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**NANYANG
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BUILDING A LEWIS ACIDIC PHOSPHORUS

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School of Physical and Mathematical Sciences

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School of Physical and Mathematical Sciences

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Construction d'acides de Lewis à base de phosphore dicoordiné

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Abstract

This work involves the synthesis and characterization of phosphonium cations whose stability reflects the σ - and π - donating properties of carbene ligands. A coordinatively unsaturated P(III)-containing dication, $[\text{iPr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$, has been synthesized and fully characterized by single crystal X-ray diffraction and theoretical calculations. Its reactivity towards DMAP, PMe_3 , H_2O , MeOH , and CoCp_2 is presented; no reactions were observed with 2-butyne, dimethylbutadiene and anisole. Two other putative Ph- and Cl-substituted dications $[\text{XPC}(\text{PPh}_3)_2]^{2+}$ were targeted. These could not be observed directly, but evidence for their formation has been obtained through trapping with alkynes and 1,3-dienes to form dicationic species containing phosphirene and phospholene rings, respectively. Reduction of $[\text{Me}_2\text{C}_2\text{PClC}(\text{PPh}_3)_2]^{2+}$ with elemental magnesium resulted in the formation of $[\text{Me}_2\text{C}_2\text{PC}(\text{PPh}_3)_2]^+$, while the dehydrohalogenation of $[\text{Me}_2\text{C}_4\text{H}_4\text{PClC}(\text{PPh}_3)_2]^{2+}$ by 2-methylpyridine resulted in the formation of a phosphole. Preliminary studies on the hydrolysis of the Cl-substituted phosphirenium salt, $[\text{Me}_2\text{C}_2\text{PClC}(\text{PPh}_3)_2]^{2+}$ shows a possible formation of a stable phosphirene oxide.

A French version of the abstract is presented on the next page.

Sommaire

Ce travail porte sur la synthèse et la caractérisation de dications phosphorés dont la stabilité résulte de la présence de ligands carbodiphosphoranes (carbones) qui présentent une capacité σ - et π - donneuse forte. Un dication phosphoré $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$ a été synthétisé et entièrement caractérisé par structure aux RX et par DFT. Sa réactivité *vis-à-vis* de la DMAP, PMe_3 , H_2O , MeOH , et CoCp_2 est décrite; il manifeste aucune réactivité évidente avec le but-2-yne, le dimethylbuta-1,3-diène et l'anisole. Deux analogues: $[\text{XP}(\text{C}(\text{PPh}_3)_2)]^{2+}$ ($\text{X} = \text{Ph}, \text{Cl}$) ont également été ciblés. Bien qu'impossibles à isoler, une réactivité compatible avec leur existence a été mise en évidence dans les réactions avec des alcynes et 1,3-diènes, qui mènent respectivement aux dications contenant les cycles phosphirènes et phospholènes. Le dication $[\text{Me}_2\text{C}_2\text{PClC}(\text{PPh}_3)_2]^{2+}$, réduit par la magnesium, mène au complexe de phosphirène $[\text{Me}_2\text{C}_2\text{PC}(\text{PPh}_3)_2]^+$, et une réaction de déshydrohalogénéation de $[\text{Me}_2\text{C}_4\text{H}_4\text{PClC}(\text{PPh}_3)_2]^{2+}$ fournit le phosphole correspondant. Des études préliminaires de l'hydrolyse du complexe $[\text{Me}_2\text{C}_2\text{PClC}(\text{PPh}_3)_2]^{2+}$ suggèrent la possibilité de synthétiser un oxyde de phosphirene stable.

Summary

Carbodiphosphorane, also known as carbene, ligands have the ability to act as strong 2-electron σ - and 2-electron π -donors.¹ A coordinatively unsaturated P(III)-containing dication, $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$, has been synthesized and fully characterized by single crystal X-ray diffraction.² Planarity is observed along the C_2NPCP_2 fragment, and this places both the amino and the carbene lone pair, which have π symmetry, in an ideal position to interact with the formally vacant P(3p) orbital in $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$. Theoretical calculations have been used to delineate the structural and electronic features of the dication. Its HOMO-12 (-12.90 eV), the molecular orbital that most adequately represents the lone pair located on the central P atom of $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$ is quite destabilized with respect to the analogous orbital of $[\text{P}(\text{NMe}_2)_2]^+$ (-13.52 eV). This suggests that $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$ is a better σ -donor than the phosphonium cation. The LUMO (-7.77 eV) for $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$ is again more stabilized than the LUMO (-6.91 eV) for $[\text{P}(\text{NMe}_2)_2]^+$ thus implying that $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$ is also a better Lewis acid than $[\text{P}(\text{NMe}_2)_2]^+$. The reactivity of $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$ towards DMAP, PMe_3 , H_2O , MeOH ,³ and CoCp_2 is presented, with the $\text{BAr}^{\text{F}}_4^-$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$) anion being used in these experiments so as to remove any potential for interference from the more commonly used AlCl_4^- counterion. A dication•DMAP adduct was formed via the reaction of $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$ and DMAP. For the reaction between $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$ and PMe_3 , it was possible to obtain a van't Hoff plot by Variable Temperature (VT) ^{31}P NMR spectroscopy, from which the thermodynamic parameters $\Delta H = -30.5 \text{ kJ mol}^{-1}$ and $\Delta S = -77.7 \text{ eu}$ have been extracted. In addition, $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$ is also observed to activate both water and methanol under conditions which are uncommon for other systems with non-metal centres. In an attempt to reduce our $[^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$, CoCp_2 was used. Theoretical calculations showed that an electron should initially add at the dicoordinate P

center, but the system undergoes an interesting activation of a CH bond of one of the triphenylphosphine rings to generate a compound containing a stable 5-membered ring. It is also shown that $[\text{Pr}_2\text{NPC}(\text{PPh}_3)_2]^{2+}$ shows no reactivity at room temperature over protracted periods with substrates such as 2-butyne, 2,3-dimethylbutadiene and anisole. Attempts have been made to extend the series of P(III)-containing dications to carbene-containing analogues that lack the stabilizing diisopropylamino group, with $[\text{XPC}(\text{PPh}_3)_2]^{2+}$ ($\text{X} = \text{Ph}, ^4\text{Cl}$) being targeted. The putative Ph- and Cl-substituted dications $[\text{XPC}(\text{PPh}_3)_2]^{2+}$ could not be observed directly, but evidence for their formation has been obtained through reactions with alkynes and 1,3-dienes that result in the formation of dicationic species containing phosphirene and phospholene rings, respectively. The single crystal X-ray structures of the Ph-substituted dicationic species with phosphirene and phospholene rings have been obtained. To generate further chemistry, reduction of $[\text{Me}_2\text{C}_2\text{PClC}(\text{PPh}_3)_2]^{2+}$ with magnesium resulted in the formation of a $\sigma^3\lambda^3$ -phosphirene, $[\text{Me}_2\text{C}_2\text{PC}(\text{PPh}_3)_2]^+$, while the dehydrohalogenation of $[\text{Me}_2\text{C}_4\text{H}_4\text{PClC}(\text{PPh}_3)_2]^{2+}$ by 2-methylpyridine resulted in the formation of a $\sigma^3\lambda^3$ -phosphole, $[\text{Me}_2\text{C}_4\text{H}_2\text{PC}(\text{PPh}_3)_2]^+$. The single crystal X-ray structures of both the phosphirene and the phosphole have been obtained. Preliminary studies on the hydrolysis of the Cl-substituted phosphirenium salt, $[\text{Me}_2\text{C}_2\text{PClC}(\text{PPh}_3)_2]^{2+}$ shows possible formation of a stable phosphirene oxide. Reaction of the putative Ph-substituted dication with anisole resulted in an unexpected product and the mechanism for the reaction was proposed.

A French version of the summary is presented on the next 2 pages.

Résumé

Les ligands carbodiphosphorane ('carbones') présentent une capacité à agir en tant que donneurs de 2 ou de 4 ($2x\sigma$, $2x\pi$) électrons.¹ Le travail qui est résumé dans cette thèse porte sur la synthèse et la caractérisation d'ions phosphéniums cationiques dont la stabilité résulte de l'aptitude de ces ligands carbones à fournir des électrons à travers les systèmes σ et π . Un dication phosphoré [$i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2$]²⁺ a été synthétisé et entièrement caractérisé par diffraction aux rayons-X.² Sa structure, dans laquelle une coplanéité des atomes du fragment C_2NPCP_2 est trouvée, présente une configuration idéale pour maximiser l'interaction de l'orbitale π du carbone, occupée, avec l'orbitale 3P du phosphore dicoordiné. Selon une analyse computationnelle, effectuée par DFT pour expliquer les aspects structuraux et électroniques de la structure du dication, l'orbitale HOMO-12 (-12.90 eV) qui correspond au 'doublet' du phosphore dicoordiné de [$i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2$]²⁺ est assez fortement déstabilisée par rapport à son orbitale homologue (-13.52 eV) dans le cation phosphénium diazoté [$\text{P}(\text{NMe}_2)_2$]⁺; ceci suggère que la capacité du dication [$i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2$]²⁺ à agir en tant que σ - donneur est plus grande. Cependant, la LUMO, située à -7.77 eV dans [$i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2$]²⁺ est stabilisée par rapport à celle de [$\text{P}(\text{NMe}_2)_2$]⁺ (-6.91 eV), ce qui implique un caractère d'acide de Lewis plus prononcé pour [$i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2$]²⁺ que [$\text{P}(\text{NMe}_2)_2$]⁺. La réactivité de [$i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2$]²⁺ vis-à-vis de la DMAP, PMe_3 , H_2O , MeOH ,³ et CoCp_2 est décrite en présence de deux contreanions différents AlCl_4^- et $\text{BAr}^{\text{F}}_4^-$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$). Un adduit [$i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2$]²⁺•DMAP se forme après addition de la DMAP; l'interaction avec la triméthylphosphine est associée aux valeurs de $\Delta H = -30.5 \text{ kJ mol}^{-1}$ and $\Delta S = -77.7 \text{ eu}$ selon une analyse de van 't Hoff issue des expériences de RMN ^{31}P à différentes températures. Le dication [$i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2$]²⁺ est également capable de l'activation de l'eau et du méthanol dans des conditions réactionnelles qui sont assez rares avec des

centres nonmétalliques. Une étude de la réduction du dication, effectuée par le cobaltocène, a été menée. D'après les calculs DFT, l'électron excédentaire devrait se localiser principalement sur l'atome du phosphore dicoordiné ; l'expérience montre que la réduction initiale est suivie d'une cyclophosphination qui résulte de l'activation par le phosphore dicoordiné d'une liaison ortho-CH associé à un cycle phényle du groupement PPh₃. Le produit ainsi obtenu, stable, incorpore un cycle à 5 contenant deux atomes du phosphore. [Pr₂NPC(PPh₃)₂]²⁺ reste inchangé après interaction en solution à température ambiante avec des substrats tels que le 2-butyne, le diméthylbutadiène et l'anisole. Par la suite, deux analogues en série dicationique: [XP(C(PPh₃)₂)₂]²⁺ (X= Ph,⁴ Cl) ont été ciblés, dans lesquels le substituant amino, fortement stabilisant, est absent. Bien qu'impossibles à isoler, une réactivité compatible avec leur existence a été mise en évidence dans les réactions avec des alcynes et 1,3-diènes, qui mènent respectivement aux dications contenant les cycles phosphirènes et phospholènes. La structure des cycles phospholènes et phosphirènes obtenues en série [PhP(C(PPh₃)₂)₂]²⁺ ont été établis par diffraction aux rayons-X. Le dication [Me₂C₂PClC(PPh₃)₂]²⁺, réduit par le magnésium, mène au complexe de σ³λ³- phosphirène [Me₂C₂PC(PPh₃)₂]⁺, et une réaction de déshydrohalogénéation de [Me₂C₄H₄PClC(PPh₃)₂]²⁺ fournit le σ³λ³-phosphole correspondant [Me₂H₂C₄PC(PPh₃)₂]⁺. Dans les deux cas, des études structurales ont été menées par diffraction aux rayons-X. Des études préliminaires de l'hydrolyse du complexe [Me₂C₂PClC(PPh₃)₂]²⁺ suggèrent la possibilité de synthétiser un oxyde de phosphirène stable. Enfin, une mécanisme réactionnelle qui permet d'expliquer le produit surprenant issu de la réaction entre l'anisole et la combinaison AlCl₃/[XPhPC(PPh₃)₂]⁺AlCl₄⁻ est proposée.

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Symbols and Abbreviations

δ	NMR chemical shift in Hz
λ	lambda
σ	sigma
$^{\circ}$	degrees
$^{\circ}\text{C}$	degree Celsius
$\text{\AA}$	angstrom(s)
br	broad
<i>ca.</i>	circa = approximately
calcd	calculated
CCDC	Cambridge Crystallographic Data Centre
Cy	cyclohexyl
d	doublet
DCM	dichloromethane
dd	doublet of doublets
DOT	Degree of Travel
dt	doublet of triplets
DFT	Density Functional Theory
ESD	Estimated Standard Deviation
ES-MS	Electrospray Mass Spectrometry
Ext	Exocyclic Atom bound to the Ring Phosphorus
FTIR	Fourier Transform Infrared Spectroscopy
g	gram(s)
h	hour(s)
HOMO	Highest Occupied Molecular Orbital
HRMS	High Resolution Mass Spectrometry
<i>in situ</i>	on site
<i>i</i> Pr	iso-propyl
kcal	kilocalorie
kJ	kilojoule

LUMO	Lowest Unoccupied Molecular Orbital
<i>m</i>	<i>meta</i>
m	multiplet
Me	methyl
mL	millilitre(s)
mmol	millimole(s)
m/z	mass-to-charge ratio
NBO	Natural Bond Orbital
NMR	Nuclear Magnetic Resonance
NPA	Natural Population Analysis
NRT	Natural Resonance Theory
<i>o</i>	<i>ortho</i>
<i>p</i>	<i>para</i>
Ph	phenyl
ppm	parts per million
q	quartet
Q-TOF	Quadrupole-Time-of-Flight
s	singlet
sept	septet
^t Bu	tert-butyl
t	triplet
THF	tetrahydrofuran
vbr	very broad
<i>vide infra</i>	see below
<i>vide supra</i>	see above

CHAPTER 1

INTRODUCTION

Section 1.1. Main Group Polycations

Recently, the field of main group polycations has been expanding rapidly and it has become a major area of study in synthetic chemistry.⁵ Main group polycations with a formal charge of +2 or more on the central atom have attracted attention due to the ability of these electropositive centres to interact with small organic molecules⁶ or act as strong π -acceptor ligands for transition metals.⁷ There have been notable successes in the isolation of p-block polycations. These include Groups 13, 14, 15 and low oxidation state group 16 polycations which use neutral ligands to coordinate the central element, filling the valence shell and delocalizing the positive charge to the peripheral atoms.^{8,9,10,11} These ligands include pyridines,^{8a, 8b} polyethers,^{9c, 9d} N-heterocyclic carbenes (NHCs)^{10c, 10e} and diimines.^{11a, 11c, 11e} The syntheses of polycations are generally performed in the presence of neutral ligands and halide abstracting agents.¹² Although there are a wide variety of synthetic methods for these polycations, nitrogen-based ligands have remained the dominant support for these cations.⁵ Some of these examples are depicted in Figure 1.1.

Figure 1.1. An example of group 13, 14, 15 and 16 polycations, (left to right), respectively.

In 2014, Ong and co-workers reported the first example of a three-coordinate dicationic hydrido boron complex, supported by two carbodicarbene ligands,¹³ depicted in Figure 1.2. Interestingly, the unprecedented reaction involved the use of carbodicarbene ligands and BH₃, without the need of a more electrophilic Lewis acidic precursor.

Figure 1.2. First example of a dicationic hydrido boron complex.

With respect to P(III) chemistry, several examples of NHC-stabilized dicationic^{10e} and tricationic^{10c} compounds have been discovered. As it is the case with many main group polycations, these P(III)-based polycations are coordinatively saturated^{8a, 8d} and therefore resemble classical Lewis bases.^{9e} Hence, this renders them inactive as Lewis acids.^{10c, 10e} Although dication $[\text{PL}_2\text{R}]^{2+}$ ($\text{R} = \text{Cl}$; $\text{L} = \text{NHC}$) was subjected to chloride substitution^{10e} (Scheme 1.1) and trication $[\text{PL}_3]^{3+}$ ($\text{L} = \text{NHC}$) showed exciting coordination chemistry,^{10c} (Scheme 1.2) they ultimately resemble Lewis basic neutral phosphines.

Scheme 1.1. Example showing chloride substitution in dication $[\text{L}_2\text{PCl}]^{2+}$.

Scheme 1.2. Example showing the coordination chemistry of trication $[\text{PL}_3]^{3+}$.

Section 1.2. Phosphenium Ions

Prior to our work, there were no examples of coordinatively unsaturated P(III) polycations even though monocationic phosphorus (i.e. phosphenium) chemistry (R_2P^+) has been extensively developed.

Schmidpeter suggested that R_2P^+ can be divided to two groups depending on their differences in the charge distribution within the π -electron system.¹⁴ For the first type of cations (Figure 1.3), the positive charge is mainly localized on the substituents.¹⁴ The phosphorus atom is neutral or has a negative π -charge and is hence expected to be a nucleophilic centre. These cations can be represented by 2-phosphaallylic cations and phosphamethine cyanines. Dimroth and Hoffmann reported the first dicoordinate phosphorus cation in 1964,¹⁵ as shown in Figure 1.3. Subsequently, numerous phosphamethine cyanines have been synthesized (Figure 1.3).¹⁶ However, the ^{31}P NMR spectra and reactivity of these cations suggest extensive charge delocalization.

Figure 1.3. Resonance structures of first type of cations with positive charge mainly localized on substituents (top) and first example of dicoordinate phosphorus cation (bottom, left) and another example of phosphamethine cyanine (bottom, right).

On the other hand, for the second type of cations (Figure 1.4), the phosphorus atom shows a positive π -charge and may have an ambiphilic centre with both electrophilic and nucleophilic character.¹⁴ These cations can be represented by aminophosphenium ions.

Figure 1.4. Resonance structures of second type of cations with positive π -charge on phosphorus atom.

Recently, Schmidpeter and Thiele discovered a novel heterocyclic bis-phosphenio-isophosphindolide cation containing both phosphenium and phosphide type structures¹⁷ (Figure 1.5). The two-coordinate phosphorus may still be considered as an ambiphilic centre but with lesser electrophilic character.¹⁴ This novel heterocycle can be considered a hybrid between the first two classes of cations.

Figure 1.5. Resonance structures of third type of cations with hybrid between the first and second type.

An extensive array of phosphenium ions has been synthesized and their synthetic methodologies are presented below.

Firstly, Phosphorus-Halogen Bond Heterolysis is the most common and versatile method of phosphenium ion synthesis which involves chloride abstraction from chlorophosphines by Al_2Cl_6 , as shown in Scheme 1.3.¹⁸

Scheme 1.3. Chloride abstraction by Al_2Cl_6 .

Other examples of chloride ion acceptors like GaCl_3 ,¹⁹ FeCl_3 ²⁰ and PCl_5 ²¹ have also been used. Generally, phosphenium ions can be prepared by allowing a mixture of

chlorophosphines and a stoichiometric amount of Al_2Cl_6 in CH_2Cl_2 solution to warm slowly from -78°C to room temperature. The progress of the reaction can be tracked via ^{31}P NMR spectroscopy. Methylene chloride is chosen as the solvent due to its non-coordinating properties and a high dielectric constant to ensure the solubility of the phosphonium salts. The reaction of Fc_2PCl (Fc = ferrocenyl) with Al_2Cl_6 also resulted in the formation of Fc_2P^+ .²²

Fluoride ion abstraction from P–F bonds is also a useful approach for phosphonium ion synthesis.¹⁸ PF_5 and BF_3 can be used for this purpose.^{19, 23} However, when AsF_5 is used, the oxidizing properties of As^{5+} may affect the outcome of the reaction. For example, when $(\text{Me}_2\text{N})(\text{R})\text{PF}$ ($\text{R} = \text{Me}_2\text{N}$, $t\text{Bu}$) was reacted with AsF_5 , a four-coordinate difluorophosphonium cations rather than a phosphonium ion was formed (Scheme 1.4).²⁴ Although the mechanism for the net F^+ transfer is unknown, it is speculated that oxidative fluorination of the fluorophosphine resulted in the formation of a trifluorophosphorane, followed by fluoride ion abstraction by AsF_3 or (AsF_5) .

Scheme 1.4. Formation of a four-coordinate difluorophosphonium cation.

The second method of phosphonium ion synthesis is the Protic Attack of Phosphorus–Nitrogen Bonds.¹⁸ This is another novel and promising approach towards phosphonium ion synthesis via the cleavage of P–N bonds with strong acids.²⁵ Trifluoromethanesulfonic acid acts as a proton source due to the low nucleophilicity of the triflate, $[\text{CF}_3\text{SO}_3]^-$, anion. However, covalent products are formed even in the presence of this anion unless the phosphonium ion is stabilized extensively by electron

delocalization for instance when $X = Y = \text{Me}_2\text{N}$. A complex example of equilibria is shown in Scheme 1.5.

Scheme 1.5. Equilibria involving $\text{CF}_3\text{SO}_3\text{H}$.

The third method of phosphonium ion synthesis involves the Electrophilic Attack of Element-Phosphorus Double Bonds (Scheme 1.6).¹⁸

Scheme 1.6. Electrophilic Attack.

However, there are only two examples using this approach. Niecke and Kröher prepared an acyclic zwitterion by reacting AlCl_3 with a phosphorus-nitrogen double bond in $(\text{Me}_3\text{Si})_2\text{N}-\text{P}=\text{N}(\text{SiMe}_3)$.²⁶ Subsequently, the zwitterion was converted to a cyclic zwitterion upon thermolysis at 70°C (Scheme 1.7). Despite the zwitterionic nature, both compounds showed considerable localization of positive charge at phosphorus.

Scheme 1.7. Reaction of AlCl_3 and a phosphorus-nitrogen double bond in $(\text{Me}_3\text{Si})_2\text{N}-\text{P}=\text{N}(\text{SiMe}_3)$ resulting in the formation of cyclic zwitterion.

In another example, protic attack of the phosphorus-phosphorus double bond of $(2,4,6\text{-}^t\text{Bu})_3\text{C}_6\text{H}_2\text{P}=\text{PC}_6\text{H}_2(2,4,6\text{-}^t\text{Bu})_3$ resulted in the formation of phosphonium ion.²⁷

It was suggested that the labile phosphonium ion undergoes intramolecular C–H oxidative addition of an *o*-*t*Bu group to the P⁺ centre (Scheme 1.8). Although the product was detectable by multinuclear NMR experiments at -78°C, the isolated product is a monophosponium salt.

Scheme 1.8. Monophosponium salt formation.

Lastly, there are also miscellaneous methods for the synthesis of phosphonium ions.¹⁸ Schmidpeter and co-workers have reported the extrusion of a halide anion spontaneously from a cyclic halophosphine derivative.²⁸ For instance, reaction of the hydrazone with PCl₃ resulted in the formation of an interesting cyclic product which is a precursor for the final product. The final product is stable due to the 6π- electron system (Scheme 1.9).

Scheme 1.9. Formation of 6π-electron system after extrusion of a halide anion.

Numerous phosphonium ions have been characterized by X-ray crystallography. The data obtained from the solid state analysis of [(*i*Pr₂N)₂P]⁺ showed that the central phosphorus atom is sp² hybridized.²⁹ Reduction of the N–P–N angle from the ideal value of 120° to 114.8(2)° can be attributed to the repulsions between the lone pair on

phosphorus and the P–N bonds (Figure 1.6). The C₂NPNC₂ fragment is almost planar, thus maximizing dative π bonding between the the nitrogen lone pairs and the formally vacant P(3p) orbital. Such conjugation is supported by the fact that within experimental error, the inner C–N–P angle is much greater than the other two. However, calculations showed a similar trend of bond angles on the virtually strain-free model cation [(H₂N)₂P]⁺ (Figure 1.6).²⁴

Figure 1.6. Bond angles in the planar fragments in [(*i*Pr₂N)₂P]⁺ and [(H₂N)₂P]⁺.

Furthermore, Figure 1.7 demonstrates a similar pattern of bond angles that can be observed in the isovalent N, N, N', N'-tetramethylformadinium cation.³⁰

Figure 1.7. N, N, N', N'-tetramethylformadinium cation.

Pohl has determined the structure of the cyclic zwitterionic phosphonium ion (final product in Scheme 1.7).³¹ Both nitrogen atoms take a trigonal planar geometry and within experimental error, the P–N bond length (1.614(6) Å) is the same as that in [(*i*Pr₂N)₂P]⁺. The relatively small N–P–N bond angle of (97.4(4) °) in the zwitterionic phosphonium ion resulted in the cyclic structure.

In Figure 1.8, the bond angle at the phosphorus of the diazaphospholium cation is much smaller at (90.4(1)°) and the P–N bond length is longer at (1.674(2) Å) than

$[(^i\text{Pr}_2\text{N})_2\text{P}]^+$ or cyclic zwitterionic phosphonium ion (final product in Scheme 1.7).^{28c} The planarity of the ring and the pattern of the bond lengths are due to the 6π -delocalization.

Figure 1.8. Diazaphospholium cation.

Phosphenium ions are defined by a high degree of positive charge accumulation at the two-coordinate phosphorus centre.^{18, 32} They potentially allow the possibility of having both acidic and basic sites on one atom. The localization of charge at the phosphorus can be observed from a δ_{P} chemical shift range of +200 to +500 ppm.¹⁸ Since the positive charge of phosphamethine cyanines (Figure 1.9) is not mainly located on the phosphorus, they are outside the scope of phosphenium chemistry.¹⁸ The same applies for a new series of triphosphorus cations (Figure 1.10) reported by Schmidpeter.³³

Figure 1.9. Delocalization of positive charge on phosphamethine cyanines.

Figure 1.10. Triphosphorus cations.

Phosphenium ions can constitute a member of the isoelectronic series extending from silylenium³⁴ to chloronium³⁵ ions as depicted in Figure 1.11.¹⁸

Figure 1.11. Isoelectronic series.

Another perspective is the parallel among the singlet states of phosphonium ions, carbenes and silylenes as shown in Figure 1.12.¹⁸ This draws attention to the lone pair of electrons on phosphorus and the formally vacant P(3p) orbital. Phosphonium cations are related to carbenes whereby isovalent P^+ replaces the central carbon atom. Carbenes can be stabilized when R^1 and R^2 are atoms or groups such as NR_2 which can act as π -electron donors to the carbon atom.¹⁴ This is similar for the electronically isovalent phosphonium analogues.³⁶

Figure 1.12. Isovalent series of carbene, silylene and phosphonium ion.

Phosphonium ions can be represented by the resonance structures depicted in Figure 1.13.

Figure 1.13. Resonance structures of phosphonium ions.

Fluoride ion affinity (FIA) calculations have been performed to discover the relative Lewis acidity of phosphonium ions.³⁷ The results have demonstrated that they are often more Lewis acidic than neutral species but are less Lewis acidic than cations like Me_3C^+ or Me_3Si^+ .³⁷ The stabilization of phosphonium ions by adjacent heteroatoms or

intermolecular donors such as nitrogen or phosphorus is rather common. Some phosphonium salts have also been prepared in the presence of different anions, resulting in significant steric interactions between cation and anion which affect the ability of the anion to approach cationic centre.³⁶

The energy of the Lowest Unoccupied Molecular Orbital (LUMO) in Ph_2P^+ is also reported to be lower than that in $(\text{Me}_2\text{N})_2\text{P}^+$.³⁸ Computational data and experimental data from solid state structures also demonstrate that Ph_2P^+ acts as a better Lewis acid than diaminophosphonium analogues, $(\text{R}_2\text{N})_2\text{P}^+$.³⁸

Phosphenium ions have been seen as reactive intermediates.³⁹ The presence of prominent peaks in the mass spectra of, for instance, phosphinous halides and diphosphines are attributed to these species.⁴⁰ Fleming, Jekot and Lupton discovered the first example of a stabilized phosphenium salt.²³ Maryanoff and Hutchins then developed a second stabilized cation.²¹ These examples are depicted in Figure 1.14. Both the cyclic phosphenium ions were prepared by halide ion abstraction from diaminohalophosphines.¹⁸ Subsequently, Parry prepared the first examples of acyclic phosphenium ions, $[(\text{Me}_2\text{N})_2\text{P}]^+$ and $[(\text{Me}_2\text{N})(\text{Cl})\text{P}]^+$.¹⁹

Figure 1.14. First (left) and second (right) example of phosphenium ions reported.

Macdonald also prepared N-Heterocyclic phosphenium salts by using N-Heterocyclic bromophosphines as precursors.⁴¹

Using generalized valence bond (GVB) wave functions, Harrison and co-workers investigated the electronic structures of the model phosphenium ions $[\text{H}_2\text{P}]^+$, $[(\text{H})(\text{F})\text{P}]^+$

and $[\text{F}_2\text{P}]^+$.⁴² These GVB calculations predict that each cation has a singlet ground state. Furthermore, the singlet-triplet separations increase with increasing ligand electronegativity as expected: $[\text{H}_2\text{P}]^+$ (20.4kcal/mol), $[(\text{H})(\text{F})\text{P}]^+$ (42.6kcal/mol) and $[\text{F}_2\text{P}]^+$ (84.0kcal/mol).

First principle calculations on $[(\text{H}_2\text{N})_2\text{P}]^+$ and $[(\text{H}_2\text{N})(\text{H})\text{P}]^+$ resulted in satisfactory agreement with both the observed ground-state geometry of $[(^i\text{Pr}_2\text{N})_2\text{P}]^+$ and earlier extended Hückel calculations¹⁹ on $[(\text{Me}_2\text{N})_2\text{P}]^+$.^{24, 43} In addition, all the calculations support the idea that dative π -bonding takes places between the nitrogen lone pair(s) and the formally vacant P(3p) orbital. Ab initio²⁴ and Fenske-Hall calculations⁴⁴ on $[(\text{H}_2\text{N})_2\text{P}]^+$ and $[\text{PN}(\text{R})\text{CH}_2\text{CH}_2\text{NR}]^+$ (R = H, Me), respectively, produce an orbital sequence shown in Figure 1.15. The HOMO which is non-bonding possesses an a_2 symmetry and has an out-of-phase combination of N(2p) AOs. The LUMO which has b_1 symmetry is π -antibonding. The a_1 MO depicts the phosphorus lone pair which is perpendicular to the N(2p) AOs. At lowest energy, the $4b_1$ depicts a three-center π -bonding MO.

Figure 1.15. Molecular orbitals of model $[(\text{H}_2\text{N})_2\text{P}]^+$ cation.

Simple mononuclear phosphonium ions that do not form part of delocalized systems all have at least one amido substituent. Thermodynamic stabilization of phosphonium ions by means of ligand $\rightarrow$ P⁺ π -bonding is important. For diazaphospholium

cations, this π -bonding makes up part of a more extensive 6π -delocalization. For the corresponding carbocations, the ferrocenyl substituent brings about stabilization via the dispersion of positive charge.⁴⁵ The marginal stability of $[(\text{Me}_5\text{C}_5)(^t\text{Bu})\text{P}]^+$ can be attributed to multihapto bonding between the Me_5C_5 ligand and P^+ and the concomitant delocalization of positive charge.⁴⁶

Other substituents such as halogens and alkoxy groups are able to conjugatively stabilize phosphonium ions. However, these groups do not have enough π -donor character unless the phosphonium ions are coordinated to a transition metal moiety to obtain the necessary thermodynamic stabilization. Hence, the reactions of PX_3 ($\text{X} = \text{Cl}, \text{F}$) with Al_2Cl_6 resulted in donor-acceptor complexes of the type X_3PAlCl_3 rather than phosphonium ions.⁴⁷

Sufficient bonding support is also necessary in the preparation of polyphosphonium cations. Treating compound **A** in Figure 1.16 with an excess of Al_2Cl_6 results in abstraction of only one chloride ion and formation of the monocation.¹⁸ Nöth and Ullmann, on the other hand, discovered that compound **B** in Figure 1.16 forms a bis AlCl_3 adduct which can be known as the AlCl_4^- salt of the corresponding bis(phosphonium) ion.⁴⁸ As shown, at least four nitrogen atoms are necessary to satisfy the conjugative requirements of two phosphonium ion centers within the same molecule.

Figure 1.16. Precursors for the preparation of polyphosphonium cations.

Since the mid 1970s, the interest in phosphonium chemistry has grown steadily due to the cations' ability to act as useful reagents, potential ligands^{11b} and their high

versatility.¹⁸ The electrophilic character of these cations is also of great interest. The phosphorus lone pair allows dative bonding to transition metals, hence creating rich coordination chemistry.¹⁸ In fact, the nucleophilic character of a phosphonium centre can be used for complex formation as shown by the synthesis of a first cationic phosphonium complex by Parry in 1978 (Figure 1.17).⁴⁹ The coordination chemistry of aminophosphonium ions was further developed, encouraged by the perception that these cations are isolobal and isovalent analogues of singlet silylenes and carbenes.¹⁴ These complexes are of great interest in the area of organometallic chemistry.¹⁴

Figure 1.17. First cationic phosphonium complex.

Over time, many phosphonium ions have been crystallographically elucidated.^{14, 29, 50} Some of these examples were reported by the groups of Gudat¹⁴, Cowley,²⁹ and Gruetzmacher (Figure 1.18).⁵⁰

Figure 1.18. Examples of phosphonium ions which have been crystallographically established.

Many groups use ligands to stabilize main group compounds, including phosphonium ions.^{4b} These may include N-heterocyclic carbenes (NHCs),⁵¹ mesoionic carbenes,⁵² cyclic alkyl amino carbenes.⁵³ Amongst these ligands, NHCs are the most widely used, playing a crucial role in synthetic organic chemistry since the discoveries by

Bertrand⁵⁴ and Arduengo.^{51b, 51c} They are strong 2-electron σ -donors and poor π -acceptors.^{4b} On the other hand, carbodiphosphoranes, also known as carbones, are less widely used. They act as strong 2-electron σ -donors and 2-electron π -donors.^{4b}

Section 1.3. Reason for the use of Carbone

The stability of phosphonium cations that contain two -NR_2 (amino) substituents seems to be independent on the nature of the counterion i.e. $[\text{R}_2\text{N-P-NR}_2]^+$ is synthetically viable in the presence of so-called non-coordinating anions such as $\text{BAr}^{\text{F}}_4^-$ or $\text{BAr}^{\text{Cl}}_4^-$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$; $\text{Ar}^{\text{Cl}} = 3,5\text{-Cl}_2\text{-C}_6\text{H}_3$). On the other hand, it is observed that phosphonium cations with either one or no NR_2 substituents always have coordinating anions such as AlCl_4^- to presumably stabilize them.^{14, 18, 24, 55} Burford reported that other than steric factors, anionic factors can create electrostatic interactions that are maintained to a certain degree in solution to protect phosphorus cationic centres.⁵⁶ As reported by Vidovic and co-workers, counterions such as EX_4^- ($\text{E} = \text{B, Al, Ga}$; $\text{X} = \text{F, Cl, Br}$) or OTf^- ($\text{Tf} = \text{O}_2\text{SCF}_3$) could not only provide added stability but participate in the further reactivity of NHC-stabilized dichloroborenum cations.⁵⁷ Building on the pretext of the necessity of coordinating anions to stabilize phosphonium cations which have either one or no NR_2 groups present, it was our objective to establish a ligand system to stabilize a two-coordinate P(III)-containing dication with a formally vacant P(3p) orbital and potentially exhibiting Lewis acidic properties (Figure 1.19).⁵⁸ As already mentioned, the most stable two-coordinate P(III)-centred monocations, also known as phosphonium cations, have been reported to contain one, if not both, R substituents such as amino groups with strong π -donating properties.^{14, 18, 24, 55, 59} Therefore, it was proposed that both the R and L ligands would need to be good π -donors in order to obtain the target dicationic compounds.² The use of a dialkylamino R substituent was predetermined⁶⁰ and

the neutral carbene ligand was suitable to act as the L substituent.² Based on computational and experimental studies, the two lone pairs of electrons with σ and π symmetry in the carbene ligand are ideal for bonding.⁶¹

Figure 1.19. Proposed ligand system for stabilizing a two-coordinate P(III)-containing dication.

Section 1.4. Structural and Electronic Properties of Carbone

The central divalent C atom retains all four electrons and gains an electron octet by the use of two electron pairs after the coordination of two neutral Lewis bases **L**, resulting in the class of compounds of general type CL_2 (Figure 1.20).⁶² For **L**, usually neutral ligands like ER_3 ($E = N, P, As, Sb, Bi$) or ER_2 ($E = O, S, Se, Te$) or those with a free pair of electrons are possible but only a few are known.⁶³ Based on the nature of **L**, it is possible to observe bent or linear geometry with allene-like properties for the central fragment of these exciting molecules.⁶³ The majority of σ donors have a bent geometry but if **L** acts as a very good π acceptor in addition to the electron pair donor ability, for instance in CO, the linear arrangement is energetically favored.⁶⁴ In carbon suboxide, $C(CO)_2$, the strong acceptor properties of CO lead to a quasilinear structure with a bending angle in the gas phase of about 156° .⁶⁵

Figure 1.20. CL_2 type compounds.

The bonding in CL_2 compounds can include charges or formal charges.⁶³ In some cases, to denote the fact that the carbon atom accepts two pairs of electrons from L and donates one or two pairs to Lewis acids, $L \rightarrow C$ dative bonds are used to demonstrate the possible electron flow.⁶³ CL_2 compounds, such as the carbene $C(PPh_3)_2$, are best represented by a double ylid with a bent conformation that is easily available and stable over long periods under an inert gas atmosphere at room temperature.⁶⁶ In fact, carbenes can be represented using different resonance structures, either as a carbon(0) compound or a bis(ylid) analogue as shown in Figure 1.21.^{4b}

Figure 1.21. Resonance hybrids of carbene ligand.

NBO and DFT studies have demonstrated that the carbon atom has two high lying occupied MOs of σ and π symmetry, HOMO and HOMO-1.^{61d, 63}

Figure 1.22. MOs of carbene ligand.

It is best known as a divalent carbon (0) compound with two lone pairs of electrons.⁶³ This is valid for numerous CL_2 compounds including the cases where L is not PPh_3 . Due to the electronic situation in CL_2 , the term “carbenes” was introduced as compared to carbenes with only one HOMO orbital of σ symmetry and an electron sextet at the carbon atom.⁶² The p orbital at the sp^2 C(II) atom in carbenes is empty and the

second electron pair of the carbon atom is engaged in electron sharing with two neighboring atoms.⁶⁷ Recently, new theoretical studies on carbones and heavier homologues (tetrylones) EL_2 ($E = C, Si, Ge, Sn, Pb$) have also been reported.^{61a, 68} Theoretical investigations have predicted that NHC, widely used in catalysis,⁶⁹ could also be used for the preparation of carbones.⁷⁰ Indeed, this was synthetically confirmed with the preparation of the first examples of carbodicarbenes.⁷¹

A captodative formalism is used for carbones. This involves σ -donation from the ligand **L** to the carbon atom and π -back donation from the lone pair of the carbon atom to the ligand, just like a metal. Hence, in a similar fashion to complexes of metals, carbones can also be seen as complexes of carbon (0).⁷²

The lone pairs of electrons allow carbones to bind to electron deficient Lewis acids, resulting in mono or double addition compounds. Reviews on transition metal complexes with carbone as ligands including bonding analyses have been performed.^{61b} Double transition metal addition compounds have also been discovered by Alcarazo.⁷³

Scheme 1.10. Synthesis of carbone.

In 1961, Ramirez reported the first synthetic procedure for carbones via potassium reduction of monocationic precursor, methylidenebis-(triphenylphosphonium) bromide in diglyme.^{66a} To a stirred suspension of potassium, methylidenebis-(triphenylphosphonium) bromide was quickly added. This resulted in gas evolution. Filtration and cooling of the

orange-yellow hot solution from potassium bromide gave the product.^{66a} The synthesis of monocationic precursor has been patented by Gastrock in 1976,⁷⁴ which reported the use of sodium carbonate to reduce the dicationic precursor (Scheme 1.10).

The essential properties of carbenes with two lone pairs of electrons are their proton affinities (PAs).⁶³ The first PA of $\text{C}(\text{PPh}_3)_2$ is 280 kcal/mol and that of the second PA is 186 kcal/mol, which is also amazingly high. Similarly, PA calculations of allenes showed that $(\text{Me}_2\text{N})_2\text{C}=\text{C}=\text{C}(\text{NMe}_2)_2$, an electron rich allene with a linear configuration, also gave high PA values of 283 kcal/mol and 152 kcal/mol, respectively.⁶³ Despite having different configurations, both $\text{C}(\text{PPh}_3)_2$ and $\text{C}(\text{C}(\text{NMe}_2)_2)_2$ can be known as superbases. To put this into perspective stable carbenes like NHCs demonstrate a first PA of about 260 kcal/mol, but a low second PA of less than 100 kcal/mol which suggested that the diprotonation of NHCs is highly unlikely.⁶³

Experimentally, there are no examples of a carbene coordinated to two main group fragments except for a proton or proton/methyl group. Despite this, the reaction of $\text{C}(\text{PPh}_3)_3$ and B_2H_6 in toluene results in a precipitate that consists of $[\text{H}_3\text{B}\{\text{C}(\text{PPh}_3)_2\}]$ and the bis-adduct $[(\text{H}_3\text{B})_2\{\text{C}(\text{PPh}_3)_2\}]$. The isolation of the final product may suggest that the bis-adduct, which then undergoes the observed reaction is the main product in toluene (Scheme 1.11).^{61c}

Scheme 1.11. Suggested reaction pathway for the final product from carbodiphosphorane and bis-borane.

After Ramirez's discovery, there has been extensive research on carbenes and numerous compounds containing the carbene moiety have been isolated.⁷⁵ The bonding of carbene compounds was usually represented as double bonds $\text{R}_3\text{P}=\text{C}=\text{PR}_3$ and

compared with carbenes or ylides.⁷⁵ Despite being described as having two lone pairs at carbon, the nature of the donor-acceptor bonding $R_3P \rightarrow C \leftarrow PR_3$ in carbenes has not been fully accepted.^{63, 76} The compounds CL_2 can be viewed as very strong Lewis bases which form strongly bonded adducts with main-group Lewis acids. They also result in strongly bonded ligands in transition-metal complexes.⁷⁷ From the calculations of proton affinities, the basicity of divalent $C(0)$ compounds are also observed to be very high.⁷⁸

Some research groups have used the electron donating properties of carbene ligands to coordinate to main group elements in boron,^{1a} silicon^{1b} and germanium compounds.^{1c} Alcarazo reported the formation of dihydridoborenium cation.^{1a} The stability of these electron deficient compounds is attributed to the σ - and π - electron donating properties of the carbene ligands.¹ These examples are presented in Figure 1.23.

Figure 1.23. Other main group compounds containing carbene moiety.

Matthews⁷⁹ and Schmidpeter⁸⁰ have succeeded in synthesizing phosphorus compounds shown in Figure 1.24.

Figure 1.24. Phosphorus compounds containing carbene moiety.

Recently, Weigand and his co-workers have also reported the use of carbodiphosphoranes in the formation of highly Lewis acidic phosphonium salts which may be useful for organocatalysis.⁸¹

Hence, carbones appear to be ideal candidates for the support of our coordinatively unsaturated phosphorus (III)-containing dications by using their π and σ electron donating properties.

CHAPTER 2

Synthesis, Structural and Electronic Properties of Phosphenium Cations

Section 2.1. Targeted Synthesis of Dication

Scheme 2.1. Targeted synthesis of dication. Key reagents/conditions: a) R'PCl₂, R = NⁱPr or NCy or Ph or Cl (excess), benzene for X = Cl, addition of AlCl₃ (or NaBAr^F₄) (1.0 equiv), CH₂Cl₂ for X = AlCl₄ (or BAr^F₄); b) 1.0 equiv of AlCl₃ (or NaBAr^F₄) for X = AlCl₄ (or BAr^F₄) and 2.0 equiv of AlCl₃ (or NaBAr^F₄) if X = Cl in CH₂Cl₂.

A general synthetic procedure for the preparation of the target dications is shown in Scheme 2.1. The very first reaction we performed involved the addition of C(PPh₃)₂ to a benzene solution containing excess ⁱPr₂NPCl₂.² Chloride displacement resulted in the formation of [2a⁺]Cl (Scheme 2.1). The ES-MS experiment gave a peak at m/z 702.2339 (calcd. for 2a⁺ = 702.2370) with the correct isotopic pattern. The room temperature ³¹P{¹H} NMR spectrum gave two second order signals at δ_P = 25.9 (d) and 133.4 ppm (t), which gave 3 doublets of doublets upon lowering the temperature to - 90°C. This is consistent with the carbene-for-chloride exchange and the formation of carbene-stabilized phosphenium cation 2a⁺.

Figure 2.1. Molecular structure of $[i\text{Pr}_2\text{NPCl}(\text{C}(\text{PPh}_3)_2)]^+$, $[2\text{a}^+]\text{AlCl}_4^-$. Ellipsoids set at 50% probability. For clarity, only one of the molecules in the asymmetric unit is shown and the $[\text{AlCl}_4]^-$ counterion together with hydrogen atoms have been omitted for clarity.

The identity of 2a^+ , as a tetrachloroaluminate salt, was confirmed by single crystal X-ray diffraction. One of the two independent cationic molecules is shown in Figure 2.1. The average P–N bond is 1.656(5) Å and is comparable to the average P–N bond length in $[(i\text{Pr}_2\text{N})_2\text{P}(\text{DBN})]^+$ (DBN=1,5-diazabicyclo[4.3.0]-non-5-ene)⁸² of 1.663(4) Å.³⁸ The average $\text{P}_{\text{central}}\text{--C}_{\text{carbone}}$ bond distance of 1.814(6) Å is slightly shorter than that of the average P–C bond distance of 1.838(6) Å for carbene-stabilized mono- and dicationic three-coordinate P(III)-centred compounds, but is within the expected values for P–C single bonds.^{10e} The sum of bond angles around the $\text{P}_{\text{central}}$ was 318.9(2)°, hence indicating a pyramidal geometry for 2a^+ .

Halide abstraction from $[2\text{a}^+]\text{Cl}$ using 2.0 equivalents of AlCl_3 resulted in the formation of dication 3a^{2+} (Scheme 2.1). The most indicative evidence for the heterolytic P–Cl bond cleavage in 2a^+ and the formation of dication 3a^{2+} was the appearance of a downfield shifted signal at $\delta_{\text{P}} = 355.7$ ppm in the ^{31}P NMR spectrum, which is within the range of 200–500 ppm known for two-coordinate phosphonium cations.^{14, 18, 24, 59} In addition, depleted electron density at the dication was also evident from the ^{13}C NMR

spectrum whereby the C_{carbone} signal ($\delta_c = 67.8$ ppm) was about 50 ppm downfield shifted as compared to the same signal for $2a^+$ ($\delta_c = 19.5$ ppm). This may also suggest an increase in electron donation from the carbone lone pair with π symmetry to the newly created and formally vacant P(3p) orbital.

Figure 2.2. Molecular structure of $[iPr_2NP(C(PPh_3)_2)[AlCl_4]_2, [3a^{2+}][AlCl_4]_2$. Ellipsoids set at 50% probability. For clarity, only one of the molecules in the asymmetric unit is shown and the $[AlCl_4]^-$ counterions together with hydrogen atoms have been omitted for clarity.

The molecular structure of $3a^{2+}$ (one of the two molecules in the asymmetric unit, as shown in Figure 2.2) demonstrates planarity along the C_2NPCP_2 fragment. This places both the amino and the carbone lone pair with π symmetry in an ideal position to interact with the formally vacant P(3p) orbital. This $N \rightarrow P \leftarrow C$ π -interaction results in the shortening of the average $P_{\text{central}}-N$ (1.623(6) Å for $3a^{2+}$ vs 1.656(5) for $2a^+$) and $P_{\text{central}}-C_{\text{carbone}}$ bonds (1.745(7) Å for $3a^{2+}$ vs 1.813(6) Å for $2a^+$) with respect to the precursor. The fact that the P–N bond is between that of a single and double bond and the average P–C bond for $3a^{2+}$ is very similar to that in a phosphaaalkene⁸³ of 1.7376(14) Å, suggests that the NPC fragment in $3a^{2+}$ is allene-like, thus bringing the necessary thermodynamic stabilization for the dication.

Subsequently, various analogues of dications were also targeted and synthesized by a similar two-step process shown in Scheme 2.1. The first step involved the preparation of monocationic precursors, $[R'PCl(PPh_2R)_2][Cl]$ (**[2b]** $[Cl]$: $R = \frac{1}{2} (CH_2)_3$, $R' = N^iPr_2$; **[2c]** $[Cl]$: $R = Ph$, $R' = NCy_2$; **[2d]** $[Cl]$: $R = \frac{1}{2} (CH_2)_3$, $R' = NCy_2$) by adding a carbene ligand $C(PPh_3)_2$, **1a** or $C(PPh_2(CH_2)_3PPh_2)$, **1b** in benzene solution containing excess of the corresponding aminodichlorophosphine ($R'PCl_2$; $R' = ^iPr_2N$ or Cy_2N). The carbene-for-chloride exchange was successful for all attempts except for that in **[2d⁺]** $[Cl]$. This may be due to the highest steric demand of the corresponding reactant combination as compared to the rest.

Similarly, the formation of dication **[3b²⁺]** $[X]_2$ and **[3c²⁺]** $[X]_2$ ($X = AlCl_4^-$ or BAr^F_4 ; $Ar^F_4 = 3,5-(CF_3)_2-C_6H_3$) was achieved with addition of 2.1 equivalents of either $AlCl_3$ or $Na[BAr^F_4]$ to the DCM mixture containing **[2b⁺]** $[Cl]$ or **[2c⁺]** $[Cl]$, respectively. It is noteworthy that the δ_P values for the central P atom were independent of the nature of the counterion ($AlCl_4^-$ vs $BAr^F_4^-$). This suggests that there is an absence of interion close contacts in the solution state.

Similar NMR spectroscopic data were observed for these monocationic and dicationic compounds as compared with **[2a⁺]** $[X]$ and **[3a²⁺]** $[AlCl_4]_2$, respectively. However, as the synthesis of **[2d⁺]** $[Cl]$ was not viable using the abovementioned procedure, the corresponding dication **3d²⁺** was not prepared.

The monocationic precursor, **[2c⁺]** $[BAr^F_4]$ and dicationic species, **[3c²⁺]** $[AlCl_4]_2$ have also been elucidated by single crystal X-ray diffraction and their crystal structures are presented in Figure 2.3.

Figure 2.3. Molecular structure of $[\text{Cy}_2\text{NPCl}(\text{C}(\text{PPh}_3)_2)][\text{BAR}^{\text{F}}_4]$, $[\text{2c}^+][\text{BAR}^{\text{F}}_4]$ (left) and $[\text{Cy}_2\text{NP}(\text{C}(\text{PPh}_3)_2)][\text{AlCl}_4]_2$, $[\text{3c}^{2+}][\text{AlCl}_4]_2$ (right). Ellipsoids set at 50% probability. For clarity, only one of the asymmetric units (for the case of $[\text{3c}^{2+}][\text{AlCl}_4]_2$) is shown and the $[\text{BAR}^{\text{F}}_4]^-$ counterions (for the case of $[\text{2c}^+][\text{BAR}^{\text{F}}_4]$) or $[\text{AlCl}_4]^-$ (for the case of $[\text{3c}^{2+}][\text{AlCl}_4]_2$) together with hydrogen atoms have been omitted for clarity.

The monocation adopted the usual pyramidal geometry around the central phosphorus. The sum of the bond angles around the P atom for 2c^+ was found to be 316° , which was similar to that in 2a^+ at 319° . With reference to 3a^{2+} , elimination of the chloride ligand and the formation of the dication 3c^{2+} was also manifested by the shortening of the P–C and P–N bond distances. These bond reductions were presumably due to increased electron donation from both amino and carbene substituents to the central P atom possessing π -symmetry lone pairs considering that the C_2NPCP_2 fragment is virtually planar, it is then not difficult to envision the electron density “flow” from the amino and carbene substituents to the formally vacant p_z orbital on the central P atom after chloride abstraction. In addition, the allene-like characteristics of the NPC fragment seemed to be mainly responsible for the room temperature stability of these species and the yellow colour that they exhibited both in solution and solid state. This bonding description for the NPC fragment was confirmed by detailed theoretical investigations.

Section 2.2. Counterions interference

Since AlCl_4^- anions, which are coordinating, can interfere with the reactivity of $\mathbf{3a}^{2+}$, we decided to synthesize our dication in the presence of non-coordinating borate, $\text{BAr}_4^{\text{F}-}$ counterions. Their respective crystal structures were obtained and presented in Figure 2.4. A careful examination of the solid states of $[\mathbf{3a}^{2+}][\text{AlCl}_4]_2$ and $[\mathbf{3a}^{2+}][\text{BAr}_4^{\text{F}-}]_2$ revealed (i) minimal interion interactions for $[\mathbf{3a}^{2+}][\text{AlCl}_4]_2$ as only one $\text{P}\cdots\text{Cl}$ interaction of 3.54 Å was within the sum of van der Waals (vdW) radii for P and Cl (3.72 Å) and (ii) for $[\mathbf{3a}^{2+}][\text{BAr}_4^{\text{F}-}]_2$, no interaction between $\text{BAr}_4^{\text{F}-}$ and dication and both $\text{P}\cdots\text{F}$ contacts (3.47 and 4.34 Å) were outside the sum of van der Waals (vdW) radii for P and F (3.36 Å) (Figure 2.4).

Figure 2.4. Interior close contacts for $[3a^{2+}][AlCl_4]_2$ (top) and $[3a^{2+}][BAr^F_4]_2$ (bottom).

Section 2.3. Computational Analysis

A series of Density Functional Theory (DFT) calculations have been performed to gain more insights on the structural or electronic features of dication $\mathbf{3a}^{2+}$. The optimized structural parameters for $\mathbf{3a}^{2+}$, including the C_2NPCP_2 fragment, are in very good agreement with the experimental values. The delocalized nature of the HOMO orbital for $\mathbf{3a}^{2+}$ (Figure 2.5) along the N–P–C fragment was very different from the HOMO of $[\text{P}(\text{NMe}_2)_2]^+$, which is non-bonding in nature. HOMO-12 (-12.90 eV), the molecular orbital that resembles the lone pair located on the central P atom of $\mathbf{3a}^{2+}$ is quite destabilized with respect to the analogous orbital of $[\text{P}(\text{NMe}_2)_2]^+$ (-13.52 eV). This suggests that $\mathbf{3a}^{2+}$ is a better σ -donor than the phosphonium cation.

HOMO-14 (-13.93 eV), the most bonding π -orbital is more stabilized in $\mathbf{3a}^{2+}$ than that in $[\text{P}(\text{NMe}_2)_2]^+$ (-13.45 eV). This implies a more effective π interaction along the N(2p)–P(3p)–C(2p $_{\pi}$) fragment for $\mathbf{3a}^{2+}$ than the analogous N(2p)–P(3p)–N(2p) fragment in $[\text{P}(\text{NMe}_2)_2]^+$.³⁸ Nevertheless, the LUMO (π^* , Figure) (-7.77 eV) for $\mathbf{3a}^{2+}$ is more stabilized than the LUMO (-6.91 eV) for $[\text{P}(\text{NMe}_2)_2]^+$, suggesting that $\mathbf{3a}^{2+}$ should also be a better Lewis acid (e^- acceptor) than $[\text{P}(\text{NMe}_2)_2]^+$.

Figure 2.5. Selected Molecular Orbitals for $3a^{2+}$. a) LUMO (top, left), b) HOMO (top, right), c) HOMO-12 (bottom, left), d) HOMO-14 (bottom, right).

In order to better understand the electronic structure of the dication, its structural features were analyzed computationally with emphasis on the NPC functionality. Firstly, B3PW91/6-31G(d) level geometries were optimized for ${}^i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2^{2+}$, $3a^{2+}$, and its model $\text{H}_2\text{NPC}(\text{PH}_3)_2^{2+}$, $3f^{2+}$, whereby hydrogen atoms replaced the diisopropylamino groups and the phosphorane phenyl groups. Both $3a^{2+}$ and $3f^{2+}$ show similar geometries, including the near-planarity about the NPC moiety and are in good agreement with the experimental X-ray structure. The NP–C (1.745 and 1.742 Å for $3a^{2+}$ and $3f^{2+}$, respectively) and N–P (1.647 and 1.629 Å) bond distances are somewhere between typical single and double bond lengths. As mentioned previously, a heteroallene

description is suggested which formally results from the presence of one electron pair on each terminal atom (N and C) and a vacant p_π orbital on the central phosphorus.

This description is confirmed by a Natural Bond Orbital (NBO) analysis, which gave a quantitative description of the electronic structure in terms of localized electron-pair bonding units.⁸⁴ NBO analysis for **3a**²⁺ and **3f**²⁺ indicates that the NPC moiety showed a 3-center/ 4 π -electron bond so that the electronic structure can be described on the basis of two resonance forms: (i) one having a C=P double bond and a π -lone pair (LP) on the nitrogen atom and (ii) the other having a carbon π -lone pair and a P=N double bond (Figure 2.6). Each resonance structure results in lone pairs that have low electron occupancy (between 1.54 and 1.69 electrons) and a large $LP \rightarrow \pi^*$ second-order interaction energy (with E(2) values being between 200 and 257 kJ mol⁻¹). These observations are also consistent with a 3-center/ 4 π -electron description. A natural resonance theory (NRT) analysis,⁸⁵ confined to the NPC fragment of **3a**²⁺ and **3f**²⁺, confirms the co-existence of two resonance structures having high weights. When the same analysis is performed for H₂N–P=CH₂, there is much lesser delocalization of the nitrogen lone pair into the π P=C bond (E(2) = 81 kJ mol⁻¹) and the weights of the canonical H₂N–P=CH₂ resonance structure (92.1 %) and of the zwitterionic structure ⁺H₂N=P–CH₂⁻ (6.7%) are very different.

Figure 2.6. NBO/NRT resonance structures of $3a^{2+}$ and $3f^{2+}$ calculated at the B3PW91/6-311+G(d,p)//B3PW91/6-31g(d) level.

The Lewis representation of these resonance structures suggests a formal neutral charge on the NPC-phosphorus center, and hence a non-electrophilic character. This would be in a disagreement with spectroscopic data and the reactivity of $3a^{2+}$. Examination of the π -bond polarization helps to explain this discrepancy well (Table 2.1). Both the NP and PC π -bonds are highly polarized, toward the carbon and nitrogen atoms, respectively. This resulted in the π -population on the phosphorus center (0.70 and 0.61 electron for $3a^{2+}$ and $3f^{2+}$, respectively) being significantly lower than in other compounds containing P=X double bonds such as $\text{HP}=\text{CH}_2$ (0.92 electron), $\text{H}_2\text{N}-\text{P}=\text{CH}_2$ (0.86 electron) or $\text{HP}=\text{NH}$ (0.73 electron) (Table 2.1). Replacing either of the two π -donor groups, NR_2^- or $(\text{PR}_3)_2\text{C}$, by a hydride results in an even lower π -population at the phosphorus center. This highlights the role of both of these groups in stabilizing $3a^{2+}$.

The total π -population at the NPC fragment is slightly smaller than 4.00 in the case of $\mathbf{3a}^{2+}$ and $\mathbf{3f}^{2+}$, and 2.00 for $\text{HP}=\text{C}(\text{PH}_3)_2^{2+}$, but essentially perfect values are obtained for the other molecules in Table 2.1. This suggests an interaction between the PR_3 groups and the π -MOs of the NPC fragment. The degree of hyperconjugation that this provokes between the σ^* R–P bond and the π P=C bond (or the π lone-pair on C) can be estimated through computation of second-order interaction energies which are found to be 78, 92 and 66 kJ mol^{-1} for $\mathbf{3a}^{2+}$, $\mathbf{3f}^{2+}$ and $\text{HP}=\text{C}(\text{PH}_3)_2^{2+}$, respectively. This hyperconjugation explains why the C– PR_3 bond lengths lie between single and double bond values (mean lengths being 1.818, 1.781 and 1.813 Å for $\mathbf{3a}^{2+}$, $\mathbf{3f}^{2+}$ and $\text{HP}=\text{C}(\text{PH}_3)_2^{2+}$, respectively). In addition, it depicts that the participation of the NR_2 group in $\mathbf{3a}^{2+}$ and $\mathbf{3f}^{2+}$ in the π -system diminishes π -donation from the carbon atom to the NPC-phosphorus center, which results in notable hyperconjugation into the $\text{C}(\text{PR}_3)_2$ fragment.

	% P ^[a]	C	P	N	$\Sigma\text{pop}^{[b]}$
$\text{H}_2\text{C}=\text{PH}$	46.4	1.07	0.92	-	1.99
$\text{H}_2\text{C}=\text{P}-\text{NH}_2$	39.0	1.26	0.86	1.84	3.96
$\text{HN}=\text{PH}$	36.8	-	0.73	1.26	1.99
$\mathbf{3a}^{2+}$	22.4/20.8	1.53	0.70	1.63	3.86
$\mathbf{3f}^{2+}$	19.5/18.3	1.57	0.61	1.68	3.86
$(\text{PH}_3)_2\text{C}=\text{PH}^{2+}$	27.2	1.40	0.53	-	1.93
$\text{H}_2\text{N}=\text{PH}^+$	22.4	-	0.44	1.55	1.99
[a] Percentage contribution of the P atom in the π C=P/N=P bond.					
[b] Sum of the π -population at the C, P and N atoms.					

Table 2.1. NBO bond polarization and NPA π population at the C, P and N atoms of the CPN moiety (in electron), calculated at the B3PW91/6-311+G(d,p)//B3PW91/6-31G(d) level.

The energy required to cause rotation about the NP and PC bonds provides another estimate of the π character of the bonds containing the NPC fragment. The bulk of the substituents in $\mathbf{3a}^{2+}$ is likely to cause significant steric bias, so this analysis was performed for $\mathbf{3f}^{2+}$. A planarized analogue of $\mathbf{3f}^{2+}$, which we labelled as $\mathbf{3f_p}^{2+}$ was

computed and found to be 7.9 kJ mol⁻¹ higher in energy than **3f**²⁺ itself. A rotation of 90° around the PC bond was performed. Subsequent optimization without full relaxation of the geometry, so that the planarity at the N and C atoms is retained, leads to **3fc**²⁺ whilst a similar rotation about PN bond gave **3fn**²⁺ (Figure 2.7). In both cases, changes with significant π -bonding were observed, with the bond undergoing the rotation lengthening and the other bond simultaneously shortening slightly. For **3fc**²⁺, where rotation blocks any delocalization of the PCP carbon π -electron density onto the phosphorus atom, a shorter C–PR₃ bond is also observed. This is indicative of hyperconjugation. The opposite trend is observed for **3fn**²⁺, where the nitrogen lone pair no longer attenuates this delocalization of the PCP carbon π -electron density. The relative energies of **3fc**²⁺ (66.4 kJ mol⁻¹) and **3fn**²⁺ (66.8 kJ mol⁻¹) relative to **3fp**²⁺ (Figure 2.7), confirm that NP and PC π bonds have similar strength, i.e. both C=P–N and C–P=N resonance forms have similar weight, so that this analysis is in good agreement with the NBO results above.

Figure 2.7. Optimized geometries and relative energies (kJ mol⁻¹) computed at the B3LYP/6-311+G(d,p)//B3PW91/6-31G(d) level.

One last concern for the nature of the CP σ bond in **3a**²⁺ and **3f**²⁺ has also been addressed. Several structural formulae, with or without donor-acceptor interactions, can be used to describe these molecules. An assembly of several closed-shell chemical groups through the use of dative bonds is a modern way of representing molecules, and **3a**²⁺ and **3f**²⁺ can be depicted in this way as an assembly of a carbodiphosphorane (being built from

one carbon atom in its ^1D excited state and 2 phosphane ligands) and a dicationic $P-NR_2$ group that formally has one lone pair and 2 vacant orbitals at the phosphorus center. Equally, a more conventional description involving only covalent bonds is also possible. In fact, both representations make up highly limiting descriptions of the true electronic structure. “Extreme” model representations of $3a^{2+}$ and $3f^{2+}$ are presented in Figure 2.8.

Figure 2.8. “Extreme” model representations of $3a^{2+}$ and $3f^{2+}$.

A precise description of the bonds can be obtained via the examination of the σ -bond polarization through NBO analysis.

PC bonds	Bond Length (Å)	% P[a]	PN bonds	Bond Length (Å)	% P[a]
H_3C-PH_2	1.867	39.2	H_2N-PH_2	1.719	28.9
$H_2C=PH$	1.671	37.5	$HN=PH$	1.590	30.5
$H_2C=P-NH_2$	1.661	38.2	$H_2C=P-NH_2$	1.687	25.9
$(Ph_3P)_2C-P-N^iPr_2^{2+}$ ($3a^{2+}$)	1.743	31.8	$(Ph_3P)_2C-P-N^iPr_2^{2+}$ ($3a^{2+}$)	1.647	23.8
$(H_3P)_2C-P-NH_2^{2+}$ ($3f^{2+}$)	1.742	30.9	$(H_3P)_2C-P-NH_2^{2+}$ ($3f^{2+}$)	1.629	26.1
$(H_3P)_2C-PH^{2+}$	1.712	30.1	$H_2N=PH^+$	1.617	24.7
$(Ph_3P)_2C-P-N^iPr_2^{2+}$ ($3a^{2+}$)	1.821	37.6			
$(H_3P)_2C-P-NH_2^{2+}$ ($3f^{2+}$)	1.781	38.8			
$(H_3P)_2C-PH$	1.813	38.9			
[a] Percentage contribution of the P atom in the σ CP/NP bond.					

Table 2.2. NBO polarization of the PC and PN σ bond calculated at the B3PW91/6-311+G(d,p)/B3PW91/6-31G(d) level.

Data in Table 2.2 indicate that the C–PNR₂ σ bonds in **3a**²⁺, **3f**²⁺ and (H₃P)₂C=PH²⁺ are highly polarized toward the carbon atom, with greater than usual electron density on the C atom.

On this basis, the carbon is implied to retain more electron density than the σ PC bond in H₃C–PH₂, H₂C=PH or H₂C=P–NH₂, the carbene–P bond can have a certain degree of dative character. However, the σ R₃P–C bonds in **3a**²⁺, **3f**²⁺ and (H₃P)₂C=PH²⁺ show a polarization that is similar to a classical σ PC bond. This implies that the R₃P→C description is not consistent with the electronic structure. The PN σ bonds present an even stronger polarization toward N, but a dative bond description has never been proposed for such bonds. The high polarization of both the σ and π components with the NP and PC bonds that comprise the NPC fragment of **3a**²⁺ and **3f**²⁺ results in a little charge transfer from the (R₃P)₂C to the formally dicationic phosphorus center in the “dative” resonance hybrid. Consequently, the NPA atomic charge remains significantly positive on P (+1.19 and +1.27 e[−] for **3a**²⁺ and **3f**²⁺, respectively) and a negative charge at the central carbon atom (−1.42 and −1.40 e[−]). Finally, the NR₂ group is almost neutral (−0.14 and −0.16 e[−]) due to the opposing “pull” of σ and “push” of π electron density. The NPA atomic/group electronic charge (in electron) of **3a**²⁺ and **3f**²⁺ are presented in Table 2.3.

	3a ²⁺	3f ²⁺
P ^[a]	+1.19	+1.27
NR ₂	−0.14	−0.16
C	−1.42	−1.40
PR ₃	+1.18	+1.14
[a] phosphorus atom of the CPN moiety.		

Table 2.3. NPA atomic/group electronic charge (in electrons) of **3a²⁺ and **3f**²⁺ calculated at the B3PW91/6-311+G(d,p)//B3PW91/6-31G(d) level.**

In view of these investigations and in order to enhance the Lewis acidic properties of our dication, we attempted to synthesize [PhP(C(PPh₃)₂)₂]²⁺.^{4a} The addition of C(PPh₃)₂, **1a** to a benzene solution containing excess PhPCl₂ resulted in the formation of the

monocationic compound, $[\mathbf{2e}][\text{Cl}]$ via a chloride displacement reaction. The formation of $[\mathbf{2e}^+][\text{Cl}]$ was elucidated from ES-MS and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy experiments. The ES-MS experiment gave a peak at m/z 679.1635 (calcd. for $\mathbf{2e}^+$: 679.1635) exhibiting the correct isotopic pattern predicted for $\mathbf{2e}^+$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two second order signals at δ_{P} 26.4 (multiplet) and 114.8 (triplet) ppm.

Unfortunately, no reaction was observed when $[\mathbf{2e}^+][\text{Cl}]$ was mixed with 2.1 equivalents of $\text{Na}[\text{BAr}^{\text{F}}_4]$. However, experiments conducted at elevated temperatures suggested that the targeted dication might exist but only as a transient intermediate.^{4a} More evidence for its existence was generated by trapping the dication $[\text{PhP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ with PMe_3 to form an acid-base adduct, $[\mathbf{3e}^{2+}\cdot\text{PMe}_3][\text{BAr}^{\text{F}}_4]_2$. This compound was elucidated from ES-MS and $^{31}\text{P}\{^1\text{H}\}$ NMR experiments. The ES-MS experiment showed a peak at m/z 360.1197 (calcd. for $\mathbf{3e}^{2+}\cdot\text{PMe}_3$: 360.1191) exhibiting the correct isotopic pattern predicted for $\mathbf{3e}^{2+}\cdot\text{PMe}_3$. The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed three second order signals at δ_{P} -6.4 (doublet of triplets), 11.4 (doublet of triplets) and 28.7 (doublets) ppm. The formation of this adduct enhances the fact that a stronger Lewis acid than the $^i\text{Pr}_2\text{N}$ dication (Scheme 2.1) could be synthesized. It is also acknowledged that an associative mechanism should not be completely ruled out.

Figure 2.9. Molecular view of $[3e^{2+} \cdot PMe_3][BAr^F_4]_2$: Ellipsoids set at 50% probability. For clarity, the $[BAr^F_4]^-$ counterions together with hydrogen atoms have been omitted for clarity.

To gain a deeper understanding on the reactivity and stability of $3e^{2+}$, theoretical investigations were performed using the Gaussian 09 package. The dicationic structure was fully optimized by the B3PW91 method with 6-31G(d) basis set. The frontier orbitals of $3e^{2+}$ are shown in Figure 2.10.

Figure 2.10. Frontier orbitals for $3e^{2+}$.

The lowest unoccupied molecular orbitals (LUMOs) correspond to the π^* for the allene-like CPC fragment in $3e^{2+}$. On the other hand, the highest occupied molecular orbitals (HOMOs) appear to be non-bonding in the same fragment, with a possibility of

mixing from the lone-pair orbital on the central phosphorus forming a helical-like MO. The energy level of HOMO for $\mathbf{3e^{2+}}$ (-11.92 eV) was similar to that in $[^i\text{Pr}_2\text{NP}(\text{CPh}_3)_2]^{2+}$, $\mathbf{3a^{2+}}$ (-11.99 eV). However, the LUMOs for $\mathbf{3e^{2+}}$ (-8.50 eV) was discovered to be at a lower energy level and hence more accessible than that in $\mathbf{3a^{2+}}$ (-7.77 eV). Similar observations were made when the amino substituents for bis(amino)phosphenium cations were replaced by Ph substituents.³⁸ Hence, this also explains the more Lewis acidic nature of the central P atom of $\mathbf{3e^{2+}}$ and hence the need of PMe_3 ligand to trap it. Interestingly, according to natural bond order analysis, the partial charges of the central phosphorus for $\mathbf{3e^{2+}}$ (+0.99) was less positive compared to $\mathbf{3a^{2+}}$ (+1.19) as shown in Table 2.4. This might be a result of the electron density over-compensation from the carbene substituent to the central phosphorus in $\mathbf{3e^{2+}}$ compared to that in $\mathbf{3a^{2+}}$.^{2, 4a} Certainly, the electronegativity difference between N (for $\mathbf{3a}$) and C (for $\mathbf{3e}$) could also contribute to the positive charge discrepancy of the central P. Despite this, it suggested that Lewis acid type behaviour of a compound might not necessarily be a result of its electron depletion at the central element but by the availability of the LUMO.

	R= NⁱPr₂ 3a²⁺	R= Ph 3e²⁺
Bond lengths (Å)		
R–P ₁	1.647	1.789
P ₁ –C ₁	1.745	1.722
C ₁ –P ₂	1.827	1.841
C ₁ –P ₃	1.810	1.826
Angles (°)		
RP ₁ C ₁	109.0	118.0
ΣC ₁	359.3	359.6
RP ₁ C ₁ P ₃	16.6	6.0
C _(cis) XP ₁ C ₁ (X=N or Ph)	7.6	18.0
Atom (group) NBO charge (-e)		
R	-0.78 (-0.14)	-0.46 (-0.11)
P ₁	+1.18	+0.99
C ₁	-1.42	-1.30
P ₂ (PPh ₃)	+1.66 (+1.20)	+1.65 (+1.22)
P ₃ (PPh ₃)	+1.64 (+1.17)	+1.63 (+1.20)
π population (e)		
N (3a ²⁺) or Cl (3g ²⁺)	1.63	-
P ₁	0.70	0.68
C ₁	1.53	1.41
Σ	3.86	2.09

Table 2.4. Comparison between 3a²⁺ and 3e²⁺ based on theoretical calculations at B3PW91/6-311+G(d,p)//B3PW91/6-31G(d) level.

To further understand the case, a comparison between [NⁱPr₂NP(CPPH₃)₂]²⁺, **3a²⁺** and [PhP(CPPH₃)₂]²⁺, **3e²⁺** was performed for their bond lengths, atomic charges and π population. The results based on theoretical calculations are tabulated in Table 2.4. This shows that the π donation from the carbene to P₁R is higher in **3e²⁺** than in **3a²⁺**.

1) the donation to PPh₃ groups is smaller in **3e²⁺** than in **3a²⁺** (slightly larger C₁–PPh₃ bond length and positive charge on PPh₃ groups in **3e²⁺** than in **3a²⁺**);

2) the C₁ atom is less populated in **3e²⁺** than in **3a²⁺** (decrease of the negative atomic charge and of the π population in **3e²⁺** than in **3a²⁺**);

3) the π donation from C₁ to P₁R is larger in **3e**²⁺ (smaller P₁–C₁ bond length) and this almost compensates for the loss of the donation due to the absence of the NⁱPr₂ π -donor group in **3e**²⁺, as compared to **3a**²⁺ (-NⁱPr₂ group).

In other words, difference between **3a**²⁺ and **3e**²⁺ is almost similar to the difference between **3f_P**²⁺ and **3f_N**²⁺ above.

CHAPTER 3

Reactivity of $3a^{2+}$

Section 3.1. Reaction with DMAP and PMe_3

Scheme 3.1. Reaction involving $3a^{2+}$ and DMAP.

In Scheme 3.1, reactions involving dication $3a^{2+}$ and dimethylaminopyridine (DMAP) are presented,² including the influence of the counterion on the overall outcome of the reaction. The reaction between $[3a^{2+}][AlCl_4]_2$ and DMAP resulted in the formation of $[2a^+][AlCl_4]$ and $DMAP \cdot AlCl_3$, which is consistent with the Hard and Soft (Lewis) Acids and Bases (HSAB) concept regarding these substrates.¹⁴

To remove the $AlCl_4^-$ counterion interference, we attempted the same reaction using $[3a^{2+}][BAr^F_4]_2$ ($Ar^F = 3,5-(CF_3)_2-C_6H_3$). The introduction of 1.0 equivalent of DMAP in a solution containing $[3a^{2+}][BAr^F_4]_2$ resulted in the formation of the target adduct, $[3a^{2+} \cdot DMAP]$ ($\delta_P = 131.2$ ppm).

Scheme 3.2. Reaction involving $3a^{2+}$ and PMe_3 and its proposed equilibria.

In order to explore the Lewis acidic properties of the dication, 1 or 2 equivalents of PMe_3 were added into a dichloromethane solution containing $[\mathbf{3a}^{2+}][\text{AlCl}_4]_2$.² It was evident that a simple Lewis acid-base adduct formation did not happen but a more complex reaction mixture was developing. Variable temperature $^{31}\text{P}\{\text{H}\}$ NMR spectroscopy was performed and showed the formation of not only the $\mathbf{3a}^{2+}\cdot\text{PMe}_3$ adduct ($\delta_{\text{P}} = 40.7$ ppm) but also the $\mathbf{2a}^+$ precursor, suggesting a dynamic equilibrium system (Scheme 3.2).

Even though the anion interference was eliminated when $\text{BAr}^{\text{F}_4}_4^-$ was used as the counterion, the equilibrium between the free dication and the corresponding adduct was still present for further studies. It was possible to obtain the van't Hoff plot, by Variable Temperature (VT) $^{31}\text{P}\{\text{H}\}$ NMR spectroscopy, from which the thermodynamic parameters $\Delta H = -30.5$ kJ mol⁻¹ and $\Delta S = -77.7$ J K⁻¹ mol⁻¹ have been extracted. The value for the enthalpy for the adduct i.e. the P–P bond formation was significantly less than the same value established for a single P–P bond (~ 200 kJ mol⁻¹) suggesting a very weak P–P bond, which is consistent with the equilibrium nature of this system (Scheme 3.2).⁸⁶

Additionally, similar thermodynamic parameters ($\Delta H = -37.5$ kJ mol⁻¹ and $\Delta S = -110.5$ J K⁻¹ mol⁻¹) were obtained when PMe_3 was added to the DCM solution containing $[\mathbf{3c}^{2+}][\text{BAr}^{\text{F}_4}_4]_2$. The graphs of $\ln K$ vs $1/T$ (K⁻¹) for the reactions of PMe_3 and $[\textit{i}\text{Pr}_2\text{NPC}(\text{PPh}_3)_2][\text{BAr}^{\text{F}_4}_4]_2$ and $[\text{Cy}_2\text{NPC}(\text{PPh}_3)_2][\text{BAr}^{\text{F}_4}_4]_2$, respectively, are presented in Figure 3.1.

Figure 3.1. Graphs of $\ln K$ vs $1/T$ (K^{-1}) of $[iPr_2NPC(PPh_3)_2][BAr^F_4]_2$ (top) and $[Cy_2NPC(PPh_3)_2][BAr^F_4]_2$ (bottom) with PMe_3 .

Hence, the unprecedented equilibrium system (Scheme 3.2), especially the equilibrium involving heterolytic P–P bond formation or cleavage for phosphonium chemistry revealed that PMe_3 has a higher preference to interact with $AlCl_4^-$ than with the cation but the preference can be changed with a decrease in temperature. Based on our knowledge, the equilibrium between dication and dication- PMe_3 adduct is the very first heterolytic P–P bond formation or cleavage in the absence of any intermolecular⁸⁷ or intramolecular⁸⁸ assistance. The presence of a partially vacant P3p orbital on 3^{2+} , resulting in the Lewis acidic nature of the dication was confirmed by the formation of $3^{2+} \cdot PMe_3$ and $3^{2+} \cdot DMAP$.

Section 3.2. Activation of Water and Methanol

Advances in the chemistry of main group systems have been remarkable in recent years. These include stabilization of unusual oxidation states, transformation of a Lewis acid into a Lewis base and the preparation of unsaturated homoleptic molecules.⁸⁹ One of the most promising results in this research field involved the use of main group systems for the activation of small molecules such as H₂, NH₃ and CO₂.⁹⁰ Frustrated Lewis pairs (FLPs) can perform reactions such as hydrogenations and have thus obtained the most attention. This poses a challenge to the well-established catalytic chemistry of transition metals.⁹¹ However, unlike transition metal-based catalysis, two sites, a Lewis acid and a Lewis base are required for FLPs, for activation and subsequent utilization of these small molecules. Compounds based on divalent Group 14 elements have exhibited remarkable activity with respect to single site activation of small molecules. These examples include the activation of H₂ and/or NH₃ by amino alkyl carbenes,^{90d} bisaryl stannylenes as well as by germylenes^{90e} and acyclic^{90f} and cyclic^{90a} silylenes.

One of the most appealing scientific challenges with respect to our global fuel needs is that of water activation and subsequent splitting into hydrogen and oxygen.⁹² A multistep procedure has been proposed as the organometallic solution to this problem and several of these steps have been performed independently.⁹³ However, no organometallic catalyst is known to be able to efficiently complete the entire proposed catalytic cycle. Water coordination is relatively common. However, the activation that follows which is oxidative addition, proves to be challenging and in fact, is one of the most crucial steps in the overall cycle (Scheme 3.3).^{92,94} The only examples of complexes reported to perform classical oxidative addition at the metal centre using equimolar amounts of water comprise of low valent ruthenium ((PMe₃)₄Ru(CH₂CH₂)) and gallium

([HC(CMe)₂(N(2,6-ⁱPr₂C₆H₃))₂]₂Ga) complexes.⁹⁵ Excess substrate and/or ligand assistance are often necessary for activation to occur in other metal complexes.⁹²⁻⁹⁴

Scheme 3.3. Coordination and activation (oxidative addition) of water to a transition metal moiety.

Other than the above mentioned gallium compound, silylene and phosphinidene centres are also used for the addition of water to the respective single site main group elements.⁹⁶ Experimental results suggested a different scenario despite the theoretical ab initio calculations which described the absence of the O–H bond cleavage before the addition of water and other substrates to the parent phosphinidene (P–H).⁹⁷ Specifically, non-equimolar amounts of substrates, addition of activators such as boranes, long reaction times and high temperatures are required for the addition of water to these main group centres, suggesting that the O–H bond cleavage occurred before the coordination or addition.⁹⁷ The same reaction conditions were necessary for the addition of alcohols to these compounds. However, there are exceptions for the case of a hypervalent phosphorus molecule ([N(CH)₂(C^tBuO)₂]₂P) and a few difluorophosphines (RPF₂; R = H or Ph), which were able to react with 1 equivalent of methanol without any activators.⁹⁸ Nevertheless, facile rearrangements to different products ensued after the additions. In fact, these compounds hydrolysed in the presence of water. Thus, our group decided to report our work on a room temperature, activator-free and facile addition or activation of water or methanol to **[3a]**[BAr^F₄]₂ by the use of equimolar amounts of the substrate, showing no cleavage of O–H bond before the addition.³

Scheme 3.4. Reactions involving activation of water and methanol. Key reagents/conditions: a) HOR (1 equiv; R = H, Me), CH₂Cl₂; b) NEt₃ (1 equiv), CH₂Cl₂.

As phosphorus is oxophilic, the activation of water was attempted. An immediate colour change was observed when 1.0 equivalent of H₂O was added to a bright yellow CD₂Cl₂ solution of **3a²⁺**. No noticeable difference was observed with respect to the rates when water was added at temperatures as low as -78°C. The ³¹P{¹H} NMR spectrum of the pale yellow reaction mixtures showed the absence of the signal at around 356 ppm assigned to the central P atom in **3a²⁺**. In addition to the signal typical for the carbene (C(PPh₃)) ligand (δ_P = 24.1 ppm), the new spectrum also contained a signal at δ_P 31.8 ppm (broad) which split into a doublet when the proton decoupler was turned off. The P–H coupling of 642 Hz is typical for a ¹J_{P(V)–H} coupling constant, suggesting an oxidation of the central phosphorus from P(III) to P(V) (Scheme 3.4). The ¹H NMR spectrum of the reaction mixture also contained a doublet at δ_H 7.58 ppm with the same coupling constant which confirmed the formation of a “P–H” fragment. Furthermore, infra-red (FT-IR) spectroscopy revealed a signal at approximately 3550 cm⁻¹, suggesting the presence of an O–H group.

A stock solution of D₂O or CD₃OD in CH₂Cl₂ or CD₂Cl₂ was used in the subsequent experiments. Even though “dried” solvents were used, some minimal H/D exchange inevitably occurred with trace amounts of H₂O. Hence, complete elimination of the signals due to deuteration was not possible but diminished δ_H signal intensities were clearly evident.

Repeating the experiment using D₂O instead of H₂O showed not only P–H/D and O–H/D fragments but also the fact that these fragments originated from water. Firstly, the intensities of the initial P–H (δ_{H} 7.58 ppm) and O–H (FT-IR: approximately 3550 cm⁻¹) signals decreased dramatically when D₂O was used. Secondly, the ²H NMR and FT-IR spectra of the deuterated reaction mixture contained signals at δ_{D} 7.54 ppm (¹J_{PD} = 89.6 Hz) and approximately 2630 cm⁻¹, respectively. This was consistent with the D-for-H replacement.

Similar results were obtained under the same reaction conditions when methanol was used instead of water. The colour change was immediate upon adding 1.0 equivalent of substrate to a solution of **3a**²⁺ in CH₂Cl₂. The ¹H NMR spectrum of the isolated solid (yield: ca. 90%) gave signals corresponding to “P–H” (δ_{H} 7.42 ppm, ¹J_{PH} = 580 Hz) and “P–OMe” (δ_{H} 3.31 ppm, ³J_{PH} = 14.5 Hz) fragments, as well as, for the amino and phenyl (carbone) groups.

The use of CD₃OD strongly suggested that the H and OMe fragments originated from methanol. High-resolution mass spectrometry identified a signal at m/z 349.6431 consistent with [((Ph₃P)₂C)(ⁱPr₂N)P(H)OMe]²⁺ (**3a**²⁺-(H)OMe) having a +2 charge (calcd. for (C₄₄H₄₈NOP₃)²⁺: m/z 349.6474). The δ_{P} signal for the central phosphorus was found at 41.3 ppm, which was in a good agreement with the analogous signal in **3a**²⁺-(H)OH.

It was observed that the δ_{P} signal for the central P atom in **3a**²⁺-(H)OH (31.8 ppm) was broader than the analogous signal observed for **3a**²⁺-(H)OMe (41.3 ppm), providing evidence for a fluxional process in **3a**²⁺-(H)OH involving the hydroxo proton. Addition of 1.0 equivalent of NEt₃ to a CH₂Cl₂ solution containing **3a**²⁺-(H)OH further showed that the hydroxo proton was responsible for the observed fluxionality. Firstly, the peak typical for an O–H group was absent from the newly collected FT-IR spectrum. Next, the amine addition not only resulted in a sharper δ_{P} signal corresponding to the central P

(17.4 ppm) but it also retained the P-H ($^1J_{\text{PH}} = 527$ Hz) fragment. In addition, it was possible to identify a broad δ_{H} signal at approximately 6.3 ppm, typical for the NH proton of the triethylammonium cation. This implies that the added amine abstracted the fluxional proton. ^2H NMR spectroscopy confirmed this observation as the **3a²⁺-(D)OD/NEt₃** system produced a broad δ_{D} signal at about 6.6 ppm. Crystals suitable for single crystal X-ray diffraction were obtained after layering the reaction mixture with hexane (Figure 3.2). The existence of a $[\text{((Ph}_3\text{P)}_2\text{C)(}^i\text{Pr}_2\text{N)P(H)O}]^+$ (**3a²⁺-(H)O**) unit strengthened the case that the addition of H₂O to the central phosphorus was preferred with respect to possible hydrolysis (Figure 3.2). The P1–O1 bond length of 1.498(3) Å is much shorter than the analogous bond distance of 1.584(2), 1.629(1) and 1.630(1) Å observed for $[\text{((MeC((CMe)(NDipp))}_2\text{P-OH)}]^+$, $(\text{C}_2\text{F}_5)_2\text{P-OH}$ and $(\text{CF}_3)_2\text{P-OH}$, respectively, which is consistent with a P–O double bond and confirmed the absence of an O-bound proton for the **3a²⁺-(H)O** fragment (the FT-IR spectrum, *vide supra*).⁹⁹ The asymmetric unit also included a triethylammonium cation (^1H and ^2H NMR, *vide supra*), which supported the idea that the missing proton has been abstracted by NEt₃. The distance of 2.717(5) Å between the oxygen (O1) of **3a²⁺-(H)O** and the ammonium nitrogen (N2) is typical for a system with hydrogen bonding between “P–O” and “H–N” fragments (Figure 3.2).¹⁰⁰ Hence, by solid-state analysis, the ammonium cation was hydrogen bonded to **3a²⁺-(H)O** cation, forming a very rare system made up of two different cationic moieties of hydrogen bound to each other.^{100d} Moreover, single crystal X-ray analysis of a crystal obtained for the deuterated analogue showed the analogous interaction between two cationic units (O1–N2 2.698(1) Å) with virtually identical structural parameters, particularly the P1–O1 (1.497(2) Å) distance.

Figure 3.2. Molecular structure of $[i\text{Pr}_2\text{NP}(\text{H})\text{OHNEt}_3(\text{C}(\text{PPh}_3)_2)][\text{BAR}^{\text{F}}_4]_2$, $[\mathbf{3a}^{2+}-(\text{H})\text{O}--\text{HNEt}_3][\text{BAR}^{\text{F}}_4]_2$. Ellipsoids set at 50% probability. For clarity, the $[\text{BAR}^{\text{F}}_4]^-$ counterions together with hydrogen atoms, except H(1) and H(2) have been omitted for clarity.

The evidence mentioned above indicated that the hydroxo proton was responsible for the fluxionality observed in $\mathbf{3a}^{2+}-(\text{H})\text{OH}$. A comparison of the variable temperature (VT) ^1H NMR spectra of $\mathbf{3a}^{2+}-(\text{H})\text{OH}$ and its deuterio analogue ($\mathbf{3a}^{2+}-(\text{D})\text{OD}$) it was possible to identify the other site for the fluxional proton. Three new signals at δ_{H} 2.68, 3.16 and 3.32 ppm appeared when the temperature of the sample containing $\mathbf{3a}^{2+}-(\text{H})\text{OH}$ was lowered to -50°C (Figure 3.3).

The analogous experiment with $\mathbf{3a}^{2+}-(\text{D})\text{OD}$ showed the appearance of only the signal at δ_{H} 3.32 ppm. This suggests that the two other signals could be attributed to the fluxional proton (Figure 3.3). The more dominant signal (δ_{H} 2.68 ppm) could be assigned to the OH proton. This is because the corresponding signal for $(\text{CO})_5\text{W}(\text{P}(\text{H})(\text{OH})\text{Ph})$ was at δ_{H} 2.35 ppm.^{96a} The value for the less intense signal of δ_{H} 3.16 ppm is similar to that of the NH signal of δ_{H} 2.93 ppm in $i\text{Pr}_2\text{HN}\cdot\text{BH}_3$. This implied that the $i\text{Pr}_2\text{N}$ substituent in $\mathbf{3a}^{2+}-(\text{H})\text{OH}$ was the second site for the fluxional proton forming $[(\text{Ph}_3\text{P})\text{C}(i\text{Pr}_2\text{HN})\text{P}(\text{H})\text{O}]^{2+}$ ($\mathbf{3a}^{2+}-(\text{H})\text{NH}$, Figure 3.4).¹⁰¹ Furthermore, the theoretically

calculated δ_{H} values for the O–H (**3a**²⁺–(**H**)OH) and N–H (**3**²⁺–(**H**)NH) protons of 2.84 and 3.43 ppm, respectively, are slightly overstated as compared to their experimental values (See Chapter 5). Nevertheless, the relative positions of these two signals and their separation of 0.5–0.6 ppm is identical regardless of the methods. Therefore, this evidence strongly supports a fluxional process shown by a dynamic 1,3-proton shift. This could be the main reason for the instability of **3a**²⁺–(**H**)OH and **3a**²⁺–(**D**)OD due to the creation of a very potent Brønsted acid.

In order to discover more about the advantage of **3a**²⁺ as a water activator with respect to analogous phosphonium cations, [(ⁱPr₂N)PCl]⁺[AlCl₄][–], **4**, and [(ⁱPr₂N)₂P]⁺[B(3,5-(CF₃)₂-C₆H₃)₄][–], **5**, were reacted with 1 equivalent of H₂O.²⁹ For both cases, the products showed a “P–H” fragment that showed that the target addition were only minor species (less than 10%). This was the case even after 72h, based on ³¹P NMR spectroscopy. In fact, based on ²⁷Al and ³¹P NMR spectroscopy, the reaction involving **4** demonstrated anion interference while **5** did not react any further. Attempts to identify the products were unsuccessful because of the presence of multiple products or low yields. Nevertheless, these monocations seem to be inferior to the analogous dication for water activation.

Figure 3.3. Variable temperature ^1H NMR for $3\text{a}^{2+}\text{-H(OH)}$ (top) and $3\text{a}^{2+}\text{-D(OD)}$ (bottom).

Figure 3.4. Proposed fluxional process.

Section 3.3. Reduction by the use of Cobaltocene

Since the N^iPr_2 dication, 3a^{2+} has 6 valence electrons about the central P atom, the possibility of forming a monocationic compound by the addition of 1 electron to it was attempted. DFT calculations using the B3PW91 method with 6-31G(d) basis set depict the difference in charges on the various fragments between the monocationic radical and dication 3a^{2+} (Table 3.1).

Fragments	Charges		ΔQ
	Dication	Monocationic radical	Monocationic radical - Dication
ⁱ Pr ₂ N	-0.13	-0.31	-0.18
Central P	1.13	0.71	-0.42
Carbone C	-1.41	-1.46	-0.05
Ph ₃ P <i>cis</i> - to ⁱ Pr ₂ N	1.20	0.98	-0.22
Ph ₃ P <i>trans</i> - to ⁱ Pr ₂ N	1.21	1.08	-0.13
Overall	2.00	1.00	-1.00

Table 3.1. Difference in charges calculated using the B3PW91 method with 6-31G(d) basis set.

Prior to our studies, all the phosphonium monocations had a formal charge of +1 but not a partial charge of +1 on P. Interestingly, we managed to synthesize the first phosphonium dication which allows a partial +1 charge on the central P. From Table 3.1, it is also observed that the largest change in charge can be found on the central P atom. Hence, this suggests that the electron is highly likely being added to the vacant π^* orbital on the P atom on the dication **3a**²⁺.

DFT calculations were also performed to obtain the spin densities on the respective fragments on the monocationic radical (Table 3.2).

Fragments	Spin density
ⁱ Pr ₂ N	0.17
Central P	0.61
Carbone C	0.06
Ph ₃ P <i>cis</i> to ⁱ Pr ₂ N	0.13
Ph ₃ P <i>trans</i> to ⁱ Pr ₂ N	0.03
Overall	1

Table 3.2. Spin density of monocationic radical.

The highest spin density was also found on the central P atom. Hence, this further supports the idea that the electron is highly likely being added into the vacant π^* orbital of the dication.

Scheme 3.5. Attempted reduction of dication using cobaltocene.

In order to test the concept experimentally, 1.2 equivalents of cobaltocene was added to $3a^{2+}$ in difluorobenzene. Scheme 3.5 demonstrates our attempts in reducing our dication. A monocationic radical could possibly be formed which undergoes an equilibrium to form a dimer. The monocationic radical then undergoes a ring cyclization reaction to form a stable 5-membered ring compound, 6^+ , which was elucidated via X-ray crystallography (Figure 3.5). After isolation and purification, the room temperature $^{31}P\{^1H\}$ NMR spectrum of 6^+ showed three sets signals at δ_P 25.7 (doublet of doublets), 40.9 (doublet of doublets) and 66.4 (doublet of doublets), ppm, which can be attributed to P_2 , P_3 and P_1 , respectively (Figure 3.5). However, there was insufficient product for

further NMR and ES-MS studies. Future attempts to scale up this experiment will be performed by the Vidovic group.

Figure 3.5. Molecular structure of $[i\text{Pr}_2\text{NPPPh}_2(\text{C}_6\text{H}_4)(\text{C}(\text{PPh}_3))][\text{BAr}^{\text{F}}_4]$, $[6^+][\text{BAr}^{\text{F}}_4]$. Ellipsoids set at 50% probability. For clarity, the $[\text{BAr}^{\text{F}}_4]^-$ counterion together with hydrogen atoms have been omitted for clarity.

Figure 3.6. X-ray crystal structures of dication (left) and 5-membered ring compound (right).

Figure 3.6 shows both the X-ray crystal structures of the N^iPr_2 dication and the final product containing the 5-membered ring. By a simple comparison of these crystal structures, a simple rotation of the two P–C bonds on the dication (left structure) allows it to be superimposed onto the 5-membered ring compound (right structure). Hence, this allows the 5-membered ring cyclization reaction to take place.

Figure 3.7. $^{31}\text{P}\{\text{H}\}$ NMR stacked at the start, 3rd, 6th and 9th hour (bottom to top), labels on the top spectrum.

Figure 3.8. ^{31}P NMR stacked at the start, 3rd, 6th and 9th hour (bottom to top), labels on the top spectrum.

The $^{31}\text{P}\{\text{H}\}$ (Figure 3.7) and ^{31}P NMR spectra (Figure 3.8) were collected on an NMR sample comprising of 1.2 equivalents of cobaltocene and dication. Hourly experiments were conducted and the progression of the experiment was tracked. In the spectra above, every 3rd hour of experimentation is stacked, from the start to the 9th hour. The peaks indicated with an * are unknown but they contain P–H coupling. It was also difficult assigning the identity of the initial peaks that existed in solution. However, it was postulated to be a “dimer-like” compound, which was in equilibrium with the possible monocationic radical. Subsequently, by the 9th hour, the peaks due to **6**⁺, a 5-membered ring containing product was observed (Scheme 3.5).

Similar samples were prepared and maintained at -95°C in a cold acetone bath. These samples managed to retain the initial product due to the reaction of 1.2 equivalents of cobaltocene and dication. However, it was also difficult to isolate the product after numerous attempts.

Despite the multiple reactivity of the $i\text{Pr}_2\text{N}$ dication, it does not react with unsaturated molecules such as alkynes and dienes or anisole over prolonged periods.

CHAPTER 4

Further Developments towards the Synthesis of Carbene-Containing Compounds

Section 4.1. Background

Recently, we have been interested in developing the chemistry of carbodiphosphoranes, “carbones” as supports for phosphorus centres. It has been known since the pioneering early work of Matthews¹⁰² that carbones can behave as nucleophiles towards phosphorus halides and a small series of cationic phosphorus compounds $[XYP\{C(PPh_3)_2\}]^+$ ($X = Y = Ph$,¹⁰² Cl ;¹⁰³ $X = Cl$, $Y = N^iPr_2$)² that are derived from $C(PPh_3)_2$ ^{66a} has been reported.

Figure 4.1. Synthesis of cationic phosphorus compounds.

Complexes containing a carbene bound to phosphorus are, in fact, interesting from a synthetic standpoint in as much as they are very readily available via a simple addition of the easily accessible carbene to a class of compounds containing a phosphorus halogen bond. To a first- and very gross- approximation, the products can be easily assimilated into the larger family of $RPCl_2$ compounds and might show good potential as precursors for phosphorus chemistry. Therefore, it is a surprise that there seem to be no reports of the behaviour of carbones in such a context, and this Chapter constitutes an initial attempt to treat this area.

The potential benefits of the Ramirez carbene $C(PPh_3)_2$ within this framework reflects its position towards more the more stable end of the carbene class with respect to

hydrolysis and oxidation,¹⁰⁴ and straightforward preparation from triphenylphosphine which is both easily accessible and cheap. The triphenylphosphine components also make this kind of carbene quite bulky, which is significant. As shown initially most elegantly by Yoshifuji,¹⁰⁵ but also by Bickelhaupt,¹⁰⁶ Bertrand,¹⁰⁷ Karsch¹⁰⁸ and to a lesser degree Cowley,¹⁰⁹ the use of bulky substituents at phosphorus centres provides the means to access an atypical and rich chemistry that is showing increasing potential. Bertrand¹⁰⁷ has remained impressively present at the forefront of this area, together with Weigand,^{10d, 10e} and has more recently spearheaded the use of bulky NHCs and related ligands as supports for phosphorus centres that has allowed durable innovation.¹¹⁰ Traditionally, the archetypal hindering precursor for phosphorus chemistry has been “YoshPCl₂” (or PAr*Cl₂ where Ar* = C₆H₂-2,4,6-*i*Bu₃), which is a compound that requires a non-negligible degree of synthetic competence to prepare.¹¹¹ As a result, it is conceivable that carbene-derived compounds such as [PCl₂{C(Ph₃P)₂}]⁺ cations might provide an alternative and, perhaps, slightly more synthetically expedient access to hindered phosphorus centres for unusual chemistry. Being very good donors, carbenes may also provide an alternative to systems based on NHCs and related supports.

The very wide chemistry of PRC₂ species means that any number of systems might be considered for an introductory study of the reactivity of PCl₂(carbene)⁺. We have chosen to explore their capacity to support unsaturated phosphirene (3-membered)¹¹² and phosphole (5-membered)¹¹³ ring systems, for two reasons. Firstly, and prosaically, both are compound classes that are very familiar to the École Polytechnique laboratory. More importantly, both have well described electronic configurations whose geometries are liable to vary in ways that are understood as a function of the electronegativity and/or the bulk of the P- substituent. From a synthetic standpoint, both have value. Phospholes serve as precursors for phosphorus analogues of metallocenes,¹¹⁴

and they can be used as sources of complexed singlet phosphinidenes, which have a broad chemistry.¹¹⁵ They also provide ligands for coordination chemistry that show unusual properties; these include low P- inversion energies¹¹⁶ and a good capacity for forming bridged species.¹¹⁷ Finally, and most notably, their use in molecular electronics is under widespread study.¹¹⁸ Phosphirenes, whose chemistry is significantly less developed, are nonetheless already useful precursors for ring expansion¹¹⁹ and retrocyclisation¹²⁰ reactions.

Figure 4.2. Structures of Phosphirene (Left) and Phosphole (Right) respectively.

To provide a reasonable degree of chemical flexibility for our studies, three distinct carbene- containing precursors: $[YPCl\{C(PPh_3)_2\}]^+$ ($Y = Ph$,^{4a} Cl ,⁸⁰ N^iPr_2)² were employed. The first, $[PhPCl\{C(PPh_3)_2\}]^+$,^{4a} which has been very recently reported by our group, constitutes what might be considered to be one of the closest representatives of a carbene- bearing species to the ubiquitous Ph_2PCl .⁷⁹ The second, $[PCl_2\{C(PPh_3)_2\}]^+$ ⁸⁰ is useful because the cycloaddition reactions under investigation generate formal phosphorus (V) species; these can be reduced easily to their desirable trivalent analogues only if the precursor has two properly adapted leaving groups and these are provided by $[PCl_2\{C(PPh_3)_2\}]^+$ (*vide infra*).⁸⁰ Finally, the electron- rich cation $[^iPr_2NPCl\{C(PPh_3)_2\}]^+$ was also used,² in the hope that it might be possible to follow reaction mechanisms cleanly by employing a preformed stabilised phosphonium ion as a starting material (Scheme 2.1).

Section 4.2. Interactions of Phosphenium Ions with C- Unsaturated Species (Alkynes, Dienes)

Fongers, Hogeveen and Kingma first worked on the addition of *in situ*- generated phosphenium ions to alkynes.¹²¹ Their methodology, which forms the basis of the best and simplest current route to phosphirenium salts and phosphirenes, involves the addition of RPCl_2 to AlCl_3 and subsequent [2+1] cheletropic addition to the alkyne.¹²¹ Within the context of our study, it is instructive to note that this addition reaction works well when the phosphorus substituent is aryl, alkyl or, importantly, $-\text{NR}_2$.¹²² Some examples are presented in Scheme 4.1.

Scheme 4.1. First examples depicting the reactions between phosphonous dichlorides and alkynes.

Breslow and Deuring almost simultaneously published the reactions of $\text{R}_2\text{PCl}/\text{AlCl}_3$ mixtures ($\text{R} = \text{Ph}, \text{Et}$) with $\text{EtC}\equiv\text{CEt}$ and $\text{PhC}\equiv\text{CPh}$,¹²³ whilst investigating the potential electronic structure of phosphirenium cations, which they supposed to be susceptible to stabilisation through a 3-center, 2-electron delocalization involving a $\text{C}=\text{C}$ bond and a phosphorus d-orbital (Figure 4.3). As will be discussed below, such potential for stabilisation is real, but it is now ascribed to σ^* -aromaticity¹²⁴ rather than the intervention of d-orbitals. With respect to the syntheses of phosphirenes without the involvement of phosphenium ions, they have been reported by Mathey^{112a} and Lammertsma.¹²⁵

Figure 4.3. A phosphirenium cation.

In the early 1950s, McCormack¹²⁶ discovered that dihalophosphines react with 1,3-dienes and produce phospholene oxides upon hydrolysis. Although the McCormack reaction allows a useful synthesis of phosphorus heterocycles, it requires long reaction time with most standard dienes¹²⁶ unless pressure is applied.¹²⁷ In cases where several isomeric products could arise, this “McCormack” cyclization reaction produces only those that are consistent with a genuine, concerted cheletropic addition.¹²⁸ The reaction is known to be quite sensitive to hindrance but can occur in favourable cases upon simple addition of a dihalophosphine to a diene.¹²⁹ Should this primary variant fail (for example in cases where hindered phosphorus centers or dienes whose equilibrium configuration is unsuited to cycloaddition are used),¹²⁶ then replacing the dihalophosphine by a phosphenium source frequently allows the reaction to proceed acceptably^{122a} as illustrated in SooHoo and Baxter¹³⁰ and Cowley’s¹³¹ early preparations of phosphenium ions from dienes, AlCl_3 and chlorophosphines. In such cases, reaction times are reduced drastically (Scheme 4.2). As in the more classical McCormack reaction, both steric and electronic factors affect the reaction rate. For instance, the highly stabilised $[(\text{Me}_2\text{N})_2\text{P}]^+$ reacts completely with 2,3-dimethyl-1,3-butadiene or isoprene in about 1 h after warming from -78 to +25 °C but complete reaction of the more sterically encumbered *trans*-1,3-pentadiene and *trans*-2-*trans*-4-hexadiene with the bulkier phosphenium ion $[(i\text{Pr}_2\text{N})_2\text{P}]^+$ requires 3 and 9 days, respectively.¹⁸ Increased reactivity can be due to a decrease in the bulk of the phosphenium ion substituents, or equally to an increase in the electrophilicity

at phosphorus. Hence, $[(^i\text{Pr}_2\text{N})(\text{Cl})\text{P}]^+$ reacts much more quickly than $[(^i\text{Pr}_2\text{N})_2\text{P}]^+$ and its reaction with 2,3-dimethyl-1,3-butadiene is complete in about 30 min at ambient temperature.¹⁸

Scheme 4.2. Examples depicting reactions between phosphonium ions and 1,3-dienes.

Less stabilised phosphonium ions also react with 1,4-dienes. Kashman¹³² has reported that complexes of the type $\text{RPX}_2 \cdot \text{AlX}_3$ ($\text{R} = \text{Me}, \text{Ph}$; $\text{X} = \text{Cl}, \text{Br}$), for instance, react with 1,4-dienes to produce phosphorus-containing heterocycles. It was believed that phosphonium ions are involved but they were not detected by ^{31}P NMR spectroscopy when PRCl_2 was reacted with AlCl_3 . Further studies of the reactivity of stabilized phosphonium ions towards the non-conjugated 1,4-diene class showed that, $[(^i\text{Pr}_2\text{N})\text{PCl}]^+$ reacts readily with 1,4-pentadiene or 1,4-hexadiene, resulting in two configurational isomers in each case.¹³³ The X-ray crystal structure of the predominant isomer from the 1,4-pentadiene reaction showed a proximal relationship between the $^i\text{Pr}_2\text{N}$ and cyclopropane moieties.¹³³

Figure 4.4. Configurational isomers.

Phosphenium ion reactions have also been extended to the heteroatom systems MeCH=CHCH=NNMe_2 , $\text{Me}_2\text{C=NN=CMe}_2$, $\text{Me}_2\text{NN=C(Me)C(Me)=NNMe}_2$. MeCH=CHCH=NNMe_2 reacts readily with $[i\text{Pr}_2\text{NPCI}]^+$ to give the heterocycle in Figure 4.5 which is obtained upon partial hydrolysis of the initial product.¹³⁴

Figure 4.5. Heterocycle from MeCH=CHCH=NNMe_2 and $[i\text{Pr}_2\text{NPCI}]^+$.

$\text{Me}_2\text{C=NN=CMe}_2$ and $\text{Me}_2\text{NN=C(Me)C(Me)=NNMe}_2$ are reacted with $[i\text{Pr}_2\text{NPCI}]^+$. Large amounts of $i\text{Pr}_2\text{NPCI}_2$ are detected by ^{31}P NMR spectroscopy in each case as a result of competing attachment of AlCl_3 units to imino or, more probably, amino lone pairs.¹⁸

In this section, our objective was to establish the degree to which carbene-substituted cations resemble more classical phosphenium ions in terms of their reactivity. To date, there appear to be few reports of the reactivity of carbene supported phosphorus centers.⁷⁹⁻⁸⁰ In principle, we might find the corresponding reaction of alkynes with $[\text{PY}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ ($\text{Y} = \text{Ph, Cl, N}^i\text{Pr}_2$) to be simple, in that there is no obvious reaction that competes with phosphirenium ion synthesis unless the alkyne employed is very electron poor.¹³⁵

However, interaction with dienes is potentially complex. Both Schmidpeter and Gruetzmacher have made extensive studies of phosphorus centres supported by ylids and it is revealing that one of Gruetzmacher's ylid- supported compounds (Figure 4.6) undergoes 4+2 cycloaddition with dienes, a reaction that reveals a phosphalkene- type reactivity for cation X, rather than the more classical 4+1 reactivity described in the cases above.⁵⁰ It is not therefore clear, *a priori*, what kind of reactivity to expect from dications such as **3e**²⁺ and **3g**²⁺.

Figure 4.6. 4+2 cycloaddition reaction involving Gruetzmacher's ylid.

In order to ascertain if our dications behave more like a phosphalkene or phosphonium cations, and therefore to obtain further indirect experimental evidence concerning the nature of the bond between the phosphorus and the carbene carbon atom, their behaviour towards alkynes and dienes was therefore studied.

Section 4.3. Results and Discussion

Initially, we prepared and characterized two carbene- based monocations possessing phenyl (Ph) and chloro (Cl) groups at phosphorus $[P\{C(PPh_3)_2\}XY]^+Cl^-$ ($XY = Cl_2$;⁸⁰ Cl, Ph).^{4a} Given the much diminished capacity for π donation that results from the replacement of the N^iPr_2 group in $[^iPr_2NP\{C(PPh_3)_2\}]^{2+}$ by Ph or Cl groups, these were expected to give rise to dications $[YP\{C(PPh_3)_2\}]^{2+}$ showing a more lively electrophilic behaviour than $[^iPr_2NPCl\{C(PPh_3)_2\}]^+$ and to provide a much more representative picture of the stability brought to a formally $\lambda^2\sigma^2$ - phosphorus cation by the $C(PPh_3)_2$ group alone. $[PCl_2\{C(PPh_3)_2\}]^+Cl^-$ was prepared from the carbene and PCl_3 by Schmidpeter's

method,⁸⁰ whilst $[\text{PhPCl}\{\text{C}(\text{PPh}_3)_2\}]^+\text{Cl}^-$ was obtained analogously from $\text{C}(\text{PPh}_3)_2$ and PhPCl_2 .^{4a} Both of these compounds give classical ^{31}P NMR spectra that are entirely analogous to those observed for $[\text{Pr}_2\text{NPCl}\{\text{C}(\text{PPh}_3)_2\}]^+\text{Cl}^-$. They show simple triplets for the $\lambda^3\sigma^3$ -phosphorus that indicate free rotation about the P–“carbone” carbon bond in room temperature solution.

$[\text{PCl}_2\{\text{C}(\text{PPh}_3)_2\}]^+\text{Cl}^-$ was characterised by an X ray diffraction study, as its tetrachloroaluminate salt, which shows a trigonal pyramidal geometry about P(1) (Figure 4.7).

Figure 4.7. Molecular structure of $[\text{PCl}_2\{\text{C}(\text{PPh}_3)_2\}][\text{AlCl}_4]$, $[2\text{g}^+][\text{AlCl}_4]$. Ellipsoids set at 50% probability. For clarity, the $[\text{AlCl}_4]^-$ counterion and the hydrogen atoms have been omitted for clarity.

	R= NⁱPr₂ 3a²⁺	R= Ph 3e²⁺	R= Cl 3g²⁺
Bond lengths (Å)			
R-P ₁	1.647	1.789	2.037
P ₁ -C ₁	1.745	1.722	1.706
C ₁ -P ₂	1.827	1.841	1.842
C ₁ -P ₃	1.810	1.826	1.847
Angles (°)			
RP ₁ C ₁	109.0	118.0	108.0
ΣC ₁	359.3	359.6	359.7
RP ₁ C ₁ P ₃	16.6	6.0	7.1
C _(cis) XP ₁ C ₁ (X=N or Ph)	7.6	18.0	-
Atom (group) NBO charge (-e)			
R	-0.78 (-0.14)	-0.46 (-0.11)	-0.17
P ₁	+1.18	+0.99	+0.98
C ₁	-1.42	-1.30	-1.28
P ₂ (PPh ₃)	+1.66 (+1.20)	+1.65 (+1.22)	+1.65 (+1.26)
P ₃ (PPh ₃)	+1.64 (+1.17)	+1.63 (+1.20)	+1.63 (+1.24)
π population (e)			
N (3a ²⁺) or Cl (3g ²⁺)	1.63	-	1.86
P ₁	0.70	0.68	0.75
C ₁	1.53	1.41	1.35
Σ	3.86	2.09	3.96

Table 4.1. Theoretical calculations at B3PW91/6-311+G(d,p)//B3PW91/6-31G(d) level comparing 3g²⁺ with 3a²⁺ and 3e²⁺ (presented in Table 2.4 above).

To estimate the effect of replacing the quite stabilizing NⁱPr₂ group at phosphorus by a simple phenyl or halide, a computational comparison between [PCl₂(CPhPh₃)₂]²⁺, 3g²⁺, with [iPr₂NP(CPhPh₃)₂]²⁺, 3a²⁺, and [PhP(CPhPh₃)₂]²⁺, 3e²⁺, was performed at B3PW91/6-311+G(d,p)//B3PW91/6-31G(d) level, with particular attention being paid to bond lengths, atomic charges and π- population. Some results of the theoretical calculations are tabulated in Table 4.1. The principal conclusions are:

- 1) the shortening of the C₁ to P₁ bond in both 3g²⁺ and 3e²⁺ relative to 3a²⁺ is consistent with a significantly increased π donation from the carbene carbon to the P₁

atom. To a degree, this offsets the stabilization of the π - system that is lost in the absence of the strongly π -donor N^iPr_2 group.

2) the C_1 atom π - population decreases along the series $\mathbf{3a}^{2+} > \mathbf{3e}^{2+} > \mathbf{3g}^{2+}$, which is reasonable in terms of the anticipated capacity for π - donation from the respective groups at bound to phosphorus, given that these groups compete with C_1 as a donor to P.

3) the negative hyperconjugation from the C_1 atom to the PPh_3 groups is smaller in $\mathbf{3g}^{2+}$ and $\mathbf{3e}^{2+}$ than in $\mathbf{3a}^{2+}$ (as is demonstrated by both the slightly increased $\text{C}_1\text{--PPh}_3$ bond lengths and slight increase in overall positive charges on the PPh_3 groups). This reflects the changing π -population at C_1 , as was discussed previously with respect to the data for $\mathbf{3a}^{2+}$ in Table 2.4.

Overall, a comparison of the degree of donation from the carbene to the phosphorus atom over the three compounds seems to be consistent with the proposal that the degree of electron deficiency within the π - system follows the order $\mathbf{3g}^{2+} < \mathbf{3e}^{2+} < \mathbf{3a}^{2+}$, as might be deduced intuitively from considering the nature of the R groups.

Section 4.3.1. Experimental Studies Pertaining to the Possible Existence of $[\text{PX}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ (X= Ph, Cl)

Our initial interest in this area was directed towards the possibility of isolating dicationic species analogous to $[\text{}^i\text{Pr}_2\text{NP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ in cases where the highly stabilizing $\text{}^i\text{Pr}_2\text{N-}$ group was replaced by either Ph- or Cl- substituents. There is precedence from Schmidpeter's work⁸⁰ which states that $[\text{PCl}_2\{\text{C}(\text{PPh}_3)_2\}]^+$ shows no significant spectroscopic change upon treatment with AlCl_3 in dichloromethane; consistently, in a number of our experiments conducted by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, neither the position of the resonance, nor the linewidth, changed to any significant degree upon addition of 2.5 equivalents of AlCl_3 to samples of $[\text{YPCl}\{\text{C}(\text{PPh}_3)_2\}]^+$ (Y= Ph, Cl) in dichloromethane. No spectroscopic evidence for the presence of $[\text{YP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ (Y=

Ph, Cl) dications could therefore be obtained. In an attempt to delineate some of the fundamental reactivity patterns of $[^i\text{Pr}_2\text{NP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ and related species, we therefore performed reactivity studies of $[^i\text{Pr}_2\text{NP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ and potential precursors for $[\text{YP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ (Y= Cl, Ph) towards three typical reagents from classes that are normally good substrates for phosphorus cations: alkynes, 1,3-dienes and activated aromatics.

A potential for low reactivity is a direct corollary of the straightforward synthesis and isolation of $[^i\text{Pr}_2\text{NP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$, and early experiments with $[^i\text{Pr}_2\text{NP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ showed that this dication is disappointingly unreactive. In dichloromethane solution at room temperature, no reaction was observed when pre-formed $[^i\text{Pr}_2\text{NP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ (as its $\text{BAR}^{\text{F}}_4^-$ or AlCl_4^- salts) was mixed with either diphenylacetylene or 2-butyne. The same lack of reactivity was also observed when the $[^i\text{Pr}_2\text{NP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ dication was generated *in situ* by Hogeveen's method¹²¹ from $[^i\text{Pr}_2\text{NPCl}\{\text{C}(\text{PPh}_3)_2\}]^+ \text{AlCl}_4^-$ and AlCl_3 , or when $[^i\text{Pr}_2\text{NPCl}\{\text{C}(\text{PPh}_3)_2\}]^+ \text{Cl}^-$ was treated *in situ* with 2.5 equivalents of AlCl_3 prior to reaction. Equally, though less remarkably, no reaction was found between the same alkynes and the monocationic P- chloro and P- phenyl substituted species $[\text{P}\{\text{C}(\text{PPh}_3)_2\}(\text{Y})\text{Cl}]^+ \text{AlCl}_4^-$ (Y= Ph, Cl).

This situation changes when the electrophile comprises 2.5 equivalents of AlCl_3 and 1 equivalent of $[\text{PhPCl}\{\text{C}(\text{PPh}_3)_2\}]^+ \text{Cl}^-$. In this case, the appearance of a highly characteristic low- frequency shifted phosphorus resonance showed the formation of a phosphirenium salt **7e**²⁺ ($\delta_{\text{P}(\text{central})} = -101.7\text{ppm}$ in dichloromethane with 2-butyne) (Scheme 4.3). This formulation was confirmed through spectroscopic analysis and an X-ray diffraction study of the 2-butyne derived product $[\text{PhP}(\text{CMe})_2\{\text{C}(\text{PPh}_3)_2\}][\text{AlCl}_4]_2$. (Figure 4.8) Analogously, reaction of 2.5 equivalents of AlCl_3 with 1 equivalent of $[\text{PCl}_2\{\text{C}(\text{PPh}_3)_2\}]^+ \text{Cl}^-$ followed by addition of alkyne gave **7g**²⁺, which showed the

slightly less upfield shifted resonance ($\delta_{\text{P(central)}} = -69.8 \text{ ppm}$ in dichloromethane for 2-butyne) (Scheme 4.3) that would be expected for the corresponding P-chlorophosphirenium analogues. These products were characterized spectroscopically and via electrospray HRMS.

Scheme 4.3. Synthesis of phosphirenium salts ($7e^{2+}$ and $7g^{2+}$) and phosphirene ($8g^+$). Key reagents/conditions: a) AlCl_3 (2.5 equiv) and 2-butyne (1.0 equiv), DCM; b) Magnesium (10 equiv), THF.

For comparison, a parallel [4+1] cycloaddition with 2,3-dimethyl-1,3-butadiene was also attempted. As noted above, this "McCormack cyclization" produces only products that are consistent with a genuine, concerted cheletropic addition.¹²⁸ Initial experiments clearly showed that the room temperature reaction of simple carbene supported chlorophosphines $[\text{YPCl}\{\text{C}(\text{PPh}_3)_2\}]^+$ (Y = Ph, Cl, N^iPr_2) with freshly dried, distilled, inhibitor-free 2,3-dimethyl-1,3-butadiene gave no product over 4 days. More surprisingly, neither the stabilized dication $[\text{N}^i\text{Pr}_2\text{NP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}[\text{BAr}^{\text{F}}_4]_2$, nor a mixture of $[\text{N}^i\text{Pr}_2\text{NPCl}\{\text{C}(\text{PPh}_3)_2\}]^+\text{Cl}^-$ and AlCl_3 showed any reactivity towards the same diene, although these failures may reflect operational (solubility) difficulties. However, good reactivity was observed in reactions with 2,3-dimethyl-1,3-butadiene when the mixtures of 2.5 equivalents of AlCl_3 with 1 equivalent of $[\text{XPCl}\{\text{C}(\text{PPh}_3)_2\}]^+\text{Cl}^-$ (X = Ph, Cl) of the

sort that were used in the phosphirenium ion case, were employed. These gave **9e**²⁺ (X= Ph) and **9g**²⁺ (X= Cl) (Scheme 4.4). Compound **9e**²⁺ showed $\delta_{\text{P(central)}} = 32.2\text{ppm}$ while **9g**²⁺ showed a more downfield shifted signal $\delta_{\text{P(central)}} = 88.9\text{ppm}$. Again, the phenyl-substituted carbene provided suitable crystals for an X ray diffraction analysis of the phospholenium salt, and this is shown in Figure 4.10.

In addition to the primary P(V) cycloaddition products, the corresponding P(III) compounds were also prepared; this was by reduction of **7g**²⁺ using PMe₃ or Mg in THF to give phosphirene **8g**⁺ (Scheme 4.4) and through a classical picoline- induced dehydrohalogenation¹²⁹ of **9g**²⁺ to give the phosphole **10g**⁺ (Scheme 4.4). **8g**⁺ showed $\delta_{\text{P(central)}} = -138.5$ while **10g**⁺ showed a more upfield shifted signal $\delta_{\text{P(central)}} = -13.5\text{ppm}$. Crystals were again grown for both products (**8g**⁺, Figure 4.9 and **10g**⁺, Figure 4.11), and these were also analyzed structurally.

Scheme 4.4. Synthesis of phospholenium salts (9e**²⁺ and **9g**²⁺) and phosphole (**10g**⁺).** Key reagents/conditions: a) AlCl₃ (2.5 equiv) and 2,3-dimethyl-1,3-butadiene (1.0 equiv), DCM; b) 2-picoline (2.0 equiv), DCM.

Section 4.3.2. Crystal structures

Figure 4.8. Molecular structure of $[\text{PhP}(\text{C}(\text{CH}_3)_2)_2\{\text{C}(\text{PPh}_3)_2\}][\text{AlCl}_4]_2$, $[\text{7e}^{2+}][\text{AlCl}_4]_2$. Ellipsoids set at 50% probability. For clarity, only one of the asymmetric units is shown and the $[\text{AlCl}_4]^-$ counterions together with hydrogen atoms have been omitted for clarity. A molecule of *n*-pentane was removed from the crystal structure of 7e^{2+} using "squeeze".

Figure 4.9. Molecular structure of $[\text{P}(\text{C}(\text{CH}_3)_2)_2\{\text{C}(\text{PPh}_3)_2\}][\text{AlCl}_4]$, $[\text{8g}^+][\text{AlCl}_4]$. Ellipsoids set at 50% probability. For clarity, the $[\text{AlCl}_4]^-$ counterion together with hydrogen atoms have been omitted for clarity.

Figure 4.10. Molecular structure of $[\text{PhP}(\text{CH}_2\text{C}(\text{CH}_3)_2)\text{C}(\text{PPh}_3)_2][\text{AlCl}_4]_2$, $[\text{9e}^{2+}][\text{AlCl}_4]_2$. Ellipsoids set at 50% probability. For clarity, the $[\text{AlCl}_4]^-$ counterions together with hydrogen atoms have been omitted for clarity.

Figure 4.11. Molecular structure of $[\text{P}(\text{ChC}(\text{CH}_3)_2)\text{C}(\text{PPh}_3)_2][\text{Cl}]$, $[\text{10g}^+][\text{AlCl}_4]$. Ellipsoids set at 50% probability. For clarity, the $[\text{AlCl}_4]^-$ counterion together with hydrogen atoms have been omitted for clarity.

Section 4.3.3. Structural Data Concerning the Three Membered Rings

The structures of these compounds can be interpreted against a background of thorough theoretical and computational investigations.^{124, 136} The geometries of free

phosphirenes are governed principally by the need to attenuate any antiaromatic 4π interactions between the lone pair with the C=C bond and, for this reason, the phosphorus bond to the exocyclic substituent in phosphirenes tends to be oriented almost perpendicular to the CPC plane. In this configuration, it attenuates any destabilising P: $\leftrightarrow$ C=C overlap by ensuring that the lone pair is in an orbital having extremely high s-character and therefore does not have the correct symmetry to interact with the π orbital of C=C bond.^{124, 137} It is noteworthy that a classical phosphirene inversion involving coplanarity of the PR substituent with the PCC plane, which would induce such $P\pi \leftrightarrow C=C$ antiaromaticity, is so heavily forbidden that the inversion of a 1-*H*-phosphirene has been computed to occur through a T-shaped intermediate instead.¹³⁸

On the contrary, a major driver of geometry in σ^4, λ^4 -phosphirenium salts is a non-classical σ^* - aromaticity that results from negative hyperconjugation between the exocyclic PR bonds and the ring C=C π electrons. This σ^* - aromaticity increases as the electron- withdrawing character of the R groups rises, because the increasing positive charge in the vicinity of the phosphorus atom that such electron withdrawal means that the two π -electrons that are normally associated with the phosphirene double bond can then be distributed more equally about the three centres of the PCC system. The geometries of phosphirenes and phosphirenium cations are therefore dependent upon rather different electronic criteria, so that drawing conclusions concerning the electronic configurations of the two structural types through comparing their geometries is extremely difficult.¹²⁴ However, comparisons within the individual phosphirene or phosphirenium salt classes can be made.

Phosphirenium salts

Crystallographically characterized phosphirenium salts are rare. Once Erker's small and rather unrepresentative class¹³⁹ that bear highly electron- withdrawing (perfluorophenyl)borane substituents at the ring carbons is excluded, only two simple phosphirenium salts are currently present on CCDC. The structures of these compounds are quite nonsymmetrical with respect to the phosphirene plane, with one P- substituent forming a much smaller Ct-P-substituent angle than the other; the more perpendicular substituent is a chlorostilbene in the rather poorly defined $C_{34}H_{34}ClNP^+$ (**GAHYET**),¹⁴⁰ and a phenyl in both $C_{11}H_{14}P^+$ (**NESMAZ**)¹⁴¹ and $7e^{2+}$, the case under study. These configurations appear to follow steric demand in placing the larger group closer to the phosphirenium plane, and it should be noted that the phosphirene ring is twisted relative to the potential π donor orbital on the carbene and Ph groups of $7e^{2+}$, presumably so as to diminish any antiaromatic repulsion. Nonetheless, the ring P-C bonds in $7e^{2+}$, which should be sensitive indicators of aromaticity, are much longer than in the "classical" species $C_{11}H_{14}P^+$ ¹⁴¹ (1.754 vs 1.728 Å). The bond lengthening in $7e^{2+}$ appears to be more pronounced than is the case with the NⁱPr₂- containing $C_{34}H_{34}ClNP^+$,¹⁴⁰ but it should be noted that the Estimated Standard Deviations (ESDs) in Cowley's case are very high. Unexpectedly, the C=C distances, which are admittedly a far less sensitive probe, are somewhat shorter in $C_{11}H_{14}P^+$ ¹⁴¹ than in $7e^{2+}$. The angle between the extracyclic substituents at the ring phosphorus, which is not thought to vary predictably as a function of substituent electronegativity, increases when π - donor substituents are present. This increases orthogonality between the substituents and the ring, but interpreting the significance of this parameter is complicated by the bulky nature of the substituents in $C_{34}H_{34}ClNP^+$ ¹⁴⁰ and $7e^{2+}$.

Figure 4.12. Structures of NESMAZ, GAHYET, 7e²⁺ (left to right).

	R1	R2	P-C	C=C	P-R1	P-R2	CtPR1	CtPR2	CPC(int)
NESMAZ ¹⁴¹	Ph	Me	1.727(5) 1.729(5)	1.305(7)	1.81(2)	1.76(2)	120.9	125.8	44.3(3)
GAHYET ¹⁴⁰	NiPr ₂	CPh=CPhCl	1.73(1) 1.73(1)	1.36(1)	1.643(9)	1.80(1)	128.0	119.7	46.2(5)
7e²⁺ (molecule 1)	Carbone	Ph	1.745(4) 1.756(4)	1.316	1.7502	1.7950	128.65	116.06	44.14
7e²⁺ (molecule 2)	Carbone	Ph	1.756(4) 1.760(4)	1.331	1.747	1.786	127.43	117.56	44.47
7e²⁺ (Average)	Carbone	Ph	1.754	1.3235	1.7486	1.7905	128.04	116.81	44.305

Ct refers to the mid- point of the C(1)C(2) ring bonds

Table 4.2. Comparisons among NESMAZ, GAHYET and 7e²⁺.

Phosphirenes

Good reference structures that are suitable for comparison with **8g⁺** are also rare in CCDC. Among these, the data for the P-chloro substituted compound C₁₂H₁₄ClP (**KISMEE**)¹⁴² are spectacularly different from those of both C₂₀H₁₅P (**CARWIB**)¹⁴³ and **8g⁺**, which have carbon-based substituents and more closely resemble each other. This divergence of structure presumably reflects the potential for polarizing the P–Cl bond in C₁₂H₁₄ClP,¹⁴² which accentuates a cationic (stabilizing) character in the phosphirene ring. Consistently, it should be noted that the P–Cl bond in C₁₂H₁₄ClP, at 2.166(2) Å, is very long. The carbone has an opposite effect to the halogen substituent: where the halogen shortens the P–C intracyclic bonds, lengthens the C=C, and induces a relatively acute Ct–P–Cl angle, the carbone- derived fragment does the opposite in every case, as might be expected for an electron donor.

Figure 4.13. Structures of NOCZIO, CARWIB, KISMEE and 8g⁺ (left to right).

	P: R	C: R1 R2	P–CR1	P–CR2	P–R	C=C	CtPR	CPC(int)
NOCZIO ¹⁴⁴	$\eta(P=C)Co$	2xtBu	1.836(4)	1.848(4)	2.237(1)	1.282(5)	100.61	40.74(2)
CARWIB ¹⁴³	Ph	2xPh	1.819(3)	1.802(2)	1.841(6)	1.297(9)	106.2	41.79(
KISMEE ¹⁴²	Cl	PhtBu	1.783(2)	1.781(4)	2.166(2)	1.303(5)	105.04	42.9(2)
8g⁺	Carb/ph	2xMe	1.821(4)	1.820(4)	1.876(3)	1.295(5)	110.15	41.7(2)

Ct refers to the mid- point of the C(1)C(2) ring bonds

Table 4.3. Comparisons among NOCZIO, CARWIB, KISMEE and 8g⁺.

Section 4.3.3.1. Comparison between Phosphirene- and Phosphole- Based Ring Systems

A comparison of the two neutral phosphole (**10g⁺**) and phosphirene (**8g⁺**) rings shows that the extracyclic P–carbone bond length is much greater in the phosphirene 1.876(3) Å than the phosphole 1.809(2) Å. The angles made by the P–carbone bond with its trace on the planes made by PC1C2 for the phosphirene (110.2 °) and PC2C5 for the phosphole (126.1 °) are also very different. To a degree, these differences might be expected, given that the hybridization of the phosphorus atom is likely to change significantly upon passing from phosphirene to phosphole in order to accommodate the CPC intracyclic angle required for ring closure (this is likely to have quite large effects, given the strain in the phosphirene. However, it is significant that the difference between the data for **10g⁺** and **8g⁺** is much greater than is found, for instance, when comparing the classical P- phenylated phosphirene C₂₀H₁₅P¹⁴³ (1.841(6) Å and 106.2°) with the P- phenylated phosphole C₁₂H₁₃P (**LEHPAQ**)¹⁴⁵ (1.843(2) Å and 110.75°), respectively.

Section 4.3.4. Structural Data Concerning the Five Membered Rings

Figure 4.14. Structures of VUMZEJ, EDIJOQ, LEHPAQ, EDUWEF, EDIJUW, 10g⁺.

Phospholes with 2,5-diH-3,4-diMe functionality

	R	PC1	PC2	C=C1	C=C2	C-C	Planes C ₄ /C ₂ P	CtPExt	PExt	CPC	Σ P
VUMZEJ 146	NPN	1.78 8(2)	1.78 3(2)	1.360(2)	1.366(2)	1.451(2)	2.74	87.75	2.356(1)	89.19	267.8
EDIJOQ 147	CN	1.79 4	1.79 4	1.348(3)	1.348(3)	1.484(2)	10.14	105.02	1.802	90.90	291.84
LEHPAQ 145	Ph	1.79 4(3)	1.79 3(3)	1.344(4)	1.355(4)	1.480(3)	8.84	110.75	1.843(2)	90.01	299.1
EDUWEF 122a	N ⁱ Pr ₂	1.79 2(2)	1.79 6(2)	1.344(3)	1.339(3)	1.473(3)	11.20	116.19	1.669(2)	89.59	306.2
EDIJUW 147	O	1.80 1(2)	1.79 8(3)	1.349(2)	1.343(2)	1.474(2)	14.90	119.49	1.624(2)	89.92	310.9(1)
10g⁺	carb	1.77 8(3)	1.77 9(3)	1.351(4)	1.358(4)	1.466(4)	14.05	126.07	1.809(2)	91.3(1))	319.90

Note: Ct-P-Ext in phospholes listed in Table 4.4 refers to Ct(C2C5)-P-Ext.

Pyramidity (°): as estimated through the measurement of Ct-P-Ext or (in parentheses) Ct(PC₄)-P-Ext where Ext is the exocyclic atom bound to the ring phosphorus: **VUMZEJ**: 87.75 (88.66); **EDIJOQ**: 105.02 (108.35); **LEHPAQ**: 110.75 (113.65); **EDUWEF**: 116.19 (119.84); **EDIJUW**: 119.49 (124.60); **10g⁺**: 126.07 (130.74), where Ct(C2C5) refers to the mid- point of the C(2)C(5) vector, Ct(PC₄) is the centroid made by all of the phosphole atoms, planes C₄/C₂P refer to the interplane made between the plane of the four carbon atoms of the phosphole and the plane defined by the phosphole P and the two C_α atoms.

Table 4.4. Comparisons among VUMZEJ, EDIJOQ, LEHPAQ, EDUWEF, EDIJUW, 10g⁺.

Figure 4.15. Structures of NIFZUX, JEJFIO and REGWUV.

Phospholes with 2,4,5-triH-3-Me functionality

	R	PC1 (Me)	PC2	C=C1 (Me)	C=C2	C-C	Planes C ₄ /C ₂ P	CtP Ext	PExt	CP C	ΣP
NIFZUX ¹⁴⁸	<i>i</i> Pr ₃	1.783(4)	1.778(5)	1.339(6)	1.366(5)	1.436(5)	12.75	121.85	1.836(4)	91.1	314.6
JEJFIO ¹⁴⁹	Ar	1.768(4)	1.762(4)	1.343(5)	1.332(5)	1.427(5)	13.26	123.92	1.839(3)	91.0	317.0
REGWUV ¹⁵⁰	<i>t</i> Bu ₃	1.746(9)	1.741(9)	1.347(12)	1.352(12)	1.402(12)	12.86	135.76	1.813(7)	91.7	331.6

Note: Ct-P-Ext in phospholes listed in Table 4.5 refers to Ct(C₂C₅)-P-Ext.

Ar= 2,4-*t*Bu-6-MeC₆H₂. Pyramidity: (in degrees) as estimated through the measurement of Ct-P-Ext or (in parentheses) Ct(PC₄)-P-Ext: **NIFZUX**: 121.85 (126.04); **JEJFIO**: 123.92 (128.29); **REGWUV**: 135.76 (140.09).

Table 4.5. Comparisons among NIFZUX, JEJFIO and REGWUV.

Unlike the relatively rare phosphirenes, phospholes comprise one of the most thoroughly studied series of all phosphorus heterocycles and a huge number of crystallographic determinations of phospholes have been made. For this reason, **10g⁺** can be compared with very similar structures that contain either an identically C- substituted phosphole ring (Table 4.4) or a very closely related series having only one β - methyl group (Table 4.5).

It is evident from a comparison with other phospholes having a 3,4-dimethyl substitution pattern makes that the carbene substituent is unusual; the P–C bonds in **10g⁺** are the shortest among the structures available, whilst the ring C=C bonds are longer and the C–C bond shorter than in any other 3,4-dimethyl- substituted phosphole except Gudat's C₂₆H₃₂N₂P₂ (**VUMZEJ**).¹⁴⁶ C₂₆H₃₂N₂P₂ can be considered to be an entirely unrepresentative compound in that it contains a highly stable and delocalised 1,3,2-

diazaphosphenium fragment that is 'bound' to the phosphole moiety by an extraordinarily long P-P bond (2.356(1) Å). The compound is therefore probably significantly ionised and its geometry can be safely be assumed to result from a degree of classical aromaticity of the sort that is found in dissociated alkali metal phospholide anions (note the classical planarity in the PC₄ ring). It therefore contains what can effectively be viewed as a planar, formally negatively charged, two- coordinate phosphorus atom in something close to a phospholide anion. This explanation is clearly not transferable to **10g**⁺, which has a strongly bound carbene substituent and shows a significant deviation from planarity about the PC₄ system. Instead, the structural effects in **10g**⁺ seem to have their roots in the bulk of the carbene, in that they are comparable with a range of very bulky phospholes prepared and studied by Quin and Keglevich, wherein the hindrance of the phosphole P- substituent directly affects the nature of the phosphole ring through the steric effects that it imposes.¹⁵⁰

Section 4.4. Computation

Because of the complexity of the effects that bear upon the structures of phospholes and phosphirenes, a complementary computational study was undertaken. To a degree, this provided compensation for the relative lack of crystallographic data relating to phosphirenes, and it also provided the means to look into the ring structures in more depth. Its main objective was to compare the carbene-substituted rings that have been prepared here with analogues containing the very bulky mes* (2,4,6-*t*Bu₃C₆H₂) substituent. To provide insight into simpler non- hindered aryl substituents whose electronics are not influenced by the sterical effects imposed by the *t*Bu groups, phospholes and phosphirenes having simple P- phenyl substituents were also calculated.

So as to avoid confusion with experimental structures, the computed structures are denoted by letters in place of numbers.

The six structures **A** to **F** shown in Figure 4.16 were computed at B3PW91/6-311+G(d,p)//B3PW91/6-31G(d) level and their structures (Figure 4.17) are in good agreement with those relevant crystal data that are available. To provide an insight into the potential for π bonding between the substituent and the ring in the computed structures, planes that are formed by atoms taking part in extended π - delocalization are also shown in Figure 4.18.

Figure 4.16. Phospholes and phosphirenes investigated by computation.

Phospholes

A comparison of the computed ring metrics for the carbene substituted phosphole with those of the mes^{*} and phenyl substituted analogues are given in Table 4.6, where R= Ph, mes^{*} and C(PPh₃)₂⁺. In the bottom line, values pertaining to the carbene- derived phosphole are expressed as a percentage of the linear degree of travel (DOT) along the vector of bond distances that links the values for the phospholes substituted by Ph and

mes* groups. The bond lengths within the carbene- substituted phosphole ring lie between those of the phenyl phosphole and its mes* analogue in all cases. For the phosphole having the carbene- derived substituent, the ring C=C and C-C bond lengths that are normally used as the simple gauge of "Bird" aromaticity^{136a} travel only about 30% of the distance along the bond length vector linking the Ph to the mes* substituted phosphole. The parameter that changes the most is the distance from the phosphorus to the exocyclic substituent, which is very significantly shorter for the carbene than for the aryl groups.

R	PC1	PC2	C=C	C=C	C-C	Planes C4/C2P	CtPExt	PExt	CPC	ΣP
Mes* (A)	1.7753	1.7728	1.3721	1.3696	1.4567	13.89	140.63	1.8548	92.26	329.83
Carb (B⁺)	1.7893	1.7893	1.3631	1.3620	1.4698	14.52	134.44	1.8166	91.42	321.35
Ph (C)	1.8034	1.8034	1.3575	1.3575	1.4750	10.18	117.65	1.8450	90.02	301.58
% DOT of B⁺ on Ph to mes* vector	+50.1	+46.1	+38.4	+37.2	+28.4	+117.0	+73.1	-289.8	+62.5	+67.8

Table 4.6. Computed bond lengths and angles pertaining to the heterocycle components in the mes* (A), carbene (B⁺), and phenyl (C),- substituted phospholes under study.

Figure 4.17. Computed structures for the carbene (upper) Mes* (middle) and phenyl (lower) derived phosphirenes (left) and phospholes (right) drawn so as to give an indication of the nature of the rings. The planes shown are : a) perpendicular to the ring (phosphole, phosphirene) best plane and including the substituent atom bound to P (blue), and b) defined either by the six carbon atoms of the aryl groups, or the PCP atoms of the triphenylphosphonium groups and the sp^2 carbon of the bis(phosphoranyl)carbon substituent (red). Interplane angles ($^\circ$): **E⁺**: top left: 68.74; **B⁺**: top right: 3.29; **D**: mid left: 79.31; **A**: mid right: 27.11; **F**, **C**: bottom: 0.00 in both cases. Note the deviation of the 'Bu groups from the arene plane in the case of the Mes* derivatives **D** and **A**.

Figure 4.18. Computed structures for the carbene (upper) meso* (middle) and phenyl- (lower) derived phosphirenes (left) and phospholes (right). The planes highlighted are those containing the atoms giving rise to those delocalized π systems that, in principle, should be most favourable for π interactions: a) those of the phosphorus containing rings (phosphole- as defined by the ring carbons-, and phosphirene as the PC_2 unit) in blue, and b) those defined either by the five (ipso excluded) carbon atoms of the

aryl groups, or the PCP atoms of the triphenylphosphonium groups and the sp^2 carbon of the bis(phosphoranyl)carbon substituent, in red. Interplane angles ($^\circ$): **B**⁺: top left: 62.27; **E**⁺: top right: 86.95; **D**: mid left: 81.22; **A**: mid right: 88.77; **F**, **C**: bottom: 90.00 in both cases. Note the rather poor potential for π interactions, and the bending of the arene about the C2C6 vector in the mes* derivatives **A** and **D** that leads to the displacement of the phosphorus atom from the arene plane.

Substituent	PC1	PC2	C=C	CtPExt	PExt	C1PC2	ΣP
mes*(D)	1.8422	1.8455	1.3070	105.32	1.8974	41.53	250.16
Carb (E ⁺)	1.8354	1.8382	1.3085	110.31	1.9034	41.73	259.58
Ph (F)	1.8395	1.8395	1.3071	105.54	1.8619	41.62	250.64
% DOT of E ⁺ along Ph to mes* vector	-151.9	-28.3	-1600	-2169	+116.9	-122.2	-1862

Table 4.7. Computed bond lengths and angles within the heterocycle components in the mes* (D**), carbene (**E**⁺), and phenyl (**F**),- substituted phosphirenes under study.**

For the phosphirenes, the results are quite different (Table 4.7). Whilst it should be emphasized that all effects for the phosphirenes are very small relative to the phosphole case, the data generated by the carbene-derived ring lie far *outside* the locus of the two sets of quite similar values generated by the aryl groups. Again, the most striking data concern the extracyclic PC bond.

Two clear conclusions appear when comparing the data sets:

1) from the pyramidity ΣP (and CtPExt) data, the carbene can be seen to behave as a "bulky" group with respect to both the phosphole and the phosphirene, in as much as it causes significant angular deformations at the ring phosphorus in both cases. On the contrary, the mes* group is massively hindering in the case of the phosphole but shows little difference in ΣP with respect to phenyl in the case of the phosphirene;

2) Replacing the phenyl substituent by the carbene causes an increase in Bird aromaticity in both the phosphole (shortened C–C bond, lengthened C=C bonds) and the phosphirene (shortened P–C bonds, lengthened C=C bond) cases.

The reasons for these differences are quite complex. It has been well established by Quin, Keglevic and their coworkers¹⁵⁰ that sterical hindrance in phospholes that is generated by bulky P- substituents can be released by increasing planarity at the phosphorus atom (*ie* by moving the P- substituent towards to the phosphole plane). It has also been established by the same authors that ring aromaticity in the phosphole increases as this process occurs, so that the increase in phosphole ring strain that accompanies planarisation is offset by increased aromaticity.¹⁵⁰ This phenomenon has not previously been treated computationally. The calculations here show that, relative to the simple P- phenyl substituted phosphole, *i*) a significant opening of the CtParyl angle (to 140.6°) occurs in the presence of the mes* group and *ii*) the phosphole ring C=C and C-C bond lengths equalise, so that aromaticity rises. This is in agreement with earlier experimental data.¹⁵⁰ The calculations also show that a large part of steric strain within the molecule is accommodated by deforming the mes* group (the angle between the planes made by the ipso carbon and its two ortho carbons with the five non-ipso carbon rings reaches 9.3° in **A**, as can be seen in Figure 4.18); this is an important datum that was not visible from the earlier experimental data.¹⁵⁰ The clear implication from both our experimental and computational data is that the carbene does not induce such high steric crowding upon a phosphole. Thus, the aromaticity of the carbene- substituted phosphole remains moderate, as is indicated by the modest equalisation of the ring C=C and C-C separations in **B**⁺ (Table 4.6). To explore this hypothesis further, supplementary computational analyses were performed, which aimed to establish the degree of steric stress that the phosphole group induces within its P- substituent. Firstly, the distorted conformation of the tri(*tert*-

butyl)phenyl group that was found in the phosphole was fixed and the phosphole group was then replaced by a hydrogen, to give a twisted form of tri(*tert*-butyl)benzene. Comparison with the relaxed computed tri(*tert*-butyl)benzene structure showed that deforming the tri(*tert*-butyl)phenyl group to give the configuration found in the phosphole resulted in an energy increase of 44.3 kJ mol⁻¹. When the same approach was applied to the carbene- derived fragment in **B**⁺, the increase in energy upon moving from the relaxed protonated carbene to the stressed form showing the geometry found in the phosphole derivative was much lower, at 14.9 kJ mol⁻¹. For comparison, the strain energy in the phenyl ring of 1-phenyl-3,4-dimethylphosphole was calculated by the same method as being only 0.3 kJ mol⁻¹.

For phosphirenes, any analogous deviation of the CtPC(mes*) angle from 90° is likely to be a high energy process. Unlike the phosphole, where planarisation is accompanied by increasing aromaticity, the planarisation process for phosphirenes is doubly disfavoured: any planarisation of the phosphorus atom will increase ring strain within the three membered ring *and* also increase antiaromaticity.¹³⁸ For this reason, the phosphirene fragment can be regarded as a very “rigid” structural component. This analysis is borne out in the changes when moving from the unhindered phenyl substituted phosphirene **F** to the mes* derivative **D**: the ring bond lengths and angles vary little, and the phosphirene simply rotates around the P-Cipso vector into an out- of- plane position that minimises hindrance with the ^tBu groups. It is important to note that the CtPExt angle remains almost perfectly invariant during this process (Table 4.7). However, a very large increase of tension in the aryl group of **D** is observed (with the angle between the planes made by the *ipso* carbon and its two ortho carbons with the five non-*ipso* carbon rings becoming 15.7°; this is again very visible in Figure 4.18), and it is therefore clear that the geometrical changes resulting from the steric strain within the molecule are largely

confined to the tri(*tert*-butyl)phenyl substituent. This is not the case for the carbene. With the carbene, the phosphirene is again found in a relatively hindrance-free pocket (see **E**⁺ Figure 4.17), but nonbonding interactions between the phosphirene and the carbene also appear to be lowered by an opening of the CtPExt angle, a process which seems to be forbidden for the aryl groups (Table 4.7). This difference in behaviour is attributed to tolerance of changes in the nature of the carbene-C₁P₁ bond. When this bond lengthens and polarises in its natural $\delta\text{-C-P}^{\delta+}$ sense, phosphirene aromaticity rises and bending becomes facilitated; simultaneously, the increased electron density that accrues at the carbene carbon generates an enhanced negative hyperconjugation towards the triphenylphosphonium centres, which translates into the observed shortening of the C-PPh₃ bonds (Table 4.8). When the same computational analysis that was used to estimate the ring strain in the phosphole is applied to the phosphirene, the strain energy associated with the mes* fragment is greater than in the phosphole at *ca* 49.5 kJ mol⁻¹, whilst the strain taken up by the carbene fragment is also increased by a similar increment, to 18.7 kJ/mol⁻¹.

	P1C1	P3C1	P2 C1	P2 C1P3	P1C1P2	P1C1P3	Σ at C1
B⁺ phosphole	1.8166	1.7610	1.7550	124.77	123.35	111.80	359.92
E⁺ phosphirene	1.9034	1.7423	1.7413	124.24	119.98	115.01	359.23

Table 4.8. Computed bond lengths about the central carbon atom of the carbene-derived fragment in carbene-derived phosphole and phosphirene. P1 denotes the phosphorus of the attached ring; P2 and P3 are the phosphorus atoms of the triphenylphosphonium groups, C1 the central carbon derived from the carbene.

Section 4.5. Conclusion

In conclusion, the data drawn from this Chapter show that carbene fragments can provide useful supports for trivalent phosphorus centres undergoing classical cycloaddition reactions, and that the first-formed P(V) products can be transformed into

classical phosphorus heterocycles of types that are known to generate further chemistry. This means that carbene supported phospholes and phosphirenes are now quite easily accessible.

When using carbene- derived species such as $[^i\text{Pr}_2\text{NP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ for synthetic purposes, an important question that arises concerns the correct choice of valence tautomer when programming a synthetic scheme. In this context, it is interesting to consider the nature of the relationship between $[^i\text{Pr}_2\text{NP}\{\text{C}(\text{PPh}_3)_2\}]^{2+}$ and Wittig reagents substituted by phosphonium cations, a class that has been synthesized and studied extensively by Schmidpeter, Gruetzmacher and their coworkers (Figure 4.19). Formally, the carbene- derived species is obtained from the corresponding Wittig reagent by simple substitution of a hydride by a triphenylphosphine group, and it might naively be anticipated that the two series of compounds could show comparable reactivity. In practice, a strong divergence in reactivity appears; classical phosphonium cations are normally expected to undergo [4+1] cycloadditions to give phospholenes with dimethylbutadiene, but Gruetzmacher has convincingly demonstrated that dimethylbutadiene gives [4+2] cycloaddition reactivity with the Wittig- derived phosphonium ion, thus demonstrating a “phosphaalkene- type” behaviour (Scheme 4.5). The data that we obtain here confirm that it is more valid in synthetic terms to view the carbene- derived reagents through their phosphonium ion resonance hybrid than the alternative bis(phosphoranyl)phosphaalkene formulation (Figure 4.19). However, it also seems likely that the distinction between the two may not be entirely clear- cut, and might be shifted easily through relatively modest changes in electronics.

Scheme 4.5. [4+2] cycloaddition reaction.

Figure 4.19. Carbene support vs ylide (top); phosphonium ion resonance hybrid vs bis(phosphoranyl)phosphaalkene (bottom).

The influence of the carbene once it is incorporated into the phosphirene and phosphole structures is subtle and quite difficult to describe in simple terms. A major problem associated with defining the "bulk" of the carbene-derived fragment with respect to hindered aromatics (for example, the tri(*tert*-butyl)phenyl ring treated above) is that whilst the "pure" spatial bulk of the ligand can be computed geometrically, the "effective" bulk of the carbene fragment is liable to reflect a contribution that arises from the significant electronic differences existing between the aromatic and carbene-based systems. Even the simplest valence bond formulation would suggest that the carbene-derived functionality should be significantly different in electronic terms from the aromatic ring. In this light, it is relatively easy to make an argument that whilst "pure" steric bulk should be essentially invariant, the "effective bulk" in terms of geometrical parameters- once electronics are factored in- is likely to vary significantly upon passing

from phosphirenes to phospholes. Given that the aromaticity within a phosphirene ring (which has two carbon- based π electrons) should increase when electron- withdrawing groups are present at phosphorus whilst, in the carbon- based 4 π - electron phosphole system, the reverse effect is to be expected, it follows that any given carbene might effectively appear to be more "bulky" when attached to a phosphole than to a phosphirene.

This effect is almost certainly the cause of the difference in the geometries of the phosphole and phosphirene substituted carbenes that was highlighted in Tables 4.3 - 4.5. In practice, it is difficult to fully quantify this argument from the data that we have; the phosphirene- ring based systems are currently difficult to evaluate from purely structural effects because there is very little related data in the literature. In both the phosphirene and phosphirenium ion cases, the analysis suggests that it is perfectly reasonable to consider the carbene to be "bulky" enough to cause significant structural effects. However, the lack of useful reference structures means that there may be a significant chance of overinterpreting the data with respect to phosphirenes.

On the other hand, the case for phospholes is better understood and the available literature is more complete. The classical analysis of phosphole geometry is that introducing steric hindrance at the phosphorus substituent causes planarization, so as to eliminate unfavourable interactions with the phosphole α - and β - carbon atoms (and their substituents). In general terms, when planarization occurs, the ring strain increases rapidly because the rehybridisation of the P(s) with a P(p) orbital that is required to move towards the flattened sp^2 configuration at phosphorus is a high energy process, and so the overall energy of the phosphole rises. Nonetheless, this phosphorus rehybridization improves hyperconjugation of the extracyclic PC bond with the butadiene π system, thus increasing aromaticity.¹⁵¹ Within this framework, it has been calculated that a normally

pyramidalised- unhindered- phosphole has 42% of the aromaticity of pyrrole, whilst the corresponding fully planarised phosphole has 108%.¹⁵²

This ability to control the degree of phosphole aromaticity through variation of hindrance is potentially a useful phenomenon, and the first serious attempts to employ hindrance to increase the aromaticity of phospholes for reactivity purposes were initiated by Quin.¹⁵⁰ Shortly after, Mathey took the complementary approach of inducing antiaromaticity into phospholes, so as to increase their reactivity in cycloaddition reactions.^{136a} In his initial paper, Quin sets out a number of characteristics which could be considered typical of “aromatized” bulky phospholes. These include quite a large coupling to the C β with methyl group attached (d, $^2J_{CP}$ = 23.4 Hz, for C₂₃H₃₅P, **REGWUV**),¹⁵⁰ a large coupling to exocyclic methyl protons (d, $^4J_{HP}$ = 7.3 Hz) and β carbons that are upfield shifted by 9 ppm relative to unhindered phospholes. To a degree, these are met by **10g**⁺ (d, $^4J_{HP}$ = 5.4 Hz), although the size of the effects is smaller in the carbene- supported case and close to C₂₀H₂₉P, **NIFZUX**.¹⁵³ He also analyses the Bird Index criteria.^{136a} These imply that C₂₃H₃₅P,¹⁵⁰ being calculated to have 57% of the aromaticity of benzene, is more aromatic than furan (43%) and close to pyrrole (56%), as has been projected by Elguero above.^{152a} On the Bird index scale, C₂₀H₂₉P¹⁴⁸ shows 40.4% of the aromaticity of benzene, whilst the non- hindered unsubstituted 1-benzylphosphole is estimated at 36%. The data that we obtain for **10g**⁺ gives approximately 39%. Given that the aromatised rings prepared by Quin and Keglevich give non-typical chemical behaviour (aromatic substitution reactions at the phosphole ring, and also atypical coordination chemistry), they have a particular value. The data available at present suggest that the carbene used here, when associated with a phosphole, has an effective bulk which is significant and close to that of the 2,4,6- tri *iso*-propyl substituted phenyl group.

A further interesting question concerns the nature- and potential existence- of the poorly stabilized dications $[XP\{C(PPh_3)_2\}]^{2+}$ (X= Ph, Cl). No fully convincing proof has been obtained for their existence during these studies. Nonetheless, control experiments to probe the formation of phosphirenium and phospholenium ions through interaction of $[PX\{C(PPh_3)_2\}P]^{2+}$ with alkynes or dienes failed under conditions where a combination of $[XPCl\{C(PPh_3)_2\}]^+Cl^-$ and $AlCl_3$ successfully gave the desired cycloaddition products (X= Ph, Cl). Whilst this also does not constitute a proof of existence (in as much as we have no way of disproving a left-sided equilibrium which is drawn to completion after formation of a P(V) intermediate through a highly favoured formation of a tetrachloroaluminate salt, for example), it nonetheless seems reasonable to expect that such dications can exist in solutions of $[^iPr_2NPCl\{C(PPh_3)_2\}]^+Cl^-$ and $AlCl_3$, and that their existence should allow a wide range of chemistry to be achieved in predictable fashion. This presages some useful applications: whilst, at the present time, it can be assumed that the carbene- derived fragments used here are slightly less hindering than the archetypal $C_6H_2'Bu_3$ group, these and related species may be of considerable use in cases where the $C_6H_2'Bu_3$ group is too reactive to provide adequate stability, such as when phosphonium intermediates are involved. In this regard, the synthesis of other bulkier carbenes seems also to be a promising and vast new area for study.

Section 4.6. Addendum: Generation of a Stable Phosphirene Oxide?

In 1972, Stille reported what was claimed to be the first synthesis of a stable phosphirene oxide.¹⁵⁴ It was postulated that the cyclization of a phosphine oxide bearing two (α -bromobenzyl) groups occurred according to the uppermost equation in Scheme 4.7. Based on a mass spectrum, and- particularly- the conversion into diphenylacetylene

upon pyrolysis at 120°C, the product was assigned as having a cyclic structure. It could not be obtained in the pure state.

Later, Quast demonstrated that the compound observed by Stille was the DBN adduct of an open-chain derivative (DBN= 1,5-diazabicyclo[4.3.0]non-5-ene) that is shown in the lower half of Scheme 4.6.¹⁵⁵ The potential intermediacy of the genuine phosphirene oxide in this reaction, which is implied by the presence of a stilbene- based sidechain in the product, shows that the cyclization of C–P–C units may have potential for the synthesis of phosphirene derivatives. Further, it points to the possibility of preparing a phosphirene oxide under appropriate conditions.

Scheme 4.6. Postulated synthesis of a phosphirene oxide, as reported by Stille, (top) and the reaction outcome proposed after reinvestigation by Quast (bottom).

Breslow has described a similar ring opening in the case of phosphirenium salts, which was instantaneous at room temperature.¹²³

Scheme 4.7. Breslow's observation of a phosphirenium salt ring opening reaction.

Stable tricoordinate 1-*H*-phosphirenes are known and can be isolated. However, ring opening reactions occur when triphenylphosphirene is oxidised by aqueous hydrogen peroxide, and no stable phosphirene oxide is known to date.¹⁵⁶ On the other hand, the reaction with sulphur in the presence of N-methylimidazole as a catalyst results in a stable P-sulfide.¹⁵⁶

Scheme 4.8. Synthesis of stable phosphirene P-sulfide.

This chemistry led us to briefly look into the possibility of synthesizing a phosphirene oxide supported by a carbene- derived group.

Scheme 4.9. Postulated synthesis of phosphirene oxide, $11g^+$.

When $7g^{2+}$ was stirred in damp acetonitrile, a phosphirene oxide $11g^+$ is proposed to be formed as shown in Scheme 4.8 above. The ES-MS experiment gave a peak at 637.1962 (calculated for $11g^+ = 637.1974$) which showed the correct isotopic pattern. The room temperature $^{31}P\{^1H\}$ NMR spectrum gave signals at -61.8 ppm (t) and $\delta_P = 23.4$ (d). Given the well known high- field shifts for tricoordinate phosphirenes¹⁴³ ($\delta^{31}P$ -190.3 ppm in C_6D_6 for triphenylphosphirene), and the pentacoordinate phosphirene sulfide¹⁵⁶ ($\delta^{31}P$ -79.0 ppm in C_6D_6), the values obtained here are quite strongly supportive of a

phosphirene oxide structure. However, multiple attempts at crystallisation have not produced monocrystals suitable for an X-ray diffraction study, so no crystal structure has yet been obtained to verify the structure of the final product, **11g**⁺.

Section 4.7. Attempts to use Carbene- Supported Phosphenium Ions in a “Friedel-Crafts” Reaction

Scheme 4.10. Possible synthesis of a coordinatively saturated phosphorus cation. Key reagents/conditions: a) AlCl₃ (2.0 equiv) and anisole (1.2 equiv)

One of the most characteristic of all reactions involving carbocations is the Friedel Crafts acylation of aromatics.¹⁵⁷ Recognising that the intermediate phosphorus dication (**3e**²⁺ or **3g**²⁺) is a potential analogue of a carbocation, an electrophilic aromatic phosphination was attempted. Such reactions have recedent in, for example, the synthesis of chlorodiphenylphosphine from benzene and dichlorophenylphosphine in a thermal reaction in the presence of AlCl₃.¹⁵⁸ In the experiments undertaken here, , 2.0 equiv of AlCl₃ and 1.2 equiv of anisole were added to **2e**⁺ and **2g**⁺, respectively in dichloromethane according to Scheme 4.9. No NMR data consistent with either **13e**⁺ or **13g**⁺ were obtained. In the case of the Cl analogue (**2g**⁺), only the starting materials were

observed by ^{31}P NMR spectroscopy. More interesting results were obtained with the phenyl substituted homologue $\mathbf{2e}^+$, where reaction took place. The ES-MS experiment gave a peak for the molecular ion of the product at 347.0865 (calculated for $\mathbf{12e}^+ = 347.0932$) which showed the correct mass and isotope pattern for a simple product of quaternisation at phosphorus. The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum gave signals at $\delta_{\text{P}} = 70.3$ ppm (t) and 24.1 (d). However, despite multiple attempts, no crystal structure has been obtained of the final product, $\mathbf{12e}^+$, whose connectivity awaits final proof. It is well precedented that phosphide anions very cleanly and efficiently demethylate anisole methyl groups,¹⁵⁹ and one potential mechanism here involves the coordination of AlCl_3 to the anisole, so as to generate an abnormally electrophilic methyl group which is then attacked by the phosphorus lone pair (Scheme 4.11). Within such a mechanistic framework, the reaction can be viewed as a variation upon the well- established Kinnear-Perren synthesis¹⁶⁰ of alkylphosphonic acids through the hydrolysis of mixtures containing ethers, phosphorus halides and aluminium chloride.^{160a}

Scheme 4.11 A potential mechanism for the formation of P- methylated products under "Friedel Crafts conditions".

A second, though probably less likely, mechanism for the formation of $\mathbf{12e}^+$ is proposed in Scheme 4.12, with the reaction going through a kinetically favoured coordination of the anisole oxygen atom to the phosphonium centre followed by evolution. In neither case is the expected Wheland intermediate intervening and, overall, it seems clear that the phosphorus atom acts essentially as a nucleophile, rather than

showing the electrophilic behaviour that was expected within the "Friedel Crafts" conceptual framework.

Scheme 4.12. Proposed mechanism for the synthesis of $12e^+$.

CHAPTER 5

EXPERIMENTAL

Section 5.1. General Procedures

All solvents were distilled over sodium benzophenone ketyl, except for dichloromethane, which was distilled over CaH_2 , and degassed prior to use. An M-Braun or VAC Vacuum Atmosphere argon-filled drybox was used for the manipulation of all solid reagents. All reactions were performed under conditions free from both moisture and oxygen using standard Schlenk or drybox techniques. To ensure the absence of water, all glassware was dried overnight in a 120°C oven, flame-dried and cooled under vacuum before use.

Water and water- d_2 were only degassed prior to use. Methanol (anhydrous) and methanol- d_4 were purchased from a commercial source, stored over sieves and degassed prior to use. Other commercial products (triphenylphosphine, trimethylphosphine, aluminium trichloride, P,P-dichlorophenylphosphine, 4-dimethylaminopyridine, cobaltocene and 2-butyne) were used without further purification. 2,3-dimethyl-1,3-butadiene was distilled over sodium borohydride, anisole was distilled over sodium benzophenone ketyl and 2-methylpyridine was distilled over CaH_2 before use. The carbodiphosphorane ligands^{66a, 74} and $\text{NaBAr}^{\text{F}}_4$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$)¹⁶¹ were prepared according to the literature procedures.

Section 5.2. Physical Measurements

High resolution mass spectra were measured on a Waters Q-TOF Premier Micromass Spectrometer, using the electrospray ionization (ESI) mode. The FTIR spectra were measured on a Shimadzu *IR* Prestige-21 spectrometer. ^1H , ^{11}B , ^{13}C , ^{19}F , ^{27}Al and ^{31}P

NMR spectra were recorded at 293 K on a JEOL ECA 400 (^1H NMR at 400 MHz; ^{13}C NMR at 100 MHz; ^{11}B NMR at 128 MHz; ^{19}F NMR at 376 MHz; ^{31}P NMR at 161 MHz) or Bruker Avance 300 (^1H NMR at 300 MHz; ^{13}C NMR at 75.5 MHz; ^{31}P NMR at 121.5 MHz) spectrometer. NMR data was recorded immediately upon the removal of samples from the dry box unless otherwise stated. Variable ^1H and ^{31}P were recorded from across the range of 178 K to 293 K, at every 5 K change in temperature using the JEOL ECA 400 spectrometer. Dichloromethane- d_2 was dried over molecular sieves thrice while chloroform- d was distilled over CaH_2 and stored away from light. The solvents were degassed before use. ^1H and ^{13}C NMR spectra were reported relative to tetramethylsilane (0.00 ppm) and referenced to the solvent. ^{11}B NMR spectra was referenced and reported relative to $\text{BF}_3\cdot\text{OEt}_2$ (0.00 ppm) while ^{19}F NMR spectra was referenced and reported relative to CFCl_3 . The ^{27}Al NMR were reported and referenced relative to AlCl_3 in D_2O solution while ^{31}P NMR spectra were referenced and reported relative to H_3PO_4 (85%).

Section 5.3. X-Ray Crystallography

Suitable single crystals were covered with a perfluorinated polyether oil to minimize exposure to oxygen. They were mounted on quartz fiber and the X-ray intensity data were collected on a Bruker X8 APEX system, using $\text{Mo K}\alpha$ radiation, with the SMART suite of programs. Data was processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS. Structural solution and refinement were carried out with the SHELXTL suite of programs. All structures were solved by direct method and refined for all data by full-matrix least squares on F^2 . All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters. The total

number of reflections, collection ranges, and final R-values for each molecule were listed in the appropriate crystallographic data tables.

Section 5.4. DFT Calculations

DFT calculations were performed with the Gaussian 09 package. The products have been fully optimized by B3LYP method with 6-31G+(d,p) basis sets. NMR chemical shifts were calculated with the GIAO method and B3LYP/6-31g+(d,p) with fine integration grids.

Section 5.5. Experimental Procedures and Spectroscopic Data

Preparation of [$^i\text{Pr}_2\text{NPClC}(\text{PPh}_3)_2$][Cl], [2a^+][Cl]. 3.0 g (5.59mmol) of $\text{C}(\text{PPh}_3)_2$, (**1a**) was added to about 3.0 equiv of $^i\text{Pr}_2\text{NPCl}_2$ in 60 mL of benzene at room temperature. After stirring overnight, the solution was filtered and the resulting white solid was washed thrice using 10 mL of *n*-hexane to remove the excess $^i\text{Pr}_2\text{NPCl}_2$. The solid was then dried under vacuum. Yield = 3.5 g (85 %). Unfortunately, numerous attempts to crystallize this product failed. ^1H NMR (400 MHz, CDCl_3 , 20°C): δ 0.72 (d, $^3J_{\text{HH}} = 6.4$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 3.39 (sept, $^3J_{\text{HH}} = 6.4$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 7.3-7.7 (Ph, 30H). ^1H NMR (400 MHz, CD_2Cl_2 , - 90°C): δ 0.110 (d, $^3J_{\text{HH}} = 5.4$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.146 (d, $^3J_{\text{HH}} = 5.0$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.960 (d, $^3J_{\text{HH}} = 5.5$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.043 (d, $^3J_{\text{HH}} = 6.4$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 3.01 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.74 (br, 1H, $\text{CH}(\text{CH}_3)_2$), 7.2-7.7 (Ph, 30H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CDCl_3 , 20°C): δ 19.5 (dt, $^1J_{\text{P}(\text{central})\text{C}} = 88.2$ Hz and $^1J_{\text{P}(\text{carbone})\text{C}} = 76.7$ Hz, $\text{C}(\text{PPh}_3)$), 22.5 (d, $^2J_{\text{PC}} = 9.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 49.9 (d, $^2J_{\text{PC}} = 7.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 125.9 (apparent triplet AA'X, $^1J_{\text{PC}} + ^2J_{\text{PC}} = 88.7$ Hz, *ipso*-C), 128.4 (s, *p*-C), 129.3 (virtual triplet, *o*-C), 134.0 (s, *m*-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3 , 20°C): δ 25.9 (second order doublet, P(carbone)), 133.4 (second order triplet, P(central)). $^{31}\text{P}\{^1\text{H}\}$

NMR (161 Hz, CD₂Cl₂, - 90°C): δ 24.79 (dd, $^2J_{\text{P(central)P(carbone)}} = 17.5$ Hz and $^2J_{\text{P(carbone)P(carbone)}} = 43.8$ Hz, P(carbone)), 26.14 (dd, $^2J_{\text{P(central)P(carbone)}} = 188.3$ Hz and $^2J_{\text{P(carbone)P(carbone)}} = 43.8$ Hz, P(carbone)), 133.2 (dd, $^2J_{\text{P(central)P(carbone)}} = 188.3$ Hz and $^2J_{\text{P(central)P(carbone)}} = 17.5$ Hz, P(central)). ES-MS calcd. for [C₄₃H₄₄ClNP₃]⁺ (**2a**⁺): m/z 702.2370; found: 702.2339.

Preparation of [*i*Pr₂NPClC(PPh₃)₂][AlCl₄], [2a**⁺][AlCl₄].** Quantitative conversion of [**2a**⁺][Cl] to [**2a**⁺][AlCl₄] is achieved by adding 1.0 equiv of AlCl₃ to 20 mL dichloromethane (DCM) solution containing 0.20 g (0.37 mmol) of [**2a**⁺][Cl]. The crystals suitable for single crystal X-ray diffraction were grown out of DCM solution layered with hexane. ¹H NMR (400 MHz, CD₂Cl₂, 20°C): δ 0.74 (br, 12H, CH(CH₃)₂), 3.45 (br, 2H, CH(CH₃)₂), 7.3-7.7 (Ph, 30H). ¹³C{¹H} NMR (100.5 MHz, CD₂Cl₂, 20°C): δ 22.3 (br, CH(CH₃)₂), 49.9 (br, CH(CH₃)₂), 126.0 (vbr, *ipso*-C), 129.9 (br, *p*-C), 133.5 (br, *o*-C), 134.7 (br, *m*-C), C(carbone) not observed. ²⁷Al NMR (104 MHz, CD₂Cl₂, 20°C): δ 106.4. ³¹P{¹H} NMR (161 MHz, CD₂Cl₂, 20°C): δ 25.9 (second order doublet, P(carbone)), 133.6 (second order triplet, P(central)).

Preparation of [*i*Pr₂NPClCPh₂(CH₂)₃PPh₂][Cl], [2b**⁺][Cl].** 1.0 g (2.36 mmol) of C(PPh₂(CH₂)₃PPh₂), (**1b**) was added to 3 equiv (1.43 g, 7.08 mmol) of *i*Pr₂NPCl₂ in 60 mL of benzene at room temperature. After stirring overnight, the solution was filtered and the resulting white solid was washed thrice using 10 mL of *n*-hexane to remove the excess *i*Pr₂NPCl₂. The solid was then dried under vacuum. Yield 0.81 g (55%). ¹H NMR (400 MHz, CD₂Cl₂, 20°C): 0.56 (br, 12H, CH₃), 2.07 (m, 2H, CH₂), 3.30 (br, 4H, CH₂), 3.73 (br, 2H, CH), 7.2-7.8 (20H, Ph) ppm. ¹³C{¹H} NMR (400 MHz, CD₂Cl₂, 20°C): δ_c 14.8 (m, PCP, cyclic carbone), 15.3 (s, CH₂(CH₂)₂, cyclic carbone) 22.3 (br, CH(CH₃)₂), 26.2

(second order triplet, $\text{CH}_2(\text{CH}_2)_2$, cyclic carbene), 48.2 (br, $\text{CH}(\text{CH}_3)_2$); 128.3 – 134.3 (m, $\text{C}_1\text{-C}_4$, Ph of cyclic carbene) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CD_2Cl_2 , 20°C): δ_{P} 16.3 (second order doublet, $\text{P}_{\text{carbene}}$), 138.0 (second order triplet, $\text{P}_{\text{central}}$) ppm. MS (ES^+): m/z 590 (M^+). HRMS (ES^+): calcd. for $\text{C}_{34}\text{H}_{40}\text{NP}_3\text{Cl}$, m/z 590.2062; found 590.2054.

Preparation of $[\text{Cy}_2\text{NPClC}(\text{PPh}_3)_2][\text{Cl}]$, $[\mathbf{2c}^+][\text{Cl}]$. 1.0 g (1.86 mmol) of $\text{C}(\text{PPh}_3)_2$, **1a** was added to 3 equiv (1.58 g, 5.58 mmol) of Cy_2NPCl_2 in 60 mL of benzene at room temperature. After stirring overnight, the solution was filtered and the resulting white solid was washed thrice using 10 mL of *n*-hexane to remove Cy_2NPCl_2 . The solid was then dried under vacuum. Yield 1.23 g (81%). ^1H NMR (400 MHz, CD_2Cl_2 , 20°C): δ_{H} 0.7-1.4 (20H, $\text{CH}_2\text{-Cy}$), 2.84 (br, 2H, CH-Cy), 7.2-7.5 (br, 30H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CD_2Cl_2 , 20°C): δ_{C} 19.9 (dt, $^1J_{\text{P}(\text{carbene})\text{C}} = 78$ Hz, $^1J_{\text{P}(\text{carbene})\text{C}} = 104$ Hz, $\text{C}(\text{PPh}_3)_2$); 25.1 (s, $\delta\text{-CH}_2\text{-Cy}$), 25.8 (s, $\gamma\text{-CH}_2\text{-Cy}$), 33.0 (br, $\beta\text{-CH}_2\text{-Cy}$), 59.1 (br, CH-Cy), 125.7 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 92$ Hz, *ipso*-C, Ph of $\text{C}(\text{PPh}_3)_2$); 129.3 (virtual triplet, *o*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 134.6 (br, *m*-C, Ph of $\text{C}(\text{PPh}_3)_2$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CD_2Cl_2 , 20°C): δ_{P} 26.1 (second order doublet, $\text{P}_{\text{carbene}}$), 140.5 (second order triplet, $\text{P}_{\text{central}}$) ppm. MS (ES^+): m/z 720 (M^+). HRMS (ES^+): calcd. for $\text{C}_{49}\text{H}_{52}\text{NPCl}$, m/z 720.3526; found 720.3536.

Preparation of $[\text{PhPClC}(\text{PPh}_3)_2][\text{Cl}]$, $[\mathbf{2e}^+][\text{Cl}]$. 0.50 g (0.93 mmol) of $\text{C}(\text{PPh}_3)_2$ (**1a**) was added to a 60 mL benzene solution containing 3.0 equiv of PhPCl_2 . The reaction was stirred overnight followed by filtration. The resulting white solid was dried under vacuum. Yield 0.65 g (98%). ^1H NMR (CD_2Cl_2 , 500 MHz): δ 7.0-7.5 (m, 35 H). $^{13}\text{C}\{^1\text{H}\}$ (CD_2Cl_2 , 100.6 MHz): δ 22.5 (m, $\text{C}_{(\text{carbene})}$), 124.2 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 90$ Hz, *ipso*-C, $\text{Ph}_{(\text{carbene})}$) 128.5 (s, *m*-C, Ph), 128.7 (d, $^2J_{\text{P}(\text{central})\text{C}} = 3.1$ Hz, *o*-C, Ph), 129.0 (s,

p-C, Ph), 129.2 (virtual triplet, *o*-C, Ph_(carbonyl)), 133.6 (s, *p*-C, Ph_(carbonyl)), 134.3 (virtual triplet, *m*-C, Ph_(carbonyl)), 139.3 (dt, $^1J_{\text{P(central)C}} = 37.3$ Hz, $^3J_{\text{P(carbonyl)C}} = 10.3$ Hz, *ipso*-C, Ph). $^{31}\text{P}\{^1\text{H}\}$ (CD₂Cl₂, 202 MHz): δ 25.6 (second order doublet, P_(carbonyl)), 110.5 (second order triplet, P_(central)). ES-MS calcd. for [C₄₃H₃₅ClP₃]⁺ (**2e**⁺): *m/z* 679.1640; found: 679.1592.

Preparation of [ⁱPr₂NPC(PPh₃)₂][AlCl₄]₂, [3a**²⁺][AlCl₄]₂.** 0.36 g (2.71 mmol) of AlCl₃ were added to a 50 mL dichloromethane solution containing 1.0 g (1.35 mmol) of [**2a**⁺][Cl]. After the mixture was stirred for about 1h, all volatilities were removed under reduced pressure resulting in 0.89 g (66%) of a yellow solid identified as [**3a**²⁺][AlCl₄]₂. Crystals suitable for single crystal X-ray diffraction were obtained by layering a saturated difluorobenzene solution of [**3a**²⁺][AlCl₄]₂ with hexane. ^1H NMR (400 MHz, CD₂Cl₂, 20°C): δ 0.54 (br, 6H, CH(CH₃)₂), 1.27 (br, 6H, CH(CH₃)₂), 3.81 (vbr, 2H, CH(CH₃)₂), 7.3-7.9 (Ph, 30H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD₂Cl₂, 20°C): δ 20.5 (br, CH(CH₃)₂), 27.9 (br, CH(CH₃)₂), 54.1 (br, CH(CH₃)₂), 61.9 (br, CH(CH₃)₂), 67.8 (vbr, C(PPh₃)), 119.8 (apparent triplet AA'X, $^1J_{\text{PC}} + 3J_{\text{PC}} = 94.0$ Hz, *ipso*-C, Ph), 130.9 (br, *p*-C, Ph), 134.3 (br, *o*-C, Ph), 135.7 (br, *m*-C, Ph). ^{27}Al NMR (104 MHz, CD₂Cl₂, 20°C): δ 106.4. $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CD₂Cl₂, 20°C): δ 26.2 (second order doublet, P(carbonyl)), 355.7 (second order triplet, P(central)). ES-MS: All attempts to detect this dication were unsuccessful.

Preparation of [ⁱPr₂NPC(PPh₃)₂][BAR^F₄]₂, [3a**²⁺][BAR^F₄]₂.** 2.0 equiv of Na[BAR^F₄] was added to a DCM solution (50 mL) containing 0.80 g (1.08 mmol) of [**2a**⁺][Cl]. The solution was stirred for 1 h, filtered and layered with about 50 ml of hexane. The formation of a yellow oil layer was observed after 24 h. All the solvents were decanted. The yellow oil was subjected to reduced vacuum, resulting in the formation of a yellow

powder. Yield 0.91 g (35%). Crystals suitable for single crystal X-ray diffraction were obtained from a saturated dichloromethane solution of $[\mathbf{3a}^{2+}][\text{BAr}^{\text{F}}_4]_2$. ^1H NMR (400 MHz, CD_2Cl_2 , 20°C): δ 0.44 (d, $^3J_{\text{HH}} = 6.4$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.13 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 3.74 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.92 (sept, $^3J_{\text{HH}} = 6.4$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 7.3-7.9 (Ph, 52H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2 , 20°C): δ 20.3 (s, $\text{CH}(\text{CH}_3)_2$), 27.7 (d, $\text{CH}(\text{CH}_3)_2$, $^3J_{\text{PC}} = 17.3$ Hz), 55.0 (d, $\text{CH}(\text{CH}_3)_2$, $^2J_{\text{PC}} = 27.9$ Hz), 61.9 (d, $\text{CH}(\text{CH}_3)_2$, $^2J_{\text{PC}} = 15.3$ Hz), 68.9 (m, C(PPh₃)), 117.5 (*p*-C of $\text{BAr}^{\text{F}}_4^-$), 119.2 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 93$ Hz, *ipso*-C, Ph of C(PPh₃)), 124.6 (q, $^1J_{\text{CF}} = 274$ Hz, CF_3 of $\text{BAr}^{\text{F}}_4^-$), 129.0 (q, $^2J_{\text{CF}} = 31$ Hz, *m*-C, $\text{BAr}^{\text{F}}_4^-$), 130.8 (m, *p*-C, Ph of C(PPh₃)), 133.8 (m, *o*-C, Ph of C(PPh₃)), 134.8 (*o*-C, $\text{BAr}^{\text{F}}_4^-$), 136.3 (*m*-C, Ph of C(PPh₃)), 161.8 (q, $^1J_{\text{CB}} = 50$ Hz, *ipso*-C of $\text{BAr}^{\text{F}}_4^-$). $^{11}\text{B}\{^1\text{H}\}$ (161 MHz, CD_2Cl_2 , 20°C): δ -7.6 ($\text{BAr}^{\text{F}}_4^-$). $^{19}\text{F}\{^1\text{H}\}$ NMR (376.3 MHz, CD_2Cl_2 , 20°C): δ -62.7 ($\text{BAr}^{\text{F}}_4^-$). $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CD_2Cl_2 , 20°C): δ 26.7 (second order doublet, P(carbone)), 356.5 (second order triplet, P(central)).

Preparation of $[\text{Pr}_2\text{NP}(\mathbf{4}\text{-NMe}_2\text{-C}_5\text{H}_4\text{N})\text{C}(\text{PPh}_3)_2][\text{BAr}^{\text{F}}_4]_2$, $[\mathbf{3a}^{2+}\cdot\text{DMAP}][\text{BAr}^{\text{F}}_4]_2$.

Addition of 1.0 equiv of DMAP to an NMR tube containing 0.030 g (0.0125 mmol) of $[\mathbf{3a}^{2+}][\text{BAr}^{\text{F}}_4]_2$ in 1 mL of CD_2Cl_2 resulted in a complete conversion to $[\mathbf{3a}^{2+}\cdot\text{DMAP}][\text{BAr}^{\text{F}}_4]_2$ as observed by multinuclear NMR. ^1H NMR (400 MHz, CD_2Cl_2 , 20°C): δ 0.90 (vbr, 12H, $\text{CH}(\text{CH}_3)_2$), 3.52 (s, 6H, NMe_2 of DMAP), 3.73 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 6.33 (vbr, 2H, *m*-CH of DMAP), 7.09 (vbr, 2H, *o*-CH of DMAP), 7.3-7.9 (aryl, 54H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2 , 20°C): δ 22.6 (s, $\text{CH}(\text{CH}_3)_2$), 23.0 (vbr, C(PPh₃)), 31.6 (s, $\text{CH}(\text{CH}_3)_2$), 40.0 (NMe_2 of DMAP), 107.3 (*m*-C of DMAP), 117.5 (*p*-C of $\text{BAr}^{\text{F}}_4^-$), 124.6 (q, $^1J_{\text{CF}} = 273$ Hz, CF_3 of $\text{BAr}^{\text{F}}_4^-$), 124.7 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 94$ Hz, *ipso*-C, Ph of C(PPh₃)), 128.9 (q, $^2J_{\text{CF}} = 35$ Hz, *m*-C, $\text{BAr}^{\text{F}}_4^-$), 129.4 (*p*-C, Ph of C(PPh₃)), 129.9 (*m*-C, Ph of C(PPh₃)), 134.1 (*o*-C, Ph of C(PPh₃)) 134.8 (*o*-C,

BAR^F₄⁻), 161.8 (q, ¹J_{CB} = 51 Hz, ipso-C of BAR^F₄⁻). ¹¹B{¹H} (161 MHz, CD₂Cl₂, 20°C): δ - 7.6 (BAR^F₄⁻). ¹⁹F{¹H} NMR (376.3 MHz, CD₂Cl₂, 20°C): δ -62.7 (BAR^F₄⁻). ³¹P{¹H} NMR (161 MHz, CD₂Cl₂, 20°C): δ 25.5 (second order doublet, P(carbone)), 131.2 (vbr, P(central)).

Reactivity of [3a²⁺][AlCl₄]₂ with PMe₃. Samples 1 and 2 were made by mixing [3a²⁺][AlCl₄]₂ and PMe₃ in a 1:1 or 1:2 ratio, respectively, in about 1 mL of dichloromethane using J. Young NMR tube. The reaction progress was monitored by ²⁷Al and ³¹P NMR.

Sample 1. 0.030 g of [3a²⁺][AlCl₄]₂ was transferred to a 1 mL CH₂Cl₂ solution (J. Young NMR tube) containing 1 equiv of PMe₃. After the sample was allowed to equilibrate for about 15 min, the following observations have been made: ²⁷Al NMR (CD₂Cl₂, 104 MHz, 23°C): δ 106.4, 81.3. ³¹P{¹H} NMR (CD₂Cl₂, 161 MHz, 23°C): δ 324.2 (vbr), 133.2 (br), 26.3 (second order doublet), - 38.7 (s). ³¹P{¹H} NMR (CD₂Cl₂, 161 MHz, - 60°C): δ 350.2 (br), 132.4 (second order doublet), 43.6 (br) 28.2 (second order doublet), 7.7 (br), - 37.0 (s). ³¹P{¹H} NMR (CH₂Cl₂, 161 MHz, - 95°C): δ 348.5 (d, P(central), ²J_{P(central)P(carbone)} = 40.171 Hz, 3a²⁺), 40.7 (dd, (P(central), ¹J_{P(central)PMe₃} = 446.0 Hz, ²J_{P(central)P(carbone)} = 235.0 Hz, 3a²⁺•PMe₃) 29.9 (dt, P(carbone), ²J_{P(central)P(carbone)} = 235.0 Hz, ³J_{P(carbone)P(carbone)} = ³J_{P(carbone)PMe₃} = 50.6 Hz, 3a²⁺•PMe₃), 29.5 (P(carbone), overlapping with the previous signal, 3a²⁺), 25.9 (d, P(carbone), ³J_{P(carbone)P(carbone)} = 50.4 Hz), 8.19 (dd, PMe₃, ¹J_{P(central)PMe₃} = 446.0 Hz, ³J_{P(carbone)PMe₃} = 50.6 Hz, 3a²⁺•PMe₃), - 37.8 (vbr, Me₃P•AlCl₃).

Sample 2. 0.030 g of $[\mathbf{3a}^{2+}][\text{AlCl}_4]_2$ was transferred to a 1 mL CH_2Cl_2 solution (J. Young NMR tube) containing 2 equiv of PMe_3 . After the sample was allowed to equilibrate for about 15 min, the following observations have been made: ^{27}Al NMR (CD_2Cl_2 , 104 MHz, 23°C): δ 106.4, 65.4. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161 MHz, 23°C): δ 133.2 (br), 26.1 (second order doublet), - 41.9 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161 MHz, -60°C): δ 132.4 (second order doublet), 43.6 (vbr), 28.2 (m), - 37.4 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161 MHz, -95°C): δ 132.1 (d, P(central), $^2J_{\text{P(central)P(carbone)}} = 183$ Hz, $\mathbf{2a}^+$), 40.7 (dd, 43.6 (P(central), $^1J_{\text{P(central)PMe}_3} = 446.0$ Hz, $^2J_{\text{P(central)P(carbone)}} = 235.0$ Hz, $\mathbf{3a}^{2+}\cdot\text{PMe}_3$) 29.9 (dt, P(carbone), $^2J_{\text{P(central)P(carbone)}} = 235.0$ Hz, $^3J_{\text{P(carbone)P(carbone)}} = ^3J_{\text{P(carbone)PMe}_3} = 50.6$ Hz, $\mathbf{3a}^{2+}\cdot\text{PMe}_3$), 25.4 (m, P(carbone), $\mathbf{2a}^+$), 8.19 (dd, PMe_3 , $^1J_{\text{P(central)PMe}_3} = 446.0$ Hz, $^3J_{\text{P(carbone)PMe}_3} = 50.6$ Hz, $\mathbf{3a}^{2+}\cdot\text{PMe}_3$), - 38.2 (br, $\text{Me}_3\text{P}\cdot\text{AlCl}_3$), - 59.4 (br, PMe_3).

Figure 5.1. DFT calculations of $[i\text{Pr}_2\text{NP}(\text{C}(\text{PPh}_3)_2)[\text{X}]_2]$, $[3\text{a}^{2+}][\text{X}]_2$.

Reactivity of $[3a^{2+}][\text{Bar}^{\text{F}_4}]_2$ and H_2O . To a 1 mL of yellow CD_2Cl_2 solution containing 0.050 g (0.021 mmol) of $[3a^{2+}][\text{Bar}^{\text{F}_4}]_2$ (J. Young NMR tube), 1 equiv of H_2O (diluted in CD_2Cl_2 , 0.111M) was added. The yellow colour faded instantaneously. Attempts to isolate the resulting product were unsuccessful due to progressive decomposition. The following observations were made immediately following the addition of water: ^1H NMR (400 MHz, CD_2Cl_2 , 25°C): δ 0.65 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.83 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 3.66 (sept, $^3J_{\text{HH}} = 6.6$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 7.3-7.7 (Ph, 54H), 7.58 (d, $^1J_{\text{P}(\text{central})\text{H}} = 642$ Hz, PH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2 , -90°C): δ 3.3 (m, $\text{C}(\text{PPh}_3)$), 20.3 (br, $\text{CH}(\text{CH}_3)_2$), 47.6 (br, $\text{CH}(\text{CH}_3)_2$), 113.0 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 93$ Hz, *ipso*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 117.6 (*p*-C of Bar^{F_4-}), 124.5 (q, $^1J_{\text{CF}} = 273$ Hz, CF_3 of Bar^{F_4-}), 128.7 (q, $^2J_{\text{CF}} = 33$ Hz, *m*-C, Bar^{F_4-}), 130.0 (br, *p*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 133-136 (br, *o*-C and *m*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 134.7 (*o*-C, Bar^{F_4-}), 161.9 (q, $^1J_{\text{CB}} = 50$ Hz, *ipso*-C of Bar^{F_4-}). $^{11}\text{B}\{^1\text{H}\}$ (161 MHz, CD_2Cl_2 , 25°C): δ - 7.6 (Bar^{F_4-}). $^{19}\text{F}\{^1\text{H}\}$ NMR (376.3 MHz, CD_2Cl_2 , 25°C): δ - 62.7 (Bar^{F_4-}). ^{31}P NMR (CD_2Cl_2 , 161 MHz, 25°C): δ 24.1 (br, P(carbone)), 31.8 (d, $^1J_{\text{P}(\text{central})\text{H}} = 642$ Hz). MS (ES^+): m/z 684 ($\text{M}^{2+}\text{-H}^+$). HRMS (ES^+): calcd. for $\text{C}_{43}\text{H}_{45}\text{NOP}_3$, m/z 684.2714; found 684.2694. FTIR (KBr pellets): 3545 cm^{-1} (O-H stretch). NMR data obtained at -50°C and assigned to (i) $[\text{iPr}_2\text{NPH}(\text{OH})(\text{C}(\text{PPh}_3)_2)][\text{Bar}^{\text{F}_4}]_2$, $[3a^{2+}\text{-(H)OH}][\text{Bar}^{\text{F}_4}]_2$: ^1H NMR (400MHz, CD_2Cl_2 , -50°C): δ 0.49 (br, 3H, $\text{CH}(\text{CH}_3)_2$), 0.78 (d, $^3J_{\text{HH}} = 5.4$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 2.68 (s, OH), 3.66 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 7.3-7.7 (Ph, 54H), 7.59 d, $^1J_{\text{P}(\text{central})\text{H}} = 605$ Hz, PH); ^{31}P NMR (CD_2Cl_2 , 161 MHz, -50°C): δ 23.1 (br, P(carbone)), 29.8 (d, $^1J_{\text{P}(\text{central})\text{H}} = 605$ Hz), and (ii) $[\text{iPr}_2\text{NH}]\text{PH}(\text{O})(\text{C}(\text{PPh}_3)_2)[\text{Bar}^{\text{F}_4}]_2$, $[3a^{2+}\text{-(H)NH}][\text{Bar}^{\text{F}_4}]_2$: ^1H NMR (400MHz, CD_2Cl_2 , -50°C): δ 0.26 (br, 3H, $\text{CH}(\text{CH}_3)_2$), 0.58 (br, 3H, $\text{CH}(\text{CH}_3)_2$), 3.16 (s, NH), 3.29 (br, 2H, $\text{CH}(\text{CH}_3)_2$), 7.3-7.7 (Ph, 54H), 7.31 (dd, $^1J_{\text{P}(\text{central})\text{H}} = 554$ Hz, $^3J_{\text{HH}} = 22.4$ Hz,

PH); ^{31}P NMR (CD_2Cl_2 , 161 MHz, -50°C): δ 22.6 (d, $^1J_{\text{P}(\text{central})\text{H}} = 554$ Hz), 26.5 (br, $\text{P}_{(\text{carbone})}$).

Signal	$3\text{a}^{2+}\text{-(H)OH}$	$3\text{a}^{2+}\text{-(H)NH}$
P-H	7.91 (7.59)	6.36 (7.31)
O-H	2.84 (2.68)	N/A
N-H	N/A	3.43 (3.16)

Table 5.1. Summary of ^1H NMR data obtained from DFT calculations. Corresponding experimental data are in parenthesis.

Reactivity of $[3\text{a}^{2+}][\text{BAr}^{\text{F}_4}]_2$ and D_2O . To a 1 mL of yellow CD_2Cl_2 solution containing 0.050 g (0.021 mmol) of $[3\text{a}^{2+}][\text{BAr}^{\text{F}_4}]_2$ (J. Young NMR tube), 1 equiv of D_2O (diluted in CD_2Cl_2 , 0.050 M) was added. The yellow colour faded instantaneously. Attempts to isolate the resulting product were unsuccessful due to progressive decomposition. The following observations were made immediately following the addition of heavy water: ^1H NMR (400 MHz, CD_2Cl_2 , 25°C): δ 0.65 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.83 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 3.64 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 7.3-7.7 (Ph, 54H). ^2H NMR (61.4 MHz, CH_2Cl_2 , 25°C): δ 7.54 (d, $^1J_{\text{PD}} = 90.6$ Hz). Note: the sample was prepared in CH_2Cl_2 . $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2 , -90°C): δ 3.6 (m, $\text{C}(\text{PPh}_3)$), 21.2 (br, $\text{CH}(\text{CH}_3)_2$), 47.4 (br, $\text{CH}(\text{CH}_3)_2$), 113.0 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 81$ Hz, *ipso*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 117.7 (*p*-C of BAr^{F_4-}), 124.5 (q, $^1J_{\text{CF}} = 273$ Hz, CF_3 of BAr^{F_4-}), 128.7 (q, $^2J_{\text{CF}} = 34$ Hz, *m*-C, BAr^{F_4-}), 130.0 (br, *p*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 133-136 (br, *o*-C and *m*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 134.7 (*o*-C, BAr^{F_4-}), 161.9 (q, $^1J_{\text{CB}} = 49$ Hz, *ipso*-C of BAr^{F_4-}). $^{11}\text{B}\{^1\text{H}\}$ (161 MHz, CD_2Cl_2 , 25°C): δ - 7.6 (BAr^{F_4-}). $^{19}\text{F}\{^1\text{H}\}$ NMR (376.3 MHz, CD_2Cl_2 , 25°C): δ - 62.7 (BAr^{F_4-}). ^{31}P NMR (CD_2Cl_2 , 161 MHz, 25°C): δ 24.1 (br, $\text{P}_{(\text{carbone})}$), 30.4 (vbr, $\text{P}_{(\text{central})}$). FTIR (KBr pellets): 2627 cm^{-1} (O-D stretch). ^1H NMR

spectrum taken at -50°C was identical as for the water addition except that the peaks initially observed at δ 2.68 and 3.16 ppm were missing. ^{31}P NMR spectra taken at this temperature was also virtually identical except for (i) added broadness due to the presence of a P-D fragment and (ii) virtual absence of the “P-H” fragments.

Preparation of $[\text{}^i\text{Pr}_2\text{NPH}(\text{OCH}_3)\text{C}(\text{PPh}_3)_2][\text{BAr}^{\text{F}_4}]_2$, $[\mathbf{3a}^{2+}\text{-(H)OMe}][\text{BAr}^{\text{F}_4}]_2$. 0.20 g (0.083 mmol) of $[\mathbf{3a}^{2+}][\text{BAr}^{\text{F}_4}]_2$ was dissolved in about 20 ml of CH_2Cl_2 followed by addition of 1 equiv of CH_3OH (diluted in CH_2Cl_2 , 0.110 M). The colour change was instantaneous. The ^{31}P NMR spectrum obtained right after the addition showed a complete consumption of the starting material. Then, all volatilities were removed under reduced pressure and the resulting solid was washed with 3 x 5 mL of hexane. Yield 0.18 g (89%). ^1H NMR (400 MHz, CD_2Cl_2 , 25°C): δ 0.70 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.90 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 3.31 (d, $^3J_{\text{P}(\text{central})\text{H}} = 14.5$ Hz, 3H, OCH_3) 3.56 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 7.3-7.7 (Ph, 54H), 7.41 (d, $^1J_{\text{P}(\text{central})\text{H}} = 580$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2 , 25°C): δ 7.9 (m, $\text{C}(\text{PPh}_3)_2$), 21.9 (s, $\text{CH}(\text{CH}_3)_2$), 24.1 (s, $\text{CH}(\text{CH}_3)_2$) 48.9 (s, $\text{CH}(\text{CH}_3)_2$), 57.8 (d, OCH_3 , $^2J_{\text{PC}} = 7.3$ Hz), 117.5 (*p*-C of BAr^{F_4-}), 121.2 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 95$ Hz, *ipso*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 124.3 (q, $^1J_{\text{CF}} = 274$ Hz, CF_3 of BAr^{F_4-}), 128.9 (q, $^2J_{\text{CF}} = 32$ Hz, *m*-C, BAr^{F_4-}), 130.4 (m, *p*-C, Ph of $\text{C}(\text{PPh}_3)$), 133.8 (m, *o*-C, Ph of $\text{C}(\text{PPh}_3)$), 134.8 (*o*-C, BAr^{F_4-}), 135.4 (s, *m*-C, Ph of $\text{C}(\text{PPh}_3)$), 161.8 (q, $^1J_{\text{CB}} = 50$ Hz, *ipso*-C of BAr^{F_4-}). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 104 MHz, 25°C): δ -7.6 (BAr^{F_4-}). $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 104 MHz, 25°C): δ -62.7 (BAr^{F_4-}). ^{31}P NMR (CD_2Cl_2 , 161 MHz, 25°C): δ 24.4 (br, $\text{P}(\text{carbone})$), 41.3 (doublet of multiplets, $^1J_{\text{P}(\text{central})\text{H}} = 580$ Hz). MS (ES^+): m/z 350 (M^{2+}). HRMS (ES^+): calcd. for $(\text{C}_{44}\text{H}_{48}\text{NOP}_3)^{2+}$: m/z 349.6474; found 349.6431.

Preparation of $[\text{Pr}_2\text{NPD}(\text{OCD}_3)\text{C}(\text{PPh}_3)_2][\text{BAr}^{\text{F}}_4]_2$, $[\mathbf{3a}^{2+}\text{-(D)}\text{OCD}_3][\text{BAr}^{\text{F}}_4]_2$. 0.20 g (0.083 mmol) of $[\mathbf{3a}^{2+}][\text{BAr}^{\text{F}}_4]_2$ was dissolved in about 20 mL of CH_2Cl_2 followed by addition of 1 equiv of CD_3OD (diluted in CH_2Cl_2 , 0.110 M). The colour change was instantaneous. The ^{31}P NMR spectrum obtained right after the addition showed a complete consumption of the starting material. Then, all volatilities were removed under reduced pressure and the resulting solid was washed with 3 x 5 mL of hexane. Yield 0.17 g (87%). ^1H NMR (400 MHz, CD_2Cl_2 , 25°C): δ 0.70 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.90 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 3.56 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 7.3-7.7 (Ph, 54H). ^2H NMR (61.4 MHz, CH_2Cl_2 , 25°C): δ 3.23 (s, OCD_3), 7.39 (d, $^1J_{\text{PD}} = 85$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2 , 25°C): δ 8.3 (m, $\text{C}(\text{PPh}_3)_2$), 21.9 (s, $\text{CH}(\text{CH}_3)_2$), 24.1 (s, $\text{CH}(\text{CH}_3)_2$), 48.9 (s, $\text{CH}(\text{CH}_3)_2$), 117.5 (*p*-C of $\text{BAr}^{\text{F}}_4^-$), 121.2 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 94$ Hz, *ipso*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 124.3 (q, $^1J_{\text{CF}} = 274$ Hz, CF_3 of $\text{BAr}^{\text{F}}_4^-$), 128.9 (q, $^2J_{\text{CF}} = 32$ Hz, *m*-C, $\text{BAr}^{\text{F}}_4^-$), 130.4 (m, *p*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 133.8 (m, *o*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 134.8 (*o*-C, $\text{BAr}^{\text{F}}_4^-$), 135.4 (s, *m*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 161.8 (q, $^1J_{\text{CB}} = 50$ Hz, *ipso*-C of $\text{BAr}^{\text{F}}_4^-$). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 104 MHz, 25°C): δ -7.6 ($\text{BAr}^{\text{F}}_4^-$). $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 104 MHz, 25°C): δ -62.7 ($\text{BAr}^{\text{F}}_4^-$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161 MHz, 25°C): δ 24.4 (second order doublet, $^3J_{\text{PP}} \sim 30$ Hz, $\text{P}_{(\text{carbone})}$), 40.7 (tt, $^1J_{\text{PD}} = 85$ Hz, $^2J_{\text{PP}} \sim 30$ Hz, $\text{P}_{(\text{central})}$).

Preparation of $[\text{Pr}_2\text{NPH}(\text{O})\text{C}(\text{PPh}_3)_2][\text{HNEt}_3][\text{BAr}^{\text{F}}_4]_2$, $[\mathbf{3a}^{2+}\text{-(H)}\text{O}\cdots\text{HNEt}_3][\text{BAr}^{\text{F}}_4]_2$. 0.20 g (0.083 mmol) of $[\mathbf{3a}^{2+}][\text{BAr}^{\text{F}}_4]_2$ was dissolved in about 20 mL of CH_2Cl_2 followed by the addition of 1 equiv of H_2O (diluted in CH_2Cl_2 , 0.111 M). After stirring for 5 min, 1 equiv of NEt_3 was added. The mixture was stirred for another 5 min. The solution was then filtered and layered with 5 mL of hexane. Colourless crystals formed after 3 days. Yield 0.12g (57%). ^1H NMR (400 MHz, CD_2Cl_2 , 25°C): δ 0.53 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H,

CH(CH₃)₂)), 0.97 (d, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂)), 1.08 (m, 9H, HN(CH₂CH₃)₃), 2.79 (br, 6H, HN(CH₂CH₃)₃), 3.59 (sept, ³J_{HH} = 6.8 Hz, 2H, CH(CH₃)₂)), 6.28 (vbr, 1H, HN(CH₂CH₃)₃), 7.3-7.7 (Ph, 54H), 7.55 (dd, ¹J_{P(central)H} = 537 Hz, ³J_{PH} = 4 Hz, PH). ¹³C{¹H} NMR (100.5 MHz, CD₂Cl₂, 25°C): δ 9.0 (s, HN(CH(CH₃)₂)₃), 21.9 (s, N(CH(CH₃)₂)₂), 23.7 (s, N(CH(CH₃)₂)₂), 46.5 (s, N(CH(CH₃)₂)₂), 47.8 (s, HN(CH(CH₃)₂)₃), 117.5 (*p*-C of BAr^F₄⁻), 124.6 (q, ¹J_{CF} = 274 Hz, CF₃ of BAr^F₄⁻), 124.8 (apparent triplet AA'X, ¹J_{PC} + ³J_{PC} = 95 Hz, *ipso*-C, Ph of C(PPh₃)₂), 129.3 (q, ²J_{CF} = 35 Hz, *m*-C, BAr^F₄⁻), 129.4 (m, *p*-C, Ph of C(PPh₃)), 133.6 (s, *o*-C, BAr^F₄⁻), 134.2 (m, *o*-C, Ph of C(PPh₃)), 134.8 (s, *m*-C, Ph of C(PPh₃)), 161.8 (q, ¹J_{CB} = 50 Hz, *ipso*-C of BAr^F₄⁻). ¹¹B NMR (CD₂Cl₂, 104 MHz, 25°C): δ -7.7. ¹⁹F NMR (CD₂Cl₂, 104 MHz, 25°C): δ -62.8. ³¹P NMR (CD₂Cl₂, 161 MHz, 25°C): δ 17.4 (d, ¹J_{P(central)H} = 537 Hz), 22.9 (br, P_(carbonyl)). MS (ES⁺): *m/z* 684 (M²⁺-HNEt₃) HRMS (ES⁺): calcd. for C₄₃H₄₅NOP₃, *m/z* 684.2714; found 684.2686.

Preparation of [¹Pr₂NPD(O)C(PPh₃)₂][DNEt₃][BAr^F₄]₂, [3a²⁺-(D)O...DNEt₃][BAr^F₄]₂.

0.20 g (0.083 mmol) of [3a²⁺][BAr^F₄]₂ was dissolved in about 20 mL of CH₂Cl₂ followed by the addition of 1 equiv of D₂O (diluted in CH₂Cl₂, 0.050 M). After stirring for 5 min, 1 equiv of NEt₃ was added. The mixture was stirred for another 5 min. The solution was then filtered and layered with 5 mL of hexane. Colourless crystals formed after 3 days. Yield 0.13 g (62%). ¹H NMR (400 MHz, CD₂Cl₂, 25°C): δ 0.50 (d, ³J_{HH} = 6.7 Hz, 3H, CH(CH₃)₂)), 0.97 (d, ³J_{HH} = 2.7 Hz, 3H, CH(CH₃)₂)), 1.08 (d, ³J_{HH} = 6.8 Hz, 9H, HN(CH₂CH₃)₃), 2.61 (m, 3H, HN(CH₂CH₃)₃), 3.61 (m, 2H, CH(CH₃)₂)), 7.3-7.7 (Ph, 54H). ²H NMR (61.4 MHz, CH₂Cl₂, 25°C): δ 6.8 (br, DN(CH₂CH₃)₃), 7.68 (d, ¹J_{PD} = 77 Hz, P-D). ¹³C{¹H} NMR (100.5 MHz, CD₂Cl₂, 25°C): δ 8.4 (s, HN(CH(CH₃)₂)₃), 21.8 (d, ³J_{PC} = 5 Hz, N(CH(CH₃)₂)₂), 23.9 (d, ³J_{PC} = 4 Hz, N(CH(CH₃)₂)₂), 46.6 (s,

$\text{N}(\text{CH}(\text{CH}_3)_2)_2$, 46.6 (s, $\text{HN}(\text{CH}(\text{CH}_3)_2)_3$), 117.5 (s, *p*-C of $\text{BAr}^{\text{F}_4^-}$), 124.5 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 95$ Hz, *ipso*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 124.6 (q, $^1J_{\text{CF}} = 274$ Hz, CF_3 of $\text{BAr}^{\text{F}_4^-}$), 128.9 (q, $^2J_{\text{CF}} = 32$ Hz, *m*-C, $\text{BAr}^{\text{F}_4^-}$), 129.5 (m, *p*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 133.8 (s, *o*-C, $\text{BAr}^{\text{F}_4^-}$), 134.0 (m, *o*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 134.8 (s, *m*-C, Ph of $\text{C}(\text{PPh}_3)_2$), 161.8 (q, $^1J_{\text{CB}} = 50$ Hz, *ipso*-C of $\text{BAr}^{\text{F}_4^-}$). ^{11}B NMR (CD_2Cl_2 , 104 MHz, 25°C): δ -7.7. ^{19}F NMR (CD_2Cl_2 , 104 MHz, 25°C): δ -62.8. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161 MHz, 25°C): δ 17.1 (tt, $^1J_{\text{PD}} = 80$ Hz, $^3J_{\text{PP}} = 18.4$, $\text{P}_{(\text{central})}$), 22.9 (d, $^3J_{\text{PP}} = 18.4$, $\text{P}_{(\text{carbone})}$).

Preparation of $[\text{iPr}_2\text{NPCPPh}_2(\text{CH}_2)_3\text{PPh}_2][\text{X}]_2$, $[\mathbf{3b}^{2+}][\text{X}]_2$ ($\text{X} = \text{AlCl}_4$, BAr^{F_4}). To a DCM solution containing 1.0 g (1.60 mmol) of $[\mathbf{2b}][\text{Cl}]$, 2.1 equiv of AlCl_3 or $\text{Na}[\text{BAr}^{\text{F}_4}]$ was added. The reaction mixture was stirred for 6h and filtered (when $\text{Na}[\text{BAr}^{\text{F}_4}]$ was used). The solvent was removed under reduced pressure yielding yellow solid. It is worth noting that regardless of the nature of the counterion, the multinuclear NMR data for the dicationic moieties ($\mathbf{3b}^{2+}$) was essentially identical so the data for ion pairs is reported separately. Yield 0.84 g (59 %) as AlCl_4^- salt and 2.19 g (60 %) as $[\text{BAr}^{\text{F}_4}]^-$ salt. ^1H NMR (400 MHz, CD_2Cl_2 , 20°C): δ_{H} 0.49 (d, $^3J_{\text{HH}} = 6.4$ Hz, CH_3), 1.18 (d, $^3J_{\text{HH}} = 6.8$ Hz, CH_3), 2.35 (m, 2H, CH_2), 2.85 (m, 4H, CH_2), 3.73 (m, 1H, CH), 3.92 (m, 1H, CH) 7.3-7.9 (20H, Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 20°C): δ_{C} 14.9 (s, $\text{CH}_2(\text{CH}_2)_2$, cyclic carbone), 20.8 (br, $\text{CH}(\text{CH}_3)_2$), 23.9 (second order triplet, $\text{CH}_2(\text{CH}_2)_2$, cyclic carbone), 27.9 (d, $^3J_{\text{PC}} = 15$ Hz, $\text{CH}(\text{CH}_3)_2$), 54.6 (d, $^2J_{\text{PC}} = 24$ Hz, $\text{CH}(\text{CH}_3)_2$), 62.8 (d, $^2J_{\text{PC}} = 15$ Hz, $\text{CH}(\text{CH}_3)_2$), 131.5 - 132.6 (m, $\text{C}_1\text{-C}_4$, Ph of cyclic carbone) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CD_2Cl_2 , 20°C): δ_{P} 19.1 (second order doublet, $\text{P}_{\text{carbone}}$), 351.5 (second order triplet, $\text{P}_{\text{central}}$) ppm.

Counterions. AlCl_4^- : ^{27}Al NMR (104 MHz, CD_2Cl_2 , 20°C): δ 106.4 ppm. $[\text{BAr}^{\text{F}_4}]^-$: ^1H NMR (400 MHz, CD_2Cl_2 , 20°C): δ 7.3-7.9 (24H, Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz,

CD₂Cl₂, 20°C): δ 117.5 (*p*-C), 124.6 (q, $^1J_{CF}$ = 272 Hz, CF₃), 128.9 (q, $^2J_{CF}$ = 35 Hz, *m*-C), 137.1 (*o*-C), 161.8 (q, $^1J_{CB}$ = 50 Hz, *ipso*-C) ppm. ^{11}B { ^1H } NMR (161 MHz, CD₂Cl₂, 20°C): δ_B - 7.6. ^{19}F { ^1H } NMR (376 MHz, CD₂Cl₂, 20°C): δ_F - 62.8 ppm.

Preparation of [Cy₂NPC(PPh₃)₂][X]₂, [3c²⁺][X]₂ (X = AlCl₄, BAr^F₄). To a DCM solution containing 1.0 g (1.22 mmol) of [2c][Cl], 2.1 equiv of AlCl₃ or Na[BAr^F₄] was added. The reaction mixture was stirred for 6h and filtered (when Na[BAr^F₄] was used). The solvent was removed under reduced pressure yielding yellow solid. It is worth noting that regardless of the nature of the counterion, the multinuclear NMR data for the dicationic moieties (3c²⁺) was essentially identical so the data for ion pairs is reported separately. Yield 0.81 g (61 %) as AlCl₄⁻ salt and 1.78 g (59 %) as [BAr^F₄]⁻ salt. ^1H NMR (400 MHz, CD₂Cl₂, 20°C): δ 0.47-1.72 (br. m, 2H, CH₂-Cy), 3.36 (br, 1H, CH-Cy), 3.53 (br, 1H, CH-Cy), 7.3-7.9 (30H, Ph) ppm. ^{13}C { ^1H } NMR (400 MHz, CD₂Cl₂, 20°C): δ 23.7 (s, δ -CH₂-Cy), 24.4 (s, δ -CH₂-Cy), 25.0 (s, γ -CH₂-Cy), 26.2 (s, γ -CH₂-Cy), 30.9 (br, β -CH₂-Cy), 39.6 (d, $^3J_{PC}$ = 18 Hz, br, β -CH₂-Cy), 64.1 (d, $^2J_{PC}$ = 22 Hz, CH-Cy), 66.0 (m, C(PPh₃)₂), 119.4 ('apparent triplet AA'X, $^1J_{PC}$ + $^3J_{PC}$ = 94 MHz, *ipso*-C, Ph of C(PPh₃)₂), 130.9 (*p*-C, Ph of C(PPh₃)₂), 133.8 (t, $^3J_{PC}$ = 5.8 Hz, *o*-C, Ph of C(PPh₃)₂), 137.7 (*m*-C, Ph of C(PPh₃)₂) ppm. ^{31}P { ^1H } NMR (161 MHz, CD₂Cl₂, 20°C): δ_P 26.0 (second order doublet, P_{carbonyl}), 360.4 (second order triplet, P_{central}) ppm.

Counterions. AlCl₄⁻: ^{27}Al NMR (104 MHz, CD₂Cl₂, 20°C): δ 106.4 ppm. [BAr^F₄]⁻: ^1H NMR (400 MHz, CD₂Cl₂, 20°C): δ 7.3-7.9 (24H, Ph) ppm. ^{13}C { ^1H } NMR (100 MHz, CD₂Cl₂, 20°C): δ 117.5 (*p*-C), 124.6 (q, $^1J_{CF}$ = 272 Hz, CF₃), 128.9 (q, $^2J_{CF}$ = 35 Hz, *m*-C), 137.1 (*o*-C), 161.8 (q, $^1J_{CB}$ = 50 Hz, *ipso*-C) ppm. ^{11}B { ^1H } NMR (161 MHz, CD₂Cl₂, 20°C): δ_B - 7.6. ^{19}F { ^1H } NMR (376 MHz, CD₂Cl₂, 20°C): δ_F - 62.8 ppm.

Preparation of $[\text{Me}_3\text{P}\cdot\text{PPhC}(\text{PPh}_3)_2][\text{BAr}^{\text{F}}_4]_2$, $[\text{3e}^{2+}\cdot\text{PMe}_3][\text{BAr}^{\text{F}}_4]_2$. 120 mg (0.167 mmol) of $[\text{2e}^+]\text{Cl}$ was dissolved in about 10 ml of 1,2-difluorobenzene followed by the addition of 1 equiv of PMe_3 and 2.1 equiv of $\text{NaBAr}^{\text{F}}_4$. The reaction mixture was stirred for 6 h followed by filtration and removal of all volatilities. Yield 0.214 g (59 %). Few crystals suitable for single crystal X-ray diffraction were obtained by re-dissolving the solid in 1,2-difluorobenzene and layering with hexane. ^1H NMR (CD_2Cl_2 , 400 MHz): δ 1.13 (dd, $^2J_{\text{PH}} = 13$ Hz, $^3J_{\text{PH}} = 5$ Hz, 9H, PMe_3), 7.0-8.0 (35H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): δ 11.7 (dd, $^1J_{\text{PC}} = 40$ Hz, $^2J_{\text{PC}} = 14$ Hz, PMe_3), 117.7 (*p*-C, $\text{BAr}^{\text{F}}_4^-$), 123.4 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 92$ Hz, *ipso*-C, $\text{Ph}_{(\text{carbone})}$), 128-130 (*o*-, *m*- and *p*-C, Ph), 124.8 (q, $^1J_{\text{CF}} = 271$ Hz, CF_3 , $\text{BAr}^{\text{F}}_4^-$), 129.0 (q, $^2J_{\text{CF}} = 15$ Hz, *m*-C, $\text{BAr}^{\text{F}}_4^-$), 130.1 (virtual triplet, *o*-C, $\text{Ph}_{(\text{carbone})}$), 134.3 (s, *p*-C, $\text{Ph}_{(\text{carbone})}$), 135.0 (*o*-C of $\text{BAr}^{\text{F}}_4^-$ and *m*-C of $\text{Ph}_{(\text{carbone})}$), 162.2 (*ipso*-C, $^1J_{\text{CB}} = 50$ Hz, $\text{BAr}^{\text{F}}_4^-$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202 MHz): δ -6.4 (second order dt, $P_{(\text{central})}$), 11.4 (second order dt, PMe_3), 28.7 (second order d, $P_{(\text{carbone})}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 160 MHz): δ -7.5 (s). ^{19}F NMR (CD_2Cl_2 , 470 MHz): δ -62.5 (s, CF_3).

Reaction between $[\text{}^i\text{Pr}_2\text{NPCI}]^+ / [(\text{}^i\text{Pr}_2\text{N})_2\text{P}]^+$ and H_2O . Both phosphonium cations have been prepared and used in situ (J. Young NMR tube). $[\text{}^i\text{Pr}_2\text{NPCI}][\text{AlCl}_4]$, **4**, was prepared by reacting 0.020 g (0.10 mmol) $^i\text{Pr}_2\text{NPCI}_2$ of with 1 equiv of AlCl_3 in 1 mL of DCM while $[(\text{}^i\text{Pr}_2\text{N})_2\text{P}][\text{BAr}^{\text{F}}_4]$, **5**, by reacting 0.020 g (0.075 mmol) of $(\text{}^i\text{Pr}_2\text{N})_2\text{PCl}$ with 1 equiv of $\text{Na}[\text{BAr}^{\text{F}}_4]$ in 1 mL of DCM. The second reaction was filtered to remove NaCl . The formation of the target phosphonium was confirmed by ^{31}P NMR spectroscopy. To the solutions of both cations 1 equiv of H_2O (diluted in CH_2Cl_2 , 0.110 M) was added and the reaction progression in was followed by ^{31}P NMR spectroscopy. The ^{31}P NMR spectra for each reaction taken immediately after water addition and after 72h were virtually the

same. [$^i\text{Pr}_2\text{NPCl}$][AlCl_4]/ H_2O : ^{31}P NMR (CH_2Cl_2 , 161 MHz, 25°C): δ 21.1 (d, $^1J_{\text{PH}} = 718$ Hz), 170.3 (s, potentially $^i\text{Pr}_2\text{NPCl}_2$), 220.1 (s); ^{27}Al NMR (CH_2Cl_2 , 103 MHz, 25°C): δ 91.1 (s), 95.0 (br), 106.4 (s, $[\text{AlCl}_4]^-$). [$^i\text{Pr}_2\text{N}$] ^+P][BAr^{F}_4]/ H_2O : ^{31}P NMR (CH_2Cl_2 , 161 MHz, 25°C): δ 5.72 (d, $^1J_{\text{PH}} = 553$ Hz), 324.2 (s, unreacted phosphonium cation).

Preparation of [$^i\text{Pr}_2\text{NPPPh}_2(\text{C}_6\text{H}_4)\text{C}(\text{PPh}_3)$][BAr^{F}_4], [6^+][BAr^{F}_4]. Quantitative conversion of [3a^{2+}][BAr^{F}_4] $_2$ to [6^+][BAr^{F}_4] is achieved by adding 10 mL of difluorobenzene solution to 1.0 equiv (0.1 g, 0.042 mmol) of [3a^{2+}][BAr^{F}_4] $_2$ and 1.2 equiv (0.009 g, 0.050 mmol) of cobaltocene. The reaction was stirred overnight and layered with hexane to precipitate the impurities. The solution was decanted and the solvent was removed under reduced pressure. Yield 0.03 g (46%). The crystals suitable for single crystal X-ray diffraction were obtained from a saturated difluorobenzene solution. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2 , 20°C): δ 25.7 (dd, $^2J_{\text{PP}} = 113.9\text{ Hz}$, $^2J_{\text{PP}} = 50.6\text{ Hz}$, PPh_3), 40.9 (dd, $^2J_{\text{PP}} = 50.6\text{ Hz}$, $^2J_{\text{PP}} = 25.3\text{ Hz}$, $\text{PPh}_2(\text{C}_6\text{H}_4)$), 66.4 (dd, $^2J_{\text{PP}} = 113.9\text{ Hz}$, $^2J_{\text{PP}} = 25.3\text{ Hz}$, P(central)). Insufficient product was obtained for further NMR and ES-MS studies.

Preparation of [$\text{PhP}(\text{C}(\text{CH}_3)_2\text{C}(\text{PPh}_3)_2$][AlCl_4] $_2$ (THF), [7e^{2+}][AlCl_4] $_2$ (THF). Quantitative conversion of [2e^+][Cl] to [7e^{2+}][AlCl_4] $_2$ is achieved by adding 60 mL dichloromethane (DCM) solution to 1.0 equiv (1.0 g, 1.40 mmol) of [2e^+][Cl], 2.5 equiv (0.47 g, 3.50 mmol) of AlCl_3 and 1.0 equiv (0.11 mL, 1.40 mmol) of 2-butyne. The reaction mixture was stirred for 30 min. Solvent removal under reduced pressure, followed by washing with 10 mL of diethyl ether 3 times yielded a mixture of [7e^{2+}][AlCl_4] $_2$ and protonated carbene. Tetrahydrofuran (THF) was then added to the mixture to precipitate the protonated carbene. Filtration and removal of solvent under

reduced pressure yielded the pure product. Yield = 0.9g (62 %). The crystals suitable for single crystal X-ray diffraction were grown out of DCM solution layered with pentane. ^1H NMR (300 MHz, CD_2Cl_2 , 20°C): δ 1.75 (br, 4H, THF- β - CH_2), 1.82 (d, $^2J_{\text{HP}} = 7.81\text{Hz}$, 6H, $(\text{C}(\text{CH}_3))_2$), 3.72 (br, 4H, THF- α - CH_2), 7.3-7.8 (Ph, 35H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2 , 20°C): δ 10.74 (s, $(\text{C}(\text{CH}_3))_2$), 25.7 (s, THF), 68.3 (s, THF), 120.8 (d, $^1J_{\text{CP}} = 94.4\text{Hz}$, ipso-C of carbene Ph), 126.13 (d, $^1J_{\text{CP}} = 105.9\text{Hz}$, ipso-C of Ph), 130.8 (second order triplet, o-C of carbene Ph), 131.5 (d, $^2J_{\text{CP}} = 6.0\text{Hz}$, o-C of Ph), 132.2 (d, $^1J_{\text{CP}} = 13.9\text{Hz}$, $(\text{C}(\text{CH}_3))_2$), 133.8 (d, $^3J_{\text{CP}} = 5.7\text{Hz}$, m-C of Ph), 134.4 (second order triplet, m-C of carbene Ph), 135.0 (d, $^4J_{\text{CP}} = 4.0\text{Hz}$, p-C of Ph), 135.9 (br, p-C of carbene Ph), C(carbene) not observed. Note: THF peaks were present in the spectra and all attempts to pump them away were unsuccessful. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2 , 20°C): δ -101.7 (t, $^2J_{\text{PP}} = 20.3\text{Hz}$, P(central)), 26.4 (d, $^2J_{\text{PP}} = 20.3\text{Hz}$, P(carbene)). ES-MS calcd. for $[\text{C}_{47}\text{H}_{41}\text{P}_3]^{2+}$ (**7e** $^{2+}$): m/z 349.1205; found: 349.1721.

Preparation of $[\text{PCl}(\text{C}(\text{CH}_3))_2\text{C}(\text{PPh}_3)_2][\text{AlCl}_4]_2$, $[\mathbf{7g}^{2+}][\text{AlCl}_4]_2$. Quantitative conversion of $[\mathbf{2g}^+][\text{Cl}]$ to $[\mathbf{7g}^{2+}][\text{AlCl}_4]_2$ is achieved by adding 60 mL dichloromethane (DCM) solution to 1.0 equiv (1.0g, 1.48 mmol) of $[\mathbf{2g}^+][\text{Cl}]$, 2.5 equiv (0.49g, 3.70 mmol) of AlCl_3 and 1.2 equiv (0.14 mL, 1.78 mmol) of 2-butyne. The reaction mixture was stirred for 30 min. Removal of solvent under reduced pressure yielded the pure product. Yield = 0.8g (54%). ^1H NMR (300 MHz, CD_2Cl_2 , 20°C): δ 1.73 (d, 6H, $^2J_{\text{HP}} = 25.2\text{Hz}$, $(\text{C}(\text{CH}_3))_2$), 7.4-7.8 (Ph, 30H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2 , 20°C): δ 11.8 (d, $^2J_{\text{CP}} = 2.6\text{Hz}$, $(\text{C}(\text{CH}_3))_2$), 119.5 (d, $^1J_{\text{CP}} = 95.3\text{Hz}$, ipso-C of carbene Ph), 131.2 (second order triplet, m-C of carbene Ph), 134.4 (second order triplet, o-C of carbene Ph), 136.3 (br, p-C of carbene Ph), 151.8 (second order doublet of triplet, $(\text{C}(\text{CH}_3))_2$), C(carbene) not observed. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2 , 20°C): δ 25.2 (d, $^2J_{\text{PP}} = 21.1\text{Hz}$,

P(carbone)), -69.8 (t, $^2J_{PP} = 21.1\text{Hz}$, P(central)). ES-MS calcd. for $[\text{C}_{41}\text{H}_{36}\text{ClP}_3]^{2+}$ (**7g** $^{2+}$): m/z 328.0854; found: 328.0851.

Preparation of $[\text{P}(\text{C}(\text{CH}_3)_2\text{C}(\text{PPh}_3)_2][\text{AlCl}_4]$, $[\mathbf{8g}^+][\text{AlCl}_4]$. Quantitative conversion of $[\mathbf{7g}^{2+}][\text{AlCl}_4]_2$ to $[\mathbf{8g}^+][\text{AlCl}_4]$ is achieved by adding 60 mL tetrahydrofuran (THF) solution to 1.0 equiv (1.0g, 1.00 mmol) of $[\mathbf{7g}^{2+}][\text{AlCl}_4]_2$ and 10.0 equiv (0.24g, 10.00 mmol) of Magnesium. The reaction mixture was sonicated for an hour. Filtration and removal of solvent under reduced pressure yielded the pure product. Yield = 0.6g (76 %). The crystals suitable for single crystal X-ray diffraction were obtained from a saturated THF solution of $[\mathbf{8g}^+][\text{AlCl}_4]$. ^1H NMR (395.9 MHz, CD_2Cl_2 , 25°C): δ 1.50 (br, 6H, $(\text{C}(\text{CH}_3)_2)_2$), 7.2-7.5 (Ph, 30H). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, CD_2Cl_2 , 25°C): δ 11.2 (d, $^2J_{CP} = 8.6\text{Hz}$, $(\text{C}(\text{CH}_3)_2)_2$), 127.1 (d, $^1J_{CP} = 95.6\text{Hz}$, ipso-C of carbone Ph), 129.2 (second order doublet of triplet, o-C of carbone Ph), 133.0 (second order triplet, m-C of carbone Ph), 134.2 (br, p-C of carbone Ph), 137.6 (d, 12.4 Hz, $(\text{C}(\text{CH}_3)_2)_2$), C(carbone) not observed. $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, $\text{C}_4\text{D}_8\text{O}$, 25°C): δ 26.0 (d, $^2J_{PP} = 34.9\text{Hz}$, P(carbone)), -138.5 (t, $^2J_{PP} = 34.9\text{Hz}$, P(central)). ES-MS calcd. for $[\text{C}_{41}\text{H}_{36}\text{P}_3]^+$ (**8g** $^+$): m/z 626.2024; found: 626.2026.

Preparation of $[\text{PhP}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{PPh}_3)_2][\text{AlCl}_4]_2$, $[\mathbf{9e}^{2+}][\text{AlCl}_4]_2$. Quantitative conversion of $[\mathbf{2e}^+][\text{Cl}]$ to $[\mathbf{9e}^{2+}][\text{AlCl}_4]_2$ is achieved by adding 60 mL dichloromethane (DCM) solution to 1.0 equiv (1.0g, 1.40 mmol) of $[\mathbf{2e}^+][\text{Cl}]$, 2.5 equiv (0.47g, 3.50 mmol) of AlCl_3 and 1.0 equiv (0.16 mL, 1.40 mmol) of 2,3-dimethyl-1,3-butadiene. The reaction mixture was stirred for 30 min. Solvent removal under reduced pressure, followed by washing with 10mL of diethyl ether 3 times yielded a mixture of $[\mathbf{9e}^{2+}][\text{AlCl}_4]_2$ and protonated carbone. Tetrahydrofuran (THF) was then added to the mixture to precipitate

the protonated carbene. Filtration and removal of solvent under reduced pressure yielded the pure product. Yield = 0.95g (64 %). The crystals suitable for single crystal X-ray diffraction were grown out of DCM solution layered with pentane. ^1H NMR (300 MHz, CD_2Cl_2 , 20°C): δ 1.57 (br, 6H, $(\text{CH}_2\text{C}(\text{CH}_3))_2$), 1.82 (br, 4H, THF- β - CH_2), 2.47 (dd, $^1J_{\text{HP}} = 19.5\text{Hz}$, $^3J_{\text{HP}} = 10.5\text{Hz}$, 2H at carbene side), 3.39 (dd, $^1J_{\text{HP}} = 18.0\text{Hz}$, $^3J_{\text{HP}} = 9.0\text{Hz}$, 2H at Ph side), 3.68 (br, 4H, THF- α - CH_2), 7.4-7.8 (Ph, 35H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2 , 20°C): δ 15.9 (d, $^3J_{\text{CP}} = 13.6\text{Hz}$, $(\text{C}(\text{CH}_3))_2$), 25.7 (s, THF), 43.0 (d, $^1J_{\text{CP}} = 56.6\text{Hz}$, $\text{P}(\text{CH}_2)_2$), 67.9 (s, THF), 121.5 (d, $^1J_{\text{CP}} = 93.3\text{Hz}$, ipso-C of carbene Ph), 126.2 (d, $^1J_{\text{CP}} = 83.8\text{Hz}$, ipso-C of Ph), 128.7 (d, $^2J_{\text{CP}} = 7.6\text{Hz}$, $(\text{C}(\text{CH}_3)_2)_2$), 129.7 (d, $^2J_{\text{CP}} = 9.8\text{Hz}$, o-C of Ph), 130.7 (second order triplet, m-C of carbene Ph), 131.0 (d, $^3J_{\text{CP}} = 13.6\text{Hz}$, m-C of Ph), 134.5 (second order triplet, o-C of carbene Ph), 134.9 (d, $^4J_{\text{CP}} = 3.0\text{Hz}$, p-C of Ph), 135.5 (br, p-C of carbene Ph), C(carbene) not observed. Note: THF peaks were present in the spectra and all attempts to pump them away were unsuccessful. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2 , 20°C): δ 25.5 (d, $^2J_{\text{PP}} = 18.7\text{Hz}$, $\text{P}(\text{carbene})$), 32.2 (t, $^2J_{\text{PP}} = 18.7\text{Hz}$, $\text{P}(\text{central})$). ES-MS calcd. for $[\text{C}_{49}\text{H}_{45}\text{P}_3]^{2+}$ (9e^{2+}): m/z 363.1362; found: 363.1364.

Preparation of $[\text{CIP}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{PPh}_3)_2][\text{AlCl}_4]_2$, $[\mathbf{9g}^{2+}][\text{AlCl}_4]_2$. Quantitative conversion of $[\mathbf{2g}^+][\text{Cl}]$ to $[\mathbf{9g}^{2+}][\text{AlCl}_4]_2$ is achieved by adding 60 mL dichloromethane (DCM) solution to 1.0 equiv (1.0g, 1.48 mmol) of $[\mathbf{2g}^+][\text{Cl}]$, 2.5 equiv (0.49g, 3.70 mmol) of AlCl_3 and 1.2 equiv (0.20 mL, 1.78 mmol) of 2,3-dimethyl-1,3-butadiene. The reaction mixture was stirred for 30 min. Removal of solvent under reduced pressure yielded the pure product. Yield = 0.7g (46%). ^1H NMR (300 MHz, CD_2Cl_2 , 20°C): δ 1.55 (br, 6H, $(\text{CH}_2\text{C}(\text{CH}_3))_2$), 1.76 (br, 2H at carbene side), 3.29 (d, $^2J_{\text{HP}} = 18.2\text{Hz}$, 2H at Cl side), 7.6-7.8 (Ph, 30H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2 , 20°C): δ 15.9 (d, $^3J_{\text{CP}} = 16.0\text{Hz}$,

(C(CH₃))₂), 47.2 (d, ¹J_{CP} = 60.3Hz, P(CH₂)₂), 119.6 (d, ¹J_{CP} = 93.7Hz, ipso-C of carbone Ph), 127.1 (d, ²J_{CP} = 10.8Hz, (C(CH₃)₂)₂), 131.0 (second order triplet, m-C of carbone Ph), 134.8 (second order triplet, o-C of carbone Ph), 136.2 (br, p-C of carbone Ph), C(carbone) not observed. ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 20°C): δ 24.9 (d, ²J_{PP} = 13.4Hz, P(carbone)), 88.9 (t, ²J_{PP} = 13.4Hz, P(central)). ES-MS: All attempts to detect this dication were unsuccessful due to hydrolysis of the product.

Preparation of [P(ChC(CH₃))₂C(PPh₃)₂][AlCl₄], [10g⁺][AlCl₄]. Quantitative conversion of [9g²⁺][AlCl₄]₂ to [10g⁺][AlCl₄] is achieved by adding 60 mL dichloromethane (DCM) solution to 1.0 equiv (1.0g, 0.98 mmol) of [9²⁺][AlCl₄]₂, followed by 2.0 equiv (0.19 mL, 1.96 mmol) of 2-picoline. The reaction mixture was stirred for 30 min. Removal of solvent under reduced pressure yielded the pure product. Yield = 0.5g (63%). The crystals suitable for single crystal X-ray diffraction were grown out of DCM solution layered with pentane. It was difficult to remove the slight excess of 2-picoline present. Heating at 40 °C under vacuum overnight did not result in any improvement. Attempts to remove excess 2-picoline at 60°C overnight decomposed the product. ¹H NMR (395.9 MHz, CD₂Cl₂, 25°C): δ 1.58 (d, ²J_{HP} = 5.5Hz, 6H, (ChC(CH₃))₂), 2.91 (br, CHP), 6.10 (d, ¹J_{HP} = 38.1 Hz, 2H, (PChC(CH₃)₂), 7.4-7.6 (Ph, 30H). ¹³C{¹H} NMR (99.5 MHz, CD₂Cl₂, 25°C): δ 17.1 (d, ⁴J_{CP} = 5.7Hz, (C(CH₃))₂), 125.0 (d, ¹J_{CP} = 96.3Hz, ipso-C of carbone Ph), 129.0 (second order triplet, m-C of carbone Ph), 133.3 (br, p-C of carbone Ph), 134.0 (second order triplet, o-C of carbone Ph), 134.6 (br, (PChC(CH₃)₂), 154.1 (br, PChC(CH₃)₂), C(carbone) not observed. ³¹P{¹H} NMR (160.3 MHz, CD₂Cl₂, 25°C): δ -13.5 (t, ²J_{PP} = 59.5Hz, P(central)), 25.2 (d, ²J_{PP} = 59.5Hz, P(carbone)). ES-MS calcd. for [C₄₃H₃₈P₃]⁺ (10g⁺): m/z 647.2181; found: 647.1960.

Section 5.6. Figures and Tables of X-ray Crystallographic Data

Figure 5.2. Molecular structure of $[i\text{Pr}_2\text{NPCl}(\text{C}(\text{PPh}_3)_2)]^+[\text{AlCl}_4]^-$, $[2a^+][\text{AlCl}_4]^-$. Ellipsoids set at 50% probability. For clarity, only one of the asymmetric units is shown and the $[\text{AlCl}_4]^-$ counterion together with hydrogen atoms have been omitted for clarity.

Table 5.2. Crystal data and structure refinement for [*i*Pr₂NPClC(PPh₃)₂][AlCl₄], [2a⁺][AlCl₄].

Identification code	dv87	
Empirical formula	C ₈₆ H ₈₉ Al ₂ Cl ₁₀ N ₂ P ₆	
Formula weight	1744.87	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.4253(10) Å	α = 94.175(3)°.
	b = 15.6778(15) Å	β = 91.888(3)°.
	c = 22.844(2) Å	γ = 91.116(3)°.
Volume	4434.7(7) Å ³	
Z	2	
Density (calculated)	1.307 Mg/m ³	
Absorption coefficient	0.486 mm ⁻¹	
F(000)	1810	
Crystal size	0.36 x 0.34 x 0.18 mm ³	
Theta range for data collection	1.63 to 26.53°.	
Index ranges	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -27 ≤ l ≤ 28	
Reflections collected	60062	
Independent reflections	18161 [R(int) = 0.0749]	
Completeness to theta = 26.53°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9176 and 0.8444	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	18161 / 0 / 963	
Goodness-of-fit on F ²	1.093	
Final R indices [I > 2σ(I)]	R1 = 0.0816, wR2 = 0.2251	
R indices (all data)	R1 = 0.1227, wR2 = 0.2508	
Largest diff. peak and hole	1.356 and -1.155 e.Å ⁻³	

Figure 5.3. Molecular structure of $[\text{Cy}_2\text{NPClC}(\text{PPh}_3)_2][\text{BAr}^{\text{F}}_4]$, $[2\text{c}^+][\text{BAr}^{\text{F}}_4]$. Ellipsoids set at 50% probability. For clarity, only one of the $[\text{BAr}^{\text{F}}_4]^-$ counterions together with hydrogen atoms have been omitted for clarity.

Table 5.3. Crystal data and structure refinement for [Cy₂NPClC(PPh₃)₂][BAr^F₄], [2c⁺][BAr^F₄].

Identification code	dv79	
Empirical formula	C ₈₁ H ₆₄ B Cl F ₂₄ N P ₃	
Formula weight	1646.50	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.2522(11) Å	α = 110.232(2)°.
	b = 16.1257(11) Å	β = 103.504(2)°.
	c = 21.1731(18) Å	γ = 96.434(2)°.
Volume	3730.4(5) Å ³	
Z	2	
Density (calculated)	1.466 Mg/m ³	
Absorption coefficient	0.222 mm ⁻¹	
F(000)	1680	
Crystal size	0.40 x 0.32 x 0.26 mm ³	
Theta range for data collection	1.07 to 25.00°.	
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -25 ≤ l ≤ 25	
Reflections collected	54505	
Independent reflections	13122 [R(int) = 0.0546]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9445 and 0.9164	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13122 / 145 / 1002	
Goodness-of-fit on F ²	1.290	
Final R indices [I > 2σ(I)]	R1 = 0.0536, wR2 = 0.1560	
R indices (all data)	R1 = 0.0739, wR2 = 0.1834	
Largest diff. peak and hole	1.048 and -0.619 e.Å ⁻³	

Figure 5.4. Molecular structure of $[\text{PCl}_2\text{C}(\text{PPh}_3)_2][\text{AlCl}_4]$, $[2\text{g}^+][\text{AlCl}_4]$. Ellipsoids set at 50% probability. For clarity, and the $[\text{AlCl}_4]^-$ counterion together with hydrogen atoms have been omitted for clarity.

Table 5.4. Crystal data and structure refinement for [PCl₂C(PPh₃)₂][AlCl₄], [2g⁺][AlCl₄].

Identification code	dv89	
Empirical formula	C ₃₇ H ₃₀ Al Cl ₆ P ₃	
Formula weight	807.20	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.7481(5) Å	α = 108.087(2)°.
	b = 11.7348(5) Å	β = 100.841(2)°.
	c = 16.2249(7) Å	γ = 99.951(2)°.
Volume	1851.05(14) Å ³	
Z	2	
Density (calculated)	1.448 Mg/m ³	
Absorption coefficient	0.645 mm ⁻¹	
F(000)	824	
Crystal size	0.40 x 0.20 x 0.16 mm ³	
Theta range for data collection	1.88 to 30.60°.	
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -23 ≤ l ≤ 22	
Reflections collected	35142	
Independent reflections	11282 [R(int) = 0.0594]	
Completeness to theta = 30.60°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9038 and 0.7824	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11282 / 0 / 424	
Goodness-of-fit on F ²	1.060	
Final R indices [I > 2σ(I)]	R1 = 0.0498, wR2 = 0.1144	
R indices (all data)	R1 = 0.0832, wR2 = 0.1411	
Largest diff. peak and hole	0.872 and -0.590 e.Å ⁻³	

Figure 5.5. Molecular structure of $[i\text{Pr}_2\text{NPC}(\text{PPh}_3)_2][\text{AlCl}_4]_2$, $[\mathbf{3a}^{2+}][\text{AlCl}_4]_2$. Ellipsoids set at 50% probability. For clarity, only one of the asymmetric units is shown and the $[\text{AlCl}_4]^-$ counterions together with hydrogen atoms have been omitted for clarity.

Table 5.5. Crystal data and structure refinement for [$\text{Pr}_2\text{NPC}(\text{PPh}_3)_2$][AlCl_4] $_2$, [3a^{2+}][AlCl_4] $_2$.

Identification code	dv85_0t	
Empirical formula	C ₅₅ H ₅₂ Al ₂ Cl ₈ F ₄ N P ₃	
Formula weight	1233.45	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 16.809(12) Å	$\alpha = 90.50(2)^\circ$.
	b = 17.553(10) Å	$\beta = 90.082(19)^\circ$.
	c = 21.603(16) Å	$\gamma = 113.53(2)^\circ$.
Volume	5844(7) Å ³	
Z	4	
Density (calculated)	1.402 Mg/m ³	
Absorption coefficient	0.548 mm ⁻¹	
F(000)	2528	
Crystal size	0.38 x 0.22 x 0.14 mm ³	
Theta range for data collection	1.57 to 25.00°.	
Index ranges	-19 ≤ h ≤ 19, -20 ≤ k ≤ 20, 0 ≤ l ≤ 25	
Reflections collected	26908	
Independent reflections	26908 [R(int) = 0.0000]	
Completeness to theta = 25.00°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9273 and 0.8189	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	26908 / 186 / 1370	
Goodness-of-fit on F ²	1.018	
Final R indices [I > 2σ(I)]	R1 = 0.0727, wR2 = 0.1717	
R indices (all data)	R1 = 0.1149, wR2 = 0.2017	
Largest diff. peak and hole	0.820 and -0.607 e.Å ⁻³	

Figure 5.6. Molecular structure of $[i\text{Pr}_2\text{NP}(\text{H})\text{OHNET}_3\text{C}(\text{PPh}_3)_2][\text{BAr}^{\text{F}}_4]_2$, $[\text{3a}^{2+} \cdot (\text{H})\text{O} \cdots \text{HNET}_3][\text{BAr}^{\text{F}}_4]_2$. Ellipsoids set at 50% probability. For clarity, the $[\text{BAr}^{\text{F}}_4]^-$ counterions together with hydrogen atoms have been omitted for clarity.

Table 5.6. Crystal data and structure refinement for [Pr₂NP(H)OHNEt₃(C(PPh₃)₂)[BAr^F₄]₂, [3a²⁺-(H)O--HNEt₃][BAr^F₄]₂.		
Identification code	dv141s	
Chemical formula	C _{114.75} H _{88.50} B ₂ Cl _{3.50} F ₄₈ N ₂ OP ₃	
Formula weight	2661.98	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.320 x 0.380 x 0.400 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 15.0786(8) Å	α = 78.026(2)°
	b = 16.6056(8) Å	β = 82.727(2)°
	c = 24.0728(11) Å	γ = 86.888(2)°
Volume	5846.5(5) Å ³	
Z	2	
Density (calculated)	1.512 g/cm ³	
Absorption coefficient	0.258 mm ⁻¹	
F(000)	2691	
Theta range for data collection	1.25 to 28.39°	
Index ranges	-20 ≤ h ≤ 20, -22 ≤ k ≤ 22, -32 ≤ l ≤ 31	
Reflections collected	127668	
Independent reflections	29190 [R(int) = 0.0659]	
Max. and min. transmission	0.9220 and 0.9040	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(F _o ² - F _c ²) ²	
Data / restraints / parameters	29190 / 5491 / 2301	
Goodness-of-fit on F ²	1.065	
Δ/σ _{max}	0.005	
Final R indices	17689 data; I > 2σ(I)	R1 = 0.0862, wR2 = 0.2299
	all data	R1 = 0.1444, wR2 = 0.2742
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.1159P) ² + 15.9839P] where P = (F _o ² + 2F _c ²)/3	
Largest diff. peak and hole	1.294 and -0.981 eÅ ⁻³	
R.M.S. deviation from mean	0.107 eÅ ⁻³	

Figure 5.7. Molecular structure of $[\text{Cy}_2\text{NPC}(\text{PPh}_3)_2][\text{AlCl}_4]_2$, $[\text{3c}^{2+}][\text{AlCl}_4]_2$. Ellipsoids set at 50% probability. For clarity, only one of the asymmetric units is shown and the $[\text{AlCl}_4]^-$ counterions together with hydrogen atoms have been omitted for clarity.

Table 5.7. Crystal data and structure refinement for [Cy₂NP(C(PPh₃)₂)[AlCl₄]₂, [3c²⁺][AlCl₄]₂.

Identification code	dv123s
Chemical formula	C ₁₁₀ H ₁₁₃ Al ₄ Cl ₁₆ F ₄ N ₂ P ₆
Formula weight	2399.96
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.380 x 0.380 x 0.400 mm
Crystal habit	colorless block
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 18.0978(8) Å α = 90° b = 34.1490(13) Å β = 103.9510(10)° c = 19.2540(7) Å γ = 90°
Volume	11548.4(8) Å ³
Z	4
Density (calculated)	1.380 g/cm ³
Absorption coefficient	0.547 mm ⁻¹
F(000)	4948
Theta range for data collection	1.16 to 29.21°
Index ranges	-18 ≤ h ≤ 24, -46 ≤ k ≤ 46, -24 ≤ l ≤ 26
Reflections collected	92486
Independent reflections	30787 [R(int) = 0.0712]
Coverage of independent reflections	98.3%
Absorption correction	multi-scan
Max. and min. transmission	0.8190 and 0.8108
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	30787 / 0 / 1279
Goodness-of-fit on F ²	1.051
Δ/σ _{max}	0.001
Final R indices	18254 data; I > 2σ(I) R1 = 0.0570, wR2 = 0.1318 all data R1 = 0.1171, wR2 = 0.1796
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0797P) ² + 0.0000P] where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	0.872 and -1.157 eÅ ⁻³
R.M.S. deviation from mean	0.146 eÅ ⁻³

Figure 5.8. Molecular view of $[3e^{2+} \cdot PMe_3][BAr^F_4]_2$. Ellipsoids set at 50% probability. For clarity, the $[BAr^F_4]^-$ counterions together with hydrogen atoms have been omitted for clarity.

Table 5.8. Crystal data and structure refinement for [3e²⁺·PMe₃][BAr^F₄]₂.

Identification code	dv78_sq
Empirical formula	C110 H68 B2 F48 P4
Formula weight	2447.14
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 13.4628(7) Å α = 84.742(2)°. b = 17.6007(10) Å β = 81.149(2)°. c = 24.4781(15) Å γ = 80.723(2)°.
Volume	5642.9(6) Å ³
Z	2
Density (calculated)	1.440 Mg/m ³
Absorption coefficient	0.193 mm ⁻¹
F(000)	2460
Crystal size	0.320 x 0.270 x 0.220 mm ³
Theta range for data collection	1.40 to 28.33°.
Index ranges	-17<=h<=14, -22<=k<=23, -32<=l<=32
Reflections collected	91093
Independent reflections	27611 [R(int) = 0.0850]
Completeness to theta = 28.33°	98.2 %
Absorption correction	None
Max. and min. transmission	0.96 and 0.94
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	27611 / 672 / 1654
Goodness-of-fit on F ²	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0829, wR2 = 0.1975
R indices (all data)	R1 = 0.1520, wR2 = 0.2389
Largest diff. peak and hole	1.052 and -0.680 e.Å ⁻³

Figure 5.9. Molecular structure of $[\text{Pr}_2\text{NPPPh}_2(\text{C}_6\text{H}_4)\text{C}(\text{PPh}_3)]^+[\text{BARF}_4]^-$, $[\mathbf{6}]^+[\text{BARF}_4]^-$. Ellipsoids set at 50% probability. For clarity, the $[\text{BARF}_4]^-$ counterion together with hydrogen atoms have been omitted for clarity.

Table 5.9. Crystal data and structure refinement for [Pr₂NPPPh₂(C₆H₄)C(PPh₃)] [Bar^F₄], [6⁺][Bar^F₄].

Identification code	dv55	
Empirical formula	C ₇₈ H _{57.50} B F _{24.50} N P ₃	
Formula weight	1577.97	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 19.3811(9) Å	α = 90°.
	b = 15.0133(8) Å	β = 99.281(3)°.
	c = 25.5121(13) Å	γ = 90°.
Volume	7326.2(6) Å ³	
Z	4	
Density (calculated)	1.431 Mg/m ³	
Absorption coefficient	0.188 mm ⁻¹	
F(000)	3212	
Crystal size	0.18 x 0.14 x 0.14 mm ³	
Theta range for data collection	1.58 to 27.12°.	
Index ranges	-24 ≤ h ≤ 24, -19 ≤ k ≤ 19, -32 ≤ l ≤ 32	
Reflections collected	65997	
Independent reflections	16161 [R(int) = 0.1661]	
Completeness to theta = 27.12°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9741 and 0.9669	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	16161 / 881 / 1212	
Goodness-of-fit on F ²	0.941	
Final R indices [I > 2σ(I)]	R1 = 0.0766, wR2 = 0.1783	
R indices (all data)	R1 = 0.2045, wR2 = 0.2543	
Largest diff. peak and hole	0.640 and -0.594 e.Å ⁻³	

Figure 5.10. Molecular structure of $[\text{PhP}(\text{C}(\text{CH}_3))_2(\text{C}(\text{PPh}_3)_2)][\text{AlCl}_4]_2$, $[\text{7e}^{2+}][\text{AlCl}_4]_2$. Ellipsoids set at 50% probability. For clarity, only one of the asymmetric units is shown and the $[\text{AlCl}_4]^-$ counterions together with hydrogen atoms have been omitted for clarity. A molecule of *n*-pentane was removed from the crystal structure of 7e^{2+} using "squeeze".

Table 5.10. Crystal data and structure refinement for [PhP(C(CH₃))₂C(PPh₃)₂][AlCl₄]₂, [7e²⁺][AlCl₄]₂.

Compound	mt111_a_sq
Molecular formula	C ₄₇ H ₄₁ P ₃ ,2(AlCl ₄), C ₄ H ₈ O
Molecular weight	1108.37
Crystal habit	colorless plate
Crystal dimensions(mm)	0.400x0.400x0.220
Crystal system	triclinic
Space group	P -1
a(Å)	15.0412(4)
b(Å)	18.2160(4)
c(Å)	21.3292(4)
α(°)	110.058(1)
β(°)	94.924(1)
γ(°)	102.001(1)
V(Å ³)	5290.4(2)
Z	4
d(g·cm ⁻³)	1.392
F(000)	2280
μ(cm ⁻¹)	0.587
Absorption corrections	multi-scan; 0.878095 min, 1.26491 max
Diffractometer	Kappa APEX II
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.483
HKL ranges	-19 19 ; -23 14 ; -27 27
Reflections measured	54116
Unique data	23473
Rint	0.0465
Reflections used	19081
Criterion	I > 2σ(I)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	1085
Reflections / parameter	17
wR2	0.1725
R1	0.0760
Weights a, b	0.0337 ; 19.815
GoF	1.141
difference peak / hole (e Å ⁻³)	1.117(0.091) / -0.605(0.091)

Figure 5.11. Molecular structure of $[\text{P}(\text{C}(\text{CH}_3)_2\text{C}(\text{PPh}_3)_2)]^+[\text{AlCl}_4]^-$, $[\text{8g}^+][\text{AlCl}_4]^-$. Ellipsoids set at 50% probability. For clarity, the $[\text{AlCl}_4]^-$ counterion together with hydrogen atoms have been omitted for clarity.

Table 5.11. Crystal data and structure refinement for [P(C(CH₃))₂C(PPh₃)₂][AlCl₄], [8g⁺][AlCl₄].

Compound	mt117_a
Molecular formula	2(C ₄₁ H ₃₆ P ₃) ₂ (AlCl ₄),CH ₂ Cl ₂
Molecular weight	1665.70
Crystal habit	colorless plate
Crystal dimensions(mm)	0.240x0.140x0.100
Crystal system	triclinic
Space group	P -1
a(Å)	10.2394(3)
b(Å)	12.0345(4)
c(Å)	17.3855(5)
α(°)	75.451(2)
β(°)	78.249(2)
γ(°)	80.760(2)
V(Å ³)	2016.61(11)
Z	1
d(g-cm ⁻³)	1.372
F(000)	858
μ(cm ⁻¹)	0.531
Absorption corrections	multi-scan; 0.950279 min, 1.05654 max
Diffractionmeter	Kappa APEX II
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.511
HKL ranges	-12 13 ; -15 15 ; -22 22
Reflections measured	12910
Unique data	8560
R _{int}	0.0327
Reflections used	7372
Criterion	I > 2σ(I)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	462
Reflections / parameter	15
wR ₂	0.1475
R ₁	0.0608
Weights a, b	0.0390 ; 5.2451
GoF	1.056
difference peak / hole (e Å ⁻³)	0.653(0.077) / -1.078(0.077)

Figure 5.12. Molecular structure of $[\text{PhP}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{PPh}_3)_2)]_2[\text{AlCl}_4]_2$, $[\text{9e}^{2+}][\text{AlCl}_4]_2$. Ellipsoids set at 50% probability. For clarity, the $[\text{AlCl}_4]^-$ counterions together with hydrogen atoms have been omitted for clarity.

Table 5.12. Crystal data and structure refinement for [PhP(CH₂C(CH₃))₂C(PPh₃)₂][AlCl₄]₂, [9e²⁺][AlCl₄]₂.

Compound	mt94_a
Molecular formula	C ₄₉ H ₄₅ P ₃ ,2(AlCl ₄)
Molecular weight	1064.32
Crystal habit	colorless block
Crystal dimensions(mm)	0.400x0.400x0.360
Crystal system	monoclinic
Space group	P 2 ₁ /c
a(Å)	15.2815(3)
b(Å)	15.9653(4)
c(Å)	21.8282(5)
α(°)	90
β(°)	107.552(1)
γ(°)	90
V(Å ³)	5077.6(2)
Z	4
d(g-cm ⁻³)	1.392
F(000)	2184
μ(cm ⁻¹)	0.607
Absorption corrections	multi-scan; 0.774916 min, 1.21896 max
Diffractometer	Kappa APEX II
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	396(2)
Scan mode	phi and omega scans
Maximum θ	30.029
HKL ranges	-14 20 ; -22 13 ; -30 30
Reflections measured	33123
Unique data	14231
Rint	0.0391
Reflections used	11131
Criterion	I > 2σ(I)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	561
Reflections / parameter	19
wR2	0.1549
R1	0.0668
Weights a, b	0.0401 ; 11.148
GoF	1.080
difference peak / hole (e Å ⁻³)	0.881(0.082) / -0.822(0.082)

Figure 5.13. Molecular structure of $[\text{P}(\text{CHC}(\text{CH}_3)_2\text{C}(\text{PPh}_3)_2)]^+[\text{Cl}]^-$, $[\text{10g}^+][\text{AlCl}_4]^-$. Ellipsoids set at 50% probability. For clarity, the $[\text{AlCl}_4]^-$ counterion together with hydrogen atoms have been omitted for clarity.

Table 5.13. Crystal data for [P(CHC(CH₃))₂C(PPh₃)₂][Cl], [10g⁺][AlCl₄].

Compound	mt112_a
Molecular formula	C ₄₃ H ₃₈ P ₃ AlCl ₄
Molecular weight	816.42
Crystal habit	colorless block
Crystal dimensions(mm)	0.220x0.200x0.200
Crystal system	monoclinic
Space group	P 2 ₁ /n
a(Å)	12.0942(2)
b(Å)	19.5934(3)
c(Å)	17.3142(3)
α(°)	90
β(°)	99.317(1)
α(°)	90
V(Å ³)	4048.76(12)
Z	4
d(g·cm ⁻³)	1.339
F(000)	1688
μ(cm ⁻¹)	0.463
Absorption corrections	multi-scan; 0.899425 min, 1.14339 max
Diffractometer	Kappa APEX II
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.030
HKL ranges	-17 17 ; -27 22 ; -21 24
Reflections measured	40227
Unique data	11740
Rint	0.0492
Reflections used	9332
Criterion	I > 2σ(I)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	468
Reflections / parameter	19
wR2	0.1454
R1	0.0629
Weights a, b	0.0378 ; 7.7585
GoF	1.045
difference peak / hole (e Å ⁻³)	0.937(0.075) / -0.943(0.075)

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Appendix

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ACADEMIC PUBLICATIONS

1. Chapter 4 of thesis, manuscript in preparation.
2. “Preparation, Structural Analysis and Reactivity Studies of Phosphenium Dications”. **Tay, M. Q. Y.**; Ilić, G.; Werner-Zwanziger, U.; Lu, Y.; Ganguly, R.; Ricard, L.; Frison, G.; Carmichael, D.; Vidović, D., *Organometallics*. **2015**, DOI: 10.1021/acs.organomet.5b00763.
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