7-5-2012

A proposed palladium-catalyzed cycle for the epoxidation of alkenes

Marie Vernell Parkes

Marie Vernell Parkes
Candidate

Chemistry and Chemical Biology
Department

This dissertation is approved, and it is acceptable in quality and form for publication:

Approved by the Dissertation Committee:

Richard Kemp , Chairperson

Martin Kirk

Wei Wang

David Bear

A Proposed Palladium-Catalyzed Cycle for the Epoxidation of Alkenes

by

Marie Vernell Parkes

Bachelor of Science, Chemistry, California Institute of Technology, 2000
Master of Science, Chemistry, University of California, Los Angeles, 2004

DISSERTATION

Submitted in Partial Fulfillment of the
Requirements for the Degree of

Doctor of Philosophy
Chemistry

The University of New Mexico
Albuquerque, New Mexico

May, 2012

ACKNOWLEDGMENTS

First and foremost, I must acknowledge my wonderful husband, Dale, for enthusiastically supporting me during my long journey through graduate school. Thank you for always doing what is best for our family. You are my best friend, my love, and my partner in everything I do. I love you and would not be here without you.

When I started graduate school at UNM, I was so fortunate to find an advisor who was not only doing interesting research, but also a supportive, encouraging, and understanding mentor in Rick Kemp. Without Rick's guidance in my chemical research, support in choosing an atypical approach to my project, and patience and understanding as my personal life and academic career collided so many times, I wouldn't have made it through grad school. Rick, "thank you" isn't quite strong enough for the appreciation I feel.

To my three wonderful daughters, Adelaida, Cordelia, and Estella, you bring joy to my life and a smile to my face. You are strong, beautiful, smart, happy girls and I will always love you.

I have been blessed with a strong support network in my family. To my parents, Annette Rawlinson, Mikel Rawlinson, Steve Fox, Mary Jo Fox, and Charlotte Parkes, thank you for your unconditional love and continued support through the years. I am so fortunate to have such loving parents! The love,

support, and friendship of my siblings, Bill Nadeau, Rachel Nadeau, Michael Fox, Sami Ezzo, BJ Murphy, Rachel Murphy, Richard Parkes, and Laura Parkes, has meant so much to me through the years. And to my nieces and nephews, Billy, Elizabeth, Sarah, Benjamin, and Simon, you are all precious and beloved children. I have great hopes for your futures!

I have had several mentors, both in chemistry and in life, without whose support, guidance, and concern I would be lost. A few of those mentors who have had the greatest impact on my life are Orville Chapman, Teresita McCarty, Craig Merlic, Ken Houk, and Jack Roberts. I appreciate each of you taking the time and effort to guide me at various stages of my life.

The members of my dissertation committee have provided valuable suggestions and advice about my dissertation project and graduate career. Discussions with Karen Goldberg and her group at the University of Washington have been particularly useful in generating and expanding on new ideas on this project. Additionally, the computational-chemistry-related assistance and direction provided by Rick Muller and Hua Guo have been particularly important throughout the course of this research project. I've really appreciated having each of you to turn to over the past several years.

Finally, I need to thank the members of the Kemp group for their support, assistance, and willingness to share information with me over the years. Thank you all.

A Proposed Palladium-Catalyzed Cycle for the Epoxidation of Alkenes

Marie Vernell Parkes

Bachelor of Science, Chemistry, California Institute of Technology, 2000

Master of Science, Chemistry, University of California, Los Angeles, 2004

Doctor of Philosophy, Chemistry, The University of New Mexico, 2012

ABSTRACT

Epoxides are an important chemical functional group, used in a wide variety of processes, from the small-scale production of pharmaceuticals to the large-scale production of propylene oxide. Current methods for production of epoxides require costly multi-step syntheses that use toxic or explosive reagents, result in low yields, and produce co-products that must be removed and often disposed. The development of an atom-efficient general method, preferably catalytic, for converting alkenes to epoxides using safe, cheap, and readily available molecular oxygen as the stoichiometric oxidant would be a great advance in both industrial and academic chemistry.

Presented here is a proposed catalytic cycle in which molecular oxygen is used as the stoichiometric oxidant for the epoxidation of alkenes. The cycle begins with a palladium hydride bearing a tridentate ligand. Molecular oxygen adds to the palladium hydride, forming a palladium hydroperoxide that will act as the active oxidant in the catalytic cycle. This palladium hydroperoxide then transfers one oxygen atom to an alkene, producing palladium hydroxide and the desired epoxide. Finally, the palladium hydride is regenerated from palladium hydroxide by addition of hydrogen gas and elimination of water.

Each individual step of this proposed catalytic cycle was studied computationally using density functional theory calculations. Specifically, the palladium-hydrogen bond dipole and the palladium-hydrogen bond length were examined in relation to formation of the palladium hydroperoxide; the effect of the electrophilicity of the alkene on the epoxidation was studied; and the relationship between the characteristics of the tridentate ligand and the mechanism of palladium-hydride regeneration were examined. Computational results and suggested direction for future experimental focus are presented.

Table of Contents

List of Figures x

Chapter 1: Background and Proposed Catalytic Cycle 1

Functionalization of Organic Substrates 1

Importance of Epoxides 2

Transition Metal Peroxides as Oxidants 3

Structure of Transition Metal Peroxides 5

Formation and Reactivity of Transition Metal Peroxides 7

Oxygen Transfer to Organic Substrates 9

Proposed Catalytic Cycle 12

Chapter 2: Methods and Methods Verification 19

Description of Methods Used for Geometry Optimizations 19

Description of Methods Used for Transition States 20

Description of Methods Used to Find Minimum Energy Crossing Points (MECP) 21

Confirmation of Geometry Optimizations 22

Confirmation of Reaction Coordinates 37

Chapter 3: Insertion of Molecular Oxygen into a Palladium-Hydride Bond to Form a Palladium Hydroperoxide 39

First Step of Proposed Catalytic Cycle 39

Computational Insight into Reaction Mechanism 40

Orientation of Oxygen and Palladium Hydride during Oxygen Insertion .. 46

Methods Verification by Reproduction of Known Computational Results 48

Palladium-Hydrogen Bond Dipole as a Proxy for Activation Barrier to Oxygen Insertion 55

Bond Dipoles Obtained Using CHELPG Charges 61

Bond Dipoles Obtained Using Mulliken Charges 62

Reaction Coordinates Determined for Six Complexes 64

Correlation between Transition State Barrier and Bond Dipole 70

Transition State Barrier Correlates Well with Palladium-Hydrogen Bond Length 73

Conclusions and Direction for Future Experimental Work 75

Chapter 4: Oxygen Atom Transfer from a Palladium Hydroperoxide to an Alkene to form an Epoxide 77

Second Step of Proposed Catalytic Cycle 77

Experimental Evidence for Oxygen Atom Transfer 78

Partial Negative Charge of Proximal Oxygen Atom in Palladium Hydroperoxide 80

Reaction Mechanism Determined for Model System 81

Effect of Nucleophilicity of Alkene on Activation Energy 84

Conclusions and Direction for Future Experimental Work 89

Chapter 5: Palladium Hydride Regeneration from Palladium Hydroxide and Hydrogen 91

Third Step of Proposed Catalytic Cycle 91

Possible Mechanisms Considered for Hydrogenolysis of Palladium Hydroxide 92

Reaction Coordinate Reproduced for Model System 94

Effect of Ligand Atoms of Attachment on Reaction Mechanism 95

Conclusions and Direction for Future Experimental Work 103

Chapter 6: Conclusions 105

Proposed Catalytic Cycle 105

Computational Results for Each Step of the Proposed Catalytic Cycle 106

Summary of Results 110

List of Appendices 113

Appendix A: Abbreviations and Symbols 114

Appendix B: Optimized Geometries of Selected Complexes 119

References 372

List of Figures

Figure 1-1: Examples of organic transformations accomplished using peracids. All abbreviations and symbols used are listed in Appendix A: Abbreviations and Symbols. 3

Figure 1-2: Classes of transition metal oxides and peroxides 6

Figure 1-3: Electronic consideration of early and late transition metal peroxides . 7

Figure 1-4: Examples of oxygen-transfer reactions accomplished by transition metal peroxides 8

Figure 1-5: (a) The Sharpless asymmetric oxidation efficiently converts allylic alcohols to epoxides. (b) The proposed active oxidant is a binuclear titanium alkyl peroxide complex. 9

Figure 1-6: Generic mechanism for the transition-metal mediated epoxidation of an alkene with alkyl peroxide 10

Figure 1-7: Mechanisms of epoxidation proposed by (a) Sharpless[31] and (b) Mimoun[32] 11

Figure 1-8: Frenking's calculations[33] suggest the intermediate proposed by Mimoun will decompose to an aldehyde or ketone rather than an epoxide 12

Figure 1-9: Proposed catalytic cycle for the epoxidation of an alkene using molecular oxygen as the stoichiometric oxidant..... 14

Figure 1-10: Insertion of oxygen into palladium hydride bond demonstrated by Goldberg, Kemp, and coworkers[36] 15

Figure 1-11: Transfer of oxygen atom from palladium hydroperoxide to alkene, producing an epoxide..... 16

Figure 1-12: Regeneration of palladium hydride from palladium hydroxide has been demonstrated by Goldberg, Kemp, and coworkers[40] 17

Figure 2-1: The minimum energy crossing point (MECP) is the point along the reaction coordinate at which the singlet and triplet potential energy surfaces intersect..... 22

Figure 2-2: Structure overlay geometry agreement between crystal structure[68] (green) and computationally optimized geometry (blue) for (bis(4-fluoro-2-(di-isopropylphosphino)phenyl)amide-N,P,P')palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay. 24

Figure 2-3: Structure overlay geometry agreement between crystal structure[69] (green) and computationally optimized geometry (blue) for (2,5-bis((di-*tert*-butylphosphino)methyl)ferrocen-1-yl-C,P,P')palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay. 25

Figure 2-4: Structure overlay geometry agreement between crystal structure[70] (green) and computationally optimized geometry (blue) for (bis(4-methyl-2-(di-isopropylphosphino)phenyl)amide-N,P,P')palladium hydroperoxide. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay. 26

Figure 2-5: Structure overlay geometry agreement between crystal structure[71] (green) and computationally optimized geometry (blue) for (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay..... 27

Figure 2-6: Structure overlay geometry agreement between crystal structure[72] (green) and computationally optimized geometry (blue) for (1,3-bis(2-(di-isopropylphosphino-P)phenyl)imidazolidin-2-ylidene)palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay. 28

Figure 2-7: Analysis of palladium-hydrogen bond distances in crystal structures in the Cambridge Structural Database[73] based on four-coordinate palladium hydride complexes in which the hydride is bound only to palladium 29

Figure 2-8: Structure overlay geometry agreement between crystal structure[74] (green) and computationally optimized geometry (blue) for (2-(diisopropylphosphino)-N-(2-(diisopropylphosphino)-4-methylphenyl)-4-methylaniline)palladium hydride. Circled atoms were used to prepare the

structure overlay. Color scale shows difference in atom position (in Å) for structure overlay. 30

Figure 2-9: Structure overlay geometry agreement between crystal structure[75] (green) and computationally optimized geometry (blue) for (P,P-bis(3-diethylphosphinopropyl)phenylphospino)palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay..... 31

Figure 2-10: (a) Structure overlay geometry agreement between crystal structure[76] (green) and computationally optimized geometry (blue) for (2,6-bis(di-isopropylphosphinomethyl)phenyl)palladium hydride, and (b) view of crystal structure (green) and computationally optimized geometry (blue) projected along the hydrogen-palladium bond. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay. 33

Figure 2-11: Analysis of *ortho*-carbon, *ipso*-carbon, palladium, phosphorus dihedral angles in crystal structures, in the Cambridge Structural Database[73] based on four-coordinate palladium complexes containing a tridentate ligand bound to palladium through two phosphorus atoms and a phenyl ring 34

Figure 2-12: (a) Structure overlay geometry agreement between crystal structure[36] (green) and computationally optimized geometry (blue) for (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydroperoxide, and (b) view of crystal structure (green) and computationally optimized geometry (blue) projected along the palladium-*ipso*-carbon bond. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay. 35

Figure 3-1: First step of proposed catalytic cycle is insertion of oxygen into palladium-hydride bond..... 39

Figure 3-2: Experimental evidence for insertion of oxygen into palladium-hydride bond demonstrated by Goldberg, Kemp, and coworkers[36] 40

Figure 3-3: Reaction coordinate determined by the Goddard group[38] for insertion of oxygen into palladium-hydride bond. Reprinted with permission from Keith, Jason M.; Muller, Richard P.; Kemp, Richard A.; Goldberg, Karen I.; Goddard, William A., III; Oxgaard, Jonas. Mechanism of Direct Molecular

Oxygen Insertion in a Palladium(II)-Hydride Bond. *Inorganic Chemistry* 2006, *45*, 9631-9633. Copyright 2006 American Chemical Society. 41

Figure 3-4: Kinetic isotope experiment performed by Goldberg, Kemp, and coworkers[36] for oxygen insertion into palladium-hydrogen bond..... 42

Figure 3-5: Reaction coordinate prepared by Goddard and coworkers in 2005[37] for insertion of oxygen into a palladium-hydride bond with a lone-pair-bearing ligand. Reprinted with permission from Keith, Jason M.; Nielsen, Robert J.; Oxgaard, Jonas; Goddard, William A., III. Pd-Mediated Activation of Molecular Oxygen in a Nonpolar Medium. *Journal of the American Chemical Society* 2005, *127*, 13172-13179. Copyright 2005 American Chemical Society. 44

Figure 3-6: Oxygen insertion pathway proposed by Stahl and coworkers[87] for palladium hydrides containing a lone-pair-bearing ligand 44

Figure 3-7: Further insight into the reaction coordinate of oxygen insertion into a palladium-hydride bond provided by Russo and coworkers,[78] showing both the triplet and singlet potential energy surfaces. Reprinted from *Chemical Physics Letters*, *443*, Chowdhury, Sugata; Rivalta, Ivan; Russo, Nino; Sicilia, Emilia, On the Insertion Mechanism of Molecular Oxygen into a Pd(II)-H Bond. Something to Add, pages 183-189, Copyright 2007, with permission from Elsevier..... 46

Figure 3-8: Three ways in which the palladium hydride and oxygen can interact: (a) oxygen approaches the hydrogen atom in the plane of the molecule; (b) oxygen approaches the palladium hydride above the plane of the molecule with oxygen parallel to the palladium-hydride bond, and (c) oxygen approaches the palladium hydride above the plane of the molecule with oxygen perpendicular to the palladium-hydride bond (note that all hydrogen atoms other than the palladium-bound hydrogen have been omitted for clarity) 47

Figure 3-9: Reaction coordinate for insertion of oxygen into palladium-hydride bond, as calculated in this research and by Goddard and coworkers[38] ... 49

Figure 3-10: Optimized geometries of reactant palladium hydride (10) and transition state structure (11) for insertion of oxygen into palladium-hydride bond..... 51

Figure 3-11: Optimized geometries of intermediate (12) and minimum energy crossing point structure (13) for insertion of oxygen into palladium-hydride bond 53

Figure 3-12: Optimized geometry of singlet product palladium hydroperoxide (14) 54

Figure 3-13: Examples of palladium hydride complexes with (a) anionic tridentate ligand and with (b) neutral tridentate ligand and counterion 56

Figure 3-14: All PCP complexes examined computationally 57

Figure 3-15: All PNP complexes examined computationally 58

Figure 3-16: All PPP, PSiP, PCN, PCO, OCO, and SCS complexes examined computationally 59

Figure 3-17: All CCC and CNC complexes examined computationally 59

Figure 3-18: All NNN and NCN complexes examined computationally 60

Figure 3-19: The bond dipole is calculated as the differences in atomic charge between the palladium and hydrogen atoms, multiplied by the palladium-hydrogen bond length 61

Figure 3-20: Bond dipoles from CHELPG charges, grouped by atoms of attachment of the tridentate ligand 62

Figure 3-21: Bond dipoles from Mulliken charges, grouped by atoms of attachment of the tridentate ligand 63

Figure 3-22: Bond dipoles from Mulliken charges and bond dipoles from CHELPG charges plotted against each other 64

Figure 3-23: Six complexes chosen for further study, based on CHELPG-charge-derived palladium-hydride bond dipoles 65

Figure 3-24: Reaction coordinate for oxygen insertion into (2,6-bis((difluorophosphino)methyl)phenyl-C-P-P')palladium hydride (18) 66

Figure 3-25: Reaction coordinate for oxygen insertion into (bis(4-methyl-2-(di-isopropylphosphino)phenyl)amide-N,P,P')palladium hydride (29) 67

Figure 3-26: Reaction coordinate for oxygen insertion into bis(1,3-bis(2-pyridylmethyl)imidazol-2-ylidene-C-N-N')palladium hydride (56) 68

Figure 3-27: Reaction coordinate for oxygen insertion into (2,6-bis(3-N-methylimidazol-2-ylidene-1-yl)phenyl-C-C'-C'')palladium hydride (41) 69

Figure 3-28: Reaction coordinate for oxygen insertion into ((2-(methoxymethyl)-6-((di-*tert*-butylphosphino)methyl))phenyl-C-O-P)palladium hydride (38) ... 70

Figure 3-29: Transition state energy plotted against CHELPG-charge-derived palladium-hydrogen bond dipole 71

Figure 3-30: Transition state energy plotted against Mulliken-charge-derived palladium-hydrogen bond dipole 72

Figure 3-31: Correlation between transition state energy and palladium-hydrogen bond length 74

Figure 3-32: Analysis of palladium-hydrogen bond lengths in calculated structures, with points representing complexes containing neutral ligands circled 75

Figure 3-33: Palladium hydride complexes with relatively long palladium-hydrogen bonds that should be examined further experimentally 76

Figure 4-1: Second step of proposed catalytic cycle is oxygen atom transfer from palladium hydroperoxide to an alkene, forming an epoxide 77

Figure 4-2: Oxygen atom transfer from palladium hydroperoxide to isocyanide to form isocyanate has been demonstrated[39] 79

Figure 4-3: Oxygen atom transfer from palladium hydroperoxide to triphenylphosphine to form phosphine oxide has been demonstrated[91] .. 79

Figure 4-4: Seven palladium hydroperoxides examined for CHELPG charge on proximal oxygen, with CHELPG charges indicated 81

Figure 4-5: Reaction coordinate for epoxidation of propene (81) 82

Figure 4-6: Representations of (a) palladium hydroperoxide and alkene reactants, (b) “butterfly” transition state, and (c) palladium hydroxide and epoxide products 83

Figure 4-7: Alkenes examined for epoxidation range from electron-rich to electron-poor..... 84

Figure 4-8: Reaction coordinate for epoxidation of methoxyethene (85) 85

Figure 4-9: Reaction coordinate for epoxidation of styrene (86)..... 86

Figure 4-10: Reaction coordinate for epoxidation of methylacrylate (87)..... 87

Figure 4-11: Reaction coordinate for epoxidation of acrylonitrile (88)..... 89

Figure 5-1: Third step of proposed catalytic cycle is regeneration of palladium hydride from palladium hydroxide and hydrogen 91

Figure 5-2: Conversion of (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P’)palladium hydroxide (96) to the corresponding palladium hydride 16, demonstrated by Kemp, Goldberg, and coworkers[40] 92

Figure 5-3: Two reaction mechanisms for the hydrogenolysis of palladium hydroxide 96 proposed by Kemp, Goldberg, and coworkers:[40] a) oxidative addition and reductive elimination through an octahedral palladium(IV) intermediate 97, and b) internal electrophilic substitution through a four-center transition state 98..... 93

Figure 5-4: Reaction coordinate for conversion of palladium hydroxide 96 and hydrogen to palladium hydride 16 and water, as calculated in this research and by Kemp, Goldberg, and coworkers[40] 95

Figure 5-5: Palladium hydroxides considered for hydrogenolysis..... 96

Figure 5-6: Reaction coordination for regeneration of palladium hydride 41 from the corresponding palladium hydroxide 99 97

Figure 5-7: Reaction coordination for regeneration of palladium hydride 54 from the corresponding palladium hydroxide 100 98

Figure 5-8: Reaction coordination for regeneration of palladium hydride 40 from the corresponding palladium hydroxide 102 99

Figure 5-9: Reaction coordination for regeneration of palladium hydride 39 from the corresponding palladium hydroxide 101 101

Figure 5-10: Possible mechanism for the addition of hydrogen to ((2-(methoxymethyl)-6-((di-*tert*-butylphosphino)methyl))phenyl-C-O-P)palladium hydroxide, as proposed by Goldberg, Kemp, and coworkers[98] 103

Figure 6-1: Proposed catalytic cycle for the epoxidation of an alkene using molecular oxygen as the stoichiometric oxidant..... 106

Figure 6-2: First step of proposed catalytic cycle is insertion of oxygen into palladium-hydride bond..... 107

Figure 6-3: Second step of proposed catalytic cycle is oxygen atom transfer from palladium hydroperoxide to an alkene, forming an epoxide 109

Figure 6-4: Third step of the proposed catalytic cycle is regeneration of palladium hydride from palladium hydroxide and hydrogen 110

Chapter 1: Background and Proposed Catalytic Cycle

Functionalization of Organic Substrates

Petroleum feedstocks serve as the primary source of organic materials, accounting for over 90% of the world's industrial organic chemicals.[1] Petroleum-based hydrocarbons are cheap, readily available starting materials that can be converted into almost any organic product: plastics, pharmaceuticals, insecticides, and detergents, for example.[1,2] However, the chemicals obtained from petroleum feedstocks are relatively unfunctionalized and require selective derivatization in order to be converted into useful products. Functionalization occurs through oxidation, reduction, carbon-carbon bond formation, and carbon-carbon bond cleavage; of these, perhaps the most useful is oxidation.

The greatest challenges associated with the oxidation of hydrocarbons are selectivity in the atoms that are oxidized and in avoiding the complete combustion of the hydrocarbon. Effective partial-oxidation of a hydrocarbon will lead to oxidation of only the desired atoms without complete combustion to carbon dioxide.[3] Oxidation generally occurs by the elimination of hydrogen from an organic molecule or the replacement of a carbon-bound hydrogen atom with a more electronegative element such as oxygen, nitrogen, or a halide.[2,3] The addition of oxygen to a hydrocarbon is a special case of oxidation termed

oxygenation. The conversion of an alkene to an epoxide is one such example of a partial-oxidation oxygenation reaction in which a carbon-carbon double bond is converted to a carbon-carbon single bond with the addition of an oxygen atom.

Importance of Epoxides

Epoxides are important functional groups in both industrial and academic chemistry, used in a wide variety of processes, from the small-scale production of pharmaceuticals to the large-scale production of propylene oxide for the conversion to polyurethane and propylene glycol. With the potential for simultaneous introduction of two chiral centers when prepared from alkenes, chiral epoxides are important precursors in the synthesis of enantiomerically pure organic molecules.[4-6] Commercially, only ethylene oxide, butadiene mono-epoxide, and butadiene di-epoxide can be prepared in single-step pathways using molecular oxygen as oxidant without producing significant amounts of co-products.[7,8] Epoxidations of other alkenes require costly multi-step syntheses that use toxic or explosive reagents, result in low yields, and produce co-products that must be removed and often disposed. The development of an atom-efficient general method, preferably catalytic, for converting alkenes to epoxides using safe, cheap, and readily available molecular oxygen as the stoichiometric oxidant would be a great advance in both industrial and academic chemistry.

Transition Metal Peroxides as Oxidants

For years, chemists have used organic peracids to stoichiometrically oxidize organic substrates.[6] Peracids are extremely reactive and versatile oxidants, and derivatives have been used to effect the transformations of tertiary amines to amine oxides, ketones to esters, sulfides to sulfoxides, phosphines to phosphine oxides, and alkenes to epoxides, among other oxidations (see Figure 1-1).[9,10] Each of these oxidations involves the transfer of the distal peracid oxygen to the organic substrate.[6]

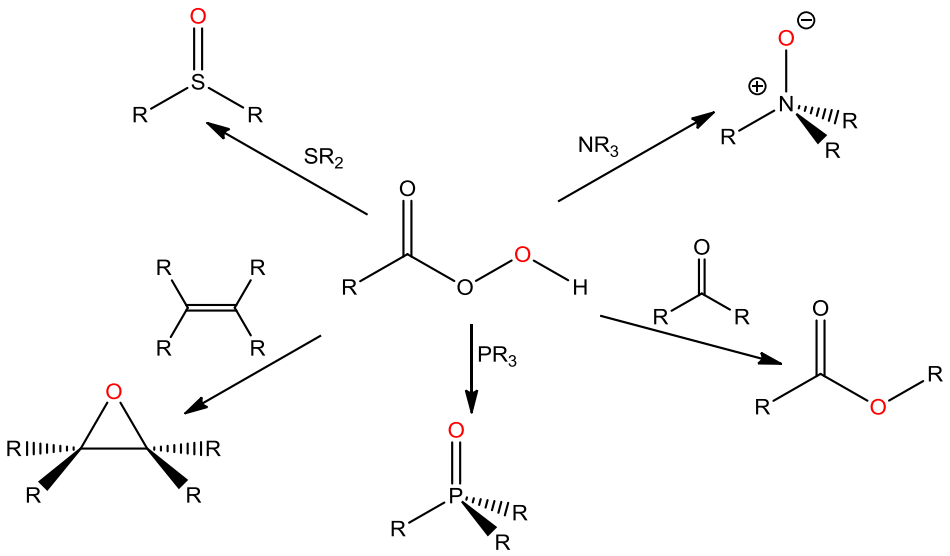


Figure 1-1: Examples of organic transformations accomplished using peracids. All abbreviations and symbols used are listed in Appendix A: Abbreviations and Symbols.

Despite their versatility in synthesis, organic peracids have a number of drawbacks: they are not highly selective and attempts to use them for

asymmetric epoxidations have met with limited success.[2,10] Furthermore, organic peracids suffer from safety concerns because the peroxide bond is easily cleaved, making the peracid explosively unstable to heat, moisture, light, air, and shock.[2,10] Therefore, extreme care must be taken in the preparation, storage, and use of peracids. Due to these limitations, alternatives to peracids are in high demand.

Some alternatives to peracids that have been investigated are molecular oxygen, alkyl peroxides, and hydrogen peroxide.[11] In particular, the selective oxidation of hydrocarbons with molecular oxygen has been one of the most sought-after transformations in catalysis. Oxygen is a known oxidant, but because it is a ground-state triplet,[12] reactions between molecular oxygen and most organic compounds are spin-forbidden.[12] Alkyl peroxides and hydrogen peroxide are cheaper than peracids, but are much less reactive and are not able to accomplish the wide variety of oxidations that can be achieved with peracids.[11]

Transition metals can be used to overcome the problems encountered by both molecular oxygen and alkyl peroxides. With large spin-orbit coupling constants,[13] transition metals are able to overcome the spin-forbidden prohibition of reaction between triplet molecular oxygen and singlet substrates and increase the reactivity of alkyl peroxides and hydrogen peroxides.[11,12] Transition metal peroxides have both advantages and disadvantages as oxidation reagents. Advantageously, they are more stable than peracids, can be used catalytically, and can be used as heterogeneous catalysts, which are easy to recover from a

reaction and reuse.[12] However, their relative expense and difficulty in preparation must be considered as drawbacks.

Structure of Transition Metal Peroxides

The broad class of transition metal peroxides can take a number of different forms, the most common of which are shown in Figure 1-2.[14] The term "peroxometal" generally refers to the η^2 species[15-19] and will be used as such here. A superoxometal species consists of the transition metal bound to only one oxygen atom, with the distal oxygen bearing an unpaired electron.[15] Superoxometal species are generally less stable than peroxometals and form only when coordination of the distal oxygen is sterically hindered.[15] Structurally, transition metal alkylperoxides or hydroperoxides adopt a conformation along a continuum between a side-on-bonded structure and an end-on bonded structure. In a side-on bonded structure, the distances between the transition metal atom and two oxygen atoms are identical; an end-on-bonded structure has one oxygen atom that is so far away from the transition metal that it cannot be considered a bonding interaction.[15]

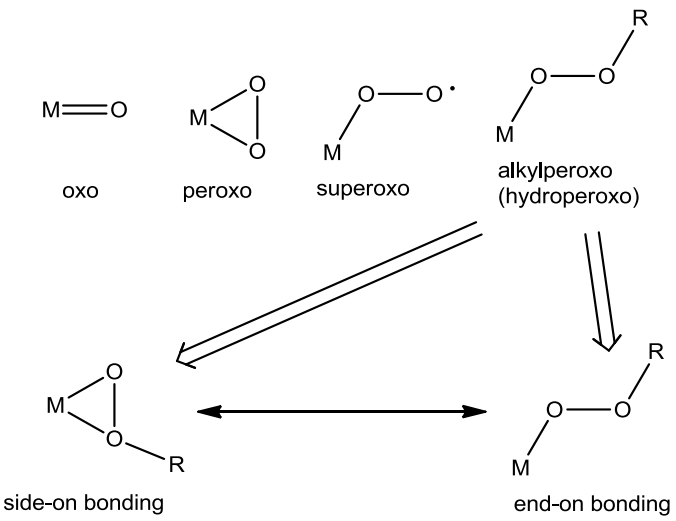


Figure 1-2: Classes of transition metal oxides and peroxides

Transition metal peroxides are typically divided into two groups: early transition metal peroxides and late transition metal peroxides. Early transition metals have empty d-orbitals, allowing the lone pair of electrons on oxygen to donate into the empty d-orbitals, resulting in a partial positive charge on oxygen and an electrophilic oxygen.[20] Late transition metals have filled d-orbitals, the electrons of which can donate into the empty oxygen-oxygen π^* orbital, resulting in a partial negative charge on oxygen and a nucleophilic oxygen.[20] Examples of both types of interactions are shown in Figure 1-3.

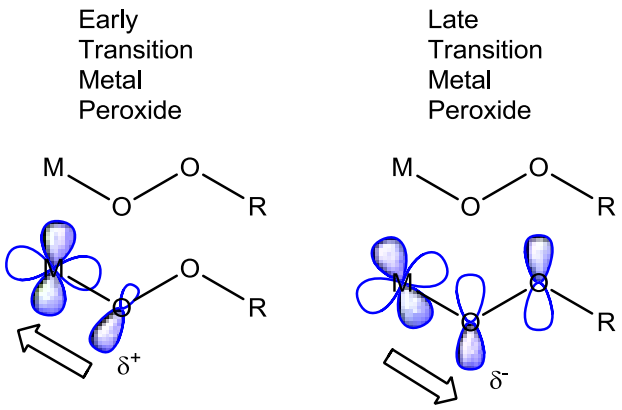


Figure 1-3: Electronic consideration of early and late transition metal peroxides

Formation and Reactivity of Transition Metal Peroxides

Transition metal peroxides have traditionally been prepared by either of two methods: addition of molecular oxygen to a transition metal or reaction of a transition metal with hydrogen peroxide.[21,22] Because the resulting product complexes are indistinguishable, the distinction between them has become less important in recent years.[23]

Transition metal peroxides can accomplish a variety of oxidations, including both oxygenations and oxidations that do not involve oxygen-transfer. Examples of oxygen-transfer reactions that use transition metal peroxides are epoxidation, oxygenation of nitrogen and sulfur, and addition of molecular oxygen to dienes.[24-28] Several examples are shown in Figure 1-4.

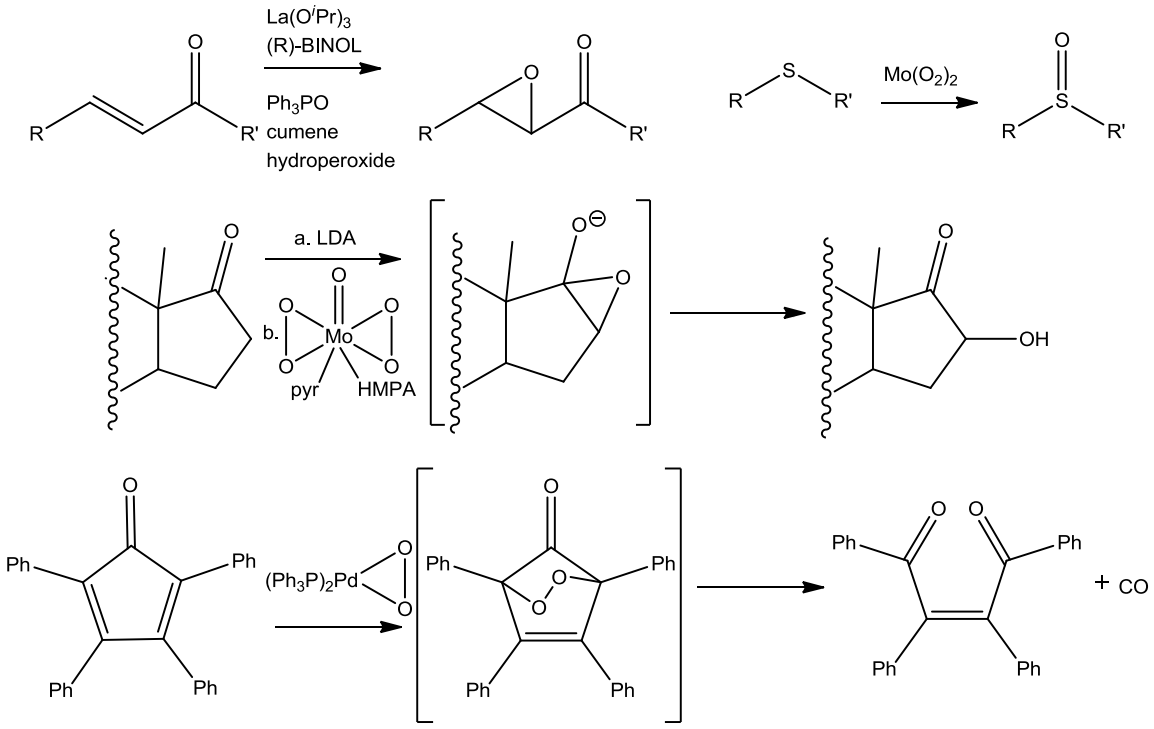


Figure 1-4: Examples of oxygen-transfer reactions accomplished by transition metal peroxides

One of the most-studied applications of transition metal peroxide oxidation is the Sharpless asymmetric epoxidation system. In this process, an allylic alcohol is epoxidized with reasonably high yield and very high enantioselectivity using titanium tetra-*iso*-propoxide, *tert*-butyl peroxide, and either enantiomer of diethyltartrate.[29] The oxidant is the achiral *tert*-butyl peroxide; asymmetric induction comes from the contribution of diethyltartrate as the chiral auxiliary.[29] The active oxidant is believed to be a binuclear titanium alkyl peroxide as shown in Figure 1-5.[30]

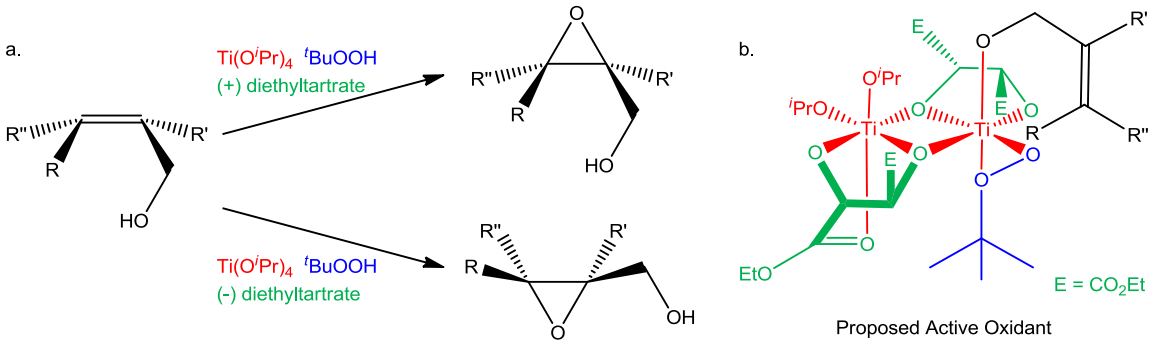


Figure 1-5: (a) The Sharpless asymmetric oxidation efficiently converts allylic alcohols to epoxides. (b) The proposed active oxidant is a binuclear titanium alkyl peroxide complex.

Oxygen Transfer to Organic Substrates

It is well known that, although alkyl peroxides are poor oxidizers, alkyl peroxides in the presence of transition metals are excellent oxidizers.[11] It has therefore been proposed that a peroxometal species, which is much more reactive than the original alkyl peroxide, is the active species in such reactions.[5] The proposed mechanism of oxidation for a generic epoxidation involves, at the most basic level, three steps:

1. the complexation of a metal to a peroxide, resulting in an alkylperoxometal,
2. the introduction of an alkene to the metal species, forming some intermediate metal-peroxide-alkene complex, and
3. the release of an epoxide and regeneration of the initial metal species.

This most basic mechanism is shown in Figure 1-6.

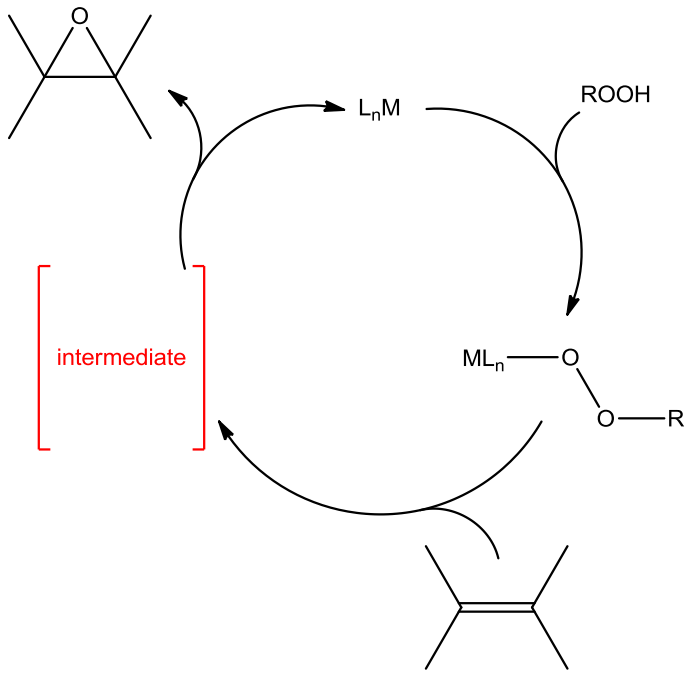


Figure 1-6: Generic mechanism for the transition-metal mediated epoxidation of an alkene with alkyl peroxide

There has been considerable controversy regarding the nature of the metal-peroxide-alkene intermediate. Two mechanisms have been proposed: one by Sharpless and the other by Mimoun. Sharpless proposed a nucleophilic attack of substrate on the peroxide oxygen, through a “butterfly” transition state, followed by loss of ligand and simultaneous release of the epoxide.[31] This is shown in Figure 1-7a. Mimoun proposed that the reaction begins with loss of ligand, occurs through a peroxometallocycle intermediate, and results in the same epoxide, as shown in Figure 1-7b.[32]

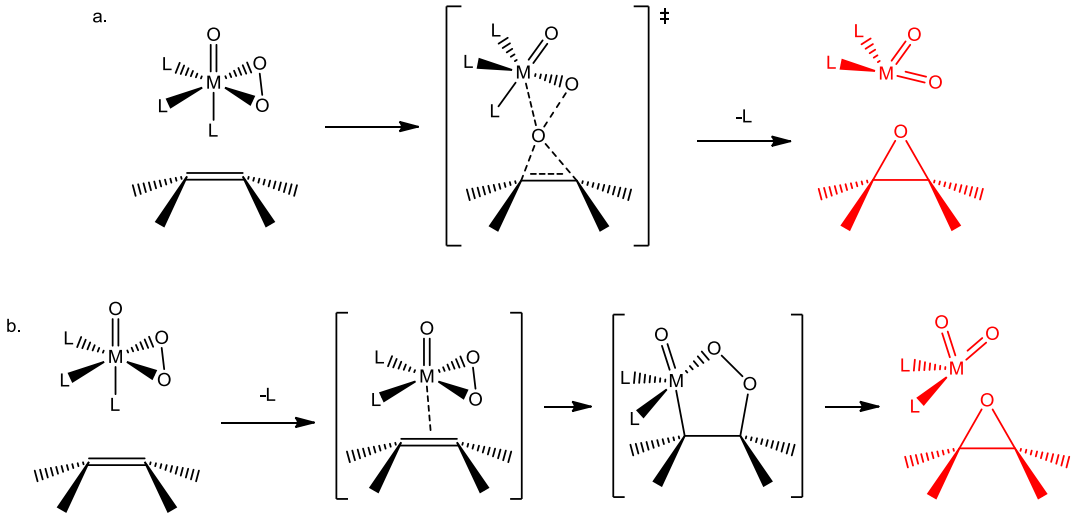


Figure 1-7: Mechanisms of epoxidation proposed by (a) Sharpless[31] and (b) Mimoun[32]

For many years, fierce debate raged over the correct mechanism for epoxidation. In 2000, however, Frenking and coworkers performed computations that show that the peroxometallocycle intermediate proposed by Mimoun would decompose to the ketone or aldehyde with alkyl migration rather than to an epoxide, as shown in Figure 1-8.[33] This strongly suggests that the mechanism proposed by Mimoun, with two discrete intermediates, is not a likely pathway for the epoxidation of an alkene.

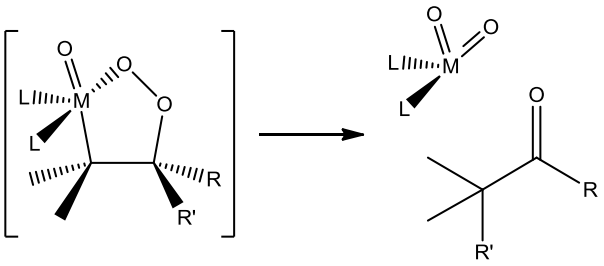


Figure 1-8: Frenking's calculations[33] suggest the intermediate proposed by Mimoun will decompose to an aldehyde or ketone rather than an epoxide

Proposed Catalytic Cycle

The selective functionalization of organic substrates, achieved cheaply, cleanly, and employing reusable materials, has long been a goal of synthetic chemists.[5] Although transition metal peroxides are known to epoxidize specific, functionalized alkenes (such as allylic alcohols, homoallylic alcohols, enolates, and enones), an efficient transition metal peroxide reagent for the epoxidation of nonfunctionalized alkenes using molecular oxygen as the primary oxidant is not known.[24,34,35]

The goal of this research is to develop a transition-metal-mediated catalytic cycle in which molecular oxygen is used as a stoichiometric oxidant in the epoxidation of alkenes. There are four key features of this goal: the transition-metal-mediation, the catalytic nature of the reaction, the use of molecular oxygen as the stoichiometric oxidant, and the resulting epoxidation of an alkene. Each of these key features is discussed in more detail below.

First, the epoxidation should be mediated by a transition metal. A reaction between molecular oxygen and an organic substrate would be spin-forbidden, but a transition metal's large spin-orbit coupling constant can overcome this limitation.[13] Second, the reaction should be catalytic in the metal. Transition metals are relatively expensive and generally not abundant, so the ability to use them efficiently is important in making the reaction attractive for use, both in research settings and in industry. Third, molecular oxygen will be used as the stoichiometric oxidant. Molecular oxygen is cheap, readily available, and a known oxidant. Finally, the net result of the reaction should be to transfer an oxygen atom to an organic substrate, ideally converting an alkene to an epoxide.

The proposed generic catalytic cycle, in which a shorthand notation is used to indicate a tridentate ligand bound to palladium by three atoms of attachment, is shown in Figure 1-9. Each of the steps of this catalytic cycle will be examined computationally to guide the experimental research being done in this field. Performing these calculations can offer several benefits. For example, computational results may indicate that certain palladium hydrides are better suited to this cycle than other palladium hydrides, thus allowing experimentalists to focus on the complexes most likely to achieve the desired epoxidation. If, on the other hand, the calculations confidently indicate that the cycle has a fundamental flaw that cannot be overcome, the results may allow the experimentalists to avoid wasting a significant amount of time and money on a cycle that is doomed to fail. Studying the individual steps of the proposed

catalytic cycle will contribute significantly to the fundamental understanding of partial oxidation catalysis.

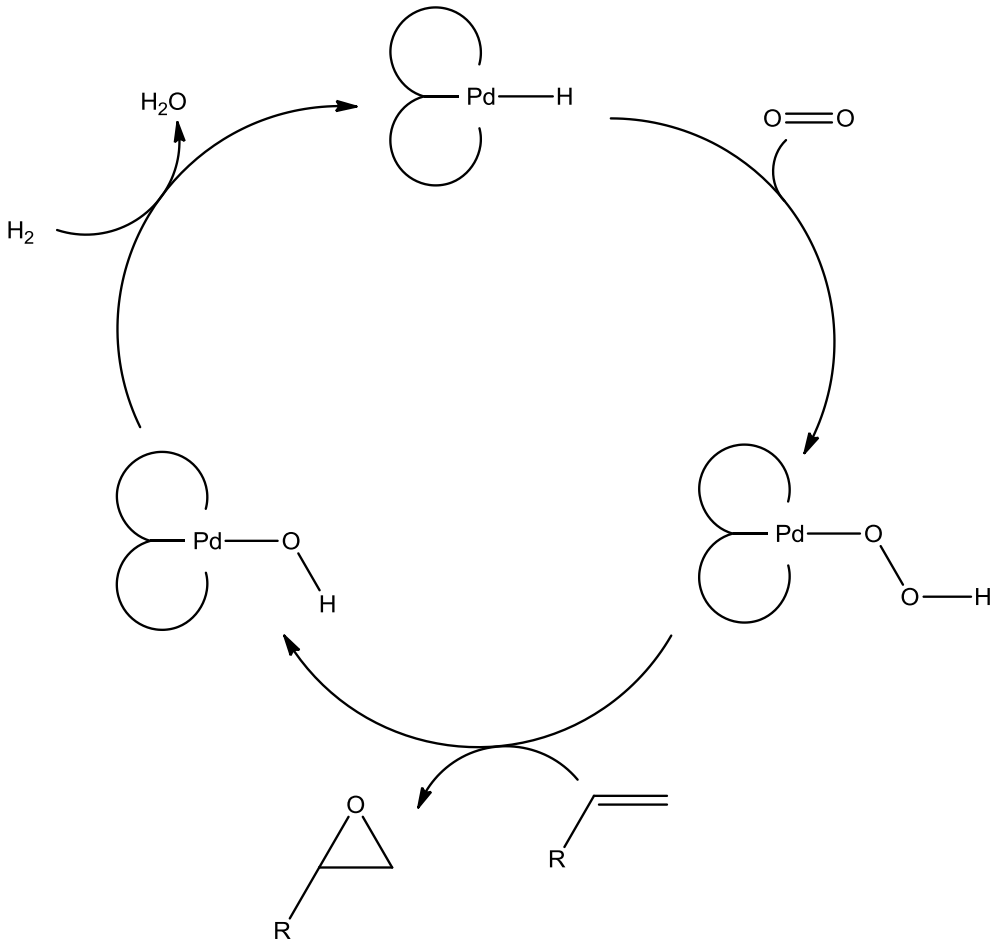


Figure 1-9: Proposed catalytic cycle for the epoxidation of an alkene using molecular oxygen as the stoichiometric oxidant

The proposed cycle begins with a tridentate-ligand-bearing palladium hydride that serves as the initial pre-catalyst. Oxygen gas is added to the palladium hydride to produce a palladium hydroperoxide, which will be the active oxidant. An oxygen atom is then transferred from the palladium hydroperoxide to

an organic substrate, leaving a palladium hydroxide. The palladium hydride is regenerated from the palladium hydroxide by the addition of hydrogen gas and elimination of water.

The first step of the proposed catalytic cycle is the addition of oxygen to a palladium hydride to generate the palladium hydroperoxide. This reaction has been demonstrated for the conversion of (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydride (**1**) to the corresponding palladium hydroperoxide **2**, as shown in Figure 1-10.[36] Although initial computational studies by Goddard and coworkers indicated that it was necessary for the ligand to have a lone pair of electrons,[37] experimental work by Goldberg, Kemp, and coworkers demonstrated that this was not the case.[36]

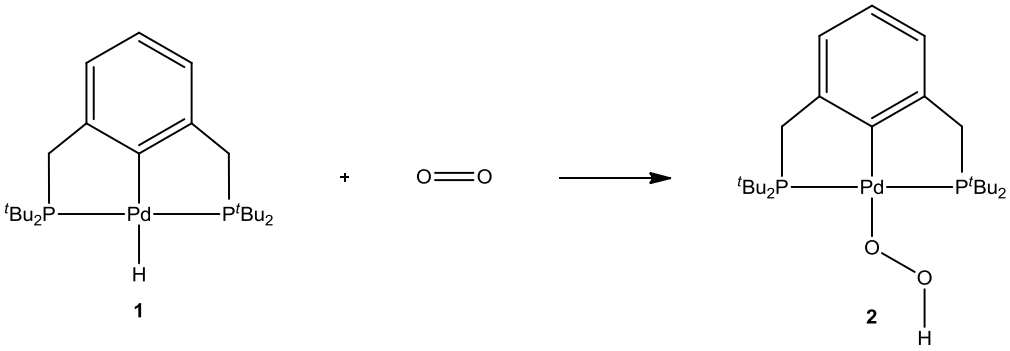


Figure 1-10: Insertion of oxygen into palladium hydride bond demonstrated by Goldberg, Kemp, and coworkers[36]

Computational mechanistic studies have been done on a model system related to this reaction,[38] and a wide variety of tridentate palladium hydrides (or their analogs) are known. These tridentate palladium hydrides will be examined

in this research to determine the effect of ligand electronics on the mechanism of this reaction.

The second step in this catalytic cycle is the transfer of an oxygen atom from palladium hydroperoxide to an alkene, as shown in Figure 1-11. Although oxygen atom transfer to an alkene has not yet been experimentally demonstrated, there is evidence that the oxygen atom will transfer from a palladium hydroperoxide to an isocyanide to form the isocyanate.[39] This evidence of oxygen atom transfer to an organic substrate is encouraging; by tuning the electrophilicity of the alkene, it should be possible to demonstrate oxygen atom transfer to an alkene as well. The effect of the electrophilicity of the alkene on the reaction will be explored, to determine if the reaction proceeds more readily with electron-rich alkenes or with electron-poor alkenes.

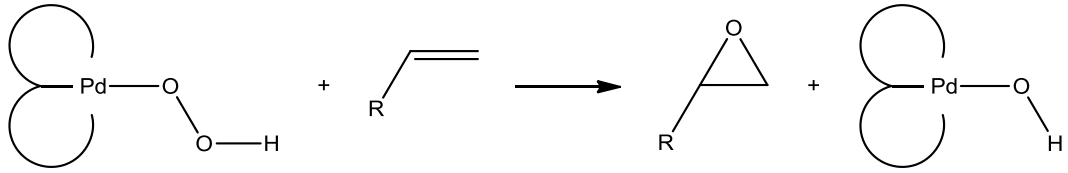


Figure 1-11: Transfer of oxygen atom from palladium hydroperoxide to alkene, producing an epoxide

Finally, in order to complete the catalytic cycle, the palladium hydride must be regenerated from the palladium hydroxide. This conversion has been demonstrated experimentally for the regeneration of (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydride (**1**) from the

corresponding palladium hydroxide,[40] as shown in Figure 1-12. Mechanistic studies have suggested that, for a model system, this reaction occurs through internal electrophilic substitution,[40] proceeding through a two-electron, four-center transition state rather than through an oxidative addition/reductive elimination mechanism. The effect of ligand atoms of attachment on the activation barrier of this reaction will be explored.

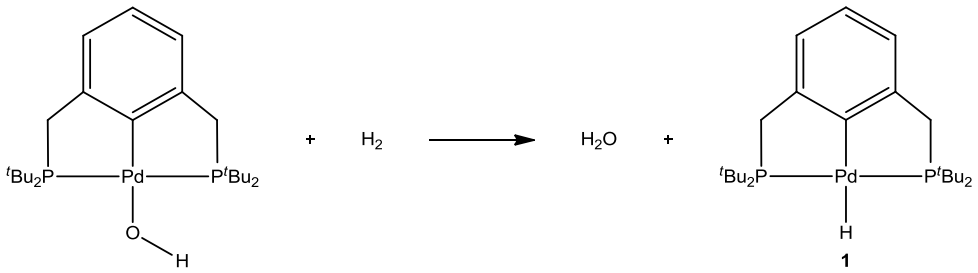


Figure 1-12: Regeneration of palladium hydride from palladium hydroxide has been demonstrated by Goldberg, Kemp, and coworkers[40]

Computational chemistry will be used to guide future experimental work on the catalytic cycle proposed above. Evaluating a palladium hydride for potential oxygen insertion experimentally can be very difficult and time-consuming, especially since preparing the palladium hydride pre-catalyst can be synthetically challenging. The additional uncertainty surrounding inserting oxygen into the palladium hydride makes the experimental testing of these complexes a shot in the dark. Likewise, conclusions drawn solely from theoretical work can be trusted only to the extent that the theory is valid. The extension of computational results that have been validated by comparison with experimental work will provide a

strong foundation for conclusions and guidance for further experimental progress on the proposed catalytic cycle.

This research is designed to streamline the experimental work by examining each step of the proposed catalytic cycle computationally to determine if the individual steps are chemically feasible. First, a variety of palladium hydrides will be studied computationally to determine how easily oxygen can be inserted into the palladium-hydride bond. Next, oxygen atom transfer from a model palladium hydroperoxide to several alkenes will be considered computationally. The electrophilicity and nucleophilicity of the carbon-carbon bonds will be correlated to the transition state barrier for epoxidation. Finally, computational methods will be used to examine the effect of the atom of attachment *cis* to the hydroxide in palladium hydride regeneration reactions. Each of these steps can be studied computationally much faster and more easily than they can be examined experimentally.

Chapter 2: Methods and Methods Verification

Description of Methods Used for Geometry Optimizations

In an effort to quickly and efficiently identify palladium complexes that might be suitable for use as oxygen transfer catalysts, density functional theory (DFT) calculations were used to optimize geometries and calculate energies of both stable species and transition states. Geometry optimizations for all complexes and frequency calculations for transition states were performed at the density functional level of theory, employing Becke's three-parameter hybrid functional[41,42] combined with the Lee, Yang, and Parr correlation functional[43] (B3LYP). The hybrid DFT functional B3LYP is known to produce good descriptions of reaction profiles for transition-metal-containing compounds[44] and the energies provided by this level of theory have proved reproducible for neutral molecules.[45] All computations were performed using the Gaussian03 program.[46] Palladium, iron, and bromine were described with the LANL2DZ effective core potential and double-ζ valence basis set.[47,48] All other elements were described including the core electrons, using Pople's 6-31+g(d) basis set.[49-51]

Atomic charges were estimated using both the Mulliken charge method[52,53] and the CHELPG charge method.[54] Both methods are commonly used to estimate atomic point charges, with charges assigned to individual atoms

based on very different techniques. Mulliken charge assignment makes use of the basis functions that are used to represent the wave functions; because of this, charges assigned by the Mulliken method are very dependent on the basis set used.[55-57] CHELPG charges are derived by measuring the electrostatic potential at grid points in space and assigning the resulting charges back to atoms in the molecule.[55] It is commonly acknowledged that different methods of atomic charge assignment produce widely varying values and cannot be compared against each other.[56] Although the CHELPG charges are considered more reliable than Mulliken charges,[55,56] Mulliken charges are still useful for predicting trends among similar molecules[57] and were therefore considered as well. All energies were evaluated at 0 K and are presented relative to reactants along the reaction coordinate. Optimized geometries, calculated energies, and other relevant data for all complexes examined are included in Appendix B: Optimized Geometries of Selected Complexes.

Description of Methods Used for Transition States

Transition state geometries were optimized and evaluated for the correct number of imaginary frequencies through vibrational frequency calculations; the presence of exactly one imaginary frequency corresponds to a transition structure. All transition states were carefully checked using intrinsic reaction coordination calculations to confirm that the transition state structure smoothly

connected the reactants and products along the reaction coordinate, and the vibrational mode associated with the imaginary frequency was examined to confirm that it corresponded to the correct movement of involved atoms.[58-60]

Description of Methods Used to Find Minimum Energy Crossing Points (MECP)

The first step of the catalytic cycle is the addition of molecular oxygen to a palladium hydride. Palladium hydrides are ground-state singlets and molecular oxygen is a ground-state triplet.[12] The product palladium hydroperoxides are much more stable as singlets than as triplets, making the overall conversion formally spin-forbidden, as shown in Figure 2-1. The large spin-orbit coupling constant of palladium allows the reaction to cross from the triplet surface of reactants to the singlet surface of the palladium hydroperoxide product;[13] this is particularly important when the singlet and triplet potential energy surfaces intersect near a transition state. To locate the minimum energy crossing point between these two potential energy surfaces, the methodology introduced by Harvey and coworkers[61-63] was employed. This technique combines the energies and gradients of the singlet and triplet surfaces into effective gradients that can be followed to locate the geometry and energy of the MECP structure.

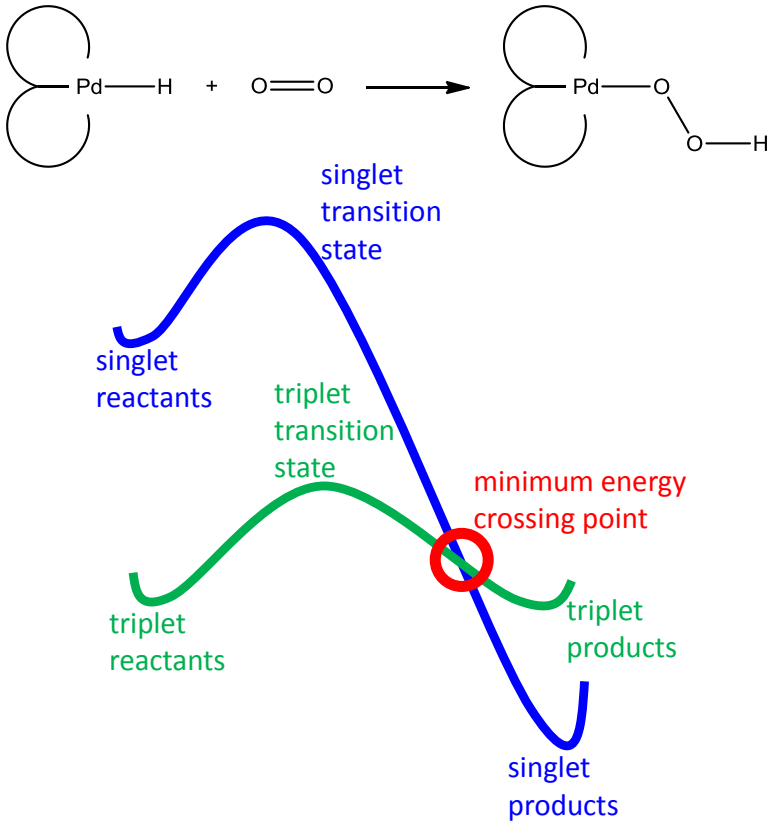


Figure 2-1: The minimum energy crossing point (MECP) is the point along the reaction coordinate at which the singlet and triplet potential energy surfaces intersect

Confirmation of Geometry Optimizations

The vast majority of the palladium complexes examined are proposed complexes that have not been prepared experimentally. However, there are seven palladium hydrides and two palladium hydroperoxides with published crystal structures. For each of those nine complexes, the published crystal

structures were compared with the optimized calculated geometries obtained in computationally to confirm that the calculated geometries were reasonable.

The comparisons were done using the “calculate structure overlay” feature in the Mercury[64-67] structural visualization program. Calculated geometries of these complexes were optimized in the gas phase, while the crystal structures are taken from solid-state structures in which crystal packing forces may alter the geometry of peripheral groups. Rather than comparing every atom in the complex, only the palladium, metal-bound hydrogen (if located crystallographically), atoms directly attached to palladium, and other core atoms were compared. Counterions, hydrogen atoms other than the palladium-bound hydrogen, and other remote atoms were not compared. Comparisons of the crystal structures and optimized calculated geometries are described below.

Figure 2-2 shows the structure overlay for (bis(4-fluoro-2-(di-isopropylphosphino)phenyl)amide-N,P,P’)palladium hydride (**3**), a complex reported by Ozerov and coworkers in 2004.[68] The core atoms of the calculated structure provide an excellent atomic position match with the corresponding atoms in the crystal structure, with less than 0.1 Å difference for each atom in the structure overlay and root-mean-square (RMS) difference of 0.03 Å. The palladium-bound hydride was not included in the structure overlay because it could not be crystallographically located in the crystal structure.

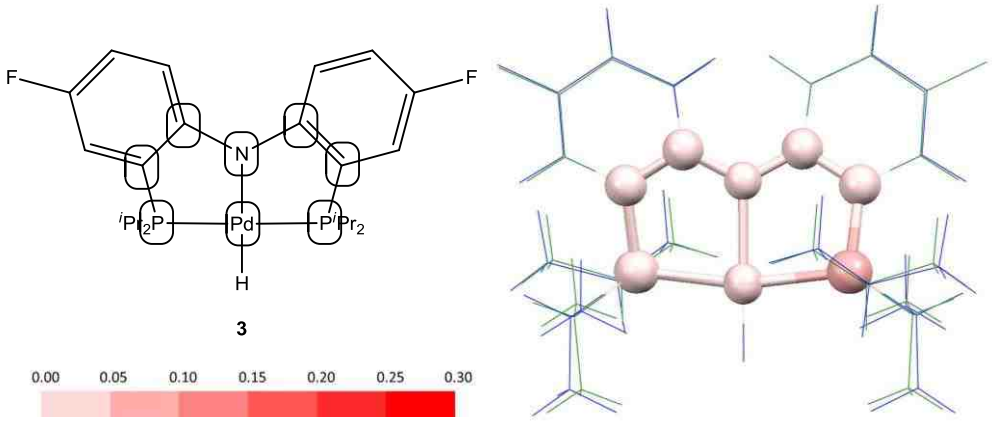


Figure 2-2: Structure overlay geometry agreement between crystal structure[68] (green) and computationally optimized geometry (blue) for (bis(4-fluoro-2-(di-isopropylphosphino)phenyl)amide-N,P,P')palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay.

The structure overlay for (2,5-bis((di-*tert*-butylphosphino)methyl)ferrocen-1-yl-C,P,P')palladium hydride[69] (**4**) is shown in Figure 2-3. The core atoms of the calculated structure, including iron, match excellently with the corresponding atoms in the crystal structure, with less than 0.1 Å difference in the positions of all atoms in the structure overlay. The RMS difference in core atom position was 0.04 Å. Because the hydride atom bridged the palladium atom and borane in the crystal structure, it was not included in the structure overlay.

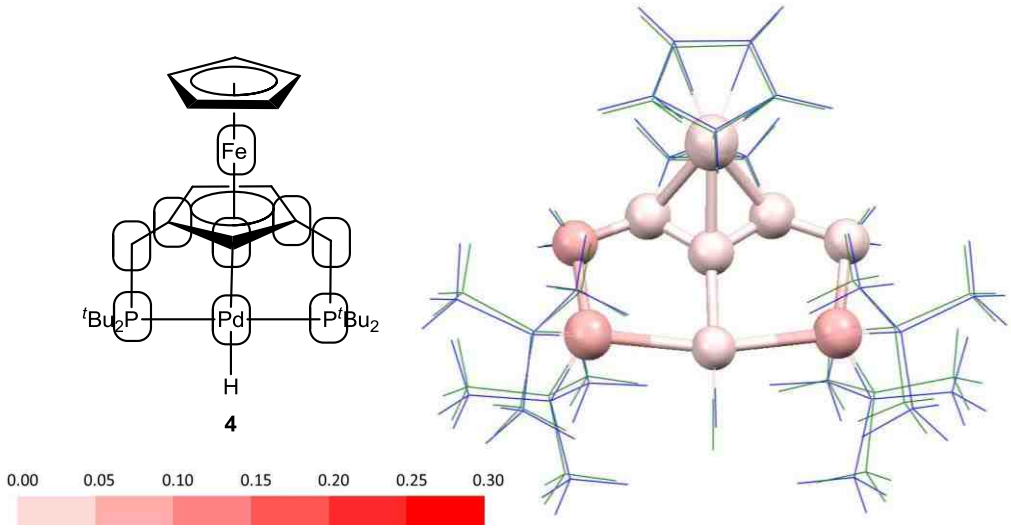


Figure 2-3: Structure overlay geometry agreement between crystal structure[69] (green) and computationally optimized geometry (blue) for (2,5-bis((di-*tert*-butylphosphino)methyl)ferrocen-1-yl-C,P,P')palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay.

Figure 2-4 shows the structure overlay for (bis(4-methyl-2-(di-isopropylphosphino)phenyl)amide-N,P,P')palladium hydroperoxide[70] (**5**). The core atoms of the calculated structure match very well with the corresponding atoms in the crystal structure, with less than 0.1 Å difference for all atoms in the structure overlay and RMS difference of 0.05 Å. The hydroperoxide oxygen and hydrogen atoms were not included in the structure overlay due to the inherent flexibility of that group.

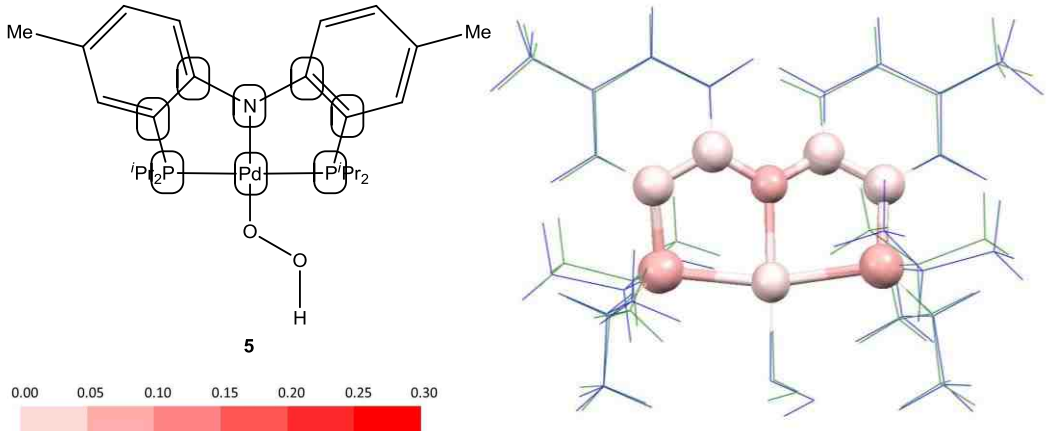


Figure 2-4: Structure overlay geometry agreement between crystal structure[70] (green) and computationally optimized geometry (blue) for (bis(4-methyl-2-(di-isopropylphosphino)phenyl)amide-N,P,P')palladium hydroperoxide. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay.

The structure overlay for (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydride[71] (**1**) is shown in Figure 2-5 below. The core atoms of the calculated structure provide an excellent atomic position match with the corresponding atoms in the crystal structure, with less than 0.1 Å difference for all atoms in the structure overlay and RMS difference in core atom position 0.05 Å. The palladium-bound hydrogen atom position was not used for the structure overlay because it could not be crystallographically located in the crystal structure.

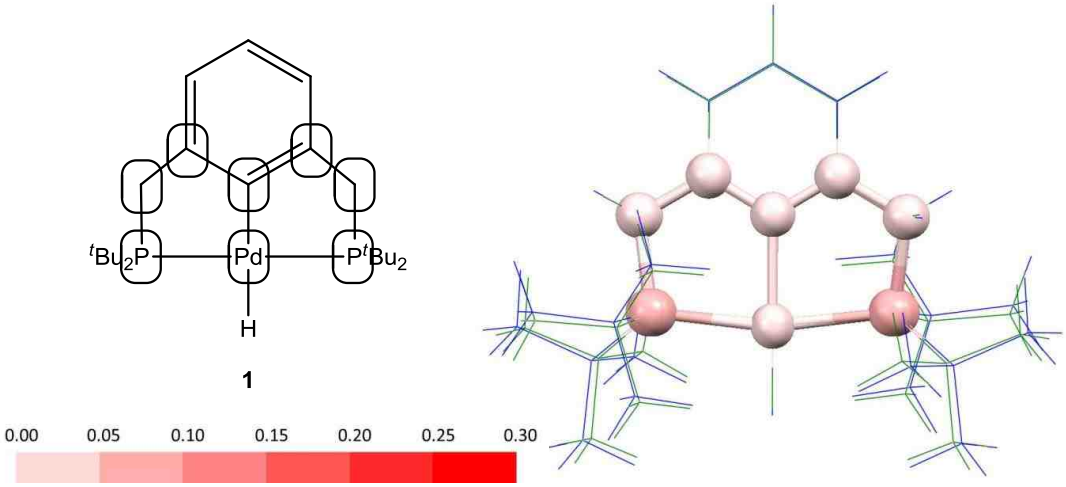


Figure 2-5: Structure overlay geometry agreement between crystal structure[71] (green) and computationally optimized geometry (blue) for (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay.

The computed geometry and crystal structure for (1,3-bis(2-(di-isopropylphosphino-P)phenyl)imidazolidin-2-ylidene)palladium hydride[72] (**6**) are shown in Figure 2-6. The core atoms of the calculated structure provide a very good atomic position match with the corresponding atoms in the crystal structure, with less than 0.1 Å difference in all of the core atoms in the structure overlay. The RMS difference in core atom position was 0.08 Å. The palladium-hydrogen bond length in the crystal structure of **6** is significantly longer than the corresponding bond in the optimized calculated geometry (1.77 Å in the crystal structure, 1.61 Å in the computed geometry), differing by 0.16 Å. Although the position of the hydride was located and refined isotropically in the crystal structure,[72] the palladium-hydrogen bond is quite long. An analysis of similar structures (four-coordinate palladium hydrides with the hydride bound only to

palladium) in the Cambridge Structural Database[73] revealed that **6** has an unusually long palladium-hydrogen bond: of the seventeen similar palladium hydrides included in the analysis, the palladium-hydrogen bond in **6** is almost 0.12 Å longer than the next longest palladium-hydride bond. The mean bond length among similar complexes is 1.56 Å, with fifty percent of complexes having bond lengths between 1.52 Å and 1.61 Å (see Figure 2-7). The bond distance in the computed geometry is typical of bond distances in crystal structures of similar complexes. Although the authors of this crystal structure mentioned that the palladium-hydride bond distance was unusually long,[72] they did not provide an explanation for it.

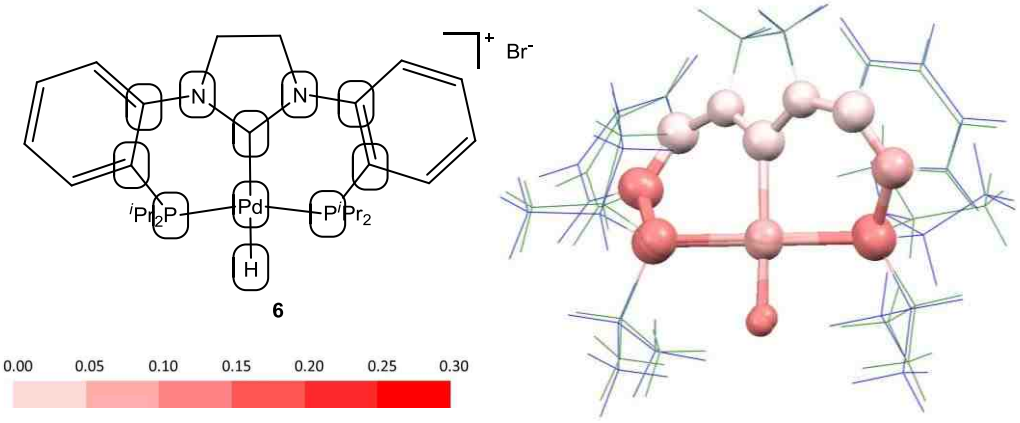


Figure 2-6: Structure overlay geometry agreement between crystal structure[72] (green) and computationally optimized geometry (blue) for (1,3-bis(2-(di-isopropylphosphino-P)phenyl)imidazolidin-2-ylidene)palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay.

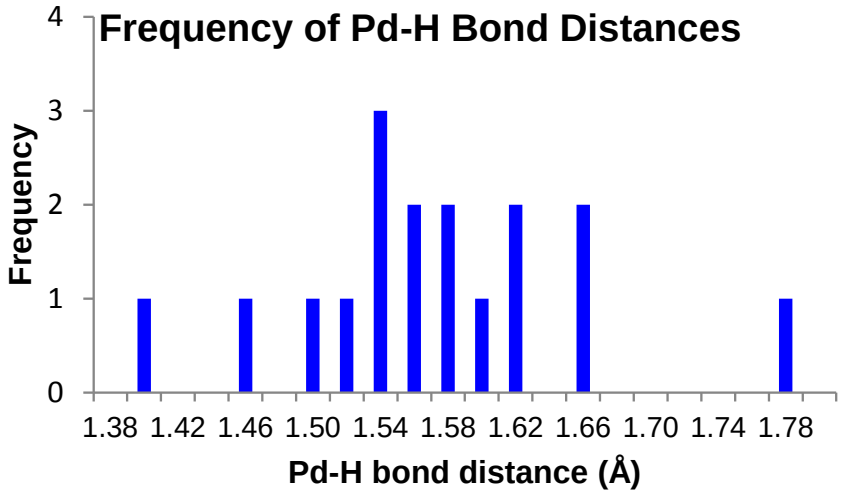


Figure 2-7: Analysis of palladium-hydrogen bond distances in crystal structures in the Cambridge Structural Database[73] based on four-coordinate palladium hydride complexes in which the hydride is bound only to palladium

Figure 2-8 shows the structure overlay for (2-(diisopropylphosphino)-N-(2-(diisopropylphosphino)-4-methylphenyl)-4-methylaniline)palladium hydride[74] (**7**). The core atoms of the calculated structure match very well with the corresponding atoms in the crystal structure, with less than 0.15 Å difference for all atoms in the structure overlay and RMS difference of 0.08 Å. The palladium-hydrogen bond lengths in the crystal structure and optimized calculated geometry are remarkably similar, differing by only 0.03 Å (1.54 Å in the crystal structure, 1.57 Å in the computed geometry).

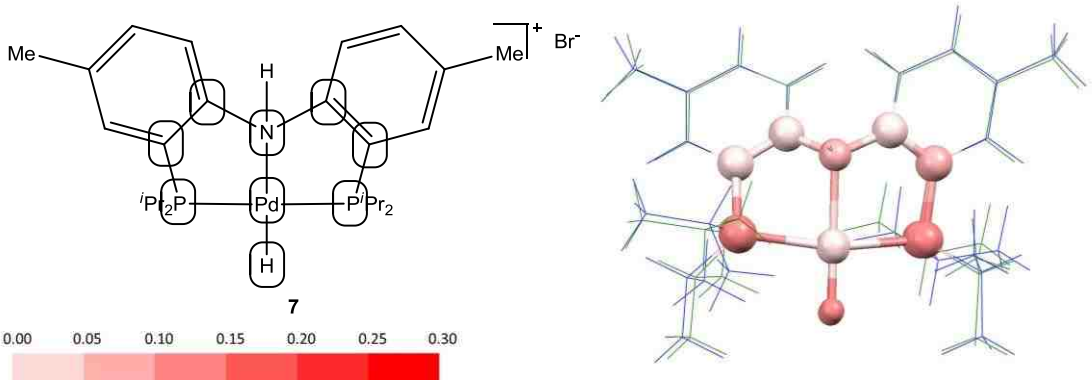


Figure 2-8: Structure overlay geometry agreement between crystal structure[74] (green) and computationally optimized geometry (blue) for (2-(diisopropylphosphino)-N-(2-(diisopropylphosphino)-4-methylphenyl)-4-methylaniline)palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay.

Figure 2-9 shows the structure overlay for (P,P-bis(3-diethylphosphinopropyl)phenylphospino)palladium hydride[75] (**8**). The flexibility of the propyl linkers makes this complex particularly conformationally sensitive to its local environment. Because of this, only the palladium, palladium-bound hydrogen, and three phosphorus atoms were included in the structure comparison. The computed and crystal structure geometries still match relatively well, with an RMS difference of only 0.11 Å and a maximum difference less than 0.15 Å for every compared atom. It is apparent from the figure, however, that the remote atoms do not align well with one another; this discrepancy is attributed to the packing of the crystal structure in this very flexible molecule. The palladium-hydrogen bond lengths in the crystal structure and optimized calculated geometry are very similar, differing by only 0.05 Å (1.65 Å in the crystal structure, 1.59 Å in the computed geometry).

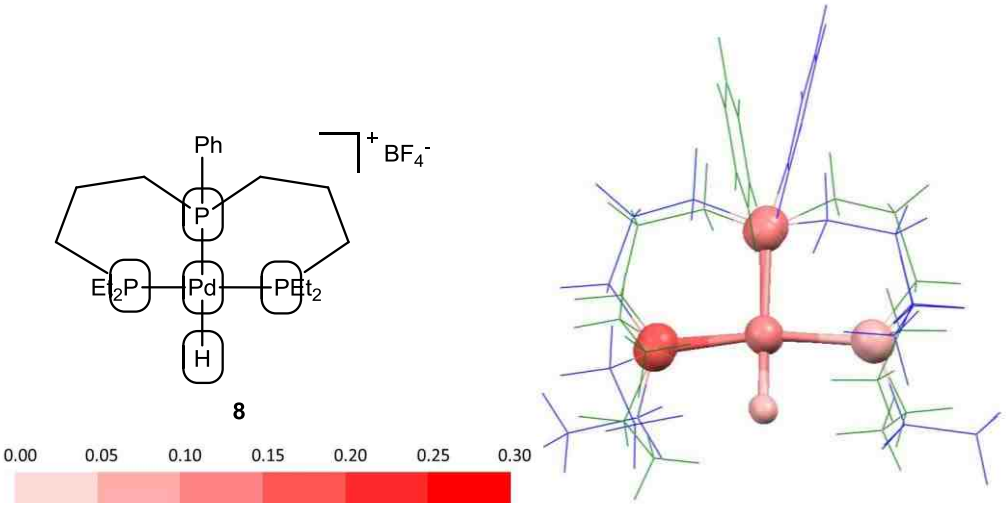


Figure 2-9: Structure overlay geometry agreement between crystal structure[75] (green) and computationally optimized geometry (blue) for (P,P-bis(3-diethylphosphinopropyl)phenylphospino)palladium hydride. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay.

The computed geometry and crystal structure for (2,6-bis(di-isopropylphosphinomethyl)phenyl)palladium hydride[76] (**9**) are shown in Figure 2-10a. Although the RMS difference in atom locations is only 0.11 Å, the two phosphorus atoms and one methylene carbon have only moderately good overlap, with location differences of 0.16 Å to 0.17 Å for these three atoms. This discrepancy is due to the difference in "twist" of the two geometries: when the dihedral angles formed from the *ortho* phenyl carbon, *ipso* phenyl carbon, palladium, and phosphorus are compared, the crystal structure geometry has a significantly smaller dihedral angle than the optimized calculated geometry (5.3º for crystal structure geometry, 12.0º for calculated geometry). This can be seen

by viewing the complexes along the hydrogen-palladium bond, as in Figure 2-10b below. An analysis of similar structures (four-coordinate palladium complexes containing a tridentate ligand bound to palladium through two phosphorus atoms and a phenyl ring) in the Cambridge Structural Database[73] revealed that the dihedral angle of the calculated geometry is typical of similar complexes: of the thirty-four structures included in the analysis, only five have dihedral angles 5.3º or smaller. The average dihedral angle for similar crystal structures is 11.1º, with fifty percent of complexes having dihedral angles between 5.9º and 15.8º (see Figure 2-11). It is important to note that the crystal structure of this complex was found to be a dimer, and the palladium hydride fragment co-crystalized with two molecules of K-Selectride® reagent (potassium tri-*sec*-butylborohydride). It is possible that the presence of K-Selectride reagent forced the complex into a conformation in which the aromatic ring and the plane defined by palladium and the two phosphorus atoms were closer to co-planarity than they would have been in the gas phase or in the absence of K-Selectride complex. Despite the fact that the K-Selectride fragment is complexed to the hydride in the crystal structure, the palladium-hydrogen bond lengths in the crystal structure and optimized calculated geometry are nearly identical at 1.65 Å.

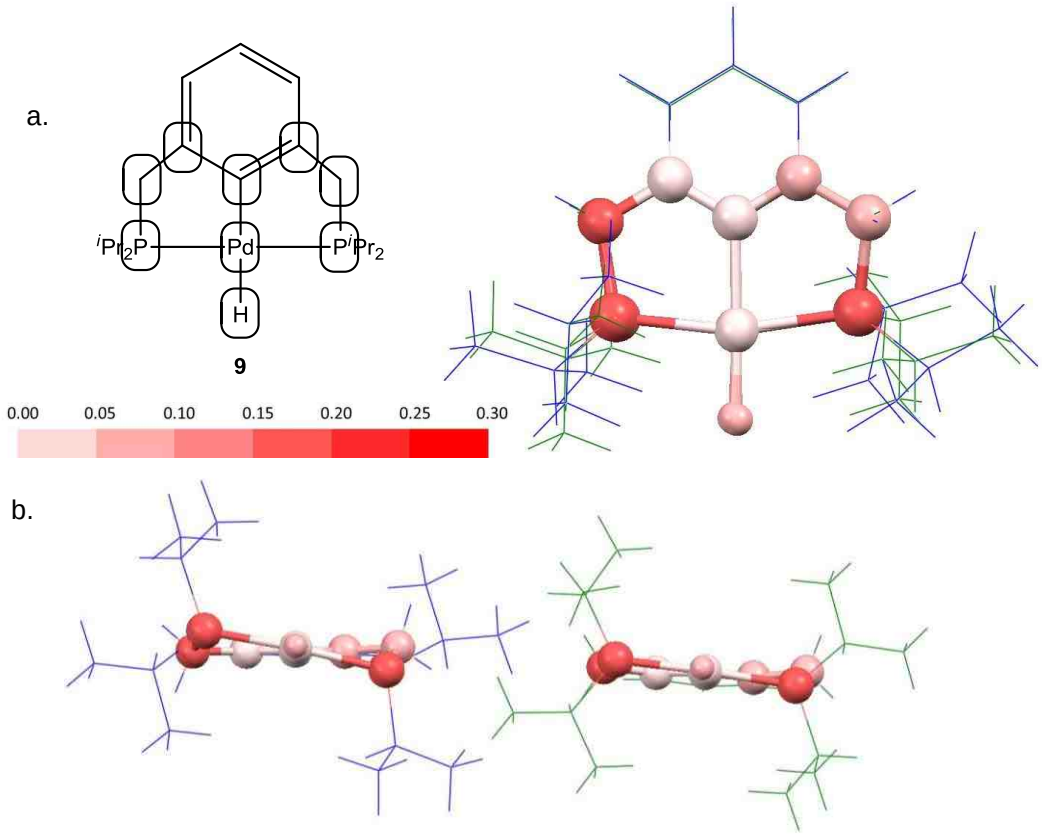


Figure 2-10: (a) Structure overlay geometry agreement between crystal structure[76] (green) and computationally optimized geometry (blue) for (2,6-bis(di-isopropylphosphinomethyl)phenyl)palladium hydride, and (b) view of crystal structure (green) and computationally optimized geometry (blue) projected along the hydrogen-palladium bond. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay.

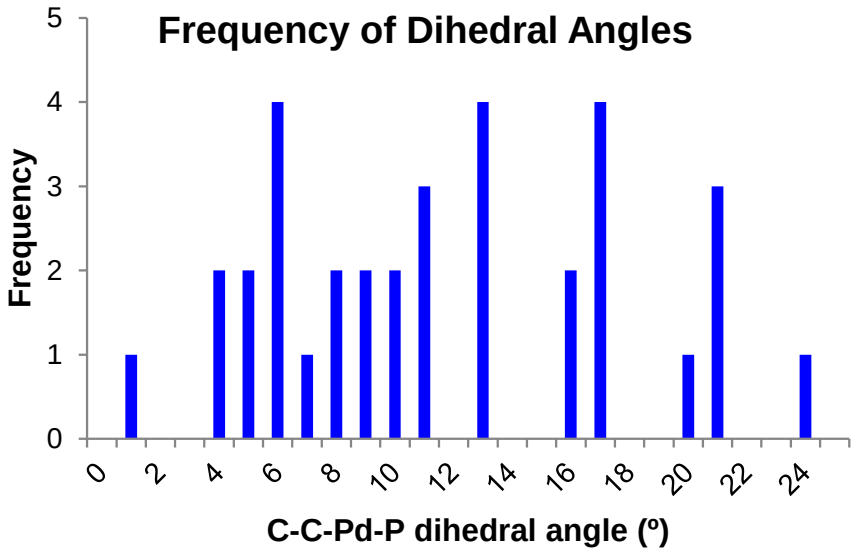


Figure 2-11: Analysis of *ortho*-carbon, *ipso*-carbon, palladium, phosphorus dihedral angles in crystal structures, in the Cambridge Structural Database[73] based on four-coordinate palladium complexes containing a tridentate ligand bound to palladium through two phosphorus atoms and a phenyl ring

The structure overlay for (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydroperoxide[36] (**2**) is shown in Figure 2-12. With an RMS difference in atom locations of 0.17 Å, these two geometries match only moderately well, with the two phosphorus atoms and one methylene carbon providing the largest discrepancies in the overlay. This large discrepancy is again due to the dihedral angle formed from the *ortho*-carbon, *ipso*-carbon, palladium, and phosphorus: the crystal structure has an unusually small dihedral angle, relative to both the calculated geometry and other similar crystal structures. Crystal structures of similar complexes have a significantly larger dihedral angle (see Figure 2-11 above for an analysis of the dihedral angles in crystal structures

of similar complexes). The crystal structure for this complex has a dihedral angle of only 0.6º, the smallest dihedral angle in the Cambridge Structural Database.[73] The calculated structure has a dihedral angle of 10.6º, which is much more typical of the crystal structures of similar complexes.

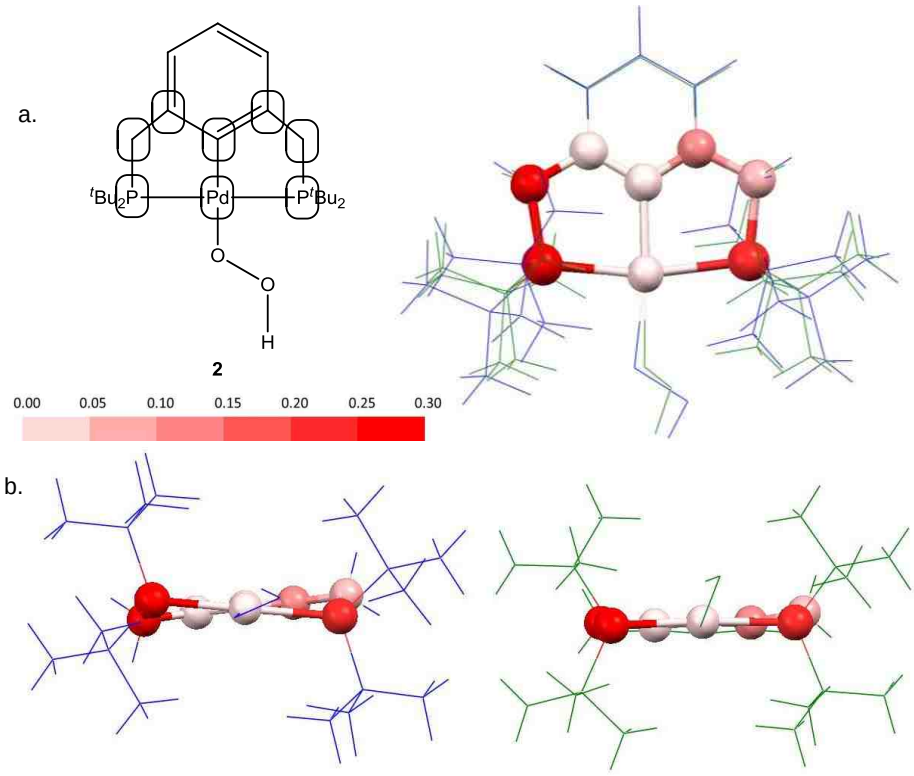


Figure 2-12: (a) Structure overlay geometry agreement between crystal structure[36] (green) and computationally optimized geometry (blue) for (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydroperoxide, and (b) view of crystal structure (green) and computationally optimized geometry (blue) projected along the palladium-*ipso*-carbon bond. Circled atoms were used to prepare the structure overlay. Color scale shows difference in atom position (in Å) for structure overlay.

This analysis shows that the calculated optimized geometries presented here match extremely well with known experimental geometries, with RMS

distance differences of less than 0.17 Å for core atoms. The three structures in which the geometries matched least well are worth noting. For **8** (shown in Figure 2-9 above), the ligand is particularly flexible, making the conformation very sensitive to packing in the crystal structure. In the crystal structure of **9** (shown in Figure 2-10 above), the dihedral angle formed by the *ortho*-carbon, *ipso*-carbon, palladium, and phosphorus is significantly smaller than the corresponding dihedral angle of the computed geometry. Significantly, the dihedral angle of the computed geometry is much more typical of dihedral angles found in similar structures than is the dihedral angle of the crystal structure itself. The crystal structure of this particular complex is a dimer co-crystalized with two molecules of K-Selectride reagent, which was likely responsible for coplanarity of the aromatic ring and the plane defined by palladium and two phosphorus atoms in the crystal structure. Likewise, the dihedral angle formed by the *ortho*-carbon, *ipso*-carbon, palladium, and phosphorus is significantly smaller than the corresponding dihedral angle of the computed geometry in **2**. This can be seen in Figure 2-12 above. Again, the dihedral angle of the computed geometry is much more typical of similar dihedral angles found in related structures than is the dihedral angle of the crystal structure itself.

For three of the four palladium hydride complexes in which the palladium-bound hydrogen was crystallographically determined, the calculated palladium-hydrogen bond lengths matched exceptionally well with corresponding bonds in the crystal structures (within 0.05 Å). For the fourth complex, the palladium-

hydrogen bond distance did not match well, but the palladium-hydrogen bond distance in the crystal structure was noted by the authors to be unusually long. As noted above, the calculated palladium-hydrogen bond distance was very similar to palladium-hydrogen bond distances found in similar crystal structures.

Overall, these results confirm that the geometry optimizations presented here are providing appropriate and reasonable representations of the complexes being examined. This validation provided the confidence necessary to draw conclusions from the geometry optimization calculations done in the following chapters.

Confirmation of Reaction Coordinates

Further verification of the methods used here was performed by reproducing the reaction coordinate presented by Goddard and coworkers[38] for the insertion of molecular oxygen into a palladium-hydride bond. Despite a slight difference in methods, the energies obtained for reactants, transition state, intermediate, and products were very similar, with energy differences of at most 2.2 kcal/mol between the energies calculated by Goddard and coworkers and the values calculated here. The predicted energies of the minimum energy crossing point (MECP), however, differed by 5.9 kcal/mol, which is significant. This 5.9 kcal/mol variation is most likely due to differences in implementation of the MECP program in the two calculations. These results will be discussed in more detail in

Chapter 3 below. Additionally, the reaction pathways considered by Goldberg, Kemp, and coworkers[40] for the regeneration of palladium hydride from palladium hydroxide were reproduced to further validate the methods used here. Energies for stable species (reactants, products, and intermediate) differed from those reported in the literature by at most 2.5 kcal/mol and energies for the transition state differed by 4.6 kcal/mol. These results will be discussed in more detail in Chapter 5 below.

Chapter 3: Insertion of Molecular Oxygen into a Palladium-Hydride Bond to Form a Palladium Hydroperoxide

First Step of Proposed Catalytic Cycle

The first step of the proposed catalytic cycle, direct insertion of molecular oxygen into a palladium-hydride bond, is known experimentally[36] and has been studied computationally.[38] A generic form of this reaction is shown in Figure 3-1.

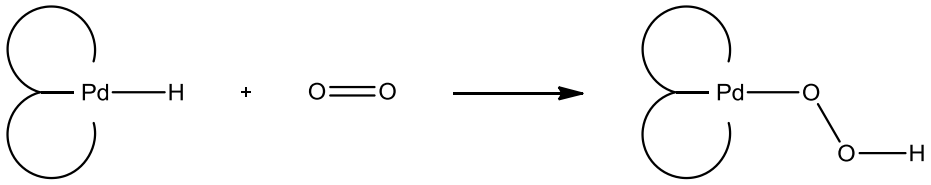


Figure 3-1: First step of proposed catalytic cycle is insertion of oxygen into palladium-hydride bond

Experimentally, this reaction was demonstrated by Goldberg, Kemp, and coworkers[36] for (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydride (**1**). The resulting palladium hydroperoxide **2** is stable in the solid phase in the absence of light, but decomposes in solution and in the presence of light to the corresponding palladium hydroxide (Figure 3-2).

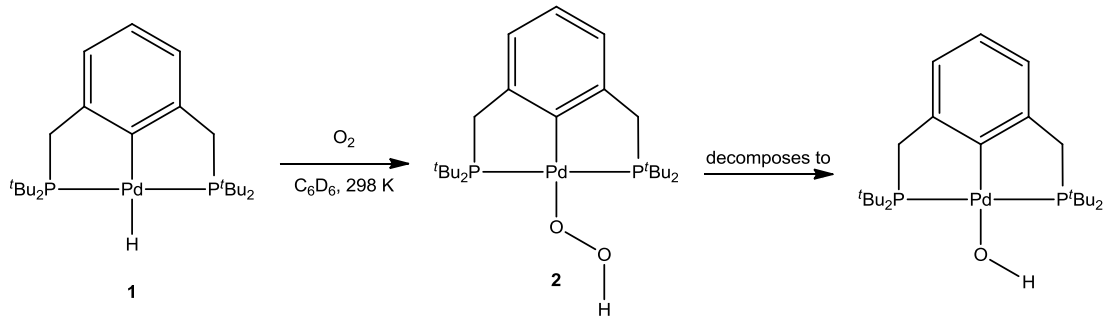


Figure 3-2: Experimental evidence for insertion of oxygen into palladium-hydride bond demonstrated by Goldberg, Kemp, and coworkers[36]

Computational Insight into Reaction Mechanism

The mechanism of oxygen insertion into palladium-hydride bonds has been the subject of several recent publications.[37,38,77-87] Goddard, Goldberg, Kemp, and coworkers elucidated the mechanism for this reaction using quantum mechanics for a model pincer-based system (2,6-bis(phosphinomethyl)phenyl-C-P-P')palladium hydride.[38] The introduction of oxygen led to a transition state with a 13 kcal/mol barrier and then to an intermediate in which the oxygen had abstracted hydrogen away from palladium. This intermediate can be thought of as a palladium(I)/hydroperoxy radical pair that are closely associated with one another. This triplet intermediate complex can then rearrange and undergo a spin flip at a minimum energy crossing point that is 12 kcal/mol higher in energy than the reactants, resulting in a singlet palladium(II) hydroperoxide that is 27 kcal/mol more stable than the initial reactants. Note that the corresponding triplet product

is almost 7 kcal/mol less stable than the reactants. This reaction coordination is shown in Figure 3-3.

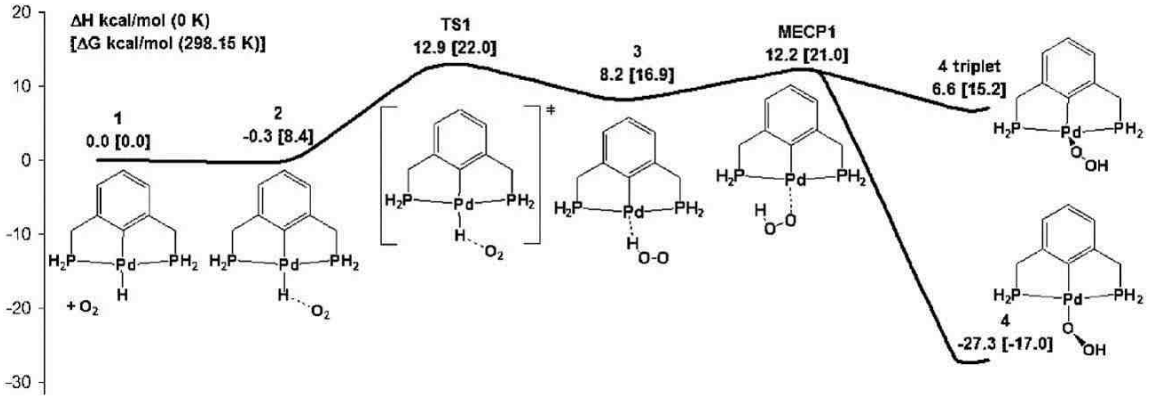


Figure 3-3: Reaction coordinate determined by the Goddard group[38] for insertion of oxygen into palladium-hydride bond. Reprinted with permission from Keith, Jason M.; Muller, Richard P.; Kemp, Richard A.; Goldberg, Karen I.; Goddard, William A., III; Oxgaard, Jonas. Mechanism of Direct Molecular Oxygen Insertion in a Palladium(II)-Hydride Bond. *Inorganic Chemistry* 2006, *45*, 9631-9633. Copyright 2006 American Chemical Society.

The reaction coordinate shown does not indicate an explicit transition state between the palladium(I)/hydroperoxy radical pair intermediate and product palladium hydroperoxides, but it is apparent that some transition state must exist on the reaction coordinate between these two stable complexes. Kinetics experiments performed by Goldberg, Kemp, and coworkers[36] provided insight into the relative energies of the first transition state, identified in the reaction coordinate above, and the second transition state, not explicitly identified but presumably located near the minimum energy crossing point. When the palladium-bound hydrogen atom was replaced by deuterium, the authors noted a

significant retardation in the observed reaction rate, corresponding to a kinetic isotope effect (k_H/k_D) of 5.8(5) (see Figure 3-4). This large observed kinetic isotope effect strongly suggests that the palladium-bound hydrogen atom is involved in the rate-determining step of the reaction. This is consistent with the first transition state along this reaction coordinate having higher energy than the second transition state.

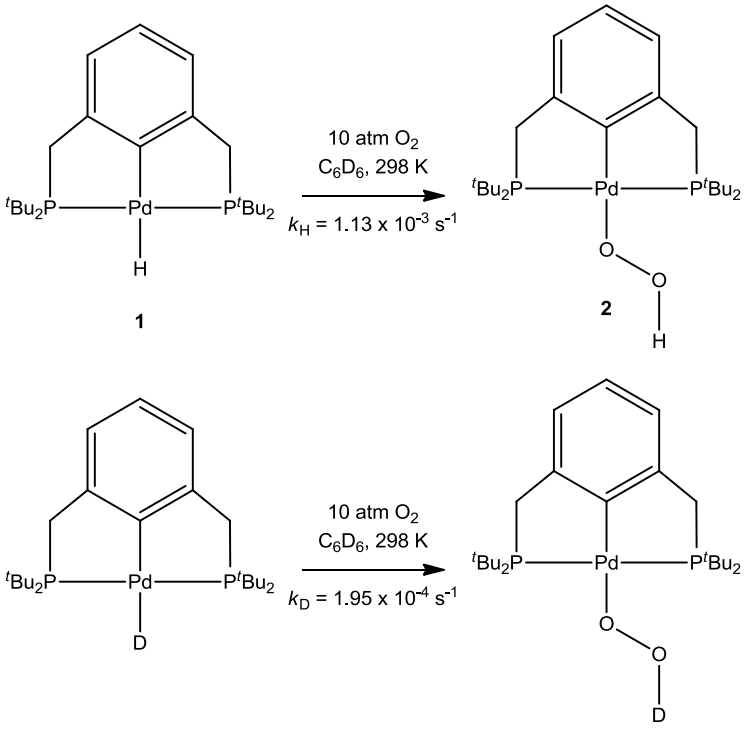


Figure 3-4: Kinetic isotope experiment performed by Goldberg, Kemp, and coworkers[36] for oxygen insertion into palladium-hydrogen bond

Experimental demonstration of this reaction for a system in which palladium was bound to a tridentate ligand without free lone pairs of electrons[36] refuted the idea initially proposed by Goddard and coworkers in 2005[37] that the

metal center must be coordinated to a ligand with a lone pair of electrons in order to facilitate oxygen insertion. For a palladium hydride containing a bidentate ligand and lone-pair-bearing chloride ligand, oxygen insertion proceeds from a transition state similar to that shown above through an intermediate in which the hydrogen atom of the palladium hydroperoxide is hydrogen-bonded to chlorine. This reaction coordinate is shown in Figure 3-5. More recent experimental and computational work by Stahl and coworkers[79,87] suggests that, for palladium hydrides with a lone-pair-bearing ligand such as chloride, the insertion of oxygen into the palladium-hydride bond will occur in three discrete steps: reductive elimination of hydrogen chloride, addition of oxygen to form an η^2 peroxopalladium species, and finally oxidative addition of hydrogen chloride, resulting in the palladium hydroperoxide. This pathway is shown in Figure 3-6.

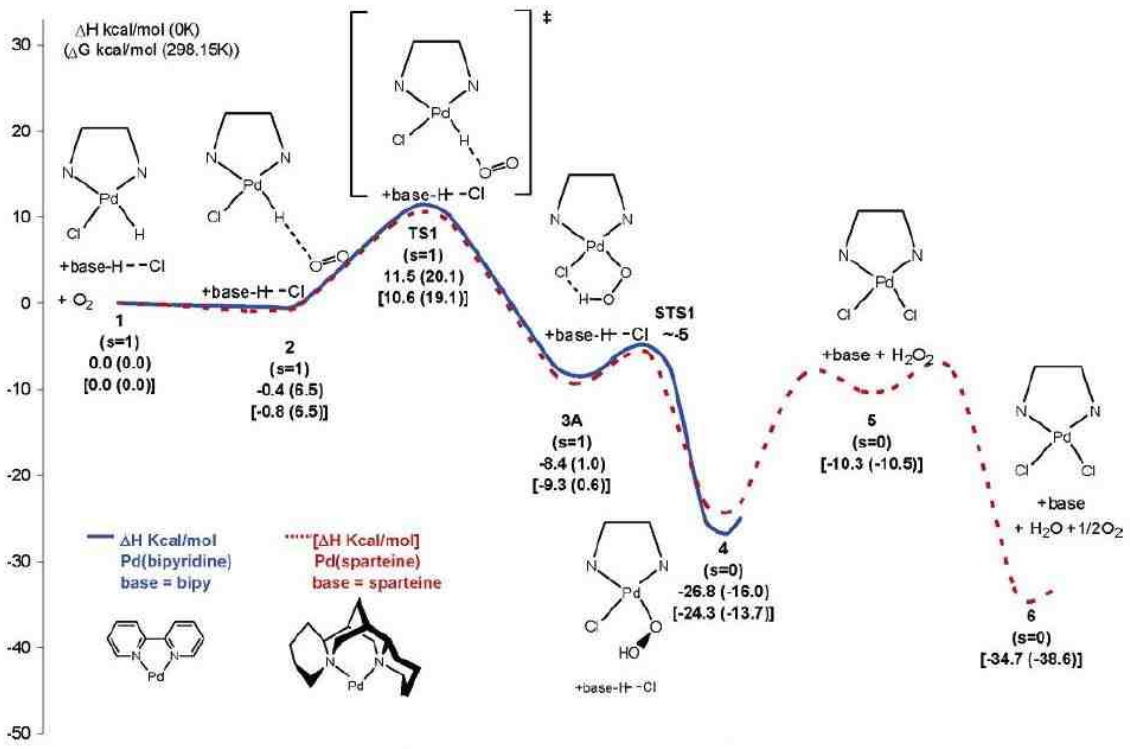


Figure 3-5: Reaction coordinate prepared by Goddard and coworkers in 2005[37] for insertion of oxygen into a palladium-hydride bond with a lone-pair-bearing ligand. Reprinted with permission from Keith, Jason M.; Nielsen, Robert J.; Oxgaard, Jonas; Goddard, William A., III. Pd-Mediated Activation of Molecular Oxygen in a Nonpolar Medium. *Journal of the American Chemical Society* 2005, *127*, 13172-13179. Copyright 2005 American Chemical Society.

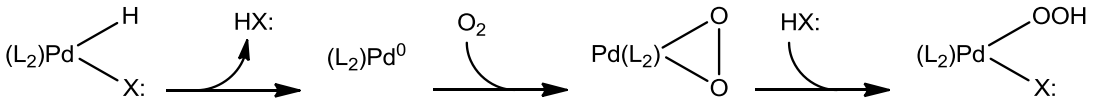


Figure 3-6: Oxygen insertion pathway proposed by Stahl and coworkers[87] for palladium hydrides containing a lone-pair-bearing ligand

Further insight into the mechanism of oxygen insertion was provided by the Russo group in 2007.[78] Russo and coworkers provided a detailed analysis of

the reaction coordinate along the singlet pathway, following the mechanism from the transition state identified by Goddard and coworkers[38] above through a very stable intermediate in which palladium is bound to the central oxygen of a hydroperoxy group. Rearrangement from this stable intermediate to the product palladium hydroperoxide is expected to be exothermic and proceeds through a low-energy transition state in which palladium is equidistant from both oxygen atoms. This reaction mechanism is shown in Figure 3-7 and reveals an alternative pathway for insertion of oxygen into the palladium hydride bond.

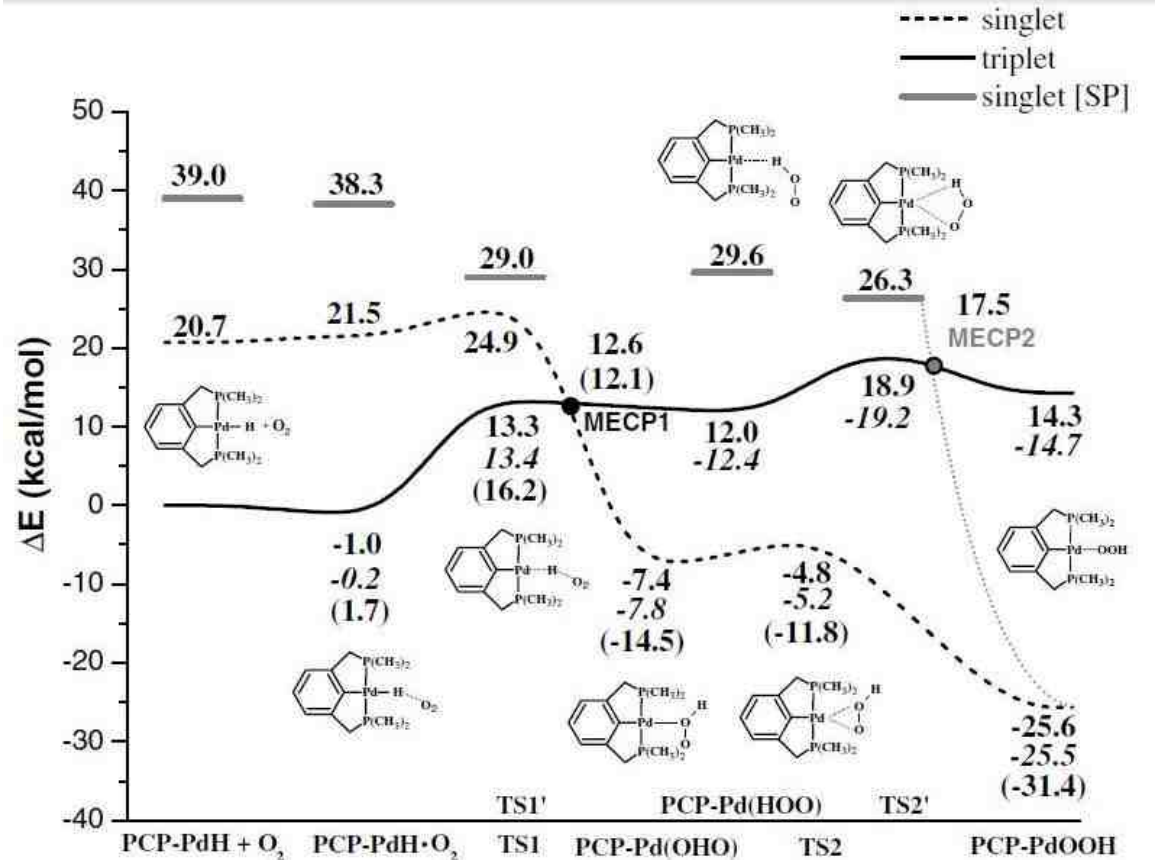


Figure 3-7: Further insight into the reaction coordinate of oxygen insertion into a palladium-hydride bond provided by Russo and coworkers,[78] showing both the triplet and singlet potential energy surfaces. Reprinted from *Chemical Physics Letters*, *443*, Chowdhury, Sugata; Rivalta, Ivan; Russo, Nino; Sicilia, Emilia, On the Insertion Mechanism of Molecular Oxygen into a Pd(II)-H Bond. Something to Add, pages 183-189, Copyright 2007, with permission from Elsevier.

Orientation of Oxygen and Palladium Hydride during Oxygen Insertion

There are several different ways in which the oxygen and palladium hydrides might interact; three of those possibilities are shown in Figure 3-8

below. First, the oxygen molecule could approach the hydrogen atom in the plane of the molecule to abstract hydrogen from palladium (Figure 3-8a). Alternatively, the oxygen molecule could approach the palladium-hydride bond above the plane of the molecule, with the two bonds parallel (Figure 3-8b) or with the oxygen-oxygen bond perpendicular to (Figure 3-8c) the palladium-hydride bond in preparation for either adding to palladium or abstracting hydrogen.

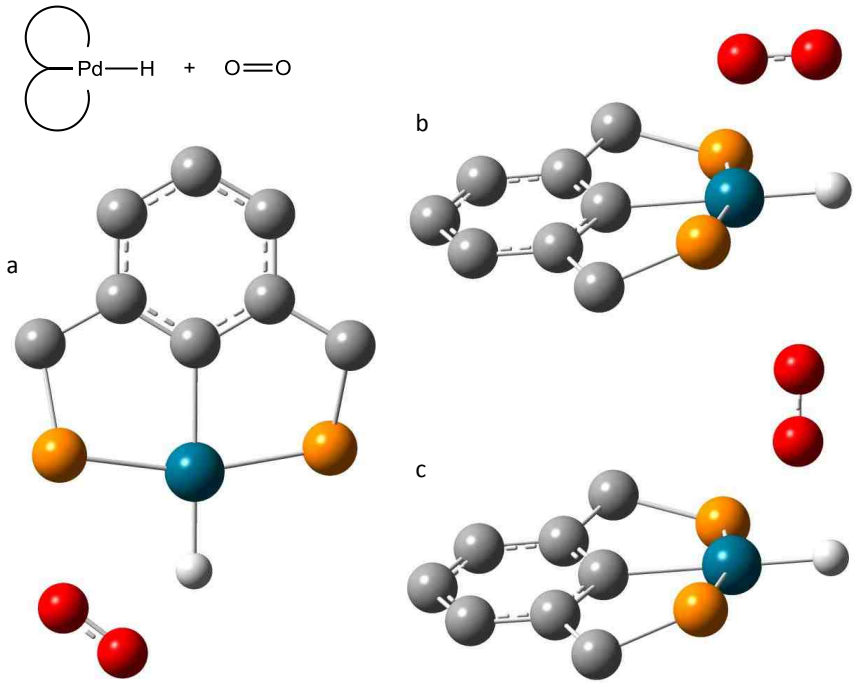


Figure 3-8: Three ways in which the palladium hydride and oxygen can interact: (a) oxygen approaches the hydrogen atom in the plane of the molecule; (b) oxygen approaches the palladium hydride above the plane of the molecule with oxygen parallel to the palladium-hydride bond, and (c) oxygen approaches the palladium hydride above the plane of the molecule with oxygen perpendicular to the palladium-hydride bond (note that all hydrogen atoms other than the palladium-bound hydrogen have been omitted for clarity)

In fact, the work done by Goddard and coworkers[38] indicates that the oxygen molecule approaches the hydrogen atom in the plane of the palladium hydride molecule in preparation for abstracting the hydrogen from the palladium. Palladium(II) has one empty d orbital, but that empty orbital is the $d_{(x^2-y^2)}$ orbital, which has lobes oriented toward the ligands and is therefore not particularly available for attack by oxygen. With attack of oxygen at the palladium atom blocked, oxygen instead abstracts the hydride, resulting in the intermediate palladium(I)/hydroperoxy radical pair shown in Figure 3-3 above.

Methods Verification by Reproduction of Known Computational Results

In order to verify the methods used here, the reaction mechanism calculations performed by Goddard and coworkers[38] were reproduced using their model system, (2,6-bis(phosphinomethyl)phenyl-C-P-P')palladium hydride (**10**). One significant difference between the methods used here and those used by the Goddard group is the software platform: Goddard and coworkers used the Jaguar 6.5 program,[88] while the calculations in this work were performed with Gaussian03.[46] The functionals used were identical (B3LYP[41,43]) and similar basis sets (LACVP*[47,49,50] in this work and LACVP** used by Goddard and coworkers[38]) were employed. Goddard and coworkers performed their calculations with implicit solvent effects for benzene using the Poisson-

Boltzmann continuum approximation, while solvent effects were ignored here. The reaction coordinates obtained by both Goddard and coworkers and in this work are shown in Figure 3-9.

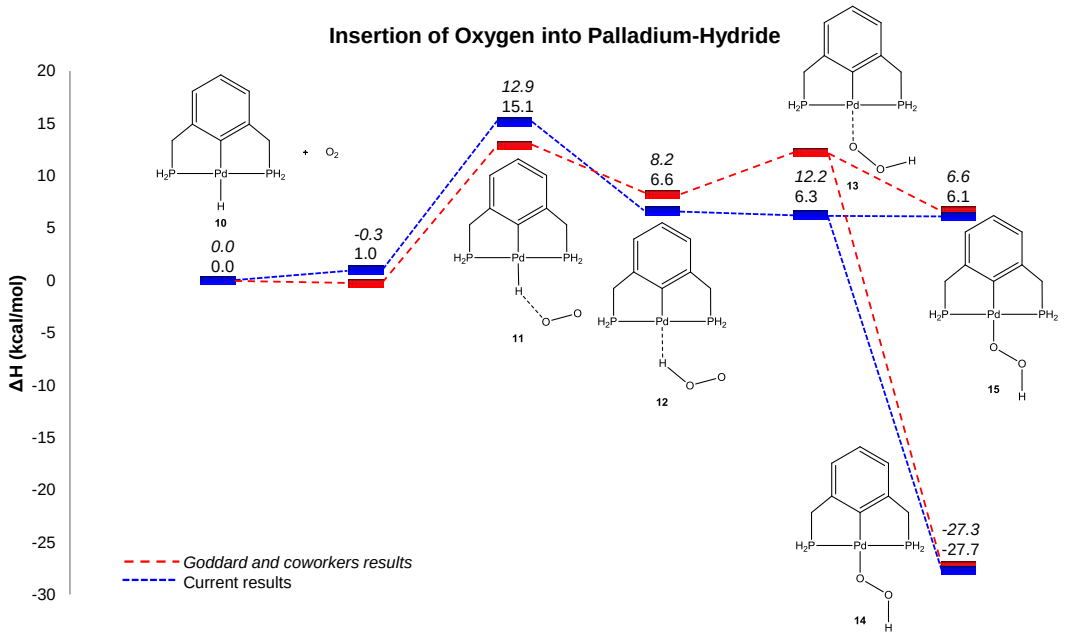


Figure 3-9: Reaction coordinate for insertion of oxygen into palladium-hydride bond, as calculated in this research and by Goddard and coworkers[38]

Despite the differences in methods, the results obtained were very similar, confirming that the methods used here are appropriate for a series of similar calculations. The energies obtained for the reactants, transition state, intermediate, and products differed from those obtained by Goddard and coworkers[38] by at most 2.2 kcal/mol, a reasonable difference considering the methods used were slightly different. At one stage of the calculations, however, the two results demonstrate considerable deviation: the predicted energies of the

minimum energy crossing point (MECP) differ significantly: 12.2 kcal/mol obtained by Goddard and coworkers[38] compared to 6.3 kcal/mol in this work. This difference is most likely due to differences in implementation of the Minimum Energy Crossing Point program between Jaguar and Gaussian.

All significant aspects of the structures of reactants, transition state, intermediate, and product are consistent with those published by Goddard and coworkers.[38] The palladium-hydrogen bond length in the optimized geometry of the reactant palladium hydride **10** is 1.63 Å; this bond length increases to 1.78 Å in the transition state **11**, with concomitant increase in oxygen-oxygen bond distance from 1.21 Å to 1.27 Å. The oxygen-hydrogen bond length in the transition state **11** is 1.35 Å, representing formation of the oxygen-hydrogen bond in the first step of the reaction. These changes can be seen in Figure 3-10.

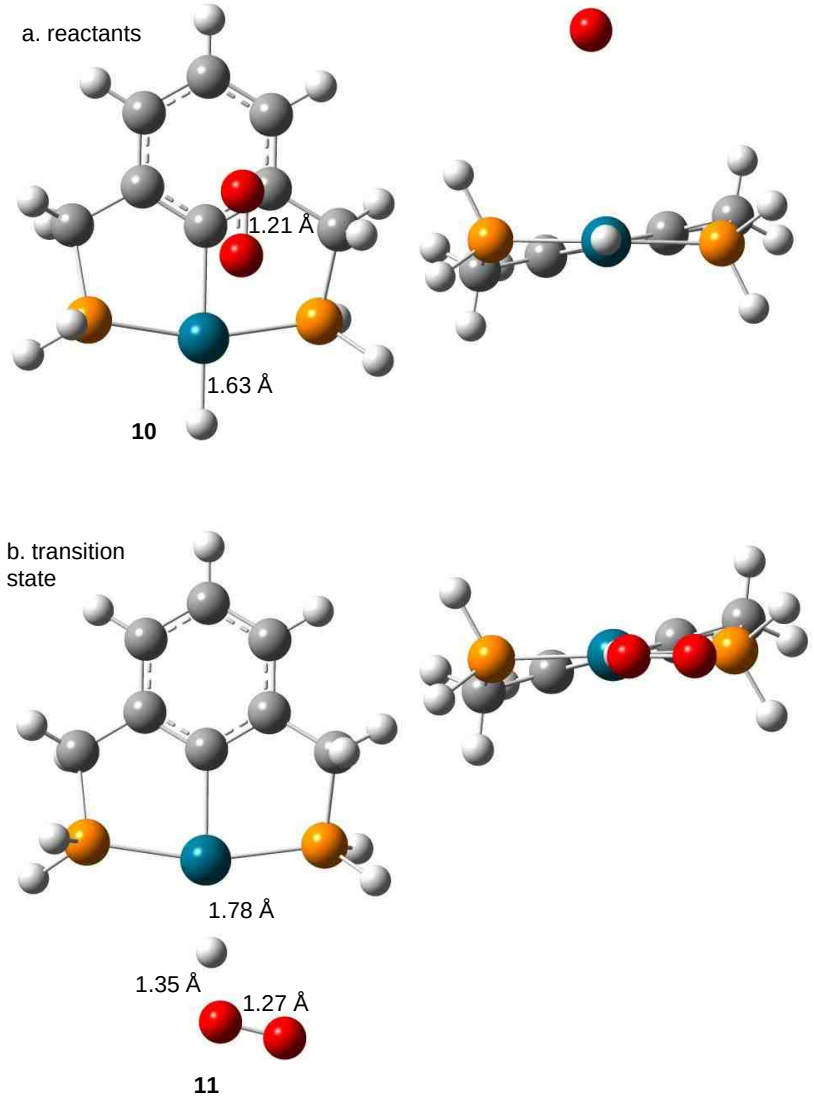


Figure 3-10: Optimized geometries of reactant palladium hydride (10) and transition state structure (11) for insertion of oxygen into palladium-hydride bond

The hydroperoxy radical in the palladium(I)/hydroperoxy radical pair intermediate **12** is orientated approximately 35° below the plane of the molecule and is 2.35 Å from the palladium atom, with the hydrogen atom of the hydroperoxy radical closest to palladium. In this intermediate, hydrogen is fully

bonded to oxygen, with a bond distance of 1.01 Å, while the oxygen-oxygen bond length has further increased to 1.33 Å. The palladium-oxygen bond length in the optimized structure at the minimum energy crossing point **13** is 2.16 Å and the oxygen-oxygen bond length is 1.42 Å. The alpha oxygen atom is 58° above the plane of the molecule. These changes can be seen in Figure 3-11.

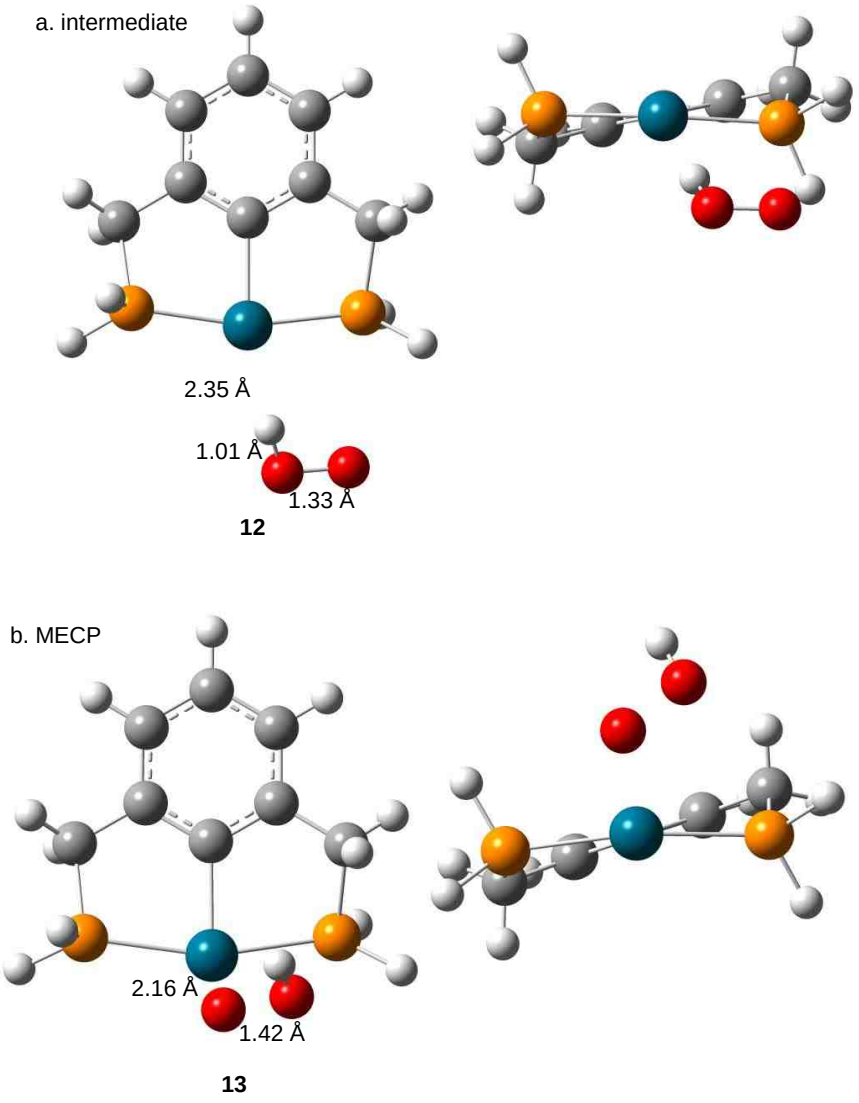


Figure 3-11: Optimized geometries of intermediate (12) and minimum energy crossing point structure (13) for insertion of oxygen into palladium-hydride bond

In proceeding from the minimum energy crossing point **13** to the singlet product palladium hydroperoxide **14**, both oxygen atoms move back into the plane of the molecule and closer to palladium, with a bond length of 2.06 Å between palladium and the alpha oxygen in the product. The oxygen-oxygen

bond length can now be described as a fully single bond, with a bond distance of 1.48 Å. The optimized geometry of the product singlet palladium hydroperoxide **14** can be seen in Figure 3-12. Note that the singlet palladium hydroperoxide is 33.8 kcal/mol more stable than the corresponding triplet palladium hydroperoxide **15**. Throughout this reaction coordinate, very little structural change occurs in the ligand or in the ligand attachments to palladium; almost all of the structural change occurs in the two oxygen atoms and hydrogen, as would be expected.

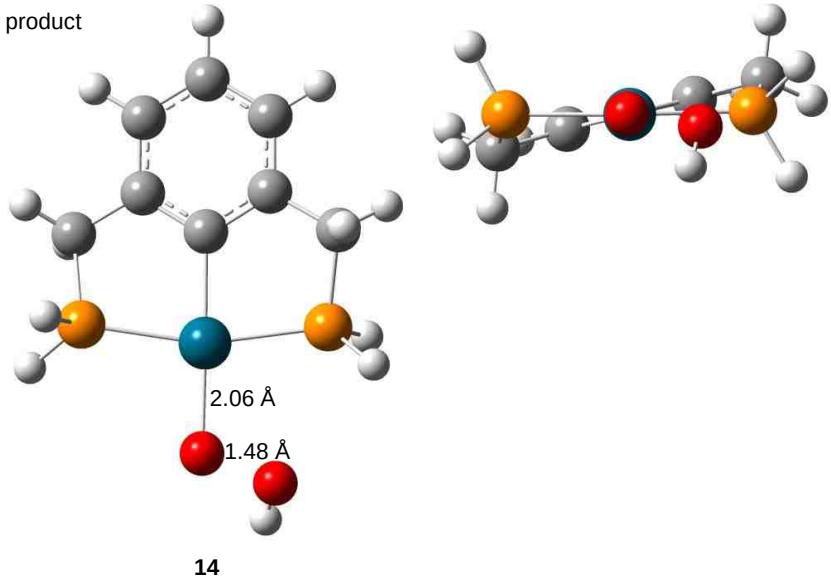


Figure 3-12: Optimized geometry of singlet product palladium hydroperoxide (14)

Palladium-Hydrogen Bond Dipole as a Proxy for Activation Barrier to Oxygen Insertion

Although the computations required to map out the reaction coordinate for insertion of molecular oxygen into a palladium-hydride bond are faster than experimental work, they still require a significant amount of time and computer resources. To further expedite the screening of these palladium hydrides, it would be advantageous to find some easily-calculated property of the palladium hydrides that could serve as a proxy for facility of oxygen insertion. One property that was hypothesized to reasonably correlate with ease of oxygen insertion is the palladium-hydride bond dipole. Recall that the first step of the oxygen insertion is abstraction of the hydrogen atom by oxygen. Because oxygen is an extremely electronegative element, more electropositive hydrogen atoms were expected to undergo hydrogen atom abstraction most readily. Therefore, palladium hydrides with relatively electropositive hydrogen atoms were expected to have the smallest transition state barrier for insertion of oxygen to form the corresponding palladium hydroperoxide. The electronegativity of the hydrogen atom is very easily determined computationally, allowing for rapid screening of the palladium hydride complexes and rapid identification of promising candidates for further experimental exploration.

To test this theory, the geometries of forty-nine palladium hydride complexes were optimized and palladium-hydride bond dipoles were calculated based on the optimized structures. The set of palladium hydrides considered all

contain a single tridentate ligand, resulting in primarily square-planar palladium hydrides. Most of the tridentate ligands studied are anionic, allowing palladium to exist in the palladium(II) oxidation state. Some of the ligands examined are neutral ligands; those complexes were modeled with a counterion to maintain the palladium(II) oxidation state. Examples of palladium hydride complexes with anionic ligands (Figure 3-13a) and neutral ligands with counterions (Figure 3-13b) are shown below.

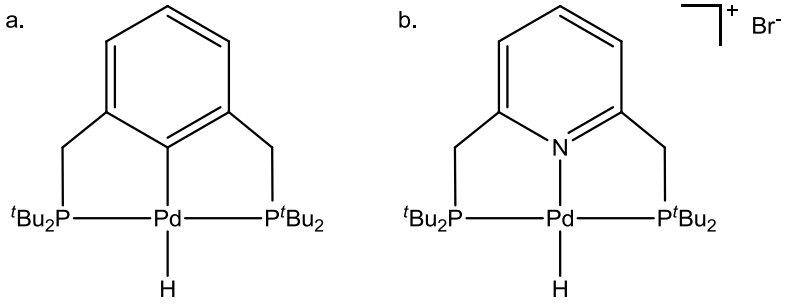


Figure 3-13: Examples of palladium hydride complexes with (a) anionic tridentate ligand and with (b) neutral tridentate ligand and counterion

The complexes examined were grouped by the atoms of attachment to palladium and are shown below. All of the complexes examined that coordinate to palladium through phosphorus-carbon-phosphorus (PCP) are shown in Figure 3-14, and the complexes that coordinate to palladium through phosphorus-nitrogen-phosphorus (PNP) are shown in Figure 3-15. Figure 3-16 shows the complexes that coordinate to palladium through either phosphorus-phosphorus-phosphorus (PPP), phosphorus-silicon-phosphorus (PSiP), phosphorus-carbon-

nitrogen (PCN), phosphorus-carbon-oxygen (PCO), oxygen-carbon-oxygen (OCO), or sulfur-carbon-sulfur (SCS). Complexes that coordinate to palladium through either carbon-carbon-carbon (CCC) or carbon-nitrogen-carbon (CNC) are shown in Figure 3-17, and the complexes that coordinate to palladium through nitrogen-nitrogen-nitrogen (NNN) or through nitrogen-carbon-nitrogen (NCN) are shown in Figure 3-18. Although very few of the palladium hydride complexes have been prepared as shown, several related species are known, such as the analogous palladium halides or other metal hydrides.

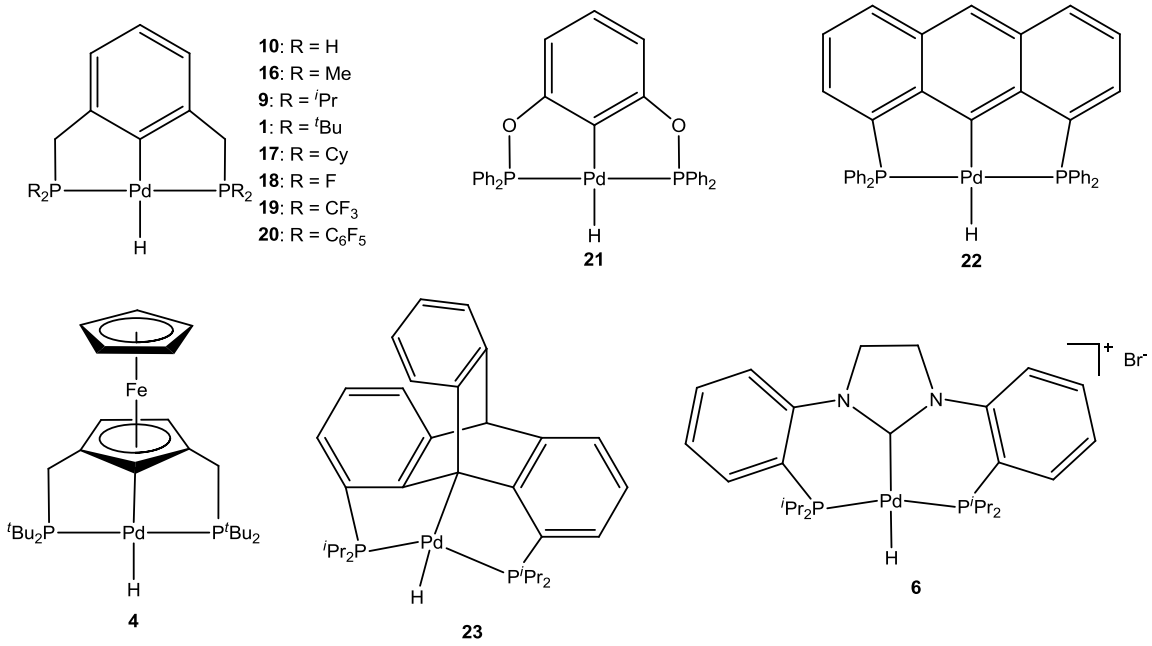


Figure 3-14: All PCP complexes examined computationally

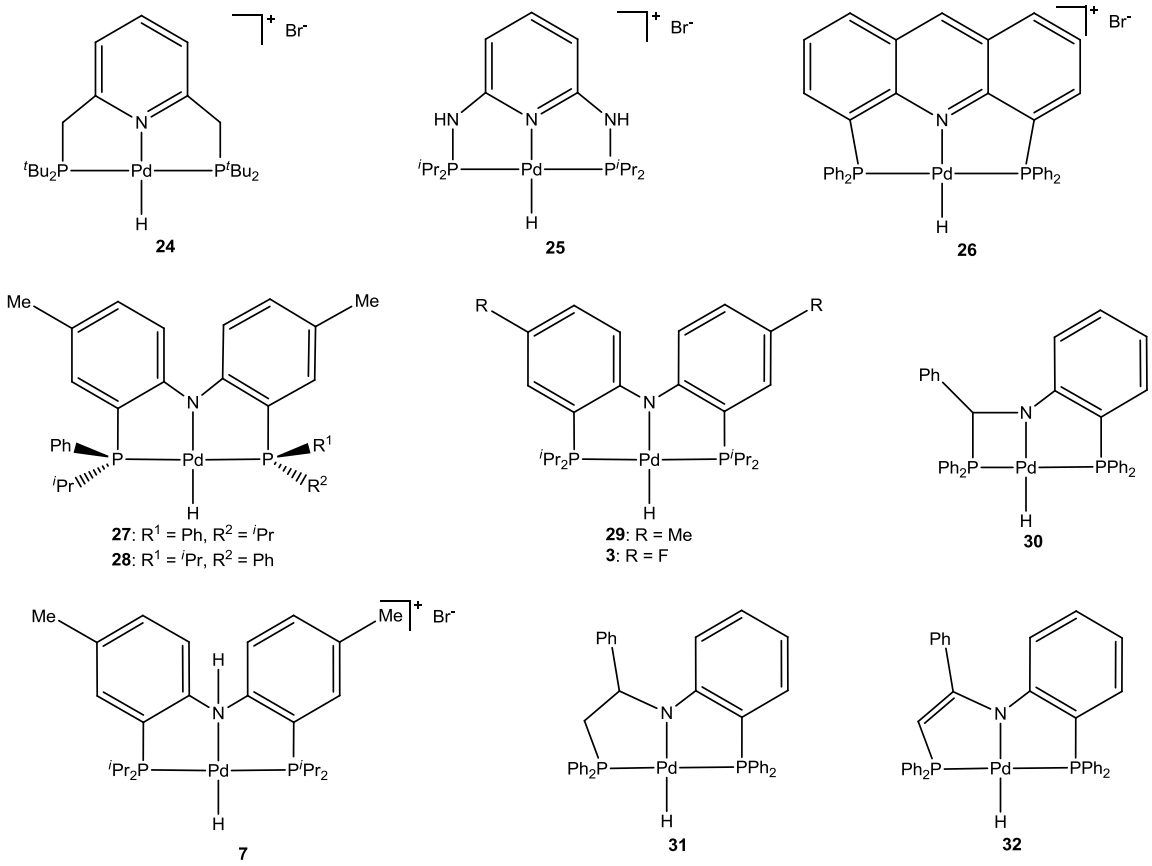


Figure 3-15: All PNP complexes examined computationally

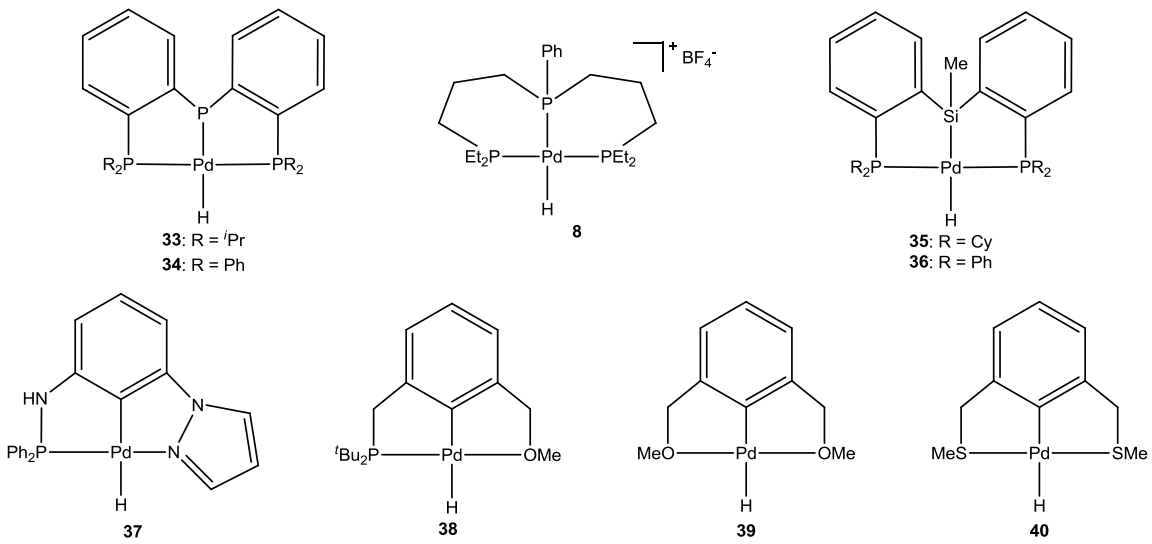


Figure 3-16: All PPP, PSiP, PCN, PCO, OCO, and SCS complexes examined computationally

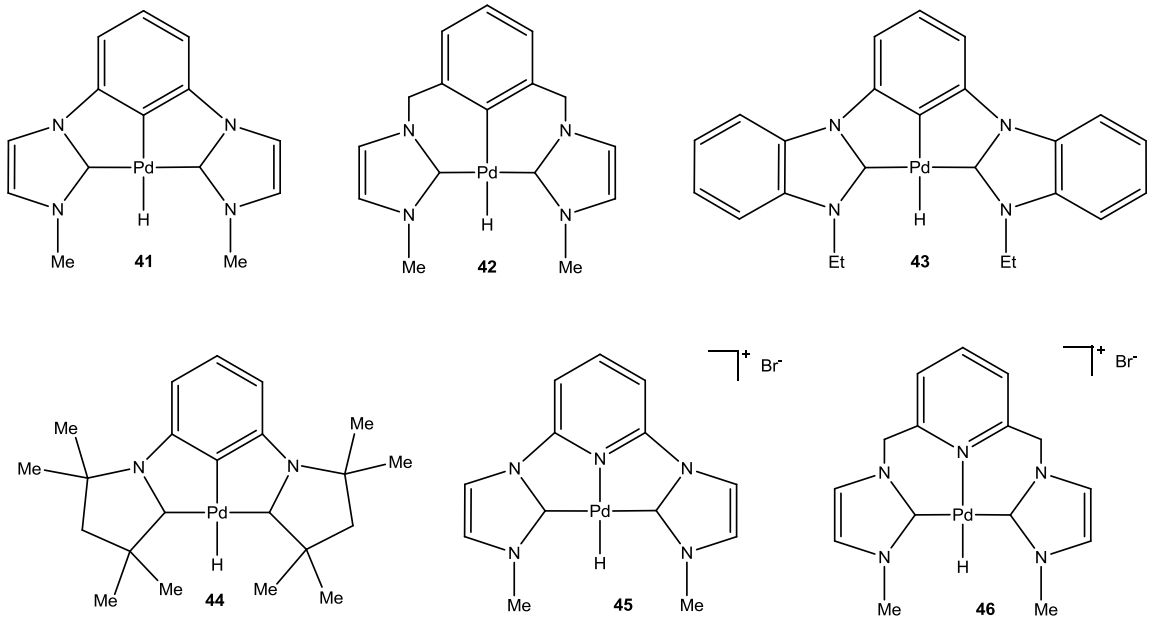


Figure 3-17: All CCC and CNC complexes examined computationally

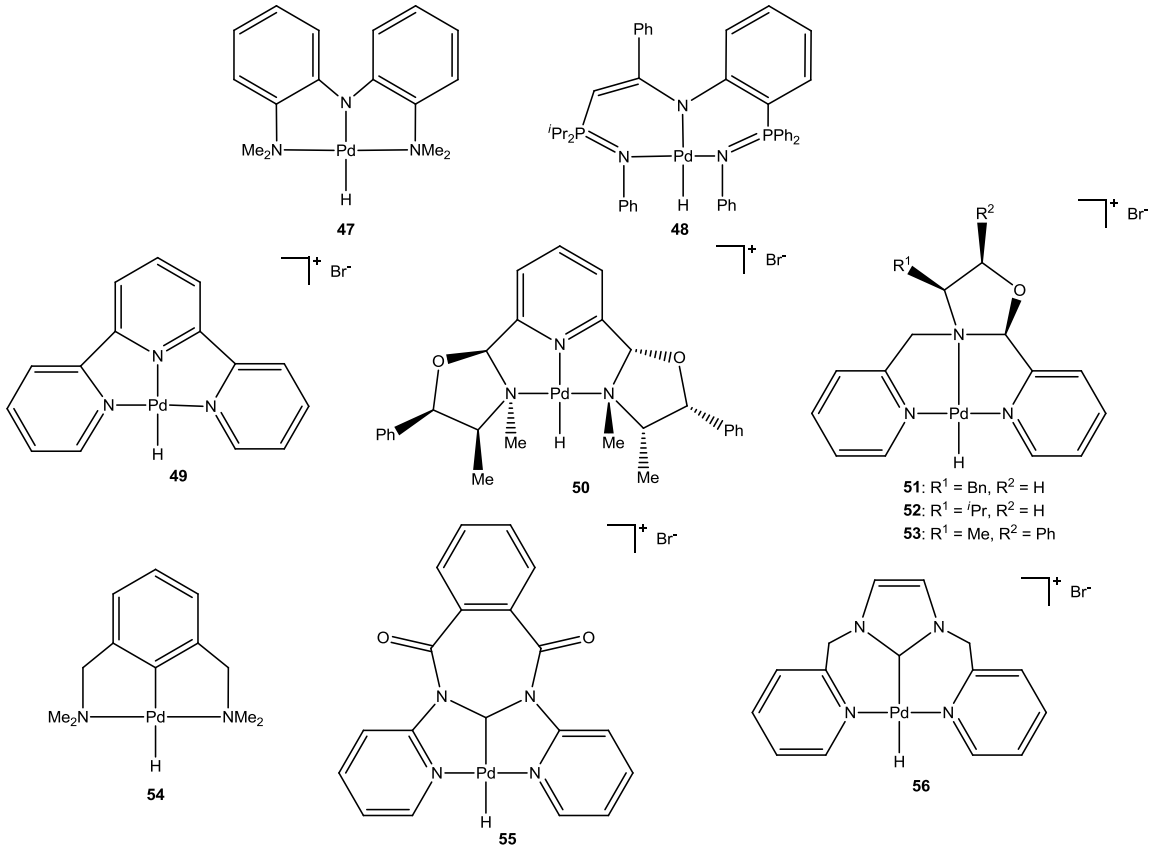


Figure 3-18: All NNN and NCN complexes examined computationally

For each palladium hydride complex examined, the geometry of the complex was first optimized, and then the palladium-hydride bond dipole was calculated using both the Mulliken charge[52,53] and the CHELPG charge.[54] The bond dipole was calculated as the difference in electron density at the palladium and hydrogen atoms, multiplied by the palladium-hydrogen bond distance (see Figure 3-19).

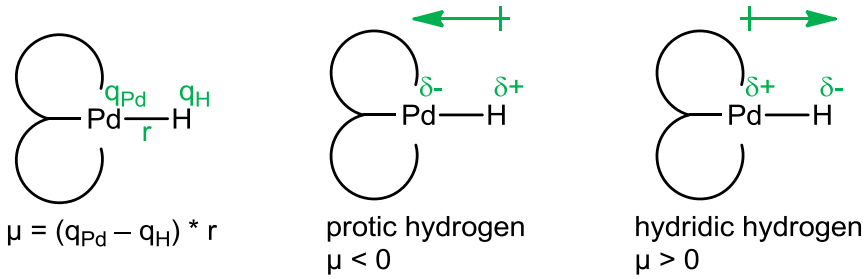


Figure 3-19: The bond dipole is calculated as the differences in atomic charge between the palladium and hydrogen atoms, multiplied by the palladium-hydrogen bond length

Bond Dipoles Obtained Using CHELPG Charges

Bond dipoles calculated using CHELPG charges[54] ranged from -0.23 Debye (protic hydrogen atom with more electronegative palladium) to +0.97 Debye (hydridic hydrogen atom with more electropositive palladium), with most dipoles in the range -0.1 Debye to +0.5 Debye. The strongest factor influencing the bond dipole was the nature of the atoms of attachment of the tridentate ligand. The calculated bond dipoles, grouped by the atoms of attachment of the tridentate ligand, are shown in Figure 3-20. Generally, palladium-hydride complexes with ligands that have more electronegative atoms attached to palladium have smaller palladium-hydrogen bond dipoles and therefore more protic hydrogen atoms. Complexes with ligands that have less electronegative atoms attached to palladium have larger palladium-hydrogen bond dipoles and therefore more hydridic hydrogen atoms. At the far end of this scale are the

complexes with hemilabile ligands; they have the largest palladium-hydrogen bond dipoles and the most hydridic hydrogen atoms.

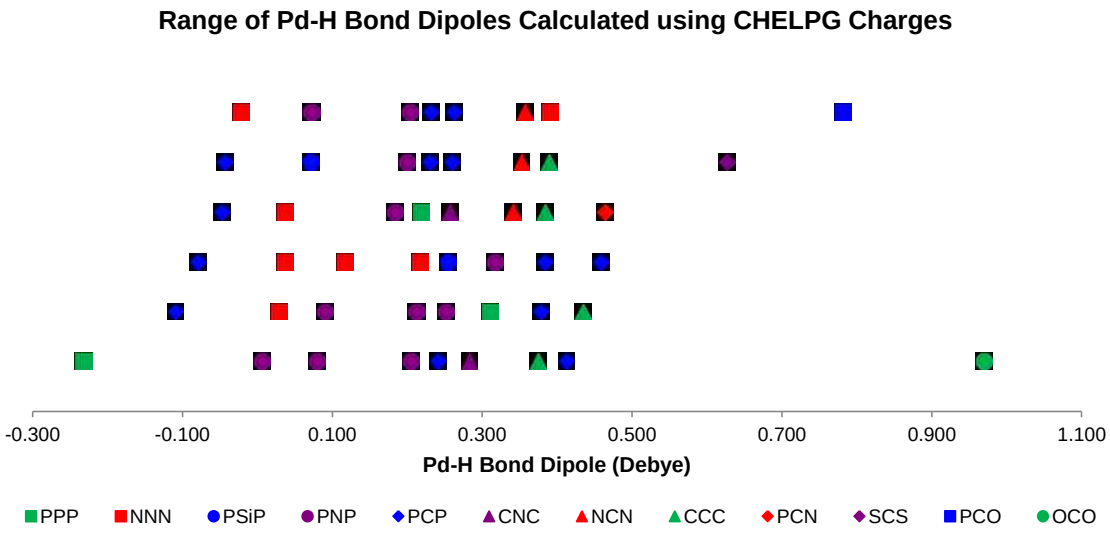


Figure 3-20: Bond dipoles from CHELPG charges, grouped by atoms of attachment of the tridentate ligand

Bond Dipoles Obtained Using Mulliken Charges

Using Mulliken charges,[52,53] bond dipoles ranged from -3.3 Debye (very protic hydrogen atom with more electronegative palladium) to 0.0 Debye (hydrogen atom and palladium atom equally electronegative) and are shown in Figure 3-21, grouped by atoms of attachment of the tridentate ligand. Unlike with the CHELPG charges calculated above, the correlation between the bond dipole obtained from Mulliken charges and the ligand atoms of attachment is weak; in

fact, the bond dipoles obtained from Mulliken charges did not appear to correlate well with any properties of the ligand.

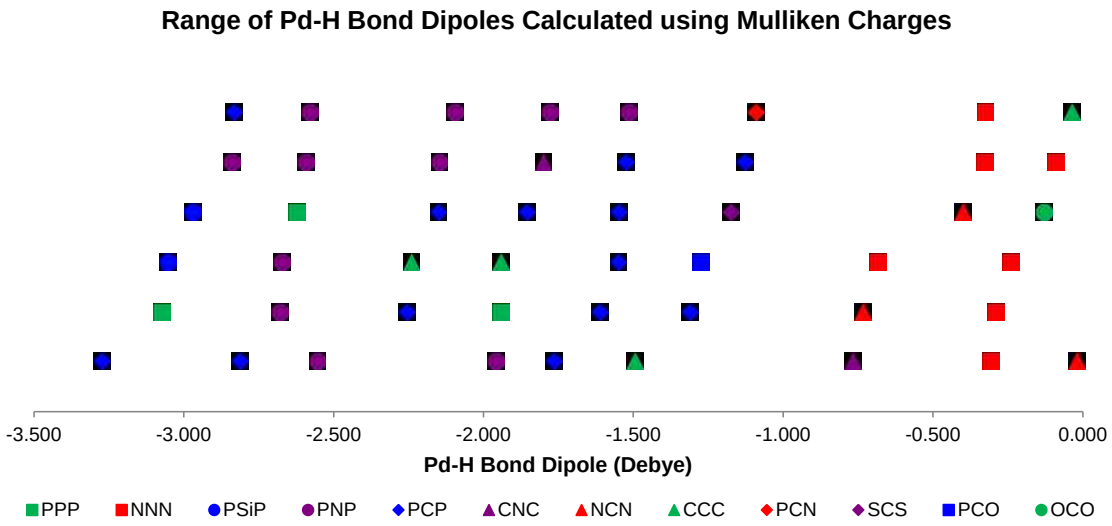


Figure 3-21: Bond dipoles from Mulliken charges, grouped by atoms of attachment of the tridentate ligand

Although Mulliken charges and CHELPG charges are designed as measures of the same properties, there was essentially no correlation between the bond dipoles obtained from the two different methods. This lack of correlation is widely acknowledged in other systems[55] and is seen in Figure 3-22. Because the CHELPG charges are assigned by fitting the measured molecular electrostatic potential while Mulliken charges are assigned based on the theoretical wavefunction, it is not surprising that bond dipoles from these two measures are not well correlated.

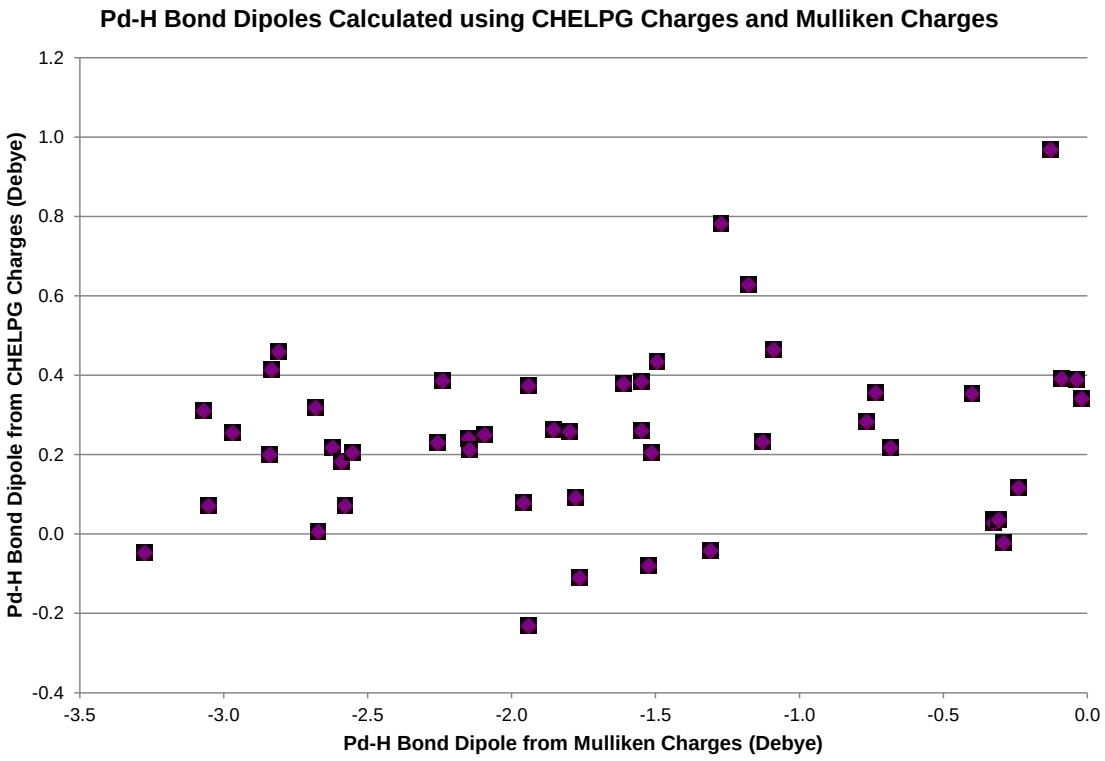


Figure 3-22: Bond dipoles from Mulliken charges and bond dipoles from CHELPG charges plotted against each other

Reaction Coordinates Determined for Six Complexes

With the bond dipoles calculated, six species were chosen for further consideration and complete reaction coordinates were calculated for oxygen insertion of those six species. Because the CHELPG-derived charges are considered more reliable than Mulliken charges,[55,56] bond dipoles resulting from the CHELPG charges were used as the basis of selection for complexes to

examine further. The six complexes chosen for further consideration were selected because they span the range of CHELPG-charge-derived palladium-hydride bond dipoles. To ensure representation of the wide variety of palladium hydride complexes considered above, one complex with a neutral ligand and one with a hemilabile ligand were included. The complexes chosen are shown in Figure 3-23. The reaction coordinate for the insertion of oxygen into **10** was discussed above (see Figure 3-9).

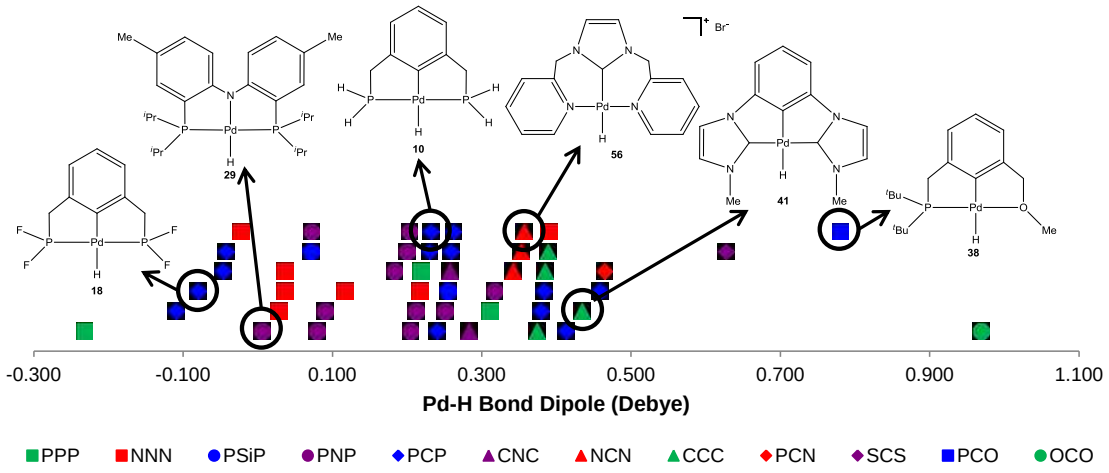


Figure 3-23: Six complexes chosen for further study, based on CHELPG-charge-derived palladium-hydride bond dipoles

For each of these six complexes, the oxygen insertion reaction coordinate was mapped, including reactants, transition state, intermediate, MECP structure, and products. The resulting reaction coordinates for the five complexes not already discussed above are presented below.

Figure 3-24 shows the reaction coordinate for (2,6-bis((difluorophosphino)methyl)phenyl-C-P-P')palladium hydride (**18**). The reaction proceeds through a transition state **57** that is 17.1 kcal/mol higher in energy than the reactants. The final singlet palladium hydroperoxide **58** is 24.0 kcal/mol more stable than the reactants and 29.5 kcal/mol more stable than the corresponding triplet **59**.

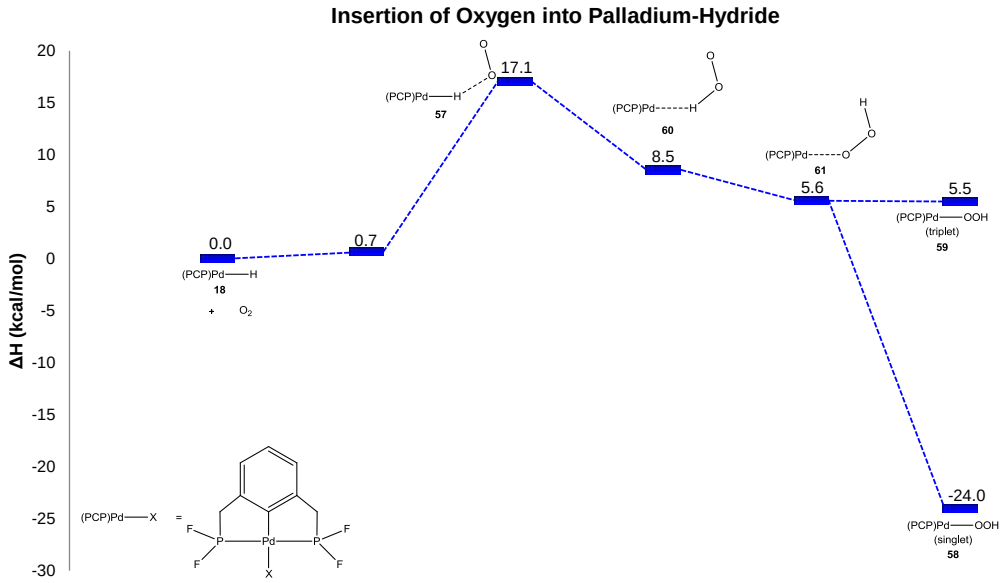


Figure 3-24: Reaction coordinate for oxygen insertion into (2,6-bis((difluorophosphino)methyl)phenyl-C-P-P')palladium hydride (18)

The insertion of molecular oxygen into (bis(4-methyl-2-(di-isopropylphosphino)phenyl)amide-N,P,P')palladium hydride (**29**) is shown in Figure 3-25. The transition state **62** barrier of 19.9 kcal/mol is the largest seen in this set of palladium hydrides and the product singlet palladium hydroperoxide **5**

is 22.4 kcal/mol lower in energy than the reactants and 33.4 kcal/mol lower in energy than the corresponding triplet **63**. Interestingly, the minimum energy crossing point structure **64** for this reaction is relatively high in energy: 3.7 kcal/mol higher in energy than the palladium(I)/hydroperoxy radical pair intermediate **65** and 7.1 kcal/mol higher in energy than the triplet palladium hydroperoxide product **63**.

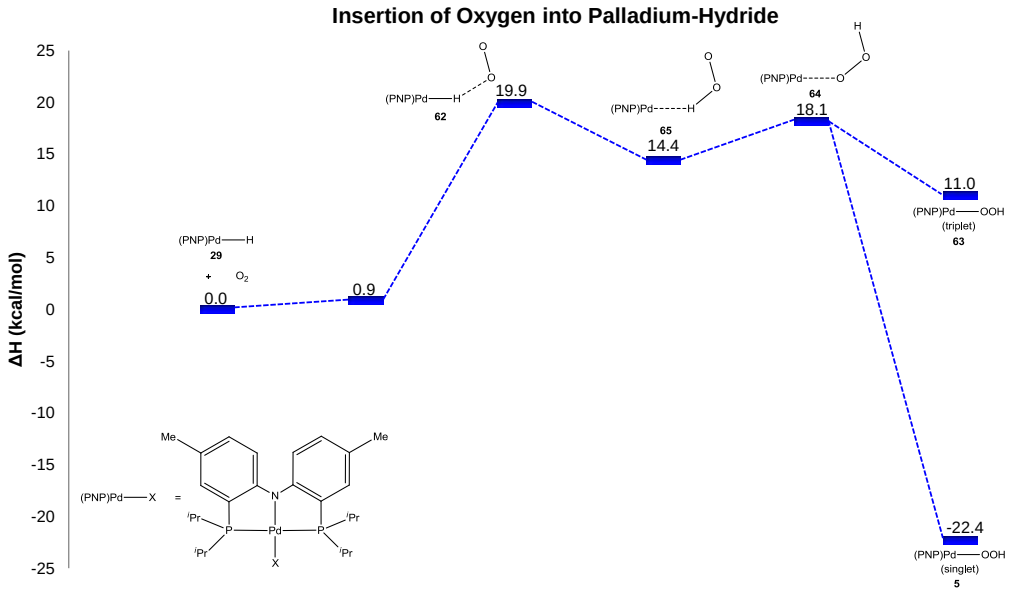


Figure 3-25: Reaction coordinate for oxygen insertion into (bis(4-methyl-2-(di-isopropylphosphino)phenyl)amide-N,P,P')palladium hydride (29)

The reaction coordinate for insertion of oxygen into bis(1,3-bis(2-pyridylmethyl)imidazol-2-ylidene-C-N-N')palladium hydride (**56**) is shown in Figure 3-26. The abstraction of hydrogen proceeds through a transition state **66** that is 16.8 kcal/mol higher in energy than the reactants. The

palladium(I)/hydroperoxy radical pair intermediate **67**, the minimum energy crossing point **68**, and the final product singlet palladium hydroperoxide **69** are all progressively lower in energy, ending at the singlet palladium hydroperoxide **69** that is 35.9 kcal/mol lower in energy than the reactants and 37.5 kcal/mol lower in energy than the corresponding triplet palladium hydroperoxide **70**.

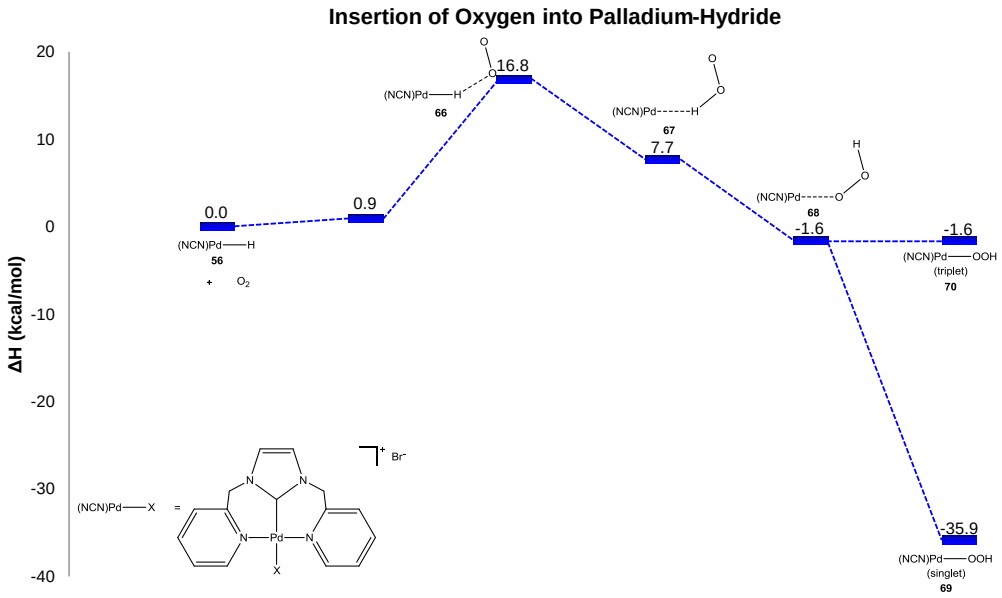


Figure 3-26: Reaction coordinate for oxygen insertion into bis(1,3-bis(2-pyridylmethyl)imidazol-2-ylidene-C-N-N')palladium hydride (56)

Figure 3-27 shows the reaction coordinate for the reaction of oxygen and (2,6-bis(3-N-methylimidazol-2-ylidene-1-yl)phenyl-C-C'-C'')palladium hydride (**41**). Although the transition state **71** is relatively low in energy (15.1 kcal/mol higher energy than the reactants), the palladium(I)/hydroperoxy radical pair intermediate **72** is only 2.4 kcal/mol lower in energy than the transition state **71**.

The product singlet palladium hydroperoxide **74** is 36.8 kcal/mol more stable than the reactants and 42.7 kcal/mol more stable than the corresponding triplet palladium hydroperoxide **75**.

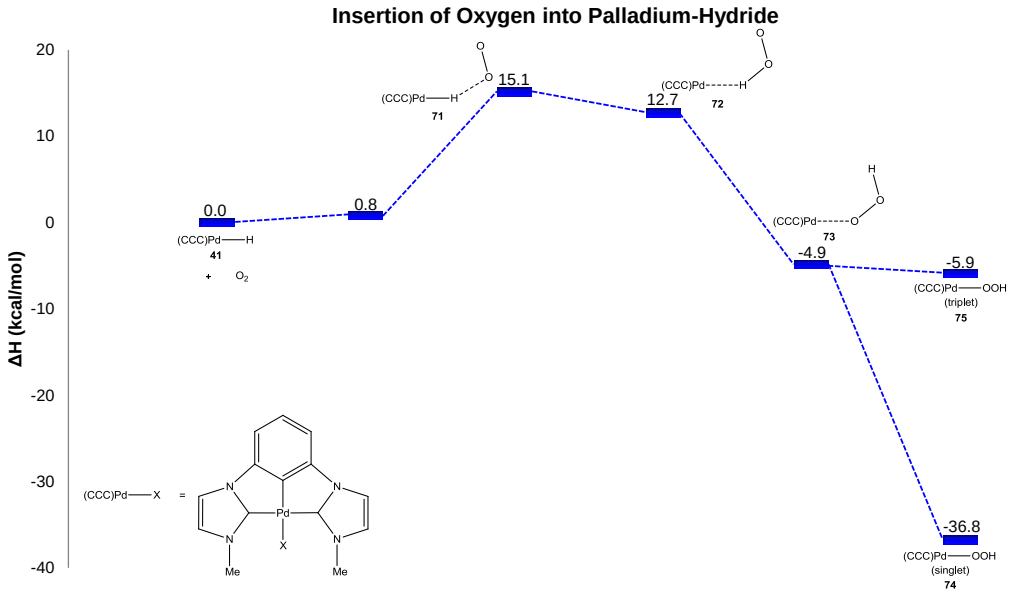


Figure 3-27: Reaction coordinate for oxygen insertion into (2,6-bis(3-N-methylimidazol-2-ylidene-1-yl)phenyl-C-C'-C'')palladium hydride (41)

The insertion of molecular oxygen into ((2-(methoxymethyl)-6-((di-*tert*-butylphosphino)methyl))phenyl-C-O-P)palladium hydride (**38**) is the most favored reaction among those examined here. The transition state **76** barrier is only 14.6 kcal/mol and the final product singlet palladium hydroperoxide **79** is 36.1 kcal/mol more stable than both the reactants and the triplet palladium hydroperoxide **80**. This reaction coordinate is shown in Figure 3-28.

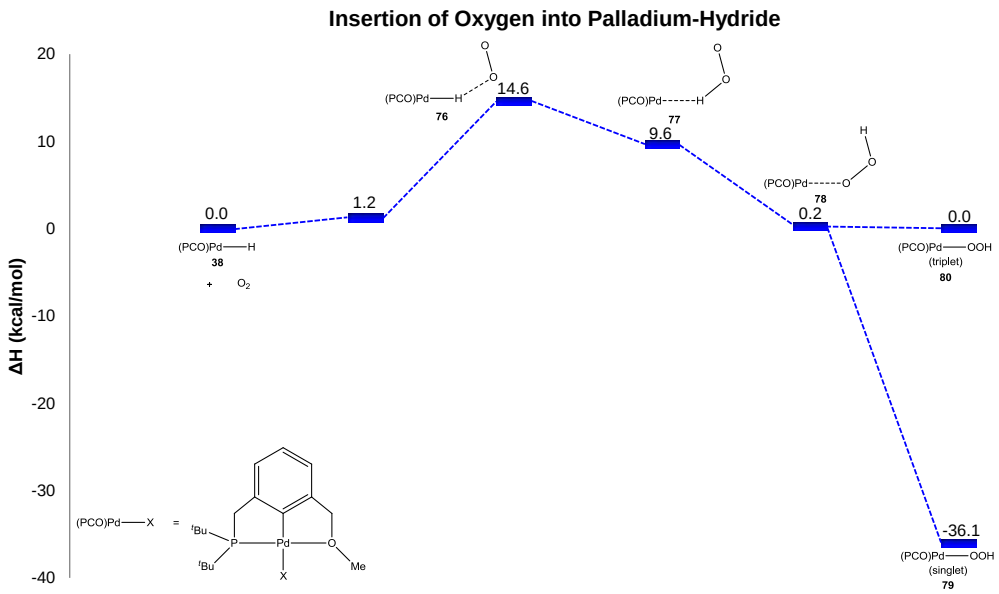


Figure 3-28: Reaction coordinate for oxygen insertion into ((2-(methoxymethyl)-6-((di-*tert*-butylphosphino)methyl))phenyl-C-O-P)palladium hydride (38)

Correlation between Transition State Barrier and Bond Dipole

After determining the transition state barriers for insertion of molecular oxygen into each of the six palladium hydrides shown above, the energies of the transition states were compared with the palladium-hydrogen bond dipoles previously calculated using CHELPG charges. A plot of transition state energy versus CHELPG-charge-derived palladium-hydrogen bond dipole is shown in Figure 3-29. The expected strong correlation between transition state energies and palladium-hydrogen bond dipoles was not seen.

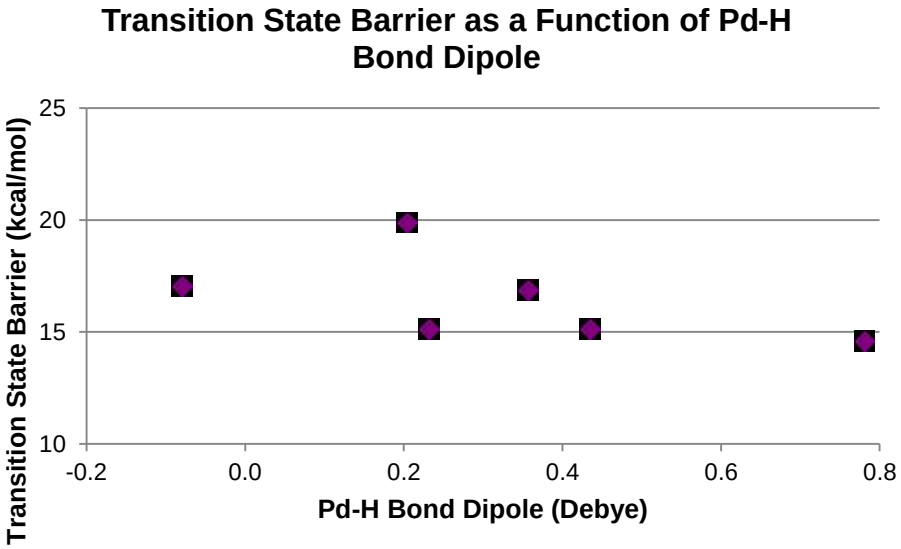


Figure 3-29: Transition state energy plotted against CHELPG-charge-derived palladium-hydrogen bond dipole

Since the Mulliken charges and CHELPG charges were so different and the palladium-hydride bond dipoles had already been calculated for Mulliken charges, a plot of the transition state energies against the Mulliken-charge-derived palladium-hydride bond dipoles was prepared. The results are shown in Figure 3-30, but again there is no correlation seen between the two.

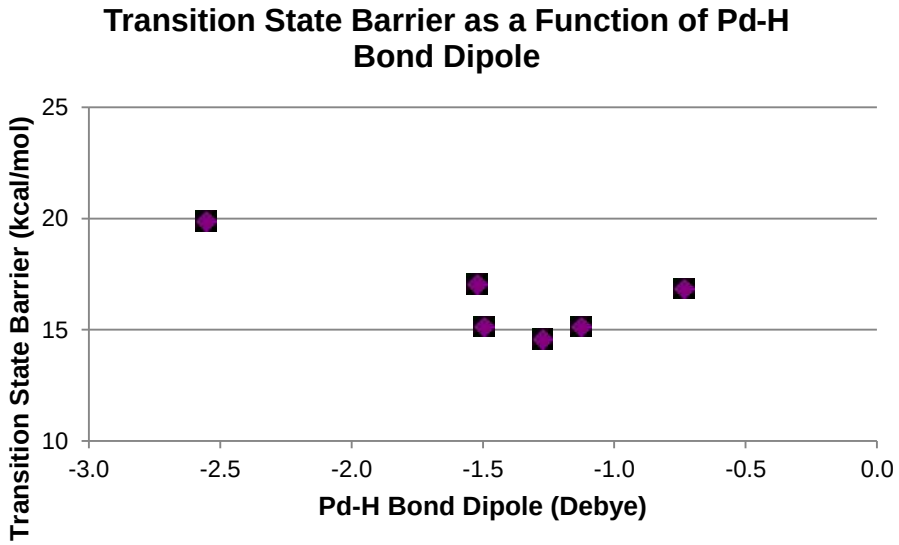


Figure 3-30: Transition state energy plotted against Mulliken-charge-derived palladium-hydrogen bond dipole

Although the palladium-hydrogen bond dipoles were expected to correlate well with the transition state barrier for oxygen insertion, no correlation was found and the palladium-hydrogen bond dipole is not a good surrogate measure for the energy required to insert molecular oxygen into the palladium-hydrogen bond. This lack of correlation can be rationalized by considering the reaction mechanism. The high-energy transition state for this reaction is for the first step of the reaction: abstraction of a hydrogen atom from palladium leading to a palladium(I)/hydroperoxy radical pair intermediate. Importantly, the rate-determining step involves the abstraction of a *hydrogen atom*, not a proton. If the rate-determining step were abstraction of a proton, it is likely that less energy would be required to abstract a proton from a palladium hydride with an electropositive palladium-bound hydrogen and conversely, abstracting a proton

from a palladium hydride with an electronegative palladium-bound hydrogen would require more energy. Since the mechanism in question involves the abstraction of a hydrogen atom rather than a proton, it is reasonable that the palladium-hydrogen bond dipole is not correlated with the activation energy of the reaction. Instead, the activation energy should be correlated with some measure of how tightly bound the hydrogen atom is to the palladium. A palladium hydride with a more weakly bound hydrogen atom should undergo hydrogen atom abstraction more easily than a palladium hydride with a more strongly bound hydrogen atom. Since bond length and bond strength are inversely proportional and bond length is often considered a measure of bond strength,[89,90] a plot of the transition state energies versus palladium-hydrogen bond lengths was prepared.

Transition State Barrier Correlates Well with Palladium-Hydrogen Bond Length

The palladium-hydrogen bond lengths had been calculated as part of the initial geometry optimization for each of the forty-nine palladium hydride complexes; excellent agreement was found between the calculated palladium-hydrogen bond lengths and published crystal structures for the four palladium hydrides in which the hydrogen atom was crystallographically located. After realizing that the transition state barriers did not correlate well with the palladium-hydrogen bond dipole, other measurable properties of the palladium hydride

complexes were considered for correlation with the transition state barriers. Since the transition state involves abstraction of the hydrogen atom from palladium, the transition state barrier was plotted against palladium-hydrogen bond length; a relatively strong correlation ($R^2 = 0.85$) was seen, as shown in Figure 3-31. Complexes with longer, weaker palladium-hydride bonds have lower barriers to insertion and thus undergo more facile oxygen insertion than do the complexes with shorter, stronger palladium-hydride bonds.

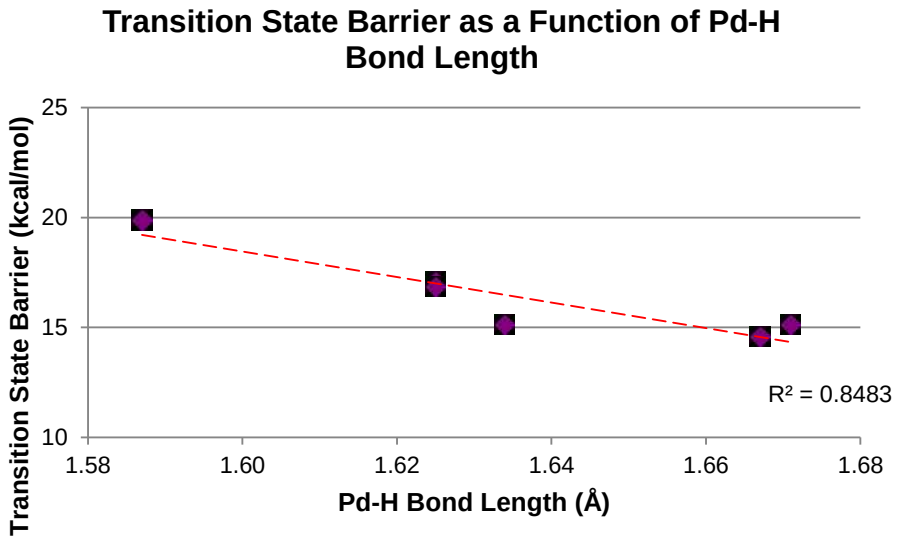


Figure 3-31: Correlation between transition state energy and palladium-hydrogen bond length

For addition of molecular oxygen to palladium hydrides, complexes with a relatively long palladium-hydrogen bond are expected to undergo oxygen insertion more readily than complexes with a relatively short palladium-hydrogen bond. Palladium-hydrogen bond lengths for the complexes considered ranged

from 1.55 Å to 1.69 Å and are shown in Figure 3-32. Notably, complexes with neutral ligands and a counterion tended to have relatively short palladium-hydrogen bonds.

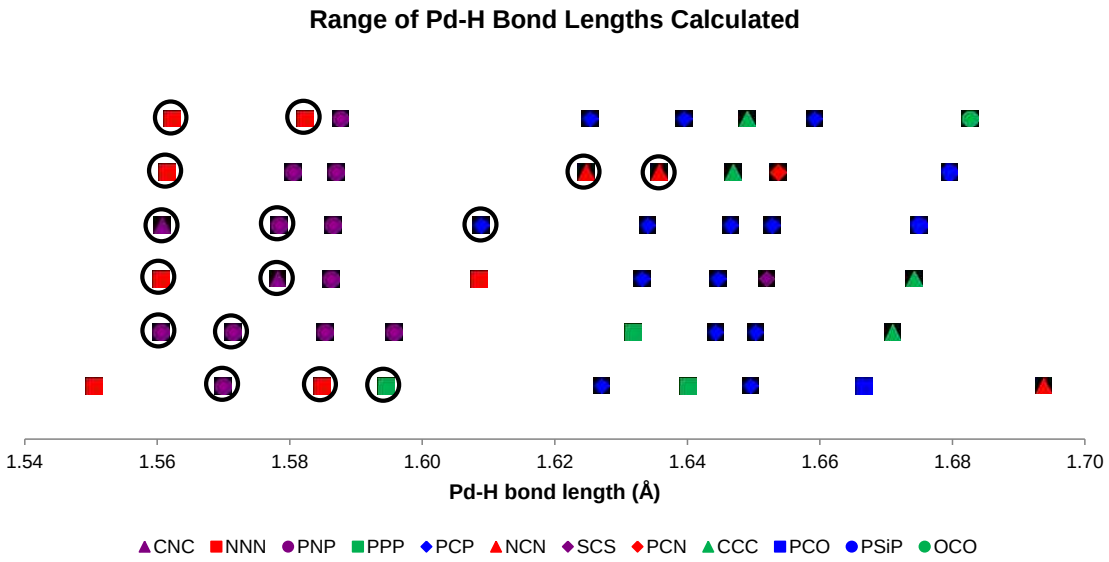


Figure 3-32: Analysis of palladium-hydrogen bond lengths in calculated structures, with points representing complexes containing neutral ligands circled

Conclusions and Direction for Future Experimental Work

The transition state barriers calculated here are all less than 20 kcal/mol, and the oxygen insertion reactions should therefore proceed at a reasonable rate at room temperature. Furthermore, the palladium hydroperoxide products are much lower in energy than the corresponding reactants, so the reaction is

thermodynamically favored. The work presented here supports future experimental work in this area focusing on palladium-hydride complexes with relatively long palladium-hydrogen bonds. Since palladium hydride complexes with neutral ligands and a counterion tended to have relatively short palladium-hydrogen bonds, they should be avoided. Specifically, complexes with the longest palladium-hydrogen bonds that should be examined experimentally based on the calculations performed here include those shown in Figure 3-33. Note that two of these complexes have hemilabile ligands; although complexes with hemilabile ligands might be preferred for oxygen insertion, hemilabile ligands are not suitable for the palladium hydride regeneration step and therefore will not be suitable complexes for the catalytic cycle (see Chapter 5).

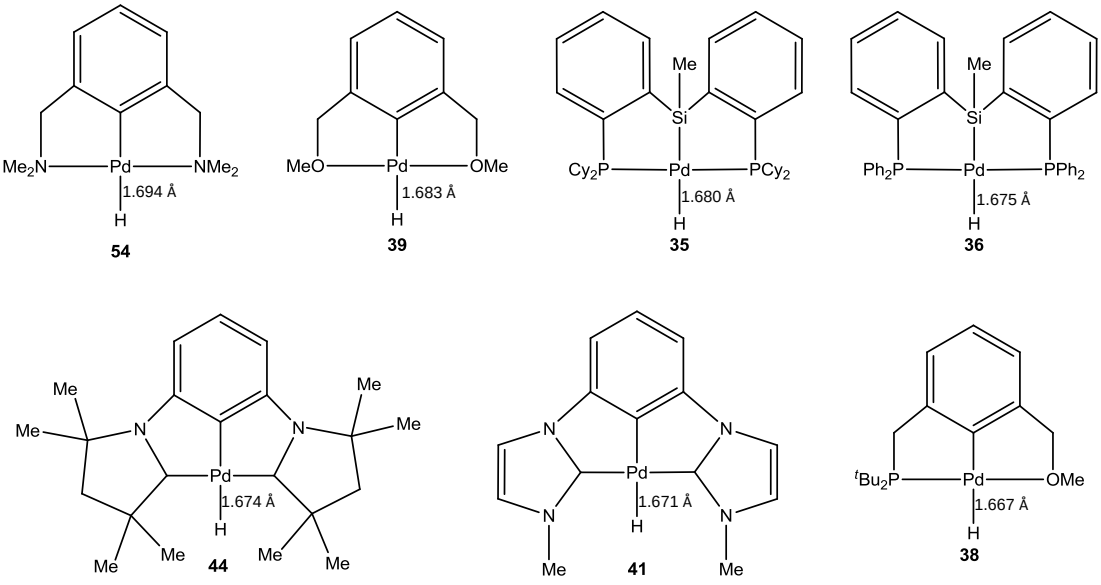


Figure 3-33: Palladium hydride complexes with relatively long palladium-hydrogen bonds that should be examined further experimentally

Chapter 4: Oxygen Atom Transfer from a Palladium Hydroperoxide to an Alkene to form an Epoxide

Second Step of Proposed Catalytic Cycle

The second step of the proposed catalytic cycle is the oxygen atom transfer from a palladium hydroperoxide to an organic substrate. This is arguably the most important step of the catalytic cycle since the organic alkene is converted to an epoxide in this step. A generic form of this reaction is shown in Figure 4-1.

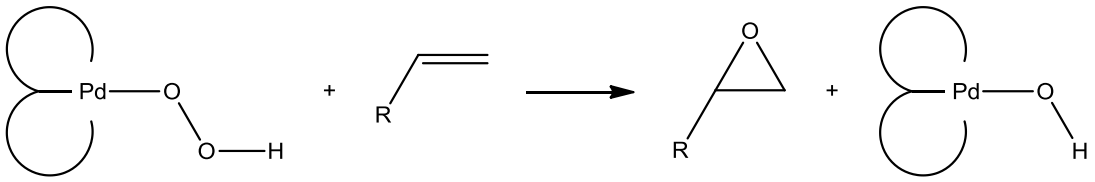


Figure 4-1: Second step of proposed catalytic cycle is oxygen atom transfer from palladium hydroperoxide to an alkene, forming an epoxide

Experimentally, oxygen transfer to an alkene is the one step of the proposed catalytic cycle that has not yet been demonstrated. Since oxygen transfer is critical to the entire catalytic cycle, there was concern about whether this step is thermodynamically allowed. Because it was not feasible for the

experimentalists to examine every palladium hydroperoxide, with every alkene, in every solvent, at every temperature, under all possible conditions to find a combination in which they could demonstrate epoxidation of an alkene, computational results were particularly important for this step of the reaction.

Experimental Evidence for Oxygen Atom Transfer

Although oxygen atom transfer from a palladium hydroperoxide to an alkene has not yet been demonstrated experimentally, there is evidence that the oxygen atom will transfer from a presumed palladium hydroperoxide, formed *in situ*, to an isocyanide to form the isocyanate (see Figure 4-2).[39] *tert*-Butyl isocyanide was added to a solution containing (2,6-bis((dicyclohexylphosphino)methyl)phenyl-C-P-P')palladium hydride (**17**); the resulting solution was pressurized with oxygen, presumably generating *in situ* (2,6-bis((dicyclohexylphosphino)methyl)phenyl-C-P-P')palladium hydroperoxide, which then transferred one oxygen atom to *tert*-butyl isocyanide to generate the corresponding isocyanate. The identity of the resulting palladium complex was not clear, but was presumed to be the palladium hydroxide. The experimental verification that the oxygen atom can transfer to an organic substrate is encouraging and suggests that, under the right conditions and with the right alkene, epoxidation of an alkene should be possible.

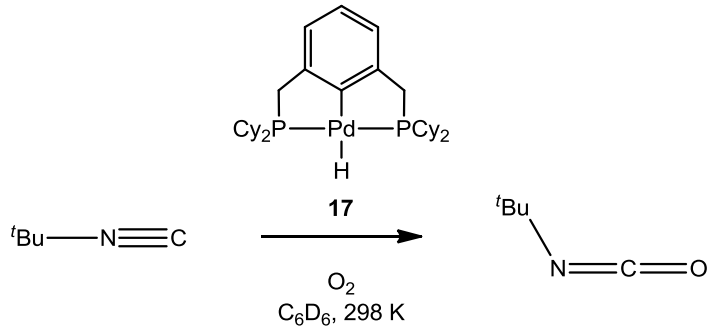


Figure 4-2: Oxygen atom transfer from palladium hydroperoxide to isocyanide to form isocyanate has been demonstrated[39]

Additionally, oxygen atom transfer to an inorganic substrate has been demonstrated. Smythe, in her Ph.D. work at the University of Washington in the Goldberg group, obtained triphenylphospine oxide from triphenylphosphine in the presence of (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydroperoxide[91] (**2**), as shown in Figure 4-3. This conversion is likely driven by formation of the strong phosphine oxide bond.

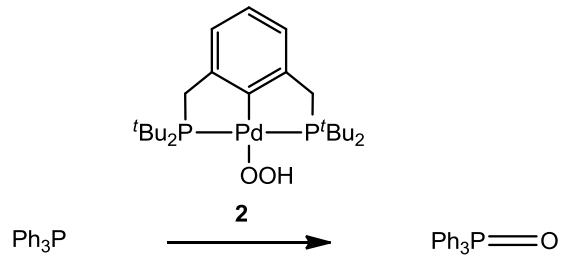


Figure 4-3: Oxygen atom transfer from palladium hydroperoxide to triphenylphosphine to form phosphine oxide has been demonstrated[91]

Partial Negative Charge of Proximal Oxygen Atom in Palladium Hydroperoxide

The oxygen atom transfer reaction has not yet been examined computationally or experimentally, and so the mechanism is not yet known. It is reasonable to suggest, however, that the oxygen proximal to the transition metal is the one transferred to the alkene. Proximal oxygen atom transfer is seen in several analogous epoxidations with transition metal alkyl peroxides.[6,92,93]

As a late transition metal, palladium is electron-rich and can donate electrons into the empty oxygen-oxygen π^* orbital, resulting in a partial negative charge on oxygen and thus enabling nucleophilic addition of the proximal oxygen to the carbon-carbon double bond. The partial negative charge of the oxygen atom proximal to palladium in palladium hydroperoxides was confirmed by determining the CHELPG charges of the oxygen atoms in the seven palladium hydroperoxides shown in Figure 4-4. The CHELPG charges for the oxygen proximal to palladium ranged from -0.32 Debye to -0.44 Debye, showing all to be strongly electron-rich. This electron-rich oxygen was expected to transfer most readily to electron-deficient alkenes rather than electron-rich alkenes.

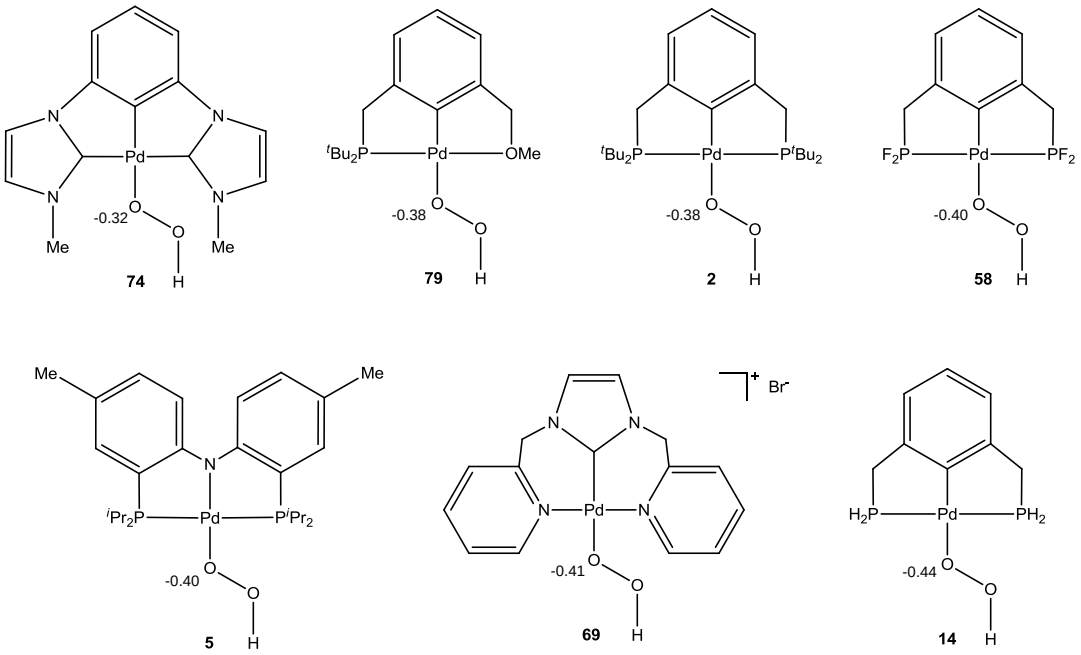


Figure 4-4: Seven palladium hydroperoxides examined for CHELPG charge on proximal oxygen, with CHELPG charges indicated

Reaction Mechanism Determined for Model System

The reaction mechanism for oxygen atom transfer to an alkene was first examined for (2,6-bis(phosphinomethyl)phenyl-C-P-P')palladium hydroperoxide (**14**), with propene (**81**) as the oxygen atom acceptor. The double bond in propene is very slightly electron-donating. The reaction coordinate for this reaction is shown in Figure 4-5. The oxygen atom transfers in a simple concerted manner, through transition state **82** in which the oxygen atom proximal to palladium complexes to the alkene in a "butterfly" formation. This transition state

barrier is 25.1 kcal/mol and the resulting product palladium hydroxide **83** and epoxide **84** are 41.5 kcal/mol lower in energy than the reactants.

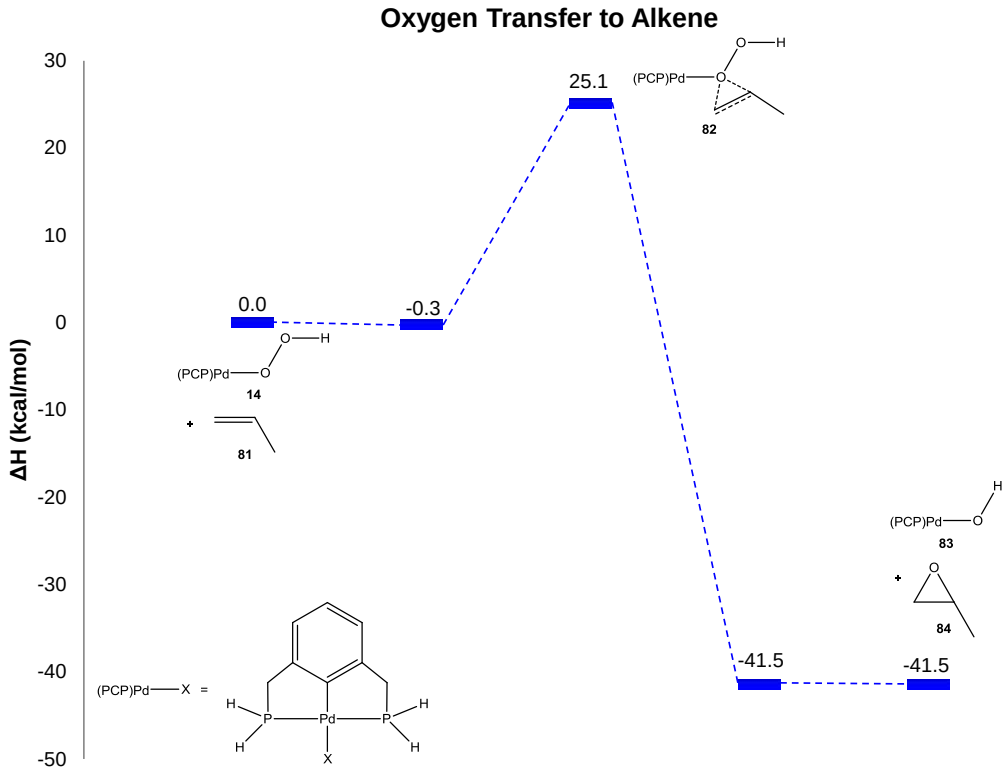
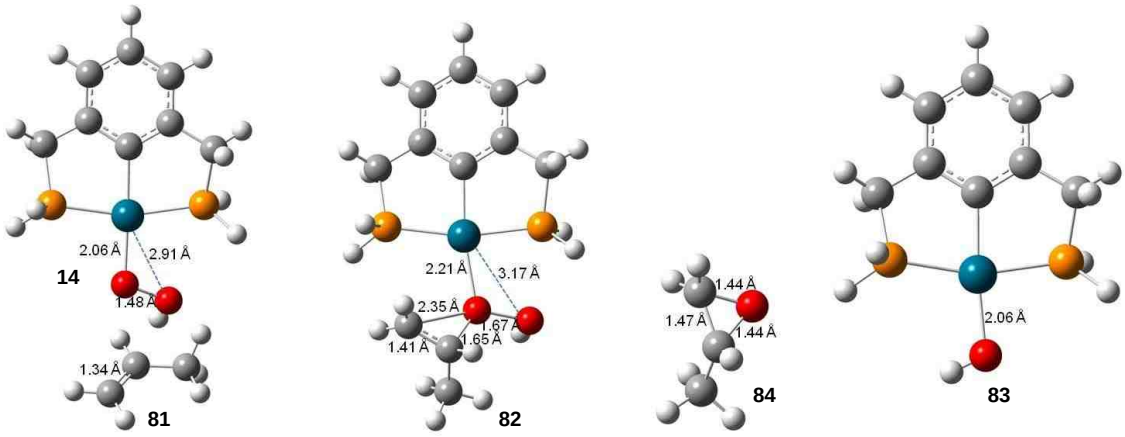


Figure 4-5: Reaction coordinate for epoxidation of propene (81)

Several changes occur as the reaction progresses, as seen in Figure 4-6. Notably, the distance between palladium and the proximal oxygen atom increases from 2.06 Å in the palladium hydroperoxide **14** to 2.21 Å in the transition state **82** as the oxygen-oxygen bond distances increases from 1.48 Å to 1.67 Å. The carbon-carbon bond in the alkene increases from 1.34 Å (typical double bond) in the alkene reactant **81** to 1.41 Å in the transition state **82** to 1.47

Å (typical single bond) in the epoxide product **84**. From the transition state **82** to the product epoxide **84**, the oxygen-carbon bond lengths decrease from 2.35 Å and 1.65 Å to 1.44 Å each as the carbon-oxygen bonds are formed. As expected, the oxygen atom proximal to palladium is transferred to the alkene. The oxygen atom is transferred in a simple concerted manner through a “butterfly” transition state. Interestingly, the distance between palladium and the oxygen atom distal to palladium is longer in the transition state **82** than it is in either the reactants or products: it first increases from 2.91 Å in the palladium hydroperoxide **14** to 3.17 Å in the transition state **82** before decreasing to a typical palladium-oxygen bond length of 2.06 Å in the product palladium hydroxide **83**. This suggests that there is some interaction between the palladium and distal oxygen atom in the palladium hydroperoxide **14** that diminishes in the transition state **82**.



a. Reactants b. Transition State c. Products

Figure 4-6: Representations of (a) palladium hydroperoxide and alkene reactants, (b) “butterfly” transition state, and (c) palladium hydroxide and epoxide products

Effect of Nucleophilicity of Alkene on Activation Energy

Knowing the general mechanism of the reaction, the effect of the alkene nucleophilicity on the activation energy for this reaction was next considered. Five different alkenes were examined, ranging from electron-rich to electron-poor, as shown in Figure 4-7. Methoxyethene (**85**) has a very electron-rich carbon-carbon double bond due to electron donation from the neighboring methoxy group. Both propene (**81**) and styrene (**86**) have carbon-carbon double bonds that are neither particularly electron-rich nor particularly electron-deficient: the methyl group adjacent to the double bond in propene (**81**) is very slightly electron-donating through the inductive effect and the phenyl ring in styrene (**86**) is very slightly electron-donating through the resonance effect, but these effects are very small and the alkenes are essentially neither electron-rich nor electron-poor. Both methyl acrylate (**87**) and acrylonitrile (**88**) have very electron-rich carbon-carbon double bonds.

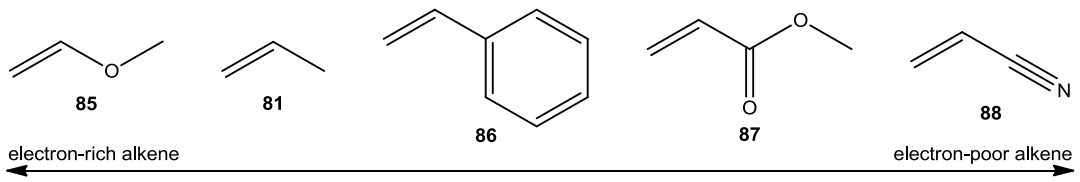


Figure 4-7: Alkenes examined for epoxidation range from electron-rich to electron-poor

The single electron-rich alkene examined, methoxyethene (**85**), proceeds through a transition state **89** with an activation barrier of 25.7 kcal/mol, the largest activation barrier in the series of alkenes examined. This reaction coordinate is shown in Figure 4-8. Like the analogous reaction coordinate for epoxidation of propene (**81**), the products of this reaction (palladium hydroxide **83** and epoxide **90**) are more stable than the reactant palladium hydroperoxide **14** and methoxyethene (**85**).

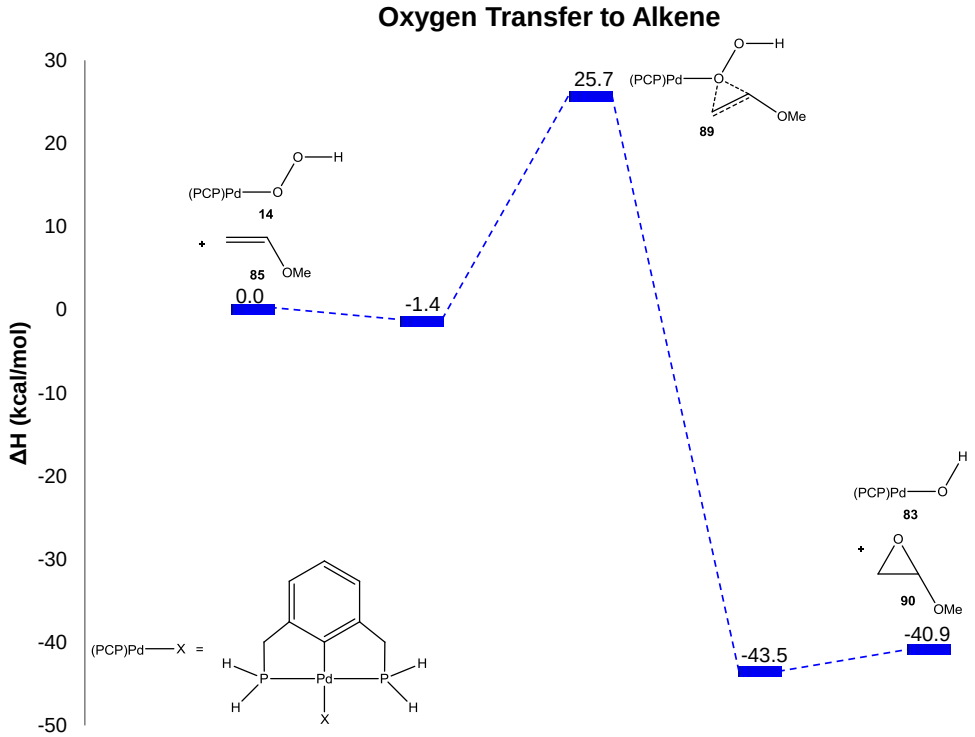


Figure 4-8: Reaction coordinate for epoxidation of methoxyethene (85)

Like propene (**81**), the carbon-carbon double bond of styrene (**86**) is neither particularly electron-rich nor electron-deficient. The phenyl group on

styrene (**86**) has some ability to both donate and accept electron density from the alkene, but the effect on the double bond is weak relative to the more electron-rich methoxyethene (**85**) and the electron-deficient methyl acrylate (**87**) and acrylonitrile (**88**). The 22.1 kcal/mol activation barrier for oxygen atom transfer to styrene (**86**) is lower than it is for methoxyethene (**85**) and propene (**81**); like methoxyethene (**85**) and propene (**81**), the reactants (palladium hydroperoxide **14** and alkene **86**) are significantly higher in energy than the products of this reaction, palladium hydroxide **83** and epoxide **92** (see Figure 4-9).

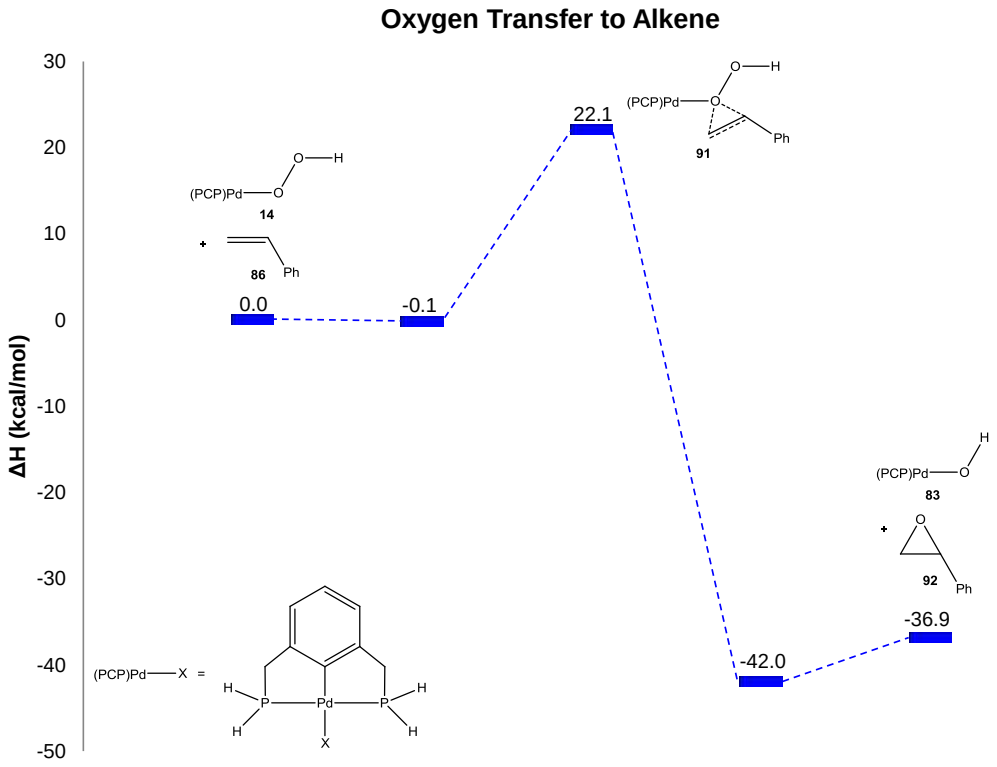


Figure 4-9: Reaction coordinate for epoxidation of styrene (86)

Methyl acrylate (**87**) has a very electron-deficient carbon-carbon double bond. *A priori*, oxygen atom transfer to methyl acrylate (**87**) was expected to be favored over oxygen atom transfer to more electron-rich alkenes. Indeed, epoxidation of methyl acrylate (**87**) has the smallest activation barrier of all the alkenes examined: the transition state **93** is only 13.9 kcal/mol higher in energy than the reactants. This activation barrier is more than 8 kcal/mol smaller than for the epoxidation of styrene (**86**) and is shown in Figure 4-10. The product epoxide **94** and palladium hydroxide **83** are significantly lower in energy than the reactant alkene **87** and palladium hydroperoxide **14**.

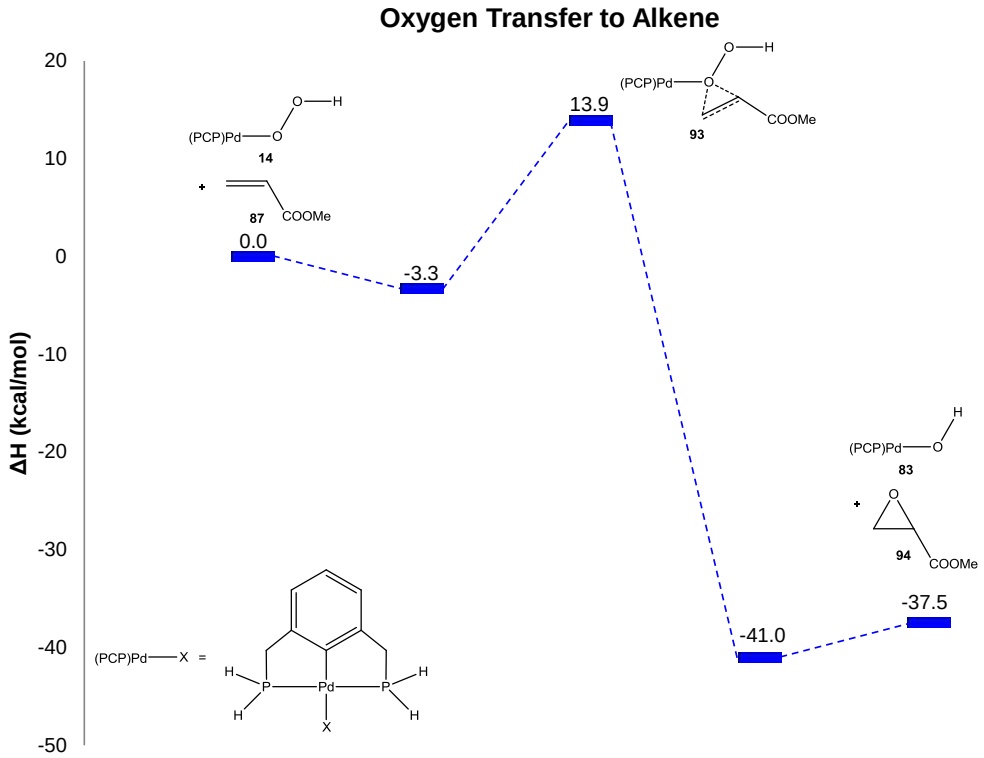


Figure 4-10: Reaction coordinate for epoxidation of methylacrylate (87)

The last of the five alkenes, acrylonitrile (**88**), is the most electron-deficient alkene examined. Despite several attempts to find the transition state for oxygen atom transfer to acrylonitrile, the transition state calculation did not converge. This could be because the epoxidation of acrylonitrile is so facile and the transition state barrier is so small that the transition state could not be located. Like the other epoxidation reactions examined, the products (epoxide **95** and palladium hydroxide **83**) are significantly more stable than the reactants (alkene **88** and palladium hydroperoxide **14**), by 35.1 kcal/mol. This is shown in Figure 4-11.

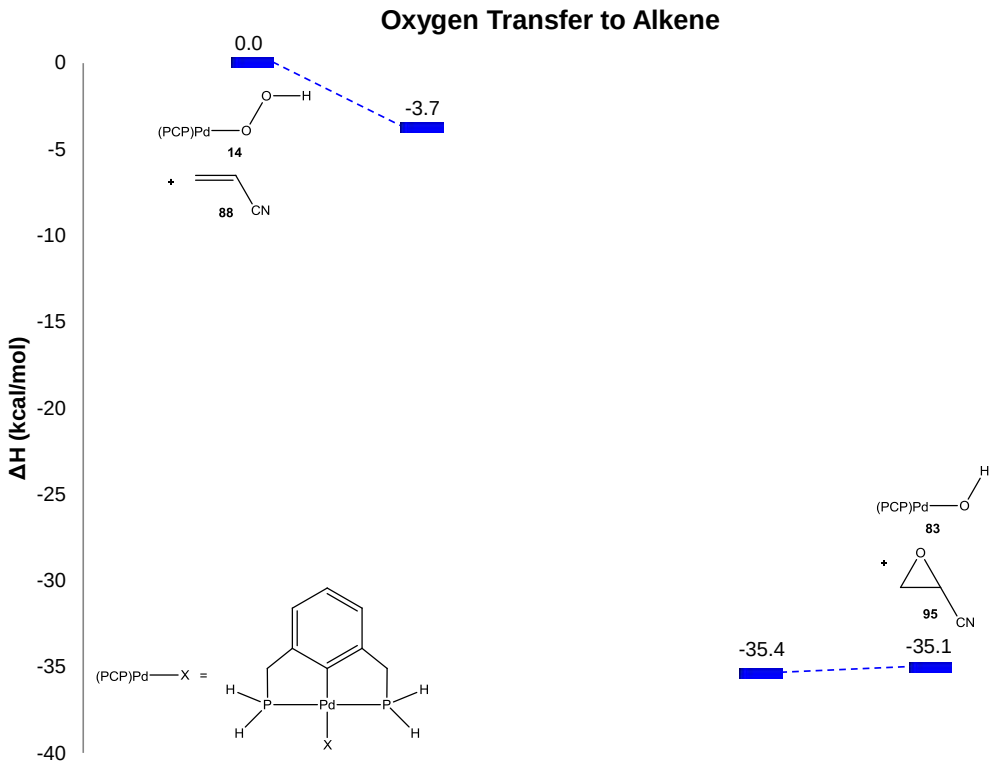


Figure 4-11: Reaction coordinate for epoxidation of acrylonitrile (88)

Conclusions and Direction for Future Experimental Work

The transition state barriers calculated here range from 13.9 kcal/mol for the epoxidation of methyl acrylate (**87**) to 25.7 kcal/mol for the epoxidation of methoxyethene (**85**); clearly, epoxidation of electron-deficient alkenes is significantly favored over epoxidation of electron-rich alkenes. Thermodynamically, the epoxidation reaction is favored for all alkenes: the products are significantly lower in energy than the reactants. These calculations

strongly support future experimental work focusing on epoxidation of electron-deficient alkenes such as methyl acrylate. Although a transition state for the epoxidation of acrylonitrile (**88**) could not be identified computationally, acrylonitrile has a very electrophilic carbon-carbon double bond and would be a good candidate for further experimental work. Other alkenes to consider that were not examined here include cyclohexenone, acrylic acid, methyl isopropenyl ketone, methacrylonitrile, and N,N-dimethylmethacrylamide: all have electron-deficient carbon-carbon double bonds and therefore the activation barrier for epoxidation is expected to be low.

Chapter 5: Palladium Hydride Regeneration from Palladium Hydroxide and Hydrogen

Third Step of Proposed Catalytic Cycle

The final step of the proposed catalytic cycle is the regeneration of palladium hydride from palladium hydroxide. A generic form of this reaction is shown below, in Figure 5-1. This reaction has been demonstrated experimentally for the conversion of (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydroxide (**96**) to the corresponding palladium hydride[40] **16** (see Figure 5-2 below). On addition of 7.0 atm of hydrogen at room temperature, the palladium hydroxide **96** was converted to palladium hydride **16** quantitatively over the course of 60 hours. Kinetic studies and preliminary computational mechanistic studies were also performed by Kemp, Goldberg, and coworkers.[40]

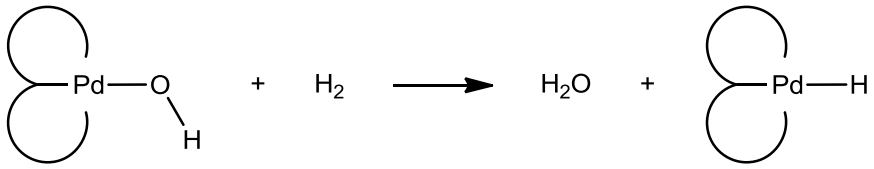


Figure 5-1: Third step of proposed catalytic cycle is regeneration of palladium hydride from palladium hydroxide and hydrogen

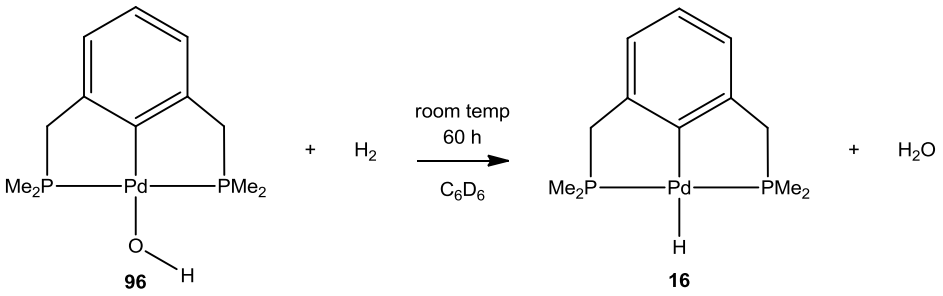


Figure 5-2: Conversion of (2,6-bis((di-*tert*-butylphosphino)methyl)phenyl-C-P-P')palladium hydroxide (96) to the corresponding palladium hydride 16, demonstrated by Kemp, Goldberg, and coworkers[40]

Possible Mechanisms Considered for Hydrogenolysis of Palladium Hydroxide

Several mechanisms for this reaction were considered, including oxidative addition of hydrogen to the palladium hydroxide **96**, forming an octahedral palladium(IV) intermediate **97**, followed by reductive elimination of water to give the palladium hydride **16** as shown in Figure 5-3a. A second mechanism considered was internal electrophilic substitution,[94,95] in which an electrophilic metal activates the hydrogen-hydrogen bond by pulling electron density from the metal-bound hydrogen atom while the lone pair of electrons on the hydroxide group abstracts the second hydrogen. This mechanism involves direct proton transfer from molecular hydrogen to the hydroxide oxygen with simultaneous dissociation of the palladium-oxygen bond and formation of a palladium-

hydrogen bond and would occur through a four-center transition state **98**, as shown in Figure 5-3b. The authors turned to computational methods to distinguish between the two potential pathways and found that the four-center transition state **98** is significantly lower in energy than the octahedral palladium intermediate **97**, suggesting that the reaction occurs through a concerted internal electrophilic substitution pathway.[40]

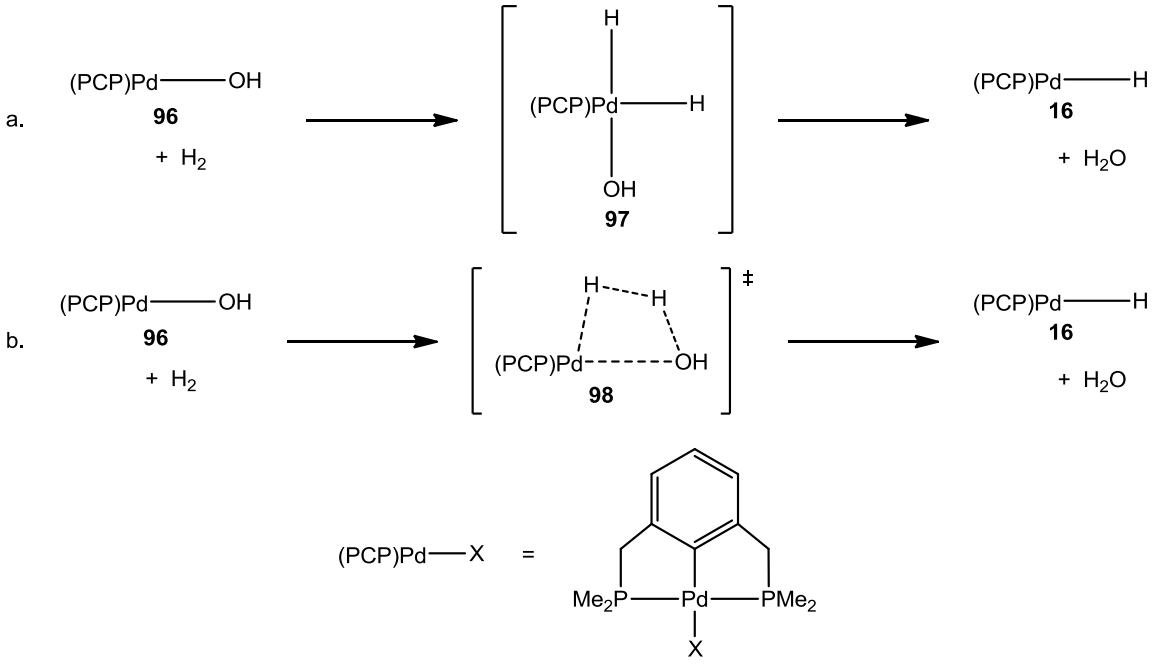


Figure 5-3: Two reaction mechanisms for the hydrogenolysis of palladium hydroxide 96 proposed by Kemp, Goldberg, and coworkers:[40] a) oxidative addition and reductive elimination through an octahedral palladium(IV) intermediate 97, and b) internal electrophilic substitution through a four-center transition state 98

Reaction Coordinate Reproduced for Model System

As further verification of methods, the calculations performed by Kemp, Goldberg, and coworkers[40] to determine the energies of the octahedral palladium intermediate **97** and four-center transition state **98** were reproduced and are shown in Figure 5-4 for (2,6-bis(phosphinomethyl)phenyl-C-P-P')palladium hydroxide (**96**). There is a 2.5 kcal/mol difference in the energies determined for the octahedral palladium intermediate **97** and a 4.6 kcal/mol difference in the energies determined for the four-center internal electrophilic substitution transition state **98**; these energy differences are in opposite directions, resulting in a 7.1 kcal/mol difference in the stabilization of the four-center transition state **98** over the octahedral intermediate **97**. If the results obtained here are more accurate, then the internal electrophilic substitution reaction is only favored by 6.1 kcal/mol, rather than 13.2 kcal/mol as initially reported by Kemp, Goldberg, and coworkers.[40] The discrepancies seen between the two sets of calculations may be due to slight differences in basis sets used to describe main-group atoms (Kemp, Goldberg, and coworkers used "a valence double zeta plus polarization basis set"[40] while Pople's 6-31+g(d) split-valence double-ζ basis set with polarization and diffuse functions was used here). The palladium atom was described with the same basis set here and by Kemp, Goldberg, and coworkers,[40] and all other computational methods were identical to the extent described by Kemp, Goldberg, and coworkers. The transition state obtained here contains exactly one imaginary frequency and intrinsic reaction coordinate

calculations were performed to confirm that the transition state obtained connects the reactants and products and involves movement of the appropriate atoms.

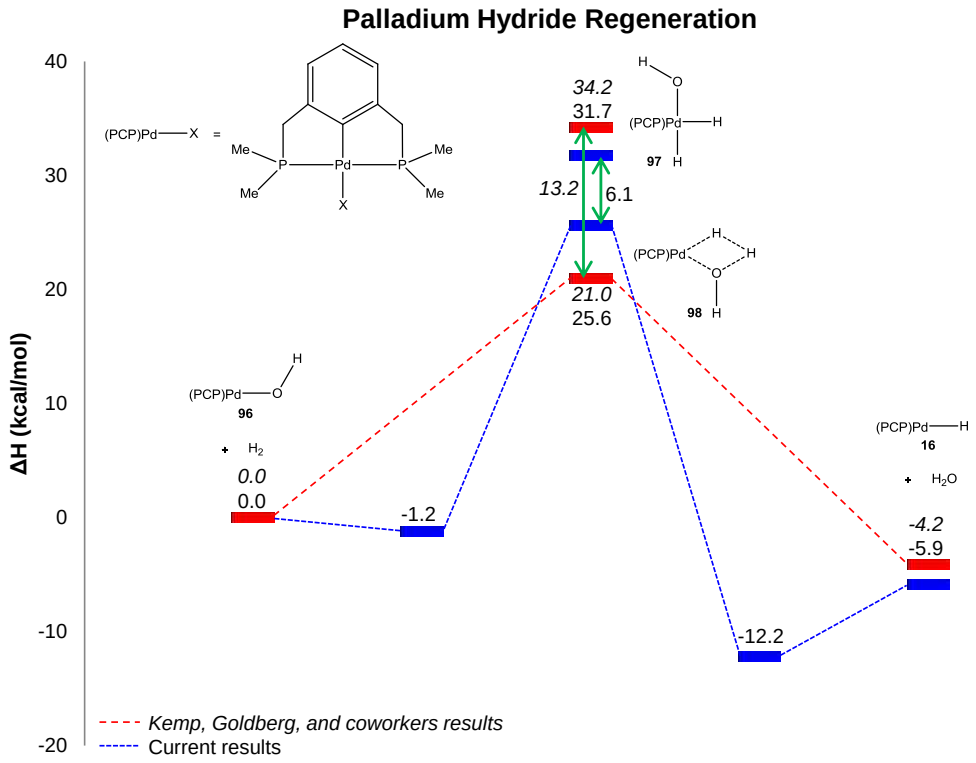


Figure 5-4: Reaction coordinate for conversion of palladium hydroxide 96 and hydrogen to palladium hydride 16 and water, as calculated in this research and by Kemp, Goldberg, and coworkers[40]

Effect of Ligand Atoms of Attachment on Reaction Mechanism

In an effort to determine the effect of the atoms attached to palladium *cis* to the hydroxide and to provide guidance for the experimentalists working on this

project, the hydrogenolysis of a series of palladium hydroxides was examined. The palladium hydroxides considered are shown in Figure 5-5 and include ligands with carbon, nitrogen, oxygen, phosphorus, and sulfur atoms attached to palladium *cis* to the hydroxide. The mechanism of hydrogenolysis of (2,6-bis(phosphinomethyl)phenyl-C-P-P')palladium hydroxide is discussed above; reaction coordinates for hydrogenolysis of the other palladium hydroxides will be presented below.

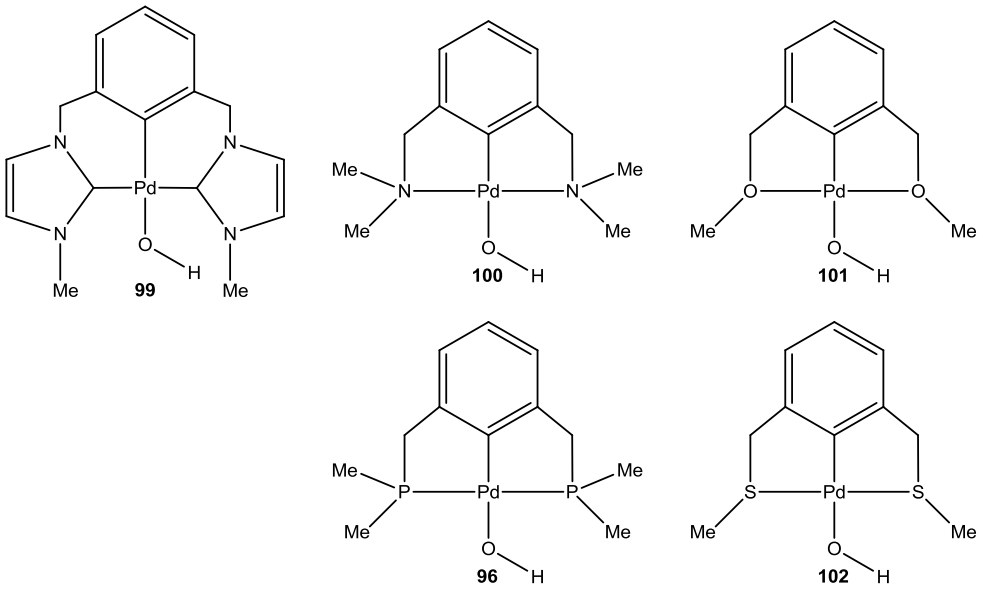


Figure 5-5: Palladium hydroxides considered for hydrogenolysis

The four-center transition state **103** and the octahedral intermediate **104** in the hydrogenolysis of (2,6-bis(N-methyl-imidazol-2-ylidene)methylphenyl-C-C'-C'')palladium hydroxide (**99**) are close enough in energy that the reaction could reasonably undergo either internal electrophilic substitution or oxidative-

addition/reductive elimination to produce the desired palladium hydride **41** (see Figure 5-6). With an energy difference of only 7.5 kcal/mol, neither pathway is strongly favored over the other. The energy of the products is close to the energy of reactants, and so this reaction is not strongly favored thermodynamically.

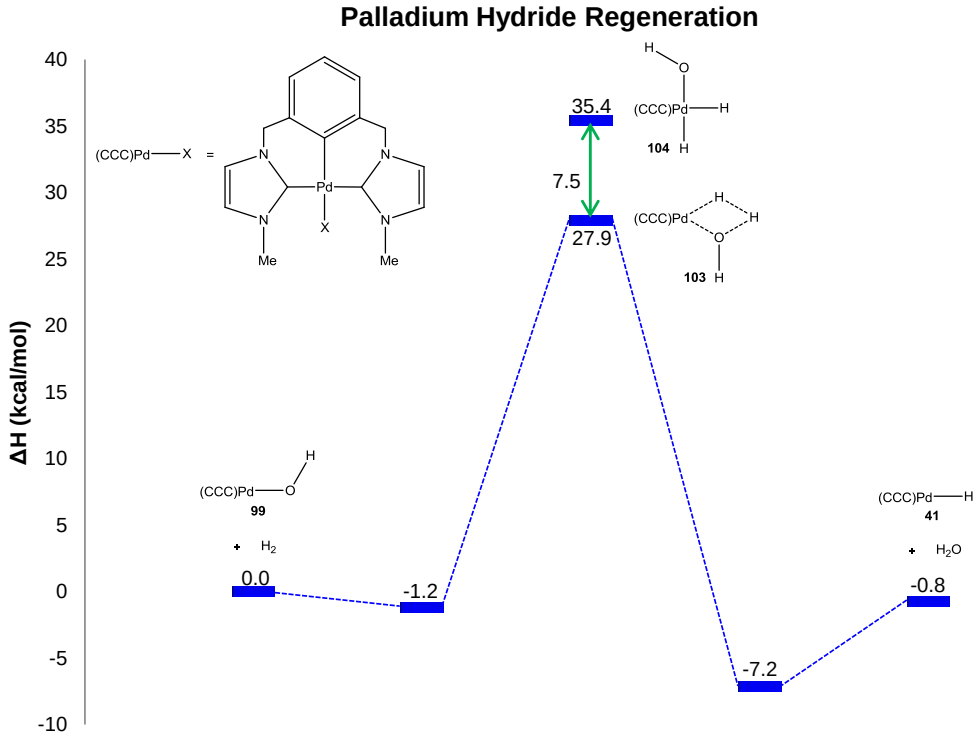


Figure 5-6: Reaction coordination for regeneration of palladium hydride 41 from the corresponding palladium hydroxide 99

The calculated reaction mechanism for the hydrogenolysis of (2,6-bis((di-methylamino)methyl)phenyl-C-N-N')palladium hydroxide (**100**) is shown in Figure 5-7. For the hydrogenolysis of this palladium hydroxide **100**, the difference in energies between the octahedral palladium intermediate **105** and the four-center

transition state **106** is quite large and the reaction would be expected to undergo hydrogenolysis only through the internal electrophilic substitution pathway. The products, palladium hydride **54** and water, are slightly higher in energy than the reactants, palladium hydroxide **100** and hydrogen.

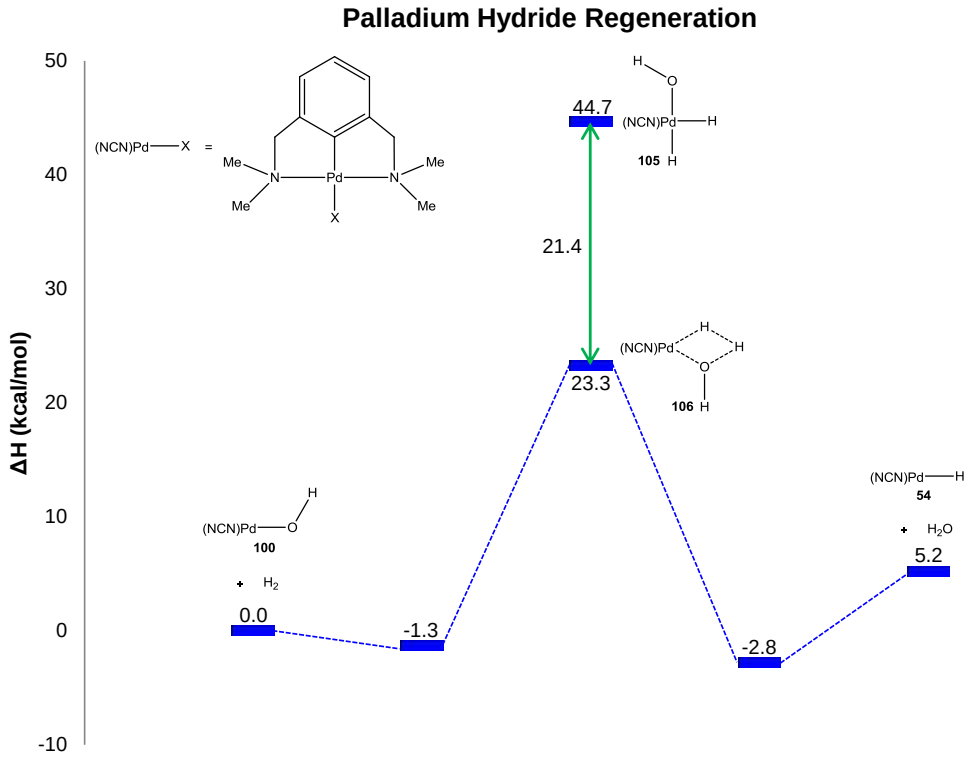


Figure 5-7: Reaction coordination for regeneration of palladium hydride 54 from the corresponding palladium hydroxide 100

At 15.5 kcal/mol, the difference in energy between the octahedral palladium intermediate **107** and the four-center transition state **108** for the hydrogenolysis of (2,6-bis(methylthiomethyl)phenyl-C-S-S')palladium hydroxide (**102**) is large enough that the system is unlikely to undergo oxidation-

addition/reductive-elimination (see Figure 5-8). Like the other palladium hydroxides examined, the reactants (palladium hydroxide **102** and hydrogen) and products (palladium hydride **40** and water) are very similar in energy and the internal electrophilic substitution transition state barrier is moderately large.

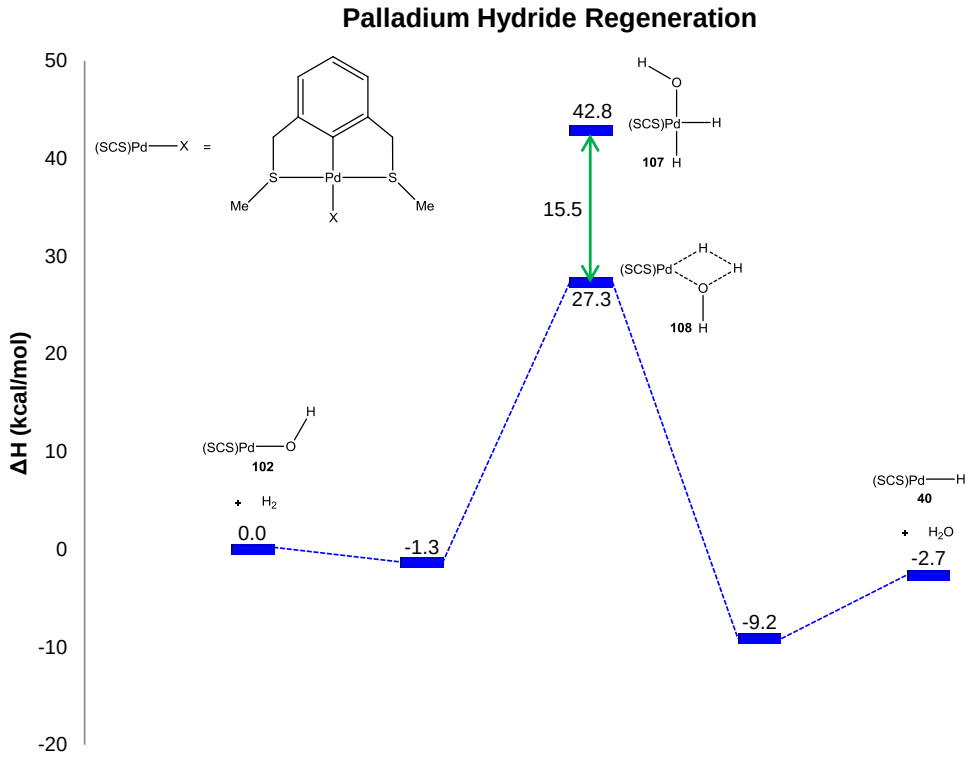


Figure 5-8: Reaction coordination for regeneration of palladium hydride 40 from the corresponding palladium hydroxide 102

In addition to the palladium hydroxides discussed above, the reaction coordinate for conversion of (2,6-bis(methoxymethyl)phenyl-C-O-O')palladium hydroxide (**101**) to the corresponding palladium hydride **39** was examined (see Figure 5-9). Despite several efforts, however, the transition state along the

internal electrophilic substitution pathway for this reaction could not be located. Instead, when hydrogen is added to the palladium hydroxide **101**, hydrogen adds across the palladium-oxygen bond and one methoxy arm of the ligand dissociates, leaving palladium bound to the aromatic ring, one methoxy arm, hydrogen, and water (intermediate **109**). This intermediate **109** is over 26 kcal/mol more stable than the reactants, suggesting that this particular palladium hydroxide **101** would undergo hydrogenation across the palladium-oxygen bond rather than hydrogenolysis. The octahedral palladium intermediate **110** is 56.6 kcal/mol higher in energy than the palladium hydroxide **101** and hydrogen reactants, making hydrogenolysis through an oxidative-addition/reductive-elimination pathway highly unlikely. The difficulty finding a transition state for the hydrogenolysis of **101** could be due to the coordinatively labile methoxy arms on the ligand. Ethers are known to be particularly labile and can be incorporated into a ligand to facilitate reversible binding of small molecules to the metal center.[96,97] Although that is often desired, the hydrogenation of the palladium hydroxide **101** allowed by the lability of the methoxy arm is counterproductive to the desired reaction here.

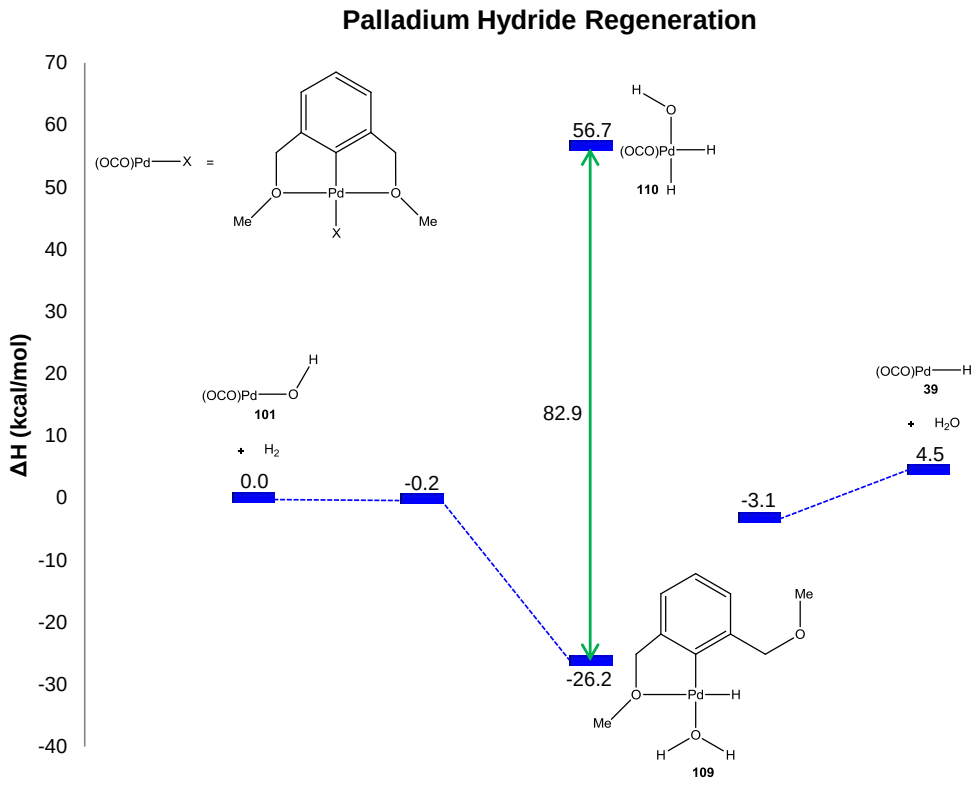


Figure 5-9: Reaction coordination for regeneration of palladium hydride 39 from the corresponding palladium hydroxide 101

A similar reaction was seen by Goldberg, Kemp, and coworkers for ((2-(methoxymethyl)-6-((di-*tert*-butylphosphino)methyl))phenyl-C-O-P)palladium hydroxide, which has a hemilabile ligand.[98] Upon addition of hydrogen gas to the palladium hydroxide, the authors noted formation of a palladium(0) species containing two (2-(methoxymethyl)-6-((di-*tert*-butylphosphino)methyl))phenyl ligands, bound to palladium in monodentate fashion through the phosphorus atoms.[98] This is shown in Figure 5-10. Although the authors presented three potential mechanisms, they concluded that the mechanism shown in Figure 5-10 was most likely based on the results of hydrogen/deuterium scrambling

experiments. The proposed four-coordinate hydro-hydridopalladium intermediate in which the methoxy arm of the ligand has dissociated from palladium is analogous to the stable hydro-hydridopalladium species **109** calculated for the addition of hydrogen to palladium hydroxide **101** in Figure 5-9 above. This similarity between the predicted outcome of addition of hydrogen to a palladium hydroxide complex with a hemilabile ligand and the observed experimental reaction between hydrogen and a palladium hydroxide complex with a hemilabile ligand provides further confirmation that the computational methods employed here are valid and accurately predicting experimental results.

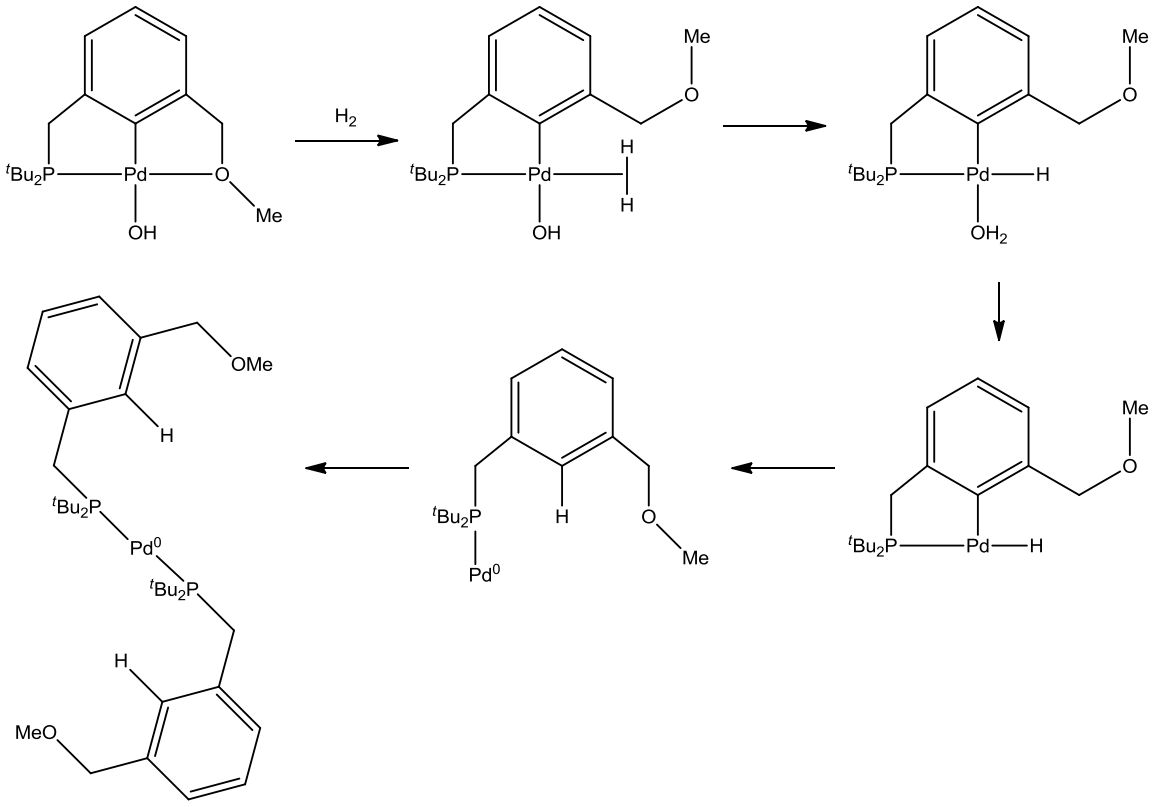


Figure 5-10: Possible mechanism for the addition of hydrogen to ((2-(methoxymethyl)-6-((di-*tert*-butylphosphino)methyl))phenyl-C-O-P)palladium hydroxide, as proposed by Goldberg, Kemp, and coworkers[98]

Conclusions and Direction for Future Experimental Work

Although the activation energies found for the regeneration of palladium hydride from palladium hydroxide are relatively large (ranging from 23.3 kcal/mol to 27.9 kcal/mol) and the products are not significantly more stable than the reactants, it is important to remember that this reaction has been demonstrated experimentally. Because the products and reactants are close in energy, the

potential exists for the reactants (palladium hydroxide and hydrogen) and products (palladium hydride and water) to exist in equilibrium. Obviously, the reverse reaction (conversion of palladium hydride to palladium hydroxide) would not be productive in the proposed catalytic cycle, so the reaction may need to be driven forward by the addition of an excess of hydrogen and the removal of water. Additionally, the choice of ligand clearly plays an important role in the regeneration of palladium hydride and hemi-labile ligands should be avoided because of the potential for hydrogenation of the palladium hydroxide rather than hydrogenolysis.

Chapter 6: Conclusions

Proposed Catalytic Cycle

The ability to selectively epoxidize alkenes using molecular oxygen as the stoichiometric oxidant is an ambitious but important goal. With large spin-orbit coupling constants, transition metals can mediate the reaction between the alkenes, which exist as singlets, and ground-state-triplet oxygen; achieving such a reaction catalytically would drastically reduce the cost and environmental impact associated with the transition metal. Accordingly, the catalytic cycle shown in Figure 6-1 was proposed and examined in its entirety computationally to determine whether such a catalytic cycle was feasible.

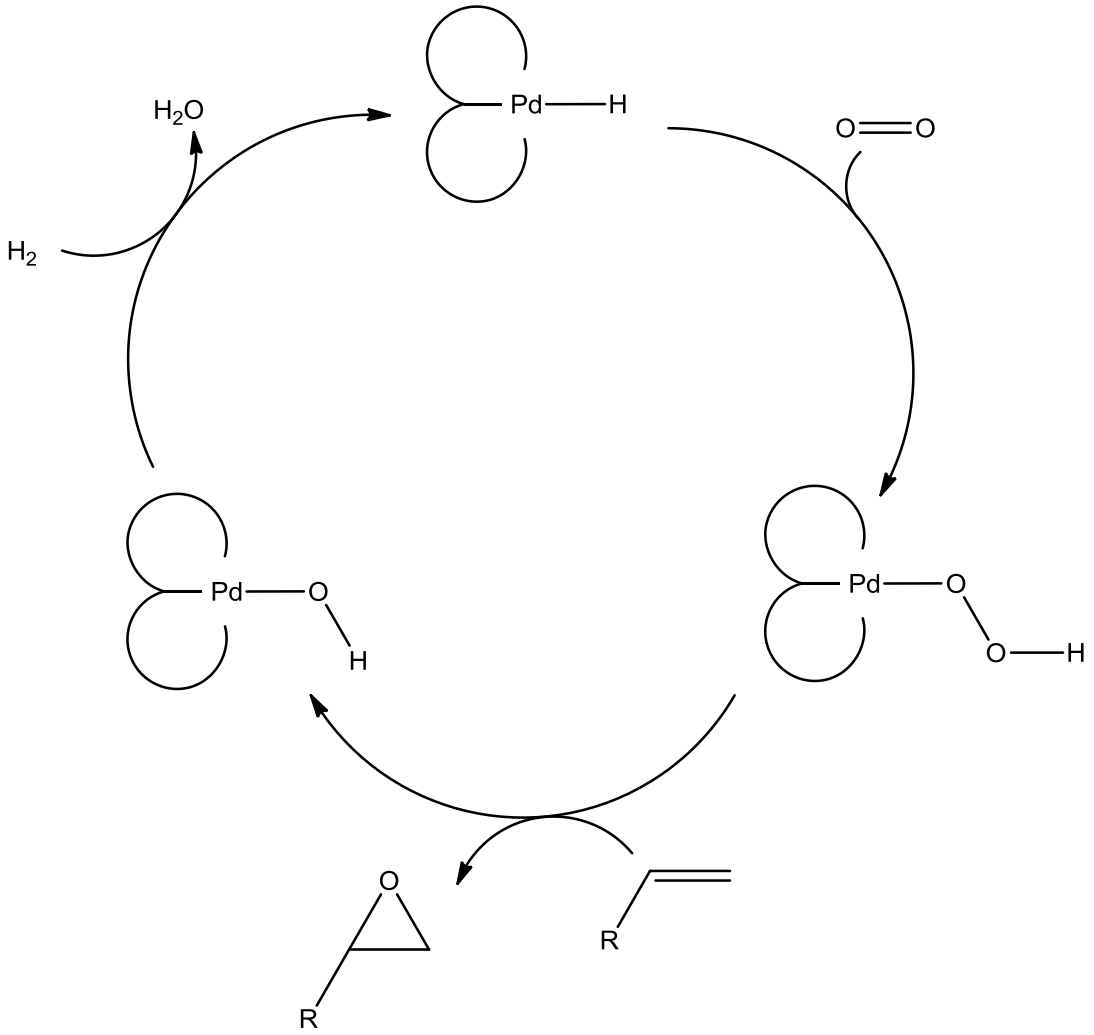


Figure 6-1: Proposed catalytic cycle for the epoxidation of an alkene using molecular oxygen as the stoichiometric oxidant

Computational Results for Each Step of the Proposed Catalytic Cycle

Each of the three steps of this proposed catalytic cycle was examined here. The first step, insertion of oxygen into a palladium-hydride bond (shown in

Figure 6-2), proceeds through a transition state that is 14-20 kcal/mol higher in energy than the corresponding reactants. Such a moderate activation barrier should be easily overcome. The product of this reaction, a singlet palladium hydroperoxide, is significantly more stable than the reactants, thermodynamically driving the reaction toward the palladium hydroperoxide product.

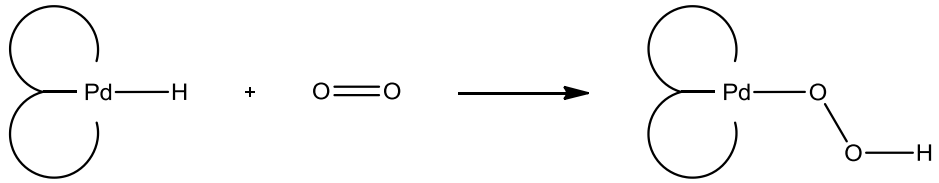


Figure 6-2: First step of proposed catalytic cycle is insertion of oxygen into palladium-hydride bond

The large number of potential tridentate ligands that could be used in this reaction effectively prohibit both the experimental and direct computational identification of the best ligand to use. Experimentally, it is both expensive and time-consuming to prepare a large number of palladium hydrides and determine the appropriate conditions under which oxygen can be inserted into the palladium-hydride bond; computationally, it is time-consuming to map out the reaction coordinates for the preparation of a large number of palladium hydroperoxides. In light of this, a physical property of the starting palladium hydrides that correlated well with the activation energy required to insert oxygen was sought. Although the activation energies did not correlate well with the palladium-hydride bond dipoles, there was a good correlation between the

activation energies and lengths of the palladium-hydride bonds, making the bond length an appropriate proxy for the ease with which oxygen can be inserted into the palladium-hydride bond. Complexes with longer palladium-hydride bonds should undergo oxygen insertion more rapidly than complexes with shorter palladium-hydride bonds. Experimental focus for this step should concentrate on palladium hydrides with relatively long palladium-hydride bonds.

The second step of the catalytic cycle, transfer of oxygen from the palladium hydroperoxide to an alkene (shown in Figure 6-3), is arguably the most important step in the cycle, as it is the one accomplishing the desired conversion of an alkene to an epoxide. If necessary, the palladium hydroperoxide could be prepared differently or the palladium hydride could be regenerated from palladium hydroxide in a different way, but without the oxygen transfer step the catalytic cycle will not accomplish the desired conversion of alkenes to epoxides. Several alkenes were examined to determine whether oxygen transfer to electron-rich or electron-deficient alkenes would be more facile. With the oxygen atom proximal to the palladium relatively electron-rich, it was anticipated that oxygen transfer to electron-deficient alkenes would be most readily accomplished. Indeed, the calculations performed confirmed this: an activation barrier of 14 kcal/mol was found for oxygen atom transfer to electron-deficient alkenes, while up to 26 kcal/mol was required for oxygen transfer to electron-rich alkenes. Fortunately, the products of this reaction are considerably more stable than the reactants (41-44 kcal/mol more stable), providing a thermodynamic

driving force for oxygen transfer. Because this reaction has not yet been demonstrated experimentally and is vital to the success of the proposed catalytic cycle, experimentalists should focus on this reaction, first attempting epoxidation of electron-deficient alkenes.

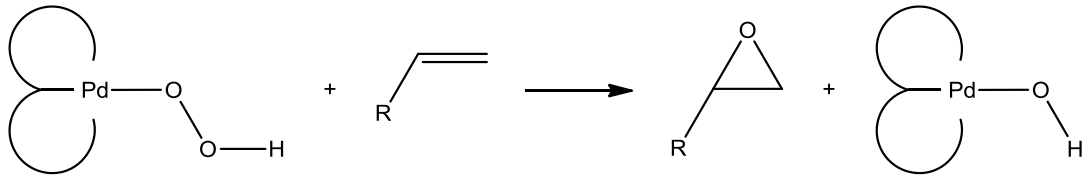


Figure 6-3: Second step of proposed catalytic cycle is oxygen atom transfer from palladium hydroperoxide to an alkene, forming an epoxide

The last step of the catalytic cycle, regeneration of palladium hydride from palladium hydroxide (shown in Figure 6-4), is one that has been demonstrated experimentally. The effect of the ligand atoms of attachment *cis* to the hydride was explored. Despite the fact that activation barriers for this reaction are moderate (23-27 kcal/mol) and the products are not significantly more stable than the reactants, this reaction is feasible. However, hemilabile ligands should be avoided, as they may allow for hydrogenation of the palladium-hydride bond rather than hydrogenolysis, leading to undesired reactions.

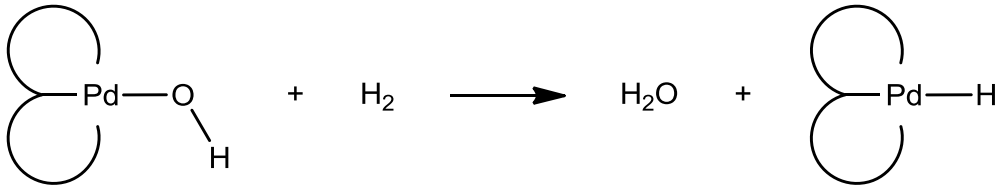


Figure 6-4: Third step of the proposed catalytic cycle is regeneration of palladium hydride from palladium hydroxide and hydrogen

Summary of Results

To summarize the results obtained above, experimentalists should keep the following points in mind when attempting to demonstrate the individual steps of the catalytic cycle:

- for oxygen insertion into a palladium-hydride bond:
    - the reaction is favored thermodynamically and the transition state barriers are all less than 20 kcal/mol, indicating that this reaction should occur readily at or near room temperature,
    - to increase ease of oxygen insertion, focus on palladium hydride complexes with relatively long palladium-hydride bonds, as calculated in Chapter 3 above,
    - complexes with neutral ligands and a counterion tended to have relatively short palladium-hydrogen bonds, so should be avoided, and

    - palladium-hydrogen bond dipoles, whether calculated from Mulliken charges or CHELPG charges, were not a good predictor of activation energy for oxygen insertion;
- for epoxidation of an alkene by palladium hydroperoxide:
    - the reaction is thermodynamically favored,
    - activation barriers for epoxidation range from 14 kcal/mol for the most electron-deficient alkene to 26 kcal/mol for the most electron-rich alkene, therefore electron-deficient alkenes clearly undergo epoxidation more readily than electron-rich alkenes, and
    - since this is the most important step of the proposed catalytic cycle and since epoxidation of an alkene by palladium hydroperoxide has not yet been demonstrated experimentally, experimental efforts should be focused on this key step; and
- for the regeneration of palladium hydride from palladium hydroxide:
    - transition state barriers are relatively large (23-28 kcal/mol), so heat may be required for this step of the proposed catalytic cycle,
    - it may be necessary to add an excess of hydrogen and remove water as it is formed to drive the potential equilibrium toward palladium hydride, since the products (palladium hydride and

water) and reactants (palladium hydroxide and hydrogen) are close in energy, and

- complexes with hemilabile ligands should be avoided because they have the potential to undergo hydrogenation of the palladium hydroxide rather than hydrogenolysis.

In conclusion, no fundamental flaw was found in the catalytic cycle proposed and experimental work on this project should continue. The calculations performed here can provide guidance to the experimentalists working to demonstrate oxygen transfer from a palladium hydroperoxide to an alkene and attempting to prepare a fully functional transition-metal-mediated catalytic cycle in which molecular oxygen is used as a stoichiometric oxidant in the epoxidation of alkenes.

List of Appendices

Appendix A: Abbreviations and Symbols 114

Appendix B: Optimized Geometries of Selected Complexes 119

Appendix A: Abbreviations and Symbols

°	Degree
‡	Transition state indicator
6-31+g(d)	Pople's split-valence double-ζ basis set with six primitive Gaussians comprising each core atomic orbital basis function and valence orbitals composed of two basis functions each, the first one composed of a linear combination of three primitive Gaussian functions and the other composed of one primitive Gaussian function, with polarization and diffuse functions added
δ^-	Partial negative charge
δ^+	Partial positive charge
ΔE	Change in energy
ΔG	Change in Gibbs free energy
ΔH	Change in enthalpy
ζ	Basis function applied to an atomic orbital
η	Hapticity of a ligand complexed to a transition metal
μ	Bond dipole
π	Bonding molecular orbital
π^*	Antibonding molecular orbital
Å	Angstroms

APT	Atomic polar tensor atomic charge calculation scheme
atm	Atmospheres of pressure
B3LYP	Becke's three-parameter hybrid functional combined with the Lee, Yang, and Parr correlation functional
bipy	2,2'-Bipyridine
Bn	Benzyl group
(CCC)	Tridentate ligand attached to transition metal through three carbon atoms
CHELPG	Charges from electrostatic potentials using a grid-based method, an atomic charge calculation scheme
(CNC)	Tridentate ligand attached to transition metal through two carbon atoms and a central nitrogen atom
Cy	Cyclohexyl group
$d(_{x^2-y^2})$	d-Orbital with lobes aligned along the x- and y-axes
DFT	Density functional theory computational method
Et	Ethyl group
h	Hours
HMPA	Hexamethylphosphoramide
^{i}Pr	Isopropyl group
K	Kelvin
kcal/mol	Kilocalories per mole
L	Any ligand
L_n	Any number of ligands

LACVP*	A basis set that uses the 6-31g(d) basis set for atoms H – Ar and the LANL2DZ basis set for atoms heavier than argon
LACVP**	A basis set that uses the 6-31g(d,p) basis set for atoms H – Ar and the LANL2DZ basis set for atoms heavier than argon
LANL2DZ	Los Alamos National Laboratories second-order double-ζ basis set of contracted Gaussian functions
LDA	Lithium diisopropylamide
M	Any transition metal
Me	Methyl group
MECP	Minimum energy crossing point
(NCN)	Tridentate ligand attached to transition metal through two nitrogen atoms and a central carbon atom
(NNN)	Tridentate ligand attached to transition metal through three nitrogen atoms
(OCO)	Tridentate ligand attached to transition metal through two oxygen atoms and a central carbon atom
(PCN)	Tridentate ligand attached to transition metal through a phosphorus atom, a carbon atom, and a nitrogen atom
(PCO)	Tridentate ligand attached to transition metal through a phosphorus atom, a carbon atom, and an oxygen atom
(PCP)	Tridentate ligand attached to transition metal through two phosphorus atoms and a central carbon atom
Ph	Phenyl group

(PNP)	Tridentate ligand attached to transition metal through two phosphorus atoms and a central nitrogen atom
(PPP)	Tridentate ligand attached to transition metal through three phosphorus atoms
(PSiP)	Tridentate ligand attached to transition metal through two phosphorus atoms and a central silicon atom
pyr	Pyridine
q_H	Atomic charge on hydrogen
q_{Pd}	Atomic charge on palladium
r	Bond length
R	Any organic substituent
R’	Any organic substituent
R’’	Any organic substituent
R^1	Any organic substituent
R^2	Any organic substituent
R^2	Coefficient of determination
(R)-BINOL	Optically active (R)-enantiomer of 1,1’-Bi-2-naphthol
RMS	Root-mean-square value
s	Spin
(SCS)	Tridentate ligand attached to transition metal through two sulfur atoms and a central carbon atom
SP	Single-point
STS	Spin transition state
^{t}Bu	*tert*-Butyl group

TS	Transition state
X	Any ligand
X:	A ligand with a lone pair of electrons

Appendix B: Optimized Geometries of Selected Complexes

This appendix contains additional structural information for selected complexes studied and presented in this dissertation. The information is included to provide the reader with a more complete understanding of the optimized geometry of each complex and to assist with reproduction of the work presented. For each complex, the appendix contains:

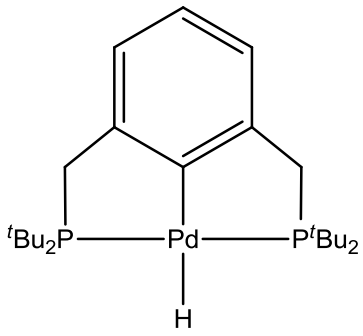
- the complex number, as referenced in the dissertation,
- the figures in which the complex was presented,
- a graphical representation of the complex, with most hydrogen atoms omitted,
- a ball-and-stick representation of the complex, presented in the optimized geometry, with atoms labeled by center number and element,
- the energy of the complex, in hartrees,
- palladium-hydrogen bond length, for palladium hydrides, and
- a table that lists, for each atom in the complex, the following:
    - the center number and element,
    - x,y,z coordinates,
    - Mulliken atomic charge,

- CHELPG atomic charge (where applicable),
- Mulliken atomic spin density (where applicable), and
- APT atomic charge (where applicable).

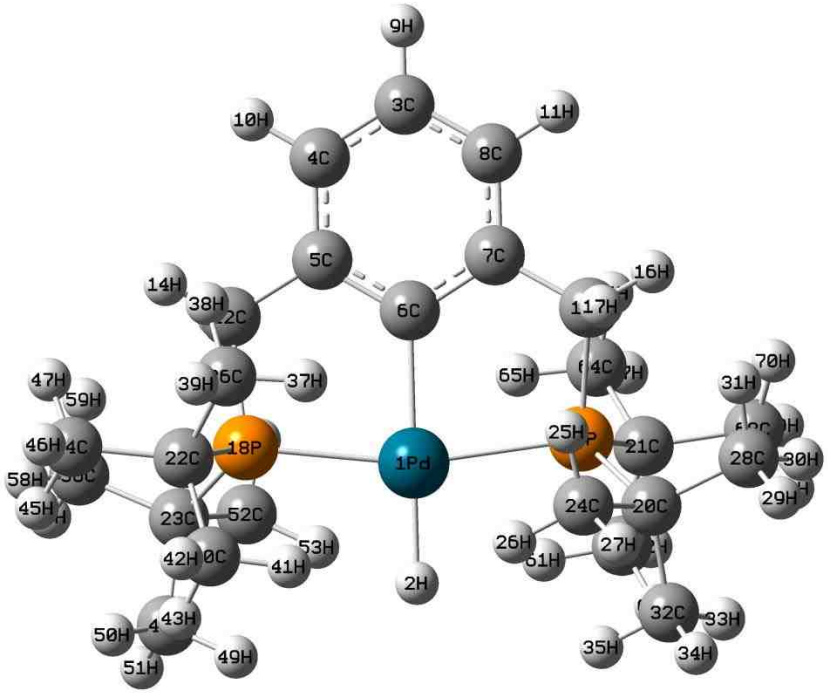
*** *** ***

(PCP) palladium hydride **1**

(see Figure 1-10, Figure 1-12, Figure 2-5, Figure 3-2, Figure 3-14)



1



Energy: -1750.55930362 hartrees

Palladium-hydrogen bond length: 1.652 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-0.4985	0.0000	-1.6987	-0.0086		
2H	0.0000	-2.1513	0.0001	0.0020	-0.2863		
3C	0.0000	4.4356	-0.0001	-0.2472	-0.0719		
4C	-1.1837	3.7349	-0.2477	-0.3258	-0.2956		
5C	-1.1863	2.3316	-0.2541	0.6291	0.2056		
6C	0.0000	1.6036	-0.0001	1.0428	-0.3235		
7C	1.1863	2.3316	0.2540	0.6291	0.2057		
8C	1.1837	3.7349	0.2475	-0.3257	-0.2957		
9H	0.0000	5.5232	-0.0001	0.1676	0.1077		
10H	-2.1027	4.2866	-0.4435	0.1619	0.1163		
11H	2.1027	4.2866	0.4433	0.1619	0.1163		
12C	-2.4665	1.5782	-0.5823	-1.7285	-0.0403		
13C	2.4665	1.5782	0.5821	-1.7285	-0.0401		
14H	-3.3524	2.0512	-0.1388	0.2484	0.0311		

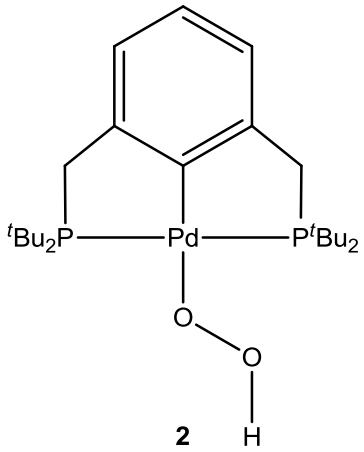
15H	-2.6325	1.5914	-1.6673	0.2509	0.0271		
16H	3.3524	2.0512	0.1385	0.2484	0.0310		
17H	2.6326	1.5916	1.6671	0.2509	0.0271		
18P	-2.3064	-0.2255	-0.0811	0.9648	-0.0468		
19P	2.3064	-0.2255	0.0811	0.9648	-0.0479		
20C	3.2490	-1.1727	1.4506	-0.4613	0.6512		
21C	3.1638	-0.3458	-1.6261	-0.4136	0.6250		
22C	-3.1638	-0.3457	1.6261	-0.4136	0.6240		
23C	-3.2489	-1.1728	-1.4506	-0.4613	0.6510		
24C	2.3166	-1.1434	2.6842	-0.4763	-0.2690		
25H	2.1184	-0.1240	3.0350	0.2169	0.0525		
26H	1.3559	-1.6189	2.4635	0.2589	0.0451		
27H	2.7947	-1.6887	3.5097	0.2111	0.0414		
28C	4.6052	-0.5469	1.8376	-0.4246	-0.4048		
29H	5.0283	-1.1077	2.6826	0.2164	0.0731		
30H	5.3356	-0.5833	1.0255	0.2165	0.0758		
31H	4.5071	0.4956	2.1590	0.2206	0.0621		
32C	3.4523	-2.6440	1.0388	-0.5066	-0.3980		
33H	4.2008	-2.7517	0.2470	0.2166	0.0707		
34H	3.8125	-3.2144	1.9060	0.2126	0.0713		
35H	2.5151	-3.0990	0.7005	0.2580	0.0842		
36C	-2.5475	0.7633	2.5096	-0.6074	-0.1892		
37H	-1.4585	0.6761	2.5700	0.2519	0.0115		
38H	-2.7825	1.7691	2.1471	0.2375	0.0260		
39H	-2.9561	0.6717	3.5253	0.2113	0.0265		
40C	-2.8317	-1.7093	2.2695	-0.6297	-0.3702		
41H	-1.7512	-1.8761	2.3127	0.2521	0.0668		
42H	-3.2272	-1.7279	3.2946	0.2081	0.0649		
43H	-3.2777	-2.5486	1.7286	0.2160	0.0709		
44C	-4.6911	-0.1528	1.5799	-0.3854	-0.4297		
45H	-5.1973	-0.9827	1.0777	0.2230	0.0841		
46H	-5.0789	-0.1098	2.6071	0.2184	0.0774		
47H	-4.9817	0.7806	1.0837	0.2248	0.0758		
48C	-3.4523	-2.6441	-1.0386	-0.5066	-0.3999		
49H	-2.5151	-3.0990	-0.7002	0.2580	0.0848		
50H	-4.2008	-2.7517	-0.2468	0.2166	0.0713		
51H	-3.8126	-3.2145	-1.9058	0.2126	0.0719		
52C	-2.3166	-1.1437	-2.6841	-0.4763	-0.2717		
53H	-1.3559	-1.6191	-2.4633	0.2589	0.0457		

54H	-2.7947	-1.6890	-3.5095	0.2111	0.0422		
55H	-2.1183	-0.1243	-3.0350	0.2169	0.0533		
56C	-4.6052	-0.5470	-1.8376	-0.4246	-0.4038		
57H	-5.0282	-1.1079	-2.6826	0.2164	0.0730		
58H	-5.3355	-0.5833	-1.0255	0.2165	0.0755		
59H	-4.5070	0.4954	-2.1591	0.2206	0.0618		
60C	2.8317	-1.7095	-2.2693	-0.6297	-0.3707		
61H	1.7512	-1.8764	-2.3125	0.2521	0.0669		
62H	3.2271	-1.7282	-3.2944	0.2081	0.0649		
63H	3.2778	-2.5487	-1.7284	0.2160	0.0710		
64C	2.5474	0.7631	-2.5097	-0.6074	-0.1892		
65H	1.4584	0.6758	-2.5700	0.2519	0.0116		
66H	2.7823	1.7690	-2.1473	0.2375	0.0259		
67H	2.9560	0.6714	-3.5254	0.2113	0.0264		
68C	4.6911	-0.1528	-1.5799	-0.3854	-0.4302		
69H	5.0789	-0.1099	-2.6071	0.2184	0.0774		
70H	4.9817	0.7806	-1.0839	0.2248	0.0759		
71H	5.1973	-0.9827	-1.0776	0.2230	0.0842		

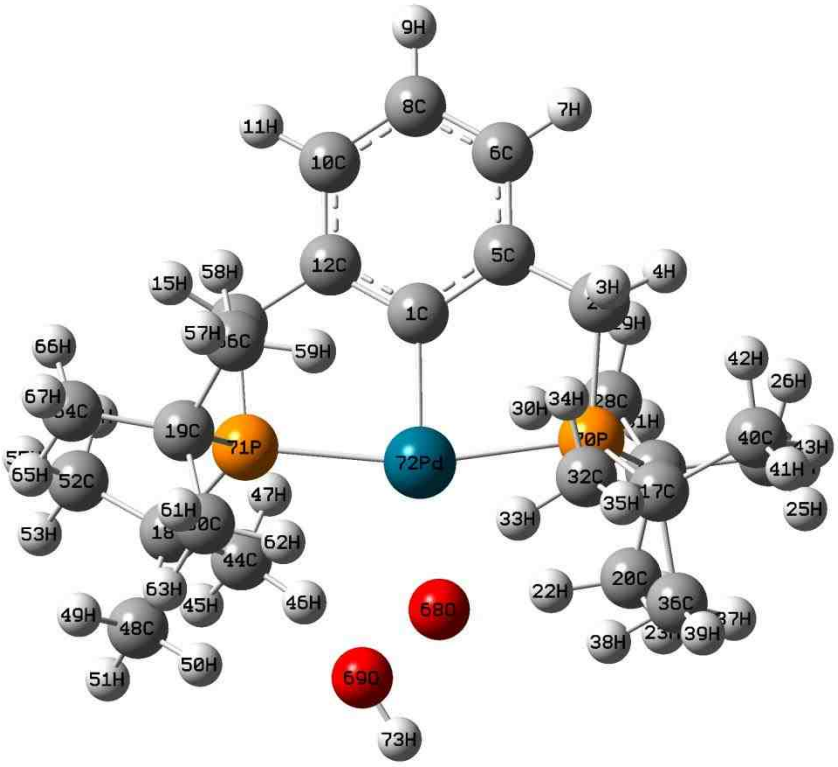
*** *** ***

(PCP) palladium hydroperoxide **2**

(see Figure 1-10, Figure 2-12, Figure 3-2, Figure 4-3, Figure 4-4)



2



Energy: -1900.93546116 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	0.0577	1.7330	-0.0414	1.5199	-0.5044		
2C	2.5295	1.7196	0.5626	-1.6462	-0.1976		
3H	2.6860	1.7394	1.6488	0.2574	0.0563		
4H	3.4135	2.1965	0.1205	0.2524	0.0685		
5C	1.2483	2.4578	0.2189	0.5282	0.3584		
6C	1.2532	3.8605	0.2055	-0.3352	-0.3615		
7H	2.1784	4.3994	0.4048	0.1659	0.1336		
8C	0.0808	4.5728	-0.0507	-0.2836	-0.0314		
9H	0.0892	5.6601	-0.0548	0.1716	0.1072		
10C	-1.1031	3.8766	-0.2997	-0.3719	-0.3629		
11H	-2.0207	4.4282	-0.4992	0.1662	0.1358		
12C	-1.1199	2.4740	-0.3021	0.5476	0.4247		
13C	-2.4085	1.7491	-0.6316	-1.8349	-0.4064		
14H	-2.5390	1.7274	-1.7208	0.2574	0.1045		

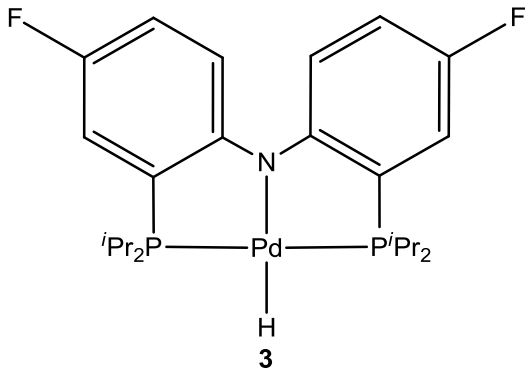
15H	-3.2886	2.2684	-0.2314	0.2505	0.1118		
16C	3.1852	-0.2241	-1.6481	-0.5632	0.5295		
17C	3.2971	-1.0372	1.4343	-0.6235	0.6769		
18C	-3.3949	-0.9439	-1.3798	-0.5950	0.7172		
19C	-3.1029	-0.0813	1.6640	-0.5083	0.5305		
20C	2.8030	-1.5860	-2.2680	-0.6356	-0.4232		
21H	3.1711	-1.6220	-3.3028	0.2078	0.0855		
22H	1.7184	-1.7300	-2.2802	0.2630	0.0873		
23H	3.2423	-2.4294	-1.7294	0.2219	0.0938		
24C	4.7173	-0.0676	-1.6243	-0.3704	-0.3861		
25H	5.2104	-0.8984	-1.1110	0.2275	0.0775		
26H	5.0349	0.8692	-1.1511	0.2246	0.0670		
27H	5.0918	-0.0543	-2.6571	0.2195	0.0735		
28C	2.5824	0.8922	-2.5309	-0.6431	-0.1392		
29H	2.8490	1.8952	-2.1821	0.2353	0.0134		
30H	1.4908	0.8305	-2.5747	0.2532	-0.0028		
31H	2.9724	0.7807	-3.5516	0.2137	0.0250		
32C	2.3590	-1.0226	2.6646	-0.4749	-0.2090		
33H	1.4182	-1.5374	2.4480	0.2845	0.0164		
34H	2.1290	-0.0056	3.0048	0.2120	0.0311		
35H	2.8560	-1.5413	3.4960	0.2107	0.0287		
36C	3.5039	-2.5049	1.0074	-0.5460	-0.3513		
37H	4.2525	-2.6019	0.2141	0.2117	0.0539		
38H	2.5622	-2.9532	0.6741	0.2893	0.0702		
39H	3.8714	-3.0762	1.8712	0.2101	0.0555		
40C	4.6495	-0.4053	1.8244	-0.3994	-0.4927		
41H	5.0848	-0.9864	2.6491	0.2188	0.0916		
42H	4.5443	0.6264	2.1775	0.2183	0.0815		
43H	5.3727	-0.4117	1.0047	0.2178	0.0948		
44C	-2.4716	-1.1370	-2.6053	-0.5204	-0.3856		
45H	-3.0458	-1.6059	-3.4166	0.2091	0.0684		
46H	-1.6258	-1.7856	-2.3592	0.2793	0.0797		
47H	-2.0818	-0.1858	-2.9883	0.2125	0.0553		
48C	-3.8471	-2.3321	-0.8835	-0.5090	-0.4038		
49H	-4.6168	-2.2618	-0.1077	0.2121	0.0578		
50H	-3.0064	-2.9182	-0.5051	0.2870	0.1115		
51H	-4.2912	-2.8771	-1.7284	0.2073	0.0609		
52C	-4.6408	-0.1372	-1.8082	-0.3750	-0.4615		
53H	-5.1917	-0.7204	-2.5591	0.2187	0.0849		

54H	-4.3884	0.8221	-2.2711	0.2157	0.0786		
55H	-5.3271	0.0556	-0.9787	0.2216	0.0796		
56C	-2.3749	0.9827	2.5166	-0.6492	-0.1830		
57H	-2.7587	0.9308	3.5447	0.2121	0.0313		
58H	-2.5409	2.0015	2.1507	0.2382	0.0217		
59H	-1.2950	0.8090	2.5472	0.2497	0.0060		
60C	-2.8343	-1.4690	2.2884	-0.6807	-0.3011		
61H	-3.1385	-1.4487	3.3442	0.2058	0.0486		
62H	-1.7744	-1.7383	2.2371	0.2748	0.0614		
63H	-3.3994	-2.2641	1.7961	0.2277	0.0488		
64C	-4.6121	0.2243	1.6798	-0.3743	-0.4175		
65H	-5.1974	-0.5439	1.1671	0.2272	0.0806		
66H	-4.8456	1.1955	1.2279	0.2221	0.0693		
67H	-4.9601	0.2586	2.7214	0.2185	0.0811		
68O	0.2661	-2.3836	0.2839	-0.2033	-0.3761		
69O	-0.8111	-3.1857	-0.3343	-0.6687	-0.4978		
70P	2.3687	-0.0715	0.0727	1.5705	0.0899		
71P	-2.3203	-0.0328	-0.0774	1.4716	0.2227		
72Pd	0.0416	-0.3202	0.0112	-2.1303	0.0894		
73H	-0.3279	-4.0141	-0.4911	0.5038	0.3660		

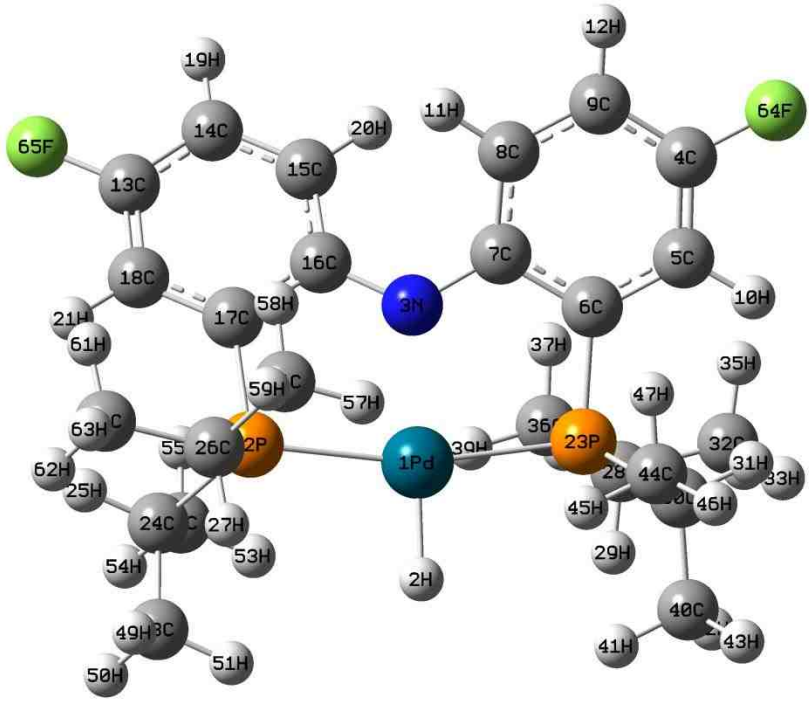
*** *** ***

(PNP) palladium hydride **3**

(see Figure 2-2, Figure 3-15)



3



Energy: -1999.60962913 hartrees

Palladium-hydrogen bond length: 1.585 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-1.1975	0.0000	-1.5521	-0.0987		
2H	0.0000	-2.7829	0.0000	0.0819	-0.2144		
3N	0.0000	0.9414	0.0000	0.3583	-0.1769		
4C	3.7110	2.7643	0.8197	-0.2539	0.4612		
5C	3.6628	1.4510	0.3848	0.1563	-0.4298		
6C	2.4245	0.8459	0.1174	-0.5099	0.1158		
7C	1.2010	1.5796	0.2616	0.6221	0.0247		
8C	1.3153	2.9071	0.7614	-0.1385	-0.1309		
9C	2.5469	3.4941	1.0333	-0.7701	-0.3437		
10H	4.5948	0.9036	0.2816	0.1956	0.1918		
11H	0.4179	3.4722	0.9826	0.2002	0.1382		
12H	2.6071	4.5049	1.4265	0.1979	0.1833		
13C	-3.7110	2.7643	-0.8198	-0.2539	0.4611		
14C	-2.5470	3.4941	-1.0333	-0.7702	-0.3436		

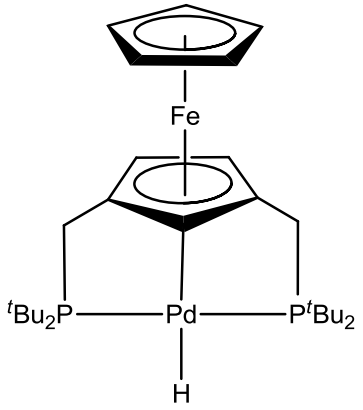
15C	-1.3154	2.9071	-0.7614	-0.1384	-0.1311		
16C	-1.2010	1.5796	-0.2616	0.6221	0.0251		
17C	-2.4245	0.8459	-0.1175	-0.5103	0.1151		
18C	-3.6629	1.4509	-0.3848	0.1566	-0.4294		
19H	-2.6071	4.5049	-1.4264	0.1979	0.1833		
20H	-0.4179	3.4722	-0.9825	0.2002	0.1382		
21H	-4.5948	0.9035	-0.2817	0.1956	0.1917		
22P	-2.2788	-0.9322	0.3194	1.4309	0.1457		
23P	2.2788	-0.9322	-0.3194	1.4311	0.1454		
24C	-3.4745	-1.8454	-0.7944	-0.0105	0.3904		
25H	-4.4648	-1.3889	-0.6638	0.2148	-0.0578		
26C	-2.9131	-1.1555	2.0750	-0.3936	0.2815		
27H	-2.7876	-2.2309	2.2599	0.2273	-0.0368		
28C	2.9132	-1.1556	-2.0750	-0.3936	0.2806		
29H	2.7878	-2.2310	-2.2598	0.2273	-0.0361		
30C	3.4745	-1.8453	0.7945	-0.0106	0.3904		
31H	4.4647	-1.3887	0.6641	0.2149	-0.0578		
32C	4.3902	-0.7863	-2.2859	-0.6127	-0.2027		
33H	5.0660	-1.3490	-1.6320	0.2136	0.0302		
34H	4.6796	-1.0066	-3.3217	0.2131	0.0478		
35H	4.5606	0.2830	-2.1192	0.2385	0.0416		
36C	2.0043	-0.3955	-3.0562	-0.7507	-0.2423		
37H	2.0683	0.6873	-2.8977	0.2394	0.0435		
38H	2.3156	-0.6031	-4.0879	0.2081	0.0650		
39H	0.9559	-0.6911	-2.9474	0.2350	0.0386		
40C	3.5605	-3.3310	0.4055	-0.7890	-0.3746		
41H	2.5740	-3.8066	0.4564	0.2441	0.0927		
42H	3.9596	-3.4793	-0.6040	0.2152	0.0797		
43H	4.2255	-3.8568	1.1023	0.2120	0.0795		
44C	3.0519	-1.6829	2.2643	-0.7885	-0.2354		
45H	2.0700	-2.1381	2.4387	0.2360	0.0472		
46H	3.7796	-2.1826	2.9165	0.2062	0.0513		
47H	2.9982	-0.6308	2.5621	0.2368	0.0345		
48C	-3.5602	-3.3312	-0.4055	-0.7890	-0.3748		
49H	-3.9591	-3.4796	0.6041	0.2152	0.0799		
50H	-4.2253	-3.8570	-1.1022	0.2120	0.0794		
51H	-2.5737	-3.8065	-0.4565	0.2441	0.0928		
52C	-3.0522	-1.6829	-2.2643	-0.7885	-0.2354		
53H	-2.0702	-2.1379	-2.4388	0.2360	0.0471		

54H	-3.7799	-2.1826	-2.9163	0.2062	0.0513		
55H	-2.9987	-0.6307	-2.5620	0.2368	0.0345		
56C	-2.0043	-0.3952	3.0561	-0.7508	-0.2425		
57H	-0.9558	-0.6907	2.9473	0.2350	0.0386		
58H	-2.0685	0.6876	2.8975	0.2394	0.0434		
59H	-2.3156	-0.6028	4.0879	0.2081	0.0651		
60C	-4.3901	-0.7864	2.2859	-0.6127	-0.2029		
61H	-4.5607	0.2829	2.1191	0.2385	0.0415		
62H	-5.0658	-1.3493	1.6320	0.2136	0.0302		
63H	-4.6795	-1.0067	3.3217	0.2131	0.0479		
64F	4.9238	3.3404	1.0793	-0.3699	-0.2846		
65F	-4.9238	3.3403	-1.0794	-0.3699	-0.2846		

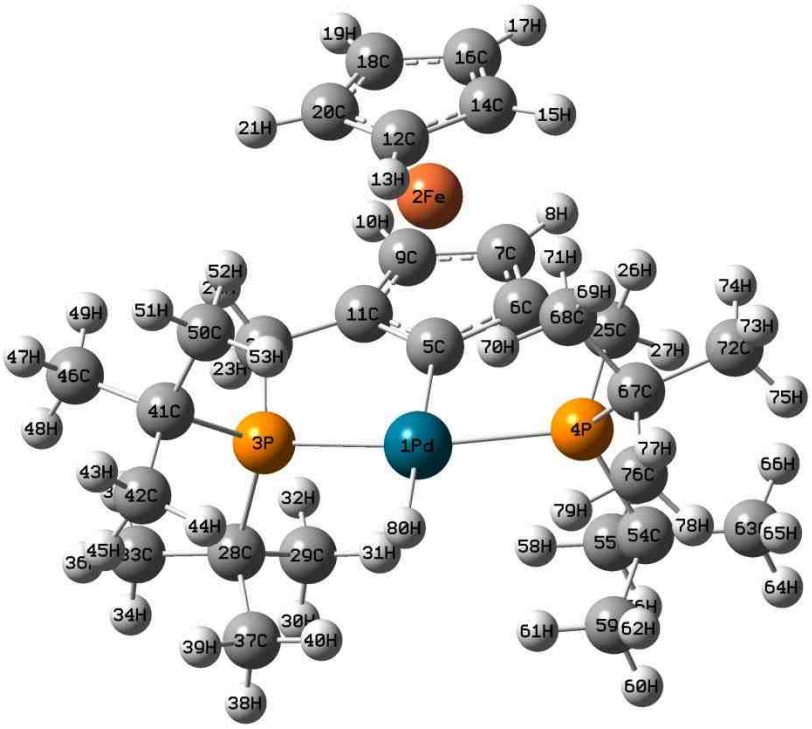
*** *** ***

(PCP) palladium hydride **4**

(see Figure 2-3, Figure 3-14)



4



Energy: -2028.81802534 hartrees

Palladium-hydrogen bond length: 1.659 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0001	-1.0113	0.4563	-1.6989	-0.0405		
2Fe	-0.0002	2.7235	-0.5867	-1.7151	0.0283		
3P	-2.3242	-0.8287	0.0926	0.5157	0.0092		
4P	2.3244	-0.8283	0.0925	0.5160	0.0114		
5C	0.0000	0.5851	-0.8215	1.9722	-0.2688		
6C	1.1573	1.1827	-1.4087	0.7590	0.1385		
7C	0.7200	2.1153	-2.4128	0.3321	-0.2282		
8H	1.3456	2.7427	-3.0377	0.1737	0.1266		
9C	-0.7202	2.1152	-2.4128	0.3315	-0.2286		
10H	-1.3459	2.7426	-3.0377	0.1737	0.1265		
11C	-1.1574	1.1826	-1.4087	0.7578	0.1396		
12C	0.0017	3.2869	1.4312	-0.0474	-0.1796		

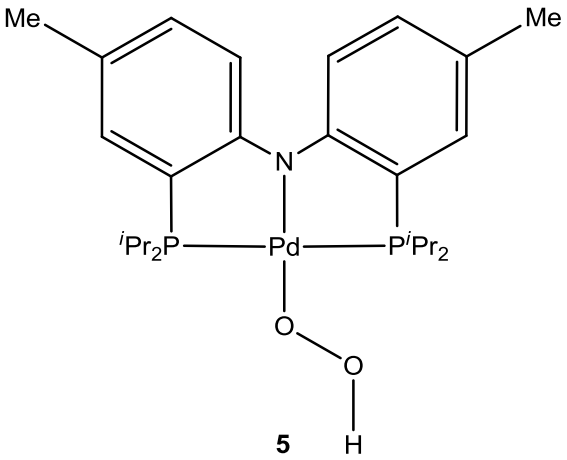
13H	0.0036	2.5932	2.2611	0.1946	0.1258		
14C	1.1548	3.8136	0.7707	-0.1577	-0.1336		
15H	2.1865	3.5976	1.0178	0.1689	0.1143		
16C	0.7120	4.6626	-0.2900	-0.0161	-0.1139		
17H	1.3462	5.1887	-0.9921	0.1828	0.1092		
18C	-0.7172	4.6606	-0.2880	-0.0168	-0.1149		
19H	-1.3547	5.1850	-0.9884	0.1828	0.1099		
20C	-1.1547	3.8104	0.7739	-0.1586	-0.1339		
21H	-2.1851	3.5915	1.0238	0.1689	0.1142		
22C	-2.5339	0.7383	-0.9711	-2.1061	-0.0878		
23H	-3.1959	0.5328	-1.8210	0.2514	0.0338		
24H	-3.0369	1.5032	-0.3715	0.2461	0.0483		
25C	2.5339	0.7385	-0.9713	-2.1065	-0.0876		
26H	3.0370	1.5035	-0.3719	0.2461	0.0481		
27H	3.1957	0.5329	-1.8214	0.2514	0.0339		
28C	-2.9876	-2.2361	-1.0279	-0.5399	0.6465		
29C	-2.2214	-2.1283	-2.3669	-0.5181	-0.2496		
30H	-2.4974	-2.9812	-3.0015	0.2148	0.0363		
31H	-1.1385	-2.1567	-2.2144	0.2410	0.0472		
32H	-2.4593	-1.2152	-2.9221	0.2289	0.0405		
33C	-4.4995	-2.1622	-1.3144	-0.3649	-0.4076		
34H	-4.7599	-2.9205	-2.0660	0.2187	0.0745		
35H	-4.8072	-1.1890	-1.7146	0.2246	0.0702		
36H	-5.0988	-2.3733	-0.4237	0.2233	0.0756		
37C	-2.6440	-3.6037	-0.3997	-0.6350	-0.4220		
38H	-2.8970	-4.3995	-1.1141	0.2066	0.0719		
39H	-3.2052	-3.7967	0.5183	0.2139	0.0892		
40H	-1.5789	-3.6735	-0.1604	0.2647	0.0816		
41C	-3.4387	-0.5293	1.6198	-0.4376	0.5812		
42C	-3.6280	-1.8409	2.4080	-0.4836	-0.3063		
43H	-4.0792	-1.6106	3.3829	0.2139	0.0621		
44H	-2.6729	-2.3454	2.5891	0.2604	0.0543		
45H	-4.3007	-2.5366	1.8958	0.2176	0.0469		
46C	-4.8189	0.0843	1.3043	-0.3604	-0.4304		
47H	-5.3553	0.2555	2.2482	0.2187	0.0851		
48H	-5.4422	-0.5693	0.6892	0.2191	0.0851		
49H	-4.7412	1.0529	0.7993	0.2157	0.0706		
50C	-2.6467	0.4567	2.5078	-0.4349	-0.3179		
51H	-3.2330	0.6825	3.4093	0.2118	0.0496		

52H	-2.4439	1.4031	1.9964	0.2244	0.1083		
53H	-1.6874	0.0284	2.8165	0.2513	0.0525		
54C	2.9878	-2.2359	-1.0277	-0.5396	0.6442		
55C	2.2213	-2.1285	-2.3666	-0.5183	-0.2489		
56H	2.4972	-2.9816	-3.0011	0.2148	0.0362		
57H	2.4589	-1.2155	-2.9221	0.2289	0.0404		
58H	1.1384	-2.1569	-2.2138	0.2410	0.0471		
59C	2.6445	-3.6034	-0.3992	-0.6350	-0.4220		
60H	2.8974	-4.3993	-1.1134	0.2066	0.0721		
61H	1.5794	-3.6732	-0.1596	0.2647	0.0816		
62H	3.2059	-3.7961	0.5187	0.2139	0.0893		
63C	4.4996	-2.1620	-1.3147	-0.3650	-0.4067		
64H	4.7599	-2.9202	-2.0663	0.2187	0.0745		
65H	5.0992	-2.3730	-0.4241	0.2233	0.0753		
66H	4.8072	-1.1887	-1.7150	0.2246	0.0699		
67C	3.4391	-0.5285	1.6195	-0.4375	0.5799		
68C	2.6476	0.4584	2.5070	-0.4354	-0.3124		
69H	3.2338	0.6840	3.4086	0.2118	0.0483		
70H	1.6879	0.0308	2.8155	0.2512	0.0510		
71H	2.4457	1.4048	1.9953	0.2245	0.1064		
72C	4.8196	0.0845	1.3037	-0.3602	-0.4313		
73H	5.3559	0.2563	2.2474	0.2187	0.0854		
74H	4.7422	1.0526	0.7977	0.2157	0.0707		
75H	5.4428	-0.5700	0.6892	0.2191	0.0854		
76C	3.6280	-1.8398	2.4085	-0.4836	-0.3057		
77H	4.0793	-1.6091	3.3832	0.2139	0.0617		
78H	4.3003	-2.5359	1.8965	0.2176	0.0470		
79H	2.6727	-2.3438	2.5898	0.2604	0.0539		
80H	0.0002	-2.3358	1.4555	0.0086	-0.2893		

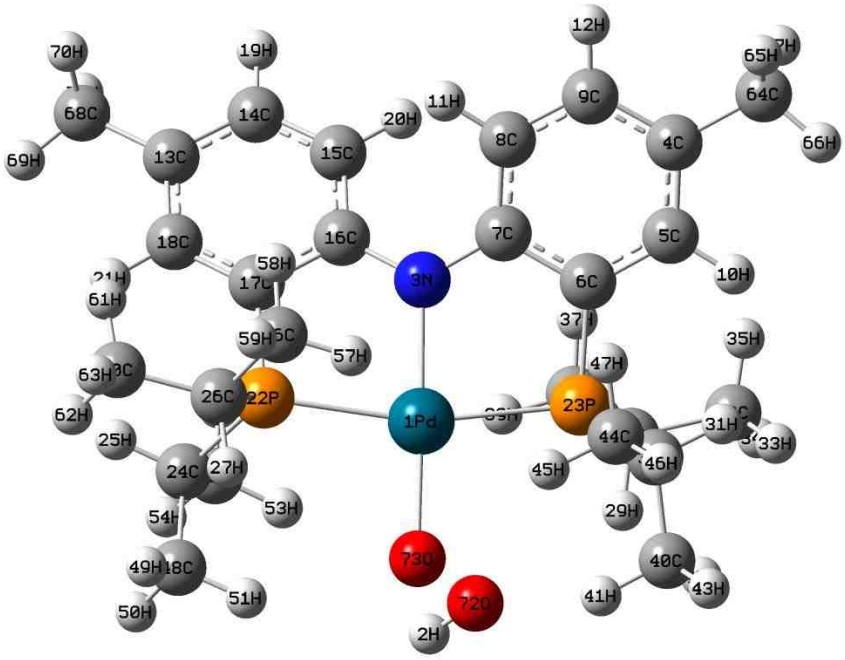
*** *** ***

(PNP) palladium hydroperoxide **5**

(see Figure 2-4, Figure 3-25, Figure 4-4)



5



Energy: -2030.12719742 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.0031	-1.0173	0.0322	-2.0101	0.0763		
2H	0.1438	-4.0198	-1.4760	0.4852	0.3965		
3N	-0.0512	1.0641	-0.0395	0.5000	-0.4878		
4C	3.6107	3.1135	0.7679	-0.1702	0.2011		
5C	3.5793	1.7775	0.3619	-0.1095	-0.3012		

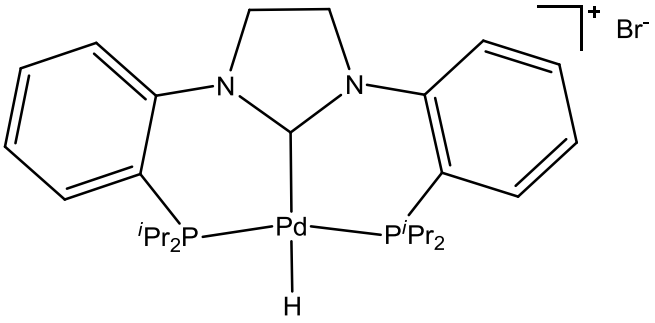
6C	2.3802	1.0948	0.1014	-0.5813	-0.1841		
7C	1.1250	1.7605	0.2198	0.4701	0.3368		
8C	1.1656	3.1006	0.6880	-0.0073	-0.2361		
9C	2.3681	3.7467	0.9450	-0.8740	-0.2310		
10H	4.5234	1.2446	0.2680	0.1690	0.1591		
11H	0.2380	3.6249	0.8868	0.1991	0.1405		
12H	2.3396	4.7710	1.3145	0.1739	0.1395		
13C	-3.8210	2.8419	-0.9859	-0.1310	0.2064		
14C	-2.6136	3.5167	-1.2403	-0.8455	-0.2341		
15C	-1.3763	2.9617	-0.9392	-0.0032	-0.2305		
16C	-1.2610	1.6761	-0.3462	0.6271	0.2742		
17C	-2.4809	0.9652	-0.1449	-0.6333	-0.0414		
18C	-3.7172	1.5561	-0.4510	0.0052	-0.3476		
19H	-2.6417	4.5005	-1.7071	0.1746	0.1408		
20H	-0.4791	3.5109	-1.2007	0.2008	0.1417		
21H	-4.6308	0.9872	-0.2884	0.1679	0.1673		
22P	-2.3029	-0.7640	0.4102	1.6395	0.2081		
23P	2.3061	-0.6930	-0.2700	2.0356	0.4140		
24C	-3.4835	-1.7985	-0.6080	-0.1550	0.4552		
25H	-4.4871	-1.3647	-0.4997	0.2149	-0.0757		
26C	-2.8885	-0.8957	2.1904	-0.3848	0.3189		
27H	-2.7206	-1.9518	2.4416	0.2349	-0.0425		
28C	2.9950	-0.9972	-1.9862	-0.4589	0.2598		
29H	2.8967	-2.0841	-2.1014	0.2522	-0.0146		
30C	3.4739	-1.5233	0.9377	-0.2741	0.3966		
31H	4.4387	-1.0037	0.8531	0.2131	-0.0770		
32C	4.4669	-0.5976	-2.1773	-0.6190	-0.2569		
33H	5.1350	-1.0891	-1.4612	0.2154	0.0381		
34H	4.7983	-0.8845	-3.1842	0.2111	0.0560		
35H	4.6003	0.4862	-2.0844	0.2336	0.0502		
36C	2.0943	-0.3222	-3.0343	-0.8163	-0.2320		
37H	2.1132	0.7695	-2.9328	0.2371	0.0453		
38H	2.4462	-0.5718	-4.0437	0.2062	0.0604		
39H	1.0548	-0.6529	-2.9422	0.2366	0.0139		
40C	3.6797	-3.0115	0.6062	-0.7382	-0.3155		
41H	2.7300	-3.5543	0.6075	0.2849	0.1168		
42H	4.1490	-3.1594	-0.3725	0.2101	0.0485		
43H	4.3397	-3.4608	1.3598	0.2037	0.0502		
44C	2.9477	-1.3450	2.3724	-0.7426	-0.3425		

45H	1.9914	-1.8645	2.4990	0.2489	0.0644		
46H	3.6650	-1.7743	3.0839	0.2043	0.0800		
47H	2.8062	-0.2902	2.6312	0.2314	0.0548		
48C	-3.5051	-3.2499	-0.0935	-0.7486	-0.3649		
49H	-3.9242	-3.3259	0.9159	0.2146	0.0647		
50H	-4.1287	-3.8663	-0.7540	0.2067	0.0690		
51H	-2.4940	-3.6728	-0.0738	0.2737	0.0989		
52C	-3.0891	-1.7367	-2.0934	-0.7629	-0.3826		
53H	-2.0945	-2.1687	-2.2530	0.2352	0.0993		
54H	-3.8090	-2.3102	-2.6917	0.2052	0.0801		
55H	-3.0770	-0.7094	-2.4719	0.2379	0.0635		
56C	-1.9912	-0.0395	3.1001	-0.7573	-0.2060		
57H	-0.9355	-0.3098	2.9973	0.2394	0.0243		
58H	-2.0920	1.0267	2.8658	0.2391	0.0346		
59H	-2.2816	-0.1827	4.1488	0.2079	0.0504		
60C	-4.3742	-0.5635	2.4041	-0.5814	-0.2506		
61H	-4.5835	0.4859	2.1679	0.2363	0.0471		
62H	-5.0397	-1.1912	1.8009	0.2139	0.0377		
63H	-4.6395	-0.7231	3.4575	0.2128	0.0533		
64C	4.9100	3.8403	1.0303	-0.6838	-0.1918		
65H	4.9069	4.3344	2.0106	0.2139	0.0522		
66H	5.7627	3.1522	1.0091	0.2000	0.0471		
67H	5.0984	4.6193	0.2787	0.2200	0.0513		
68C	-5.1582	3.4733	-1.2993	-0.6696	-0.1880		
69H	-5.9757	2.7528	-1.1824	0.1993	0.0464		
70H	-5.3717	4.3224	-0.6354	0.2204	0.0503		
71H	-5.1959	3.8537	-2.3285	0.2145	0.0521		
72O	0.8264	-3.5941	-0.9296	-0.5612	-0.5022		
73O	0.0059	-3.0456	0.1578	-0.1580	-0.3974		

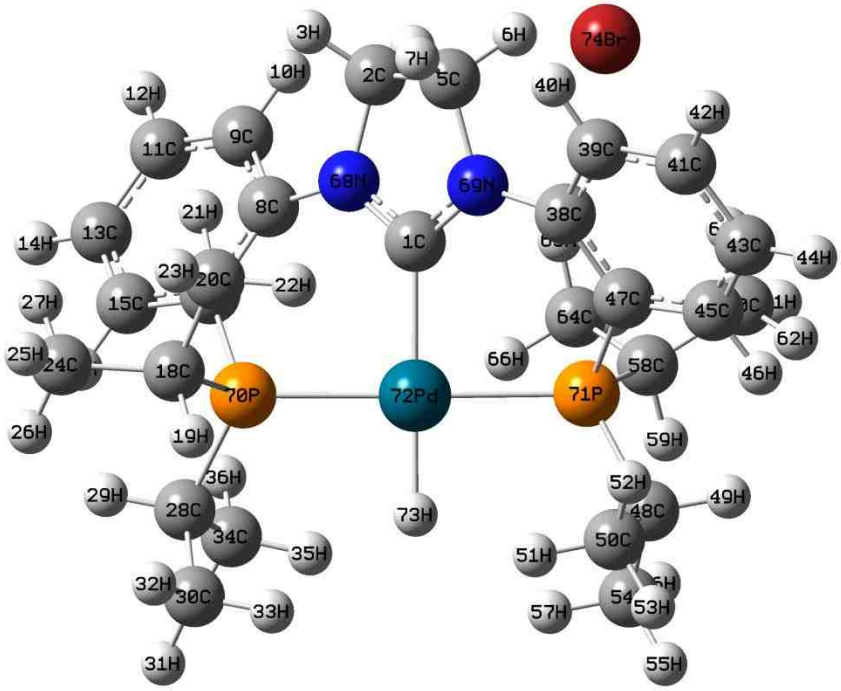
*** *** ***

(PCP) palladium hydride **6**

(see Figure 2-6, Figure 3-14)



6



Energy: -1985.77542003 hartrees

Palladium-hydrogen bond length: 1.609 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	0.0323	0.6843	0.6103	0.3729	0.0727		
2C	0.1256	2.9915	1.0602	-0.4342	-0.0173		
3H	-0.5208	3.6323	1.6657	0.2192	0.0380		
4H	0.5946	3.5494	0.2403	0.2882	0.0738		
5C	1.2136	2.2934	1.8582	-0.2619	0.0718		

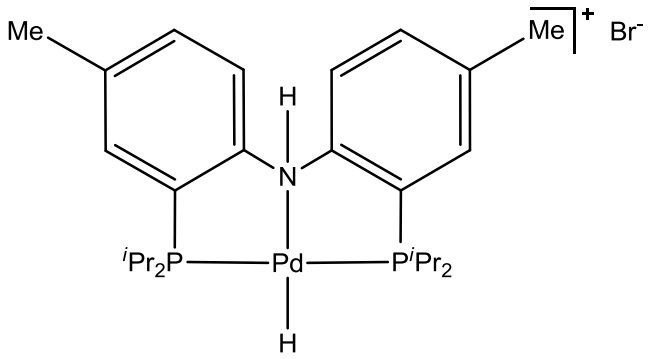
6H	2.1919	2.7252	1.6275	0.3075	0.0664		
7H	1.0094	2.2855	2.9361	0.2009	0.0106		
8C	-1.9029	2.0967	-0.1188	0.3529	0.0319		
9C	-2.0838	3.3940	-0.6346	-0.1764	-0.1503		
10H	-1.2568	4.0930	-0.6214	0.2147	0.1334		
11C	-3.2944	3.7973	-1.1911	-0.4729	-0.0870		
12H	-3.3877	4.8044	-1.5879	0.1953	0.1261		
13C	-4.3681	2.9102	-1.2389	-0.6179	-0.1646		
14H	-5.3246	3.2109	-1.6570	0.1863	0.1250		
15C	-4.1931	1.6163	-0.7513	0.2925	-0.1008		
16H	-5.0329	0.9327	-0.8089	0.1763	0.0973		
17C	-2.9799	1.1701	-0.1969	-0.5616	0.0486		
18C	-3.3784	-0.6817	2.1083	-0.4520	0.1896		
19H	-3.3286	-1.7541	2.3386	0.2319	-0.0149		
20C	-2.4013	0.0448	3.0469	-0.7578	-0.0773		
21H	-2.3849	1.1231	2.8505	0.2353	0.0106		
22H	-1.3815	-0.3393	2.9485	0.2378	-0.0363		
23H	-2.7189	-0.0971	4.0875	0.2134	0.0378		
24C	-4.8197	-0.1936	2.3252	-0.6850	-0.1669		
25H	-5.0944	-0.3173	3.3805	0.2174	0.0472		
26H	-5.5495	-0.7536	1.7309	0.2154	0.0305		
27H	-4.9219	0.8695	2.0791	0.2431	0.0114		
28C	-4.1018	-1.5457	-0.6559	-0.0618	0.4329		
29H	-5.0732	-1.0674	-0.4813	0.2072	-0.0580		
30C	-4.1937	-2.9969	-0.1511	-0.7326	-0.3843		
31H	-4.9179	-3.5467	-0.7648	0.2154	0.0823		
32H	-4.5307	-3.0622	0.8891	0.2142	0.0794		
33H	-3.2263	-3.5040	-0.2351	0.2485	0.0916		
34C	-3.7935	-1.5127	-2.1625	-0.6935	-0.2519		
35H	-2.8361	-2.0020	-2.3704	0.2526	0.0617		
36H	-3.7472	-0.4935	-2.5589	0.2312	0.0355		
37H	-4.5788	-2.0509	-2.7083	0.2083	0.0484		
38C	2.2502	0.0298	1.5669	-0.1049	0.0336		
39C	3.0543	0.3451	2.6776	-0.0060	-0.2028		
40H	2.7810	1.1712	3.3211	0.1845	0.1386		
41C	4.2153	-0.3633	2.9704	-0.4759	-0.0409		
42H	4.8092	-0.0798	3.8348	0.1883	0.1127		
43C	4.6128	-1.4118	2.1448	-0.5730	-0.1958		
44H	5.5287	-1.9624	2.3389	0.1849	0.1243		

45C	3.8138	-1.7442	1.0533	0.2514	-0.0212		
46H	4.1359	-2.5624	0.4192	0.1763	0.1012		
47C	2.6248	-1.0631	0.7403	-0.4402	-0.0304		
48C	2.0135	-3.4888	-0.8426	-0.1214	0.3707		
49H	3.0945	-3.5641	-1.0215	0.2169	-0.0565		
50C	1.6498	-4.2589	0.4383	-0.7445	-0.1636		
51H	0.5706	-4.2029	0.6210	0.2429	0.0211		
52H	2.1651	-3.8777	1.3245	0.2323	-0.0082		
53H	1.9189	-5.3164	0.3208	0.2069	0.0425		
54C	1.2938	-4.1164	-2.0503	-0.7973	-0.4280		
55H	1.5395	-5.1848	-2.0971	0.2110	0.0971		
56H	1.5908	-3.6725	-3.0054	0.2072	0.0927		
57H	0.2075	-4.0213	-1.9498	0.2416	0.1080		
58C	2.2787	-0.8829	-2.2712	-0.4515	0.4145		
59H	2.1681	-1.7023	-2.9930	0.1970	-0.0697		
60C	3.7640	-0.4955	-2.1841	-0.8558	-0.3436		
61H	4.1108	-0.2028	-3.1831	0.2166	0.0796		
62H	4.3987	-1.3219	-1.8421	0.1982	0.0290		
63H	3.9069	0.3682	-1.5265	0.3049	0.1161		
64C	1.4198	0.2968	-2.7566	-0.6692	-0.2444		
65H	1.5541	1.1793	-2.1217	0.3042	0.0825		
66H	0.3573	0.0310	-2.8053	0.2024	-0.0054		
67H	1.7470	0.5816	-3.7649	0.2116	0.0512		
68N	-0.6570	1.8453	0.5199	0.1047	0.0176		
69N	1.1526	0.9050	1.3255	0.2302	0.0387		
70P	-2.8044	-0.5942	0.3144	1.3296	0.1288		
71P	1.6078	-1.6570	-0.6804	1.8654	0.1626		
72Pd	-0.5951	-1.1597	-0.1367	-2.0013	-0.1840		
73H	-1.0658	-2.5955	-0.6896	0.0327	-0.1549		
74Br	3.0070	3.2878	-0.9048	-0.5717	-0.7584		

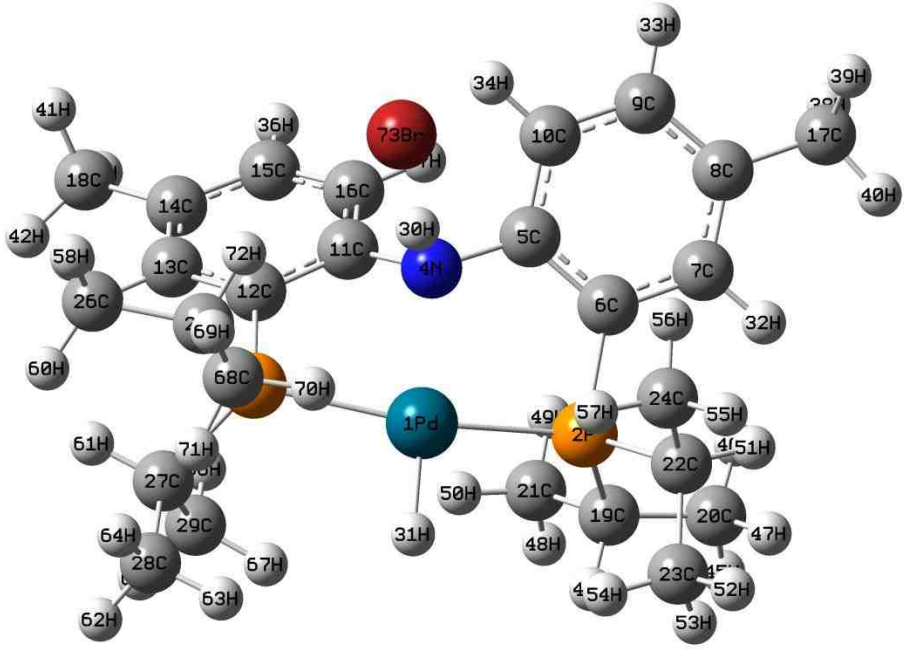
*** *** ***

(PNP) palladium hydride **7**

(see Figure 2-8, Figure 3-15)



7



Energy: -1893.55689849 hartrees

Palladium-hydrogen bond length: 1.570 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.0344	-1.3047	0.1818	-1.5991	-0.1554		
2P	2.2350	-1.3076	-0.2492	1.8975	0.1174		
3P	-2.3316	-0.8515	0.1820	1.2469	0.1437		
4N	0.1081	0.8858	-0.0244	0.0392	0.2502		
5C	1.4666	1.3906	-0.1848	0.4163	-0.2196		

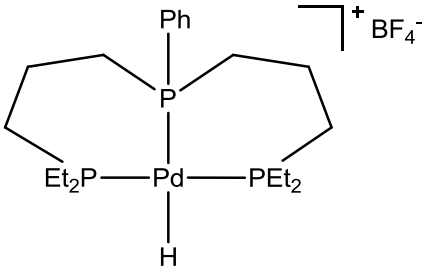
6C	2.5525	0.5092	-0.3386	-0.6552	0.2001		
7C	3.8551	1.0385	-0.4059	-0.0293	-0.4754		
8C	4.1071	2.4097	-0.3077	-0.1923	0.3667		
9C	3.0110	3.2617	-0.0998	-0.5917	-0.3831		
10C	1.7144	2.7622	-0.0250	-0.0304	0.1163		
11C	-0.9289	1.3051	-0.9601	0.1735	-0.0830		
12C	-2.1933	0.6714	-0.8689	-0.3738	0.0150		
13C	-3.2448	1.1345	-1.6704	0.1546	-0.3044		
14C	-3.0815	2.1696	-2.6011	-0.1703	0.2532		
15C	-1.8038	2.7249	-2.7252	-0.9341	-0.2672		
16C	-0.7457	2.3100	-1.9135	0.0562	-0.0721		
17C	5.5133	2.9586	-0.3863	-0.6928	-0.2414		
18C	-4.2399	2.6634	-3.4373	-0.7081	-0.2229		
19C	2.7588	-2.0808	-1.8796	-0.4694	0.2913		
20C	4.2541	-1.9767	-2.2204	-0.5847	-0.2076		
21C	1.8888	-1.5354	-3.0248	-0.7734	-0.2364		
22C	3.4090	-1.9447	1.0615	-0.1461	0.4337		
23C	3.3646	-3.4813	1.1262	-0.8018	-0.3217		
24C	3.0583	-1.3180	2.4224	-0.7274	-0.3108		
25C	-3.2027	-0.3357	1.7606	-0.2967	0.3862		
26C	-4.6987	-0.0363	1.5850	-0.5721	-0.3306		
27C	-3.4479	-2.0084	-0.7852	-0.0894	0.4331		
28C	-3.7060	-3.3063	0.0001	-0.7467	-0.4100		
29C	-2.8482	-2.3257	-2.1656	-0.7480	-0.2728		
30H	-0.1955	1.2250	0.9447	0.3216	0.1340		
31H	-0.1587	-2.8660	0.2898	0.1024	-0.1595		
32H	4.7013	0.3637	-0.5025	0.1762	0.1932		
33H	3.1767	4.3280	0.0383	0.1887	0.1709		
34H	0.8862	3.4247	0.2038	0.2513	0.0822		
35H	-4.2183	0.6550	-1.6004	0.1715	0.1676		
36H	-1.6253	3.5060	-3.4614	0.1806	0.1494		
37H	0.2243	2.7776	-2.0331	0.2018	0.0989		
38H	5.6549	3.5612	-1.2929	0.2276	0.0628		
39H	5.7355	3.6066	0.4702	0.2273	0.0785		
40H	6.2573	2.1551	-0.4020	0.2036	0.0585		
41H	-4.7229	3.5322	-2.9698	0.2318	0.0713		
42H	-5.0068	1.8903	-3.5592	0.2071	0.0541		
43H	-3.9110	2.9725	-4.4359	0.2106	0.0621		
44H	2.5057	-3.1400	-1.7368	0.2340	-0.0318		

45H	4.4633	-2.5612	-3.1256	0.2160	0.0485		
46H	4.5455	-0.9411	-2.4268	0.2306	0.0418		
47H	4.8993	-2.3643	-1.4243	0.2166	0.0302		
48H	2.1100	-2.0802	-3.9513	0.2124	0.0696		
49H	2.0910	-0.4732	-3.2062	0.2359	0.0321		
50H	0.8209	-1.6463	-2.8099	0.2372	0.0324		
51H	4.4224	-1.6294	0.7780	0.2185	-0.0755		
52H	4.0219	-3.8332	1.9310	0.2170	0.0688		
53H	3.7010	-3.9534	0.1963	0.2138	0.0624		
54H	2.3502	-3.8361	1.3420	0.2443	0.0740		
55H	3.7666	-1.6719	3.1821	0.2074	0.0733		
56H	3.1028	-0.2249	2.4027	0.2513	0.0559		
57H	2.0491	-1.6027	2.7407	0.2450	0.0698		
58H	-5.0892	0.3877	2.5185	0.2243	0.0799		
59H	-4.8820	0.7000	0.7945	0.2212	0.0505		
60H	-5.2849	-0.9371	1.3634	0.2155	0.0572		
61H	-4.4067	-1.4917	-0.9257	0.2227	-0.0717		
62H	-4.3172	-3.9857	-0.6076	0.2093	0.0864		
63H	-2.7653	-3.8185	0.2342	0.2411	0.0976		
64H	-4.2409	-3.1295	0.9374	0.2213	0.0971		
65H	-3.5389	-2.9684	-2.7270	0.2064	0.0543		
66H	-2.6685	-1.4241	-2.7593	0.2337	0.0413		
67H	-1.8975	-2.8611	-2.0615	0.2370	0.0594		
68C	-2.9241	-1.3057	2.9215	-0.8490	-0.2264		
69H	-3.3144	-0.8679	3.8481	0.2198	0.0680		
70H	-1.8491	-1.4564	3.0584	0.2388	0.0224		
71H	-3.4004	-2.2833	2.7848	0.1977	0.0263		
72H	-2.6819	0.6005	2.0077	0.2933	-0.0215		
73Br	-0.6389	2.1325	2.8431	-0.4661	-0.6889		

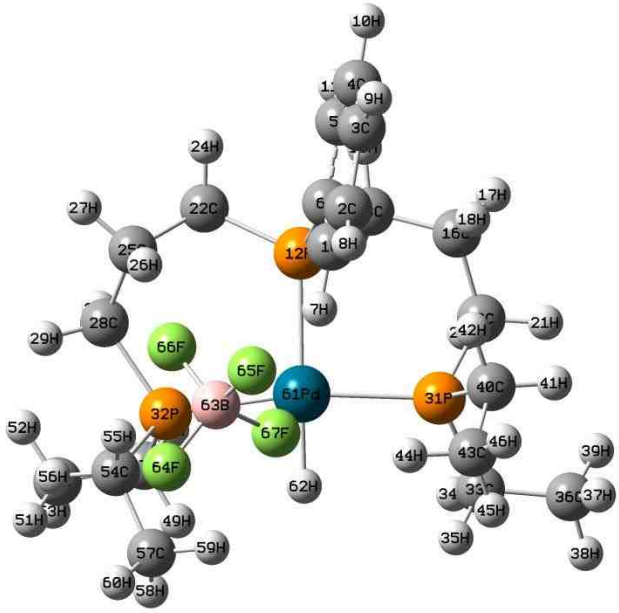
*** *** ***

(PPP) palladium hydride **8**

(see Figure 2-9, Figure 3-16)



8



Energy: -2360.41287169 hartrees

Palladium-hydrogen bond length: 1.595 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-1.8637	-2.0759	0.2703	1.3122	-0.0578		
2C	-2.6841	-3.1187	0.7165	-0.2957	-0.1353		
3C	-3.6034	-3.7070	-0.1526	-0.0623	-0.1015		
4C	-3.6979	-3.2615	-1.4778	-0.3381	-0.1264		
5C	-2.8708	-2.2326	-1.9284	-0.1687	-0.2359		
6C	-1.9478	-1.6260	-1.0545	-1.8559	0.1519		
7H	-1.1410	-1.6420	0.9514	0.2555	0.1234		
8H	-2.5692	-3.4734	1.7362	0.2279	0.1545		

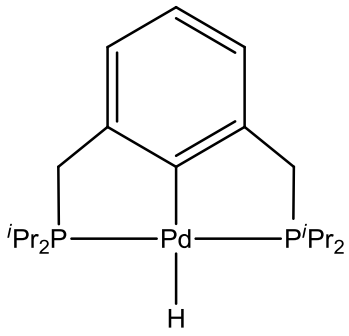
9H	-4.2383	-4.5193	0.1924	0.1834	0.1158		
10H	-4.4077	-3.7221	-2.1608	0.1774	0.1175		
11H	-2.9476	-1.9126	-2.9654	0.1699	0.1380		
12P	-0.8115	-0.3016	-1.6344	1.1052	0.2519		
13C	-1.9196	0.8225	-2.6262	-0.5950	-0.1094		
14H	-1.2720	1.5521	-3.1310	0.2312	0.0332		
15H	-2.4126	0.2403	-3.4148	0.2280	0.0297		
16C	-2.9948	1.5519	-1.7916	-0.5938	0.1213		
17H	-3.7247	1.9773	-2.4934	0.2135	0.0032		
18H	-3.5527	0.8220	-1.1915	0.2439	-0.0346		
19C	-2.5042	2.7120	-0.8974	-0.7725	-0.2135		
20H	-1.9350	3.4292	-1.5046	0.2345	0.0678		
21H	-3.3815	3.2497	-0.5152	0.2312	0.0692		
22C	0.2232	-1.1427	-2.9315	-0.7866	-0.1367		
23H	0.5205	-0.3858	-3.6709	0.2182	0.0388		
24H	-0.4112	-1.8689	-3.4534	0.2450	0.0476		
25C	1.4720	-1.8484	-2.3562	-0.3978	0.0421		
26H	1.2305	-2.3729	-1.4241	0.2911	0.0343		
27H	1.7771	-2.6224	-3.0725	0.2074	0.0141		
28C	2.6829	-0.9171	-2.1481	-0.9859	-0.1311		
29H	3.5848	-1.5275	-2.0154	0.2454	0.0367		
30H	2.8402	-0.3167	-3.0552	0.2279	0.0667		
31P	-1.4187	2.2691	0.5531	1.3176	0.2648		
32P	2.6097	0.2653	-0.7005	1.9256	0.3341		
33C	-1.0266	3.9225	1.3116	-0.4890	0.1166		
34H	-0.4046	4.4450	0.5741	0.2366	-0.0265		
35H	-0.3625	3.7053	2.1557	0.2565	0.0180		
36C	-2.1985	4.8059	1.7595	-0.7718	-0.1479		
37H	-2.8084	4.3196	2.5285	0.2220	0.0333		
38H	-1.8156	5.7389	2.1904	0.2174	0.0397		
39H	-2.8568	5.0789	0.9271	0.2109	0.0317		
40C	-2.5737	1.4410	1.7480	-0.5454	0.2751		
41H	-3.4592	2.0793	1.8718	0.2228	-0.0528		
42H	-2.9113	0.5141	1.2701	0.2586	-0.0716		
43C	-1.9285	1.1184	3.1054	-0.8813	-0.2275		
44H	-1.0647	0.4563	2.9926	0.3013	0.0730		
45H	-1.6054	2.0270	3.6272	0.2069	0.0449		
46H	-2.6571	0.6118	3.7489	0.2174	0.0431		
47C	3.6970	1.6715	-1.2623	-0.6040	-0.0825		

48H	3.1570	2.1715	-2.0767	0.2255	-0.0034		
49H	3.7184	2.3870	-0.4327	0.2465	0.0378		
50C	5.1245	1.3157	-1.7027	-0.7190	0.0397		
51H	5.7038	0.8742	-0.8848	0.2225	-0.0045		
52H	5.1351	0.6103	-2.5414	0.2174	-0.0192		
53H	5.6529	2.2203	-2.0278	0.2118	0.0060		
54C	3.5670	-0.6046	0.6220	-0.5306	0.3742		
55H	3.0284	-1.5342	0.8260	0.3124	-0.0430		
56H	4.5409	-0.8754	0.1917	0.2154	-0.0898		
57C	3.7406	0.1909	1.9210	-0.9397	-0.2241		
58H	4.2659	1.1416	1.7627	0.1902	0.0168		
59H	2.7701	0.3922	2.3810	0.2726	0.0715		
60H	4.3221	-0.4054	2.6322	0.2314	0.0523		
61Pd	0.4673	1.0402	-0.1083	-1.1432	-0.2809		
62H	1.3160	2.0475	0.7902	0.0746	-0.1355		
63B	0.9569	-2.4675	2.3059	1.5599	0.8683		
64F	2.1376	-2.6104	3.0403	-0.5623	-0.4431		
65F	-0.0792	-3.2587	2.8192	-0.5903	-0.4476		
66F	1.1997	-2.8177	0.9406	-0.6037	-0.4369		
67F	0.5465	-1.0936	2.3237	-0.5899	-0.3798		

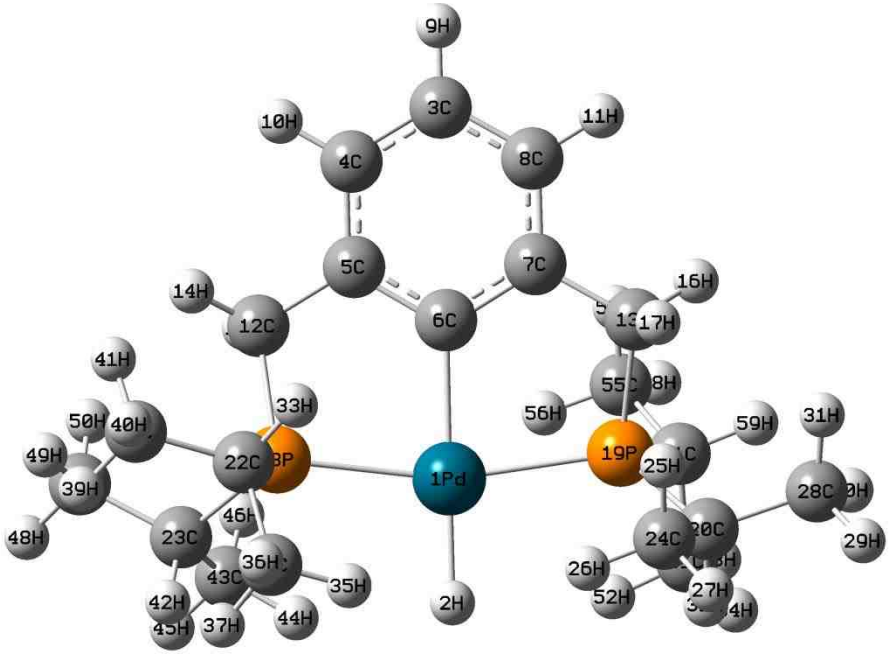
*** *** ***

(PCP) palladium hydride **9**

(see Figure 2-10, Figure 3-14)



9



Energy: -1593.32259113 hartrees

Palladium-hydrogen bond length: 1.650 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0600	-0.6576	-0.0598	-0.9702	-0.0623		
2H	0.0946	-2.3068	-0.0675	0.0053	-0.2923		
3C	-0.0377	4.2781	0.0345	-0.6548	-0.0302		
4C	-1.2043	3.5584	-0.2417	0.6877	-0.3292		
5C	-1.1728	2.1570	-0.2875	0.5951	0.2303		
6C	0.0263	1.4494	-0.0332	-0.7750	-0.3953		
7C	1.1954	2.1953	0.2460	0.5112	0.2282		
8C	1.1601	3.5985	0.2719	0.6340	-0.3027		
9H	-0.0620	5.3651	0.0626	0.1692	0.0961		
10H	-2.1332	4.0942	-0.4339	0.1616	0.1302		
11H	2.0652	4.1662	0.4853	0.1623	0.1153		
12C	-2.4195	1.3709	-0.6621	-1.2345	-0.1206		
13C	2.4925	1.4600	0.5500	-1.8389	-0.0152		
14H	-3.3425	1.8582	-0.3232	0.2265	0.0425		
15H	-2.4944	1.2923	-1.7565	0.2545	0.0599		

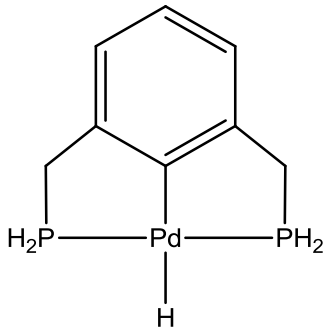
16H	3.3613	1.9397	0.0786	0.2427	0.0127		
17H	2.6883	1.4702	1.6317	0.2513	0.0155		
18P	-2.2432	-0.3780	-0.0241	0.8815	0.1406		
19P	2.3427	-0.3358	0.0301	1.0745	0.1276		
20C	3.3726	-1.2986	1.2692	-0.2129	0.3907		
21C	3.2970	-0.4336	-1.5811	-0.0727	0.3360		
22C	-2.8720	-0.3216	1.7473	-0.1667	0.4058		
23C	-3.4324	-1.4437	-1.0196	-0.2715	0.4217		
24C	2.6535	-1.3530	2.6286	-0.7268	-0.3035		
25H	2.5914	-0.3623	3.0962	0.2132	0.0670		
26H	1.6363	-1.7432	2.5221	0.2445	0.0529		
27H	3.2048	-2.0063	3.3173	0.2039	0.0647		
28C	4.8216	-0.8044	1.4147	-0.6026	-0.2693		
29H	5.3610	-1.4339	2.1347	0.2100	0.0545		
30H	5.3746	-0.8409	0.4696	0.2098	0.0430		
31H	4.8604	0.2259	1.7891	0.2241	0.0439		
32H	3.3855	-2.3192	0.8649	0.2240	-0.0511		
33H	-2.2216	0.4464	2.1886	0.2370	-0.0563		
34C	-2.5863	-1.6533	2.4646	-0.8507	-0.3847		
35H	-1.5368	-1.9458	2.3656	0.2464	0.0788		
36H	-2.8260	-1.5618	3.5320	0.2041	0.0898		
37H	-3.2015	-2.4679	2.0610	0.2090	0.0756		
38C	-4.3332	0.1093	1.9522	-0.6188	-0.2985		
39H	-5.0330	-0.6587	1.6026	0.2188	0.0582		
40H	-4.5239	0.2575	3.0233	0.2123	0.0601		
41H	-4.5747	1.0504	1.4461	0.2079	0.0592		
42H	-3.6820	-2.2724	-0.3417	0.2169	-0.0638		
43C	-2.7098	-2.0376	-2.2426	-0.7044	-0.3092		
44H	-1.8039	-2.5758	-1.9495	0.2527	0.0575		
45H	-3.3777	-2.7297	-2.7725	0.2004	0.0605		
46H	-2.4194	-1.2516	-2.9521	0.2153	0.0644		
47C	-4.7366	-0.7449	-1.4461	-0.6586	-0.3055		
48H	-5.3988	-1.4686	-1.9394	0.2096	0.0606		
49H	-5.2855	-0.3125	-0.6053	0.2075	0.0524		
50H	-4.5401	0.0571	-2.1673	0.2216	0.0551		
51C	3.4380	-1.8877	-2.0617	-0.8395	-0.2797		
52H	2.4544	-2.3525	-2.1954	0.2466	0.0547		
53H	3.9607	-1.9117	-3.0267	0.2058	0.0613		
54H	4.0115	-2.5063	-1.3624	0.2075	0.0504		

55C	2.6272	0.4386	-2.6569	-0.7889	-0.1801		
56H	1.6256	0.0640	-2.8953	0.2367	0.0326		
57H	2.5241	1.4827	-2.3438	0.2311	0.0293		
58H	3.2285	0.4187	-3.5754	0.2014	0.0308		
59H	4.2978	-0.0254	-1.3794	0.2119	-0.0611		

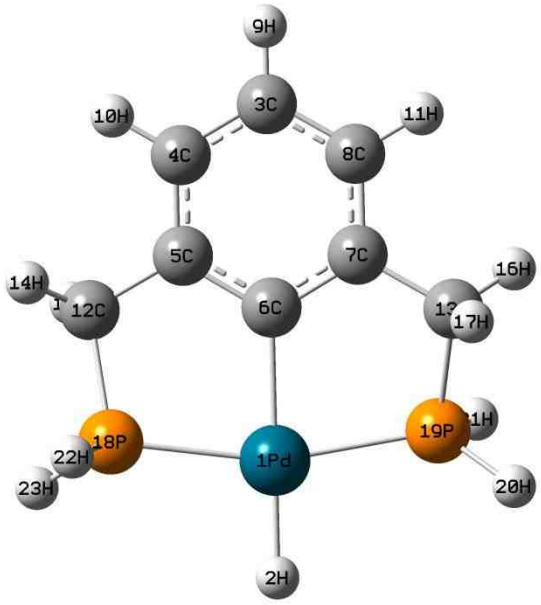
*** *** ***

(PCP) palladium hydride **10**

(see Figure 3-9, Figure 3-10, Figure 3-14, Figure 3-23)



10



Energy: -1121.52539922 hartrees

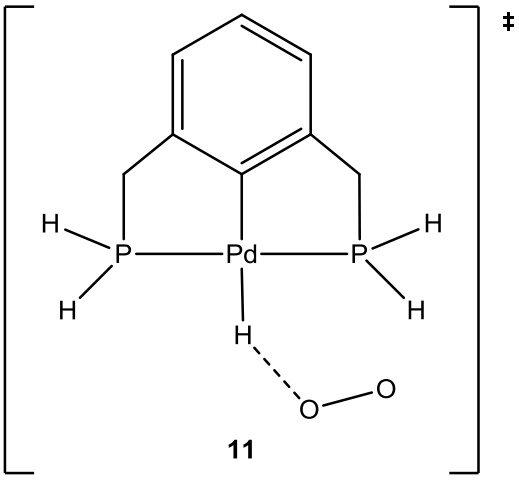
Palladium-hydrogen bond length: 1.634 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-1.3690	0.0001	0.0000	-0.6664	-0.1332		
2H	-3.0033	0.0003	0.0001	0.0226	-0.2755		
3C	3.5871	-0.0004	0.0001	-0.0117	-0.0054		
4C	2.8880	1.2034	-0.1196	-0.2604	-0.3296		
5C	1.4853	1.2065	-0.1317	-0.1743	0.2280		
6C	0.7582	-0.0001	-0.0001	0.9259	-0.4183		
7C	1.4850	-1.2068	0.1317	-0.1744	0.2290		
8C	2.8877	-1.2040	0.1196	-0.2602	-0.3291		
9H	4.6745	-0.0005	0.0001	0.1719	0.0937		
10H	3.4399	2.1374	-0.2149	0.1677	0.1389		
11H	3.4394	-2.1381	0.2150	0.1677	0.1387		
12C	0.7310	2.5131	-0.3258	-0.8465	-0.0075		
13C	0.7305	-2.5133	0.3257	-0.8465	-0.0084		
14H	1.2011	3.3559	0.1948	0.2360	0.0122		
15H	0.6901	2.7810	-1.3913	0.2478	0.0232		
16H	1.2004	-3.3561	-0.1951	0.2360	0.0122		
17H	0.6897	-2.7814	1.3911	0.2478	0.0234		
18P	-1.0355	2.2552	0.2224	0.3418	0.3655		
19P	-1.0360	-2.2550	-0.2223	0.3418	0.3654		
20H	-1.7444	-3.2972	0.4184	0.0294	-0.0334		
21H	-1.0582	-2.7721	-1.5374	0.0373	-0.0281		
22H	-1.0572	2.7720	1.5376	0.0373	-0.0282		
23H	-1.7437	3.2977	-0.4179	0.0294	-0.0335		

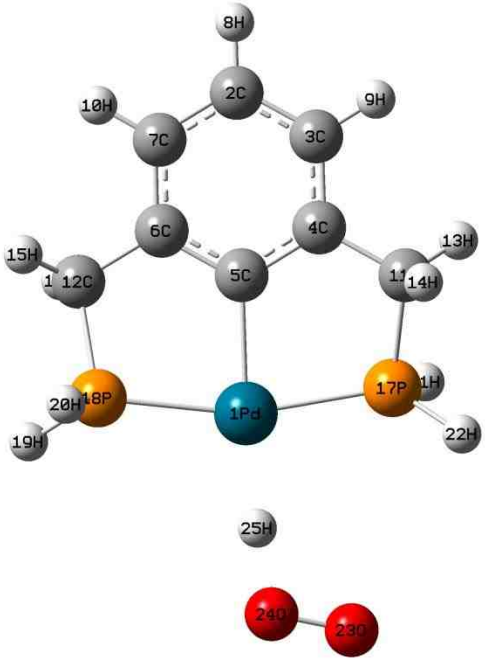
*** *** ***

(PCP) transition state **11**

(see Figure 3-9, Figure 3-10)



11



Energy: -1271.82887188 hartrees

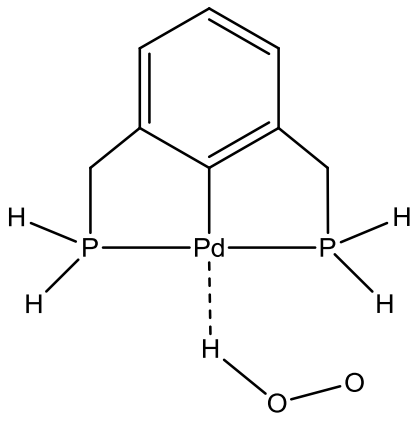
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.8409	0.2522	0.0302	-0.6472		0.1608	-0.1787
2C	4.0193	-0.6401	-0.0517	0.0230		-0.0163	-0.0716
3C	3.1167	-1.6975	0.0904	-0.3457		0.0338	-0.0225
4C	1.7363	-1.4486	0.1284	-0.3642		-0.0714	-0.1130

5C	1.2564	-0.1286	-0.0004	0.9504		0.3836	0.0571
6C	2.1720	0.9320	-0.1570	-0.0255		-0.0491	-0.0956
7C	3.5507	0.6710	-0.1696	-0.2734		0.0430	-0.0370
8H	5.0881	-0.8380	-0.0707	0.1756		0.0004	0.0104
9H	3.4914	-2.7158	0.1816	0.1721		0.0031	-0.0110
10H	4.2612	1.4884	-0.2820	0.1719		0.0031	-0.0119
11C	0.7559	-2.5910	0.3462	-0.7561		-0.0085	-0.0310
12C	1.6573	2.3494	-0.3521	-0.8458		-0.0131	-0.0285
13H	1.0624	-3.5098	-0.1671	0.2392		-0.0010	-0.0162
14H	0.6838	-2.8339	1.4158	0.2515		-0.0003	-0.0185
15H	2.2896	3.0978	0.1394	0.2388		-0.0010	-0.0211
16H	1.6340	2.6047	-1.4210	0.2507		-0.0003	-0.0225
17P	-0.9494	-2.0389	-0.1816	0.3323		0.0438	0.7450
18P	-0.1112	2.4383	0.2454	0.3289		0.0528	0.8145
19H	-0.6005	3.6129	-0.3731	0.0332		0.0072	-0.2013
20H	0.0148	2.9428	1.5598	0.0412		-0.0002	-0.1600
21H	-1.0799	-2.5610	-1.4876	0.0422		-0.0001	-0.1484
22H	-1.8126	-2.9331	0.4897	0.0416		0.0060	-0.1672
23O	-4.4705	-0.6452	-0.1603	-0.2195		0.7874	-0.4362
24O	-3.9568	0.5106	-0.0099	-0.0284		0.6663	0.3644
25H	-2.6108	0.4479	0.0271	0.2132		-0.0299	-0.1991

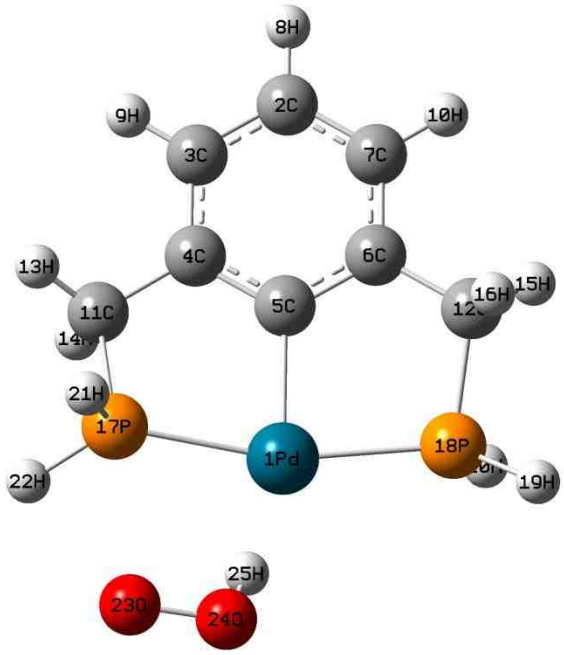
*** *** ***

(PCP) palladium(I)/hydroperoxy radical pair intermediate **12**

(see Figure 3-9, Figure 3-11)



12



Energy: -1271.84245371 hartrees

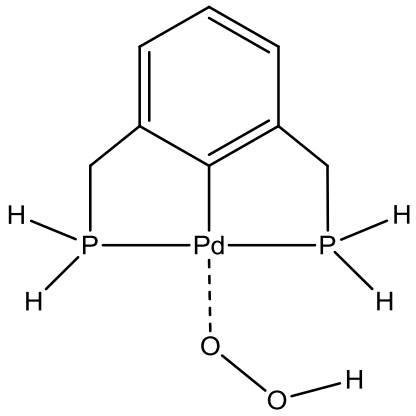
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.7729	0.4519	-0.3667	-0.5495		0.4198	
2C	-3.8093	-1.1332	0.4915	-0.0513		-0.0137	
3C	-2.8075	-2.0469	0.1504	-0.2343		0.0037	
4C	-1.5012	-1.6007	-0.1017	-0.3215		0.0523	
5C	-1.2044	-0.2299	0.0101	1.0976		0.3121	
6C	-2.2069	0.6878	0.3717	-0.2659		-0.0188	
7C	-3.5138	0.2289	0.5983	-0.1747		-0.0217	
8H	-4.8217	-1.4837	0.6766	0.1751		0.0005	
9H	-3.0482	-3.1062	0.0729	0.1718		0.0041	
10H	-4.3010	0.9312	0.8686	0.1712		0.0041	
11C	-0.4129	-2.5743	-0.5265	-0.7851		-0.0005	
12C	-1.8599	2.1572	0.5551	-0.8724		0.0016	
13H	-0.5239	-3.5547	-0.0491	0.2362		-0.0013	
14H	-0.4529	-2.7419	-1.6122	0.2487		0.0001	
15H	-2.6733	2.8193	0.2372	0.2377		-0.0013	
16H	-1.6703	2.3728	1.6162	0.2506		-0.0002	
17P	1.2670	-1.8260	-0.1754	0.2717		0.0787	

18P	-0.2655	2.5510	-0.3445	0.2465		0.1091	
19H	0.0806	3.8027	0.2258	0.0285		0.0168	
20H	-0.7318	3.0400	-1.5880	0.0385		-0.0016	
21H	1.5540	-2.3111	1.1190	0.0514		0.0004	
22H	2.1316	-2.6755	-0.9064	0.0337		0.0126	
23O	4.2072	-0.7837	0.9157	-0.1852		0.7194	
24O	3.8943	0.5045	0.8649	-0.2887		0.3039	
25H	2.9644	0.5459	0.4708	0.4695		0.0200	

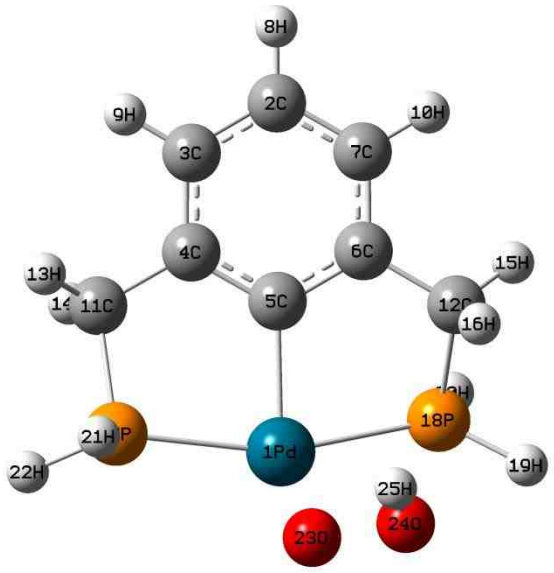
*** *** ***

(PCP) minimum energy crossing point structure **13**

(see Figure 3-9, Figure 3-11)



13



Energy: -1271.84301549 hartrees

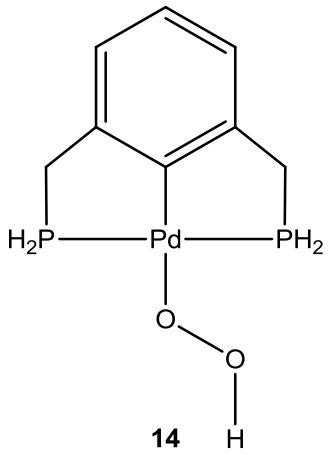
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.9997	0.3825	-0.4104	-0.2960		0.7806	
2C	3.6524	-0.9571	0.5223	-0.0715		0.0008	
3C	3.3513	0.3926	0.3227	-0.2890		0.0357	
4C	2.0354	0.7903	0.0345	-0.9670		0.1131	
5C	1.0187	-0.1790	-0.0338	0.7609		0.3153	
6C	1.3207	-1.5392	0.1757	0.6267		-0.1572	
7C	2.6438	-1.9223	0.4421	-0.1156		-0.0323	
8H	4.6745	-1.2580	0.7380	0.1743		-0.0004	
9H	4.1451	1.1364	0.3829	0.1706		0.0044	
10H	2.8879	-2.9726	0.5975	0.1710		0.0044	
11C	1.7264	2.2542	-0.2415	-0.7257		-0.0191	
12C	0.2060	-2.5724	0.1471	-0.8863		0.0016	
13H	2.3186	2.9224	0.3941	0.2381		-0.0007	
14H	1.9788	2.5037	-1.2819	0.2472		0.0005	
15H	0.5690	-3.5640	-0.1443	0.2316		-0.0007	
16H	-0.2460	-2.6728	1.1441	0.2531		0.0010	
17P	-0.1048	2.5923	-0.0576	0.2211		0.1705	
18P	-1.1753	-1.9749	-0.9622	0.3058		0.1685	
19H	-2.1801	-2.9435	-0.7159	0.0319		0.0141	

20H	-0.7435	-2.4521	-2.2255	0.0286		0.0105	
21H	-0.2007	3.0110	1.2897	0.0426		-0.0071	
22H	-0.1946	3.8790	-0.6555	0.0215		0.0287	
23O	-2.4500	0.5396	1.1881	-0.2049		0.4625	
24O	-2.7093	-0.7180	1.7849	-0.4321		0.1081	
25H	-2.2782	-0.6225	2.6552	0.4633		-0.0027	

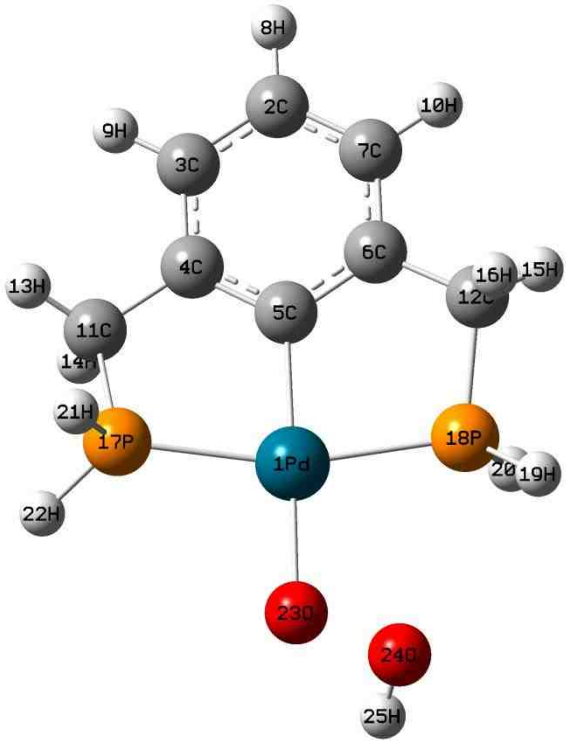
*** *** ***

(PCP) palladium hydroperoxide **14**

(see Figure 3-9, Figure 3-12, Figure 4-4, Figure 4-5, Figure 4-6, Figure 4-8, Figure 4-9, Figure 4-10, Figure 4-11)



14



Energy: -1271.89717798 hartrees

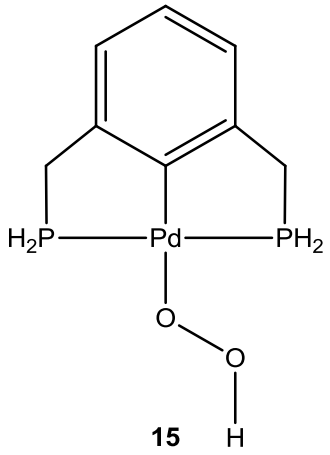
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.9243	0.2317	0.0385	-0.5307	0.0269		
2C	3.9121	-0.5988	-0.0763	0.0242	-0.0042		
3C	3.4205	0.7016	-0.2020	-0.4440	-0.3636		
4C	2.0400	0.9450	-0.1793	-0.1111	0.4069		
5C	1.1200	-0.1183	-0.0018	1.5276	-0.6559		
6C	1.6384	-1.4312	0.1340	-0.6102	0.4528		
7C	3.0207	-1.6611	0.0833	-0.4796	-0.3731		
8H	4.9831	-0.7831	-0.1036	0.1752	0.1023		
9H	4.1150	1.5305	-0.3288	0.1720	0.1477		
10H	3.4041	-2.6755	0.1804	0.1722	0.1531		
11C	1.5255	2.3598	-0.3838	-0.7266	-0.2170		
12C	0.6935	-2.5989	0.3674	-0.6208	-0.3478		
13H	2.1765	3.1153	0.0700	0.2388	0.0633		
14H	1.4587	2.5946	-1.4555	0.2528	0.0678		
15H	1.0225	-3.5123	-0.1411	0.2387	0.0899		

16H	0.6336	-2.8352	1.4392	0.2532	0.0937		
17P	-0.2089	2.4282	0.2772	0.3882	0.4678		
18P	-1.0078	-2.0622	-0.1515	0.3174	0.6060		
19H	-1.9028	-2.8628	0.5846	0.0534	-0.0299		
20H	-1.1931	-2.6206	-1.4345	0.0384	-0.0756		
21H	-0.0599	2.9313	1.5886	0.0430	-0.0352		
22H	-0.7865	3.5662	-0.3287	0.0381	-0.0339		
23O	-2.9422	0.6143	0.1067	-0.3685	-0.4434		
24O	-3.6887	-0.6066	-0.2588	-0.4970	-0.4741		
25H	-4.2620	-0.2500	-0.9582	0.4552	0.3753		

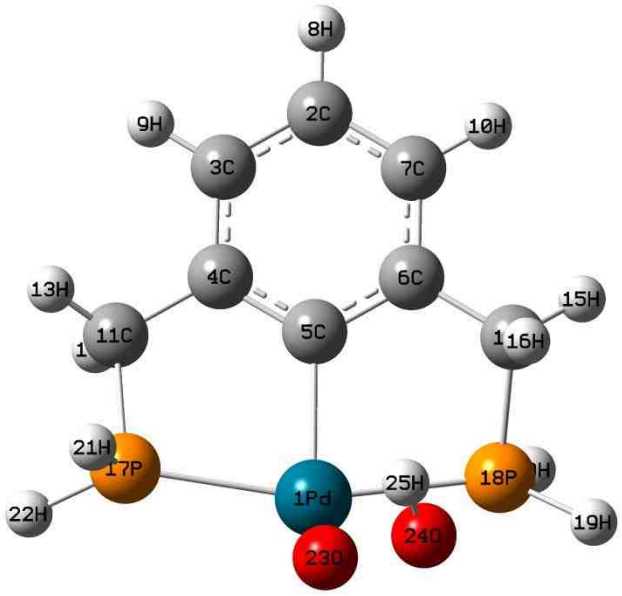
*** *** ***

(PCP) triplet palladium hydroperoxide **15**

(see Figure 3-9)



15



Energy: -1271.84323324 hartrees

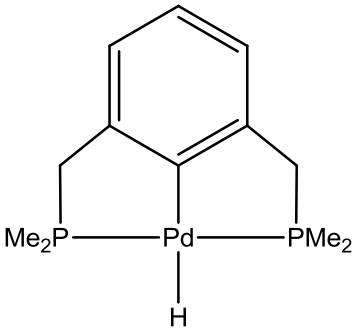
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-1.0051	0.3904	-0.4248	-0.2829		0.7817	
2C	3.6480	-0.9709	0.5065	-0.0721		-0.0012	
3C	3.3488	0.3806	0.3167	-0.2528		0.0349	
4C	2.0314	0.7837	0.0443	-0.9328		0.1095	
5C	1.0099	-0.1805	-0.0151	0.7530		0.3149	
6C	1.3102	-1.5423	0.1830	0.5594		-0.1483	
7C	2.6347	-1.9315	0.4327	-0.1294		-0.0303	
8H	4.6716	-1.2766	0.7087	0.1741		-0.0003	
9H	4.1456	1.1214	0.3699	0.1704		0.0043	
10H	2.8764	-2.9833	0.5786	0.1709		0.0043	
11C	1.7299	2.2494	-0.2333	-0.7141		-0.0212	
12C	0.1945	-2.5746	0.1519	-0.8888		0.0015	
13H	2.3251	2.9150	0.4021	0.2379		-0.0007	
14H	1.9864	2.4959	-1.2737	0.2467		0.0004	
15H	0.5595	-3.5655	-0.1400	0.2313		-0.0007	
16H	-0.2596	-2.6770	1.1477	0.2531		0.0010	
17P	-0.0991	2.6051	-0.0570	0.2215		0.1694	
18P	-1.1881	-1.9845	-0.9620	0.2993		0.1655	

19H	-2.1834	-2.9633	-0.7124	0.0321		0.0144	
20H	-0.7499	-2.4699	-2.2204	0.0287		0.0101	
21H	-0.1990	2.9956	1.2986	0.0438		-0.0072	
22H	-0.1572	3.9082	-0.6248	0.0212		0.0295	
23O	-2.4091	0.5365	1.2213	-0.1990		0.4617	
24O	-2.6764	-0.7141	1.8149	-0.4343		0.1096	
25H	-2.2360	-0.6319	2.6822	0.4627		-0.0028	

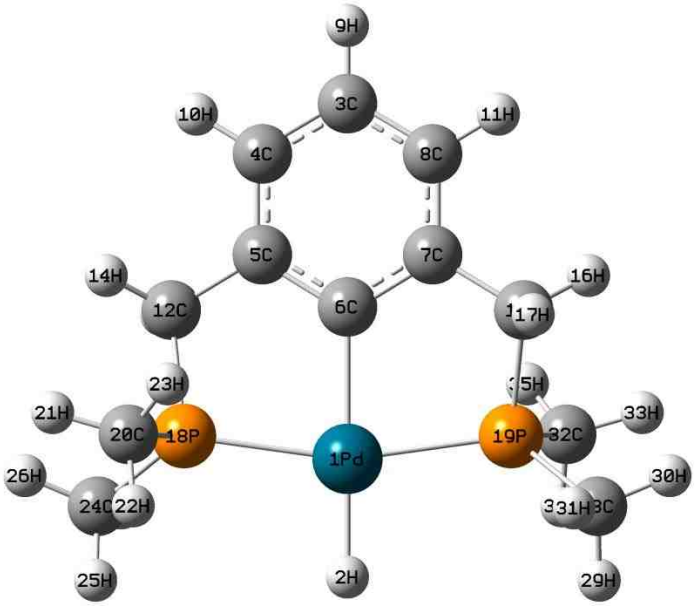
*** *** ***

(PCP) palladium hydride **16**

(see Figure 3-14, Figure 5-2, Figure 5-3, Figure 5-4)



16



Energy: -1278.82791142 hartrees

Palladium-hydrogen bond length: 1.645 Å

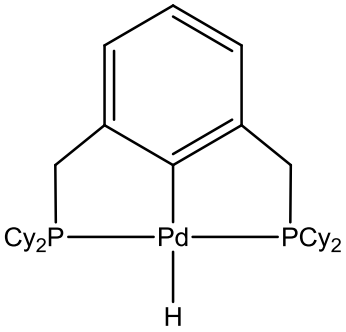
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-1.0592	0.0000	-0.7938	-0.3185		
2H	0.0000	-2.7039	0.0000	0.0024	-0.2926		
3C	0.0000	3.8847	0.0000	-0.2229	-0.0644		
4C	-1.1850	3.1853	-0.2471	-0.0610	-0.2824		
5C	-1.1867	1.7824	-0.2586	0.2464	0.1951		
6C	0.0000	1.0559	0.0000	0.1811	-0.3555		
7C	1.1867	1.7824	0.2586	0.2464	0.1951		
8C	1.1850	3.1853	0.2471	-0.0611	-0.2824		
9H	0.0000	4.9722	0.0000	0.1690	0.1000		
10H	-2.1035	3.7375	-0.4421	0.1639	0.1263		
11H	2.1035	3.7375	0.4421	0.1639	0.1263		
12C	-2.4561	1.0126	-0.5907	-1.0141	-0.1191		
13C	2.4561	1.0126	0.5907	-1.0141	-0.1191		
14H	-3.3606	1.4933	-0.1926	0.2237	0.0289		
15H	-2.5885	0.9480	-1.6812	0.2412	0.0385		
16H	3.3606	1.4933	0.1925	0.2237	0.0290		
17H	2.5885	0.9481	1.6811	0.2412	0.0386		
18P	-2.2791	-0.7411	0.0267	0.8244	0.6439		
19P	2.2791	-0.7411	-0.0267	0.8244	0.6439		
20C	-3.0544	-0.7170	1.7034	-0.8995	-0.2641		
21H	-4.1078	-0.4144	1.6555	0.2255	0.0696		
22H	-2.9855	-1.7124	2.1533	0.2441	0.0698		
23H	-2.5071	-0.0145	2.3392	0.2521	0.0582		
24C	-3.4845	-1.7184	-0.9736	-0.8248	-0.4099		
25H	-3.5089	-2.7483	-0.6035	0.2441	0.1142		
26H	-4.4943	-1.2927	-0.9230	0.2251	0.0960		
27H	-3.1568	-1.7426	-2.0178	0.2411	0.1004		
28C	3.4845	-1.7183	0.9737	-0.8247	-0.4099		
29H	3.5087	-2.7483	0.6037	0.2441	0.1142		
30H	4.4943	-1.2927	0.9229	0.2251	0.0960		
31H	3.1569	-1.7423	2.0178	0.2411	0.1004		
32C	3.0544	-0.7171	-1.7034	-0.8995	-0.2641		

33H	4.1077	-0.4143	-1.6555	0.2255	0.0696		
34H	2.9857	-1.7125	-2.1532	0.2441	0.0698		
35H	2.5070	-0.0147	-2.3393	0.2521	0.0582		

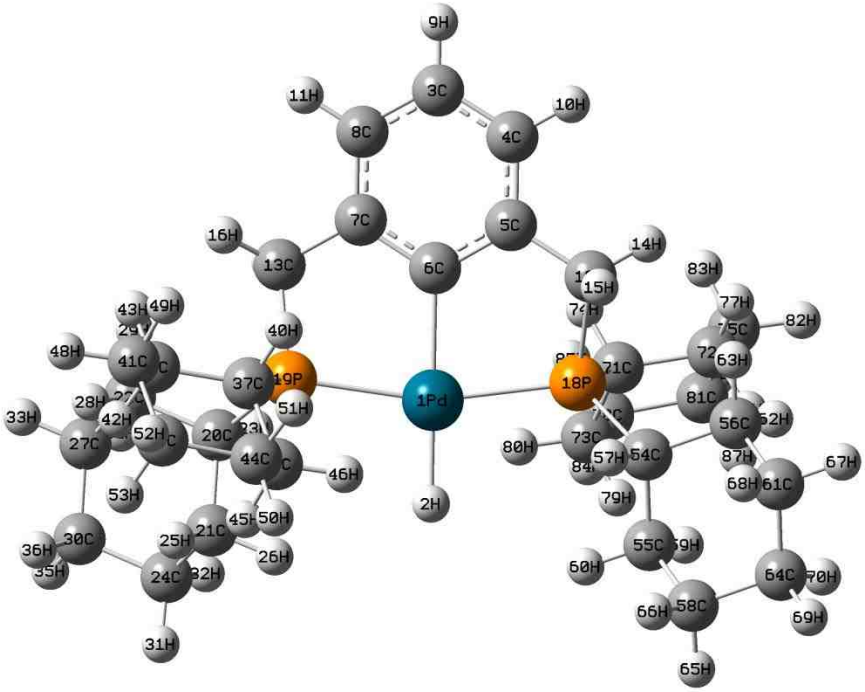
*** *** ***

(PCP) palladium hydride **17**

(see Figure 3-14, Figure 4-2)



17



Energy: -2060.26487525 hartrees

Palladium-hydrogen bond length: 1.650 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-0.0008	-0.1048	-1.2923	-0.1150		
2H	-0.0001	0.0000	-1.7551	0.0103	-0.2608		
3C	0.0001	-0.0038	4.8296	-0.1324	-0.0264		
4C	1.1429	-0.4021	4.1295	-0.4699	-0.3040		
5C	1.1428	-0.4127	2.7263	0.1073	0.2027		
6C	0.0001	-0.0019	2.0003	1.0206	-0.3720		
7C	-1.1427	0.4080	2.7269	0.1054	0.2063		
8C	-1.1427	0.3955	4.1300	-0.4717	-0.3026		
9H	0.0001	-0.0045	5.9173	0.1671	0.0904		
10H	2.0287	-0.7147	4.6814	0.1600	0.1222		
11H	-2.0285	0.7074	4.6824	0.1599	0.1216		
12C	2.3581	-0.9103	1.9588	-1.1360	-0.1253		
13C	-2.3579	0.9068	1.9601	-1.1407	-0.1328		
14H	3.3018	-0.6514	2.4567	0.2349	0.0544		
15H	2.3347	-2.0079	1.8892	0.2513	0.0566		
16H	-3.3016	0.6471	2.4577	0.2350	0.0557		
17H	-2.3344	2.0044	1.8921	0.2513	0.0570		
18P	2.2809	-0.2656	0.2026	1.6744	0.2468		
19P	-2.2808	0.2645	0.2030	1.6743	0.2603		
20C	-3.2020	1.5438	-0.8150	-0.4508	0.0081		
21C	-3.3434	1.1280	-2.2943	-0.3026	-0.0344		
22C	-4.5436	2.0735	-0.2621	-0.0155	0.0503		
23H	-2.4834	2.3795	-0.7841	0.2232	0.0194		
24C	-3.8682	2.2958	-3.1481	-0.6942	0.0525		
25H	-4.0470	0.2863	-2.3727	0.2120	0.0170		
26H	-2.3781	0.7765	-2.6756	0.2482	0.0007		
27C	-5.0608	3.2457	-1.1183	-0.5403	0.0732		
28H	-5.2939	1.2733	-0.2667	0.2111	-0.0261		
29H	-4.4362	2.3992	0.7799	0.2053	-0.0343		
30C	-5.1902	2.8540	-2.5985	-0.4633	0.0479		
31H	-3.9965	1.9666	-4.1879	0.1965	-0.0187		
32H	-3.1128	3.0960	-3.1649	0.2019	-0.0137		
33H	-6.0284	3.5896	-0.7284	0.1955	-0.0327		
34H	-4.3666	4.0948	-1.0252	0.1993	-0.0264		

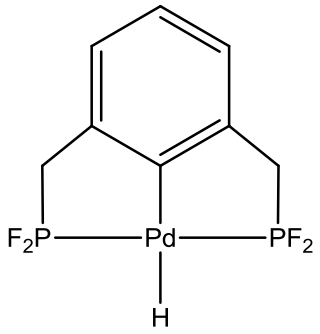
35H	-5.5154	3.7186	-3.1924	0.1946	-0.0277		
36H	-5.9762	2.0900	-2.7020	0.1946	-0.0268		
37C	-3.1809	-1.3823	0.2876	-0.4603	0.0991		
38C	-4.7023	-1.3492	0.5397	-0.1250	-0.0673		
39C	-2.8504	-2.2994	-0.9108	-0.3271	0.0436		
40H	-2.7022	-1.8262	1.1758	0.2359	-0.0031		
41C	-5.2537	-2.7691	0.7688	-0.8212	0.0650		
42H	-5.2069	-0.9119	-0.3323	0.2184	0.0271		
43H	-4.9469	-0.7133	1.3998	0.2090	-0.0019		
44C	-3.4070	-3.7165	-0.6909	-0.5848	0.0727		
45H	-3.2837	-1.8793	-1.8295	0.2105	-0.0225		
46H	-1.7664	-2.3311	-1.0659	0.2380	-0.0503		
47C	-4.9171	-3.7014	-0.4054	-0.4956	0.0212		
48H	-6.3406	-2.7240	0.9215	0.1949	-0.0241		
49H	-4.8233	-3.1782	1.6954	0.2015	-0.0182		
50H	-3.1921	-4.3393	-1.5695	0.1957	-0.0223		
51H	-2.8818	-4.1808	0.1578	0.2006	-0.0277		
52H	-5.2771	-4.7179	-0.1982	0.1946	-0.0195		
53H	-5.4519	-3.3568	-1.3040	0.1946	-0.0217		
54C	3.2034	-1.5427	-0.8169	-0.4510	0.0143		
55C	3.3442	-1.1251	-2.2957	-0.3024	-0.0337		
56C	4.5457	-2.0715	-0.2646	-0.0153	0.0494		
57H	2.4858	-2.3792	-0.7869	0.2231	0.0191		
58C	3.8704	-2.2912	-3.1508	-0.6941	0.0531		
59H	4.0467	-0.2824	-2.3733	0.2120	0.0161		
60H	2.3784	-0.7742	-2.6766	0.2482	0.0009		
61C	5.0643	-3.2421	-1.1222	-0.5404	0.0652		
62H	5.2949	-1.2704	-0.2681	0.2111	-0.0247		
63H	4.4384	-2.3986	0.7770	0.2054	-0.0345		
64C	5.1931	-2.8483	-2.6020	-0.4633	0.0474		
65H	3.9984	-1.9607	-4.1903	0.1965	-0.0189		
66H	3.1161	-3.0923	-3.1685	0.2019	-0.0142		
67H	6.0323	-3.5853	-0.7327	0.1955	-0.0300		
68H	4.3710	-4.0921	-1.0301	0.1993	-0.0237		
69H	5.5195	-3.7118	-3.1969	0.1946	-0.0272		
70H	5.9782	-2.0832	-2.7044	0.1946	-0.0260		
71C	3.1795	1.3819	0.2897	-0.4590	0.1059		
72C	4.7008	1.3499	0.5425	-0.1251	-0.0706		
73C	2.8487	2.3000	-0.9079	-0.3277	0.0450		

74H	2.6999	1.8243	1.1781	0.2359	-0.0031		
75C	5.2508	2.7700	0.7734	-0.8212	0.0632		
76H	5.2063	0.9139	-0.3297	0.2184	0.0276		
77H	4.9455	0.7133	1.4021	0.2090	-0.0012		
78C	3.4041	3.7174	-0.6862	-0.5848	0.0700		
79H	3.2828	1.8814	-1.8268	0.2105	-0.0223		
80H	1.7648	2.3310	-1.0634	0.2380	-0.0508		
81C	4.9140	3.7032	-0.4000	-0.4956	0.0213		
82H	6.3376	2.7257	0.9266	0.1949	-0.0233		
83H	4.8196	3.1777	1.7003	0.2015	-0.0177		
84H	3.1890	4.3410	-1.5642	0.1957	-0.0216		
85H	2.8781	4.1804	0.1627	0.2006	-0.0274		
86H	5.2731	4.7198	-0.1915	0.1946	-0.0191		
87H	5.4495	3.3600	-1.2987	0.1946	-0.0216		

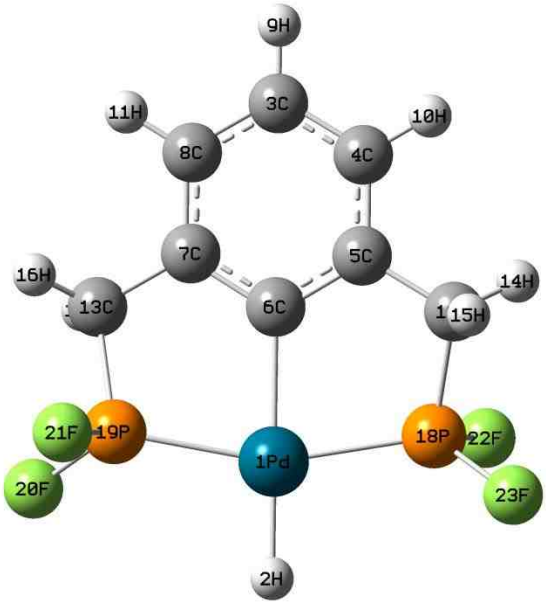
*** *** ***

(PCP) palladium hydride **18**

(see Figure 3-14, Figure 3-23, Figure 3-24)



18



Energy: -1518.63906536 hartrees

Palladium-hydrogen bond length: 1.625 Å

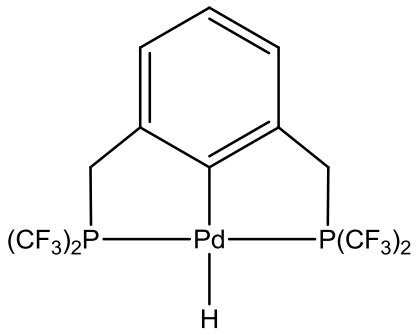
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-1.1173	0.0000	-0.8792	-0.2595		
2H	0.0001	-2.7427	-0.0001	0.0575	-0.2107		
3C	-0.0001	3.8543	0.0000	-0.0016	-0.0693		
4C	1.1903	3.1568	0.2179	-0.3788	-0.2191		
5C	1.1923	1.7555	0.2302	-0.3168	0.1372		
6C	0.0000	1.0295	0.0000	1.3634	-0.3748		
7C	-1.1924	1.7554	-0.2302	-0.3167	0.1396		
8C	-1.1904	3.1568	-0.2179	-0.3788	-0.2185		
9H	-0.0001	4.9411	0.0000	0.1820	0.1140		
10H	2.1133	3.7076	0.3882	0.1784	0.1263		
11H	-2.1134	3.7076	-0.3882	0.1784	0.1258		
12C	2.4801	0.9976	0.5217	-1.0601	-0.0927		
13C	-2.4801	0.9975	-0.5217	-1.0601	-0.0958		
14H	3.3639	1.4319	0.0381	0.2602	0.0731		
15H	2.6862	0.9535	1.6014	0.2682	0.0557		
16H	-3.3640	1.4318	-0.0382	0.2602	0.0738		
17H	-2.6862	0.9534	-1.6015	0.2682	0.0564		

18P	2.2249	-0.7332	-0.0357	1.4448	0.8895		
19P	-2.2249	-0.7333	0.0357	1.4448	0.8896		
20F	-3.3386	-1.5378	-0.7999	-0.3830	-0.2877		
21F	-2.9455	-0.7518	1.4735	-0.3740	-0.2825		
22F	2.9456	-0.7518	-1.4734	-0.3740	-0.2825		
23F	3.3385	-1.5377	0.8000	-0.3830	-0.2879		

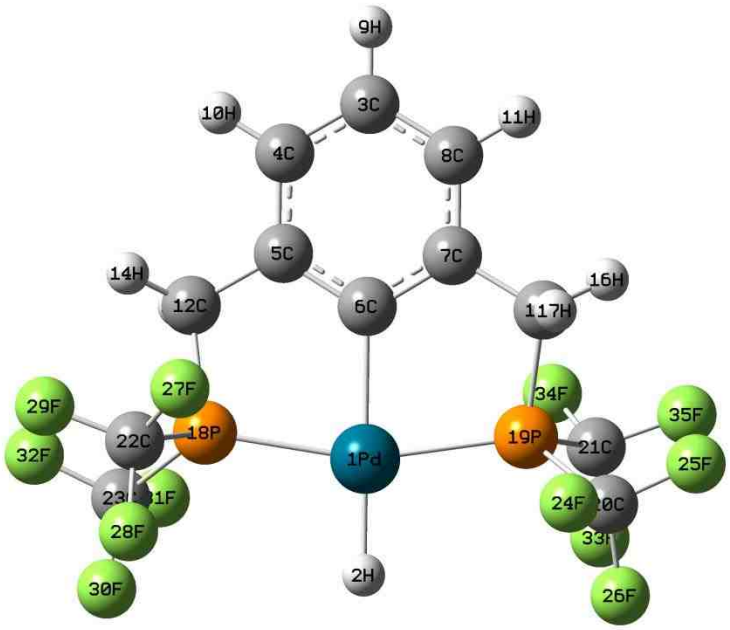
*** *** ***

(PCP) palladium hydride **19**

(see Figure 3-14)



19



Energy: -2469.70807324 hartrees

Palladium-hydrogen bond length: 1.627 Å

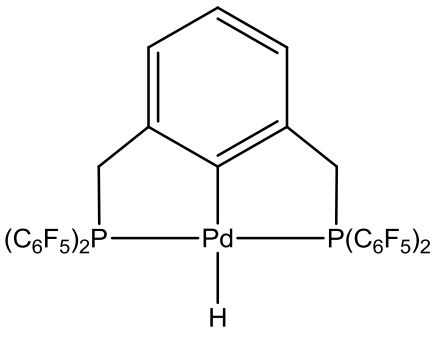
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-0.5621	-0.0002	-0.8841	0.0091		
2H	0.0000	-2.1891	-0.0001	0.0664	-0.2269		
3C	-0.0001	4.3973	-0.0001	-0.2186	-0.0265		
4C	-1.1817	3.6994	-0.2601	0.3512	-0.2916		
5C	-1.1820	2.2978	-0.2711	1.1083	0.1817		
6C	0.0000	1.5715	-0.0002	-2.1734	-0.3228		
7C	1.1819	2.2979	0.2708	1.1082	0.1799		
8C	1.1815	3.6995	0.2598	0.3524	-0.2893		
9H	-0.0001	5.4841	-0.0001	0.1838	0.1150		
10H	-2.0979	4.2508	-0.4628	0.1779	0.1458		
11H	2.0977	4.2508	0.4626	0.1779	0.1451		
12C	-2.4631	1.5530	-0.6175	-1.3253	-0.0078		
13C	2.4630	1.5531	0.6171	-1.3257	-0.0070		
14H	-3.3578	1.9905	-0.1605	0.2779	0.0429		
15H	-2.6334	1.5449	-1.7033	0.2814	0.0609		
16H	3.3577	1.9906	0.1600	0.2779	0.0428		

17H	2.6335	1.5452	1.7029	0.2814	0.0608		
18P	-2.2463	-0.2235	-0.1101	1.0265	0.0677		
19P	2.2463	-0.2234	0.1100	1.0267	0.0677		
20C	3.4132	-1.1511	1.2915	0.6407	0.6984		
21C	3.2295	-0.3525	-1.5160	0.4417	0.6909		
22C	-3.2292	-0.3522	1.5161	0.4417	0.6907		
23C	-3.4134	-1.1514	-1.2912	0.6408	0.6987		
24F	2.8612	-1.1408	2.5255	-0.2655	-0.2240		
25F	4.6306	-0.5702	1.3914	-0.2236	-0.2440		
26F	3.5938	-2.4286	0.9194	-0.2552	-0.2164		
27F	-2.6064	0.3866	2.4579	-0.2403	-0.2294		
28F	-3.2983	-1.6219	1.9512	-0.2470	-0.2268		
29F	-4.4935	0.1159	1.4051	-0.2363	-0.2224		
30F	-3.5941	-2.4288	-0.9186	-0.2552	-0.2165		
31F	-2.8616	-1.1415	-2.5253	-0.2655	-0.2241		
32F	-4.6308	-0.5705	-1.3911	-0.2236	-0.2440		
33F	3.2988	-1.6223	-1.9508	-0.2470	-0.2269		
34F	2.6068	0.3860	-2.4581	-0.2403	-0.2295		
35F	4.4937	0.1158	-1.4048	-0.2363	-0.2225		

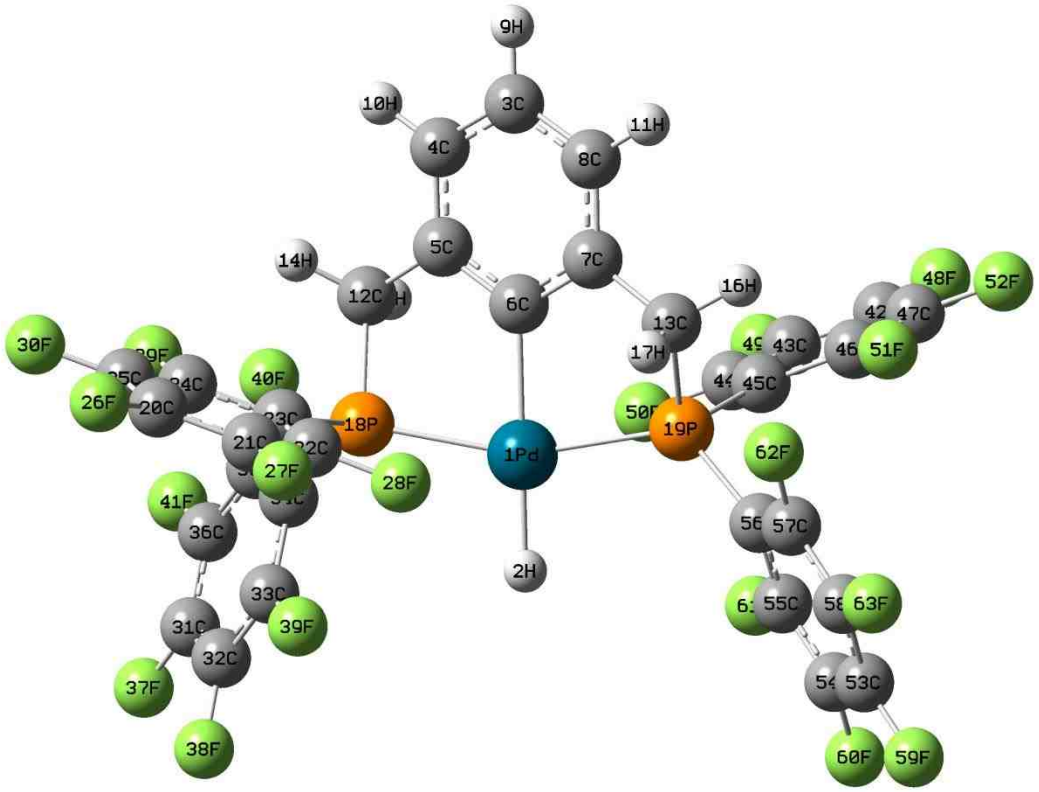
*** *** ***

(PCP) palladium hydride **20**

(see Figure 3-14)



20



Energy: -4030.41990746 hartrees

Palladium-hydrogen bond length: 1.633 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0001	-0.0011	0.0814	-1.0259	-0.3074		
2H	0.0002	-0.0013	1.7146	0.0536	-0.2406		
3C	-0.0003	-0.0005	-4.8496	-0.0154	-0.0987		
4C	-1.0723	-0.5695	-4.1539	-0.2725	-0.2058		
5C	-1.0643	-0.5853	-2.7517	0.2793	0.0753		
6C	-0.0001	-0.0008	-2.0352	0.4867	-0.2434		
7C	1.0639	0.5840	-2.7517	0.2788	0.0762		
8C	1.0718	0.5684	-4.1539	-0.2722	-0.2059		
9H	-0.0004	-0.0004	-5.9366	0.1786	0.1150		
10H	-1.8989	-1.0124	-4.7068	0.1752	0.1256		
11H	1.8982	1.0115	-4.7069	0.1752	0.1256		
12C	-2.1679	-1.2670	-1.9598	-0.9763	-0.1892		

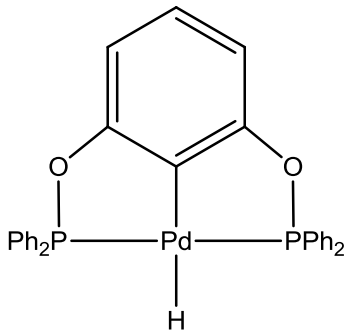
13C	2.1675	1.2659	-1.9600	-0.9754	-0.1910		
14H	-3.1331	-1.2887	-2.4729	0.2659	0.0876		
15H	-1.8906	-2.3032	-1.7370	0.2797	0.0964		
16H	3.1327	1.2877	-2.4731	0.2659	0.0881		
17H	1.8901	2.3021	-1.7373	0.2797	0.0970		
18P	-2.2335	-0.3768	-0.3140	0.7296	0.9386		
19P	2.2334	0.3760	-0.3140	0.7297	0.9384		
20C	-4.8942	3.3644	-1.2540	0.7083	0.1579		
21C	-3.5990	3.5349	-0.7733	-0.3576	0.1492		
22C	-2.8107	2.4199	-0.4881	-0.1493	0.2150		
23C	-3.2781	1.1122	-0.6729	0.4683	-0.4121		
24C	-4.5876	0.9843	-1.1560	0.3115	0.2279		
25C	-5.3954	2.0781	-1.4469	-0.0643	0.1235		
26F	-5.6539	4.4267	-1.5290	-0.3304	-0.1260		
27F	-3.1169	4.7696	-0.5857	-0.3291	-0.1396		
28F	-1.5800	2.6602	-0.0210	-0.2221	-0.1548		
29F	-5.1165	-0.2398	-1.3563	-0.2487	-0.1434		
30F	-6.6407	1.9056	-1.9086	-0.3293	-0.1429		
31C	-4.7885	-2.6350	2.8923	0.5670	0.1959		
32C	-4.3118	-1.3432	3.1082	0.0435	0.0934		
33C	-3.5907	-0.7061	2.1041	-1.0129	0.3120		
34C	-3.3218	-1.3045	0.8644	1.4771	-0.5658		
35C	-3.8245	-2.5971	0.6838	0.6477	0.3016		
36C	-4.5448	-3.2630	1.6739	0.0298	0.1032		
37F	-5.4814	-3.2631	3.8453	-0.3312	-0.1338		
38F	-4.5493	-0.7280	4.2730	-0.3288	-0.1382		
39F	-3.1525	0.5402	2.3494	-0.2505	-0.1519		
40F	-3.6374	-3.2605	-0.4728	-0.2906	-0.1724		
41F	-5.0082	-4.5006	1.4560	-0.3285	-0.1400		
42C	4.8966	-3.3637	-1.2527	0.7081	0.1577		
43C	3.6015	-3.5350	-0.7722	-0.3579	0.1494		
44C	2.8124	-2.4203	-0.4874	-0.1493	0.2144		
45C	3.2791	-1.1124	-0.6724	0.4683	-0.4115		
46C	4.5885	-0.9838	-1.1554	0.3116	0.2278		
47C	5.3971	-2.0772	-1.4459	-0.0641	0.1234		
48F	5.6571	-4.4256	-1.5273	-0.3304	-0.1260		
49F	3.1202	-4.7699	-0.5843	-0.3291	-0.1396		
50F	1.5818	-2.6613	-0.0204	-0.2221	-0.1545		
51F	5.1167	0.2406	-1.3558	-0.2487	-0.1436		

52F	6.6423	-1.9040	-1.9075	-0.3293	-0.1426		
53C	4.7862	2.6363	2.8926	0.5670	0.1966		
54C	4.3102	1.3443	3.1086	0.0429	0.0946		
55C	3.5898	0.7066	2.1045	-1.0140	0.3105		
56C	3.3209	1.3045	0.8645	1.4781	-0.5644		
57C	3.8228	2.5974	0.6838	0.6487	0.3008		
58C	4.5426	3.2640	1.6740	0.0294	0.1028		
59F	5.4785	3.2650	3.8456	-0.3312	-0.1342		
60F	4.5477	0.7294	4.2735	-0.3288	-0.1386		
61F	3.1522	-0.5399	2.3498	-0.2505	-0.1517		
62F	3.6358	3.2605	-0.4730	-0.2906	-0.1721		
63F	5.0053	4.5017	1.4559	-0.3285	-0.1399		

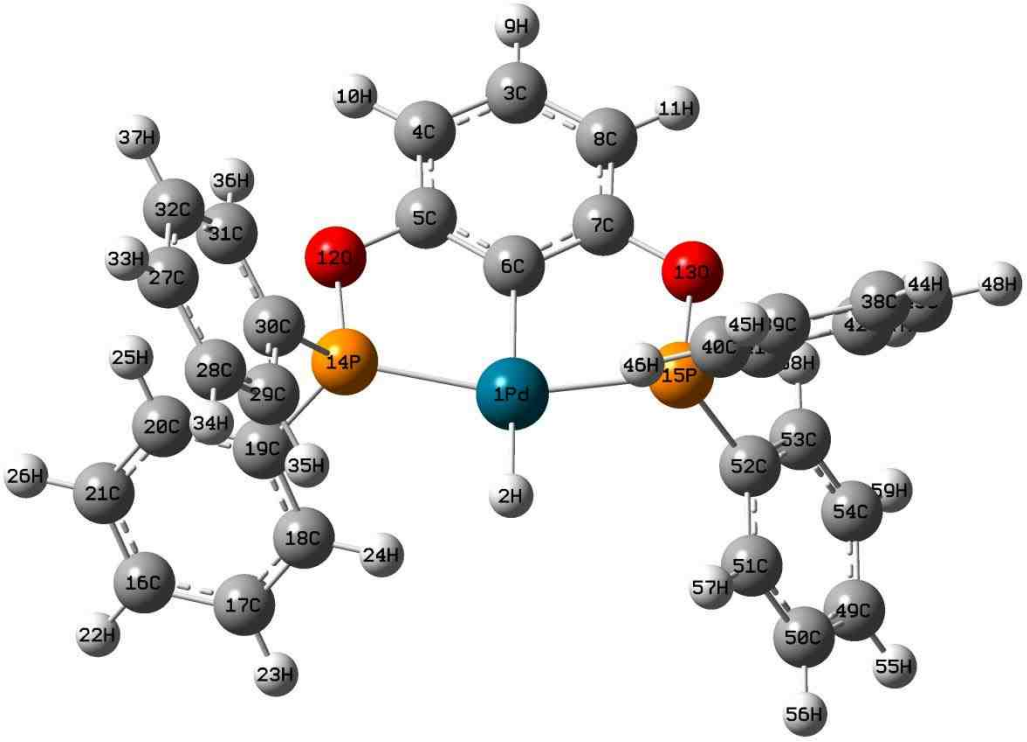
*** *** ***

(PCP) palladium hydride **21**

(see Figure 3-14)



21



Energy: -2117.62108935 hartrees

Palladium-hydrogen bond length: 1.647 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0001	-0.0046	-0.3860	-1.3436	-0.1343		
2H	0.0003	-0.0034	-2.0326	0.0261	-0.2742		
3C	0.0016	-0.0053	4.4872	-0.0658	-0.0432		
4C	-1.2210	0.0219	3.8042	-0.5317	-0.3512		
5C	-1.1923	0.0189	2.4075	0.0282	0.4251		
6C	0.0008	-0.0054	1.6845	0.4936	-0.4591		
7C	1.1943	-0.0293	2.4068	0.0358	0.4211		
8C	1.2237	-0.0322	3.8034	-0.5310	-0.3499		
9H	0.0019	-0.0053	5.5742	0.1740	0.1147		
10H	-2.1656	0.0464	4.3389	0.1793	0.1567		
11H	2.1686	-0.0565	4.3377	0.1793	0.1565		
12O	-2.4011	0.0375	1.7078	-0.4381	-0.4044		
13O	2.4026	-0.0473	1.7064	-0.4357	-0.4014		

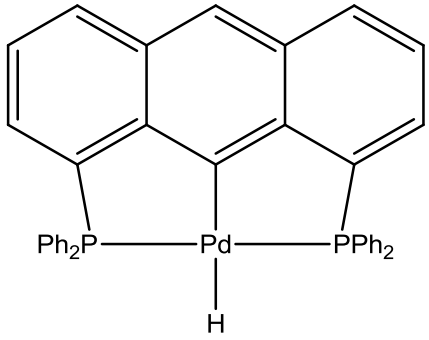
14P	-2.2606	0.0443	0.0286	0.8782	0.6113		
15P	2.2608	-0.0482	0.0272	0.8726	0.6109		
16C	-4.6659	3.8208	-1.1506	-0.0717	-0.1468		
17C	-3.3247	3.6901	-1.5186	-0.3690	-0.0537		
18C	-2.6099	2.5423	-1.1622	0.3519	-0.1619		
19C	-3.2384	1.5183	-0.4387	-0.5205	0.0403		
20C	-4.5892	1.6519	-0.0756	-0.0148	-0.1799		
21C	-5.2971	2.8014	-0.4273	-0.2491	-0.0503		
22H	-5.2215	4.7134	-1.4272	0.1820	0.1173		
23H	-2.8326	4.4789	-2.0815	0.1850	0.1066		
24H	-1.5670	2.4321	-1.4483	0.2225	0.0990		
25H	-5.0855	0.8611	0.4803	0.1968	0.1236		
26H	-6.3412	2.9015	-0.1417	0.1828	0.0998		
27C	-4.9030	-3.5608	-1.1917	-0.2081	-0.1306		
28C	-4.1971	-2.8313	-2.1553	-0.3847	-0.0258		
29C	-3.4008	-1.7516	-1.7717	-0.9601	-0.2048		
30C	-3.3167	-1.3824	-0.4188	0.7103	-0.0335		
31C	-4.0186	-2.1198	0.5458	0.1263	-0.0536		
32C	-4.8094	-3.2057	0.1564	-0.1136	-0.1335		
33H	-5.5174	-4.4061	-1.4913	0.1811	0.1152		
34H	-4.2581	-3.1101	-3.2042	0.1833	0.0965		
35H	-2.8361	-1.2018	-2.5208	0.2048	0.1209		
36H	-3.9389	-1.8476	1.5935	0.2182	0.1007		
37H	-5.3490	-3.7746	0.9095	0.1831	0.1162		
38C	4.6814	-3.8110	-1.1643	-0.0724	-0.1442		
39C	3.3391	-3.6854	-1.5299	-0.3648	-0.0626		
40C	2.6199	-2.5415	-1.1700	0.3605	-0.1495		
41C	3.2449	-1.5164	-0.4451	-0.5321	0.0309		
42C	4.5969	-1.6448	-0.0846	-0.0066	-0.1735		
43C	5.3093	-2.7903	-0.4400	-0.2543	-0.0519		
44H	5.2405	-4.7005	-1.4438	0.1820	0.1175		
45H	2.8496	-4.4751	-2.0938	0.1850	0.1084		
46H	1.5760	-2.4353	-1.4543	0.2224	0.0963		
47H	5.0906	-0.8530	0.4722	0.1967	0.1217		
48H	6.3543	-2.8864	-0.1562	0.1828	0.0997		
49C	4.8856	3.5725	-1.1842	-0.2050	-0.1217		
50C	4.1647	2.8564	-2.1467	-0.3868	-0.0362		
51C	3.3731	1.7722	-1.7655	-0.9525	-0.1914		
52C	3.3091	1.3853	-0.4165	0.7130	-0.0451		

53C	4.0259	2.1094	0.5472	0.1168	-0.0440		
54C	4.8117	3.1999	0.1604	-0.1131	-0.1400		
55H	5.4962	4.4213	-1.4817	0.1811	0.1130		
56H	4.2102	3.1491	-3.1925	0.1834	0.0982		
57H	2.7959	1.2332	-2.5129	0.2054	0.1183		
58H	3.9609	1.8240	1.5924	0.2179	0.0990		
59H	5.3628	3.7586	0.9128	0.1831	0.1168		

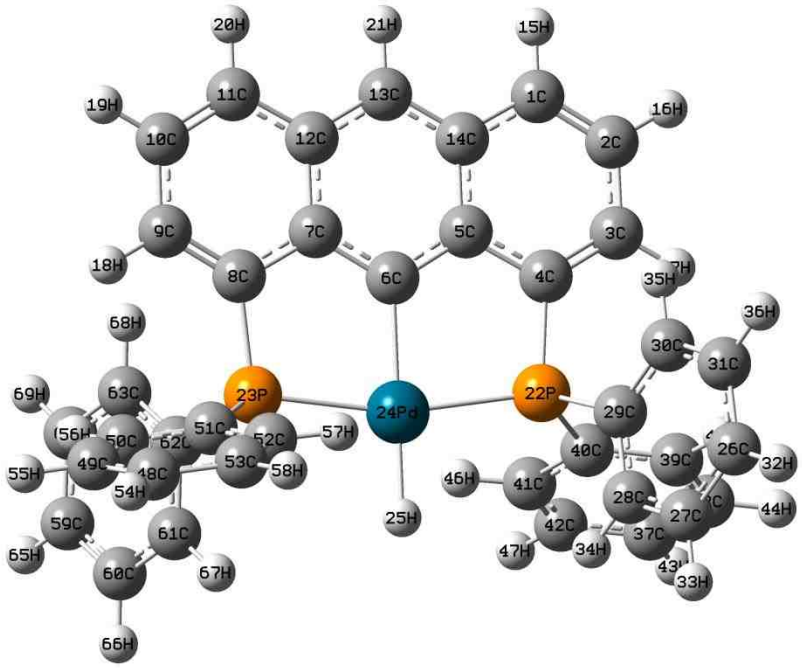
*** *** ***

(PCP) palladium hydride **22**

(see Figure 3-14)



22



Energy: -2274.42746196 hartrees

Palladium-hydrogen bond length: 1.644 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	2.4715	4.3364	-0.2654	-0.1773	-0.2151		
2C	3.6461	3.6326	-0.3805	-0.7421	-0.1419		
3C	3.6479	2.2073	-0.3264	0.2194	-0.0960		
4C	2.4661	1.5200	-0.1644	-0.1778	-0.1200		
5C	1.2100	2.2179	-0.0852	-0.2098	0.1250		
6C	0.0000	1.4919	-0.0010	0.2783	-0.3954		
7C	-1.2100	2.2181	0.0819	-0.2109	0.1213		
8C	-2.4661	1.5202	0.1621	-0.1747	-0.1168		
9C	-3.6480	2.2078	0.3230	0.2191	-0.1030		
10C	-3.6461	3.6332	0.3750	-0.7415	-0.1342		
11C	-2.4715	4.3368	0.2589	-0.1776	-0.2197		
12C	-1.2168	3.6647	0.1092	0.6350	0.2204		
13C	0.0000	4.3547	-0.0032	-0.2686	-0.4240		
14C	1.2168	3.6645	-0.1147	0.6351	0.2179		
15H	2.4800	5.4242	-0.2982	0.1805	0.1306		

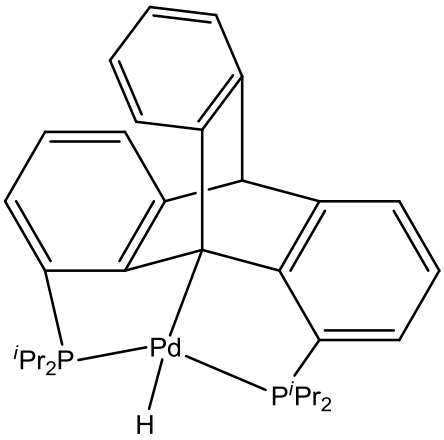
16H	4.5881	4.1600	-0.5087	0.1786	0.1188		
17H	4.5924	1.6764	-0.4151	0.1919	0.0958		
18H	-4.5925	1.6770	0.4125	0.1920	0.0971		
19H	-4.5881	4.1608	0.5024	0.1786	0.1171		
20H	-2.4800	5.4247	0.2900	0.1805	0.1314		
21H	0.0000	5.4434	-0.0041	0.1755	0.1699		
22P	2.2932	-0.3152	-0.0351	-0.1743	0.4935		
23P	-2.2932	-0.3151	0.0355	-0.1760	0.4975		
24Pd	0.0000	-0.5987	0.0005	-1.0870	-0.1219		
25H	0.0001	-2.2430	0.0017	0.0404	-0.2814		
26C	4.4178	-1.7477	3.8481	-0.2466	-0.1467		
27C	3.8265	-2.6581	2.9640	-0.5515	-0.0457		
28C	3.2027	-2.2032	1.8023	-0.9058	-0.1851		
29C	3.1790	-0.8303	1.4961	1.2883	0.0356		
30C	3.7651	0.0767	2.3905	0.4342	-0.1817		
31C	4.3801	-0.3819	3.5613	-0.5694	-0.0606		
32H	4.8973	-2.1026	4.7569	0.1797	0.1126		
33H	3.8414	-3.7224	3.1850	0.1828	0.0993		
34H	2.7208	-2.9134	1.1352	0.2084	0.1168		
35H	3.7398	1.1415	2.1813	0.2104	0.1212		
36H	4.8281	0.3334	4.2467	0.1813	0.0969		
37C	4.7437	-2.0275	-3.5934	-0.1335	-0.0998		
38C	5.4061	-1.6958	-2.4074	-0.2816	-0.1341		
39C	4.6874	-1.1941	-1.3190	-0.1333	-0.0998		
40C	3.2969	-1.0199	-1.4078	0.0616	-0.0148		
41C	2.6367	-1.3697	-2.5961	0.0065	-0.1406		
42C	3.3581	-1.8650	-3.6851	-0.3805	-0.0848		
43H	5.3040	-2.4202	-4.4383	0.1799	0.1063		
44H	6.4818	-1.8310	-2.3263	0.1807	0.1134		
45H	5.2098	-0.9554	-0.3963	0.1967	0.1013		
46H	1.5562	-1.2664	-2.6572	0.2145	0.0964		
47H	2.8357	-2.1342	-4.5996	0.1832	0.1117		
48C	-4.7439	-2.0221	3.5963	-0.1340	-0.0958		
49C	-5.4061	-1.6923	2.4097	-0.2802	-0.1368		
50C	-4.6874	-1.1923	1.3206	-0.1339	-0.0967		
51C	-3.2969	-1.0178	1.4092	0.0630	-0.0178		
52C	-2.6368	-1.3656	2.5982	0.0061	-0.1401		
53C	-3.3583	-1.8593	3.6879	-0.3808	-0.0882		
54H	-5.3041	-2.4135	4.4418	0.1799	0.1053		

55H	-6.4819	-1.8277	2.3288	0.1807	0.1138		
56H	-5.2097	-0.9551	0.3975	0.1967	0.1005		
57H	-1.5563	-1.2622	2.6591	0.2144	0.0974		
58H	-2.8359	-2.1270	4.6029	0.1832	0.1126		
59C	-4.4179	-1.7541	-3.8452	-0.2461	-0.1411		
60C	-3.8248	-2.6628	-2.9606	-0.5520	-0.0512		
61C	-3.2008	-2.2060	-1.7998	-0.9040	-0.1782		
62C	-3.1788	-0.8327	-1.4949	1.2865	0.0287		
63C	-3.7667	0.0727	-2.3899	0.4358	-0.1742		
64C	-4.3819	-0.3879	-3.5598	-0.5715	-0.0676		
65H	-4.8975	-2.1105	-4.7534	0.1797	0.1118		
66H	-3.8383	-3.7273	-3.1806	0.1828	0.1001		
67H	-2.7175	-2.9148	-1.1324	0.2085	0.1152		
68H	-3.7427	1.1377	-2.1817	0.2104	0.1194		
69H	-4.8313	0.3261	-4.2456	0.1813	0.0983		

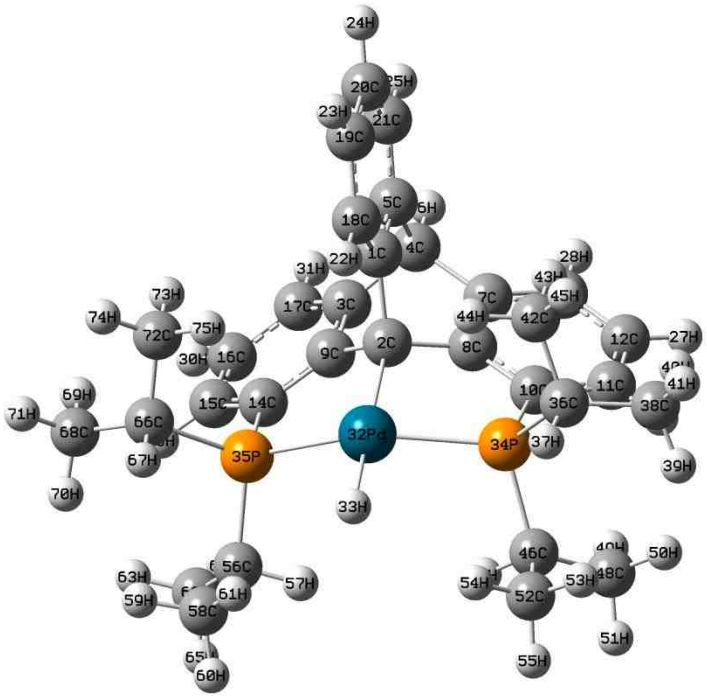
*** *** ***

(PCP) palladium hydride **23**

(see Figure 3-14)



23



Energy: -2053.00349139 hartrees

Palladium-hydrogen bond length: 1.640 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	0.0002	2.0952	0.9244	-0.9873	0.1025		
2C	0.0000	0.8659	-0.0106	1.5544	-0.0199		
3C	-1.2305	2.3333	-1.5968	-0.4322	-0.0061		
4C	0.0001	3.1792	-1.2863	1.1892	0.0728		
5C	0.0002	3.3329	0.2415	-0.8523	0.0429		
6H	0.0001	4.1404	-1.8091	0.1785	0.0615		
7C	1.2306	2.3331	-1.5970	-0.4322	-0.0073		
8C	1.2366	1.1164	-0.8868	-0.0132	-0.0293		
9C	-1.2366	1.1165	-0.8867	-0.0134	-0.0294		
10C	2.3651	0.2850	-0.9243	-0.7364	-0.0198		
11C	3.4642	0.6705	-1.7229	-0.0107	-0.1054		
12C	3.4265	1.8518	-2.4638	-0.6057	-0.1799		
13C	2.3080	2.6972	-2.3959	-0.0728	-0.1315		
14C	-2.3652	0.2853	-0.9242	-0.7371	-0.0202		

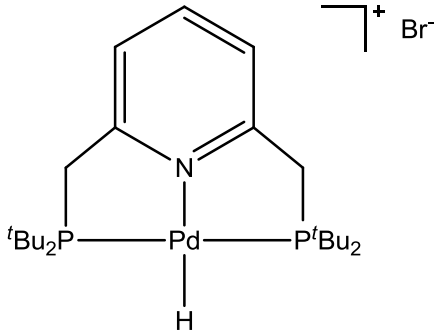
15C	-3.4643	0.6710	-1.7225	-0.0102	-0.1046		
16C	-3.4267	1.8523	-2.4634	-0.6054	-0.1781		
17C	-2.3080	2.6976	-2.3956	-0.0729	-0.1342		
18C	0.0003	2.0910	2.3174	-0.1302	-0.1102		
19C	0.0004	3.3036	3.0254	-0.0010	-0.2061		
20C	0.0004	4.5209	2.3419	-0.2311	-0.0855		
21C	0.0003	4.5368	0.9381	0.3971	-0.2431		
22H	0.0003	1.1438	2.8505	0.1834	0.1375		
23H	0.0005	3.2921	4.1130	0.1717	0.1216		
24H	0.0005	5.4574	2.8943	0.1721	0.1084		
25H	0.0004	5.4840	0.4014	0.1690	0.1222		
26H	4.3532	0.0511	-1.7729	0.1911	0.1232		
27H	4.2776	2.1277	-3.0817	0.1759	0.1198		
28H	2.2972	3.6364	-2.9460	0.1766	0.1066		
29H	-4.3534	0.0517	-1.7725	0.1911	0.1224		
30H	-4.2778	2.1283	-3.0811	0.1759	0.1193		
31H	-2.2972	3.6368	-2.9457	0.1766	0.1074		
32Pd	-0.0001	-1.1539	0.7518	-0.9331	-0.1121		
33H	-0.0002	-2.7101	1.2681	0.0112	-0.2705		
34P	2.2498	-1.1966	0.1762	1.0403	0.0561		
35P	-2.2499	-1.1964	0.1761	1.0402	0.0558		
36C	3.6168	-1.0697	1.4672	-0.2460	0.4152		
37H	3.5157	-2.0157	2.0161	0.2301	-0.0719		
38C	5.0601	-0.9581	0.9506	-0.6376	-0.2444		
39H	5.3405	-1.7877	0.2946	0.2116	0.0425		
40H	5.2187	-0.0198	0.4083	0.2310	0.0334		
41H	5.7539	-0.9645	1.8020	0.2105	0.0423		
42C	3.2956	0.0762	2.4415	-0.7336	-0.2344		
43H	3.3342	1.0511	1.9420	0.2401	0.0471		
44H	2.3002	-0.0360	2.8811	0.2289	0.0091		
45H	4.0311	0.0884	3.2566	0.2054	0.0499		
46C	2.5816	-2.7454	-0.8630	-0.2606	0.4387		
47H	1.5976	-2.8968	-1.3244	0.2310	-0.0567		
48C	3.6118	-2.6614	-2.0004	-0.6249	-0.2951		
49H	3.3687	-1.8714	-2.7162	0.2374	0.0343		
50H	4.6312	-2.4947	-1.6356	0.2117	0.0577		
51H	3.6160	-3.6137	-2.5478	0.2100	0.0603		
52C	2.8506	-3.9536	0.0512	-0.7791	-0.3044		
53H	3.8494	-3.9060	0.5018	0.2198	0.0506		

54H	2.1065	-4.0264	0.8511	0.2481	0.0757		
55H	2.8033	-4.8784	-0.5382	0.2078	0.0564		
56C	-2.5818	-2.7452	-0.8632	-0.2606	0.4366		
57H	-1.5978	-2.8966	-1.3246	0.2310	-0.0560		
58C	-2.8509	-3.9534	0.0509	-0.7790	-0.3043		
59H	-3.8497	-3.9057	0.5016	0.2198	0.0506		
60H	-2.8038	-4.8781	-0.5386	0.2078	0.0565		
61H	-2.1068	-4.0264	0.8508	0.2481	0.0757		
62C	-3.6119	-2.6609	-2.0007	-0.6250	-0.2926		
63H	-4.6312	-2.4941	-1.6359	0.2117	0.0573		
64H	-3.3686	-1.8709	-2.7164	0.2375	0.0336		
65H	-3.6162	-3.6132	-2.5481	0.2100	0.0598		
66C	-3.6167	-1.0696	1.4673	-0.2458	0.4152		
67H	-3.5154	-2.0156	2.0163	0.2301	-0.0719		
68C	-5.0601	-0.9583	0.9509	-0.6376	-0.2425		
69H	-5.2189	-0.0202	0.4084	0.2310	0.0331		
70H	-5.3407	-1.7881	0.2952	0.2116	0.0423		
71H	-5.7538	-0.9644	1.8024	0.2105	0.0415		
72C	-3.2956	0.0764	2.4415	-0.7338	-0.2343		
73H	-3.3345	1.0513	1.9420	0.2401	0.0469		
74H	-4.0308	0.0884	3.2568	0.2054	0.0500		
75H	-2.3000	-0.0355	2.8807	0.2289	0.0091		

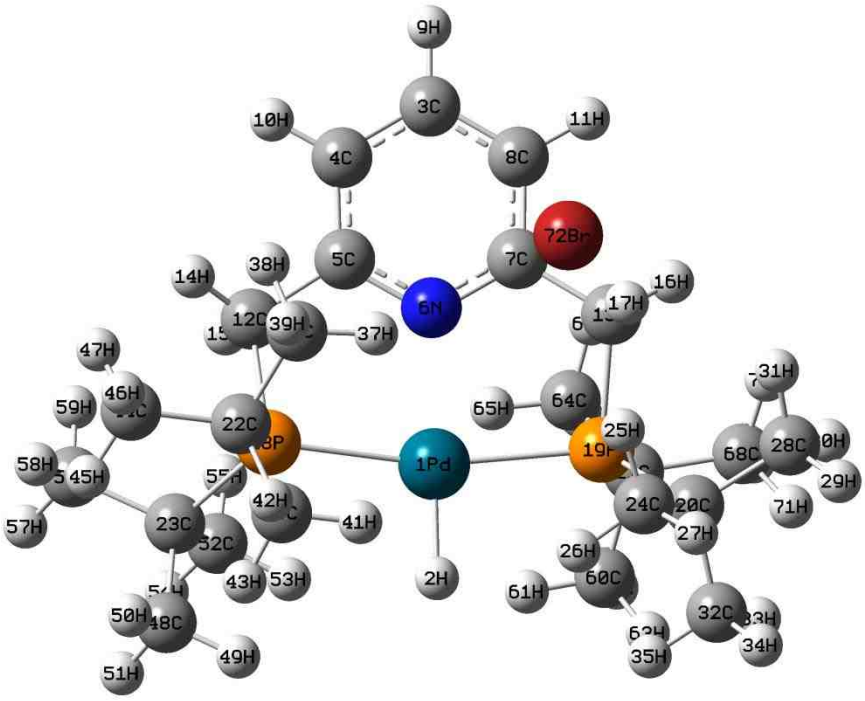
*** *** ***

(PNP) palladium hydride **24**

(see Figure 3-15)



24



Energy: -1780.42590061 hartrees

Palladium-hydrogen bond length: 1.571 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.2286	-0.8285	-0.2833	-1.6979	-0.0420		
2H	0.3346	-1.8151	-1.5019	0.1092	-0.1691		
3C	-0.1597	2.2963	3.5022	-0.2393	0.0410		
4C	1.0950	1.8249	3.1119	-0.3310	-0.3147		
5C	1.1798	0.9209	2.0543	0.3341	0.2195		
6N	0.0664	0.5090	1.4031	0.6860	-0.1620		
7C	-1.1542	0.9744	1.7542	-0.2477	0.3616		
8C	-1.2931	1.8681	2.8216	-0.6941	-0.3313		
9H	-0.2468	3.0107	4.3161	0.1957	0.1251		
10H	1.9969	2.1547	3.6186	0.1887	0.1492		
11H	-2.2747	2.2559	3.0715	0.2023	0.1555		
12C	2.5115	0.3262	1.6369	-1.3476	-0.0654		
13C	-2.3358	0.6154	0.8930	-1.2441	-0.0181		
14H	3.3182	1.0504	1.7950	0.2678	0.0602		

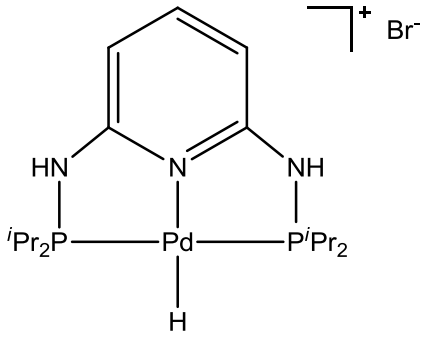
15H	2.7301	-0.5231	2.2967	0.2650	0.0363		
16H	-3.2621	0.5991	1.4774	0.2445	0.0154		
17H	-2.4087	1.4705	0.1865	0.3225	0.0893		
18P	2.5132	-0.3569	-0.1161	1.8306	-0.0083		
19P	-2.1041	-0.9231	-0.1387	1.8543	-0.0480		
20C	-3.1279	-0.6058	-1.7148	-0.5235	0.6769		
21C	-2.7644	-2.3694	0.9224	-0.6348	0.5498		
22C	3.1144	1.0701	-1.2328	-0.6527	0.6136		
23C	3.7260	-1.8285	-0.0205	-0.6310	0.6110		
24C	-2.2682	0.3173	-2.6089	-0.4462	-0.3264		
25H	-2.0127	1.2677	-2.1253	0.2984	0.0922		
26H	-1.3408	-0.1797	-2.9131	0.2289	0.0523		
27H	-2.8430	0.5531	-3.5152	0.2119	0.0499		
28C	-4.4687	0.0989	-1.4144	-0.4978	-0.2863		
29H	-5.0039	0.2456	-2.3620	0.2223	0.0570		
30H	-5.1208	-0.4837	-0.7570	0.2126	0.0321		
31H	-4.3187	1.0900	-0.9760	0.2632	0.0349		
32C	-3.3805	-1.9255	-2.4711	-0.5399	-0.4288		
33H	-4.0716	-2.5918	-1.9448	0.2174	0.0743		
34H	-3.8332	-1.6883	-3.4425	0.2238	0.0817		
35H	-2.4491	-2.4689	-2.6671	0.2365	0.0848		
36C	2.3280	2.3374	-0.8257	-0.5892	-0.2601		
37H	1.2389	2.2295	-0.8724	0.3138	0.0861		
38H	2.5929	2.6885	0.1776	0.2207	0.0456		
39H	2.5897	3.1425	-1.5242	0.2299	0.0518		
40C	2.7579	0.7261	-2.6955	-0.6106	-0.4025		
41H	1.6835	0.5559	-2.8111	0.2565	0.0762		
42H	3.0345	1.5740	-3.3352	0.2233	0.0921		
43H	3.2888	-0.1563	-3.0662	0.2147	0.0780		
44C	4.6230	1.3586	-1.1125	-0.3959	-0.4483		
45H	5.2421	0.5413	-1.4957	0.2219	0.0925		
46H	4.8567	2.2507	-1.7082	0.2303	0.0945		
47H	4.9273	1.5717	-0.0809	0.2226	0.0763		
48C	4.0391	-2.3261	-1.4461	-0.5229	-0.3683		
49H	3.1244	-2.5231	-2.0157	0.2483	0.0846		
50H	4.6510	-1.6141	-2.0076	0.2302	0.0676		
51H	4.6036	-3.2658	-1.3835	0.2197	0.0750		
52C	2.9838	-2.9564	0.7332	-0.4818	-0.3137		
53H	2.0594	-3.2408	0.2214	0.2559	0.0475		

54H	3.6355	-3.8388	0.7868	0.2190	0.0636		
55H	2.7298	-2.6781	1.7629	0.2111	0.0699		
56C	5.0397	-1.5147	0.7267	-0.4244	-0.3787		
57H	5.6427	-2.4309	0.7852	0.2223	0.0733		
58H	5.6439	-0.7578	0.2218	0.2271	0.0792		
59H	4.8639	-1.1802	1.7552	0.2209	0.0586		
60C	-2.3216	-3.7093	0.2959	-0.6527	-0.3221		
61H	-1.2346	-3.7495	0.1707	0.2416	0.0477		
62H	-2.6198	-4.5324	0.9595	0.2137	0.0618		
63H	-2.7799	-3.8911	-0.6793	0.2254	0.0708		
64C	-2.0971	-2.2489	2.3110	-0.5355	-0.1474		
65H	-1.0047	-2.2217	2.2367	0.2380	-0.0249		
66H	-2.4255	-1.3581	2.8563	0.2377	-0.0171		
67H	-2.3720	-3.1245	2.9140	0.2185	0.0443		
68C	-4.2945	-2.3532	1.1065	-0.3875	-0.4085		
69H	-4.5807	-3.1571	1.7986	0.2205	0.0731		
70H	-4.6516	-1.4109	1.5375	0.2304	0.0957		
71H	-4.8300	-2.5247	0.1684	0.2324	0.0838		
72Br	-1.3890	3.5863	-0.6532	-0.5333	-0.7611		

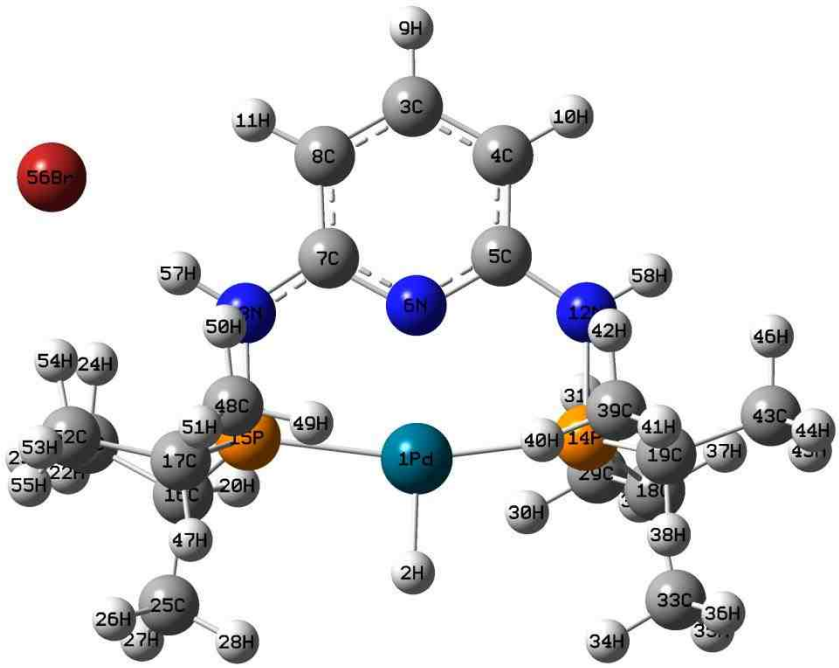
*** *** ***

(PNP) palladium hydride **25**

(see Figure 3-15)



25



Energy: -1655.31201182 hartrees

Palladium-hydrogen bond length: 1.578 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.9827	-0.8496	0.1400	-1.5229	-0.1441		
2H	1.3742	-2.3538	0.4144	0.1103	-0.1899		
3C	-0.4372	3.7415	-0.6732	-0.6228	0.0941		
4C	0.9352	3.4529	-0.6155	-0.3711	-0.4359		
5C	1.3054	2.1287	-0.3874	-0.4560	0.3114		
6N	0.3823	1.1541	-0.2286	0.2879	-0.0818		
7C	-0.9480	1.4329	-0.2930	-0.6233	0.3154		
8C	-1.3950	2.7517	-0.5174	-0.3034	-0.3336		
9H	-0.7566	4.7659	-0.8461	0.1967	0.1108		
10H	1.6840	4.2287	-0.7389	0.1760	0.1718		
11H	-2.4628	2.9461	-0.5554	0.2602	0.1550		
12N	2.6413	1.7219	-0.3084	-0.9187	-0.4321		
13N	-1.8235	0.3910	-0.1378	-0.5275	-0.4815		
14P	3.1167	0.0811	-0.0139	2.4032	0.3169		

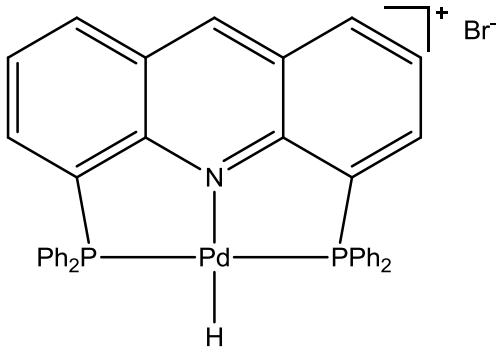
15P	-1.3096	-1.2281	0.1271	2.1624	0.3407		
16C	-1.9368	-2.2242	-1.3270	-0.2933	0.3166		
17C	-2.1006	-1.7896	1.7214	-0.2700	0.3195		
18C	4.2214	-0.3398	-1.4601	-0.2445	0.2444		
19C	4.2295	0.1703	1.4873	-0.3629	0.2420		
20H	-1.2554	-1.8916	-2.1227	0.2235	-0.0454		
21C	-3.3754	-1.9233	-1.7839	-0.6203	-0.1642		
22H	-3.5297	-2.3802	-2.7703	0.2061	0.0369		
23H	-4.1207	-2.3444	-1.1043	0.2233	0.0473		
24H	-3.5825	-0.8527	-1.8687	0.2809	0.0158		
25C	-1.6955	-3.7259	-1.0900	-0.7005	-0.3695		
26H	-2.3567	-4.1197	-0.3093	0.2283	0.0811		
27H	-1.9131	-4.2800	-2.0110	0.2175	0.0911		
28H	-0.6590	-3.9397	-0.8048	0.2272	0.0813		
29C	3.4007	-0.3399	-2.7608	-0.7915	-0.1889		
30H	2.6332	-1.1221	-2.7399	0.2379	0.0433		
31H	2.9022	0.6197	-2.9326	0.2320	0.0182		
32H	4.0609	-0.5342	-3.6149	0.2144	0.0603		
33C	4.9193	-1.6930	-1.2351	-0.6975	-0.2667		
34H	4.1871	-2.4951	-1.0855	0.2436	0.0629		
35H	5.5190	-1.9490	-2.1169	0.2200	0.0731		
36H	5.5938	-1.6807	-0.3720	0.2177	0.0607		
37H	4.9838	0.4496	-1.5256	0.2158	-0.0275		
38H	4.5752	-0.8648	1.6163	0.2301	-0.0258		
39C	3.4030	0.5570	2.7257	-0.7499	-0.2131		
40H	2.5544	-0.1193	2.8715	0.2345	0.0420		
41H	4.0335	0.5117	3.6220	0.2138	0.0636		
42H	3.0139	1.5783	2.6419	0.2358	0.0413		
43C	5.4531	1.0854	1.3145	-0.6576	-0.1796		
44H	6.0646	1.0610	2.2248	0.2246	0.0540		
45H	6.0960	0.7831	0.4808	0.2204	0.0338		
46H	5.1549	2.1301	1.1597	0.2154	0.0306		
47H	-1.6630	-2.7867	1.8769	0.2246	-0.0645		
48C	-1.6259	-0.8694	2.8616	-0.7717	-0.2147		
49H	-0.5333	-0.7911	2.9006	0.2124	0.0312		
50H	-2.0446	0.1367	2.7514	0.2561	0.0424		
51H	-1.9721	-1.2727	3.8209	0.2123	0.0566		
52C	-3.6357	-1.9028	1.7014	-0.7254	-0.2232		
53H	-3.9833	-2.1566	2.7114	0.2036	0.0453		

54H	-4.1177	-0.9637	1.4045	0.2988	0.0625		
55H	-3.9820	-2.6937	1.0298	0.2061	0.0451		
56Br	-4.8855	1.4175	-0.1383	-0.5209	-0.7181		
57H	-2.8479	0.6556	-0.1447	0.3324	0.3586		
58H	3.3288	2.4531	-0.4518	0.4457	0.2827		

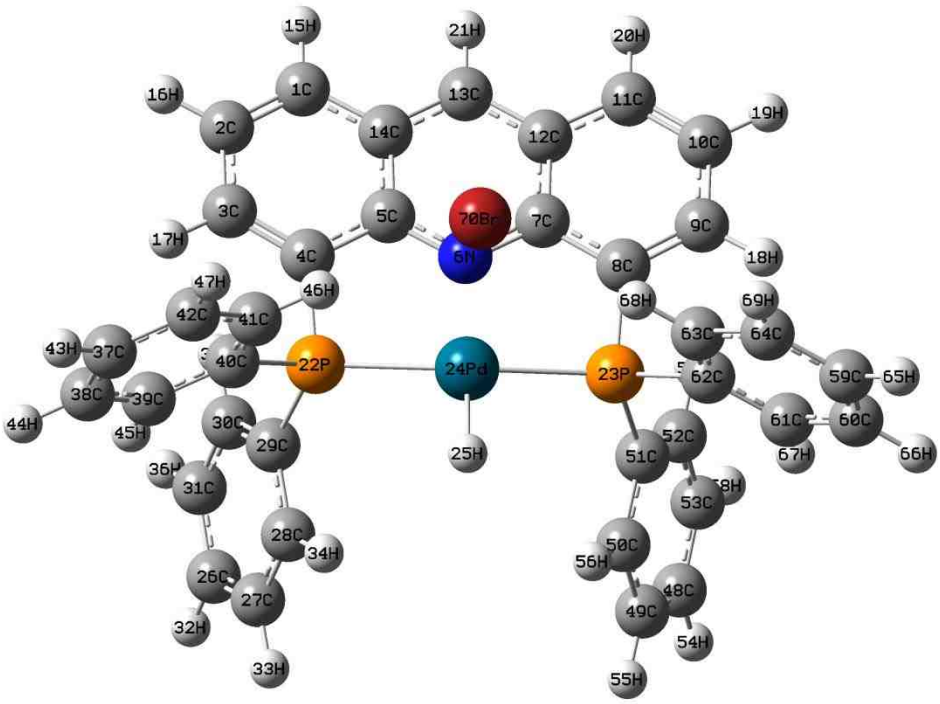
*** *** ***

(PNP) palladium hydride **26**

(see Figure 3-15)



26



Energy: -2304.28846645 hartrees

Palladium-hydrogen bond length: 1.561 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-2.4842	-1.7697	3.8703	0.1640	-0.2150		
2C	-3.6438	-1.5053	3.1877	-0.5480	-0.1078		
3C	-3.5993	-0.8699	1.9127	0.1155	-0.0805		
4C	-2.4076	-0.4941	1.3323	-0.1378	0.0335		
5C	-1.1766	-0.7964	2.0124	-1.6403	0.0871		
6N	-0.0006	-0.5117	1.4141	0.8599	-0.1074		
7C	1.1755	-0.8002	2.0105	-1.6165	0.0827		
8C	2.4064	-0.5004	1.3291	-0.1511	0.0379		
9C	3.5978	-0.8815	1.9066	0.1166	-0.0812		
10C	3.6422	-1.5193	3.1804	-0.5341	-0.1063		
11C	2.4831	-1.7800	3.8651	0.1653	-0.2195		
12C	1.2163	-1.4389	3.3001	0.6384	0.1527		
13C	-0.0005	-1.7386	3.9227	0.6665	-0.2380		
14C	-1.2173	-1.4341	3.3025	0.6358	0.1492		

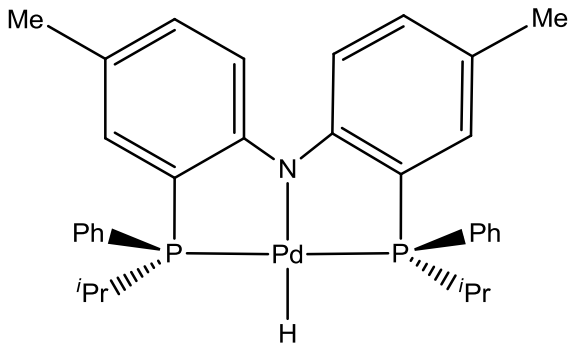
15H	-2.5082	-2.2599	4.8406	0.1933	0.1446		
16H	-4.6056	-1.7835	3.6090	0.1921	0.1242		
17H	-4.5332	-0.6906	1.3857	0.2113	0.0983		
18H	4.5313	-0.7043	1.3783	0.2114	0.0974		
19H	4.6038	-1.8020	3.5994	0.1921	0.1245		
20H	2.5071	-2.2713	4.8348	0.1933	0.1458		
21H	-0.0005	-2.2373	4.8900	0.1993	0.1611		
22P	-2.2827	0.3304	-0.3259	0.3723	0.2922		
23P	2.2813	0.3310	-0.3255	0.3608	0.2916		
24Pd	-0.0007	0.0657	-0.6756	-1.2449	-0.0173		
25H	-0.0008	0.5793	-2.1492	0.1304	-0.1534		
26C	-3.5542	4.7775	0.2191	-0.2311	-0.1021		
27C	-2.9405	4.3301	-0.9565	-0.5086	-0.0636		
28C	-2.5646	2.9930	-1.0863	-0.7933	-0.0959		
29C	-2.8173	2.0748	-0.0510	0.6338	-0.2121		
30C	-3.4303	2.5322	1.1249	0.5785	-0.0200		
31C	-3.7929	3.8772	1.2592	-0.4778	-0.1156		
32H	-3.8369	5.8218	0.3243	0.1817	0.1052		
33H	-2.7430	5.0256	-1.7683	0.1838	0.1000		
34H	-2.0621	2.6594	-1.9908	0.2052	0.1115		
35H	-3.6238	1.8467	1.9439	0.1992	0.0628		
36H	-4.2622	4.2167	2.1794	0.1810	0.1043		
37C	-5.6150	-1.6507	-2.8749	-0.1100	-0.1693		
38C	-5.8597	-0.4078	-2.2836	-0.0963	-0.0559		
39C	-4.8697	0.2087	-1.5128	0.0397	-0.3139		
40C	-3.6259	-0.4186	-1.3311	-0.5463	0.3474		
41C	-3.3772	-1.6638	-1.9353	0.1370	-0.4473		
42C	-4.3756	-2.2743	-2.6977	-0.2397	0.0578		
43H	-6.3853	-2.1280	-3.4760	0.1794	0.1159		
44H	-6.8184	0.0862	-2.4227	0.1778	0.0972		
45H	-5.0670	1.1793	-1.0667	0.2020	0.1683		
46H	-2.4127	-2.1536	-1.8031	0.2537	0.2354		
47H	-4.1753	-3.2377	-3.1594	0.1937	0.0822		
48C	3.5476	4.7769	0.2415	-0.2357	-0.0957		
49C	2.9210	4.3376	-0.9303	-0.4944	-0.0610		
50C	2.5464	3.0007	-1.0664	-0.7498	-0.1024		
51C	2.8133	2.0749	-0.0415	0.6197	-0.2102		
52C	3.4391	2.5242	1.1307	0.5600	-0.0226		
53C	3.8005	3.8689	1.2716	-0.4957	-0.1195		

54H	3.8294	5.8210	0.3518	0.1817	0.1019		
55H	2.7123	5.0393	-1.7339	0.1838	0.0995		
56H	2.0336	2.6730	-1.9671	0.2052	0.1125		
57H	3.6437	1.8326	1.9419	0.1994	0.0644		
58H	4.2799	4.2021	2.1888	0.1810	0.1058		
59C	5.6172	-1.6293	-2.8865	-0.1147	-0.1760		
60C	5.8575	-0.3869	-2.2924	-0.1270	-0.0521		
61C	4.8664	0.2228	-1.5175	0.0905	-0.3165		
62C	3.6259	-0.4108	-1.3344	-0.5099	0.3516		
63C	3.3817	-1.6555	-1.9414	0.1069	-0.4520		
64C	4.3812	-2.2592	-2.7079	-0.2496	0.0647		
65H	6.3883	-2.1013	-3.4907	0.1794	0.1169		
66H	6.8134	0.1121	-2.4323	0.1778	0.0966		
67H	5.0604	1.1930	-1.0692	0.2022	0.1691		
68H	2.4198	-2.1502	-1.8085	0.2534	0.2359		
69H	4.1842	-3.2222	-3.1718	0.1936	0.0808		
70Br	0.0080	-2.9940	-0.9885	-0.4467	-0.6804		

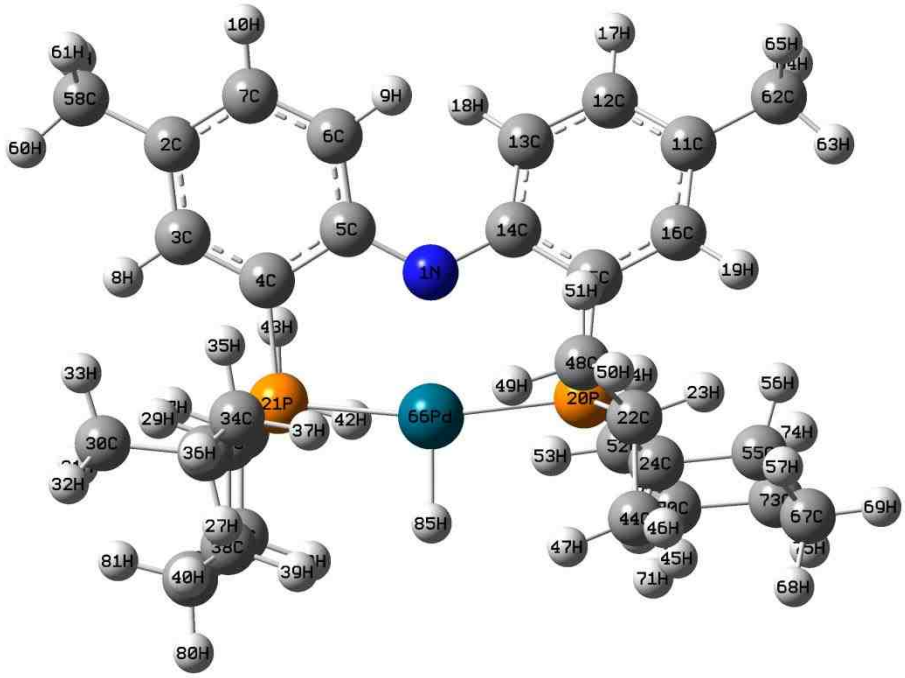
*** *** ***

(PNP) palladium hydride **27**

(see Figure 3-15)



27



Energy: -2113.23441993 hartrees

Palladium-hydrogen bond length: 1.588 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1N	-0.1308	1.3607	-0.2159	0.4007	-0.3574		
2C	-4.0107	3.0485	-0.8478	-0.0610	0.2760		
3C	-3.8270	1.7276	-0.4348	0.0227	-0.4508		
4C	-2.5605	1.1839	-0.1630	-0.7659	0.1387		
5C	-1.3717	1.9521	-0.3895	0.8827	0.1370		
6C	-1.5835	3.3234	-0.7113	0.0149	-0.1851		
7C	-2.8529	3.8416	-0.9314	-1.1438	-0.2926		
8H	-4.7061	1.0991	-0.3105	0.1652	0.1770		
9H	-0.7361	3.9964	-0.7561	0.1948	0.1429		
10H	-2.9473	4.8999	-1.1727	0.1713	0.1466		
11C	3.6128	2.9303	-1.5640	-0.0153	0.2683		
12C	2.4059	3.3036	-2.1811	-0.9827	-0.2826		
13C	1.1797	2.7934	-1.7766	-0.0840	-0.1968		
14C	1.0644	1.8590	-0.7073	0.7320	0.1561		
15C	2.3056	1.3703	-0.1830	-0.9200	0.0994		

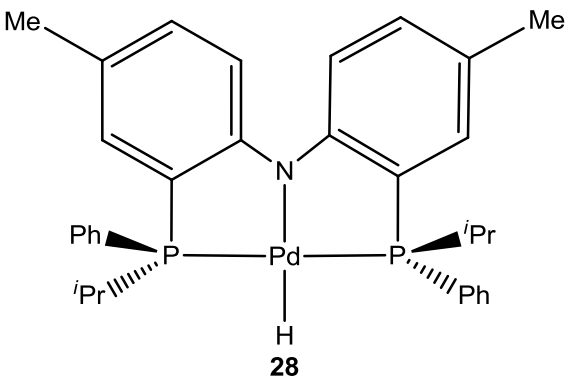
16C	3.5259	1.9401	-0.5839	0.0495	-0.4287		
17H	2.4261	4.0140	-3.0069	0.1710	0.1441		
18H	0.2909	3.0960	-2.3164	0.1955	0.1436		
19H	4.4460	1.5915	-0.1204	0.1649	0.1641		
20P	2.2214	-0.0738	0.9398	1.5240	0.1631		
21P	-2.3493	-0.4731	0.5860	2.0217	0.1363		
22C	3.0778	0.4145	2.5338	0.0119	0.3035		
23H	4.0963	0.7300	2.2672	0.2205	-0.0385		
24C	3.2359	-1.4770	0.2089	-0.5062	0.1183		
25H	3.0258	-2.3036	0.9049	0.2336	-0.0111		
26C	-3.3193	-0.5306	2.2003	-0.2964	0.3750		
27H	-3.0452	-1.5152	2.6030	0.2317	-0.0549		
28C	-3.1656	-1.7073	-0.5585	-0.3097	0.0786		
29H	-4.2149	-1.3950	-0.6755	0.2210	-0.0026		
30C	-4.8516	-0.4591	2.0985	-0.7182	-0.2445		
31H	-5.2681	-1.1952	1.4016	0.2183	0.0321		
32H	-5.2909	-0.6583	3.0850	0.2120	0.0462		
33H	-5.1868	0.5362	1.7891	0.2268	0.0518		
34C	-2.7791	0.5381	3.1656	-0.7636	-0.2488		
35H	-2.9830	1.5481	2.7917	0.2427	0.0396		
36H	-3.2641	0.4359	4.1452	0.2023	0.0537		
37H	-1.6975	0.4391	3.3068	0.2331	0.0337		
38C	-3.1372	-3.1359	0.0257	-0.3873	-0.0115		
39H	-2.0936	-3.4174	0.2243	0.2387	-0.0093		
40H	-3.6601	-3.1720	0.9897	0.2036	-0.0021		
41C	-2.4983	-1.6718	-1.9507	-0.2699	-0.0089		
42H	-1.4288	-1.9006	-1.8401	0.2280	-0.0024		
43H	-2.5610	-0.6622	-2.3727	0.2323	-0.0266		
44C	3.1619	-0.7718	3.5087	-0.8382	-0.2383		
45H	3.7487	-1.6053	3.1073	0.2181	0.0519		
46H	3.6408	-0.4519	4.4433	0.2094	0.0482		
47H	2.1618	-1.1487	3.7527	0.2422	0.0470		
48C	2.3540	1.6097	3.1763	-0.8753	-0.2934		
49H	1.3289	1.3417	3.4578	0.2303	0.0715		
50H	2.8854	1.9206	4.0851	0.2045	0.0717		
51H	2.3054	2.4694	2.5001	0.2392	0.0452		
52C	2.6685	-1.8813	-1.1692	-0.2455	0.0372		
53H	1.5861	-2.0411	-1.0912	0.2247	-0.0334		
54H	2.8168	-1.0543	-1.8776	0.2384	-0.0309		

55C	4.7656	-1.2962	0.1324	-0.0578	-0.0021		
56H	5.0054	-0.4721	-0.5513	0.2143	0.0025		
57H	5.1818	-1.0318	1.1127	0.2047	-0.0269		
58C	-5.3787	3.6060	-1.1676	-0.6211	-0.2135		
59H	-5.5261	3.7285	-2.2501	0.2190	0.0529		
60H	-6.1742	2.9452	-0.8037	0.1989	0.0529		
61H	-5.5312	4.5921	-0.7102	0.2096	0.0526		
62C	4.9314	3.5526	-1.9622	-0.6280	-0.2066		
63H	5.7773	3.0028	-1.5335	0.1989	0.0520		
64H	5.0617	3.5643	-3.0523	0.2110	0.0512		
65H	5.0107	4.5938	-1.6191	0.2193	0.0506		
66Pd	-0.0565	-0.4686	0.8871	-1.5983	-0.0346		
67C	5.4441	-2.5782	-0.3878	-0.7240	0.0561		
68H	5.2865	-3.3921	0.3363	0.1991	-0.0228		
69H	6.5293	-2.4214	-0.4514	0.1962	-0.0248		
70C	3.3549	-3.1496	-1.7061	-0.6281	0.0706		
71H	3.0961	-4.0011	-1.0583	0.1985	-0.0319		
72H	2.9636	-3.3862	-2.7045	0.1965	-0.0204		
73C	4.8829	-2.9968	-1.7554	-0.4819	0.0305		
74H	5.1472	-2.2331	-2.5027	0.1991	-0.0183		
75H	5.3494	-3.9341	-2.0866	0.1946	-0.0241		
76C	-3.1420	-2.6884	-2.9088	-0.7452	0.1032		
77H	-4.1844	-2.3943	-3.1064	0.1977	-0.0381		
78H	-2.6224	-2.6618	-3.8758	0.1981	-0.0283		
79C	-3.7726	-4.1534	-0.9394	-0.6607	0.0807		
80H	-3.6960	-5.1619	-0.5115	0.1968	-0.0272		
81H	-4.8475	-3.9373	-1.0392	0.1978	-0.0345		
82C	-3.1167	-4.1100	-2.3278	-0.4790	0.0282		
83H	-2.0728	-4.4491	-2.2454	0.1998	-0.0131		
84H	-3.6210	-4.8097	-3.0077	0.1936	-0.0291		
85H	0.0000	-1.8288	1.7040	0.0894	-0.2346		

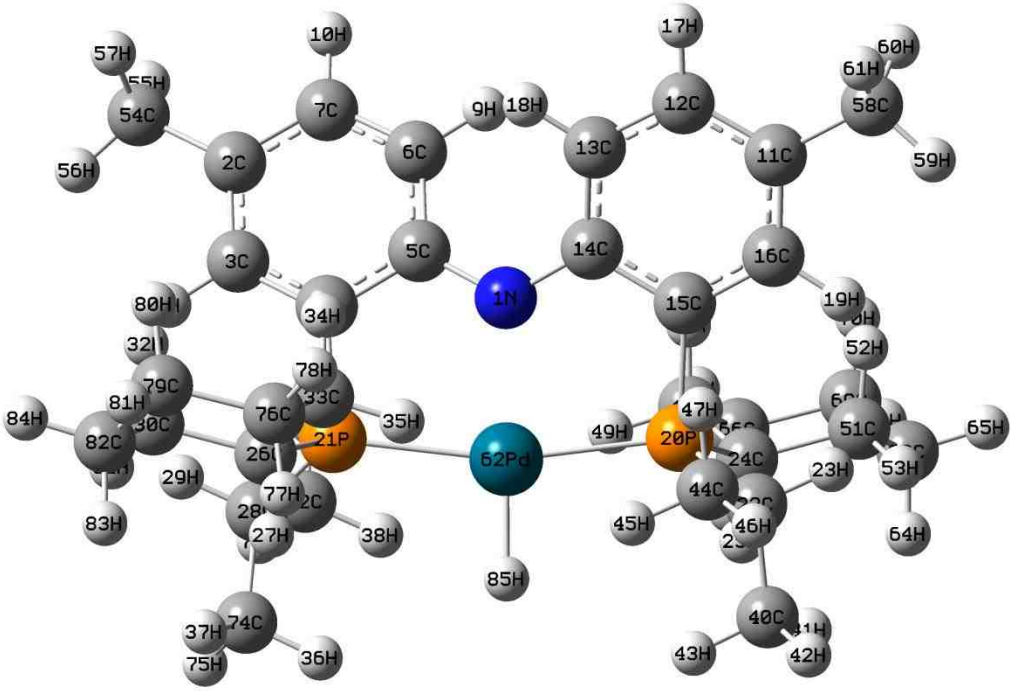
*** *** ***

(PNP) palladium hydride **28**

(see Figure 3-15)



28



Energy: -2113.23835223 hartrees

Palladium-hydrogen bond length: 1.587 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1N	0.0001	1.0268	0.0000	0.5690	-0.2682		
2C	-3.2163	2.8691	-2.1261	-0.0170	0.2428		
3C	-3.2755	1.5482	-1.6755	-0.0594	-0.3961		

4C	-2.2216	0.9363	-0.9786	-0.7278	0.0754		
5C	-1.0282	1.6643	-0.6722	0.9142	0.1179		
6C	-0.9624	2.9910	-1.1816	-0.0906	-0.1887		
7C	-2.0196	3.5635	-1.8770	-0.9904	-0.2718		
8H	-4.1691	0.9681	-1.8978	0.1657	0.1596		
9H	-0.0469	3.5597	-1.0669	0.1956	0.1379		
10H	-1.9038	4.5788	-2.2550	0.1720	0.1445		
11C	3.2160	2.8683	2.1273	-0.0115	0.2414		
12C	2.0194	3.5628	1.8782	-0.9997	-0.2742		
13C	0.9622	2.9906	1.1824	-0.0935	-0.1867		
14C	1.0282	1.6642	0.6725	0.9127	0.1179		
15C	2.2215	0.9360	0.9788	-0.7264	0.0755		
16C	3.2753	1.5476	1.6762	-0.0513	-0.3959		
17H	1.9034	4.5779	2.2567	0.1720	0.1450		
18H	0.0468	3.5593	1.0679	0.1956	0.1375		
19H	4.1687	0.9674	1.8986	0.1657	0.1596		
20P	2.2430	-0.8393	0.5170	1.1811	0.1773		
21P	-2.2430	-0.8391	-0.5173	1.1822	0.1756		
22C	2.9667	-1.7556	1.9829	0.1574	0.3791		
23H	3.9383	-1.2989	2.2148	0.2152	-0.0562		
24C	3.4563	-1.0747	-0.8972	-0.6205	0.0263		
25H	3.4222	-2.1568	-1.0947	0.2287	-0.0025		
26C	-3.4562	-1.0750	0.8970	-0.6210	0.0313		
27H	-3.4218	-2.1571	1.0943	0.2287	-0.0035		
28C	-2.9668	-1.7550	-1.9834	0.1573	0.3840		
29H	-3.9384	-1.2983	-2.2150	0.2152	-0.0581		
30C	-4.9155	-0.6783	0.5951	-0.0679	0.0568		
31H	-5.2958	-1.2209	-0.2799	0.2059	-0.0300		
32H	-4.9554	0.3916	0.3501	0.2323	-0.0173		
33C	-2.9444	-0.3524	2.1623	-0.1215	0.0611		
34H	-2.8952	0.7278	1.9658	0.2375	-0.0289		
35H	-1.9214	-0.6763	2.3875	0.2294	-0.0339		
36H	-2.2485	-3.7159	-1.3437	0.2439	0.0914		
37H	-3.9221	-3.3880	-0.8534	0.2168	0.0777		
38H	-1.0668	-2.0408	-3.0178	0.2359	0.0494		
39H	-1.8990	-0.5393	-3.4675	0.2384	0.0362		
40C	3.1869	-3.2411	1.6512	-0.8972	-0.3739		
41H	3.9224	-3.3881	0.8526	0.2168	0.0789		
42H	3.5567	-3.7681	2.5402	0.2094	0.0779		

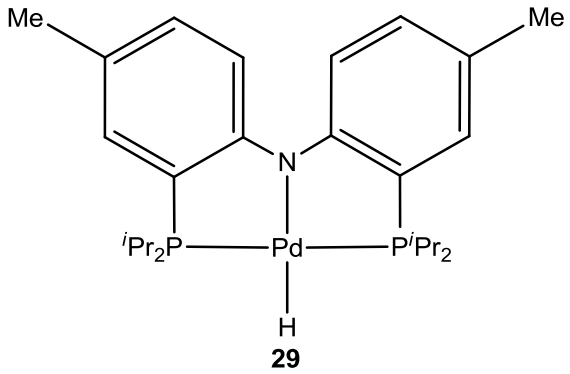
43H	2.2486	-3.7163	1.3423	0.2439	0.0928		
44C	2.0489	-1.5931	3.2064	-0.8441	-0.2387		
45H	1.0667	-2.0418	3.0171	0.2359	0.0488		
46H	2.4929	-2.0985	4.0740	0.2028	0.0492		
47H	1.8987	-0.5404	3.4673	0.2384	0.0352		
48C	2.9445	-0.3521	-2.1625	-0.1215	0.0653		
49H	1.9216	-0.6761	-2.3879	0.2294	-0.0346		
50H	2.8950	0.7281	-1.9659	0.2375	-0.0297		
51C	4.9156	-0.6778	-0.5951	-0.0679	0.0591		
52H	4.9552	0.3921	-0.3499	0.2323	-0.0172		
53H	5.2959	-1.2204	0.2798	0.2059	-0.0300		
54C	-4.3664	3.5161	-2.8637	-0.6626	-0.1912		
55H	-4.0400	3.9662	-3.8106	0.2132	0.0481		
56H	-5.1500	2.7861	-3.0975	0.1979	0.0472		
57H	-4.8308	4.3170	-2.2715	0.2183	0.0489		
58C	4.3664	3.5153	2.8645	-0.6634	-0.1836		
59H	5.1445	2.7829	3.1088	0.1980	0.0444		
60H	4.8384	4.3080	2.2673	0.2183	0.0471		
61H	4.0380	3.9759	3.8055	0.2128	0.0466		
62Pd	0.0000	-1.1129	-0.0002	-1.2406	-0.0709		
63C	5.8295	-0.9481	-1.8053	-0.7876	0.0305		
64H	5.8741	-2.0322	-1.9914	0.1979	-0.0196		
65H	6.8541	-0.6289	-1.5716	0.1964	-0.0240		
66C	3.8632	-0.6123	-3.3687	-0.6365	0.0555		
67H	3.8122	-1.6783	-3.6390	0.1974	-0.0285		
68H	3.4961	-0.0518	-4.2386	0.1984	-0.0218		
69C	5.3220	-0.2358	-3.0681	-0.4760	0.0694		
70H	5.3935	0.8529	-2.9223	0.1994	-0.0240		
71H	5.9634	-0.4800	-3.9253	0.1940	-0.0350		
72C	-2.0490	-1.5920	-3.2069	-0.8443	-0.2426		
73H	-2.4931	-2.0972	-4.0746	0.2028	0.0499		
74C	-3.1869	-3.2407	-1.6522	-0.8972	-0.3704		
75H	-3.5568	-3.7674	-2.5412	0.2094	0.0767		
76C	-3.8630	-0.6130	3.3686	-0.6365	0.0575		
77H	-3.8116	-1.6790	3.6387	0.1974	-0.0287		
78H	-3.4959	-0.0525	4.2385	0.1984	-0.0218		
79C	-5.3218	-0.2368	3.0681	-0.4760	0.0658		
80H	-5.3936	0.8518	2.9225	0.1994	-0.0231		
81H	-5.9632	-0.4813	3.9253	0.1940	-0.0343		

82C	-5.8293	-0.9491	1.8052	-0.7877	0.0343		
83H	-5.8735	-2.0332	1.9912	0.1979	-0.0207		
84H	-6.8540	-0.6301	1.5718	0.1964	-0.0247		
85H	0.0000	-2.6995	-0.0003	0.0793	-0.2293		

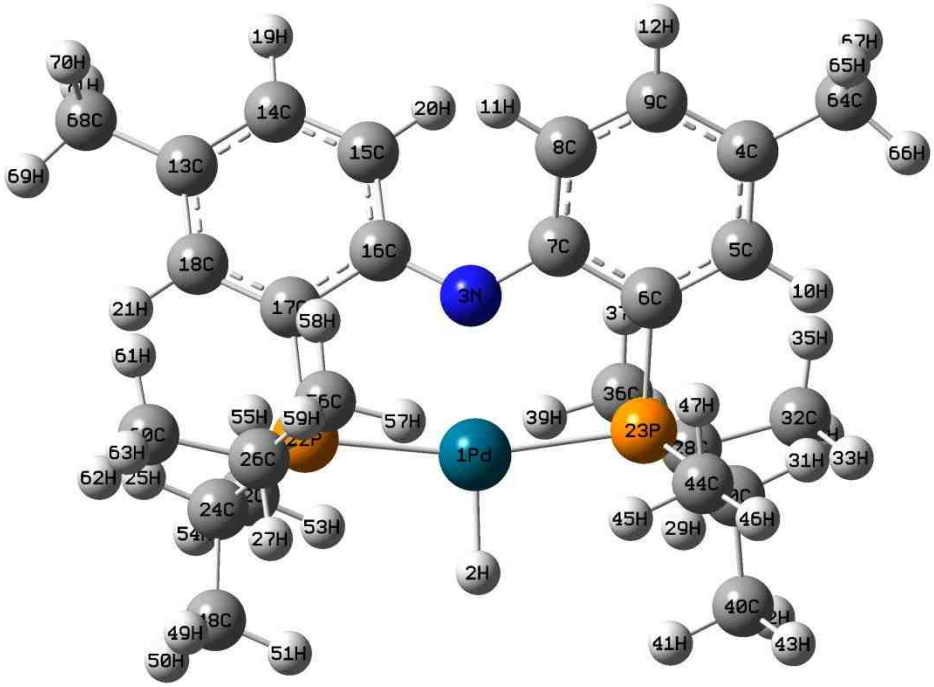
*** *** ***

(PNP) palladium hydride **29**

(see Figure 3-15, Figure 3-23, Figure 3-25)



29



Energy: -1879.76399120 hartrees

Palladium-hydrogen bond length: 1.587 Å

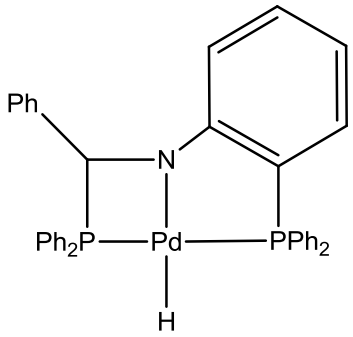
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-1.2058	-0.0007	-1.5316	-0.0900		
2H	0.0001	-2.7929	-0.0010	0.0768	-0.2191		
3N	-0.0001	0.9328	-0.0004	0.3721	-0.1990		
4C	3.7736	2.7798	0.7861	-0.1327	0.2552		
5C	3.6635	1.4561	0.3543	-0.1059	-0.4462		
6C	2.4269	0.8414	0.0995	-0.6057	0.1461		
7C	1.2036	1.5704	0.2475	0.7664	0.0487		
8C	1.3300	2.8988	0.7406	-0.0525	-0.1506		
9C	2.5687	3.4736	0.9938	-0.9099	-0.2842		
10H	4.5773	0.8769	0.2352	0.1648	0.1844		
11H	0.4367	3.4680	0.9697	0.1947	0.1290		
12H	2.5997	4.4906	1.3836	0.1721	0.1442		
13C	-3.7741	2.7796	-0.7860	-0.1323	0.2551		
14C	-2.5693	3.4735	-0.9939	-0.9102	-0.2843		
15C	-1.3305	2.8988	-0.7409	-0.0528	-0.1506		
16C	-1.2039	1.5704	-0.2479	0.7672	0.0488		
17C	-2.4271	0.8413	-0.0997	-0.6067	0.1448		
18C	-3.6639	1.4558	-0.3543	-0.1043	-0.4451		
19H	-2.6005	4.4905	-1.3837	0.1721	0.1443		
20H	-0.4373	3.4681	-0.9702	0.1947	0.1290		
21H	-4.5776	0.8766	-0.2350	0.1648	0.1837		
22P	-2.2784	-0.9371	0.3217	1.3597	0.1175		
23P	2.2785	-0.9370	-0.3219	1.3597	0.1153		
24C	-3.4739	-1.8485	-0.7953	-0.0202	0.4031		
25H	-4.4653	-1.3966	-0.6583	0.2137	-0.0699		
26C	-2.9075	-1.1858	2.0767	-0.4048	0.3027		
27H	-2.7793	-2.2628	2.2497	0.2256	-0.0450		
28C	2.9091	-1.1860	-2.0763	-0.4047	0.3021		
29H	2.7810	-2.2631	-2.2492	0.2256	-0.0450		
30C	3.4729	-1.8482	0.7963	-0.0204	0.4039		
31H	4.4645	-1.3963	0.6601	0.2137	-0.0708		
32C	4.3861	-0.8221	-2.2956	-0.6085	-0.2047		

33H	5.0623	-1.3800	-1.6377	0.2116	0.0279		
34H	4.6728	-1.0523	-3.3303	0.2100	0.0440		
35H	4.5579	0.2483	-2.1375	0.2376	0.0380		
36C	2.0002	-0.4344	-3.0638	-0.7594	-0.2392		
37H	2.0651	0.6496	-2.9145	0.2403	0.0403		
38H	2.3093	-0.6520	-4.0945	0.2050	0.0594		
39H	0.9516	-0.7278	-2.9500	0.2351	0.0382		
40C	3.5524	-3.3379	0.4220	-0.8008	-0.3574		
41H	2.5637	-3.8082	0.4777	0.2442	0.0860		
42H	3.9495	-3.4973	-0.5867	0.2136	0.0746		
43H	4.2158	-3.8608	1.1228	0.2090	0.0705		
44C	3.0545	-1.6699	2.2655	-0.7706	-0.2204		
45H	2.0708	-2.1188	2.4461	0.2354	0.0419		
46H	3.7811	-2.1665	2.9216	0.2025	0.0437		
47H	3.0055	-0.6142	2.5514	0.2381	0.0267		
48C	-3.5530	-3.3381	-0.4204	-0.8008	-0.3618		
49H	-3.9494	-3.4972	0.5886	0.2136	0.0756		
50H	-4.2169	-3.8612	-1.1207	0.2090	0.0717		
51H	-2.5643	-3.8084	-0.4767	0.2442	0.0873		
52C	-3.0567	-1.6705	-2.2648	-0.7706	-0.2219		
53H	-2.0731	-2.1195	-2.4461	0.2354	0.0424		
54H	-3.7839	-2.1673	-2.9202	0.2025	0.0443		
55H	-3.0079	-0.6149	-2.5510	0.2381	0.0270		
56C	-1.9976	-0.4341	3.0634	-0.7595	-0.2387		
57H	-0.9492	-0.7276	2.9488	0.2352	0.0379		
58H	-2.0625	0.6499	2.9140	0.2403	0.0403		
59H	-2.3060	-0.6515	4.0943	0.2050	0.0593		
60C	-4.3842	-0.8216	2.2970	-0.6088	-0.2094		
61H	-4.5560	0.2488	2.1387	0.2376	0.0391		
62H	-5.0609	-1.3797	1.6399	0.2116	0.0294		
63H	-4.6701	-1.0514	3.3320	0.2100	0.0453		
64C	5.1140	3.4306	1.0412	-0.6971	-0.1853		
65H	5.1553	3.9001	2.0328	0.2128	0.0473		
66H	5.9284	2.6989	0.9877	0.1978	0.0424		
67H	5.3316	4.2170	0.3049	0.2187	0.0480		
68C	-5.1146	3.4303	-1.0408	-0.6969	-0.1854		
69H	-5.9289	2.6985	-0.9877	0.1979	0.0425		
70H	-5.3323	4.2163	-0.3041	0.2187	0.0480		
71H	-5.1560	3.9003	-2.0322	0.2128	0.0473		

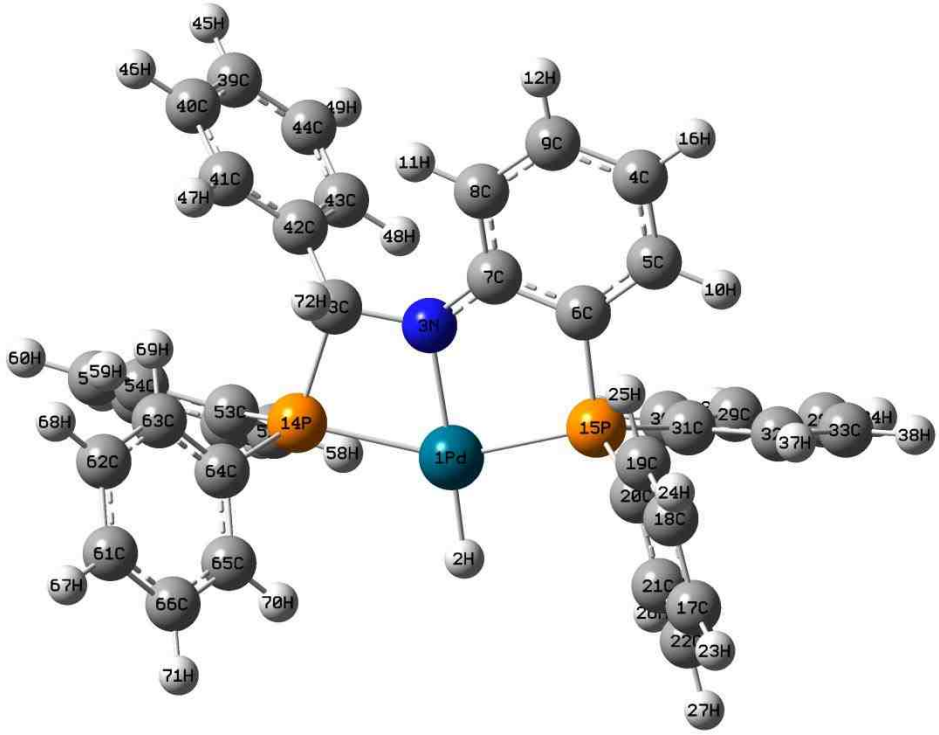
*** *** ***

(PNP) palladium hydride **30**

(see Figure 3-15)



30



Energy: -2292.85116221 hartrees

Palladium-hydrogen bond length: 1.596 Å

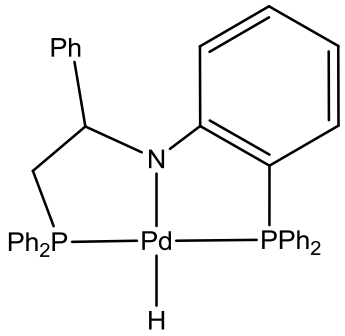
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.3604	0.4522	-0.8842	-0.8767	-0.1046		
2H	-0.7417	1.1758	-2.2544	0.0721	-0.2322		
3N	0.2162	-0.4906	0.8851	0.5290	-0.4221		
4C	-2.7329	-1.8386	3.5768	-0.7747	-0.1978		
5C	-3.0701	-1.3397	2.3174	0.1670	-0.1331		
6C	-2.0933	-0.8304	1.4532	-0.1091	-0.0611		
7C	-0.7030	-0.8737	1.8143	-0.3031	0.1936		
8C	-0.3883	-1.3517	3.1179	0.0398	-0.2556		
9C	-1.3846	-1.8201	3.9672	-0.1857	-0.0734		
10H	-4.1135	-1.3307	2.0092	0.1850	0.1080		
11H	0.6488	-1.3850	3.4362	0.1885	0.1193		
12H	-1.1047	-2.1924	4.9507	0.1722	0.1075		
13C	1.6230	-0.2427	1.1629	-2.2760	0.3237		
14P	1.9575	0.7295	-0.4765	0.8360	0.2790		
15P	-2.4872	-0.0547	-0.1617	0.1684	0.3885		
16H	-3.5003	-2.2235	4.2422	0.1690	0.1088		
17C	-5.0906	3.7312	0.5588	-0.2099	-0.1387		
18C	-4.5629	3.0453	1.6543	-0.5491	-0.0686		
19C	-3.7963	1.8902	1.4618	0.3766	-0.1864		
20C	-3.5501	1.4125	0.1665	1.5839	0.0562		
21C	-4.0697	2.1191	-0.9330	-1.0273	-0.1766		
22C	-4.8418	3.2639	-0.7374	-0.6645	-0.0647		
23H	-5.6876	4.6271	0.7103	0.1789	0.1123		
24H	-4.7454	3.4047	2.6641	0.1815	0.1019		
25H	-3.3903	1.3640	2.3201	0.2217	0.1229		
26H	-3.8631	1.7764	-1.9438	0.2000	0.1169		
27H	-5.2411	3.7974	-1.5964	0.1813	0.1027		
28C	-5.1343	-3.1119	-2.4541	-0.0938	-0.1223		
29C	-3.7523	-3.0595	-2.6606	-0.3191	-0.0490		
30C	-2.9781	-2.1164	-1.9811	-0.1293	-0.2152		
31C	-3.5756	-1.2204	-1.0803	-0.0038	0.0483		
32C	-4.9649	-1.2739	-0.8838	-0.0182	-0.1195		
33C	-5.7387	-2.2155	-1.5678	-0.2528	-0.1160		
34H	-5.7383	-3.8420	-2.9869	0.1801	0.1107		
35H	-3.2777	-3.7458	-3.3573	0.1812	0.1050		
36H	-1.9062	-2.0631	-2.1548	0.2019	0.1266		

37H	-5.4482	-0.5743	-0.2073	0.1978	0.1078		
38H	-6.8138	-2.2461	-1.4085	0.1816	0.1114		
39C	4.1530	-3.6961	1.8495	-0.1205	-0.1337		
40C	4.4388	-2.4781	2.4733	-0.1770	-0.0879		
41C	3.6145	-1.3712	2.2539	0.0577	-0.2454		
42C	2.4984	-1.4584	1.4085	0.9206	0.1206		
43C	2.2165	-2.6869	0.7944	-0.0482	-0.0630		
44C	3.0364	-3.7960	1.0131	-0.6346	-0.1463		
45H	4.7882	-4.5615	2.0215	0.1751	0.1126		
46H	5.2954	-2.3919	3.1378	0.1741	0.1057		
47H	3.8323	-0.4325	2.7618	0.1684	0.1196		
48H	1.3382	-2.7669	0.1607	0.2140	0.0628		
49H	2.8001	-4.7428	0.5333	0.1767	0.1193		
50C	5.1015	-1.4698	-3.0903	-0.1082	-0.1300		
51C	3.7367	-1.5486	-3.3783	-0.4270	-0.0717		
52C	2.8126	-0.8717	-2.5776	-0.1828	-0.1605		
53C	3.2447	-0.1146	-1.4767	0.1050	0.0376		
54C	4.6191	-0.0357	-1.1978	0.1142	-0.1482		
55C	5.5407	-0.7102	-2.0006	-0.3899	-0.0695		
56H	5.8219	-1.9923	-3.7146	0.1807	0.1128		
57H	3.3897	-2.1295	-4.2291	0.1821	0.1087		
58H	1.7512	-0.9180	-2.8091	0.2149	0.1065		
59H	4.9761	0.5563	-0.3604	0.1947	0.1006		
60H	6.6020	-0.6425	-1.7753	0.1805	0.1011		
61C	3.6605	4.9263	0.5616	0.0235	-0.0891		
62C	4.0613	3.8257	1.3251	-0.7394	-0.1514		
63C	3.5638	2.5526	1.0350	0.5975	-0.0545		
64C	2.6556	2.3655	-0.0208	0.2817	-0.0337		
65C	2.2487	3.4799	-0.7735	-0.4405	-0.1210		
66C	2.7547	4.7506	-0.4884	-0.4748	-0.0992		
67H	4.0472	5.9164	0.7891	0.1822	0.1101		
68H	4.7601	3.9566	2.1477	0.1830	0.1169		
69H	3.8840	1.7085	1.6394	0.1869	0.0898		
70H	1.5264	3.3503	-1.5753	0.2117	0.1057		
71H	2.4310	5.6038	-1.0790	0.1855	0.1158		
72H	1.7718	0.4682	1.9952	0.2321	-0.0551		

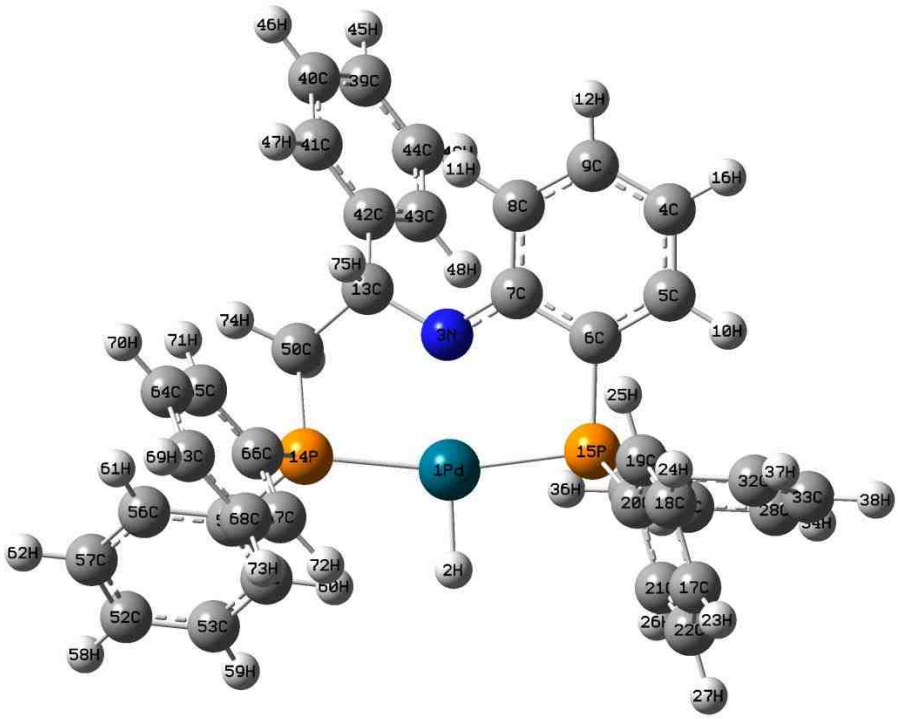
*** *** ***

(PNP) palladium hydride **31**

(see Figure 3-15)



31



Energy: -2332.18586013 hartrees

Palladium-hydrogen bond length: 1.586 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge

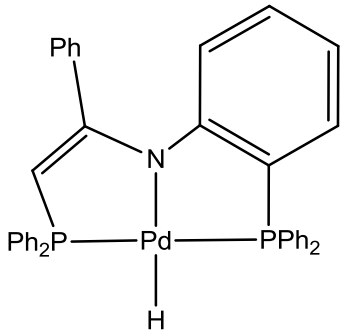
1Pd	-0.0363	-0.6839	0.4940	-1.0276	-0.1532		
2H	-0.2044	-2.0634	1.2588	0.0930	-0.2103		
3N	0.1444	1.1834	-0.5421	0.4605	-0.4897		
4C	-3.3405	2.6030	-2.5116	-0.8763	-0.1778		
5C	-3.4025	1.5687	-1.5795	0.0462	-0.1581		
6C	-2.2474	1.0565	-0.9742	0.0121	-0.0817		
7C	-0.9501	1.6225	-1.2378	-0.1600	0.2529		
8C	-0.9189	2.6483	-2.2329	0.0308	-0.2858		
9C	-2.0775	3.1171	-2.8398	-0.1762	-0.0739		
10H	-4.3684	1.1330	-1.3328	0.1791	0.1164		
11H	0.0267	3.0949	-2.5135	0.1858	0.1384		
12H	-1.9935	3.9073	-3.5836	0.1700	0.1032		
13C	1.4570	1.7590	-0.8318	-1.1863	0.3661		
14P	2.2602	-0.7348	0.2786	0.6537	0.4655		
15P	-2.2972	-0.3644	0.1653	0.3993	0.4590		
16H	-4.2426	2.9843	-2.9811	0.1678	0.1005		
17C	-4.3565	-3.9458	-1.9743	-0.2440	-0.1194		
18C	-3.8904	-2.8647	-2.7257	-0.2751	-0.0738		
19C	-3.3016	-1.7654	-2.0918	0.0219	-0.1740		
20C	-3.1724	-1.7374	-0.6949	1.5487	0.0065		
21C	-3.6314	-2.8359	0.0532	-0.9736	-0.1242		
22C	-4.2251	-3.9277	-0.5810	-0.6129	-0.1005		
23H	-4.8172	-4.7976	-2.4683	0.1784	0.1076		
24H	-3.9849	-2.8705	-3.8087	0.1809	0.1028		
25H	-2.9451	-0.9291	-2.6851	0.2219	0.1194		
26H	-3.5241	-2.8394	1.1349	0.1960	0.1031		
27H	-4.5803	-4.7668	0.0122	0.1797	0.1074		
28C	-4.9593	0.8535	3.7785	-0.1338	-0.1052		
29C	-3.5651	0.8646	3.8767	-0.2627	-0.0779		
30C	-2.7831	0.4704	2.7876	-0.3019	-0.1338		
31C	-3.3863	0.0680	1.5856	0.2620	-0.0224		
32C	-4.7881	0.0534	1.4977	0.0822	-0.1149		
33C	-5.5688	0.4447	2.5878	-0.4219	-0.1179		
34H	-5.5687	1.1555	4.6266	0.1800	0.1059		
35H	-3.0848	1.1723	4.8022	0.1816	0.1051		
36H	-1.6989	0.4644	2.8666	0.2060	0.0962		
37H	-5.2745	-0.2739	0.5830	0.1943	0.1100		
38H	-6.6529	0.4281	2.5073	0.1813	0.1106		
39C	1.9378	6.0114	-0.0241	-0.1124	-0.1102		

40C	2.6529	5.4034	-1.0598	-0.0793	-0.1291		
41C	2.4738	4.0426	-1.3278	0.1133	-0.2042		
42C	1.5834	3.2696	-0.5706	0.9233	0.1236		
43C	0.8700	3.8885	0.4642	-0.3467	-0.0707		
44C	1.0443	5.2480	0.7348	-0.6045	-0.1758		
45H	2.0692	7.0702	0.1847	0.1733	0.1074		
46H	3.3450	5.9871	-1.6624	0.1735	0.1137		
47H	3.0250	3.5786	-2.1451	0.1681	0.1033		
48H	0.1628	3.2992	1.0414	0.2086	0.0723		
49H	0.4744	5.7147	1.5350	0.1762	0.1244		
50C	2.5434	1.0855	0.0511	-1.3932	-0.0908		
51H	2.4770	1.4904	1.0683	0.2758	-0.0043		
52C	5.1262	-1.8816	3.7524	-0.1511	-0.1259		
53C	3.7440	-1.8341	3.9506	-0.4747	-0.0658		
54C	2.8939	-1.5080	2.8894	-0.1737	-0.1539		
55C	3.4213	-1.2187	1.6215	0.0826	0.0190		
56C	4.8117	-1.2767	1.4279	0.3207	-0.1552		
57C	5.6586	-1.6046	2.4885	-0.3651	-0.0883		
58H	5.7870	-2.1394	4.5762	0.1821	0.1129		
59H	3.3241	-2.0583	4.9280	0.1839	0.1060		
60H	1.8169	-1.4875	3.0352	0.2221	0.1050		
61H	5.2369	-1.0778	0.4475	0.1926	0.1066		
62H	6.7329	-1.6476	2.3274	0.1818	0.1080		
63C	3.7508	-3.0182	-3.4871	-0.1554	-0.0910		
64C	4.2351	-1.7318	-3.2375	-0.3784	-0.1466		
65C	3.8006	-1.0239	-2.1124	0.2400	-0.0876		
66C	2.8730	-1.5942	-1.2263	0.0029	-0.0302		
67C	2.3806	-2.8834	-1.4943	-0.1564	-0.1660		
68C	2.8229	-3.5928	-2.6122	-0.3631	-0.0688		
69H	4.0880	-3.5672	-4.3626	0.1820	0.1064		
70H	4.9495	-1.2750	-3.9179	0.1823	0.1172		
71H	4.1858	-0.0231	-1.9391	0.1750	0.1118		
72H	1.6405	-3.3234	-0.8309	0.2092	0.1093		
73H	2.4334	-4.5888	-2.8064	0.1853	0.1108		
74H	3.5476	1.3270	-0.3163	0.2315	-0.0004		
75H	1.7325	1.5864	-1.8896	0.2068	-0.0752		

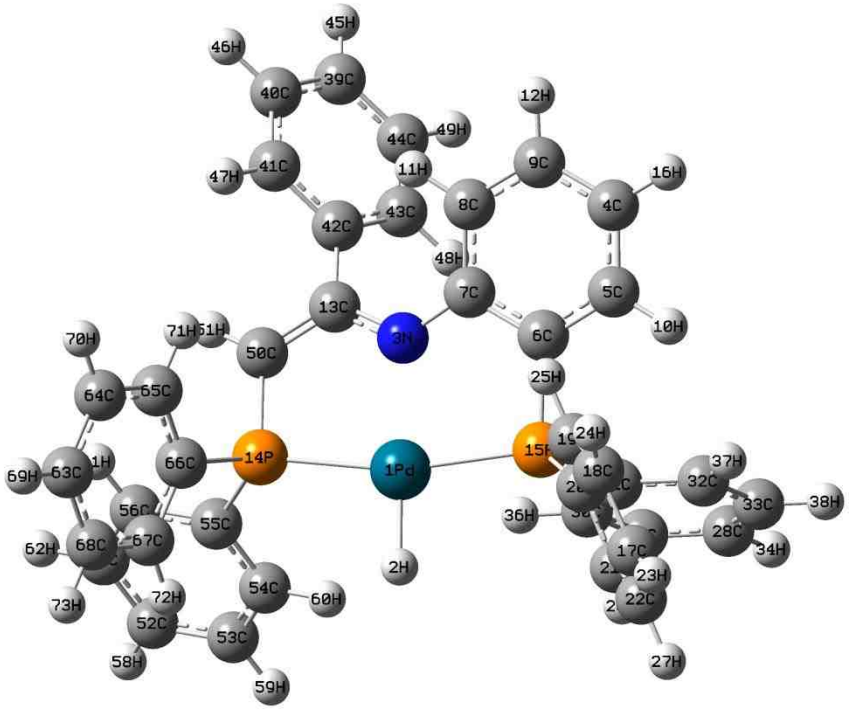
*** *** ***

(PNP) palladium hydride **32**

(see Figure 3-15)



32



Energy: -2330.97846933 hartrees

Palladium-hydrogen bond length: 1.581 Å

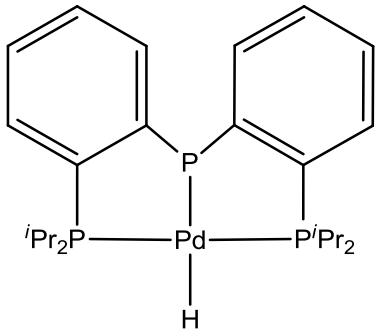
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.0132	-0.8399	0.1498	-1.1413	-0.1569		
2H	-0.0849	-2.3436	0.6311	0.0968	-0.2070		
3N	0.0794	1.2222	-0.4581	0.3285	-0.1589		
4C	-3.5106	2.8777	-2.0183	-0.8360	-0.1543		
5C	-3.5118	1.6979	-1.2781	0.0235	-0.1623		
6C	-2.3210	1.1346	-0.7972	-0.0319	-0.0569		
7C	-1.0639	1.7879	-1.0039	-0.1134	0.1099		
8C	-1.0867	2.9525	-1.8190	-0.0672	-0.1600		
9C	-2.2782	3.4823	-2.3003	-0.4040	-0.0993		
10H	-4.4541	1.1876	-1.0938	0.1841	0.1219		
11H	-0.1567	3.4386	-2.0829	0.2033	0.1135		
12H	-2.2421	4.3774	-2.9175	0.1763	0.1059		
13C	1.3059	1.8246	-0.3352	-0.1503	0.0377		
14P	2.3067	-0.6986	0.0710	0.8419	0.5034		
15P	-2.2961	-0.4809	0.0710	0.4140	0.3852		
16H	-4.4394	3.2972	-2.3942	0.1734	0.1064		
17C	-4.7269	-3.5452	-2.4429	-0.2847	-0.1393		
18C	-4.1530	-2.4329	-3.0640	-0.2239	-0.0674		
19C	-3.4578	-1.4839	-2.3091	-0.2621	-0.2004		
20C	-3.3319	-1.6345	-0.9188	1.3284	0.0715		
21C	-3.9002	-2.7635	-0.3039	-0.7041	-0.1717		
22C	-4.5967	-3.7080	-1.0600	-0.2902	-0.0664		
23H	-5.2685	-4.2815	-3.0312	0.1801	0.1140		
24H	-4.2440	-2.2997	-4.1390	0.1819	0.1062		
25H	-3.0158	-0.6251	-2.8049	0.2114	0.1272		
26H	-3.7995	-2.9084	0.7683	0.1965	0.1169		
27H	-5.0340	-4.5731	-0.5678	0.1805	0.1006		
28C	-4.4690	0.1808	4.1297	-0.1197	-0.1178		
29C	-3.0785	0.0575	4.0701	-0.3127	-0.0731		
30C	-2.4472	-0.1679	2.8434	-0.1364	-0.1620		
31C	-3.1993	-0.2658	1.6625	0.1556	0.0342		
32C	-4.5974	-0.1456	1.7323	0.0322	-0.1382		
33C	-5.2273	0.0759	2.9587	-0.4661	-0.1030		
34H	-4.9615	0.3525	5.0835	0.1815	0.1114		
35H	-2.4835	0.1312	4.9769	0.1838	0.1095		
36H	-1.3664	-0.2738	2.7956	0.2128	0.1023		

37H	-5.2000	-0.2349	0.8327	0.1937	0.1065		
38H	-6.3100	0.1651	2.9996	0.1822	0.1103		
39C	1.8254	6.0974	0.0058	-0.2178	-0.1052		
40C	2.6016	5.3706	-0.9011	-0.3951	-0.1730		
41C	2.4243	3.9897	-1.0289	0.0358	-0.0953		
42C	1.4610	3.3171	-0.2616	0.3791	0.2012		
43C	0.6849	4.0567	0.6462	-0.2192	-0.1613		
44C	0.8691	5.4331	0.7818	-0.5108	-0.1179		
45H	1.9636	7.1708	0.1079	0.1763	0.1081		
46H	3.3467	5.8765	-1.5104	0.1768	0.1201		
47H	3.0269	3.4283	-1.7383	0.1925	0.0945		
48H	-0.0615	3.5459	1.2481	0.2020	0.1103		
49H	0.2640	5.9886	1.4942	0.1776	0.1123		
50C	2.4499	1.0781	-0.1295	-0.7765	-0.4310		
51H	3.3957	1.5786	0.0542	0.2125	0.1075		
52C	4.7412	-1.7729	3.8847	-0.1248	-0.0979		
53C	3.3698	-2.0317	3.8277	-0.4867	-0.0745		
54C	2.6434	-1.7201	2.6732	-0.4628	-0.2038		
55C	3.2837	-1.1468	1.5652	0.3002	0.0279		
56C	4.6657	-0.8966	1.6279	0.0696	-0.1042		
57C	5.3888	-1.2053	2.7810	-0.3519	-0.1368		
58H	5.3059	-2.0151	4.7816	0.1795	0.1063		
59H	2.8626	-2.4792	4.6790	0.1816	0.1032		
60H	1.5778	-1.9280	2.6226	0.2204	0.1426		
61H	5.1808	-0.4656	0.7727	0.1895	0.1159		
62H	6.4569	-1.0059	2.8181	0.1810	0.1127		
63C	4.4879	-2.8194	-3.4518	-0.1362	-0.1461		
64C	4.0912	-1.4852	-3.5726	-0.5679	-0.0697		
65C	3.4576	-0.8407	-2.5055	0.5051	-0.1550		
66C	3.2199	-1.5232	-1.3036	0.5823	0.0217		
67C	3.6143	-2.8670	-1.1920	-0.6670	-0.2422		
68C	4.2468	-3.5089	-2.2581	-0.2988	-0.0223		
69H	4.9805	-3.3206	-4.2813	0.1783	0.1092		
70H	4.2736	-0.9430	-4.4974	0.1791	0.0988		
71H	3.1483	0.1970	-2.6004	0.2069	0.1149		
72H	3.4311	-3.4133	-0.2700	0.1911	0.1367		
73H	4.5503	-4.5481	-2.1574	0.1797	0.0927		

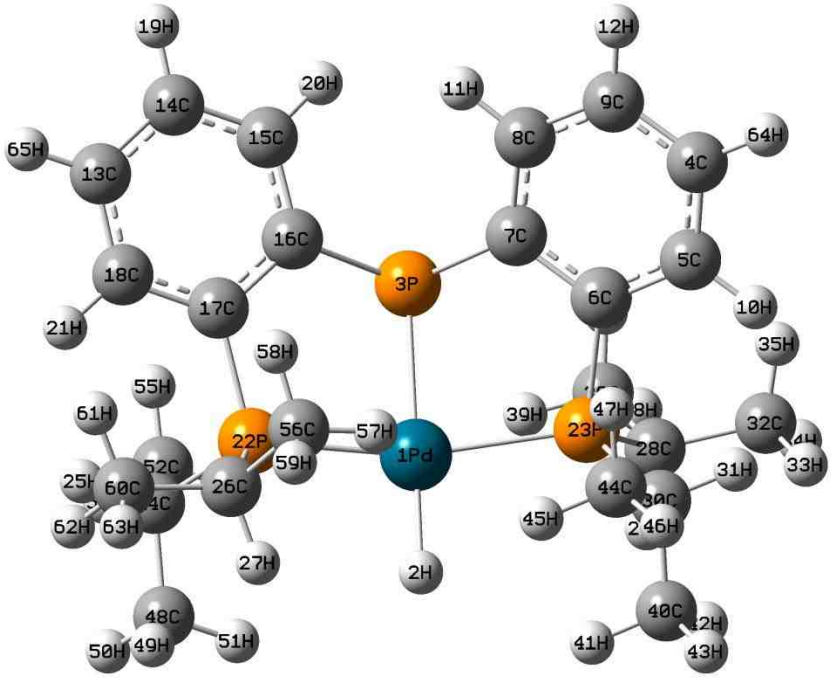
*** *** ***

(PPP) palladium hydride **33**

(see Figure 3-16)



33



Energy: -2087.72430873 hartrees

Palladium-hydrogen bond length: 1.640 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0421	-1.0327	-0.2564	-1.8658	-0.0878		

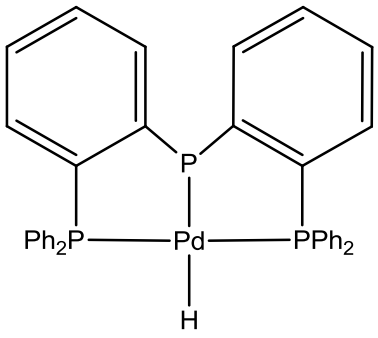
2H	0.0531	-2.5718	0.3105	0.0069	-0.2776		
3P	0.0177	1.2128	-1.0782	0.5305	-0.3424		
4C	3.7139	3.0295	1.1605	-0.6119	-0.1167		
5C	3.6605	1.6793	0.8087	0.0988	-0.1857		
6C	2.5077	1.1234	0.2308	-0.1094	0.0607		
7C	1.3836	1.9495	-0.0535	0.2507	0.1291		
8C	1.4614	3.3072	0.3132	0.0155	-0.2421		
9C	2.5982	3.8378	0.9232	-0.7729	-0.1080		
10H	4.5191	1.0489	1.0243	0.1764	0.1178		
11H	0.6196	3.9647	0.1224	0.1633	0.1579		
12H	2.6153	4.8880	1.2063	0.1767	0.1132		
13C	-4.2650	2.8282	-0.1135	-0.5007	-0.0704		
14C	-3.2371	3.7234	-0.4284	-0.2309	-0.1322		
15C	-1.9425	3.2528	-0.6427	0.1049	-0.2030		
16C	-1.6147	1.8882	-0.4967	-0.5203	0.0945		
17C	-2.6587	0.9926	-0.1475	-0.1805	0.1165		
18C	-3.9726	1.4699	0.0093	0.0479	-0.2619		
19H	-3.4522	4.7833	-0.5425	0.1786	0.1178		
20H	-1.1815	3.9533	-0.9746	0.1739	0.1436		
21H	-4.7804	0.7787	0.2323	0.1773	0.1360		
22P	-2.2350	-0.7960	0.0775	1.5628	0.2677		
23P	2.3465	-0.6945	-0.0990	1.3777	0.1782		
24C	-3.4304	-1.7275	-1.0260	-0.0221	0.2912		
25H	-4.4446	-1.3956	-0.7644	0.2129	-0.0608		
26C	-2.6955	-1.2426	1.8490	-0.3992	0.2479		
27H	-2.3341	-2.2767	1.9211	0.2400	-0.0137		
28C	3.4325	-1.0954	-1.5876	-0.2771	0.3690		
29H	3.3331	-2.1847	-1.6852	0.2265	-0.0857		
30C	3.1986	-1.5299	1.3533	-0.0035	0.3591		
31H	4.2122	-1.1139	1.4227	0.2059	-0.0412		
32C	4.9200	-0.7487	-1.4163	-0.6167	-0.2395		
33H	5.3730	-1.2373	-0.5463	0.2113	0.0365		
34H	5.4780	-1.0763	-2.3032	0.2109	0.0486		
35H	5.0657	0.3328	-1.3173	0.2391	0.0298		
36C	2.8607	-0.4540	-2.8628	-0.8477	-0.1125		
37H	2.8902	0.6404	-2.8098	0.2417	0.0011		
38H	3.4576	-0.7637	-3.7307	0.2037	0.0195		
39H	1.8223	-0.7507	-3.0369	0.2408	-0.0085		
40C	3.3034	-3.0475	1.1278	-0.8770	-0.4042		

41H	2.3105	-3.4847	0.9721	0.2529	0.1040		
42H	3.9309	-3.3029	0.2666	0.2110	0.0846		
43H	3.7499	-3.5212	2.0116	0.2070	0.0843		
44C	2.4551	-1.2238	2.6635	-0.7778	-0.3094		
45H	1.4438	-1.6444	2.6378	0.2404	0.1025		
46H	2.9917	-1.6772	3.5072	0.2024	0.0610		
47H	2.3763	-0.1482	2.8533	0.2312	0.0413		
48C	-3.3265	-3.2449	-0.7968	-0.8107	-0.2167		
49H	-3.5894	-3.5346	0.2265	0.2142	0.0405		
50H	-4.0118	-3.7690	-1.4754	0.2075	0.0479		
51H	-2.3093	-3.6003	-0.9954	0.2490	0.0305		
52C	-3.1667	-1.3704	-2.4989	-0.8884	-0.2033		
53H	-2.1557	-1.6691	-2.7994	0.2365	0.0402		
54H	-3.8824	-1.8977	-3.1428	0.2051	0.0436		
55H	-3.2720	-0.2967	-2.6870	0.2339	0.0244		
56C	-1.8781	-0.3873	2.8318	-0.7739	-0.2371		
57H	-0.8071	-0.4406	2.6136	0.2380	0.0143		
58H	-2.1824	0.6651	2.7906	0.2349	0.0272		
59H	-2.0385	-0.7434	3.8577	0.2037	0.0721		
60C	-4.1887	-1.2190	2.2136	-0.5619	-0.2226		
61H	-4.5800	-0.1968	2.2516	0.2248	0.0503		
62H	-4.8086	-1.8008	1.5225	0.2143	0.0335		
63H	-4.3217	-1.6522	3.2138	0.2133	0.0440		
64H	4.6061	3.4385	1.6273	0.1762	0.1024		
65H	-5.2835	3.1823	0.0232	0.1777	0.0987		

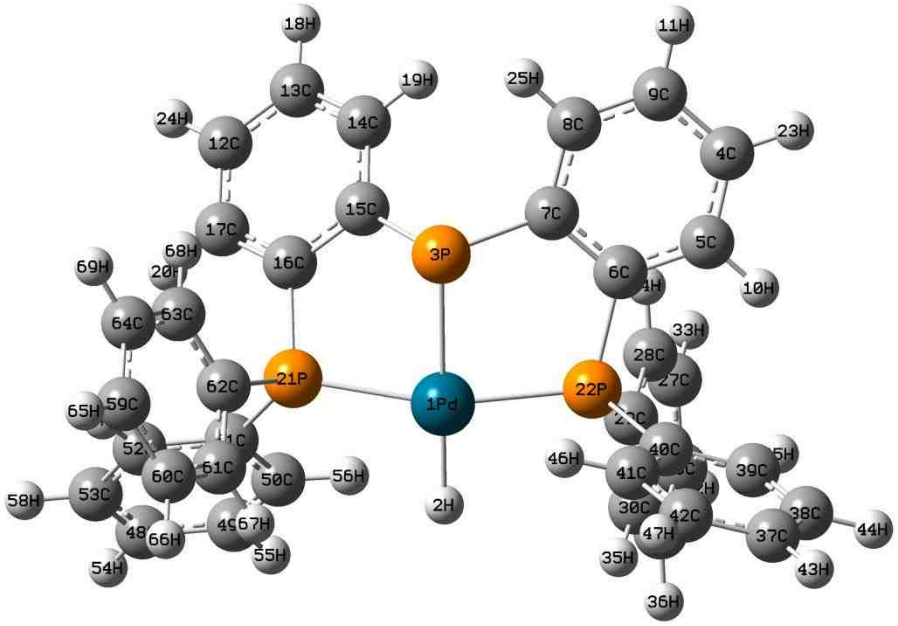
*** *** ***

(PPP) palladium hydride **34**

(see Figure 3-16)



34



Energy: -2540.16774091 hartrees

Palladium-hydrogen bond length: 1.632 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0015	0.1430	0.6346	-1.5667	-0.1203		
2H	-0.0638	1.5659	1.4310	0.0397	-0.2541		
3P	0.0953	-1.9558	-0.5486	0.6040	-0.4010		
4C	-4.2141	-2.4815	-2.3133	-0.5941	-0.1125		
5C	-3.9508	-1.4661	-1.3958	-0.1408	-0.1528		
6C	-2.6422	-1.2315	-0.9391	-0.0263	-0.0620		

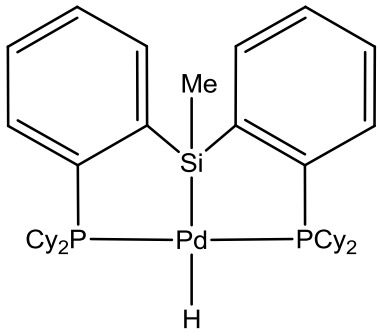
7C	-1.5722	-2.0511	-1.3707	-0.5779	0.2100		
8C	-1.8715	-3.0920	-2.2753	0.1916	-0.2267		
9C	-3.1635	-3.2927	-2.7584	-0.2186	-0.1026		
10H	-4.7686	-0.8442	-1.0409	0.1928	0.1210		
11H	-3.3583	-4.1009	-3.4597	0.1799	0.1116		
12C	3.4407	-0.8531	-3.6486	-0.6132	-0.0830		
13C	2.3721	-1.6549	-4.0597	-0.7712	-0.1373		
14C	1.3375	-1.9639	-3.1744	0.1804	-0.1706		
15C	1.3208	-1.4641	-1.8592	0.1825	0.1079		
16C	2.3995	-0.6266	-1.4618	-0.1631	-0.0234		
17C	3.4480	-0.3434	-2.3478	0.4159	-0.1982		
18H	2.3426	-2.0442	-5.0750	0.1766	0.1146		
19H	0.5257	-2.5964	-3.5199	0.1688	0.1341		
20H	4.2572	0.3118	-2.0366	0.2001	0.1203		
21P	2.2981	0.1301	0.2246	0.5248	0.3519		
22P	-2.2674	0.1267	0.2599	0.7507	0.4986		
23H	-5.2280	-2.6471	-2.6682	0.1799	0.1058		
24H	4.2471	-0.6095	-4.3351	0.1775	0.1002		
25H	-1.0857	-3.7812	-2.5728	0.1808	0.1513		
26C	-3.6403	4.1179	-1.7031	-0.2757	-0.0919		
27C	-3.5152	2.9730	-2.4921	-0.2761	-0.0951		
28C	-3.1324	1.7566	-1.9152	0.2326	-0.1341		
29C	-2.8699	1.6745	-0.5400	1.8951	-0.1216		
30C	-2.9762	2.8375	0.2434	-1.5843	0.0084		
31C	-3.3697	4.0458	-0.3313	-0.8002	-0.1460		
32H	-3.9406	5.0615	-2.1516	0.1800	0.1036		
33H	-3.7138	3.0201	-3.5599	0.1814	0.1071		
34H	-3.0380	0.8758	-2.5422	0.2117	0.1046		
35H	-2.7429	2.7992	1.3041	0.2053	0.0708		
36H	-3.4553	4.9339	0.2899	0.1821	0.1121		
37C	-5.0887	-0.7106	3.8620	-0.1078	-0.1306		
38C	-5.5843	-0.0038	2.7620	-0.4749	-0.0809		
39C	-4.7527	0.2764	1.6745	0.0397	-0.1859		
40C	-3.4143	-0.1480	1.6766	0.0471	0.0751		
41C	-2.9212	-0.8458	2.7907	-0.1319	-0.2319		
42C	-3.7552	-1.1299	3.8747	-0.2337	-0.0417		
43H	-5.7367	-0.9261	4.7078	0.1808	0.1115		
44H	-6.6179	0.3331	2.7499	0.1817	0.1044		
45H	-5.1468	0.8392	0.8328	0.1967	0.1203		

46H	-1.8792	-1.1557	2.8098	0.2096	0.1288		
47H	-3.3601	-1.6705	4.7310	0.1844	0.1037		
48C	4.5253	4.1973	-0.1509	-0.1371	-0.0972		
49C	3.1362	4.1239	-0.2928	-0.6028	-0.1118		
50C	2.4802	2.8980	-0.1573	0.0254	-0.1269		
51C	3.2093	1.7282	0.1062	-0.2880	-0.0020		
52C	4.6037	1.8099	0.2550	-0.0664	-0.0596		
53C	5.2569	3.0391	0.1284	-0.0873	-0.1425		
54H	5.0342	5.1532	-0.2472	0.1797	0.1073		
55H	2.5597	5.0229	-0.4960	0.1823	0.1176		
56H	1.3974	2.8451	-0.2328	0.2293	0.1120		
57H	5.1816	0.9181	0.4825	0.2033	0.0725		
58H	6.3360	3.0904	0.2513	0.1806	0.1127		
59C	4.8672	-2.4495	3.1200	-0.1793	-0.1957		
60C	4.1422	-1.3469	3.5872	-0.5126	0.0170		
61C	3.3829	-0.5818	2.7013	-0.6753	-0.3298		
62C	3.3507	-0.9000	1.3318	0.9234	0.2815		
63C	4.0733	-2.0100	0.8719	0.3837	-0.2972		
64C	4.8284	-2.7798	1.7638	-0.6356	-0.0364		
65H	5.4530	-3.0497	3.8117	0.1794	0.1227		
66H	4.1609	-1.0884	4.6430	0.1816	0.0971		
67H	2.8090	0.2635	3.0738	0.2000	0.1264		
68H	4.0465	-2.2793	-0.1799	0.2160	0.1570		
69H	5.3821	-3.6396	1.3946	0.1817	0.1016		

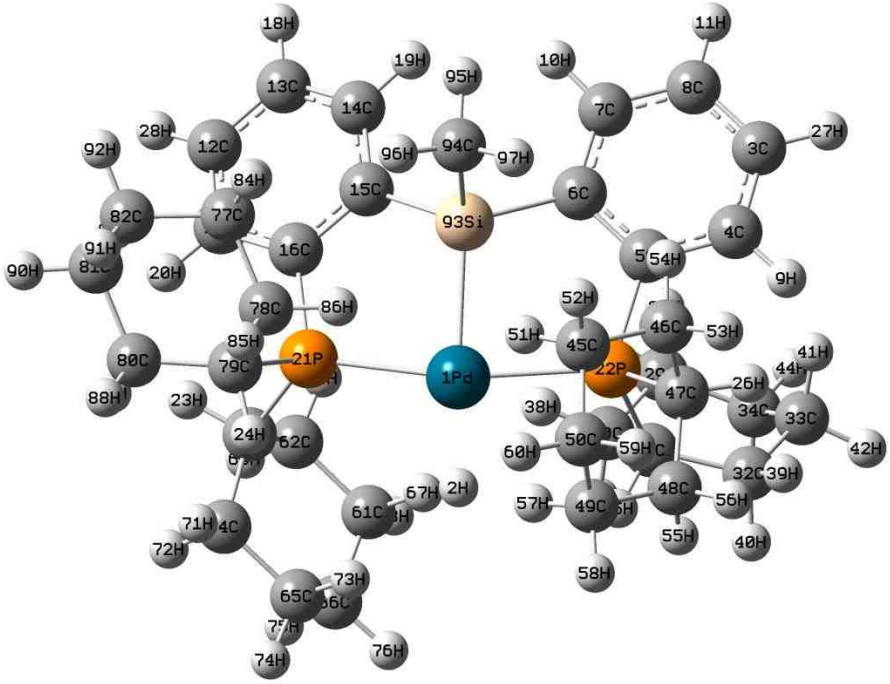
*** *** ***

(PSiP) palladium hydride **35**

(see Figure 3-16, Figure 3-33)



35



Energy: -2542.71411319 hartrees

Palladium-hydrogen bond length: 1.680 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0024	0.5090	0.5284	-1.7977	-0.0747		
2H	-0.1590	2.1319	0.9302	-0.0295	-0.2266		
3C	-4.2956	-3.0975	-1.1868	-0.7984	-0.0304		
4C	-4.0265	-1.9251	-0.4807	-0.1691	-0.2357		

5C	-2.7089	-1.4575	-0.3340	-0.2347	0.2174		
6C	-1.6260	-2.2212	-0.8325	-0.3818	-0.2300		
7C	-1.9261	-3.3946	-1.5519	0.2822	-0.0461		
8C	-3.2399	-3.8226	-1.7490	-0.6105	-0.1954		
9H	-4.8558	-1.3769	-0.0432	0.1789	0.1130		
10H	-1.1186	-4.0055	-1.9497	0.1664	0.1055		
11H	-3.4399	-4.7316	-2.3119	0.1781	0.1207		
12C	3.8475	-1.9030	-3.0927	-0.7935	-0.1057		
13C	2.8932	-2.9205	-3.1698	-0.6171	-0.1389		
14C	1.7816	-2.8859	-2.3259	0.4035	-0.1454		
15C	1.5776	-1.8421	-1.4034	-0.0051	-0.1218		
16C	2.5564	-0.8177	-1.3295	-0.3985	0.1294		
17C	3.6786	-0.8650	-2.1753	0.0236	-0.1236		
18H	3.0152	-3.7338	-3.8817	0.1784	0.1168		
19H	1.0552	-3.6927	-2.3943	0.1659	0.1307		
20H	4.4360	-0.0877	-2.1369	0.1776	0.0919		
21P	2.2631	0.5857	-0.1154	1.4686	-0.0416		
22P	-2.3094	0.1550	0.5158	1.4396	0.0717		
23H	3.9490	1.6912	-1.4014	0.1950	-0.0076		
24H	3.1475	1.3879	1.8801	0.2340	-0.0068		
25H	-2.6660	2.4063	0.1283	0.2473	0.0043		
26H	-4.3451	-0.1063	1.7670	0.2056	-0.0364		
27H	-5.3209	-3.4419	-1.2988	0.1800	0.0913		
28H	4.7188	-1.9143	-3.7432	0.1795	0.1044		
29C	-3.2920	0.9605	-2.9699	-0.3639	-0.0506		
30C	-2.5068	1.7097	-1.8826	-0.5406	0.0378		
31C	-3.0990	1.5845	-0.4545	-0.3535	0.0783		
32C	-4.6359	1.8039	-0.4666	-0.3625	0.0864		
33C	-5.4125	1.1326	-1.6147	-0.3286	-0.0424		
34C	-4.7653	1.3911	-2.9823	-0.6103	0.1315		
35H	-3.2285	-0.1231	-2.8069	0.2310	-0.0070		
36H	-2.8281	1.1581	-3.9455	0.1929	0.0025		
37H	-2.5009	2.7793	-2.1423	0.2066	-0.0037		
38H	-1.4588	1.3921	-1.8774	0.2215	-0.0422		
39H	-5.0854	1.5361	0.4975	0.2061	-0.0405		
40H	-4.7813	2.8912	-0.5635	0.2113	-0.0221		
41H	-5.4734	0.0507	-1.4584	0.1916	0.0062		
42H	-6.4458	1.5059	-1.6045	0.1935	-0.0156		
43H	-4.8306	2.4631	-3.2261	0.1946	-0.0380		

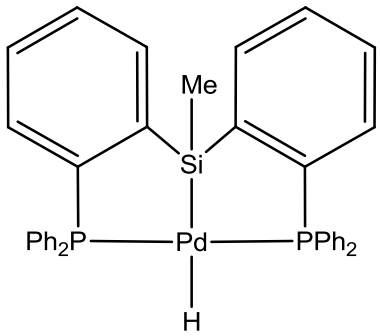
44H	-5.3171	0.8561	-3.7665	0.1932	-0.0426		
45C	-1.6320	-0.9218	3.8047	-0.2541	0.3087		
46C	-2.9204	-1.1454	2.9960	-0.6003	-0.1950		
47C	-3.3150	0.0620	2.1099	-0.0833	0.2311		
48C	-3.3085	1.3668	2.9464	-0.3608	-0.0165		
49C	-2.0293	1.5762	3.7750	-0.3702	0.1991		
50C	-1.7181	0.3554	4.6530	-0.6553	-0.1217		
51H	-0.7746	-0.8447	3.1220	0.2349	-0.1000		
52H	-1.4500	-1.7965	4.4437	0.1893	-0.0655		
53H	-3.7499	-1.3148	3.7005	0.2059	0.0115		
54H	-2.8437	-2.0574	2.3919	0.2252	0.0175		
55H	-3.4923	2.2427	2.3130	0.2134	-0.0288		
56H	-4.1668	1.3048	3.6344	0.2059	-0.0217		
57H	-1.1844	1.7691	3.1020	0.2577	-0.0867		
58H	-2.1511	2.4727	4.3982	0.1873	-0.0485		
59H	-2.5057	0.2348	5.4141	0.1922	-0.0043		
60H	-0.7778	0.5126	5.1979	0.1952	-0.0031		
61C	0.9760	3.3404	-2.1277	-0.4674	0.1977		
62C	2.1744	2.4066	-2.3605	-0.4847	-0.0468		
63C	2.9712	2.0640	-1.0748	-0.2978	0.1930		
64C	3.2594	3.3516	-0.2567	-0.2870	-0.0127		
65C	2.0498	4.2756	-0.0496	-0.4257	0.1867		
66C	1.3826	4.6220	-1.3873	-0.5412	-0.0926		
67H	0.2171	2.8211	-1.5338	0.2365	-0.0453		
68H	0.5196	3.5833	-3.0973	0.1849	-0.0468		
69H	2.8753	2.9034	-3.0501	0.2040	-0.0230		
70H	1.8505	1.4897	-2.8680	0.2207	-0.0304		
71H	3.7209	3.1162	0.7081	0.2083	-0.0196		
72H	4.0246	3.9080	-0.8220	0.2068	-0.0263		
73H	1.3156	3.7870	0.6007	0.2419	-0.0685		
74H	2.3841	5.1894	0.4610	0.1843	-0.0540		
75H	2.0772	5.2095	-2.0098	0.1889	-0.0096		
76H	0.5010	5.2545	-1.2178	0.1925	-0.0077		
77C	3.8535	-2.0135	1.9820	-0.3191	0.1438		
78C	3.1436	-0.6956	2.3316	-0.5324	-0.0242		
79C	3.4567	0.4703	1.3618	-0.2024	0.1369		
80C	4.9856	0.5783	1.1180	-0.2789	0.0499		
81C	5.6978	-0.7531	0.8210	-0.3890	0.0895		
82C	5.3718	-1.8192	1.8750	-0.7628	-0.1169		

83H	3.4775	-2.4062	1.0285	0.2330	-0.0123		
84H	3.6168	-2.7651	2.7469	0.1986	-0.0311		
85H	3.4805	-0.3835	3.3327	0.2049	-0.0131		
86H	2.0599	-0.8426	2.4068	0.2322	-0.0105		
87H	5.2156	1.3076	0.3334	0.2128	-0.0462		
88H	5.4188	0.9929	2.0422	0.2107	-0.0173		
89H	5.4029	-1.1302	-0.1653	0.2208	-0.0340		
90H	6.7809	-0.5743	0.7779	0.1931	-0.0281		
91H	5.7737	-1.5095	2.8524	0.1952	0.0152		
92H	5.8619	-2.7678	1.6190	0.1958	0.0070		
93Si	0.1177	-1.7624	-0.1569	1.8753	0.2593		
94C	0.4052	-3.2195	1.0593	-1.0765	-0.0958		
95H	0.4283	-4.1761	0.5180	0.2255	0.0021		
96H	1.3456	-3.1281	1.6110	0.2328	-0.0161		
97H	-0.4106	-3.2765	1.7903	0.2308	0.0031		

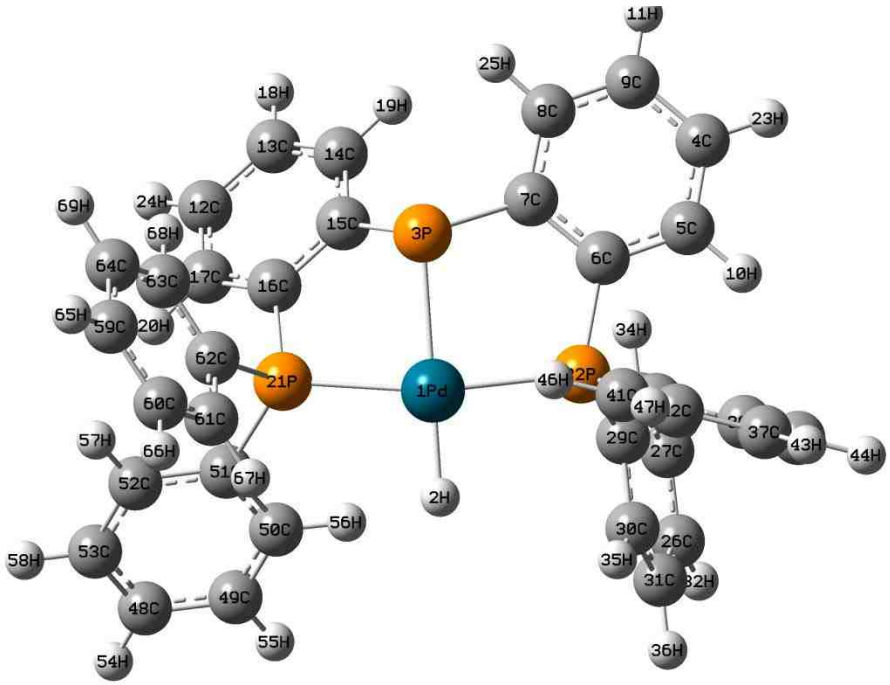
*** *** ***

(PSiP) palladium hydride **36**

(see Figure 3-16, Figure 3-33)



36



Energy: -2332.18586013 hartrees

Palladium-hydrogen bond length: 1.586 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.0175	0.3061	0.5738	-1.8118	-0.2271		
2H	-0.0974	1.8364	1.2502	0.0095	-0.2700		
3C	-4.2995	-2.4606	-2.3053	-0.6637	-0.0618		
4C	-4.0182	-1.4053	-1.4380	-0.2545	-0.1577		
5C	-2.7077	-1.1935	-0.9758	-0.1803	-0.0167		
6C	-1.6572	-2.0548	-1.3650	-0.5027	-0.0078		
7C	-1.9728	-3.1172	-2.2353	0.2393	-0.1683		
8C	-3.2701	-3.3180	-2.7094	-0.3397	-0.1290		
9H	-4.8239	-0.7466	-1.1253	0.1913	0.1104		
10H	-1.1942	-3.8140	-2.5399	0.1699	0.1511		
11H	-3.4830	-4.1457	-3.3822	0.1783	0.1063		
12C	3.7540	-1.1868	-3.4514	-0.6736	-0.0713		
13C	2.7755	-2.1170	-3.8120	-0.6672	-0.1475		
14C	1.6742	-2.3284	-2.9771	0.3388	-0.1009		
15C	1.5116	-1.6185	-1.7745	0.0037	-0.0321		

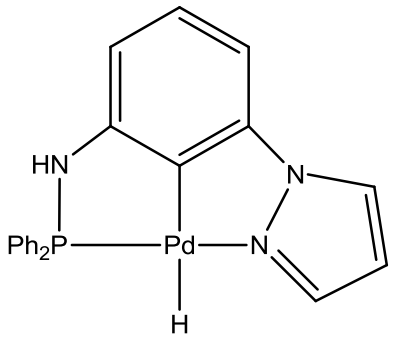
16C	2.5167	-0.6826	-1.4229	-0.3884	-0.0413		
17C	3.6255	-0.4730	-2.2571	0.4131	-0.1535		
18H	2.8658	-2.6699	-4.7444	0.1776	0.1133		
19H	0.9206	-3.0514	-3.2819	0.1680	0.1005		
20H	4.3808	0.2618	-1.9927	0.2021	0.1055		
21P	2.2683	0.2518	0.1675	0.4079	0.3577		
22P	-2.2897	0.1946	0.1920	0.8839	0.3883		
23H	-5.3154	-2.6163	-2.6600	0.1804	0.0937		
24H	4.6086	-1.0087	-4.0997	0.1799	0.0980		
25Si	0.0590	-1.8195	-0.5295	1.7205	0.0549		
26C	4.7729	-1.8999	3.4513	-0.1377	-0.1129		
27C	3.8969	-0.8567	3.7729	-0.5151	-0.0800		
28C	3.1582	-0.2269	2.7702	-0.1899	-0.2172		
29C	3.2962	-0.6223	1.4275	0.3160	0.1273		
30C	4.1728	-1.6710	1.1134	0.1846	-0.0605		
31C	4.9066	-2.3063	2.1218	-0.3737	-0.1427		
32H	5.3427	-2.3949	4.2337	0.1798	0.1095		
33H	3.7825	-0.5387	4.8062	0.1827	0.1133		
34H	2.4666	0.5720	3.0274	0.2100	0.1102		
35H	4.2830	-1.9985	0.0838	0.2116	0.0833		
36H	5.5803	-3.1199	1.8641	0.1809	0.1085		
37C	4.4411	4.3108	-0.5363	-0.1523	-0.1155		
38C	3.0570	4.1982	-0.6994	-0.7111	-0.0949		
39C	2.4183	2.9783	-0.4624	-0.1932	-0.1645		
40C	3.1604	1.8516	-0.0774	0.1495	0.0195		
41C	4.5491	1.9743	0.0952	-0.0366	-0.0546		
42C	5.1850	3.1981	-0.1323	-0.1152	-0.1321		
43H	4.9361	5.2630	-0.7108	0.1785	0.1116		
44H	2.4697	5.0636	-0.9961	0.1820	0.1132		
45H	1.3374	2.9001	-0.5439	0.2339	0.1301		
46H	5.1372	1.1208	0.4220	0.2002	0.0493		
47H	6.2595	3.2816	0.0116	0.1788	0.1119		
48C	-4.9923	-0.5671	3.9057	-0.1285	-0.1316		
49C	-3.6352	-0.9008	3.9186	-0.2174	-0.0640		
50C	-2.8403	-0.6444	2.7983	0.0591	-0.1913		
51C	-3.3948	-0.0609	1.6485	-0.0501	0.0734		
52C	-4.7570	0.2799	1.6477	-0.2139	-0.1705		
53C	-5.5503	0.0279	2.7697	-0.4187	-0.0944		
54H	-5.6104	-0.7602	4.7789	0.1801	0.1140		

55H	-3.1912	-1.3512	4.8027	0.1826	0.1067		
56H	-1.7794	-0.8823	2.8174	0.2094	0.1275		
57H	-5.1994	0.7613	0.7800	0.1935	0.1122		
58H	-6.6026	0.3011	2.7573	0.1805	0.1093		
59C	-3.8049	4.1193	-1.8091	-0.2240	-0.1379		
60C	-3.6411	2.9720	-2.5872	-0.3942	-0.0574		
61C	-3.2169	1.7750	-1.9985	0.4277	-0.2238		
62C	-2.9511	1.7139	-0.6227	2.0965	0.0486		
63C	-3.0946	2.8809	0.1485	-1.7300	-0.0764		
64C	-3.5299	4.0693	-0.4372	-0.8525	-0.1136		
65H	-4.1374	5.0480	-2.2662	0.1784	0.1139		
66H	-3.8414	3.0019	-3.6554	0.1795	0.0998		
67H	-3.0932	0.8931	-2.6189	0.2065	0.1267		
68H	-2.8528	2.8620	1.2075	0.2079	0.0836		
69H	-3.6429	4.9603	0.1754	0.1814	0.1123		
70C	0.3747	-3.4600	0.4025	-1.0799	-0.0996		
71H	-0.4169	-3.6464	1.1390	0.2238	0.0111		
72H	0.4005	-4.3187	-0.2832	0.2218	0.0176		
73H	1.3319	-3.4303	0.9370	0.2348	-0.0038		

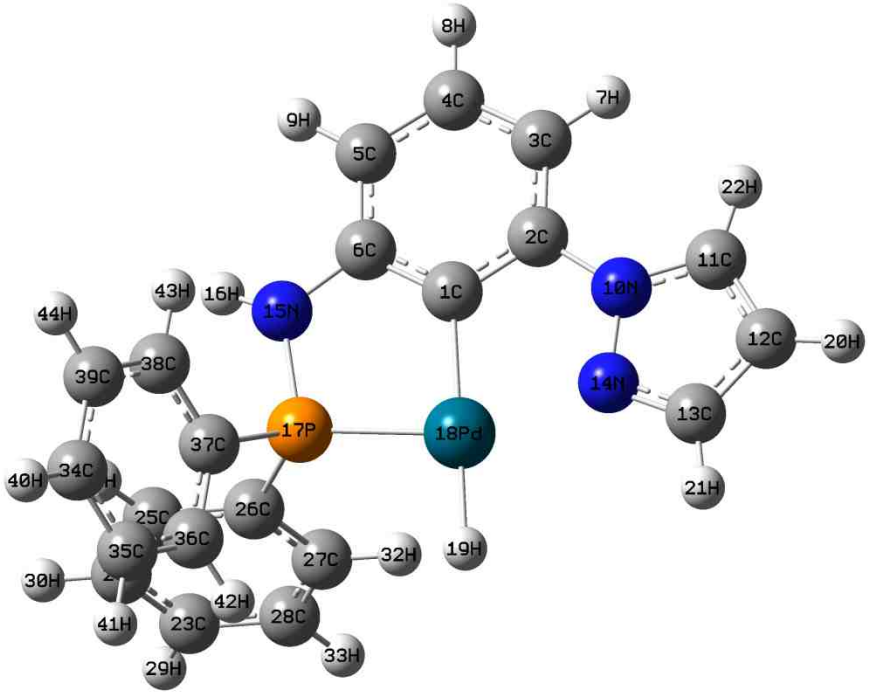
*** *** ***

(PCN) palladium hydride **37**

(see Figure 3-16)



37



Energy: -1443.44536066 hartrees

Palladium-hydrogen bond length: 1.654 Å

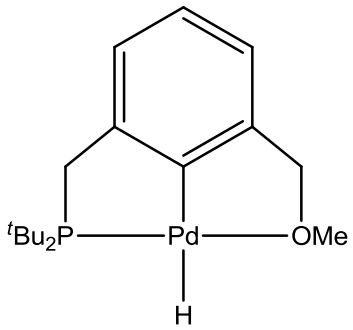
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	1.6057	-0.0464	0.8929	0.1070	-0.3494		
2C	2.9847	-0.0449	1.0376	0.2801	0.1968		
3C	3.6052	-0.0194	2.2950	-0.2433	-0.2798		
4C	2.7754	0.0018	3.4214	-0.5155	-0.0844		
5C	1.3756	-0.0048	3.3124	-0.5344	-0.3004		
6C	0.7973	-0.0283	2.0350	0.1129	0.3140		
7H	4.6852	-0.0095	2.4126	0.1619	0.1375		
8H	3.2271	0.0229	4.4097	0.1730	0.1145		
9H	0.7632	0.0054	4.2118	0.1648	0.1397		
10N	3.7006	-0.0528	-0.2025	0.2492	0.1338		
11C	5.0271	-0.0774	-0.4815	-0.0648	-0.1801		
12C	5.1680	-0.0758	-1.8615	-0.1396	-0.1807		
13C	3.8515	-0.0488	-2.3605	-0.3683	-0.1346		
14N	2.9695	-0.0352	-1.3598	0.0386	0.0298		

15N	-0.5940	-0.0576	1.7834	-0.7228	-0.4380		
16H	-1.2278	0.2103	2.5288	0.4237	0.2579		
17P	-1.0933	-0.0003	0.1236	0.6429	0.4446		
18Pd	0.8427	-0.0044	-1.0031	-0.6454	-0.0098		
19H	0.2133	0.0644	-2.5308	0.0140	-0.2907		
20H	6.0904	-0.0926	-2.4236	0.1978	0.1500		
21H	3.4955	-0.0389	-3.3808	0.2137	0.1663		
22H	5.7654	-0.0959	0.3064	0.2055	0.1823		
23C	-3.7786	3.7799	-0.0730	-0.0698	-0.1060		
24C	-4.2647	2.6240	0.5473	-0.3516	-0.1312		
25C	-3.4798	1.4694	0.5887	0.3356	-0.1149		
26C	-2.1970	1.4643	0.0149	-0.5060	0.0348		
27C	-1.7195	2.6242	-0.6141	-0.2624	-0.1566		
28C	-2.5078	3.7774	-0.6555	-0.1223	-0.0730		
29H	-4.3927	4.6762	-0.1093	0.1825	0.1103		
30H	-5.2570	2.6185	0.9913	0.1832	0.1171		
31H	-3.8744	0.5692	1.0539	0.1964	0.1029		
32H	-0.7376	2.6101	-1.0801	0.2218	0.1018		
33H	-2.1314	4.6698	-1.1488	0.1860	0.1103		
34C	-3.8992	-3.6518	-0.4545	-0.2449	-0.1335		
35C	-3.8176	-2.6528	-1.4320	-0.3271	-0.0518		
36C	-2.9836	-1.5512	-1.2408	-0.8042	-0.2076		
37C	-2.2280	-1.4314	-0.0620	0.6584	0.0443		
38C	-2.3032	-2.4401	0.9084	0.1375	-0.1109		
39C	-3.1395	-3.5447	0.7126	-0.1275	-0.1092		
40H	-4.5469	-4.5114	-0.6071	0.1811	0.1155		
41H	-4.3985	-2.7360	-2.3469	0.1838	0.1033		
42H	-2.9122	-0.7889	-2.0126	0.2028	0.1341		
43H	-1.7006	-2.3638	1.8087	0.2137	0.0885		
44H	-3.1908	-4.3216	1.4714	0.1817	0.1125		

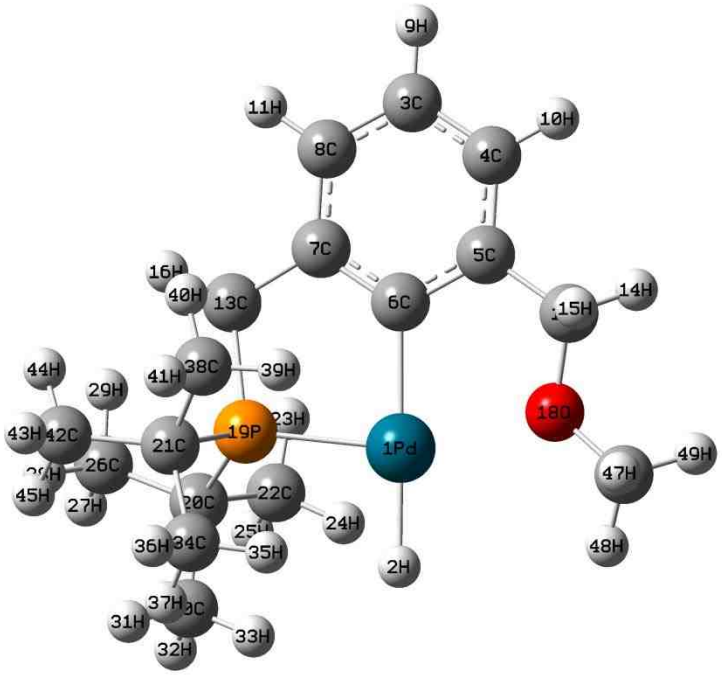
*** *** ***

(PCO) palladium hydride **38**

(see Figure 3-16, Figure 3-23, Figure 3-28, Figure 3-33)



38



Energy: -1208.59726383 hartrees

Palladium-hydrogen bond length: 1.667 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.5366	-1.0856	-0.0429	-0.7862	0.1690		
2H	-0.2550	-2.5503	0.0346	-0.0232	-0.2996		
3C	2.9182	3.1392	-0.3700	-0.5418	-0.0464		
4C	3.6042	1.9339	-0.1827	0.2423	-0.2662		
5C	2.8861	0.7358	-0.0681	0.3524	0.1381		

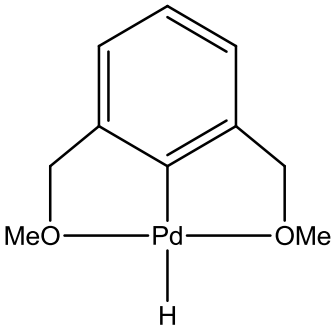
6C	1.4834	0.7340	-0.1556	-1.0744	-0.3878		
7C	0.8036	1.9499	-0.3594	0.3277	0.2646		
8C	1.5209	3.1513	-0.4572	0.7945	-0.3074		
9H	3.4740	4.0699	-0.4553	0.1712	0.0998		
10H	4.6925	1.9382	-0.1249	0.1633	0.1182		
11H	1.0022	4.0967	-0.6119	0.1638	0.1181		
12C	3.5939	-0.5738	0.1982	-0.3880	0.1058		
13C	-0.7070	1.8940	-0.5112	-1.2702	-0.0709		
14H	4.5001	-0.6848	-0.4158	0.1941	0.0360		
15H	3.8927	-0.6521	1.2563	0.2017	0.0439		
16H	-1.2219	2.6672	0.0740	0.2483	0.0396		
17H	-0.9880	2.0711	-1.5568	0.2451	0.0428		
18O	2.7100	-1.6780	-0.0967	-0.2687	-0.1784		
19P	-1.3114	0.1658	-0.0412	0.8839	-0.0733		
20C	-2.5958	-0.2768	-1.3826	-0.3548	0.6335		
21C	-2.0601	0.3542	1.7080	-0.3481	0.5754		
22C	-1.7737	-0.5695	-2.6602	-0.5813	-0.1726		
23H	-1.1768	0.2913	-2.9830	0.2215	0.0184		
24H	-1.0948	-1.4142	-2.5085	0.2640	-0.0193		
25H	-2.4640	-0.8189	-3.4775	0.2117	0.0353		
26C	-3.6002	0.8561	-1.6853	-0.4122	-0.3801		
27H	-4.2326	0.5479	-2.5288	0.2190	0.0650		
28H	-4.2646	1.0699	-0.8444	0.2162	0.0714		
29H	-3.1086	1.7901	-1.9773	0.2177	0.0595		
30C	-3.3634	-1.5569	-0.9970	-0.6249	-0.3428		
31H	-4.0714	-1.3819	-0.1803	0.2145	0.0557		
32H	-3.9450	-1.8983	-1.8639	0.2123	0.0562		
33H	-2.6801	-2.3613	-0.7066	0.2653	0.0805		
34C	-2.3473	-1.0383	2.3090	-0.6638	-0.2692		
35H	-1.4547	-1.6702	2.2943	0.2651	0.0086		
36H	-2.6724	-0.9140	3.3512	0.2077	0.0504		
37H	-3.1409	-1.5697	1.7770	0.2149	0.0562		
38C	-0.9806	1.0378	2.5790	-0.6358	-0.1569		
39H	-0.0401	0.4786	2.5686	0.2527	0.0158		
40H	-0.7664	2.0630	2.2607	0.2323	0.0178		
41H	-1.3427	1.0817	3.6149	0.2134	0.0210		
42C	-3.3436	1.2067	1.7388	-0.3798	-0.4064		
43H	-3.6248	1.3905	2.7846	0.2193	0.0722		
44H	-3.2136	2.1846	1.2610	0.2235	0.0790		

45H	-4.1874	0.6987	1.2622	0.2233	0.0782		
46C	3.2322	-2.9486	0.2852	-0.3479	0.0159		
47H	3.3773	-2.9975	1.3735	0.1971	0.0402		
48H	2.4981	-3.6934	-0.0217	0.2324	0.0664		
49H	4.1899	-3.1304	-0.2221	0.1890	0.0289		

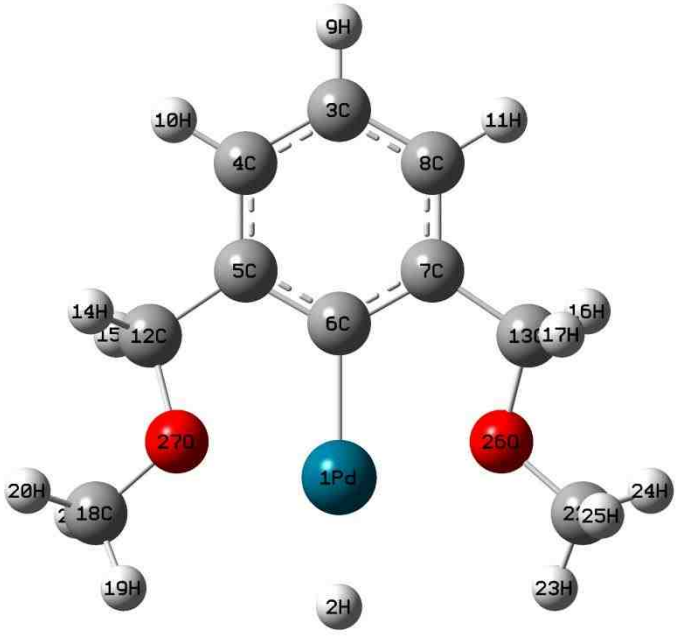
*** *** ***

(OCO) palladium hydride **39**

(see Figure 3-16, Figure 3-33, Figure 5-9)



39



Energy: -666.60917298 hartrees

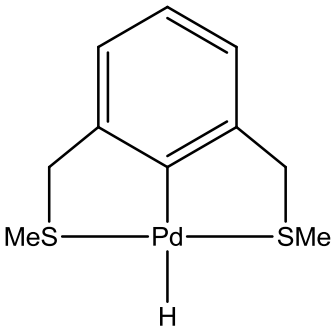
Palladium-hydrogen bond length: 1.683 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-1.2022	0.0000	-0.1377	0.2306		
2H	0.0001	-2.8849	-0.0001	-0.0613	-0.3455		
3C	-0.0001	3.5815	0.0000	-0.0798	-0.0540		
4C	-1.2199	2.8906	-0.0080	-0.5606	-0.2573		
5C	-1.2167	1.4894	-0.0178	-0.0527	0.1473		
6C	0.0000	0.8025	0.0000	0.6044	-0.3320		
7C	1.2166	1.4894	0.0178	-0.0527	0.1474		
8C	1.2198	2.8907	0.0080	-0.5606	-0.2573		
9H	-0.0001	4.6685	0.0000	0.1741	0.1019		
10H	-2.1539	3.4513	-0.0135	0.1706	0.1213		
11H	2.1538	3.4513	0.0135	0.1706	0.1213		
12C	-2.4645	0.6430	-0.0889	-0.2420	0.1132		
13C	2.4645	0.6431	0.0890	-0.2420	0.1131		
14H	-3.2383	0.9613	0.6244	0.2007	0.0407		
15H	-2.9024	0.6588	-1.0990	0.2054	0.0463		
16H	3.2383	0.9614	-0.6242	0.2007	0.0407		
17H	2.9023	0.6589	1.0991	0.2054	0.0464		
18C	-3.1734	-1.6674	-0.0229	-0.3191	0.0395		
19H	-2.8116	-2.6410	0.3042	0.2414	0.0684		
20H	-4.0612	-1.3749	0.5533	0.1898	0.0280		
21H	-3.4161	-1.6992	-1.0933	0.2006	0.0370		
22C	3.1735	-1.6673	0.0231	-0.3191	0.0394		
23H	2.8116	-2.6410	-0.3039	0.2414	0.0684		
24H	4.0612	-1.3749	-0.5532	0.1898	0.0280		
25H	3.4162	-1.6989	1.0934	0.2006	0.0370		
26O	2.1159	-0.7354	-0.2228	-0.2840	-0.1850		
27O	-2.1158	-0.7355	0.2228	-0.2840	-0.1851		

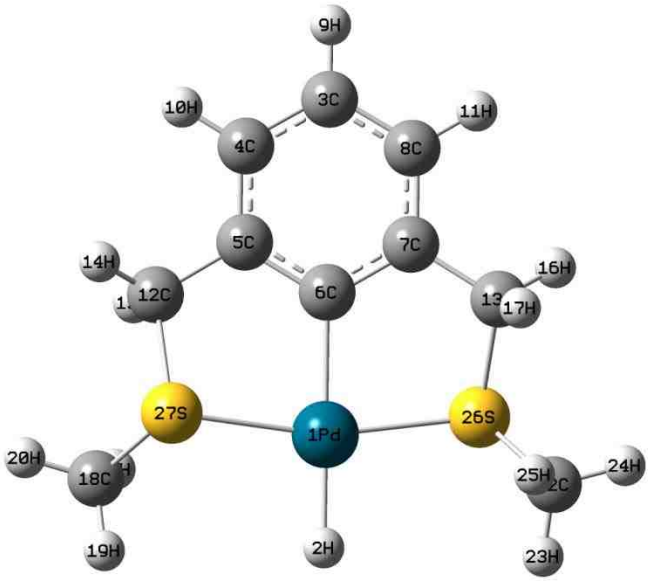
*** *** ***

(SCS) palladium hydride **40**

(see Figure 3-16, Figure 5-8)



40



Energy: -1312.61879843 hartrees

Palladium-hydrogen bond length: 1.652 Å

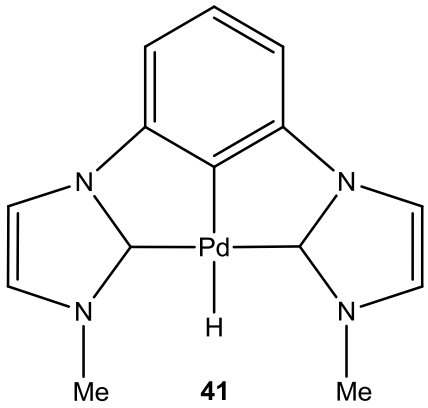
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-1.1035	0.0000	-0.7421	0.1191		
2H	0.0000	-2.7555	0.0000	-0.0132	-0.2607		
3C	0.0000	3.7851	0.0000	-0.1489	0.0060		
4C	-1.2131	3.0883	0.0082	-0.1990	-0.2963		
5C	-1.2126	1.6858	-0.0108	0.4970	0.0917		
6C	0.0000	0.9704	0.0000	-0.1017	-0.2604		
7C	1.2126	1.6858	0.0108	0.4969	0.0917		

8C	1.2131	3.0883	-0.0082	-0.1991	-0.2963		
9H	0.0000	4.8723	0.0000	0.1729	0.0878		
10H	-2.1505	3.6427	0.0143	0.1688	0.1243		
11H	2.1505	3.6427	-0.0143	0.1688	0.1243		
12C	-2.5046	0.9047	-0.0980	-1.1381	0.2296		
13C	2.5045	0.9047	0.0980	-1.1381	0.2296		
14H	-3.3263	1.3732	0.4551	0.2377	0.0017		
15H	-2.8226	0.7812	-1.1406	0.2482	0.0047		
16H	3.3263	1.3732	-0.4550	0.2377	0.0017		
17H	2.8225	0.7811	1.1406	0.2482	0.0047		
18C	-3.3381	-1.7896	-0.5210	-0.8709	0.1267		
19H	-3.2010	-2.8379	-0.2479	0.2584	0.0401		
20H	-4.3798	-1.4980	-0.3564	0.2336	0.0008		
21H	-3.0605	-1.6501	-1.5682	0.2522	0.0000		
22C	3.3381	-1.7896	0.5212	-0.8709	0.1266		
23H	3.2012	-2.8379	0.2480	0.2584	0.0401		
24H	4.3798	-1.4979	0.3565	0.2336	0.0008		
25H	3.0604	-1.6500	1.5683	0.2522	0.0000		
26S	2.2443	-0.8183	-0.5780	0.7286	-0.1692		
27S	-2.2443	-0.8182	0.5781	0.7286	-0.1692		

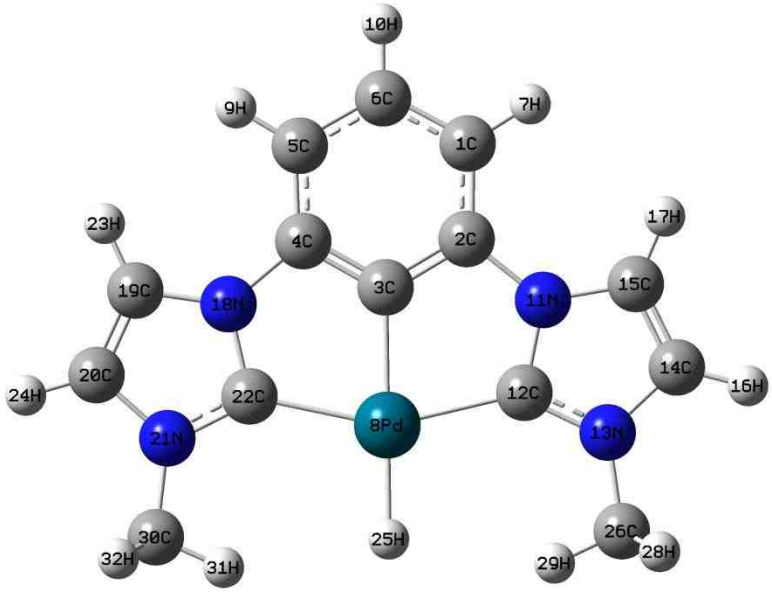
*** *** ***

(CCC) palladium hydride **41**

(see Figure 3-17, Figure 3-23, Figure 3-27, Figure 3-33, Figure 5-6)



41



Energy: -887.64208132 hartrees

Palladium-hydrogen bond length: 1.671 Å

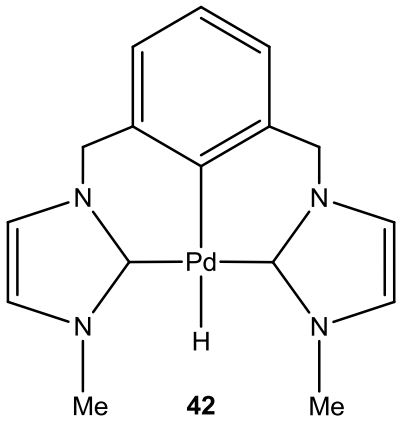
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	1.2316	3.0935	0.0002	-0.6711	-0.2562		
2C	1.1994	1.6959	0.0002	0.7245	0.1626		
3C	0.0000	1.0026	0.0002	0.0886	-0.2310		
4C	-1.1994	1.6959	0.0000	0.7245	0.1625		
5C	-1.2316	3.0935	-0.0001	-0.6711	-0.2561		
6C	0.0000	3.7726	0.0000	-0.7743	-0.0980		
7H	2.1604	3.6593	0.0002	0.1677	0.1354		
8Pd	0.0000	-1.0147	0.0001	-0.9565	-0.0284		
9H	-2.1604	3.6593	-0.0002	0.1677	0.1354		
10H	0.0000	4.8592	0.0000	0.1728	0.1087		
11N	2.3087	0.7878	0.0003	-0.0736	0.2128		
12C	2.0180	-0.5670	0.0004	0.1141	-0.2140		
13N	3.2330	-1.1655	-0.0004	-0.1444	0.2962		
14C	4.2602	-0.2255	-0.0008	-0.0761	-0.2568		
15C	3.6744	1.0050	-0.0005	0.0482	-0.2583		
16H	5.3020	-0.5088	-0.0012	0.2041	0.1861		

17H	4.1135	1.9907	-0.0009	0.2042	0.1981		
18N	-2.3087	0.7878	-0.0002	-0.0736	0.2130		
19C	-3.6744	1.0050	0.0002	0.0482	-0.2589		
20C	-4.2602	-0.2255	0.0001	-0.0761	-0.2557		
21N	-3.2330	-1.1655	-0.0001	-0.1444	0.2951		
22C	-2.0180	-0.5669	-0.0003	0.1141	-0.2136		
23H	-4.1136	1.9907	0.0003	0.2042	0.1982		
24H	-5.3020	-0.5087	0.0003	0.2041	0.1858		
25H	0.0001	-2.6857	-0.0003	-0.0624	-0.2887		
26C	3.4212	-2.6125	0.0006	-0.4368	-0.1708		
27H	3.9765	-2.9203	-0.8914	0.2164	0.0674		
28H	3.9697	-2.9201	0.8969	0.2168	0.0675		
29H	2.4294	-3.0689	-0.0029	0.2719	0.0987		
30C	-3.4212	-2.6125	-0.0004	-0.4368	-0.1704		
31H	-2.4294	-3.0689	0.0000	0.2719	0.0986		
32H	-3.9737	-2.9203	0.8934	0.2166	0.0675		
33H	-3.9727	-2.9200	-0.8949	0.2166	0.0674		

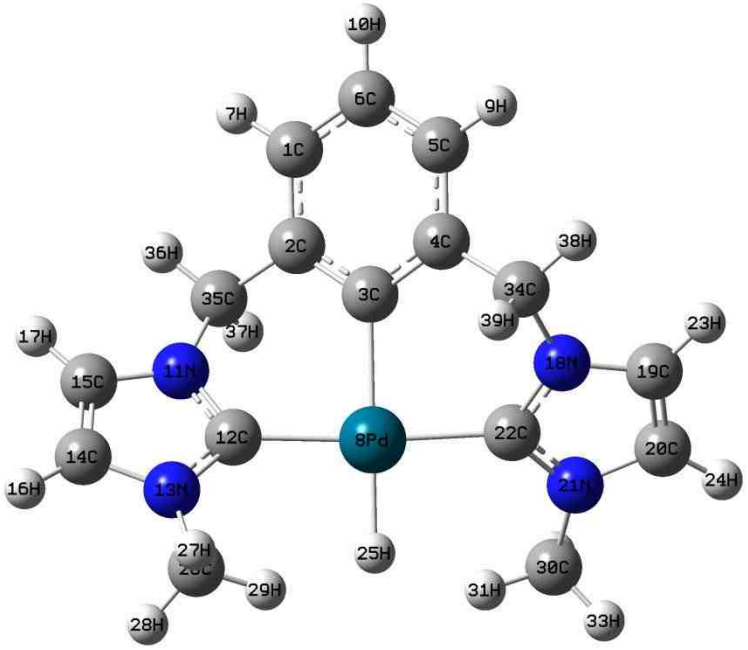
*** *** ***

(CCC) palladium hydride **42**

(see Figure 3-17)



42



Energy: -966.27904548 hartrees

Palladium-hydrogen bond length: 1.649 Å

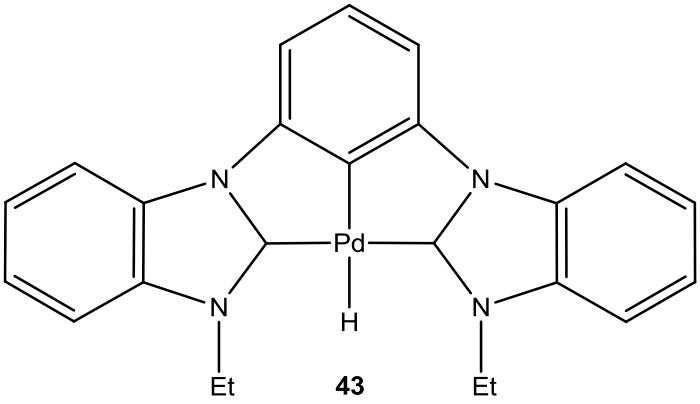
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-1.0157	3.4225	-0.6470	-0.6304	-0.3200		
2C	-1.0085	2.0197	-0.6479	1.1644	0.1718		
3C	0.0000	1.2800	0.0000	-0.6534	-0.2768		
4C	1.0084	2.0197	0.6479	1.1644	0.1717		
5C	1.0156	3.4225	0.6470	-0.6303	-0.3198		
6C	0.0000	4.1305	0.0000	0.0533	-0.0244		
7H	-1.8126	3.9677	-1.1529	0.1573	0.1290		
8Pd	0.0000	-0.8405	0.0000	-0.7941	-0.0033		
9H	1.8125	3.9677	1.1529	0.1573	0.1289		
10H	-0.0001	5.2178	0.0000	0.1671	0.0913		
11N	-2.7411	0.2216	-0.6155	-0.0256	0.2222		
12C	-2.0401	-0.7683	0.0024	-0.0050	-0.2299		
13N	-2.9957	-1.5336	0.6040	-0.0432	0.2561		
14C	-4.2659	-1.0256	0.3653	-0.0656	-0.2275		
15C	-4.1039	0.0818	-0.4083	-0.0420	-0.3024		

16H	-5.1575	-1.4862	0.7635	0.2000	0.1787		
17H	-4.8284	0.7654	-0.8248	0.2019	0.1962		
18N	2.7411	0.2217	0.6156	-0.0256	0.2222		
19C	4.1039	0.0819	0.4084	-0.0420	-0.3023		
20C	4.2660	-1.0255	-0.3652	-0.0656	-0.2275		
21N	2.9958	-1.5335	-0.6040	-0.0432	0.2562		
22C	2.0401	-0.7683	-0.0024	-0.0050	-0.2299		
23H	4.8284	0.7655	0.8249	0.2019	0.1961		
24H	5.1575	-1.4861	-0.7634	0.2000	0.1787		
25H	0.0001	-2.4896	0.0000	-0.0573	-0.2392		
26C	-2.7224	-2.7051	1.4272	-0.4850	-0.1163		
27H	-2.8195	-2.4586	2.4904	0.2203	0.0545		
28H	-3.4266	-3.5038	1.1734	0.2038	0.0541		
29H	-1.7000	-3.0248	1.2174	0.2605	0.0728		
30C	2.7225	-2.7050	-1.4273	-0.4850	-0.1163		
31H	1.7000	-3.0247	-1.2175	0.2605	0.0728		
32H	2.8197	-2.4586	-2.4904	0.2203	0.0545		
33H	3.4267	-3.5037	-1.1733	0.2038	0.0541		
34C	2.1020	1.2857	1.4062	-0.8978	0.0226		
35C	-2.1020	1.2857	-1.4062	-0.8978	0.0227		
36H	-2.8949	1.9736	-1.7152	0.1878	0.0491		
37H	-1.6908	0.8208	-2.3100	0.2407	0.0151		
38H	2.8948	1.9737	1.7152	0.1878	0.0491		
39H	1.6907	0.8208	2.3100	0.2407	0.0151		

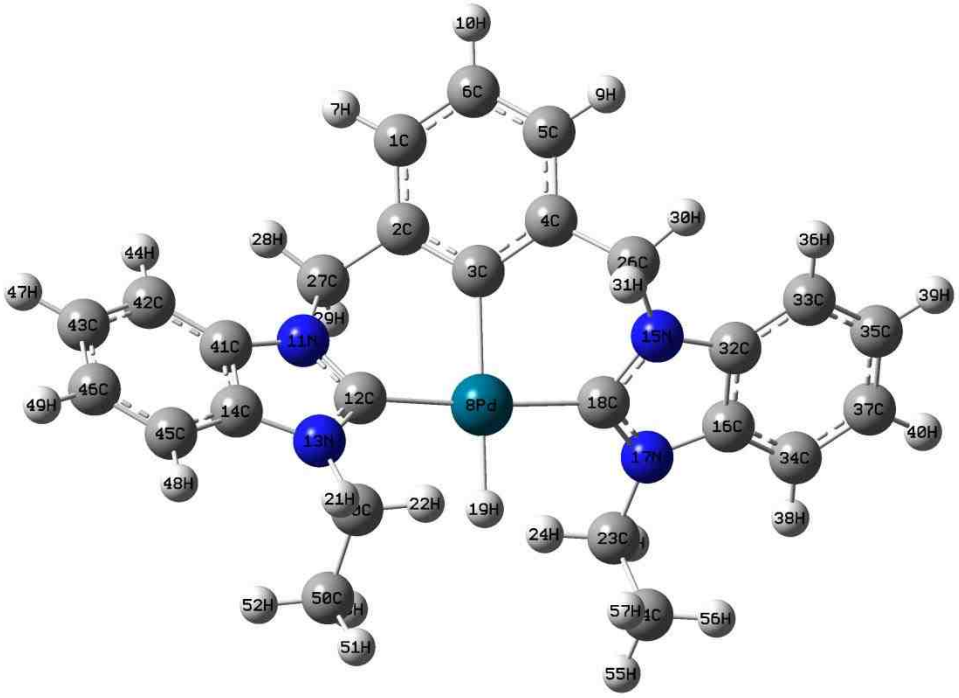
*** *** ***

(CCC) palladium hydride **43**

(see Figure 3-17)



43



Energy: -1352.21929817 hartrees

Palladium-hydrogen bond length: 1.647 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-1.0047	3.7319	-0.6691	-0.9421	-0.3214		
2C	-0.9971	2.3294	-0.6702	1.4829	0.1944		
3C	-0.0009	1.5942	-0.0014	-0.1551	-0.3243		

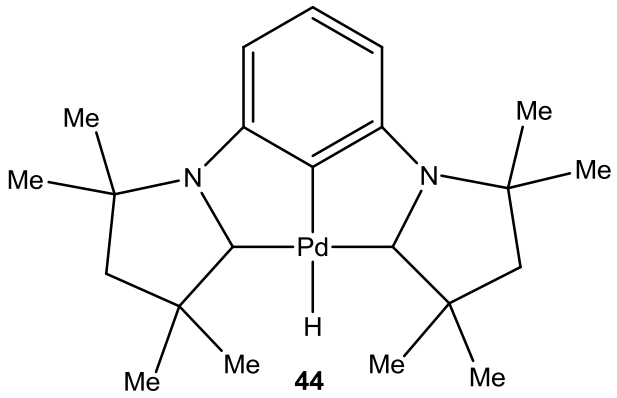
4C	0.9945	2.3298	0.6680	1.4815	0.1964		
5C	1.0009	3.7324	0.6676	-0.9440	-0.3233		
6C	-0.0021	4.4391	-0.0006	-0.1543	-0.0196		
7H	-1.7911	4.2777	-1.1902	0.1578	0.1287		
8Pd	0.0002	-0.5217	-0.0028	-1.3964	0.0278		
9H	1.7868	4.2786	1.1891	0.1578	0.1295		
10H	-0.0026	5.5263	-0.0004	0.1691	0.0924		
11N	-2.7287	0.5296	-0.6604	0.0704	0.0589		
12C	-2.0376	-0.4479	-0.0092	0.0165	-0.1006		
13N	-2.9746	-1.2203	0.6141	-0.0354	-0.1297		
14C	-4.2585	-0.7406	0.3599	0.7765	0.1895		
15N	2.7275	0.5311	0.6595	0.0707	0.0605		
16C	4.2598	-0.7392	-0.3571	0.7778	0.1875		
17N	2.9766	-1.2190	-0.6142	-0.0354	-0.1289		
18C	2.0380	-0.4466	0.0069	0.0180	-0.1004		
19H	0.0007	-2.1687	-0.0040	-0.0366	-0.2058		
20C	-2.6747	-2.4070	1.4193	-0.2900	0.3834		
21H	-3.2862	-2.3561	2.3282	0.1992	-0.0644		
22H	-1.6243	-2.3261	1.7028	0.2542	-0.0603		
23C	2.6787	-2.4056	-1.4203	-0.2898	0.3829		
24H	1.6288	-2.3250	-1.7059	0.2541	-0.0607		
25H	3.2920	-2.3544	-2.3279	0.1992	-0.0636		
26C	2.0703	1.5887	1.4446	-0.9361	0.0121		
27C	-2.0729	1.5876	-1.4463	-0.9375	0.0164		
28H	-2.8544	2.2752	-1.7789	0.1844	0.0653		
29H	-1.6439	1.1169	-2.3389	0.2412	0.0174		
30H	2.8511	2.2770	1.7776	0.1844	0.0664		
31H	1.6410	1.1180	2.3370	0.2412	0.0184		
32C	4.1002	0.3910	0.4665	0.4471	0.0592		
33C	5.2035	1.1233	0.9107	-0.3127	-0.2245		
34C	5.5235	-1.1660	-0.7708	-0.5511	-0.2318		
35C	6.4680	0.6946	0.5000	-0.4025	-0.1045		
36H	5.0926	1.9948	1.5482	0.1869	0.1464		
37C	6.6263	-0.4310	-0.3289	-0.3230	-0.1403		
38H	5.6499	-2.0351	-1.4090	0.1917	0.1588		
39H	7.3463	1.2439	0.8273	0.1799	0.1152		
40H	7.6245	-0.7358	-0.6306	0.1802	0.1180		
41C	-4.1009	0.3895	-0.4642	0.4482	0.0605		
42C	-5.2052	1.1217	-0.9059	-0.3121	-0.2267		

43C	-6.4688	0.6928	-0.4923	-0.4022	-0.1030		
44H	-5.0959	1.9931	-1.5438	0.1869	0.1472		
45C	-5.5213	-1.1676	0.7764	-0.5482	-0.2323		
46C	-6.6251	-0.4327	0.3369	-0.3229	-0.1435		
47H	-7.3479	1.2420	-0.8177	0.1799	0.1150		
48H	-5.6461	-2.0367	1.4149	0.1917	0.1597		
49H	-7.6225	-0.7376	0.6409	0.1801	0.1193		
50C	-2.9175	-3.7117	0.6580	-0.6420	-0.0934		
51H	-2.7057	-4.5657	1.3124	0.2036	0.0139		
52H	-3.9531	-3.7973	0.3098	0.2085	0.0018		
53H	-2.2498	-3.7677	-0.2076	0.2391	0.0189		
54C	2.9204	-3.7105	-0.6587	-0.6423	-0.0931		
55H	2.7101	-4.5643	-1.3138	0.2036	0.0136		
56H	3.9552	-3.7957	-0.3083	0.2085	0.0022		
57H	2.2508	-3.7668	0.2054	0.2391	0.0187		

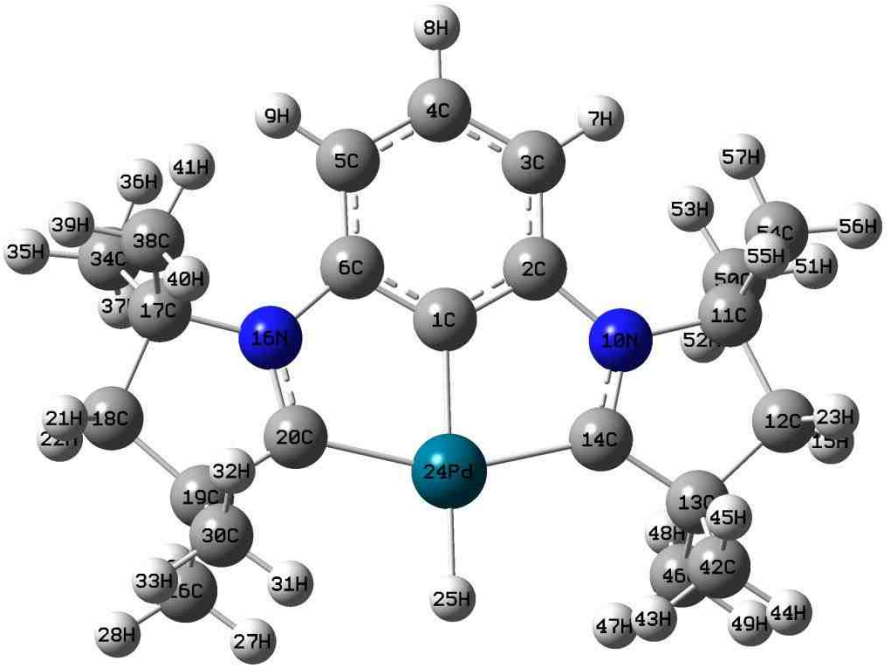
*** *** ***

(CCC) palladium hydride **44**

(see Figure 3-17, Figure 3-33)



44



Energy: -1093.82896495 hartrees

Palladium-hydrogen bond length: 1.674 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	0.0000	0.8659	-0.0003	0.6829	-0.2231		
2C	1.2116	1.5424	0.0215	0.1254	0.2380		
3C	1.2324	2.9432	0.0135	-0.4988	-0.2785		
4C	0.0000	3.6174	0.0001	-0.8989	-0.1368		
5C	-1.2324	2.9432	-0.0135	-0.4986	-0.2784		
6C	-1.2116	1.5424	-0.0219	0.1249	0.2378		
7H	2.1457	3.5276	0.0162	0.1656	0.1677		
8H	0.0000	4.7042	0.0002	0.1723	0.1184		
9H	-2.1458	3.5276	-0.0159	0.1656	0.1677		
10N	2.3202	0.6085	0.0466	0.4345	-0.2393		
11C	3.7863	0.9570	0.0442	-0.2162	0.7902		
12C	4.4357	-0.4495	0.1698	-0.4123	-0.5254		
13C	3.2991	-1.5003	0.0009	0.6873	0.7303		
14C	2.0241	-0.6926	0.0301	-0.1077	-0.1205		
15H	5.2272	-0.5796	-0.5762	0.2205	0.0696		

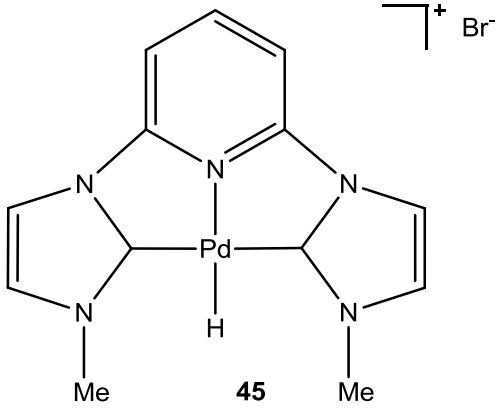
16N	-2.3202	0.6085	-0.0470	0.4344	-0.2386		
17C	-3.7863	0.9570	-0.0442	-0.2164	0.7893		
18C	-4.4356	-0.4495	-0.1701	-0.4122	-0.5252		
19C	-3.2991	-1.5003	-0.0007	0.6871	0.7291		
20C	-2.0241	-0.6926	-0.0304	-0.1077	-0.1203		
21H	-5.2276	-0.5796	0.5753	0.2205	0.0697		
22H	-4.9034	-0.5548	-1.1554	0.2181	0.0812		
23H	4.9041	-0.5548	1.1547	0.2182	0.0811		
24Pd	0.0000	-1.1299	-0.0003	-1.2051	-0.0607		
25H	0.0001	-2.8041	-0.0001	-0.0459	-0.2843		
26C	-3.2904	-2.5422	-1.1370	-0.7791	-0.2989		
27H	-2.4340	-3.2143	-1.0279	0.2589	0.0565		
28H	-4.2171	-3.1303	-1.1117	0.2061	0.0440		
29H	-3.2192	-2.0594	-2.1193	0.2122	0.0371		
30C	-3.3695	-2.2340	1.3595	-0.7653	-0.2617		
31H	-2.4975	-2.8829	1.4852	0.2569	0.0384		
32H	-3.3946	-1.5297	2.1996	0.2132	0.0334		
33H	-4.2791	-2.8469	1.4006	0.2100	0.0394		
34C	-4.1534	1.8346	-1.2533	-0.5839	-0.3224		
35H	-5.2447	1.9267	-1.3076	0.2242	0.0583		
36H	-3.7385	2.8438	-1.1934	0.2137	0.0495		
37H	-3.8047	1.3755	-2.1848	0.2356	0.0621		
38C	-4.1613	1.6436	1.2814	-0.5501	-0.3428		
39H	-5.2394	1.8424	1.2971	0.2213	0.0582		
40H	-3.9207	1.0005	2.1346	0.2342	0.0776		
41H	-3.6411	2.5962	1.4178	0.2237	0.0522		
42C	3.2901	-2.5414	1.1379	-0.7792	-0.3000		
43H	2.4337	-3.2136	1.0291	0.2589	0.0567		
44H	4.2168	-3.1296	1.1131	0.2061	0.0443		
45H	3.2189	-2.0580	2.1198	0.2122	0.0373		
46C	3.3696	-2.2349	-1.3588	-0.7654	-0.2616		
47H	2.4976	-2.8839	-1.4842	0.2569	0.0384		
48H	3.3948	-1.5311	-2.1994	0.2132	0.0333		
49H	4.2793	-2.8478	-1.3994	0.2100	0.0394		
50C	4.1616	1.6441	-1.2811	-0.5501	-0.3433		
51H	5.2398	1.8427	-1.2965	0.2213	0.0583		
52H	3.9211	1.0012	-2.1345	0.2342	0.0778		
53H	3.6417	2.5968	-1.4173	0.2237	0.0523		
54C	4.1531	1.8342	1.2537	-0.5840	-0.3227		

55H	3.8045	1.3747	2.1851	0.2356	0.0621		
56H	5.2443	1.9267	1.3082	0.2242	0.0584		
57H	3.7378	2.8433	1.1943	0.2137	0.0495		

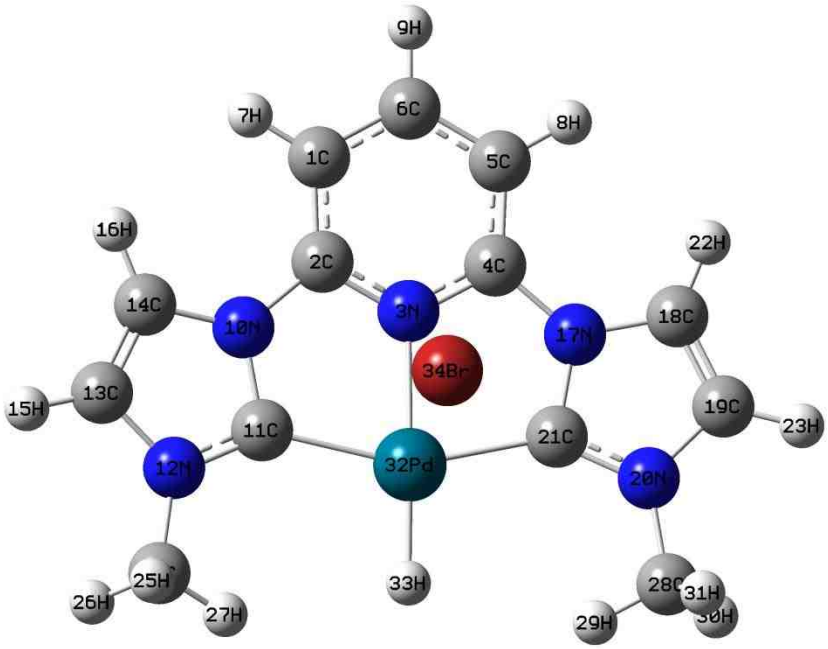
*** *** ***

(CNC) palladium hydride **45**

(see Figure 3-17)



45



Energy: -917.49380162 hartrees

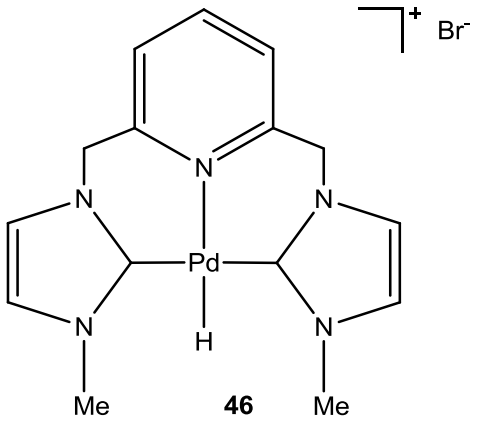
Palladium-hydrogen bond length: 1.578 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-1.2177	3.1296	-0.2588	0.5829	-0.5068		
2C	-1.1639	1.7482	-0.4390	0.0600	0.5384		
3N	0.0070	1.1219	-0.5371	-0.1633	-0.3869		
4C	1.1776	1.7467	-0.4291	0.0629	0.5369		
5C	1.2319	3.1280	-0.2478	0.5785	-0.5099		
6C	0.0071	3.8039	-0.1683	-1.4976	0.1705		
7H	-2.1565	3.6644	-0.1717	0.1906	0.2085		
8H	2.1706	3.6615	-0.1522	0.1905	0.2100		
9H	0.0072	4.8795	-0.0190	0.1972	0.0962		
10N	-2.2417	0.8446	-0.5126	-0.1753	0.0999		
11C	-1.9918	-0.5267	-0.6328	-0.0681	-0.2614		
12N	-3.2127	-1.0883	-0.5436	-0.0959	0.3280		
13C	-4.2074	-0.1269	-0.3588	-0.0546	-0.2381		
14C	-3.6019	1.0858	-0.3376	0.0272	-0.2197		
15H	-5.2493	-0.3904	-0.2568	0.2115	0.1893		
16H	-4.0144	2.0739	-0.2082	0.2075	0.1912		
17N	2.2550	0.8415	-0.4943	-0.1758	0.1004		
18C	3.6146	1.0815	-0.3129	0.0292	-0.2240		
19C	4.2192	-0.1317	-0.3321	-0.0555	-0.2306		
20N	3.2245	-1.0921	-0.5220	-0.0959	0.3182		
21C	2.0044	-0.5293	-0.6171	-0.0720	-0.2521		
22H	4.0274	2.0691	-0.1812	0.2076	0.1921		
23H	5.2604	-0.3962	-0.2254	0.2116	0.1874		
24C	-3.4393	-2.5300	-0.5450	-0.4314	-0.0890		
25H	-3.7258	-2.8629	0.4574	0.2398	0.0820		
26H	-4.2269	-2.7824	-1.2616	0.2116	0.0184		
27H	-2.5035	-3.0116	-0.8300	0.2569	0.0821		
28C	3.4505	-2.5340	-0.5274	-0.4305	-0.0868		
29H	2.5134	-3.0144	-0.8102	0.2573	0.0807		
30H	4.2353	-2.7854	-1.2475	0.2121	0.0190		
31H	3.7408	-2.8694	0.4731	0.2391	0.0816		
32Pd	0.0063	-0.9538	-0.6350	-0.4487	0.0229		
33H	0.0066	-2.5083	-0.9077	0.0372	-0.1567		
34Br	-0.0315	-0.3518	2.4017	-0.4464	-0.5915		

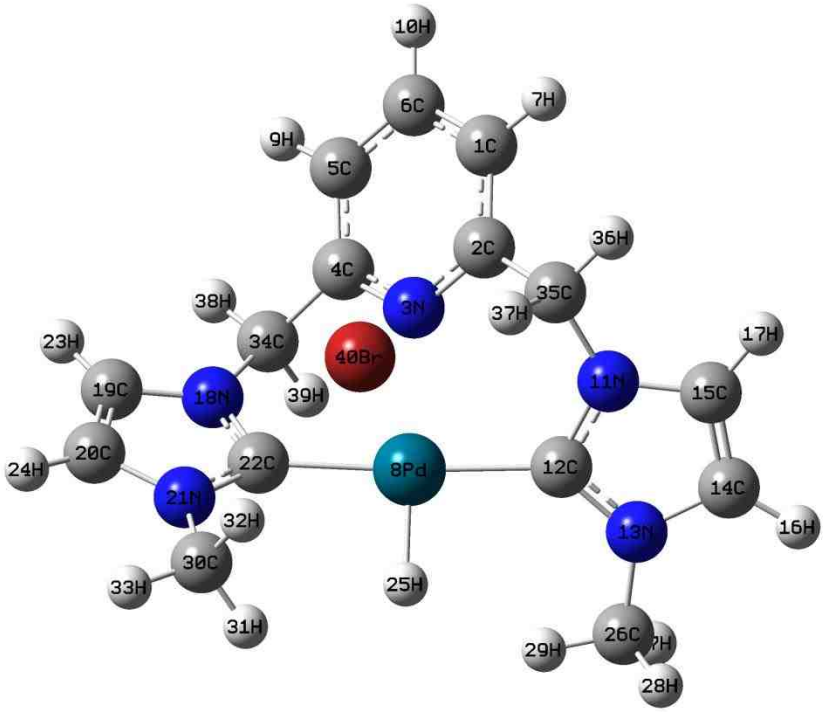
*** *** ***

(CNC) palladium hydride **46**

(see Figure 3-17)



46



Energy: -996.14606055 hartrees

Palladium-hydrogen bond length: 1.561 Å

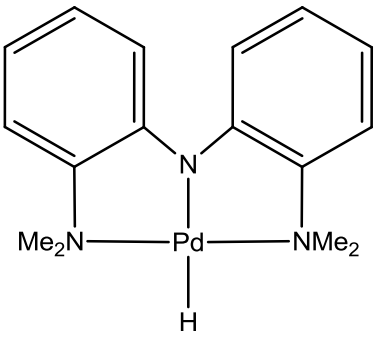
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	0.8339	3.4536	0.6743	-0.4484	-0.3500		
2C	0.9151	2.0761	0.4424	0.4978	0.1758		
3N	0.0686	1.4583	-0.4029	0.1573	-0.0686		
4C	-0.8869	2.1690	-1.0318	0.5098	0.2357		
5C	-1.0324	3.5421	-0.8322	-0.0307	-0.3181		
6C	-0.1535	4.1957	0.0326	-0.3857	0.0823		
7H	1.5282	3.9267	1.3618	0.1937	0.1818		
8Pd	0.1858	-0.7641	-0.6882	-1.0907	0.0447		
9H	-1.8206	4.0868	-1.3435	0.1887	0.1465		
10H	-0.2420	5.2647	0.2055	0.1965	0.1037		
11N	2.7147	0.3348	0.3905	0.0605	0.2077		
12C	2.2084	-0.6339	-0.4229	0.1794	-0.2933		
13N	3.3038	-1.2707	-0.9185	-0.0996	0.2243		
14C	4.4733	-0.7143	-0.4164	-0.1477	-0.1428		
15C	4.1011	0.2993	0.4101	0.0991	-0.3466		
16H	5.4513	-1.0842	-0.6848	0.2050	0.1557		
17H	4.6914	0.9746	1.0107	0.2072	0.2194		
18N	-2.4949	0.2982	-1.3890	0.0229	0.1411		
19C	-3.8657	0.1960	-1.1820	-0.0649	-0.2033		
20C	-4.0605	-0.9908	-0.5466	-0.0493	-0.3362		
21N	-2.8146	-1.5779	-0.3841	-0.0246	0.3515		
22C	-1.8397	-0.7856	-0.8860	0.1175	-0.2284		
23H	-4.5651	0.9521	-1.5050	0.2017	0.1712		
24H	-4.9663	-1.4591	-0.1932	0.2058	0.2234		
25H	0.2631	-2.2872	-1.0199	0.0615	-0.1202		
26C	3.2682	-2.3856	-1.8576	-0.5506	-0.0368		
27H	3.7321	-2.0970	-2.8068	0.2200	0.0206		
28H	3.8010	-3.2445	-1.4373	0.2217	0.0685		
29H	2.2238	-2.6487	-2.0242	0.2552	0.0361		
30C	-2.5542	-2.7986	0.3813	-0.5385	-0.1787		
31H	-1.8747	-3.4376	-0.1861	0.2232	0.0594		
32H	-2.0902	-2.5196	1.3340	0.2922	0.1585		
33H	-3.5027	-3.3155	0.5454	0.1847	0.0469		
34C	-1.7867	1.4187	-2.0009	-0.9667	0.0641		

35C	1.8816	1.2140	1.2193	-0.5403	0.0745		
36H	2.5523	1.8409	1.8106	0.1849	0.0210		
37H	1.2708	0.5878	1.9012	0.2973	0.1129		
38H	-2.5302	2.1000	-2.4216	0.2032	0.0787		
39H	-1.1760	1.0258	-2.8224	0.2593	-0.0518		
40Br	-0.7357	-0.5644	2.7131	-0.5087	-0.7310		

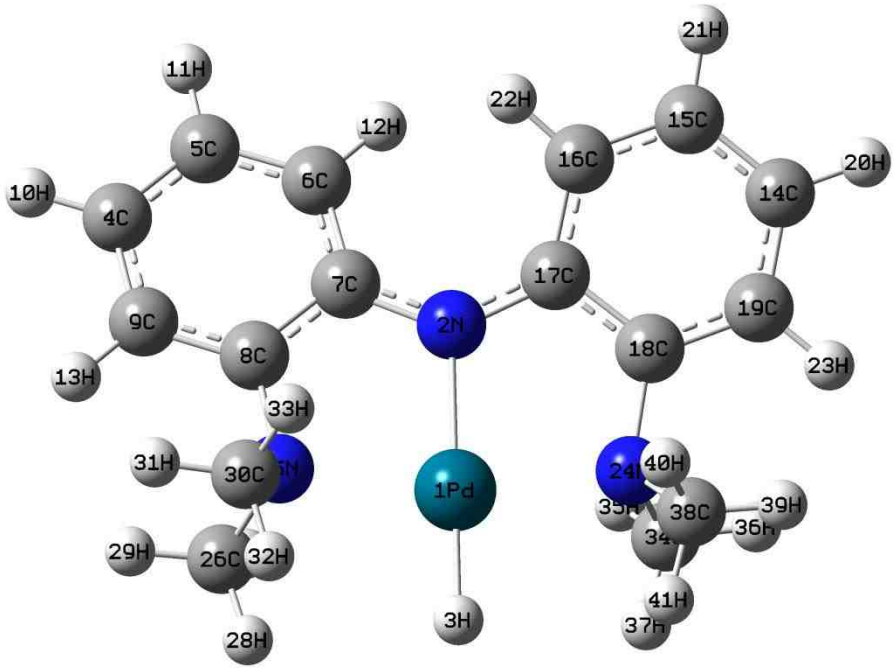
*** *** ***

(NNN) palladium hydride **47**

(see Figure 3-18)



47



Energy: -913.34604436 hartrees

Palladium-hydrogen bond length: 1.609 Å

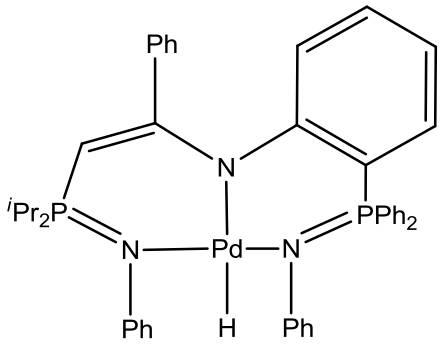
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-1.3712	0.0000	-0.1743	-0.2198		
2N	0.0000	0.6748	0.0000	-0.2595	-0.4573		
3H	0.0000	-2.9798	0.0000	0.0271	-0.2379		
4C	-3.9570	2.1526	-0.2208	-0.3497	-0.1814		
5C	-2.8904	3.0351	-0.4084	-0.4757	-0.0990		
6C	-1.5708	2.5933	-0.3455	0.0373	-0.2599		
7C	-1.2511	1.2334	-0.0860	0.3349	0.3072		
8C	-2.3597	0.3382	0.0374	-0.4250	-0.1616		
9C	-3.6725	0.8001	-0.0082	-0.1197	-0.1618		
10H	-4.9857	2.4983	-0.2580	0.1724	0.1159		
11H	-3.0834	4.0854	-0.6151	0.1731	0.1151		
12H	-0.7781	3.3009	-0.5445	0.1710	0.1391		
13H	-4.4959	0.1012	0.1120	0.1730	0.1288		
14C	3.9570	2.1526	0.2208	-0.3497	-0.1813		

15C	2.8904	3.0351	0.4084	-0.4757	-0.0990		
16C	1.5708	2.5933	0.3455	0.0373	-0.2599		
17C	1.2511	1.2334	0.0860	0.3349	0.3072		
18C	2.3597	0.3382	-0.0374	-0.4250	-0.1616		
19C	3.6725	0.8001	0.0082	-0.1197	-0.1618		
20H	4.9857	2.4983	0.2580	0.1724	0.1159		
21H	3.0835	4.0854	0.6151	0.1731	0.1151		
22H	0.7781	3.3009	0.5445	0.1710	0.1391		
23H	4.4959	0.1011	-0.1120	0.1730	0.1288		
24N	2.0949	-1.1192	-0.2183	-0.2059	0.6203		
25N	-2.0949	-1.1192	0.2183	-0.2059	0.6203		
26C	-2.8045	-1.9340	-0.8086	-0.3308	-0.2148		
27H	-2.5051	-1.5941	-1.8012	0.2406	0.0482		
28H	-2.5148	-2.9781	-0.6822	0.2397	0.0697		
29H	-3.8941	-1.8413	-0.7066	0.2057	0.0459		
30C	-2.5045	-1.5620	1.5822	-0.3307	-0.2071		
31H	-3.5861	-1.4280	1.7237	0.2150	0.0421		
32H	-2.2461	-2.6154	1.7053	0.2361	0.0558		
33H	-1.9692	-0.9675	2.3243	0.2420	0.0550		
34C	2.5045	-1.5620	-1.5822	-0.3307	-0.2071		
35H	1.9693	-0.9675	-2.3243	0.2420	0.0550		
36H	3.5861	-1.4281	-1.7237	0.2150	0.0421		
37H	2.2460	-2.6154	-1.7053	0.2361	0.0558		
38C	2.8045	-1.9340	0.8086	-0.3308	-0.2148		
39H	3.8941	-1.8413	0.7066	0.2057	0.0459		
40H	2.5050	-1.5941	1.8012	0.2406	0.0482		
41H	2.5148	-2.9781	0.6822	0.2397	0.0697		

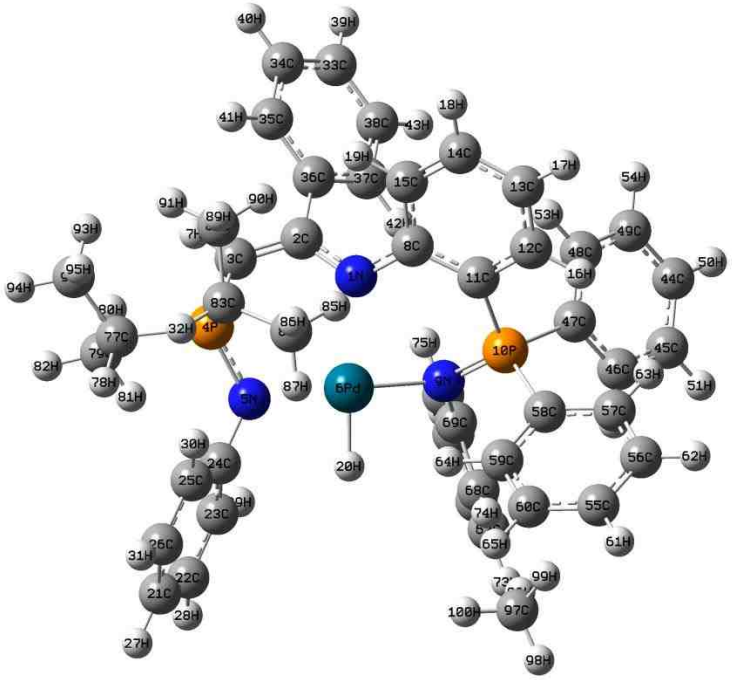
*** *** ***

(NNN) palladium hydride **48**

(see Figure 3-18)



48



Energy: -2677.51075044 hartrees

Palladium-hydrogen bond length: 1.550 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1N	-0.4980	1.2906	0.3637	-0.2632	-0.3308		
2C	-1.3671	2.1802	-0.2130	0.4963	0.3462		
3C	-2.6860	1.8610	-0.4308	-0.8124	-0.6596		
4P	-3.4997	0.4138	0.1977	0.9814	0.5792		

5N	-2.7083	-0.9688	-0.2266	0.0019	-0.4537		
6Pd	-0.6085	-0.7924	-0.3901	0.0438	0.1355		
7H	-3.2864	2.4957	-1.0742	0.2145	0.1974		
8C	0.4220	1.6966	1.2998	0.5465	0.3826		
9N	1.4475	-0.6596	-0.7358	-0.0444	-0.4811		
10P	2.3667	-0.3162	0.5525	-0.3963	0.7038		
11C	1.6231	0.9707	1.5910	0.3550	-0.2881		
12C	2.4080	1.3267	2.7076	-0.2415	-0.1026		
13C	2.1031	2.4128	3.5176	-0.8060	-0.1631		
14C	0.9695	3.1761	3.2012	-0.6614	-0.1006		
15C	0.1591	2.8246	2.1347	-0.1895	-0.2275		
16H	3.2975	0.7456	2.9363	0.1933	0.1028		
17H	2.7294	2.6599	4.3695	0.1753	0.1081		
18H	0.7034	4.0380	3.8095	0.1783	0.1129		
19H	-0.7403	3.4000	1.9435	0.1853	0.1157		
20H	-0.5809	-2.2573	-0.8973	0.1004	-0.1167		
21C	-4.7349	-4.6906	-0.6759	-0.1079	-0.0942		
22C	-3.8327	-4.2278	-1.6439	-0.5213	-0.2489		
23C	-3.1760	-3.0104	-1.4825	-0.0532	0.0213		
24C	-3.3893	-2.2072	-0.3410	-0.4717	0.1723		
25C	-4.2919	-2.6912	0.6285	0.5095	-0.1294		
26C	-4.9580	-3.9112	0.4592	-0.7453	-0.1848		
27H	-5.2457	-5.6413	-0.8043	0.1684	0.1028		
28H	-3.6422	-4.8201	-2.5363	0.1726	0.1366		
29H	-2.4722	-2.6606	-2.2308	0.2014	0.0617		
30H	-4.4631	-2.1250	1.5392	0.1685	0.0981		
31H	-5.6435	-4.2533	1.2318	0.1692	0.1147		
32H	-4.7322	0.0507	2.2266	0.2288	-0.1079		
33C	0.1273	5.8831	-1.8598	-0.2966	-0.1067		
34C	-1.1317	5.8495	-1.2529	-0.3400	-0.1556		
35C	-1.6160	4.6580	-0.7076	-0.2292	-0.0622		
36C	-0.8493	3.4821	-0.7533	0.4559	-0.0171		
37C	0.4172	3.5295	-1.3602	0.0124	-0.0710		
38C	0.8983	4.7170	-1.9134	-0.3863	-0.1311		
39H	0.5049	6.8093	-2.2859	0.1764	0.1078		
40H	-1.7351	6.7525	-1.1980	0.1770	0.1170		
41H	-2.5881	4.6426	-0.2213	0.1891	0.0770		
42H	1.0105	2.6211	-1.4087	0.2140	0.0615		
43H	1.8751	4.7316	-2.3910	0.1789	0.1192		

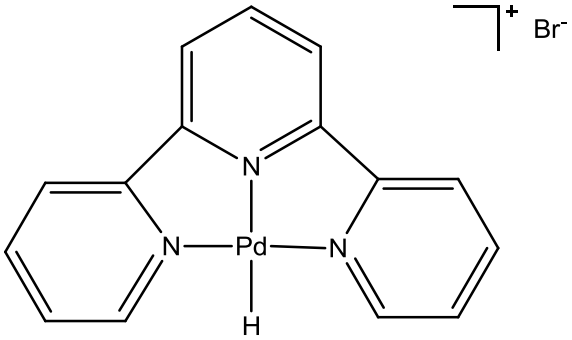
44C	6.4190	1.2746	-1.0654	-0.0677	-0.0710		
45C	6.1656	-0.0996	-1.0374	-0.3283	-0.1872		
46C	4.9656	-0.5810	-0.5096	0.2534	0.0292		
47C	4.0037	0.3091	-0.0007	-0.0695	-0.0710		
48C	4.2627	1.6889	-0.0414	-0.1102	-0.1077		
49C	5.4654	2.1669	-0.5676	-0.3660	-0.1290		
50H	7.3542	1.6481	-1.4749	0.1828	0.1105		
51H	6.8982	-0.7997	-1.4302	0.1853	0.1282		
52H	4.7804	-1.6505	-0.5028	0.2138	0.0405		
53H	3.5307	2.3912	0.3450	0.2256	0.1184		
54H	5.6555	3.2370	-0.5859	0.1840	0.1137		
55C	3.1342	-3.9416	3.3721	-0.1518	-0.0801		
56C	4.1420	-2.9880	3.2053	-0.6032	-0.1731		
57C	3.9422	-1.8981	2.3530	0.2065	-0.0448		
58C	2.7304	-1.7514	1.6583	-0.1028	-0.0656		
59C	1.7221	-2.7154	1.8307	0.0651	-0.0311		
60C	1.9247	-3.8023	2.6836	-0.0667	-0.1441		
61H	3.2911	-4.7901	4.0334	0.1824	0.1120		
62H	5.0861	-3.0913	3.7344	0.1823	0.1245		
63H	4.7393	-1.1712	2.2267	0.2034	0.0713		
64H	0.7812	-2.6119	1.2940	0.2546	0.0568		
65H	1.1369	-4.5411	2.8067	0.1900	0.1253		
66C	2.9918	-2.4565	-4.2631	-0.1533	-0.2158		
67C	2.8391	-3.2225	-3.1023	-0.3335	-0.0831		
68C	2.3358	-2.6449	-1.9345	-0.2945	-0.1870		
69C	1.9821	-1.2850	-1.9031	0.1735	0.4217		
70C	2.1311	-0.5258	-3.0744	-0.0039	-0.3760		
71C	2.6310	-1.1058	-4.2430	-0.6078	-0.0057		
72H	3.3784	-2.9089	-5.1729	0.1705	0.1227		
73H	3.1037	-4.2776	-3.1070	0.1729	0.1004		
74H	2.1910	-3.2514	-1.0453	0.2027	0.0976		
75H	1.8409	0.5208	-3.0560	0.1839	0.1635		
76H	2.7368	-0.4996	-5.1398	0.1726	0.0934		
77C	-5.1974	0.4162	-0.5856	-0.2202	0.3539		
78H	-5.6402	-0.5320	-0.2568	0.2482	-0.0786		
79C	-5.0790	0.3689	-2.1206	-0.7423	-0.1666		
80H	-4.6669	1.3004	-2.5250	0.2245	0.0269		
81H	-4.4436	-0.4559	-2.4537	0.2561	0.0053		
82H	-6.0761	0.2279	-2.5567	0.2089	0.0397		

83C	-3.7702	0.5599	2.0627	-0.1239	0.4569		
84C	-2.6871	-0.1877	2.8610	-0.6438	-0.2267		
85H	-1.7126	0.2971	2.7533	0.2601	0.0300		
86H	-2.9542	-0.1838	3.9260	0.2037	0.0421		
87H	-2.5752	-1.2256	2.5372	0.2411	0.0096		
88C	-3.8998	2.0109	2.5587	-0.7668	-0.3855		
89H	-4.1962	2.0109	3.6160	0.2105	0.0730		
90H	-2.9415	2.5319	2.4797	0.2439	0.0820		
91H	-4.6407	2.5923	2.0029	0.2145	0.0696		
92C	-6.1216	1.5572	-0.1269	-0.7596	-0.3247		
93H	-5.7071	2.5446	-0.3622	0.2301	0.0644		
94H	-7.0829	1.4728	-0.6495	0.2161	0.0696		
95H	-6.3304	1.5211	0.9467	0.2245	0.0602		

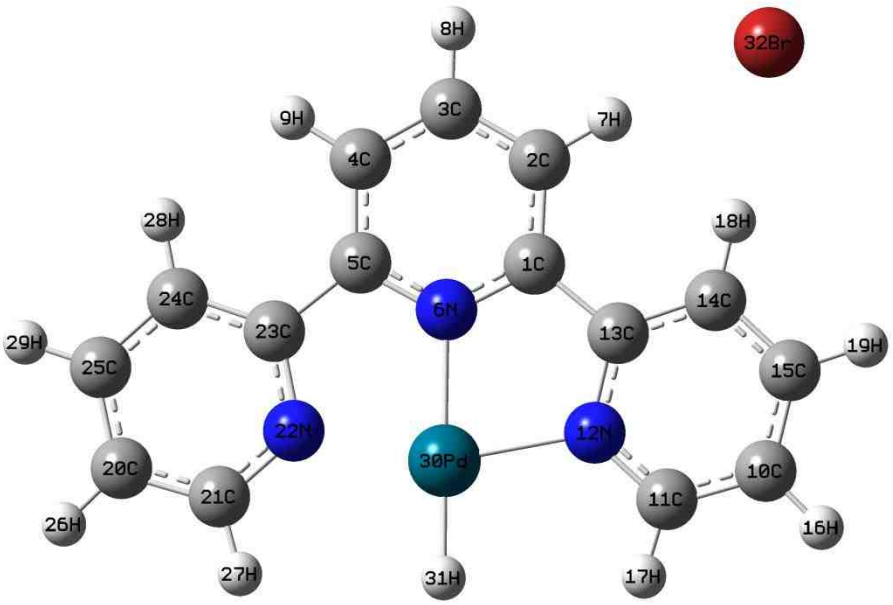
*** *** ***

(NNN) palladium hydride **49**

(see Figure 3-18)



49



Energy: -883.04876431 hartrees

Palladium-hydrogen bond length: 1.582 Å

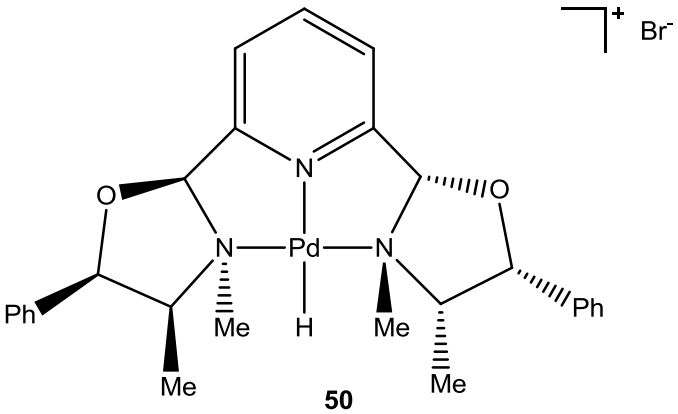
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	0.7338	-0.3847	0.0086	0.4955	0.1289		
2C	1.4798	-1.5732	0.0111	-0.7139	-0.1125		
3C	0.7690	-2.7780	0.0107	-0.7501	-0.0137		
4C	-0.6305	-2.8056	0.0083	-0.5388	-0.1818		
5C	-1.3140	-1.5840	0.0053	0.6986	0.0944		
6N	-0.6065	-0.4452	0.0056	-0.1157	-0.0440		
7H	2.5780	-1.5735	0.0107	0.2307	0.1434		
8H	1.3275	-3.7100	0.0121	0.2251	0.1200		
9H	-1.1598	-3.7526	0.0081	0.1960	0.1405		
10C	2.1042	3.6323	0.0021	-0.2001	-0.1141		
11C	0.7503	3.2909	-0.0019	-0.0395	-0.0665		
12N	0.3356	2.0157	0.0007	0.1723	0.0230		
13C	1.2678	1.0025	0.0075	-0.2898	0.1037		
14C	2.6351	1.2789	0.0131	0.2578	-0.1216		
15C	3.0528	2.6128	0.0098	-0.3668	-0.0008		
16H	2.3906	4.6793	-0.0006	0.2035	0.1248		

17H	-0.0300	4.0423	-0.0073	0.2168	0.1379		
18H	3.3746	0.4684	0.0194	0.2310	0.1526		
19H	4.1163	2.8343	0.0133	0.2267	0.1135		
20C	-5.4952	-0.7953	-0.0066	-0.2792	-0.0889		
21C	-4.5258	0.2068	-0.0064	-0.0300	-0.0639		
22N	-3.2106	-0.0609	-0.0027	0.1478	0.0441		
23C	-2.7845	-1.3657	0.0011	0.0049	0.1239		
24C	-3.7130	-2.4099	0.0011	0.1529	-0.1613		
25C	-5.0783	-2.1256	-0.0028	-0.4614	-0.0524		
26H	-6.5466	-0.5279	-0.0096	0.2103	0.1258		
27H	-4.7911	1.2574	-0.0093	0.2275	0.1434		
28H	-3.3692	-3.4384	0.0041	0.2023	0.1463		
29H	-5.8031	-2.9344	-0.0029	0.2106	0.1290		
30Pd	-1.6271	1.3198	-0.0025	-0.0711	-0.0739		
31H	-2.4112	2.6943	-0.0093	0.0795	-0.1478		
32Br	4.9724	-1.3866	-0.0087	-0.5332	-0.7519		

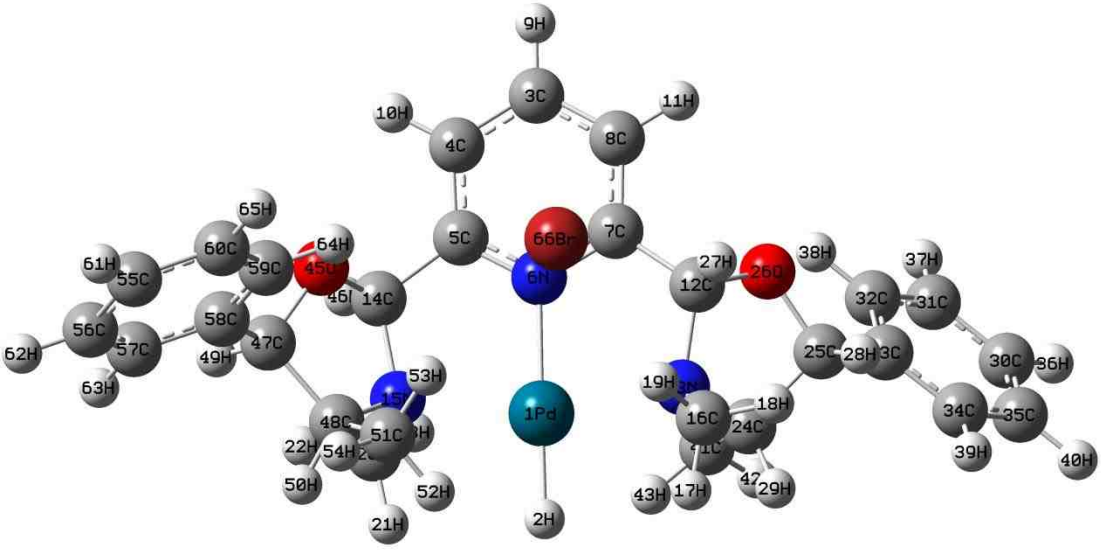
*** *** ***

(NNN) palladium hydride **50**

(see Figure 3-18)



50



Energy: -1502.78231421 hartrees

Palladium-hydrogen bond length: 1.585 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.1366	-1.0663	-0.7230	-0.3367	-0.0300		
2H	-0.1805	-1.9215	-2.0567	0.0936	-0.1674		
3C	-0.1060	1.4699	3.3288	-0.3140	0.0602		
4C	0.8619	0.4816	3.1223	-0.1810	-0.2209		
5C	0.8193	-0.2390	1.9310	0.2157	0.0747		
6N	-0.1304	0.0053	1.0259	0.3512	-0.2393		
7C	-1.0385	0.9723	1.1803	0.1220	0.2818		
8C	-1.0669	1.7296	2.3504	-0.4356	-0.2810		
9H	-0.0930	2.0561	4.2431	0.2001	0.1083		
10H	1.6418	0.2948	3.8532	0.2084	0.1415		
11H	-1.8008	2.5184	2.4753	0.2125	0.1623		
12C	-1.9745	1.2016	0.0091	-0.2038	0.5049		
13N	-1.8349	0.1871	-1.1446	-0.0079	0.1974		
14C	1.8520	-1.2854	1.5469	-0.2727	0.4973		
15N	1.6279	-1.9577	0.1783	0.1624	0.0583		
16C	-1.5207	0.9264	-2.4124	-0.3785	-0.1323		
17H	-1.4025	0.1970	-3.2143	0.2330	0.0552		

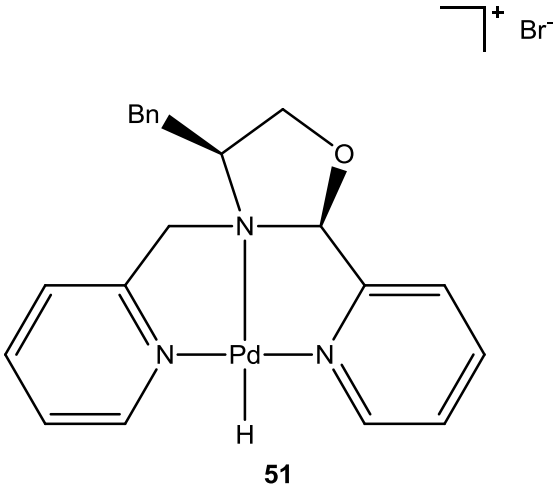
18H	-2.3280	1.6280	-2.6633	0.2224	0.0224		
19H	-0.5900	1.4841	-2.2657	0.3133	0.0668		
20C	1.3585	-3.4093	0.3784	-0.4133	-0.1598		
21H	1.1855	-3.8720	-0.5934	0.2511	0.0790		
22H	2.2015	-3.9069	0.8800	0.2292	0.0472		
23H	0.4586	-3.5304	0.9864	0.2390	0.0403		
24C	-3.1968	-0.4649	-1.2277	-0.3263	-0.0016		
25C	-4.1052	0.6444	-0.6314	-0.5851	0.3474		
26O	-3.3148	1.1132	0.4643	-0.1934	-0.6028		
27H	-1.7632	2.1927	-0.4102	0.2888	-0.0162		
28H	-4.2097	1.4535	-1.3714	0.2003	-0.0114		
29H	-3.4157	-0.6240	-2.2873	0.2143	0.0201		
30C	-8.0625	-0.5764	0.5972	-0.1934	-0.1122		
31C	-7.0481	-0.4534	1.5507	-0.4045	-0.1554		
32C	-5.7638	-0.0535	1.1693	-0.3229	-0.0848		
33C	-5.4829	0.2312	-0.1728	0.6815	0.0848		
34C	-6.5087	0.1211	-1.1229	-0.1160	-0.2095		
35C	-7.7893	-0.2871	-0.7434	-0.1362	-0.0850		
36H	-9.0603	-0.8862	0.8968	0.1809	0.1129		
37H	-7.2560	-0.6650	2.5965	0.1817	0.1215		
38H	-4.9794	0.0516	1.9116	0.2093	0.1105		
39H	-6.3082	0.3618	-2.1655	0.1754	0.1088		
40H	-8.5739	-0.3683	-1.4913	0.1827	0.1112		
41C	-3.2752	-1.7947	-0.4840	-0.7644	-0.0843		
42H	-4.2669	-2.2398	-0.6182	0.2315	0.0458		
43H	-2.5217	-2.4821	-0.8799	0.2489	-0.0001		
44H	-3.1018	-1.6688	0.5894	0.2402	-0.0120		
45O	3.0973	-0.6503	1.4903	-0.0976	-0.4110		
46H	1.8730	-2.0963	2.2948	0.2028	-0.0467		
47C	3.9278	-1.3854	0.5822	-0.4649	-0.0729		
48C	2.9446	-1.7528	-0.5694	-0.5890	0.4402		
49H	4.2539	-2.3162	1.0758	0.1762	0.0542		
50H	3.2240	-2.7272	-0.9840	0.2076	-0.0711		
51C	2.8423	-0.7364	-1.6995	-0.7834	-0.3728		
52H	2.1186	-1.0885	-2.4408	0.2331	0.0619		
53H	2.5243	0.2541	-1.3556	0.3155	0.1536		
54H	3.8172	-0.6386	-2.1892	0.2282	0.0667		
55C	7.4295	0.9068	-0.4620	-0.1035	-0.1606		
56C	7.5214	-0.4746	-0.2714	-0.1920	-0.0707		

57C	6.3824	-1.2047	0.0804	-0.1799	-0.2572		
58C	5.1446	-0.5655	0.2308	0.6221	0.2499		
59C	5.0558	0.8229	0.0421	-0.0017	-0.2048		
60C	6.1975	1.5502	-0.3015	-0.5290	-0.0552		
61H	8.3136	1.4798	-0.7306	0.1776	0.1171		
62H	8.4759	-0.9822	-0.3856	0.1765	0.1046		
63H	6.4604	-2.2784	0.2442	0.1645	0.1127		
64H	4.1033	1.3347	0.1551	0.2685	0.1610		
65H	6.1174	2.6240	-0.4482	0.1950	0.1060		
66Br	1.2308	2.7377	-0.6987	-0.5300	-0.7590		

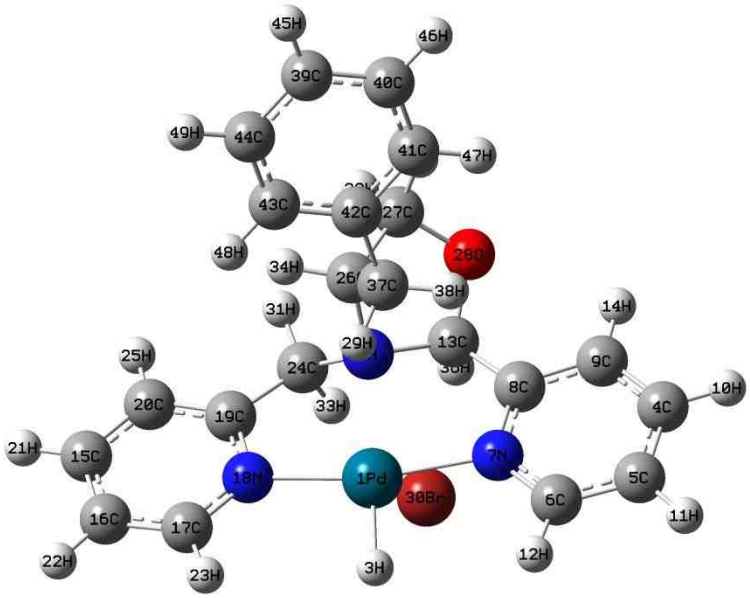
*** *** ***

(NNN) palladium hydride **51**

(see Figure 3-18)



51



Energy: -1192.91563621 hartrees

Palladium-hydrogen bond length: 1.561 Å

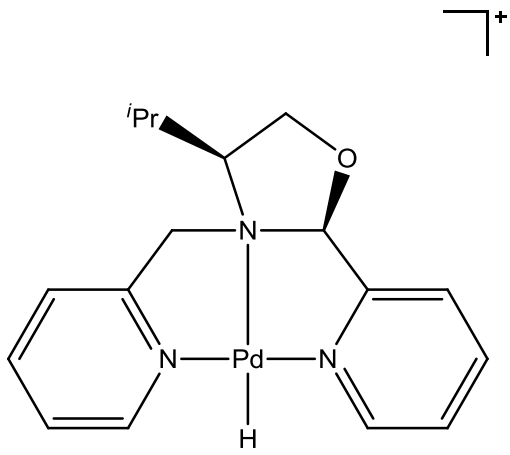
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.9354	0.2182	1.2715	-0.1024	-0.0840		
2N	-0.0292	0.1174	-0.7183	-0.1457	0.1377		
3H	-1.6054	0.2977	2.6787	0.0937	-0.1078		
4C	-0.5684	-4.5560	0.6805	-0.4234	0.0023		
5C	-0.8988	-4.0955	1.9570	-0.2039	-0.1706		
6C	-1.0058	-2.7254	2.1657	-0.0820	-0.0047		
7N	-0.8029	-1.8333	1.1769	0.4290	-0.0585		
8C	-0.4879	-2.2689	-0.0681	0.0512	0.1787		
9C	-0.3608	-3.6319	-0.3411	-0.5010	-0.2128		
10H	-0.4825	-5.6206	0.4818	0.2023	0.1137		
11H	-1.0781	-4.7802	2.7796	0.1995	0.1379		
12H	-1.2625	-2.3088	3.1318	0.2160	0.1282		
13C	-0.3837	-1.2459	-1.2004	-0.0145	0.5480		
14H	-0.1100	-3.9443	-1.3485	0.2253	0.1490		
15C	-1.1037	4.8224	-0.1589	-0.3647	0.0305		
16C	-1.2764	4.5847	1.2068	-0.2497	-0.1888		

17C	-1.2304	3.2725	1.6656	-0.0525	0.0013		
18N	-1.0303	2.2306	0.8379	0.3662	-0.0568		
19C	-0.8652	2.4440	-0.4972	0.1440	0.2734		
20C	-0.8914	3.7426	-1.0139	-0.2947	-0.2972		
21H	-1.1344	5.8346	-0.5523	0.2020	0.1128		
22H	-1.4482	5.3951	1.9077	0.2002	0.1410		
23H	-1.3615	3.0249	2.7122	0.2178	0.1253		
24C	-0.7733	1.2318	-1.3876	-0.1532	0.0139		
25H	-0.7612	3.8934	-2.0811	0.1996	0.1567		
26C	1.4517	0.2166	-0.9390	-0.9552	-0.1336		
27C	1.6104	-0.6016	-2.2308	-0.3096	0.2652		
28O	0.6400	-1.6481	-2.1183	-0.2138	-0.5626		
29H	1.9107	0.1520	1.1602	0.2453	-0.0864		
30Br	-3.7874	-0.4552	-1.3351	-0.4987	-0.7203		
31H	-0.3295	1.4957	-2.3560	0.2075	0.0255		
32H	1.4003	0.0044	-3.1232	0.2038	-0.0045		
33H	-1.8096	0.8649	-1.5613	0.2751	0.0435		
34H	1.7005	1.2703	-1.0930	0.2204	0.0061		
35H	2.5984	-1.0556	-2.3387	0.2187	0.0270		
36H	-1.3702	-1.2032	-1.6875	0.2856	-0.0445		
37C	2.2814	-0.3252	0.2451	-0.8084	0.1532		
38H	2.1072	-1.4010	0.3566	0.2277	-0.0385		
39C	6.5217	0.4473	-0.2401	-0.1089	-0.0966		
40C	6.0173	-0.8411	-0.4339	-0.3469	-0.1025		
41C	4.6505	-1.0912	-0.2740	-0.2775	-0.2234		
42C	3.7652	-0.0626	0.0799	0.9704	0.1241		
43C	4.2872	1.2262	0.2778	-0.0563	-0.1505		
44C	5.6512	1.4817	0.1189	-0.3409	-0.1490		
45H	7.5839	0.6434	-0.3611	0.1813	0.1099		
46H	6.6863	-1.6540	-0.7053	0.1829	0.1124		
47H	4.2687	-2.1002	-0.4170	0.1800	0.1405		
48H	3.6207	2.0356	0.5712	0.1770	0.1129		
49H	6.0353	2.4856	0.2815	0.1816	0.1227		

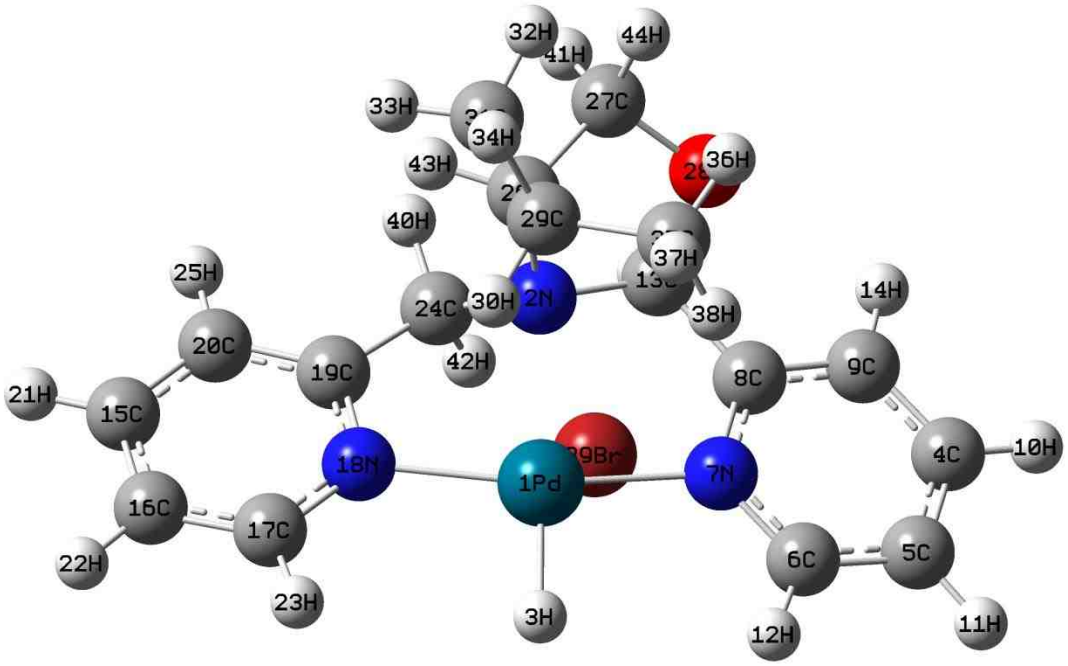
*** *** ***

(NNN) palladium hydride **52**

(see Figure 3-18)



52



Energy: -1040.48423702 hartrees

Palladium-hydrogen bond length: 1.561 Å

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.3209	0.0122	1.3082	-0.0975	-0.1261		
2N	-0.3097	0.5350	-0.8201	-0.1125	0.0903		

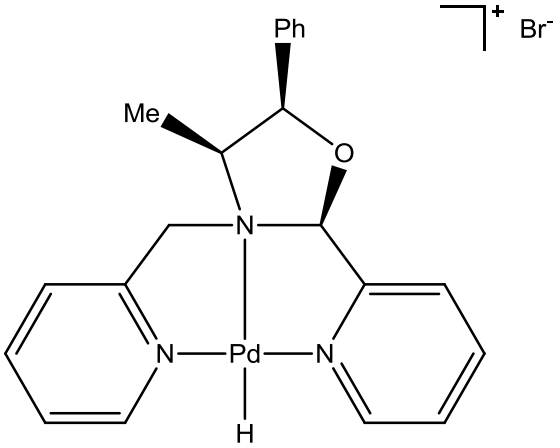
3H	-0.3303	-0.4254	2.8070	0.0886	-0.1121		
4C	4.4260	0.3916	0.6563	-0.3437	-0.0081		
5C	3.9645	0.3395	1.9739	-0.1444	-0.1564		
6C	2.5947	0.3224	2.2014	-0.1479	-0.0254		
7N	1.6995	0.3744	1.1936	0.3896	0.0224		
8C	2.1369	0.4303	-0.0866	1.6078	0.1222		
9C	3.5012	0.4336	-0.3814	-0.9202	-0.1930		
10H	5.4908	0.3844	0.4418	0.2008	0.1218		
11H	4.6491	0.2937	2.8146	0.1976	0.1348		
12H	2.1789	0.2578	3.1989	0.2124	0.1238		
13C	1.1383	0.5018	-1.2379	-1.4077	0.6351		
14H	3.8170	0.4520	-1.4186	0.2175	0.1454		
15C	-4.5963	-1.6457	-0.1809	-0.3453	-0.0018		
16C	-4.4674	-1.4159	1.1912	-0.2174	-0.1730		
17C	-3.2631	-0.9114	1.6712	-0.1117	-0.0298		
18N	-2.2261	-0.6400	0.8585	0.2876	0.0247		
19C	-2.3344	-0.8578	-0.4818	0.2496	0.1913		
20C	-3.5228	-1.3584	-1.0218	-0.2210	-0.2510		
21H	-5.5210	-2.0428	-0.5901	0.2025	0.1209		
22H	-5.2772	-1.6274	1.8816	0.2008	0.1412		
23H	-3.0995	-0.7209	2.7253	0.2175	0.1281		
24C	-1.1036	-0.6328	-1.3210	-0.4317	0.0933		
25H	-3.5899	-1.5315	-2.0915	0.2020	0.1502		
26C	-0.8693	1.8413	-1.3359	-0.3880	-0.3186		
27C	0.1307	2.1683	-2.4548	-0.3806	0.3536		
28O	1.3787	1.7233	-1.9355	-0.1952	-0.5972		
29C	-1.0832	2.9527	-0.2798	0.2304	0.6335		
30H	-1.5910	2.4675	0.5653	0.2092	-0.1575		
31C	-2.0389	4.0165	-0.8529	-0.7358	-0.3049		
32H	-1.5980	4.5367	-1.7137	0.2118	0.0427		
33H	-2.9911	3.5776	-1.1777	0.2036	0.0450		
34H	-2.2635	4.7759	-0.0954	0.2147	0.0622		
35C	0.1929	3.6162	0.2618	-0.6864	-0.3572		
36H	0.7561	4.1267	-0.5280	0.2205	0.0879		
37H	-0.0783	4.3673	1.0136	0.2037	0.0636		
38H	0.8608	2.8962	0.7400	0.2416	0.0191		
39Br	1.4745	-2.9497	-1.0995	-0.5154	-0.7338		
40H	-1.3773	-0.5078	-2.3778	0.2113	0.0142		
41H	-0.1158	1.6302	-3.3831	0.2004	-0.0313		

42H	-0.4477	-1.5303	-1.2514	0.2822	0.0070		
43H	-1.8538	1.6132	-1.7568	0.1961	0.0380		
44H	0.2244	3.2332	-2.6787	0.2132	0.0261		
45H	1.3023	-0.3708	-1.8822	0.2893	-0.0613		

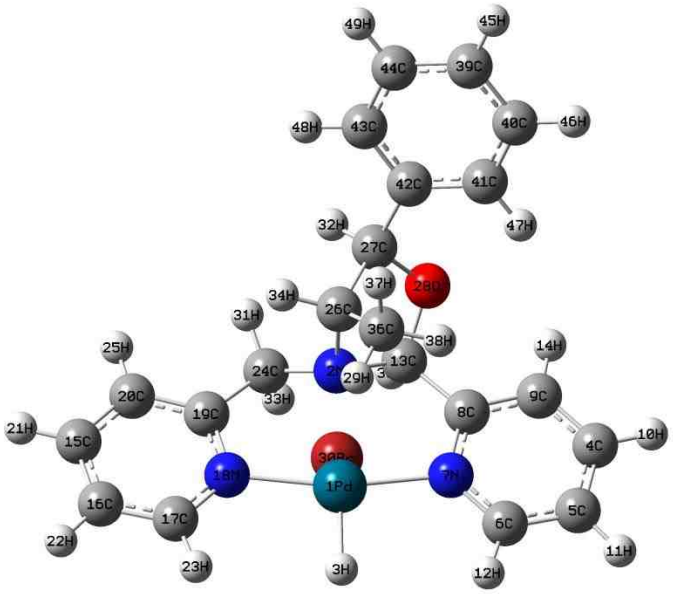
*** *** ***

(NNN) palladium hydride **53**

(see Figure 3-18)



53



Energy: -1192.91764688 hartrees

Palladium-hydrogen bond length: 1.562 Å

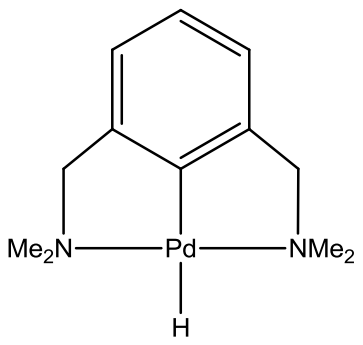
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-1.4979	0.2429	-1.2965	-0.1154	-0.0868		
2N	-0.0147	-0.4501	0.1519	-0.1684	0.0242		
3H	-2.5857	0.7404	-2.3014	0.0925	-0.1105		
4C	1.1001	4.2633	-0.7038	-0.3488	-0.0152		
5C	0.1895	4.2423	-1.7631	-0.2141	-0.1488		
6C	-0.5609	3.0921	-1.9750	-0.0893	-0.0047		
7N	-0.4333	1.9998	-1.1955	0.4010	-0.0601		
8C	0.4487	2.0076	-0.1657	0.2401	0.1529		
9C	1.2287	3.1349	0.1018	-0.3973	-0.1928		
10H	1.6939	5.1505	-0.5025	0.2027	0.1174		
11H	0.0510	5.1017	-2.4110	0.2005	0.1315		
12H	-1.2890	3.0193	-2.7734	0.2163	0.1259		
13C	0.5079	0.8029	0.7703	-0.3618	0.5955		
14H	1.9130	3.1134	0.9428	0.2246	0.1535		
15C	-3.3065	-4.0280	0.0201	-0.2958	0.0189		
16C	-3.8141	-3.4695	-1.1558	-0.2643	-0.1744		
17C	-3.3146	-2.2426	-1.5790	-0.0516	0.0032		
18N	-2.3659	-1.5794	-0.8920	0.3025	-0.0578		
19C	-1.8616	-2.1083	0.2573	0.2673	0.2537		
20C	-2.3202	-3.3434	0.7263	-0.2417	-0.2807		
21H	-3.6748	-4.9840	0.3818	0.2021	0.1146		
22H	-4.5847	-3.9670	-1.7354	0.2007	0.1361		
23H	-3.6712	-1.7567	-2.4792	0.2175	0.1236		
24C	-0.8939	-1.2676	1.0474	-0.3192	0.0358		
25H	-1.9119	-3.7476	1.6475	0.2005	0.1569		
26C	1.2156	-1.1949	-0.2784	-0.7444	0.1135		
27C	2.1950	-0.8105	0.8681	-0.3913	0.2644		
28O	1.8737	0.5586	1.1300	-0.2458	-0.5878		
29H	0.8928	-0.9973	-2.4071	0.2375	-0.0210		
30Br	-2.3615	1.4028	2.6827	-0.5038	-0.7223		
31H	-0.3088	-1.8967	1.7302	0.2072	0.0076		
32H	1.9404	-1.4086	1.7569	0.1944	-0.0019		

33H	-1.4828	-0.5527	1.6675	0.2692	0.0524		
34H	0.9856	-2.2642	-0.2503	0.2151	-0.0368		
35H	-0.1058	1.0432	1.6553	0.2797	-0.0579		
36C	1.6916	-0.8193	-1.6806	-0.7396	-0.0762		
37H	2.5591	-1.4287	-1.9534	0.2353	0.0343		
38H	1.9883	0.2313	-1.7485	0.2450	-0.0007		
39C	6.3921	-1.4088	0.0195	-0.1925	-0.1383		
40C	5.8301	-0.1372	-0.1242	-0.5871	-0.1059		
41C	4.4766	0.0733	0.1551	-0.3567	-0.1594		
42C	3.6695	-0.9873	0.5848	0.8979	0.1654		
43C	4.2434	-2.2573	0.7429	0.0464	-0.2462		
44C	5.5934	-2.4708	0.4555	-0.0903	-0.0658		
45H	7.4451	-1.5697	-0.1965	0.1811	0.1162		
46H	6.4473	0.6964	-0.4499	0.1812	0.1118		
47H	4.0444	1.0635	0.0567	0.2082	0.1178		
48H	3.6331	-3.0849	1.1009	0.1717	0.1172		
49H	6.0228	-3.4612	0.5831	0.1814	0.1075		

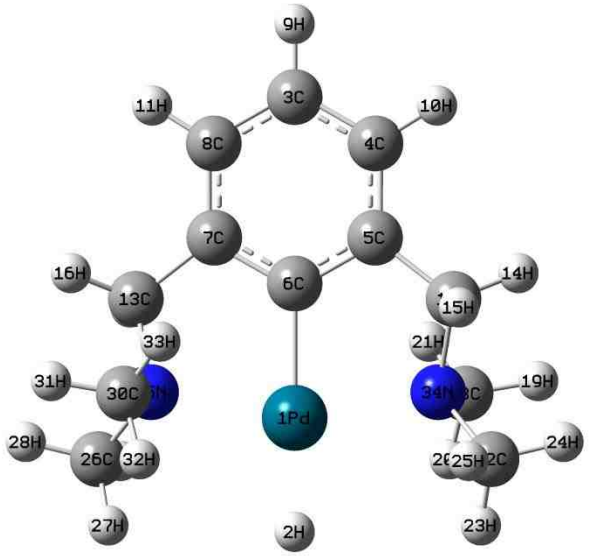
*** *** ***

(NCN) palladium hydride **54**

(see Figure 3-18, Figure 3-33, Figure 5-7)



54



Energy: -705.53965417 hartrees

Palladium-hydrogen bond length: 1.694 Å

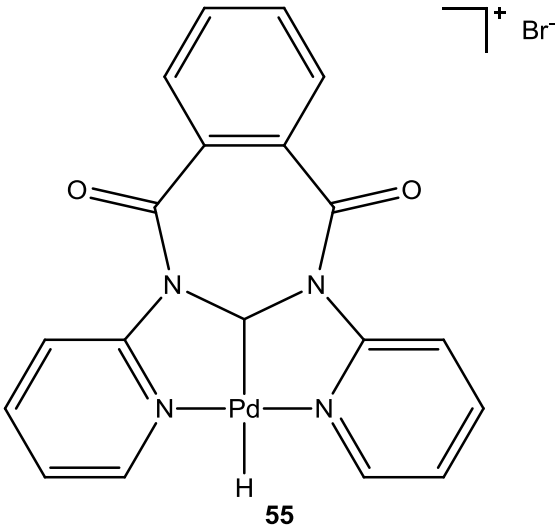
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0000	-1.0734	0.0000	-0.2998	-0.1584		
2H	0.0000	-2.7671	0.0001	-0.0640	-0.3665		
3C	0.0000	3.6935	0.0000	-0.0479	-0.0534		
4C	1.2060	3.0048	0.2112	-0.1822	-0.3178		
5C	1.1989	1.6038	0.2221	0.3423	0.2763		
6C	0.0000	0.9234	-0.0001	-0.5458	-0.4263		
7C	-1.1989	1.6038	-0.2222	0.3428	0.2762		
8C	-1.2059	3.0048	-0.2112	-0.1825	-0.3178		
9H	0.0000	4.7809	0.0001	0.1705	0.1031		
10H	2.1240	3.5688	0.3735	0.1684	0.1366		
11H	-2.1239	3.5689	-0.3734	0.1684	0.1366		
12C	2.3686	0.6945	0.5370	-0.6025	-0.1775		
13C	-2.3686	0.6945	-0.5371	-0.6025	-0.1774		
14H	3.3376	1.0783	0.1796	0.2043	0.0407		
15H	2.4518	0.5685	1.6232	0.2196	0.0575		
16H	-3.3376	1.0784	-0.1798	0.2043	0.0406		
17H	-2.4517	0.5684	-1.6233	0.2196	0.0576		

18C	2.5495	-0.7126	-1.4609	-0.4501	-0.0858		
19H	3.6324	-0.5257	-1.5509	0.2020	0.0081		
20H	2.3106	-1.6886	-1.8877	0.2408	0.0301		
21H	2.0031	0.0596	-2.0049	0.2441	0.0256		
22C	2.9364	-1.6866	0.7182	-0.4483	-0.1362		
23H	2.7774	-2.6713	0.2771	0.2443	0.0606		
24H	4.0088	-1.4316	0.6885	0.2018	0.0125		
25H	2.5961	-1.7132	1.7555	0.2264	0.0333		
26C	-2.9366	-1.6867	-0.7182	-0.4484	-0.1376		
27H	-2.7780	-2.6713	-0.2767	0.2443	0.0609		
28H	-4.0090	-1.4315	-0.6888	0.2018	0.0130		
29H	-2.5961	-1.7136	-1.7554	0.2264	0.0335		
30C	-2.5494	-0.7124	1.4611	-0.4503	-0.0860		
31H	-3.6324	-0.5260	1.5511	0.2020	0.0081		
32H	-2.3101	-1.6882	1.8881	0.2408	0.0301		
33H	-2.0034	0.0602	2.0049	0.2441	0.0257		
34N	2.1409	-0.6913	-0.0342	-0.2173	0.4866		
35N	-2.1410	-0.6913	0.0342	-0.2173	0.4872		

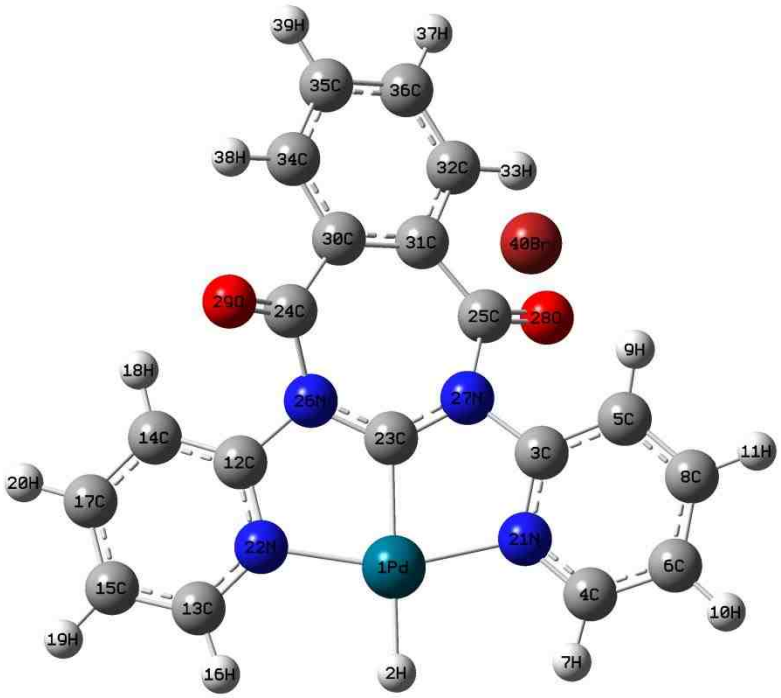
*** *** ***

(NCN) palladium hydride **55**

(see Figure 3-18)



55



Energy: -1241.23468085 hartrees

Palladium-hydrogen bond length: 1.636 Å

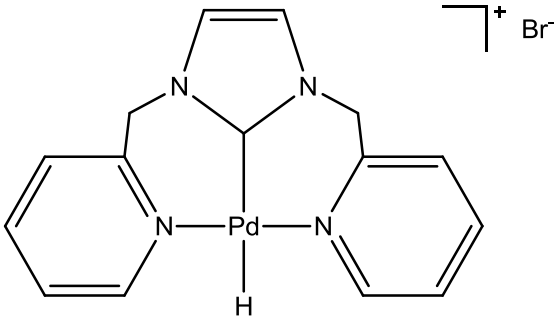
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	2.3174	1.1026	-0.0520	-0.0111	-0.0157		
2H	3.6972	1.9781	0.0222	-0.0001	-0.2246		
3C	-0.3421	2.1472	-0.3670	-0.5264	0.2404		
4C	1.1530	3.9355	-0.1839	-0.2401	-0.0158		
5C	-1.4379	3.0062	-0.3145	0.7268	-0.1516		
6C	0.1122	4.8542	-0.1607	-0.2272	-0.1553		
7H	2.1935	4.2272	-0.1193	0.2246	0.1346		
8C	-1.1977	4.3747	-0.2142	-0.6002	-0.0175		
9H	-2.4418	2.6067	-0.3107	0.2719	0.1936		
10H	0.3296	5.9145	-0.0860	0.2015	0.1341		
11H	-2.0401	5.0583	-0.1670	0.2103	0.1167		
12C	2.1206	-1.7656	0.0436	-0.3544	0.3983		
13C	4.3785	-1.1672	0.1671	-0.2088	-0.0300		
14C	2.4572	-3.1191	-0.0405	0.2831	-0.2834		

15C	4.7825	-2.4946	0.1209	-0.2561	-0.1941		
16H	5.0804	-0.3455	0.2343	0.2328	0.1479		
17C	3.8003	-3.4803	0.0022	-0.2880	0.0483		
18H	1.6872	-3.8732	-0.1247	0.2241	0.1715		
19H	5.8376	-2.7423	0.1652	0.2073	0.1483		
20H	4.0736	-4.5297	-0.0567	0.2091	0.1134		
21N	0.9297	2.6097	-0.2852	0.1458	-0.0459		
22N	3.0792	-0.8098	0.1282	0.1621	-0.0264		
23C	0.6329	0.0369	-0.1867	0.0613	0.1634		
24C	-0.2834	-2.2062	0.5027	-0.7394	0.7514		
25C	-1.6984	0.1979	-1.1293	-0.0421	0.5139		
26N	0.7580	-1.3114	-0.0345	-0.0107	-0.4263		
27N	-0.4904	0.7080	-0.4448	-0.1400	-0.1049		
28O	-2.1469	0.9135	-2.0027	-0.3118	-0.5045		
29O	0.0524	-2.9691	1.3832	-0.3321	-0.4654		
30C	-1.6094	-2.2172	-0.1349	0.7241	-0.2893		
31C	-2.1940	-1.1892	-0.9074	1.0313	0.1805		
32C	-3.4187	-1.4486	-1.5494	-0.0697	-0.2326		
33H	-3.8611	-0.6541	-2.1377	0.2291	0.1716		
34C	-2.3117	-3.4247	0.0502	-0.4631	-0.0107		
35C	-3.5350	-3.6511	-0.5674	-0.2270	-0.1284		
36C	-4.0803	-2.6597	-1.3893	-0.2825	-0.0040		
37H	-5.0322	-2.8205	-1.8875	0.1930	0.1021		
38H	-1.8622	-4.1855	0.6783	0.2182	0.1060		
39H	-4.0545	-4.5925	-0.4141	0.1930	0.1149		
40Br	-3.0674	0.6552	1.5302	-0.4184	-0.6242		

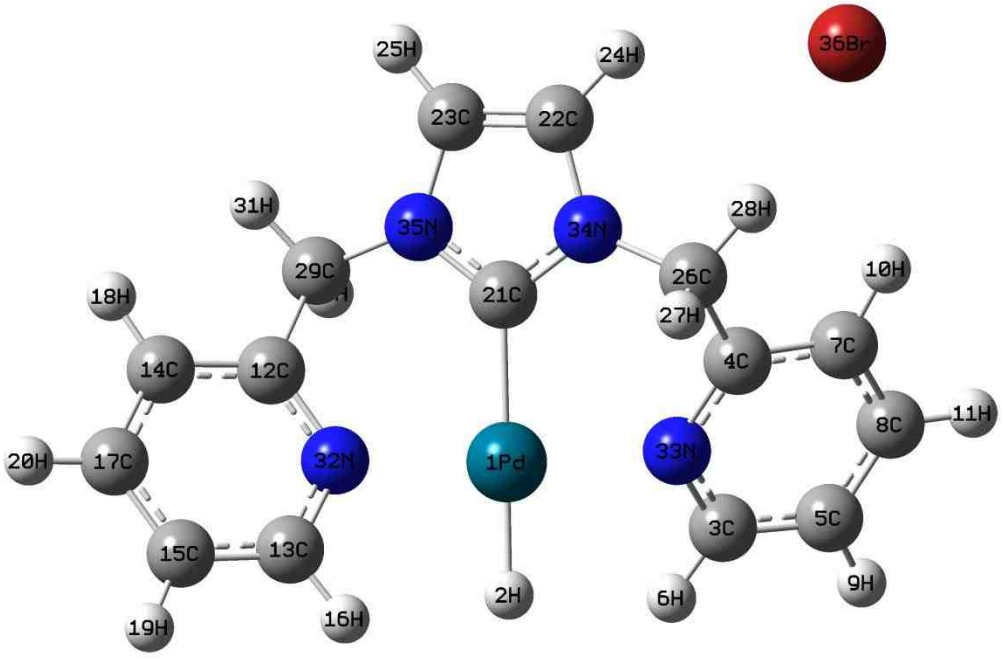
*** *** ***

(NCN) palladium hydride **56**

(see Figure 3-18, Figure 3-33, Figure 5-7)



56



Energy: -939.57806527 hartrees

Palladium-hydrogen bond length: 1.625 Å

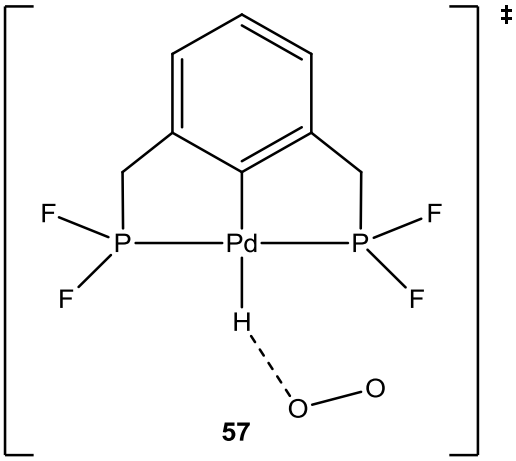
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-1.3092	1.0816	-0.0793	-0.4582	-0.0041		
2H	-2.0261	2.5377	-0.1545	-0.0069	-0.2239		
3C	0.7222	3.1909	0.5073	-0.0428	0.0007		
4C	1.7375	1.2637	-0.3319	0.1548	0.2694		
5C	1.9538	3.7670	0.8006	-0.1484	-0.1926		

6H	-0.2085	3.7054	0.7055	0.2186	0.1283		
7C	3.0037	1.7758	-0.0322	0.0635	-0.2664		
8C	3.1161	3.0423	0.5390	-0.4959	0.0484		
9H	1.9852	4.7607	1.2366	0.1978	0.1340		
10H	3.8713	1.1447	-0.2227	0.2709	0.1779		
11H	4.0948	3.4491	0.7782	0.2089	0.1101		
12C	-3.3177	-1.1825	0.4612	0.1320	0.1386		
13C	-4.1961	0.6469	-0.6873	-0.0224	0.0152		
14C	-4.5245	-1.8698	0.3030	0.1430	-0.2168		
15C	-5.4205	0.0120	-0.8751	-0.1862	-0.1506		
16H	-4.0128	1.6491	-1.0520	0.2359	0.1299		
17C	-5.5900	-1.2749	-0.3716	-0.3065	0.0128		
18H	-4.6221	-2.8718	0.7092	0.1998	0.1417		
19H	-6.2141	0.5275	-1.4060	0.2095	0.1356		
20H	-6.5281	-1.8077	-0.4981	0.2087	0.1154		
21C	-0.4104	-0.7484	0.0482	-0.1436	-0.1640		
22C	1.1745	-2.3504	0.0471	0.0095	-0.1974		
23C	0.0631	-2.8673	0.6469	-0.1637	-0.2592		
24H	2.1754	-2.7364	-0.1183	0.2841	0.2140		
25H	-0.1145	-3.8371	1.0866	0.2086	0.1923		
26C	1.6639	-0.0738	-1.0394	-0.6307	0.0026		
27H	1.2348	0.0602	-2.0399	0.2399	0.0092		
28H	2.6748	-0.4942	-1.1206	0.2574	0.0772		
29C	-2.2113	-1.8369	1.2799	-0.7557	0.0140		
30H	-2.1193	-1.3055	2.2368	0.2617	0.0571		
31H	-2.4995	-2.8668	1.5007	0.2141	0.0799		
32N	-3.1609	0.0719	-0.0373	0.1265	-0.0231		
33N	0.6043	1.9604	-0.0419	0.1803	-0.0797		
34N	0.8420	-1.0494	-0.3169	-0.0483	0.2099		
35N	-0.9082	-1.8583	0.6250	-0.0477	0.1396		
36Br	4.6944	-1.5574	-0.2106	-0.5687	-0.7760		

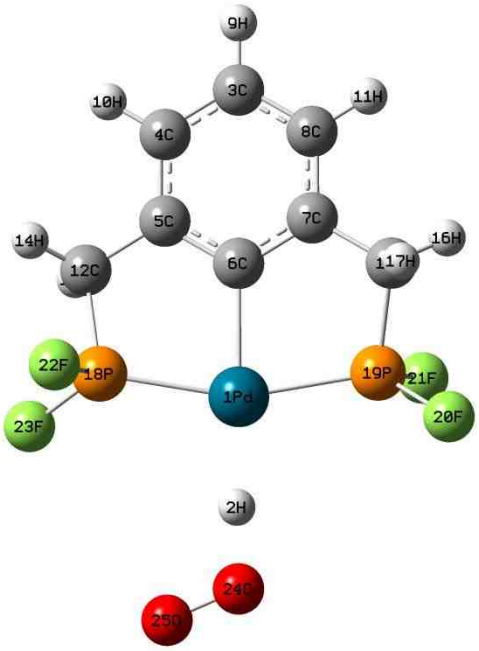
*** *** ***

(PCP) transition state **57**

(see Figure 3-24)



57



Energy: -1668.93946480

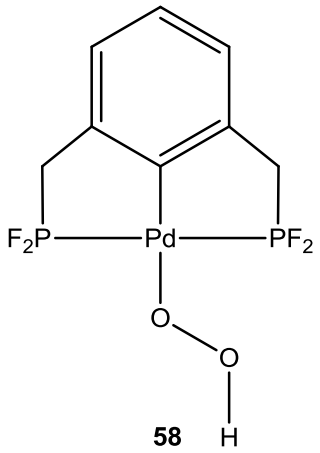
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.6378	0.3636	0.0226	-0.9370		0.1342	-0.2667
2H	2.2632	1.1068	0.0188	0.2338		-0.0688	-0.2592
3C	-3.8395	-1.7872	-0.0541	0.0409		-0.0175	-0.0610
4C	-2.6933	-2.5567	-0.2673	-0.4286		0.0432	-0.0260
5C	-1.4269	-1.9549	-0.2465	-0.3375		-0.0705	-0.1218

6C	-1.3077	-0.5727	0.0053	1.4164		0.3677	0.0696
7C	-2.4698	0.1943	0.2301	-0.2999		-0.0637	-0.1111
8C	-3.7314	-0.4158	0.1895	-0.4743		0.0443	-0.0354
9H	-4.8191	-2.2571	-0.0782	0.1845		0.0008	0.0219
10H	-2.7880	-3.6240	-0.4575	0.1817		0.0025	-0.0004
11H	-4.6299	0.1750	0.3559	0.1816		0.0026	-0.0007
12C	-0.1797	-2.7775	-0.5339	-0.9758		0.0082	-0.1390
13C	-2.3397	1.6770	0.5456	-0.9783		0.0048	-0.1431
14H	-0.1980	-3.7721	-0.0713	0.2621		-0.0009	0.0095
15H	-0.0370	-2.9222	-1.6150	0.2701		-0.0005	0.0126
16H	-3.1244	2.2910	0.0869	0.2614		-0.0010	0.0077
17H	-2.3716	1.8600	1.6299	0.2696		-0.0005	0.0117
18P	1.2739	-1.8234	0.0588	1.4154		0.0658	1.8125
19P	-0.6820	2.2224	-0.0263	1.3641		0.0720	1.9215
20F	-0.4854	3.6012	0.7843	-0.3715		-0.0033	-0.7439
21F	-1.0077	2.8386	-1.4777	-0.3606		-0.0032	-0.6709
22F	1.5455	-2.4743	1.5054	-0.3626		-0.0037	-0.6549
23F	2.4777	-2.5173	-0.7524	-0.3694		-0.0040	-0.6822
24O	3.4431	1.7000	0.0059	-0.0075		0.6619	0.5102
25O	4.3876	0.8703	-0.1492	-0.1783		0.8295	-0.4612

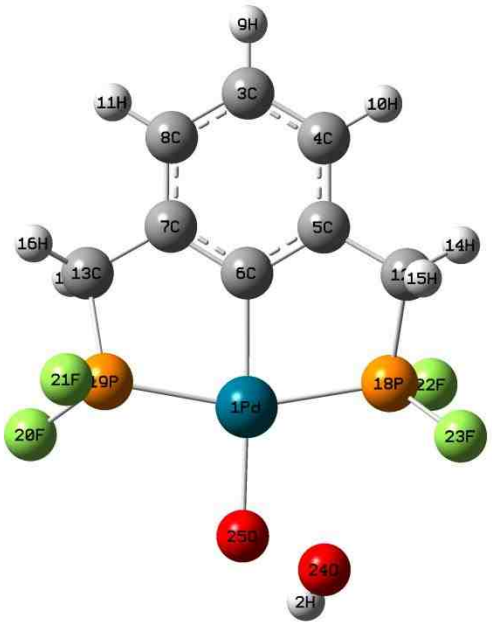
*** *** ***

(PCP) palladium hydroperoxide **58**

(see Figure 3-24, Figure 4-4)



58



Energy: -1669.00494162 hartrees

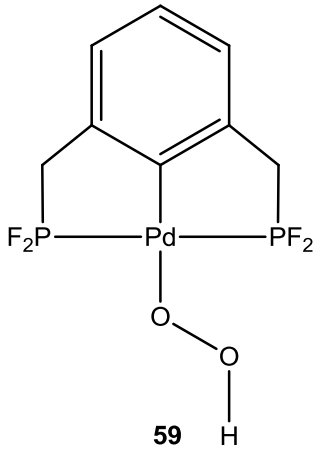
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.3195	-0.7391	0.0244	-0.5687	-0.0842		
2H	2.6753	-2.9886	-1.0602	0.4669	0.3792		
3C	-1.9666	3.6340	-0.0947	-0.0021	-0.0163		
4C	-0.5978	3.5650	0.1674	-0.4960	-0.3085		
5C	0.0534	2.3254	0.2234	-1.0018	0.4054		
6C	-0.6608	1.1254	-0.0099	2.1163	-0.6600		
7C	-2.0460	1.2168	-0.2870	-0.3189	0.3709		
8C	-2.6895	2.4611	-0.3154	-0.4052	-0.3104		
9H	-2.4677	4.5976	-0.1266	0.1848	0.1115		
10H	-0.0352	4.4797	0.3415	0.1819	0.1462		
11H	-3.7564	2.5149	-0.5220	0.1819	0.1462		
12C	1.5356	2.2774	0.5627	-0.8359	-0.4162		
13C	-2.8433	-0.0448	-0.5808	-0.9890	-0.3253		
14H	2.1111	3.0930	0.1091	0.2614	0.1444		
15H	1.6990	2.3214	1.6497	0.2734	0.1187		
16H	-3.8497	-0.0359	-0.1454	0.2628	0.1284		
17H	-2.9507	-0.2113	-1.6629	0.2717	0.1027		
18P	2.1438	0.6440	0.0127	1.3156	1.0874		

19P	-1.8559	-1.4363	0.0691	1.4153	0.9850		
20F	-2.4346	-2.7086	-0.7183	-0.3729	-0.2851		
21F	-2.5211	-1.7158	1.5042	-0.3545	-0.2838		
22F	2.8456	0.9629	-1.3959	-0.3686	-0.3218		
23F	3.4541	0.4203	0.8999	-0.3651	-0.2751		
24O	2.6303	-2.4211	-0.2712	-0.4990	-0.4422		
25O	1.2139	-2.5639	0.0795	-0.3542	-0.3971		

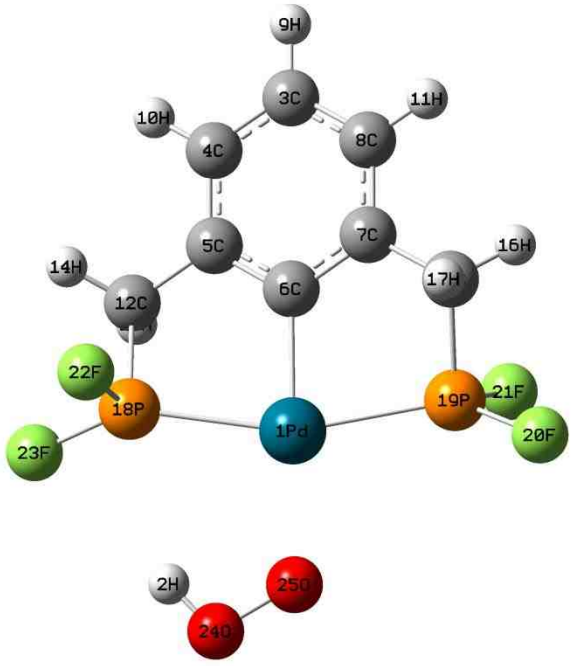
*** *** ***

(PCP) triplet palladium hydroperoxide **59**

(see Figure 3-24)



59



Energy: -1668.95786962 hartrees

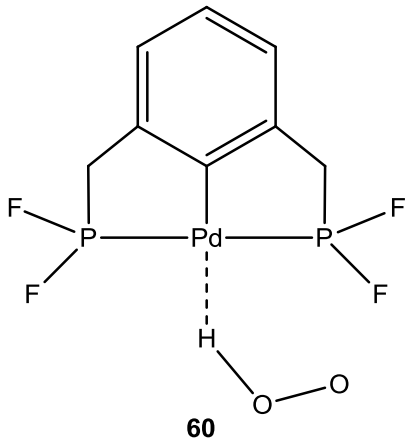
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.1936	-0.8087	-0.0075	-0.5774		0.4622	
2H	-2.6228	-2.3373	-0.1085	0.4602		0.0145	
3C	1.2996	3.8681	-0.0295	0.0356		0.0126	
4C	-0.0275	3.5575	-0.3319	-0.4946		-0.0444	
5C	-0.4584	2.2237	-0.3287	0.0489		0.1153	
6C	0.4358	1.1841	0.0082	1.3731		0.0590	
7C	1.7726	1.5141	0.3252	-0.2108		0.0496	
8C	2.1987	2.8492	0.2909	-0.5866		-0.0335	
9H	1.6327	4.9026	-0.0434	0.1821		0.0003	
10H	-0.7263	4.3534	-0.5813	0.1795		0.0016	
11H	3.2322	3.0942	0.5269	0.1794		0.0016	
12C	-1.8876	1.8880	-0.7030	-1.0515		-0.0008	
13C	2.7447	0.4192	0.7234	-1.0994		0.0106	
14H	-2.6075	2.6515	-0.3831	0.2580		-0.0012	
15H	-2.0035	1.7683	-1.7909	0.2630		0.0007	
16H	3.7802	0.6374	0.4353	0.2550		-0.0018	
17H	2.7337	0.2507	1.8106	0.2641		0.0002	

18P	-2.3568	0.2756	0.0410	1.0376		0.2474	
19P	2.1944	-1.1563	-0.0440	1.2503		0.1960	
20F	3.2666	-2.1797	0.6362	-0.3686		-0.0050	
21F	2.8803	-1.0273	-1.5070	-0.3674		-0.0034	
22F	-2.6818	0.7225	1.5641	-0.3485		-0.0067	
23F	-3.9153	0.2242	-0.5061	-0.3577		-0.0106	
24O	-2.1861	-3.2293	-0.0851	-0.3304		0.2818	
25O	-0.8754	-2.9692	-0.0257	0.0063		0.6541	

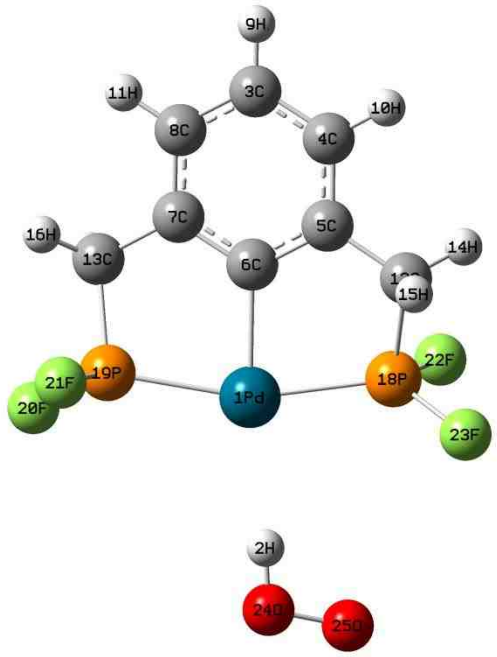
*** *** ***

(PCP) palladium(I)/hydroperoxy radical pair intermediate **60**

(see Figure 3-24)



60



Energy: -1668.95302824 hartrees

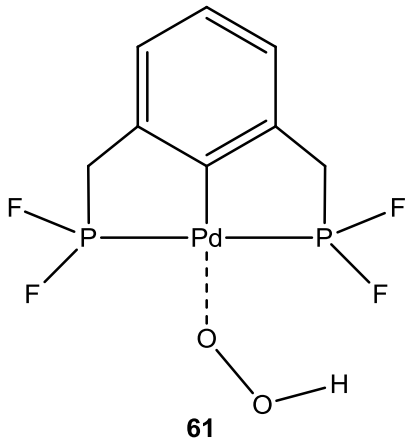
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.5451	0.4428	0.0373	-0.8583		0.3185	
2H	-2.7640	1.4930	0.0295	0.4670		0.0106	
3C	3.6403	-2.1765	-0.0783	0.0375		-0.0260	
4C	2.4251	-2.8181	0.1735	-0.4447		0.0572	
5C	1.2338	-2.0794	0.2209	-0.3507		-0.0486	
6C	1.2716	-0.6920	-0.0127	1.4344		0.4229	
7C	2.4936	-0.0475	-0.2806	-0.2213		-0.0718	
8C	3.6786	-0.7974	-0.2982	-0.4014		0.0538	
9H	4.5609	-2.7535	-0.1035	0.1853		0.0012	
10H	2.4064	-3.8928	0.3435	0.1829		0.0035	
11H	4.6301	-0.3075	-0.4949	0.1828		0.0035	
12C	-0.0862	-2.7563	0.5554	-1.0042		0.0002	
13C	2.5131	1.4427	-0.5830	-1.0535		-0.0017	
14H	-0.1869	-3.7512	0.1046	0.2619		-0.0012	
15H	-0.2051	-2.8769	1.6423	0.2697		-0.0006	
16H	3.3823	1.9586	-0.1567	0.2617		-0.0013	
17H	2.5231	1.6267	-1.6675	0.2696		-0.0006	

18P	-1.4640	-1.6696	0.0033	1.3480		0.1139	
19P	0.9582	2.1895	0.0538	1.3512		0.1562	
20F	0.9521	3.6017	-0.7356	-0.3677		-0.0088	
21F	1.4262	2.7251	1.5029	-0.3664		-0.0072	
22F	-1.8017	-2.2857	-1.4479	-0.3630		-0.0061	
23F	-2.6969	-2.2995	0.8341	-0.3634		-0.0069	
24O	-3.6454	1.9702	0.0388	-0.2828		0.2963	
25O	-4.5574	1.0556	-0.2678	-0.1744		0.7430	

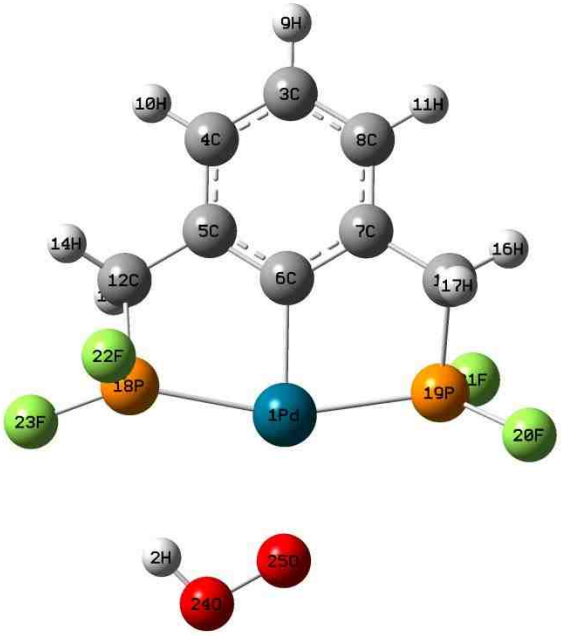
*** *** ***

(PCP) minimum energy crossing point **61**

(see Figure 3-24)



61



Energy: -1668.95769677 hartrees

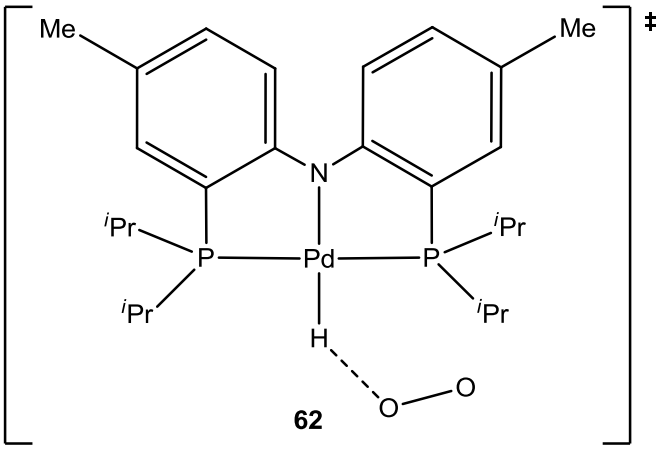
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.1969	-0.8103	-0.0021	-0.5738		0.4730	
2H	-2.6185	-2.3639	-0.1178	0.4626		0.0133	
3C	1.2963	3.8704	-0.0319	0.0303		0.0151	
4C	-0.0305	3.5584	-0.3343	-0.4875		-0.0464	
5C	-0.4601	2.2244	-0.3318	0.0218		0.1032	
6C	0.4343	1.1845	0.0067	1.3895		0.0566	
7C	1.7711	1.5166	0.3228	-0.2115		0.0634	
8C	2.1964	2.8517	0.2886	-0.5762		-0.0314	
9H	1.6280	4.9054	-0.0436	0.1822		0.0002	
10H	-0.7309	4.3539	-0.5818	0.1795		0.0016	
11H	3.2293	3.0979	0.5271	0.1795		0.0016	
12C	-1.8903	1.8885	-0.7056	-1.0510		0.0008	
13C	2.7440	0.4211	0.7207	-1.0985		0.0095	
14H	-2.6093	2.6535	-0.3871	0.2577		-0.0013	
15H	-2.0070	1.7644	-1.7929	0.2629		0.0008	
16H	3.7799	0.6390	0.4337	0.2548		-0.0018	
17H	2.7301	0.2503	1.8074	0.2640		0.0002	

18P	-2.3523	0.2771	0.0437	1.0338		0.2501	
19P	2.1886	-1.1506	-0.0506	1.2519		0.1977	
20F	3.2475	-2.1855	0.6298	-0.3682		-0.0054	
21F	2.8785	-1.0224	-1.5110	-0.3668		-0.0036	
22F	-2.6872	0.7262	1.5633	-0.3489		-0.0067	
23F	-3.9059	0.2004	-0.5076	-0.3558		-0.0118	
24O	-2.1574	-3.2411	-0.1024	-0.3381		0.2744	
25O	-0.8489	-2.9449	-0.0007	0.0057		0.6470	

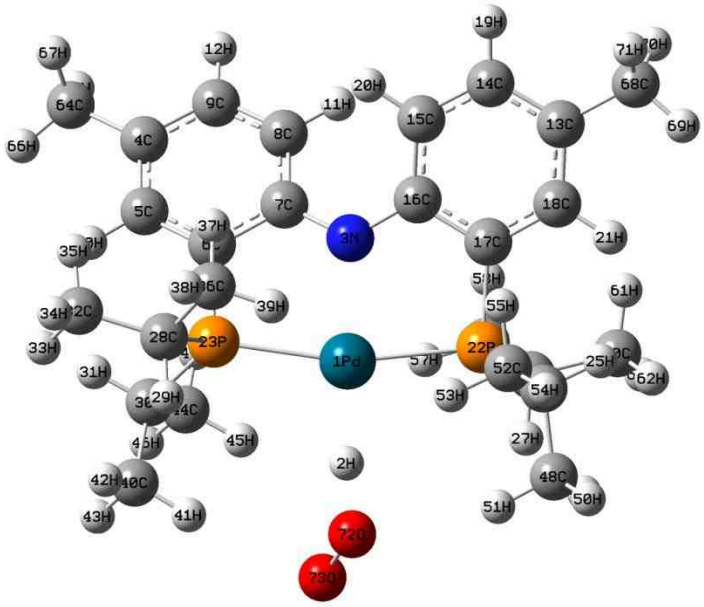
*** *** ***

(PNP) transition state **62**

(see Figure 3-25)



62



Energy: -2030.05990829 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.0035	-0.9857	0.0514	-1.5769		0.2600	0.0373
2H	-0.0080	-2.7693	0.1088	0.2617		-0.0210	-0.1349
3N	0.0265	1.1652	-0.0173	0.4128		0.1749	-1.1710
4C	-3.7034	3.0475	-0.8896	-0.1517		0.0001	-0.1709
5C	-3.6235	1.7419	-0.3997	-0.1183		-0.0011	0.0646
6C	-2.4016	1.1101	-0.1166	-0.6012		0.0169	-0.4659
7C	-1.1667	1.8063	-0.2973	0.7270		-0.0136	0.6989
8C	-1.2590	3.1131	-0.8504	-0.0895		0.0114	-0.2423
9C	-2.4840	3.7052	-1.1278	-0.8649		-0.0003	0.1532
10H	-4.5506	1.1914	-0.2547	0.1654		0.0001	0.0135
11H	-0.3508	3.6505	-1.0977	0.1975		-0.0004	0.0318
12H	-2.4926	4.7050	-1.5602	0.1739		0.0007	0.0011
13C	3.8081	2.9894	0.7533	-0.1567		-0.0014	-0.1779
14C	2.6074	3.6948	0.9467	-0.8589		0.0004	0.1537
15C	1.3663	3.1232	0.6996	-0.0814		0.0106	-0.2448
16C	1.2369	1.7882	0.2265	0.7935		-0.0115	0.7148
17C	2.4523	1.0481	0.0919	-0.5574		0.0114	-0.4789
18C	3.6916	1.6601	0.3414	-0.1226		-0.0006	0.0719

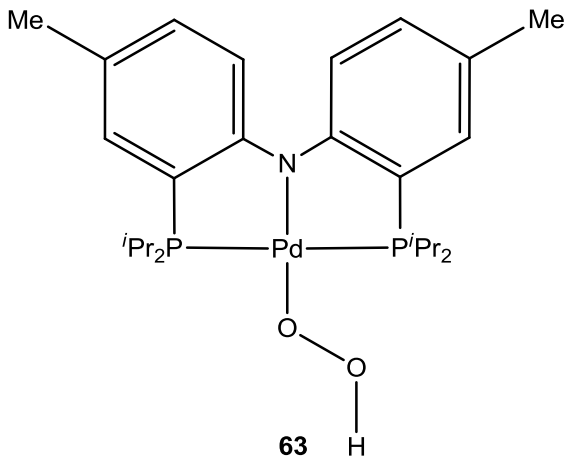
19H	2.6437	4.7179	1.3191	0.1740		0.0007	0.0007
20H	0.4736	3.7007	0.9102	0.1976		-0.0004	0.0322
21H	4.6024	1.0751	0.2318	0.1655		0.0001	0.0134
22P	2.2959	-0.7348	-0.3038	1.1870		0.0977	0.9505
23P	-2.2974	-0.6524	0.3814	1.3027		0.0510	0.9300
24C	3.5283	-1.6162	0.8013	-0.1700		-0.0463	-0.1278
25H	4.5035	-1.1331	0.6542	0.2146		0.0016	-0.0613
26C	2.8960	-0.9973	-2.0678	-0.3537		0.0151	-0.1245
27H	2.7859	-2.0789	-2.2254	0.2282		0.0001	-0.0382
28C	-2.9017	-0.7914	2.1584	-0.3712		0.0140	-0.1156
29H	-2.8252	-1.8651	2.3783	0.2271		0.0002	-0.0403
30C	-3.5636	-1.5504	-0.6705	-0.1256		-0.0285	-0.1260
31H	-4.5176	-1.0191	-0.5537	0.2131		0.0012	-0.0568
32C	-4.3543	-0.3440	2.3862	-0.6113		0.0038	0.0386
33H	-5.0690	-0.8924	1.7623	0.2144		0.0000	-0.0097
34H	-4.6332	-0.5177	3.4338	0.2117		0.0002	-0.0536
35H	-4.4744	0.7264	2.1865	0.2393		0.0000	0.0090
36C	-1.9383	-0.0432	3.0956	-0.7466		-0.0074	0.0319
37H	-1.9504	1.0347	2.8971	0.2407		0.0000	0.0051
38H	-2.2403	-0.1969	4.1397	0.2073		-0.0001	-0.0461
39H	-0.9074	-0.3942	2.9811	0.2330		0.0003	0.0045
40C	-3.7532	-3.0065	-0.2125	-0.7172		0.0205	0.0399
41H	-2.8194	-3.5730	-0.2933	0.2511		0.0000	0.0224
42H	-4.1149	-3.0815	0.8189	0.2138		0.0001	-0.0114
43H	-4.4941	-3.4981	-0.8559	0.2122		-0.0002	-0.0388
44C	-3.1511	-1.4886	-2.1513	-0.7214		0.0088	0.0340
45H	-2.2045	-2.0169	-2.3148	0.2395		0.0007	0.0078
46H	-3.9181	-1.9722	-2.7698	0.2057		-0.0001	-0.0441
47H	-3.0342	-0.4580	-2.5020	0.2365		0.0000	0.0067
48C	3.6578	-3.1034	0.4295	-0.6887		0.0214	0.0412
49H	4.0364	-3.2512	-0.5878	0.2159		0.0000	-0.0110
50H	4.3612	-3.5930	1.1151	0.2122		0.0000	-0.0410
51H	2.6963	-3.6223	0.5129	0.2484		0.0012	0.0210
52C	3.1235	-1.4474	2.2756	-0.6975		0.0117	0.0353
53H	2.1569	-1.9258	2.4736	0.2344		0.0006	0.0080
54H	3.8731	-1.9206	2.9229	0.2064		-0.0001	-0.0461
55H	3.0466	-0.3932	2.5611	0.2383		0.0000	0.0074
56C	1.9573	-0.2752	-3.0496	-0.7583		-0.0064	0.0317
57H	0.9160	-0.5871	-2.9182	0.2344		0.0003	0.0032

58H	2.0032	0.8117	-2.9144	0.2402		0.0000	0.0054
59H	2.2553	-0.4993	-4.0819	0.2080		-0.0001	-0.0452
60C	4.3620	-0.6084	-2.3157	-0.6075		0.0046	0.0428
61H	4.5152	0.4670	-2.1739	0.2394		0.0000	0.0090
62H	5.0591	-1.1445	-1.6617	0.2134		0.0000	-0.0110
63H	4.6363	-0.8471	-3.3517	0.2122		0.0003	-0.0536
64C	-5.0292	3.7163	-1.1725	-0.6942		0.0000	0.1502
65H	-5.0610	4.1420	-2.1840	0.2140		0.0001	-0.0525
66H	-5.8598	3.0066	-1.0859	0.1989		0.0000	-0.0228
67H	-5.2267	4.5394	-0.4718	0.2198		0.0002	-0.0672
68C	5.1516	3.6354	1.0040	-0.6910		0.0001	0.1524
69H	5.9633	2.9011	0.9471	0.1987		0.0000	-0.0229
70H	5.3684	4.4216	0.2676	0.2197		0.0001	-0.0667
71H	5.1978	4.1038	1.9959	0.2144		0.0000	-0.0539
72O	0.1115	-4.0242	0.2358	-0.0468		0.6046	0.3252
73O	-0.5367	-4.6503	-0.6735	-0.1349		0.7917	-0.4255

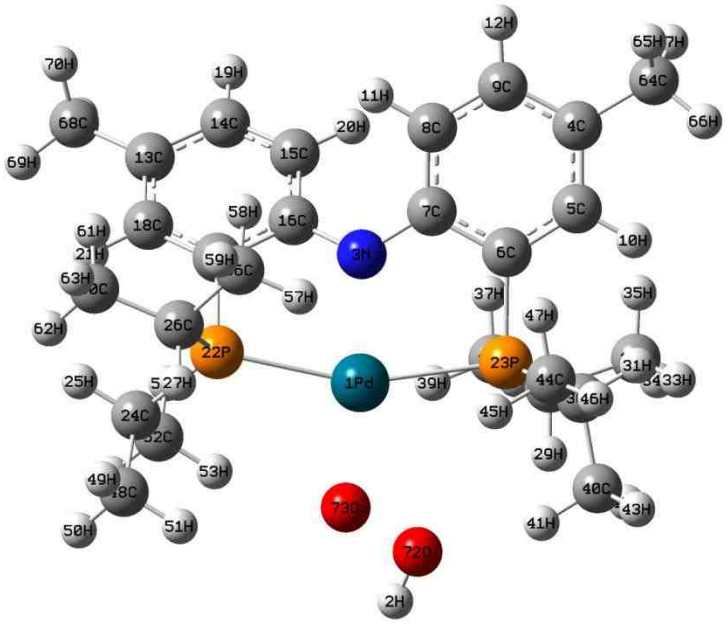
*** *** ***

(PNP) triplet palladium hydroperoxide **63**

(see Figure 3-25)



63



Energy: -2030.07405482 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.0173	-1.1535	0.0337	-1.3529		0.7671	
2H	0.5681	-4.6281	-1.3786	0.4957		-0.0019	
3N	-0.0491	1.0101	-0.0034	0.3797		0.2901	
4C	3.5541	3.1249	0.8270	-0.1054		0.0649	
5C	3.5585	1.7854	0.4219	0.0517		-0.0123	
6C	2.3865	1.0694	0.1367	-0.6685		0.0721	
7C	1.1194	1.7245	0.2318	0.5057		-0.0410	
8C	1.1204	3.0691	0.6876	0.0073		0.0744	
9C	2.3009	3.7422	0.9731	-0.9220		-0.0367	
10H	4.5185	1.2805	0.3428	0.1692		0.0015	
11H	0.1739	3.5726	0.8514	0.2006		-0.0031	
12H	2.2471	4.7696	1.3303	0.1756		0.0020	
13C	-3.7231	2.7434	-1.2821	-0.0662		0.0884	
14C	-2.4973	3.3755	-1.5485	-0.8258		-0.0511	
15C	-1.2904	2.8319	-1.1279	-0.1133		0.0905	
16C	-1.2350	1.6121	-0.4038	0.7908		-0.0369	
17C	-2.4746	0.9350	-0.1758	-0.7469		0.0956	

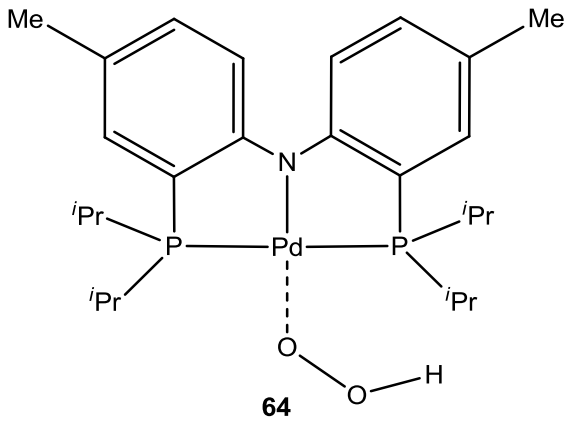
18C	-3.6735	1.5176	-0.6060	0.1770		-0.0395	
19H	-2.4860	4.3076	-2.1117	0.1766		0.0022	
20H	-0.3658	3.3349	-1.3896	0.2026		-0.0040	
21H	-4.6101	0.9943	-0.4275	0.1700		0.0019	
22P	-2.3873	-0.7503	0.5672	1.2177		0.0908	
23P	2.3879	-0.7349	-0.2385	1.2628		0.1131	
24C	-3.7699	-1.7308	-0.2410	-0.1368		0.0098	
25H	-4.7186	-1.1925	-0.1144	0.2069		0.0037	
26C	-2.9104	-0.5397	2.3702	-0.3453		-0.0061	
27H	-2.8704	-1.5622	2.7700	0.2240		0.0003	
28C	3.0139	-0.9185	-2.0061	-0.3144		-0.0055	
29H	3.0235	-2.0070	-2.1509	0.2419		0.0007	
30C	3.7441	-1.4505	0.8505	-0.1251		0.0035	
31H	4.6627	-0.8671	0.7019	0.2067		0.0060	
32C	4.4212	-0.3634	-2.2722	-0.6255		0.0040	
33H	5.1789	-0.7975	-1.6098	0.2118		-0.0001	
34H	4.7211	-0.5892	-3.3046	0.2076		0.0013	
35H	4.4472	0.7259	-2.1529	0.2350		-0.0001	
36C	1.9896	-0.3256	-2.9881	-0.8488		-0.0017	
37H	1.9050	0.7613	-2.8679	0.2317		0.0000	
38H	2.3051	-0.5234	-4.0210	0.2046		-0.0003	
39H	0.9958	-0.7619	-2.8443	0.2420		0.0002	
40C	4.0256	-2.9155	0.4714	-0.7313		0.0052	
41H	3.1117	-3.5182	0.5075	0.2644		0.0004	
42H	4.4486	-3.0104	-0.5348	0.2122		0.0000	
43H	4.7506	-3.3447	1.1755	0.2035		0.0001	
44C	3.3288	-1.3381	2.3277	-0.7107		0.0009	
45H	2.4183	-1.9177	2.5212	0.2336		0.0007	
46H	4.1255	-1.7351	2.9706	0.2029		-0.0002	
47H	3.1413	-0.3010	2.6256	0.2313		-0.0001	
48C	-3.8924	-3.1101	0.4337	-0.7134		-0.0005	
49H	-4.1792	-3.0381	1.4889	0.2106		0.0000	
50H	-4.6631	-3.7030	-0.0759	0.2061		0.0001	
51H	-2.9461	-3.6602	0.3699	0.2593		0.0005	
52C	-3.4858	-1.8893	-1.7453	-0.6793		-0.0097	
53H	-2.5466	-2.4311	-1.9050	0.2569		0.0002	
54H	-4.2957	-2.4617	-2.2168	0.1994		-0.0002	
55H	-3.4165	-0.9230	-2.2557	0.2305		0.0000	
56C	-1.8691	0.3013	3.1274	-0.7490		0.0076	

57H	-0.8609	-0.1129	3.0257	0.2329		0.0005	
58H	-1.8476	1.3332	2.7577	0.2363		0.0000	
59H	-2.1217	0.3337	4.1953	0.2051		-0.0003	
60C	-4.3272	0.0158	2.5779	-0.6759		0.0077	
61H	-4.4139	1.0362	2.1871	0.2374		-0.0002	
62H	-5.0955	-0.6010	2.0981	0.2113		0.0000	
63H	-4.5591	0.0520	3.6511	0.2084		0.0024	
64C	4.8364	3.8746	1.1053	-0.7035		-0.0054	
65H	4.7934	4.4047	2.0653	0.2147		0.0020	
66H	5.6967	3.1968	1.1368	0.2024		0.0002	
67H	5.0396	4.6279	0.3313	0.2224		0.0036	
68C	-5.0335	3.3550	-1.7197	-0.6954		-0.0087	
69H	-5.8677	2.6608	-1.5698	0.2026		0.0002	
70H	-5.2604	4.2698	-1.1549	0.2228		0.0046	
71H	-5.0153	3.6306	-2.7820	0.2169		0.0030	
72O	0.9504	-3.8517	-0.9318	-0.5841		0.0819	
73O	-0.2386	-3.1877	-0.4737	-0.0798		0.3598	

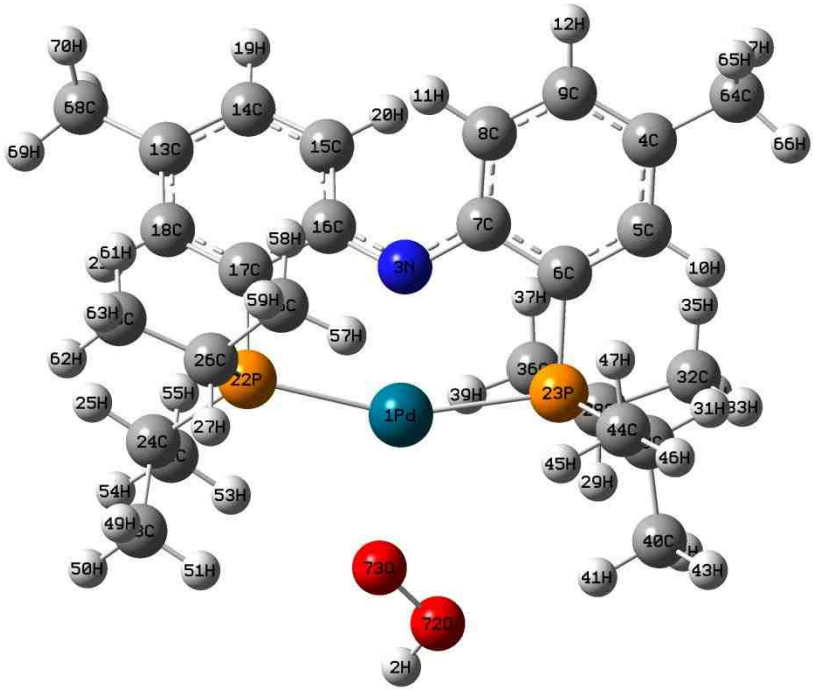
*** *** ***

(PNP) minimum energy crossing point structure **64**

(see Figure 3-25)



64



Energy: -2030.06267809 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.0118	-1.1556	0.1756	-1.3190		0.6652	
2H	0.0613	-4.9699	-1.7567	0.4912		-0.0057	
3N	-0.0265	1.0851	-0.0470	0.2994		0.2284	
4C	3.6408	3.1232	0.6866	-0.1272		0.0343	
5C	3.5968	1.7622	0.3682	0.0324		0.0041	
6C	2.4023	1.0708	0.1156	-0.7164		0.0486	
7C	1.1523	1.7727	0.1525	0.7828		-0.0243	
8C	1.2072	3.1472	0.5192	-0.1178		0.0509	
9C	2.4087	3.7933	0.7736	-0.9216		-0.0201	
10H	4.5387	1.2195	0.3317	0.1635		0.0008	
11H	0.2799	3.6955	0.6450	0.1978		-0.0019	
12H	2.3892	4.8440	1.0605	0.1733		0.0014	
13C	-3.7347	2.7496	-1.3074	-0.1017		0.0500	
14C	-2.5202	3.3928	-1.6013	-0.8514		-0.0283	
15C	-1.3005	2.8699	-1.1944	-0.1946		0.0622	
16C	-1.2114	1.6594	-0.4510	1.0182		-0.0284	

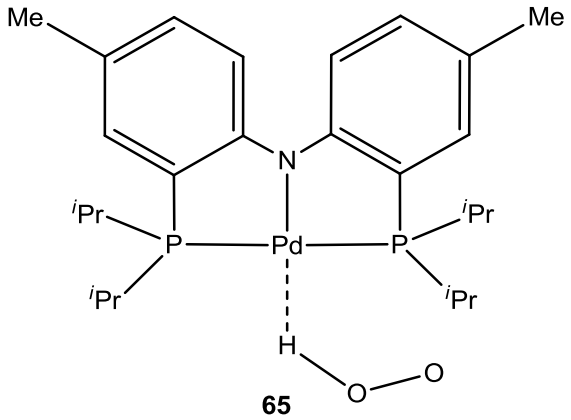
17C	-2.4444	0.9698	-0.1989	-0.7624		0.0618	
18C	-3.6568	1.5331	-0.6191	0.1215		-0.0128	
19H	-2.5298	4.3194	-2.1739	0.1739		0.0016	
20H	-0.3878	3.3817	-1.4793	0.1991		-0.0025	
21H	-4.5857	1.0042	-0.4173	0.1647		0.0012	
22P	-2.3479	-0.6896	0.6017	1.2241		0.1096	
23P	2.3631	-0.7472	-0.1758	1.0692		0.0738	
24C	-3.7624	-1.6757	-0.1498	-0.1171		0.0014	
25H	-4.6989	-1.1187	-0.0178	0.2088		0.0030	
26C	-2.8561	-0.4083	2.4005	-0.3381		-0.0039	
27H	-2.8222	-1.4146	2.8407	0.2198		0.0003	
28C	2.9403	-0.9841	-1.9605	-0.2931		-0.0078	
29H	2.9437	-2.0752	-2.0891	0.2310		0.0004	
30C	3.7568	-1.4481	0.8756	-0.0915		0.0086	
31H	4.6850	-0.9038	0.6572	0.2093		0.0041	
32C	4.3414	-0.4420	-2.2789	-0.6183		0.0038	
33H	5.1178	-0.8744	-1.6370	0.2092		0.0000	
34H	4.6059	-0.6787	-3.3185	0.2074		0.0007	
35H	4.3778	0.6478	-2.1696	0.2405		-0.0001	
36C	1.8951	-0.4007	-2.9268	-0.7940		-0.0014	
37H	1.8238	0.6883	-2.8224	0.2384		0.0000	
38H	2.1809	-0.6197	-3.9642	0.2032		-0.0002	
39H	0.8991	-0.8195	-2.7487	0.2404		0.0005	
40C	3.9790	-2.9351	0.5453	-0.7286		-0.0010	
41H	3.0592	-3.5152	0.6890	0.2441		0.0005	
42H	4.3154	-3.0893	-0.4860	0.2161		0.0000	
43H	4.7477	-3.3528	1.2088	0.2073		-0.0001	
44C	3.4241	-1.2664	2.3664	-0.7046		0.0055	
45H	2.5084	-1.8100	2.6299	0.2286		0.0005	
46H	4.2415	-1.6610	2.9844	0.2029		-0.0001	
47H	3.2788	-0.2134	2.6293	0.2366		0.0000	
48C	-3.9004	-3.0320	0.5651	-0.7163		-0.0036	
49H	-4.1688	-2.9248	1.6220	0.2127		0.0000	
50H	-4.6881	-3.6273	0.0845	0.2062		0.0000	
51H	-2.9655	-3.6022	0.5061	0.2481		0.0004	
52C	-3.5243	-1.8821	-1.6562	-0.6887		-0.0082	
53H	-2.6031	-2.4503	-1.8285	0.2480		0.0001	
54H	-4.3593	-2.4485	-2.0902	0.1989		-0.0002	
55H	-3.4452	-0.9327	-2.1955	0.2360		0.0000	

56C	-1.7976	0.4522	3.1113	-0.7663		0.0096	
57H	-0.7943	0.0259	3.0104	0.2326		0.0005	
58H	-1.7713	1.4676	2.6992	0.2404		0.0000	
59H	-2.0355	0.5293	4.1804	0.2037		-0.0003	
60C	-4.2631	0.1709	2.6054	-0.6668		0.0069	
61H	-4.3446	1.1743	2.1723	0.2412		-0.0001	
62H	-5.0465	-0.4564	2.1645	0.2097		0.0000	
63H	-4.4775	0.2555	3.6794	0.2083		0.0014	
64C	4.9478	3.8394	0.9385	-0.7083		-0.0025	
65H	4.9347	4.3850	1.8912	0.2142		0.0011	
66H	5.7874	3.1359	0.9714	0.1994		0.0001	
67H	5.1659	4.5745	0.1513	0.2196		0.0018	
68C	-5.0610	3.3404	-1.7263	-0.7060		-0.0046	
69H	-5.8843	2.6427	-1.5363	0.1996		0.0001	
70H	-5.2826	4.2676	-1.1795	0.2200		0.0026	
71H	-5.0747	3.5885	-2.7957	0.2147		0.0018	
72O	0.6078	-4.2964	-1.2989	-0.4868		0.1978	
73O	-0.2868	-3.4801	-0.6961	-0.0713		0.5108	

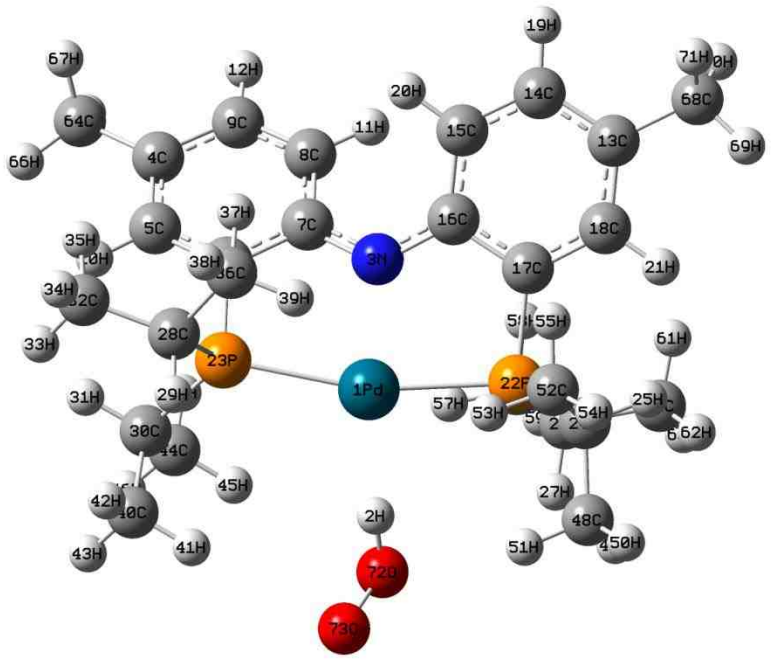
*** *** ***

(PNP) palladium(I)/hydroperoxy radical pair intermediate **65**

(see Figure 3-25)



65



Energy: -2030.06866670 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0013	-0.9972	0.2927	-1.6761		0.4192	
2H	0.0240	-2.8302	-1.0529	0.4757		0.0128	
3N	0.0171	1.1423	-0.0431	0.3544		0.2261	
4C	-3.7076	2.8567	-1.2183	-0.1233		0.0070	
5C	-3.6285	1.6288	-0.5566	-0.0081		-0.0002	
6C	-2.4093	1.0500	-0.1689	-0.6898		0.0320	
7C	-1.1750	1.7265	-0.4245	1.0272		-0.0054	
8C	-1.2653	2.9494	-1.1445	-0.1166		0.0209	
9C	-2.4888	3.4896	-1.5182	-0.8949		-0.0049	
10H	-4.5546	1.0943	-0.3554	0.1668		0.0002	
11H	-0.3553	3.4579	-1.4419	0.1969		-0.0007	
12H	-2.4962	4.4244	-2.0776	0.1741		0.0009	
13C	3.7913	3.0428	0.5452	-0.1280		-0.0048	
14C	2.5888	3.7656	0.6391	-0.9277		0.0000	
15C	1.3508	3.1684	0.4431	-0.0355		0.0132	
16C	1.2268	1.7872	0.1267	0.7138		-0.0173	
17C	2.4441	1.0377	0.0834	-0.6790		0.0107	

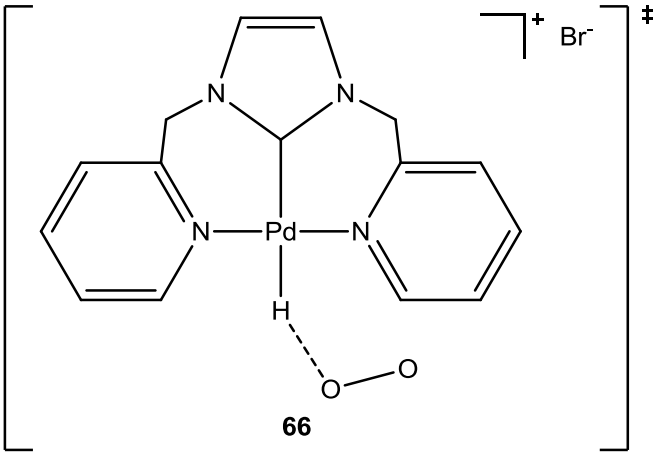
18C	3.6796	1.6762	0.2803	-0.0635		0.0012	
19H	2.6214	4.8249	0.8913	0.1743		0.0009	
20H	0.4547	3.7646	0.5731	0.1972		-0.0004	
21H	4.5912	1.0833	0.2454	0.1652		0.0001	
22P	2.3047	-0.7749	-0.1501	1.0227		0.1458	
23P	-2.3136	-0.6229	0.5800	1.4012		0.1187	
24C	3.5665	-1.5559	0.9976	-0.0205		-0.0330	
25H	4.5464	-1.1143	0.7731	0.2142		0.0020	
26C	2.8954	-1.1587	-1.9000	-0.3459		0.0047	
27H	2.7705	-2.2460	-1.9936	0.2374		-0.0001	
28C	-2.8966	-0.4706	2.3675	-0.3913		0.0022	
29H	-2.8193	-1.4945	2.7586	0.2211		0.0005	
30C	-3.6166	-1.6607	-0.2845	-0.1584		-0.0404	
31H	-4.5839	-1.1599	-0.1462	0.2123		0.0024	
32C	-4.3441	0.0141	2.5402	-0.6487		0.0040	
33H	-5.0697	-0.6356	2.0383	0.2114		0.0000	
34H	-4.6026	0.0303	3.6072	0.2106		0.0003	
35H	-4.4699	1.0323	2.1549	0.2403		0.0000	
36C	-1.9195	0.4153	3.1591	-0.7516		-0.0074	
37H	-1.9303	1.4462	2.7871	0.2421		0.0000	
38H	-2.2096	0.4359	4.2176	0.2066		-0.0002	
39H	-0.8907	0.0460	3.0931	0.2298		0.0003	
40C	-3.6963	-3.0627	0.3453	-0.6988		0.0230	
41H	-2.7374	-3.5886	0.2666	0.2501		0.0007	
42H	-3.9839	-3.0318	1.4022	0.2122		0.0002	
43H	-4.4487	-3.6626	-0.1824	0.2121		0.0000	
44C	-3.3320	-1.7470	-1.7934	-0.6537		0.0240	
45H	-2.3819	-2.2556	-1.9910	0.2316		0.0006	
46H	-4.1251	-2.3246	-2.2855	0.2067		-0.0001	
47H	-3.2932	-0.7581	-2.2607	0.2407		0.0000	
48C	3.6473	-3.0745	0.7622	-0.7610		0.0110	
49H	3.9772	-3.3265	-0.2513	0.2206		0.0000	
50H	4.3642	-3.5209	1.4630	0.2128		0.0000	
51H	2.6753	-3.5544	0.9295	0.2361		0.0005	
52C	3.2165	-1.2430	2.4622	-0.7278		-0.0017	
53H	2.2435	-1.6712	2.7322	0.2265		0.0004	
54H	3.9728	-1.6806	3.1266	0.2060		-0.0001	
55H	3.1790	-0.1660	2.6544	0.2397		0.0000	
56C	1.9671	-0.4823	-2.9235	-0.6849		0.0021	

57H	0.9178	-0.7544	-2.7696	0.2372		0.0005	
58H	2.0419	0.6096	-2.8629	0.2419		0.0000	
59H	2.2518	-0.7850	-3.9391	0.2100		-0.0001	
60C	4.3651	-0.8045	-2.1751	-0.6338		0.0074	
61H	4.5330	0.2753	-2.0973	0.2393		0.0000	
62H	5.0579	-1.3106	-1.4936	0.2120		0.0000	
63H	4.6316	-1.1074	-3.1962	0.2127		0.0005	
64C	-5.0326	3.4688	-1.6117	-0.7015		-0.0009	
65H	-5.0524	3.7458	-2.6738	0.2143		0.0002	
66H	-5.8605	2.7723	-1.4359	0.1991		0.0000	
67H	-5.2448	4.3819	-1.0383	0.2198		0.0005	
68C	5.1317	3.7130	0.7433	-0.6940		0.0007	
69H	5.9463	2.9797	0.7474	0.1987		0.0000	
70H	5.3460	4.4370	-0.0550	0.2196		0.0000	
71H	5.1754	4.2615	1.6935	0.2152		0.0000	
72O	0.0950	-3.6445	-1.6502	-0.2414		0.2888	
73O	-0.3965	-4.6634	-0.9528	-0.1544		0.7311	

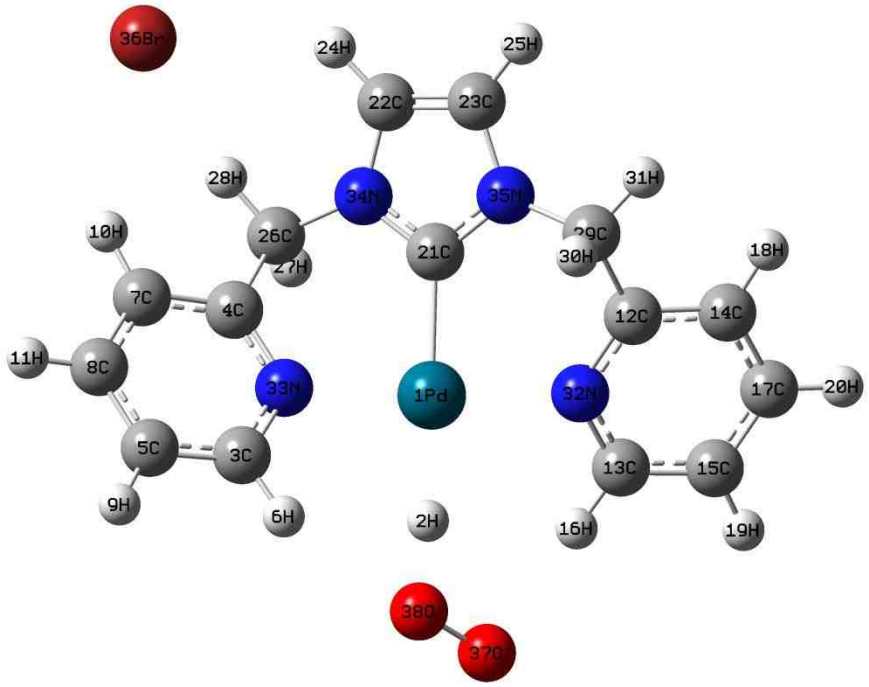
*** *** ***

(NCN) transition state **66**

(see Figure 3-26)



66



Energy: -1089.87880403 hartrees

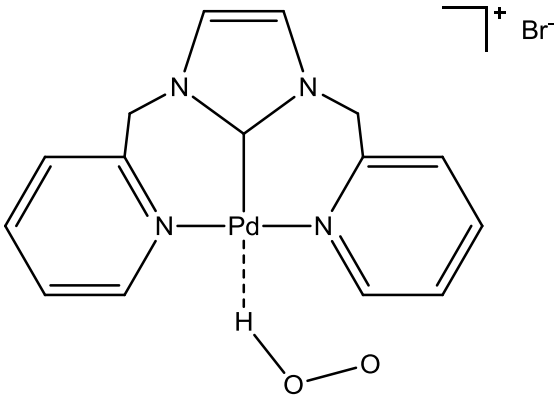
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-1.1945	0.6508	0.0081	-0.6674		0.3700	0.3744
2H	-2.1926	2.1402	-0.0334	0.2128		-0.0079	0.0077
3C	0.5452	3.0263	0.6234	-0.0108		0.0324	0.0252
4C	1.7975	1.2811	-0.2879	0.1124		-0.0078	0.1402
5C	1.6912	3.7552	0.9240	-0.1036		-0.0457	-0.0782
6H	-0.4387	3.4179	0.8523	0.2160		-0.0006	0.0625
7C	2.9874	1.9500	0.0146	0.1148		-0.0059	-0.2032
8C	2.9360	3.2019	0.6261	-0.5820		0.0042	0.1325
9H	1.5946	4.7299	1.3921	0.2018		0.0001	0.0419
10H	3.9301	1.4503	-0.2072	0.2713		-0.0001	0.1652
11H	3.8542	3.7298	0.8684	0.2114		0.0001	0.0485
12C	-2.8547	-1.9064	0.4797	0.0156		-0.0137	0.1344
13C	-4.0193	-0.1745	-0.5636	-0.0039		0.0228	0.0314
14C	-3.9337	-2.7686	0.2723	0.1906		-0.0045	-0.1300
15C	-5.1268	-0.9873	-0.7957	-0.1141		-0.0469	-0.0569
16H	-4.0233	0.8687	-0.8631	0.2477		-0.0028	0.0913
17C	-5.0833	-2.3129	-0.3744	-0.3551		0.0038	0.0937

18H	-3.8685	-3.7955	0.6182	0.1998		0.0002	0.0481
19H	-5.9960	-0.5733	-1.2962	0.2137		0.0000	0.0586
20H	-5.9230	-2.9817	-0.5404	0.2102		0.0001	0.0521
21C	-0.0456	-1.0437	0.0498	-0.0688		0.2294	0.2881
22C	1.7591	-2.3840	-0.0031	0.0081		-0.0036	-0.0607
23C	0.7442	-3.0757	0.5923	-0.1788		0.0020	-0.0455
24H	2.8049	-2.6112	-0.1867	0.2839		0.0007	0.2326
25H	0.7192	-4.0716	1.0081	0.2110		0.0014	0.0822
26C	1.8894	-0.0322	-1.0389	-0.5492		0.0003	0.2081
27H	1.4144	0.0708	-2.0218	0.2414		-0.0004	-0.0307
28H	2.9458	-0.3051	-1.1600	0.2588		-0.0002	0.1996
29C	-1.6549	-2.4152	1.2690	-0.6763		-0.0031	0.3812
30H	-1.6273	-1.9059	2.2415	0.2616		-0.0003	-0.0243
31H	-1.7842	-3.4828	1.4582	0.2156		-0.0001	0.0049
32N	-2.9033	-0.6159	0.0550	0.1092		0.0447	-0.1316
33N	0.5852	1.8103	0.0344	0.1768		0.0306	-0.1479
34N	1.2326	-1.1382	-0.3322	-0.0446		-0.0066	-0.4034
35N	-0.3687	-2.2251	0.6034	-0.0380		-0.0080	-0.4235
36Br	5.1043	-1.1176	-0.2927	-0.5627		0.0039	-0.8949
37O	-3.9988	3.1094	-0.6080	-0.1372		0.7860	-0.4512
38O	-2.8420	3.2655	-0.0807	-0.0918		0.6255	0.1774

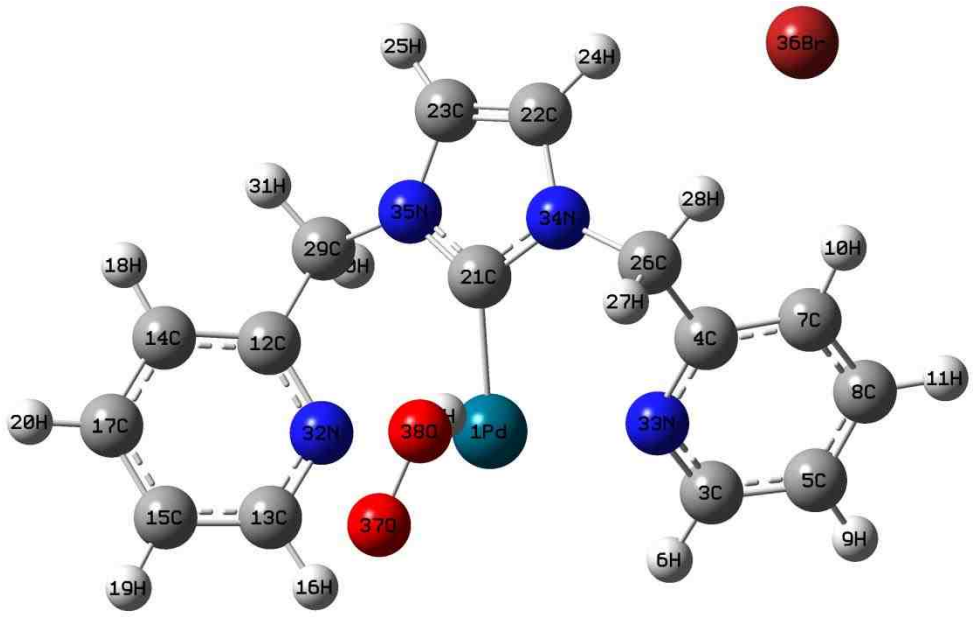
*** *** ***

(NCN) palladium(I)/hydroperoxy radical pair intermediate **67**

(see Figure 3-26)



67



Energy: -1089.89338089 hartrees

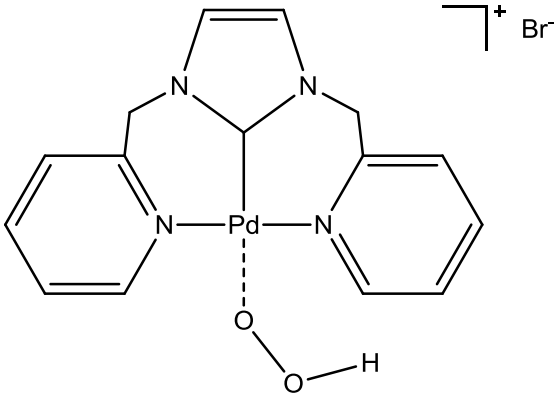
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	1.1497	1.0238	-0.3100	-0.4688		0.5824	
2H	1.5153	0.3837	1.8992	0.5188		-0.0130	
3C	-0.9895	3.1502	-0.8213	-0.0076		0.0264	
4C	-1.9198	1.2681	0.1872	-0.0119		-0.0030	
5C	-2.2433	3.6800	-1.1112	-0.0755		0.0046	
6H	-0.0832	3.6812	-1.0968	0.1902		-0.0002	
7C	-3.2106	1.7264	-0.0968	0.1165		0.0037	
8C	-3.3746	2.9467	-0.7520	-0.5977		-0.0028	
9H	-2.3191	4.6381	-1.6164	0.1968		0.0005	
10H	-4.0562	1.0928	0.1707	0.2690		0.0002	
11H	-4.3717	3.3124	-0.9813	0.2101		0.0002	
12C	3.1403	-1.3245	-0.8156	-0.0802		0.0125	
13C	4.1916	0.6203	-0.0875	-0.1053		0.0343	
14C	4.2984	-2.0610	-0.5594	0.2271		-0.0023	
15C	5.3806	-0.0541	0.1830	-0.0426		-0.0012	
16H	4.1044	1.6855	0.0963	0.2140		-0.0006	
17C	5.4338	-1.4250	-0.0523	-0.3947		0.0116	
18H	4.3084	-3.1285	-0.7570	0.1992		0.0007	

19H	6.2313	0.4916	0.5779	0.2090		0.0008	
20H	6.3366	-1.9929	0.1530	0.2091		-0.0007	
21C	0.2955	-0.8314	-0.0586	-0.4242		0.2502	
22C	-1.4083	-2.3091	-0.0901	0.1332		0.0091	
23C	-0.3443	-2.8871	-0.7173	-0.3334		0.0056	
24H	-2.4323	-2.6290	0.0856	0.2819		0.0009	
25H	-0.2410	-3.8596	-1.1748	0.2108		0.0017	
26C	-1.7697	-0.0134	0.9906	-0.3679		0.0043	
27H	-1.2842	0.2073	1.9481	0.2458		-0.0009	
28H	-2.7654	-0.4373	1.1711	0.2676		-0.0003	
29C	1.9456	-2.0169	-1.4538	-0.5856		-0.0231	
30H	1.7598	-1.5680	-2.4387	0.2555		0.0012	
31H	2.1910	-3.0697	-1.6111	0.2138		0.0000	
32N	3.0920	0.0121	-0.5743	0.0995		0.0425	
33N	-0.8194	1.9695	-0.1904	0.2367		0.0449	
34N	-0.9799	-1.0456	0.3061	-0.0004		0.0053	
35N	0.7032	-1.9596	-0.6777	-0.0568		-0.0094	
36Br	-4.8680	-1.5273	0.3294	-0.5601		0.0028	
37O	2.9054	1.1513	2.8829	-0.1001		0.7103	
38O	1.8538	0.3370	2.8409	-0.2923		0.3011	

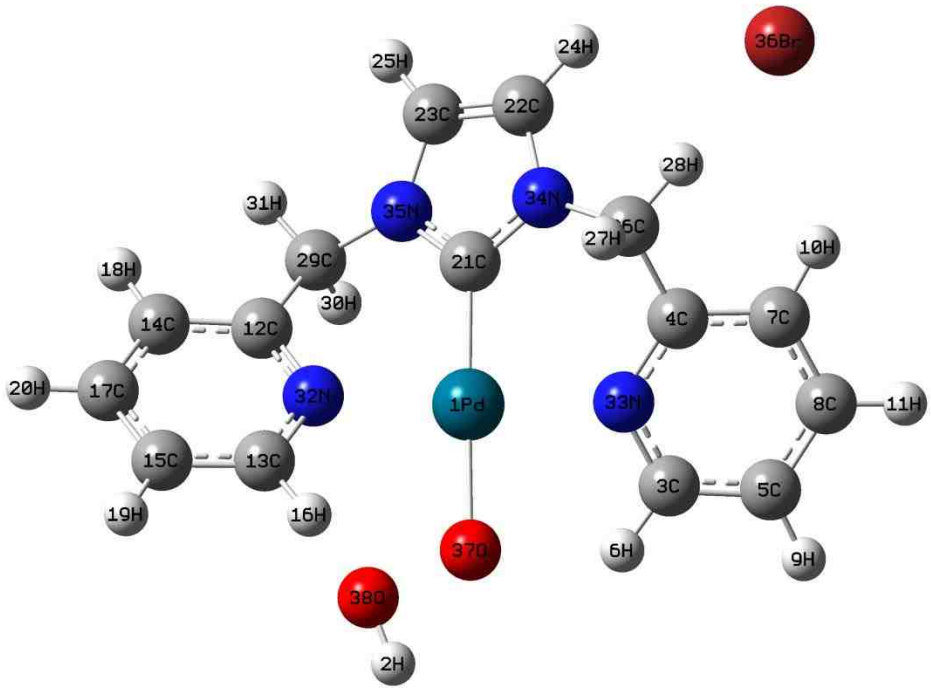
*** *** ***

(NCN) minimum energy crossing point structure **68**

(see Figure 3-26)



68



Energy: -1089.90819125 hartrees

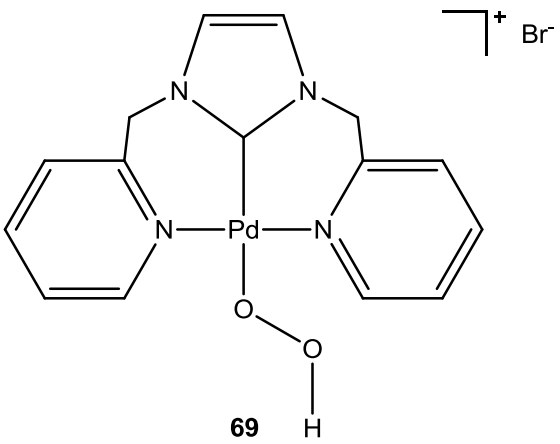
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-1.1527	0.7466	-0.1682	-0.4998		0.0464	
2H	-3.7981	3.1229	0.9848	0.4637		-0.0244	
3C	0.6268	3.0443	0.4294	0.0322		0.0092	
4C	1.8680	1.2361	-0.3814	0.1437		0.0083	
5C	1.7825	3.7718	0.6940	-0.1940		-0.0017	
6H	-0.3627	3.4462	0.6193	0.2425		-0.0020	
7C	3.0650	1.9024	-0.1087	0.0877		-0.0063	
8C	3.0220	3.1863	0.4343	-0.5741		0.0017	
9H	1.6987	4.7707	1.1100	0.2037		0.0001	
10H	4.0012	1.3780	-0.2943	0.2726		0.0000	
11H	3.9445	3.7155	0.6566	0.2119		0.0001	
12C	-2.9849	-1.6508	0.4089	0.1215		0.0061	
13C	-3.9411	0.0448	-0.8764	-0.0224		0.0123	
14C	-4.1514	-2.4093	0.3058	0.0097		-0.0024	
15C	-5.1302	-0.6659	-1.0174	-0.0881		0.0075	
16H	-3.8167	1.0321	-1.2989	0.2463		-0.0010	

17C	-5.2388	-1.9163	-0.4173	-0.3573		0.0075	
18H	-4.2037	-3.3783	0.7923	0.1981		0.0001	
19H	-5.9473	-0.2305	-1.5827	0.2101		0.0001	
20H	-6.1498	-2.5013	-0.5053	0.2082		0.0000	
21C	-0.1199	-0.9289	0.0369	-0.1244		-0.0406	
22C	1.5925	-2.3824	0.0958	0.0427		0.0018	
23C	0.5218	-2.9739	0.7000	-0.1622		0.0036	
24H	2.6260	-2.6837	-0.0473	0.2867		-0.0002	
25H	0.4212	-3.9411	1.1685	0.2157		-0.0004	
26C	1.9202	-0.1170	-1.0524	-0.5140		0.0001	
27H	1.5041	-0.0480	-2.0650	0.2449		0.0004	
28H	2.9624	-0.4635	-1.0967	0.2546		0.0000	
29C	-1.8445	-2.1579	1.2760	-0.6358		-0.0031	
30H	-1.8308	-1.5881	2.2146	0.2735		0.0004	
31H	-2.0199	-3.2062	1.5248	0.2190		0.0000	
32N	-2.8900	-0.4393	-0.1872	0.2471		-0.0118	
33N	0.6676	1.8004	-0.0922	0.2261		0.0019	
34N	1.1585	-1.1269	-0.3113	0.0223		0.0046	
35N	-0.5314	-2.0570	0.6456	0.0152		0.0058	
36Br	5.0133	-1.3158	-0.1133	-0.5598		0.0009	
37O	-2.1591	2.4746	-0.3202	-0.2828		1.2230	
38O	-3.6198	2.1686	1.0666	-0.6853		0.7520	

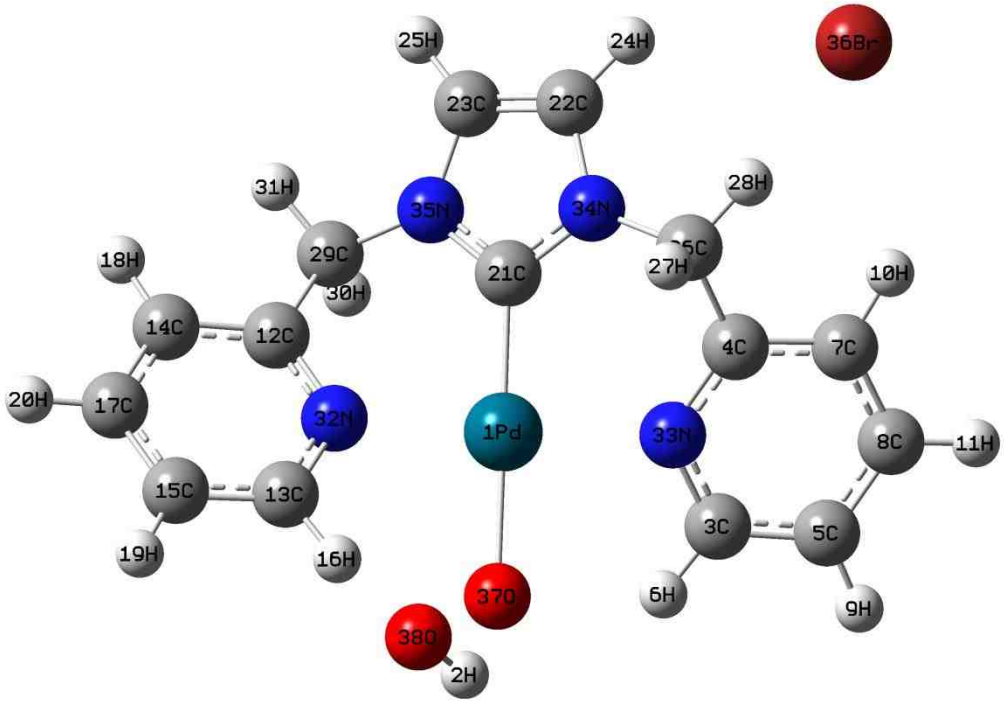
*** *** ***

(NCN) palladium hydroperoxide **69**

(see Figure 3-26, Figure 4-4)



69



Energy: -1089.96278644 hartrees

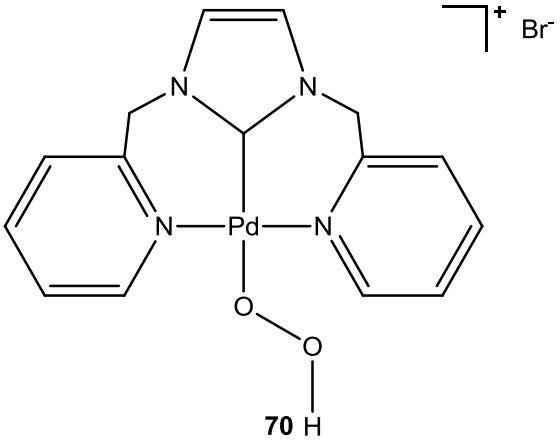
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-1.1682	0.7372	-0.0913	-0.4325	0.2540		
2H	-2.9631	3.1405	1.4051	0.4862	0.3822		
3C	0.6140	3.0718	0.3662	0.0450	-0.0120		
4C	1.8501	1.2326	-0.3761	0.1102	0.2785		

5C	1.7712	3.8105	0.5927	-0.2511	-0.2117		
6H	-0.3806	3.4748	0.5208	0.2465	0.1673		
7C	3.0487	1.9082	-0.1333	0.0833	-0.2634		
8C	3.0096	3.2125	0.3589	-0.5849	0.0589		
9H	1.6898	4.8293	0.9586	0.1996	0.1388		
10H	3.9837	1.3783	-0.3082	0.2724	0.1804		
11H	3.9335	3.7490	0.5564	0.2100	0.1095		
12C	-3.0057	-1.6879	0.4028	0.1162	0.1683		
13C	-3.9607	0.0726	-0.7989	-0.0918	0.0528		
14C	-4.1619	-2.4520	0.2358	0.0421	-0.2280		
15C	-5.1412	-0.6398	-0.9954	-0.0146	-0.1503		
16H	-3.8203	1.0839	-1.1647	0.2702	0.1486		
17C	-5.2438	-1.9264	-0.4726	-0.3864	0.0020		
18H	-4.2101	-3.4506	0.6590	0.1981	0.1473		
19H	-5.9548	-0.1826	-1.5487	0.2109	0.1369		
20H	-6.1464	-2.5148	-0.6108	0.2079	0.1190		
21C	-0.1357	-0.9469	0.0549	-0.0740	-0.3952		
22C	1.5724	-2.4122	0.0654	0.0135	-0.1742		
23C	0.5010	-3.0199	0.6488	-0.1598	-0.2812		
24H	2.6044	-2.7121	-0.0885	0.2861	0.2020		
25H	0.3968	-4.0014	1.0855	0.2128	0.1983		
26C	1.9075	-0.1283	-1.0297	-0.5253	-0.0920		
27H	1.5055	-0.0635	-2.0487	0.2432	0.0417		
28H	2.9510	-0.4724	-1.0627	0.2525	0.0921		
29C	-1.8634	-2.2280	1.2478	-0.6444	-0.0552		
30H	-1.8521	-1.7007	2.2112	0.2647	0.0819		
31H	-2.0359	-3.2868	1.4512	0.2180	0.0847		
32N	-2.9183	-0.4416	-0.1167	0.1987	-0.0389		
33N	0.6507	1.8044	-0.0965	0.2256	-0.0758		
34N	1.1424	-1.1411	-0.2986	0.0031	0.3174		
35N	-0.5504	-2.0973	0.6235	0.0171	0.2559		
36Br	5.0112	-1.3314	-0.1182	-0.5646	-0.7711		
37O	-2.2464	2.4749	-0.2377	-0.3640	-0.4094		
38O	-3.2781	2.4433	0.8047	-0.5407	-0.4602		

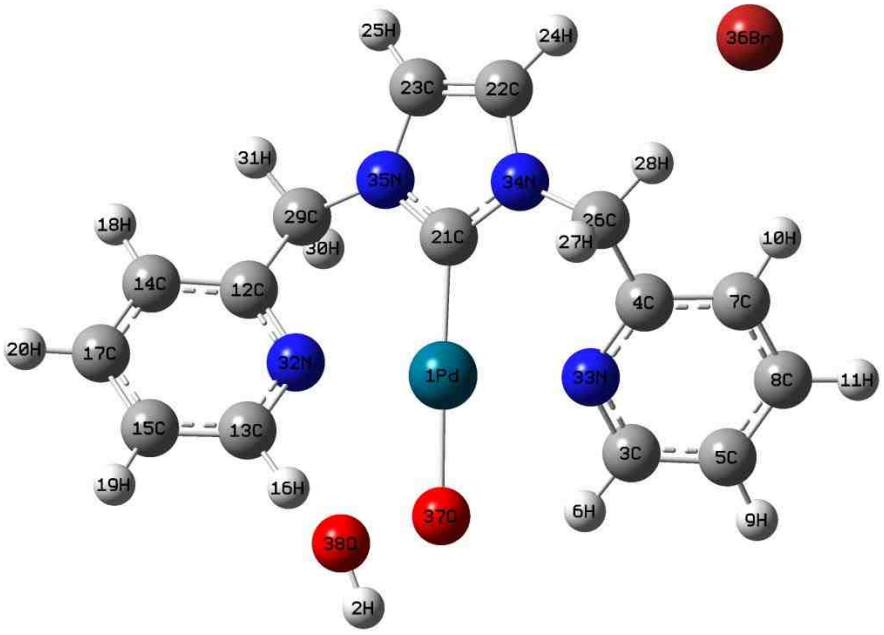
*** *** ***

(NCN) triplet palladium hydroperoxide **70**

(see Figure 3-26)



70



Energy: -1089.90825018 hartrees

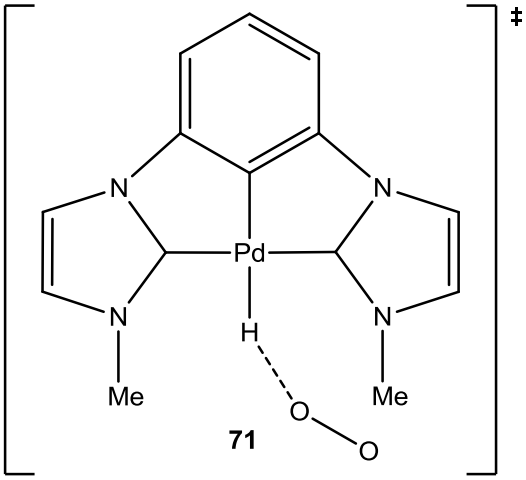
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-1.1513	0.7471	-0.1699	-0.5007		0.0476	
2H	-3.7979	3.1219	0.9854	0.4625		-0.0244	
3C	0.6269	3.0440	0.4297	0.0338		0.0095	
4C	1.8682	1.2358	-0.3810	0.1431		0.0080	

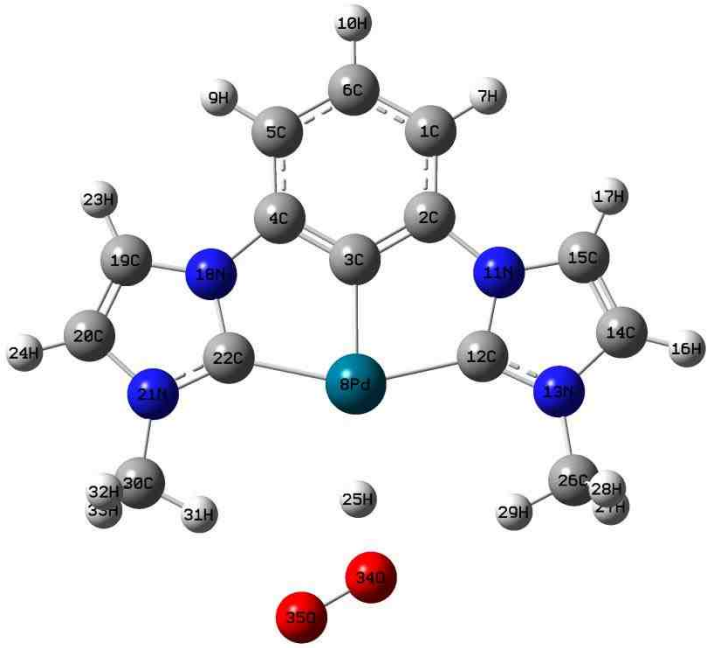
5C	1.7824	3.7715	0.6944	-0.1956		-0.0010	
6H	-0.3623	3.4466	0.6196	0.2420		-0.0021	
7C	3.0650	1.9021	-0.1083	0.0885		-0.0058	
8C	3.0219	3.1860	0.4347	-0.5733		0.0016	
9H	1.6985	4.7704	1.1104	0.2038		0.0001	
10H	4.0011	1.3777	-0.2940	0.2726		0.0000	
11H	3.9443	3.7152	0.6569	0.2119		0.0001	
12C	-2.9851	-1.6506	0.4092	0.1229		0.0060	
13C	-3.9414	0.0449	-0.8757	-0.0238		0.0123	
14C	-4.1516	-2.4091	0.3062	0.0111		-0.0025	
15C	-5.1305	-0.6658	-1.0170	-0.0895		0.0073	
16H	-3.8176	1.0322	-1.2986	0.2460		-0.0010	
17C	-5.2390	-1.9162	-0.4169	-0.3579		0.0071	
18H	-4.2040	-3.3781	0.7927	0.1981		0.0001	
19H	-5.9475	-0.2303	-1.5824	0.2101		0.0001	
20H	-6.1501	-2.5012	-0.5050	0.2082		0.0000	
21C	-0.1202	-0.9292	0.0379	-0.1247		-0.0409	
22C	1.5922	-2.3826	0.0962	0.0434		0.0018	
23C	0.5214	-2.9743	0.7004	-0.1628		0.0039	
24H	2.6257	-2.6838	-0.0470	0.2867		-0.0002	
25H	0.4209	-3.9414	1.1689	0.2158		-0.0004	
26C	1.9200	-0.1173	-1.0520	-0.5129		-0.0001	
27H	1.5039	-0.0482	-2.0645	0.2450		0.0004	
28H	2.9622	-0.4639	-1.0962	0.2545		0.0000	
29C	-1.8449	-2.1580	1.2765	-0.6380		-0.0026	
30H	-1.8312	-1.5881	2.2150	0.2736		0.0004	
31H	-2.0203	-3.2063	1.5253	0.2190		0.0000	
32N	-2.8899	-0.4390	-0.1870	0.2508		-0.0117	
33N	0.6680	1.8001	-0.0920	0.2259		0.0014	
34N	1.1582	-1.1272	-0.3107	0.0232		0.0048	
35N	-0.5316	-2.0573	0.6464	0.0146		0.0061	
36Br	5.0127	-1.3160	-0.1129	-0.5597		0.0009	
37O	-2.1496	2.4771	-0.3301	-0.2876		1.2203	
38O	-3.6325	2.1661	1.0774	-0.6805		0.7529	

*** *** ***

(CCC) transition state **71**

(see Figure 3-27)





Energy: -1037.94556348 hartrees

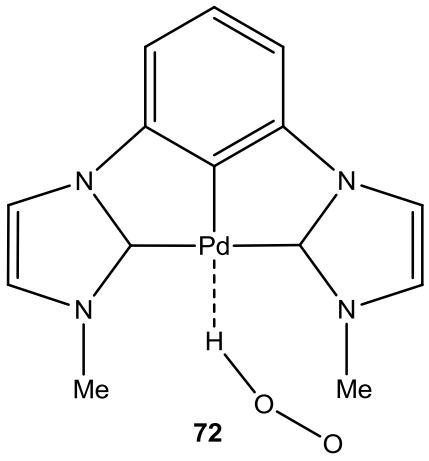
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	1.6930	3.2769	-0.0063	-0.6844		0.0176	-0.0750
2C	1.4853	1.8940	-0.0006	0.7495		-0.0324	0.3221

3C	0.2055	1.3713	0.0024	0.1754		0.4847	-0.2180
4C	-0.9009	2.2003	-0.0004	0.7652		-0.0365	0.3117
5C	-0.7511	3.5907	-0.0067	-0.6802		0.0225	-0.0722
6C	0.5574	4.1059	-0.0090	-0.7929		-0.0330	-0.0936
7H	2.6859	3.7200	-0.0090	0.1712		0.0035	0.0081
8Pd	-0.0523	-0.6332	0.0017	-0.8522		0.3558	0.0287
9H	-1.5992	4.2712	-0.0096	0.1715		0.0035	0.0090
10H	0.6956	5.1835	-0.0136	0.1768		0.0005	0.0162
11N	2.4701	0.8542	0.0011	-0.0884		0.0244	-0.4006
12C	2.0240	-0.4581	0.0002	0.0191		-0.0678	0.4103
13N	3.1643	-1.1904	0.0020	-0.1625		-0.0228	-0.4328
14C	4.2921	-0.3742	0.0058	-0.1111		0.0009	-0.0897
15C	3.8516	0.9142	0.0045	0.1024		-0.0122	0.0756
16H	5.2944	-0.7756	0.0079	0.2077		0.0008	0.0818
17H	4.4006	1.8432	0.0047	0.2069		-0.0001	0.0908
18N	-2.1159	1.4438	0.0014	-0.0773		0.0247	-0.3965
19C	-3.4372	1.8512	0.0021	0.0863		-0.0186	0.0754
20C	-4.1881	0.7153	0.0039	-0.0984		0.0056	-0.0830
21N	-3.3043	-0.3599	0.0045	-0.1742		-0.0206	-0.4193
22C	-2.0169	0.0603	0.0028	-0.0203		-0.0740	0.3999
23H	-3.7334	2.8888	0.0014	0.2060		-0.0001	0.0906
24H	-5.2593	0.5798	0.0050	0.2077		0.0007	0.0819
25H	-0.2676	-2.4892	-0.0075	0.2185		0.0863	0.0686
26C	3.2076	-2.6502	0.0069	-0.4122		-0.0082	0.3135
27H	3.7630	-3.0098	-0.8649	0.2239		0.0001	-0.0203
28H	3.6909	-3.0083	0.9215	0.2266		0.0001	-0.0203
29H	2.1850	-3.0246	-0.0339	0.2796		0.0009	0.0613
30C	-3.7190	-1.7614	0.0065	-0.4272		-0.0110	0.2922
31H	-2.8307	-2.3957	0.0092	0.2846		0.0017	0.0722
32H	-4.3168	-1.9698	0.8995	0.2215		0.0000	-0.0196
33H	-4.3140	-1.9733	-0.8875	0.2217		0.0000	-0.0190
34O	-0.2338	-3.7732	-0.0293	-0.1143		0.5599	-0.0097
35O	-1.4298	-4.2721	-0.0002	-0.2265		0.7430	T

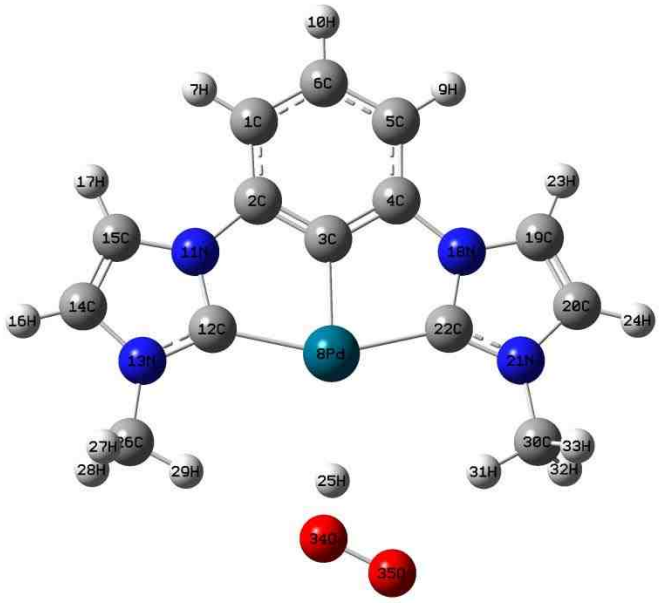
*** *** ***

(CCC) palladium(I)/hydroperoxy radical pair intermediate **72**

(see Figure 3-27)



72



Energy: -1037.94943914 hartrees

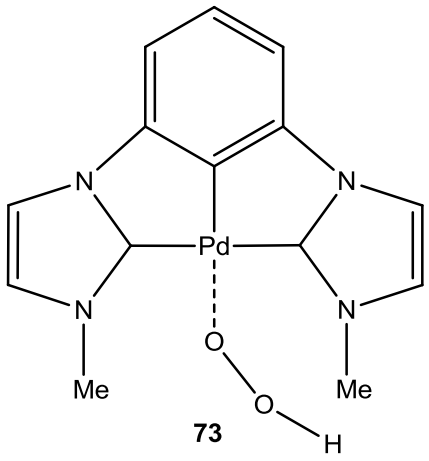
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-1.7377	-3.2640	-0.0078	-0.6873		0.0233	
2C	-1.5115	-1.8836	-0.0019	0.6939		-0.0218	
3C	-0.2259	-1.3808	0.0019	0.2782		0.5408	
4C	0.8703	-2.2204	-0.0016	0.7115		-0.0294	
5C	0.7033	-3.6091	-0.0074	-0.6760		0.0285	
6C	-0.6121	-4.1072	-0.0102	-0.7821		-0.0411	

7H	-2.7357	-3.6960	-0.0107	0.1695		0.0046	
8Pd	0.0590	0.6298	0.0046	-0.8369		0.5048	
9H	1.5418	-4.3019	-0.0101	0.1698		0.0046	
10H	-0.7641	-5.1831	-0.0146	0.1753		0.0008	
11N	-2.4846	-0.8309	0.0001	-0.0994		0.0330	
12C	-2.0338	0.4818	0.0029	-0.0069		-0.0461	
13N	-3.1782	1.2126	0.0044	-0.1624		-0.0309	
14C	-4.3068	0.3978	0.0026	-0.1304		0.0132	
15C	-3.8659	-0.8899	-0.0003	0.1057		-0.0194	
16H	-5.3093	0.7991	0.0034	0.2065		0.0013	
17H	-4.4147	-1.8190	-0.0023	0.2059		-0.0001	
18N	2.0968	-1.4793	0.0007	-0.0923		0.0328	
19C	3.4076	-1.9188	0.0003	0.0914		-0.0243	
20C	4.1871	-0.8030	0.0030	-0.1167		0.0174	
21N	3.3292	0.2930	0.0047	-0.1679		-0.0272	
22C	2.0283	-0.0924	0.0033	-0.0605		-0.0551	
23H	3.6773	-2.9636	-0.0018	0.2052		-0.0001	
24H	5.2614	-0.6944	0.0037	0.2064		0.0012	
25H	0.3260	2.8652	-0.0124	0.4125		0.1049	
26C	-3.2292	2.6707	0.0077	-0.3805		-0.0289	
27H	-3.7508	3.0309	-0.8847	0.2254		0.0002	
28H	-3.7483	3.0271	0.9031	0.2255		0.0002	
29H	-2.2076	3.0502	0.0070	0.2604		0.0018	
30C	3.7841	1.6806	0.0088	-0.3982		-0.0272	
31H	2.9136	2.3381	0.0022	0.2700		0.0014	
32H	4.3790	1.8755	0.9070	0.2220		0.0002	
33H	4.3927	1.8759	-0.8800	0.2215		0.0002	
34O	0.2900	3.9101	-0.0203	-0.2695		0.3038	
35O	1.5397	4.3509	-0.0172	-0.1896		0.7326	

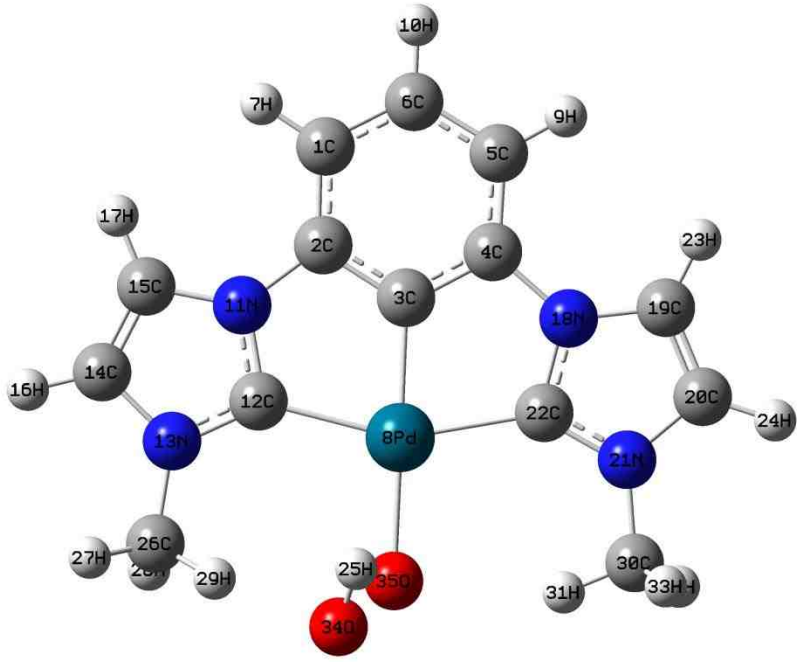
*** *** ***

(CCC) minimum energy crossing point structure **73**

(see Figure 3-27)



73



Energy: -1037.97748962 hartrees

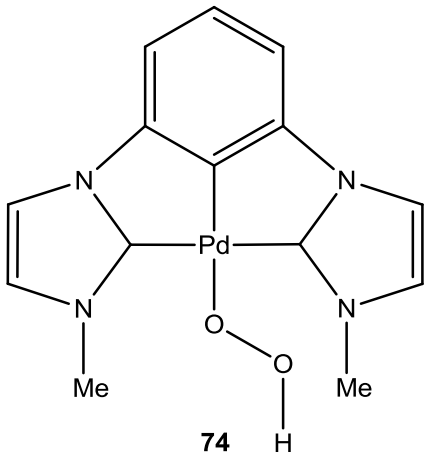
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-0.9502	3.4449	0.1354	-0.6752		-0.0048	
2C	-1.0242	2.0531	0.0415	0.7893		0.0053	
3C	0.1260	1.2732	0.0159	0.3175		-0.0617	
4C	1.3745	1.8791	0.0839	0.8075		0.0064	
5C	1.5011	3.2668	0.1827	-0.6472		-0.0041	

6C	0.3238	4.0327	0.2065	-0.8233		0.0059	
7H	-1.8375	4.0719	0.1560	0.1759		-0.0001	
8Pd	-0.0150	-0.6951	-0.1362	-0.7921		0.0597	
9H	2.4682	3.7581	0.2416	0.1751		-0.0001	
10H	0.4011	5.1136	0.2840	0.1801		-0.0002	
11N	-2.1976	1.2429	-0.0340	0.0043		-0.0028	
12C	-2.0061	-0.1210	-0.1121	-0.0818		0.0161	
13N	-3.2469	-0.6468	-0.1383	-0.1750		0.0008	
14C	-4.2072	0.3589	-0.0874	-0.0377		-0.0001	
15C	-3.5469	1.5498	-0.0185	0.0341		0.0008	
16H	-5.2649	0.1419	-0.0996	0.2100		0.0001	
17H	-3.9234	2.5592	0.0452	0.2079		0.0000	
18N	2.4206	0.9061	0.0378	-0.0002		-0.0031	
19C	3.8002	1.0131	0.0725	0.1217		0.0019	
20C	4.2844	-0.2583	-0.0146	-0.1047		0.0011	
21N	3.1871	-1.1113	-0.1013	-0.1634		0.0005	
22C	2.0336	-0.4123	-0.0699	-0.1136		0.0218	
23H	4.3176	1.9567	0.1530	0.2098		0.0000	
24H	5.3004	-0.6239	-0.0238	0.2114		0.0001	
25H	-0.6510	-2.7157	1.8022	0.4253		-0.0203	
26C	-3.5264	-2.0839	-0.2498	-0.4020		0.0115	
27H	-4.4506	-2.3039	0.2915	0.2010		0.0002	
28H	-3.6454	-2.3557	-1.3035	0.2298		0.0001	
29H	-2.6938	-2.6449	0.1891	0.3403		-0.0031	
30C	3.2504	-2.5693	-0.2143	-0.4742		0.0099	
31H	2.2316	-2.9455	-0.3300	0.2934		-0.0009	
32H	3.8493	-2.8455	-1.0875	0.2221		-0.0002	
33H	3.6974	-2.9962	0.6887	0.2299		-0.0001	
34O	-0.9382	-3.4819	1.2711	-0.6738		0.6966	
35O	-0.1679	-2.7047	-0.3862	-0.2221		1.2628	

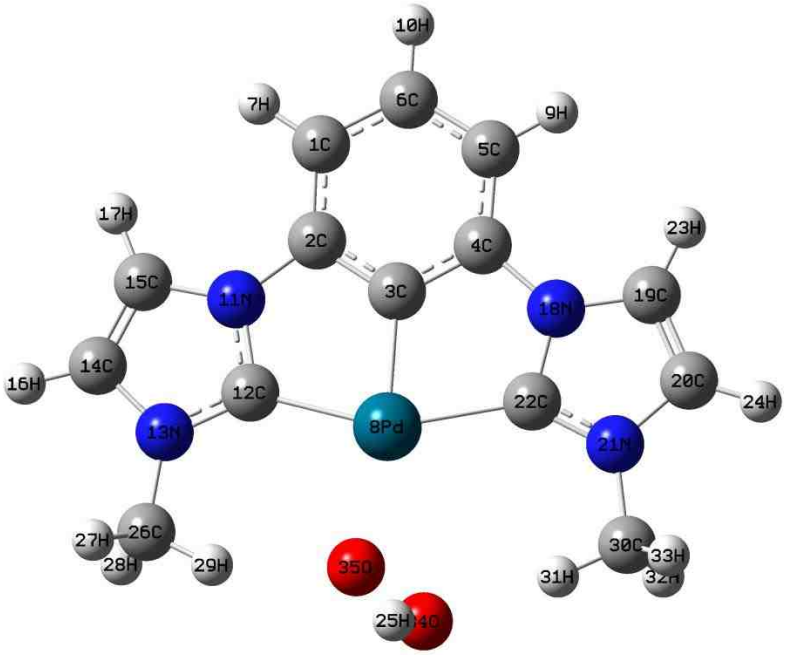
*** *** ***

(CCC) palladium hydroperoxide **74**

(see Figure 3-27, Figure 4-4)



74



Energy: -1038.02826307 hartrees

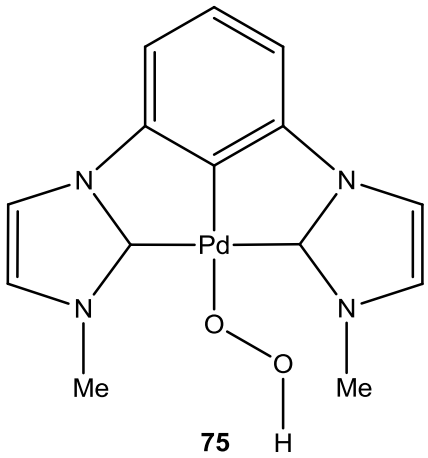
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-1.4188	3.3066	0.0670	-0.6956	-0.3425		
2C	-1.3228	1.9139	0.0257	0.8802	0.2971		
3C	-0.0888	1.2702	0.0155	0.2701	-0.4659		
4C	1.0739	2.0291	0.0489	0.7670	0.3708		

5C	1.0330	3.4254	0.0919	-0.6405	-0.3590		
6C	-0.2259	4.0471	0.1003	-0.8078	-0.0257		
7H	-2.3771	3.8197	0.0743	0.1721	0.1565		
8Pd	-0.0040	-0.7025	-0.0083	-0.4907	0.1759		
9H	1.9361	4.0296	0.1175	0.1709	0.1585		
10H	-0.2787	5.1316	0.1329	0.1765	0.1059		
11N	-2.3935	0.9723	-0.0113	-0.0147	0.1895		
12C	-2.0405	-0.3599	-0.0392	-0.1611	-0.2178		
13N	-3.2144	-1.0256	-0.0775	-0.1820	0.2475		
14C	-4.2877	-0.1386	-0.0738	-0.0767	-0.2340		
15C	-3.7695	1.1213	-0.0316	0.0766	-0.2468		
16H	-5.3127	-0.4770	-0.1016	0.2071	0.1773		
17H	-4.2595	2.0825	-0.0148	0.2061	0.1929		
18N	2.2321	1.2002	0.0202	-0.0313	0.0921		
19C	3.5769	1.5194	-0.0317	0.0825	-0.2174		
20C	4.2437	0.3352	-0.1062	-0.0887	-0.2744		
21N	3.2885	-0.6767	-0.0963	-0.1769	0.3449		
22C	2.0356	-0.1686	-0.0170	-0.0903	-0.1953		
23H	3.9435	2.5339	-0.0126	0.2053	0.1898		
24H	5.3011	0.1244	-0.1639	0.2066	0.1969		
25H	0.6504	-3.7945	1.3274	0.4535	0.3682		
26C	-3.3208	-2.4847	-0.1328	-0.5379	-0.0097		
27H	-3.9228	-2.8405	0.7095	0.2141	0.0326		
28H	-3.7956	-2.7847	-1.0724	0.2208	0.0361		
29H	-2.3092	-2.9008	-0.0752	0.3261	0.0353		
30C	3.6075	-2.0992	-0.2149	-0.4803	-0.3384		
31H	2.6953	-2.6763	-0.0459	0.3347	0.2432		
32H	4.0026	-2.3065	-1.2151	0.2234	0.1029		
33H	4.3602	-2.3659	0.5341	0.2088	0.0809		
34O	0.9224	-3.5805	0.4192	-0.5317	-0.5442		
35O	-0.2241	-2.7765	-0.0279	-0.3961	-0.3236		

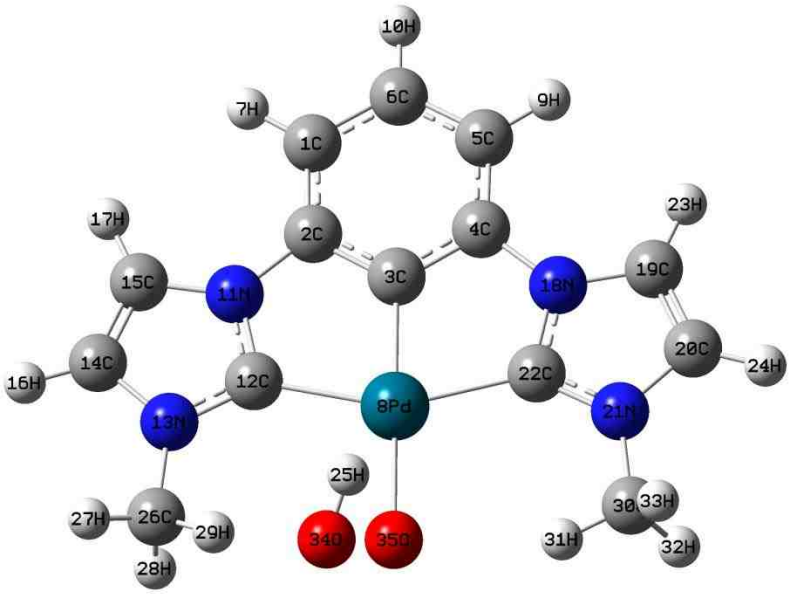
*** *** ***

(CCC) triplet palladium hydroperoxide **75**

(see Figure 3-27)



75



Energy: -1037.97910993 hartrees

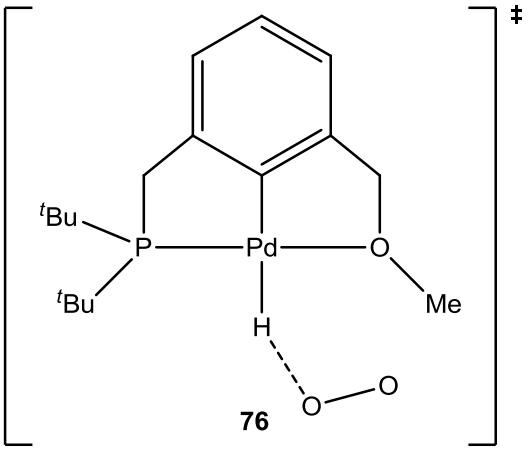
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-0.9186	3.4539	0.1408	-0.6722		-0.0047	
2C	-1.0037	2.0631	0.0414	0.7844		0.0038	
3C	0.1398	1.2730	0.0178	0.3244		-0.0642	
4C	1.3928	1.8683	0.0918	0.8030		0.0048	
5C	1.5315	3.2547	0.1937	-0.6473		-0.0038	
6C	0.3605	4.0301	0.2166	-0.8186		0.0053	

7H	-1.8012	4.0878	0.1606	0.1761		-0.0002	
8Pd	-0.0192	-0.6950	-0.1574	-0.8062		0.0679	
9H	2.5035	3.7374	0.2535	0.1752		-0.0001	
10H	0.4467	5.1101	0.2943	0.1801		-0.0001	
11N	-2.1830	1.2630	-0.0428	0.0089		-0.0034	
12C	-2.0012	-0.1010	-0.1330	-0.0660		0.0245	
13N	-3.2446	-0.6203	-0.1465	-0.1737		0.0004	
14C	-4.1983	0.3907	-0.0770	-0.0310		0.0007	
15C	-3.5306	1.5774	-0.0082	0.0320		0.0003	
16H	-5.2570	0.1794	-0.0761	0.2101		0.0001	
17H	-3.8994	2.5884	0.0685	0.2078		0.0000	
18N	2.4304	0.8864	0.0452	0.0023		-0.0034	
19C	3.8106	0.9810	0.0838	0.1217		0.0017	
20C	4.2840	-0.2941	-0.0079	-0.1038		0.0011	
21N	3.1792	-1.1369	-0.1013	-0.1653		-0.0005	
22C	2.0319	-0.4274	-0.0692	-0.1100		0.0270	
23H	4.3356	1.9197	0.1704	0.2099		0.0000	
24H	5.2963	-0.6694	-0.0142	0.2115		0.0001	
25H	-0.6530	-2.7400	1.8472	0.4257		-0.0219	
26C	-3.5332	-2.0569	-0.2452	-0.4096		0.0099	
27H	-4.4614	-2.2633	0.2940	0.2002		0.0003	
28H	-3.6493	-2.3401	-1.2961	0.2293		0.0000	
29H	-2.7090	-2.6190	0.2099	0.3428		-0.0026	
30C	3.2331	-2.5949	-0.2119	-0.4750		0.0093	
31H	2.2139	-2.9658	-0.3379	0.2918		-0.0011	
32H	3.8376	-2.8776	-1.0788	0.2226		-0.0002	
33H	3.6687	-3.0233	0.6958	0.2303		-0.0001	
34O	-1.0495	-3.4934	1.3708	-0.6559		0.7133	
35O	-0.1827	-2.6826	-0.4249	-0.2555		1.2357	

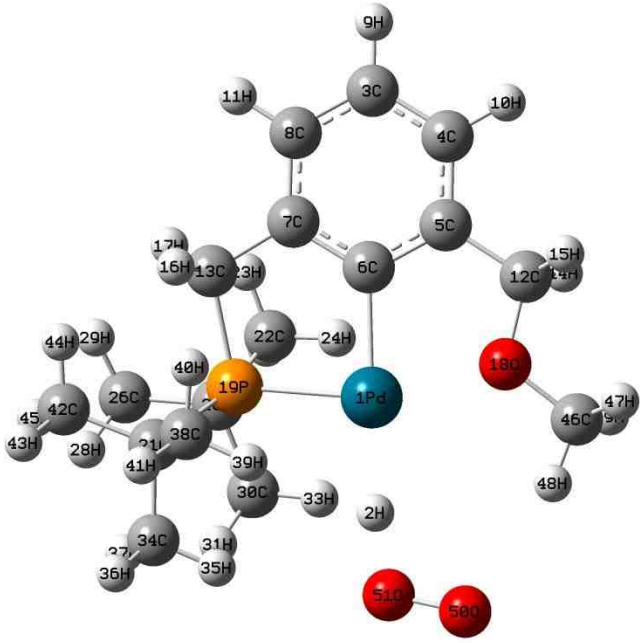
*** *** ***

(PCO) transition state **76**

(see Figure 3-28)



76



Energy: -1358.90161470 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.5527	0.7739	-0.0608	-0.8047	0.1728	0.0846	
2H	-0.3132	2.3770	0.0194	0.2138	0.0384	-0.0028	
3C	3.0147	-3.3949	-0.3240	-0.5495	-0.0199	-0.0865	
4C	3.6824	-2.1758	-0.1620	0.3145	0.0507	-0.0142	
5C	2.9467	-0.9851	-0.0756	0.2587	-0.0450	-0.1243	

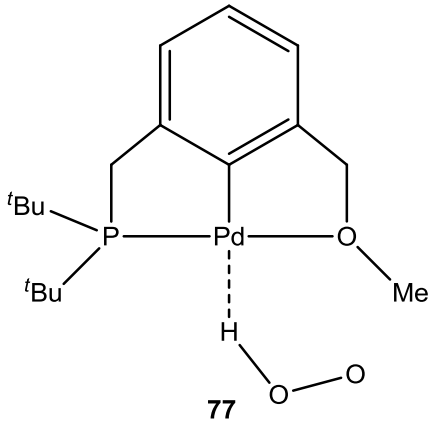
6C	1.5499	-1.0273	-0.1658	-0.9589	0.3106	0.0441	
7C	0.8776	-2.2456	-0.3470	0.3815	0.0139	-0.0737	
8C	1.6180	-3.4351	-0.4166	0.7520	0.0335	-0.0165	
9H	3.5861	-4.3178	-0.3858	0.1754	0.0005	0.0059	
10H	4.7703	-2.1618	-0.1010	0.1680	0.0034	-0.0200	
11H	1.1165	-4.3924	-0.5528	0.1674	0.0032	-0.0101	
12C	3.6294	0.3464	0.1540	-0.4349	-0.0046	0.4806	
13C	-0.6324	-2.2115	-0.5152	-1.2367	0.0178	-0.1063	
14H	3.9840	0.4311	1.1939	0.2048	-0.0008	-0.0622	
15H	4.4974	0.4783	-0.5089	0.1994	-0.0008	-0.0598	
16H	-0.8890	-2.3790	-1.5686	0.2488	-0.0009	-0.0254	
17H	-1.1385	-3.0056	0.0488	0.2518	-0.0013	-0.0265	
18O	2.7039	1.4244	-0.0908	-0.2781	0.0015	-0.7158	
19P	-1.3008	-0.5063	-0.0445	0.9432	0.0837	0.9314	
20C	-2.0287	-0.7167	1.7119	-0.3740	-0.0666	-0.0633	
21C	-2.6206	-0.1367	-1.3769	-0.6160	-0.0068	-0.0743	
22C	-0.9288	-1.3778	2.5739	-0.6179	-0.0078	-0.0045	
23H	-0.6953	-2.3979	2.2524	0.2326	0.0000	0.0024	
24H	-0.0003	-0.7987	2.5596	0.2521	-0.0001	0.0165	
25H	-1.2823	-1.4312	3.6122	0.2162	0.0002	-0.0395	
26C	-3.2949	-1.5932	1.7559	-0.3776	-0.0028	0.0306	
27H	-3.5681	-1.7741	2.8042	0.2211	0.0005	-0.0487	
28H	-4.1511	-1.1070	1.2786	0.2257	0.0000	-0.0095	
29H	-3.1457	-2.5719	1.2856	0.2243	0.0000	-0.0022	
30C	-2.3358	0.6722	2.3119	-0.6446	0.0401	0.0160	
31H	-3.1306	1.1981	1.7765	0.2236	0.0000	0.0010	
32H	-2.6648	0.5459	3.3524	0.2130	0.0008	-0.0372	
33H	-1.4490	1.3136	2.3093	0.2560	-0.0005	0.0133	
34C	-3.4595	1.0958	-0.9825	-0.5060	0.0019	0.0156	
35H	-2.8333	1.9526	-0.7141	0.2611	0.0004	0.0237	
36H	-4.0799	1.3927	-1.8386	0.2176	-0.0001	-0.0352	
37H	-4.1378	0.8838	-0.1497	0.2194	0.0001	-0.0138	
38C	-1.8296	0.2022	-2.6628	-0.5701	0.0033	-0.0087	
39H	-1.1973	1.0848	-2.5242	0.2575	0.0004	0.0198	
40H	-1.1878	-0.6231	-2.9919	0.2218	0.0000	0.0004	
41H	-2.5406	0.4120	-3.4732	0.2164	-0.0002	-0.0393	
42C	-3.5619	-1.3242	-1.6730	-0.4233	0.0042	0.0219	
43H	-4.2280	-1.0459	-2.5008	0.2211	0.0012	-0.0502	
44H	-3.0202	-2.2231	-1.9850	0.2186	0.0000	0.0017	

45H	-4.1953	-1.5867	-0.8222	0.2187	0.0000	-0.0033	
46C	3.2176	2.7185	0.2360	-0.3679	0.0072	0.4512	
47H	4.0977	2.9379	-0.3836	0.1935	0.0021	-0.0496	
48H	2.4217	3.4364	0.0316	0.2584	-0.0010	0.0529	
49H	3.4950	2.7632	1.2984	0.1946	0.0003	-0.0440	
50O	0.1825	4.4786	0.0228	-0.1724	0.7547	-0.4407	
51O	-0.7734	3.6139	0.0538	-0.1100	0.6117	0.0941	

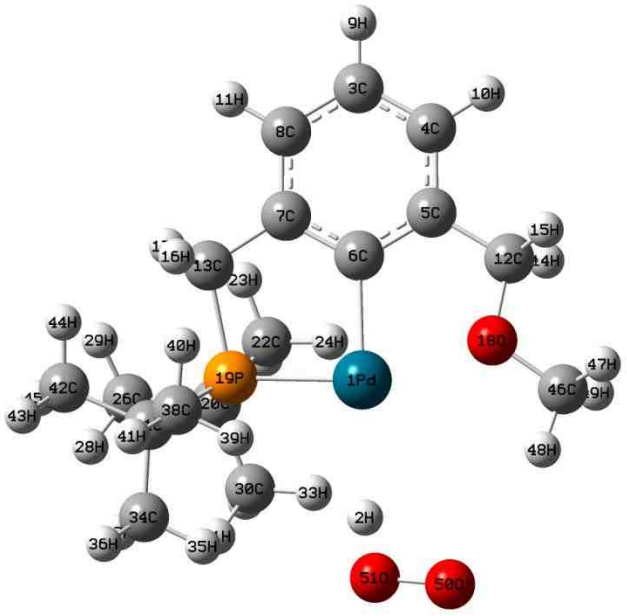
*** *** ***

(PCO) palladium(I)/hydroperoxy radical pair intermediate **77**

(see Figure 3-28)



77



Energy: -1358.90955424 hartrees

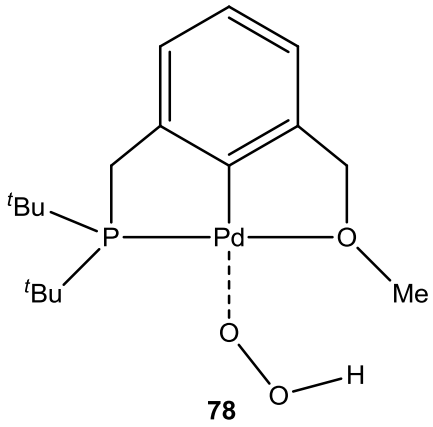
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.5812	0.7850	-0.0738	-0.7384		0.3305	
2H	-0.5357	2.7868	0.0331	0.4454		0.0618	
3C	2.9893	-3.4205	-0.3436	-0.5364		-0.0242	
4C	3.6867	-2.2191	-0.1740	0.2949		0.0631	
5C	2.9792	-1.0105	-0.0897	0.1487		-0.0176	
6C	1.5853	-1.0215	-0.1903	-0.7221		0.3795	
7C	0.8811	-2.2182	-0.3812	0.2904		-0.0001	
8C	1.5920	-3.4257	-0.4475	0.7462		0.0300	
9H	3.5375	-4.3576	-0.4027	0.1737		0.0006	
10H	4.7744	-2.2329	-0.1048	0.1660		0.0048	
11H	1.0683	-4.3705	-0.5896	0.1655		0.0042	
12C	3.6943	0.3039	0.1490	-0.4013		-0.0222	
13C	-0.6271	-2.1501	-0.5706	-1.2721		-0.0003	
14H	4.0574	0.3674	1.1878	0.2023		-0.0011	
15H	4.5637	0.4158	-0.5165	0.1969		-0.0011	
16H	-0.8589	-2.2629	-1.6369	0.2481		-0.0010	
17H	-1.1498	-2.9691	-0.0595	0.2499		-0.0017	

18O	2.8020	1.4117	-0.0799	-0.2754		0.0008	
19P	-1.3185	-0.4660	-0.0468	0.7430		0.2135	
20C	-2.0126	-0.7540	1.7176	-0.3716		-0.0972	
21C	-2.7028	-0.1488	-1.3382	-0.6536		0.0061	
22C	-0.8885	-1.4265	2.5377	-0.6049		-0.0043	
23H	-0.6536	-2.4350	2.1826	0.2348		0.0000	
24H	0.0347	-0.8391	2.5167	0.2515		-0.0001	
25H	-1.2171	-1.5112	3.5825	0.2140		0.0004	
26C	-3.2657	-1.6484	1.7635	-0.4033		0.0006	
27H	-3.5151	-1.8629	2.8118	0.2194		0.0012	
28H	-4.1389	-1.1630	1.3171	0.2241		0.0000	
29H	-3.1112	-2.6108	1.2629	0.2251		0.0000	
30C	-2.3252	0.6102	2.3688	-0.6209		0.0446	
31H	-3.1185	1.1566	1.8510	0.2235		-0.0001	
32H	-2.6566	0.4478	3.4037	0.2139		0.0011	
33H	-1.4362	1.2489	2.3953	0.2435		-0.0003	
34C	-3.6068	1.0167	-0.8885	-0.4475		-0.0170	
35H	-3.0304	1.9132	-0.6355	0.2424		0.0004	
36H	-4.2841	1.2832	-1.7109	0.2180		-0.0002	
37H	-4.2303	0.7519	-0.0285	0.2215		0.0002	
38C	-1.9732	0.2754	-2.6338	-0.5220		-0.0022	
39H	-1.3753	1.1800	-2.4815	0.2465		0.0006	
40H	-1.3050	-0.5058	-3.0139	0.2228		0.0001	
41H	-2.7175	0.4827	-3.4146	0.2157		-0.0004	
42C	-3.5794	-1.3818	-1.6474	-0.4289		0.0047	
43H	-4.2928	-1.1183	-2.4405	0.2186		0.0025	
44H	-2.9935	-2.2316	-2.0119	0.2200		-0.0001	
45H	-4.1614	-1.7157	-0.7851	0.2187		0.0000	
46C	3.3751	2.6788	0.2404	-0.3595		0.0073	
47H	4.2590	2.8649	-0.3857	0.1934		0.0021	
48H	2.6120	3.4325	0.0411	0.2427		-0.0006	
49H	3.6643	2.7161	1.3004	0.1950		0.0003	
50O	0.1515	4.5528	0.0051	-0.1538		0.7284	
51O	-0.8981	3.7429	0.0744	-0.2645		0.3025	

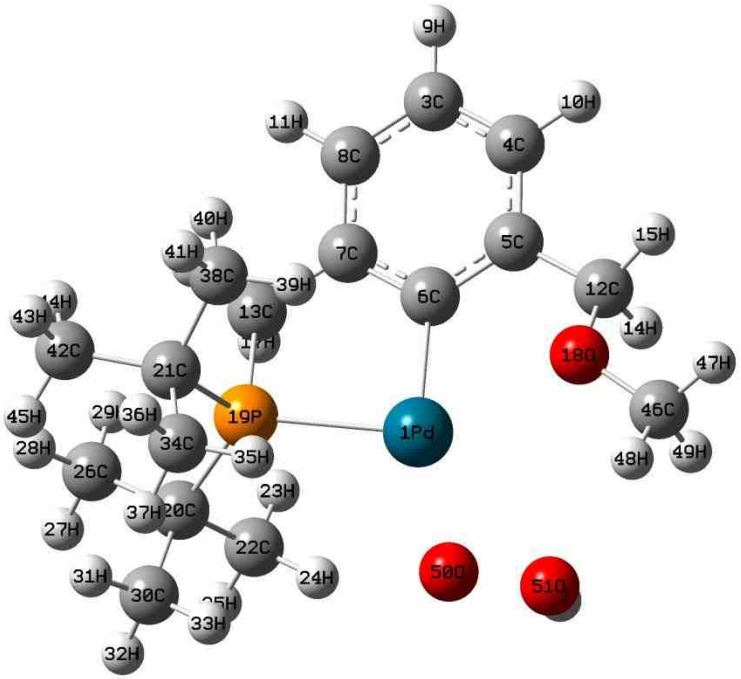
*** *** ***

(PCO) minimum energy crossing point structure **78**

(see Figure 3-28)



78



Energy: -1358.92448548 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.6887	-0.8709	0.2371	-0.6012		1.0143	
2H	1.7112	-3.5302	-1.7072	0.4628		-0.0004	
3C	2.2157	3.5924	-1.0354	-0.5159		0.0092	

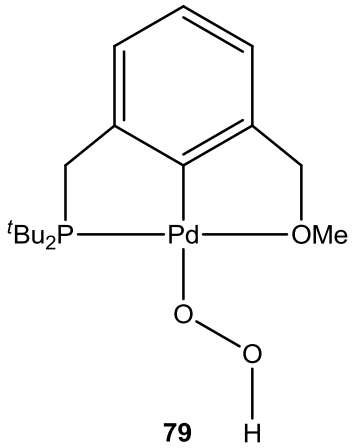
4C	3.1470	2.6244	-0.6473	0.0160		0.0279	
5C	2.7314	1.3086	-0.3997	0.5130		0.0395	
6C	1.3740	0.9618	-0.5185	-0.3128		0.2297	
7C	0.4370	1.9405	-0.9009	0.3607		-0.0518	
8C	0.8660	3.2525	-1.1606	0.4359		0.0094	
9H	2.5395	4.6133	-1.2239	0.1736		-0.0009	
10H	4.1953	2.8975	-0.5311	0.1670		0.0049	
11H	0.1454	4.0160	-1.4535	0.1639		0.0043	
12C	3.7524	0.2527	-0.0390	-0.5395		0.0456	
13C	-1.0351	1.5813	-1.0636	-1.7438		-0.0277	
14H	4.0151	-0.3428	-0.9302	0.1982		0.0015	
15H	4.6789	0.7167	0.3354	0.1780		-0.0003	
16H	-1.6778	2.4528	-0.8864	0.2457		0.0007	
17H	-1.2158	1.2794	-2.1029	0.2543		-0.0004	
18O	3.2209	-0.6273	0.9546	-0.2385		-0.0144	
19P	-1.5523	0.1203	-0.0010	1.3719		0.2144	
20C	-2.9150	-0.7231	-1.0523	-0.6373		0.0285	
21C	-2.2319	0.9005	1.6148	-0.5055		-0.0026	
22C	-2.1716	-1.4219	-2.2158	-0.5426		-0.0189	
23H	-1.6565	-0.7084	-2.8699	0.2118		0.0000	
24H	-1.4318	-2.1428	-1.8556	0.2775		-0.0001	
25H	-2.9067	-1.9560	-2.8335	0.2114		-0.0005	
26C	-3.9644	0.2403	-1.6445	-0.4569		-0.0001	
27H	-4.6488	-0.3308	-2.2873	0.2169		0.0043	
28H	-4.5700	0.7309	-0.8783	0.2142		-0.0002	
29H	-3.5093	1.0175	-2.2683	0.2232		-0.0002	
30C	-3.6245	-1.8067	-0.2159	-0.4688		-0.0082	
31H	-4.2590	-1.3764	0.5656	0.2183		0.0001	
32H	-4.2747	-2.3995	-0.8739	0.2168		-0.0003	
33H	-2.9112	-2.4944	0.2522	0.2477		0.0001	
34C	-2.3746	-0.2135	2.6756	-0.6205		0.0160	
35H	-1.4268	-0.7389	2.8367	0.2354		0.0002	
36H	-2.6783	0.2347	3.6318	0.2143		0.0001	
37H	-3.1304	-0.9564	2.4053	0.2184		0.0000	
38C	-1.1610	1.8997	2.1095	-0.6025		0.0103	
39H	-0.1744	1.4345	2.2082	0.2473		-0.0006	
40H	-1.0571	2.7632	1.4453	0.2396		0.0001	
41H	-1.4571	2.2746	3.0987	0.2147		0.0003	
42C	-3.5715	1.6458	1.4701	-0.4203		0.0104	

43H	-3.8064	2.1511	2.4176	0.2182		0.0046	
44H	-3.5400	2.4151	0.6896	0.2247		-0.0002	
45H	-4.4013	0.9663	1.2519	0.2225		-0.0002	
46C	4.0686	-1.7327	1.2342	-0.3420		-0.0050	
47H	5.0345	-1.3941	1.6390	0.1793		0.0011	
48H	3.5555	-2.3438	1.9801	0.2089		0.0006	
49H	4.2391	-2.3380	0.3327	0.2056		0.0003	
50O	0.4412	-2.7845	-0.5317	-0.2086		0.3673	
51O	1.7088	-3.3968	-0.7406	-0.4512		0.0873	

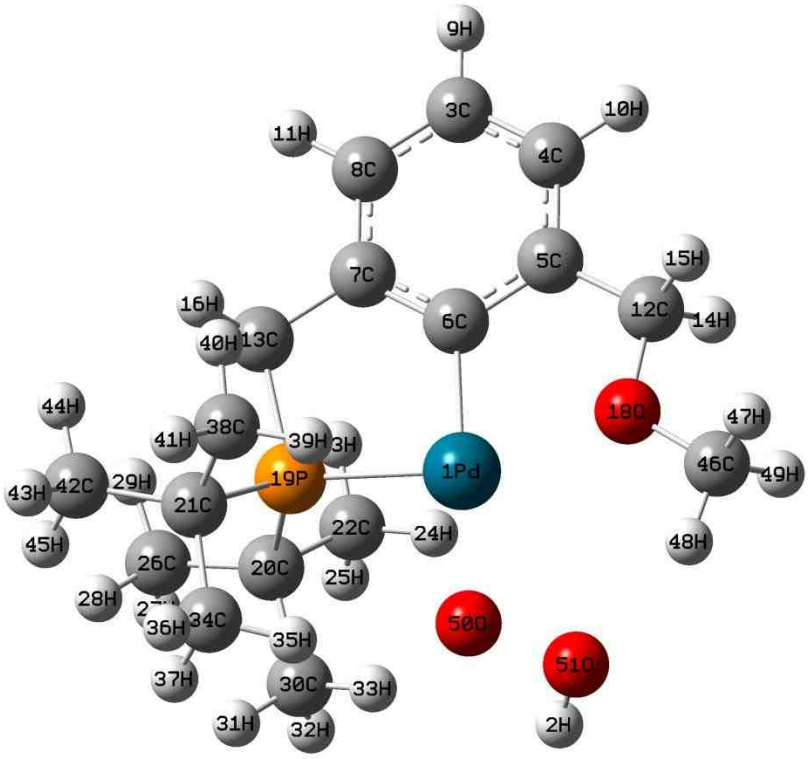
*** *** ***

(PCO) palladium hydroperoxide **79**

(see Figure 3-28, Figure 4-4)



79



Energy: -1358.98236696 hartrees

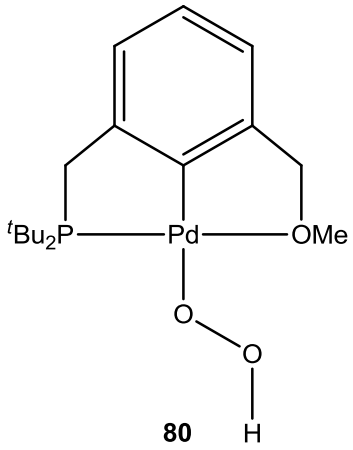
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.5532	-0.7804	-0.0731	0.3174	0.3174		
2H	0.1389	-3.8247	1.2833	0.3765	0.3765		
3C	-2.8521	3.4613	0.0248	-0.0102	-0.0102		
4C	-3.5541	2.2529	0.0353	-0.3143	-0.3143		
5C	-2.8621	1.0349	0.0097	0.3000	0.3000		
6C	-1.4544	1.0167	-0.0300	-0.6104	-0.6104		
7C	-0.7550	2.2418	-0.0532	0.4171	0.4171		
8C	-1.4551	3.4561	-0.0211	-0.3676	-0.3676		
9H	-3.3929	4.4042	0.0462	0.0999	0.0999		
10H	-4.6433	2.2631	0.0618	0.1326	0.1326		
11H	-0.9132	4.4007	-0.0367	0.1302	0.1302		
12C	-3.6312	-0.2661	0.0328	-0.0863	-0.0863		
13C	0.7602	2.2130	-0.1353	-0.1529	-0.1529		
14H	-4.1483	-0.4063	0.9963	0.0785	0.0785		
15H	-4.3946	-0.2899	-0.7607	0.0743	0.0743		

16H	1.1079	2.6465	-1.0811	0.0500	0.0500		
17H	1.2224	2.8142	0.6571	0.0600	0.0600		
18O	-2.7318	-1.3627	-0.1635	-0.0178	-0.0178		
19P	1.3459	0.4326	-0.0280	0.0172	0.0172		
20C	2.2585	0.2966	1.6433	0.5259	0.5259		
21C	2.4398	0.1495	-1.5633	0.5886	0.5886		
22C	1.2059	0.6464	2.7221	-0.0975	-0.0975		
23H	0.8143	1.6644	2.6219	0.0051	0.0051		
24H	0.3575	-0.0445	2.6920	-0.0181	-0.0181		
25H	1.6779	0.5689	3.7105	0.0188	0.0188		
26C	3.4581	1.2544	1.7810	-0.3305	-0.3305		
27H	3.8434	1.1951	2.8079	0.0669	0.0669		
28H	4.2798	0.9859	1.1118	0.0646	0.0646		
29H	3.1920	2.3015	1.5954	0.0534	0.0534		
30C	2.7209	-1.1589	1.8714	-0.5013	-0.5013		
31H	3.6145	-1.4020	1.2896	0.1127	0.1127		
32H	2.9747	-1.2904	2.9318	0.1018	0.1018		
33H	1.9392	-1.8767	1.6022	0.1326	0.1326		
34C	3.0252	-1.2792	-1.5384	-0.1832	-0.1832		
35H	2.2643	-2.0358	-1.3174	0.0176	0.0176		
36H	3.4541	-1.5004	-2.5252	0.0253	0.0253		
37H	3.8333	-1.3756	-0.8067	0.0151	0.0151		
38C	1.4887	0.2617	-2.7790	-0.1259	-0.1259		
39H	0.6959	-0.4912	-2.7362	-0.0308	-0.0308		
40H	1.0190	1.2481	-2.8634	0.0092	0.0092		
41H	2.0712	0.0952	-3.6948	0.0301	0.0301		
42C	3.5765	1.1805	-1.7200	-0.4780	-0.4780		
43H	4.0670	1.0187	-2.6893	0.0874	0.0874		
44H	3.2175	2.2161	-1.7081	0.0915	0.0915		
45H	4.3452	1.0767	-0.9496	0.0985	0.0985		
46C	-3.3597	-2.6450	-0.1889	-0.1578	-0.1578		
47H	-4.0537	-2.7015	-1.0390	0.0534	0.0534		
48H	-2.5628	-3.3803	-0.2851	0.1643	0.1643		
49H	-3.9091	-2.8161	0.7475	0.0650	0.0650		
50O	0.3495	-2.6578	-0.2185	-0.3838	-0.3838		
51O	-0.4820	-3.5740	0.5786	-0.5148	-0.5148		

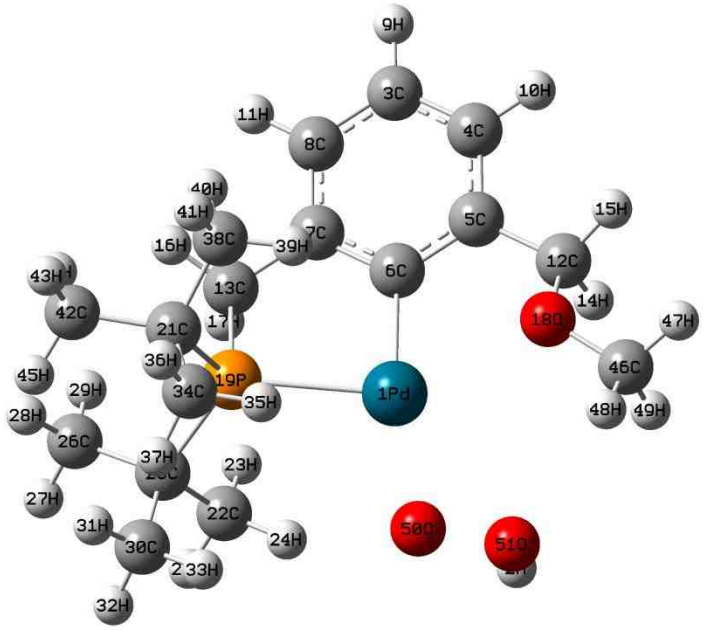
*** *** ***

(PCO) triplet palladium hydroperoxide **80**

(see Figure 3-28)



80



Energy: -1358.92488357 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.6898	-0.8705	0.1825	-0.6232		1.0151	
2H	1.6665	-3.6790	-1.6056	0.4638		-0.0003	

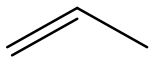
3C	2.2303	3.6047	-1.0093	-0.5091		0.0158	
4C	3.1531	2.6282	-0.6217	0.0254		0.0208	
5C	2.7265	1.3152	-0.3799	0.4653		0.0483	
6C	1.3664	0.9804	-0.5048	-0.2726		0.2314	
7C	0.4381	1.9676	-0.8856	0.3651		-0.0596	
8C	0.8779	3.2763	-1.1397	0.4475		0.0054	
9H	2.5624	4.6232	-1.1956	0.1737		-0.0011	
10H	4.2031	2.8933	-0.5028	0.1667		0.0049	
11H	0.1641	4.0454	-1.4335	0.1640		0.0043	
12C	3.7343	0.2466	-0.0188	-0.5333		0.0507	
13C	-1.0345	1.6143	-1.0465	-1.7302		-0.0354	
14H	4.0223	-0.3263	-0.9171	0.1990		0.0018	
15H	4.6499	0.6945	0.3982	0.1786		-0.0002	
16H	-1.6767	2.4816	-0.8480	0.2456		0.0007	
17H	-1.2243	1.3281	-2.0888	0.2543		-0.0002	
18O	3.1701	-0.6576	0.9345	-0.2361		-0.0148	
19P	-1.5363	0.1368	-0.0008	1.3476		0.2137	
20C	-2.9015	-0.7048	-1.0499	-0.6378		0.0282	
21C	-2.2096	0.8953	1.6283	-0.5017		-0.0008	
22C	-2.1591	-1.4009	-2.2156	-0.5421		-0.0188	
23H	-1.6358	-0.6871	-2.8627	0.2126		0.0000	
24H	-1.4261	-2.1289	-1.8555	0.2761		-0.0001	
25H	-2.8951	-1.9269	-2.8392	0.2109		-0.0006	
26C	-3.9521	0.2600	-1.6381	-0.4503		-0.0004	
27H	-4.6382	-0.3091	-2.2814	0.2163		0.0043	
28H	-4.5567	0.7504	-0.8712	0.2142		-0.0002	
29H	-3.4979	1.0374	-2.2619	0.2224		-0.0002	
30C	-3.6041	-1.7915	-0.2120	-0.4784		-0.0085	
31H	-4.2361	-1.3648	0.5735	0.2179		0.0000	
32H	-4.2550	-2.3871	-0.8663	0.2163		-0.0003	
33H	-2.8844	-2.4756	0.2513	0.2486		0.0001	
34C	-2.3485	-0.2302	2.6768	-0.6216		0.0151	
35H	-1.3988	-0.7548	2.8280	0.2360		0.0002	
36H	-2.6491	0.2071	3.6389	0.2139		0.0001	
37H	-3.1038	-0.9717	2.4017	0.2178		0.0000	
38C	-1.1385	1.8882	2.1346	-0.6042		0.0085	
39H	-0.1539	1.4191	2.2317	0.2477		-0.0005	
40H	-1.0305	2.7584	1.4797	0.2392		0.0001	
41H	-1.4376	2.2535	3.1265	0.2143		0.0003	

42C	-3.5496	1.6414	1.4884	-0.4222		0.0099	
43H	-3.7849	2.1424	2.4382	0.2177		0.0048	
44H	-3.5179	2.4146	0.7121	0.2242		-0.0002	
45H	-4.3795	0.9638	1.2663	0.2228		-0.0002	
46C	4.0181	-1.7603	1.2259	-0.3398		-0.0043	
47H	4.9715	-1.4152	1.6542	0.1791		0.0012	
48H	3.4935	-2.3802	1.9558	0.2110		0.0006	
49H	4.2134	-2.3566	0.3239	0.2049		0.0003	
50O	0.4005	-2.8114	-0.5084	-0.2035		0.3722	
51O	1.6630	-3.4616	-0.6545	-0.4545		0.0878	

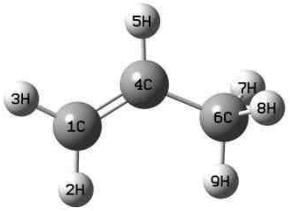
*** *** ***

Propene (**81**)

(see Figure 4-5, Figure 4-6, Figure 4-7)



81



Energy: -117.91392362 hartrees

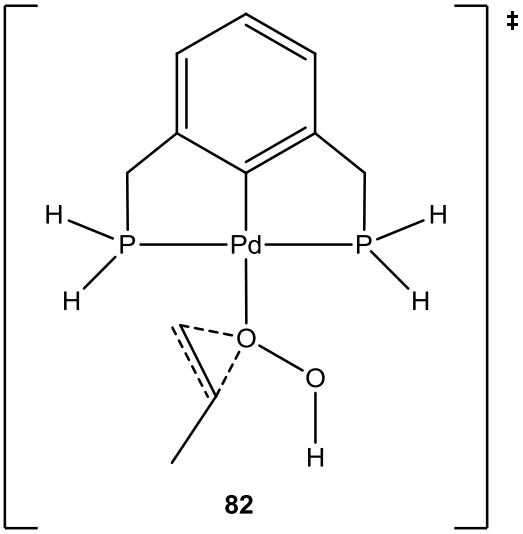
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-1.2858	0.2207	-0.0001	-0.4602			
2H	-1.3097	1.3095	0.0000	0.1759			
3H	-2.2466	-0.2880	0.0007	0.1803			
4C	-0.1327	-0.4558	-0.0003	0.1923			
5H	-0.1642	-1.5469	0.0004	0.1753			
6C	1.2370	0.1633	0.0000	-0.8820			
7H	1.8123	-0.1504	0.8819	0.2084			

8H	1.8136	-0.1515	-0.8806	0.2084			
9H	1.1835	1.2578	-0.0005	0.2016			

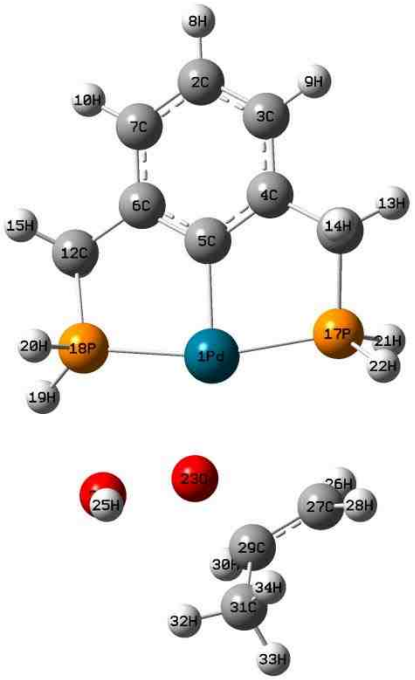
*** *** ***

(PCP) transition state **82**

(see Figure 4-5, Figure 4-6)



82



Energy: -1389.77117467 hartrees

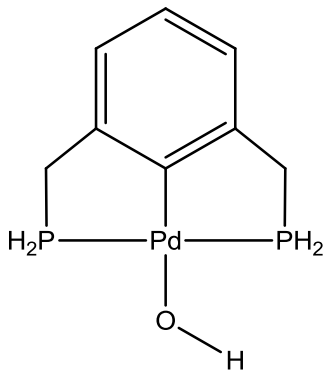
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.3139	0.0163	-0.0103	-0.9258			0.0038
2C	-4.5595	-0.1251	-0.0037	-0.3889			-0.0720
3C	-3.8282	-1.2951	-0.2123	0.0782			-0.0217
4C	-2.4259	-1.2678	-0.2228	-0.8109			-0.1032
5C	-1.7349	-0.0517	0.0006	2.0288			0.0322
6C	-2.4881	1.1296	0.2233	-0.8382			-0.0809
7C	-3.8897	1.0811	0.2075	0.0374			-0.0302
8H	-5.6462	-0.1529	-0.0056	0.1773			0.0114
9H	-4.3514	-2.2352	-0.3779	0.1709			-0.0013
10H	-4.4613	1.9928	0.3719	0.1711			-0.0020
11C	-1.6519	-2.5411	-0.5090	-0.6416			-0.0676
12C	-1.7883	2.4466	0.5172	-0.6754			-0.0704
13H	-2.1074	-3.4221	-0.0417	0.2392			-0.0180
14H	-1.6211	-2.7359	-1.5907	0.2502			-0.0207
15H	-2.3133	3.3016	0.0757	0.2369			-0.0219
16H	-1.7550	2.6225	1.6021	0.2517			-0.0184

17P	0.1121	-2.2743	0.0384	0.4155			0.9423
18P	-0.0222	2.3037	-0.0546	0.4819			0.8740
19H	0.6958	3.2419	0.7094	0.0541			-0.1583
20H	-0.0071	2.9361	-1.3130	0.0422			-0.1500
21H	0.1807	-2.9236	1.2890	0.0423			-0.1574
22H	0.8421	-3.1988	-0.7372	0.0369			-0.1859
23O	2.4732	0.4486	-0.1282	-0.0043			0.0768
24O	2.6860	2.0160	-0.6683	-0.6978			-0.8537
25H	2.9576	1.7851	-1.5732	0.4500			0.1741
26H	2.5783	-1.7532	1.8579	0.1841			0.0292
27C	3.0560	-1.5787	0.8996	-0.4152			-0.4799
28H	3.1664	-2.4207	0.2215	0.1713			0.0219
29C	3.7026	-0.3536	0.6238	-0.1091			0.3619
30H	3.8656	0.3000	1.4834	0.1798			-0.0483
31C	4.8525	-0.3242	-0.3653	-0.8127			0.0751
32H	5.0426	0.6945	-0.7200	0.2137			-0.0017
33H	5.7684	-0.6928	0.1137	0.2053			-0.0241
34H	4.6367	-0.9651	-1.2289	0.2009			-0.0153

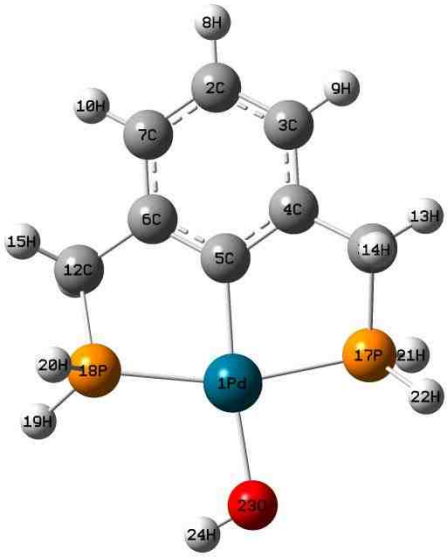
*** *** ***

(PCP) palladium hydroxide **83**

(see Figure 4-5, Figure 4-6, Figure 4-8, Figure 4-9, Figure 4-10, Figure 4-11)



83



Energy: -1196.75917942 hartrees

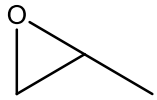
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-1.1560	0.0391	-0.0027	-0.3433			
2C	3.7528	-0.0995	-0.0109	-0.0097			
3C	3.0154	-1.2753	0.1409	-0.4063			
4C	1.6140	-1.2402	0.1611	-0.5658			
5C	0.9188	-0.0142	0.0027	1.6062			
6C	1.6859	1.1655	-0.1618	-0.2990			
7C	3.0870	1.1189	-0.1556	-0.3558			
8H	4.8393	-0.1328	-0.0164	0.1749			
9H	3.5348	-2.2253	0.2547	0.1721			
10H	3.6613	2.0361	-0.2749	0.1718			
11C	0.8334	-2.5251	0.3841	-0.7413			
12C	0.9765	2.4908	-0.3764	-0.7704			
13H	1.3154	-3.3959	-0.0742	0.2374			
14H	0.7394	-2.7377	1.4584	0.2528			
15H	1.5044	3.3343	0.0824	0.2379			
16H	0.8826	2.7127	-1.4489	0.2529			
17P	-0.8894	-2.2414	-0.2499	0.3802			
18P	-0.7527	2.2986	0.2748	0.2884			
19H	-1.4725	3.3718	-0.3012	0.0308			
20H	-0.6750	2.7870	1.5985	0.0417			

21H	-0.8740	-2.7738	-1.5578	0.0389			
22H	-1.6968	-3.2107	0.3827	0.0419			
23O	-3.2051	-0.1140	-0.0292	-0.8572			
24H	-3.6119	0.7655	-0.0232	0.4209			

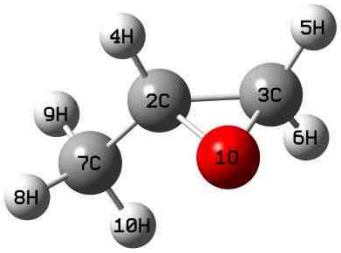
*** *** ***

Epoxide **84**

(see Figure 4-5, Figure 4-6)



84



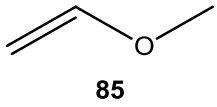
Energy: -193.11813086 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1O	0.8298	-0.7907	-0.2422	-0.3428			
2C	-0.1537	-0.0354	0.4882	0.1629			
3C	1.0453	0.6184	-0.0593	-0.2394			
4H	-0.1542	-0.2596	1.5574	0.1829			
5H	1.8777	0.8763	0.5957	0.1880			
6H	0.9614	1.2170	-0.9671	0.1853			
7C	-1.5136	0.0995	-0.1489	-0.7646			
8H	-2.0803	-0.8343	-0.0509	0.2134			
9H	-2.0889	0.8975	0.3376	0.2067			
10H	-1.4224	0.3340	-1.2149	0.2076			

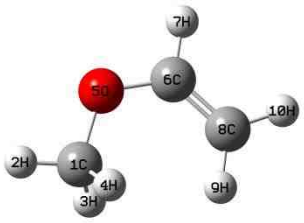
*** *** ***

Methoxyethene (**85**)

(see Figure 4-7, Figure 4-8)



85



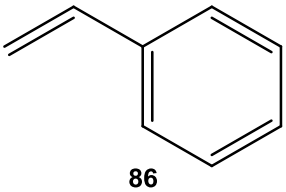
Energy: -193.12441604 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-1.3875	0.4763	-0.0001	-0.4206			
2H	-2.4299	0.1531	-0.0011	0.2049			
3H	-1.1861	1.0758	0.8973	0.1991			
4H	-1.1846	1.0763	-0.8968	0.1991			
5O	-0.6061	-0.7130	0.0002	-0.3217			
6C	0.7443	-0.5664	-0.0001	0.0367			
7H	1.2189	-1.5438	-0.0003	0.1825			
8C	1.4562	0.5696	0.0000	-0.4488			
9H	1.0137	1.5595	0.0004	0.1802			
10H	2.5387	0.5061	-0.0002	0.1887			

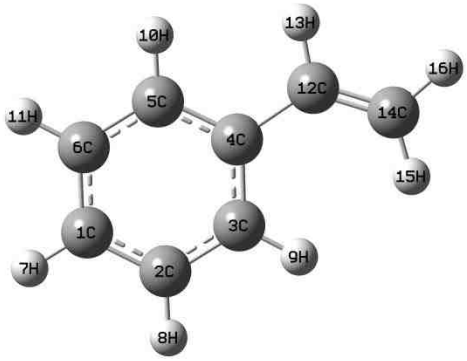
*** *** ***

Styrene (**86**)

(see Figure 4-7, Figure 4-9)



86



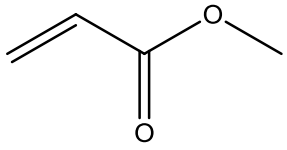
Energy: -309.66127429 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-2.2687	0.2620	0.0001	-0.2061			
2C	-1.3644	1.3310	0.0000	-0.2903			
3C	0.0086	1.0934	-0.0002	-0.4898			
4C	0.5158	-0.2204	-0.0001	0.7822			
5C	-0.4066	-1.2825	0.0000	-0.2295			
6C	-1.7830	-1.0475	0.0001	-0.2201			
7H	-3.3392	0.4505	0.0001	0.1791			
8H	-1.7324	2.3541	-0.0002	0.1793			
9H	0.6923	1.9377	-0.0005	0.1691			
10H	-0.0360	-2.3057	0.0000	0.1768			
11H	-2.4740	-1.8868	0.0003	0.1801			
12C	1.9567	-0.5297	-0.0003	-0.2869			
13H	2.1889	-1.5953	-0.0006	0.1740			
14C	2.9823	0.3356	0.0003	-0.4868			
15H	2.8469	1.4143	0.0010	0.1805			
16H	4.0087	-0.0196	0.0002	0.1886			

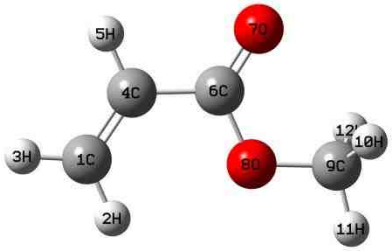
*** *** ***

Methylacrylate (**87**)

(see Figure 4-7, Figure 4-10)



87



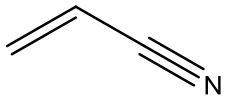
Energy: -306.48183062 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	2.2046	-0.7731	0.0479	-0.4605			
2H	1.6648	-1.6824	-0.1156	0.2256			
3H	3.2666	-0.7991	0.1758	0.1998			
4C	1.5478	0.4115	0.0935	0.0269			
5H	2.0876	1.3208	0.2570	0.2132			
6C	0.0193	0.4490	-0.0907	0.3420			
7O	-0.5970	1.5453	-0.0495	-0.4516			
8O	-0.7022	-0.7662	-0.3091	-0.3596			
9C	-2.0291	-0.6329	0.2068	-0.3694			
10H	-2.5869	0.0380	-0.4125	0.2258			
11H	-2.5064	-1.5906	0.2155	0.2025			
12H	-1.9871	-0.2464	1.2037	0.2054			

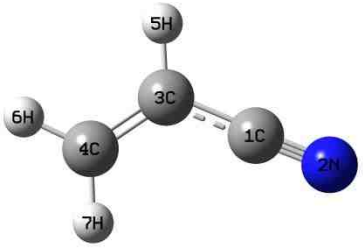
*** *** ***

Acrylonitrile (**88**)

(see Figure 4-7, Figure 4-11)



88



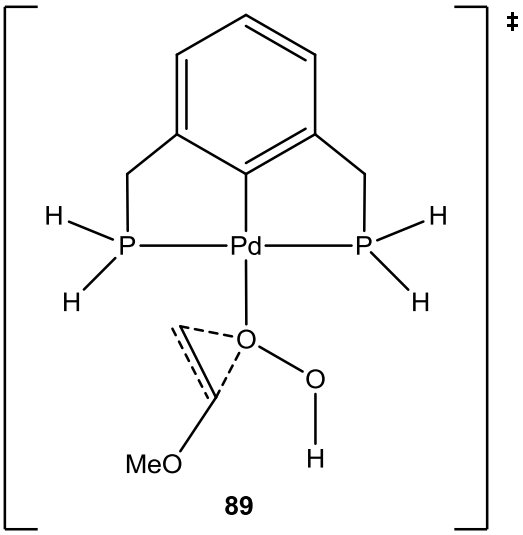
Energy: -170.84030224 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	0.7838	0.0884	0.0000	0.0938			
2N	1.9051	-0.2240	0.0000	-0.4902			
3C	-0.5863	0.5056	0.0000	0.1504			
4C	-1.6121	-0.3578	0.0000	-0.4051			
5H	-0.7538	1.5804	0.0000	0.2272			
6H	-2.6361	0.0032	0.0000	0.2072			
7H	-1.4579	-1.4327	0.0000	0.2167			

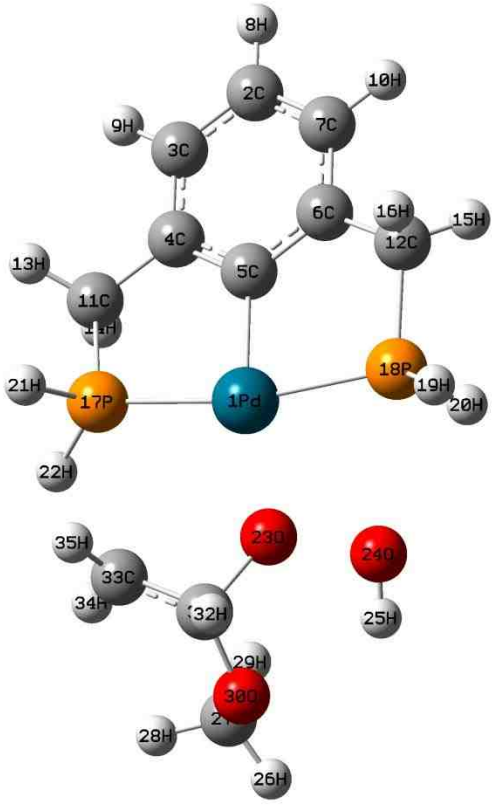
*** *** ***

(PCP) transition state **89**

(see Figure 4-8)



89



Energy: -1646.98063737 hartrees

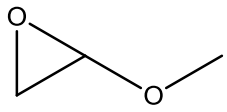
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge

1Pd	-0.1017	0.0403	-0.1230	-0.9358			-0.0177
2C	4.7411	-0.2236	0.2862	-0.3667			-0.0705
3C	3.9731	-1.3879	0.3100	0.1674			-0.0191
4C	2.5759	-1.3263	0.1996	-0.8166			-0.1105
5C	1.9302	-0.0749	0.0425	2.2200			0.0505
6C	2.7209	1.1024	0.0049	-1.1280			-0.0813
7C	4.1143	1.0141	0.1384	0.0451			-0.0316
8H	5.8225	-0.2805	0.3808	0.1782			0.0119
9H	4.4620	-2.3535	0.4249	0.1717			-0.0007
10H	4.7140	1.9222	0.1153	0.1720			-0.0019
11C	1.7674	-2.6069	0.2852	-0.6744			-0.0777
12C	2.0860	2.4638	-0.2252	-0.6402			-0.0593
13H	2.2224	-3.4236	-0.2880	0.2428			-0.0174
14H	1.7058	-2.9510	1.3274	0.2508			-0.0210
15H	2.5565	3.2441	0.3840	0.2407			-0.0202
16H	2.2150	2.7656	-1.2742	0.2528			-0.0185
17P	0.0204	-2.2434	-0.2723	0.4107			0.9968
18P	0.2535	2.3328	0.0731	0.4694			0.8457
19H	-0.3242	3.3128	-0.7541	0.0643			-0.1487
20H	0.0493	2.9199	1.3376	0.0444			-0.1497
21H	-0.0674	-2.8403	-1.5473	0.0438			-0.1601
22H	-0.7422	-3.1701	0.4664	0.0354			-0.1877
23O	-2.2703	0.5751	-0.2649	0.0664			0.0776
24O	-2.5816	2.2147	0.0098	-0.7507			-0.8927
25H	-3.3782	2.0627	0.5519	0.4828			0.2122
26H	-5.1517	-0.2731	2.1465	0.1917			-0.0182
27C	-4.3978	-0.6990	1.4793	-0.3814			0.4225
28H	-4.6227	-1.7631	1.3256	0.1876			-0.0318
29H	-3.4058	-0.5949	1.9376	0.2049			-0.0299
30O	-4.4910	0.0311	0.2631	-0.3528			-0.7337
31C	-3.4834	-0.1923	-0.7010	-0.2983			0.7906
32H	-3.8342	0.3128	-1.6033	0.1846			-0.0409
33C	-2.9034	-1.4984	-0.8789	-0.3583			-0.5357
34H	-2.9957	-2.2537	-0.1090	0.1812			0.0527
35H	-2.6581	-1.8214	-1.8841	0.1946			0.0157

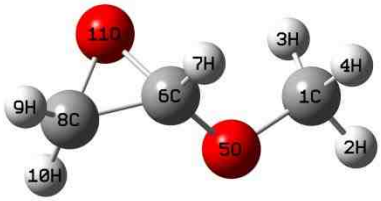
*** *** ***

Epoxide **90**

(see Figure 4-8)



90



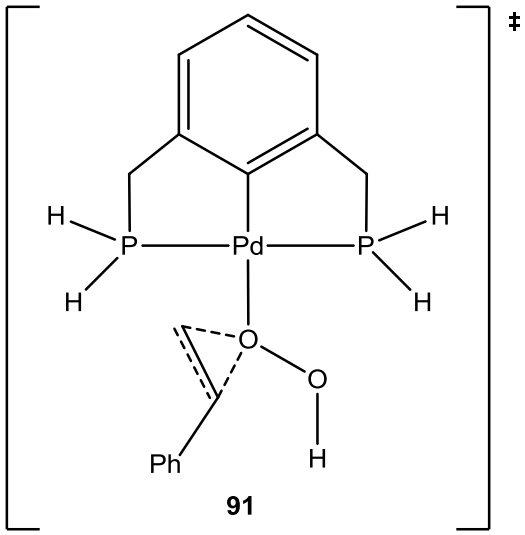
Energy: -268.32762264 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	1.9405	0.2053	-0.0437	-0.3789			
2H	2.7614	-0.3297	-0.5249	0.2035			
3H	1.7828	1.1689	-0.5427	0.2124			
4H	2.1863	0.3743	1.0148	0.1840			
5O	0.7856	-0.6271	-0.1715	-0.3472			
6C	-0.3253	-0.1230	0.4661	0.1512			
7H	-0.1873	0.0572	1.5360	0.1780			
8C	-1.6390	-0.4203	-0.0951	-0.2495			
9H	-2.5139	-0.4934	0.5501	0.1921			
10H	-1.6845	-0.9698	-1.0338	0.2072			
11O	-1.0608	0.9047	-0.1989	-0.3530			

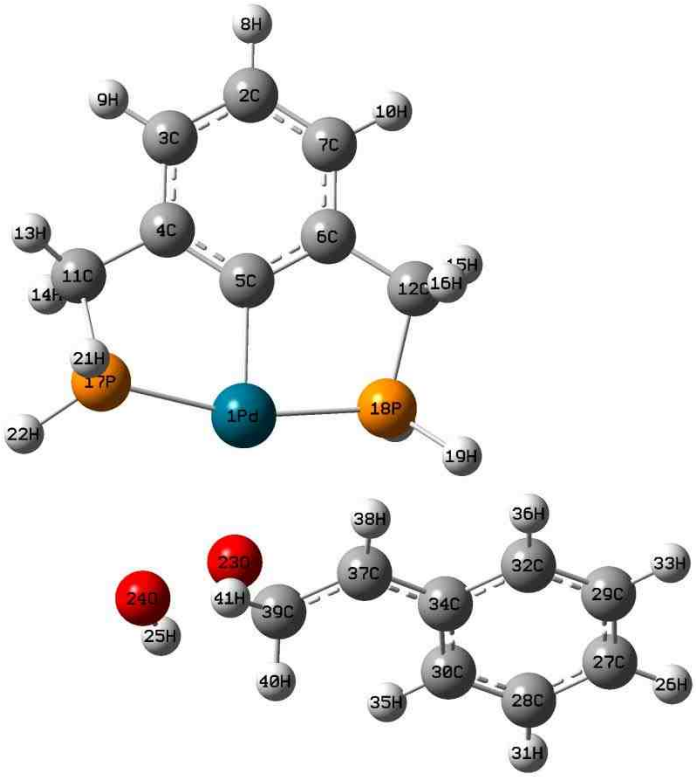
*** *** ***

(PCP) transition state **91**

(see Figure 4-9)



91



Energy: -1581.52328823 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge

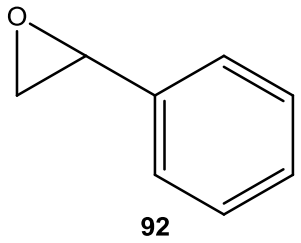
1Pd	-0.6826	-0.5763	-0.1102	-0.9375			0.0696
2C	-4.4804	2.4890	0.0603	-0.4568			-0.0703
3C	-4.6911	1.1092	0.0634	0.1009			-0.0450
4C	-3.6066	0.2223	0.0002	-0.6548			-0.0715
5C	-2.2817	0.7193	-0.0450	1.5739			-0.0454
6C	-2.0803	2.1208	-0.0363	-0.4849			-0.1504
7C	-3.1793	2.9910	0.0054	0.1605			-0.0041
8H	-5.3265	3.1700	0.1011	0.1800			0.0117
9H	-5.7062	0.7188	0.1063	0.1725			-0.0103
10H	-3.0159	4.0670	0.0035	0.1740			0.0000
11C	-3.8582	-1.2739	-0.0500	-0.6970			-0.0317
12C	-0.6710	2.6805	-0.0428	-0.7591			-0.0272
13H	-4.7450	-1.5694	0.5213	0.2389			-0.0203
14H	-4.0172	-1.6035	-1.0863	0.2553			-0.0145
15H	-0.5884	3.6093	-0.6183	0.2420			-0.0116
16H	-0.3404	2.9080	0.9803	0.2574			-0.0032
17P	-2.3120	-2.1224	0.5375	0.4475			0.8804
18P	0.4607	1.3503	-0.6764	0.4082			0.7141
19H	1.7581	1.7212	-0.2608	0.0681			-0.0411
20H	0.5571	1.6153	-2.0607	0.0343			-0.1417
21H	-2.5537	-2.3327	1.9142	0.0378			-0.2108
22H	-2.4229	-3.4521	0.0774	0.0499			-0.2151
23O	0.9850	-2.0133	-0.3466	-0.0099			0.1739
24O	0.5248	-3.3302	-1.0025	-0.5930			-0.8060
25H	1.0574	-3.2902	-1.8167	0.4570			0.1677
26H	6.3608	2.2347	-0.7897	0.1644			0.0099
27C	5.5690	1.6056	-0.3920	-0.2601			-0.2907
28C	5.2363	0.3923	-1.0137	-0.3419			0.1270
29C	4.8541	1.9871	0.7490	-0.2308			0.1861
30C	4.2217	-0.4186	-0.5130	-0.6305			-0.2135
31H	5.7732	0.0786	-1.9071	0.1640			-0.0002
32C	3.8393	1.1763	1.2584	-0.1568			-0.3089
33H	5.0925	2.9222	1.2524	0.1647			0.0009
34C	3.4934	-0.0669	0.6583	0.6204			0.5315
35H	3.9797	-1.3413	-1.0344	0.1562			0.0272
36H	3.3145	1.4813	2.1628	0.1608			0.0167
37C	2.4545	-0.8802	1.2329	0.2381			-0.6013
38H	1.9410	-0.4779	2.1041	0.1585			0.0125
39C	2.1026	-2.1939	0.8107	-0.8515			0.4593

40H	2.8604	-2.7704	0.2757	0.1878			-0.0221
41H	1.5770	-2.8066	1.5449	0.1914			-0.0315

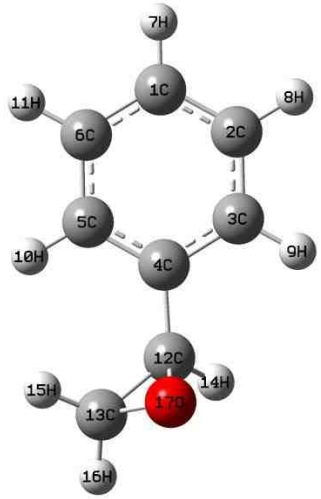
*** *** ***

Epoxide **92**

(see Figure 4-9)



92



Energy: -384.85802898 hartrees

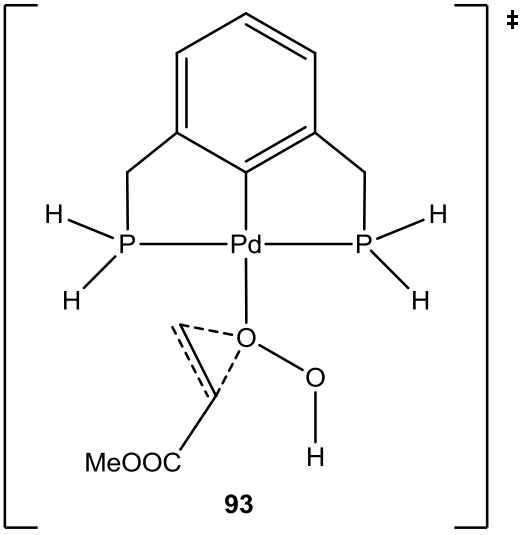
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	2.6153	0.1873	0.1572	-0.1638			
2C	2.0685	-1.0954	0.0492	-0.1254			
3C	0.6960	-1.2545	-0.1460	0.0292			
4C	-0.1529	-0.1391	-0.2264	0.3530			
5C	0.4067	1.1421	-0.1255	-0.5499			

6C	1.7815	1.3047	0.0667	-0.2453			
7H	3.6846	0.3145	0.3056	0.1805			
8H	2.7108	-1.9699	0.1155	0.1824			
9H	0.2732	-2.2535	-0.2300	0.1829			
10H	-0.2286	2.0198	-0.2049	0.1707			
11H	2.2008	2.3049	0.1405	0.1809			
12C	-1.6180	-0.3683	-0.4238	-0.2036			
13C	-2.6650	0.6218	-0.1266	-0.2556			
14H	-1.8585	-1.1313	-1.1667	0.1955			
15H	-2.4019	1.5950	0.2857	0.1870			
16H	-3.6036	0.5906	-0.6811	0.1904			
17O	-2.4462	-0.4827	0.7609	-0.3090			

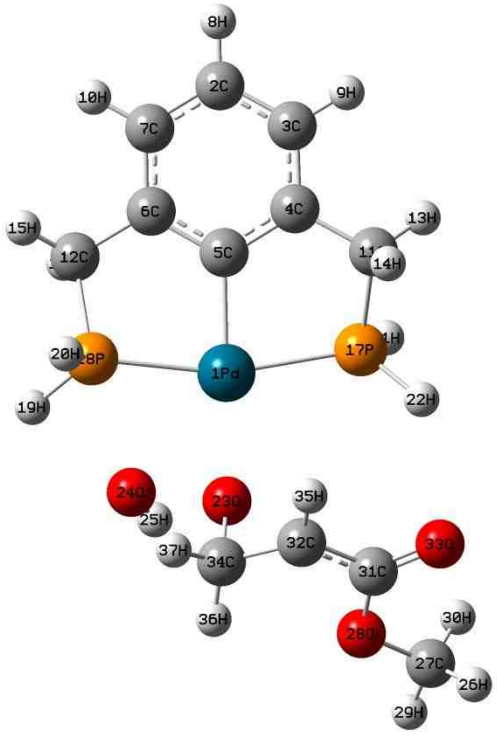
*** *** ***

(PCP) transition state **93**

(see Figure 4-10)



93



Energy: -1578.35690345 hartrees

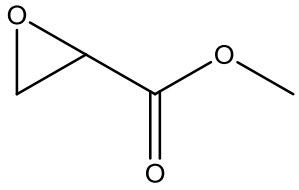
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.2671	-0.3473	0.0275	-0.9451			0.1932
2C	4.7906	1.4304	0.0148	-0.4635			-0.0597
3C	3.7011	2.2987	-0.0662	0.1128			-0.0264
4C	2.3905	1.8004	-0.0784	-0.3015			-0.0856
5C	2.1615	0.4057	0.0084	1.5931			0.1051
6C	3.2735	-0.4661	0.1078	-0.6312			-0.0777
7C	4.5754	0.0539	0.0982	0.0339			-0.0275
8H	5.8033	1.8250	0.0156	0.1815			0.0177
9H	3.8690	3.3722	-0.1257	0.1753			0.0079
10H	5.4252	-0.6223	0.1661	0.1749			0.0065
11C	1.2157	2.7520	-0.1998	-0.7598			-0.0329
12C	3.0478	-1.9590	0.2515	-0.7630			-0.0407
13H	1.4014	3.7148	0.2883	0.2415			-0.0087
14H	0.9908	2.9625	-1.2545	0.2605			-0.0070
15H	3.8580	-2.5523	-0.1858	0.2361			-0.0125

16H	2.9710	-2.2382	1.3112	0.2651			0.0014
17P	-0.2654	1.8711	0.4887	0.4703			0.6778
18P	1.3891	-2.3217	-0.4992	0.4519			0.7517
19H	0.9928	-3.5886	-0.0378	0.0804			-0.1072
20H	1.7039	-2.6091	-1.8478	0.0276			-0.1776
21H	-0.3160	2.2734	1.8412	0.0392			-0.1448
22H	-1.4084	2.5245	-0.0174	0.0890			-0.0748
23O	-1.7450	-1.1881	0.2382	-0.1367			0.1959
24O	-1.0405	-2.6794	1.2269	-0.7872			-1.0077
25H	-1.6572	-2.5345	1.9648	0.4528			0.1561
26H	-6.2058	1.4708	0.1235	0.2109			-0.0360
27C	-5.6296	0.8862	0.8470	-0.3356			0.5566
28O	-4.6837	0.0425	0.1818	-0.3119			-0.8937
29H	-6.2838	0.2095	1.3996	0.1939			-0.0163
30H	-5.1232	1.5720	1.5340	0.2043			-0.0400
31C	-3.7504	0.6802	-0.5845	0.2689			1.4192
32C	-2.8027	-0.2104	-1.2080	-0.0110			-0.6323
33O	-3.7491	1.9077	-0.7189	-0.4945			-0.9214
34C	-2.6027	-1.6075	-0.8316	-0.4168			0.3553
35H	-2.0953	0.2601	-1.8809	0.2045			0.0322
36H	-3.4703	-2.1267	-0.4198	0.2117			-0.0162
37H	-2.0741	-2.2291	-1.5616	0.1777			-0.0297

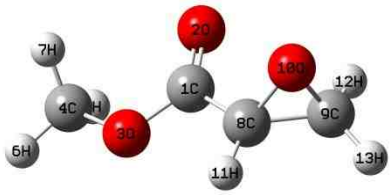
*** *** ***

Epoxide **94**

(see Figure 4-10)



94



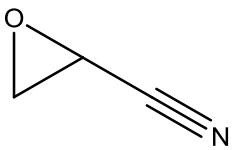
Energy: -381.67951181 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-0.3287	0.1740	0.0423	0.1921			
2O	-0.5785	1.3790	-0.2204	-0.3736			
3O	-1.3429	-0.8186	-0.1334	-0.2973			
4C	-2.6297	-0.2257	0.0599	-0.3609			
5H	-2.8500	0.4241	-0.7610	0.2284			
6H	-3.3720	-0.9945	0.1154	0.2060			
7H	-2.6302	0.3368	0.9701	0.2073			
8C	1.0656	-0.2353	0.5523	0.0021			
9C	2.0754	-0.7686	-0.3580	-0.1437			
10O	2.1572	0.6033	0.0640	-0.2868			
11H	1.1035	-0.4495	1.6365	0.2229			
12H	1.8643	-0.8922	-1.4364	0.2048			
13H	2.9033	-1.4002	0.0140	0.1987			

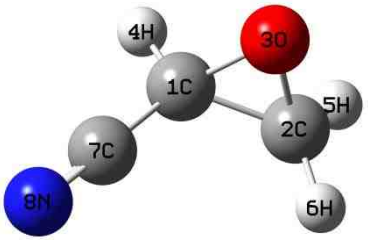
*** *** ***

Epoxide **95**

(see Figure 4-11)



95



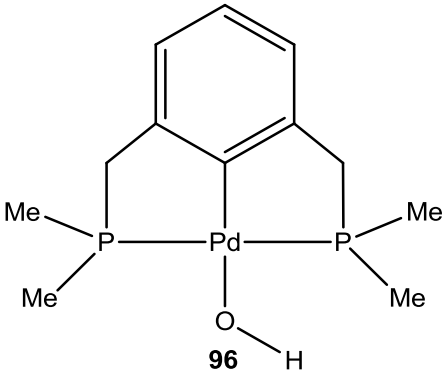
Energy: -246.03417421 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	0.2511	-0.1686	0.5353	0.0870			
2C	1.3215	0.6736	-0.0407	-0.2432			
3O	1.1700	-0.6942	-0.4298	-0.2910			
4H	0.3672	-0.5636	1.5436	0.2335			
5H	2.1963	0.8913	0.5703	0.2089			
6H	1.0677	1.4041	-0.8066	0.2179			
7C	-1.1279	-0.0103	0.1066	0.2783			
8N	-2.2371	0.1219	-0.2108	-0.4913			

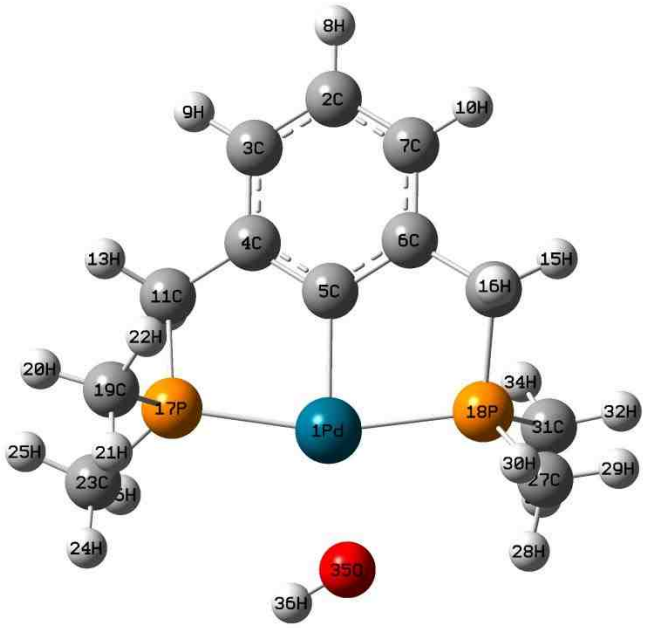
*** *** ***

(PCP) palladium hydroxide **96**

(see Figure 5-2, Figure 5-3, Figure 5-4, Figure 5-5)



96



Energy: -1354.06564195 hartrees

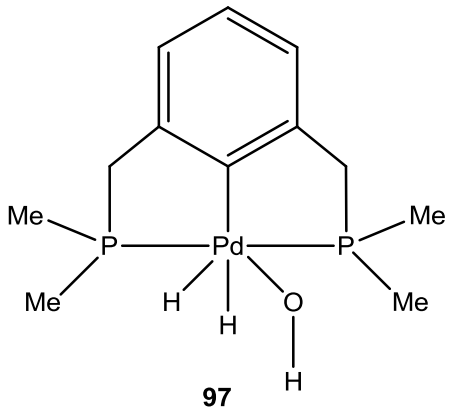
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.0617	-0.8806	-0.0196	-0.6503			
2C	-0.2642	4.0019	-0.0022	-0.5221			
3C	-1.3948	3.2262	-0.2682	0.2939			
4C	-1.3078	1.8269	-0.2835	-0.1132			
5C	-0.0817	1.1732	-0.0065	1.4633			
6C	1.0547	1.9777	0.2694	-0.7791			
7C	0.9572	3.3766	0.2592	0.1884			
8H	-0.3340	5.0870	-0.0001	0.1724			
9H	-2.3461	3.7138	-0.4764	0.1652			
10H	1.8378	3.9828	0.4666	0.1657			
11C	-2.5249	0.9890	-0.6350	-1.0021			
12C	2.3796	1.3103	0.6102	-0.9672			
13H	-3.4625	1.4352	-0.2767	0.2251			
14H	-2.6168	0.8883	-1.7267	0.2443			
15H	3.2419	1.8682	0.2216	0.2266			
16H	2.5069	1.2483	1.7010	0.2447			
17P	-2.2651	-0.7258	0.0342	0.7758			

18P	2.3156	-0.4355	-0.0217	0.9395			
19C	-3.0237	-0.6921	1.7180	-0.8889			
20H	-4.0946	-0.4585	1.6750	0.2260			
21H	-2.8865	-1.6645	2.2019	0.2451			
22H	-2.5137	0.0638	2.3228	0.2548			
23C	-3.4242	-1.8016	-0.9211	-0.8460			
24H	-3.3991	-2.8191	-0.5164	0.2407			
25H	-4.4546	-1.4284	-0.8732	0.2301			
26H	-3.1062	-1.8450	-1.9675	0.2456			
27C	3.4066	-1.4795	1.0233	-0.8552			
28H	3.2342	-2.5215	0.7342	0.2873			
29H	4.4666	-1.2242	0.9078	0.2208			
30H	3.1161	-1.3726	2.0729	0.2388			
31C	3.1445	-0.4160	-1.6671	-0.9464			
32H	4.1976	-0.1199	-1.5863	0.2279			
33H	3.0818	-1.4176	-2.1043	0.2587			
34H	2.6214	0.2825	-2.3272	0.2486			
35O	0.5086	-2.9101	-0.0187	-0.8951			
36H	-0.2850	-3.4450	-0.1663	0.4364			

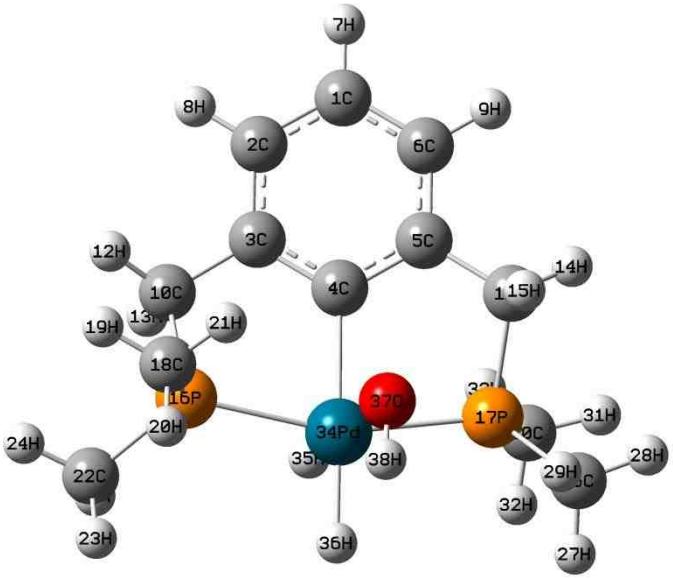
*** *** ***

(PCP) octahedral palladium intermediate **97**

(see Figure 5-3, Figure 5-4)



97



Energy: -1355.19054674 hartrees

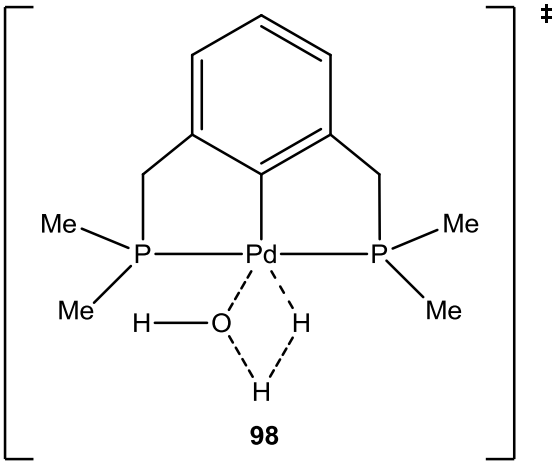
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-0.1332	3.9304	0.1312	-0.5056			
2C	-1.2911	3.2246	-0.2079	0.3753			
3C	-1.2536	1.8262	-0.3197	0.8760			
4C	-0.0564	1.1290	-0.0762	-1.7519			
5C	1.0985	1.8444	0.2927	0.9622			
6C	1.0591	3.2435	0.3817	0.7403			
7H	-0.1613	5.0147	0.2078	0.1711			
8H	-2.2183	3.7658	-0.3908	0.1640			
9H	1.9519	3.8002	0.6627	0.1648			
10C	-2.4836	1.0275	-0.7147	-1.3114			
11C	2.3465	1.0594	0.6524	-1.4043			
12H	-3.4194	1.4802	-0.3603	0.2272			
13H	-2.5580	0.9457	-1.8095	0.2455			
14H	3.2768	1.5985	0.4284	0.2179			
15H	2.3357	0.8243	1.7246	0.2855			
16P	-2.2807	-0.7072	-0.0727	1.0653			
17P	2.2912	-0.5875	-0.2057	1.4668			
18C	-2.9051	-0.7014	1.6525	-0.9189			
19H	-3.8941	-0.2324	1.7176	0.2235			

20H	-2.9653	-1.7316	2.0174	0.2432			
21H	-2.1780	-0.1725	2.2747	0.3097			
22C	-3.4775	-1.7369	-1.0189	-0.8391			
23H	-3.4373	-2.7675	-0.6528	0.2458			
24H	-4.5012	-1.3581	-0.9133	0.2307			
25H	-3.1998	-1.7397	-2.0772	0.2464			
26C	3.4031	-1.6971	0.7425	-0.8615			
27H	3.4881	-2.6620	0.2328	0.2377			
28H	4.4014	-1.2568	0.8529	0.2254			
29H	2.9539	-1.8510	1.7274	0.2825			
30C	3.1339	-0.3368	-1.8247	-0.9777			
31H	4.1740	-0.0182	-1.6857	0.2288			
32H	3.1152	-1.2682	-2.3994	0.2437			
33H	2.5950	0.4289	-2.3906	0.2578			
34Pd	0.0158	-1.0035	-0.1873	-1.3101			
35H	-0.1076	-1.0013	-1.7550	0.1893			
36H	0.0680	-2.6256	-0.3567	0.0999			
37O	0.3106	-1.0587	1.9285	-0.8047			
38H	0.2681	-1.9988	2.1626	0.4586			

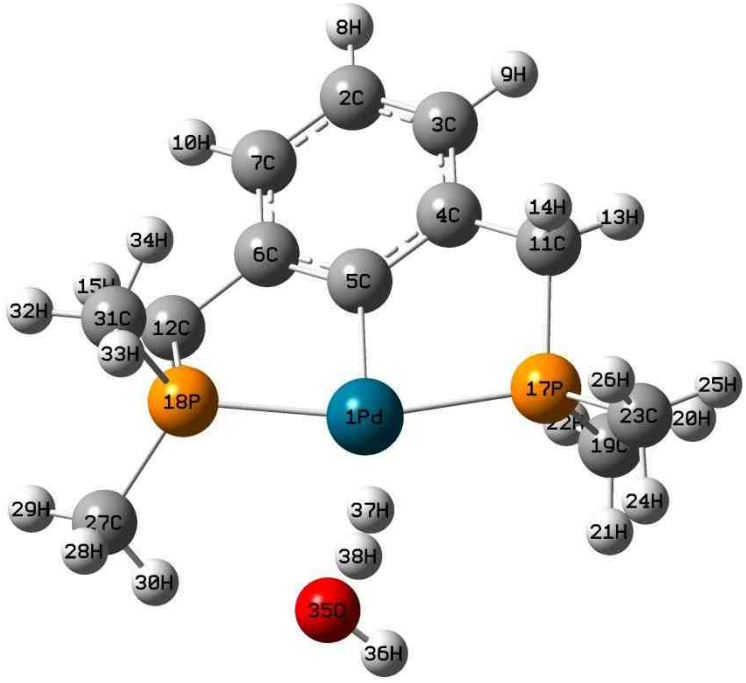
*** *** ***

(PCP) transition state **98**

(see Figure 5-3, Figure 5-4)



98



Energy: -1355.20030490 hartrees

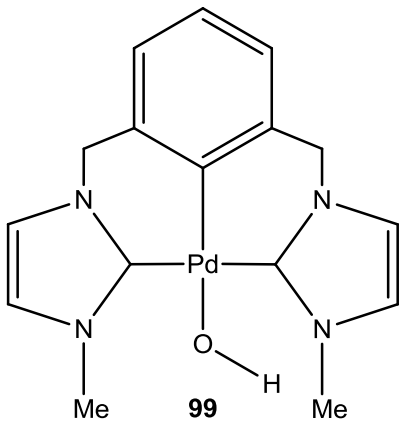
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.0648	-0.8587	0.1510	-0.8877			0.0109
2C	0.4136	3.9661	-0.2913	-0.4499			-0.0895
3C	1.5068	3.1905	0.1012	-0.0272			-0.0180
4C	1.3769	1.8031	0.2568	0.6536			-0.0615
5C	0.1364	1.1710	0.0024	0.5820			0.1416
6C	-0.9596	1.9637	-0.4182	-0.3402			-0.0674
7C	-0.8142	3.3522	-0.5484	0.3138			-0.0102
8H	0.5197	5.0423	-0.4015	0.1756			0.0098
9H	2.4655	3.6680	0.2958	0.1697			0.0007
10H	-1.6630	3.9555	-0.8655	0.1704			0.0026
11C	2.5518	0.9568	0.7055	-1.2100			-0.1035
12C	-2.2716	1.2821	-0.7547	-1.1112			-0.1172
13H	3.5172	1.3700	0.3848	0.2257			-0.0278
14H	2.5781	0.8823	1.8024	0.2485			-0.0212
15H	-3.1442	1.9185	-0.5571	0.2250			-0.0264
16H	-2.3007	1.0107	-1.8196	0.2608			-0.0102
17P	2.2594	-0.7616	0.0651	0.9108			0.9617

18P	-2.3182	-0.3113	0.1947	1.0733			0.9601
19C	3.0252	-0.7843	-1.6127	-0.8847			-0.2377
20H	4.1017	-0.5797	-1.5676	0.2274			-0.0272
21H	2.8629	-1.7634	-2.0743	0.2478			0.0308
22H	2.5381	-0.0293	-2.2368	0.2569			0.0351
23C	3.3490	-1.8719	1.0551	-0.8359			-0.2494
24H	3.2669	-2.8951	0.6746	0.2492			0.0264
25H	4.3978	-1.5548	1.0050	0.2291			-0.0354
26H	3.0203	-1.8721	2.0988	0.2487			0.0340
27C	-3.5079	-1.4357	-0.6296	-0.8962			-0.2743
28H	-3.8388	-2.1960	0.0855	0.2411			0.0182
29H	-4.3804	-0.8915	-1.0107	0.2175			-0.0296
30H	-2.9598	-1.9555	-1.4245	0.3367			0.1138
31C	-3.0889	0.1309	1.8119	-0.9441			-0.2405
32H	-4.1209	0.4774	1.6772	0.2313			-0.0278
33H	-3.0897	-0.7460	2.4672	0.2455			0.0282
34H	-2.5021	0.9201	2.2918	0.2515			0.0293
35O	-0.8586	-2.8297	-1.1723	-0.9070			-0.8782
36H	-0.2094	-3.2259	-1.7768	0.4273			0.1221
37H	-0.2107	-2.7266	1.1112	-0.0658			-0.3025
38H	-0.4227	-2.9232	0.3062	0.1409			0.3300

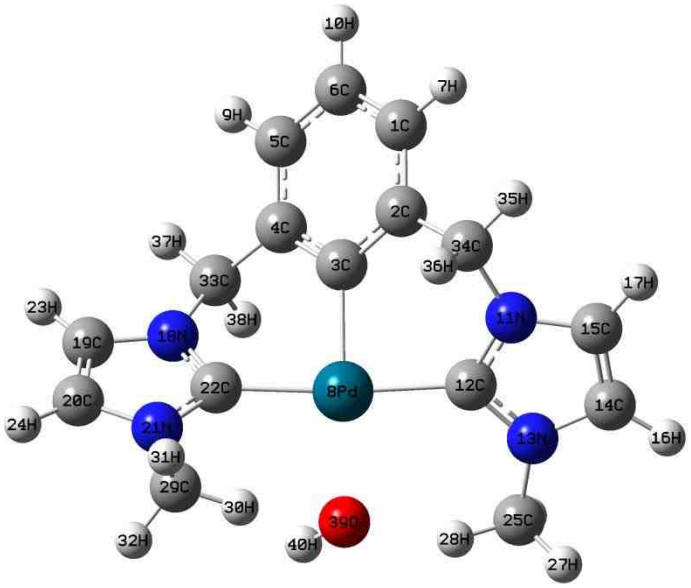
*** *** ***

(CCC) palladium hydroxide **99**

(see Figure 5-5, Figure 5-6)



99



Energy: -1041.52492167 hartrees

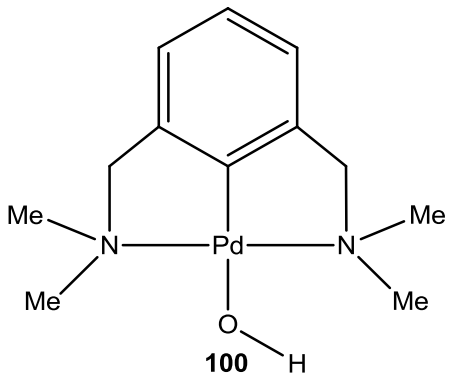
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	0.8836	3.5352	0.6353	-0.1018			
2C	0.9238	2.1334	0.6471	0.6193			
3C	-0.0534	1.3586	-0.0136	0.2896			
4C	-1.0797	2.0660	-0.6793	0.6913			
5C	-1.1226	3.4675	-0.6849	-0.1893			
6C	-0.1398	4.2109	-0.0302	-0.3613			
7H	1.6570	4.1036	1.1508	0.1600			
8Pd	0.0177	-0.6951	-0.0510	-0.5111			
9H	-1.9296	3.9830	-1.2044	0.1594			
10H	-0.1720	5.2973	-0.0372	0.1713			
11N	2.7348	0.4309	0.6277	-0.0357			
12C	2.0767	-0.5615	-0.0259	0.0288			
13N	3.0604	-1.3256	-0.5691	-0.0514			
14C	4.3124	-0.8119	-0.2634	-0.0397			
15C	4.1077	0.2971	0.4990	-0.0517			
16H	5.2244	-1.2745	-0.6096	0.2011			
17H	4.8052	0.9828	0.9560	0.2016			
18N	-2.7771	0.2602	-0.6109	-0.0095			
19C	-4.1256	0.0847	-0.3448	0.0004			

20C	-4.2155	-0.9993	0.4748	-0.1254			
21N	-2.9199	-1.4553	0.6812	-0.0887			
22C	-2.0247	-0.6773	0.0161	-0.1500			
23H	-4.8896	0.7258	-0.7583	0.2038			
24H	-5.0735	-1.4781	0.9222	0.2028			
25C	2.8282	-2.5174	-1.3877	-0.5217			
26H	2.9154	-2.2654	-2.4510	0.2120			
27H	3.5766	-3.2738	-1.1324	0.1964			
28H	1.8217	-2.8837	-1.1465	0.3556			
29C	-2.5529	-2.5658	1.5622	-0.4889			
30H	-1.5173	-2.8421	1.3344	0.3353			
31H	-2.6523	-2.2607	2.6099	0.2189			
32H	-3.2150	-3.4157	1.3686	0.2045			
33C	-2.1656	1.3153	-1.4303	-1.0020			
34C	2.0391	1.4550	1.4181	-1.0358			
35H	2.7901	2.1842	1.7355	0.1897			
36H	1.6433	0.9680	2.3177	0.2424			
37H	-2.9660	1.9932	-1.7403	0.1913			
38H	-1.7574	0.8410	-2.3307	0.2438			
39O	0.0860	-2.8068	-0.1401	-1.0181			
40H	-0.5999	-3.0727	-0.7733	0.4629			

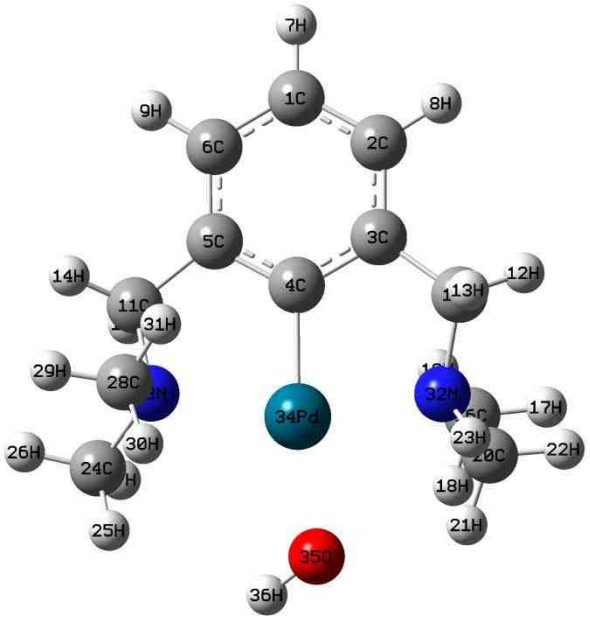
*** *** ***

(NCN) palladium hydroxide **100**

(see Figure 5-5, Figure 7-7)



100



Energy: -780.79497494 hartrees

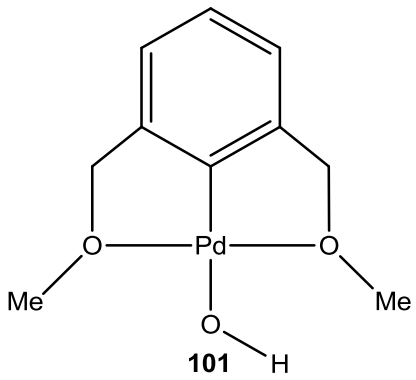
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	3.1114	-2.2615	-0.0189	-0.4119			
2C	1.8421	-2.8279	0.1803	0.1243			
3C	0.7128	-2.0002	0.2015	0.1245			
4C	0.8758	-0.6245	0.0023	-0.1559			
5C	2.1347	-0.0560	-0.2145	0.1145			
6C	3.2668	-0.8797	-0.2125	0.1256			
7H	3.9883	-2.9041	-0.0256	0.1736			
8H	1.7519	-3.9036	0.3252	0.1690			
9H	4.2626	-0.4674	-0.3701	0.1683			
10C	-0.7094	-2.4271	0.4996	-0.7069			
11C	2.0989	1.4254	-0.5196	-0.6461			
12H	-0.9652	-3.4156	0.0882	0.2055			
13H	-0.8557	-2.4827	1.5848	0.2194			
14H	2.9779	1.9747	-0.1471	0.2065			
15H	2.0583	1.5761	-1.6052	0.2215			
16C	-2.0449	-1.6776	-1.4277	-0.4559			
17H	-2.5856	-2.6352	-1.5002	0.2030			
18H	-2.6787	-0.8682	-1.7953	0.2604			

19H	-1.1353	-1.7291	-2.0297	0.2357			
20C	-2.9247	-1.3513	0.8018	-0.4455			
21H	-3.5201	-0.4988	0.4649	0.3006			
22H	-3.4877	-2.2930	0.7048	0.1980			
23H	-2.6584	-1.1922	1.8492	0.2148			
24C	0.4950	3.2761	-0.7031	-0.4658			
25H	-0.3959	3.7239	-0.2576	0.2354			
26H	1.3210	4.0045	-0.6670	0.2108			
27H	0.2802	3.0210	-1.7432	0.2319			
28C	1.0462	2.3873	1.4765	-0.4441			
29H	1.8151	3.1704	1.5789	0.2045			
30H	0.1042	2.7421	1.9001	0.2474			
31H	1.3650	1.4940	2.0159	0.2462			
32N	-1.6893	-1.3969	-0.0148	-0.1423			
33N	0.8417	2.0496	0.0450	-0.2251			
34Pd	-0.7026	0.5143	-0.0084	-0.0026			
35O	-2.5368	1.5183	-0.0236	-0.9771			
36H	-2.5226	2.4092	-0.4029	0.4375			

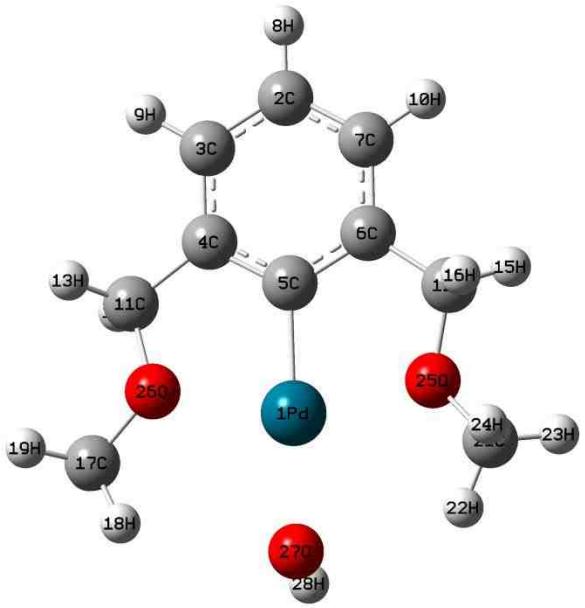
*** *** ***

(OCO) palladium hydroxide **101**

(see Figure 5-5, Figure 5-9)



101



Energy: -741.86344253 hartrees

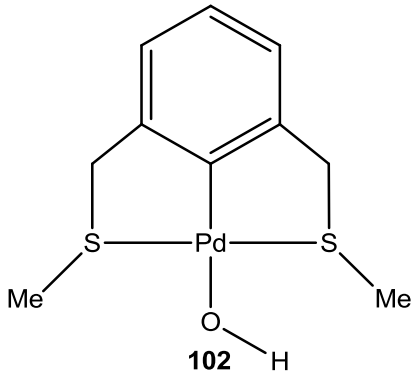
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.9662	-0.0061	-0.0296	0.1456			
2C	3.7516	0.0130	-0.0090	-0.4665			
3C	3.0568	1.2307	0.0004	-0.1889			
4C	1.6564	1.2272	-0.0027	-0.4868			
5C	0.9806	0.0022	0.0028	1.1637			
6C	1.6657	-1.2172	0.0028	-0.4011			
7C	3.0663	-1.2099	-0.0129	-0.2108			
8H	4.8383	0.0173	-0.0132	0.1782			
9H	3.6136	2.1666	0.0040	0.1720			
10H	3.6301	-2.1414	-0.0207	0.1722			
11C	0.7983	2.4702	-0.0544	-0.2214			
12C	0.8189	-2.4665	0.0682	-0.2673			
13H	1.1058	3.2327	0.6749	0.2045			
14H	0.8107	2.9262	-1.0563	0.2079			
15H	1.1348	-3.2375	-0.6481	0.2056			
16H	0.8365	-2.9056	1.0770	0.2075			
17C	-1.5649	3.0919	0.0340	-0.3750			
18H	-2.5194	2.6180	0.2699	0.2772			

19H	-1.3728	3.9426	0.6998	0.1947			
20H	-1.5537	3.4222	-1.0131	0.1940			
21C	-1.5461	-3.0725	0.1559	-0.3603			
22H	-2.5132	-2.5959	-0.0127	0.2758			
23H	-1.4329	-3.9780	-0.4532	0.1941			
24H	-1.4350	-3.3154	1.2203	0.1965			
25O	-0.5580	-2.1073	-0.2362	-0.2310			
26O	-0.5683	2.0854	0.2480	-0.2293			
27O	-3.0454	-0.0167	0.0356	-0.9814			
28H	-3.4263	0.0234	-0.8564	0.4302			

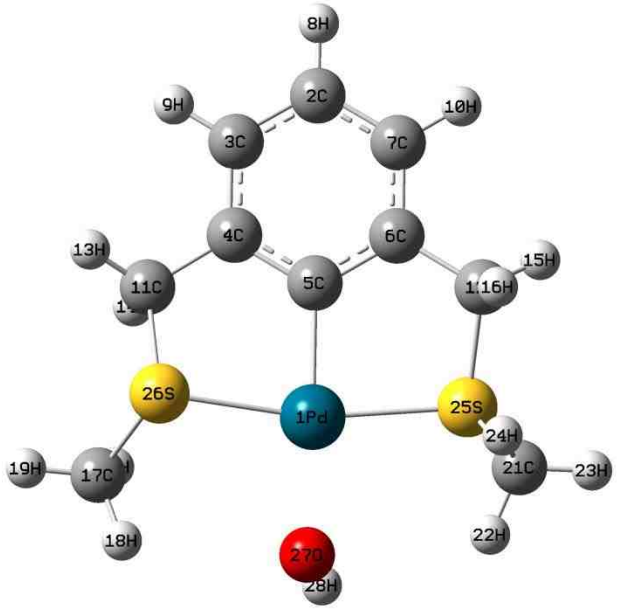
*** *** ***

(SCS) palladium hydroxide **102**

(see Figure 5-5, Figure 5-8)



102



Energy: -1387.86163226 hartrees

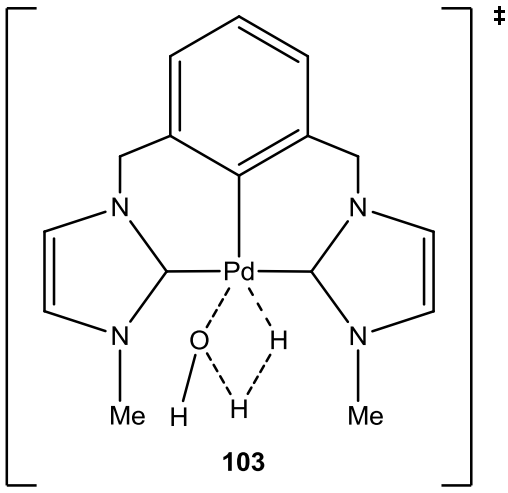
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.8882	0.1002	-0.0234	-0.5383			
2C	-3.9088	-0.4224	-0.0020	-0.0655			
3C	-3.0833	-1.5512	-0.0024	-0.3841			
4C	-1.6897	-1.4020	-0.0243	0.6729			
5C	-1.1119	-0.1156	-0.0042	0.0546			
6C	-1.9542	1.0149	0.0150	0.5149			
7C	-3.3474	0.8583	-0.0042	-0.3817			
8H	-4.9893	-0.5407	-0.0007	0.1757			
9H	-3.5294	-2.5444	0.0009	0.1734			
10H	-3.9986	1.7309	-0.0067	0.1732			
11C	-0.7754	-2.6037	-0.1216	-1.1040			
12C	-1.3268	2.3879	0.1074	-1.0758			
13H	-1.1748	-3.4836	0.3937	0.2394			
14H	-0.5895	-2.8750	-1.1680	0.2498			
15H	-1.8957	3.1517	-0.4329	0.2408			
16H	-1.2314	2.7099	1.1514	0.2501			
17C	2.0693	-3.0171	-0.4794	-0.9385			
18H	3.0277	-2.5259	-0.2900	0.2976			

19H	2.1221	-4.0796	-0.2259	0.2344			
20H	1.7967	-2.8829	-1.5291	0.2429			
21C	1.3617	3.3220	0.6296	-0.8505			
22H	2.4006	3.0019	0.5143	0.2985			
23H	1.2538	4.3883	0.4131	0.2346			
24H	1.0364	3.0980	1.6483	0.2455			
25S	0.4067	2.3330	-0.5786	0.6868			
26S	0.8779	-2.1651	0.6114	0.8503			
27O	2.9599	0.2813	0.0327	-0.9244			
28H	3.2810	0.4806	-0.8620	0.4274			

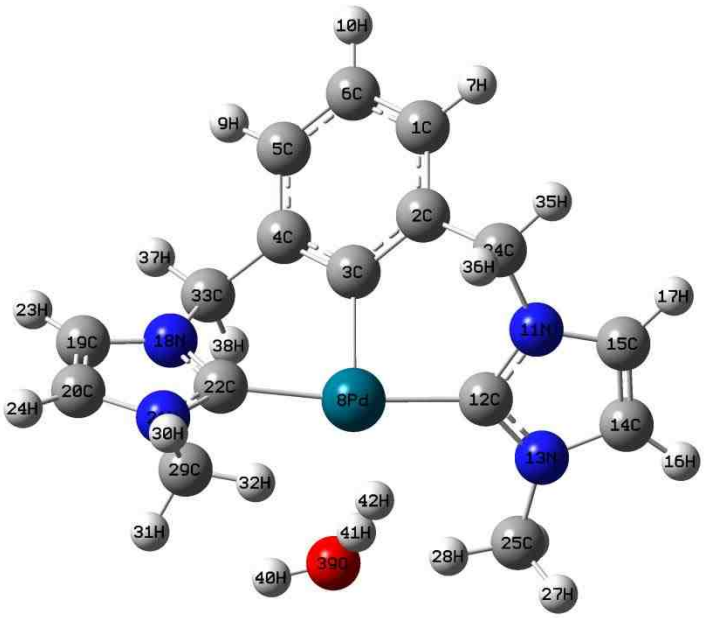
*** *** ***

(CCC) transition state **103**

(see Figure 5-6)



103



Energy: -1042.65599017 hartrees

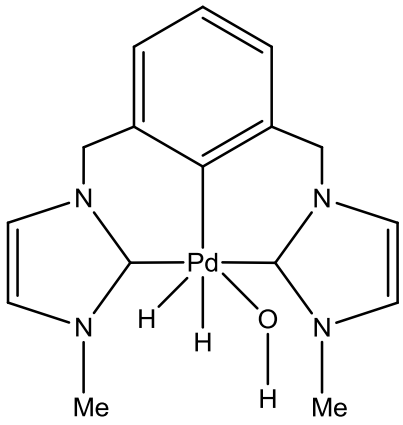
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	1.0802	3.4934	0.5671	-0.1908			0.0181
2C	1.0411	2.0952	0.6586	0.6607			-0.1436
3C	0.0547	1.3502	-0.0174	0.1440			0.1744
4C	-0.8864	2.0591	-0.7888	0.6704			-0.1450
5C	-0.8449	3.4577	-0.8760	-0.0690			0.0164
6C	0.1372	4.1818	-0.1983	-0.3588			-0.1132
7H	1.8536	4.0483	1.0964	0.1634			-0.0043
8Pd	-0.0085	-0.6805	0.1108	-0.8737			0.1752
9H	-1.5841	3.9844	-1.4780	0.1633			-0.0042
10H	0.1691	5.2659	-0.2677	0.1744			0.0129
11N	2.7463	0.3183	0.7227	-0.0384			-0.4244
12C	2.0468	-0.6263	0.0425	0.0843			0.3894
13N	2.9921	-1.3904	-0.5637	-0.0722			-0.3829
14C	4.2646	-0.9275	-0.2577	-0.0758			-0.0459
15C	4.1111	0.1536	0.5542	0.0024			0.0102
16H	5.1541	-1.4003	-0.6461	0.2036			0.0789
17H	4.8382	0.8023	1.0190	0.2034			0.0754
18N	-2.6961	0.3861	-0.6608	0.0246			-0.4211

19C	-4.0718	0.3092	-0.5234	0.0504			0.0206
20C	-4.3097	-0.6627	0.3979	-0.1315			-0.0516
21N	-3.0708	-1.1502	0.7958	-0.1143			-0.4002
22C	-2.0637	-0.5066	0.1426	-0.1516			0.3924
23H	-4.7490	0.9366	-1.0831	0.2065			0.0779
24H	-5.2351	-1.0418	0.8049	0.2055			0.0804
25C	2.7354	-2.5247	-1.4569	-0.4878			0.2594
26H	3.0801	-2.2739	-2.4661	0.2116			-0.0319
27H	3.2863	-3.3981	-1.0932	0.2082			-0.0273
28H	1.6612	-2.7457	-1.4687	0.3691			0.1714
29C	-2.9031	-2.1910	1.8062	-0.5264			0.3025
30H	-3.3079	-1.8476	2.7640	0.2181			-0.0259
31H	-3.4259	-3.1005	1.4938	0.2233			-0.0180
32H	-1.8396	-2.4044	1.9093	0.2588			0.0846
33C	-1.9592	1.3022	-1.5444	-0.7920			0.4001
34C	2.0814	1.3769	1.4938	-1.0549			0.4035
35H	2.8557	2.0682	1.8384	0.1922			-0.0226
36H	1.6208	0.9134	2.3740	0.2460			-0.0261
37H	-2.6888	1.9875	-1.9850	0.1921			-0.0225
38H	-1.5199	0.7052	-2.3518	0.2529			-0.0214
39O	-0.1986	-2.9871	-0.9985	-0.8555			-0.9329
40H	-1.1164	-3.1636	-1.2634	0.4442			0.1342
41H	-0.0577	-2.8211	0.4080	0.1238			0.3746
42H	0.1036	-2.5038	1.2272	-0.1046			-0.3875

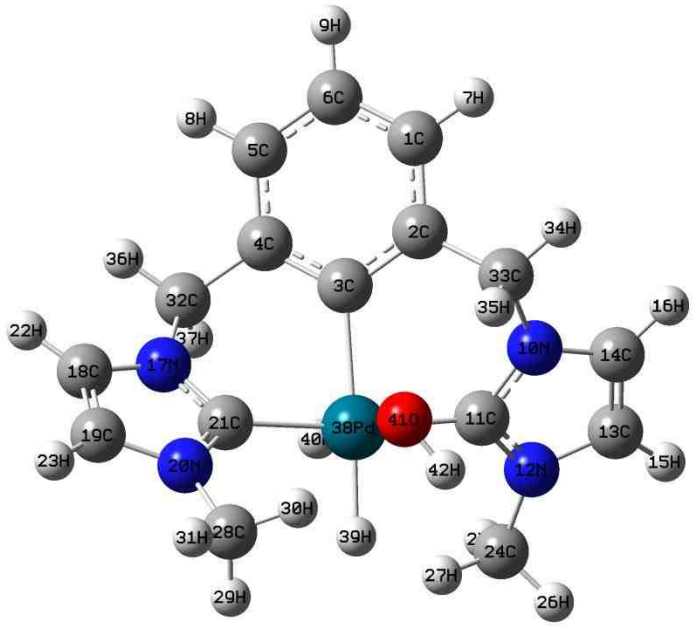
*** *** ***

(CCC) octahedral palladium intermediate **104**

(see Figure 5-6)



104



Energy: -1042.64397144 hartrees

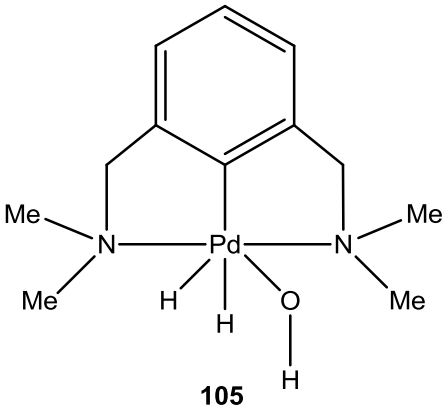
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	0.8492	3.4372	0.7506	-0.1927			
2C	0.8942	2.0379	0.6783	0.9838			
3C	-0.0640	1.3207	-0.0538	0.4109			
4C	-1.0717	2.0428	-0.7103	0.8637			
5C	-1.1265	3.4430	-0.6340	-0.2215			

6C	-0.1627	4.1437	0.0946	-0.3894			
7H	1.6001	3.9790	1.3249	0.1602			
8H	-1.9202	3.9892	-1.1431	0.1577			
9H	-0.2016	5.2286	0.1541	0.1699			
10N	2.6831	0.3165	0.5773	0.1501			
11C	2.0623	-0.6443	-0.1470	-0.0607			
12N	3.0578	-1.3128	-0.7863	-0.0640			
13C	4.2945	-0.7691	-0.4611	-0.1436			
14C	4.0545	0.2581	0.3992	0.1359			
15H	5.2181	-1.1563	-0.8640	0.2038			
16H	4.7311	0.9343	0.8994	0.2065			
17N	-2.7334	0.1979	-0.7808	-0.0633			
18C	-4.0881	0.0439	-0.5272	-0.0981			
19C	-4.2078	-1.0458	0.2801	0.0749			
20N	-2.9246	-1.5231	0.5050	0.0702			
21C	-2.0165	-0.7634	-0.1493	0.7364			
22H	-4.8327	0.7134	-0.9300	0.2043			
23H	-5.0783	-1.5090	0.7191	0.2033			
24C	2.8628	-2.4135	-1.7225	-0.6151			
25H	2.9756	-2.0625	-2.7539	0.2258			
26H	3.5985	-3.1982	-1.5218	0.2103			
27H	1.8544	-2.8033	-1.5802	0.2628			
28C	-2.5736	-2.6536	1.3654	-0.4452			
29H	-2.3736	-3.5414	0.7573	0.2214			
30H	-1.6785	-2.3660	1.9273	0.3231			
31H	-3.4103	-2.8490	2.0409	0.1894			
32C	-2.1088	1.2975	-1.5330	-1.6000			
33C	1.9560	1.2701	1.4413	-0.9365			
34H	2.7028	1.9381	1.8796	0.1781			
35H	1.4690	0.6714	2.2203	0.3292			
36H	-2.9129	1.9638	-1.8579	0.1916			
37H	-1.6443	0.8617	-2.4258	0.2464			
38Pd	0.0220	-0.8143	-0.1336	-2.1887			
39H	0.0583	-2.4326	-0.3308	0.0832			
40H	0.0037	-0.7509	-1.6966	0.1915			
41O	0.0408	-1.0171	2.0151	-0.8256			
42H	0.5999	-1.7946	2.1735	0.4599			

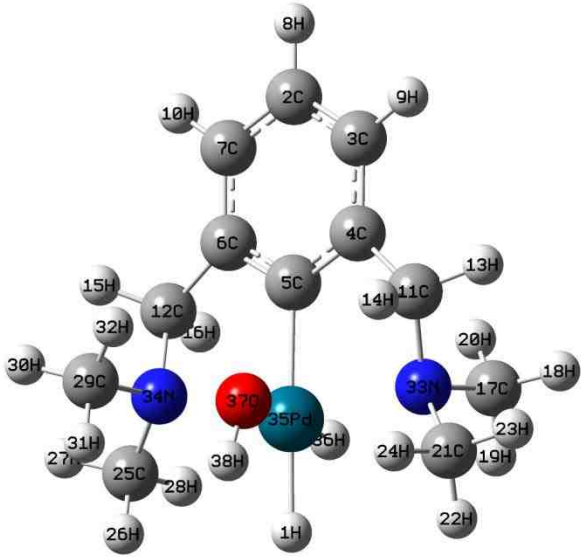
*** *** ***

(NCN) octahedral palladium intermediate **105**

(see Figure 5-7)



105



Energy: -781.89925185 hartrees

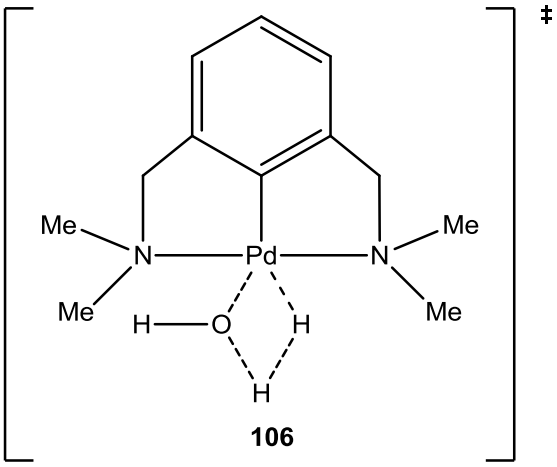
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1H	0.1331	-2.6680	-0.3467	0.0548			
2C	-0.2238	3.7433	0.1262	-0.3978			
3C	1.0110	3.1071	0.3392	0.0932			
4C	1.0845	1.7113	0.2475	0.7674			
5C	-0.0694	1.0090	-0.0761	-1.1001			

6C	-1.2985	1.6171	-0.2896	0.5061			
7C	-1.3832	3.0121	-0.1781	0.2031			
8H	-0.2839	4.8259	0.2049	0.1743			
9H	1.8876	3.7043	0.5859	0.1712			
10H	-2.3258	3.5361	-0.3291	0.1696			
11C	2.2603	0.8140	0.5508	-0.5658			
12C	-2.3864	0.6465	-0.6790	-1.1981			
13H	3.2422	1.2638	0.3419	0.2031			
14H	2.2157	0.5190	1.6029	0.2862			
15H	-3.3965	0.9626	-0.3794	0.2108			
16H	-2.3883	0.5093	-1.7668	0.2276			
17C	2.5846	-0.2659	-1.6385	-0.4373			
18H	3.6492	0.0120	-1.6517	0.2088			
19H	2.4387	-1.1870	-2.2045	0.2363			
20H	1.9930	0.5321	-2.0882	0.2495			
21C	2.9804	-1.5252	0.3995	-0.5126			
22H	2.9131	-2.4412	-0.1899	0.2302			
23H	4.0272	-1.1881	0.4432	0.2058			
24H	2.5905	-1.7021	1.4024	0.2715			
25C	-2.8510	-1.7614	-0.8278	-0.4217			
26H	-2.6447	-2.7343	-0.3805	0.2419			
27H	-3.9313	-1.5555	-0.7867	0.2103			
28H	-2.5142	-1.7749	-1.8652	0.2333			
29C	-2.5332	-0.7371	1.3457	-0.4890			
30H	-3.6103	-0.5181	1.3998	0.2007			
31H	-2.3300	-1.7211	1.7668	0.2375			
32H	-1.9544	-0.0086	1.9105	0.2907			
33N	2.1429	-0.4808	-0.2376	0.0922			
34N	-2.1070	-0.7212	-0.0792	-0.0771			
35Pd	0.0485	-1.0095	-0.1615	-0.5240			
36H	-0.0803	-1.0628	-1.7267	0.1736			
37O	0.3196	-1.0822	1.9487	-0.9000			
38H	0.2811	-2.0184	2.1960	0.4740			

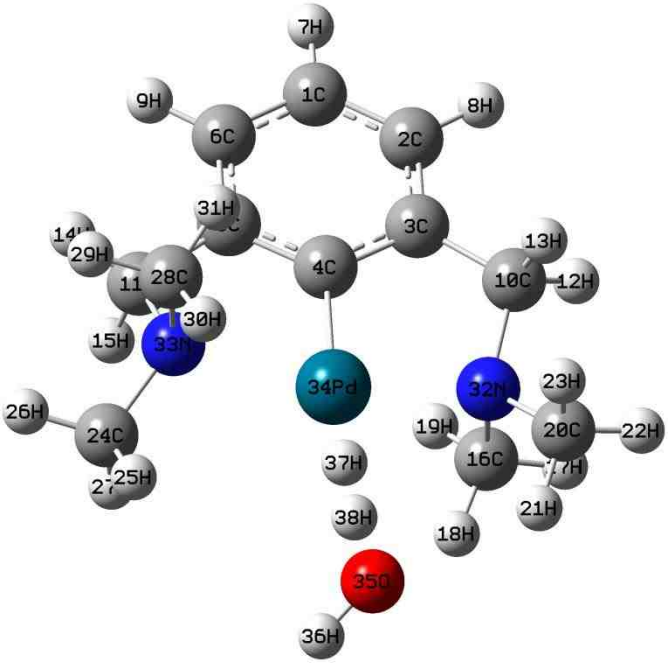
*** *** ***

(NCN) transition state **106**

(see Figure 5-7)



106



Energy: -781.93338006 hartrees

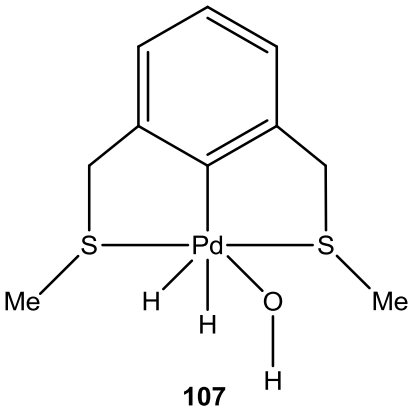
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	3.3870	-1.8659	-0.2007	-0.3991			-0.1237
2C	2.2141	-2.5797	0.0898	0.2071			0.0310
3C	0.9954	-1.8988	0.1939	0.1952			-0.0893
4C	0.9818	-0.5157	-0.0162	-0.4998			0.1247
5C	2.1395	0.2066	-0.3208	0.2452			-0.0932

6C	3.3580	-0.4780	-0.4026	0.1530			0.0221
7H	4.3324	-2.3972	-0.2726	0.1776			0.0162
8H	2.2630	-3.6569	0.2395	0.1746			0.0065
9H	4.2807	0.0532	-0.6304	0.1729			0.0053
10C	-0.3419	-2.4852	0.5792	-0.6341			0.2701
11C	1.9070	1.6712	-0.6039	-0.6367			0.2891
12H	-0.4965	-3.5093	0.2068	0.2098			-0.0451
13H	-0.4302	-2.5174	1.6720	0.2239			-0.0285
14H	2.7500	2.3160	-0.3118	0.2086			-0.0485
15H	1.7410	1.8170	-1.6779	0.2275			-0.0282
16C	-1.7552	-1.8847	-1.3478	-0.5030			0.1831
17H	-2.1983	-2.8898	-1.4300	0.1979			-0.0584
18H	-2.4541	-1.1194	-1.6961	0.3126			0.0923
19H	-0.8341	-1.8464	-1.9332	0.2253			0.0069
20C	-2.6801	-1.7424	0.8820	-0.4561			0.2209
21H	-3.4290	-1.0572	0.4787	0.3025			0.0718
22H	-3.0438	-2.7808	0.8285	0.2023			-0.0627
23H	-2.4714	-1.4809	1.9221	0.2205			0.0048
24C	0.0614	3.2990	-0.6027	-0.4709			0.2493
25H	-0.8428	3.6060	-0.0734	0.2526			0.0208
26H	0.7740	4.1385	-0.6292	0.2114			-0.0594
27H	-0.2083	3.0156	-1.6223	0.2375			0.0146
28C	0.9572	2.4983	1.4998	-0.4680			0.2288
29H	1.6290	3.3712	1.5277	0.2064			-0.0570
30H	0.0265	2.7333	2.0199	0.2509			0.0313
31H	1.4388	1.6539	1.9958	0.2444			0.0213
32N	-1.4447	-1.5900	0.0781	-0.1850			-0.4406
33N	0.6497	2.1337	0.0937	-0.2356			-0.4853
34Pd	-0.6985	0.4301	0.1320	-0.0771			0.5371
35O	-3.0449	0.8831	-0.8251	-0.9618			-0.9551
36H	-3.2741	1.6196	-1.4155	0.4544			0.1356
37H	-2.1998	1.5475	1.2010	-0.1173			-0.4270
38H	-2.6422	1.3792	0.4282	0.1305			0.4186

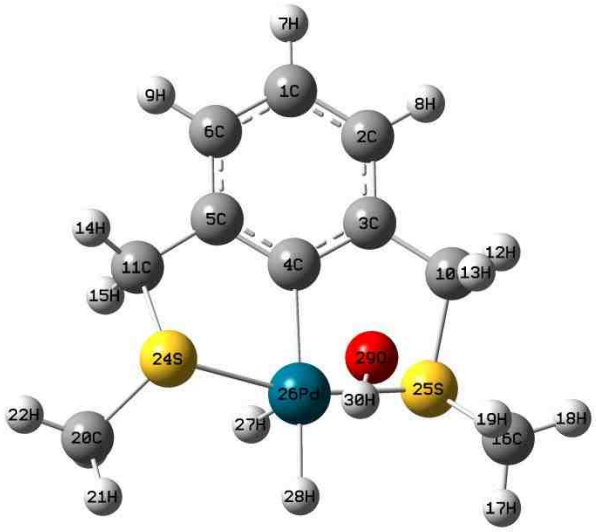
*** *** ***

(SCS) octahedral palladium intermediate **107**

(see Figure 5-8)



107



Energy: -1388.96887741 hartrees

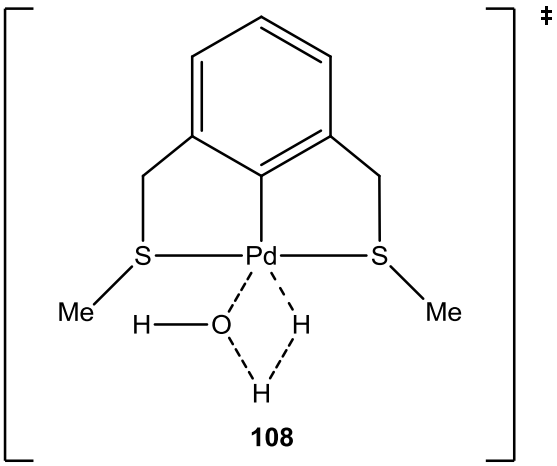
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	-0.5253	3.8195	0.0673	-0.3612			
2C	0.7664	3.2789	0.0488	0.3102			
3C	0.9390	1.8897	-0.0098	0.1216			
4C	-0.1799	1.0511	-0.0885	-0.8102			
5C	-1.4700	1.5923	-0.0716	1.2135			
6C	-1.6443	2.9821	0.0227	-0.1141			
7H	-0.6590	4.8966	0.1256	0.1755			
8H	1.6282	3.9422	0.0999	0.1706			
9H	-2.6428	3.4151	0.0527	0.1699			

10C	2.2923	1.2329	0.1049	-1.1673			
11C	-2.6372	0.6417	-0.1854	-1.5262			
12H	3.1158	1.8422	-0.2829	0.2332			
13H	2.4878	0.9589	1.1470	0.3031			
14H	-3.5279	0.9814	0.3542	0.2437			
15H	-2.9101	0.4610	-1.2326	0.2551			
16C	3.4098	-1.3567	0.2224	-0.9520			
17H	3.4976	-2.3474	-0.2289	0.2456			
18H	4.3886	-0.8675	0.2401	0.2297			
19H	2.9524	-1.4163	1.2157	0.3320			
20C	-3.1051	-2.1392	-0.5500	-0.9688			
21H	-2.8208	-3.1577	-0.2780	0.2613			
22H	-4.1718	-1.9900	-0.3566	0.2379			
23H	-2.8705	-1.9642	-1.6018	0.2603			
24S	-2.1400	-1.0162	0.5201	1.2578			
25S	2.2794	-0.3836	-0.8286	1.0349			
26Pd	0.1086	-1.0264	-0.1482	-1.0567			
27H	-0.3310	-1.1279	-1.6558	0.1925			
28H	0.2998	-2.6503	-0.2775	0.0864			
29O	0.8284	-0.9402	1.8512	-0.8440			
30H	0.6357	-1.7980	2.2592	0.4658			

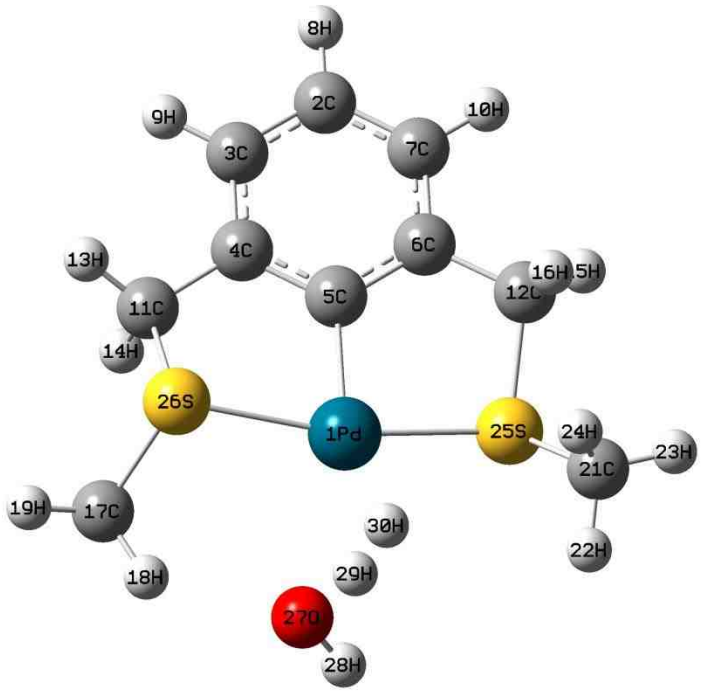
*** *** ***

(SCS) transition state **108**

(see Figure 5-8)



108



Energy: -1388.99362340 hartrees

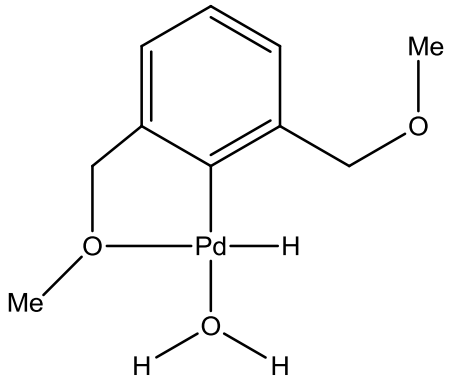
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	0.7661	0.3658	0.1004	-0.6305			0.3541
2C	-3.6372	-1.5705	-0.1349	-0.1294			-0.1061
3C	-2.5109	-2.3968	-0.1123	-0.3550			0.0169
4C	-1.2241	-1.8425	-0.0709	0.0798			-0.1102
5C	-1.0623	-0.4425	-0.0108	0.4988			0.1356
6C	-2.2045	0.3848	-0.0092	0.6340			-0.1104
7C	-3.4833	-0.1826	-0.0934	-0.2870			0.0123
8H	-4.6313	-2.0066	-0.1841	0.1797			0.0183
9H	-2.6344	-3.4778	-0.1401	0.1773			0.0083
10H	-4.3622	0.4591	-0.1122	0.1767			0.0079
11C	0.0010	-2.7178	-0.1373	-1.1449			0.1443
12C	-2.0236	1.8742	0.1337	-1.1573			0.1550
13H	-0.1445	-3.6877	0.3495	0.2420			-0.0099
14H	0.3004	-2.8968	-1.1767	0.2537			-0.0353
15H	-2.8021	2.4495	-0.3778	0.2419			-0.0124
16H	-2.0106	2.1702	1.1895	0.2586			-0.0353

17C	2.8368	-2.2601	-0.3951	-0.9079			0.0019
18H	3.5021	-1.3900	-0.3748	0.3504			0.1188
19H	3.3165	-3.1644	-0.0112	0.2310			-0.0150
20H	2.4991	-2.4032	-1.4241	0.2363			0.0004
21C	0.1245	3.7004	0.5583	-0.9042			0.0183
22H	1.1405	3.9856	0.2783	0.2659			0.0399
23H	-0.5514	4.5487	0.4138	0.2351			-0.0091
24H	0.1238	3.3650	1.5971	0.2686			0.0180
25S	-0.3653	2.3373	-0.5587	0.7450			0.0782
26S	1.4151	-1.8305	0.6742	0.8171			0.0778
27O	3.1305	0.7184	-0.6660	-0.8508			-0.8939
28H	3.3008	1.4216	-1.3151	0.4391			0.1531
29H	2.7356	1.2330	0.5021	0.1366			0.4079
30H	2.2377	1.4294	1.2781	-0.1007			-0.4294

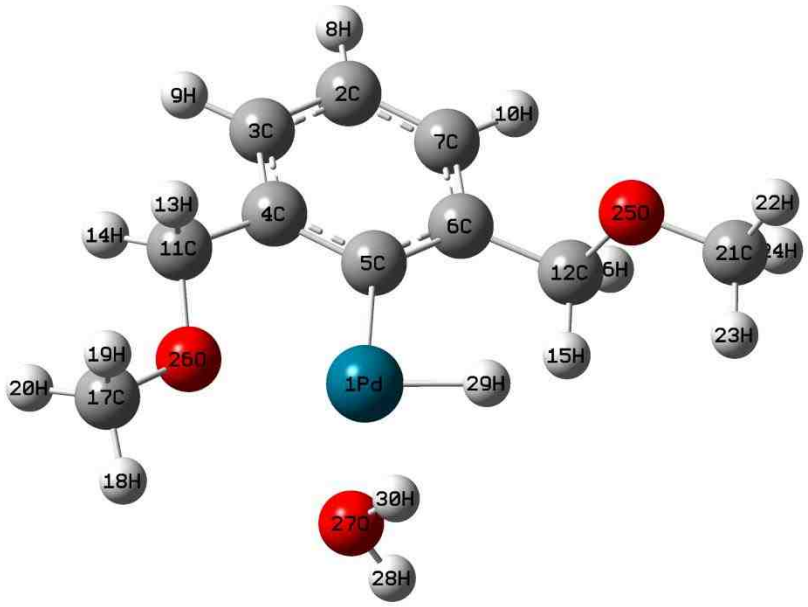
*** *** ***

(OC) palladium hydride **109**

(see Figure 5-9)



109



Energy: -743.08072474 hartrees

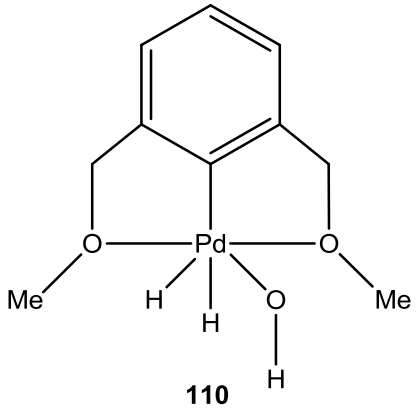
Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1Pd	-0.8510	-0.9029	-0.0737	-0.5424			
2C	1.8331	3.0930	-0.0935	-0.5105			
3C	0.4568	3.0783	0.1337	-0.1469			
4C	-0.2410	1.8649	0.1594	0.7092			
5C	0.4218	0.6332	-0.0665	1.2974			
6C	1.8094	0.6598	-0.3190	-0.9475			
7C	2.4941	1.8875	-0.3207	-0.2000			
8H	2.3784	4.0332	-0.1102	0.1728			
9H	-0.0782	4.0141	0.2906	0.1642			
10H	3.5660	1.8893	-0.5087	0.1737			
11C	-1.7174	1.8935	0.4704	-0.2939			
12C	2.6276	-0.5800	-0.5887	-0.7004			
13H	-1.8985	1.7908	1.5528	0.2048			
14H	-2.1793	2.8331	0.1353	0.1871			
15H	1.9998	-1.3678	-1.0240	0.1837			
16H	3.4369	-0.3478	-1.3024	0.1651			
17C	-3.7461	0.6621	0.1346	-0.2935			
18H	-4.1232	-0.2079	-0.4060	0.2182			

19H	-3.8804	0.5108	1.2152	0.1970			
20H	-4.2957	1.5601	-0.1793	0.1921			
21C	3.9822	-2.2118	0.4471	-0.3594			
22H	4.3846	-2.4891	1.4255	0.1908			
23H	3.3719	-3.0441	0.0589	0.1756			
24H	4.8197	-2.0382	-0.2500	0.1716			
25O	3.2092	-1.0446	0.6307	-0.2828			
26O	-2.3669	0.7935	-0.1950	-0.3033			
27O	-2.3541	-2.6567	-0.0807	-0.9437			
28H	-2.0662	-3.1647	-0.8576	0.5309			
29H	0.3289	-1.8930	0.0842	0.0573			
30H	-2.0467	-3.1674	0.6870	0.5328			

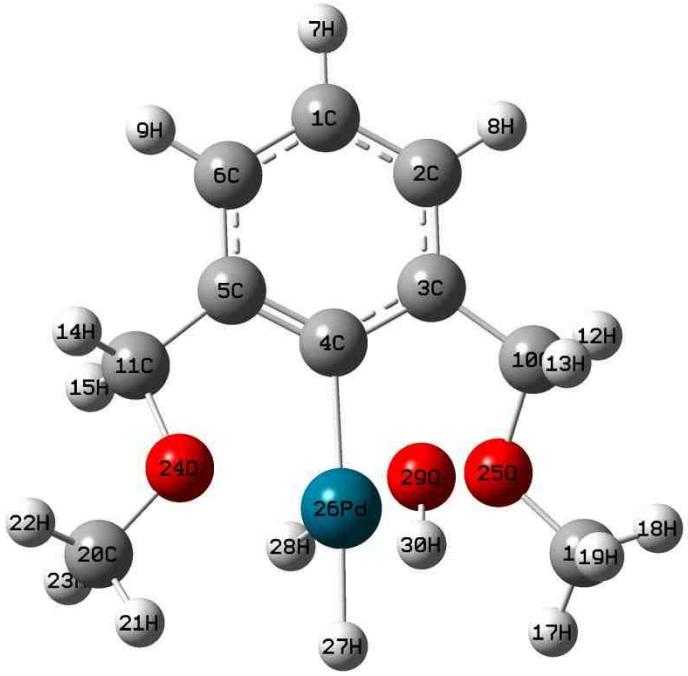
*** *** ***

(OCO) octahedral palladium intermediate **110**

(see Figure 5-9)



110



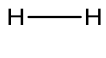
Energy: -742.94864249 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1C	3.5477	-0.9428	0.0626	-0.2199			
2C	2.5580	-1.9380	0.0594	-0.3328			
3C	1.2099	-1.5635	-0.0026	0.5768			
4C	0.9132	-0.2123	-0.0963	-0.3559			
5C	1.8670	0.7929	-0.0844	0.7329			
6C	3.2160	0.4180	0.0041	-0.6436			
7H	4.5933	-1.2328	0.1221	0.1794			
8H	2.8467	-2.9855	0.1223	0.1763			
9H	4.0060	1.1667	0.0233	0.1760			
10C	0.0126	-2.4631	0.1047	-0.4676			
11C	1.3334	2.1922	-0.2037	-0.8152			
12H	0.1340	-3.4408	-0.3776	0.1984			
13H	-0.2790	-2.5850	1.1537	0.2675			
14H	1.8488	2.9165	0.4394	0.2096			
15H	1.3640	2.5520	-1.2427	0.2174			
16C	-2.3725	-2.4238	-0.3002	-0.3344			

17H	-3.1171	-1.9062	-0.9033	0.2320			
18H	-2.2983	-3.4754	-0.6022	0.1901			
19H	-2.6034	-2.3302	0.7649	0.2493			
20C	-0.7695	3.3963	-0.0300	-0.2513			
21H	-1.7656	3.2772	0.3929	0.2420			
22H	-0.2338	4.2092	0.4742	0.1974			
23H	-0.8372	3.5872	-1.1072	0.2135			
24O	-0.0702	2.1671	0.2187	-0.1240			
25O	-1.1079	-1.7878	-0.5777	-0.0937			
26Pd	-1.0415	0.3082	-0.1829	-0.2825			
27H	-2.6391	0.7742	-0.3458	0.0599			
28H	-1.1187	0.6695	-1.7206	0.2017			
29O	-1.2028	-0.2540	1.8515	-0.8643			
30H	-2.0394	0.0895	2.1982	0.4649			

*** *** ***

Hydrogen

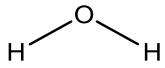


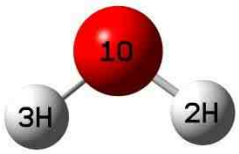
Energy: -1.17548239 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1H	0.0000	0.0000	0.3714	0.0000			
2H	0.0000	0.0000	-0.3714	0.0000			

*** *** ***

Water



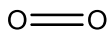


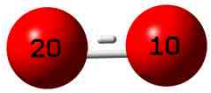
Energy: -76.42257235 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1O	0.0000	0.1173	0.0000	-0.9276			
2H	0.7713	-0.4692	0.0000	0.4638			
3H	-0.7713	-0.4692	0.0000	0.4638			

*** *** ***

Triplet oxygen





Energy: -150.32757696 hartrees

Center number and element	x-coord.	y-coord.	z-coord.	Mulliken atomic charge	chelpg atomic charge	Mulliken atomic spin density	APT atomic charge
1O	0.0000	0.0000	0.6077	0.0000		1.0000	
2O	0.0000	0.0000	-0.6077	0.0000		1.0000	

*** *** ***

References

1. Stahl, Shanon S. Palladium Oxidase Catalysis: Selective Oxidation of Organic Chemicals by Direct Dioxygen-Coupled Turnover. *Angewandte Chemie International Edition* **2004,** *43*, 3400-3420.

2. Sheldon, Roger A.; Kochi, Jay K., *Metal-Catalyzed Oxidations of Organic Compounds*. Academic Press: New York, 1981.

3. Gates, Bruce C.; Katzer, James R.; Schuit, G. C. A., *Chemistry of Catalytic Processes*. McGraw-Hill Book Company: New York, NY, 1979; p 464.

4. Xia, Q.-H.; Ge, H.-Q.; Ye, C.-P.; Liu, Z.-M.; Su, K.-X. Advances in Homogeneous and Heterogeneous Catalytic Asymmetric Epoxidation. *Chemical Reviews* **2005,** *105*, 1603-1662.

5. Punniyamurthy, T.; Velusamy, Subbarayan; Iqbal, J. Recent Advances in Transition Metal Catalyzed Oxidation of Organic Substrates with Molecular Oxygen. *Chemical Reviews* **2005,** *105*, 2329-2363.

6. Jørgensen, Karl Anker. Transition-Metal-Catalyzed Epoxidations. *Chemical Reviews* **1989,** *89*, (3), 431-458.

7. Monnier, John R. The Direct Epoxidation of Higher Olefins Using Molecular Oxygen. *Applied Catalysis A: General* **2001,** *221*, 73-91.

8. Matar, Sami; Hatch, Lewis F., *Chemistry of Petrochemical Processes*. Second Edition ed.; Gulf Professional Publishing: Boston, MA, 2001; p 392.

9. *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*. Kluwer Academic Publishers: Dordrecht, 1992.

10. *The Chemistry of Peroxides, Part 2*. John Wiley & Sons Ltd.: Chichester, 2006; Vol. 2.

11. *Organic Peroxides*. John Wiley & Sons: Chichester, 1992.

12. Mimoun, Hubert. The Role of Peroxymetallation in Selective Oxidative Processes. *Journal of Molecular Catalysis* **1980,** *7*, 1-29.

13. Vijayakumar, M.; Gopinathan, M. S. Spin-Orbit Coupling Constants of Transition Metal Atoms and Ions in Density Functional Theory. *Journal of Molecular Structure (Theochem)* **1996,** *361*, 15-19.

14. Xiao, Jianliang; Santarsiero, Bernard D.; Vaartstra, Brian A.; Cowie, Martin. Structure and Reactivity Studies of the Unusual Peroxo-Bridged Complex, $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(Ph_2PCH_2PPh_2)_2]$: The First Compound Having a Peroxide Moiety Bridging a Metal-Metal Bond. *Journal of the American Chemical Society* **1993,** *115*, 3212-3220.

15. Vaska, Lauri. Dixoygen-Metal Complexes: Toward a Unified View. *Accounts of Chemical Research* **1976,** *9*, 175-183.

16. Dickman, Michael H.; Pope, Michael T. Peroxo and Superoxo Complexes of Chromium, Molybdenum, and Tungsten. *Chemical Reviews* **1994,** *94*, 569-584.

17. Conte, Valeria; Floris, Barbara. Vanadium and Molybdenum Peroxides: Synthesis and Catalytic Activity in Oxidation Reactions. *Dalton Transactions* **2011,** *40*, 1419-1436.

18. Pecoraro, Vincent L.; Baldwin, Michael J.; Gelasco, Andrew. Interaction of Manganese with Dioxygen and Its Reduced Derivatives. *Chemical Reviews* **1994,** *94*, 807-826.

19. Akita, Munetaka; Fujisawa, Kiyoshi; Hikichi, Shiro; Moro-oka, Yoshihiko. Chemistry of $\mu\text{-}\eta^2\text{:}\eta^2$-Peroxo Dimetal Complexes: A Bioinorganic Model Triggers a New Trend of Transition Metal Peroxo Species. *Research on Chemical Intermediates* **1998,** *24*, (3), 291-307.

20. Siegbahn, Per E. M. Binding in Second-Row Transition Metal Dioxides, Trioxides, Tetraoxides, Peroxides, and Superoxides. *Journal of Physical Chemistry* **1993,** *97*, 9096-9102.

21. Lane, Benjamin S.; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chemical Reviews* **2003,** *103*, (7), 2457-2473.

22. Crabtree, Robert H., *The Organometallic Chemistry of the Transition Metals*. Third ed.; John Wiley & Sons, Inc.: New York, 2001.

23. Bosnich, B.; Jackson, W. G.; Lo, S. T. D.; McLaren, J. W. Dissymmetric Arsine Complexes. Monomeric and Dimeric Dioxygen Complexes of Cobalt. *Inorganic Chemistry* **1974,** *13*, (11), 2605-2611.

24. Vedejs, E. A Method for Direct Hydroxylation of Enolates. Transition Metal Peroxide Reactions. *Journal of the American Chemical Society* **1974,** *96*, (18), 5944-5946.

25. Campestrini, S.; Conte, V.; Di Furia, F.; Modena, G.; Bortolini, O. Metal Catalysis in Oxidation by Peroxides. 30. Electrophilic Oxygen Transfer from Anionic, Coordinatively Saturated Molybdenum Peroxo Complexes. *Journal of Organic Chemistry* **1988,** *53*, 5721-5724.

26. Porter, Michael J.; Skidmore, John. Asymmetric Epoxidation of Electron-Deficient Olefins. *Chemical Communications* **2000**, 1215-1225.

27. Møller, Eval Rud; Jørgensen, Karl Anker. Chemistry of Molybdenaoxaziridines. A Study of Oxo(*N*-phenylhydroxylamido-*O*,*N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) and Its Catalytic Properties. *Journal of the American Chemical Society* **1993,** *115*, 11814-11822.

28. Dagonneau, M.; Fauvarque, J. F. Oxidation of Dienes by Triphenylphosphine Peroxopalladium. *Journal of Organometallic Chemistry* **1983,** *241*, 113-118.

29. Katsuki, Tsutomu; Sharpless, K. Barry. The First Practical Method for Asymmetric Epoxidation. *Journal of the American Chemical Society* **1980,** *102*, 5974-5976.

30. Burns, Christopher J.; Martin, Cheryl A.; Sharpless, K. Barry. Tartrate-Like Ligands in the Asymmetric Epoxidation. *Journal of Organic Chemistry* **1989,** *54*, 2826-2834.

31. Chong, A. O.; Sharpless, K. Barry. On the Mechanism of the Molybdenum and Vanadium Catalyzed Epoxidation of Olefins by Alkyl Hydroperoxides. *Journal of Organic Chemistry* **1977,** *42*, (9), 1587-1590.

32. Mimoun, Hubert. Oxygen Transfer from Inorganic and Organic Peroxides to Organic Substrates: A Common Mechanism? *Angewandte Chemie International Edition in English* **1982,** *21*, 734-750.

33. Deubel, Dirk V.; Sundermeyer, Jörg; Frenking, Gernot. Mechanism of the Olefin Epoxidation Catalyzed by Molybdenum Diperoxo Complexes: Quantum-Chemical Calculations Give an Answer to a Long-Standing Question. *Journal of the American Chemical Society* **2000,** *122*, 10101-10108.

34. Makita, Naoya; Hoshino, Yujiro; Yamamoto, Hisashi. Asymmetric Epoxidation of Homoallylic Alcohols and Application in a Concise Total Synthesis of (-)-α-Bisabolol and (-)-8-*epi*-α-Bisabolol. *Angewandte Chemie International Edition* **2003,** *42*, (8), 941-943.

35. Mukhopadhyay, Sudip; Bell, Alexis T. Direct Liquid-Phase Sulfonation of Methane to Methanesulfonic Acid by SO_3 in the Presence of a Metal Peroxide. *Angewandte Chemie* **2003,** *115*, (9), 1049-1051.

36. Denney, Melanie C.; Smythe, Nichole A.; Cetto, Kara L.; Kemp, Richard A.; Goldberg, Karen I. Insertion of Molecular Oxygen into a Palladium(II) Hydride Bond. *Journal of the American Chemical Society* **2006,** *128*, 2508-2509.

37. Keith, Jason M.; Nielsen, Robert J.; Oxgaard, Jonas; Goddard, William A., III. Pd-Mediated Activation of Molecular Oxygen in a Nonpolar Medium. *Journal of the American Chemical Society* **2005,** *127*, 13172-13179.

38. Keith, Jason M.; Muller, Richard P.; Kemp, Richard A.; Goldberg, Karen I.; Goddard, William A., III; Oxgaard, Jonas. Mechanism of Direct Molecular Oxygen Insertion in a Palladium(II)-Hydride Bond. *Inorganic Chemistry* **2006,** *45*, 9631-9633.

39. Boro, Brian Joseph. Investigations of Pincer-Ligated Transition Metal Complexes for the Activation of Molecular Oxygen. Dissertation, The University of New Mexico, Albuquerque, NM, 2009.

40. Fulmer, Gregory R.; Muller, Richard P.; Kemp, Richard A.; Goldberg, Karen I. Hydrogenolysis of Palladium(II) Hydroxide and Methoxide Pincer Complexes. *Journal of the American Chemical Society* **2009,** *131*, 1346-1347.

41. Becke, Axel D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *Journal of Chemical Physics* **1993,** *98*, (7), 5648-5652.

42. Becke, Axel D. A New Mixing of Hartree-Fock and Local Density-Functional Theories. *Journal of Chemical Physics* **1993,** *98*, (2), 1372-1377.

43. Lee, Chengteh; Yang, Weitao; Parr, Robert G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Physical Review B* **1988,** *37*, (2), 785-789.

44. Niu, Shuqiang; Hall, Michael B. Theoretical Studies on Reactions of Transition-Metal Complexes. *Chemical Reviews* **2000,** *100*, 353-405.

45. Johnson, Benny G.; Gill, Peter M. W.; Pople, John A. The Performance of a Family of Density Functional Methods. *Journal of Chemical Physics* **1993,** *98*, (7), 5612-5626.

46. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, J.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, J. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pompelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Maklick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

47. Hay, P. Jeffrey; Wadt, Willard R. Ab initio Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. *Journal of Chemical Physics* **1985,** *82*, (1), 299-310.

48. Wadt, Willard R.; Hay, P. Jeffrey. *Ab initio* Effective Core Potentials for Molecular Calculations. Potentials for Main Group Elements Na to Bi. *Journal of Chemical Physics* **1985,** *82*, (1), 284-298.

49. Francl, Michelle M.; Pietro, William J.; Hehre, Warren J.; Binkley, J. Stephen; Gordon, Mark S.; DeFrees, Douglas J.; Pople, John A. Self-Consistent Molecular Orbital Methods. XXIII. A Polarization-Type Basis Set for Second-Row Elements. *Journal of Chemical Physics* **1982,** *77*, (7), 3654-3665.

50. Hehre, Warren J.; Ditchfield, R.; Pople, John A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *Journal of Chemical Physics* **1972,** *56*, (5), 2257-2261.

51. Hariharan, P. C.; Pople, John A. The Effect of d-Functions on Molecular Orbital Energies for Hydrocarbons. *Chemical Physics Letters* **1972,** *16*, (2), 217-219.

52. Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I. *Journal of Chemical Physics* **1955,** *23*, (10), 1833-1840.

53. Mulliken, R. S. Criteria for the Construction of Good Self-Consistent-Field Molecular Orbital Wave Functions, and the Significance of LCAO-MO Population Analysis. *Journal of Chemical Physics* **1962,** *36*, (12), 3428-3439.

54. Breneman, Curt M.; Wiberg, Kenneth B. Determining Atom-Centered Monopoles from Molecular Electrostatic Potentials. The Need for High Sampling Density in Formamide Conformational Analysis. *Journal of Computational Chemistry* **1990,** *11*, (3), 361-373.

55. Wiberg, Kenneth B.; Rablen, Paul R. Comparison of Atomic Charges Derived via Different Procedures. *Journal of Computational Chemistry* **1993,** *14*, (12), 1504-1518.

56. Heinz, Hendrik; Suter, Ulrich W. Atomic Charges for Classical Simulations of Polar Systems. *Journal of Physical Chemistry B* **2004,** *108*, 18341-18352.

57. Mullay, John. A Simple Method for Calculating Atomic Charge in Molecules. *Journal of the American Chemical Society* **1986,** *108*, 1770-1775.

58. Gonzalez, Carlos; Schlegel, H. Bernhard. An Improved Algorithm for Reaction Path Following. *Journal of Chemical Physics* **1989,** *90*, (4), 2154-2161.

59. Fukui, Kenichi. A Formulation of the Reaction Coordinate. *Journal of Physical Chemistry* **1970,** *74*, (23), 4161-4163.

60. Gonzalez, Carlos; Schlegel, H. Bernhard. Reaction Path Following in Mass-Weighted Internal Coordinates. *Journal of Physical Chemistry* **1990,** *94*, 5523-5527.

61. Poli, Rinaldo; Harvey, Jeremy N. Spin Forbidden Chemical Reactions of Transition Metal Compounds. New Ideas and New Computational Challenges. *Chemical Society Reviews* **2003,** *32*, 1-8.

62. Harvey, Jeremy N.; Aschi, Massimiliano; Schwarz, Helmut; Koch, Wolfram. The Singlet and Triplet States of Phenyl Cation. A Hybrid Approach for Locating Minimum Energy Crossing Points Between Non-Interacting Potential Energy Surfaces. *Theoretical Chemistry Accounts* **1998,** *99*, 95-99.

63. Harvey, Jeremy N.; Aschi, Massimiliano. Spin-Forbidden Dehydrogenation of Methoxy Cation: A Statistical View. *Physical Chemistry Chemical Physics* **1999,** *1*, 5555-5563.

64. Bruno, Ian J.; Cole, Jason C.; Edgington, Paul R.; Kessler, Magnus; Macrae, Clare F.; McCabe, Patrick; Pearson, Jonathan; Taylor, Robin. New Software for Searching the Cambridge Structural Database and Visualizing Crystal Structures. *Acta Crystallographica Section B* **2002,** *B58*, 389-397.

65. Macrae, Clare F.; Bruno, Ian J.; Chisholm, James A.; Edgington, Paul R.; McCabe, Patrick; Pidcock, Elna; Rodriguez-Monge, Lucia; Taylor, Robin; Van de Streek, Jacco; Wood, Peter A. *Mercury CSD 2.0* -- New Features for the Visualization and Inestigation of Crystal Structures. *Journal of Applied Crystallography* **2008,** *41*, 466-470.

66. Taylor, Robin; Macrae, Clare F. Rules Governing the Crystal Packing on Mono- and Dialcohols. *Acta Crystallographica Section B* **2001,** *B57*, 815-827.

67. Macrae, Clare F.; Edgington, Paul R.; McCabe, Patrick; Pidcock, Elna; Shields, Greg P.; Taylor, Robin; Towler, Matthew; van de Streek, Jacco. *Mercury*: Visualization and Analysis of Crystal Structures. *Journal of Applied Crystallography* **2006,** *39*, 453-457.

68. Ozerov, Oleg V.; Guo, Chengyun; Fan, Lei; Foxman, Bruce M. Oxidative Addition of N-C and N-H Bonds to Zerovalent Nickel, Palladium, and Platinum. *Organometallics* **2004,** *23*, 5573-5580.

69. Koridze, A. A.; Kuklin, S. A.; Sheloumov, A. M.; Kondrashov, M. V.; Dolgushin, F. M.; Peregudov, A. S.; Petrovskii, P. V. Synthesis and Structure of Palladium P,C,P Pincer Complexes Based on Ferrocene. *Russian Chemical Bulletin, International Edition* **2003,** *52*, (12), 2754-2756.

70. Lansing, Raymond B., Jr. Investigations into Late Transition Metal Pincer Complexes as Possible Direct Partial Oxidation Catalysts. Dissertation, The University of New Mexico, Albuquerque, NM, 2010.

71. Johansson, Roger; Wendt, Ola F. Synthesis and Reactivity of (PCP) Palladium Hydroxy Carbonyl and Related Complexes toward CO_2 and Phenylacetylene. *Organometallics* **2007,** *26*, (9), 2426-2430.

72. Steinke, Tobias; Shaw, Bryan K.; Jong, Howard; Patrick, Brian O.; Fryzuk, Michael D. Synthesis and Coordination Chemistry of a Tridentate *o*-Phenylene-Bridged Diphosphine-NHC System. *Organometallics* **2009,** *28*, 2830-2836.

73. Allen, Frank H. The Cambridge Structural Database: A Quarter of a Million Crystal Structures and Rising. *Acta Crystallographica Section B* **2002,** *B58*, 380-388.

74. Gregor, Lauren C.; Chen, Chung-Hsing; Fafard, Claudia M.; Fan, Lei; Guo, Chengyun; Foxman, Bruce M.; Gusev, Dmitry G.; Ozerov, Oleg V. Heterolytic Splitting of H-X Bonds at a Cationic (PNP)Pd Center. *Dalton Transactions* **2010,** *39*, 3195-3202.

75. Wander, Sheryl A.; Miedaner, Alex; Noll, Bruce C.; Barkley, Robert M.; DuBois, Daniel L. Chelate Bite Effects for [Pd(triphosphine)(solvent)]$(BF_4)_2$ Complexes in Electrochemical CO_2 Reduction and the Heterolytic Cleavage of Molecular Hydrogen. *Organometallics* **1996,** *15*, 3360-3373.

76. Boro, Brian J.; Duesler, Eileen N.; Goldberg, Karen I.; Kemp, Richard A. An Unprecedented Bonding Mode for Potassium within a PCP-Pincer Palladium Hydride-K-Selectride Complex. *Inorganic Chemistry Communications* **2008,** *11*, 1426-1429.

77. Chowdhury, Sugata; Rivalta, Ivan; Russo, Nino; Sicilia, Emilia. The Recognition of a New Pathway for the Reaction of Molecular Oxygen with a Pd(II)-Hydride to Produce a Pd(II)-Hydroperoxide. *Chemical Physics Letters* **2008,** *456*, 41-46.

78. Chowdhury, Sugata; Rivalta, Ivan; Russo, Nino; Sicilia, Emilia. On the Insertion Mechanism of Molecular Oxygen into a Pd(II)-H Bond. Something to Add. *Chemical Physics Letters* **2007,** *443*, 183-189.

79. Konnick, Michael M.; Decharin, Nattawan; Popp, Brian V.; Stahl, Shanon S. O_2 Insertion into a Palladium(II)-Hydride bond: Observation of MNechanistic Crossover between HX-Reductive-Elimination and Hydrogen-Atom-Abstraction Pathways. *Chemical Science* **2011,** *2*, 326-330.

80. Chowdhury, Sugata; Rivalta, Ivan; Russo, Nino; Sicilia, Emilia. Theoretical Investigation of the Mechanism of Acid-Catalyzed Oxygenation of a Pd(II)-Hydride to Produce a Pd(II)-Hydroperoxide. *Journal of Chemical Theory and Computation* **2008,** *4*, 1283-1292.

81. Keith, Jason M.; Goddard, William A., III. Mechanism for Activation of Molecular Oxygen by *cis*- and *trans*-$(Pyridine)_2Pd(OAc)H$: Pd^0 versus Direct Insertion. *Journal of the American Chemical Society* **2009,** *131*, 1416-1425.

82. Konnick, Michael M.; Gandhi, Bhavesh A.; Guzei, Ilia, A.; Stahl, Shanon S. Reaction of Molecular Oxygen with a Pd^{II}-Hydride to Produce a Pd^{II}-Hydroperoxide: Acid Catalysis and Implications for Pd-Catalyzed Aerobic Oxidation Reactions. *Angewandte Chemie International Edition* **2006,** *45*, 2904-2907.

83. Popp, Brian V.; Stahl, Shanon S. Mechanism of $Pd(OAc)_2$/Pyridine Catalyst Reoxidation by O_2: Influence of Labile Monodentate Ligands and Identification of a Biomimetic Mechanism for O_2 Oxidation. *Chemistry: A European Journal* **2009,** *15*, 2915-2922.

84. Popp, Brian V.; Stahl, Shanon S. Insertion of Molecular Oxygen into a Palladium-Hydride Bond: Computational Evidence for Two Nearly Isoenergetic Pathways. *Journal of the American Chemical Society* **2007,** *129*, 4410-4422.

85. Konnick, Michael M.; Stahl, Shanon S. Reaction of Molecular Oxygen with a Pd^{II}-Hydride to Produce a Pd^{II}-Hydroperoxide: Experimental Evidence for an HX-Reductive-Elimination Pathway. *Journal of the American Chemical Society* **2008,** *130*, 5753-5762.

86. Keith, Jason M.; Goddard, William A., III; Oxgaard, Jonas. Pd-Mediated Activation of Molecular Oxygen: Pd(0) versus Direct Insertion. *Journal of the American Chemical Society* **2007,** *129*, 10361-10369.

87. Decharin, Nattawan; Popp, Brian V.; Stahl, Shanon S. Reaction of O_2 with [(-)-Sparteine]Pd(H)Cl: Evidence for an Intramolecular $[H\text{-}L]^+$ "Reductive Elimination" Pathway. *Journal of the American Chemical Society* **2011,** *133*, 13268-13271.

88. *Jaguar, version 7.0*, New York, NY, 2007.

89. Pauling, Linus, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*. Second Edition ed.; Cornell University Press: Ithaca, NY, 1944; p 450.

90. Gibbs, G. V.; Hill, F. C.; Boisen, M. B.; Downs, R. T. Power Law Relationship between Bond Length, Bond Strength and Electron Density Distributions. *Physics and Chemistry of Minerals* **1998,** *25*, 585-590.

91. Goldberg, Karen I.; Smythe, Nichole A., personal communication from K.I.G. regarding the oxidation of triphenylphosphine from ^{tBu}PCPPdOOH performed by N.A.S.; 25 Jan 2012.

92. Bach, Robert D.; Wolber, Gregory J.; Coddens, Barry A. On the Mechanism of Metal-Catalyzed Epoxidation: A Model for the Bonding in Peroxo-Metal Complexes. *Journal of the American Chemical Society* **1984,** *106*, 6098-6099.

93. Deubel, Dirk V.; Frenking, Gernot; Gisdakis, Philip; Herrmann, Wolfgang A.; Rösch, Notker; Sundermeyer, Jörg. Olefin Epoxidation with Inorganic Peroxides. Solutions to Four Long-Standing Controversies on the Mechanism of Oxygen Transfer. *Accounts of Chemical Research* **2004,** *37*, 645-652.

94. Oxgaard, Jonas; Tenn, William J., III; Nielsen, Robert J.; Periana, Roy A.; Goddard, William A., III. Mechanistic Analysis of Iridium Heteroatom C-H Activation: Evidence for an Internal Electrophilic Substitution Mechanism. *Organometallics* **2007,** *26*, 1565-1567.

95. Cundari, Thomas R.; Grimes, Thomas V.; Gunnoe, T. Brent. Activation of Carbon-Hydrogen Bonds via 1,2-Addition across M-X (X = OH or NH_2) Bonds of d^6 Transition Metals as a Potential Key Step in Hydrocarbon Functionalization: A Computational Study. *Journal of the American Chemical Society* **2007,** *129*, 13172-13182.

96. Bader, Armin; Lindner, Ekkehard. Coordination Chemistry and Catalysis with Hemilabile Oxygen-Phosphorus Ligands. *Coordination Chemistry Reviews* **1991,** *108*, 27-110.

97. Slone, Caroline S.; Weinberger, Dana A.; Mirkin, Chad A. The Transition Metal Coordination Chemistry of Hemilabile Ligands. *Progress in Inorganic Chemistry* **1999,** *48*, 233-350.

98. Fulmer, Gregory R.; Kaminsky, Werner; Kemp, Richard A.; Goldberg, Karen I. Syntheses and Characterization of Palladium Complexes with a Hemilabile "PCO" Pincer Ligand. *Organometallics* **2011,** *30*, 1627-1636.