A Silicon−Cobalt Cluster with an Unusually Short Cross-Ring Silicon−Silicon Distance

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Received February 21, 1997⊗

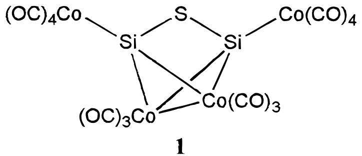
Summary: $[\mu\text{-}((CH_3)Si(CH_2)-)_2](Co(CO)_3)_2$ *was formed in the reaction of 2,5-disilahexane with dicobalt octacarbonyl. The complex was fully characterized, and the X-ray diffraction crystal structure indicates a very short Si···Si transannular distance.*

Silicon−transition-metal chemistry is involved in catalytic processes as well as in the preparation of organometallic precursors of materials. Silicon−cobalt compounds, in particular, have been widely investigated, since $Co_2(CO)_8$ is a known hydrosilylation catalyst.[1−3]

We report here the synthesis and structural characterization of an unusual cobalt−silyl complex with a short cross-ring Si···Si distance. This new type of complex is easily prepared by reaction of a 2,5-disilahexane with dicobalt octacarbonyl.

From the pioneering work of Chalk and Harrod,[1b] it is well-known that Si−Co bonds are easily formed by reaction of Si−H compounds with dicobalt octacarbonyl, accompanied by elimination of dihydrogen and carbon monoxide. Numerous Si−Co-containing compounds have been prepared by such reactions of trialkylsilanes or $R^1R^2SiH-R-SiHR^3R^4$.[4−9] However, when dihydrosilanes R_2SiH_2 ($R =$ alkyl, phenyl) are used, the reaction is more complex; the expected $R_2HSiCo(CO)_4$ is formed, but other polynuclear complexes are formed as well.[2] For example, diphenylsilane reacts with iron pentacarbonyl to form the dimeric complex $(OC)_4Fe(\mu\text{-}SiPh_2)_2Fe(CO)_4$[10a] but, with $Co_2(CO)_8$, the unexpected complex $[Ph_2Si\{Co(CO)_4\}OCCo_3(CO)_9]$[10b] is obtained. The formation of the dimeric cyclic complex $(OC)_3Co(\mu\text{-}SiR_2)_2Co(CO)_3$ occurs only when a disilane, $(CH_3)_2HSi-SiH(CH_3)_2$, is treated with dicobalt octacarbonyl.[11]

This type of dimeric complex, $(OC)_3Co(\mu\text{-}ER_2)_2Co(CO)_3$, was reported for other group 14 elements such as Sn and Ge.[12,13] Recently, the fully characterized complex $(OC)_3Co[\mu\text{-}((CO)_4Co)Si-S-Si(Co(CO)_4)]Co(CO)_3$, (**1**) was prepared by the reaction of $H_3Si-S-SiH_3$ with $Co_2(CO)_8$.[14]



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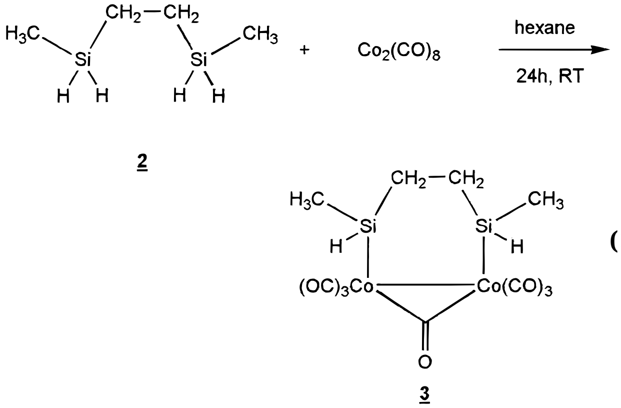
In the course of our investigations of the preparation of organometallic precursors of ceramics,[15,16] we happened to study the reaction of 2,5-disilahexane,[17] (**2**), with dicobalt octacarbonyl. A complicated mixture of products was expected from the reaction because four reactive Si−H functions were present in the silane. However, when the reaction was carried out at room temperature using equimolar amounts of the reactants with hexane as solvent, we found that a rather simple reaction had occurred, leading mainly to formation of complex **3** (eq 1). This compound could not be isolated or purified; however, the proposed structure for **3** is consistent with the NMR and IR spectroscopic analysis of the crude mixture.[18]



(1)

Longer stirring (3 or 4 days) at room temperature or heating to 60 °C for 24 h of this reaction mixture led to the formation of complex **4** along with other uncharacterized metal complexes (eq 2). When the reaction was carried out with an excess of silane (ca. 2 equiv), after 20 h at reflux, **4** could be isolated in 70% yield.[19] The

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⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1997.

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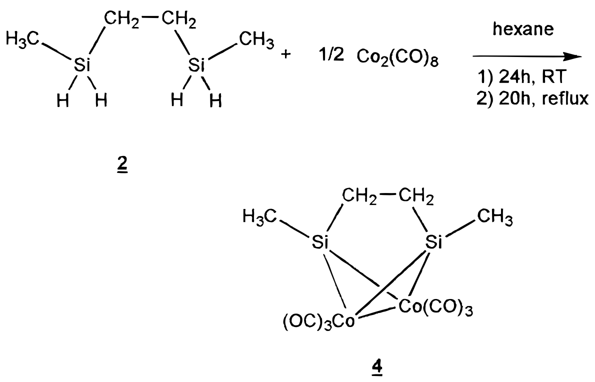
(17) The procedure for 2,5-disilahexane (**2**) is supplied as Supporting Information.

S0276-7333(97)00127-1 CCC: $14.00



(2)

effect of an excess of the silane is not understood, but it improves the yield and the selectivity of the reaction.

Complex **4** was isolated from cold hexane as yellow crystals. It is poorly stable to air and heat but can be stored for several weeks at −20 °C in hexane under dinitrogen.

Compound **4** was fully characterized by X-ray diffraction crystal structure analysis.[20] The ORTEP drawing and the main bond lengths and bond angles are given in Figure 1. The structure is very close to C_{2v} symmetry, as shown by the presence of a dihedral angle $-Si-CH_2-CH_2-Si-$ of 2.4° (Figure 2). The thermal parameter values for the silicon atoms ($U_{iso} = 0.020$ and 0.026 Å, respectively) suggested that the near-eclipsing of the silicon atoms was real and was not the averaging of the alternative staggered conformation. Each silicon atom is bonded to two cobalt atoms, and the average Si−Co bond length is 2.28 Å, close to the 2.254(3) or 2.381(7) Å observed for the single Si−Co bonds in $Cl_3Si-Co(CO)_4$[21] and $H_3Si-Co(CO)_4$.[22] The Co−Co bond length (2.612(1) Å) is longer than that in the dicobalt octacarbonyl crystal (2.524(2) Å)[23] or in $(R_2C_2)Co_2(CO)_6$ (R = *t*-Bu, Ph; 2.463(1) Å[24a] and 2.47 Å,[24b] respectively). However, this distance is close to the Co−Co distance in **1** (2.623(1) Å) or **5** (2.61 Å (average)).[14]

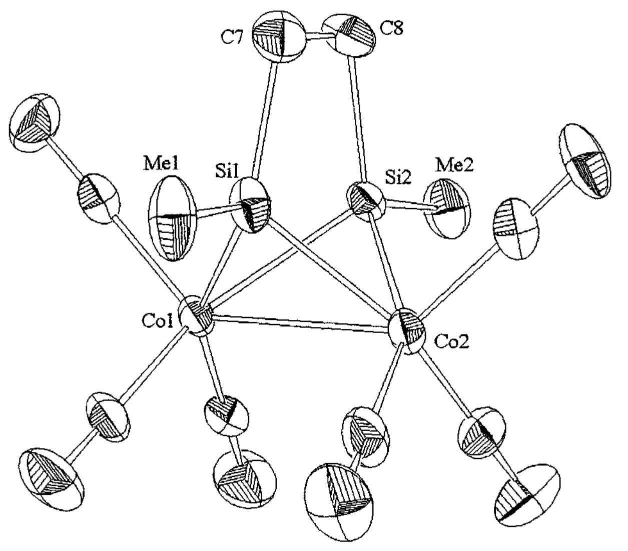


Figure 1. ORTEP drawing of complex **4**. Selected bond distances (Å) and angles (deg) are as follows: Co1−Co2, 2.612(1); Co1−Si, 2.284(1); Co1−Si2, 2.278(2); Co2−Si1, 2.281(1); Co2−Si2, 2.275; Si1···Si2, 2.691(2); Si1−Me1, 1.855(5); Si1−C7, 1.882; C7−C8, 1.534; Si1−Co1−Si2, 72.29(5); Si1−Co2−Si2, 72.39; Si1−Co1−Co2, 55.05(4); Si1−Co2−Co1, 55.16(4); Co1−Si1−Co2, 69.80(4); Me1−Si1−Co1, 124.2(2); Me1−Si1−Co2, 123.4(2); Me1−Si1···Si2, 176.5(2); Me1−Si1−C7, 111.3(2); Co1−Si1−C7, 111.0(2); Co2−Si1−C7, 111.1(2).

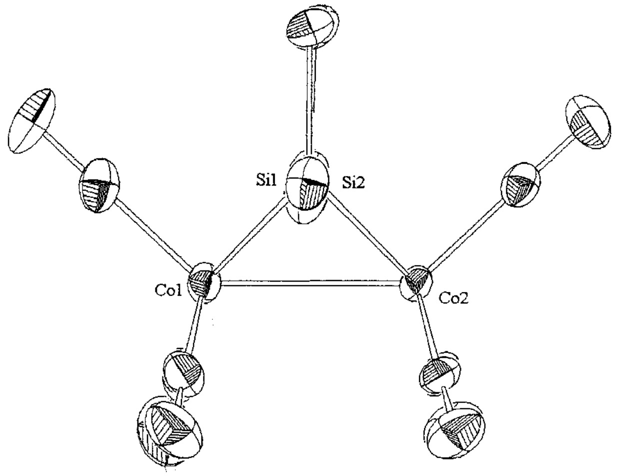


Figure 2. View of **4** along the Si···Si axis.

More interesting is the presence of a very short transannular Si···Si distance of 2.691(2) Å, which is in the range of the longest known single Si−Si bonds (e.g., $(t\text{-Bu})_6Si_2$, 2.697 Å).[25] This distance is one of the shortest cross-ring Si···Si distances known in a silicon−metal four-membered ring. The shortness of the Si···

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(18) Due to paramagnetism of the solution, ^{1}H NMR gave only very broad signals (C_6D_6; δ, ppm): 3.36; 1.23); 0.88; 0.29. ^{13}C NMR (C_6D_6; δ, ppm): 206.35; 198.98; 196.82; 16.32; 6.95; −2.79. ^{29}Si NMR (C_6D_6; δ, ppm): 60.50; 57.25; 48.84. IR (hexane; cm^{-1}): 2120; 2091; 2072; 2054; 2028.5; 1990; 1835. The ^{1}H NMR spectrum showed a Si−H signal (multiplet at 3.36 ppm) and no Si−Co−H signal, expected in the range 0 to −15 ppm. From the ^{29}Si NMR spectrum, the dominant signal at 60.5 ppm is attributed to **3**. The small signal at 45.8 ppm is attributed to $(OC)_4CoSiH(CH_3)CH_2CH_2SiH(CH_3)Co(CO)_4$, by reference to $(OC)_4CoSi(CH_3)_2CH_2CH_2Si(CH_3)_2Co(CO)_4$ (47.1 ppm).[7] The tiny signal at 57.25 ppm was not assigned. The FT-IR spectrum showed the presence of Si−H (2120 cm^{-1}) and bridging CO ligands (1835 cm^{-1}).

(19) Procedure for (2,5-disilahexane)hexacarbonyldicobalt (**4**): to 120 mL of hexane was added 5.13 g (15 mmol) of dicobalt octacarbonyl, and 3.54 g (30 mmol) of 2,5-disilahexane was added dropwise. The mixture was stirred for 24 h at room temperature and then heated at reflux for 20 h. The mixture was filtered quickly through Celite. The solution was concentrated and kept at −20 °C. Compound **4** crystallized as pale yellow needles. Yield: 4.15 g (69%). ^{1}H NMR ($CDCl_3$; δ, ppm): 1.36 (4H, s); 1.14 (6H, s). ^{13}C NMR (C_6D_6; δ, ppm): 201.5 (CO); 199.9 (CO); 16.98 (CH_3); 6.49 (CH_2). ^{29}Si NMR (C_6D_6; δ, ppm): 210. IR (hexane, cm^{-1}) 2072.6; 2031.9; 2017.7; 1993.5; 1983.2 sh. Mass spectrum (EI, 30 eV; *m/e*): parent ion M^+ 400. Elemental analyses were not reproducible due to the decomposition of the crystals at room temperature in sealed vials.

(20) Crystal data for **4**: $C_{10}H_{10}Co_2O_6Si_2$, $M_r = 400.1$, monoclinic, space group $P2_1/n$, $a = 7.683(2)$ Å, $b = 23.717(3)$ Å, $c = 8.910(2)$ Å, $\beta = 108.76(2)°$, $V = 1537.3(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.729$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 23.3 cm^{-1}, crystal dimensions 0.12 × 0.12 × 0.20 mm^3. Data were collected on a Nonius CAD 4 automated diffractometer at 163 K. A total of 2046 reflections having $F_o > 3\sigma(F)$ were considered to be observed ($4 < 2\theta < 52°$). The absorption corrections were neglected in view of the small size and the regular shape of the crystal. Direct methods (SHELXS-86 program) succeeded in locating 17 out of the 20 non-hydrogen atoms. The three remaining atoms were located in a Fourier map. After six least-squares refinement cycles with anisotropic thermal parameters for all atoms ($R = 0.0453$), hydrogen atoms were then positioned by calculation (SHELX-76 program). After four more least-squares cycles, the refinement converged to the final R value of 0.0386 ($R_w = 0.0421$). The calculated hydrogen atom coordinates are available as Supporting Information.

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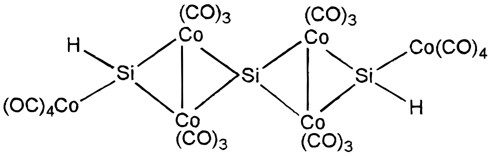

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Si distance may depend on the presence of the wingtip–wingtip bridge. From the clusters presented in Table 1, the presence of a bridge seems to force the two silicon atoms close to each other. In the absence of a bridge (complex **5**), a rather long distance is observed (2.85 Å (average)), while with the same geometry, sulfur and ethylene bridges shorten the bond to respectively 2.498(2) and 2.691(2) Å. According to the reviewers, "In the present case, it is the optimization of the Co–Si bonding which forces the Si–Co–Si angles to be small. A component involving overlap of a filled Co d orbital, bisecting the Si–Co–Si angle with empty σ^* orbitals located mainly on the Si's is responsible." It is well-known that M_2Si_2 complexes where M = Pt[26,27] have a short cross-ring Si···Si distance. However, care must be taken, since these clusters have a different geometry.

The simplicity of the infrared (CO) stretching vibrations is related to the symmetrical arrangement of these ligands. With an overall molecular symmetry close to C_{2v}, five stretching modes are expected and are effectively observed. Two other vibrations of very weak intensity are attributed to the ^{13}C isotope. The vibrational frequencies are reported in Table 2 along with those for the related germanium and tin compounds $[\mu\text{-}M(CH_3)_2]_2(Co(CO)_3)_2$ (M = Ge, Sn).[13]

The other vibrational frequencies of the spectrum are related to the organosilyl bridging part of the complex.

We note also that the ^{29}Si NMR spectrum of **4** exhibits a signal at δ 210 ppm, which is one of the highest reported values for a silicon chemical shift. This particularly high value is related to the presence of two Si–Co bonds at each silicon atom. To our knowledge, higher values have only previously been reported for a few silylene–ruthenium species.[28]

Table 1. Crystal Data of Cobalt–Silyl Butterfly Four-Membered Rings

compd	bridge	Si–Si dist (Å)	angle (deg)	
			Si–M–Si	M–Si–M
complex **1**[a]	–S–	2.498		70
complex **4**[b]	$-CH_2CH_2-$	2.691	72	70
complex **5**[a]	no bridge	2.85		69

[a] Reference 14. [b] Present work.

Table 2. Infrared (CO) Stretching Vibrations (cm^{-1})

$[\mu\text{-}((CH_3)Si(CH_2)-)_2]\text{-}(Co(CO)_3)_2$	$[(Ge(CH_3)_2]_2\text{-}(Co(CO)_3)_2$[b]	$[(Sn(CH_3)_2]_2\text{-}(Co(CO)_3)_2$[b]
2073 s	2072 s	2063 s
2031 sv	2035 vs	2025 vs
2017 vs	2014 vs	2005 vs
1993 vs	1994 vs	1980 s
1983 s	1984 m	1974 m
1966 vw[a]	1964 vw[a]	
1948 vw[a]	1947 vw[a]	

[a] Isotopic ^{13}C satellite. [b] Reference 13.

The ^{1}H NMR spectrum was recorded between 15 and −20 ppm. Only signals at 1.36 ppm and 1.14 ppm were observed corresponding to the $-CH_2-$ and $-CH_3$ groups, which confirms the absence of Si–H···Co or Si···H–Co links that have been reported for some transition-metal–silyl complexes.[29]

Clusters of this type are currently under investigation in our laboratory. They can be used as ceramic precursors or as cross-linking catalysts for preceramic polymers.[15]

Acknowledgment. We thank the reviewers for their fruitful suggestions.

Supporting Information Available: Text giving the synthetic procedure for compound **2** and tables giving all the fractional atomic coordinates, interatomic distances and bond angles, anisotropic parameters for all non-hydrogen atoms, and calculated hydrogen atom coordinates for **4** (5 pages). Ordering information is given on any current masthead page.

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