COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

N-H cleavage vs. Werner complex formation: reactivity of cationic Group 14 tetrelenes towards amines

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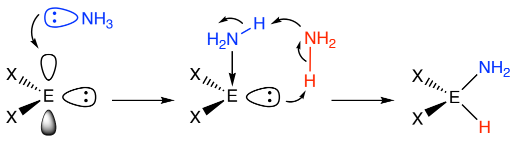
β-Diketiminate ligands featuring backbone NMe$_2$ groups have been exploited to access a series of two-coordinate cations of the type [(N-nacnac)E]$^+$ (E = Si, Ge, Sn), whose reactivity towards N-H bonds has been investigated. While the heavier group 14 systems react via simple adduct formation, N-H oxidative addition occurs for E = Si consistent with differences in E^{II}/E^{IV} redox potentials. The structurally characterized Ge/Sn adducts can be viewed as models for the corresponding (transient) Si systems [(N-nacnac)Si·(NH$_2$R)]$^+$ (R = H, ^{t}Bu) - which are potential intermediates in the formation of [(N-nacnac)Si(H)(NHR)]$^+$ via a proton-shuttling mechanism.

Activation of the N-H bonds in ammonia via oxidative addition at a metal centre represents an attractive target in synthetic chemistry with relevance to a number of important industrial processes.[1] Nonetheless, N-H bond cleavage in this manner remains a significant challenge: the scarcity of transition metal systems capable of effecting such a transformation reflects the competing tendency of ammonia to form classical Werner complexes at unsaturated metal centres.[2]

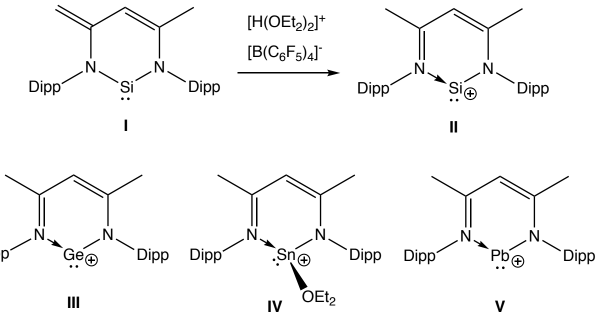
Recently, main group compounds have emerged which will cleave ammonia to give a primary amido/hydride derivative,[3,4] including a number of carbene and related heavier group 14 species in the +2 oxidation state.[3] The presence of a low-lying formally vacant pπ orbital in such systems allows for simple coordination of ammonia (akin to *d*-block metal complexes). However, subsequent N-to-E proton shuttling has been shown to offer a facile route to generate the E(H)(NH$_2$) function without the need for ammonia dissociation (Scheme 1).[3e,3h,5,6]

Although N-H bond cleavage of this type has been reported for charge-neutral tetrelenes, EX$_2$,[3] isoelectronic cations of the type [X(L)E]$^+$ might be expected to offer potential advantages stemming from enhanced Lewis acidity.[7] Thus, the presence of a net positive charge should promote initial coordination of ammonia and enhance the acidity of the NH protons of the coordinated NH$_3$ molecule.



Scheme 1: A coordination/proton-shuttling mechanism for the oxidative addition of the N-H bond in ammonia at divalent Group 14 species of the type EX$_2$.[3e,3h,5,6]

Mononuclear cations of the type [X(L)E]$^+$ can be accessed for a range of systems featuring sterically encumbered β-diketiminate ('Nacnac') supporting ligand frameworks (Scheme 2).[8-12] However, systems of this type featuring backbone Me groups (e.g. **II** - **V**) are known to be very susceptible to deprotonation. Silyliumylidene system **II**, for example, is accessed from the corresponding neutral Si^{II} compound (**I**) via protonation with the extremely strong acid [H(OEt$_2$)$_2$][B(C$_6$F$_5$)$_4$].[9]



Scheme 2: Structurally characterized examples of cationic β-diketiminate E^{II} (and related) systems for E = Si-Pb. (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$; counterions omitted for clarity).

With this in mind, and in order to target systems which would be resistant to backbone deprotonation by ammonia (and related amines), we turned instead to amine-functionalized N-nacnac systems (**VI**, Scheme 3).[12a] Martin and co-workers have previously synthesized a carbene system of this type (i.e. E = C) via deprotonation of the corresponding C-H conjugate acid,[8] but we perceived that a halide abstraction approach exploiting precursors of the type **VII** might prove to be optimal for the heavier group 14 elements. Our studies aimed at isolating system of this type (for E = Si, Ge and Sn) are reported here, together with their contrasting reactivities towards substrates containing N-H bonds.

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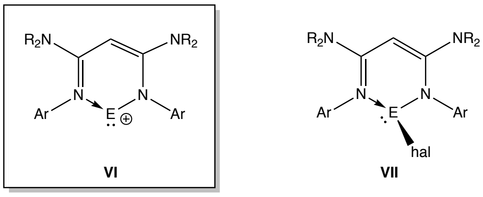
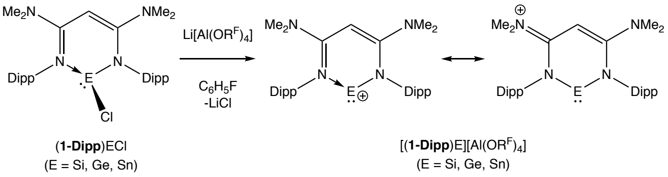
Electronic Supplementary Information (ESI) available: synthetic and computational details; X-ray CIFs (CCDC: 1981261-1981268). See DOI: 10.1039/x0xx00000x



Scheme 3: Cationic systems targeted in the current study (**VI**, E = Si, Ge, Sn) and their halide-containing precursors **VII**.

Halide abstraction from the chlorotetrelenes (**1-Dipp**)ECl (E = Si, Ge, Sn; **1-Dipp** = [HC{(Me$_2$N)C(Dipp)N}$_2$])[12] using Li[Al(OR^F)$_4$][13] affords the corresponding two-coordinate cations [(**1-Dipp**)E]$^+$ as the [Al(OR^F)$_4$]$^-$ salts, in isolated yields ranging from 62% (Si) to 23% (Ge) (Scheme 4). Each of these compounds has been characterized by standard analytical techniques and has been structurally characterized in the solid state by X-ray crystallography.



Scheme 4: Syntheses of two coordinate silicon, germanium and tin cations [(**1-Dipp**)E]$^+$, where E = Si, Ge or Sn (counterions omitted for clarity; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$; R^F = C(CF$_3$)$_3$).

In solution, the pattern of ^{1}H NMR resonances is consistent with a higher degree of symmetry than the (**1-Dipp**)ECl precursors. The signals associated with the Dipp ^{i}Pr protons in each case feature two 12 H doublets and a single septet signal integrating to 4H, consistent with the presence of two planes of symmetry on the NMR timescale.

The ^{29}Si NMR resonance of [(**1-Dipp**)Si][Al(OR^F)$_4$] (δ_{Si} = 80.0 ppm) is shifted significantly downfield from its chloro precursor (δ_{Si} = 1.8 ppm), consistent with decreased shielding of the silicon centre, and is similar to the chemical shifts reported for the two-coordinate silicon compounds **I** and **II** by Driess and co-workers (δ_{Si} = 69.3 and 88.4 ppm, respectively).[9,14] The similarity to the shifts of neutral silylene systems implies a significant contribution from resonance structures in which the cationic charge resides on the backbone NMe$_2$ functions (Scheme 4). By contrast, the ^{119}Sn resonance measured for [(**1-Dipp**)Sn][Al(OR^F)$_4$] (δ_{Sn} = -313 ppm) is shifted *upfield* compared to the chloro-stannylene starting material (δ_{Sn} = -192 ppm). A wide range of ^{119}Sn chemical shifts have been reported for β-diketiminate stabilized Sn^{II} cations by Fulton and co-workers, depending strongly on the nature of the accompanying counterion (δ_{Sn} = +197 for [B(C$_6$F$_5$)$_4$]$^-$, to -627 ppm for [AlCl$_4$]$^-$).[11] In the case of [(**1-Dipp**)Sn]$^+$, the enhanced degree of shielding compared to its three-coordinate precursor implies a degree of secondary coordination at tin in solution; the closest contacts determined crystallographically in the solid state, however, are ca. 3.0 Å (intramolecular Sn···H) and 3.4 Å (intermolecular Sn···F).

At a molecular level, crystallographic studies (Figure 1) reveal features common to all three cations in the solid state. Most notable is the very close approach of the central heterocycle to planarity (sum of all internal angles ≈ 720°), with the group 14 element centre in each case lying much closer to the least-squares NC$_3$N mean plane than in the chloro-tetrelene precursor (largest out-of-plane deviation ca. 0.06 Å). In addition, chloride abstraction brings about marked contraction of the E–N bonds, presumably reflecting the reduced coordination number at E and increased potential for N-to-E π bonding (particularly in the case of E = Si). E–N bond contraction brings with it widening of the N–E–N angle as the group 14 centre is drawn closer into the β-diketiminate ligand chelate (e.g. 1.765(2)/1.768(2) Å and 99.1(1)° for [(**1-Dipp**)Si][Al(OR^F)$_4$], *cf.* 1.846(1)/1.859(1) Å and 96.8(1)° for (**1-Dipp**)SiCl).

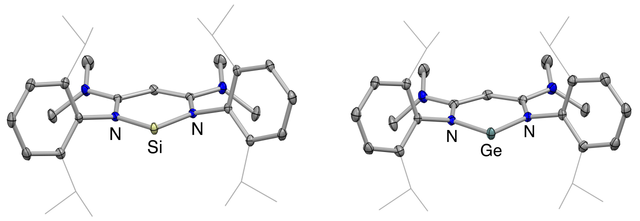


Figure 1. Molecular structures of [(**1-Dipp**)E][Al(OR^F)$_4$] (E = Si (left), Ge (right), Sn (ESI)) in the solid state as determined by X-ray crystallography. [Al(OR^F)$_4$]$^-$ anions and hydrogen atoms omitted and isopropyl groups shown in wireframe format for clarity. Key bond lengths (Å) and angles (°): (for [(**1-Dipp**)Si][Al(OR^F)$_4$]) Si-N 1.765(2), 1.768(2), N-Si-N 99.1(1); (for [(**1-Dipp**)Ge][Al(OR^F)$_4$]) Ge-N 1.881(2), 1.882(2), N-Ge-N 96.0(1); (for [(**1-Dipp**)Sn][Al(OR^F)$_4$]) Sn-N 2.089(2), 2.095(2), N-Sn-N 90.1(1).

In terms of frontier orbitals, DFT studies reveal that the LUMO for each of these cationic species is comprised predominantly of an E-centred *np* orbital lying approximately perpendicular to the C$_3$N$_2$E plane (Figure 2), while the lone pair of the respective tetrel contributes to relatively low-energy occupied orbitals (HOMO-4 and HOMO-5 for the silylene, HOMO-6 and HOMO-7 for the germylene, HOMO-7 for the stannylene), consistent with the stabilizing effect of the cationic charge. While these calculations suggest that the energetic gap between the key frontier orbitals in these cations ($\Delta E_{n\text{-}\pi^*}$) is relatively wide (e.g. 5.58 eV, 538 kJ mol^{-1} for [(**1-Dipp**)Si]$^+$), they also suggest that they might show interesting reactivity as potent Lewis acids. Consistently, the partial positive charges calculated at the group 14 element centre using the NPA method (Si: +1.310; Ge: 1.280; Sn: 1.546) are noticeably higher than in their chlorotetrelene precursors (+1.011, +1.040 and +1.209, respectively).

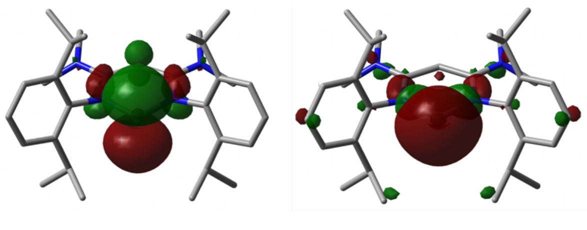
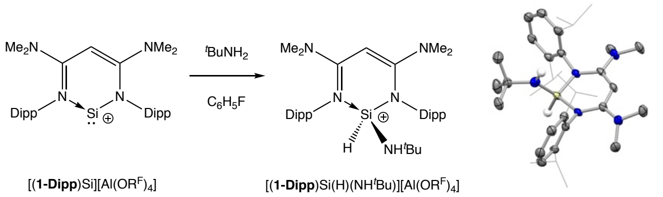


Figure 2. DFT-calculated frontier orbitals for [(**1-Dipp**)Si]$^+$: (left) LUMO at -4.62 eV (-446 kJ mol^{-1}); (right) HOMO-5 at -10.20 eV (-984 kJ mol^{-1}). Analogous frontier orbitals for [(**1-Dipp**)Ge]$^+$ and [(**1-Dipp**)Sn]$^+$ can be located at energies of -4.99 eV (-481 kJ mol^{-1}) / -10.88 eV (1051 kJ mol^{-1}) and -5.25 eV (-507 kJ mol^{-1}) / -10.87 (1049 kJ mol^{-1}).

With this in mind, we examined the reactivity of [(**1-Dipp**)E][Al(OR^F)$_4$] (E = Si, Ge, Sn) towards amines, RNH$_2$. These substrates are known to be activated by a small number of charge-neutral E^{II} systems to give amido E^{IV} hydride products, and both computational and experimental studies have suggested a mechanism involving initial coordination of the amine followed by proton shuttling to E.[3e,3h,5,6] As such, we perceived that the strongly Lewis acid nature of the [(**1-Dipp**)E]$^+$ cations should promote coordination of the amine, enhance the acidity of the bound NH protons, and (subject to the redox properties of E) offer a facile pathway for the formation of the tetravalent systems [(**1-Dipp**)E(H)(NHR)]$^+$.

Initial experiments with [(**1-Dipp**)Si][Al(OR^F)$_4$] carried out using ammonia were hampered by problems controlling the reaction stoichiometry, and the consequent formation of the protio-ligand (**1-Dipp**)H via Si-N bond protonolysis. Small quantities of the N-H activation product [(**1-Dipp**)Si(H)(NH$_2$)][Al(OR^F)$_4$] could be obtained from one reaction (see ESI). However, problems with yield and reproducibility led us to employ ^{t}BuNH$_2$ as a more convenient amine substrate.

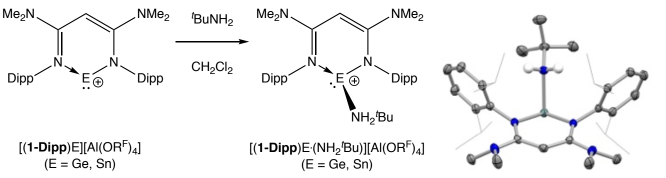
The reactivity of [(**1-Dipp**)E][Al(OR^F)$_4$] (E = Si, Ge, Sn) towards ^{t}BuNH$_2$ is strongly dependent on the nature of E. Thus, in the case of the silicon cation, the reaction with one equivalent of the amine generates an analogous product to that obtained with NH$_3$ – albeit in more reasonable isolated yield (ca. 50%). The product of this reaction, [(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^F)$_4$] (Scheme 5), has been characterized by standard spectroscopic and analytical techniques,[§] and its structure in the solid state determined by X-ray crystallography. A significant upfield shift in the ^{29}Si resonance (to δ_{Si} = -44.5 ppm) is observed, and the appearance of a pair of mutually coupled doublets at δ_H = 0.97 and 5.50 ppm (the latter featuring ^{29}Si satellites with $^1J_{SiH}$ = 285 Hz) is consistent with the formation of the Si(H)(NH^{t}Bu) moiety via formal N-H oxidative addition. The identity of the product, [(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^F)$_4$], was ultimately confirmed by X-ray crystallography (Scheme 5). To our knowledge this system represents the first example of oxidative addition at a two-coordinate Si^{II} cation.[15] Related N-H activation chemistry has been reported for cyclic charge-neutral silylenes such as **II** and the acyclic system {(Me$_3$Si)$_3$Si}{Dipp(Me$_3$Si)N}Si.[3c,3f,3h]



Scheme 5: (upper) Oxidative addition of the N-H bond in ^{t}BuNH$_2$ at [(**1-Dipp**)Si]$^+$ to generate [(**1-Dipp**)Si(H)(NH^{t}Bu)]$^+$ (counterions omitted for clarity). (lower) Molecular structure of [(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^F)$_4$] in the solid state as determined by X-ray crystallography. [Al(OR^F)$_4$]$^-$ anion and most hydrogen atoms omitted and isopropyl groups shown in wireframe format for clarity. Key bond lengths (Å) and angles (°): (for [(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^F)$_4$]) Si-N 1.761(3), 1.775(3), Si-N(H) 1.670(4), Si-H 1.36(6), N-Si-N 103.3(2).

By contrast, the corresponding reactions between [(**1-Dipp**)E][Al(OR^F)$_4$] (E = Ge or Sn) and ^{t}BuNH$_2$ lead not to N-H bond cleavage, but to simple adduct formation (Scheme 6). Each of [(**1-Dipp**)E·(NH$_2{}^t$Bu)] [Al(OR^F)$_4$] (E = Ge, Sn) has been characterized by multinuclear NMR, microanalysis and single crystal X-ray diffraction. In solution, coordination of the amine is reflected in a lowering of the symmetry of the ^{1}H/^{13}C NMR signals associated with the Dipp substituents, and the retention of both N-H bonds is signalled by a single ^{t}BuNH_2 resonance integrating to 2H at 2.30/1.97 ppm (for Ge/Sn).

Descriptions of both compounds as classical Werner coordination complexes are supported by the relatively long E-N distances associated with the ^{t}BuNH$_2$ ligand. Thus, in the cases of both [(**1-Dipp**)Ge·(NH$_2{}^t$Bu)][Al(OR^F)$_4$] and [(**1-Dipp**)Sn·(NH$_2{}^t$Bu)][Al(OR^F)$_4$] the E-N separation [2.168(2) and 2.327(4) Å, respectively] is significantly longer than the sum of the respective covalent radii (1.92 and 2.11 Å),[16] while for [(**1-Dipp**)Si(H)(NH^{t}Bu)][Al(OR^F)$_4$] the reverse is the case, with the Si-N(H)^{t}Bu bond [1.670(4) Å] being markedly shorter than the sum of the respective radii (1.87 Å). In addition the orientation of the E-N coordinate bond with respect to the [(1- **Dipp**)E]$^+$ fragment in [(**1-Dipp**)E·(NH$_2{}^t$Bu)][Al(OR^F)$_4$] (E = Ge, Sn) (e.g. ∠N-Ge-N(H) = 92.7(1), 90.5(1)° for the Ge case) is consistent with the formation of a donor/acceptor interaction via donation from the amine into the vacant $p\pi$ orbital at E (i.e. the LUMO of the cation; Figure 2).



Scheme 6: (left) Coordination of ^{t}BuNH$_2$ at [(**1-Dipp**)E]$^+$ (E = Ge, Sn) to generate [(**1-Dipp**)E·(NH$_2{}^t$Bu)]$^+$ (counterions omitted for clarity). (right) Molecular structure of [(**1-Dipp**)Ge·(NH$_2{}^t$Bu)][Al(OR^F)$_4$] in the solid state as determined by X-ray crystallography. [Al(OR^F)$_4$]$^-$ anion and most hydrogen atoms omitted, and isopropyl groups shown in wireframe format for clarity. Key bond lengths (Å) and angles (°): Ge-N 1.958(2), 1.965(2), Ge-N(H) 2.168(2), N-Ge-N 93.6(1), N-Ge-N(H) 92.7(1), 90.5(1). See ESI for the corresponding structure of [(**1-Dipp**)Sn·(NH$_2{}^t$Bu)][Al(OR^F)$_4$].

For neither [(**1-Dipp**)E·(NH$_2{}^t$Bu)]$^+$ species (E = Ge, Sn) is any evidence seen for N-to-E proton migration under more forcing conditions to give a formal E^{IV} oxidative addition product analogous to that found in the silicon case. This contrasts with the neutral boryl-substituted Sn^{II} system {(HCDippN)$_2$B}$_2$Sn·NH$_3$ which undergoes proton migration from nitrogen to tin in the presence of excess NH$_3$ to give {(HCDippN)$_2$B}$_2$Sn(H)(NH$_2$). These observations presumably reflect differences in E^{II}/E^{IV} redox chemistry on descending group 14, modulated by the very strong σ donor boryl ligand (cf. weaker donor **1-Dipp**) which is capable of supporting formal oxidation to Sn^{IV}.[3h,17] As such, the adducts [(**1-Dipp**)E·(NH$_2{}^t$Bu)]$^+$ (E = Ge, Sn) can be viewed as models for the corresponding (transient) silicon systems [(**1-Dipp**)Si·(NH$_2$R)]$^+$ (R = H, ^{t}Bu) - which are potential intermediates in the formation of [(**1-Dipp**)Si(H)(NHR)] via a proton-shuttling mechanism.

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