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Novel silacyclohexadienyl chromium and iron complexes bearing a bulky substituent on the central silicon atom*

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Abstract: Novel hydrido(silacyclohexadienyl)chromium complexes bearing a bulky substituent, Tbt (2,4,6-tris[bis(trimethylsilyl)methyl]phenyl), were synthesized using formal insertion reactions of Cr(0) into C–H or Si–H bond. When the reactions of 1-silacyclohexa-2,4-dienes bearing a hydroxy or chloro group on the silicon atom with $[Cr(CH_3CN)_3(CO)_3]$ were performed, the corresponding hydrido(1-silacyclohexa-2,4-dienyl) complexes were obtained as the sole product. A similar reaction of a hydrosilane having a similar skeleton with $[Cr(CH_3CN)_3(CO)_3]$ gave an unprecedented type of silacyclohexadienyl complex, hydrido(1-silacyclohexa-1,3-dienyl)chromium bearing a three-center bonding interaction among the silicon, hydrogen, and chromium atoms. These are the first syntheses of silacyclohexadienyl complexes by the formal insertion reaction toward the corresponding silacyclohexadienes. Furthermore, the isolation of the silacyclohexadienyl anion was achieved; it was applied to synthesis of the corresponding sandwich-type iron complex. Structures of the newly obtained complexes were revealed based on their NMR and IR spectroscopic data and X-ray diffraction study.

Keywords: bulky substituents; chromium; hydrido complexes; iron; sandwich complexes; silacyclohexadienyl ligands.

INTRODUCTION

Monoanionic tridentate ligands such as cyclopentadienyl are widely used as ancillary ligands in transition-metal catalysts [1]. Similarly, η^5-cyclohexadienyl ligands are monoanionic and tridentate; their complexes are obtained usually by nucleophilic addition toward arene complexes [2]. For example, the reactions of $[Cr(\eta^6\text{-benzene})(CO)_3]$ with alkyllithiums afford the corresponding anionic complexes; $Li[(\eta^5\text{-cyclohexadienyl})Cr(CO)_3]$ [3]. Although silacyclohexadienyl complexes having similar tridentate ligands are intriguing for their steric and electronic character, few reports describe their syntheses because of the limited synthetic methods [4]. They are synthesized only through a deprotonation reaction of the corresponding silacyclohexadienes followed by a simple metathesis reaction with MX_n (M = transition metal, X = halogen or alkoxy). Nevertheless, we synthesized and isolated kinetically stabilized silaaromatic compounds and their group 6 transition-metal complexes by taking advantage of an extremely bulky protecting group; Tbt (2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) [5]. Recently,

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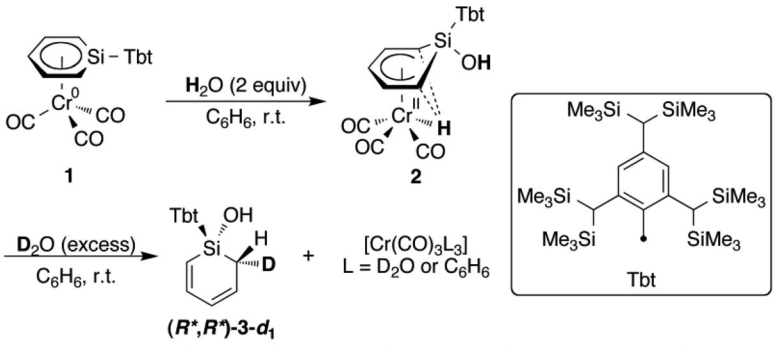
[(H)(η^5-silacyclohexadienyl)Cr(CO)$_3$] (**2**) was isolated as a key intermediate in the hydration reaction of [Cr(η^6-silabenzene)(CO)$_3$] (**1**) (Scheme 1) [6]. Herein, we report the syntheses and structures of novel chromium and iron complexes bearing a silacyclohexadienyl ligand. The complexes were obtained using the formal insertion reactions of Cr(0) to C–H or Si–H bond of some silacyclohexadienes and the complexation of the isolated silacyclohexadienyllithium with $FeCl_2$, respectively. Development of the new synthetic strategies for silacyclohexadienyl complexes enables us to elucidate their structural and electronic features in detail.



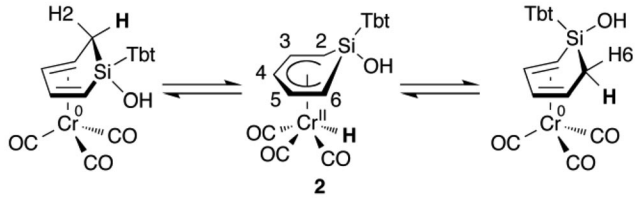
Scheme 1 Stereoselective and regioselective hydration of silabenzene complex **1**.

RESULTS AND DISCUSSION

Reactions of hydroxy- and chlorosilane with [Cr(CH$_3$CN)$_3$(CO)$_3$]

We previously reported that silacyclohexadienyl complex **2** exists as an equilibrated mixture in benzene, as depicted in Scheme 2 [6,7]. This equilibrium suggests that silacyclohexadienyl complex is obtainable using the reaction of silacyclohexadiene with Cr(0) complex having three replaceable ligands such as a solvent molecule. We subsequently investigated the reactions of several 1-silacyclohexa-2,4-dienes **3–5** with [Cr(CH$_3$CN)$_3$(CO)$_3$]. As expected, 1-silacyclohexa-2,4-dienyl complex **2**, which is the key intermediate for the hydration reaction of [Cr(1-Tbt-η^6-silabenzene)(CO)$_3$], was obtained using the treatment of silanol **3** with [Cr(CH$_3$CN)$_3$(CO)$_3$] (Scheme 3). Although the yield of **2** was low, only the isomer having Tbt group situated at the *exo* position toward the metal center was formed selectively, probably because of the steric repulsion between the bulky Tbt group with the Cr(CO)$_3$ unit. To our knowledge, only one report in the relevant literature describes the reaction of silacyclohexadiene with zerovalent group 6 transition-metal complex [8], in which the reaction of [M(CH$_3$CN)$_3$(CO)$_3$] (M = Mo, W) with 1,1-dialkyl-, 1-alkyl-1-aryl-, or 1-alkyl-1-chloro-1-silacyclohexa-2,4-diene afforded the bis(η^2,η^2-1-silacyclohexa-2,4-diene) complex. In our case, no generation of bis(silacyclohexadiene) complex was observed, probably because the extreme bulkiness of the Tbt group prevented the coordination of two silacyclohexadiene units toward the central chromium atom. A similar reaction of chlorosilane **4** gave the corresponding complex **6** (Scheme 3). The structure of **6** was determined based on its NMR and IR spectra together with results of elemental analysis and X-ray crystallographic study. In the ^{1}H NMR spectrum of **6** in benzene-d_6, the signals assignable to the Cr–H and the protons on the silacyclohexadienyl ring were observed, respectively, at –8.73 (t, Cr–H), 2.30 (dd, H2 and H6), 5.00 (dd, H3 and H5), and 5.28 (t, H4) ppm. Equivalent observation of H2 and H6 protons as well as H3 and H5 indicates the delocalization of π electrons in the dienyl unit. The H2 and H6 protons and Cr–H are mutually coupled (^2J = 9.0 Hz), showing that complex **6** would have agostic interaction resembling that of **2**, as described in Scheme 3. In the ^{13}C NMR spectrum of **6**, the signals of three carbons in the carbonyl ligands were observed equivalently at 230.4 ppm, suggesting the existence of rapid

rotation of $Cr(CO)_3$ unit around axis through Cr and centroid in the SiC_5 ring with agostic interaction. In the IR spectrum of **6**, the wavenumbers of the carbonyl stretchings (2002, 1929, and 1897 cm^{-1}) are higher than those observed for the related complex **2** bearing a hydroxyl group on the silicon atom (1991, 1910, and 1888 cm^{-1}) [6]. This result indicates that the electron-donating ability of the η^5-1-chloro-1-silacyclohexa-2,4-dienyl ligand is smaller than that of the η^5-1-hydroxy-1-silacyclohexa-2,4-dienyl ligand and that electronic properties of silacyclohexadienyl ligands were controllable by changing a substituent on the silicon atom. Crystals of **6** suitable for X-ray diffraction analysis were obtained by slow evaporation from its benzene solution. Although two independent molecules were found in the unit cell, their structures were mutually similar. The results of X-ray diffraction study of **6** are presented in Table 1 and Fig. 1.



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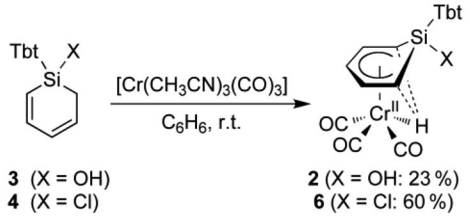
Scheme 2 Equilibrium of **2** in benzene.



Scheme 3 Reactions of silacyclohexadienes **3** and **4** with $[Cr(CH_3CN)_3(CO)_3]$.

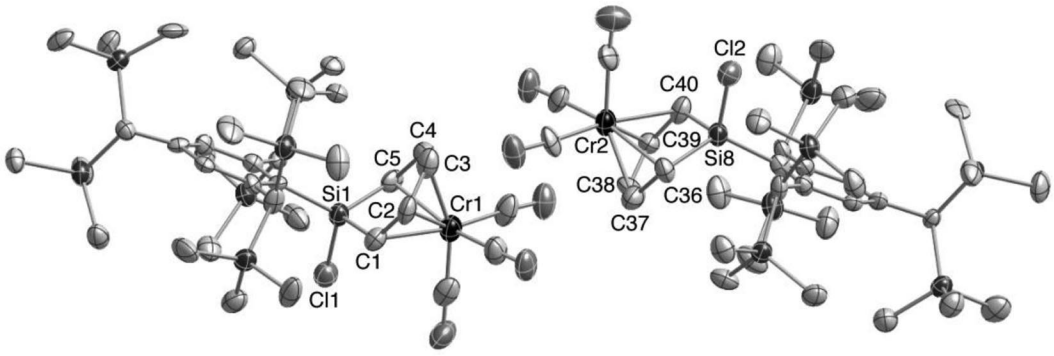


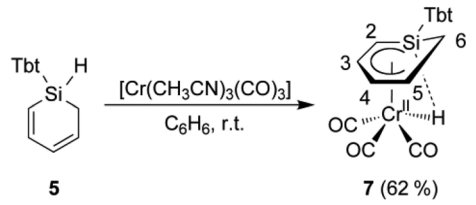
Fig. 1 Thermal ellipsoid plot of **6** (30 % probability). Two independent molecules found in the unit cell are shown. Hydrogen atoms are omitted for clarity. The hydrido ligand position was not determined. Selected bond lengths [Å]. Si1–C1 1.853(6), C1–C2 1.410(8), C2–C3 1.414(9), C3–C4 1.390(8), C4–C5 1.501(8), C5–Si1 1.879(5), C1–Cr1 2.272(6), C2–Cr1 2.162(6), C3–Cr1 2.187(6), C4–Cr1 2.178(6), C5–Cr1 2.306(5), Si8–C36 1.855(6), C36–C37 1.411(8), C37–C38 1.414(9), C38–C39 1.397(8), C39–C40 1.473(8), C40–Si8 1.866(5), C36–Cr2 2.293(5), C37–Cr2 2.164(6), C38–Cr2 2.179(6), C39–Cr2 2.159(6), and C40–Cr2 2.304(5).

Table 1 Crystal data and structure refinements for **6–9**.

	6	**7**	**8**	**9**
Empirical formula	$C_{35}H_{65}ClCrO_3Si_7$	$C_{35}H_{66}CrO_3Si_7$	$C_{72}H_{146}Li_2O_2Si_{14}$	$C_{64}H_{130}FeSi_{14}$
Formula weight	817.95	783.51	1451.03	1348.79
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1$ (#4)	P-1 (#2)	P-1 (#2)	$P2_1/a$ (#14)
a (Å)	9.3740(2)	9.0609(3)	11.6997(8)	18.6573(3)
b (Å)	48.5601(12)	11.1057(5)	12.8287(10)	12.8793(2)
c (Å)	11.1626(4)	23.8055(11)	18.3307(19)	35.4996(5)
α (°)		84.971(2)	84.698(4)	
β (°)	114.3297(14)	79.172(3)	74.736(5)	97.3153(7)
γ (°)		72.840(2)	70.744(3)	
V (Å^3)	4630.0(2)	2246.77(16)	59.532(8)	8460.9(2)
Z	4	2	1	4
d_{calc} (Mg m^{-3})	1.173	1.158	1.055	1.059
μ (Mo $K\alpha$) (mm^{-1})	0.516	0.471	0.233	0.409
Crystal size (mm)	0.15 × 0.10 × 0.02	0.30 × 0.10 × 0.05	0.20 × 0.10 × 0.03	0.20 × 0.10 × 0.05
Reflections collected	36076	18612	18947	79928
Independent reflections	15323 [R(int) = 0.0591]	7796 [R(int) = 0.0735]	7920 [R(int) = 0.0833]	14862 [R(int) = 0.0707]
Parameters	883	481	429	797
R_1 [$I > 2\sigma(I)$]	0.0548	0.0579	0.0573	0.0502
wR_2 (all data)	0.1409	0.1572	0.1457	0.1175
GOF	1.091	1.014	1.004	1.097
Largest peak, hole (e Å^{-3})	0.546, –0.403	0.687, –0.708	0.335, –0.441	0.415, –0.492

Reaction of hydrosilane with $[Cr(CH_3CN)_3(CO)_3]$

The reaction of hydrosilane **5** with $[Cr(CH_3CN)_3(CO)_3]$ in benzene produced a new type of silacyclohexadienyl complex **7**, [(H)(η^5-1-silacyclohexa-1,3-dienyl)$Cr(CO)_3$], in 62 % yield (Scheme 4). The structure of **7** was determined using NMR, IR, and UV–vis spectroscopic study, elemental analysis, and X-ray diffraction study, and differed markedly from those of complexes **2** and **6**. To disclose the structure of product **7** in detail, we conducted a variable-temperature ^{1}H NMR analysis of **7** in toluene-d_8 (–50 to 50 °C, Fig. 2). As the temperature was raised, the signals assignable to the protons on the SiC_5 ring except for H4 were dramatically changed. The two individual signals for H3 and H5 (H2 and H6) coalesced to one broad signal. On the other hand, the signal for H4 was almost unchanged. As for the Cr–H moiety, multiplicity of the signal was changed from doublet to triplet with increasing temperature. In the variable-temperature ^{29}Si NMR analysis, the chemical shifts of the signal assignable to the central silicon atom were unchanged (–49.5 ppm) at any temperature. These results indicate the presence of the rapid 1,5-H-migration between two carbon atoms (C2 and C6) at higher temperature, as depicted in Scheme 5 [7]. Finally, the complete characterization of **7** in toluene was conducted using the results of NMR spectra at –50 °C. In the ^{1}H NMR spectrum of **7** at –50 °C in toluene-d_8, the signals of the protons on the silacyclohexadienyl ring were observed at 5.82 (dd, J = 9.3 Hz, J = 4.8 Hz, H3), 4.21 (m, H4), 3.54 (m, H5), 3.27 (d, J = 9.3 Hz, H2), and 1.51 (m, $H6_a$ and $H6_b$), which values differed slightly from those of the related η^5-cyclohexadienyl chromium complex showing no 1,5-H-migration [7], because the silicon atom is incorporated in the cyclohexadienyl unit in complex **7**. The signal for Cr–H observed at –7.39 (doublet with Si satellites, $^1J_{HSi}$ = 92 Hz, $^3J_{HH}$ = 9.3 Hz) indicates that complex **7** can be described as a novel type of hydrido(silacyclohexadienyl) complex containing an Si–H–Cr three-centered interaction, as portrayed in Scheme 4. The coupling constant $^1J_{HSi}$ (92 Hz) is



Scheme 4 Reaction of hydrosilane with $[Cr(CH_3CN)_3(CO)_3]$.

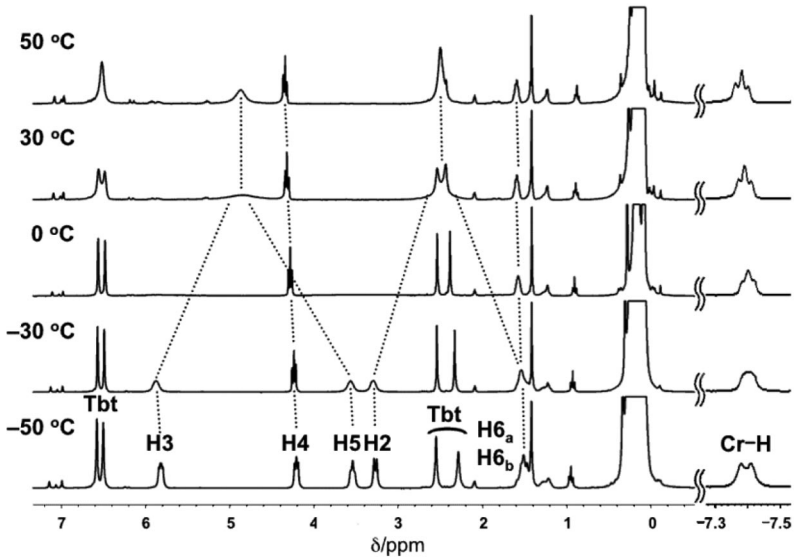
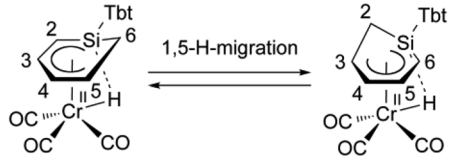


Fig. 2 Variable-temperature ^{1}H NMR spectra of **7**.



Scheme 5 Equilibrium of **7** in toluene.

much smaller than those observed between sp^3-hybridized silicon and hydrogen atoms in general hydrosilanes (ca. 200 Hz) [9], showing a weak Si–H bonding of **7**. Its value is larger than that of the related silacyclopentadienyl ruthenium complex bearing an Si–H–Ru three-centered interaction ($^1J_{HSi}$ = 41 Hz) [10]. In the ^{13}C NMR spectrum of **7** at –50 °C, the signals of the carbons in the carbonyl ligands were observed as three nonequivalent signals at 238.5, 231.4, and 229.3 ppm, suggesting that the rotation of $Cr(CO)_3$ unit around the axis through Cr and centroid in the SiC_5 ring is slow on the NMR time scale at –50 °C.

The UV–vis spectra of **7** in hexane showed characteristic absorptions at 395 and 497 nm, which were assigned by the time-dependent density function theory (TD-DFT) calculations [TD-B3LYP/6-311+G(2df,2p)//B3LYP/6-31G(d,p); Tbt was replaced by 2,6-dimethylphenyl] (Fig. 3). The absorption at 395 nm is derived from some degree of the transition from π–π* orbital in the dienyl unit together with the orbitals of the central chromium atom. That at 497 nm is assignable to the charge transfer from

the central chromium to the ligand (MLCT). In the IR spectrum of **7**, the wavenumbers of the carbonyl stretchings (1993, 1910, and 1885 cm^{-1}) resemble those for **2** and are smaller than those observed for complex **6** (2002, 1929, and 1897 cm^{-1}). This result indicates the increased electron-donating ability of the 1-silacyclohexa-1,3-dienyl ligand in **7** compared to **6**. Results of X-ray diffraction study of **7** are presented in Table 1 and Fig. 4. The X-ray analysis of **7** revealed that the silicon atom is certainly located in the dienyl unit (the deviation of the silicon atom from the plane defined by C1–C4 is 0.049 Å). The Si(1)–C(1) bond length is 1.822(4) Å, the value of which is slightly less than the average value of the silicon(sp^3)–carbon(sp^2) bond lengths (ca. 1.85 Å) [11]. It can be noted that **7** is the first example of a transition-metal complex bearing a 1-silacyclohexa-1,3-dienyl ligand.

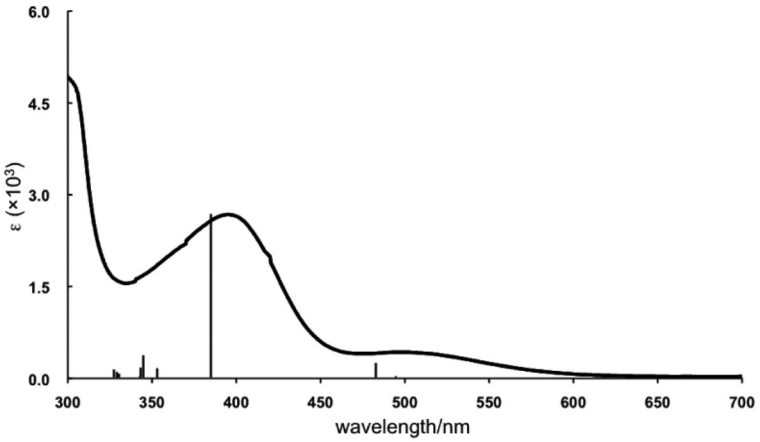


Fig. 3 Experimental UV–vis spectrum of **7** in hexane and calculated electron transitions (bars) for the model compound bearing a 2,6-dimethylphenyl substituent instead of Tbt.

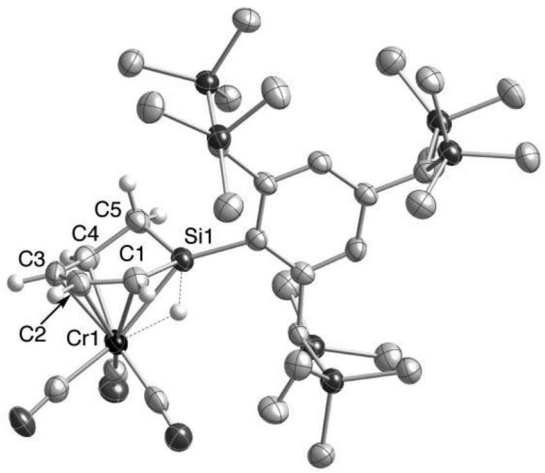
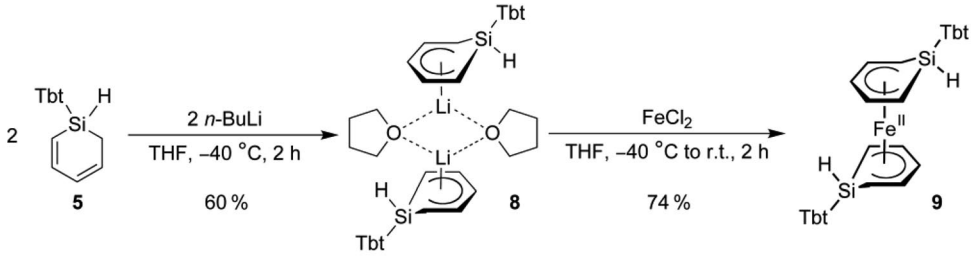


Fig. 4 Thermal ellipsoid plot of **7** drawn at the 50 % probability level. Hydrogen atoms except for hydrogen atoms on the SiC_5 ring and Si–H–Cr are omitted for clarity. Selected bond lengths [Å]. Si1–C1 1.822(4), C1–C2 1.385(6), C2–C3 1.426(6), C3–C4 1.381(6), C4–C5 1.520(6), C5–Si1 1.853(5), Si1–H1 1.52(3), Cr1–H1 1.76(3), Si1–Cr1 2.5480(12), C1–Cr1 2.256(4), C2–Cr1 2.200(4), C3–Cr1 2.186(4), and C4–Cr1 2.330(5).

Isolation of silacyclohexadienyllithium and its application to the synthesis of sandwich-type iron complex

We have described two methods for the synthesis of silacyclohexadienyl complex bearing a bulky substituent on the silicon atom. One is hydration of silabenzene complex, as shown in Scheme 1 [6]. The other is the formal insertion reaction of Cr(0) to C–H or Si–H bond of silacyclohexadiene (Schemes 3 and 4). Next, we examined the isolation of Tbt-substituted silacyclohexadienyllithium, because such an anionic species generally plays an important role in the synthesis of the corresponding silacyclohexadienyl transition-metal complex [4]. The treatment of hydrosilane **5** with *n*-BuLi afforded the corresponding anionic species **8** in a moderate yield as depicted in Scheme 6. The structure of **8** was confirmed by the NMR and IR spectra and X-ray diffraction study. The chemical shifts for **8** in the ^{1}H and ^{13}C NMR spectra closely resemble those of the reported silacyclohexadienide except for the signals assignable to the hydrogen on the silicon atom. The ^{1}H NMR chemical shift of SiH group was observed at 6.95 ppm, which is shifted downfield by ca. 1.2 ppm compared with the reported silacyclohexadienyl anion bearing a hydrogen atom and a *tert*-butyl group on the silicon atom, probably because of the ring current effect of Tbt group. In the ^{29}Si NMR spectrum, the signal of the central silicon atom was observed at –51.5 ppm, the value of which was similar to that of silacyclohexadiene **5** (–45.4 ppm). The ^{7}Li signal was observed at –4.4 ppm, although it is known that the signal of typical alkyl lithium was observed as 0–2 ppm [12]. The upfield shift probably resulted from the ring current effect of the η^5-coordinated SiC_5 ring in solution. The structure of **8** was finally determined using X-ray crystallographic



Scheme 6 Synthesis of bis(silacyclohexadienyl)iron complex **9** via silacyclohexadienyllithium **8**.

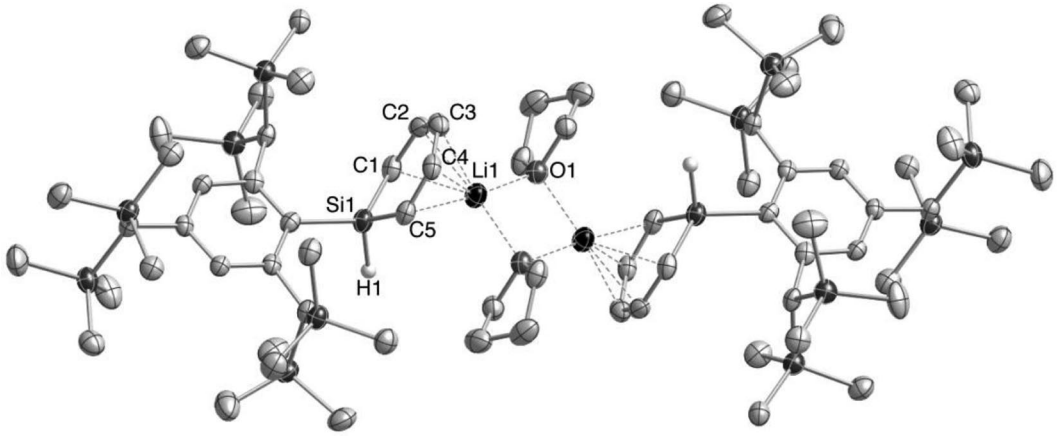


Fig. 5 Thermal ellipsoid plot of **8** drawn at the 50 % probability level. Hydrogen atoms except for Si–H are omitted for clarity. Selected bond lengths [Å]. Si(1)–C(1) 1.837(4), C1–C2 1.400(5), C2–C3 1.409(5), C3–C4 1.409(5), C4–C5 1.374(5), C5–Si1 1.852(4), C1–Li1 2.421(7), C2–Li1 2.290(7), C3–Li1 2.269(7), C4–Li1 2.302(7), and C5–Li1 2.457(7).

analysis (Fig. 5 and Table 1); the crystal structure of **8** showed a dimeric structure bridged by two tetrahydrofuran (THF) molecules between the two silacyclohexadienyllithium units [13].

To elucidate the reactivity of **8**, the reaction of **8** with anhydrous $FeCl_2$ was performed according to the reported procedure for the synthesis of a sandwich-type bis(silacyclohexadienyl)iron complex [4c]. The expected product **9** was obtained as orange crystals in 66 % isolated yield (Scheme 6). The ^1H and ^{13}C NMR spectral data for the dienyl unit of **9** closely resembles those for the similar type of complex having two methyl groups on the silicon atom [4b], indicating that the electronic effect of the Tbt group toward the dienyl unit is negligible. The thermal ellipsoid plot of **9** is depicted in Fig. 6. Each Tbt group on the central silicon atoms is located at the *exo* positions to the metal moiety to avoid its steric repulsion.

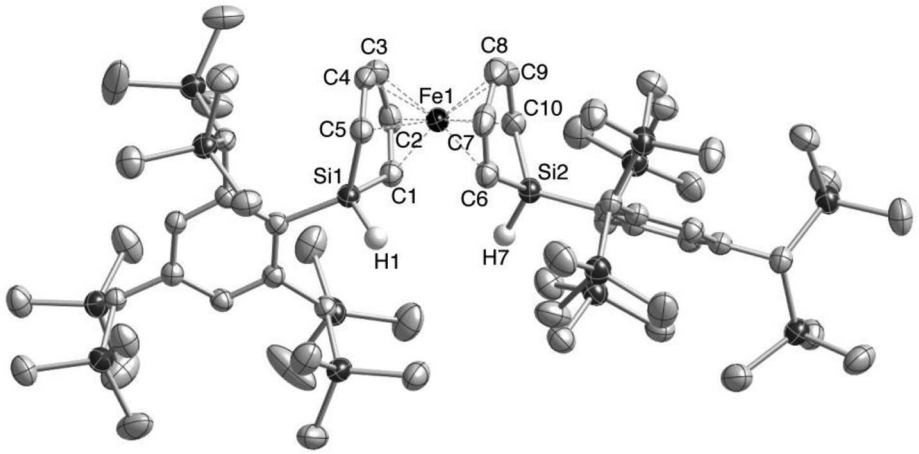


Fig. 6 Thermal ellipsoid plot of **9** drawn at the 50 % probability level. Hydrogen atoms except for Si–H are omitted for clarity. Selected bond lengths [Å]. Si1–C1 1.836(3), C1–C2 1.415(4), C2–C3 1.414(5), C3–C4 1.405(5), C4–C5 1.410(5), C5–Si1 1.847(3), Si2–C6 1.835(3), C6–C7 1.415(4), C7–C8 1.414(6), C8–C9 1.407(6), C9–C10 1.404(5), C10–Si2 1.843(3), C1–Fe1 2.126(3), C2–Fe1 2.075(3), C3–Fe1 2.067(3), C4–Fe1 2.055(3), and C5–Fe1 2.142(3).

CONCLUSION

In summary, two types of silacyclohexadienyl chromium complexes bearing a bulky Tbt group on the silicon atom, **2**, **6**, and **7**, were synthesized using the formal insertion reactions of Cr(0) into C–H or Si–H bonds. These complexes were fully characterized based on the spectroscopic data, elemental analyses, and X-ray structural study. 1-Silacyclohexa-1,3-dienyl complex **7** was found to have an unprecedented structure in which the dienyl moiety certainly consists of four carbon and one silicon atoms with an Si–H–Cr three-centered interaction. Additionally, we synthesized and isolated a silacyclohexadienyl anion **8** and showed its application to the synthesis of sandwich-type iron complex **9**. Compound **8** might be a useful building block to synthesize transition-metal complexes and functionalized silabenzenes of various kinds.

EXPERIMENTAL

General experimental details

All experiments were performed under an argon atmosphere unless otherwise noted. Solvents used for the reactions were purified using The Ultimate Solvent System (Glass Contour Co.) [14]. The THF, benzene, C_6D_6, and toluene-d_8 used as solvent were dried over a K mirror and distilled using the

trap-to-trap method. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured in C_6D_6 and $C_6D_5CD_3$ using a spectrometer (JNM AL-300; JEOL). Signals attributable to C_6D_5H (7.15 ppm) and $C_6D_5CD_2H$ (2.09 ppm) in ^{1}H NMR and C_6D_6 (128.0 ppm) and $C_6D_5CD_3$ (20.3 ppm) in ^{13}C NMR were used as references. The ^{29}Si NMR (59 MHz) spectra were measured in C_6D_6 and $C_6D_5CD_3$ using a spectrometer (AL-300; JEOL) with a signal for tetramethylsilane in C_6D_6 (0 ppm) as an external standard. Multiplicity of signals in ^{13}C NMR was determined using distortionless enhancement by polarization transfer (DEPT) technique. The IR spectra were recorded on a spectrometer (FT/IR-5300; Jasco Inc.). All melting points were determined on a Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were conducted at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. High-resolution mass spectral data were obtained using a spectrometer (JMS-700; JEOL). Gel permeation liquid chromatography (GPLC) was performed (LC-908 and LC-918 Systems; Japan Analytical Industry Co., Ltd.) with JAIGEL 1H and 2H columns (eluent: $CHCl_3$). 1-Silacyclohexadienes **3–5** were prepared according to the reported procedures [15]. Scaling up of the reactions described in this text might be possible, even though all reactions were performed at milligram scale.

*Synthesis of [(H)(1-Tbt-1-hydroxy-1-silacyclohexa-2,4-dienyl)Cr(CO)$_3$] (**2**)*

To a solution of **3** (30.3 mg, 0.0457 mmol) in C_6H_6 (2.0 ml) was added $[Cr(CH_3CN)_3(CO)_3]$ (13.0 mg, 0.0502 mmol). The reaction mixture was stirred at room temperature for 20 h. After removal of the solvent, *n*-hexane was added to the residue. The resulting suspension was filtered through Celite®; the solvent was removed. The residue was washed with *n*-hexane (1 ml × 5) to give a pale orange solid of **2** (8.3 mg, 23 %). **2**: mp. 122 °C (decomp.); ^{1}H NMR (300 MHz, C_6D_6): δ 6.42 (br s, 1H), 6.31 (br s, 1H), 5.30 (t, J = 6.0 Hz, 1H), 4.97 (dd, J = 9.3 Hz, J = 6.0 Hz, 2H), 2.15 (dd, J = 9.3 Hz, J = 9.0 Hz, 2H), 2.02 (s, 1H), 1.98 (s, 1H), 1.66 (s, 1H), 1.37 (s, 1H), 0.10 (br, 54H), –9.04 (t, J = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ 231.34 (s), 150.92 (s), 150.46 (s), 146.21 (s), 129.03 (s), 127.14 (d), 122.26 (d), 97.77 (d), 97.16 (d), 42.34 (d), 31.01 (d), 28.74 (d), 28.26 (d), 1.24 (q), 0.96 (q), 0.93 (q), 0.85 (q); ^{29}Si NMR (59 MHz, C_6D_6): δ 2.13, 2.04, –7.24; IR (KBr) 1991, 1910, 1888 cm^{-1} (C≡O stretching). Anal. calcd. for $C_{35}H_{66}CrO_4Si_7$: C, 52.58; H, 8.32 Found: C, 52.75; H, 8.40.

*Synthesis of [(H)(1-Tbt-1-chloro-1-silacyclohexa-2,4-dienyl)Cr(CO)$_3$] (**6**)*

To a solution of **4** (42.6 mg, 0.0625 mmol) in C_6H_6 (3.0 ml) was added $[Cr(CH_3CN)_3(CO)_3]$ (19.4 mg, 0.0748 mmol). The reaction mixture was stirred at room temperature for 20 h. After removal of the solvent, *n*-hexane was added to the residue. The resulting suspension was filtered through Celite; the solvent was removed. The residue was washed with *n*-hexane (1 ml × 5) to give a pale orange solid of **6** (30.5 mg, 60 %). **6**: m.p. 161 °C (decomp.); ^{1}H NMR (300 MHz, C_6D_6): δ 6.44 (br s, 1H), 6.32 (br s, 1H), 5.28 (t, J = 6.3 Hz, 1H), 5.00 (dd, J = 9.3 Hz, J = 6.3 Hz, 2H), 2.30 (dd, J = 9.3 Hz, J = 9.0 Hz, 2H), 2.04 (s, 2H), 1.37 (s, 1H), 0.13 (s, 18H), 0.11 (s, 18H), 0.08 (s, 18H), –8.73 (t, J = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ 230.42 (s), 151.73 (s), 151.26 (s), 147.40 (s), 127.50 (d), 125.92 (s), 122.59 (d), 97.12 (d), 96.13 (d), 41.07 (d), 31.27 (d), 29.10 (d), 28.53 (d), 1.46 (q), 1.12 (q), 0.86 (q); ^{29}Si NMR (59 MHz, C_6D_6): δ 4.83, 2.56, 2.19; IR (KBr) 2002, 1929, 1897 cm^{-1} (C≡O stretching). Anal. calcd. for $C_{35}H_{65}ClCrO_3Si_7$: C, 51.39; H, 8.01. Found: C, 51.59; H, 8.03.

*Synthesis of [(H)(1-Tbt-1-silacyclohexa-1,3-dienyl)Cr(CO)$_3$] (**7**)*

To a solution of **5** (46.2 mg, 0.0715 mmol) in C_6H_6 (2.2 ml) was added $[Cr(CH_3CN)_3(CO)_3]$ (20.4 mg, 0.0787 mmol). The reaction mixture was stirred at room temperature for 9 h. After removal of the solvent, *n*-hexane was added to the residue. The resulting suspension was filtered through Celite; the solvent was removed. The residue was washed with *n*-hexane (1 ml × 5) to give a pale orange solid of **7** (34.5 mg, 62 %). **7**: m.p. 202 °C (decomp.); ^{1}H NMR (300 MHz, C_7D_8, –50 °C): δ 6.58 (s, 1H), 6.51 (s, 1H), 5.82 (dd, J = 9.3 Hz, J = 4.8 Hz, 1H), 4.21 (m, 1H), 3.54 (m, 1H), 3.27 (d, J = 9.3 Hz, 1H), 2.55 (s, 1H), 2.29 (s, 1H), 1.51 (m, 2H), 1.42 (s, 1H), 0.27 (s, 9H), 0.22 (s, 9H), 0.17 (s, 9H), 0.12 (s, 9H), 0.10 (s, 9H), 0.08 (s, 9H), –7.39 (d, with Si satelites, $^1J_{HSi}$ = 92.1 Hz, $^3J_{HH}$ = 9.3 Hz,

Cr–H); ^{1}H NMR (300 MHz, C_7D_8, 50 °C): δ 6.52 (br s, 2H), 4.87 (br s, 2H), 4.34 (t, J = 6.6 Hz, 1H), 2.50 (br s, 4H), 1.59 (m, 1H), 1.42 (s, 1H), 0.16 (s, 36H), 0.08 (s, 18H), –7.38 (t, with Si satelites, $^1J_{HSi}$ = 91.2 Hz, $^3J_{HH}$ = 5.7 Hz, Cr–H); ^{13}C NMR (75 MHz, C_7D_8, –50 °C): δ 238.48 (s), 231.35 (s), 229.30 (s), 152.87 (s), 152.61 (s), 147.39 (s), 126.64 (d), 121.39 (d), 117.14 (d), 100.71 (s), 95.28 (d), 75.38 (d), 61.87 (d), 32.44 (d), 31.58 (d), 30.73 (d), 21.70 (t), 0.86 (q), 0.75 (q), 0.54 (q), 0.49 (q), 0.41 (q); ^{29}Si NMR (59 MHz, C_7D_8, –50 °C): δ 2.50, 2.19, –49.60; IR (KBr) 1993, 1910, 1885 cm^{-1} (C≡O stretching); UV/vis (hexane): λ_{max} (ε) = 395 (2.7×10^3), 497 (4.2×10^2) nm; high-resolution MS (FAB) m/z calcd. for $C_{35}H_{67}Si_7CrO_3$ 782.2802 ([M]$^+$), found 782.2807 ([M]$^+$). Anal. calcd. for $C_{35}H_{66}CrO_3Si_7$: C, 53.65; H, 8.49. Found: C, 53.44; H, 8.39.

*Synthesis of 1-Tbt-1-hydro-1-silacyclohexadienyllithium (**8**)*

To a solution of **5** (306 mg, 0.473 mmol) in THF (9.3 ml) was added *n*-BuLi (0.440 ml of 1.50 M solution in hexane, 0.660 mmol) at –40 °C. The reaction mixture was stirred and warmed gradually to room temperature for 2 h. After removal of the solvent, *n*-hexane was added to the residue. The resulting suspension was filtered through Celite; the solvent was removed. The hexane solution of the residue was cooled to give yellow crystals of **8** (206 mg, 60 %). **8**: mp. 168 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6): δ 7.21 (m, 4H, H2/H4), 6.95 (s, 2H, SiH), 6.61 (br s, 2H), 6.51 (br s, 2H), 5.02 (t, J = 7.2 Hz, 2H, H3), 4.67 (d, J = 6.0 Hz, 4H, H1/H5), 3.15 (br s, 2H), 3.14 (br s, 2H), 2.96 (m, 8H, THF), 1.50 (s, 2H), 0.99 (m, 8H, THF), 0.37 (br s, 72H), 0.22 (s, 36H); ^{7}Li NMR (75 MHz, C_6D_6): –4.4; ^{13}C NMR (100 MHz, C_6D_6): δ 150.67 (s), 150.57 (s), 143.28 (s), 140.16 (d, C2/C4), 133.97 (s), 127.33 (d), 122.39 (d), 92.60 (d, C3), 85.97 (d, C1/C5), 68.65 (t, THF), 30.54 (d), 25.92 (d), 25.66 (d), 25.07 (t, THF), 1.55 (q), 1.23 (q), 1.01 (q); ^{29}Si NMR (59 MHz, C_6D_6): δ 1.88, 1.77, –51.50. IR (KBr) 2135 cm^{-1} (Si–H stretching).

*Synthesis of [bis(1-Tbt-1-hydro-1-silacyclohexadienyl)Fe] (**9**)*

To a solution of **8** (184 mg, 0.127 mmol) in THF (3.0 ml) was added anhydrous $FeCl_2$ (19.0 mg, 0.150 mmol) at –40 °C. The reaction mixture was stirred and warmed gradually to room temperature for 2 h. After removal of the solvent, *n*-hexane was added to the residue. The resulting suspension was filtered through Celite; the solvent was removed. After separation of the side products using GPC (eluent; $CHCl_3$), the hexane solution of the residue was cooled to give orange crystals of **9** (206.1 mg, 0.142 mmol, 74 %). **9**: m.p. 218 °C (decomp.); ^{1}H NMR (300 MHz, C_6D_6): δ 6.46 (br s, 2H), 6.34 (br s, 2H), 6.06 (s, 2H. SiH), 4.84 (dd, $^2J_{HH}$ = 9.9 Hz, $^2J_{HH}$ = 6.0 Hz, 4H), 4.49 (t, $^2J_{HH}$ = 6.0 Hz, 2H), 2.98 (d, $^2J_{HH}$ = 9.9 Hz, 4H), 2.80 (s, 4H), 1.40 (s, 2H), 0.26 (br s, 72H), 0.14 (s, 36H); ^{13}C NMR (75 MHz, C_6D_6): δ 149.98 (s), 144.20 (s), 130.47 (s), 128.63 (s), 127.00 (d), 122.15 (d), 95.22 (d), 79.44 (d), 45.88 (d), 30.64 (d), 26.86 (d), 26.44 (d), 1.32 (q), 1.04 (q), 0.89 (q); ^{29}Si NMR (59 MHz, C_6D_6): δ 1.96, 1.77, –56.83; IR (KBr) 2123 cm^{-1} (Si–H stretching); high-resolution MS (FAB) m/z calcd. for $C_{64}H_{130}FeSi_{14}$ 1346.6292 ([M]$^+$), found 1346.6288 ([M]$^+$). Anal. calcd. for $C_{64}H_{130}FeSi_{14}$: C, 56.99; H, 9.72. Found: C, 57.14; H, 9.72.

X-ray crystallography

Single crystals of **6–9** were grown by the slow evaporation of their benzene solutions. Their intensity data were collected using a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71071 Å) to $2\theta_{max}$ = 50° at 103 K. Their structures were solved using the direct method (SHELXL-97) and refined using the full-matrix least-squares procedure on F^2 for all reflections (SHELXL-97) [16]. All the non-hydrogen atoms were refined anisotropically; all hydrogens were placed using AFIX instruction except for hydrogen atoms on the silicon atoms in **7–9**.

Theoretical calculations

Geometry optimization of the model compound for **7** bearing a 2,6-dimethylphenyl substituent instead of Tbt was conducted using the Gaussian 03 program [17] with DFT at the B3LYP level with 6-31G(2d) basis sets. The atomic coordinates obtained using the X-ray crystallographic analysis of **7** were used as

those for the calculations. Its TD-DFT calculations were performed at TD-B3LYP/6-311+G(2df,2p)//B3LYP/6-31G(d,p) level. The computation time was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis of **6–9** were deposited with the Cambridge Crystallographic Data Centre, as CCDC Nos. 749547 (**6**), 749544 (**7**), 749546 (**8**), and 749545 (**9**), respectively. A copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax. (int. code) +44 1223 336 033 or E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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