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The contrasting behaviour of bridged amido-cyclopentadienyl (constrained geometry) group 15 chlorides and cations derived therefrom

Robert J. Wiacek,[a] Charles L. B. Macdonald,[b] Jamie N. Jones,[a] Jeffrey M. Pietryga[a] and Alan H. Cowley*[a]

[a] *Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712, USA. E-mail: cowley@mail.utexas.edu; Fax: 512-471-6822; Tel: 512-471-7484*

[b] *Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada*

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The first group 15 amido-cyclopentadienyl (constrained geometry) cations have been prepared and structurally characterized; the structure of the stibenium cation is different from those of the corresponding phosphenium and arsenium cations.

The d- and f-block complexes that feature the linked amido-cyclopentadienyl ligand [Me$_2$Si(C$_5$Me$_4$)N-*t*-Bu)]$^{2-}$ (**1**) are the focus of much current research since they are more electronically unsaturated and sterically accessible than the corresponding metallocenes.[1–3] Some of these so-called ‘constrained geometry complexes’ have proved to be important as single-site olefin polymerization catalysts. However, in light of the foregoing, it is curious that, with the exception of a few Al(III) and Ga(III) complexes,[4] ligand **1** has not been employed in p-block chemistry. Herein we report (i) the first group 15 complexes that incorporate ligand **1**, (ii) surprising differences in the phosphorus, arsenic, and antimony chemistry of ligand **1**, and (iii) the first examples of structurally authenticated constrained geometry p-block cations.

Treatment of [Me$_2$Si(C$_5$Me$_4$)(N-*t*-Bu)](MgCl)$_2$·THF][5] with ECl$_3$ results in 50–80% yields of monochlorides of composition [Me$_2$Si(C$_5$Me$_4$)(N-*t*-Bu)]ECl (**2**, E = P; **3**, E = As; **4**, E = Sb).[6] X-ray analyses† of **3** and **4** indicate that these compounds possess the anticipated structure in the sense that there is σ-attachment of the group 15 element to the Cp ring in an α position with respect to the μ-SiMe$_2$ group, which permits the formation of five-membered E–C–C–Si–N rings (Fig. 1). Note that, unlike d- and f-block bridged amido-cyclopentadienide complexes,[1–3] **3** and **4** feature σ- rather than π-interactions with the Cp ring. Presumably, this observation is due to the absence of sufficiently low-lying π-acceptor orbitals on the part of the pnictogen atom. Consistent with the η^1(σ) Cp attachment, the C(1)–C(2) and C(3)–C(4) bond lengths for both compounds are considerably shorter than the other three. Within experimental error, the nitrogen atom of each compound is planar and the sums of bond angles at As and Sb are 294.42(7)° and 286.77(9)°, respectively. The solution phase ^{1}H and NMR data[6] for **3** and **4** are consistent with the crystal structures in the sense that such data evidence four ring-methyl resonances along with non-equivalent SiMe$_2$ signals. The SiMe$_2$ signals for **2** are also non-equivalent; however, the chemical shifts are significantly different than those for **3** and **4**, thus implying a different structure for the chlorophosphine. In fact, **2** adopts an unprecedented constrained geometry structure in which the μ-SiMe$_2$ group is attached to a methylated Cp ring carbon rather than to the unmethylated position (Fig. 1). Moreover, the double bonds in **2** are located between C(2) and C(3) and C(4) and C(5) hence the phosphorus atom is connected to a vinylic fragment.

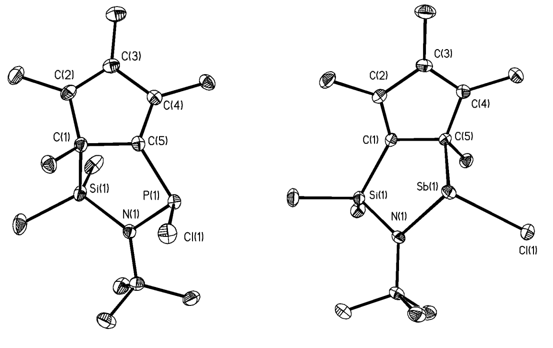

Fig. 1 Molecular structures of **2** (left) **4** (right). Important bond lengths [Å] and angles [°] **2**: P(1)–N(1) 1.689(2), P(1)–C(5) 1.790(2), N(1)–Si(1) 1.773(2), Si(1)–C(1) 1.904(2), C(1)–C(5) 1.506(2), N(1)–P(1)–C(5) 93.63(8), P(1)–N(1)–Si(1) 113.90(9), N(1)–Si(1)–C(1) 98.37(8), Si(1)–C(1)–C(5) 95.12(11), C(1)–C(5)–P(1) 120.56(13); **4**: Sb(1)–N(1) 2.036(2), Sb(1)–C(5) 2.333(3), N(1)–Si(1) 1.746(2), Si(1)–C(1) 1.870(2), C(1)–C(5) 1.504(3), N(1)–Sb(1)–C(5) 90.58(9), Sb(1)–N(1)–Si(1) 107.38(10), N(1)–Si(1)–C(1) 95.92(10), Si(1)–C(1)–C(5) 117.66(16) C(1)–C(5)–Sb(1) 84.07(14).

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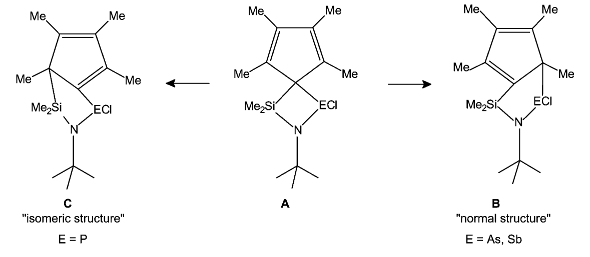
The geometry at phosphorus is pyramidal (sum of angles = 299.21(8)°) and the nitrogen geometry is trigonal planar within experimental error. Two possible steps that lead to the observed products are shown in Scheme 1. If the initially formed product is **A**, this four-membered ring species can form either the ‘normal structure’, **B**, or the ‘isomeric structure’, **C**, by a 1,2 shift of an E–Cl or a SiMe$_2$ group, respectively. Because of the bond strength sequence P–C > Si–C > As–C > Sb–C, movement of the SiMe$_2$ fragment is favoured when E = P.

Treatment of **2**–**4** with AlCl$_3$ results in chloride abstraction and formation of salts of composition [{Me$_2$Si(C$_5$Me$_4$)N-*t*-Bu}E][AlCl$_4$] (**5**, E = P; **6**, E = As; **7**, E = Sb) as evidenced by the characteristic ^{27}Al chemical shifts for the [AlCl$_4$]$^-$ anion,[7] the pattern of ^{1}H resonances and, in the case of **5**, a downfield ^{31}P chemical shift of δ 394.0. The crystalline states of **5**–**7** consist of cation–anion pairs, the closest inter-ionic contacts being ~3.3 Å. Other than the absence of the Cl$^-$ ion, the gross structure of the phosphenium ion resembles that of the precursor **2**. Focusing on the P$^+$ centre, the major changes that accompany chloride anion abstraction are a 4.2° increase in the N(1)–P(1)–C(5) angle and modest decreases in the P(1)–N(1) (~0.03 Å) and P(1)–C(5) (~0.06 Å) bond lengths.

Intriguingly, chloride ion abstraction from **4** results in a change from the ‘normal structure’ to the ‘isomeric structure’ in the related arsenium cation, **6**$^+$. The overall structural features of the two crystallographically independent **6**$^+$ cations (one of which is shown in Fig. 2) are similar to those discussed above for phosphenium cation, **5**$^+$. It is likely that the rearrangement to



Scheme 1

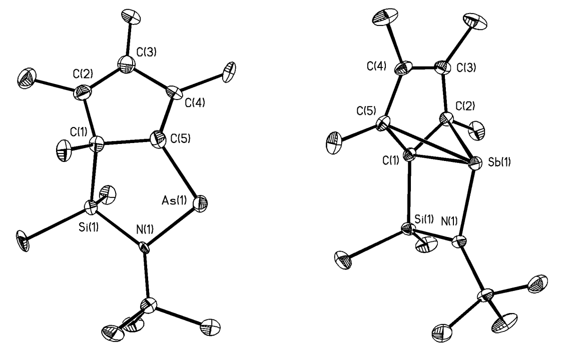


Fig. 2 Molecular structures of cations, **6**$^+$ (left) and **7**$^+$ (right). Important bond lengths [Å] and angles [°]: **5**$^+$: P(1)–N(1) 1.659(7), P(1)–C(5) 1.730(6), N(1)–Si(1) 1.862(6), Si(1)–C(1) 1.900(6), C(1)–C(5) 1.509(8), N(1)–P(1)–C(5) 97.8(3), C(1)–C(5)–P(1) 121.0(4), C(5)–C(1)–Si(1) 97.4(4), C(1)–Si(1)–N(1) 96.0(3), Si(1)–N(1)–P(1) 110.6(4); **6**$^+$: As(1)–N(1) 1.827(7), As(1)–C(5) 1.866(8), N(1)–Si(1) 1.822(7), Si(1)–C(1) 1.889(7), C(1)–C(5) 1.503(10), N(1)–As(1)–C(5) 93.9(3), C(1)–C(5)–As(1) 119.0(5), C(5)–C(1)–Si(1) 100.2(5), C(1)–Si(1)–N(1) 98.9(3), Si(1)–N(1)–As(1) 110.4(4); **7**$^+$: Sb(1)–N(1) 2.0170(1), Sb(1)–C(1) 2.230(2), Sb(1)–C(2) 2.522(2), Sb(1)–C(5) 2.460(2), N(1)–Si(1) 1.756(2), Si(1)–C(1) 1.901(2), Sb(1)–N(1)–Si(1) 101.26(7), N(1)–Si(1)–C(1) 92.38(7).

6$^+$ takes place *via* an intermediate with an η^3-structure similar to that of stibenium cation **7**$^+$ (see below).

The structure of **7**$^+$ is of interest because of the rarity of such species.[8] This cation, which possesses the 'normal structure,' features η^3-attachment of Sb to the Cp ring, the bonding in which is more delocalized than that in the precursor chloride **4**. Note however that the C(3)–C(4) bond (1.399(3) Å) is shorter than the others, which average 1.444(3) Å. Another noteworthy feature is the shortening of the N–Sb bond length by ~ 0.2 Å as **4** is converted into **7**$^+$, which suggests that donation from the amido fragment is much more important for the stabilization of this electron-deficient pnictogen in this geometry.

In conclusion, the present study demonstrates that the main group chemistry of the constrained geometry ligand is significantly different than that of d- and f-block elements. Moreover, ligand **1** shows great promise for the stabilization of a wide variety of main group cations. Reactivity and theoretical (DFT) studies are in progress.

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Notes and references

† *Crystal data.* Single crystals were covered with mineral oil and mounted on a Nonius KAPPA-CCD at 153(2) K using Mo Kα radiation (λ = 0.71073 Å). Each structure was solved by direct methods. **2**: $C_{15}H_{27}ClNPSi$, orthorhombic, *Pbca*, a = 15.304(5), b = 14.964(5), c = 15.503(5) Å, V = 3550(2) Å^3, Z = 8, D_{calcd} = 1.330 g cm^{-3}, μ (Mo Kα) = 0.407 mm^{-1}; wR$_2$ = 0.0482, R$_1$ = 0.0905. **3**: $C_{15}H_{27}AsClNSi$, monoclinic, $P2_{1/n}$, a = 6.953(5), b = 17.258(5), c = 14.991(5) Å, β = 91.669(5)°, V = 1798.1(15) Å^3, Z = 4, D_{calcd} = 1.662 g cm^{-3}, μ (Mo Kα) = 2.619 mm^{-1}; wR$_2$ = 0.0561, R$_1$ = 0.0274. **4**: $C_{15}H_{27}ClNSbSi$, monoclinic, $P2_{1/n}$, a = 8.146(5), b = 24.618(5), c = 8.984(5) Å, β = 95.488(5)°, V = 1793.4(15) Å^3, Z = 4, D_{calcd} = 1.883 g cm^{-3}, μ (Mo Kα) = 2.179 mm^{-1}; wR$_2$ = 0.0786, R$_1$ = 0.0332. **5**: $C_{15}H_{27}AlCl_4NPSi$, orthorhombic, *Pca*2(1), a = 18.064(4), b = 8.3447(17), c = 30.103(6) Å, V = 4537.6(16) Å^3, Z = 9, D_{calcd} = 1.480 g cm^{-3}, μ (Mo Kα) = 0.768 mm^{-1}; wR$_2$ = 0.2002, R$_1$ = 0.0772. **6**: $C_{15}H_{27}AlAsCl_4NSi$, orthorhombic, *Pca*2(1), a = 18.184(4), b = 8.2774(17), c = 30.284(6) Å, V = 4558.2(16) Å^3, Z = 9, D_{calcd} = 1.617 g cm^{-3}, μ (Mo Kα) = 2.306 mm^{-1}; wR$_2$ = 0.1537, R$_1$ = 0.0677. **7**: $C_{15}H_{27}AlCl_4NSbSi$, triclinic, *P*1, a = 10.064(5), b = 11.154(5), c = 12.120(5) Å, α = 92.411(5)°, β = 114.403(5)°, γ = 110.722(5)°, V = 1130.2(9) Å^3, Z = 2, D_{calcd} = 1.587 g cm^{-3}, μ (Mo Kα) = 1.784 mm^{-1}; wR$_2$ = 0.0431, R$_1$ = 0.0202. CCDC 200128–200133. See http://www.rsc.org/suppdata/cc/b2/b211591c/ for crystallographic data in CIF or other electronic format.

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6 The synthesis of compounds **2**–**4** is exemplified by that of **2**. A pale yellow solution of [$Me_2Si(C_5Me_4)$(N-*t*-Bu)]$(MgCl)_2$·THF][5] (3.192 g, 7.237 mmol) in THF (50 mL) was added slowly to a solution of PCl_3 (0.983 g, 7.158 mmol) in 70 mL of THF at room temperature. The yellow reaction mixture was stirred overnight, following which the solvent and volatiles were removed under reduced pressure. The resulting yellow solid was extracted with 50 mL of pentane and filtered through Celite® to afford a crop of yellow crystalline **2** in 47.9% yield. The yields of **3** and **4** were 83.3 and 84.4%, respectively. **2**: ^{1}H NMR (CD_2Cl_2): δ −0.55 (s, SiMe, 3H), 0.54 (s, SiMe, 3H), 1.42 (d, $NCMe_3$, 9H, $^4J_{PH}$ = 1.75 Hz), 1.44 (d, $NCMe_3$, 9H), 1.59 (s, C_5Me, 3H), 1.86 (s, C_5Me, 3H), 1.90 (s, C_5Me, 3H), 2.18 (s, C_5Me, 3H). ^{31}P NMR (CD_2Cl_2): δ 139.00 (s, PCl). **3**: ^{1}H NMR (CD_2Cl_2): δ 0.40 (s, SiMe, 3H), 0.46 (s, SiMe, 3H), 1.41 (s, $NCMe_3$ + s, C_5Me, 12H), 1.85 (s, C_5Me_2, 6H) 2.06 (s, C_5Me, 3H). **4**: ^{1}H NMR (C_6D_6): δ 0.29 (s, SiMe, 3H), 0.56 (s, SiMe, 3H), 1.23 (s, $NCMe_3$, 9H), 1.82 (s, C_5Me, 3H), 1.85 (s, C_5Me, 3H), 1.95 (s, C_5Me, 3H) 2.36 (s, C_5Me, 3H). The synthesis of compounds **5**–**7** is exemplified by that of **5**. A solution of $Me_2Si(\eta$-$C_5Me_4)$(N-*t*-Bu)PCl (0.625 g, 1.978 mmol) in CH_2Cl_2 (20 mL) was added to a stirred suspension of $AlCl_3$ (0.349 g, 2.618 mmol) in CH_2Cl_2 (20 mL) at room temperature, resulting in an orange solution. After being stirred overnight, the reaction mixture was filtered through Celite® and the filtrate was layered with an equal volume of pentane to afford a crop of red-orange crystals in 87.8% yield. **5**: ^{1}H NMR (CD_2Cl_2): δ −0.15 (s, 3H, SiMe), 0.92 (s, 3H, SiMe), 1.38 (s, 3H, C_5Me), 1.67 (s, 9H, $NCMe_3$), 2.04 (s, 3H, C_5Me), 2.18 (s, 3H, C_5Me), 2.612 (s, 3H, C_5Me); ^{27}Al NMR (CD_2Cl_2): δ 99.6 (s, $AlCl_4^-$); ^{31}P NMR (CD_2Cl_2): δ 394.0 (s, P$^+$). **6**: ^{1}H NMR (CD_2Cl_2): δ 0.85 (s, $SiMe_2$, 6H), 1.35 (s, $NCMe_3$, 9H), 2.05 (s, C_5Me_2, 6H), 2.48 (s, C_5Me_2, 6H). **7**: ^{1}H NMR (CD_2Cl_2): δ 0.72 (s, 6H, $SiMe_2$), 1.31 (s, 9H, $NCMe_3$), 1.93 (s, 6H, C_5Me), 2.53 (s, 6H, C_5Me), ^{27}Al NMR (CD_2Cl_2) δ 99.5 (s, $AlCl_4^-$).

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