ELSEVIER

Journal of Organometallic Chemistry 547 (1997) 173–182

Journal of Organometallic Chemistry

The reactions of hydrosilanes with the methoxycarbonyl complexes $Cp(L)(CO)MCO_2Me$ (M = Fe, Ru; L = CO, PPh_3) and $(L)(CO)_xMCO_2Me$ (M = Co, Mn; L = CO, PPh_3; $x = 3, 4$, with and without catalysis

M. DiBiase Cavanaugh, Brian T. Gregg, R.J. Chiulli, Alan R. Cutler *

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

Received 13 January 1997; revised 8 April 1997

Abstract

The reactivity of selected organotransition metal methoxycarbonyl complexes towards hydrosilanes differs significantly from their acetyl analogs in that hydrosilation does not occur across the methoxycarbonyl ligand. Only hydrosilane/manganese carbonyl precatalyst systems that had proved to be more active towards the acetyl ligand on $Cp(L)(CO)MC(O)CH_3$ (M = Fe, Ru; L = CO, PPh_3, PPh_3) reacted with the methoxycarbonyl complexes $Cp(CO)_2MCO_2CH_3$ (**1**, M = Fe; **2**, M = Ru). These reactions involving $PhSiH_3$/2–3% $(PPh_3)(CO)_4MnC(O)CH_3$ for **1** and **2**, or $PhMe_2SiH$/2–3% $(CO)_5MnCH_3$ for **1** afforded their η^4-cyclopentadiene compounds $(\eta^4\text{-}C_5H_6)M(CO)_3$ (M = Fe, Ru) plus methoxysilanes. Results with $PhMe_2SiD$/3% $(CO)_5MnCH_3$ support exo deuteride transfer to the Cp ligand; a mechanism is proposed. The low reactivity of methoxycarbonyl complexes under hydrosilation catalysis conditions also is consistent with the inactivity of $PhSiH_3$ or $Ph_2SiH_2/Rh(PPh_3)_3Cl$ towards **1** or **2** and with the inertness of $Cp(PPh_3)(CO)FeCO_2CH_3$ and $Cp^*(CO)_2FeCO_2CH_3$ under all attempted hydrosilation conditions.

This diminution of hydrosilane reactivity extends to cobalt and manganese carbonyl methoxycarbonyl complexes $(L)(CO)_xMCO_2CH_3$ (**3**, M = Mn, $x = 4$, L = CO; **4**, M = Co, $x = 3$, L = PPh_3; **5**, M = Co, $x = 3$, L = CO). Although their acetyl analogs $(L)(CO)_xMC(O)CH_3$ are sensitive to hydrosilanes, both **3** and **4** are inert towards $PhMe_2SiH$ or Ph_2SiH_2. Treatment of **5** with $PhMe_2SiH$ released methyl formate and left the silyl complex $(CO)_4CoSiMe_2Ph$, a result that resembles the hydrogenation chemistry of **5**. © 1997 Elsevier Science S.A.

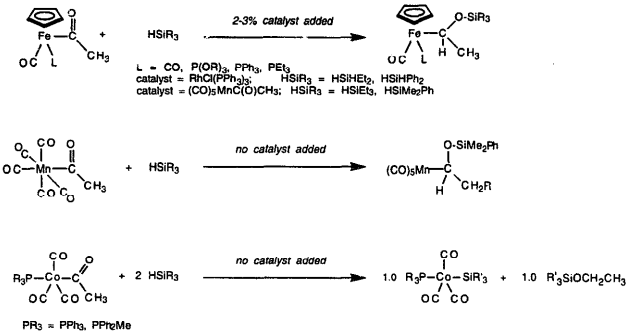
1. Introduction

In recent studies, we have observed several reactions between hydrosilanes and organometallic acyl complexes (Scheme 1) [1]. In the first type of reaction, mono- or dihydrosilanes and obligatory catalysts, e.g. $Rh(PPh_3)_3Cl$, transform the nonlabile iron acetyl complexes $Cp(CO)(L)FeC(O)CH_3$ [L = CO, PR_3] to $Cp(CO)(L)FeCH(OSiR_3)CH_3$ [1–4]. A number of these (α-siloxyethyl)iron compounds accordingly have been isolated. Two other types of hydrosilation reactions [5–8] have been documented for the labile acetyl complexes $(CO)_5MnC(O)CH_3$ [9,10] and $(PR_3)(CO)_3CoC(O)CH_3$ [11]. Both rapidly add hydrosilanes without benefit of added catalysts; the manganese acetyl affords its α-siloxyethyl derivatives, whereas the cobalt acetyl incorporates two equivalents of hydrosilanes and gives its cobalt silyl plus ethoxysilane. This latter reaction entails an intramolecular mechanism in which the second equivalent of silane adds to a coordinatively unsaturated intermediate $L_3CoCH(OSiR_3)CH_3$ and reductively eliminates $CH_3CH_2OSiR_3$ [1].

* Corresponding author. Tel.: +1-518-2768447, fax: +1-518-2764045.

[1] This mechanism also has been advanced for the hydrosilation of $(CO)_4CoC(O)CHMe_2$ [12], the $Co_2(CO)_8$-catalyzed siloxymethylation of aldehydes [13], and the hydrosilation/reduction of the acyl ligand on $Cp(L)(CO)FeC(O)CH_2CH_2Ph$ [14].

PII S0022-328X(97)00274-X

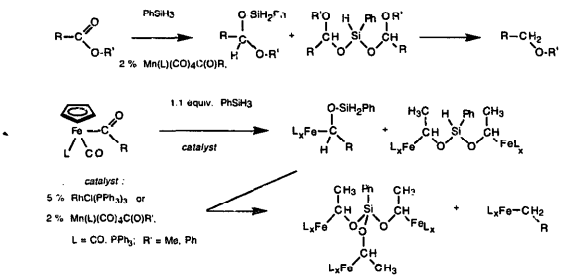


Scheme 1.

The hydrosilation of $(CO)_5MnC(O)CH_3$ engenders an intermolecular or autocatalytic pathway [10]. These reaction mixtures afford transient quantities of the coordinatively unsaturated $(CO)_4MnSiR_3$, which serves as the active (albeit unstable) catalyst [15,16]. It binds the acetyl substrate and gives the key intermediate $(CO)_5MnC(CH_3)(OSiR_3)Mn(CO)_4$; H–$SiR_3$ addition and elimination of $(CO)_5MnCH(OSiR_3)CH_3$ regenerates $(CO)_4MnSiR_3$. Autocatalysis originates via (independently established) silane-induced degradation of the product. Furthermore, these manganese acyl-hydrosilane reaction mixtures are convenient sources of extremely active hydrosilation catalysts. Treatment of catalytic concentrations of $(L)(CO)_4MnC(O)R$ [L = CO, PPh_3; R = CH_3, Ph] or $(L)(CO)_4MnCH_3$ with excess hydrosilane transforms these manganese complexes to active catalysts for the hydrosilation of $Cp(CO)(L)FeC(O)R$ [17,18] as well as organic ketones [19] and even esters [20,21].

Recently, these hydrosilation reaction mixtures using $PhSiH_3$ have been shown to further reduce the initial α-siloxyalkyl products. Treatment of organic esters with the same manganese acyl precatalysts and $PhSiH_3$ gave silyl acetals $PhSiH_{3-x}[OCH(R)OR']_x$ ($x = 1, 2$) that subsequently afforded ethers RCH_2OR' as major products, Scheme 2 [20,21]. Similar hydrosilation-then-reduction reactions, especially those using $Rh(PPh_3)_3Cl$ as the precatalyst, convert $Cp(L)(CO)FeC(O)R$ [R = Me, Ph, ^iPr, ^tBu; L = CO, PPh_3, $P(OMe)_3$, and $P(OPh)_3$] to $Cp(L)(CO)FeCH_2R$ (and $Cp(L)(CO)FeCH{=}CH_2$ byproducts where appropriate) [2,4].

In this study, we attempted to extend the $Rh(PPh_3)_3Cl$- and manganese carbonyl-catalyzed hydrosilation and subsequent reduction of acyl groups to a selection of known methoxycarbonyl complexes [22,23], $Cp(CO)_2FeC(O)OCH_3$ [$FpCO_2CH_3$] (**1**) [24,25], $Cp(CO)(PPh_3)FeCO_2CH_3$ [26], $Cp(CO)_2RuCO_2CH_3$ (**2**) [27], $(CO)_5MnCO_2CH_3$ (**3**) [28,29], $(PPh_3)(CO)_3CoCO_2CH_3$ (**4**), and $(CO)_4CoCO_2CH_3$ (**5**) [30–32]. A new methoxycarbonyl complex, $Cp^*(CO)_2FeCO_2CH_3$ [$Fp^*CO_2CH_3$], was characterized and subjected to our hydrosilation conditions. Our objective was to use these hydrosilane reactions to transform methoxycarbonyl complexes to silylacetal



Scheme 2.

$L_xMCH(OSiR_3)(OMe)$, methoxymethyl L_xMCH_2OMe [33], or fully reduced methyl L_xMCH_3 compounds [34]. Although alkoxycarbonyl complexes, in general, represent derivatives of ligated CO [22,23] and CO_2 [35–40], relatively few examples have been reported for further reducing an alkoxycarbonyl ligand [38,41,42].

2. Experimental section

Synthetic manipulations were performed in a nitrogen atmosphere using a combination of standard Schlenk line, glovebox, and vacuum line procedures [43]. Infrared spectra of benzene solutions were recorded on a Perkin-Elmer FT spectrophotometer, Model no. 1600, over the carbonyl ν(CO) frequency range, 2200–1600 cm^{-1}. NMR spectral data were obtained in C_6D_6 and were reported as δ values relative to residual C_6H_6 (^1H: 7.15 ppm) and C_6D_6 (^{13}C: 128.00 ppm) using Varian Model XL-200 and Unity 500 spectrometers.

Organic and inorganic reagents were obtained commercially and used as received; silanes and C_6D_6 were stored in a glovebox under nitrogen. Diethyl ether, hexane, and benzene were distilled from sodium benzophenone ketyl. Wilkinson's compound, $Rh(PPh_3)_3Cl$, was both purchased and prepared [44]; its purity (activity) was assayed by ^1H NMR spectral monitoring of the catalyzed Ph_2SiH_2 hydrosilation of $FpC(O)CH_3$ [2]. Samples of $Cp(CO)(PPh_3)FeCO_2CH_3$ [26], $Cp(CO)_2RuCO_2CH_3$ (2) [27], $(CO)_5MnCO_2CH_3$ (3) [28,29], $(PPh_3)(CO)_3Co-CO_2CH_3$ (4), $(CO)_4CoC(O)C(O)OCH_3$ [30–32], $(CO)_5MnCH_3$ [45–47], $(PPh_3)(CO)_4MnC(O)CH_3$ [48–50], FpK [51], and $Cp^*Fe(CO)_3^+PF_6^-$ [52,53] were prepared by literature procedures and judged pure by IR and ^1H NMR spectroscopy. Authentic samples of the methoxysilanes CH_3OSiMe_2Ph, $(CH_3O)_xSiH_{2-x}Ph_2$, and $(CH_3O)_xSiH_{3-x}Ph$ were generated by $(CO)_5MnBr$-catalyzed dehydrogenative silation of methanol [54].

2.1. Preparation of $Cp(CO)_2FeCO_2CH_3$ (1)

The following procedure, a modification of that previously reported [24,25], provided $Cp(CO)_2FeCO_2CH_3$ (1) as a stable, crystalline material. A pale orange suspension of Fp^-K^+ (10.0 g, 46.3 mmol) in 150 mL dry diethylether was cooled to −78°C and treated with methylchloroformate (3.2 mL, 46.9 mmol). The methylchloroformate was added dropwise by syringe, and after 0.5 h, the mixture was warmed slowly to room temperature (3 h). IR spectra of the resulting dark red-brown solution were consistent with the formation of $FpCO_2CH_3$ (1) [24,25], ν(CO) = 2038 (vs), 1988 (vs) and 1657 (s) cm^{-1}, and Fp_2 (ca. 20%). The diethylether was evaporated (10^{-1} mm); the resulting red-brown powder was extracted with 3 × 4 mL methylene chloride, which was filtered through a 2.5 × 2 cm pad of Celite with additional solvent.

The combined filtrates were evaporated, and the red brown powder was dissolved in the minimum volume of hexane (40 mL). After cooling for 3 h at −78°C, the hexane solution deposited light yellow-brown crystals. The supernatant hexane was removed via cannula, and the crystals were washed with 2 × 10 mL of cold hexane. After vacuum drying, this first crop afforded 5.21 g of spectroscopically pure 1: ^1H NMR (C_6D_6) δ = 5.12 (Cp) and 3.25 (CH_3); ^{13}C NMR (C_6D_6) δ = 213.3 (CO), 201.2 (C=O), 88.1 (Cp) and 58.1 (CH_3). The combined hexane supernatant and washings were combined, and the volume was reduced by one-half before cooling to −78°C (4h). This afforded slightly darker brown-yellow crystals (presumably due to < 5% Fp_2), for a combined yield of 1 of 7.36 g (67%).

2.2. Preparation of $Cp^*(CO)_2FeCO_2CH_3$

To a white suspension of Na_2CO_3 (126 mg, 1.19 mmol) in methanol (4 mL) was added a pale yellow suspension of $Cp^*Fe(CO)_3^+PF_6^-$ (100 mg, 0.238 mmol) in 4 mL of methanol. After stirring for 15 min, the suspension was filtered through a 1 g bed of Celite. The pale yellow filtrate was combined with a 4 mL methanol washing of the Celite and evaporated. Pentane extracts (3 × 3 mL) of the residue were filtered through Celite, reduced in vacuo to 5 mL, and cooled at −78°C. The yellow solid that precipitated, was collected, washed with cold pentane (2 × 1 mL, −78°C), and dried in vacuo. The resulting 55 mg of a fluffy yellow solid was identified as $Cp^*(CO)_2FeCO_2CH_3$, yield 75%, IR (pentane) 2018, 1968 and 1649 cm^{-1}; ^1H NMR (C_6D_6) δ = 3.56 (s, OCH_3) and 1.47 (s, Cp^*); $^{13}C\{^1H\}$ NMR (C_6D_6) δ = 216.4 (C ≡ O), 204.4 (C=O), 97.0 (C_5CH_3), 51.7 (CH_3) and 9.30 (C_5CH_3). Analytically calculated for $C_{14}H_{18}O_4Fe$: C, 54.93; H, 5.93. Observed: C, 54.46; H, 5.82.

2.3. Hydrosilation of $Cp(CO)_2FeCO_2CH_3$ (1) with $PhMe_2SiH$: $(CO)_5MnCH_3$ catalysis

To a 5-mL vial in the glove box was added $Cp(CO)_2FeCO_2CH_3$ (1) (500 mg, 2.12 mmol), $(CO)_5MnCH_3$ (9 mg, 0.044 mmol), and C_6D_6 (800 mg). This red-brown solution was treated with $PhMe_2SiH$ (299 mg, 2.20 mmol) and

transferred to a 5-mm NMR tube. ^1H and ^{13}C NMR spectral monitoring of the reaction revealed that **2** was replaced in 3 h by a 1:1 mixture of η^4-$(C_5H_6)Fe(CO)_3$ (**6**) [55,56] and CH_3OSiMe_2Ph [^1H NMR $\delta = 3.27$ ($SiOCH_3$) and 0.29 (SiMe); ^{13}C NMR $\delta = 50.3$ ($SiOCH_3$) and −2.1 (SiMe)] [57]. Neither gas evolution nor color change was noted; only trace concentrations of $[Cp(CO)_2Fe]_2$ and $PhMe_2SiOSiMe_2Ph$ [^1H NMR, $\delta = 0.31$, SiMe] were observed.

The reaction mixture was distilled trap-to-trap (20 mm/25°C), affording a golden yellow C_6D_6 solution as the distillate. ^1H and ^{13}C NMR spectra of this solution established the presence of **6** along with 2–3% CH_3OSiMe_2Ph. A stream of N_2 was used to remove the C_6D_6 until a constant weight was obtained, 412 mg (92% yield of **6**). Alternatively, the reaction was worked up by column chromatography on a 1 × 10 cm column of activity 3 alumina (neutral) with pentane. A yellow band was eluted cleanly with pentane; the solvent was evaporated with N_2 leaving a yellow oil that contained **6** (90% yield) and 5–7% CH_3OSiMe_2Ph. The IR and ^1H NMR spectra of **6** are in excellent agreement with the data reported by Whitesides and Shelly [56].

η^4-$(C_5H_6)Fe(CO)_3$ (**6**) IR (CCl_4) $\nu(CH_{exo}) = 2786\ cm^{-1}$, $\nu(CO) = 2045$ and 1976 (br) cm^{-1}; (pentane) $\nu(CO) = 2048$, 1981 and 1974 cm^{-1}. ^1H NMR (C_6D_6) δ(500 MHz) = 4.97 (t, $J_{AM} = 2.2$ Hz, H_A), 2.42 (m, H_M), 2.36 (dt, $J_{endo\text{-}M} = 1.9$, $J_{endo\text{-}exo} = 12.0$ Hz, H_{endo}), 1.91 (dt, $J_{exo\text{-}M} = 1.45$, $J_{exo\text{-}endo} = 12.0$ Hz, H_{exo}), triplet appearance of H_{endo} and H_{exo} absorptions was enhanced after the long-range coupling involving H_A was removed by spin decoupling at H_A. This decoupling left the H_M absorption as an apparent triplet with 1.8 and 1.6 Hz separations. Results of homonuclear 2D *J*-resolved NMR experiments confirmed the presence of the H_A–H_{exo} spin coupling, $J_{exo\text{-}A} = 0.7$ Hz, but insufficient resolution precluded other assignments. ^{13}C NMR (C_6D_6) $\delta = 212.7$ (CO), 85.5 (C_A), 54.3 (CH_M) and 45.2 (CH_2), assignments are consistent with the results of both DEPT and H,C-COSY NMR experiments [58,59].

2.4. $PhMe_2SiD$ hydrosilation of $Cp(CO)_2FeCO_2CH_3$ (1): $(CO)_5MnCH_3$ catalysis

The hydrosilation of **1** was repeated with 1.1 equivalents of $PhMe_2SiD$ (302 mg, 2.20 mmol) and 2% $(CO)_5MnCH_3$ as the catalyst. Starting **1** was consumed within 3 h (^1H NMR spectral monitoring), and a yellow oil was isolated by trap-to-trap distillation (20 mm/25°C). The oil was identified as spectroscopically pure exo-D (η^4-$C_5H_5D)Fe(CO)_3$ (**6-D**), [56] 93% yield. For **6-D**, IR (CCl_4) $\nu(CO) = 2044$ and 1976 (br) cm^{-1}; (pentane) $\nu(CO) = 2048$, 1981 and 1974 cm^{-1}. ^1H NMR (C_6D_6) δ(500 MHz) = 4.99 (t, $J_{AM} = 2.2$ Hz, H_A), 2.42 (m, H_M) and 2.34 (br s, H_{endo}), the H_M multiplet, an apparent dt, appeared as a doublet ($J_{endo\text{-}M} = 2.0$ Hz) after spin decoupling at H_A. ^{13}C NMR (C_6D_6) $\delta = 212.6$ (CO), 85.5 (C_A), 54.2 (CH_M) and 44.85 (1:1:1 t, $J_{CD} = 19.1$ Hz, *C*DH).

2.5. $PhMe_2SiH$ and Ph_2SiH_2 hydrosilation of 1: NMR spectral observations

C_6D_6 solutions (600 mg) of $Cp(CO)_2FeCO_2CH_3$ (**1**) (55 mg, 0.23 mmol), $PhMe_2SiH$ (35 mg, 0.26 mmol), and either $(CO)_5MnCH_3$ (2 mg, 9.5×10^{-3} mmol), $(PPh_3)(CO)_4MnC(O)CH_3$ (4 mg, 9.5×10^{-3} mmol), or $Rh(PPh_3)_3Cl$ (6 mg, 6.5×10^{-3} mmol) were monitored by ^1H NMR spectroscopy. No reactions were observed after 5–6 h. Similar results were noted for reactions between 200 mg of **1** (0.85 mmol) and $PhMe_2SiH$ (127 mg, 0.93 mmol) with 3% of $(PPh_3)(CO)_4MnC(O)CH_3$ (12 mg, 0.025 mmol) as the precatalyst. Treatment of C_6D_6 solutions (600 mg) containing **1** (50 mg, 0.21 mmol) and $(PPh_3)(CO)_4MnC(O)CH_3$ (3 mg, 6.0×10^{-3} mmol) with Ph_2SiH_2 (43 mg, 0.23 mmol) generated **6** (90% yield) over 3 h, whereas $Rh(PPh_3)_3Cl$ (6 mg, 6.5×10^{-3} mmol) under comparable reaction conditions was inactive.

2.6. Phenylsilane hydrosilation of $Cp(CO)_2FeCO_2CH_3$ (1)

A red-brown C_6D_6 solution (600 mg) containing $Cp(CO)_2FeCO_2CH_3$ (**1**) (50 mg, 0.21 mmol), $(PPh_3)(CO)_4MnC(O)CH_3$ (3 mg, 0.007 mmol), and the $Me_3SiOSiMe_3$ internal standard (13 mg, 0.080 mmol) was treated with $PhSiH_3$ (25 mg, 0.23 mmol). After 25 min ^1H NMR spectral monitoring of the reaction was consistent with a 92% yield of η^4-$(C_5H_6)Fe(CO)_3$ (**6**) and a 2:1 to 3:1 mixture of $Ph(CH_3O)SiH_2$ [$\delta = 5.13$ (SiH) and 3.27 ($SiOCH_3$)] and $Ph(CH_3O)_2SiH$ [$\delta = 5.11$ (SiH) and 3.40 ($SiOCH_3$)], along with the requisite concentration of $PhSiH_3$. Only trace concentrations of $[Cp(CO)_2Fe]_2$ [^1H NMR, $\delta = 0.31$] were observed.

2.7. Phenylsilane hydrosilation of $Cp(CO)_2RuCO_2CH_3$ (2)

To a solution of $Cp(CO)_2RuCO_2CH_3$ (**2**) (50 mg, 0.18 mmol), $(PPh_3)(CO)_4MnC(O)CH_3$ (3 mg, 0.007 mmol), and $Me_3SiOSiMe_3$ (11 mg, 0.070 mmol) in C_6D_6 (600 mg) was added $PhSiH_3$ (27 mg, 0.20 mmol). The yellow-brown solution was monitored by ^1H NMR spectroscopy; within 35 min **2** was consumed. Although a large number of

unassigned resonances were evident, $(\eta^4\text{-}C_5H_6)Ru(CO)_3$ (**7**) [60] was identified as the major component: ^1H NMR (C_6D_6) $\delta = 5.01$ (m, 2H, β-CH), 2.63 (m, 2H, α-CH) and 2.61 (m, 2H, CH_2); ^{13}C NMR $\delta = 199.5$ (CO), 85.8 (β-*C*H), 48.4 (α-*C*H) and 48.0 (*C*H_2); IR (pentane) 2060, 1996 and 1985 cm^{-1}. Other intense IR ν(CO) absorptions appeared at 2024 and 1965 cm^{-1}; NMR spectral data also were consistent with the absence of either $[Cp(CO)_2Ru]_2$ or $Cp(CO)_2RuH$ [61]. A 53% yield of **7** was determined by integration of the ^1H NMR $\delta = 2.63$ and 2.61 multiplets vs. the internal standard. Attempts to purify **7**, an unstable yellow oil, by chromatography on activity 3, neutral alumina-pentane inevitably produced a yellow eluate that contained **7** in addition to organic impurities.

2.8. Attempted hydrosilation of $Cp(CO)(PPh_3)FeCO_2CH_3$, $Cp^*(CO)_2FeCO_2CH_3$, $(CO)_5MnC(O)OCH_3$ (3), and $(PPh_3)(CO)_3CoC(O)OCH_3$ (4)

C_6D_6 solutions (500 mg) containing $(CO)_5MnC(O)OCH_3$ (**3**) (27 mg, 0.10 mmol) or $(PPh_3)(CO)_3CoC(O)OCH_3$ (**4**) (48 mg, 0.18 mmol) were treated with $PhMe_2SiH$ (27 mg, 0.20 mmol) or Ph_2SiH_2 (36 mg, 0.20 mmol) and transferred to NMR tubes that were securely stoppered with rubber septa. IR and ^1H NMR spectral monitoring of these four mixtures recorded that no reactions occurred over 6 h. Similar results were noted for the reactions between (a) $Cp(CO)(PPh_3)FeCO_2CH_3$ (82 mg, 0.20 mmol) and $PhSiH_3$ (25 mg, 0.23 mmol), with 3.5% of $(PPh_3)(CO)_4MnC(O)CH_3$ (3 mg, 0.072 mmol) as the precatalyst, and (b) $Cp^*(CO)_2FeCO_2CH_3$ (184 mg, 0.60 mmol) and Ph_2SiH_2 (133 mg, 0.72 mmol), with anisole as the internal standard and $(CO)_5MnCH_3$ (5 mg, 0.025 mmol) or $(PPh_3)(CO)_4MnC(O)CH_3$ (12 mg, 0.025 mmol) as the precatalysts.

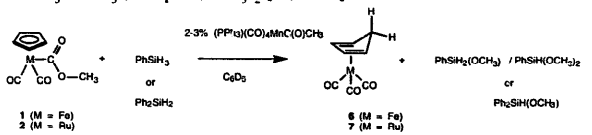
2.9. Dimethylphenylsilane hydrosilation of $(CO)_4CoC(O)OCH_3$ (5)

Starting $(CO)_4CoC(O)OCH_3$ (**5**) was generated by the decarbonylation of the oxalyl complex $(CO)_4CoC(O)C(O)OCH_3$ [30–32] as it was distilled trap-to-trap at room temperature. The yellow oil (600 mg **5**, 44% yield) then was dissolved in C_6D_6 and diluted as needed. Its concentration was quantified by ^1H NMR spectroscopy of samples containing Cp_2Fe internal standards. A yellow solution containing 30 mg of **5** (0.13 mmol) in 500 mg of C_6D_6 was treated with $HSiMe_2Ph$ (18 mg, 0.13 mmol) and transferred to an NMR tube. Within 15 min **5** was consumed in the brown solution, and the resulting 1:1 mixture of $(CO)_4CoSiMe_2Ph$ [62] and $HC(O)OCH_3$ was identified by ^1H and ^{13}C NMR spectroscopy. No other products were evident by IR or ^1H and ^{13}C NMR spectroscopy; $(CO)_4CoSiMe_2Ph$: IR $\nu(CO)(C_6D_6) = 2090$, 2070 (w), 2044 (m, sh), 2027 and 1992 (s, br) cm^{-1}; ^1H NMR (C_6D_6) $\delta = 0.71$ (s, SiMe); ^{13}C NMR $\delta = 199.5$ (CO) and 5.86 (SiMe). The yield was 91% (^1H NMR spectral integration vs. the internal standard).

3. Results and discussion

3.1. Manganese carbonyl catalyzed reactions of $PhSiH_3$, Ph_2SiH_2, or $PhMe_2SiH$ with methoxycarbonyl compounds $Cp(L)(CO)MCO_2Me$ (M = Fe, Ru; L = CO, PPh_3)

Although the methoxycarbonyl complex $Cp(CO)_2FeC(O)OCH_3$ (**1**) [24,25] in C_6D_6 solutions is inert towards $PhSiH_3$, addition of 2–3% $(PPh_3)(CO)_4MnC(O)CH_3$ rapidly reduced **1** to the known [55,56] η^4-cyclopentadiene complex $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (**6**) Eq. (1)). This was formed with over 90% yields, and the silane moiety was accounted for as mixtures of unreacted $PhSiH_3$ and the methoxysilanes $(CH_3O)PhSiH_2$ and $(CH_3O)_2PhSiH$. Similar reactions using Ph_2SiH_2 in place of $PhSiH_3$ produced 1:1 mixtures of **6** and $Ph_2SiH(OCH_3)$ (90% yields), although longer reaction times (3 h vs. 20 min) were required. With either hydrosilane, traces of Fp_2 also were evident, but NMR spectral resonances that could be attributed to $FpCH_3$ [63,64], $FpCH_2OMe$ [65,66], or silylacetal analogs, $FpCH(OSiR_3)(OCH_3)$, of $FpCH(OCH_3)_2$ [38,67–69] were not detected.

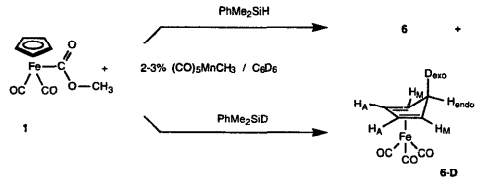


(1)

[2] The reactivity order of the hydrosilanes, $RSiH_3 \gg R_2SiH_2 \gg R_3SiH$, has been established for the $Rh(PPh_3)_3Cl$-catalyzed hydrosilation of ketones [5].

The monohydrosilane $PhMe_2SiH$ proved to be a less powerful reductant [2] towards **1** with manganese carbonyl precatalysts. Thus, $(PPh_3)(CO)_4MnC(O)CH_3$ (2–3%) was ineffective as a precatalyst, irrespective of using dilute (0.23 mmol **1**/475 mg C_6D_6) or more concentrated (0.85 mmol **1**/450 mg C_6D_6) solutions of the substrate and 1.1 equivalents of $PhMe_2SiH$. By switching to $(CO)_5MnCH_3$ as the precatalyst (2–3%), however, we quantitatively reduced **1** to **6** (> 90%) over 3 h, provided that more concentrated reaction mixtures (0.85–2.12 mmol **1**/450–600 mg C_6D_6) were used.

Further studies were carried out on the $(CO)_5MnCH_3$-catalyzed $PhMe_2SiH$ and $PhMe_2SiD$ reduction of **1**. The significant results are that (1) CH_3OSiMe_2Ph, which is produced in a 1 : 1 ratio with **6** (or **6-D**), accounts for the silicon balance (Eq. (2)), and (2) the $PhMe_2SiD$-derived deuterium adds exo to the η^5-Cp ring to yield the η^4-cyclopentadiene ligand. Our NMR spectral assignments for **6-D** are in agreement with those reported by Whitesides and Shelly [56] and confirm the exo configuration of the deuterium [58,59]. (In the Whitesides study, they substantiated the assigned structure by noting the stereoselective



(2)

abstraction of (exo) deuteride with the trityl carbocation [56].)

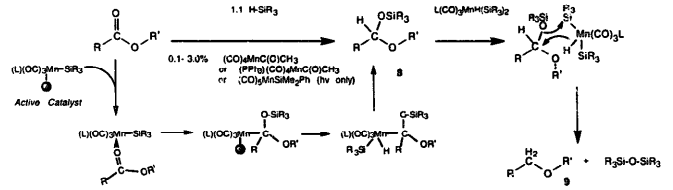
Our attempts to extend the catalytic hydrosilane reduction of **1** by manganese carbonyl complexes to the related iron methoxycarbonyl complexes $Cp(CO)(PPh_3)FeCO_2CH_3$ [27] and $Cp^*(CO)_2FeC(O)OCH_3$ [5–8] and to $Cp(CO)_2RuC(O)OCH_3$ (**2**) [28,29] were only partially successful. Both iron methoxycarbonyls were unreactive towards $PhSiH_3$ reduction even using $(PPh_3)(CO)_4MnC(O)CH_3$ as the precatalyst. Although the ruthenium analog **2** proved to be inert to $PhMe_2SiH$ with either $(CO)_5MnCH_3$ or $(PPh_3)(CO)_4MnC(O)CH_3$ precatalysts, $PhSiH_3$ reduction of **2** using 2–3% $(PPh_3)(CO)_4MnC(O)CH_3$ as the precatalyst afforded moderate yields of the known $(\eta^4\text{-}C_5H_6)Ru(CO)_3$ (**7**) (Eq. (1)) [60].

The catalytic $PhSiH_3$ reduction of **2** was quite messy, however. We determined 50% yields of **7** by ^1H NMR spectral integration (the β-H and CH_2 multiplets at $\delta \approx 2.6$ were free of interfering absorptions), but we could not account for the remaining CpRu moiety. CpRu compounds conspicuously absent included $Cp(CO)_2RuH$, $Cp(CO)_2RuCH_2OMe$ [70,71], and $[Cp(CO)_2Ru]_2$ [61]; also missing were IR and NMR spectral absorptions that could be consistent with the presence of ruthenium hydride, formyl, or siloxymethyl compounds [61,72,73].

The surprising outcome of this study was that the methoxycarbonyl ligand of $Cp(L)(CO)MCO_2Me$ (**1**, M = Fe, L = CO; L = PPh_3; **2**, M = Ru, L = CO) and $Cp^*(CO)_2FeC(O)OCH_3$ resisted hydrosilation. Our catalysis conditions – the choice of manganese carbonyl precatalyst, hydrosilane, and substrate concentration in C_6D_6 – had been effective for the hydrosilation of the iron and ruthenium acetyl complexes $Cp(L)(CO)MC(O)CH_3$ [4,17,18] (Scheme 1) and for the hydrosilation-then-reduction of organic esters (Scheme 2) [20,21]. For example, we previously established that $(CO)_5MnCH_3$ is an efficient precatalyst with $PhMe_2SiH$ for the hydrosilation of $FpC(O)CH_3$, whereas $(PPh_3)(CO)_4MnC(O)CH_3$ is preferred for Ph_2SiH_2 [17,18] and $PhSiH_3$ [4].

Even the choice of Wilkinson's compound, $Rh(PPh_3)_3Cl$, in this work followed from its use as the optimal catalyst for the $PhSiH_3$ or Ph_2SiH_2 hydrosilation-then-reduction of the iron acyl complexes $Cp(L)(CO)FeC(O)R$ to $Cp(L)(CO)FeCH_2R$ (Scheme 2) [2–4]. It thus was quite surprising when under comparable reaction conditions **1** remained inert towards $Rh(PPh_3)_3Cl$ in the presence of $PhSiH_3$, Ph_2SiH_2, or $PhMe_2SiH$.

At the inception of this study, we assumed that manganese carbonyl-catalyzed hydrosilane chemistry of $FpC(O)OCH_3$ (**1**) might resemble that of organic esters (Scheme 2) [20,21] and yield silyl acetal complexes, $FpCH(OSiR_3)(OCH_3)$, or perhaps the further reduced $FpCH_2OCH_3$ [65,66] or $FpCH_3$ [63,64]. Organotransition metal acetals have been reported: Casey et al. [67], Theys and Hossain [68], and Cutler [42]d independently synthesized $FpCH(OCH_3)_2$. This acetal is noteworthy for its BH_3 reduction to $FpCH_2OCH_3$ [42]d and for its room temperature stability, which contrasts the extreme instability of its formyl derivative, $FpC(O)H$ [35–40,74].



Scheme 3.

The ester hydrosilation chemistry entails two reactions (Scheme 3) [20,21]: (a) $(PPh_3)(CO)_4MnC(O)CH_3$-catalyzed hydrosilation of $RC(O)OR'$ to its silylacetal **8**, and (b) subsequent reduction of **8** to its ether, RCH_2OR' (**9**). Both steps apparently engender the same coordinatively unsaturated $(L)(CO)_3MnSiR_3$ as the active catalyst [15,16]; its role in the ester hydrosilation step resembles the catalytic hydrosilation of ketones [19] or $FpC(O)CH_3$ [17,18]. During catalytic $PhSiH_3$ ester hydrosilation chemistry, the silyl acetals **8** were detected only as intermediates with $PhSiH_3$, although analogous reactions using the less reactive Ph_2SiH_2 and $PhMe_2SiH$ afforded several isolated examples of **8**. These independently reduced to their ethers **9** in the presence of $PhSiH_3$ and fresh manganese precatalyst [20,21].

In Scheme 4, we outline a plausible pathway for the manganese carbonyl hydrosilane reduction of $FpC(O)OMe$ (**1**) to $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (**6**). The proposed active catalyst, $(L)(CO)_3MnSiR_3$, derives from the manganese methyl and acetyl precatalysts via documented reactions and provides the bis(silyl)manganese hydride intermediates $(L)(CO)_3MnH(SiR_3)_2$ [3] [75–78] as the hydride donor. Exo addition of hydride from this intermediate to the Cp ligand [58,59] concurrent with releasing the methoxysilane then yields **6**.

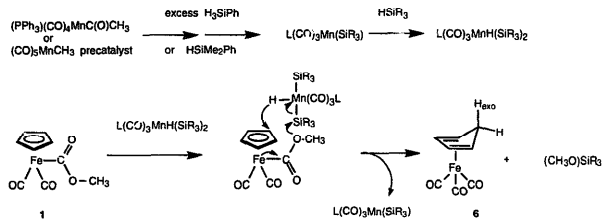
Both steps are precedented. The bimolecular addition of reactants to the exo or top face of the Cp ligand has been thoroughly documented [58,59], and we recently reported the manganese carbonyl-catalyzed $PhSiH_3$ reduction of $FpC(O)CH_3$ to $FpCH_2CH_3$ [4]. For this latter reaction, however, $Rh(PPh_3)_3Cl$ serves as a much more effective catalyst; a variety of iron acyl complexes $Cp(L)(CO)FeC(O)R'$ accordingly were reduced via α-siloxyalkyl intermediates $Cp(L)(CO)FeCH(OSiR_3)R'$ to $Cp(L)(CO)FeCH_2R'$. We proposed that in these latter reactions $(PPh_3)_2(Cl)RhH(SiR_3)_2$ transfers hydride to $Cp(L)(CO)FeCH(OSiR_3)R'$ as the requisite disiloxane byproduct forms.

3.2. *Reactions of $PhSiH_3$ or $PhMe_2SiH$ with labile manganese and cobalt methoxycarbonyl complexes $(L)(CO)_xMCO_2Me$ ($L = CO, PPh_3$)*

The labile methoxycarbonyl complexes $(CO)_5MnC(O)OCH_3$ (**3**), $(PPh_3)(CO)_3CoC(O)OCH_3$ (**4**), and $(CO)_4CoC(O)OCH_3$ (**5**) were selected for this study because their acetyl and related acyl analogs readily incorporate hydrosilanes without adding a catalyst [1]. Thus a wide variety of hydrosilanes efficiently transform $(CO)_5MnC(O)CH_3$ [9,10] and $(PPh_3)(CO)_3CoC(O)CH_3$ [11] to their respective products at room temperature (Scheme 1). Analogous reactions between $(CO)_4CoC(O)CH(CH_3)_2$ and Et_3SiH were reported by Kovács et al. [12] to give $(CO)_4CoSiEt_3$ and several organic products that are consistent with the subsequent degradation of $(CO)_3(H)(SiEt_3)CoCH(OSiEt_3)CH(CH_3)_2$.

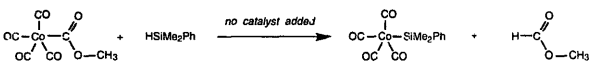
In contradistinction, both **3** and **4** proved to be inert towards $PhMe_2SiH$ or Ph_2SiH_2 for at least 5 h at room temperature. We did not detect even trace concentrations of the requisite metal silyl complexes or organic byproducts HCO_2CH_3, $CH_2(OCH_3)(OSiR_3)$, or CH_3OSiR_3 that could derive from hydrosilane cleavage of the starting methoxycarbonyl compound or its silyl acetal derivative, $L_xMCH(OCH_3)(OSiR_3)$ [12–14]. It is worth noting that we have recently established that $(PPh_3)(CO)_4MnC(O)CH_3$ catalyzes the hydrosilation-then-reduction of HCO_2CH_3 to

[3] Examples of (hydrido)(silyl)(alkyl)metal complexes have been reported or implicated as intermediates in hydrosilation catalysis [5–8].



Scheme 4.

$CH_2(OCH_3)(OSiR_3)$ and then CH_3OSiR_3 [21]. Even in the presence of 4% $(PPh_3)(CO)_4MnC(O)CH_3$ or $Rh(PPh_3)_3Cl$ precatalyst, however, **4** did not react with Ph_2SiH_2.



[No reaction with $(CO)_5MnCO_2CH_3$ (3) or with $(PPh_3)(CO)_3CoCO_2CH_3$ (4)] (3)

The (tetracarbonyl)cobalt moiety proved to be reactive towards $PhMe_2SiH$. One equivalent of $PhMe_2SiH$ rapidly cleaved $(CO)_4CoC(O)OCH_3$ (**5**) and quantitatively yielded the known silyl complex $(CO)_4CoSiMe_2Ph$ [62] and methyl formate (Eq. (3)). IR and ^1H, ^{13}C NMR spectral data for $(CO)_4CoSiMe_2Ph$ matches that for samples that were independently prepared from the reaction of two equivalents of $PhMe_2SiH$ with $Co_2(CO)_8$ [11,79–81]. The release of methyl formate from **5** previously had been observed for its uncatalyzed hydrogenation, a reaction for which **5** is more reactive than **4** [31].

This $PhMe_2SiH$ cleavage of the cobalt-acyl (Eq. (3)) is the first example that we have observed for a hydrosilane cleaving a transition organometallic acyl complex to its organic acyl compound (cf. Scheme 1). Although Wegman [82] had reported that triethylsilane cleaves acetaldehyde from $(CO)_5MnC(O)CH_3$ and $(PPh_3)(CO)_3CoC(O)CH_3$ under somewhat different reaction conditions, this work was not reproducible in our hands. This discrepancy with the results of our ongoing studies has been addressed in Refs. [10,11].

4. Conclusions

The reactivity of selected organotransition metal methoxycarbonyl complexes towards hydrosilanes differs significantly from their acetyl analogs in that we found no examples of hydrosilation of the methoxycarbonyl ligand. Although the iron and ruthenium acetyl compounds $Cp(L)(CO)MC(O)CH_3$ (L = CO, PPh_3) readily hydrosilate across the acetyl ligand (Scheme 1) with a variety of hydrosilane/$Rh(PPh_3)_3Cl$ or manganese carbonyl precatalyst systems, the corresponding methoxycarbonyls $Cp(L)(CO)MC(O)OCH_3$ were much less reactive. Only the more active hydrosilane/manganese carbonyl precatalyst systems even reacted with their methoxycarbonyl analogs $Cp(CO)_2MCO_2CH_3$ (**1**, M = Fe; **2**, M = Ru). These reactions involving $PhSiH_3$/3% $(PPh_3)(CO)_4MnC(O)CH_3$ for **1** and **2** or $PhMe_2SiH$/2–3% $(CO)_5MnCH_3$ for **1** afforded their η^4-cyclopentadiene compounds (η^4-C_5H_6) $M(CO)_3$ (**6**, M = Fe; **7**, M = Ru). As further examples of the low reactivity of methoxycarbonyl complexes under hydrosilation catalysis conditions, $PhSiH_3$ or Ph_2SiH_2/$Rh(PPh_3)_3Cl$ were ineffective towards **1** or **2**, and $Cp(PPh_3)(CO)FeCO_2CH_3$ and $Cp'(CO)_2FeC(O)OCH_3$ proved to be inert under all attempted hydrosilation conditions.

This diminution of hydrosilane reactivity extends to cobalt and manganese carbonyl methoxycarbonyl complexes $(L)(CO)_xMCO_2CH_3$ (**3**, M = Mn, $x = 4$, L = CO; **4**, M = Co, $x = 3$, L = PPh_3; **5**, M = Co, $x = 3$, L = CO). Although their acetyl analogs $(L)(CO)_xMC(O)CH_3$ are sensitive to hydrosilanes, both **3** and **4** are inert towards $PhMe_2SiH$ or Ph_2SiH_2. Treatment of **5** with $PhMe_2SiH$ released methyl formate and left the silyl complex $(CO)_4CoSiMe_2Ph$, a result that resembles the hydrogenation chemistry of **5**.

Acknowledgements

Support from the National Science Foundation, Grant CHE-8305484 is gratefully acknowledged.

References

[1] P.K. Hanna, B T. Gregg, D.L. Tarazano, J.R. Pinkes, A.R. Cutler, in: W.R. Moser, D.W. Slocum (Eds.), Homogeneous Transition Metal Catalyzed Reactions; Advances in Chemistry Series No. 230, American Chemical Society, Washington, DC, 1992, p. 491.
[2] E.J. Crawford, P.K. Hanna, A.R. Cutler, J. Am. Chem. Soc. 111 (1989) 6891.
[3] M. Akita, O. Mitani, Y. Moro-Oka, J. Chem. Soc., Chem. Commun. (1989) 527.
[4] Z. Mao, B.T. Gregg, A.R. Cutler, manuscript submitted.
[5] I. Ojima, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, Part 2, Chapt. 25.
[6] T.D. Tilley, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, Part 2, Chapt. 24.
[7] T.D. Tilley, in: S. Patai, Z. Rappoport (Eds.), The Silicon–Heteroatom Bond, Wiley, New York, 1992, Chapt. 10.
[8] B. Marciniec, J. Guliński, J. Organomet. Chem. 446 (1993) 15.
[9] B.T. Gregg, P.K. Hanna, E.J. Crawford, A.R. Cutler, J. Am. Chem. Soc. 113 (1991) 384.
[10] B.T. Gregg, A.R. Cutler, J. Am. Chem. Soc. 118 (1996) 10069.
[11] B.T. Gregg, A.R. Cutler, Organometallics 11 (1992) 4276.
[12] I. Kovács, A. Sisak, F. Ungváry, L. Markó, Organometallics 7 (1988) 1025.
[13] S. Murai, Y. Seki, J. Mol. Cat. 41 (1987) 197.
[14] M. Akita, T. Oku, M. Tanaka, Y. Moro-oka, Organometallics 10 (1991) 3080.
[15] B.T. Gregg, A.R. Cutler, Organometallics 12 (1993) 2006.
[16] Manganese alkyl and halide complexes $(L)(CO)_4MnX$ [X = CH_3, Ph, $CH(OSiR_3)CH_3$, Br; L = CO, PPh_3, PEt_3] also serve as effective precatalysts for the hydrosilation of a variety of organic and organometallic acyl compounds. Under comparable reaction conditions, neither $(CO)_5MnSiR_3$ (R_3Si=Me_2Ph, $SiHPh_2$) nor $Mn_2(CO)_{10}$, are effective precatalysts. B.T. Gregg and A.R. Cutler, manuscript in preparation.
[17] P.K. Hanna, B.T. Gregg, A.R. Cutler, Organometallics 10 (1991) 31.
[18] J.R. Pinkes, Z. Mao, A.R. Cutler, manuscript in preparation.
[19] M. DiBiase Cavanaugh, B.T. Gregg, A.R. Cutler, Organometallics 15 (1996) 2764.
[20] Z. Mao, B.T. Gregg, A.R. Cutler, J. Am. Chem. Soc. 117 (1995) 10139.
[21] Z. Mao and A.R. Cutler, Hydrosilation-then-reduction of formate esters and silyl formates, manuscript in preparation.
[22] R.J. Angelici, Acc. Chem. Res. 5 (1972) 335.
[23] P.C. Ford, A. Rokicki, Adv. Organomet. Chem. 28 (1988) 139.
[24] R.B. King, M. Bisnette, A. Fronzaglia, J. Organomet. Chem. 5 (1966) 341.
[25] L. Busetto, R.J. Angelici, Inorg. Chim. Acta 2 (1968) 391.
[26] H. Brunner, E. Schmidt, J. Organomet. Chem. 50 (1973) 219.
[27] A.E. Kruse, R.J. Angelici, J. Organomet. Chem. 24 (1970) 231.
[28] T. Kruck, M. Noack, Chem. Ber. 97 (1964) 1693.
[29] I. Kovács, C.D. Hoff, F. Ungváry, L. Markó, Organometallics 4 (1985) 1347.
[30] D. Milstein, J.L. Huckaby, J. Am. Chem. Soc. 4 (1985) 1523.
[31] F. Ungváry, L. Markó, Organometallics 2 (1983) 1608.
[32] M. Tasi, G. Pályi, Organometallics 4 (1985) 1523.
[33] D. Steinform, Angew. Chem., Int. Ed. Engl. 31 (1992) 401.
[34] A.R. Cutler, P.K. Hanna, J.C. Vites, Chem. Rev. 88 (1988) 1363.
[35] K.K. Pandey, Coord. Chem. Rev. 140 (1995) 37.
[36] P.G. Jessop, T. Ikariya, R. Noyori, Chem. Rev. 95 (1995) 259.
[37] *t*-$Cl(dmpe)_2IrCO_2^+$: R.L. Harlow, J.B. Kinney, T. Herskovitz, J. Chem. Soc., Chem. Commun. (1980) 813.
[38] $(FpCO_2)_2Mg$: T. Forschner, K. Menard, A. Cutler, J. Chem. Soc., Chem. Commun. (1984) 121.
[39] *t*-$(CO)(bpy)_2RuCO_2^+$: H. Ishida, K. Tanaka, T. Tanaka, Organometallics 6 (1987) 181.
[40] $Cp(PPh_3)(CO)FeCO_2^-$: D.H. Gibson, T.-S. Ong, M. Ye, Organometallics 10 (1991) 1811.
[41] D.H. Gibson, J.O. Franco, M.J. Harris, M.T. Ong, Organometallics 11 (1992) 1993.
[42] D.L. Thorn, Organometallics 1 (1982) 197.
[43] D.F. Shriver, M.A. Drezdon, The Manipulation of Air-Sensitive Compounds, 2nd ed., Wiley, NY, 1986.
[44] J.A. Osborn, G. Wilkinson, Inorg. Synth. 28 (1990) 77.
[45] R.D. Closson, J. Kozikowski, T.H. Coffield, J. Org. Chem. 22 (1957) 598.
[46] R.B. King, Organometallic Syntheses, Part I, Vol. 1, Academic Press, NY, 1965, p. 147.
[47] R.J. Mckinney, S.S. Crawford, Inorg. Synth. 26 (1989) 155.
[48] R.J. Mawby, F. Basolo, R.G. Pearson, J. Am. Chem. Soc. 86 (1964) 5043.
[49] C.S. Kraihanzel, P.K. Maples, Inorg. Chem. 7 (1968) 1806.
[50] K. Noack, M. Ruch, F. Calderazzo, Inorg. Chem. 7 (1968) 345.
[51] J.A. Gladysz, G.M. Williams, W. Tam, D.L. Johnson, D.W. Parker, J.C. Selover, Inorg. Chem. 18 (1979) 553.
[52] D. Catheline, D. Astruc, J. Organomet. Chem. 226 (1982) C52.
[53] D. Catheline, D. Astruc, Organometallics 3 (1984) 1094.
[54] B.T. Gregg, A.R. Cutler, Organometallics 13 (1994) 1039.
[55] R.K. Kochhar and R. Pettit, J. Organomet. Chem., 6 (1966) 272;

[56] T.H. Whitesides, J. Shelly, J. Organomet. Chem. 92 (1975) 215.
[57] W. Caseri, P.S. Pregosin, Organometallics 7 (1988) 1373.
[58] L.P. Szajek, J.R. Shapley, Organometallics 10 (1991) 2512.
[59] S.G. Davies, S.D. Moon, S.J. Simpson, S.E. Thomas, J. Chem. Soc., Dalton Trans. (1983) 1805.
[60] A.P. Humphries, S.A.R. Knox, J. Chem. Soc., Dalton Trans. (1975) 1710.
[61] N.M. Doherty, S.A.R. Knox, Inorg. Synth. 25 (1989) 179.
[62] A.C. Street, Y. Mizobe, F. Gotah, I. Mega, H. Oshita and M. Hidai, Chem. Lett. (1991) 383.
[63] T.S. Piper, G. Wilkinson, J. Inorg. Nucl. Chem. 3 (1956) 104.
[64] R.B. King, Organometallic Syntheses, Academic Press, New York, 1965, Vol. 1, p. 151.
[65] P.W. Jolly, R. Pettit, J. Am. Chem. Soc. 88 (1966) 5044.
[66] M.L.H. Green, M. Ishaq, R.N. Whiteley, J. Chem. Soc. A (1967) 1508.
[67] C.P. Casey, H. Tukada, W.H. Miles, Organometallics 1 (1982) 1083.
[68] R.D. Theys, M. Hossain, Tetrahedron Lett. 33 (1992) 3447.
[69] $(CO)_5MnCH(OPh)_2$: C. Loewe, G. Huttner, L. Zsolnai, H. Berkew, Z. Naturforsch. B: Chem. Sci. 43B (1988) 25.
[70] S. Pelling, C. Botha, J.R. Moss, J. Chem. Soc., Dalton Trans. (1983) 1495.
[71] J.R. Moss, S. Pelling, J. Organomet. Chem. 236 (1982) 221.
[72] Y.C. Lin, D. Milstein, S.S. Wreford, Organometallics 2 (1983) 1461.
[73] G.O. Nelson, C.E. Summer, Organometallics 5 (1986) 1983.
[74] D.A. Brown, W.K. Glass, M. Turkiubeid, Inorg. Chim. Acta 89 (1984) L47.
[75] C.L. Randolph, M.S. Wrighton, J. Am. Chem. Soc. 108 (1986) 3366.
[76] H. Brunner, K. Fisch, Ang. Chem., Int. Ed. Engl. 29 (1990) 1131; J. Organomet. Chem. 412 (1991) C11.
[77] M. Akita, T. Oku, M. Tanaka, Y. Moro-oka, Organometallics 10 (1991) 3080.
[78] B.K. Campion, R.H. Heyn, T.D. Tilley, A.L. Rheingold, J. Am. Chem. Soc. 115 (1993) 5527, and references therein.
[79] A.J. Chalk, J.F. Harrod, J. Am. Chem. Soc. 89 (1967) 1640.
[80] J.F. Harrod, A.J. Chalk, in: Organic Syntheses via Metal Carbonyls, Wiley, New York, 1977, Vol. 2, pp. 687–690, and references therein.
[81] A. Sisak, F. Ungváry, L. Markó, Organometallics 5 (1986) 1019.
[82] R.W. Wegman, Organometallics 5 (1986) 707.