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Manganese- and Rhodium-Catalyzed Phenylsilane Hydrosilation−Deoxygenation of Iron Acyl Complexes Cp(L)(CO)FeC(O)R (L = CO, PPh_3, $P(OMe)_3$, $P(OPh)_3$; R = CH_3, Ph, $CHMe_2$, CMe_3)

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The manganese carbonyl acyl complexes $L(CO)_4MnC(O)R$ (L = CO, R = CH_3 (**2a**); L = CO, R = Ph (**2b**); L = PPh_3, R = CH_3 (**2c**)) are precatalysts for the $PhSiH_3$ hydrosilation−deoxygenation of $Cp(CO)_2FeC(O)CH_3$ (**1a**) to $Cp(CO)_2FeCH_2CH_3$ (**6a**). Thus, **2a** (4%) and 1.1 equiv of $PhSiH_3$ reduce **1a** initially to a mixture of $[Cp(CO)_2FeCH(CH_3)O]_{3-x}H_xSiPh$ (x = 2 (**3b**), 1 (**4b**), and 0 (**5b**)) (7−8 h), which transforms to a mixture of **5b** (62%) and **6a** (35%) (12 h). Similarly, **2b** and $PhSiH_3$ transform **1a** to a mixture containing 4% **3b**, 22% **4b**, 72% **5b**, and 2% **6a** (30 min), then up to 15−20% **6a** (12 h). Use of **2c** as the precatalyst selectively yields 71% **4b** and 10% **6a** (30 min), then up to 19% **6a** (5 h). Both **4b** and **5b** were isolated by size-exclusion chromatography and characterized as mixtures of four stereoisomers, **4b** as a pair of enantiomers having a prochiral center and two meso diastereoisomers with pseudoasymmetric centers and **5b** as a diastereomeric pair of enantiomers. The $PhSiH_3$ (1.6 equiv)/$RhCl(PPh_3)_3$ (3%) system conveniently transforms Cp(L)(CO)FeC(O)R to their alkyl derivatives $Cp(L)(CO)FeCH_2R$. Seven iron acyl complexes were studied ($Cp(CO)_2FeC(O)R$, R = Me, Ph, ^iPr, ^tBu; $Cp(L)(CO)FeC(O)CH_3$, L = PPh_3, $P(OMe)_3$, and $P(OPh)_3$), which gave 49−87% isolated yields of $Cp(L)(CO)FeCH_2R$. Their modest yields correspond to the presence of byproducts, $Cp(CO)_2FeCH{=}CH_2$ (32%) and **4b** (14%) with **1a** and 10−15% of the vinyl complexes with L = PPh_3 and $P(OPh)_3$.

Introduction

Organotransition-metal acyl complexes exhibit a rich and varied reaction chemistry with hydrosilanes that depends on the metallic moiety and the choice of hydrosilane and catalyst.[1] The cyclopentadienyliron acetyl complexes $Cp(L)(CO)FeC(O)CH_3$ (L = CO (**1a**), PPh_3 (**1b**), $P(OR)_3$), for example, undergo catalytic hydrosilation with mono- or dihydrosilanes to give[1b,2,3] isolable α-siloxyethyl complexes, $Cp(CO)_2FeCH(OSiR_3)CH_3$ (Scheme 1).[1b,e] To date, the most active iron acetyl hydrosilation catalysts are the degradation product(s) that result from treating the manganese acyl complexes $L(CO)_4MnC(O)R$ (**2**) with excess hydrosilane.[4]

An interesting selectivity was noted for the hydrosilation of **1a** with 1 equiv of a di- or trihydrosilane and 2−3% of a manganese acyl **2a**−**c**. Using $(CO)_5MnC(O)CH_3$ (**2a**) or $(CO)_5MnC(O)Ph$ (**2b**) as the precatalyst with R_2SiH_2 (R = Et, Ph) gave separable mixtures of mono- and bis($Cp(CO)_2Fe$-α-siloxyethyl) complexes, **3a** and **4a**, respectively, whereas use of $(PPh_3)(CO)_4MnC(O)CH_3$ (**2c**) selectively furnished **3a**. In the presence of the more reactive $PhSiH_3$, **2a** catalytically transformed **1a** to mixtures of $[Cp(CO)_2FeCH(CH_3)O]_3SiPh$ (**5b**) and $Cp(CO)_2FeCH_2CH_3$ (**6a**).[1b]

Rhodium(I) compounds also catalyze the hydrosilation of CpFe acetyl complexes **1a** and **1b**, although the extent of reaction and types of products often differ.[2,3] For example, $RhCl(PPh_3)_3$ does not catalyze the hydrosilation of **1a** with monohydrosilanes.[2a] With excess of the more reactive dihydrosilanes,[6] $RhCl(PPh_3)_3$ converted **1a** to **3a** in the presence of competing Rh(I)-promoted

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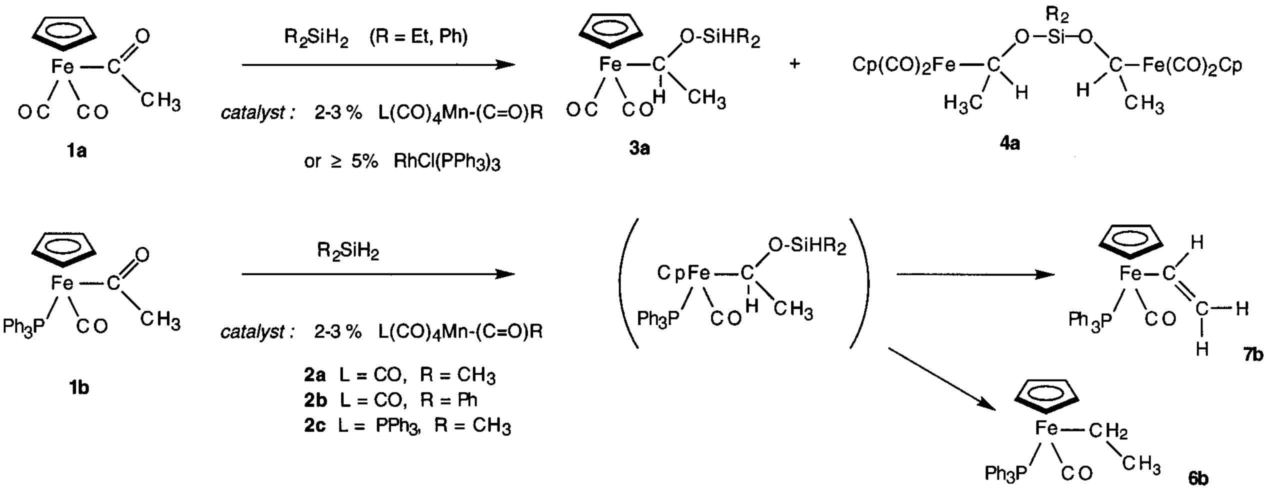
S0276-7333(97)00659-6 CCC: $15.00

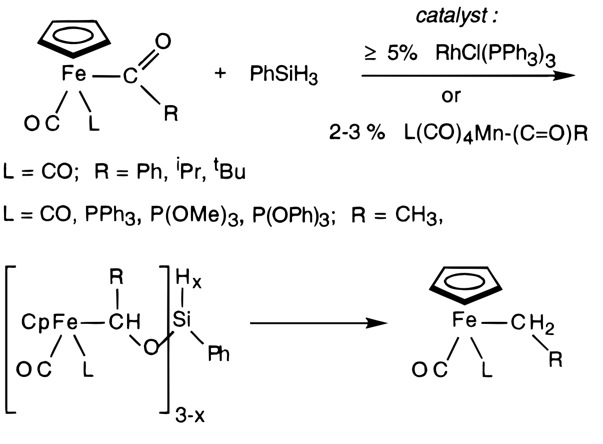
Scheme 1



silane dehydrogenative coupling.[7] Although treatment of **1b** with monohydrosilanes and **2a**−**c** yielded Cp(PPh$_3$)(CO)FeCH(OSiR$_3$)CH$_3$, RhCl(PPh$_3$)$_3$ additionally transformed these α-siloxyethyl products to the vinyl complex Cp(PPh$_3$)(CO)FeCH=CH$_2$ (**7b**). With either type of catalyst, dihydrosilanes additionally produce varying amounts of the fully reduced Cp(PPh$_3$)(CO)FeCH$_2$CH$_3$ (**6b**).[2,3b] It is this catalytic hydrosilation-then-deoxygenation of the acyl ligand on L$_x$MC(=O)R to an α-methylene group L$_x$MCH$_2$R that is of interest to the present study.

The only other procedure that we are aware of for directly reducing L$_x$MC(=O)R to its alkyl derivative L$_x$MCH$_2$R entails treatment with excess B$_2$H$_6$/C$_6$D$_6$ or BH$_3$·THF.[8] When carried out with **1b**, however, this procedure also gave 25% Cp(PPh$_3$)(CO)FeH (**8b**) relative to the major product **6b**. Direct catalytic hydrogenation (e.g., with RhCl(PPh$_3$)$_3$)[8] of these acyl complexes has not been documented.

In initiating this study, we wanted to find catalytic conditions for the PhSiH$_3$ hydrosilation-then-deoxygenation of **1a** to Cp(CO)$_2$FeCH$_2$CH$_3$ (**6a**) (eq 1) while minimizing the accumulation of α-siloxyethylCp(CO)$_2$Fe intermediates [Cp(CO)$_2$FeCH(CH$_3$)O]$_{3-x}$H$_x$SiPh (x = 2 (**3b**), 1 (**4b**), 0 (**5b**)). The precatalysts that we surveyed included the manganese acyls **2a**−**c** and RhCl(PPh$_3$)$_3$. These manganese acyls and PhSiH$_3$ are effective for the hydrosilation-then-deoxygenation of organic esters RC(=O)OR′ to give, successively, silyl acetals [RCH(OR′)O]$_{3-x}$H$_x$SiPh and ethers RCH$_2$OR′.[5b] In the present study, RhCl(PPh$_3$)$_3$ proved to be the optimal precatalyst for the deoxygenation of **1a** and the scope of this reaction was extended to Cp(CO)(L)FeC(O)CH$_3$ (L = CO, PPh$_3$, P(OMe)$_3$, P(OPh)$_3$) and Cp(CO)$_2$FeC(O)R (R = Et, n-Pr, i-Pr, t-Bu). Portions of this study have been communicated previously.[1b,2a]



(1)

Experimental Section

Synthetic manipulations were performed using a combination of standard Schlenk-line, glovebox, and vacuum-line procedures.[9] Infrared spectra of benzene solutions were recorded on a Perkin-Elmer FT spectrophotometer, model 1600, over the carbonyl ν(CO) frequency range (2200−1600 cm^{-1}). NMR spectral data were obtained in C$_6$D$_6$ and were reported as δ values relative to residual C$_6$H$_6$ (^{1}H, 7.15 ppm) and C$_6$D$_6$ (^{13}C, 128.00 ppm) using Varian model XL-200 and Unity 500 spectrometers. ^{1}H NMR spectrometer parameters had been optimized with a 38° pulse angle during quantitative analyses of known concentrations of **1** and anisole. As a result, integration traces are believed to be accurate within ±5%. Combustion microanalyses were done by Quantitative Technologies, Bound Brook, NJ.

Organic and inorganic reagents were obtained commercially and used as received; silanes and C$_6$D$_6$ were stored in a glovebox under nitrogen. THF and benzene were distilled from sodium benzophenone ketyl. Wilkinson's compound, Rh(PPh$_3$)$_3$Cl, was purchased or prepared and purified according to the literature procedure;[10] its purity (activity) was assayed by ^{1}H NMR spectral monitoring of the catalyzed H$_2$SiPh$_2$ hydrosilation of Cp(CO)$_2$FeC(O)CH$_3$.[2a] The manganese acyl complexes, (CO)$_5$MnC(O)CH$_3$ (**2a**),[11] (CO)$_5$MnC(O)Ph (**2b**),[12] and (PPh$_3$)(CO)$_4$MnC(O)CH$_3$ (**2c**),[13] and the iron acyl complexes, Cp(CO)(L)FeC(O)CH$_3$ (L = CO (**1a**), PPh$_3$ (**1b**),[14]

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$P(OMe)_3$ (**1c**), $P(OPh)_3$ (**1d**)[15]) and $Cp(CO)_2FeC(O)R$ (R = Ph[16] (**9**), i-Pr[17] (**10**), t-Bu[18] (**11**)), were prepared by literature procedures and judged pure by IR and ^1H NMR spectroscopy. Samples of $Cp(CO)_2FeCH{=}CH_2$ (**7a**)[16b] and its spectral data were available from previous studies:[19] ^1H NMR (C_6D_6) δ 7.17 (dd, J = 17.1, 9.0 Hz, Fe−CH), 6.26 (dd, J = 9.0, 0.9 Hz, E =CH), 5.76 (dd, J = 17.1, 0.9 Hz, Z =CH), 4.02 (Cp); ^{13}C NMR (C_6D_6) δ 216.53 (CO), 85.41 (Cp), 139.76 (=CH_2), 130.81 (Fe−CH=).

Hydrosilation of $Cp(CO)_2FeC(O)CH_3$ (1a) with $PhSiH_3$ and $(CO)_5MnC(O)CH_3$ (2a) as the Precatalyst. A solution containing 200 mg of **1a** (0.91 mmol), 10 mg of manganese acetyl **2a** 0.042 mmol, 4.6 mol %), and 33 mg of $C_6H_5OCH_3$ (0.31 mmol) in 600 mg of C_6D_6 was treated with $PhSiH_3$ (118 mg, 1.09 mmol). The resulting light yellow-orange solution was transferred in the glovebox to a 5-mm NMR tube that was fitted with a new rubber septum, and the first ^1H NMR spectrum was recorded within 10 min. Within 1 h, the reaction solution had turned dark red; no other physical changes were noted over 12 h. Since virtually all NMR absorptions were assigned, the reaction progress was monitored by ^1H and ^{13}C-{^1H} NMR spectroscopy.

The reaction was worked up by size-exclusion chromatography on polystyrene beads (Biorad SX-12, molecular weight range 0−400) that had been packed into a 40 × 350 mm glass column in benzene. A guard column (21 × 130 mm) also was part of the high-performance, low- to medium-pressure chromatography[20] apparatus, which was connected via 4-mm Teflon tubing and fittings. The UV−vis detector was set at 463 nm. After 12 h, the reaction mixture was injected onto the apparatus through a three-way valve and was pumped through the columns. Six orange to yellow-orange fractions, 10−15 mL each, were collected and evaporated. When combined after NMR analysis, fractions 2−4 afforded 57 mg of an orange oil that was characterized as $[Cp(CO)_2FeCH(CH_3)O]_3SiPh$ (**5b**) (24% yield). Anal. Calcd for $C_{33}H_{32}O_9SiFe_3$: C, 51.59; H, 4.20. Found: C, 52.10; H, 4.11. Fractions 5 and 6 were evaporated under a stream of nitrogen to yield 104 mg of spectroscopically pure $Cp(CO)_2FeCH_2CH_3$ (**6a**),[21] an amber oil, in 51% yield. ^1H NMR (C_6D_6) δ 4.02 (Cp), 1.58 (q, J = 7.6 Hz, $FeCH_2$), 1.36 (t, CH_3); ^{13}C NMR δ 218.25 (CO), 85.32 (Cp), 22.53 (CH_3), −2.81 ($FeCH_2$).

Hydrosilation of $Cp(CO)_2FeC(O)CH_3$ (1a) with $(CO)_5MnC(O)Ph$ (2b) as the Precatalyst. A yellow C_6D_6 solution (0.5 mL) containing 200 mg of **1a** (0.91 mmol) and 12 mg of **2b** (4.4 mol %) was treated with 118 mg of $PhSiH_3$ (1.09 mmol). The reaction solution turned yellow-orange after 15 min, and after 2 h, the red solution was evaporated to a red oil, which was extracted by hexane (2 × 1 mL). This extractant was chromatographed on a column (10 × 2 cm) of flash-grade silica gel in hexane. Elution with hexane and then 2:1 hexane−benzene brought down light orange bands that produced small amounts of $Cp(CO)_2FeCH_2CH_3$ admixed with unidentified organic residues. Continued development of the column with 2:1 hexane−benzene removed fraction 3, a dark yellow band, which provided 133 mg of a yellow gum. This gum corresponded to $[Cp(CO)_2FeCH(CH_3)O]_3SiPh$ (**5b**) (43% yield by relative integration) that was contaminated (total 30 mg) with **6a** (6%), <4% $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**), and uinidentified organic materials. Prolonged washing of the column with 2:1 hexane−benzene and then benzene gave smaller amounts of **5b** that were increasingly contaminated with **4b**, $Cp(CO)_2Fe_2$, and other unidentified residues.

Hydrosilation of 1a with $(PPh_3)(CO)_4MnC(O)CH_3$ (2c) as the Precatalyst. 1. To a 5-mL vial in the glovebox was added **1a** (44 mg, 0.20 mmol), C_6D_6 (600 mg), **2c** (3 mg, 3.2%), $PhSiH_3$ (11 or 26 mg, 0.50 and 1.20 equiv respectively), and toluene (10 mg, 0.11 mmol). The yellow solution darkened over 5 min. It was transferred to a 5-mm NMR tube that was fitted with a rubber septum, and ^1H NMR spectra were recorded within 10 min. Within 0.5 h, all of the substrate **1a** was consumed.

2. Phenylsilane (43 mg, 0.40 mmol) was added to a benzene solution (1 g) of **1a** (176 mg, 0.80 mmol) and **2c** (11 mg, 0.023 mmol, 2.9%). After 0.5 h, the darkened yellow solution was chromatographed on Biorad SX-12 (size exclusion) polystyrene beads in benzene. Four 15-mL yellow fractions were collected and evaporated. Fraction 2 offered 180 mg of a brown gum that was spectroscopically characterized as **4b** (82% yield) plus small amounts of organic residues. Further attempts to purify this fraction proved unsuccessful. Fractions 1 and 3 also contained **4b** admixed with unidentified organic residues.

Treatment of $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (4b) with $RhCl(PPh_3)_3$ and $PhSiH_3$. A yellow solution containing **1a** (44 mg, 0.20 mmol), **2c** (3 mg, 3.2%), and toluene (10.3 mg, 0.11 mmol) in 500 mg of C_6D_6 was treated with $PhSiH_3$ (11 mg, 0.10 mmol). ^1H and ^{13}C NMR spectral monitoring of the reaction mixture indicated that all of **1a** and $PhSiH_3$ were consumed within 0.5 h, leaving a mixture of **4b** (81%) and $Cp(CO)_2FeCH_2CH_3$ (**6a**) (4%). The NMR tube was brought back to the glovebox, and $RhCl(PPh_3)_3$ (3 mg) and excess $PhSiH_3$ (35 mg) were added. The results of ^1H NMR spectral monitoring over 3 h were consistent with a reduction in concentration of **4b** (70%) commensurate with an increase in **6a** (14%).

Reaction of $[Cp(CO)_2FeCH(CH_3)O]_3SiPh$ (5b) with $RhCl(PPh_3)_3$ and $PhSiH_3$. To a 0.5 mL benzene solution of **1a** (200 mg, 0.91 mmol) was added **1b** (12 mg, 4.4%) and $PhSiH_3$ (110 mg, 1.01 mmol). The yellow solution turned red over 1 h, and after 1.5 h it was chromatographed on Biorad SX-12 polystyrene beads in benzene. Five 15-mL yellow fractions were collected and evaporated, of which fraction 2 contained most of the initial yellow band. This band provided 172 mg of a yellow oil that was identified as $[Cp(CO)_2FeCH(CH_3)O]_3SiPh$ (**5b**) (0.22 mmol, 74% yield), albeit contaminated by small amounts of organic residues. This material in 600 mg of C_6D_6 was treated with $RhCl(PPh_3)_3$ (21 mg, 0.022 mmol) and $PhSiH_3$ (130 mg, 1.19 mmol). ^1H NMR spectral monitoring over 8 h indicated that none of the substrate **5b** was consumed.

Treatment of $Cp(CO)_2FeCH(OSiMe_2Ph)CH_3$ with $RhCl(PPh_3)_3$ and $PhSiH_3$. $PhMe_2SiH$ (138 mg, 1.01 mmol) was added to a benzene solution (0.50 mL) containing **1a** (200 mg, 0.91 mmol) and $(CO)_5MnC(O)CH_3$ (**2a**) (12 mg, 4.4%). After 50 min, the resulting orange solution was chromatographed on 4 × 1 cm of silica gel−pentane. The resulting yellow pentane eluate (40 mL) was evaporated to yield a 188 mg of a yellow oil, which was identified as spectroscopically pure $Cp(CO)_2FeCH(OSiMe_2Ph)CH_3$[1b] (0.53 mmol): ^1H NMR (C_6D_6) δ

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5.72 (q, *J* = 6.0 Hz, FeCH), 4.15 (Cp), 1.69 (d, CH*CH*$_3$), 0.39 (s, $SiMe_2$). To this material in C_6D_6 (500 mg) was added $RhCl(PPh_3)_3$ (15 mg, 0.016 mmol or 3.1%) and $PhSiH_3$ (57 mg, 0.53 mmol). Although gas evolution occurred during the first 0.5 h, the solution remained orange and ^1H NMR spectral monitoring over 8 h indicated that none of the $Cp(CO)_2FeCH(OSiMe_2Ph)CH_3$ was consumed.

Hydrosilation of $Cp(CO)_2FeC(O)CH_3$ (1a) with $PhSiH_3$ and $RhCl(PPh_3)_3$. The reaction was carried out in a 1 dram vial in the glovebox by adding 6 mg of $RhCl(PPh_3)_3$ (3.2%) to a C_6D_6 solution (500 mg) containing **1a** (44 mg, 0.20 mmol), $PhSiH_3$ (35 mg, 1.6 equiv), and PhMe internal standard (9 mg, 0.10 mmol). After 10 min, the yellow solution turned yellowish-green (commensurate with gas evolution), and it was transferred to a NMR tube. Within 40−60 min all of the **1a** was consumed, as judged by ^1H and ^{13}C NMR spectral monitoring. The presence of Cp ^{13}C NMR absorptions was especially informative: $Cp(CO)_2FeCH_2CH_3$ (**6a**) (δ 85.32), $Cp(CO)_2FeCH{=}CH_2$ (**7a**) (δ 85.41), **1a** (δ 86.22), $Cp(CO)_2Fe_2$ (δ 88.52). Product yields were determined via integration of the ^1H NMR spectra vs PhMe: **6a** δ 1.58 (quart, *J* = 7.6 Hz, CH_3), 1.36 (t, CH_2), (49%); **7a** δ 6.26 (*E* =CH), 5.76 (*Z* =CH) (32%); $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**) δ 6.12−6.06 (Fe−CH) (12−14%); **1a** δ 2.40 (CH_3); $Cp(CO)_2FeH$[22] (**8a**) δ −11.8 (FeH).

When the reaction was repeated with 1.1 equiv of $PhSiH_3$, 23% of **1a** remained along with **6a** (49%), **7a** (32%), and **4b** (10−12%). With 0.56 equiv of H_3SiPh, the reaction had 29% **1a** remaining after 3 h and only trace quantities of **7a**.

The reaction mixture (1.6 equiv of $PhSiH_3$) and a 1 mL of pentane rinse were poured into 5 mL of pentane and centrifuged. The supernatant solution was chromatographed on activity 2 neutral alumina (5 × 90 mm) in pentane, from which a yellow band was removed with 5:1 pentane−CH_2Cl_2. This afforded 22 mg of a yellow oil that was identified as spectroscopically pure **6a** (53% yield); NMR spectral yield vs added $(Me_3Si)_2O$, 52%.

The reaction was carried out on a 0.50 mmol scale: 110 mg of **1a** (0.50 mmol), 86 mg of $PhSiH_3$ (1.6 equiv), and 14 mg of $RhCl(PPh_3)_3$ (3.2%) were mixed in 1.0 g of C_6D_6. An NMR spectrum of the reaction mixture after 2 h indicated that all of **1a** was consumed; chromatographic yield of **6a** (4 × 1 cm alumina−pentane, eluted with pentane then 5:1 pentane−CH_2Cl_2), 52 mg, 49%.

$RhCl(PPh_3)_3$-Catalyzed $PhSiH_3$ Hydrosilation of Cp(L)(CO)FeC(O)R: $Cp(PPh_3)(CO)FeC(O)CH_3$ (1b). An NMR tube was charged with a C_6D_6 solution (600 mg) of **1b** (91 mg, 0.20 mmol), $PhSiH_3$ (35 mg, 1.6 equiv), PhMe (14 mg, 0.15 mmol), and $RhCl(PPh_3)_3$ (6 mg, 3.2%). The reaction was complete within 45 min, as judged by ^1H NMR spectroscopy: 61% $Cp(PPh_3)(CO)FeCH_2CH_3$ (**6b**),[8,23] 11% $Cp(PPh_3)(CO)FeCH{=}CH_2$ (**7b**)[24] (quantitated by integration of the vinyl absorptions at δ 6.31 (ddd, 1H), 5.86 (dt, 1H), 4.18 (d, *J* = 1.2 Hz, Cp)), and 11% $Cp(PPh_3)(CO)FeH$ (**8b**)[23a,25] (quantitated with the hydride and Cp absorptions at δ −12.85 (d, J_{PH} = 75.3 Hz) and 4.25 (d, *J* = 1.0 Hz), respectively).

$Cp(PPh_3)(CO)FeC(O)CH_3$ (**1b**) (227 mg, 0.50 mmol), $PhSiH_3$ (86 mg, 1.6 equiv), and $RhCl(PPh_3)_3$ (14 mg, 3.2%) were dissolved in 1.2 g of C_6D_6. The orange solution turned green within 15 min; NMR spectral monitoring confirmed that the reaction was complete. The reaction mixture was poured into 10 mL of pentane and centrifuged. The centrifugate plus pentane washings (2 × 5 mL) were chromatographed on activity 2 neutral alumina−pentane (2 × 5 cm column). Development with 5:1 pentane−CH_2Cl_2 eluted an orange band that gave spectroscopically pure **6b** (137 mg, 62% yield) as an orange solid. ^1H NMR (C_6D_6) δ 7.52 (m, 6H, Ph), 7.02 (m, 9H, Ph), 4.12 (d, *J* = 1.0 Hz, Cp), 1.85 (m, 1H, FeCH*H*), 1.56 (dt, *J* = 1.9, 7.3 Hz, $FeCH_2$*CH*$_3$), 1.04 (m, 1H, Fe*H*H); ^{13}C NMR (C_6D_6) δ 223.52 (d, *J* = 32.3 Hz, CO), 137.71 (d, *J* = 39.1 Hz, ipso C), 133.40 (d, *J* = 9.6 Hz, *o*-C), 129.45 (s, *p*-C), 128.21 (d, *J* = 6.9 Hz, *m*-C), 84.95 (Cp), 23.71 (d, *J* = 4.1 Hz, $FeCH_2$*C*H$_3$), −2.19 (d, *J* = 18.5 Hz, Fe*C*H$_2$).

Similar reactions, 0.20 and 0.50 mmol scale, were performed with the following iron acyls: $Cp(CO)_2FeC(O)Ph$ (**9**), $Cp(CO)_2FeC(O)CH(CH_3)_2$ (**10**), $Cp(CO)_2FeC(O)C(CH_3)_3$ (**11**), $Cp[P(OMe)_3](CO)FeC(O)CH_3$ (**1c**), and $Cp[P(OPh)_3](CO)FeC(O)CH_3$ (**1d**). Reactions were chromatographed using the above procedures; both NMR spectroscopic and isolated yields of the resulting alkyl complexes are recorded in Table 2. Salient NMR spectroscopic data, $Cp(CO)_2FeCH_2Ph$:[26] ^1H NMR (C_6D_6) δ 3.91 (Cp), 2.67 (CH_2); ^{13}C NMR (C_6D_6) δ 217.5 (CO), 86.01 (Cp), 5.42 (CH_2). $Cp(CO)_2FeCH_2CH(CH_3)_2$:[27] ^1H NMR (C_6D_6) δ 4.05 (Cp), 4.74 (m, $FeCH_2$*CH*), 1.59 (t, *J* = 1.2 Hz, Fe*CH*$_2$), 1.09 (d, *J* = 5.9 Hz, CH_3); ^{13}C NMR (C_6D_6) δ 218.39 (CO), 85.45 (Cp), 35.24 ($Cp(CO)_2FeCH_2$*C*H), 26.66 ($Cp(CO)_2Fe$*C*H$_2$), 13.71 (CH_3). $Cp(CO)_2FeCH_2C(CH_3)_3$:[28] ^1H NMR (C_6D_6) δ 4.06 (Cp), 1.73 (s, $FeCH_2$), 1.12 (s, CH_3); ^{13}C NMR (C_6D_6) δ 219.11 (CO), 85.62 (Cp), 35.40 (*C*Me$_3$), 33.40 (Fe*C*H$_2$), 19.25 (CH_3). $Cp[P(OMe)_3](CO)FeCH_2CH_3$:[29] ^1H NMR (C_6D_6) δ 4.31 (Cp), 3.26 (d, *J* = 11.3 Hz, $P(OMe)_3$), 1.58 (m, $FeCH_2$*CH*$_3$), 1.27 (m, Fe*CH*$_2$CH$_3$); ^{13}C NMR (C_6D_6) δ 221.4 (d, *J* = 47.6 Hz, CO), 83.32 (Cp), 51.13 ($P(OMe)_3$), 23.27 (d, *J* = 2.7 Hz, $FeCH_2$*C*H$_3$), −6.01 (d, *J* = 29.3 Hz, Fe*C*H$_2$). $Cp[P(OPh)_3](CO)FeCH_2CH_3$:[24a,30] ^1H NMR (C_6D_6) δ 7.25 (m, 6H, Ph), 7.02 (m, 6H, Ph), 6.85 (m, 3H, Ph), 3.90 (Cp), 1.62 (m, 5H, CH_2CH_3).

Results and Discussion

1. Manganese-Acyl-Catalyzed $PhSiH_3$ Hydrosilation of $Cp(CO)_2FeC(O)CH_3$ (1a). The $(CO)_5MnC(O)CH_3$-catalyzed $PhSiH_3$ hydrosilation of $Cp(CO)_2FeC(O)CH_3$ (**1a**) exhibited three characteristics. First, these sluggish reactions had variable reaction times under comparable conditions. With 1.1−1.2 equiv of $PhSiH_3$ and 4.4−4.6% of precatalyst **2a**, typically 20% of **1a** was depleted over 4−5 h and then 70−85% over 7−8 h. These values, averaged over a dozen runs, however, do not convey the wide rate fluctuations with which substrate **1a** was consumed. The rate of consumption of **1a** varied from 85% within 2 h to an initial 30% after 6 h followed by jumping to 85% after 7 h.

The second observation concerns the fate of the precatalyst **2a**. Most of it remained intact (as deduced from ^1H NMR spectroscopy), up to at least 85−90% consumption of the substrate **1a**. This substrate inhibition of the required hydrosilation of the precatalyst[1d] is typical of the manganese-acyl-catalyzed hydrosilation of **1**.[2] As expected,[4] a reactive precatalyst is required for the hydrosilation of **1a**; neither $(CO)_5MnSi(CH_3)_3$ nor $Mn_2(CO)_{10}$ function as viable hydrosilation catalysts toward **1** under these conditions.

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Table 1. Spectral Data for α-Siloxyethyl $Fe(CO)_2Cp$ Complexes

complex (IR)	^1H NMR (C_6D_6), δ	$^{13}C\{^1H\}$ NMR (C_6D_6), δ
$Cp(CO)_2FeCH(CH_3)OSiH_2Ph$, **3b**[a]	5.73 (q, $J = 6.0$ Hz, FeCH) 5.25 (s, 2H, SiH) 4.24 (s, Cp) 1.78 (d, $J = 6.0$ Hz, CH_3)	72.26 (CH) 34.88 (CH_3)
$[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$, **4b**[b] ($\nu$(CO) 2004, 1945 cm^{-1}(br))	7.90 (m, 2H, SiPh) 7.26 (m, 3H, SiPh) 6.07 (q, $J = 6.4$ Hz, $FeCH_A$) 6.05 (q, $J = 6.4$ Hz, $FeCH_B$) 6.04 (q, $J = 5.9$ Hz, $FeCH_C$) 6.01 (q, $J = 5.9$ Hz, $FeCH_D$) 5.47 (s, 1H, SiH) 5.42 (s, 3H, SiH) 4.24, 4.22, 4.18, 4.17 (s, Cp_{A-D}) 1.96 (d, $J = 6.4$ Hz, $CH_{3(C)}$) 1.95 (d, J = 6.4 Hz, $CH_{3(D)}$) 1.88 (d, $J = 5.9$ Hz, $CH_{3(A)}$) 1.87 (d, $J = 5.9$ Hz, $CH_{3(B)}$)	217.85, 217.55, 217.49, 217.46 (CO) 134.30, 130.56, 127.49 (*ipso*-SiPh) 86.29, 86.27, 86.24 (br) (Cp) 70.20, 70.02, 69.41, 69.40 (CH) 35.73, 35.69, 35.49, 35.42 (CH_3)
$[Cp(CO)_2FeCH(CH_3)O]_3SiPh$, **5b** ($\nu$(CO) 2008, 1951 cm^{-1}(br))	8.10 (m, 2H, Ph) 7.36 (m, 2H, Ph) 7.26 (m, 1H, Ph) 6.39 (q, $J = 6.2$ Hz, $FeCH_A$) 6.38 (q, $J = 6.2$ Hz, $FeCH_B$) 6.32 (q, $J = 5.8$ Hz, $FeCH_C$) 6.23 (q, $J = 6.1$ Hz, $FeCH_D$) 4.39, 4.38, 4.31, 4.27 (s, Cp) 2.06 (d, $J = 5.8$ Hz, $CH_{3(A)}$) 2.04 (d, $J = 5.9$ Hz, $CH_{3(C)}$) 2.01 (d, $J = 5.9$ Hz, $CH_{3(B)}$) 1.98 (d, $J = 6.1$ Hz, $CH_{3(D)}$)	218.09, 218.08, 218.05, 218.03, 217.91, 217.87, 217.82, 217.77 (CO) 138.22 (*ipso*-C, Ph) 130.06, 128.53, 127.99 (Ph) 86.36, 86.30, 86.27, 86.21 (Cp) 69.37, 69.29, 69.27, 69.10 (FeC) 36.12, 36.02, 35.97, 35.93 (CH_3)

[a] Observed as a minor component during the early stages of hydrosilation of **1a**. Carbonyl (IR, ^{13}C NMR), phenyl (^1H, ^{13}C NMR), and Cp (^{13}C NMR) absorptions were not discerned. [b] Methine absorption appears as an eight-line multiplet at δ 6.05, and two of the methyl doublets appear as an apparent triplet (δ 1.99). Double irradiation at δ 1.9 reduced the δ 6.05 multiplet to four equally intense singlets; reversing the decoupling experiment revealed four methyl resonances. Further correlation of these methine−methyl spin systems are consistent with the results of the COSY experiments.[33]

Table 2. $RhCl(PPh_3)_3$-Catalyzed $PhSiH_3$ Hydrosilation of Cp(CO)(L)FeC(O)R

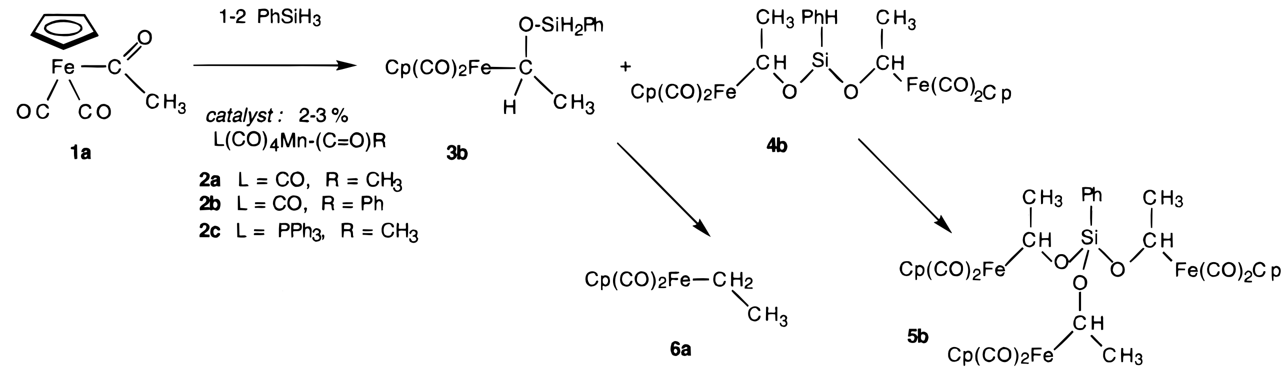
substrate	reaction scale (mmol)[a]	product	NMR yield (%)[b]	isolated yield (%)[c]
1. $Cp(CO)_2FeC(O)CH_3$ (**1a**)	0.20	$Cp(CO)_2FeCH_2CH_3$ (**6a**)	49[d]	53
	0.50			49
2. $Cp(CO)_2FeC(O)CH(CH_3)_2$ (**10**)	0.50	$Cp(CO)_2FeCH_2CH(CH_3)_2$		69
3. $Cp(CO)_2FeC(O)C(CH_3)_3$ (**11**)	0.20	$Cp(CO)_2FeCH_2C(CH_3)_3$	91	
	0.50			66
4. $Cp(CO)_2FeC(O)Ph$ (**9**)	0.20	$Cp(CO)_2FeCH_2Ph$	82	58
	0.50			73
5. $Cp(PPh_3)(CO)FeC(O)CH_3$ (**1b**)	0.20	$Cp(PPh_3)(CO)FeCH_2CH_3$ (**6b**)	61[e]	
	0.50			62
6. $Cp[P(OMe)_3](CO)FeC(O)CH_3$ (**1c**)	0.20	$Cp[P(OMe)_3](CO)FeCH_2CH_3$	75[e]	
	0.50			74
7. $Cp[P(OPh)_3](CO)FeC(O)CH_3$ (**1d**)	0.50	$Cp[P(OPh)_3](CO)FeCH_2CH_3$		87

[a] Reaction carried out in 600 mg of C_6D_6 (0.20 mmol) or 1.5 mL of C_6D_6 or C_6H_6 (0.50 mmol) with 1.6 equiv of $PhSiH_3$ and 3.2% $RhCl(PPh_3)_3$. [b] Quantified by ^1H NMR vs PhMe internal standard (±5%). [c] Isolated as spectroscopically pure material via column chromatography on activity 2 alumina using 5:1 pentane−CH_2Cl_2. [d] Also detected 32% $Cp(CO)_2FeCH{=}CH_2$ (**7a**) and 12−14% $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**). [e] Also detected 10−15% of the vinyl complexes $Cp(L)(CO)FeCH{=}CH_2$ (L = PPh_3 (**7b**) and $P(OMe)_3$ (**7c**)).

Third, results of ^1H NMR spectroscopic monitoring established that the **2a**-catalyzed hydrosilation of **1a** occurs in two stages, Scheme 2. Within the first 7−8 h, **1a** transformed to variable mixtures of $Cp(CO)_2FeCH(CH_3)OSiH_2Ph$ (**3b**), $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**), and $[Cp(CO)_2FeCH(CH_3)O]_3SiPh$ (**5b**), typically 1:1:2 at 70% depletion of **1a**. Little or no $Cp(CO)_2FeCH_2CH_3$ (**6a**) or $Cp_2(CO)_4Fe_2$ was detected. Between 8 and 12 h, the reaction mixture of **3b**−**5b** plus remaining $PhSiH_3$ produced **6a** (along with traces of $Cp_2(CO)_4Fe_2$) and left **5b**. Then **5b** evidently underwent only very slow reduction to **6a**, which was not further studied. Although the use of 2.2−2.4 equiv of $PhSiH_3$ and the same precatalyst concentration accelerated the reaction (**1a** was consumed in under 6 h), the same ratio of **6a** and **5b** formed as the final products.

Together, **6a** and **5b** constituted the final products after reaction for 12 h with 1.2 equiv of $PhSiH_3$ and accounted for virtually all of the starting **1a**. Their NMR yields of 35% and 62%, respectively (based upon **1a**), were calculated via two procedures. Results of direct quantitation of either their Cp resonances or their upfield ethyl multiplets and methyl doublets—using anisole as an internal standard—agreed with the other procedure of extrapolating the maximum yields of **6a** and **5b** that are possible from the relative integrated areas of their Cp resonances.[31] We made no attempts to account for the residual organosilane byproducts. These byproducts left no definitive NMR spectral absorptions other than broad SiH ^1H NMR absorptions at 5.2−5.4 ppm, which coincided with the buildup of substantial concentrations of **6a**.

Scheme 2



We isolated [Cp(CO)$_2$FeCH(CH$_3$)O]$_3$SiPh (**5b**) in 24% yield by size-exclusion chromatography, as outlined in the Experimental Section. This chromatography procedure, when used on 0.5−2.0 mmol scale reactions, had been used to separate similar hydrosilation reaction products involving dihydrosilanes. Both Cp(CO)$_2$FeCH(OSiHR$_2$)CH$_3$ (**3a**) and [Cp(CO)$_2$FeCH(CH$_3$)O]$_2$SiR$_2$ (**4a**) (R = Et, Ph), the R$_2$SiH$_2$ dihydrosilation products of **1a** (Scheme 1), accordingly had been isolated by size-exclusion chromatography.[1b,e] Experimental details also are outlined for working up the **1a**/PhSiH$_3$ hydrosilation reactions using the more traditional column chromatography on 40 μm (flash-grade) silica gel−hexane. Under these chromatography conditions, however, considerable decomposition occurred on the column and produced unidentified residues admixed with both **5b** and **6a**.

The isolated **5b** is a stable yellow oil that that was fully characterized as an equimolar mixture of four diastereomers. Its IR spectrum shows two broadened carbonyl υ(CO) bands at 2008 and 1951 cm^{-1}. Chemical shifts for the ^{1}H and ^{13}C NMR spectra of **5b** (Table 1) correspond to those of the fully characterized Cp(CO)$_2$FeCH(OSiHPh$_2$)CH$_3$ (**3a**) and [Cp(CO)$_2$FeCH(CH$_3$)O]$_2$SiPh$_2$ (**4a**). Both the ^{1}H and ^{13}C NMR spectra of **5b** are well resolved and further establish it as a constitutionally symmetrical molecule that has three stereogenic Cp(CO)$_2$FeCHMeO groups branching off an achiral silicon center. The resulting four stereoisomers constitute a diastereomeric pair of enantiomers [*RRR* (*SSS*) and *RRS* (*SSR*)][32] that accounts for the net 1:1:1:1 relative intensities for the Cp (and other Cp(CO)$_2$FeCHMeO) ^{1}H and ^{13}C NMR spectral resonances of **5b**.[33]

We were unable to isolate Cp(CO)$_2$FeCH(CH$_3$)OSiH$_2$Ph (**3b**) and [Cp(CO)$_2$FeCH(CH$_3$)O]$_2$SiHPh (**4b**) during the earlier stages of these reactions catalyzed by **2a**. Attempted size-exclusion chromatographic workup produced only fractions that contained varying ratios (always <1:5) of **4b** and **5b**. Although both the ^{1}H and ^{13}C NMR spectra of these reaction mixtures are rich in the number of absorptions corresponding to diastereomeric mixtures for **3b**−**5b**, the isolation of **5b** (and of **4b** from the **2c**-catalyzed reactions, vide infra) greatly simplified the assignment of their NMR spectra and spectral monitoring of these hydrosilation reactions.

NMR spectroscopic monitoring of the catalyzed PhSiH$_3$ hydrosilation of **1a** also was facilitated by spreading out of the corresponding absorptions for **3b**−**5b**. In particular, a characteristic downfield progression of the methine quartets, Cp singlets, and methyl doublets occurs in their ^{1}H NMR spectra in going from **5b** to **4b** to **3b**. These chemical shift regions for each of **3b**−**5b** are consistent with the results of COSY NMR experiments.[33]

Ethoxyphenylsilanes H$_x$Si(EtO)$_{3-x}$Ph (x = 1−3) that might have originated from continued oxidative addition of PhSiH$_3$ to **3b**−**5b** and then reductive elimination were not detected. Similar elimination of alkoxysilanes from CpFe α-siloxyethyl complexes has been observed with trialkylsilanes upon photolysis or heating.[34] ^{1}H and ^{13}C NMR spectral data of authentic samples of these ethoxysilanes, generated by **2**-catalyzed dehydrogenative silation of ethanol with PhSiH$_3$,[5a] were obtained independently. These ethoxyphenylsilanes exhibit diagnostic ^{1}H NMR absorptions at δ 3.6−3.7 and 1.0−1.2 and ^{13}C NMR resonances at δ 18−19 and 59−61 that easily would have been detected during the hydrosilation of **1a**.

Substitution of (CO)$_5$MnC(O)Ph (**2b**) as the precatalyst (4.4%) under otherwise identical reaction conditions considerably accelerated the PhSiH$_3$ hydrosilation of Cp(CO)$_2$FeC(O)CH$_3$ (**1a**)—the substrate was depleted within 30 min. In its place, a mixture containing 4% **3b**, 22% **4b**, 72% **5b**, and approximately 2% Cp(CO)$_2$FeCH$_2$CH$_3$ (**6a**) was quantified by ^{1}H NMR spectroscopy. Over 2 h, **3b** was consumed, leaving 15% **4b**, 81% **5b**, but only 4% **6a**. Prolonged sitting of the reaction mixture up to 12 h only increased the yield of **6a** to 15−20% (peak broadening of the ^{1}H NMR spectra was problematic). The higher yields of **5b** when using **2b** as the precatalyst facilitated the isolation of **5b** by size-exclusion chromatography on polystyrene beads. It

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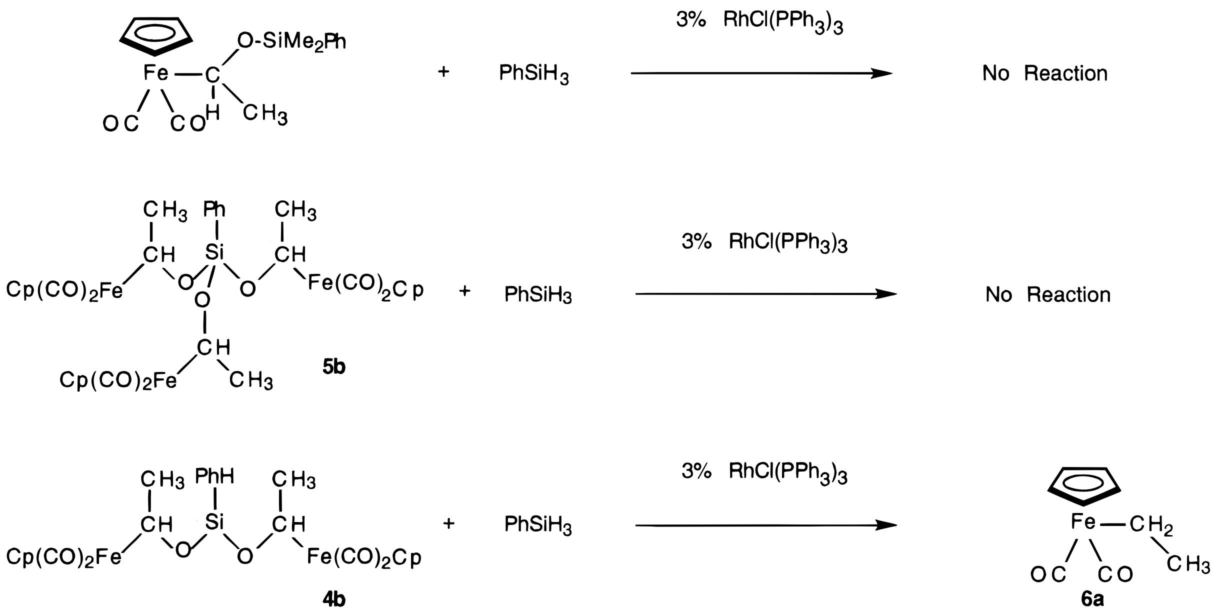
[31] The ratio of the integral traces of the Cp resonances for **5b** is 0.61 times that of Cp(CO)$_2$FeEt (**6a**) or $n_{5b} = (0.61)n_{6a}$ (n = number of moles), after accounting for the relative number of Cp rings involved. Thus, $n_{1a} = n_{6a} + 3n_{5b}$, and $n_{1a} = n_{6a} + 3(0.61)n_{6a} = 2.83n_{6a}$. This affords $n_{6a}/n_{1a} = 0.35$ or 35% and 65% yields of **6a** and **5b**, respectively, as deduced from the ratio of the Cp ligand integrations and the observation that all of the substrate **1a** had been converted to **6a** and **5b**.

[32] Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; p 68.

[33] ^{1}H NMR spectra of isolated **4b** and **5b** (with discussion of their assignments) as well as of the reaction mixtures of **2a**- and **2c**-catalyzed PhSiH$_3$ hydrosilation of **1a** are deposited in the Supporting Information.

[34] (a) Akita, M.; Oku, T.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1790. Akita, M.; Oku, T.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1991**, *10*, 3080. (b) Brunner, H.; Fisch, K. *Ang. Chem., Int. Ed. Engl.* **1990**, *29*, 1131; *J. Organomet. Chem.* **1991**, *412*, C11.

Scheme 3

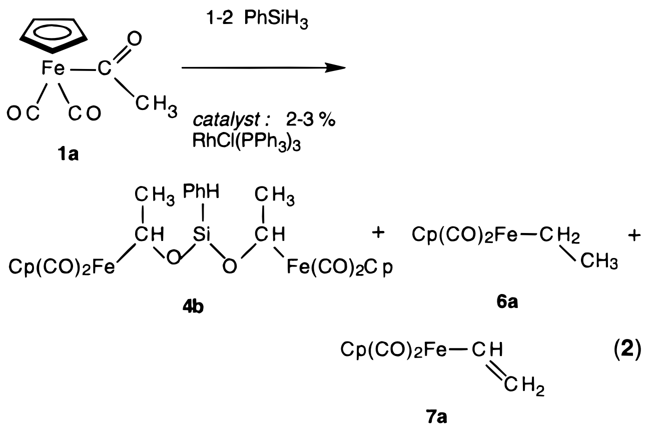


was very difficult to completely remove all of **4b**, although benzene easily eluted 100−150 mg samples of **5b** that were contaminated with 5−10% **4b**.

The precatalyst $(PPh_3)(CO)_4MnC(O)CH_3$ (**2c**) differed in activity from **2a** and **2b** in that $PhSiH_3$ hydrosilation of **1a** yielded $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**) as the major product. The use of **2c** (3.0 mol %) as the precatalyst consumed **1a** within 0.5 h and selectively yielded **4b** and **6a** as the only NMR detectable products. With 1.2 equiv of $PhSiH_3$, the yields of **4b** and **6a** went from 71% and 10% after 0.5 h to 66% and 19% after 5 h. With 0.50 equiv of $PhSiH_3$ under otherwise identical conditions, **1a** transformed to mixtures containing 73% **4b** plus 6% **6a**.[33]

The ^1H NMR spectrum of $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**) also exhibits four sets of NMR absorptions for its $Cp(CO)_2FeCHMeO$ groups. These NMR absorptions are anticipated for a constitutionally symmetrical molecule that has two stereogenic $Cp(CO)_2FeCHMeO$ groups separated by the SiHPh center. This structure affords four stereoisomers, a pair of enantiomers having a prochiral center [*R*·*R* (*S*·*S*)] and two meso diastereoisomers each with their pseudoasymmetric centers [*RrS* and *RsS*]. The meso diastereoisomers account for two sets of ^1H and ^{13}C NMR absorptions for their $Cp(CO)_2FeCHMeO$ groups, whereas the enantiomeric pair exhibits two sets of NMR absorptions due to the presence of their diastereotopic and magnetically nonequivalent $Cp(CO)_2FeCHMeO$ moieties. Detailed NMR assignments for these sets of NMR absorptions of **4b**, however, were more difficult to make than those for **5b** because of overlapping of the NMR spectral absorptions.[33]

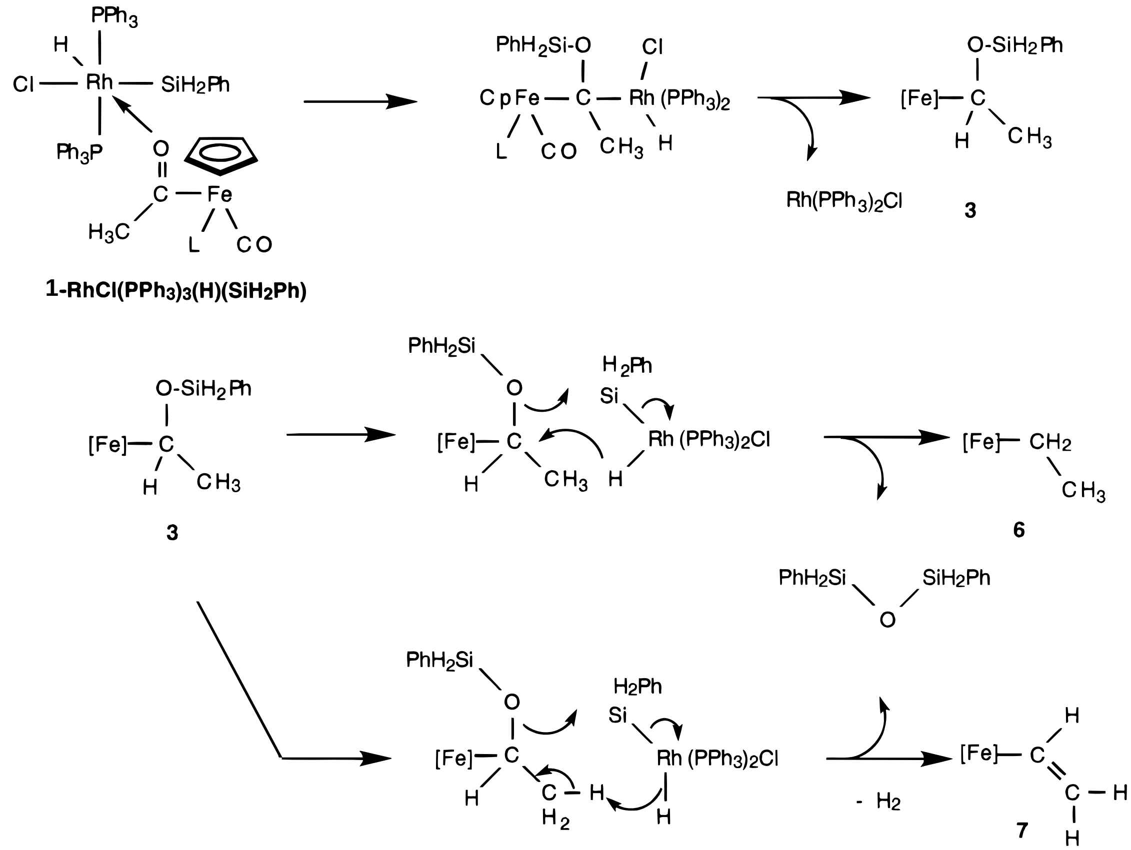
2. $RhCl(PPh_3)_3$-Catalyzed $PhSiH_3$ Hydrosilation of Iron Acyl Complexes Cp(CO)(L)FeC(O)R. The $RhCl(PPh_3)_3$-catalyzed $PhSiH_3$ hydrosilation of $Cp(CO)_2FeC(O)CH_3$ (**1a**) is the most efficient procedure for reducing it to $Cp(CO)_2FeCH_2CH_3$ (**6a**), albeit at the expense of producing another organoiron product—the known[16b,19] vinyl complex $Cp(CO)_2FeCH{=}CH_2$ (**7a**), eq 2. A mixture of **7a** (32%), **6a** (49%), and $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**) (12−14%) results from the reaction of **1a** (0.20 mmol) with 1.6 equiv of $PhSiH_3$ and 3.2% $RhCl(PPh_3)_3$ in C_6D_6, as deduced by ^1H and ^{13}C NMR spectroscopy. The catalyst and silane concentrations were optimized for the rapid depletion of substrate **1a** (40 to 60 min), conditions under which neither $Cp_2Fe_2(CO)_4$ (δ 4.22) nor $Cp(CO)_2FeH$ (δ −11.8) were detected. Isolated yields of spectroscopically pure **6a** varied from 48% (0.50 mmol scale) to 51% (0.20 mmol scale) after chromatography on alumina.



To probe the mechanism for the $RhCl(PPh_3)_3$-catalyzed $PhSiH_3$ hydrosilation of **1a**, we looked at the independent reactions of several $Cp(CO)_2Fe$-α-siloxyethyl complexes with $RhCl(PPh_3)_3/PhSiH_3$ (Scheme 3). The addition of catalytic quantities of $RhCl(PPh_3)_3$ had no effect on mixtures of $Cp(CO)_2FeCH(OSiMe_2Ph)CH_3$[1a] or $[Cp(CO)_2FeCH(CH_3)O]_3SiPh$ (**5b**) with $PhSiH_3$ over at least 3 h. We did note, however, the much slower dehydrogenative silation and oligomerization of $PhSiH_3$ to at least PhH_2SiSiH_2Ph (10%).[7]

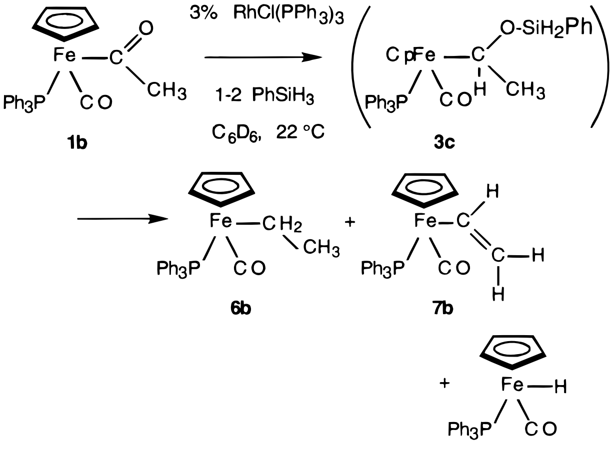
In contrast, $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**) proved to be a more responsive substrate toward $RhCl(PPh_3)_3/PhSiH_3$. The substrate **4b** was generated conveniently from **2c**-catalyzed hydrosilation of **1a** (0.50 equivalent of $PhSiH_3$) as a mixture containing 72% **4b** and 2% **6a** but no residual $PhSiH_3$. Although the addition of 3% $RhCl(PPh_3)_3$ to this mixture had no effect, repeating the

Scheme 4



same procedure and adding another 1.0 equiv of $PhSiH_3$ yielded 12% **6a** after 2 h.

Wilkinson's compound also catalyzed the $PhSiH_3$ hydrosilation–deoxygenation of $Cp(PPh_3)(CO)FeC(O)CH_3$ (**1b**). The addition of 1.6 equiv of $PhSiH_3$ and 3.2% $RhCl(PPh_3)_3$ promptly transformed **1b** to a mixture containing 61% $Cp(PPh_3)(CO)FeCH_2CH_3$ (**6b**), 11% $Cp(PPh_3)(CO)FeCH{=}CH_2$ (**7b**), and 11% $Cp(PPh_3)(CO)FeH$ (**8b**) (eq 3). A slightly higher yield of the ethyl compound **6b** (62%) was realized after column chromatography of a larger scale reaction (0.50 mmol). The presence of **7b** and **8b** was signaled by diagnostic ^1H NMR spectral absorptions for their vinyl and iron hydride spin systems, respectively.



(3)

Five other iron acyl compounds—$Cp(CO)_2FeC(O)Ph$ (**9**), $Cp(CO)_2FeC(O)CH(CH_3)_2$ (**10**), $Cp(CO)_2FeC(O)C(CH_3)_3$ (**11**), $Cp[P(OMe)_3](CO)FeC(O)CH_3$ (**1c**), and $Cp[P(OPh)_3](CO)FeC(O)CH_3$ (**1d**)—were subjected to similar hydrosilation procedures. The resulting fully reduced alkyl complexes are reported in Table 2 as both their in situ NMR spectral and isolated yields after chromatography. Both yields, in good agreement with one another, ranged from 58% (for **9**) to 87% (**1d**). The model substrate **1a** under comparable reaction conditions, in contrast, afforded somewhat lower yields of **6a**, due to the presence of **4b** and especially the vinyl complex **7a**. Of the five new iron acyl compounds, only the trimethyl-phosphite-substituted acetyl complex **1c** provided detectable concentrations of a vinyl complex, $Cp[P(OMe)_3](CO)FeCH{=}CH_2$[2a] (**7c**). Catalytic hydrosilation–deoxygenation, using $RhCl(PPh_3)_3$ and Ph_2SiH_2 in CH_2Cl_2, also has been reported by Akita, Moro-oka, and co-workers.[3] They transformed **1b** to **6b** plus varying amounts of **7b** and $Cp(CO)_2FeC(O)Ph$ (**9**) to $Cp(CO)_2FeCH_2Ph$ plus $Cp(CO)_2FeCH(OMe)Ph$ after methanolysis.

A plausible pathway for the rhodium(I)-catalyzed hydrosilation–reduction of iron acyl complexes to their fully reduced alkyl compounds (Scheme 4) has as its first step catalytic hydrosilation that gives an α-siloxyalkyl intermediate, $Cp(L)(CO)FeCH(OSiH_2Ph)R$ (**3**). In this first step, $RhCl(PPh_3)_2$ as the active catalyst promotes hydrosilation of the acyl complex analogous to the accepted mechanism for the Rh(I)-catalyzed hydrosilation of ketones.[6,35] We emphasize, however, that although this latter reaction often provides vinyl silyl ethers as byproducts (e.g., $PhC(OSiR_3){=}CH_2$ from $PhC(O)CH_3$),[36] full reduction of the acyl functionality to a methylene group is rare.[6,37]

The resulting α-siloxyalkyl intermediate **3** then continues to react with the active catalyst and $PhSiH_3$ (or Ph_2SiH_2[3]), perhaps via an active catalyst·$PhSiH_3$ adduct $(PhH_2Si)(H)RhCl(PPh_3)_2$.[6,38] This hydrido(silyl)rhodium(III) transient would transfer hydride to **3** concurrent with abstracting the α-siloxy group as a disiloxane. A potential driving force for loss of the α-siloxy group relates to the established proclivity of organometallic centers to ionize even poor leaving groups from a sp^3 hybridized α-carbon.[39] This ionization step is commonly used to produce stable alkylidene derivatives such as $Cp(L)(CO)Fe{=}CHCH_3^+$,[39a,b] which are reduced by hydride donors (giving **6**) or are deprotonated by weak bases (giving **7**).[24a] Accordingly, we hypothesize that hydrido(silyl)rhodium(III), while abstracting the α-siloxy group, also competitively deprotonates **3** to a vinyl complex **7** concurrent with releasing disiloxane and $H_2RhCl(PPh_3)_2$ (then H_2).

Supporting evidence for the ionization–deoxygenation step is available from the studies of Akita, Moro-oka, and co-workers[3] on the $RhCl(PPh_3)_2$-catalyzed reactions of Ph_2SiH_2 with iron α-methoxyalkyl complexes. They observed that $RhCl(PPh_3)_3$ in the presence of Ph_2SiH_2 catalytically deoxygenated $Cp(PPh_3)(CO)FeCH(OCH_3)R$ ($R = H, CH_3$) to give $Cp(PPh_3)(CO)FeCH_2R$, although $Cp(CO)_2FeCH_2OCH_3$ was inert. This diminution in reactivity by switching to the comparatively electron-deficient $Cp(CO)_2Fe$ moiety can be attributed to its diminished capability of promoting the alkoxide ionization or otherwise stabilizing an incipient positive charge at the α-carbon.

We propose that the $RhCl(PPh_3)_2{\cdot}PhSiH_3$ adduct preferentially reduces the mono-α-siloxyethyl intermediates $Cp(L)(CO)FeCH(OSiH_2Ph)CH_3$ (**3**), as opposed to their bis- and tris-counterparts **4** and **5**. The intermediates **3**–**5** were detected only during the catalytic $PhSiH_3$ hydrosilation of **1a**. With this substrate, choice of a manganese acyl precatalyst **2a**–**c** gave variable amounts of **3b**–**5b**, although **3b** never accumulated in more than 18% of the converted **1a** and never appeared as part of the final product array. These observations correspond to using **2a**–**c** as catalysts, whereas choice of $RhCl(PPh_3)_3$ as the precatalyst and **1a** as the substrate gave <15% $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**) as the minor byproduct to $Cp(CO)_2FeCH_2CH_3$ (**6a**) and $Cp(CO)_2FeCH{=}CH_2$ (**7a**). Nevertheless, isolated samples of **4b** when subjected to $RhCl(PPh_3)_3/PhSiH_3$ catalysis only slowly reduced to $Cp(CO)_2FeCH_2CH_3$ (**6a**); in separate reactions, **5b**, as well as $Cp(CO)_2FeCH(OSiMe_2Ph)CH_3$, remained inert. It is of course possible that acyl substrates with more electron-rich iron centers, especially **1b**, may form (undetected) mono-, bis-, and tris-α-siloxyethyl intermediates $[Cp(L)(CO)FeCH(CH_3)O]_xSiH_{3-x}Ph$ (**3**, $x = 1$; **4**, $x = 2$; **5**, $x = 3$) that undergo subsequent catalytic deoxygenation or deprotonation along with loss of disiloxane.

A reaction pathway similar to that advanced in Scheme 4 for the hydrosilation–deoxygenation of iron acyl complexes using $RhCl(PPh_3)_3$ as the catalyst also applies to the manganese acyl precatalysts **2a**–**c**. These precatalysts could afford coordinatively unsaturated $L(CO)_3MnSiH_2Ph$ ($L = CO, PPh_3$) as the presumed active catalysts.[4a] Analogous manganese silyls, generated by hydrosilation of **2a**–**c** with excess hydrosilane and by photolysis of $(CO)_5MnSiR_3$, are postulated active catalysts for the hydrosilation of ketones,[5c] esters,[5b] and $Cp(CO)_2FeC(O)R$.[1b,e] Indeed, treatment of $(CO)_5MnC(O)CH_3$ (**1a**) with $PhSiH_3$ yields α-siloxyethyl complexes $[(CO)_5MnCH(CH_3)O]_xH_{3-x}SiPh$ (**3c**–**5c**);[33] their degradation was reminescent of the hydrosilation chemistry of **2a**–**c** with other hydrosilanes to generate transient concentrations of the purported hydrosilation active catalysts.[1a,b,d] Studies in progress address the proposed use of active catalyst–hydrosilane adducts, $L(CO)_3Mn(H)(SiR_3)_2$, as reducing agents toward organic silyl acetals and organometallic α-siloxyalkyl complexes.

Conclusions

The $PhSiH_3/RhCl(PPh_3)_3$ catalytic system affords a convenient synthetic procedure for the hydrosilation then deoxygenation of organoiron acyl complexes $Cp(L)(CO)FeC(O)R$ to yield their alkyl derivatives $Cp(L)(CO)FeCH_2R$. We used the transformation of $Cp(CO)_2FeC(O)CH_3$ (**1a**) to $Cp(CO)_2FeCH_2CH_3$ (**6a**) as the control reaction for optimizing catalysis, although this substrate of the seven iron acyl complexes studied provided the lowest yields (49%) of its reduced alkyl. With 3% $RhCl(PPh_3)_3$ and 1.6 equiv of $PhSiH_3$, the reduced yields of **6a** corresponded to the presence of $Cp(CO)_2FeCH{=}CH_2$ (**7a**) (32%) and $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**) (12–14%). The other iron acyl complexes provided their fully reduced alkyl derivatives (0.50 mmol scale reactions) in 58–87% isolated yields after chromatography, for which analogous vinyl byproducts were observed with only two other iron acyl substrates.

The manganese carbonyl acyl complexes $L(CO)_4MnC(O)R$ ($L = CO$, $R = CH_3$ (**2a**); $L = CO$, $R = Ph$ (**2b**); $L = PPh_3$, $R = CH_3$ (**2c**)) also served as viable $PhSiH_3$ hydrosilation precatalysts for **1a**. With 1 equiv of $PhSiH_3$ and 3% manganese acyl precatalyst, these reactions produced $Cp(CO)_2FeCH(CH_3)OSiH_2Ph$ (**3b**), $[Cp(CO)_2FeCH(CH_3)O]_2SiHPh$ (**4b**), and $[Cp(CO)_2FeCH(CH_3)O]_3SiPh$ (**5b**) plus variable amounts of **6a** (maximum 35% with **2a**) but no **7a**. Depending on the choice of precatalyst, both **4b** and **5b** were isolated whereas

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3b was only detected by ^{1}H and ^{13}C NMR spectral monitoring. We believe that **3b**, as opposed to **4b** or **5b**, preferentially undergoes reduction to **6a** with the manganese acyls **2a**−**c** (or RhCl(PPh$_3$)$_3$) as the precatalysts. Consistent with this hypothesis, samples of **4b** and **5b** were poor substrates for PhSiH$_3$/RhCl(PPh$_3$)$_3$ reduction to **6a**. We surmise that similar intermediates Cp(L)(CO)FeCH(OSiH$_2$Ph)R (**3**) serve as precursors to other alkyl products, Cp(L)(CO)FeCH$_2$R).

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Supporting Information Available: ^{1}H NMR spectra of isolated **4b** and **5b** (with discussion of their assignments) and of the reaction mixtures of **2a**- and **2c**-catalyzed PhSiH$_3$ hydrosilation of **1a**, as well as spectroscopic data, and discussion of the reaction of **2a** and PhSiH$_3$ (9 pages). Ordering information is given on any current masthead page.

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