Novel Two-coordinate Germanium(II) Arylamides: $Ge(NHAr)_2$, $ArN[Ge(NHAr)]_2(\mu\text{-}NAr)$ and $[Ge(\mu\text{-}NAr)]_2$ 2, and the X-Ray Structures of 2 and $Sn(NHAr)_2$ ($Ar = C_6H_2Bu^t{}_3\text{-}2,4,6$)†

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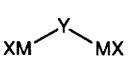
Depending on reaction conditions, treatment of $GeCl_2$(1,4-dioxane) with $[Li(\mu\text{-}NHAr)(L)]_2$ ($L = OEt_2$ or OC_4H_8) yields $Ge(NHAr)_2$ **1** or the first binuclear group 14 element(II) amides $[Ge(\mu\text{-}NAr)]_2$ **2** or $ArN[Ge(NHAr)]_2(\mu\text{-}NAr)$ **3**; X-ray structural data are presented on the tin analogue of **1** and on the germetane **2**.

We have introduced the sterically demanding secondary amido ligand ^-NHAr ($Ar = C_6H_2Bu^t{}_3\text{-}2,4,6$) into the co-ordination chemistry of Li, B, Al, Sn^{II}, P^{III}, As^{III}, $P^{III}\text{–}Li$, $P^{III}\text{–}Al_2$ and Ni^{II};[1] it has also been reported in the context of Si^{IV} amides[2a] and Sn^{IV} amides.[2b]

We now describe extensions to Ge^{II} chemistry. The crystalline, coloured amides $Ge(NHAr)_2$ **1**, $[Ge(\mu\text{-}NAr)]_2$ **2** and $[Ge(NHAr)]_2(\mu\text{-}NAr)$ **3** have been prepared (Scheme 1) and characterised.‡ Compound **2** is shown to behave as a substrate for oxidative addition {yielding $[Ge(NAr)]_2(MeI)_2$



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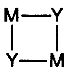

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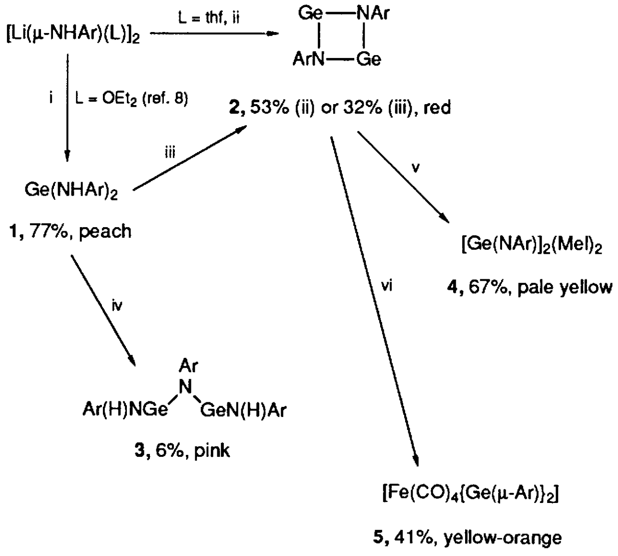

Scheme 1 $Ar = C_6H_2Bu^t{}_3\text{-}2,4,6$, *Reagents and conditions:* i, $GeCl_2$(1,4-dioxane), Et_2O, *ca.* 28 °C, 12 h; ii, $GeCl_2$(1,4-dioxane), thf, 0 to 20 °C, 1 to 24 h; iii, C_6H_{14}, reflux, *ca.* 15 min; iv, fractional crystallisation of **1** from PhMe (the isolated yield was low, because substantial co-products were **1** and **2**); v, excess of MeI, 20 °C, *ca.* 12 h; vi, $[Fe_2(CO)_9]$, thf, *ca.* 20 °C, 12 h. *Characterisation:* Compounds **1–5** are crystalline; satisfactory microanalytical **1–5** and spectroscopic **1** and **3–5** results were obtained; for the X-ray structure of **2**, see Fig. 1.

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† No reprints available.

‡ *Spectroscopic data* for compounds **1–5**: [^1H NMR in C_6D_6, 300 K; IR ν_{NH}/cm^{-1} in Nujol mulls; MS (electron impact MS at 70 eV, with rel. abundance)]. **1**; ^1H NMR: δ 1.48 (*p*-Bu^t), 1.77 (*o*-Bu^t), 5.85 (NH), 7.69 (3,5-CH's); IR ν_{NH}: 3360w, 3320m. **3** ^1H NMR: δ 1.49 (terminal *p*-Bu^t), 1.53 (bridging *p*-Bu^t), 1.77 (terminal *o*-Bu^t), 1.95 (bridging *o*-Bu^t), 5.79 (NH), 7.70 (terminal 3,5-CH's), 7.80 (bridging 3,5-CH's); IR ν_{NH}: 3360w, 3320m, 3310m. **4** ^1H NMR: 1.41 (*p*-Bu^t), 1.67 (*o*-Bu^t), 1.81 (Me), 7.56 (3,5-CH's). **5** IR ν_{CO}/cm^{-1} (in C_6H_{14}): 2060s, 1995vs, 1988vs, 1983sh, 1978vs; MS 832 $[P]^+$, 776 $[P - 2CO]^+$, 748 $[P - 3CO]^+$, 720 $[P - 4CO]^+$. **2** MS: 666 $[P]^+$ (4%), 333 ($[ArN{=}Ge]^+$, 33%), 318 (28%), 261 ($[ArNH_2]^+$, 27%), 246 ($[ArH]^+$, 100%).

Table 1 Selected X-ray diffraction data on germanium(II) amides

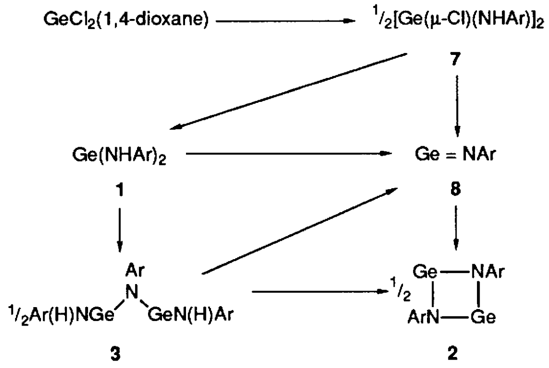
Compound[a]	<Ge–N>/Å	<N–Ge–N'>/°	Ge–N–Ge'/°	Ref.
$Ge[N(SiMe_3)_2]_2$	1.89(1) (gas)[b] 1.875(5) (cryst.)	101(1.5) gas)[b] 107.1(2) (cryst.)		5 14
$Ge[NCMe_2(CH_2)_3CMe_2]_2$	1.88(2)	111.4(5)		6
$[Ge(\mu\text{-}NAr')]_3$	1.859(2)	101.84(1)	138.0(2)	11
$[Ge(\mu\text{-}NAr)]_2$	1.849(4)	86.3(1)	93.7(1)	This work

[a] Abbreviations: R = $SiMe_3$, Ar = $C_6H_2Bu^t{}_3$-2,4,6; Ar' = $C_6H_3Pr^i{}_2$-2,6. [b] Gas electron diffraction data.

4} and as a ligand, affording $[Fe(CO)_4\{Ge(\mu\text{-}NAr)\}_2]$ **5**, Scheme 1. X-Ray structural data on the germetane **2** (Fig. 1) and $Sn(NHAr)_2$ **6** (Fig. 2), the tin analogue of **1**, are presented.§

V-Shaped monomeric, coloured, diamagnetic metal(II) amides of the heavier Group 14 elements have been known since 1974.[3] These include the tertiary amido-metal(II) complexes $M[N(SiMe_3)_2]_2$ (M = Ge, Sn or Pb),[3-5] $M[NCMe_2(CH_2)_3CMe_2]_2$,[6] and $Sn[N(Bu^t)SiMe_2NBu^t]$.[7] The only secondary amido analogue previously reported was $Sn(NHAr)_2$ **6**.[8] The N–Sn–N' bond angle appears to be significantly smaller than that found in crystalline $Sn[N(SiMe_3)_2]_2$, 104.7(2)°,[5] but may well be affected by the disorder, while the average Sn–N distance in **6** is similar to that found in the latter, 2.09(1) Å[5] or in $Sn[N(Bu^t)SiMe_2NBu^t]$, 2.091(8) Å.[7]

Metal amides L_nM–NHR, derived from a primary amine, are relatively rare compared with those from a secondary amine, L_nM–NR_2.[9] Doubtless $Ge(NHAr)_2$ is kinetically stable with respect to $ArNH_2$ elimination for steric reasons. Compounds $[Ge(NHAr)]_2(\mu\text{-}NAr)$ **3** and $[Ge(\mu\text{-}NAr)]_2$ **2** are the first binuclear Ge^{II} [or indeed, more generally, group 14 element(II)] amides. They are expected to be the forerunners of the wider classes of acyclic **A** and cyclic **B** group 14 metal(II) (M) complexes (X^- and Y^{2-} being a monodentate and a bridging ligand, respectively). Plausible pathways leading to **2** and **3** from $GeCl_2$ and Li(NHAr) are shown in Scheme 2. Direct evidence is not available for $[Ge(\mu\text{-}Cl)(NHAr)]_2$ **7** or Ge=NAr **8**. For the former, our proposal is based on analogy with $[Sn(\mu\text{-}Cl)\{N(SiMe_3)_2\}]_2$,[10] while the latter (the Ge analogue of an isonitrile) is supported by a high intensity cationic species observed in the mass spectral fragmentation pattern of **2**.‡ A trinuclear Ge^{II} amide $[Ge(\mu\text{-}NHAr')]_3$ (Ar' = $C_6H_3Pr^i{}_2$-



Scheme 2 Alternative pathways to the acyclic **3** and cyclic **2** binuclear amido-germanium compounds from $GeCl_2$(1,4-dioxane) and $[Li(\mu\text{-}NHAr)(L)]_2$.

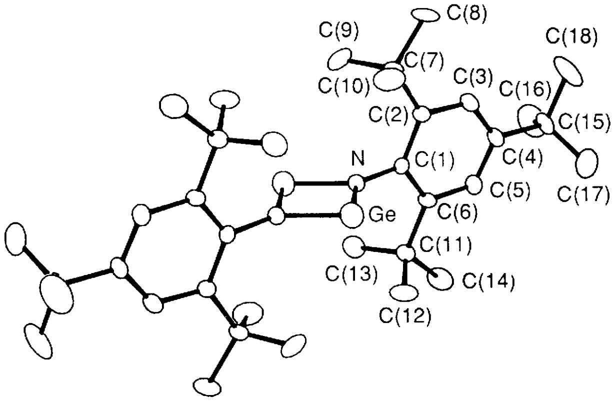


Fig. 1 X-ray structure of $[Ge(\mu\text{-}NAr)]_2$ (Ar = $C_6H_2Bu^t{}_3$-2,4,6) **2**, with numbering scheme. Selected intramolecular bond lengths (Å) and angles (°): Ge–N 1.844(3), Ge–N' 1.855(3), N–C(1) 1.438(4), C(1)–C(2) 1.423(4), C(1)–C(6) 1.418(4), C(2)–C(3) 1.401(4), C(3)–C(4) 1.370(5), C(4)–C(5) 1.383(5), C(5)–C(6) 1.399(4); N–Ge–N' 86.3(1), Ge–N–Ge' 93.7(1), Ge–N–C(1) 136.1(2), Ge'–N–C(1) 130.2(2), N–C(1)–C(2) 120.1(3)°; angle between GeNGe'N' and C(1) to C(6) planes 89.6°.

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§ *Crystal data* for **2** and **6** [in square brackets]; $C_{36}H_{58}Ge_2N_2$ ($C_{36}H_{60}N_2Sn$), *M* 664.1 [639.6], triclinic [triclinic], a = 5.938(6) [5.954(4)], b = 10.727(4) [10.721(4)], c = 14.569(3) [14.855(14)] Å, α = 76.38(2) [77.71(5)], β = 84.16(6) [83.94(7)], γ = 74.45(6) [73.95(4)]°, U = 868.2 [889.3] Å^3, space group $P\bar{1}$ [$P\bar{1}$], Z = 1 [1], D_c = 1.27 [1.19 g cm^{-3}], $F(000)$ = 352 [340]. Monochromated Mo-Kα radiation, λ = 0.71069 Å, μ = 18.6 [7.4] cm^{-1}. Data were measured on an Enraf-Nonius CAD4 diffractometer using a crystal of size *ca.* 0.95 × 0.30 × 0.15 [0.40 × 0.20 × 0.08] mm, sealed in a Lindemann capillary under argon. There was no crystal decay during collection. Intensities for $h \pm k \pm l$ [$h \pm k \pm l$] reflections with $2 < \theta < 25°$ [$2 < \theta < 20°$] were measured by an $\omega - 2\theta$ scan with a max. scan time of 1 min. No correction was made for absorption. Out of 3056 [1755] reflections measured, 2501 [1232] unique reflections with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (PI)^2]^{\frac{1}{2}}/Lp$ (P = 0.02 for **2** and P = 0.04 for **6**).

The structures, which are isomorphous, were solved by routine heavy atom methods and refined by full-matrix least-squares analysis with anisotropic temperature factors. The weighting scheme was $w = 1/\sigma^2(F)$ and R = 0.077 [0.12] and R_w = 0.119 [0.17]. A final difference map for **2** had peaks of up to 1 eÅ^{-3} near the Ge atom (**6** showed uninterpretable electron density of up to 1.1 e Å^{-3} near the inversion centres at ½, 0, 0 and 0, 0, 0, which was presumed to be due to disordered solvent molecules). All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP-Plus program system.

The structure of **6** at first appeared to show a four-membered $(SnN)_2$ ring lying across an inversion centre at ½, ½, 0. However, refinement of the occupancy of Sn sites converged at 0.5, indicating that there is only one Sn atom disordered equally over the two sites.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

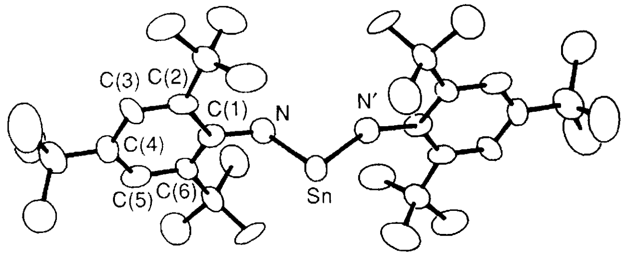

Fig. 2. X-Ray structure of $Sn(NHAr)_2$ (Ar = $C_6H_2Bu^t_3$-2,4,6) **6**, with numbering scheme. Selected intramolecular bond lengths (Å) and angles (°): Sn–N 1.99(2), Sn–N' 2.06(2), N–C(1) 1.42(3), C(1)–C(2) 1.44(2), C(1)–C(6) 1.41(3), C(2)–C(3) 1.38(3), C(3)–C(4) 1.43(4), C(4)–C(5) 1.38(3), C(5)–C(6) 1.41 (3), N–Sn–N' 89.6(6), Sn–N–C(1) 143(1), Sn–N'–C(1)' 127(1), N–C(1)–C(2) 120(2)°. The aryl rings are orthogonal to the SnN_2 plane.

2,6) has recently been reported by Bartlett and Power;[11] the smaller ring size in **2** is attributable to the greater steric effect of Ar compared with Ar'; *cf.*[9] the 6-membered borazines $[RB(\mu\text{-}NR')]_3$ and the 4-membered boretanes $[RB(\mu\text{-}NR')]_2$. Crystalline $[Sn(\mu_3\text{-}NBu^t)]_4$ has a cubane-like structure with three-coordinate Sn and N.[12] Other interesting Ge^{II} amides recently reported are $:Ge[N(Bu^t)Si(Me)N(Bu^t)][N(Bu^t)\text{-}Si(Me)NBu^t]$ and its Ge-bound complexes to $Fe(CO)_4$ or $NSiMe_3$ fragments.[13]

Geometric parameters for $[Ge(\mu\text{-}NAr)]_2$ **2** are compared (Table 1) with those of other Ge^{II} amides having two-coordinate Ge and three-coordinate N. Compound **2**, surprisingly and unlike **1** or **3**, is sparingly soluble in hydrocarbons, but is soluble in tetrahydrofuran (THF); this may be due to intermolecular contacts of 3.6 Å between the Ge atoms of adjacent molecules along the short *a* axis of the unit cell. Similar contacts of 3.4 Å occur in the structure of **6**.

We thank the SERC for a studentship for A. J. T.

Received, 2nd July 1990; Com. 0/02941F

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