

Synthesis, characterization and reactivity of $\text{Cp}(\text{C}_2\text{H}_4)\text{Co}(o\text{-Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2)$; a model compound of selective double silylation

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Abstract

o-Bis(dimethylsilyl)benzene (**1**) reacts with cyclopentadienylobis(ethylene)cobalt at room temperature. This reaction results in overall double Si–H activation, generating the disilacobaltacycle complex $\text{Cp}(\text{C}_2\text{H}_4)\text{Co}(o\text{-Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2)$ (**3**). Complex **3** was characterized by X-ray diffraction. 1,2,4,5-Tetrakis(dimethylsilyl)benzene reacts with $\text{CpCo}(\text{C}_2\text{H}_4)_2$ to give 4,12,6,10-benzo-1,1,3,3,7,7,8,9,9-nonamethyl-1,3-disilacobaltacycle-7,8-disilacyclopent-6-ene (**4**). Complex **4** was characterized by X-ray diffraction and found to contain a 6,10-benzo-7,7,8,9,9-pentamethyl-7,9-disilacyclopent-6-ene via 1,1-double silylation.

Keywords: Cobalt; Disilacobaltacycle; Double silylation; Silicon

1. Introduction

Silyl transition metal complexes now constitute a well recognized class of reagents and intermediates in organic synthesis [1]. Rhodium [2], nickel [3], palladium [4] and platinum complexes [5,6] catalyze various synthetic organic reactions such as hydrosilylation and dehydrogenative double silylation. Of particular importance among transition metal complex catalyzed syntheses of silicon compounds is the double silylation of unsaturated hydrocarbons with silanes. In the double silylation process, the cyclic bis(silyl)metal moiety is thought to play an important role as a reactive intermediate [3–6]. However, a few studies have been directed towards the preparation of complexes in which two silicon atoms are joined to a metal in a cyclic structure [7]. We report herein the first example of monomeric disilacobaltacycle complexes that contain bis(silyl)groups and ethylene in a proximal position.

2. Experimental, results and discussion

Treatment of $\text{CpCo}(\text{C}_2\text{H}_4)_2$ [**1**] with an equimolar amount of **1** in toluene at room temperature gave the disilacobaltacycle complex **3** in 32% yield, which was obtained as a yellow crystalline solid. In the solid state **3** seems to be indefinitely stable when kept under N_2 . In common organic solvents, however, the complex is slowly decomposed. Analytical and spectral data are in accord with the proposed formulation.

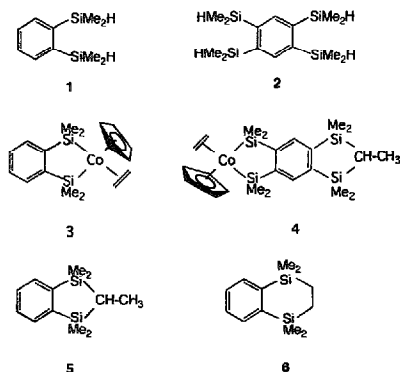
$[\text{CpCo}(\text{Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2)(\text{C}_2\text{H}_4)]$ **3** was prepared as follows. Toluene (40 ml) was added to a flask containing $\text{CpCo}(\text{C}_2\text{H}_4)_2$ (1.02 g, 5.67 mmol) and **1** (1.10 g, 5.67 mmol) under ethylene atmosphere. The mixture was stirred for four days at room temperature and all volatiles were removed in vacuo. The reaction mixture was subjected to a chromatographic work-up (silica gel, hexane) under nitrogen. X-ray suitable crystals were obtained from hexane at -15°C .

Selected spectroscopic data for **3**. ^1H NMR (300 MHz, C_6D_6 , at 25°C): δ 7.67 (2H, Ph), 7.40 (2H, Ph), 4.532 (5H, C, H₃), 1.82 (4H, C, H₁), 1.11 (6H, Si–Me), 0.77 (6H, Si–Me). ^{13}C NMR (C_6D_6): δ 152.26, 151.86, 130.13, 86.13, 36.65, 8.37, 5.32. ^{29}Si NMR

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(C_6D_6): δ 50.52. MS m/z 344 (28%, M^+), 316 (92%, $M^+ C_2H_4$). Satisfactory analytical data were obtained.

The 1H NMR spectrum of **3** shows two sets of peaks due to the hydrogens of the Si–Me groups. The peaks can be assigned to the two sets of methyl groups situated on opposite sides of the Si(1)–Si(2) vector.



In addition, the 1H NMR spectrum of **3** included two sets of peaks, arising from the non-equivalent carbons of coordinated ethylene at δ 2.74 and 0.90 at $-15^\circ C$. Upon warming the solution at $25^\circ C$, these two peaks coalesced to one broad resonance at 1.82 ppm. This result is consistent with the presence of a coordinated ethylene molecule, and is similar to that reported for other transition metal complexes involving a coordinated ethylene molecule, and is similar to that reported for other transition metal complexes involving a coordinated ethylene [12]. The ^{13}C NMR spectrum is also consistent with the presence of the two sets of methyl groups situated on opposite sides and a symmetrical ethylene fragment. Its formulation was confirmed by X-ray diffraction.

Crystal data for **3**. $C_{17}H_{25}Si_2Co$, $M = 344.49$, space group $P2_1/c$ (No. 14), $a = 8.525(4)$, $b = 15.003(5)$, $c = 13.490(3)$ Å, $\beta = 93.60(3)^\circ$, $V = 1722(1)$ Å³, $D_{calc} = 1.329$ g cm⁻³, $Z = 4$. Of the 3358 unique reflections collected ($48.56^\circ < 2\theta < 49.91^\circ$) with Mo K α ($\lambda = 0.71069$ Å), the 2388 with $I > 3.00\sigma(I)$ were used in the final least-squares refinement to yield $R = 0.032$ and $R_w = 0.048$. The non-hydrogen atoms were refined anisotropically. As shown in the ORTEP diagram (Fig. 1), the complex has a square-pyramidal geometry about the cobalt with two silyl groups and ethylene forming the base of a square pyramid with the C_5H_5 ligand in the capping position. The olefin and Si(1)–Co–Si(2) vectors are nearly parallel. The Co–Si bond distances of

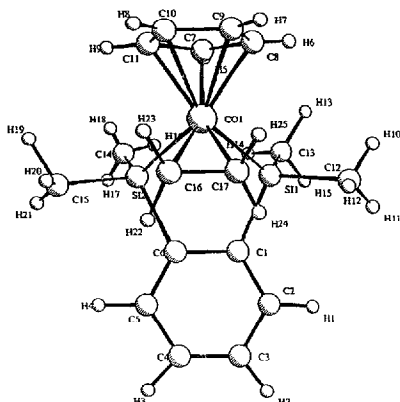


Fig. 1. Molecular structure of **3**. Selected bond distances (Å) and angles ($^\circ$): Co–Si(1) 2.290(1), Co–Si(2) 2.293(1), Co–C(16) 2.035(3), Co–C(17) 2.035(3), Si–C(1) 1.893(3), Si(2)–C(16) 1.897(3), C(16)–C(17) 1.399(5), Si(1)–Co–Si(2) 81.33(5), Co–Si(1)–C(1) 105.3(1), C(16)–Co–C(17) 40.2(1), Co–C(16)–C(17) 69.9(2).

12.290(1) and 2.293(1) Å are shorter than those of the platinum complex with 1,2-disilylbenzene [12.428(2) and 2.383(1) Å] [8], $ReH_3(disil)(PPh_3)_2$ [2.495(2) and 2.489(3) Å] [9], and $Rh_4Si_2Me_2CH_2CH_2SiMe_2[CH_2(PMe_3)]_2$ [2.832(2) and 2.839(2) Å] [10]. The C(16)–C(17) bond distance [1.399(5) Å] of ethylene in **3** is directly comparable with that found in $Co(C_6H_6)(C_2H_4)(PMe_3)_3$ [1.431(1) Å] [13] and $(C_2Me_5)Rh(C_2H_4)(PPh_3)_3$ [1.408(16) Å] [14]. The Co–C(16)/C(17) distance [2.035 Å] falls well within the range commonly observed for ethylene cobalt complexes.

Complex **4** can readily be prepared by the reaction of **2** with two molar amounts of $CpCo(CO)_2H_4$ in toluene in 12% yield, and its structure can be ascertained by NMR spectroscopy.

Selected spectroscopic data for **4**. 1H NMR (300 MHz, C_6D_6 , at $25^\circ C$): δ 7.55 (2H, Ph), 4.90 (5H, C_5H_5), 1.93 (4H, C_2H_4), 1.52 (d, 3H, CH_3), 1.26 (6H, Si–Me), 1.15 (6H, Si–Me), 0.87 (6H, Si–Me), 0.66 (6H, Si–Me), 0.50 (q, 1H, CH). ^{13}C NMR (C_6D_6): δ 154.28 (2C, aromatic Si–C), 131.42 (2C), 129.38 (2C), 88.22 (Cp), 37.92 (CH_2), 8.84 ($CHCH_3$), 8.46, 8.34, 5.52, 5.42 (Si– CH_3), –1.44 ($CHCH_3$). ^{29}Si NMR(C_6D_6): δ 47.82, 2.06. Satisfactory analytical data were obtained.

The observation of four Me singlets for the Si–Me in the 1H NMR spectrum is in agreement with the existence of four non-equivalent CH_3 groups. The ^{13}C NMR spectrum of **4** reveals four resonances at 8.46, 8.34, 5.52 and 5.42 ppm attributed to four non-equivalent CH_3 carbons, and two resonances at 8.84 and

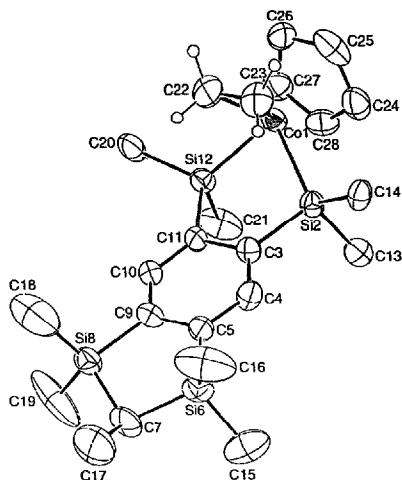


Fig. 2. Molecular structure of **4**. Selected bond distances (Å) and angles (°): Co(1)–Si(2) 2.304(3), Co(1)–Si(12) 2.283(3), Co(1)–C(22) 2.039(12), Co(1)–C(23) 2.307(13), Si(2)–C(3) 1.868(10), Si(12)–C(11) 1.8909(10), Si(6)–C(7) 1.993(28), Si(8)–C(7) 1.837(27); Si(2)–Co(1)–Si(12) 82.4(1), C(22)–Co(1)–C(23) 39.5(5), Si(6)–C(7)–Si(8) 103.5(12).

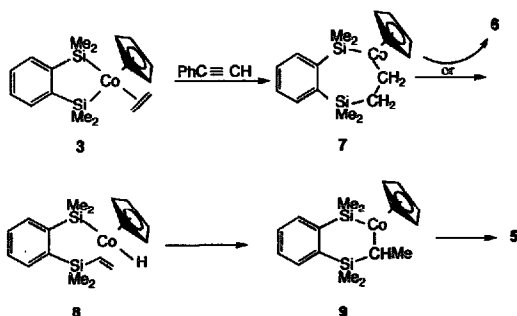
–1.44 ppm due to MeC carbons. These data are in accord with the structure in **4**, which has been unequivocally established by an X-ray study.

Crystal data for **4**. $\text{CoC}_{23}\text{H}_{29}\text{Si}_4$, sp...c group $P2_12_12_1$, $a = 12.44206(6)$, $b = 17.7380(8)$, $c = 12.2910(5)$ Å, $V = 2712.6(2)$ Å³, $D_{\text{calc}} = 1.496$ g cm⁻³, $Z = 4$. Of the 19418 reflections collected ($0.0^\circ < 2\theta < 48.7^\circ$) with Mo K α ($\lambda = 0.7107$ Å), a total of 2196 unique reflections with $I > 3.00\sigma(I)$ were used in the

final least-squares refinement to yield $R = 0.0754$ and $R_w = 0.0901$. The non-hydrogen atoms were refined anisotropically.

An ORTEP representation of the molecule of **4** is shown in Fig. 2, which also includes the atom labelling scheme. The molecular structure of **4** around Co shows this complex to be an isostructural species with that of **3**. The Co–Si bond distances of 12.304(3) and 2.283(3) Å are similar to those of complex **3**. The C(22)–C(23) bond distance of ethylene in **4** [1.376(19) Å] is comparable with that found in **3**. An intriguing feature of the structure of **4** is that the complex contains two different moieties; the formation of disilacobaltacycle and the linkage of two silyl groups by a coordinated olefin. The structural configuration strongly suggests that the reaction of $\text{CpCo}(\text{C}_2\text{H}_4)_2$ with **2** proceeds via a double silylation reaction. Tanaka et al. [6] recently reported the hydrogenative reaction of olefins with **1** in the presence of $(\text{C}_2\text{H}_5)_3\text{Pt}(\text{PPh}_3)_2$, proceeding to give the 4,5-benzo-1,1,3,3-tetramethyl-2-alkyl-1,3-disilacyclopent-4-ene via 1,1-double silylation. They proposed the reaction mechanism as intramolecular insertion of a C=C bond into the Pt–H or Pt–Si bond. In this regard, the complex **4** provides an excellent model for the mechanistic study of the double silylation.

In an effort to obtain some information concerning the formation of **4**, we have investigated the reaction of **3** in the presence or absence of a phenylacetylene. When a mixture of phenylacetylene and **3** was heated at 70°C for 6 h, 1,1- and 1,2-double silylation occurred to form a mixture of **5** and **6** in an approximate 76:24 ratio in 92% yield, together with 1,3,5-triphenylbenzene. However, when the complex **3** was heated at 70°C in the absence of a phenylacetylene, an intractable product was obtained. The structures of **5** and **6** have been determined from spectral data and confirmed by comparison with authentic compounds prepared by another route.



Scheme 1.

Selected spectroscopic data for **5**. ^1H NMR (300 MHz, CDCl_3): δ 7.48 (m, 2H, Ph), 7.28 (m, 2H, Ph), 1.26 (d, 3H, CH_3 , $J = 6.9$ Hz), 0.57 (6H, Si-Me), 0.41 (q, 1H, CH, $J = 6.9$ Hz), 0.38 (6H, Si-Me). ^{13}C NMR (CDCl_3): δ 147.42 (2C, aromatic, Si-C), 131.36 (2C), 130.94 (2C), 8.74 (CH_3), 3.08 (CH), 0.82 (2C, SiMe), -0.64 (2C, SiMe). MS m/z 220 (M^+). Satisfactory analytical data were obtained.

A plausible mechanism for the formation of **5** and **6** is shown in Scheme 1. Compound **3** would involve the insertion of a coordinated ethylene into a cobalt-silicon bond, facilitated by the close proximity of these two ligands in the same plane. The formation of a seven-membered intermediate **7** then allows rearrangement of ethylene to give 3,4-benzo-2,2,5,5,6-pentamethyl-1-cobalta-2,5-disilacyclohex-3-ene **9** via an intermediate **8**. The liberation of a CpCo fragment from intermediates **7** and **9** is concomitant with the linkage of silicon-carbon bonds, leading to the complexes **6** and **5** respectively. The role of a phenylacetylene would be to promote the insertion of a coordinated ethylene into a cobalt-silicon bond. However, we must await further investigations to elucidate a detailed reaction mechanism.

In summary, two novel disilacobaltacycle complexes **3** and **4** can be prepared by the reaction of $\text{CpCo}(\text{C}_2\text{H}_4)_2$ with *o*-bis(dimethylsilyl)benzene and 1,2,4,5-tetrakis(dimethylsilyl)benzene respectively. The complexes **3** and **4** provide not only model complexes of the mechanistic rationale of known double silylation, but also a clue to developing unknown catalytic reactions starting from olefins and disilanes.

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