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Preparations and Thermal Isomerization of Some Tricarbonyl(1-silacyclohexadiene) Iron Complexes. Silyl and Hydrogen Migration in the Diene and the Diene Complex[1]

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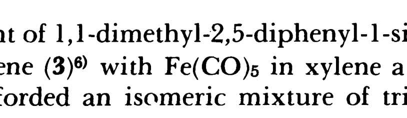
The reaction of 1,1-dimethyl-2,5-diphenyl-1-silacyclohexa-2,4-diene with iron pentacarbonyl or diiron nonacarbonyl gave a mixture of tricarbonyl(1,1-dimethyl-2,5-diphenyl-1-silacyclohexa-2,4-diene)iron and tricarbonyl(1,1-dimethyl-3,6-diphenyl-1-silacyclohexa-2,4-diene)iron. Similarly, on treatment with iron pentacarbonyl 1,1-dimethyl-2,5-diphenyl-4-trimethylsilyl-1-silacyclohexa-2,5-diene yielded a mixture of tricarbonyl(1,1-dimethyl-3,6-diphenyl-4-trimethylsilyl-1-silacyclohexa-2,4-diene)iron, tricarbonyl(1,1-dimethyl-2,5-diphenyl-4-trimethylsilyl-1-silacyclohexa-2,4-diene)iron, and tricarbonyl(1,1-dimethyl-2,5-diphenyl-6-trimethylsilyl-1-silacyclohexa-2,4-diene)iron as a result of migration of the hydrogen on the ligand competing with silyl migration. On thermolysis, 1,1-dimethyl-2,5-diphenyl-4-trimethylsilyl-1-silacyclohexa-2,5-diene underwent only 1,3-silyl-migration to yield 1,1-dimethyl-2,5-diphenyl-6-trimethylsilyl-1-silacyclohexa-2,4-diene. The mechanism of transition-metal assisted hydrogen-migration is discussed.

We have reported previously an interesting chemistry of the transition-metal complexes of silacyclopentadienes,[2] which has been followed by several other workers.[3] Our investigations of tricarbonyl(silacyclopentadiene)iron complexes have shown that the exo-substituent on the silicon is highly activated toward electrophilic substitution; for example, tricarbonyl(1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene)iron (**1**) is readily converted stereospecifically into the silanol complex **2** by the treatment with mercury(II) acetate in the presence of perchloric acid.[2] There are a few reports on the homologous complex, namely the transition-metal complexes of 1-silacyclohexadienes.[4,5] We now describe our own result on the preparation and thermal isomerization of some tricarbonyl(1-silacyclohexadiene)iron complexes as well as of their ligands, 1-silacyclohexadienes.



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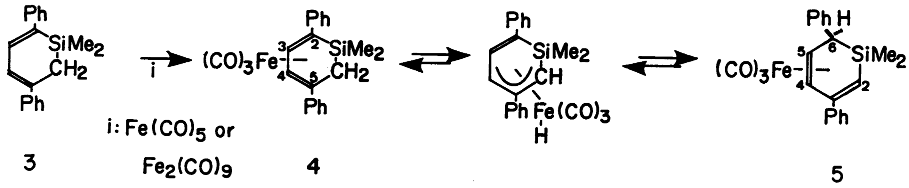
Results and Discussions

Treatment of 1,1-dimethyl-2,5-diphenyl-1-silacyclohexa-2,4-diene (**3**)[6] with $Fe(CO)_5$ in xylene at 130 °C for 30 h afforded an isomeric mixture of tricarbonyl(1,1-dimethyl-3,6-diphenyl-1-silacyclohexa-2,4-diene)iron (**5**) in 48.7% yield together with tricarbonyl(1,1-dimethyl-2,5-diphenyl-1-silacyclohexa-2,4-diene)iron (**4**) in 39.0% yield. **5** is a product of 1,5-H shift. These isomers could be separated each other by TLC on silica gel. Spectral properties, in particular NMR spectra served to distinguish between the two isomers, **4** and **5**. **4** shows two olefinic proton signals (H_3 and H_4) at 5.90 and 6.17 as doublet ($J_{3,4}=5.4$ Hz) together with AB type methylene proton signals (H_{6N} and H_{6X}, $J_{6N,6X}=16.5$ Hz) at 2.10 and 1.25, respectively. In contrast, with only one "internal" olefinic proton signal H_4 at 5.88, **5** has two "outside" complexed olefinic proton signals (H_2 and H_5) at 2.19 and 3.15, respectively. One proton signal due to H_6 is observed at 2.93. The configuration of H_6 is endo as described below. When **3** was allowed to react with diiron nonacarbonyl in benzene for 5 h at 90 °C, only **4** could be isolated in 78% yield together with the unreacted diene **3**. The equilibration between **4** and **5** was demonstrated as follows. When **4** was heated in a sealed tube at 130 °C for 48 h, it was converted into a 56:44 mixture of **4** and **5** without appreciable decomposition. Similarly, the thermolysis under similar conditions (140 °C, 22 h in a sealed tube), **5** gave a 48:52 mixture of **4** and **5**.[7] These isomer ratios were determined after careful TLC separation of these thermolysates on silica gel. Inspection of these findings above indicates that treatment of the diene **3** with an iron carbonyl reagent gives **4** at first, which is then isomerized thermally to **5**, and the equilibrium constant between **4** and **5** is nearly unity.

1,1-Dimethyl-2,5-diphenyl-4-trimethylsilyl-1-silacyclohexa-2,5-diene (**6**) was obtained quantiatively by quenching the anion derived from **3** with trimethylchlorosilane. Thermolysis of **6** in a sealed tube at 170 °C for 38 h caused 1,3-sila-allyl rearrangement and gave 1,1-dimethyl-2,5-diphenyl-6-trimethylsilyl-1-silacyclohexa-2,4-diene (**7**) in high yield.[8,9] The other possible isomers such as **8** and **9** were not detected in the reaction mixture and this shows that the trimethylsilyl group migrates to C_6 not to C_2 and 1,3- or 1,5-hydrogen migration does not compete with 1,3-silaallyl rearrangement effectively.[10] 1,1-

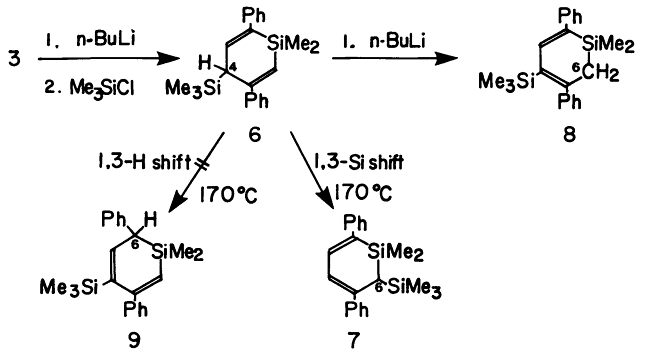


Scheme 1.

Table 1. Thermal Interconversion between 4 and 5

Complex	Temp	Time	Fe(CO)$_3$(diene)		
	°C	h	% yield[a]		Relative yield
			4	**5**	**4**:**5**
4	130	48	52	42	56:44
5	140	22	41	43	48:52

a) Isolated Yields by TLC.



Scheme 2.

Dimethyl-2,5-diphenyl-4-trimethylsilyl-1-silacyclohexa-2,4-diene (**8**) was obtained by quenching the anion derived from **6** with water.

Treatment of dienes **6**, **7**, and **8** with Fe(CO)$_5$ led to the mixtures of complexes **10**, **11**, and **12** as shown in Table 2 and Scheme 3. These isomers could be separated by careful TLC on silica gel and their structures were readily characterized on the basis of NMR spectra. Thermolyses of **11** and **12** resulted in isomerization to give the equilibrium mixture as shown in Table 3. The results obtained here indicate that 1,3 and 1,5-hydrogen shift is considerably enhanced by the transition metal and can compete with the sila-allyl migration observed in thermolysis of **6**. This can be explained by assuming the intermediacy of a (π-allyl)metal hydrides such as **13**.[7,11] Coordination of the metal complex should occur from the less sterically hindered side of the diene and hence the trimethylsilyl group necessarily turns out to be exo in **10**.[15] This always allows to migrate the endo hydrogen to the metal center to form a π-allyl metal hydride such as **13**, which reverts to the diene complex, either **11** or **12**.

Table 2. Reactions of Dienes **6**, **7**, and **8** with Fe(CO)$_5$

Diene	Temp	Time	Fe(CO)$_3$(diene)			
	°C	h	% yield[a]			
			10	**12**	**11**	**7**[b]
6	165	20	20.5	trace	26.4	42.0
7	170	37	44.0			34.3
8	160	22		23.4	37.5	

a) Isolated yields by TLC. b) A trace amount of **12** was detected on TLC.

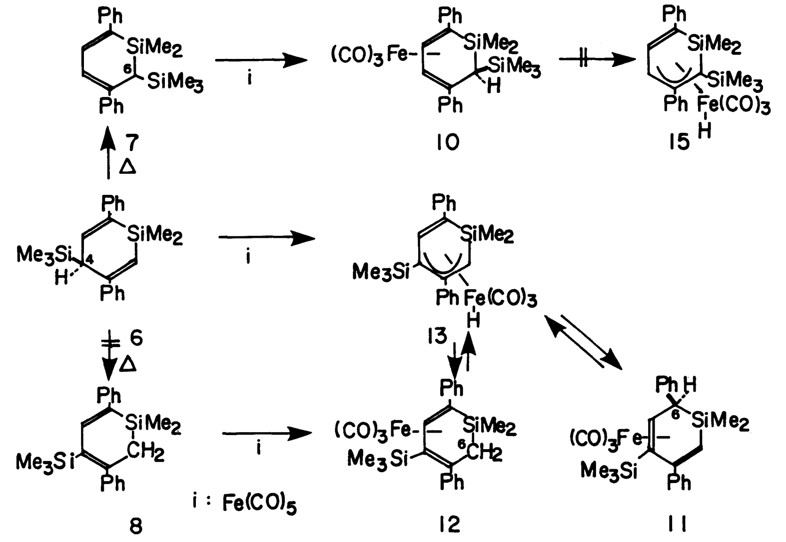
Table 3. Thermal Interconversion of **11** and **12**

Complex	Temp	Time	Fe(CO)$_3$(diene)		
	°C	h	% yield[a]		Relative yield
			11	**12**	**11**:**12**
11	170	7	71	27	72:28
12	155—180	123	50	24	68:32

a) Isolated yields by TLC.

On the other hand, **10** did not isomerize thermally, namely no metal-assisted hydrogen migration was observed. This may be ascribed to a large steric hindrance emerging in **15**. To examine the reactivity of the substituent on the silicon of the tricarbonyl(silacyclohexadiene)iron complex, **4** was allowed to react with Hg(OAc)$_2$ in presence of HClO$_4$,[2] and was found to remain unchanged under these conditions.[12]

It is noteworthy to add some comments on NMR signals, especially Si–Me signals of these carbonyl(silacyclohexadiene)iron complexes (Table 4). The assignment of these Si–Me signals is made by analogy to that made in tricarbonyl(silacyclopentadiene)iron complexes in which exo Si–Me resonance always occurs at higher field than the endo one.[13] The difference in chemical shift between endo- and exo-Me signals is similar in these two types of diene complexes. The similar trend is observed in the chemical shifts of C$_6$-methylene protons in **4**, and **12**.[14] The endo-proton signal always appears at lower field.[15]



Scheme 3.

Table 4. NMR Spectra of Tricarbonyl(silacyclohexadiene)iron Complexes (δ in CCl_4)

Complex	Si-Me exo	Si-Me endo	H_{6X}[a]	H_{6N}[a]	H_2	H_3	H_4	H_5	$SiMe_3$
4	−0.02	0.44	1.25	2.10		6.17	5.90		
5	−0.42	0.35		2.93	2.19		5.88	3.14	
10	−0.05	0.38		1.71		6.03	5.91		−0.32
11	−0.22	0.47		3.00	1.91			3.25	0.05
12	0.06	0.42	1.37	1.73		5.91			0.20

a) H_{6X} and H_{6N} denote the exo- and endo-hydrogens at C_6, respectively.

Experimental

General Remarks. NMR spectra were obtained by using Varian A-60 and HA-100 instruments. Mass spectra were obtained by a Hitachi RMU-6 instrument. Infrared spectra were recorded on a Hitachi EPI-G2 grating spectrometer. NMR spectra were recorded in CCl_4 and chemical shift data are given in δ value. IR spectra were measured in a KBr disk and IR data are given in cm^{-1}.

Reaction of 1,1-Dimethyl-2,5-diphenyl-1-silacyclohexa-2,4-diene (3) with $Fe(CO)_5$. A mixture of **3** (478.5 mg, 1.73 mmol), $Fe(CO)_5$ (5 ml, ≈35 mmol) and dry xylene (5 ml) was heated in a small autoclave at 130 °C for 30 h. Solvent and excess $Fe(CO)_5$ were removed in vacuum and the residue was separated by TLC on silica gel. **4** (289.0 mg, 39.0%) and **5** (359.0 mg, 48.7%) were obtained. **4**: mp 80 °C; MS *m/z* M^+ 416; ^1H NMR −0.02 (3H, s, *exo*-SiMe), 0.44 (3H, s, *endo*-SiMe), 1.25 (1H, d, H_{6N}, $J_{6X,6N}$=16.5 Hz), 2.10 (1H, d, H_{6N}, $J_{6X,6N}$=16.5 Hz), 5.90 (1H, d, H_4, $J_{3,4}$=5.4 Hz), 6.17 (1H, d, H_3, $J_{3,4}$=5.4 Hz), 7.0—7.6 (10H, m, Ph); IR 2040, 1975, 1965 (CO), 1250 (SiMe); Anal. Calcd for $C_{22}H_{20}O_3SiFe$: C, 63.47; H, 4.84. Found: C, 63.49; H, 4.72, **5**: Mp 107 °C; MS *m/z* M^+ 416; ^1H NMR −0.42 (3H, s, *exo*-SiMe), 0.35 (3H, s, *endo*-SiMe), 2.19 (1H, d, H_2, $J_{2,4}$=1.8 Hz), 2.93 (1H, d, H_6, $J_{5,6}$=3.9 Hz), 3.14 (1H, dd, H_5, $J_{4,5}$=6.8 Hz, $J_{5,6}$=3.9 Hz), 5.88 (1H, dd, H_4, $J_{4,5}$=6.8 Hz, $J_{2,4}$=1.8 Hz), 6.8—7.6 (10H, m, Ph); IR 2050, 1990, 1970 (CO), 1250 (SiMe); Found: C, 63.39; H, 4.90%. Calcd for $C_{22}H_{20}O_3SiFe$: C, 63.47; H, 4.84%.

Reaction of 1,1-Dimethyl-2,5-diphenyl-1-silacyclohexa-2,4-diene (3) with $Fe_2(CO)_9$. A mixture of **3** (81.2 mg, 0.294 mmol), $Fe_2(CO)_9$ (148.2 mg, 0.407 mmol) and dry benzene (5 ml) was heated in an autoclave at 90 °C for 5 h. The solvent was removed under reduced pressure. The residual oil was separated by TLC on silica gel. Unchanged **3** (45.5 mg, 56.0%) was recovered and **4** (41.8 mg, 77.7%) was obtained.

Thermolysis of 4. **4** (54.0 mg, 0.130 mmol) was sealed under vacuum in a Pyrex tube and heated in an oil bath at 130 °C for 48 h. **4** (28.4 mg, 52.0%) were recovered and **5** (22.6 mg) were separated from the reaction mixture by TLC.

Thermolysis of 5. **5** (30.0 mg, 0.072 mmol) was sealed under vacuum in a Pyrex tube and heated in an oil bath at 140 °C for 22 h. The reaction mixture was separated by TLC. Starting material **5** (13.0 mg) was recovered and isomer **4** (12.2 mg) was obtained.

Preparation of 1,1-Dimethyl-2,5-diphenyl-4-trimethylsilyl-1-silacyclohexa-2,5-diene (6). In a 20 ml-flask was placed **3** (261.2 mg, 0.945 mmol) dissolved in dry ether (10 ml) containing *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (0.5 g, ≈4 mmol). Then butyllithium in hexane was added to the mixture and was stirred magnetically at room temperature for 10 min. Then excess amount of trimethylchlorosilane was added to the reaction mixture, and was hydrolyzed after 10 min and was extracted with ether. The ethereal solution was evaporated to dryness in vacuum. The residue was purified by TLC on silica gel to give **6** (301.0 mg, 91.4%). **6**: an oil; MS *m/z* M^+ 348; UV (hexane) $\lambda_{max}(\varepsilon)$ 245.5 nm (23900); ^{1}H NMR −0.08 (9H, s, $\mathrm{SiMe_3}$), 0.27 (3H, s, SiMe), 0.41 (3H, s, SiMe), 3.70 (1H, d, H_4, $J_{3,4}$=5.4 Hz), 5.90 (1H, s, H_6), 6.83 (1H, d, H_3, $J_{3,4}$=5.3 Hz), 7.0—7.5 (10H, m, Ph); Found: C, 75.79; H, 8.29%. Calcd for $\mathrm{C_{22}H_{28}Si_2}$: C, 75.59; H, 8.10%.

Preparation of 1,1-Dimethyl-2,5-diphenyl-6-trimethylsilyl-1-silacyclohexa-2,4-diene (7). **6** (121.2 mg, 0.248 mmol) was sealed under vacuum in a Pyrex tube and heated in an oil bath at 170 °C for 38 h. The reaction mixture was purified by TLC on silica gel. **7** (105.6 mg, 87.1%) was afforded as an oil. Other isomers such as **6** or **9** were not detected on TLC. **7**: an oil; MS *m/z* M^+ 348; UV (hexane) $\lambda_{max}(\varepsilon)$ 238 nm (14800), 350 nm (16800); ^{1}H NMR 0.02 (9H, s, $\mathrm{SiMe_3}$), 0.43 (3H, s, SiMe), 0.45 (3H, s, SiMe), 1.89 (1H, s, H_6), 6.46 (1H, d, H_4, $J_{3,4}$=6.4 Hz), 6.83 (1H, d, H_3, $J_{3,4}$=6.4 Hz), 7.0—7.5 (10H, m, Ph); Found: C, 75.77; H, 8.10%. Calcd for $\mathrm{C_{22}H_{28}Si_2}$: C, 75.79; H, 8.10%.

Preparation of 1,1-dimethyl-2,5-diphenyl-4-trimethylsilyl-1-silacyclohexa-2,4-diene (8). In a 30 ml-flask was placed 1,1-dimethyl-2,5-diphenyl-4-trimethylsilyl-1-silacyclohexa-2,4-diene (**6**) (166.5 mg, 0.478 mmol) dissolved in dry ether (10 ml) containing TMEDA (0.5 g, 4 mmol). Then butyllithium in hexane was added to the mixture and was stirred magnetically at room temperature for 10 min. The mixture was hydrolyzed and was extracted with ether. The ethereal solution was evaporated to dryness in vacuum. The residue was separated by TLC on silica gel to give unreacted **6** (61.0 mg, 36.6%) and **8** (55.5 mg, 52.6%). **8**: Mp 100 °C; MS *m/z* M^+ 348; UV (hexane) $\lambda_{max}(\varepsilon)$ 233 nm (11400), 322 nm (13200); ^{1}H NMR −0.16 (9H, s, $\mathrm{SiMe_3}$), 0.25 (6H, s, $\mathrm{SiMe_2}$), 1.96 (2H, s, H_6), 6.95 (1H, s, H_3), 7.0—7.4 (10H, m, Ph); Found: C, 75.89; H, 8.19%. Calcd for $\mathrm{C_{22}H_{28}Si_2}$: C, 75.79; H, 8.10%.

Reaction of 4 with $\mathrm{Hg(OAc)_2}$. In a 20 ml-flask equipped with a condenser and a nitrogen inlet tube, a mixture of **4** (38.0 mg, 0.0913 mmol), $\mathrm{Hg(OAc)_2}$ (36.0 mg, 0.113 mmol), dioxane (10 ml) and one drop of 70% aq perchloric acid was placed and stirred magnetically at room temperature for 10 min. After addition of water, the reaction mixture was extracted with ether. The ethereal solution was evaporated to dryness to give an oil (37.0 mg). NMR spectrum of this oil indicated almost 100% recovery of **4**.

Reaction of 6 with $\mathrm{Fe(CO)_5}$. In a small autoclave **6** (255.0 mg, 0.731 mmol), $\mathrm{Fe(CO)_5}$ (5 ml, 35 mmol), dry toluene (10 ml) were heated at 165 °C for 20 h. The solvent and excess amount of $\mathrm{Fe(CO)_5}$ are removed under vacuum and the residual oil was separated by TLC on silica gel. **10** (73.0 mg, 20.5%), **11** (94.0 mg, 26.4%) and **7** (107.4 mg, 42.0%) were afforded. Since **7** and **12** show same R_f value on TLC under various conditions, **7** thus obtained remained to be contaminated with a small amount of **12**. **10**: mp 140 °C; MS *m/z* M^+ 488; ^{1}H NMR −0.32 (9H, s, $\mathrm{SiMe_3}$), −0.05 (3H, s, *exo*-SiMe), 0.38 (3H, s, *endo*-SiMe), 1.71 (1H, s, H_6), 5.91 (1H, d, H_4, $J_{3,4}$=5.1 Hz), 6.03 (1H, d, H_3, $J_{3,4}$=5.1 Hz), 6.9—7.4 (10H, m, Ph); IR 2040, 1975, 1950 (ν CO), 1250 (δ SiMe); Found: C, 61.64; H, 5.83%. Calcd for $\mathrm{C_{25}H_{28}O_3Si_2Fe}$: C, 61.47; H, 5.78%. **11**: mp 95 °C; MS *m/z* M^+ 488; ^{1}H NMR −0.22 (3H, s, *exo*-SiMe), 0.05 (9H, s, $\mathrm{SiMe_3}$), 0.47 (3H, s, *endo*-SiMe), 1.91 (1H, s, H_2), 3.00 (1H, d, H_6, $J_{5,6}$=4.2 Hz), 3.25 (1H, d, H_5, $J_{5,6}$=4.2 Hz), 6.8—7.6 (10H, m, Ph); IR 2050, 1980, 1970, 1960 (ν CO), 1260, 1250 (δ SiMe); Found: C, 61.73, H, 5.77%. Calcd for $\mathrm{C_{25}H_{28}O_3Si_2Fe}$: C, 61.47; H, 5.78%. **12**: an oil; MS *m/z* M^+ 488; ^{1}H NMR 0.06 (3H, s, *exo*-SiMe), 0.20 (9H, s, $\mathrm{SiMe_3}$), 0.42 (3H, s, *endo*-SiMe), 1.37 (1H, d, H_{6X}, $J_{6X,6N}$=16.5 Hz, 5.91 (1H, s, H_3), 7.0—7.6 (10H, m, Ph); IR (liquid film) 2050, 1975 (ν CO), 1250 (δ SiMe).

Reaction of 7 with $\mathrm{Fe(CO)_5}$. A mixture of **7** (105.6 mg, 0.303 mmol), $\mathrm{Fe(CO)_5}$ (2 ml, 14 mmol) and dry xylene (4 ml) was heated in an autoclave at 170 °C for 37 h. The solvent and excess $\mathrm{Fe(CO)_5}$ were removed in vacuum. The residual oil was separated by TLC to give **7** (36.0 mg, 34.3%) and **10** (66.0 mg, 68.3%).

Reaction of 8 with $\mathrm{Fe(CO)_5}$. A mixture of **8** (74.1 mg, 0.213 mmol), $\mathrm{Fe(CO)_5}$ (2 ml, 14 mmol) and dry toluene (6 ml) was heated in an autoclave to 160 °C for 22 h. Solvent and unchanged $\mathrm{Fe(CO)_5}$ were removed in vacuum. The residual oil was separated by TLC to afford **11** (39.1 mg, 37.5%) and **12** (24.3 mg, 23.4%). **12** was always contaminated with a trace of unidentified compound, which shows same R_f value as **12** on TLC under various conditions.

Thermolysis of 11. **11** (49.0 mg, 0.100 mmol) was sealed under vacuum in a Pyrex tube and was heated in an oil bath at 170 °C for 7 h. The reaction mixture was separated by TLC to give recovered **11** (34 mg) and isomer **12** (13.4 mg).

Thermolysis of 12. In an autoclave the mixture (87 mg) of **12** (0.0462 mmol) containing **7** (0.1848 mmol), $\mathrm{Fe(CO)_5}$ (2 ml, 14 mmol) and dry toluene (5 ml) were placed, and heated in an oil bath at 155—180 °C for 123 h. The solvent and excess $\mathrm{Fe(CO)_5}$ were removed in vacuum. The residual oil was separated by TLC to give **10** (43.2 mg, 0.0885 mmol), **11** (11.5 mg, 0.0236 mmol), and the mixture (21.0 mg) of **12** and **7**.

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15) This enables us to assign the H_6 methylene proton signals in NMR spectra of these complexes. Since H_{6N} signal of **10** is located at 1.71, the higher field signal (1.25 in **4** and 1.37 in **12**) and the lower field signal (2.10 in **4** and 1.73 in **12**) can be assigned to those of H_{6N} and H_{6N}, respectively, by considering the substituent effect of the trimethylsilyl group on the chemical shift of H_{6N}. The chemical shift of H_6 signal is almost the same in **5** and **11**, and this shows that the configuration of H_6 should be same in these two complexes. On considerations of the effect of the α-phenyl group on the chemical shift of the H_6 signal, H_6 is reasonably assigned to be endo in both **5** and **11**.