Synthetic, structural and theoretical studies of amidinate and guanidinate stabilised germanium(I) dimers†

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Received (in Cambridge, UK) 25th July 2006, Accepted 24th August 2006
First published as an Advance Article on the web 8th September 2006
DOI: 10.1039/b610645e

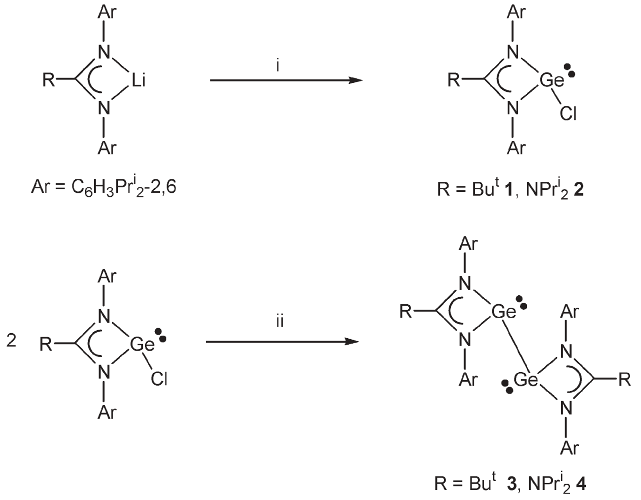
The neutral germanium(I) dimers, $[\{Ge(Piso)\}_2]$ and $[\{Ge(Giso)\}_2]$, Piso = $[(ArN)_2CBu^t]^-$, Giso = $[(ArN)_2CNPr^i_2]^-$, Ar = $C_6H_3Pr^i_2$-2,6, which are stabilised by bulky amidinate and guanidinate ligands respectively, have been prepared by reduction of the corresponding germanium(II) chlorides, [Ge(Piso)Cl] and [Ge(Giso)Cl]; theoretical studies suggest that the Ge–Ge bonds of $[\{Ge(Piso)\}_2]$ and $[\{Ge(Giso)\}_2]$ are associated with their HOMOs, whilst their LUMOs have substantial Ge–Ge π-bonding character.

The heavier group 14 analogues of alkynes have attracted much interest in recent years.[1] A number of compounds of the type REER (E = Si,[2] Ge,[3,4] Sn[5] or Pb;[6] R = bulky monodentate organyl) have now been prepared, mainly by reduction of REX, X = halide. When less bulky substituents are employed in these reductions, oligomeric cage compounds, $(RE)_n$, are often formed.[7] The nature of the E–E bonds in REER, especially with respect to multiple bonding, has been analysed in many theoretical studies.[8] Unlike alkynes, these compounds display *trans*-bent geometries with decreasing CEE angles as the molecular weight of the group 14 element increases. In the case of digermynes, recent theoretical studies point towards Ge–Ge interactions having bond orders of *ca.* 2 and partial singlet diradicaloid character,[8a] the latter of which is consistent with the results of digermyne reactivity studies.[9] Distannynes and diplumbynes, on the other hand, probably have E–E bond orders close to 1, little or no diradicaloid character and LUMOs corresponding to empty E–E π-bonding orbitals.[8a] Indeed, when distannynes are doubly reduced, their Sn–Sn interactions can shorten.[10]

We have had recent successes in using bulky amidinate and guanidinate ligands in the stabilisation of group 13 metal(I) compounds.[11] It seemed that such ligands may also have utility in the stabilisation of novel dimeric germanium(I) compounds, analogous to digermynes, RGeGeR. Our preliminary efforts in this direction are reported herein.

The reactions of the lithium amidinate and guanidinate salts, Li[Piso] and Li[Giso],[11] Piso = $[(ArN)_2CBu^t]^-$, Giso = $[(ArN)_2CNPr^i_2]^-$, Ar = $C_6H_3Pr^i_2$-2,6, with $GeCl_2$·dioxane yielded the germanium(II) complexes, **1** and **2**,[12] in good yields (Scheme 1).† The spectroscopic data for both complexes are consistent with their solid state structures. That for **1** is depicted in Fig. 1‡ and shows it to be monomeric with a chelating, delocalised amidinate ligand and a Cl–heterocycle plane angle of 104.6° (*cf.* **2** 102.8°). The structures of **1** and **2** are reminiscent of related β-diketiminate complexes, *e.g.* $[GeCl\{[(Ar)NC(Me)]_2CH\}]$.[13]

Reductions of **1** and **2** with potassium mirrors in toluene at room temperature over 3–4 hours afforded deeply coloured solutions of the germanium(I) dimers, **3** and **4**, respectively.



Scheme 1 *Reagents and conditions*: i, $GeCl_2$·dioxane, − LiCl; ii, excess K, − KCl.

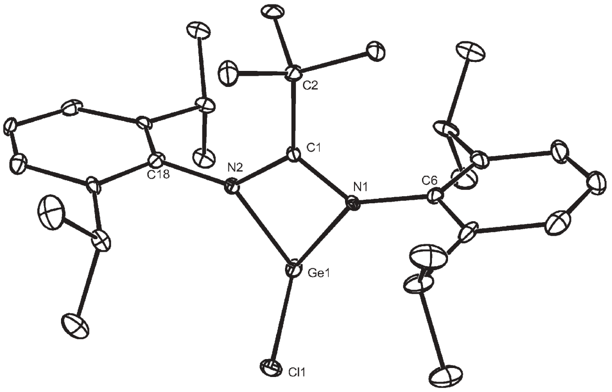


Fig. 1 Molecular structure of **1** (hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ge(1)–Cl(1) 2.174(2), Ge(1)–N(1) 2.005(3), Ge(1)–N(2) 2.003(4), N(1)–C(1) 1.334(5), N(2)–C(1) 1.356(5); N(1)–C(1)–N(2) 106.9(3), N(2)–Ge(1)–N(1) 65.25(14), N(2)–Ge(1)–Cl(1) 101.83(18), N(1)–Ge(1)–Cl(1) 98.21(18).

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† Electronic supplementary information (ESI) available: Full synthetic details for **1**–**4**, spectroscopic data for **1** and **2**, molecular structures of **2** and **4**, and details of the theoretical study. See DOI: 10.1039/b610645e

Recrystallisation of the crude products from these reactions afforded dichromic, green–red crystals of **3**, and lime-green crystals of **4**, in low yield (Scheme 1). They are both remarkably thermally stable, with decomposition temperatures > 200 °C, but are extremely sensitive towards oxygen and moisture. It is of note that attempts to prepare Si, Sn and Pb analogues of **3** and **4** by similar routes have so far been unsuccessful.

The NMR spectra§ of the complexes indicate that their solid state structures are retained in solution. Of most note are their ^1H and $^{13}C\{^1H\}$ NMR spectra which display signals for four chemically inequivalent Ar methyl, and two chemically inequivalent Ar methine centres. As both compounds have closely related structures, only that for **3** is shown here (Fig. 2). As in **1**, its amidinate ligand is apparently delocalised but it has longer Ge–N interactions than in that compound, presumably because of the expected larger covalent radii of its Ge(I) centres. The Ge–Ge bond length of **3** (2.6380(8) Å, *cf.* 2.6721(13) Å for **4**) is in the normal region for single Ge–Ge interactions (2.61 Å mean[14]) but significantly longer than is typical for digermenes, R_2GeGeR_2 (2.21–2.51 Å[14]) and the two structurally characterised digermynes (2.2850(6) Å[3] and 2.2060(8) Å[4]). These observations suggest there is no Ge–Ge multiple bond character in **3** and **4**, as do their rather acute C(1)–Ge–Ge angles of 100.7° and 100.8° respectively (*cf.* 128.7° mean in Ar*GeGeAr*, Ar* = $C_6H_3(Ar)_2$-2,6[3]). In fact, these angles resemble more the CPbPb angles (94.3° mean) in the singly Pb–Pb bonded compound, Ar″PbPbAr″, Ar″ = $C_6H_3(Trip)_2$-2,6; Trip = $C_6H_2Pr^i_3$-2,4,6.[6]

In order to shed light on the nature of the Ge–Ge interactions in **3** and **4**, DFT calculations were performed on the model complex $[\{Ge[(Ar'N)_2CMe]\}_2]$ (Ar′ = $C_6H_3Me_2$-2,6).† The optimised structure is in good agreement with the geometries of **3** and **4**, though with slightly overestimated Ge–Ge and Ge–N bond lengths (2.679 Å; 2.133–2.137 Å respectively). An NBO analysis of the model showed the Ge–Ge bond to be associated with the HOMO (Fig. 3b) and to be largely derived from Ge p-orbital overlap (s 17.43%, p 81.74%). Therefore, this bond is almost exclusively σ in character, as is the case for the Pb–Pb bonds in diplumbynes.[8a] In the LUMO, empty p-orbitals at the Ge centres combine to form a Ge–Ge π-bonding component (Fig. 3a), which is anti-bonding toward the Ge–ligand interactions. Similar π-bonding LUMOs have been calculated for distannynes.[8a] The lone pairs at the Ge centres (Fig. 3c) are high in s-character ($sp^{0.31/0.30}$) but have some directionality, whilst the Ge–N bonds are heavily polarised (Ge +0.54, N −0.69 mean) towards the

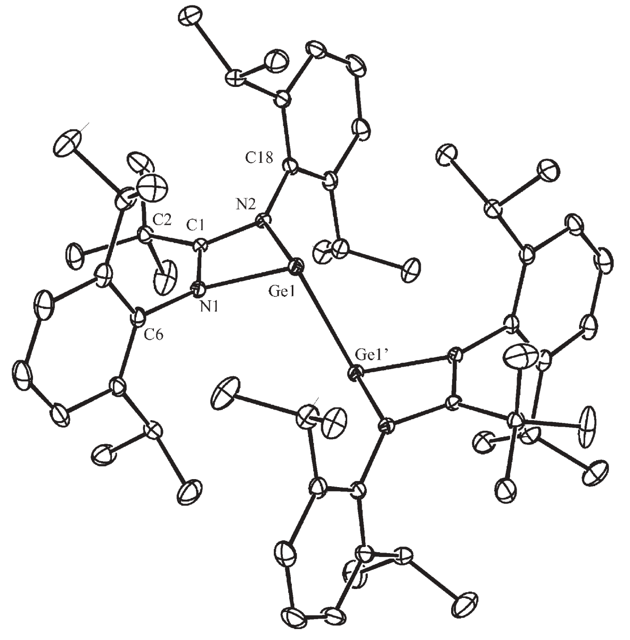

Fig. 2 Molecular structure of **3** (hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ge(1)–Ge(1)′ 2.6380(8), Ge(1)–N(1) 2.032(2), Ge(1)–N(2) 2.049(2), N(1)–C(1) 1.339(3), N(2)–C(1) 1.339(3); N(2)–C(1)–N(1) 106.9(2), N(1)–Ge(1)–N(2) 63.61(9), N(1)–Ge(1)–Ge(1)′ 96.74(7), N(2)–Ge(1)–Ge(1)′ 97.70(7). Symmetry operation′: −x + 2, y, −z + ½.

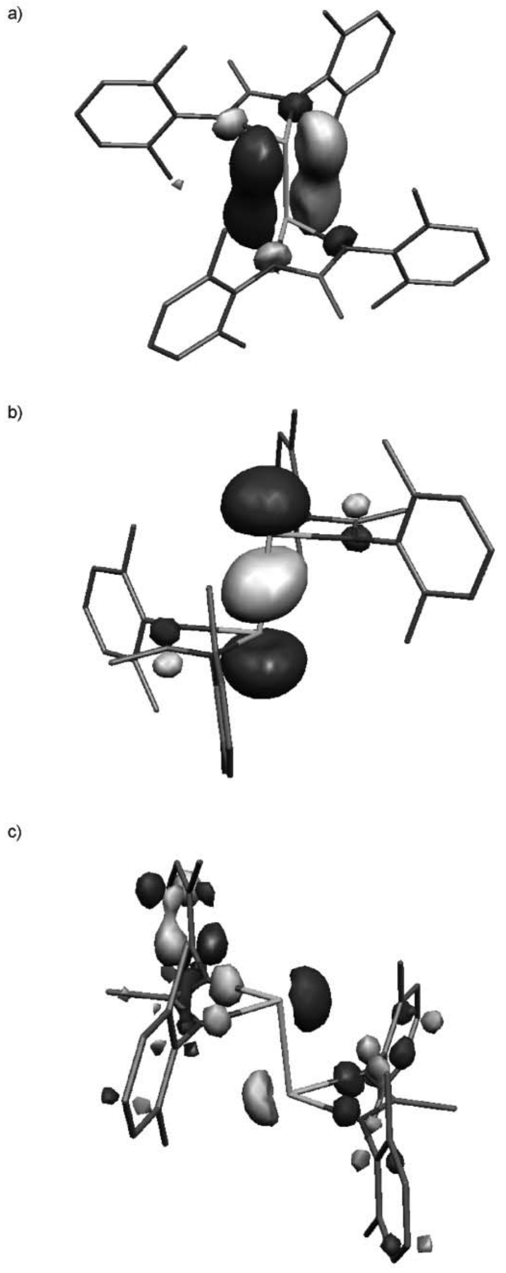

Fig. 3 Representations and energies of (a) the LUMO, (b) the HOMO and (c) the HOMO-4 of the model system $[\{MeC(NAr')_2Ge\}_2]$ (Ar′ = 2,6-$Me_2C_6H_3$).

nitrogen atoms (97% mean N-electron contribution). In addition, a Wiberg bonding analysis revealed a Ge–Ge bond order of 0.8525 and an average Ge–N bond order of 0.439. Finally, the HOMO–LUMO gap (1.913 eV; equiv. to λ_{max} 647 nm) is of a similar energy to an absorption band observed in the visible spectrum of **3** (λ_{max} 568 nm).

In light of the π-bonding LUMO of the model germanium dimer and the fact that heavier group 14 alkyne analogues can be singly or doubly reduced,[10] DFT calculations were carried out on the anionic species, $[\{Ge[(Ar'N)_2CMe]\}_2]^{1\text{ or }2-}$. For the optimised singly reduced model complex, the Ge–Ge bond length shortened by 0.09 Å, while one Ge–N bond at each metal centre lengthened by *ca.* 0.5 Å. This is to be expected since a population analysis showed the molecular orbital energies and ordering to be close to those of the neutral dimer, but with the additional electron populating the LUMO which possesses bonding character between the Ge centres and anti-bonding character between the Ge centres and the amidinate ligands. Optimisation was unsuccessful for the doubly reduced species, but it may be reasonable to propose further strengthening of the Ge–Ge bond and destabilisation of the Ge–ligand interactions. This is in line with our experimental observation that reduction of **3** and **4** leads to their decomposition to mixtures of products, including elemental germanium, K[Piso] or K[Giso].

In summary, we have prepared novel germanium(I) dimers which are stabilised by bulky amidinate and guanidinate ligands. Theoretical studies on a model complex suggest their Ge–Ge bonds show no multiple bond character but their LUMOs are π-bonding in nature, as is the case for distannynes. We are currently exploring the further chemistry of germanium(I) dimers and comparing it with that of "diradicaloid" digermynes.

We gratefully acknowledge financial support from the Leverhume Trust (postdoctoral fellowship for AS), the EPSRC (partial studentship for SPG) and the ERASMUS scheme of the European Union (travel grant for K.-A.L). Thanks also go to the EPSRC Mass Spectrometry Service.

Notes and references

‡ *Crystal data* for **1**: $C_{29}H_{43}ClGeN_2$, M = 527.69, orthorhombic, space group $Pna2_1$, a = 18.515(4), b = 8.3709(17), c = 18.448(4) Å, V = 2859.2(10) Å^3, Z = 4, D_c = 1.226 g cm^{-3}, $F(000)$ = 1120, μ(Mo-Kα) = 1.183 mm^{-1}, 150(2) K, 4919 unique reflections [R_{int} 0.0845], R (on F) 0.0548, wR (on F^2) 0.1133 ($I > 2\sigma(I)$); **2**: $C_{31}H_{48}ClGeN_3$, M = 570.76, monoclinic, space group Cc, a = 17.620(4), b = 12.441(3), c = 14.419(3) Å, β = 100.69(3)°, V = 3106.1(11) Å^3, Z = 4, D_c = 1.221 g cm^{-3}, $F(000)$ = 1216, μ(Mo-Kα) = 1.095 mm^{-1}, 150(2) K, 6076 unique reflections [R_{int} 0.0401], R (on F) 0.0643, wR (on F^2) 0.1349 ($I > 2\sigma(I)$); **3**·(THF): $C_{62}H_{94}Ge_2N_4O$, M = 1056.59, monoclinic, space group $C2/c$, a = 19.051(4), b = 16.770(3), c = 19.911(4) Å, β = 95.77(3)°, V = 6329(2) Å^3, Z = 4, D_c = 1.109 g cm^{-3}, $F(000)$ = 2264, μ(Mo-Kα) = 0.989 mm^{-1}, 150(2) K, 6871 unique reflections [R_{int} 0.0488], R (on F) 0.0504, wR (on F^2) 0.1112 ($I > 2\sigma(I)$); **4**: $C_{62}H_{96}Ge_2N_6$, M = 1070.63, monoclinic, space group $P2_1/n$, a = 11.818(2), b = 14.892(3), c = 17.589(4) Å, β = 103.72(3)°, V = 3007.3(10) Å^3, Z = 2, D_c = 1.182 g cm^{-3}, $F(000)$ = 1148, μ(Mo-Kα) = 1.041 mm^{-1}, 150(2) K, 5573 unique reflections [R_{int} 0.0960], R (on F) 0.0761, wR (on F^2) 0.1116 ($I > 2\sigma(I)$). CCDC 616057–616060. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610645e

§ *Selected data for* **3**: Yield: 16%. Mp > 300 °C. ^1H NMR (400 MHz, C_6D_6, 298 K): δ 0.41 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 0.96 (s, 18 H, $C(CH_3)_3$), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.62 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 3.56 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 3.79 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 6.81–7.21 (m, 12 H, Ar*H*); $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6, 298 K): δ 23.5 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 28.4 ($CH(CH_3)_2$), 28.8 ($CH(CH_3)_2$), 29.9 ($C(CH_3)_3$), 42.5 ($C(CH_3)_3$), 123.6, 123.7, 126.1, 141.5, 144.2, 145.0 (Ar*C*), 165.5 (backbone CN_2); UV/Vis: λ_{max}/nm (c = 0.006 mol l^{-1}): 348 (intense), 438 (ε = 501), 568 (ε = 103); MS (EI 70 eV), *m*/*z* (%): 493.4 (½ M$^+$, 36), 420.4 (PisoH$^+$, 6), 244.3 (PisoH$^+$ − ArNH, 100); IR *v*/cm^{-1} (Nujol): 1616 (s), 1586 (m), 1322 (m), 1260 (m), 1211 (m), 1171 (m), 1028 (m), 799 (s), 760 (m); **4**: Yield: 13%. Mp 200–203 °C (decomp.); ^1H NMR (400 MHz, C_6D_6, 298 K): δ 0.70 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 0.93 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, $CH(CH_3)_2$), 1.33 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.53 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.78 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 3.89 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 4.03 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 4.21 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 6.98–7.38 (m, 12 H, Ar*H*); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 20.4 ($CH(CH_3)_2$), 20.7 ($CH(CH_3)_2$), 21.3 ($CH(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 26.6 ($CH(CH_3)_2$), 26.7 ($CH(CH_3)_2$), 27.5 ($CH(CH_3)_2$), 46.5 ($NCH(CH_3)_2$), 121.4, 122.0, 126.5, 138.6, 144.5, 147.3 (Ar*C*), 152.3 (backbone CN_2); IR *v*/cm^{-1} (Nujol): 1614 (m), 1581 (m), 1330 (s), 1280 (s), 1125 (s), 1046 (m), 800 (s), 756 (s); MS (EI 70 eV), *m*/*z* (%): 536.3 (½ M$^+$, 1), 420.3 (½ M$^+$ − Ge − Pr^i, 100); Acc. Mass. EI: calc. for ½ M$^+$: $C_{31}H_{48}N_3Ge_1$: 536.3055, found 536.3059.

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