8-31-2011

I. The synthesis and coordination chemistry of novel 6n-electron ligands. II. Improvement of student writing skills in chemistry lab reports through the use of Calibrated Peer Review

Wilson William

Wilson Ngambeki William
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:

Prof. David G. Bear Chairperson

Dr. Joseph K. Ho

Prof. Kathryn Watkins

Prof. Stephen E. Cabaniss

Prof. Reddy V. Prakash

I. THE SYNTHSIS AND COORDINATION CHEMISTRY OF NOVEL 6π-ELECTRON LIGANDS

II. IMPROVEMENT OF STUDENT WRTING SKILLS IN CHEMISTRY LAB REPORTS THROUGH THE USE OF CALIBRATED PEER REVIEW

WILSON NGAMBEKI WILLIAM

B.Sc.(Hons), Education, University of Dar es Salaam, 1991
M.Sc. Chemistry, University of Dar es Salaam, 1996

DISSERTATION

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy
CHEMISTRY

The University of New Mexico
Albuquerque, New Mexico

July 2011

DEDICATION

To my beloved wife Jane Barongo, and our children Joseline, Nelson, Catherine and Cuthbert. To my dearest parent Martha, brothers and sisters.

ACKNOWLEDGMENTS

As anyone who has been through this process knows, completing the requirement for Ph.D. cannot be accomplished without support from many people. To begin with I am grateful to Dr. Joseph K. Ho for your guidance and encouragement during the course of this work.

Many thanks to members of my committee on studies: Professors David G. Bear, Kathryn Watkins, Stephen E. Cabaniss and Reddy V. Prakash for their constructive contributions and comments.

I wish to express my most sincere appreciation to the University of New Mexico, Department of Chemistry and Chemical Biology in particular for granting me assistanceship and support for research. I am indebted to ACS-PRF for funding my research for six months as well.

Special thanks to Dr. Eileen Duesler, Ken Sherrell, and Dr. Kanen Ann Smith for their invaluable help with, X-ray crystal structures, Mass spectrometry and nuclear magnetic resonance spectroscopy respectively. This includes both Dr. Doris G. Wagner and Dr. Jamal Martin for editing the work. I would like to thank Dr. Admasu Shunkuri for his encouragement and support during my studies.

Lastly I wish my deepest heartfelt thanks to all my family members, friends both in Tanzania and here in the USA whose immense moral and material support made it possible for me to accomplish this work.

I. The Synthesis and Coordination Chemistry of Novel 6π-Electron Ligands

II. Improvement of Student Writing Skills in General Chemistry Lab Reports Through the Use of Calibrated Peer Review

By

WILSON NGAMBEKI WILLIAM

B.Sc. (Hons), Education, University of Dar es Salaam, 1991

M.Sc., Chemistry, University of Dar es Salaam, 1996

Ph.D., Chemistry, University of New Mexico, 2011

ABSTRACT I

The goal of this study was to synthesize and characterize a set of coordination complexes containing 6π-cationic ligands. These compounds could be extremely useful as catalysts for the polymerization of olefins that are widely used in the synthetic polymer industry. The original strategy was to synthesize the 6π-cationic ligands using $(Ph_2P)_3CH$ (**1**) and $(Me_2P)_3CH$ (**10**) as precursors; however, both precursors **1** and **10** were found to be highly reactive leading to the fragmentation products $(Ph_2P)_2CH_2$ and $(Me_2P)_2CH_2$ respectively. In trying to control the reactivity, precursor **1** was coordinated to the group 6B metal carbonyl in two modes, $Mo(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$ and $W(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$. In these novel compounds, two of the three phosphorus atoms are chelated to the metal. These complexes were isolated and

characterized by X-ray analysis, elemental analysis, NMR and infrared spectroscopy. When these metal complexes were reacted with $B(C_6F_5)_3$, the complexes were stabilized, and no molecular fragmentation was observed. Instead, a second mode of coordination was observed by $^{31}P\{^1H\}$ NMR spectroscopy, where all three phosphorus atoms are bonded to the metal in a tridentate fashion, yielding the novel product $EtCNB(C_6F_5)_3$, which was characterized by X-ray analysis. However, because there was no hydride abstraction from the tertiary carbon in either compound, further studies will be required to develop a strategy for hydride abstraction to produce a cationic ligand.

Another strategy for the synthesis of 6π-cationic ligands was to directly synthesize the halogenated version of the tertiary carbon atom of compound **10**. Fractional recrystallization of the crude product yielded two compounds of 2,4,6-trimethypyridinium bromide and $(PMe_2)_3CBr$. $(PMe_2)_3CBr$ was determined to be pure as revealed by $^{31}P\{^1H\}$ NMR. It is expected that oxidation of the bromide should yield the 6π-cationic ligand.

In the next strategy, density function theory calculations (DFT) were used to predict the possibility that the 6π-cationic ligand of guanidinium analog would coordinate with a group 6B metal carbonyl. However, attempts to synthesize the predicted complex were unsuccessful; when neodymium nitrate was reacted with the 6π-cationic ligand of guanidinium salt, a completely novel diguanidinium diaquapentakis(nitrato)neodymiate(III) was produced, as characterized by X-ray analysis, NMR, elemental analysis, and infrared spectroscopy.

In the next approach, the synthesis of the 6π-cationic ligand of guanidinium analog tripiperidine carbenium tetrafluoroborate was attempted; again the ligand could not be obtained; however, other novel compounds, 1-tritylpiperidine and diphenyldipiperidin-1-ylmethane were obtained as indicated by single crystal X-ray analysis.

The last strategy was to synthesize a 6π-anionic phosphorus-based complex using 2,4,6-tri-*tert*-butylaniline and PI_5. While the desired complex was not obtained, another novel compound, 2,4,6-tri-*tert*-butylbenzenaminium iodide, was produced and characterized by single crystal X-ray analysis and ^1H NMR.

In conclusion, new strategies that combine DFT with novel synthetic approaches will be required to successfully produce coordination complexes containing 6π-cationic ligands.

ABSTRACT II

The goal of this study was to assess effectiveness of using Calibrated Peer Review (CPR) for submitting post-lab reports. According to the literature the use of CPR could help improve students' writing skills (WS), conceptual understanding (CU) and critical thinking (CT). The first strategy of this study was to divide all students into two groups and required one group to use CPR for writing post-lab reports. The performances of the post-lab between the two groups were then compared. In second strategy I used an essay (pretest/posttest) to objectively assess students' writing skills that showed an improvement of 19% from students' who used CPR and 11% from students' who did not use CPR. When we compared the percentage of students who were not proficient in any areas (WS, CU, or CT) between the pre- and post-test, the CPR group has more improvement (22%) over the non-CPR group, which is 17%. Statistical analyses (t-test and ANOVA) for pretest and posttest scores have also shown significant differences in means and variances for CPR and non CPR students. In the third strategy we collected feedback from students through survey questions regarding the usefulness of CPR from their point of view. We have obtained low rating (2 on a five point Likert scale) about the use of CPR for writing post-lab report from students.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

Abbreviation	Definition
Å	Angstrom
ANOVA	Analysis of Variance
AR	Analytical Reagent
Bp	Boiling Point
Br	Broad
^{o}C	Degrees Celsius
Ca.	Approximately
C_6D_6	Deuterated Benzene
$CDCl_3$	Deuterated Chloroform
CD_2Cl_2	Deuterated Methyl Chloride
CD_3COCD_3	Deuterated Acetone
CD_3CN	Deuterated Acetonitrile
Cp-	Cyclopentadienyl
CPR	Calibrated Peer Review
CU	Conceptual Understanding
CT	Critical Thinking
d	doublet

δ	Chemical Shift
DCM	Dichloromethane
DME	Dimethoxyethane
DMSO	Deuterated Dimethyl Sulfoxide
DPPM	Diphenylphosphinomethane
df	Degree of Freedom
ESI	Electrospray Ionization
Et_2O	Diethyl Ether
F	Quotient of the Squares of the Standard Deviations
G	Grams
h	hour
H_o	Null Hypothesis
HMPT	Hexametylphosphorustriamide
HSAB	Hard/Soft Acid/Base
Hz	Hertz
IR	Infrared Spectroscopy
k	Set of scores in a given section
min.	Minutes
m (IR)	Medium
MHz	Mega Hertz
MeOH	Methanol
mL	Milliliter

mmol	Millimole
mp	Melting Point
MS	Mean Square
N	Number of populations
NBS	N-bromosuccinimide
NMR	Nuclear Magnetic Resonance
m (NMR)	Multiplet
P(I)	Group One
P(II)	Group Two
PTA	1,3,5-triaza-7-phosphaadamantane
Ppm	Parts per Million
Q	Quartet
RT	Room Temperature
s	Strong
s (NMR)	Singlet
sep	Septet
SS	Sums of Squares
t	Triplet
‘‘t’’	Apparent Triplet
TA	Teaching Assistant
THF-d_8	Deuterated Tetrahydrofuran
THF	Tetrahydrofuran

TMEDA	Tetramethylenediamine
TPM	Tris(diphenylphosphinol)methane
URL	Uniform Resource Locator
υ	Frequency
w	Weak
WS	Writing Skills
$\overline{X_1}$	The Mean Value for Pretest
$\overline{X_2}$	The Mean Value for Posttest
μ	Population mean
σ^2	Variance

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

CHAPTER ONE

Introduction, literature review, and Statement of Research Problem

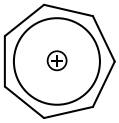
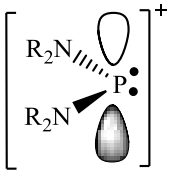
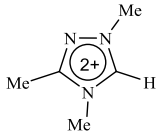
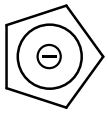
1.1. Introduction

This chapter contains a literature review on the types of ligands and their bonding modes. It also introduces the concepts of the carbenium ion, guanidinium ion, photolysis and lanthanides. In the subsequent chapter, the ‘’attempted syntheses’’ of 6π-cationic ligands $[(PR_2)_3C]$,$^+$ $[(NH_2)_3C]^+$ and the 6π-anionic ligand $[P(=NR)_3]^-$ are described. In the third chapter, the results and discussion are described together with conclusions, future work and a summary of synthesized novel compounds (Appendix I).

A ligand is an atom, ion or molecule that donates one or more electrons through a coordinate covalent bond to one or more central atoms or ions (these ligands act as Lewis bases.)[1] In general, ligands donate electron density to the electron-deficient central atom; that is, the highest occupied molecular orbital (HOMO) of the ligand overlaps with the lowest unoccupied molecular orbital (LUMO) of the central atom.[1,2] Thus, the ligand acts as a Lewis base by donating electron density (electron pairs) to a central atom that is acting as a Lewis acid. Some ligand molecules are able to bind to a metal ion through multiple sites because they have free lone electron pairs on more than one atom.[1,2,3] Ligands that bind to more than one site are referred to as **multi-hapto**, and can be **chelating** if they form more than one attachment to a single metal atom, thereby resulting in ring formation. Beyond the classical definition of Lewis bases and anions, unsaturated molecules can also be ligands, utilizing their π-electrons to form coordinate bonds.[1]

Table 1.0 contains examples of three types of ligands with two bonding modes.[4-8]

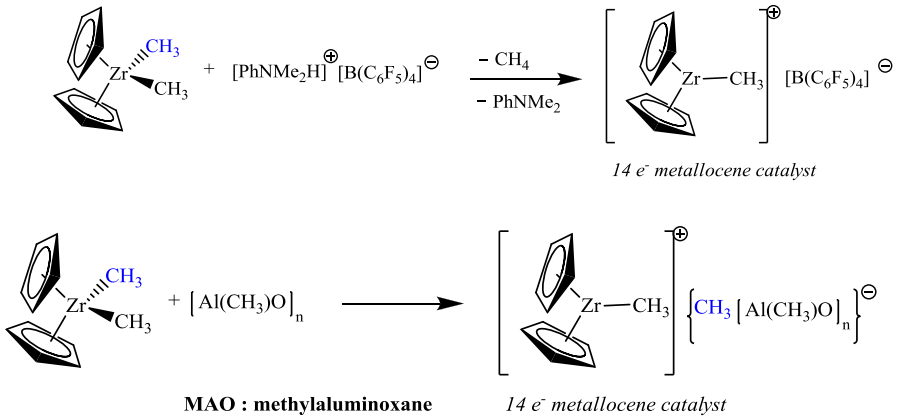
Table 1.0: Ligands and their bonding modes

Type	Cationic	Neutral	Anionic
σ-bond	NO^+  tropylium ion  Phosphenium ion  1,2,3,4-tetramethyl-1,2,4-triazolium cation	H_2O PR_3 NR_3 MeCN CO 2,2-bipyridine	Halides PR_2^- NR_2^-
π-bond	NOT KNOWN	Benzene olefin	Cp- 

As shown in **Table 1.0**, π-bonding cationic ligands have not been identified. The main goal of the studies described in this dissertation was to develop a novel 6π-electron ligand synthesis using alternative ligands to the traditional cyclopentadienyl anions. Group 4B Cp-containing metallocene catalysts Cp_2MX_2 (M = Ti, Zr, Hf; X= halide) have been shown to exhibit catalytic olefin polymerization activity.[9-12] However, the chemical and physical properties of metallocene catalysts can be significantly modified by the

substituents on cyclopentadienyl ring. Even one substituent is sufficient to introduce novel features into the catalytic behavior of these complexes, including the reactivity as well as the stability.[13,14] We also anticipated that the successful development of these compounds would reduce the cost for catalyst synthesis because conventional metallocene catalysts require co-catalysts in order to be activated. This activation is achieved by using of ammonium tetraarylborates or large excesses of methylaluminoxanes (MAO)[15-20] (see **Figure 1.0**). Excess MAO probably induces the formation of large counteranions, which increases the distance between the anion and the catalytically active cation.[21] The more "naked" the cationic catalyst, the more active it will be towards alkene insertion.[9] However, co-catalysts are generally expensive. Methylaluminoxane, for example, is the most active, but its synthesis is complicated and irreproducible, resulting in dramatic differences in catalytic performance.[21-22] We anticipated that the use of 6π-cationic ligands would allow catalysts to be prepared in fewer steps, and using lower oxidation state precursors than those currently found in conventional metallocene catalysts.

Figure 1.0. Activated Metallocene Catalysts[23]



1.2. Literature Review

1.2.1. Carbenium ion $[(R_2P)_3C]^+$ and anionic ion $[(R_2C=)_3P]^-$ or $[(RN=)_3P]^-$

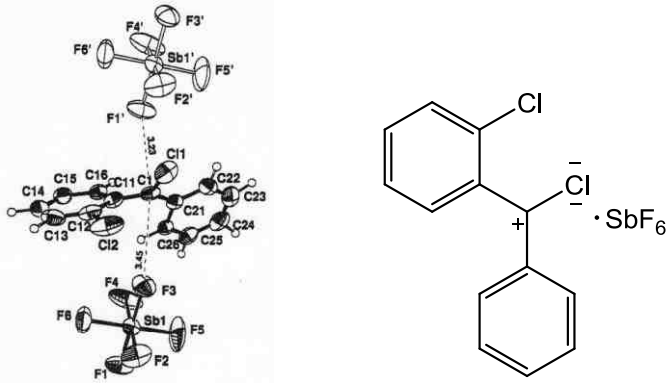
The coordination chemistry of neutral or anionic phosphorus compounds that have three phosphorus atoms $(R_2P)_3CH$ (R = Me, Ph) attached to the same carbon atom is relatively new.[24] The first syntheses of analogs of tris(diphenylphosphino)methane $(Ph_2P)_3CH$ was reported by Issleib *et al.*[25] paving the way for use of these ligands in various aspects of synthetic chemistry. Subsequently, additional analogs were synthesized and characterized.[26-32] In addition, coordination complexes with neutral ligands, where phosphorus is bonded to the metal in a tridentate fashion, were prepared.[33,34] Anionic ligands that are obtained after removal of a methine proton to generate $[(R_2P)_3C]^-$, $[R_2P(S)]_3C^-$ anions, and which are potentially tridentate, i.e., anionic tripod ligand, have also been documented.[35-42] On the other hand, the removal of the methine *hydride* to generate a carbenium ligand with 6π-electrons, $[(R_2P)_3C]^+$ (R = Me, Ph), has not yet been reported. The effects of such ligands, when used as a substitute for cyclopentadienyl in early transition metal complexes of group (4-6)B, are unknown. Early transition metals such as group (4-6)B form the nucleus of the Ziegler-Natta family of catalysts for olefin polymerization.[43]

Carbenium ions are usually very short lived, and most are present in solution only as intermediates that are quickly converted to more stable molecules.[44] However, long-lived carbenium ions (trivalent carbocations) have been prepared and studied as stable entities in solution,[43,44] and, in a few cases, they persist even in solid state.[43] In solution, carbenium ions with the general formula $[R_3C]^+$ may be uncoordinated (this is more

likely in polar solvents in which it is solvated) or they may exist as an ion pair, which indicates a close associated with their gegenion(s).[45] The carbon atom of the carbenium ion assumes an sp^2-state of hybridization and therefore it is planar.[46]

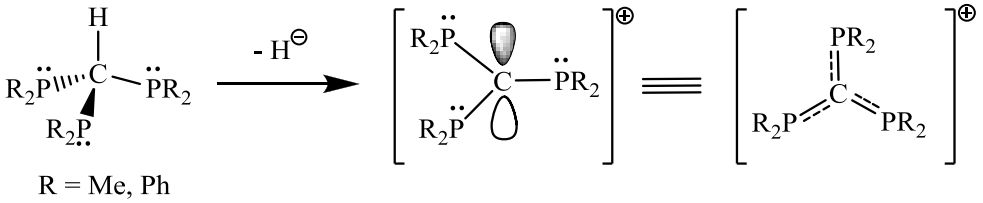
Some of the best known of these cationic species include alkylcarbenium ion,[47,48] diphenylfluorocarbenium ion,[49] bis(dialkylamido) phosphenium ions,[50] phosphenium iron tetracarbonyl complex ions,[51] and nitrogen substituted carbenium ions like iminium $[R_2NCR_2]^+$, amidinium ion $[(R_2N)_2CR]^+$ [52-54] and triphenylcarbenium ion.[55] However, isolation and crystallization of carbocations as salts remain a challenging problem. Recently the stabilization of chloro-substituted carbocations has been examined experimentally by Olah[56] (NMR spectroscopy) and Vancik and Sunk[57] (IR spectroscopy) and theoretically by Schaefer[58] and Reynolds[59] (*ab initio* calculations). Laube *et al* made a comparison of theoretical predictions concerning the structure of carbocations with experimental data obtained by X-ray analysis.[60] The first α-chloro-carbocation crystal structure obtained by Laube's group (see **Figure 1.1**) and was followed *tert*-butyl cation determined by same latter.[60]

Figure 1.1. The First Crystal Structure of Chloro-substituted Carbocation



The majority of the carbenium ions known today were generated by using SbF_5 as a Lewis acid [61], or by superacids[62] and concentrated sulfuric acid.[55,63,64] In all cases tertiary carbon is bonded to three other carbons $[R_3C]^+$, or two carbons and a nitrogen $[R_2CNH_2]^+$, or one carbon and two halides $[RCX_2]^+$. There is no single case where a phosphorus based $[(R_2P)_3C]^+$ has been studied using the above techniques to generate such carbenium. Thus, in the next chapter I will present studies that attempted to synthesize such carbenium ions using different approaches including Lewis acids and hydride abstracting agent such as trityl(tetrakis)pentafluorophenylborate as shown in **Figure 1.2**.

Figure 1.2. General Route for Cationic P Containing Species



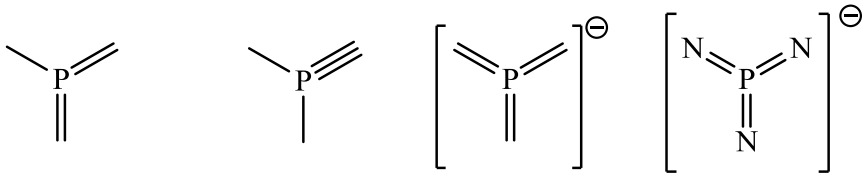
The carbenium ions of the type $[(R_2P)_3C]^+$ shown in **Figure 1.2** with dialkyl or diarylphosphine substituents have not been previously reported. Stabilization of tricoordinated carbenium ion of this type is greatly enhanced by the π-donation from non-bonding electron pairs residing on the phosphorus atoms at α-position. [65,66]

Carbenium ions with three-fold coordinated carbon centers are very useful for synthetic chemists because upon combination with electron rich molecules they will form a salt through metathesis reaction.[60] Carbenium ions being highly reactive cationic species can be stabilized by incorporation into the coordination sphere of transition metal

complexes. Preparing carbenium ions with cationic 6π-electron ligands rather than conventional anionic 6π-electron ligands afford the possibility to make unique metal-ligand combinations, particularly with early transition metals.[67,68,] These combinations should form highly reactive cationic complexes (*e.g.* olefin polymerization catalysts) in an entirely new way using metal complexes of lower oxidation state that could not be used previously. From some previous studies, examples of cationic ligands that can σ-bond to metals includes NO^+ [69] and triazolium cation[8] (see **Table 1.1**). On the other hand, it is not clear how the 6π-cationic ligands bond with the metal complexes.

1.2.2. Oxidation states of phosphorus

The simple hybridization scheme that is employed for carbon, nitrogen and oxygen can also be useful in phosphorus chemistry, a point that was not at all evident some time ago. Phosphorus can form a variety of compounds as a neutral species P^o, as a phosphonium P^+ ion, or as phosphate P^- ion.[70] Pentavalent phosphorus compounds generally have the coordination numbers of 4, 5, or 6.[71] Compounds in which pentavalent phosphorus is coordinated by three or fewer ligands have recently been synthesized.[72] Examples of such systems, which are characterized by double or triple bonds, can exhibit the structure types **A**,[72-75] **B**,[76] **C**,[71] and **D** are shown in below.



A **B** **C** **D**

The central PC_3 group in structure **C** is planar and the C-P-C angles are almost identical.[71] The three double-bonded C atoms that surround the central phosphorus atom are in a propeller-like manner (sp^2 hybridization).[71] New ligand types **C** and **D**, which have 6π-electrons and which will be the focus of the studies in this dissertation, should be a good substitute for 6π-electron cyclopentadienyl ligands in early transition metal spheres. Once **C** and **D** are synthesized, we plan to examine the interaction of these ligands with metals to form cationic complex analogs of the homogeneous Ziegler-Natta catalyst, $[Cp_2M\text{-}R]^+$. This should be favored as the active site consists of electron-deficient metal atoms.[77] As well, these new 6π-electron ligands will be used to replace cyclopentadienyl in electron-deficient organolanthanide species Cp_2MCH_3 (M = Gd, Yb, Lu), which are known to be excellent models for the active site of Ziegler-Natta catalysts.[78]

1.2.3. Guanidinium cation

The guanidinium ion $[(R_2N)_3C]^+$ is a well known ‘’rock stable’’ cation that has found wide spread use in synthetic chemistry.[52-54] The properties of guanidine **1** and its guanidinium cation **2** (see **Figure 1.3**) have attracted the interest of both theoretical and synthetic chemists.[79-80] Guanidine is among the strongest organic bases (pKa = 13.6) known in chemistry.[85] While guanidinium cation has three resonance structures that are chemically equivalent, guanidine has three resonance structures that are not chemically equivalent[79] (see **Figure 1.4**). The resonance energy difference is estimated to be 6-8 kcal/mol, which significantly increases the strength of the base.[79] Guanidine and its

derivatives are biologically and industrially important chemicals.[86] The biological activity of guanidine, high basicity in aqueous solution, its particular thermodynamic stability and applications in synthesis have been the subject of discussion for many years.[87-91] Although fairly toxic by itself, guanidine derivatives have a number of applications in chemotherapy.[86,92] They have also demonstrated, anti-inflammatory, antibacterial, antiviral and antifungal properties.[93] Most of the biological properties of guanidine and its derivatives are related to their strong basicity.

The guanidinium ion $[C(NH_2)_3]^+$ is of biochemical interest. This is due to its role as an essential fragment in a variety of larger biochemical compounds whose applications are dependent upon the properties of the ion.[94-99] Guanidinium cation has been shown to bind a number of biochemically important anions,[100] including nitrates, phosphates and sulfates through both charge pairing interactions and hydrogen bonding. There are several reasons why the guanidinium group binds so tightly to anions. First, a very high pKa value of 12-13.6 allows it to remain protonated over a wide pH range.[101] Furthermore, its geometry allows it to align well with anionic species, and results in a highly stable complex. The cationic ligand **2 Figure 1.3** is particularly interesting because of its high symmetry, planarity, Y aromatic character, and because the three amino groups that it contains can easily form inter-ionic hydrogen bonds with various proton acceptors.[102] In industry, guanidine is used as an electrolyte in batteries, photoelectrochemical cells, electroplating and other wet electrochemical devices.[103] Guanidine salts have been employed as fertilizers, antioxidants for textiles, and as catalysts in chemical processes (e.g. guanidium hydrochloride).[87]

Figure 1.3. Schematic Representation of the Y-conjugated Molecules **1**, **2**[88]

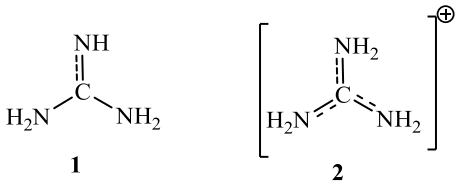
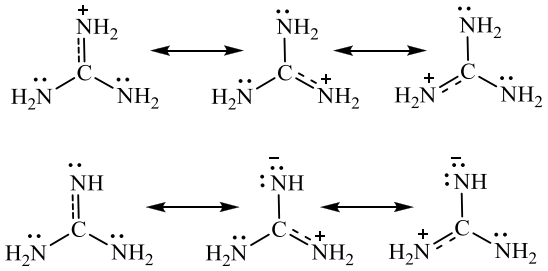


Figure 1.4. Resonance Structures for Guanidinium Cation and Guanidine[80]



The Y-shaped guanidinium compound **2** in **Figure 1.3** is conjugated with a high stability 6π-electron system.[90] The source of stability of the aminocarbocation is due to the π-donation of the nitrogen pair of electrons into an empty 2p(π)-orbital of the adjacent carbon center.[104] The stabilities of Y-conjugated compounds were analyzed by Klein,[105] and he concluded that favorable coulombic interactions rather than Y-aromaticity are the main sources of stability. This was supported by theoretical studies done by Schleyer *et al.*[106] who found that the preference of Y-delocalized isomers is caused by a more favorable π charge distribution. One of the main foci in my study is to synthesize 6π-cationic ligand of Y-shaped **2** analogs and to coordinate it with group 6B metal carbonyl complexes. Such coordination has not been reported in literature despite the fact that, such 6π-cationic ligand has been known for a long time. Therefore; this will

be an important step towards synthesis of novel catalysts.

1.2.4. Photolysis of transition metal carbonyl complexes

Photochemistry is the study of the physical processes or chemical changes that occur in molecules upon absorption of ultraviolet-visible radiation.[107] Chemical change is not a requirement, however, **fluorescence** (light emitted from a species which has absorbed radiation) and **chemiluminescence** (light emitted as a product of a chemical reaction) can occur.[108] Photochemical reactions are commonly used in the formation of four-membered rings [2 + 2] inter-and intra molecular cycloaddition.[109-112] Photochemical reactions have also been useful to obtain highly strained compounds whose thermodynamic instability is not favorable under thermal reaction conditions.[108]

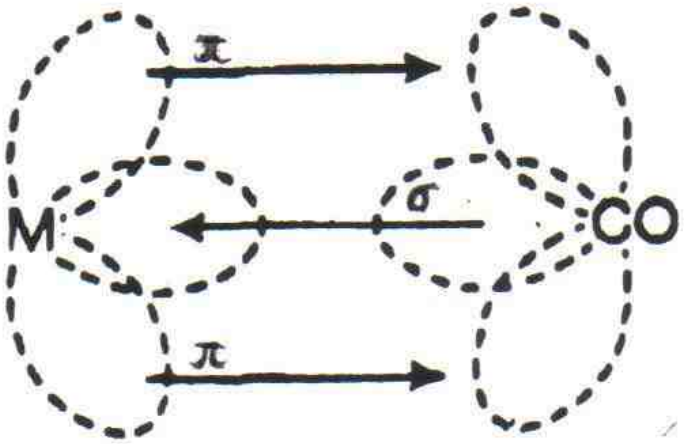
It is apparent that transition metal carbonyl complexes are among the most photo-reactive chemical species. Metal carbonyl photoprocesses include electronic absorption phenomena, luminescence, non-radioactive decay, energy transfer, and chemical reaction.[113] Metal carbonyl complexes are low-valent, and include d^4, d^5, d^6, d^7, d^8, d^9, and d^{10} oxidation states. Our focus in the studies presented in this dissertation will be on group 6B metal carbonyl complex derivatives, which are among the most well studied.[113] The approach I will present is more hypothetically advantageous than a thermal approach because a photo-chemical substitution route can be carried out at room temperature or below, thereby avoiding the use of high temperatures that may lead to decomposition of unstable ligands and complexes.[108,114] In our synthesis, however, we will use a lamp with a wavelength that ranges between 200 to 400 nm, a range used most often for inducing

photolysis in the UV region.[106]

The bonding between CO and a metal is a combination of σ and π bonding.[112,113] Delocalization of π-d electrons from the central metal into the π* CO orbitals gives rise to π-back-bonding (see **Figure 1.5**), and overlap of vacant **d** orbitals of the metal and CO lone pair electrons yielding a strong σ donor interaction.[115,116] The back-bonding from filled metal **d** orbitals into the π* CO orbitals result in partial cancellation of C to O bonding.[117] This results in the reduction of the bond order of CO and reduces the force constant between C to O. Consequently, the bond between C and O can be stretched with less energy. Another possible factor affecting the stretching frequency of the complexed CO is that the more highly positively charged metal makes it more difficult to allow its **d** orbital electrons to participate in back-bonding.[117] This will result in less cancellation of C to O bonding and more of the carbon-oxygen triple bond character. More triple bonding character results in a higher CO stretching frequency.

It is believed that stronger π-back-bonding with lower valent metals is the reason that these metals have greater tendency to delocalize electron density into the ligand. Due to a large degree of delocalization of the electrons from the central metal into the ligand, these compounds are highly covalent.[113] Electronic transitions involving these electrons are the reason for the extreme photosensitivity of these compounds.[113]

Figure 1.5. Bonding M-CO[113]



Metal carbonyl derivatives have been demonstrated to readily lose a carbonyl ligand upon photolysis.[108,113-117] Photolysis of metal carbonyl complexes involves ligand exchange, and substitution dominates the excited state processes.[113] The resulting substitution products include those formed utilizing ligands that function as electron donors[118,119] and those produced through replacement of metal carbonyl groups. There is a combination of factors that makes substituted complexes possible; this includes final product stability and photolabilization of the CO at intermediate stages of substitution.[113] The loss of CO to yield stable low-valent complexes requires an entering ligand capable of stabilizing the low-valent metal complex.[113] In the process of coordinating 6π-cationic guanidinium analog ligands through photolysis, we expect step wise loss of CO groups or other weakly coordinated ligands to the metal complexes.[120-126] It is assumed that the guanidinium cation has a high propensity to accept any excess charge accumulated on the metal atom; therefore, it can stabilize the low-valent metal complex. The presence of

such a ligand will certainly weaken the M-CO bonds.[113] This will result in loss of CO or other weakly coordinated ligands to most likely yield an anticipated novel stable low-valent cationic metal complex.

1.2.5. Lanthanides

The lanthanide or lanthanoid series in the periodic table consists of fifteen elements including lanthanum. These elements have atomic numbers from 57 to 71 (lanthanum to lutetium).[127,128] They are generally classified as lanthanides because the lighter elements in the series are chemically similar to lanthanum.[127] Strictly speaking lanthanum is a group 3B element. Its electronic configuration is $[Xe]5d^16s^2$ with three electrons in the highest energy 5d and 6s orbitals.[129,130] Therefore the ion La^{3+} has no *f* electrons, which is the case for the rest of the fourteen elements.

The generally accepted electronic configuration of lanthanide elements, with minor exceptions, is $[Xe]4f^n5d^06s^2$.[126,130] The chemistry of lanthanides differs from both main group and transition metals due to the nature of 4*f* orbitals. These orbitals are towards the inside of the atom and are shielded from the atom's environment by 4d and 5d electrons. The sum of the first three ionization enthalpies of lanthanides is relatively low, so that the elements are highly positive.[127,130,133] They readily form 3+ ions in solids, in aqueous solution ion and in complexes with other species.[127,131] Oxidation state 3+ is the most dominant state due to the stabilizing effects exerted on different orbitals by increasing ionic charge. In a few cases, oxidation states of 2+ and 4+ can be obtained. For example, it has been observed that Eu^{2+} is formed when Eu^{3+} gains an electron to form an

f^7 configuration, which has extra stability of a half-filled shell. Ce^{4+} is formed when Ce^{3+} loses its single *f* electron to obtain the electronic configuration of xenon.[128] Both Eu^{2+} and Ce^{4+} are stable in water and they are strong oxidizing and reducing agents respectively.[129,131] In addition, Ln^{2+} ions (Ln = Nd, Eu, Dy, Tm, Yb) and Ln^{4+} ions (Ln = Pr, Tb) are also formed in the solid state, but these are unstable in water.[127,129,130,131]

Lanthanides are silvery in appearance and become dull or discolored when exposed to air due to the formation of their oxides. The lower atomic number lanthanide elements are rather soft, but increase in hardness across the series. Also, their conductivities are appreciably lower than those of other close-packed metals.[131] The ionic radii of lanthanides decrease across the period, due to a phenomenon called lanthanide contraction, which is due to the imperfect shielding of the 4*f* electron by another 4*f* electron.[131] The directional characteristics of the 4*f* orbitals cause the $4f^n$ electrons to shield themselves and other electrons from the nuclear charge imperfectly.[131] As the nuclear charge and 4*f* electron population increases; the imperfect shielding occurs due to The lanthanides coordination number 6 for Ln^{x+} ion is rare; instead larger coordination numbers 7-12 are common.[133-135] This is possibly due to the space available around these larger cations. The coordination modes of the lanthanides with the 6π-cationic ligands of guanidinium analogs are the subject of the studies presented in this dissertation.

1.3. Preliminary studies

1.3.1. DFT calculations of $[(R_2P)_3C]^+$

To gain more insight into how the 6π-cationic ligand coordinates with transition metal complexes, our group undertook a theoretical study using density functional theory (DFT) calculations on the model reactions showed in **Figure 1.6, Figure 1.7** and **Figure 1.8**. We hoped that the knowledge gained from these would be helpful in a rational design of new catalysts.

All DFT calculations were done by Richard, M a corworker[136] of Sandia National Laboratory. He performed the calculations using the B3LYP density function,[137] that combines the Becke GGA exchange function[138] with some exact exchange and the GGA correlation function to describe the species.[139] He used a valence double zeta plus polarization basis set to describe the electronic degrees of freedom.[136] He also used small core effective core potentials for the transition metal atom's core electrons.[140]

Initial calculations B3LYP density function level was done on $[(R_2P)_3C]^+$ (R = Me) revealed a planar central C atom. **Figure 1.6** shows that the geometry of the optimized structure has a planar C atom, with pseudo-tetrahedral P atoms. The calculations were made for cationic ligand $[(R_2P)_3C]^+$ mixed with $Cr(CO)_3$ to form $\{[(R_2P)_3C]Cr(CO)_3\}^+$ as a model complex.

Figure 1.6. Geometry-Optimized Structure for $[(R_2P)_3C]^+$

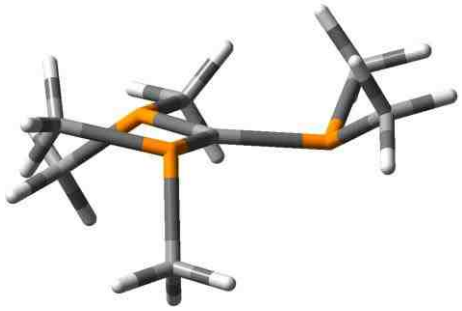
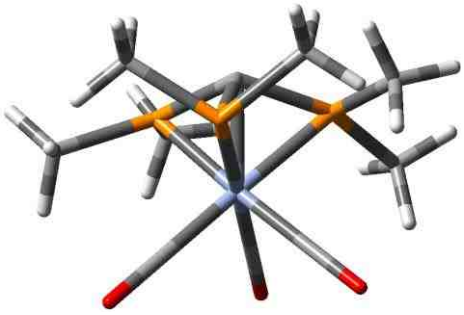


Figure 1.7 shows the geometry-optimized structure of $\{[(R_2P)_3C]Cr(CO)_3\}^+$ (**A**) and a neutral complex $\{[(R_2P)_3CH]Cr(CO)_3\}$ (**B**). Interestingly, net bonding interactions between the $[(R_2P)_3C]^+$ ligand and the $Cr(CO)_3$ fragment in **A** are observed. This signifies that 6π-cationic ligand should bind to a metal fragment. Distinctive changes in geometry around the core P_3C-Cr portion of molecule **A** can be observed. While the calculated P-C-P bond angle in **A** is 111^o on the other hand in **B** it is 93.4^o. The bond angle in cationic complex **A** has flattened from planarity (120^o) by approximately 10^o. Further, P-C bond length has shortened from 1.90 Å of neutral complex **B** to 1.82 Å of the cationic complex **A**.

Figure 1.7. Geometry-Optimized Structure of **A** and **B**

$\{[(R_2P)_3C]Cr(CO)_3\}^+$ (**A**)



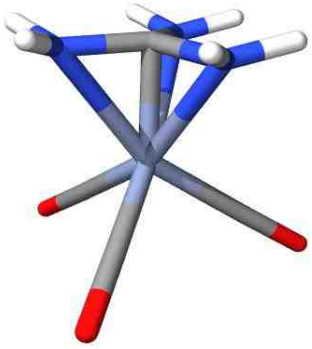
$\{[(R_2P)_3CH]Cr(CO)_3\}$ (**B**)

1.3.2. DFT calculations of $[(H_2N)_3C]^+$

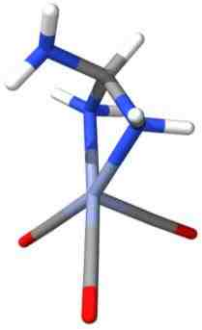
With the above concepts in mind and in an effort to better understanding those empirical contributions that lead to electron rich species to bind to the guanidinium cation, we undertook theoretical calculations of how 6π-cationic ligand coordinates with group 6B metal carbonyl complexes for example, $Cr(CO)_3$. It is true that, such types of metal complexes are not electron rich, as is the case for NO_3^- or SO_4^{2-} but, they are not electron poor either. Theoretical calculations done on mixing $Cr(CO)_3$ and guanidinium ion,[136] revealed the following in **Figure 1.8**. The calculations show the geometry of the $\{[(H_2N)_3C]Cr(CO)_3\}^+$ (**C**) analog to contain a planar sp^2 central carbon atom, binding to the metal in three-fold symmetrical π-bonding when compared with di-hepto σ-bonding seen in the parent $\{[(H_2N)_3CH]Cr(CO)_3\}$ complex (**D**) **Figure 1.8**. Theoretical study following by structure shown such possibility of 6π-cationic ligand to coordinate with a group 6B metal carbonyl is a good sign towards our target in the next chapter.

Figure 1.8. Comparison of Coordinated Guanidinium Cationic and Neutral Guanidine to $Cr(CO)_3$

$\{[(H_2N)_3C]Cr(CO)_3\}^+$ (**C**)



$\{[(H_2N)_3CH]Cr(CO)_3\}$ (**D**)



1.4. Statement of research problem

Traditional 6π-electron ligands like cyclopenatadienyl and its derivatives have been used for synthetic chemistry for many years. Yet, there exists opportunities to prepare new ligands with new chemical properties. We will synthesize and characterize metal complexes of two new ligand types-anionic 6π-electron ligands that are more similar to cyclopentadienyl anion, and 6π-cationic ligands, which should lead to novel routes to new organometallic species. The key questions that I wished to explore are the following:

1. Can we abstract hydrogen in form of *hydride* (H^-) instead of proton (H^+) from $(R_2P)_3CH$ (R = Me, Ph) to form 6π-cationic ligands?
2. Can a synthesized cationic 6π-electron ligand work as a substitute for cyclopentadienyl anion?
3. Will 6π-cationic ligands bond with group 6B metal complexes in a unique way?

1.5. Hypothesis

The 6π-electron cationic ligand will form unique complexes with early transition metals and will be useful as a catalyst for a wide variety of applications in synthetic chemistry.

1.6. References

1. Von Zelewsky, A. "Stereochemistry of Coordination Compounds" John Wiley: Chichester, **1995**.
2. Miessler, G. L.;Tarr, D. A. *Inorganic Chemistry* 2nd ed. Prentice Hall, Upper Saddle River, New Jersey, **1998**
3. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 6th ed. John Wiley and Sons, Inc. New York, **1999**.
4. Mata, J. A.; Peris, E.; Incarvito, C.; Robert, H. *Chem. Commun*. **2003**, *2*, 184.
5. Shao, L.; Steven, J.; Paul. D.; Cooper, N. J. *J. Am. Chem. Soc*. **2002**, *124*, 14812.
6. Catherine, S; Claude, P. George, G. *J. Organomet. Chem*. **1974**, *77*, 49.
7. Mccaffery, E.; Natishan, P. M.; Hubter, G. K. *Corrosion*, **1997**, *53*, 556.
8. Chaumonnot, A.; Donnadieu. B.; Sabo-Etienne, S.; Chaudret, B.; Buron, C.; Bertrand, G.; Metivier, P. *Organometallics*, **2001**, *20*, 5614.
9. Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc*. **1990**, *112*, 1566.
10. Sehling, U.; Diebold, J.; Kirsten, R.; Roll, W.; Brintzinger, H. H. *Organometallics*, **1994**, *13*, 964.
11. Resconi, L.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Zeigler, R. *Macromolecules*, **1995**, *28*, 6667.
12. Cavallo, L.; Guerra, G. *Macromolecules*, **1996**, *29*, 2729.
13. Mallin, D. T.; Rausch, M. D.; Mintz, E. A.; Rheingold, A. L. *J. organomet. Chem*. **1990**, *381*, 35.
14. Mohring, P. C.; Coville, N. J. *J. Organomet. Chem*. 1994, *479*, 1.

15. Piccolrovazzi, N.; Pino, P.; Consignoli, G.; Sironi, A.; Moret, M. *Organometallics*, **1990**, *9*, 309.

16. Lee, I. M.; Gauthier, W. J.; Ball, J. M.; Lyengar, B.; Collins, S. *Organometallics*, **1992**, *11*, 2115.

17. Spaleck, W.; Kuber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics*, **1994**, *13*, 954.

18. Spaleck, W.; Aulbach, M.; Bachmann, B.; Kuber, F.; Winter, A. *Makromol. Chem. Macromol. Symp.* **1995**, *89*, 237.

19. Coates, G. W.; Waymouth, R. M. *Science*, **1995**, *267*, 217.

20. Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc*. **1995**, *117*, 11586.

21. Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143.

22. Bochmann, M. *J. Chem. Soc. Dalton Trans*. **1996**, 255.

23. Marks, T. J.; Sishta, C.; Hathorn, R. M. *J. Am. Chem. Soc*. **1992**, *114*, 1112.

24. Grim, S. O.; Smith, P. H.; Nittolo, S.; Ammon, H. L.; Satek, L. C.; Sangokoya, S. A.; Khanna, R. K.; Colquhoun, I. J.; McFarlane, W.; Holden, J. R. *Inorg. Chem*. **1985**, *24*, 2889.

25. Issleib, K.; Abicht, H. P. *J. Prakt. Chem*. **1970**, *312*, 456.

26. Karsch, H. H.; Schubert, U.; Neugebauer, D. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 484.

27. Karsch, H. H.; Zimmer-Gasser, B.; Schubert, U.; Neugebauer, D. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 484.

28. Karsch, H. H. *Z. Naturforsch, B: Anorg. Chem. Org. Chem*. **1979**, *34B*, 1178.

29. Grim, S. O.; Sateke, L. C.; Mitchell, J. D. *Z. Naturforsch, B: Anorg. Chem. Org. Chem.* **1980**, *35B*, 832.

30. Grim, S. O.; Walton, E. D. *Phosphorus Sulfur*, **1980**, *9*, 123.

31. Colquhoun, I. J.; Grim, S. O.; McFarlane, W.; Mitchell, J. D. *J. Magn. Reson*. **1981**, *42*, 1986.

32. Colquhoun, I. J.; Grim, S. O.; McFarlane, W.; Bassett, J. M.; Grim, S. O. *J. Chem. Soc. Dalton Trans*. **1980**, 1645.

33. Selegue, J. P.; Goodrich, J. O. *Organometellics*, **1985**, *4*, 798.

34. Smith, A. K.; Gaperet, C.; Rida, A. M. *J. Organomet. Chem*. **2001**, *628*, 1.

35. Forniers, J.; Martinez, F.; Navarro, R.; Tomas, M.; Urriolabeitia, E. P. *J. Chem. Soc. Dalton Trans*. **1994**, 505.

36. Trofimenko, S. *Acc. Chem. Res*. **1971**, *4*, 17.

37. Karsch, H. H.; Zimmer-Gasser, B.; Schubert, U.; Neugebauer, D.; Schubert, U. *Angew. Chem.* **1979**, *91*, 519.

38. Grim, S. O.; Smith, P. H.; Satek, L. C. *Polyhedron*, **1982,** *1*, 137.

39. Laguna, A.; Gimeno, M. C.; Laguna, M.; Fernandez, E. J.; Olmos, E.; Jones, P. G. *J. Chem. Soc, Dalton Trans*. **1994**, 2891.

40. Karsch, H. H.; Appelt, A. *Angew. Chem. Int. Ed. Engl*. **1985**, *24*, 402.

41. Karsch, H. H.; Appelt, A.; Muller, G.; Riede, J. *Organometallics*, **1987**, *6*, 316.

42. Fernandez, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.;

LopezdeLuzuriaga, J. M. *J. Chem. Soc. Dalton Trans*. **1993**, 3401.

43. March, J. *Advanced Organic Chemistry Reaction Mechanism and Structure*, Mcgrw-Hill Book, New York, **1969**.
44. Olah, G. A. *Top. Curr. Chem*. **1979**, *80*, 19.
45. Olah, G. A.; Pittman, Jr., C. U. *J. Am. Chem. Soc*. **1966**, *88*, 2331.
46. Evans, A. G. *Trans. Faraday Soc*. **1946**, *42*, 719.
47. Olah, G. A.; Baker, E. B.; Evans, J. C.; Tolgyesi, W. S.; McIntyre, J. S.; Bastien, I. J. *J. Am. Chem. Soc.* **1964**, *86*, 1360.
48. Olah, G. A.; Comisarow, M. B. *J. Am. Chem. Soc*. **1965**, *87*, 2998.
49. Olah, G. A.; Cupas, C. A.; Comisaro, M. B. *J. Am. Chem. Soc*. **1966**, *88*, 362. 49. 49.
50. Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem*. **1972**, *11*, 2534.
51. Coweley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem*. **1981**, *20*, 4289.
52. Olah, G. A.; Schley, P. R. *Carbonium Ions, Vol. I-V*, Wiley, New York, **1976**.
53. Volkmann, R. A.; Trost, B. M.; Fleming, I.; Schreiber, S. L. *Comprehensive Organic Synthesis, Vol. 1*, Pergamon Press, Oxford, **1991**, pp 355.
54. Kleinman, E. F.; Heaney, H.; Volkmann, R. A.; Overman, L. A.; Ricca, D. J.; Hiemstra, H.; Speckamp, W. N.; Ugi, I.; Lohberger, S.; Karl, R.; Trost, B. M.; Fleming, I.; Schreiber, S. L. (Eds) *Comprehensive Organic Synthesis, Vol. 2*, Pergamon Press Oxford, **1991**, pp 893.
55. Baeyer, A. V.; Villiger, V. *Chem. Ber.* **1902**, *34*, 1189.
56. Olah , G. A.; Heilinger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1989**, *111*, 8020.
57. Vancik, H.; Percac, K.; Sunko, D. E. *J. Am. Chem Soc*. **1990**, *112*, 7418.

58. Hamliton, T. P.; Schaefer III, H. F. *J. Am. Chem. Soc*. **1991**, *113*, 7147.

59. Reynolds, C. H. *J. Am. Chem. Soc*. **1992**, *114*, 8676.

60. (a) Laube, T.; Bannwart, E.; Hollenstein, S. *J. Am. Chem. Soc.* **1993**, *115*, 1731. (b) Laube, T.; Hollenstein, S. *J. Am. Chem. Soc.* **1993**, *115*, 7240.

61. Olah, G. A. *Angew. Chem. Int. Ed. Engl*. **1973**, *2*, 173.

62. Olah, G. A.; Sommer, S. J. *Superacids.* Willey, New York, **1985**.

63. Norris, J, F.; Sounders, W. W. *J. Am. Chem. Soc*. **1901**, *25*, 54.

64. Kehrmann, F.; Wentzel, F. *Chem. Ber.* **1901**, *24*, 3815.

65. Grutzmacher, H.; Marchand, C. M. *Coord. Chem. Rev*. **1997**, *163*, 287.

66. Christe, K. O.; Hoge, B.; Boatz, J. A.; Prakash, G. K. S.; Olah, G. A.; Sheehy, J. A. *Inorg. Chem.* **1999**, *38*, 3132.

67. Cossee, P. *Tetrahedron Lett*. **1960**, *17*, 12.

68. Cossee, P. *J. Catal.* **1964**, *3*, 80.

69. Praneeth, V. K. K.; Nather, C.; Peters, G.; Lehnert, N. *Inorg. Chem*. **2006**, *45*, 2795.

70. Wolf, R. *Pure and Appl. Chem*. **1980**, *52*, 1141.

71. Appel, R.; Gaitzsch, E.; Knoch, F. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 589.

72. Niecke, E.; Flick, W. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 589.

73. Scherer, O. J.; Kuhn, N. *J. Organomet. Chem*. **1974**. C17, 78.

74. Appel, R.; Peters, J.; Westerhaus, A. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 80.

75. Navech, J.; Majoral, J. P.; Kreamer, R. *Tetrahedron Lett.* **1983**, *24*, 5885.

76. Yoshifuji, M.; Shibayama, K.; Inamoto, W. *Chem. Lett*. **1984**, 603.

77. Bertrand, G. *J. Am. Chem*. Soc. **1984**, *106*, 6008.

78. Ziegler, K. *Organometallic Chem*. ACS monograph, **1960**, No 147, 194.

79. Parshall, G. W.; Watson, P. L. *Acc. Chem. Res.* **1985**, *18*, 51.

80. Pauling, L. *Nature of Chemical Bond*, 3rd ed. Cornel University Press: Ithaca, NY, **1960**, pp 286.

81. Gund, P. *J. Chem. Educ*. **1972**, *49*, 100.

82. Sapse, A. M.; Massa, L. J. *J. Org. Chem.* **1980**, *45*, 719.

83. Ohwada, T.; Itai, A.; Ohta, T.; Shudo, K. *J. Am. Chem. Soc*. **1987**, *109*, 7036.

84. Sreerama, N.; Vishveshwara, S. *J. Mol. Struct*. **1989**, *194*, 61.

85. Weiberg, K. B. *J. Am. Chem. Soc*. **1990**, *112*, 4177.

86. Angyal, S. J.; Warburton, W. K. *J. Chem. Soc*. **1951**, 2492.

87. American Cyanamid Co. *Chemistry of Guanidine*, Wayne, *Vol. IV*, **1950**.

88. Guand, P. *J. Chem. Educ*. **1972**, *49*, 100.

89. Weiberg, B. K. *J. Am. Chem. Soc*. **1993**, *112*, 4177.

90. Gobbi, A.; Frenking, G. *J. Am. Chem. Soc*. **1993**, *115*, 2362.

91. Ohwada, T.; Kagawa, H.; Ichikawa, H. *Bull. Chem. Soc. Jpn*. **1997**, *70*, 2411.

92. Krygowski, M. T.; Cyranski, K. M.; Anulewiez, R. O. *Pol. J. Chem*. **2001**, *75*, 1939.

93. Schafer, G. *In International Encyclopedia of Pharmacology and Therapeutics* Erecinsk. M (ed). Pergamon Press: Oxford, **1981**, pp 165.

94. Palagiano, E.; Demarino, S.; Minale, L.; Riccio, R.; Zollo, F.; Iorizzi, M.; Carre, B. J.; Debitus, C.; Lucarain, L.; Provost, J. *Tetrahedron*, **1995**, *51*, 3675.

95. Subramanian, S.; Sarma, T. S.; Balasubrananian, D.; Ahluwalia, J. C. *J. Chem. Phys.* **1971**, *75*, 815.

96. Swanson, C. A. *Arch. Biochem. Biophys.* **1966**, *117*, 494.

97. Katz, S. *Biochim. Acta*, **1968**, *154*, 468.

98. Capitani, J. F.; Pedersen, L. *Chem. Phys. Lett.* **1978**, *54*, 547.

99. Kollman, P.; Mckelvey, J.; Gund, P. *J. Am. Chem. Soc.* **1975**, *97*, 1640.

100. Best, M. D.; Tobey, S.L.; Anslyn, E. V. *Coord. Chem. Rev.* **2003**, *240*. 3.

101. Rozas, R.; Kruger, P. E. *J. Chem. Theory. Comput.* **2005**, *1*, 1055.

102. Kozak, A.; Grottel, M.; Koziol, A. E.; Pajak, Z. *J. Phys. C: Solid State Phys.* **1987**, *20*, 5433.

103. (a) Fuller, J.; Carlin, R. T.; Osteryoung, R. A. *J. Electrochem. Soc.* **1997**, *144*, 3881 (b) Kosmulski, M.; Osteryoung, R. A.; Ciszkowska, M. *J. Electrochem. Soc*. **2000**, *147*, 1454.

104. Kato, T.; Gornitzka, H.; Baceiredo, A. Scoeller, W. W.; Bertrand, G. *J. Am. Chem. Soc*. **2002**, *124*, 2506.

105. Klein, J. *Tetrahedron*, **1988**, *44*, 503.

106. Clark, T.; Wilhelm, D.; Schleyer, P. V. R. *Tetrahedron Lett*. **1982**, *23*, 3547.

107. Wells, C. H. J. *Introduction to Molecular Photochemistry*, Chapman and Hall Ltd. 11 New Fetter Lane, London, **1972**.

108. Wayne, P. R. *Principle and Applications of Photochemistry*, Oxford. Univ. Press: Oxford, **1988**, pp 1.

109. Penn, J. H.; Gan, L.; Chan, E. Y.; Lossel, P. D. *J. Org. Chem.* **1989**, *54*, 601.

110. Padwa, A.; Rieker, W. F. *J. Org. Chem.* **1979**, *44*, 3273.

111. Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc*. **1979**, *101*, 3390.

112. Lee, C. K.; Ahn, Y. M. *J. Org. Chem*. **1990**, *55*, 3957.

113. Wrighton, M. *Chem. Rev*. **1974**, *74*, 401.

114. Geoffroy, G. L. *J. Chem. Educ.* **1983**, *60*, 861.

115. Abel, E. W.; Stone, F. G. A. *Quart. Rev. Chem. Soc.* **1969**, *23*, 325.

116. Miessler, G. L.; Tarr, D, A. *Inorganic Chemistry*, **1999**, pp 435.

117. Orchin, M.; Jaffe, H. H. *The importance of Antibonding Orbitals*, **1967**, pp 49.

118. Dobson, G. R.; Amr El Sayed, M. F.; Stolz, I. W.; Sheline, R. K. *Inorg. Chem*. **1962**, *1*, 526.

119. Mannershantz, H. C. E.; Wilkinson, G. *J. Chem. Soc*. **1962**, 4454.

120. Strohmeler, W. *Angew. Chem. Int. Ed. Engl*. **1964**, *3*, 730.

121. Koerner von Gustorf, E.; Grevels, F. W. *Fortschr. Chem. Forsch*. **1969**, *13*, 366.

122. King, R. B.; Pannell, K. H. *Inorg. Chem.* **1968**, *7*, 273.

123. King, R. B.; Korenowski, T. F. *Inorg. Chem.* **1971**, *10*, 1188.

124. Muller, F. J.; Herberhol, M. *J. Organomet. Chem*. **1968**, *13*, 399.

125. Muller, F. J.; Fenderl, K. *J. Organomet. Chem*. **1969**, *19*, 123.

126. Nasielski, J.; Colas, A. *Inorg. Chem*. **1978**, *17*, 237.

127. Cotton, F. A.; Wilkinson, G. F. R. *Advance Inorganic Chemistry, A Comprehensive Text*, 4th ed. Published by John Wiley & Sons. **1988**, pp 981.

128. Shone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Porg. Inorg. Chem*. **1999**, *48*, 233.

129. Shriver, D. F.; Atkins, P. W.; Overton, T. L.; Rourker, J. P.; Weller, M. T.; Armstrong, F. A. *Inorganic Chemistry*, 3rd ed. **2000**, pp. 320.

130. Bailar, J. C.; Emeleus, H. J.; Sir Nyholm, R.; Dickenson, A. F. *Comprehensive Inorganic Chemistry-Lanthanide Transition Metal Compounds*, Edited by Emeleus, H. J.; Nyholm, R.; Trotman-Dickenson, A. F and Published by Pergamon Press, **1973**, *4*, pp 1.

131. Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, Published by Pergamon Press. Oxford, New York, Toront, Sydney, Paris, and Frunkfurt, **1984**, pp. 1423.

132. Jorgensenn, K. C. J. *Inorg. Chem*. **1955**, *1*, 301.

133. Moeller, T.; Martin, D. F.; Thompson, L. C.; Ferrus, R.; Feistel, G. R.; Randal, W. J. *Chem. Rev*. **1965**, *65*, 1.

134. Sinha, S. P. *Complexes of the Rare Earths*, Pergamon Press, New York, **1966**.

135. Mnetteries, E. L.; Wright, C. M. *Quart. Rev*. (London), **1967**, *21*, 109

136. Richard, M. DFT Calculations on 6π-Cationic Ligands, Unpublished Report, **2008**.

137. Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.

138**.** Becke, A. D. *Phys. Rev*. **1988**, *38*, 3098.

139. Lee, C.; Yang, W.; Parr, R. G. *PRB*, **1988**, *37*, 785.

140. Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *85*, 299.

CHAPTER TWO

Materials, Methods, and Protocols

2.1. Reagents

Analytical reagent (AR) grade aniline, MeI, Me_2PCl, $(Me_2P)_2CH_2$, PCl_5, and guanidinium carbonate were supplied by Alfa Aesa Johnson Metthey Company. AR tricarbonyl(1,2,3,4-tetrahydronaphthalene)chromium(0), tricarbonyl(cycloheptatriene) chromium (0), tricarbonyl(mesitylene)tungsten(0), CD_3Cl, C_6D_6, tetramethylenediamine (TMEDA), Br_2, HBF_4, $[(C_2H_5)_2N]_3P$, Me_3SiCl, SbF_5, TaF_5, and benzoyl peroxide were supplied by Aldrich Chemicals. AR grade $[Ph_3C]^+[B(C_6F_5)_4]^-$, THF-d_8, DMSO, CD_3COCD_3 and tricarbonylcycloheptatrienemolybdenum(0) were supplied by Acros Organics Fisher Scientific. AR grade 2,4,6-tri-*tert*-butylaniline, AgOTf, $B(C_6F_5)_3$, $Cr(CO)_6$, $Mo(CO)_6$, PCl_3, Ph_2PCl, $(Ph_2P)_2CH_2$, $Nd(NO_3)_3.6H_2O$, $Tb(NO_3)_3.5H_2O$, $YbCl_3$, $Yb(NO_3)_3.5H_2O$ and $W(CO)_6$ were supplied by Strem Chemicals.

2.2. Physical measurements and instrumentation

Infrared spectra were obtained on a Nicolet 6700 FT-IR. ^1H NMR spectra (and proton decoupled phosphorus-31), as well as decoupled ^{13}C NMR and decoupled ^{11}B NMR spectra were obtained on an AC-250 MHz, 101.3, 62.9, and 80.2 MHz respectively. ^1H and ^{13}C chemical shifts are referenced to external tetramethylsilane (δ 0.0), and phosphorus chemical shifts are referenced to external 85% H_3PO_4 (δ 0.0). All NMR spectra were obtained at ambient probe temperature (Ca. 298 K).

Elemental analyses were performed by Columbia Analytical Services. X-ray analyses were performed on a X 8 APEX II. Mass spectra were carried out on a LCT Premier Electrospray mass spectrometer in the positive mode. Photolysis was carried out by a Pen-Ray Mercury Lamp 90-0012-01, (Model $11SC^{-1}$) with current of 18 mA AC.

2.3. General procedures for synthesis

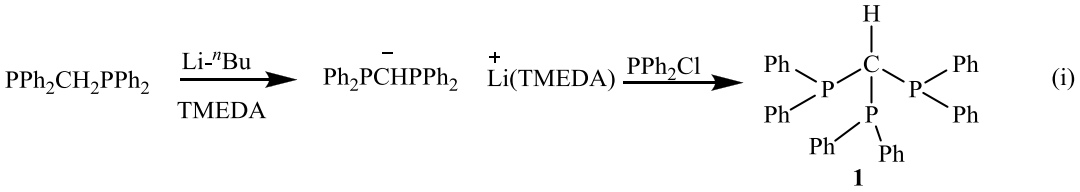
All operations were carried out under an argon atmosphere using standard Schlenk techniques, or in a vacuum atmosphere dry box. All solvents were appropriately dried and some were distilled before use and stored under argon. Solvents for NMR were also dried prior to use and stored under argon.

Phosphine-based ligands play a predominant role in transition metal coordination chemistry.[1] In this chapter I will focus on the description for the preparation of analogs of 6π-electron cyclopentadienyl ligand with structures below, cationic $[(R_2P)_3C]^+$ and anionic $[(RN=)_3P]^-$ (R = Me, Ph). The goal was to study their impact on coordination chemistry to group 6B transition metal carbonyl complexes. In addition, studies of the coordination of a known 6π-cationic ligand of guanidinium[2] analog $[(H_2N)_3C]^+$ with group 6B transition metal carbonyl complexes and lanthanides will be described. Finally, studies on the coordination of neutral tris(diphenylphosphino)methane with group 6B metal carbonyl complexes as well as the reaction of complex formed with Lewis acid, tris(pentafluorophenyl)borane $\{B(C_6F_5)_3\}$, will be described, which includes the attempted synthesis of 6π-cationic ligand of guanidinium analog tripiperidine carbenium

tetrafluoroborate.

2.4. Description of synthetic schemes

2.4.1. Synthesis of tris(diphenylphosphino) methane (compound 1)



(i)

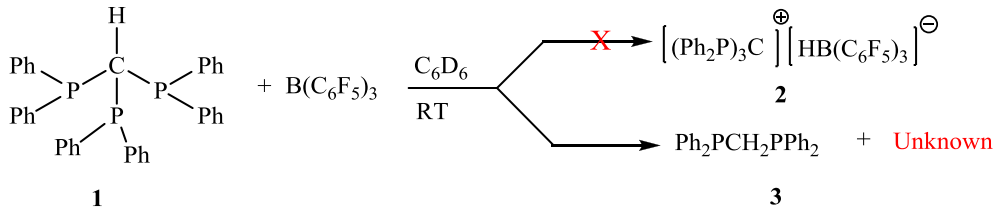
The synthesis of precursor **1** has been reported.[3,4] A (0.80 mL, 5.3 mmol) sample of tetramethylenediamine (TMEDA) was mixed with 2 mL of dry toluene and this solution was added dropwise over a period of 15 minutes to 2.50 M ^{n}Bu-Li in hexane solution (2.20 mL, 5.30 mmol) in a 50 mL flask with a magnetic stirrer. This resulted in an orange-red solution of ^{n}BuLi(TMEDA). Bis(diphenyphosphono)methane powder (2.00 g, 5.30 mmol) was added to the ^{n}BuLi(TMEDA) in several aliquots, and the mixture was stirred vigorously for 1h at room temperature in the dry box. The salt of $(Ph_2P)_2CH^-(LiTMEDA)^+$ precipitated as pale yellow crystals, and was filtered, washed with dry hexane (2 x 10 mL) and dried in *vacuo* to yield 2.00 g of dry solid material (2.00 g, 4.00 mmol).

The resulting $(Ph_2P)_2CH^-(LiTMEDA)^+$ salt was dissolved in 7 mL of dry-distilled tetrahydrofuran (THF) and added to a 50 mL flask over a magnetic stirrer. This mixture was treated with Ph_2PCl (1.00 mL, 5.30 mmol) diluted in 1 mL of THF in a dropwise fashion under argon for 1h. The mixture was stirred for 3h. The resultant pale yellow solution was evaporated under *vacuo* to dryness, yielding a pale yellow solid.

The dry pale yellow solid was treated with 16 mL of toluene and the resultant solution filtered through celite contained in a sintered frit. The clear yellow filtrate was collected and concentrated in *vacuo* to almost half of the original volume and left to stand for 12h in a freezer, which yielded colorless crystals of $(Ph_2P)_3CH$. The crystals were captured by filtration and washed with 2 mL of cold toluene and several times with hexane (4 x 3 mL), and then dried in *vacuo* for 12h. The washings were collected and additional crystals were recovered by repeating the filtration procedure, producing a further crop of crystals. This procedure yielded 1.2 g with a 53% yield, mp = 176-178 ^{o}C. The ^{1}H NMR spectrum (250 MHz, $CDCl_3$, 298K, ppm): δ = 4.1 (s, 1H, CH); 7.10-7.40 (m, 30H Ar-H). The $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, CDCl, 298 K, ppm): δ = -8.2 (s) with H_3PO_4 as a reference. The $^{13}C\{^{1}H\}$ NMR spectrum (62.9 MHz, CDCl, 298 K, ppm): δ = 24.2-26.6 (q, $^{2}J_{P-C}$ = 48.00 Hz), 134.9 (d, J = 1.70 Hz), 135.1 (d, J = 1.76 Hz), 135.3 (d, J = 1.50 Hz), and 137.4 (dt, J = 4.60 Hz).

2.4.2. Synthesis of 6π-cationic ligand using precursor 1

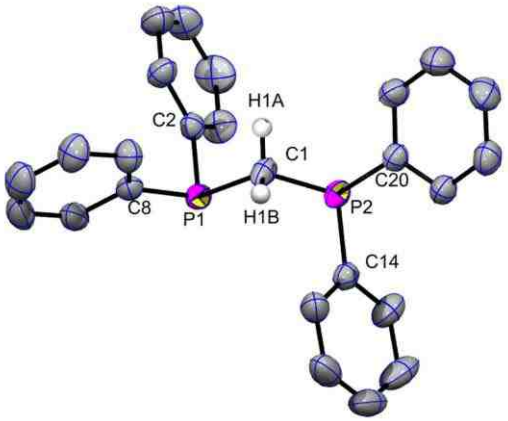
Scheme 1. Attempted synthesis of **2**

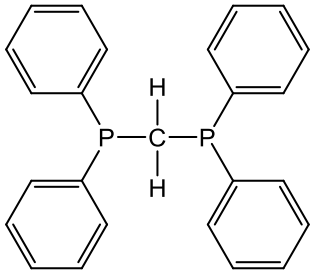


A sample of compound **1** (0.10 g, 0.18 mmol) was added to a 100 mL flask with a magnetic stirrer, then followed by of $B(C_6F_5)_3$ (0.10 g, 0.18 mmol), and the mixture was

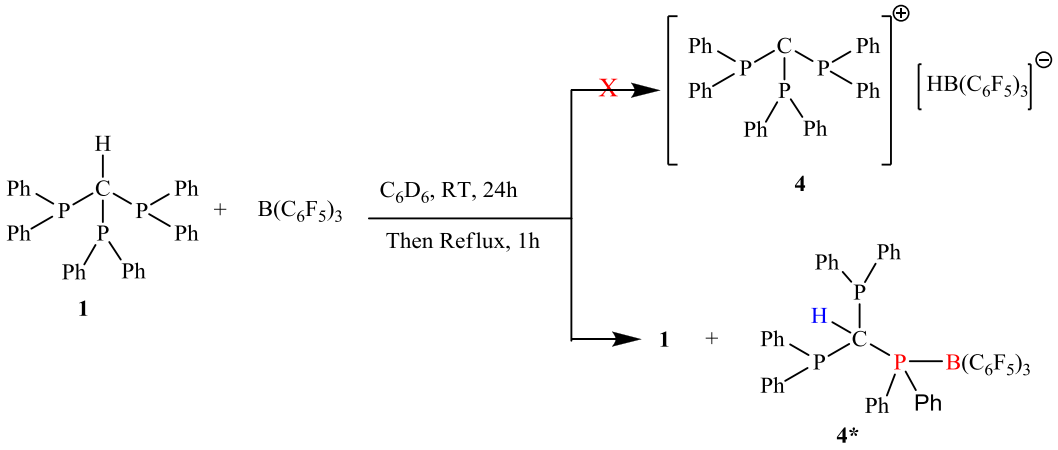
dissolved in 7 mL of benzene-d_6. The mixture was stirred at room temperature inside the dry box. From the mixture, an aliquot was removed for NMR spectroscopy analysis every 12h. After 145h, NMR analysis showed the formation of $Ph_2PCH_2PPh_2$ (compound **3)** with a $^{31}P\{^1H\}$ NMR spectrum at -21.8 (ppm) (s) and ‘’unidentified’’ compound at 37.4 (ppm) (s). Phosphorus-hydrogen coupled NMR spectrum showed two peaks: -21.8 (ppm) (s), and 37.4 (ppm) (d, $^1J_{P\text{-}H}$ = 518.7 Hz). These two compounds were separated by column chromatography using 100% dichloromethane as the eluent to separate **3**. The unidentified compound, which seemed to be slightly polar, was further separated using an eluent of a 2.5% MeOH and 97.5% DCM mixture. After recrystallization of **3**, single-crystal X-ray analysis revealed the structure shown in **Figure 2.1**. The NMR analysis for the unknown showed a ^1H NMR spectrum 250 MHz, $CDCl_3$, 298 K, ppm): δ = 4.3 (s, 1H, CH) and 6.8-8.7 (m, 30H, Ar-H). The $^{31}P\{^1H\}$ NMR spectrum for pure compound (101.3 MHz, C_6D_6, 298 K, ppm): δ = 17.8 (s) and the ^{31}P hydrogen-coupled NMR spectrum showed peaks at 17.8 (d, $^1J_{P\text{-}H}$ = 474 Hz) relative to H_3PO_4 as reference. $^{11}B\{^1H\}$ NMR spectrum (80.2 MHz, C_6C_6, 298 K, ppm): δ = -2.7 (s) for coordinated $\{HB(C_6F_5)_3\}^-$ and a single peak which is 50.2 (s) for uncoordinated $B(C_6F_5)_3$.

Figure 2.1. Molecular Structure of $(Ph_2P)_2CH_2$(**3**), Showing the Numbering Scheme. Hydrogen Atoms are Omitted for Clarity





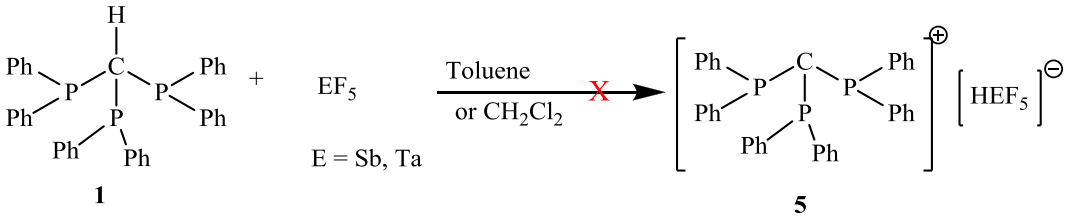
Scheme 2. Attempted synthesis of **4**



A sample of **1** (0.05 g, 0.09 mmol) was dissolved in 4 mL of benzene-d_6 and added to a 50 mL flask with a magnetic stirrer in the dry box and $B(C_6F_5)_3$ (0.02 g, 0.09 mmol) dissolved in 6 mL of benzene-d_6 was added dropwise. After stirring for 2h, no color change observed. The mixture was refluxed for 1h and left stirring overnight. The following day solvent was evaporated under *vacuo* for 12h. NMR of dry crude product of

the mixture showed a $^{31}P\{^{1}H\}$ NMR (101.3 MHz, C_6D_6, 298 K, ppm): δ = -8.9 (s) for the starting material compound **1** and 9.4 (t, $^{2}J_{p\text{-}p}$ = 43.3 Hz) and 15.4 δ (ppm): (d, $^{2}J_{p\text{-}p}$ = 43.0 Hz) for **4*** in ***Scheme 2***.

Scheme 3. Attempted synthesis of **5**

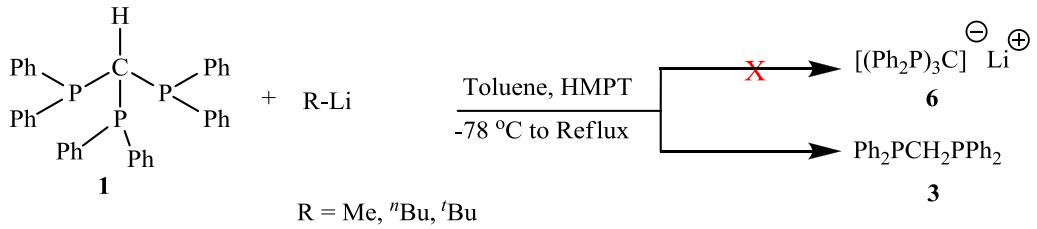


Antimony pentafluoride or tantalum pentafluoride (0.06 mL, 0.88 mmol) was added to a 25 mL flask with a magnetic stirrer in the dry box. The flask was cooled in an ice bath to keep the antimony pentafluoride just above its freezing point 5-7 ^{o}C with stirring under argon. Compound **1** (0.10 g, 0.18 mmol) was dissolved in deuterated benzene and was added to the cold antimony solution in a dropwise manner for 15 minutes using a syringe. Upon addition of **1** to the cold antimony solution while stirring under argon, the solution changed from colorless to a black/brown mixture containing a sticky solid. After solvent evaporation, NMR of the product with SbF_5 showed a $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, DMSO, 298 K, ppm): δ = -9.8 (s), for bis(diphenylphosphino)methane (compound **3**), at -22.9 (s), and 25.2 (s) for the other unknown compound, which was not characterized.

When TaF_5 was used in the reaction instead of SbF_5, the $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, DMSO, 298 K, ppm): δ = 46.7 (s), 36.7 (s), 29.2 (s), 25.4 (s) and 19.8 (s) for un identified product mixtures, and -9.8 (s) for a starting material.

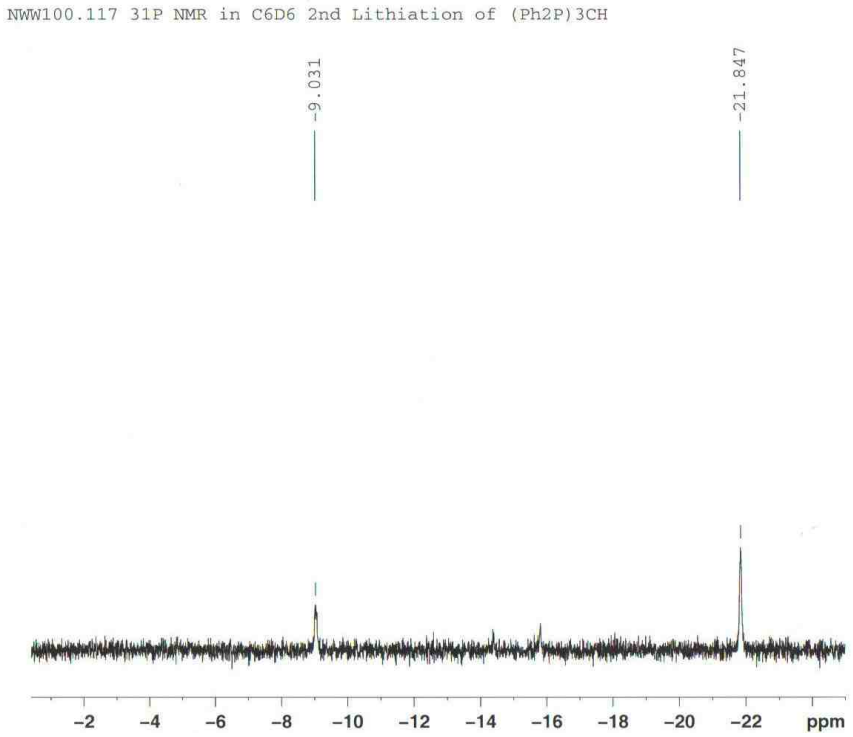
2.4.3. Synthesis of lithium salt using precursor 1

Scheme 4. Attempted synthesis of **6**



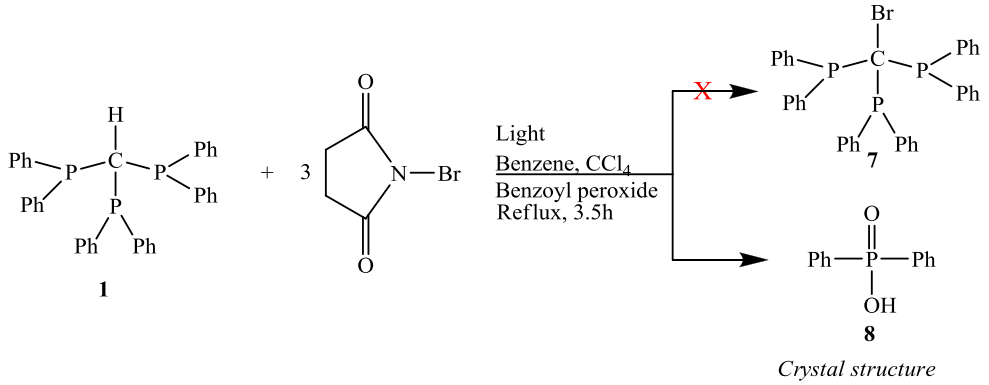
Compound **1** (0.20 g, 0.35 mmol) was dissolved in 7 mL of dry toluene and added to a 25 mL flask with a magnetic stir bar in the dry box and stirred for 5 minutes. To this mixture, 0.10 mL of hexamethylphosphorustriamide (HMPT) was added drop-wise by a syringe for 5 minutes. The mixture was placed in a cold bath at -78 ^{o}C under argon and stirred for 10 minutes. Thereafter, 1.70 M ^{t}BuLi (0.30 g, 0.50 mmol) in pentane was added to the cold mixture by syringe over 5 minutes. The mixture turned from colorless to yellow, and it was left to warm to room temperature for 30 minutes. $^{31}P\{^{1}H\}$ NMR analysis of the mixture revealed the presence of starting material. Thereafter the mixture was refluxed for 1h, and the solution remained yellow throughout the reflux period. The yellow solution was left to cool to room temperature while stirring overnight. The following day the solvent was evaporated under *vacuo* for 8h. $^{31}P\{^{1}H\}$ NMR of the dry solid revealed a peak at -21.8 (ppm) (s) which should be compound **3** and - 9.0 (ppm) (s), which is for the starting material. The ratio of the peak intensity was 2:1 (see **Figure 2.2**).

Figure 2.2. ^{31}P NMR for the Product of Lithiation of Precursor **1**



2.4.4. Synthesis of the brominated form of precursor 1

Scheme 5. Attempted synthesis of **7**



Crystal structure

NBS (0.12 g, 0.67 mmol) was dissolved in 4 mL of carbon tetrachloride in a 25 mL flask with a magnetic stirrer in a dry box. Compound **1** (0.12 g, 0.22 mmol) was dissolved in 2 mL of dry benzene followed by the addition of 0.02 g of

dibenzoylperoxide as a radical initiator. The flask containing the mixture of compound **1** and NBS was attached to a reflux condenser, then exposed to a flashlight and refluxed for 3.5h. After cooling to room temperature, the brown mixture was filtered through a celite pad in a fritted glass filter, which left behind a black residue. The filtrate was evaporated under *vacuo* for 6h. The crude brown solid was insoluble in most non-polar solvents except for CH_3CN and DMSO. The sample was impure based on NMR. ^{1}H NMR spectrum (250 MHz, DMSO, 298 K, ppm): δ = 2.57 (s) (s, succinimide) and 7.36-7.77 (m, Ar-H). $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, DMSO, 298 K, ppm): δ = 25 (s), and 39.4 (s) with a 3:1 peak intensity ratio. From recrystallization of crude product in CH_3CN, the first peak was shown to be diphenylphosphinic acid (compound **8**) by single crystal X-ray analysis (see **Figure 2.3** and a summary for the hydrogen bonding distances and bond angles in **Table 2.1**). The second peak 39.4 (ppm) (s) in the mixture remained in mother liquor of the recrystallization process and was not further characterized.

Figure 2.3. Molecular Structure of Ph_2POOH (**8**) and its Hydrogen Bonding

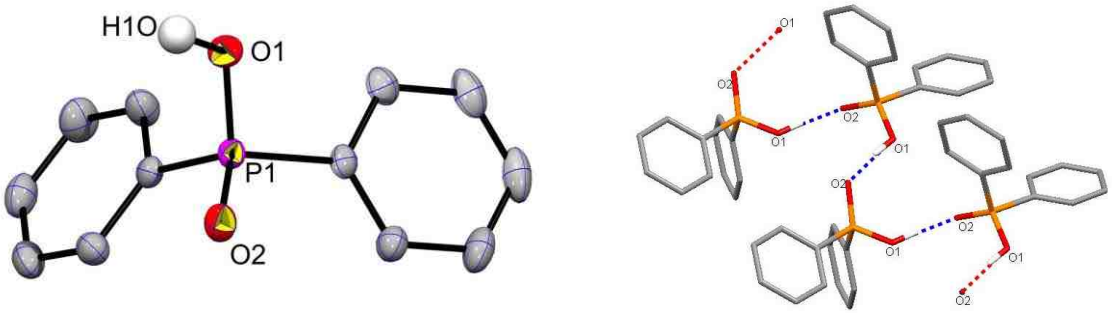
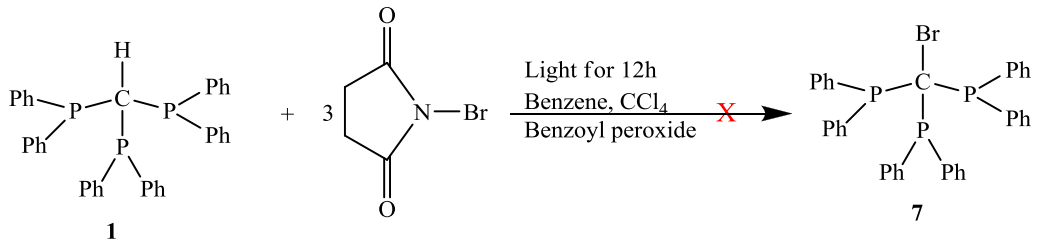


Table 2.1: Hydrogen bonds [Å] and angles [°] for **8**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...O(2)#1	0.88(3)	1.60(3)	2.4776(12)	173(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1/2

Scheme 6. Attempted synthesis of **7** without reflux



NBS (0.14 g, 0.78 mmol) was dissolved in 10 mL of carbon tetrachloride and added to a 25 mL flask with a magnetic stirrer in the dry box. Compound **1** (0.15 g, 0.26 mmol) was dissolved in 5 mL of dry benzene, followed by addition of 0.02 g of dibenzoyl peroxide as a radical initiator. The mixture while stirring under argon remained colorless, but slowly started changing in color from colorless to yellow upon exposure to a flashlight. After 12h of stirring, the color changed from faint yellow to brown/black with some black solids suspended on the sides of the flask. The brown/black mixture was filtered through a celite pad in a fritted glass filter, leaving behind a black precipitate on top of celite. A small amount of filtrate was collected. Both the black residue and the filtrate were dried under *vacuo* for 8h. The NMR spectrum of the black residue and the residue from the filtrate were found to have similar peaks. The $^{31}P\{^{1}H\}$ spectrum of the black celite residue (101.3 MHz, DMSO, 298 K, ppm): δ = 4.5 δ (d, J = 13 Hz), 32.5 (d, J = 41.5 Hz) and 33.4 (s). The ratio of the two doublet peaks was 3:1. The filtrate

$^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, DMSO, 298 K, ppm): δ = 25.0 (s), 29.0 (s), and 24.5 (d, J = 13 Hz). The singlet peaks showed an intensity ratio of 1:2. The first singlet showed the exact the same chemical shift as compound **8** derived from ***Scheme 5***.

2.4.5. Synthesis of tris(dimethylphosphino)methane precursor (compound 10)

$$(Me_2P)_2CH_2 + {}^{n}Bu\text{-}Li \xrightarrow[RT]{Pentane} \underset{\mathbf{9}}{[(Me_2P)_2\bar{C}H\,]\dot{Li}} \qquad \text{(ii)}$$

The synthesis of precursor **10** has been previously reported.[5] An aliquot (4.8 mL, 11.80 mmol) of 2.50 M ^{n}BuLi in a hexane solution was added to a 100 mL round bottom flask. 1 mL of dry pentane was added to the flask with a magnetic stirrer in an argon atmosphere. A solution of bis(dimethylphosphino)methane (1.8 mL, 11.80 mmol) was then added dropwise from syringe over a period of 10 minutes at room temperature, during which the solution changed from colorless to a milky white precipitate. The reaction mixture was kept stirring for 3h. Thereafter, the solvent evaporated under *vacuo* for 12h, yielding compound **9**. This procedure yielded 1.1 g, 68% yield, mp > 200 ^{o}C. The $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, THF-d_8, 298 K, ppm): δ = -45.3 (s).

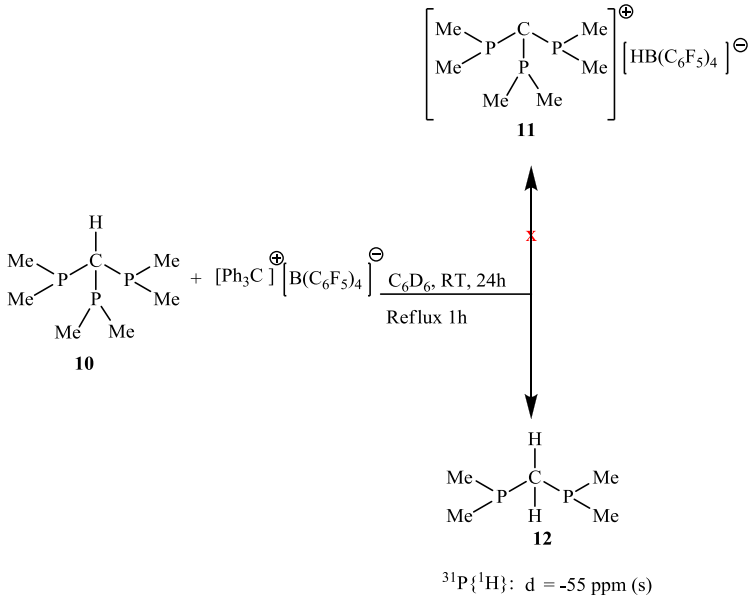
$$\underset{\mathbf{9}}{[(Me_2P)_2\bar{C}H\,]\dot{Li}} + Me_2PCl \xrightarrow[-78\ ^{o}C]{Ether} \underset{\mathbf{10}}{(Me_2P)_3CH} \qquad \text{(iii)}$$

To obtain compound **10**, compound **9** (1.48 g, 10.40 mmol) was dissolved in 30 mL of diethyl ether and placed in a 100 mL round bottom flask with a magnetic stirrer and cooled to -78 ^{o}C (acetone ice bath). While stirring under an argon atmosphere, dimethylchlorophosphine (1.00 g, 10.40 mmol) was added dropwise by syringe over a

period of 30 minutes. After 1h of stirring, the reaction was allowed to come to room temperature, and the solvent was evaporated. The dry residue was dissolved in 59 mL of pentane and filtered with fine fritted glass filter. The filtrate was evaporated under *vacuo* for 24h, and the faint yellow crystal residue was slowly sublimated in an evacuated apparatus by gradually reducing the temperature, yielding compound **10** (1.00 g, 49% yield). The colorless crystals had an mp = 45-47 ^{o}C. The ^{1}H NMR spectrum (250 MHz, C_6D_6, 298 K, ppm): δ = 0.59 (q, $^{2}J_{(PCH)}$ = 1.50 Hz) and 1.14 ("t", $J_{(PCH3)}$ = 2.00 Hz). The $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, C_6D_6, 298 K, ppm): δ = -48.0 (s) with H_3PO_4 as a reference. The $^{13}C\{^{1}H\}$ NMR spectrum (62.9 MHz, C_6D_6, 298 K, ppm): δ = 13.2 (sep. J = 47.25 Hz, PCH_3) and 33.3 (q, $^{1}J_{P-C}$ = 41.20 Hz). The $^{13}C\{^{1}H\}$ NMR spectrum from the literature δ = 13.2 (''sep'' ($AA_2'X$) N = 45.9 Hz (distance between outer lines), PCH_3) and 33.3 (q, $^{1}J_{P-C}$ = 39.0 Hz).The literature spectrum did not include the spectrometer frequency used.

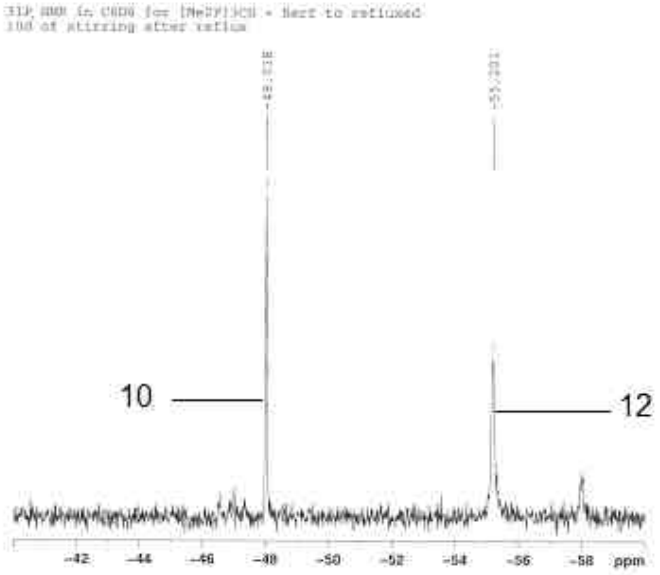
2.4.6. Synthesis of precursor 11

Scheme 7. Attempted synthesis of **11**



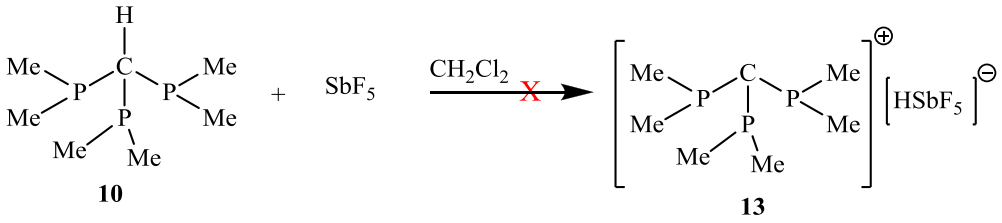
Compound **10** (0.01 g, 0.03 mmol) was dissolved in 4 mL of dry C_6D_6 and was added to a 50 mL flask with a magnetic stirrer in the dry box. Trityl tetrakis pentafluorophenyl borate (0.03 g, 0.03 mmol) was added to compound **10,** causing the mixture to turn from colorless to orange. After stirring overnight in the dry box, the mixture was analyzed by $^{31}P\{^{1}H\}$ NMR and shown to be unreacted. The mixture was then refluxed for 1h and the $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, C_6D_6, 298 K, ppm): δ = -48.0 (s) and -55.0 (s) with a 5:1 ratio of intensities. These peaks corresponded to compound **10** and $PMe_2CH_2PMe_2$ (compound **12**) respectively. This reaction was allowed to continue 10 days while monitored by NMR every 12 h. The $^{31}P\{^{1}H\}$ NMR spectrum on the tenth day revealed two peaks: -48.0 (ppm) (s) and -55.2 (ppm) (s) with a ratio of peak intensities of 2:1 (**Figure 2.4**).

Figure 2.4. ^{31}P NMR for the Product of $(PMe_2)_3CH$ (**10**) Reacted With Lewis Acid



2.4.7. Synthesis of precursor 13

Scheme 8. Attempted Synthesis of **13**



SbF_5 (0.09 mL, 1.28 mmol) was added to a 25 mL flask with a magnetic stirrer in the dry box. While stirring under argon, the mixture was cooled in an ice bath to keep the SbF_5 just above its freezing point of 5-7 ^oC. Compound **10** (0.05 g, 0.26 mmol) was dissolved in 2 mL of dichloromethane and added dropwise to the SbF_5 by syringe. The reaction yielded a colorless to a white/brown sticky solid, and was allowed to proceed

under argon overnight. The following day, the solvent was evaporated under *vacuo* for 6h. The $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, DMSO, 298 K, ppm): δ = 74.2 (s), 64.5 (s), and 42.4 (s). The 42.4 (s) peak was three times more intense than the other peaks.

2.4.8. Synthesis of lithium tris(dimethylphosphino)methanide (compound 14)

$$\underset{\mathbf{10}}{(Me_2P)_3CH} + {}^{t}Bu\text{-}Li \xrightarrow[RT]{Pentane} \underset{\mathbf{14}}{[(Me_2P)_3\bar{C}]\overset{+}{Li}} \qquad \text{(iv)}$$

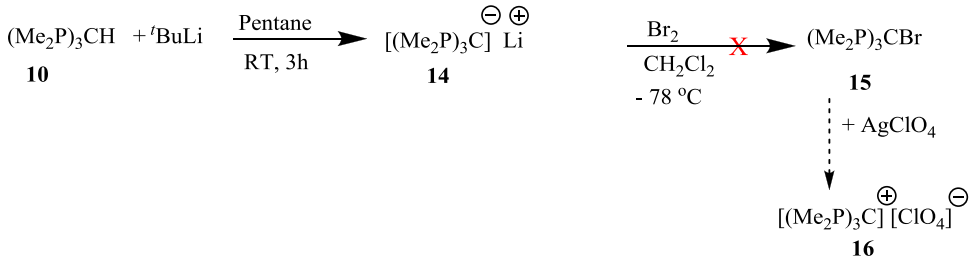
The synthesis of precursor **14** has been previously reported.[6] Compound **10** (0.20 g, 1.02 mmol) was added to a 50 mL flask with a magnetic stirrer in the dry box. Pentane (5 mL) was added while stirring to dissolve the solid. ^{t}BuLi (1 mL, 2.04 mmol) was added by syringe over a period of 20 minutes. The colorless solution became turbid as the reaction proceeded, forming a white precipitate. The mixture was left stirring under argon for 3h. The precipitate was filtered and washed with dry diethyl ether. The product, compound **14,** was dried under *vacuo* for 7h. This procedure yielded a white solid 0.14 g, 67% mp > 200 ^{o}C. The $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, THF-d_8, 298 K, ppm): δ = -26.6 (s) with H_3PO_4 as a reference. The elemental analysis of compound **14** is shown below (in **Table 2.2**).

Table 2.2: Elemental analysis for $(Me_2P)_3C^{-}Li^{+}$ (compound **14**)

Atom	C	H
Calculated	41.60	8.98
Found	41.15	8.44

2.4.9. Synthesis of compound 16

Scheme 9. Attempted synthesis of **16**

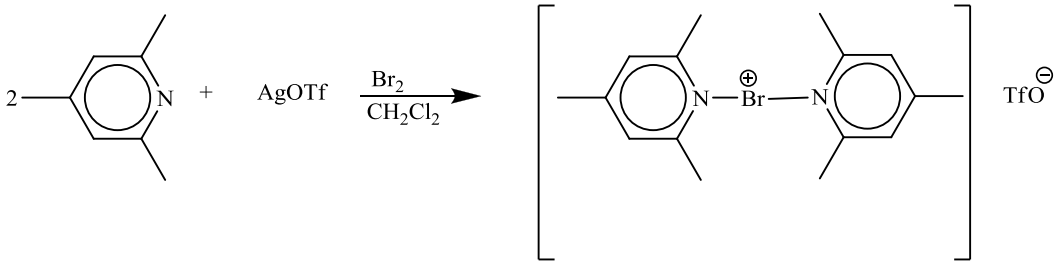


Compound **14** (0.18 g, 0.89 mmol) was added to a 50 mL flask with a magnetic stirrer in the dry box and was dissolved in 8 mL of THF. The flask was transferred to a cold bath at -110 to -120 ^{o}C. After stirring the mixture under argon for 30 minutes, a bromine (0.05 mL, 0.89 mmol) dissolved in 3 mL of THF was slowly added by syringe and the reaction mixture was left stirring for 5h while warming to room temperature.

The solution was filtered and the pink filtrate was collected and dried under *vacuo* for 12h. The pink solid was dissolved in DMSO. The $^{1}P\{^{1}H\}$ NMR spectrum (101.3 MHz, DMSO, 298 K, ppm): δ = 60.4 (s) 41.7, 38.1 (s), 33.5 (s), 32.5 (s) and -48.0 (s) with H_3PO_4 at the reference. The -48.0 (s) is the starting material, compound **10,** and has 50% greater intensity than the other peaks.

2.4.10. Synthesis of bis(sym-collidine)bromonium triflate (compound 17)

Scheme 10. Attemped synthesis of compound **17**



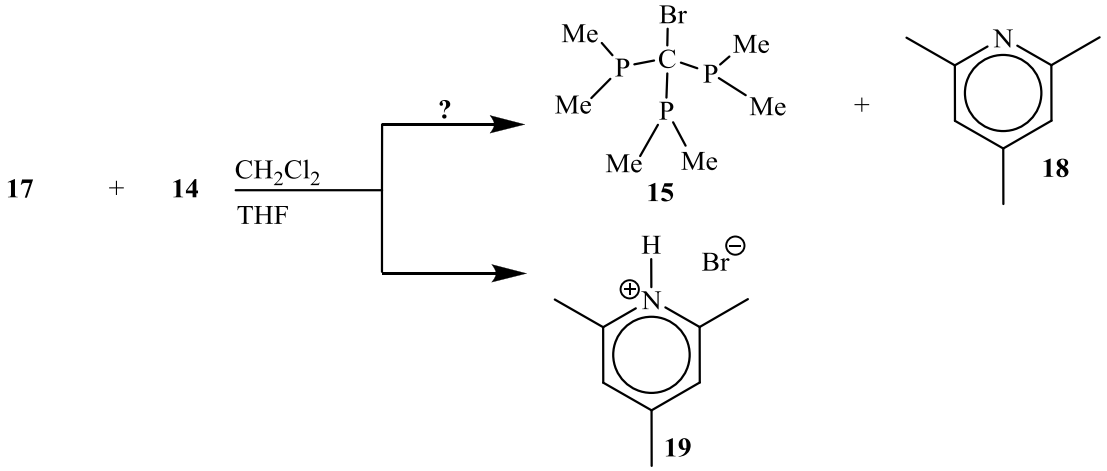
17

The synthesis of precursor **17** has been previously reported.[7] Silver triflate (1.41 g, 5.48 mmol) was dissolved in 20 mL of dry dichloromethane and added to a 100 mL flask with a magnetic stirrer in the dry box. 2,4,6-collidine (1.45 mL, 10.97 mmol) was added to the flask, and a clear solution is formed. Bromine (0.88 g, 5.47 mmol) in 5 mL of dry dichloromethane was added to this mixture and stirred under argon. After 10 minutes, a yellow precipitate formed and was removed by filtration through a celite pad. The filtrate was partially evaporated by an argon stream and 2 mL of dry hexane was added with stirring. The reaction formed white crystals, which were filtered and washed with dry hexane. The white crystalline solid was dried under *vacuo* for 2h. The dry solid was recrystallized from a dichloromethane/hexane solvent system and the flask was placed in the freezer overnight. The following day, the solvent was cannulated and the crystals dried for 3h. This procedure yielded 1.58 g, of a white crystalline product 61%, mp = 108-110 ^{o}C. ^{1}H NMR spectrum (250 MHz, CD_2Cl_2, 298 K, ppm): δ = 2.43

(s, 6H, CH_3), 2.82 (s), 2.82 (s, 6H, $2CH_3$), and 7.21 (s, 2H, Ar-H). The $^{13}C\{^1H\}$ NMR spectrum (62.9 MHz, CD_2Cl_2, 298 K, ppm): δ = 21.7 (s), 25.7 (s), 126.5 (s), 155.0 (s), and 156.8 (s).

2.4.11. Synthesis of halogenated compound 15

Scheme 11. Attempted synthesis of **15**



Compound **14** (0.02 g, 0.11 mmol) was dissolved in 5 mL of dry THF and placed to a 50 mL flask with a magnetic stirrer in the dry box. Compound **17** (0.02 g, 0.11 mmol) was dissolved in 5mL of dry dichloromethane and added dropwise to the reaction by syringe at -78 ^oC over a period of 10 minutes. The reaction mixture was left to stir under a cold bath for 5h, and then allowed to warm to room temperature for 30 minutes. The mixture was filtered with sintered fine filter by gravity inside the dry box. Both filtrate and gelatinous precipitates were collected. The filtrate as well as the gelatinous precipitate was evaporated under *vacuo* for four days to ensure that the 2,4,6-collidine (compound **18**) was removed due to its very high boiling point (bp = 172 ^oC). The ^1H

NMR of crude dry solid obtained after vacuum evaporation revealed peaks, which include compound **17** as well as an unknown compound. $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, DMSO, 298 K, ppm): δ = 39.0 (s) and 21.6 (s) with a 7:1 peak intensity ratio with H_3PO_4 as a reference. Recrystallization of the crude product was carried out in a mixture of solvent systems: THF/CH_3CN, CH_3CN/Et_2O, CH_3CN/CH_2Cl_2 and THF/CH_3CN/CH_2Cl_2 and petroleum ether. Only the latter solvent system combination resulted in crystals, but only after more than five weeks. Single crystal X-ray analysis confirmed the compound to be 2,4,6-trimethylpyridinium bromide (**19**) in ***Scheme 11***, which was previously reported. The crystal structure (see **Figure 2.5** below) is shown with both disordered and non-disorded appearances. A summary of selected bond lengths is shown in **Table 2.3**, and the hydrogen bonds are described in **Table 2.4**.

Figure 2.5. Molecular Structure of 2,4,6-trimethylpyridinium bromide Showing the Numbering Scheme Structure **19**

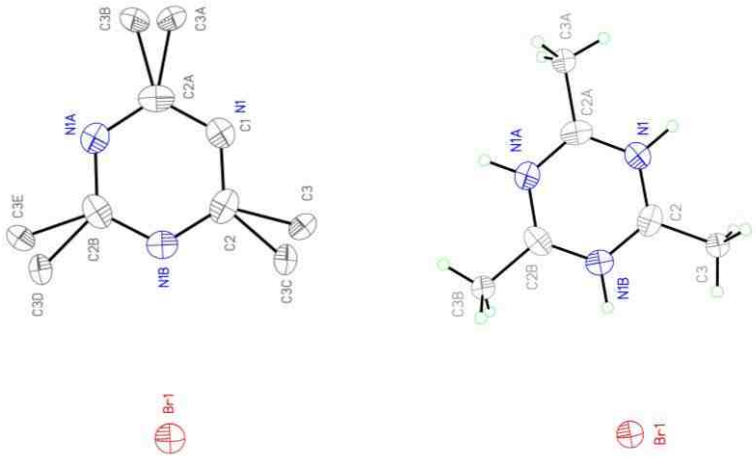


Table 2.3: Bond lengths [Å] and angles [°] for **19**

N(1)-C(2)	1.368(4)
C(2)-C(3)	1.519(11)
C(3)-H(3A)	0.9605
C(3)-H(3B)	0.9598
C(3)-H(3C)	0.9598
C(2)-C(3)-H(3C)	111.7
H(3A)-C(3)-H(3C)	107.1
H(3B)-C(3)-H(3C)	107.7

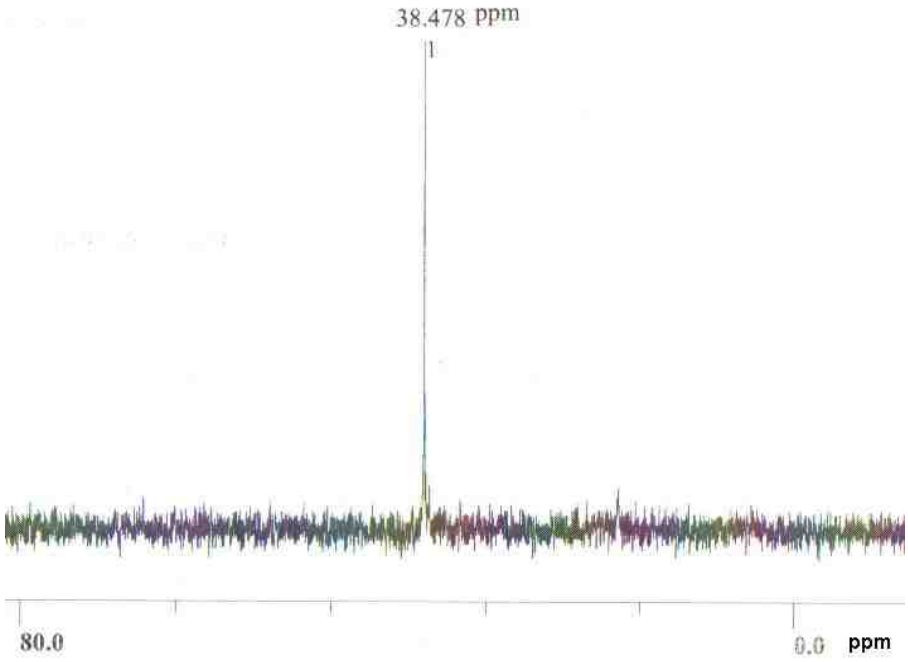
Table 2.4: Hydrogen bonds [Å] and angle [°] for **19**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1)...Br(1)#4	0.95	2.67	3.618(7)	180.0

Symmetry transformations used to generate equivalent atoms:
#1 -y,x-y,z #2 -x+y,-x,z #3 -x+y,y,z #4 x-1,y,z

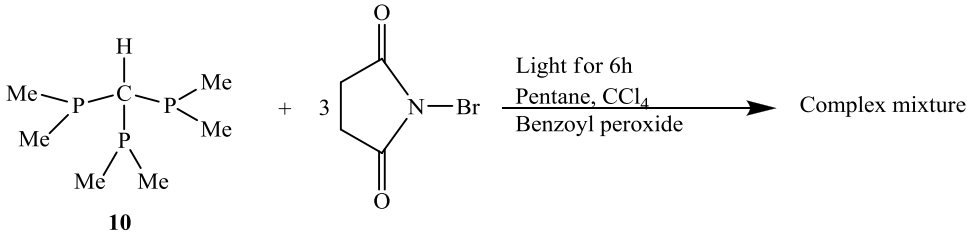
The mother liquor from which the crystals of compound **19** were derived, contained a number of impurities, including the starting material, compound **17** and compound **19**. A second recrystallization did not produce a pure product. The filtrate was left in the freezer in a vial to form crystals for about two months. This mixture in the vial resulted in a white precipitate that was isolated by filtration over celite. The filtrate was concentrated and allowed to evaporate slowly in the dry box. White crystalline needles formed producing 48 mg of product (mp = 180-182 ^{o}C). The $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, CD_3CN, 298 K, ppm): δ = 38.5 (s) with H_3PO_4 as a reference (see **Figure 2.6**). Most probably this is compound **15** which should have single peak in $^{31}P\{^{1}H\}$ NMR.

Figure 2.6. ^{31}P NMR for Brominated Product Derived from Lithium Salt **14**



2.4.12. Synthesis of brominated precursor 10

Scheme 12. Attempted synthesis of tris(dimethylphosphino)bromomethane



Compound **10** (0.16 g, 0.82 mmol) was dissolved in 15 mL of pentane and added to a 25 mL flask with a magnetic stirrer in the dry box. To this mixture, was added NBS (0.44 g, 2.46 mmol) followed by the addition of 12.00 mL of carbon tetrachloride plus 0.02 g of dibenzoyl peroxide as a radical initiator. During stirring the mixture under

argon it remained colorless, but upon exposing a flashlight to it, slowly the mixture started changing from colorless to a yellow solid (see a general reaction in ***Scheme 12***). Yellow solid was evaporated under *vacuo* for 8h. The final solid which is insoluble in non polar solvents, but soluble in DMSO was collected and its $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, DMSO, 298 K, ppm): δ = 45.4 (s), 41.0 (s) and 38.3 (s) in the ratio 1:1.2:1 peak intensity ratio. The chemical shift of the last NMR peak is similar to that obtained when compound **14** is brominated with bromine solution (***Scheme 9***) or with bromonium triflate (***Scheme 11***), which are 38.1, (ppm) (s) and 38.5 (ppm) (s) respectively.

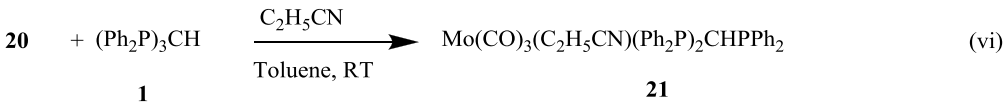
2.4.13. Synthesis of tricarbonyltris(propionitrile)molybdenum(0) (compound 20)

$$Mo(CO)_6 + 3\ C_2H_5CN \longrightarrow \underset{\mathbf{20}}{Mo(CO)_3(C_2H_5CN)_3} + 3\ CO \qquad (v)$$

The synthesis of compound **20** has been previously reported.[8] A mixture of $Mo(CO)_6$ (6.00 g, 22.7 mmol) and propionitrile (60 mL) was added to a 250 mL flask equipped with a magnetic stirrer and a reflux condenser with an exhaust port for removal of CO. The reaction mixture was refluxed for 24h. After 14h of refluxing, the color of this mixture changed from colorless to brown/black. Upon completion of the refluxing, the reaction mixture was left to cool to room temperature for 45 minutes and reduced to half the volume under *vacuo*. Dry diethyl ether was added slowly using a cannula, resulting in a purple-colored precipitate, which was placed in the freezer overnight. The following day, filtrate was cannulated and the precipitate was dried under *vacuo* for 6h. This procedure yielded 5.9 g of crystalline product with a 75% yield (mp = 138-140 ^{o}C).

While the reaction was in progress, an aliquot was diluted with propionitrile and analyzed by IR spectroscopy. The spectrum showed two υCO bands at 1917.7 (s) cm^{-1} and 1795 (s) cm^{-1}, respectively. The expected band due to hexacarbonylmolybdenum was not seen at υCO = 2000 cm^{-1}, suggesting that the reaction had gone to completion. The IR spectrum of the final product, prepared as a Nujol mull for dry solid $Mo(CO)_3(C_2H_5CN)_3$ showed two υCO bands at 1909 (s) cm^{-1} and 1778 (s) cm^{-1}

2.4.14. Synthesis of $Mo(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$ (compound 21)



Compound **20** (0.06 g, 17 mmol), ($Mo(CO)_3(C_2H_5CN)_3$), was dissolved in 4 mL of propionitrile and was added to a 25 mL flask with a magnetic stirrer in the dry box. To this mixture, compound **1** (0.10 g, 17 mmol) was dissolved in 4 mL of toluene and added to the flask via a syringe. The flask was immersed to an ultrasonic bath for 5 minutes to speed up the reaction. The mixture changed in color from dark brown to greenish yellow. This mixture was allowed to proceed at 20 ^oC, and then left to stir at room temperature overnight. The reaction produced a green precipitate, which was collected by filtration, dissolved in 15 mL of diethyl ether, and stirred for 2h to complete the precipitation. The precipitates was separated in a fritted glass filter and washed with 20 mL of diethyl ether, which was evaporated under *vacuo* for 6h. This procedure yielded 0.08 g of a green solid product 58% yield; mp = 148-150 ^oC). The IR spectroscopy of a Nujol mull of compound **21** showed two υCO bands at 1930 (s) cm^{-1} and 1785 (s) cm^{-1}.

The ^{1}H NMR spectrum (250 MHz, DMSO, 298 K, ppm): δ = 0.95 (t, $^{3}J_{H-H}$ = 7.5 Hz, CH_3), 1.10-1.18 (q, $^{3}J_{H-H}$ = 7.5 Hz, CH_2), 4.75 (s) (s, 1H, CH), 6.89 - 7.78 (m, 30H, Ar-H). The $^{31}P\{^{1}H\}$NMR spectrum (101.3 MHz, DMSO, 298 K, ppm): δ = 22.7 (d, $^{2}J_{p-p}$ = 25 Hz) and -24.8 (t, $^{2}J_{p-p}$ = 25 Hz). The $^{13}C\{^{1}H\}$ NMR spectrum (62.9 MHz, CD_2Cl_2, 298 K, ppm): δ = 58.1 δ (s), 58.6 (s), 59.3 (s), 124.9 (s), 129.5 (s) 154.3 (s), 175.2 (s). Recrystallization of the crude product in dichloromethane after slow evaporation in the freezer resulted in crystals suitable for crystallography, which revealed novel structure in (see **Figure 2.7** and a summary of selected bond lengths shown in **Table 2.6**).

Figure 2.7. Molecular Structure of $Mo(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$ Showing the Numbering Scheme Structure **21**. Hydrogen Atoms are Omitted for Clarity

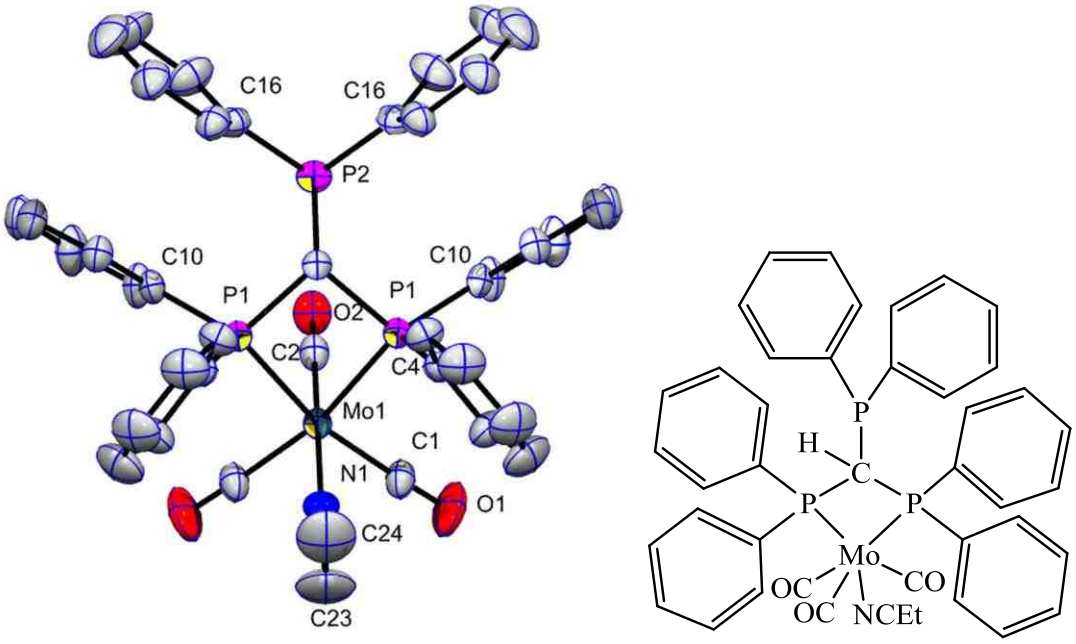


Table 2.5: Elemental analysis for $Mo(CO)_3(C_2H_5CN)$ $(Ph_2P)_2CHPPh_2$

Atom	C	H	N
Calculated	64.27	4.52	1.74
Found	64.25	4.37	1.39

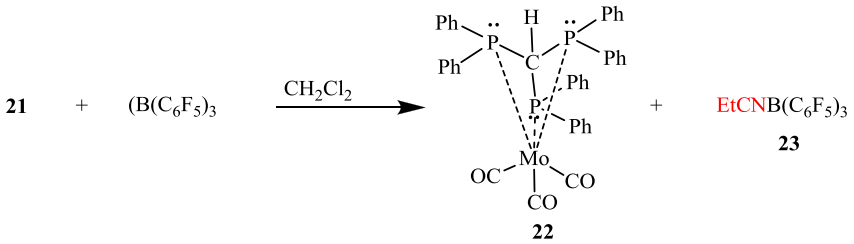
Table 2.6: Bond lengths [Å] and angles [°] for **21**

Mo(1)-C(2)	1.946(3)
Mo(1)-C(1)	1.977(2)
Mo(1)-N(1)	2.201(3)
Mo(1)-P(1)	2.4962(6)
P(1)-C(10)	1.827(2)
P(1)-C(4)	1.830(2)
P(2)-C(16)	1.842(2)
P(2)-C(3)	1.864(3)
N(1)-C(22)	1.128(4)
O(1)-C(1)	1.151(3)
O(2)-C(2)	1.170(4)
C(4)-C(5)	1.386(3)
C(5)-C(6)	1.387(3)
C(5)-H(5)	0.9500
C(7)-C(8)	1.374(4)
C(8)-C(9)	1.380(4)
C(10)-C(11)	1.393(3)
C(10)-C(15)	1.390(3)
C(16)-C(21)	1.386(3)
C(16)-C(17)	1.394(3)
C(18)-C(19)	1.364(4)
C(19)-C(20)	1.378(5)
C(20)-C(21)	1.392(4)
C(2)-Mo(1)-C(1)	87.46(10)
C(2)-Mo(1)-N(1)	178.57(11)
C(1)-Mo(1)-N(1)	91.57(9)
C(2)-Mo(1)-P(1)	92.68(8)

C(1)-Mo(1)-P(1)	99.47(7)
N(1)-Mo(1)-P(1)	88.51(6)
C(10)-P(1)-C(4)	100.16(10)
C(10)-P(1)-Mo(1)	122.76(7)
C(4)-P(1)-C(3)	105.70(11)
C(3)-P(1)-Mo(1)	96.77(7)
C(16)-P(2)-C(3)	101.92(9)
O(1)-C(1)-Mo(1)	177.6(2)
O(2)-C(2)-Mo(1)	176.8(3)
C(22)-N(1)-Mo(1)	174.5(3)
P(2)-C(3)-P(1)	113.04(10)
P(1)#1-C(3)-P(1)	94.34(12)
P(2)-C(3)-H(3)	111.8
C(7)-C(6)-C(5)	120.9(3)
C(11)-C(10)-C(15)	118.4(2)
C(12)-C(11)-C(10)	120.9(2)
C(14)-C(13)-C(12)	119.8(2)
C(13)-C(14)-C(15)	120.5(2)
C(14)-C(15)-C(10)	120.4(2)
C(21)-C(16)-C(17)	117.8(2)
C(18)-C(17)-C(16)	121.2(2)

2.4.15. Synthesis of compounds 22 and 23

Scheme 13. Attempted synthesis of **22** and **23**



Compound **21** (0.01 g, 0.01 mmol) was dissolved in 2 mL of dichloromethane and

was added to a 25 mL flask with a magnetic stirrer in the dry box. $B(C_6F_5)_3$ (0.01 g, 0.01 mmol) was dissolved in 2 mL of dichloromethane and added to the reaction via a syringe. The reaction was allowed to proceed for 2h; the color of the mixture changed from light brown to deep brown. The reaction was left to stir overnight, and the following day the solvent was slowly evaporated off in the glove box for 12h, which was dissolved in CD_2Cl_2. The ^1H NMR spectrum (250 MHz, CD_2Cl_2, 298 K, ppm): δ = 7.41 - 7.62 (m, 30H, Ar-H). The $^{31}P\{^1H\}$ NMR spectrum (101.3 MHz, CD_2Cl_2, 298 K, ppm): δ = 11 (s) (see **Figure 2.9**). The sample was left in the NMR tube and placed in the freezer for several weeks to obtain crystals. The yield of the crystals was not enough to carry out further analysis. It is likely that the crystals **23** formed at low temperature were in a mixture of liquid compound **22** (***Scheme 13***). Single-crystal X-ray analysis revealed a novel structure that is referred to as compound **23** (see **Figure 2.8**) with bond lengths described in **Table 2.7** that did not correspond to the structure of the expected product predicted from the NMR spectra.

Figure 2.8. Molecular Structure of $EtCNB(C_6F_5)_3$ Showing the Numbering Scheme For Structure **23**. Hydrogen Atoms are Omitted for Clarity

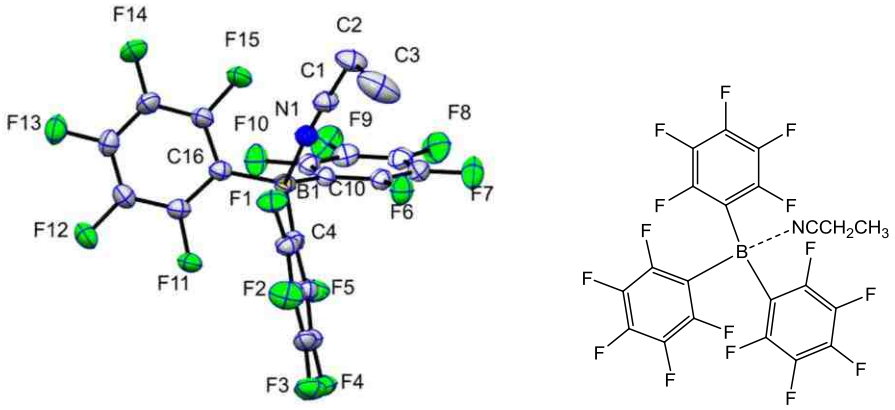


Table 2.7: Bond lengths [Å] and angles [°] for **23**

N(1)-C(1)	1.136(2)
N(1)-B(1)	1.596(2)
F(1)-C(5)	1.3497(17)
B(1)-C(16)	1.630(2)
B(1)-C(4)	1.631(2)
B(1)-C(10)	1.636(2)
C(1)-C(2)	1.442(2)
C(2)-C(3)	1.510(3)
C(2)-H(2B)	1.387(2)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(4)-C(5)	1.384(2)
C(4)-C(9)	1.387(2)
C(16)-C(21)	1.386(2)
C(16)-C(17)	1.387(2)
C(1)-N(1)-B(1)	173.90(16)
N(1)-B(1)-C(16)	105.72(12)
N(1)-B(1)-C(4)	105.99(12)
C(16)-B(1)-C(4)	112.15(12)
N(1)-B(1)-C(10)	101.56(12)
C(16)-B(1)-C(10)	116.26(12)
C(4)-B(1)-C(10)	113.67(12)
N(1)-C(1)-C(2)	176.75(18)
C(1)-C(2)-C(3)	109.85(17)
C(1)-C(2)-H(2A)	109.7
C(3)-C(2)-H(2A)	109.7
C(1)-C(2)-H(2B)	109.7
C(3)-C(2)-H(2B)	109.7
H(2A)-C(2)-H(2B)	108.2
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5

H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(5)-C(4)-C(9)	114.23(13)
C(15)-C(10)-C(11)	113.86(14)
C(15)-C(10)-B(1)	126.42(14)
C(11)-C(10)-B(1)	119.61(13)
F(6)-C(11)-C(10)	119.05(14)
C(12)-C(11)-C(10)	124.44(15)
C(21)-C(16)-C(17)	113.59(14)
C(21)-C(16)-B(1)	121.27(13)
C(17)-C(16)-B(1)	125.12(13)
F(11)-C(17)-C(16)	121.06(14)
C(18)-C(17)-C(16)	123.67(14)

Figure 2.9. A Comparison of $^{31}P\{^{1}H\}$ NMR for Uncoordinated Tris(diphenylphosphino)methane (**1**) and Coordinated Structure **22**

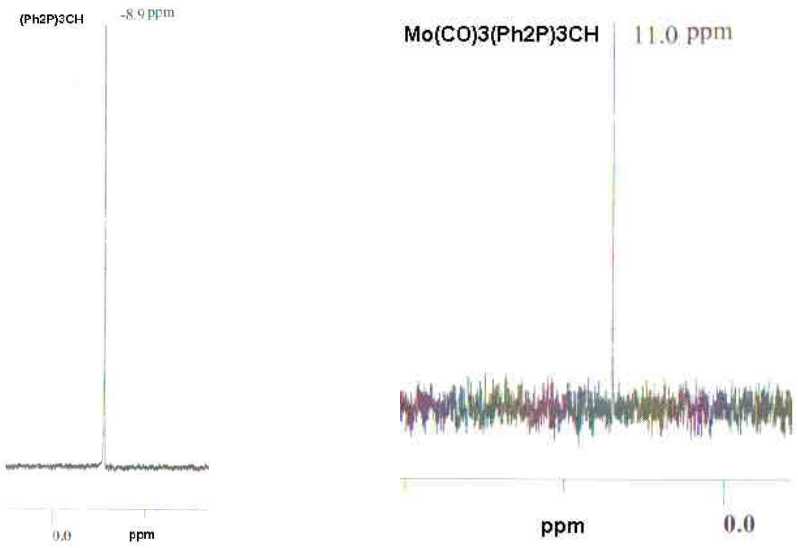


Figure 2.9 shows the comparison of δ for uncoordinated precursor **1** and when its two phosphorus atoms are coordinated to group 6B metal carbonyl in structure **21**. The uncoordinated to coordinated has shown the shift from -8.9 (ppm) (s) to 11.0 (ppm) (s)

2.4.16. Synthesis of tricarbonyltris(propionitrile)tungsten(0) (compound 24)

$$W(CO)_6 + 3\ C_2H_5CN \longrightarrow W(CO)_3(C_2H_5CN)_3 + 3\ CO \qquad \text{(vii)}$$

24

The synthesis of precursor **24** has been previously reported.[8] $W(CO)_6$ (6.00 g, 23.0 mmol) was dissolved in 86 mL of propionitrile and added to a 250 mL flask equipped with a magnetic stirrer and a reflux condenser with an exhaust port for removal of CO. The reaction mixture was gently refluxed causing the mixture to change from colorless to yellow, and then to dark brown-red. After 4 days, IR spectroscopy of an aliquot (diluted with propionitrile by 10:1) revealed multiple bands corresponding to the intermediate with the structure $W(CO)_4(C_2H_5CN)_2$ {υCO = 2021 (s) cm^{-1}, 1898 (br) cm^{-1}, and 1840 cm^{-1})}; thus, the reaction was allowed to proceed for another three days. The IR spectrum of the product was consistent with the reaction going to completion to form the expected product, $W(CO)_3(C_2H_5CN)_3$, with two υ(CO) bands at 1910 (s) cm^{-1}, and 1793 (s) cm^{-1}. The solution was cooled to 45-55 ^oC and the solvent volume was reduced to half under *vacuo*. This resulted in a small number of fine yellow crystal needles. 80 mL of diethyl ether was added to complete the crystallization in the freezer overnight. The following day, the mixture was filtered in the dry box, and the light yellow crystalline solid was washed three times with 20 mL of diethyl ether and dried for 20 minutes. This

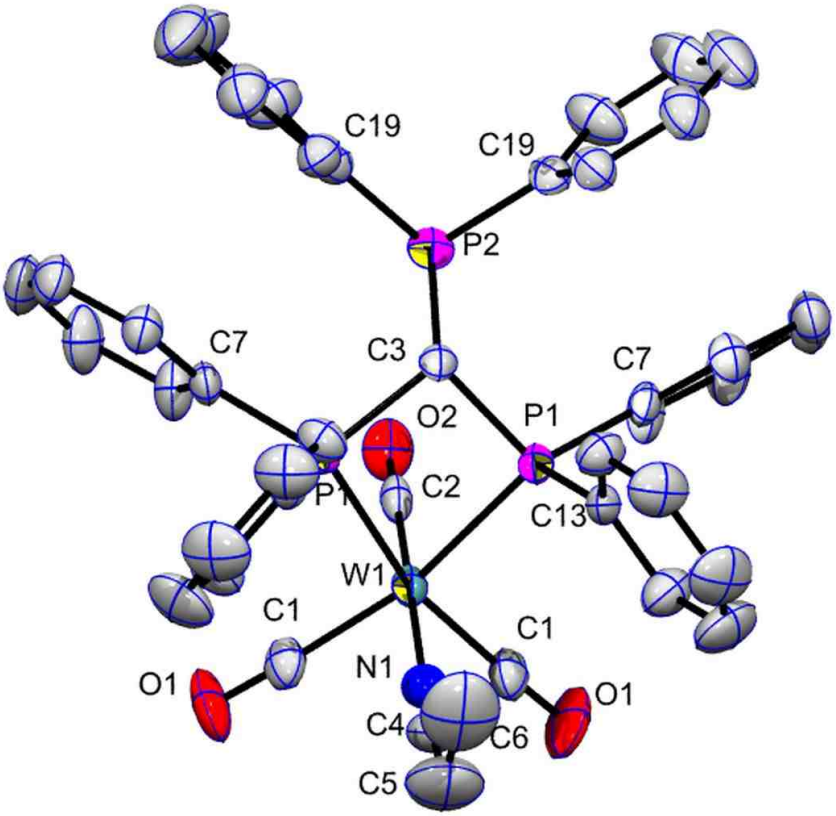
yielded 7.00 g, of product (71% yield, mp = 128-130 ^{o}C). The IR spectrum, as a Nujol mull for $W(CO)_3(C_2H_5CN)_3$ product showed two υCO bands: 1890 (s) cm^{-1} and 1770 (br) cm^{-1}, indicating that compound **24** had been obtained.

2.4.17. Synthesis of $W(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$ (compound 25)

Compound **24** (0.08 g, 0.18 mmol) is dissolved in 3 mL of dichloromethane and was added to a 25 mL flask with a magnetic stirrer in the dry box. To this mixture, compound **1** (0.10 g, 0.18 mmol) was dissolved in 4 mL of toluene and added via syringe. The flask was immersed in an ultrasonic bath for 5 minutes to increase the reaction rate. The mixture changed from colorless to brown, and was left stirring at 20 ^{o}C for 1h; the reaction was then stirred at room temperature overnight. The following day, the mixture was added 15 mL of diethyl ether and stirred for 1h. The precipitate that formed was separated by filtration and washed with 10 mL of diethyl ether. The final precipitate compound **25** was dried under *vacuo* for 8h. This procedure yielded 0.12 g, of a yellowish-brown solid product (75% yield, mp = 147-149 ^{o}C. An IR spectrum as a Nujol mull, for **25** showed two υCO bands: 1924 (s) cm^{-1} and 1781 (s) cm^{-1}. The ^{1}HNMR spectrum (250 MHz, CD_3COCD_3, 298 K, ppm): δ = 1.30 δ (ppm) (t, $^{3}J_{H-H}$ = 7.8 Hz, CH_3), 2.42-2.50 (q, $^{3}J_{H-H}$ = 7.8 Hz, CH_2), 5.60 (s, 1H, CH), 7.00-7.80 (m, 30H, Ar-H). The $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, CD_3COCD_3, 298 K, ppm): δ = 18.7 (d, $^{2}J_{p-p}$ = 30 Hz), and -21.9 (t, $^{2}J_{p-p}$ = 30 Hz). Recrystallization of the crude product in

dichloromethane resulted in crystals. Single crystal X-ray analysis revealed novel structure (see **Figure 2.10** and a summary of selected bond lengths in **Table 2.9**).

Figure 2.10. Molecular Structure of $W(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$ Showing the Numbering Scheme Structure **25**. Hydrogen Atoms are Omitted for Clarity



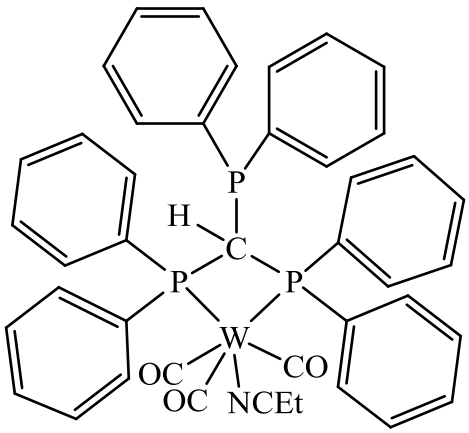


Table 2.8: Elemental analysis for $W(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$

Atom	C	H	N
Calculated	57.73	4.39	1.57
Found	56.22	4.11	1.20

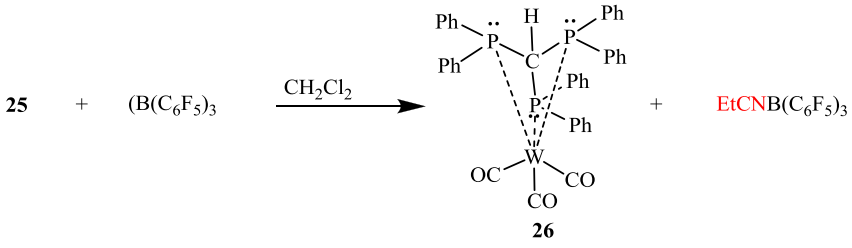
Table 2.9: Bond lengths [Å] and angles [°] for **25**

W(1)-C(2)	1.952(7)
W(1)-C(1)	1.971(5)
W(1)-N(1)	2.179(6)
W(1)-P(1)	2.4866(10)
P(1)-C(13)	1.824(4)
P(1)-C(7)	1.832(4)
P(1)-C(3)	1.880(4)
P(2)-C(19)	1.848(4)
P(2)-C(3)	1.863(6)
N(1)-C(4)	1.121(8)
O(1)-C(1)	1.153(5)
O(2)-C(2)	1.173(7)
C(3)-H(3)	0.9800
C(4)-C(5)	1.464(10)
C(13)-C(18)	1.381(5)
C(13)-C(14)	1.388(6)
C(19)-C(20)	1.386(6)
C(19)-C(24)	1.388(6)
C(2)-W(1)-C(1)	88.17(18)
C(2)-W(1)-N(1)	178.8(2)
C(1)-W(1)-N(1)	91.04(17)
C(1)-W(1)-P(1)	99.07(13)
P(1)#1-W(1)-P(1)	67.23(5)
C(13)-P(1)-C(7)	100.35(19)
C(13)-P(1)-C(3)	106.0(2)
C(7)-P(1)-C(3)	111.4(2)
C(13)-P(1)-W(1)	118.94(14)
C(7)-P(1)-W(1)	122.51(13)

C(3)-P(1)-W(1)	96.88(13)
C(19)-P(2)-C(3)	101.90(18)
C(4)-N(1)-W(1)	175.6(6)
O(1)-C(1)-W(1)	177.4(5)
O(2)-C(2)-W(1)	177.8(5)
P(2)-C(3)-P(1)	113.3(2)
P(1)-C(3)-P(1)#1	94.2(3)
P(2)-C(3)-H(3)	111.6
P(1)-C(3)-H(3)	111.6
N(1)-C(4)-C(5)	175.1(8)
C(6)-C(5)-C(4)	113.8(7)
C(4)-C(5)-H(5A)	108.8
C(4)-C(5)-H(5B)	108.8
C(18)-C(13)-C(14)	117.5(4)
C(18)-C(13)-P(1)	126.2(3)
C(14)-C(13)-P(1)	116.3(3)
C(13)-C(18)-H(18)	119.4
C(20)-C(19)-C(24)	118.4(4)
C(20)-C(19)-P(2)	125.7(3)
C(24)-C(19)-P(2)	115.8(3)
C(21)-C(20)-C(19)	120.9(4)
C(19)-C(20)-H(20)	119.5
C(23)-C(24)-C(19)	119.8(5)

2.4.18. Synthesis of tridentate compound 26

Scheme 14. Attempted synthesis of **26**



26

Compound **25** (0.02 g, 0.02 mmol) was added to a 25 mL flask with a magnetic stir bar and dissolved in 10 mL of dried acetone. The reaction was stirred overnight and produced a yellowish brown mixture that still contained solid material. $B(C_6F_5)_3$ (0.01 g, 0.02 mmol) was dissolved in 2 mL of acetone and added to the reaction via a syringe. The reaction was continued at room temperature for two days; the mixture changed slightly from yellowish-brown to deep brown. A sticky brown solid was isolated after solvent evaporation under *vacuo* for 7h. The $^{31}P\{^1H\}$ spectrum of brown solid (101.3 MHz, CD_3CN, 298 K, ppm): δ = -1.2 (s) showing the formation of compound **26** (see **Figure 2.11**).

Figure 2.11. A Comparison of $^{31}P\ \{^1H\}$ NMR for Uncoordinated Tris(diphenylphosphino)methane (**1**) and Coordinated Structure **26**

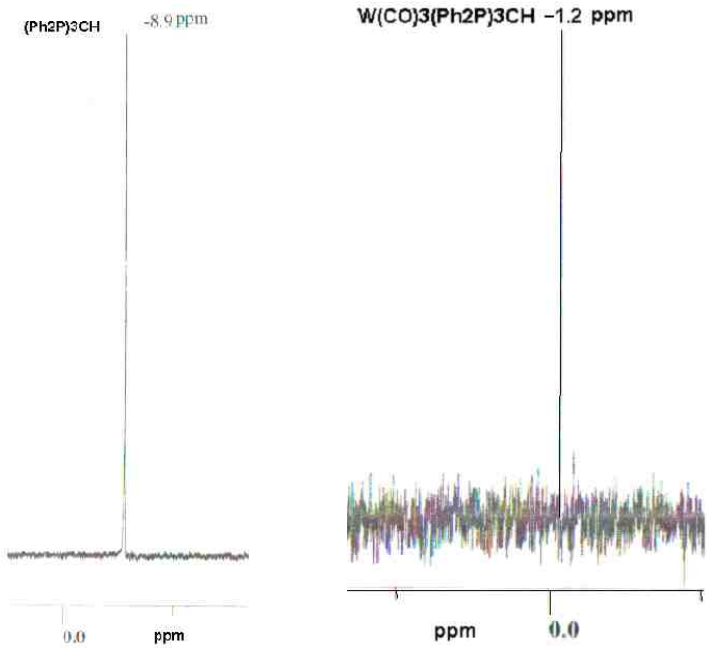
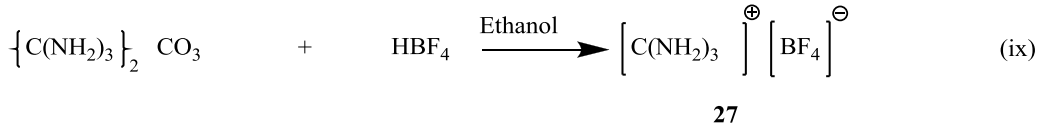


Figure 2.11 shows the comparison of δ for uncoordinated precursor **1** and when its two phosphorus atoms are coordinated to group 6B metal carbonyl in structure **26**. The uncoordinated to coordinated has shown the shift from -8.9 (ppm) (s) to -1.2 (ppm) (s).

2.5. Synthesis of guanidinium tetrafluoroborate (compound 27)



(ix)

27

The synthesis of precursor **27** has been previously reported.[2] Guanidinium carbonate (1.80 g, 10.00 mmol) was dissolved in 25 mL of dry ethanol and added to a 100 mL flask with a magnetic stirrer. To this mixture, a small excess of tetrafluoroboric acid (48-50% in diethyl ether) was added drop wise until pH = 3-4. The product was dissolved by stirring for 20 minutes and the remaining solid was removed by gravity filtration. The filtrate was slowly evaporated to dryness. Crystallization of the products was induced by the addition of 5 mL of acetone followed by addition of 15mL of ethyl acetate. The reaction mixture was evaporated under *vacuo* to half of the original volume (or until the crystals start to form). Some of the solvent was removed through evaporation under argon overnight at room temperature. The rest of solvents and solids were removed by using cannula, dried in *vacu*o for 4h. This procedure yielded 1.38 g of a white crystalline product 94%, mp = 176-178 ^{o}C. The ^{1}H NMR spectrum (250 MHz, CD_3COCD_3, 298 K, ppm): δ = peak at 6.87 (s, 6H, ($3xNH_2$). The $^{13}C\{^{1}H\}$ NMR spectrum (62.9 MHz, CD_3COCD_3, 298 K, ppm): δ = 159 (s). IR spectroscopy of the

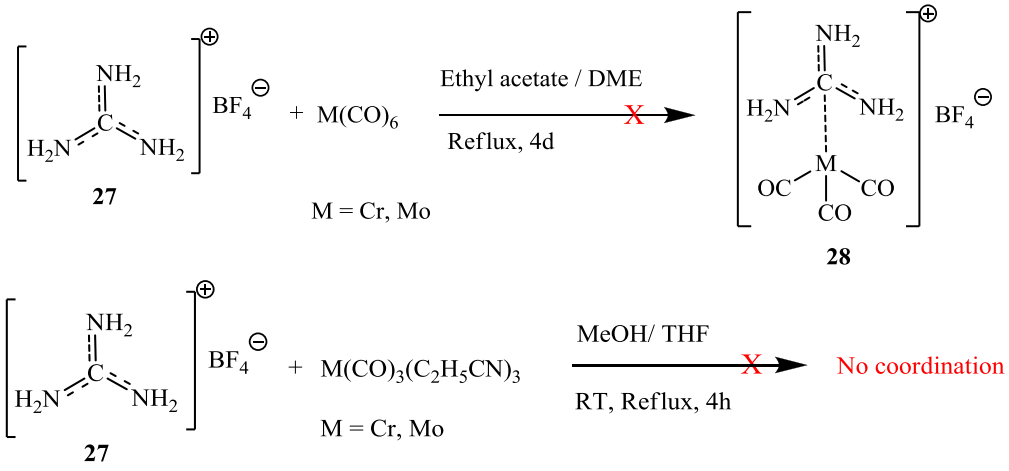
Nujol mull of the product showed four υN-H bands: 3483 (w) cm^{-1}, 3394 (w) cm^{-1} 1684 (m-s) cm^{-1}, and 1570 (w) cm^{-1}.

Table 2.10: Elemental analysis for $[(NH_2)_3C]^+[BF_4]^-$ **27**

Atom	C	H	N
Calculated	8.78	3.76	28.23
Found	8.18	4.12	28.61

2.5.1. Synthesis of cationic compound 28 using precursor 27

Scheme 15. Attempted coordination of group 6B metal carbonyl complexes with **27**

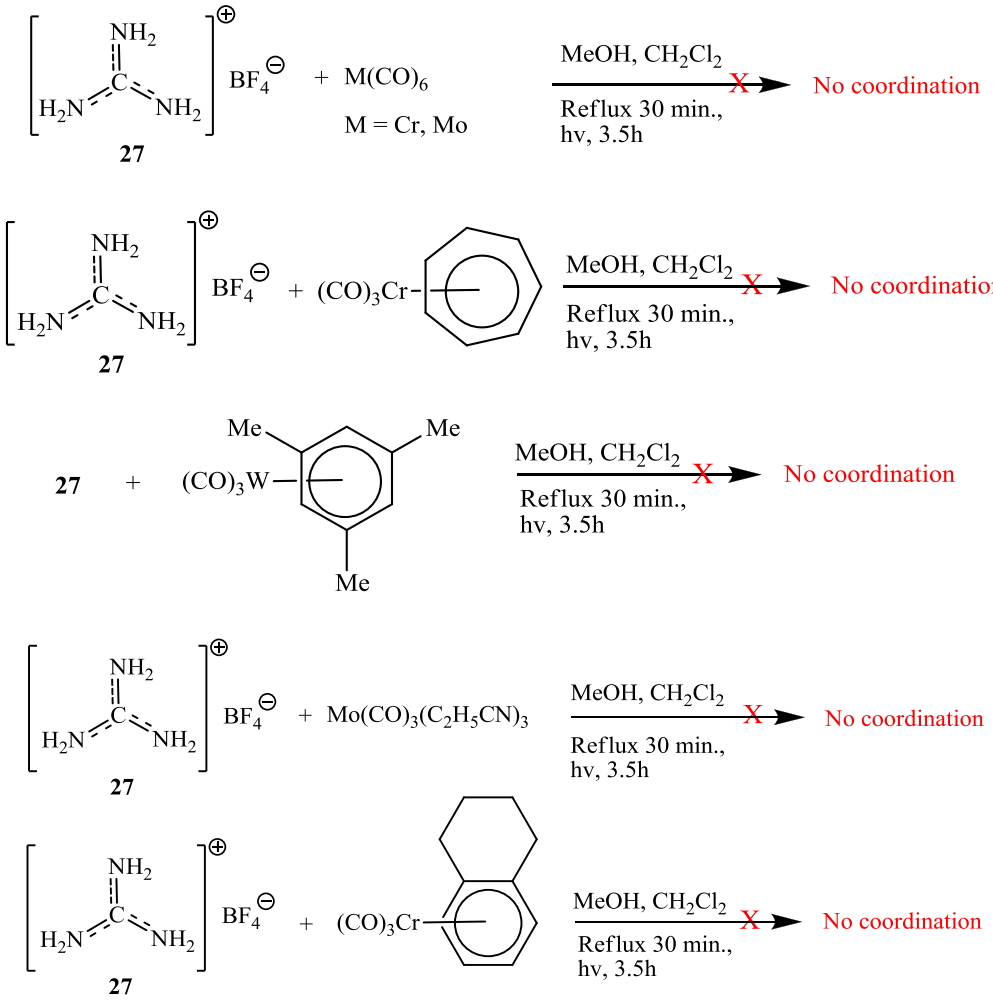


Compound **27** (0.05 g, 0.34 mmol) was dissolved in 5 mL of MeOH and was added to a 50 mL flask with a magnetic stirrer in the dry box. In the other 25 mL flask, molybdenum hexacarbonyl (0.10 g, 0.37 mmol) dissolved in 10 mL of methanol and left stirring overnight as well. The following day the two mixtures were combined together and stirred for 24h. No color change observed. When this mixture was refluxed in a bath of ethyl acetate/DME mixture for 1h, the color changed from colorless to yellow. This mixture was left to cool to room temperature while stirring under argon overnight. The

next day a white crystalline undissolved starting material was observed and filtered with fritted glass filter. The yellow filtrate was evaporated under *vacuo* for 8h. IR spectroscopy of the Nujol mull confirmed the existence of starting material and this indicates that, the synthesis protocol had failed.

2.5.2. Photolysis of compound 27 with group 6B metal carbonyl

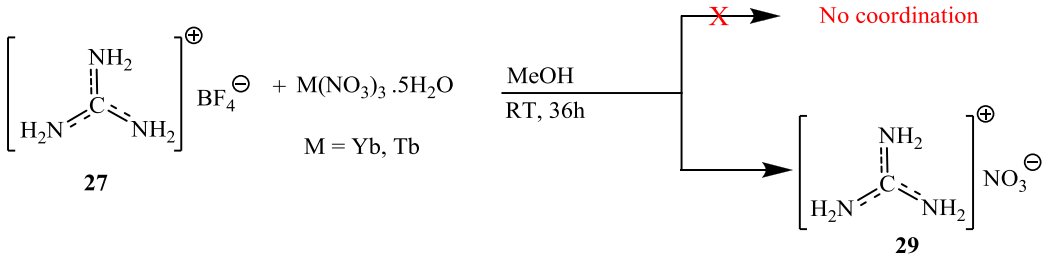
Scheme 16. Attempted photolysis of the mixture of **27** with group 6B metal carbonyl complexes



1,2,3,4-tetrahydronapthalene chromium(0)tricarbonyl (0.02 g, 0.07 mmol) was dissolved in 5 mL of dichloromethane and added to a 25 mL flask with a magnetic stirrer, and was left to stir overnight in the dry box. Compound **27** (0.02 g, 0.12 mmol) dissolved in 5 mL of methanol was added to a second 25 mL flask with a magnetic stirrer and left stirring overnight in the dry box as well. The following day the two mixtures were combined and refluxed for 30 minutes. During reflux of this mixture, the color changed from colorless to faint yellow. The faint yellow solution was exposed to ultraviolet light for 3.5h. After photolysis, the mixture did not show any further significant change in color. However, during transfer of the mixture using a pipette to 25 mL flask under argon, the faint yellow solution changed to green. The mixture was evaporated under *vacuo* for 6h. IR spectroscopy of the Nujol mull revealed the existence of uncoordinated **27** in all of the attempted reactions (***Scheme 16***).

2.5.3. The coordination of 27 with lanthanide salts

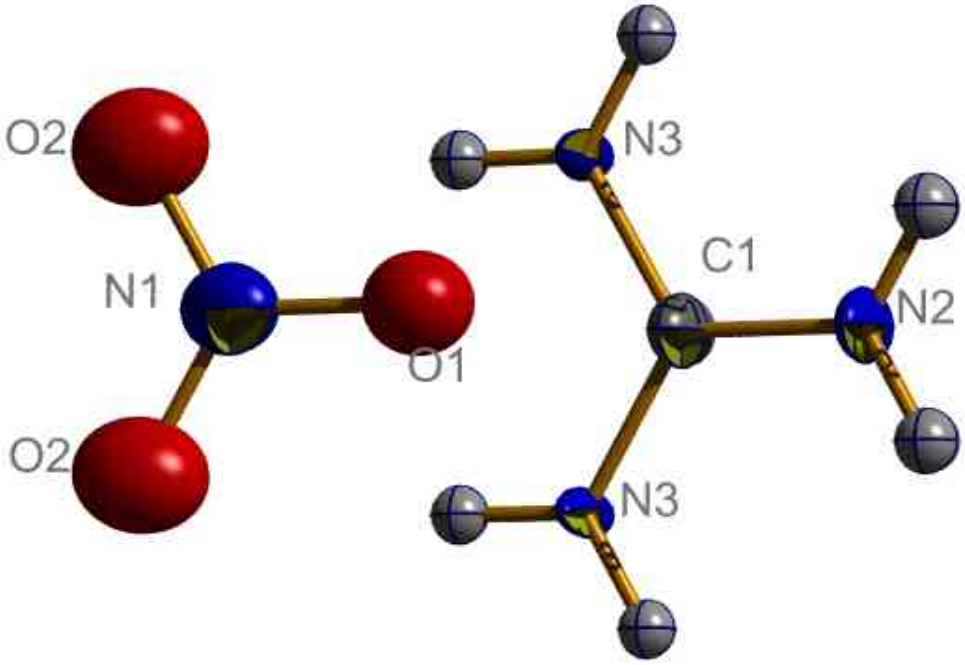
Scheme 17. Attempted synthesis of lanthanide guanidinium complex



Ytterbium nitrate hexahydrate (0.06 g, 0.22 mmol) was dissolved in 5 mL of methanol and was added to a 25 mL flask with a magnetic stirrer in the dry box. Compound **27** (0.03 g, 0.22 mmol) dissolved in 5 mL of methanol was added and left

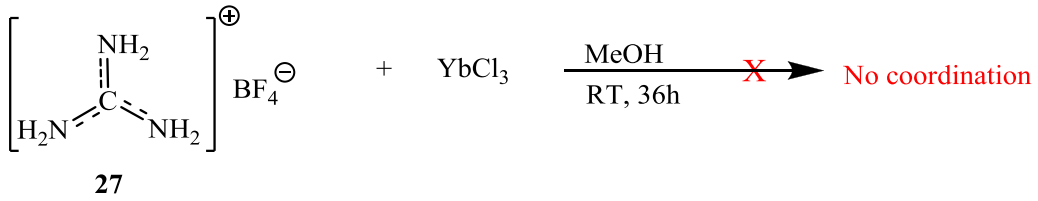
stirring overnight at room temperature. The following day, white crystals suspended on top of the solution in the flask were observed. The solvent was canullated and the solid dried under *vacuo* for 8h. IR spectroscopy of the Nujol mull showed two υN-H bands: 3462 (w) cm^{-1} and 1670 (w) cm^{-1}, suggesting the formation of compound **29** (***Scheme 17***). Recrystallization of crude product was carried out in methanol and allowed to evaporate slowly at room temperature. Single crystal X-ray analysis revealed the structure shown in **Figure 2.12**.

Figure 2.12. Molecular Structure of Guanidinium Nitrate **29**



2.5.4. Synthesis of ytterbium guanidinium complex

Scheme 18. Attempted synthesis of ytterbium guanidinium complex

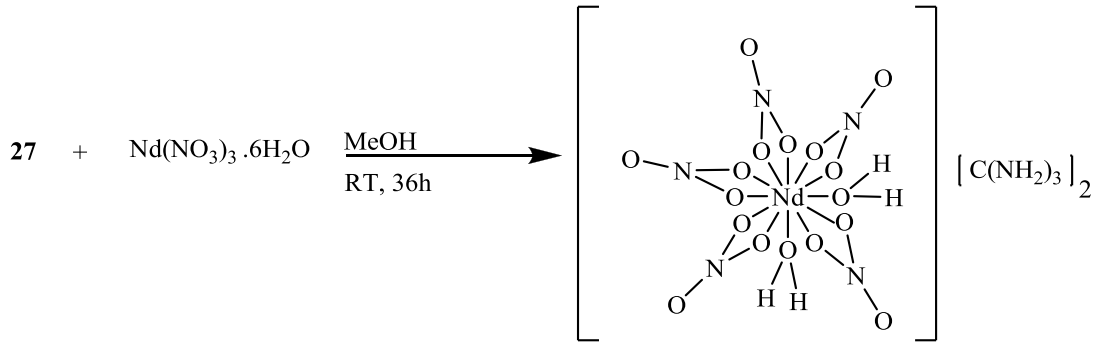


27

Ytterbium chloride (0.06 g, 0.22 mmol) was dissolved in 5 mL of methanol and added to a 25 mL flask with a magnetic stirrer in the dry box. Compound **27** (0.03 g, 0.22 mmol) was dissolved in 5 mL of methanol and added to the reaction, and the reaction was left to stir overnight. This mixture was further stirred for an additional 36h. The solvent was evaporated under *vacuo* for 6h. Recrystallization of dry solid in different solvent systems resulted crystals; however, X-ray analysis revealed that the crystals were the compound **27** starting material.

2.5.5. Synthesis of compound 30 from compound 27 and neodymium nitrate

Scheme 19. Attempted synthesis of complex **30**



30

Neodymium nitrate hexahydrate (0.01 g, 0.22 mmol) was dissolved in 8 mL of methanol and added to a 25 mL flask with a magnetic stirrer in the dry box. Compound **27** (0.03 g, 0.23 mmol) was dissolved in 5 mL of methanol and added to the reaction, and the colorless mixture was stirred at room temperature overnight. The following day this mixture was concentrated using argon stream, producing a suspension of white crystals. The crystals were left to evaporate in air at room temperature. This procedure yielded 0.09 g of a white crystalline product (69% yield; mp > 200 ^{o}C). IR spectroscopy of the Nujol mull showed two υN-H bands: 3374 (w) cm^{-1}, and 1653 (w) cm^{-1}. Single crystal X-ray analysis revealed a novel structure designated compound **30**, whose structure is shown in **Figure 2.13**, along with and a summary of selected bond lengths in Table **2.12**, and hydrogen bonds in **Table 2.13**.

Figure 2.13. Molecular Structure of Diguanidinium diaquapentakis(nitrato) neodymiate(III) **30**

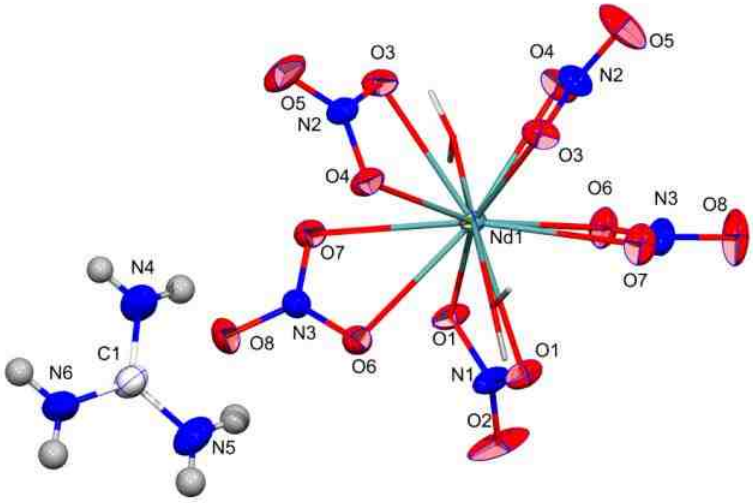


Table 2.11: Elemental analysis for **30**

Atom	C	H	N
Calculated	3.94	2.64	25.24
Found	4.65	2.50	23.52

Table 2.12: Bond lengths [Å] and angles [°] for **30**

Nd(1)-O(9)	2.4917(10)
Nd(1)-O(4)	2.5543(10)
Nd(1)-O(1)	2.6050(10)
Nd(1)-O(6)	2.6588(11)
Nd(1)-O(3)	2.6826(11)
Nd(1)-O(7)	2.7109(11)
O(9)-H(9A)	0.84(3)
O(9)-H(9B)	0.79(3)
N(1)-O(2)	1.219(2)
N(1)-O(1)	1.2729(12)
N(2)-O(5)	1.2184(16)
N(2)-O(3)	1.2573(16)
N(2)-O(4)	1.2734(15)
N(3)-O(8)	1.2362(17)
N(3)-O(7)	1.2565(16)
N(3)-O(6)	1.2578(16)
C(1)-N(4)	1.314(2)
C(1)-N(6)	1.318(2)
C(1)-N(5)	1.327(2)
N(4)-H(4A)	0.79(3)
N(4)-H(4B)	0.82(3)
N(5)-H(5A)	0.82(3)
N(5)-H(5B)	0.78(3)
N(6)-H(6A)	0.79(3)
N(6)-H(6B)	0.86(3)
Nd(1)-O(9)-H(9A)	121.8(17)
Nd(1)-O(9)-H(9B)	127.2(18)

H(9A)-O(9)-H(9B)	107(2)
O(1)-Nd(1)-O(6)	65.33(4)
O(9)-Nd(1)-O(3)	66.31(3)
O(4)-Nd(1)-O(3)	48.43(3)
O(1)-Nd(1)-O(3)	164.21(4)
O(6)-Nd(1)-O(3)	100.34(3)
O(2)-N(1)-O(1)	121.75(8)
N(1)-O(1)-Nd(1)	97.19(8)
O(5)-N(2)-O(3)	122.58(13)
O(5)-N(2)-O(4)	120.99(13)
O(3)-N(2)-O(4)	116.43(11)
N(2)-O(3)-Nd(1)	94.51(8)
N(2)-O(4)-Nd(1)	100.28(8)
O(8)-N(3)-O(7)	121.77(13)
O(8)-N(3)-O(6)	120.41(13)
O(7)-N(3)-O(6)	117.83(12)
N(3)-O(6)-Nd(1)	98.63(8)
N(4)-C(1)-N(6)	119.79(16)
N(4)-C(1)-N(5)	120.25(19)
N(6)-C(1)-N(5)	119.95(18)
C(1)-N(4)-H(4A)	119(2)
C(1)-N(4)-H(4B)	121.0(19)
H(4A)-N(4)-H(4B)	119(3)
C(1)-N(5)-H(5B)	118(2)
H(5A)-N(5)-H(5B)	122(3)
C(1)-N(6)-H(6A)	120(2)
H(6A)-N(6)-H(6B)	119(3)

Table 2.13: Hydrogen bonds [Å] and angles [°] for **30**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(9)-H(9B)...O(2)#2	0.77(3)	2.56(3)	3.066(3)	124(3)
O(9)-H(9B)...O(1)#2	0.77(3)	2.15(3)	2.9170(16)	175(3)
O(9)-H(9A)...O(3)#3	0.84(3)	2.08(3)	2.9078(16)	172(3)
N(5)-H(5A)...O(8)#4	0.82(3)	2.27(4)	3.057(3)	161(3)
N(6)-H(6A)...O(6)#4	0.80(3)	2.20(3)	2.982(2)	169(3)
N(5)-H(5A)...O(5)#5	0.82(3)	2.56(3)	2.869(2)	104(3)
N(6)-H(6B)...O(7)#6	0.86(3)	2.20(3)	3.022(2)	162(3)
N(4)-H(4B)...O(8)#6	0.81(3)	2.10(3)	2.907(3)	173(3)
N(4)-H(4A)...O(4)#7	0.79(3)	2.08(3)	2.852(2)	168(3)

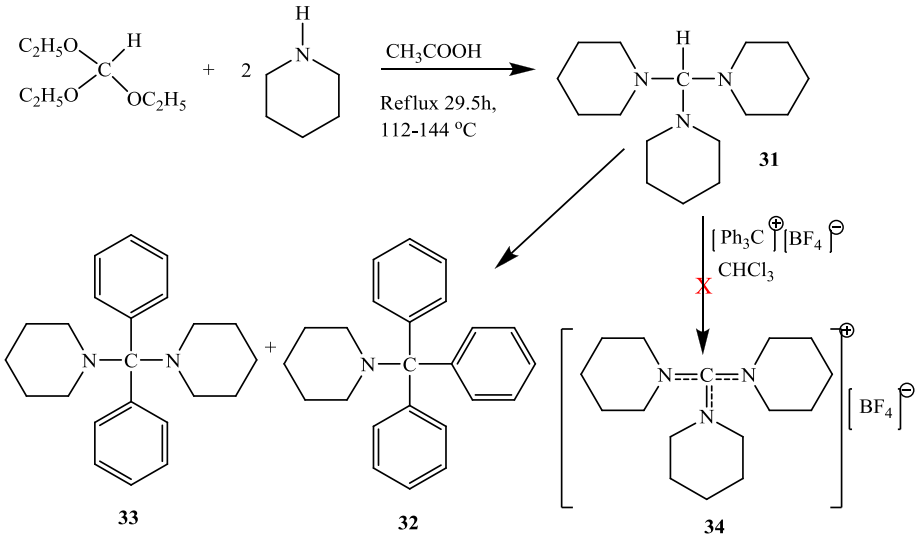
Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+3/2 #2 x+1/2,y+1/2,z #3 -x+3/2,y-1/2,-z+3/2

#4 -x+1,-y+1,-z+1 #5 x,y-1,z #6 -x+3/2,-y+3/2,-z+1

#7 x+1/2,y-1/2,z

2.5.6. Synthesis of 6π-cationic ligand 34 of guanidinium analog

Scheme 20. Attempted synthesis of 6π-cationic ligand **34**

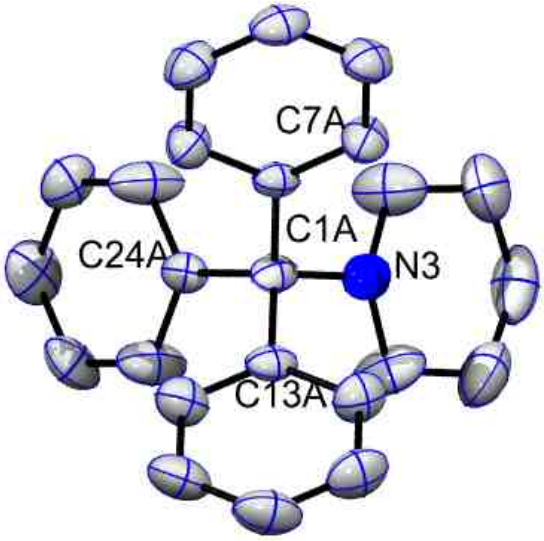


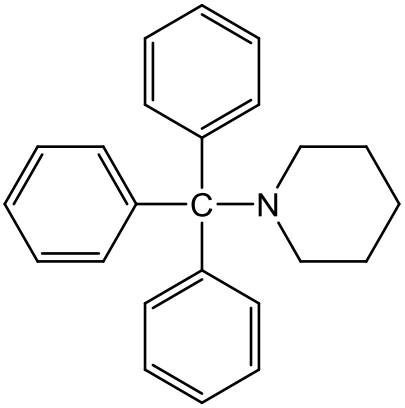
The synthesis of precursor **31** has been previously reported.[9] Piperidine (88.92 mL, 0.90 mmol) was added in a 250 mL flask with a magnetic stirrer in the dry box. Triethyl orthoformate (74.86 mL, 0.45 mmol) was added dropwise to the reaction. While this mixture, was stirring under argon, acetic acid (1.72 mL, 0.03 mmol) was added dropwise by syringe to the reaction vessel. Upon addition of the acetic acid to the mixture, a white precipitate formed, but disappeared upon further stirring. The mixture was refluxed at 112 ^{o}C, and the temperature was gradually increased during the 29.5h of reflux; the final pot temperature was 144 ^{o}C. The mixture was concentrated for 12h to remove N-formylpiperidine, and the following day the mixture was distilled under vacuum. A small amount of white dense product was collected (50 mg; 42% yield). ^{1}H NMR spectrum (250 MHz, $CDCl_3$, 298 K, ppm): δ = (250 MHz, 1.46 (br s, 18H, $(CH_2)_3$), 2.80 (br s, 12H, CH_2N), and 3.11 (s, 1H, $HC(N)_3$), confirming the synthesis of compound **31**.

Tripiperidinomethane (compound **31**) (12 mg, 0.045 mmol) was dissolved in 4 mL of dry deuterated chloroform and added to a 25 mL flask with a magnetic stirrer in the dry box. Triphenyl tetrafluoroborate (15mg, 0.045 mmol) of was added to the mixture, causing the color to change gradually from colorless to dark red. The reaction was left to stir at room temperature overnight under argon. The solvent was evaporated under *vacuo* for 6h and recrystallization was carried out in $CDCl_3$/hexane. The ^{1}H NMR spectrum (250 MHz, $CDCl_3$, 298 K, ppm): δ = 1.74 (br s, 18H, $(CH_2)_3$), 3.63 (br s, 12H, CH_2N), and 7.11-7.73 (m, Ar-H). The $^{11}B\{^{1}H\}$ spectrum (80.2 MHz, $CDCl_3$, 298 K, ppm): δ =- 1.30 (s). Single crystal X-ray analysis revealed that each unit cell contained

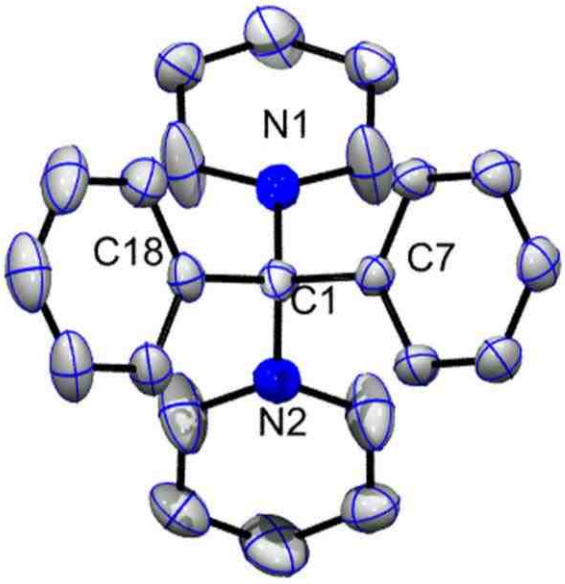
the two novel structures shown **Figure 2.14**, and a summary of selected bond length parameters are given in **Table 2.14**.

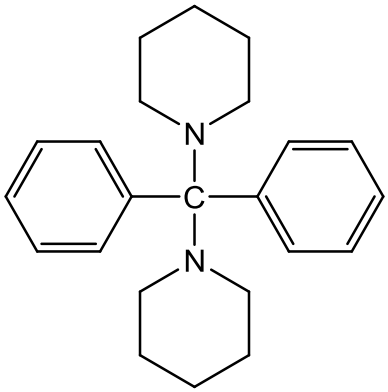
Figure 2.14. Molecular Structure of **32** and **33** Showing the Numbering Scheme. Hydrogen Atoms are Omitted for Clarity





32





33

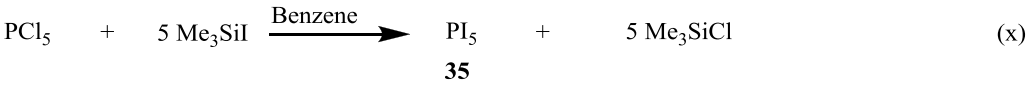
Table 2.14: Bond lengths [Å] and angles [°] for **32 and 33**

C(1)-N(1)	1.507(3)
C(1)-N(2)	1.510(3)
C(1)-C(18)	1.538(3)
C(1)-C(7)	1.544(3)
N(1)-C(6)	1.408(4)
N(1)-C(2)	1.412(4)
C(7)-C(12)	1.384(4)
C(7)-C(8)	1.391(3)
N(2)-C(17)	1.407(4)
N(2)-C(13)	1.420(4)
C(13)-C(14)	1.406(5)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(18)-C(19)	1.390(4)
C(18)-C(23)	1.395(4)
C(1A)-N(3)	1.493(4)
C(1A)-C(19A)	1.521(3)
C(1A)-C(13A)	1.536(4)
C(1A)-C(7A)	1.549(3)
N(3)-C(6A)	1.431(4)
N(3)-C(2A)	1.437(4)
C(2A)-C(3A)	1.445(6)
C(7A)-C(8A)	1.381(4)
C(7A)-C(12A)	1.391(4)
C(13A)-C(18A)	1.381(4)
C(13A)-C(14A)	1.401(4)
C(17A)-C(18A)	1.392(4)
C(17A)-H(17C)	0.9500
C(24A)-H(24A)	0.9500
N(1)-C(1)-N(2)	109.37(19)
N(1)-C(1)-C(18)	111.9(2)
N(2)-C(1)-C(18)	110.9(2)

N(1)-C(1)-C(7)	110.34(19)
N(2)-C(1)-C(7)	111.5(2)
C(18)-C(1)-C(7)	102.67(18)
C(2)-N(1)-C(1)	117.7(2)
N(1)-C(2)-C(3)	116.7(3)
N(1)-C(2)-H(2A)	108.1
C(3)-C(2)-H(2A)	108.1
N(1)-C(2)-H(2B)	108.1
N(1)-C(6)-C(5)	116.9(3)
N(1)-C(6)-H(6A)	108.1
N(1)-C(6)-H(6B)	108.1
C(12)-C(7)-C(8)	118.0(2)
C(12)-C(7)-C(8)	118.0(2)
C(12)-C(7)-C(1)	121.3(2)
C(8)-C(7)-C(1)	120.3(2)
C(9)-C(8)-C(7)	120.9(2)
C(7)-C(8)-H(8)	119.5
C(7)-C(12)-C(11)	120.9(3)
C(7)-C(12)-H(12)	119.6
C(14)-C(13)-H(13A)	107.5
N(2)-C(13)-H(13A)	107.5
C(14)-C(13)-H(13B)	107.5
N(2)-C(13)-H(13B)	107.5
H(13A)-C(13)-H(13B)	107.0
C(13)-C(14)-C(15)	118.6(3)
C(13)-C(14)-H(14A)	107.7
C(13)-C(14)-H(14B)	107.7
N(2)-C(17)-C(16)	119.6(3)
N(2)-C(17)-H(17A)	107.4
C(16)-C(17)-H(17A)	107.4
N(2)-C(17)-H(17B)	107.4
C(18)-C(19)-H(19)	119.6
C(18)-C(23)-H(23)	119.7

N(3)-C(1A)-C(19A)	108.5(2)
N(3)-C(1A)-C(13A)	110.7(2)
N(3)-C(1A)-C(7A)	110.3(2)
C(19A)-C(1A)-C(7A)	112.1(2)
C(6A)-N(3)-C(2A)	112.9(3)
C(6A)-N(3)-C(1A)	117.5(2)
C(2A)-N(3)-C(1A)	117.3(3)
N(3)-C(2A)-C(3A)	115.5(4)
N(3)-C(2A)-H(2A1)	108.4
N(3)-C(2A)-H(2A2)	108.4
N(3)-C(6A)-C(5A)	116.7(3)
N(3)-C(6A)-H(6A1)	108.1
N(3)-C(6A)-H(6A2)	108.1
C(7A)-C(8A)-C(9A)	121.1(3)
C(7A)-C(8A)-H(8A)	119.4
C(11A)-C(12A)-C(7A)	120.7(3)
C(7A)-C(12A)-H(12A)	119.7
C(18A)-C(13A)-C(14A)	118.1(3)
C(18A)-C(13A)-C(1A)	121.4(2)
C(14A)-C(13A)-C(1A)	119.8(3)
C(24A)-C(23A)-H(23A)	120.0

2.6. Synthesis of phosphoruspentaiodide (compound 35)

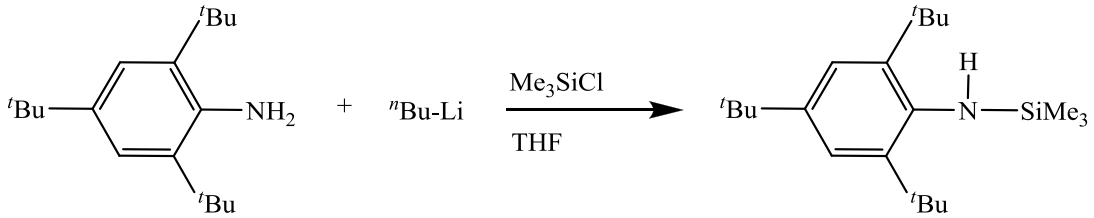


The synthesis of precursor **35** has been previously reported.[10] Phosphoruspentachloride (1.00 g, 4.80 mmol) was dissolved in 50 mL of dry benzene and was added to a 100 mL flask with a magnetic stirrer covered with aluminum foil in a

dry box. This mixture remained colorless and was transferred to a cold bath at 16-18 ^{o}C for 10 minutes. While this mixture stirring under argon trimethylsilyiodide (3.42 g, 24.01 mmol) was added dropwise by syringe over the course of 6 minutes, causing the color of the mixture to change from colorless to purple. The reaction mixture was left stirring at cold bath for 1h, and then allowed to warm to room temperature for 30 minute. The reaction was filtered and the filtrate was evaporated under *vacuo* for 20 minutes. The dry solid was washed with benzene and dried for 8h. This procedure yielded 2.10 g, of a purple solid product (66% yield, mp = 39-42 ^{o}C). The $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, CH_3I, 298 K, ppm): δ = 181.1 (s), which is comparable with reported value of 182 (ppm) (s) with H_3PO_4 as a reference.

2.6.1. Synthesis of precursor 36

Scheme 21. Attempted synthesis of 2,4,6-tri-*tert*-butyl trimethylsilylaniline compound **36**



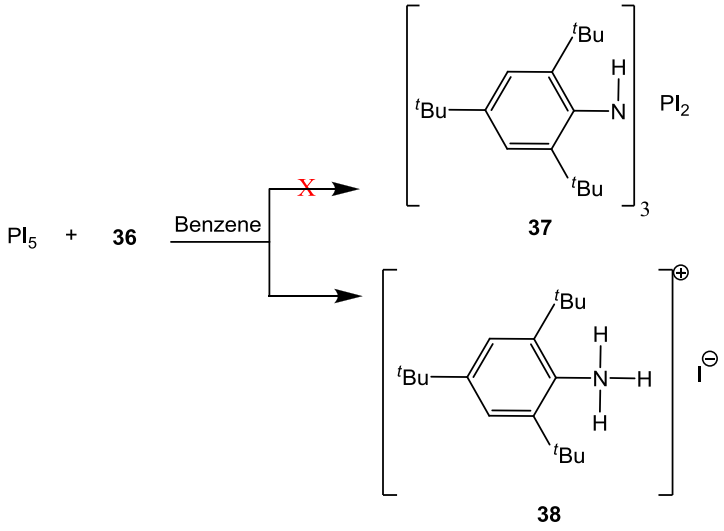
36

The synthesis of precursor **36** has been previously reported.[11] 2,4,6-tri-*tert*-butylaniline (4.00 g, 15.30 mmol) was dissolved in 30 mL of dry THF and was added to a 250 mL flask with a magnetic stirrer. While stirring this mixture in the dry box at room temperature, 2.50 M ^{n}BuLi was (6.40 mL, 15.90 mmol), provided by Aldrich Chemicals in hexane was added to the reaction dropwise for 20 minutes. The mixture was placed at

0 ^{o}C for 10 minutes, and chlorotrimethylsilane (2.47 g, 22.80 mmol) dissolved in 8 mL dry THF was added dropwise for 20 minutes. The reaction mixture was allowed to warm to room temperature for 1h, and then was cannulated over a celite pad in a fritted glass filter. The solvent in the filtrate was evaporated off, and residue dried under *vacuo* for 10h. The dried residue was recrystallized in hexane and placed in the freezer over night. The following day, the solvent was cannulated and the crystals were dried for 10h under *vacuo*. This procedure yielded a pink solid product (4.00 g, 78% yield, mp = 93-95 ^{o}C). ^{1}H NMR spectrum (250 MHz, $CDCl_3$, 298 K, ppm): δ = 0.18 (s, 9H, Me_3Si), 1.30 (s, 9H, p-^{t}Bu), 1.48 (s, 18H, o-^{t}Bu), 2.21 (s, 1H, N-H), and 7.31 δ (s, 2H, Ar-H), consistent with the expected NMR spectrum for compound **36**.

2.6.2. Synthesis of 37 using both 35 and 36

Scheme 22. Attempted synthesis of **37**



Compound **35** (0.35 g, 0.53 mmol) was dissolved in 4 mL of dry benzene and transferred to a 100 mL flask with a magnetic stirrer in the dry box. The mixture turned deep purple-red. Compound **36** (0.53 g, 1.59 mmol) dissolved in 2 mL of benzene was added dropwise to the reaction over the course of 10 minutes. The mixture was transferred to cold bath at 17-20 ^{o}C, stirred under argon for 2h, refluxed for 4h, and left to cool at room temperature overnight while stirring under argon. The next day, the mixture was refluxed for 1h and the solvent was evaporated. The ^{1}H NMR spectrum of the product in C_6D_6 revealed a number of impurities. Therefore, column chromatography separation was carried out using an eluent of a 10% MeOH/ 90% CH_2Cl_2 mixture. The product was isolated and analyzed by thin-layer chromatography. The ^{1}H NMR spectrum (250 MHz, C_6D_6, 298 K, ppm): δ = 1.37 (s, 9H, p-^{t}Bu), 1.44 (s, 18H, o-^{t}Bu), 5.22 (br (s), 3H, N-H), and 7.42 (s, 2H, Ar-H). The ^{13}C{^{1}H} NMR spectrum (62.9 MHz, THF-d_8, 298 K, ppm): δ = 30.1 (s), 31.6 (s), 34.8 (s), 102.6 (s), 133.5 (s) 138.5 (s), and 141.7 (s). Based on these data, the expected product, compound **37**, was not obtained. Instead, a novel compound **38**, 2,4,6-tri-tert-butylbenzenaminium iodide, was obtained. The product isolated after column separation and was recrystallized in THF. Because of low purity of crystals, both melting point and percentage yield were not determined. Single crystal X-ray analysis revealed the structure of 2,4,6-tri-*tert*-butylbenzenaminium iodide **38** to be as shown in **Figure 2.15**. A summary of selected bond lengths and hydrogen bonding are shown in **Table 2.15** and **Table 2.16**, respectively.

Figure 2.15. Molecular Structure for 2,4,6-tri-*tert*-butylbenzenaminium Iodide **38**

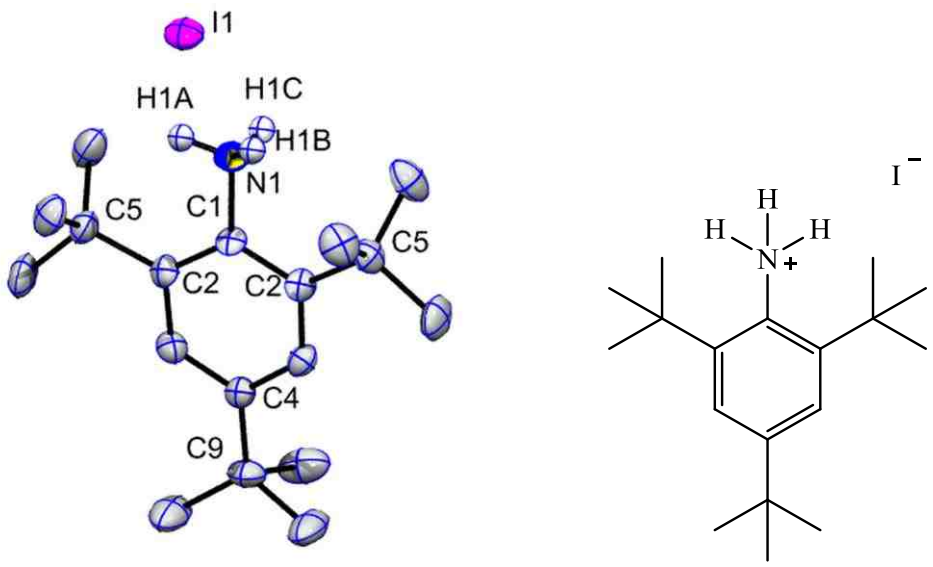


Table 2.15: Bond lengths [Å] and angles [°] for 2,4,6-tri-*tert*-butyl benzenaminium iodide

N(1)-C(1)	1.477(9)
N(1)-H(1A)	0.9100
N(1)-H(1B)	0.9100
N(1)-H(1C)	0.9100
C(2)-C(3)	1.387(7)
C(2)-C(5)	1.547(7)
C(3)-C(4)	1.391(6)
C(4)-C(9)	1.523(10)
C(5)-C(6)	1.531(8)
C(5)-C(8)	1.534(8)
C(5)-C(7)	1.540(8)
C(9)-C(10)	1.498(13)
C(1)-N(1)-H(1A)	109.5
C(1)-N(1)-H(1B)	109.5
H(1A)-N(1)-H(1B)	109.5
C(1)-N(1)-H(1C)	109.5
H(1A)-N(1)-H(1C)	109.5
H(1B)-N(1)-H(1C)	109.5

C(3)-C(2)-C(1)	116.1(5)
C(3)-C(2)-C(5)	120.1(5)
C(1)-C(2)-C(5)	123.5(5)
C(1)-C(2)-C(5)	123.5(5)
C(1)-C(2)-C(5)	123.5(5)
C(2)-C(3)-C(4)	123.4(5)
C(2)-C(3)-H(3)	118.3
C(4)-C(3)-H(3)	118.3
C(3)-C(4)-C(9)	121.4(3)
C(6)-C(5)-C(8)	106.6(5)
C(6)-C(5)-C(7)	110.2(5)
C(8)-C(5)-C(7)	105.4(5)
C(6)-C(5)-C(2)	109.8(5)
C(8)-C(5)-C(2)	111.1(5)
C(7)-C(5)-C(2)	113.4(5)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
C(5)-C(8)-H(8A)	109.5
C(5)-C(8)-H(8B)	109.5
C(4)-C(9)-C(10)	116.2(12)
C(4)-C(9)-C(10A)	108.2(12)
C(10)-C(9)-C(10A)	105.6(9)
C(9)-C(10)-H(10C)	109.6
C(9)-C(11)-H(11A)	111.5

Table 2.16: Hydrogen bonds [Å] and angles [°] for 2,4,6-tri-*tert*-butyl benzenaminium iodide.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1B)...I(1)	0.91	2.86	3.390(7)	118.6
N(1)-H(1C)...I(1)#2	0.91	2.64	3.505(7)	160.1
C(7)-H(7A)...N(1)	0.98	2.47	3.028(7)	116.1

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z #2 x,y,z-1

2.6.3. Synthesis of trianilinodiiodophosphorane (**compound 40**)

$$PI_5 + \underset{\textbf{39}}{6\ C_6H_5NH_2} \xrightarrow{\text{Benzene}} \underset{\textbf{40}}{(C_6H_5NH)_3PI_2} + 3\ C_6H_5NHI \qquad \text{(xi)}$$

The synthesis of precursor **40** has been previously reported.[12] Compound **35** (1.75 g, 2.63 mmol) was dissolved in 13 mL of dry benzene and added to a 100 mL flask with a magnetic stirrer in the dry box. Compound **39** (1.44 mL, 15.80 mmol) was dissolved in 7 mL of benzene and added to the reaction. The mixture color changed from faint yellow to bright yellow. The reaction was transferred to a cold bath at 19-20 ^{o}C and stirred for 2h, warmed to room temperature, refluxed for 1.5h, and left to cool to room temperature for 1h. The mixture was filtered through a fritted glass filter using a hand-pressure bulb, and the residue was washed with ice-cold water. The residue was dried under *vacuo* for 12h, yielding 0.80 g of dry a yellow solid (54% yield, mp > 200^{o}C). The ^{1}H NMR spectrum (250 MHz, $C_6D_5NO_2$, 298 K, ppm): δ = 7.00-8.13 (m, 5H, H-Ar), and 9.30 (d, $^{2}J_{P\text{-}H}$ = 15.50 Hz). The $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, $C_6D_5NO_2$, 298 K, ppm): δ = 6.9 (s) with H_3PO_4 as a reference. These analyses confirmed the synthesis of compound **40**.

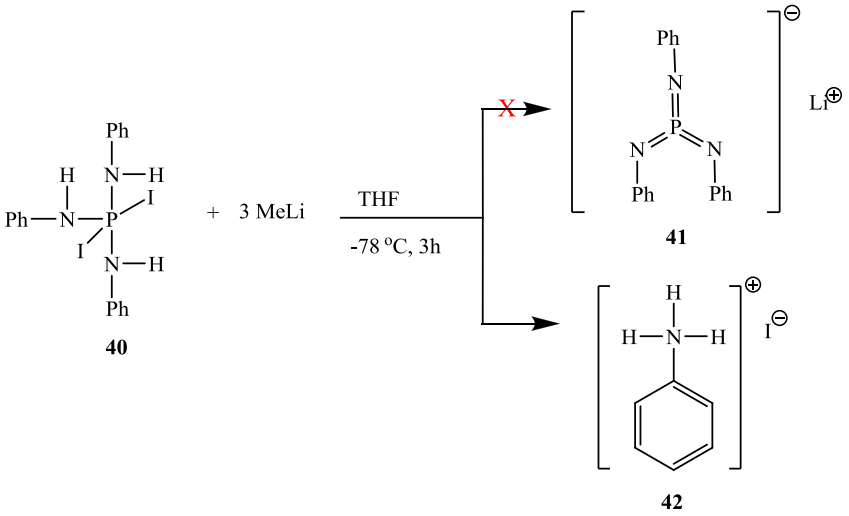
Elemental analysis for compound **40** is shown in **Table 2.17**.

Table 2.17: Elemental analysis for **40**

Atom	Carbon	Hydrogen	Nitrogen
Calculated	38.56	3.25	7.49
Found	40.46	3.99	7.10

2.6.4. Synthesis of anionic ligand 41

Scheme 23. Attempted lithiation of trianilinodiiodophosphorane (compound **40**)



Compound **40** (0.10 g, 0.18 mmol) dissolved in 15 mL of dry THF was added to a 50 mL flask with a magnetic stirrer in the dry box. Compound **40** was relatively insoluble in THF, and was allowed to stir for 2h to ensure that a significant amount of the solid was dissolved. The reaction vessel was kept under argon, and was transferred to a cold bath at -78 ^{o}C for 30 minutes. Methyllithium in ether (0.48 mL, 0.77 mmol), plus an extra 30% of either, were mixed for 15 minutes and added dropwise to the reaction over a 15 minute period. During addition of the base to the mixture, the color changed from faint yellow to deep yellow. The mixture was left stirring for 3h, warmed to room temperature for 30 minutes, and filtered through a medium fritted glass filter. The filtrate was evaporated

under *vacuo* for 8h and a dry yellow solid was obtained. Both melting point and percentage yield were not determined. Recrystallization of crude product was done in THF/hexane. However, the majority of product was powder rather than crystalline. The ^{1}H NMR spectrum (250 MHz, THF-d_8, 298 K, ppm): δ = 3.80 (s, 3H, NH), and 6.83-7.32 (m, 5H, Ar-H). Single crystal X-ray analysis revealed that, rather than the expected product, compound **41**, the actual product was a known compound[13] (compound **42**) with the structure shown in **Figure 2.16**. A summary of the selected bond lengths is shown in **Table 2.18**.

Figure 2.16. Molecular Structure of Benzenaminium Iodide (**42**)

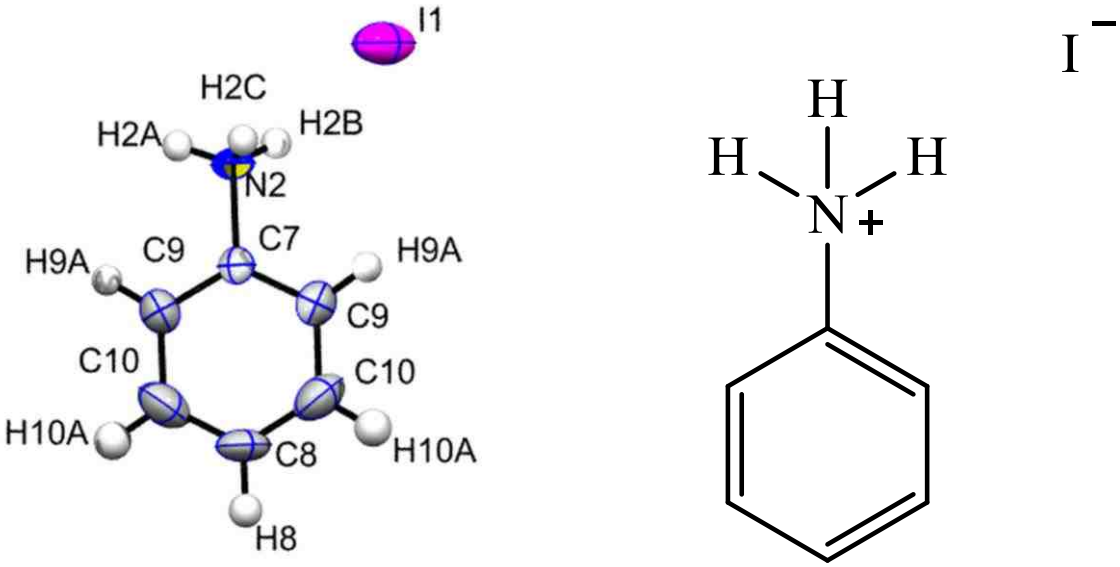


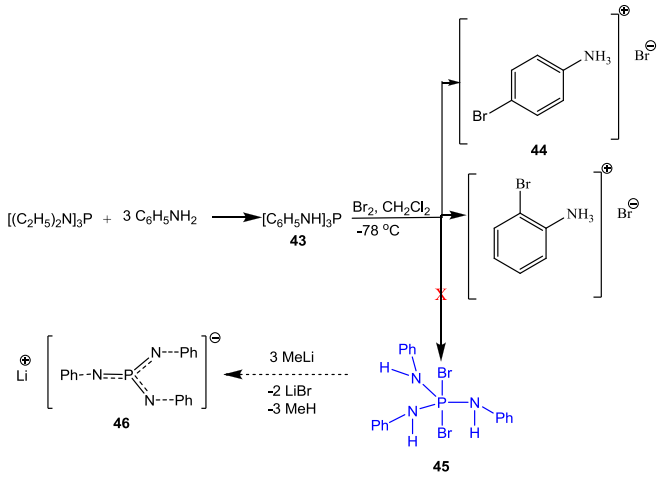
Table 2.18: Bond lengths [Å] and angles [°] for 42

N(1)-C(1)	1.42(3)
N(1)-H(1A)	0.9100
N(1)-H(1B)	0.9100
N(2)-C(7)	1.492(18)
C(7)-C(9)	1.363(13)
C(7)-C(11)	1.370(13)
C(8)-C(10)	1.372(15)
C(8)-C(12)	1.373(14)
C(1)-N(1)-H(1A)	109.5
C(7)-N(2)-H(2A)	109.5
C(7)-N(2)-H(2B)	109.5
H(2A)-N(2)-H(2B)	109.5
C(7)-N(2)-H(2C)	109.5
C(9)-C(7)-C(11)	41.5(12)
C(9)-C(7)-N(2)	116.7(13)
C(10)-C(9)-H(9A)	121.9
C(8)-C(10)-C(9)	119(3)
C(12)-C(11)-C(7)	120(2)
C(11)-C(12)-C(8)	116(2)
C(7)-C(9)-C(10)	116(3)
C(8)-C(10)-C(9)	119(3)

The numbers in parentheses are estimated standard deviations of the least significant digits as they can be seen in all Tables (2.1 to 2.18). Also a summary of novel compounds can be found in the appendix I page 137.

2.7. Synthesis of anionic ligand compound 46

Scheme 24. Attempted synthesis of N-[bis(phenylamino)phosphino] benzenamine compound **43** and its bromination



The synthesis of precursor **43** has been previously reported.[14] N,N,N',N',N'',N''-hexaethylphosphinetriamine (14.80 g, 67 mmol) was added to a 250 mL flask with a magnetic stirrer in the dry box. Aniline (16 mL, 180 mmol) was added in a dropwise fashion to dissolve the solid compound **43**. Upon addition of the aniline, the color of the mixture gradually changed from colorless to light green/yellow. The reaction was heated at 55 ^{o}C for 6h. Periodically (every 30 minutes), the volatile components were removed by vacuum into a cold trap before reaching the end of the schlenk line trap, yielding 10 mL of condensed diethylamine side-product. After cooling overnight, a white crystalline solid was detected on the walls of the reaction flask. The solid dried under *vacuo* for 23h to ensure that of the aniline was removed. The dry solid was dissolved in 150 mL of diethyl ether and undissoved residue was removed by filtration. The filtrate was placed at 6 ^{o}C for 15h. White crystals were formed and collected by filtration. This procedure

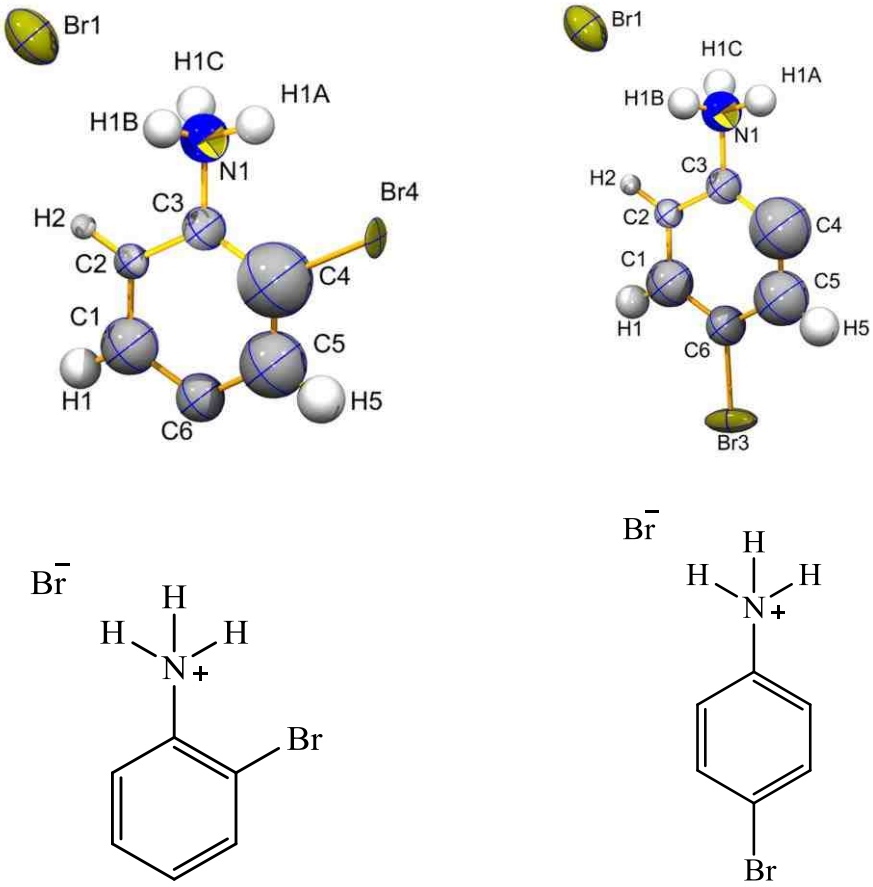
resulted in 1.5 g of product (7.5% yield, mp = 108-111 ^{o}C). The ^{1}H NMR spectrum (250 MHz, CD_2Cl_2, 298 K, ppm): δ = 5.51.82 (s) (s, 3H, NH), 7.50-7.90 (m, 15H, Ar-H). The $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz, CD_2Cl_2, 298 K, ppm): δ = 69 (s) with H_3PO_4 as a reference. The mass spectrum showed the most intense peak of the parent molecular ion [$M+H^+$] to be at *m/e* = 308.1. All of these analyses were consistent with the structure of compound **43**.

2.7.1. Bromination of N-(bis(phenylamino)phosphino)benzenamine compound 43

Compound **43** (0.10 g, 0.33 mmol) was added to a 25 mL flask with a magnetic stirrer in the dry box and dissolved in 10 mL 80:20 diethyl ether:dichloromethane. This mixture was stirred under argon and placed at -78 ^{o}C for 10 minutes. Then to the mixture, bromine (0.02 g, 0.33 mmol) dissolved in 2 mL of 80:20 diethyl ether:dichloromethane was added dropwise for 10 minutes. During addition, the color of the mixture changed from colorless to yellow. Ultimately, a red precipitate was generated. This reaction mixture was allowed to stir under argon at room temperature overnight. After 14h, the mixture contained red oil droplets. After another 12h, a yellow precipitate began to form. The reaction was continued for another 40h, yielding a light yellow precipitate. The reaction was filtered in the dry box using fine fritted glass filter. Both filtrate and solid were dried under *vacuo* for 12h. Both melting point and percentage yield were not determined because recrystallized product contained mixture of crystalline and powder. Recrystallization of crude solid in THF resulted in compound **44**. The ^{1}H NMR spectrum (250 MHz, THF-d_8, 298 K, ppm): δ = 3.82 (s, 3H, NH), and

6.68-7.06 (m, 15H, Ar-H). The ^{31}P {^{1}H} NMR spectrum (101.3 MHz, THF-d_8, 298 K, ppm): δ = 6.0 (s) with H_3PO_4 as a reference. Single crystal X-ray analysis revealed a co-crystal of the ortho and para structures of the known compound,[15-17] designated compound **44**, as shown in **Figure 2.17**, which are both known compounds.

Figure 2.17. Molecular Structure for Bromobenzenaminium bromide



2.8. References

1. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
2. Haasnoot, G. J.; Veldhuiezen, Y. S. J.; Veldman, N.; Spek, A. L.; Faulmann, C.; Reedijk, J. *Inorg. Chem*. **1995**, *34*, 140.
3. Issleib, K.; Abicht, H. P. *J. Prakt. Chem.* **1970**, *312*, 456.
4. Osborn, J. A.; Bahsoun, A. A.; Voelker, C.; Bonnet, J. T.; Lavigne, G. *Organometallics*, **1982**, *1*, 1114.
5. Neugebauer, D.; Karsch, H. H. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 484.
6. Karsch, H. H. *Z. Naturforsch*, **1979**, *34B*, 1178.
7. Brown, R. S.; Neverov, A. A. *J. Org. Chem*. **1998**, *63*, 5977.
8. Kubas, G. J.; Van der Sluys, L. S. *Inorg. Synth.* **1990**, *28*, 29.
9. Swaringen, Jr., R. A.; Eaddy, J. F.; Henderson, T. R. *J. Org. Chem*. **1980**, *45*, 3986.
10. Romanenko, V. D.; Tovstenko, V. I.; Markovski, L. N. *Synthesis*, **1980**, 823.
11. Romanenko, V. D.; Ruban, V.; Ikasanova, S. V.; Polyachenko, L. K.; Markoski, N. L. *Phosphorus and Sulfur and the Related Elements*, **1985**, *22*, 365.
12. Kostina, V. G.; Feschchenko, N. G. *Zhurnal Obshchei Khimii*. **1979**, *49*, 2452.
13. Fecher, G.; Weiss, A. *Ber. Bunsenges. Phys. Chem*. **1986**, *90*, 1.
14. Norman, A. D.; Tarassoli A.; Haltwanger, R. C. *Inorg. Chem*. **1982**, *21*, 2684.
15. Willet, R. D. *Inorg. Chem.* **2001**, *40*, 966.
16. Gray, L.; Jones, P. G. *Z. Naturforsch., B*: *Chem. Sci*. **2002**, *57*, 61.
17. Jones, P. G.; Lozano, V. *Acta Crystallogr. Sect. E: Struct. Rep*. **2003**, *59*, 1092.

CHAPTER THREE

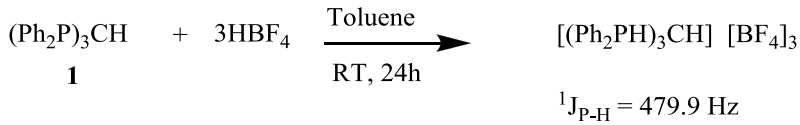
Results, Discussion, Conclusions and Future Directions

The goal of this study was to synthesize and characterize a set of coordination complexes containing 6π-cationic ligands. These compounds could be extremely useful as catalysts for the polymerization of olefins that are widely used in the synthetic polymer industry.

3.1. A synthetic approach to 6π-cationic ligands using phosphorus-based ligands

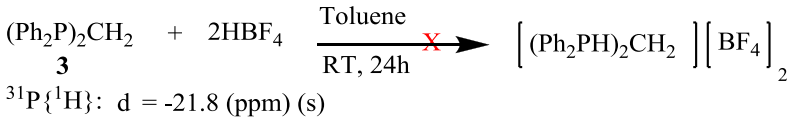
The original strategy for the synthesis of 6π-cationic ligands was to use $(Ph_2P)_3CH$ (**1**) and $(Me_2P)_3CH$ (**10**) as precursors. Analysis of the products using ***Scheme 1*** by thin layer chromatography and NMR analysis showed that this scheme leads to a mixture contains two different compounds. These were separated by column chromatography, starting with 100% dichloromethane (DCM), followed by 25% methanol (MeOH)/DCM as eluents. The first fraction contains the known compound $Ph_2PCH_2PPh_2$[1] (**3**) and the second contains an unknown compound that is slightly polar. Compound **3** was recrystallized in DCM and single crystal X-ray analysis confirmed the structure as shown in **Figure 2.1**. We tried to identify the unknown compound using NMR; however, because the small size of crystals collected, they were unsuitable for X-ray analysis. Despite our failure to obtain a crystal structure, the ^{31}P hydrogen-coupled NMR spectrum supports the possibility that the unknown is phosphonium. This is based on a comparison of phosphorus-hydrogen coupling of the unknown which is $^1J_{P\text{-}H}$ = 474.0 Hz and the one I obtained in experimental ***Equation xii*** for comparison, which

has revealed high phosphorus-hydrogen coupling constant value. I confirmed this by synthesizing phosphonium using the scheme shown below:



(xii)

The $^{1}J_{P\text{-}H}$ value for the unknown compound is comparable with the compound formed in equation xii above. Also a similar reaction was done by using bis(diphenylphosphino) methane compound **3** as follows:



(xiii)

From the ^{31}P NMR spectrum, there was no phosphorus-hydrogen coupling noted in equation xiii. This was carried out in order to establish if the phosphorus-hydrogen coupling value of the unknown (unidentified) compound match with both protonation reactions ***Equation xii***, and ***Equation xiii***.

In order to understand if $B(C_6F_5)_3$ is bound to the unknown complex as a counter anion, $^{11}B\{^{1}H\}$ NMR analysis of the unknown compound was carried out. This revealed that boron is at a higher field i.e., -2.7 (ppm) (s), which implies it is more shielded and probably is in the form of $\{HB(C_6F_5)_3\}^{-}$. It is also coordinated when compared with neutral $B(C_6F_5)_3$, which is at low field (50.2 (ppm) (s)). Thus, with no crystal structure, at this point, it is difficult to know definitively the identity of the unknown complex.

The fact that the targeted 6π-cationic ligand compound **2** was not formed in

Scheme 1 may be due to several reasons. The Lewis acid may either abstract hydride ion or react at the phosphorus center.[2] Also as phosphino substituents increase at methane carbon, nucleophilicity of that carbon should decrease both for steric and electronic effects.[3] This might have contributed to phosphorus reactivity and consequently led to the formation of $Ph_2PCH_2PPh_2$ (**3**) that exists as a stable compound. It is also possible that an unanticipated disproponationality might have happened, which resulted in unusual reactivity of $(Ph_2P)_3CH$ (**1**) leading to similar results even at different reaction conditions. In addition, *such facile P-C bond cleavage* has been observed by Grim[4] and his co-workers when

they attempted to oxidize compound **1** with H_2O_2 ***Equation xiv***.

$$\underset{\mathbf{1}}{(Ph_2P)_3CH} + H_2O_2 \text{ (excess)} \xrightarrow[H_2O]{\text{Acetone}} [Ph_2P(O)]_2CH_2 \qquad \text{(xiv)}$$

I next attempted ***Scheme 2***. I posited that this would lead to the synthesis of compound **4.** However, instead, I obtained starting material **1** and compound **4***. From the $^{31}P\{^1H\}$ NMR spectrum, the phosphorous atom in the compound was shown to be bound in a monodentate fashion of phosphorus atom to the Lewis acid $B(C_6F_5)_3$. Such bonding has 9.4 (t), 15.4 (d) ($^2J_{P\text{-}P}$ = 43 Hz) and phosphorus atoms are coupled to each other.

I next attempted to synthesize compound **5** using ***Scheme 3*** by reacting the phosphine compounds PMe_3 and PPh_3 with the Lewis acids (EF_5 E = Sb, Ta) to examine if they might react with phosphorus. However, in both cases there were no reaction observed, as revealed by $^{31}P\{^1H\}$ NMR spectroscopy. Compound **5** in ***Scheme 3*** could

not be isolated due to the fragmentation of the starting material $(Ph_2P)_3CH$ (**1**), into $Ph_2PCH_2PPh_2$ (**3**), as well as many other compounds whose identities are not known because of limited solubility of the final products in DMSO. These results again underscore the unusual reactivity of compound **1**.

I then attempted to synthesize compound **6** through lithiation of compound **1** in ***Scheme 4***, and lastly to form a halogenated form of compound $(Ph_2P)_3CBr$ (compound **7**) using ***Scheme 5***. Neither scheme was successful. The reactivity competition probably resulted in Ph_2P- cleavage, followed by the rearrangement, leading to the formation of **1** and **3** as stable compounds, with ration of the $^{31}P\{^1H\}$ NMR peaks intensity ratio of 1:2 respectively (see **Figure 2.2**). Abstraction of methine proton (H^+) attempted by Grim *et al*. showed that even with a phosphorus compound $(Ph_2P{=}S)_3CH$ protected by reacting with a variety of base to form $[(Ph_2P{=}S)_3C]^-$ the synthesis was unsuccessful.[5] These investigators were only able to isolate a product in the form $(Ph_2P{=}S)_3CHgCl$ when they mixed $(Ph_2P{=}S)_3CH$ with mercuric halide in ethanol.[5] These results demonstrate how difficult it is to abstract a tertiary proton from precursor **1** using any base.

In ***Scheme 5***, when compound **1** reacted with NBS in 1:2 mole ratio, the reaction produced the starting material, as indicated by ^1H NMR spectrum. However, $^{31}P\{^1H\}$ NMR spectrum showed new peaks. When the reaction mole ratio was changed to 1:3, the ^1H NMR spectrum did not show a tertiary P_3C-H at 4.30 (ppm) (s), unlike the first attempt. The extra addition of NBS in the bromination reaction seemed to be necessary in order to obtain the required product.[6,7] Nevertheless, the intended compound **7** in ***Scheme 5*** was not isolated. Instead, diphenylphosphinic acid (compound **8**) was

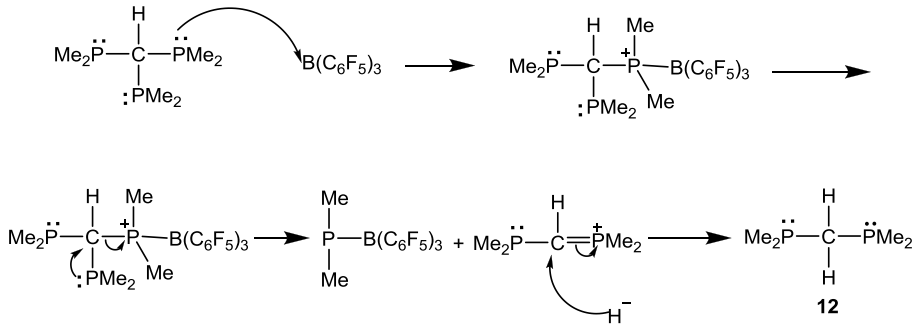
produced in a yield of about 60%, based on observed $^{31}P\{^{1}H\}$ NMR peak intensity ratio was isolated. The dry crude product isolated was insoluble in non-polar organic solvents, but soluble in DMSO and acetonitrile (CH_3CN). Recrystallization of the crude product, which was subsequently shown to be two compounds, was done in CH_3CN. Single crystal X-ray analysis revealed compound **8** to be a known compound.[8,9] The structure of compound **8** possesses strong **intermolecular** hydrogen bonding in a self-assembled complex, which has not been previously reported in the literature (see **Figure 2.3**, and **Table 2.1**). Such hydrogen bonding appears to be quite strong based on O(2)-H(1)**….**O(2) bond angle 173^{o}, which is close to 180^{o}. In addition, the second compound in the mixture did not crystallize.

A product, similar to compound **8** was obtained in ***Scheme 6***, though under slightly different reaction conditions. In ***Scheme 6***, compound **8** was produced in relatively less amounts compared to ***Scheme 5***. Also another compound with $^{31}P\{^{1}H\}$ NMR at 24.5 (d, J = 13 Hz), which was not observed in ***Scheme 5*** was revealed in ***Scheme 6*** . The source of oxygen that led to the formation of **8** is not clear; it may be from the solvents, dibenzoyl peroxide decomposition during the reaction, or dibenzoyl peroxide oxidized phosphorus (as it is a good oxidant). It is possible that this problem could be addressed in the future by purifying all solvents to eliminate the possible source of the oxygen. Alternatively, azobis(isobutyronitrile) (AIBN) could be employed as a radical initiator, which has no oxygen in its molecular structure.

I next used ***Scheme 7*** to attempt to produce the 6π-cationic ligand, compound **11.** However, again molecular fragmentation occurred at the Me_2P- groups and resulted in

$(PMe_2)_3CH$ (**10**) and the formation of $Me_2PCH_2PMe_2$ (**12**). The starting material **10** was has converted to **12** with a 50% yield, based on $^{31}P\{^1H\}$ NMR peaks intensity ratio shown in Figure 2.4. According to previous published work,[2,3] it is well known that $(Me_2P)_3CH$ (**10**) is among a rare class of compounds with three nucleophilic centers, which may compete for electrophiles when three phosphorus atoms are linked to the same carbon atom. When compound **10** or compound **1** were reacted with the Lewis acid $B(C_6F_5)_3$, which is electrophilic in nature, ***Scheme 25*** might be a possible mechanistic route for the stable formation of $Me_2PCH_2PMe_2$ (**12**) or $(Ph_2P)_2CH_2$ (**3**). However, the bond formed between P-B is derived from the interaction of a soft base with a hard acid, and its strength is undefined, based on the Pearson principle.[10] If the P-B bond formed between the two atoms is not strong enough, it may easily cleave, resulting in the formation of Me_2P- or Ph_2P- ions in solution. Step 1 of the proposed mechanism (***Scheme 25***) is supported by reaction step observed in ***Scheme 2***, where compound **4*** was identified by $^{31}P\{^1H\}$ NMR. The possible source of hydride (H^-) in ***Scheme 25*** is most likely coming from the solvent mixtures or during disproponation reaction if it happened.

Scheme 25. Possible mechanism route for the formation of $Me_2PCH_2PMe_2$ (compound **12**) or $Ph_2PCH_2PPh_2$ (compound **3**)



3.2. The attempted synthesis of 6π-cationic ligands using halogenated version of compound 10.

Another strategy for the synthesis of 6π-cationic ligands was to synthesize the halogenated version of the tertiary carbon atom of compound **10**. I reasoned that by halogenating the tertiary carbon atom of compound **10**, it would become easier to oxidize and to form the cationic ligand. ***Scheme 9*** shows my approach. However, the predicted product, compound **13** (***Scheme 8***) was not produced. When **10** reacted with strong Lewis acid (SbF_5) it resulted in a white/brown sticky solid, which was only soluble in DMSO. $^{31}P\{^1H\}$ NMR revealed three peaks, which could not be characterized due to the insolubility of the product.

Scheme 9 is a second approach to the halogenation to precursor **10**. I first synthesized the lithimun salt $(Me_2P)_3C^-Li^+$ (compound **14**), which as shown in equation iv was isolated in good yield using an established method.[11] Elemental analysis for compound **14** is shown in **Table 2.2**. The bromination of $(Me_2P)_3C^-Li^+$ (compound **14**) resulted in a mixture of products, based on observed $^{31}P\{^1H\}$ NMR peaks. The $^{31}P\{^1H\}$ NMR peak at 38.1 (ppm) (s) corresponds to those peaks observed in ***Scheme 10*** and **Scheme 12**. Also, a mass balance after bromination showed ~10% higher weight for the product than expected. The mass spectrum (ESI) *m/e* (fragment relative intensity) showed the following peaks: $(M + Na^+) = 297.1$ and $(M + Na^+) = 377$. Based on an exact mass of 274, both mono and dibrominated products appear to have been produced. I could not determine the structure of dibrominated product. There is a possibility that the

phosphorus atoms along with the nucleophilic carbon atom were brominated. Similar observations have been previously reported.[12] However; it is clear that the intended compound **16** product was not produced. .

The next approach that I took to the bromination reaction is shown in ***Scheme 11***. The lithium salt, compound **14**, was reacted with compound **17**. X-ray analysis revealed the unexpected product, compound **19**, which was 2,4,6-trimethylpyridinium bromide (see **Figure 2.5**). The structure has not been previously reported in the literature. In compound **19**, both the NH and the CH_3 groups were disordered. The ring has a positive charge due to the H atom attached on the N; this balances the Br- ion. The ions are held together by hydrogen bonds (see **Table 2.4**). The bond length for N-C is 1.368(4) Å, which is slightly longer than 1.338(3) Å observed by Ishida[13] and 1.355(7) Å observed by Kalateh *et al.*[14] for the related compounds. The reason for such differences in bond length is most likely due to the disordered structure of compound **19**.

Several fractional recrystallizations were carried out on the crude product to ensure that all traces of compound **19** were separated from the mixture. After extensive recrystallization, $^{31}P\{^{1}H\}$ NMR of the product revealed two unknown compounds, which. $^{31}P\{^{1}H\}$ peak intensity ratio ((39.0 (ppm) (s) and 21.6 (ppm) (s)) of 7:1. The impure product was re-dissolved in the solvent system of THF, CH_3CN, CH_2Cl_2, and petroleum ether and placed a freezer for two months. A precipitate formed, which turned out to be 2,4,6-trimethylpyridinium bromide (compound **19**), as confirmed by ^{1}H NMR. The evaporated filtrate had a $^{31}P\{^{1}H\}$ NMR spectrum that showed a clean single peak at 38.5 ppm (s) (see **Figure 2.6**). This suggests that the mixture contains probably compound

$(PMe_2)_3CBr$ (compound **15**), which was my intended target product, although contaminated with compound **19**. The impure product was further re-dissolved in a solvent system of THF, CH_3CN, CH_2Cl_2, petroleum ether and placed in the freezer for an additional month. The products were by filtration and the filtrate was further fractionated using column chromatography. I was unable to go further in the purification process. However, if compound **15** could be obtained, ***Scheme 9*** would be a very viable procedure for the synthesis of the 6π-cationic ligand compound **16**.

I next approached the bromination reaction by using NBS, as shown in ***Scheme 12***. This produced a mixture of products, as indicated by $^{31}P\{^1H\}$ NMR. The spectrum included a peak at 38.3 (ppm) (s), which corresponds to the peak at 38.5 (ppm) (s) obtained in ***Scheme 11*** (see **Figure 2.6**). This peak is most likely compound **15** based on the comparison of the $^{31}P\{^1H\}$ NMR spectra for the products derived from the three experiments done at totally different reaction conditions in ***Scheme 9, Scheme 11*** and ***Scheme 12*** respectively.

3.3. Use of group 6B metal carbonyl complexes to stabilize precursor 1

I reasoned that if I coordinated compound **1** with group 6B metal carbonyl complexes, it would be easier to reduce the reactivity of the phosphorus atoms and stabilize the ligand.

Complex **21** was formed by reacting $Mo(CO)_3(C_2H_5CN)_3$ (compound **20**) with $(Ph_2P)_3CH$ (compound **1**) in 1:1 stoichiometry as indicated in ***Equation vi***. Recrystallization of the crude product was carried out in dichloromethane and the mixture

was left to evaporate slowly to half of the volume in the dry box. The reaction was then placed in the freezer for over a week, and crystals were obtained. Elemental analysis of the product, designated compound **21**, $Mo(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$, is shown in **Table 2.5**, and is in good agreement with the calculated values. Single crystal X-ray analysis revealed a novel structure (see **Figure 2.7** and **Table 2.6**). The crystal structure has a crystallographic mirror plane passing through Mo(1), P(2), C(3), C(22)-C(24), and the molybdenum has an approximately octahedral coordination. The restricted bite angle of the phosphine, which is 67.24(3)^o, results in distortion of the P-Mo-P structure. This bite angle is smaller than that which is observed in the square-planar complex $[Pt\{(PPh_2)_2CHPPh_2\}_2][BF_4]_2$,[15] (72.2(1)^o), where both ligands chelate the metal center. Similar values for the following molybdenum compounds have been observed: 67.3(1)^o for $[Mo(CO)_4\{(PPh_2)_2CH_2\}]$[16]; 67.77(4)^o for $[Mo(CO)_4\{(PPh_2)_2CHPPh_2AuCl\}]$[17]; 67.829(11)^o for $[Mo(CO)_4\{PPh_2CH(Pr)PPh_2\}]$[18] and 67.941(12)^o for $[Mo(CO)_4\{PPh_2CMe(Et)PPh_2\}]$.[18] The chelate ring formed in compound **21** by Mo, P(1), C(3) P(1) is approximately planar, but is folded about the P**….**P axis. The strain of the four-membered chelate ring in the P(1)-C(3)-P(1) angle of 94.34(12)^o represents a significant deviation from ideal tetrahedral geometry at C(3). All three Mo-O separations in compound **21** lie in the range 3.110-3.128 Å. The angles Mo-C-O, in the range of 176.8-177.6^o, can be compared with values in other metal complexes in the solid state.[19] The Mo-C bond lengths in the hexacarbonyl and tricarbonyl are 2.06 and 1.94 Å respectively.[20] The values of 1.990,[21] 1.96-2.07,[22], 1.95-1.96,[23] 1.95,[24] 1.93-2.01,[25] and 1.93 Å[26] for the Mo-C bond have been reported for other molybdenum carbonyl

complexes. In compound **21** the Mo-C distances of 1.946(3) and 1.977(2) Å fall into two distinct groups whose values can be placed on the two extremes of the Mo-C bond lengths cited. The *trans* CO group to Mo-P(1) has a longer Mo-C(1) 1.977(2) Å bond length than CO {Mo-C(2) 1.946(3) Å}, which is not *trans* to Mo-P(1). The reason is probably because carbon is a better π-acceptor than phosphorus. The carbonyl group also has a large *trans* effect, in the formation of this complex.[16] The Mo-C bond *trans* to the Mo-P bond in $Mo(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$ (**21**) is expected to receive a greater share of the d_π orbital electron density, leaving only less for the Mo-P d_π-d_π back-bonding.[16] It is, therefore, the difference in the extent of π-bonding that accounts for such differences in the Mo-C bond lengths. The Mo-P distance of 2.4962(6) Å is relatively shorter than 2.71 Å, the sum of the covalent single-bond radii (1.61 Å for the Mo^o atom and 1.10 Å[27] for the phosphorus atom). This shortening is most probably due to the presence of d_π-d_π back-bonding. The values of 2.51,[21] 2.517,[22] 2.518-2.537,[25] and 2.476 Å[24] have been observed in other molybdenum complexes. The P-C(sp^3) bond distance of 1.864(3) Å for compound **21** is comparable with values of 1.88(1) Å,[15] 1.77(6) Å,[17] and estimated single bond lengths of about 1.87 Å by Pauling[28] and Kojima *et al.*[29] The mean C-C bond length and C-C-C bond angle for the six phenyl groups in structure **21** are 1.383 Å and 119.9° respectively. These values are comparable to those observed by Cheung *et al.*[16] which is 1.37 Å and 120.0° respectively. Furthermore, the crystal structure **21** is disordered in the hydrogens of the terminal methyl group.

The ^1H NMR spectrum of the crystal structure for compound **21** revealed triplets and a quartet with ($^3J_{H\text{-}H}$ = 7.5 Hz, $CH_3CH_2^-$), which means the protons are coupled to

each other. The $^{13}C\{^{1}H\}$ NMR spectrum was not informative, particularly the signal of the carbonyl carbon, due to a very poor signal-to-noise ratio. A similar situation has been encounted by Mague *et al.*[30] when they tried to determine $^{13}C\{^{1}H\}$ of $\{Mo(CO)_4TPM\}$ and also by Braterman *et al.*[31] Phosphorus atoms are bonded to the metal in bidentate fashion for $[Mo(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$ -24.8 (t), 22.7 (d) ($^{2}J_{P\text{-}P}$ = 25 Hz)] and they are coupling with each other with a coupling constant of 25 Hz.

The IR υCO for compound **21** has high frequency because of the relative increase in the CO force constant. This is due to the fact that phosphine ligand, like CO, has two bonding modes. First, is sigma donation of a phosphine lone pair to an empty orbital on the metal. Second, is backdonation from a filled metal **d** orbital to an empty orbital on the phosphine ligand.[32,33] As electron withdrawing groups are attached to the phosphorus atom, the sigma-donating ability of the phosphorus tends to decrease. On the other hand, the pi-antibonding on phosphorus is lowered in energy; this allows the backbonding capacity to increase.[32,33] In the crystal structure of compound **21,** phosphorus is bonded with a benzene ring that is not a good electron withdrawing group, but electrons are delocalized in the ring, perhaps some how contributing to lowering the sigma-donating capacity and enhancing backbonding from metal **d** orbitals to the pi-acceptor (sigma*) phosphorus. This suggests an increase in the CO force constant is observed. Another possible reason for the observed increase in the υCO is the following: In general, when electronegative groups are attached to the phosphorus atoms, a decrease in υC=O, by withdrawing electrons from the metal is observed, thus increasing the triply bonded resonance form, between C and O ($C \equiv O$)[34] relative to the doubly-bonded form between

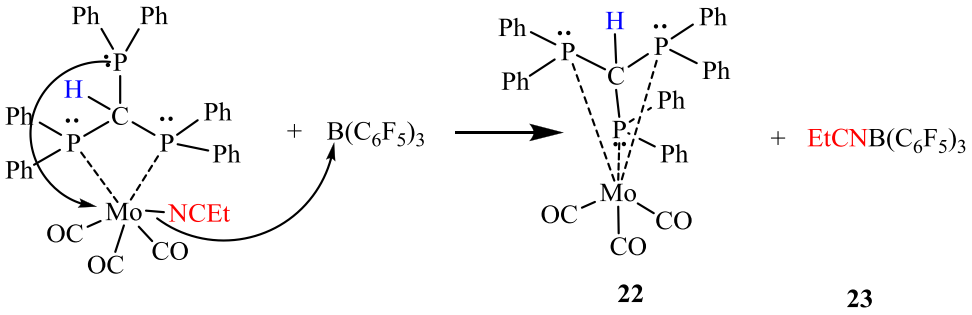
C=O. The observed strong υCO frequencies in compound **21 (**1930 (s) cm^{-1} and 1785 (s) cm^{-1}) are closely related to those observed by Chatt *et al.*[34] in $[Mo(CO)_4\{C_2H_4(PPh_2)_2\}]$ (1843 (s) cm^{-1} and 1774 (s) cm^{-1}).

When compound **21** was reacted with the Lewis acid $B(C_6F_5)_3$, $CH_3CH_2CNB(C_6F_5)_3$ (compound **23**) was generated as a crystal, while leaving compound **22** in CD_2Cl_2 solution. The crystal structure of novel compound **23** was established by X-ray analysis. The structure and a summary of selected bond lengths for compound **23** are shown in **Figure 2.8** and **Table 2.7**. The boron coordination geometry in compound **23** is slightly distorted tetrahedral geometry with average N-B-C(aryl) angles of 105.85(12)^o. The latter is relatively close to the tetrahedral geometry compared to $CH_3CNB(C_6F_5)_3$ which has an average N-B-C(aryl) angles of 114.3(2)^o observed by Jacobsen *et al.*[35] The crystal structure of compound **23** is close to linear, with the bond angles C(1)-N(1)-B(1) 173.90(16)^o and C(2)-C(1)-N(1) 176.75(18)^o both being close to 180^o. The observed N-B-C(aryl) angle for compound **23** is not a linear as that for $CH_3CNB(C_6F_5)_3$ (C(2)-N(1)-B(1) 177.1(2)^o and C(2)-C(1)-N(1) 178.9(3)^o) observed by Jacobsen *et al.*[35]. Furthermore, the C(2)-C(1) bond length is 1.442(2) Å for compound **23**, and thus is the expected C(sp^3)-C(sp) single bond range which is 1.459 Å measured by Costain *et al.*[36] However, the C(1)-N(1) 1.136(2) Å bond length of compound **23** is slightly higher by 0.012 Å than the one observed by Jacobsen *et al.*[35] for $CH_3CNB(C_6F_5)_3$.

Compound **23** was unable to be completely separated from $Mo(CO)_3(C_2H_5CN)(Ph_2P)_3CH$ (compound **22**), although I was able to pick a single

crystal for the crystallization to obtain the X-ray structure. The reason for the side reaction that formed compound **23** is possibly due to the fact that, when all other things are equal, the hard base binds to the hard acid to form a bond with substantial ionic character.[37-40] This was a driving force for the reaction when the hard base nitrogen bonded to the hard acid boron in the formation of crystals of **23** as well as **22,** which did not crystallize. This is the only possible route for the formation of compound **23** (see ***Scheme 26*** below). According to Pearson[10], phosphorus is a relatively "soft" base, and cannot easily bond with the "hard" acid boron, but the bonding between a soft acid and a hard base has not been clearly defined. Phosphorus can donate its lone pair into the benzene ring, which will make the phosphorus atom partially positive. The neighboring tertiary carbon is relatively electronegative, but being bonded to three phosphorus atoms, there is no way that it is electron rich. Therefore, the chance of abstracting a hydride from such carbon is low. Despite obtaining a crystal structure for compound **23** using the single crystal, both elemental analysis and percentage yield were unable to be determined due to the scarcity of pure material.

Scheme 26. Possible route for the formation of **23**



The $^{31}P\{^{1}H\}$ NMR spectrum of novel compound **22**, $Mo(CO)_3(Ph_2P)_3CH$, has is shown in **Figure 2.9**. However, crystallization was not achieved. Initial NMR characterization revealed that the phosphorus is bonded in a tridentate fashion to the metal, which is based on the observed $^{31}P\{^{1}H\}$ NMR peak at 11.0 (ppm) (s).

The novel compound **25**, $W(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$, was formed when $W(CO)_3(C_2H_5CN)_3$ (**24)** reacted with $(Ph_2P)_3CH$ (**1**) in a 1:1 metal complex-to-ligand stoichiometry (shown in equation viii). Elemental analysis for compound **25** (see **Table 2.8**) was in good agreement with the calculated values for only nitrogen and hydrogen. However, the difference in % carbon between experimental and calculated values was significant, most likely due to partial decomposition as well as due to impurities that may have been trapped in the crystal lattice. Recrystallization in dichloromethane carried out in the dry box for a longer period yielded a few crystals suitable for X-ray analysis. A single crystal X-ray analysis yielded a novel structure as shown in **Figure 2.10** and **Table 2.9**. The crystal structure has a mirror plane passing through W carbonyl of C(2)-O(2), NCEt and the ligand through P(2) and C(3). The coordination of the tungsten atom, by the two phosphorus atoms of the ligand, CH_3CH_2CN, and three carbonyl groups displayed an approximately octahedral arrangement. The bite angle of the phosphine, P-W-P $67.23(5)^{o}$ is comparable with those observed for $[W(CO)_4\{(Cy_2PCH_2PCy_2\}]$,[18] and $[W(CO)_4\{(Ph_2P)_2C{=}HCH{=}HCPh\}]$,[40] which are $67.20(2)^{o}$ and $68.1,^{o}$ respectively. The chelate ring formed by W, P(1), C(3), P(1) in compound **25** is approximately planar, but it is folded about the P**…..**P axis. There is strong strain of the four-membered chelate

ring in the P(1)-C(3)-P(1) angle of 94.2(3)^{o}, which is a significantly reduced from the tetrahedral geometry at C(3) by 15.3^{o}. This is slightly contrary to the geometry reported for $[W(CO)_4\{(Ph_2P)_2C=HCH=HCPh\}]$,[40] which has a P(2)-C(13)-P(1) angle of 100.7(4)^{o} and $[W(CO)_4\{(Cy_2PCH_2PCy_2\}]$[18] that has P(2)-C(13)-P(1) angle of 98.21(13)^{o}. In both cases the angles are reduced by 8.5^{o} and 11.29^{o} from tetrahedral geometry, respectively.

All three W-O separations in compound **25** are in the range of 3.124-3.125 Å, which is comparable to 3.142-3.176 Å observed by Cheung *et al*.[16] The angles W-C-O in the range 177.4-177.8^{o} can be compared with values for other metal complexes, for example, 172.4-176.3^{o} [16] and 173.4-175.9^{o}.[41] The W-C bond lengths for other tungsten carbonyl complexes have been reported for the following: $[W(CO)_4\{(Ph_2P)_2C=HCH=HCPh\}]$[40] in the range of 1.980-2.036 Å,[41] $[W(CO)_4(PTA\text{-}PPh_2)]$[42] in the range of 1.972-2.048 Å[42], and $[W(CO)_4(DPPM)]$[42] is in the range of 1.980-2.036 Å[42]. In compound **25** the W-C bond distances of 1.952(7) Å and 1.971(5) Å fall into one distinct group observed by Wong *et al*.[42] The *trans* CO group to W-P(1) has relatively longer W-C(1) 1.971(5) Å than CO {W-C(2) 1.952(7) Å }, which is not *trans* to W-P(1). The W-C(1) *trans* to the W-P(1) in **25** has a long bond length because there is a relatively large d_π electron density donated to carbon (W-C) through back-donation.[16] This implies less of d_π-d_π electron density has been donated to the phosphorus atom through W-P. Therefore the observed W-C bond length difference is due to variations in the extent of π-bonding. The W-P bond distance of 2.4866(10) Å found in compound **25** is slightly shorter when compared to the values of 2.501 Å and 2.535 Å,[16] 2.5070 Å and 2.5291 Å,[42] 2.500 Å and 2.525 Å, [43] and 2.5187 Å and 2.5324 Å,[14] observed in other

tungsten complexes. The P-C(sp^3) distance of 1.880(4) Å for compound **25** is comparable with values of 1.830(7) Å,[39] 1.852(19) Å,[41] and estimated single bond lengths of about 1.87 Å by Pauling[28] and Kojima *et al.*[29] The mean C-C bond length and C-C-C bond angle for the six phenyl groups in structure **25** are 1.401 Å and 118.6°, respectively. In addition, the crystal structure **25** is disordered in the hydrogens of the terminal methyl group.

The ^{1}H NMR spectrum of compound **25** revealed triplets and a quartet with ($^3J_{H-H}$ = 7.8 Hz, $CH_3CH_2^-$), which means the protons are coupled. The ^{1}H NMR revealed the hydrogen that attached at the tertiary carbon of $(Ph_2P)_3CH$ (**1**) has shifted more downfield. This suggests that the tertiary carbon is relatively deshielded in this complex, if compared with an uncoordinated precursor **1,** which is on their respective chemical shifts 5.6 (ppm) (s) for the complex and 4.1 (ppm) (s) for uncoordinated compound **1**. The $^{13}C\{^1H\}$ NMR spectrum of compound **25** was uninterpretable due to poor signal-to-noise. This most likely due to the combination of the considerable splitting of the $^{13}C\{^1H\}$ resonances by the phosphine and the unfavorable relaxation time for the carbonyl carbon atoms on tungsten. A similar problem was observed by Braterman *et al.*[31] in related tungsten carbonyl complexes. Phosphorus atoms are bonded to the metal in bidentate fashion in compound **25** with two peaks (-21.9 (t), 18.7 (d) ($^2J_{P-P}$ = 30 Hz), and they are coupled to each other with a coupling constant of 30 Hz. The W-P coupling could not be observed due to extremely poor signal-to-noise. The solubility of compound **25** might also have contributed to the problem. In addition, ^{183}W abundance being 2.1% is too low

to observe its coupling with ^{31}P under such circumstance.

The IR υCO for the compound **25** has high frequency due to a relatively increased CO force constant. The reason for observed high frequency in υCO is similar to compound **21** as discussed above for a phosphine contained ligand when it is bonded to the metal carbonyls.[32,33] The low sigma-donating capacity from phosphorus has enhanced back-bonding from filled metal **d** orbitals into the pi-acceptor (sigma*) on phosphorus and not into π* of CO. If this would have had happened to π* of the CO, it could have reduced the bond order, and resulted in a reduction of the force constant between C, and O. Another possible reasoned is that in compound **25**, when electronegative groups are attached to the phosphorus atoms, there is a progressive decrease in υC=O by withdrawing electrons from the metal, thereby increasing the triply bonded resonance form between C and O ($C \equiv O$),[34] relative to the doubly-bonded form between C=O. The observed strong υCO in compound **25** (1924 (s) cm^{-1} and 1781 (br) cm^{-1}) are similar to those observed by Chatt *et al.*[34] in $[W(CO)_4\{C_2H_4(PPh_2)_2\}]$ (1847 (s) cm^{-1} and 1782 (s) cm^{-1}).

The novel compound $W(CO)_3(Ph_2P)_3CH$, designated compound **26** was generated by the reaction shown in ***Scheme 14***. Compound **26** could only be partially characterized by $^{31}P\{^1H\}$ NMR, because was not isolated, and we were still looking for the appropriate solvent for recrystallization. Initial characterization revealed that the phosphorus is bonded in tridentate fashion to the metal, as suggested by the peak at -1.2 (ppm) (s) as seen in **Figure 2.11**.

3.4. The coordination of 6π-cationic guanidinium ligands with group 6B metal carbonyl complexes

With the very limited success of the prior strategies utilizing phosphorus-based ligands, I explored the use of guanidinium ligands to form coordination complexes with 6B metal carbonyls**.** Density function theory calculations (DFT) were used to predict the possibility that the 6π-cationic ligand of guanidinium analogs would coordinate with a group 6B metal carbonyl in a stable manner. The coordination chemistry of 6π-cationic guanidinium ligand analog $[C(NH_2)_3]^+[BF_4]^-$ (**27**) with group 6B metal carbonyl complexes was attempted at room temperature, but ultimately, the reactions were carried out under reflux and photolysis. However, all of the synthetic approaches to coordinate the guanidinium ligand with the group 6B metal carbonyl failed, including those described in ***Scheme 15*** and ***Scheme 16***.

Next, I turned to a strategy that employed the electron-deficient lanthanide salts. Compound **27** was reacted with the lanthanide nitrate salts, $Yb(NO_3)_3$ and $Tb(NO_3)_3$, in 1:1 metal complex to ligand stoichiometry as shown in ***Scheme 17***. The complex $[C(NH_2)_3]^+[NO_3]^-$ (compound **29**) was formed. IR spectrum of the Nujol mull of compound **29** showed that the υN-H band shifts to a low frequency as the result of the N-H**….**O bond weakening by intermolecular hydrogen bonding. Hydrogen from guanidinium cation interacts with the oxygen donor from nitrate (NO_3^-). This results in increasing N-H bond length and consequently a weak force constant between nitrogen and hydrogen. Recrystallization of the crude product was carried out methanol. Single crystal X-ray analysis revealed the structure shown in **Figure 2.12**. Compound

$[C(NH_2)_3]^+[NO_3]^-$ (**29**) has previously been reported in the literature using a different synthetic strategy.[44,45] The C(1) and N(2) atoms of the cation and the N(1) and O(1) atoms of the anions lie on the special positions and the ions have Cs symmetry.

Next, I used $Nd(NO_3)_3$ to react with compound **27** in 1:1 metal complex to ligand stoichiometry as shown in ***Scheme 19***, which yielded the complex of diguanidinium diaquapentakis(nitrato)neodymiate(III) (compound **30**). Crystals were formed through slow evaporation of the solvent at room temperature. The novel crystal structure of complex **30** was determined by single-crystal X-ray analysis (see **Figure 2.13** and **Table 2.12**). As seen in **Figure 2.13**, the asymmetric unit is composed of one $[Nd(NO_3)_5.2H_2O]^{2-}$ anion and half of guanidinium cation $[(NH_2)_3C].^+$ The ions are held together by N-H**….**O hydrogen bonds as shown in **Table 2.13**.

The neodymium in compound **30** is coordinated to twelve oxygen atoms from five nitrate ions, and two water molecules. The nitrate ligand coordination around the neodymium does not seem vary from other similar Nd complexes in terms of either the Nd-O bond lengths or O-Nd-O bite angles. The average Nd-O bond length is 2.6643 Å, which is only about 0.02 Å greater than that observed by Chesman *et al*.[46] [2.555(3)-2.642(2) Å][46] in a related complex. The average O-Nd-O bite angle in compound **30** is $48.43(3)^o$, which is close to 49.09^o that has been observed in $[Me_4N]_3[Nd(NO_3)_6]$.[46] The nitrate ligands in the $[Nd(NO_3)_5.2H_2O]^{2-}$ anion are positioned in a pseudo-octahedral around the metal center in an arrangement which minimizes repulsion between ligands; this has also been observed by Chesman *et al*.[47] The nitrate ligands are oriented

perpendicular to each other around the metal center. A similar arrangement of the ligands has been observed in hexanitratolanthanate(III) complexes containing structures with terpyridinium,[48] and in a methyl pyridinium-based caunter-cation.[49] The bond distance N-O for compound **30** is in the range 1.2190(2)-1.2734(15) Å as well as O-N-O bond angles are in the range 116.43(11)^{o}-122.58(13)^{o}. These results are in agreement with those of diimidazolium aquapentakis(nitrito)neodymate(III) observed by Zhang *et al.*[50], which are 1.216(2)-1.271(2) Å and 116.25(14)-122.37(15)^{o}, respectively. The guanidinium N-H and water H atoms in the compound **30** are engaged in hydrogen bonds with an oxygen atom of the nitrate groups. The hydrogen bond distances for the OH (from the water) with the O(from nitrate) and N-H(from guanidinium) with the O (from nitrate) are 2.9078(16)-3.066(3) Å and 2.852(2)-3.057(3) Å, respectively. Hydrogen bonding in compound **30** are fairly strong based on the bond angles 168(3)-173(3)^{o} for the N-H**….**O bond (nitrate) and 172(3)-175(3)^{o} for the O-H**….**O bond (nitrate). These two angles approach 180^{o}, implying that the straight line is the result of the strong stretching. The observed hydrogen bonding interaction is one of the most important non-covalent properties of the 6π-cationic ligand of guanidinium analogs.

The IR spectrum of the Nujol mull of compound **30** showed a υN-H shift to a lower frequency, which is a result of the guanidinium N-H bond weakening by inter-hydrogen bonding when hydrogen is interacting with the oxygens of nitrate (NO_3^-). Elemental analysis of compound **30** for carbon and hydrogen content (see **Table 2.11**) is in good agreement with the expected values; however, there is a slight difference in the nitrogen content. This may be due to several reasons that include the following:

(1) During analysis, it is possible that not all the nitrogens were recovered with 100% efficiency from NO_3^-. (2) The other nitrogen of the guanidinium cation is not directly chemically bound to the metal, which would make it easy for the nitrogen to be lost.

3.5. The attempted synthesis of the 6π-cationic ligand of guanidinium analog tripiperidine carbenium tetrafluoroborate

I was concerned that the failure to obtain the expected product in ***Scheme 15*** and ***Scheme 16*** might have been due to the relative insolubility of compound **27**. Thus, I attempted to synthesize the guanidinium analog tripiperidine carbenium tetrafluoroborate as shown in ***Scheme 20***. However, instead of obtaining the intended produce, compound **34**, the products compound **32** (1-tritylpiperidine) and compound **33** (diphenyldipiperidin-1-ylmethane) were obtained, neither of which have been previously reported. Single-crystal X-ray analysis revealed structures for compound **32** and **33** as shown in **Figure 2.14** and **Table 2.14**. There are two different molecules in asymmetric unit: 4 molecules per unit cell with 2 of each compound. While the C(1A) is well aligned, the C(1) atom has some unresolved disorder. In addition, the 1NC(5) unit cells are not wholly occupied, and show some phenyl group disorder. The mean bond length C-N is 1.509 Å, which is comparable with 1.502(2) Å of 1-[(3-methylpiperidin-1-yl)(phenyl)-methyl]-2-naphthol previously observed by *Wang et al.*[51] On the other hand, the C-N mean bond length is slightly longer than 1.493(2) Å of 3-[(2-hydroxy-1-naphthyl)(piperidin-1-yl)methyl]benzonitrile observed by Qu.[52]. The bond distance between central carbon C(1) and aromatic carbon C(7) and C(18) for compound **33** is in the range of 1.538(3)-1.544(3) Å, which is almost identical to the C-C(sp^3) (1.544 Å)

observed by Costain *et al.*[36] While N(1)-C(1)-N(2) bond angle in compound **33** is 109.37(2)^{o}, which is almost the same as a tetrahedral geometry, the rest of the angles N(2)-C(1)-C(7), N(2)-C(1)-C(18), C(7)-C(1)-N1), and N(1)-C(1)-C(18) are slightly above tetrahedral geometry by about 1.4-2.0^{o}. Similar deviations in the tetrahedral angle values (1.01-3.31)^{o} have been observed by Wang *et.al.*[51] for closely related compounds.

The ^{1}H NMR spectrum of the products in the reaction did not reveal the presence of a tertiary hydrogen of tripiperidine methane (**31**) $HC(N)_3$ at 3.11 δ (ppm) (s). Nonetheless, $^{11}B\{^{1}H\}$ NMR spectrum showed a 0.25 ppm difference in chemical shift between the starting material and the product after the reaction, indicating that BF_4^- did not abstract hydride from the tertiary carbon of the starting material **31**. Because of the presence of more than one compound in the mixture, the percentage yield, melting point, and elemental analysis were not determined.

The possible reasons for the formation of 1-tritylpiperidine (compound **32**) and diphenyldipiperidin-1-ylmethane (compound **33**), rather than the intended compound **34** are the following: First, a rearrangement with an unknown mechanism may have occurred. Second, the methane hydrogen of compound **31** is not easily accessible to the triphenyl carbenium due to some steric effects. A similarly low reactivity of the tertiary carbon-hydrogen with triphenyl carbenium tetrafluoroborate has been previously observed by Slutsky *et al.*[53] in the reaction of $[Ph_3C]^+[BF_4]^-$ with orthoamide, which appears to be as sterically hindered as compound **31**.

3.6. The attempted synthesis of precursor for 6π-anionic ligand in phosphorus-based complex using 2,4,6-tri-*tert*-butylaniline and PI_5

The last strategy that I to attempted, was to synthesize a 6π-anionic ligand from phosphorus-based complex using 2,4,6-tri-*tert*-butylaniline and PI_5. While this was a change from the original concept of a 6π-cationic ligand, the anionic ligands might also be useful in the synthesis of catalysts. While the desired anionic complex product (compound **37**) as shown in ***Scheme 22*** was not obtained, another novel compound, 2,4,6-tri-*tert*-butylbenzenaminium iodide (compound **38**) was produced and characterized by single crystal X-ray analysis and ^{1}H NMR. The $^{31}P\{^{1}H\}$ NMR spectrum of the crude produce revealed a signal at 5 δ (ppm) (s). After purification of the crude product by column chromatography, no phosphorus-containing compound was isolated. The filtrate was evaporated under *vacuo* and the dry solid was recrystallized in THF, resulting in a mixture of both crystals and powder.

The novel crystal structure of the compound **38** was determined by single-crystal X-ray analysis as shown in **Figure 2.15** and **Table 2.15**. In the crystal structure both the cation and anion are situated on mirror planes. The aromatic ring shows mirror symmetry, through NH_3, C(1), C(4), C(9), which includes the t-butyl group on the mirror plane. The hydrogens on N(1) are disordered as well as those on t-butyl group at C(9). The bond distance for N(1)-C(1) is 1.477(9) Å, and is slightly higher than 1.42(2) Å found in the related compound, benzenaminium iodide (compound **42**; see ***Scheme 23*** below). The mean bond length for N-H for **38** is 0.9100 Å, which is exactly the same as compound **42**, but is slightly higher than 0.89 Å for 2,4,6-trimethylanilinium iodide

observed by Lemmerer *et al*.[54]

The mean C-C bond length and C-C-C bond angle for the benzene ring of compound **38** are 1.389 Å and 119.8^{o}, respectively. Compound **38** has a similar packing arrangement to 2,4,6-trimethylanilinium iodide observed by Lemmerer *et al*.[54] In the crystal structure of compound **38** the ions are linked together by N-H**....**I hydrogen bonds (see **Table 2.16**), with a bond distance ranging between 3.390(7)-3.505(7) Å. This bond distance range is slightly shorter than that observed by Lemmerer *et al*.[54] in 2,4,6-trimethylanilinium iodide, which is 3.5570(8)-3.562(2) Å. The bond angle between N-H**….**I in compound **38** ranges between 118.6^{o}-160.1^{o}, which is lower compared to 180^{o}, and implies that this may not necessarily be a strong hydrogen bonding stretch. On the other hand, this bond angle is almost equal to the one observed by Lemmerer *et al*.[54] which ranges between 143^{o}-155^{o}.

The failure to obtain the expected product, compound **37**, was most likely due to the steric constrains of the starting material, which has three t-butyl substituent groups. Furthermore, the extra hydrogen attached on the nitrogen in compound **38** most likely came from the solvent together with the effect of using dry solvents. It is also possible that this proton came from the methanol used during column chromatography separation of the product.

In a different strategy to form the anionic ligand, I decided to use aniline (compound **39**) to form a less bulky precursor for further syntheses (see ***Equation xi***). Synthesis of compound **40** (trianilinodiiodophosphorane) has been previously described.[55] The observed ^{1}H NMR spectrum of compound **40** revealed doublets that

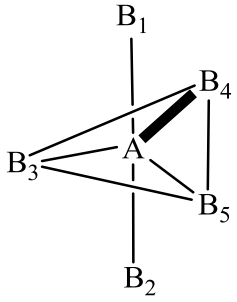
appear to be due to N-H coupled with phosphorus $^{2}J_{P\text{-}H}$ = 15.50 Hz. This was confirmed by the addition of deuterated water (D_2O) in the same NMR tube containing compound **40**, where the hydrogen exchange with deuterium occurred, eliminating the doublet peaks. Elemental analysis for compound **40** has showed good agreement with the expected values, although experimentally determined carbon values are slightly higher (see **Table 2.17**). The previous description of the synthesis of compound **40** did not include a spectroscopic analysis.

I used compound **40** to attempt to synthesis the anionic ligand complex, compound **41**, as shown in ***Scheme 23***. Although I started with a 5% excess of the required amount of methyl lithium, the reaction failed and I ended up with starting material. In the second attempt, I used a 30% excess MeLi, which resulted in molecular fragmentation. Although the $^{31}P\{^{1}H\}$ NMR spectrum of the crude product showed a signal at -13.0 (ppm) (s), this was not observed in NMR spectrum of the crystals after recrystallization of the crude products. Only a small amount of crystals were formed in the recrystallization. Single-crystal X-ray analysis revealed the structure of the crystal product to be compound **42**, benzenaminium iodide (see **Figure 2.16**), rather than the expected compound **41**. The source of extra hydrogen attached on the nitrogen in compound **42** most likely came from the solvent. The crystal structure of compound **42** has been previously reported[56]. Both the cation and anion lie on the mirror planes. The crystal structure **42** is disordered at the position of the aromatic ring. The ring on N(2) C(7)-C(9)-C(10)-C(8)-C(10A)-C(9A)-C(7) is occupied 59.5% of time and N(2) C(7)-C(11)-C(12)-C(8)-C(12A)-C(11)-C(7) is occupied 40.5% of time. The mean C-C bond

length and C-C-C bond angle for the benzene ring is 1.367 Å and 119.8^{o}, respectively.

There are several possible explanations for compound **40** fragmentation upon reacting with MeLi in ***Scheme 23***. In general the bonding in phosphorus(V) compounds shows a trigonal bipyramidal geometry (see **Figure 3.1**), whereby the two axial positions are different from the three equatorial positions.[57,58] The two apical atoms B_1 and B_2 are equivalent, but distinct from the three equatorial atoms B_3, B_4, B_5 are equivalent among themselves.

Figure 3.1. General Structure for Trigonal Bipyramid (A = Phosphorus) [58]



The literature suggest that the most electronegative substituent should occupy axial positions of the trigonal bipyramid.[57,58-63] Those axial positions of a trigonal bipyramid are most preferred by electronegative substituents because of the presence of the most electron density.[63] This leaves electropositive groups occupying equatorial positions because of **s** character in the equatorial phosphorus hybrid orbitals.[59] This is supported by ^{19}F NMR,[59,64,65] dipole moment measurements,[66] and infrared and Raman spectroscopy[67] of pentacoordinated phosphorus(V) derivative compounds, and indicates that the more stable isomers are those with the more electronegative substituent occupying axial positions. It has been observed that the axial bonds are weaker than equatorial bonds for those hybridizations of phosphorus in which the **s** character is

located in the plane.[68] Phosphorus in compound **40** is directly bonded with nitrogen and iodine. It is therefore expected that more electronegative nitrogen groups will be at the axial position and iodine, which is relatively electropositive, will occupy the equatorial position. The steric nature of the group attached on nitrogen has forced all three nitrogen groups to be attached on phosphorus at the equatorial and two iodines at the axial positions, contrary to their electronegativities strengths.

The B_3-A-B_4 angle at equatorial position, in a perfect trigonal bipyramid molecule, (see **Figure 3.1**), is supposed to be 120^o and B_1-A-B_3 angle at axial is supposed to be 90^o.[58] The trianilinodiiodophosphorane (compound **40)** has very bulky anilinyl groups, these ligands may have caused the deviation from 120^o and 90^o of the bond angles at the equatorial and axial positions. I used the software package called "Marvin Sketch" (ChemAxon Kft, Budapest Hungary)[69] to calculate the optimal angles for structure of compound **40**. The Marvin space was used to estimate the three N-P-N and I-P-N bond angles in the optimized structure, which range between 115^o-126^o, and 79^o-106^o (top face or bottom face) respectively. These results suggest that phosphorus-nitrogen bond can be easily cleaved due to the existing strain, consequently leading to the observed formation of benzenaminium iodide (compound **42**). Furthermore, compound **40** having P-N and P-I bond polarizability, is expected to be highly reactive due to an appreciable partial positive charge at the phosphorus atom.[70] Nitrogen, which has a lone pair of electrons, contributes to the stereochemical effect around the phosphorus-nitrogen bonds.[71] Compound **40** possesses some steric and lone pair-lone pair repulsion effects.

The combinations of all these steric effects most likely contributed to the high energy state of compound **40**. When such a precursor is reacted with a strong base, it will result in the formation of adducts that are lower in energy and more stable, one example being compound **42**. In ***Scheme 23***, it is most likely that the strong base caused the fragmentation of **40**, thereby leading to the formation of compound **42**. Therefore, a less nucleophilic strong base, for instance diazabicyclo[5.4.0]undecane (DBU) and lithium diisopropylamide (LDA) may be the next choice of reactants to address this problem in future studies.

Another approach to the synthesis of an anionic ligand was to synthesize a phosphine-based ligand followed by bromination. This precursor would then be lithiated to form the 6π-anionic ligand.

I synthesized N-[bis(phenylamino)phosphino]benzenamine (compound **43**) according to the literature[56] as depicted in ***Scheme 24***, with the main target being compound **46**. Reaction of compound **43** with bromine solution in a 1:1 mole ratio, yielded rather unexpected results. The bromobenzenaminium bromide (compound **44**) was obtained and not the intended brominated intermediate, compound **45**. $^{31}P\{^{1}H\}$ NMR spectroscopy of the crude product revealed a peak at 6.0 (ppm) (s). After recrystallization of the crude product in THF/hexane, $^{31}P\{^{1}H\}$ NMR spectroscopy of the crystals did not reveal the presence of a phosphorus, which apparently remained in the mother liquor. Single-crystal X-ray analysis revealed the formation of compound **44**, as shown in **Figure 2.17**, which is a known compound obtained by an alternate synthetic route.[72-74] Compound **44** is attached by the bromide ion at either **ortho** or **para** positions.

In this case, the ration of **ortho and para** substituted products was 40:60. However, each product contains one bromide at either **ortho** or **para** position. The third hydrogen attached on the nitrogen most likely came from the solvent.

Because of purity concern, the percentage yield and melting point were not determined. An explanation for the failure to obtain the intended compound **45** is that the amino group attached on the benzene ring has a strong electron donating resonance effect that is most pronounced at the **ortho** and **para** positions.[75,76] These two positions (**ortho** and **para**) permit a more **nucleophilic** attack on the electrophile than the phosphorus lone pairs. The three nitrogen atoms attached to the phosphorus are causing the phosphorus to be highly polarized, such that cannot behave as good nucleophile for the attack of the electrophile (Br^+), thereby inhibiting the bromination reaction originally predicted in ***Scheme 24***.

3.7. Conclusions

Conclusion 1. ***Experimental results have revealed that $(Ph_2P)_3CH$ (compound 1) possesses unanticipated reactivity when it is reacted with strong Lewis acids to abstract hydride or a strong base to form lithium salt.*** I had originally wanted to use this as a step towards the synthesis of 6π-cationic ligand by converting the tertiary P_3C-H compound to P_3C-Br. Such instability was a major stumbling block in the synthesis of the 6π-cationic ligand using the hydride abstraction approach due to the molecular fragmentation and formation of the more stable compound $Ph_2PCH_2PPh_2$ (compound **3**).

The reaction mechanism that may cause compound **1** upon reaction with a strong

Lewis acid or strong base to cleave into compound **3** in ***Scheme 1***, ***Scheme 3***, and ***Scheme 4*** are unknown. However, I propose the following explanation: Precursor **1** belongs to a rare class of compounds with three nucleophilic groups (Ph_2P-) directly connected at one center. Based on Pearson principle[6], the three nucleophilic centers may react with Lewis acid $B(C_6F_5)_3$ directly, though with slightly unidefined bonding interactions soft base/hard acid (P-B), instead of Lewis acid abstracting hydride as we expected. Phosphorus, being directly bonded to the benzene ring, has a lone electron pair that may participate in the resonance within the ring and cause appreciable partial positive charge on phosphorus, which will make it more reactive with the base, instead of the base abstracting the tertiary hydrogen. Presumably both incidences may contribute to the fragmentation of Ph_2P-, and result in the formation of compound **3** as a stable product at various reaction conditions.

When the precursor $(Me_2P)_3CH$ (compound **10**), three nucleophiles (PMe_2P-) connected at one center, is exposed to the Lewis acid ($B(C_6F_5)_3$), there will be a reaction with the phosphorus atoms rather than intended abstraction of the tertiary C-H by the Lewis acid. Such a reaction will weaken the P-C(sp^3) bond and cause cleavage of Me_2P- (see ***Scheme 25***), and results in the formation of $Me_2PCH_2PMe_2$ (compound **12**) as a stable product.

Thus, at this point, the use of the tertiary C-H hydride abstraction as a pathway to the formation of the 6π-cationic ligand from precursors $(Ph_2P)_3CH$ (compound **1**) and $(Me_2P)_3CH$ (compound **10**) is not a viable approach. The understanding of why both

precursors **1** and **10** are cleaving under these reaction conditions requires extensive DFT calculations to determine the charge distribution around tertiary carbon at both precursors. This will hopefully suggest alternative approaches for abstracting the *hydride* at the tertiary carbon.

Bromination of precursors **1** and **10** using NBS in catalytic amounts of benzoyl peroxide resulted in a mixture of products, including the diphenylphosphinic acid (compound **8**), which crystallized out and was characterized by single crystal X-ray analysis. Benzoyl peroxide, under the reaction conditions used in my studies, may be the source of oxidizing phosphorus. There is no evidence that tertiary hydrogen P_3C-H has been converted to P_3C-Br upon using this reaction condition. Bromination of $(PMe_2)_3C^-Li^+$ (**14**) in ***Scheme 9***, resulted in a mixture of products based on $^{31}P\{^1H\}$ NMR spectroscopy, mass balance, and exact mass, indicating that both phosphorus and nucleophilic carbon were unequivocally brominated.

Bromination of lithium salt compound **14** using bromonium triflate compound **17** according to ***Scheme 11*** unexpectedly yielded the novel compound 2,4,6-trimethylpyridinium bromide (compound **19**), as indicated by single-crystal X-ray analysis as shown in **Figure 2.5**. Repeated fractional recrystallization of the crude product yielded a clean $^{31}P\{^1H\}$ NMR spectrum as shown in **Figure 2.6**, which will most likely be $(PMe_2)_3CBr$ (compound **15**) when the compound is finally isolated. This assumption is based on the same $^{31}P\{^1H\}$ NMR chemical shift observed in other two different reactions in ***Schemes 9 and 12***. The chance of the nucleophilic carbon of the lithium salt attacking electrophile (Br^+) as depicted in ***Scheme 11*** is high. The product

obtained still requires additional fractional recrystallization workup before a pure $(PMe_2)_3CBr$ (compound **15**) can be isolated and characterized. Based on these results, it is likely that ***Scheme 11*** carried out under the right conditions and separation procedures has a much greater chance of yielding a single product than the other bromination schemes attempted.

Conclusion 2. Even when compound 1 is stabilized by the coordination to group 6B metal carbonyl complexes, the hydride is still refractory to abstraction.

Upon slight changes of strategy by coordinating two phosphorus atoms of precursor $(Ph_2P)_3CH$ (compound **1)** to group 6B metal carbonyl, the novel compounds $Mo(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$ (**21**), $W(CO)_3(C_2H_5CN)(Ph_2P)_2CHPPh_2$ (**25**), as shown in **Figure 2.7** and **Figure 2.10** were isolated, respectively. When these bidentate coordinated **21** and **25** compounds reacted with the same Lewis acid as shown in ***Scheme 13*** and ***Scheme 14***, no molecular cleavage – the same result as observed in the case of ***Scheme 1*** for uncoordinated compound **1**. Preliminary results indicate that the formation of novel compound **23** occurs instead of abstracting hydride from the tertiary carbon. In addition, as indicated from $^{31}P\{^1H\}$ NMR spectroscopy, the phosphorus is bonded in a tridentate fashion to group 6B metal carbonyls in both compounds $Mo(CO)_3(C_2H_5CN)(Ph_2P)_3CH$ (compound **22**) and $W(CO)_3(C_2H_5CN)(Ph_2P)_3CH$ (compound **26**). In the future, if these novel compounds can be isolated, they may react with the strong Lewis acid ($B(C_6F_5)_3$) allowing the abstraction of hydride(s) attached on the tertiary carbon without molecular fragmentation, and perhaps yielding the 6π-cationic ligand.

Conclusion 3. Coordination of the 6π-cationic guanidinium ligand $[C(NH_2)_3]^+[BF_4]^-$ (27) with group 6B metal carbonyl complexes formed at room or under reflux and photolysis, although predicted by DFT calculations, did not result in coordination. It is possible that a high intensity light source could promote the coordination reaction. The failure of the guanidinium analogs to coordinate with group 6B metal carbonyl complexes indicates that these analogs cannot substitute for cyclopentadienyl. When $[C(NH_2)_3]^+[BF_4]^-$ (compound **27)** was reacted with electron poor lanthanides salts, guanidinium nitrate was isolated in as shown in **Figure 2.12**. When neodymium nitrate was reacted with 6π-cationic ligand of guanidinium analog **27**, a novel diguanidinium diaquapentakis (nitrato)neodymiate(III) (compound **30**) was isolated. Single crystal X-ray analysis showed that the coordination between lanthanide and guanidinium cation is through the hydrogen bonding. Nitrate oxygens are partially bonded to the hydrogens of guanidinium cation (N-H**….**ONO_2^-).

The attempt to synthesize 6π-cationic ligand of guanidinium analog compound **34** in ***Scheme 20*** was unsuccessful, most likely due to the steric effects of the piperidine and phenyl groups. Instead, novel compounds 1-tritylpiperidine (compound **32**), and diphenyldipiperidin-1-ylmethane (compound **33**) were obtained, as indicated by single-crystal X-ray analysis.

Conclusion 4. Attempts to synthesize a 6π-anionic phosphorus-based complex using 2,4,6-tri-tert-butylaniline or aniline with PI_5 did not produce the desired products. The reaction with 2,4,6-tri-*tert*-butylaniline yielded the compound **38**, 2,4,6-tri-*tert*-butylbenzenaminium iodide, which was characterized by single crystal X-ray

analysis and ^{1}H NMR spectroscopy. It is likely that the alternative to the expected product was due to the steric factors induced by the large ring structures. When the smaller precursor aniline (compound **39**) was used, the expected product trianilinodiiodophosphorane (compound **40**) was formed. When compound **40** was used to synthesize the 6π-anionic ligand, the expected product, compound **41,** was not formed; instead, a previously characterized compound[55], benzenaminium iodide (compound **42**) was isolated. The combination of factors that include weak bonds caused by steric effects of the three nitrogens bonded to phosphorus N-P at equatorial position in **40**, N-P bond polarizability, as well as the lone pair-lone pair repulsion of nitrogen around phosphorus atom, most likely contributed to the fragmentation of compound **40** and resulted in the formation of a stable benzenaminium iodide (compound **42**). Because of the relatively low purity of **40**, the chance of isolating **41** even by using a less steric precursor is precluded, most likely due to the reactive nature of **40** when is subjected to such strong basic conditions.

When the synthesis of a phosphorus based 6π-anionic ligand using bromination of a phosphorus(III) derivative precursor was attempted, molecular cleavage occurred, resulting in the formation of bromobenzenaminium bromide (compound **44**), most likely due to nitrogen lone pairs of precursor **40** being involved in resonance in the benzene ring. This made the **ortho** and **para** positions of the benzene ring more nucleophilic towards electrophilic bromide (Br^{+}) than phosphorus lone pairs, yielding a ratio of **ortho** and **para** isomers in the ratio of 40:60. In this case phosphorus lone pairs are a relatively weak nucleophile to attack the electrophile Br^{+} when compared with the negatively

charged carbons of the benzene ring at both **ortho** and **para** positions.

3.8. Future directions

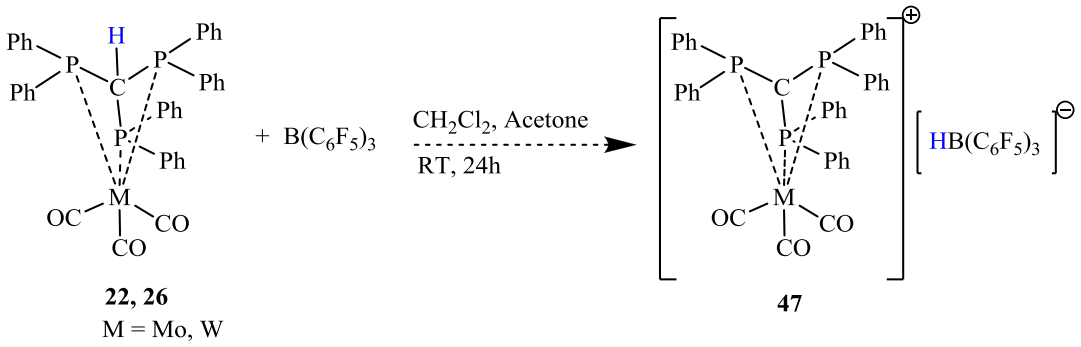
I wish to end this section of the dissertation by proposing a set of future studies that might be carried out to complete the work that I initiated.

The ability to use the precursors $(Ph_2P)_3CH$ (**1**), and $(PMe_2)_3CH$ (**10**) for formation of 6π-cationic ligands will require a thorough and profound understanding of how their electronic and steric effects influence their reactivity with bases and Lewis acids. Density function theory calculations should be used to determine the extent of electron density at each tertiary carbon, which will provide information on the ability for hydride abstraction in forming 6π-cationic ligand.

Purification of the product obtained in ***Scheme 11*** is required so that the brominated version of $(PMe_2)_3CBr$ (**15**) may be isolated. This will be a milestone toward synthesis of 6π- cationic ligand in ***Scheme 9***.

Compound **22** and **26,** which have been identified in solution based on observed $^{31}P\{^1H\}$ NMR spectroscopy must be isolated and characterized. Thereafter, an attempt should be made to produce the 6π-cationic ligand, compound **47,** perhaps using an approach similar to ***Scheme 27.***

Scheme 27. Synthesis for 6π-cationic complex **47**

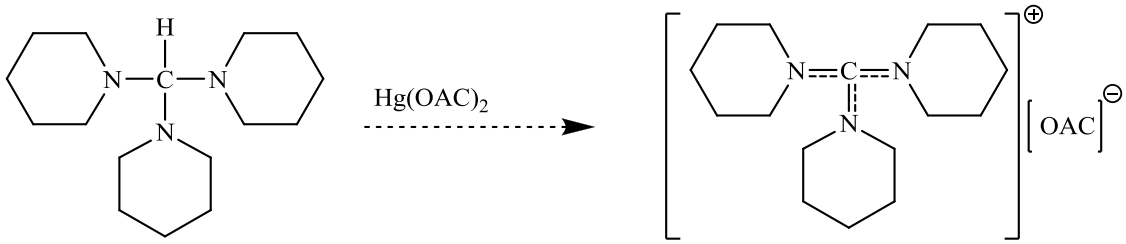


22, 26
M = Mo, W

47

Compound **34** may be formed under the reaction conditions that seemed to work when orthoamide was reacted with mercury acetate to form guanidinium acetate (***Scheme 28***).[77] When **34** is isolated, it will be reacted with group 6B metal carbonyl by using a photolysis technique, shown in ***Scheme 29***. This will reveal any coordination possibilities between group 6B metal carbonyl and 6π-cationic ligand **34**.

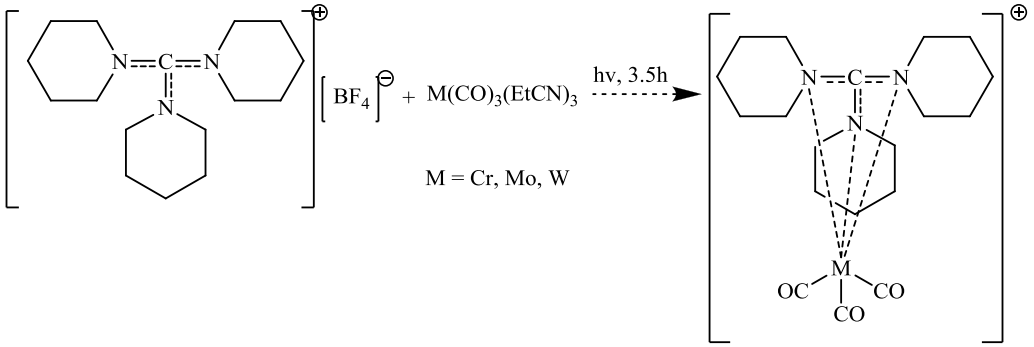
Scheme 28. Synthesis for 6π-cationic ligand **34**



31

34

Scheme 29. Synthesis to be attempted for 6π-cationic complex **48**



48

3.9. References

1. Dinicola, C.; Fazarol, F.; Pettinari, C.; Skelton, W. B.; Somers, N.; White, H. A. *Inorg. Chem. Acta*, **2005**, *358*, 720.
2. (a) Karsch, H. H.; Weber. L.; Wewers, D.; Boese, R.; Muller, G. *Z. Naturforsch, B: Anorg, Chem. Org. Chem.* **1984**, *39B*, 1518. (b) Karsch, H. H. *Chem. Ber*. **1984**, *117*, 783. (c) Karsch, H. H.; Muller,G.; Kruger, C. *J. Organomet. Chem.* **1984**, *273*, 195.
3. Karsch, H. H.; Appelt, A.; Rlede, J.; Muller. G. *Organometallics*, **1987**, *6*, 316.
4. Grim, S. O.; Walton, E. D. *Phosphorus Sulfur*, **1980**, *9*, 123.
5. Grim, S. O.; Smith, P. H.; Nittolo, S.; Ammon, H. L.; Satek, L. C.; Sangokoya, S. A.; Khanna, R. K.; Colquhoun, I. J.; McFarlane, W.; Holden, J. R. *Inorg. Chem*. **1985**, *24*, 2889.
6. Stevens, C. V.; Vaan Heecke, G.; Barbero, C.; Patora, K.; De Kimpe, N.; Verhe, R. *Synlett*. **2002**, *7*, 1089.
7. Alper, H.; Bensimon, C.; Goldberg, Y. *J. Org. Chem*. **1992**, *57*, 6374.
8. Fenske, D.; Mattes, R.; Lons, J.; Tebbe, K. F. *Chem. Ber*. **1973**, *106*, 1139.
9. Siasios, G.; Tiekink, E. T. R. *Z. Kristallogr*. **1994**, *209*, 547.
10. http://www.meta-synthesis.com/webbook/43-hsab/HSAB.html
11. Karsch, H. H. *Z. Naturforsch*, **1979**, *34B*, 1178.
12. (a) Issleib, K.; Abicht, H. P. *J. Prakt. Chem.* **1970**, *312*, 456. (b) Appel, R.; Haubrich, G.; Knoch, F. *Chem. Ber*. **1984**, *177*, 2068.
13. Ishida, H. *Acta cryst*. **2004**, *E60*, o2005.
14. Kalateh, K.; Ebadi, A.; Abedi, A.; Aman, V.; Khavasi, H. R. *Acta Cryst*. **2008**, *E68*,

m1267.

15. Beckett, K. J.; Loeb, S. J. *Can, J. Chem. Soc*. **1988**, *66*, 1073.
16. Cheung, K. K.; Lai, T. F.; Mok, K. S. *J. Chem. Soc. (A)*, **1971**, 1644.
17. Fernandez, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Olmos, E. *J. Chem. Soc. Dalton Trans*. **1994**, 2891.
18. Hogarth, G.; Kilmartin, J. *J. Organomet. Chem*. **2007**, *692*, 5655.
19. Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc*. **1966**, 1095.
20. Najarian, G. M. *Ph.D. Thesis*, Califonia Institute of Technology, **1957**.
21. Payne, D. S.; Mokuolo, J. A. A.; Speakman, J. C. *Chem. Comm*. **1965**, 599.
22. Luth, H.; Truter, M. R. *J. Chem. Soc. (A*), **1969**, 28.
23. Mais, R. H.; Owston, P. G.; Thompson, D. T. *J. Chem. Soc. (A)*, **1967**, 1735.
24. Cheung, K. K.; Lai, T. F.; Lam, S. Y. *J. Chem. Soc*. **1970**, 3345.
25. Bush, M. A.; Woodward, P. *J. Chem. Soc*. **1968**, 1221.
26. Doedens, R. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1965**, *87*, 2576.
27. Doedens, R. J.; Robinson, W. T.; Ibers, J. A. *J. Am. Chem. Soc*. **1967**, *89*, 4223.
28. Pauling, L. *Nature of Chemical Bond*, 3rd ed. Cornel University Press: Ithaca, NY, **1960**, pp 286.
29. Kojima, T.; Breig, E. L.; Lim, C. C. *J. Chem. Phys*. **1961**, *35*, 2139.
30. Mague, J. T.; Dessens, S. E. *J. Organomet. Chem*. **1984**, *262*, 374.
31. Braterman, P. S.; Milne, D. W.; Randall, E. W.; Rosenberg, E. *J. Chem*. *Soc. Dalton Trans.* **1973**, 1027.

32. Chatt, J. *Nature*, **1950**, *165*, 637.

33. Toreki, R. "*Phosphine Complexes"in: Organometallic Hyper TexBook*. Lexington, KY: Interactive Leaning Paradigms, Inc. URL. Accessed Date 16/02/2006.

34. Chatt, J.; Watson, H. R. *J. Chem. Soc*. **1961**, 4980.

35. Jacobsen, H.; Berke, H.; Doring, S.; Kehr, G.; Erker, G., Flohlich, R.; Meyer, O. *Organometallics*, **1999**, *18*, 1724.

36. Costain, C. C.; Stoicheff, B. P. *J. Chem. Phys*. **1959**, *30*, 777.

37. Pearson, R. G. *J. Am. Chem. Soc*. **1963**, *85*, 3533.

38.Pearson, R. G. *Science*, **1966**, *151*, 172.

39. Pearson, R. G. *J. Chem. Educ*. **1968**, *45*, 581.

40. Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643.

41. Shaw, B. L.; Hassan, F. S. M.; Pett, M. T. *J. Chem. Soc. Dalton Trans.* **1988**, 89.

42. Wong, G. W.; Harkreader, J. L.; Mebi, C. A.; Frost, B. J. *Inorg. Chem*. **2006**, *45*, 6748.

43. Schenk, W. A.; Nielsen, K.; Burzlaff, N. I.; Hagel, M. *Inorg. Chem*. **2002**, *41*, 1079.

44. Katrusiak, A.; Szafransk, M. *Acta Crystallogr. Sect. C. Crystat. Struct. Commun.* **1994**, *50*, 1161.

45. Katrusiak, A.; Szafransk, M. *J. Mol. Struct.* **1996**, *378*, 205.

46. Chesman, A. S. R.; Turner, D. R.; Deacon, G. B.; Batten, S. R. *J. Coord. Chem*. **2007**, 2191.

47. Chesman, A. S. R.; Turner, D. R.; Deacon, G. B.; Batten, S. R. *Acta Cryst*. **2006**, *E62*,

m1942.

48. Drew, M. G. B.; Iveson, P. B.; Hudson, M. J.; Liljenzin, J. O.; Spjuth, L.; Cordier, P.Y.; Enarsson, A.; Hill, C.; Madic, C. *J. Chem. Soc. Dalton Trans*. **2000**, 821.
49. Jing, H.; Wang, Y.; Hou, Z.; Chen. S.; Li, D. *Polyhedran*, **1994**, *13*, 1035.62. Zhang, H.; Wu, Y.; Fang, L. *Acta Cryst*. **2006**, *E62*, m854.
50. Zhang, H.; Wu,Y.; Fang, L. *Acta Cryst*. **2006**, *E62*, m854.
51. Wang, X. W.; Zhao, H. *Acta Cryst*. **2009**, *E65*, o1277.
52. Qu, Z. R. *Acta Cryst*. **2007**, *E63*, o3429.
53. Slutsky, J.; Bingham, R. C.; Schleyer, P. V. R.; Dickason, W. C.; Brown, H. C. *J. Am. Chem. Soc*. **1974**, *96*, 1969.
54. Lemmerer, A.; Billing, D. G. *Acta cryst*. **2007**, *E63*, o929.
55. Kostina, V. G.; Feschchenko, N. G. *Zhurnal Obshchei Khimii*. **1979**, *49*, 2452.
56. Norman, A. D.; Tarassoli A.; Haltwanger, R. C. *Inorg. Chem*. **1982**, *21*, 2684.
57. Van Der Voorn, P. C.; Drago, R. A. *J. Am. Chem. Soc*. **1966**, *88*, 3255.
58. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed. John Wiley and Sons, Inc. New York, **1980**, pp 1219.
59. Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem*. **1963**, *2*, 613.
60. (a) Gillespie, R. J.; Nyholm, R. S. *Quar. Rev. Chem. Soc*. **1957**, *11*, 339. (b) Gillespie, R. J. *Can. J. Chem*. **1960**, *38*, 818. (c) Gillespie, R. J. *Can. J. Chem*. **1961**, *39*, 318. (d) Gillespie, R. J. *J. Chem. Soc*. **1963**, 4672. (e) Gillespie, R. J. *Inorg. Chem*. **1966**, *5*, 1634. (f) Gillespie, R. J. *Chem. Educ*. **1963**, *40*, 295. (g) Gillespie, R. J. *J. Am.*

Chem. Soc. **1963**, *85*, 4672.

61. (a) Rundle, R. E. *J. Am. Chem. Soc*. **1963**, *85*, 112. (b) Rundle, R. E. *Rec. Chem. Progr*. **1962**, *23*, 195. (c) Rundle, R. E. *Acta Crystallogr*. **1961,** *14*, 585. (d) Rundle, R. E. *Surv. Progr. Chem*. **1963**, *1*, 81. (e) Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc*. **1951,** *73*, 4321.
62. Muetterties, E. L.; Schunn, R. A. *Quart. Rev. Chem*. Soc. **1966**, *20*, 245.
63. (a) Bartell, L. S.; Hansen, K. W. *Inorg. Chem*. **1965**, *4*, 1777. (b) Hansen, K. W.; Bartell, L. S. *Inorg. Chem*. **1965**, *4*, 1775. (c) Bartell, L. S. *Inorg. Chem*. **1966**, *5*, 1635. (d) Bartell, L. S. *J. Am. Chem. Soc*. **1968**, *45*, 754.
64. Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc*. **1972**, *94*, 3047.
65. Muetterties, E. L.; Mahler, W.; Packer, K. J.; Schmutzler, R. *Inorg. Chem*. **1964**, *3*, 1298.
66. Holmes, R. R.; Carter, Jr., R. P. Abstracts, Inorganic Division, 148th National Meeting on the American Chemical Society, Chicago. III. **1964**.
67. Griffiths, J. E.; Carter, Jr., R. P.; Holmes, R. R. *J. Chem. Phys*. **1964**, *41*, 863.
68. Cotton, F. A. *J. Chem. Phys*. **1961**, *35*, 228.
69. ChemAxon Ltd. **2006**. Marvin Sketch Version 4.1.1 & Marvin Space Version 1.3.1, ChemAxon Ltd, Budapest, Hungary**.** http://www.chemaxon.com/marvin
70. Ahlrichs, R.; Schifler. H. *J. Am. Chem. Soc*. **1985**, *107*, 6494.
71. Cowley, A. H.; Dewar, M. J.; Jackson, W. R.; Jennings, W. B. *J. Am. Chem. Soc*. **1970**, *92*, 5206.
72. Willet, R. D. *Inorg. Chem.* **2001**, *40*, 966.

73. Gray, L.; Jones, P. G. *Z. Naturforsch., B*: *Chem. Sci*. **2002**, *57*, 61.

74. Jones, P. G.; Lozano, V. *Acta Crystallogr. Sect. E: Struct. Rep*. **2003**, *59*, 1092.

75. McMurry, J. *Organic Chemistry*, 6th ed. **2004**, pp 546.

76. Smith, B. M. *Organic Synthesis*, **1994**, pp 189.

77. Erhardt, J. M.; Grover, E. R.; Wuest, J. D. *J. Am. Chem. Soc*. **1980**, *102*, 6369.

3.10. Appendix I

Compound	**21**	**23**
Empirical Formula	$C_{43}H_{36}MoNO_3$	$P_3C_{21}H_5BF_{15}N$
Fw	803.58	567.07
Cryst. Size (mm)	0.25x0.07x0.07	0.23x0.18x0.07
Cryst Syst	Orthorhombic	Monoclinic
Space Group	Pnma	P2(1)/c
a,Å	16. 5382(3)	11. 4513(3)
b,Å	20. 6594(4)	9. 1670(2)
c,Å	11. 3661(2)	21.6015(6)
α,deg	90	90
β,deg	90	90
γ,deg	90	90
Volume A^3	3883.48(12)	2035.96(9)
Z	4	4
Calc. density $mg.M^{-3}$	1.374	1.850
μ(MoKα)	0.501	0.205
Indep Reflecns	84431 [R(Int)=0.091	6797 [R(Int)=0.0913]
T,K	188(2)	188(2)
RI, WR_2(all data)	0.0707, 0.0885	0.0748, 0.1224
RI, WR_2 [I>2σ(I)]	0.0383, 0.0753	0.422, 0.1047
GOF on F^2	0.992	1.024

Compound	**25**	**30**
Empirical Formula	$C_{43}H_{36}WNO_3P_3$	$C_2H_{16}N_{11}NdO_{17}$
Fw	891.49	610.50
Cryst. Size (mm)	0.25x0.02x0.02	0.621x0.23x0.184
Cryst Syst	Orthorhombic	Monoclinic
Space Group	Pnma	C2(1)/c
a,Å	16. 4570(5)	10. 8926(6)
b,Å	20. 7161(6)	9. 0004(6)
c,Å	11. 3192(4)	20.4621(11)
α,deg	90	90
β,deg	90	90. 535(3)
γ,deg	90	90
Volume A^3	3859.0(2)	1999.8(2)
Z	4	4
Calc. density $mg.M^{-3}$	1.534	2.028
μ(MoKα)	3.158	2.701
Indep Reflecns	4929 [R(Int)=0.091	4435 [R(Int)=0.0913]
T,K	296(2)	228(2)
RI, WR_2(all data)	0.0819, 0.0734	0.0167, 0.0397
RI, WR_2 [I>2σ(I)]	0.0376, 0.0618	0.0167, 0.0397
GOF on F^2	1.036	1.408

Compound	**32, 33**	**38**	**19**
Empirical Formula	$C_{23.5}H_{27.5}N_{1.5}$	$C_{18}H_{32}IN$	$C_8H_{12}BrN$
Fw	330.97	389.35	202.10
Cryst. Size (mm)	0.34x0.28x0.10	0.437x0.081x0.03	0.18x0.16x0.14
Cryst Syst	Triclinic	Orthorhombic	Hexagonal
Space Group	P-1	Pnma	P6(3) mmc
a,Å	10. 2675(4)	22. 1960(7)	8. 6200(4)
b,Å	11. 3630(4)	14.8228(5)	8. 6200(4)
c,Å	16. 6373(6)	5.8533(2)	6.9118(3)
α,deg	74.357(2)	90	90
β,deg	88.743(2)	90	90
γ,deg	85.162(2)	90	120
Volume A^3	1862.15(12)	1925.78(11)	444.77(3)
Z	4	4	2
Calc. density $mg.M^{-3}$	1.180	1.343	1.509
μ(MoKα)	0.068	1.657	4.550
Indep Reflecns	9232 [R(Int)=0.0374]	2475 [R(Int)=0.0625]	268 [R(Int)=0.0266]
T,K	183(2)	188(2)	183(2)
RI, WR_2(all data)	0.1287, 0.2754	0.0702, 0.1355	0.0530, 0.1132
RI, WR_2 [I>2σ(I)]	0.0857, 0.2414	0.0541, 0.1287	0.0464, 0.1082
GOF on F^2	1.019	1.189	1.097

CHAPTER FOUR

Improvement of Student Writing Skills in General Chemistry Lab Reports Through the Use of Calibrated Peer Review

4. 1. Introduction

In this rapidly changing world, one of the most important challenges in education is the development of effective techniques that help students learn difficult concepts through writing. Since the College Board offered its first writing examinations in 1901, there have been obvious declines in the writing abilities among students at different educational levels.[1] Over the ensuing decades, the effort to improve student writing skills has been a principal focus of secondary and college-level education. The literature shows that regardless of the type of discipline, students gain a more profound understanding of conceptual material when they write about what they are learning.[2,3] In general, the teaching of writing can enable instructors to meet the essential teaching challenges that include (1) assisting students in developing conceptual understanding of subject matter (2) enhancing communication skills and (3) providing opportunities for critical thinking.[4]

However, teaching writing to students with diverse of educational backgrounds, abilities, and interests is an especially difficulty task for faculty at larger colleges and universities, especially in introductory science courses. Many of these challenges are not adequately addressed through lectures, discussions, laboratories, and problem sets that are part of the traditional first-year college-level science course. Teaching of writing techniques has been traditionally used in chemistry laboratory course to reinforce student engagement in concepts and critical thinking.[4-8] However, it has been observed that the

writing of technical reports is often poor and students are lacking in motivation to improve their writing.[9]

There are undeniable challenges specifically related to large laboratory courses that include high grading burdens and lack of sufficient instructor expertise in creating and evaluating writing assignments.[10,11] The idea of "peer review" has been employed as a new approach for teaching oral and written communication skills, and is grounded in the philosophies of active learning.[12] Peer review reduces an instructor's grading load and maximizes the use of teaching resources. [13,14] Through peer review, students build their writing skills from the joint construction of knowledge through writing reviews of each other's work. Freshman chemistry laboratory courses, where students from diverse backgrounds must gain skills in scientific writing and critical thinking at the earliest stage of their college careers, may be best suited for the application of peer-review teaching methodologies. Chemistry faculty interested in implementing writing in a laboratory course usually face many challenges[4], which include (1) design of effective assignments, (2) knowing how and where to use writing within the laboratory curriculum, and (3) how to provide feedback that improves the students' understanding of content and critical thinking. Over the past two decades, a number of chemistry educators have demonstrated the value of a specific peer review technique referred to as "calibrated peer review" (CPR). CPR is a comprehensive approach which not only promotes student understanding through frequent writing assignments, but also develops student critical thinking skills through the process of peer-review and self-review.

CPR has been shown to be an effective method to improve student writing in

chemistry lecture assignments[8,15-17] and laboratory reports.[5,6,18,19-22] CPR is a web-based delivery tool that manages the submission and evaluation of students' written assignments.[23] It was developed in 1998 to foster science literacy, constructivist learning, and critical thinking in introductory chemistry classrooms in California colleges and universities.[24] It is currently being adopted by more than 800 institutions and used by more than 120,000 students[2,25,26] in many disciplines, class sizes and levels of education.

4.1.1. How CPR works

CPR as web-based instructional tool provides students autonomy in line with offering continual feed-back through guided exercises, peer evaluations and final performance reports.[24] The CPR's guided peer review process goes through the following two parts (instructor and student):[2,27]

In the first part of CPR, the instructor designs a writing assignment with essential guidelines. He or she can use CPR's built in authoring tools or can use or modify assignments that other users have deposited in CPR's library. CPR offers also an assignment authoring tool which help instructors in writing and reviewing the activities.[23] There are created and published library assignments by other faculty members this often helps instructor to select appropriate topics for his or her class. The instructor may also decide to author his or her new assignment whenever he or she has convenient time to do so. When CPR is used it will prepare a very detailed report summary for instructors about the class and individual performance.[23] The instructor can reevaluate the individual document any time if needed because he or she has the access.

In the second part of CPR, the students use the CPR program to complete the

assignment using the following steps:[2,27]

Step One. Each student begins an assignment based on the instructor's guidelines. Instead of turning in a printed report to the instructor, the written work is submitted electronically to the CPR program.

Step Two. After each student has submitted his or her work, the program provides a guided tutorial on peer review of that particular assignment. Students learn to calibrate their review skills by going through three essays on that particular assignment that has been chosen by the instructor as examples of different qualities of performance: a low-range essay, a mid-range essay and a high-range essay. Through guided questions students evaluate the essays. The questions may include for example, "Is the information organized into paragraphs: yes or no" or "Rank the quality of the introductory sentence: (a) vaguely related to the essay topic (b) mostly related to the essay topic (c) perfectly related to the essay topic." Students will receive a rating for their ability to identify the quality of the calibration essays correctly. If a student is able to correctly identify the quality of the essays to match the instructor's perception, the student will be considered as a reliable grader and awarded a "Reviewer Competency Index'' (RCI) of 6 points. Thereafter, each student will receive detailed feedback regarding his or her evaluation skills. Each student however, must complete calibration exercises before he or she can be allowed to move to the next step.

Step Three. Once a student has completed step two and has an understanding of

the criteria for a high quality assignment (calibration), he or she is given the opportunity to apply this knowledge by reviewing three essays from other students, which are presented arbitrarily and anonymously,[28] although the instructor has full access to the identity of the authors of the essays. The CPR grades the student on his or her ability to correctly identify the quality of the essay. If the assessment by the student and the CPR program are in agreement, then the student will receive full credit for this step in the assignment.

Step Four. Last but not least, the students grade their own essays using the same standards they previously employed in evaluating their peers' essays.

Step Five. At the end of each assignment, CPR prepares and provides each student with a summarized report that shows all his or her reviewers' assessments, grades, and comments.

In the studies that I will describe in this chapter, I wanted to apply CPR for teaching writing skills and critical thinking in the preparation of lab reports in a first-semester laboratory course that accompanies a traditionally taught general chemistry lecture course (Chem 123L) at the University of New Mexico.

4.2. Literature review

4.2.1. The function of CPR

CPR is applicable across all disciplines in helping students develop their writing skills and easing the instructor's workload. It is equally effective to both classes with small (20) and large (500) numbers of students.[23] In addition, students become well

prepared in reading for content. This mastery has been observed from the student's ability to answer the content questions much more correctly towards the end of an assignment than they did at the beginning.[18] CPR enables students to develop a number of skills that include: abstracting, persuading, developing logical arguments, describing, assessing, criticizing, analyzing, and reviewing.[18] These are important higher-order thinking skills as described by Bloom.[29] More importantly, through writing and reviewing, students develop critical thinking.[30,31]

Our focus will be on lab reports will include writing skills and critical thinking. We expect at least some of the basic fundamentals of competent writing to be achieved.[32,33] This includes good sentence construction (organization, clarity and style); grammar, which includes verb agreement, proper use of pronouns, adjectives and adverbs; punctuation; and spelling. Critical thinking has broad applications in academic and non-academic activities including reading, analysis, argumentation and logical reasoning. The complexity of critical thinking activity is reflected in its definitions, and is the source of some disagreement on what it is all about by most critical thinking advocates.[34,35,,36] There are a number of perspectives on the definition of critical thinking.[37,38] The general definition that we will use for critical thinking in our study is as follows: [34,36,39] *Critical thinking* is a way of thinking and a set of skills that encourage an informed, aware, systematic, considered and logical approach to deciding what to believe or to do.[39] Furthermore, critical thinking leads to arguments and conclusions that are valid, substantiated and resistant to criticism. Critical thinking enables students to

adequately accomplish certain intellectual tasks that include the ability to analyze arguments and judgment making on the credibility of the issues and make valid conclusions.

4.2.2. Documented students learning progress as a result of using CPR

Based on previous studies, students from Chemistry, Biology, Economics, and Physiology courses taught using CPR have performed approximately 10% better on the examinations than students taught through traditional methods.[40,41,] This finding was the same for all students who participated in the studies, and was independent of the type of examination questions given in the courses.[18] It has also been noted from research that the reviewing process in CPR enhanced learning.[43] Repeated studies revealed that the reviewing step dramatically enables the weakest students to understand the content beyond their learning gain from the essay writing.[43]

4.2.3. CPR impact on higher education

The use of the CPR program is growing rapidly. For example, in the year 2001, there were 101 universities and colleges that used CPR. During this time, CPR served more than 520 courses, enrolled more than 16,000 students, and had about 175 library assignments in its data base.[44] In the year 2004, the CPR user report showed that 500 institutions used CPR to support 1900 courses, which had a total enrollment of over 72,000 students.[44] In 2005, the report showed that CPR has been adopted by over 800 institutions and served more than 120,000 students.[18] More importantly, the assignment

library of CPR has expanded exponentially to 1275 assignments. Further, progress has been made among faculty members in each discipline to develop and share discipline specific assignments.[23]

4.3. Research question

4.3.1. How effective is CPR?

Quantitative studies have revealed that students who learn by CRP have improved test scores over those who are taught using traditional lecture approach.[40,41,42] Other research suggests that CPR led to improvement of students' performance in both essay writing and critical thinking.[45-50] Some supportive literature suggested that well-written CPR assignments can facilitate course content mastery,[51-54] and can be as effective as other methods of teaching writing skills.[45,55] In addition, Palaez[56] noted that human-physiology majors performed significantly better on both multiple choice and essay portions of their midterm examinations for topics taught using CPR than those taught in the traditional method.

On the other hand, other studies have disputed the value of CPR. Walvoord *et al*[24] reported that CPR did not improve students technical writing skills, nor did it improve their scientific understanding of written summaries from publications.[24] An analysis carried out by Reynolds *et al*[57] revealed that the use of CPR did not match the expectations to improve student learning.

By reviewing the literature, it is apparent that there are some conflicting views on the effectiveness of CPR as an instructional tool for teaching. While the Department of

Chemistry and Chemical Biology is intrigued with the possibility of using CPR in teaching lecture and laboratory courses, we fell it is necessary for us to carry out our own research to determine the effectiveness of using CPR in the context of our own courses to for improving writing skills and critical thinking. The remainder of the chapter describes preliminary studies to determine if our own experience in using CPR for teaching laboratory courses supports its use as a suitable alternative method for submitting post-lab reports for a large, general chemistry lab course.

4.3.2. Statement of research problem

The teaching of freshman general chemistry lab faces many challenges: large numbers of students (greater than 2,000 per semester), large faculty workloads in grading essays, and limited number of instructors. The following key questions were explored:

1) Can CPR improve the ability of students to master writing skills over a semester?
2) Can CPR help students develop skills in both conceptual understanding and critical thinking?
3) Is the CPR program a feasible tool for students to submit post-lab reports?

4.3.3. Hypothesis

Using the CPR program in laboratory teaching can improve students' writing skills, conceptual understanding, and critical thinking.

4.4. Methods

This study was designed to determine the effectiveness of implementing the CPR program in teaching of a first-semester, general chemistry laboratory (CHEM 123L). The course contained a total of eight experiments. There were 26 sections. Eleven sections (Group I) carried out the first four experiments using the CPR process and then reverted to the traditional process for the remaining four experiments. Fifteen sections (Group II) carried out the first four experiments without CPR and then used CPR in the remaining four experiments. Students took a pretest before doing each experiment. The students then conducted the experiment. For those experiments conducted by groups who did not use CPR, the students submitted their post-lab reports through the traditional hard-copy process. For those groups who underwent CPR, the students submitted their post-lab reports through the CPR program. Each group was then given a posttest. The performances on the pretest and the posttest were then compared within each group and between the two groups. At the end of the semester, all students were asked to fill out a questionnaire on their opinions of the CPR process.

At the beginning of the course, the teaching assistants or instructor gave a presentation to the students on the general concepts of CPR and how it works. The presentation included information about instructor's ability to see all comments and reviews made by the students. Students completed the laboratory experiment in three hours. Students who submitted a traditional post-lab report handed in their report within seven days. Students who submitted their post-lab report through the CPR program had

approximately two weeks to complete the assignment. All essay questions were instructor-developed items for topics addressed in the experiment. Each assignment was designed with goals, source materials, guiding questions, and three example essays to help students "calibrate" their ability for peer review. The CPR system automatically managed the peer review process. However, the TA or instructor was able to monitor the progress of the assignment on-line.

4.4.1. Data collection

The following are examples in post-lab questions answered and submitted through CPR program:

1) Describe the hypothesis you wrote in the pre-lab and write a conclusion for your experiment. Include the data and an explanation of whether your hypothesis was supported or not supported. Comment on the sources of experimental error and possible ways to prevent this error. If you find you have no error, comment on precautions you may have taken to avoid the error.
2) What is the empirical formula of magnesium oxide according to your calculations based on your experimental data? Describe steps taken and show calculations made to determine this formula.
3) Based on your experimental data calculate the empirical formula of zinc ferrocyanide. Provide a logical step-by-step explanation of how you reached your result.

A complete set of post-lab questions and the rubric for grading are attached in the

appendix II (Section 4.13). The grading system for the CPR process was the following: text entry submitted through the CPR program consists of the following break down: 70% of the grade was given for the quality of report as entered by the student. 13% of the grade was based on the reviewing process in the calibration performance. 12% of the grade was based on the review of the student's classmate's work. 5% of the grade was based on self-evaluation. The CPR processes counted for 20% of the course grade. The remaining 80% of the course grade was based on TA evaluations, pre-lab report and post-lab questions separate from the CPR process.

To assess the value of CPR, I asked a single question at the beginning of the course and after the completion of the first four experiments of the course. The grading rubric was used to award a possible 10 points.

The following is a student's lab procedure, observation and experimental data from the preparation of a 100 mL of 0.4 M glucose solution. Comment on this student's preparation of the solution. Describe the problems of preparation and how to correct the problems. Write the answers in essay format with clear logic and correct spelling and grammar. (10pts)

Making 100 mL of a 0.4 M sugar solution	
Experiments	**Observations**
1. Prepare a clean and dry, 100 mL volumetric flask with a stopper.	1. Obtained a vol. flask from the drawer. Cleaned it with soap and dried it with paper towel.
2. Weigh 720 g of glucose by using a weight boat and record the mass. 0.4 M x 100 mL = 40 moles 40 moles x 180 g/mole = 720 g	2. The mass of glucose is 719.980 g = (740.01 g – 20.03 g of weight boat).
3. Transfer all the glucose into vol.	3. Although I was very careful, I lost some

flask	glucose during the transfer. It was hard not to spill it; the flask opening is too small.
4. Add the water to the vol. flask to the mark.	4. The water line was just below the mark.
5. Shake the flask to make all sugar dissolve.	5. A little water was leak out of the stopper during the mixing. It is very hard to dissolve the entire solid. It took me almost 40 minutes to dissolve it.

The following is an example of expected essay from students and its respective rubric designed for instructor to grade the essay:

Making 100 mL of a 0.4 M Sugar Solution

In this preparation, a student needs a rubber stopper, a cleaned 100 milliliter (mL) volumetric flask rinsed with de-ionize water, and drying the flask with paper towel. In order to obtain the actual mass of glucose needed to make 0.4 M of glucose solution in the 100 mL volumetric flask, it is important to determine the correct number of moles contained in a 100 mL volumetric flask. The number of moles contained is (0.4 moles)/1000 mL x 100 mL = 0.04 moles, and not 40 moles as indicated in the preparation. Having calculated that number of moles, therefore the mass of glucose to be weighed is (180 g/moles) x 0.04 moles = 7.2 g. This implies that both experiment, and observations made by the student were incorrect. Instead, it should have read as 7.2 g weight of glucose, and an observed mass of glucose as 7.2 g (tare the empty weight boat instead of weighing it). The correct calculated amount of glucose was transferred from weight boat by using a metal spatula to a dry beaker and a minimum amount of water used to dissolve before transferring to a labeled 100 mL volumetric flask. After all the solution was transferred, the beaker was rinsed and the solution added to the 100 mL flask. Then more of the de-ionized water was slowly added to fill up to the 100 mL mark on the volumetric flask (it is important to ensure that the bottom

of the meniscus is exactly at the line). Then the volumetric flask was capped with the appropriate stopper to avoid possible solution leaking, carefully inverted to thoroughly dissolve all solids, and the 0.4 M glucose solution was left to stand at room temperature. Since the amount of glucose that can be dissolved at room temperature in a 100 mL volumetric flask is 7.2 g, an attempt to dissolve 720 g would have resulted in a saturated glucose solution that would not have dissolved during the 40-minute time limit of the experiment.

Grading Rubric for Pre-Test and Post-Test

Points

i. Writing in essay format (in a paragraph form)……..……..…….0.5

ii. Calculating both correct number of moles and mass of glucose with their respective units; 0.04 moles, 7.2 g of glucose…….…….....2.5

iii. Tare the empty weight boat to zero, instead of weighing it……..0.5

iv. Suggesting how to transfer glucose from weight boat to 100 mL volumetric flask with less or no spill, dissolve glucose in beaker with minimum water first, then transfer to 100 mL volumetric flask ……..……...0.5

v. The addition of de-ionized water in 100 mL volumetric flask should be at the bottom of the meniscus exactly on the marked line……..…0.5

vi. Using an appropriate stopper to avoid solution leaking during thorough shaking of the mixture…….…….……..0.5

vii. The reason for why it was impossible for a student to dissolve 720 g of glucose in 100 mL volumetric flask (over saturation)……..…….….. 2

viii. Good sentence construction (organization, clarity, and style) and proper use of

pronouns, adjective, and verbs…….……....1.5

ix. Good writing mechanics (spelling and punctuation)……..……..1.5

4.4.2. Data analysis for post-lab (reports submitted using CPR) and pretest/posttest scores

The scores of all eight post-lab reports obtained through the CPR process and the pretest and posttest scores were analyzed using "Student's" t-test, Analysis of Variance (ANOVA-single factor),[58] and the Fisher box plot. The t-test was used to confirm whether the mean of two normally distributed scores are equal. Our null hypothesis states that the mean values from pretest and posttest are not statistically different (i.e., $H_o : \mu_1 = \mu_2$).

The ANOVA-single factor analysis was used in comparing the mean of more than two samples to determine whether differences in the means are real or just random errors. This was done in a single test with ANOVA rather than pair wise comparisons using the t-test approach. ANOVA helped to compare the means and standard deviations of more than two groups (in these case scores on pretest and posttest for students who used or did not use CPR) and determined whether there was significance difference in variance from one group to another. Our *null hypothesis* for ANOVA was that all pretest and posttest variances are equal (i.e., $H_o : \sigma_1^{\,2} = \sigma_2^{\,2} = \sigma_3^{\,2} = \ldots\ldots = \sigma_k^{\,2}$) and ***k*** stands for a set of scores in a give section.

The Minitab Program under Fisher Multiple Comparison package provided extra

information, which could not be obtained through both t-test and ANOVA. We used a box plot to analyze each individual section's score distribution. The plot shows the values of mean and median of every section including outlier(s).

4.4.3. Data analysis on student questionnaire statements

Questionnaires regarding the effectiveness of writing skills, critical thinking, and the overall value of using CPR were filled out by the students at the end of semester. The questionnaire statements were written in positive manner (see Appendix II Section 4.13). Each statement was rated by a student on a five point Likert-scale where **one** represents strong disagreement, **two** represents more disagreement than agreement, **three** is in between, **four** is more agreement than disagreement and **five** represents a strong agreement. The mean and standard deviation of each statement from questionnaires were computed. These data have revealed the general opinions of students about the effectiveness of CPR for improving writing skills, critical thinking and overall value of using CPR as an instructional tool.

4.5. Results and Discussion

4.5.1 Comparison of CPR Post-lab reports submitted by Groups I and II

First, I compared the scores of the post-lab reports graded by the CPR program for all sections in Group I. ANOVA and the Fisher multiple comparison box plot were used to analyze average score of the two best post-lab reports (Group I) and (Group II) out of four submitted by two groups using CPR. This analysis revealed that variance in

scores between the individual sections in Group I was not significant (see **Table 4.1**), indicating that the overall performance of these groups was approximately the same (F = 0.87, p > 0.57 at 0.05 alpha level), which is consistent with the null hypothesis ($H_o : \sigma_1^2 = \sigma_2^2 = \sigma_3^2 = ... = \sigma_k^2$). This conclusion remained the same even when Section 28, the one with the lowest mean, was excluded in the analysis.

From the box plot in **Figure 4.1** for Group I, the majority (8 out of 11 sections) had mean scores above 16 (out of a possible 20 points), suggesting that the students had a good learning outcome from the CPR process, even though the students only completed four CPR reports. In the box plot shown in **Figure 4.1,** the median values of more than half of the sections (12, 15, 16, 20, 27 and 34) are higher than the mean values. The reason for these higher values appears to be due to outliers who had particularly higher scores. The mean and median scores for Sections 24, 29, 30 and 31 are symmetrical, indicating that the scores in those sections show an almost normal distribution. The majority of students in Section 28 of in Group I scored below the mean (**Figure 4.1**). A similar trend was also observed in **Figure 4.9** when the same section did posttest objective essay. This indicates that Section 28 was weaker than the rest or that the TA in the section was ineffective.

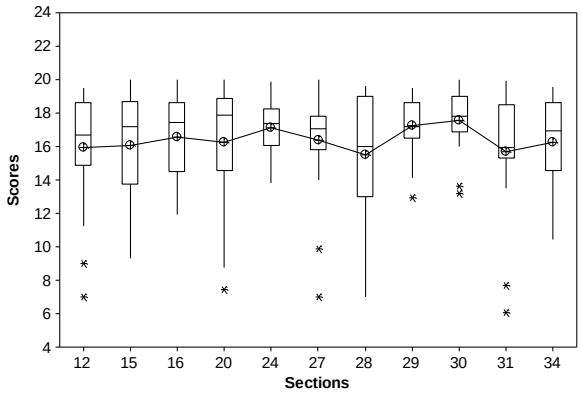
Table 4.1: One way analysis of variance of average post-lab scores for Group I students who submitted assignments 1-4 using the CPR program

Sections	No. of Students	Sum total of scores	Average scores	Variance
12	19.00	303.02	15.95	11.92
15	15.00	242.08	16.07	12.22
16	14.00	232.09	16.58	6.35
20	21.00	340.98	16.24	14.54
24	17.00	291.61	17.15	2.82
27	21.00	344.00	16.38	9.12
28	11.00	170.60	15.51	16.53
29	20.00	345.34	17.27	3.04
30	20.00	351.80	17.59	3.17
31	19.00	298.37	15.70	12.83
34	16.00	259.85	16.24	7.60

ANOVA

Source of Variation	SS	df	MS	F	P-value	F-crit.
Between Groups	76.90	10.00	7.69	0.87	0.57	1.88
Within Groups	1614.70	182.00	8.87			
Total	1691.61	192.00				

Figure 4.1. Post-lab Group I Scores for Students Who Submitted Assignments 1-4 Using the CPR Program



Note: A box plot is depicting sections of numerical scores through the following summaries: (1) The smallest score (sample minimum) (2) The lower quartile (3) median (4) The upper quartile (5) The largest score (sample maximum) (6) The data not included between whiskers symbolizes as a star, stand for outlier (7) The dot inside the box represent the mean of the score in a section, in addition, a dash (-) representing the median.

Comparison of Group II score variances (see **Table 4.2)** revealed there was a significant difference between the sections in this group F-value being significant at (F = 2.07, p < 0.01, 0.05 alpha level), and were consistent with the rejection of the null hypothesis ($H_o : \sigma_1^2 = \sigma_2^2 = \sigma_3^2 = ... = \sigma_k^2$). This result could have been due to a variation in student ability or variation in the quality of the TAs. However when Sections 18 and 37 were excluded, the variances in scores decreased significantly. Without these two sections, $H_o : \sigma_1^2 = \sigma_2^2 = \sigma_3^2 = ... = \sigma_k^2$ for Group II is accepted.

Table 4.2: One-way analysis of variance of average post-lab for Group II scores of students who submitted assignments 5-8 using the CPR program

Sections	No. of Students	Sum total of scores	Average scores	Variance
11	21.00	355.40	16.92	5.11
14	15.00	240.06	16.00	4.62
17	18.00	298.28	16.57	4.43
18	17.00	228.74	13.46	20.59
21	17.00	277.74	16.34	7.67
22	20.00	319.89	15.99	13.27
23	19.00	312.94	16.47	12.57
25	18.00	311.20	17.29	2.91
26	20.00	318.28	15.91	10.17
32	18.00	273.17	15.18	8.03
33	22.00	337.46	15.34	9.98
37	15.00	205.37	13.69	17.44
38	15.00	223.00	14.87	10.70
39	20.00	306.35	15.32	9.22
41	11.00	173.14	15.74	9.89

ANOVA

Sources of variation	F	p-value	F-crit.	Comments
All sections	2.07	0.01	1.73	There is significant difference
Excluding section 37	1.79	0.05	1.76	There is significant difference
Excluding section 18	1.61	0.08	1.76	There is insignificant difference
Excluding sections 18 and 37	1.10	0.36	1.80	There is insignificant difference

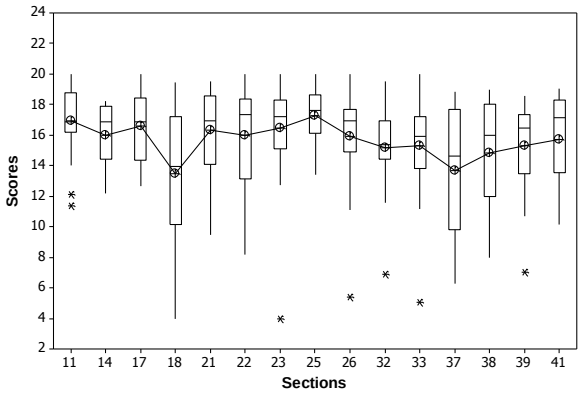
The box plot in **Figure 4.2** for Group II revealed that the majority (12 out of 15 sections) of the students mean scores were above 15 out of 20 points. Sections 18 and 37 had the mean scores of less than 14 points. Based on only four post-lab reports submitted by the students' using CPR, these mean scores are only marginally lower than the Group I scores, and can be considered to be moderately good based on average percentage score, which is about 75%.

The values of medians of nine out of fifteen sections are higher than the means in their respective sections, in which the majority of the students in these sections scored above the average score. The median and mean values for Sections 11, 17, 18, and 32 are almost symmetrical (scores are normally distributed). Regardless of the presence of outliers in some sections, the effects appear to be cancelled out by some of the higher scores in a given section. Section 18 showed similar results in post-lab (II), pretest and posttest scores (**Figure 4.2, Figure 4.10** and **Figure 4.11**), suggesting that this section may have significantly weaker students or an ineffective TA.

Looking at both **Figure 4.1** and **Figure 4.2**, it appears that the average CPR performances of Group I and Group II are similar (Group = 16; Group = 15). This

suggests that both groups are approximately the same in terms of ability (with the exception of Sections 18 and 37) and that the levels of difficulty of the lab assignments are approximately the same.

Figure 4.2. Post-lab Group II Scores for Students Who Submitted Assignments 5-8 Using the CPR Program



Note: A box plot is depicting sections of numerical scores through the following summaries: (1) The smallest score (sample minimum) (2) The lower quartile (3) median (4) The upper quartile (5) The largest score (sample maximum) (6) The data not included between whiskers symbolizes as a star, stand for outlier (7) The dot inside the box represent the mean of the score in a section, in addition, a dash (-) representing the median.

4.6. Comparison of pretest and posttest scores in response to CPR

Table 4.3 shows the score distribution of 523 students on an objective essay question done as a pretest before using CPR. The objective essay question consists of the following three major areas of focus (with a break down of the points associated with the answers): writing skills (3.5 points), conceptual understanding (4.5 points), and critical thinking (2 points). In regard to writing skills, the main focus was on good sentence construction (organization, clarity, and style), spelling, grammar (proper use of pronouns, adjectives and verbs), and punctuation. For conceptual understanding, students were

expected to recognize the error in the description of the solution protocol described in the experiment, and to calculate the correct amount of glucose required to make the appropriate concentration solution. The student was expected to then correct the protocol, describing the correct method for weighing the solute and preparing the solution. For the critical thinking portion the students were expected to explain why the original amount of glucose described in the incorrect protocol would have led to a saturated solution with undissolved solute.

The grades as shown in **Table 4.3** ranged from 0 to 9 out of a possible 10 points. The means score for the pre-test for all sections was 3.24 ± 1.59 (see the histogram in **Figure 4.3)**. Descriptive statistics were used to check the extent to which the scores were normally distributed, and skewness of the score distribution was determined. The overall skewness of the score distribution is 0.53, and thus, the scores appear to fit a normal distribution (**Figure 4.3**).

Figure 4.3. Frequency Histogram on Pretest Objective Essay Performance for all Students

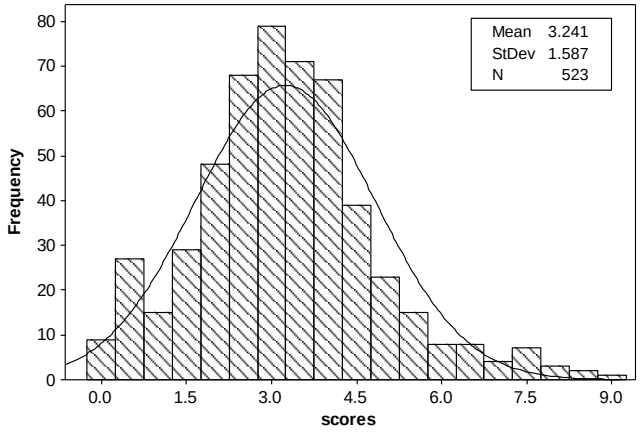


Table 4.3: Frequency and points for student performance on pretest objective essay

Frequency	Points
9	0
28	0.5
17	1
30	1.5
49	2
69	2.5
80	3
72	3.5
68	4
40	4.5
24	5
16	5.5
9	6
9	6.5
5	7
9	7.5
4	8
3	8.5
1	9
0	10

Table 4.4: Student pretest performance before using CPR Group I

Title	WS	CU	CT	WS + CU	WS + CT	CU + CT	WS + CU + CT	WO
Stud.	92	17	11	2	3	1	1	73
%	41	8	5	-	-	-	-	46

Writing skills = WS Conceptual understanding = CU Critical thinking = CT
Obtained less than minimum points in all three areas = WO

Table 4.5: Student pretest performance before using CPR Group II

Title	WS	CU	CT	WS + CU	WS + CT	CU + CT	WS + CU + CT	WO
Stud.	120	17	12	20	12	9	5	151
%	40	6	4	-	-	-	-	50

Writing skills = WS Conceptual understanding = CU Critical thinking = CT
Obtained less than minimum points in all three areas = WO

We divided students into eight different categories based on their performance of the objective essay as shown in **Table 4.4** and **Table 4.5**. The students considered in this classification are those who were able to obtain points between 2.5-3.5 for writing skills (WS), 3.5-4.5 for conceptual understanding (CU), 1.5-2 for critical thinking (CT), and those who obtained less than the minimum points in all three areas (WO).

Quantitative analysis of the above results (**Table 4.4**) of Group I with a total of 223 students in eleven sections revealed that 92 out of 223 students (41%) displayed good writing skills, 17 out 223 students (8%) did well in conceptual understanding, and 11 out of 223 students (5%) were good at critical thinking.

The same analysis (in **Table 4.5**) for Group II with a total of 300 students in fifteen sections showed that 120 out of 300 students (40%) had good writing skills, 17 out 300 students (6%) did well in conceptual understanding, and 12 out 300 students (4%) were good at critical thinking.

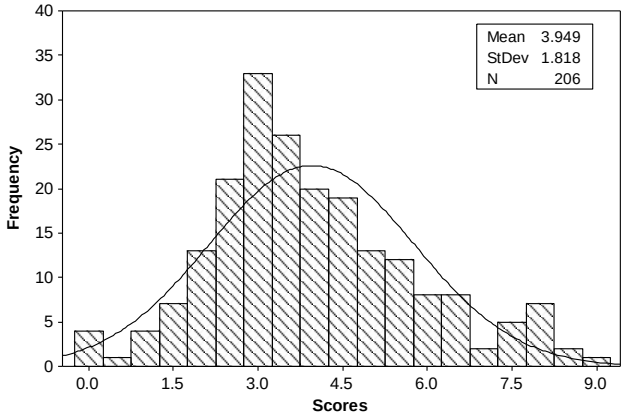
Students in both groups displayed some sort of problem with writing skills that required improvement. The most common issues included incorrect capitalization, formatting errors, incorrect use of the singular and plural pronouns (see **Table 4.4** and **Table 4.5)**. Only 6-8% of the students in both groups did well on conceptual understanding, most commonly due to difficulties with the understanding of the mole concept and improper distinction between units of volume (liters and milliliters). On the critical thinking part, only 4-5% of the students did well, most likely due to the complexity of the problem. It is well known by almost every educator that critical

thinking skills develops slowly as the student gains expertise in a subject.[34] Critical thinking requires evaluative and judgmental aspects, such as analyzing arguments, and judging credibility of the event, which are developed over time.

Table 4.6: Frequency and points of student performance for Group I on posttest after submission of assignments 1-4 using CPR

Frequency	Points
4	0
1	0.5
4	1
7	1.5
13	2
21	2.5
33	3
26	3.5
20	4
19	4.5
13	5
12	5.5
8	6
8	6.5
2	7
5	7.5
7	8
2	8.5
1	9
-	10

Figure 4.4. Frequency Histogram for Students Performance for Group I on Posttest after Submission of Assignments 1-4 Using CPR



In the posttest analysis the total of students decreased from 523 to 424 due to attrition during course. Analysis of the scores revealed that Group I (using CPR) had a mean score of 3.95 ± 1.82, and Group II (not using CPR) had a mean score of 3.94 ± 1.73 (see **Table 4.6** and **Table 4.7**; **Figure 4.4** and **Figure 4.5)**.

Figure 4.5. Frequency Histogram for Group II Student Performance on Posttest without Use of CPR

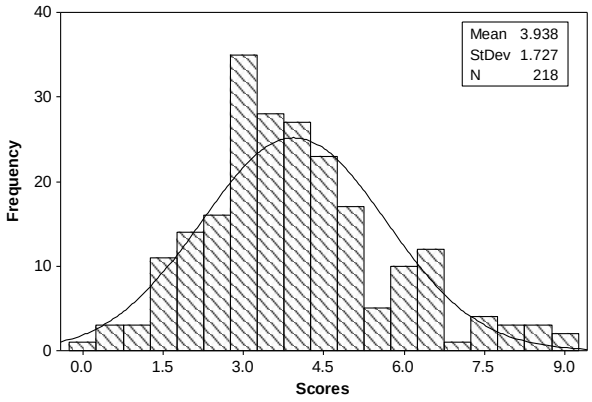


Table 4.7: Frequency and points of Group II student performance on posttest without use of CPR

Frequency	Points
1	0
3	0.5
3	1
11	1.5
14	2
16	2.5
35	3
28	3.5
27	4
23	4.5
17	5
5	5.5
10	6
12	6.5
1	7
4	7.5
3	8
3	8.5
2	9
-	10

Descriptive statistics performed on scores of both groups (**Figure 4.4** and **Figure 4.5**) for students who used or not used CPR, has revealed the extent of skewness for scores distribution being 0.53 and 0.63 respectively. In both cases values are small and close to zero which is a value for perfect normal distribution curve. This is generally reflecting that students' abilities are approximately falling within the theoretical normal curve. Because both means (**Table 4.6** and **Table 4.7**) look approximately the same, we cannot infer anything at this moment until when qualitative analysis is carried out later.

Next we wished to compare the scores for writing skills, conceptual understanding, and critical thinking for Groups I and II (**Table 4.4** and **Table 4.8**, **Table 4.5** and **Table 4.9).** We found that students in Group I, who used CPR, showed an increase in writing skills (from 41% on the pretest to 60% on the posttest). We found a very slight decrease in conceptual understanding (from 8% on the pretest to 7% on the posttest) and a slight increase in critical thinking (from 5% on the pretest to 9% on the posttest). The number of students in Group I who scored less than minimum points in all three skills (WO) decreased from 46% on the pretest to 24% on the posttest with CPR intervention (**Table 4.4** and **Table 4.8**).

Even though students in Group II did not use CPR, the posttest scores for the group as a whole showed significant improvement. Writing skills improvement increased from 40% for the pretest to 51% for the posttest; critical thinking skills improved from 4% for the pretest to 10% for the posttest; and number of students who obtained less than the minimum points in three areas (WO) decreased from 50% on the pretest to 33% on the posttest (see Table **4.5** and **Table 4.9**.) However, the there was no improvement in conceptual understanding for this group.

Group I with CPR intervention showed a significant improvement in writing skills compared to Group II. Group I improved by 19% in writing skills, while Group II only improved by 11%. However, the improvement in conceptual understanding for both groups was nearly identical with and without the use of CPR. In the case of critical thinking, Group I with CPR training improved by 4% while Group II without CPR improved by 6%. These findings suggest that CPR had no effect on conceptual

understanding or critical thinking.

Table 4.8: Student performance on posttest for Group I after submission of assignments 1-4 using of CPR

Title	WS	CU	CT	WS + CU	WS + CT	CU + CT	WS + CU + CT	WO
Stud.	123	15	19	10	11	3	3	49
%	60	7	9	-	-	-	-	24

Writing skills = WS Conceptual understanding = CU Critical thinking = CT
Obtained less than minimum points in all three areas = WO

Table 4.9: Students performance on posttest for Group II after submission of assignments 1-4 without using CPR

Title	WS	CU	CT	WS + CU	WS + CT	CU + CT	WS + CU + CT	WO
Stud.	111	13	22	10	8	3	2	72
%	51	6	10	-	-	-	-	33

Writing skills = WS Conceptual understanding = CU Critical thinking = CT
Obtained less than minimum points in all three areas = WO

For the purpose of comparison of individual student pretest and posttest scores, we carried out different analyses on the results using t-test, ANOVA-single factor, and Minitab program under Fisher multiple comparison box plot. The results are as follows:

i) The t-test

The t-test treatment of an objective essay results was carried out under null hypothesis, which states that both pretest and posttest compared have an equal mean (i.e., $H_o : \mu_1 = \mu_2$). Furthermore, it is reasonable to assume that posttest scores would be expected to be greater than pretest scores. The results in **Table 4.10** and **Table 4.11** are based on t-one tail that is directional. Through comparison of pretest and posttest scores for Group I students who submitted assignment 1-4 using CPR, the results from the t-test are summarized in **Table 4.10**. The table consists of four out of eleven sections (15,

16, 20 and 24), which were shown to have significant differences between pretest and posttest score means. These four sections have means that are above the theoretical t-value as shown in the histogram in **Figure 4.6**. The analysis has revealed that 36.4% of the sections have significant mean differences, as opposed to 63.6% of sections with insignificant mean differences. However, the summation of all sections scores (pretest and posttest for students who used CPR) revealed a t-test value ($t = 4.18$, $p < 2x10^{-5}$) that was statistically significant. Thus, the null hypothesis $H_o : \mu_1 = \mu_2$ is rejected.

Table 4.10: The t-test results (pretest-posttest comparison) for Group I students who did the posttest after using CPR

Section	Students	$\overline{X_1}$	$\overline{X_2}$	t-test calculated	t-one tail	t-two tail	P one tail	P two tail
12	16	2.25	3.28	1.50	1.69	2.04	0.07	0.14
15	11	2.82	4.82	**2.37**	1.72	2.08	0.01	0.02
16	8	3.13	4.69	**2.14**	1.76	2.14	0.02	0.05
20	19	2.89	4.18	**2.47**	1.69	2.03	0.01	0.02
24	13	3.50	4.58	**1.73**	1.71	2.06	0.05	0.10
27	18	4.06	4.61	0.90	1.69	2.03	0.19	0.37
28	15	4.53	4.00	0.69	1.70	2.05	0.25	0.50
29	22	4.52	4.75	0.40	1.68	2.02	0.35	0.70
30	17	3.68	4.32	1.43	1.69	2.04	0.08	0.16
31	16	3.66	3.75	0.21	1.70	2.04	0.42	0.83
34	11	2.86	2.68	0.29	1.72	2.09	0.39	0.78

Figure 4.6. The t-test Statistics Frequency Histogram for Students Performance on Pretest-posttest after Submission Assignments 1-4 Using CPR with Theoretical Value of t at 1.7 (t-one tail)

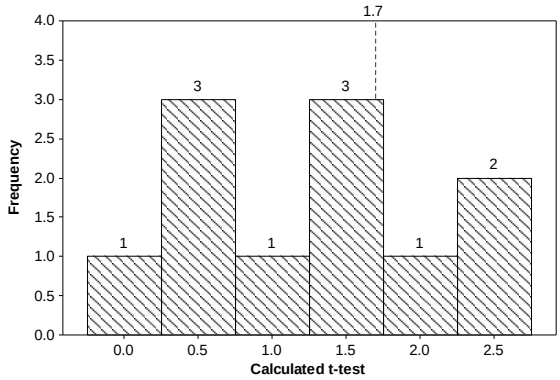
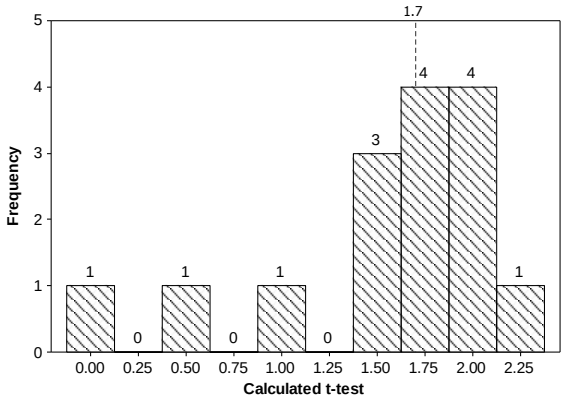


Table 4.11: The t-test results (pretest-posttest comparison) for Group II students who did posttest without the use of CPR

Section	Students	$\overline{X_1}$	$\overline{X_2}$	t-test calculated	t-one tail	t-two tail	P one tail	P two tail
11	20	3.28	3.95	1.40	1.69	2.02	0.08	0.17
14	15	2.90	4.23	**1.99**	1.70	2.05	0.03	0.06
17	16	3.22	4.16	**2.06**	1.69	2.04	0.02	0.05
18	18	2.33	3.31	**1.87**	1.69	2.03	0.03	0.06
21	15	2.90	3.87	1.42	1.70	2.05	0.08	0.16
22	14	3.29	4.32	**2.37**	1.70	2.05	0.01	0.02
23	16	3.50	3.06	0.90	1.69	2.04	0.18	0.37
25	17	3.65	4.38	1.54	1.69	2.03	0.06	0.13
26	20	3.50	2.50	0.05	1.68	2.04	0.48	0.96
32	18	2.72	3.42	**1.77**	1.69	2.03	0.04	0.08
33	15	2.90	3.93	**1.82**	1.70	2.05	0.04	0.08
37	15	2.93	4.27	**2.04**	1.70	2.05	0.02	0.05
38	13	2.54	3.85	**1.90**	1.71	2.06	0.03	0.07
38	22	4.41	4.11	0.49	1.68	2.01	0.31	0.62
41	11	3.23	4.41	**1.72**	1.72	2.08	0.12	0.24

Figure 4.7. The t-test Statistics Frequency Histogram for Student Performance on Pretest-posttest without Use of CPR Theoretical Value at 1.7 (t-one tail)



Among students who did not use CPR, the t-test revealed significant differences between pretest and posttest scores from nine out of fifteen sections (**Table 4.11** and **Figure 4.7**). Hence, it can be concluded that only 60.0% of the sections have significant differences in the mean, leaving 40.0% of the sections with a mean difference that is insignificant. On other hand, the t-test analysis performed on the sum of all sections scores (pretest and posttest for students who did not use CPR) yielded a value ($t = 6.30$ $p < 7x10^{-10}$) that was statistically significant. Thus, the null hypothesis $H_o : \mu_1 = \mu_2$ is rejected.

The overall t-test analysis performed on the pretest and posttest for both Group I and II students revealed statistically significant improvements from both groups with $\overline{X_2}$ - $\overline{X_1}$ (Posttest - pretest) = 0.63 for students who used CPR and $\overline{X_2}$ - $\overline{X_1}$ = 0.71 for students who did not use CPR. There is insignificant difference of means between these two groups when t-test was used to compare these two changes in means

ii) ANOVA

ANOVA-single factor analysis was performed on the Group I and Group II pretest and posttest) scores. This test was applied based on the null hypothesis that all scores in each section have equal variance (i.e., $H_o : \sigma_1^2 = \sigma_2^2 = \sigma_3^2 = ... = \sigma_k^2$). A separate analysis was performed to identify difference in performance between Group I and Group II. The calculated F-values indicate the existence of significant differences in variances for the two groups, which can be seen in **Table 4.12**, ($F = 2.94$, $p < 3x10^{-5}$) and **Table 4.13** ($F = 2.20$, $p < 4x10^{-4}$). Thus, the null hypothesis $H_o : \sigma_1^2 = \sigma_2^2 = \sigma_3^2 = ... = \sigma_k^2$ is rejected for both Group I and Group II.

Table 4.12: One-way analysis of variance of scores for Group I students who did pretest and posttest after using CPR

Groups	Count	Sum	Average	Variance
BF12	16.00	36.00	2.25	3.40
AF CPR	16.00	52.00	3.28	4.17
BF 15	11.00	31.00	2.82	3.76
AF CPR	11.00	51.00	4.68	3.06
BF 16	8.00	25.00	3.13	1.91
AF CPR	8.00	37.00	4.69	2.35
BF 20	19.00	55.00	2.89	1.24
AF CPR	19.00	79.00	4.18	3.92
BF 24	13.00	45.50	3.50	0.92
AF CPR	13.00	59.00	4.58	4.12
BF 27	18.00	73.00	4.06	4.64
AF CPR	18.00	83.00	4.61	3.19
BF 28	15.00	68.00	4.53	3.55
AF CPR	15.00	60.00	4.00	3.46
BF 29	22.00	99.50	4.52	3.08
AF CPR	22.00	104.50	4.75	4.21
BF 30	17.00	62.50	3.68	0.84
AF CPR	17.00	73.50	4.32	2.62
BF 31	16.00	58.50	3.66	0.69
AF CPR	16.00	60.00	3.75	2.40
BF 34	11.00	31.50	2.86	3.35

AF CPR	11.00	29.50	2.68	0.96

ANOVA

Source of Variation	SS	df	MS	F	p-value	F-crit.
Between Groups	180.29	21.00	8.59	2.94	0.00003	1.59
Within Groups	905.47	310.00	2.92			
Total	1085.76	331.00				

BF: pretest, AF CPR : posttest for student who submitted assignment 1-4 using CPR program, AF-No CPR : posttest for students who did not use the CPR program

Table 4.13: One-way analysis of variance for scores of Group II students who did pretest and posttest without the use of CPR

Groups	Count	Sum	Average	Variance
BF 11	20.00	65.50	3.28	1.51
AF-No CPR	20.00	79.00	3.95	3.13
BF 14	15.00	43.50	2.90	2.04
AF-No CPR	15.00	63.50	4.23	4.67
BF 17	16.00	51.50	3.22	1.20
AF-No CPR	16.00	66.50	4.16	2.12
BF 18	18.00	59.50	3.31	2.83
AF-No CPR	18.00	43.50	2.90	2.04
BF 21	15.00	43.50	2.90	2.04
AF-No CPR	15.00	58.00	3.87	4.87
BF 22	14.00	46.00	3.29	0.72
AF-No CPR	14.00	60.50	4.32	1.95
BF 23	16.00	56.00	4.32	1.95
AF-No CPR	16.00	49.00	3.50	2.10
BF 25	17.00	62.00	3.65	1.40
AF-No CPR	17.00	74.50	4.38	2.45
BF 26	20.00	70.50	3.53	1.46
AF-No CPR	20.00	71.00	3.55	3.63
BF 32	18.00	49.00	2.72	1.39
AF-No CPR	18.00	61.50	3.42	2.54
BF 33	15.00	43.50	2.90	2.54
AF-No CPR	15.00	59.00	3.93	2.25
BF 37	15.00	44.00	2.93	3.96
AF-No CPR	15.00	64.00	4.27	2.42
BF 38	13.00	33.00	2.54	1.60
AF-No CPR	13.00	50.00	3.85	4.64
BF 39	22.00	97.00	4.41	4.47

AF-No CPR	22.00	90.50	4.11	3.36
BF 41	11.00	35.50	3.23	4.97
AF-No CPR	11.00	48.50	4.41	5.54

ANOVA

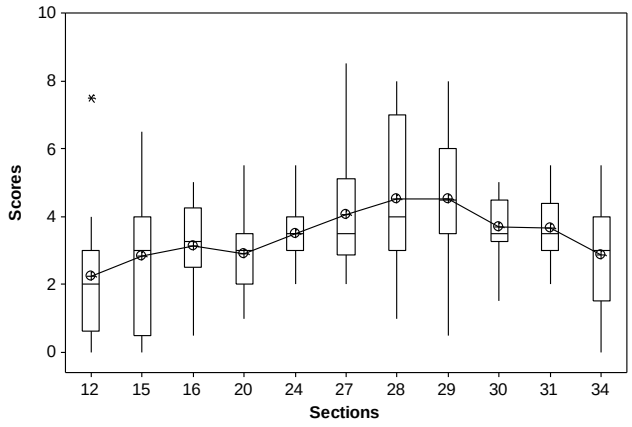
Source of Variation	SS	df	MS	F	p-value	F crit.
Between Groups	167.88	29.00	5.79	2.20	0.0004	1.49
Within Groups	1207.83	460.00	2.63			
Total	1375.72	489.00				

iii) Fisher multiple comparisons

The Fisher multiple comparisons package provided extra information that cannot be obtained through use of both t-test and ANOVA. The part of the package that was most useful to us was a box plot, which shows the score distribution of the various laboratory sections. The plot displays the values of mean and median of every section including any outliers.

The box plot scores for Group I are shown in **Figure 4.8** and reveals that the mean and median scores for the majority of sections are almost identical, with the exception of slight differences noted in Sections 27 and 28. In these two sections, three or more students in each section obtained relatively high grades (7 to 8 out of 10 points) as compared to other students in their respective sections. It is apparent from the box plot in **Figure 4.8** that the majority of student scores are clustered around the mean.

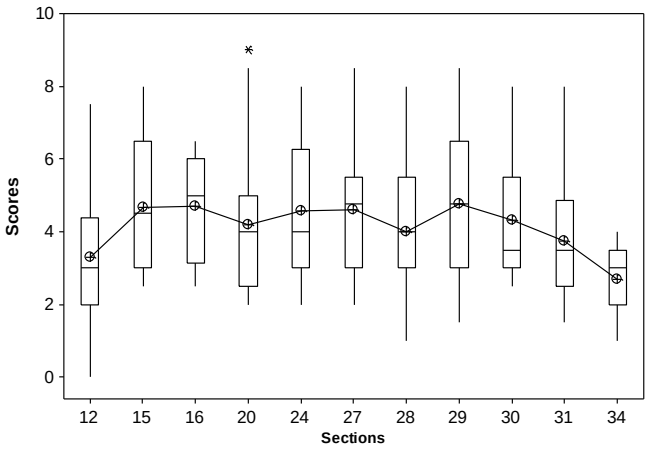
Figure 4.8. The Plot for Pretest Performance of Group I Students Who Later Submitted Assignments 1-4 Using CPR



Note: A box plot is depicting sections of numerical scores through the following summaries: (1) The smallest score (sample minimum) (2) The lower quartile (3) median (4) The upper quartile (5) The largest score (sample maximum) (6) The data not included between whiskers symbolizes as a star, stand for outlier (7) The dot inside the box represent the mean of the score in a section, in addition, a dash (-) representing the median.

The scores box plot presented in **Figure 4.9** for posttest scores of Group I students indicates that most of the sections showed nearly identical mean and median values, the exceptions being Sections 24 and 30, whose medians are lower than their respective means. This is due to the significantly higher score increases of three students. In general, all sections had mean scores slightly above 4 points, as compared to the scores in the pretest. Many students in Section 20 had above-average scores, including one outlier who had 9 points (**Figure 4.9**). The plot shows that the posttest performance of Section 34 remained almost the same pretest, whereas Sections 28 and 34 had lower posttest means in comparison with their pretest mean scores.

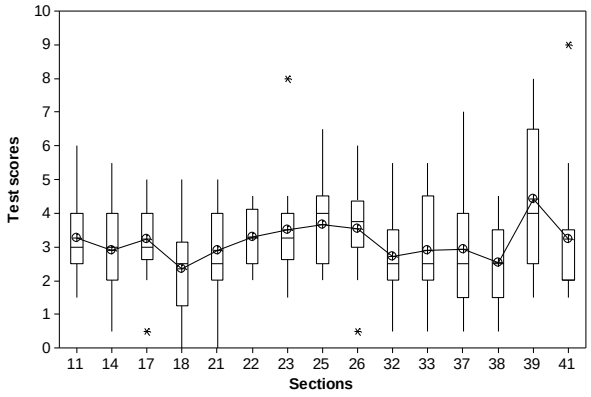
Figure 4.9. The Plot for Group I Student Posttest Performance after Submission Assignments 1-4 Using CPR



Note: A box plot is depicting sections of numerical scores through the following summaries: (1) The smallest score (sample minimum) (2) The lower quartile (3) median (4) The upper quartile (5) The largest score (sample maximum) (6) The data not included between whiskers symbolizes as a star, stand for outlier (7) The dot inside the box represent the mean of the score in a section, in addition, a dash (-) representing the median.

The box plot shown in **Figure 4.10** pretest for Group II shows that the medians of eight out fifteen sections are different from their respective means. This is due to the fluctuation of student scores, whereby a few individuals in the sections obtained higher grades as compared to the majority of students in the respective sections. The median values for Sections 17, 23, 33, 37 and 39 are lower than their respective means. Only the median of Section 25 is higher than its mean value. Section 39 had both the highest mean and the highest median.

Figure 4.10. The Plot for Group II Student Pretest Performance Who later Submitted Assignment 1-4 without Use of CPR

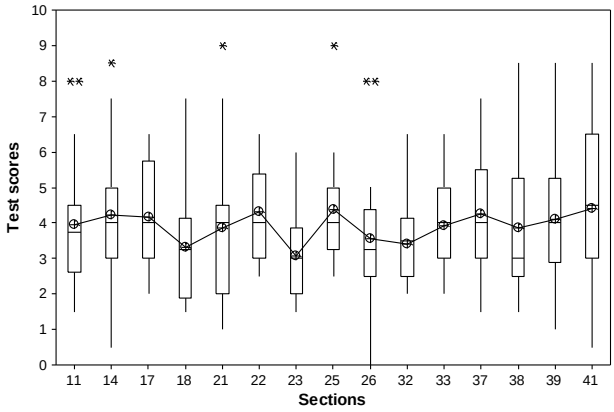


Note: A box plot is depicting sections of numerical scores through the following summaries: (1) The smallest score (sample minimum) (2) The lower quartile (3) median (4) The upper quartile (5) The largest score (sample maximum) (6) The data not included between whiskers symbolizes as a star, stand for outlier (7) The dot inside the box represent the mean of the score in a section, in addition, a dash (-) representing the median.

The box plot in **Figure 4.11** for Group II posttest scores shows that for most of the sections, both means and medians are the same. Sections 26 and 38, which have mean and median differences, are the exceptions. In both cases the mean values are higher than the median. The variations between means and medians observed in these two sections are due to outliers. This can be observed in Section 26, where students changed their scores from 2.5 to 8 and two students in Section 38 changed their scores from 2.5 to 8.5.

The general performance on the posttest appears to be wave-like from one section to the next (see **Figure 4.11**). Sections 23 and 39 had lower mean scores in the posttest as compared to the pretest. It is not clear why the mean for Section 39 dropped when it had the highest pretest score.

Figure 4.11. The Plot for Group II Student Posttest Performance Who did not Use CPR



Note: A box plot is depicting sections of numerical scores through the following summaries: (1) The smallest score (sample minimum) (2) The lower quartile (3) median (4) The upper quartile (5) The largest score (sample maximum) (6) The data not included between whiskers symbolizes as a star, stand for outlier (7) The dot inside the box represent the mean of the score in a section, in addition, a dash (-) representing the median.

4.7. Results of the questionnaire on student attitudes about the CPR process

4.7.1. Do peer reviews improve writing skills?

Students did not feel that the CPR program contributed to their writing skills (see **Table 4.14**). The mean rating scores for each of the writing skills statements ranged between 1.6 and 2.0 on 1-to-5-point Likert scales. The overall mean rating falls within two choices, strong disagreement and more disagreement than agreement, which suggests that, for some reason, the students did not like using the CPR program as a tool for submitting post-lab reports. This finding is contrary to the observation by Walvoord *et al*.[24] that students generally agreed (more than they disagreed) that their writing skills had improved with CPR and that they preferred submitting their papers using the CPR

program rather than turning in papers in the traditional way. However, contrary to the students' opinion in our questionnaire, the students' posttest on an objective essay after the use of CPR showed some improvement over the pretest results.

Table 4.14: Student ratings of the value of CPR in improving writing skills; the scale for this instrument ran from 1 (strong disagreement) to 5 (strong agreement)

	Writing Skill Statement	**Mean (N=400)**	**sd**
1.	Peer review processes in CPR helped increase my writing skill.	1.6	0.9
2.	My reviews of my peers' papers in CPR were helpful to me in learning how other students organize their points in writing.	2.0	1.1
3.	My reviews in CPR of my peers' papers enabled me to identify errors in spelling.	1.9	1.1
4.	Comments from my peer reviewers from CPR of my papers were helpful in writing chemistry reports.	1.7	1.0
5.	Comments provided by my peer reviews in CPR of my papers were helpful to me for identifying proper use of chemistry terms.	1.8	1.0
6.	Comments provided by my peer reviewers from CPR of my papers were beneficial to me such that it is unlikely I will commit the same mistakes in the future.	1.8	1.0
7.	Learning through multiple exposures to the assignment-related material has helped my writing skills.	1.9	1.1

It was my general observation that in the pretest, the majority of students were not able to write an essay with the format required in the question, but after using the CPR program a slight improvement in writing skills was noted. Quantitatively, these changes amounted to a 19% improvement in writing skills. This slight improvement answers our research question, although it somehow contradicts the students' own responses on the

questionnaire. Observable gains in writing skills do not happen suddenly. We can expect real gains in writing skills only when we consistently demand coherent writing. Then we should see improved writing abilities in our students.

4.7.2. Does CPR improve critical thinking?

The mean rating ranged from 1.8 to 2.2 on a scale of 1-to-5 point Likert scales (**Table 4.15**). The mean average rating indicates that students disagreed more than agreed that the use of the CPR program helped to develop their critical thinking, self-assessment, and/or active learning.

Table 4.15: Student ratings of the value of CPR in improving critical thinking skills; the scale for this instrument ran from 1 (strong disagreement) to 5 (strong agreement)

	Critical Thinking Skills Statement	**Mean (N=400)**	**sd**
1.	The peer review process in CPR helped me to develop critical thinking skills.	1.9	1.1
2.	My reviews in CPR of my peers' papers required careful reading and in the process I developed critical thinking skills.	2.1	1.1
3.	The comments written by my peer reviews provided me an opportunity to engage in conceptual understanding.	1.8	0.8
4.	The comments written by my peers' reviews from CPR pressured me to be responsible about reading the content.	2.1	1.2
5.	Comments provided by my peers' reviews from CPR pressured me to think critically during my assignment writing.	2.0	1.2
6.	Comments from my peers' reviewers from CPR have provided me a sense of accountability and active learning.	1.9	1.1
7.	Critiquing peers' enhances my self-critique and promotes realistic self-assessment.	2.2	1.2

A similar opinion was observed by Walvoord *et al*.[24] , whose student population

also exhibited more disagreement than agreement about the helpfulness of the CPR program in enhancing critical thinking. Given the attitude of the students, it is difficult to know if the CPR program actually enabled them to improve their critical thinking skills. As previously mentioned,[34] critical thinking develops slowly, through constant practice, so one cannot expect the submission of four post-lab reports using the CPR program to effect radical changes in critical thinking. In our case, the students who submitted their post-lab reports using the CPR program did not exhibit superior critical thinking skills on the posttest objective essay than those students who did not use CPR.

Table 4.16: Student ratings of the value of using CPR to submit post-lab reports; the scale on this instrument ran from 1 (strong disagreement) to 5 (strong agreement)

	Values of Using CPR Statement	**Mean (N=400)**	**sd**
1	The calibrated peer review (CPR) program is the best and most convenient tool to use in submitting Chem. 123L assignments.	1.3	0.7
2.	The CPR program enables high levels of interaction between students themselves as well as students' with the instructor.	1.5	0.9
3.	Using the CPR program helped me to identify and fill in knowledge gaps in my skill and abilities.	1.7	1.0
4.	Through using CPR one can significantly improve writing skills.	1.7	1.0
5.	The CPR program saves time and has provided me the chance to build my self-confidence in writing scientific reports.	1.4	0.9
6.	Using the CPR program in doing my assignments has promoted higher orders of thinking abilities.	1.7	0.9

The questionnaire aimed to discover the students' attitudes on the use of the CPR

program submit their post-lab reports. Generally, the rating of the benefits in using the CPR program fell within the mean range of 1.3 to 1.7 on a 1-to-5-point Likert scale (see **Table 4.16**). The students' responses basically expressed strong disagreement that CPR as a timesaving tool when submitting laboratory assignments, and also disagreed that the CPR program promotes interactions among students and/or improves critical thinking ability. This attitude has also been noted by other research groups,[54] perhaps because of the students' perception is that using the CPR program is too much work. Although CPR has proven to be a worthwhile tool that enhances or promotes writing skills, critical thinking, and interaction among students, for beginners it appears to be a waste of time.

Although the students were not given a formal opportunity to make extra comments on the questionnaire, approximately 15% of the anonymous respondents wrote comments, expressing their view that the CPR program required too much work. Walvoord and his co-researchers[24] reported that approximately 10% of their respondents held the same attitude. In our case study, some of the students expressed their anger and feared that their grades would be lowered because of the dishonesty of some of their peers, who they felt lacked grading experiences and did not take their work seriously. Others presumed that the grading was inconsistent and unfair, while still others said that they already knew how to write, and that, in any case, the course was a chemistry course, not an English class. Other complaints included the lack of clear, detailed explanations of how to use the CPR program. Generally speaking, the negative comments by the students outnumbered the positive ones. This overall low rating of the CPR program by the students, which appears to be typical for this type of questionnaire, was also observed by

other research groups.[50,59]

Positive comments were given by less than 1% of the respondents, who said that CPR helped them understand all aspects of laboratory work. Few respondents, however, stated that the use of the CPR program was educational. Others mentioned that the work involved in using CPR was equivalent to a three-credit course, rather than just one credit. On the positive side, students did not complain about a lack of computers or CPR accessibility. In the past, one of the major problems in implementing similar technologies to CPR had been a lack of computers.[60.61]

4.7.3. Students' attitude towards using the CPR program and its consequences

Student animosity toward using the CPR program, particularly among first-time users, seems to be common phenomenon. There may be a number of reasons for this: e.g., the newness and unfamiliarity of the method and/or a general lack of attention when reading the first essay, which is critical for the later calibration step. If the initial evaluation is poor, it will affect the calibration of the final individual score. The system appears "unfriendly" to some students, who prefer to submit their assignments at the last minute, despite the fact that sufficient time is provided (from days to weeks) for them to accomplish each of the assignments. Work performed under such circumstances is likely to receive a low score, since more time is probably needed to comprehend the questions being asked. Such shortcuts taken by students when submitting assignments will undoubtedly undermine the anticipated results of their learning.

Students frequently lack the ability to write well, since they have not had sufficient opportunity to communicate their thoughts in essays. The CPR program offers them the opportunity to improve their writing skills, although it is a fact that students are concerned about being over-worked.

Understanding early on that honesty is a basic prerequisite of using the CPR program is important, if one is to avoid being penalized by the program. Penalization often happens when a student awards a grade that is too low or too high a grade, either during calibration or when reviewing one's own work or the work of peers. The CPR program awards points to students based on how closely the grades they have provided agree with the weighted average from their own reviewers, not from the grades they have awarded themselves.

During the fall of 2010 semester both instructors and TAs were constantly reviewing as many students' reports and reviews as possible. Some students were also contacting the instructor to request a review of their grades.

4.8. What can be done to improve student attitudes towards CPR?

Due to the complexity of the CPR program (and the amount of time it takes to use it), students have negative attitudes toward the program. Such negative attitudes, which have also been observed by other research groups,[18,49,60,61] remain a problem in our findings. Students may well have a negative attitude to any writing assignment that requires the use of new technology (e.g., CPR) for the first time; we should therefore make an effort to encourage and help students who are still resistant to using such

technology. We should also help those students who have difficulties in adapting to the active and independent approach to learning that is promoted by the CPR program, since, in the end, such work is quite worthwhile.

Changing the negative attitudes of students to using CPR will require a conscious effort. It is important to catch the students' interest in CPR at the very beginning of a course. This will require a detailed explanation of its advantages and benefits, including the goal of using CPR, namely, to improve writing skills and critical thinking/reading. One should also provide students with the available data from previous courses that compare scores obtained using the CPR program with essay assignments graded by the instructor, pointing out that the use of CPR could largely reduces the subjective nature of evaluating written work. This can be important, since essays graded by instructors may well be influenced by extraneous factors, such as, essay length or handwriting quality.[62-65] At times a grade may also be influenced by whether the student is attractive or unattractive,[66] male or female,[67] or bright, persistent or lazy.[68] Under such circumstances, it is obvious that a grade may not necessarily be representative of a student's actual ability.

The literature provides evidence of dramatic variations in scores awarded identical essays by different raters.[62,69] There are numerous instances of rater inconsistencies, not only between or among different raters, but also by the same rater on different occasions.[70] The sources of instructor grading errors are many (e.g., leniency or

inconsistency, particularly when grading a large class). The CPR program might to a large extent provide a more objective-grading alternative to the course than having the instructor grade the reports. Currently, such problems can perhaps best be alleviated by adopting the CPR program, since the CPR program provides final grades automatically and, more importantly, makes the assessment more consistent and objective.

By awarding extra credit for the first assignment, learning how the system works, one can reduce the number of student complaints.[24,50] Some literature reveals that, as students used CPR for a second or third time, they naturally became more conversant with the program; and the number of complaints dropped dramatically.[50,54] To ensure that students are comfortable with the CPR program, before starting recording students' grades. This should be done when students have sufficient experience with the system and understand the settings that work best for their class. Furthermore, there should be concise written questions in the CPR that cover all essential criteria, and address the topic, of the writing assignment that the students are working on at the time.

At the beginning of the course, it should be explained to the students that careful reading and an understanding content is fundamental to using the CPR program. Unless students comprehend what they read, they can hardly answer the questions. In such a case, they will receive a low score in the calibration step.

Instructors should always be flexible in adjusting deadlines as circumstances requires. For day-to-day follow-up, the students should know when the CPR site is inaccessible. This will reduce student frustration, particularly when the system will be inaccessible close to an assignment deadline. It is also important for the TAs to have

better training on how the CPR program works, since this will enable them to better assist students in need. Deadline sheets for all assignments should be distributed to the students, and reminders should be sent to them by email. Furthermore, students should be made aware that, after they have submitted their assignment through CPR, they can continue to revise it until the specified deadline.

Despite the fact that, according to student opinion, using the CPR program requires too much work, at the moment there is no other appropriate method that is able to address the writing problems encountered in courses taken by large number of students; and instructors frequently silently accept poor writing because of the labor-intensive nature of teaching basic writing skills. Extensive laboratory work contributes to the problem, as does the acceptance of mathematics as a language, all adding up to poor writing in the chemistry curriculum.

As mentioned before, writing skills develop over time, as students are given writing assignments in their courses, so it would be a mistake to expect radical changes in student writing skills after a submission of only four post-lab reports. Also, we should remember that it is a general tendency for human beings to resist change in working habits. If a great effort is invested, however, and if the advantages of a new phenomenon (CPR) are made known to them, change is almost always inevitable.

Our study has one important limitation to bear in mind, namely, its assessment on the use of the CPR program was limited to first-year chemistry students over the course of one semester. Our findings are therefore restricted to a one-semester timeframe, since our project design did not allow a continuous assessment of the same students for more

than one semester. We believe that this limited timeframe has influenced the responses to some of our research questions (on conceptual and critical thinking), notably those that require a certain amount of assessment time in order to obtain comprehensive answers.

4.9. Conclusions

Conclusion 1. ***The results have shown that Group I and Group II students who took general Chemistry (CHEM 123L) in the fall 2010 and submitted four post-lab reports using the CPR program, showed average scores of 80% and 75% respectively, based on the two highest scores.*** This implies that students gained a better understanding of how to use the CPR program, but the knowledge gained by using CPR did not seem to improve student performance on the posttest (as we will discuss later). Also, the low rating that the students gave the CPR program on the questionnaire does not correlate with the good post-lab scores obtained by the students. We will need to investigate this phenomenon further in order to determine the sources of such an inconsistent relationship.

Conclusion 2. ***From the results of quantitative analyses, we agree that there is evidence that CPR improves writing skills, as previously reported[45-50]. CPR increases the proficiency of students who were deficient in all three areas: writing skills, conceptual understanding and critical thinking.*** Our investigation has found that, for students in Group I who used the CPR program before posttest, their writing skills improved by 19% from the pre-test, whereas the students in Group II who did not use CPR improved by 11%. This implies that CPR had a direct impact on student writing

skills, which answers our first research question. Furthermore, there was a 22% improvement in students who were not proficient in any of the areas (WS, CU and CT) but who used CPR; non-proficient students who did not use CPR improved by only 17%. This suggests that CPR may have the largest effect on those students with the weakest preparation. However, our results indicate that CPR had little effect on conceptual understanding or critical thinking. This answers our second research question regarding the potential impact of CPR on CU and CT.

Our study has revealed non-quantifiable qualities during my grading of the student essays, particularly for those students who used CPR before writing the posttest. I observed that the students' writing in the posttest essay was good (students were able to starting write a paragraph and connecting points together in essay format) compared to their pretest, in which most of them were unable to write in the essay format as it was asked in the essay question (pretest or posttest). A majority of students in the group that took the posttest without using CPR could not write in essay format; their grades seemed to improve, however, because some of them were able to obtain the correct calculation requested in the posttest, which they had not obtained in the pretest.

Conclusion 3. Statistical analyses (t-test and ANOVA) of pretest and posttest scores show significant differences for both CPR-users and non-CPR-users. This implies that the improvement noted in posttest performance is not necessarily due to the use of CPR. When t-test analysis was performed on the sum total scores (pretest and posttest for students with or without use of CPR) revealed significant mean differences in

pretest and posttest for both groups i.e., $H_o : \mu_1 = \mu_2$ is rejected. The results imply that, the posttest performances for students with or without use of CPR have some improvements compared to pretest results.

The statistical analysis comparison performed by using ANOVA on the pretest and posttest scores of both groups (CPR-users and non-CPR-users) revealed the existence of significant variance differences; i.e., $H_o : \sigma_1^2 = \sigma_2^2 = \sigma_3^2 = ... = \sigma_k^2$ is rejected.

Both t-test and ANOVA analyses have therefore revealed existing differences between pretest and posttest scores, regardless of whether or not the group used CPR to submit their post-lab reports. The statistical analysis gave us little reason to link the use of the CPR program and student improvement. The establishment of such a link would require continuing, long-term research on both students who are using CPR and those who are not, since our (limited) study of the two groups has shown the same results.

Our study indicates a slow learning-transfer among students, particularly among those students who used the CPR program for submitting four post-lab reports before taking the posttest. These students were expected to do better than non-CPR-users because the program contains basic necessary requirements that should have helped them in responding to the posttest. The concept of learning transfer should therefore be explained to students at the beginning of the course.

Conclusion 4. Feedback from students on the survey questions regarding the usefulness of CPR indicates that students have a low opinion of the program as rated on 1-to- 5-point Likert scale. This basically means that students were not comfortable

using CPR to submit post-lab reports. On the questionnaire, students gave low ratings on the issue of whether CPR helped them improve their writing skills. The majority of students strongly disagreed or disagreed more than agreed to the notion that CPR

improved their writing skills, with their ratings ranging from 1.7 to 2.2 on a 1-to-5-point Likert scale. Student attitudes to the CPR program remain a major challenge in our study, regardless of whether it can help students to learn or not.

The students also gave a low rating to the idea of CPR being a time-saving tool for submitting chemistry laboratory reports. This was the response by the majority of the students, who strongly disagree that CPR is time-saving tool that promote interactions among students. As previously reported, this seems to be a common response among beginners,[24,50,54] which may be due to a general lack of enthusiasm for, and preconceived notions about, the CPR program. The low rating (1.7 to 2.2) by students on this issue, indicates that the students generally disagree with our suggestion that CPR is a useful tool for submitting post-lab reports (Question 3).

4.10. Future directions

In conclusion, I should like to propose some suggestions for changing the way students view the use of the CPR program. First, a concerted effort should be made to offer an intensive training to all prospective CPR-users at least 2 hours before they are to start using the program. Ideally, this would be augmented by a copy of basic instructions, which should be helpful during implementation. The CPR program will surely be more

effective if adequate training on the program is also provided to the TAs. If such steps are taken, utilizing the CPR program should become less of problem over time. This has been observed by other research groups who used web-based technology (information communication technology-ICT,[71] web-based self- and peer-assessment system-Web-SPA[72], WebCT™[73]) similar to CPR.[74]

Second, continuous and rigorous evaluation of student views of CPR should also be performed during the course of a semester. A data collection for multi-semester changes in student writing skills, both CPR-users and non-CPR-users, would also be important. As other research groups have noted,[75,76] an evaluation of new methodologies from viewpoint of usability and educational effectiveness is also important when a new instructional technology (e.g. CPR) is initiated. One should also consider incorporating more subjective questions into the questionnaire and measure how they impact the students writing skills. Thus, in order to better implement the CPR program, one should also take the students' suggestions into account.

Third, the CPR program should be used not only by freshman in a single course, but rather continuously during the entire course of their college life, since even second-year students, who are expected to have good writing skills, have been found to exhibit varying qualities of writing (Kovac *et al.*[5]). Continuous training in writing will make the tracking of student progress using CPR quite easy. This should gradually enhance student interest in taking responsibility for their own learning through mutual collaboration and increasing knowledge with fellow students.

4.11. References

1. Breland, H. M.; Gaynor, J. L. A Comparison of Direct and Indirect Assessment of Writing Skill, *Journal of Educational Measurement*, **1979**, *16*, 119.
2. www. educause. edu/eli
3. Zinsser, W. Writing to Learn; Harper and Row: New York, **1988**.
4. Kovac, J.; Sherwood, D. W. *J. Chem. Educ*. **1999**, *76*, 1399.
5. Kovac, J.; Sherwood, D. W. Writing Across the Chemistry Curriculum: An Instructor's Handbook; Printice Hall: Upper Saddle River. NJ, **2001**.
6. Rosenthal, L. C. *J. Chem. Educ*. **1987**, *64*, 996.
7. Oliver-Hoyo, M. T. *J. Chem. Educ*. **2003**, *80*, 889.
8. Schepmann, H. G.; Hughes, L. A. *J. Chem. Educ*. **2006**, *83*, 1024.
9. Doody, T. C.; Gibbens, V. E. *J. Chem. Educ*. **1954**, *31*, 8.
10. Hobson, E. H.; Schafermeyer, K. W. Writing-to-Learn in Large Classes. American *Journal of Pharmaceutical Education*, **1994**, *58*, 423.
11. Walvoord, B. E.; Hunt, L. L.; Dowling, H. F.; McMahon, J. D. *In the Long Run*: *A Study of Faculty in Three Writing- Across the Curriculum Programs*. Urban, IL: National Council of Teachers of English, **1997**.
12. Piaget, J. *Science of Education and the Psychology of the Child*. Longman: London, **1971**.
13. Bound, D. Developing Student Autonomy in Learning 2nd ed. London: Kogan Page, **1988**.

14. Falchikov, N. Product Comparisons and Process Benefits of Collaborative Self and Peer Group Assessments. *Assessment and Evaluation in Higher Education*, **1986**, *11*, 146.
15. Shibley, I. A., Jr.; Milakofsky, L. M.; Nicotera, C. L. *J. Chem. Educ*. **2001**, *78*, 50.
16. Nilson, I. B. *College Teaching*, **2003**, *51*, 34.
17. Guilford, W. H. *Adv. Physiol. Educ*. **2001**, *25*, 167.
18. Hollenbeck, J. J.; Wixson, N. E.; Geske, G. D.; Dodge, M. W; Tseng, T. A.; Clauss, A. D.; Blackwell, H. E. *J. Chem. Educ*. **2006**, *83*, 1835.
19. Fawkes, K. L.; Berry, D. E. *Positive Pedagogy*, **2001**, *1*, 1496.
20. Widstrand, C. G.; Nordell, K. J.; Ellis, A. B. *J. Chem. Educ*. **2001**, *78*, 1044.
21. Koprowiski, J. L. *Coll. Sci. Teach.* **1997**, *27*, 133.
22. Barnett, R. W.; Blumner, J. S. (eds) *Writing Centers and Writing Across the Curiculum Programs*, West Port, CT: Greenwoood Press, **1999**.
23. Russell, A. A. "Calibrated Peer Review $^{TM\ A}$ Writing and Critical Thinking Instructional Tool" (Invention and Impact): Building Excellence in Undergraduate Science Technology, Engineering and Mathematics (STEM) Education. Washington DC: American Association for the Advancement of Science, **2005**.
24. Russell, A. A.; Chapman, O. L.; Wagner, P. A. *J. Chem. Educ*. **1998**, *75,* 578.
25. The Regents of the University of California, **2001**. who uses CPR? http://cpr.molsci. ucla. edu/who-uses-cpr.asp
26. Russell, A. A. *Growth Charts on History of Uses of CPR* Los Angeles: UCLA, **2005**.
27. Walvoord, M. E.; Hoefnagels, M. H.; Goffin, D. D.; Chumchal, M. M.; Long, D. A.

Journal of College Science Teaching, **2008**, 66.

28. Lightfoot, J. T. A. Different Method of Teaching Peer Review Systems. *Advances in Physiology Education*, **1998**, *274*, S57.
29. Bloom, B. S. (Ed), *Taxonomy of Educational Objectives, Cognitive Domain Longmans*, Green and Company, New York, **1956**.
30. Bean, J. C. *Engaging, Ideas, The Professor's Guide to Intergratating Writing Critical Thinking and Active Learning in the Classroom* Jossey-Bass, San Francisco, **1996**.
31. Falchikov, N.; Goldfinch, J. "Student Peer Assessment in Higher Education: A Meta-Analysis Comparing Peer and Teacher Marks" *Review of Educational Research*, **2000**, *70*, 287.
32. Lunsford, A. A. (Ed). Easy Writer, 2nd ed. Boston: Bedford ST. Martin's, **2002**.
33. Maimon, E. P.; Peritz, J. H. (Ed). A Writer's Resource. New York: McGraw-Hill. **2002**.
34. Bailin, S.; Case, R.; Coombs, J. R.; Daniels, L. B. *J. Curriculum Studies*, **1999**, *31*, 285.
35. Johnson, R. H. "The Problem of Defining Critical Thinking" in Norris, S. P. (eds) *The Generalizability of Critical Thinking,* Teacher College Press, New York, **1992**, 38.
36. http://www.patrickonions. Org/docs/academic/2009%20Thinking%20Critically.pdf
37. Beyer, B. Practical Strategies for the Teaching Thinking, Ally and Bacon, Boston, **1987**.
38. Browne, M.; Keeley, S. *Asking the Right Questions: A Guide to Critical Thinking*, Prentice-Hall, Upper Saddle River, N. J. **2001**.

39. Ennis, R. H. A Taxonomy of Critical Thinking Dispositions and Abilities. In Baron, J. B and Sternberg, R. J. (Eds), Teaching Thinking Skills: Theory and Practice New York: Freeman, **1987**, 9.
40. Russell, A. A. The Evaluation of CPR, Prepared for HP e-Education; Business Development, UCLA, **2001**.
41. Chapman, K. Impact of CPR in Economics 200, California State University, Northridge, **2000**.
42. Palaez, N. "Problem-Based Writing with Peer Review Improves Academic Performance in Physiology" Advances in Physiology Education, **2002**, *26*, 174.
43. Murphy, P. "Collaborative Innovations: New UC-Wide Partnerships are Transforming the Teaching and Learning Experiences" http://www.uctltc.org/news /**2001**/12/feature-6.htm.
44. Volume IV: What works, what matters, what last http://www.kpkal.org/template2.cfm?c_id=1317
45. Heise, E. A.; Palmer-Julson, A.; Su, T. M. Calibrated Peer Review Writing Assignment for Introductory Geology Courses. Abstract with Programs (Geological Society of America), **2002**, *34*, A-345.
46. McCarty, T.; Parkes, M. V.; Anderson, T. T.; Mines, J.; Skipper, B. J.; Grebosky, J. *Academic Medicine*, **2005**, *80*. S67.
47. Carlson, P. A.; Berry, F. C. Calibrated Peer Review and Assessing Learning Outcomes. Paper Presented at the 33rd ASEE/IEEE Frontiaers in Education Conference, Boulder, Co. **2003**.

48. Carlson, P. A.; Berry, F. C.; Voltmer, D. Incorporating Student Peer-review into an Introduction to Engineering Design Course. Paper Presented at the 35th ASEE/IEEE Frontiers in Education Conference, Indianapolis, IN, **2005**.

49. Donovan, J. B. My Computer, my Writing Coach. *Howard Hughes Medical Institute* (*HHMI*) *Bulletin*, **2003**, *16*, 7.

50. Robinson, R. Calibrated Peer Review an Application to Increase Student Reading and Writing Skills American Biology Teacher, **2001**, *63*, 474.

51. Furman, B.; Robinson, W. Improving Engineering Report Writing with Calibrated Peer Review. Paper presented at the 33rd ASEE/IEEE Frontiers in Education Conference, Boulder, Co. **2003**.

52. Gerdeman, R, D.; Russell, A. A.; Worden, K. J. Web-based Student Writing and Reviewing in a Large Biology Lecture Course, *Journal of College Science Teaching*, **2007**, *36*, 46.

53. Kim, S. H.; Wise, J.; Hillsley, M. Learning Technical Writing Skills Through Peer Review: Use of Calibrated Peer Review in unit Operation Laboratory. Paper Presented at AIChE Annual Meeting, Conference Proceedings, **2005**.

54. Margerum, L. D.; Gulsud, M.; Manlapez, R.; Rebong, R.; Love, A. Application of Calibrated Peer Review Writing Assignments to Enhance Experiments with an Environmental Chemistry Focus, *J. Chem. Educ*. **2007**, *84*, 292.

55. Plutsky, S.; Wilson, B. A. Comparison of Three Methods for Teaching and Evaluating Writing: Aquasi-experimental Study. *Delta pi Epsilon*, **2004**, *46*, 50.

56. Palaez, N. Calibrated Peer Review in General Education Undergraduate Human

Physiology. In Proceedings of Annual International Conference of the Association for the Education of Teachers in Science, Costa Mesa. California, **2001**, 8.

57. Reynolds, J.; Moskovitz, C. *Journal of College Science Teaching*, **2008**, 60.
58. Devore, J.; Farnum, N. Applied Statistics for Engineers and Scientists, 2nd ed. **2005**, 402.
59. Nickle, T. Association for Biology Laboratory Education, Proceedings, **2006**, *27*, 328.
60. Slotte, V.; Wangel, M.; Lonka, K. Information Technology in Medical Education: A Nationalwide Project on Opportunities of the New Technology. *Medical Education*, **2001**, *35*, 990.
61. Dewhurst, D. G.; Macleod, H. A.; Norris, T. A. Independent Student Learning Aided by Computers: An Acceptable Alternative to Lectures? *Computers&Education*, **2000**, *35*, 223.
62. Shepherd, E. M. The Effect of Quality of Penmanship on Grades. *Journal of Educational Research,* **1926**, *19*, 102.
63. Chase, C. I. The Impact of Some Obvious Variables on Essay Test Scores. *Journal of Educational Measurement*, **1968**, *5*, 315.
64. Briggs, D. Influence of Handwriting on Assessment. *Educational Research*, **1970**, *13*, 50.
65. Soloff, S. Effect on Non-content Factors on the Grading of Essays, *Graduate Research in Education and Related Disciplines*, **1973**, *6*, 44.
66. Clifford, M. M.; Walster, E. The Effect of Physical Attractiveness on Teacher

Expectations, *Socialogy of Education,* **1973**, *46*, 248.

67. Austin, D. E.; Clark, V. B.; Fitchett, G. W. Reading Right for Boys, New: Appleton-Century-Crofts, **1971**.
68. NEA Research Division. Marking and Reporting Pupil Progress. *Today's Education*, **1970**, *59*, 55.
69. Markham, L. R. Influences of Handwriting Quality on Teacher Evaluation of Written Work. *American Educational Research Journal,* **1976**, *13*, 227.
70. Coffman, W. E. Essay Examinations, In Educational Measurement 2nd ed. R. L. Thorndike, ed. Washington, DC.: American Council on Education, **1971**.
71. Masiello, I.; Ramberg, R.; Lonka, K. Attitudes on the Application of a Web-based Learning System in a Microbiology Course, *Computers & Education,* **2005**, *45*, 171.
72. Sung, Y. T.; Chang, K. E.; Chiou, S. K.; Hou, H. T. The Design and Application of a Web-based self-and Peer-assessment System, *Computers & Education*, **2005**, *45*, 187.
73. Holtzman, J. M.; Elliot, N.; Biber, C. L.; Sanders, R. M. Computerized Assessment of Dental Student Writing Skills, *Journal of Dental Education*, **2005**, *69*, 285.
74. Jolliffe, A.; Ritter, J.; Stevens, D. The Online Leaning Handbook-devoloping and Using Web-basd Learning London: Kogan Page Limited, **2001**.
75. Pelgrum, W. J. Obstacles to the Integration of ICT in Education: Results from a Worldwide Educational Assessment. *Computers & Education*, **2001**, *37*, 163.
76. Ward, J. P. T.; Gordon, J.; Field, M. J.; Lehmann, H. P. Communication and Information Technology in Medical Education. *The Lancet*, **2001**, *357*, 792.

4.12. Appendix II

The determination of empirical formula from experimental data.

Top

Use your actual data from lab to answer all of the following questions. Use your lab manual for help with calculations. Instructions for CPR and grading can be found in WebCT.

Top

Top

Based on your experimental data from your lab Experiment 4, answer the following questions. You need to address the questions listed in the next section. You should NOT give your answers without providing a logical explanation according to the principles of stoichiometry and the experiment.

Download the data submission template from webCT for this experiment. Before submitting your essay make sure you have included all of your data in the essay as laid out in the template. Your data will be necessary to the students that are grading, and you will be marked off points if your data is not clearly displayed.

Top

1. Describe the hypothesis you wrote in the pre-lab and write a conclusion for your experiment and include data and explanation whether your hypothesis was supported or not supported. Comment on experiment error and possible ways to prevent this error. If you find you have no error, comment on precautions taken to avoid the error.

2. What is the empirical formula of magnesium oxide according to your calculations based on your experimental data? Describe steps taken and show calculations made to determine this formula.

3. Based on your experimental data calculate the empirical formula of Zinc ferrocyanide. Provide a logical step-by-step explanation of how you reached your result.

Top

Again, do not forget to present calculation steps and logical reasons for your answers. The answer for each question should be labeled clearly in separate paragraphs (to create separate paragraphs insert the tag < p > or < br > without spaces). Please also check your writing for (1) errors in the tenses used in the verbs, (2) run-on sentences, (3) sentence fragments, and (4) abbreviations

Assignment Preview Close

Title: Duplicate of Experiment 4: Stoichiometry

NOTE: This preview only displays saved data.

Assignment Goals

Source Material

Source Material Resources:

Instructions for CPR - Getting started and useful tips

URL:

http://cpr.molsci.ucla.edu/cpr/data/designers/y/y11162/assignments/200019/resources/res001/file/RelativeResourceManager.pdf

Instructions for grading CPR - How to determine the "rating" for each text. The rating is

determined only by the formula, not by judgment and it is NOT ARBITRARY.

URL:

http://cpr.molsci.ucla.edu/cpr/data/designers/y/y11162/assignments/200019/resources/res002/file/Instructions for grading using the rubric.pdf

Student Instructions

Guiding Questions

Writing Prompt

Preview Assignment Page 1 of 10

http://cpr.molsci.ucla.edu/cpr/cpr/designer/activation/preview_all.asp?loginID=y11162&i_... 3/23/2011

that is not defined.

Remember to check the Student Instructions for HTML tags.

An easy way to generate an HTML-coded essay is to write the essay in Microsoft Word. Go to **File**, **Save As** and select **Web page** in the **Save as Type** box. Then in your browser open the file you just saved under **File** and **Open**. Then select the essay you just wrote from where it was saved. Once open right click on the essay and select **View source** and scroll down to find your essay. The essay usually begins after the tag "body" and ends after "/body" tag. Copy your essay and paste it into the CPR text box.

Top

Average Calibration Word Count = 438

Calibrations and Answer Keys

High Quality Calibration

1. Hypothesis: If the molar ratio can be determined from weight measurements and combustion, and the combustion goes to completion, the empirical formula can be calculated. Based on the oxidation states of these two elements, I hypothesize the empirical formula will be MgO. Also, the stochiometric ratio between zinc and ferrocyanide can be indicated by the color of the complexing agent and will be $Zn_2(Fe(CN)_6)$ based on the charges of the intermediate species. From my experimental data, one mole of oxygen reacted with one mole of Mg after converting all of the data into moles. This data supports my hypothesis because I found the exact empirical formula I had guessed. For the second part of the experiment, my data do not support my hypothesis because the zinc ferrocyanide formed as an ion not in a double replacement reaction. The correct stoichiometric relationship was seen in the test tubes at the transition point between the colors. Those test tubes had the correct 3:2 mole ratio for Zn and ferrocyanide. Possible sources of error may include the reaction with magnesium and diatomic nitrogen or not allowing the Mg to fully combust. Also in the second part of the experiment, if measurement was not very careful, the stoichiometric ratio could have been altered. I found there was no error in the empirical formula of MgO found. I prevented problems by allowing full combustion with oxygen available. I checked and rechecked the mass of my crucible until no mass change was present. I converted all of the Mg nitride into MgO. I made sure there were few sources for contamination. 2. The empirical formula of magnesium oxide is MgO. From the experimental data, the number of grams of Mg is the difference between the empty crucible and the crucible with Mg. The mole of Mg present is the mass divided by the atomic mass of Mg.

17.849g-17.539g= .310g Mg

.310g/24.305g/mol= .01276mol Mg.

The grams of oxygen reacted would be the difference between the crucible with Mg and the crucible with products. The moles of O reacted will be the difference in mass divided by the atomic mass of O.

18.016g-17.840g= .176g O

.176g/16.0g/mol= .011 mol O To find the mole ratio I will set the number of moles of each as a ratio and find the smallest whole number ratio.

.0128/.011= 1.16

The mole ratio is very close to 1:1. This means that the empirical formula contains 1 mole of Mg and 1 mole of O, because empirical formulae are the simplest molar ratios of the elements in question. So the empirical formula is MgO. 3. To find the empirical formula of Zinc ferrocyanide, the color transition in the two sets of test tubes must be carefully analyzed. For the first set of test tubes, the zinc concentration was kept constant. The color transition between whiteish and green occurred in test tube 4 because 5 was completely white and 3 was already very green. For the second set of tests the ferrocyanide was kept constant and the zinc was added. Here the transition between whiteish and blueish happened in test tube 7 because 6 was completely white and 8 was already blue. Therefore, the correct ratios are in test tubes 4 and for 3 mL Zn to every 2 mL ferrocyanide. To calculate the empirical formula from this we need to find the number of moles of each reagent in that volume. To get moles of both reagents, I will

multiply the molarity of the solution by the volume in the correct ratio to get the number of moles. Then to get the mole ratio I will divide the number of moles of Zn by the number of moles of ferrocyanide.

Zn: .1 M*.003L=.0003 mol

$Fe(CN)_6$: .1 M*.002L=.0002 mol

.0003/.0002=3:2 mole ratio.

From this mole ratio the empirical formula of Zinc ferrocyanide is $Zn_3(Fe(CN)_6)_2$

-2 because the mole ratio is always expressed as the simplest ratio of whole numbers.

1. For question 1 the following should be present: hypothesis statement; data supporting or not supporting the hypothesis and explanation; concluding statements.

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: A

Feedback : Great detailed hypothesis, evidence of data supporting is present and

explanation of data.

2. For question 1: Was there a meaningful explanation presented for the potential experimental error in determining the empirical formula? Did the essay include steps that could be taken to avoid the same experimental error next time?

Examples of meaningful explanations include: incomplete combustion of magnesium due to not letting the reaction run long enough magnesium reacting with something other than oxygen magnesium sample containing an impurity

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: A

Feedback : Possible errors and precautions taken to avoid errors are described in detail.

3. For Question 2: Was the empirical formula of magnesium oxide presented? Was the empirical formula of magnesium oxide presented correct as MgO?

A: It was presented and is correct

B: It was not correct but is present

c: It is not present

A

B

C

Answer: A

Feedback : Yes the correct formula is present.

4. Did the essay include a reasonable written description of how the empirical formula of magnesium oxide was determined? For example, the explanation of how the mass of oxygen was calculated from the experimental data should be included. Were the calculation steps for empirical formula of magnesium oxide presented in detail? Appropriate detail would include calculations of: masses of magnesium and oxygen number of moles of magnesium and oxygen the simplest molar ratio of magnesium to oxygen

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: A

Feedback : Student describes using before and after measurements to find the mass of oxygen, student converted masses of both species into moles and found the ratio.

Description is detailed.

5. For question 3 the following requirements should be present: explanation of how

to determine the test tube with the correct mole ratio, determination of mole ratio from the contents of the test tube with both explanation and calculations, the empirical formula of Zinc ferrocyanide (ok if not correct for this question).

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: A

Feedback : Yes explanation of the observations leading to the correct combination was detailed. Explanation and calculations are clear. The empirical

6. Was the empirical formula for zinc ferrocyanide correct? It is $Zn_3(Fe(CN)_6)_2$

A: Correct

B: Present but not correct

C: Not present

A

B

C

Answer: A

Feedback : Correct and present

7. Download the excel template for this assignment from here. Use the template to plug in the student's data to see if the student calculated their result correctly. Compare their result listed in their essay with the one you just calculated. Is the result correct?

A: Result is correct or differs only slightly (may be from rounding error or sigfigs)

B: Result is incorrect but all necessary data is clearly displayed and the student may have just performed a wrong calculation.

C: Student did not display enough data to use the template to get a result.

A

B

C

Answer: A

Feedback : Result and calculations are correct

8. Are the questions answered in paragraph format using complete sentences with correct grammar? Is everything spelled correctly?

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: A

Feedback : none

9. For all calculations: were the calculations steps shown in detail (work shown)? Is every calculation explained in writing in addition to the work shown?

A: All calculations have explanations in writing and have calculation steps shown.

B: Most calculation steps are shown, explanation not present for every calculation but some.

C: Little work shown and little to no explanation provided.

A

B

C

Answer: A

Feedback : All calculations are explained in words before they are performed. Calculations steps are easy to follow

10. How would you rate this text?

10 Highest

9

8

7

6

5

Top

3

2

1 Lowest

Rating: 10

Feedback : Rating: 18*10/18=10

This essay meets or exceeds all requirements. It is written in detail and all calculations and data manipulations are explained.

Mid Quality Calibration

1.In this experiment I believe it will be very difficult and near impossible to get to the original mass of Magnesium (Mg) after adding water to it. I also predict that in the second part of the experiment there will be no similar chemical in the test tubes. (Mixed with potassium ferrocyanide) The colors will be different, the denser it gets, with the help of the indicator; they will become darker and cloudier. The densities will clearly be different escalating little by little indicated by color change.

2. The final empirical formula we got for the final product was Mg_2O. We got this formula by calculating the mass of the crucible+lid+product which ended up being 18.882g on the second trial. (The goal of this section was to get it to be relatively close

to the first mass you acquired before adding in the water droplets from the pipette.) After subtracting the mass of the empty crucible+cover from the mass of the crucible+cover+Mg, we arrived at the mass of the Mg sample.

a) After knowing the basic information listed above, you can begin the process of finding the empirical formula. We start by dividing he mass of the Mg sample (0.25 g) by 24 g/mol (the atomic mass of Mg) (0.25)g/(24 g/mol)RMM= 0.0104 mol b)Second I will calculate how much O is left in the final product by subracting the initial mass weighed, 18.873g from the final mass of 18.882g/ Here we arrive at 0.009g. After this we will divide 0.009 g by Oxygens RMM 16. 18.882g-18.873g= 0.009 0.009/16=0.0056 mol

c) Now that we have obtained our two answers of 0.0104 mol and 0.0056 mol we will have to find the simplest ratios. We find this by dividing by the smallest number. #1 0.0140/0.0056=1.8, which rounds to approximately 2 #2 0.0056/0.0056= 1 Therefore the simplest ratio comes out to 2:1 This indicates that for every two moles of magnesium used there is one mole of oxygen needed. ---

>The product here is Mg_2O

3. First let's write out the balanced equation for the reaction of Zinc Nitrate and Potasssium Ferrocyanide. a)2 $Zn(NO_3)_2$ + $K_4Fe(CN)_6$ ----> Zn_2 $Fe(CN)_6$ + 4KNO_3 For now we will be looking only into the $Zn_2Fe(CN)_6$. (You reach this result by balancing your equation.) Calculation of molar mass: Zn- 2 x 65.38 = 130.76 Fe- 1 x 55.85 = 55.85 C- 6 x 12.01 = 72.06 N- 6 x 14.01= 84.06

You will then need to divide the answers you just got by the smallest number to get the simplest ratio. The smallest number/result is 55.85. Therefore Zn- 2 Fe- 1 C- 1 N- 2 The

empirical formula is as follows $Zn_2Fe(CN)_6$

1. For question 1 the following should be present: hypothesis statement; data supporting or not supporting the hypothesis and explanation; concluding statements.

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: C

Feedback: Hypothesis statement is unclear, or is not present. Student talks about densities of the zinc and ferrocyanide reaction which is not correct. No concluding statements other than that.

2. For question 1: Was there a meaningful explanation presented for the potential experimental error in determining the empirical formula? Did the essay include steps that could be taken to avoid the same experimental error next time?

Examples of meaningful explanations include: incomplete combustion of magnesium due to not letting the reaction run long enough magnesium reacting with something other than oxygen magnesium sample containing an impurity

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: C

Feedback : No mention of experimental error

3. For Question 2: Was the empirical formula of magnesium oxide presented? Was the empirical formula of magnesium oxide presented correct as MgO?

A: It was presented and is correct

B: It was not correct but is present

c: It is not present

A

B

C

Answer: B

Feedback : listed as Mg_2O

4. Did the essay include a reasonable written description of how the empirical formula of magnesium oxide was determined? For example, the explanation of how

the mass of oxygen was calculated from the experimental data should be included. Were the calculation steps for empirical formula of magnesium oxide presented in detail?

Appropriate detail would include calculations of: masses of magnesium and oxygen number of moles of magnesium and oxygen he simplest molar ratio of magnesium to oxygen

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: A

Feedback : Description of method of finding the empirical formula was detailed.

Calculations are explained and calculation work is present and easy to follow

5. For question 3 the following requirements should be present: explanation of how to determine the test tube with the correct mole ratio, determination of mole ratio from the contents of the test tube with both explanation and calculations, the empirical formula of Zinc ferrocyanide (ok if not correct for this question).

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: C

Feedback : Student did not consider the combinations in the test tubes and just balanced a reaction.

6. Was the empirical formula for zinc ferrocyanide correct? It is $Zn_3(Fe(CN)_6)_2$

-2

A: Correct

B: Present but not correct

C: Not present

A

B

C

Answer: B

Feedback : Present no correct.

7. Download the excel template for this assignment from here. Use the template to plug in the student's data to see if

Top

the student calculated their result correctly. Compare their result listed in their essay with the one you just calculated. Is the result correct?

A: Result is correct or differs only slightly (may be from rounding error or sigfigs)

B: Result is incorrect but all necessary data is clearly displayed and the student may have just performed a wrong calculation.

C: Student did not display enough data to use the template to get a result.

A

B

C

Answer: B

Feedback : Data is displayed but the student manipulated it in the wrong way.

8. Are the questions answered in paragraph format using complete sentences with correct grammar? Is everything spelled correctly?

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: A

Feedback : none

9. For all calculations: were the calculations steps shown in detail (work shown)? Is every calculation explained in writing in addition to the work shown?

A: All calculations have explanations in writing and have calculation steps shown.

B: Most calculation steps are shown, explanation not present for every calculation but some.

C: Little work shown and little to no explanation provided.

A

B

C

Answer: A

Feedback : All calculations are described

10. How would you rate this text?

10 Highest

9

8

7

6

5

4

3

2

1 Lowest

Rating: 6

Feedback : Rating calculated as points scored multiplied by 10 over the total pts possible(2 x # of questions) 10x10/18=5.55~6

The student had a detailed and correct explanation for determining the empirical formula of magnesium oxide but was confused on how to write a hypothesis and conclusion and also on how to determine the empirical formula of zinc ferrocyanide from the experiment.

Low Quality Calibration

1. An indicator was used to help determine the reaction for zinc and ferrocynide. It led to physical colors that were documented and used in the results. The mangesium oxide was made into a pure substance by carefully doing a combustion reaction. This required repetition and the addition of water due to the uncontrollable force of nitrogen leaving the compound while over the burner. The hypothesis therefore was supported in this experiment. Errors occurred such as spilling a tiny amount of the magnesium oxide out of the crucible while making it into a pure substance. This did not dramatically change the results but did make it a bit more difficult to determine the pure substance in the end.

2. The empirical formula for Magnesium Oxide according to our data was Mg4O. This was derived by using the amount of solutions

required (which was in the lab manual), and from here the concentrations were necessary. These concentrations were determined by using M1V1=M2V2 The calculations are the

number of moles of magnesium divided by the number of grams of oxygen. Then the number of moles of magnesium are multiplied by 16 grams. These are then multiplied by 2 and 3.

3. The molecular weight must first be determined by multiplying the atomic masses of each element by the number of each element in the reaction. These calculations are then added to one another. The molar mass of this compound is 342.7674 g/mol.

Now we derive the formula by using M1V1=M2V2 to get the concentration

zinc ferrocyanide.

65.409x2 + 55.845 + (12.0107 + 14.0067)x6= 342.7674 g/mol

Empirical formula= $Zn_2Fe(CN)_6$

1. For question 1 the following should be present: hypothesis statement; data supporting or not supporting the hypothesis and explanation; concluding statements.

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: C

Feedback : Student's hypothesis is not clear. Concluding statements are not present or are unclear. Statements about what happened in the experiment are not concluding

statements.

2. For question 1: Was there a meaningful explanation presented for the potential experimental error in determining the empirical formula? Did the essay include steps that could be taken to avoid the same experimental error next time?

Examples of meaningful explanations include: incomplete combustion of magnesium due to not letting the reaction run long enough magnesium reacting with something other than oxygen magnesium sample containing an impurity

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: B

Feedback : One statement about experimental error is present, but their conclusions about this statement are incorrect.

3. For Question 2: Was the empirical formula of magnesium oxide presented? Was the empirical formula of

magnesium oxide presented correct as MgO?

A: It was presented and is correct

B: It was not correct but is present

c: It is not present

A

B

C

Answer: B

Feedback: present, not correct

4. Did the essay include a reasonable written description of how the empirical formula of magnesium oxide was determined?

For example, the explanation of how the mass of oxygen was calculated from the experimental data should be included. Were the calculation steps for empirical formula of magnesium oxide presented in detail?

Appropriate detail would include calculations of:

Masses of magnesium and oxygen number of moles of magnesium and oxygen

the simplest molar ratio of magnesium to oxygen

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: C

Feedback : Student attempted to explain how the formula was determined but was confused on which part of the experiment the determination comes from. There is no mention of weighing the product of magnesium. Explanation is incorrect

5. For question 3 the following requirements should be present: explanation of how to determine the test tube with the correct mole ratio, determination of mole ratio from the contents of the test tube with both explanation and calculations, the empirical formula of Zinc ferrocyanide (ok if not correct for this question).

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: C

Feedback : Student again is confused on how to find the empirical formula. Explanation is unclear and not correct.

6. Was the empirical formula for zinc ferrocyanide correct? It is $Zn_3(Fe(CN)_6)_2$

-2

A: Correct

B: Present but not correct

C: Not present

A

B

C

Answer: B

Feedback : Present but incorrect

7. Download the excel template for this assignment from here. Use the template to plug in the student's data to see if the student calculated their result correctly. Compare their result listed in their essay with the one you just calculated. Is the result correct?

A: Result is correct or differs only slightly (may be from rounding error or sigfigs)

B: Result is incorrect but all necessary data is clearly displayed and the student may have just performed a wrong calculation.

C: Student did not display enough data to use the template to get a result.

A

B

C

Answer: C

Feedback : Missing data for question 2

8. Are the questions answered in paragraph format using complete sentences with correct grammar? Is everything

spelled correctly?

A: All requirements are addressed in detail

B: Most requirements present with some detail

C: Some requirements addressed

A

B

C

Answer: B

Feedback : Several run on sentences and spelling mistakes

9. For all calculations: were the calculations steps shown in detail (work shown)? Is every calculation explained in writing in addition to the work shown?

A: All calculations have explanations in writing and have calculation steps shown.

B: Most calculation steps are shown, explanation not present for every calculation but some.

C: Little work shown and little to no explanation provided.

Top

A

B

C

Answer: B

Feedback : Calculations were incorrect but there is explanations and some work shown.

10. How would you rate this text?

10 Highest

9

8

7

6

5

4

3

2

Lowest

The following are some questionnaire statements in assessing writing skills:

1. Peer review processes in CPR helped increase my writing skill.
2. My reviews of my peers' papers in CPR were helpful to me in learning how other students organize their points in writing.
3. My reviews in CPR of my peers' papers enabled me to identify errors in spelling.
4. Comments from my peer reviewers from CPR of my papers were helpful in writing chemistry reports.
5. Comments provided by my peer reviews in CPR of my papers were helpful to me for identifying proper use of chemistry terms.
6. Comments provided by my peer reviewers from CPR of my papers were beneficial to

me such that it is unlikely I will commit the same mistakes in the future.

7. Learning through multiple exposures to the assignment-related material has helped my writing skills.

The following are questionnaire statements in assessing critical thinking skills:

1. The peer review process in CPR helped me to develop critical thinking skills.
2. My reviews in CPR of my peers' papers required careful reading and in the process I developed critical thinking skills.
3. The comments written by my peer reviews provided me an opportunity to engage in conceptual understanding.
4. The comments written by my peers' reviews from CPR pressured me to be responsible about reading the content.
5. Comments provided by my peers' reviews from CPR pressured me to think critically during my assignment writing.
6. Comments from my peers' reviewers from CPR have provided me a sense of accountability and active learning.
7. Critiquing peers' enhances my self-critique and promotes realistic self-assessment.

The following are questionnaire statements in assessing values of using CPR:

1. The calibrated peer review (CPR) program is the best and most convenient tool to use in submitting CHEM 123L assignments.
2. The CPR program enables high levels of interaction between students themselves as

3. Using the CPR program helped me to identify and fill in knowledge gaps in my skill and abilities.
4. Through using CPR one can significantly improve writing skills.
5. The CPR program saves time and has provided me the chance to build my self confidence in writing scientific reports.
6. Using the CPR program in doing my assignments has promoted higher orders of thinking abilities.