Synthesis and Properties of η^6-Silabenzene−M(CO)$_3$ Complexes (M = Cr, Mo)

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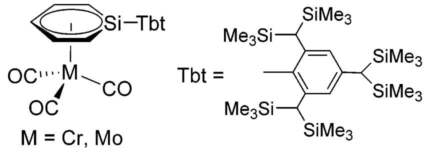
Received March 10, 2005

Synthesis of the first neutral η^6-silabenzene complexes [M(η^6-C_5H_5SiTbt)(CO)$_3$] (M = Cr (**2**), Mo (**3**); Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) was achieved by the ligand exchange reactions of [M(CH_3CN)$_3$(CO)$_3$] (M = Cr, Mo) with the kinetically stabilized silabenzene **1**. X-ray crystallographic analysis of **2** revealed that the η^6-coordinated silabenzene rings of the complexes have almost planar geometries with delocalized π-electron structures. The structures of η^6-silabenzene complexes **2** and **3** were fully characterized by NMR, UV/vis, and IR spectroscopic analysis. All the ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts of the SiC_5H_5 rings of **2** and **3** were shifted to upper field relative to those for silabenzene **1**, due to the π-coordination of the silabenzene ring to the metal center. The carbonyl stretching frequencies of **2** and **3** were observed in a region of lower wavenumber as compared to those of the corresponding group 6 metal complexes of benzene. In the UV/vis spectra of **2** and **3**, the absorption maxima were slightly red-shifted compared to those for the corresponding benzene complexes. The formation of η^6-silabenzene complexes **2** and **3** is very important from the viewpoints of the novel chemical reactivity of silaaromatics. Silabenzene complexes **2** and **3** were thermally stable under an inert atmosphere but air and moisture sensitive. These compounds underwent ready addition reactions with water exclusively at their 1,2-positions to give the corresponding hydroxysilane **8a**. The high regioselectivity observed for the addition reactions to **2** and **3** is in a sharp contrast to the competitive 1,2- and 1,4-addition reactions of free silabenzene **1** with water.

Introduction

Silaaromatic compounds have been of great interest as heavier element analogues of aromatic compounds. However, such species have been elusive until recently, despite the theoretical predictions suggesting their significant aromatic character.[1] Meanwhile, we have succeeded in the synthesis of a series of stable silaaromatic species, such as silabenzene, 1- and 2-silanaphthalenes, and 9-silaanthracene, by taking advantage of kinetic stabilization using an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt group; Chart 1).[2,3] As judged by the results of spectroscopic analysis, we revealed that the silaaromatic compounds possess fully delocalized π-electron ring systems.

Chart 1



On the other hand, complexation with transition metals is one of the most popular reactions of aromatic compounds,[4] and it may be a useful method for the thermodynamic stabilization of reactive silaaromatic compounds. Märkl and co-workers have reported the observation of an Fe complex of silabenzene, [Fe{4-Cy-(C_5H_4SiMe)}]$^{\bullet+}$ (Cy = cyclohexyl), in the mass spectrum.[5] Tilley and co-workers succeeded in the synthesis of transition-metal complexes with a η^5-coordinated

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10.1021/om0501778 CCC: $30.25

silolyl anion, which have the conjugated six-π-electron type ligand.[6] Recently, they reported the characterization of the first cationic silabenzene−Ru complex, $[Ru\{C_5H_5Si(t\text{-}Bu)\}Cp^*][BH(C_6F_5)_3]$ ($Cp^* = C_5Me_5$),[7] in which the bonding of the silabenzene moiety could be described as an η^5:η^1 interaction with limited delocalization of the silabenzene π-electrons.

We have already succeeded in the synthesis of the first neutral η^6-germabenzene−group 6 transition metal complexes by the ligand exchange reactions of $[M(CH_3CN)_3(CO)_3]$ (M = Cr, Mo, W) with the kinetically stabilized germabenzene $TbtGeC_5H_5$.[8,9] These experimental results are of great importance as a new finding on the chemical reactivity of the germaaromatic compound. As an extension of our chemistry on metallaaromatic species, we became interested in the synthesis of transition-metal complexes of silaaromatic compounds. We describe here the synthesis and properties of the first neutral η^6-silabenzene complexes coordinated with a group 6 metal center having three carbonyl ligands.

Experimental Section

All manipulations were performed under an argon atmosphere unless otherwise noted. THF, hexane, and benzene were dried over a K mirror and distilled by trap-to-trap distillation. The ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL AL-300 spectrometer using $CHCl_3$ (7.25 ppm) or C_6D_5H (7.15 ppm) for ^1H NMR and $CDCl_3$ (77.0 ppm) or C_6D_6 (128.0 ppm) for ^{13}C NMR as an internal standard. The multiplicity of signals in ^{13}C NMR spectra was determined by the DEPT technique. The ^{29}Si NMR (59 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL AL-300 spectrometer using tetramethylsilane as an external standard. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 instrument (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent $CHCl_3$). Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. The electronic spectra were recorded on a JASCO V-570 instrument. IR spectra were measured at room temperature on a JASCO FT/IR-460 plus spectrometer. Melting points were measured by a Yanaco Micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Silabenzene **1**[2,10] and $[M(CH_3CN)_3(CO)_3]$ (M = Cr, Mo)[11] were prepared according to the reported procedure.

Computational Details. Geometry optimization and GIAO calculations for **4** and **5** were carried out using the Gaussian 98 program.[12] Geometries were optimized with density functional theory at the B3LYP level. 6-31G(d) for Si, C, H, and O, and LANL2DZ for Cr and Mo were used as basis sets. GIAO calculations were operated at B3LYP/6-311G(d) for C, H, and O, 6-311G(3d) for Si, TVZ (17s10p6d)[6s3p3d] for Cr, and TVZ (19s14p9d)[8s6p5d] for Mo levels.[13]

Synthesis of $[Cr(\eta^6\text{-}C_5H_5SiTbt)(CO)_3]$ (2). Silabenzene **1** (70.8 mg, 0.109 mmol) and $[Cr(CH_3CN)_3(CO)_3]$ (32.3 mg, 0.125 mmol) were dissolved in benzene (2 mL). After the mixture was stirred for 2 days at room temperature, the solvent was removed in vacuo. The residue was recrystallized from hexane at −40 °C to give **2** (42.2 mg, 50%). **2**: yellow powder, mp 238 °C dec; ^1H NMR (300 MHz, C_6D_6) δ 0.12 (s, 18H), 0.18 (s, 18H), 0.20 (s, 18H), 1.49 (s, 1H), 2.75 (br s, 1H), 2.93 (br s, 1H), 3.23 (d, J = 10.8 Hz, 2H), 4.83−4.89 (m, 3H), 6.61 (br s, 1H), 6.69 (br s, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 0.66 (q), 0.77 (q), 0.97 (q), 31.83 (d), 35.35 (d), 35.75 (d), 74.05 (d), 85.03 (d), 101.59 (d), 116.74 (s), 122.16 (d), 127.14 (d), 149.52 (s), 154.13 (s), 154.50 (s), 234.50 (s); ^{29}Si NMR (59 MHz, C_6D_6) δ 2.39, 2.81, 52.62; IR (Nujol) 1958, 1897, 1863 cm^{-1} (C≡O stretching); UV/vis (hexane) λ_{max} 228 ($\epsilon = 5.9 \times 10^4$), 306 ($8.7 \times 10^3$), 340 nm ($7.3 \times 10^3$); high-resolution FAB-MS m/z calcd for $C_{35}H_{65}O_3CrSi_7$ ($[M + H]^+$) 781.2724, found 781.2759. Anal. Calcd for $C_{35}H_{64}O_3CrSi_7$: C, 53.79; H, 8.25. Found: C, 53.62; H, 8.15.

Synthesis of $[Mo(\eta^6\text{-}C_5H_5SiTbt)(CO)_3]$ (3). The Mo complex **3** was synthesized by the same route as for **2** in 58% yield (51.5 mg) from silabenzene **1** (72.4 mg, 0.112 mmol) and $[Mo(CH_3CN)_3(CO)_3]$ (34.3 mg, 0.112 mmol). **3**: yellow powder, mp 240 °C dec; ^1H NMR (300 MHz, C_6D_6) δ 0.08 (s, 18H), 0.15 (s, 18H), 0.19 (s, 18H), 1.48 (s, 1H), 2.67 (br s, 1H), 2.90 (br s, 1H), 3.34 (d, J = 12 Hz, 2H), 4.77 (t, J = 7.3 Hz, 1H), 5.09 (dd, J = 12, 7.3 Hz, 2H), 6.59 (s, 1H), 6.66 (br s, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 0.63 (q), 0.79 (q), 0.94 (q), 31.77 (d), 35.85 (d), 35.97 (d), 72.08 (d), 83.06 (d), 104.16 (d), 117.22 (s), 122.11 (d), 127.19 (d), 149.39 (s), 154.14 (s), 154.18 (s), 221.48 (s); ^{29}Si NMR (59 MHz, C_6D_6) δ 2.39, 2.89, 52.47; IR (Nujol) 1966, 1898, 1870 cm^{-1} (C≡O stretching); UV/vis (hexane) λ_{max} 230 ($\epsilon = 6.1 \times 10^4$), 306 ($1.0 \times 10^4$), 339 nm ($1.5 \times 10^4$); high-resolution FAB-MS m/z calcd for $C_{35}H_{64}O_3{}^{98}MoSi_7$ ($[M]^+$) 826.2294, found 826.2266. Although we have performed the elemental analysis of **3** several times, the results have not been commensurate with the calculated values for **3**, due to its highly moisture sensitive properties.

Reaction of Silabenzene 1 with H_2O. In a glovebox filled with argon, the silabenzene **1** (50.7 mg, 0.0782 mmol) was dissolved in THF (2 mL), and then H_2O (0.5 mL) was added to the solution. The mixture was stirred for 2 h, and the solvent was evaporated. Separation of the mixture by PTLC (THF: hexane = 1:10) and GPLC ($CHCl_3$) afforded 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,4-diene-1-ol (**6a**; 15.6 mg, 30%) and 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,5-diene-1-ol (**6b**; 28.1 mg, 54%). **6a**: colorless powder, mp 182−185 °C; ^1H NMR (300 MHz, $CDCl_3$) δ −0.01 (s, 18H), 0.03 (s, 36H), 1.30 (s, 1H), 1.65 (s, 1H), 1.82−1.84 (m, 2H), 2.47 (s, 2H), 5.95−6.00 (m, 1H), 6.07−6.14 (m, 1H), 6.23 (br s, 1H), 6.25 (d, J = 14 Hz, 1H), 6.35 (br s, 1H), 6.76 (dd, J = 14, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.65 (q), 0.71 (q). 0.99 (q), 1.13 (q), 19.87 (t), 27.94 (d), 28.20 (d), 30.34 (d), 122.03 (d), 125.47 (d), 126.82 (s), 127.03 (d), 129.89 (d), 130.47 (d), 140.08 (d), 144.74 (s), 151.31 (s), 151.71

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(s); ^{29}Si NMR (59 MHz, C$_6$D$_6$) δ −12.48, 1.61, 1.75, 2.15. Anal. Calcd for C$_{32}$H$_{66}$OSi$_7$: C, 57.93; H, 10.03. Found: C, 57.82; H, 10.04. **6b**: colorless powder, mp 174−176 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.00 (s, 18H), 0.02 (s, 27H), 0.03 (s, 9H), 1.29 (s, 1H), 1.65 (s, 1H, Si−O*H*), 2.46 (br s, 1H), 2.57 (br s, 1H), 2.87−2.98 (m, 1H), 3.01−3.13 (m, 1H), 6.23 (br s, 1H), 6.24 (dd, *J* = 15, 2.1 Hz, 2H), 6.34 (br s, 1H), 6.77 (dd, *J* = 15, 3.6 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.64 (q), 0.72 (q), 0.98 (q), 27.54 (d), 27.76 (d), 30.32 (d), 33.49 (t), 122.04 (d), 126.10 (s), 127.04 (d), 129.73 (d), 144.63 (s), 133.80 (d) 151.56 (s), 151.95 (s); ^{29}Si NMR (59 MHz, C$_6$D$_6$) δ −30.99, 1.73, 1.76. Anal. Calcd for C$_{32}$H$_{66}$OSi$_7$: C, 57.93; H, 10.03. Found: C, 57.96; H, 10.13.

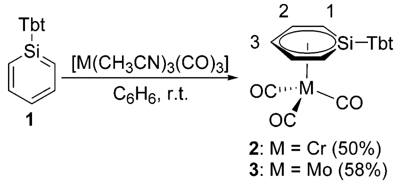
Reaction of Cr Complex 2 with H$_2$O. To a solution of **2** (24.9 mg, 0.0319 mmol) in C$_6$H$_6$ (1 mL) was added 0.5 mL of water at room temperature, and the solution was stirred for 1 h. After the solvent was removed, purification of the residue by PTLC afforded **6a** (15.2 mg, 72%).

Reaction of Mo Complex 3 with H$_2$O. To a solution of **3** (22.5 mg, 0.0272 mmol) in C$_6$H$_6$ (1 mL) was added 1.0 mL of water at room temperature, and the solution was stirred for 1 h. After the solvent was removed, purification of the residue by PTLC afforded **6a** (11.7 mg, 65%).

Reaction of Silabenzene 1 with Phenylacetylene. In a glovebox filled with argon, silabenzene **1** (32.1 mg, 0.0495 mmol) was dissolved in C$_6$D$_6$ (0.6 mL) and the solution was put into a 5 mm i.d. NMR tube. After phenylacetylene (0.5 mL, distilled from CaH$_2$ under Ar prior to use) was added to the solution, the NMR tube was degassed and sealed. The NMR signals of silabenzene **1** disappeared after the mixture stood for 2 days. Then, the tube was opened and the solvent was evaporated. Purification of the residue by PTLC afforded 3-phenyl-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silabicyclo[2.2.2]octa-2,5,7-triene (**7a**; 20.6 mg, 55%) and 1-(phenylethynyl)-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,4-diene (**7b**; 6.2 mg, 17%). **7a**: colorless powder, mp 151−153.0 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.05 (s, 36H), 0.08 (s, 18H), 1.38 (s.1H), 2.35 (br s, 2H), 5.30 (m, 1H), 6.36 (br s, 1H), 6.49 (br s, 1H), 6.71 (d, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 10.6 Hz, 2H), 7.15−7.43 (m, 5H), 7.49 (dd, *J* = 10.6, 6.9 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.77 (q), 1.03 (q), 28.97 (d), 29.13 (d), 30.62 (d), 51.76 (d), 121.55 (s), 121.95 (d), 124.89 (d), 126.86 (d), 127.29 (d), 128.39 (d), 131.49 (d), 137.32 (d), 141.96 (s), 145.50 (s), 151.07 (d), 152.44 (s), 152.79 (s), 162.56 (s); ^{29}Si NMR (59 MHz, C$_6$D$_6$) δ 1.49, 1.87, 2.06. Anal. Calcd for C$_{40}$H$_{70}$Si$_7$: C, 64.26; H, 9.44. Found: C, 63.99; H, 9.55. **7b**: colorless powder, mp 59−61 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.01 (s, 9H), 0.03 (s, 9H), 0.04 (s, 18H), 0.05 (s, 9H), 0.06 (s, 9H), 1.30 (s, 1H), 1.91 (ddd, *J* = 19.2, 5.7, 1.5 Hz, 1H), 2.09 (ddd, *J* = 19.2, 4.5, 2.1 Hz, 1H), 2.65 (br s, 1H), 2.67 (br s, 1H), 5.91−5.96 (m, 1H), 6.00−6.05 (m, 1H), 6.247 (br s, 1H), 6.252 (d, *J* = 13.8 Hz, 1H), 6.36 (br s, 1H), 6.67 (dd, *J* = 13.8, 6.0 Hz, 1H), 7.26−7.28 (m, 3H), 7.41 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.76 (q), 0.77 (q), 0.83 (q), 1.13 (q), 1.19 (q), 17.31 (t), 27.96 (d), 28.03 (d), 30.40 (d), 95.52 (s), 109.33 (s), 122.17 (d), 123.62 (s), 123.97 (s), 125.93 (d), 127.22 (d), 127.55 (d), 128.11 (d), 128.35 (d), 128.43 (d), 131.77 (d), 138.69 (d), 144.87 (s), 152.03 (s), 152.38 (s); ^{29}Si NMR (59 MHz, C$_6$D$_6$) δ −47.05, 1.80, 1.92, 2.29; high-resolution FAB-MS *m/z* calcd for C$_{40}$H$_{70}$Si$_7$ ([M]$^+$) 746.3862, found 746.3871.

Reaction of Silabenzene Complexes 2 with Phenylacetylene. In a glovebox filled with argon, the silabenzene Cr complex **2** (10.0 mg, 0.0128 mmol) was dissolved in C$_6$D$_6$ (0.6 mL) and the solution was put into a 5 mm i.d. NMR tube. After phenylacetylene (0.5 mL, distilled from CaH$_2$ under Ar prior to use) was added to the solution, the NMR tube was degassed and sealed. No reaction occurred even on standing for 2 days.

Scheme 1. Synthesis of η^6-Silabenzene Complexes



X-ray Data Collection. Single crystals of **2**·0.5C$_6$H$_6$ were grown at room temperature from the corresponding saturated solution in C$_6$H$_6$. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å). The structure of **2**·0.5C$_6$H$_6$ was solved by direct methods (SHELXS-97)[14] and refined by full-matrix least-squares methods on F^2 for all reflections (SHELXL-97).[14] The occupancies of the disordered trimethylsilyl group at the para position of the Tbt group were refined so that the sum of them is 1 (0.53:0.47). All hydrogen atoms were placed using AFIX instructions, while all the non-hydrogen atoms were refined anisotropically. Crystallographic data for **2** are given in Table 2.

Results and Discussion

The ligand exchange reactions of silabenzene **1** with [M(CH$_3$CN)$_3$(CO)$_3$] (M = Cr, Mo) at room temperature in benzene resulted in the formation of the corresponding neutral η^6-silabenzene−transition metal tricarbonyl complexes, [M(η^6-C$_5$H$_5$SiTbt)(CO)$_3$] (M = Cr (**2**) Mo (**3**); Scheme 1). These complexes were isolated as stable yellow crystals by recrystallization from hexane in the yields of 50% (for **2**) and 58% (for **3**), respectively. Unfortunately, the reaction of silabenzene **1** with [W(CH$_3$CN)$_3$(CO)$_3$] afforded a complicated mixture.

Although the complexes **2** and **3** were highly air and moisturesensitive, they are thermally stable even at 120 °C in solution under an inert atmosphere. The structures of **2** and **3** were confirmed by their spectroscopic analyses, and the η^6-coordinated geometries were determined by X-ray crystallographic analysis (Figure 1).[15] In the structure of the silabenzene ring of **2**, the silicon atom adopts a nearly planar geometry, where the sum of the bond angles around the central Si atom and the sum of the interior bond angles of the silabenzene ring are 359.8 and 719.8°, respectively. The bond lengths of the silabenzene ring of **2** (1.781(4), 1.797(4) Å for Si−C and 1.396(6)−1.414(5) Å for C−C) were longer than those of the free silabenzene **1** (1.770(4), 1.765(4) Å for Si−C and 1.381(6)−1.399(6) Å for C−C).[2e] The Si−Cr distance (2.4864(13) Å) of **2** was somewhat longer than that of the base-stabilized silylene complex HMPA(*t*-BuO)$_2$SiCr(CO)$_5$ (2.431 Å).[16,17] The distance between the center of the silabenzene ring of **2** and the chromium atom was 1.692(2) Å, which was longer than those reported for some arene complexes.[18] The dihedral angle between the silabenzene core and the benzene ring of the Tbt group was 37.8(3)°. A projection of three carbonyl groups and the chromium atom onto the silabenzene ring revealed deviations from idealized

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[14] Sheldrick, G. M. University of Göttingen, Göttingen, Germany, 1997.

[15] The molecular geometry of **3** was also determined by X-ray crystallographic analysis. Although the crystal data of **3** were rather poor, the geometry of **3** was almost analogous to that of **2**.

[16] Zybill, C.; Müller, G. *Organometallics* **1988**, *7*, 1368.

[17] For reviews on complexes containing bonds between silicon atoms and transition metals, see: Corey, J. Y.; Braddock-Wiking, J. *Chem. Rev.* **1999**, *99*, 175.

[18] Hunter, A. D.; Shilliday, L.; Furey, W. S.; Zaworotko, M. J. *Organometallics* **1992**, *11*, 1550.

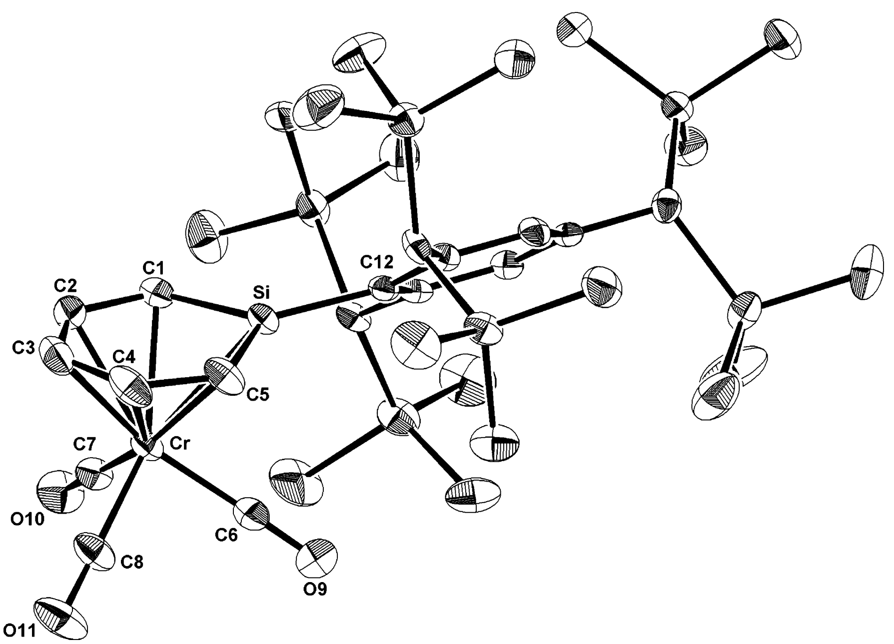

Figure 1. ORTEP drawing of [Cr(η^6-C_5H_5SiTbt)$(CO)_3$] (**2**; 50% probability ellipsoids). The hydrogen atoms and the fragment of solvated benzene were omitted for clarity. Selected bond lengths (Å) and angles (deg): Si−C1 = 1.781(4), C1−C2 = 1.414(5), C2−C3 = 1.396(6), C3−C4 = 1.404(6), C4−C5 = 1.397(6), C5−Si = 1.797(4), Si−Cr = 2.4864(13), Cr−C6 = 1.839(4), Cr−C7 = 1.841(4), Cr−C8 = 1.840(4), C6−O9 = 1.156(5), C7−O10 = 1.157(4), C8−O11 = 1.158(4); C1−Si−C5 = 102.56(18), C5−Si−C12 = 126.89(17), C1−Si−C12 = 130.36(16).

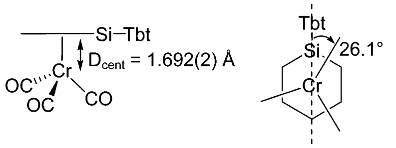

Figure 2. Distance (D_{cent}) between the silabenzene ring and the Cr center (left) and the projection of $Cr(CO)_3$ onto the silabenzene ring plane (right).

geometry, and the angle of Si−Cr−C is about 26.1° for **2** (Figure 2). Since the theoretically optimized structure of silabenzene−Cr complex **4**, [Cr(η^6-C_5H_5SiH)$(CO)_3$], showed completely syn-eclipsed geometry,[12] the staggered structure of **2** was most likely explained by the steric repulsion between the Tbt group and the three CO ligands.[4,19,20]

Arene tricarbonyl complexes generally showed upfield-shifted chemical shifts in the NMR spectra compared with those for the free aromatic compounds, due to the reduction of π-electron density in the arene ring moiety.[21] In solution, the silabenzene complexes **2** and **3** were found to have a C_s symmetry with a mirror plane vertical to the silabenzene rings containing the Si−C3 axis, as judged by the NMR spectra.[20] The protons on the silabenzene ring of **2** resonated at 3.23 (H1) and 4.83−4.89 ppm (H2 and H3), and those of **3** were observed at 3.34 (H1), 4.77 (H3), and 5.09 ppm (H2). The ^{13}C NMR spectra showed peaks at 74.05 (C1), 101.59 (C2), and 85.03 ppm (C3) for **2** and at 72.08 (C1), 104.16 (C2), and 83.06 ppm (C3) for **3** (Table 1). All of the ^1H and ^{13}C NMR signals for **2** and **3** were clearly shifted to upper field relative to those for silabenzene **1** (6.71, 7.11, and 8.00 ppm for ^1H NMR and 116.1, 122.2, and 143.4 ppm for ^{13}C NMR, respectively).[2e] The ^{13}C NMR signals of carbonyl carbons were assignable to 234.50 ppm for **2** and 221.48 ppm for **3**. These signals appeared in a region quite similar to those for [M(η^6-mesitylene)$(CO)_3$] (M = Cr (δ 235.1 ppm), Mo (δ 223.7 ppm)).

Tilley and co-workers reported that the interaction between the silabenzene moiety and the ruthenium center in [Ru{C_5H_5Si(t-Bu)}Cp*][BH$(C_6F_5)_3$] may be described as an η^5:η^1 interaction with limited delocalization in the silabenzene ligand. The ^{13}C NMR spectra showed the C1 atom for the Ru complex to be at higher field at 39.8 ppm than C2 (92.5 ppm) and C3 (83.3 ppm).[7] Taking into account the differences in ^{13}C NMR chemical shifts between our complexes (**2** and **3**) and Tilley's Ru complex, it can be considered that the bonding between the central metals (Cr, Mo) and the silabenzene rings for **2** and **3** can be described as fully delocalized η^6 coordination.

Notably, the ^{29}Si NMR resonances in the silabenzene rings of **2** (δ 52.6) and **3** (δ 52.5) lay in an upfield region as compared with that of **1** (δ 93.6). These upfield shifts observed for **2** and **3** strongly suggested the π-coordination of the silabenzene ring to the Cr and Mo center, since the ^{29}Si NMR chemical shifts of **2** and **3** were comparable to those of the Hf (δ 49.7) and Zr (δ 48.9) complexes of the η^5-silolyl anion.[6] In addition, ^{29}Si NMR

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(19) It was known that disubstituted π-complexes normally adopted a fully staggered structure due to the steric repulsion. See: (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) Heppert, J. A.; Morgenstern, M. A.; Scherubel, D. M.; Takusagawa, F.; Shaker, M. R. *Organometallics* **1988**, *7*, 1715.

(20) We measured the VT-NMR spectra of the toluene-d_8 solution of the complex **2** in the range of −100 to +25 °C. As a result, neither obvious changes nor peak separations were observed even at −100 °C, though the ortho protons of the silabenzene ring slightly shifted to the upper field region (δ 4.88 (+25 °C), δ 4.63 (−100 °C)). Although the reason for the slight upper-field shift is not clear at present, it was indicated that the rotation barrier of the $Cr(CO)_3$ unit should be quite low. We are grateful to a reviewer for a kind comment concerning this matter.

(21) (a) Mcfarlane, W.; Grim, S. O. *J. Organomet. Chem.* **1966**, *5*, 147. (b) Emanel, R. V.; Randall, E. W. *J. Chem. Soc. A* **1969**, 3002. (c) Mann, B. E. *J. Chem. Soc., Chem. Commun.* **1971**, 976. (d) Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1973**, 2012.

Table 1. Observed and Calculated NMR Chemical Shifts for Silabenzene and Silabenzene Complexes[a]

compd	Si	C1	C2	C3
Observed				
silabenzene **1**[b]	93.6	122.2	143.6	116.1
[Cr(η^6-C_5H_5SiTbt)$(CO)_3$] (**2**)	52.6	74.1	101.6	85.0
[Mo(η^6-C_5H_5SiTbt)$(CO)_3$] (**3**)	52.5	72.1	104.2	83.1
[Ru{C_5H_5Si(*t*-Bu)}Cp*][BH$(C_6F_5)_3$][c]	−23.1	39.8	92.5	83.3
Calculated				
[Cr(η^6-C_5H_5SiH)$(CO)_3$] (**4**)[d]	52.0	74.3	115.7	84.8
[Mo(η^6-C_5H_5SiH)$(CO)_3$] (**5**)[d]	46.2	76.5	118.1	85.8

[a] C1 is the carbon ortho to silicon in a ring, C2 is in the meta position, and C3 is para to silicon. [b] See ref 6e. [c] See ref 5. [d] B3LYP/6-311G(d) (C, H, O), 6-311G(3d) (Si), TVZ (17s10p6d)-[6s3p3d] (Cr), and TVZ (19s14p9d)[8s6p5d] (Mo)//B3LYP/6-31G(d) (C, H, O, Si) and LANL2DZ (Cr, Mo).[13]

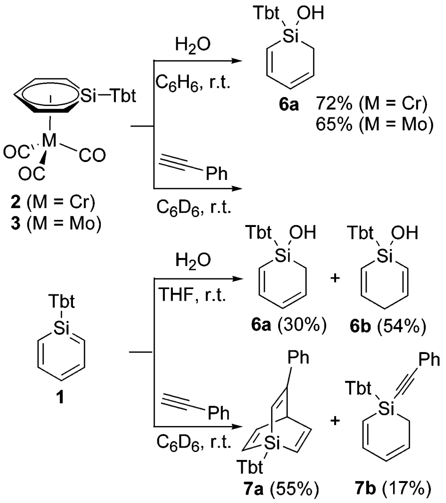
Table 2. Crystallographic Data for 2

formula	$C_{35}H_{64}O_3CrSi_7 \cdot 0.5C_6H_6$
formula wt	820.55
cryst size (mm)	0.20 × 0.20 × 0.20
cryst syst, space group	monoclinic, $P2_1/n$ (No. 14)
a (Å)	12.635(5)
b (Å)	32.737(13)
c (Å)	12.691(5)
β (deg)	116.605(4)
V (Å^3)	4693.3(3)
Z	4
D_{calcd} (g cm^{-3})	1.161
θ range (deg)	1.89−25.00
μ (mm^{-1})	0.454
F(000)	1764
no. of rflns measd	40 504
no. of unique rflns	8249 ($R_{int} = 0.051$)
no. of params	620
R1 ($I > 2\sigma(I)$)	0.057
wR2 (all data)	0.149
largest diff peak and hole (e Å^{-3})	0.405 and −0.509
goodness of fit	1.24

chemical shifts of **2** and **3** were reasonably supported by the comparison of the experimentally observed chemical shifts with those calculated for the model molecules, hydrogen-substituted silabenzene complexes **4** (Cr) and **5** (Mo) (Table 1).[13] The J_{SiC} coupling constants of η^6-silabenzene complexes **2** (67 Hz) and **3** (65 Hz) were smaller than that of silabenzene **1** (83 Hz). The results of the NMR study for **2** and **3** imply a decrease of the π-bonding characters in the silabenzene ring upon coordination with the transition-metal unit.

Comparisons of the IR spectra between the complexes of silabenzene and benzene can explain the features of silabenzene **1** as an η^6 ligand. The IR spectrum for **2** showed characteristic C≡O stretching frequencies at 1958, 1897, and 1863 cm^{-1}, while that for **3** showed similar frequencies at 1966, 1898, and 1870 cm^{-1}. In both cases, the carbonyl stretching frequencies were observed at a region of lower wavenumber as compared to those of the corresponding benzene complexes [M(η^6-C_6H_6)$(CO)_3$] (M = Cr, 1982, 1915 cm^{-1}; M = Mo, 1983, 1913 cm^{-1}).[22] Similar spectral features were observed for $\nu_{C\equiv O}$ stretching of the Tbt-substituted η^6-germabenzene complexes [M(η^6-C_5H_5GeTbt)$(CO)_3$].[9] In the case of the heterobenzene−Mo complexes [Mo(EC_5H_5)$(CO)_3$] (E = As, Sb), $\nu_{C\equiv O}$ stretchings were observed at 1996, 1926 cm^{-1} (E = As) and 1990, 1919 cm^{-1} (E = Sb).[23] The IR spectra for **2** and **3** demonstrate that silabenzene might be a weaker π-acceptor than benzene and heterobenzenes for π-back-bonding from the Cr and Mo metal centers.

Scheme 2. Comparisons of Reactivities of Silabenzene Complexes (2 and 3) with Those of Silabenzene 1



The UV/vis spectra of **2** and **3** in hexane showed three absorption maxima (**2**, λ_{max} 228 (ϵ, 5.9 × 10^4), 306 (8.7 × 10^3), 340 nm (7.3 × 10^3); **3**, λ_{max} 230 (ϵ, 6.1 × 10^4), 306 (1.0 × 10^4), 339 nm (1.5 × 10^4)). These values are slightly red-shifted compared to those for the corresponding benzene complexes: 217 (ϵ, 23 700), 263 (6720), and 315 nm (9450) for [Cr(η^6-C_6H_6)$(CO)_3$]; 220 (ϵ, 17 900), 240 (10 560), 282−287 (3980), and 323 nm (18 400) for [Mo(η^6-C_6H_6)$(CO)_3$].[24] The prominent bands of **2** and **3** at around 340 nm can be assigned to the metal-to-ligand charge transfer (MLCT) bands, in accordance with the calculated and experimental electronic spectra of [Cr(η^6-C_6H_6)$(CO)_3$].[25]

The reactivity of η^6-silabenzene complexes was different from that of the free silabenzene **1** previously reported.[2d] Silabenzene complexes **2** and **3** reacted with H_2O at only their 1,2-positions to give the corresponding hydrolysis product **6a** in 72 and 65% yields, respectively (Scheme 2). The high regioselectivity observed for the addition of water to **2** is in sharp contrast to the competitive 1,2- (**6a**, 30%) and 1,4-addition reactions (**6b**, 54%) of water with the free silabenzene **1**.[26] Although silabenzene **1** reacted with phenylacetylene to afford the two isomers **7a** (55%) and **7b** (17%), the silabenzene complex **2** did not react with phenylacetylene under the same conditions.

In summation, the novel η^6-silabenzene complexes **2** and **3** were successfully synthesized by the ligand exchange reactions of silabenzene **1** with [M$(CH_3CN)_3$-$(CO)_3$] (M = Cr, Mo). The structures of η^6-silabenzene complexes were experimentally determined by spectro-

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(22) (a) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154. (b) Nesmeyanov, A. N.; Krivykh, V. V.; Kaganovich, V. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1975**, *102*, 185.

(23) (a) Ashe, A. J., III; Colburn, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 8099. (b) Elschenbroich, C.; Kroker, J.; Nowotny, M.; Behrendt, A.; Metz, B.; Harms, K. *Organometallics* **1999**, *18*, 1495.

(24) Evdokimova, M. G.; Yavorskii, B. M.; Trembouler, V. N.; Baranetskaya, N. K.; Krivyk, V. U.; Zaslavskaya, G. B. *Dokl. Phys. Chem.* **1978**, *19*, 154.

(25) (a) Carroll, D. G.; McGlynn, S. P. *Inorg. Chem.* **1968**, *7*, 1285. (b) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10338.

scopic data and X-ray crystallographic analysis. These results are the first examples showing the feature of the silaaromatics undergoing complexation with a transition metal in the η^6 form. Further investigations on the synthesis and properties of the novel transition-metal complexes of silaaromatic compounds are currently under way.

Acknowledgment. This work was partially supported by Grants-in-Aid for COE Research on Elements Science (No. 12CE2005), Scientific Research on Priority Areas (No. 14078213), Scientific Research A (No. 1424064), and the 21st Century COE Program on Kyoto University Alliance for Chemistry (No. 14212101) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We thank Central Glass Co. Ltd. for a generous gift of tetrafluorosilane.

Supporting Information Available: X-ray structural data of **2**, as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) In the hydrolysis of the complex **2**, the selective formation of **6a** may be due to the Cr-catalyzed conversion process of **6b** to **6a**. Therefore, we have performed the reaction of a mixture of the silabenzene **1** and the Cr complex **2** with H_2O. To a benzene solution (2.5 mL) of a 1:1 mixture of silabenzene **1** (9.3 mg, 0.014 mmol) and the Cr complex **2** (11.5 mg, 0.014 mmol) was added H_2O (0.4 mL, 22 mmol). After the mixture was stirred for 2 h and the solvents were evaporated, the reaction mixture was separated by PTLC (THF:hexane = 1:40) to afford **6a** (10.0 mg, 54%) and **6b** (7.0 mg, 39%). Therefore, it can be considered that the hydrolysis of the complex **2** selectively afforded only the 1,2-adduct **6a** and that this did not occur via the metal-catalytic conversion process of **6b** to **6a**. We are grateful to a reviewer for fruitful discussions on this matter.