Reaction of Silyl(carbonyl)iron Complexes with $\mathrm{LiAlH_4}$ Giving Methylsilanes: Reduction of a Carbonyl Ligand and Coupling with a Silyl Group

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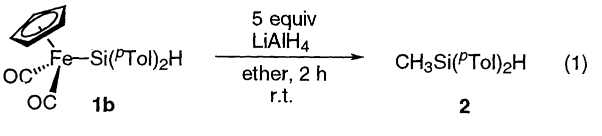
Treatment of $\mathrm{CpFe(CO)_2SiR_3}$ ($\mathrm{R_3} = (^p\mathrm{Tol})_2\mathrm{H}$, $(^p\mathrm{Tol})_2\mathrm{Me}$, MePh(1-Nap); 1-Nap = 1-naphthyl) with $\mathrm{LiAlH_4}$ in ether or THF at room temperature gave $\mathrm{CH_3SiR_3}$ as a major product in moderate to high yield. The labeling experiments using $\mathrm{LiAlD_4}$ and $\mathrm{CpFe(^{13}CO)_2SiR(^pTol)_2}$ (R = H, Me) proved unambiguously that the carbonyl ligand is reduced with $\mathrm{LiAlH_4}$ and coupled with the silyl group to give the methylsilane.

Reactions of hydride-transfer reagents with transition metal carbonyl complexes have attracted much attention. They usually give formyl complexes,[1] but there are also a few examples reported in which a carbonyl ligand is further reduced to a methyl group: Treichel and Shubkin described that $\mathrm{[CpM(CO)_3PPh_3]PF_6}$ (M = Mo, W) reacted with $\mathrm{NaBH_4}$ in THF to give $\mathrm{CpM(CO)_2PPh_3(CH_3)}$,[2] and Wong and Atwood found that treatment of $\mathrm{CpFe(CO)_2R}$ (R = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, $\mathrm{CH_3C(O)}$) with $\mathrm{LiAlH_4}$ produced $\mathrm{CH_3CH_3}$ mainly.[3]

As to silyl carbonyl transition-metal complexes, reactions with hydride-transfer reagents were reported to result in substitution of transition metal moieties with a hydride to give the corresponding hydrosilanes,[4] and participation of the CO reduction has not been demonstrated. We report here the first clear evidence for the reduction of a carbonyl ligand: a reaction of silyl(carbonyl)iron complexes with $\mathrm{LiAlH_4}$ giving *methylsilanes*.

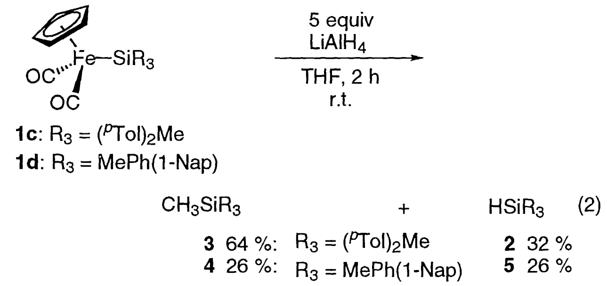
Treatment of $\mathrm{FpSi(^pTol)_2Cl}$ (**1a**)[5] (Fp = $\mathrm{CpFe(CO)_2}$) with $\mathrm{LiAlH_4}$ in refluxing THF afforded $\mathrm{CH_3Si(^pTol)_2H}$ (**2**)[6] in 42 % yield. The formation of methylsilane was unexpected because the reduction of chlorosilyl-Fp complexes to hydrosilyl-Fp complexes,[7] and also the above-mentioned nucleophilic substitution of Fp to H on silyl-Fp complexes[4] have been well established, whereas the formation of methylsilane was unprecedented. An analogous reaction of **1a** with $\mathrm{LiAlD_4}$ gave $\mathrm{CD_3Si(^pTol)_2D}$ (**2-*d*$_4$**; ~100%D). This suggested a possibility that the reaction of **1a** with $\mathrm{LiAlH_4}$ proceeded through the reduced intermediate $\mathrm{FpSi(^pTol)_2H}$ (**1b**). In fact, the reaction of **1b** with $\mathrm{LiAlH_4}$ occurred under milder conditions, *i.e.*, in diethylether at room temperature, to give **2** in 73 % yield (eq 1). The yield of **2** was dependent on the solvent and temperature: 48 % in refluxing THF; 21 % in refluxing DME.



Interestingly, the reaction of **1b** with $\mathrm{LiAlD_4}$ exclusively produced $\mathrm{CHD_2Si(^pTol)_2D}$ (**2-*d*$_3$**; ~100%D), which was characterized by the ^{1}H NMR spectrum showing the Si-C*H*$\mathrm{D_2}$ signal at 0.51 ppm as a quintet ($^2J_{\mathrm{HD}}$ = 2.0 Hz) and the mass spectrum giving the molecular ion peak at *m/z* 229. This result suggests that the source of two of the hydrogen atoms of the methyl group in **2** is $\mathrm{LiAlH_4}$ while that of the third one is a hydrogen on the silyl group which may migrate onto the carbonyl carbon in the course of the reaction.

The conversion of a carbonyl ligand in **1b** to a methyl group in **2** was further confirmed by the ^{13}C labeling experiments. Reaction of **1b-^{13}CO** (**1b** enriched with ^{13}CO to 32 %)[8] with $\mathrm{LiAlH_4}$ afforded **2** in which the methyl carbon was enriched with ^{13}C. The ^{1}H NMR signal of the $\mathrm{Si^{13}C}H_3$ of ^{13}C-enriched **2** appeared at 0.53 ppm as a double doublet coupled with a ^{13}C and an Si-H ($^1J_{\mathrm{CH}}$ = 120.4, $^3J_{\mathrm{HH}}$ = 3.7 Hz).

The reactions of silyl complexes without Si-H bonds, namely $\mathrm{FpSi(^pTol)_2Me}$ (**1c**)[5] and FpSiMePh(1-Nap) (**1d**),[4] with $\mathrm{LiAlH_4}$ also gave methylsilanes, $\mathrm{SiMe_2(^pTol)_2}$ (**3**)[6] and $\mathrm{SiMe_2Ph}$(1-Nap) (**4**),[6] respectively, although, in these cases, the by-products in which Fp was merely replaced with H, namely $\mathrm{HSi^pTol_2Me}$ (**2**) and HSiMePh(1-Nap) (**5**), were formed (eq 2).



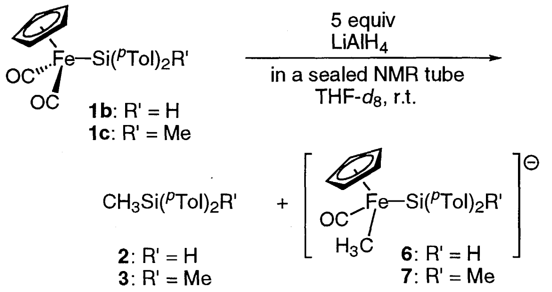
1c: $\mathrm{R_3} = (^p\mathrm{Tol})_2\mathrm{Me}$
1d: $\mathrm{R_3}$ = MePh(1-Nap)

3 64 %: $\mathrm{R_3} = (^p\mathrm{Tol})_2\mathrm{Me}$ **2** 32 %
4 26 %: $\mathrm{R_3}$ = MePh(1-Nap) **5** 26 %

Treatment of **1c** with $\mathrm{LiAlD_4}$ yielded $\mathrm{(CD_3)Si(^pTol)_2Me}$ (**3-*d*$_3$**; ~100%D) and $\mathrm{DSi(^pTol)_2Me}$ (**2-*d***; ~100%D) in 63 and 37 % yields, respectively. In this case, all the three hydrogens of a methyl group in **3-*d*$_3$** are deuterated, indeed, due to the absence of hydrogen on the Si of **1c**. Reduction of **1c-^{13}CO** (**1c** enriched with ^{13}CO to 46 %)[8] afforded a ^{13}C-enriched **3**, *i.e.*, $\mathrm{(^{13}CH_3)Si(^pTol)_2Me}$.

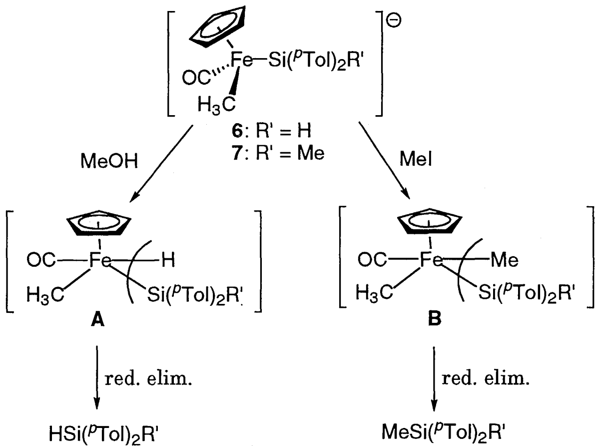
Employment of $\mathrm{NaBH_4}$, $\mathrm{LiBEt_3H}$, or KH as a hydride-transfer reagent in refluxing THF did not convert **1b** to the methyl- or hydride-substituted silane, but resulted in the partial recovery of **1b** and the formation of $\mathrm{Fp_2}$ and some unidentified products. This implies that these reagents are not strong enough either to reduce the carbonyl ligand to a methyl group or to attack the silyl group nucleophilically.

The NMR tube reaction of **1b** with $\mathrm{LiAlH_4}$ in THF-*d*$_8$ showed, besides the signals of **2**, the signals of another product which can be assigned to an anionic species $\mathrm{[CpFe(CO)(CH_3)Si(^pTol)_2H]^-}$ (**6**) (eq 3).[9] The molar ratio of **2** to **6** was ca. 1 : 2. A similar reaction of **1c** with $\mathrm{LiAlH_4}$ gave **3** and $\mathrm{[CpFe(CO)(CH_3)Si(^pTol)_2Me]^-}$ (**7**)[9] in ca. 16 : 1 molar ratio (eq 3). In the latter case, only a trace amount of **2** was observed by ^{1}H and ^{29}Si NMR spectroscopy. The ^{1}H and ^{13}C NMR signals of the Fe-*Me* groups in **6** and **7** appear clearly at fairly high field (^{1}H NMR **6**: -0.71, **7**: -0.65 ppm; ^{13}C NMR **6**: -23.5, **7**: -24.6 ppm). All other ^{1}H NMR signals of **6** and **7** except those of *p*-tolyl groups also shift to higher field compared to the corresponding signals of **1b** and **1c**, respectively. These high-field shift of ^{1}H NMR signals is consistent with the anionic character of **6** and **7**.



(3)

Besides these spectroscopic evidences, the reactions of **6** and **7** with MeOH or MeI afforded further evidences for the structures. Addition of MeOH to the NMR tube reaction mixture containing **6** or **7** caused exclusive conversion of the anionic species to $H_2Si(^p\mathrm{Tol})_2$ or $CH_3Si(^p\mathrm{Tol})_2H$ (**2**), respectively. In a similar manner, addition of MeI resulted in the formation of **2** and $SiMe_2(^p\mathrm{Tol})_2$ (**3**), respectively. These results can be rationalized by the mechanism involving the electrophilic attack of H^+ or Me^+ to the anionic iron center followed by the reductive elimination from the resulting neutral intermediate **A** or **B** (Scheme 1).



Scheme 1.

Indeed, the reductive elimination of silanes from the neutral Fe(IV) species **A** would be much easier than that from more electron-rich and less oxidized anionic Fe(II) species **6** or **7**. The formation of hydrosilanes instead of methylsilanes on treatment with MeOH may be attributable to the tendency that reductive elimination of Si-H species is easier than that of Si-Me species.[10]

Interestingly, even on heating to the boiling point of THF-d_8, the conversion of **6** or **7** in the reaction mixture to the methylated product **2** or **3** was not observed. This result suggests that **6** and **7** are *not* the intermediates for the formation of methylsilanes. The mechanism for the formation of methylsilanes is under active investigation.

We demonstrated in this paper that LiAlH$_4$ transfers more than one H$^-$ to a carbonyl ligand, and when the metal has a silyl group on it, the reduced carbonyl ligand is coupled with it to give a methylsilane in fair yield. We are now investigating the generality of this reaction for a variety of carbonyl complexes containing a silyl ligand.

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References and Notes

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5 Selected data. **1a**: ^{1}H NMR (300 MHz, C_6D_6): δ 2.07 (s, 6H, *p*-*Me*C_6H_4), 4.09 (s, 5H, Cp), 7.05-7.08, 7.86-7.89 (Abq, *J* = 8.1 Hz, 4H x 2, *p*-MeC_6H_4).). ^{29}Si NMR (59.6 MHz, C_6D_6) δ 70.8. **1b**: ^{1}H NMR (300 MHz, C_6D_6): δ 2.12 (s, 6H, *p*-*Me*C_6H_4), 4.05 (s, 5H, Cp), 6.02 (s, 1H, SiH), 7.05-7.08, 7.86-7.89 (Abq, *J* = 8.1 Hz, 4H x 2, *p*-MeC_6H_4). ^{29}Si NMR (59.6 MHz, C_6D_6) δ 26.2. Anal. Found: C, 64.83; H, 5.36%. Calcd for $C_{21}H_{20}FeO_2Si$: C, 64.95; H, 5.19%. **1c**: ^{1}H NMR (300 MHz, C_6D_6): δ 1.01 (s, 3H, SiMe), 2.15 (s, 6H, *p*-*Me*C_6H_4), 4.02 (s, 5H, Cp), 7.10-7.12, 7.67-7.69 (Abq, *J* = 8.1 Hz, 4H x 2, *p*-MeC_6H_4). ^{29}Si NMR (59.6 MHz, C_6D_6) δ 34.8. Anal. Found: C, 65.87; H, 5.68%. Calcd for $C_{22}H_{22}FeO_2Si$: C, 65.67; H, 5.51%.
6 Satisfactory elemental analyses were obtained for **2** - **3**. **2**: ^{1}H NMR (300 MHz, C_6D_6): δ 0.51 (d, $^3J_{HH}$ = 3.8 Hz, 3H, SiMe), 2.09 (s, 6H, *p*-*Me*C_6H_4), 5.21 (q, $^3J_{HH}$ = 3.8 Hz, 1H, SiH), 7.01-7.04, 7.49-7.51 (Abq, *J* = 8.1 Hz, 4H x 2, *p*-MeC_6H_4). (THF-d_8): δ 0.53 (d, $^3J_{HH}$ = 3.8 Hz, 3H, SiMe), 2.30 (s, 6H, *p*-*Me*C_6H_4), 4.86 (q, $^3J_{HH}$ = 3.8 Hz, 1H, SiH), 7.12-7.15, 7.38-7.40 (Abq, *J* = 8.1 Hz, 4H x 2, *p*-MeC_6H_4). ^{29}Si NMR (59.6 MHz, THF-d_8) δ -18.1. IR (KBr) ν_{Si-H} 2118 cm^{-1}. **3**: ^{1}H NMR (300 MHz, C_6D_6): δ 0.50 (s, 6H, SiMe), 2.12 (s, 6H, *p*-*Me*C_6H_4), 7.05-7.07, 7.46-7.49 (Abq, *J* = 8.1 Hz, 4H x 2, *p*-MeC_6H_4). (THF-d_8): δ 0.48 (s, 6H, SiMe), 2.30 (s, 6H, *p*-*Me*C_6H_4), 7.11-7.13, 7.36-7.39 (Abq, *J* = 8.1 Hz, 4H x 2, *p*-MeC_6H_4). ^{29}Si NMR (59.6 MHz, THF-d_8) δ -8.67. **4**: ^{1}H NMR (300 MHz, C_6D_6): δ 0.60 (s, 6H, SiMe), 7.11-8.08 (m, 12H, Ph, 1-Nap). ^{29}Si NMR (59.6 MHz, C_6D_6) δ -7.04.
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8 Photolysis of **1b** under a ^{13}CO atmosphere for 5 min gave **1b-^{13}CO** in which the CO ligands were enriched with ^{13}CO, together with a *cis-trans* mixture of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Si^p\mathrm{Tol}_2)$ enriched with ^{13}CO. Similarly, the photolysis of **1c** under ^{13}CO atmosphere afforded **1c-^{13}CO** enriched with ^{13}CO. The ^{13}C contents of **1b-^{13}CO** and **1c-^{13}CO** were estimated from those of **2** and **3** determined by ^{1}H NMR spectroscopy, respectively.
9 **6**: ^{1}H NMR (300 MHz, THF-d_8): δ -0.71 (s, 3H, FeMe), 2.13, 2.15 (s, 3H x 2, *p*-*Me*C_6H_4), 3.84 (s, 5H, Cp), 4.72 (s, 1H, SiH), 6.77-7.37 (m, 8H, *p*-MeC_6H_4). ^{29}Si NMR (59.6 MHz, THF-d_8) δ 44.6. **7**: ^{1}H NMR (300 MHz, THF-d_8): δ -0.65 (s, 3H, FeMe), 0.32 (s, 3H, Si-Me), 2.21 (s, 6H, *p*-*Me*C_6H_4), 3.88 (s, 5H, Cp), 6.86-7.37 (m, 8H, *p*-MeC_6H_4).). ^{29}Si NMR (59.6 MHz, THF-d_8) δ 41.4.
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