Synthesis and reactivity of electron-deficient phosphorus(III) compounds

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SYNTHESIS AND REACTIVITY OF
ELECTRON-DEFICIENT PHOSPHORUS(III)
COMPOUNDS**

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School of Physical and Mathematical Sciences

2017

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COMPOUNDS**

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School of Physical and Mathematical Sciences

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partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2017

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Abstract

Our work reflects efforts to increase the Lewis acidity of two-coordinate phosphorus(III)-based compounds for the purpose of small molecule activation. In this view, we tuned the electronic properties of phosphonium ions by increasing their overall positive charge and by varying the extent of π -donation from the neighboring substituents to the central P atom. Synthetic methodology for generation of di- and tricationic phosphonium salts is based on exceptional electron-donating properties of carbene ligands. Initial attempts to generate isolable phenyl- ($[(\text{Ph}_3\text{P})_2\text{C}^+\text{PR}]^{2+}$, R = Ph, **[1a]**²⁺), 4-fluorophenyl- (R = 4-F-Ph, **[1b]**²⁺), methoxy- (R = OMe, **[1e]**²⁺), and *tert*-butyl-substituted (R = ^tBu, **[1d]**²⁺) phosphonium dications stabilized by carbodiphosphorane $(\text{Ph}_3\text{P})_2\text{C}$, **1** are described. Transient formation of **[1a]**²⁺ and **[1b]**²⁺ is evidenced by activating C-F bonds of trifluorotoluene and $[\text{BAr}^{\text{F}}_4]^-$ ($\text{Ar}^{\text{F}} = (\text{CF}_3)_2\text{-C}_6\text{H}_3$) anion. The replacement of carbodiphosphorane **1** with more nucleophilic and sterically less demanding carbodicarbene ligand $\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}$, **2** resulted in a series of P-dications $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{PR}]^{2+}$ (R = NⁱPr₂, Ph, OMe, ^tBu, Cl) whose spectroscopic and structural features are presented. Uniting electron donor capabilities of two carbodicarbene molecules afforded the first example of two-coordinate phosphonium trication $[(\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C})_2\text{P}]^{3+}$, **[(2)₂P]**³⁺ whose interesting bonding features are studied using modern computational methods. In addition to the increased overall positive charge, cooperative enhancement of Lewis acidity by bringing two dicationic P centers in close proximity is also attempted. However, these attempts yielded reaction products derived from an unexpected P-N bond cleavage whose mechanistic details are disclosed. The last portion of this work is focused on the activation of enthalpically strong E-H bonds (E = B, Si, C) using carbodicarbene-stabilized P-dications. Reaction products formally derived from E-H insertion and/or hydride abstraction are isolated and fully characterized. The preference of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{PPh}]^{2+}$, **[2a]**²⁺ and $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{PN}^i\text{Pr}_2]^{2+}$, **[2c]**²⁺ to cleave rather than to insert into Si-H bond, as well as the surprising formation of carbodicarbene-supported parent phosphonium ion $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{PH}_2]^+$, **[2PH₂]**⁺ are experimentally verified.

Biographical Sketch

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- "Bis(carbodicarbene)phosphenium Trication: The Case Against Hypervalency", **Đorđević, N.**; Ganguly, R.; Petković, M.; Vidović, D., Abstract of Papers, Singapore Inorganic Chemistry Symposium – SICS 2016, Singapore, Singapore, July 15, **2016**.
- "Bis(carbodicarbene)phosphenium Trication: The Case Against Hypervalency", **Đorđević, N.**; Ganguly, R.; Petković, M.; Vidović, D. *Chem. Commun.* **2016**, 52, 9789.
- "Chemistry of Electron Deficient Phosphenium Dications", **Đorđević, N.** and Vidović, D., Abstract of Papers, Pure and Applied Chemistry Conference 2016 – PACCON

2016, Bangkok, Thailand, February 9-11, **2016**, BITEC.

- “Extending the Chemistry of Carbenes: P-N Bond Cleavage via an S_N2'-like mechanism”, Gurnani, C.; **Đorđević, N.**; Muthaiah, S.; Dimić, D.; Ganguly, R.; Petković, M.; Vidović, D. *Chem. Commun.* **2015**, 51, 10762.
- “C-F Bond Activation by Transient Phosphenium Dications”, Vidović, D.; **Đorđević, N.**; Tay, M. Q. Y.; Dimić, D.; Muthaiah, S., Abstracts of Papers, 250th ACS National Meeting & Exposition, Boston, MA, United States, August 16-20, **2015**, INOR-212.
- “C-F Bond Activation by Transient Phosphenium Dications”, **Đorđević, N.**; Tay, M. Q. Y.; Muthaiah, S.; Ganguly, R.; Dimić, D.; Vidović, D. *Inorg. Chem.* **2015**, 54, 4180.

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Abbreviations and Symbols

δ	NMR chemical shift in ppm
γ	Valence electron equivalent
η	Eta – ligand coordination through multiple atoms
μL	Microliter
π	Pi
ρ	Electron density
σ	Sigma
∞	Infinity
$^{\circ}$	Degree
$^{\circ}\text{C}$	Degree Celsius
$\text{\AA}$	Angstrom
∇^2	Laplacian
br	Broad
B3LYP	Becke's -3 parameter functional with Lee-Yang-Parr correlation
B3PW91	Becke's -3 parameter functional with Perdew and Wang 91 correlation
calcd	Calculated
d	Doublet
DCM	Dichloromethane
dd	Doublet of doublets
DI	Delocalization index
Dipp	2,6-diisopropylphenyl
dt	Doublet of triplets
E_a	Activation energy
ESI-MS	Electrospray Mass Spectrometry
eV	Electronvolt
FLP	Frustrated Lewis pair

g	Gram
HOMO	Highest occupied molecular orbital
HR-MS	High Resolution Mass Spectrometry
ⁱ Pr	<i>Iso</i> -propyl
<i>in situ</i>	On site
K	Kelvin
kcal	Kilocalorie
kJ	Kilojoule
LUMO	Lowest unoccupied molecular orbital
Me	Methyl
MeO	Methoxy
Mes	Mesityl - 2,4,6-trimethylphenyl
Mes*	Supermesityl - 2,4,6-tri(<i>tert</i> -butyl)phenyl
mg	Milligram
mL	Milliliter
mmol	Millimol
m/z	Mass to charge ratio
NBO	Natural Bond Orbital
NHC	N-heterocyclic carbene
NMR	Nuclear Magnetic Resonance
<i>o</i>	Ortho
<i>p</i>	Para
Ph	Phenyl
ppm	Parts per million
q	Quartet
Q-TOF	Quadruple-time of flight
QTAIM	Quantum theory of atoms in molecules
r	Bond distance
s	Singlet
sept	Septet
S _N 2'	Bimolecular nucleophilic substitution

t	Triplet
^t Bu	<i>Tert</i> -butyl
THF	Tetrahydrofuran
TOF	Time of flight

Legend

Mes = 2,4,6-(Me)₃-C₆H₂

Mes* = 2,4,6-(^tBu)₃-C₆H₂

Dipp = 2,6-(ⁱPr)₂-C₆H₃

CHAPTER 1

Introduction

Section 1.1. General

Since the discovery of the first isolable cationic two-coordinate phosphorus compound by Fleming, Jekot, and Lupton,¹ the chemistry of phosphonium ions has grown rapidly. A term “phosphonium” is used to emphasize a low-coordination number at the positively charged P center.² The central P atom possesses a formally vacant 3p atomic orbital and a lone pair of electrons highlighting the structural parallel between the phosphonium and the more popular carbene molecules.³ It is then not surprising that phosphonium cations exhibit versatile chemistry as both Lewis acids/bases and ligands for transition metal complexes.⁴

In many cases, phosphonium ions were envisaged as reactive intermediates.⁵ Their high reactivity could be mainly attributed to the coordinatively unsaturated nature of the central P atom. Significant efforts were made to develop an adequate substitution pattern that would allow the isolation of phosphonium ions in the condensed phase. Regarding the nature of surrounding groups R, phosphonium cations could be classified into several categories (Figure 1.1).^{4b,c} The most prominent class is certainly aminophosphonium cations (Figure 1.1a). This group is represented by delocalized 3-centre 4π -electron systems in which the P atom is positively charged and has an ambiphilic character.^{4a} It is fundamentally different from the central P atom of phosphine-substituted phosphonium cations (Figure 1.1b) that carry a predominantly negative charge and act as nucleophiles.⁶ The latter system includes three adjacent P atoms among which only 2π -electrons are shared. With extension of conjugated π -system additional groups of phosphonium cations based on delocalization of positive charge could be identified. These include the 5-centre 4π -electron phosphaaallylphosphines^{7, 4b} (Figure 1.1c) and the 5-centre 6π -electron phosphamethine cyanines (Figure 1.1d).⁸ The latter class is comparable to triphosphonium cations (Figure 1.1b) as both groups could be depicted using a phosphide-like resonance form. However, formal charges should always be taken cautiously as they often contradict partial charge values obtained by experimental and/or computational means. Moreover, if

only the middle resonance form for all groups of compounds is considered (Figure 1.1), it can be concluded that bisamino (a) and phosphaaallylic (c) ions feature an electron-deficient central P (six-valent electrons) and thus represent the “classic” phosphonium cations.^{4a}

Figure 1.1. Bonding modes of phosphonium cations with respect to charge distribution within the π -electron system.

Following the discovery of the first aminophosphonium ion (Figure 1.2, **I**),¹ Maryanoff and Hutchins identified another cyclic bisamino-substituted P-cation (**II**).⁹ As expected, both compounds were shifted downfield (δ_{P} 264 ppm for **I** and 222 ppm for **II**) in the ^{31}P NMR spectrum. Furthermore, both of these species were prepared via chloride abstraction from the respective halophosphines. Interestingly, Hutchins and co-workers pointed out that acyclic bisaminophosphonium cation $[(\text{Me}_2\text{N})_2\text{P}]^+$ (**III**) could not be synthesized using the corresponding chlorophosphine and PCl_5 due to the severe steric interaction that precluded coplanar orientation of amino groups.⁹ However, in 1976, Parry and co-workers detected the first examples of acyclic phosphonium cations **III** and $[(\text{Me}_2\text{N})\text{PCl}]^+$ (**IV**) by reacting the corresponding chlorophosphines with AlCl_3 .¹⁰ Other Lewis acids such as GaCl_3 , FeCl_3 , BF_3 , and PF_5 were subsequently utilized to confirm the identity of **III** and **IV**.^{10c} Two years after the discovery of acyclic aminophosphonium salts, Parry and co-workers also demonstrated their potential as supporting ligands for preparation of several iron-carbonyl complexes.¹¹ Therefore, their communication could be considered as a stepping-stone for modern coordination chemistry of cationic phosphonium complexes.

Figure 1.2. First examples of stabilized cyclic (**I**, **II**) and acyclic (**III**, **IV**) phosphonium cations.

Regarding the compounds presented in Figure 1.2, one could infer that stable phosphonium salts contain at least one amino group.^{4a} Groups with strong π -donor characteristics attached to the central P are essential as they impart the thermodynamic stabilization.⁴ In this view, other π -donating groups such as alkoxy, halo, and aryl were considered as viable substituents in preparation of phosphonium cations. For instance, oxygen atom possesses two lone pairs of electrons rendering O-based substituents particularly suitable to engage in conjugation with the central P. Nevertheless, only two examples of P-cations bearing aryloxy and/or siloxy groups directly attached to the central P have been isolated to date. While aminooxyphosphonium cation (Figure 1.3, **V**) was prepared via alcoholysis of the corresponding iminophosphonium salt,^{12a} trimethylsiloxy-substituted phosphonium ion (**VI**) was formed in an unusual siloxy group transfer from $\text{Me}_3\text{Si-CNO}$ to the starting chloro-phosphonium ion $[(\text{Me}_3\text{Si})_2\text{N=PCl}]^+$ followed by formal elimination of “CNCl” fragment.^{13b} Other examples of O-substituted P-cations such as $[(\text{MeO})_2\text{P}]^+$ and $[(\text{Mes}^*\text{O})(\text{Cp}^*)\text{P}]^+$ were registered as parts of inner coordination spheres of molybdenum- and cobalt-based transition metal complexes, respectively, suggesting that O-based substituents solely or without an assistance from amino groups were not able to stabilize phosphonium cations.^{12c,d}

Figure 1.3. Aminoaryloxy (**V**) and amino(trimethylsiloxy)-substituted (**VI**) phosphonium cations.

Similarly, stable phosphonium ions containing two halogen atoms (e.g. PX_2^+ , where X = halogen) were not observed so far.¹⁴ This can be attributed to the inferior ability of halogens with respect to amino groups to engage their π -symmetry lone pair(s) in bonding with the central P.⁴ However, the P-center of an amino-supported phosphonium ion could carry a chloro-substituent as well, as demonstrated by groups of Parry (Figure 1.2, **IV**)^{10a,b} and Cowley.¹⁵ In 2012, another example of aminochlorophosphonium ion (Figure 1.4, **VII**) was prepared by Villinger's group.^{13a} This species represents the first crystallographically elucidated halogen-substituted phosphonium cation formed exclusively upon crystallization. In fact, cation **VII** exists only in the solid state at temperatures below -50°C rendering the preparation of halophosphonium cations highly challenging.

Figure 1.4. The first structurally characterized chloro-substituted phosphonium cation (**VII**).

In 1995, Reed and co-workers have isolated the first example of amino-supported phosphonium cation featuring a bulky aryl ring directly attached to the central P in η^1 -coordination mode (Figure 1.5, **VIII**).^{16a} Shortly after, another electron-rich aryl group was employed in the synthesis of phosphanyl-stabilized phosphonium ion **IX** (Figure 1.5) by Grützmacher's group.^{16b} Cation **IX** was prepared via methylation of the corresponding

diphosphene molecule using 35 fold excess of methylating agent. Apart from the fact that electronic properties of both amino and phosphanyl groups proved adequate for stabilization of aryl-substituted phosphonium cations, these communications also indicated that aryl rings do not engage significantly in conjugation with the central P atom as judged by the values of the corresponding C-P bond lengths.¹⁶ The same explanation was used to depict the bonding situation in cation **X** (Figure 1.5) that was prepared by Bertrand and co-workers.^{16c} Furthermore, crystal structure of **X** featured two short P...F contacts suggesting that the presence of phenyl-based substituents could significantly alter the electrophilicity of phosphonium cations.^{16c} Moreover, these P...F electrostatic interactions were subsequently envisaged as starting points for *hitherto* unknown phosphonium-induced C-F bond activation.^{17a}

Figure 1.5. Structural formulas of phosphonium cations featuring mesityl (**VIII**), phosphanyl (**IX**), and bis(trifluoromethyl)phenyl-moieties (**X**).

While the use of amino groups was predetermined, bulky aryl substituents appeared successful providing kinetic stabilization to phosphonium cations **VIII** and **IX**. Using the same substitution pattern (amino group + bulky group), Cowley and co-workers succeeded preparing the first example of an alkyl-substituted phosphonium ion (Figure 1.6, **XI**).¹⁸ Interestingly, the compound **XI** witnessed the largest ³¹P NMR chemical shift (δ_P 513 ppm) ever registered in phosphonium chemistry. Clearly, this observation was attributed to the non-conjugating character of *tert*-butyl substituent.^{4a} The same alkyl group was subsequently combined with pentamethylcyclopentadienyl-ligand (Cp^{*}) in the preparation of the corresponding P-cation **XII**.¹⁹ However, spectroscopic and computational investigations revealed a multihapto bonding between the central P and Cp^{*}

moiety thus indicating the three-coordinate nature of **XII**. These examples implied that the stable phosphonium cation could contain at most one non-conjugating group (i.e. ^tBu) directly attached to the central P only if significant π -donation is imparted by other substituent.

Figure 1.6. Amino(*tert*-butyl)phosphenium (**XI**) and η^2 -pentamethylcyclopentadienyl(*tert*-butyl)phosphenium cation (**XII**).

Previous examples demonstrated the influence of delocalization on the thermodynamic stability of coordinatively unsaturated phosphorus compounds. If conjugation is reduced by steric and/or electronic modification of supporting substituents, the resulting phosphonium cations might be either transient¹⁹ or stable under extremely inert conditions for a limited period of time.¹³ These factors certainly pose a challenge for today's synthetic chemists working in the field of phosphonium chemistry.

Section 1.2. Synthesis of Phosphenium Cations

Versatile chemical behavior could surely be regarded as one of the key reasons behind the great variety of phosphenium ions known today. Their synthetic methodologies are described in the following examples.

Scheme 1.1. P-X bond cleavage by strong Lewis acids.

The most popular synthetic method involves phosphorus-halogen bond cleavage of the starting halophosphine induced by a Lewis acid that is more halophilic than the target phosphenium cation (Scheme 1.1). This method is considered convenient, as variety of readily available Lewis acids such as AlCl_3 , GaCl_3 ,¹⁰ FeCl_3 ,²⁰ PCl_5 ,⁹ PF_5 ,¹⁰ and BF_3 ¹ have been successfully employed so far. As a consequence of the electron-deficient nature of phosphenium ions, P-X (X = halogen) bond heterolysis is commonly carried out in polar non-coordinating solvents, such as dichloromethane (DCM). Its high dielectric constant affords high solubility of phosphenium salts even at temperatures as low as -78°C ensuring their spectroscopic detection.^{4a}

In a slightly modified procedure, $\text{Na}[\text{BPh}_4]$ was also utilized for P-X bond cleavage to yield the corresponding phosphenium ion accompanied by a $[\text{BPh}_4]^-$ anion, followed by elimination of insoluble NaCl .²¹ These examples demonstrated that a variety of anions with different steric and coordinating properties could be delivered via P-X bond heterolysis. In turn, this method offers an opportunity to significantly enrich the current knowledge of stability and reactivity of phosphenium cations.

Scheme 1.2. Electrophilic attack on phosphorus-element double bond.

Apart from halide abstraction, phosphonium salts were formed in an electrophilic attack on phosphorus-phosphorus or phosphorus-nitrogen double bonds (Scheme 1.2).²² For example, Niecke and Kröher prepared phosphonium zwitterion **XIII** by treating the corresponding iminophosphane with AlCl₃ (Scheme 1.3). On heating, compound **XIII** released Me₃SiCl to form the cyclic zwitterion **XIV**. Based on spectroscopic data (³¹P NMR spectroscopy) it was concluded that the positive charge was mainly located on P-atoms thus suggesting the phosphonium character of **XIII** and **XIV**.^{4a}

Scheme 1.3. Electrophilic attack on P=N bond leading to the formation of acyclic (**XIII**) and cyclic (**XIV**) zwitterionic phosphonium ions.

Another example based on this methodology was observed during protonation of diphosphene with HBF₄·Et₂O at low temperatures (Scheme 1.4).²³ Cowley and co-workers initially observed the formation of compound **A**, which upon warming underwent P-P bond cleavage to give the monophosphonium salt **B**. To explain the formation of **A**, the authors proposed that protonation of diphosphene initially led to the formation of labile phosphonium cation **XV**. As both insertion of phosphonium cations into C-H bonds²⁴ and the feasibility of 2,4,6-(^tBu)₃-C₆H₂ group towards P-centered ring-closure were previously reported,²⁵ it was suggested that the two-coordinate P atom of cation **XV** inserted into C-H bond of *ortho*-positioned *tert*-butyl group to give compound **A**.

Scheme 1.4. Electrophilic attack on P=P bond leading to the transient phosphonium ion (**XV**) that subsequently undergoes intramolecular C-H insertion and P-P bond cleavage. Due to clarity, only the molecular structure of R group undergoing C-H insertion was presented.

While the previous example described protonation of a P=P bond, addition of H^+ to the amino substituent (e.g. NMe_2) and subsequent P-N bond cleavage was also identified as a successful strategy for preparation of phosphonium cations. This method was established by Dahl who treated various amino-substituted phosphines with trifluoromethanesulfonic acid (HSO_3CF_3) due to the low nucleophilicity of triflate $[\text{CF}_3\text{SO}_3]^-$.²⁶ While this synthetic approach proved viable, it also established that the existence of P-salts (i.e. $[(\text{R}_1)(\text{R}_2)\text{P}]^+$) was strongly dependent on the nature of supporting R groups. For example, when $\text{R}_1 = \text{R}_2 =$ amino group, a positively charged P-ion bearing non-coordinated $[\text{CF}_3\text{SO}_3]^-$ was registered in the solution. On the other hand, the replacement of either R_1 or R_2 by groups less electron donating than amino (e.g. $-\text{Ph}$ and $-\text{Cl}$) resulted in an equilibrium between the “free” phosphonium and the corresponding triflate-substituted phosphines (Scheme 1.5).

Scheme 1.5. Protic attack on P-N bond leading to the formation of equilibrium between the “free” phosphonium ion and its phosphine analogue bearing covalently bound triflate.

Over the years, several miscellaneous methods for the synthesis of phosphonium cations have emerged. Thus, spontaneous chloride extrusion from both cyclic²⁷ and acyclic²⁸ halophosphines resulted in the formation of target phosphonium ions as demonstrated by Schmidpeter’s group. The synthesis of cyclic phosphonium cation **XVI** involved the initial formation of heterocycle **C** followed by chloride dissociation and 1,3-H-migration (Scheme 1.6a). On the other hand, acyclic analogue **XVII** was prepared in the condensation reaction between the corresponding phosphonium salt and PCl_3 followed by elimination of Me_3SiCl (Scheme 1.6b). The generation of **XVII** was attributed to the spontaneous dissociation of chloride from the transient halophosphine **D**. Interestingly, coordinatively unsaturated P-centers of **XVI** and **XVII** were inert in the presence of rather

nucleophilic chloride anion. This somewhat unusual phenomenon could be attributed to the dispersion of positive charge across the whole molecule of these phosphonium salts.

Scheme 1.6. Miscellaneous methods associated with spontaneous chloride dissociation to yield cyclic **XVI** (a) and acyclic **XVII** (b) phosphonium compounds.

In 2007, Cowley and co-workers discovered another miscellaneous method for the synthesis of N-heterocyclic phosphonium ions (NHPs).^{29a} The preparation of NHPs **XVIII** was achieved through a one-step redox process between the corresponding diimine and the PI_3 in DCM solution (Scheme 1.7). In a similar fashion, Macdonald *et al.* discovered that reaction of diimine with PBr_3 in the presence of excess cyclohexene yields N-heterocyclic bromophosphines, which can be further transformed to NHPs by means of halide abstraction.^{29b} Newly discovered processes appeared very attractive as simple high yielding procedures.

Scheme 1.7. General redox route for preparation of NHPs (**XVIII**).

Lastly, chloride-for-pseudohalogen exchange proved to be an effective procedure

for preparation of labile pseudohalogen-substituted phosphonium cations.¹³ Following the preparation of chloro-substituted phosphonium cation **VII**, Schulz and co-workers have discovered that chloride could be replaced if **VII** was treated with an appropriate trimethylsilylpseudohalide (Me₃Si-X). In a metathesis reaction between **VII** and Me₃Si-X, the phosphorus-pseudohalide (P-X) bond formation was followed by elimination of chlorinated silane (Me₃SiCl) leading to the target pseudohalophosphonium ions (Scheme 1.8). This procedure was initially applied for isolation of the first azidophosphonium ion (**XIX**).^{13a} The discovery of **XIX** prompted the synthesis of other pseudohalophosphonium species. Although, a broad scope of pseudohalides was tested, only aminoisocyanato (**XX**) and aminoisothiocyanatophosphonium (**XXI**) cations were isolated and structurally characterized.^{13b} These cations underwent Lewis acid-base complexation when treated with strong σ -donors, while their carbenoid-like reactivity was established in [1+4]-cyclization reactions.^{13b}

Scheme 1.8. Halogen-pseudohalogen exchange leading to the isolation of pseudohalophosphonium cations (**XIX – XXI**).

In recent years, multiply charged P(III) cations have drawn significant scientific interest. In particular, three-coordinate P(III) trications (**XXII**, Figure 1.7) were very attractive as they structurally resemble phosphines, the most commonly employed ligands in transition metal catalysis. Groups of Engel^{30a} and Bertrand^{30b} used N-based two-electron donor ligands for the stabilization of P³⁺-center (**a-c**, Figure 1.7). The resulting compounds were isolated and their structures were determined spectroscopically and chemically. In 2011, Alcarazo and co-workers prepared the first example of crystallographically characterized [L₃P]³⁺.^{30c} Triply-charged phosphine supported by carbene ligands (**d**) was synthesized using Bertrand's "onio-substituent transfer" methodology^{30b} and its coordinating ability was subsequently explored in reactions with

electron-rich transition metals such as Pd and Pt.

Figure 1.7. Three-coordinate P(III) trications (**XXII**) stabilized by: 4-(dimethylamino)pyridine (**a**), quinuclidine (**b**), 1,5-diazabicyclo[4.3.0]non-5-ene (**c**), and carbene (**d**).

The versatility of “onio-transfer” reagents was further demonstrated in preparation of doubly charged P-species. While phenyl-substituted phosphorus dication (**XXIII**) was prepared using CO₂-masked N-heterocyclic carbene (NHC) by Cattey and co-workers,^{31a} Weigand’s group synthesized Cl-containing P-dication (**XXIV**) via stepwise chloride-for-NHC replacement followed by Me₃SiCl removal (Scheme 1.9).^{31b} The presence of chlorine on the P atom of **XXIV** allowed further halide exchange resulting in azido- and cyano-substituted dicationic phosphines.^{31b}

Scheme 1.9. The synthesis of phenyl- (**XXIII**) and chloro-substituted (**XXIV**) dications employing “onio-transfer” method.

If the dative bonding model³² is used to describe the previously mentioned P-polycations, these compounds could be regarded as three-coordinate trication (**XXII**) and dications (**XXIII** and **XXIV**) stabilized by the corresponding two-electron donor ligand L

(Figure 1.8). In other words, these species resemble triply and doubly charged phosphonium cations supported by strong nitrogen base or a carbene-type donor, respectively. A logical question that arises from this bonding situation is whether phosphonium di- and trications could be isolated in their “free” form.

Figure 1.8. Three-coordinate P trication (XXII) and dications (XXIII and XXIV) depicted using donor-acceptor bonding model.

In 2013, our group pioneered the synthesis of two-coordinate aminophosphonium dication $[(\text{Ph}_3\text{P})_2\text{C}^+\text{P}^+\text{N}^i\text{Pr}_2][\text{AlCl}_4]_2$, **[1c]** $[\text{AlCl}_4]_2$, supported by hexaphenylcarbodiphosphorane ligand **1**.³³ The dication **[1c]** $^{2+}$ was obtained in a stepwise procedure involving 1-for-Cl substituent exchange leading to the monocation $[(\text{Ph}_3\text{P})_2\text{C}^+\text{P}^+\text{N}^i\text{Pr}_2\text{Cl}][\text{Cl}]$, **[1c-Cl]** $[\text{Cl}]$ followed by subsequent chloride abstraction (Scheme 1.10). The molecular structure of **[1c]** $^{2+}$ was analyzed using both crystallographic and computational methods. It was revealed that both C-P and P-N bond lengths possess significant double bond character derived from an extensive π -electron delocalization across the CPN fragment. Furthermore, theoretical analysis demonstrated that increased positive charge of **[1c]** $^{2+}$ resulted in a greater stabilization of its frontier orbitals compared to Parry’s bisaminophosphonium cation **III**. In fact, this particular result implied a greater Lewis acidic character of **[1c]** $^{2+}$ with respect to its bisaminophosphonium analogue **III**. This communication was followed by another article in which detailed theoretical studies on the bonding situation in **[1c]** $^{2+}$ was reported.^{33b} Interestingly, the extent of π -donation from amino group and carbene ligand (**1**) to the formally empty P(3p) atomic orbital appeared almost identical thus indicating that both substituents attributed equally to the thermodynamic stabilization of **[1c]** $^{2+}$. As ability of amino groups to stabilize phosphonium ions was well documented previously, one could argue that unique electron-donating properties of neutral carbene ligand **1** had a decisive role in maintaining the two-

coordinate nature while increasing the positive charge of phosphonium cation. This argument is supported by the fact that all previously reported P-polycations were at least three-coordinate (Figure 1.8).

Scheme 1.10. The stepwise synthesis of hexaphenylcarbodiphosphorane-stabilized aminophosphenium dication **[1c][AlCl₄]₂**.

Section 1.3. Carbones as Supporting Ligands for Main Group Lewis Acids

The effect of **1** on the thermodynamic stability of phosphonium dication [**1c**]²⁺ could be better interpreted by taking a closer look at the unique electronic structure of carbone ligands. Carbones (CL₂, L = 2 electron donor) differ from other carbon-centered electron donors by the number of lone electron pairs at the central carbon atom. For example, carbenes, ylides, allenylidenes, and cumulenylidenes possess one electron pair available for bonding.^{35d} However, the central carbon atom of carbones has two lone pairs of electrons, one with σ and the other with π symmetry. Therefore, the term “carbone”³⁴ highlights the presence of a “naked” carbon atom in the CL₂ class of compounds, thus providing a clear distinction between carbones and more popular carbenes.³⁵

The bonding situation in carbones (L→C←L) is best described in terms of donor-acceptor interactions between the two L σ -electron donors and a zero-valent C atom in its ¹D excited state. This concept was first proposed by Yuri Varshavsky in 1980,³⁶ whose Russian version of the original article was not widely known in the community. The theoretical background for Yuri’s hypothesis came from an independent computational investigation performed by Frenking and co-workers.³⁷ Intensive theoretical research on the nature of carbone’s L-C bonds has not only confirmed the presence of dative bonding, but also established the donor-acceptor bonding model for other often debated compounds.³² Thus, bending around the central C atom of CL₂ compounds such as hexaphenylcarbodiphosphorane (**1**, L = PPh₃) and carbon suboxide (L = CO) could not be accounted for within the traditional covalent bonding model. While covalent bonding imparts the linear environment around the central carbons of **1** (Ph₃P=C=PPh₃) and carbon suboxide (O=C=C=C=O), the dative bonding model explains the deviation from the linear geometry by considering these molecules as Ph₃P⁻ and / or CO-stabilized C(0) complexes (e.g. L→C←L, L = PPh₃, CO). The larger bending angle of C(CO)₂ (156°) with respect to **1** (136°) could then be explained by stronger π -backdonation from the central C to the CO moiety (OC←C→CO) of C(CO)₂ thus indicating the analogy between carbone molecules and transition metal complexes.³²

In view of the previous captodative description, the central carbon atom of CL₂ retains all valent electrons as none of them is involved in the corresponding L→C←L

bonds. The same atom thus differs from the carbene's carbon CR_2 whose valence electrons form R-C-R electron sharing (covalent) bonds. Formally regarded, while the central C of CL_2 has an electron octet, carbene's C is surrounded by six electrons. This particular bonding portrayal renders carbenes as σ -donors but π -acceptors, whereas carbones are regarded as both σ - and π -donors.^{35d}

The presence of two electron pairs on the central C atom of **1** (the first known example of carbones) could be depicted using Lewis structures as well (Figure 1.9).^{35d} The most appropriate resonance form is **D** where central carbon atom carries two formal negative charges along with the formal positive charge on each phosphane ligand. It is noteworthy that this structure was first proposed by Kaska *et al.* in 1973.³⁸ Furthermore, forms **B** and **C** represent structures with $\text{C}=\text{P}$ double bond where C has a formal negative charge, while form **A** has two $\text{C}=\text{P}$ double bonds and no formal charges. Form **A** is widely used in the literature as it complies with the often-stated rule that the most suitable Lewis structure contains the least formal charges. However, the presence of purely covalent $\text{C}=\text{P}$ double bonds in **1** (as in form **A**) is strongly disfavored if modern computational methods³⁷ and reactivity of this strongly nucleophilic ligand are considered.³⁹

Figure 1.9. The bonding situation in hexaphenylcarbodiphosphorane (**1**) described using resonance forms.

Even though, hexaphenylcarbodiphosphorane **1** was originally synthesized by Ramirez in 1961,⁴⁰ its classification as a carbene compound was established in 2005 when Frenking and co-workers analyzed the nature of C-C bonds in the corresponding CX_2 -carbene adducts (e.g. $[\mathbf{1}\cdot\text{CX}_2]$, $\text{X} = \text{O}, \text{S}$).⁴¹ With the use of modern computational methods, the bonding between **1** and CX_2 was identified as dative (i.e. $[\mathbf{1}\rightarrow\text{CX}_2]$) with a predominant σ - and a weaker π -component leading to the bond distances shorter than the standard C-C single bond. This finding brought the idea about double electron pair donor ability of **1** and related carbodiphosphorane molecules (i.e. $\text{C}(\text{PR}_3)_2$).^{35c}

Apart from **1**, other CL_2 compounds were known for a long period of time (Figure

1.10). For example, Schmidbaur and co-workers have reported a series of carbodiphosphoranes (**XXV**) supported by PMe_3 ,^{42a} PPhMe_2 ,^{42b} and PPh_2Me .^{42c} The same group has described cyclic carbodiphosphoranes (**XXVI**), which could be formally regarded as $\text{C}(0)$ -complexes of the corresponding chelating diphosphines.⁴³ It's noteworthy that Baceiredo's group has also contributed to the development of cyclic carbodiphosphoranes and their chemistry.⁴⁴ In addition, Baceiredo and co-workers have isolated the first example of mixed phosphorus sulfur bisylide (**XXVII**).⁴⁵ This example indicated that other σ -donors apart from (or combined with) phosphines could be a good fit for the preparation of carbene compounds. Prompted by this finding, Fürstner *et al.* have reported a series of mixed bisylides $\text{C}(\text{PPh}_3)(\text{L})$ in which PPh_3 was combined with other two-electron donors such as CO , CNPh , cyclic (**XXX**) and acyclic carbenes (**XXVIII** and **XXIX**).⁴⁶ This work delivered an experimental contribution to the concept of "coordination chemistry at carbon". Moreover, its authors have demonstrated that the replacement of PPh_3 by certain heteroatom-stabilized carbenes (**XXVIII**) did not affect the "true" carbene character of the central C atom.⁴⁶

Figure 1.10. Molecular formulas of acyclic (**XXV**) and cyclic (**XXVI**) carbodiphosphoranes, P, S-mixed bisylide (**XXVII**), and P, carbene-mixed bisylides (**XXVIII-XXX**).

The concept of "coordination chemistry at carbon" coupled with experimental studies indicating that phosphines and NHCs have similar σ -donating properties,⁴⁶ led to the theoretical prediction of carbodicarbenes $\text{C}(\text{NHC})_2$.^{37a} Shortly after, Bertrand's group prepared the first example of benzoannulated carbodicarbene **2** in a two step procedure

involving methylation of N-heterocycles followed by double deprotonation to give the target compound (Scheme 1.11).⁴⁷ The C-C bond lengths of **2** (1.343(2) Å) were significantly shorter than the standard C-C single bond and slightly longer than the corresponding C=C double bonds of allenes (1.31 Å).⁴⁸ Therefore, the central CCC fragment of **2** could be described using two extreme resonance forms **2^a** and **2^b**. This representation indicates some backdonation of electron density from the central C to the formally empty C(2p) atomic orbitals of NHC-moieties. Furthermore, the experimentally observed CCC bond angle of **2** (134.8°) was found to be very close to the theoretically predicted value (~138°) and even closer to an analogous angle observed for **1** (136°). These features suggested that, as in case of carbodiphosphoranes, the central C of **2** should be equipped with two lone pairs of electrons corresponding to the HOMO and HOMO-1 orbitals of π - and σ -symmetry, respectively.^{37a}

Scheme 1.11. The synthesis of the first carbodicarbene (**2**) ligand and its representation using two extreme resonance forms (**2^{a-b}**).

Apart from carbodicarbene **2**, Bertrand's group has also succeeded in preparation of "bent allenes", a class of compounds whose cumulene CCC bonding motif is incorporated in five- and even four-membered heterocycles (Figure 1.11, **XXXI** and **XXXII**, respectively).⁴⁹ As NHCs are known as strong σ -donors, carbodicarbene **2** is sometimes termed "push-push allene".⁴⁷ Nonetheless, "push-pull" allene in which an amino group was replaced by an electron-withdrawing oxygen atom, has also been reported by the same research group (**XXXIII**).⁵⁰ Further structural modification of **2** were investigated by Ong and co-workers (**XXXIV**).⁵¹ The most prominent examples include the preparation of tridentate bis(pirydine)carbodicarbene (**XXXV**),^{51b} as well as a series of

unsymmetrical carbodicarbene molecules CL^1L^2 where L^1 and L^2 are different NHC ligands (**XXXVI**).^{51c} The most recent example of carbodicarbene ligands was carbodicyclopropenylidene (**XXXVII**), compound that unlike its predecessors was based solely on carbon atoms.⁵²

Figure 1.11. Bent allenes (**XXXI** and **XXXII**), push-pull allene (**XXXIII**), N-modified carbodicarbene (**XXXIV**), tridentate pyridine-substituted carbodicarbene (**XXXV**), unsymmetrical carbodicarbenes (**XXXVI**), and carbodicyclopropenylidene (**XXXVII**) as new class of carbene compounds. For simplicity, covalent bonding representations are used.

To prove the concept of “coordination chemistry at carbene” and thus verify the presence of two lone electron pairs on the central C, several computational and experimental assessments have been developed. Frenking and co-workers have studied the binding strength of carbodiphosphoranes $[C(PR_3)_2]$ towards H^+ and main group Lewis acids by means of computational methods.³⁷ It was calculated that carbodiphosphoranes and NHCs had similar values of the first proton affinity (PA), however, values for the 2nd PA of carbodiphosphoranes appeared significantly higher than those observed for NHCs. This observation was in agreement with the notion of two lone pairs on the central C of carbenes. Fürstner *et al.* have verified this finding by preparing carbene complexes in which the central C was bound to two transition metal (AuCl) fragments.⁴⁶ Even though, carbenes have been successfully implemented as Lewis basic components of Frustrated Lewis Pairs (FLPs),⁵³ as well as supporting ligands for transition metal catalysis,⁵⁴ we

focused our interest on their ability to donate both electron pairs to the coordinatively unsaturated main group Lewis acids.

Although, carbenes (especially NHCs) are commonly used for stabilization of highly Lewis acidic main group species, the superior electron donating character of carbones over carbenes was demonstrated over the years. In 2009, Petz and co-workers synthesized borane adduct of carbodiphosphorane $\mathbf{1}\cdot\text{BH}_3$ (Scheme 1.12a) by treating $\mathbf{1}$ with excess of B_2H_6 .⁵⁵ Exposure of $\mathbf{1}\cdot\text{BH}_3$ to an excess of diborane led to the formation of a complicated mixture from which the hydride-bridged bisadduct $[\mathbf{1}\cdot\text{B}_2\text{H}_4(\mu\text{-H})]^+$ was isolated and structurally characterized.⁵⁵ Its formation most likely proceeded by B_2H_6 -promoted hydride abstraction from the initially formed bisadduct $\mathbf{1}(\text{BH}_3)_2$. Nevertheless, the bisadduct $[\mathbf{1}\cdot\text{B}_2\text{H}_4(\mu\text{-H})]^+$ represents the first example of a complex in which two main group Lewis acids different than H^+ or Me^+ are attached to the central C atom of carbone.

Another example of hydride abstraction from $\mathbf{1}\cdot\text{BH}_3$ adduct was reported by Alcarazo's group.⁵⁶ In this case, the treatment of $\mathbf{1}\cdot\text{BH}_3$ with 1 equiv. of $\text{B}(\text{C}_6\text{F}_5)_3$ yielded carbone-stabilized borenium cation $[\mathbf{1}\cdot\text{BH}_2]^+$ (Scheme 1.12a). Based on crystallographic and theoretical analyses, it was concluded that C atom of $\mathbf{1}$ donated both of its lone electron pairs to the corresponding σ - and π -orbitals of BH_2^+ moiety.⁵⁶ In order to prove that peculiar donor properties of $\mathbf{1}$ were essential for the isolation of borenium cation, authors reacted NHC-stabilized borane adduct $\text{NHC}\cdot\text{BH}_3$ with $\text{B}(\text{C}_6\text{F}_5)_3$ (Scheme 1.12b). The formation of bridged cation $[\text{NHC}\cdot\text{BH}_2(\mu\text{-H})\text{BH}_2\cdot\text{NHC}]^+$ stabilized by two bulky NHC ligands was a striking evidence demonstrating different electron donating abilities of carbenes and carbones. Moreover, the presence of π -bonding component between $\mathbf{1}$ and BH_2^+ fragments indicated that carbones are not only capable of binding two Lewis acids, but also capable of simultaneous σ - and π -donation to the same Lewis acidic center.

Scheme 1.12. Differences in reactivity of carbodiphosphorane- (a) and NHC-stabilized (b) borane adducts.

Other examples where the two-fold donating character of **1** was directed to a single main group center include Tonner's borenium ion $[\mathbf{1} \cdot \text{BF}_2]^+$,⁵⁷ Alcarazo's Ge(II) monocation $[\mathbf{1} \cdot \text{GeCl}]^+$,⁵⁸ and Petz's carbocation $[\mathbf{1} \cdot \text{CH}_2]^{2+}$ (Figure 1.12).⁵⁹ While bonding in both $[\mathbf{1} \cdot \text{BF}_2]^+$ and $[\mathbf{1} \cdot \text{GeCl}]^+$ was better described using dative rather than covalent depiction as judged by modern computational methods, the same theoretical approach suggested that the C=C double bond of $[\mathbf{1} \cdot \text{CH}_2]^{2+}$ was comprised of essentially covalent interactions.⁵⁹ These included σ and π electron-sharing C-C bonds between two fragments ($\mathbf{1}^{2+}$ and $:\text{CH}_2$) in their triplet states. Nevertheless, these examples demonstrated that highly reactive main group cations, previously regarded as transient, are now isolable due to the unique coordinating ability of hexaphenylcarbodiphosphorane **1**.

Figure 1.12. Boron ($[1\cdot\text{BF}_2]^+$), germanium ($[1\cdot\text{GeCl}]^+$), and carbon ($[1\cdot\text{CH}_2]^{2+}$) cations stabilized by carbodiphosphorane ligand **1**.

Despite the fact that both carbodiphosphoranes and carbodicarbenes belong to the same group of carbene compounds, certain difference in their reactivity was noted. This relates to the dicationic boron compound recently described by Ong and co-workers $[\text{BH}(\text{XXXIV})_2]^{2+}$.⁶⁰ Unlike Alcarazo's $[1\cdot\text{BH}_2]^+$, $[\text{BH}(\text{XXXIV})_2]^{2+}$ was prepared in an unusual one-pot synthesis involving the treatment of the appropriate boron source (THF·BH₃) with carbodicarbene **XXXIV** ligand (Scheme 1.13). The bonding analysis of $[\text{BH}(\text{XXXIV})_2]^{2+}$ revealed that two carbodicarbene ligands formally donate six electrons to the BH²⁺-fragment via two σ ($\text{XXXIV} \rightarrow \text{BH}^{2+} \leftarrow \text{XXXIV}$) and one π -type allenic interaction.⁶⁰ Furthermore, the partial positive charge of +0.36 on the B atom was significantly reduced with respect to the overall charge of the molecule as seen from the natural population analysis. In fact, each benzimidazolyl moiety carried positive charge of 0.72-0.78, thus, further enhancing the stability of the dicationic boron center. Lastly, $[\text{BH}(\text{XXXIV})_2]^{2+}$ represents the only compound isolated so far in which two carbene ligands are attached to the same main group Lewis acidic center.

Scheme 1.13. One-pot synthesis of biscarbodicarbene-stabilized borenium dication $[\text{BH}(\text{XXXIV})_2]^{2+}$.

As presented above, the use of carbene ligands enabled isolation of *hitherto* unknown positively charged main group species, thus, opening the pathway for novel Lewis acid-directed chemical transformations.

Section 1.4. Electrophilicity and “Carbene Analogue” Character of Phosphenium Cations

Phosphenium ions feature a planar, formally sp^2 -hybridized P center with a lone pair of electrons in a σ -type orbital and an unhybridized, formally vacant P(3p) atomic orbital. The population of the latter orbital induced by adjacent π -donor ligands (e.g. NR_2) reduces the electron accepting ability/Lewis acidic character of the coordinatively unsaturated P-center. In addition, this phenomenon imparts 3-center 4-electron π -bonding around the P-atom, resulting in a more stable singlet ground state. The same method was typically applied towards the preparation of stable carbenes and analogous species.

Phosphenium ions are often considered as carbene analogues because of their similar reactivity patterns, as well as their isolobal relationship. The latter claim is based on the similarity of the HOMO (lone pair of electrons on the central element) and LUMO (empty np orbital) between the two model compounds H_2P^+ and CH_2 .⁶¹ However, closer examination of the frontier orbitals of other P-cations reveals that this analogy is not preserved at all times. In fact, the nature of substituents around the P atom directs the sequence of frontier orbital of phosphenium ions.^{17b} For example, the carbene-like orbital sequence is observed for phosphenium ions with small to moderate π -stabilization such as $[(H)(R)P]^+$ (where R = any group) and $[(H_2N)(R)P]^+$ (where R = Cl, OH, and CH_3).^{17b} On the other hand, cations with both strong π -donating groups $[(ER_n)_2P]^+$ ($ER_n = NH_2, NMe_2$, and SH) have the frontier orbital sequence of an allyl anion (Figure 1.13).^{61, 17c} The LUMO (π^*) of $[(H_2N)_2P]^+$ has π -antibonding character, while the HOMO (π_2), essentially nonbonding, is comprised from an out-of-phase combination of N(2p) atomic orbitals with a node at phosphorus. The lone pair orbital has σ -symmetry and it is usually located at 0.5-2.4 eV below the HOMO. The energy gap between the lone pair orbital and the HOMO can be altered by alkylation of N-center, which results in the inductive destabilization of the lone pair.^{17b} Lastly, the 3-center π -bonding molecular orbital (π_1), comprised from an in-phase combination of N(2p) and P(3p) atomic orbitals, is found at the lowest energy.

Figure 1.13. Allylic frontier orbital sequence of bisaminophosphenium model cation $[(\text{H}_2\text{N})_2\text{P}]^+$.

That the frontier orbital representation of phosphonium ions is strongly dependent on the nature of surrounding substituents was also confirmed in a theoretical study by Macdonald and co-workers.^{17d} These authors compared orbital energy levels of the experimentally known bis(dimethylamino)phosphonium $[(\text{Me}_2\text{N})_2\text{P}]^+$ (**III**) and the transient diphenylphosphonium cation $[\text{Ph}_2\text{P}]^+$. Investigation revealed that the LUMO of $[\text{Ph}_2\text{P}]^+$ was more stabilized than an analogous orbital of **III**, thus indicating better electron accepting ability of phenyl-substituted cation. This observation was a consequence of an ineffective π -conjugation between the P-center and phenyl groups in $[\text{Ph}_2\text{P}]^+$. Furthermore, the σ -type lone pair orbital of **III** was on a significantly lower energy level than the corresponding orbital of $[\text{Ph}_2\text{P}]^+$. This was somewhat expected considering the greater σ -electron withdrawing character of amino substituents. The same study demonstrated the lower relative energy of HOMO in case of aminophosphonium ion, thus suggesting that $[\text{Ph}_2\text{P}]^+$ could be a better electron donor than **III**. Overall, it could be concluded that replacement of amino by phenyl substituents resulted in a smaller HOMO-LUMO (singlet-triplet) energy gap rendering $[\text{Ph}_2\text{P}]^+$ not only as a better Lewis acid, but also as a stronger Lewis base with respect to bisaminophosphonium cation **III**.

Phosphenium ions act as electrophiles in reactions such as cycloaddition, C-H and C-C bond insertion, as well as complex formation with Lewis bases. Their nucleophilic character comes to the fore in formation of transition metal complexes.⁴ On the other hand, the propensity of carbenes to undergo [1 + 4] cycloaddition reactions, various bond insertions, as well as to support the preparation of various transition metal catalysts is well established.⁶² Despite the difference in frontier orbital sequence between phosphenium ions and carbenes, these two groups of compounds exhibit the same reactivity pattern in most of chemical transformations. An exception is the reactivity towards Lewis bases wherein, unlike phosphenium cations, carbenes and other group 14 metallylenes do not form stable adducts.^{17b} The richer acceptor chemistry of phosphenium ions is not unexpected considering the greater positive charge and the larger size of phosphorus relative to carbon.

The fact that phosphenium ions manifest carbene-like reactivity pattern towards various substrates can be explained considering frontier orbital interactions when former species act as Lewis acids. For instance, electrophilic behavior of phosphenium ions involves the interaction between the LUMO of P-cation and the HOMO of the reaction partner. Since LUMO is always localized at the more electropositive P-atom, the reactivity of different phosphenium salts remains the same regardless of allyl anion- or carbene-like frontier orbital sequence.^{17b} As a reminder, these two orbital orders differ only in the relative energies of molecular orbital resembling P-lone pair, which is responsible for the nucleophilic (ambiphilic) behavior of cations.^{17b,d} Based on this, one could conclude that phosphenium ions (P-center stabilized by two strong π -donors) whose order of frontier orbitals is different than that of carbenes, still exhibit carbene-like reactivity because they prefer to act as electrophiles rather than nucleophiles.^{17b}

Section 1.5. Main-group Compounds for Small Molecule Activation

Over the past decade, small molecule activation by main group compounds became increasingly popular as alternatives to traditional transition metal complexes.⁶³ This led to the discovery of Frustrated Lewis Pairs (FLPs),⁶⁴ as well as a variety of abundant, inexpensive, and less toxic group 13⁶⁵ and 14-centered species⁶⁶ suitable for activation of enthalpically strong σ bonds. Moreover, some of these species appeared capable of carrying out small molecule activation tasks catalytically.⁶⁷

Certainly, one of the most remarkable findings in this area was the ability of acyclic (**XXXVIII**) and cyclic alkylamino carbenes (**XXXIX**) to split H-H and N-H bonds of dihydrogen and ammonia, respectively (Scheme 1.14).⁶⁸ In the following communication, Bertrand and co-workers demonstrated that the replacement of σ -withdrawing and π -donating amino group (**XL**) with σ -donating and π -inert alkyl moieties (**XXXIX**) led to the increased nucleophilic (destabilized HOMO) and increased electrophilic (stabilized LUMO) character of alkylamino carbenes. As a consequence of a smaller HOMO-LUMO gap, it was reasonable to assume that latter species represented a more suitable candidate for transition metal-like reactivity than traditional N-heterocyclic carbene (**XL**). Indeed, while **XL** remained chemically inert, alkylamino carbenes **XXXVIII** and **XXXIX** facilitated the activation of non-polar molecules such as H₂ and NH₃ under mild experimental conditions. Unlike transition metals that favor electrophilic activation and proton transfer pathways,⁶⁹ oxidative addition of H₂ and NH₃ by carbenes was found to proceed via nucleophilic activation,^{68a} thus creating hydride and pseudo-amide-like moieties, which then shift to the positively polarized carbene carbon. The nucleophilicity of cyclic alkylamino (**XXXIX**) and N-heterocyclic carbenes (**XL**) was also utilized for activation of Si-H, B-H, and P-H bonds.^{68b}

Scheme 1.14. Activation of enthalpically strong σ -bonds by acyclic alkylamino (XXXVIII), cyclic alkylamino (XXXIX), and N-heterocyclic (XL) carbenes.

Similarly, singlet tetrelenes based on heavier Group 14 elements possess a lone pair of electrons and a formally vacant orbital providing a platform for transition metal-like reactivity. For example, Aldridge's acyclic silylene (**XLI**) undergoes oxidative addition of hydrogen molecule under ambient conditions (Figure 1.14).^{66e} Furthermore, when heated gently, the silicon center inserts intramolecularly into C-H bond of boryl's Dipp-moiety. Interestingly, the observed reactivity is attributed to the electrophilic nature of **XLI** consistent with electron density transfer from HOMO of H₂ to the LUMO of **XLI**.^{66e} The same mechanistic pathway takes place in the activation of H₂ by neutral germylene (**XLII**, Figure 1.14).^{66d} In addition, **XLII** also facilitates N-H bond activation of ammonia via two-step N-to-Ge coordination/proton transfer mechanism. The role of a second molecule of NH₃ in the formal oxidative addition of N-H bond to the heavy Group 14 elements was suggested based on the theoretical investigation conducted by Power and co-workers.^{66d} This claim was experimentally confirmed by Aldridge *et al.* whose stannylene (**XLIII**, Figure 1.14) enabled the isolation of compounds such as **XLIII**·NH₃ and [**XLIII**(NH₂)]⁺, as well as their subsequent conversion to the formal oxidative addition product **XLIII**(H)(NH₂).^{66f} Apart from N-H, stannylene **XLIII** was capable of activating other strong E-H bonds (E = H, B, Si, and O). Its remarkable activity towards small molecule activation originates from small HOMO-LUMO energy gap imparted by

strong σ -donating properties of boryl substituents.^{66f}

Figure 1.14. Silylene (**XLI**), germylene (**XLII**) and stannylene (**XLIII**) used for small molecule activation.

The enhancement of small molecule activation via positively charged heavier group 14 carbene analogues was pioneered by Tobita and co-workers (Figure 1.15, **XLIV**).^{70a} These authors proposed that increased overall positive charge would result in the stabilization of relative energy levels of both HOMO and LUMO. Thus, the lowered LUMO of **XLIV** would be more susceptible to the interaction with the σ -bonding orbital of H₂ leading to the more feasible electrophilic activation pathway. Indeed, cationic metallocermylene **XLIV** (Figure 1.15) inserted not only into hydridic B-H and Si-H bonds, but also into non-polar H-H bond. Remarkably, the insertion into former bonds was found to be reversible, a characteristic attributable to the small HOMO-LUMO gap of **XLIV**.^{70a} The oxidative flexibility of cationic germylenes was once again demonstrated by Aldridge's group.^{70b} In a subsequent communication, Aldridge and co-workers described the preparation of a positively charged germylene **XLV** (Figure 1.15) featuring no π -donating atoms in α -position with respect to the Ge-center. As a consequence, **XLV** has a relatively small HOMO-LUMO energy separation and exhibits rich oxidation chemistry including [2+1] cycloadditions and single insertion into C-Cl bond of dichloromethane (DCM). Nevertheless, these examples demonstrated that increased electrophilicity of the main group atom imposed by introduction of the positive charge had significant contribution to the facile splitting of strong σ -bonds.

Figure 1.15. Cationic metallogermylene (**XLIV**) and Aldridge's germylene with no π -stabilization (**XLV**).

Apart from the two-coordinate heavier carbene analogues, the concept of small molecule activation induced by means of increased electrophilicity/Lewis acidity was also established for coordinatively saturated P(V)-based cations. For example, phosphonium monocation **XLVII** (Scheme 1.15) exhibits exceptional fluorophilicity owing to the low-lying σ^* orbital located opposite to the fluorine substituent.⁷¹ As such, **XLVII** undergoes facile C-F bond activation via fluoride abstraction and in combination with an equimolar amount of triethylsilane rapidly catalyzes hydrodefluorination reactions of alkyl fluorides.^{71a} However, the high reactivity of **XLVII** necessitates the presence of strong electron-withdrawing substituents attached to the central P, thus limiting the tunability of this phosphonium salt. To address this issue, Stephan and co-workers prepared NHC-stabilized fluorophosphonium dication **XLVI**.⁷² Reaction of **XLVI** with (C₆F₅)₃PF₂ resulted in fluoride abstraction leading to the formation of the corresponding difluorophosphorane and previously mentioned fluorophosphonium monocation **XLVII** (Scheme 1.15). This example clearly demonstrated that phosphonium dication **XLVI** was more fluorophilic (electrophilic) than **XLVII**. Consequently, **XLVI** was found to catalyze hydrodefluorination and hydrosilylation of various substrates under mild experimental conditions.⁷² Based on this, one could conclude that increased positive charge played a greater role in cleaving the strong bonds (e.g. C-F and P-F) than electron-withdrawing substituents.⁷³

* Mes = 2,4,6-(Me)₃-C₆H₂

Scheme 1.15. Reaction of fluorophosphonium dication (**XLVI**) with (C₆F₅)₃PF₂ yielding the corresponding difluorophosphorane and fluorophosphonium monocation (**XLVII**). Counterion ([B(C₆F₅)₄]⁻) was omitted for clarity.

Another example of P(V)-based dication (**XLVIII**) utilized in the activation/cleavage of enthalpically strong σ -bonds was reported by Stephan's group (Scheme 1.16).⁷⁴ To improve the electrophilicity of **XLVIII**, authors combined the effect of increased positive charge along with the proximity of two Lewis acidic phosphorus centers. It was previously demonstrated that proximal distance between two electrophiles led to the cooperative enhancement of overall Lewis acidity.⁷⁵ In combination with Lewis basic phosphines, dication **XLVIII** activated dihydrogen, as well as hydridic B-H and Si-H bonds (Scheme 1.16). Furthermore, it also facilitated activation of C-H bonds of 1,4-cyclohexadiene and 1,3,5-cycloheptatriene. Although, this was not a typical single site molecular activation, these reactions were initiated by hydride abstraction thus inferring a remarkable hydridophilicity of P-dication **XLVIII**. It should be noted that **XLVIII** does not react with basic phosphines such as Ph₃P or ^tBu₃P indicating the existence of all-phosphorus-based FLPs as active species in the solution.⁷⁴ Interestingly, the dication **XLVIII** could be formally depicted as phosphine-stabilized doubly charged P(V)-center (**XLVIII'**, Scheme 1.16), in which only the more Lewis acidic component of P-P linkage showed activity in small molecule activation.

Scheme 1.16. Small molecule activation initiated by doubly charged diphosphonium cation (**XLVIII**) as a Lewis acidic component of an all-phosphorus-based FLP. Anions $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ were omitted for clarity.

In 2004, Gudat and co-workers prepared phosphide-stabilized N-heterocyclic phosphonium molecule **XLIX** that features a strongly polarized homoatomic P-P bond (Figure 1.16).⁷⁶ Chemically active P-P moiety was then employed for activation of polar O-H (H_2O and $i\text{PrOH}$) and C-Cl (DCM) bonds. The splitting of these bonds proceeded via metathesis in which both Lewis acidic and basic P centers featured a new bond formation followed by P-P bond cleavage.⁷⁶ This example revealed that apart from subvalent group 14 compounds, polar E-H and E-Cl bonds ($\text{E} = \text{O}$ and C) of small substrates could be activated/cleaved by cooperative involvement of group 15 reactive centers in their lower oxidation states (**XLIX'**).

Figure 1.16. Resonance structures of P-P polarized phosphide-complexed phosphonium compound (**XLIX** and **XLIX'**).

Recently, it was shown that pincer-like P(III)-containing species exhibit redox

P(III)-to-P(V) behavior to cleave a range of polarized E-H bonds ($E = O$ or N).⁷⁷ Using the planar T-shaped tridentate ONO ligand system, Radosevich and co-workers successfully incorporated the reversible P(III) / P(V) redox cycle of **L** towards activation of ammonia-borane and subsequent hydrogen transfer to azobenzene.^{77a,b} This observation demonstrated that main group species were not only capable of undergoing formal oxidative addition but also integrating this elementary reaction step to catalyze further chemical transformations. Additional examples of redox active P(III)-species with distorted geometry include Radosevich's NNN- (**LI**)^{77c} and Kinjo's NPN-ligated (**LII**)^{77d} phosphines (Figure 1.17). It is noteworthy that activation of ammonia by **LII**, as well as protic E-H bonds ($E = N$ or O) by **LI**, both proceeded through a ligand-assisted mechanism. Conversely, Aldridge and Goicoechea studied the effect of aromatic backbone of ONO-ligand on the redox activity of distorted **LIII** compound.^{77e} Consistent with previous findings, **LIII** was capable of activating N-H and O-H bonds of ammonia and water, respectively. These results clearly indicated the potential of geometrically distorted P(III)-based compounds to undergo formal oxidative addition of polar protic bonds.

Figure 1.17. Radosevich's ONO (**L**) and NPN-ligated (**LI**) phosphines, Kinjo's NPN-substituted phosphine (**LII**), and Aldridge's and Goicoechea's phosphine with aromatic backbone on the ONO-ligand (**LIII**).

Even though, group 15 compounds containing phosphorus in its formal +3 oxidation state certainly demonstrated the potential for insertion into enthalpically strong polar bonds (e.g. O-H and N-H), the activation of non-polar H-H bonds by these species was rarely documented. Indeed, the only example of dihydrogen cleavage was recently described by Stephan *et al.*⁷⁸ Authors discovered that the exposure of 2,4,6-(tBu)₃-1,3,5-

triphosphabenzene (**LIV**) to H₂ resulted in the formation of an isomeric mixture of bicyclic product comprised of fused five- and three-membered rings (Scheme 1.17). Variable temperature data coupled with computational studies confirmed the role of phosphorus as a Lewis acid in 1,4-addition of H₂ (**LIV'**) to the triphosphabenzene derivative. This chemical transformation proceeds via cooperative involvement of formally positive P(III)-center and formally negative *para*-C and hence resembles an FLP-type mechanism.⁷⁴

Scheme 1.17. Dihydrogen activation facilitated by Stephan's triphosphabenzene derivative.

Lewis acidic phosphonium cations possess a formally vacant P(3p) atomic orbital orthogonal to the lone pair of electrons and are thus expected to exhibit insertion into σ -bonds.⁴ However, examples are limited to intramolecular C-H activation of Cp-substituted phosphonium ion (**XII**),¹⁹ transient zwitterion **LV** (Scheme 1.18)^{24b} and previously mentioned transient monocation **XV** formed by protonation of the corresponding diphosphene (Scheme 1.4).²³ These reactions were most likely governed by the proximity effect between the P-center and the potentially activated C-H bond as only one case of intermolecular bond insertion in phosphonium chemistry was reported to date. Namely, Cowley and co-workers observed the insertion of bis(diisopropylamino)phosphonium cation (**[3]**⁺, Scheme 1.18) into C-H bonds of stannocene and plumbocene.^{24a} The molecular composition of the insertion products was elucidated by means of multinuclear NMR and no structural evidence was presented. Nonetheless, considering the isolobal relationship between phosphonium and group 14 metallylenes and their oxidative flexibility, one should expect that enthalpically strong bonds other than C-H could be activated by phosphonium cations.

Scheme 1.18. Examples of intra- (**XII** and **LV**) and intermolecular (**[3]⁺**) C-H bond insertion in phosphonium chemistry. Anions $[\text{AlCl}_4]^-$ were omitted for clarity.

Indeed, our group observed that carbene-stabilized aminophosphonium dication **[1c]²⁺** successfully inserts into O-H bonds of H_2O and MeOH giving the corresponding dicationic phosphonium salts (Scheme 1.19).⁷⁹ Remarkably, reaction proceeded with equimolar amounts of substrates under room temperature suggesting that **[1c]²⁺** is both oxophilic and highly Lewis acidic. The effect of increased Lewis acidity imparted by dicationic charge was demonstrated in parallel experiments involving the treatment of **[3]⁺** and $[\text{iPr}_2\text{NPCI}]^+$ with equivalent amount of H_2O . Both phosphonium monocations remained inert towards the substrate even after extended reaction times. This particular example indicates that carbene or transition metal-like behavior of phosphonium cations could be significantly enriched by simply increasing their Lewis acidity.

Scheme 1.19. Water and methanol activation by amino-substituted phosphonium dication $[\mathbf{1c}]^{2+}$. Anion $[\text{BAr}^{\text{F}}_4]^-$ ($\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3-(\text{CF}_3)_2$) was omitted due to clarity.

Section 1.6. Aims of Thesis

The preparation of stable phosphonium cations requires the presence of at least one (if not both) amino substituent on the P-atom. The ligand $\rightarrow$ P π -conjugation increases the overall electron density on the central P thus diminishing its electrophilic character and causing it to react preferably via its lone pair of electrons. As a consequence, non-amino-supported isolable phosphonium cations that potentially exhibit Lewis acidic behavior remain rather scarce. This research aims to establish a ligand system that enables the preparation of stable multiply charged two-coordinate P(III) cations. In addition, it improves the overall electrophilicity of phosphonium molecules by means of increased positive charge and proximity of two P Lewis acidic centers. Lewis acidity of newly synthesized species will be explored in small molecule activation, a task previously reserved exclusively for transition metals.

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- ¹ Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534.
- ² (a) Olah proposed that suffix “enium” and “onium” should be given to cations with lower and higher coordination number, respectively. (b) Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808.
- ³ For structural parallels between phosphonium and carbene ligands see: Rosenberg, L. *Coord. Chem. Rev.* **2012**, *256*, 606, and references therein.
- ⁴ For reviews on phosphonium chemistry see: (a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. (b) Gudat, D. *Coord. Chem. Rev.* **1997**, *163*, 71. (c) Burford, N.; Ragogna, P. J. *J. Chem. Soc., Dalton. Trans.* **2002**, 4307.
- ⁵ (a) Jungermann, E.; McBride, J. J., Jr.; Clutter, R.; Mais, A. *J. Org. Chem.* **1962**, *27*, 606. (b) Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Pakulski, M. *J. Am. Chem. Soc.* **1983**, *105*, 4845. (c) Tsang, C.-W.; Rohrick, C. A.; Saini, T. S.; Patrick, B. O.; Gates, D. P. *Organometallics* **2004**, *23*, 5913. (d) Soleilhavoup, M.; Guerret, O.; Faure, J.-L.; Baceiredo, A.; Bertrand, G. *Phosphorus, Sulfur, and Silicon* **1997**, *123*, 161.
- ⁶ (a) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 226. (b) Schmidpeter, A.; Lochschmidt S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 253.
- ⁷ Gudat, D. *Eur. J. Inorg. Chem.* **1998**, 1087.
- ⁸ (a) Schmidpeter, A. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Georg Thieme Verlag: New York, 1990; pp. 149. (b) Dimroth, K. *Top. Curr. Chem.* **1973**, *38*, 1.
- ⁹ Maryanoff, B. E.; Hutchins, R. O. *J. Org. Chem.* **1972**, *37*, 3475.
- ¹⁰ (a) Kopp, R. W.; Bond, A. C.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3042. (b) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046.
- ¹¹ Montemayor, R. G.; Sauer, D. T.; Fleming, Sr. S.; Bennet, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231.
- ¹² For alkoxy- and aryloxyphosphonium cations see: (a) Huang, T.; Liu, L.; Zhang, J.; Xu, X.; Huang, W.; Chen, R.; Wang, K.; Yu, X.; Liu, X. *Phosphorus, Sulfur, and Silicon* **1998**, *140*, 183; (b) Burford, N.; Cameron, T. S.; Clyburne, J. A. C.; Eichele, K.; Robertson, K. N.; Sereda, S.; Wasylishen, R. E.; Whitla, W. A. *Inorg. Chem.* **1996**, *35*, 5460; (c) Muetterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. L.; Abdel-Meguid, S.; Tavanaiepour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056; (d) Lang, H.; Eberle, U.; Leise, M.; Zsolnai, I. *J. Organomet. Chem.* **1996**, *519*, 137.

¹³ For pseudohalophosphenium cations see: (a) Hering, C.; Schulz, A.; Villinger, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 6241; (b) Hering, C.; Schulz, A.; Villinger, A. *Inorg. Chem.* **2013**, *52*, 5214.

¹⁴ It should be noted that $[P_2Cl_5]^+$ cation isolated by Krossing *et al.* can be formally regarded as dichlorophosphenium ion $[PCl_2]^+$ stabilized by PCl_3 . See: Gonsior, M.; Krossing, I.; Müller, L.; Raabe, I.; Jansen, M.; Wüllen, L. V. *Chem. Eur. J.* **2002**, *8*, 4475.

¹⁵ Cowley, A. H.; Stewart, C. A.; Whittlesey, B. R.; Wright, T. C. *Tetrahedron Lett.* **1984**, *25*, 815.

¹⁶ For aryl-substituted phosphonium cations see: (a) Reed, R. W.; Xie, Z.; Reed, C. A. *Organometallics* **1995**, *14*, 5002; (b) Loss, S.; Widauer, C.; Grützmacher, H. *Angew. Chem.* **1999**, *111*, 3546; *Angew. Chem. Int. Ed.* **1999**, *38*, 3329; (c) Dumitrescu, A.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Eur. J. Inorg. Chem.* **2002**, 1953.

¹⁷ For computational investigations on stability and electrophilicity of phosphonium cations see: (a) Hussein, S.; Slattery, J. M. *Dalton Trans.* **2012**, *41*, 1808; (b) Gudat, D. *Eur. J. Inorg. Chem.* **1998**, 1087; (c) Schoeller, W. W.; Tubbesing, U. *J. Mol. Struct. (Theochem)* **1995**, *343*, 49; (d) Ellis, B. D.; Ragona, P. J.; Macdonald, C. L. B. *Inorg. Chem.* **2004**, *43*, 7857.

¹⁸ Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784.

¹⁹ Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1983**, *105*, 2074.

²⁰ Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994.

²¹ (a) Burford, N.; Losier, P.; Macdonald, C.; Kyrimis, V.; Bakshi, P. K.; Cameron, T. S. *Inorg. Chem.* **1994**, *33*, 1434; (b) Veith, M.; Kruhs, W.; Huch, V. *Phosphor, Sulfur Silicon Relat. Elem.* **1995**, *105*, 217.

²² Niecke, E.; Kröher, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 692.

²³ Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Pakulski, M.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4845.

²⁴ For insertion of phosphonium ions into C-H bonds see: (a) Cowley, A. H.; Kemp, R. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 3239. (b) Tsang, C.-W.; Rohrick, C. A.; Saini, T. S.; Patrick, B. O.; Gates, D. P. *Organometallics* **2004**, *23*, 5913.

²⁵ (a) Baceiredo, A.; Bertrand, G.; Mazerolles, P.; Majoral, J.-P. *J. Chem. Soc., Chem. Commun.* **1981**, 1197; (b) Yoshifuji, M.; Shima, I.; Ando, K.; Inamoto, N. *Tetrahedron Lett.* **1983**, *24*, 933; (c) Cadogan, J. I. G.; Cowley, A. H.; Gosney, I.; Pakulski, M.;

Yaslak, S. *J. Chem. Soc., Chem. Commun.* **1983**, 1408; (d) Cowley, A. H.; Pakulski, M. *Tetrahedron Lett.* **1984**, 25, 2125.

²⁶ Dahl, O. *Tetrahedron Lett.* **1982**, 23, 1493.

²⁷ (a) Luber, J.; Schmidpeter, A. *Angew. Chem., Int. Ed. Engl.* **1976**, 15, 111; (b) Luber, J.; Schmidpeter, A. *J. Chem. Soc., Chem. Commun.* **1976**, 886; (c) Friedrich, P.; Huttner, G.; Luber, J.; Schmidpeter, A. *Chem. Ber.* **1978**, 111, 1558; (d) Weinmaier, J. H.; Brunnhuber, G.; Schmidpeter, A. *Angew. Chem.* **1979**, 91, 442.

²⁸ (a) Schmidpeter, A.; Jochem, G. *Tetrahedron Lett.* **1992**, 33, 471; (b) Schmidpeter, A.; Jochem, G.; Klinger, C.; Robl, C.; Nöth, H. *J. Organomet. Chem.* **1997**, 529, 87.

²⁹ For preparation of NHPs, see: (a) Reeske, G.; Cowley, A. H. *Inorg. Chem.* **2007**, 46, 1426; (b) Dube, J. W.; Farrar, G. J.; Norton, E. L.; Szekely, K. L. S.; Cooper, B. F. T.; Macdonald, C. L. B. *Organometallics* **2009**, 28, 4377.

³⁰ For three-coordinate P-trications see: (a) Weiss, R.; Engel, S. *Synthesis* **1991**, 1077; (b) Bouhadir, G.; Reed, R. W.; Reau, R.; Bertrand, G. *Heteroat. Chem.* **1995**, 6, 371; (c) Petuskova, J.; Patil, M.; Holle, S.; Lehman, C. W.; Thiel, W.; Alcarazo, M. *J. Am. Chem. Soc.* **2011**, 133, 20758.

³¹ For three-coordinate P-dications see: (a) Azouri, M.; Andrieu, J.; Picquet, M.; Cattey, H. *Inorg. Chem.* **2009**, 48, 1236; (b) Weigand, J. J.; Feldmann, K.-O.; Henne, F. D. *J. Am. Chem. Soc.* **2010**, 132, 16321.

³² Frenking, G. *Angew. Chem. Int. Ed.* **2014**, 53, 6040.

³³ For carbodiphosphorane-stabilized phosphonium cations see: (a) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidović, D. *Angew. Chem. Int. Ed.* **2013**, 52, 3132; (b) Tay, M. Q. Y.; Ilić, G.; W.-Zwanziger, U.; Lu, Y.; Ganguly, R.; Ricard, L.; Frison, G.; Carmichael, D.; Vidović, D. *Organometallics* **2016**, 35, 439; (c) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Frison, G.; Ricard, L.; Vidović, D.; Carmichael, D. *Phosphor, Sulfur Silicon Relat. Elem.* **2015**, 190, 785.

³⁴ The term carbon was first introduced by Frenking: Tonner, R.; Heydenrych, G.; Frenking, G. *Chem. Phys. Chem.* **2008**, 9, 1474.

³⁵ For recent reviews on carbene molecules, see: (a) Frenking, G.; Tonner, R.; Klein, S.; Takagi, N.; Shimizu, T.; Krapp, A.; Pandey, K. K.; Parameswaran, P. *Chem. Soc. Rev.* **2014**, 43, 5106; (b) Petz, W. *Coord. Chem. Rev.* **2015**, 291, 1; (c) Frenking, G.; Hermann, M.; Andrada, D. M.; Holzmann, N. *Chem. Soc. Rev.* **2016**, 45, 1129; (d) Petz, W.; Frenking, G. *Top. Organomet. Chem.* **2010**, 30, 49.

³⁶ Varshavskii, Y. S. *Russ. J. Gen. Chem.* **1980**, 50, 406.

-
- ³⁷ (a) Tonner, R.; Frenking, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 8695; (b) Deshmukh, M. M.; Gadre, S. R.; Tonner, R.; Frenking, G. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2298; (c) Tonner, R.; Frenking, G. *Chem. - Eur. J.* **2008**, *14*, 3260; (d) Takagi, N.; Shimizu, T.; Frenking, G. *Chem. - Eur. J.* **2009**, *15*, 8593; (e) Frenking, G.; Tonner, R.; *Pure Appl. Chem.* **2009**, *81*, 597; (f) Takagi, N.; Shimizu, T.; Frenking, G. *Chem. - Eur. J.* **2009**, *15*, 3448; (g) Tonner, R.; Frenking, G. *Chem. - Eur. J.* **2008**, *14*, 3273.
- ³⁸ Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F. *J. Organomet. Chem.* **1973**, *47*, 391.
- ³⁹ The first time unique electronic properties of carbones were experimentally achieved: Dyker, C. A.; Lavallo, B.; Donnadiou, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3206.
- ⁴⁰ Ramirez, F.; Desai, N. B.; Hansen, B.; McKelvie N. *J. Am. Chem. Soc.* **1961**, *83*, 3539.
- ⁴¹ Petz, W.; Kutschera, C.; Heitbaum, M.; Frenking, G.; Tonner, R.; Neumüller, B. *Inorg. Chem.* **2005**, *44*, 1263.
- ⁴² (a) Gasser, O.; Schmidbaur, H. *J. Am. Chem. Soc.* **1975**, *97*, 6281; (b) Schmidbaur, H.; Gasser, O.; Hussain, M. S. *Chem. Ber.* **1977**, *110*, 3501; (c) Schubert, U.; Kappenstein, C.; M.-Marhla, B.; Schmidbaur, H. *Chem. Ber.* **1981**, *114*, 3070.
- ⁴³ (a) Schmidbaur, H.; Costa, T.; M.-Marhla, B.; Schubert, U. *Angew. Chem.* **1980**, *92*, 557; *Angew. Chem., Int. Ed. Engl.* **1980**, *92*, 555; (b) Schmidbaur, H.; Costa, T. *Chem. Ber.* **1981**, *114*, 3063.
- ⁴⁴ (a) Marrot, S.; Kato, T.; Gornitzka, H.; Baceiredo, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 2598; *Angew. Chem.* **2006**, *118*, 2660; (b) Marrot, S.; Kato, T.; Cossio, F. P.; Gornitzka, H.; Baceiredo, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 7607; *Angew. Chem.* **2006**, *118*, 7447.
- ⁴⁵ Pascual, S.; Assay, M.; Illa, O.; Kato, T.; Bertrand, G.; S.-Merceron, N.; Branchadell, V.; Baceiredo, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 9078; *Angew. Chem.* **2007**, *119*, 9236.
- ⁴⁶ Alcarazo, M.; Lehmann, C. W.; Anoop, A.; Thiel, W.; Fürstner, A. *Nature Chem.* **2009**, *1*, 295.
- ⁴⁷ Dyker, C. A.; Lavallo, V.; Donnadiou, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3206; *Angew. Chem.* **2007**, *120*, 3250.
- ⁴⁸ Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, G.; Taylor, R.; *J. Chem. Soc. Perkin Trans.* **1987**, *2*, S1-S19.
- ⁴⁹ (a) Melaimi, M.; Parameswaran, P.; Donnadiou, B.; Frenking, G.; Bertrand, G. *Angew. Chem.* **2009**, *121*, 4886; (b) Lavallo, V.; Dyker, C. A.; Donnadiou, B.; Bertrand, G.

Angew. Chem., Int. Ed. **2008**, *47*, 5411; (c) Fernandez, I.; Dyker, C. A.; DeHope, A.; Donnadiu, B.; Frenking, G.; Bertrand, G. *J. Am. Chem. Soc.* **2009**, *131*, 11875.

⁵⁰ Ruiz, D. A.; Melaimi, M.; Bertrand, G. *Chem. Asian J.* **2013**, *8*, 2940.

⁵¹ (a) Chen, W.-C.; Hsu, Y.-C.; Lee, C.-Y.; Yap, G. P. A.; Ong, T.-G. *Organometallics* **2013**, *32*, 2435; (b) Hsu, Y.-C.; Shen, J.-S.; Lin, B.-C.; Chen, W.-C.; Chan, Y.-T.; Ching, W.-M.; Yap, G. P. A.; Hsu, C.-P.; Ong, T.-G. *Angew. Chem., Int. Ed.* **2015**, *54*, 2420; (c) Chen, W.-C.; Chen, W.-C.; Jurca, T.; Peng, C.-J.; Lin, Y.-H.; Wang, Y.-P.; Shih, W.-C.; Yap, G. P. A.; Ong, T.-G. *Angew. Chem., Int. Ed.* **2015**, *54*, 15207.

⁵² Prankevicius, C.; Liu, L.; Bertrand, G.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2016**, *55*, 5536.

⁵³ Alcarazo, M.; Gomez, C.; Holle, S.; Goddard, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 5788.

⁵⁴ Prankevicius, C.; Fan, L.; Stephan, D. W. *J. Am. Chem. Soc.* **2015**, *137*, 5582; (b) Roberts, C. C.; Matias, D. M.; Goldfogel, M. J.; Meek, S. J. *J. Am. Chem. Soc.* **2015**, *137*, 6488; (c) Goldfogel, M. J.; Roberts, C. C.; Meek, S. J. *J. Am. Chem. Soc.* **2014**, *136*, 6227.

⁵⁵ Petz, W.; Öxler, F.; Neumüller, B.; Tonner, R.; Frenking, G. *Eur. J. Inorg. Chem.* **2009**, 4507.

⁵⁶ Ines, B.; Patil, M.; Carreras, J.; Goddard, R.; Thiel, W.; Alcarazo, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 8400.

⁵⁷ Münzer, J. E.; O.-Burgos, P.; A.-Campos, F. M.; Neumüller, B.; Tonner, R.; Fernandez, I.; Kuzu, I. *Eur. J. Inorg. Chem.* **2016**, 3852.

⁵⁸ Khan, S.; Gopakumar, G.; Thiel, W.; Alcarazo, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 5644.

⁵⁹ Celik, M. A.; Frenking, G.; Neumüller, B.; Petz, W. *ChemPlusChem* **2013**, *78*, 1024.

⁶⁰ Chen, W.-C.; Lee, C.-Y.; Lin, B.-C.; Hsu, Y.-C.; Shen, J.-S.; Hsu, C.-P.; Yap, G. P. A.; Ong, T.-G. *J. Am. Chem. Soc.* **2014**, *136*, 914.

⁶¹ (a) Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. C.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789; (b) Trinquier, G.; Marre, M. R.; *J. Phys. Chem.* **1983**, *87*, 1903.

⁶² For similarity in the chemistry of phosphonium and carbene molecules, see: Rosenberg, L. *Coord. Chem. Rev.* **2012**, *256*, 606.

⁶³ For recent reviews, see: (a) Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2015**, *54*, 6400; *Angew. Chem.* **2015**, *127*, 6498; (b) Power, P. P. *Chem. Rev.* **2012**, *12*, 238; (c) Mandal, S. K.; Roesky, H. W. *Acc. Chem. Res.* **2012**, *45*, 298; (d) Power, P. P. *Acc. Chem. Res.* **2011**, *44*, 627; (e) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354; (f) Yao, S.; Xiong, Y.; Driess, M. *Organometallics* **2011**, *30*, 1748; (g) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389; (h) Power, P. P. *Nature* **2010**, *463*, 171; (i) Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 46; *Angew. Chem.* **2010**, *122*, 50.

⁶⁴ Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124.

⁶⁵ Zhu, Z.; Wang, X.; Peng, Y.; Lei, H.; Fettingner, J. C.; Rivard, E.; Power, P. P. *Angew. Chem. Int. Ed.* **2009**, *48*, 2031; *Angew. Chem.* **2009**, *121*, 2065.

⁶⁶ For small molecule activation by heavier group 14 elements, see: (a) Spikes, G. H.; Fettingner, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232; (b) Peng, Y.; Brynda, M.; Ellis, B. D.; Fettingner, J. C.; Rivard, E.; Power, P. P. *Chem. Commun.* **2008**, 6042; (c) Peng, Y.; Ellis, B. D.; Wang, X.; Power, P. P. *J. Am. Chem. Soc.* **2008**, *130*, 12268; (d) Peng, Y.; Guo, J.-D.; Ellis, B. D.; Zhu, Z.; Fettingner, J. C.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2009**, *131*, 16272; (e) Protchenko, A. V.; Birjkumar, K. H.; Dange, D.; Schwarz, A. D.; Vidović, D.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldridge, S. *J. Am. Chem. Soc.* **2012**, *134*, 6500; (f) Protchenko, A. V.; Bates, J. I.; Saleh, L. M. A.; Blake, M. P.; Schwarz, A. D.; Kolychiev, E. L.; Thompson, A. L.; Jones, C.; Mountford, P.; Aldridge, S. *J. Am. Chem. Soc.* **2016**, *138*, 4555.

⁶⁷ (a) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2007**, *46*, 8050; *Angew. Chem.* **2007**, *119*, 8196; (b) Chen, D.; Wang, Y.; Klankermayer, J. *Angew. Chem. Int. Ed.* **2010**, *49*, 9475; *Angew. Chem.* **2010**, *122*, 9665; (c) Greb, L.; O-Burgos, P.; Schirmer, B.; Grimme, S.; Stephan, D. W.; Paradies, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 10164; *Angew. Chem.* **2012**, *124*, 10311; (d) Chernichenko, K.; Madarasz, A.; Papai, I.; Nieger, M.; Leskela, M.; Repo, T. *Nat. Chem.* **2013**, *5*, 718; (e) Mahdi, T.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2013**, *52*, 12418; *Angew. Chem.* **2013**, *125*, 12644; (f) Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2014**, *136*, 3028.

⁶⁸ (a) Frey, G. D.; Lavallo, V.; Donnadiou, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439; (b) Frey, G. D.; Masuda, J. D.; Donnadiou, B.; Donnadiou, B.; *Angew. Chem. Int. Ed.* **2010**, *49*, 9444.

⁶⁹ (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451; (b) Kubas, G. J. *Adv. Inorg. Chem.* **2004**, *56*, 127; (c) Kubas, G. J. *J. Organomet. Chem.* **2001**, *635*, 37; (d) McGrady, G. S.; Guilera, G. *Chem. Soc. Rev.* **2003**, *32*, 383; (e) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95; (f) Kubas, G. J. *Science* **2006**, *314*, 1096.

-
- ⁷⁰ (a) Inomata, K.; Watanabe, T.; Miyazaki, Y.; Tobita, H. *J. Am. Chem. Soc.* **2015**, *137*, 11935; (b) Rit, A.; Tirfoin, R.; Aldridge, S. *Angew. Chem. Int. Ed.* **2015**, *54*, 378.
- ⁷¹ (a) Caputo, C. B.; Hounjet, L. J.; Dobrovetsky, R.; Stephan, D. W. *Science* **2013**, *341*, 1374; (b) Gabbai, F. P. *Science* **2013**, *341*, 1348.
- ⁷² Holthausen, M.; Mehta, M.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 6538.
- ⁷³ Bayne, J. M.; Stephan, D. W. *Chem. Soc. Rev.* **2016**, *45*, 765.
- ⁷⁴ Holthausen, M.; Bayne, J. M.; Mallov, I.; Dobrovetsky, R.; Stephan, D. W. *J. Am. Chem. Soc.* **2015**, *137*, 7298.
- ⁷⁵ Hudnall, T. W.; Kim, Y. M.; Bebbington, M. W. P.; Bourissou D.; Gabbai, F. P. *J. Am. Chem. Soc.* **2008**, *130*, 10890.
- ⁷⁶ Burck, S.; Gudat, D.; Nieger, M. *Angew. Chem. Int. Ed.* **2004**, *43*, 4801.
- ⁷⁷ For pincer-like P(III)-induced bond activation, see: (a) Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, *134*, 11330; (b) McCarthy, S. M.; Lin, Y.-C.; Devarajan, D.; Chang, J. W.; Yennawar, H. P.; Rioux, R. M.; Ess, D. H.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136*, 4640; (c) Zhao, W.; McCarthy, S. M.; Lai, T. Y.; Yennawar, H. P.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136*, 17634; (d) Cui, J.; Li, Y.; Ganguly, R.; Inthirarajah, A.; Hirao, H.; Kinjo, R. *J. Am. Chem. Soc.* **2014**, *136*, 16764; (e) Robinson, T. P.; De Rosa, D. M.; Aldridge, S.; Goicoechea, J. M. *Angew. Chem., Int. Ed.* **2015**, *54*, 13758.
- ⁷⁸ Longobardi, L. E.; Russell, C. A.; Green, M.; Townsend, N. S.; Wang, K.; Holmes, A. J.; Duckett, S. B.; McGrady, J. E.; Stephan, D. W. *J. Am. Chem. Soc.* **2014**, *136*, 13453.
- ⁷⁹ Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidović, D. *Chem. Eur. J.* **2014**, *20*, 6628.

CHAPTER 2

The Synthesis and Reactivity of Transient Carbodiphosphorane-stabilized Phosphenium Dications

Section 2.1. Towards The Synthesis of Carbodiphosphorane-stabilized Phosphenium Dications

Inspired by recent findings of our group that carbodiphosphoranes were able to support the isolation of the first doubly charged phosphenium cation $[(\text{Ph}_3\text{P})_2\text{C}^+\text{PN}^i\text{Pr}_2]^{2+}$, **[1c]**²⁺,¹ we wanted to investigate the scope of substituents different than amino groups, which in combination with carbodiphosphorane (**1**) would be able to support the formation of phosphenium species potentially more Lewis acidic than **[1c]**²⁺. The chosen examples of phenyl- (Ph), 4-fluorophenyl- (4-F-Ph), methoxy- (MeO), and *tert*-butyl-substituents (^tBu) were delivered in the form of dichlorophosphines (e.g. $\text{R}(\text{PCl}_2)_2$), which were subsequently treated with **1** according to the procedure previously described for the synthesis of **[1c]**²⁺. The first step, ligand-for-chloride displacement, occurred smoothly to give the corresponding carbene-stabilized P-monocations (Scheme 2.1). However, the chloride abstraction step using AlCl_3 , Na- or even Ag-salts did not result in the formation of the target dications. Nevertheless, the transient nature of phenyl- (**[1a]**²⁺) and 4-F-phenyl-substituted (**[1b]**²⁺) phosphenium dications was subsequently confirmed in C-F bond activation reactions, as well as in a trapping experiment employing PMe_3 as a Lewis base.

Scheme 2.1. Attempted synthesis of novel phosphenium dications. Reagents and conditions: (a) excess of $\text{R}(\text{PCl}_2)_2$, benzene, ambient temperature; (b) AlCl_3 , $\text{Na}[\text{BAr}^{\text{Cl}}_4]$, $\text{Ag}[\text{BAr}^{\text{Cl}}_4]$ ($\text{Ar}^{\text{Cl}} = 3,5\text{-(Cl)}_2\text{-C}_6\text{H}_3$), $\text{Na}[\text{BAr}^{\text{F}}_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$) (2 or 3 equiv), dichloromethane (DCM) or 1,2-difluorobenzene, ambient temperature.

Since the synthetic route for the preparation of $[\mathbf{1c}]^{2+}$ appeared as a high-yielding procedure, we decided to use the same method for the preparation of our target molecules. The corresponding monocations $[(\text{Ph}_3\text{P})_2\text{C}^+\text{P}(\text{R})\text{Cl}][\text{Cl}]$ ($[\mathbf{1a-Cl}][\text{Cl}]$, $\text{R} = \text{Ph}$; $[\mathbf{1b-Cl}][\text{Cl}]$, $\text{R} = 4\text{-FPh}$) were prepared by adding the free carbene ligand $(\text{Ph}_3\text{P})_2\text{C} \mathbf{1}$ to the benzene solution containing an excess of the respective dichlorophosphine RPCl_2 ($\text{R} = \text{Ph}$, 4-F-Ph) as depicted in Scheme 2.1. Ligand-for-chloride exchange was primarily evidenced from the ^{31}P NMR spectrum where a triplet (~ 111 ppm) and a doublet (~ 25 ppm) corresponding to the central and carbene's phosphorus atoms, respectively, were observed. Furthermore, the diluted solutions of $[\mathbf{1a-Cl}]^+$ and $[\mathbf{1b-Cl}]^+$ were prepared and analyzed via ESI-MS. The obtained data was consistent with the spectroscopic measurements. Signals at m/z 679.1592 (calculated for $\text{C}_{43}\text{H}_{35}\text{ClP}_3$: m/z 679.1640) and 697.1511 (calculated for $\text{C}_{43}\text{H}_{34}\text{ClFP}_3$: m/z 697.1546) further confirmed the coordination of $\mathbf{1}$ to the corresponding P-fragments $[\mathbf{1a-Cl}]^+$ and $[\mathbf{1b-Cl}]^+$, respectively. The structural identities of these monocations were unambiguously elucidated from single crystal X-ray diffraction analysis. X-ray quality crystals for $[\mathbf{1a-Cl}]^+$ and $[\mathbf{1b-Cl}]^+$ (Figures 2.1 and 2.2, respectively) were obtained after the non-coordinating chloride anion was replaced with hexafluoroantimonate(V) anion ($[\text{SbF}_6]$). The crystal structure of compound $[\mathbf{1a-Cl}][\text{SbF}_6]$ revealed a high degree of disorder and hence its structural parameters are exempted from further discussion.

Figure 2.1. Single crystal X-ray structure of $[1a-Cl][SbF_6]$ at 50% probability. The counterion, hydrogen atoms as well as the observed disorder were omitted for clarity. The closest contact between the central P and the anion is 4.839 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.856(8), P1-Cl1, 2.002(10), P1-C2, 1.838(10), C2-P1-C1, 105.5(9), C2-P1-Cl1, 101.4(7), C1-P1-Cl1, 108.1(5).

Figure 2.2. Single crystal X-ray structure of $[1b-Cl][SbF_6]$ at 50% probability. The counterion and hydrogen atoms were omitted for clarity. The closest contact between the central P and the anion is 4.904 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.7828(13), P1-Cl1, 2.1271(5), P1-C2, 1.8290(14), C2-P1-C1, 104.31(6), C2-P1-Cl1, 100.55(5), C1-P1-Cl1, 107.15(5).

The molecular structure of monocation $[\mathbf{1b-Cl}]^+$ presented in Figure 2.2, reveals the pyramidal geometry around the central phosphorus atom with the sum of interligand angles of $312.01(7)^\circ$. The P1-Cl bond length is $1.7828(13)$ Å and the bond distance for P1-Cl1 is $2.1271(5)$ Å. Both values are relatively short with respect to the analogous bond lengths found in $[\mathbf{1c-Cl}]^+$ [$1.812(5)$ and $2.173(2)$ Å, respectively].^{1a} This observation was somewhat expected considering that both Ph and 4-F-Ph substituents are weaker π -donors than diisopropylamino group. Nonetheless, a shorter P-Cl bond distance for $[\mathbf{1b-Cl}]^+$ (and presumably for $[\mathbf{1a-Cl}]^+$) indicated that chloride abstraction from $[\mathbf{1a-Cl}]^+ / [\mathbf{1b-Cl}]^+$, potentially leading to the target dication $[\mathbf{1a}]^{2+} / [\mathbf{1b}]^{2+}$, might be more demanding than in the case of the amino-substituted analogue $[\mathbf{1c-Cl}]^+$.

Indeed, the addition of 2 or even 3 equiv of $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ ($\text{Ar}^{\text{Cl}} = 3,5\text{-(Cl)}_2\text{-C}_6\text{H}_3$) or $\text{Na}[\text{BAr}^{\text{F}}_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{F}_3$) to either dichloromethane or 1,2-difluorobenzene solutions of $[\mathbf{1a-Cl}][\text{Cl}] / [\mathbf{1b-Cl}][\text{Cl}]$ did not result in P-Cl bond cleavage under ambient conditions. Further attempts to heterolytically cleave the P-Cl bond involved the addition of 2 equiv of AlCl_3 to a dichloromethane solution of either $[\mathbf{1a-Cl}][\text{Cl}]$ or $[\mathbf{1b-Cl}][\text{Cl}]$. Reaction progress was monitored by ^{31}P NMR spectroscopy and in both instances no signals in the range typical for phosphonium salts were registered.² In fact, very complicated ^{31}P NMR spectra was obtained after the addition of AlCl_3 whereas $\text{Na}[\text{BAr}^{\text{Cl}}_4] / \text{Na}[\text{BAr}^{\text{F}}_4]$ did not react with the inner-sphere chloride atom under the same reaction conditions. These observations suggested that (i) Na-based salts might not be chlorophilic enough to abstract the chloride atom from inner sphere of phenyl- and 4-fluorophenyl-substituted P-monocations at ambient conditions, (ii) upon formation, $[\mathbf{1a}]^{2+}$ and $[\mathbf{1b}]^{2+}$ might be very reactive leading to the formation of a complicated reaction mixture when 2 equiv of AlCl_3 were used.

In order to remove the chlorine atoms from the inner coordination spheres of $[\mathbf{1a-Cl}]^+ / [\mathbf{1b-Cl}]^+$, we decided to use silver-based reagents instead of sodium-based ones. Ag salts are well known halogen abstracting agents due to the exceptionally high lattice potential energies of silver halides.³ Therefore, the formation of silver halides provides a large driving force leading to more feasible ionization of the substrate.³ In view of these considerations, we have synthesized $\text{Ag}[\text{BAr}^{\text{Cl}}_4]$ according to the previously described procedure.⁴ The addition of 2 equiv of $\text{Ag}[\text{BAr}^{\text{Cl}}_4]$ to a 1,2-difluorobenzene solution of

$[\mathbf{1a-Cl}][\text{Cl}]/[\mathbf{1b-Cl}][\text{Cl}]$ resulted in the formation of 2 new signals as judged by ^{31}P NMR spectroscopy. The doublet corresponding to the P-atoms of carbene ligand (δ_{P} 25 ppm) was shifted slightly downfield to δ_{P} 27 ppm, while the triplet assigned to the central P of $[\mathbf{1a-Cl}]^+ / [\mathbf{1b-Cl}]^+$ (δ_{P} 110 ppm) appeared upfield at δ_{P} 87 ppm. For comparison, the same reaction was carried in DCM resulting in a slightly changed ^{31}P NMR spectrum with respect to the starting materials $[\mathbf{1a-Cl}]^+ / [\mathbf{1b-Cl}]^+$. The doublet at δ_{P} 25 ppm exhibited a similar value, while the triplet at δ_{P} 110 ppm was shifted slightly upfield to δ_{P} 107 ppm. These observations support the claim that (i) Ag-based reagents are superior to Na-salts with respect to the chloride abstraction from inner spheres of $[\mathbf{1a-Cl}]^+ / [\mathbf{1b-Cl}]^+$, and that (ii) highly reactive nature of newly formed $[\mathbf{1a}]^{2+}$ and $[\mathbf{1b}]^{2+}$ gave rise to new P-containing species. However, one should also note that Ag^+ ion might not always be the most suitable reagent for halide abstraction as under certain conditions this cation was found to oxidize the substrate.⁵ Unfortunately, numerous attempts to grow crystals from these reaction mixtures were not successful, thus providing no conclusions about the nature of the newly formed products.

Next, we focused our efforts on obtaining methoxy-substituted phosphonium dication. Using the same synthetic procedure, we prepared $[(\text{Ph}_3\text{P})_2\text{C}^+\text{P}(\text{OMe})\text{Cl}][\text{Cl}]$, $[\mathbf{1e-Cl}][\text{Cl}]$ in excellent yield (Scheme 2.1). The ^{31}P NMR spectrum displayed a doublet at δ_{P} 22 ppm corresponding to the P-atoms of **1** and a triplet at δ_{P} 216 ppm consistent with the central phosphorus. The latter signal was downfield-shifted for more than 100 ppm with respect to $[\mathbf{1a-Cl}]^+ / [\mathbf{1b-Cl}]^+$ (δ_{P} 110 ppm) and more than 80 ppm compared to the value observed for $[\mathbf{1c-Cl}]^+$ (δ_{P} 133 ppm).^{1a} Furthermore, the central P atom of $[\mathbf{1e-Cl}][\text{Cl}]$ appeared about 40 ppm downfield with respect to the δ_{P} of the starting dichlorophosphine (MeOPCl_2 , δ_{P} 180 ppm). So far, only one example of P-centered chloride-for-carbene exchange leading to the more downfield chemical shift of the monocationic product has been reported.⁶ The ^1H NMR spectrum of $[\mathbf{1e-Cl}][\text{Cl}]$ showed a doublet at δ_{H} 3.09 ppm corresponding to the methoxy group attached to the central P. Finally, the molecular structure of $[\mathbf{1e-Cl}]^+$ was elucidated after replacing the chloride with $[\text{SbF}_6]^-$ anion (Figure 2.3). The P1-Cl1 bond of $[\mathbf{1e-Cl}]^+$ (2.1558(15) Å) was found to be longer than the analogous bond for $[\mathbf{1b-Cl}]^+$ (2.1271(5) Å) but shorter than the corresponding P-Cl bond

of $[\mathbf{1c-Cl}]^+$ (2.173(2) Å).^{1a} The elongation of the P-Cl bond in the following order $[\mathbf{1b-Cl}]^+ < [\mathbf{1e-Cl}]^+ < [\mathbf{1c-Cl}]^+$ compares well with the π -donor strength of the respective substituents attached to the central P-atom (4-F-Ph < OMe < NⁱPr₂). Moreover, this observation might indicate the feasibility of the potential ionization of P-monocations towards the target dication molecules.

Figure 2.3. Single crystal X-ray structure of $[\mathbf{1e-Cl}][\text{SbF}_6]$ at 50% probability. The counterion and hydrogen atoms were omitted for clarity. The closest contact between the central P and the anion is 4.710 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.781(3), P1-Cl1, 2.1558(15), P1-O1, 1.631(3), O1-P1-C1, 96.71(16), O1-P1-Cl1, 98.15(12), C1-P1-Cl1, 106.30(12).

Unfortunately, the addition of 2 equiv of AlCl_3 or $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ to a DCM solution of $[\mathbf{1e-Cl}][\text{Cl}]$ at ambient temperature did not give the desired dication $[\mathbf{1e}]^{2+}$. Instead, a single resonance at δ_{P} 19 ppm corresponding to $[(\text{Ph}_3\text{P})_2\text{CH}]^+$ was observed in the $^{31}\text{P}\{^1\text{H}\}/^{31}\text{P}$ NMR spectra.⁷ This observation suggested that despite being a better π -donor than 4-F-Ph- and Ph-substituents, the methoxy group does not possess sufficient electron-donating character for thermodynamic stabilization of the target dication. In fact, electron-depletion on the P-center induced by the high electronegativity of the neighboring oxygen atom might be the reason behind the instability of $[\mathbf{1e}]^{2+}$ under ambient conditions.

The use of moderately strong electron-donor substituents (4-F-Ph, Ph, and OMe) in combination with carbene (**1**) was not sufficient for the preparation of phosphonium

dications. While *tert*-butyl (^tBu) group is considered as strong σ-donor, its non-conjugating character might be the prevailing factor in the synthesis of the target dication [(Ph₃P)₂C^tBP^tBu]²⁺, [**1d**]²⁺. Nevertheless, we prepared its precursor [(Ph₃P)₂C^tBP(^tBu)Cl][Cl], [**1d-Cl**][Cl] by treating the benzene solution of **1** with an excess of ^tBuPCl₂. The identity of [**1d-Cl**][Cl] was established using spectroscopic methods. A multiplet derived from two second order doublets at δ_P 23 ppm and a second order triplet at δ_P 132 ppm corresponding to the carbene's and central P-atoms, respectively, were registered in the ³¹P NMR spectrum. Furthermore, coupling of ^tBu-protons with the central ³¹P nucleus gave rise to a doublet at δ_H 0.6 ppm (³J_{PH} = 15 Hz) in the ¹H NMR spectrum. The identity of [**1d-Cl**]⁺ was also confirmed by ESI-MS analysis where a signal at *m/z* 659.1955 (calculated for C₄₁H₃₉ClP₃; *m/z* 659.1953) with a matching isotope pattern was registered. As speculated, the addition of 2 or even 3 equiv of AlCl₃/Na[BAr^{Cl}₄] to a DCM solution of [**1d-Cl**][Cl] did not give the target phosphonium dication [**1d**]²⁺. Instead, the ³¹P NMR spectrum revealed [(Ph₃P)₂CH]⁺ as only P-containing species in the solution. This result indicated that electron-donating characteristics of ^tBu-group, as well as methoxy and phenyl-based substituents, combined with those of **1**, were not sufficient for thermodynamic stabilization of P-dications presumably due to their extremely electrophilic nature. Therefore, we sought to exploit Lewis acidity of the target phosphonium salts to gather experimental evidence for their transient nature.

2.2. C-F Bond Activation by Transient Phosphenium Dications

Since the isolation of elemental fluorine in 1886, fluorinated building blocks have been of utmost importance in both industrial and academic research. High significance of these compounds is reflected by their wide application in areas such as materials science, polymer chemistry, catalysis, crop protection, medicine, pharmacy, and biochemistry.⁸ Moreover, the extreme electronegativity and small size of fluorine induce high ionic character and render carbon–fluorine bond the strongest single bond that carbon forms with any element.⁹ Therefore, the introduction of fluorine atom into simple hydrocarbon molecules represents an important tool for the design of various commercial products whose physicochemical properties significantly differ from those of starting hydrocarbons. For instance, poly(tetrafluoroethylene) and high performance lubricants are known as extremely useful durable goods.

High kinetic and thermodynamic inertness of C-F bonds has certainly found many useful applications, however, it is also the main cause behind environmental persistency and potential toxicity of perfluorinated compounds.¹⁰ Their contribution to global warming (greenhouse gases) and depletion of ozone layer (chlorofluorocarbons – CFCs) are generally accepted.^{11a} With an atmospheric half-life greater than 5×10^4 years for CF_4 , the disposal of organofluorine waste remains a challenge.^{11b}

There is a growing interest in developing different pathways for C–F bond activation. Transition metals are currently dominating this field,¹² as they can be used for both stoichiometric and catalytic transformations. Transition metal catalyzed replacement of fluorine by other organic groups is very attractive as it allows the synthesis of partially fluorinated synthetic intermediates from rather inactive per- or oligofluorinated species.^{13d} However, it should be noted that transition metal complexes have showed preference for polyfluoroarenes and fluoroalkenes,^{12a-d} with very few examples being able to transform fundamentally more challenging alkyl- and perfluoroalkyl compounds.^{12p,q}

Scheme 2.2. General approaches towards C-F bond activation

Recently, main-group Lewis acids have emerged as a very effective method for selective C–F bond cleavage of saturated fluorocarbons. While single-electron transfer or oxidative addition to an electron-rich metal center are preferred pathways for most metal-based systems, main group Lewis acids combine both Lewis acidity and fluorine affinity for heterolysis of C(sp³)-F bonds via fluoride abstraction (Scheme 2.2). For example, high dissociation energy of Si-F bond (~140 kcal/mol) renders electron deficient silicon compounds (e.g. R₃Si⁺) particularly suitable for C-F bond activation (Figure 2.4, **LVI**).¹³ In fact, silanes are the most commonly used fluorine scavengers in catalytic C-F functionalizations.¹⁴ Boron- (**LVII**) and aluminium-based Lewis acids (**LVIII**) are also reported to be effective in C–F bond activation (Figure 2.4).¹⁵ Their Lewis acidic behavior is induced by the presence of a formally vacant p atomic orbital located on the main group atom. Recent reports from Stephan and co-workers have demonstrated that organofluorophosphonium cations (i.e. P(V)-based cations) could be used in catalytic C–F activation (**XLVI** and **XLVII**). This is the very first example of C–F activation performed at Lewis acidic P-centers with a full valence of eight electrons. Their fluorophilicity originates from an empty coordination site formally defined as σ* orbital whose lobe is mainly located on the phosphorus center.¹⁶ However, no examples of P(III)-based compounds used for C–F bond cleavage have been reported to date. We postulated that phosphonium dication could be a suitable candidate, as they possess both a formally vacant 3p atomic orbital and a positively charged phosphorus atom.² Therefore, we investigated the reactivity of transient P(III)-based dication towards C–F bond cleavage

using $[\text{BAr}^{\text{F}}_4]^-$ anion $[\text{Ar}^{\text{F}} = (\text{CF}_3)_2\text{-C}_6\text{H}_3]$ and α,α,α -trifluorotoluene (PhCF_3) as fluoride source.

Figure 2.4. Silicon- (**LVI**), boron- (**LVII**), aluminum- (**LVIII**), and phosphorus-based (**XLVI** and **XLVII**) Lewis acids used in C-F bond activation. Note: anions were deleted for clarity.

As previously mentioned, target phosphonium dications $[\mathbf{1a}]^{2+}$ and $[\mathbf{1b}]^{2+}$ were not formed upon the addition of either 2 or 3 equiv of $\text{Na}[\text{BAr}^{\text{F}}_4]$ to a solution containing either of monocations $[\mathbf{1a}\text{-Cl}]^+ / [\mathbf{2b}\text{-Cl}]^+$ at room temperature. Nonetheless, when reaction mixture of $[\mathbf{1a}\text{-Cl}][\text{Cl}]$ and 3 equiv of $\text{Na}[\text{BAr}^{\text{F}}_4]$ in 1,2-difluorobenzene was heated at 100°C overnight (Scheme 2.3), apart from evident disappearance of the triplet signal assigned to $[\mathbf{1a}\text{-Cl}]^+$ (δ_{P} 110.5 ppm), a new doublet of triplets at δ_{P} 162.2 ppm appeared (Figure 2.5). While carbene ligand caused the triplet splitting of the newly formed signal, its chemical shift value indicated the presence of a stronger electron-withdrawing substituent at the three-coordinate central P atom. Furthermore, the value for the doublet coupling constant ($^1J_{\text{P-F}} = 976.4$ Hz) suggested the formation of a P-F bond.

* Ar^F = 3,5-(CF₃)₂-C₆H₃; Ar^{Cl} = 3,5-(Cl)₂-C₆H₃

Scheme 2.3. General synthetic procedures.

Figure 2.5. ³¹P NMR Spectra of $[\mathbf{1a-Cl}]^+$ (upper) and $[\mathbf{1a-F}]^+$ (bottom).

An additional evidence for the formation of a P–F fragment was observed in the ^{19}F NMR spectrum (δ_{F} -161.2 ppm; $^1J_{\text{F-P}} = 976.4$ Hz). Next, the crude reaction mixture was investigated by electrospray mass spectrometry (ESI-MS). A signal at m/z 663.2006 (calculated for $\text{C}_{43}\text{H}_{35}\text{FP}_3$: m/z 663.1936) whose isotope pattern was ideally aligned with a carbene-stabilized fluorinated P-monocation $[(\text{Ph}_3\text{P})_2\text{C}(\text{Ph})\text{F}]^+$, $[\mathbf{1a-F}]^+$ was observed. Unfortunately, all attempts to elucidate the identity of $[\mathbf{1a-F}]^+$ by means of X-ray diffraction were not successful. However, the identity of $[\mathbf{1a-F}]^+$ was confirmed by treating $[\mathbf{1a-Cl}][\text{BAr}^{\text{Cl}}_4]$ with an excess of KF. Fluoride-for-chloride displacement resulted in identical ^{31}P and ^{19}F NMR spectra observed previously for the crude reaction mixture.

Even though it was not immediately evident whether the solvent or the anion was the source of fluoride, we assumed that highly reactive nature of the transient phosphonium dication $[(\text{Ph}_3\text{P})_2\text{C}(\text{Ph})\text{P}]^{2+}$, $[\mathbf{1a}]^{2+}$ might be responsible for the observed C–F bond cleavage. To gain an insight about the existence of these interesting species, we performed a trapping experiment based on the formation of an acid-base adduct. The addition of a Lewis base (PMe_3) to a solution containing $[\mathbf{1a-Cl}][\text{Cl}]$ and 2 equiv of $\text{Na}[\text{BAr}^{\text{F}}_4]$ gave adduct $[(\text{Ph}_3\text{P})_2\text{C}(\text{Ph})\text{P}(\text{PMe}_3)][\text{BAr}^{\text{F}}_4]_2$, $[\mathbf{1a-PMe}_3][\text{BAr}^{\text{F}}_4]_2$. The identity of this compound was elucidated using both solution- and solid-state characterization techniques. The ^{31}P NMR spectrum revealed the presence of three second order signals at δ_{P} -6.4 (doublet of triplets), 11.4 (doublet of triplets), and 28.7 (doublet), while ESI-MS signal at m/z 360.1197 (calculated for $[\text{C}_{46}\text{H}_{44}\text{P}_4]^{2+}$: m/z 360.1191) further supported the formation of the expected reaction product. In addition, crystal structure of $[\mathbf{1a-PMe}_3][\text{BAr}^{\text{F}}_4]_2$ (Figure 2.6)¹⁷ revealed that P1–C1 [1.792(4) Å] and P1–C2 [1.826(4) Å] bond lengths were very similar to those of the monocationic precursor $[\mathbf{1b-Cl}]^+$, while P1–P4 bond distance [2.217(2) Å] was comparable with the value [2.187(2) Å] previously observed for $[\text{Ph}_2\text{P-PMe}_3]^+$ adduct.¹⁸

Figure 2.6. Molecular structure for $[4a \cdot PMe_3][BAR^F_4]_2$ drawn at 50% probability. The counterions, hydrogen atoms and disordered solvent molecules have been omitted for clarity. The closest contact between the central P and the anion is 5.322 Å. Selected bond lengths [Å]: P1-C1, 1.792(4); P1-C2, 1.826(4); P1-P4, 2.2173(1).

To gain further insight into the origin of the fluoride anion, $Na[BAR^F_4]$ was replaced with fluorine-free chloride abstracting agent $Na[BAR^{Cl}_4]$, thus leaving the solvent as only fluorine source present in the reaction mixture. In fact, the non-coordinating chloride anions of the monocationic precursors $[1a-Cl][Cl]$ and $[1b-Cl][Cl]$ were first replaced by $[BAR^{Cl}_4]^-$ to give $[1a-Cl][BAR^{Cl}_4]$ and $[1b-Cl][BAR^{Cl}_4]$, respectively (Scheme 2.3). Next, to a 1,2-difluorobenzene solution containing either of these two monocations 2 equiv of $Na[BAR^{Cl}_4]$ were added. The resulting mixture was heated at 100°C overnight, and then investigated by means of ^{31}P and ^{19}F NMR Spectroscopy. None of the reaction mixtures showed formation of any “P-F” fragments, thus eliminating the solvent as fluoride source in the original experiment. Then, to the same reaction mixtures 1 equiv of $PhCF_3$ was introduced followed by heating at 100°C for several hours. In this case, the formation of fluorinated monocations $[1a-F]^+$ and $[(Ph_3P)_2C^+P(4-F-Ph)F]^+$, $[1b-F]^+$ was evident (Scheme 2.3). These observations clearly indicated that the source of the fluoride in the initial experiment was $[BAR^F_4]^-$ anion.¹⁹

In order to inspect whether phosphonium dications $[1a]^{2+}$ or $[1b]^{2+}$ formed *in situ* were responsible for the observed C–F bond cleavage, a 1:1 molar mixture of $Na[BAR^{Cl}_4]$ and $PhCF_3$ was allowed to react under the same experimental conditions. As expected, ^{19}F

NMR spectroscopy showed no reactivity hence, confirming the potential of doubly charged P(III)-species to cleave C–F bonds of fluorinated compounds (PhCF₃ and [BAr^F₄][–]). Unfortunately, when other organofluorine substrates such as C₆F₅Br, (CF₃CH₂)₂O, and (CF₃)(CF₂)₆CHF₂ were introduced to reaction mixtures containing either of monocations [1a-Cl][BAr^{Cl}₄] or [1b-Cl][BAr^{Cl}₄] and 2 equiv of Na[BAr^{Cl}₄] under the same experimental conditions, no evidence for the formation of the corresponding P–F fragments was gathered. This was presumably due to the absence of a phenyl group adjacent to the potentially cleaved C–F bond, as phenyl rings were found to assist in stabilization of the corresponding carbocations.²⁰ The same holds true for the observed selectivity of transient phosphonium dications towards activation of PhCF₃ and [BAr^F₄][–] anion. Nevertheless, this work features the first example of P(III)-based compounds capable of activating α-phenyl C–F bonds.

To better understand the difference in the electronic and structural properties between the transient [1a]²⁺ and [1b]²⁺, and the isolable dication [1c]²⁺, a detailed computational analysis using the *Gaussian 09* package was performed. The dications were fully optimized by the B3PW91 method with 6-31G(d) basis set. As the nature of the frontier orbitals for all compounds appeared to be virtually identical, only molecular orbitals of [1a]²⁺ are displayed in Figure 2.7.

Figure 2.7. Frontier molecular orbitals for [1a]²⁺.

The lowest unoccupied molecular orbitals (LUMOs) were virtually quite comparable to the π^* for the allene-like CPX bonding motif (X = C for [1a]²⁺/[1b]²⁺; X =

N for $[1c]^{2+}$). The highest occupied molecular orbitals (HOMOs) are mainly non-bonding with helical-like shape, presumably as a result of the slight mixing of the atomic orbital that resembles the lone pair on the central phosphorus and orbitals on the adjacent atoms of the CPX moiety.²¹ Apart from the identical shape, HOMOs of the respective dications possess similar energy levels as well: -0.43791, -0.43854, and -0.43453 eV for $[1a]^{2+}$, $[1b]^{2+}$, and amino-substituted dication $[1c]^{2+}$, respectively. However, LUMO(s) for transient dications $[1a]^{2+}$ (-0.31248 eV) and $[1b]^{2+}$ (-0.31315 eV) appeared to be more stabilized with respect to an analogous orbital of $[1c]^{2+}$ (-0.28129 eV). The same trend was observed when amino groups of the bis(amino)phosphenium monocation were replaced by phenyl substituents.²² These observations indicated that more accessible LUMOs of transient phenyl-substituted phosphenium dications were not only responsible for their transient nature, but also for ability to activate enthalpically strong C-F bond. Moreover, isolable amino-substituted phosphenium dication was chemically inert towards organofluorine compounds under the same experimental conditions.

Surprisingly, according to the NBO analysis, the central phosphorus atom of $[1a]^{2+}$ (+1.02e) and $[1b]^{2+}$ (+1.02e) appeared to have a less positive partial charge with respect to an analogous atom for $[1c]^{2+}$ (+1.22e). The higher electron deficiency at the central phosphorus of $[1c]^{2+}$ might be due to electron density overcompensation from the carbene ligand to the central phosphorus atom of $[1a]^{2+}$ or $[1b]^{2+}$. However, the difference in electronegativity between the nitrogen (N^iPr_2) and carbon atoms (Ph and 4-F-Ph) of the corresponding substituents should not be ruled out. Nevertheless, this observation indicates that the Lewis acidity of a compound might not necessarily be affected by the electron depletion at the central atom as much as by the accessibility of its LUMO.

In this chapter, we demonstrated that a combination of carbodiphosphorane ligand with alkyl, alkoxy, and phenyl-based substituents was not sufficiently electron donating to enable the isolation of the corresponding two-coordinate P-dications. The transient nature of phenyl ($[1a]^{2+}$) and 4-fluorophenyl ($[1b]^{2+}$) phosphenium dications was utilized in the activation of enthalpically strong α -phenyl C-F bonds. Theoretical analysis revealed that higher fluorophilicity of transient dications $[1a]^{2+}$ / $[1b]^{2+}$ compared to amino-substituted analogue $[1c]^{2+}$ was due to the greater accessibility of their LUMOs. In order to overcome a rather limited scope of thermodynamically stable phosphenium dications and explore

further their reactivity as strong Lewis acids, we turned our efforts towards finding a more suitable (stronger electron-donor) carbene-type ligand.

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- ¹ (a) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidović, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 3132; (b) Tay, M. Q. Y.; Ilić, G.; W.-Zwanziger, U.; Lu, Y.; Ganguly, R.; Ricard, L.; Frison, G.; Carmichael, D.; Vidović, D. *Organometallics* **2016**, *35*, 439; (c) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Frison, G.; Ricard, L.; Vidović, D.; Carmichael, D. *Phosphorus, Sulfur Silicon Relat. Elem.* **2015**, *190*, 785.
- ² (a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367; (b) Gudat, D. *Coord. Chem. Rev.* **1997**, *163*, 71.
- ³ Raabe, I.; Krossing, I. *Angew. Chem. Int. Ed.* **2004**, *43*, 2066.
- ⁴ Ag[BAr^{Cl}₄] was synthesized according to the modified preparation procedure for Ag[BAr^F₄]: Miller, K. J.; Kitagawa, T. T.; Abu-Omar, M. M. *Organometallics* **2001**, *20*, 4403.
- ⁵ Conolly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
- ⁶ Loh, Y. K.; Gurnani, C.; Ganguly, R.; Vidović, D. *Inorg. Chem.* **2015**, *54*, 3087.
- ⁷ (a) Driscoll, J. S.; Grisley, D. W. Jr.; Pustinger, J. V.; Harris, J. E.; Matthews, C. N. J. *Org. Chem.* **1964**, *29*, 2427; (b) Zybil, C.; Müller, G. *Organometallics* **1987**, *6*, 2489.
- ⁸ (a) Welch, J. T.; Eswarakrishnan, S. *Fluorine in Bioorganic Chemistry*; John Wiley & Sons: 1991. (b) Nakajima, T.; Zemva, B.; Tressaud, A. *Advanced Inorganic Fluorides: Synthesis, Characterization and Applications*; Elsevier Science: Amsterdam, 2000. (c) Banks, R. E. *Fluorine Chemistry at the Millennium: Fascinated by Fluorine*; Elsevier: Amsterdam, 2000. (d) Ameduri, B.; Boutevin, B. *Well-Architected Fluoropolymers: Synthesis, Properties and Applications*; Elsevier Science: 2004. (e) Kirsch, P. *Modern Fluoroorganic Chemistry: Synthesis, Reactivity and Applications*; Wiley-VCH: Weinheim, 2004. (f) Chambers, R. D. *Fluorine in Organic Chemistry*; Blackwell, 2004. (g) Nakajima, T.; Groult, H. *Fluorinated Materials for Energy Conversion*; Elsevier: 2005. (h) Gladysz, J. A.; Curran, D. P.; Horvath, I. T. *Handbook of Fluorous Chemistry*; Wiley-VCH: Weinheim, 2006. (i) Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881. (j) Paquette, L. A. *Handbook of Reagents for Organic Synthesis: Fluorine-Containing Reagents*; Wiley: New York, 2007. (k) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320. (l) Hagmann, W. K. *J. Med. Chem.* **2008**, *51*, 4359. (m) Tressaud, A.; Haufe, G. *Fluorine and Health: Molecular Imaging, Biomedical Materials and Pharmaceuticals*; Elsevier Science: 2008. (n) Bégué, J. P.; Bonnet-Delpon, D. *Bioorganic and Medicinal Chemistry of Fluorine*; John Wiley & Sons, Inc.: Hoboken, New York, 2008. (o) Petrov, V. A. *Fluorinated Heterocyclic Compounds: Synthesis, Chemistry, and Applications*; Wiley: 2009. (p) Tressaud, A. *Functionalized Inorganic Fluorides: Synthesis, Characterization and Properties of Nanostructured Solids*; Wiley: 2010. (q) O'Hagan, D. *J. Fluorine Chem.* **2010**, *131*, 1071. (r) Lee, E.; Kamlet, A. S.; Powers, D. C.; Neumann, C. N.; Boursalian, G. B.; Furuya, T.; Choi, D. C.; Hooker, J. M.; Ritter, T. *Science* **2011**, *334*, 639. (s) Tredwell, M.; Gouverneur, V.

Angew. Chem. **2012**, *124*, 11590. (t) Tredwell, M.; Gouverneur, V. *Angew. Chem. Int. Ed.* **2012**, *51*, 11426. (u) Stenhagen, I. S. R.; Kirjavainen, A. K.; Forsback, S. J.; Jorgensen, C. G.; Robins, E. G.; Luthra, S. K.; Solin, O.; Gouverneur, V. *Chem. Commun.* **2013**, *49*, 1386. (v) Sanford, G. *Philos. Trans. R. Soc. London Ser. A* **2000**, *358*, 455.

⁹ (a) Smart, B. E. *Mol. Struct. Energ.* **1986**, *3*, 141. (b) Hudlicky, M. *Chemistry of Organic Fluorine Compounds*; Prentice-Hall: New York, 1992; p 175. (c) Hiyama, T. *Organofluorine Compounds Chemistry and Applications*; Springer: New York, 2000. (d) Uneyama, K. *Organofluorine Chemistry*; Blackwell: Oxford, U.K., 2006. (e) O'Hagan, D. *Chem. Soc. Rev.* **2008**, *37*, 308.

¹⁰ (a) Banks, R. E.; Smart, B. E.; Tatlow, J. C. *Organofluorine chemistry, Principles and Commercial Applications*; Plenum: New York, 1994. (b) So, M. K. *et al.*, *Env. Sci. Tech.* **2004**, *38*, 4056.

¹¹ (a) Hong, Y. C.; Uhm, H. S. *Phys. Plasmas* **2003**, *10*, 3410. (b) Ravishankara, A. R.; Solomon, S.; Turnipseed, A. A.; Warren, R. F. *Science* **1993**, *259*, 194.

¹² For example, see: (a) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373. (b) Amil, H.; Uneyama, K. *Chem. Rev.* **2009**, *109*, 2119. (c) Furuya, T.; Benitez, D.; Tkatchouk, E.; Strom, A. E.; Tang, P.; Goddard III, W. A.; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 3793. (d) Torrents, H. *Coord. Chem. Rev.* **2005**, *249*, 1957. (e) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber.* **1997**, *130*, 145. (f) Richmond, T. G. in *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer: New York, 1999; Vol. 3, pp. 243. (g) Reinhold, M.; McGrady, J. E.; Perutz, R. N. *J. Am. Chem. Soc.* **2004**, *126*, 5268, and references within. (h) Perutz, R. N.; Braun, T. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007; Vol. 1, p 725. (i) Kuehnel, M. F.; Lentz, D.; Braun, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 3328. (j) Hughes, R. P. *Eur. J. Inorg. Chem.* **2009**, 4591. (k) Mazurek, U.; Schwarz, H. *Chem. Commun.* **2003**, 1321. (l) Jones, W. D. *Dalton Trans.* **2003**, 3991. (m) Braun, T.; Perutz, R. N. *Chem. Commun.* **2002**, 2749. (n) Richmond, T. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 3241. (o) Ahrens, T.; Kohlmann, J.; Ahrens, M.; Braun, T. *Chem. Rev.* **2015**, *115*, 931 and references cited therein. (p) Mo, Z.; Zhang, Q.; Deng, L. *Organometallics* **2012**, *31*, 6518. (q) Choi, J.; Wang, D. Y.; Kundu, S.; Choliy, Y.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *Science* **2011**, *332*, 1545.

¹³ (a) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325. (b) Azhakar, R.; Roesky, H. W.; Wolf, H.; Stalke, D. *Chem. Commun.* **2013**, *49*, 1841. (c) Stahl, T.; Klare, H. F. T.; Oestreich, M. *J. Am. Chem. Soc.* **2013**, *135*, 1248. (d) Stahl, T.; Klare, H. F. T.; Oestreich, M. *ACS Catal.* **2013**, *3*, 1578 and references cited therein.

¹⁴ For example, see: (a) Yang, J.; Brookhart, M. *J. Am. Chem. Soc.* **2007**, *129*, 12656. (b) Reade, S. P.; Mahon, M. F.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2009**, *131*, 1847. (c) Kuehnel, M. F.; Holstein, P.; Kliche, M.; Krüger, J.; Matthies, S.; Nitsch, D.; Schutt, J.; Sparenberg, M.; Lentz, D. *Chem. Eur. J.* **2012**, *18*, 10701.

¹⁵ (a) Hirano, K.; Fujita, K.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Tetrahedron Lett.* **2004**, *45*, 2555. (b) Caputo, C. B.; Stephan, D. W. *Organometallics* **2012**, *31*, 27. (c) Vol'plin, M. E.; Shevchenko, N. V.; Bolestova, G. I.; Zeifman, Y. V.; Fialkov, Y. A.; Parnes, N. A. *Mendeleev Commun.* **1991**, *1*, 118. (d) Terao, J.; Begum, S. A.; Shinohara, Y.; Tomita, M.; Naitoh, Y.; Kambe, N. *Chem. Commun.* **2007**, 855. (e) Klahn, M.; Fischer, C.; Spannenberg, A.; Rosenthal, U.; Krossing, I. *Tetrahedron Lett.* **2007**, *48*, 8900. (f) Gu, W.; Haneline, M. R.; Douvris, C.; Ozerov, O. V. *J. Am. Chem. Soc.* **2009**, *131*, 11203.

¹⁶ (a) Hounjet, L. J.; Caputo, C. B.; Stephan, D. W. *Dalton Trans.* **2013**, *42*, 2629. (b) Caputo, C. B.; Hounjet, L. J.; Dobrovetsky, R.; Stephan, D. W. *Science* **2013**, *341*, 1374. (c) Holthausen, M. H.; Mehta, M.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 6538. (d) Gabbaï, F. P. *Science* **2013**, *341*, 1348.

¹⁷ The crystal structure of $[\mathbf{1a}^{\text{PMe}_3}][\text{BAR}^{\text{F}}_4]_2$ was obtained by my group colleague and further details can be found at: (a) Đorđević, N.; Tay, M. Q. Y.; Muthaiah, S.; Ganguly, R.; Dimić, D.; Vidović, D. *Inorg. Chem.* **2015**, *54*, 4180; (b) Tay, M. Q. Y. PhD thesis, Nanyang Technological University, 2015.

¹⁸ Burford, N.; Ragona, P. J.; McDonald, R.; Ferguson, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 14404.

¹⁹ For $[\text{BAR}^{\text{F}}_4]^-$ decomposition reports, see: (a) Bahr, S. R.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 4514; (b) Ferraris, D.; Cox, C.; Anand, R.; Lectka, T. *J. Am. Chem. Soc.* **1997**, *119*, 4319.

²⁰ El-Nahas, A. M.; Clark, T. *J. Org. Chem.* **1995**, *60*, 8023.

²¹ It is worth mentioning that orbitals found on the Ph rings of the carbene ligand are also involved in formation of the HOMO

²² Ellis, B. D.; Ragona, P. J.; Macdonald, C. L. B. *Inorg. Chem.* **2004**, *43*, 7857.

CHAPTER 3

The Synthesis and Characterization of Carbodicarbene-stabilized Electron-deficient Phosphorus Compounds

As described in the previous chapter, our initial goal involving the synthesis of carbodiphosphorane-stabilized phosphenium dications by employing weaker π -donors than amino group ($R = \text{Ph}$, 4-F-Ph, OMe, ^tBu) was not successful. In order to provide sufficient thermodynamic stabilization, necessary for isolation of highly Lewis acidic species such as doubly charged P-cations, we decided to replace **1** with a potentially stronger carbene-type donor. An ideal ligand for this role would thus be a stronger electron-donor that prefers to share its lone pairs of electrons with a substrate rather than with supporting groups (Ph_3P in case of **1**) via π -backdonation.

Phosphines are considered strong σ -donors and weak π -acceptors. They are quite comparable with carbenes, particularly N-heterocyclic carbenes (NHCs), as both groups of ligands represent monodentate, two-electron donors. Even though, the carbon atom of NHCs possesses a formally empty 2p atomic orbital, NHCs are usually regarded as weaker π -acceptors and stronger σ -donors than phosphines.¹ The explanation for this rather unusual claim comes from the theoretical studies suggesting that the NCN moiety of NHCs can be regarded as a 3-center, 4-electron π -system formed by electron donation from nitrogen atoms to the formally vacant 2p atomic orbital of the carbene carbon.² The $\text{N} \rightarrow \text{C}$ π -electron donation increases upon coordination of the carbene to a metal/Lewis acidic center, thus preventing the carbene carbon to accept the electron density from the metal via π -backdonation.³ Taking into account that carbene molecules are considered as donor-acceptor complexes $\text{L} \rightarrow \text{C} \leftarrow \text{L}$ ($\text{L} = \text{Ph}_3\text{P}$, NHC) between zero-valent central carbon atom and strong σ -donors (L),⁴ it is reasonable to assume that replacement of Ph_3P with NHC would decrease the π -backdonation from the central carbon atom of carbene ligand to the neighboring carbene carbons ultimately resulting in a stronger π -bonding with electron-deficient P-fragment (Figure 3.1). Therefore, we identified carbodicarbene ligand ($\{\text{C}_6\text{H}_4(\text{NMe})_2\}_2\text{C}$, **2**) as a more suitable candidate for thermodynamic stabilization of the target phosphenium dications.

Figure 3.1. The replacement of Ph_3P with NHC forces the central carbon atom to use its σ - and π -lone pairs preferably for bonding with the P-fragment of phosphonium dications. Benzene rings in the backbonding of carbodienophile **2** were omitted for clarity.

In the following chapter we demonstrate that the electronic properties of **2** are not only sufficient for the preparation of P-dications bearing alkyl (^tBu), alkoxy (OMe), and aryl (Ph) groups, but also for isolation of the first example of a two-coordinate triply charged phosphonium cation. Furthermore, we have also demonstrated that nucleophilicity of both **1** and **2** was responsible for the P-N bond splitting that occurred via an $\text{S}_{\text{N}}2'$ -like mechanism

Section 3.1. The Synthesis and Characterization of Carbodicarbene-stabilized Phosphenium Dications

Scheme 3.1. General synthetic procedure for preparation of novel carbodicarbene-stabilized phosphenium dications. Reagents and conditions: (a) excess of RPCl_2 , benzene, ambient temperature; (b) AlCl_3 , AgSbF_6 , $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ ($\text{Ar}^{\text{Cl}} = 3,5\text{-(Cl)}_2\text{-C}_6\text{H}_3$), $\text{Na}[\text{BAr}^{\text{F}}_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$) (2 or 3 equiv), CH_2Cl_2 or 1,2-difluorobenzene, ambient temperature.

The synthetic route for the preparation of carbodicarbene-supported P-dications is depicted in Scheme 3.1. As in the case of carbodiphosphorane **1**, we decided to use similar synthetic procedure involving the reaction of **2** with an excess of the corresponding dichlorophosphine RPCl_2 (R = Ph, NⁱPr₂, ^tBu, OMe, Cl). Thus, $[\{\text{C}_6\text{H}_4(\text{NMe})_2\text{C}\}_2\text{C}^+\text{P}(\text{Ph})\text{Cl}][\text{Cl}]$, **[2a-Cl][Cl]** was synthesized by treating a benzene solution of **2** with an excess of PhPCl_2 . The formation of **[2a-Cl][Cl]** was registered by ³¹P NMR spectroscopy where a new signal at δ_{P} 101 ppm was detected. It is noteworthy that the P-atom of **[2a-Cl][Cl]** was about 10 ppm more shielded than the analogous signal observed for **[1a-Cl][Cl]** (δ_{P} 111 ppm). Furthermore, coordination of carbodicarbene ligand to the P-containing fragment was indicated by the complete disappearance of a signal corresponding to the NMe groups of free carbodicarbene (δ_{H} 2.89 ppm) and appearance of an analogous signal at δ_{H} 3.64 ppm according to the ¹H NMR spectrum of **[2a-Cl][Cl]**. The downfield shift of methyl protons suggested that imidazolium rings of **2**, upon coordination of the carbone to the Lewis acidic center, might stabilize the cation through delocalization/accumulation of the positive charge.⁵ Nonetheless, the identity of

this compound was confirmed crystallographically (Figure 3.2) when chloride anion of $[2\mathbf{a}\text{-Cl}][\text{Cl}]$ was replaced with $[\text{SbF}_6]$ (i.e. $[2\mathbf{a}\text{-Cl}][\text{SbF}_6]$).

Figure 3.2. Single crystal X-ray structure of $[2\mathbf{a}\text{-Cl}][\text{SbF}_6]$ at 50% probability. The counterion and hydrogen atoms were omitted for clarity. The closest contact between the cation (P1) and the anion is 4.040 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.776(6), P1-Cl1, 2.120(2), P1-C4, 1.836(6), C1-C2, 1.422(7), C1-C3, 1.437(7), C4-P1-C1, 101.7(3), C4-P1-Cl1, 100.6(2), C1-P1-Cl1, 107.2(2).

The sum of the bond angles around the central P-atom of $[2\mathbf{a}\text{-Cl}]^+$ ($309.5(5)^\circ$) confirmed the expected pyramidal geometry of this monocation. The values for P1-C1 (1.776(6) Å) and P1-Cl1 (2.120(2) Å) bond lengths for $[2\mathbf{a}\text{-Cl}]^+$ are very similar to the analogous bond distances observed for 4-fluorophenyl substituted carbodiphosphorane-stabilized monocation $[1\mathbf{b}\text{-Cl}]^+$ (1.7828(13) and 2.1271(5) Å, respectively). However, the P1-C4 (1.836(6) Å) bond distance for $[2\mathbf{a}\text{-Cl}]^+$ appeared somewhat longer than the corresponding bond length for $[1\mathbf{b}\text{-Cl}]^+$ (1.8290(14) Å). Nonetheless, to demonstrate the superior π -electron donating character of **2** over **1**, necessary for stabilization of target dication, we focused our efforts on chloride abstraction from $[2\mathbf{a}\text{-Cl}]^+$.

The removal of chlorine atom from inner sphere of $[2\mathbf{a}\text{-Cl}]^+$ was attempted using highly halophilic reagents such as AlCl_3 , AgSbF_6 , $\text{Na}[\text{BAR}^{\text{Cl}}_4]$ ($\text{Ar}^{\text{Cl}} = 3,5\text{-(Cl)}_2\text{-C}_6\text{H}_3$), and $\text{Na}[\text{BAR}^{\text{F}}_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$), as these salts appeared to be effective in preparation of amino-substituted phosphonium dication $[1\mathbf{c}]^{2+}$. The reaction progress was investigated

by ^{31}P NMR spectroscopy that is considered as an ideal tool for the identification of phosphonium ions due to their characteristic downfield chemical shift.⁶ To our delight, addition of 2 equiv of AlCl_3 to a DCM solution of $[\mathbf{2a-Cl}][\text{Cl}]$ resulted in the formation of the target dication $[\mathbf{2a}][\text{AlCl}_4]_2$ as evidenced by the signal at δ_{P} 393 ppm in the ^{31}P NMR spectrum. The formation of $[\mathbf{2a}]^{2+}$ was also evidenced from the ^{13}C NMR spectrum. Namely, the signal corresponding to the central carbon of carbodicarbene ligand in $[\mathbf{2a}][\text{AlCl}_4]_2$ (δ_{C} 129 ppm) was shifted downfield by 75 ppm with respect to the same signal observed for $[\mathbf{2a-Cl}][\text{Cl}]$ (δ_{C} 54 ppm). These observations directly suggested that carbodicarbene **2** afforded sufficient thermodynamic stabilization to support the preparation of doubly charged phenylphosphonium ion $[\mathbf{2a}]^{2+}$.

The thermodynamic stabilization of $[\mathbf{2a}]^{2+}$ by means of π -donation was best inferred from the metrical parameters of X-ray structure of $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ (Figure 3.3). Crystals of $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ suitable for single crystal X-ray diffraction were obtained when chloride abstraction from $[\mathbf{2a-Cl}][\text{Cl}]$ was performed using 2 equiv of $\text{Na}[\text{BAr}^{\text{Cl}}_4]$. The shortening of the P1-C1 bond length from 1.776(6) Å ($[\mathbf{2a-Cl}]^+$) to 1.701(5) Å in $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ is consistent with the significant amount of $\text{C}_{\text{carbone}} \rightarrow \text{P}$ electron density flow. The same electron flow was further supported by the elongation of the average C1-C2/3 bond distances from 1.343(2) Å in free carbodicarbene (**2**) to 1.462(7) Å upon formation of $[\mathbf{2a}]^{2+}$. In fact, this observation suggested minimal, if any, π -backdonation from the central carbon atom (C1) to the carbene carbons (C2/3) considering that average value for the C1-C2/3 bond distance (1.462(7) Å) corresponds well with $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ single bond distances. In addition, the P1-C4 bond length of $[\mathbf{2a}]^{2+}$ (1.784(6) Å) appeared to be somewhat shorter than the corresponding bond of $[\mathbf{2a-Cl}]^+$ (1.836(6) Å), presumably due to a higher positive charge of former species; however, a certain degree of π -conjugation between the Ph group and the P-atom of $[\mathbf{2a}]^{2+}$ could not be ruled out. Therefore, the CPC fragment of $[\mathbf{2a}]^{2+}$ could be regarded as phosphalkene-like, considering only the significant double bond character of $\text{C}_{\text{carbone}}\text{-P}$ bond,⁷ or allene-like in the case of extended π -delocalization across both carbodicarbene and phenyl substituents.

Figure 3.3. Single crystal X-ray structure of $[2a][BAr^{Cl}_4]_2$ set at 50% probability. Counterions and hydrogen atoms were omitted for clarity. The closest contact between the cation (P1) and the anion is 3.711 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.701(5), C1-C2, 1.463(8), C1-C3, 1.461(7), P1-C4, 1.784(6), C4-P1-C1, 110.9(3), C2-C1-C3, 115.6(5), C2-C1-P1, 132.5(4), C3-C1-P1, 111.7(4).

In order to ascertain whether $[2a]^{2+}$ is better described as a phosphonium dication or a doubly charged phosphalkene, we decided to test its reactivity towards 2,3-dimethyl-1,3-butadiene. It is well established that conjugated dienes undergo [4+1] cycloaddition with phosphonium cations to give the corresponding phospholenium salts.^{6a} On the other hand, the product arising from [4+2] cycloaddition reaction was observed when 2,3-dimethyl-1,3-butadiene reacted with a cationic phosphalkene.⁸ This assessment could potentially provide experimental evidence about the nature of the bonding between the C-atom of carbodicarbene and central P. The reaction of $[2a][AlCl_4]_2$ with 1 equiv of 2,3-dimethyl-1,3-butadiene under ambient conditions led to the immediate formation of a single reaction product according to the ^{31}P NMR spectrum (δ_P 31 ppm). The identity of the newly formed compound as phospholenium salt $[\{C_6H_4(MeN)_2\}_2C \cdot P \{ (CH_2CCH_3)_2 \} Ph][AlCl_4]_2$, $[2a-h][AlCl_4]_2$, was established upon X-ray diffraction analysis (Figure 3.4). The crystal structure of $[2a-h][AlCl_4]_2$ revealed that cycloaddition reaction took place exclusively on the P-atom of $[2a]^{2+}$ indicating its phosphonium nature. The average bond length (1.518(8) Å) for C3-C4 and C5-C6 bonds

as well as the value for C4-C5 bond distance (1.333(9) Å) were consistent with the bonding pattern expected for [4+1] cycloaddition product. Nonetheless, this experiment indicated that $[2a]^{2+}$ is significantly more Lewis acidic than the previously reported amino-substituted dication $[1c]^{2+}$, considering that $[1c]^{2+}$ showed no reactivity towards 2,3-dimethyl-1,3-butadiene over the period of 4 days.⁹

Figure 3.4. Single crystal X-ray structure of $[2a-h][AlCl_4]_2$ set at 50% probability. Counterions and hydrogen atoms were omitted for clarity. The closest contact between the cation (P1) and the anion is 4.883 Å. Selected bond lengths [Å]: P1-C1, 1.737(6), P1-C2, 1.817(6), P1-C3, 1.817(6), P1-C6, 1.817(6), C3-C4, 1.511(8), C4-C5, 1.333(9), C5-C6, 1.524(8).

Encouraged by higher electron-donating ability of **2** compared to **1**, as demonstrated by the synthesis and isolation of $[2a]^{2+}$, we decided to attempt the preparation of other highly Lewis acidic phosphonium dications. Thus, methoxy-substituted P-monocation $[\{C_6H_4(MeN)_2C\}_2C^+P(OMe)Cl][Cl]$, $[2e-Cl][Cl]$ was prepared according to the previously established procedure. Its identity was deduced using multinuclear NMR spectroscopy and ESI-MS. The coupling between the methoxy protons and the central P atom of $[2e-Cl][Cl]$ ($^3J_{PH} = 15$ Hz) was indicated by appearance of analogous signals in ^{31}P (br q, δ_P 200 ppm) and 1H NMR (d, δ_H 3.73 ppm) spectra. Lastly, the formation of $[2e-Cl]^+$ was confirmed by ESI-MS signal at m/z 401.1297 (calculated for $C_{20}H_{23}ClN_4OP$: m/z 401.1298) with the matching isotope pattern. It is noteworthy that

[**2e-Cl**][Cl] was formed along with [$\{C_6H_4(MeN)_2C\}_2CPCl_2$][Cl], [**2g-Cl**][Cl]¹⁰ due to the presence of small amount of PCl₃ in MeOPCl₂. Similar boiling points of these phosphines, as well as the similar solubility of [**2e-Cl**][Cl] and [**2g-Cl**][Cl] in common organic solvents, prohibited further purification and presumably crystallization of [**2e-Cl**]⁺. Nonetheless, chloride abstraction leading to the target dication [**2e**]²⁺ was attempted by adding 2 equiv of AlCl₃ to a DCM solution of [**2e-Cl**][Cl]. Surprisingly, the ³¹P NMR spectrum displayed a major signal at δ_P 373 ppm suggestive of methoxy-substituted P-dication [**2e**][AlCl₄]₂, whose molecular structure was obtained by slow evaporation from the corresponding saturated DCM solution (Figure 3.5). Interestingly, X-ray analysis revealed that crystals were comprised of [**2e**][AlCl₄]₂ and [$\{C_6H_4(MeN)_2C\}_2CPCl$][AlCl₄]₂, [**2g**][AlCl₄]₂ (Figure 3.6) in the respective 93:7 ratio manifested via partial occupancy. The P1-C1 bond distance of [**2e**][AlCl₄]₂ (1.687(2) Å) was shorter than the analogous bond of [**2a**][BAr^{Cl}₄] (1.701(5) Å), but within the range expected for a P-C double bond.⁷ Furthermore, the P1-O1 bond length (1.599(4) Å) also suggested the presence of double bond character.¹¹ Considering the double bond character of P1-C1 and P1-O1 bonds, it was reasonable to assume that electron density delocalization across the CPO moiety of [**2e**][AlCl₄]₂ supported its thermodynamic stabilization. Nevertheless, appearance of chloro-substituted P-dication [**2g**]²⁺ in a crystalline form along with the methoxy-substituted analogue [**2e**]²⁺, prompted us to attempt the synthesis of highly electron-deficient halophosphenium dications.

Figure 3.5. Single crystal X-ray structure of $[2e][AlCl_4]_2$ set at 50% probability. Counterions and hydrogen atoms were omitted for clarity. The closest contact between the cation (P1) and the anion is 3.549 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.687 (2), C1-C2, 1.467(3), C1-C3, 1.465(3), P1-O1, 1.599(4), O1-P1-C1, 100.65(16), C2-C1-C3, 116.29(19), C2-C1-P1, 117.09(16), C3-C1-P1, 126.58(16).

Figure 3.6. Single crystal X-ray structure of $[2g][AlCl_4]_2$ set at 50% probability. Counterions and hydrogen atoms were omitted for clarity. The closest contact between the cation (P1) and the anion is 3.549 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.687 (2), C1-C2, 1.467(3), C1-C3, 1.465(3), P1-Cl1, 1.984(13), Cl1-P1-C1, 113.9(4), C2-C1-C3, 116.29(19), C2-C1-P1, 117.09(16), C3-C1-P1, 126.58(16).

In view of previous findings, we identified chloro- and bromo-substituted phosphonium dications as potential target molecules. The respective P-monocations $[\{C_6H_4(MeN)_2C\}_2C^+PCl_2][Cl]$, $[2g-Cl][Cl]$, and $[\{C_6H_4(MeN)_2C\}_2C^+PBr_2][Br]$, $[2f-$

Br][Br], were synthesized by reacting **2** with an excess of PCl₃ and PBr₃, respectively. Both compounds were identified spectroscopically ($\delta_P \sim 160$ ppm for [**2g-Cl**]⁺ and [**2f-Br**]⁺) and crystallographically. While X-ray structure of [**2f-Br**]⁺ was obtained with bromide in the outer sphere (Figure 3.7), [**2g-Cl**]⁺ crystallized upon standard [Cl]-to-[SbF₆] anion exchange ([**2g-Cl**][SbF₆], Figure 3.8). Crystals of [**2g-Cl**][SbF₆] were disordered and hence, we excluded their parameters from further discussion. On the other hand, the P1-C1 bond length (1.748(8) Å) of [**2f-Br**][Br] appeared somewhat shorter than the corresponding bond distance (1.776(6) Å) observed for Ph-analogue [**2a-Cl**]⁺. This P-C bond contraction suggested a more pronounced C_(carbone)→P electron density flow in [**2f-Br**]⁺, which was expected considering the presence of two electron-withdrawing Br substituents on the central P.

Figure 3.7. Molecular view of [**2f-Br**][Br] in the solid state. Only one of the molecules in the asymmetric unit is shown, while hydrogen atoms and counterion are omitted for clarity. The closest contact between the cation (P1) and the anion is 4.032 Å. Selected bond lengths (Å) and angles (°): P1-C1, 1.746(8) (1.748(8)), P1-Br1, 2.238(2) (2.228(2)), P1-Br2, 2.341(2) (2.397(2)), C1-P1-Br1, 110.4(3) (110.0(3)), C1-P1-Br2, 101.4(3) (101.5(3)).

Figure 3.8. Molecular view of $[2\mathbf{g}\text{-Cl}][\text{SbF}_6]$ in the solid state. Hydrogen atoms and counterion are omitted for clarity. The closest contact between the cation (P1) and the anion is 4.336 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.772 (8), P1-Cl1, 2.063(5), P1-Cl2, 2.117(6), Cl1-P1-C1, 101.7(3), Cl2-P1-C1, 112.0(4).

The halide abstraction from inner spheres of $[2\mathbf{g}\text{-Cl}][\text{Cl}]$ and $[2\mathbf{f}\text{-Br}][\text{Br}]$ was performed using AlCl_3 and AlBr_3 compounds, respectively. The addition of 2 equiv of AlCl_3 to a DCM solution of $[2\mathbf{g}\text{-Cl}][\text{Cl}]$ gave the expected chloro-substituted P-dication $[2\mathbf{g}][\text{AlCl}_4]_2$ according to the signal at δ_{P} 361 ppm in the ^{31}P NMR spectrum. On the other hand, when $[2\mathbf{f}\text{-Br}][\text{Br}]$ was treated with 2 equiv of AlBr_3 , the ^{31}P NMR spectrum displayed a single resonance at δ_{P} 229 ppm consistent with the starting PBr_3 . However, immediate color change (orange to red) and formation of thick oil insoluble in DCM suggested that $[2\mathbf{f}\text{-Br}][\text{Br}]$ and AlBr_3 yielded a reaction product whose insufficient solubility or stability prevented our spectroscopic measurements. A more detailed description of reactivity between $[2\mathbf{f}\text{-Br}][\text{Br}]$ and different halide-abstracting reagents is presented in Section 3.3. In addition, attempts to isolate chlorophosphenium salt $[2\mathbf{g}][\text{AlCl}_4]_2$ in the solid state were not successful prompting us to explore whether anions different than $[\text{AlCl}_4]$ could be found in the outer sphere of $[2\mathbf{g}]^{2+}$. Unfortunately, treatment of $[2\mathbf{g}\text{-Cl}][\text{Cl}]$ with 2 (or 3) equiv of $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ did not give $[2\mathbf{g}][\text{BAr}^{\text{Cl}}_4]_2$ inferring that existence of hypothetically more electrophilic chlorophosphenium dication $[2\mathbf{g}]^{2+}$ is not only limited to the solution state, but also to the presence of rather stabilizing $[\text{AlCl}_4]$ anion. This observation was not unusual considering that $[\text{MCl}_4]$ -type anions

(M=Al, Ga) are well known for their ability to stabilize reactive phosphonium centers via electrostatic anion-cation interactions.¹² Even though, we did not detect hypothetical bromo-P-dication $[\{C_6H_4(MeN)_2C\}_2C^+PBr]^{2+}$, $[2f]^{2+}$, we successfully prepared Cl- ($[2g]^{2+}$), Ph- ($[2a]^{2+}$), and MeO-substituted ($[2e]^{2+}$) phosphonium ions, indicating that carbodicarbene **2** provides access to novel chemical entities unknown in phosphonium chemistry. Encouraged by our findings, we attempted the synthesis of *tert*-butyl-substituted P-dication that appeared to be unstable when carbodiphosphorane **1** was used as a supporting ligand.

Using the established procedure, we synthesized *tert*-butyl-substituted P-monocation $[\{C_6H_4(MeN)_2C\}_2C^+P(tBu)Cl][Cl]$, $[2d-Cl][Cl]$ in high yield. The $^{31}P\{^1H\}$ NMR spectrum of $[2d-Cl][Cl]$ showed singlet at δ_P 124 ppm, which was shifted upfield by about 80 ppm with respect to the starting material $tBuPCl_2$ (δ_P 199 ppm). This observation was consistent with P-centered carbene-for-Cl displacement that was also confirmed by ESI-MS analysis (calculated for $C_{23}H_{29}ClN_4P$: m/z 427.1818; found: 427.1797). Furthermore, the molecular structure of $[2d-Cl]^+$ was obtained upon $[Cl]$ -for- $[SbF_6]$ anion exchange ($[2d-Cl][SbF_6]$). While the P1-C1 bond distance (1.768(2) Å) of $[2d-Cl]^+$ was somewhat shorter than analogous bond of $[2a-Cl]^+$ (1.776(6) Å), the P1-C2 bond of $[2d-Cl]^+$ (1.873(3) Å) appeared longer than the corresponding bond (P1-C4: 1.836(6) Å) of Ph-substituted P-monocation. The P-C(substituent) bond elongation is consistent with the $C(sp^2)$ (Ph-group from $[2a-Cl]^+$) for $C(sp^3)$ (tBu from $[2d-Cl]^+$) carbon atom replacement. However, the value for P1-Cl1 bond length of 2.1632(9) Å ($[2a-Cl]^+$: 2.120(2) Å) suggested that $[2d-Cl]^+$ might be a suitable starting material for the preparation of the target tBu -substituted dication $[2d]^{2+}$.

Figure 3.9. Molecular view of $[2\mathbf{d}\text{-Cl}][\text{SbF}_6]$ in the solid state. Hydrogen atoms and counterion are omitted for clarity. The closest contact between the cation (P1) and the anion is 5.366 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.768(2), P1-Cl1, 2.1632(9), P1-C2, 1.873(3), Cl1-P1-C1, 109.00(8), C2-P1-C1, 109.17(11), C2-P1-Cl1, 98.89(8).

We were quite fortunate that the treatment of $[2\mathbf{d}\text{-Cl}][\text{Cl}]$ with 2 equiv of AlCl_3 generated the target dication $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{P}^+\text{Bu}][\text{AlCl}_4]_2$, $[2\mathbf{d}][\text{AlCl}_4]_2$, as demonstrated by the signal at δ_{P} 474 ppm in the ^{31}P NMR spectrum. The P-center of $[2\mathbf{d}]^{2+}$ was the most deshielded of all phosphonium salts described in our research. Its δ_{P} signal was shifted more than 80 ppm with respect to $[2\mathbf{a}]^{2+}$ (δ_{P} 393 ppm) and more than 100 ppm downfield from $[2\mathbf{e}]^{2+}$ (δ_{P} 373 ppm) and $[2\mathbf{g}]^{2+}$ (δ_{P} 360 ppm). This observation was consistent with the inability of ^tBu -group to act as a π -donor. The formation of $[2\mathbf{d}]^{2+}$ was further confirmed by the corresponding ESI-MS signal at m/z 196.1086 (calculated for $\text{C}_{23}\text{H}_{29}\text{N}_4\text{P}^{2+}$: m/z 196.1086). ^tBu -dication $[2\mathbf{d}][\text{AlCl}_4]_2$ was stable in solution under ambient conditions for 24 hours, which hampered our attempts to structurally verify its identity. In addition, we attempted the preparation of $[2\mathbf{d}]^{2+}$ using weakly coordinating anions (WCAs) such as $[\text{BAr}^{\text{Cl}}_4]$ or $[\text{BAr}^{\text{F}}_4]$. The addition of 2 (or 3) equiv of $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ or $\text{Na}[\text{BAr}^{\text{F}}_4]$ to a DCM solution of $[2\mathbf{d}\text{-Cl}][\text{Cl}]$ gave a complicated reaction mixture, whose ^{31}P NMR spectrum revealed no signals in the region expected for $[2\mathbf{d}]^{2+}$ indicating the significance of electrostatic anion-cation interactions upon the stability of $[2\mathbf{d}]^{2+}$.

Nevertheless, $[\mathbf{2d}][\text{AlCl}_4]_2$ represents the first example of a doubly charged phosphonium ion with non-conjugating ^tBu group directly attached to the central P.

The stability of methoxy ($[\mathbf{2e}]^{2+}$), chloro ($[\mathbf{2g}]^{2+}$), and *tert*-butyl ($[\mathbf{2d}]^{2+}$) phosphonium ions appeared closely related with the nature of counterion. However, the presence of weakly coordinating anions (WCAs) did not affect the existence of Ph-dication $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]$. Furthermore, our group demonstrated that WCAs did not interfere with the Lewis acidity of N^iPr_2 -dication $[\mathbf{1c}][\text{BAr}^{\text{F}}_4]_2$ towards dimethylaminopyridine (DMAP), leading to the formation of acid-base adduct $[\mathbf{1cDMAP}][\text{BAr}^{\text{F}}_4]_2$. On the other hand, the reaction between DMAP and $[\mathbf{1c}][\text{AlCl}_4]_2$ gave $\text{DMAP}\cdot\text{AlCl}_3$ and $[\mathbf{1c-Cl}][\text{AlCl}_4]$.^{12b} To expand the scope of doubly charged phosphonium salts compatible with WCAs and subsequently explore their electrophilicity, we also synthesized amino-substituted analogue $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\cdot\text{PN}^i\text{Pr}_2][\text{BAr}^{\text{Cl}}_4]_2$, $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$. The corresponding P-monocation $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\cdot\text{P}(\text{N}^i\text{Pr}_2)\text{Cl}][\text{Cl}]$, $[\mathbf{2c-Cl}][\text{Cl}]$ was prepared by treating the benzene solution of **2** with an excess of $^i\text{Pr}_2\text{NPCl}_2$. The identity of $[\mathbf{2c-Cl}]^+$ was confirmed by multinuclear NMR and X-ray diffraction methods upon replacing the chloride with $[\text{SbF}_6]$ counterion ($[\mathbf{2c-Cl}][\text{SbF}_6]$, Figure 3.10). The P-atom of $[\mathbf{2c-Cl}]^+$ was registered at δ_{P} 138 ppm in the ^{31}P NMR spectrum, which was similar to the value previously observed for analogous amino-substituted monocation $[\mathbf{1c-Cl}][\text{Cl}]$ (δ_{P} 133 ppm). Besides, the similarity between $[\mathbf{2c-Cl}]^+$ and $[\mathbf{1c-Cl}]^+$ was also reflected by P1-C1 ($[\mathbf{2c-Cl}]^+$: 1.820(4) Å vs. $[\mathbf{1c-Cl}]^+$: 1.812(5) Å), P1-N1 (1.651(4) Å vs. 1.660(4) Å), respectively and P1-Cl1 (2.1914(14) Å vs. 2.173(2) Å, respectively) bond distances.^{12b} Chloride-abstraction leading to the formation of $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$ was completed by adding 2 equiv of $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ to either DCM or 1,2-difluorobenzene solutions of $[\mathbf{2c-Cl}][\text{Cl}]$. The resulting ^{31}P NMR spectrum displayed a signal at δ_{P} 328 ppm corresponding to the central P, while central carbon atom of carbodicarbene ligand was identified at δ_{C} 86 ppm in the ^{13}C NMR spectrum of $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$. The latter resonance appeared downfield compared to an analogous signal (δ_{C} 68 ppm) previously reported for $[\mathbf{1c}]^{2+}$, thus suggesting a greater $\text{C}_{\text{carbone}}\rightarrow\text{P}$ electron density flow directed by the more electron-donating carbodicarbene ligand **2**. The identity of $[\mathbf{2c}]^{2+}$ was also established by ESI-MS (calculated for $\text{C}_{25}\text{H}_{34}\text{N}_5\text{P}^{2+}$: m/z 217.6271; found: 217.6272). Nevertheless, we successfully prepared $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$, which together with Ph-dication $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$,

enables assessment of the influence of structural modifications influence upon the electrophilicity of phosphonium dications without anion interference.

Figure 3.10. Single crystal X-ray structure of $[2c-Cl][SbF_6]$ at 50% probability. The counterion and hydrogen atoms were omitted for clarity. The closest contact between the cation (P1) and the anion is 4.743 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.820(4), P1-Cl1, 2.1914(14), P1-N1, 1.651(4), N1-P1-C1, 105.56(18), N1-P1-Cl1, 109.71(13), C1-P1-Cl1, 87.49(13).

Section 3.1.1. Anion dependence

While preparation of Ph- and N^iPr_2 -substituted phosphonium dications was achieved irrespective of the counterion employed, phosphonium dications bearing less electron-donating tBu -, MeO -, and Cl -substituents were detected only in the presence of coordinating $[AlCl_4]$ anions. As expected, the solid state structure of methoxyphosphonium cation $[2e][AlCl_4]_2$ revealed two $P \cdots Cl$ interactions (Figure 3.11a) (3.372 and 3.549 Å) that were well within the sum of van der Waals (vdW) radii for P and Cl atoms (3.72 Å).¹³ The corresponding contacts provided significant stabilization of the electron-deficient P-center of $[2e][AlCl_4]_2$. Even though phenylphosphonium salt $[2a]^{2+}$ appeared to be stable in presence of either coordinating $[AlCl_4]$ or weakly coordinating $[BAr^{Cl}_4]$ anions, we carefully examined the X-ray structure of $[2a][BAr^{Cl}_4]_2$. Interestingly, three close contacts between the P atom and lone pairs of neighboring chlorine atoms were observed (Figure 3.11b). While two of them (3.803 and 3.769 Å) were outside, a

minimal cation-anion interaction with distance of 3.711 Å appeared to be within the sum of vdW radii for P and Cl. However, it should be noted that $[2a]^{2+}$ exhibited the same δ_P value 393 ppm independent of the counterion ($[AlCl_4]$, $[SbF_6]$, $[BAr^{Cl}_4]$) indicating than these contacts might be minimal or even nonexistent in solution.

Figure 3.11. Cation-anion electrostatic interactions for (a) $[2e][AlCl_4]_2$ and (b) $[2a][BAr^{Cl}_4]_2$.

Section 3.1.2. Computational Analysis

To gain an insight about the electronic properties of newly prepared phosphonium dications,¹⁴ we carried out a theoretical analysis using density functional theory. The effect of increased positive charge, as well as different electron donating characteristics of supporting substituents (N^iPr_2 , Ph, ^tBu) were comparatively assessed by analyzing relative energy levels of frontier orbitals for singly $[(^i\text{Pr}_2\text{N})_2\text{P}]^+$, $[\mathbf{3}]^+$ and doubly charged P-species $[\mathbf{2c}]^{2+}$, $[\mathbf{2a}]^{2+}$, $[\mathbf{2d}]^{2+}$ (Figure 3.12). Thus, the relative energy levels of LUMOs for dications $[\mathbf{2c}]^{2+}$ (-8.56 eV), $[\mathbf{2a}]^{2+}$ (-9.25 eV), and $[\mathbf{2d}]^{2+}$ (-9.17 eV) were significantly stabilized with respect to the corresponding molecular orbital of monocation $[\mathbf{3}]^+$ (-6.17 eV). Furthermore, LUMOs of $[\mathbf{2a}]^{2+}$ and $[\mathbf{2d}]^{2+}$ appeared more accessible than an analogous orbital of $[\mathbf{2c}]^{2+}$, which was expected considering the inferior π -donating character of Ph and ^tBu compared to N^iPr_2 group. If only π -donor strength of substituents is considered, one would also expect the LUMO of *tert*-butyl P-dication $[\mathbf{2d}]^{2+}$ to be on a lower relative energy level than equivalent orbital of phenyl-substituted analogue $[\mathbf{2a}]^{2+}$. However, this was not the case likely due to the electron density overcompensation from carbodicarbene ligand **2** to the P atom of $[\mathbf{2d}]^{2+}$. Increasing the positive charge also resulted in the stabilization of HOMO for all doubly charged species (Figure 3.12), but to a markedly lesser degree relative to the LUMO(s), thus reducing the HOMO-LUMO (i.e. singlet-triplet) gap in the following order $[\mathbf{3}]^+ > [\mathbf{2d}]^{2+} \sim [\mathbf{2c}]^{2+} > [\mathbf{2a}]^{2+}$. Consequently, the frontier orbitals separation energy of $[\mathbf{2a}]^{2+}$ (67.5 kcal/mol) appeared quite comparable with the value reported for cationic metallocgermylene **XLIV** (64.1 kcal/mol) capable of inserting into B-H and Si-H bonds.¹⁵

Figure 3.12. Relative energy levels of frontier orbitals of phosphonium mono- ($[3]^+$) and dicationic ($[2c]^{2+}$, $[2d]^{2+}$ and $[2a]^{2+}$).

Section 3.2. Bis(carbodicarbene)phosphonium trication: the case against hypervalency

Considering the unprecedented electron-donating properties of carbene ligands (σ - and π -donors),⁴ we envisaged that two carbene molecules would provide an adequate thermodynamic stabilization for the preparation of phosphonium trication $[L_2P]^{3+}$. With both carbodiphosphorane (**1**) and carbodicarbene (**2**) in our hands, we decided to use **2** because it was not only shown to be more nucleophilic¹⁶ but it is also significantly less sterically demanding. Steric factors represent an important factor in the synthesis of $[L_2P]^{3+}$ due to its expected bent geometry derived from the presence of a lone pair on a two-coordinate phosphorus atom.⁶ Furthermore, the only molecule consisting of two **1** ligands bound to the central atom was found to be linear (Figure 3.13, $[Ag(\mathbf{1})_2]^+$).¹⁷ On the other hand, fitting two **2** ligands in non-linear fashion has already been reported ($[BH(\mathbf{XXXIV})_2]^{2+}$).¹⁸

Figure 3.13. Carbodiphosphorane-stabilized silver monocation ($[\text{Ag}(\mathbf{1})_2]^+$) and carbodicarbene-stabilized hydridoborenium dication ($[\text{BH}(\text{XXXIV})_2]^{2+}$).

In view of previous carbene-for-halogen substituent replacements, we hypothesized that sequential binding of two carbodicarbene ligands to the P-based fragment followed by halide abstraction, might give the target trication (Scheme 3.2). Therefore, we identified previously described bromo-substituted P-monocation $[\mathbf{2f}\text{-Br}][\text{Br}]$ (Figure 3.7) as a starting point for the synthesis of our target molecule. However, when $[\mathbf{2f}\text{-Br}][\text{Br}]$ (δ_{P} 163 ppm) was treated with 1 equivalent of **2** (Scheme 3.2a), instead of the target P-dication $[\text{L}_2\text{PBr}]^{2+}$, $[\mathbf{2f}\mathbf{2}]^{2+}$, the ^{31}P NMR spectrum revealed the formation of several unanticipated products.

Scheme 3.2. General synthetic procedure. Reaction conditions: (a) 1 equiv of **2**, 1,2-difluorobenzene or acetonitrile; (b) 2 equiv of AgSbF_6 , acetonitrile.

Before obtaining the crystal structure of $[\mathbf{2f}\text{-Br}][\text{Br}]$, we attempted to replace its non-coordinating bromide anion with $[\text{SbF}_6]$ as this was our standard procedure for crystalizing similar P-monocations. Interestingly, when 1 equiv of AgSbF_6 was introduced to an equimolar amount of $[\mathbf{2f}\text{-Br}][\text{Br}]$ in acetonitrile, apart from the monocation (δ_{P} 163

ppm), we also observed the formation of at least two new compounds as judged by the ^{31}P NMR signals at 228 and 302 ppm (Figure 3.14a). While the resonance at 228 ppm was most likely PBr_3 , it seemed reasonable to assume that compound identified by the signal at 302 ppm was bromophosphenium dication $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\cdot\text{PBr}]^{2+}$, $[\mathbf{2f}]^{2+}$, as similar chemical shift values were reported for other halo- and pseudohalophosphenium salts.^{12a,19} This assumption was somewhat supported by complete disappearance of the $[\mathbf{2f}\cdot\text{Br}]^+$ signal at δ_{p} 163 ppm when 2 (or even 3) equivalents of AgSbF_6 were used (Figure 3.14b). However, PBr_3 also became the major reaction product in this instance inferring a more complex reaction mechanism than a simple bromide abstraction. Fortunately, a few red X-ray quality crystals were formed upon layering an acetonitrile solution of the former (1 equiv AgSbF_6) reaction mixture with diethyl-ether.

Figure 3.14. ^{31}P NMR Spectrum of the reaction mixture between $[\mathbf{2f}\cdot\text{Br}][\text{Br}]$ and: (a) 1 equiv AgSbF_6 ; (b) 2 equiv AgSbF_6 . Red stars represent unidentified products.

To our delight, X-ray analysis revealed the target trication molecule supported by two carbodicarbene moieties $[\mathbf{L}_2\mathbf{P}]^{3+}$, $[(\mathbf{2})_2\mathbf{P}]^{3+}$ (Figure 3.15). This in turn contradicted the assumption that signal at δ_{p} 302 ppm belonged to the postulated dication $[\mathbf{2f}]^{2+}$. Even though, the precise reaction mechanism is not known at the moment, we firmly believe that one of the key mechanistic steps leading to the formation of the trication and PBr_3 was carbene-for-bromide substituent replacement. It is noteworthy that P-centered substituent exchange has been the subject of several previously published reports

including a recent article on carbene-for-chloride ligand exchange.²⁰ Furthermore, the highly reactive nature of the trication prevented all attempts to obtain this compound in a pure form.

Figure 3.15. Molecular view of $[(2)_2P]^3+$ in the solid state. Hydrogen atoms and counterions are omitted for clarity. The closest contact between the cation (P1) and the anion (Br) is 3.424 Å. Selected bond lengths (Å) and angles (°): P1-C1, 1.733(4), P1-C4, 1.747(4), C4-C5, 1.462(5), C4-C6, 1.444(5), C1-C2, 1.443(5), C1-C3, 1.441(5), C1-P1-C4 111.0(2).

The nature of the trication $[(2)_2P]^3+$ could be described using both dative and covalent bonding methods. If dative bonding model was considered, the trication could be depicted as a bis(carbene) capture of a $P(III)^{3+}$ fragment, i.e. $2 \rightarrow P^{3+} \leftarrow 2$.²¹ The values for the P1-C1 (1.733(4) Å) and the P1-C4 (1.747(4) Å) bond lengths implied a significant double bond character. This observation complies with Frenking's recent critical assessment that dative/donor-acceptor bonds could be quite strong and short, generated by substantial amount of electron density flow from the electron donating to the electron accepting fragment/atom.²¹ The carbodicarbene-to- P^{3+} electron density flow in the trication was further supported by the lengthening of the corresponding C1-C2/3 and C4-C5/6 bond lengths. The average value for these bonds increased from 1.343(2) Å in the free carbodicarbene to 1.448(6) Å in the trication suggesting the relocation of the electron density from the imidazolyl substituents to the triply charged phosphorus atom. The double bond character of the central C-P bonds was also studied using Bader's Quantum

Theory of Atoms in Molecules, QTAIM.²² Obtained data was subsequently implemented to calculate ellipticity values for the trication model compound $[(2')_2P]^{3+}$ ($2' = C(NMe)_2(CH)_2$), as well as for compounds containing traditionally accepted single and double P-C bonds (Table 3.1). The value of 0.31 for $[(2')_2P]^{3+}$ correlated well with values obtained for other single and double P-C bonds, thus, confirming the double bond character among the C-P-C fragment. Considering all mentioned above, it was then not surprising that QTAIM partial charge of the central P of $[(2')_2P]^{3+}$ was reduced from the formal value of $+3e$ to only $+1.45e$, with approximately $+0.7e$ delocalized on each imidazolyl ring.

Table 3.1. Ellipticity values for selected P-C bonds of several compounds.

Compound
Ellipticity value	0.15	0.03 (P-C) 0.49 (P=C)	0.05 (P-C) 0.50 (P=C)	0.31

On the other hand, if covalent bonding model was considered, the entire trication could be described using numerous resonance forms.²³ For simplicity, we used resonance forms only to describe the central C-P-C fragment (Figure 3.16).²⁴ Thus, considering only the double bond character of P-C bonds the overall resonance depiction of the trication should be significantly shifted towards the hypervalent form **A**. The other extreme, fully ionic form **E**, closely resembles the dative bonding portrayal of the trication. Finally, the resonance form **B** is considered covalent as it obeys the octet rule, while resonance forms **C** and **D** are partially ionic.

Figure 3.16. Canonical forms for the central C-P-C fragment of $[(2)_2P]^{3+}$.

In order to examine if P-atom of the trication is indeed hypervalent or the covalent form **B** provides a more accurate bonding description or P-C bonds possess significant degree of ionic character, we used Durrant's method for assessing covalency and/or hypervalency.²⁵ This method is solely based on the atomic charges that could be generated either by experimental or computational means. In this work, we used QTAIM as charges obtained this way are almost identical to those found experimentally.^{25,26} Once generated, partial atomic charge of the atom of interest is then used to calculate the parameter named the valence electron equivalent (γ) for that particular atom.²⁵ If $\gamma = 8$ (or close to it) the compound is best described using the covalent form. When γ is higher than 8 then the central atom is hypervalent while the values of γ lower than 8 indicate the presence of ionic bonding. We found a significant degree of ionic bonding around the central P-atom of the trication, as its $\gamma(P)$ was found to be 5.1. Interestingly, this value was calculated using only the two extreme resonance forms **A** and **E** in the respective ratio of 39:61. This suggested that the central C-P-C fragment of the trication is more accurately described using ionic form(s). The properties of the P-C bond critical point reveal bond's character – a positive Laplacian (+ 0.143 au) implies depletion of electron density in the internuclear region, which indicates bond's ionic nature.²⁷ However, significant electron density (0.166 au) suggests presence of a charge-shift bond, as demonstrated by Shaik and Hiberty.²⁸ Overall, this analysis revealed that ionic resonance forms **C**, **D**, and **E** had a major role when the covalent bonding model was used to describe the nature of the trication. As fully ionic form **E** is quite comparable with dative bonding depiction ($2 \rightarrow P^{3+} \leftarrow 2$), one could

also conclude that dative contribution to the overall bonding portrayal of the title compound is significant.

Inspired by newly acquired results and the fact that hypervalent resonance form **A** represents a hypervalent phosphorane, we decided to explore whether phosphorane molecules are indeed hypervalent as stated in the literature.²⁹ Common representatives of this class of compounds possess ten valent electrons around the four coordinate P-center (10-P-4 phosphoranes). Therefore, a couple of simple 10-P-4 phosphoranes (**a** and **b**, Table 3.2), as well as simplified models of recently reported cationic (**c**),^{29b} anionic (**d**),^{29c} and neutral (**e**)^{29b} phosphorane molecules were subjected to Durrant's method. In addition, bonding around the P-center of 10-P-3 phosphorane (**f**)^{29a} and hypothetical bis(methylene)phosphorane anion (10-P-2, **g**), which closely resembles the form **A** of our trication, was also investigated. Partial atomic charges for these species were generated using QTAIM method. Interestingly, $\gamma(P)$ parameter for most of these compounds was lower than 6 indicating the presence of ionic bonding around the central P rather than its hypervalent character.²⁹ In fact, this particular observation suggested that simple 10-P-4 phosphoranes would be more appropriately described as $X^{\cdot-}\cdots PX_2^+\cdots X^{\cdot-}$ or $PX_3^{\cdot-}\cdots X^{\cdot-}$ than the commonly adopted $PX_4^{\cdot-}$ ($X = Cl, Br$). Furthermore, it was found that the relationship between the $\gamma(P)$ and the partial charge on the central P-atom is linear (Figure 3.17). This allowed us to generate an equation $y = -2.01x + 8.01$ ($R^2 = 0.9998$) from which the $\gamma(P)$ (y) for any phosphorane can be calculated if partial charge (x) on the central P is known.

Table 3.2. Calculated QTAIM partial charges and the valence electron equivalent parameter γ for the central P-atom of several phosphorane molecules. In each case only the hypervalent form is drawn.

		Partial charge	$\gamma(P)$
a	+1.12	5.76
b	+0.88	6.24

c	+1.40	5.2
d	+1.48	5.04
e	+1.12	5.78
f	+1.52	4.96
g	+1.31	5.38

Figure 3.17. Graph: valence electron equivalent parameter $\gamma(P)$ vs. QTAIM charge.

Section 3.3. Towards the Synthesis of Phosphorus-based tetracation: P–N bond cleavage via an S_N2'-like mechanism

As mentioned earlier, our group utilized hexaphenylcarbodiphosphorane **1** for preparation of aminophosphenium dication [**1c**]²⁺ (Figure 3.18). Its synthesis was based on carbene-for-chloride exchange between **1** and ⁱPr₂NPCl₂ to give a monocationic precursor [**1c-Cl**][Cl], which was then subjected to chloride abstraction.^{12b,30} The feasibility of this synthetic pathway prompted us to attempt the preparation of a molecule consisting of two such phosphonium dications bridged by a mutual amino group (**LIX**, Figure 3.18). The target tetracation would, thus, be the first molecule that combines the proximity of two phosphorus Lewis acidic centers with overall positive charge higher than 2.³¹ In turn, the proposed synthetic methodology revealed an unusual P–N bond splitting reaction. Detailed theoretical investigation revealed that this process follows an S_N2'-like mechanism.

Figure 3.18. Aminophosphenium dication [**1c**]²⁺ and target tetracation **LIX**.

We hypothesized that synthesis of **LIX** should begin with carbene-induced chloride displacement between MeN(PCl₂)₂ and **1** to give the anticipated product [{(Ph₃P)₂C·PCl}NMe(PCl₂)][Cl], [**1·P_e**][Cl] (Scheme 3.3). The same reaction would be repeated at the adjacent PCl₂ fragment of [**1·P_e**][Cl] leading to the dication [{(Ph₃P)₂C·PCl}NMe(ClP·C(PPh₃)₂)]²⁺. The second step would be followed by dual halide abstraction to complete the synthesis of **LIX**.

Scheme 3.3. Proposed carbene-for-chloride displacement as initial step in the synthesis of tetracation **LIX**.

However, when **1** was introduced to the benzene solution of MeN(PCl₂)₂, the ³¹P NMR spectrum revealed a single resonance at δ_P 173 ppm that is inconsistent with the expected product [**1**⁺**P_e**][Cl]. Surprisingly, the same signal was observed even when the ratio between reactants was varied (**1**:MeN(PCl₂)₂ = 1:1, 1:2 or 2:1). According to the published reports on the reactivity of **1** with chloro-containing P(III) compounds, we discovered that Schmidpeter and co-workers have observed essentially identical signal for the central P-atom of [(Ph₃P)₂CPCl₂][Cl], [**1g-Cl**][Cl].³² Indeed, we isolated and structurally confirmed³³ the identity of this cation upon replacing the non-coordinating chloride with [AlCl₄]⁻ anion ([**1g-Cl**][AlCl₄], Figure 3.19).³⁴

Figure 3.19. Molecular view of [1g-Cl][AlCl₄] in the solid state. Hydrogen atoms and counterion are omitted for clarity. The closest contact between the cation (P1) and the anion is 5.092 Å.

If the overall reaction stoichiometry between **1** and MeN(PCl₂)₂ is considered, apart from the formation of experimentally observed [1g-Cl]⁺, P-N bond cleavage should also give a “MeNPCI” fragment (Scheme 3.4). As “RNPCI” compounds are well known by their ability to dimerize/oligomerize,³⁵ we performed the same reaction in the presence of a trapping agent 2,3-dimethylbutadiene. However, ¹H NMR signals corresponding to 2,3-dimethylbutadiene remained virtually identical after the formation of [1g-Cl]⁺ suggesting the transient character of “MeNPCI”.

Scheme 3.4. Carbene-induced P-N bond splitting of RN(PCl₂)₂-type of substrates.

As discussed previously, the reaction of **1** with several RPCl₂-type phosphines (R = ⁱPr₂N,^{12b,30a,b} Cy₂N,^{12b} Ph, 4-F-Ph, N=C(N^tBu)₂(CH)₂,^{30c} ^tBu, and OMe) always resulted in a simple substituent exchange yielding the expected carbene-stabilized chlorophosphenium cations. This suggested that newly discovered selectivity of **1** to cleave the P-N rather than the P-Cl bond, was most likely affected by the presence of two PCl₂ units in MeN(PCl₂)₂. To gain an additional evidence about the overall reaction mechanism, we performed a couple of test experiments in which (i) a similar substrate (PhN(PCl₂)₂), and (ii) a carbene ligand (**2**) with different electronic and steric properties were used.¹⁶ The reaction between **2** and MeN(PCl₂)₂ did not give the expected product, but rather followed P-N bond cleavage pathway to yield [2g-Cl][Cl], whose spectroscopic and structural details (Figure 3.8) were discussed in Section 3.1. Similarly, the treatment of PhN(PCl₂)₂ with **1** gave [1g-Cl][Cl] as major reaction product. These observations confirmed that nature of the substrate directed the outcome of carbene-induced P-N bond heterolysis reactions.

In order to explain the formation of experimentally observed products [1g-Cl][Cl] and [2g-Cl][Cl], we conducted a detailed computational investigation. We supposed that chloride displacement initially resulted in the formation of the predicted [1⁺P_e][Cl] and

$[2\cdot\mathbf{P_e}][\text{Cl}]$ compounds. These species then undergo a 1,3-chloride shift to give $[1\mathbf{g}\text{-Cl}][\text{Cl}]/[2\mathbf{g}\text{-Cl}][\text{Cl}]$ and “ $\text{R}'\text{NPCl}$ ” fragment ($\text{R}' = \text{Me, Ph}$) (Scheme 3.5). This assumption was somewhat supported by higher thermodynamic stability of experimentally observed $[1\mathbf{g}\text{-Cl}][\text{Cl}]$ and $[2\mathbf{g}\text{-Cl}][\text{Cl}]$ (by 93 and 50 kJ/mol, respectively) with respect to the expected products $[1\cdot\mathbf{P_e}][\text{Cl}]$ and $[2\cdot\mathbf{P_e}][\text{Cl}]$.³⁶ However, numerous attempts to identify the low energy pathway that could convert $[1\cdot\mathbf{P_e}][\text{Cl}]$ and $[2\cdot\mathbf{P_e}][\text{Cl}]$ into $[1\mathbf{g}\text{-Cl}][\text{Cl}]$ and $[2\mathbf{g}\text{-Cl}][\text{Cl}]$, respectively, and “ $\text{R}'\text{NPCl}$ ” were not successful, thus eliminating the ligand exchange as the initial step in the formation of the P-N bond cleavage products.

Scheme 3.5. Proposed reaction mechanism involving the initial carbene-for-chloride replacement (P-Cl cleavage) followed by 1,3-chloride migration.

Theoretical calculations were then used to examine the nature of structural changes that $\text{MeN}(\text{PCl}_2)_2$ underwent as the central carbon atom (C_A) of ligands **1** and **2** approached one of the substrate's phosphorus atoms (P_A) (Scheme 3.6a).³⁷ The most prominent changes were observed for the $\text{P}_A\text{-N}_A$, $\text{P}_B\text{-N}_A$, and average $\text{P}_B\text{-Cl}$ ³⁸ bond lengths. While the $\text{P}_A\text{-C}_A$ bond distance was systematically reduced, the $\text{P}_A\text{-N}_A$ and $\text{P}_B\text{-Cl}_{(\text{ave})}$ bonds elongated followed by the contraction of the $\text{P}_B\text{-N}_A$ bond (Scheme 3.6b). This trend continued throughout the transition state ultimately leading to the complete dissociation of the $\text{P}_A\text{-N}_A$ and one of the $\text{P}_B\text{-Cl}$ bonds while forming a double bond between the P_B and N_A atoms. These findings were consistent with the formation of the isolable $[1\mathbf{g}\text{-Cl}][\text{Cl}]/[2\mathbf{g}\text{-Cl}][\text{Cl}]$ and presumably MeNPCl . In addition, the $\text{C}_A\text{-P}_A\text{-N}_A$ angle was close to 180° during the entire ligand approach suggesting the preference of C_A to interact with P_A exclusively *trans* to N_A .³⁹ This in turn allows the interaction of C_A with the σ^* orbital of the $\text{P}_A\text{-N}_A$ bond and explains the preference of carbene ligands to cleave the P-N rather than the P-Cl bond of $\text{RN}(\text{PCl}_2)_2$ -type phosphines.

Scheme 3.6. (a) Proposed mechanistic pathway; (b) theoretically calculated values for P-N and P-Cl bond lengths during the ligand's (1 or 2) approach to the substrate's (MeN(PCl₂)₂) P atom.

The observed bond elongation and contraction pattern was consistent with the concerted S_N2' mechanism traditionally accepted for nucleophilic substitution manifested by allylic shift.⁴⁰ More reminiscent pathways involving σ -bond cleavage and π -bond formation were established for intramolecular Grob fragmentation (Scheme 3.7a)⁴¹ and for the last step in the synthesis of alkyl chlorides in the presence of a base (Scheme 3.7b).⁴² In fact, nucleophilic attack of chloride anion followed by S=O bond formation and extrusion of the leaving group is essentially identical to the mechanism depicted in Scheme 3.6a. However, it seems that this mechanism was not previously observed during hydrolysis,^{43a-d} alcoholysis,^{43f-h} or acidolysis,^{43e,f} of various P-N bonds. Furthermore, P-N bond activations caused by Fe-Fe oxidative bond cleavage⁴⁴ or small molecule (e.g. CS₂, CO₂, isocyanates, aldehydes, etc.) insertions also do not follow an S_N2' pathway.⁴⁵ Nonetheless, this work features a novel P-N bond cleavage method prompted by nucleophilic substitution at the nitrogen fragment without preceding N-protonation or P-oxidation. Furthermore, it highlights the ability of carbenes to cleave the P-N bonds via an S_N2'-like mechanism.

Scheme 3.7. Mechanisms for: (a) intramolecular Grob fragmentation; (b) the last step in the synthesis of alkyl chlorides in the presence of a base.

In summary, we successfully expanded the palette of isolable doubly charged phosphonium ions by replacing the carbodiphosphorane **1** with a more nucleophilic carbodicarbene ligand **2**. Computational analysis of newly prepared species validated that increased positive charge led to the significant stabilization of their LUMOs with respect to the relative energy level of the corresponding molecular orbital for P-monocation [(ⁱPr₂N)₂P]⁺, [**3**]⁺. Intrinsic nucleophilicity of carbodicarbene **2** was further employed for isolation of the triply charged phosphonium cation [(**2**)₂P]³⁺. The combination of X-ray data and Durant's method for assessing covalency/hypervalency suggested that [(**2**)₂P]³⁺ is best described using dative bonds (**2**→P³⁺←**2**). In addition, unique electronic properties of carbones (**1** and **2**) were also demonstrated in reactions with RN(PCl₂)₂ (R = Me, Ph) wherein instead of the anticipated P-Cl bond cleavage, P-N bond cleavage occurred. Control experiments revealed that the presence of two adjacent PCl₂-moieties in the substrate was responsible for the observed P-N bond heterolysis, which, according to the computational studies, proceeds via an S_N2'-like mechanism. These findings demonstrated novel reactivity of carbone molecules, as well as their remarkable ability to stabilize highly Lewis acidic phosphonium dications.

¹ (a) Schwarz, J.; Bohm, V. P. W.; Gardiner, M. G.; Grosche, M.; Hermann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *6*, 1773; (b) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H.; *Organometallics* **1999**, *18*, 1596; (c) Lappert, M. F. J. *J. Organomet. Chem.* **1975**, *100*, 139; (d) Lappert, M. F. J. *J. Chem. Soc. Dalton* **1977**, 2172; (e) Lappert, M. F. J. *J. Organomet. Chem.* **1988**, 358, 185; (f) Öfelle, K.; Hermann, W. A.; Mihalios, D.; Elison, M.; Herdtweck, E.; Scherer, W.; Mink, J. *J. Organomet. Chem.* **1993**, *459*, 177; (g) Perrin, L.; Clot, E.; Einstein, O.; Loch, J.; Crabtree, R. H. *Inorg. Chem.* **2001**, *40*, 5806; (h) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Hermann, W. A. *Angew. Chem. Int. Ed.* **1999**, *38*, 2416; (i) Termante, A. T.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Chem. Eur. J.* **2003**, *9*, 3577; (j) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485.

² Tafipolsky, M.; Scherer, W.; Öfelle, K.; Artus, G.; Pedersen, B.; Hermann, A. W.; McGrady, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 5865.

³ (a) Fröhlich, N.; Pidun, U.; Stahl, M.; Frenking, G. *Organometallics* **1997**, *16*, 442; (b) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801; (c) Lee, M.-T.; Hu, C.-H. *Organometallics* **2004**, *23*, 976.

⁴ For recent reviews on carbene molecules, see: (a) Frenking, G.; Tonner, R.; Klein, S.; Takagi, N.; Shimizu, T.; Krapp, A.; Pandey, K. K.; Parameswaran, P. *Chem. Soc. Rev.* **2014**, *43*, 5106; (b) Petz, W. *Coord. Chem. Rev.* **2015**, *291*, 1; (c) Frenking, G.; Hermann, M.; Andrada, D. M.; Holzmann, N. *Chem. Soc. Rev.* **2016**, *45*, 1129; (d) Petz, W.; Frenking, G. *Top. Organomet. Chem.* **2010**, *30*, 49.

⁵ (a) Wilson, D. J. D.; Couchman, S. A.; Dutton, J. L. *Inorg. Chem.* **2012**, *51*, 7657; (b) Holthausen, M. H.; Surmiak, S. K.; Jerabek, P.; Frenking, G.; Weigand, J. *J. Angew. Chem.* **2013**, *125*, 11284; *Angew. Chem. Int. Ed.* **2013**, *52*, 11078.

⁶ For reviews on phosphonium chemistry see: (a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. (b) Gudat, D. *Coord. Chem. Rev.* **1997**, *163*, 71. (c) Burford, N.; Ragnogna, P. J. *J. Chem. Soc., Dalton. Trans.* **2002**, 4307.

⁷ The C_{carbene}-P bond distance (1.701(5) Å) of [2a]²⁺ falls well within the range for a typical C-P double bond of phosphalkenes (1.65-1.76 Å): Weber, L. *Eur. J. Inorg. Chem.* **2000**, 2425.

⁸ Grützmacher, H.; Pritzkow, D. *Angew. Chem. Int. Ed.* **1991**, *30*, 709.

⁹ Tay, M. Q. Y. PhD thesis, Nanyang Technological University, 2015.

¹⁰ [2g-Cl][Cl] was prepared in a separate procedure using 2 and PCl₃ as the only P-source available in the reaction mixture

- ¹¹ The corresponding P-O bond distance (1.599(4) Å) is between the P=O bond length of triphenylphosphine oxide (1.479(2) Å; Al-Farhan, K. A. *Journal of Crystallographic and Spectroscopic Research* **1992**, 22, 687) and the P-O single bond distance of three-coordinate phosphines (1.721(1) Å; Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, 134, 11330. Furthermore, it is quite comparable with the P-O bond distance of other two-coordinate phosphonium systems (See ref. 12a).
- ¹² (a) Hering, C.; Schulz, A.; Villinger, A. *Inorg. Chem.* **2013**, 52, 5214; (b) Tay, M. Q. Y.; Ilić, G.; W.-Zwanziger, U.; Lu, Y.; Ganguly, R.; Ricard, L.; Frison, G.; Carmichael, D.; Vidović, D. *Organometallics* **2016**, 35, 439.
- ¹³ Alvarez, S. *Dalton Trans.* **2013**, 42, 8617.
- ¹⁴ Methoxy- [2e]²⁺ and chlorophosphonium [2g]²⁺ dications were not analyzed by computational methods due to their intrinsic instability.
- ¹⁵ Inomata, K.; Watanabe, T.; Miyazaki, Y.; Tobita, H. *J. Am. Chem. Soc.* **2015**, 137, 11935.
- ¹⁶ For computational studies on carbones, see: (a) Tonner, R.; Frenking, G. *Angew. Chem., Int. Ed.* **2007**, 46, 8695; (b) Deshmukh, M. M.; Gadre, S. R.; Tonner, R.; Frenking, G. *Phys. Chem. Chem. Phys.* **2008**, 10, 2298; (c) Tonner, R.; Frenking, G. *Chem. - Eur. J.* **2008**, 14, 3260; (d) Takagi, N.; Shimizu, T.; Frenking, G. *Chem. - Eur. J.* **2009**, 15, 8593; (e) Frenking, G.; Tonner, R.; *Pure Appl. Chem.* **2009**, 81, 597; (f) Takagi, N.; Shimizu, T.; Frenking, G. *Chem. - Eur. J.* **2009**, 15, 3448; (g) Tonner, R.; Frenking, G. *Chem. - Eur. J.* **2008**, 14, 3273.
- ¹⁷ Petz, W.; Oexler, F.; Neumueller, B. *J. Organomet. Chem.* **2009**, 694, 4094.
- ¹⁸ Chen, W.-C.; Lee, C.-Y.; Lin, B.-C.; Hsu, Y.-C.; Shen, J.-S.; Hsu, C.-P.; Yap, G. P. A.; Ong, T.-G. *J. Am. Chem. Soc.* **2014**, 136, 914.
- ¹⁹ (a) Hering, C.; Schulz, A.; Villinger, A. *Angew. Chem.* **2012**, 124, 6345; *Angew. Chem., Int. Ed.* **2012**, 51, 6241; (b) Holthausen, M. H.; Weigand, J. J. Z. *Anorg. Allg. Chem.* **2012**, 638, 1103; (c) Mazieres, M. P.; Roques, C.; Sanchez, M.; Majoral, J. P.; Wolf, R. *Tetrahedron* **1987**, 43, 2109.
- ²⁰ See for example: (a) Fluck, E.; Van Wazer, J. R.; Groenweghe, C. D. *J. Am. Chem. Soc.* **1959**, 81, 6363; (b) Azouri, M.; Andrieu, J.; Picquet, M.; Cattey, H. *Inorg. Chem.* **2009**, 48, 1236.
- ²¹ Frenking, G. *Angew. Chem., Int. Ed.* **2014**, 53, 6040.
- ²² Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: Oxford, 2003.

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- ²³ Himmel, D.; Krossing, I.; Schnepf, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 370.
- ²⁴ It should be noted that the resonance forms **B** and **D** have two indistinguishable forms.
- ²⁵ Durrant, M. C. *Chem. Sci.* **2015**, *6*, 6614.
- ²⁶ (a) Bader, R. F. W.; Matta, C. F. *J. Phys. Chem. A* **2004**, *108*, 8385; (b) Bader, R. F. W.; Matta, C. F. *Found. Chem.* **2013**, *15*, 253.
- ²⁷ *The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design*; ed. Matta, C. F.; Boyd, R. J.; WILEY-VCH: Weinham, 2007.
- ²⁸ Shaik, S.; Danovich, D.; Wu, W.; Hiberty, P. C. *Nature Chem.* **2009**, *1*, 443.
- ²⁹ See for example: (a) Märkl, G.; Martin, C. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 408; (b) Schwedtmann, K.; Holthausen, M. H.; Feldmann, K.-O.; Weigand, J. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 14204; (c) Heift, D.; Benkő, Z.; Grützmacher, H.; Jupp, R. J.; Goicoechea, J. M. *Chem. Sci.* **2015**, *6*, 4017.
- ³⁰ (a) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidović, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 3132; (b) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Frison, G.; Ricard, L.; Vidović, D.; Charmichael, D. *Phosphorus, Sulfur Silicon Relat. Elem.* **2015**, *190*, 785; (c) Loh, Y. K.; Gurnani, C.; Ganguly, R.; Vidović, D. *Inorg. Chem.* **2015**, *54*, 3087.
- ³¹ (a) Holthausen, M. H.; Hiranandani, R. R.; Stephan, D. W. *Chem. Sci.* **2015**, *6*, 2016; (b) Holthausen, M. H.; Bayne, J. M.; Mallov, I.; Stephan D. W. *J. Am. Chem. Soc.* **2015**, *137*, 7298.
- ³² Schmidpeter, A.; Nöth, H.; Jochem, G.; Schrödel, H.-P.; Karaghiosoff, K. *Chem. Ber.* **1995**, *128*, 379.
- ³³ X-ray structure of [**1g-Cl**][AlCl₄] was obtained by my co-worker Dr. Chitra Gurnani. Further crystallographic details can be found: Gurnani, C.; Đorđević, N.; Muthaiah, S.; Dimić, D.; Ganguly, R.; Petković, M.; Vidović, D. *Chem. Commun.* **2015**, *51*, 10762.
- ³⁴ The reaction of **1** with phosphorus species is normally performed in benzene, thus causing precipitation of the target monocationic compound.
- ³⁵ (a) Balakrishna, M. S.; Eisler, D. J.; Chivers, T. *Chem. Soc. Rev.* **2007**, *36*, 650, and references therein. (b) Niecke, E.; Gudat, D.; Symalla, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 834. (c) Niecke, E.; Rüger, R.; Krebs, B.; Dartmann, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 552.

³⁶ For theoretical investigation we used the formation of the monomeric MeNPCI. The use of the dimeric form did not affect the conclusions.

³⁷ The P_A–C_A was fixed at a certain distance (the *x*-axis for the graph in Scheme 3.6) and the rest of the system was optimized.

³⁸ As (i) the optimized structures for [1g-Cl][Cl] and [2g-Cl][Cl] contain two Cl atoms at approximately equal distance from the central P and (ii) both P–Cl bonds showed elongation during the mechanism it was then appropriate to use the average value for the two P–Cl bonds to construct the graph.

³⁹ We have tried to initially place C_A *trans* to one of the Cl atoms of MeN(PCl₂)₂ but partial optimization would always orient C_A *trans* to N_A.

⁴⁰ (a) Magid, R. M. *Tetrahedron*, **1980**, 36, 1901; (b) Paquette, L. A.; Stirling, C. J. M. *Tetrahedron*, **1992**, 48, 7383.

⁴¹ Grob, C. A.; Schiess, P. W. *Angew. Chem., Int. Ed. Engl.* **1967**, 6, 1.

⁴² Brown, G. W. in *The Chemistry of the Hydroxyl Group*; Interscience: London **1971**, part 1, p. 592.

⁴³ See for example: (a) Hart, W. A.; Sisler, H. H. *Inorg. Chem.* **1964**, 3, 617; (b) Balakrishna, M. S.; Santarsiero, B. D.; Cavell, R. G. *Inorg. Chem.* **1994**, 33, 3079; (c) Slawin, A. M. Z.; Wainwright, M.; Woollins, J. D. *New J. Chem.* **2000**, 24, 69; (d) Burck, S.; Gudat, D.; Nieger, M.; Schalley, C. A.; Weilandt, T. *Dalton Trans.* **2008**, 3478; (e) Greenhalg, R.; Blanchfied, J. R. *Can. J. Chem.* **1966**, 44, 501; (f) Dyer, P. W.; Fawcett, J.; Hanton, M. J.; Kemmitt, R. D. W.; Padda, R.; Singh, N. *Dalton Trans.* **2003**, 104; (g) Bhattacharyya, P.; Slawin, A. M. Z.; Woollins, J. D. *Inorg. Chem. Commun.* **2001**, 4, 198; (h) Ohkubo, A.; Kuwayama, Y.; Kudo, T.; Tsunoda, H.; Seio, K.; Sekine, M. *Org. Lett.* **2008**, 10, 2793.

⁴⁴ Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1977**, 100, 1632.

⁴⁵ (a) Hudson, R. F. *Chem. Commun.* **1967**, 1249; (b) Cavell, R. G.; The, K. I.; Vande Griend, L. *Inorg. Chem.* **1981**, 20, 3813; (c) Wang, Y.; Goekjian, P. G.; Ryckman, D. M.; Kishi, Y. *J. Org. Chem.* **1988**, 53, 4154; (d) Priya, S.; Balakrishna, M. S.; Mague, J. T. *Inorg. Chem. Commun.* **2001**, 4, 437; (e) Priya, S.; Balakrishna, M. S.; Mague, J. T.; Mobin, S. M. *Inorg. Chem.* **2003**, 42, 1272; (f) Priya, S.; Balakrishna, M. S.; Mobin, S. M. *Polyhedron* **2005**, 24, 1641; (g) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Tetrahedron Lett.* **2007**, 48, 5227; (h) Biricik, N.; Kayana, C.; Gümgüm, B. *Helv. Chim. Acta* **2014**, 97, 1158.

CHAPTER 4

E-H (E = Si, B, C) Bond Activation by Phosphenium Cations

To experimentally assess the potential of phosphenium salts for small molecule activation,¹ we studied the reactivity of Ph- ($[2a]^{2+}$), N^iPr_2 - ($[2c]^{2+}$), and tBu -substituted ($[2d]^{2+}$) dications² towards hydridic aminoboranes ($N = 10.01-7.97$, where N is nucleophilicity parameter of various hydride donors), less nucleophilic silanes ($N = 3.58-2.65$), and substrates containing slightly hydridic C-H bonds ($N = 0.64-0.52$).³ In order to comparatively determine the effects of not only P-centered substituent exchange but also increasing the positive charge on phosphenium-induced small substrate activation, we further included bis(diisopropylamino)phosphenium monocation $[3][BAr^{Cl}_4]$, which was synthesized via chloride abstraction from chlorophosphine $(^iPr_2N)_2PCl$ employing $Na[BAr^{Cl}_4]$.⁴ Apart from spectroscopic methods, the identity of $[3][BAr^{Cl}_4]$ was confirmed using crystallographic techniques (Figure 4.1). While all phosphenium salts activated B-H bonds via oxidative addition and/or hydride abstraction, increased electrophilicity of N^iPr_2 - ($[2c]^{2+}$) and Ph-dications ($[2a]^{2+}$) enabled the activation of less hydridic Si-H and $C(sp^3)$ -H bonds, respectively. Preliminary experimental studies indicated that phosphenium dications ($[2a]^{2+}$ and $[2c]^{2+}$) preferred heterolytic cleavage over oxidative addition of the Si-H bond, while combination of steric and electronic factors controlled the outcome of B-H and C-H bond activation less predictable.

Figure 4.1. Molecular view of $[3][\text{BAr}^{\text{Cl}}_4]$ set at 50% probability. Counterion and hydrogen atoms were omitted for clarity. The closest contact between the cation (P1) and the anion is 3.709 Å. Selected bond lengths [Å] and angle [°]: N1-P1, 1.6183(10), N2-P1, 1.6252(10), N1-P1-N2, 110.65(5).

Section 4.1. B-H Bond Activation of Lewis Base Stabilized Boranes

The addition of 1 equivalent⁵ of trimethylamino ($\text{H}_3\text{B}\cdot\text{NMe}_3$) or pyridine borane complexes ($\text{H}_3\text{B}\cdot\text{Py}$) to the DCM solution of P-monocation $[3][\text{BAr}^{\text{Cl}}_4]$ (Scheme 4.1) gave rise to broad signals in $^{31}\text{P}\{^1\text{H}\}$ (δ_{P} 16.1 (NMe₃) and 20.3 ppm (Py)) and $^{11}\text{B}\{^1\text{H}\}$ (δ_{B} – 10.4 and –13.4 ppm, respectively) NMR spectra suggestive of P-B bond formation. Furthermore, ^{31}P NMR spectra revealed broad doublets implying the presence of P-H fragments whose characteristic appearance as doublets of triplets ($^1J_{\text{P-H}} = 432$ Hz and $^3J_{\text{H-H}} = 2$ Hz in both instances) in ^1H NMR spectra (δ_{H} 6.96 (NMe₃) and 7.06 ppm (Py)) indicated attachment of $-\text{BH}_2\cdot\text{LB}$ (LB = NMe₃, Py) moieties directly to the P atom. These results were consistent with the formation of B-H bond insertion products $[(^i\text{Pr}_2\text{N})_2\text{P}(\text{H})(\text{BH}_2\cdot\text{NMe}_3)][\text{BAr}^{\text{Cl}}_4]$, **[3-j]** $[\text{BAr}^{\text{Cl}}_4]$ and $[(^i\text{Pr}_2\text{N})_2\text{P}(\text{H})(\text{BH}_2\cdot\text{Py})][\text{BAr}^{\text{Cl}}_4]$, **[3-i]** $[\text{BAr}^{\text{Cl}}_4]$, whose structural identities were further elucidated by standard crystallographic methods (Figures 4.2. and 4.3).

Scheme 4.1. B-H bond activation by [3][BAr^{Cl}₄]. Reagents and conditions: (a) 1 equiv of H₃B·LB (LB = NMe₃, Py), DCM or 1,2-difluorobenzene, ambient temperature.

Figure 4.2. Molecular view of [3-j][BAr^{Cl}₄] set at 50% probability. Counterion and hydrogen atoms except H1-3 were omitted for clarity. The closest contact between the cation (P1) and the anion is 4.419 Å. Selected bond lengths [Å] and angles [°]: N1-P1, 1.6615(16), N2-P1, 1.6547(15), P1-B1, 1.9576(19), B1-N3, 1.605(2), N1-P1-B1, 113.66(8), N2-P1-B1, 108.91(8), N1-P1-N2, 116.77(8).

Figure 4.3. Molecular view of $[3-i][BAr^{Cl}_4]$ set at 50% probability. Counterion and hydrogen atoms except H1-3 were omitted for clarity. The closest contact between the cation (P1) and the anion is 5.813 Å. Selected bond lengths [Å] and angles [°]: N1-P1, 1.6480(18), N2-P1, 1.6427(18), P1-B1, 1.942(3), B1-N3, 1.578(3), N1-P1-B1, 112.17(10), N2-P1-B1, 114.24(11), N1-P1-N2, 115.19(9).

On the other hand, the reaction of doubly charged N^iPr_2 analogue $[2c][BAr^{Cl}_4]_2$ with $H_3B\cdot NMe_3$ (Scheme 4.2), other than formal oxidative addition product $[\{C_6H_4(MeN)_2C\}_2C\cdot P(H)(BH_2\cdot NMe_3)N^iPr_2][BAr^{Cl}_4]_2$, $[2c-j][BAr^{Cl}_4]_2$ (δ_P –15.4 ppm), yielded another P-H-based species as inferred from the corresponding doublet (δ_P –12.3 ppm) in the ^{31}P NMR spectrum. The latter compound exhibited a $^1J_{P-H}$ coupling constant value of 225 Hz typical of primary phosphines. Its identity as carbene-supported aminohydridophosphenium monocation $[\{C_6H_4(MeN)_2C\}_2C\cdot P(N^iPr_2)H]^+$, $[2c-H]^+$ was subsequently established by ESI-MS analysis of the respective reaction mixture (calcd. for $C_{25}H_{35}N_5P^+$: m/z 436.2630, found: 436.2632) and by independent treatment of $[2c][BAr^{Cl}_4]_2$ with an equimolar amount of tributyltin-hydride (nBu_3SnH).⁶ Furthermore, the 1H NMR spectrum of $[2c-j][BAr^{Cl}_4]_2$ displayed PH proton as doublet of doublets (δ_H 7.16 ppm, $^1J_{P-H}$ = 351 Hz and $^3J_{H-H}$ = 4 Hz) indicating 1H - 1H coupling with only one of the two vicinal BH_2 protons. The same phenomenon also occurred for an analogous B-H insertion product $[\{C_6H_4(MeN)_2C\}_2C\cdot P(H)(BH_2\cdot NMe_3)Ph]^{2+}$, $[2a-j]^{2+}$ (δ_H 7.06 ppm, $^1J_{P-H}$ = 383 Hz and $^3J_{H-H}$ = 7 Hz) whose identity was undoubtedly confirmed by single crystal

X-ray diffraction (Figure 4.4). Careful structural examination of $[2a-j]^{2+}$ revealed a rather elongated P-B single bond (1.973(6) Å; 1.9576(19) and 1.942(3) Å observed for $[3-j]^+$ and $[3-i]^+$, respectively)⁷ with carbodicarbene and trimethylamino group in quasi-*trans* disposition (C-P-B-N dihedral angle 137.7 °) due to steric factors. Accordingly, this prevented the rotation around the P-B bond forcing the PH proton to couple exclusively with the vicinal BH proton in the *trans* disposition as judged by the Karplus curve (H-P-B-H dihedral angles 78.1 and 163.1 °).⁸ In addition to $[2a-j][BAr^{Cl}_4]_2$, the reaction mixture between phenylphosphenium dication $[2a][BAr^{Cl}_4]_2$ and $H_3B \cdot NMe_3$ also revealed a formal hydride abstraction product $\{[C_6H_4(MeN)_2C\}_2C \cdot P(Ph)H[BAr^{Cl}_4]$, $[2a-H][BAr^{Cl}_4]$, as a minor constituent. The presence of analogous doublets in ^{31}P (δ_P -52.0 ppm, $^1J_{P-H}$ = 226 Hz) and 1H (δ_H 5.59 ppm) NMR spectra is diagnostic of P-H bond formation, while structural characterization of $[2a-H]^+$ (Figure 4.5) was accomplished using the hydride donating reagent nBu_3SnH .⁹ The P1-C1 bond distance of $[2a-H]^+$ (1.807(8) Å) was longer than the corresponding bond of $[2a-Cl]^+$ (1.776(6) Å), which was somewhat expected considering the greater $C_{\text{carbone}} \rightarrow P$ electron-density flow in $[2a-Cl]^+$ induced by higher electronegativity of Cl vs. H atom. It is also noteworthy that larger hydridophilicity of P-dications $[2a]^{2+}$ and $[2c]^{2+}$ compared to the monocation $[3]^+$ as witnessed by the formation of H-abstraction products $[2a-H]^+$ and $[2c-H]^+$ was in agreement with the more accessible LUMOs of doubly charged species (Figure 3.11).

Scheme 4.2. B-H bond activation by $[2a][BAr^{Cl}_4]$ and $[2c][BAr^{Cl}_4]$. Reagents and conditions: (a) 1 equiv of $H_3B \cdot LB$ (LB = NMe_3 , Py), DCM or 1,2-difluorobenzene, ambient temperature.

Figure 4.4. Molecular view of $[2a-j][AlCl_4]_2$ set at 50% probability. Counterions and hydrogen atoms apart from H1-3 were omitted for clarity. The closest contact between the cation (P1) and the anion is 3.998 Å. Selected bond lengths [Å] and angle [°]: P1-C1, 1.775(5), P1-B1, P1-C2, 1.810(5), 1.973(6), B1-N1, 1.585(8), C1-P1-B1, 108.7(2).

Figure 4.5. Molecular view of $[2a-H][AlCl_4]$ set at 50% probability. The counterion and hydrogen atoms apart from H1 were omitted for clarity. The closest contact between the cation (P1) and the anion is 4.370 Å. Selected bond lengths [Å] and angles [°]: P1-C1, 1.807(8), P1-C2, 1.838(9), C1-P1-C2, 106.0(4).

Likewise, the introduction of BH_3Py to either DCM or 1,2-difluorobenzene solutions of $[2a][BAr^{Cl}_4]_2$ or $[2c][BAr^{Cl}_4]_2$ (Scheme 4.2), apart from formal hydride-

abstraction $[\mathbf{2a-H}][\text{BAr}^{\text{Cl}}_4]$ and $[\mathbf{2c-H}][\text{BAr}^{\text{Cl}}_4]$, traditionally afford BH bond insertion products $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\cdot\text{P}(\text{H})(\text{BH}_2\cdot\text{Py})\text{Ph}][\text{BAr}^{\text{Cl}}_4]_2$, $[\mathbf{2a-i}][\text{BAr}^{\text{Cl}}_4]_2$ ($\delta_{\text{P}} -13.5$ ppm, $^1J_{\text{P-H}} = 395$ Hz; calcd. for $\text{C}_{30}\text{H}_{33}\text{BN}_5\text{P}^{2+}$: m/z 252.6280, found: 252.6292) or $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\cdot\text{P}(\text{H})(\text{BH}_2\cdot\text{Py})\text{N}^i\text{Pr}_2][\text{BAr}^{\text{Cl}}_4]_2$, $[\mathbf{2c-i}][\text{BAr}^{\text{Cl}}_4]_2$ ($\delta_{\text{P}} -1.8$ ppm, $^1J_{\text{P-H}} = 423$ Hz; calcd. for $\text{C}_{30}\text{H}_{42}\text{BN}_6\text{P}^{2+}$: m/z 264.1648, found: 264.1658), respectively, as observed from ^{31}P and ESI-MS spectra. However, notably higher amounts of $[\mathbf{2a-H}]^{+10}$ and $[\mathbf{2c-H}]^+$ with respect to the corresponding BH-insertion products were formed after $\text{H}_3\text{B}\cdot\text{NMe}_3$ (the ratio of insertion vs. hydride abstraction products was 9:1 for $[\mathbf{2a}]^{2+}$ and 23:1 for $[\mathbf{2c}]^{2+}$) was replaced with the more powerful hydride donor $\text{BH}_3\cdot\text{Py}$ ($[\mathbf{2a}]^{2+}$: 4:1; $[\mathbf{2c}]^{2+}$: 10:1).³ These results suggested that the relative ratio of the B-H bond activation products was dominantly influenced by electronic factors between phosphonium cations and Lewis base-stabilized boranes, however, steric effects should not be completely excluded (see Section 4.2). Additionally, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture between $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$ and $\text{BH}_3\cdot\text{Py}$ also showed a minor signal at $\delta_{\text{P}} -133.4$ ppm that resolved into a triplet after the proton decoupler was turned off. Furthermore, the ^1H NMR spectrum featured an analogous doublet at $\delta_{\text{H}} 4.15$ ppm with the same $^1J_{\text{P-H}}$ coupling constant value of 212 Hz diagnostic of a phosphine-like PH_2 fragment.¹¹ Its identity as carbodicarbene-stabilized parent phosphonium ion $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\cdot\text{PH}_2]^+$, $[\mathbf{2}\cdot\text{PH}_2]^+$ was initially suggested by ESI-MS analysis (calcd. for $\text{C}_{19}\text{H}_{22}\text{N}_4\text{P}^+$: m/z 337.1582; found: 337.1583) and subsequently crystallographically confirmed (Figure 4.6) by treating $[\mathbf{2f-Br}][\text{Br}]$ with 2 equiv of AlCl_3 ($\text{Na}[\text{BAr}^{\text{Cl}}_4]$) and $^n\text{Bu}_3\text{SnH}$ (Scheme 4.3). The P1-C1 bond distance of $[\mathbf{2}\cdot\text{PH}_2][\text{AlCl}_4]$ (1.811(4) Å) appeared shorter than the corresponding bond length (1.840(4) Å) of recently reported NHC-stabilized dihydridophosphonium cation,¹¹ which was not unusual considering the greater electron donating character of carbenes relative to NHC-type ligands.

Scheme 4.3. Reaction routes leading to the formation $[2\cdot\text{PH}_2]^+$. Reagents and conditions: (a) 1 equiv of H_3BPy , DCM or 1,2-difluorobenzene, ambient temperature; (b) 2 equiv of $\text{AlCl}_3/\text{Na}[\text{BARCl}_4]$, 2 equiv of $^n\text{Bu}_3\text{SnH}$, 1,2-difluorobenzene, ambient temperature.

Figure 4.6. Molecular view of $[2\cdot\text{PH}_2][\text{AlCl}_4]$ set at 50% probability. Counterion and hydrogen atoms except H1-2 were omitted for clarity. The closest contact between the cation (P1) and the anion is 3.743 Å. Selected bond length [Å]: P1-C1, 1.811(4).

Unlike its Ph- and N^iPr_2 -correspondents, *tert*-butylphosphenium dication $[2\text{d}][\text{AlCl}_4]_2$ oxidatively inserted into B-H bonds of aminoborane complexes to give $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}(\text{P}(\text{H})(\text{BH}_2\text{NMe}_3)^t\text{Bu})][\text{AlCl}_4]_2$, $[2\text{d-j}][\text{AlCl}_4]_2$ ($\delta_{\text{P}} -11.3$ ppm, $^1J_{\text{P-H}} = 372$ Hz) or $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}(\text{P}(\text{H})(\text{BH}_2\text{Py})^t\text{Bu})][\text{AlCl}_4]_2$, $[2\text{d-i}][\text{AlCl}_4]_2$ ($\delta_{\text{P}} 2.2$ ppm, $^1J_{\text{P-H}} = 383$ Hz) as the only P-containing species in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Scheme 4.4). In addition, ^1H NMR spectra of $[2\text{d-j}][\text{AlCl}_4]_2$ and $[2\text{d-i}][\text{AlCl}_4]_2$ revealed *PH* resonances ($\delta_{\text{H}} 6.16$ and 6.21 ppm, respectively) as doublet of doublets due to ^1H - ^{31}P ($^1J_{\text{P-H}} = 372$ Hz and $^1J_{\text{P-H}} = 383$ Hz) and ^1H - ^1H coupling ($^3J_{\text{H-H}} = 4$ Hz and $^3J_{\text{H-H}} = 2$ Hz, respectively) with only one of the two vicinal protons from BH_2 -moiety. As discussed previously, the latter observation was likely a consequence of restricted rotation around the P-B bond caused by steric factors. Nevertheless, molecular compositions of doubly charged B-H insertion products $[2\text{d-j}]^{2+}$ and $[2\text{d-i}]^{2+}$ were validated by ESI-MS signals at m/z 232.6590

(calculated for $\text{C}_{26}\text{H}_{41}\text{BN}_5\text{P}^{2+}$: m/z 232.6591) and 242.6447 (calculated for $\text{C}_{28}\text{H}_{37}\text{BN}_5\text{P}^{2+}$: m/z 242.6435), respectively. Considering a somewhat similar hydridophilicity of phosphonium dications as judged by the relatively close energy levels of their LUMOs ($[\mathbf{2a}]^{2+}$: -9.25 ; $[\mathbf{2c}]^{2+}$: -8.56 ; $[\mathbf{2d}]^{2+}$: -9.17 eV), one would expect that the treatment of ^tBu -dication with hydridic aminoboranes, in addition to B-H insertion give H-abstraction products as well. However, absence of anticipated carbodicarbene-stabilized *tert*-butylhydridophosphonium cation $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{P}(^t\text{Bu})\text{H}]$, $[\mathbf{2d-H}]^+$, in the respective reaction mixtures may be attributed to its inherited instability as established in a control experiment between $[\mathbf{2d}][\text{AlCl}_4]_2$ and 1 equiv of $^n\text{Bu}_3\text{SnH}$.¹²

Although, mechanistic details regarding the formation of formal H-abstraction and B-H insertion products remain unknown, it is reasonable to assume that the nature of the initial interaction between phosphonium cations and amino borane complexes enabled the overlapping of two distinctive pathways. However, to the best of our knowledge, single site B-H bond activation via H-abstraction and/or insertion has no precedent in P(III) chemistry.

Scheme 4.4. B-H bond activation by $[\mathbf{2d}][\text{AlCl}_4]$. Reagents and conditions: (a) 1 equiv of $\text{H}_3\text{B} \cdot \text{LB}$ (LB = NMe_3 , Py), DCM, ambient temperature.

Section 4.2. Si-H Bond Activation of Primary, Secondary, and Tertiary Silanes

Next, we explored the electrophilicity of phosphonium cations towards significantly less hydridic tertiary (Et_3SiH and Ph_3SiH for which $N = 3.58$ and 2.65 , respectively), secondary (Ph_2SiH_2 , $N = 1.52$), and primary (PhSiH_3 , $N = 0.06$) silanes.³ While ^tBu -dication $[\mathbf{2d}][\text{AlCl}_4]_2$ gave a very complex mixtures of unstable products presumably due to the $[\text{AlCl}_4]$ anion interference,¹³ the monocation $[\mathbf{3}][\text{BAr}^{\text{Cl}}_4]$ did not react with tertiary and secondary silanes and its treatment with 1 equiv of PhSiH_3 gave a very complicated mixture of products.¹⁴ On the other hand, introduction of Et_3SiH or

Ph₃SiH to the DCM solution of NⁱPr₂-dication [2c][BAr^{Cl}₄]²⁺ resulted in a slight conversion (approximately 20 % based on ³¹P{¹H} NMR spectrum) to the previously identified H-abstraction product [2c-H][BAr^{Cl}₄]⁺ (Scheme 4.5).¹⁵ Interestingly, the conversion rate was significantly improved when sterically less demanding Ph₂SiH₂ (40 %) and PhSiH₃ (95 %) silanes were employed as substrates. This observation indicated that relative hydricity of silanes and [2c]²⁺-to-[2c-H]⁺ conversion followed reverse trends (i.e. less nucleophilic substrate yielded more H-abstraction product), thus suggesting that steric factors had a major contribution to the outcome of the aminophosphenium [2c][BAr^{Cl}₄]₂ induced Si-H bond activation.

Scheme 4.5. Si-H bond activation by [2a][BAr^{Cl}₄]₂ and [2c][BAr^{Cl}₄]₂. Reagents and conditions: (a) 1 equiv of the corresponding silane (Et₃SiH, Ph₃SiH, Ph₂SiH₂, PhSiH₃), DCM, ambient temperature.

Furthermore, the treatment of more electrophilic Ph-dication [2a][BAr^{Cl}₄]₂ with primary, secondary, or tertiary silanes resulted in a complete conversion to [2a-H][BAr^{Cl}₄]. It is noteworthy that ²⁹Si NMR spectrum did not reveal any visible signals corresponding to R'₃Si⁺-units (R' = Et, Ph, H) even after extended scanning time (48 hours) inferring the transient nature of cationic Si-based compounds in non-coordinating solvents such as dichloromethane.¹⁶ Overall, these results demonstrated the preference of doubly charged P-cations [2a][BAr^{Cl}₄]₂ and [2c][BAr^{Cl}₄]₂ to activate Si-H bonds via hydride abstraction unlike their isolobal group 14 analogues that favor oxidative insertion.

Inspired by somewhat unexpected reactivity of phosphonium dications towards silanes, we attempted the synthesis of hypothetical Si-H insertion product [ⁱC₆H₄(MeN)₂C]₂C·P(H)(SiEt₃)Ph]²⁺, [2a(H)(SiEt₃)]²⁺. For this purpose, we reacted secondary phosphine [2a-H][BAr^{Cl}₄] and [(Et₃Si)toluene][B(C₆F₅)₄] hoping to observe the P-Si bond formation (Scheme 4.5). However, virtually identical ³¹P{¹H}/³¹P NMR

spectra of $[\mathbf{2a-H}]^+$ observed upon reaction with cationic Si-source refuted any reactivity between the two building blocks. This observation suggested that formation of the formal Si-H oxidative addition products might be restricted by thermodynamic (steric) and/or kinetic (energy of transition states) factors. Overall, these experimental observations strongly support the preference of Ph- $[\mathbf{2a}]^{2+}$ and N^iPr_2 -phosphenium $[\mathbf{2c}]^{2+}$ dications to abstract hydride rather than to insert into Si-H bonds.

Section 4.3. C-H Bond Activation of 1,3,5-cycloheptatriene and Xanthene

Prompted by inherent hydridophilicity of newly prepared P-dications, we also attempted activation of several substrates with moderately hydridic C-H bonds.¹⁷ While aminophosphenium mono- $[\mathbf{3}][\text{BAr}^{\text{Cl}}_4]$ and dication $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$ appeared chemically inert toward C-H bond activation, the ^tBu -congener $[\mathbf{2d}][\text{AlCl}_4]_2$ reacted with 1,3,5-cycloheptatriene ($N = 0.52$)³ to yield a very complex mixture of unstable reaction products. However, when DCM solution of phenylphosphenium salt $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ was exposed to the same substrate, the ^{31}P NMR spectrum revealed products formally derived from [4+1] cycloaddition, $\text{C}(\text{sp}^3)$ -H oxidative addition, and H-abstraction (Scheme 4.6). The cycloaddition product $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C-P}(\{\text{CH}\}_6\text{CH}_2)\text{Ph}][\text{BAr}^{\text{Cl}}_4]_2$, $[\mathbf{2a-k}][\text{BAr}^{\text{Cl}}_4]_2$, was the major constituent of the respective reaction mixture which enabled its isolation and full characterization using spectroscopic and crystallographic techniques (Figure 4.7). The X-ray structure of $[\mathbf{2a-k}][\text{BAr}^{\text{Cl}}_4]_2$ was disordered and hence, its structural parameters were exempted from further discussion.

* only trace amounts of this reaction product were observed

Scheme 4.6. Reaction between $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ and 1,3,5-cycloheptatriene leading to the formation of [4+1] cycloaddition ($[\mathbf{2a-k}][\text{BAr}^{\text{Cl}}_4]_2$), $\text{C}(\text{sp}^3)$ -H insertion ($[\mathbf{2a-l}][\text{BAr}^{\text{Cl}}_4]_2$), and H-abstraction ($[\mathbf{2a-H}][\text{BAr}^{\text{Cl}}_4]$) products.

Figure 4.7. Molecular view of $[2a-k][BAr^{Cl_4}]_2$ set at 50% probability. Counterions and hydrogen atoms were omitted for clarity. The closest contact between the cation (P1) and the anion is 4.500 Å. Selected bond lengths [Å]: P1-C1, 1.674(16), P1-C2, 1.796(10), C1-P1-C2, 107.2(8).

Furthermore, the formal C-H bond insertion product $[\{C_6H_4(MeN)_2C\}_2C^+P(H)(C_7H_7)Ph]^{2+}$, $[2a-l]^{2+}$ was very unstable under given experimental conditions. To confirm the identity of $[2a-l]^{2+}$, we performed an independent synthesis using its building blocks such as formal H-abstraction product $[2a-H][BAr^{Cl_4}]$ and commercially available tropylium cation $[C_7H_7][BF_4]$ (Scheme 4.7). Appearance of the previously observed doublet at $\delta_P - 18.9$ ppm with a coupling constant value of $^1J_{P-H} = 498$ Hz verified the ability of Ph-substituted dication $[2a][BAr^{Cl_4}]_2$ to insert into polarized $C(sp^3)-H$ bonds.

Scheme 4.7. Independent preparation of C-H bond insertion product $[2a-l][BAr^{Cl_4}][BF_4]$ from its building blocks $[2a-H][BAr^{Cl_4}]$ and tropylium-tetrafluoroborate salt $[C_7H_7][BF_4]$.

In addition to 1,3,5-cycloheptatriene, Ph-dication $[2a][\text{BAR}^{\text{Cl}}_4]_2$ also inserted into C(sp³)-H bond of xanthene ($N = 0.64$)³ to give $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{P}(\text{H})(\text{CH}\{\text{C}_6\text{H}_4\}_2\text{O})\text{Ph}\}]^{2+}$, $[2a-m]^{2+}$ as the only P-based product present in the solution (Scheme 4.8). Its identity was suggested based on the correlated doublets in the ³¹P (δ_P 4.4 ppm) and ¹H (δ_H 7.65 ppm, $^1J_{P-H} = 485$ Hz) NMR spectra. Moreover, the H atom attached to the C(sp³)-PH moiety of $[2a-m]^{2+}$ was shifted downfield to 5.79 ppm (xanthene: δ_H 4.04) because of the increased overall positive charge. It is noteworthy that spectroscopic analyses of $[2a-m]^{2+}$ were performed *in situ* due to its apparent solution and solid state instability. Thus, the ESI-MS spectrum of $[2a-m]^{2+}$, instead of the corresponding molecular ion, showed signals characteristic of its structural fragments $[2a-H]^+$ and $[\text{CH}\{\text{C}_6\text{H}_4\}_2\text{O}]^+$ (calcd. for $\text{C}_{13}\text{H}_9\text{O}^+$: m/z 181.0648; found: 181.0653) (Scheme 4.8). Similarly, building blocks $[\text{CH}\{\text{C}_6\text{H}_4\}_2\text{O}]^+$ and $[2d-H]^+$ (393.2229; calcd. for $\text{C}_{23}\text{H}_{30}\text{N}_4\text{P}^+$: m/z 393.2203) were observed in the ESI-MS spectrum of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{P}(\text{H})(\text{CH}\{\text{C}_6\text{H}_4\}_2\text{O})^t\text{Bu}\}]^{2+}$, $[2d-m]^{2+}$ formed upon formal oxidative insertion of ^tBu-dication $[2d][\text{AlCl}_4]_2$ into C(sp³)-H bond of xanthene (Scheme 4.8). The identity of $[2d-m]^{2+}$ was also confirmed by the ³¹P{¹H} NMR signal at δ_P 31.9 ppm, which resolved into the corresponding doublet ($^1J_{P-H} = 466$ Hz) upon cancelling the proton decoupling effect. The described reactivity of electronically tuned phosphonium ions towards CH-based substrates certainly advances the synthetic application of P(III) electrophiles.

Scheme 4.8. The insertion of Ph- $[2a]^{2+}$ and ^tBu-substituted $[2d]^{2+}$ dications into C(sp³)-H bond of xanthene; dissociation of the insertion products $[2a-m]^{2+}$ and $[2d-m]^{2+}$ to the respective building blocks $[2a-H]^+$ and $[2d-H]^+$ and aromatic $[\text{CH}\{\text{C}_6\text{H}_4\}_2\text{O}]^+$ ion under ESI-MS conditions.

In this chapter, we investigated the effect of increasing the positive charge, as well as steric and electronic influences of various substituents, on P-centered small molecule activation. While all phosphonium salts activated aminoborane complexes via BH-insertion to give the corresponding phosphonium salts, Ph- $[2a]^{2+}$ and N^iPr_2 -dications $[2c]^{2+}$ were also capable of abstracting the hydride as witnessed by the formation of the respective monocationic primary phosphines. Moreover, reaction between $[2c][BAr^{Cl}_4]_2$ and $PyBH_3$, apart from formal oxidative addition and H-abstraction products, yielded the first example of a thermodynamically-stable parent phosphonium cation $[2\text{-}PH_2]^+$. In addition, $[2a]^{2+}$ and $[2c]^{2+}$ activated Si-H bonds of primary, secondary, and tertiary silanes via H-abstraction. Additional experimental assessments supported the absence of Si-H insertion products suggesting that the rather unusual outcome of Si-H bond activation was affected by thermodynamic (steric) and/or kinetic (activation energy) factors. High electrophilicity of phenylphosphenium dication $[2a]^{2+}$ also manifested in C-H bond activation of 1,3,5-cycloheptatriene and xanthene. While the former reaction also gave [4+1]-cycloaddition and H-abstraction products, the latter reaction confirmed the tendency of $[2a]^{2+}$ to oxidatively insert into $C(sp^3)$ -H bonds. Therefore, we described a novel approach of adapting P(III)-based compounds, commonly regarded as Lewis bases, for chemical transformations typically achieved by Lewis acidic transition metal complexes.

¹ MeO- $[2e]^{2+}$ and Cl-substituted $[2g]^{2+}$ P-dications always gave complicated mixtures of inseparable reaction products upon reacting with hydride donating substrates used in this research.

² We did not obtain any spectroscopic evidence for the P-H bond formation after reacting $[2a]^{2+}$, $[2c]^{2+}$, and $[2d]^{2+}$ with H₂, H₂O, primary and secondary amines, and Ph₂PH.

³ For studies on nucleophilicity *N* of hydride donors see: a) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500; b) Mayr, H.; Lang, G.; Ofial, A. R. *J. Am. Chem. Soc.* **2002**, *124*, 4076; c) Richter, D.; Mayr, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 1958; *Angew. Chem.* **2009**, *121*, 1992; d) Ammer, J.; Lang, G.; Ofial, A. R. *J. Am. Chem. Soc.* **2012**, *134*, 13902; e) Horn, M.; Schappele, L. H.; L.-Wittkowski, G.; Mayr, H.; Ofial, A. R. *Chem. Eur. J.* **2013**, *19*, 249.

⁴ For preparation of the corresponding phosphonium monocation with $[AlCl_4]^-$ anion see: Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784.

⁵ Increasing the number of equivalents of amino borane complexes did not affect significantly the reactivity of monocation $[3][BAr^{Cl}_4]$, as well as the ratio between hydride abstraction and BH-insertion products derived from dications $[2a]^{2+}$, $[2c]^{2+}$, and $[2d]^{2+}$.

⁶ ⁿBu₃SnH was previously used for trapping of two-coordinate cationic P-species. Back, O.; Celik, M. A.; Frenking, G.; Melaimi, M.; Donnadieu B.; Bertrand, G. *J. Am. Chem. Soc.* **2010**, *132*, 10262.

⁷ The P-C single bond length of 1.917 Å was observed for Ph₃PBH₃; Huffman, J. C.; Skupinski, W. A.; Caulton, K. G. *Cryst. Struct. Commun.* **1982**, *11*, 1435.

⁸ This phenomenon was also described upon insertion of phosphinidene into B-H bonds of Lewis stabilized borane complexes. Tian, R.; Mathey, F. *Chem. Eur. J.* **2012**, *18*, 11210.

⁹ Crystals of $[2a-H]^+$ were obtained when $[BAr^{Cl}_4]$ was replaced by $[AlCl_4]$ anion. This was achieved in a separate procedure by treating $[2a][AlCl_4]_2$ with stoichiometric amount of ⁿBu₃SnH.

¹⁰ A significantly higher amount of H-abstraction product formed in the reaction between $[2a][BAr^{Cl}_4]_2$ and H₃BPy along with the similar solubility of $[2a-H]^+$ and $[2a-i]^{2+}$ imparted by the presence of the weakly coordinating $[BAr^{Cl}_4]$ anion(s) prevented the isolation of latter reaction product by means of fractional precipitation.

¹¹ Liu, L.; Ruiz, D. A.; Dahcheh F.; Bertrand, G. *Chem. Commun.* **2015**, *51*, 12732.

¹² [**2d-H**]⁺ was only spectroscopically registered (³¹P{¹H}: δ_P -34.9 ppm; ³¹P: δ_P -34.9 ppm, d, ¹J_{P-H} = 226 Hz) among other compounds when [**2d**][AlCl₄]₂ reacted with ⁿBu₃SnH in dichloromethane.

¹³ [**2a**][AlCl₄]₂ also yielded a mixture of unstable products under identical experimental conditions.

¹⁴ Multinuclear NMR analysis of the corresponding reaction mixture did not reveal the P-H bond formation derived from Si-H bond activation of phenylsilane PhSiH₃.

¹⁵ Si-H bond activation by [**2c**][BAr^{Cl}₄]₂ was also accompanied by minor hydrolysis (~10 %) of the starting dication (δ_P 12.9 ppm, ¹J_{P-H} = 560 Hz). The product of hydrolysis [**2c(O)(H)**][BAr^{Cl}₄] was prepared and fully characterized in an independent experiment by treating [**2c**][BAr^{Cl}₄]₂ with stoichiometric amount of H₂O.

¹⁶ Holthausen, M. H.; Bayne, J. M.; Mallov, I.; Dobrovetsky, R.; Stephan, D. W. *J. Am. Chem. Soc.* **2015**, *137*, 7298. In the following publications authors attributed the inability to observe the ²⁹Si NMR signal of (R'₃Si)⁺ ion due to its transient nature in CD₂Cl₂. On the other hand, if the strongly coordinating solvent such as CD₃CN was used, solvated adduct [(R'₃Si)CD₃CN]⁺ was detected. Unfortunately, coordinatively unsaturated nature of phosphonium dication [**2a**]²⁺ prevented the use of CD₃CN as solvent.

¹⁷ It should be noted that both 1,4-cyclohexadiene (*N* = 0.09) and triphenylmethane did not react with any of phosphonium salts used in this research.

CHAPTER 5

Experimental Details

Section 5.1. General Procedure

All preparations and manipulations were carried out using standard Schlenk techniques under an inert atmosphere of anhydrous N₂ and a dry-box under an argon atmosphere. All glassware was kept in the oven at 120°C overnight, flame-dried and cooled under vacuum before use. Solvents (acetonitrile, benzene, CDCl₃, CD₂Cl₂, CD₃CN, C₆D₆, dichloromethane, diethyl-ether, n-pentane, n-hexane, tetrahydrofuran, toluene, and 1,2-difluorobenzene) were dried using standard procedures, distilled under N₂, degassed under Ar, and kept over 4Å molecular sieves in storage flasks prior to use.

The commercial products (aluminium trichloride, borane trimethylamine complex, borane pyridine complex, bis(diisopropylamino)chlorophosphine, fluorobenzene, phenylsilane, phosphorus(V)-oxychloride, silver hexafluoroantimonate, sodium amide, sodium hexafluoroantimonate, tributyltin hydride, triethylsilane, triphenylsilane, tropylium tetrafluoroborate, xanthene, and α,α,α -trifluorotoluene) were used without further purification. Cycloheptatriene and 2,3-dimethyl-1,3-butadiene were distilled before use. Phosphines such as phosphorus tribromide, phosphorus trichloride, P,P-dichlorophenylphosphine, and *tert*-butyldichlorophosphine) were distilled prior to use, while ¹Pr₂NPCl₂,¹ (PhN(PCl₂)₂),² and (*para*-fluorophenyl)dichlorophosphine³ were prepared according to the literature methods. Methyl dichlorophosphite, MeN(PCl₂)₂, trimethylphosphine, and triphenylphosphine were purchased from Sigma Aldrich and used without further purification. Ligands (carbodiphosphorane and carbodicarbene),⁴ Na[BAr^{Cl}₄] (Ar^{Cl} = 3,5-Cl₂-C₆H₃),⁵ and Na[BAr^F₄] (Ar^F = 3,5-(CF₃)₂-C₆H₃)⁶ were prepared according to the described procedures.

NMR spectra were obtained on a Brüker Avance III 400, Brüker Avance 500, and JEOL ECA 400 instrument. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal - tetramethylsilane for ¹H and ¹³C{¹H}, and external standards: 85% phosphoric acid for ³¹P, α,α,α -trifluorotoluene for ¹⁹F, and BF₃·OEt₂ for ¹¹B. Mass spectra were obtained on Waters Q-TOF Premier MS and Agilent Technologies 6230 TOF LC/MS mass spectrometers using the electrospray ionization (ESI) mode.

Section 5.2. Preparation Procedures and Spectroscopic Data

Preparation of $[(\text{Ph}_3\text{P})_2\text{C}(\text{P}(\text{Ph})\text{Cl})][\text{X}]$; **[1a-Cl][X]**, $\text{X} = \text{Cl}, \text{BAr}^{\text{Cl}}_4, \text{SbF}_6$. The chloride salt of this compound was synthesized by adding 0.50 g (0.93 mmol) of $(\text{Ph}_3\text{P})_2\text{C}$ (**1**) to a 100 mL benzene solution containing 0.38 mL (2.79 mmol) of PhPCl_2 . The reaction was stirred overnight followed by filtration. The resulting white solid was dried under vacuum to yield 0.65 g (98%) of **[1a-Cl][Cl]**. The most suitable counterion for crystallization of this species was $[\text{SbF}_6]$, which was quantitatively exchanged with the chloride anion by the addition of 9 mg (0.03 mmol) of NaSbF_6 to a DCM solution (0.8 mL) of **[1a-Cl][Cl]** (25 mg, 0.03 mmol) followed by layering with n-pentane (**[1a-Cl][SbF₆]**). Quantitative anion exchange with $[\text{BAr}^{\text{Cl}}_4]$ was also achieved in the same manner by using $\text{NaBAr}^{\text{Cl}}_4$. The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for the monocation were essentially identical irrespective of the nature of counterion. Therefore, we only report the multinuclear NMR data for **[1a-Cl][Cl]** as the NMR spectroscopic details for $[\text{SbF}_6]$ and $[\text{BAr}^{\text{Cl}}_4]$ anions can be found in numerous published reports.

^1H NMR (CD_2Cl_2 , 500 MHz, 298 K): δ 7.0-7.5 (m, 35 H). $^{13}\text{C}\{^1\text{H}\}$ (CD_2Cl_2 , 100 MHz, 298 K): δ 22.5 (m, $\text{C}_{(\text{carbonyl})}$), 124.2 (apparent triplet AA'X, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 90$ Hz, *ipso-C*, $\text{Ph}_{(\text{carbonyl})}$), 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*, $\text{Ph}_{(\text{carbonyl})}$), 133.6 (s, *p-C*, $\text{Ph}_{(\text{carbonyl})}$), 134.3 (virtual triplet, *m-C*, $\text{Ph}_{(\text{carbonyl})}$), 139.3 (dt, $^1J_{\text{P}(\text{central})\text{C}} = 37.3$ Hz, $^3J_{\text{P}(\text{carbonyl})\text{C}} = 10.3$ Hz, *ipso-C*, Ph). $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2 , 202 MHz, 298 K): δ 25.6 (second order doublet, $\text{P}_{(\text{carbonyl})}$), 110.5 (second order triplet, $\text{P}_{(\text{central})}$). HR-MS Calculated for $[\text{C}_{43}\text{H}_{35}\text{ClP}_3]^+$ (**1a-Cl**⁺): m/z 679.1640. Found: 679.1592.

Preparation of $[(\text{Ph}_3\text{P})_2\text{C}(\text{P}(4\text{-F-Ph})\text{Cl})][\text{X}]$; **[1b-Cl][X]**, $\text{X} = \text{Cl}, \text{BAr}^{\text{Cl}}_4, \text{SbF}_6$. The chloride salt of this compound was synthesized by adding 0.50 g (0.93 mmol) of $(\text{Ph}_3\text{P})_2\text{C}$ (**1**) to a 100 mL benzene solution containing 0.40 mL (2.79 mmol) of 4-F- PhPCl_2 . The reaction was stirred overnight followed by filtration. The resulting white solid was dried under vacuum to yield 0.68 g (98%) of **[1b-Cl][Cl]**. The most adequate counterion for crystallization of this species was found to be $[\text{SbF}_6]$, which was quantitatively exchange with the chloride anion by the addition of 9 mg (0.03 mmol) of NaSbF_6 to a DCM

solution (0.8 mL) of [**1b-Cl**][Cl] (25 mg, 0.03 mmol) followed by layering with n-hexane ([**1b-Cl**][SbF₆]). Quantitative anion exchange with [BAr^{Cl}₄] was also achieved in the same manner by using NaBAr^{Cl}₄. Multinuclear NMR spectra for this monocation were essentially identical irrespective of the nature of counterion. Therefore, we only report the multinuclear NMR data for [**1b-Cl**][Cl] as the NMR spectroscopic details for [SbF₆] and [BAr^{Cl}₄] anions can be found in numerous published reports.

¹H NMR (CD₂Cl₂, 500 MHz, 298 K): δ 6.8-7.5 (m, 34 H). ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz, 298 K): δ 115.9 (dd, ²J_{P(central)C} = 21.3 Hz, ³J_{CF} = 4.2 Hz, *o*-C, 4-F-Ph), 124.2 (apparent triplet AA'X, ¹J_{PC} + ³J_{PC} = 91.4 Hz, *ipso*-C, Ph_(carbonyl)), 129.3 (virtual triplet, *o*-C, Ph_(carbonyl)), 131.3 (dd, ³J_{P(central)C} = 8.2 Hz, ²J_{CF} = 21.9 Hz, *m*-C, 4-F-Ph) 133.6 (s, *p*-C, Ph_(carbonyl)), 134.3 (virtual triplet, *m*-C, Ph_(carbonyl)), 162.9 (d, ¹J_{CF} = 249.9 Hz, *p*-C, 4-F-Ph). C_(carbonyl) and *ipso*-C for 4-F-Ph were not observed presumably due to the quaternary nature of these atoms and coupling to P and / or F atoms. ³¹P{¹H} NMR (CD₂Cl₂, 202 MHz, 298 K): δ 25.6 (second order doublet, P_(carbonyl)), 110.6 (second order triplet, P_(central)). ¹⁹F{¹H} NMR (CD₂Cl₂, 470 MHz, 298 K): δ -113.7 (s, F-Ph). HR-MS Calculated for [C₄₃H₃₄ClFP₃]⁺ (**1b-Cl**⁺): m/z 697.1546. Found: 697.1511.

Preparation of [(Ph₃P)₂C^tBuCl]Cl; [1d-Cl**][Cl].** A benzene solution of (PPh₃)₂C (**1**) 0.10 g (0.19 mmol) was added to a toluene solution (20 mL) containing 90 mg (0.57 mmol) of ^tBuPCl₂. The reaction was stirred overnight and it resulted in the formation of white precipitate. The resulting solution was filtered off and white precipitate was washed with toluene twice and finally with n-hexane and dried *in vacuo* to yield [**1d-Cl**][Cl] as a white solid. Yield: 0.11 g (90 %).

¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.40-7.69 (m, 30H, Ph), 0.57 (d, 9H, ³J_{PH} = 15.6 Hz, CCH₃). ¹³C{¹H} (CD₂Cl₂, 100 MHz, 298 K): δ 27.9 (d, ²J_{P(central)C} = 33.6 Hz, CCH₃), 40.4 (dt, ¹J_{P(central)C} = 72 Hz, ³J_{P(carbonyl)C} = 11 Hz, CCH₃), 124.4 (br m, *ipso*-C, Ph), 129.1 (virtual triplet, *o*-C, Ph), 133.7 (s, *p*-C, Ph), 134.6 (virtual triplet, *m*-C, Ph). ³¹P{¹H} (CD₂Cl₂, 202 MHz, 298 K): δ 23.42 (multiplet - a set of second order doublets, P_(carbonyl)), 131.55 (second order triplet, P_(central)). HR-MS Calculated for [C₄₁H₃₉ClP₃]⁺ (**1d-Cl**⁺): m/z 659.1953. Found: 659.1955.

Preparation of $[(\text{Ph}_3\text{P})_2\text{C}(\text{OMe})\text{Cl}][\text{X}]$, $[\mathbf{1e-Cl}][\text{X}]$, $[\text{X}] = [\text{Cl}], [\text{SbF}_6]$. 0.5 g (0.93 mmol) of $(\text{Ph}_3\text{P})_2\text{C}$ (**1**) was dissolved in 200 mL of benzene. The resulting solution was then transferred to a Schlenk flask containing 0.27 mL (2.79 mmol) of MeOPCl_2 . The reaction mixture was stirred overnight, followed by filtration and drying *in vacuo* to yield 0.61 g (98 %) of $[\mathbf{1e-Cl}][\text{Cl}]$ as a white solid. The most adequate counterion for crystallization of this species was found to be $[\text{SbF}_6]$ which was quantitatively exchanged with the chloride anion by addition of 10 mg (0.03 mmol) of NaSbF_6 to a DCM solution (0.8 mL) containing 25 mg (0.03 mmol) of $[\mathbf{1e-Cl}][\text{Cl}]$ followed by layering with n-hexane ($[\mathbf{1e-Cl}][\text{SbF}_6]$).

^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ 3.09 (d, $^3J_{\text{PH}} = 14$ Hz, 3H, OCH_3), 7.43-7.65 (m, 30H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K): δ 55.3 (d, $^2J_{\text{CP}} = 18$ Hz, OCH_3), 123.9 (br t, $^1J_{\text{CP}} = 47$ Hz, *ipso*-C, Ph), 129.2 (t, $^2J_{\text{CP}} = 6$ Hz *o*-C, Ph), 133.6 (s, *p*-C, Ph), 134.3 (t, $^3J_{\text{CP}} = 5$ Hz, *m*-C, Ph). The signal corresponding to the PCP resonance was not observed in $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum. ^{31}P NMR (160 MHz, CD_2Cl_2 , 298 K): δ 21.7 (d, $^2J_{\text{PP}} = 74$ Hz, $\text{P}_{(\text{carbone})}$), 215.6 (t, $^2J_{\text{PP}} = 74$ Hz, $\text{P}_{(\text{central})}$). HR-MS Calculated for $[\text{C}_{38}\text{H}_{33}\text{ClOP}_3]^+$ ($\mathbf{1e-Cl}^+$): m/z 633.1433. Found: 633.1427.

Preparation of $[(\text{Ph}_3\text{P})_2\text{C}\{\text{Ph}\}\text{P}(\text{PMe}_3)][\text{BAr}^{\text{F}}_4]_2$, $[\mathbf{1a-PM}_3][\text{BAr}^{\text{F}}_4]_2$. 120 mg (0.17 mmol) of $[\mathbf{1a-Cl}][\text{Cl}]$ was dissolved in about 10 mL of 1,2-difluorobenzene followed by addition of 17 μL (0.17 mmol) of PMe_3 and 316 mg (0.36 mmol) of $\text{Na}[\text{BAr}^{\text{F}}_4]$, respectively. 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, 298 K): 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, 298 K): δ 11.7 (dd, $^1J_{\text{PC}} = 40$ Hz, $^2J_{\text{PC}} = 14$ Hz, PMe_3), 117.7 (*p*-C, BAr^{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 , BAr^{F}_4), 129.0 (q, $^2J_{\text{CF}} = 15$ Hz, *m*-C, BAr^{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 BAr^{F}_4 and *m*-C of $\text{Ph}_{(\text{carbone})}$), 162.2 (*ipso*-C, $^1J_{\text{CB}} = 50$ Hz, BAr^{F}_4). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202 MHz, 298 K): δ -6.4 (second order dt, $\text{P}_{(\text{carbone})}$),

11.4 (second order dt, PMe_3), 28.7 (second order d, $\text{P}_{(\text{carbone})}$). HR-MS Calculated for $[\text{C}_{46}\text{H}_{44}\text{P}_4]^{2+}$ ($\mathbf{1a} \cdot \text{PMe}_3^{2+}$): m/z 360.1197. Found: 360.1191.

Figure 5.1. ^{31}P NMR spectrum of $[\mathbf{1a} \cdot \text{PMe}_3][\text{BAr}^{\text{F}}_4]_2$.

Preparation of $[(\text{Ph}_3\text{P})_2\text{C}(\text{Ph})\text{F}][\text{BAr}^{\text{Cl}}_4]$; $[\mathbf{1a-F}][\text{BAr}^{\text{Cl}}_4]$. This compound was obtained as a main product in the reaction of the corresponding monocation and PhCF_3 , and for comparison of NMR data, $[\mathbf{1a-F}][\text{BAr}^{\text{Cl}}_4]$ was synthesized using KF as the fluoride source. Both reaction pathways are described below. The multinuclear NMR spectroscopic data was taken from the latter reaction as it was cleaner.

- *Reaction of $[\mathbf{1a-Cl}][\text{BAr}^{\text{Cl}}_4]$ and PhCF_3 .* 1 mL of 1,2-difluorobenzene was added to 30 mg (0.02 mmol) of $[\mathbf{1a-Cl}][\text{BAr}^{\text{Cl}}_4]$ and 30 mg (0.04 mmol) of $\text{NaBAr}^{\text{Cl}}_4$ followed by addition of 3 μL of PhCF_3 (J. Young NMR tube). After 5 hours at 100°C , the reaction was completed. Yield: 26 %. Note that the yield for $[\mathbf{1a-F}][\text{BAr}^{\text{Cl}}_4]$ was estimated by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy by addition of 5 mg (0.02 mmol) of PPh_3 after reaction completion. Unfortunately, numerous attempts to purify this compound were unsuccessful.

- *Preparation of [1a-F][BAr^{Cl}₄]* using KF as a fluoride source. 1 mL of 1,2-difluorobenzene was added to 64 mg (0.05 mmol) of [1a-Cl][BAr^{Cl}₄] and 31 mg (0.53 mmol) of KF (J. Young NMR tube). The solution was heated at 100°C for 6 days. More than 95 % yield was obtained based on ³¹P{¹H} NMR Spectroscopy. ¹H NMR (CDCl₃, 500 MHz, 298 K): δ 6.9-7.5 (m, 47 H). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 298 K): δ 123.1 (s, *p*-C, BAr^{Cl}₄), 124.5 (br m, *ipso*-C, Ph_(carbonyl)), 128-130.5 (*o*-, *m*-, *p*-C, Ph), 129.2 (virtual triplet, *o*-C, Ph_(carbonyl)), 132.9 (q, ²J_{CB} = 4 Hz, *o*-C, BAr^{Cl}₄) 133.2 (s, *m*-C, BAr^{Cl}₄), 133.5 (s, *p*-C, Ph_(carbonyl)), 134.0 (virtual triplet, *m*-C, Ph_(carbonyl)), 150.5 (dd, ²J_{CF} = 249.1 Hz, ¹J_{P(central)C} = 14 Hz, *ipso*-C, 4-F-Ph), 164.7 (q, ¹J_{CB} = 49 Hz, *ipso*-C, BAr^{Cl}₄). ³¹P{¹H} NMR (CDCl₃, 202 MHz, 298 K): δ 23.4 (second order doublet, P_(carbonyl)), 162.2 (doublet of second order triplets, ¹J_{PF} = 977 Hz, P_(central)). ¹⁹F{¹H} NMR (CDCl₃, 376.5 MHz, 298 K): δ -161.2 (d, ¹J_{PF} = 977 Hz, P-F). HR-MS Calculated for [C₄₃H₃₅ClFP₃]⁺ (1a-F⁺): m/z 663.1930. Found: 663.1904.

Preparation of [(Ph₃P)₂C·P(4-F-Ph)F][BAr^{Cl}₄], [1b-F][BAr^{Cl}₄]. Compound [1b-F][BAr^{Cl}₄] was registered as the main product in the reaction of [1b-Cl][BAr^{Cl}₄] and PhCF₃. Reaction conditions are as following: 1 mL of 1,2-difluorobenzene was added to 35 mg (0.03 mmol) of [1b-Cl][BAr^{Cl}₄] and 34 mg (0.05 mmol) of NaBAr^{Cl}₄ followed by addition of 3.5 μL of PhCF₃ (J. Young NMR tube). After 5 hours at 100°C, reaction was completed. Yield: 55 %. Note that the yield for [1b-F][BAr^{Cl}₄] was estimated by ³¹P{¹H} NMR spectroscopy by addition of 8 mg (0.03 mmol) of PPh₃ after reaction completion. Unfortunately, numerous attempts to purify this compound were unsuccessful. The ¹⁹F and ³¹P NMR signals were recorded *in situ*.

³¹P{¹H} NMR (161 MHz, 298 K): δ 24.8 (second order doublet, P_(carbonyl)), 162.7 (doublet of second order triplets, ¹J_{PF} = 985 Hz, P_(central)). ¹⁹F{¹H} NMR (376 MHz, 298 K): δ -160.4 (d, ¹J_{PF} = 985 Hz, P-F), -113.7 (s, F-Ph). HR-MS Calculated for [C₄₃H₃₄F₂P₃]⁺ (1b-F⁺): m/z 681.1841. Found: 681.1150.

Figure 5.2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{1b-F}][\text{BAr}^{\text{Cl}}_4]$.

Figure 5.3. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{1b-F}][\text{BAr}^{\text{Cl}}_4]$.

Preparation of [$\{C_6H_4(MeN)_2C\}_2CP(N^iPr_2)Cl$][X], [**2c-Cl**][X], X = Cl, SbF₆. Benzene (200 mL) solution of $\{C_6H_4(MeN)_2C\}_2C$, **2** (0.50 g, 1.65 mmol) was transferred to a Schlenk flask containing 0.8 g (4.12 mmol) of iPr_2NPCl_2 . The reaction was stirred overnight followed by filtration. The resulting yellow solid was dried under vacuum to yield 0.76 g (92%) of [**2c-Cl**][Cl]. The most adequate counterion for crystallization of [**2c-Cl**]⁺ was [SbF₆], which was quantitatively exchanged with the chloride anion by adding 10 mg (0.04 mmol) of NaSbF₆ to a DCM solution (0.8 mL) of [**2c-Cl**][Cl] (20 mg, 0.04 mmol) followed by layering with n-hexane ([**2c-Cl**][SbF₆]).

¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ 1.18 (d, ³J_{HH} = 6 Hz, 9H, CH₃ - ⁱPr), 1.29 (m, 3H, CH₃ - ⁱPr), 3.25 (br m, 2H, CH - ⁱPr), 3.81 (s, 12H, NCH₃), 7.47-7.65 (m, 8H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ 18.4 (s, CH₃ - ⁱPr), 23.3 (d, ²J_{CP} = 9 Hz, CH - ⁱPr), 34.2 (d, ⁴J_{PC} = 8 Hz, NCH₃), 48.8 (d, ¹J_{PC} = 7 Hz, CCC), 111.6 (s, CH arom.), 125.5 (s, CH arom.), 132.4 (s, CH arom.), 153.7 (d, ²J_{PC} = 19 Hz, NCN). ³¹P NMR (202 MHz, CD₂Cl₂, 298 K): δ 137.9 (s). HR-MS Calculated for [C₂₅H₃₄N₅PCl]⁺ (**2c-Cl**⁺): m/z 470.2240. Found: 470.2255.

Preparation of [$\{C_6H_4(MeN)_2C\}_2CP(Ph)Cl$][X], [**2a-Cl**][X], X = Cl, SbF₆. The chloride salt of this compound was synthesized by adding benzene solution (200 mL) of **2** (0.50 g, 1.65 mmol) to 0.56 mL (4.12 mmol) of PhPCl₂. The reaction was stirred overnight followed by filtration. The resulting light-yellow solid was dried under vacuum to yield 0.77 g (97%) of [**2a-Cl**][Cl]. The most adequate counterion for crystallization of [**2a-Cl**]⁺ was [SbF₆], which was quantitatively exchanged with the chloride anion by adding 10 mg (0.04 mmol) of NaSbF₆ to a DCM solution (0.8 mL) of [**2a-Cl**][Cl] (20 mg, 0.04 mmol) followed by layering with n-hexane ([**2a-Cl**][SbF₆]).

¹H NMR (500 MHz, CDCl₃, 298 K): δ 3.64 (s, 12H, NCH₃), 7.16-7.53 (m, 13H). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K): δ 33.7 (d, ⁴J_{PC} = 8 Hz, NCH₃), 54.2 (d, ¹J_{PC} = 62 Hz, CCC), 111.6 (s, CH arom.), 125.7 (s, CH arom.), 128.7 (d, ³J_{PC} = 4 Hz, *m*-C, Ph), 129.8 (d, ²J_{PC} = 20 Hz, *o*-C, Ph), 131.7 (s, CH arom.), 132.7 (s, *p*-C, Ph), 136.2 (d, ¹J_{PC} = 28 Hz, *ipso*-C, Ph), 153.2 (d, ²J_{PC} = 18 Hz, NCN). ³¹P NMR (202 MHz, CD₂Cl₂, 298 K): δ 101.7 (s). HR-MS Calculated for [C₂₅H₂₅N₄PCl]⁺ (**2a-Cl**⁺): m/z 447.1526. Found: 447.1505.

Preparation of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{CP}(\text{tBu})\text{Cl}][\text{X}]$, **[2d-Cl][X]**, X = Cl, SbF₆. Benzene solution (200 mL) of **2** (0.50 g, 1.65 mmol) was transferred to a Schlenk flask containing 0.65 g (4.12 mmol) of ^tBuPCl₂. The reaction mixture was stirred overnight during which time a light yellow precipitate formed. The precipitate was isolated by filtration and subsequently dried *in vacuo* to yield 0.72 g (94%) of **[2d-Cl][Cl]**. The most adequate counterion for crystallization of **[2d-Cl]⁺** was [SbF₆], which was quantitatively exchanged with chloride anion by adding 11 mg (0.04 mmol) of NaSbF₆ to a DCM solution (0.8 mL) of **[2d-Cl][Cl]** (20 mg, 0.04 mmol) followed by layering with n-hexane (**[2d-Cl][SbF₆]**).

¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ 1.17 (d, ³J_{PH} = 14 Hz, 9H, ^tBu), 3.80 (br d, 12H, NCH₃), 7.48 (m, 4H, CH arom.), 7.63 (br s, 4H, CH arom.). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ 27.4 (d, ²J_{CP} = 18 Hz, CH₃ - ^tBu), 33.6 (br s, NCH₃), 37.5 (d, ¹J_{CP} = 29 Hz, C - ^tBu), 48.8 (d, ¹J_{CP} = 73 Hz, C_{CC}), 111.1 (s, CH arom.), 112.1 (s, CH arom.), 125.5 (s, CH arom.), 126.8 (s, CH arom.), 131.7 (s, CH arom.), 132.4 (s, CH arom.), 153.3 (d, ²J_{CP} = 2 Hz, N_{CC}N), 156.7 (d, ²J_{CP} = 45 Hz, N_{CC}N). ³¹P NMR (121 MHz, CD₂Cl₂, 298 K): δ 123.5 (br d). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K): δ 124.6 (s). HR-MS Calculated for [C₂₃H₂₉ClN₄P]⁺ (**2d-Cl⁺**): m/z 427.1818. Found: 427.1797.

Preparation of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{CP}(\text{OMe})\text{Cl}][\text{Cl}]$, **[2e-Cl][Cl]**. Benzene solution (200 mL) of **2** (0.50 g, 1.65 mmol) was transferred to a Schlenk flask with 0.4 mL (4.12 mmol) of MeOPCl₂. The resulting mixture was stirred overnight followed by filtration. Isolated orange solid was dried under vacuum to give 0.67 g (94 %) of **[2e-Cl][Cl]**.

¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 3.73 (d, ³J_{PH} = 15 Hz, 3H, OCH₃), 3.79 (s, 12H, NCH₃), 7.50-7.68 (m, 8H, CH arom.). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ 33.8 (s, NCH₃), 33.9 (s, NCH₃), 56.1 (d, ²J_{CP} = 20 Hz, OCH₃), 111.7 (s, CH arom.), 125.6 (s, CH arom.), 132.3 (s, CH arom.), 152.1 (d, ²J_{CP} = 20 Hz, N_{CC}N). ³¹P NMR (160 MHz, CD₂Cl₂, 298 K): δ 194.7 (br q, ³J_{PH} = 15 Hz). ³¹P{¹H} NMR (202 MHz, CD₃CN, 298 K): δ 200.0 (s). HR-MS Calculated for [C₂₀H₂₃ClN₄OP]⁺ (**2e-Cl⁺**): m/z 401.1298. Found: 401.1297.

Preparation of $[(\text{Ph}_3\text{P})_2\text{CPCl}_2][\text{AlCl}_4]$, **[1g-Cl][AlCl₄]**. The chloride salt of this compound was synthesized by adding toluene solution (80 mL) of (Ph₃P)₂C (**1**) (0.10 g,

0.19 mmol) to 88 mg (0.38 mmol) of MeN(PCl₂)₂ or 112 mg (0.38 mmol) PhN(PCl₂)₂. The reaction was stirred overnight followed by filtration. The resulting white solid was dissolved in 1,2-difluorobenzene and quantitative counterion conversion was achieved by adding 25 mg (0.19 mmol) of AlCl₃. Single crystals of [**1g-Cl**][AlCl₄] suitable for X-ray analysis were obtained by layering the above solution with n-hexane. Note: compound [**1g-Cl**][Cl] can also be prepared by reacting **1** with PCl₃.

¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ 7.19-7.72 (m, 30H, Ph). ¹³C{¹H} (100 MHz, CD₂Cl₂, 298 K): δ 124.0 (br, m, *ipso*-C, Ph_(carbonyl)), 129.9 (virtual triplet, *o*-C, Ph_(carbonyl)), 133.6 (s, *p*-C, Ph_(carbonyl)), 134.3 (virtual triplet, *m*-C, Ph_(carbonyl)). ³¹P{¹H} (121 MHz, CD₂Cl₂, 298 K): δ 23.85 (d, P_(carbonyl)), 173.53 (t, P_(central)). ²⁷Al{¹H} (104 MHz, CD₂Cl₂, 298 K): δ 107.05 (s).

Preparation of [**2g-Cl**][X], [**2g-Cl**][X], X = Cl, SbF₆ or BAr^{Cl}₄. The chloride salt of this compound was synthesized by adding benzene solution (100 mL) of **2** (0.10 g, 0.33 mmol) to 153 mg (0.66 mmol) of MeN(PCl₂)₂. The reaction was stirred overnight followed by filtration. The resulting light yellow solid was dried under vacuum to yield 0.14 g (98%) of [**2g-Cl**][Cl]. The most adequate counterion for crystallization of [**2g-Cl**]⁺ was [SbF₆], which was quantitatively exchanged with the chloride anion by introducing 12 mg (0.04 mmol) of NaSbF₆ to a DCM solution (0.8 mL) of [**2g-Cl**][Cl] (20 mg, 0.04 mmol) followed by layering with n-hexane ([**2g-Cl**][SbF₆]). Note: [**2g-Cl**][Cl] can also be prepared by reacting **2** with PCl₃.

³¹P{¹H} (CD₂Cl₂, 160 MHz, 298 K): δ 160.0 (s). HR-MS Calculated for [C₁₉H₂₀Cl₂N₄P]⁺ (**2g-Cl**⁺): m/z 405.0803. Found: 405.0804. Due to surprisingly low solubility of [**2g-Cl**][X] (X = Cl and SbF₆) in common organic solvents (C₆D₆, CD₂Cl₂, CD₃CN,) we have quantitatively converted [**2g-Cl**][Cl] to [**2g-Cl**][BAr^{Cl}₄]. This conversion was achieved by adding 70 mg (0.11 mmol) of Na[BAr^{Cl}₄] to the THF solution (10 mL) of [**2g-Cl**][Cl] (50 mg, 0.11 mmol) followed by precipitation with n-pentane, and subsequent filtration and removal of all volatiles to get [**2g-Cl**][BAr^{Cl}₄] as a yellow solid. ¹H NMR (400 MHz, CD₂Cl₂, 298K): δ 3.68 (s, 12H, NCH₃), 6.80-6.94 (m, 12H, BAr^{Cl}₄), 7.38-7.52 (m, 8H, CH arom.). ¹³C{¹H} (100 MHz, CD₂Cl₂, 298K): δ 32.8 (s, NCH₃), 111.8 (s, CH arom.), 122.9 (s, *p*-C, BAr^{Cl}₄), 127.3 (br s, CH arom.), 132.0 (s, *m*-C, BAr^{Cl}₄), 132.9 (q, ²J_{CB} = 4

Hz, *o*-C, BAr^{Cl}₄), 164.7 (q, ¹J_{CB} = 49 Hz, *ipso*-C, BAr^{Cl}₄). Signals corresponding to the NCN and CCC resonances were not observed in the ¹³C{¹H} Spectrum.

Preparation of [$\{C_6H_4(MeN)_2C\}_2C^+PBr_2][Br]$, [**2f-Br**][Br]. Benzene solution (200 mL) of **2** (0.50 g, 1.64 mmol) was added to 0.39 mL (4.1 mmol) of PBr₃. The reaction mixture was stirred overnight followed by filtration. The resulting orange solid was dried under vacuum to yield 0.87 g (92 %) of [**2f-Br**][Br]. The crystallization of [**2f-Br**][Br] was achieved by layering the saturated acetonitrile solution of this compound with diethyl ether.

¹H NMR (500 MHz, CD₃CN, 298 K): δ 3.83 (d, ⁵J_{PH} = 2 Hz, 12H, NCH₃), 7.59-7.73 (m, 8H). ¹³C{¹H} NMR (100 MHz, CD₃CN, 298 K): δ 33.6 (d, ⁴J_{PC} = 8 Hz, NCH₃), 56.5 (d, ¹J_{PC} = 89 Hz, CCC), 112.4 (s, CH arom.), 126.0 (s, CH arom.), 132.3 (s, CH arom.), 150.8 (d, ²J_{PC} = 23 Hz, NCN). ³¹P NMR (CD₃CN, 202 MHz, 298 K): δ 163.79 (s). HR-MS Calculated for [C₁₉H₂₀⁷⁹Br⁸¹BrN₄P]⁺ (**2f-Br**⁺): m/z 494.9772. Found: 494.9787.

Preparation of [$\{C_6H_4(MeN)_2C\}_2C^+PN^iPr_2][BAr^{Cl}_4]_2$, [**2c**][BAr^{Cl}₄]₂. [**2c-Cl**][Cl] (100 mg, 0.19 mmol) and Na[BAr^{Cl}₄] (256 mg, 0.40 mmol) were weighed inside a glove box (Schlenk flask) followed by addition of DCM (20 mL). The reaction mixture was stirred for 10 min and then filtered to remove NaCl. DCM was subsequently removed leaving an orange solid, which was dried *in vacuo* to give 200 mg (63%) of [**2c**][BAr^{Cl}₄]₂.

¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ 1.03 (d, 6H, ³J_{HH} = 6 Hz, CH₃ - ⁱPr), 1.59 (d, ³J_{HH} = 6 Hz, 6H, CH₃ - ⁱPr), 3.17 (br m, 1H, CH - ⁱPr), 3.55 (s, 6H, NCH₃), 3.63 (s, 6H, NCH₃), 4.05 (br m, 1H, CH - ⁱPr), 6.94 (m, 8H, *p*-H, BAr^{Cl}₄), 7.07 (m, 16H, *o*-H, BAr^{Cl}₄), 7.41 (m, 2H), 7.50 (m, 2H), 7.73 (m, 4H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ 21.6 (s, CH₃ - ⁱPr), 28.3 (d, ³J_{CP} = 12 Hz, CH₃ - ⁱPr), 33.4 (d, ⁴J_{CP} = 6 Hz, NCH₃), 33.5 (s, NCH₃), 51.4 (s, CH - ⁱPr), 61.1 (d, ²J_{CP} = 14 Hz, CH - ⁱPr), 85.6 (d, ¹J_{CP} = 65 Hz, CCC), 112.7 (s, CH arom.), 112.9 (s, CH arom.), 123.2 (s, *p*-C, BAr^{Cl}₄), 129.5 (s, CH arom.), 130.1 (s, CH arom.), 131.1 (s, CH arom.), 132.0 (s, CH arom.), 133.1 (m, *o*-C, *m*-C, BAr^{Cl}₄), 144.6 (s, NCN), 145.7 (d, ²J_{CP} = 37 Hz, NCN), 164.7 (q, ¹J_{CB} = 49 Hz, *ipso*-C, BAr^{Cl}₄). ³¹P NMR (CD₂Cl₂, 160 MHz, 298 K): δ 327.7 (s). HR-MS Calculated for [C₂₅H₃₄N₅P]²⁺ (**2c**²⁺): m/z 217.6271. Found: 217.6272.

Preparation of $[\{C_6H_4(MeN)_2C\}_2C^+PPh][X]_2$, $[2a][X]_2$, $[X] = [AlCl_4]$, $[SbF_6]$, and $[BAr^{Cl}_4]$. The 1H , $^{13}C\{^1H\}$, and ^{31}P NMR spectra of this compound were identical irrespective of the nature of counterion, and therefore, we only report multinuclear NMR data for $[2a][AlCl_4]_2$ as spectroscopic NMR details for $[SbF_6]$ and $[BAr^{Cl}_4]$ anions can be found in numerous published reports. $AlCl_3$ (11 mg, 0.08 mmol) was added to CD_2Cl_2 solution (0.7 mL) of $[2a-Cl][Cl]$ (20 mg, 0.04 mmol) to form the dication $[2a][AlCl_4]_2$ (J. Young NMR tube). The solvent was removed and the resulting orange solid was dried *in vacuo*. Yield: 22 mg (73%). Single crystals of $[2a][BAr^{Cl}_4]_2$ were obtained in a separate procedure: $Na[BAr^{Cl}_4]$ (21 mg, 0.03 mmol) was added to 1,2-difluorobenzene solution (0.7 mL) of $[2a-Cl][BAr^{Cl}_4]$ (35 mg, 0.03 mmol); the resulting solution was filtered (NaCl removal) and layered with n-hexane ($[2a][BAr^{Cl}_4]_2$).

1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ 3.71 (s, 6H, NCH_3), 4.11 (s, 6H, NCH_3), 7.38 (br t, $^3J_{HH} = 9$ Hz, 2H, *o*-H, Ph), 7.45 (t, $^3J_{HH} = 10$ Hz, 2H, *m*-H, Ph), 7.68 (t, $^3J_{HH} = 10$ Hz, 1H, *p*-H, Ph), 7.75-7.84 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2 , 298 K): δ 34.5 (s, NCH_3), 35.3 (d, $^4J_{PC} = 5$ Hz, NCH_3), 114.1 (d, $^4J_{CP} = 5$ Hz, CH arom.), 129.2 (d, $^1J_{PC} = 65$ Hz, CCC), 129.9 (s, CH arom.), 130.1 (s, CH arom.), 131.0 (d, $^3J_{CP} = 6$ Hz, *m*-C, Ph), 132.0 (s, CH arom.), 132.9 (d, $^2J_{CP} = 18$ Hz, *o*-C, Ph), 133.2 (s, *p*-C, Ph), 136.7 (s, CH arom.), 138.2 (d, $^1J_{CP} = 54$ Hz, *ipso*-C, Ph), 143.6 (d, $^4J_{CP} = 8$ Hz, CH arom.), 145.3 (d, $^2J_{PC} = 26$ Hz, NCN). ^{31}P NMR (CD_2Cl_2 , 202 MHz, 298 K): δ 393.4 (s). HR-MS Calculated for $[C_{25}H_{25}N_4P]^{2+}$ ($2a^{2+}$): m/z 206.0903. Found: 206.0903.

Preparation of $[\{C_6H_4(MeN)_2C\}_2C^+P^tBu][AlCl_4]_2$, $[2d][AlCl_4]_2$. $AlCl_3$ (14 mg, 0.10 mmol) was added to CD_2Cl_2 solution (0.7 mL) of $[2d-Cl][Cl]$ (25 mg, 0.05 mmol) to give the target $[2d][AlCl_4]_2$ (J. Young NMR tube). This compound was found to be very reactive in solution at various temperatures. Therefore, multinuclear NMR data were recorded using the sample of $[2d][AlCl_4]_2$ formed *in situ*.

1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ 1.36 (d, $^3J_{PH} = 12$ Hz, 9H, tBu), 4.11 (s, 6H, NCH_3), 4.14 (s, 6H, NCH_3), 7.85 (m, 4H, CH arom.), 7.89 (br s, 4H, CH arom.). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2 , 298 K): δ 27.8 (d, $^2J_{CP} = 10$ Hz, $CH_3 - ^tBu$), 34.6 (d, $^4J_{CP} = 5$ Hz, NCH_3), 34.8 (s, NCH_3), 46.6 (d, $^1J_{CP} = 62$ Hz, C - tBu), 113.6 (s, CH arom.), 113.8 (s,

CH arom.), 129.3 (s, CH arom.), 129.8 (s, CH arom.), 131.6 (s, CH arom.), 132.6 (s, CH arom.), 141.9 (s, NCN), 144.0 (d, $^2J_{\text{CP}} = 24$ Hz, NCN). Signal corresponding to the CCC resonance was not observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum. ^{31}P NMR (202 MHz, CD_2Cl_2 , 298 K): δ 474.2 (br s). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): δ 473.8 (s). HR-MS Calculated for $[\text{C}_{23}\text{H}_{29}\text{N}_4\text{P}]^{2+}$ (**2d**⁺): m/z 196.1086. Found: 196.1086.

Preparation of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{POMe}][\text{AlCl}_4]_2$, **[2e]** $[\text{AlCl}_4]_2$. AlCl_3 (15 mg, 0.11 mmol) was added to CD_2Cl_2 solution (0.7 mL) of **[2e-Cl]** $[\text{Cl}]$ (25 mg, 0.06 mmol) to give the target dication **[2e]** $[\text{AlCl}_4]_2$ (J. Young NMR tube). Based on the multinuclear NMR data, this compound was very reactive in solution, which prevented its complete characterization. In fact, based on ^{31}P NMR a very complicated mixture of **[2e]**²⁺, MeOPCl_2 , and $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{PCl}]^{2+}$, **[2g]**²⁺ among other present species, was formed. We were quite fortunate that few single crystals suitable for x-ray diffraction formed after slow evaporation from saturated DCM solution. Surprisingly, these crystals were composed of **[2e]** $[\text{AlCl}_4]_2$ and **[2g]** $[\text{AlCl}_4]_2$ in 93:7 respective ratio.

^{31}P NMR (202 MHz, CD_2Cl_2 , 298 K): δ 373.4 (br s). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): δ 372.4 (s). HR-MS Calculated for $[\text{C}_{20}\text{H}_{23}\text{N}_4\text{OP}]^{2+}$ (**2e**²⁺): m/z 183.0799. Numerous attempts to detect this species via ESI-MS were unsuccessful.

Preparation of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{PCl}][\text{AlCl}_4]_2$, **[2g]** $[\text{AlCl}_4]_2$. AlCl_3 (23mg, 0.17 mmol) was added to CD_2Cl_2 solution (0.7 mL) of **[2g-Cl]** $[\text{Cl}]$ (25 mg, 0.06 mmol). Upon mixing, the thick red oil formed. Reaction mixture was investigated by $^{31}\text{P}/^{31}\text{P}\{^1\text{H}\}$ NMR Spectroscopy. Even though, the target dication $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{PCl}][\text{AlCl}_4]_2$, **[2g]** $[\text{AlCl}_4]_2$ was the major constituent, all attempts to isolate this species by fractional precipitation and/or crystallization were unsuccessful.

^{31}P NMR (202 MHz, CD_2Cl_2 , 298 K): δ 361.6 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): δ 361.6 (s). HR-MS Calculated for $[\text{C}_{19}\text{H}_{20}\text{ClN}_4\text{P}]^{2+}$ (**2g**²⁺): m/z 185.0552. All attempts to detect this compound via ESI-MS failed.

Preparation of $[\{\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\}_2\text{P}][\text{SbF}_6]_2[\text{Br}]$, **[(2)₂P]** $[\text{SbF}_6]_2[\text{Br}]$. The formation of **[(2)₂P]** $[\text{SbF}_6]_2[\text{Br}]$ was observed upon addition of 1 or 2 molar equivalents of AgSbF_6

to the acetonitrile solution of **[2f-Br][Br]** as shown by the copies of the ^{31}P NMR spectra (Figures 3.13) recorded right after the addition of the silver salt. A small crop of crystals suitable for single crystal X-ray diffraction were obtained using the former solution as describe below. However, the title compound could not be isolated in its pure form even though numerous attempts (re-crystallization, precipitation etc.) have been made. It appears that the trication is extremely unstable in solution resulting in the formation of a substantial amount of “di-protonated” ligand even though the only P-containing species soluble in this reaction mixture is the trication. In fact, during the data collection for the ^{13}C NMR spectrum (overnight collection) it was noticed that the solution changed color from the usual red to orange suggesting the decomposition of the trication and the only δ_{C} signals that could be resolved belonged to deprotonated carbodicarbene. Lastly, as both preparatory methods differ only in the amount of the silver salt added we described only the former one.

- *Synthesis of **[(2)₂P][SbF₆]₂[Br]** using 1 molar equivalent of AgSbF₆.* CD₃CN (0.7 mL) was added to **[2f-Br][Br]** (15 mg, 0.026 mmol) and AgSbF₆ (9 mg, 0.026 mmol) (J. Young NMR tube). Immediately upon addition, the solution changed color from orange to red. The white precipitate (AgBr) was filtered-off and the resulting red solution was layered with diethyl ether. Few crystals of **[(2)₂P][SbF₆]₂[Br]** suitable for X-ray analysis were formed at room temperature after 3 days.

^1H NMR (400 MHz, CD₃CN, 298 K): δ 3.69 (s, 24H, NCH₃), 7.73-7.86 (m, 16H). ^{31}P NMR (CD₃CN, 202 MHz, 298 K): δ 302.18 (s). HR-MS: numerous attempts to detect **[(2)₂P]³⁺** were not successful.

Preparation of **[(C₆H₄(MeN)₂C)₂C=P{(CH₂CCH₃)₂}Ph][AlCl₄]₂, **[2a-h][AlCl₄]₂.** AlCl₃ (11 mg, 0.08 mmol) was added to CD₂Cl₂ solution (0.7 mL) of **[2a-Cl][Cl]** (20 mg, 0.04 mmol) followed by 2,3-dimethyl-1,3-butadiene (5 μL , 0.04 mmol) (J. Young NMR tube). The solvent was removed and the resulting beige precipitate was dried *in vacuo* to afford 25 mg (77 %) of **[2a-h][AlCl₄]₂**. Single crystals suitable for X-Ray analysis were obtained upon layering the saturated DCM solution of **[2a-h][AlCl₄]₂** with n-hexane.**

^1H NMR (500 MHz, CD₂Cl₂, 298 K): δ 1.85 (s, 6H, CCH₃), 3.53 (br m, 4H, CH₂), 3.79 (s, 12H, NCH₃), 7.64 (m, 13H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD₂Cl₂, 298 K): δ 15.9 (s, CCH₃),

16.1 (s, CCH₃), 23.0 (d, ¹J_{CP} = 115 Hz, CCC), 34.2 (s, NCH₃), 39.0 (d, ¹J_{CP} = 56 Hz, CH₂), 112.6 (s, CH arom.), 127.6 (s, CH arom.), 128.9 (s, *p*-C, Ph), 130.9 (d, ²J_{CP} = 10 Hz, *o*-C, Ph), 131.4 (d, ³J_{CP} = 8 Hz, *m*-C, Ph), 131.7 (s, CH arom.), 135.8 (br s, *ipso*-C, Ph), 149.3 (d, ²J_{CP} = 10 Hz, NCN). ³¹P NMR (CD₂Cl₂, 202 MHz, 298 K): δ 30.7 (s). ³¹P{¹H} NMR (CD₂Cl₂, 202 MHz, 298 K): δ 31.1 (s). HR-MS Calculated for [C₃₁H₃₅N₄P]²⁺ (**2a-h**²⁺): m/z 247.1294. Found: 247.1295.

Preparation of [(ⁱPr₂N)₂P][BAr^{Cl}₄], [3**][BAr^{Cl}₄].** Na[BAr^{Cl}₄] (38 mg, 0.06 mmol) was added to CD₂Cl₂ (0.5 mL) solution of (ⁱPr₂N)₂PCl (15 mg, 0.06 mmol) to give [(ⁱPr₂N)₂P][BAr^{Cl}₄], [**3**][BAr^{Cl}₄] (J. Young NMR tube), which was used in subsequent reactions. Single crystals suitable for X-ray diffraction were grown by slow evaporation from saturated 1,2-difluorobenzene solution of [**3**][BAr^{Cl}₄].

¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ 1.44 (d, ³J_{HH} = 7 Hz, 24H, CH₃ - ⁱPr), 4.13 (m, 4H, CH - ⁱPr), 7.04 (m, 12H, BAr^{Cl}₄). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, 298 K): δ 19.5 (s, CH₃ - ⁱPr), 24.8 (d, ²J_{CP} = 8 Hz, CH - ⁱPr), 123.1 (s, *p*-C, BAr^{Cl}₄), 132.9 (q, ²J_{CB} = 4 Hz, *o*-C, BAr^{Cl}₄), 133.1 (s, *m*-C, BAr^{Cl}₄), 164.7 (q, ¹J_{CB} = 49 Hz, *ipso*-C, BAr^{Cl}₄). ³¹P NMR (160 MHz, CD₂Cl₂, 298 K): δ 300.3 (s). HR-MS Calculated for [C₁₂H₂₈N₂P]⁺ (**3**⁺): m/z 231.1985. Found: 231.1992.

Reactions of [2c][BAr^{Cl}₄]₂ with tertiary (Et₃SiH, Ph₃SiH), secondary (Ph₂SiH₂), and primary (PhSiH₃) silanes – general procedure. Na[BAr^{Cl}₄] (51 mg, 0.08 mmol) was added to CD₂Cl₂ (0.7 mL) solution of [2c-Cl][Cl] (20 mg, 0.04 mmol) (J. Young NMR tube) to form the dication [2c][BAr^{Cl}₄]₂. Subsequently, the corresponding silane [Et₃SiH: 7 μL (0.04 mmol); Ph₃SiH: 11 mg (0.04 mmol); Ph₂SiH₂: 8 μL (0.04 mmol); PhSiH₃: 5 μL (0.04 mmol)] was added and the reaction mixture was investigated by ³¹P/³¹P{¹H} NMR spectroscopy and ESI-MS. In all instances, we observed the formation of [{C₆H₄(MeN)₂C}₂C·P(H)NⁱPr₂]⁺, [2c-H]⁺ whose identity was confirmed in a separate procedure using ⁿBu₃SnH as a hydride source.

Reaction of [2c][BAr^{Cl}₄]₂ with ⁿBu₃SnH. Na[BAr^{Cl}₄] (51 mg, 0.08 mmol) was added to CD₂Cl₂ solution (0.7 mL) of [2c-Cl][Cl] (20 mg, 0.04 mmol) (J. Young NMR tube),

followed by addition of $^n\text{Bu}_3\text{SnH}$ (11 μL , 0.04 mmol). The resulting mixture was analyzed by $^{31}\text{P}/^{31}\text{P}\{^1\text{H}\}$ NMR Spectroscopy and ESI-MS. $[\mathbf{2c-H}][\text{BAr}^{\text{Cl}}_4]$ was the major reaction product, whose high reactivity in solution prevented our isolation attempts.

$[\mathbf{2c-H}][\text{BAr}^{\text{Cl}}_4]$: ^{31}P NMR (202 MHz, CD_2Cl_2 , 298 K): δ -12.3 (br d, $^1J_{\text{PH}} = 225$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): δ -12.3 (br s). HR-MS Calculated for $[\text{C}_{25}\text{H}_{35}\text{N}_5\text{P}]^+$ ($\mathbf{2c-H}^+$): m/z 436.2630. Found: 436.2632.

Reactions of $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ with tertiary (Et_3SiH , Ph_3SiH), secondary (Ph_2SiH_2), and primary (PhSiH_3) silanes – general procedure. $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ (52 mg, 0.08 mmol) was added to CD_2Cl_2 (0.7 mL) solution of $[\mathbf{2a-Cl}][\text{Cl}]$ (20 mg, 0.04 mmol) to form the dication $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ (J. Young NMR tube). Then, the corresponding silane [Et_3SiH : 7 μL (0.04 mmol); Ph_3SiH : 11 mg (0.04 mmol); Ph_2SiH_2 : 8 μL (0.04 mmol); PhSiH_3 : 5 μL (0.04 mmol)] was added and the resulting mixture was investigated by $^{31}\text{P}/^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and ESI-MS. In all instances, a single reaction product $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\cdot\text{P}(\text{H})\text{Ph}][\text{BAr}^{\text{Cl}}_4]$, $[\mathbf{2a-H}][\text{BAr}^{\text{Cl}}_4]$ was observed.

Preparation of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\cdot\text{P}(\text{H})\text{Ph}][\text{X}]$, $[\mathbf{2a-H}][\text{X}]$, $\text{X} = \text{AlCl}_4$ and BAr^{Cl}_4 . 1,2-difluorobenzene (35 mL) was added to a Schlenk flask containing $[\mathbf{2a-Cl}][\text{Cl}]$ (100 mg, 0.21 mmol) and $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ (268 mg, 0.43 mmol). The reaction mixture was stirred for 10 min followed by addition of $^n\text{Bu}_3\text{SnH}$ (57 μL , 0.21 mmol). After 2 hours of stirring at ambient temperature, NaCl was filtered off. The resulting solution was treated with n-hexane (100 mL) to afford the formation of $[\mathbf{2a-H}][\text{BAr}^{\text{Cl}}_4]$ as a light yellow precipitate, which was isolated by filtration and subsequently dried under vacuum. Yield: 78 mg (37 %). $[\text{AlCl}_4]$ appeared to be the most suitable anion for crystallization of $[\mathbf{2a-H}]^+$. This anion was introduced in a separate experimental procedure: $[\mathbf{2a-Cl}][\text{Cl}]$ (20 mg, 0.04 mmol) and AlCl_3 (11 mg, 0.08 mmol) were dissolved in 1,2-difluorobenzene (0.7 mL) (J. Young NMR tube) to form the dication $[\mathbf{2a}][\text{AlCl}_4]_2$, which was then treated with $^n\text{Bu}_3\text{SnH}$ (11 μL , 0.04 mmol). The resulting solution was layered with n-hexane to afford single crystals of $[\mathbf{2a-H}][\text{AlCl}_4]$.

^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ 3.53 (s, 12H, NCH_3), 5.59 (d, 1H, $^1J_{\text{PH}} = 226$ Hz), 6.94 (br s, 4H, $p\text{-H}$, BAr^{Cl}_4), 7.05-7.44 (m, 21H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298

K): δ 33.1 (d, $^4J_{\text{CP}} = 6$ Hz, NCH_3), 42.6 (d, $^1J_{\text{CP}} = 23$ Hz, $\text{C}\equiv\text{C}$), 110.5 (s, CH arom.), 123.0 (s, *p*-C, BAr^{Cl}_4), 125.4 (s, CH arom.), 128.3 (s, *p*-C, Ph), 129.1 (d, $^3J_{\text{PC}} = 5$ Hz, *m*-C, Ph), 129.8 (d, $^2J_{\text{PC}} = 15$ Hz, *o*-C, Ph), 132.1 (s, CH arom.), 132.9 (q, $^2J_{\text{CB}} = 4$ Hz, *o*-C, BAr^{Cl}_4), 133.1 (s, *m*-C, BAr^{Cl}_4), 135.7 (d, $^1J_{\text{PC}} = 6$ Hz, *ipso*-C, Ph), 155.5 (d, $^2J_{\text{PC}} = 17$ Hz, $\text{N}\equiv\text{N}$), 164.7 (q, $^1J_{\text{CB}} = 49$ Hz, *ipso*-C, BAr^{Cl}_4). ^{31}P NMR (202 MHz, CD_2Cl_2 , 298 K): δ -52.7 (d, $^1J_{\text{PH}} = 226$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): δ -52.7 (s). HR-MS Calculated for $[\text{C}_{25}\text{H}_{26}\text{N}_4\text{P}]^+$ (**2a-H**⁺): m/z 413.1890. Found: 413.1892.

Figure 5.4. ^1H NMR spectrum of **[2a-H][BAr^{Cl}₄]**.

Figure 5.5. ^{31}P NMR spectrum of $[\mathbf{2a-H}][\text{BAr}^{\text{Cl}}_4]$.

Figure 5.6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{2a-H}][\text{BAr}^{\text{Cl}}_4]$.

Preparation of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{PH}_2][\text{X}]$, $[\mathbf{2}^+\text{PH}_2][\text{X}]$, $\text{X} = \text{AlCl}_4$, BAr^{Cl}_4 . This species was synthesized using $[\mathbf{2f-Br}][\text{Br}]$ as a starting material. CD_2Cl_2 (0.7 mL) was added to

[**2f-Br**][Br] (22 mg, 0.04 mmol) and Na[BAr^{Cl}₄] (47 mg, 0.08 mmol) followed by addition of ⁿBu₃SnH (21 μ L, 0.08 mmol) (J. Young NMR tube). Thus formed [**2·PH₂**][BAr^{Cl}₄] was used for multinuclear NMR analyses. [AlCl₄] appeared to be the most suitable anion for crystallization of [**2·PH₂**]⁺. This anion was introduced in a separate procedure: [**2f-Br**][Br] (22 mg, 0.04 mmol) and AlCl₃ (10 mg, 0.08 mmol) were dissolved in 1,2-difluorobenzene (0.8 mL) followed by addition of ⁿBu₃SnH (21 μ L, 0.08 mmol) to give [**2·PH₂**][AlCl₄]. Crystals suitable for single X-ray diffraction were grown by layering the saturated 1,2-difluorobenzene solution of [**2·PH₂**][AlCl₄] with n-hexane.

¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ 3.51 (s, 12H, NCH₃), 4.15 (d, 2H, ¹J_{PH} = 212 Hz), 6.91 (br s, *p*-H, BAr^{Cl}₄), 7.04 (br s, *o*-H, BAr^{Cl}₄), 7.34 (m, 4H), 7.44 (m, 4H). ³¹P NMR (121 MHz, CD₂Cl₂, 298 K): δ -133.1 (t, ¹J_{PH} = 212 Hz). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K): δ -134.1 (s). HR-MS Calculated for [C₁₉H₂₂N₄P]⁺ (**2·PH₂**⁺): *m/z* 337.1582. Found: 337.1583. Note: multiple attempts to isolate this species by means of fractional precipitation were unsuccessful, presumably due to the similar solubility of all present species induced by the non-coordinating anion – [BAr^{Cl}₄]. Crystals of [**2·PH₂**][AlCl₄] were not soluble in common organic solvents.

Figure 5.7. ³¹P NMR spectrum of [**2·PH₂**][BAr^{Cl}₄].

Figure 5.8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{2}\cdot\text{PH}_2][\text{BAr}^{\text{Cl}}_4]$.

Preparation of $[(^i\text{Pr}_2\text{N})_2\text{P}(\text{H})(\text{BH}_2\text{Py})][\text{BAr}^{\text{Cl}}_4]$, $[\mathbf{3-i}][\text{BAr}^{\text{Cl}}_4]$. $(^i\text{Pr}_2\text{N})_2\text{PCl}$ (75 mg, 0.28 mmol) and $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ (174 mg, 0.28 mmol) were placed to a Schlenk flask followed by addition of 1,2-difluorobenzene (35 ml). The resulting mixture was stirred for 5 minutes at room temperature after which PyBH_3 (30 μL , 0.28 mmol) was added. After 2 hours of stirring, NaCl was filtered-off and subsequent addition of n-hexane (80 mL) led to the precipitation of $[\mathbf{3-i}][\text{BAr}^{\text{Cl}}_4]$ as a white solid that was dried *in vacuo*. Yield: 104 mg (40%). Single crystals suitable for X-ray analysis were obtained by layering the DCM solution of $[\mathbf{3-i}][\text{BAr}^{\text{Cl}}_4]$ with n-hexane.

^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ 0.99 (d, $^3J_{\text{HH}} = 7$ Hz, 12H, $\text{CH}_3 - ^i\text{Pr}$), 1.26 (d, $^3J_{\text{HH}} = 7$ Hz, 12H, $\text{CH}_3 - ^i\text{Pr}$), 3.22 (br d, 2H, $\text{BH}_2\text{-Py}$), 3.49 (sept, $^3J_{\text{HH}} = 7$ Hz, 4H, $\text{CH} - ^i\text{Pr}$), 7.02 (m, 12H, BAr^{Cl}_4), 7.06 (dt, $^1J_{\text{PH}} = 432$ Hz and $^3J_{\text{HH}} = 2$ Hz, 1H, PH), 7.68 (t, $^3J_{\text{HH}} = 7$ Hz, 2H, *m*-H, Py), 8.13 (dd, $^3J_{\text{HH}} = 7$ Hz and $^5J_{\text{HH}} = 1$ Hz, 1H, *p*-H, Py), 8.40 (d, $^3J_{\text{HH}} = 6$ Hz, 2H, *o*-H, Py). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K): δ 22.8 (d, $^3J_{\text{CP}} = 2$ Hz, $\text{CH}_3 - ^i\text{Pr}$), 22.9 (d, $^3J_{\text{CP}} = 2$ Hz, $\text{CH}_3 - ^i\text{Pr}$), 48.1 (d, $^2J_{\text{CP}} = 4$ Hz, $\text{CH} - ^i\text{Pr}$), 123.0 (s, *p*-C, BAr^{Cl}_4), 127.6 (s, *p*-C, Py), 132.9 (q, $^2J_{\text{CB}} = 4$ Hz, *o*-C, BAr^{Cl}_4), 133.1 (s, *m*-C, BAr^{Cl}_4),

143.3 (d, $^4J_{CP} = 2$ Hz, *m*-C, Py), 147.4 (d, $^3J_{CP} = 7$ Hz, *o*-C, Py), 164.7 (q, $^1J_{CB} = 49$ Hz, *ipso*-C, BAr^{Cl}₄). ^{11}B (128 MHz, CD₂Cl₂, 298K): δ - 7.1 (s, BAr^{Cl}₄), - 13.5 (br dd). $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, CD₂Cl₂, 298K): δ - 7.1 (s, BAr^{Cl}₄), - 13.4 (br d). ^{31}P NMR (160 MHz, CD₂Cl₂, 298 K): δ 20.4 (br dd). $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, CD₂Cl₂, 298 K): δ 20.3 (br d). HR-MS Calculated for [C₁₇H₃₆BN₃P]⁺ (**3-i**⁺): *m/z* 324.2740. Found: 324.2741.

Preparation of [(ⁱPr₂N)₂P(H)(BH₂NMe₃)] [BAr^{Cl}₄], [**3-j**] [BAr^{Cl}₄]. 1,2-difluorobenzene (35 mL) was added to a Schlenk flask with (ⁱPr₂N)₂PCl (75 mg, 0.28 mmol) and Na[BAr^{Cl}₄] (174 mg, 0.28 mmol) followed by addition of Me₃NBH₃ (21 mg, 0.28 mmol). The reaction was stirred for additional 2 hours followed by filtration to remove NaCl. Subsequent addition of 80 mL of n-hexane led to the precipitation of a white solid that was dried *in vacuo* to yield 124 mg (49%) of [**3-j**] [BAr^{Cl}₄]. The crystallization was performed by layering the DCM solution of [**3-j**] [BAr^{Cl}₄] with n-hexane.

^1H NMR (300 MHz, CD₂Cl₂, 298 K): δ 1.24 (d, $^3J_{\text{HH}} = 7$ Hz, 12H, CH₃ - ⁱPr), 1.30 (d, $^3J_{\text{HH}} = 7$ Hz, 12H, CH₃ - ⁱPr), 2.40 (dd or br q, 2H, BH₂-Py), 3.60 (sept, $^3J_{\text{HH}} = 7$ Hz, 4H, CH - ⁱPr), 6.96 (dt, $^1J_{\text{PH}} = 432$ Hz and $^3J_{\text{HH}} = 2$ Hz, 1H, PH), 7.03 (m, 12H, BAr^{Cl}₄). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD₂Cl₂, 298 K): δ 22.9 (d, $^3J_{CP} = 4$ Hz, CH₃ - ⁱPr), 23.5 (d, $^3J_{CP} = 3$ Hz, CH₃ - ⁱPr), 49.0 (d, $^2J_{CP} = 3$ Hz, CH - ⁱPr), 54.4 (d, $^3J_{CP} = 8$ Hz, NMe₃), 123.0 (s, *p*-C, BAr^{Cl}₄), 132.9 (q, $^2J_{CB} = 4$ Hz, *o*-C, BAr^{Cl}₄), 133.1 (s, *m*-C, BAr^{Cl}₄), 164.7 (q, $^1J_{CB} = 49$ Hz, *ipso*-C, BAr^{Cl}₄). ^{11}B (96 MHz, CD₂Cl₂, 298K): δ - 7.3 (s, BAr^{Cl}₄), - 10.4 (br q). $^{11}\text{B}\{^1\text{H}\}$ (96 MHz, CD₂Cl₂, 298K): δ - 7.3 (s, BAr^{Cl}₄), -10.4 (br d). ^{31}P NMR (121 MHz, CD₂Cl₂, 298 K): δ 15.6 (br dd). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD₂Cl₂, 298 K): δ 16.1 (br d). HR-MS Calculated for [C₁₅H₄₀BN₃P]⁺ (**3-j**⁺): *m/z* 304.3053. Found: 304.3051.

Figure 5.9. ¹H NMR spectrum of [3-j][BArCl₄].

Figure 5.10. ³¹P NMR spectrum of [3-j][BArCl₄].

Figure 5.11. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{3-j}][\text{BAr}^{\text{Cl}}_4]$.

Reaction of $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$ with PyBH_3 . $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ (50 mg, 0.08 mmol) was added to a CD_2Cl_2 (0.7 mL) solution of $[\mathbf{2c-Cl}][\text{Cl}]$ (20 mg, 0.04 mmol) (J. Young NMR tube) to give the dication $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$. Next, PyBH_3 (4 μL , 0.04 mmol) was added and the resulting mixture was investigated by $^{31}\text{P}/^{31}\text{P}\{^1\text{H}\}$ NMR Spectroscopy and ESI-MS. Both $[\mathbf{2c-H}]^+$ and $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}(\text{P}(\text{H})(\text{BH}_2\text{Py})\text{N}^i\text{Pr}_2)][\text{BAr}^{\text{Cl}}_4]_2$, $[\mathbf{2c-i}][\text{BAr}^{\text{Cl}}_4]_2$ reaction products were observed. Unfortunately, all attempts to isolate the later compound by means of fractional precipitation were unsuccessful presumably due to the similar solubility of all present species imparted by the non-coordinating $[\text{BAr}^{\text{Cl}}_4]$ anion.

$[\mathbf{2c-i}][\text{BAr}^{\text{Cl}}_4]_2$: ^{31}P NMR (121 MHz, CD_2Cl_2 , 298 K): δ -1.8 (br d, $^1J_{\text{PH}} = 423$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2 , 298 K): δ -1.8 (s). HR-MS Calculated for $[\text{C}_{30}\text{H}_{42}\text{BN}_6\text{P}]^{2+}$ ($\mathbf{2c-i}^{2+}$): m/z 264.1648. Found: 264.1658.

Reaction of $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$ with $\text{Me}_3\text{N}\cdot\text{BH}_3$ – general procedure. $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ (50 mg, 0.08 mmol) was added to a CD_2Cl_2 (0.7 mL) solution of $[\mathbf{2c-Cl}][\text{Cl}]$ (20 mg, 0.04 mmol) to give the dication $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$ (J. Young NMR tube). Then, 3 mg (0.04 mmol) of

Me₃NBH₃ was added subsequently and the resulting mixture was explored by ³¹P/³¹P{¹H} NMR Spectroscopy and ESI-MS.

Preparation of [$\{C_6H_4(MeN)_2C\}_2C^+P(H)(BH_2NMe_3)N^iPr_2\}[BAr^{Cl}_4]_2$, [**2c-j**][BAr^{Cl}₄]₂. Na[BAr^{Cl}₄] (256 mg, 0.40 mmol) was added to 1,2-difluorobenzene solution (35 mL) of [**2c-Cl**][Cl] (100 mg, 0.19 mmol) to give the dication [**2c**][BAr^{Cl}₄]₂. The resulting mixture was treated with Me₃NBH₃ (15 mg, 0.21 mmol) and stirred for 2 hours. Filtration to remove NaCl was followed by addition of n-hexane (80 mL) to precipitate [**2c-j**][BAr^{Cl}₄]₂ as a light yellow solid, which was isolated by filtration and dried under vacuum. Yield: 123 mg (37%).

¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 0.88 (d, ³J_{HH} = 6 Hz, 6H, CH₃ - ⁱPr), 1.16 (d, ³J_{HH} = 6 Hz, 6H, CH₃ - ⁱPr), 2.66 (d, ⁴J_{HH} = 1 Hz, 9H, NMe₃), 3.49 (br s, 12H, NCH₃), 3.72 (sept, ³J_{HH} = 6 Hz, 2H, CH - ⁱPr), 6.93 (br s, 8H, *p*-H, BAr^{Cl}₄), 6.94 (m, 16H, BAr^{Cl}₄), 7.16 (dd, ³J_{HH} = 4 Hz and ¹J_{PH} = 351 Hz, 1H), 7.05 (br m, 4H), 7.40 (m, 4H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ 18.5 (s, CH₃ - ⁱPr), 22.54 (d, ²J_{CP} = 3 Hz, CH - ⁱPr), 23.02 (d, ³J_{CP} = 2 Hz, CH₃ - ⁱPr), 32.9 (br s, NCH₃), 54.4 (d, ³J_{CP} = 7 Hz, NMe₃), 111.9 (s, CH arom.), 123.1 (s, *p*-C, BAr^{Cl}₄), 127.7 (s, CH arom.), 131.2 (s, CH arom.), 132.9 (q, ²J_{CB} = 4 Hz, *o*-C, BAr^{Cl}₄), 133.0 (s, *m*-C, BAr^{Cl}₄), 151.9 (br s, NCN), 164.2 (q, ¹J_{CB} = 49 Hz, *ipso*-C, BAr^{Cl}₄). The signal corresponding to the central carbon atom (CCC) was not detected. ¹¹B (128 MHz, CD₂Cl₂, 298K): δ -6.9 (s, BAr^{Cl}₄), -9.4 (br q). ¹¹B{¹H} (128 MHz, CD₂Cl₂, 298K): δ -6.9 (s, BAr^{Cl}₄), -9.3 (br s). ³¹P NMR (202 MHz, CD₂Cl₂, 298 K): δ -15.4 (br d). ³¹P{¹H} NMR (160 MHz, CD₂Cl₂, 298 K): δ -15.3 (br s). HR-MS Calculated for [C₂₈H₄₆BN₆P]²⁺ (**2c-j**²⁺): m/z 254.1804. Found: 254.1811.

Figure 5.12. ¹H NMR spectrum of [2c-j][BAr^{Cl}₄]₂.

Figure 5.13. ³¹P NMR spectrum of [2c-j][BAr^{Cl}₄]₂.

Figure 5.14. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{2c-j}][\text{BAr}^{\text{Cl}}_4]_2$.

Reaction of $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ with $\text{Py}\cdot\text{BH}_3$ – general procedure. $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ (52 mg, 0.08 mmol) was added to a CD_2Cl_2 (0.7 mL) solution of $[\mathbf{2a-Cl}][\text{Cl}]$ (20 mg, 0.04 mmol) (J. Young NMR tube) to form $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$. Subsequently, $\text{Py}\cdot\text{BH}_3$ (4 μL , 0.04 mmol) was added and the reaction mixture was analyzed by $^{31}\text{P}/^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and HR-MS. Both $[\mathbf{2a-H}]^+$ and $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\cdot\text{P}(\text{H})(\text{BH}_2\cdot\text{Py})\text{Ph}][\text{BAr}^{\text{Cl}}_4]_2$, $[\mathbf{2a-i}][\text{BAr}^{\text{Cl}}_4]_2$ reaction products were observed. Unfortunately, all attempts to isolate $[\mathbf{2a-i}][\text{BAr}^{\text{Cl}}_4]_2$ by fractional precipitation were unsuccessful presumably due to the similar solubility of all present species imparted by the non-coordinating $[\text{BAr}^{\text{Cl}}_4]$ anion.

$[\mathbf{2a-i}][\text{BAr}^{\text{Cl}}_4]_2$: ^{31}P NMR (160 MHz, CD_2Cl_2 , 298 K): δ -13.5 (br d, $^1J_{\text{PH}} = 395$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, CD_2Cl_2 , 298 K): δ -13.5 (s). HR-MS Calculated for $[\text{C}_{30}\text{H}_{33}\text{BN}_5\text{P}]^{2+}$ ($\mathbf{2a-i}^{2+}$): m/z 252.6280. Found: 252.6292.

Reaction of $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ with $\text{Me}_3\text{N}\cdot\text{BH}_3$ – general procedure. $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ (52 mg, 0.08 mmol) was added to a CD_2Cl_2 (0.7 mL) solution of $[\mathbf{2a-Cl}][\text{Cl}]$ (20 mg, 0.04 mmol) to form $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ (J. Young NMR tube). In situ formed $[\mathbf{2a}][\text{BAr}^{\text{Cl}}_4]_2$ was then treated

with Me₃N·BH₃ (3 mg, 0.04 mmol) and the resulting mixture was investigated by ³¹P/³¹P{¹H} NMR spectroscopy and ESI-MS.

Preparation of [$\{C_6H_4(MeN)_2C\}_2CP(H)(BH_2NMe_3)Ph\}[X]_2$, [**2a-j**][X]₂, X = AlCl₄ and BAr^{Cl}₄. Na[BAr^{Cl}₄] (268 mg, 0.43 mmol) was added to 1,2-difluorobenzene (35 ml) solution of [**2a-Cl**][Cl] (100 mg, 0.21 mmol) (Schlenk flask) to give [**2a**][BAr^{Cl}₄]₂. Then, 15 mg (0.21 mmol) of Me₃N·BH₃ was added and the resulting mixture was stirred over night followed by filtration to remove NaCl. The filtrate was treated with n-hexane (80 mL) to precipitate [**2a-j**][BAr^{Cl}₄]₂ as a light yellow solid, which was isolated by filtration and subsequently dried under vacuum. Yield 220 mg (64 %). The most adequate counterion for crystallization of [**2a-j**]²⁺ was [AlCl₄]. Following the procedure described above, [AlCl₄] was introduced when AlCl₃ was used instead of Na[BAr^{Cl}₄]. Colorless crystals suitable for X-Ray analysis were obtained by layering the saturated 1,2-difluorobenzene solution of [**2a-j**][AlCl₄]₂ with n-hexane.

¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ 2.39 (br d, 2H), 2.63 (d, ⁴J_{HH} = 1 Hz, 9H, NMe₃), 3.50 (s, 12H, NCH₃), 6.93 (t, ⁴J_{HH} = 2 Hz, 8H, *p*-H, BAr^{Cl}₄), 7.04 (m, 16H, BAr^{Cl}₄), 7.06 (dd, ³J_{HH} = 7 Hz and ¹J_{PH} = 383 Hz, 1H), 7.37-7.61 (m, 13H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ 24.9 (d, ¹J_{CP} = 94 Hz, C_{CC}), 33.3 (s, NCH₃), 54.6 (d, ³J_{CP} = 6 Hz, N(C_{CH₃)₃), 111.9 (s, CH arom.), 123.1 (s, *p*-C, BAr^{Cl}₄), 123.7 (s, *p*-C, Ph), 127.7 (s, CH arom.), 131.3 (d, ¹J_{PC} = 14 Hz, *ipso*-C, Ph), 131.4 (d, ²J_{PC} = 13 Hz, *o*-C, Ph), 132.9 (q, ²J_{CB} = 4 Hz, *o*-C, BAr^{Cl}₄), 133.1 (s, *m*-C, BAr^{Cl}₄), 134.6 (d, ³J_{CP} = 3 Hz, *m*-C, Ph), 150.8 (d, ²J_{PC} = 8 Hz, N_{CCN}), 164.7 (q, ¹J_{CB} = 49 Hz, *ipso*-C, BAr^{Cl}₄). ¹¹B (128 MHz, CD₂Cl₂, 298K): δ - 7.5 (s, BAr^{Cl}₄), -10.8 (br). ¹¹B{¹H} (128 MHz, CD₂Cl₂, 298K): δ - 7.5 (s, BAr^{Cl}₄), -11.1 (br s). ³¹P NMR (202 MHz, CD₂Cl₂, 298 K): δ -30.5 (br d). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K): δ -30.5 (s). HR-MS Calculated for [C₂₈H₃₇BN₅P]²⁺ (**2a-j**²⁺): m/z 242.6435. Found: 242.6440.}

Figure 5.15. ¹H NMR spectrum of [2a-j][BArCl₄]₂.

Figure 5.16. ³¹P NMR spectrum of [2a-j][BArCl₄]₂.

Figure 5.17. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{2a-j}][\text{BAR}^{\text{Cl}}_4]_2$.

Preparation of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{P}(\text{H})(\text{BH}_2\text{Py})^t\text{Bu}][\text{AlCl}_4]_2$, $[\mathbf{2d-i}][\text{AlCl}_4]_2$. AlCl_3 (15 mg, 0.11 mmol) was added to CD_2Cl_2 solution (0.7 mL) of $[\mathbf{2d-Cl}][\text{Cl}]$ (25 mg, 0.05 mmol) to form the dication $[\mathbf{2d}][\text{AlCl}_4]_2$, which was subsequently treated with PyBH_3 (6 μL , 0.06 mmol). According to $^{31}\text{P}/^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy only $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^+\text{P}(\text{H})(\text{BH}_2\text{Py})^t\text{Bu}][\text{AlCl}_4]_2$, $[\mathbf{2d-i}][\text{AlCl}_4]_2$ was present in the solution. Its characterization was performed *in situ* as all attempts to isolate this species gave mixtures of several other compounds.

^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ 1.18 (d, $^3J_{\text{PH}} = 17$ Hz, 9H, $\text{CH}_3 - ^t\text{Bu}$), 3.79 (br s, 12H, NCH_3), 6.21 (dd, $^1J_{\text{PH}} = 383$ Hz and $^3J_{\text{HH}} = 2$ Hz, 1H, PH), 7.64 (br s, 8H, CH arom.), 7.80 (dd, $^3J_{\text{HH}} = 8$ Hz and $^3J_{\text{HH}} = 5$ Hz, 2H, *m*-H, Py), 8.24 (dt, $^3J_{\text{HH}} = 8$ Hz and $^5J_{\text{HH}} = 2$ Hz, 1H, *p*-H, Py), 8.57 (d, $^3J_{\text{HH}} = 6$ Hz, 2H, *o*-H, Py). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K): δ 26.9 (d, $^2J_{\text{CP}} = 3$ Hz, $\text{CH}_3 - ^t\text{Bu}$), 34.0 (br s, NCH_3), 34.7 (d, $^1J_{\text{CP}} = 37$ Hz, $\text{C} - ^t\text{Bu}$), 112.2 (s, CH arom.), 127.2 (s, CH arom.), 128.1 (s, *p*-C, Py), 131.5 (s, CH arom.), 144.0 (d, $^4J_{\text{CP}} = 2$ Hz, *m*-C, Py), 148.0 (d, $^3J_{\text{CP}} = 4$ Hz, *o*-C, Py), 152.0 (br s, NCN). ^{11}B (128 MHz, CD_2Cl_2 , 298K): δ -13.5 (br). $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, CD_2Cl_2 , 298K): δ -12.8 (br s). ^{31}P NMR (160 MHz, CD_2Cl_2 , 298 K): δ 2.2 (br d). $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz,

CD₂Cl₂, 298 K): δ 2.2 (br s). HR-MS Calculated for [C₂₈H₃₇BN₅P]²⁺ (**2d-i**²⁺): m/z 242.6435. Found: 242.6447.

Preparation of [{C₆H₄(MeN)₂C}₂C⁺P(H)(BH₂NMe₃)^tBu}][AlCl₄]₂, [**2d-j**][AlCl₄]₂. 1,2-difluorobenzene (40 mL) was added to a Schlenk flask charged with [**2d-Cl**][Cl] (105 mg, 0.23 mmol) and AlCl₃ (60 mg, 0.45 mmol). The resulting mixture was stirred for 5 minutes to form [**2d**][AlCl₄]₂, which was then treated with Me₃NBH₃ (20 mg, 0.27 mmol) followed by additional stirring for 2 hours. The addition of n-pentane (around 100 mL) caused the formation of yellow oil, which crystallized under vacuum to yield 79 mg (43 %) of [**2d-j**][AlCl₄]₂ as a yellow crystalline solid.

¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ 1.24 (d, ³J_{PH} = 18 Hz, 9H, CH₃ – ^tBu), 2.29 (br d, 2H, BH₂), 2.80 (s, 9H, NMe₃), 3.76 (br s, 12H, NCH₃), 6.16 (dd, ¹J_{PH} = 372 Hz and ³J_{HH} = 4 Hz, 1H, PH), 7.66 (br s, 8H, CH arom.). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ 24.9 (d, ¹J_{CP} = 62 Hz, C_{CC}), 26.9 (d, ²J_{CP} = 2 Hz, CH₃ – ^tBu), 34.7 (br s, NCH₃), 34.9 (d, ¹J_{CP} = 32 Hz, C – ^tBu), 54.9 (d, ³J_{CP} = 5 Hz, NMe₃), 112.3 (s, CH arom.), 127.3 (s, CH arom.), 131.5 (s, CH arom.), 151.9 (br s, N_{CN}). ¹¹B (128 MHz, CD₂Cl₂, 298K): δ -11.5 (br). ¹¹B{¹H} (128 MHz, CD₂Cl₂, 298K): δ -11.4 (br s). ³¹P NMR (160 MHz, CD₂Cl₂, 298 K): δ -11.3 (br d). ³¹P{¹H} NMR (160 MHz, CD₂Cl₂, 298 K): δ -11.3 (br s). HR-MS Calculated for [C₂₆H₄₁BN₅P]²⁺ (**2d-j**²⁺): m/z 232.6591. Found: 232.6590.

tBu Me3N-BH3 AV500 CD2Cl2 7-10-1
1H

Figure 5.18. ^1H NMR spectrum of $[2\text{d-j}][\text{AlCl}_4]_2$.

Figure 5.19. ^{31}P NMR spectrum of $[2\text{d-j}][\text{AlCl}_4]_2$.

Figure 5.20. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{2d-j}][\text{AlCl}_4]_2$.

Reaction of $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$ with H_2O – preparation of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}^*\text{P}(\text{O})(\text{H})\text{N}^i\text{Pr}_2][\text{BAr}^{\text{Cl}}_4]$, $[\mathbf{2c-O(H)}][\text{BAr}^{\text{Cl}}_4]$. When $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$ reacted with silanes and stannane, apart from the formation of reaction products whose identities were confirmed, we also observed a signal at +12 ppm in the $^{31}\text{P}\{^1\text{H}\}/^{31}\text{P}$ NMR spectrum, which was derived from slight hydrolysis (less than 10% in abundance) of the starting dication $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$. $\text{Na}[\text{BAr}^{\text{Cl}}_4]$ (256 mg, 0.40 mmol) was added to 1,2-difluorobenzene solution (40 mL) of $[\mathbf{2c-Cl}][\text{Cl}]$ (100 mg, 0.19 mmol) to form the dication $[\mathbf{2c}][\text{BAr}^{\text{Cl}}_4]_2$. The resulting solution was treated with 4 μL (0.19 mmol) of H_2O followed by additional stirring for 2 hours. NaCl was removed by filtration and n-pentane (around 100 mL) was added to the filtrate to precipitate $[\mathbf{2c-O(H)}][\text{BAr}^{\text{Cl}}_4]$ as a light yellow solid that was isolated by filtration and dried under vacuum. Yield: 186 mg (93%).

^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ 0.90 (br s, 6H, $\text{CH}_3 - ^i\text{Pr}$), 1.39 (br s, 6H, $\text{CH}_3 - ^i\text{Pr}$), 3.42 (br s, 12H, NCH_3), 3.78 (br m, 2H, $\text{CH} - ^i\text{Pr}$), 6.89 (t, $^4J_{\text{HH}} = 2$ Hz, 8H, $p\text{-H}$, BAr^{Cl}_4), 7.03 (m, 16H, BAr^{Cl}_4), 7.31 (br s, 4H), 8.13 (d, $^1J_{\text{HP}} = 560$ Hz, PH), 7.57 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K): δ 23.0 (s, $\text{CH}_3 - ^i\text{Pr}$), 23.6 (s, $\text{CH}_3 - ^i\text{Pr}$), 32.9

(br s, NCH₃), 47.2 (s, CH - ⁱPr), 111.8 (s, CH arom.), 122.9 (s, *p*-C, BAr^{Cl}₄), 127.6 (s, CH arom.), 131.2 (s, CH arom.), 132.9 (br s, *o*-C, BAr^{Cl}₄), 133.0 (s, *m*-C, BAr^{Cl}₄), 150.4 (br s, NCN), 164.7 (q, ¹J_{CB} = 49 Hz, *ipso*-C, BAr^{Cl}₄). ³¹P NMR (160 MHz, CD₂Cl₂, 298 K): δ 12.3 (d, ¹J_{PH} = 560 Hz). ³¹P{¹H} NMR (160 MHz, CD₂Cl₂, 298 K): δ 12.9 (s). HR-MS Calculated for [C₂₅H₃₅N₅OP]⁺ (**2c-(O)(H)**⁺): m/z 452.2574. Found: 452.2576.

Reaction of [2a][BAr^{Cl}₄]₂ with 1,3,5-cycloheptatriene [CH₂(C₆H₆)] – general procedure. Na[BAr^{Cl}₄] (52 mg, 0.08 mmol) was added to CD₂Cl₂ (0.7 mL) solution of [2a-Cl][Cl] (20 mg, 0.04 mmol) to give the dication [2a][BAr^{Cl}₄]₂ (J. Young NMR tube). The resulting solution was introduced to 1,3,5-cycloheptatriene (5 μL, 0.05 mmol), and the reaction mixture was investigated by ³¹P/³¹P{¹H} NMR spectroscopy.

Preparation of [{C₆H₄(MeN)₂C}₂C P{(CH)₆CH₂}Ph][BAr^{Cl}₄]₂, [2a-k][BAr^{Cl}₄]₂. Na[BAr^{Cl}₄] (268 mg, 0.43 mmol) was added to 1,2-difluorobenzene solution (45 mL) of [2a-Cl][Cl] (100 mg, 0.21 mmol) to yield [2a][BAr^{Cl}₄]₂. The reaction mixture was then treated with 1,3,5-cycloheptatriene (22 μL, 0.21 mmol) followed by overnight stirring. The resulting solution was filtered followed by addition of n-hexane (around 100 mL) to precipitate [{C₆H₄(MeN)₂C}₂C P{(CH)₆CH₂}Ph][BAr^{Cl}₄]₂, [2a-k][BAr^{Cl}₄]₂ as a light yellow solid that was isolated by filtration and dried *in vacuo*. Yield: 109 mg (31 %). Single crystals of [2a-k][BAr^{Cl}₄]₂ suitable for X-ray diffraction were grown by slow evaporation from 1,2-difluorobenzene solution. Surprisingly, once precipitated, [2a-k][BAr^{Cl}₄]₂ was only sparingly soluble in common deuterated solvents (CDCl₃, CD₂Cl₂, CD₃CN).

¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ 2.37 (br m, 1H), 2.73 (br m, 1H), 3.55 (br s, 12H, NCH₃), 5.23 (br m, 1H), 5.58 (br m, 1H), 6.36 (m, 2H), 6.85 (m, 1H), 7.01 (t, ⁴J_{HH} = 2 Hz, 8H, *p*-H, BAr^{Cl}₄), 7.13 (m, *o*-H, 16H, BAr^{Cl}₄), 7.34-7.82 (m, 14H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ 123.3 (s, *p*-C, BAr^{Cl}₄), 125.8 (s), 125.9 (s), 126.9 (s), 127.9 (s), 131.0 (s), 132.1 (br d), 132.9 (br s, *o*-C, BAr^{Cl}₄), 133.3 (m, *m*-C, BAr^{Cl}₄), 133.5 (s), 134.6 (s), 135.0 (br d), 135.5 (br t), 137.1 (s), 142.4 (br s), 154.5 (s), 164.7 (q, ¹J_{CB} = 49 Hz, *ipso*-C, BAr^{Cl}₄). ³¹P NMR (202 MHz, CD₂Cl₂, 298 K): δ 39.8 (br s). HR-MS Calculated for [C₃₂H₃₃N₄P]²⁺ (**2a-k**²⁺): m/z 252.1216. Found: 252.1218.

Reaction of [2a-H][BAr^{Cl}₄] with tropylium tetrafluoroborate. [C₇H₇][BF₄] (6 mg, 0.03 mmol) was added to CD₂Cl₂ solution (0.7 mL) of [2a-H][BAr^{Cl}₄] (30 mg, 0.03 mmol). The reaction mixture was kept at ambient temperature for 3 hours and then analyzed by ³¹P/³¹P{¹H} NMR Spectroscopy. C-H bond insertion product [C₆H₄(MeN)₂C}₂C·P(H)(C₇H₇)Ph][BAr^{Cl}₄]₂, [2a-I][BAr^{Cl}₄]₂ identified by the signal at -18.9 ppm was unstable and always formed in a mixture with [2a-H][BAr^{Cl}₄]. Attempts to improve the ratio between [2a-H][BAr^{Cl}₄] and [2a-I][BAr^{Cl}₄]₂ using larger amount of tropylium salt, higher temperature, as well as ultrasound bath, were all unsuccessful.

Reaction of [2a][BAr^{Cl}₄]₂ with Xanthene – synthesis of [{C₆H₄(MeN)₂C}₂C·P(H)(CH{C₆H₄}₂O)Ph][BAr^{Cl}₄]₂, [2a-m][BAr^{Cl}₄]₂. Na[BAr^{Cl}₄] (52 mg, 0.08 mmol) was added to CD₂Cl₂ (0.7 mL) solution of [2a-Cl][Cl] (20 mg, 0.04 mmol) to form [2a][BAr^{Cl}₄]₂ (J. Young NMR tube). The resulting mixture was treated with xanthene (8 mg, 0.04 mmol) and subsequently investigated by multinuclear NMR spectroscopy and ESI-MS. ³¹P/³¹P{¹H} NMR spectra revealed the presence of [{C₆H₄(MeN)₂C}₂C·P(H)(CH{C₆H₄}₂O)Ph][BAr^{Cl}₄]₂, [2a-m][BAr^{Cl}₄]₂ as only P-containing species, however, attempts to purify this reaction mixture always gave yellow oil which when dissolved in CD₂Cl₂ showed the presence of multiple P-based reaction products. It is also noteworthy that [2a-m][BAr^{Cl}₄]₂ is moderately stable in solution at ambient temperature over the period of 24 hours after which it decomposes to give the complicated mixture. Therefore, all spectroscopic data were obtained *in situ*.

¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ 3.10 (s, 12H, NCH₃), 5.79 (br s, 1H), 6.92 (t, ⁴J_{HH} = 2 Hz, 8H, *p*-H, BAr^{Cl}₄), 7.07 (m, 16H, *o*-H, BAr^{Cl}₄), 7.65 (d, ¹J_{PH} = 485 Hz, 1H, PH), 7.36-7.82 (m, 21H, CH arom.). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ 32.7 (s, NCH₃), 110.7 (s, CH arom.), 111.9 (s, CH arom.), 112.9 (s, CH arom.), 117.6 (s, CH arom.), 118.03 (s, CH arom.), 123.1 (s, *p*-C, BAr^{Cl}₄), 125.8 (s, CH arom.), 126.46 (s, CH arom.), 128.3 (s, CH arom.), 130.3 (s, CH arom.), 131.1 (s, CH arom.), 131.3 (s, CH arom.), 131.7 (s, CH arom.), 132.1 (s, CH arom.), 133.0 (br s, *o*- and *m*-C, BAr^{Cl}₄), 147.8 (br s, N₂CN), 164.7 (q, ¹J_{CB} = 49 Hz, *ipso*-C, BAr^{Cl}₄). ³¹P NMR (160 MHz, CD₂Cl₂, 298 K): δ 4.4 (br d). ³¹P{¹H} NMR (160 MHz, CD₂Cl₂, 298 K): δ 4.5 (s). HR-MS calculated for: [C₃₈H₃₄N₄OP]⁺ (**M-H**⁺): m/z 593.2465; found: 593.2469; [C₂₅H₂₆N₄P]⁺ (**2a-H**⁺): m/z

413.1890; found: 413.1892; $[\text{C}_{13}\text{H}_9\text{O}]^+$ ($\text{CH}\{\text{C}_6\text{H}_4\}_2\text{O}^+$): m/z 181.0648; found: 181.0653. Although, we were not able to detect the molecular ion $[\mathbf{2a-m}]^{2+}$ at the respective m/z value (calcd 327.1738), we managed to clearly observe its fragments $[\mathbf{2a-H}]^+$ and $[\text{CH}\{\text{C}_6\text{H}_4\}_2\text{O}]^+$, as well as $(\mathbf{M-H}^+)$ ion.

Figure 5.21. ^1H NMR spectrum of $[\mathbf{2a-m}][\text{BAr}^{\text{Cl}}_4]_2$.

Figure 5.22. ^{31}P NMR spectrum of $[\mathbf{2a-m}][\text{BAr}^{\text{Cl}}_4]_2$.

Figure 5.23. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\mathbf{2a-m}][\text{BAr}^{\text{Cl}}_4]_2$.

Reaction of $[\mathbf{2d}][\text{AlCl}_4]_2$ with Xanthene – preparation of $[\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}\cdot\text{P}(\text{H})(\text{CH}\{\text{C}_6\text{H}_4\}_2\text{O})^t\text{Bu}][\text{AlCl}_4]_2$, $\mathbf{2d-m}][\text{AlCl}_4]_2$. AlCl_3 (12 mg, 0.09

mmol) was added to CD₂Cl₂ solution (0.7 mL) of [**2d-Cl**][Cl] (21 mg, 0.04 mmol) to form the dication [**2d**][AlCl₄]₂. The resulting mixture was treated with xanthene (9 mg, 0.05 mmol) and subsequently assessed by ³¹P/³¹P{¹H} NMR Spectroscopy and ESI-MS. Based on spectroscopic results, C-H bond insertion product [**2d-m**][AlCl₄]₂ was major compound in the solution, however, its high reactivity/instability prevented our isolation attempts.

³¹P (202 MHz, CD₂Cl₂, 298 K): δ 31.9 (d, ¹J_{PH} = 466 Hz). ³¹P{¹H} (202 MHz, CD₂Cl₂, 298 K): δ 31.9 (s). HR-MS calculated for [C₃₆H₃₉N₄OP]²⁺ (**2d-m**²⁺): m/z 287.1425; this ion was not found. [C₂₃H₃₀N₄P]⁺ (**2d-H**⁺): m/z 393.2203; found: 393.2229. [C₁₃H₉O]⁺ (CH{C₆H₄}₂O⁺): m/z 181.0648; found: 181.0653. Even though, molecular ion [**2d-m**]²⁺ at the respective m/z value (calcd 287.1425) was not detected, species derived from its fragmentation – [**2d-H**]⁺ and [CH{C₆H₄}₂O]⁺ were apparent.

Section 5.3. X-Ray Crystallography

Single crystals were mounted on quartz fiber and the X-ray intensity data was collected on a Bruker X8 APEX system, using Mo K α radiation, with the SMART suite of programs.⁷ Data were processed and corrected for Lorentz and polarization effects with SAINT⁸ and for absorption effects with SABADS.⁹ Structural solution and refinement were carried out with the SHELXTL suite of programs.¹⁰ The structures were solved by direct method and refined for all data by full-matrix least-squares methods 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. Further crystallographic details for each molecular structure are listed in the corresponding crystallographic data tables.

Table 5.1. Crystal data and structure refinement for $[(\text{Ph}_3\text{P})_2\text{C}(\text{P}(\text{Ph})\text{Cl})][\text{SbF}_6]$, [**1a-Cl**][SbF_6].

Identification code	dv255s
Chemical formula	$\text{C}_{43}\text{H}_{35}\text{ClF}_6\text{P}_3\text{Sb}$
Formula weight	915.82 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.120 x 0.180 x 0.200 mm
Crystal habit	colorless block
Crystal system	monoclinic
Space group	$P 1 2_1/n 1$
Unit Cell Dimensions	$a = 10.5582(4) \text{ Å}$ $\alpha = 90^\circ$ $b = 18.6784(8) \text{ Å}$ $\beta = 99.4721(13)^\circ$ $c = 20.2317(7) \text{ Å}$ $\gamma = 90^\circ$
Volume	$3935.5(3) \text{ Å}^3$
Z	4
Density (calculated)	1.546 g/cm^3
Absorption coefficient	0.951 mm^{-1}
F(000)	1840
Theta range for data collection	1.49 to 31.08°
Index ranges	$-15 \leq h \leq 14$, $-27 \leq k \leq 27$, $-29 \leq l \leq 29$
Reflections collected	78917
Independent reflections	12591 [$R(\text{int}) = 0.0796$]
Coverage of independent reflections	99.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.894 and 0.8330
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014 (Sheldrick, 2014)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	12591 / 1885 / 904
Goodness-of-fit on F^2	1.109
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0560$, $wR2 = 0.1415$
R indices (all data)	$R1 = 0.1095$, $wR2 = 0.1991$
Largest diff. peak and hole	1.902 and -1.940 eÅ^{-3}
R.M.S. deviation from mean	0.214 eÅ^{-3}

Table 5.2. Crystal data and structure refinement for [(Ph₃P)₂CP(4-F-Ph)Cl][SbF₆], [**1b-Cl**][SbF₆].

Identification code	dv256
Chemical formula	C ₄₃ H ₃₄ ClF ₇ P ₃ Sb
Formula weight	933.81 g/mol
Temperature	93(2) K
Wavelength	0.71073 Å
Crystal size	0.300 x 0.320 x 0.400 mm
Crystal habit	colorless block
Crystal system	triclinic
Space group	P -1
Unit Cell Dimensions	$a = 11.7973(4) \text{ Å}$ $\alpha = 89.7362(13)^\circ$ $b = 13.4325(5) \text{ Å}$ $\beta = 79.2458(13)^\circ$ $c = 13.4603(5) \text{ Å}$ $\gamma = 66.8080(12)^\circ$
Volume	1920.60(12) Å ³
Z	2
Density (calculated)	1.615 g/cm ³
Absorption coefficient	0.979 mm ⁻¹
F(000)	936
Theta range for data collection	2.99 to 31.29°
Index ranges	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -19 ≤ l ≤ 19
Reflections collected	45847
Independent reflections	12411 [R(int) = 0.0309]
Coverage of independent reflections	98.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7580 and 0.6950
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	12411 / 0 / 496
Goodness-of-fit on F ²	1.032
Final R indices [I>2σ(I)]	R1 = 0.0244, wR2 = 0.0591
R indices (all data)	R1 = 0.0293, wR2 = 0.0616
Largest diff. peak and hole	0.567 and -0.447 eÅ ⁻³
R.M.S. deviation from mean	0.077 eÅ ⁻³

Table 5.3. Crystal data and structure refinement for [(Ph₃P)₂C⁺P(OMe)Cl][SbF₆], [**1e-Cl**][SbF₆].

Identification code	dv390s
Chemical formula	C ₃₈ H ₃₃ ClF ₆ OP ₃ Sb
Formula weight	869.75 g/mol
Temperature	103(2) K
Wavelength	1.54178 Å
Crystal size	0.010 x 0.080 x 0.100 mm
Crystal habit	colorless plate
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit Cell Dimensions	$a = 10.3999(2) \text{ Å}$ $\alpha = 90^\circ$ $b = 24.6134(3) \text{ Å}$ $\beta = 108.6273(8)^\circ$ $c = 15.3029(2) \text{ Å}$ $\gamma = 90^\circ$
Volume	3711.99(10) Å ³
Z	4
Density (calculated)	1.556 g/cm ³
Absorption coefficient	8.309 mm ⁻¹
F(000)	1744
Theta range for data collection	3.54 to 66.65°
Index ranges	-12 ≤ h ≤ 12, -29 ≤ k ≤ 29, -18 ≤ l ≤ 18
Reflections collected	45733
Independent reflections	6574 [R(int) = 0.0587]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9220 and 0.4900
Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6574 / 0 / 452
Goodness-of-fit on F ²	1.071
Final R indices [I > 2σ(I)]	R1 = 0.0398, wR2 = 0.0956
R indices (all data)	R1 = 0.0433, wR2 = 0.0975
Largest diff. peak and hole	1.528 and -0.724 eÅ ⁻³
R.M.S. deviation from mean	0.083 eÅ ⁻³

Table 5.4. Crystal data and structure refinement for [$\{C_6H_4(MeN)_2C\}_2CP(Ph)Cl$][SbF_6], [**2a-Cl**][SbF_6].

Identification code	dv294
Chemical formula	$C_{53}H_{56}Cl_8F_{12}N_8P_2Sb_2$
Formula weight	1622.09 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.120 x 0.200 x 0.240 mm
Crystal habit	colorless block
Crystal system	triclinic
Space group	P -1
Unit Cell Dimensions	$a = 8.5429(8)$ Å $\alpha = 107.4440(19)^\circ$ $b = 15.9590(15)$ Å $\beta = 98.8580(19)^\circ$ $c = 24.892(2)$ Å $\gamma = 91.986(2)^\circ$
Volume	$3187.2(5)$ Å ³
Z	2
Density (calculated)	1.690 g/cm ³
Absorption coefficient	1.312 mm ⁻¹
F(000)	1612
Theta range for data collection	1.34 to 29.27°
Index ranges	$-11 \leq h \leq 11$, $-21 \leq k \leq 21$, $-34 \leq l \leq 34$
Reflections collected	40964
Independent reflections	17232 [R(int) = 0.0566]
Coverage of independent reflections	99.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8600 and 0.6800
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	17232 / 0 / 774
Goodness-of-fit on F ²	1.033
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0659, wR2 = 0.1553
R indices (all data)	R1 = 0.1066, wR2 = 0.1793
Largest diff. peak and hole	2.859 and -2.259 eÅ ⁻³
R.M.S. deviation from mean	0.168 eÅ ⁻³

Table 5.5. Crystal data and structure refinement for $[\{C_6H_4(MeN)_2C\}_2C \cdot P(N^iPr_2)Cl][SbF_6]$, **[2c-Cl][SbF₆]**.

Identification code	dv351
Chemical formula	$C_{52}H_{72}Cl_6F_{12}N_{10}P_2Sb_2$
Formula weight	1583.33 g/mol
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal size	0.100 x 0.140 x 0.320 mm
Crystal habit	yellow block
Crystal system	triclinic
Space group	P -1
Unit Cell Dimensions	$a = 9.9510(2) \text{ Å}$ $\alpha = 70.4820(11)^\circ$ $b = 18.1607(5) \text{ Å}$ $\beta = 88.0745(12)^\circ$ $c = 19.4532(4) \text{ Å}$ $\gamma = 82.4796(14)^\circ$
Volume	$3284.82(13) \text{ Å}^3$
Z	2
Density (calculated)	1.601 g/cm^3
Absorption coefficient	1.192 mm^{-1}
F(000)	1592
Theta range for data collection	1.34 to 27.00°
Index ranges	$-12 \leq h \leq 12$, $-23 \leq k \leq 23$, $-24 \leq l \leq 24$
Reflections collected	68666
Independent reflections	14331 [R(int) = 0.0584]
Coverage of independent reflections	100.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8900 and 0.7020
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	14331 / 264 / 828
Goodness-of-fit on F^2	1.068
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0464$, $wR2 = 0.1195$
R indices (all data)	$R1 = 0.0674$, $wR2 = 0.1505$
Largest diff. peak and hole	2.532 and -1.971 eÅ^{-3}
R.M.S. deviation from mean	0.168 eÅ^{-3}

Table 5.6. Crystal data and structure refinement for [$\{C_6H_4(MeN)_2C\}_2C(^tBu)Cl$][SbF₆], [2d-Cl][SbF₆].

Identification code	dv346s
Chemical formula	C ₉₆ H ₁₂₄ Cl ₁₂ F ₂₄ N ₁₆ P ₄ Sb ₄
Formula weight	2994.38 g/mol
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal size	0.180 x 0.280 x 0.360 mm
Crystal habit	colorless plate
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit Cell Dimensions	$a = 15.6185(18) \text{ Å}$ $\alpha = 90^\circ$ $b = 16.8892(19) \text{ Å}$ $\beta = 103.2159(18)^\circ$ $c = 11.5723(13) \text{ Å}$ $\gamma = 90^\circ$
Volume	2971.7(6) Å ³
Z	1
Density (calculated)	1.673 g/cm ³
Absorption coefficient	1.312 mm ⁻¹
F(000)	1496
Theta range for data collection	2.41 to 27.11°
Index ranges	-20 ≤ h ≤ 19, -21 ≤ k ≤ 21, -14 ≤ l ≤ 14
Reflections collected	36593
Independent reflections	6545 [R(int) = 0.0539]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7980 and 0.6500
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6545 / 0 / 359
Goodness-of-fit on F ²	1.039
$\Delta/\sigma_{\max}$	0.001
Final R indices [I > 2σ(I)]	R1 = 0.0623, wR2 = 0.1467
R indices (all data)	R1 = 0.1660, wR2 = 0.2257
Largest diff. peak and hole	1.452 and -1.064 eÅ ⁻³
R.M.S. deviation from mean	0.087 eÅ ⁻³

Table 5.7. Crystal data and structure refinement for [$\{C_6H_4(MeN)_2C\}_2C^+PBr_2][Br^-]$, [**2f-Br**][Br].

Identification code	dv354s
Chemical formula	$C_{40}H_{43}Br_6N_9P_2$
Formula weight	1191.23 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.180 x 0.200 x 0.240 mm
Crystal habit	orange block
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit Cell Dimensions	$a = 15.790(3)$ Å $\alpha = 90^\circ$ $b = 17.796(3)$ Å $\beta = 104.672(4)^\circ$ $c = 16.457(3)$ Å $\gamma = 90^\circ$
Volume	$4473.6(14)$ Å ³
Z	4
Density (calculated)	1.769 g/cm ³
Absorption coefficient	5.497 mm ⁻¹
F(000)	2344
Theta range for data collection	1.76 to 27.90°
Reflections collected	12317
Independent reflections	12317 [R(int) = 0.1157]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.4380 and 0.3520
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	12317 / 6 / 524
Goodness-of-fit on F^2	1.062
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0771$, $wR2 = 0.1104$
R indices (all data)	$R1 = 0.1305$, $wR2 = 0.1274$
Largest diff. peak and hole	1.239 and -1.033 eÅ ⁻³
R.M.S. deviation from mean	0.231 eÅ ⁻³

Table 5.8. Crystal data and structure refinement for [$\{C_6H_4(MeN)_2C\}_2CPCl_2][SbF_6]$, [**2g-Cl**][SbF_6].

Identification code	dv299s
Chemical formula	$C_{19}H_{20}Cl_2F_6N_4PSb$
Formula weight	642.01 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.080 x 0.100 x 0.140 mm
Crystal habit	yellow block
Crystal system	orthorhombic
Space group	P b c a
Unit Cell Dimensions	$a = 11.6300(9)$ Å $\alpha = 90^\circ$ $b = 19.1931(14)$ Å $\beta = 90^\circ$ $c = 21.1940(13)$ Å $\gamma = 90^\circ$
Volume	$4730.8(6)$ Å ³
Z	8
Density (calculated)	1.803 g/cm ³
Absorption coefficient	1.523 mm ⁻¹
F(000)	2528
Theta range for data collection	1.92 to 26.43°
Index ranges	$-14 \leq h \leq 14$, $-22 \leq k \leq 23$, $-26 \leq l \leq 26$
Reflections collected	69640
Independent reflections	4854 [$R(\text{int}) = 0.1168$]
Coverage of independent reflections	99.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8880 and 0.8150
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4854 / 166 / 359
Goodness-of-fit on F^2	1.068
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0604$, $wR2 = 0.1577$
R indices (all data)	$R1 = 0.1188$, $wR2 = 0.2044$
Largest diff. peak and hole	1.703 and -1.035 eÅ ⁻³
R.M.S. deviation from mean	0.149 eÅ ⁻³

Table 5.9. Crystal data and structure refinement for [$\{C_6H_4(MeN)_2C\}_2CPh\}[BAr^{Cl}_4]_2$, **[2a]**[BAr^{Cl}_4]₂.

Identification code	dv308s
Chemical formula	C ₈₅ H ₅₇ B ₂ Cl ₁₆ F ₄ N ₄ P
Formula weight	1830.13 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.060 x 0.080 x 0.120 mm
Crystal habit	orange block
Crystal system	triclinic
Space group	P -1
Unit Cell Dimensions	$a = 13.4121(11) \text{ Å}$ $\alpha = 84.027(3)^\circ$ $b = 13.9406(12) \text{ Å}$ $\beta = 82.751(3)^\circ$ $c = 22.8317(19) \text{ Å}$ $\gamma = 76.978(3)^\circ$
Volume	4113.2(6) Å ³
Z	2
Density (calculated)	1.478 g/cm ³
Absorption coefficient	0.611 mm ⁻¹
F(000)	1856
Theta range for data collection	0.90 to 28.00°
Index ranges	-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -30 ≤ l ≤ 30
Reflections collected	77999
Independent reflections	19869 [R(int) = 0.1461]
Coverage of independent reflections	100.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9640 and 0.9300
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	19869 / 78 / 1013
Goodness-of-fit on F ²	1.000
Final R indices [I>2σ(I)]	R1 = 0.0705, wR2 = 0.1609
R indices (all data)	R1 = 0.1707, wR2 = 0.2483
Largest diff. peak and hole	0.676 and -0.533 eÅ ⁻³
R.M.S. deviation from mean	0.122 eÅ ⁻³

Table 5.10. Crystal data and structure refinement for [$\{C_6H_4(MeN)_2C\}_2C^+POMe\}[AlCl_4]_2$, **[2e]** $[AlCl_4]_2$.

Identification code	dv352r
Chemical formula	$C_{19.93}H_{22.78}Al_2Cl_{8.07}N_4O_{0.93}P$
Formula weight	704.28 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.200 x 0.320 x 0.420 mm
Crystal habit	yellow block
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit Cell Dimensions	$a = 12.1375(13)$ Å $\alpha = 90^\circ$ $b = 9.5726(10)$ Å $\beta = 99.186(2)^\circ$ $c = 27.119(3)$ Å $\gamma = 90^\circ$
Volume	$3110.5(6)$ Å ³
Z	4
Density (calculated)	1.504 g/cm ³
Absorption coefficient	0.861 mm ⁻¹
F(000)	1424
Theta range for data collection	1.52 to 28.36°
Index ranges	$-16 \leq h \leq 16$, $-12 \leq k \leq 12$, $-36 \leq l \leq 36$
Reflections collected	45443
Independent reflections	7761 [R(int) = 0.0518]
Coverage of independent reflections	99.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8470 and 0.7140
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7761 / 7 / 340
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0418$, $wR2 = 0.1016$
R indices (all data)	$R1 = 0.0543$, $wR2 = 0.1099$
Largest diff. peak and hole	1.009 and -0.571 eÅ ⁻³
R.M.S. deviation from mean	0.084 eÅ ⁻³

Table 5.11. Crystal data and structure refinement for $[\{ \{ \text{C}_6\text{H}_4(\text{MeN})_2\text{C} \}_2\text{C} \}_2\text{P}][\text{SbF}_6]_2[\text{Br}]$, $[(\mathbf{2})_2\text{P}][\text{SbF}_6]_2[\text{Br}]$.

Identification code	dv353
Chemical formula	$\text{C}_{84}\text{H}_{94}\text{Br}_2\text{F}_{24}\text{N}_{19}\text{O}_{0.50}\text{P}_2\text{Sb}_4$
Formula weight	2542.54 g/mol
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal size	0.100 x 0.140 x 0.160 mm
Crystal habit	orange block
Crystal system	triclinic
Space group	P -1
Unit Cell Dimensions	$a = 12.1048(3) \text{ Å}$ $\alpha = 108.8842(16)^\circ$ $b = 13.7318(4) \text{ Å}$ $\beta = 98.2298(14)^\circ$ $c = 16.1379(5) \text{ Å}$ $\gamma = 102.7525(14)^\circ$
Volume	$2407.61(12) \text{ Å}^3$
Z	1
Density (calculated)	1.754 g/cm^3
Absorption coefficient	2.075 mm^{-1}
F(000)	1255
Theta range for data collection	2.90 to 31.06°
Index ranges	$-17 \leq h \leq 17$, $-19 \leq k \leq 19$, $-23 \leq l \leq 23$
Reflections collected	47167
Independent reflections	15411 [R(int) = 0.0828]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8190 and 0.7330
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	15411 / 198 / 670
Goodness-of-fit on F^2	1.017
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0532, wR2 = 0.1000
R indices (all data)	R1 = 0.1170, wR2 = 0.1195
Largest diff. peak and hole	1.326 and -1.378 eÅ^{-3}
R.M.S. deviation from mean	0.135 eÅ^{-3}

Table 5.12. Crystal data and structure refinement for $[\{C_6H_4(MeN)_2C\}_2C \cdot P\{(CH_2CCH_3)_2\}Ph][AlCl_4]_2$, **[2a-h]** $[AlCl_4]_2$.

Identification code	dv323
Chemical formula	$C_{32}H_{37}Al_2Cl_{10}N_4P$
Formula weight	917.08 g/mol
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal size	0.060 x 0.120 x 0.160 mm
Crystal habit	colorless plate
Crystal system	monoclinic
Space group	$P 1 21/n 1$
Unit Cell Dimensions	$a = 9.5886(4) \text{ Å}$ $\alpha = 90^\circ$ $b = 36.6578(17) \text{ Å}$ $\beta = 98.046(3)^\circ$ $c = 12.1022(7) \text{ Å}$ $\gamma = 90^\circ$
Volume	$4212.0(4) \text{ Å}^3$
Z	4
Density (calculated)	1.446 g/cm^3
Absorption coefficient	0.771 mm^{-1}
F(000)	1872
Theta range for data collection	1.79 to 25.88°
Index ranges	$-11 \leq h \leq 9$, $-44 \leq k \leq 45$, $-14 \leq l \leq 14$
Reflections collected	44804
Independent reflections	8081 [$R(\text{int}) = 0.1497$]
Coverage of independent reflections	98.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9550 and 0.8870
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8081 / 0 / 448
Goodness-of-fit on F^2	1.009
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0607$, $wR2 = 0.1619$
R indices (all data)	$R1 = 0.1615$, $wR2 = 0.2401$
Largest diff. peak and hole	0.558 and -0.665 eÅ^{-3}
R.M.S. deviation from mean	0.133 eÅ^{-3}

Table 5.13. Crystal data and structure refinement for [(ⁱPr₂N)₂P][BAr^{Cl}₄], [**3**][BAr^{Cl}₄].

Identification code	dv411
Chemical formula	C ₃₆ H ₄₀ BCl ₈ N ₂ P
Formula weight	826.08 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.360 x 0.400 x 0.420 mm
Crystal habit	yellow block
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit Cell Dimensions	$a = 9.7448(3) \text{ Å}$ $\alpha = 90^\circ$ $b = 13.9148(4) \text{ Å}$ $\beta = 95.6699(14)^\circ$ $c = 29.7605(8) \text{ Å}$ $\gamma = 90^\circ$
Volume	4015.7(2) Å ³
Z	4
Density (calculated)	1.366 g/cm ³
Absorption coefficient	0.629 mm ⁻¹
F(000)	1704
Theta range for data collection	1.38 to 33.24°
Index ranges	-15 ≤ h ≤ 14, -21 ≤ k ≤ 21, -45 ≤ l ≤ 45
Reflections collected	116505
Independent reflections	15393 [R(int) = 0.0294]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8050 and 0.7780
Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	15393 / 130 / 471
Goodness-of-fit on F ²	1.081
Final R indices [I > 2σ(I)]	R1 = 0.0348, wR2 = 0.0848
R indices (all data)	R1 = 0.0414, wR2 = 0.0881
Largest diff. peak and hole	1.439 and -0.672 eÅ ⁻³
R.M.S. deviation from mean	0.063 eÅ ⁻³

Table 5.14. Crystal data and structure refinement for [$\{C_6H_4(MeN)_2C\}_2C \cdot P(H)Ph$][$AlCl_4$], [**2a-H**][$AlCl_4$].

Identification code	dv344s
Chemical formula	$C_{50}H_{53}Al_2Cl_8N_8P_2$
Formula weight	1165.50 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.060 x 0.100 x 0.120 mm
Crystal habit	yellow block
Crystal system	orthorhombic
Space group	$Pca2_1$
Unit Cell Dimensions	$a = 21.0177(16)$ Å $\alpha = 90^\circ$ $b = 22.3251(16)$ Å $\beta = 90^\circ$ $c = 11.6657(9)$ Å $\gamma = 90^\circ$
Volume	$5473.8(7)$ Å ³
Z	4
Density (calculated)	1.414 g/cm ³
Absorption coefficient	0.546 mm ⁻¹
F(000)	2404
Theta range for data collection	1.82 to 25.57°
Index ranges	$-26 \leq h \leq 26$, $-14 \leq k \leq 14$, $-27 \leq l \leq 22$
Reflections collected	10242
Independent reflections	10242 [$R(int) = 0.1152$]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9680 and 0.9370
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	10242 / 1 / 646
Goodness-of-fit on F^2	1.064
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0561$, $wR2 = 0.1276$
R indices (all data)	$R1 = 0.1080$, $wR2 = 0.1637$
Absolute Structure Parameter	0.2(1)
Largest diff. peak and hole	0.747 and -0.523 eÅ ⁻³
R.M.S. deviation from mean	0.129 eÅ ⁻³

Table 5.15. Crystal data and structure refinement for $[\{C_6H_4(MeN)_2C\}_2C^*P(H)(BH_2NMe_3)Ph][AlCl_4]_2$, **[2a-j]** $[AlCl_4]_2$.

Identification code	dv335
Chemical formula	$C_{28}H_{37}Al_2BCl_8N_5P$
Formula weight	822.96 g/mol
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal size	0.280 x 0.340 x 0.420 mm
Crystal habit	colorless block
Crystal system	triclinic
Space group	P -1
Unit Cell Dimensions	$a = 11.0690(7)$ Å $\alpha = 90.450(3)^\circ$ $b = 18.5787(13)$ Å $\beta = 105.030(3)^\circ$ $c = 19.7880(13)$ Å $\gamma = 90.613(3)^\circ$
Volume	$3929.7(5)$ Å ³
Z	4
Density (calculated)	1.391 g/cm ³
Absorption coefficient	0.686 mm ⁻¹
F(000)	1688
Theta range for data collection	1.10 to 26.54°
Index ranges	$-13 \leq h \leq 13$, $-23 \leq k \leq 23$, $-24 \leq l \leq 24$
Reflections collected	130301
Independent reflections	16208 [R(int) = 0.0625]
Coverage of independent reflections	99.2%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8310 and 0.7610
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	16208 / 844 / 889
Goodness-of-fit on F ²	1.122
Final R indices [I>2σ(I)]	R1 = 0.0703, wR2 = 0.2133
R indices (all data)	R1 = 0.0951, wR2 = 0.2356
Largest diff. peak and hole	0.907 and -0.933 eÅ ⁻³
R.M.S. deviation from mean	0.124 eÅ ⁻³

Table 5.16. Crystal data and structure refinement for $[(^i\text{Pr}_2\text{N})_2\text{P}(\text{H})\text{BH}_2\cdot\text{Py}][\text{BAr}^{\text{Cl}}_4]$, **[3-i]** $[\text{BAr}^{\text{Cl}}_4]$.

Identification code	dv396
Chemical formula	$\text{C}_{41}\text{H}_{48}\text{B}_2\text{Cl}_8\text{N}_3\text{P}$
Formula weight	919.01 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.240 x 0.300 x 0.420 mm
Crystal habit	colorless block
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit Cell Dimensions	$a = 14.6575(6)$ Å $\alpha = 90^\circ$ $b = 13.5987(5)$ Å $\beta = 106.9035(14)^\circ$ $c = 23.7606(9)$ Å $\gamma = 90^\circ$
Volume	$4531.4(3)$ Å ³
Z	4
Density (calculated)	1.347 g/cm ³
Absorption coefficient	0.566 mm ⁻¹
F(000)	1904
Theta range for data collection	1.45 to 31.03°
Index ranges	$-18 \leq h \leq 21$, $-19 \leq k \leq 19$, $-34 \leq l \leq 34$
Reflections collected	71364
Independent reflections	14451 [R(int) = 0.1219]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8760 and 0.7970
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	14451 / 0 / 516
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0547, wR2 = 0.1285
R indices (all data)	R1 = 0.0870, wR2 = 0.1492
Largest diff. peak and hole	0.914 and -0.690 eÅ ⁻³
R.M.S. deviation from mean	0.104 eÅ ⁻³

Table 5.17. Crystal data and structure refinement for $[(^i\text{Pr}_2\text{N})_2\text{P}(\text{H})\text{BH}_2\cdot\text{NMe}_3][\text{BAr}^{\text{Cl}}_4]$, **[3-j][BAr^{Cl}₄]**.

Identification code	dv395
Chemical formula	$\text{C}_{39}\text{H}_{52}\text{B}_2\text{Cl}_8\text{N}_3\text{P}$
Formula weight	899.02 g/mol
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal size	0.320 x 0.380 x 0.440 mm
Crystal habit	colorless block
Crystal system	triclinic
Space group	P -1
Unit Cell Dimensions	$a = 12.7943(5) \text{ Å}$ $\alpha = 96.1461(14)^\circ$ $b = 12.8697(5) \text{ Å}$ $\beta = 109.8769(14)^\circ$ $c = 15.7309(6) \text{ Å}$ $\gamma = 108.7461(14)^\circ$
Volume	$2237.60(15) \text{ Å}^3$
Z	2
Density (calculated)	1.334 g/cm^3
Absorption coefficient	0.571 mm^{-1}
F(000)	936
Theta range for data collection	1.42 to 33.33°
Index ranges	$-19 \leq h \leq 19$, $-19 \leq k \leq 19$, $-24 \leq l \leq 24$
Reflections collected	105482
Independent reflections	17242 [R(int) = 0.1075]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8380 and 0.7870
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	17242 / 0 / 498
Goodness-of-fit on F^2	1.014
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0511$, $wR2 = 0.1189$
R indices (all data)	$R1 = 0.0823$, $wR2 = 0.1390$
Largest diff. peak and hole	1.402 and -0.594 eÅ^{-3}
R.M.S. deviation from mean	0.081 eÅ^{-3}

Table 5.18. Crystal data and structure refinement for [$\{\text{C}_6\text{H}_4(\text{MeN})_2\text{C}\}_2\text{C}(\text{PH}_2)[\text{AlCl}_4]$, $[\mathbf{2} \cdot \text{PH}_2][\text{AlCl}_4]$.

Identification code	dv376s
Chemical formula	$\text{C}_{19}\text{H}_{22}\text{AlCl}_4\text{N}_4\text{P}$
Formula weight	506.15 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.100 x 0.180 x 0.220 mm
Crystal habit	orange block
Crystal system	monoclinic
Space group	$P 1\ 21/n\ 1$
Unit Cell Dimensions	$a = 10.4946(9)\ \text{Å}$ $\alpha = 90^\circ$ $b = 14.2035(15)\ \text{Å}$ $\beta = 100.966(3)^\circ$ $c = 16.6481(15)\ \text{Å}$ $\gamma = 90^\circ$
Volume	$2436.3(4)\ \text{Å}^3$
Z	4
Density (calculated)	$1.380\ \text{g/cm}^3$
Absorption coefficient	$0.601\ \text{mm}^{-1}$
F(000)	1040
Theta range for data collection	1.90 to 27.11°
Index ranges	$-13 \leq h \leq 12$, $-18 \leq k \leq 18$, $-21 \leq l \leq 19$
Reflections collected	30724
Independent reflections	5364 [$R(\text{int}) = 0.0694$]
Coverage of independent reflections	99.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9420 and 0.8790
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5364 / 1 / 272
Goodness-of-fit on F^2	1.068
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0581$, $wR2 = 0.1656$
R indices (all data)	$R1 = 0.0911$, $wR2 = 0.1842$
Largest diff. peak and hole	1.012 and $-0.727\ \text{eÅ}^{-3}$
R.M.S. deviation from mean	$0.113\ \text{eÅ}^{-3}$

Table 5.19. Crystal data and structure refinement for $[\{C_6H_4(MeN)_2C\}_2C \cdot P(\{CH\}_6CH_2)Ph][BAr^{Cl}_4]_2$, [**2a-k**][BAr^{Cl}_4]₂.

Identification code	dv386s
Chemical formula	C ₉₂ H ₆₇ B ₂ Cl ₁₆ F ₄ N ₄ P
Formula weight	1924.28 g/mol
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal size	0.080 x 0.160 x 0.200 mm
Crystal habit	yellow block
Crystal system	triclinic
Space group	P -1
Unit Cell Dimensions	$a = 13.3965(11) \text{ Å}$ $\alpha = 93.476(5)^\circ$ $b = 13.4151(12) \text{ Å}$ $\beta = 101.749(5)^\circ$ $c = 25.380(2) \text{ Å}$ $\gamma = 101.070(5)^\circ$
Volume	4358.9(7) Å ³
Z	2
Density (calculated)	1.466 g/cm ³
Absorption coefficient	0.581 mm ⁻¹
F(000)	1960
Theta range for data collection	4.77 to 26.16°
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 15, -31 ≤ l ≤ 31
Reflections collected	72340
Independent reflections	17104 [R(int) = 0.0978]
Coverage of independent reflections	99.3%
Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	17104 / 171 / 1096
Goodness-of-fit on F ²	1.051
Final R indices [I > 2σ(I)]	R1 = 0.0997, wR2 = 0.2567
R indices (all data)	R1 = 0.1240, wR2 = 0.2787
Largest diff. peak and hole	0.892 and -0.816 eÅ ⁻³
R.M.S. deviation from mean	0.133 eÅ ⁻³

Section 5.4. Computational Methods

Computational calculations in **Section 2.2** were performed with the Gaussian 09 package.¹¹ The geometry of the free ligand **1**, $[\mathbf{1a}]^{2+}$, $[\mathbf{1b}]^{2+}$, and $[\mathbf{1c}]^{2+}$ were fully optimized by B3PW91¹² method with the 6-31G(d) basis set using atom coordinates from the solid state analysis. Harmonic frequency calculation was performed to validate the optimized geometry in local minimum on the potential energy surface by yielding zero imaginary vibrational frequency.

Table 5.20. Molecular orbitals and the relative energies of Ph- $[\mathbf{1a}]^{2+}$, 4-F-Ph- $[\mathbf{1b}]^{2+}$, and NⁱPr₂-substituted $[\mathbf{1c}]^{2+}$ phosphonium dications.

Compound	LUMO	HOMO	P-lone pair orbital
$[\mathbf{1a}]^{2+}$	- 0.31 eV	- 0.44 eV	- 0.47 eV
$[\mathbf{1b}]^{2+}$	- 0.31 eV	- 0.44 eV	- 0.47 eV
$[\mathbf{1c}]^{2+}$	- 0.28 eV	- 0.43 eV	- 0.47 eV

Theoretical analysis in **Section 3.1** was performed with the Gaussian 09¹⁵ suite of programs using default convergence criteria for optimization and an ultrafine integration grid. Cartesian coordinates of the structures optimized at B3LYP/6-31G* level are reported.

Table 5.21. Frontier molecular orbitals and the relative energies of P-monocation $[3]^+$, carbodicarbene-stabilized Ph- $[2a]^{2+}$, N^iPr_2 - $[2c]^{2+}$, and tBu -substituted $[2d]^{2+}$ phosphonium dications.

Compound	LUMO	HOMO	P-lone pair orbital
$[3]^+$	- 6.17 eV	- 10.60 eV	- 11.96 eV
$[2a]^{2+}$	- 9.25 eV	- 12.18 eV	- 14.00 eV
$[2c]^{2+}$	- 8.56 eV	- 11.87 eV	- 14.14 eV

All quantum chemical calculations in **Section 3.2** were performed with the Gaussian program package.¹³ Frequency calculations on all optimized structures confirmed that they represent minima on potential energy hypersurfaces. QTAIM analysis was carried out with the AIMAll software package.¹⁴

Table 5.22. Selected bonding and antibonding molecular orbitals for the trication model compound $[(2')_2P]^{3+}$.

Quantum chemical calculations in **Section 3.3** were performed with the Gaussian program package¹⁵ at the B3LYP/6-31G(d) level. Frequency calculations performed on the optimized structures revealed absence of imaginary frequency for the stable species, and a single imaginary frequency for each transition state. Intrinsic reaction coordinate calculations confirmed that the optimized transition states connect the structures of interest. Analysis of electron density and its Laplacian in the bond critical points and computation of delocalization index were performed with the AIMAll program package.¹⁶

Table 5.23. Activation energy values for reactions of carbodiphosphorane **1** and carbodicarbene **2** with MeN(PCl₂)₂.

Ligand	E _a : kJ/mol (kcal/mol)
1	54 (12.9)
2	44 (10.4)

Table 5.24. Change in various bond distances (r), their electron densities (ρ_{BCP}), Laplacians ($\nabla^2\rho_{\text{BCP}}$), and delocalization indexes (DI) as **1** is approaching P_A of MeN(PCl₂)₂. Values highlighted in green are for the transition state while those ones in orange are for the final product(s).

P _A -C _A				P _A -N _A				P _B -N _A			
r	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	DI	R	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	DI	r	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	DI
1.845	0.152	-0.157	0.93	/	/	/	/	1.534	0.208	1.236	1.58
2.071	0.105	-0.097	0.77	2.254	0.066	0.060	0.48	1.608	0.190	0.798	1.09
2.100	0.100	-0.074	0.73	2.179	0.075	0.044	0.53	1.616	0.188	0.758	1.07
2.200	0.082	-0.017	0.63	2.017	0.100	-0.030	0.65	1.640	0.181	0.658	1.00
2.300	0.068	0.018	0.54	1.933	0.115	-0.068	0.70	1.655	0.177	0.592	0.97
2.400	0.056	0.037	0.47	1.882	0.124	-0.044	0.73	1.666	0.174	0.551	0.95
2.500	0.047	0.047	0.40	1.848	0.130	0.006	0.75	1.675	0.172	0.515	0.93
3.000	0.020	0.039	0.18	1.770	0.147	0.203	0.81	1.698	0.165	0.429	0.89
3.500	0.009	0.020	0.08	1.744	0.153	0.282	0.83	1.708	0.162	0.394	0.87
4.000	0.004	0.010	0.03	1.733	0.155	0.316	0.84	1.713	0.161	0.380	0.86
∞	/	/	/	1.720	0.159	0.358	0.85	1.720	0.159	0.358	0.85

Table 5.25. Change in various bond distances (r), their electron densities (ρ_{BCP}), Laplacians ($\nabla^2\rho_{\text{BCP}}$), and delocalization indexes (DI) as **2** is approaching P_A of MeN(PCl₂)₂. Values highlighted in green are for the transition state while those ones in orange are for the final product(s).

P _A -C _A				P _A -N _A				P _B -N _A			
r	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	DI	R	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	DI	r	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	DI
1.860	0.152	-0.199	0.83	/	/	/	/	1.534	0.208	1.236	1.58
2.008	0.119	-0.154	0.73	2.264	0.065	0.061	0.47	1.608	0.190	0.791	1.09
2.100	0.100	-0.077	0.64	2.067	0.092	-0.002	0.61	1.633	0.183	0.687	1.02
2.200	0.083	-0.021	0.56	1.966	0.109	-0.058	0.68	1.649	0.179	0.616	0.98
2.300	0.069	0.013	0.49	1.905	0.120	-0.062	0.72	1.662	0.175	0.567	0.96
2.400	0.057	0.035	0.42	1.863	0.128	-0.018	0.74	1.671	0.173	0.530	0.94
2.500	0.047	0.045	0.36	1.833	0.133	0.038	0.76	1.678	0.171	0.502	0.92
3.000	0.019	0.037	0.16	1.762	0.148	0.228	0.81	1.700	0.164	0.423	0.89
3.500	0.008	0.018	0.07	1.737	0.154	0.305	0.83	1.710	0.161	0.389	0.87
4.000	/	/	0.02	1.720	0.159	0.359	0.85	1.725	0.157	0.340	0.85
∞	/	/	/	1.720	0.159	0.358	0.85	1.720	0.159	0.358	0.85

Section 5.5. Determination of the valence electron equivalent (γ)

Molecule: $[(2')_2P]^{3+}$

Summary of charge map (the total charge is +3)

Two resonance forms are required to reproduce this distribution

Portions: $[(0.3875) \times \mathbf{A}] + [(0.6125) \times \mathbf{B}]$

Such that charge on P = $(0.3875 \times -1) + (0.6125 \times +3) = +1.45$

Then $\gamma(P) = (0.3875 \times 10) + (0.6125 \times 2) = 5.10$

Molecules: **a** and **b**

Contributing resonance forms

For X = Cl, charges: P +1.12, Cl -0.53 (average)

This is reproduced by $[0.47 \times \mathbf{A}] + [0.53 \times \mathbf{B}]$

Such that charge on P = $(0.47 \times -1) + (0.53 \times +3) = +1.12$

Then $\gamma(P) = (0.47 \times 10) + (0.53 \times 2) = 5.76$

For X = Br, charges: P +0.88, Br -0.47 (average)

This is reproduced by $[0.53 \times \mathbf{A}] + [0.47 \times \mathbf{B}]$

Such that charge on P = $(0.53 \times -1) + (0.47 \times +3) = +0.88$

Then $\gamma(\text{P}) = (0.53 \times 10) + (0.47 \times 2) = 6.24$

Molecule: **c**

Summary of charge map (the total charge is +1)

Charge on P = +1.40

Four resonance forms are required to reproduce this distribution

Portions: $[(0.26) \times \mathbf{A}] + [(0.08) \times \mathbf{B}] + [(0.16) \times \mathbf{C}] + [(0.5) \times \mathbf{D}]$

Such that charge on P = $(0.26 \times -1) + (0.08 \times 0) + (0.16 \times +1) + (0.5 \times +3) = +1.40$

Then $\gamma(\text{P}) = (0.26 \times 10) + (0.08 \times 8) + (0.16 \times 6) + (0.5 \times 2) = 5.2$

Molecule: **d**

Summary of charge map (the total charge is -1)

Two resonance forms are required to reproduce this distribution

Portions: $[(0.38) \times \mathbf{A}] + [(0.62) \times \mathbf{B}]$

Such that charge on P = $(0.38 \times -1) + (0.62 \times +3) = +1.48$

Then $\gamma(\text{P}) = (0.38 \times 10) + (0.62 \times 2) = 5.04$

Molecule: **e**

Summary of charge map (the total charge is 0)

Three resonance forms are required to reproduce this distribution

Portions: $[(0.26) \times \mathbf{A}] + [(0.283) \times \mathbf{B}] + [(0.457) \times \mathbf{C}]$

Such that charge on P = $(0.26 \times -1) + (0.283 \times 0) + (0.457 \times +3) = +1.12$

Then $\gamma(\text{P}) = (0.26 \times 10) + (0.283 \times 8) + (0.457 \times 2) = 5.778$

Molecule: **f**

Summary of charge map (the total charge is -1)

Three resonance forms are required to reproduce this distribution

(P has 10 e) (P has 4 e) (P has 2 e)

Portions: $[(0.35) \times \mathbf{A}] + [(0.08) \times \mathbf{B}] + [(0.57) \times \mathbf{C}]$

Such that charge on P = $(0.35 \times -1) + (0.08 \times +2) + (0.57 \times +3) = +1.52$

Then $\gamma(\text{P}) = (0.35 \times 10) + (0.08 \times 4) + (0.57 \times 2) = 4.96$

Molecule: **g**

Summary of charge map (the total charge is -1)

Two resonance forms are required to reproduce this distribution

Portions: $[(0.4225) \times \mathbf{A}] + [(0.5775) \times \mathbf{B}]$

Such that charge on P = $(0.4225 \times -1) + (0.5775 \times +3) = +1.31$

Then $\gamma(\text{P}) = (0.4225 \times 10) + (0.5775 \times 2) = 5.38$

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- ¹ Stadlbauer, S.; Frank, R.; Maulana, I.; Lönnecker, P.; Kirchner, B.; Hey-Hawkins, E. *Inorg. Chem.* **2009**, *48*, 6072.
- ² Davies, A. R.; Dronsfield, A. T.; Haszeldine, R. N.; Taylor, D. R. *J. Chem. Soc., Perkin Trans.* **1973**, *1*, 379.
- ³ Schindbauer H. *Monatshefte für Chemie - Chemical Monthly* **1965**, *96*, 1936.
- ⁴ (a) Ramirez, F.; Desai, N. B.; Hansen, B.; McKelvie, N. *J. Am. Chem. Soc.*, **1961**, *83*, 3539; (b) Dyker, C. A.; Lavallo, V.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 3206.
- ⁵ Chaplin, A. B.; Weller, A. S. *Eur. J. Inorg. Chem.* **2010**, *32*, 5124.
- ⁶ Coucouvanis, D. *Inorganic Syntheses [electronic resource]*. New York: Wiley-Interscience: 2002, p 85. K₂CO₃ was replaced by Na₂CO₃ in order to obtain the target Na[BAr^F₄].
- ⁷ SMART version 5.628; Bruker AXS Inc.: Madison, WI, **2001**.
- ⁸ SAINT+ version 6.22a; Bruker AXS Inc.: Madison, WI, **2001**.
- ⁹ Sheldrick, G. M. SADABS; **1996**.
- ¹⁰ SHELXTL version 5.1; Bruker AXS Inc.: Madison, WI, **1997**.
- ¹¹ Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2010**.
- ¹² (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; (b) Perdew, J. P. In *Electronic Structure of Solids '91* (Eds: P. Ziesche, H. Eschrig) Akademie Verlag: Berlin, **1991**, pp 11; (c) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B: Condens. Matter* **1996**, *54*, 16533; (d) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.;

Singh, D. J.; Fiolhais, C. *Phys. Rev. B: Condens. Matter* **1992**, *46*, 6671; (e) Perdew, J. P. J.; Chevary, A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B: Condens. Matter* **1993**, *48*, 4987.

¹³ Frisch, M. J. *et al.* Gaussian 09 Revision D.01, Gaussian Inc. Wallingford, CT, **2009**.

¹⁴ Keith, T. A. AIMAll (Version 27.09.15), TK Gristmill Software, Overland Park KS, USA, **2015** <http://aim.tkgristmill.com>.

¹⁵ Frisch, M. J. *et al.* Gaussian 09 Revision D.01, Gaussian Inc. Wallingford, CT, **2013**.

¹⁶ Keith, T. A. AIMAll (Version 14.11.23), TK Gristmill Software, Overland Park KS, USA, **2014** (<http://aim.tkgristmill.com>).

CHAPTER 6

Overall Conclusions and Future Work

First, we demonstrated that the combination of carbodiphosphorane ligand **1**, with phenyl-based substituents yielded transient phosphonium dications $[\mathbf{1a}]^{2+}$ and $[\mathbf{1b}]^{2+}$, whose highly electrophilic nature was subsequently employed for the C-F bond activation of trifluorotoluene and $[\text{BAr}^{\text{F}}_4]^-$ anion (Scheme 6.1). The observed reactivity has no precedent in the P(III) chemistry, and it was attributed to the low-lying LUMOs of $[\mathbf{1a}]^{2+}$ and $[\mathbf{1b}]^{2+}$.

Scheme 6.1. C-F bond cleavage of trifluorotoluene induced by transient phosphonium dications $[\mathbf{1a}]^{2+}$ and $[\mathbf{1b}]^{2+}$.

By replacing the carbodiphosphorane **1**, with a more nucleophilic and electron-donating carbodicarbene ligand **2**, we prepared a series of stable two-coordinate P(III)-based dications, as well as the first example of a triply charged phosphonium ion $[(\mathbf{2})_2\text{P}]^{3+}$ (Scheme 6.2). According to the computational studies, the combination of the increased overall positive charge and amino-for-aryl/alkyl ligand replacement resulted in the significant stabilization of LUMOs with an overall reduction of a HOMO-LUMO gap of P-dications.

Scheme 6.2. Ligand replacement, P-based di- and trications, respectively.

Attempts to generate a P-based tetracation by bridging two phosphonium ions, revealed a novel P-N bond cleavage route that proceeds via an S_N2'-like mechanism (Scheme 6.3). This represents a unique reactivity mode for both carbenes and bis(dichlorophosphino)amines.

Scheme 6.3. Carbene-induced P-N bond cleavage via an S_N2'-like mechanism.

Lastly, modification of electronic properties of phosphonium ions enabled the activation of enthalpically strong E-H (E = B, Si, C) bonds, leading to the formation of bond insertion and hydride-abstraction products. The described reactivity suggested that P-dications could be to phosphonium chemistry as cyclic(alkyl)(amino) carbenes (cAACs) are to carbene chemistry.¹

Scheme 6.4. E-H (E = B, Si, C) bond activation by phosphonium dications.

While phosphonium dications activated enthalpically strong hydridic σ -bonds, their increased electrophilicity appeared inadequate towards more challenging homopolar H-H and C-C bonds.² To expand the substrate scope beyond polar covalent bonds, further efforts to reduce the HOMO-LUMO gap of phosphonium salts are recommended. These should aim to destabilize the HOMO³ while preserving the availability of LUMO imposed by the increased overall positive charge. This could be potentially accomplished by combining ancillary substituents based on relatively electropositive boron and silicon

atoms⁴ with carbodicarbene ligand, which appeared crucial in stabilizing the two-coordinate doubly, and even triply charged P-species. The improved oxidative flexibility of P(III)/P(V) redox pair could not only deliver the insertion into nonpolar σ -bonds, but also promote the P-centered reductive elimination, which has yet to be observed in the chemistry of phosphonium ions.⁵

¹ Lavallo, V.; Canac, Y.; Präsang, C.; Donnadiou, B.; Bertrand, G. *Angew. Chem.* **2005**, *117*, 5851; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705.

² Phosphenium dications $[2a]^{2+}$, $[2c]^{2+}$, and $[2d]^{2+}$ were chemically inert towards insertion into H-H and C-C bonds of H₂ and 1,2-biphenylene, respectively.

³ Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

⁴ (a) Zhu, J.; Lin, Z.; Marder, T. B. *Inorg. Chem.* **2005**, *44*, 9384; (b) Braunschweig, H.; Dewhurst, R. D.; Schneider, A. *Chem. Rev.* **2010**, *110*, 3924.

⁵ For potential redox-based bond modifications at phosphorus, see: (a) Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, *134*, 11330; (b) Zeng, G.; Maeda, S.; Taketsugu, T.; Sakaki, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 4633; (c) Cui, J.; Li, Y.; Ganguly, R.; Inthirarajah, A.; Hirao, H.; Kinjo, R. *J. Am. Chem. Soc.* **2014**, *136*, 16764; (d) Zhao, W.; McCarthy, S. M.; Lai, T. Y.; Yennawar, H. P.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136*, 17634; (e) Robinson, T. P.; De Rosa, D. M.; Aldridge, S.; Goicoechea, J. M. *Angew. Chem. Int. Ed.* **2015**, *54*, 13758.