Synthesis and Characterisation of Phosphenium Ions with Aromatic Amido Substituents

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Synthesis and Characterisation of Phosphenium Ions with Aromatic Amido Substituents

Thesis submitted for the Degree of Master of Science

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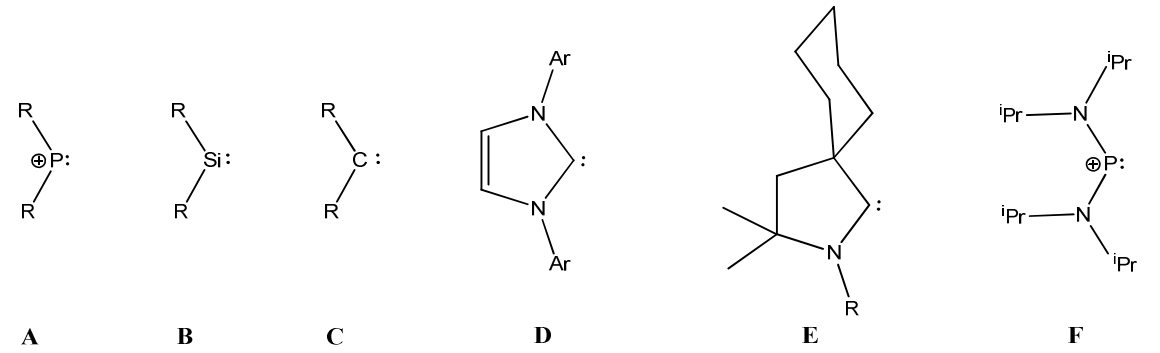
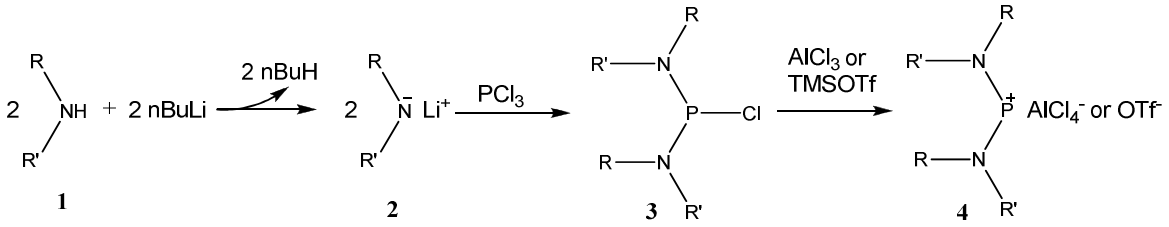
Abstract

$\sigma^2\lambda^3$-Phosphenium cations **A** are valence isoelectronic and isolobal with silenes **B** and hence, carbenes **C**. Notably, the chemistry of these divalent phosphorus cations mirrors that of their carbon-based analogues (*e.g.* cycloaddition chemistry, C-H insertions, *etc*.), making them versatile reagents in a variety of transformations and reactions. Just as for carbenes (*e.g.* amino carbenes **D** and **E)**, a combination of kinetic and electronic stabilisation has been used to prepare and isolate stable phosphenium ions such as **F**, with amido substituents. This approach is also followed in this work. In particular, the synthesis, characterisation, and properties of a range of phosphenium ions (**4**) with alkyl or aryl amido substituents (R_2N, R = alkyl or aryl) is described.



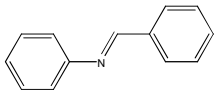
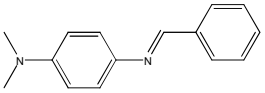
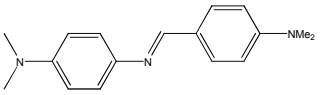
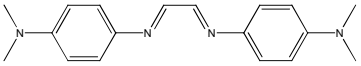
The desired phosphenium ions **4** are synthesized in three steps by reacting the secondary amines **1** with nBuLi, which results in the production of the appropriate lithium amide salts (**2**) followed by subsequent reaction with PCl_3, which yields the chlorophosphines **3**. Reaction of **3** with a halogen abstracting reagent such as $AlCl_3$ (or TMSOTf) results in the formation of phosphenium ions (**4**), which were studied by NMR spectroscopy and X-ray diffraction.



Abbreviations

- Ar: General aryl group
- Bnz: Benzyl group
- Cp: Cyclopentadienyl group
- DCM: Dichloromethane
- HOMO: Highest occupied molecular orbital
- iPr: isopropyl group
- LUMO: Lowest unoccupied molecular orbital
- Me: Methyl group
- nBuLi: n-butyllithium
- NMR: nuclear magnetic resonance
- OTf: Trifluoromethanesulphonate group
- Ph: Phenyl group
- R: General organic group
- tBu: tert butyl group
- TMS: Trimethylsilyl group
- TMSCl: Trimethylsilyl chloride

Table of Compounds

IMINES			
 (ImI)	 (ImII)	 (ImIII)	 (ImIV)
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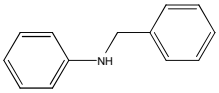
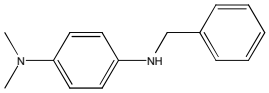
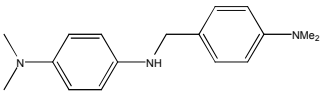
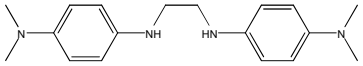
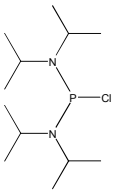
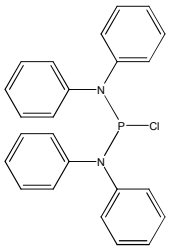
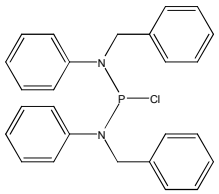
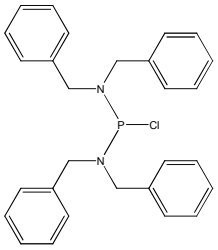
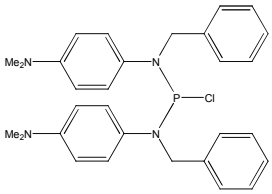
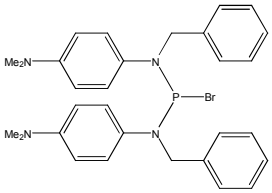
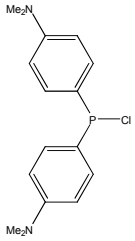
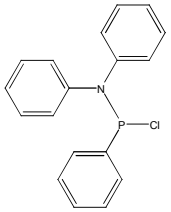
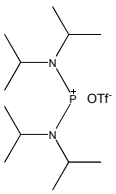
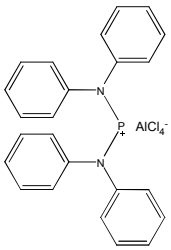
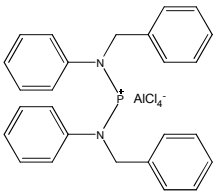
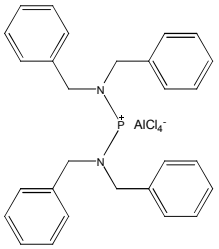
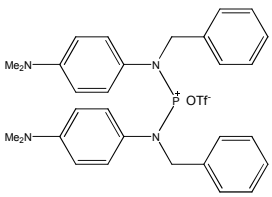
 (AmI)	 (AmII)	 (AmIII)	 (AmIV)
BIS(AMINO)HALOPHOSPHINES			
 (N2PCl I)	 (N2PCl II)	 (N2PCl III)	 (N2PCl IV)
 (N2PCl V)	 (N2PBr I)	 (C2PCl I)	 (CNPCl I)
BIS(AMINO)PHOSPHENIUM IONS			
 (N2P+ I)	 (N2P+ II)	 (N2P+ III)	 (N2P+ IV)	 (N2P+ V)

1. General Review of Phosphenium Cations

This chapter will focus on giving a broad overview of the synthesis, structure, and reactivity of phosphenium ions (R_2P^+). It is not intended as an exhaustive review, but rather as an introduction to important general aspects of phosphenium ion chemistry.

1.1 Electronic Structure and Stability

1.1.1 General Factors for the Stabilization of Phosphenium Ions

$\sigma^2\lambda^3$-Phosphenium ions (R_2P^+) contain a positively charged phosphorus centre in the +3 oxidation state, connected to two organic substituents. The hybridization of the central phosphorous atom can be regarded as being approximately sp^2 (because of the smaller than 120° RPR bond angles observed), with a lone electron pair in the free sp^2 orbital and a vacant p_z orbital as described in Figure 1.[1] From the above description, it is evident that phosphenium ions are isolobal and isoelectronic with singlet carbenes, singlet silenes, and nitrenium ions (Figure 1),[2,3] which means that these species are likely to have similar chemistry and properties.

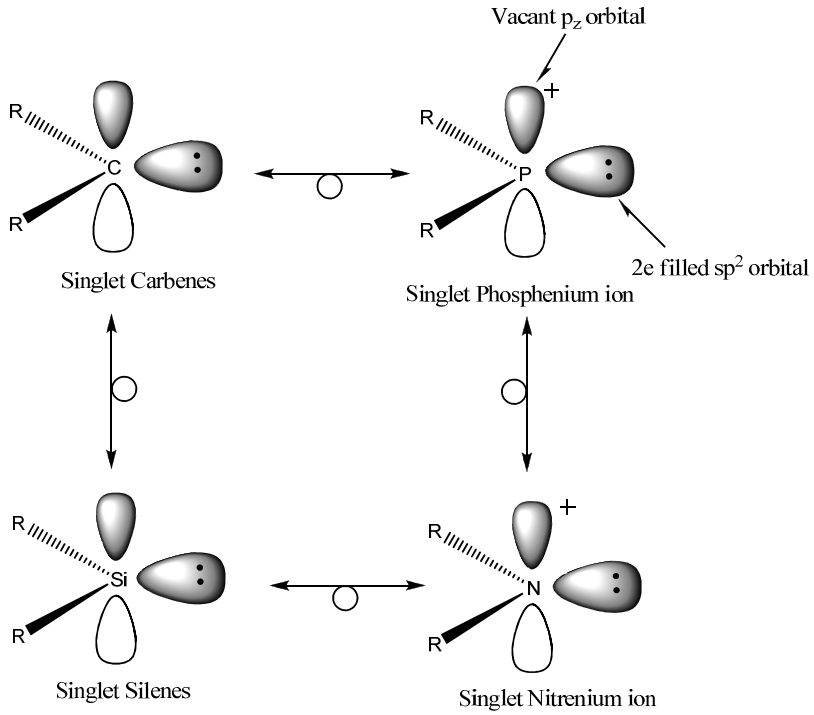
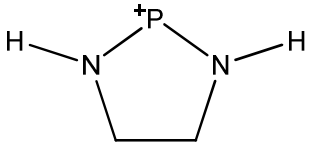


Figure 1: *Phosphenium ions and related species*

For example, it has been shown through *ab initio* calculations by Harrison (1981) that the model phosphenium ion PH_2^+ has a singlet ground energy state with a singlet-triplet separation of about 16 Kcal/mol.[4] More recent calculations by Boyd *et al*. (1998) on the model ion **5** are qualitatively in agreement with Harrisons studies, but have shown that **5** has a singlet state that is more stable than the triplet by 73.6 Kcal/mol. The larger singlet-triplet separation calculated for **5** compared to PH_2^+ is attributed to the π donating amido groups and the acute NPN angle the five membered ring induces. Both of these factors exert a stabilizing effect on the singlet energy state.[5]



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In just the same way, carbenes can also adopt ground triplet states having unpaired electrons as shown in Figure 2. Here too the multiplicity of the carbene ground state also depends on the nature of the substituents. Electronegative and π-electron donating groups energetically favour the singlet ground energy state just as is the case for phosphenium ions.[6]

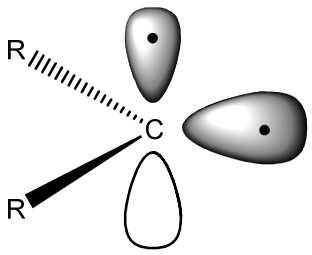


Figure 2: *A triplet carbene*

Phosphenium ions are highly reactive species due to the extreme lack of electron density at the phosphorus centre. As a result, electron-donating substituents connected to the phosphorus atom are necessary in order to isolate them. Usually amido groups bonded to the phosphorus are employed and, as a result of N→P donation, this results in a trigonal geometry around the nitrogen, which maximizes the interaction of the two filled nitrogen p_z orbitals with the vacant phosphorus p_z orbital (Figure 3), relieving the positive charge on the phosphorus atom through transfer of electron density from the amido groups.[7] Nevertheless, even unstable phosphenium ions like Cl_2P^+ can be observed by EI mass spectrometry of their precursor halophosphines as the species with the highest intensity.[8]

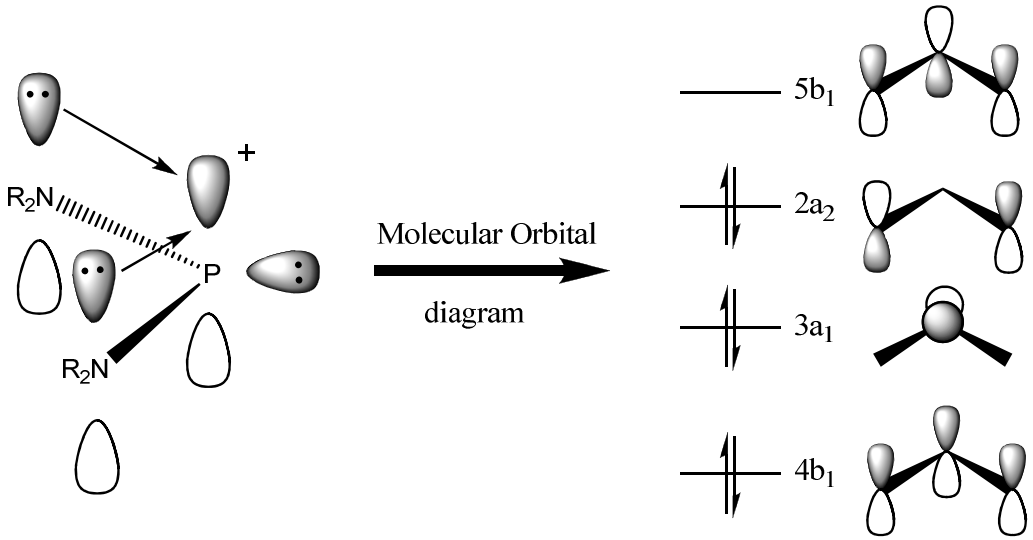
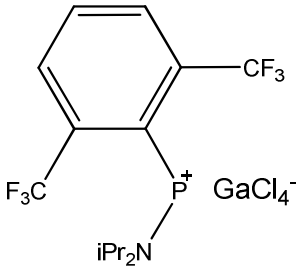


Figure 3: *Molecular orbital diagram of an amido-stabilized phosphenium ion*

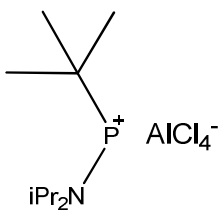
By including the interaction of the amido p_z orbitals with the orbitals of the phosphorus atom the molecular orbital diagram shown in Figure 3 may be constructed, where the a_2 symmetry HOMO is non-bonding in character, while the b_1 symmetry LUMO is anti-bonding. The phosphorus lone pair orbital corresponds to the $3a_1$ molecular orbital.[9] Although the π bonding between the N and P atoms is crucial for the phosphenium ions' stability, rotation around the P-N bond is allowed at room temperature with a rotational barrier of approximately 11.5 Kcal/mol being estimated (depending on the method used for the calculation), which often results in broad peaks in their ^{13}C and ^{1}H NMR spectra.[10]

1.1.2 Selected Stable, Mono (Amido)-Substituted Phosphenium Ions

Phosphenium ions do not necessarily require two amido substituents in order to be stable. For example, Bertrand *et al.* (2002) have successfully synthesized the mono(amido) phosphenium ion **6** with the 2,6-*bis*(trifluoromethyl)phenyl moiety as the second substituent,[11] while Cowley *et al.* synthesized its tert-butyl equivalent **7**, which exhibits the highest frequency ^{31}P NMR resonance of 513.2 ppm amongst related species.[12]



6

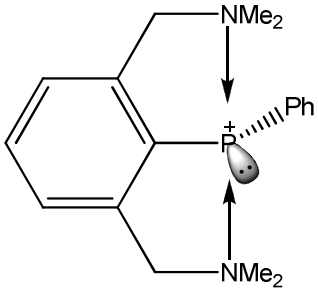


7

The ^{31}P NMR spectroscopic chemical shift of 423 ppm for phosphenium **6** is characteristic of the ionic nature of the bond between the phosphorus centre and the counterion $GaCl_4^-$. Another interesting feature of compound **6** is that the aromatic ring is perpendicularly orientated with respect to the NPN plane in the solid state, making any π-interaction, which could potentially lead to the electronic stabilization of the compound, impossible. This behaviour is attributed to steric factors and also to a weak interaction of the phosphorus centre with the fluorine atoms, which is observed in the crystal structure (P···F = 2.554 Å while the sum of the van der Waals radii is 3.37 Å).[11]

1.1.3 Stabilization of Phosphenium Ions Through Adduct Formation

It must be mentioned that P-N covalent bonding is not always necessary in order to obtain a stable phosphenium ion, provided there is another way for the molecule to relieve the positive charge at the phosphorus atom. This may also be achieved by *intra*-molecular N→P σ-coordination as shown in cations **8** and **9**. In some cases such as in the tetrafluoroborate salt of cation **9**, the stabilization is enough to make the compound air and moisture stable.[13,14]



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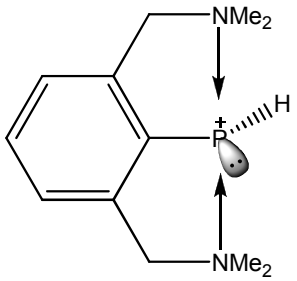
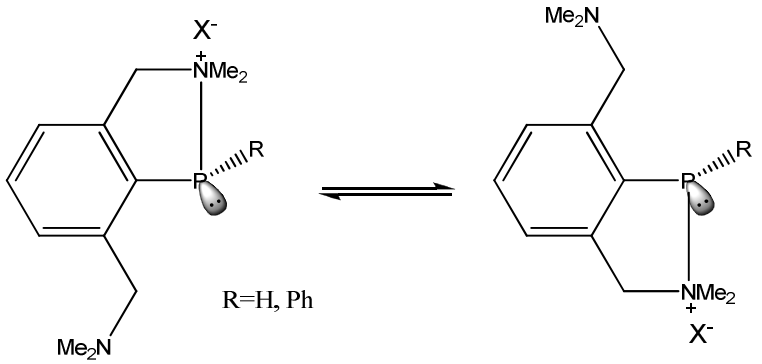


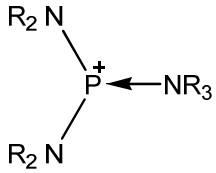
9

Cations **8** and **9** though, may also be regarded as ammonium salts as depicted in Scheme 1. Nevertheless, if that was the case, then the two Me groups in each arm would be equivalent, because of the exchange process shown in scheme 1, giving rise to a single resonance in the ^{1}H NMR spectrum for the NMe_2 protons. On the contrary, two resonances are observed in the ^{1}H NMR spectrum, one for each Me group, implying that the actual structure is like **8** or **9** where the Me groups on each arm are inequivalent since there is no plane of symmetry that relates the two of them due to the single electron pair of the phosphorus atom. [13]



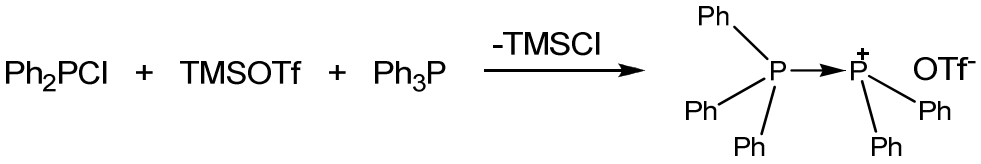
Scheme 1: *The possible exchange process for cations **8** and **9***

Notably phosphenium ions may also be stabilised in the same way as described above for **8** and **9** by coordination to a discrete amine forming salts such as **10**. The synthesis of this kind of phosphenium adduct will be described later in the text (section 1.4).



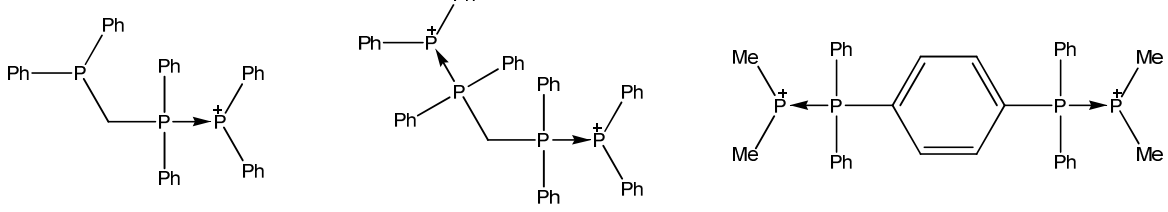
10

Phosphines can also be used as the electron donating group in order to stabilize phosphenium ions, something that results in the formation of phosphino phosphonium salts. For example, the Ph_2P^+ phosphenium ion, which can't be isolated due to its instability that arises from the lack of amido substituents, can be stabilized if it is generated in the presence of PPh_3, resulting in a phosphino phosphonium ion as described in Scheme 2.[15]



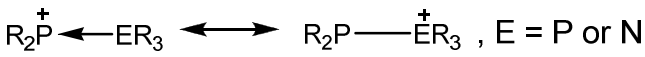
Scheme 2: *Formation of a phosphine-stabilized phosphenium ion*

Of course plenty of other phosphine-stabilized phosphenium ions have been synthesized in the same way. A number of representative examples are shown in Scheme 3.[16]



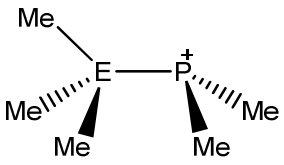
Scheme 3: *Some examples of phosphine-stabilized phosphenium ions*

The question that arises now for these adducts, concerns the nature of the bonding between the phosphenium phosphorus atom and the donating atom of the amine or phosphine used to form the adduct. So far these bonds have been drawn as dative bonds from the amine or the phosphine towards the phosphenium ion positive centre. Nevertheless, the possibility of covalent bonding between the two species giving rise to a phosphino phosphonium or a phosphino ammonium salt can't be excluded (Scheme 4).

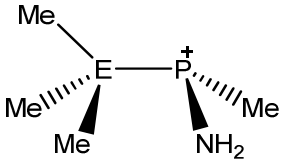


Scheme 4: *Resonance forms for the two extreme representations of the bonding in phosphenium ion/Lewis base adducts*

As always with resonance forms, the real structure of the compound lies somewhere in between the two extremes. Thus computational studies are necessary in order to draw any conclusions. This has been covered by the work of Pietsching (2007) who conducted DFT and *ab initio* calculations on the model phosphenium ion adducts **11** and **12** (E = P or N).



11



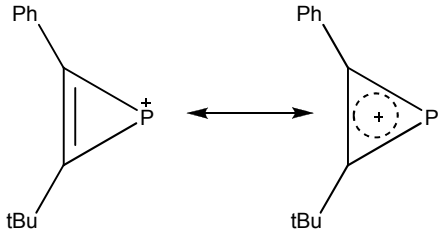
12

The most important part of this study is the calculation of the charge distribution between the E and P atoms, as well as the energy needed for homolytic or heterolytic cleavage of the P-E bond. It was found that the charge on the electron-accepting phosphorus atom is reduced by half after complexation with PMe_3 in compound **11**, compared to that for the free phosphenium ion. The same applies for the amino-substituted compounds whith E = N, but this time the decrease is much smaller. If a methyl group on the phosphenium fragment is replaced with the π-donating amido group (like in compound **12**) the decrease in the degree of positive charge is even smaller in both amino (E = N) and phosphino (E = P) adducts. Nevertheless, this charge distribution study alone doesn't provide strong enough evidence in order to distinguish whether these species should be regarded as stabilized phosphenium ions and not phosphinophosphonium and phosphinoammonium ions. The value of the P-E bond cleavage energy for the methyl-substituted species **11**, favours a homolytic cleavage pathway over a heterolytic one and thus implies covalent bonding between P and E. However, the situation is inverted if the methyl group is

replaced by the amido group (compound **12**). Here, the stabilising effect of the amido group favours the heterolytic cleavage of the P-E bond for compound **12**, which thus implies that the phosphenium ion character will be sustained. From the above, we can be concluded that for methyl-substituted systems like **11** the P-E bond is rather covalent, while for amido substituted systems the P-E bond is dative and especially when E = N.[17]

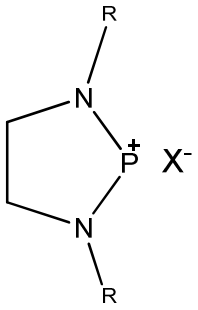
1.1.4 Stabilization of Phosphenium Ions Through Conjugation

Two examples of phosphenium ions that completely lack amido substituents are $(Me_5C_5)(t\text{-}Bu)P^+$ and the phosphirenylium cation **13**. In $(Me_5C_5)(t\text{-}Bu)P^+$ stabilization results from the η^5 attachment of the Me_5C_5 substituent, which is evident from the equivalence of the Me groups in its NMR spectra even at -90 °C.[18] Alternatively, another mode of phosphenium ion stabilization is observed for **13**. Here, stabilization is achieved through conjugation with the three membered ring double bond (like in cyclopropenium ions) and the phenyl substituent.[19]



13

In the same way, cyclic phosphenium ions like **15** are further stabilized compared to their acyclic (**14**) or to their saturated (**16**) analogues since the positive charge on phosphorus is more delocalized. Denk *et al.*[20] and Gudat *et al.*[21] conducted crystallographic, spectroscopic, conductometric and computational studies examining the alteration of bond lengths about the heterocyclic ring, the deshielding of ring protons in the NMR spectra, the aromatic delocalization energy, the influence of substituents and various other parameters of species like **15**. The results of these studies suggest that **15** is not a genuine aromatic system like benzene, but does have partial aromatic character with some electron density being delocalized from the double bond and the nitrogen atoms to the positively charged phosphorus centre.



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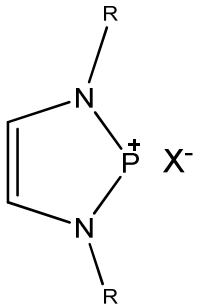

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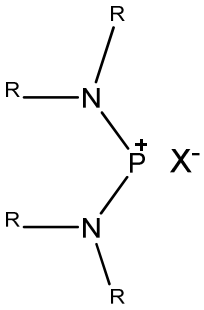
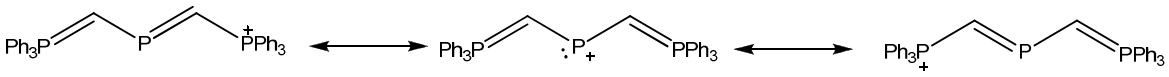


16

A final characteristic example of phosphenium ions stabilized through conjugation are the *bis*(ylide)-substituted phosphenium halides such as **17**, where the central phosphorus atom is stabilized through delocalization of its positive charge to the phosphonium groups as is evident from the possible resonance forms shown in Scheme 5.[22]



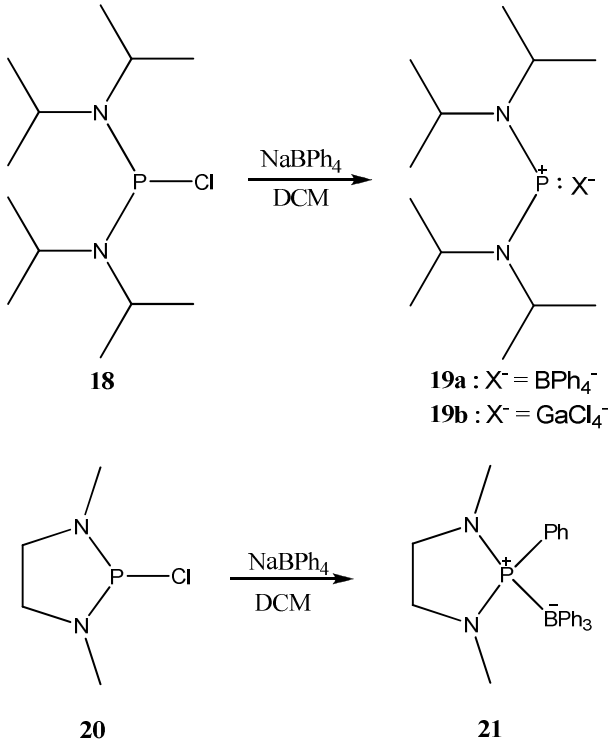
17

Scheme 5: *A stable, non-nitrogen-containing phosphenium ion*

This mode of stabilization is so effective that compound **17** can even be handled in air for some time, and that the phosphenium ion loses part of its characteristic reactivity. Hence, **17** does not react with 2,3-dimethylbutadiene, while diaminophosphenium ions such as $(iPr_2N)_2P^+$,[1] participate in cycloaddition reactions with this substrate.

1.1.5 Kinetic Stabilization and the Effect of the Counter Ion on the Stability of Phosphenium ions

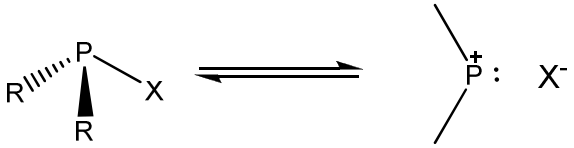
Phosphenium ions can also be kinetically stabilized with incorporation of bulky substituents. For example, the phosphenium salt 1**9a** can be easily synthesized by treating the corresponding chlorophosphine 1**8** with $NaBPh_4$. In contrast, the less bulky, tied-back diaminochlorophosphine **20** reacts with $NaBPh_4$ to give the adduct **21**. This occurs through an oxidative addition of the B-Ph bond to the phosphenium intermediate as described in Scheme 6. The difference in the way **18** and **20** react with $NaBPh_4$ is attributed to the fact that the resulting phosphenium ion **19a** is kinetically stabilized by the bulky isopropyl substituents, which protect the phosphorus centre. On the other hand in compound **20** this kind of protection is absent, resulting in the high reactivity of the phosphorus centre, thus facilitating the oxidative addition of the tetraphenylborate ion.



18 **20** **21**

Scheme 6: *Effect of steric hindrance on the formation/reactivity of phosphenium ions*

Another important factor that influences the stability of phosphenium ions is the nature of the counter anion. Hence, while the phosphenium tetrachlorogallate salt **19b** is stable in DCM, the tetraphenylborate salt (**19a**) undergoes oxidative addition of the C-Cl bond of DCM giving rise to a phosphonium adduct: $[(iPr_2N)_2P(Cl)(CH_2Cl)]^+$. The stabilizing effect of the tetrachlorogallate anion is attributed to the free electron pairs of the chlorine atoms, which interact with the positively charged phosphorus center.[23] This type of anion/cation interaction is reminiscent of the weak electrolytic behaviour of certain phosphenium salts depending on the counter anion and the stability of the phosphenium ion formed (Scheme 7).[24] There are cases (most commonly when OTf^- is used as the counter ion) where the counter ion is weakly interacting with the phosphenium ion leading to an equilibrium between the two species as described in Scheme 7. This interaction can be experimentally observed by the strong dependence of the ^{31}P NMR spectrum chemical shift from the concentration of the solution.

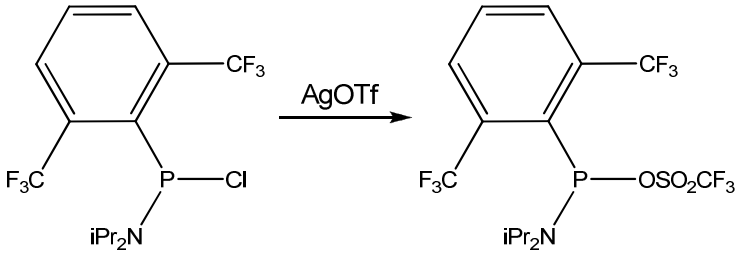


Scheme 7: *Equilibrium between covalent and ionic form of a phosphenium 'salt'*

1.2 Selected Syntheses

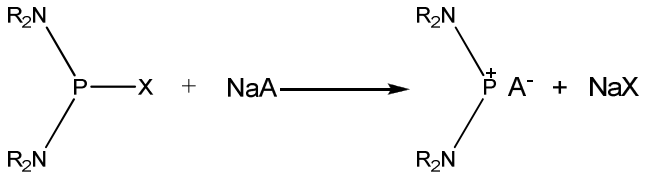
1.2.1 Synthesis of Phosphenium Ions by Halide Abstraction

Phosphenium ions are most commonly synthesized from the corresponding halophosphine by abstraction of the halogen atom using a strong Lewis acid (A). The Lewis acid is usually $AlCl_3$ or TMSOTf (which releases TMSX as a volatile liquid), but $GaCl_3$, $FeCl_3$, PCl_5 and $AgPF_6$ have also been employed successfully.[1] Which Lewis acid is the most appropriate for a particular halophosphine must be determined experimentally since a phosphenium ion might not necessarily form (or be stable) with all of the above reagents. For example, it is found that $GaCl_3$ sometimes gives cleaner reactions compared to $AlCl_3$, although the rationale behind this observation is not readily apparent.[20] One important aspect regarding the use of TMSOTf as a Lewis acid is that it can sometimes lead to covalent products, where the triflate anion (OTf^-) binds strongly to the positively charged phosphorus centre. A characteristic example of such covalent bonding is observed during the reaction outlined in Scheme 8, where the synthesis of the corresponding phosphenium ion is attempted.[11, 25]



Scheme 8: *Formation of a covalent phosphenium triflate species*

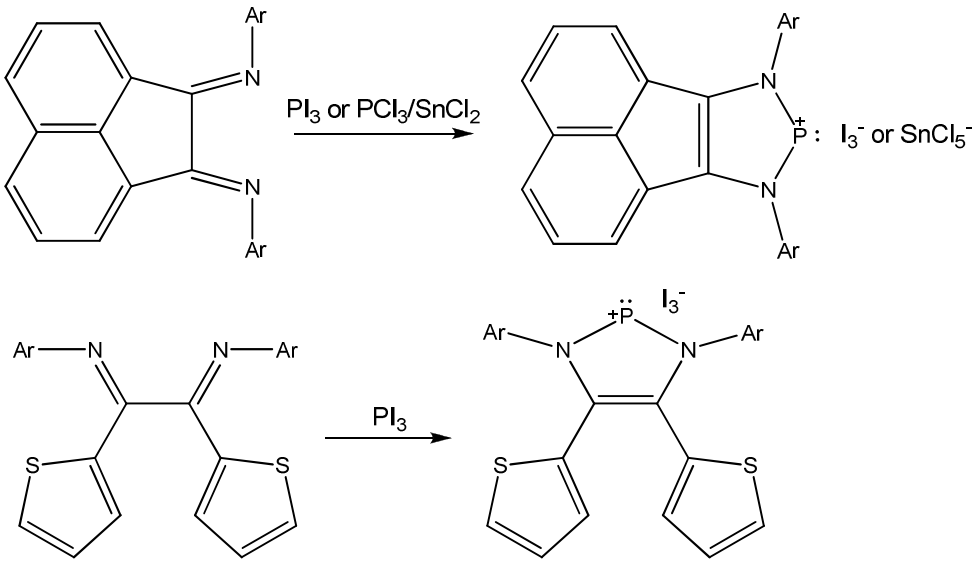
Another synthetic methodology for the preparation of phosphenium ions, similar to the one just mentioned, uses salts with weakly coordinating anions such as $NaBPh_4$.[23] The driving force of this reaction is the formation of insoluble sodium halide salts (Scheme 9).



Scheme 9: *Common synthetic route to a phosphenium ion*

1.2.2 Synthesis of Phosphenium Ions Through Oxidative Coupling Reactions

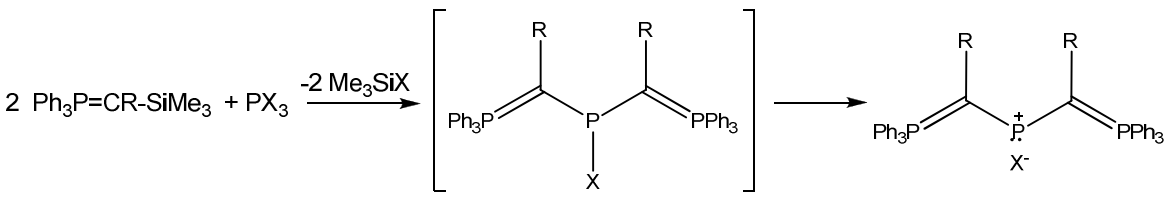
The phosphenium ion syntheses described so far require a halophosphine as a starting material. However, this is not always the case, especially for the synthesis of cyclic phosphenium ions. For example, reaction of a conjugated diimine with PI_3 or an equimolar mixture of $PCl_3/SnCl_2$ results in the formation of cyclic phosphenium ions as described in Scheme 10. It is speculated that the mechanism of this transformation involves the initial formation of a diamidophosphine iodide centre and I_2, which is followed by abstraction of the I atom by the I_2 produced in order to form I_3^-.[26,27,28]



Scheme 10: *Formation of cyclic phosphenium ions directly from a conjugated diimine*

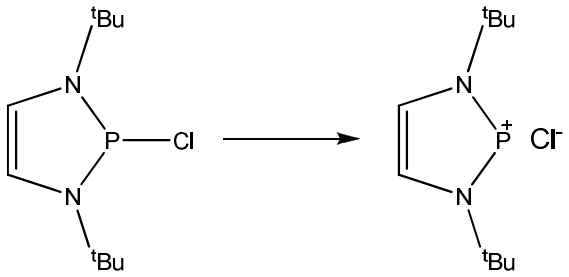
1.2.3 Synthesis of Phosphenium Ions Through Autoionisation of The Precursor Halophosphine

Sometimes, a phosphenium ion, if it is stable enough, can form spontaneously from the corresponding halophosphine without the need of a halide abstracting reagent. For example, the *bis*(ylide)-substituted phosphenium ions that have already been mentioned in section 1.1 are synthesized as described in Scheme 11.



Scheme 11: *Synthesis of bis (ylide)-substituted phosphenium ions*

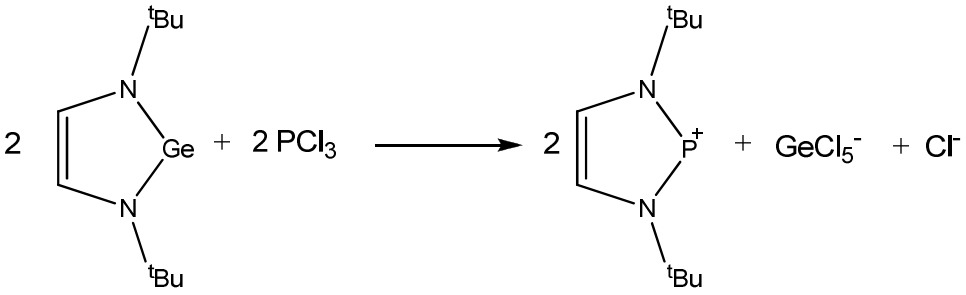
Here, the halophosphine is generated by abstraction of two molecules of trimethylsilyl halide. Rearrangement of the halophosphine follows, resulting in the formation of the phosphenium ion. The ionic nature of the phosphorus-halogen bond is evident from the ^{31}P NMR chemical shift of the central phosphorus atom, which is observed at approximately 300 ppm (depending on the R groups).[22] The autoionization process described in Scheme 11 is also observed with cyclic halophosphines as outlined in Scheme 12. The driving force for this process is the formation of an aromatic-like system (as described in section 1.1), which further stabilizes the resulting phosphenium ion.[20]



Scheme 12: *The autoionization process of an N-heterocyclic chlorophosphine affording a phosphenium ion*

1.2.4 Synthesis of Phosphenium Ions Through Atom (Ge) Displacement

Phosphenium ions can also be generated by reacting a germylene with PCl_3 as outlined in Scheme 13. At the start of the reaction the germanium atom is displaced by phosphorus trichloride resulting in the formation of a cyclic chlorophosphine, which is further autoionized to yield a phosphenium ion as described in Section 1.2.3. The driving force for the autoionization observed is the formation of a partially aromatic system (the charge is less localized compared to completely aromatic systems), which stabilizes the phosphenium ion formed.[29]



Scheme 13: *Synthesis of a cyclic phosphenium ion from a germylene*

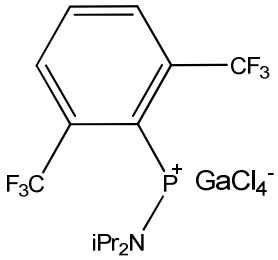
1.3 Spectroscopic and Crystallographic Properties

Many different types of phosphenium ions have been structurally characterized, and a good survey of these data is presented by Cowley.[1] The majority of phosphenium ions are *bis*-or *mono*-(amido)-substituted of the type $(R_2N)_2P^+$ or $(R_2N)XP^+$, where X usually is carbon chlorine or silicon. Thus, in this section primarily the *mono*- and *bis*-(amido) phosphenium ions will be discussed.

1.3.1 Crystallographic Properties

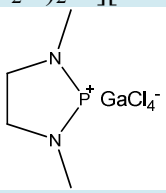
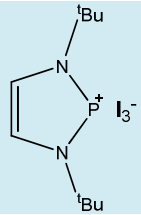
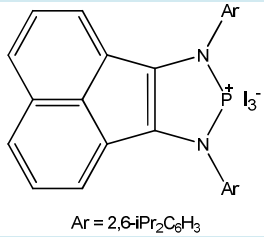
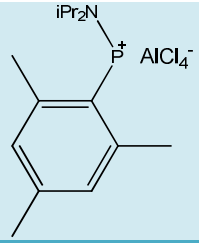
In Table I, the most important geometric characteristics of some representative examples of phosphenium ions are outlined. From a crystallographic point of view, apart from the planar NPN configuration and the approximate sp^2 hybridization of the phosphorus atom already mentioned for phosphenium ions, a deviation of the NPN angle from the ideal value of 120° is observed in the majority of acyclic phosphenium ions. For example, for the $[(iPr_2N)_2P]^+$ ion the NPN angle has a value of only 114.8°.[30] This has been attributed to the repulsions between the two P-N bonds and the phosphorus lone electron pair.

Another important piece of information obtained from the crystallographic analysis of phosphenium ions concerns the nature of the interaction between the phosphorus centre and the counterion. By comparing the distance between the phosphorus atom and the closest atom of the counteranion with the sum of the van der Waals radii of the two, one can decide if the bonding is covalent (the phosphorus-counterion distance is smaller than the Van der Waals radii) or ionic (the phosphorus-counterion distance is larger than the Van der Waals radii). For example, in phosphenium ion **22** the value of the shortest P···Cl contact is 3.378(9) Å, while the sum of the van der Waals radii between phosphorus and chlorine is 3.55 Å. The P···Cl interaction is shorter than the sum of the van der Waals radii of phosphorus and chlorine by 0.17 Å, which means that there is some covalent bonding present between the phosphorus centre and $GaCl_4^-$. Nevertheless, since the difference between the sum of the van der Waals radii of phosphorus and chlorine and the observed P···Cl interaction is fairly small, the bond between phosphorus and $GaCl_4^-$ can be considered ionic enough in order for **22** to be considered as a phosphenium ion.[11]



22

Table I. Selected Bond Lengths (Ångstroms) and Angles (Degrees) for some common phosphenium ions where X = N' or C

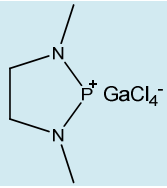
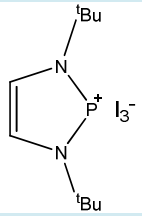
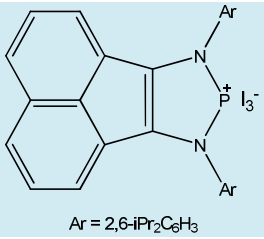
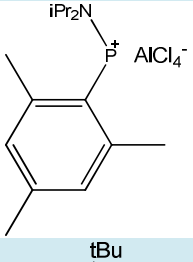
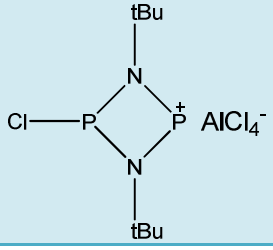
Phosphenium Ion	Bond lengths (P-X)		Bond angles (NPX)	Reference
	P-N	P-X		
$[(iPr_2N)_2P^+][AlCl_4^-]$	1.611(4)	1.615(4)	114.8(2)	30
$[(iPr_2N)_2P^+][GaCl_4^-]$	1.601(13)	1.587(12)	117.0(7)	23
	1.56(2)	1.58(2)	99.0(11)	23
	1.664(3)	1.663(4)	90.14(17)	28
	1.694(4)	1.689(4)	90.23(17)	26
	1.617(5)	1.787(6)	107.0(3)	25

1.3.2 The ^{31}P NMR Spectra of Phosphenium Ions

The most important spectroscopic technique applied in order to characterise and identify phosphenium ions is ^{31}P NMR spectroscopy. Most phosphenium ions resonate at high frequency due to their lack of electron density at phosphorus, usually giving rise to sharp singlet resonances in the region of +111.0 to +513.2 ppm. The lower value of this

range, +111.0 ppm, corresponds to the phosphenium ion $[(Me_5C_5)(Me_2N)P]^+$.[31] This unusual chemical shift is attributed to the multihapto coordination mode of the $Me_5C_5^-$ substituent. The $(iPr_2N)_2P^+$ ion resonates at 313 ppm in its ^{31}P NMR spectrum (somewhere in the middle of the range), while the higher value of 513.2 ppm corresponds to the mono-amido substituted phosphenium ion $[(iPr_2N)(tBu)P^+][AlCl_4^-]$ and results from the lack of an electron donating amido substituent. In Table II the ^{31}P NMR chemical shifts of some common phosphenium ions are outlined.

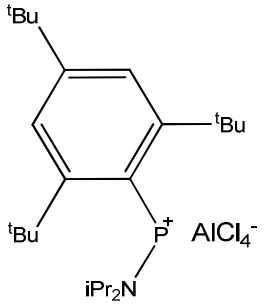
Table II. ^{31}P NMR Chemical Shifts (ppm) for some common phosphenium ions

Phosphenium Ion	^{31}P NMR Chemical Shift	Reference
$[(Me_2N)_2P^+][AlCl_4^-]$	264	32
$[(Et_2N)_2P^+][AlCl_4^-]$	263	33
$[(iPr_2N)_2P^+][AlCl_4^-]$	313	1
$[(iPr_2N)(Cl)P^+][AlCl_4^-]$	334	34
$[(Me_2N)(tBu)P^+][AlCl_4^-]$	513.2	12
	269	23
	204.3	28
	234.5	26
	500	25
	365.7	12

Generally, the ^{31}P NMR chemical shifts of phosphenium ions are affected in a predictable way by varying the groups bonded to the phosphorus. Thus, replacing an NMe_2 group for a Cl in $[(Me_2N)_2P]^+$ results in deshielding of the phosphorus atom due to the higher electronegativity of the Cl atom, while replacing the Cl atom with a t-Bu group results in an even greater deshielding due to the inability of the t-Bu group to π-donate.

Another trend observed is that an increase in bulk of the NR_2 substituents leads to higher frequency shifts in the ^{31}P NMR spectra. For example, the phosphenium ion $[(Me_2N)_2P^+][AlCl_4^-]$ has a ^{31}P NMR chemical shift of 264 ppm, which is 49 ppm to lower frequency compared to $[(iPr_2N)_2P^+][AlCl_4^-]$, which resonates at 313 ppm. This results from the steric constraints/repulsion created by these isopropyl substituents, which force the P-N bonds to rotate. As a consequence the nitrogen p_z orbital and the phosphorus p_z orbital overlap less effectively lowering the degree of N→P electron donation.[1]

In some rare cases coupling of the phosphorus to the nitrogen of the amido ligands is observed in the ^{31}P NMR spectra. For example a broad resonance is observed in the ^{31}P NMR spectrum of compound **23** at 423 ppm,[11] while for compound **24**, a 1:1:1 triplet resonance is observed at 500 ppm. This is attributed to coupling of the phosphorus with the nitrogen atom (J_{PN} = 65 Hz). Although nitrogen is a quadrupolar nucleus and doesn't always give rise to observable coupling with other nuclei sometimes coupling is observed.[25] This is probably due to the low electric field gradient of the nitrogen atom in phosphenium ion **24**, which therefore allows it to couple with the phosphorus atom.



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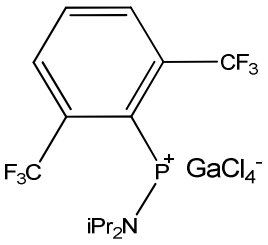
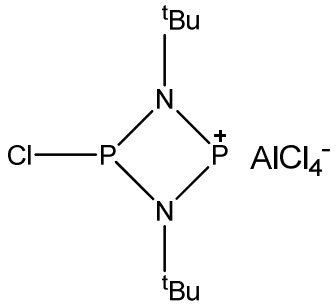


23

Another example of a phosphenium ion with a broad ^{31}P NMR resonance is the cyclic phosphenium ion **25**. At - 40 °C an AB type spectrum is observed, while at 70 °C there is only one broad resonance apparent. It is speculated that this broadening stems from the intramolecular transfer of the Cl atom between the two phosphorus centers.[9]

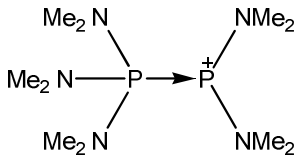


25

1.3.3 The ^{1}H NMR and ^{13}C NMR Spectra of Phosphenium Ions

In the ^{1}H NMR or ^{13}C NMR spectra of phosphenium ions broadening is sometimes observed (depending on the nature of the NR_2 groups), which diminishes their diagnostic utility at ambient temperature. Sometimes this broadening is associated with the rotation of the NR_2 group around the P-N bond at a rate equivalent to the spectroscopic time-scale. Hence, at lower temperatures where the rotation is slower, the peaks become sharper. For example, the phosphenium ion $(iPr_2N)_2P^+$ displays a very broad resonance in its ^{1}H NMR spectrum at 290 K. However, when the temperature is lowered to 220 K, two sharp doublets are revealed.[10]

Broadening of the NMR spectra is even observed for phosphenium ion adducts such as compound **26**. In the ^{1}H NMR spectrum of this compound at ambient temperature only one broad resonance is observed for the methyl groups instead of the expected two quartets (due to coupling with the two phosphorus atoms) for the two proton environments. Indeed in, the ^{31}P NMR spectrum no peak could be observed due to extreme broadening. When the spectra are recorded at -50 °C the expected signals were evident. This behaviour was assigned to a rapid exchange process where one NMe_2 group moves from one phosphorus to the other and diminishes the differences between the two phosphorus centers.[35]



26

1.3.4 The ^{35}Cl NMR Spectra of Phosphenium Ions

It has been mentioned in Section 1.2 that sometimes a phosphenium ion, if stable enough, might form directly from the precursor halophosphine with automatic abstraction of a Cl^- ion. Nevertheless, there is still an interaction between the positively charged phosphorus centre and the Cl^- anion. It is crucial to determine if this interaction is weak enough in solution in order to consider the compound as a phosphenium ion and not as a chlorophosphine with an elongated P-Cl bond. This can be determined in solution with the help of ^{35}Cl NMR spectroscopy. Although coupling between phosphorus and chlorine can't be observed due to the rapid quadrupolar relaxation of the latter (and thus one can't compare the J_{PCl} coupling constants), comparison of the linewidths of the signal in the ^{35}Cl NMR spectra can be used to determine whether the Cl atom is in its ionic or in covalent form. The low electric field gradient in the highly symmetric Cl^- ion results in sharp resonances in the NMR spectra, while in a highly asymmetric chlorophosphine broad resonances should be observed. Thus broad ^{35}Cl NMR resonances indicate covalent bonding while sharp resonances indicate presence of free Cl^-.[21]

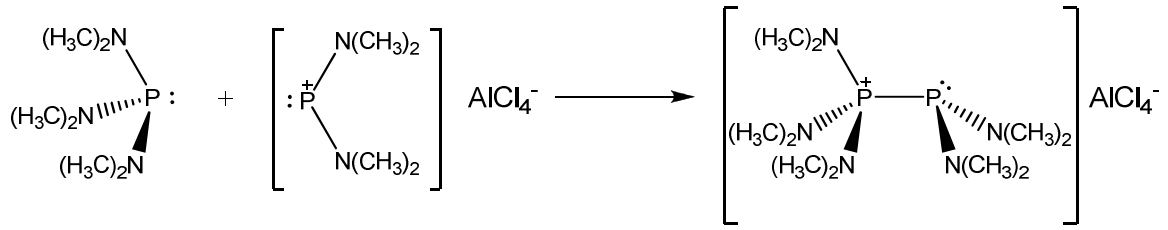
1.4 Characteristic Reactions of Phosphenium ions

Since phosphenium ions have an empty p_z orbital on the phosphorus atom along with a filled sp^2 orbital, they can act as both Lewis acids and Lewis bases. This ambiphilic character is evident from the capability of phosphenium ions to participate in complexation reactions with metals where the phosphenium ion acts as a Lewis base,[36,37] or in cycloadditions to alkynes and alkenes where they act as Lewis acids.[38] Because of these properties phosphenium ions are versatile reagents and participate in a wide variety of reactions, which are too numerous to describe here, but which have been reviewed.[1] A summary of various general types of reaction are given below.

1.4.1 Reactions with Phosphines

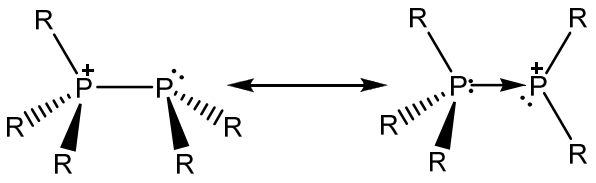
Due to their strong Lewis acidity, phosphenium ions react with phosphines to afford phosphinophosphonium ions (or phosphine-stabilized phosphenium ions) as described in Scheme 14. These diphosphorus-containing salts can be identified *via* ^{31}P

NMR spectroscopy at -50 °C (at ambient temperature no signal is observed probably due to an exchange process between the NMe_2 groups) from the characteristic doublet of doublets pattern arising from coupling between the two phosphorus atoms.[39,35]



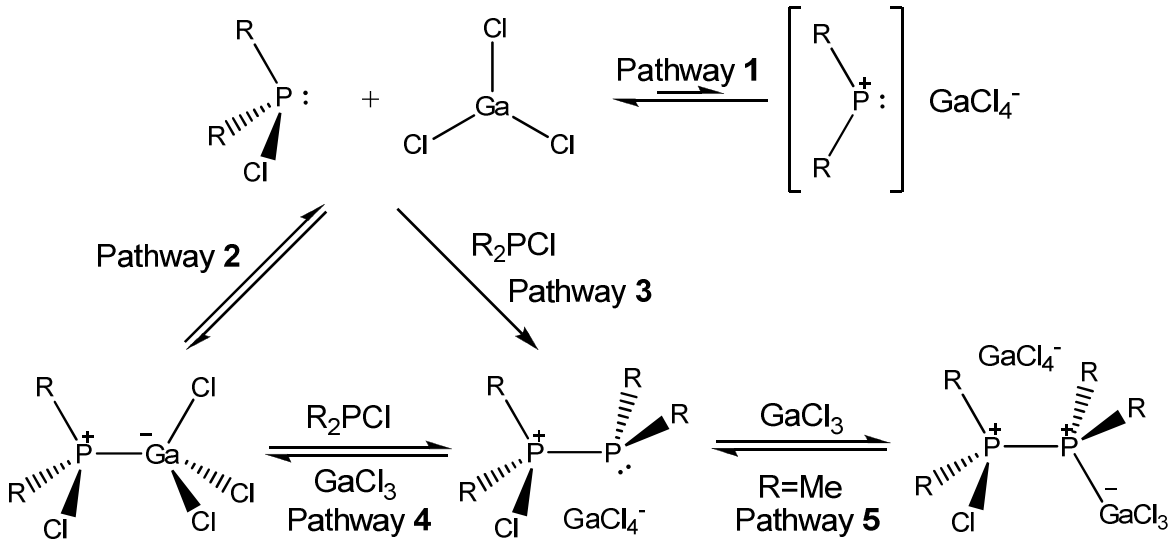
Scheme 14: *Synthesis of a phosphinophosphonium ion*

This type of reaction can also occur during the formation of a phosphenium ion between the unreacted chlorophosphine and the phosphenium ion that has formed so far (from this point of view phosphinophosphonium ions can be considered as intermediate species during phosphenium ion formation). Of course, it would be expected that formation of a phosphinophosphonium ion would occur if a chlorophosphine is reacted with half an equivalent of a Lewis acid such as $AlCl_3$ or $GaCl_3$. This is indeed often the case, but not always, because phosphinophosphonium ions **27** can also be regarded as complexes of phosphenium ions with phosphines **28** as has already been mentioned earlier in the text.



27 **28**

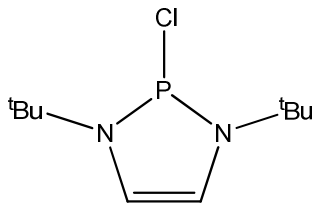
Hence, the formation of the P-P bond can be reversible giving rise to various types of equilibria and interactions with the compounds in the reaction mixture. A characteristic example of such behaviour is the case of the (dialkyl/diaryl)chlorophosphine-gallium chloride system, which is described below (Scheme 15).



Scheme 15: *The (dialkyl/diaryl)chlorophosphine-gallium chloride system*

The formation of each product described in Scheme 15 is favoured depending on the nature of the R substituents and the stoichiometry between the gallium chloride and the chlorophosphine. Thus, if the stoichiometry is 1:1, amido groups would favour Pathway 1 due to stabilization of the resulting phosphenium ion, while alkyl or aryl substituens would favour Pathway 2. If half an equivalent of gallium chloride (stoichiometry 1:2) is added, then Pathway 3 is favoured resulting in the formation of a phosphinophosphonium ion, which can also be formed by addition of R_2PCl through Pathway 4. Lastly, if R=Me and the molar ratio $GaCl_3$: chlorophosphine is 2:1 the phosphinophosphonium ion can further react through Pathway 5.[40]

The observations described in Scheme 15 imply that coexistence of a phosphenium ion with its precursor chlorophosphine in the same solution results in the formation of phosphine-phosphonium ions (Pathway 3 and 4). Nevertheless, this is not always the case. For example, when phosphenium triflate **30** is added to a solution of the corresponding chlorophosphine **29**, one resonance is observed in the ^{31}P NMR spectrum of the reaction mixture (even at – 70 °C), the chemical shift moving to higher frequency with addition of the phosphenium triflate.



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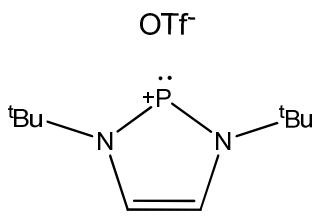
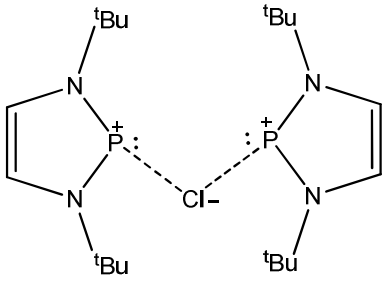


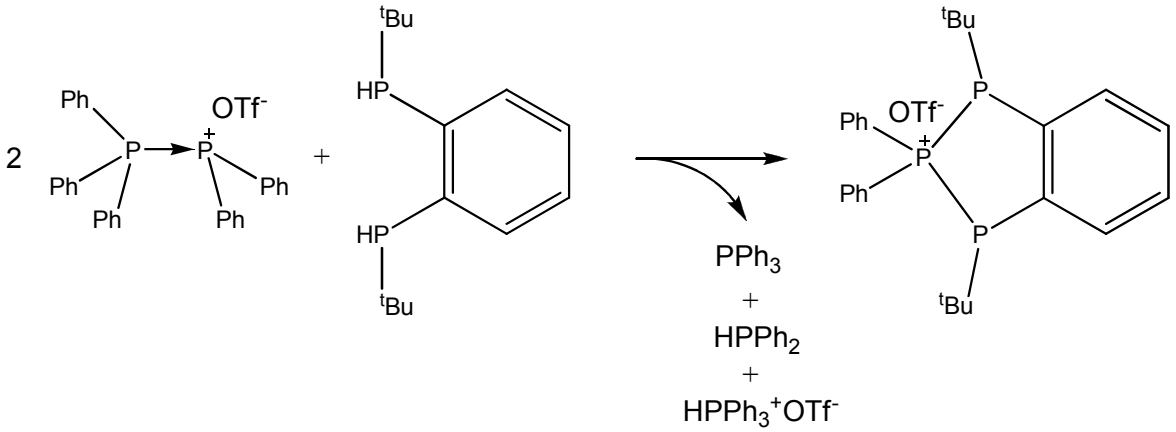
30

This result along with computational studies led to the conclusion that a symmetrical product **31** could be present instead of the expected phosphinophosphonium ion. Adduct **31** can be regarded as two phosphenium ions coordinated to a chloride anion, which acts as a bridge, just as for a Cl-bridged bimetallic complex. This kind of bonding explains the singlet resonance observed in the ^{31}P NMR spectrum since the two phosphorus atoms are now equivalent.[38]



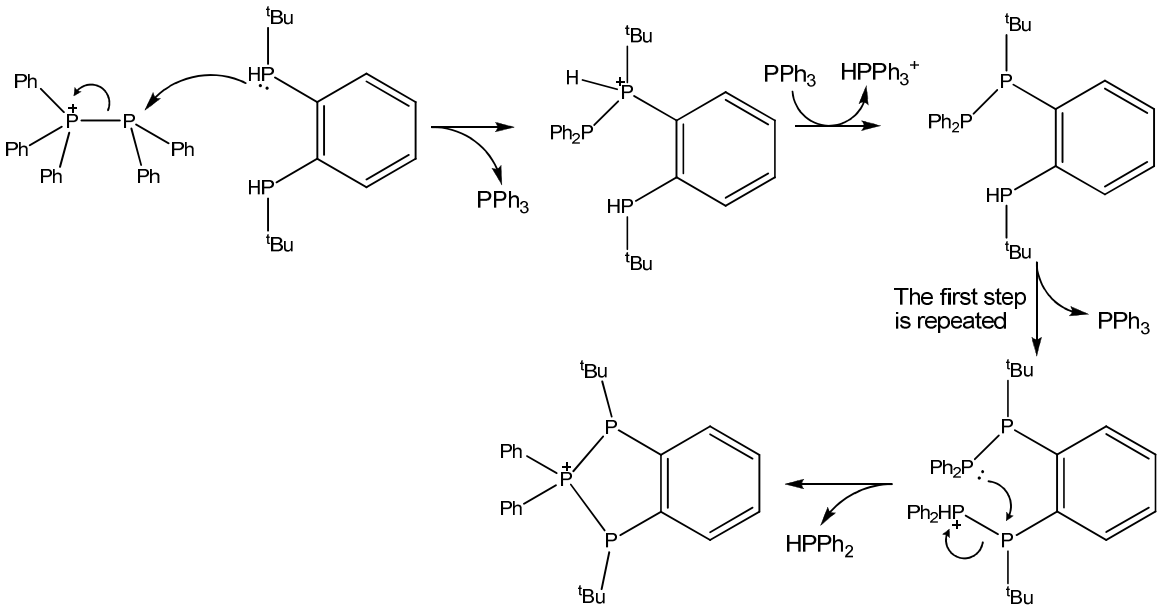
31

Phosphine-stabilised phosphenium ions can further react with various substrates. A characteristic example is the reaction between triphenylphosphine-diphenylphosphenium trifluoromethanesulfonate and 1,2-*bis*(di-*tert*-butylphosphino)benzene outlined in Scheme 16.



Scheme 16: *Reaction of a phosphinophosphenium ion with an aromatic diphosphine*

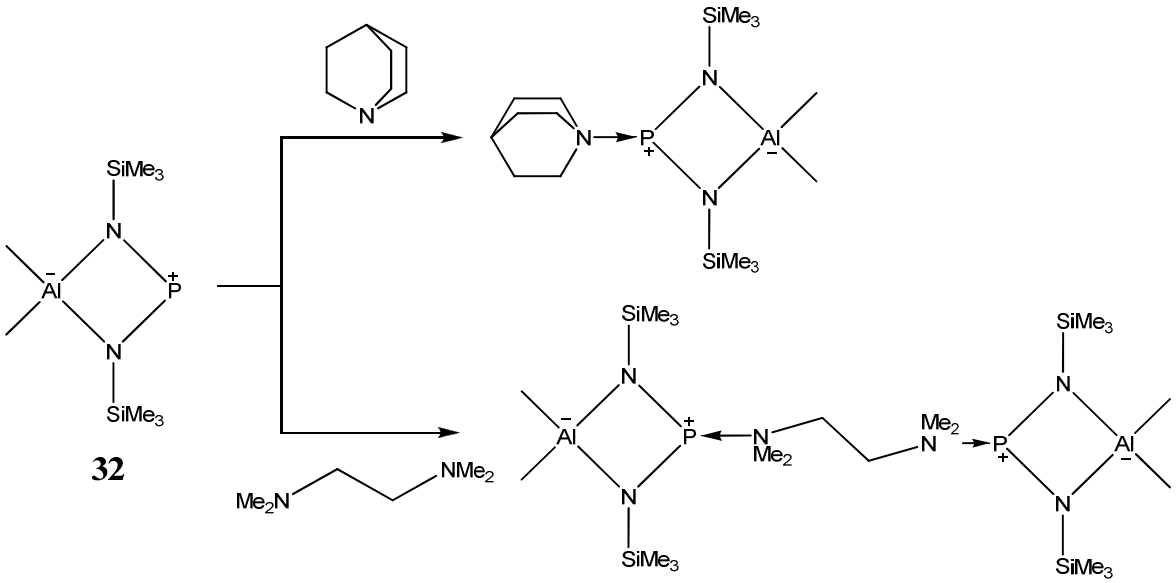
On monitoring this reaction by ^{31}P NMR spectroscopy, the formation of PPh_3 (δ = -5 ppm), $HPPh_2$ (δ = -40 ppm) and Ph_3PH^+ (δ = 2 ppm) is observed. This lead to the proposed mechanism described in Scheme 17. It is evident that the reaction is equivalent to the dehydrogenation of the diphosphine, which further reacts with the phosphenium ion "Ph_2P^+" towards the final product.[15]



Scheme 17: *Modified scheme describing the reaction mechanism of a phosphine stabilized phosphenium ion with an aromatic diphosphine taken from Burford et al. (2003)*[15]

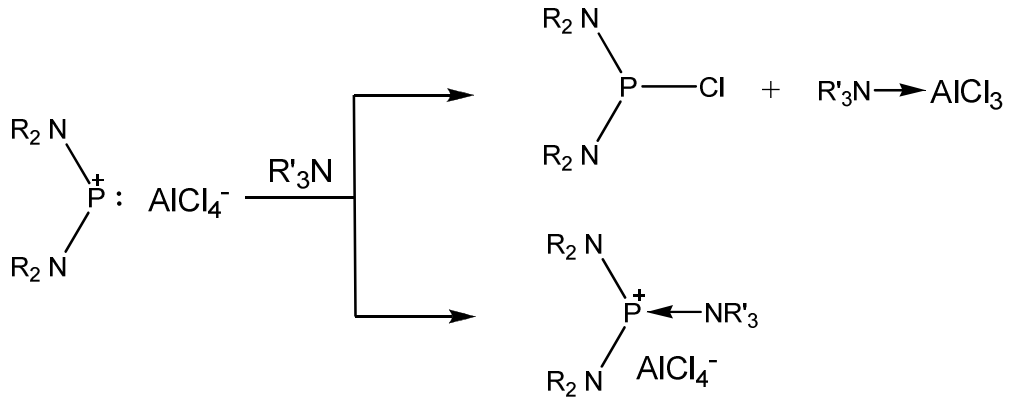
1.4.2 Reactions with Amines

Since amines posses a basic electron pair, it is reasonable to assume that they will form adducts analogous to the ones formed by reacting phosphenium ions with phosphines. For example, the Zwitterionic phosphenium ion **32** readily reacts with quinuclidine or tetramethylethylenediamine as outlined in Scheme 18.[41]



Scheme 18: *Reactions of a phosphenium ion with tertiary amines*

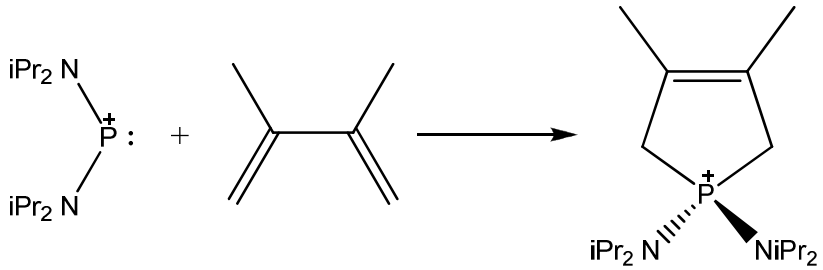
Nevertheless, the aluminate salts of phosphenium ions will not always react with amines in the expected way, namely through an elecrophilic attack of the amine nitrogen lone pair at the phosphorus centre. Instead, the amine can also attack the $AlCl_4^-$ ion displacing a Cl^- ion, which binds with the phosphenium centre in order to yield the chlorophosphine as described in Scheme 19. The way in which the phosphenium tetrachloroaluminate will react with an amine, depends on the basicity of the amine towards the counterion and the steric bulk of the substituents of the amine used.[32]



Scheme 19: *Reaction of a phosphenium tetrachloroaluminate salt with tertiary amines where R, R' = aryl or alkyl groups*

1.4.3 Cycloaddition Reactions

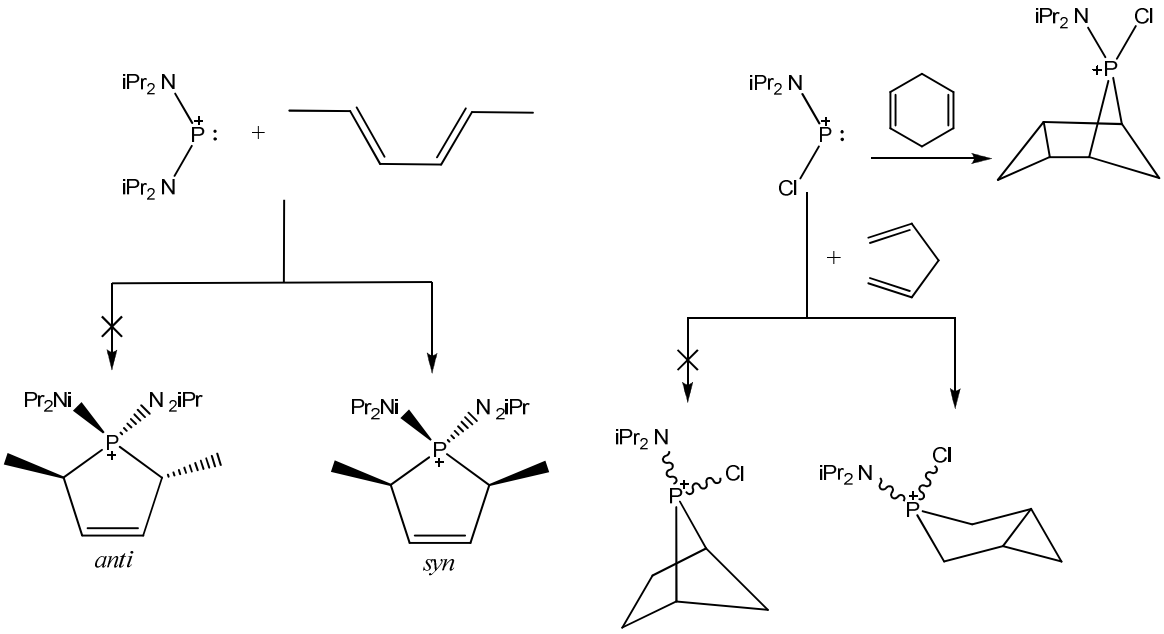
One of the most characteristic reactions of phosphenium ions is their cycloaddition with dienes. Thus, $(iPr_2N)_2P^+$ reacts with 2,3-dimethyl-1,3-butadiene as described in Scheme 20.



Scheme 20: *Reaction of a phosphenium ion with a 1,3-diene*

The characteristics of this type of reaction strongly depend on both the groups on the diene and those on the phosphenium ion, with bulky substituents resulting in longer reaction times. For example, reaction of $(iPr_2N)_2P^+$ with *trans*-2-*trans*-4-hexadiene takes 9 days to reach completion. In contrast, the less bulky $(Me_2N)_2P^+$ phosphenium ion also reacts within one hour with the less bulky isoprene.[42,43]

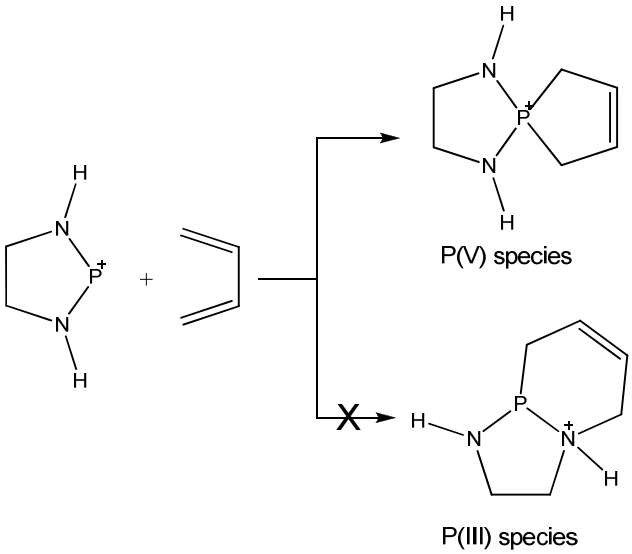
Another interesting aspect of these types of cycloaddition reactions is their stereoselectivity. Thus, reaction of $(iPr_2N)_2P^+$ with *trans*-2-*trans*-4-hexadiene results in the formation of only one product, namely the one with the methyl groups in a *syn* conformation (Scheme 21), which points towards a [2+4] chelotropic cycloaddition mechanism.[42,43]



Scheme 21: *Stereospecific reactions of phosphenium ions with dienes*

Phosphenium ions can also react with 1,4 dienes. For example, $(iPr_2N)ClP^+$ reacts with 1,4-pentadiene as described in Scheme 21. This reaction proceeds with a specific topology by 1,5-cycloaddition and not by 2,4-cycloaddition, which could be an alternative pathway, for unknown reasons.[42,43] As expected, $(iPr_2N)ClP^+$ can also react with 1,4-cyclohexadiene resulting in the formation of a tricyclic compound with a three-membered ring according to the reaction outlined in Scheme 21.[34] One question that arises regarding the reaction of phosphenium ions with dienes, is why the formation of a P(V) species through a cheletropic cycloaddition is preferred over the formation of a P(III) species through a Diels-Alder cycloaddition as described in Scheme 22, since formation of a C-N (75.0 Kcal/mol) and a C-P (66 Kcal/mol) bond is thermodynamically favoured over the formation of two C-P (131.8 Kcal/mol) bonds by comparing the empirical bond energies. The question becomes even more interesting if one considers that both chelotropic and Diels-Alder mechanisms are possible in respect of the interactions between the π-type and lone pair frontier orbitals of the reactants. Nevertheless, computational studies have shown

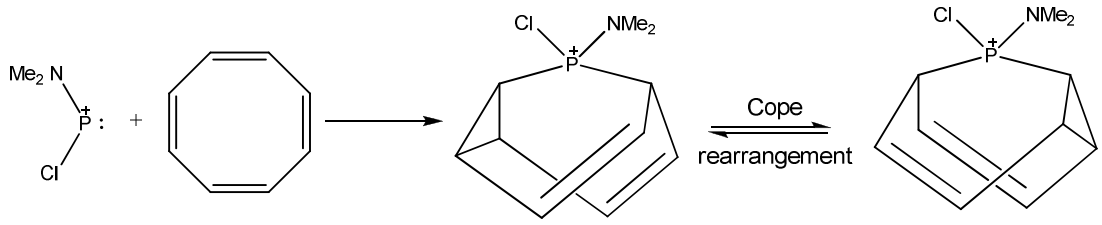
that the P(V) species is more thermodynamically stable compared to the P(III) species by 12 Kcal/mol and thus is formed preferentially.[5]



Scheme 22: *The two possible pathways for the reaction between a phosphenium ion and a diene*

1.4.4 Reactions with other Unsaturated Systems

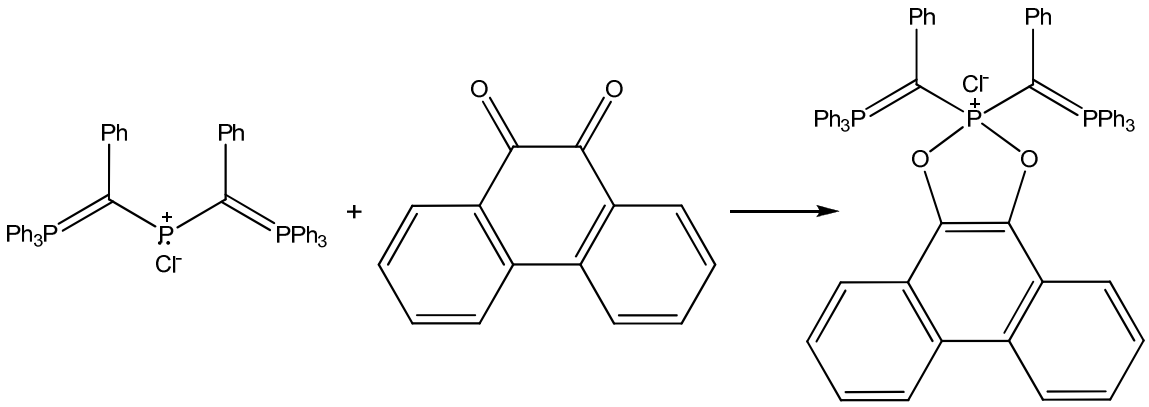
Another example demonstrating the unique reactivity of phosphenium ions towards unsaturated systems is outlined in Scheme 23, where the reaction of $[(Me_2N)ClP^+][AlCl_4^-]$ with cyclooctatetraene[44] is described. Here, cyclooctatetraene is added to $[(Me_2N)ClP^+][AlCl_4^-]$ affording the phosphonium ion **33**, which is an interesting species since it undergoes Cope rearrangement with a barrier of 12 ± 1.7 Kcal/mol.



33

Scheme 23: *Reaction of phosphenium ions with cyclooctatetraene and cyclo-octa-1,5-diene*

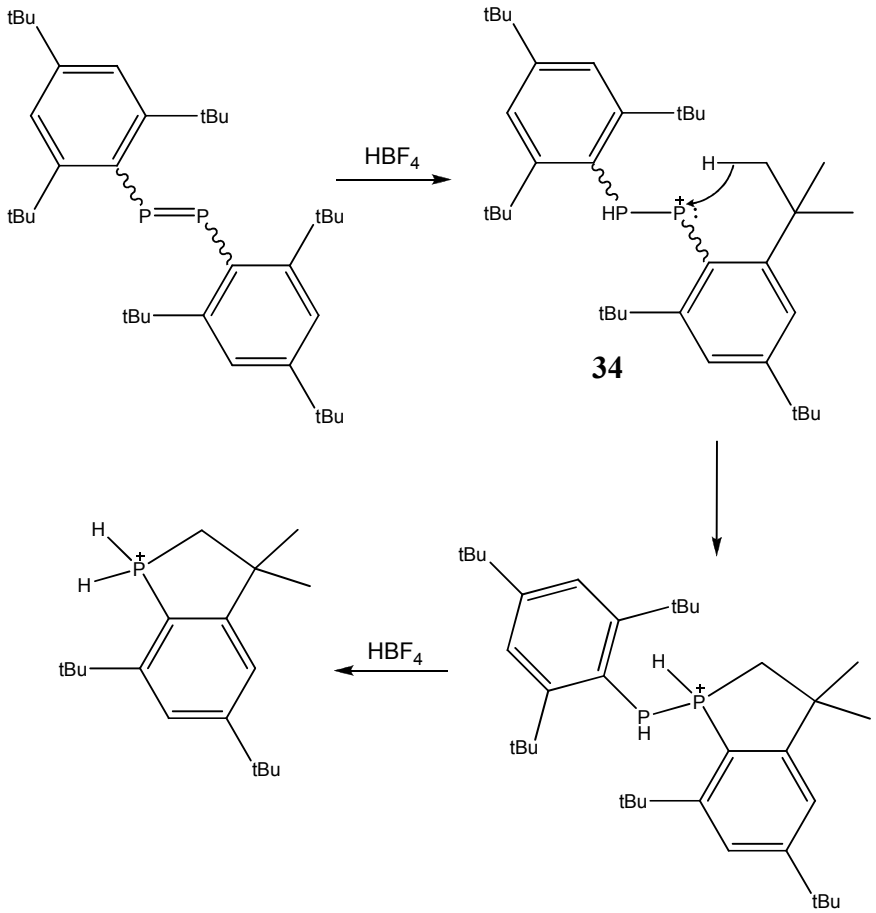
Nevertheless, not all phosphenium ions are reactive towards dienes. For example some of the *bis*(ylide)-substituted phosphenium ions mentioned in Section 1.1 are stable enough in order not to react with a diene. Instead, they require a more reactive substrate, such as an orthoquinone, as described in Scheme 24. These reactions occur strictly by a [4+2] cycloaddition.[22]



Scheme 24: *Reaction of a bis(ylide)-substituted phosphenium ion with an orthoquinoline*

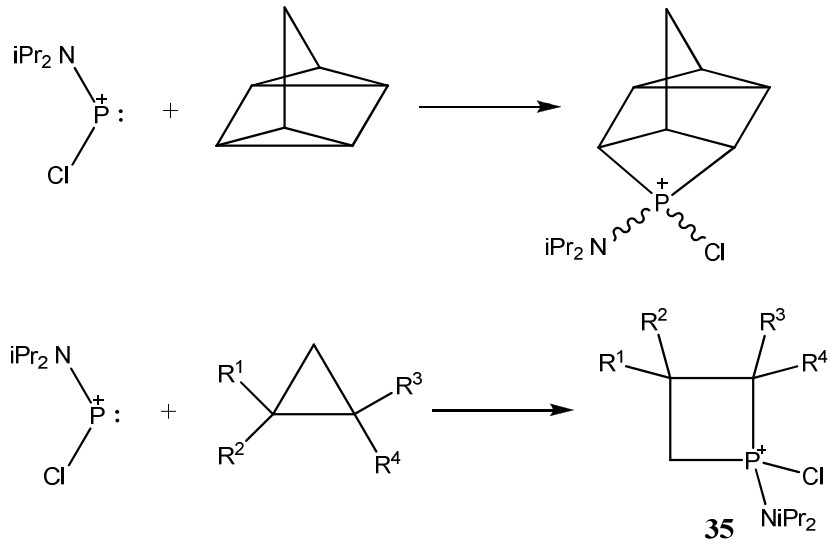
1.4.5 C-C and C-H Oxidative Additions

Phosphenium ions sometimes are intermediate species in various reactions and thus can be used in order to predict the reaction's mechanism. For example, treatment of (2,4,6-$(tBu)_3C_6H_2$)P=P(2,4,6-$(tBu)_3C_6H_2$) with an equimolar amount of dry, gaseous HCl results in formation of a reactive phosphenium ion intermediate (compound **34**), which undergoes intramolecular C-H oxidative addition in order to form a phosphonium ion (Scheme 25).[7]



Scheme 25: *A reactive phosphenium ion intermediate*

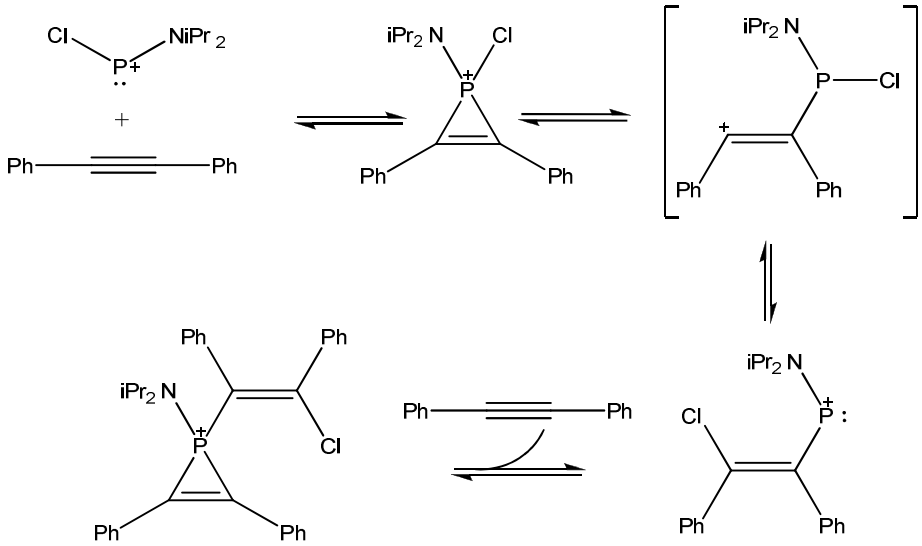
Apart from C-H oxidative addition, phosphenium ions are also capable of C-C oxidative addition reactions. Thus, addition of $(iPr_2N)ClP^+$ to a solution of a quadricyclane results in the formation of a phosphonium ion through C-C oxidative addition as described in Scheme 26. The driving force for this reaction is probably the instability of the three-membered ring.[45] The same type of reaction can occur with substituted cyclopropanes in order to yield phosphetanium ions (**35** in Scheme 26).[46]



Scheme 26: *Examples of oxidative addition of a phosphenium ion to a C-C bond*

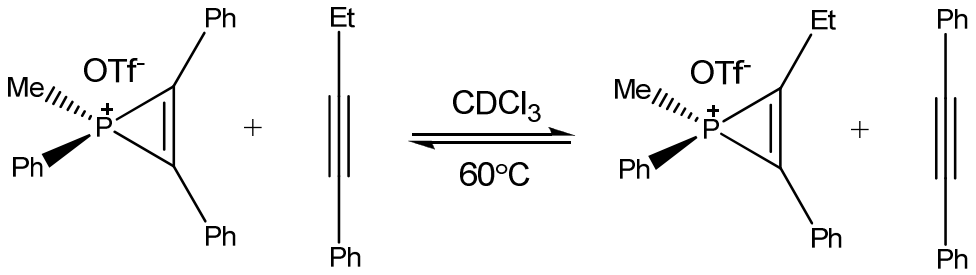
1.4.6 Reactions with Alkynes

Reaction of phosphenium ions with alkynes leads to the formation of phosphirenium ions.[47] This occurs *via* a [2+2] cycloaddition of the phosphenium ion to the triple bond. An example of such a transformation is outlined in Scheme 27.



Scheme 27: *Formation of phosphirenium ions*

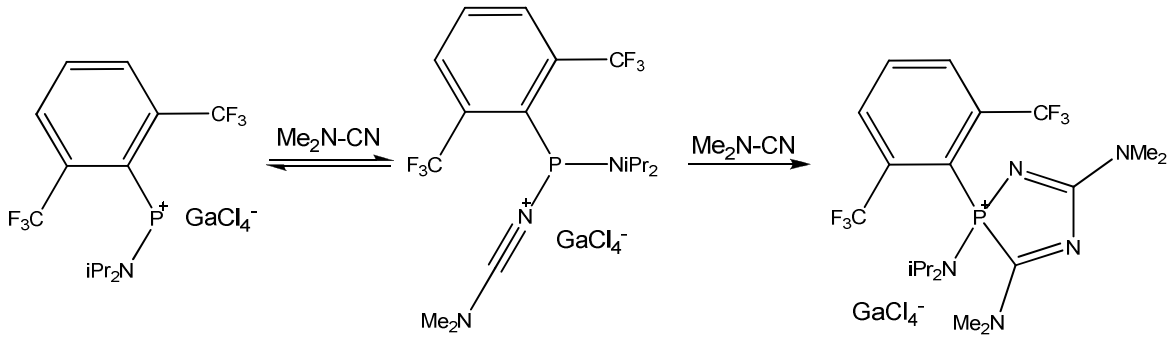
This reaction is of special interest since the phosphirenium ion initially formed undergoes ring-opening affording an intermediate vinyl cation, which rearranges to the vinyl phosphenium cation as described in Scheme 12. Addition of a second equivalent of diphenyl acetylene leads to the formation of a vinyl phosphirenium ion.[48] Phosphirenium ions are interesting species in their own right due to their potent aromaticity. An empty d orbital of the phosphorus atom can be used in order for the phosphirenium ion to form a three orbital – two electron aromatic system.[49] Also a very interesting property of phosphirenium ions that needs to be mentioned is their ability to reversibly exchange alkynes as described in Scheme 28. This exchange is thought to proceed through a phosphenium ion intermediate. This example demonstrates the importance of phosphenium ions not just as reactants, but also as reactive intermediates.[50]



Scheme 28: *Reversible exchange reaction of a phosphirenium ion with an alkyne*

1.4.7 Miscellaneous reactions

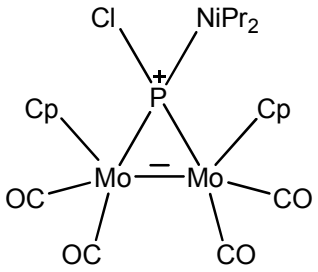
From the above discussion it is evident that phosphenium ions are versatile electrophiles and will react with almost any substrate that possesses a free, relatively basic electron pair. An example of this is the reaction of the phosphenium ion **36** with the carbodiimide Me_2N-CN described in Scheme 29. Firstly, the Me_2N-CN attacks the phosphorus centre with the lone electron pair of the nitrogen atom forming of the phosphenium adduct **37**, which further reacts with a second molecule of Me_2N-CN through a dipolar [3+2] cycloaddition in order to yield the final product **38**.[11]



36 **37** **38**

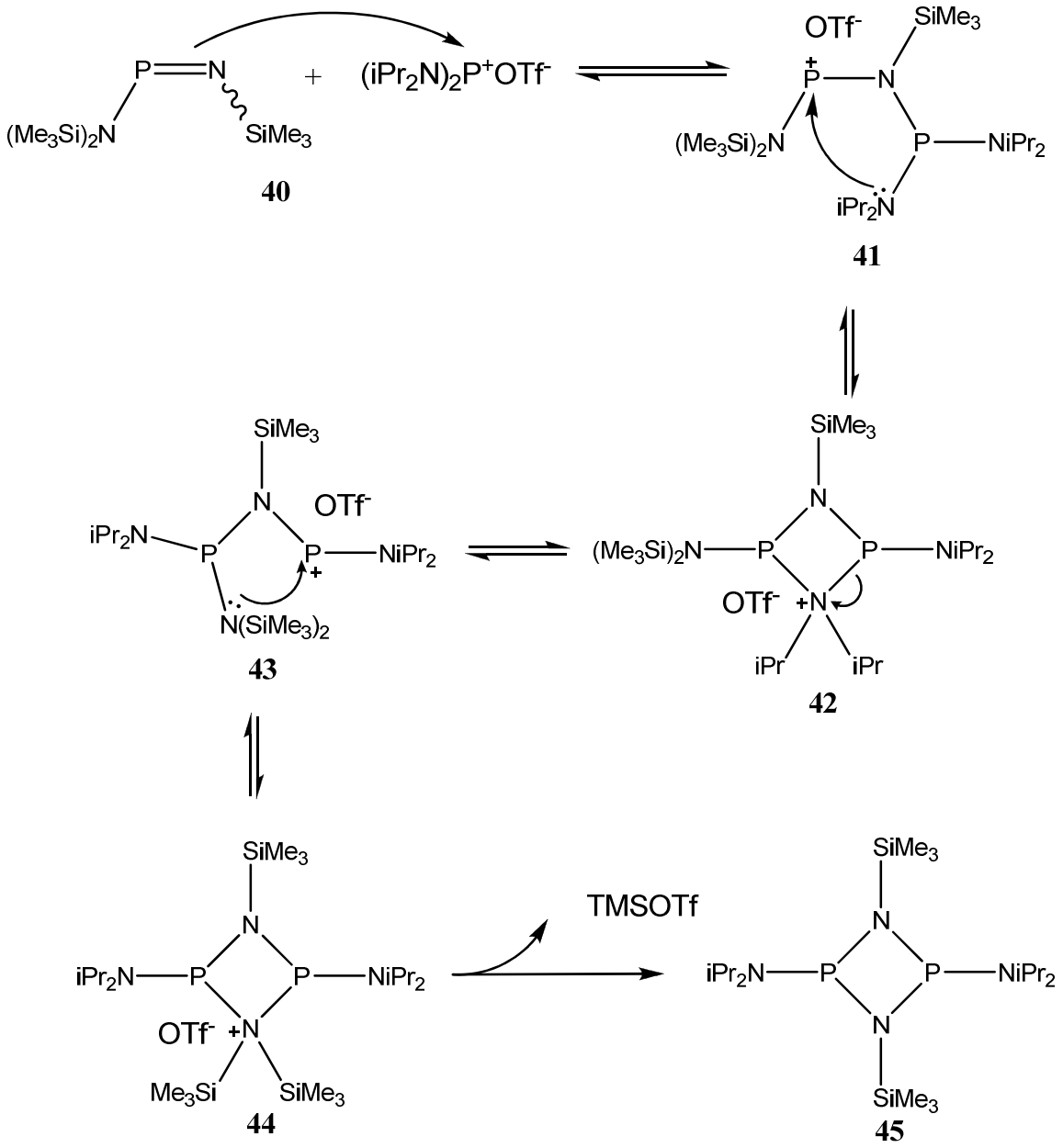
Scheme 29: *Reaction of phosphenium ion **36** with a CN group*

Having examined the reactivity of phosphenium ions towards alkynes, and if one considers the isolobal analogy between alkynes and organometallic compounds containing M-M triple bonds, phosphenium ions should also be able to react with the latter species. This is indeed the case with $Cp(CO)_2MoΞMo(CO)_2Cp$ reacting with $(iPr_2N)ClP^+$ in order to yield the dimetallaphosphirenium ion **39**. This latter reaction highlights the generality of the [2+2] cycloaddition chemistry of phosphenium salts.[1]



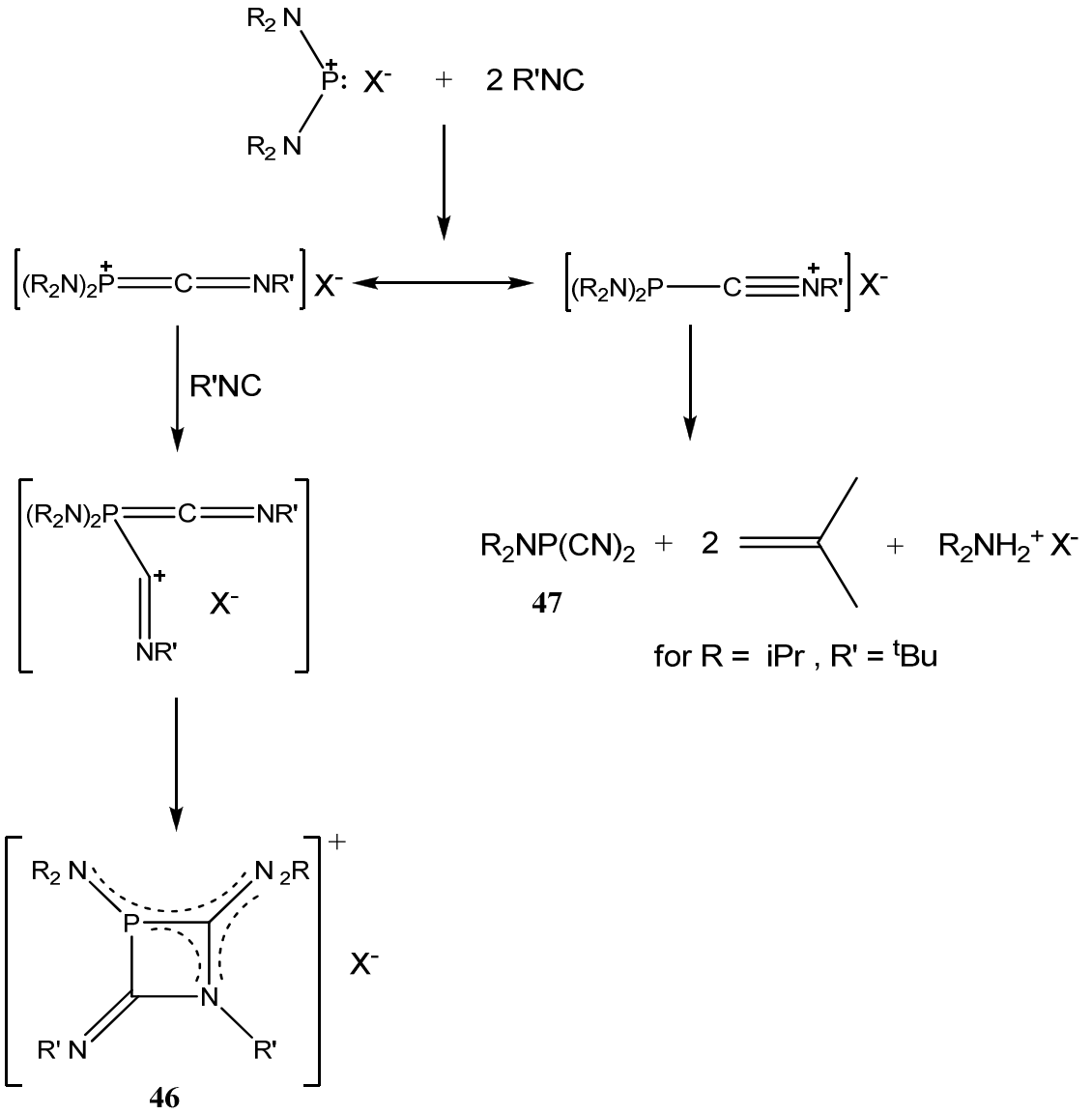
39

Phosphenium ions can also participate in more complicated and unpredictable reactions with "exotic" substrates. Thus, reaction of $(iPr_2N)_2P^+OTf^-$ with the iminophosphorane **40** yields the diazadiphosphetidine **45** by the mechanism outlined in Scheme **30**. During the first step, the $(iPr_2N)_2P^+OTf^-$ attacks the double P=N bond of the iminophosphane **40** giving rise to a second phosphenium ion intermediate **41**, which reacts in an intramolecular fashion with the diisopropylamino group to yield a four-membered cyclic intermediate **42**; this then rearranges to the phosphenium ion intermediate **43**. Intramolecular electrophilic attack at the positively charged phosphorus atom from the $N(SiMe_3)_2$ group followed by formation of TMSOTf completes the process.[51] This example highlights the diverse range of reactivity possible for phosphenium ions.



Scheme 30: *Modified scheme for the mechanism of formation of an diazadiphosphetidine from the reaction of $(iPr_2N)_2P^+OTf$ with an iminophosphorane taken from Sanchez et al.*[51]

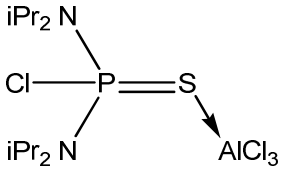
Another example that demonstrates the unique reactivity of phosphenium ions is their reaction with isocyanate compounds, where the phosphenium ion acts as the nucleophile, while the isocyanate as the electrophile. This results in the formation of either a cyclic 1-aza-3-phosphetine cation **46** or a dicyanophosphine **47** and 1,1-dimethylethene if the R and R' substituents are bulky enough as described in Scheme 31. The reaction proceeds through a phosphacumulene cation $(R_2N)_2P^+{=}C{=}NR'$, which is in resonance with the nitrilium salt $(R_2N)_2PC{\equiv}N^+R'$ and results from the nucleophilic addition of the CN group to the phosphorus centre.[52]



46

Scheme 31: *Reaction of phosphenium ions with isocyanates*

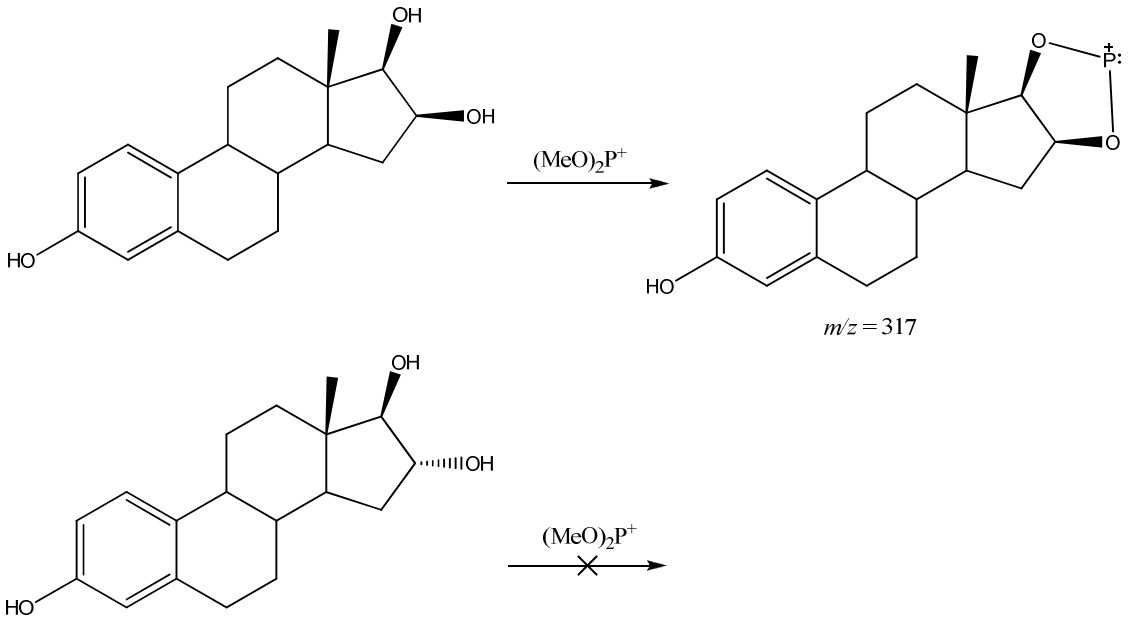
Lastly, phosphenium ions can react slowly with elemental sulfur by oxidative addition. Hence, a solution of $[(iPr_2N)_2P^+][AlCl_4^-]$ in the presence of S_8 reacts within three weeks in order to yield compound **48**.[53]



48

1.5 Applications of phosphenium ions

Apart from being versatile reagents in various reactions (cycloadditions leading to phosphorus heterocycles, formation of phosphonium salts and other phosphorus adducts, *etc*.) and good ligands in the formation of metal complexes, phosphenium ions can also be employed in other, less obvious, applications. For example, the phosphenium ion $(MeO)_2P^+$ may be generated *in situ* in a mass spectrometer and used to distinguish between *cis* and *trans* diols, such as Estriol, for example. The method is based on the fact that the phosphenium ion generated will react only with the *cis* isomer in order to form a positively charged phosphorus species with a characteristic *m/z* value as shown in Scheme 32.[54]

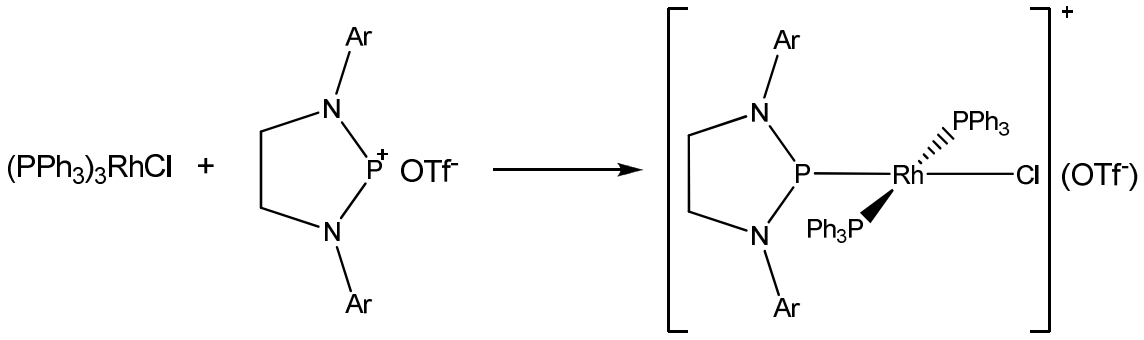


Scheme 32: *Differentiation of cis from trans estriol using a phosphenium intermediate*

It is also reported that phosphenium ions could be used in acquiring information on the charge density at metal centres by measurement of the barrier to the P-N bond rotation. In the parent phosphenium ion the phosphorus is conjugated with the nitrogen atoms. Thus, transfer of electron density into the N_2P antibonding orbitals from a metal following coordination will reduce the double bond character of the NPN system, resulting in a lowering of the P-N rotational barrier that can be measured through variable temperature NMR spectroscopic studies.[10]

Another important feature of phosphenium ions is their potential to be used as ligands for the synthesis of organometallic complexes, which could be in turn used as catalysts due to their high π acidity (*e.g.* $[(Et_2N)_2P^+][OTf^-]$ has a Tolman electronic

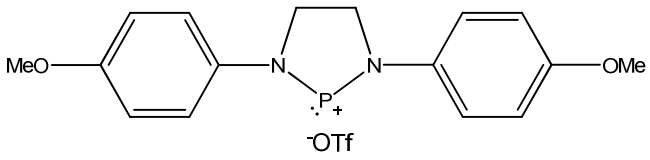
parameter χ similar to PF_3).[55] There are plenty of examples in the literature concerning transition metal complexes with phosphenium ions and their precursor halophosphines. A typical example is the reaction of the cyclic phosphenium ion **49** with Wilkinson's catalyst (Scheme 33).[36] Nevertheless, the extended discussion regarding the metal complexes of phosphenium ions is beyond the scope of this report.



49

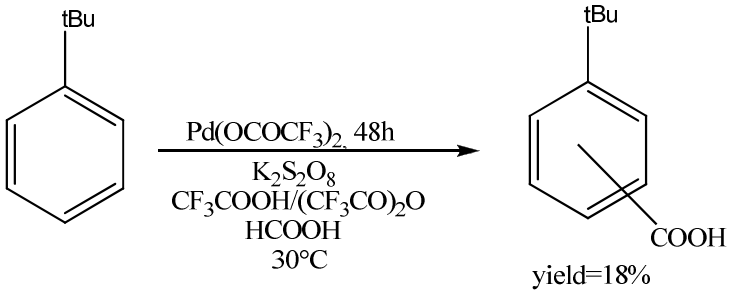
Scheme 33: *Formation of a rhodium complex with a cyclic phosphenium ion as a ligand*

Phosphenium ions have also been used as additives in catalysis (in contrast to their use as discrete ligands). Specifically, the phosphenium ion **50** is reported to greatly increase the yield in the catalytic carboxylation of aromatic rings as described in Scheme 34.



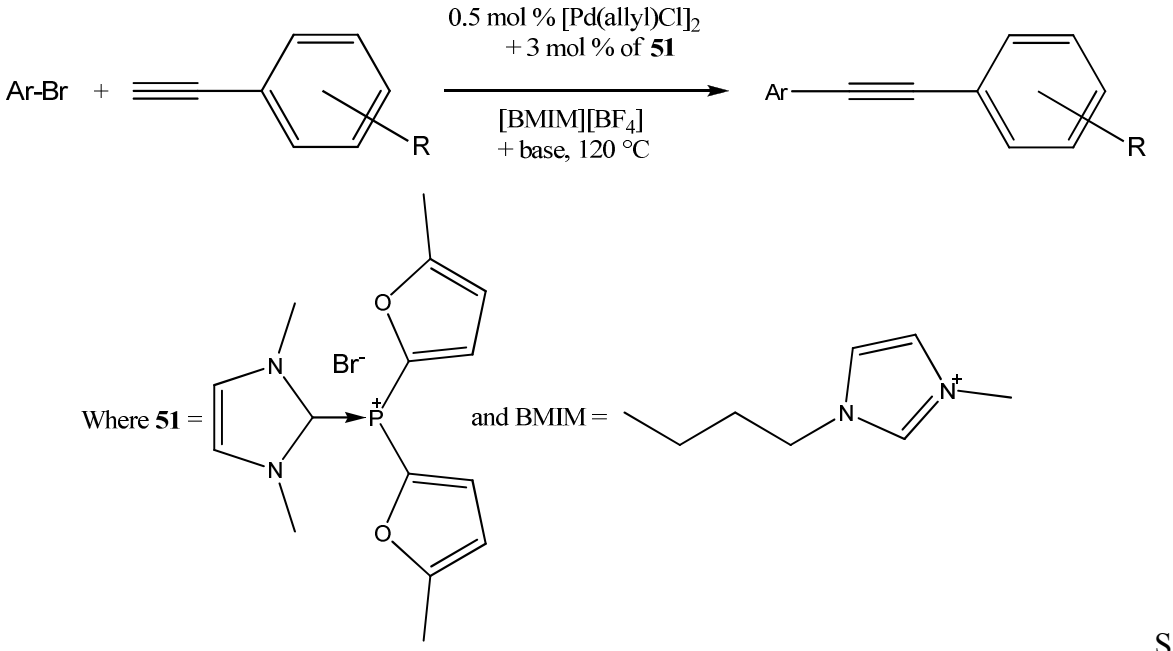
50

The yield in this reaction is 18%, but increases to 84% when 1.1 equivalents (related to the Pd catalyst) of **50** are added. Unfortunately, the reaction's exact mechanism and the role of the phosphenium adduct have not been made clear.[56]



Scheme 34: *The Pd(II)-catalysed carboxylation of aromatic rings*

Lastly, another potent application of phosphenium ions in catalysis is their use in the synthesis of Pd(0) complexes. It is known that Pd(0) – phosphine complexes participate as catalysts in a wide variety of transformations like Suzuki couplings, for example. It has been proposed that the anion $[Pd(PR_3)X]^-$ is the active species in such reactions, and would be stabilized by increasing the electron withdrawing character of the phosphinic ligands. Thus, it becomes evident that phosphenium ions should be excellent ligands from this point of view, due to their increased π-acidity. However, there are few investigations conducted on this topic to date.[57] Donor-stabilized phosphenium adducts can also be used as ligands in palladium-catalyzed reactions. For example, compound **51** has been employed as an additive for the palladium-catalyzed aryl alkynylation process in an ionic liquid phase as outlined in Scheme 35.[58]



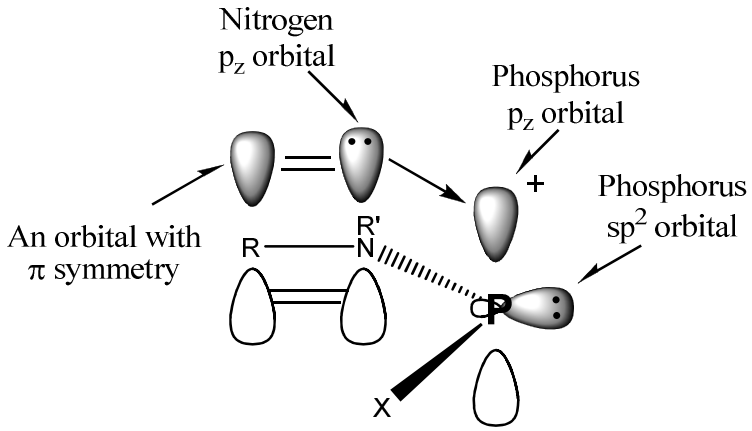
Scheme 35: *A palladium catalyzed reaction with a stabilized phosphenium ion as an additive*

Compound **51** was used instead of PPh_3 (the Pd/ PPh_3 system can also be employed as catalyst for this reaction) in order to increase the recycling ability of the system. When PPh_3 is used, leaching is observed during the extraction processes with organic solvents diminishing the recycling ability of the system. The use of **51** prevents leaching as it is more polar due to its ionic nature and thus less soluble in organic solvents.[58]

2. Results and Discussion

2.1 General Aspects: Aims and Objectives

Phosphenium ions have fascinating properties due to their planar NPX structure (where X can be nitrogen, halogen or carbon), which maximizes the π interactions in the molecule (Section 1.1.1), linking the phosphorus centre electronically with its substituents (Scheme 36). Such an arrangement means that the electronic properties of the phosphorus centre can be tuned by varying the substituents on the N and X atoms, making the phosphenium ion more or less reactive.

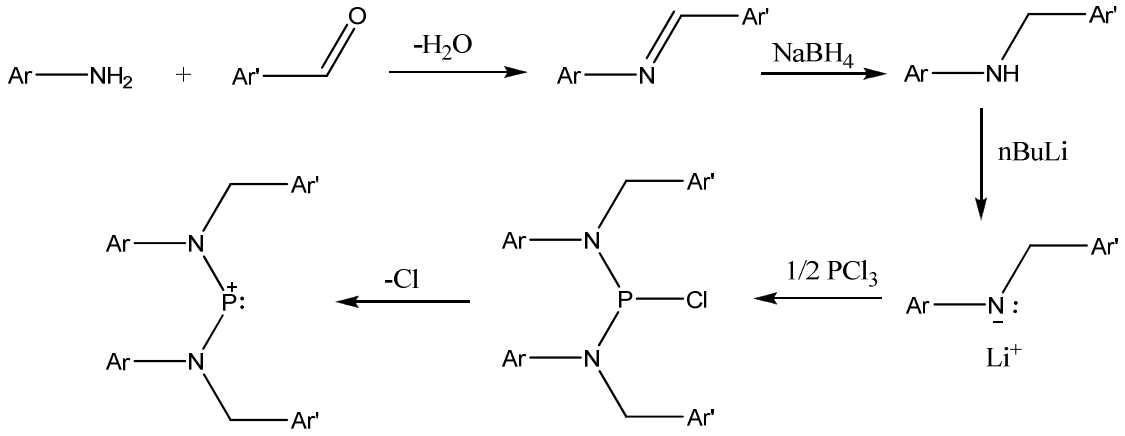


Scheme 36: *Interactions between orbitals in a phosphenium ion where R = general group which possesses π symmetric orbitals and R' = general group*

The aim of this project is to synthesize and characterize various phosphenium ions of the type $(R_2N)_2P^+$ in which the nature of the R groups is varied in a systematic fashion. Subsequently, using NMR spectroscopy and X-ray crystallography the influence of these substituents on the electronic properties of the phosphorus centre will be explored since it phosphenium ions are potentially versatile ligands for metals, utilising both the sp^2-hybidised lone pair for donation and the empty p_z orbital for back-bonding.[36]

The general synthetic strategy for the synthesis of such phosphorus-containing compounds is briefly described in Scheme 37. Applying a retro-synthetic analysis indicates that one of the most convenient ways of accessing phosphenium ions is through halide abstraction from the corresponding halophosphines. The necessary halophosphines are easily accessed from the reaction of appropriately-substituted secondary amines with PCl_3.

Similarly, the desired secondary amines can be synthesized from the reduction of the appropriate imine, themselves prepared in a straightforward fashion from condensation reactions between aldehydes with primary amines.

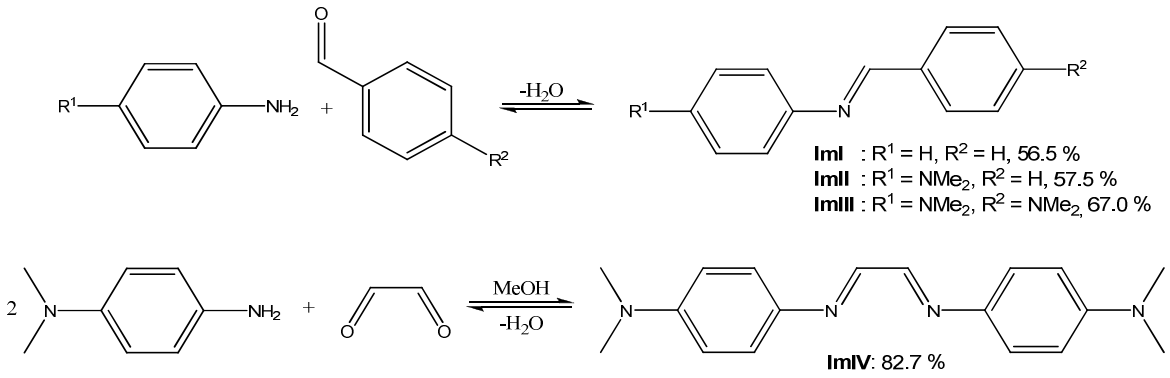


Scheme 37: *General procedure utilised for the synthesis of potentially conjugated phosphenium ions*

2.2 Phosphenium Ion Precursor Syntheses and Characterization

2.2.1 Imine preparation

The imines **ImI**, **ImII, ImIII** and **ImIV** were synthesized *via* the condensation of aniline or *N1,N1*-dimethylbenzene-1,4-diamine with benzaldehyde, 4-(dimethylamino)benzaldehyde or oxalaldehyde as outlined in Scheme 38.



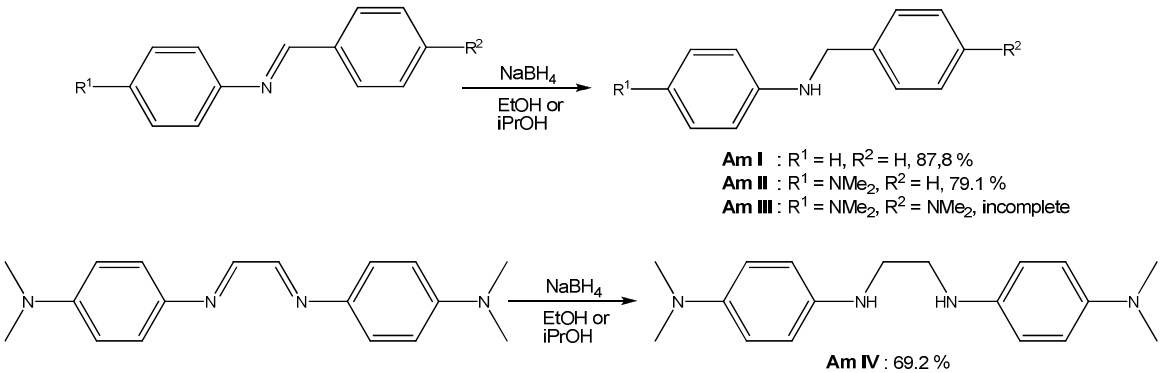
Scheme 38: *Imine **ImI**, **ImII**, **ImIII** and **ImIV** syntheses*

Two different synthetic procedures were followed for the synthesis of the imines. In the first, dry ethanol and $MgSO_4$ were employed in order to remove the water produced and to drive the equilibrium towards the imine. The use of non-dried ethanol (or methanol for **ImIV**) without any $MgSO_4$ added, resulted in a slight decrease in the yields of the desired imines by approximately 10%. An alternative method for the synthesis of the imines, used ethyl lactate as the reaction medium in accordance with the work of Bennet *et al.*[59] The use of ethyl lactate as solvent resulted in the instant precipitation of the imine out of the reaction mixture in relatively good yields (for example, the yield for **ImII** is 57.5 %) under very mild conditions without the need for either heating, dry solvents or drying agents. Indeed, irrespective of the synthetic methodology employed, the insolubility of the imine in the reaction medium (ethanol, methanol or ethyl lactate) was found to be crucial in obtaining good yields, effectively displacing the equilibrium in favour of the products.

In all cases, formation of the desired imines was monitored by ^{1}H NMR spectroscopy of the crude reaction mixture (following removal and appropriate work-up of a small aliquot), where the characteristic aldehyde resonance at ~ 10 ppm is replaced by the characteristic imine resonance at ~ 8.5 ppm. Following isolation of the crude imine products, further purification was achieved either through Sohxlet extraction (for **ImII**, and **ImIII**) using petroleum ether (80 °C), or *via* recrystallization.

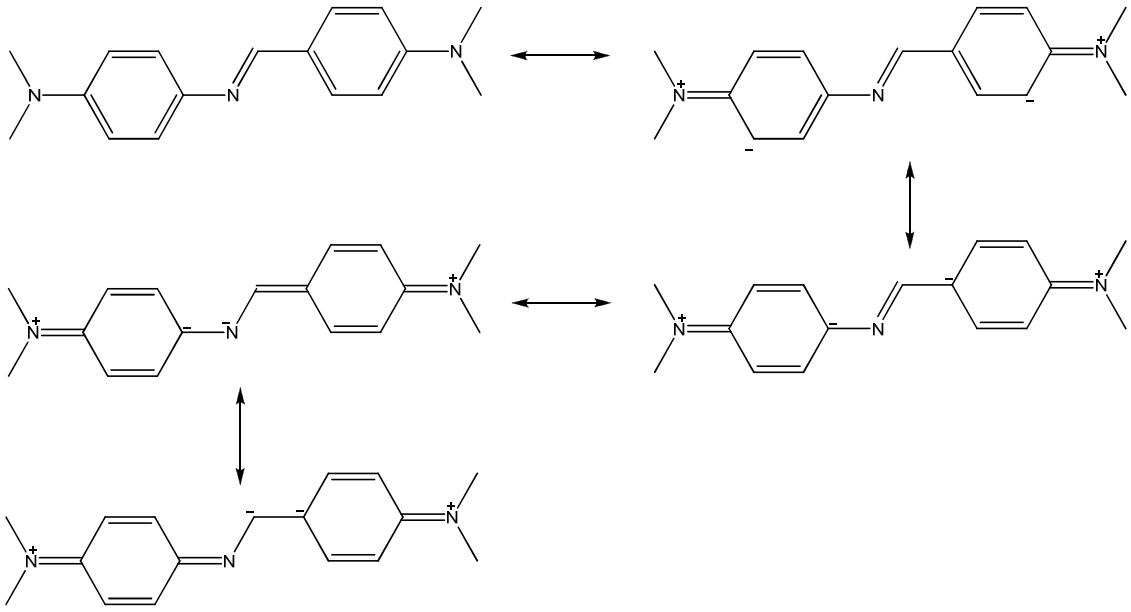
2.2.2 Secondary Amine Syntheses

The necessary secondary amines were synthesized by reducing the previously described imines with an excess of sodium borohydride as outlined in Scheme 39.



Scheme 39: *Synthesis of amines **AmI**, **AmII**, **AmIII** and **AmIV***

These reactions are essentially quantitative allowing the ensuing amines to be isolated in generally very good yields. In all cases, the extent of completion of the reactions was monitored by the disappearance of the characteristic imine resonance by ^{1}H NMR spectroscopy, which is observed at ~ 8.5 ppm and the appearance of a characteristic CH_2 resonance at around 4.3 ppm. Nevertheless **AmIII** could not be completely reduced with this method, even when a large excess of sodium borohydride was used. This is presumed to be a result of the electron donating properties of the second NMe_2 group, which leads to an increase in the electron density of the double iminic bond as can be seen from the resonance structures in Scheme 40.

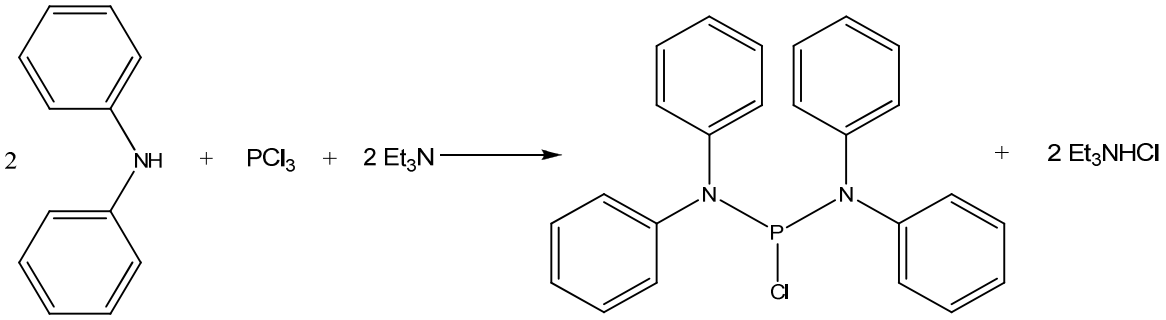


Scheme 40: *Resonance structures of **ImIV***

It is evident that there is a high accumulation of negative charge on the N or C atom of the iminic bond of **ImIV** that could hinder the hydride attack for the reduction to be complete. Consequently, the reduction reaction is slow and comparable to the rate of borohydride decomposition in ethanol. Incomplete reduction was also encountered for **ImII**, something that was solved by replacing the reaction solvent (ethanol) with isopropanol. This is due to the greater stability of borohydride in the more bulky (and thus more sterically hindered) isopropanol compared with ethanol. Thus, had time permitted, the reduction of **ImIII** in isopropanol would have been explored in order to achieve complete reduction to **AmIII**.[60]

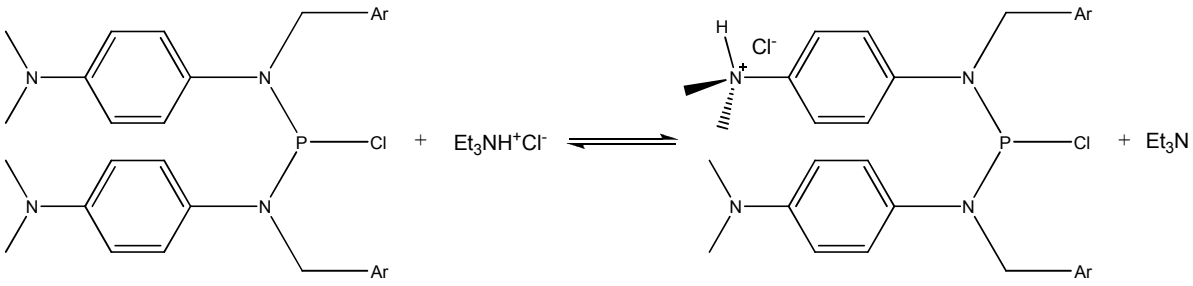
2.2.3 Halophosphine Syntheses

The most common method employed in the literature for the synthesis of bis(amido) chlorophosphines is described in Scheme 41 for the synthesis of **N2PCl II**. Here, PCl_3 is reacted with the appropriate amine in the presence of an excess of the base triethylamine in order to scavenge the HCl produced.



Scheme 41: *Synthesis of the bis(amido)chlorophosphine **N2PCl II***

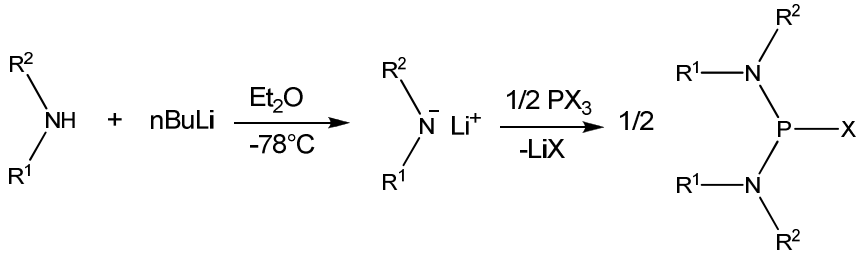
However, this reaction methodology has two disadvantages. The first is that the triethyl ammonium chloride produced is often difficult to remove from the reaction medium due to its slight solubility in many organic solvents. This results in contamination of the chlorophosphine and hence of the final target phosphenium ion. The second disadvantage is that this method is not suitable for compounds that bear basic substituents such as those required in order to synthesize compounds **N2PCl IV** and **N2PBr I** because of the presence of the NMe_2 groups, which can also competitively scavenge the HCl produced as described in Scheme 42.[61]



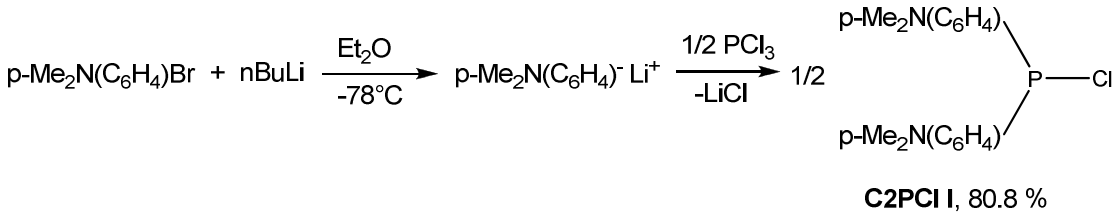
Scheme 42: *Equilibrium between a chlorophosphine containing NMe_2 groups and $Et_3NH^+Cl^-$*

For all the above reasons the chlorophosphines **N2PCl II**, **N2PCl III**, **N2PCl IV**, **N2PCl V**, **C2PCl I**, **CNPCl I**, and the bromophosphine **N2PBr I** were synthesized by first making the lithium salts of the appropriate secondary amines (or the lithium salt of 4-

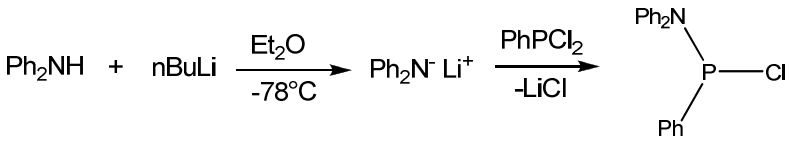
bromo-N,N-dimethylaniline for the synthesis of **N2PCl VI**), followed by reaction with PCl_3, PBr_3 or $PhPCl_2$ as described in Scheme 43.



N2PCl II: R^1 = Ph, R^2 = Ph, X = Cl, 66.8 %
N2PCl III: R^1 = Ph, R^2 = Bnz, X = Cl, 59.6 %
N2PCl IV: R^1 = Bnz, R^2 = Bnz, X = Cl, 81.6 %
N2PCl V: R^1 = p-$Me_2N(C_6H_4)$, R^2 = Bnz, X = Cl, 74.6 %
N2PBr I: R^1 = p-$Me_2N(C_6H_4)$, R^2 = Bnz, X = Br, 44.0 %



C2PCl I, 80.8 %

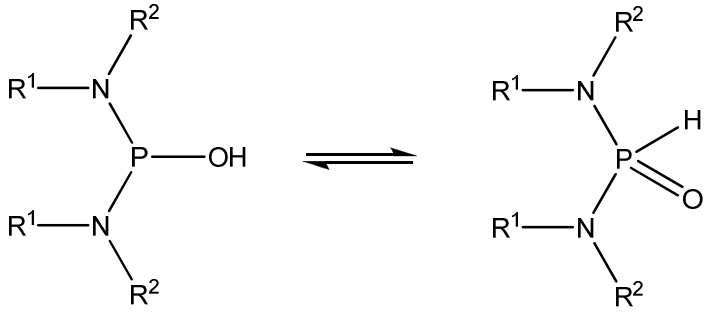


CNPCl I, 86.3 %

Scheme 43: *Synthesis of the halophosphines **N2PCl II**, **N2PCl III**, **N2PCl IV**, **N2PCl V**, **N2PBr I**, **C2PCl I** and **CNPCl I***

Each of the phosphorus nuclei in the halophosphines prepared resonates at a characteristic frequency in their ^{31}P NMR spectra of approximately 150 ppm.[62] One notable feature of these particular amido-substituted halophosphines is that they are extremely air and/or moisture sensitive, something that makes purification of the desired compounds rather challenging. By comparison, solid samples $(iPr_2N)_2PCl$ may be handled under air. This extreme sensitivity was found to be especially problematic for **N2PCl V** and **N2PBr I**. Generally, the impurities observed during the preparation of the desired chlorophosphines are the mono-substituted phosphines ($RPCl_2$), which give rise to characteristic high frequency resonances (compared with the desired compounds R_2PCl) in the ^{31}P NMR spectra, together with trace quantities of the tri-substituted phosphines (R_3P)

and/or hydrolysis products; despite the use of vigorously anaerobic and dry solvents and reaction conditions the later are observed to give rise to resonances in the region of 5-25 ppm. The formation of hydrolysis products is supported by the fact that after exposure to air, the characteristic ^{31}P NMR resonance (about 150 ppm) of the desired chlorophosphines is rapidly replaced by a peak, or peaks, in the hydrolysis region (5-25ppm). Further evidence that the peaks in the region of 5-25 ppm arise from hydrolysis products is also provided by ^{31}P [^{1}H] NMR spectroscopy, where coupling with the hydrogen is apparent ($^{1}J_{PH}$ = *ca*. 600 Hz), consistent with the hydrolysis products of the chlorophosphines as shown in Scheme 44. Purification of the desired di-substituted halophosphines is further hampered by their sticky, oily nature, which apparently prevented recrystallization. Consequently, the crude halophosphines were used in the next stages of the synthetic process towards the formation of phosphenium ions, without any complications.



Scheme 44: *Equilibrium of the halophosphine hydrolysis product*

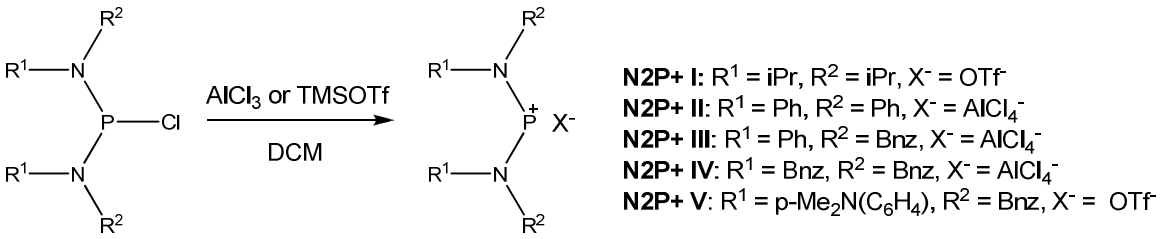
2.3 Phosphenium Ion Preparation

2.3.1 General Aspects of the Preparation of Phosphenium Ions

2.3.1.1 Syntheses

All phosphenium ions included in this report were synthesised by reacting the appropriate chlorophosphine with the chloride abstracting reagents $AlCl_3$ or TMSOTf. This approach allowed for the successful synthesis of phosphenium ions **N2P+ I**, **N2P+ II**, **N2P+ III**, **N2P+ IV** and **N2P+ V** as described in Scheme 45. The formation of the desired phosphenium ions was always accompanied by a colour change of the reaction solution.

Notably, the successful formation of the desired phosphenium ion was critically dependant on the choice of the correct halide abstracting agent as discussed in Section 1.2.1.

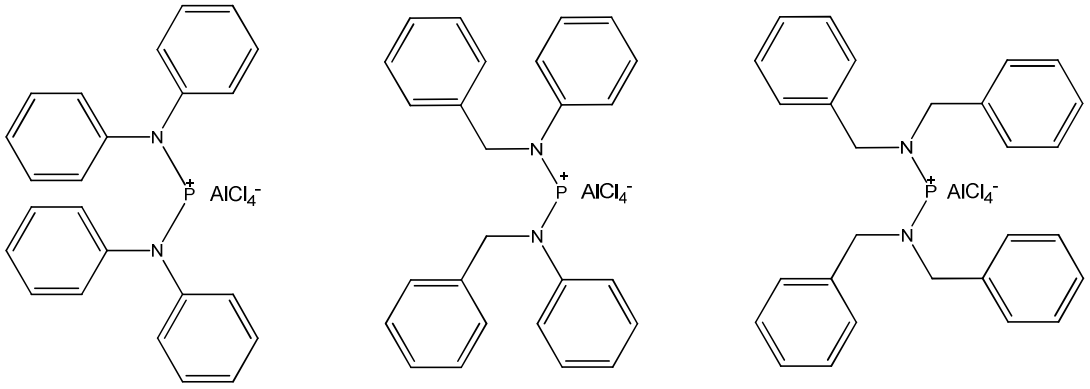


Scheme 45: *Synthesis of the phosphenium ions **N2P+ I**, **N2P+ II**, **N2P+ III**, **N2P+ IV** and **N2P+ V***

For example, the phosphenium salt **N2P+ I**, which is a pale yellow crystalline solid, was synthesised as described in the bibliography[30] by reacting the corresponding halophosphine with TMSOTf. In contrast, the salts **N2P+ II**, **N2P+ III** and **N2P+ IV** were all synthesized by using $AlCl_3$ as the chlorine abstracting agent. **N2P+ II** and **N2P+ III** are red and orange crystalline solids, respectively, while **N2P+ IV** has the form of an extremely viscous glass-like orange liquid.

2.3.1.2 The Importance of Phosphenium ions N2P+ I, N2P+ II, N2P+ III, N2P+ IV and N2P+ V

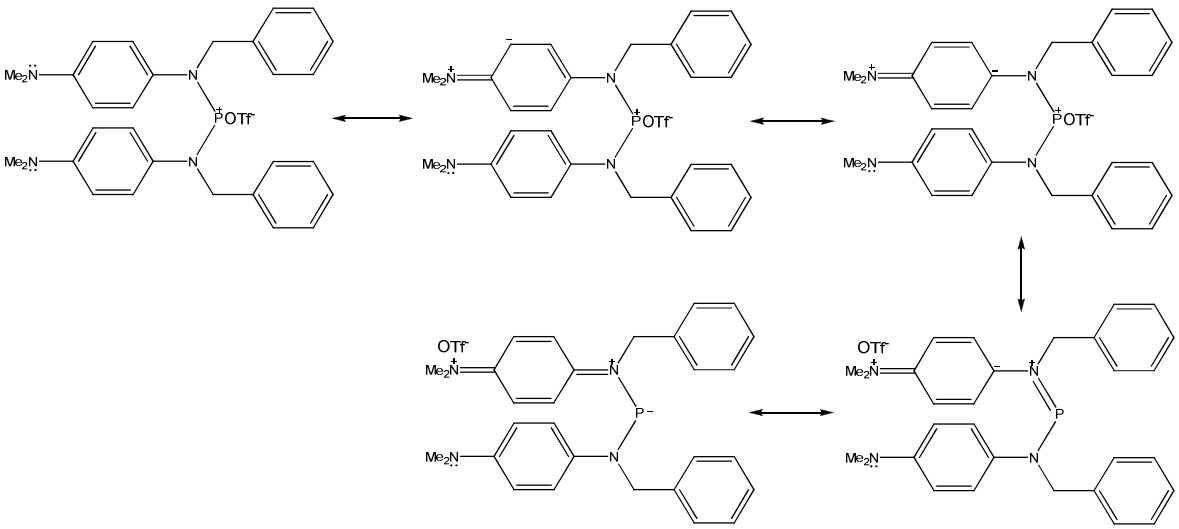
The synthesis and subsequent study of phosphenium ions **N2P+ II**, **N2P+ III** and **N2P+ IV** was undertaken in order to clarify the way in which the substituents on the nitrogen groups affect the behaviour and characteristics of the phosphorus centre in a systematic way. As can be seen in Scheme 46, compound **N2P+ II** has all four phenyl rings directly linked to the nitrogen atoms; **N2P+ III** has two phenyl rings connected directly with the nitrogen atoms and two phenyl rings connected with the nitrogen atoms through a CH_2 group; while **N2P+ IV** has all four phenyl rings linked to the nitrogen groups through a CH_2 unit.



Scheme 46: *The phosphenium ions **N2P+ II**, **N2P+ III** and **N2P+ IV***

By studying the properties of this series of compounds, it was possible to investigate the effect that the phenyl rings that are directly connected to the nitrogen substituents of the phosphenium centre may have on the electronic properties of the phosphorus centre. This is very important with respect to the future synthesis of phosphenium ion metal complexes and their application in catalysis.

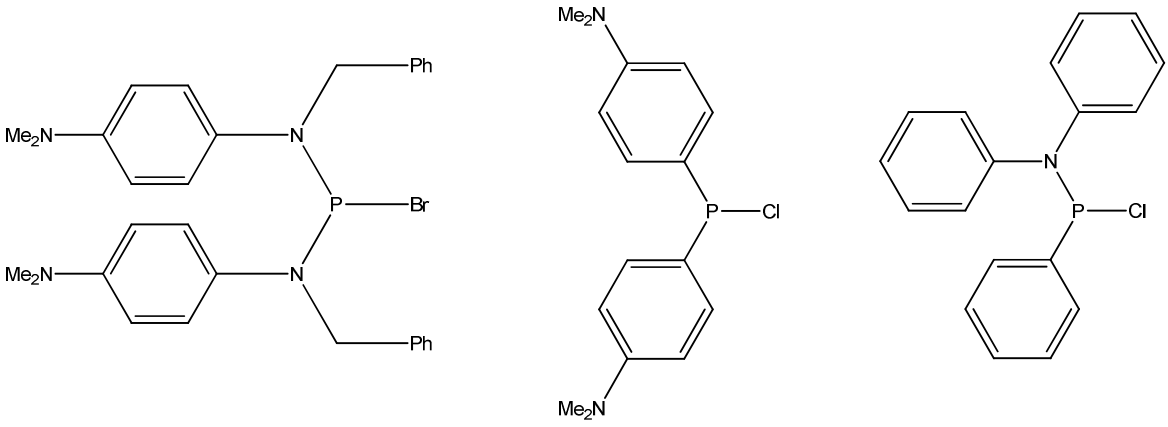
Additionally, the synthesis of the phosphenium salt **N2P+ V** was of special interest since there is the possibility that the NMe_2 groups might be able to donate electron density to the phosphorus centre through the aromatic ring as described in Scheme 47, which could further stabilize the phosphenium ion and influence its properties. However, in contrast to the compounds described above, the synthesis of **N2P+ V** with $AlCl_3$ was unsuccessful with multiple resonances being observed in the ^{31}P NMR spectrum of the ensuing reaction mixture and, in particular, a number of broad resonances in the phosphenium region above 200 ppm. This is probably due to the fact that the NMe_2 groups of **N2P+ V** interact with $AlCl_3$ (see Scheme 19 on page 24) leading to side reactions. Such a situation is supported by the fact that by repeating the same reaction using TMSOTf instead of $AlCl_3$, this resulted in a colour change to dark red accompanied by the appearance at a broad resonance of 244.7 ppm in the ^{31}P NMR spectrum, which is characteristic of the formation of the desired phosphenium ion.



Scheme 47: *Resonance forms for the phosphenium ion **N2P+ V***

2.3.1.3 Attempted Syntheses of Phosphenium Ions from the Halophosphines **C2PCl I**, **CNPCl I** and **N2PBr I**

For each of the reactions of the chlorophosphines **C2PCl I** and **CNPCl I** with $AlCl_3$ and the bromophosphine **N2PBr I** with TMSOTf (Scheme 48) the ^{31}P NMR spectra of the resulting mixtures did not include resonances that could be attributable to the desired phosphenium species. Instead, either signals from the starting materials or unattributable resonances in the region 0-100 ppm were observed.

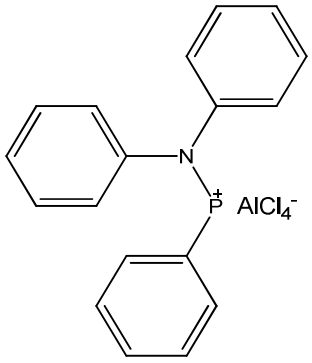


N2PBr I **C2PCl I** **CNPCl I**

Scheme 48: *The chlorophosphines **N2PBr I**, **C2PCl I** and **CNPCl I***

No reaction was observed between **N2PBr I** and TMSOTf despite the corresponding chlorophosphine (**N2PCl V**) reacting readily with TMSOTf. It is speculated that the reason for this difference in reactivity between **N2PBr I** and **N2PCl V** is that more bulky bromine atom causes steric hindrance making the reaction kinetically unfavourable.

Since there are a number of examples in the literature, for example by Bertrand *et al.*[11] and by Reed and co-workers,[25] where stable phosphenium ions may be prepared that possess only one amido substituent, it was of interest to explore whether the reaction of **CNPCl I** with $AlCl_3$ could give rise to a stable phosphenium ion. The ^{31}P NMR spectrum of the ensuing reaction mixture revealed multiple peaks in the region between -50 and 100 ppm, which suggests that the phosphenium ion of **CNPCl I** (**52**) is formed initially, but reacts further affording a number of unattributable decomposition products.

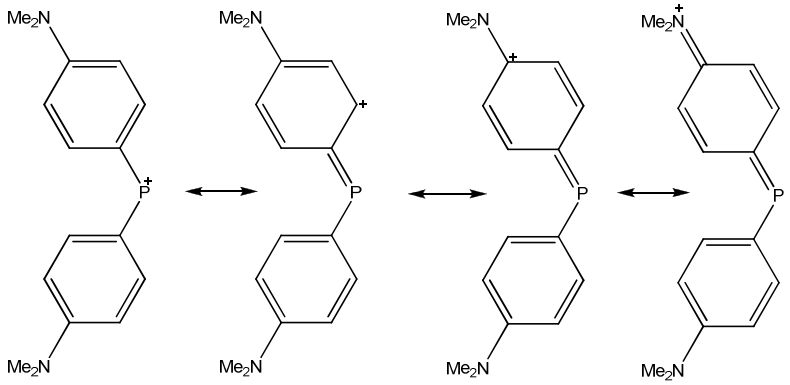


52

However, it is too early to draw any conclusions on whether phosphenium ion **52** can be synthesized or not, since other chloride abstracting reagents must be tried. Nevertheless, one factor that could prohibit the synthesis of **52**, is the low steric bulk of its substituents since it is known that bulky amido groups are generally required to provide kinetic stabilization of phosphenium ions.[23]

In an extension to this idea, it was tempting to explore whether **C2PCl I** could be used as a precursor to a stable phosphenium ion. Here, stabilization could potentially result from the potent electron donation of the NMe_2 groups to the phosphorus centre through the aromatic ring as outlined by the resonance structures in Scheme 49. However, no reaction was observed to occur between $AlCl_3$ and **C2PCl I**, presumably as a result of coordination of the pendant NMe_2 group to the Lewis acid. Due to time constraints, the reaction of **C2PCl I** with other chloride abstracting reagents such as $GaCl_3$ and TMSOTf was not

attempted, something that should be addressed in any future in attempts to prepare the corresponding phosphenium ion.



Scheme 49: *Resonance structures for a potential phosphenium ion that does not possess amido substituents*

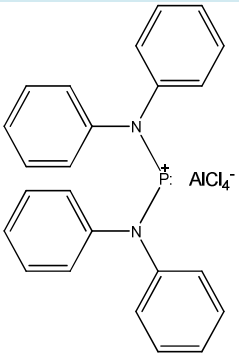
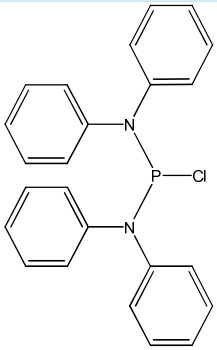
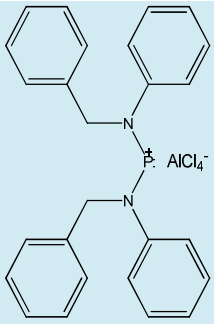
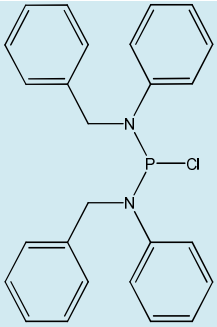
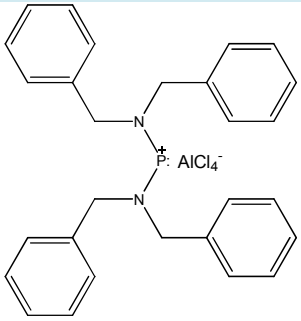
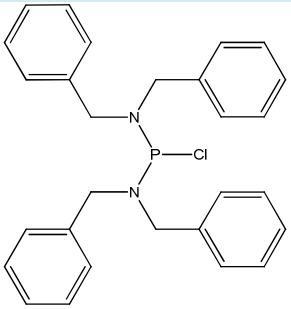
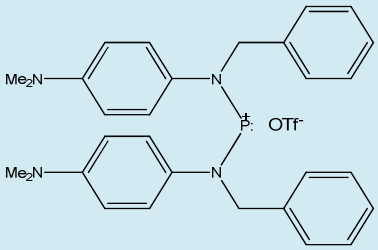
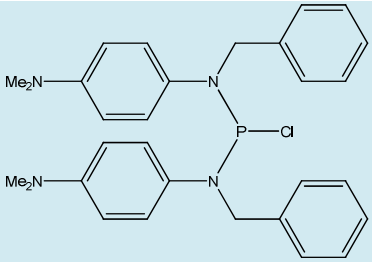
2.3.2 Characterisation of Novel Phosphenium Ions

In this section the analysis of the ^{31}P NMR spectra and the crystallographic data obtained for the successfully synthesized phosphenium ions **N2P+ I**, **N2P+ II**, **N2P+ III**, **N2P+ IV** and **N2P+ V** is described.

2.3.2.1 ^{31}P NMR Spectroscopy

^{31}P NMR spectroscopy is one of the most versatile and powerful techniques used for the study of phosphenium ions. As has already been mentioned in section 1, phosphenium ions exhibit characteristic resonances in the region between 111 and 513 ppm, which are ~100 ppm higher in frequency than their precursor halophosphines.[1] In this section of the report, the ^{31}P NMR chemical shifts of phosphenium ions **N2P+ II**, **N2P+ III**, **N2P+ IV** and **N2P+ V** in CD_2Cl_2 and of their precursor chlorophosphines **N2PCl II**, **N2PCl III**, **N2PCl IV** and **N2PCl V** in $CDCl_3$ are reported and summarized in Table III.

Table III. ^{31}P NMR chemical shifts (ppm) for the phosphenium ions **N2P+ II, N2P+ III, N2P+ IV** and **N2P+ V** and for their precursor chlorophosphines

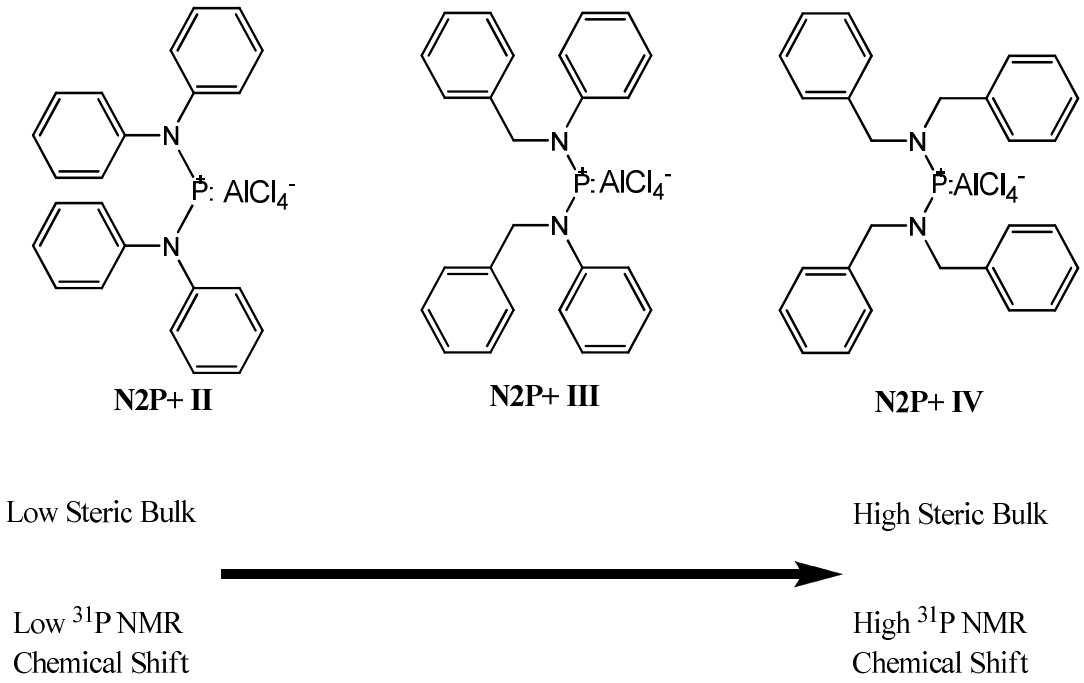
Phosphenium Ion	^{31}P NMR Chemical Shift	Chlorophosphine	^{31}P NMR Chemical Shift
 N2P+ II	234.6	 N2PCl II	124.2
 N2P+ III	249.0	 N2PCl III	137.5
 N2P+ IV	264.0	 N2PCl IV	148.2
 N2P+ V	244.7	 N2PCl V	140.1

2.3.2.1.1 ^{31}P NMR Spectroscopic Study of Compounds **N2P+ II**, **N2P+ III** and **N2P+ IV**

Using ^{31}P NMR spectroscopy to study the series of phosphenium ions **N2P+ II**, **N2P+ III** and **N2P+ IV**, a move to higher frequency of ~14 ppm is observed on replacing every pair of phenyl groups by a pair of benzyl substituents. Thus, **N2P+ VI** displays a resonance that is at ~14 ppm to higher frequency than that for **N2P+ III**, which is in turn at ~14 ppm higher frequency than **N2P+ II** (see Table III).

A number of explanations that account for this trend are possible. Firstly, the introduction of bulky substituents on the nitrogen atoms of a phosphenium ion results in an increase in the frequency of the ^{31}P NMR chemical shift. This is because bulky substituents tend to move the nitrogen atoms out of the NPN plane, which decreases their electron donating potential towards the phosphorus centre.[1] If one considers that the benzyl group is bulkier than the phenyl group, something supported by a comparison with the Tolman cone angles θ for the phosphines PPh_3, $PiPr_3$, $PBnz_3$, which are 145, 160 and 165, respectively,[63] it is evident that the steric bulk of the amido substituents for the phosphenium ions **N2P+ II**, **N2P+ III** and **N2P+ IV** increases as one moves from **N2P+ II** to **N2P+ IV**. This is thus consistent with the observed increase in the ^{31}P NMR chemical shifts (Scheme 50).

However, this interpretation of the observed trend does not explain why a very similar trend is also observed for the chlorophosphines **N2PCl II**, **N2PCl III** and **N2PCl IV**, where the substituents at nitrogen atoms are much less likely to cause significant changes in geometry at the P-centre. Moreover, if the steric bulk of the amido substituents was the only reason for the observed changes in the ^{31}P NMR chemical shifts of the phosphenium ions reported here, then one would expect that the previously reported phosphenium salts $[(Me_2N)_2P^+][AlCl_4^-]$ and $[(Et_2N)_2P^+][AlCl_4^-]$ (see Table II) would resonate to much lower frequencies compared to all the examples given here, since they posses less bulky amido groups. Nevertheless, $[(Me_2N)_2P^+][AlCl_4^-]$ resonates at 264 ppm (Table II) while $[(Et_2N)_2P^+][AlCl_4^-]$ resonates at 263 ppm (Table II). Both of these chemical shifts are comparable to that observed for compound **N2P+ IV**, which suggests that the steric bulk of the amido substituents for compounds **N2P+ II**, **N2P+ III**, **N2P+ IV**, $[(Me_2N)_2P^+][AlCl_4^-]$ and $[(Et_2N)_2P^+][AlCl_4^-]$ has a negligible effect on the electronic properties of the phosphorus centre.

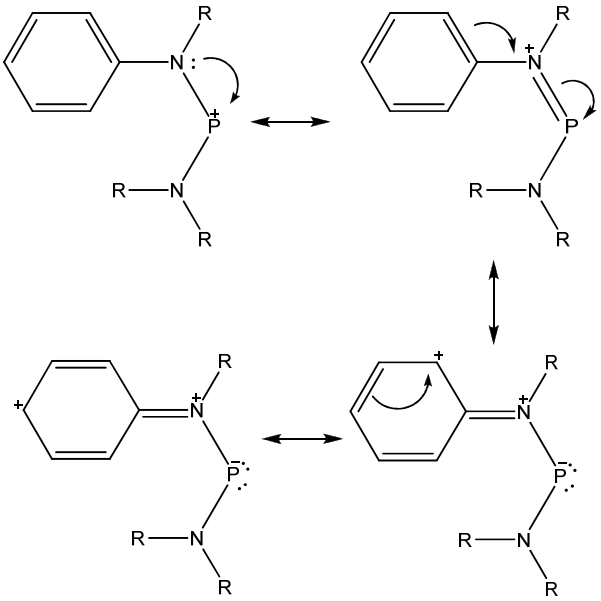


Scheme 50: *The relationship between the ^{31}P NMR chemical shift and the steric bulk of the amido substituents for phosphenium ions **N2P+ II**, **N2P+ III** and **N2P+ IV***

It needs to be mentioned though, that the above observations do not conflict with the fact that the bulk of the amido substituents can affect the ^{31}P NMR chemical shifts of phosphenium ions. For example, $[(iPr_2N)_2P^+][AlCl_4^-]$ exhibits a chemical shift of 313 ppm (Table I), which is 50 ppm to higher frequency than that for $[(Me_2N)_2P^+][AlCl_4^-]$. Here, the difference between $[(iPr_2N)_2P^+][AlCl_4^-]$ and the phosphenium ions **N2P+ II**, **N2P+ III**, **N2P+ IV**, $[(Me_2N)_2P^+][AlCl_4^-]$ and $[(Et_2N)_2P^+][AlCl_4^-]$ is that the iPr group is more rigid and hence spherical in shape compared with the Et, Ph and Bnz groups. Thus, the Et, Ph and Bnz groups can orientate themselves in the molecule in such a way as to avoid each other, while the iPr group can't.

Clearly, steric effects imposed by the amido substituents of phosphenium ions **N2P+ II**, **N2P+ III** and **N2P+ IV** have little or no impact on the electronic structure of the phosphorus centre and hence on their observed ^{31}P NMR chemical shifts. Indeed, the phosphenium ions bearing alkyl groups on the nitrogen atoms, $[(Me_2N)_2P^+][AlCl_4^-]$, $[(Et_2N)_2P^+][AlCl_4^-]$ and **N2P+ IV**, all resonate at approximately 264 ppm. However, phosphenium ions with Ph groups directly linked to the nitrogen atoms of the molecule, like **N2P+ II** and **N2P+ III**, resonate at considerably lower frequencies by ^{31}P NMR

spectroscopy. This strongly suggests that there is an electronic interaction between the Ph groups and the phosphorus centre (Scheme 51). This interaction will further delocalize the positive charge on the phosphorus centre resulting in the increase of the electron density at phosphorus and thus in the low frequency shift of the ^{31}P NMR resonances observed for compounds **N2P+ II** and **N2P+ III** .



Scheme 51: *Resonance forms demonstrating the delocalization of the positive charge of a phosphenium ions' phosphorus centre through conjugation with the phenyl ring of a Ph(R)N amido substituent, where R = Ph or alkyl.*

Moreover, this suggestion is in accordance with the already mentioned trend observed in the ^{31}P NMR spectra for compounds **N2P+ II**, **N2P+ III** and **N2P+ IV**. Thus, compound **N2P+ II** is expected to resonate at lower frequencies in the ^{31}P NMR spectrum compared to **N2P+ III** since it has two extra phenyl groups that can delocalize the positive charge of the phosphorus centre. In the same way, **N2P+ III** is expected to resonate at lower frequencies in the ^{31}P NMR spectrum compared to **N2P+ IV**. Lastly, compounds **N2P+ IV**, $[(Me_2N)_2P^+][AlCl_4^-]$ and $[(Et_2N)_2P^+][AlCl_4^-]$ are expected to resonate at around the same frequency in the ^{31}P NMR spectrum since their pendant alkyl groups are 'electronically innocent'.

2.3.2.1.2 ^{31}P NMR Spectroscopic Study of Compound N2P+ V

The phosphenium ion **N2P+ V** was synthesized in order to examine whether the NMe_2 group would be able to stabilize the phosphenium ion by donating electron density to the phosphorus centre. In **N2P+ V** the counter ion is OTf^- and not the $AlCl_4^-$ anion.

Furthermore, the molecule contains a basic NMe_2 group, which is probably going to strongly influence its properties. For the above reasons, it is not possible to examine this compound as part of the **N2P+ II**, **N2P+ III** and **N2P+ IV** series. However, the solution-state ^{31}P NMR spectrum of **N2P+ V** is interesting by itself, since instead of the usual sharp resonance observed in the region between 200 and 300 ppm at ambient temperature, a broad resonance ($\nu_{½}$ = 339 Hz) is observed at 244.7 ppm, which sharpens as the temperature of the solution is gradually lowered from ambient temperature to – 80 °C (Figure 5).

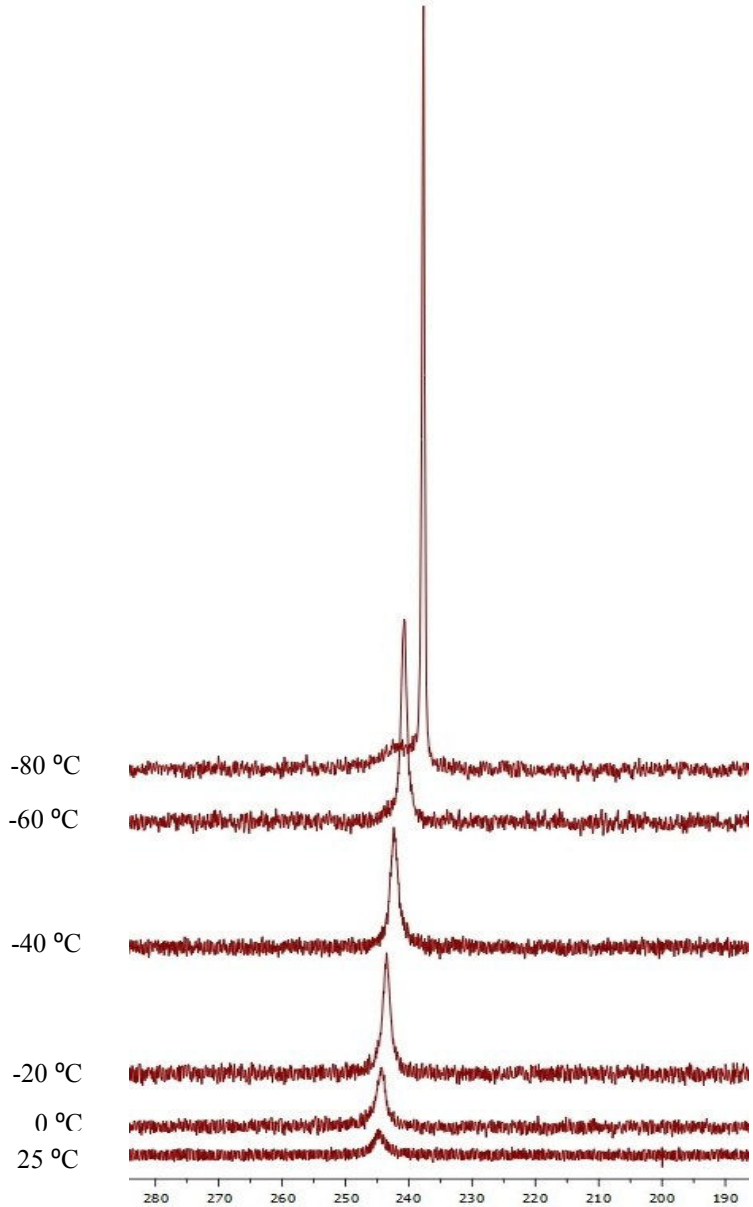
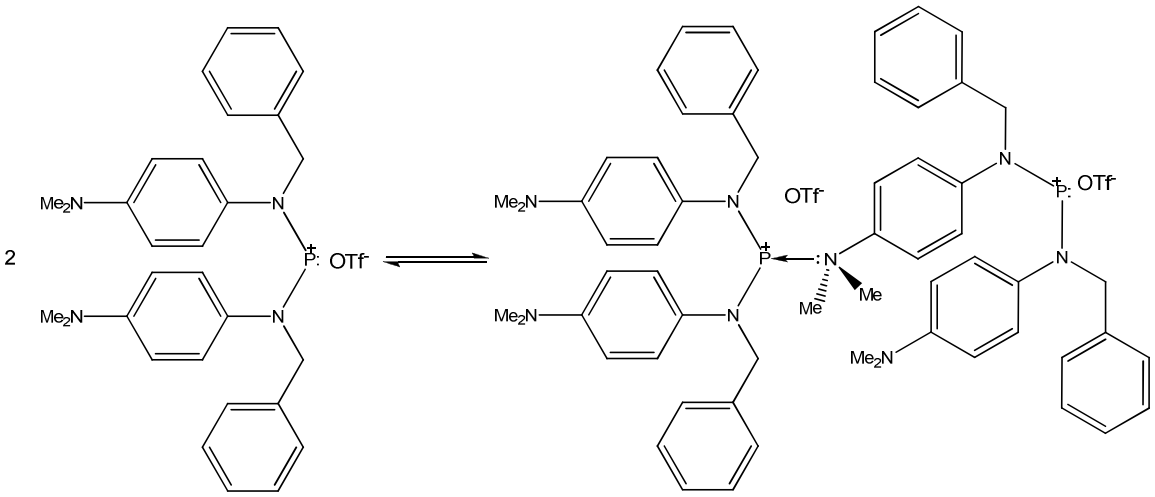


Figure 5: *The ^{31}P NMR spectra for compound **N2P+ V** at various temperatures*

This indicates that a dynamic process is taking place that causes broadening of the ^{31}P NMR resonance of **N2P+ V**. One possible explanation for this behaviour could be that the

broadening observed for **N2P+ V** in the ^{31}P NMR spectra at ambient temperature is due to dynamic intermolecular interactions between the basic NMe_2 group and the acidic N_2P^+ centre as described in Scheme 52.



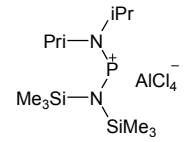
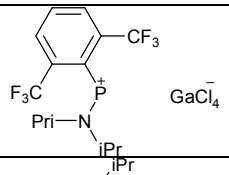
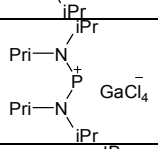
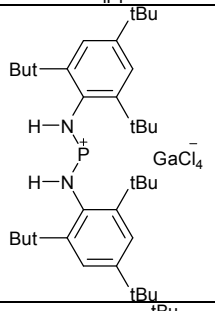
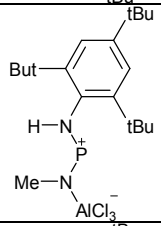
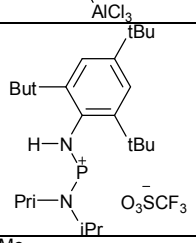
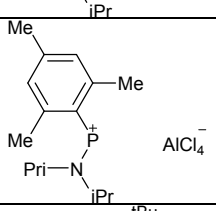
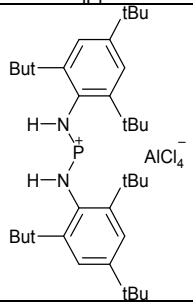
Scheme 52: *Interactions between two* **N2P+ V** *phosphenium ions*

If the rate associated with this process at ambient temperature was comparable to the NMR time scale resulting in the broad resonances observed in the ^{31}P NMR spectrum (Figure 5). As the temperature is lowered, the process is slowed down resulting in a sharper resonance in the ^{31}P NMR spectrum. Notably, a similar observation has been made for $[(iPr_2N)_2P^+][OTf^-]$ generated from $(iPr_2N)_2PCl$ and TMSOTf, where the presence of TMSCl formed by the reaction causes extreme broadening of the ^{31}P NMR resonance due to its interaction of the phosphorus centre *via* the chlorine atom of TMSCl.[64]

2.3.2.2 X-Ray Crystallographic Studies

Crystals suitable for an X-ray crystallographic study were grown from concentrated DCM solutions of the phosphenium ions **N2P+ II** and **N2P+ III** at low temperature (-30°C). The structures were subsequently determined and solved by Dr. A. Batsanov (Durham University). This achievement is important since there are comparatively few crystallographic studies described for acyclic amido-substituted phosphenium ions (Table IV). Indeed, most reported phosphenium ions are characterized only by their NMR spectra, in particular ^{31}P NMR spectroscopy.

Table IV. Molecular structures of acyclic amido-substituted phosphenium salts determined crystallographically

CSD REFCODE[a]	Structure	Reference
BEYLEX		J. P. Bezombes, K. B. Borisenko, P. B. Hitchcock, M. F. Lappert, J. E. Nycz, D. W. H. Rankin, H. E. Robertson, *Dalton Trans*., 2004, 1980
EGOYOO		A. Dumitrescu, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Eur. J. Inorg. Chem.*, 2002, 1953
KUWMOE		N. Burford, P. Losier, P. K. Bakshi, T.S. Cameron, *J. Chem.Soc., Dalton Trans.,* 1993, 201
TOPGIO		N. Burford, T.S. Cameron, J. A. C. Clyburne, K. Eichele, K. N. Roberston, S. Sereda, R. E. Wasylishen, W. A. Whitla*, Inorg. Chem.*, 1996, **35**, 5460
WIJPOU		A. B. Drapailo, A. N. Chernega, V. D. Romanenko, R. Madhouni, J.-M. Sotiropoulos, L. Lamande, M. Sanchez, J. *Chem.Soc., Dalton Trans.*, 1994, 2925
WIJPUA		A. B. Drapailo, A. N. Chernega, V. D. Romanenko, R. Madhouni, J.-M. Sotiropoulos, L. Lamande, M. Sanchez, *J. Chem. Soc., Dalton Trans.*, 1994, 2925
ZIQDIM		R. W. Reed, Z. Xie, C. A. Reed, *Organometallics*, 1995, **14**, 5002
ZOLCAE		M. Nieger, E. Niecke, R. Detsch, Z. *Kristallogr*., 1995, **210**, 971

[a] CSD: F. H. Allen, *Acta Cryst.*, B**58**, 380-388, 2002 (Nov. 2009 database)

Notably, phosphenium ion **N2P+ II** crystallizes in two very slightly different isomeric forms, namely **N2P+ IIa** and **N2P+ IIb**, which are both present in the unit cell. The ORTEP diagrams of compounds **N2P+ IIa**, **N2P+ IIb** and **N2P+ III** are presented below and are accompanied by a list of selected bond lengths and angles.

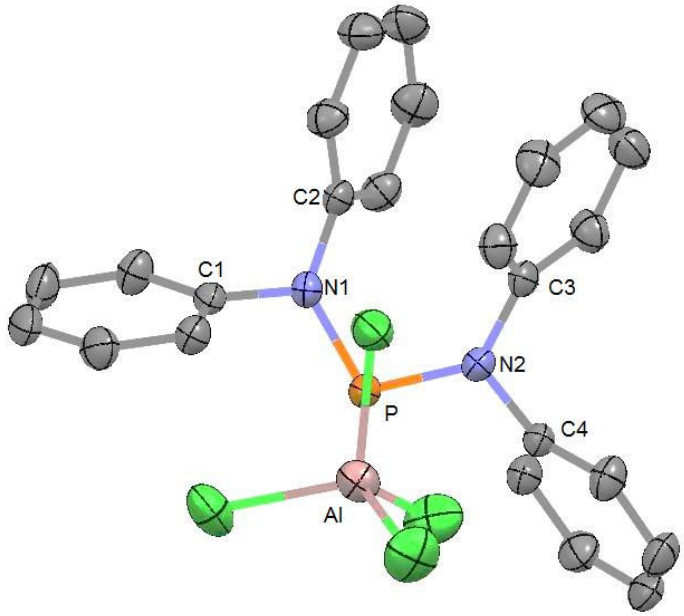


Figure 6: *ORTEP drawing of **N2P+ IIa**. The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.*

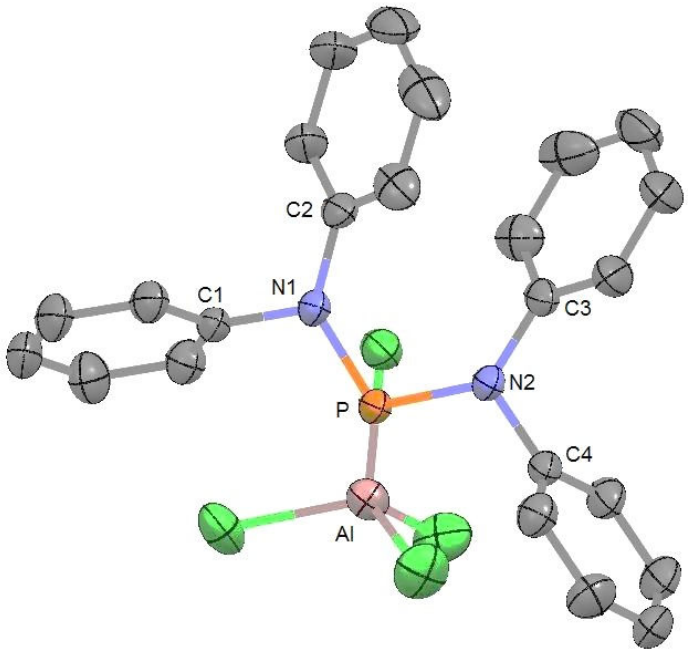


Figure 7: *ORTEP drawing of **N2P+ IIb**. The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.*

Table V. Selected Bond Lengths (Ångstroms) and Angles (Degrees) for the Phosphenium Ion **N2P+ IIa** and **N2P+ IIb**

Bond lengths			Bond angles		
	N2P+ IIa	**N2P+ IIb**		**N2P+ IIa**	**N2P+ IIb**
P-N1	1.6400(16)	1.6381(15)	**N1-P-N2**	110.10(11)	106.58(11)
P-N2	1.6401(16)	1.6380(15)	**P-N1-C1**	111.80(12)	113.52(12)
N1-C1	1.465(2)	1.446(2)	**P-N1-C2**	133.07(13)	128.05(12)
N1-C2	1.441(2)	1.443(2)	**C1-N1-C2**	115.12(15)	118.28(14)
N2-C3	1.441(2)	1.443(2)	**P-N2-C4**	111.80(12)	113.52(12)
N2-C4	1.465(2)	1.446(2)	**P-N2-C3**	133.07(13)	128.05(12)
			C3-N2-C4	115.12(15)	118.28(14)

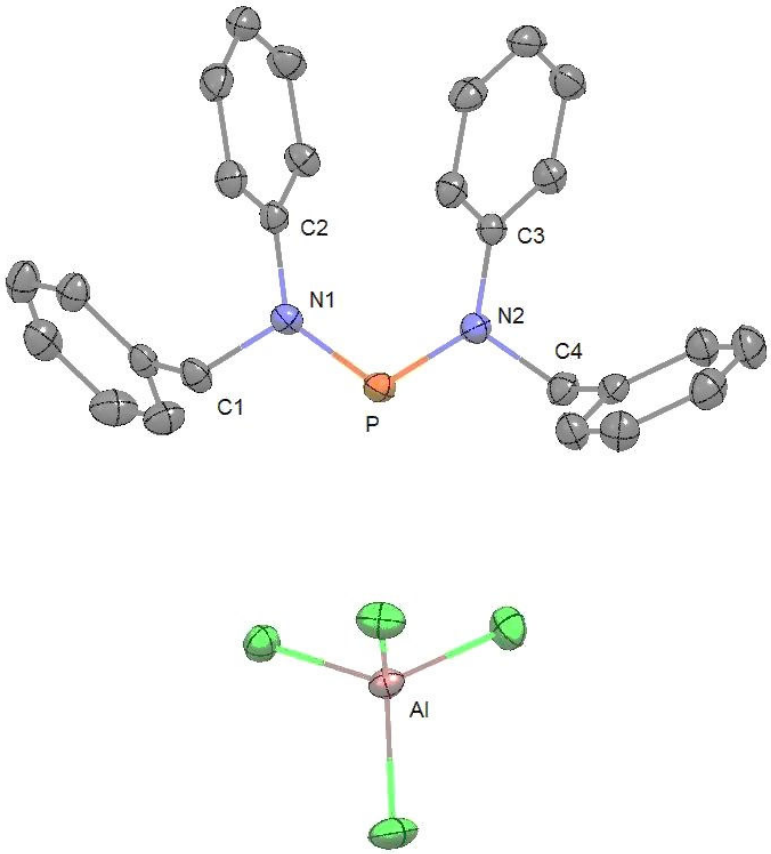


Figure 8: *ORTEP drawing of **N2P+ III**. The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.*

Table VI. Selected Bond Lengths (Ångstroms) and Angles (Degrees) for the Phosphenium Ion **N2P+ III**

Bond lengths		**Bond angles**	
P-N1	1.6219(12)	**N1-P-N2**	111.90(6)
P-N2	1.6242(12)	**P-N1-C1**	112.72(9)
N1-C1	1.5036(17)	**P-N1-C2**	132.07(9)
N1-C2	1.4433(17)	**C1-N1-C2**	115.21(10)
N2-C3	1.4487(17)	**P-N2-C4**	112.02(9)
N2-C4	1.5052(17)	**P-N2-C3**	133.14(9)
		C3-N2-C4	114.78(11)

From the data presented in Tables IV and V, it is evident that the NPN angles for the phosphenium ions **N2P+ IIa**, **N2P+ IIb** and **N2P+ III** are smaller by 9.90 °, 13.42 ° and 8.10 °, respectively, than the typical value of 120 ° for a true sp^2 hybridized atom. This lowering of the NPN angles is characteristic for all phosphenium ions and is believed to be due to the repulsions between the free electron pair of the phosphorus atom and the electron pairs of the P-N bonds.[1] Moreover, the NPN angle of a phosphenium ion is also influenced by the steric bulk of the amido substituents. For example, compound $[(iPr_2N)_2P^+][AlCl_4^-]$ has an NPN angle of 114.8 °,[30] which is 2.9 ° greater than that found for compound **N2P+ III** due to the increased steric bulk of the iPr groups. This observation is in agreement with the fact that $[(iPr_2N)_2P^+][AlCl_4^-]$ is more sterically hindered than compounds **N2PCl II**, **N2PCl III** and **N2PCl IV**, something that leads to a higher frequency resonance being observed in its ^{31}P NMR spectrum, as discussed in section 2.3.2.1. The effect of the steric bulk is also reflected by the greater value of the NPNC dihedral angle of ~ 18 ° for $[(iPr_2N)_2P^+][AlCl_4^-]$,[30] which forces the nitrogen atoms out of the NPN plane, compared to the NPNC dihedral angles of compounds **N2P+ IIa** (11.33 °) and **N2P+ III** (3.44 °). Notably, irrespective of the extent of N→P lone pair donation, the sum of the angles around the nitrogen atoms are all identical within experimental error (*e.g.* C1N1P + C1N1C2 + C2N1P) and equal to 360 ° in all the compounds examined.

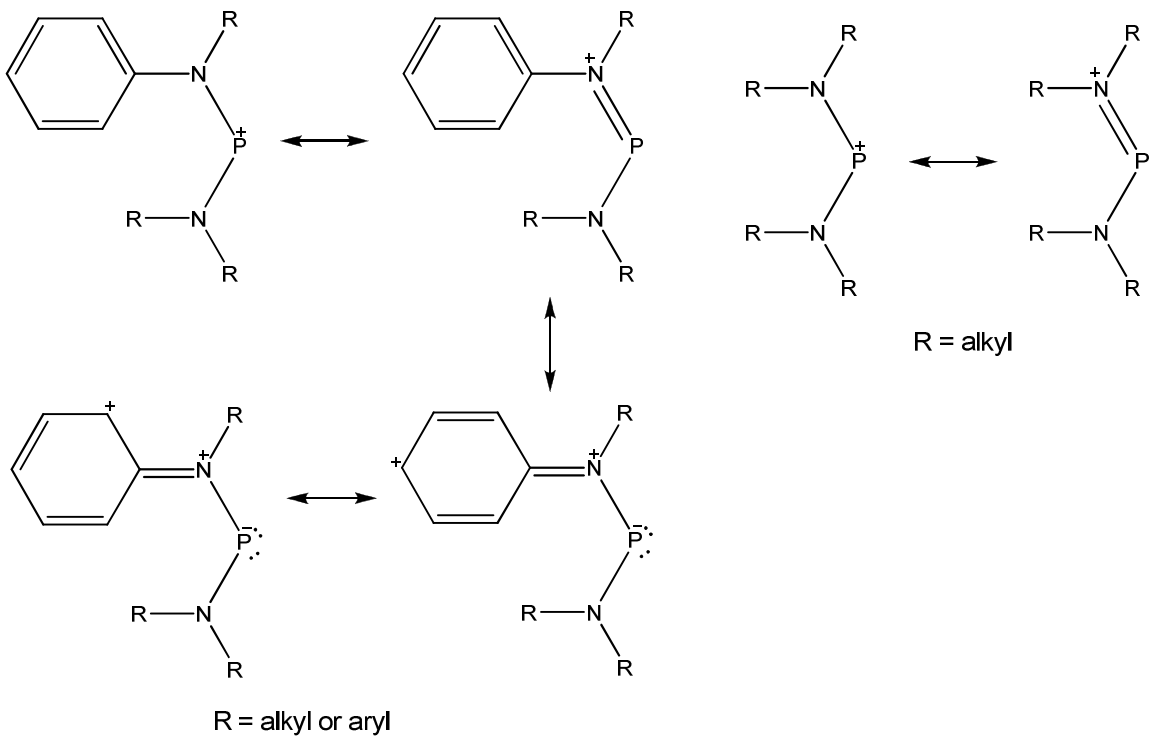
By comparing the sum of the Van der Waals radii of phosphorus and chloride atoms (3.55 Å) with the shortest interaction between the phosphorus centre and the counter ion ($AlCl_4^-$) in compounds **N2P+ IIa** (3.59 Å), **N2P+ IIb** (3.52 Å) and **N2P+ III** (3.37 Å), one can determine the extent of ionic character the compounds possess. Thus, **N2P+ IIa** is

completely ionic in character, since the $P^{+}\cdots ClAlCl_3^{-}$ interaction is longer than the sum of the Van der Waals radii, while compounds **N2P+ IIb** and **N2P+ III** are slightly less ionic, but still ionic enough in order to be considered as true phosphenium ions.[1]

A typical characteristic of phosphenium ions is the short P-N distances observed in their crystal structures compared to neutral amido phosphines in which the P-N distances are between 1.69 and 1.73 Å[65]. This trend is also observed in the examined compounds **N2P+ IIa**, **N2P+ IIb** and **N2P+ III** in which the P-N bond lengths are 1.64 Å, 1.64 Å and 1.62 Å long, respectively. The shortening of the P-N bond lengths derives from the partial double bond character, which is due to N→P lone pair donation.

Lastly, an interesting observation is that the P-N bond lengths of 1.61 Å in $[(iPr_2N)_2P^{+}][AlCl_4^{-}]$[30] are slightly shorter than the P-N bond lengths in **N2P+ IIa**, **N2P+ IIb** and **N2P+ III**. This suggest that for **N2P+ IIa**, **N2P+ IIb** and **N2P+ III** there is a degree of charge delocalization across the phenyl rings of the amido substituents, since such extended delocalization will disperse the electron density off the P-N bonds reducing their double bond character. This argument was also used in section 2.3.2.1 in order to explain the ^{31}P NMR chemical shift data obtained for these compounds and is supported by examination of the resonance forms for these compounds presented in Scheme 53. In the case where the *bis*(amido) phosphenium ion has alkyl substituents (*e.g.* for **N2P+ IV**), only two resonance forms contribute to the actual structure of the molecule, one with a P-N double bond and one with a P-N single bond. On the other hand, if aryl groups are present (like in compound **N2P+ II)** another two resonance forms contribute to the actual structure of the phosphenium ion both of which contain a P-N single bond and an N-C double bond. This suggests that addition of aryl substituents should result in an increase of the P-N bond lengths as already mentioned.

It must be noted, that the conjugation of the aryl substituents with the NPN system will be stronger when the aryl groups become coplanar with the NPN plane. From Figures 6, 7 and 8 it is evident that the phenyl rings are not parallel to the NPN plane in the solid state. However, they are also not vertical; in which case the interactions described in Scheme 53 would be completely prohibited.



Scheme 53: *Resonance forms of a phosphenium ion with aryl substituents (left) and alkyl substituents (right)*

2.4 Summary and Conclusions.

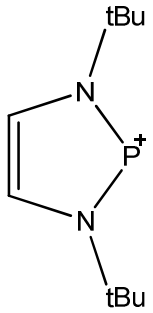
It is evident that the ^{31}P NMR spectra obtained for phosphenium ions **N2P+ II**, **N2P+ III** and **N2P+ IV** seem to be in agreement with the crystallographic data. Both studies suggest that there can be an electronic interaction between the positively charged phosphorus centre and the aryl groups of the aryl amido substituents. This interaction most probably results from the presence of some degree of conjugation between the phosphorus centre and the aryl groups through the nitrogen atom. However, more experiments must be conducted in order to verify this suggestion, especially since it is difficult to compare the results of a solid-state technique such as X-ray diffraction with a solution-state technique like NMR. In order to create a more solid correlation between the results obtained with these two methods, the solid state NMR of **N2P+ II**, **N2P+ III** and **N2P+ IV** should also be obtained and compared with the solution state data, since a better correlation with the structural data may be made.

2.5 Outlook and Future Work

From the above discussions it becomes clear that although phosphenium ions were discovered 25 years ago, they are still an area of great interest. Nevertheless, there is still a significant amount of research required in order to completely understand the properties

and the potential of phosphenium ions. In particular, their combined σ-donating and good π-accepting properties (a rare combination in a single ligand moiety) they could act as ligands for the synthesis of various metal complexes that could be further used as catalysts.

One particular aspect of the chemistry of phosphenium ions that remains crucial to explore is the way in which the counter ion affects the reactivity/properties of phosphenium ions. Also, the fact that specific phosphenium ions form only with certain halide extracting agents needs to be probed in greater depth. For example, phosphenium ion **53** can be synthesized by using $GaCl_3$ as the chloride abstracting agent, but not by using $AlCl_3$, which leads to side reactions.[20]



53

Clearly other chloride abstracting agents apart from $AlCl_3$ should be used to explore whether the phosphenium ions described in this thesis are anion specific. This study might lead to the synthesis of new phosphenium ions derived from the chlorophosphines **C2PCl I** and **CNPCl I**, which failed to form a phosphenium ion when they were treated with $AlCl_3$. In conjunction with this study, an exploration of the properties of the various phosphenium salts by both UV-Vis spectroscopy and cyclic voltametry would be useful in order to assess not only the bonding, but also the redox behaviour of these potentially ambiphilic compounds.

Undoubtedly, it is important that all the above studies be accompanied by theoretical DFT calculations, which will help in understanding the bonding associated with the various phosphenium ion structures, since the crystallographic analysis provides us with only one out of the various conformations a compound may obtain. From these studies new approaches for the synthesis of novel phosphenium ions might also result.

Lastly, after having extensively understood the chemistry and the behaviour of phosphenium ions, it will be possible to use them, or their precursor chlorophosphines, as

ligands for the synthesis of various organometallic complexes, which will have direct applications in catalysis.

3. Experimental

3.1 Experimental Details

All operations were conducted under an atmosphere of dry nitrogen using standard Schlenk and canula techniques, or in a Saffron Scientific nitrogen-filled glove box, unless otherwise stated. Bulk solvents were purified using an Innovative Technologies SPS facility, except dry ethanol, which was purified by distillation from Mg and I_2.[66] Deuterated solvents were distilled from P_2O_5. All solvents were degassed prior to use, unless otherwise stated. DCM-d2 was purchased from Goss Scientific and benzene-d6 from Apollo Scientific. Aniline, *N*^{1},*N*^{1}-dimethylbenzene-1,4-diamine, oxalaldehyde, sodium borohydride, ethyl lactate, benzaldehyde, 4-(dimethylamino)benzaldehyde, isoproplyl alcohol, 4-bromo-N,N-dimethylaniline, butyl lithium solutions in hexane, 2,4,6-trimethylbenzaldehyde, methanol, formic acid and aluminium trichloride were purchased from Aldrich and used as received. Trimethylsilyl trifluoromethanesulfonate was purchased from Aldrich and degassed prior to use. Diphenylamine was purchased from Aldrich and was recrystalized from pentane prior to use. Dibenzylamine was purchased from Alfa-Aesar, dried under molecular sieves (3Å) and degassed. Phosphorus trichloride, phosphorus tribromide and phenylphosphorus dichloride were purchased from Aldrich and were distilled and degassed prior to use.

Solution phase NMR spectra were collected on a Varian Mercury 400, 300 or 200, a Varian Inova 500, a Varian VNMRS-700 and a Bruker Avance 400 at ambient probe temperatures (290 K) unless otherwise stated. Chemical shifts were referenced to residual proton impurities in the deuterated solvent (^{1}H), ^{13}C shift of the solvent (^{13}C) or to external 85% H_3PO_4 aqueous solution. Solvent proton shifts (ppm): $CDCl_3$, 7.26 (s); C_6D_6, 7.15 (s); CD_2Cl_2, 5.32 (s). Solvent carbon shifts (ppm): $CDCl_3$, 77.36 (t); C_6D_6, 128.62 (t); CD_2Cl_2, 54.00 (quin). ^{1}H NMR and ^{13}C NMR spectra were assigned with the aid of COSY, HSQC and HMBC experiments. Chemical shifts are reported in ppm and coupling constants in Hz. Monitoring of reactions by ^{31}P NMR spectroscopy was achieved in non-deuterated solvents using a sealed capillary tube containing C_6D_6 added to obtain a deuterium lock.

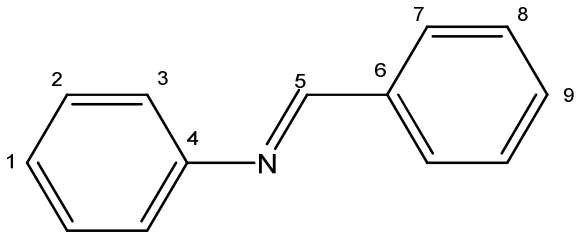
Mass spectra (ES) were obtained using a Micromass Autospec instrument. GC-MS analysis was performed on an Agilent Technologies 5973N MSD Mass Spectrometric

instrument. Elemental analyses were performed by the Analytical Services Department of Chemistry Department, Durham University.

Estimates of the purity of the chlorophosphines and phosphenium ions synthesised here were established by ^{31}P NMR, ^{1}H NMR and ^{13}C NMR spectroscopy only. Despite repeated attempts the chlorophosphines couldn't be purified further due to their air and moisture sensitive nature and their inability to be recrystallized. Hence a combination of these factors meant that satisfactory elemental analyses could not be obtained. Similarly, the analyses of the phosphenium ions synthesised were unsatisfactory (even for single crystals) possibly due to their incomplete burning in the elemental analyzer and/or their extreme sensitivity. A characteristic ^{31}P NMR spectrum for one of the phosphenium ions and its corresponding chlorophosphine is presented later in the text for reference. In the following pages only the most optimal synthetic procedure for each compound is reported. Nevertheless the yields are not optimized.

3.2 Imine Syntheses

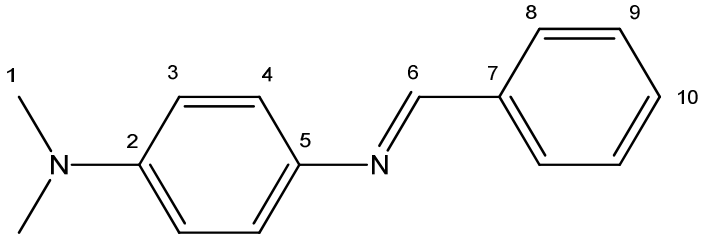
3.2.1 *N*-Benzylideneaniline (**ImI**)



The compound was synthesized as reported in the literature.[67] Specifically, aniline (5.00 mL, 5.11 g, 54.9 mmol) was added to benzaldehyde (5.82 mL, 6.08 g, 57.3 mmol) in a 50 mL flask with vigorous stirring. After a few seconds evolution of heat was observed and separation of water apparent. The mixture was left to stand for 15 minutes and was then poured into ethanol (9.0 mL) with vigorous stirring. Scratching the beaker's walls with a glass rod results in the formation of white crystals. The almost solid mixture was left in an ice bath for 30 minutes, the solid removed by filtration with a Buchner funnel and air dried. The product **ImI** was recrystalized from warm ethanol. **Unoptimized Yield** (5.93g, 56.5%), **m.p:** 48.5-50 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.48 (s, 1H, H^5), 7.94 – 7.92 (m, 2H, H^7), 7.52 – 7.48 (m, 3H, $H^{8,\ 9}$), 7.44 – 7.40 (m, 2H, H^2), 7.23 – 7.28 (m, 3H, $H^{1,3}$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 160.72 (C^5), 152.38 (C^4), 136.50 (C_6), 131.69 (C^9), 129.46 (C^7), 129.11(C^8), 129.08 (C^2), 126.25(C^1), 121.18 (C^3). **GC**: t (min) = 16.65 (100%). **MS** (EI, CH_3CN) m/z: M^+ - 1 = 180.1 (98%). **Anal.** Found: C, 86.03; H, 6.15; N, 7.71. Calc: C, 86.15; H, 6.12; N, 7.73.

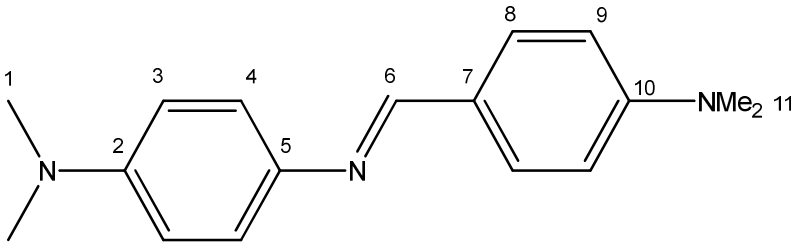
3.2.2 N^1-Benzylidene-N^4,N^4-dimethylbenzene-1,4-diamine (ImII)



ImII was synthesized following the method described by Bennett *et al.*[59] N^1,N^1-dimethylbenzene-1,4-diamine (15.00 g, 110 mmol) was dissolved in ethyl lactate (50 mL) followed by addition of benzaldehyde (11.2 mL, 110 mmol) with vigorous stirring. The imine precipitated out of the solution almost instantly yielding, after Buchner filtration, a dark yellow solid. The crude product was purified by Sohxlet extraction with petroleum ether at 80 °C yielding a clear yellow solution that afforded yellow crystals. The mixture was further cooled down to -30 °C overnight, and the resulting solid was isolated by Buchner filtration followed by air drying resulting in a yellow crystalline solid. **Yield** (14.2 g, 57.5 %), **m.p:** 93-94 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.52 (s, 1H, H^6), 7.89 (dd, $^3J_{HH}$=7.6, $^4J_{HH}$=1.9, 2H, H^8), 7.47 – 7.42 (m, 3H, $H^{9,10}$), 7.28 (d, J_{HH}=9.0, 2H, H^4), 6.77 (d, J_{HH}=8.9, 2H, H^3), 2.99 (s, 6H, H^1). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 156.35 (C^6), 149.87(C^2), 141.21 (C^5), 137.18 (C^7), 130.86 (C^{10}), 128.99 (C^9), 128.66 (C^8), 122.60 (C^4), 113.21 (C^3), 41.11 (C^1). **GC**: t (min) = 21.93 (100%). **MS** (EI, CH_3CN) m/z: M^+ = 223.8 (100%). **Anal.** Found: C, 80.29; H, 7.21; N, 12.55. Calc: C, 80.32; H, 7.19; N, 12.49.

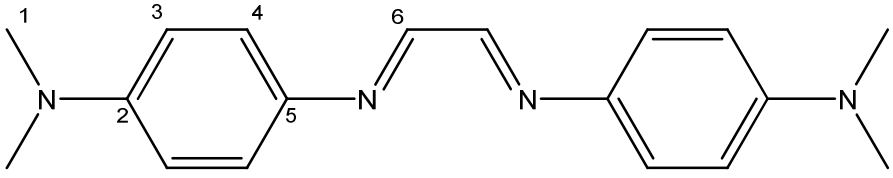
3.2.3 N^1-(4-(Dimethylamino)benzylidene)-N4,N4-dimethylbenzene-1,4-diamine (**ImIII**)



A two-neck flask with an attached condenser was loaded with *N1,N1*-dimethylbenzene-1,4-diamine (5.00 g, 36.7 mmol) and magnesium sulphate (5g). The whole system was vacuum dried and placed under nitrogen. Dry ethanol (70mL) and 4-(dimethylamino)benzaldehyde (5.40 g, 36.2 mmol) was added and the mixture heated at reflux overnight. This led to the formation of a dark precipitate. The mixture was condensed in a rotary evaporator and dried under reduced pressure. This resulted in the isolation of **ImIV** as dark coloured crystalline spheres after purification *via* Sohxlet extraction using petroleum ether (80 °C). **Yield** (5.92 g, 67.0%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (s, 1H, H^6), 7.76 (d, $^3J_{HH}$=8.9, 2H, $H^{4 \text{ or } 8}$), 7.22 (d, $^3J_{HH}$=8.9, 2H, $H^{4 \text{ or } 8}$), 6.77 (d, $^3J_{HH}$=8.9, 2H, $H^{3 \text{ or } 9}$), 6.74 (d, ^3J=8.9, 2H, $H^{3 \text{ or } 9}$), 3.04 (s, 6H, $H^{1 \text{ or } 11}$), 2.97 (s, 6H, $H^{1 \text{ or } 11}$).

3.2.4 (N^1,N^1,N^1,N^1')-*N1,N1'*-(Ethane-1,2diylidene)bis(N^4,N^4-dimethylbenzene-1,4-diamine) (**ImIV**)



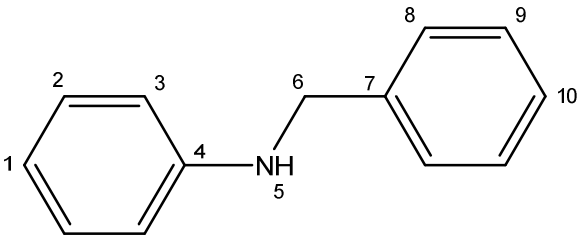
This compound was synthesized according to the literature procedure.[68] N^1,N^1-Dimethylbenzene-1,4-diamine (10.00 g, 73.42 mmol) was dissolved in methanol (80 mL). Oxalaldehyde (40% w/w solution, 4.21 mL, 1.68 g, 29.0 mmol) was added to the solution along with three drops of formic acid with vigorous stirring. This resulted in the formation of a brown solid. The reaction was left to reach completion (3h) and the product was

isolated by Buchner filtration as a brown solid. The crude solid was recrystalized from a DCM/ethanol mixture, isolated by filtration, washed with cold toluene and air dried. **Unoptimized Yield** (7.06 g, 82.7%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.47 (s, 2H, H^6), 7.35 (d, $^{3}J_{HH}$=9.1, 4H, $H^{3\text{ or }4}$), 6.73 (d, $^{3}J_{HH}$=9.1, 4H, $H^{3\text{ or }4}$), 3.01 (s, 12H, H^1).

3.3 Secondary Amine Synthesis

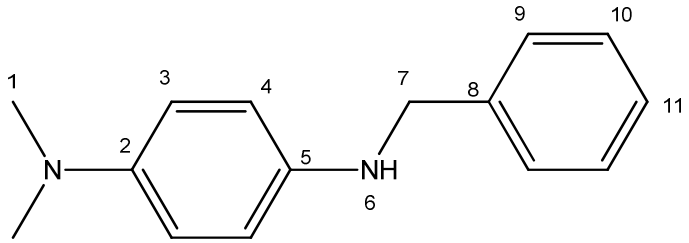
3.3.1 *N*-Benzylaniline (**AmI**)



This is a known compound which is commercially available from Sigma – Aldrich. Here, it was synthesized in the following way: A two-neck flask fitted with a condenser was loaded with crushed *N*-benzylideneaniline (**ImI**) (3.66 g, 20.2 mmol) and unpurified ethanol (60 mL), which was followed by slow addition of sodium borohydride (3.00 g, 79.3 mmol). The mixture was heated at reflux overnight, with evolution of gas being observed. After cooling to room temperature, the reaction was quenched by addition of water followed by neutralization of the mixture by dropwise addition of concentrated hydrochloric acid (37% w/w). Formation of a salt (NaCl) is observed, which is dissolved with further addition of water. The aqueous solution was extracted with DCM (3 x 30 mL) followed by drying of the organic layer over $MgSO_4$. The clear colourless DCM solution that resulted was condensed on a rotary evaporator leaving behind a pale yellow oil, which on standing in air overnight solidifies to yield a crystalline pale yellow solid of **AmI**. **Unoptimized Yield** (3.25 g, 87.8%), **m.p:** 36-37 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.10 (m, 7H, $H^{Aromatic}$), 6.87 – 6.43 (m, 3H, $H^{Aromatic}$), 4.35 (s, 2H, H^6), 4.04 (s, broad $\nu_{½}$ = 27 Hz, 1H, H^5). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.46 (s, C^4), 139.74 (s, C^7), 129.59 (s, C^8), 128.96 (s, C^2), 127.83 (s, C^9), 127.55 (s, C^{10}), 117.88 (s, C^1), 113.16 (s, C^3), 48.64 (s, C^6).

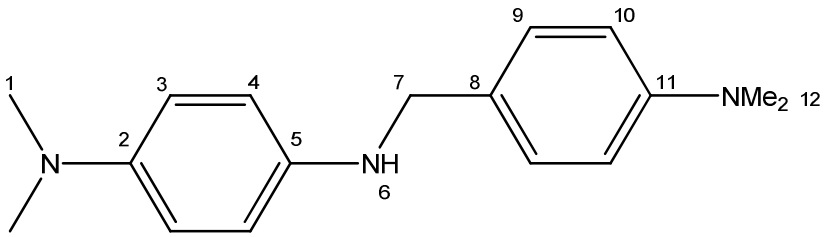
3.3.2 N^1-Benzyl-N^4,N^4-dimethylbenzene-1,4-diamine (**AmII**)



This compound has been synthesized before by reacting N^1,N^1-Dimethylbenzene-1,4-diamine with benzylalcohol.[69] Here, a modified procedure was followed: A two-neck flask fitted with a condenser was loaded with crushed **ImII** (14.2 g, 63.3 mmol) and analytical grade isopropanol (60 mL), which was followed by slow addition of sodium borohydride (10.0 g, 222.0 mmol). The mixture was heated at reflux overnight, which was accompanied by evolution of gas. After cooling to room temperature, the reaction was quenched by addition of water followed by neutralization of the mixture by dropwise addition of concentrated hydrochloric acid (37% w/w). Formation of a salt (NaCl) is observed, which is dissolved with further addition of water. The aqueous solution was extracted with DCM (3 x 40 mL) followed by drying of the organic layer over $MgSO_4$. The clear colourless DCM solution that resulted after filtration was condensed on a rotary evaporator leaving behind a dark brown yellowish oil, which on standing in air overnight solidifies to yield a dark brown yellowish solid of **AmII**. **Unoptimized Yield** (11.34 g, 79.1%). **m.p:** 41-43 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.40 (m, 5H, $H^{Aromatic}$), 6.77 (d, J_{HH}=8.2, 2H, $H^{3\text{ or }4}$), 6.65 (d, J_{HH}=7.7, 2H, $H^{3\text{ or }4}$), 4.30 (s, 2H, H^7), 3.72 (s, broad $\nu_{½}$ = 68 Hz , 1H, H^6), 2.84 (s, 6H, H^1). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.57 (s, C^2), 141.12 (s, C^5), 140.30 (s, C^8), 128.87 (s, C^{10}), 127.91 (s, $C^{9\text{ or }11}$), 127.40 (s, $C^{9\text{ or }11}$), 116.23 (s, C^4), 114.67 (s, C^3), 49.74 (s, C^7), 42.58 (s, C^1). **MS** (ES+, CH_3CN) m/z = 227.0 $(M + H)^+$.

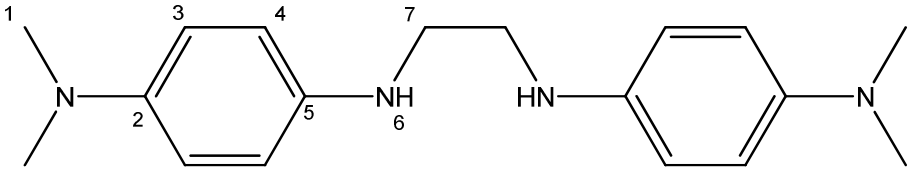
3.3.3 N^1-(4-(Dimethylamino)benzyl)-*N4,N4*-dimethylbenzene-1,4-diamine (**AmIII**)



Crushed **ImIII** (5.70 g, 21.3 mmol) was treated with sodium borohydride (4.00 g, 105.8 mmol) under the same conditions as described in section 3.3.1. In this case the starting mixture had a dark brown-yellowish colour, which became brownish-orange after heating at reflux. The final product has the form of a dark brown-yellowish oil mixed with solid, which solidifies to yield **AmIII** as an impure brown amorphous solid when left under air overnight.

Large amounts of the starting materials were found in the resulting product by ^{1}H NMR spectroscopy indicating incomplete reaction. The reaction wouldn't go to completion even when large amounts of $NaBH_4$ (tenfold) were used.

3.3.4 N^1,$N^{1\prime}$-(Ethane-1,2-diyl)bis(*N4,N4*-dimethylbenzene-1,4-diamine) (**AmIV**)



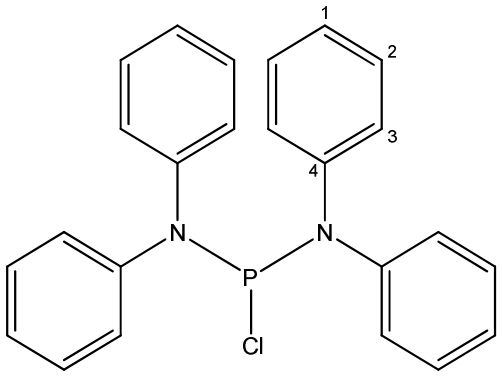
Crushed **ImIV** (3.16 g, 10.7 mmol) was treated with sodium borohydride (3.50 g, 92.5 mmol) under the same conditions as described in section 3.3.1. In this case the starting mixture has a brown colour, which became brownish-orange after heating at reflux. The final product was isolated as a black solid, which was recrystalized from a DCM/pentane solution in order to yield silver flakes of **AmIV**. **Unoptimized Yield** (2.21 g, 69.2 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.75 (d, $^3J_{HH}$=8.9, 4H, $H^{3\text{ or }4}$), 6.65 (d, $^3J_{HH}$=8.9, 4H, $H^{3\text{ or }4}$), 3.33 (s, 4H, H^7), 2.82 (s, 12H, H^1), 1.73 (s, 2H, H^6). **^{13}C NMR** (101 MHz, $CDCl_3$) δ =

144.33 (s, C^2), 140.67 (s, C^5), 115.94 (s, C^4), 114.71 (s, C^3), 44.65 (s, C^7), 42.25 (s, C^1). **MS** (ES+, CH_3CN) m/z = 299.3 $(M + H)^+$, 150.3.

3.4 Chlorophosphine Synthesis

3.4.1 1-Chloro-*N,N,N′,N′*-tetraphenylphosphinediamine (**N2PCl II**)



The synthesis of 1-chloro-*N,N,N′,N′*-tetraphenylphosphinediamine has been reported previously.[70, 71] Here, it was synthesized using the following procedure: Diphenylamine (5.00 g, 29.5 mmol) previously recrystallized from petroleum ether (80 °C) was loaded into a Schlenk along with diethyl ether (40 mL) and cooled to -78 °C. Dropwise addition of butyl lithium (1.6M in hexane, 18.50 mL, 29.6 mmol) was undertaken with vigorous stirring. The reaction was left at room temperature (2h), yielding a pale yellow solution with a white precipitate. A second Schlenk was loaded with a solution of trichlorophosphine (1.30 mL, 2.05 g, 14.9 mmol) in diethyl ether (20 mL) and cooled to -78 °C. Dropwise addition of the lithium salt to the cold trichlorophosphine solution with vigorous stirring resulted in the formation of a white precipitate. The reaction was left to react overnight. The volatile components were removed under reduced pressure and the residue was washed with toluene using a canula filter yielding **N2PCl II** as a pale yellow toluene solution, which after drying *in vacuo* formed a pale yellow viscous liquid. The final product contains less than 10% impurities (calculated by integrating the ^{31}P NMR spectrum of the final product) **Yield** (4.01 g, 66.8 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 6.70 (m, 20H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.35 (d, $^2J_{PC}$ = 10.2, C^4), 129.31 (s, $C^{1 \text{ or } 2}$), 126.29 (d, J = 8.6, C^3), 125.21 (s, $C^{1 \text{ or } 2}$). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 124.2 (s). The ^{31}P NMR spectrum is submitted in Figure 9.

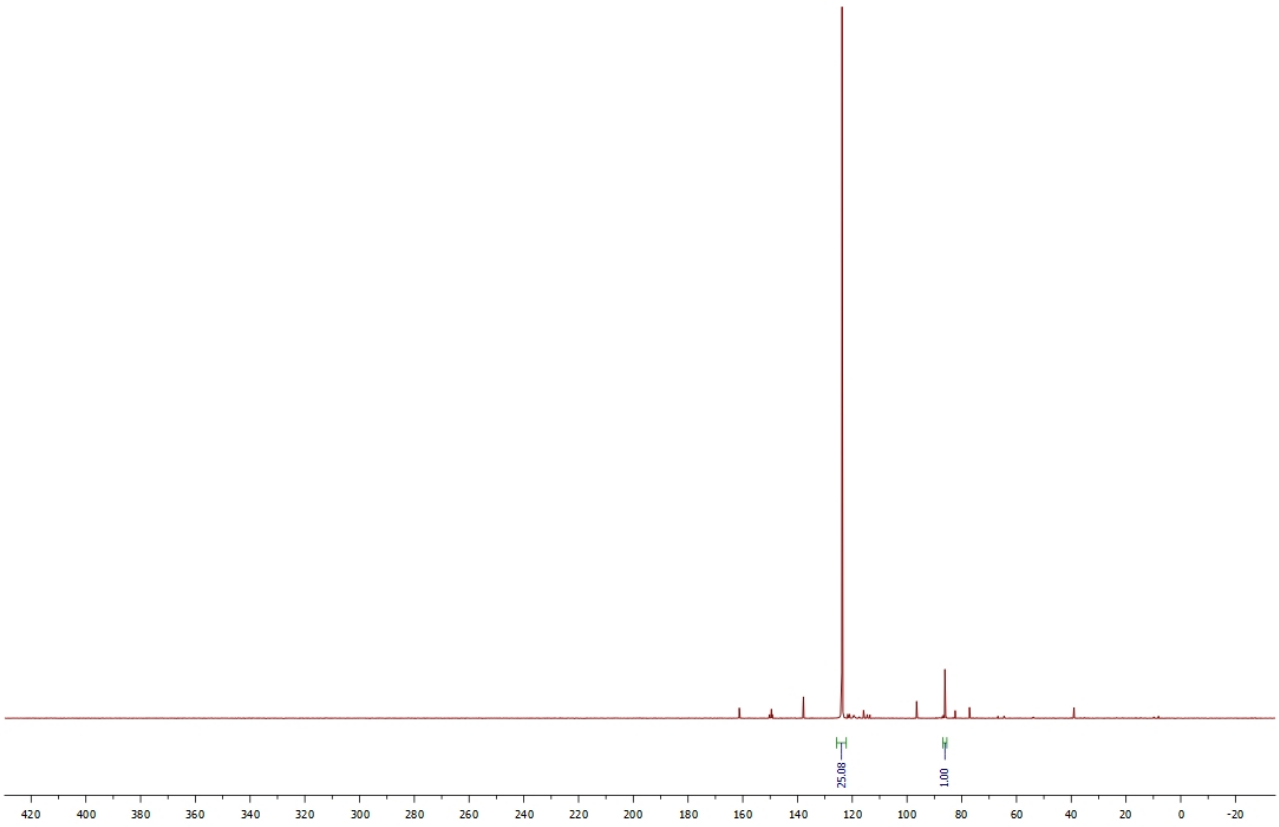
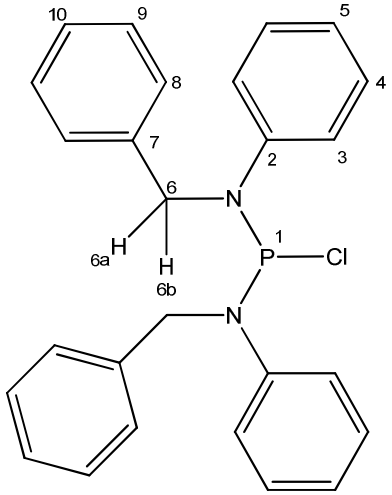


Figure 9: *The ^{31}P NMR spectrum of the chlorophosphine N2PCl II.*

3.4.2 *N,N′*-Dibenzyl-1-chloro-*N,N′*-diphenylphosphinediamine (**N2PCl III**)

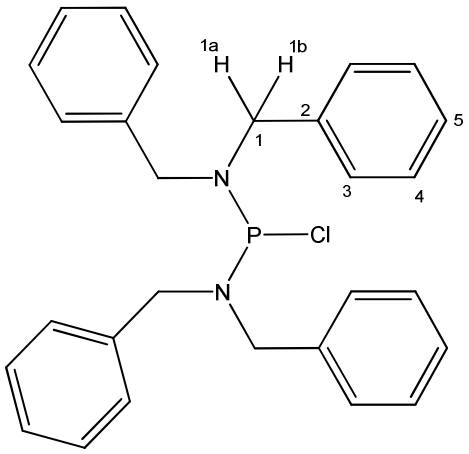


A Schlenk was loaded with *N*-benzylaniline (**AmI**) (3.00 g, 16.4 mmol), diethyl ether (20 mL) and cooled to -78 °C, which was followed by dropwise addition of butyl

lithium (1.6M in hexane, 10.23 mL, 16.4 mmol) with vigorous stirring. The reaction was left to react at room temperature (2h) yielding a pale yellow solution of the corresponding lithium salt. A second Schlenk was loaded with a solution of trichlorophosphine (0.71 mL, 1.12 g, 8.18 mmol) in diethyl ether (20 mL) and cooled to -78 ºC. Dropwise addition of the lithium salt to the cold trichlorophosphine solution with vigorous stirring resulted in the formation of a white precipitate. The reaction was left to react overnight. The volatile components were removed under reduced pressure and the residue was washed with toluene using a canula filter yielding **N2PCl III** as a pale yellow toluene solution, which after drying *in vacuo* formed a pale yellow viscous liquid. **Yield** (2.1 g, 59.6 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.10 (m, 20H, $H^{Aromatic}$), 4.82 (dd, J_{HH} = 15.9, $^{3}J_{PH}$ = 7.5, 1H, $H^{6a\ or\ 6b}$), 4.36 (dd, J_{HH} = broad, $^{3}J_{PH}$ = 10.1, 1H, $H^{6a\ or\ 6b}$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.61 (d, $^{2}J_{PC}$ = 12.5, C^{2}), 137.89 (d, $^{3}J_{PC}$ = 5.2, C^{7}), 129.33 (s, $C^{Aromatic}$), 128.42 (s, $C^{Aromatic}$), 127.25 (s, $C^{Aromatic}$), 125.78 (s, $C^{Aromatic}$), 125.68 (s, $C^{Aromatic}$), 125.15 (d, $^{3}J_{PC}$ = 1.8, C^{3}), 53.77 (d, $^{2}J_{PC}$ = 11.8, C^{6}). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 137.5 (s).

3.4.3 *N,N,N′,N′*-tetrabenzyl-1-chlorophosphinediamine (N2PCl IV)

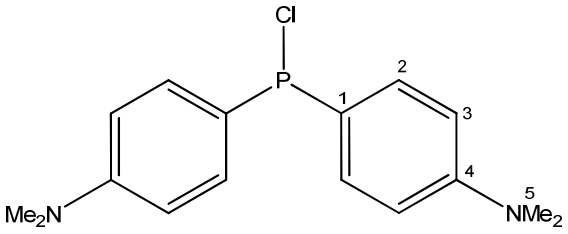


Dibenzylamine (10,0 mL, 10.26 g, 22.4 mmol) was dried over molecular sieves (3 Å), loaded in a Schlenk along with diethyl ether (60 mL) and cooled to -78 ºC. Subsequently, dropwise addition of butyl lithium (2.5M in hexane, 20.8 mL, 26.0 mmol) with vigorous stirring was carried out. The mixture was left to react at room temperature (2h), yielding a red solution and a white precipitate. A second Schlenk was loaded with a

solution of trichlorophosphine (2.26 mL, 26.0 mmol) in diethyl ether (20 mL) and cooled to -78 °C. Dropwise addition of the lithium salt to the cold trichlorophosphine solution under vigorous stirring resulted in the formation of a yellow solution with a white precipitate. The mixture was left to react overnight. The volatile components were removed under reduced pressure and the residue was washed with toluene using a cannula filter yielding **N2PCl IV** as a yellow toluene solution which after drying *in vacuo* formed a yellow viscous liquid. **Yield** (9.73 g, 81.6 %)

^{1}H NMR (400 MHz, CDCl3) δ 7.54 – 7.25 (m, 20H, $H^{Aromatic}$), 4.52 – 4.45 (m, broad, 4H, $H^{1a\ or\ 1b}$), 4.28 – 4.21 (m, broad, 4H, $H^{1a\ or\ 1b}$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.57 (d, $^{3}J_{PC}$ = 2.8, C^{2}), 128.90 (s, $C^{Aromatic}$), 128.68 (s, $C^{Aromatic}$), 127.59 (s, $C^{Aromatic}$), 51.44 (d, $^{2}J_{PC}$= 19.0, C^{1}). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 148.2 (s).

3.4.4 4,4'-(chlorophosphinediyl)bis(*N*,*N*-dimethylaniline) (C2PCl I)

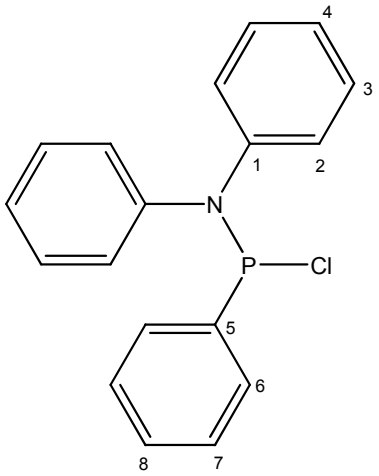


The lithium salt of 4-bromo-N,N-dimethylaniline used in this preparation was made according to the literature procedure.[72] A Schlenk was loaded with 4-bromo-N,N-dimethylaniline (5.00 g, 25.0 mmol), diethyl ether (40 mL) and cooled to -78 °C, which was followed by dropwise addition of butyl lithium (2.5M in hexane, 11.00 mL, 27.5 mmol) with vigorous stirring. The mixture was left to react at room temperature (2h), yielding a pale yellow solution of the corresponding lithium salt.[72] A second Schlenk was loaded with a solution of trichlorophosphine (1.10 mL, 12.5 mmol) in diethyl ether (40 mL) and cooled to -78 °C. Dropwise addition of the lithium salt to the cold trichlorophosphine solution with vigorous stirring resulted in the formation of a yellow

solution with a white precipitate. The mixture was left to react overnight. The volatile components were removed under reduced pressure and the residue was washed with DCM using a canula filter yielding **C2PCl I** as a yellow DCM solution, which after drying *in vacuo* formed a dark yellow viscous liquid. **Yield** (3.10 g, 80.8 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, $^{3}J_{PH}$ = 13.8, $^{3}J_{HH}$ = 9.2, 4H, H^2), 6.78 (dd, $^{3}J_{HH}$ = 9.2, $^{4}J_{PH}$ = 3.5, 4H), 3.09 (s, 12H, H^5). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.80 (d, $^{4}J_{PC}$ = 2.5, C^4), 135.01 (d, $^{3}J_{PC}$ = 14.4, C^3), 112.38 (d, $^{2}J_{PC}$ = 15.7, C^2), 102.74 (d, $^{1}J_{PC}$ = 113.2, C^1), 40.32 (s, C^5). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 64.2 (s)

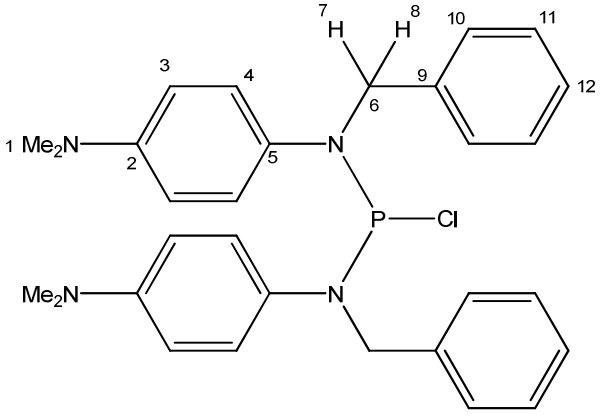
3.4.5 1-Chloro-*N*,*N*,1-triphenylphosphinamine (**CNPCl I**)



Diphenylamine (7.24 g, 42.8 mmol) previously recrystalized from petroleum ether (80 °C) was loaded into a Schlenk along with diethyl ether (40 mL) and cooled to -78 °C, followed by dropwise addition of butyl lithium (2.5 M in hexane, 17.1 mL, 42.8 mmol) followed by vigorous stirring. The mixture was left to react at room temperature (2h), yielding a pale yellow solution with a white precipitate of the corresponding lithium salt. A second Schlenk was loaded with a solution of dichloro(phenyl)phosphine (5.8 mL, 7.7 g, 42.8 mmol) in diethyl ether (20 mL) and cooled to -78 °C. Dropwise addition of the lithium salt to the cold dichloro(phenyl)phosphine solution with vigorous stirring resulted in the formation of a white precipitate. The reaction was left to reach completion overnight. The volatile components were removed under reduced pressure and the residue was washed with DCM using a canula filter yielding **CNPCl I** as a pale yellow DCM solution, which after drying *in vacuo* formed a pale yellow viscous liquid. **Yield** (11.5 g, 86.3 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H, $H^{Aromatic}$), 7.42 – 7.23 (m, 7H, $H^{Aromatic}$), 7.22 – 7.13 (m, 6H, $H^{Aromatic}$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.05 (d, $^{2}J_{PC}$ = 6.0, C^{1}), 137.39 (d, $^{1}J_{PC}$ = 27.9, C^{5}), 131.56 (d, $^{2}J_{PC}$ = 26.0, C^{6}), 130.56 (s, $C^{3,4\text{ or }8}$), 129.18 (s, $C^{3,4\text{ or }8}$), 128.35 (d, $^{3}J_{PC}$ = 6.6, $C^{2\text{ or }7}$), 125.83 (d, $^{3}J_{PC}$ = 8.9, $C^{2\text{ or }7}$), 125.24 (s, $C^{3,4\text{ or }8}$). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 118.2 (s).

3.4.6 *N*^{1},*N*^{1}'-(Chlorophosphinediyl)bis(*N*^{1}-benzyl-*N*^{4},*N*^{4}-dimethylbenzene-1,4-diamine) (**N2PCl V**)



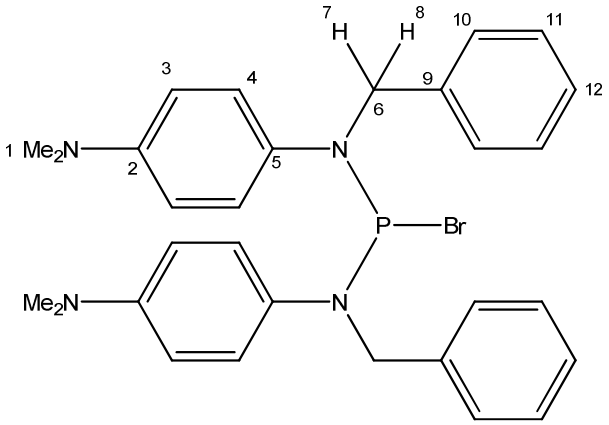
A Schlenk was loaded with **AmII** (10.00 g, 44.2 mmol), diethyl ether (70 mL) and cooled to -78 °C, which was followed by dropwise addition of butyl lithium (2.5 M in hexane, 17.7 mL, 44.2 mmol) with vigorous stirring. The mixture was left to react at room temperature (2h), which was accompanied by a colour change from dark brown-yellow to pale pink. A second Schlenk was loaded with a solution of trichlorophosphine (1.93 mL, 22.1 mmol) in diethyl ether (70 mL) and cooled to -78 °C. Dropwise addition of the lithium salt to the cold trichlorophosphine solution with vigorous stirring resulted in a colour change to orange along with formation of a gray precipitate. The volatile components were removed under reduced pressure and the precipitate was washed with DCM using a canula filter yielding **N2PCl V** as a dark greenish-orange solution, which after drying *in vacuo* formed a sticky dark solid. **Yield** (8.53 g, 74.6 %)

^{1}H NMR (700 MHz, C_6D_6) δ = 7.24 (d, J_{HH}=8.1, 4H, H^{4}), 7.21 (d, J_{HH}=7.1, 4H, H^{10}), 7.01 (t, J_{HH} =7.6, 6H, H^{11}), 6.94 (d, J_{HH}=7.37, 2H, H^{12}), 6.36 (d, J_{HH} =9.0, 4H, H^{3}), 4.88 (dd, J_{HH}=15.0, $^{3}J_{PH}$=7.8, 2H, $H^{7\text{ or }8}$), 4.31 (dd, J_{HH}=15.0, $^{3}J_{PH}$=2.2, 2H, $H^{7\text{ or }8}$), 2.36 (s, 12H, H^{1}). **^{13}C NMR** (176 MHz, C_6D_6) δ = 149.45 (s, C^{2}), 139.49 (d, $^{3}J_{PC}$ =5.6, C^{9}), 134.25 (d, $^{2}J_{PC}$=11.5, C^{5}), 129.67 (s, C^{10}), 129.44 (d, $^{3}J_{PC}$=7.1, C^{4}), 128.86 (s, C^{11}), 127.66 (s, C^{12}),

113.69 (s, C^3), 55.80 (d, $^2J_{PC}$=13.7, C^6), 40.12 (s, C^1). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 140.1 (s).

3.5 *bis*(Amino)bromophosphine Synthesis

3.5.1 $N^1,N^{1\prime}$-(Bromophosphinediyl)bis(N^1-benzyl-N^4,N^4-dimethylbenzene-1,4-diamine) (**N2PBr I**)

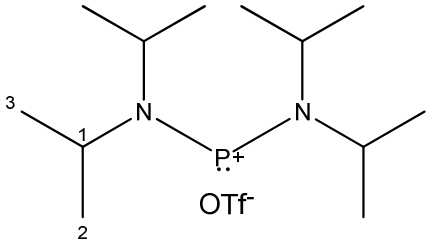


AmII (2.19 g, 9.67 mmol) was treated with butyl lithium (1.6 M in hexane, 6.10 mL, 9.76 mmol) and tribromophosphine (0.46 mL, 1.32 g, 4.89 mmol) under the same conditions as described in Section 3.4.6. **Unoptimized Yield** (1.19 g, 44.0 %).

^{1}H NMR (700 MHz, C_6D_6) δ = 7.25 (dd, $^3J_{HH}$=8.9, $^4J_{PH}$ =0.9, 4H, H^4), 7.14 (d, $^3J_{HH}$=7.0, 4H, H^{10}), 6.99 – 6.95 (m, 4H, H^{11}), 6.92 – 6.88 (m, 2H, H^{12}), 6.30 (d, $^3J_{HH}$=8.8, 4H, H^3), 4.82 (s, broad $\nu_{½}$ = 44Hz, 2H, $H^{7\text{ or }8}$), 4.34 (s, broad $\nu_{½}$ = 45Hz, 2H, $H^{7\text{ or }8}$), 2.31 (s, 12H, H^1). **^{13}C NMR** (176 MHz, C_6D_6) δ = 148.73 (s, C^2), 137.71 (d, $^3J_{PH}$=5.9, C^9), 132.62 (s, C^5), 128.79 (s, C^{10}), 128.30 (d, $^3J_{PH}$=6.9, C^4), 127.80 (s, C^{11}), 126.72 (s, C^{12}), 112.56 (s, C^3), 56.34 (d, $^2J_{PC}$=15.1, C^6), 39.65 (s, C^1). **^{31}P NMR** (81 MHz, benzene) δ = 159.1 (s).

3.6 Phosphenium Cation Syntheses

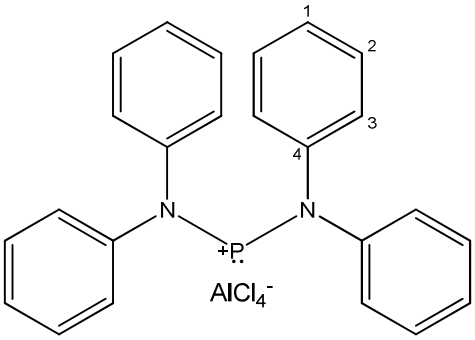
3.6.1 *N,N,N′,N′*-Tetraisopropylphospheniumdiamine Triflate (**N2P+ I**)



This compound was synthesized according to literature procedures.[64] **N2PCl I** (0.5 g, 1.24 mmol) was dissolved in DCM (5 mL) yielding a colourless solution, which after dropwise addition of TMSOTf (0.38 mL, 0.47 g, 2.10 mmol) becomes pale yellow. After the volatile components were thoroughly removed under reduced pressure, DCM (5 mL) was added and the resulting solution was dried *in vacuo* leaving behind a pale yellow solid, which was recrystalized from DCM yielding pale yellow crystals of **N2P+ I**.

^{31}P NMR (162 MHz, benzene) δ = 312.1 (s).

3.6.2 *N,N,N′,N′*-Tetraphenylphospheniumdiamine Tetrachloroaluminate (**N2P+ II**)



N2PCl II (1.00g, 2.48 mmol) was mixed in a Schlenk along with $AlCl_3$ (0.364 g, 2.73 mmol). Subsequent addition of DCM (5 mL) resulted in a pale yellow solution, which gradually turns blood red as the reaction goes to completion. Red crystals of **N2P+ II** were grown from the solution upon cooling at -30 °C, which were found suitable for an X-ray crystallographic analysis.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.57 (s), 7.41-7.36 (m, broad), 7.19 (s, broad $\nu_{½}$ = 21 Hz).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 141.18 (s, broad $\nu_{½}$ = 25 Hz , C^4), 131.23 (s), 131.03 (s),

126.85 (s). **^{31}P NMR** (162 MHz, benzene) δ = 234.6 (s). The ^{31}P NMR spectrum is submitted in Figure 10.

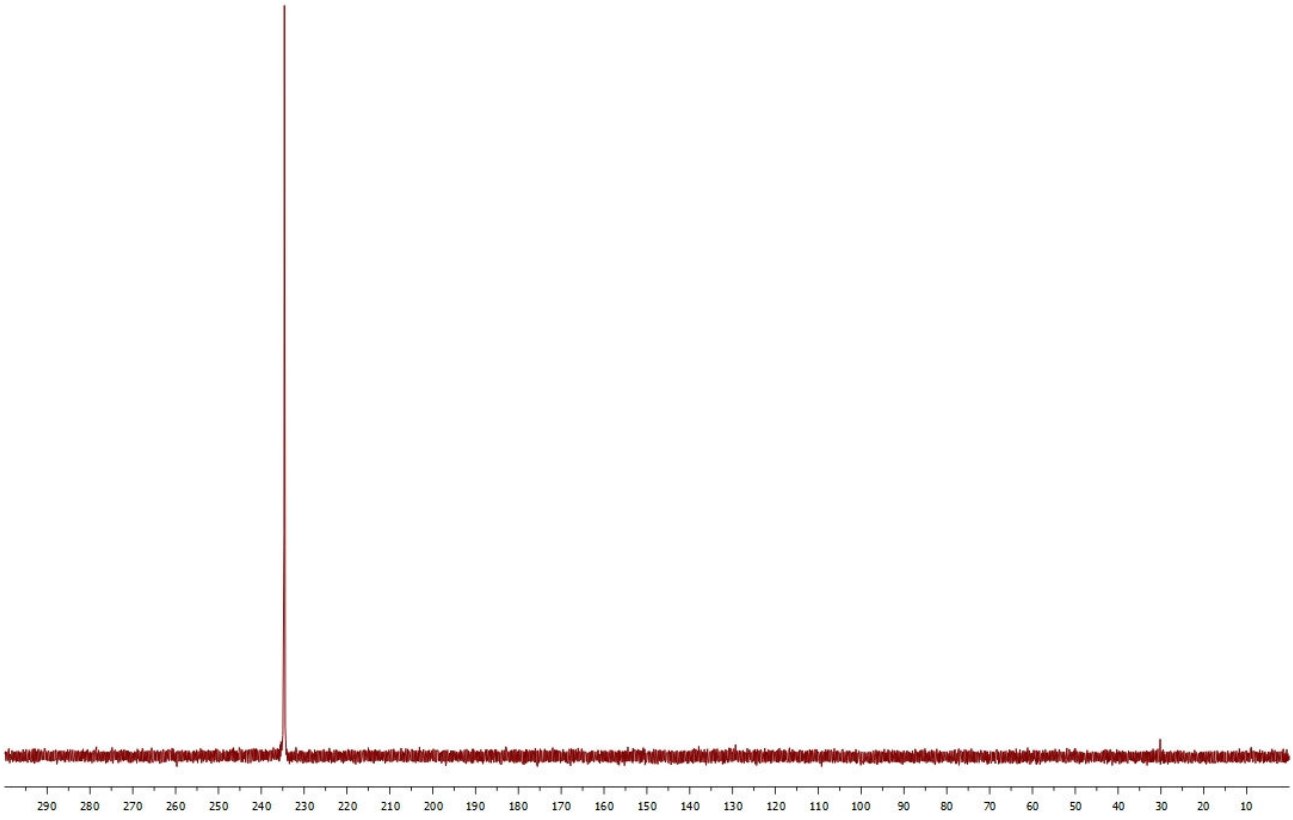
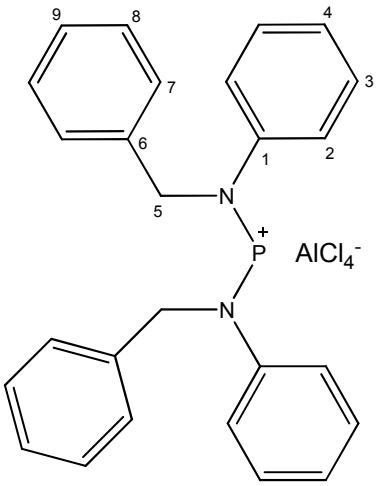


Figure 10: *The ^{31}P NMR spectrum of the phosphenium ion N2P+ II.*

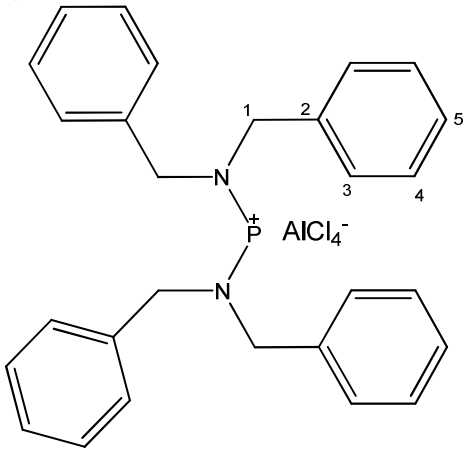
3.6.3 *N,N′*-dibenzyl-*N,N′*-diphenylphospheniumdiamine tetrachloroaluminate (**N2P+ III**)



N2PCl III (1.00g, 2.32 mmol) was mixed in a Schlenk along with $AlCl_3$ (0.342 g, 2.56 mmol). Subsequent addition of DCM (5 mL) resulted in a pale yellow solution, which gradually turns yellow as the reaction goes to completion. Yellow crystals of **N2P+ III** were grown from the solution upon cooling at -30 °C, which were found suitable for an X-ray crystallographic analysis.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 – 6.55 (m, $H^{Aromatic}$ broads, 20H), 5.10 (s, H^{5} broad $\nu_{½}$ = 36 Hz, 4H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 138.66 (s, C^{1}), 132.56 (d, $^{3}J_{PC}$ = 5.2, C^{6}), 130.12 (s, $C^{Aromatic}$), 129.86 (s, $C^{Aromatic}$), 129.53 (s, $C^{Aromatic}$), 129.47 (s, $C^{Aromatic}$), 129.19 (s, $C^{Aromatic}$), 127.07(s, $C^{Aromatic}$), 61.84 (d, $^{2}J_{PC}$ = 31.0, C^{5}). **^{31}P NMR** (162 MHz, CD_2Cl_2) δ 249.0 (s, slightly broad $\nu_{½}$ = 85 Hz).

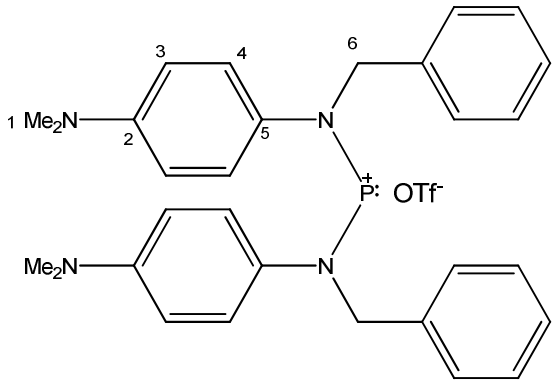
3.6.4 *N,N′*-dibenzyl-*N,N′*-diphenylphospheniumdiamine tetrachloroaluminate (**N2P+ IV**)



$(Bnz_2N)_2PCl$ (1.00g, 2.18 mmol) was mixed in a Schlenk along with $AlCl_3$ (0.320 g, 2.40 mmol). Subsequent addition of DCM (5 mL) resulted in a pale yellow solution, which gradually turns orange as the reaction goes to completion. The volatile components were removed under reduced pressure resulting in an orange viscous oil.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.64 – 7.34 (m, 12H, $H^{4,5}$), 7.27 – 7.10 (m, 8H, H^{3}), 4.74 (d, $^{3}J_{PH}$ = 9.3, 8H, H^{1}). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 132.38 (d, $^{3}J_{PC}$ = 3.4, C^{2}), 130.18 (s, $C^{4\text{ or }5}$), 130.05 (s, $C^{4\text{ or }5}$), 128.54 (s, C^{3}), 55.65 (d, $^{2}J_{PC}$ = 12.6, C^{1}). **^{31}P NMR** (162 MHz, CD_2Cl_2) δ 264.0 (s).

3.6.5 *N*^{1},*N*^{1}′-(Phospheniumdiyl)bis(*N*^{1}-benzyl-*N*^{4},*N*^{4}-dimethylbenzene-1,4-diamine) Triflate (**N2P+ V**)



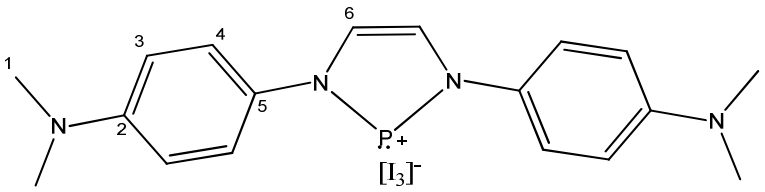
N2PCl V (0.5 g, 0.97 mmol) was dissolved in DCM (5 mL) yielding an orange solution, which after dropwise addition of TMSOTf (0.19 mL, 1.06 mmol) becomes blood

red. The reaction was left to reach completion for one hour. After the volatile components were thoroughly removed under reduced pressure, DCM (5 mL) was added and the resulting solution was dried *in vacuo* leaving behind a red solid.

^{1}H NMR (500 MHz, CD_2Cl_2, 0 °C) δ 7.25 (m, 5H), 6.73 (m, 2H), 6.27 (s, broad, 2H), 4.91 (d, $^{3}J_{PH}$ = 10.1, 2H), 2.82 (s, 6H). **^{31}P NMR** (202 MHz, CD_2Cl_2, 0 °C) δ 244.46 (s, broad $\nu_{½}$ = 339 Hz) + impurities. **^{31}P NMR** (202 MHz, CD_2Cl_2, – 80 °C) at δ 237.8 (s) + impurities.

3.7 Cyclic Phosphenium Cation Synthesis

3.7.1 4,4'-(1,3,2-Diazacyclophospholenium-1,3(2H)-diyl)bis(*N*,*N*-dimethylaniline) Triiodide



An **ImIV** (0.894 g, 3.04 mmol) and a triiodophosphine (1.250 g, 3.04 mmol) solution were prepared in DCM (30 mL). Dropwise addition of the triiodophosphine solution to the diamine solution was undertaken over the period of 30 minutes. An instant colour change of the solution from brown to dark greenish yellow was observed, which became dark yellow after the reaction was left to reach completion overnight.

No reaction was observed. The PI_3 resonance remained unchanged even after leaving the mixture to react for 3 days.

4. Appendix I

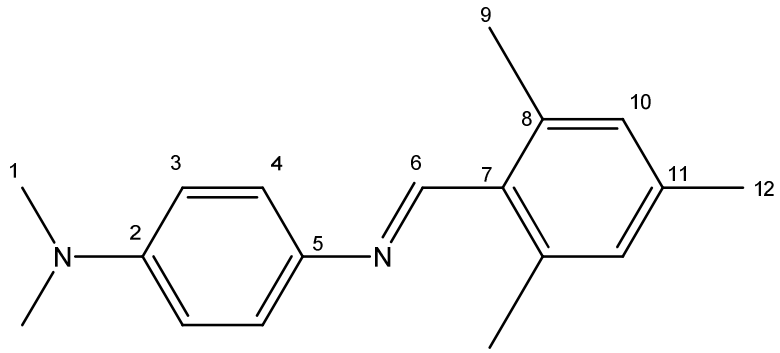
In this section are reported some additional compounds prepared, but not discussed in this report.

4.1 Phosphorus Triiodide Synthesis

A two-neck flask fitted with a condenser was dried under reduced pressure and loaded with DCM (40mL), PCl_3 (5.00 mL, 7.87 g, 57.3 mmol) and KI (30.0 g, 180.7 mmol). The mixture was heated at reflux for 3 days. This resulted to the formation of a bright red crystalline solid (PI_3) and a fine white precipitate (KCl). The product was isolated by Sohxlet distillation with DCM and carefully dried under reduced pressure because of the compound's low sublimation point.

^{31}P NMR (162 MHz, benzene): δ = 174.8 (s, PI_3), 103.41 (s, P_2I_4).

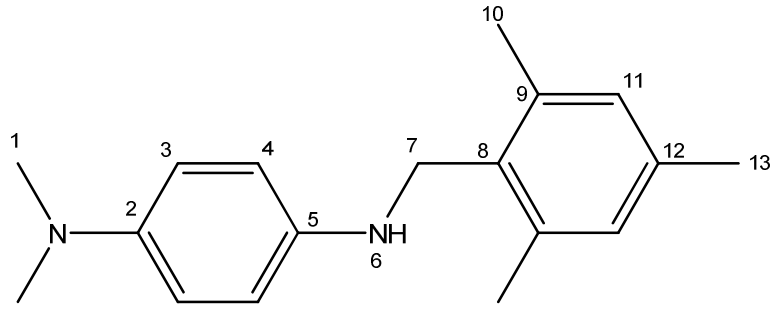
4.2 *N1,N1*-Dimethyl-*N4*-(2,4,6-trimethylbenzylidene) benzene-1,4-diamine



N1,N1-Dimethylbenzene-1,4-diamine (5.00 g, 36.7 mmol) was treated with 2,4,6-trimethylbenzaldehyde (4.9 mL, 5.00 g, 33.8 mmol) under the same conditions as described in Section 3.2.2. This resulted in the isolation of **ImIII** as, shiny yellowish-brown crystals. **Unoptimized Yield** (6.19 g, 68.8%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.81 (s, 1H, H^6), 7.22 (d, $^{3}J_{HH}$=8.5, 2H, $H^{3\text{ or }4}$), 6.91 (s, 2H, H^{10}), 6.79 (d, $^{3}J_{HH}$=8.7, 2H, $H^{3\text{ or }4}$), 2.98 (s, 6H, H^1), 2.51 (s, 6H, H^9), 2.31 (s, 3H, H^{12}).

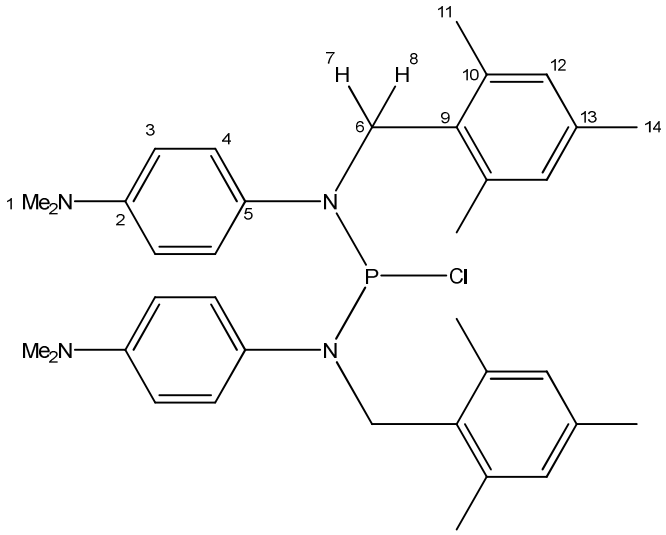
4.3 *N1,N1*-Dimethyl-*N4*-(2,4,6-trimethylbenzyl)benzene-1,4-diamine



Crushed **ImIII** (6.19 g, 23.2 mmol) was treated with sodium borohydride (4.00 g, 105.8mmol) under the same conditions as described in Section 3.3.2. In this case the starting mixture had a dark brown-yellowish color, which became darker after heating under reflux. The final product is a dark oil, which solidifies to yield **AmIII** as a black amorphous solid when left under air overnight. **Unoptimized Yield** (5.15 g, 82.7 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.90 (s, 2H, H^{11}), 6.81 (d, $^{3}J_{HH}$=8.2, 2H, $H^{3\ or\ 4}$), 6.67 (d,$^{3}J_{HH}$=8.2, 2H, $H^{3\ or\ 4}$), 4.16 (s, 2H, H^{7}), 2.85 (s, 6H, H^{1}), 2.36 (s, 6H, H^{10}), 2.29 (s, 3H, H^{13}). **^{13}C NMR** (101 MHz, CDCl3) δ = 144.29 (s), 141.83 (s), 137.71 (s), 137.34 (s), 132.91 (s), 129.30 (s), 116.46 (s), 114.09 (s), 43.57 (s), 42.76 (s), 21.24 (s), 19.72 (s). **MS** (ES+, CH_3CN) m/z = 269.1 $(M + H)^{+}$.

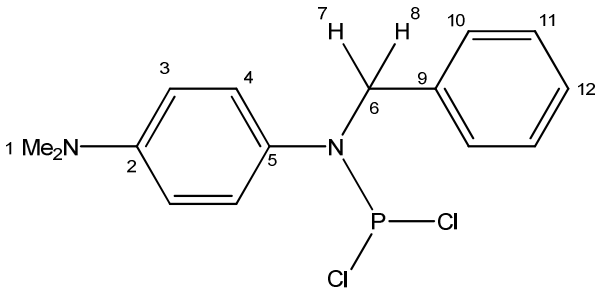
4.4 *N1,N1'*-(Chlorophosphinediyl)bis(*N4,N4*-dimethyl-*N1*-(2,4,6-trimethylbenzyl)benzene-1,4-diamine)



AmIII (2.35 g, 8.66 mmol) was treated with butyl lithium (1.6 M in hexane, 5.47 mL, 8.75 mmol) and trichlorophosphine (0.38 mL, 0.60 g, 4.36mmol) under the same

conditions as described in Section 3.4.6. In this case the starting mixture had a black colour, which became dark brown after the butyl lithium addition. The final product has the form of a gray like solid. **^{31}P NMR** (81 MHz, benzene) δ = 146.01 (s). **Solid State ^{31}P NMR** (162 MHz) δ = 148.3 (s).

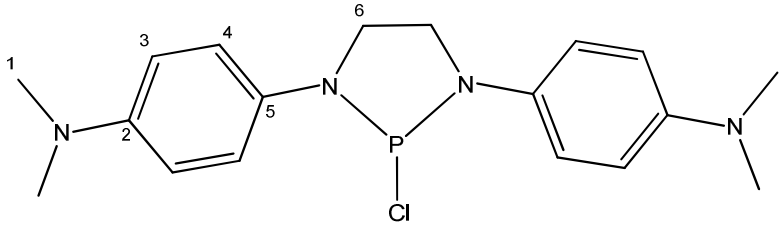
4.5 *N1*-Benzyl-*N1*-(dichlorophosphino)-*N4,N4*-dimethylbenzene-1,4-diamine



AmII (1.00 g, 4.42 mmol) was treated with butyl lithium (1.6 M in hexane, 2.76 mL, 4.46 mmol) and trichlorophosphine (0.39 mL, 0.61 g, 4.47 mmol) under the same conditions as described in Sectin 3.4.6, resulting in the formation of an orange viscous liquid.

^{1}H NMR (700 MHz, CD_2Cl_2) δ = 7.38 – 7.15 (m, 5H, $H^{Aromatic}$), 6.97 (d, *J*=7.8, 2H, $H^{Aromatic}$), 6.62 (s, broad, 2H), 4.79 (d, $^{3}J_{PH}$ =4.6, 2H, $H^{7,8}$), 2.91 (s, 6H, H^{1}). **^{13}C NMR** (176 MHz, CD_2Cl_2) δ = 136.42 (d, *J*=2.4), 128.85 (s), 128.82 (s), 128.24 (s), 127.42 (s), 112.56 (s), 54.16 (s), 40.33 (s), 28.71 (s), 22.46 (s), 13.72 (s). **^{31}P NMR** (162 MHz, benzene) δ = 155.1 (s)

4.6 4,4'-(2-Chloro-1,3,2-diazaphospholidine-1,3-diyl)bis(*N,N*-dimethylaniline)

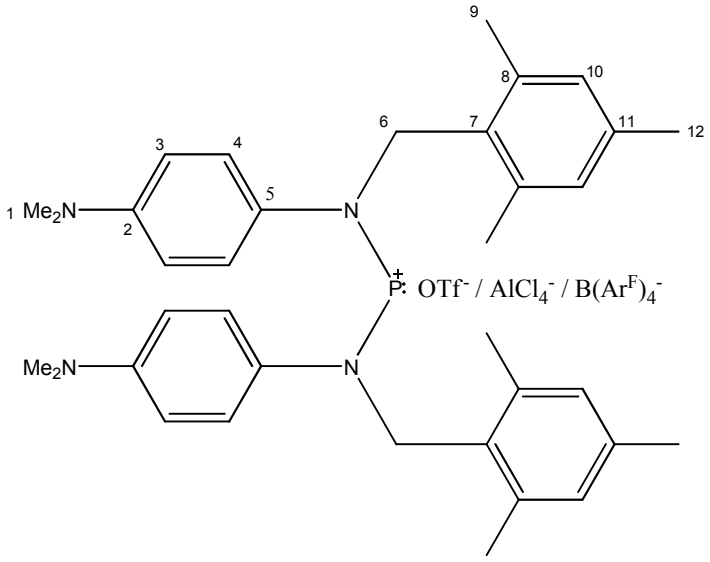


DAmI (1.00 g, 3.35 mmol) was treated with butyl lithium (1.6 M in hexane, 4.19 mL, 6.70 mmol) and trichlorophosphine (0.29 mL, 0.46 g, 3.32 mmol) under the same conditions as described in Section 3.4.6. In this case the starting mixture had an orange-brownish color, which became dark green after the butyl lithium addition. The final

product has an olive oil-like color in DCM solution from which pale yellow urchin-like crystals form upon cooling at -30 °C.

^{31}P NMR (162 MHz, Benzene) δ = 143.7 (s, broad).

4.7 *N1,N1'*-(Phospheniumdiyl)bis(*N4,N4*-dimethyl-*N1*-(2,4,6-trimethylbenzyl)benzene-1,4-diamine)Cation



- Counter ion = OTf$^-$: **N2PCl IV** (0.250g, 0.42 mmol) was treated with TlOTf (0.150 g, 0.42 mmol). In this case the DCM solution turns blood red upon addition of the TlOTf.

  ^{31}P NMR (162 MHz, benzene): No signal apparent.

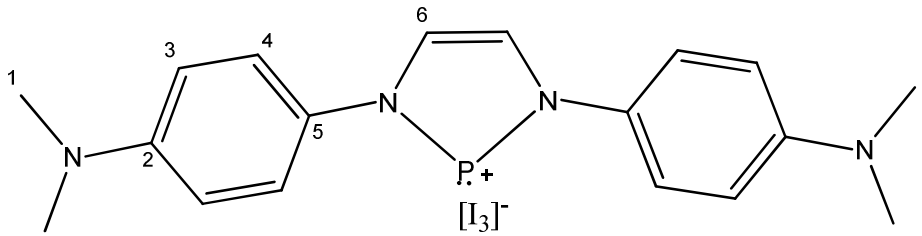
- Counter ion = $AlCl_4^-$: **N2PCl IV** (0.290g, 0.48 mmol) was treated with $AlCl_3$ (0.90 g, 6.70 mmol) under the same conditions as described in section 3.10.2. In this case the DCM solution turns blood red upon addition of the $AlCl_3$.

  ^{31}P NMR (202 MHz, CD_2Cl_2) δ = 264.87 (s, broad), 249.34 (s, broad, barely visible), **^{31}P NMR** (202 MHz,-80 °C, CD_2Cl_2) δ = 264.87 (s, broad), 249.34 (s, sharp), **Solid State ^{31}P NMR** (162 MHz) δ = 247.54 (s with satellites), **Solid State ^{27}Al NMR** (104.2 MHz) δ = 102.3 ($AlCl_4^-$), 87.7($AlCl_3$).

- Counter ion = $B(Ar^F)_4^-$: N2PCl IV (0.150g, 0.25 mmol) was treated with $LiB(Ar^F)_4$ (0.342 g, 0.50 mmol) in DCM. In this case the DCM solution turns blood red upon addition of the $LiB(Ar^F)_4$.

^{31}P NMR (162 MHz, benzene): No signal apparent.

4.8 4,4'-(1,3,2-Diazacyclophospholenium-1,3(2H)-diyl)bis(*N*,*N*-dimethylaniline) Triiodide



A **DImI** (0.894 g, 3.04 mmol) and a triiodophosphine (1.250 g, 3.04 mmol) solution were prepared in DCM (30 mL). Dropwise addition of the triiodophosphine solution in the diamine solution follows over the period of 30 minutes. An instant color change of the solution from brown to dark greenish yellow was observed, which became dark yellow after the reaction was left to reach completion overnight.

No reaction observed.

5. Appendix II

In this appendix the postgraduate first year modules, chemistry colloquia attended at Durham University and external inorganic conferences attended are listed.

I) Postgraduate first year modules

Practical Spectroscopy – 56% (pass)

Introduction to Organometallic Chemistry – 64% (pass)

II) External Inorganic Conferences Attended

Dalton Division Main Group Discussion Meeting, University of Manchester, 11th September, 2009

6th European Workshop on Phosphorus Chemistry, March 26-27th, 2009 at University of Florence, Florence, Italy.

III) Chemistry Colloquia Attended at Durham University Chemistry Department

Prof. Dr. Manfred Scheer, University of Regensburg, Germany.
"Complexed Main Group-Congeners of Hydrocarbons in Molecular and Supramolecular Environments"

Prof. Erick M. Carreira, ETH Zurich, Switzerland.
"Discovery and Surprises with Small Molecules"

Dr. Chris Russell, Bristol.
"Novel Structure, Bonding and Reactivity for Pnictogens in Low Coordinate Environments. Is Phosphorus a Carbon Copy?"

Dr. Jason Riley, Imperial.
"Nanomaterials for Displays - What can an electrochemist contribute?"

Prof. Mark Weller, Southampton.
"From Greenland to Grenoble; The Structural Chemistry of New Frameworks and All Sorts of Hydrogen Compounds"

Prof. Todd Marder, Durham.

"Metal Catalysed Synthesis of Retinoids for Stem Cell Differentiation Including Applications of Novel C-H Bond Functionalisation Processes"

Dr. Andrew Sutherland, Glasgow.

"New stereoselective rearrangement processes for the synthesis of natural products"

Prof. Stuart Macgregor, Heriot Watt.

"Computational studies on bond activation reactions at transition metal centres"

Prof. Paul Beer, Oxford University.

"Anion templated assembly of interlocked structures and ion-pair recognition"

Prof. Naokazu Kano, University of Tokyo, Japan.

"Development of organic fluorescent materials by taking advantage of N-B interaction"

Prof. Mike Ward, Sheffield University.

"Self-assembly and host-guest chemistry of polyhedral coordination cages"

Prof. Rob Field, John Innes Centre.

"From biofuels to homeland security: challenges for chemistry and chemical biology"

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