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Phosphine and carbene azido-cations: $[(L)N_3]^+$ and $[(L)_2N_3]^+\dagger$ Daniel Winkelhaus,^{‡a} Michael H. Holthausen,^{‡a} Roman Dobrovetsky^b
and Douglas W. Stephan^{*a}

The cationic N_3 -species $[(p\text{-HC}_6\text{F}_4)_3\text{PN}_3]^+$ (**1**) featuring a perfluoro-arene phosphonium group serves as a N_3^+ -source in stoichiometric reactions with several Lewis bases (L) allowing for the stepwise formation of $[(L)N_3]^+$ and $[(L)_2N_3]^+$ cations (L = phosphine, carbene) with liberation of $(p\text{-HC}_6\text{F}_4)_3\text{P}$. X-Ray diffraction analysis and computational studies provide insight into the bonding in these remarkably stable azido-cations.

Introduction

A major component of the recent renaissance in p-block chemistry¹ has been the use of neutral, two electron donors like carbenes or phosphines for the stabilization of homoatomic, low valent main group element fragments.² Most recently Cummins used an anthracene stabilized P_2 for the synthesis of an aromatic $[P_2N_3]^+$.³ Species of the form $(L)_2E_2$ (E = B,⁴ C,⁵ Si,⁶ Ge,⁷ Sn,⁸ N,⁹ P,¹⁰ As,¹¹ Sb;¹² L = carbene, phosphine) have been prepared affording ligand stabilization of unique diatomic main group fragments. In addition, the groups of Robinson, Bertrand and Roesky have exploited these donors for isolation of dications and radical cations of type $[(\text{carbene})_2E_2]^{n+}$ (E = C,⁵ P,¹³ As;¹⁴ n = 1, 2) while Burford, Weigand, Jones and Grützmacher prepared $[(\text{carbene})_2P_3]^{+15}$ or bicyclic $[(L)_2P_4]^{2+}$ species (L = carbene, AsPh_3 , PPh_3).¹⁶ The latter compound is of special interest since L can be exchanged for more basic donors. A similar donor exchange was reported for $[(\text{Ph}_3\text{P})\text{PPh}_2]^+$ affording $[(\text{carbene})\text{PPh}_2]^+$.¹⁷ The nature of these and related systems, especially the L-E and E-E bonding, has sparked vigorous debate.¹⁸

Our recent studies of highly electrophilic phosphonium cations (EPCs) have demonstrated that species such as the fluorophosphonium cation $[(\text{C}_6\text{F}_5)_3\text{PF}]^{+19}$ exhibit remarkable Lewis acidity and thus act as effective catalysts in a range of Lewis acid mediated transformations.²⁰ At the same time, we were motivated to probe the utility of these EPCs as synthons for cationic

azides. Herein we describe the synthesis of $[(p\text{-HC}_6\text{F}_4)_3\text{PN}_3]^+$ (**1**) and its use as a synthon to species of the form $[(L)N_3]^+$ and $[(L)_2N_3]^+$ (L = phosphine, carbene).

Results and discussion

Compound $[(p\text{-HC}_6\text{F}_4)_3\text{PN}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) was readily prepared in quantitative yield by the reaction of $[(p\text{-HC}_6\text{F}_4)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ with Me_3SiN_3 in CH_2Cl_2 (Scheme 1).§ The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of **1** in CD_2Cl_2 gives rise to a broad singlet resonance ($\delta(^{31}\text{P}) = 17.5$ ppm, $\Delta\nu_{1/2} = 30$ Hz).

The presence of the *para* hydrogen substituents in **1** is crucial as the fully fluorinated derivative $[(\text{C}_6\text{F}_5)_3\text{PF}]^+$ is prone to nucleophilic attack at this position.²¹ The formulation of compound **1** was subsequently confirmed by an X-ray crystallographic study (Fig. 1).

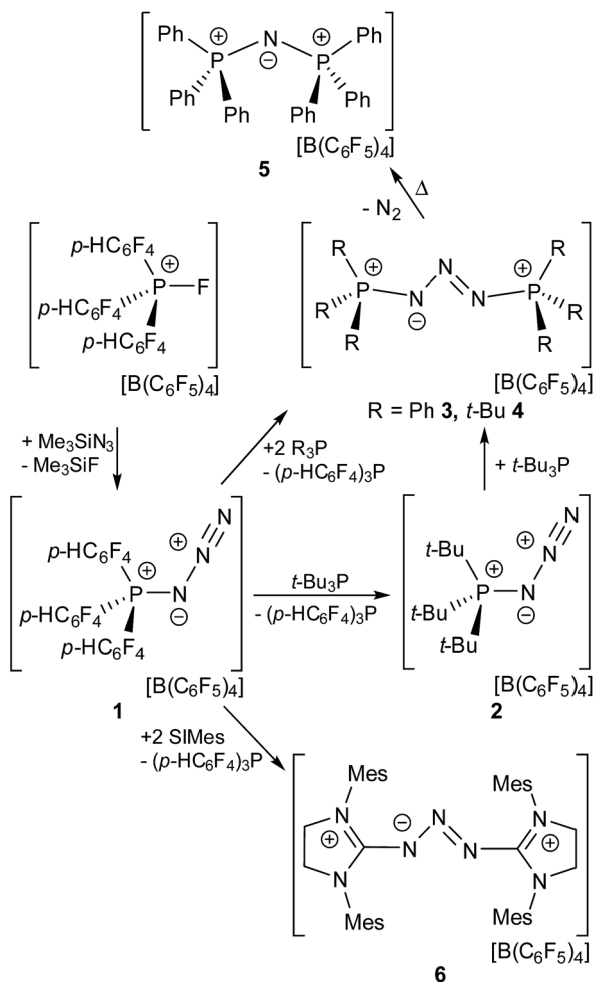
The molecular structure of **1** shows a distorted tetrahedral environment about the phosphorus atom with angles at P ranging from $102.3(1)$ – $112.6(1)^\circ$. The P(1)–N(1) bond length of $1.651(2)$ Å is shorter than those observed in azido-substituted phosphonium cations (1.67 Å)²² and azido-phosphines (1.73 Å),²³ consistent with the electron deficient nature of the phosphonium center and the strongly polarized nature of the P–N bond. The azido moiety shows an N(1)–N(2)–N(3) angle that slightly deviates from the ideal 180° ($172.4(2)^\circ$) while the N(1)–N(2) ($1.260(2)$ Å) and N(2)–N(3) bond length ($1.114(2)$ Å) are in the expected range for azide substituents. Compound **1** is a rare example of a crystallographically characterized salt of a cationic azido-phosphonium species²⁴ while several neutral, azido-substituted P(III) and P(V) derivatives have been reported to date.²⁵ Other examples of monocationic nitrogen species, reported in the literature, include diazonium ions,²⁶ the homoleptic $[\text{N}_5]^+$ of Christie,²⁷ $[\text{N}_2\text{F}]^+$,²⁸ Hünig's stable tri-azanium ions $[\text{R}_2\text{N}_3\text{R}_2]^{+29}$ and aminodiazonium ions of the form $[(\text{R}_2\text{N})\text{N}_2]^{+30}$ (R = H, silyl, alkyl, aryl).

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Scheme 1 Preparation of 1–6.

To gain further insights into the nature of **1**, the geometry of the cation was optimized at the wb97XD/def2-TZV level of theory (see ESI†). The *p*-type HOMO of **1** is located at the P-bonded N atom while the LUMO is part of two sets of degenerated π^* -type orbitals involving the *p*-HC₆F₄-groups (LUMO to LUMO+9). The first accessible acceptor orbital is a π^* -type orbital located at the terminal N₂ moiety (LUMO+10). This stands in contrast to other EPCs where the accessible acceptor orbital involves the P–F σ^* orbital at the P center.¹⁹ The corresponding P–N σ^* orbital in **1** is much higher in energy (LUMO+11). NBO analysis reveals that the P–N single bond in **1** is occupied by 1.92 electrons, while the P-bonded N atom features two lone pairs of *p* and *sp*^{0.69} type. Donation of electron density from these lone pairs into σ^* orbitals of the adjacent P–C bonds occurs ($\text{LP}(\text{p})_{\text{N1}} \rightarrow \sigma^*_{\text{P-C7}}$ 11.2 kcal mol^{−1}, $\text{LP}(\text{p})_{\text{N1}} \rightarrow \sigma^*_{\text{P-C7}}$ 7.4 kcal mol^{−1}, $\text{LP}(\text{sp}^{0.69})_{\text{N1}} \rightarrow \sigma^*_{\text{P-C7}}$ 3.7 kcal mol^{−1}). The secondary interactions of these lone pairs may account for the observed shortening of the P–N bond in **1** in comparison to other P-azido species.^{22,23}

Compound **1** reacts with the Lewis base *t*-Bu₃P in CH₂Cl₂ solution (Scheme 1).§ The ³¹P{¹H} NMR spectrum of the reaction mixture showed a septet resonance at $\delta(^{31}\text{P}) = -72.3$ ppm (³*J*_{PF} = 36.4 Hz)^{19b} which corresponds to (*p*-HC₆F₄)₃P and a new

singlet resonance at low field ($\delta(^{31}\text{P}) = -85.9$ ppm) which is in the typical chemical shift range for an *N*-substituted trialkylphosphonium derivative.³¹ Collectively, these observations indicate the formal transfer of the N₃⁺-moiety in **1** to *t*-Bu₃P yielding [*t*-Bu₃PN₃][B(C₆F₅)₄] (**2**) which was isolated in 98% yield. The nature of **2** was confirmed by X-ray single crystallography and the metrics were found similar to **1** (see ESI†). Interestingly, **2** and **1** are very stable and do not show any signs of degradation on heating in C₆D₅Br solution to 100 °C for 24 h. Attempts to independently synthesize **2** from the reaction of [*t*-Bu₃PF][B(C₆F₅)₄]¹⁹ with Me₃SiN₃ failed even after prolonged reaction times at 100 °C in C₆D₅Br solution. This reflects the increased steric demand of the [*t*-Bu₃PF]⁺ cation.

The corresponding reaction of **1** with Ph₃P in CH₂Cl₂ was monitored by ³¹P{¹H} NMR spectroscopy revealing the complete consumption of Ph₃P and the liberation of only 0.5 equivalents of (*p*-HC₆F₄)₃P, leaving approximately 50% of **1** unreacted. Addition of another equivalent of Ph₃P resulted in its complete consumption. Collectively, this indicates the formation of a bis-adduct [(Ph₃P)₂(N₃)]+[B(C₆F₅)₄] (**3**, Scheme 1). While the proposed intermediate [Ph₃PN₃]⁺ was independently synthesized by the reaction of [Ph₃PF][B(C₆F₅)₄]^{20c} and Me₃SiN₃ (see ESI†), this species was not observed in the reaction of **1** with Ph₃P. This indicates that reaction of [Ph₃PN₃]⁺ with a second equivalent of Ph₃P is rapid, in agreement with Wiberg who described the [(Ph₃P)₂(N₃)]⁺ cation in 1967.^{24c} Compound **3** was isolated in high yields (97%). The *t*-Bu-substituted analog **4** was obtained from **1** with two equivalents of *t*-Bu₃P or by reaction of **2** with one equivalent of *t*-Bu₃P (Scheme 1). Species **4** was also obtained by reaction of **3** with two equivalents of *t*-Bu₃P with concurrent release of Ph₃P. All methods furnish **4** in high yields (76–99%). Compounds **3** and **4** show ³¹P{¹H} NMR resonances at 30.6 and 56.5 ppm that are between the chemical shift ranges of phosphinimine and *N*-substituted phosphonium derivatives.³¹ X-Ray structure determination confirmed the formulations (Fig. 2). The P₂N₃-moiety adopts a W-shaped geometry with all five atoms almost located within one plane (largest deviation: **3**: 0.013(2) Å for N₂, **4**: 0.039(1) Å for N₂). The acute N–N–N angles (**3**: 113.2(4)°, **4**: 110.8(1)°) are in the typical range for phosphazides.³² The two P–N–N angles in each compound are **3**: 114.5(3)°/114.7(3)°; **4**: 118.1(1)°/118.9(1)° with the larger angles in **4** reflecting the increased steric congestion. Similarly, the P–N bond lengths of 1.648(3) Å and 1.643(3) Å and 1.675(2) Å and 1.673(2) Å seen in **3** and **4**, respectively, range between those of phosphinimine and *N*-substituted phosphonium derivatives.³¹ The N–N bonds in **3** and **4** were found to be 1.298(4) Å, 1.309(4) Å and 1.309(2) Å, 1.300(2) Å,²⁸ which are intermediate between single and double bond distances. A similar conformation is observed for several crystallographically characterized organo-phosphazides R₃PN₃R,³² formed in the initial step of a Staudinger reaction.³³

It is of interest to note that, similar to **1** and **2**, **4** is thermally stable and can be heated to 120 °C in C₆D₅Br solution over several days without decomposition. In contrast, compound **3** is not temperature stable, decomposing quantitatively with release of N₂ within 3 h at 100 °C.^{24c} The ³¹P{¹H} NMR spectrum shows only one resonance at $\delta(^{31}\text{P}) = 21.1$ ppm assignable to



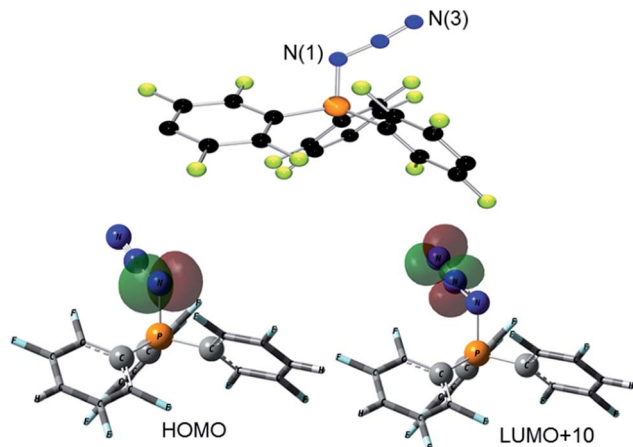


Fig. 1 POV-ray depiction of the cation in **1** (top). Hydrogen atoms are omitted for clarity. Selected bond distances and angles: P(1)–N(1) 1.651(2), P(1)–C(13) 1.783(2), P(1)–C(1) 1.789(2), P(1)–C(7) 1.789(2), N(1)–N(2) 1.260(2), N(2)–N(3) 1.114(2), N(1)–P(1)–C(13) 111.6(2), N(1)–P(1)–C(1) 102.3(2), C(13)–P(1)–C(1) 112.6(2), N(1)–P(1)–C(7) 109.8(2), C(13)–P(1)–C(7) 110.5(2), C(1)–P(1)–C(7) 109.7(2), N(2)–N(1)–P(1) 120.9(2), N(3)–N(2)–N(1) 172.4(2). Graphical presentation of the HOMO and LUMO+10 of **1** calculated at the wB97XD/def2-TZV level of theory (surface iso-value = 0.05).

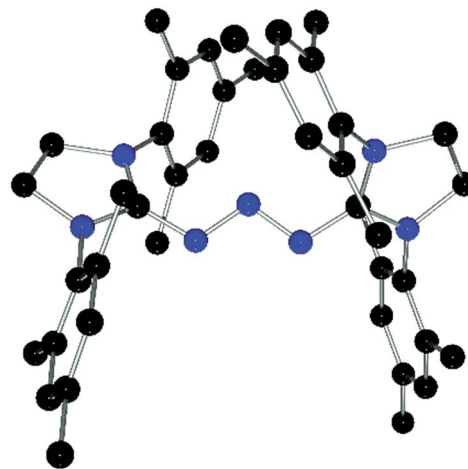


Fig. 3 POV-ray depiction of the cation in **6**. Hydrogen atoms are omitted for clarity. Selected bond distances and angles: C(1)–N(4) 1.332(3), C(1)–N(5) 1.346(2), C(1)–N(1) 1.359(2), C(22)–N(7) 1.335(2), C(22)–N(6) 1.337(2), C(22)–N(3) 1.369(2), N(1)–N(2) 1.309(2), N(2)–N(3) 1.311(2), N(4)–C(1)–N(5) 111.1(2), N(4)–C(1)–N(1) 119.3(2), N(5)–C(1)–N(1) 129.4(2), N(7)–C(22)–N(6) 111.7(2), N(7)–C(22)–N(3) 119.9(2), N(6)–C(22)–N(3) 128.2(2), N(2)–N(1)–C(1) 113.6(2), N(1)–N(2)–N(3) 110.4(2), N(2)–N(3)–C(22) 111.9(2).

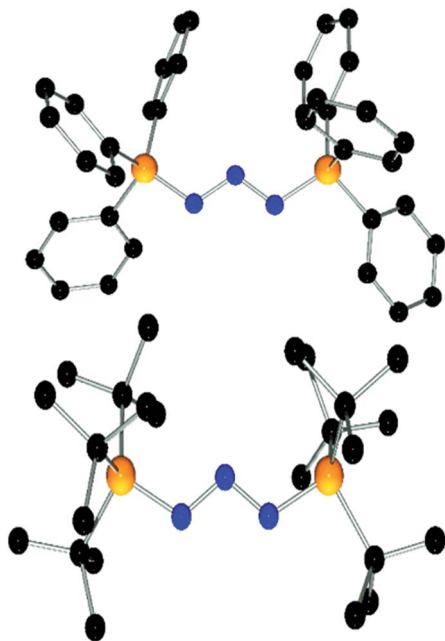


Fig. 2 POV-ray depiction of the cations in **3** (top) and **4** (bottom). Hydrogen atoms are omitted for clarity. Selected bond distances and angles for **3**: N(1)–P(1) 1.648(3), N(3)–P(2) 1.643(3), N(1)–N(2) 1.298(4), N(2)–N(3) 1.309(4), N(2)–N(1)–P(1) 114.5(3), N(1)–N(2)–N(3) 113.2(4), N(2)–N(3)–P(2) 114.7(3), for **4**: P(1)–N(3) 1.675(2), P(2)–N(1) 1.673(2), N(1)–N(2) 1.309(2), N(3)–N(2) 1.230(2), N(2)–N(1)–P(2) 118.1(2), N(2)–N(3)–P(1) 118.9(2), N(3)–N(2)–N(1) 110.8(2).

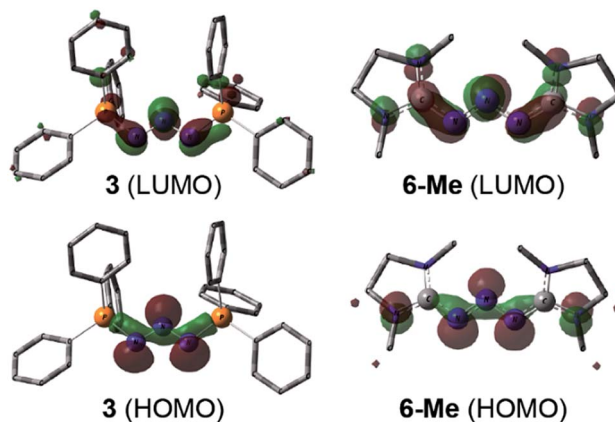


Fig. 4 Graphical presentation of the LUMO (top) and HOMO (bottom) of the cations in **3** and **6-Me** calculated at the wB97XD/def2-TZVPP level of theory (surface iso-value = 0.05).

$[(\text{Ph}_3\text{P})_2\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**5**) (Scheme 1).³⁴ N_2 elimination is thought to follow isomerization of the W-shaped **3** to a U-shaped isomer. It is noteworthy that compound **3** was isolated as a mixture of

both isomers in a 4 : 1 ratio. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the minor isomer gave two resonances at $\delta(^{31}\text{P}) = 28.4$ and 11.0 ppm ($^4J_{\text{PP}} = 5.5$ Hz). At elevated temperatures, rapid conversion of the cation **3** to $[(\text{Ph}_3\text{P})_2\text{N}]^+$ **5** was observed. Nonetheless, the ratio of the isomers of **3** is unchanged inferring the rate of N_2 -loss is comparable to the rate of isomerization of **3**. Computations at the wB97XD/def2-TZV level of theory with addition of the conductor-like polarizable continuum solvation model (CPCM)³⁵ showed only a small energy difference between the W and U-shaped isomers of **3** ($\Delta G_{\text{R}}^{298} = -2.6$ kcal mol^{−1}).

Compound **1** also reacts with two equivalents of 1,3-dimesitylimidazolidin-2-ylidene (SIMes) in $\text{C}_6\text{D}_5\text{Br}$ solution with liberation of $(p\text{-HC}_6\text{F}_4)_3\text{P}$ as evidenced by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows a new resonance for the C-2 carbon



atom at $\delta(^{13}\text{C}) = 162.2$ ppm.³⁶ Collectively, the NMR data indicate the formation of $[(\text{SImes})_2\text{N}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**6**) which was isolated in 70% yield. Interestingly, **6** was the only product obtained from the reaction using a 1 : 1 stoichiometry. This contrasts with the reactivity observed for *t*-Bu₃P and is likely a result of the low solubility of **1** in bromobenzene. Interestingly, compound **6** was also obtained in high yields by reaction of **3** or $[\text{Ph}_3\text{PN}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ with SImes in 1 : 2 stoichiometry (see ESI†). Compound **6** is thermally stable even under prolonged heating to 120 °C for several days in C₆D₅Br solution. The nature of compound **6** was further confirmed by single crystal X-ray diffraction (Fig. 3). The structure features a W-shaped N₃-chain terminated by imidazolidiniumyl-groups with a N–N–N angle (110.4(2)°) comparable to that seen for **3** and **4**. The planes of the imidazole-rings are skewed with respect to the N₃-plane (38.3(7)°/41.2(5)°) and the torsion angles involving the C–N bonds (N5–C1–N1–N2: 27.6°, N6–C22–N3–N2: 35.0°) deviate from those expected for a C=N double bond. This indicates that electron delocalization across the imidazole and azide moiety may be hampered by the steric demands of the Mes substituents. The N–N (1.309(2) Å/1.311(2) Å) and C–N (1.359(2) Å/1.369(2) Å) bond distances involving the W-type fragment of **6** fall in the range between those expected for single and double bonds.³⁷

DFT calculations (wb97XD/def2-TZV, see ESI†) carried out on **3** and the model compound **6-Me**, (mesityl-substituents replaced by methyl groups) showed similar molecular orbitals for both compounds (Fig. 4). The HOMOs exhibit strong *n* character comprised primarily of the lone pairs of the N-atoms. The LUMOs are π -type orbitals delocalized across the N₃-linkage and the L donors. This is in contrast to the isolated P₃-allyl anion frontier orbitals reported for $[(\text{carbene})_2\text{P}_3]^+$.¹⁵ Interestingly these frontier orbitals are also reminiscent of the HOMO and HOMO–1 of neutral triazenes (NHC)N₃R.³⁸

Conclusions

In summary, the EPC $[(p\text{-C}_6\text{F}_4\text{H})_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ is used to prepare the phosphonium ion salt **1** which serves as a precursor for the formal transfer of $[\text{N}_3]^+$ to other donors affording stable and isolable mono- and bis-adducts of the form $[(\text{L})\text{N}_3]^+$ and $[(\text{L})_2\text{N}_3]^+$. The reactivity of these species containing terminal and bridging azide-fragments is the subject of continuing studies. In addition, the exploration of the reactivity of EPCs as synthetic building blocks for other unusual main group cations is ongoing.

Acknowledgements

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Notes and references

§ Extra precaution must be taken when working with azides in CH₂Cl₂ solution as they are potentially dangerous and can result in the possible formation of dangerous and explosive diazidomethane.

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