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Communications

X-ray and Molecular Structure of the First Germacyclopentenyl Compound η^1- and η^3-Coordinated to Two Cobalt Carbonyl Fragments

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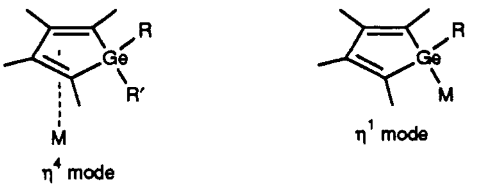
Summary: Thermal reaction of $Co_2(CO)_8$ with 1-phenyl-2,3,4,5-tetramethylgermole gave rise to the first germacyclopentenyl compound coordinated to two cobalt(I) carbonyl fragments, in an η^1 mode to $Co(CO)_4$ and in an η^3 mode to $Co(CO)_3$. The complex has been structurally characterized.

1,1-R,R′-substituted germoles are usually bonded to metal centers in the η^4 mode (Chart I). The result may be either isolation and characterization of the molecule as its metal complex[1] or nucleophilic regioselective substitution reactions at the germanium atom if R and R′ are convenient substituents (Cl, OMe).[1b,c,f,2] Hydrogermoles (R = H; R′) on the other hand, like the corresponding hydrosiloles, coordinate oxidatively to metal centers in the η^1 mode, a reaction that has precedents in catalytic hydrosilylation reactions of olefins.[3,4] However, this coordination may destabilize the germole by a ring-opening reaction.[5]

Chart I



It was thus of interest to study the reaction of 1-phenyl-2,3,4,5-tetramethylgermole with $Co_2(CO)_8$, which is well-known to be a hydrosilylation and hydrogermylation catalyst precursor.[6] Interestingly, the reaction of 1-methyl-2,5-diphenylsilole with $Co_2(CO)_8$ has been reported, giving a bimetallic complex, in which the tetraphenylsilole is η^1-bonded to $Co(CO)_4$ and η^4-bonded to $Co_2(CO)_6$.[7]

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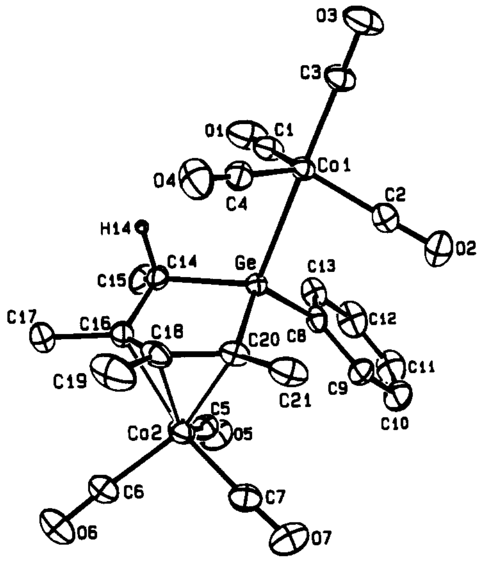
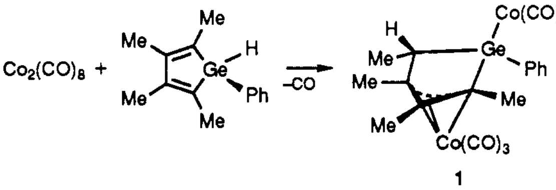


Figure 1. ORTEP drawing of 1. The main distances (Å) are as follows: Ge–Co1 = 2.467 (1), Ge–C14 = 1.971 (5), Ge–C8 = 1.948 (5), Ge–C20 = 1.958 (5), C14–C16 = 1.520 (7), C16–C18 = 1.414 (8), C18–C20 = 1.419 (7), C14–H14 = 1.12 (5), Co1–C1 = 1.785 (6), Co1–C2 = 1.789 (6), Co1–C3 = 1.806 (5), Co1–C4 = 1.783 (6), Co2–C16 = 2.140 (5), Co2–C18 = 2.010 (5), Co2–C20 = 2.120 (5), Co2–C5 = 1.806 (6), Co2–C6 = 1.802 (6), Co2–C7 = 1.777 (7). Angles (deg) are as follows: around Ge, Co1–Ge–C8 = 109.7 (1), Co1–Ge–C14 = 111.1 (1), Co1–Ge–C20 = 111.2 (1), C8–Ge–C14 = 117.6 (2), C20–Ge–C14 = 91.1 (2), C20–Ge–C8 = 115.1 (2); in the ring, Ge–C14–C16 = 101.7 (3), Ge–C14–C15 = 118.6 (4), C14–C16–C18 = 116.9 (4), C16–C18–C20 = 113.9 (4), C18–C20–Ge = 106.8 (4), Ge–C14–H14 = 101 (3); around Co1, Ge–Co1–C3 = 175.5 (2), C1–Co1–C2 = 123.3 (3), C1–Co1–C4 = 117.6 (3), C2–Co1–C4 = 114.2 (3), Ge–Co1–C1 = 79.3 (2), Ge–Co1–C2 = 83.5 (2), Ge–Co1–C4 = 85.5 (2); around Co2, C6–Co2–C5 = 103.3 (3), C6–Co2–C7 = 97.6 (3), C5–Co2–C7 = 99.1 (2).

We describe here the reaction that gives rise to the synthesis of the first germacyclopentenyl complex 1, in which the germole acts as a (3 + 1)-electron donor toward two cobalt carbonyl fragments (reaction 1).

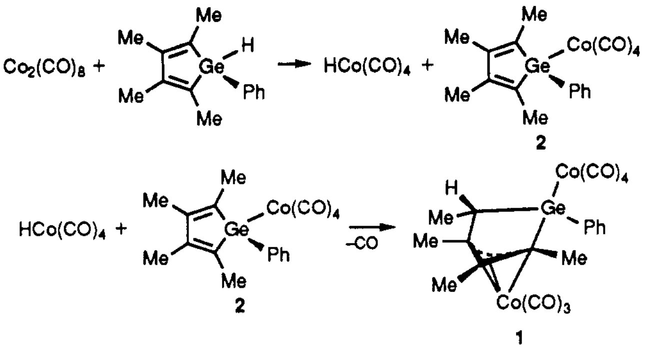


(1)

1

A solution of 1-phenyl-2,3,4,5-tetramethylgermole (0.350 g, 1.28 mmol) in pentane was treated with $Co_2(CO)_8$ (0.220 g, 0.643 mmol) and stirred at 35 °C for 48 h. The solution was concentrated in vacuo. Cooling overnight at −20 °C gave rise to 1, as black-brown, air-stable crystals (yield 65%), which were fully characterized by IR and NMR spectroscopy, elemental analysis,[8] and X-ray diffraction measurement.[9]

Scheme I



The molecular geometry is illustrated in Figure 1. It consists of a germacyclopentenyl ring bridging two cobalt carbonyl fragments, $Co(CO)_4$, in an η^1 fashion via germanium (Co1–Ge = 2.467 (1) Å) and $Co(CO)_3$ in an η^3 mode through the carbons C16, C18, and C20 of the allylic portion of the cycle. The variations in the Co2–allyl distances are as usually observed in cobalt η^3-allyl complexes, i.e. M–C(terminal) (2.120 (5), 2.140 (5) Å) > M–C(central) (2.010 (5) Å).[10] The η^3-enylic C–C bond lengths at 1.414 (8) Å are normal. The germanium is tetrahedral, as indicated by the angles around Ge (average 109.3°). Nevertheless, the Ge–C distances (1.958 and 1.971 Å) are slightly longer than those observed in η^4 metal coordinated germole. The ring is hinged at the terminal allylic carbons into two planes, with the interplanar angle being 28 (2)°. The methyl carbon C15, which lies toward the metal atom Co2, has probably been forced into this position by the steric requirement of the $Co(CO)_4$ fragment. Consequently, the proton H14 is located at 1.12 (5) Å from C14 toward Co1, as expected.

The geometry around Co1 is trigonal bipyramidal, with GeR_3, a σ-donor ligand, in an axial position as expected.[11] The Co1–C distances are not significantly different and are as usual, as are the angles around Co1. The environment of Co2 is best described as a distorted-square-pyramidal geometry, with the three Co2–C distances not significantly different and similar to that observed in $(\eta^3\text{-}C_3H_5)Co(CO)_3$. The allylic fragment occupies two basal coordination sites, in a staggered orientation with respect to the C5C6C7 face, which is the most stable conformation for $(\eta^3\text{-allyl})ML_3$ systems.[12]

A probable mechanism for the reaction is as shown in Scheme I.

The first step parallels the usual hydrosilylation reaction: thermally induced cleavage of $Co_2(CO)_8$ and hydrogen transfer from 1-phenyl-2,3,4,5-tetramethylgermole to give the mononuclear $HCo(CO)_4$ and the η^1 Ge–Co complexes. The absence of the characteristic absorption bands of $HCo(CO)_4$ in the IR spectrum of the reaction mixture[13]

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(8) Characterization of $GeCO_2O_7C_{21}H_{18}$: ^{1}H NMR (200 MHz; CD_2Cl_2) δ 1.53 (C14-Me, d, ^3J = 7.1 Hz), 1.81, 2.03, 2.19 (C16,C18,C20-Me, s), 1.99 (C14-H, q, ^3J = 7.1 Hz), 7.36, 7.54 (H-Ph, 2 m); ^{13}C NMR (50.32 MHz, C_6D_6) δ 15.5, 16.1, 20.3, 22.5 (C14,C16,C18,C20-CH_3), 44 (C14), 96, 79 (C16,C18,C20), 135.4, 129.1, 128.7, 125 (CPh); IR (pentane) ν(CO) = 2081 (s), 2049 (s), 2021 (s), 1990 (s) cm^{-1}. Anal. Calcd for $GeCO_2O_7C_{21}H_{18}$: C, 44.03; H, 3.17. Found: C, 43.97; H, 3.12.

(9) Crystal data at 20 °C for $GeCo_2O_7C_{21}H_{18}$, grown from pentane at −20 °C: a = 8.733 (2) Å, b = 14.697 (2) Å, c = 18.561 (3) Å, β = 101.48 (2)°, V = 2335 (1) Å^3, Z = 4, d_{calc} = 1.219 g cm^{-3}, space group $P2_1/c$, Mo Kα radiation, μ = 26.20 cm^{-1}. Of the 6218 unique data, 3743 with $I > 3\sigma(I)$ were used in refinement. Anisotropic thermal parameters were used for all non-hydrogen atoms. Refinement converged at R = 0.0360 and R_w = 0.0419.

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could indicate that this strong electrophile[3b] may be immediately trapped by the germole **2**, with loss of CO, to give **1**, i.e. the germacyclopentenyl moiety η^3-coordinated to $Co(CO)_3$. Precedents of these reactions have been reported in the action of dienes with metal hydrido complexes.[14]

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Supplementary Material Available: Listings of crystal data and data collection and refinement details, fractional atomic coordinates, bond distances and angles, and anisotropic thermal parameters (7 pages); a table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Synthesis and Solid-State Structure of $(Me_3Si)_3CGeCH(SiMe_3)_2$, a Monomeric Dialkylgermylene

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Summary: The reaction of $Me_5C_5GeCH(SiMe_3)_2$ with $LiC(SiMe_3)_3$ affords $(Me_3Si)_3CGeCH(SiMe_3)_2$ (**2**), the first unsymmetrically substituted dialkylgermylene, which is stable at ambient temperature. In the solid state, the germylene **2** is monomeric, whereas Lappert's germylene $[(Me_3Si)_2CH]_2Ge$ (**1**) shows a dimeric structure with a Ge═Ge double bond. Steric effects of the additional trimethylsilyl group in **2** are responsible for these drastic changes in the structure. The germylene $Me_3SiCH_2GeCH(SiMe_3)_2$ (**3**) decomposes at about −20 °C.

Germylenes—the germanium analogues of carbenes—have been extensively studied during the last 15 years.[1] Most of these compounds are unstable under normal conditions and thus have been used as reactive intermediates.[2] A noticeable stabilization is possible by using π-ligands[3] or bulky ligands such as $-NR_2$, $-OR$, or $-SR$;[4] compounds of this type are stable at ambient temperature, and some of them are monomeric in the solid state and in the gas phase. In the class of dialkylgermylenes, the stable compound $[(Me_3Si)_2CH]_2Ge$ (**1**) was described in 1976 by Lappert and co-workers.[5] This species has interesting structural features: It is a monomer in solution and in the gas phase[6] and a dimer in the solid state. The dimerization is caused by a Ge–Ge interaction that has been interpreted as a new type of double bond.[7] Up to

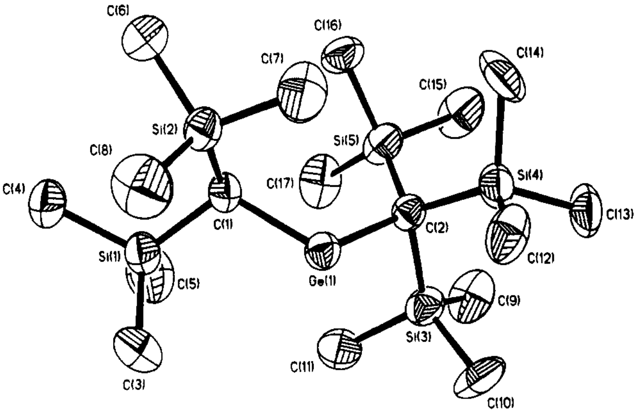

Figure 1. X-ray structure of $(Me_3Si)_2CHGeC(SiMe_3)_3$ (**2**). Selected bond distances (Å) and angles (deg): Ge(1)–C(1) = 2.012 (6), Ge(1)–C(2) = 2.067 (4), Si(1)–C(1) = 1.883 (4), Si(2)–C(1) = 1.887 (5), Si(2)–C(6) = 1.857 (9), Si(3)–C(2) = 1.928 (6), Si(4)–C(2) = 1.871 (4), Si(5)–C(2) = 1.881 (6); C(1)–Ge(1)–C(2) = 111.3 (2), Ge(1)–C(1)–Si(1) = 115.2 (3), Ge(1)–C(1)–Si(2) = 103.3 (2), Ge(1)–C(2)–Si(3) = 95.2 (2), Ge(1)–C(2)–Si(4) = 109.0 (3), Ge(1)–C(2)–Si(5) = 117.4 (3).

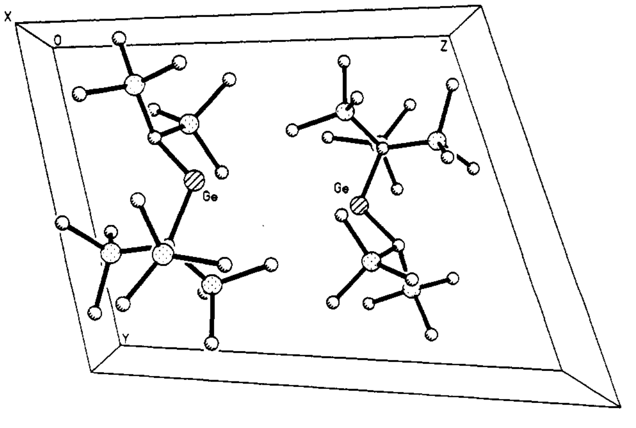

Figure 2. Unit cell diagram of $(Me_3Si)_2CHGeC(SiMe_3)_3$ (**2**).

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