Novel Reaction of Silyl Carbonyl Complexes with Hydride-Transfer Reagents: Reduction of a Carbonyl Ligand and Coupling with a Silyl Group

Rie Shiozawa, Hiromi Tobita,* and Hiroshi Ogino*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Received March 20, 1998

Treatment of $CpFe(CO)_2SiR_3$ ($Cp = \eta^5$-C_5H_5; $R_3 = {}^pTol_2Cl$, ${}^pTol_2H$, ${}^pTol_2Me$, MePh(1-Nap), and $(n$-$C_5H_{11})_2H$; 1-Nap = 1-naphthyl) with $LiAlH_4$ in ether or THF at room temperature gave CH_3SiR_3 as the major product in moderate to high yield together with $HSiR_3$. Reaction of $CpFe(CO)_2SiMes_2H$ with $LiAlH_4$ afforded only H_2SiMes_2. Labeling experiments using $LiAlD_4$ gave the deuterated methylsilanes. These results proved that the hydrogen source for the methyl group is $LiAlH_4$. Furthermore, the reduction of $CpFe(*CO)_2Si^pTol_2R'$ ($*C = {}^{13}C$ enriched; $R' = H$, Me) produced $*CH_3Si^pTol_2R'$ where the methyl group introduced on Si was ^{13}C-enriched. These experimental results suggested that the carbonyl ligand was reduced by $LiAlH_4$ and coupled with the silyl group to give the methylsilane. $Cp^*Fe(CO)_2Si^pTol_2H$ ($Cp^* = \eta^5$-C_5Me_5), having a Cp* ligand which is bulkier and more electron-donating than a Cp ligand, did not react with $LiAlH_4$ at room temperature, but it did so at 50 °C to give $CH_3Si^pTol_2H$ and HSi^pTol_2H, probably because nucleophilic attack of $LiAlH_4$ at a carbonyl ligand was retarded both sterically and electronically by the Cp* ligand. When the reactions were performed in sealed NMR tubes and monitored by NMR spectroscopy, the signals due to the anionic complexes $Li^+[CpFe(CO)(CH_3)Si^pTol_2R']^-$ were observed in addition to those of silane products. These anionic complexes are considered *not* to be intermediates but to be byproducts because the anionic complexes did not change to methylsilanes on heating. The anionic complexes reacted with MeOH and MeI to give hydrosilanes HSi^pTol_2R' and methylsilanes $CH_3Si^pTol_2R'$, respectively.

Introduction

Reactions of hydride-transfer reagents with transition-metal carbonyl complexes have attracted much attention. They usually give transition-metal hydrides,[1] transition-metal anions,[2] and formyl−transition-metal complexes,[3] but there are also a few examples reported in which a carbonyl ligand is further reduced to a methyl group. Thus, Treichel and Shubkin reported that $[CpM(CO)_3PPh_3]PF_6$ (M = Mo, W) reacted with $NaBH_4$ in THF to give $CpM(CO)_2PPh_3(CH_3)$.[4] The reduction of carbonyl ligands by hydride-transfer reagents accompanied by subsequent C−C coupling also was reported: Wong and Atwood found that treatment of $Cp_2Fe_2(CO)_4$ with $LiAlH_4$ produced CH_4, $CH_2{=}CH_2$, CH_3CH_3, $CH_2{=}CHCH_3$, $CH_3CH_2CH_3$, C_4H_8, and C_4H_{10}.[5] The exact ratio depended on the amount of $LiAlH_4$ used and the reaction time. Employment of $LiAlD_4$ resulted in formation of CD_3CH_3. Treatment of potential intermediates $CpFe(CO)_2R$ ($R = CH_3$, C_2H_5, CH_3CO) with $LiAlH_4$ produced CH_3CH_3 mainly. These reactions also occurred with $NaBH_4$ or $LiBEt_3H$, and the reactivity for the reduction of a carbonyl ligand decreased in the order $LiAlH_4 > NaBH_4 > LiBEt_3H$. van der Woude *et al.* also observed the reduction of carbonyl ligands in $M_n(CO)_m$ ($n = 1$, $m = 6$, M = Cr, Mo, W; $n = 3$, $m = 12$, M = Ru) by $LiAlH_4$, AlH_3/THF, or BH_3/THF to hydrocarbons with chain lengths up to C_4.[6]

With regard to (silyl)carbonyliron complex $CpFe(CO)_2$-SiMePh(1-Nap), reaction with hydride-transfer reagents was reported to result in substitution of the $CpFe(CO)_2$ moiety with a hydride to give the corresponding hydrosilane HSiMePh(1-Nap),[7a] but CO reduction was not demonstrated. Reactions of other metal complexes such as $Co(CO)_4SiPh_3$,[7b] $Co(CO)_4SiMePh$(1-Nap),[7c] (η^5-MeCp)$Mn(CO)_2(H)$SiMePh(1-Nap),[7d] and $Mn(CO)_5SiMePh$-(1-Nap)[7e] with $LiAlH_4$ also produced the corresponding hydrosilanes.

Recently we found a novel reaction of (silyl)carbonyliron complexes $CpFe(CO)_2SiR_3$ with $LiAlH_4$ which gave methylsilanes CH_3SiR_3, the mechanism of which involves the reduction of a CO ligand and migration to the Si atom.[8] We report herein the reactions of several

---

[1] Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

[2] Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

[3] Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

[4] Treichel, P. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328.

[5] (a) Wong, A.; Atwood, J. D. *J. Organomet. Chem.* **1980**, *199*, C9. (b) Wong, A.; Atwood, J. D. *J. Organomet. Chem.* **1981**, *210*, 395.

[6] van der Woude, C.; van Doorn, J. A.; Masters, C. *J. Am. Chem. Soc.* **1979**, *101*, 1633.

[7] (a) Cerveau, G.; Colomer, E.; Corriu, R. J. P.; Douglas, W. E. *J. Organomet. Chem.* **1977**, *135*, 373. (b) Colomer, E.; Corriu, R. J. P.; Vioux, A. *J. Chem. Soc., Chem. Commun.* **1976**, 175. (c) Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.* **1977**, *139*, 159. (d) Colomer, E.; Corriu, R. J. P.; Vioux, A. *Inorg. Chem.* **1979**, *18*, 159. (e) Cerveau, G.; Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.* **1982**, *236*, 33.

S0276-7333(98)00211-8 CCC: $15.00 © 1998 American Chemical Society
Publication on Web 07/03/1998

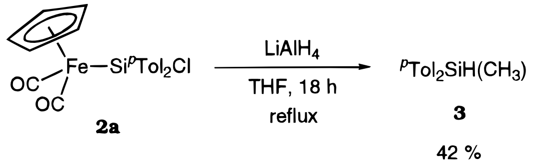
Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 3, 1998 on http://pubs.acs.org | doi: 10.1021/om9802111

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 3, 1998 on http://pubs.acs.org | doi: 10.1021/om9802111

(silyl)carbonyliron complexes having different ligands and substitutions with $LiAlH_4$ and some other hydride-transfer reagents.

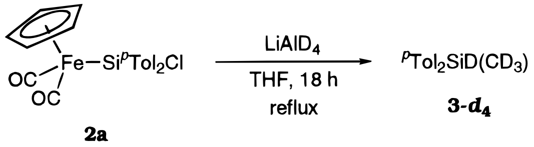
Results and Discussion

Reactions of $CpFe(CO)_2Si^{p}Tol_2Cl$ (2a) with $LiAlH_4$. Treatment of **2a** with an excess of $LiAlH_4$ in refluxing THF afforded $^{p}Tol_2SiH(CH_3)$ (**3**) in 42% yield (eq 1). The formation of a methylsilane was unexpected because a number of closely related reactions had been reported to give different products: reduction of chlorosilyl−metal complexes $Cp'M(CO)_nSiCl_mR_{3-m}$ ($Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$; $n = 3$, M = Mo, W; $n = 2$, M = Fe, Ru; R = H, alkyl, aryl) to hydrosilyl−metal complexes $Cp'M(CO)_nSiH_mR_{3-m}$ with $LiAlH_4$ has been reported by Malisch.[9] Moreover, the nucleophilic substitution of the $CpFe(CO)_2$ fragment by hydride on $CpFe(CO)_2SiR_3$[7] has been well-established by Corriu *et al.* In our case, the reaction in eq 1 required more forcing conditions than Malisch's reactions. This is probably because the nucleophilic attack of $LiAlH_4$ at the Si atom in **2a** was inhibited by the bulky substituents, ^{p}Tol and Cl.



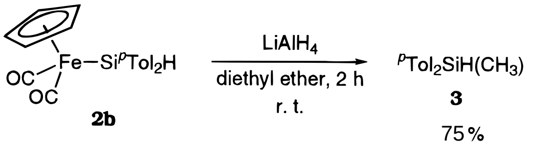
(1)

The reaction of **2a** with $LiAlD_4$ produced $^{p}Tol_2SiD(CD_3)$ (**3-*d*$_4$**; ~100%D) (eq 2). The formation of **3-*d*$_4$** unambiguously proved that the hydrogen source for the methyl group on the Si atom is $LiAlH_4$. A possible intermediate in the formation of **3** is the hydrosilyliron complex $CpFe(CO)_2Si^{p}Tol_2H$ (**2b**). Thus, we next examined the reaction of **2b** with several other hydride-transfer reagents.



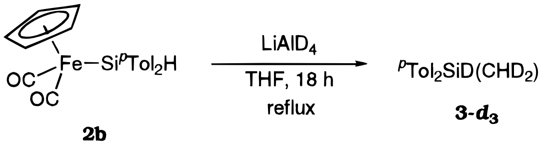
(2)

Reactions of $CpFe(CO)_2Si^{p}Tol_2H$ (2b) with Hydride-Transfer Reagents. $CpFe(CO)_2Si^{p}Tol_2H$ (**2b**) was synthesized by reaction of $^{p}Tol_2SiHCl$ (**1b**) with $K[CpFe(CO)_2]$. The reaction of **2b** with $LiAlH_4$ proceeded at room temperature in diethyl ether to give **3** in 75% yield (eq 3). The yield of **3** was 48% in refluxing THF and 21% in refluxing DME.



(3)

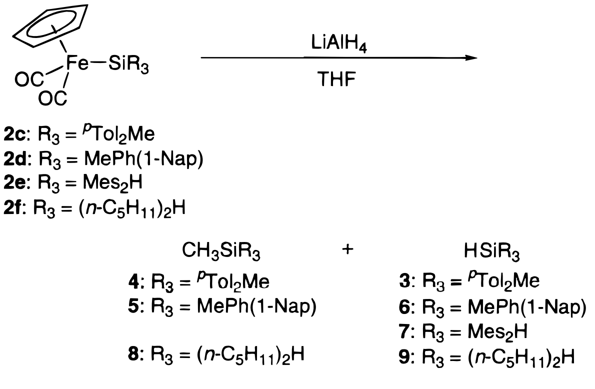
Interestingly, the reaction of **2b** with $LiAlD_4$ exclusively produced $^{p}Tol_2SiD(CHD_2)$ (**3-*d*$_3$**), which was characterized by its ^{1}H NMR spectrum showing the Si−C*H*D$_2$ signal at 0.51 ppm as a quintet ($^2J_{HD} = 2.0$ Hz) and the mass spectrum showing the molecular ion peak at *m*/*z* 229 (eq 4). This result suggests that the source of two of the hydrogen atoms of the methyl group in **3** is $LiAlH_4$, while the third hydrogen on the silyl group may migrate from Si to the carbonyl carbon during the course of the reaction.



(4)

Employment of $NaBH_4$, $LiBEt_3H$, or KH as a hydride-transfer reagent in refluxing THF did not convert **2b** to the methyl- or hydride-substituted silanes but resulted in partial recovery of **2b** and formation of $Cp_2Fe_2(CO)_4$ and some unidentified products. Use of $Na[(CH_3OCH_2CH_2O)_2AlH_2]$ or DIBAL-H (diisobutylaluminum hydride) gave no reaction. This implies that these reagents are not strong enough either to reduce the carbonyl ligand to a methyl group or to attack the silyl group nucleophilically.

Reactions of (Silyl)carbonyliron Complexes Having Various Substituents on the Si Atom with $LiAlH_4$. To investigate the generality of the formation of a methylsilane, we synthesized (silyl)carbonyliron complexes having various substituents on the Si atom and carried out reactions of these with $LiAlH_4$ (eq 5).



(5)

Table 1 summarizes the reaction conditions, products, and their yields. Reactions of **2c**, **2d**, and **2f** with $LiAlH_4$ produced not only the corresponding methylsilanes CH_3SiR_3 but also hydrosilanes $HSiR_3$, and in the case of **2e**, only the hydrosilane Mes_2SiH_2 (**7**) was formed. Corriu *et al.* reported the formation of only the hydrosilane HSiMePh(1-Nap) (**6**) in the reaction of **2d** with $LiAlH_4$ in diethyl ether, but in our case, we observed the formation of an appreciable amount of a methylsilane, CH_3SiMePh(1-Nap) (**5**), together with HSiMePh(1-Nap) (**6**). These results seem to indicate that the ratio of methylated product to hydrogenated product increases as the bulkiness of substituents on the silicon atom decreases.

---

[8] Tobita, H.; Shiozawa, R.; Ogino, H. *Chem. Lett.* **1997**, 805.

[9] (a) Wekel, H.-U.; Malisch, W. *J. Organomet. Chem.* **1984**, *264*, C10. (b) Malisch, W.; Lankat, R.; Schmitzer, S.; Pikl, R.; Posset, U.; Kiefer, W. *Organometallics* **1995**, *14*, 5622. (c) Malisch, W.; Neumayer, M.; Fey, O.; Adam, W.; Schuhmann, R. *Chem. Ber.* **1995**, *128*, 1257. (d) Möller, S.; Fey, O.; Malisch, W.; Seelbach, W. *J. Organomet. Chem.* **1996**, *507*, 239. (e) Malisch, W.; Lankat, R.; Seelbach, W.; Reising, J.; Noltemeyer, M.; Pikl, R.; Posset, U.; Kiefer, W. *Chem. Ber.* **1995**, *128*, 1109. (f) Malisch, W.; Möller, S.; Fey, O.; Wekel, H.-U.; Pikl, R.; Posset, U.; Kiefer, W. *J. Organomet. Chem.* **1996**, *507*, 117.

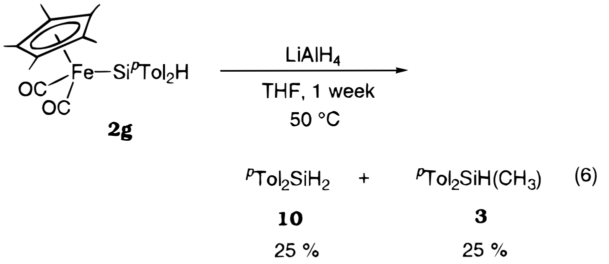
Table 1. Reaction of (Silyl)iron Complexes 2a−g with $LiAlH_4$

complex	reacn conditions	product yield (%)	
		$HSiR_3$	CH_3SiR_3
$CpFe(CO)_2Si^pTol_2Cl$ (**2a**)	THF, reflux, 18 h		42
$CpFe(CO)_2Si^pTol_2H$ (**2b**)	ether, room temp, 2 h		75
$CpFe(CO)_2Si^pTol_2Me$ (**2c**)	THF, room temp, 2 h	32	64
$CpFe(CO)_2SiMePh(1\text{-}Nap)$ (**2d**)	ether, room temp, 48 h	14	72
$CpFe(CO)_2SiMePh(1\text{-}Nap)$ (**2d**)	THF, room temp, 20 h	26	26
$CpFe(CO)_2SiMes_2H$ (**2e**)	THF, room temp, 16 h	65	
$CpFe(CO)_2Si(n\text{-}C_5H_{11})_2H$ (**2f**)	THF, room temp, 46 h	5.3	42
$Cp^*Fe(CO)_2Si^pTol_2H$ (**2g**)	THF, 50 °C, 1 week	25	25

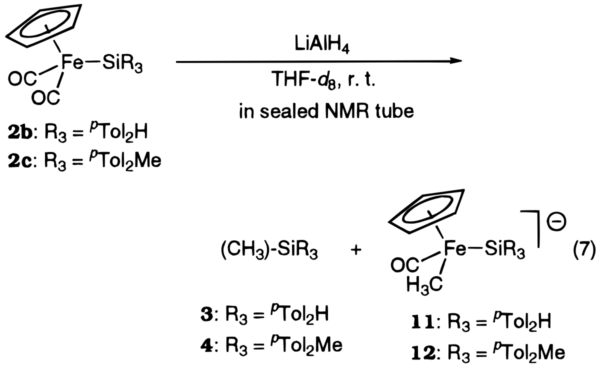
Treatment of **2c** with $LiAlD_4$ yielded $^pTol_2SiMe(CD_3)$ (**3-*d*$_3$**; ~100%D) and $^pTol_2SiDMe$ (**3-*d***; ~100%D) in 63 and 37% yields, respectively. In this case, all the three hydrogens of the methyl group in **3-*d*$_3$** are deuterated, since a Si−H bond was not present in **2c**.

Employment of $Na[(CH_3OCH_2CH_2O)_2AlH_2]$ or DIBAL-H as a hydride-transfer reagent in a sealed tube also did not convert **2c** to the methyl- or hydride-substituted silanes.

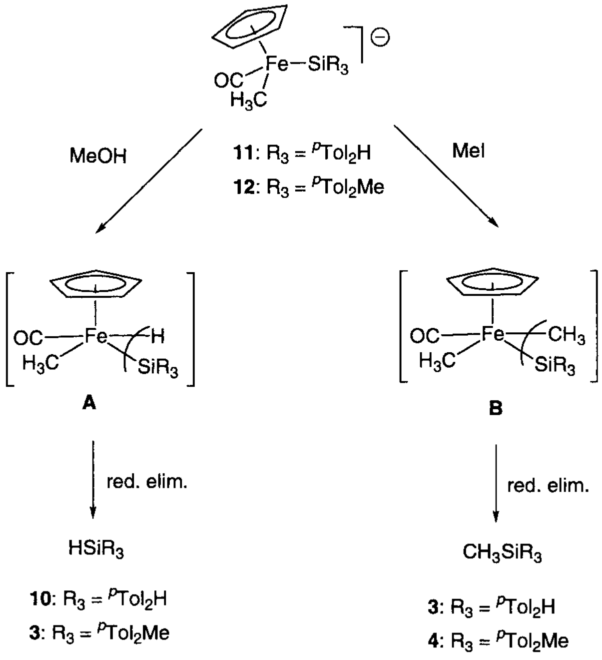
Reaction of $Cp^*Fe(CO)_2Si^pTol_2H$ (2g) with $LiAlH_4$. The reaction of **2g**, which contains a Cp* (=η^5-C_5Me_5) ligand which is bulkier and more electron-donating than a Cp ligand, did not proceed at room temperature but did so on heating at 50 °C to give not only **3** but also hydrosilane $^pTol_2SiH_2$ (**10**) (eq 6). This result can be explained by the following factors. (1) The carbonyl ligands on **2g** are less vulnerable to nucleophiles than those on **2b** because a Cp* ligand is much more electron-donating than a Cp ligand. This is clearly reflected in the shift of ν(CO) values to the lower wavenumber side in the IR spectra (**2b**, 1988, 1934 cm^{-1}; **2g**, 1978, 1917 cm^{-1}). (2) The carbonyl ligands on **2g** are sterically protected against attack of $LiAlH_4$ by the bulky Cp* ligand more effectively than by a Cp ligand in **2b**.



NMR Tube Reactions. The reaction of **2b** with $LiAlH_4$ in THF-d_8 in a sealed NMR tube showed, besides the signals due to **3**, those of another product which can be assigned to the anionic complex $Li[CpFe(CO)(CH_3)Si^pTol_2H]$ (**11**) (eq 7). The molar ratio of **3** to **11** was *ca.* 1:2. A similar reaction of **2c** with $LiAlH_4$ gave **4** and $Li[CpFe(CO)(CH_3)Si^pTol_2Me]$ (**12**) in a *ca.* 16:1 molar ratio. In the latter case, unlike the reaction in an open system under nitrogen, only a trace amount of **3** was observed by ^1H and ^{29}Si NMR spectroscopy. The reason for the difference so far is unclear. The ^1H and ^{13}C NMR signals of the Fe-*Me* groups in **11** and **12** appear at fairly high field (^1H NMR, −0.71 (**11**), −0.65 ppm (**12**); ^{13}C NMR, −23.5 (**11**), −24.6 ppm (**12**)). All other ^1H NMR signals of **11** and **12** except those of *p*-tolyl groups also are shifted to higher field compared to the corresponding signals of **2b** and **2c**, respectively. These high-field shifts of ^1H NMR signals are consistent with the anionic character of **11** and **12**.



Scheme 1



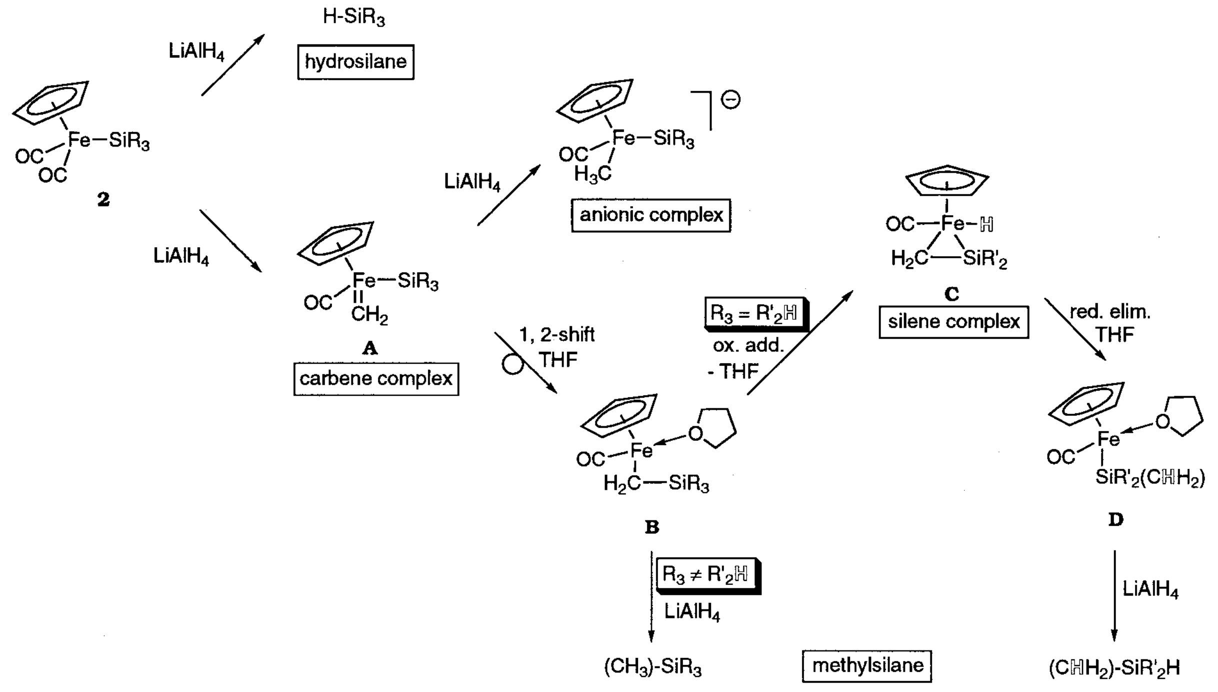
Besides this spectroscopic evidence, the reactions of **11** and **12** with MeOH or MeI afforded further evidence for the structures. Addition of MeOH to the NMR tube reaction mixture containing **11** or **12** caused exclusive conversion of the anionic species to $^pTol_2SiH_2$ (**10**) or $^pTol_2SiH(CH_3)$ (**3**), respectively. In a similar manner, addition of MeI resulted in the formation of **3** or $^pTol_2SiMe_2$ (**4**), respectively. These results can be rationalized by a mechanism involving nucleophilic attack of the anionic iron center on these reagents followed by reductive elimination from the resulting neutral intermediate **A** or **B** (Scheme 1).

The reductive elimination of silanes from the neutral Fe(IV) species **A** and **B** would be much easier than that from more electron-rich and lower valent anionic Fe-

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 3, 1998 on http://pubs.acs.org | doi: 10.1021/om9802111

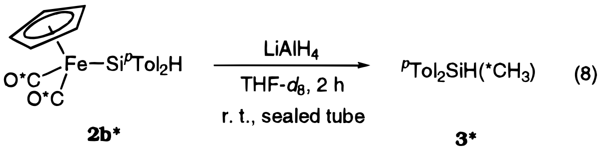
Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 3, 1998 on http://pubs.acs.org | doi: 10.1021/om9802111

Scheme 2



(II) species **11** and **12**. The formation of hydrosilanes instead of methylsilanes on treatment with MeOH may be attributable to the more facile reductive elimination of Si−H compared with Si−Me species.[10] Even on heating to the boiling point of THF-d_8, the conversion of **11** or **12** in the reaction mixture to the methylated product **3** or **4** was not observed. This result suggests that **11** and **12** are *not* the intermediates in the formation of methylsilanes.

^{13}C-Labeling Experiments. The conversion of a carbonyl ligand in **2b** to a methyl group in **3** was further confirmed by the ^{13}C-labeling experiments. Reaction of CpFe(*CO)$_2$Si^{p}Tol$_2$H (**2b***) (*C = a carbon atom enriched with ^{13}C to 32%) with LiAlH$_4$ produced **3***, in which the methyl carbon was enriched with ^{13}C (eq 8). The ^{1}H NMR signal of the Si-^{13}CH_3 of **3*** appeared at 0.53 ppm as a double doublet coupled with ^{13}C and Si−H ($^1J_{CH}$ = 120.4, $^3J_{HH}$ = 3.7 Hz). Similarly, reaction of CpFe(*CO)$_2$-Si^{p}Tol$_2$Me (**2c***) (*C = a carbon atom enriched with ^{13}C to 46%) with LiAlH$_4$ afforded ^{13}C-enriched ^{p}Tol$_2$SiMe(*CH$_3$) (**4***).



(8)

Possible Mechanism. Because of a number of technical problems, we have not yet succeeded in observing the intermediates of this complicated reaction. At present, we can only suggest the possible mechanism illustrated in Scheme 2, which is consistent with the above-mentioned experimental results.

Because the formation of substantial amounts of CH$_3$-SiR$_3$ and HSiR$_3$ was observed in a sealed tube, a mechanism involving their formation by hydrolysis of unstable products during workup can be ruled out. Moreover, as mentioned above, the anionic complex Li[CpFe(CO)(CH$_3$)SiR$_3$] is not an intermediate in the formation of CH$_3$SiR$_3$, so that the direct reductive elimination of CH$_3$SiR$_3$ from this anionic complex can be ruled out. On the basis of these facts, we assume a 1,2-silyl shift on the silyl−methylene complex **A** to form silylmethyl complex **B**. From **B**, if complex **B** has an Si−H bond, that is, R$_3$ = R′$_2$H, the oxidative addition of the Si−H bond of **B** occurs to give the silene complex **C**. This complex subsequently undergoes reductive elimination of a C−H bond to produce the THF-coordinated methylsilyl complex **D**. This type of rearrangement already has been reported by Pannell[11] and Wrighton.[12] Finally, nucleophilic attack of LiAlH$_4$ at the Si atom of **D** occurs to afford the methylsilane. This mechanism reasonably explains the incorporation of one hydrogen atom into a deuterated methyl group by the reaction of **2b** with LiAlD$_4$, giving ^{p}Tol$_2$SiD(CHD$_2$) (**3-*d*$_3$**). If complex **B** does not have an Si−H bond, a carbon of the methylene group in **B** is attacked by LiAlH$_4$ to yield the methylsilane.

Conclusion

(Silyl)carbonyliron complex Cp′Fe(CO)$_2$SiR$_3$ (**2**) reacts with LiAlH$_4$ to give not only the hydrosilane HSiR$_3$ but also the methylsilane CH$_3$SiR$_3$ *via* the reduction of the CO ligand and subsequent migration. The facility of this reaction and the ratio of products depend on the steric and the electronic properties of the Cp′ ligand and the bulkiness of the substituents on the silicon atom. We propose a possible mechanism for the formation of CH$_3$SiR$_3$ involving a 1,2-silyl shift on a (silyl)methyleneiron intermediate to give a (silylmethyl)iron complex, followed by the substitution of the iron fragment by H$^-$.

---

[10] (a) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.* **1993**, *115*, 2373. (b) Okazaki, M.; Tobita, H.; Ogino, H. *Organometallics* **1996**, *15*, 2790.

[11] Pannell, K. H. *J. Organomet. Chem.* **1970**, *21*, 17.

[12] Randolph, C. L.; Wrighton, M. S. *Organometallics* **1987**, *6*, 365.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 3, 1998 on http://pubs.acs.org | doi: 10.1021/om9802111

Experimental Section

General Remarks. All manipulations were carried out under a dry nitrogen atmosphere using Schlenk-tube techniques. Reagent-grade toluene, hexane, diethyl ether, benzene, DME (dimethoxyethane), and THF were distilled from sodium–benzophenone ketyl immediately before use. Benzene-d_6 and THF-d_8 were dried over a potassium mirror and transferred into an NMR tube under vacuum. $Cp_2Fe_2(CO)_4$,[13] $^{p}Tol_2SiCl_2$ (**1a**),[14] $K[CpFe(CO)_2]$,[15] $Na[CpFe(CO)_2]$,[16] $CpFe(CO)_2SiMe_3$,[17] $CpFe(CO)_2SiMePh$(1-Nap) (**2d**),[18] and $CpFe(CO)_2SiMes_2H$ (**2e**)[19] were prepared according to the literature procedures. $LiAlH_4$ and $NaBH_4$ were purchased from Kanto Chemical Co., Inc.; $LiBEt_3H$, $NaBH_3CN$, DIBAL-H (diisobutylaluminum hydride), $Na[(CH_3OCH_2CH_2O)_2AlH_2]$, and ^{13}CO were purchased from Aldrich. Other chemicals were purchased from Wako Pure Chemical Industries, Ltd., and used as received. NMR spectra were recorded on a Bruker ARX-300 spectrometer. ^1H, ^{13}C, and ^{29}Si NMR data were referenced to $SiMe_4$. ^{29}Si NMR spectra were obtained using the DEPT pulse sequence. IR spectra were recorded on a Horiba FT-200 spectrometer. Mass spectra were recorded on a Hitachi M-2500S mass spectrometer and a Shimadzu GCMS-QP5050A mass spectrometer.

Preparation of $CpFe(CO)_2Si^{p}Tol_2Cl$ (2a). A THF (50 mL) solution of $Cp_2Fe_2(CO)_4$ (1.01 g, 2.85 mmol) was stirred for 2 h over $NaK_{2.8}$ alloy (3.4 mmol) prepared from Na (79.0 mg, 3.44 mmol) and K (372 mg, 9.51 mmol). The solution of $K[CpFe(CO)_2]$ thus obtained was cooled to −43 °C; then $^{p}Tol_2SiCl_2$ (**1a**) (1.85 g, 6.57 mmol, 94% purity) was added to it. The mixture was stirred at room temperature, and the reaction was monitored by silica gel TLC (1/3 benzene/hexane as eluent). After 17 h, the solvent was removed from the reaction mixture under reduced pressure. The residue was extracted with hexane (100 mL); then the extract was filtered through a Celite pad under a nitrogen atmosphere. The filtrate was evaporated under reduced pressure, and the residue was purified by silica gel flash chromatography (36 mm o.d. × 270 mm) with 1/3 benzene/hexane as eluent to give **2a** (1.15 g, 2.71 mmol) as a yellow powder in 48% yield. ^1H NMR (300 MHz, C_6D_6): δ 2.07 (s, 6H, p-$CH_3C_6H_4$), 4.09 (s, 5H, η^5-C_5H_5), 7.05−7.08, 7.86−7.89 (AB q, J = 8.1 Hz, 4H × 2, p-$CH_3C_6H_4$). ^{13}C NMR (75.5 MHz, C_6D_6): δ 21.3 (p-$CH_3C_6H_4$), 85.3 (η^5-C_5H_5), 128.9, 134.2, 135.0, 139.9 (p-$CH_3C_6H_4$), 214.3 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 70.8. IR (cm^{-1}, KBr): ν(CO) 2015, 1963. Mass (EI, 70 eV): m/z 422 (M^+, 1), 394 ($M^+ - CO$, 5), 366 ($M^+ - 2CO$, 100), 245 ($M^+ - CpFe(CO)_2$, 60). Anal. Found: C, 59.92; H, 5.10. Calcd for $C_{21}H_{19}ClFeO_2Si$: C, 59.66; H, 4.93.

Preparation of $CpFe(CO)_2Si^{p}Tol_2H$ (2b). A 2 L four-necked flask was equipped with a condenser, a mechanical stirrer, and a dropping funnel. A THF solution of $^{p}TolMgCl$ (3.76 M, 450 mL, 1.69 mol) placed in the funnel was added dropwise to $SiHCl_3$ (117 g, 0.86 mol) in THF (150 mL) over 2 h; then the solution was refluxed for an additional 2 h. After the reaction mixture was cooled to room temperature, it was filtered and the salt was washed with diethyl ether (50 mL × 3). The filtrate was distilled under reduced pressure to give $^{p}Tol_2SiHCl$ (**1b**; 27.6 g, 0.112 mol, 12%) as a colorless oil. Bp: 133 °C/1 mmHg. ^1H NMR (300 MHz, C_6D_6): δ 2.01 (s, 6H, p-$CH_3C_6H_4$), 5.89 (s, 1H, Si-H), 6.93−6.96, 7.53−7.56 (AB q, J = 8.1 Hz, 4H × 2, p-$CH_3C_6H_4$). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT): δ −4.83.

Complex **2b** was prepared from **1b** (1.76 g, 7.14 mmol) and $K[CpFe(CO)_2]$ (0.144 M in THF, 50 mL, 7.18 mmol) in the same manner as that used for **2a**. **2b** (1.35 g, 3.47 mmol) was obtained as a yellow powder in 73% yield. ^1H NMR (300 MHz, C_6D_6): δ 2.12 (s, 6H, p-$CH_3C_6H_4$), 4.05 (s, 5H, η^5-C_5H_5), 6.02 (s, 1H, Si-H), 7.05−7.08, 7.86−7.89 (AB q, J = 8.1 Hz, 4H × 2, p-$CH_3C_6H_4$). ^{13}C NMR (75.5 MHz, THF-d_8): δ 21.3 (p-$CH_3C_6H_4$), 85.3 (η^5-C_5H_5), 129.0, 135.3, 138.5, 148.9 (p-$CH_3C_6H_4$), 215.6 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT): δ 26.2. IR (cm^{-1}, KBr pellet): ν(Si−H) 2096, ν(CO) 1988, 1934. Mass (EI, 70 eV): m/z 388 (M^+, 1), 360 ($M^+ - CO$, 32), 332 ($M^+ - 2CO$, 100), 211 ($M^+ - CpFe(CO)_2$, 30). Anal. Found: C, 64.83; H, 5.36. Calcd for $C_{21}H_{20}FeO_2Si$: C, 64.95; H, 5.19.

Preparation of $CpFe(^{*}CO)_2Si^{p}Tol_2H$ (2b*; *C = Carbon Atom Enriched with ^{13}C). A Pyrex tube (18 mm o.d.) was charged with **2b** (60 mg, 155 μmol) and connected to a vacuum line. Pentane (20 mL) degassed on the vacuum line by a freeze−pump−thaw method was added by a trap-to-trap-transfer technique to it. Then the tube was filled with ^{13}CO. The tube was sealed with a Teflon stopcock, and the mixture was irradiated with a 450 W medium-pressure Hg lamp at 14 °C. The color of the solution changed from yellow to red during irradiation. After 5 min, the solvent was removed in vacuo and the residue was purified by silica gel flash chromatography (24 mm o.d. × 120 mm) with 1/1 benzene/hexane as eluent to give $CpFe(^{*}CO)_2Si^{p}Tol_2H$ (**2b***; 29 mg, 72.5 μmol, 32% enriched with ^{13}CO)[20] in 48% yield and *cis*- and *trans*-$Cp_2Fe_2(^{*}CO)_2(\mu$-$^{*}CO)(\mu$-$Si^{p}Tol_2)$ (**14***; 75 mg, 209 μmol) in 27% yield. **14*** in solution underwent thermal *cis*−*trans* isomerization at room temperature, and on the basis of the relative intensity of the methyl signals in p-tolyl groups, the ratio of isomers in equilibrium was determined to be ***cis*-14***:***trans*-14*** = 4:5 at room temperature. **14*** was identified by comparing the spectroscopic data with those of the unlabeled authentic sample of **14** synthesized as follows. A mixture of $^{p}Tol_2SiH_2$ (**10**; 640 mg, 3.02 mmol) and $CpFe(CO)_2SiMe_3$ (1.51 g, 6.04 mmol) was dissolved in pentane (40 mL), and the solution was irradiated with a 450 W medium-pressure Hg lamp at 4 °C. The yellow solution changed to red with evolution of CO, and a red powder precipitated out during irradiation. The mother liquor was removed via a cannula, and the precipitate was washed with pentane (20 mL) and then dried under vacuum to give **14** (674 mg, 1.26 mmol) as a red powder in 42% yield. ^1H NMR (300 MHz, C_6D_6): δ 2.05, 2.22 (s, 3H × 2, p-$CH_3C_6H_4$ of ***cis*-14**), 2.19 (s, 6H, p-$CH_3C_6H_4$ of ***trans*-14**), 4.27 (s, 10H, η^5-C_5H_5 of ***cis*-14**), 4.31 (s, 10H, η^5-C_5H_5 of ***trans*-14**), 7.03−7.05, 7.26−7.29, 7.38−7.41, 7.76−7.78 (AB q, J = 8.1 Hz, 2H × 4, p-$CH_3C_6H_4$ of ***cis*-14**), 7.15−7.18, 7.85−7.88 (AB q, J = 8.1 Hz, 4H × 2, p-$CH_3C_6H_4$ of ***trans*-14**). ^{13}C NMR (75.5 MHz, C_6D_6): δ 20.9, 21.4 (p-$CH_3C_6H_4$ of ***cis*-14**), 21.3 (p-$CH_3C_6H_4$ of ***trans*-14**), 85.7, 86.6 (Cp), 128.7, 136.2, 138.3, 146.9 (p-$CH_3C_6H_4$ of ***trans*-14**), 128.2, 128.9, 136.1, 136.5, 138.8, 138.8, 144.4, 147.9 (p-$CH_3C_6H_4$ of ***cis*-14**), 213.1, 214.2 (terminal CO), 276.2, 277.5 (bridging CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 220.7, 234.4. IR (cm^{-1}, KBr pellet): ν(terminal CO) 1956, 1921, ν(bridging CO) 1751. Mass (EI, 70 eV): m/z 536 (M^+, 8), 508 ($M^+ - CO$, 7), 480 ($M^+ - 2CO$, 73), 452 ($M^+ - 3CO$, 100). Exact mass: calcd for $C_{27}H_{24}Fe_2O_3Si$ 536.0194, found 536.0164.

Preparation of $CpFe(CO)_2Si^{p}Tol_2Me$ (2c). Chlorosilane $^{p}Tol_2SiMeCl$ (**1c**) was prepared from $^{p}TolMgCl$ (5.25 M in THF, 200 mL, 1.05 mol) and $SiMeCl_3$ (78.3 g, 0.52 mol) in a manner analogous to that used for **1b**. Distillation under reduced pressure gave the colorless liquid **1c** (77.6 g, 0.297 mol) in 57% yield, bp 121 °C/0.15 mmHg. ^1H NMR (300 MHz, C_6D_6): δ 0.92 (s, 3H, Si−CH_3), 2.39 (s, 6H, p-$CH_3C_6H_4$), 7.23−7.25,

---

(13) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 110.
(14) Steel, A. R.; Kipping, F. S. *J. Chem. Soc.* **1929**, 357.
(15) Ellis, J. E.; Folm, E. A. *J. Organomet. Chem.* **1975**, *99*, 263.
(16) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.
(17) King, R. B.; Pannell, K. H. *Inorg. Chem.* **1968**, *7*, 1510.
(18) Cerveau, G.; Colomer, E.; Corriu, R. J. P.; Douglas, W. E. *J. Chem. Soc., Chem. Commun.* **1975**, 410.
(19) Tobita, H.; Izumi, H.; Ohnuki, S.; Ellerby, M. C.; Kikuchi, M.; Inomata, S.; Ogino, H. *J. Am. Chem. Soc.* **1995**, *117*, 7013.

(20) The ^{13}C contents in the carbonyl ligands in **2b*** and **2c*** were determined after conversion of them to $Li[CpFe(^{*}CO)(^{*}CH_3)Si^{p}Tol_2R]$ (**11***; R = H, **12***; R = CH_3) by treatment with $LiAlH_4$. The ^{13}C contents in the Fe−$^{*}CH_3$ groups in **11*** and **12*** determined from the ^1H NMR spectra correspond to those in the carbonyl ligands in **2b*** and **2c***.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 3, 1998 on http://pubs.acs.org | doi: 10.1021/om9802111

7.54−7.56 (AB q, $J = 8.1$ Hz, 4H × 2, p-$CH_3C_6H_4$). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT): δ 10.8.

A THF solution of K[CpFe(CO)$_2$] (0.244 M, 50 mL, 12.2 mmol) was cooled to −43 °C; then **1c** (3.35 g, 12.8 mmol) was added to it. The mixture was stirred at room temperature and the reaction was monitored by silica gel TLC (1/3 benzene/hexane as eluent). After 17 h, the solvent was removed from the reaction mixture under reduced pressure. The residue was extracted with hexane (100 mL), the extract filtered through a Celite pad under a nitrogen atmosphere, and the filtrate evaporated under reduced pressure. The residue was purified by silica gel flash chromatography (60 mm o.d. × 300 mm) with 1/3 benzene/hexane as eluent to give **2c** (1.74 g, 4.34 mmol) as a yellow powder in 60% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 1.01 (s, 3H, Si−CH_3), 2.15 (s, 6H, p-C$H_3C_6H_4$), 4.02 (s, 5H, η^5-C_5H_5), 7.10−7.12, 7.67−7.69 (AB q, $J = 8.1$ Hz, 4H × 2, p-$CH_3C_6H_4$). ^{13}C NMR (75.5 MHz, C_6D_6): δ 5.70 (Si−CH_3), 21.3 (p-$CH_3C_6H_4$), 84.4 (η^5-C_5H_5), 128.9, 134.7, 137.9, 141.2 (p-$CH_3C_6H_4$), 216.0 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT): δ 34.8. IR (cm^{-1}, KBr pellet): ν(CO) 1992, 1940. Mass (EI, 70 eV): m/z 402 (M$^+$, 1), 374 (M$^+$ − CO, 6), 346 (M$^+$ − 2CO, 21), 225 (M$^+$ − CpFe(CO)$_2$, 100). Anal. Found: C, 65.87; H, 5.68. Calcd for $C_{22}H_{22}FeO_2Si$: C, 65.67; H, 5.51.

Preparation of CpFe(*CO)$_2$Si^{p}Tol$_2$Me (2c*). In a manner analogous to the preparation of **2b***, a pentane (40 mL) solution of **2c** (106 mg, 264 μmol) in a Pyrex tube (18 mm o.d.) was irradiated with a 450 W medium-pressure Hg lamp under ^{13}CO atmosphere at 14 °C. After 15 min, the solvent was removed in vacuo. The residue was purified by recrystallization from toluene/hexane to give CpFe(*CO)$_2$Si^{p}Tol$_2$Me (**2c***; 80 mg, 198 μmol, 46% enriched with ^{13}CO)[20] in 75% yield.

Preparation of CpFe(CO)$_2$Si(n-C$_5$H$_{11}$)$_2$H (2f). Chlorosilane (n-C_5H_{11})$_2$SiHCl (**1f**) was prepared from (n-C_5H_{11})MgCl (4.81 M in THF, 200 mL, 961 mmol) and SiHCl$_3$ (78.3 g, 0.52 mol) in a manner analogous to that used for **1b**. Distillation under reduced pressure gave the colorless liquid **1f** (13.3 g, 64.6 mmol) in 11% yield, bp 80 °C/14 mmHg. ^{1}H NMR (300 MHz, C_6D_6): δ 0.68−1.49 (m, 22H, n-C_5H_{11}), 4.83 (quintet, $^3J_{H-H} = 3.3$ Hz, 1H, Si-H). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT): δ 15.7.

A THF (15 mL) solution of $Cp_2Fe_2(CO)_4$ (495 mg, 1.40 mmol) was stirred for 2 h over a sodium amalgam prepared from Na (95.9 mg, 4.13 mmol) and Hg (1 mL). The resultant THF solution of Na[CpFe(CO)$_2$] was slowly cannulated away from the Na/Hg into a cooled (−93 °C) THF (30 mL) solution of **1f** (548 mg, 2.66 mmol) over 5 min. The mixture was warmed to room temperature and stirred for 21 h. The solvent was removed in vacuo, the residue was extracted with hexane (30 mL), and the extract was filtered through a Celite pad under nitrogen. After removal of the solvent *in vacuo*, the residue was purified by silica gel flash chromatography (20 mm o.d. × 200 mm) with 1/1 toluene/hexane as eluent to give **2f** (670 mg, 1.82 mmol) as a yellow oil in 68% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 0.93−1.66 (m, 22H, n-C_5H_{11}), 4.08 (s, 5H, η^5-C_5H_5), 4.80 (quintet, $^3J_{H-H} = 3.3$ Hz, 1H, Si−H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 14.3, 19.8, 22.8, 27.0, 36.0 (n-C_5H_{11}), 83.3 (η^5-C_5H_5), 215.5 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT): δ 31.4. IR (cm^{-1}, KBr pellet): ν(Si−H) 2056, ν(CO) 1992, 1942. Mass (EI, 70 eV): m/z 348 (M$^+$, 2), 320 (M$^+$ − CO, 100), 291 (M$^+$ − H-2CO, 12), 287 (M$^+$ − (n-C_5H_{11}), 24), 286 (M$^+$ − (n-C_5H_{11}) − H, 32). Anal. Found: C, 58.50; H, 8.17. Calcd for $C_{17}H_{28}FeO_2Si$: C, 58.62; H, 8.11.

Preparation of Cp*Fe(CO)$_2$Si^{p}Tol$_2$H (2g). A THF (20 mL) solution of Cp*$_2$Fe$_2$(CO)$_4$ (500 mg, 1.01 mmol) was stirred for 2 h over NaK$_{2.8}$ alloy prepared from Na (116 mg, 5.04 mmol) and K (406 mg, 10.4 mmol). A solution of K[Cp*Fe(CO)$_2$] was cooled to −43 °C; then **1b** (587 mg, 2.63 mmol) was added to it. The solution was stirred at room temperature overnight, and the solvent was removed *in vacuo*. The residue was extracted with hexane (30 mL), and the extract was filtered through a Celite pad under nitrogen. The filtrate was evaporated under reduced pressure, and the residue was purified by silica gel flash chromatography (20 mm o.d. × 150 mm) with 1/3 toluene/hexane as eluent to give **2g** (272 mg, 612 μmol) as a yellow powder in 34% yield together with recovered Cp*$_2$Fe$_2$(CO)$_4$ (102 mg, 206 μmol). ^{1}H NMR (300 MHz, THF-d_8): δ 1.72 (s, 15H, η^5-$C_5(CH_3)_5$), 2.25 (s, 6H, p-C$H_3C_6H_4$), 5.25 (s, 1H, Si−H), 7.01−7.03, 7.49−7.52 (AB q, $J = 8.1$ Hz, 4H × 2, p-$CH_3C_6H_4$). ^{13}C NMR (75.5 MHz, C_6D_6): δ 9.32 (η^5-$C_5(CH_3)_5$), 21.4 (p-$CH_3C_6H_4$), 94.9 (η^5-$C_5(CH_3)_5$), 129.1, 134.9, 137.8, 140.2 (p-$CH_3C_6H_4$), 217.5 (CO). ^{29}Si NMR (59.6 MHz, THF-d_8, DEPT): δ 37.9. IR (cm^{-1}, KBr pellet): ν(Si−H) 2031, ν(CO) 1978, 1917. Mass (EI, 70 eV): m/z 458 (M$^+$, 6), 430 (M$^+$ − CO, 89), 402 (M$^+$ − 2CO, 100), 211 (M$^+$ − Cp*Fe(CO)$_2$, 18). Anal. Found: C, 68.67; H, 6.51. Calcd for $C_{26}H_{30}FeO_2Si$: C, 68.12; H, 6.60.

Reaction of CpFe(CO)$_2$Si^{p}Tol$_2$Cl (2a) with LiAlH$_4$ in THF. To a suspension of LiAlH$_4$ (309 mg, 8.13 mmol) in THF (50 mL) was added a THF solution (80 mL) of CpFe(CO)$_2$Si^{p}Tol$_2$Cl (**2a**; 533 mg, 1.26 mmol). The reaction mixture was refluxed, and the reaction was monitored by silica gel TLC (1/3 benzene/hexane as eluent). After 18 h, the solvent was removed *in vacuo*, the residue was extracted with hexane (30 mL), and the extract was filtered through a Celite pad under nitrogen. The filtrate was evaporated *in vacuo*, and the residue was purified by silica gel preparative TLC (1/3 benzene/hexane as eluent) to give ^{p}Tol$_2$SiH(CH$_3$) (**3**; 119 mg, 527 μmol) in 42% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 0.51 (d, $^3J_{H-H} = 3.8$ Hz, 3H, Si−CH_3), 2.09 (s, 6H, p-C$H_3C_6H_4$), 5.21 (q, $^3J_{H-H} = 3.8$ Hz, 1H, Si−H), 7.01−7.04, 7.49−7.51 (AB q, $J = 8.1$ Hz, 4H × 2, p-$CH_3C_6H_4$). ^{13}C NMR (75.5 MHz, THF-d_8): δ −4.83 (Si−CH_3), 21.4 (p-$CH_3C_6H_4$), 128.9, 135.2, 146.6, 147.8 (p-$CH_3C_6H_4$). ^{29}Si NMR (59.6 MHz, THF-d_8, DEPT): δ −18.1. IR (cm^{-1}, hexane solution): ν(Si−H) 2118. Mass (EI, 70 eV): m/z 226 (M$^+$, 37), 225 (M$^+$ − H, 13), 211 (M$^+$ − CH$_3$, 51), 134 (M$^+$ − ^{p}Tol − H, 100). Anal. Found: C, 79.32; H, 7.90. Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01.

Reaction of CpFe(CO)$_2$Si^{p}Tol$_2$Cl (2a) with LiAlD$_4$ in THF. To a suspension of LiAlD$_4$ (33 mg, 786 μmol) in THF (15 mL) was added a THF solution (5 mL) of CpFe(CO)$_2$Si^{p}Tol$_2$Cl (**2a**; 131 mg, 310 μmol). The reaction mixture was refluxed and worked up in a manner similar to that for the reaction with LiAlH$_4$. The crude product was purified by preparative silica gel TLC (1/3 benzene/hexane as eluent) to give ^{p}Tol$_2$SiD(CD$_3$) (**3-*d*$_4$**; 21 mg, 91.3 μmol) in 29% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 2.09 (s, 6H, p-C$H_3C_6H_4$), 7.01−7.04, 7.49−7.51 (AB q, $J = 8.1$ Hz, 4H × 2, p-$CH_3C_6H_4$). Mass (EI, 70 eV): m/z 230 (M$^+$, 40), 228 (M$^+$ − D, 10), 212 (M$^+$ − CD$_3$, 35), 137 (M$^+$ − ^{p}Tol − D, 100).

Reaction of CpFe(CO)$_2$Si^{p}Tol$_2$H (2b) with LiAlH$_4$ in Diethyl Ether. To a suspension of LiAlH$_4$ (69 mg, 1.82 mmol) in diethyl ether (15 mL) was added a diethyl ether solution (5 mL) of CpFe(CO)$_2$Si^{p}Tol$_2$H (**2b**; 135 mg, 348 μmol). The reaction mixture was stirred at room temperature, and the reaction was monitored by silica gel TLC (1/3 benzene/hexane as eluent). After 2 h, the solvent was removed in vacuo and the residue was extracted with hexane (30 mL) and filtered through a Celite pad under nitrogen. The filtrate was evaporated in vacuo to give ^{p}Tol$_2$SiH(CH$_3$) (**3**; 59 mg, 261 μmol) in 75% yield.

Reaction of CpFe(CO)$_2$Si^{p}Tol$_2$H (2b) with LiAlH$_4$ in THF. To a suspension of LiAlH$_4$ (67 mg, 1.76 mmol) in THF (15 mL) was added a THF solution (5 mL) of CpFe(CO)$_2$Si^{p}Tol$_2$H (**2b**; 106 mg, 273 μmol). The reaction mixture was refluxed and worked up in a manner similar to that for the reaction in diethyl ether to give ^{p}Tol$_2$SiH(CH$_3$) (**3**; 30 mg, 132 μmol) in 48% yield.

Reaction of CpFe(CO)$_2$Si^{p}Tol$_2$H (2b) with LiAlH$_4$ in DME. To a suspension of LiAlH$_4$ (110 mg, 2.89 mmol) in DME (10 mL) was added a DME solution (5 mL) of CpFe(CO)$_2$Si^{p}Tol$_2$H (**2b**; 109 mg, 281 μmol). The reaction mixture was refluxed and worked up in a manner similar to that for the

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 3, 1998 on http://pubs.acs.org | doi: 10.1021/om9802111

reaction in diethyl ether to give $^{p}Tol_2SiH(CH_3)$ (**3**; 13 mg, 57.5 μmol) in 21% yield.

Reaction of $CpFe(CO)_2Si^{p}Tol_2H$ (2b) with $LiAlD_4$ in THF. To a suspension of $LiAlD_4$ (35 mg, 833 μmol) in THF (10 mL) was added a THF solution (5 mL) of $CpFe(CO)_2$-$Si^{p}Tol_2H$ (**2b**; 53.9 mg, 139 μmol). The reaction mixture was refluxed for 18 h and worked up in a manner similar to that for the reaction with $LiAlH_4$ to give $^{p}Tol_2SiD(CHD_2)$ (**3-d_3**; 8 mg, 34.9 μmol) in 25% yield. **3-d_3**: ^1H NMR (300 MHz, C_6D_6): δ 0.48 (quintet, 1H, Si$-$CHD_2), 2.09 (s, 6H, p-C$H_3C_6H_4$), 7.01$-$7.04, 7.49$-$7.51 (AB q, $J = 8.1$ Hz, 4H × 2, p-$CH_3C_6H_4$). Mass (EI, 70 eV): m/z 229 (M^+, 41), 227 ($M^+ - D$, 7), 212 ($M^+ - CHD_2$, 54), 136 ($M^+ - {}^{p}Tol - D$, 100).

Reaction of $CpFe(CO)_2Si^{p}Tol_2H$ (2b) with $LiAlH_4$ in a Sealed Tube. To **2b** (10.4 mg, 26.9 μmol) and $LiAlH_4$ (5.33 mg, 140 μmol) in a Pyrex NMR tube (5 mm o.d.) connected to a vacuum line was added THF-d_8 (0.4 mL) by the trap-to-trap-transfer technique. The tube was flame-sealed under vacuum. The reaction was monitored by ^1H NMR spectroscopy. The signals assigned to $^{p}Tol_2SiH(CH_3)$ (**3**) and $Li[CpFe(CO)(CH_3)$-$Si^{p}Tol_2H]$ (**11**) were observed. The sealed tube was then heated to 40 °C, resulting in an increase in the intensity of the signal of **11**, compared to that of **3**. After the tube was opened in a glovebag, MeOH (60 μL) was added to the reaction mixture. The signal of **11** disappeared, and the signal of $^{p}Tol_2SiH_2$ (**10**) newly appeared. Data for **11** are as follows. ^1H NMR (300 MHz, THF-d_8): δ -0.71 (s, 3H, Fe$-$CH_3), 2.13, 2.15 (s, 3H × 2, p-C$H_3C_6H_4$), 3.84 (s, 5H, η^5-C_5H_5), 4.72 (s, 1H, Si-H), 6.77$-$6.80, 6.80$-$6.83, 7.32$-$7.34, 7.34$-$7.37 (AB q, $J = 8.1$ Hz, 2H × 4, p-$CH_3C_6H_4$). ^{13}C NMR (75.5 MHz, THF-d_8): δ -23.5 (Fe$-$$CH_3$), 21.1, 21.1 ($p$-$CH_3C_6H_4$), 81.8 ($\eta^5$-$C_5H_5$), 126.9, 126.9, 134.1, 134.2, 135.3, 135.6, 135.7, 136.1 (p-$CH_3C_6H_4$), 224.0 (CO). ^{29}Si NMR (59.6 MHz, THF-d_8, DEPT): δ 44.6.

Reaction of $Li[CpFe(CO)(CH_3)Si^{p}Tol_2H]$ (11) with CH_3I. To **2b** (3.02 mg, 7.78 μmol) and $LiAlH_4$ (1.31 mg, 34.5 μmol) in a Pyrex NMR tube (5 mm o.d.) connected to a vacuum line was added THF-d_8 (0.4 mL) by the trap-to-trap-transfer technique. The tube was flame-sealed under vacuum. After the tube was opened in a glovebag, MeI (4 μL) was added to the reaction mixture. The signal of **11** disappeared, and the signal of $^{p}Tol_2SiHMe$ (**3**) increased.

Reaction of $CpFe(^*CO)_2Si^{p}Tol_2H$ (2b*) with $LiAlH_4$ in a Sealed Tube. To **2b*** (32% enriched with ^{13}CO; 14.5 mg, 37.2 μmol) and $LiAlH_4$ (5.50 mg, 145 μmol) in a Pyrex NMR tube (5 mm o.d.) connected to a vacuum line was added THF-d_8 (0.4 mL) by the trap-to-trap-transfer technique. The tube was flame-sealed under vacuum. The reaction was monitored by ^1H NMR spectroscopy. After 2 h, the signals of **2b*** disappeared and signals assigned to $^{p}Tol_2SiH(^*CH_3)$ (**3***) and $Li[CpFe(^*CO)(^*CH_3)Si^{p}Tol_2H]$ (**11***) were observed. Data for **3** are as follows. ^1H NMR (300 MHz, THF-d_8): δ 0.53 (dd, $^1J_{C-H} = 120.4$ Hz, $^3J_{H-H} = 3.7$ Hz, 3H, Si$-^{13}$CH_3), 2.29 (s, 6H, p-C$H_3C_6H_4$), 4.84 (q, $^3J_{H-H} = 3.8$ Hz, 1H, Si-H), 7.12$-$7.15, 7.38$-$7.40 (AB q, $J = 8.1$ Hz, 2H × 4, p-$CH_3C_6H_4$). Data for **11** are as follows. ^1H NMR (300 MHz, THF-d_8): δ -0.64 (d, $^1J_{C-H} = 119.6$ Hz, 3H, Fe$-^{13}$CH_3), 2.19, 2.21 (s, 3H × 2, p-C$H_3C_6H_4$), 3.82 (s, 5H, η^5-C_5H_5), 4.77 (s, 1H, Si$-H$), 6.77$-$6.80, 6.80$-$6.83, 7.32$-$7.34, 7.34$-$7.37 (AB q, $J = 8.1$ Hz, 2H × 4, p-$CH_3C_6H_4$).

Reaction of $CpFe(CO)_2Si^{p}Tol_2H$ (2b) with $NaBH_4$ in THF. To a suspension of $NaBH_4$ (60 mg, 1.58 mmol) in THF (15 mL) was added a THF solution (5 mL) of $CpFe(CO)_2$-$Si^{p}Tol_2H$ (**2b**; 97 mg, 250 μmol). The reaction mixture was refluxed, and the reaction was monitored by silica gel TLC (1/3 benzene/hexane as eluent). After 4 days, the solvent was removed *in vacuo* and the residue was extracted with hexane (30 mL) and filtered through a Celite pad under nitrogen. The filtrate was evaporated *in vacuo*. The crude product was purified by preparative silica gel TLC (1/3 benzene/hexane as eluent) to give $Cp_2Fe_2(CO)_4$ (26 mg, 73.4 μmol) as a reddish purple powder in 59% yield and **2b** (32 mg, 82.5 μmol) with 33% recovery.

Reaction of $CpFe(CO)_2Si^{p}Tol_2H$ (2b) with $LiBEt_3H$ in THF. To a suspension of $LiBEt_3H$ (1 mL of its 1 M THF solution, 1.00 mmol) was added a THF solution (20 mL) of $CpFe(CO)_2Si^{p}Tol_2H$ (**2b**; 56 mg, 144 μmol). The reaction mixture was refluxed for 3 days and worked up in a manner similar to that for the reaction with $NaBH_4$ to give Cp_2Fe_2-$(CO)_4$ (14 mg, 39.5 μmol) in 55% yield and **2b** (15 mg, 38.7 μmol) with 27% recovery.

A similar reaction of KH (125 mg, 93.8 μmol) with a THF solution (20 mL) of $CpFe(CO)_2Si^{p}Tol_2H$ (**2b**; 56 mg, 144 μmol) (reflux for 1 day) gave $Cp_2Fe_2(CO)_4$ in 41% yield.

Reaction of $CpFe(CO)_2Si^{p}Tol_2Me$ (2c) with $LiAlH_4$ in THF. To a suspension of $LiAlH_4$ (42 mg, 1.11 mmol) in THF (15 mL) was added a THF solution (5 mL) of $CpFe(CO)_2Si^{p}Tol_2$-Me (**2c**; 80 mg, 199 μmol). The reaction mixture was stirred at room temperature, and the reaction was monitored by silica gel TLC (1/3 benzene/hexane as eluent). After 2 h, the solvent was removed in vacuo and the residue was extracted with hexane (30 mL) and filtered through a Celite pad under nitrogen. The filtrate was evaporated *in vacuo* to give a mixture of $^{p}Tol_2SiH(CH_3)$ (**3**; 14.4 mg, 63.7 μmol) in 32% yield and $^{p}Tol_2Si(CH_3)_2$ (**4**; 30.6 mg, 128 μmol) in 64% yield. The yields were determined from the intensity ratio of the Si$-$CH$_3$ signals in a ^1H NMR spectrum of the product mixture. **4** was identified by comparing the spectroscopic data with those of the authentic sample synthesized as follows. $^{p}Tol_2SiMeCl$ (**1c**; 4.35 g, 16.7 mmol) in diethyl ether was cooled to -43 °C, and a diethyl ether solution of MeLi (1.37 M, 13 mL, 17.8 mmol) was added dropwise to it via a syringe over 5 min. The mixture was stirred at room temperature for 20 h and then cooled in an ice bath. Water (15 mL) was added dropwise to quench an excess of MeLi. The white precipitate was filtered by frit and washed with diethyl ether (20 mL × 3). The filtrate and washings were combined and placed in a separatory funnel. The organic layer was washed with saturated $NaHCO_3$ solution (10 mL × 2), water (10 mL), and saturated NaCl solution (10 mL) and then dried over $MgSO_4$. After removal of solvent, the residue was distilled under reduced pressure to give **4** (3.89 g, 16.2 mmol, 97%) as a colorless oil, bp 108 °C/0.2 mmHg. ^1H NMR (300 MHz, THF-d_8): δ 0.48 (s, 6H, Si$-$CH_3), 2.30 (s, 6H, p-C$H_3C_6H_4$), 7.11$-$7.13, 7.36$-$7.39 (AB q, $J = 8.1$ Hz, 4H × 2, p-$CH_3C_6H_4$). ^{13}C NMR (75.5 MHz, THF-d_8): δ -2.08 (Si-CH_3), 21.5 (p-$CH_3C_6H_4$), 128.9, 135.2, 146.6, 147.8 (p-$CH_3C_6H_4$). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT): δ -8.22. Mass (EI, 70 eV): m/z 240 (M^+, 20), 225 ($M^+ - CH_3$, 100), 149 ($M^+ - {}^{p}Tol$, 3). Anal. Found: C, 79.76; H, 8.25. Calcd for $C_{16}H_{20}Si$: C, 79.93; H, 8.38.

Reaction of $CpFe(CO)_2Si^{p}Tol_2Me$ (2c) with $LiAlD_4$ in THF. To a suspension of $LiAlD_4$ (45 mg, 1.07 mmol) in THF (15 mL) was added a THF solution (5 mL) of $CpFe(CO)_2Si^{p}Tol_2$-Me (**2c**; 83.0 mg, 204 μmol). The reaction mixture was stirred at room temperature for 2 h and worked up in a manner similar to that for the reaction with $LiAlH_4$ to give a mixture of $^{p}Tol_2SiD(CH_3)$ (**3-d**; 17.2 mg, 75.8 μmol) in 37% yield and $^{p}Tol_2Si(CH_3)(CD_3)$ (**4-d_3**; 39.8 mg, 164 μmol) in 63% yield. The yields were determined from the intensity ratio of the Si$-$CH$_3$ signals in a ^1H NMR spectrum of the product mixture. Data for **3-d** are as follows. ^1H NMR (300 MHz, C_6D_6): δ 0.51 (s, 3H, Si$-$CH_3), 2.09 (s, 6H, p-C$H_3C_6H_4$), 7.01$-$7.04, 7.49$-$7.51 (AB q, $J = 8.1$ Hz, 4H × 2, p-$CH_3C_6H_4$). Data for **4-d_3** are as follows. ^1H NMR (300 MHz, C_6D_6): δ 0.49 (s, 3H, Si$-$CH_3), 2.12 (s, 6H, p-C$H_3C_6H_4$), 7.04$-$7.07, 7.45$-$7.48 (AB q, $J = 8.1$ Hz, 4H × 2, p-$CH_3C_6H_4$).

Reaction of $CpFe(CO)_2Si^{p}Tol_2Me$ (2c) with $LiAlH_4$ in a Sealed Tube. To **2c** (6.75 mg, 16.8 μmol) and $LiAlH_4$ (4.35 mg, 110 μmol) in a Pyrex NMR tube (5 mm o.d.) connected to a vacuum line was added THF-d_8 (0.4 mL) by the trap-to-trap-transfer technique. The tube was flame-sealed under vacuum. The reaction was monitored by ^1H NMR spectroscopy. After

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 3, 1998 on http://pubs.acs.org | doi: 10.1021/om9802111

3 h, the signal of **2c** disappeared and the signals assigned to ^{p}Tol$_2$Si(CH$_3$)$_2$ (**4**) and Li[CpFe(CO)(CH$_3$)Si^{p}Tol$_2$Me] (**12**) appeared. After the tube was opened in a glovebag, MeI (7 μL) was added to the reaction mixture. The signal of **12** disappeared, and the signal of ^{p}Tol$_2$SiMe$_2$ (**4**) increased. Data for **12** are as follows. ^{1}H NMR (300 MHz, THF-d_8): δ −0.65 (s, 3H, Fe−CH_3), 0.32 (s, 3H, Si−CH_3), 2.21 (s, 6H, p-CH_3C$_6$H$_4$), 3.88 (s, 5H, η^5-C$_5$$H_5$), 6.86−6.89, 7.35−7.37 (AB q, J = 8.1 Hz, 4H × 2, p-CH$_3$C$_6$$H_4$). ^{13}C NMR (75.5 MHz, THF-d_8): δ −24.6 (Fe-CH$_3$), 8.35 (Si−CH$_3$), 21.1 (p-CH$_3$C$_6$H$_4$), 83.0 (η^5-C_5H$_5$), 126.9, 134.1, 135.3, 135.6 (p-CH$_3$$C_6H_4$), 224.0 (CO). ^{29}Si NMR (59.6 MHz, THF-d_8, DEPT): δ 41.4.

Reaction of Li[CpFe(CO)(CH$_3$)Si^{p}Tol$_2$Me] (12) with MeOH. To **2c** (10.3 mg, 25.6 μmol) and LiAlH$_4$ (4.00 mg, 105 μmol) in a Pyrex NMR tube (5 mm o.d.) connected to a vacuum line was added THF-d_8 (0.4 mL) by the trap-to-trap-transfer technique. The tube was flame-sealed under vacuum. After the tube was opened in a glovebag, MeOH (10 μL) was added to the reaction mixture. The signal of **12** disappeared, and the signal of ^{p}Tol$_2$SiHMe (**3**) newly appeared.

Reaction of CpFe(*CO)$_2$Si^{p}Tol$_2$Me (2c*) with LiAlH$_4$ in a Sealed Tube. To **2c*** (46% enriched with ^{13}CO; 14.0 mg, 34.7 μmol) and LiAlH$_4$ (5.20 mg, 137 μmol) in a Pyrex NMR tube (5 mm o.d.) connected to a vacuum line was added THF-d_8 (0.4 mL) by the trap-to-trap-transfer technique. The tube was flame-sealed under vacuum. The reaction was monitored by ^{1}H NMR spectroscopy. After 2 h, the signals of **2c*** disappeared and the signals assigned to ^{p}Tol$_2$SiMe(*CH$_3$) (**4***) and Li[CpFe(*CO)(*CH$_3$)Si^{p}Tol$_2$Me] (**12***) were observed. Data for **4*** are as follows. ^{1}H NMR (300 MHz, THF-d_8): δ 0.46 (s, 3H, Si−CH_3), 0.46 (d, $^1J_{\mathrm{C-H}}$ = 119.4 Hz, 3H, Si−^{13}CH_3), 2.30 (s, 6H, p-CH_3C$_6$H$_4$), 7.11−7.13, 7.36−7.39 (AB q, J = 8.1 Hz, 4H × 2, p-CH$_3$C$_6$$H_4$). Data for **12*** are as follows. ^{1}H NMR (300 MHz, THF-d_8): δ −0.66 (d, $^1J_{\mathrm{C-H}}$ = 125.4 Hz, 3H, Fe−^{13}CH_3), 0.36 (s, 3H, Si−CH_3), 2.20 (s, 6H, p-CH_3C$_6$H$_4$), 3.88 (s, 5H, η^5-C$_5$$H_5$), 6.77−6.80, 6.80−6.83, 7.32−7.34, 7.34−7.37 (AB q, J = 8.1 Hz, 2H × 4, p-CH$_3$C$_6$$H_4$).

Reaction of CpFe(CO)$_2$SiMePh(1-Nap) (2d) with LiAlH$_4$ in Diethyl Ether. To a suspension of LiAlH$_4$ (74.5 mg, 1.96 mmol) in diethyl ether (15 mL) was added a diethyl ether solution (5 mL) of CpFe(CO)$_2$SiMePh(1-Nap) (**2d**; 204 mg, 480 μmol) at 0 °C. The mixture was warmed to room temperature and was stirred for 48 h. Then the reaction mixture was cooled to 0 °C and was hydrolyzed with water (5 mL). The solvent was removed *in vacuo*, and the residue was recrystallized from pentane to give a mixture of Ph(1-Nap)SiH(CH$_3$) (**6**; 17.2 mg, 69.4 μmol) in 14% yield and Ph(1-Nap)Si(CH$_3$)$_2$ (**5**; 90.9 mg, 347 μmol) in 72% yield. The yields were determined from the intensity ratio of the Si−CH$_3$ signals in a ^{1}H NMR spectrum of the product mixture. **5**[21] and **6**[22] are known compounds. **5** and **6** were identified by comparison of the ^{1}H, ^{13}C, and ^{29}Si NMR and mass spectra with those of the authentic samples.

Reaction of CpFe(CO)$_2$SiMePh(1-Nap) (2d) with LiAlH$_4$ in THF. To a suspension of LiAlH$_4$ (48.0 mg, 1.26 mmol) in THF (10 mL) was added a THF solution (10 mL) of CpFe(CO)$_2$SiMePh(1-Nap) (**2d**; 96.9 mg, 229 μmol) at −93 °C. The mixture was warmed to room temperature and was stirred for 20 h. The reaction mixture was worked up in a manner similar to that for the reaction of **2c** to give a mixture of Ph(1-Nap)SiH(CH$_3$) (**6**; 14.9 mg, 60.2 μmol) in 26% yield and Ph(1-Nap)Si(CH$_3$)$_2$ (**5**; 15.8 mg, 60.2 μmol) in 26% yield. The yields were determined from the intensity ratio of the Si−CH$_3$ signals in a ^{1}H NMR spectrum of the product mixture.

Reaction of CpFe(CO)$_2$SiMes$_2$H (2e) with LiAlH$_4$ in THF. To a suspension of LiAlH$_4$ (171 mg, 4.50 mmol) in THF (15 mL) was added a THF solution (5 mL) of CpFe(CO)$_2$SiMes$_2$H (**2e**; 480 mg, 1.07 μmol). The reaction mixture was stirred at room temperature, and the reaction was monitored by silica gel TLC (1/3 toluene/hexane as eluent). After 16 h, the solvent was removed in vacuo and the residue was extracted with hexane (30 mL) and filtered through a Celite pad under nitrogen. The filtrate was evaporated *in vacuo* to give Mes$_2$SiH$_2$ (**7**;[23] 186 mg, 696 μmol) in 65% yield.

Reaction of CpFe(CO)$_2$Si(n-C$_5$H$_{11}$)$_2$H (2f) with LiAlH$_4$ in THF. To a suspension of LiAlH$_4$ (27.3 mg, 718 μmol) in THF (10 mL) was added a THF solution (10 mL) of CpFe(CO)$_2$Si(n-C$_5$H$_{11}$)$_2$H (**2f**; 59.6 mg, 162 μmol) at −93 °C. The reaction mixture was stirred at room temperature for 46 h and worked up in a manner similar to that for the reaction of **2c** to give a mixture of (n-C$_5$H$_{11}$)$_2$SiH$_2$ (**9**; 1.47 mg, 8.55 μmol) in 5.3% yield and (n-C$_5$H$_{11}$)$_2$SiH(CH$_3$) (**8**; 12.7 mg, 68.3 μmol) in 42% yield. The yields were determined from the intensity ratio of the Si−H signals in a ^{1}H NMR spectrum of the product mixture. **8**[24] and **9**[25] are known compounds. **8** and **9** were identified by comparison of the ^{1}H, ^{13}C, and ^{29}Si NMR and mass spectra with those of the authentic samples.

Reaction of Cp*Fe(CO)$_2$Si^{p}Tol$_2$H (2g) with LiAlH$_4$ in THF. To a suspension of LiAlH$_4$ (36.0 mg, 947 μmol) in THF (15 mL) was added a THF solution (5 mL) of Cp*Fe(CO)$_2$Si^{p}Tol$_2$H (**2g**; 103 mg, 225 μmol) at −93 °C. The reaction mixture was warmed to 50 °C. After 1 week, the mixture was worked up in a manner similar to that for the reaction of **2c** to give a mixture of ^{p}Tol$_2$SiH(CH$_3$) (**3**; 12.7 mg, 56.2 μmol) in 25% yield and ^{p}Tol$_2$SiH$_2$ (**10**; 11.9 mg, 56.2 μmol) in 25% yield. The yields were determined from the intensity ratio of the Si−H signals in a ^{1}H NMR spectrum of the product mixture. **10**[26] is a known compound. **10** was identified by comparison of the ^{1}H, ^{13}C, and ^{29}Si NMR and mass spectra with those of the authentic sample.

Reaction of Cp*Fe(CO)$_2$Si^{p}Tol$_2$H (2g) with LiAlH$_4$ in a Sealed Tube. To **2g** (5.80 mg, 13.1 μmol) and LiAlH$_4$ (2.61 mg, 68.4 μmol) in a Pyrex NMR tube (5 mm o.d.) connected to a vacuum line was added THF-d_8 (0.4 mL) by the trap-to-trap-transfer technique. The tube was flame-sealed under vacuum. The reaction was monitored by ^{1}H NMR spectroscopy. After the sealed tube was heated at 50 °C for 3 days, signals assigned to ^{p}Tol$_2$SiH(CH$_3$) (**3**), ^{p}Tol$_2$SiH$_2$ (**10**), and Li[Cp*Fe(CO)(CH$_3$)Si^{p}Tol$_2$H] (**13**) were observed. Data for **13** are as follows. ^{1}H NMR (300 MHz, THF-d_8): δ −0.75 (s, 3H, Fe−CH_3), 1.87 (s, 15H, η^5-C$_5$(CH_3)$_5$), 2.22, 2.25 (s, 3H × 2, p-CH_3C$_6$H$_4$), 4.84 (s, 1H, Si−H), 6.73−6.75, 6.85−6.87, 7.42−7.45, 7.57−7.59 (AB q, J = 8.1 Hz, 2H × 4, p-CH$_3$C$_6$$H_4$). ^{13}C NMR (75.5 MHz, THF-d_8): δ −21.5 (Fe−CH$_3$), 15.5 (η^5-C$_5$(CH$_3$)$_5$), 24.4, 24.5 (p-CH$_3$C$_6$H$_4$), 91.5 (η^5-C_5(CH$_3$)$_5$), 129.9, 130.2, 136.9, 137.2, 138.9, 139.5, 151.2, 151.7 (p-CH$_3$$C_6H_4$), 236.5 (CO). ^{29}Si NMR (59.6 MHz, THF-d_8, DEPT): δ 45.6.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (Nos. 09440223 and 09440245) and a Grant-in-Aid for Scientific Research on Priority Area “The Chemistry of Inter-element Linkage” (No. 09239105) from the Ministry of Education, Science, Sports and Culture of Japan and a Kurata Research Grant from the Kurata Foundation. We thank Shin-Etsu Chemical Co., Ltd., for a gift of silicon compounds.

OM9802111

---

[21] (a) Corriu, R. J. P.; Moreau, J. J. B. *Bull. Soc. Chim. Fr.* **1975**, *3*, 901. (b) Sommer, L. H.; Michael, K. W.; Korte, K. W. *J. Am. Chem. Soc.* **1967**, *89*, 868.

[22] Fearon, F. W. G.; Gilman, H. *J. Organomet. Chem.* **1967**, *9*, 403.

[23] Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531.

[24] Kovalev, I. F.; Arbuzova, U. A.; Voronkov, M. G.; Khudobin, Yu. I.; Kharitonov, N. R. *Dokl. Akad. Nauk SSSR* **1968**, *179*, 126.

[25] Opitz, H. E.; Peake, J. S.; Nebergall, W. H. *J. Am. Chem. Soc.* **1956**, *78*, 292.

[26] Tour, J. M.; John, J. A.; Stephans, E. B. *J. Organomet. Chem.* **1992**, *429*, 301.