ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2016, **52**, 5746

Received 26th February 2016,
Accepted 29th March 2016

DOI: 10.1039/c6cc01759b

www.rsc.org/chemcomm

# Protonation of carbene-stabilized diphosphorus: complexation of $HP_2^+$†

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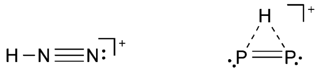
**Reaction of carbene-stabilized diphosphorus, L:P–P:L (5) (L: = :C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$) with pyridine hydrochloride yields [L:(H)P–P:L]Cl (6), a salt containing the $HP_2^+$ cation—the elusive phosphorus analogue of the well known diazonium cation, $HN_2^+$. In addition to reporting the synthesis and structure, the nature of (6) was further probed by DFT computations. Interestingly, carbenes may be employed to deprotonate (6), affording the starting material (5).**

In contrast to aromatic diazonium cations, $RN_2^+$ (R = aryls), which have been extensively utilized in palladium-catalyzed cross-coupling reactions,[1] the parent diazonium cation, $HN_2^+$, is elusive in the condensed state, having only been observed in the gas phase.[2] Similarly, the phosphorus analogue of $HN_2^+$, the parent phosphaphosphenium (or phosphanediylphophenium) cation,[3] $HP_2^+$, is also highly reactive and has only been investigated in the gas phase[4] or computationally.[5] Ion cyclotron resonance spectroscopy (ICR) studies have suggested that $HP_2^+$ may be prepared (in the gas phase) by reaction of $PH_3$ with $P^+$ or $H_2P^+$ ions.[4a] While direct protonation of $P_2$ to produce $HP_2^+$ has been theoretically proposed,[5c] experimental studies have not been reported. In contrast to $N_2$, which undergoes end-on (or linear) protonation (Fig. 1a), $P_2$ is predicted to favor an edge-on (or cyclic) $HP_2^+$ structure (Fig. 1b).[5c]

As phosphorus analogues of carbenes, phosphenium ions, $[R_2P:]^+$, have been extensively utilized as ligands in the synthesis of coordination complexes.[6] In addition, phosphenium ions have also functioned as electrophiles in reactions with Lewis bases and transition metals.[6c,7] Employing a very sterically demanding carbene, Bertrand, in an interesting turn, recently stabilized the highly reactive parent phosphenium cation, $H_2P^+$.[8]



(a) (b)

Fig. 1 (a) End-on protonation of $N_2$; (b) edge-on protonation of $P_2$.

While a series of carbene-stabilized $P_n$ ($n$ = 1–4, 8, and 12) molecules have recently been reported,[9] carbene-stabilized diphosphorus L:P–P:L [L: = :C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$][9b,10] (5), prepared *via* potassium graphite reduction of L:$PCl_3$, is particularly relevant as it provides a convenient platform to study the protonation of diphosphorus. Herein, we report the synthesis,[11] structure,[11] and computations[11] of carbene-stabilized $HP_2^+$, $[L:(H)P–P:L]^+Cl^-$; [L: = :C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$] (6).

We have previously utilized $HCl{\cdot}NEt_3$ to protonate the C2 carbon atoms of both anionic NHDC–borane complexes (1) and $SiCl_3$-modified (at C4 carbon) N-heterocyclic carbenes (2), giving abnormal carbene (aNHC)-based borane (3) and silicon chloride derivatives (4), respectively (Fig. 2, R = 2,6-diisopropylphenyl).[12] These studies encouraged us to investigate a series of amine-complexed HCl salts. Consequently, we discovered that pyridine hydrochloride salt ($HCl{\cdot}NC_5H_5$) is an ideal protonation agent for carbene-stabilized $P_2$ (5).

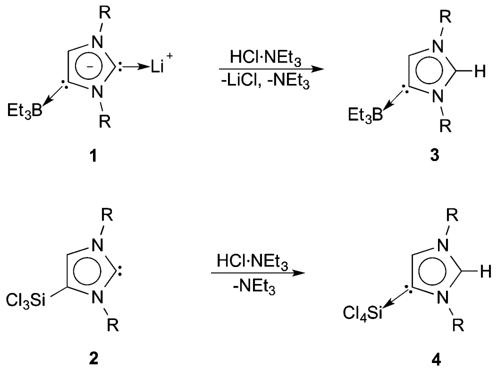


Fig. 2 $HCl{\cdot}NEt_3$ as a protonation agent in the synthesis of aNHC-based main group complexes.

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† Electronic supplementary information (ESI) available: Synthetic and computational details and structural and spectral characterization. CCDC 1454832. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc01759b

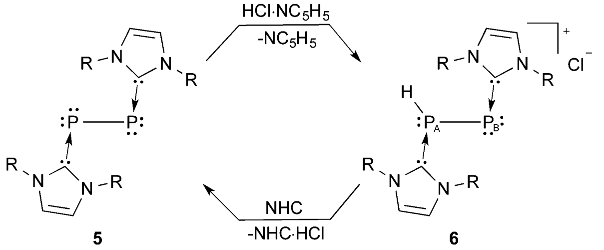

Fig. 3 Synthesis of carbene-stabilized $HP_2^+$ ion **6** and its deprotonation to give **5**.

Reaction of **5** (red crystals) with $HCl·NC_5H_5$ (1 : 1 molar ratio) in toluene at ambient temperature quantitatively gives **6** (yellow powder) (Fig. 3, R = 2,6-diisopropylphenyl). Significantly, the 1 : 2 reaction of **5** with $HCl·NC_5H_5$ does not result in the diprotonated salt $[L{:}(H)P–P(H){:}L]^{2+}[Cl^-]_2$, affording only **6**. Computations, however, suggest that the free $[H_2P_2]^{2+}$ dication is stable toward proton loss.[5a] Both $H_2S$ and $H_2O$ have been reported to deprotonate $HP_2^+$ (in the gas phase) affording free $P_2$ molecules.[4c] Notably, we observed that the N-heterocyclic carbene [NHC = $:C[Pr^iNC(Me)]_2$] serves to deprotonate **6**, quantitatively giving **5** (Fig. 3). Interestingly, **6** is less air- and moisture-sensitive than **5**. In addition, **5** shows two reversible oxidations at $E_{1/2} = -1.408$ and $-0.178$ V (*vs.* $Fc^+/Fc$),[13] whereas **6** exhibits a quasi-reversible redox couple at $E_{1/2} = -1.60$ V (*vs.* $Fc^+/Fc$; scan rate 100 mV $s^{-1}$) (Fig. S1 and S2, ESI†).

In contrast to the singlet $^{31}P$ NMR resonance of **5** (−52.4 ppm), the $^{31}P\{^1H\}$ spectrum of **6** [Fig. 4(I)] shows two coupled resonances at −105.2 (for $P_A$, Fig. 3) and −109.8 (for $P_B$, Fig. 3) ppm ($|^1J_{PP}|$ = 235 Hz). The $^1H$-coupled $^{31}P$ NMR spectrum of **6** is shown in Fig. 4(II) with $|^1J_{P(A)-H}|$ = 204 Hz and $|^2J_{P(B)-H}|$ = 11 Hz, which are consistent with the P–H coupling constants observed in $^1H$ NMR spectrum of **6** ($|^1J_{P(A)-H}|$ = 205 Hz and $|^2J_{P(B)-H}|$ = 10 Hz).

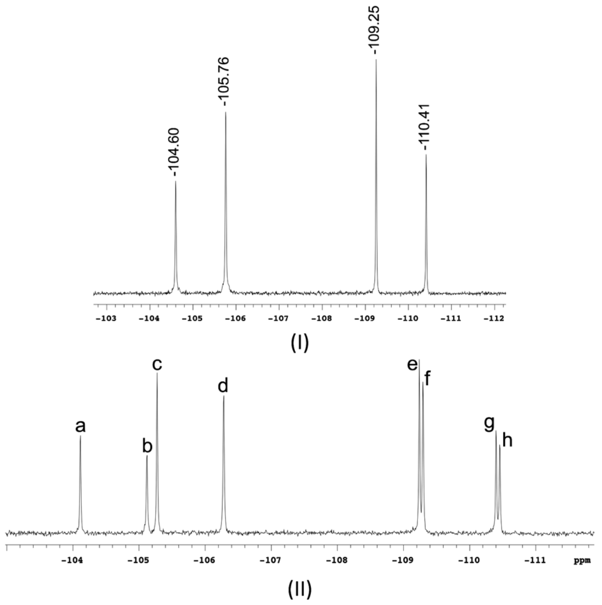

Fig. 4 (I) Proton-decoupled $^{31}P$ NMR spectrum of **6**; (II) proton-coupled $^{31}P$ NMR spectrum of **6** [$\delta$ (ppm): a = −104.11; b = −105.12; c = −105.28; d = −106.28; e = −109.24; f = −109.29; g = −110.40; h = −110.45].

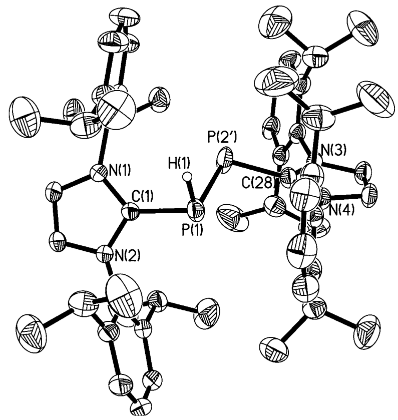

Fig. 5 Molecular structure of $\mathbf{6}^+$ [thermal ellipsoids represent 30% probability; hydrogen atoms on carbons and the disordered P(2) atom (with 30.0% occupancy) omitted for clarity]. Selected bond distances (Å) and angles (deg): P(1)–C(1) = 1.830(3), P(1)–P(2′) = 2.160(6), P(1)–P(2) = 2.098(13), P(2′)–C(28) = 1.795(7), P(2)–C(28) = 1.760(14); C(1)–P(1)–P(2′) = 97.87(19), C(1)–P(1)–P(2) = 95.2(4), P(1)–P(2′)–C(28) = 101.1(3), P(1)–P(2)–C(28) = 104.7(5), C(1)–P(1)–H(1) = 95(2), H(1)–P(1)–P(2′) = 99(2), H(1)–P(1)–P(2) = 114(2).

Single crystal X-ray structural analysis shows that the $HP_2^+$ core in **6** adopts a bent geometry due to the coordination of two carbene ligands (Fig. 5).[11] The H(1) atom was located from the difference Fourier map. The two-coordinate phosphorus atom is disordered [denoted as P(2) (30.0% occupancy) and P(2′) (70.0% occupancy), respectively] and adopts a bent geometry, whereas the three-coordinate phosphorus atom, P(1), has a pyramidal geometry. The average P–P bond distance of **6** (2.141 Å) is shorter than the P–P single bond distances in **5** (2.205 Å) and $P_4$ (2.21 Å),[9b,14] but longer than typical P=P double bond distances in diphosphenes (*ca.* 2.00 Å).[15] Notably, the short P–P single bonds have also been observed in 1,2-diborylphosphanes (*ca.* 2.11 Å)[16] and in a neutral diphosphanide $[(^{Cl}Im^{Dipp})P–P(Cl)(Dipp)]$ ($^{Cl}Im^{Dipp}$ = 4,5-dichloro-1,3-bis(Dipp)-imidazol-2-yl; Dipp = 2,6-diisopropylphenyl) [2.1327(9) Å] and its cationic derivative $[(^{Cl}Im^{Dipp})P–P(PMe_3)(Dipp)]^+$ [2.151(1) Å].[17] The latter may be regarded as a phosphaphosphenium P–PR (R = Dipp) ion, which is coordinated by two Lewis base ligands (*i.e.*, carbene and phosphine). The single carbene-complexed phosphaphosphenium $[(^{Cl}Im^{Dipp})P{=}P(Dipp)]^+$ containing a P=P double bond [2.038(1) Å] has also been reported by the same group.[17]

While the average P–C(28) bond distance in **6** (1.784 Å) compares to that in **5** (1.750 Å), the P(1)–C(1) bond distance (1.830 Å) in **6** is elongated to the range for normal P–C single bonds.[9b] The P–C bond elongation may be ascribed to the formation of P(1)–H(1) bond, inhibiting the p–π back donation of the lone pair of electrons of P(1) into the vacant p orbital of C(1). It is noteworthy that this type of elongation has also been observed in a cyclic $L_2P_2$-complexed boronium salt, $[L{:}P(\mu\text{-}BH_2)P{:}L]^+[B_2H_7]^-$ [L: = $:C\{N(2,6\text{-}Pr^i_2C_6H_3)CH\}_2$] (1.83 Å).[18]

In an effort to further probe the nature of **6**, DFT computations at the B3LYP/6-311+G** level on the simplified model $[\mathbf{6\text{-}Me}]^+$ [L: = $:C\{N(Me)CH\}_2$, Fig. S3, ESI†] were performed.[11] While the $C_{NHC}–P_H$ bond distance for $[\mathbf{6\text{-}Me}]^+$ (1.841 Å) compares well to that for **6** (1.830 Å), both the P–P bond (2.225 Å) and $P(2)–C_{NHC}$

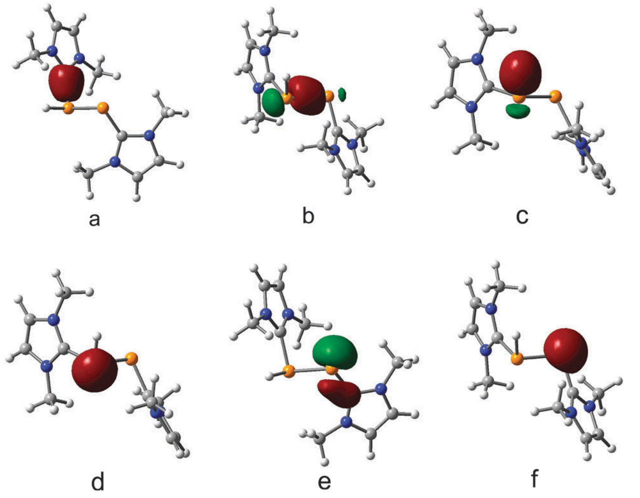

Fig. 6 Selected localized molecular orbitals (LMOs) of **[6-Me]**$^+$: (a) $C_{NHC}$–P(H) σ-bonding orbital; (b) P–P σ-bonding orbital; (c) P–H σ-bonding orbital; (d) lone pair orbital of three-coordinate P; (e) and (f) lone pair orbitals of two-coordinate P.

(1.815 Å) in **[6-Me]**$^+$ (Fig. S3, ESI†) are longer than those in **6** [$d_{\text{P–P}}$ = 2.141 Å (av); $d_{\text{C(28)–P}}$ = 1.784 Å (av)], respectively (Fig. 5). This suggests that the electronic and steric properties of the ligand may play a partial role in the change of the P–P and P–C bond distances. For instance, in **6** the imidazole ring, bound to the two coordinate phosphorus, is almost coplanar to the central P–P bond with a N(3)–C(28)–P(2)–P(1) torsion angle of 170.1° (av), which should favour p–π back donation of the lone pair of electrons of phosphorus into the empty p orbital of the carbene carbon [*i.e.*, C(28)] (Fig. 5). However, for **[6-Me]**$^+$, the corresponding N(6)–C(12)–P(2)–P(1) torsion angle of 142.46° (Fig. S3, ESI†) somewhat decreases the p–π back donation mentioned above (as shown in Fig. 6e) and thus gives a longer P(2)–$C_{NHC}$ bond.

Selected localized molecular orbitals (LMOs) of **[6-Me]**$^+$ are presented (Fig. 6). Natural bond orbital (NBO) analysis shows that the positive charge is largely delocalized [P(1) bears only +0.25 positive charge]. The WBI of the central P–P single bond (1.021), in which P(1) and P(2) have 85.0% and 89.3% p character, respectively, (Fig. 6b), compares well to that of **5** (1.004).[9b] While the P(1)–C(7) bond (Fig. S3, ESI†) is a typical single bond (WBI = 0.937, Fig. 6a), the P(2)–C(12) bond (Fig. S3, ESI†) has modest double bond character (WBI = 1.128). The P–C σ bond polarization is *ca.* 67% toward carbon and *ca.* 33% toward phosphorus.

Considering the cyclic $HP_2^+$ structure (Fig. 1b) is favoured in the gas phase,[5c] we also computed the model of **[6-Me]**$^+$ in $C_2$ symmetry, containing a bridging hydrogen between two phosphorus atoms. Our study shows that the model in $C_2$ symmetry represents a transition state, which is 29.1 kcal mol$^{-1}$ higher in energy than the model with a terminal hydrogen and thus does not support a dynamic hydrogen shift between two phosphorus atoms.

We have synthesized the first carbene-stabilized parent phosphaphosphenium ion ($HP_2^+$) (**6**) *via* $HCl{\cdot}NC_5H_5$ protonation of carbene-complexed diphosphorus (**5**). Both structural and computational studies show that the $HP_2^+$ core in **6** adopts a bent geometry. The redox capabilities of this unique carbene-stabilized $HP_2^+$ cation are under investigation.

We are grateful to the National Science Foundation for support: CHE-1565676 (G. H. R., Y. W.) and CHE-1361178 (H. F. S.). We also want to thank Prof. Todd C. Harrop for his assistance with the cyclic voltammetric measurements.

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