Chemical Science

EDGE ARTICLE

View Article Online
View Journal | View Issue

Open Access Article. Published on 21 July 2015. Downloaded on 3/16/2026 9:03:57 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Cite this: *Chem. Sci.*, 2015, **6**, 6367

Received 28th June 2015
Accepted 20th July 2015

DOI: 10.1039/c5sc02336j

www.rsc.org/chemicalscience

# Phosphine and carbene azido-cations: $[(L)N_3]^+$ and $[(L)_2N_3]^+$†

Daniel Winkelhaus,‡[a] Michael H. Holthausen,‡[a] Roman Dobrovetsky[b] and Douglas W. Stephan*[a]

The cationic $N_3$-species $[(p\text{-}HC_6F_4)_3PN_3]^+$ (**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 $(p\text{-}HC_6F_4)_3P$. 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 chemistry[1] 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 $[(carbene)_2E_2]^{n+}$ (E = C,[5] P,[13] As;[14] $n$ = 1, 2) while Burford, Weigand, Jones and Grützmacher prepared $[(carbene)_2P_3]^+$[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 $[(Ph_3P)PPh_2]^+$ affording $[(carbene)PPh_2]^+$.[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 $[(C_6F_5)_3PF]^+$[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 $[(p\text{-}HC_6F_4)_3PN_3]^+$ (**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 $[(p\text{-}HC_6F_4)_3PN_3][B(C_6F_5)_4]$ (**1**) was readily prepared in quantitative yield by the reaction of $[(p\text{-}HC_6F_4)_3PF][B(C_6F_5)_4]$ with $Me_3SiN_3$ in $CH_2Cl_2$ (Scheme 1).§ The $^{31}P\{^1H\}$ NMR spectrum of **1** in $CD_2Cl_2$ gives rise to a broad singlet resonance ($\delta(^{31}P)$ = 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 $[(C_6F_5)_3PF]^+$ 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)°. The P(1)–N(1) bond length of 1.651(2) Å is shorter than those observed in azido-substituted phosphenium 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)°) 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 species[24] 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 $[N_5]^+$ of Christe,[27] $[N_2F]^+$,[28] Hünig's stable triazenium ions $[R_2N_3R_2]^+$[29] and aminodiazonium ions of the form $[(R_2N)N_2]^+$[30] (R = H, silyl, alkyl, aryl).

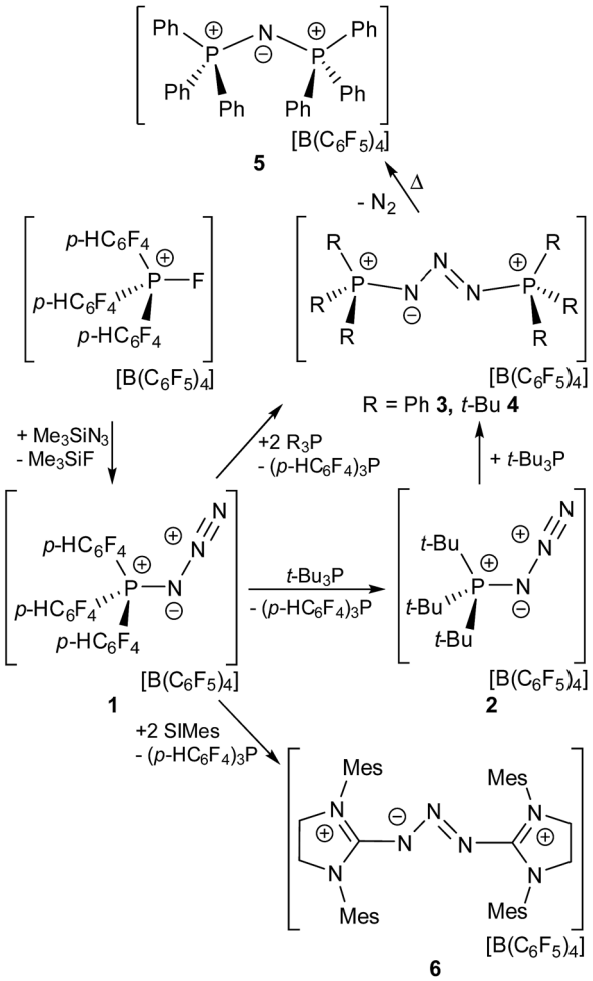
[a]Department of Chemistry, University of Toronto, 80 St. George St, Toronto, Ontario M5S3H6, Canada. E-mail: dstephan@chem.utoronto.ca

[b]School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel

† Electronic supplementary information (ESI) available: Details on VT NMR experiments, preparation of **5**, quantum chemical calculations and X-ray crystallography. CCDC 1403531–1403535. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc02336j

‡ These authors contributed equally.

Open Access Article. Published on 21 July 2015. Downloaded on 3/16/2026 9:03:57 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.




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*-$HC_6F_4$-groups (LUMO to LUMO+9). The first accessible acceptor orbital is a π*-type orbital located at the terminal $N_2$ 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-bound 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 ($LP(p)_{N1} \rightarrow \sigma^*_{P-C7}$ 11.2 kcal $mol^{-1}$, $LP(p)_{N1} \rightarrow \sigma^*_{P-C7}$ 7.4 kcal $mol^{-1}$, $LP(sp^{0.69})_{N1} \rightarrow \sigma^*_{P-C7}$ 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*-$Bu_3P$ in $CH_2Cl_2$ solution (Scheme 1).§ The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a septet resonance at $\delta(^{31}P) = -72.3$ ppm ($^3J_{PF} = 36.4$ Hz)[19b] which corresponds to $(p\text{-}HC_6F_4)_3P$ and a new singlet resonance at low field ($\delta(^{31}P) = -85.9$ 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 $N_3^+$-moiety in **1** to *t*-$Bu_3P$ yielding $[t\text{-}Bu_3PN_3][B(C_6F_5)_4]$ (**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 $C_6D_5Br$ solution to 100 °C for 24 h. Attempts to independently synthesize **2** from the reaction of $[t\text{-}Bu_3PF][B(C_6F_5)_4]$[19] with $Me_3SiN_3$ failed even after prolonged reaction times at 100 °C in $C_6D_5Br$ solution. This reflects the increased steric demand of the $[t\text{-}Bu_3PF]^+$ cation.

The corresponding reaction of **1** with $Ph_3P$ in $CH_2Cl_2$ was monitored by $^{31}P\{^1H\}$ NMR spectroscopy revealing the complete consumption of $Ph_3P$ and the liberation of only 0.5 equivalents of $(p\text{-}HC_6F_4)_3P$, leaving approximately 50% of **1** unreacted. Addition of another equivalent of $Ph_3P$ resulted in its complete consumption. Collectively, this indicates the formation of a bis-adduct $[(Ph_3P)_2(N_3)][B(C_6F_5)_4]$ (**3**, Scheme 1). While the proposed intermediate $[Ph_3PN_3]^+$ was independently synthesized by the reaction of $[Ph_3PF][B(C_6F_5)_4]$[20c] and $Me_3SiN_3$ (see ESI†), this species was not observed in the reaction of **1** with $Ph_3P$. This indicates that reaction of $[Ph_3PN_3]^+$ with a second equivalent of $Ph_3P$ is rapid, in agreement with Wiberg who described the $[(Ph_3P)_2(N_3)]^+$ 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*-$Bu_3P$ or by reaction of **2** with one equivalent of *t*-$Bu_3P$ (Scheme 1). Species **4** was also obtained by reaction of **3** with two equivalents of *t*-$Bu_3P$ with concurrent release of $Ph_3P$. All methods furnish **4** in high yields (76–99%). Compounds **3** and **4** show $^{31}P\{^1H\}$ 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 $P_2N_3$-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 $R_3PN_3R$,[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 $C_6D_5Br$ solution over several days without decomposition. In contrast, compound **3** is not temperature stable, decomposing quantitatively with release of $N_2$ within 3 h at 100 °C.[24c] The $^{31}P\{^1H\}$ NMR spectrum shows only one resonance at $\delta(^{31}P) = 21.1$ ppm assignable to

Open Access Article. Published on 21 July 2015. Downloaded on 3/16/2026 9:03:57 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

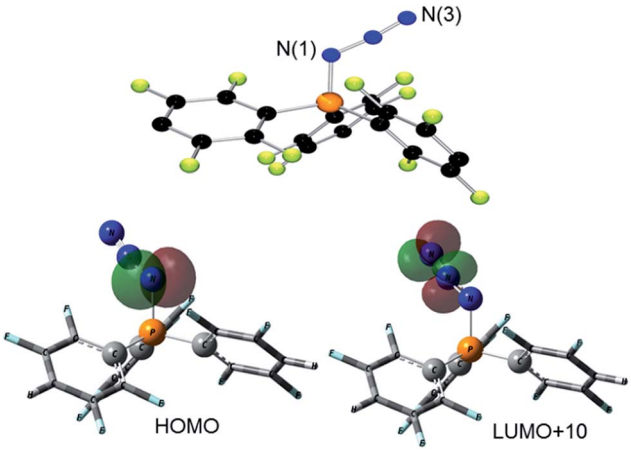



Fig. 1 POV-ray depiction of the cation in **1** (top). Hydrogen atoms are omitted for clarity. Selected bond distances and angles: P(1)–N(1) 1.651(2), P(1)–C(13) 1.783(2), P(1)–C(1) 1.789(2), P(1)–C(7) 1.789(2), N(1)–N(2) 1.260(2), N(2)–N(3) 1.114(2), N(1)–P(1)–C(13) 111.6(2), N(1)–P(1)–C(1) 102.3(2), 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).

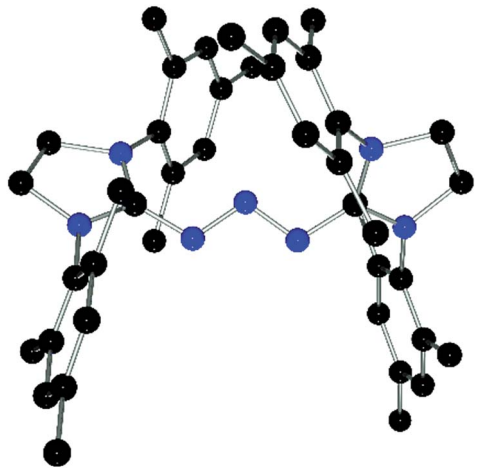


Fig. 3 POV-ray depiction of the cation in **6**. Hydrogen atoms are omitted for clarity. Selected bond distances and angles: C(1)–N(4) 1.332(3), C(1)–N(5) 1.346(2), C(1)–N(1) 1.359(2), C(22)–N(7) 1.335(2), C(22)–N(6) 1.337(2), C(22)–N(3) 1.369(2), N(1)–N(2) 1.309(2), N(2)–N(3) 1.311(2), N(4)–C(1)–N(5)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

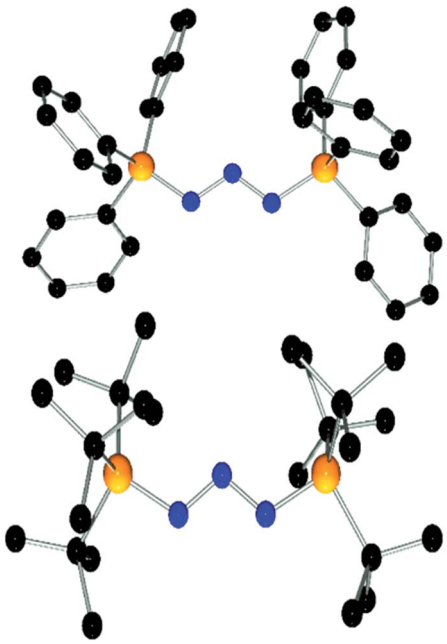


Fig. 2 POV-ray depiction of the cations in **3** (top) and **4** (bottom). Hydrogen atoms are omitted for clarity. Selected bond distances and angles for **3**: N(1)–P(1) 1.648(3), N(3)–P(2) 1.643(3), N(1)–N(2) 1.298(4), N(2)–N(3) 1.309(4), N(2)–N(1)–P(1) 114.5(3), N(1)–N(2)–N(3) 113.2(4), N(2)–N(3)–P(2)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

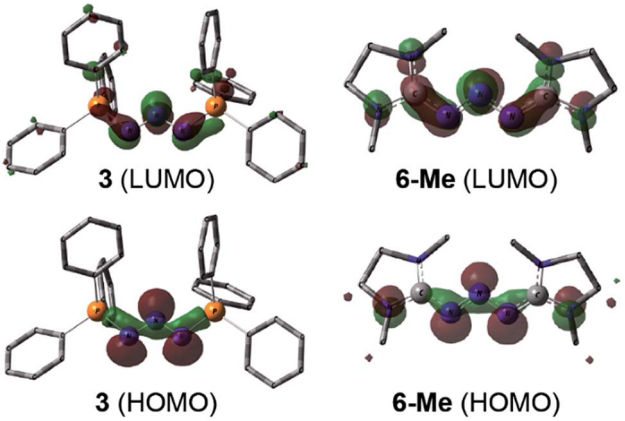



Fig. 4 Graphical presentation of the LUMO (top) and HOMO (bottom) of the cations in **3** and **6-Me** calculated at the wB97XD/def2-TZVPP level of theory (surface iso-value = 0.05).

$[(Ph_3P)_2N][B(C_6F_5)_4]$ (**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 $^{31}P\{^1H\}$ NMR spectrum of the minor isomer gave two resonances at $\delta(^{31}P) = 28.4$ and 11.0 ppm ($^4J_{PP} = 5.5$ Hz). At elevated temperatures, rapid conversion of the cation **3** to $[(Ph_3P)_2N]^+$ **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** ($\Delta G_R^{298} = -2.6$ kcal mol$^{-1}$).

Compound **1** also reacts with two equivalents of 1,3-dimesityl-imidazolidin-2-ylidene (SIMes) in $C_6D_5Br$ solution with liberation of $(p\text{-}HC_6F_4)_3P$ as evidenced by the $^{31}P\{^1H\}$ NMR spectrum. The $^{13}C\{^1H\}$ NMR spectrum shows a new resonance for the C-2 carbon

Open Access Article. Published on 21 July 2015. Downloaded on 3/16/2026 9:03:57 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

atom at $\delta(^{13}C) = 162.2$ ppm.[36] Collectively, the NMR data indicate the formation of $[(SIMes)_2N_3][B(C_6F_5)_4]$ (**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 $t$-$Bu_3P$ 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 $[Ph_3PN_3][B(C_6F_5)_4]$ with SIMes in 1 : 2 stoichiometry (see ESI†). Compound **6** is thermally stable even under prolonged heating to 120 °C for several days in $C_6D_5Br$ solution. The nature of compound **6** was further confirmed by single crystal X-ray diffraction (Fig. 3). The structure features a W-shaped $N_3$-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 $N_3$-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 $N_3$-linkage and the L donors. This is in contrast to the isolated $P_3$-allyl anion frontier orbitals reported for $[(carbene)_2P_3]^+$.[15] Interestingly these frontier orbitals are also reminiscent of the HOMO and HOMO−1 of neutral triazenes $(NHC)N_3R$.[38]

## Conclusions

In summary, the EPC $[(p\text{-}C_6F_4H)_3PF][B(C_6F_5)_4]$ is used to prepare the phosphonium ion salt **1** which serves as a precursor for the formal transfer of $[N_3]^+$ to other donors affording stable and isolable mono- and bis-adducts of the form $[(L)N_3]^+$ and $[(L)_2N_3]^+$. 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

D. W. S. gratefully acknowledges the financial support of the NSERC of Canada and the award of a Canada Research Chair. M. H. H. thanks the Alexander von Humboldt Foundation for a Feodor Lynen Research Fellowship.

## Notes and references

§ Extra precaution must be taken when working with azides in $CH_2Cl_2$ solution as they are potentially dangerous and can result in the possible formation of dangerous and explosive diazidomethane.

1 (*a*) Y. Z. Wang and G. H. Robinson, *Inorg. Chem.*, 2011, **50**, 12326–12337; (*b*) C. D. Martin, M. Soleilhavoup and G. Bertrand, *Chem. Sci.*, 2013, **4**, 3020–3030; (*c*) C. A. Dyker and G. Bertrand, *Science*, 2008, **321**, 1050–1051; (*d*) Y. Wang and G. H. Robinson, *Inorg. Chem.*, 2014, **53**, 11815–11832.
2 D. J. D. Wilson, S. A. Couchman and J. L. Dutton, *Inorg. Chem.*, 2012, **51**, 7657–7668.
3 A. Velian and C. C. Cummins, *Science*, 2015, **348**, 1001–1004.
4 H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki and A. Vargas, *Science*, 2012, **336**, 1420–1422.
5 (*a*) Y. Li, K. C. Mondal, P. P. Samuel, H. Zhu, C. M. Orben, S. Panneerselvam, B. Dittrich, B. Schwederski, W. Kaim, T. Mondal, D. Koley and H. W. Roesky, *Angew. Chem., Int. Ed.*, 2014, **53**, 4168–4172; *Angew. Chem.*, 2014, **126**, 4252–4256; (*b*) L. Jin, M. Melaimi, L. Liu and G. Bertrand, *Org. Chem. Front.*, 2014, **1**, 351–354.
6 Y. Z. Wang, Y. M. Xie, P. R. Wei, R. B. King, H. F. Schaefer, P. V. Schleyer and G. H. Robinson, *Science*, 2008, **321**, 1069–1071.
7 A. Sidiropoulos, C. Jones, A. Stasch, S. Klein and G. Frenking, *Angew. Chem., Int. Ed.*, 2009, **48**, 9701–9704; *Angew. Chem.*, 2009, **121**, 9881–9884.
8 C. Jones, A. Sidiropoulos, N. Holzmann, G. Frenking and A. Stasch, *Chem. Commun.*, 2012, **48**, 9855–9857.
9 N. Holzmann, D. Dange, C. Jones and G. Frenking, *Angew. Chem., Int. Ed.*, 2013, **52**, 3004–3008; *Angew. Chem.*, 2013, **125**, 3078–3082.
10 (*a*) Y. Z. Wang, Y. M. Xie, P. R. Wei, R. B. King, H. F. Schaefer, P. V. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2008, **130**, 14970–14971; (*b*) O. Back, G. Kuchenbeiser, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2009, **48**, 5530–5533; *Angew. Chem.*, 2009, **121**, 5638–5641; (*c*) J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *J. Am. Chem. Soc.*, 2007, **129**, 14180–14181; (*d*) J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2007, **46**, 7052–7055; *Angew. Chem.*, 2007, **119**, 7182–7185.
11 M. Y. Abraham, Y. Z. Wang, Y. M. Xie, P. R. Wei, H. F. Schaefer, P. V. Schleyer and G. H. Robinson, *Chem.–Eur. J.*, 2010, **16**, 432–435.
12 R. Kretschmer, D. A. Ruiz, C. E. Moore, A. L. Rheingold and G. Bertrand, *Angew. Chem., Int. Ed.*, 2014, **53**, 8176–8179; *Angew. Chem.*, 2014, **126**, 8315–8318.
13 O. Back, B. Donnadieu, P. Parameswaran, G. Frenking and G. Bertrand, *Nat. Chem.*, 2010, **2**, 369–373.
14 M. Y. Abraham, Y. Wang, Y. Xie, R. J. Gilliard Jr, P. Wei, B. J. Vaccaro, M. K. Johnson, H. F. Schaefer III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2013, **135**, 2486–2488.
15 (*a*) M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking and J. J. Weigand, *Angew. Chem., Int. Ed.*, 2013, **52**, 11078–11082; *Angew. Chem.*, 2013, **125**, 11284–11288; (*b*) A. M. Tondreau, Z. Benko, J. R. Harmer and H. Grützmacher, *Chem. Sci.*, 2014, **5**, 1545–1554.
16 (*a*) M. Donath, E. Conrad, P. Jerabek, G. Frenking, R. Fröhlich, N. Burford and J. J. Weigand, *Angew. Chem.,*

 This journal is © The Royal Society of Chemistry 2015

Open Access Article. Published on 21 July 2015. Downloaded on 3/16/2026 9:03:57 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

*Int. Ed.*, 2012, **51**, 2964–2967; *Angew. Chem.*, 2012, **124**, 3018–3021; (*b*) A. Sidiropoulos, B. Osborne, A. N. Simonov, D. Dange, A. M. Bond, A. Stasch and C. Jones, *Dalton Trans.*, 2014, **43**, 14858–14864.

17 N. Burford, T. S. Cameron and P. J. Ragogna, *J. Am. Chem. Soc.*, 2001, **123**, 7947–7948.

18 (*a*) D. Himmel, I. Krossing and A. Schnepf, *Angew. Chem., Int. Ed.*, 2014, **53**, 370–374; *Angew. Chem.*, 2014, **126**, 378–382; (*b*) D. Himmel, I. Krossing and A. Schnepf, *Angew. Chem., Int. Ed.*, 2014, **53**, 6047–6048; *Angew. Chem.*, 2014, **126**, 6159–6160; (*c*) G. Frenking, *Angew. Chem., Int. Ed.*, 2014, **53**, 6040–6046; *Angew. Chem.*, 2014, **126**, 6152–6158.

19 (*a*) C. B. Caputo, L. J. Hounjet, R. Dobrovetsky and D. W. Stephan, *Science*, 2013, **341**, 1374–1377; (*b*) C. B. Caputo, D. Winkelhaus, R. Dobrovetsky, L. J. Hounjet and D. W. Stephan, *Dalton Trans.*, 2015, **44**, 12256–12264; (*c*) M. Perez, Z. W. Qu, C. B. Caputo, V. Podgorny, L. J. Hounjet, A. Hansen, R. Dobrovetsky, S. Grimme and D. W. Stephan, *Chem.–Eur. J.*, 2015, **21**, 6491–6500.

20 (*a*) M. Perez, C. B. Caputo, R. Dobrovetsky and D. W. Stephan, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 10917–10921; (*b*) M. Perez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 18308–18310; (*c*) M. H. Holthausen, R. R. Hiranandani and D. W. Stephan, *Chem. Sci.*, 2015, **6**, 2016–2021; (*d*) M. H. Holthausen, M. Mehta and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2014, **53**, 6538–6541; *Angew. Chem.*, 2014, **126**, 6656–6659.

21 L. J. Hounjet, C. B. Caputo and D. W. Stephan, *Dalton Trans.*, 2013, **42**, 2629–2635.

22 C. Hering, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2012, **51**, 6241–6245; *Angew. Chem.*, 2012, **124**, 6345–6349.

23 (*a*) J. J. Weigand, K.-O. Feldmann and F. D. Henne, *J. Am. Chem. Soc.*, 2010, **132**, 16321–16323; (*b*) D. Michalik, A. Schulz, A. Villinger and N. Weding, *Angew. Chem., Int. Ed.*, 2008, **47**, 6465–6468; *Angew. Chem.*, 2008, **120**, 6565–6568.

24 Only two examples were crystallographically characterized: (*a*) C. Hering, A. Schulz and A. Villinger, *Inorg. Chem.*, 2013, **52**, 5214–5225; for derivatives that were not characterized by X-ray see: (*b*) K. Bott, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 695; *Angew. Chem.*, 1965, **77**, 683; (*c*) N. Wiberg and K. H. Schmid, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 953–954; *Angew. Chem.*, 1967, **79**, 938; (*d*) A. Schmidt, *Chem. Ber.*, 1968, **101**, 4015–4021; (*e*) A. Schmidt, *Chem. Ber.*, 1970, **103**, 3923–3927; (*f*) W. Buder and A. Schmidt, *Chem. Ber.*, 1973, **106**, 3812–3816; (*g*) C. Hering, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2012, **51**, 6241–6245.

25 (*a*) U. Müller, *Chem. Ber.*, 1977, **110**, 788–791; (*b*) H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, *Z. Naturforsch., B: Chem. Sci.*, 1986, **41**, 803–807; (*c*) D. Schomburg, U. Wermuth and R. Schmutzler, *Chem. Ber.*, 1987, **120**, 1713–1718; (*d*) A. H. Cowley, F. Gabbaï, R. Schluter and D. Atwood, *J. Am. Chem. Soc.*, 1992, **114**, 3142–3144; (*e*) U. Englert, P. Paetzold and E. Eversheim, *Z. Kristallogr.*, 1993, **208**, 307–309; (*f*) J. R. Goerlich, M. Farkens, A. Fischer, P. G. Jones and R. Schmutzler, *Z. Anorg. Allg. Chem.*, 1994, **620**, 707–715; (*g*) A. H. Cowley, F. P. Gabbaï, G. Bertrand, C. J. Carrano and M. R. Bond, *J. Organomet. Chem.*, 1995, **493**, 95–99; (*h*) M. Larbig, M. Nieger, V. von der Gönna, A. V. Ruban and E. Niecke, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 460–462; *Angew. Chem.*, 1995, **107**, 505; (*i*) C. Aubauer, T. M. Klapötke, H. Noth, A. Schulz, M. Suter and J. Weigand, *Chem. Commun.*, 2000, 2491–2492; (*j*) N. Götz, S. Herler, P. Mayer, A. Schulz, A. Villinger and J. J. Weigand, *Eur. J. Inorg. Chem.*, 2006, 2051–2057; (*k*) A. Schulz and A. Villinger, *Eur. J. Inorg. Chem.*, 2008, 4199–4203; (*l*) X. Zeng, M. Gerken, H. Beckers and H. Willner, *Inorg. Chem.*, 2010, **49**, 3002–3010; (*m*) X. Zeng, E. Bernhardt, H. Beckers and H. Willner, *Inorg. Chem.*, 2011, **50**, 11235–11241; (*n*) C. Hering, M. Hertrich, A. Schulz and A. Villinger, *Inorg. Chem.*, 2014, **53**, 3880–3892.

26 (*a*) A. Roglans, A. Pla-Quintana and M. Moreno-Mañas, *Chem. Rev.*, 2006, **106**, 4622–4643; (*b*) S. Mahouche-Chergui, S. Gam-Derouich, C. Mangeney and M. M. Chehimi, *Chem. Soc. Rev.*, 2011, **40**, 4143–4166.

27 (*a*) K. O. Christe, W. W. Wilson, J. A. Sheehy and J. A. Boatz, *Angew. Chem., Int. Ed.*, 1999, **38**, 2004–2009; (*b*) K. O. Christe, W. W Wilson, J. A. Sheehy and J. A. Boatz, *Angew. Chem., Int. Ed.*, 1999, **111**, 2112–2118.

28 D. Moy and A. R. Young, *J. Am. Chem. Soc.*, 1965, **87**, 1889–1892.

29 H. Hansen, S. Hünig and K.-I. Kishi, *Chem. Ber.*, 1979, **112**, 445–461.

30 (*a*) A. Mertens, K. Lammertsma, A. Massoud and G. A. Olah, *J. Am. Chem. Soc.*, 1983, **105**, 5657–5660; (*b*) K. O. Christe, W. W. Wilson, D. A. Dixon, S. I. Khan, R. Bau, T. Metzenthin and R. Lu, *J. Am. Chem. Soc.*, 1993, **115**, 1836–1842; (*c*) A. Schulz and A. Villinger, *Chem.–Eur. J.*, 2010, **16**, 7276–7281; (*d*) C. W. Huh and J. Aube, *Chem. Sci.*, 2014, **5**, 699–706.

31 M. H. Holthausen, I. Mallov and D. W. Stephan, *Dalton Trans.*, 2014, **43**, 15201–15211.

32 (*a*) L. LePichon and D. W. Stephan, *Inorg. Chem.*, 2001, **40**, 3827–3829; (*b*) G. C. Fortman, B. Captain and C. D. Hoff, *Inorg. Chem.*, 2009, **48**, 1808–1810; (*c*) P. Molina, C. López-Leonardo, J. Llamas-Botía, C. Foces-Foces and C. Fernández-Castaño, *Tetrahedron*, 1996, **52**, 9629–9642; (*d*) R. D. Kennedy, *Chem. Commun.*, 2010, **46**, 4782–4784; (*e*) C. G. Chidester, J. Szmuszkovicz, D. J. Duchamp, L. G. Laurian and J. P. Freeman, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1988, **44**, 1080–1083; (*f*) C. Reddy, V. Reddy, B. M. Fetterly and J. G. Verkade, *Energy Fuels*, 2007, **21**, 2466–2472; (*g*) M. W. P. Bebbington and D. Bourissou, *Coord. Chem. Rev.*, 2009, **253**, 1248–1261.

33 H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635.

34 S. Cameron and M. Peach, *J. Chem. Crystallogr.*, 1998, **28**, 919–924.

35 (*a*) V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001; (*b*) M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669–681; (*c*) J. Andzelm, C. Kölmel and A. Klamt, *J. Chem. Phys.*, 1995, **103**, 9312–

9320; (*d*) A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, 1993, 799.
36 M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi and I. A. Fallis, *Organometallics*, 2008, **27**, 3279–3289.
37 A. F. Holleman and E. Wiberg, *Lehrbuch der Anorganischen Chemie*, ed. von Nils Wiberg, de Gruyter, Berlin, 2007.
38 (*a*) J. E. Leffer and R. D. Temple, *J. Am. Chem. Soc.*, 1967, **89**, 5235–5246; (*b*) J. G. Gololobov, L. F. Kasukhin and U. S. Petrenko, *Phosphorus Sulfur Relat. Elem.*, 1987, **30**, 393–396; (*c*) H. Bock and M. Schnöller, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 636–637; *Angew. Chem.*, 1968, **80**, 667.

Open Access Article. Published on 21 July 2015. Downloaded on 3/16/2026 9:03:57 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.


This journal is © The Royal Society of Chemistry 2015