The synthesis of phosphonium indenylides and an investigation of their coordination to group 4 metals

by

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Abstract

A class of phosphonium cyclopentadienylide ligands was first reported in 1956 by Ramirez and Levy, who synthesized triphenylphosphonium cyclopentadienylide. They discovered that this ylide was unusually inert, for instance being unreactive with ketones; they attributed this unusual stability to its ability to undergo charge delocalization. It was subsequently found that the ylide coordinates to metals in η^5 fashion, and thus one might anticipate a rich chemistry involved with these ligands, although surprisingly little research on this fascinating ligand has been reported over the past 50 years. More recently, the coordination chemistry of its analogous compound, methyldiphenylphosphonium cyclopentadienylide, has been investigated, specifically using group six transition metals. As an extension of the latter work, we have now successfully developed a general synthetic route to similar phosphonium 1-indenylide compounds, $IndPL_3$ (L_3 = Ph_3, $PMePh_2$, PMe_2Ph).

The coordination of these compounds is of particular interest given that the compounds that form exhibit planar chirality and, as a result, enantioselective catalytic properties are anticipated. Furthermore, reactions involving two molar equivalents of phosphonium 1-indenylide, where two ligands coordinate, would produce diastereomers.It was our attempt to extend this work to group 4 metal halides, specifically to form coordination compounds of the type $[TiCl_3(IndPL_3)]Cl$ and $[TiCl_2(IndPL_3)_2]Cl_2$. These compounds could be of great importance as enantioselective polymerization catalysts, or alternatively anti-cancer agents.

Acknowledgements

I would like to begin by thanking my supervisor, Mike Baird, for giving me the opportunity to work in his lab and for being my mentor throughout this journey. Mike was always very eager to teach me what I needed to be a chemist, and his enthusiasm for research always motivated me.

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List of Abbreviations

br	broad
Bu	butyl
Bz	benzyl
COSY	Correlation Spectroscopy
Cp	cyclopentadiene
Cp*	pentamethylcyclopentadiene
d	doublet
DMSO	dimethylsulfoxide
DRIFT	Diffuse Reflectance Infrared Fourier Transform
Et	ethyl
FT	Fourier Transform
HMBC	Heteronuclear Multiple Bond Coherence
HSQC	Heteronuclear Single Quantum Coherence
Ind	indenyl
IR	Infrared
L	ligand
M	metal
m	multiplet
Me	methyl
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser Effect Spectroscopy
Ph	phenyl
ppm	parts per million
R	alkyl substituent
s	singlet
sep	septet
t	triplet
TDEAT	tetrakis(diethylamido)titanium
THF	tetrahydrofuran
TMS	tetramethylsilane
tol	toluene
UV	Ultraviolet
X	halide

Chapter 1. Introduction

1.1 The Ramirez Ylide

A class of phosphonium cyclopentadienylide ligands was first reported in 1956 by Ramirez and Levy,[1] who synthesized and explored the chemistry of triphenylphosphonium cyclopentadienylide, the "Ramirez ylide".[2-6] They discovered, among other things, that the compound was unusually inert; unlike typical ylides it does not undergo a Wittig reaction with ketones.[7] This remarkable stability was attributed to its ability to undergo charge delocalization, with the negative charge distributed over the cyclopentadiene ring, as implied by the resonance structures seen below in Figure 1:

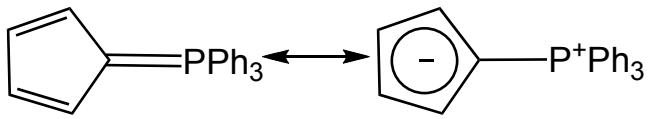


Figure 1. Resonance of triphenylphosphonium cyclopentadienylide, the "Ramirez ylide"

Structure **b** is consistent with the relatively high observed dipole moment of 7.0 D.[3,4] Further evidence for such extensive delocalization was found in the crystal structure, which showed a lengthened P-C_5H_4 bond, somewhere between that of a single and a double bond.[8] In addition, the ^{13}C NMR spectrum showed a highly shielded ylide carbon with a large $^1J_{C\text{-}P}$ value, typical of an aliphatic-type carbon.[9]

From an organometallic point of view, one of the most interesting features of this compound becomes apparent when resonance structure **b** from Figure 1 is

examined. This resonance form is structurally comparable and isoelectronic with the cyclopentadienyl (Cp) ligand, a ligand ubiquitous in organometallic chemistry and catalysis. With different steric and electronic properties than those of the Cp ligand, the Ramirez ylide was anticipated to lend itself to the tuning of catalysts by giving unique reactivities to coordination complexes. After the initial discovery of the ligand, there were several reports investigating the coordination capabilities of the ligand; the ylide was shown to coordinate via the cyclopentadienyl ring in a η^5 or η^1 fashion with a number of different metals (Figure 2).[10-18] In the following years, however, research seemed to have idled; very few reports can be found on the coordination of this type of potentially very interesting ligand in the past 30 years.

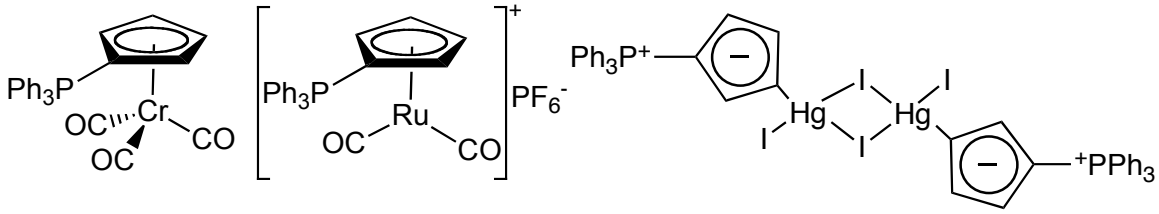


Figure 2. Examples of coordination of Ramirez ylide; Group 6 η^5-complex,[10] Group 8 η^5-complex,[18] η^1-Group 11 complex[11]

1.1.1 Synthesis of Phosphonium Cyclopentadienylides

There exist several different preparations of the Ramirez ylide and variations thereof in the literature. The following section deals with the different synthetic pathways to the phosphonium cyclopentadienylides that have been reported to date.

1.1.1.1 Synthesis of the Ramirez Ylide

The original synthetic preparation by Ramirez and Levy, seen below in Figure 3, involved the bromination of cyclopentadiene followed by substitution with triphenylphosphine to form the diphosphonium salt.[1] Deprotonation of the salt by the addition of two molar equivalents of aqueous sodium hydroxide afforded the desired ylide in an overall yield of 41%.[1,3]

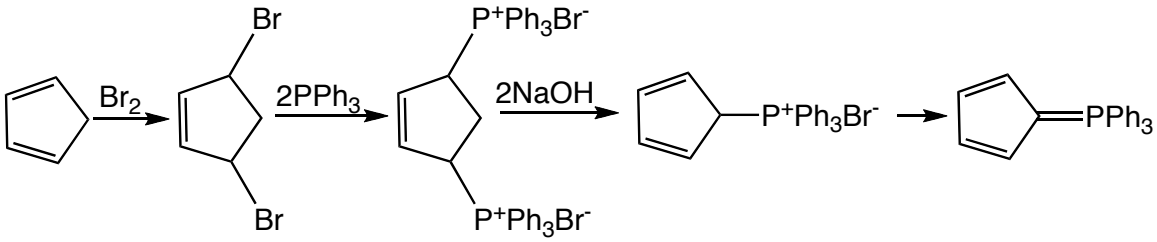


Figure 3. The original synthetic procedure of the Ramirez ylide

Aside from one report which follows the Ramirez methodology to synthesize tri-*n*-propylphosphonium cyclopentadienylide,[19] no other reports following this synthetic procedure exist for variations of the Ramirez ylide. Recent attempts at extending this method to other phosphines resulted in unidentified black materials which were presumed to be polymeric materials.[20]

1.1.1.2 Synthesis via Diazocyclopentadienes

Shortly after their initial discovery of the ylide, Ramirez and Levy considered an alternative route to the phosphonium cyclopentadienylide, which involved the reaction of triphenylphosphine and diazocyclopentadiene, which

would yield a phosphazine intermediate that was expected to lose nitrogen gas and form the ylide upon heating (Figure 4).[21] The phosphazine was easily collected and characterized in a good yield, but all attempts at thermal decomposition to afford the desired ylide failed, and this route was thus abandoned.

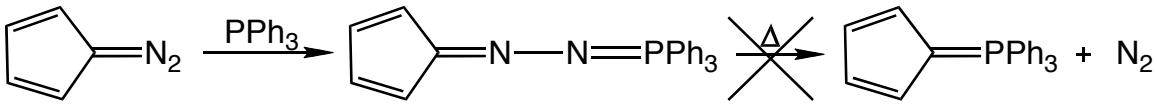
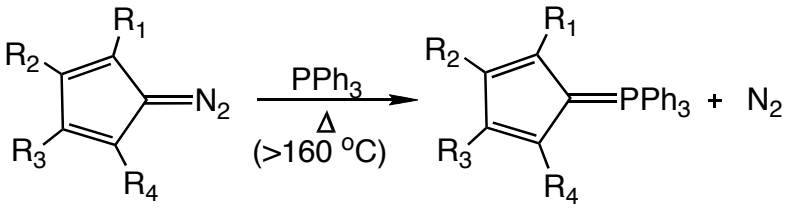


Figure 4. Attempted synthesis of the Ramirez ylide by thermal decomposition of the corresponding phosphazine

Lloyd and co-workers re-investigated this method in 1971 with substituted C_5-cyclopentadienyl derivatives, initially finding that thermal decomposition of diazo-2,3,4-triphenylcyclopentadiene at 140°C would not occur to yield triphenylphosphonium triphenylcyclopentadienylide.[22] Several years later, however, repeated reactions by Lloyd *et al.* with increased temperatures, extended reaction times and a large excess of triphenylphosphine resulted in successful decomposition of the phosphazine to the ylide.[23] This method was also extended to a few other di-, tri- and tetra-phenyl substituted C_5-cyclopentadienylides (Figure 5).[23,24] While a number of compounds could be synthesized in this manner, the reaction did not appear to be a general one, since it would not proceed for the less substituted ylides, including the original Ramirez ylide.



$R_1 = R_3 = Ph, R_2 = R_4 = H$
$R_1 = R_2 = R_3 = Ph, R_4 = H$
$R_1 = R_2 = R_4 = Ph, R_3 = H$
$R_1 = Me, R_2 = R_3 = R_4 = Ph$
$R_1 = Bz, R_2 = R_3 = R_4 = Ph$
$R_1 = R_2 = R_3 = Ph, R_4 = p\text{-}MeC_6H_4$

Figure 5. Synthesis of C_5-substituted cyclopentadienylides from decomposition of corresponding diazocyclopentadienes

1.1.1.3 Synthesis via Chlorodiphenylphosphine

In the following years, an alternative synthetic procedure for a derivative of the Ramirez ylide was developed by Mathey and Lampin, who synthesized methyldiphenylphosphonium cyclopentadienylide and explored much of its organic chemistry.[25] The first step of this synthesis, as seen in Figure 6, involved the formation of cyclopentadienyldiphenylphosphine by the reaction of TlCp and chlorodiphenylphosphine. The phosphine was then alkylated with methyl iodide to form the phosphonium salt, which was then deprotonated with *n*-butyllithium to form the desired ylide.

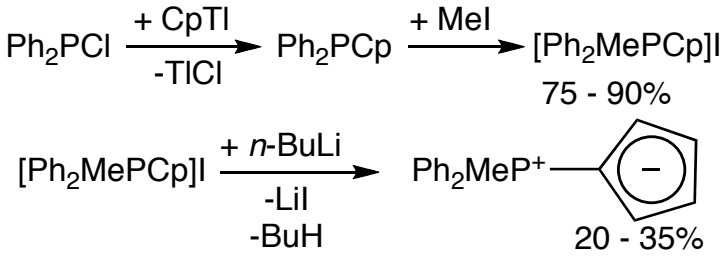


Figure 6. Preparation of methyldiphenylphosphonium cyclopentadienylide

More recently, this procedure was further developed and the compound was more properly characterized by Brownie and coworkers.[26] Through spectroscopic and crystallographic evidence the ylide was found to have properties consistent with the Ramirez ylide; for example the ylide P-C_5H_4 bond length of 1.727 Å is comparable to the Ramirez ylide at 1.718 Å,[8] which indicates that it also has significant contributions from both resonance structures. The slight elongation is believed to be a result of the more donating methyl group present in place of the phenyl group.[26] One of the main advantages of using this mixed alkyl-aryl cyclopentadienylidene over the Ramirez ylide is that this ylide is more amenable to NMR characterization; a characteristic doublet in the aliphatic region of the ^{1}H NMR for the methyl group ($J_{C\text{-}P} \approx 13$ Hz) can easily be used as a "tag" for the compound and its coordination complexes.[26]

While this synthetic procedure was successful in the development of the aforementioned ylide, its application to other cyclopentadienylide derivatives is limited in the sense that chlorodiphenylphosphine is the only disubstituted chlorophosphine that is commercially available at a reasonable cost. Another drawback is that compounds of the type $CpPR_2$ have been found to be generally unstable at room temperature, possibly due to Diels-Alder dimerization and thus it is imperative that deprotonation to generate the phosphonium salt be carried out immediately after synthesizing the $CpPPh_2$ intermediate.[27] These limitations prevent this method from providing a general route to phosphonium cyclopentadienylides. Different alkyl halides could in theory be used to generate derivatives with substituents other then the methyl group, but this approach does not yet seem to have been assessed.

1.1.2 Coordination of the Ramirez Ylide and Derivatives

A number of coordination complexes have been reported for the phosphonium cyclopentadienylides with transition metals. This review will focus only on the coordination complexes of group 4 and 6 metals.

1.1.2.1 Group 4 Complexes

Group 4 complexes of the phosphonium cyclopentadienylides, in particular the bis-ylide species, are highly anticipated for their potential as catalyst precursors for olefin polymerization, due to their structural similarities to metallocene complexes of the type Cp_2MX_2. A large number of different titanocene and zirconocene based precatalysts have been prepared and have been shown to be very effective at polymerizing a number of different olefins to give a variety of polymers (some examples of the catalyst precursors can be seen below in Figure 7).[28-32] Once coordinated, the phosphonium cyclopentadienylide group 4 compounds are expected to open a new class of olefin polymerization catalysts, similar to the Cp derivatives already known.

Furthermore, since titanocene dichloride and many of its Cp derivatives have been found to be active anti-tumour reagents, all such bis-ylide species could potentially act as anti-cancer drugs.[33-35]

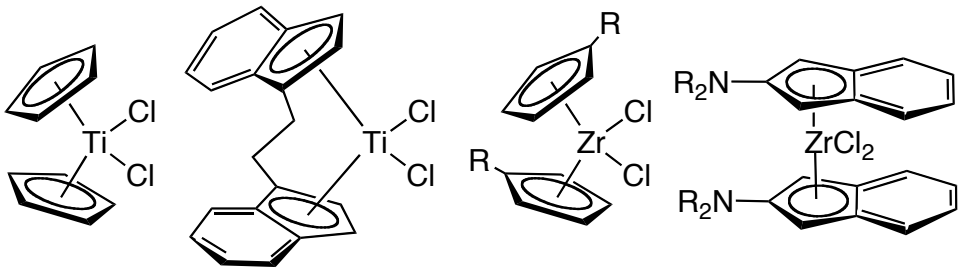


Figure 7. Examples of known group 4 metallocene-based precatalysts for olefin polymerization

The first report of a phosphonium cyclopentadienylide group 4 coordination complex was in 1977, by Holy *et al*.,[36] who described the reaction of the Ramirez ylide with group 4 metal halides, illustrated in the following equation:

$$n\mathrm{CpPPh_3} + \mathrm{MCl_x} \longrightarrow (\mathrm{CpPPh_3})_n\mathrm{MCl_x}$$

M = Ti, Zr, Hf
x = 3, 4
n = 1, 2

(eq. 1)

The titanium(IV) compound was synthesized using titanium tetrachloride and two equivalents of ylide to yield an air sensitive precipitate; the product was characterized by melting point, IR, ^{1}H NMR and elemental analyses and determined to be $[(\eta^5\text{-CpPPh}_3)_2\mathrm{TiCl_2}]\mathrm{Cl_2}$. The ^{1}H NMR showed a multiplet centered at δ 7.95 for the cyclopentadienyl protons, a considerable shift downfield from that of the free ylide at δ 6.40. However, on the low field instrument full assignments of each proton was not possible. All attempts at recrystallization resulted in decomposition, and thus no X-ray analysis could be obtained to confirm this structure. Preparation of the Ti(III) compound was done using titanium trichloride with one equivalent of ylide, and yielded a product identified

only by elemental analysis as $CpPPh_3TiCl_3 \cdot 4H_2O$. All attempts to prepare the titanium(II) compound failed.[36]

A zirconium(IV) complex was synthesized in the same manner, but the product isolated was presumed to be the mono-ylide complex. The compound had low solubility in a number of solvents, apart from DMSO, which limited its characterization to elemental analysis and did not allow for recrystallization. A hafnium(IV) complex was also obtained as a mono-ylide species and exhibited similar solubility problems. The reported elemental analyses for both the Zr and Hf compounds did not in fact agree with the calculated values, and the discrepancies were attributed to problems with combustion.[36]

The synthesis of the titanium(IV) compounds by this methodology was later repeated in 2008 with the alkyl-aryl derived ylide, methyldiphenylphosponium cyclopentadienylide,[20] but findings were not consistent with the Holy *et al*. report.[36] Most notably, the ^{1}H NMR resonances did not match those reported for the complex, and a ^{31}P NMR of the product showed at least four major species had formed. The product could not be purified, and so could not conclusively be characterized.[36]

In 2000, a series of cationic ansa-zirconocene and hafnocene derivatives of a phosphonium-bridged bis-permethylcyclopentadienyl ligand were prepared and were characterized by X-ray crystallography (Figure 8).[37]

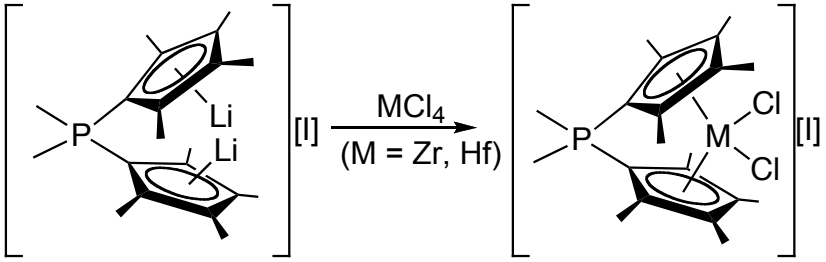


Figure 8. Synthesis of group 4 phosphonium bridged cyclopentadienyl complex

The phosphonium-bridged bis(tetramethylcyclopentadienyl) ligand, $[Me_2P(C_5Me_4)_2]^-$, was synthesized sequentially as in the following reaction scheme:

$$MePCl_2 + 2\ Li(C_5Me_4H) \longrightarrow MeP(C_5Me_4H)_2 \xrightarrow{MeI} [Me_2P(C_5Me_4H)_2][I]$$

$$[Me_2P(C_5Me_4H)_2][I] \xrightarrow{2\ n\text{-BuLi}} [Me_2P(C_5Me_4Li)_2][I] \qquad \text{(eq. 2)}$$

Subsequent treatment of the ligand with $ZrCl_4$ and $HfCl_4$ yielded the phosphonium bridged cyclopentadienyl complex, as in Figure 8. Although no parallels were drawn between these complexes and the Ramirez ylide in the report, by looking at the resonance structures of the ligand, seen below in Figure 9, the similarities become evident.

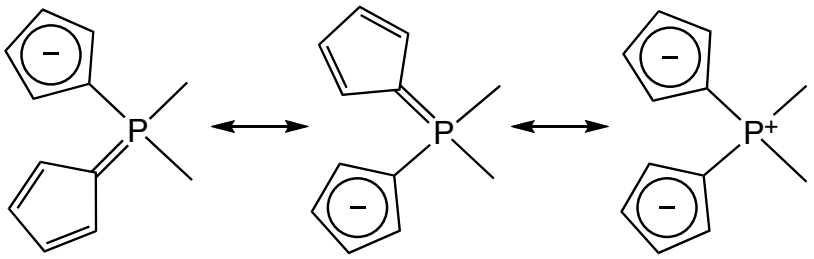


Figure 9. Resonance forms of the phosphonium-bridged permethylcyclopentadienyl ligand (methyl groups omitted for clarity)

1.1.2.2 Group 6 Complexes

The group 6 phosphonium cyclopentadienyl complexes are the most thoroughly investigated compounds of the Ramirez ligand and its derivatives. The first complex of this type was explored by Wilkinson and co-workers,[10] who recognized that the resonance structure **b** of the ylide (Figure 1) was isoelectronic with benzene and thus that the ylide would be expected to form compounds analogous to $(\eta^6\text{-}C_6H_6)M(CO)_3$ (M = Cr, Mo, W). The complexes $(C_5H_4PPh_3)M(CO)_3$ (M = Cr, Mo, W) were synthesized by addition of the ylide to the metal carbonyls in diglyme, and were characterized by IR, ^{1}H NMR and elemental analyses;[10] η^5-structures were proposed but not confirmed until several years later by X-ray crystallography.[12]

In 1970, Kotz and Pedrotty reviewed the synthesis of the group 6 tricarbonyl ylide complexes,[12] and successfully coordinated the ylide to chromium and molybdenum following the previously described procedure by Wilkinson, in yields between 60 – 80%.[12] However, attempts to synthesize the tungsten analogue by this procedure resulted in the formation of little or no product, and a

modification of the procedure was developed which involved the addition of the ylide to a solution of the tris-acetonitrile tricarbonyl tungsten complex, $W(CO)_3(CH_3CN)_3$ in diglyme and heating to 110 °C.[12] A detailed reaction scheme for these complexes can be seen below in Figure 10. Much of the chemistry of these complexes was further explored in the following years, in particular their Lewis basicity by the formation of Lewis acid-base adducts, which will not be discussed further here.[12,16,38,39]

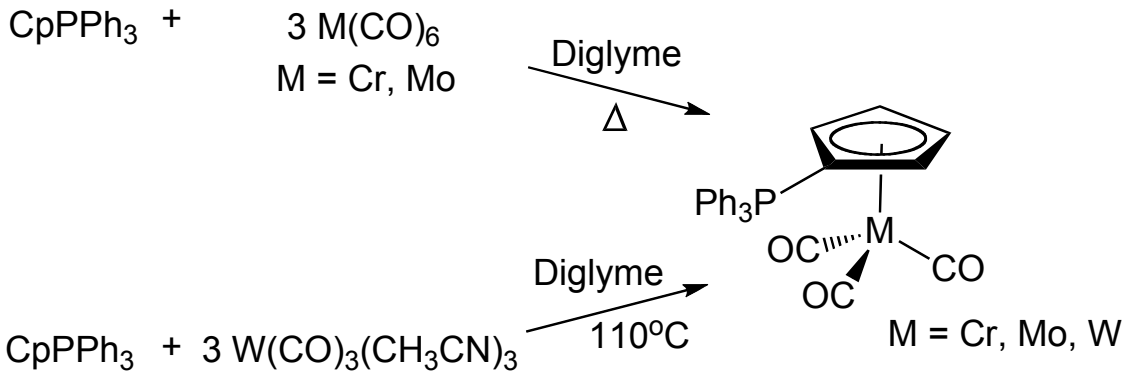


Figure 10. General reaction scheme for the coordination of the Ramirez ylide to group 6 metals

The reaction of the ylide with group 6 metal compounds in higher oxidation states was first reported by Nalesnik *et al.* in 1977, who reacted the Ramirez ylide with group 6 metal halides to form metallocene-like complexes.[13] The synthesis was performed by reacting tungsten hexachloride with triphenylphosphonium cyclopentadienylide in dry benzene to give a product, which by elemental analysis was confirmed to be $(CpPPh_3)_2WCl_6$, the structure of which was proposed as in Figure 11 below.

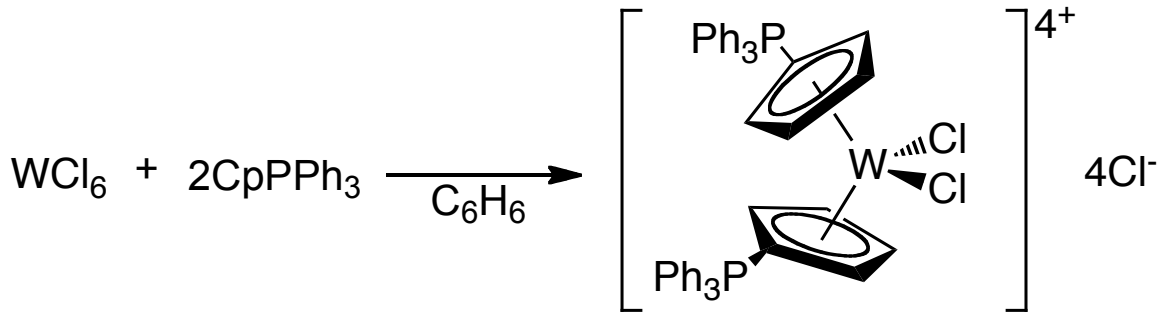


Figure 11. Synthesis of tungsten ylide metallocene complex

Evidence of this structure is seen in the ^{1}H NMR, which shows the signals for the cyclopentadienyl protons shifted from a multiplet centered at 6.20 ppm in the free ylide, to one centered at 8.57 ppm.[13] The ^{13}C NMR spectrum is also consistent with this structure, as it shows a considerable downfield shift for the cyclopentadienyl carbons.[13] No crystal structure was obtained to confirm this structure.

A molybdenum complex was prepared in an analogous manner by reacting molybdenum pentachloride with the Ramirez ylide in dry benzene. Elemental analysis indicated the product had a stoichiometry of $(CpPPh_3)_3MoCl_3(OH)_2$.[13] The presence of hydroxyls in this compound were attributed to trace amounts of water present in the solvents used for recrystallization, but the product was not as well characterized as the tungsten analogue.[13] Attempts to prepare the chromium complex from chromium dichloride failed, presumably due to the large amount of steric hindrance generated by the bulky ylide groups.[13]

An in-depth study into the bonding and reactivities of the group 6 metal complexes of the ylide was recently carried out by Brownie *et al*., using the

derivative of the Ramirez ylide, methyldiphenylphosphonium cyclopentadienylide, to prepare (η^5-CpPMePh$_2$)M(CO)$_3$ (M = Cr, Mo, W) as in the complexes prepared in Figure 11.[26,40] The complexes were characterized spectroscopically (IR and ^{1}H, ^{13}C, ^{31}P NMR) and crystallographically, making this series of compounds one of the best characterized series of phosphonium cyclopentadienylide metal complexes available.[26] One of the interesting features studied in these complexes was the carbonyl stretching frequencies, which act as a good indication as to the donor properties of the ylide. The IR spectra exhibited two strong carbonyl stretching bands, consistent with a 3-fold –M(CO)$_3$ moiety, at frequencies of approximately 1915 and 1810 cm^{-1} for all three metal complexes.[26] These values are of great significance since they lie between those of the analogous η^6-C$_6$H$_6$ neutral ligand group 6 tricarbonyl complexes (~1970, ~1890 cm^{-1})[41] and those of the η^5-C$_5$H$_5$ anionic ligand group 6 tricarbonyl complexes (~1900, 1780 cm^{-1}).[42] This suggests that the donor properties of the phosphonium cyclopentadienylide ligand lie somewhere between those of benzene and Cp$^-$, and likely more closer to the latter.[26]

1.2 Indenyl-derived ylides

One of the most notable problems that may have limited the exploration of this class of ligands is the lack of a general synthetic route, as none of the discussed procedures are generally applicable to all phosphines and related systems. In an attempt to revive the use of this class of ligand, an investigation into the use of its indenyl-derived ylide analogue has recently been carried out.

The ylide was expected to exist as the resonance structures seen below in Figure 12, similar to the cyclopentadienyl ylides.

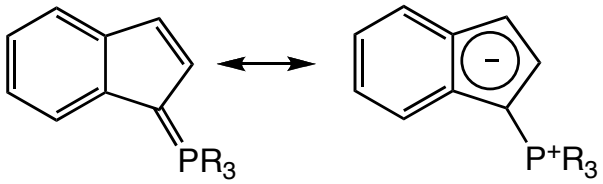


Figure 12. Resonance of indenyl-derived ylide

There are some advantages of this ylide system in comparison with the cyclopentadienyl ylide ligands. Generally, yields are much higher for the synthesis of these compounds, presumably because of the increased stability of both the starting materials as well as the products.[43,44] Furthermore, the more extensive delocalization with the additional benzene ring seems to allow for the compound to be more soluble in aromatic solvents, a drawback encountered when working with the relatively insoluble cyclopentadienyl derivatives.

1.2.1 Croft's Synthesis of the Indenylide

The first report of this type of compound was done by Crofts and Williamson in 1967, who synthesized 1-indenylidenetriphenylphosphorane and explored its reactions with diazonium salts.[45] The first step of the synthesis was the formation of 1-bromoindene, done by refluxing *trans*-1,2-bromoindane in an excess of 2,6-lutadine. Addition of triphenylphosphine and standing for 3 weeks under nitrogen gave a yellow solution; work-up with water, hydrochloric acid, then sodium hydroxide afforded the desired ylide in a 9% overall yield (Figure 13). The

compound was analyzed by melting point, UV and elemental analyses. Low analytical figures for carbon were obtained, and the structure could only be confirmed by the ultraviolet spectrum, which was found to be similar to the Ramirez ylide.[45]

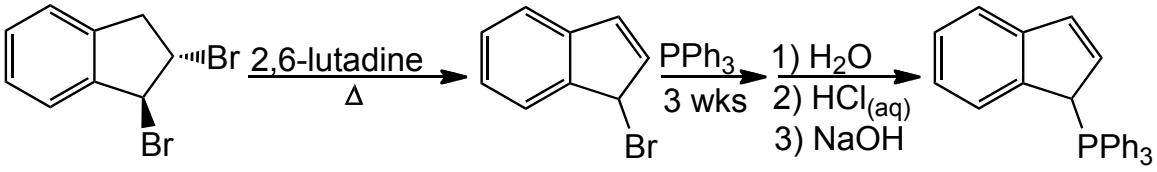


Figure 13. Croft's synthesis for triphenylphosphonium indenylide

The compound was never definitively characterized, and much of its chemistry was left unexplored. Furthermore, this reaction was never extended to any other phosphines.

1.2.2 Rufanov Synthesis of the Indenylide

In an extension of Mathey's previous work towards the synthesis of methyldiphenylcyclopentadienylide (Figure 6),[25] Rufanov and co-workers developed a synthesis for the analogous indenyl-derived ylides in the same manner (Figure 14).[43] They seem to have, however, been unaware of Mathey's earlier report, and draw no comparisons to the Ramirez-type ylides.

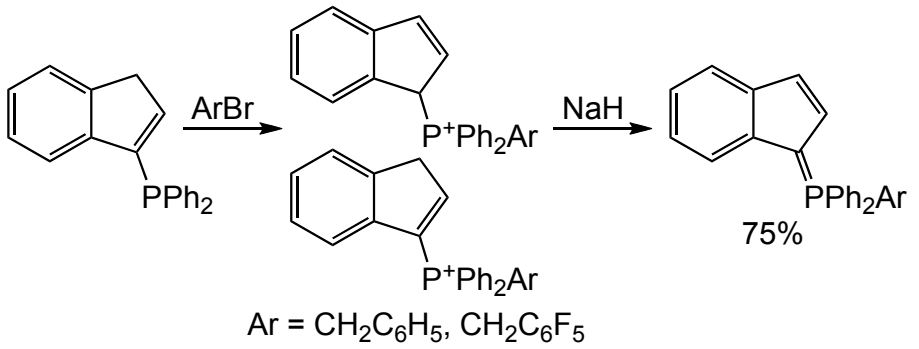


Figure 14. The synthesis of indenyl derived phosphonium ylides

In this procedure, the starting phosphine, $IndPPh_2$, was quaternized using an excess of benzyl bromide. The corresponding phosphonium salt isomers were then deprotonated with excess sodium hydride, to afford the desired ylide in an overall yield of 75%. The ylide was fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR as well mass spectrometry, elemental analysis and X-ray crystallography.[43]

1.2.3 Brownie Synthesis of the Indenylide

Using a protocol very similar to their synthesis of the cyclopentadien-ylides,[25,26] the analogous indenyl ylide, methyldiphenylphosphonium indenylide, was synthesized by Brownie *et al.* (Figure 15).[44]

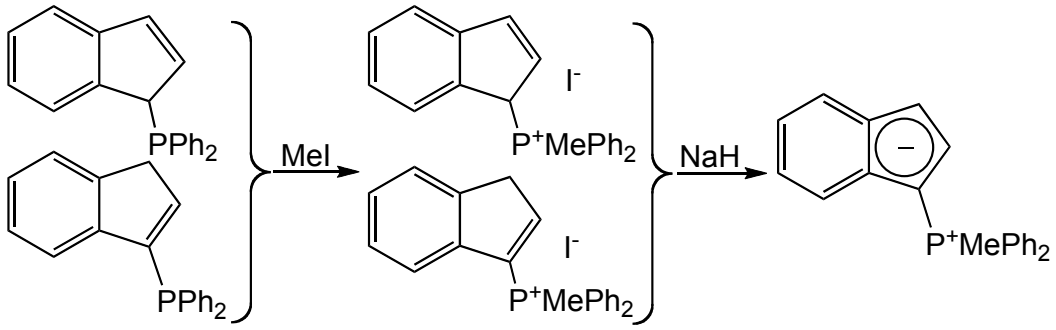


Figure 15. Synthesis of methyldiphenylphosphonium indenylide

The starting phosphine isomers of $IndPPh_2$ were synthesized from indenyl lithium and chlorodiphenylphosphine, and were alkylated with methyl iodide to obtain the phosphonium salt in a 75% yield as a mixture of the two isomers. The salt was then deprotonated with excess sodium hydride to yield the desired ylide in an 87% yield. The ylide was fully characterized by ^{1}H, ^{13}C and ^{31}P NMR, as well as IR, elemental analysis and X-ray crystallography. The molecular structure of the ylide showed that the P-C_9H_6 bond length, at 1.711 Å, was shorter than the analogous Cp derived ylide (1.727 Å)[26] and the Ramirez ylide (1.718 Å).[8] The shortening of the P-C bond indicates that it has more double character than the corresponding Cp ylides; it is, however, much longer than a typical example of a non-resonance stabilized ylide, $Ph_3P{=}CH_2$ (1.66 Å), which may be taken as a good indication of a true carbon-phosphorus double bond length.[46] Therefore, much like the analogous Cp derived ylides, the indenyl ylide is expected to have significant contributions from both resonance structures, seen previously in Figure 12.

Once again this synthesis is limited to the availability of the only commercially available starting phosphine, chlorodiphenylphosphine. Thus, while it does provide an efficient route to this particular ylide, this synthetic route cannot be generally applied to any phosphorus-substituted indenylide.

1.2.4 Coordination Complexes of Indenylides

Similar to the cyclopentadienylide derivatives, indenylides were expected to coordinate in an η^5-manner, and thus the possibility exists of using them as

ligands for various catalysts. Several reports have concluded that using an indenyl-derived ligand in place of a cyclopentadienyl ligand in various organometallic complexes for olefin polymerization actually results in significant enhancement of the rate of ligand substitution, thus leading to an overall increase in catalytic activity.[47-54] These indenyl-derived ylides are thus highly anticipated ligands for catalysts, particularly the bis-ylide metallocene-like complexes.

While this class of indenylide compounds is expected to open the doors to some very interesting organometallic chemistry, until very recently in the Baird lab, no transition metal complexes of this type had been reported. What makes them even more desirable as a ligand is the fact that the ylides are prochiral; coordination compounds formed would exhibit planar chirality. This would lead to the mono-ylide complex to be formed as a mixture of two enantiomers, and the bis-ylide complex a mixture of two diastereomers (Figure 16). If the respective enantiomers/diastereomers could be separated, the complexes may behave as potential enantioselective olefin polymerization catalysts or pre-catalysts.

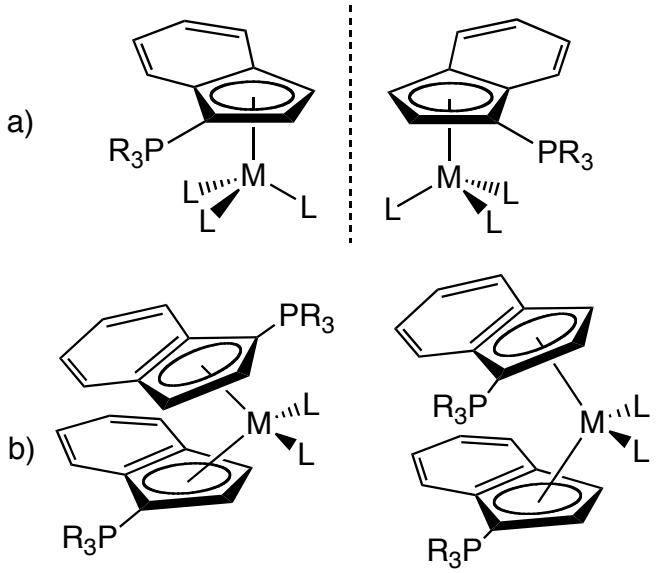


Figure 16. a) Coordination of mono-ylide metal complex, demonstrating the planar chirality of the resulting compound b) Coordination of bis-ylide metal complex, demonstrating two of the diastereomers formed

1.2.4.1 Coordination to Group VI metals

The only coordination compounds that exist for the indenylide are those to group 6 transition metals, synthesized and characterized in this lab by Brownie *et al.* in 2008.[44] The chromium complex was synthesized by refluxing the ylide in diglyme with an excess of $Cr(CO)_6$, as seen below in Figure 17.

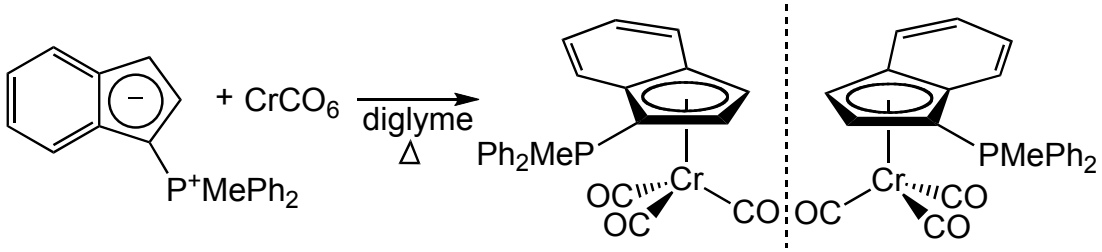


Figure 17. Synthesis of the chromium indenylide complex

The compound was fully characterized by elemental analysis, IR and ^{1}H, ^{13}C and ^{31}P NMR, as well as X-ray crystallography. The crystal data showed that upon coordination, the P-C_9H_6 bond undergoes elongation (1.753 Å) when compared to the free ylide (1.711 Å), an observation consistent with the coordination of the Cp-derived ylide chromium complexes (1.759 Å for the complex, 1.727 Å for the free ylide).[26,40] This bond lengthening is due to the greater contribution of the zwitterionic resonance structure, indicating a greater degree of aromatic character upon coordination to a metal centre. The IR spectrum of this Cr complex exhibits stretching frequencies nearly identical to those of the related Cp-derived ylide complexes, demonstrating that the indenyl-derived ylide has similar donor properties to the Cp-ylide systems.[44] Unfortunately, the coordination of these ligands to any other metal has not been explored, which leaves its potential as a ligand for olefin polymerization catalysts to be as of yet unknown.

1.3 Aims of Present Research

A problem that has certainly limited the exploration into this class of ligands is the lack of a general synthetic route. The initial objective of this thesis was to develop an efficient, reproducible synthetic pathway that can be applied to, in theory, any ylide derivative of the indenyl system. This will be done following a modified procedure of that developed by Crofts and coworkers (Figure 13), using 1-bromoindene as the precursor to the triphenylphosphonium indenylide.[45] Since this reaction was not particularly efficient, having a reaction time of over 3 weeks and yields of approximately 9%, it will be further developed

and optimized for this particular ylide, at which point it can then be extended to other phosphines and systems. Specifically, the synthesis will initially be extended to the methyldiphenylphosphine derivative, an indenylide previously characterized by Brownie *et al.*,[44] as well as the dimethylphenylphosphine indenylide derivative, which has not yet been reported in literature. All ylides will be fully characterized by spectroscopic and crystallographic analysis. Presumably, once the synthesis of these ylides has been accomplished, this procedure could, in theory, be applied to any phosphine system. This includes but is not limited to any alkyl/aryl phosphine, as well as bidentate phosphines.

Once a synthesis for the ylides has been successfully developed, the coordination complexes of the ylides to group 4 metals will be investigated. In particular, the coordination of the ligand to titanium in the +4 oxidation state will be attempted. While other oxidation states of titanium would also be of interest, the complexes formed would be paramagnetic and would thus not be amenable to NMR characterization. Any η^5-ylide titanium complexes that are formed are expected to resemble known olefin polymerization catalysts or precatalysts, thus the complexes obtained are anticipated to make up a library of new potential catalysts.

Chapter 2. Experimental

2.1 General Conditions

Unless otherwise noted, all syntheses were carried out under a dry, deoxygenated argon atmosphere, using standard Schlenk line techniques. Argon was deoxygenated by passage through a heated BASF copper catalyst column, and then dried by passage through a column of 4 Å molecular sieves. Handling and storage of air-sensitive compounds was done using an MBraun Labmaster glove box.

Anhydrous solvents (ethyl ether, methylene chloride, toluene, hexanes, THF) were purchased from Aldrich in 18 L reservoirs packaged under nitrogen, and were dried by passage through columns of activated alumina (Innovative Technology Solvent Purification System). THF, ether, and methylene chloride were then stored over 3 Å molecular sieves to remove residual water. All solvents were tested for appropriately low moisture content by Karl-Fischer titrations.

NMR spectra were recorded using Bruker AV 300, 400, 500 and 600 spectrometers. ^{1}H and ^{13}C NMR spectra were referenced to carbons or residual protons present in the deuterated solvents with respect to TMS at δ 0. $^{31}P\{^{1}H\}$ NMR spectra were referenced to external 85% H_3PO_4. Samples were prepared in 5 mm diameter tubes with approximately 0.6 mL of selected deuterated solvent. All 1D spectra were processed using Bruker XWIN-NMR or Mestrec (version 2.3) software, while 2D spectra were processed using Bruker XWIN-NMR or Spinworks (version 2.5) software. IR spectra were acquired on a Varian 640 FT-IR using Diffuse Reflectance Infrared Fourier Transform; samples were prepared

as a KBr mixture. Elemental analyses were conducted by the Canadian Microanalytical Service Ltd., of Delta, BC.

Most chemicals were purchased from Sigma Aldrich or Strem Chemicals and were used as received, or purified by established procedures as indicated. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Chloroform-d and DMSO-d_6 were dried by adding them to activated 3 Å molecular sieves in a Schlenk under argon for 24 hours, degassing, and then transferring to fresh 3 Å molecular sieves for storage. Benzene-d_6 and methylene chloride-d_2 were dried over calcium hydride, transferred by trap-to-trap distillation and degassed under vacuum and stored over 3 Å molecular sieves. Toluene-d_8 was dried over sodium metal, transferred by trap-to-trap distillation and degassed under vacuum and stored over 3 Å molecular sieves. THF-d_8 was purchased dry in an ampule stored under nitrogen. D_2O and methanol-d_4 were used as received.

2.2 X-ray Crystal Structure Determinations

X-ray crystallographic structure determinations were performed by Dr. Ruiyao Wang in the X-ray Crystallography Laboratory at Queen's University. Crystals were mounted on a glass fiber with grease and cooled to -93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). No significant decay was observed during the data collections. Data were processed on a Pentium PC using the Bruker AXS Crystal Structure Analysis Package.[55] Neutral atom

scattering factors were taken from Cromer and Waber.[56] The structures were solved by direct methods. Full-matrix least-square refinements minimizing the function $\sum w (F_o^2 - F_c^2)^2$ were applied to the compounds. All non-hydrogen atoms were refined anistropically, and all H atoms were placed in geometrically calculated positions.

2.3 Preparation of the Ligands of the Type $C_9H_6PR_3$

2.3.1 Synthesis of 1-Bromoindene

1-Bromoindene was prepared for its use as a precursor to the indenylide compounds. Synthetic routes following variations of published procedures were used and are described below.

2.3.1.1 Synthesis of Indenyl Lithium[43]

A solution of 4.0 mL indene (34 mmol) in 100 mL hexanes was stirred vigorously at 0 °C while 15 mL of 2.5 M *n*-BuLi in hexanes (38 mmol) was added dropwise via syringe over a period of 30 minutes. The mixture was stirred overnight at room temperature, over which time a white precipitate developed. The precipitate was filtered off, washed with dry hexanes (3 x 10 mL), and dried *in vacuo* for several hours to yield 3.52 g of a white solid (85% yield).

2.3.1.2 Synthesis of Trimethylsilyl(indene)[54,57,58]

A suspension of 3.5 g indenyllithium (29 mmol) in 100 mL hexanes was cooled to 0 °C and 3.65 mL chlorotrimethylsilane (29 mmol) was added dropwise

via syringe over a period of 15 minutes. The resulting beige solution was allowed to stir overnight at room temperature. The solution was filtered through a Celite plug to remove LiCl, and pumped to dryness *in vacuo* to yield 4.2 g of a yellow oil (80% yield). The 1-(trimethylsilyl)indene obtained was relatively pure (NMR) and thus used without purification; the product could be stored at -30 °C under an inert atmosphere. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.58 – 7.28 (m, 4H, aromatic), 6.95 (d, 1H, **H**C=CHCHSiMe$_3$), 6.65 (d of d, 1H, C=C**H**CHSiMe$_3$), 3.45 (s, 1H, C**H**SiMe$_3$), 0.00 (s, 9H, Si(C**H**$_3$)$_3$). Literature^{1}H NMR ($CDCl_3$, 80 MHz)[54] : δ 7.5 – 7.15 (m, 4H, aromatic), 6.95 (d, 1H, sp^2 3-position), 6.65 (d, 1H sp^2 2-position), 3.55 (s, 1H, sp^3 1-position), 0.01 (s, 9H, Si(CH$_3$)$_3$).

2.3.1.3 Synthesis of Dioxane Dibromide[59]

In an Erlenmeyer flask in air, 10 mL of bromine was added dropwise to 15 mL dioxane (170 mmol, distilled over sodium) with vigorous stirring. The warm solution was poured into approximately 50 mL hexanes pre-cooled to -78 °C, at which point an orange precipitate was immediately noted. The precipitate was filtered off under suction as quickly as possible to avoid loss of the volatile product. Dioxane dibromide was collected as 39.0 g of an orange crystalline solid (92% yield) and was stored at -20 °C in air.

2.3.1.4 Synthesis of 1-(bromoindene)[60]

A solution of 4.2 g 1-(trimethylsilyl)indene (23 mmol) in 50 mL THF in a round bottom flask was fitted with an addition funnel containing 6.3 g dioxane

dibromide (25 mmol) dissolved in 20 mL THF with the entire apparatus covered in aluminum foil to exclude light. While stirring and chilling the contents of the roundbottom flask to -78 °C, the dioxane dibromide solution was added dropwise over a period of 5 minutes. The solution was allowed to stir overnight at room temperature, after which the orange solution was concentrated to a brown oil by removing the solvent *in vacuo*. The remaining oil, which is air stable, was placed on top of a silica gel column (70 – 250 mesh) and eluted with hexanes. The pale yellow fraction was collected and the solvent was removed on the rotary evaporator to yield 2.68 g of a deep yellow oil (60% yield). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.33-7.25 (m, 4H, aromatic), 6.84 (d, 1H, **H**C=CHCHBr), 6.48 (d of d, 1H, C=C**H**CHBr), 5.53 (s, 1H, C**H**Br). Literature ^{1}H NMR ($CDCl_3$)[60]: δ 7.67 – 7.13 (m, 4H, aromatic), 6.82 (d, 1H, **H**C=CHCHBr), 6.6 (d of d, 1H, C=C**H**CHBr), 5.48 (br s, 1H, C**H**Br).

2.3.2 Synthesis of Phosphonium Salts of the Type $[C_9H_7PR_3]^+X^-$

2.3.2.1 Synthesis of $[C_9H_7PPh_3]^+Br^-$ (Ia)

A solution of 5.14 g triphenylphosphine (19.6 mmol, recrystallized from ethanol) in 50 mL toluene was stirred at room temperature while 3.5 g 1-(bromoindene) (18 mmol) was injected into the solution. The reaction was placed in an oil bath at 50 °C and left for 72 hours, over which time an off-white precipitate developed. The precipitate was filtered off, washed with toluene (3 x 10 mL), and dried *in vacuo* for an hour. The two phosphonium salt isomers were thus obtained as 3.97 g of an off-white solid (49% yield). ^{1}H NMR ($CDCl_3$, 600

MHz): δ 7.8 – 7.7 (m, Ph), 8.2 – 6.8 (m, olefinic), 6.7 (m, **H**-C-P^+Ph_3 of isomer B), 4.1 (m, $\mathbf{H}_2$C-CH=C-P^+ of isomer A). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 242.5 MHz): δ 26.6 (isomer B), 12.5 (isomer A). Elemental analysis for $C_{27}H_{22}PBr$: Found: C 70.43, H 4.93; Calculated: C 70.95, H 4.85. The relative intensities of the ^{31}P NMR signals indicate a 74 : 26 ratio of isomer A : isomer B.

2.3.2.2 Synthesis of $[C_9H_7PMePh_2]^+Br^-$ (Ib)

The reaction was carried out similar to the synthesis of **Ia**, starting from 4.84 mL methyldiphenyl phosphine (25.7 mmol) and 5.03 g 1-(bromoindene) (25.7 mmol) using 75 mL of toluene. The reaction proceeded in three hours at room temperature to yield 8.90 g of a white, air sensitive solid (88% yield). The ^1H and ^{31}P NMR are consistent with the literature values for the phosphonium iodide salt analogues.[44] ^1H NMR (CD_2Cl_2, 500 MHz): δ 8.0 – 7.6 (m, Ph), 8.2 – 6.9 (m, olefinic), 6.6 (m, **H**-C-$P^+(MePh_2)$ of isomer B), 3.9 (br s, $\mathbf{H}_2$C-CH=C-P^+ of isomer A) 3.1 (d, $P^+C\mathbf{H}_3$ of isomer A, $^2J_{P-H}$ = 13.1 Hz), 2.8 (d, $P^+C\mathbf{H}_3$ of isomer B, $^2J_{P-H}$ = 13.1 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 25.9 (isomer B), 13.6 (isomer A). The relative intensities of the ^1H NMR doublets and the ^{31}P NMR signals indicate a 42 : 58 ratio of isomer A : isomer B. Literature ^1H NMR $[C_9H_7PMePh_2]^+I^-$ ($CDCl_3$, 300 MHz)[44]: δ 8.10 – 6.90 (m, Ph, possibly olefinic), 6.7 – 6.15 (m, olefinic), 3.18 (d, PMe $^2J_{H-P}$ = 13.3Hz).

2.3.2.3 Synthesis of $[C_9H_7PMe_2Ph]^+Br^-$ (Ic)

The reaction was carried out similar to the synthesis of **Ia**, starting from 2.13 mL dimethylphenyl phosphine (15 mmol) and 2.93 g 1-(bromoindene) (15 mmol) using 50 mL of toluene. The reaction proceeded in one hour at room temperature to yield 2.40 g of a white, air sensitive solid (48% yield). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.0 – 7.4 (m, Ph), 8.1 – 6.3 (m, olefinic), 6.6 (br m, **H**-C-$P^+(Me_2Ph)$ of isomer B), 3.9 (br s, $\mathbf{H}_2$C-CH=C-P^+ of isomer A), 2.9 (d, $P^+(C\mathbf{H}_3)_2$ of isomer A, $^2J_{P\text{-}H}$ = 13.1 Hz), 2.5 (d, $P^+C\mathbf{H}_3$ of isomer B, $^2J_{P\text{-}H}$ = 13.1 Hz) 2.4 (d, $P^+C\mathbf{H}_3$ of isomer B, $^2J_{P\text{-}H}$ = 13.1 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 27.4 (isomer B), 13.4 (isomer A). Elemental analysis for $C_{17}H_{18}PBr$: Found: C 58.97, H 4.99; Calculated: C 61.28, H 5.44. The relative intensities of the ^{1}H NMR doublets and the ^{31}P NMR signals indicate a 32 : 68 ratio of isomer A : isomer B.

2.3.2.4 Synthesis of $[C_9H_7PMePh_2]^+PF_6^-$ (Id)

To a suspension of 1.30 g **Ib** (3.3 mmol) in 100 mL methylene chloride, 0.605 g potassium hexafluorophosphate (3.3 mmol) was added. The reaction mixture was stirred for 12 hours and then filtered; the solvent was then removed from the filtrate *in vacuo* to yield 1.21 g of a white solid (80% yield). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.8 – 7.4 (m, Ph), 8.0 – 6.9 (m, olefinic), 6.5 (s, **H**-C-P^+Ph_3 of isomer B), 3.9 (s, $\mathbf{H}_2$C-CH=C-P^+ of isomer A), 2.8 (d, P^+-CH_3 of isomer A), 2.3 (d, P^+-CH_3 of isomer B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 25.42 (isomer B), 12.98 (isomer A), -143.70 (PF_6^- sep). The relative intensities of the ^{1}H NMR doublets and the ^{31}P NMR signals indicate a 91 : 9 ratio of isomer A : isomer B.

2.3.3 Synthesis of Indenyl Ylides, $C_9H_6PR_3$

2.3.3.1 Synthesis of $C_9H_6PPh_3$ (IIa)

To a suspension of 0.63 g sodium hydride (26.3 mmol) in 60 mL THF, 3.97 g of **Ia** (8.69 mmol) was added. The development of a green colour was immediately noted, and the solution was stirred at room temperature for 48 hours, over which time the green colour deepened. The solution was filtered through a Celite plug to remove any sodium bromide and unreacted sodium hydride. The filtrate was pumped down to dryness *in vacuo* to yield 2.58 g of a dark green solid (65% yield) which could be stored in air without decomposition. X-ray quality crystals were obtained by crystallization from a concentrated CH_2Cl_2 solution layered with hexanes. ^1H and ^{13}C NMR data are listed in the Results and Discussion section in Table 1. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 242.5 MHz): δ 10.39. Elemental analysis for $C_{27}H_{21}P$: Found: C 84.74, H 5.50; Calculated: C 86.10, H 5.62. IR (DRIFT-IR): 3040, 2980, 2854, 1587, 1435, 1406, 1104, 697 cm^{-1}.

2.3.3.2 Synthesis of $C_9H_6PMePh_2$ (IIb)

The reaction was carried out similarly to **IIa** using 7.85 g **Ib** (19.9 mmol) and 0.53 g NaH (22.0 mmol) in 150 mL THF. The reaction proceeded over 24 hours at room temperature to yield 5.32 g of a pale green, air sensitive solid (85% yield). Pure material (NMR) could be obtained by crystallization from a concentrated CH_2Cl_2 solution layered with hexanes. NMR analysis agreed with literature values.[44] $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 5.69. IR (DRIFT-IR): 3047, 2914, 1588, 1411, 1307, 1173, 876, 733, 710 cm^{-1}. Literature ^1H NMR ($CDCl_3$): δ

7.68 (m, 1H), 7.67 – 7.63 (m, 2H) 7.67 – 7.53 (m, 1H), 7.55 – 7.52 (m, 2H), 7.04 (d, 1H), 6.97 (t, 1H), 6.84 (t, 1H), 6.74 (t, 1H) 6.64 (t, 1H), 2.5 (d, 3H).[20]

2.3.3.3 Synthesis of $C_9H_6PMe_2Ph$ (IIc)

The reaction was carried out similarly to **IIa** using 2.390 g **Ic** (7.2 mmol) and 0.19 g NaH (7.92 mmol) in 60 mL THF. The reaction proceeded over 24 hours at room temperature to yield 1.82 g of a yellow-green, air sensitive solid (94% yield). X-ray quality crystals were obtained by crystallization from a concentrated CH_2Cl_2 solution layered with hexanes. ^1H and ^{13}C NMR data are listed in the Results and Discussion section in Table 2. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 242.5 MHz): δ 1.78. Elemental analysis for $C_{17}H_{17}P$: Found: C 79.38, H 6.69; Calculated: C 80.93, H 6.79. IR (DRIFT-IR): 3046, 2983, 2895, 1586, 1413, 1303, 1166, 919, 742, 709 cm^{-1}.

2.4 Coordination of Ligands to Group 4 Metals

2.4.1 Synthesis of $TiCl_4(THF)_2$[61]

To a solution of 3.0 mL $TiCl_4$ (27 mmol) in 50 mL CH_2Cl_2, 10 mL THF (123 mmol) was slowly added by syringe. Addition of 50 mL hexanes and storing at -20 °C for 1 hour results in the formation of a bright yellow precipitate which was collected by filtration to yield 8.06 g of a yellow crystalline solid (90% yield).

2.4.2 Attempted Coordination of One Equivalent of Ylide using $TiCl_4(THF)_2$

A solution of 162 mg **IIc** (0.64 mmol) in 10 mL CH_2Cl_2 was syringed into a solution of 214 mg $TiCl_4(THF)_2$ (0.64 mmol) in 10 mL CH_2Cl_2. The reaction was stirred overnight, over which time a light brown precipitate formed from the dark brown solution. The precipitate was filtered and dried *in vacuo* to give 0.147 g of a pale brown solid. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded in D_2O. The NMR spectra showed that several products had formed, with at least seven methyl doublets resonances in the ^1H NMR spectrum. The product was readily soluble in DMSO and water, and slightly soluble in methanol and ethanol. Attempts to recrystallize the product by dissolving in minimal amounts of ethanol and adding ether dropwise resulted in an orange powder, the ^1H NMR spectrum of which showed four prominent doublets. No crystals sufficient for X-ray analysis could be obtained. In another attempt to recrystallize the product, the chloride anion was exchanged for the bulkier anion, PF_6^-, by dissolving the product in water and adding excess sodium hexafluorophosphate. The $^{31}P\{^1H\}$ NMR spectrum (DMSO-d_6) of the resultant precipitate showed more than seven environments, and no further attempt to purify the material was made.

An NMR scale reaction using the ylide $IndPMePh_2$ in CD_2Cl_2 was also attempted following this method. ^1H NMR experiments were immediately collected at intervals of 2 minutes after the titanium solution was injected into the ylide solution. The NMR spectra showed that all of the ylide starting material was immediately consumed and five new methyl doublets immediately formed, and remained for several hours.

2.4.3 Attempted Coordination of Two Equivalents of Ylide using $TiCl_4(THF)_2$

A solution of 375 mg **IIb** (1.20 mmol) in 40 mL THF was syringed over to a solution of 200 mg $TiCl_4(THF)_2$ (0.60 mmol) in 60 mL THF and stirred overnight at room temperature. As the reaction proceeded, a dark brown precipitate formed and the filtrate became light pink. The reaction was filtered and the precipitate was dried *in vacuo* for several hours. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded in DMSO-d_6. Many phosphorus resonances were observed in the ^{31}P NMR spectrum, but only two appeared to be the major species. The product was poorly soluble, aside from in DMSO, water and acetone; recrystallization attempts by slow evaporation in acetone resulted in crystals which appear to be the result of the ylide reacting with acetone (**III**). ^1H NMR (D_2O, 400 MHz): δ 7.81 (br d, 1H), 7.73 (t, 2H), 7.65 (d of d, 4H), 7.55 (m, 5H), 7.25 (t, 1H), 7.02 (t, 1H), 6.89 (d, 1H), 2.68 (d, 3H), 2.40 (s, 3H), 2.26 (s, 3H).

Anion exchange of the crude material was attempted by dissolving the compound in water and adding an excess of sodium hexafluorophosphate or sodium tetraphenylborate, but pure material could not be obtained from either attempt (NMR). Similar results were obtained when repeating the reaction with the alternative ylides, $IndPPh_3$ and $IndPMe_2Ph$.

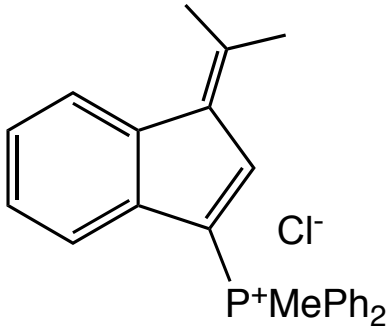


Figure 18. The resulting compound (III) from recrystallization attempts in acetone

2.4.4 Attempted Synthesis of [$TiCl_3$(IndPMePh_2)]Cl from $TiCl_4$

To a solution of 300 mg **IIb** (0.95 mmol) in 40 mL toluene, a solution of 105 μL $TiCl_4$ (0.95 mmol) in 10 mL toluene was injected and immediately the solution turned red. The reaction was refluxed for 48 hours, over which time a brown precipitate formed from the red solution. The reaction was allowed to cool before the solvent was decanted from the precipitate. The brown precipitate was dried *in vacuo* and 0.31 g of solid was collected. ^1H and $^{31}P\{^1H\}$ NMR were recorded in methanol-d_4; the ^{31}P NMR showed more than ten resonances present and no attempts at purification were made due to the number of species that had formed.

2.4.5 Attempted Synthesis of [$TiCl_2$Cp*(IndPMePh_2)]Cl from Cp*$TiCl_3$

A mixture of 500 mg **IIb** (1.59 mmol) and 460 mg Cp*$TiCl_3$ (1.59 mmol) in 50 mL chlorobenzene was refluxed for four hours and then cooled to room temperature. The solution was pumped to down dryness *in vacuo* and 0.69 g of a dark brown solid was collected. ^1H and $^{31}P\{^1H\}$ NMR were recorded in $CDCl_3$.

The NMR spectra showed two prominent resonances in the ^{31}P NMR spectrum, two methyl doublets in the ^{1}H NMR, and two Cp* resonances. Attempts to recrystallize gave titanium oxide products, presumably from small amounts of residual water present in the solvents.

The reaction was also attempted in THF which gave similar results, as well as on an NMR scale in CD_2Cl_2, which showed more than four different species immediately forming in the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra.

2.4.6 Attempted Syntheses of $[TiCl_3(IndPR_3)]Cl$ using $TiCl_3(THF)_3$

$TiCl_3(THF)_3$ was prepared by fellow lab-mate Andrew Fraser, following the patent by Strickler in 1994.[62] A solution of 315 mg **IIb** (1.0 mmol) in 30 mL THF was added dropwise to a solution of 373 mg $TiCl_3(THF)_3$ (1.0 mmol) in 10 mL THF at -78 °C. The reaction was warmed to room temperature and stirred for three hours, as a white precipitate developed from the dark purple solution. To oxidize the Ti(III) to Ti(IV), 1 mL carbon tetrachloride was added and the reaction stirred for 10 minutes. The resulting white precipitate was filtered off and the filtrate was pumped down to dryness *in vacuo* to yield 338 mg of a magenta solid. ^{1}H and $^{31}P\{^{1}H\}$ spectra were collected in THF-d_8. The ^{31}P NMR spectrum showed at least six species and the ^{1}H NMR spectrum showed several methyl doublets as well as evidence of coordinated THF. Attempts to purify the resulting mixture by recrystallization from a CH_2Cl_2 solution layered with hexanes at -20 °C resulted in decomposition.

2.4.7 Attempted Syntheses of $[TiCl_2(IndPR_3)_2]Cl_2$ using $TiCl_3(THF)_3$

In a procedure similar to that described above, a solution of 716 mg **IIb** (2.3 mmol) in 50 mL THF was added dropwise to a solution of 422 mg $TiCl_3(THF)_3$ (1.1 mmol) in 10 mL THF at -78 °C. The reaction was stirred for four hours. 0.2 mL carbon tetrachloride was then added and the reaction was stirred for an additional hour. The reaction was filtered and the filtrate was pumped to dryness *in vacuo* to yield 564 mg of a deep purple solid. ^1H and $^{31}P\{^1H\}$ NMR spectra were collected in toluene-d_8. The NMR spectra showed that several products had formed, with several prominent resonances in the ^{31}P spectrum. The reaction was also repeated at reflux to give similar results.

2.4.8 Attempted Syntheses of $[Ti(NEt_2)_3(IndPR_3)]Br$ using Tetrakis(diethylamido)titanium (TDEAT)

1.01 mL TDEAT (2.8 mmol) was added dropwise to a suspension of 1.11 g **Ib** (2.8 mmol) in 125 mL dry toluene at -10 °C. The reaction was gradually warmed to room temperature and stirred for 12 hours. As the reaction proceeded, a pale green precipitate formed from the dark brown solution. The precipitate was collected by filtration to yield 0.40 g of a green solid. ^1H and $^{31}P\{^1H\}$ NMR spectra were collected in CD_2Cl_2 and are consistent with the free ylide, $IndPMePh_2$ (**IIb**). The solvent was removed from the filtrate *in vacuo* to yield a brown oil, which appeared to be $TiBr(NEt_2)_3(NHEt_2)$ by NMR. ^1H NMR (tol-d_8, 500 MHz): δ 3.61 (q, 6H, Ti-NC**H**$_2$CH$_3$), 3.57 (q, 2H, Ti←HNC**H**$_2$CH$_3$), 2.10 (s, 1H, Ti←**H**NCH$_2$CH$_3$), 1.15 (t, 9H, Ti-NCH$_2$C**H**$_3$), 1.08 (t, 3H, Ti←HNCH$_2$C**H**$_3$).

2.4.9 Attempted Synthesis of $[Ti(NEt_2)_3(IndPR_3)]PF_6$ using TDEAT

0.94 mL TDEAT (2.6 mmol) was added dropwise to a suspension of 1.20 g **Id** (2.6 mmol) in 50 mL chlorobenzene at 0 °C. The reaction was warmed to room temperature and stirred for 1 hour, during which time the phosphonium salt was consumed. The reaction was then refluxed for an additional hour, during which no further observable change was noted. After cooling to room temperature, the reaction was pumped down to dryness *in vacuo* to yield a green/brown oily product. The product was identified as free $IndPMePh_2$ (**IIb**), $NHEt_2$ and a titanium product which appeared to be $[Ti(NEt_2)_3(NHEt_2)]PF_6$ by NMR. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 – 7.40 (Ph of **IIb**), 7.05 – 6.60 (Ind of **IIb**), 3.70 (q, Ti-NC**H**$_2$CH$_3$), 3.55 (q, Ti←HNC**H**$_2$CH$_3$), 2.65 (HNC**H**$_2$CH$_3$), 2.50 (d, P-C**H**$_3$ of **IIb**), 1.15 (br t, Ti-NCH$_2$C**H**$_3$, Ti←HNCH$_2$C**H**$_3$, HNC**H**$_2$CH$_3$).

Chapter 3. Results and Discussion

3.1 The Synthesis and Characterization of Phosphonium Indenylides

One of the most significant problems that limited the exploration of the class of phosphonium ylide ligands is the lack of a general synthetic route, since published synthetic procedures are not generally applicable to other phosphines or the ylide derivatives.[1,2] In an attempt to revive this class of ligand, an investigation into the use of the indenyl-derived ylide was recently conducted by Brownie *et al.*;[44] specifically the synthesis, characterization, and coordination to group VI metals of methyldiphenylphosphonium indenylide was explored (Section 1.2.3). While Brownie and coworkers were able to successfully synthesize the aforementioned ylide in high yields, the synthetic route was limited in that it is limited to that particular ylide due to dichlorophenylphosphine being the only commercially available starting phosphine.[20-26,44]

The synthesis of an indenyl-derived ylide by a potentially more general route was reported by Crofts and Williamson, who prepared triphenylphosphonium indenylide (**IIa**).[45] The compound was synthesized by reacting an excess of triphenylphosphine with 1-bromoindene to obtain the ylide in an overall yield of ~9%.[45] The compound was not definitively characterized and much of its chemistry was left unexplored, presumably due to the procedure being so inefficient.

We report herein a variation of this procedure by Crofts *et al.*[45] to synthesize the ylide, **IIa**, from 1-bromoindene. Instead of simply reacting

triphenylphosphine with 1-bromoindene for an extended period of time, harsher reaction conditions were employed, and the phosphonium salt intermediate was collected and characterized prior to being converted to the ylide. Furthermore, this procedure was extended to other phosphine derivatives of the indenylide system to demonstrate that it is indeed a more general route to the indenyl-derived ylides.

3.1.1 Synthesis and Characterization of Phosphonium Salts $[C_9H_6PR_3]^+Br^-$

1-Bromoindene was initially prepared from trimethylsilyl(indene)[54,57,58] and dioxane dibromide,[59] and purified by column chromatography according to the procedure by Woell and Boudjouk (Figure 19).[60]

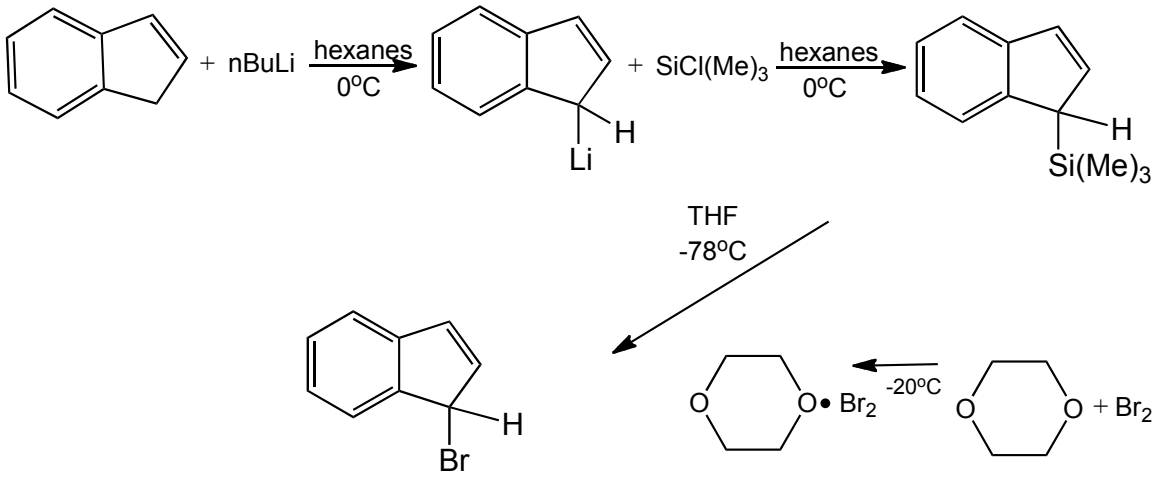


Figure 19. Synthesis of 1-bromoindene

Reacting 1-bromoindene with triphenylphosphine at 60 °C for 72 hours generated the phosphonium salt as a mixture of two isomers (**Ia; A** & **B**) which were isolated in a 49% yield as a white powder (Figure 20). Compounds **Ib** and

Ic were prepared in the same manner with methyldiphenylphosphine (3 hours, 88% yield) and dimethylphenylphosphine (1 hour, 48 % yield), respectively at room temperature. Of the three phosphines utilized, triphenylphosphine is the least nucleophilic[63] and therefore it is reasonable to expect that it required the harshest reaction conditions. With increasing nucleophilicity (PPh_3 < $PMePh_2$ < PMe_2Ph),[63] the reaction can be completed at lower temperatures and with shorter reaction times.

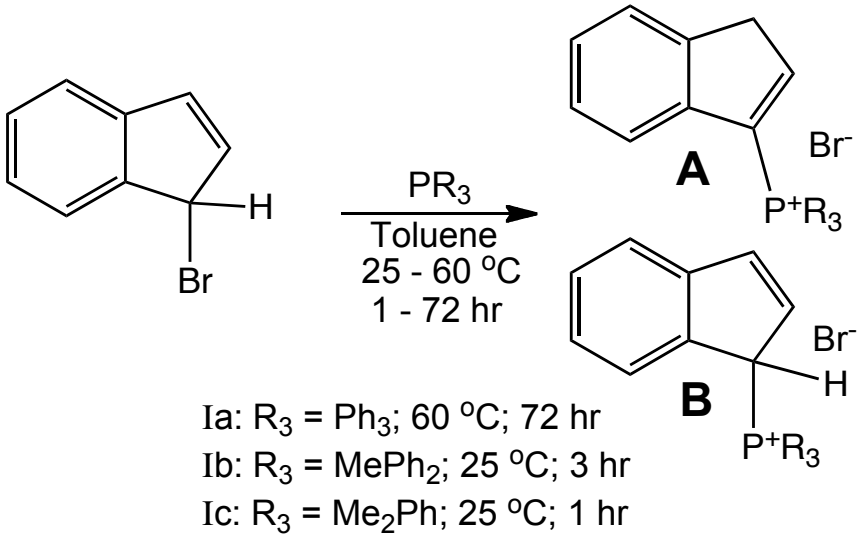


Figure 20. Synthesis of phosphonium salt isomers Ia, Ib and Ic, A and B

For all three salts, the two isomers were characterized by ^1H and ^{31}P NMR spectroscopy in $CDCl_3$. Characterization of **Ib** and **Ic** was done initially since they are more amenable to NMR characterization due to the presence of the methyl doublet "tags" visible in the aliphatic region of the ^1H NMR spectrum.

For compound **Ic**, three methyl doublets appear between 3.0 and 2.4 ppm in the ^1H NMR spectrum. Since isomer **B** bears a chiral carbon centre, the two

methyl groups are rendered inequivalent and thus the protons appear as two doublets of equal intensity at 2.5 and 2.4 ppm. The broad shift at 6.6 ppm has a relative integration of 1 when compared to the methyl doublets of isomer **B**, and by a NOESY NMR experiment it is confirmed that this signal belongs to the single proton present on the chiral carbon of isomer **B**. The two equivalent methyl groups of isomer **A** appear at 2.9 ppm. Integrating the broadened singlet at 3.9 ppm with respect to the methyl doublet of isomer **A** shows a 2 : 6 relative integration, and thus this signal is assigned to the two equivalent aliphatic protons of isomer **A** (**H_2**C-CH=C-P^+). All methyl doublets have coupling constants of 13.1 Hz, consistent with $^2J_{H\text{-}P}$ coupling.[64] The overlap of the indenyl and phenyl protons from both isomers makes the spectrum very complicated above 7.0 ppm and it is therefore not possible to definitively assign this region of the NMR spectrum. The relative intensities of the methyl doublets in the ^{1}H NMR spectrum indicate a 30 : 70 ratio of isomer **A** : isomer **B**, yet this ratio does vary slightly from experiment to experiment. Using the relative intensities, it is possible to assign the two phosphorus environments in the $^{31}P\{^1H\}$ NMR spectrum; isomer **B** appears at 27.4 ppm while isomer **A** appears at 13.4 ppm. These assignments are consistent with what one would expect for a positively charged phosphorus atom adjacent to an sp^3 carbon (shifted downfield) versus a positively charged phosphorus atom adjacent to an sp^2 carbon (shifted upfield).[64]

For phosphonium salt **Ib**, the two methyl doublets present at 3.1 and 2.8 ppm were integrated with respect to the peak present at 3.9 ppm. A 3 : 2 relative integration ratio is found between the peak at 3.9 and the doublet at 3.1 ppm; thus the singlet is assigned as the two equivalent aliphatic protons of isomer **A**

and the doublet at 3.1 ppm is assigned to the $–CH_3$ of isomer **A**. The doublet at 2.8 ppm is thus the methyl ($–CH_3$) protons of isomer **B**. Once again, coupling constants of 13.1 Hz were calculated for both methyl doublets, consistent with $^2J_{H\text{-}P}$ coupling. The broad singlet present at 6.6 ppm is assigned as the single aliphatic proton present in isomer **B**, shifted considerably downfield by the nearby positively charged phosphorus. This assignment is confirmed by a 2D NOESY NMR experiment, which shows correlation between the broad singlet at 6.6 ppm and the methyl doublet at 3.1 ppm. The indenyl and phenyl region of the NMR spectrum is again very complicated due to overlapping shifts of both isomers in such a small region, therefore these peaks could not be definitely assigned. The relative integration of the methyl doublets to one another were calculated in order to determine the ratio of the isomers; the ratio is approximately 40 : 60 for isomer **A** : **B,** but does vary slightly from experiment to experiment. Using the relative integration data, the ^{31}P NMR signals can also be assigned to isomer **A** and isomer **B** (13.6 and 25.9 ppm respectively).

Phosphonium salt **Ia** is the most difficult to assign in the ^{1}H NMR spectrum, since it lacks the methyl doublets "tags" that can be easily assigned for the other two compounds. Thus, the signals at 6.7 ppm (**H**C-P^+ of isomer **B**) and at 4.1 ppm (**H_2**C-CH=C-P^+ of isomer **A**) were assigned based on the assignments in the other two phosphonium salts. Once again, the indenyl/phenyl region of the spectrum appears very complicated due to the presence of the two isomers, and thus cannot be assigned. The ^{31}P NMR spectrum is also assigned based on the previous phosphonium salts; isomer **B** appearing downfield at 26.6 ppm and

isomer **A** appearing upfield at 12.5 ppm. The relative intensities of the signals in the ^{31}P NMR spectrum indicate a 75 : 25 ratio of isomer **A** : **B**.

3.1.2 The Synthesis of Ylide $C_9H_6PR_3$

The ylides **IIa**, **IIb**, and **IIc**, were synthesized from their respective phosphonium salts by deprotonation using an excess of NaH in THF. The three ylides were obtained in good yields, with increasing yields for the less bulky phosphines. This could be due to the increased sterics hindering the deprotonation with the larger phosphines, or possibly due to the fact that with increasing bulkiness of the phosphine, isomer **A** becomes the more predominant species, which could in turn be harder to deprotonate than isomer **B**. In order to confirm this theory, isomer **A** and **B** would have to be separated before deprotonation, although this area was not further explored in this project.

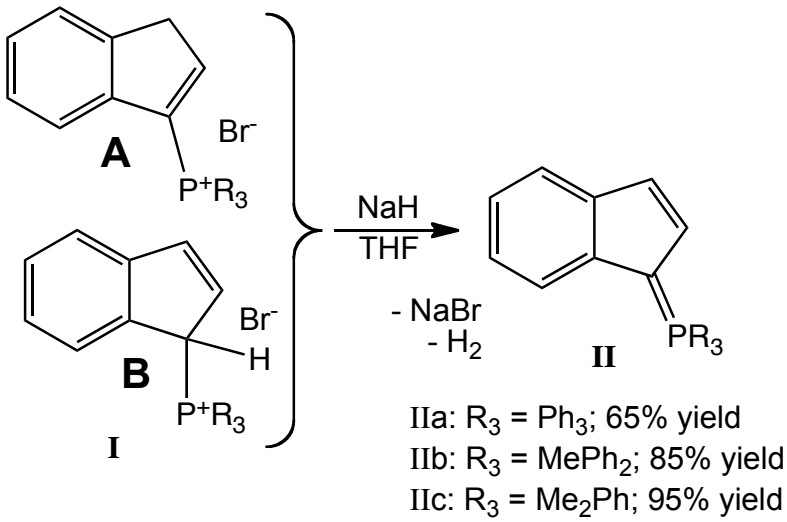


Figure 21. Synthesis of indenylide compounds: triphenylphosphonium indenylide, methyldiphenylphosphonium indenylide, and dimethylphenylphosphonium indenylide

Analytically pure material and X-ray quality crystals of **IIa** and **IIc** were obtained by recrystallization from CH_2Cl_2 solution layered with hexanes. Since analytical and X-ray crystallographic data for **IIb** already appear in the literature,[44] the product was determined to be pure by NMR spectroscopy, after recrystallization by layering a concentrated solution in CH_2Cl_2 with hexanes. Complete ^1H, ^{13}C and ^{31}P NMR spectral data for the ylides **IIa** and **IIc** are described below in Section 3.1.3.

The notable advantage of using this preparation as opposed to that developed by Brownie is its applicability to a range of possible indenylides, since there are many commercially available starting phosphines which could be used in this synthesis. Brownie's synthesis is limited to the methyldiphenyl derivative due to chlorodiphenylphosphine being the only practical available starting material.[44] While only three ylides were synthesized and characterized for this project, this route is in theory only limited to the availability of a phosphine (PR_3), of which there are many commercially available.

3.1.3 NMR Characterization of Ylide $C_9H_6PR_3$ (IIa, IIc)

Compounds **IIa** and **IIc** were characterized fully by NMR spectroscopy, elemental analysis and X-ray crystallography. Since compound **IIb** has already been reported and characterized, a full characterization was not necessary and the compound was determined to be the desired one by comparing ^1H and $^{31}P\{^1H\}$ NMR to reported values.[44]

In addition to standard 1D ^{1}H, ^{13}C and ^{31}P NMR spectra, 2D NOESY, COSY, HSQC and HMBC were collected for **IIa** and **IIc** to assist in NMR characterization. The assignments of the NMR peaks are described as follows in full detail for **IIc**; labeling schemes for both **IIc** and **IIa** can be seen below in Figure 22 and Figure 28 respectively, and a summary of the assignments for both ylides can be seen in Table 1 and Table 2.

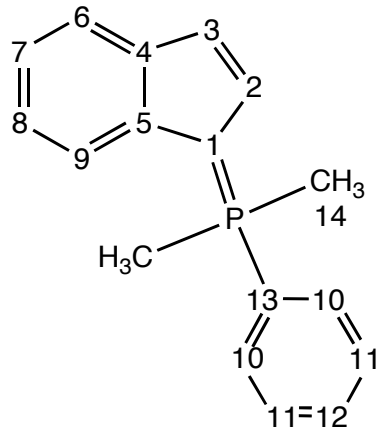


Figure 22. Dimethylphenylphosphonium indenylide with labeling for NMR characterization

Table 1. ^{1}H and ^{13}C NMR chemical shifts (ppm) and coupling constants for dimethylphenylphosphonium indenylide.

Position	δ (^{1}H)	Mult.	J (Hz)	δ (^{13}C)	Mult.	J (Hz)
1	-	-	-	66.69	d	$^{1}J_{C-P}$ = 121
2	6.98	t	$^{3}J_{H-H}$ = 4.5 $^{4}J_{H-P}$ = 4.5	124.2	d	$^{2}J_{C-P}$ = 16.5
3	6.64	t	$^{3}J_{H-H}$ = 4.5 $^{3}J_{H-P}$ = 4.5	105.8	d	$^{3}J_{C-P}$ = 14.8
4	-	-	-	134.4	d	$^{3}J_{C-P}$ = 14.8
5	-	-	-	137.1	d	$^{2}J_{C-P}$ = 13.0
6	6.68	d	$^{3}J_{H-H}$ = 8.7	120.6	d	$^{4}J_{C-P}$ = 1.9
7	6.95	t	$^{3}J_{H-H}$ = 7.6	116.9	s	-
8	6.87	t	$^{3}J_{H-H}$ = 7.6	117.6	s	-
9	7.18	d	$^{3}J_{H-H}$ = 7.9	116.8	d	$^{3}J_{C-P}$ = 1.9
10	7.64	d of d	$^{3}J_{H-H}$ = 7.3 $^{3}J_{H-P}$ = 13.0	131.0	d	$^{2}J_{C-P}$ = 11.1
11	7.49	t of d	$^{3}J_{H-H}$ =7.6 $^{4}J_{H-P}$ = 2.3	129.3	d	$^{3}J_{C-P}$ = 12.0
12	7.58	t	$^{3}J_{H-H}$ = 7.9	132.6	d	$^{4}J_{C-P}$ = 2.8
13	-	-	-	128.3	d	$^{1}J_{C-P}$ = 84.2
14	2.21	d	$^{2}J_{H-P}$ = 13.	12.92	d	$^{2}J_{C-P}$ = 61.0

The first step in the assignment of the ^{1}H NMR spectrum (Figure 23) of **IIc** began with the assignment of the phosphorus doublet at δ 2.21; the HSQC spectrum (Figure 24) shows these protons belong to the signal at δ 12.92 in the ^{13}C spectrum (carbon **14**). The ylidic carbon (carbon **1**) can also be easily assigned as it appears shifted upfield as a doublet at δ 67 ($^{1}J_{C-P}$ = 121 Hz). The HSQC spectrum confirms this is indeed a quaternary carbon signal.

The HMBC spectrum (Figure 25) shows correlation of the methyl protons to the quaternary carbon shift at δ128.3, which has a large J_{C-P} coupling of 84 Hz and therefore must be carbon **13** of the phenyl group. The HMBC spectrum shows further correlation of this carbon to the protons at δ 7.49 (2H) and δ 7.64

(2H), which are thus assigned to the phenyl protons. NOESY interactions (Figure 27) are observed between the protons at δ 7.64 and the methyl group, allowing this to be assigned as **10** and the shift at δ 7.49 as **11**. The COSY NMR spectrum (Figure 26) shows correlation of **10** and the broad triplet at δ 7.58 (1H), which can thus be assigned to the final phenyl proton **12**. The phenyl carbons were assigned using the HSQC spectrum.

The NOESY spectrum (Figure 27) was then used to assign the protons **2** and **9**, which were the only protons of the indenyl fragment that showed through-space correlation to the protons of the methyl group at δ 6.98 and δ 7.18. The shift at δ 6.98 also showed HMBC coupling to the ylidic carbon and is thus assigned as proton **2**, and therefore the signal at δ 7.18 must be **9**. The COSY spectrum shows the only correlation between proton **2** is the shift at δ 6.64 which allows this to be assigned as **3**. Both protons **2** and **3** appear as triplets due to coupling with each other and with the nearby phosphorus.

The COSY spectrum was used to assign the remaining indenyl protons. Proton **9** correlates to the peak at δ 6.87. This peak is a triplet, as expected for proton **8**. Proton **8** correlates to the triplet at 6.95, which is then assigned as **7**. Finally, proton **6** is assigned as δ 6.68 due to its correlation to proton **7**. All indenyl carbons were assigned by HSQC coupling. The HMBC spectrum was then used to confirm all of these proton assignments.

The remaining two quaternary carbons, **4** and **5** were assigned using the HMBC spectrum. Correlation between proton **9** and the quaternary carbon signal at δ 137.1 allows this peak to be assigned as carbon **5** and the correlation

between proton **3** and the quaternary carbon signal at δ 134.4 allows this peak to be assigned as carbon **4**.

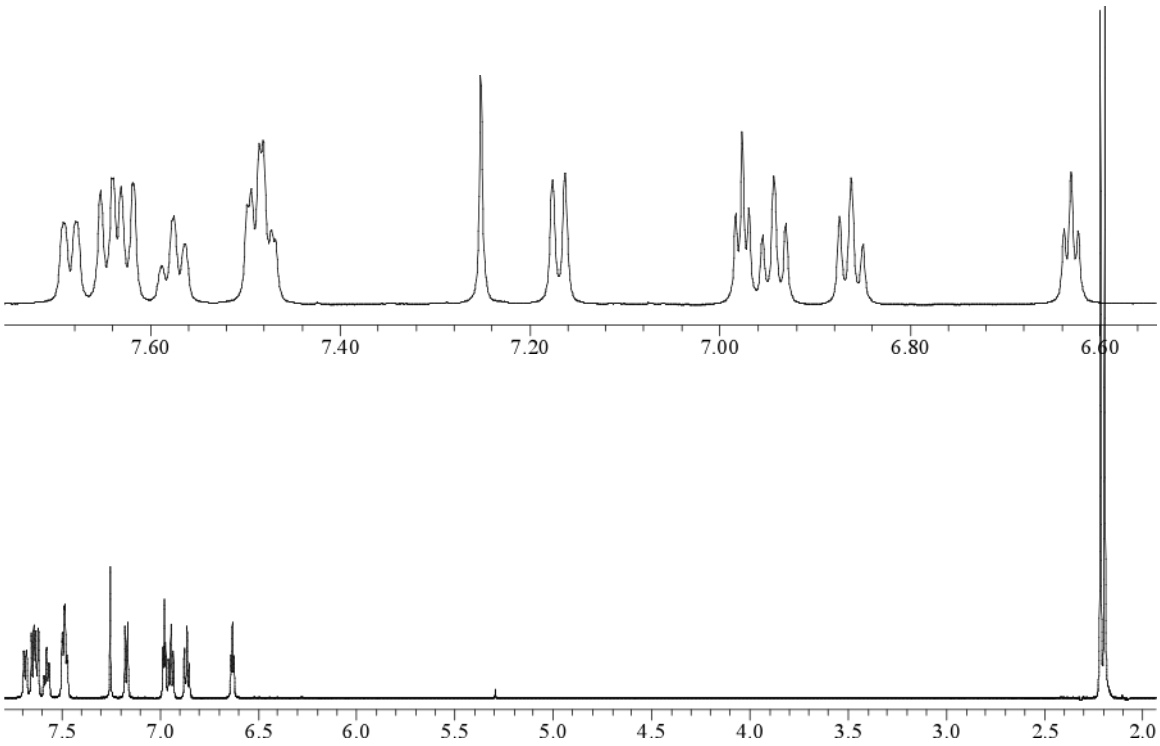


Figure 23. ^{1}H NMR spectrum of IIc, dimethylphenylphosphonium indenylide, $CDCl_3$, 600 MHz

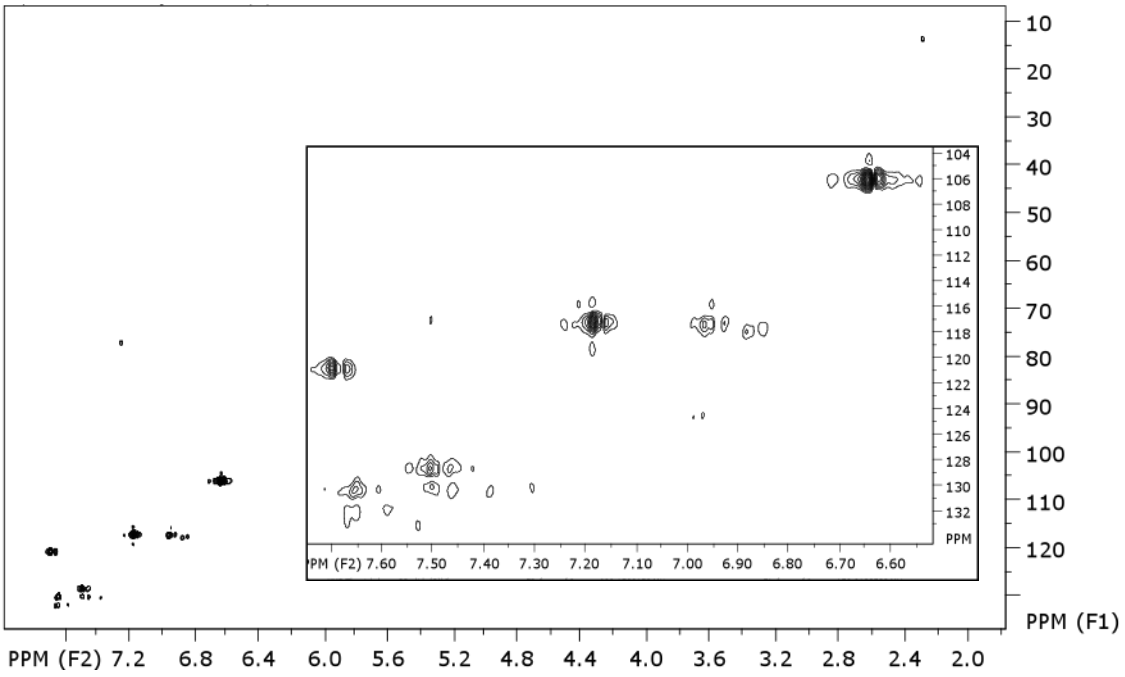


Figure 24. HSQC NMR spectrum of IIc, $CDCl_3$, 600 MHz

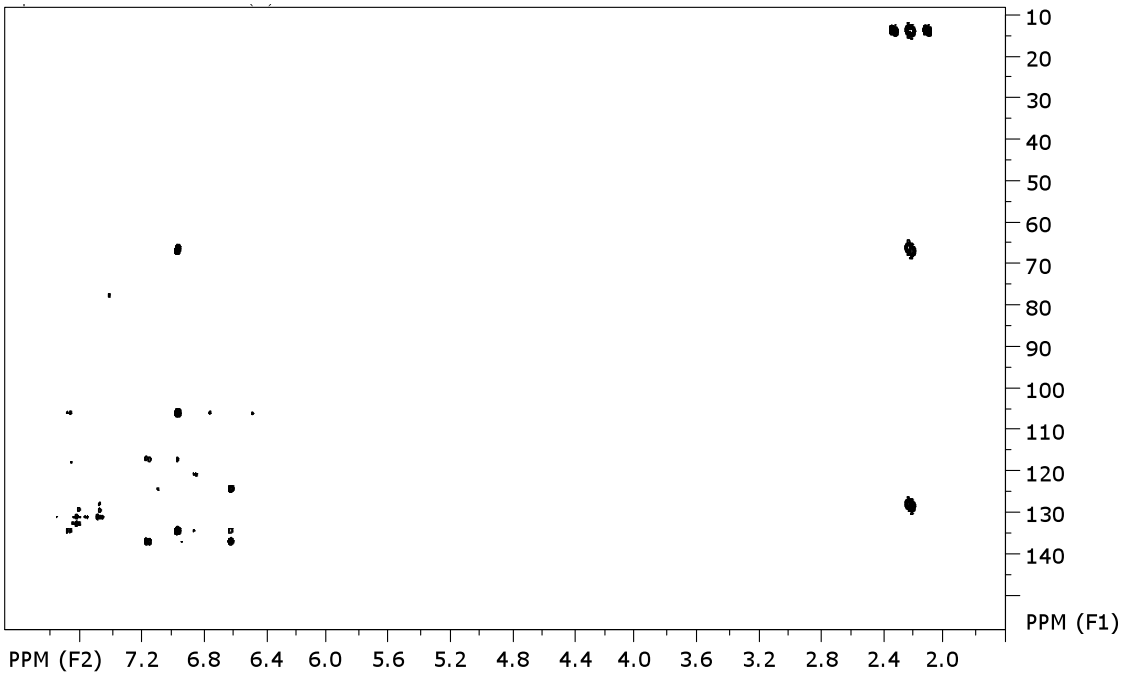


Figure 25. HMBC NMR spectrum of IIc, $CDCl_3$, 600 MHz

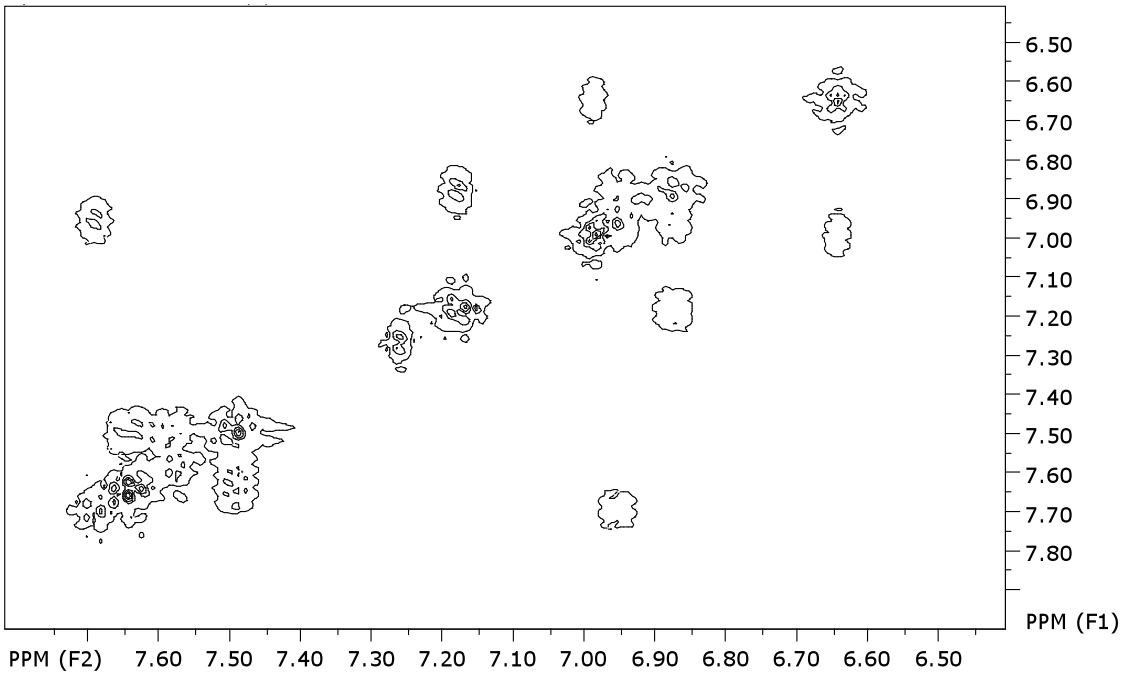


Figure 26. COSY NMR spectrum of IIc indenyl/phenyl region, $CDCl_3$, 600 MHz

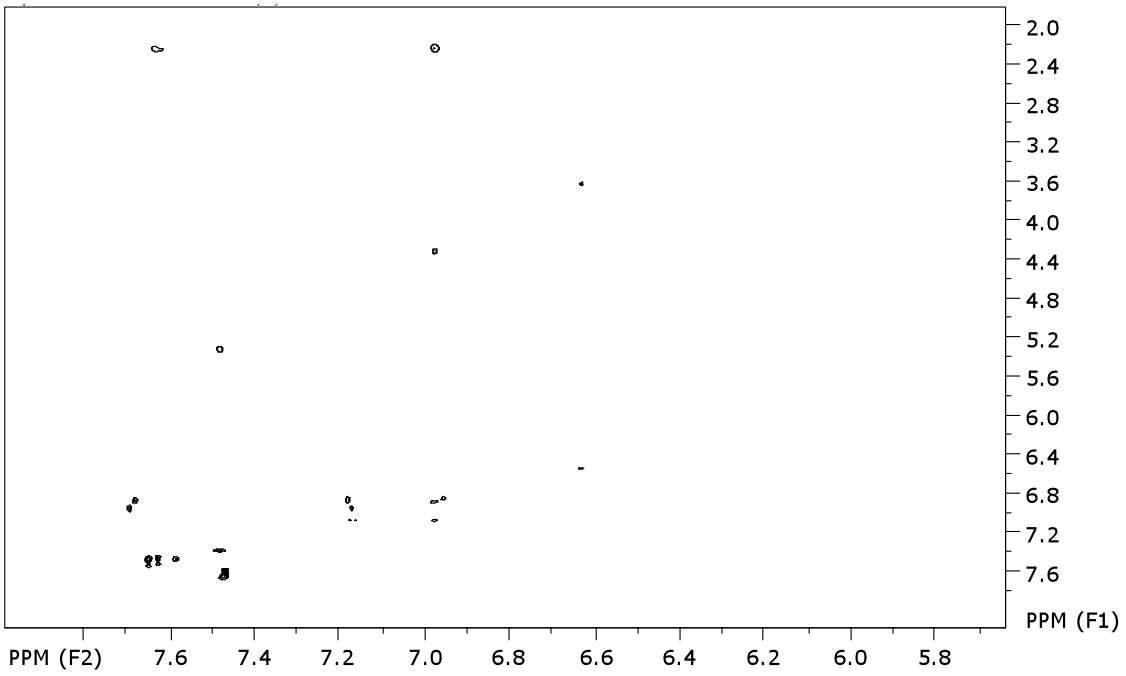


Figure 27. NOESY NMR spectrum of IIc, $CDCl_3$, 600 MHz

Assignments of the protons and carbons in **IIa** were done in a similar manner, using ^{1}H NMR accompanied with 2D HSQC, HMBC, COSY and NOESY to aid in the assignments (Figure 30, Figure 31, Figure 32, and Figure 33 respectively).

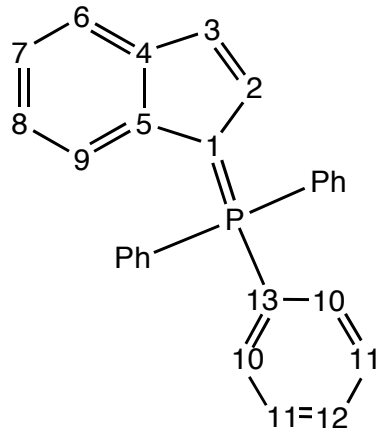


Figure 28. Triphenylphosphonium indenylide with labeling for NMR characterization

Table 2. ^{1}H and ^{13}C NMR chemical shifts (ppm) and coupling constants for triphenylphosphonium indenylide.

Position	δ (^{1}H)	Mult.	J (Hz)	δ (^{13}C)	Mult.	J (Hz)
1	-	-	-	65.52	d	$^{1}J_{C-P}$ = 123
2	6.56	t	$^{4}J_{H-P}$ = 4.2 $^{3}J_{H-H}$ = 4.2	106.4	d	$^{2}J_{C-P}$ = 16.0
3	6.61	t	$^{3}J_{H-P}$ = 4.5 $^{3}J_{H-H}$ = 4.5	128.2	d	$^{3}J_{C-P}$ = 16.0
4	-	-	-	135.7	d	$^{3}J_{C-P}$ = 13.5
5	-	-	-	137.8	d	$^{2}J_{C-P}$ = 14.8
6	6.89	d	$^{3}J_{H-H}$ = 7.9	117.2	s	-
7	6.76	t	$^{3}J_{H-H}$ = 7.2	118.0	s	-
8	6.95	t	$^{3}J_{H-H}$ = 7.2	117.7	s	-
9	7.66	m	-	120.4	s	-
10	7.68-7.65	m	-	133.8	d	$^{2}J_{C-P}$ = 9.8
11	7.51	t of d	$^{3}J_{H-H}$ = 7.9 $^{4}J_{H-P}$ = 3.0	129.1	d	$^{3}J_{C-P}$ = 12.3
12	7.62	t	$^{3}J_{H-H}$ = 7.6	133.6	d	$^{4}J_{C-P}$ = 3.7
13	-	-	-	125.8	d	$^{1}J_{C-P}$ = 89.8

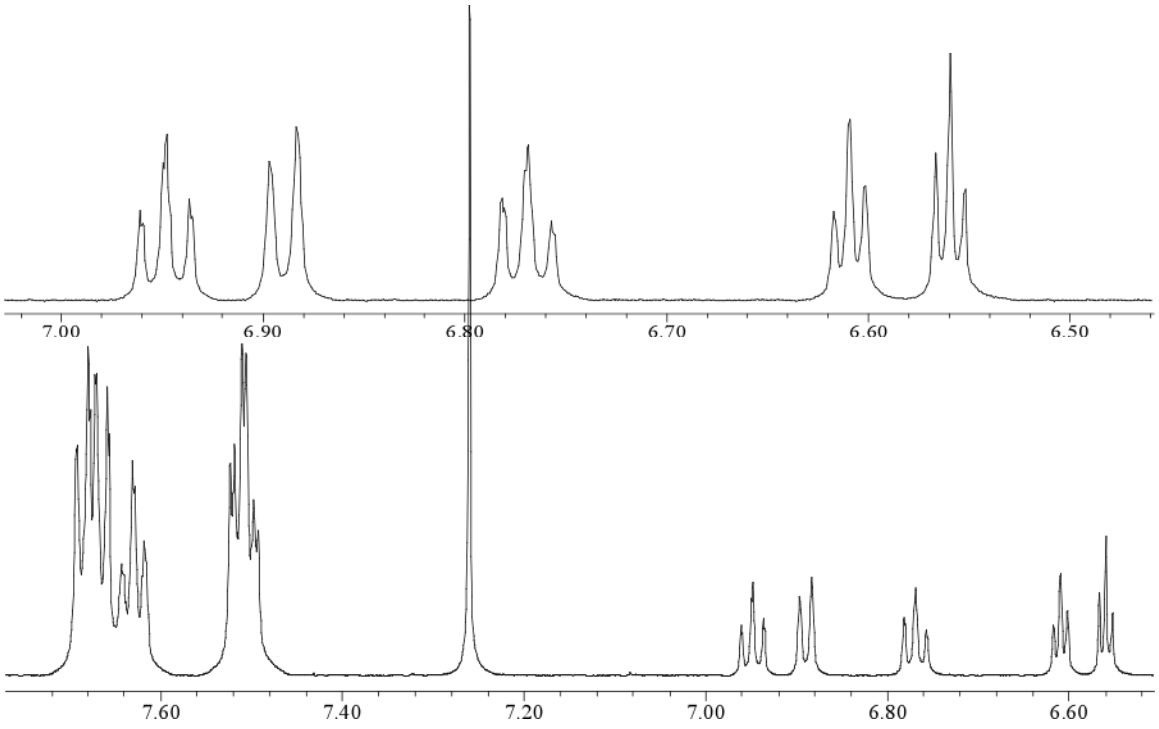


Figure 29. ^{1}H NMR spectrum of IIa, triphenylphosphonium indenylide, $CDCl_3$, 600 MHz

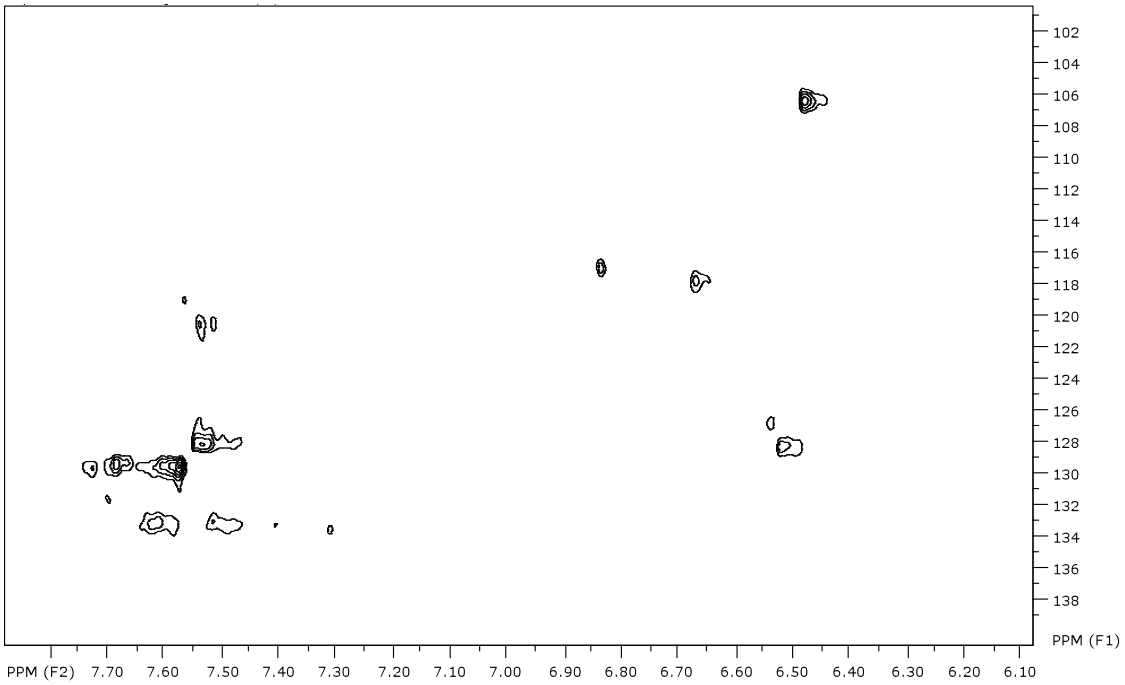


Figure 30. HSQC NMR spectrum of IIa, $CDCl_3$, 600 MHz

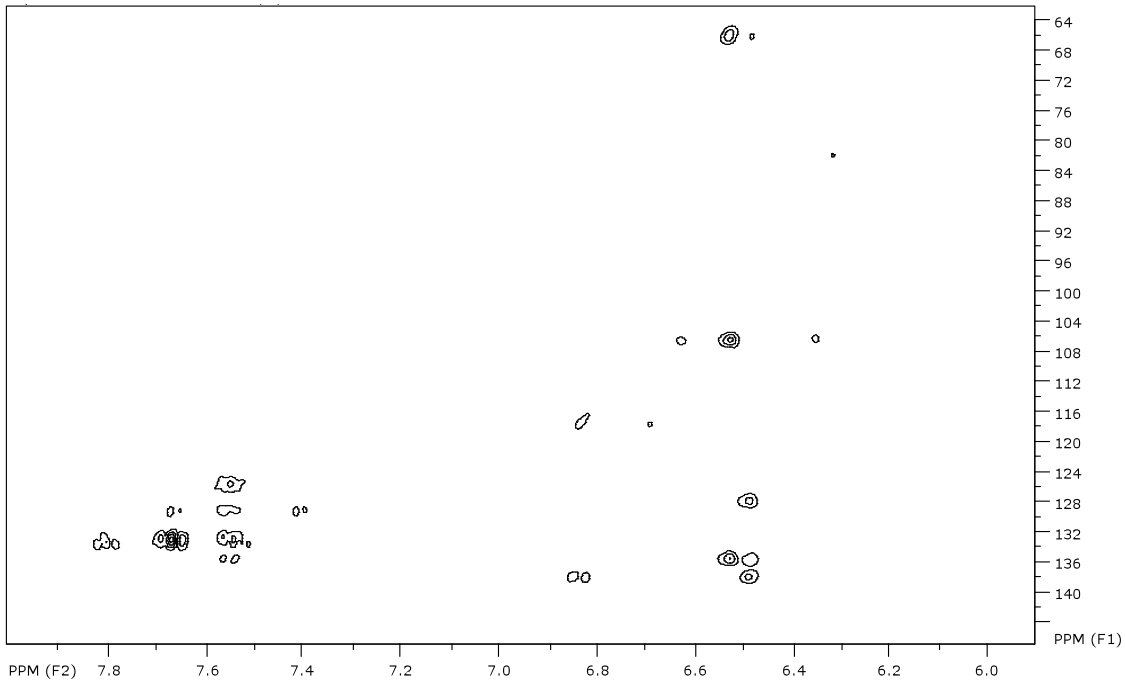


Figure 31. HMBC NMR spectrum of IIa, $CDCl_3$, 600 MHz

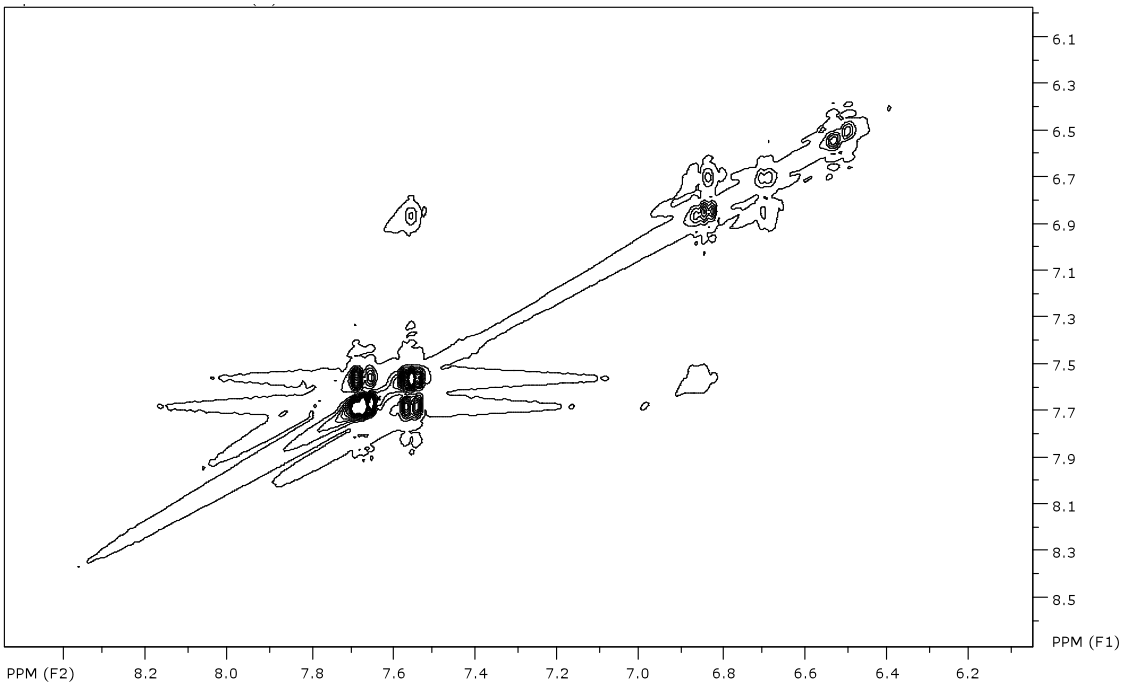


Figure 32. COSY NMR spectrum of IIa, $CDCl_3$, 600 MHz

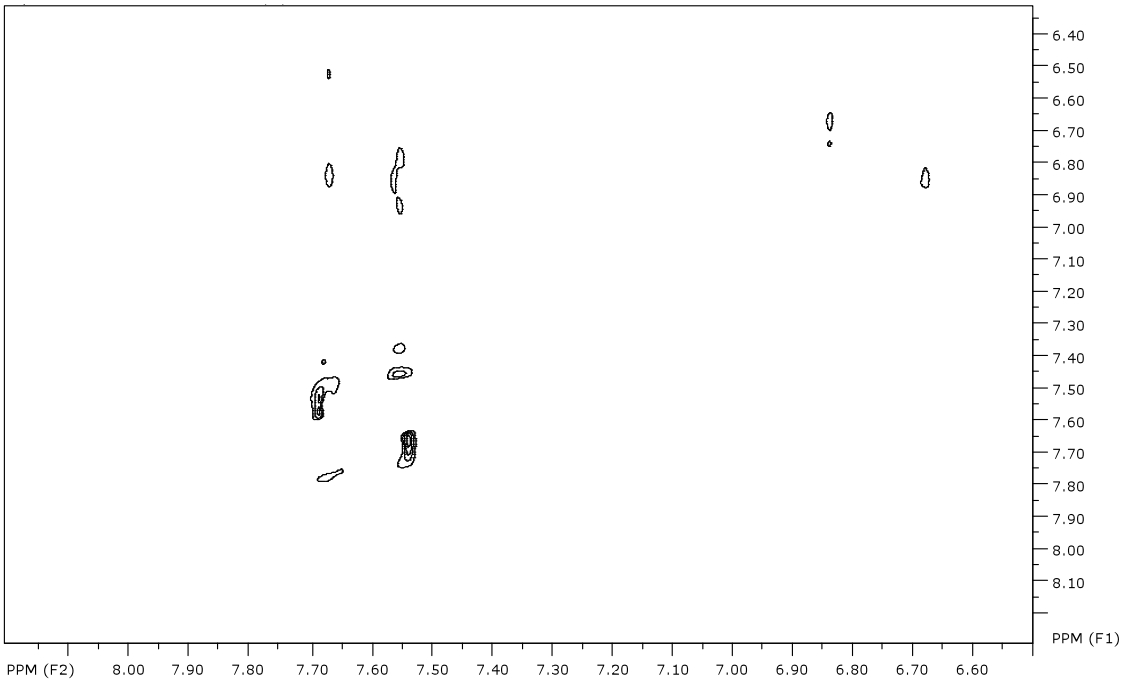


Figure 33. NOESY NMR spectrum of IIa, $CDCl_3$, 600 MHz

The NMR spectrum and peak assignments are consistent with those listed by Brownie *et al*. for methyldiphenylphosphonium indenylide[44] and Rufanov *et al.* for benzyldiphenylphosphonium indenylide.[43] The ^{13}C NMR spectrum shows that the ylidic carbon (carbon 1) appears upfield in the spectra for **IIa** (δ 65.52), **IIb** (δ 66.1)[44] and **IIc** (δ 66.69), which falls within range for carbon-phosphorus bonds with some double bond character.[64] The ^{31}P NMR resonance of **IIa** (δ 10.39) is more downfield than that of **IIb** (δ 5.69)[44], while that of **IIc** is shifted upfield (δ 1.78). This trend (δ PPh_3 > δ $PMePh_2$ > δ PMe_2Ph) is consistent with the decreasing sterics around the phosphorus atom and may be an indication of a slight increase in double bond character. The cyclopentadienyl derivative, $CpPMePh_2$, has a ^{31}P resonance of δ 7.95,[26] which falls within the range of resonances for these indenyl complexes. This implies that the donating ability of the phosphonium indenylide system would be similar to that of the related cyclopentadienyl complexes.

3.1.4 Molecular Structures of Ylide $C_9H_6PR_3$ (IIa, IIc)

X-ray quality crystals were obtained for **IIa** and **IIc** by dissolving the compounds in minimal amounts of methylene chloride and layering carefully with hexanes. Full structural data for both compounds can be found in the Appendix section, while selected bond lengths and angles are found below in Table 3. Also included in Table 3 are the literature values for bond lengths and angles for the ylide methyldiphenylphosphonium indenylide synthesized and characterized by the alternative route by Brownie *et al*.[44] The molecular structures complete with

labeling for triphenylphosphonium indenylide and dimethylphenylphosphonium indenylide are shown in Figure 34 and Figure 35, respectively. A full report of the crystal data can be found in Appendix 2.

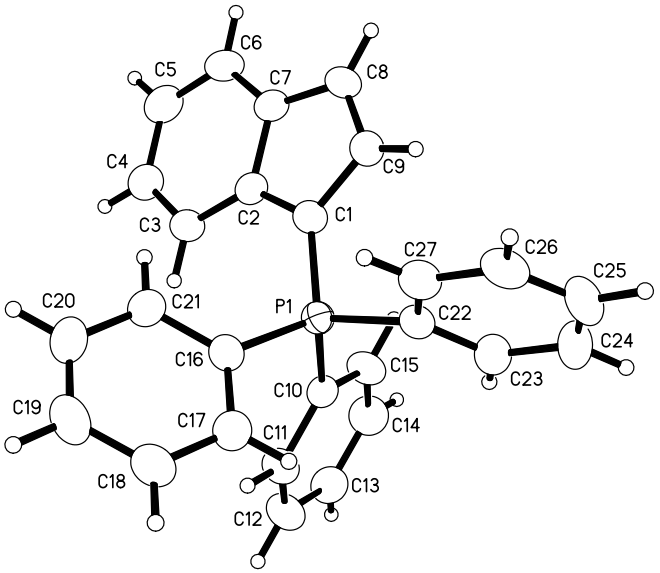


Figure 34. Molecular structure of IIa, $C_9H_6PPh_3$

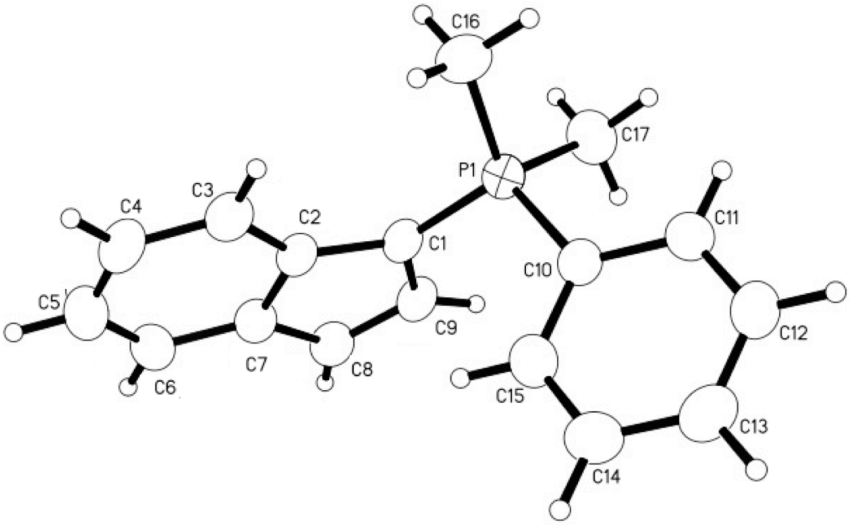


Figure 35. Molecular structure of IIc, $C_9H_6PMe_2Ph$

Table 3. Selected bond lengths and angles for IIa, IIb and IIc

Bond (Å)	IIa	IIb[20]	IIc
P(1)-C(1)	1.7284(19)	1.711(2)	1.727(3)
P-Me	-	1.787(2)	1.785(4)
P-Ph	1.8100*	1.788*	1.817(3)
C(1)-C(2)	1.435(3)	1.422(3)	1.435(4)
C(1)-C(9)	1.427(3)	1.430(3)	1.424(4)
C(9)-C(8)	1.368(3)	1.364(3)	1.374(5)
C(2)-C(7)	1.438(3)	1.423(3)	1.437(4)
C(8)-C(7)	1.429(3)	1.421(3)	1.417(5)
C(7)-C(6)	1.406(3)	1.397(3)	1.411(5)
C(6)-C(5)	1.374(3)	1.362(3)	1.368(5)
C(5)-C(4)	1.399(3)	1.394(3)	1.407(5)
C(4)-C(3)	1.372(3)	1.369(3)	1.372(5)
C(3)-C(2)	1.406(3)	1.400(3)	1.416(5)
Bond Angles (º)			
C(1)-P-Me	-	111.90(10)	112.12*
C(1)-P-Ph	110.80*	111.16*	112.31(15)
Me-P-Ph	-	107.05*	106.19*
Ph-P-Ph	108.15*	108.33(10)	-
Me-P-Me	-	-	107.45(19)
P-C(1)-C(2)	127.86(15)	174.9	129.6(3)
C(1)-C(9)-C(8)	110.12(17)	110.1(2)	110.1(3)
C(9)-C(8)-C(7)	108.50(17)	108.2(2)	108.2(3)
C(8)-C(7)-C(2)	107.47(17)	107.96(19)	108.1(3)
C(7)-C(2)-C(1)	107.22(16)	107.09(18)	107.0(3)
C(2)-C(1)-C(9)	106.67(16)	106.64(19)	106.6(3)

*denotes an average value

A good indication of the ylidic character of these molecules comes from the P(1)-C(1) bond length. Brownie *et al*. observed a bond length of 1.711(2) Å for methyldiphenylphosphonium indenylide, which was shorter than observed for the cyclopentadienylide derivative, at 1.727 Å.[44] Thus it was concluded that the indenylide derivative had more double bond character than its cyclopentadienylide counterparts, with less contribution from the zwitterionic resonance structure than the Cp derivatives.[44] The two indenylide structures

reported here, however, were found to have bond lengths of 1.7284(19) Å for **IIa** and 1.727(3) Å for **IIc**, which are considerably longer than Brownie found for his indenylide and closer to that of the cyclopentadienyl derivative, methyldiphenylcyclopentadienylide. The P(1)-C(1) bond length of for **IIa-c** is shorter than that of the indenyl derived ylide, $C_9H_6PBzPh_2$ (Bz = benzyl) reported by Rufanov *et al.* at 1.733(4) Å.[43] Thus there does not appear to be a consistent pattern for increasing sterics or electronics for this class of compounds.

It can be concluded that all of the P(1)-C(1) bond lengths for the indenylides are significantly shorter than the P-Ph bonds in the molecules (typical of a P-C single bond in phenyl phosphonium ylides), but longer than the P=C bond in $Ph_3P=CH_2$ (1.66 Å), a typical example of a non-resonance stabilized P-C double bond.[46] Therefore, the indenyl-derived ylides, much like the cyclopentadienylides, have significant contributions from both resonance structures seen previously in Figure 12.

3.2 Coordination to Titanium

There have been a few reports of titanium complexes of phosphorus cyclopentadienylides,[36] but the characterization of these complexes was largely incomplete and attempts to repeat these reported syntheses did not yield the desired products.[20] Due to the potential of the group 4 metallocene complexes to behave as catalysts for olefin polymerization, the coordination of the indenylide ligands was investigated. Several synthetic routes were examined using various

titanium (IV) and titanium (III) precursors; the attempts of these reactions are reported below.

3.2.1 Attempted Synthesis of $[TiCl_m(IndPR_3)_n]^{m+}$ by Direct Addition

Using an approach similar to the methodology reprted by Holy *et al.* to synthesize the complex $[(CpPPh_3)_2TiCl_2]Cl_2$,[36] direct addition of the ylide to a titanium source ($TiCl_4$ or $TiCl_4(THF)_2$) was attempted in hopes of generating the cationic species, $[TiCl_3(IndPR_3)]^{3+}$ or $[TiCl_2(IndPR_3)]^{2+}$ depending on the equivalent of ylide used.

In an attempt to repeat the reaction by Holy *et al.* to synthesize the cyclopentadienylide titanium complex,[36] Brownie *et al*. discovered the reaction generates a number of products from which the desired product could not be separated.[20] It therefore seemed reasonable that $TiCl_4$ may in fact be too reactive as a starting material, and its solvated complex, $TiCl_4(THF)_2$ was used in its place for the reactions as shown in Figure 36.

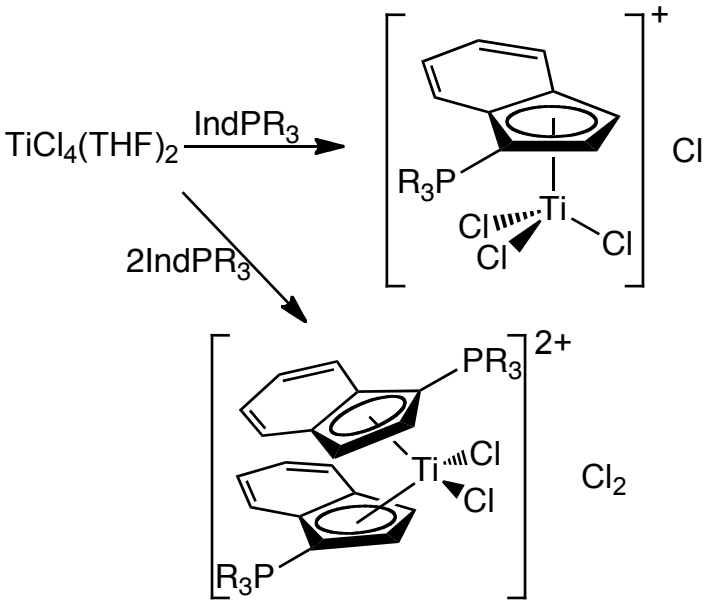


Figure 36. The attempted reactions of $TiCl_4(THF)_2$ with II

When one equivalent of ylide **IIc** was stirred with $TiCl_4(THF)_2$ in CH_2Cl_2, a brown solution with a beige precipitate resulted. ^1H and ^{31}P NMR spectra of the precipitate were collected in D_2O. The ^1H NMR spectrum showed seven methyl doublets corresponding to the P-Me group, with the peaks at δ 2.35, 2.30 and 2.25 being the most prominent (Figure 37). All doublets had J couplings of ~13 Hz, consistent with $^2J_{P\text{-}H}$ coupling of the ylide and its complexes.[26,44] The ^{31}P NMR spectrum showed two major species at δ 29.0 and 28.8 as well as several other minor species. Recrystallization of the product was difficult due to its poor solubility in a number of organic solvents. In an attempt to purify the product, the product was dissolved in water and sodium hexafluorophosphate was added in hopes of exchanging the chloride anion for the bulkier hexafluorophosphate anion. No such compound precipitated, and the resulting material had a ^{31}P NMR spectrum with at least seven phosphorus environments. Thus, no further attempt

to purify the product was made. An NMR scale reaction was also completed which showed the ylide starting material was immediately consumed upon injection; five new methyl doublets were observed which remain unchanged after several hours.

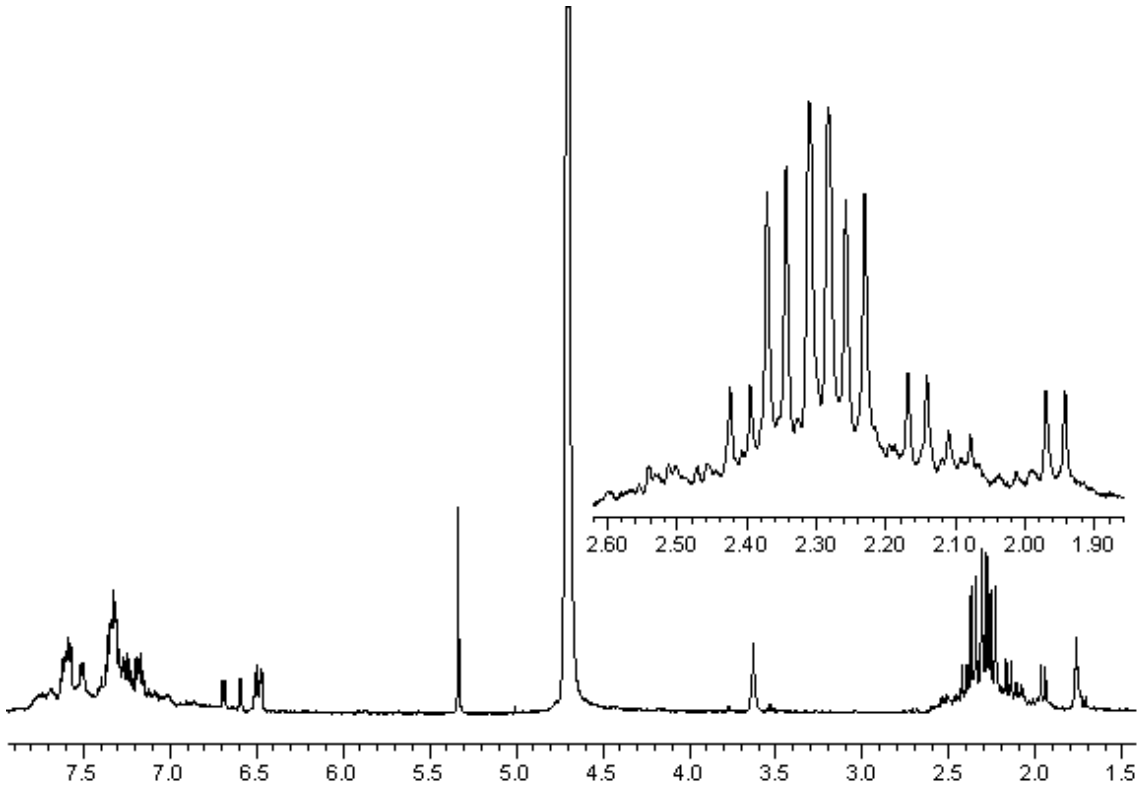


Figure 37. ^{1}H NMR spectrum of the product of the reaction between $TiCl_4(THF)_2$ and $IndPMe_2Ph$, D_2O, 500 MHz

Two equivalents of ylide **IIb** were used in reactions similar to those described above, in hopes of generating a bis-indenylide metallocene complex, which would be expected to exist as a mixture of diastereomers (Figure 38).

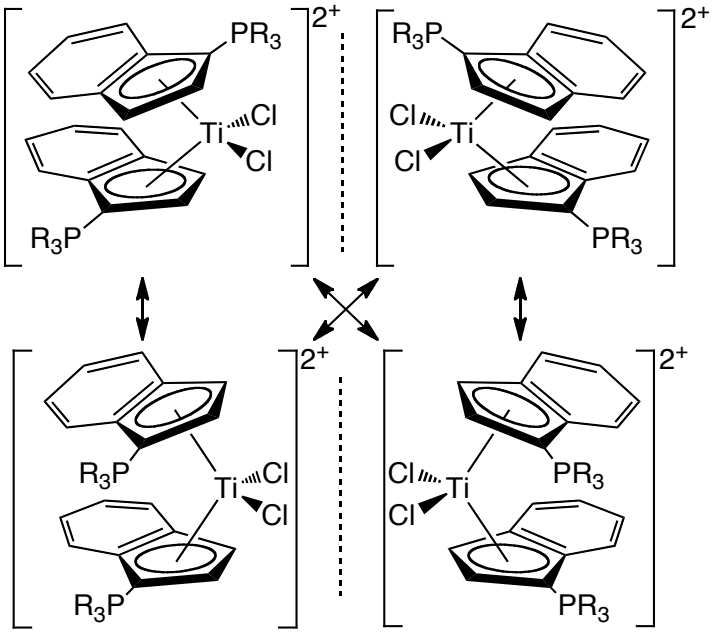


Figure 38. Bis-indenylide titanium complexes; dashed lines represent enantiomers while arrows represent diasteromers

Addition of the ylide to $TiCl_4(THF)_2$ in THF resulted in a brown precipitate which was analyzed by ^1H and ^{31}P NMR spectroscopy. Similar to the reactions involving one equivalent of ylide, the products from these reactions had poor solubility, which limited their characterization and the ability to purify them. There appeared to be two major species in the ^{31}P NMR (DMSO-d_6) (Figure 39), which would be expected for the mixture of diastereomers, although there also appeared to be several minor species present (> 5). Anion exchange was attempted by dissolving the compound in water and adding either potassium hexafluorophosphate or sodium tetraphenylborate in order to replace the small chloride anion with either hexafluorophosphate or tetraphenylborate. This would in theory make the compound more stable and therefore easier to purify; both

attempts resulted in a mixture of several phosphorus compounds (NMR), none of which appeared to be the major species.

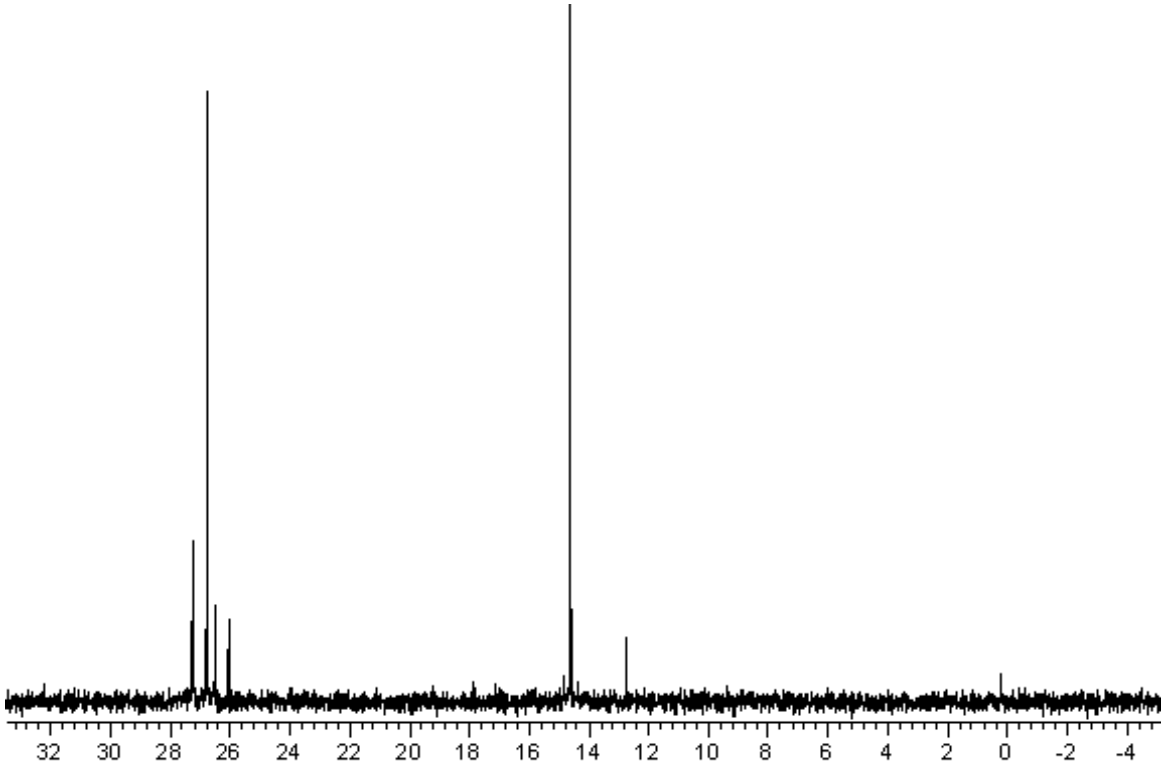


Figure 39. $^{31}P\{^{1}H\}$ NMR spectrum of reaction of $TiCl_4(THF)_2$ with two equivalents of $IndPMePh_2$, DMSO-d_6, 242.5 MHz

Recrystallization of the crude product by slow evaporation in acetone resulted in crystals which appear to be a salt of the ylide reacted with acetone (**III**), the structure of which can be seen below in Figure 40 and Figure 41. The product was characterized by ^{1}H and ^{31}P NMR, however, since this unusual product was not the desired complex and did not include any titanium, the formation of this product was not further considered. A table of selected bond

lengths and angles can be found below in Table 4; a full crystal structure report can be found in Appendix 1.

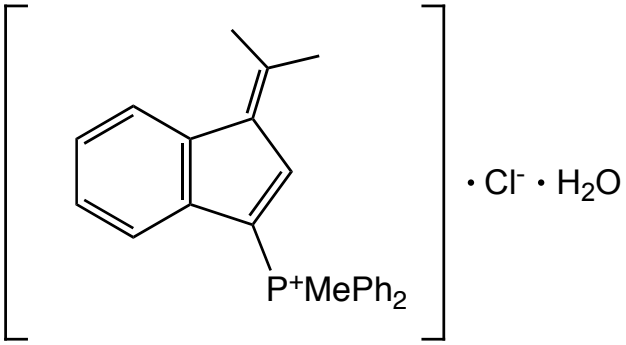


Figure 40. Molecular structure of III

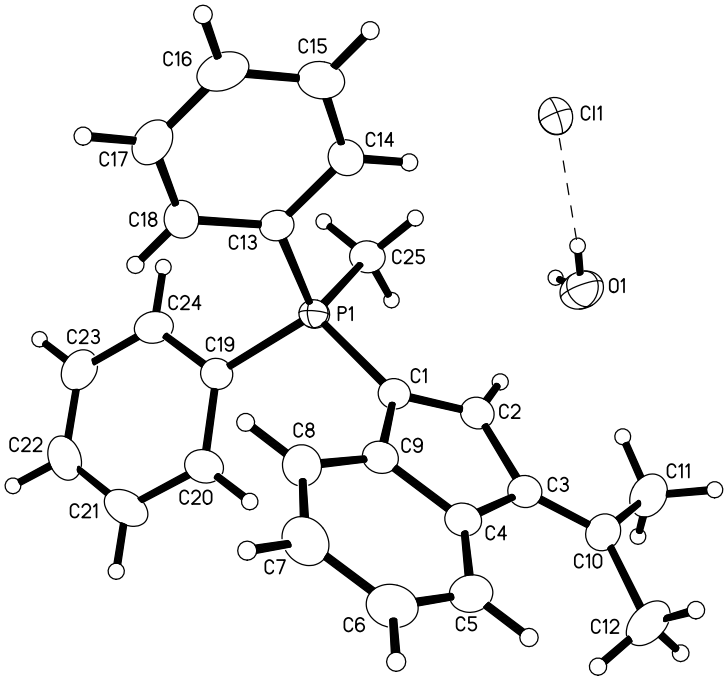


Figure 41. Crystal structure of III, what appears to be the ylide reacted with acetone

Table 4. Selected bond lengths and angles for III.

Bond	Length (Å)
P(1)-C(1)	1.7705(14)
P-Me	1.7845(15)
P-Ph	1.7999*
C(1)-C(9)	1.4736(19)
C(1)-C(2)	1.357(2)
C(2)-C(3)	1.4603(19)
C(4)-C(9)	1.416(2)
C(3)-C(4)	1.479(2)
C(4)-C(5)	1.393(2)
C(5)-C(6)	1.385(2)
C(6)-C(7)	1.388(2)
C(7)-C(8)	1.389(2)
C(8)-C(9)	1.388(2)
C(3)-C(10)	1.359(2)
C(10)-C(11)	1.491(2)
C(10)-C(12)	1.502(2)
Bond	**Angles (º)**
C(1)-P-Me	109.64(7)
C(1)-P-Ph	110.06*
Me-P-Ph	108.935*
Ph-P-Ph	109.16(7)
P-C(1)-C(9)	126.81(11)
C(1)-C(2)-C(3)	109.98(13)
C(2)-C(3)-C(4)	105.62(12)
C(3)-C(4)-C(9)	107.83(12)
C(4)-C(9)-C(1)	107.34(12)
C(9)-C(1)-C(2)	109.16(12)
C(3)-C(10)-C(11)	123.15(14)
C(3)-C(10)-C(12)	123.22(15)
C(11)-C(10)-C(12)	113.59(14)

* denotes an average value

Reactions were also attempted using direct addition of equal equivalents of the ylide to $TiCl_4$ in toluene. The reaction was refluxed with the hope this would drive the reaction to completion. Upon injection of the titanium tetrachloride, a red colour immediately formed, and after refluxing for two days a brown precipitate developed. The ^{31}P NMR spectrum of the precipitate showed more than ten

resonances; thus this reaction was abandoned. These results are similar to those that Brownie *et al.* observed when carrying out this reaction with methyldiphenylcyclopentadienylide in THF.[20]

3.2.2 Direct Addition of the Ylide to Trichloro(pentamethylcyclopentadienyl)titanium (IV)

Unsymmetrical group IV metallocene complexes bearing a C_5Me_5 ligand as well as a bulky indenyl-type ligand have been shown to be desirable for stereoselective polymerization.[65] Therefore, it seemed reasonable to attempt to synthesize one of these such complexes from Cp^*TiCl_3, using the indenylide ligand. In most literature procedures, the complexes formed bear an anionic indenyl ligand where alkyl lithium can be used to drive the reaction by deprotonating the ligand and extracting a chloride (Figure 42). The indenylide is an overall neutral ligand and thus it was anticipated that direct addition with harsh conditions (refluxing in chlorobenzene) may be a successful alternative in coordinating the ligand.

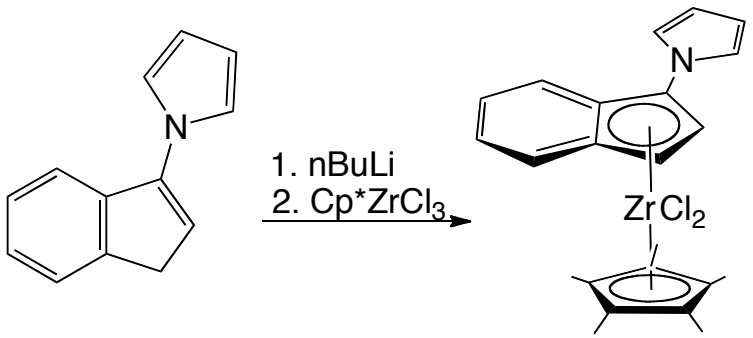


Figure 42. Lebedev *et al.* synthesized unsymmetrical group IV indenyl complexes which were demonstrated to be desirable stereoselective polymerization catalysts[65]

As the reaction proceeded using one equivalent of ylide **IIb**, a very dark solution resulted which when pumped to dryness gave a dark brown solid. The ^{31}P NMR spectrum showed two phosphorus environments and the ^{1}H NMR spectrum showed two methyl doublets and two Cp* resonances (Figure 43). While these results at first looked promising, the integrations of the Cp* peaks with respect to the methyl doublets do not match expected 5 : 1 ratios; attempts to purify and recrystallize resulted in titanium oxide products, presumably from trace amounts of water available in the solvents. The reaction was also repeated on an NMR scale in CD_2Cl_2, which showed that immediately upon collection four different phosphorus species form.

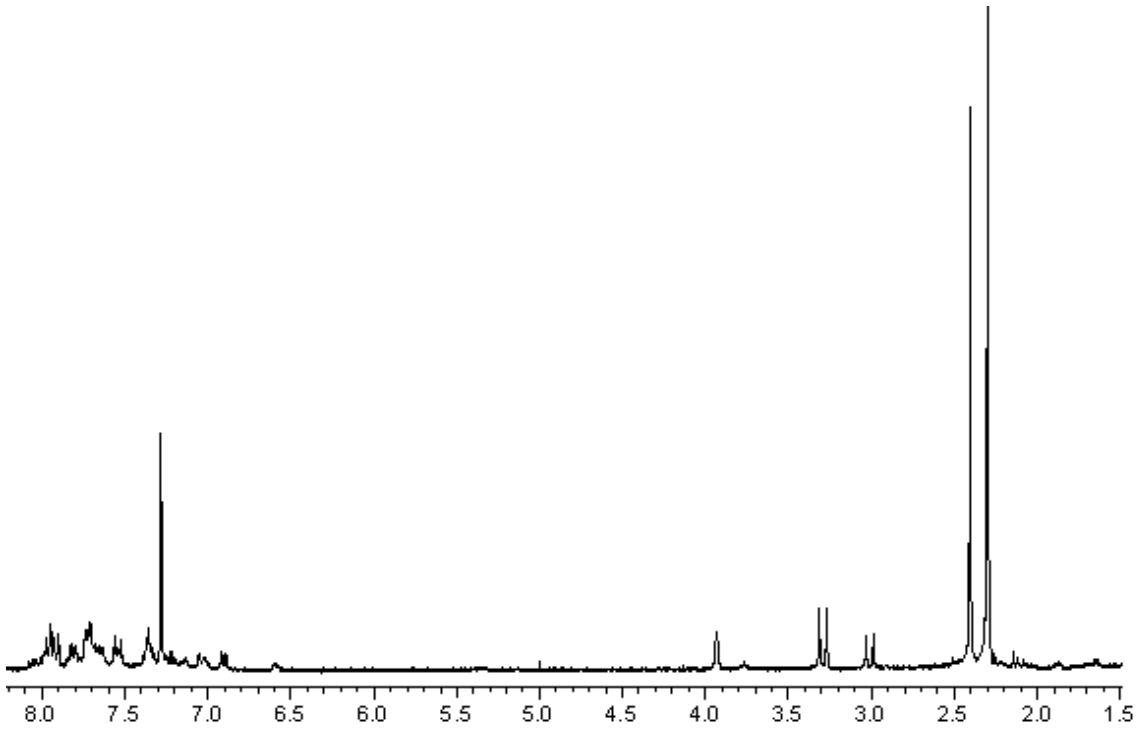


Figure 43. ^{1}H NMR of reaction with Cp^*TiCl_3 and $IndPMePh_2$, $CDCl_3$, 300 MHz

3.2.3 Coordination of Ylide using Ti(III) Followed by Oxidation

There are several reports in which bulky substituted cyclopentadienyl ligands are coordinated to titanium in the +3 oxidation state and then oxidized to Ti(IV) using various reagents. The most common way to oxidize the Ti(III) complexes is with the use of concentrated HCl;[66-70] this method however cannot be used when dealing with acid sensitive ligands. A few reports also exist in which the Ti(III) compounds are oxidized with one equivalent of CCl_4,[71,72] and this approach can easily be done while excluding air and water and thus it was attempted as in the reaction of Figure 44 below.

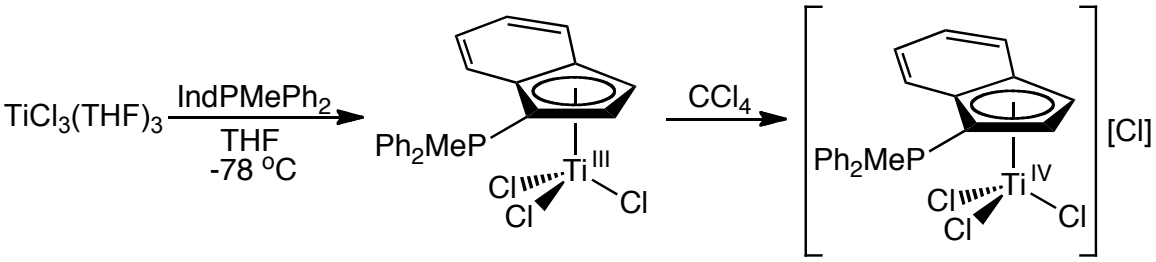


Figure 44. Coordination of indenylide to Ti(III) with subsequent oxidation to Ti(IV) using CCl_4

The addition of the ylide $IndPMePh_2$ to $TiCl_3(THF)_3$ was done dropwise at -78 °C in THF, the solution was allowed to warm to room temperature and a dark pink colour was observed which was presumed to be the Ti(III) ylide species. Since this compound would be paramagnetic it would not be amenable to NMR characterization. A ^1H NMR spectrum of this intermediate showed broad peaks and peaks outside the range of 0 to 12 ppm, indicating it was indeed paramagnetic. No attempt to isolate, purify or characterize the intermediate was made. The oxidizing agent, CCl_4, was then added at which point the colour of the

solution darkened to deep purple. The ^{1}H and ^{31}P NMR spectra showed several different products had formed, while the ^{1}H NMR showed evidence of coordinated THF, which is not expected in the desired complex due to the bulkiness of the ylide ligand. The NMR did confirm successful oxidation of Ti(III) to Ti(IV), since no indication of a paramagnetic species was found. Attempts to recrystallize the crude material resulted in decomposition of the product. Reactions were also carried out using two equivalents of $IndPMePh_2$, both at room temperature and reflux. Similar results were obtained.

3.2.4 Coordination of Ylide using Tetrakis(diethylamido)titanium(IV)

In a final attempt to coordinate the ylide to titanium, a different approach was used which involved using the phosphonium salt to coordinate to a titanium species, as opposed to direct addition of the ylide to a titanium source. This approach involved a titanium species with ligands that can act as a base, thereby deprotonating the phosphonium salt and coordinating the ylide Tetrakis(diethylamido)titanium (TDEAT) and related compounds (tetrakis(dimethylamido)titanium, tetrakis(diethylamidio)zirconium, etc.) have been shown to work in these types of reactions where coordination occurs and dialkylamine is the byproduct (Figure 45).[65] The anticipated reaction scheme for the coordination of the indenylide is shown below in Figure 46.

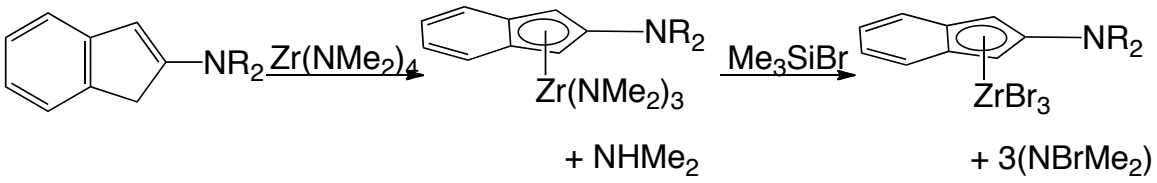


Figure 45. Coordination of an indenyl complex using tetrakis(dimethylamido)zirconium as a starting material

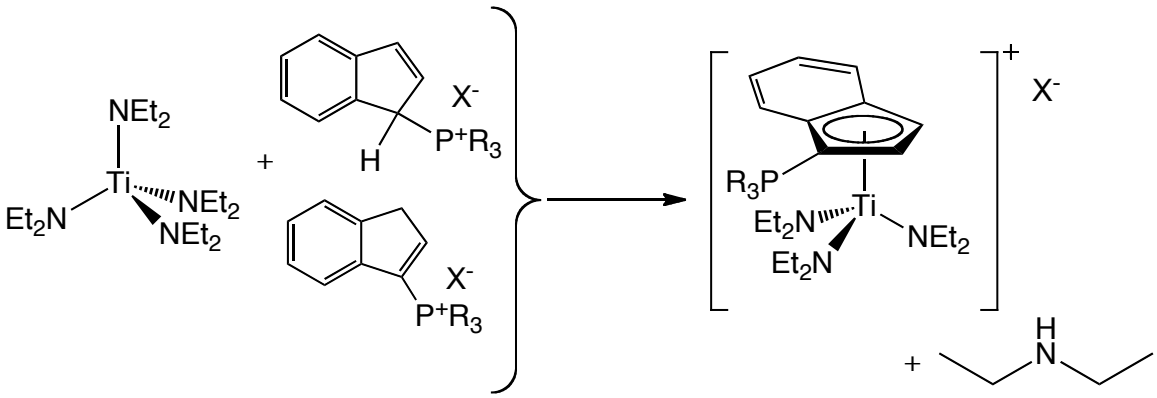


Figure 46. Attempted reaction of phosphonium salt isomers with TDEAT to generate an indenylide titanium complex

Initially this reaction was attempted by adding TDEAT dropwise to a suspension of dimethylphenylphosphonium bromide in toluene. As the reaction proceeded, a green precipitate formed from a dark brown solution. The precipitate was isolated, characterized by ^{1}H and ^{31}P NMR, and found to be the free ylide $IndPMePh_2$. The solution was pumped to dryness *in vacuo* to yield a brown oil which was also studied by ^{1}H NMR. The oil is presumed to be a product such as $TiBr(NEt_2)_3(NHEt_2)$ by analysis of the NMR spectrum, a small amount of dissolved ylide was also present (Figure 48). The ^{1}H NMR spectrum shows two ethyl environments are consistent with the three NEt_2 coordinated ligands, while two additional ethyl environments as well as a slightly broadened shift,

presumably the amine proton, are consistent with the $NHEt_2$ ligand. It is assumed that the diethylamine is indeed coordinated to titanium as opposed to existing as a free ligand, as its NMR peaks are shifted considerably downfield when compared to those of the free ligand.[73] Thus the reaction appears to have proceeded as in Figure 47.

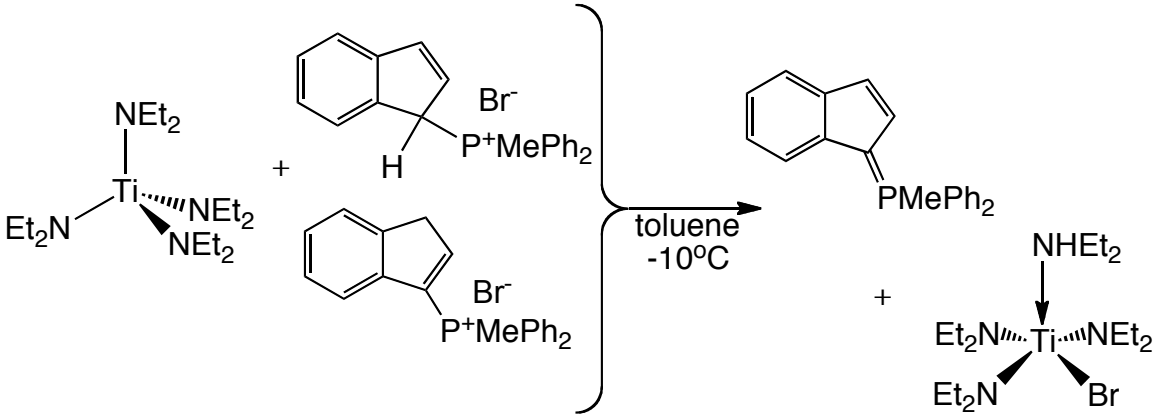


Figure 47. Result of reaction with TDEAT and phosphonium salt isomers

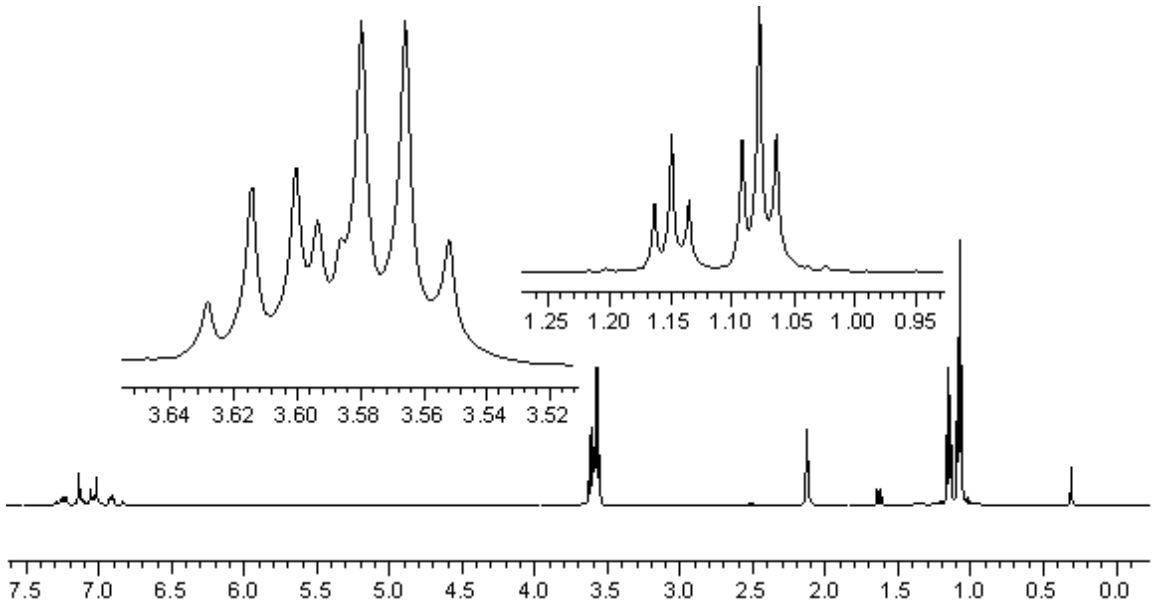


Figure 48. ^{1}H NMR spectrum of the reaction of TDEAT with phosphonium salt [IndPMePh$_2$]$^{+}$Br^{-}, toluene-d$_8$, 500 MHz

Since bromide did not act as a non-coordinating anion for the indenylide titanium complex, a bulkier, non-coordinating anion was then employed. The phosphonium salt, IndPMePh$_2^{+}$Br^{-} was dissolved in methylene chloride and potassium hexafluorophosphate was added. Potassium bromide precipitated and was separated; the filtrate was pumped to dryness *in vacuo* to result in IndPMePh$_2^{+}$PF$_6^{-}$. It was anticipated that this larger anion would be less likely to coordinate to the titanium centre as bromide appears to have in the previous reaction. Harsher reaction conditions were also used in this reaction by using chlorobenzene as a solvent and refluxing after addition of the TDEAT. The brown oily product was analyzed by ^{1}H and ^{31}P NMR. Once again, evidence of the free ylide, **IIb**, was apparent, but peaks consistent with free NHEt$_2$ were also present in a small amount, as well as peaks which have been assigned to a product

which appears to be $[Ti(NEt_2)_3(NHEt_2)]^+PF_6^-$ by integration (Figure 50). The anticipated reaction scheme can be seen below in Figure 49.

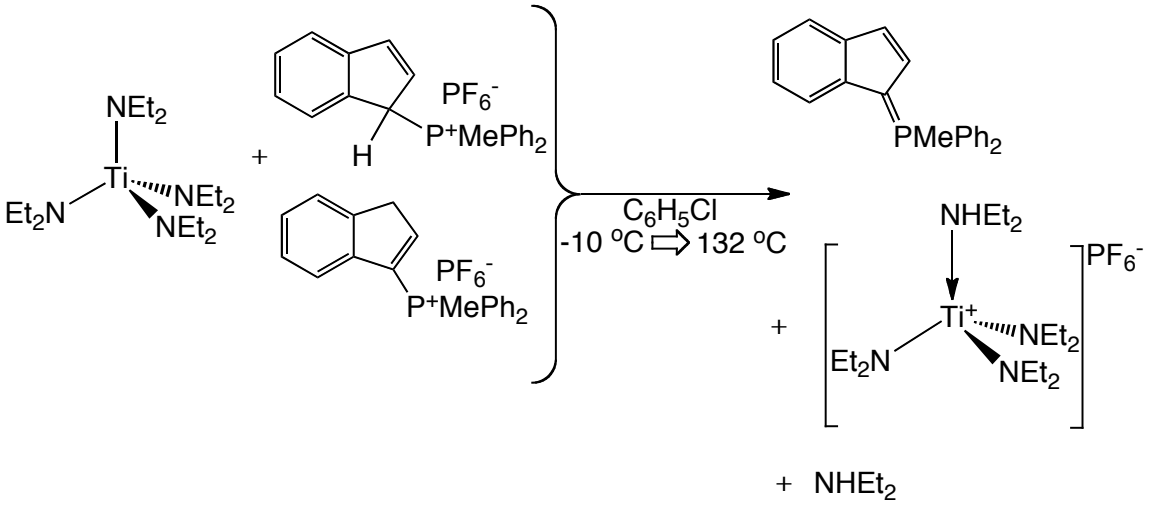


Figure 49. Result of reaction with TDEAT and phosphonium hexafluorophosphate salts

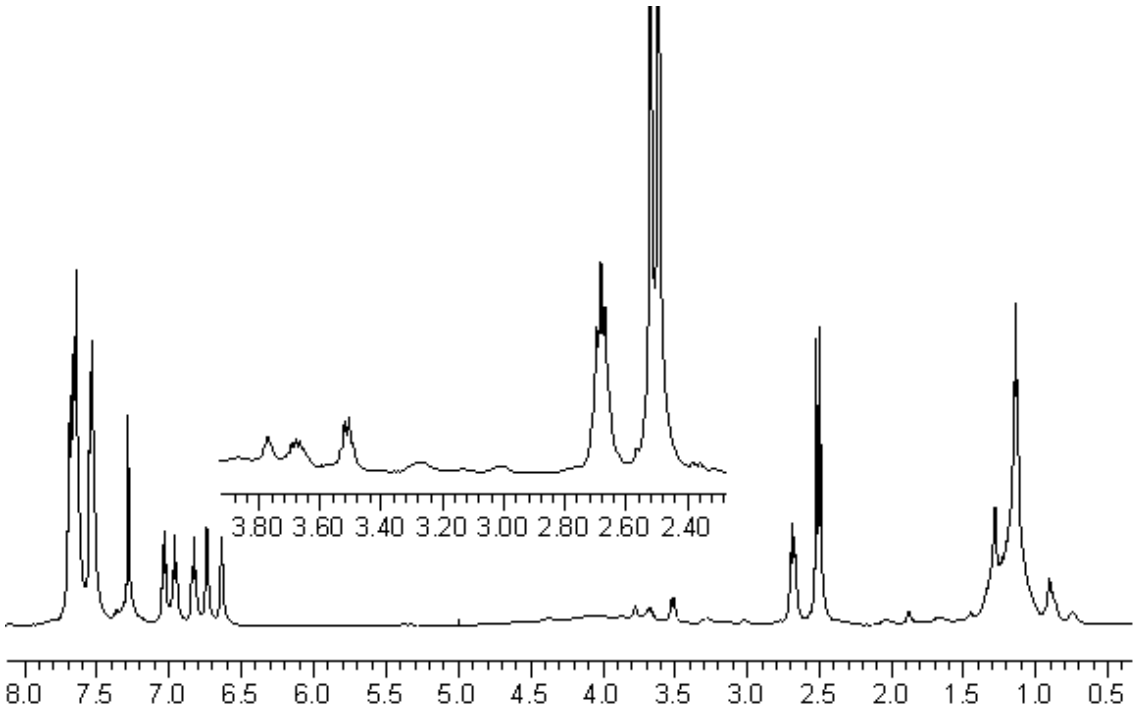


Figure 50. ^{1}H NMR of reaction of TDEAT and $[IndPMePh_2]^{+}PF_6^{-}$, $CDCl_3$, 500 MHz

Chapter 4. Conclusions

In this thesis, an effective route for the synthesis of phosphonium indenylide complexes was developed, specifically by synthesizing and characterizing three title ylides: triphenylphosphonium indenylide, methyldiphenylphosphonium indenylide, and dimethylphenylphosphonium indenylide. The ylides were all synthesized in high yields, and were fully characterized by ^{1}H, ^{31}P, ^{13}C NMR spectroscopy, IR spectroscopy, elemental analyses and X-ray crystallography. This synthetic route is in theory applicable to any commercially available phosphine, and one could use it to synthesize a number of phosphonium indenylides with varying electronic and steric properties. This would be ideal for the tuning of catalysts with phosphonium indenylide ligands.

While this study successfully developed this class of indenylide ligands, much work remains to be done on the investigation of its coordination to group IV metals. This studied focused on the coordination of the ligand particularly using titanium as the metal centre; zirconium and hafnium indenylide metallocene complexes would also be desirable for their potential as olefin polymerization catalysts.

Once a successful synthetic route is determined for attaching the indenylide ligands to group IV metals, much work on their capabilities as stereoselective polymerization catalysts remains to be accomplished. Complexes bearing two indenylide ligands are of particular interest, as they would exist as

two diastereomers, which could in theory be separated and tested individually as polymerization catalysts.

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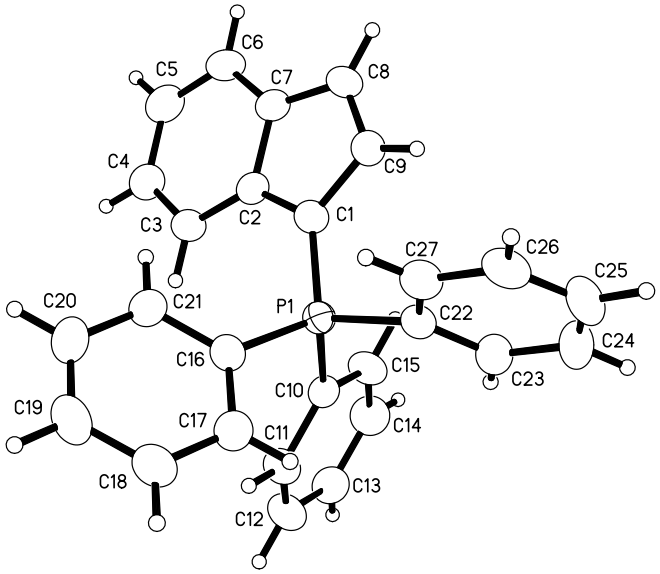
Appendix – Crystal Structure Data



Appendix Figure 1. Molecular structure of IIa

Table 1. Crystal data and structure refinement for IIa

Identification code	mb27	
Empirical formula	C27 H21 P	
Formula weight	376.41	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.7916(14) Å	a= 90°.
	b = 12.3946(16) Å	b= 90°.
	c = 14.957(2) Å	g = 90°.
Volume	2000.6(5) $Å^3$	
Z	4	
Density (calculated)	1.250 Mg/m^3	
Absorption coefficient	0.147 mm^{-1}	
F(000)	792	
Crystal size	0.30 x 0.10 x 0.08 mm^3	
Theta range for data collection	2.50 to 25.99°.	
Index ranges	-13<=h<=13, -15<=k<=15, -18<=l<=18	
Reflections collected	19833	
Independent reflections	3933 [R(int) = 0.0475]	
Completeness to theta = 25.99°	99.9 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9884 and 0.9573	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3933 / 0 / 253	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0348, wR2 = 0.0755	
R indices (all data)	R1 = 0.0420, wR2 = 0.0799	
Absolute structure parameter	0.03(9)	
Largest diff. peak and hole	0.277 and -0.194 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for IIa. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	2635(1)	9629(1)	1571(1)	29(1)
C(1)	3979(2)	9734(2)	949(1)	31(1)
C(2)	4274(2)	10521(2)	278(1)	30(1)
C(3)	3627(2)	11405(2)	-80(1)	34(1)
C(4)	4181(2)	12025(2)	-727(1)	39(1)
C(5)	5371(2)	11795(2)	-1044(2)	43(1)
C(6)	6022(2)	10927(2)	-717(1)	38(1)
C(7)	5485(2)	10262(2)	-60(1)	32(1)
C(8)	5896(2)	9310(2)	390(1)	35(1)
C(9)	5004(2)	9007(2)	990(1)	33(1)
C(10)	1298(2)	9580(2)	837(1)	30(1)
C(11)	198(2)	10128(2)	1003(1)	37(1)
C(12)	-762(2)	10086(2)	394(2)	45(1)
C(13)	-637(2)	9505(2)	-387(2)	42(1)
C(14)	446(2)	8958(2)	-558(2)	44(1)
C(15)	1410(2)	8998(2)	46(1)	40(1)
C(16)	2346(2)	10733(2)	2336(1)	30(1)
C(17)	1462(2)	10627(2)	3013(1)	36(1)
C(18)	1166(2)	11515(2)	3538(2)	40(1)
C(19)	1746(2)	12493(2)	3396(2)	43(1)
C(20)	2647(2)	12591(2)	2740(1)	41(1)
C(21)	2952(2)	11712(2)	2206(1)	34(1)
C(22)	2757(2)	8404(2)	2219(1)	32(1)
C(23)	2201(2)	7448(2)	1936(1)	39(1)
C(24)	2474(2)	6490(2)	2383(2)	47(1)
C(25)	3291(2)	6487(2)	3093(2)	50(1)
C(26)	3808(2)	7442(2)	3397(2)	45(1)
C(27)	3543(2)	8401(2)	2958(1)	40(1)

Table 3. Bond lengths [Å] and angles [°] for IIa.

P(1)-C(1)	1.7284(19)	C(17)-H(17A)	0.9500
P(1)-C(22)	1.8063(19)	C(18)-C(19)	1.380(3)
P(1)-C(16)	1.8103(19)	C(18)-H(18A)	0.9500
P(1)-C(10)	1.8134(19)	C(19)-C(20)	1.387(3)
C(1)-C(9)	1.427(3)	C(19)-H(19A)	0.9500
C(1)-C(2)	1.435(3)	C(20)-C(21)	1.390(3)
C(2)-C(3)	1.406(3)	C(20)-H(20A)	0.9500
C(2)-C(7)	1.438(3)	C(21)-H(21A)	0.9500
C(3)-C(4)	1.372(3)	C(22)-C(23)	1.393(3)
C(3)-H(3A)	0.9500	C(22)-C(27)	1.394(3)
C(4)-C(5)	1.399(3)	C(23)-C(24)	1.394(3)
C(4)-H(4A)	0.9500	C(23)-H(23A)	0.9500
C(5)-C(6)	1.374(3)	C(24)-C(25)	1.381(3)
C(5)-H(5A)	0.9500	C(24)-H(24A)	0.9500
C(6)-C(7)	1.406(3)	C(25)-C(26)	1.386(3)
C(6)-H(6A)	0.9500	C(25)-H(25A)	0.9500
C(7)-C(8)	1.429(3)	C(26)-C(27)	1.387(3)
C(8)-C(9)	1.368(3)	C(26)-H(26A)	0.9500
C(8)-H(8A)	0.9500	C(27)-H(27A)	0.9500
C(9)-H(9A)	0.9500	C(1)-P(1)-C(22)	106.91(9)
C(10)-C(11)	1.391(3)	C(1)-P(1)-C(16)	115.31(10)
C(10)-C(15)	1.392(3)	C(22)-P(1)-C(16)	107.98(9)
C(11)-C(12)	1.381(3)	C(1)-P(1)-C(10)	110.17(9)
C(11)-H(11A)	0.9500	C(22)-P(1)-C(10)	110.77(9)
C(12)-C(13)	1.378(3)	C(16)-P(1)-C(10)	105.71(9)
C(12)-H(12A)	0.9500	C(9)-C(1)-C(2)	106.67(16)
C(13)-C(14)	1.376(3)	C(9)-C(1)-P(1)	125.44(15)
C(13)-H(13A)	0.9500	C(2)-C(1)-P(1)	127.86(15)
C(14)-C(15)	1.378(3)	C(3)-C(2)-C(1)	133.32(18)
C(14)-H(14A)	0.9500	C(3)-C(2)-C(7)	119.45(18)
C(15)-H(15A)	0.9500	C(1)-C(2)-C(7)	107.22(16)
C(16)-C(21)	1.393(3)	C(4)-C(3)-C(2)	119.23(19)
C(16)-C(17)	1.398(3)	C(4)-C(3)-H(3A)	120.4
C(17)-C(18)	1.390(3)	C(2)-C(3)-H(3A)	120.4

C(3)-C(4)-C(5)	121.7(2)	C(21)-C(16)-C(17)	120.18(18)
C(3)-C(4)-H(4A)	119.2	C(21)-C(16)-P(1)	119.36(15)
C(5)-C(4)-H(4A)	119.2	C(17)-C(16)-P(1)	120.32(15)
C(6)-C(5)-C(4)	120.5(2)	C(18)-C(17)-C(16)	119.51(19)
C(6)-C(5)-H(5A)	119.8	C(18)-C(17)-H(17A)	120.2
C(4)-C(5)-H(5A)	119.8	C(16)-C(17)-H(17A)	120.2
C(5)-C(6)-C(7)	119.80(19)	C(19)-C(18)-C(17)	120.3(2)
C(5)-C(6)-H(6A)	120.1	C(19)-C(18)-H(18A)	119.9
C(7)-C(6)-H(6A)	120.1	C(17)-C(18)-H(18A)	119.9
C(6)-C(7)-C(8)	133.23(19)	C(18)-C(19)-C(20)	120.3(2)
C(6)-C(7)-C(2)	119.30(18)	C(18)-C(19)-H(19A)	119.9
C(8)-C(7)-C(2)	107.47(17)	C(20)-C(19)-H(19A)	119.9
C(9)-C(8)-C(7)	108.50(17)	C(19)-C(20)-C(21)	120.25(19)
C(9)-C(8)-H(8A)	125.8	C(19)-C(20)-H(20A)	119.9
C(7)-C(8)-H(8A)	125.8	C(21)-C(20)-H(20A)	119.9
C(8)-C(9)-C(1)	110.12(17)	C(20)-C(21)-C(16)	119.47(19)
C(8)-C(9)-H(9A)	124.9	C(20)-C(21)-H(21A)	120.3
C(1)-C(9)-H(9A)	124.9	C(16)-C(21)-H(21A)	120.3
C(11)-C(10)-C(15)	118.65(19)	C(23)-C(22)-C(27)	120.06(18)
C(11)-C(10)-P(1)	123.71(15)	C(23)-C(22)-P(1)	121.37(15)
C(15)-C(10)-P(1)	117.57(15)	C(27)-C(22)-P(1)	118.15(15)
C(12)-C(11)-C(10)	120.26(19)	C(22)-C(23)-C(24)	119.2(2)
C(12)-C(11)-H(11A)	119.9	C(22)-C(23)-H(23A)	120.4
C(10)-C(11)-H(11A)	119.9	C(24)-C(23)-H(23A)	120.4
C(13)-C(12)-C(11)	120.4(2)	C(25)-C(24)-C(23)	120.4(2)
C(13)-C(12)-H(12A)	119.8	C(25)-C(24)-H(24A)	119.8
C(11)-C(12)-H(12A)	119.8	C(23)-C(24)-H(24A)	119.8
C(14)-C(13)-C(12)	119.9(2)	C(24)-C(25)-C(26)	120.4(2)
C(14)-C(13)-H(13A)	120.1	C(24)-C(25)-H(25A)	119.8
C(12)-C(13)-H(13A)	120.1	C(26)-C(25)-H(25A)	119.8
C(13)-C(14)-C(15)	120.1(2)	C(25)-C(26)-C(27)	119.6(2)
C(13)-C(14)-H(14A)	120.0	C(25)-C(26)-H(26A)	120.2
C(15)-C(14)-H(14A)	120.0	C(27)-C(26)-H(26A)	120.2
C(14)-C(15)-C(10)	120.7(2)	C(26)-C(27)-C(22)	120.2(2)
C(14)-C(15)-H(15A)	119.7	C(26)-C(27)-H(27A)	119.9
C(10)-C(15)-H(15A)	119.7	C(22)-C(27)-H(27A)	119.9

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for IIa. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	28(1)	28(1)	31(1)	2(1)	0(1)	1(1)
C(1)	29(1)	32(1)	31(1)	3(1)	-2(1)	2(1)
C(2)	29(1)	30(1)	30(1)	-1(1)	-2(1)	-3(1)
C(3)	29(1)	36(1)	38(1)	2(1)	-1(1)	1(1)
C(4)	38(1)	37(1)	42(1)	9(1)	-5(1)	-1(1)
C(5)	45(1)	46(1)	39(1)	8(1)	5(1)	-8(1)
C(6)	30(1)	47(1)	39(1)	-1(1)	5(1)	-2(1)
C(7)	28(1)	35(1)	32(1)	-3(1)	-2(1)	-3(1)
C(8)	27(1)	37(1)	41(1)	-2(1)	-2(1)	4(1)
C(9)	32(1)	31(1)	36(1)	2(1)	-6(1)	1(1)
C(10)	29(1)	27(1)	32(1)	3(1)	1(1)	-2(1)
C(11)	35(1)	39(1)	38(1)	-10(1)	-2(1)	3(1)
C(12)	35(1)	45(1)	54(1)	-12(1)	-6(1)	7(1)
C(13)	37(1)	43(1)	45(1)	-2(1)	-10(1)	-4(1)
C(14)	50(1)	49(1)	34(1)	-8(1)	1(1)	-2(1)
C(15)	34(1)	45(1)	40(1)	-6(1)	4(1)	6(1)
C(16)	30(1)	30(1)	31(1)	1(1)	-6(1)	3(1)
C(17)	36(1)	35(1)	36(1)	3(1)	-2(1)	0(1)
C(18)	40(1)	45(1)	35(1)	-2(1)	-2(1)	7(1)
C(19)	50(1)	39(1)	39(1)	-10(1)	-14(1)	11(1)
C(20)	45(1)	33(1)	45(1)	0(1)	-14(1)	-3(1)
C(21)	32(1)	35(1)	36(1)	1(1)	-6(1)	-2(1)
C(22)	30(1)	31(1)	34(1)	3(1)	6(1)	4(1)
C(23)	45(1)	35(1)	38(1)	2(1)	8(1)	1(1)
C(24)	65(2)	29(1)	46(1)	0(1)	19(1)	2(1)
C(25)	62(2)	38(1)	49(1)	16(1)	19(1)	19(1)
C(26)	38(1)	55(1)	44(1)	13(1)	7(1)	13(1)
C(27)	35(1)	42(1)	42(1)	6(1)	0(1)	4(1)

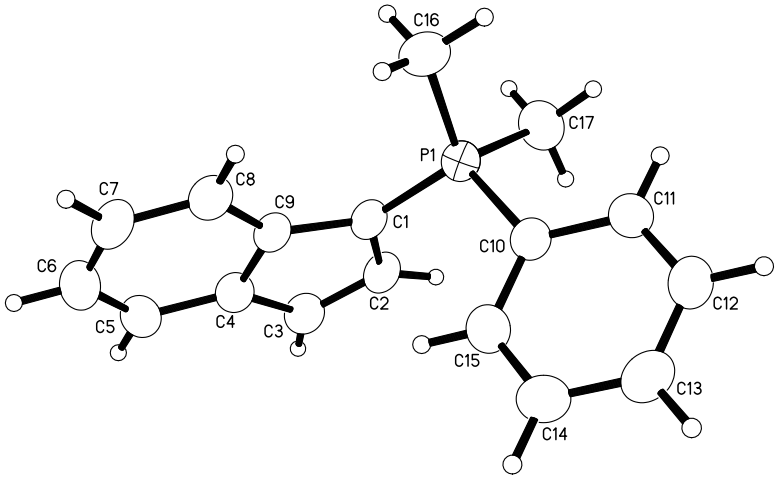
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for IIa.

	x	y	z	U(eq)
H(3A)	2815	11572	123	41
H(4A)	3746	12626	-964	47
H(5A)	5733	12241	-1490	52
H(6A)	6831	10776	-934	46
H(8A)	6659	8948	290	42
H(9A)	5059	8402	1377	40
H(11A)	106	10534	1538	45
H(12A)	-1512	10460	513	54
H(13A)	-1298	9483	-806	50
H(14A)	530	8552	-1093	53
H(15A)	2159	8625	-80	47
H(17A)	1066	9953	3114	43
H(18A)	562	11450	3997	48
H(19A)	1526	13101	3749	51
H(20A)	3057	13261	2655	49
H(21A)	3569	11780	1757	41
H(23A)	1643	7449	1445	47
H(24A)	2095	5835	2198	56
H(25A)	3501	5825	3376	59
H(26A)	4341	7441	3902	55
H(27A)	3899	9058	3162	48

Table 6. Torsion angles [°] for IIa.

C(22)-P(1)-C(1)-C(9)	-3.0(2)
C(16)-P(1)-C(1)-C(9)	117.04(18)
C(10)-P(1)-C(1)-C(9)	-123.43(18)
C(22)-P(1)-C(1)-C(2)	174.41(17)
C(16)-P(1)-C(1)-C(2)	-65.5(2)
C(10)-P(1)-C(1)-C(2)	54.0(2)
C(9)-C(1)-C(2)-C(3)	177.7(2)
P(1)-C(1)-C(2)-C(3)	-0.1(3)
C(9)-C(1)-C(2)-C(7)	-1.1(2)
P(1)-C(1)-C(2)-C(7)	-178.91(15)
C(1)-C(2)-C(3)-C(4)	179.3(2)
C(7)-C(2)-C(3)-C(4)	-2.0(3)
C(2)-C(3)-C(4)-C(5)	0.5(3)
C(3)-C(4)-C(5)-C(6)	0.4(3)
C(4)-C(5)-C(6)-C(7)	0.3(3)
C(5)-C(6)-C(7)-C(8)	178.4(2)
C(5)-C(6)-C(7)-C(2)	-1.7(3)
C(3)-C(2)-C(7)-C(6)	2.6(3)
C(1)-C(2)-C(7)-C(6)	-178.38(18)
C(3)-C(2)-C(7)-C(8)	-177.48(18)
C(1)-C(2)-C(7)-C(8)	1.5(2)
C(6)-C(7)-C(8)-C(9)	178.5(2)
C(2)-C(7)-C(8)-C(9)	-1.4(2)
C(7)-C(8)-C(9)-C(1)	0.7(2)
C(2)-C(1)-C(9)-C(8)	0.3(2)
P(1)-C(1)-C(9)-C(8)	178.15(15)
C(1)-P(1)-C(10)-C(11)	-138.49(18)
C(22)-P(1)-C(10)-C(11)	103.43(18)
C(16)-P(1)-C(10)-C(11)	-13.3(2)
C(1)-P(1)-C(10)-C(15)	38.48(18)
C(22)-P(1)-C(10)-C(15)	-79.59(17)
C(16)-P(1)-C(10)-C(15)	163.68(16)
C(15)-C(10)-C(11)-C(12)	0.4(3)
P(1)-C(10)-C(11)-C(12)	177.32(16)

C(10)-C(11)-C(12)-C(13)	-0.3(3)
C(11)-C(12)-C(13)-C(14)	0.4(3)
C(12)-C(13)-C(14)-C(15)	-0.6(3)
C(13)-C(14)-C(15)-C(10)	0.7(3)
C(11)-C(10)-C(15)-C(14)	-0.6(3)
P(1)-C(10)-C(15)-C(14)	-177.71(17)
C(1)-P(1)-C(16)-C(21)	19.17(19)
C(22)-P(1)-C(16)-C(21)	138.63(15)
C(10)-P(1)-C(16)-C(21)	-102.78(16)
C(1)-P(1)-C(16)-C(17)	-165.15(15)
C(22)-P(1)-C(16)-C(17)	-45.70(18)
C(10)-P(1)-C(16)-C(17)	72.90(17)
C(21)-C(16)-C(17)-C(18)	1.9(3)
P(1)-C(16)-C(17)-C(18)	-173.74(15)
C(16)-C(17)-C(18)-C(19)	-0.4(3)
C(17)-C(18)-C(19)-C(20)	-1.3(3)
C(18)-C(19)-C(20)-C(21)	1.6(3)
C(19)-C(20)-C(21)-C(16)	0.0(3)
C(17)-C(16)-C(21)-C(20)	-1.7(3)
P(1)-C(16)-C(21)-C(20)	174.00(15)
C(1)-P(1)-C(22)-C(23)	-97.78(18)
C(16)-P(1)-C(22)-C(23)	137.58(17)
C(10)-P(1)-C(22)-C(23)	22.3(2)
C(1)-P(1)-C(22)-C(27)	74.78(18)
C(16)-P(1)-C(22)-C(27)	-49.86(18)
C(10)-P(1)-C(22)-C(27)	-165.17(15)
C(27)-C(22)-C(23)-C(24)	-2.0(3)
P(1)-C(22)-C(23)-C(24)	170.37(16)
C(22)-C(23)-C(24)-C(25)	-0.5(3)
C(23)-C(24)-C(25)-C(26)	2.9(3)
C(24)-C(25)-C(26)-C(27)	-2.8(3)
C(25)-C(26)-C(27)-C(22)	0.3(3)
C(23)-C(22)-C(27)-C(26)	2.1(3)
P(1)-C(22)-C(27)-C(26)	-170.53(16)



Appendix Figure 2. Molecular structure of IIc

Table 7. Crystal data and structure refinement for IIb

Identification code	mb25	
Empirical formula	C17 H17 P	
Formula weight	252.28	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R-3	
Unit cell dimensions	a = 30.207(10) Å	a= 90°.
	b = 30.207(10) Å	b= 90°.
	c = 7.786(5) Å	g = 120°.
Volume	6153(5) $Å^3$	
Z	18	
Density (calculated)	1.226 Mg/m^3	
Absorption coefficient	0.180 mm^{-1}	
F(000)	2412	
Crystal size	0.12 x 0.10 x 0.08 mm^3	
Theta range for data collection	2.34 to 25.99°.	
Index ranges	-37<=h<=37, -37<=k<=37, -9<=l<=9	
Reflections collected	19404	
Independent reflections	2680 [R(int) = 0.1776]	
Completeness to theta = 25.99°	99.4 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9857 and 0.9787	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2680 / 0 / 165	
Goodness-of-fit on F^2	0.986	
Final R indices [I>2sigma(I)]	R1 = 0.0675, wR2 = 0.1541	
R indices (all data)	R1 = 0.1123, wR2 = 0.1812	
Largest diff. peak and hole	0.569 and -0.276 $e.Å^{-3}$	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for IIb. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	2490(1)	1069(1)	-301(1)	35(1)
C(1)	2691(1)	1670(1)	534(4)	34(1)
C(2)	2934(1)	2126(1)	-466(4)	38(1)
C(3)	3001(1)	2536(1)	499(4)	37(1)
C(4)	2797(1)	2356(1)	2157(4)	35(1)
C(5)	2765(1)	2606(1)	3643(5)	39(1)
C(6)	2538(1)	2331(2)	5096(5)	48(1)
C(7)	2339(1)	1799(2)	5137(4)	45(1)
C(8)	2364(1)	1542(1)	3722(4)	40(1)
C(9)	2598(1)	1813(1)	2195(4)	32(1)
C(10)	1864(1)	795(1)	-1301(4)	32(1)
C(11)	1697(1)	394(1)	-2477(4)	40(1)
C(12)	1223(1)	201(1)	-3232(5)	47(1)
C(13)	914(1)	403(1)	-2844(5)	49(1)
C(14)	1078(1)	801(1)	-1689(5)	47(1)
C(15)	1549(1)	995(1)	-929(4)	40(1)
C(16)	2450(2)	616(1)	1250(5)	49(1)
C(17)	2916(1)	1103(1)	-1950(5)	48(1)

Table 9. Bond lengths [Å] and angles [°] for IIb.

P(1)-C(1)	1.727(3)	C(17)-H(17A)	0.9800
P(1)-C(16)	1.785(4)	C(17)-H(17B)	0.9800
P(1)-C(17)	1.785(4)	C(17)-H(17C)	0.9800
P(1)-C(10)	1.817(3)		
C(1)-C(2)	1.424(4)	C(1)-P(1)-C(16)	113.92(17)
C(1)-C(9)	1.435(4)	C(1)-P(1)-C(17)	110.32(17)
C(2)-C(3)	1.374(5)	C(16)-P(1)-C(17)	107.45(19)
C(2)-H(2A)	0.9500	C(1)-P(1)-C(10)	112.31(15)
C(3)-C(4)	1.417(5)	C(16)-P(1)-C(10)	106.49(16)
C(3)-H(3A)	0.9500	C(17)-P(1)-C(10)	105.90(16)
C(4)-C(5)	1.411(5)	C(2)-C(1)-C(9)	106.6(3)
C(4)-C(9)	1.437(4)	C(2)-C(1)-P(1)	123.3(3)
C(5)-C(6)	1.368(5)	C(9)-C(1)-P(1)	129.6(3)
C(5)-H(5A)	0.9500	C(3)-C(2)-C(1)	110.1(3)
C(6)-C(7)	1.407(5)	C(3)-C(2)-H(2A)	124.9
C(6)-H(6A)	0.9500	C(1)-C(2)-H(2A)	124.9
C(7)-C(8)	1.372(5)	C(2)-C(3)-C(4)	108.2(3)
C(7)-H(7A)	0.9500	C(2)-C(3)-H(3A)	125.9
C(8)-C(9)	1.416(5)	C(4)-C(3)-H(3A)	125.9
C(8)-H(8A)	0.9500	C(5)-C(4)-C(3)	132.4(3)
C(10)-C(15)	1.391(4)	C(5)-C(4)-C(9)	119.5(3)
C(10)-C(11)	1.395(4)	C(3)-C(4)-C(9)	108.1(3)
C(11)-C(12)	1.379(5)	C(6)-C(5)-C(4)	120.1(3)
C(11)-H(11A)	0.9500	C(6)-C(5)-H(5A)	120.0
C(12)-C(13)	1.379(5)	C(4)-C(5)-H(5A)	120.0
C(12)-H(12A)	0.9500	C(5)-C(6)-C(7)	120.7(3)
C(13)-C(14)	1.380(5)	C(5)-C(6)-H(6A)	119.7
C(13)-H(13A)	0.9500	C(7)-C(6)-H(6A)	119.7
C(14)-C(15)	1.374(5)	C(8)-C(7)-C(6)	121.0(3)
C(14)-H(14A)	0.9500	C(8)-C(7)-H(7A)	119.5
C(15)-H(15A)	0.9500	C(6)-C(7)-H(7A)	119.5
C(16)-H(16A)	0.9800	C(7)-C(8)-C(9)	120.0(3)
C(16)-H(16B)	0.9800	C(7)-C(8)-H(8A)	120.0
C(16)-H(16C)	0.9800	C(9)-C(8)-H(8A)	120.0

C(8)-C(9)-C(1)	134.3(3)	C(13)-C(14)-H(14A)	120.2
C(8)-C(9)-C(4)	118.7(3)	C(14)-C(15)-C(10)	120.9(3)
C(1)-C(9)-C(4)	107.0(3)	C(14)-C(15)-H(15A)	119.5
C(15)-C(10)-C(11)	119.0(3)	C(10)-C(15)-H(15A)	119.5
C(15)-C(10)-P(1)	119.7(2)	P(1)-C(16)-H(16A)	109.5
C(11)-C(10)-P(1)	121.3(2)	P(1)-C(16)-H(16B)	109.5
C(12)-C(11)-C(10)	119.7(3)	H(16A)-C(16)-H(16B)	109.5
C(12)-C(11)-H(11A)	120.1	P(1)-C(16)-H(16C)	109.5
C(10)-C(11)-H(11A)	120.1	H(16A)-C(16)-H(16C)	109.5
C(13)-C(12)-C(11)	120.6(3)	H(16B)-C(16)-H(16C)	109.5
C(13)-C(12)-H(12A)	119.7	P(1)-C(17)-H(17A)	109.5
C(11)-C(12)-H(12A)	119.7	P(1)-C(17)-H(17B)	109.5
C(12)-C(13)-C(14)	120.1(3)	H(17A)-C(17)-H(17B)	109.5
C(12)-C(13)-H(13A)	119.9	P(1)-C(17)-H(17C)	109.5
C(14)-C(13)-H(13A)	119.9	H(17A)-C(17)-H(17C)	109.5
C(15)-C(14)-C(13)	119.7(3)	H(17B)-C(17)-H(17C)	109.5
C(15)-C(14)-H(14A)	120.2		

Table 10. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for IIb. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	37(1)	36(1)	32(1)	-2(1)	-3(1)	19(1)
C(1)	39(2)	37(2)	27(2)	-1(1)	-4(1)	19(2)
C(2)	44(2)	41(2)	27(2)	2(2)	-2(2)	21(2)
C(3)	37(2)	35(2)	36(2)	4(2)	1(2)	14(2)
C(4)	31(2)	38(2)	35(2)	-3(2)	-3(1)	16(2)
C(5)	34(2)	39(2)	43(2)	-8(2)	-4(2)	18(2)
C(6)	46(2)	61(3)	40(2)	-9(2)	-1(2)	29(2)
C(7)	44(2)	61(2)	29(2)	5(2)	3(2)	27(2)
C(8)	38(2)	46(2)	35(2)	2(2)	-1(2)	21(2)
C(9)	29(2)	39(2)	28(2)	-1(1)	-3(1)	17(2)
C(10)	35(2)	32(2)	27(2)	4(1)	3(1)	16(2)
C(11)	46(2)	41(2)	37(2)	-1(2)	-1(2)	26(2)
C(12)	53(2)	44(2)	44(2)	-10(2)	-11(2)	24(2)
C(13)	42(2)	55(2)	49(2)	-3(2)	-10(2)	23(2)
C(14)	41(2)	60(2)	48(2)	1(2)	2(2)	31(2)
C(15)	41(2)	46(2)	33(2)	1(2)	6(2)	23(2)
C(16)	56(2)	45(2)	49(2)	2(2)	-9(2)	28(2)
C(17)	37(2)	51(2)	53(3)	-6(2)	3(2)	21(2)

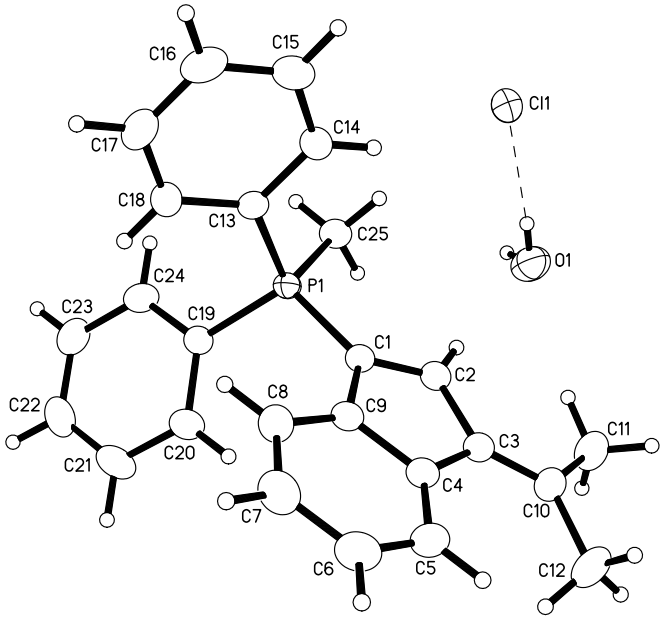
Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for IIb.

	x	y	z	U(eq)
H(2A)	3035	2143	-1631	45
H(3A)	3158	2880	120	45
H(5A)	2902	2966	3634	47
H(6A)	2514	2501	6088	57
H(7A)	2185	1615	6161	53
H(8A)	2224	1182	3766	48
H(11A)	1909	255	-2757	47
H(12A)	1108	-73	-4027	57
H(13A)	588	268	-3372	59
H(14A)	865	940	-1421	56
H(15A)	1661	1270	-137	48
H(16A)	2779	751	1843	74
H(16B)	2367	295	671	74
H(16C)	2182	552	2087	74
H(17A)	3263	1254	-1484	72
H(17B)	2913	1315	-2896	72
H(17C)	2807	758	-2376	72

Table 12. Torsion angles [°] for IIb.

C(16)-P(1)-C(1)-C(2)	155.2(3)
C(17)-P(1)-C(1)-C(2)	34.2(3)
C(10)-P(1)-C(1)-C(2)	-83.6(3)
C(16)-P(1)-C(1)-C(9)	-33.9(4)
C(17)-P(1)-C(1)-C(9)	-154.8(3)
C(10)-P(1)-C(1)-C(9)	87.3(3)
C(9)-C(1)-C(2)-C(3)	1.0(4)
P(1)-C(1)-C(2)-C(3)	173.7(2)
C(1)-C(2)-C(3)-C(4)	-0.7(4)
C(2)-C(3)-C(4)-C(5)	179.6(3)
C(2)-C(3)-C(4)-C(9)	0.1(4)
C(3)-C(4)-C(5)-C(6)	179.3(3)
C(9)-C(4)-C(5)-C(6)	-1.2(5)
C(4)-C(5)-C(6)-C(7)	0.7(5)
C(5)-C(6)-C(7)-C(8)	-0.5(5)
C(6)-C(7)-C(8)-C(9)	0.8(5)
C(7)-C(8)-C(9)-C(1)	179.4(3)
C(7)-C(8)-C(9)-C(4)	-1.2(5)
C(2)-C(1)-C(9)-C(8)	178.5(3)
P(1)-C(1)-C(9)-C(8)	6.4(6)
C(2)-C(1)-C(9)-C(4)	-1.0(3)
P(1)-C(1)-C(9)-C(4)	-173.1(2)
C(5)-C(4)-C(9)-C(8)	1.5(4)
C(3)-C(4)-C(9)-C(8)	-179.0(3)
C(5)-C(4)-C(9)-C(1)	-179.0(3)
C(3)-C(4)-C(9)-C(1)	0.6(3)
C(1)-P(1)-C(10)-C(15)	-17.6(3)
C(16)-P(1)-C(10)-C(15)	107.8(3)
C(17)-P(1)-C(10)-C(15)	-138.0(3)
C(1)-P(1)-C(10)-C(11)	160.6(3)
C(16)-P(1)-C(10)-C(11)	-74.0(3)
C(17)-P(1)-C(10)-C(11)	40.2(3)
C(15)-C(10)-C(11)-C(12)	-0.7(5)
P(1)-C(10)-C(11)-C(12)	-178.9(3)

C(10)-C(11)-C(12)-C(13)	0.5(5)
C(11)-C(12)-C(13)-C(14)	-0.1(6)
C(12)-C(13)-C(14)-C(15)	0.0(5)
C(13)-C(14)-C(15)-C(10)	-0.2(5)
C(11)-C(10)-C(15)-C(14)	0.6(5)
P(1)-C(10)-C(15)-C(14)	178.8(3)



Appendix Figure 3. Molecular structure of III

Table 13. Crystal data and structure refinement for III

Identification code	mb24	
Empirical formula	C25 H26 Cl O P	
Formula weight	408.88	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2272(10) Å	a= 107.6370(10)°.
	b = 9.7361(10) Å	b= 103.1390(10)°.
	c = 13.4523(14) Å	g = 101.7430(10)°.
Volume	1072.2(2) $Å^3$	
Z	2	
Density (calculated)	1.267 Mg/m^3	
Absorption coefficient	0.266 mm^{-1}	
F(000)	432	
Crystal size	0.35 x 0.30 x 0.25 mm^3	
Theta range for data collection	2.29 to 26.00°.	
Index ranges	-11<=h<=11, -12<=k<=12, -16<=l<=16	
Reflections collected	10644	
Independent reflections	4185 [R(int) = 0.0167]	
Completeness to theta = 26.00°	99.4 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9366 and 0.9128	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4185 / 3 / 262	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0314, wR2 = 0.0817	
R indices (all data)	R1 = 0.0369, wR2 = 0.0862	
Largest diff. peak and hole	0.381 and -0.228 $e.Å^{-3}$	

Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for III. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	7351(1)	10004(1)	3421(1)	22(1)
C(1)	5955(2)	10213(2)	2376(1)	23(1)
C(2)	5670(2)	11541(2)	2425(1)	25(1)
C(3)	4338(2)	11293(2)	1495(1)	26(1)
C(4)	3869(2)	9665(2)	826(1)	26(1)
C(5)	2731(2)	8751(2)	-167(1)	32(1)
C(6)	2575(2)	7224(2)	-590(1)	38(1)
C(7)	3538(2)	6584(2)	-43(1)	38(1)
C(8)	4700(2)	7473(2)	939(1)	31(1)
C(9)	4861(2)	9003(2)	1367(1)	24(1)
C(10)	3668(2)	12382(2)	1384(1)	31(1)
C(11)	4301(2)	13982(2)	2158(2)	41(1)
C(12)	2188(2)	12076(2)	496(2)	46(1)
C(13)	8649(2)	9088(2)	2853(1)	23(1)
C(14)	9670(2)	9898(2)	2462(1)	28(1)
C(15)	10693(2)	9249(2)	2018(1)	36(1)
C(16)	10706(2)	7807(2)	1959(1)	37(1)
C(17)	9709(2)	7010(2)	2356(1)	36(1)
C(18)	8669(2)	7642(2)	2803(1)	29(1)
C(19)	6387(2)	8893(2)	4062(1)	25(1)
C(20)	4792(2)	8187(2)	3634(1)	30(1)
C(21)	4089(2)	7230(2)	4082(1)	35(1)
C(22)	4970(2)	7002(2)	4964(1)	37(1)
C(23)	6542(2)	7746(2)	5420(1)	40(1)
C(24)	7258(2)	8689(2)	4968(1)	36(1)
C(25)	8502(2)	11817(2)	4410(1)	28(1)
Cl(1)	10731(1)	13997(1)	3248(1)	37(1)
O(1)	8019(1)	15094(2)	4086(1)	44(1)

Table 15. Bond lengths [Å] and angles [°] for III.

P(1)-C(1)	1.7705(14)	C(16)-C(17)	1.384(2)
P(1)-C(25)	1.7845(15)	C(16)-H(16A)	0.9500
P(1)-C(19)	1.7960(14)	C(17)-C(18)	1.393(2)
P(1)-C(13)	1.8038(14)	C(17)-H(17A)	0.9500
C(1)-C(2)	1.357(2)	C(18)-H(18A)	0.9500
C(1)-C(9)	1.4736(19)	C(19)-C(20)	1.390(2)
C(2)-C(3)	1.4603(19)	C(19)-C(24)	1.392(2)
C(2)-H(2A)	0.9500	C(20)-C(21)	1.387(2)
C(3)-C(10)	1.359(2)	C(20)-H(20A)	0.9500
C(3)-C(4)	1.479(2)	C(21)-C(22)	1.383(2)
C(4)-C(5)	1.393(2)	C(21)-H(21A)	0.9500
C(4)-C(9)	1.416(2)	C(22)-C(23)	1.380(3)
C(5)-C(6)	1.385(2)	C(22)-H(22A)	0.9500
C(5)-H(5A)	0.9500	C(23)-C(24)	1.386(2)
C(6)-C(7)	1.388(2)	C(23)-H(23A)	0.9500
C(6)-H(6A)	0.9500	C(24)-H(24A)	0.9500
C(7)-C(8)	1.389(2)	C(25)-H(25A)	0.9800
C(7)-H(7A)	0.9500	C(25)-H(25B)	0.9800
C(8)-C(9)	1.388(2)	C(25)-H(25C)	0.9800
C(8)-H(8A)	0.9500	O(1)-H(1WB)	0.832(9)
C(10)-C(11)	1.491(2)	O(1)-H(1WA)	0.834(9)
C(10)-C(12)	1.502(2)		
C(11)-H(11A)	0.9800	C(1)-P(1)-C(25)	109.64(7)
C(11)-H(11B)	0.9800	C(1)-P(1)-C(19)	109.85(7)
C(11)-H(11C)	0.9800	C(25)-P(1)-C(19)	110.42(7)
C(12)-H(12A)	0.9800	C(1)-P(1)-C(13)	110.27(6)
C(12)-H(12B)	0.9800	C(25)-P(1)-C(13)	107.45(7)
C(12)-H(12C)	0.9800	C(19)-P(1)-C(13)	109.16(7)
C(13)-C(18)	1.393(2)	C(2)-C(1)-C(9)	109.16(12)
C(13)-C(14)	1.400(2)	C(2)-C(1)-P(1)	123.92(11)
C(14)-C(15)	1.385(2)	C(9)-C(1)-P(1)	126.81(11)
C(14)-H(14A)	0.9500	C(1)-C(2)-C(3)	109.98(13)
C(15)-C(16)	1.384(2)	C(1)-C(2)-H(2A)	125.0
C(15)-H(15A)	0.9500	C(3)-C(2)-H(2A)	125.0

C(10)-C(3)-C(2)	123.58(14)	C(18)-C(13)-C(14)	120.24(13)
C(10)-C(3)-C(4)	130.59(14)	C(18)-C(13)-P(1)	122.61(11)
C(2)-C(3)-C(4)	105.62(12)	C(14)-C(13)-P(1)	117.15(11)
C(5)-C(4)-C(9)	118.64(14)	C(15)-C(14)-C(13)	119.56(14)
C(5)-C(4)-C(3)	133.52(14)	C(15)-C(14)-H(14A)	120.2
C(9)-C(4)-C(3)	107.83(12)	C(13)-C(14)-H(14A)	120.2
C(6)-C(5)-C(4)	119.71(15)	C(16)-C(15)-C(14)	120.29(15)
C(6)-C(5)-H(5A)	120.1	C(16)-C(15)-H(15A)	119.9
C(4)-C(5)-H(5A)	120.1	C(14)-C(15)-H(15A)	119.9
C(5)-C(6)-C(7)	121.11(15)	C(15)-C(16)-C(17)	120.25(15)
C(5)-C(6)-H(6A)	119.4	C(15)-C(16)-H(16A)	119.9
C(7)-C(6)-H(6A)	119.4	C(17)-C(16)-H(16A)	119.9
C(6)-C(7)-C(8)	120.41(15)	C(16)-C(17)-C(18)	120.30(15)
C(6)-C(7)-H(7A)	119.8	C(16)-C(17)-H(17A)	119.8
C(8)-C(7)-H(7A)	119.8	C(18)-C(17)-H(17A)	119.8
C(9)-C(8)-C(7)	118.71(15)	C(17)-C(18)-C(13)	119.35(14)
C(9)-C(8)-H(8A)	120.6	C(17)-C(18)-H(18A)	120.3
C(7)-C(8)-H(8A)	120.6	C(13)-C(18)-H(18A)	120.3
C(8)-C(9)-C(4)	121.39(13)	C(20)-C(19)-C(24)	119.84(13)
C(8)-C(9)-C(1)	131.27(13)	C(20)-C(19)-P(1)	120.57(11)
C(4)-C(9)-C(1)	107.34(12)	C(24)-C(19)-P(1)	119.54(11)
C(3)-C(10)-C(11)	123.15(14)	C(21)-C(20)-C(19)	119.79(14)
C(3)-C(10)-C(12)	123.22(15)	C(21)-C(20)-H(20A)	120.1
C(11)-C(10)-C(12)	113.59(14)	C(19)-C(20)-H(20A)	120.1
C(10)-C(11)-H(11A)	109.5	C(22)-C(21)-C(20)	119.98(15)
C(10)-C(11)-H(11B)	109.5	C(22)-C(21)-H(21A)	120.0
H(11A)-C(11)-H(11B)	109.5	C(20)-C(21)-H(21A)	120.0
C(10)-C(11)-H(11C)	109.5	C(23)-C(22)-C(21)	120.48(14)
H(11A)-C(11)-H(11C)	109.5	C(23)-C(22)-H(22A)	119.8
H(11B)-C(11)-H(11C)	109.5	C(21)-C(22)-H(22A)	119.8
C(10)-C(12)-H(12A)	109.5	C(22)-C(23)-C(24)	119.87(15)
C(10)-C(12)-H(12B)	109.5	C(22)-C(23)-H(23A)	120.1
H(12A)-C(12)-H(12B)	109.5	C(24)-C(23)-H(23A)	120.1
C(10)-C(12)-H(12C)	109.5	C(23)-C(24)-C(19)	119.96(15)
H(12A)-C(12)-H(12C)	109.5	C(23)-C(24)-H(24A)	120.0
H(12B)-C(12)-H(12C)	109.5	C(19)-C(24)-H(24A)	120.0

P(1)-C(25)-H(25A)	109.5	H(25A)-C(25)-H(25C)	109.5
P(1)-C(25)-H(25B)	109.5	H(25B)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25B)	109.5	H(1WB)-O(1)-H(1WA)	105.1(17)
P(1)-C(25)-H(25C)	109.5		

Table 16. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for III. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	18(1)	24(1)	23(1)	11(1)	5(1)	4(1)
C(1)	20(1)	27(1)	23(1)	12(1)	6(1)	5(1)
C(2)	22(1)	28(1)	25(1)	12(1)	7(1)	5(1)
C(3)	22(1)	31(1)	26(1)	14(1)	8(1)	7(1)
C(4)	22(1)	34(1)	25(1)	14(1)	9(1)	6(1)
C(5)	26(1)	42(1)	27(1)	15(1)	5(1)	7(1)
C(6)	33(1)	41(1)	26(1)	7(1)	2(1)	1(1)
C(7)	42(1)	28(1)	34(1)	5(1)	9(1)	4(1)
C(8)	32(1)	30(1)	31(1)	12(1)	8(1)	7(1)
C(9)	21(1)	29(1)	23(1)	11(1)	7(1)	5(1)
C(10)	29(1)	38(1)	32(1)	19(1)	10(1)	13(1)
C(11)	43(1)	36(1)	48(1)	19(1)	10(1)	18(1)
C(12)	42(1)	48(1)	48(1)	22(1)	2(1)	21(1)
C(13)	19(1)	27(1)	24(1)	10(1)	3(1)	6(1)
C(14)	26(1)	29(1)	31(1)	14(1)	9(1)	7(1)
C(15)	28(1)	45(1)	36(1)	16(1)	13(1)	9(1)
C(16)	29(1)	45(1)	34(1)	9(1)	9(1)	17(1)
C(17)	36(1)	30(1)	38(1)	11(1)	5(1)	15(1)
C(18)	28(1)	27(1)	33(1)	14(1)	7(1)	7(1)
C(19)	23(1)	28(1)	27(1)	13(1)	9(1)	7(1)
C(20)	26(1)	36(1)	26(1)	12(1)	8(1)	5(1)
C(21)	31(1)	36(1)	33(1)	9(1)	14(1)	0(1)
C(22)	48(1)	32(1)	43(1)	20(1)	29(1)	14(1)
C(23)	42(1)	55(1)	44(1)	35(1)	21(1)	25(1)
C(24)	25(1)	53(1)	39(1)	28(1)	11(1)	13(1)
C(25)	24(1)	27(1)	28(1)	8(1)	4(1)	4(1)
Cl(1)	31(1)	35(1)	49(1)	24(1)	11(1)	8(1)
O(1)	36(1)	41(1)	49(1)	13(1)	5(1)	11(1)

Table 17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for III.

	x	y	z	U(eq)
H(2A)	6251	12493	2983	30
H(5A)	2065	9174	-552	38
H(6A)	1796	6605	-1267	45
H(7A)	3401	5532	-342	45
H(8A)	5372	7041	1310	37
H(11A)	5328	14136	2653	61
H(11B)	3595	14216	2587	61
H(11C)	4395	14648	1741	61
H(12A)	1505	11070	333	69
H(12B)	2433	12125	-166	69
H(12C)	1662	12833	743	69
H(14A)	9661	10887	2502	34
H(15A)	11389	9795	1753	43
H(16A)	11401	7363	1645	44
H(17A)	9735	6027	2323	43
H(18A)	7981	7093	3071	35
H(20A)	4186	8359	3036	36
H(21A)	3002	6732	3783	42
H(22A)	4489	6327	5257	44
H(23A)	7133	7613	6042	47
H(24A)	8342	9196	5277	43
H(25A)	7818	12390	4674	42
H(25B)	9126	12359	4071	42
H(25C)	9194	11697	5028	42
H(1WB)	8340(20)	15340(30)	4764(8)	66
H(1WA)	8740(20)	14850(30)	3869(16)	66

Table 18. Torsion angles [°] for III.

C(25)-P(1)-C(1)-C(2)	-9.25(14)
C(19)-P(1)-C(1)-C(2)	112.28(13)
C(13)-P(1)-C(1)-C(2)	-127.37(12)
C(25)-P(1)-C(1)-C(9)	175.06(12)
C(19)-P(1)-C(1)-C(9)	-63.42(14)
C(13)-P(1)-C(1)-C(9)	56.94(13)
C(9)-C(1)-C(2)-C(3)	2.78(16)
P(1)-C(1)-C(2)-C(3)	-173.57(10)
C(1)-C(2)-C(3)-C(10)	172.56(14)
C(1)-C(2)-C(3)-C(4)	-2.75(15)
C(10)-C(3)-C(4)-C(5)	7.7(3)
C(2)-C(3)-C(4)-C(5)	-177.46(15)
C(10)-C(3)-C(4)-C(9)	-173.22(15)
C(2)-C(3)-C(4)-C(9)	1.63(15)
C(9)-C(4)-C(5)-C(6)	1.2(2)
C(3)-C(4)-C(5)-C(6)	-179.80(15)
C(4)-C(5)-C(6)-C(7)	-0.2(2)
C(5)-C(6)-C(7)-C(8)	-1.0(3)
C(6)-C(7)-C(8)-C(9)	1.0(2)
C(7)-C(8)-C(9)-C(4)	0.1(2)
C(7)-C(8)-C(9)-C(1)	179.63(15)
C(5)-C(4)-C(9)-C(8)	-1.2(2)
C(3)-C(4)-C(9)-C(8)	179.58(13)
C(5)-C(4)-C(9)-C(1)	179.19(12)
C(3)-C(4)-C(9)-C(1)	-0.06(15)
C(2)-C(1)-C(9)-C(8)	178.72(15)
P(1)-C(1)-C(9)-C(8)	-5.1(2)
C(2)-C(1)-C(9)-C(4)	-1.69(16)
P(1)-C(1)-C(9)-C(4)	174.53(10)
C(2)-C(3)-C(10)-C(11)	5.0(2)
C(4)-C(3)-C(10)-C(11)	179.08(15)
C(2)-C(3)-C(10)-C(12)	-172.60(15)
C(4)-C(3)-C(10)-C(12)	1.4(3)
C(1)-P(1)-C(13)-C(18)	-112.14(12)

C(25)-P(1)-C(13)-C(18)	128.41(12)
C(19)-P(1)-C(13)-C(18)	8.64(14)
C(1)-P(1)-C(13)-C(14)	68.39(12)
C(25)-P(1)-C(13)-C(14)	-51.07(13)
C(19)-P(1)-C(13)-C(14)	-170.84(11)
C(18)-C(13)-C(14)-C(15)	0.5(2)
P(1)-C(13)-C(14)-C(15)	179.95(11)
C(13)-C(14)-C(15)-C(16)	0.1(2)
C(14)-C(15)-C(16)-C(17)	-0.8(2)
C(15)-C(16)-C(17)-C(18)	1.0(2)
C(16)-C(17)-C(18)-C(13)	-0.4(2)
C(14)-C(13)-C(18)-C(17)	-0.3(2)
P(1)-C(13)-C(18)-C(17)	-179.77(11)
C(1)-P(1)-C(19)-C(20)	7.80(15)
C(25)-P(1)-C(19)-C(20)	128.85(13)
C(13)-P(1)-C(19)-C(20)	-113.23(13)
C(1)-P(1)-C(19)-C(24)	-174.80(12)
C(25)-P(1)-C(19)-C(24)	-53.75(15)
C(13)-P(1)-C(19)-C(24)	64.17(14)
C(24)-C(19)-C(20)-C(21)	-2.9(2)
P(1)-C(19)-C(20)-C(21)	174.52(12)
C(19)-C(20)-C(21)-C(22)	1.1(2)
C(20)-C(21)-C(22)-C(23)	1.5(2)
C(21)-C(22)-C(23)-C(24)	-2.3(3)
C(22)-C(23)-C(24)-C(19)	0.6(3)
C(20)-C(19)-C(24)-C(23)	2.0(2)
P(1)-C(19)-C(24)-C(23)	-175.38(13)

Table 19. Hydrogen bonds for III [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1WA)...Cl(1)	0.834(9)	2.379(10)	3.2113(14)	176(2)
O(1)-H(1WB)...Cl(1)#1	0.832(9)	2.448(10)	3.2797(14)	178(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+3,-z+1