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Preliminary communication

A novel tricycle with a planar tetragermanium(I) four-membered ring *

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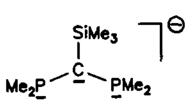
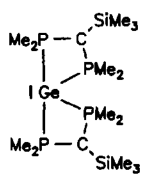
Abstract

Nucleophilic attack of Li^{t}Bu on Ge$_2$[C(PMe$_2$)$_2$(SiMe$_3$)]$_2$ leads, via formation of {Li[C(PMe$_2$)$_2$(SiMe$_3$)]}$_2$, to the novel tricycle Ge$_4$[C(PMe$_2$)$_2$(SiMe$_3$)]$_2$(^{t}Bu)$_2$, which contains a planar four-membered ring of Ge^I atoms. The compound was characterized by means of NMR spectroscopy and an X-ray diffraction study.

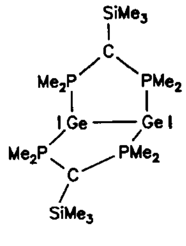
A milestone in the development of isolable molecular compounds of germanium in low oxidation states (in particular Ge^{II}) was the synthesis of Ge[HC-(SiMe$_3$)$_2$]$_2$ by Lappert and Hitchcock [1]. Only a few additional examples of stable organogermanium(II) compounds, mostly containing substituted cyclopentadienyl ligands [2], have been successfully synthesized since then, while after the first synthesis of a germanium(II) amide derivative [3], quite a number of similar compounds with bulky N-substituents have been obtained [4]. In addition, numerous analogous species containing other heteroelement ligands (OR [5a], SR [5b], SeR [5c], halogen [5d]) are known, but monomeric germylenes with PR$_2$ ligands remain elusive [6]. Another approach to stable germanium(II) compounds with organophosphorus ligands has been successfully achieved by means of diphosphinomethanide ligands, *e.g.* the species I.



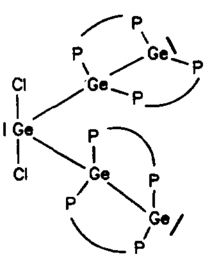
I (= P P)



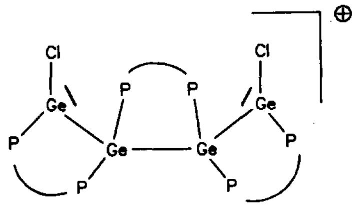
II



III



IV (= GeCl$_2$ × 2 III)



V

The mononuclear compound II [7a], as well as the dinuclear germanium(I) compound III [7b] and its bisadduct with GeCl$_2$, IV (Ge$_5$-chain) [7c], have been isolated and structurally characterized. A Ge$_4$-chain is present in the cation V [7d], demonstrating that Ge–Ge linkages in low valent germanium species are strongly stabilized by ligands of type I.

In recent years rings and cages with Ge$_4$, Ge$_6$ and Ge$_8$ cores have become accessible [8], and so isolation of germanium ring compounds stabilized by phosphinomethanide ligands were to be expected.

Whereas III is strongly nucleophilic towards Main Group and Transition Metal acceptors (*e.g.* in the formation of IV), it is quite inert towards nucleophiles. No reaction is observed with neutral donors or with LiMe, Li^{n}Bu, Li[CH(SiMe$_3$)$_2$], Na[N(SiMe$_3$)$_2$] and LiPMe$_2$. The only reaction of III with a nucleophile that could be brought about, was that with Li^{t}Bu in toluene, according to eqn. (1). Along with insoluble {Li[C(PMe$_2$)$_2$(SiMe$_3$)]}$_2$, yellow crystals of 1 were formed, and isolated in 72% yield.

The {^{1}H}^{31}P NMR spectrum of 1 shows an AA′BB′ spin system, and the ^{1}H and {^{1}H}^{13}C NMR spectra indicate the presence of a ^{t}Bu, a SiMe$_3$ group, and four different PMe groups. From these signals, and a

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* Dedicated, on the occassion of his 65th birthday, to Professor M.F. Lappert, who pioneered many aspects of organometallic chemistry; especially notable in the present context is his seminal work in the chemistry of low-valent germanium.

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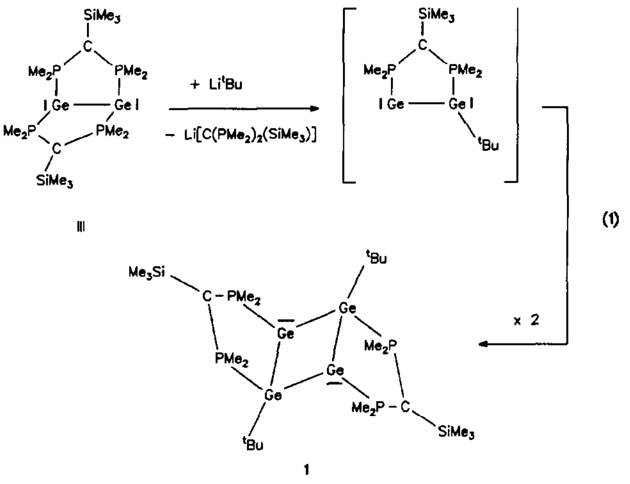

mass spectrum with the correct isotopic pattern for **1**, the structure could be deduced, and this was subsequently confirmed by an X-ray structure determination [9].

The molecular structure of centrosymmetric **1** (Fig. 1) shows a ladder shaped tricycle, formed by two diphosphinomethanide Ge–Ge bridging ligands on the opposite sides of a planar four membered germanium homocycle. Two of the germanium atoms are linked to ᵗBu groups, again at opposite sides of the ring. Thus, two of the germanium atoms are three-coordinated (Ge2) and two are four-coordinated (Ge1), and consequently, the Ge_4 ring is rhombohedral: the endocyclic angles at Ge1 are 104.2(1)° and those at Ge2 75.8(1)°. The other two angles at Ge2 are 88.9(1)° and 103.5(1)°, and the mean of 89.4° is close to the "p-only" value. The two Ge–Ge distances are slightly different (Ge1–Ge2 2.489(1) Å/Ge1–Ge2a 2.529(1) Å); the longer distance is that between the ligand bridged germanium atoms, which is comparable with the Ge–Ge distance in **III** (2.540(1) Å). The Ge2–P2 (2.363(1) Å) distance is shorter than Ge1–P1 (2.413(1) Å), but both values are close to the corresponding distance in **III** (mean 2.395(1) Å) [7b]. The Ge1–C bond length (2.018(3) Å) corresponds to that in $\{GeCH(SiMe_3)_2\}_2$ [1]. The five-membered rings formed by the diphosphinomethanide bridging ligands and the Ge–Ge moiety are almost planar, as are the carbanionic C2 atoms.

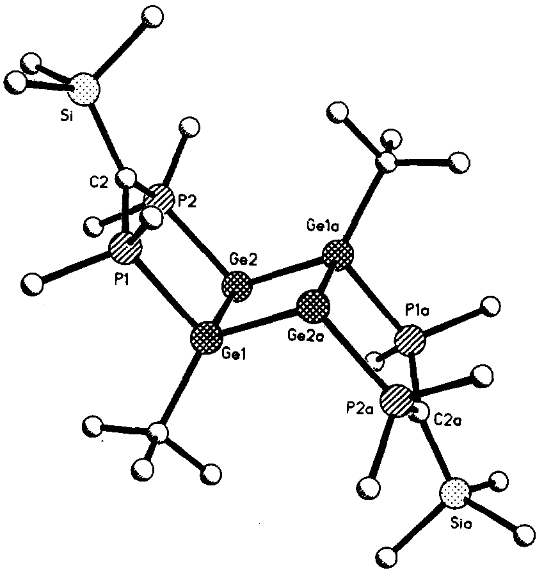

Fig. 1. Molecular structure of 1 (SHELXTL), with hydrogen atoms omitted.

The uniqueness of the four-membered ring in **1** mainly lies in the fact that it is the first germanium homocycle containing alternate three- and four-coordinated germanium atoms with an average +1 oxidation state. Thus **1** is clearly distinct from other tetragermanium homocycles made up of Ge^{II} centres [8]. The presence of the two remaining lone electron pairs in **1** should lead to interesting chemistry involving preservation of the ring. Ring-opening reactions should lead to novel low valent germanium species. The formation of **1** from **III** demonstrates that the latter does indeed have some carbene-like character, so that nucleophilic as well as electrophilic behaviour is possible.

Experimental details

To a stirred solution of 0.9 g (1.61 mmol) of **III** in 40 ml of toluene at −78°C was added 0.87 ml (1.61 mmol) of a 0.185 M ᵗBuLi/hexane solution. The mixture was allowed to warm to room temperature, and after 12 h, the volume was considerably reduced, and slow cooling gave yellow crystals (0.95 g, 72%), m.p. 207°C. Found: C, 35.18; H, 7.33. $C_{24}H_{60}Ge_4P_4Si_2$ (819.17) calc.: C, 34.96; H, 7.25%. NMR (C_6D_6, 25°C) $\{^1H\}^{31}P$: AA'BB', $\delta P_A = 23.15$, $\delta P_B = 10.60$, $J_{AA'} = 4.3$, $J_{BB'} = 6.4$, $J_{AB} = J_{A'B'} = 214.5$, $J_{A'B} = J_{AB'} = 52.8$; ^1H: $\delta PCH_3 = 2.13$d (9.8), 1.87d (8.8), 1.39d (4.9), 1.36d (3.4); $\delta CCH_3 = 1.24$d (1.5); $\delta SiCH_3 = 0.30$s; $\{^1H\}^{13}C$: $\delta CCH_3 = 31.2$s; $\delta CCH_3 = 30.05$s; $\delta PCH_3 = 22.02$d (5.8), 21.77d (6.2), 21.42d (10.7), 21.09d (10.7); $\delta SiCH_3 = 5.47$s. MS (EI, 70 eV, 25°C, ^{74}Ge): $m/e = 820$ (M^+, 2.2%), 763 ($M^+ -$ ᵗBu, 15.6%), 281 (Ge[$(Me_2P)_2C(SiMe_3)$], 43.8%), 73 ($SiMe_3$, 100%).

Acknowledgement

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9 X-ray structure determination of **2**: Enraf-Nonius: CAD 4 diffractometer, Mo-Kα radiation 0.71069 Å, graphite monochromator, $T = 22$°C; $C_{24}H_{60}Ge_4P_4Si_2$, $M_r = 819.173$. Monoclinic, C_2/c, $a = 20.851(1)$, $b = 12.865(1)$, $c = 17.302(1)$ Å, $\beta = 123.88°$, $V = 3853.18$ Å^3, $Z = 4$, ρ_{calc} 1. 412 g cm^{-3}, μ(Mo-Kα) = 33.3 cm^{-1}. (Refl. measd. 7576), refl. unique 3609, observed 3204 ($F_o \geq 3\sigma(F_o)$, $(\sin \Theta/\lambda)_{max}$ 0.617 Å^{-1}, *hkl*: +17, ±17, ±22, ω scan, $\Delta\omega = 0.9 + 0.35 \tan \Theta$). Direct methods (SHELXS-86), all non-H-atoms refined anisotropically, all H atoms refined isotropically. R (R_w) = 0.024 (0.025) (274 parameters refined). Tables of atomic coordinates, displacement parameters, and observed and calculated structure factors have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen under the number CSD-57188.