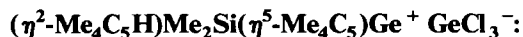


Preliminary communication



ALKENE COORDINATION AT DIVALENT GERMANIUM

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Summary

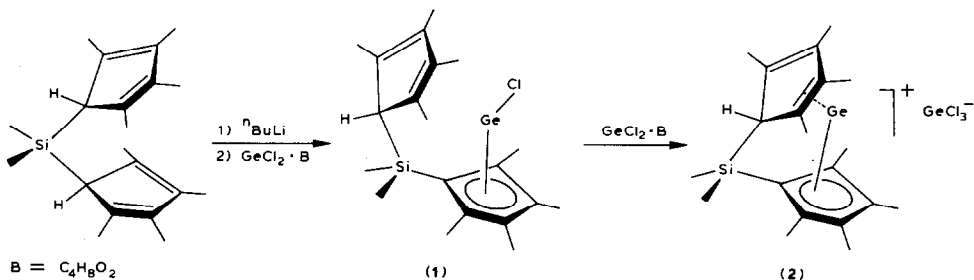
The compound $(\eta^2\text{-Me}_4\text{C}_5\text{H})\text{Me}_2\text{Si}(\eta^5\text{-Me}_4\text{C}_5)\text{Ge}^+ \text{GeCl}_3^-$ is the first example of alkene coordination at a main group element substantiated by X-ray crystallography. The complex was prepared from monometalated dimethylsilanediylbis(2,3,4,5-tetramethylcyclopenta-2,4-diene) and germanium dichloride-dioxane. The intramolecular interaction between the diene and the central germanium atom suggests that main group elements can coordinate with ordinary unsaturated hydrocarbons.

Interactions of basic organic compounds, especially unsaturated hydrocarbons, with transition metal centers form the starting point for various catalytic processes. Thus, any comparable catalytic activity of a main group element requires the ability to form π -complexes [1]. Surprisingly, crystallographic evidence has not previously been presented for an interaction between a main group element and the π -system of an ordinary carbon-carbon double-bond. The title compound dimethylsilanediyl(2,3,4,5-tetramethyl- η^2 -cyclopenta-2,4-diene)(2,3,4,5-tetramethyl- η^5 -cyclopentadienyl)germanium trichlorogermanate (**2**) provides the first example of this type of compound, since its diene is dihapto-coordinated to the germanium atom.

The essential core of the metallocenophane-like complex **2** is a cation of the type $\text{R}_5\text{C}_5\text{Ge}^+$ [2]; its electrophilic character has been revealed by its formation of adducts with certain π -acceptor ligands [3] and of covalent compounds when it bonds to counterions of even minor nucleophilicity [3,4].

The preparation of **2** started from dimethylsilanediylbis(2,3,4,5-tetramethylcyclopenta-2,4-diene) [5]. Monometalation with n-butyllithium followed by addition

of equimolar amounts of germanium dichloride-dioxane yielded the covalent chloro compound **1**; abstraction of chloride by treatment of **1** with a second equivalent of $\text{GeCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ [4] gave **2**. The two reactions can be combined, to give **2** in a one-step synthesis [6].



The air- and moisture-sensitive compound **2** was obtained as colorless crystals (from CH_2Cl_2) with properties analogous to those of $\text{Me}_5\text{C}_5\text{Ge}^+ \text{GeCl}_3^-$ [4]. From comparison of the ^1H and ^{13}C NMR data for **2** with those of **1** it can be concluded that the diene system remains coordinated to the germanium center in solution [7].

X-ray structural investigations on **2** [8] showed the coordination sphere of the central germanium atom, formed by the basal cyclopentadienyl ligand and two chlorine atoms of the counterion, to be completed by one of the carbon-carbon double bonds of the cyclopentadiene moiety (see Fig. 1). The additional contact to a more distant chlorine atom results in formation of centrosymmetric dimers (see Fig. 2), so that the central atom Ge(1) is effectively shielded by the coordination of one alkene double-bond, three chlorine atoms and the basal η^5 -cyclopentadienyl ligand.

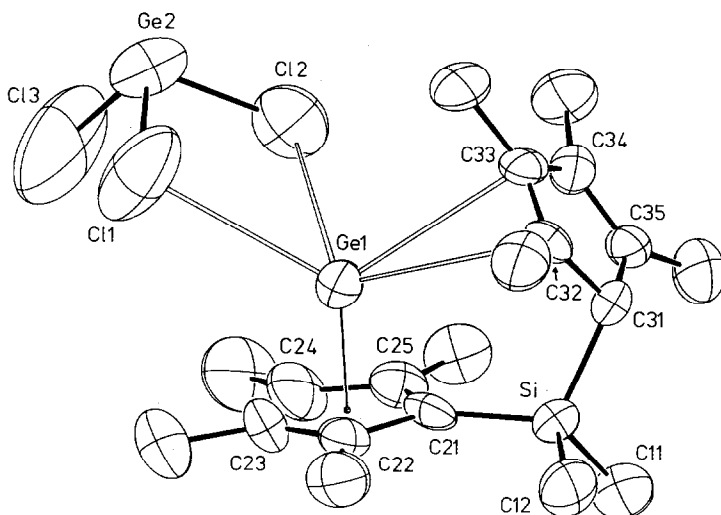


Fig. 1. Structure and labelling scheme for the non-hydrogen atoms of **2** (thermal ellipsoids 50% probability; only one of alternatives for the disordered GeCl_3^- -ion is shown). Important interatomic distances (Å): $\text{Ge}(1)\text{-C}(21)$ 2.24(1), $\text{Ge}(1)\text{-C}(22)$ 2.27(1), $\text{Ge}(1)\text{-C}(23)$ 2.31(2), $\text{Ge}(1)\text{-C}(24)$ 2.28(1), $\text{Ge}(1)\text{-C}(25)$ 2.29(1), $\text{Ge}(1)\text{-C}(32)$ 3.34(2), $\text{Ge}(1)\text{-C}(33)$ 3.18(2), $\text{Ge}(1)\text{-C}(34)$ 3.72(2), $\text{Ge}(1)\text{-C}(35)$ 4.16(2), $\text{Ge}(1)\text{-Cl}(1)$ 3.235(6), $\text{Ge}(1)\text{-Cl}(2)$ 3.394(6); interplanar angle $\text{Ge}(1)$, $\text{C}(32)$, $\text{C}(33)/\text{C}(32)$, $\text{C}(33)$, $\text{C}(34)$, $\text{C}(35)$ 80.5° .

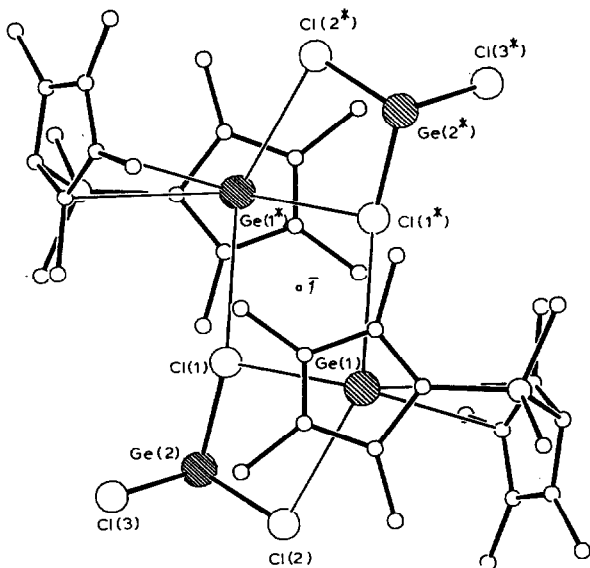


Fig. 2. Structure of the centrosymmetric dimer (Ge(1)–Cl(1*) 3.685(6) Å).

The η^2 -mode of diene coordination, revealed by the distances between Ge(1) and the carbon atoms C(32)–C(35), is associated with an almost perpendicular arrangement of the plane Ge(1), C(32), C(33) relative to the diene plane C(32), C(33), C(34), C(35). When considering the germanium–carbon bond lengths it should be noted that the metal–carbon bonds in π -complexes of main group elements [1] are in general significantly longer than the metal–carbon bonds in π -complexes of transition metals. Nevertheless, even when this is taken into account the Ge–C(32)/C(33) bonds of 3.34(2)/3.18(2) Å still appear to be unusually stretched, probably by the short and quite rigid SiMe₂ bridge. However, η^4 -coordination, effected by twisting the bridge about the Si–C(21)/C(31) axes, would involve even longer germanium–carbon distances.

As expected, the GeCl₃[−] counterions (see Fig. 1) show ψ -tetrahedral geometry. Some influence of the anion on the hapticity of diene coordination cannot be ruled out; surprisingly, the related tin compound (η^2 -Me₄C₅H)Me₂Si(η^5 -Me₄C₅)Sn⁺BF₄[−] [9] also shows cation–anion contacts, despite the markedly lower nucleophilicity of the BF₄[−]-anion.

References and Notes

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- 5 C.M. Fendrick, E.A. Mintz, L.D. Schertz, T.J. Marks and V.W. Day, *Organometallics*, 3 (1984) 819; P. Jutzi and R. Dickbreder, *Chem. Ber.*, 119 (1986) 1750.
- 6 Preparation of **2**: Dimethylsilanediy-bis(2,3,4,5-tetramethylcyclopenta-2,4-diene) (3.03 g, 10.1 mmol) in tetrahydrofuran (50 ml) was metalated with a 1.55 M solution of n-butyllithium in hexane (6.51 ml, 10.1 mmol). After 2 h stirring and cooling to -40°C a suspension of GeCl₂·C₄H₈O₂ (5.18 g, 22.4

mmol) in tetrahydrofuran (50 ml) was added. The mixture was then allowed to warm to room temperature, the solvents were evaporated in vacuo, and the residue was digested with dichloromethane (100 ml). Filtration of the dichloromethane extract, followed by concentration of the solution and cooling, gave 2.72 g (49%) of colorless crystals; m.p. 130–135°C.

7 **1**: ^1H NMR (300 MHz, CDCl_3): δ 0.28 (s, 6H, Me_2Si), 1.71, 1.77 (2 brs; $2 \times 6\text{H}$, $\text{Me}_4\text{C}_5\text{H}$), 2.03, 2.12 (2s; $2 \times 6\text{H}$, Me_4C_5), 3.04 (m; 1H, $\text{Me}_4\text{C}_5\text{H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ -0.76 (Me_2Si), 10.26, 12.79 (Me_4C_5), 11.13, 14.13 ($\text{Me}_4\text{C}_5\text{H}$), 110.50, 126.62, 130.86 (Me_4C_5), 54.74, 132.89, 136.60 ($\text{Me}_4\text{C}_5\text{H}$).

2: ^1H NMR (300 MHz, CDCl_3): δ 0.39 (s; 6H, Me_2Si), 1.81 (brs; 12H, $\text{Me}_4\text{C}_5\text{H}$), 2.15, 2.19 (2s; $2 \times 6\text{H}$, Me_4C_5), 2.98 (m; 1H, $\text{Me}_4\text{C}_5\text{H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 0.14 (Me_2Si), 10.26, 12.39 (Me_4C_5), 11.45, 14.50 ($\text{Me}_4\text{C}_5\text{H}$), 113.19, 127.51, 129.99 (Me_4C_5), 54.33, 133.15, 138.10 ($\text{Me}_4\text{C}_5\text{H}$). The main features of interest are the ^{13}C data for the unsaturated carbon atoms of the cyclopentadiene moiety $\text{Me}_4\text{C}_5\text{H}$; the values for the free ligand $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5\text{H})_2$ (δ 133.20, 136.20 ppm) are very close to those of **1**, whereas for **2** the second of these resonances shows a distinct low-field shift. There is no indication of an unsymmetric arrangement of the cyclopentadiene moiety such as is detected in the solid state.

8 Crystal structure of **2**: $\text{C}_{20}\text{H}_{31}\text{Cl}_3\text{Ge}_2\text{Si}$: $M_r = 551.10$; monoclinic, space group $P2_1/c$; a 9.866(2), b 13.535(3), c 19.246(3) Å, β 97.71(1)°, V 2546.81 Å³, $Z = 4$, D_{calcd} 1.437 g cm⁻³; $F(000) = 1120$ electrons; $\mu(\text{Mo-K}\alpha)$ 26.97 cm⁻¹. 3995 independent reflections were collected, 2227 reflections having $I \geq 2.0 \sigma(I)$ (ω scans, $\Delta\omega = 0.9^\circ$, scan velocity 0.9–29.3°/min, $(\sin \theta/\lambda)_{\text{max}} = 0.572$, $+h$, $+k$, $\pm l$, Mo- $K\alpha$, λ 0.71069 Å, T 22°C, Lp and empirical absorption correction, Syntex P2₁). The structure was solved by direct methods (MULTAN 80), $R = 0.088$, $R_w = 0.100$, $w = 1/[\sigma^2(F_0) + 0.00064F_0^2]$ (anisotropic, H constant, 253 parameters, SHELX 76). $\Delta\rho$ (fin.) = +1.06/−0.99 e/Å³. More details are available on request from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (F.R.G.); any request should be accompanied by the reference number CSD 51737, and the full literature citation for this communication.

9 F.X. Kohl, R. Dickbreder, P. Jutzi, G. Müller and B. Huber, in preparation.