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COMMUNICATION

Contrasting reductions of group 14 metal(II) chloride complexes: synthesis of a β-diketiminato tin(I) dimer†‡

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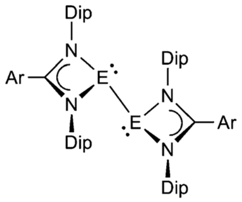
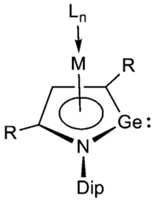
Reductions of the β-diketiminato group 14 metal(II) chloride complexes, [($^{\mathrm{Bu}^t}$MesNacnac)ECl] ($^{\mathrm{Bu}^t}$MesNacnac = [(MesNCBu^t)$_2$CH]$^-$; Mes = mesityl; E = Ge, Sn or Pb), with a magnesium(I) dimer have led to differing outcomes, which include the formation of the first β-diketiminato group 14 metal(I) dimer, [{($^{\mathrm{Bu}^t}$MesNacnac)Sn}$_2$].

The rapid development of the chemistry of low oxidation state group 14 compounds over the last decade has been one of the major driving forces behind the renaissance that is occurring in main group chemistry. This progress is typified by the heavier group 14 alkyne analogues (or ditetrelynes), REER (E = Si, Ge, Sn or Pb; R = bulky terphenyl, silyl, aryl or amide), the unusual structure, bonding and reactivity of which has been extensively investigated.[1] Over the past five years the chemistry of these two-coordinate systems has been extended to that of related three- and four-coordinate "intra-molecularly base stabilised" examples which incorporate sterically bulky, chelating N-donor ligands, *viz.* LEEL (*e.g.* L = amidinate, guanidinate, N-functionalised aryl, P-functionalised amide *etc.*).[2] Amidinato coordinated examples of these compounds are emerging as powerful reagents for the activation of small molecules, unsaturated substrates *etc.*[3] Despite this, their preparations, *via* the alkali metal reduction of group 14 halide precursors, are typically low yielding. To overcome this problem we have recently developed moderate to high yielding routes to a series of "*trans*-bent" amidinato-element(I) dimers, **1**,[2a] using soluble magnesium(I) dimers as alternative reducing agents.[4]

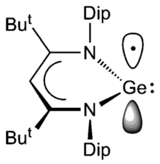
The β-diketiminate (Nacnac) class of ligand, [(R^{1}NCR^2)$_2$CR^3]$^-$ (R^{1,2,3} = H, alkyl, aryl, silyl *etc.*) is closely related to amidinates, and these ligands have been widely used to stabilise complexes containing low valent metal centers from across the periodic table.[5] In spite of this, no examples of β-diketiminato group 14 element(I) dimers, [{(Nacnac)E}$_2$], have yet been reported.[6] Attempts to prepare such compounds *via* the alkali metal reduction of metal(II) precursors, [(Nacnac)ECl] (E = Ge or Sn), have instead led to various outcomes, including disproportionation processes,[7] reductive ring contraction reactions (to give **2**[8]), and the formation of the remarkable monomeric germanium(I) radical, **3**, which is sterically "frustrated" from dimerising by its extremely bulky ligand.[9] We reasoned that utilising a slightly less bulky Nacnac system than that in **3** would allow for the formation of group 14 metal(I) dimers, while still providing sufficient kinetic protection from disproportionation processes. Here we report on the reductions of the moderately bulky metal(II) chloride complexes, [($^{\mathrm{Bu}^t}$MesNacnac)ECl] ($^{\mathrm{Bu}^t}$MesNacnac = [(MesNCBu^t)$_2$CH]$^-$; Mes = mesityl; E = Ge, Sn or Pb) which led to significantly different outcomes, including the formation of the first β-diketiminato group 14 metal(I) dimer (for E = Sn).



1 E = Si, Ge or Sn
Ar = $C_6H_4Bu^t$-4
Dip = $C_6H_3Pr^i_2$-2,6



2 R = Me or Bu^t
M = K or Li
L$_n$ = (OEt$_2$)$_2$ or THF



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The precursor complexes, [($^{\mathrm{Bu}^t}$MesNacnac)ECl] (E = Ge **4**,[10] Sn **5** or Pb **6**), were prepared by reaction of *in situ* generated [Li($^{\mathrm{Bu}^t}$MesNacnac)] with either GeCl$_2$·dioxane, SnCl$_2$ or PbCl$_2$. The tin and lead complexes have not been previously reported and, accordingly, were spectroscopically characterised. Of note here is the ^{119}Sn{^{1}H} NMR spectrum of **5** which exhibits a resonance (δ −235.5 ppm) at a field similar to that of related complexes, *e.g.* δ −252.0 ppm for [($^{\mathrm{Bu}^t}$Nacnac)SnCl] ($^{\mathrm{Bu}^t}$Nacnac = [(DipNCBu^t)$_2$CH]$^-$, Dip = $C_6H_3Pr^i_2$–2,6).[8a]

Compounds **4–6** were initially reduced by treating them with half an equivalent of the magnesium(I) dimer, [{($^{\mathrm{Mes}}$Nacnac)Mg}$_2$] ($^{\mathrm{Mes}}$Nacnac = [(MesNCMe)$_2$CH]$^-$),[4b] in toluene. The reaction with **5** afforded a moderate isolated yield (55%) of the tin(I) dimer, **7**, as a deep green crystalline solid (Scheme 1). The reduction of **4**, on the other hand, gave a low yield of the wine-red ring-contracted product, **8**, and returned a significant amount of unreacted **4**. From these observations it was clear that the reduction of **5** is a 1-electron process, whereas in the synthesis of **8**, the precursor complex **4** is doubly reduced. In view of this, the latter reduction was repeated, but with one equivalent of

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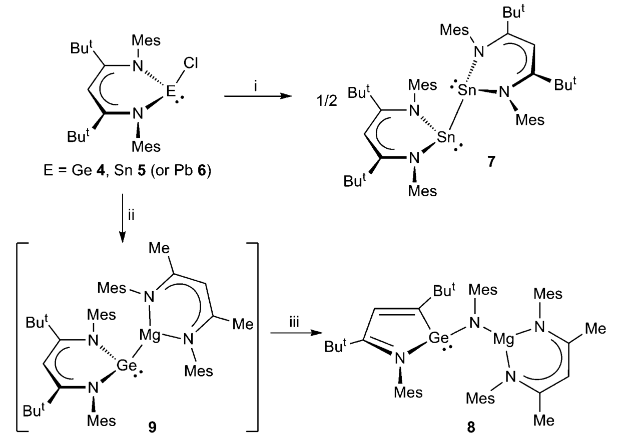

Scheme 1 Reagents and conditions: i, E = Sn, 1/2 [{($^{\mathrm{Mes}}$Nacnac)Mg}$_2$], −1/2 [{($^{\mathrm{Mes}}$Nacnac)Mg(μ-Cl)}$_2$]; ii, E = Ge, [{($^{\mathrm{Mes}}$Nacnac)Mg}$_2$], −1/2 [{($^{\mathrm{Mes}}$Nacnac)Mg(μ-Cl)}$_2$]; iii, ring contraction.

[{($^{\mathrm{Mes}}$Nacnac)Mg}$_2$], and this gave a good yield (65%) of **8**. In contrast, the reduction of **6** (or the bulkier analogue [($^{\mathrm{Bu}^t}$Nacnac)PbCl]) resulted in the deposition of lead metal and the generation of a complex mixture of soluble products, from which low yields of the homoleptic Pb$^{\mathrm{II}}$ complex, [Pb($^{\mathrm{Bu}^t}$MesNacnac)$_2$], and the dimeric adduct, [{($^{\mathrm{Mes}}$Nacnac)MgCl}$_2${($^{\mathrm{Bu}^t}$MesNacnac)PbCl}$_2$], were crystallised (see Supplementary Information for further details‡). It seems likely that this reaction does proceed *via* a lead(I) intermediate, but this is unstable towards disproportionation.

With regard to the mechanisms of formation of **7** and **8**, it is plausible that the reduction of **5** generates the transient tin(I) radical monomer, [($^{\mathrm{Bu}^t}$MesNacnac)Sn:]$^\bullet$ (*cf.* **3**), which dimerises to give **7**. If the related germanium(I) radical, [($^{\mathrm{Bu}^t}$MesNacnac)Ge:]$^\bullet$, is transiently generated in the reduction of **4**, the steric bulk of the ligand may be too great to allow it to rapidly dimerise (covalent radii: Ge 1.22 Å, Sn 1.40 Å[11]). Instead, it could undergo a second reduction with [{($^{\mathrm{Mes}}$Nacnac)Mg}$_2$] to give a germylenyl magnesium complex, **9**, which is unstable and undergoes a ring contraction reaction to give **8**. It is of note that intermediates closely related to **8** and **9** have been proposed for the mechanisms of formation of **2** from the reduction of [(Nacnac)GeCl] compounds with alkali metals.[8]

In non-coordinating solvents both **7** and **8** decompose at 20 °C over one day or several weeks respectively, to give unidentified mixtures of soluble products, and a deposit of tin metal in the case of **7**. Although the ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data for the compounds are largely consistent with the compounds retaining their solid state structures (*vide infra*) in solution, the number of resonances in the spectra does suggest more symmetrical time averaged structures for the compounds. This, in turn, implies relatively unhindered rotations of the two heterocycles in each compound about their respective Sn–Sn and N–Ge/Mg bonds. The ^{119}Sn{^{1}H} NMR spectrum of **7** exhibits a singlet resonance at δ 502.1 ppm, which is downfield from the signal for the three-coordinate precursor, **4**, by more than 730 ppm, but considerably upfield of the resonance for the closely related amidinate coordinated dimer, **1** (E = Sn, δ 777.7 ppm).[2a]

Compound **7** is the first crystallographically characterised example of a β-diketiminato-group 14 element(I) dimer (see Fig. 1). It exhibits a Sn-Sn bond length which is comparable to those in the related dimeric, singly bonded tin(I) complexes (*e.g.* **1** E = Sn, 3.0141(8) Å;[2a] ArSnSnAr, Ar = terphenyl 3.058–3.075 Å,[12] C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6 2.971(1) Å,[2c] or C$_6$H$_3$(CMeNDip)$_2$-2,6 2.898(1) Å).[2g] Unlike **1**, which has a *trans*-bent structure, compound **7** exhibits an unusual, and unsymmetrical *gauche*-bent arrangement between its two heterocycles. This situation is somewhat similar to the geometries of the higher coordinate complexes, ArSnSnAr (Ar = C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6 or C$_6$H$_3$(CMeNDip)$_2$-2,6). The tin atoms of the two heterocycles in **7** are markedly displaced from their N$_2$C$_3$ ligand backbone least squares planes (by 1.135 Å, Sn(1); and 1.228 Å, Sn(2)), while the metrical parameters within those β-diketiminate backbones suggest they are not fully delocalised. Furthermore, the unsymmetrical nature of the molecule is highlighted by the significant difference in the sum of the angles about the tin centres (Sn(1): 279.6°; Sn(2): 306.8°), though both values imply the presence of lone pairs of electrons at the metal, each having a high degree of s-character.

The molecular structure of **8** (Fig. 2) shows it to be monomeric, with a pyramidal Ge centre that by implication possesses a stereochemically active lone pair of electrons. This does not appear to be directed towards the magnesium centre, and therefore it is likely that there is little bonding character between the two atoms (Ge···Mg separation: 3.050(1) Å). The germanium heterocycle is close to planar and its metrical parameters suggest it contains largely localised C(1)–C(2) and C(3)–N(1) double bonds, in contrast to the partially delocalised Ge heterocycles in **2**.[8] There is a marked difference in the magnitude of the two Ge–N bond lengths in the compound, which is consistent with Ge(1)–N(1) being a dative interaction, while Ge(1)–N(2) is a covalent bond. The geometry of the essentially planar Mg heterocycle is unexceptional and reveals it to have a largely delocalised β-diketiminate backbone.

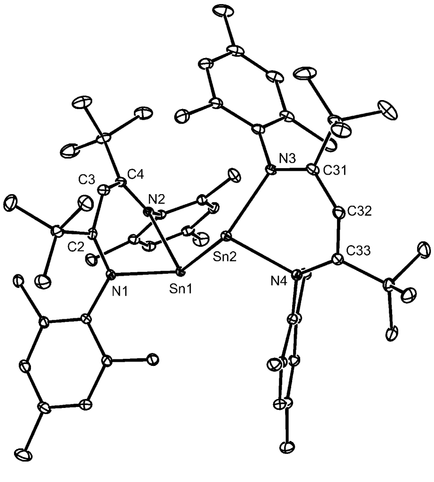

Fig. 1 Molecular structure of **7** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Sn(1)–Sn(2) 3.0685(9), Sn(1)–N(1) 2.215(2), Sn(1)–N(2) 2.2300(19), Sn(2)–N(3) 2.215(2), Sn(2)–N(4) 2.264(2), N(1)–C(2) 1.346(3), N(2)–C(4) 1.320(3), C(2)–C(3) 1.403(3), C(3)–C(4) 1.428(3), N(1)–Sn(1)–N(2) 82.29(7), N(1)–Sn(1)–Sn(2) 89.05(6), N(2)–Sn(1)–Sn(2) 108.23(5), N(3)–Sn(2)–N(4) 83.81(8), N(3)–Sn(2)–Sn(1) 116.38(5), N(4)–Sn(2)–Sn(1) 93.39(6).

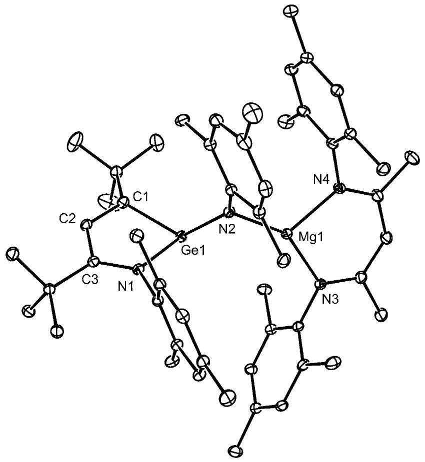

Fig. 2 Molecular structure of **8** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ge(1)–N(2) 1.8477(14), Ge(1)–C(1) 2.0079(17), Ge(1)–N(1) 2.0402(14), Mg(1)–N(2) 1.9504(16), Mg(1)–N(4) 2.0206(15), Mg(1)–N(3) 2.0216(15), N(1)–C(3) 1.311(2), C(1)–C(2) 1.356(2), C(2)–C(3) 1.451(2), N(2)–Ge(1)–C(1) 123.24(6), N(2)–Ge(1)–N(1) 103.54(6), C(1)–Ge(1)–N(1) 81.96(7), N(4)–Mg(1)–N(3) 94.65(6), Ge(1)–N(2)–Mg(1) 106.82(7).

DFT analyses (RI-BP86/def2-TZVPP/def2-SVP) of **7** and **8** in the gas phase led to optimised geometries for both molecules that are in good agreement with their solid state structures (see Supplementary Information for full details‡), though the calculated Sn-Sn distance of **7** (3.225 Å) was over-estimated by *ca.* 5%. The electronic structure of both molecules was examined, and that for **8** revealed no significant bonding interaction between its Ge and Mg centres. In the case of **7**, its HOMO almost exclusively comprises its Sn–Sn σ-bond which is of very high p-character (94.0%), whilst the highest energy orbital displaying significant Sn-lone pair character is the HOMO−11 (see Fig. 3). The LUMO + 2 and LUMO + 3 of **7** possess Sn p-orbital character, which is associated with a single tin centre in each case. The bond dissociation energy (BDE) of **7** (yielding two [(${}^{\mathrm{Bu}^t}$MesNacnac)Sn:]$^\bullet$ fragments in an electronic doublet state) was calculated at 11.9 kcal mol^{-1}, *i.e.* considerably lower than that for **1** (E = Sn), 19.9 kcal mol^{-1}, which was obtained using a similar level of theory (RI-BP86/def2-TZVPP).[2a] It should be noted, however, that the calculated Sn–Sn bond in **1** (3.111 Å) is shorter than that in **7** in the gas phase by more than 0.1 Å. This could indicate that Sn-Sn BDEs of tin(I) dimers such as **1** and **7** are sensitive to the lengths of those bonds.

In conclusion, the reductions of the group 14 metal(II) complexes, [(${}^{\mathrm{Bu}^t}$MesNacnac)ECl] (E = Ge, Sn or Pb), with a magnesium(I) dimer have led to different outcomes, which include the formation of an unprecedented β-diketiminato tin(I) dimer. The results obtained here, in combination with those from previous studies,[8,9] have revealed that subtle changes in the steric profile of β-diketiminate (Nacnac) ligands can have very marked effects on the course that reductions of compounds of the type, [(Nacnac)ECl], can take.

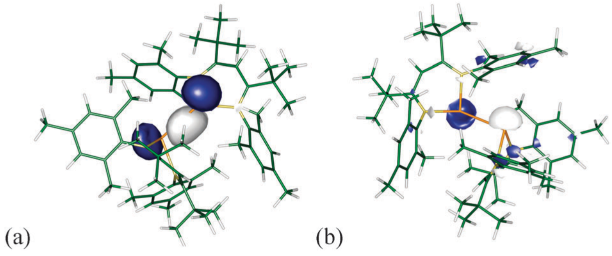
(a) (b)

Fig. 3 (a) HOMO and (b) HOMO−11 of **7**.

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