Cationic phosphorus–carbon–pnictogen cages isolobal to $[C_5R_5]^+$†

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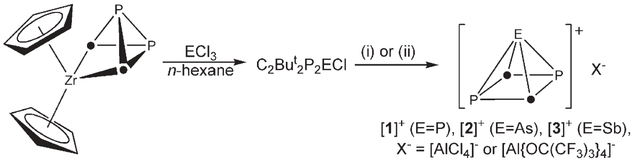
Received (in Cambridge, UK) 14th December 2005, Accepted 2nd February 2006
First published as an Advance Article on the web 17th February 2006
DOI: 10.1039/b517710c

The cationic cages *nido*-$[C_2Bu^t{}_2P_2E]^+$ (E = As, Sb), which are isolobal to the cyclopentadienyl cation, adopt square based pyramidal structures with the heavy pnictogen atom at the apex; NMR and computational methods have been used to probe the dynamic behaviour of the complexes.

At first glance, it is a curious anomaly that electron deficient group 15 cluster cations are extremely rare while their group 16 counterparts with more electronegative heteroatoms are relatively common. In fact, of the group 15 elements, only bismuth has well-established polyatomic cluster cation chemistry—the remaining members of the group show little tendency to form such complexes. Indeed the synthesis of pnictogen-containing electron deficient compounds represents a significant challenge. Our approach to this synthetic problem has focussed on synthesising heteroatomic cationic clusters involving group 15 elements and carbon units. We recently reported the first example of a mixed phosphorus–carbon cation, *nido*-$[3,5\text{-}Bu^t{}_2\text{-}1,2,4\text{-}P_3C_2]^+$, that is isoelectronic with the cyclopentadienyl cation $[C_5R_5]^+$ and obeys Wade's rules.[1] This cation adopts a square based pyramidal structure with the three phosphorus atoms occupying the apical site and two mutually *trans* positions in the diamond-shaped base—this is, of course, related to (*i.e.*, isolobal with) the classical structures of the neutral borane and carborane, B_5H_9 and $C_2B_3H_7$ respectively.[2] Herein we report the synthesis and characterisation of the isostructural clusters with As and Sb atoms at the apical positions, and the extension of the series gives us further insight into the properties of these intriguing cage cations.

Cationic cages of general formula $[P_2(CBu^t)_2E]^+$ (**[1]**$^+$, E = P; **[2]**$^+$, E = As; **[3]**$^+$, E = Sb) are readily formed by removal of the chloride anion from the monochloro cages, $ClP_2(CBu^t)_2E$‡ (E = P, As, Sb, see Scheme 1), through use of a suitable Lewis acid (*e.g.*, $AlCl_3$) or by replacement of the chloride anion with a non-coordinating anion (*e.g.*, $[Al\{OC(CF_3)_3\}_4]^-$). The products are both highly oxygen- and moisture-sensitive crystalline compounds. **[3]**$^+$ is a very rare example of an antimony containing cage cation[3] and **[2]**$^+$ is the first example of such a compound containing arsenic.



Scheme 1 • = CBu^t, (i) $AlCl_3$, (ii) $Ag[Al\{OC(CF_3)_3\}_4]$.

The $[Al\{OC(CF_3)_3\}_4]^-$ and $[AlCl_4]^-$ salts of **[1]**$^+$, **[2]**$^+$ and **[3]**$^+$ were characterised by elemental analysis, NMR and IR spectroscopies. In addition, the $[AlCl_4]^-$ salts have been structurally characterised.§ The cationic cages of these compounds are isomorphous, adopting square based pyramidal cores, with a diamond shaped C_2P_2 base featuring alternating carbon and phosphorus atoms, with the remaining group 15 element occupying the apical site. The *nido* cluster structure, based on a parent *closo* octahedron with one vertex removed, is consistent with the presence of seven polyhedral skeletal electron pairs. Cation **[1]**$^+$ forms two apical and three basal contacts to Cl atoms of the $[AlCl_4]^-$ at distances which range from 3.16 to 3.58 Å. In a subtlety different vein, the As apical site of cation **[2]**$^+$ forms three contacts with the $[AlCl_4]^-$ anion (3.47–3.58 Å) with only one contact from a Cl atom to a basal P site (3.28 Å). In contrast cation **[3]**$^+$ forms only a single long range contact to its $[AlCl_4]^-$ counteranion (to the apical Sb atom, Sb···Cl 3.68 Å). The P–C bond lengths within the C_2P_2 base are very similar (ranging from 1.796(2) to 1.809(2) Å), but the distance of the apical atom from the C_2P_2 base increases for the heavier group 15 elements (1.70 Å, 1.86 Å and 2.09 Å above the mean C_2P_2 plane for **[1]**$^+$, **[2]**$^+$ and **[3]**$^+$, respectively). The C–E–P bond angles subtended by mutually *cis* C–P pairs at the apical atom become correspondingly smaller (av. 49.9° for **[1]**$^+$, 46.9° for **[2]**$^+$, 43.1° for **[3]**$^+$). The C_2P_2 base is also slightly distorted away from planarity in all cases, with the carbon atoms displaced towards the apex giving acute angles of 11.1°, 10.1° and 10.0° between the two C_2P triangles in **[1]**$^+$, **[2]**$^+$ and **[3]**$^+$ respectively. This distortion from planarity of the 2,4-C_2P_2 fragment appears to be a feature common to square based pyramidal complexes containing this unit, whether in these cationic complexes or their neutral group 14 counterparts $[P_2(CBu^t)_2A]$, (A = Ge, 12.7°; Sn, 5.9°; Pb, 9.4°).[4,5]

The structures of **[2]**$^+$ and **[3]**$^+$ shown in Fig. 1 represent only one of six possible isomers, **A–F**, based on the *nido* cluster geometries, the structures and relative energies (computed using density functional theory[6–9]) are summarised in Fig. 2. The relative energies summarised confirm that the experimental structures (isomer **B**) *do not* correspond to the global minimum for any of the three cations: the great strength of the C–C bond dictates that isomers **A** and **D** lie lower. However, the mutually *trans* arrangement of C and P in the basal ring is pre-configured in our starting materials, the cage species, $ClP_2(CBu^t)_2E$,‡ and so our

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† Electronic supplementary information (ESI) available: Experimental details and electronic structures of all reported species. See DOI: 10.1039/b517710c

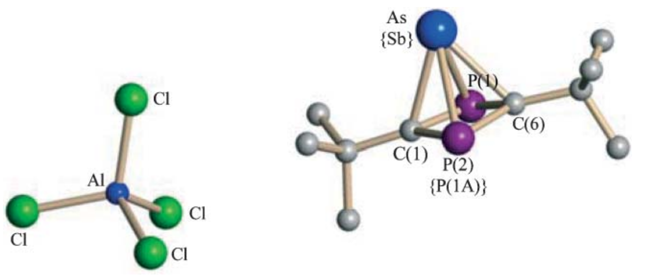


Fig. 1 Molecular structure of *nido*-[3,5-Bu^t_2-1-E-2,4-P_2C_2]$^+$[$AlCl_4$]$^-$ (E = As, [**2**]$^+$; E = Sb, [**3**]$^+$). Where more than one atom label is included, those in parentheses {} refer to the structure of [**3**]$^+$. Selected bond lengths (Å) and angles (°): for [**2**]$^+$: As(1)–C(6) 2.141(3), As(1)–C(1) 2.144(3), As(1)–P(1) 2.3578(8), As(1)–P(2) 2.3650(8), P(1)–C(6) 1.807(3), P(1)–C(1) 1.809(3), P(2)–C(1) 1.797(3), P(2)–C(6) 1.805(3), P(1)–C(1)–P(2) 99.3(1), P(1)–C(6)–P(2) 99.1(1), C(1)–P(1)–C(6) 80.1(1), C(1)–P(2)–C(6) 80.5(1); for [**3**]$^+$: Sb(1)–C(6) 2.344(3), Sb(1)–C(1) 2.348(3), Sb(1)–P(1) 2.5447(7), P(1)–C(1) 1.803(2), P(1)–C(6) 1.805(2), P(1)–C(1)–P(1A) 98.2(2), P(1)–C(6)–P(1A) 98.1(2), C(1)–P(1)–C(6) 81.4(2).

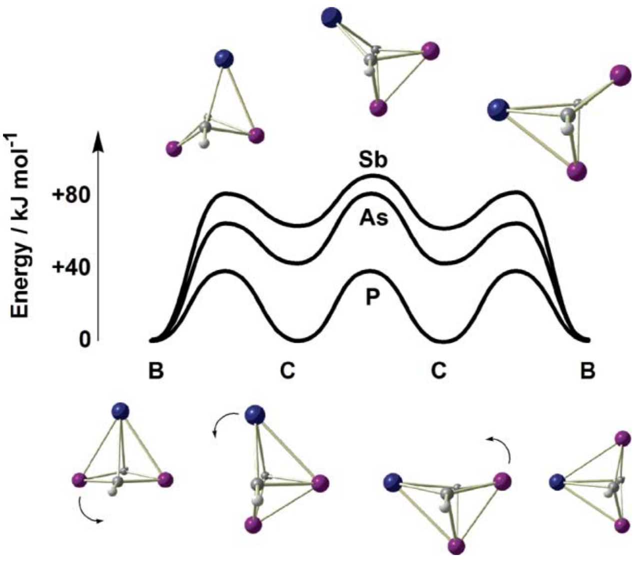
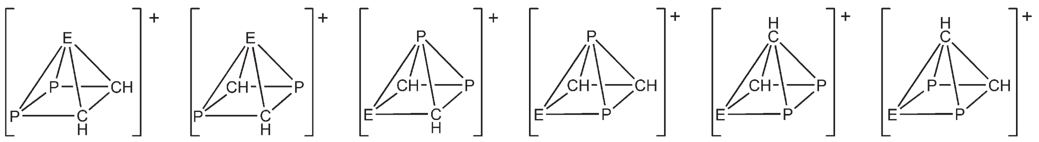


Fig. 3 Potential energy surface for the interconversion of isomers **B** and **C** in [$P_2(CH)_2E$]$^+$. Energies are given relative to isomer **B**.



Relative Energy	A	B	C	D	E	F
E = P	0.0	33.0	33.0	0.0	107.5	107.5
E = As	0.0	38.7	81.1	21.8	147.3	121.9
E = Sb	0.0	40.7	102.2	40.1	155.3	134.9

Fig. 2 Relative energy (kJ mol^{-1}) of the isomers of the model *nido* cations [$(CH)_2P_2E$]$^+$ (E = P, As, Sb).

chosen synthetic protocol necessarily leads to the formation of the kinetic (**B**) rather than thermodynamic (**A**) product. Moreover, **B** cannot be converted to **A** (or **D**) in a one-step mechanism, and subsequent isomerisation would involve a high-energy intermediate with carbon in the apical position (**B** ↔ **F** ↔ **A**).

In our previous reports,[1,10] we rationalised the absence of a signal in the ^{31}P NMR spectrum of [**1**]$^+$[$AlCl_4$]$^-$ by identifying a facile pathway for interconversion of the magnetically disparate apical and basal phosphorus atoms. In terms of the structures summarised in Fig. 2, this process involves the interconversion of isomers **B** and **C** (degenerate when E = P), for which a C_{2v}-symmetric transition state has been located only 38.4 kJ mol^{-1} above **B**. A ^{31}P NMR signal was similarly absent for [**1**]$^+$[Al{$OC(CF_3)_3$}$_4$]$^-$, whose structure was also shown to be ion-separated with a square based pyramidal cationic unit, and for which resonances were observed at δ = 1.16 ppm in the ^{1}H NMR spectrum and at δ = 29.9 (s, CH_3) and 34.0 {br. s, C–$(CH_3)_3$} ppm in the ^{13}C spectrum.[11] In marked contrast, sharp singlets were observed in the room temperature ^{31}P-{^{1}H} NMR spectra (in CH_2Cl_2) of [**2**]$^+$[$AlCl_4$]$^-$ (δ = 169.9 ppm) and of [**3**]$^+$[$AlCl_4$]$^-$ (δ = 180.3 ppm). Corresponding peaks at δ = 183.1 ppm for [**2**]$^+$[Al{$OC(CF_3)_3$}$_4$]$^-$ and δ = 176.3 ppm for [**3**]$^+$[Al{$OC(CF_3)_3$}$_4$]$^-$ presumably indicate that the cations adopt similar structures to those in [**2**]$^+$[$AlCl_4$]$^-$ and [**3**]$^+$[$AlCl_4$]$^-$. However, these ^{31}P NMR spectra do not differentiate between the cage structure undergoing rapid rearrangement (similar to that proposed for [**1**]$^+$) or a static structure on the NMR timescale, as both would lead to the observation of one ^{31}P NMR signal. To resolve this question, we have extended our analysis of the potential energy surface for the interconversion of **B** and **C** to the heteroatomic systems [$(CH)_2P_2As$]$^+$ and [$(CH)_2P_2Sb$]$^+$, where the **B** ↔ **C** rearrangement is no longer degenerate (Fig. 3). In fact, the strong preference of the heavier atom for the apical site means that **C** lies significantly higher than **B**. Moreover, complete fluxionality involves two distinct transition states with both heavy-pnictogen–phosphorus exchange (**B** ↔ **C**) and apical–basal phosphorus exchange (**C** ↔ **C**); the latter lies 81 kJ mol^{-1} (As) and 88.8 kJ mol^{-1} (Sb) above **B**, compared to the value of 38.4 kJ mol^{-1} for E = P. We therefore conclude that the cations [**2**]$^+$ and [**3**]$^+$ are conformationally far more robust than [**1**]$^+$ as a result of the strong preference of the heteroatom for the apical site.

In summary we have shown that our synthetic protocol allows access to a range of interesting cage cations that are formally isolobal to the cyclopentadienyl cation; those containing heavier pnictogens show quite different dynamic behaviour to their lighter homologues.

We thank the Royal Society (University Research Fellowship for CAR), the Universities of Bristol (MG, CAR, CF) and York (JML, CEW) and the EPSRC (RJK, DAP, CEW) for financial support.

Notes and references

‡ We have determined the structures of $ClP_2(CBu^t)_2E$ (E = As, Sb); the structure of $ClP_2(CBu^t)_2As$ is a tricyclic cage and is discussed in the

Supplementary Information linked to this paper.† In contrast $ClP_2(CBu^t)_2Sb$ form a wholly different structure based on a 1,3-diphosphabutene unit with the saturated edge bridged by a SbCl unit—this remarkable structure will be discussed in detail in a separate communication.

§ Single crystals of $[\mathbf{2}]^{+\cdot}[AlCl_4]^-$ were grown from a CH_2Cl_2–hexane mixture (*ca.* 5 : 1); crystals of $[\mathbf{3}]^{+\cdot}[AlCl_4]^-$ were grown from CH_2Cl_2 at −20 °C. The crystals were mounted in an inert oil and transferred to the cold gas stream of Bruker SMART CCD area-detector diffractometer using Mo-K$_\alpha$ radiation (λ = 0.71073 Å). Crystal data for $[\mathbf{2}]^{+\cdot}[AlCl_4]^-$: $C_{10}H_{18}AlAsCl_4P_2$, M = 443.88, monoclinic space group *C2/c*, a = 19.1632(8), b = 9.6826(4), c = 20.9520(9) Å, β = 101.2530(10)°, U = 3812.9(3) Å^3, T = 173 K, Z = 8, μ(Mo-Kα) = 2.540 mm^{-1}, 19900 reflections measured, 4359 unique (R_{int} = 0.0476) which were used in all calculations. The final R_1 [$I > 2\sigma(I)$] was 0.0330. Crystal data for $[\mathbf{3}]^+[AlCl_4]^-$: $C_{10}H_{18}AlCl_4P_2Sb$, M = 490.71, monoclinic space group $P2_1/m$, a = 9.1431(4), b = 9.8320(5), c = 11.0710(5) Å, β = 112.6970(10)°, U = 918.15(7) Å^3, T = 173 K, Z = 2, μ(Mo-Kα) = 2.289 mm^{-1}, 9862 reflections measured, 2224 unique (R_{int} = 0.0290) which were used in all calculations. The final R_1 [$I > 2\sigma(I)$] was 0.0261. CCDC 293301 and 293302. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517710c

1 J. M. Lynam, M. C. Copsey, M. Green, J. C. Jeffery, J. E. McGrady, C. A. Russell, J. M. Slattery and A. C. Swain, *Angew. Chem., Int. Ed.*, 2003, **42**, 2778.

2 For examples of these compounds and other related structures see: K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1; R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 67 and references therein.

3 M. Lindsjö, A. Fischer and L. Kloo, *Angew. Chem., Int. Ed.*, 2004, **43**, 2540.

4 M. D. Francis and P. B. Hitchcock, *Organometallics*, 2003, **22**, 2891.

5 M. D. Francis and P. B. Hitchcock, *Chem. Commun.*, 2002, 86.

6 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

7 C. Lee, W. Yang and R. Parr, *Phys. Rev. B*, 1988, **37**, 785.

8 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.

9 W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.

10 D. A. Pantazis, J. E. McGrady, J. M. Lynam, C. A. Russell and M. Green, *Dalton Trans.*, 2004, 2080.

11 No resonance was observed for the ring carbon atom in the ^{13}C NMR spectrum of $[\mathbf{1}]^+[Al\{OC(CF_3)_3\}_4]^-$, presumably on account of the broadening though direct linkage to the rapidly exchanging P centres.