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Low-Coordinate Cations

Weak Arene Stabilization of Bulky Amido-Germanium(II) and Tin(II) Monocations**

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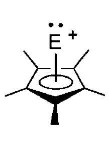
The last two decades have seen much progress in extending the chemistry of classical carbenium ions, R_3C^+, to their heavier Group 14 counterparts, R_3E^+ (E = Si, Ge, Sn, or Pb).[1] The isolation of such species at ambient temperature has generally required their pairing with large, charge diffuse, weakly coordinating anions (WCAs); while the highly electrophilic nature of the cations is at the heart of their remarkable reactivity. Despite considerable efforts, fewer advances have been made within the closely related field of Group 14 element(II) monocation ($RE\!:^+$) chemistry,[2] and one-coordinate examples of these ions remain elusive. If they could be accessed they would undoubtedly be extremely electrophilic (as there are only four valence electrons at the cationic E center), while at the same time holding the potential to act as nucleophiles through their E lone pair. Similar ambiphilic behavior is now well established for the neutral, isoelectronic Group 13 analogues of the cations, that is, the one-coordinate metal diyls, RM: (M = Al, Ga, In, or Tl).[3]

Although truly one-coordinate cations of the type $RE\!:^+$ are unknown, a variety of kinetic and/or electronic stabilization strategies have been employed to allow an entry to higher-coordinate examples. These include the use of anionic[4] or neutral[5] arene donors (as in **1** and **2**), and bi-[6–8] or polydentate[9] N-donor ligands (as in **3** and **4**). Other notable stabilization strategies involve electronic saturation of $RE\!:^+$ by very nucleophilic N-heterocyclic carbenes[10] (e.g. as in $[(NHC)_2GeCl]^+$ (NHC = :C(*i*PrNCMe)$_2$) or crown ethers[11] (e.g. as in $[GeCl([15]crown\text{-}5)]^+$), and coordination of the cation E lone pair to a transition metal fragment[12] (e.g. as in $[\{\kappa^3\text{-}C_6H_3(CH_2OMe)_2\text{-}2,6\}(THF)_2Sn\rightarrow Cr(CO)_5]^+$). Perhaps the lowest-coordinate Group 14 cation so far reported is **5**, in which the bulky terphenyl ligated Pb center has only a weak η^2-interaction with a molecule of toluene (closest Pb–$C_{toluene}$ distance: 2.832(10) Å).[13] Accordingly, this was described as a quasi-one-coordinate cation, a view that was supported by spectroscopic and crystallographic data.



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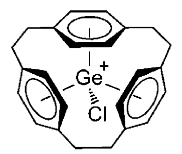

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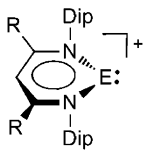

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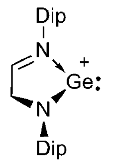

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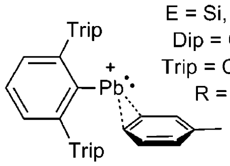

5

E = Si, Ge, Sn or Pb
Dip = $C_6H_3iPr_2$-2,6
Trip = $C_6H_2iPr_3$-2,4,6
R = Me or *t*Bu

In order to access stable one-coordinate Group 14 cations, $RE\!:^+$, it is clear that their substituent (R) would have to possess considerable steric bulk. Recently, we developed a series of extremely hindered amide ligands L (e.g. $-N(Ar^*)(SiMe_3)$, $Ar^* = C_6H_2\{C(H)Ph_2\}_2Me\text{-}2,6,4$), which we believed might be suitable for this task.[14] Moreover, we have utilized these amides in the preparation of the first monomeric amido Group 14 metal(II) halide complexes (e.g. LECl, E = Ge or Sn), which we saw as ideal precursors for the synthesis of the cations, LE^+, by halide abstraction methods. Here, we show that such cations can indeed be accessed, and that in addition to their amido linkage, their coordination sphere only includes a weak, intramolecular η^2-arene interaction in the solid state (cf. **5**). Preliminary studies of the further reactivity of the cations are also discussed.

The silver and lithium salts of the perfluorinated aluminate anion, $[Al\{OC(CF_3)_3\}_4]^-$ (PF), were chosen as chloride abstraction agents because of their ease of preparation, and because of their weakly coordinating nature.[15] Reaction of Ag[PF] with LSnCl in dichloromethane (DCM) gave the salt, **6**, in good yield as a yellow, thermally stable crystalline solid (Scheme 1).[16] In contrast, the reaction of Ag[PF] with LGeCl did not lead to chloride abstraction, but instead to the germylene donor complexes, $[\{L(Cl)Ge\}_2Ag][PF]$ and $[\{L(Cl)Ge\}Ag(\eta^2\text{-}PhF)][PF]$ (see Supporting Information for further details), when the reactions were carried out in DCM or fluorobenzene (PhF), respectively. To circumvent this

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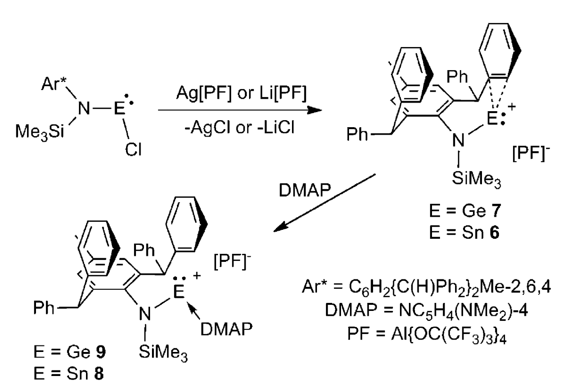
Supporting information for this article (synthesis and characterizing data for all new compounds, and full details and references for the crystallographic and computational studies) is available on the WWW under http://dx.doi.org/10.1002/anie.201204601.



Scheme 1. Synthesis of compounds **6**–**9**.

problem a synthetic route was devised whereby a solution of LGeCl in DCM was slowly added to a solution of Li[PF] in PhF, affording a good isolated yield of yellow **7**, upon work-up. It is of note that **7** could not be isolated when the reaction was carried out with the reverse addition of reagents, or when only one of the solvents was used. The latter observation results from the fact that LGeCl is poorly soluble in PhF, while Li[PF] has a low solubility in DCM.

The X-ray crystal structures of **6** and **7** were obtained and the compounds found to be isomorphous. As a result only the structure of the cation of **7** is depicted in Figure 1 (see Supporting Information for the structure of the cationic component of **6**), while metrical parameters for both compounds can be found in the caption. There are no close contacts between the anion and metal centers of **6** (closest: 3.54 Å) or **7** (closest: 3.71 Å), and their metal–N distances are only slightly shorter than those in LSnCl (2.076(3) Å) and LGeCl (1.855(3) Å), respectively.[14a] At first glance, the cations of **6** and **7** appeared to be truly one-coordinate. However, in both there is a weak η^2-interaction between the C(28)−C(33) bond and their tin (Sn−C: 2.82 Å mean) or germanium (Ge−C: 2.65 Å mean) centers (note the next closest $C_{phenyl}\cdots E$ distances are ca. 3.0 Å). While these contacts are closer than the shortest $C_{phenyl}\cdots E$ distances in the neutral species, LSnCl (3.110(3) Å) and LGeCl (3.074(3) Å),[14a] they are comparable to the shortest $Pb\cdots C_{toluene}$ separation (2.832(10) Å) in **5**.[13] Given the markedly larger covalent and dicationic radii for lead (1.54 Å/1.32 Å) relative to those of tin (1.40 Å/0.93 Å) and germanium (1.22 Å/0.90 Å),[17] and the fact that **5** is viewed as quasi-one-coordinate, it is reasonable to describe the Group 14 metal centers of **6** and **7** as having similar, if not lower, degrees of coordination than that of **5** in the solid state. This is also borne out by the fact that the η^2-C···E distances in **6** and **7** are of the same order as η^6-C···E distances in much higher coordination number arene complexes, for example, **2**,[5] and considerably longer than η^5-C···E interactions in cyclopentadienyl complexes, for example, **1**.[4]

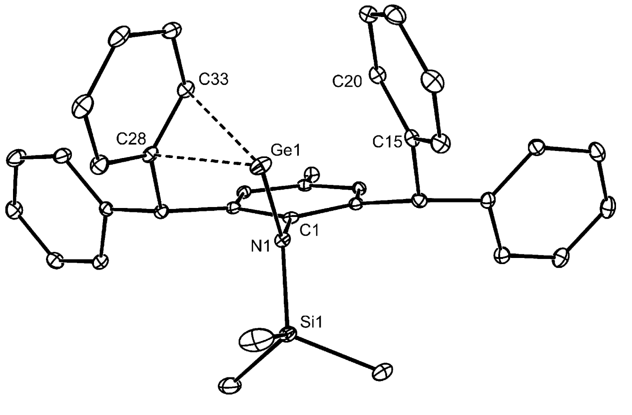


Figure 1. Structure of the cationic component of **7** (25% ellipsoids; hydrogen atoms omitted). Relevant bond lengths [Å] and angles [°] for **7**: Ge1–N1 1.8153(18), Si1–N1 1.7715(19), N1–C1 1.448(3), Ge1–C28 2.642(2), Ge1–C33 2.661(2), Ge1–C15 3.013(2), Ge1–C20 3.116(2); C1-N1-Si1 121.80(14), C1-N1-Ge1 116.00(14), Si1-N1-Ge1 122.12(10). Relevant bond lengths [Å] and angles [°] for **6**: Sn1–N1 2.0413(18), Si1–N1 1.7460(19), N1–C1 1.437(3), Sn1–C28 2.821(2), Sn1–C33 2.827(2), Sn1–C15 3.034(2), Sn1–C20 3.083(2); C1-N1-Si1 122.03(14), C1-N1-Sn1 115.67(13), Si1-N1-Sn1 122.29(10).

The solution state ^1H and $^{13}C\{^1H\}$ NMR spectra ([D$_2$]dichloromethane) of **6** and **7** acquired at room temperature are suggestive of more symmetrical structures for their cations (C_s symmetry) than is seen in the solid state (see Supporting Information for full details). Most revealing are their $^{13}C\{^1H\}$ NMR spectra which exhibit twelve aryl resonances, thus indicating that there are no arene–metal interactions that persist long enough to be observed on the NMR timescale. When the solutions were cooled to −70 °C (close to the solubility limits of the compounds), the $^{13}C\{^1H\}$ NMR spectra partially resolved, and sixteen broad aryl signals were observed. This, again, indicates time-averaged C_s symmetry for the cations of **6** and **7** (see Supporting Information, Figure S2), and therefore that the solid-state structures of the molecules (C_1 symmetry) have not "frozen out" in solution. Instead, the spectra signify that a dynamic process occurs in solution at low temperature, which likely involves a rapid exchange of weak (η^2-arene)–E interactions between both C(H)Ph$_2$ groups of either cation. Furthermore, the solution-state ^{27}Al and ^{19}F NMR spectra of **6** and **7** exhibit resonances that are very close to those previously reported for the uncoordinated anion.[15] This suggests that there are no significant cation–anion interactions in solution.

^{119}Sn NMR spectroscopy can be a useful tool to probe the coordination number of tin(II) compounds, and the electronic effects of tin-coordinated ligands.[18] Interestingly, the room-temperature solution-state ^{119}Sn NMR spectrum of **6** displayed a broad signal at $\delta = 46.3$ ppm (peak width at half height: 195 Hz), which is upfield of the signal for the neutral two-coordinate precursor complex, LSnCl ($\delta = 173.7$ ppm).[14(a)] While this may seem counterintuitive at first sight, ^{119}Sn chemical shifts for higher-coordinate tin(II) cations are typically found upfield from that for **6**. To the best of our knowledge there have been no ^{119}Sn NMR data reported for crystallographically authenticated two-coordinate cations,[19] but data for several three-coordinate (e.g. $[\{HC(MeCNDip)_2\}Sn(OEt_2)]^+$, $\delta = -139.5$ ppm),[6d] four-coordinate (e.g. $[\{C_5NH_3(MeCNDip)_2\text{-}2,6\}SnCl]^+$, $\delta = -435.0$ ppm),[9a] and higher-coordinate species[11] have been described. It is particularly noteworthy that the ^{119}Sn NMR signals for π-complexed arene–tin(II) cations can occur at very high fields. A pertinent example here is the cyclopentadienyl complex, $[Sn(\eta^5\text{-}C_5H_3tBu_2\text{-}1,3)]^+$ ($\delta = -2100$ ppm).[20] The solid-state ^{119}Sn MAS NMR spectrum of **6** was also acquired, and while the signal-to-noise ratio was low, the isotropic chemical shift for the compound was determined to be $\delta = 68$ ppm, that is, in quite good agreement with the solution spectrum. Finally, the solution-state ^{15}N NMR shift of the amide center of **6** was found to be $\delta = -188$ ppm, though ^{119}Sn satellites for this signal were not observable.

The ^{119}Sn Mössbauer spectrum of **6** was recorded at 78 K and is depicted in Figure 2. It was readily simulated as possessing a single tin signal at an isomer shift of $\delta = 3.369(4)$ mm s^{-1}, which is subjected to significant quadrupole splitting of $\Delta E_Q = 3.69(1)$ mm s^{-1}. The isomer shift depends on the s electron density at the tin nucleus, and values of around 4 mm s^{-1} typically occur for tin(II) compounds (e.g. SnS, $\delta = 3.4$ mm s^{-1}; SnF_2, $\delta = 3.6$ mm s^{-1})[21] and cations (e.g. $[SnCl([18]crown\text{-}6)]^+$, $\delta = 3.83$ mm s^{-1}).[11a] Accordingly, it is clear that the tin atom in **6** is in the +2 oxidation state. Because of the non-cubic environment of this tin center, we expect a high quadrupolar interaction associated with the electric field gradient. This is in full agreement with the high quadrupole splitting parameter observed for the compound.

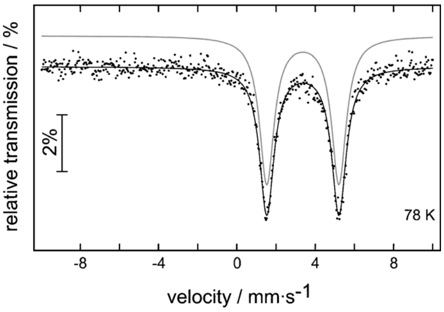


Figure 2. Experimental (bottom line) and simulated (top line) ^{119}Sn Mössbauer spectra of **6** at 78 K.

In order to gain further insight into the electronic structure of the cations of **6** and **7**, quantum-chemical calculations (BP86/RI-DFT/def2-TZVPP/def2-SVP) were carried out on the full ions in the gas phase. In both cases the geometries of the cations optimized to be close to the experimental structures, but with slightly overestimated Sn–N (2.058 Å) and Ge–N (1.841 Å) bond lengths. In addition, whereas in the solid state only one phenyl group has a weak η^2-interaction with the E center of each cation, in the calculated structures there are essentially equivalent η^2-interactions with one phenyl group from both $C(H)Ph_2$ substituents of the cations. This gives rise to C_s symmetrical structures with four E···C contacts < 3.0 Å, rather than the two contacts seen in the unsymmetrical solid-state structures. The calculated contacts (Sn···C 2.96 Å mean; Ge···C 2.84 Å mean) are longer (and apparently weaker) than in the experimental situation, as might be expected given their greater number. In fact, the calculated structures are consistent with the time-averaged solution-state structures proposed from the low-temperature (−70 °C) NMR spectroscopic studies.

Analyses of the frontier orbitals of the calculated cations revealed similar electronic structures. In the case of the cation of **7**, the LUMO largely comprises an empty p-orbital coplanar with the CNSiGe fragment, while the empty p-orbital orthogonal to that fragment is associated with LUMO+1 (Figure 3). This is directed towards a phenyl ring on each side of the cation, though there does not appear to be any significant Ge–arene bonding interaction taking place in that orbital, or any of the higher-energy filled MOs. The HOMO of the cation is essentially a ligand based orbital, while the HOMO−10 and HOMO−21 both possess character compatible with a Ge lone pair having a high s-orbital component. In contrast to the neutral precursor compound, LGeCl, the N p-orbital of **7** (HOMO−6) has a negligible π-bonding interaction with the empty p-orbital of appropriate symmetry at Ge.

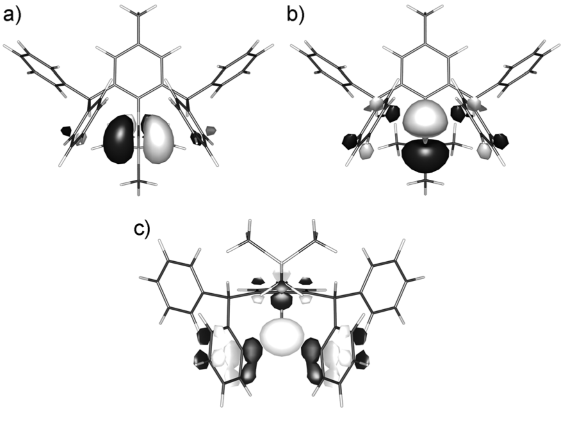


Figure 3. a) LUMO+1, b) LUMO and c) HOMO−10 of the cation of **7**.

Although an inspection of the molecular orbitals of **6** and **7** suggested negligible E···C$_{phenyl}$ interactions in the calculated cations, Wiberg bond indices (WBIs) were calculated for each in order to provide some quantification of the strengths of these interactions. The sum of the four largest E···C$_{phenyl}$ WBIs (i.e. from two η^2- interactions, involving two *ipso*-carbons, and two adjacent *ortho*-carbons) were found to be 0.423 for **6** and 0.283 for **7**. These are substantially lower than the WBIs for the E–N bonds of each (1.027 for **6** and 0.946 for **7**), and the E–C single-bond WBIs calculated for the optimized structures of :EMe_2 (E = Sn 0.920 mean, Ge 0.849 mean). These results are fully consistent with the description of the cations as being weakly arene stabilized. Moreover, to allow direct comparisons between the relative strengths of the η^2-E···C$_{arene}$ interactions in **6** and **7**, and that in Power's compound, **5**, empirical bond valence calculations were carried out using Brown's Bond Valence program[22] on the solid-state geometries of each compound. These gave the sum of the four strongest E···C$_{arene}$ interactions as 0.64 v.u. (valency units) for **5** (Pb–C$_\sigma$ 1.15 v.u.), 0.49 v.u. for **6** (Sn–N 1.08 v.u.), and 0.43 v.u. for **7** (Ge–N 1.24 v.u.), where the v.u. values can be considered to be roughly equivalent to a bond order. The results of these calculations clearly indicate that the E···C$_{arene}$ interactions in **6** and **7** are not only weak, but are apparently weaker than those in quasi-one-coordinate **5**.

In initial attempts to form complexes of the cations of **6** and **7**, they were either dissolved in THF, or their DCM solutions were treated with large excesses of styrene. However, dissolution of both salts in THF led to polymerization of the ether at 20 °C over several hours, while reactions with styrene occurred rapidly at 20 °C, generating moderate yields of polystyrene. Although these reactions presumably proceed through initial 1:1 complexes (which could not be isolated) the subsequent catalyzed polymerizations of the substrates clearly indicate the significant electrophilicity of the cations. Attention then turned to reactions of **6** and **7** with one equivalent of 4-(dimethylamino)pyridine (DMAP) in DCM solutions. These led to complexation and the formation of the salts, **8** and **9**, in good yields (Scheme 1). The multinuclear NMR spectroscopic data for the compounds are consistent with them existing as ion separate salts in solution, with the cations possessing C_s symmetry (cf. the cations of **6** and **7**). Of note is the room-temperature solution-state ^{119}Sn NMR spectrum of **8** (in [D$_2$]dichloromethane), which displays a singlet resonance significantly upfield ($\delta = -30.0$ ppm) from that of **6**, thus suggesting its tin center is more electronically satisfied, and has a higher net coordination number.

Crystal structures of both **8** and **9** were obtained and the compounds found to be isomorphous. However, only the structure of **8** was of sufficient quality to report here. Even then, the commonly encountered large atomic displacement parameters for the [PF] anion,[15] in combination with severely disordered lattice solvent molecules, led to relatively high *r*-factors for the structure. With that said, the refinement of the cation was routine and its structural parameters should be considered as reliable. Its structure (Figure 4) contains a two-coordinate cationic tin(II) center, which has no contact with the anion (closest Sn–anion separation: 5.44 Å). The Sn–N$_{\text{amide}}$ distance is significantly shorter than the Sn–N$_{\text{DMAP}}$ separation, but is very close to the Sn–N$_{\text{amide}}$ bond length in **6**. The acute N-Sn-N angle in the cation (96.3(2)°; cf. Cp*$_{\text{centroid}}$-Sn-N angle of 115.0° for [Cp*Sn(pyridine)]$^+$)[23] implies significant s-character for the tin lone pair, and indicates that DMAP complexation occurs through donation of its pyridine N-lone pair orbital into the LUMO of **6**. This complexation leads to displacement of the weak (η^2-arene)–Sn interaction in **6**, as evidenced by the closest Sn···C$_{\text{phenyl}}$ contacts in **8**, which are to the *ipso*-carbons of the two flanking phenyl groups (3.152(6) Å and 3.184(6) Å), and are longer than those in **6**.

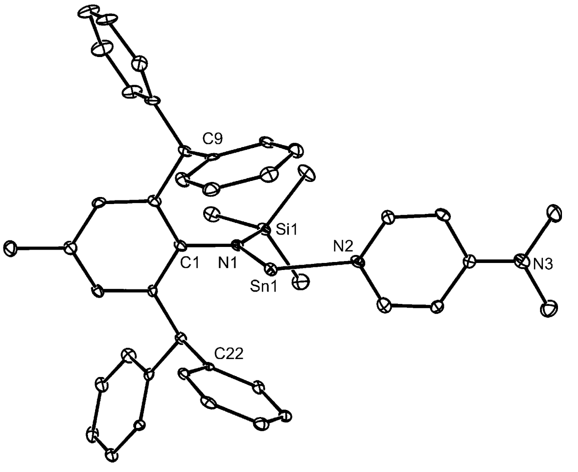


Figure 4. Structure of the cationic component of **8** (25 % ellipsoids; hydrogen atoms omitted). Relevant bond lengths [Å] and angles [°]: Sn1–N1 2.065(6), Sn1–N2 2.286(6), Si1–N1 1.755(6), N1–C1 1.462(9); N1-Sn1-N2 96.3(2), C1-N1-Si1 118.9(5), C1-N1-Sn1 108.1(4), Si1-N1-Sn1 133.0(3).

In summary, extremely bulky amido-germanium(II) and amido-tin(II) monocations, which are intramolecularly stabilized by weak η^2-arene interactions, have been prepared. The structural and electronic properties of these species have been investigated by a combination of techniques, and preliminary reactivity studies have highlighted their electrophilicity. We are currently exploiting this electrophilicity in a systematic examination of the further chemistry of **6**, **7** and related low-coordinate group 14 metal(II) cations.

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