Synthesis and structures of hypervalent species of silicon and germanium: toward heptacoordination?

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= 1.395 Å, C–H = 0.96 Å, and all angles = 120°. Other H atoms were included by using a riding model. The disordered perchlorate ions of compounds **2** and **8** were restrained to an approximately tetrahedral geometry.

Compounds **2** and **7** contained ill-defined regions of residual electron density that probably correspond to solvent, but no suitable model could be refined. Compound **7** displayed disorder of the central (gold-containing) moiety; this is described in more detail in the Discussion. Weighting schemes of the form $w^{-1} = \sigma^2(F) + gF^2$ were employed. Full details of the individual data collections and refinements are given in Table I; atom coordinates and derived bond lengths and angles are given in Tables II–IX.

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Registry No. **1**, 112596-62-0; **2**, 112596-64-2; **3**, 112596-66-4; **3a**, 112596-76-6; **4**, 112596-68-6; **5**, 112596-69-7; **6**, 112596-70-0; **7**, 112596-72-2; **8**, 112596-74-4; $\{CH(PPh_3)ClO)CH_2PPh_3\}ClO_4$, 112576-37-1; $[(Ph_3P(CH_2)_2CO](ClO_4)_2$, 107526-65-8; $[Ag\{CH(PPh_3)C(O)CH_3\}_2]ClO_4$, 112620-95-8; $[AuCl\{CH(PPh_3)C(O)CH_3\}]$, 112596-77-7; [AuCl(tht)], 39929-21-0; $[Au(acac)PPh_3]$, 98255-79-9.

Supplementary Material Available: Tables of anisotropic displacement parameters and H-atom coordinates for **2**, **3a**, **7**, and **8** and tables of bond lengths and angles for **7** and **8** (15 pages); listings of structure factor amplitudes for **2**, **3a**, **7**, and **8** (151 pages). Ordering information is given on any current masthead page.

Communications

Synthesis and Structures of Hypervalent Species of Silicon and Germanium: Toward Heptacoordination?

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Summary: The compounds $(2\text{-}Me_2NCH_2C_6H_4)_3MH$ (M = Si, Ge) have been prepared. The crystal structure of the germanium compound shows symmetrical intramolecular chelation of three NMe_2 groups to the germanium atom at the centers of the three tetrahedral faces containing the hydrogen atom, giving a pseudoheptacoordinate environment. The silicon compound appears to have the same structure.

In the course of our studies concerning hypervalent species of silicon, we have observed that penta- and hexacoordinated species display unusual reactivity toward nucleophiles.[1] The overall results of these reactions are substitution by a nucleophile at a hypervalent silicon.[2] The detailed mechanisms (and the driving force) of these reactions have not yet been elucidated. We have sought evidence for the possibility of a process involving extension of coordination; in the case of pentacoordinate silicon, the possibility of conversion to hexacoordinate species is well-documented.[3] For hexacoordinate species the question is open; dubious examples of heptacoordination have been claimed[4] whereas kinetic studies of the hydrolyses have been interpreted as involving rate-determining steps that are dissociative in nature.[5]

Scheme I

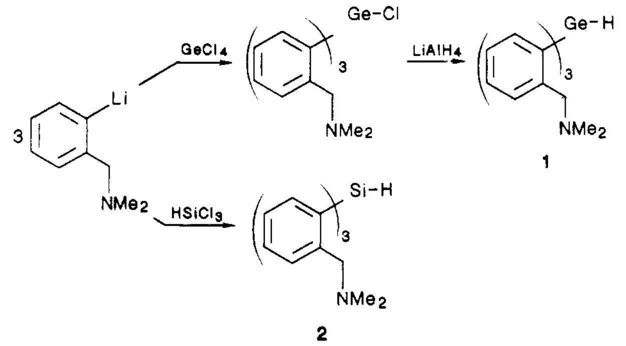

Table I. X-ray Powder Diagrams for Products 1 and 2

germane 1		silane 2	
d_{hkl}	intensity	d_{hkl}	intensity
8.8876	h	8.7677	h
7.7282	h	7.7417	h
7.6351	vh	7.6351	vh
7.2249	m	7.2366	m
6.8673	m	6.8673	m
6.5629	m	6.5532	m
6.1541	w	6.1287	w
5.9011	w	5.9168	w
4.4095	h	4.3836	h
3.9206	m	3.9621	m
3.5984	w	3.5841	w
3.5503	w	3.5309	w

Dunitz[6] has demonstrated that molecular interactions in the solid state, even if relatively weak, may well be

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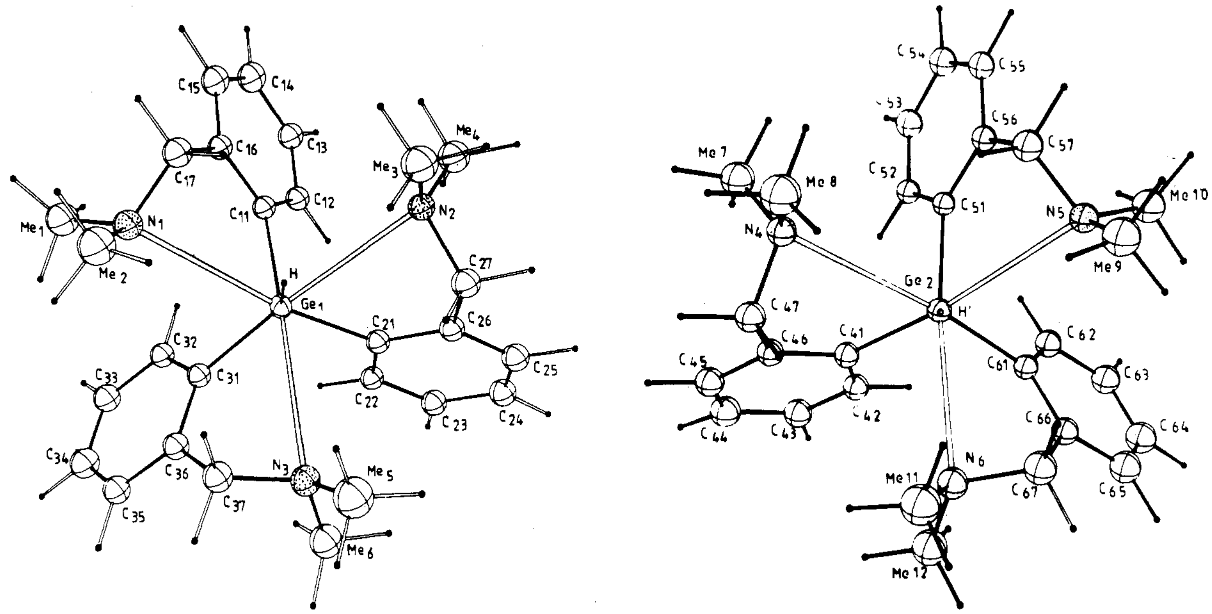


Figure 1. ORTEP drawings of the two conformations of germane 1. The spheres are at the 20% probability level. Important bond distances (Å): average N···Ge = 3.05 (1), average Ge(1)–C(Ph) = 1.959 (8), and av Ge–H = 1.58 (6). Typical angle values (deg): C(11)–Ge(1)–N(3) = 176.8 (3), C(11)–Ge(1)–N(2) = 77.7 (3), C(11)–Ge(1)–N(1) = 68.7 (3), and average N···Ge(1)–H = 68(2)°.

directly bonded and provide an indication of preferred pathways of chemical reactions. With this insight we have synthesized a silicon compound in which this atom could possibly become heptacoordinated by intramolecular donation from three chelating ligands bonded to the tetravalent silicon.

Germane 1 and silane 2 were synthesized by the reaction of (2-((dimethylamino)methyl)phenyl)lithium[7] toward halogermanes and halosilanes as shown in Scheme I.

Only the germanium derivative gave crystals of quality adequate for full X-ray structural determination, and only studies of the powder diagrams and of the thermal analysis diagrams prove the essential similarity of the two structures.

Since compound 1 exhibits two slightly different conformations in the solid state (Figures 1 and 2), only average values will be given here for interatomic distances and bonds angles.[8] The molecules of compound 1 have a propeller shape with an approximate C_3 geometry, the Ge–H bond being coincident with the axis of symmetry.

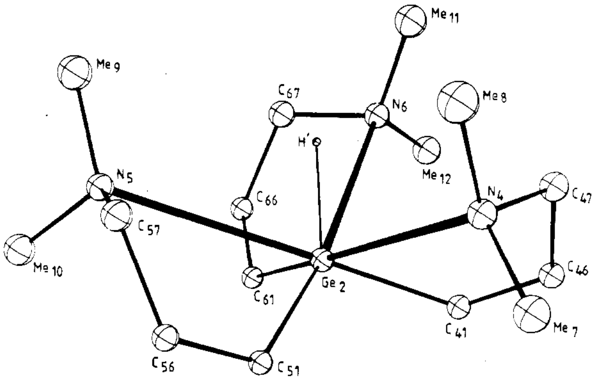
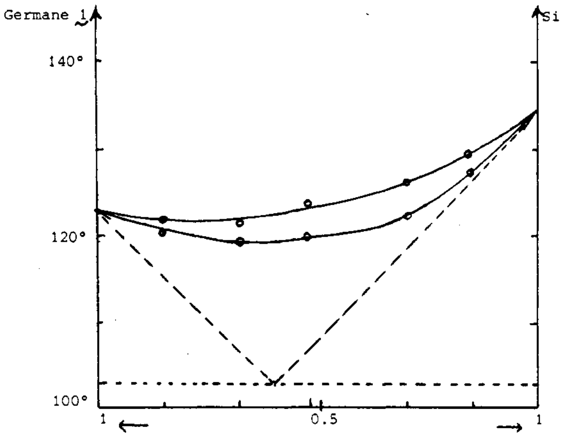


Figure 2. Perspective view of molecule 2 of germane 1. The hydrogen atoms and carbons 2–5 of the phenyl rings have been omitted for clarity. Two basic geometries are clearly present in the molecule: the antiprism C(41)–C(51)–C(61)–N(4)–N(5)–N(6) with the Ge(2)–H' bond as an axis of symmetry and the basic tetrahedal geometry of the germane $Ar_3Ge(2)$–H'.

Scheme II. Phase Diagram of Compounds 1 and 2[a]



[a] Microcalorimetric measurements (reference lithium metal) are as follows: 1, F_{inst} = 123.4 °C, ΔH_M = 9029.6 cal·mol^{-1}; 2, F_{inst} = 134.4 °C, ΔH_M = 10 258 cal·mol^{-1}. Calculated eutectic: T = 103 °C. Molar fraction of 2 in the mixture: 0.407.

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[7] Synthesis of Tris(2-((dimethylamino)methyl)phenyl)germane, (1). (2-(Dimethylamino)methyl)phenyl)lithium etherate suspension in 200 cm^3 or dry ether (prepared by ortholithiation of N,N-dimethylbenzylamide with n-butyllithium (2.5 M) in hexane [Jones, F. N.; Zinn, M. F.; Hauser, C. R. *J. Org. Chem.* **1963**, *28*, 663. van Koten, G.; Leusink, A. J.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *74*, 117]) (0.063 M, 8.7 g) was added dropwise to tetrachlorogermane (0.02 M, 4.26 g) in 100 cm^3 of ether at 0 °C. The resulting mixture was stirred at room temperature for 1 h and then added dropwise to a suspension of $LiAlH_4$ (0.001 M, 0.4g) in 200 cm^3 of ether. The resulting mixture was stirred for 12 h. After usual workup, tris(2-((dimethylamino)methyl)phenyl)germane (45%, 4.3 g) was obtained by crystallization from benzene; mp 123–124 °C. Anal. Calcd for $C_{27}H_{37}GeN_3$: C, 68.10; H, 7.82; Ge, 15.18; N, 8.82. Found: C, 68.25; H, 8.07; N, 8.68. Mass: 477, $(M-1)^+$, 476. ^1H NMR ($CDCl_3$): δ 1.95 (18 H, s, NMe_2), 3.45 (6 H, s, CH_2N), 6.05 (1 H, s, GeH), 7.1–7.4 (12 H, m aromatic). IR (CCl_4): ν 2080 cm^{-1} (GeH). Synthesis of Tris(2-((dimethylamino)methyl)phenyl)silane (2). (2-((Dimethylamino)methyl)phenyl)lithium etherate suspension in 200 cm^3 of dry ether (0.063 M, 8.7 g) was added dropwise to silicochloroform (0.021 M, 2.86 g) in 100 cm^3 of ether at 0° C. The resulting mixture was stirred at room temperature for 12 h. After usual workup, tris(2-((dimethylamino)methyl)phenyl)silane (45%, 3.45 g) was obtained by crystallization from benzene; mp 134.4 °C. Anal. Calcd for $C_{27}H_{37}SiN_3$: C, 75.47, H 8.67, Si, 6.54 N, 9.31. Found: C, 75.08; H, 8.67; N, 9.10. Mass: 432, $(M-1)^+$, 431. ^1H NMR ($CDCl_3$): δ 1.90 (18 H, s, NMe_2), 3.50 (6 H, s, CH_2N), 5.60 (1 H, s, SiH), 7.1–7.4 (12 H, m aromatic). IR (CCl_4): ν 2177 cm^{-1} (SiH). ^{29}Si NMR, ($CDCl_3$): δ −35.30 (J(SiH) = 229.3 Hz).

Compound 1 is formally seven-coordinate with the three nitrogen atoms, the carbon atoms, and the hydrogen atom forming a distorted capped antiprism, MX_3Y_3Z[9].

The basic tetrahedral geometry of the germane Ar_3GeH is retained with the angles H–Ge–Ar = 112 (2)° and Ar–Ge–Ar = 106.8 (3)°. This last angle compares well with the average of 106.3 (5)° reported by Cameron for tri-*o*-tolylgermane.[10] This should indicate that the coordination of the three nitrogen ligands are not responsible for the decrease of the Ar–Ge–Ar angle values from the theorical 109.5°. The approach of each nitrogen ligand occurs opposite to an aryl–germanium bond. The nitrogen–germanium distance varies from 3.014 to 3.088 (7) Å (mean 3.05 Å) and the Ar–Ge–N angle from 172.5 to 176.8 (3)° (mean 174.0°). This angle is comparable to other angles measured around penta-[11] or hexacoordinated silicon species[12] and depends mainly on the geometry of the five-membered rings, e.g., Ge–C(11)–C(16)–C(17)–N(1). Other angles around the germanium atom are of two types: C(11)–Ge–N(1), mean 69.4 (3)°, and C(11)–Ge–N(2), mean 78.2 (3)°. The Ge–H bond distance 1.58 (5) Å is probably underevaluated by the X-ray technique, and the Ar–Ge bonds, ranging from 1.948 (8) to 1.969 (8) Å, are slightly shorter than that reported in ref 3, mean 1.981 (7) Å. This difference falls within the range of experimental errors and cannot be attributed to any interaction of the nitrogen dative bond with the opposite aryl–germanium bond.

The identity of the X-ray powder diagrams of compounds 1 and 2 shows the two structures are isomorphous; accordingly, the molecules (and the atoms) occupy the same places in the unit cell and this isosterism demonstrates unequivocally the identity of the two species.

Moreover, the thermal analysis diagrams of the mixtures of the two hydrides (1, mp 123.4 C; 2, mp 134.4 °C) using the Fregda method[13] show a solid solution to be produced instead of the calculated eutectic (molar fraction of 2 in the eutectic mixture, 0.407 *F* 103 °C),[14] and this result leaves no doubt as to the structural identity of these two compounds because cocrystallization of isosteric silicon and germanium compounds is well-known (cocrystallization of $+\alpha$-NpMePhSiH and $+\alpha$-NpMePhGeH was studied by Brook[15]).

Finally in the ^{29}Si NMR spectrum of 2 the chemical shift of the silicon appears at δ −35.3 ($^1J(SiH)$ = 229.3 Hz) upfield from that of the model product Ph_3SiH (δ −17.8 ($^1J(SiH)$ = 200 Hz).[16] The $\Delta\delta$ = 18 ppm between these two values is in the range of those observed for other neutral hypervalent silicon species.[17,18]

We can conclude that the silicon hydride has a geometry in which the three NMe_2 groups interact with the central silicon atom.

The structure we have observed corresponds to a tetravalent atom which has suffered, therefore, nucleophilic approach. This result confirms the possible interaction of three external donor ligands with a tetravalent silicon atom. This fact means that nucleophilic attack on an hexacoordinate silicon atom is not a chemically forbidden pathway and cannot "a priori" be eliminated in the mechanistic studies.

Registry No. 1, 113404-06-1; 2, 113404-07-2; $GeCl_4$, 10038-98-9; $HSiCl_3$, 10025-78-2; dimethylbenzylamine, 103-83-3.

Supplementary Material Available: Table II, summary of crystal data, intensity collection, and refinement for compound 1; Table IV, atomic coordinates and thermal parameters for compound 1; Table V, atomic coordinates and thermal parameters for hydrogen atoms bonded to carbons atoms; Table VI, all bond distances and angles around the germanium atoms; Table VII, important angles and bond distances in the six germa five-membered rings; Table VIII, the other bond distances and bond angles in the two different molecules of compound 1 (10 pages); Table III, a list of structure factors amplitudes (10 pages). Ordering information is given on any current masthead page.

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[8] Crystallographic information for germane 1: $C_{27}H_{37}GeN_3$; a = 35.046 (5) Å, *b* = 16.787 (1) Å, *c* = 8.907 (2) Å, β = 90.26 (2)°, space group $P2_1/n$; Z = 8; Mo Kα radiation; R = 0.035 for 2179 unique observed reflections. The hydrogen atoms attached to carbon atoms were positioned by calculation (SHELX-76 program); the hydrogen atoms bonded to the germanium atoms were located by difference Fourier synthesis, and their coordinates were free to move during the last least-squares refinement cycles. Full details of this structure are available as supplementary material.

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Organometallic Compounds of the Lanthanides. 43.[1] Synthesis and X-ray Crystallographic Characterization of the First Organolanthanide Compound with a Lanthanide–Arsenic Bond

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Summary: $(C_5H_5)_2Lu(\mu\text{-}CH_3)_2Li(tmed)$ reacts with diphenylarsine in benzene to give $(C_5H_5)_2Lu(\mu\text{-}AsPh_2)_2Li(tmed)$. The molecular structure has been elucidated through complete X-ray analysis. The crystals are orthorhombic, space group *Pcnb* (nonstandard setting of *Pbcn*, No. 60), with *a* = 37.61 (1) Å, *b* = 21.065 (3) Å, *c* = 10.597 (1) Å, *V* = 8396 (3) $Å^3$, ρ_{calcd} = 1.526 g/cm^3, and *Z* = 8. The structure was solved by Patterson and Fourier techniques from 1987 observed reflections ($I \geq 3\sigma(I)$) corrected for Lorentz and polarization effects but not for absorption (μ = 37.90 cm^{-1}). The final *R* value is 0.0452 (R_w = 0.0395). Principal dimensions are as follows: Lu–Cp = 2.28 (2) and 2.32 (2) Å, Lu–As = 2.896 (2) and 2.870 (2) Å, Cp–Lu–Cp = 131.9 (7)°, and As–Lu–As = 81.14 (6)°.

Organometallic compounds of the lanthanides with bonds between the lanthanide metals and soft donor atoms like sulfur, phosphorus, and silicon and its heavier ho-

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[1] Part 43: Schumann, H.; Nickel, S.; Loebel, J.; Pickardt, J. *Organometallics*, submitted for publication.