

Phosphine Complexes of Main Group Elements. $[(\text{Me}_3\text{Si})\text{C}(\text{PMe}_2)_2]_2\text{Ge}_2\text{I}_2$, an Intramolecular Germylene (Germanediyl) Donor–Germylene Acceptor Complex with a Germylene–Phosphane Chelating Ligand

Hans H. Karsch,* Josef Hofmann, and Gerhard Müller

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, D-8046 Garching, Federal Republic of Germany

The addition of I_2 to the bis-germylene complex $[(\text{Me}_3\text{Si})\text{C}(\text{PMe}_2)_2]_2\text{Ge}_2$ ($\text{Ge}^{\text{I}}\text{–Ge}^{\text{I}}$) (**1**) surprisingly results in the oxidation of only one Ge atom and rearrangement of one of the phosphinomethanide ligands; the GeI_2 formed is complexed by a chelating germylene–phosphine ligand in the form of a homonuclear donor–acceptor complex.

During our investigations of phosphine complexes of low valent main group elements, we recently synthesized a novel type of bis-germylene (**1**), with the Ge atoms in the formal oxidation state +1 and a rather long Ge–Ge bond.¹ This peculiar situation gave rise to the question as to whether the Ge lone pairs or the Ge–Ge bond are more amenable to electrophilic attack. Furthermore, oxidation with, e.g., iodine, in principle could proceed either in a symmetrical or an unsymmetrical fashion, thereby leading to various isomeric compounds (**2**)–(**4**) or (**5**) and (**6**), respectively. Recrystallisation from toluene of the white solid† obtained in the

reaction of (**1**) with iodine gave colourless needles of the toluene solvate of (**2**), the crystal structure of which has been determined.‡

In (**2**), both iodine atoms are bound to *one* Ge atom (Figure 1), the Ge–Ge bond being retained and shortened considerably [2.458(1) Å] as compared to (**1**) [2.540(1) Å].¹ This shortening is a typical feature of the partial oxidation of low valent compounds containing Ge–Ge bonds.^{2,3} The two (axial) iodine ligands together with the (equatorial) lone pair and the Ge–Ge and one Ge–P bond constitute a pseudo trigonal bipyramidal geometry at the Ge^{II} centre $\text{Ge}(1)$,⁴

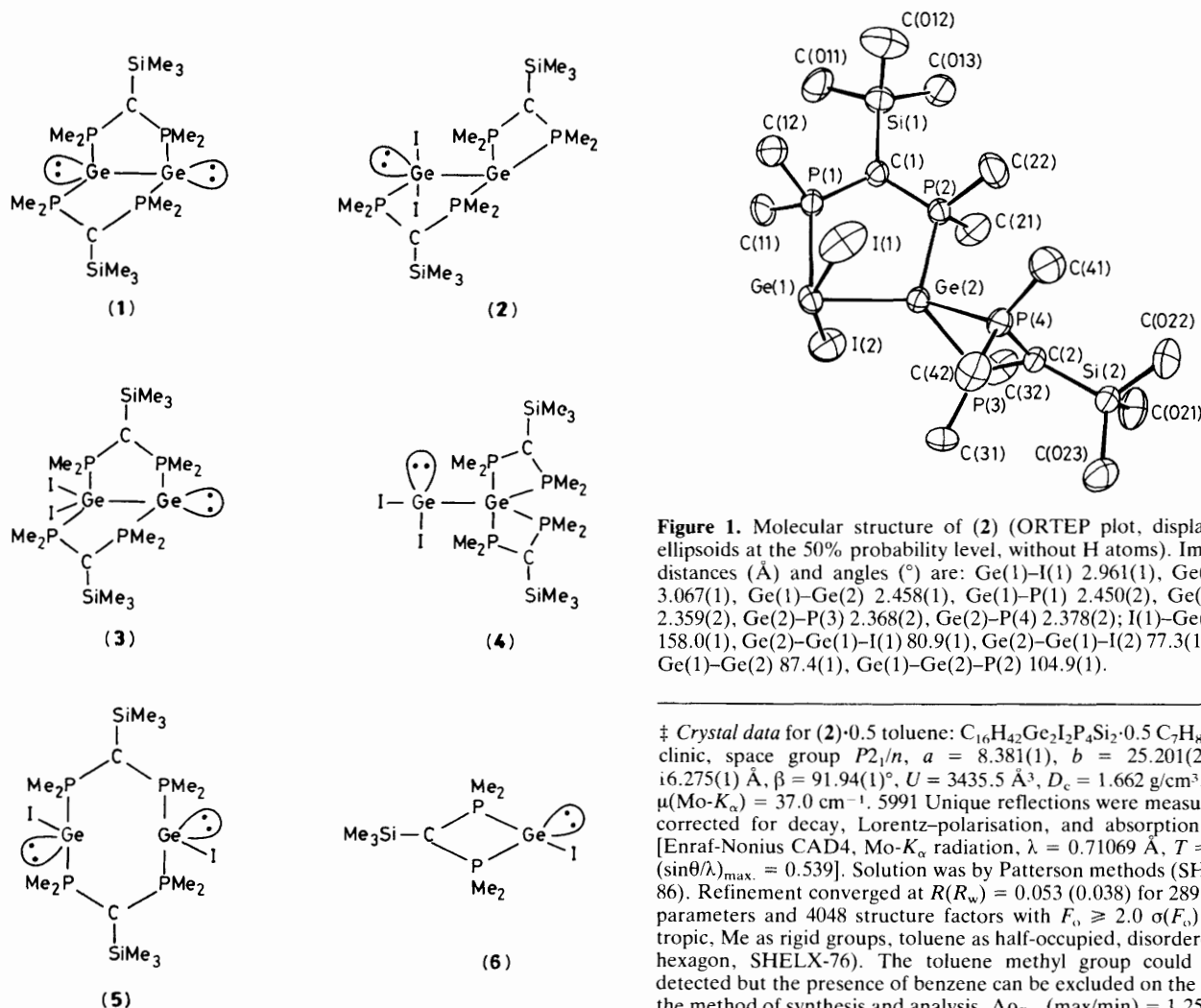


Figure 1. Molecular structure of (**2**) (ORTEP plot, displacement ellipsoids at the 50% probability level, without H atoms). Important distances (Å) and angles (°) are: Ge(1)–I(1) 2.961(1), Ge(1)–I(2) 3.067(1), Ge(1)–Ge(2) 2.458(1), Ge(1)–P(1) 2.450(2), Ge(2)–P(2) 2.359(2), Ge(2)–P(3) 2.368(2), Ge(2)–P(4) 2.378(2); I(1)–Ge(1)–I(2) 158.0(1), Ge(2)–Ge(1)–I(1) 80.9(1), Ge(2)–Ge(1)–I(2) 77.3(1), P(1)–Ge(1)–Ge(2) 87.4(1), Ge(1)–Ge(2)–P(2) 104.9(1).

‡ Crystal data for (**2**)·0.5 toluene: $\text{C}_{16}\text{H}_{42}\text{Ge}_2\text{I}_2\text{P}_4\text{Si}_2 \cdot 0.5 \text{C}_7\text{H}_8$, monoclinic, space group $P2_1/n$, $a = 8.381(1)$, $b = 25.201(2)$, $c = 16.275(1)$ Å, $\beta = 91.94(1)^\circ$, $U = 3435.5$ Å³, $D_c = 1.662$ g/cm³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 37.0$ cm⁻¹. 5991 Unique reflections were measured and corrected for decay, Lorentz-polarisation, and absorption effects [Enraf-Nonius CAD4, Mo-K α radiation, $\lambda = 0.71069$ Å, $T = 23^\circ\text{C}$, $(\sin\theta/\lambda)_{\text{max}} = 0.539$]. Solution was by Patterson methods (SHELXS-86). Refinement converged at $R(R_w) = 0.053$ (0.038) for 289 refined parameters and 4048 structure factors with $F_o \geq 2.0 \sigma(F_o)$ (anisotropic, Me as rigid groups, toluene as half-occupied, disordered rigid hexagon, SHELX-76). The toluene methyl group could not be detected but the presence of benzene can be excluded on the basis of the method of synthesis and analysis. $\Delta\rho_{\text{fin}}$ (max/min) = 1.25/–0.84 e/Å³. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

† Satisfactory C, H microanalyses were obtained.

leaving no space for another phosphine donor. Consequently, one of the bridging diphosphanomethanide ligands is rearranged to a chelating ligand at Ge(2). The geometry around Ge(2) is tetrahedral and this lower co-ordination results in significantly shorter Ge(2)–P than Ge(1)–P bonds (Figure 1). The lone pair at Ge(2), on the other hand, has to be considered as being engaged in the intramolecular dative bond at Ge(1), which together with the P(1)–Ge(1) (dative) bond constitutes a novel germylene–phosphine chelating ligand to GeI₂. The five-membered Ge₂P₂C heterocycle thus formed is essentially planar. Remarkably, although the I(1)–Ge(1)–I(2) angle of 158.0(1)° may be attributed to the lone pair repulsion of Ge(1), the I atoms clearly point towards the second Ge atom [*cf.* Ge(1)–I 2.961(1)/3.067(1) *vs.* Ge(2) · · · I 3.537(1)/3.485(1) Å]. Since this is reminiscent of a semibridging behaviour one may speculate if it contributes to some extent to the overall stability of (2). In any case, despite the unsymmetrical addition of I₂ to only one Ge atom, the structure of (2) amply proves that both Ge atoms are involved in the oxidation process; obviously, the taking up of the lone pair at one Ge atom by I₂ is balanced by the donation of the lone pair of the second Ge atom, regenerating the lone pair at the former, or in other words, both lone pairs in (1) are disposable at one

germylene atom, thus enhancing its donor ability (ligand properties) considerably.²

In conclusion, iodine adds to the bis-germylene (1) unsymmetrically, with retention of the Ge–Ge bond. Phosphinomethanide stabilized germylenes are excellent donors, forming strong intramolecular, homonuclear bonds to germylene acceptor species. This and previous work^{1–3} strongly indicates the unique ability of phosphinomethanide complexes of germanium to undergo a varied redox chemistry which is as yet unrivalled in main group chemistry.

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