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A Cobalt Silacyclobutadiene Complex

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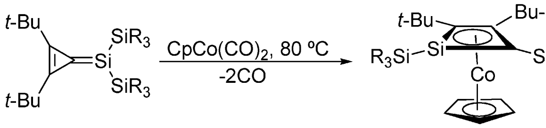
*Summary: The first silacyclobutadiene complex, (η^5-cyclopentadienyl)[η^4-1,2-bis(tert-butyldimethylsilyl)-3,4-di-tert-butyl-1-silacyclobutadiene]cobalt (**1**), was synthesized as red crystals by the reaction of the corresponding 4-silatriafulvene derivative with (cyclopentadienyl)dicarbonylcobalt at 80 °C in benzene. The X-ray analysis of **1** and theoretical calculations for a model silacyclobutadiene complex revealed that the electron accepting ability of the η^4-silacyclobutadiene ligand is significantly smaller than that of a cyclobutadiene ligand in the analogous complex.*

Much effort has recently been devoted to the synthesis of transition-metal complexes of cyclic π electron systems containing heavier group 14 elements in the ring.[1,2] Although a number of silacyclopentadienyl- and germacyclopentadienylmetal complexes[1] and several silabenzene and germabenzene complexes[2] have been synthesized and their structures have been analyzed by X-ray crystallography, complexes with sila- and germacyclobutadiene ligands are missing, despite a great interest in comparing their structural properties with known complexes having cyclobutadiene,[3,4] phosphacyclobutadiene,[5] and related ligands.[6] We wish herein to report the synthesis and characterization of the first η^4-silacyclobutadiene transition-metal complex. A difficulty in the synthesis of silacyclobutadiene complexes that arises from the unknown nature of the ligands as stable compounds was overcome by applying the isomerization of a 4-silatriafulvene to the corresponding silacyclobutadiene.[7]

The silacyclobutadiene complex (η^5-cyclopentadienyl)-[η^4-1,2-bis(*tert*-butyldimethylsilyl)-3,4-di-*tert*-butyl-1-silacyclobutadiene]cobalt (**1**)[8] was synthesized by the reaction of the 4-silatriafulvene **2** with (η^5-cyclopentadienyl)dicarbonylcobalt as red crystals in 64% yield (eq 1). The crystals of complex **1** are stable under an inert atmosphere at room temperature for several months but are moisture- and air-sensitive.



(1)

2 $R_3Si = t\text{-}BuMe_2Si$ **1**

Crystals of **1** suitable for single-crystal X-ray analysis were grown by cooling a pentane solution to 0 °C. The molecular structure of **1** determined at 223 K is shown in Figure 1.[9] The silacyclobutadiene (SiCb) and cyclopentadienyl rings (Cp) of **1** are both almost planar; the bent angle (θ) in SiCb, defined as the angle between Si1−C2−C4 and C2−C3−C4 planes, is 3.8°. Similarly to cyclobutadiene complexes,[3,4] complex **1** has a sandwich structure with two almost parallel cyclic π ligands; the dihedral angle (α), defined as the angle between the average planes of Cp and SiCb, is 2.92°. The distance between the Co atom and the SiCb plane of **1** (1.730(3) Å) is significantly longer than those of cyclobutadiene complexes **3** (1.681(1) Å)[4d] and **4** (1.692 Å)[4e,10] (Chart

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(8) A mixture of 4-silatriafulvene **2** (19 mg, 0.047 mmol) and (η^5-cyclopentadienyl)dicarbonylcobalt (40 mg, 0.22 mmol) in benzene-d_6 (0.4 mL) was heated at 80 °C for 18 h. After removal of the solvent, the residue was subjected to flash chromatography (silica gel, eluent hexane) to afford a red solid. Recrystallization from pentane gave compound **1** as red crystals (16 mg, 0.030 mmol, 64% yield). **1**: red crystals; mp 80 °C; ^{1}H NMR (C_6D_6) δ −0.13 (s, 3H), 0.30 (s, 3H), 0.33 (s, 3H), 0.35 (s, 3H), 1.05 (s, 9H), 1.09 (s, 9H), 1.14 (s, 9H), 1.37 (s, 9H), 4.93 (s, 5H, Cp); ^{13}C NMR (C_6D_6) δ −0.7, −0.6, 1.0, 1.6, 18.9, 19.0, 27.9, 29.4, 33.5, 34.0, 35.0, 35.8, 60.7 (SiCb), 79.7 (Cp), 106.9 (SiCb), 107.5 (SiCb); ^{29}Si NMR (C_6D_6) δ −15.3 (ring Si), 1.0, 6.6; HRMS calcd for $C_{28}H_{53}CoSi_3$ 532.2787, found 532.2785.

(9) Crystal data for **1** at 223 K: $C_{28}H_{53}CoSi_3$, mol wt 532.90, monoclinic, space group $P2_1/n$, $a = 12.238(4)$ Å, $b = 15.096(4)$ Å, $c = 17.226(5)$ Å, $\beta = 95.811(5)°$, $V = 3166.0(16)$ Å^3, $Z = 4$, $D_{calcd} = 1.118$ g/cm^3, R1 = 0.084 (wR2 = 0.257), GOF = 1.007.

10.1021/om0490029 CCC: $30.25

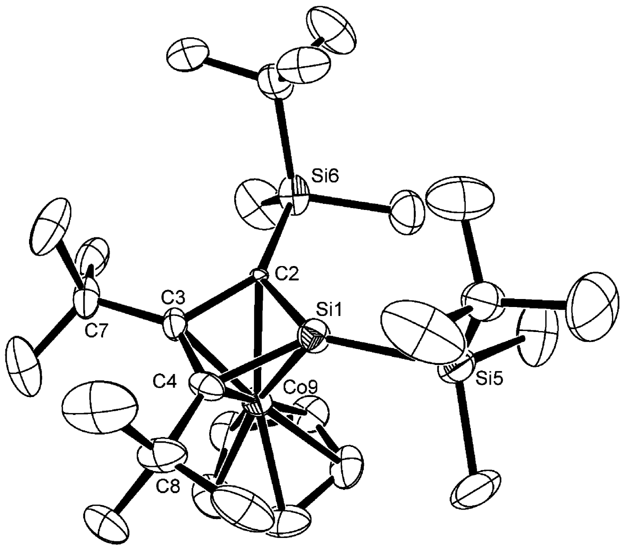
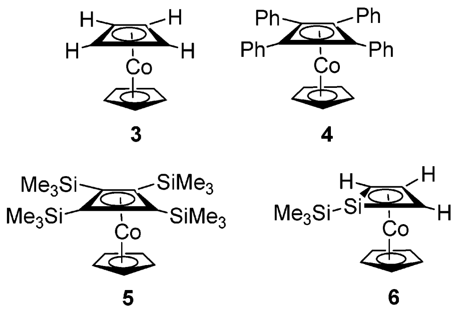


Figure 1. Molecular structure of **1** with atom-labeling scheme. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 30% level.

Chart 1. Cyclobutadiene Complexes 3−5 and the Model Silacyclobutadiene Complex 6



1), while the distance between the Cp plane and Co metal in **1** (1.681(4) Å) is comparable to the corresponding distances in **3** (1.660(1) Å)[4d] and **4** (1.679 Å).[4e,10] It is well-known that the C−C bond alternation exists in cyclobutadiene as a singlet 4π-electron system,[11] while there is no C−C bond alternation in the metal complexes.[4d−f,12] Unfortunately, an issue concerning a similar bond alternation in **1** cannot be discussed, because the structural parameters for the SiCb ring in **1** are strongly affected by the disorder of the Si1 atom at the C2 positions and the occupancy factors are not equal, which is suggested by the unusually small temperature factor for the C2 atom. While two Si−C bond lengths in the SiCb ring of **1** are similar (1.757(4) and 1.801(5) Å for the Si1−C2 and Si1−C4 bonds, respectively) and are intermediate between typical Si−C single (1.86 Å)[13] and double bonds (1.70 Å),[14] the two C−C bonds in the ring are quite different from each other (1.564(6) and 1.469(7) Å for C2−C3 and C3−C4 bonds, respectively); the C3−C4 bond length is close to the corresponding C−C bond length in cyclobutadiene complexes (1.43−1.47 Å),[3,4] but the C2−C3 bond is unusually long.

To elucidate the structural characteristics of silacyclobutadiene complexes in more detail, we performed theoretical calculations for the model complex **6** (Chart 1) at the B3PW91/6-311G(d) level.[15] In good agreement with the X-ray structure of **1**, the SiCb ring in the optimized structure of the 1-(trimethylsilyl)silacyclobutadiene complex **6** is roughly planar (bent angle θ 7.1°) with a dihedral angle α of 5.2° and distances between Cp and Co and between SiCb and Co are 1.648 and 1.701 Å, respectively. The theoretical Cb- - -Co (1.669 Å) and Cp- - -Co distances (1.649 Å) for **3** are in good accord with the experimental values (1.681(1) and 1.660(1) Å, respectively). Similarly, the theoretical SiCb- - -Co (1.701 Å) and Cp- - -Co (1.649 Å) distances for **6** are in accord with those values for complex **1** (1.730(3) and 1.681(4) Å, respectively). The significantly larger SiCb- - -Co distance in **1** as compared to the Cb- - -Co distance in **3** may be ascribed to the weaker coordination ability of SiCb rather than the steric hindrance between the SiCb ring with bulky substituents and the Co atom in **1**. The two Si−C and two C−C bonds in the SiCb ring of **6** are both equivalent, with the distances of 1.842 and 1.441 Å, respectively; hence, the ring has a mirror plane through the Si1 and C3 atoms. On the other hand, in the parent silacyclobutadiene,[16] a set of C−C and Si−C bonds is double bonds (1.351 and 1.712 Å, respectively)[16b] but another set of these bonds is single bonds (1.551 and 1.920 Å, respectively).[16b] On this basis, the silacyclobutadienes would be considered to intrinsically serve as cyclic conjugated π ligands similarly to cyclobutadienes in their complexes.

Natural population analysis (NBO/B3PW91/6-311+G(d,p)//B3PW91/6-311G(d)) for complex **6** revealed that the charge distribution is −0.062, +0.348, and −0.286 on SiCb, Co, and Cp in complex **6**, while the distribution is −0.189, +0.474, and −0.285 on Cb, Co, and Cp in complex **3**, respectively.[17] The electron-accepting ability of a silacyclobutadiene ligand from the (η^5-cyclopenta-

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[10] No standard deviation is given for the distances in ref 4e.

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dienyl)cobalt moiety is significantly smaller than that of a cyclobutadiene ligand, suggesting weaker π-back-donation from Co to SiCb than that from Co to Cb.[18]

The NMR resonances of **1** in C_6D_6 were observed at −15.3 ppm for the ring ^{29}Si nucleus and at 60.7, 106.9, and 107.5 ppm for the ring ^{13}C nuclei. The ^{29}Si and ^{13}C resonances for the ring silicon and carbon nuclei are shifted remarkably to high field from the usual values for the unsaturated silicon and carbon nuclei, but the tendency is reproducible by the theoretical calculations.[8] The values for the ^{29}Si and ^{13}C resonances for **6** calculated by the GIAO method (B3PW91/6-311+G-(d,p)//B3PW91/6-311G(d)) are −5.0 ppm for Si1 and 59.8 and 75.7 ppm for C2 (C4) and C3, respectively, while the values for the corresponding free silacyclobutadiene are 202.2 (Si1), 161.0 (C2), 167.9 (C3), and 102.7 ppm (C4). A similar tendency is found in cyclobutadiene complexes. The ^{13}C NMR resonances for the cyclobutadiene ring carbons of complex **5**[4f,19] and the corresponding free cyclobutadiene[11g,h] have been found at 82.0 and 172.0 ppm, respectively, and the GIAO calculated ^{13}C resonances for complex **3** and the corresponding free cyclobutadiene are 60.3 and 146.6 ppm, respectively.

In conclusion, a silacyclobutadiene ligand complexed with the (cyclopentadienyl)cobalt moiety serves as an η^4-cyclic conjugated π ligand but its electron-accepting ability is significantly smaller than that of the cyclobutadiene ligand.

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Supporting Information Available: Tables giving the details of the X-ray structure determination, bond lengths, and bond angles of **1** and optimized coordinates of model complexes **3** and **6**; X-ray crystallographic data for **1** are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The calculated charge distribution for complex **3** is in good agreement with the reported distribution of −0.187, +0.477, and −0.290 on Cb, Co, and Cp, respectively: Mutseneck, E. V.; Loginov, D. A.; Perekalin, D. S.; Starikova, Z. A.; Golovanov, D. G.; Petrovskii, P. V.; Zanello, P.; Corsin, M.; Laschi, F.; Kudinov, A. R. *Organometallics* **2004**, *23*, 5944. The theoretical level for the NPA calculations is not given in the paper, while the geometry optimization has been performed at the same level as ours.

(18) The charge distribution coincides with the qualitative view of the bonding of these complexes. Because silicon is more electropositive than carbon, qualitative perturbation theory predicts that the LUMO level of silacyclobutadiene will be much higher than that of cyclobutadiene, while the HOMO levels will be similar for the two π systems. Therefore, the back-donation from the CoCp to SiCb LUMO will be less effective than that from the CoCp to Cb LUMO.

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