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Manganese Carbonyl Complexes as Catalysts for the Hydrosilation of Ketones: Comparison with RhCl(PPh$_3$)$_3$

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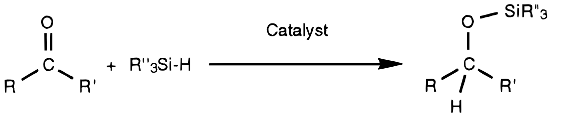
Manganese carbonyl complexes catalyze the hydrosilation of ketones with PhMe$_2$SiH and Ph$_2$SiH$_2$ in C$_6$D$_6$ solutions. Efficacy of the manganese carbonyl precatalysts (2.4 mol %) toward acetone hydrosilation with 1.1 equiv of PhMe$_2$SiH to give (CH$_3$)$_2$CH(OSiMe$_2$Ph) (**3**) varied: (PPh$_3$)(CO)$_4$MnC(O)CH$_3$ (**1**) (<5 min) $\gg$ (CO)$_5$MnC(O)Ph > (CO)$_5$MnC(O)CH$_3$ > (CO)$_5$MnCH$_3$ > (CO)$_5$MnBr (6.0 h) $\gg$ Mn$_2$(CO)$_{10}$ $\approx$ (PPh$_3$)(CO)$_4$MnBr $\approx$ (CO)$_5$MnSiMe$_2$Ph (**2**). A turnover frequency of 27 min^{-1} was measured for catalysis using 1% **1**; rapid catalysis was possible with 0.1% **1** in the absence of solvent. As a precatalyst, **1** is much more reactive than Rh(PPh$_3$)$_3$Cl for the PhMe$_2$SiH hydrosilation of acetone, acetophenone, and cyclohexanone; both catalysts exhibit similar reactivity with Ph$_2$SiH$_2$. With **1** as the precatalyst, isolated yields of the alkoxydimethylphenylsilanes exceeded 90%, with no evidence of competing dehydrogenative silation to yield vinyl silyl ethers. Photochemical activation of (CO)$_5$MnSiMe$_2$Ph (**2**) affords moderate hydrosilation catalytic activity in transforming acetone to **3**. In contrast, (CO)$_4$CoSiMe$_2$Ph (**10**) or Co$_2$(CO)$_8$ in the presence of the excess HSiMe$_2$Ph, with or without photochemical activation, were ineffective acetone hydrosilation catalysts. A reaction pathway is presented for the manganese carbonyl-catalyzed hydrosilation of ketones that involves coordinatively unsaturated manganese silyl intermediates, (L)(CO)MnSiR″$_3$, as the active catalysts.

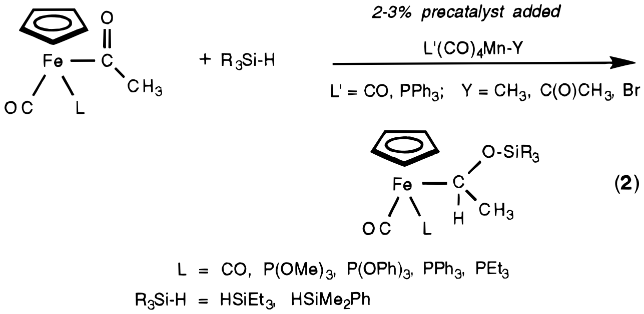
Introduction

The hydrosilation of aldehydes and ketones became an established synthetic procedure with the introduction of Wilkinson's compound, Rh(PPh$_3$)$_3$Cl, as a catalyst for this reaction, eq 1.[1] In early studies, Ojima and co-workers demonstrated that the reactivity order of the hydrosilanes decreased, RSiH$_3$ $\gg$ R$_2$SiH$_2$ $\gg$ R$_3$SiH.[2] Typical reaction conditions with the monohydrosilanes Et$_3$SiH or PhMe$_2$SiH, for example, required 0.1−5% Rh(PPh$_3$)$_3$Cl for a 1:1 mixture of ketone substrate to R$_3$SiH, with the reactions run neat or in benzene above 50 °C.[3] Rhodium complexes remain preeminent as ketone hydrosilation catalysts, although competitive dehydrogenative silation reactions that give vinyl silyl ethers (e.g., PhC(OSiMe$_2$Ph)=CH$_2$ from acetophenone)[4] remain problematic.[5]



(**1**)

In recent studies, we established that manganese carbonyl complexes efficiently catalyze the hydrosilation of nonlabile organometallic acyls Cp(CO)(L)FeC(O)CH$_3$ (L = CO, PR$_3$) to give Cp(CO)(L)FeCH(OSiR$_3$)CH$_3$ (eq 2).[6] A number of these (α-siloxyethyl)iron products were isolated, although under the appropriate conditions they further transformed to vinyl, Cp(CO)(L)FeCH=CH$_2$, and ethyl compounds, Cp(CO)(L)FeCH$_2$CH$_3$.[6b] Rh(PPh$_3$)$_3$-



(**2**)

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Cl also catalyzes some of these reactions, but only the more active manganese precatalysts promote the hydrosilation of $Cp(CO)(L)FeC(O)CH_3$ with monohydrosilanes.[7]

Evidently excess hydrosilane transforms the manganese carbonyl precatalyst to unstable, coordinatively unsaturated manganese silyls $(L)_x(CO)_{4-x}MnSiR_3$, which function as the active catalyst(s).[8] Supporting evidence for these active catalysts is available from a kinetics study on the $(CO)_5MnC(O)Ph$-catalyzed SiH/SiD isotope exchange between $EtMe_2SiH$ and $PhMe_2SiH$.[9] Although coordinatively saturated $(CO)_5MnSiMe_2Ph$ was not a viable catalyst, photolysis of the reaction mixture dissociates CO from the silyl precatalyst and promoted the SiH/SiD isotope exchange. Similar observations have been extended to the manganese carbonyl-catalyzed hydrosilation of $Cp(CO)_2FeC(O)CH_3$[6c] and even to organic esters.[10] We now report the use of manganese carbonyl precatalysts for the $PhMe_2SiH$ and Ph_2SiH_2 hydrosilation of four organic ketones: acetone, acetophenone, cyclohexanone, and 2-cyclohexen-1-one. In previous communications, we noted that manganese carbonyl acyl complexes are extremely effective as hydrosilation catalysts of acetaldehyde and benzaldehyde.[6a,7a,11]

Experimental Section

Synthetic manipulations were performed in a nitrogen atmosphere using standard Schlenk line and glovebox procedures.[12] Hydrosilation reaction mixtures were prepared in a glovebox and transferred to stoppered NMR tubes. Infrared spectra of benzene solutions were recorded on a Perkin-Elmer FT spectrophotometer, Model No. 1600. 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.

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 purified according to literature procedure.[13] Samples of $(CO)_5MnBr$,[14a] $(PPh_3)(CO)_4MnBr$,[15] $(CO)_5MnCH_3$, $(CO)_5MnC(O)CH_3$,[16] $(PPh_3)(CO)_4MnC(O)CH_3$ (**1**),[17] $(CO)_5MnSiMe_2Ph$ (**2**),[9,11] and $(CO)_5MnC(O)$-p-$C_6H_4CH_3$[18] were prepared by literature procedures and judged pure by IR and ^1H NMR spectroscopy. $(CO)_4CoSiMe_2Ph$ (**11**)[19] was prepared by the procedure of Chalk and Harrod[20] as a brown fluid: IR (hexane) ν(CO) 2090 m, 2026 s, 1993 s, br cm^{-1}; ^1H NMR δ 0.72 (SiMe), 7.17 (m, 3 H, Ph), 7.61 (m, 2 H, Ph); ^{13}C NMR (C_6D_6) δ 5.88 (SiMe), 199.58 (br s, CO), 141.45 (Ph, ipso-C), 133.22, 129.78, 128.20 (Ph).

Manganese and Cobalt Carbonyl Precatalysts for Ketone Hydrosilation: Determination of NMR Spectroscopic Yields. 1. $PhMe_2SiH$ and Acetone. To a vial containing the metal carbonyl precatalyst (Table 1) (0.011 mmol, 2.4 mol % of substrate) dissolved in C_6D_6 (600 mg) was added $PhMe_2SiH$ (68 mg, 0.50 mmol) and then acetone (26 mg, 0.45 mmol). The resulting yellow solution was transferred to an NMR tube, which was removed from the glovebox, and the ^1H and ^{13}C NMR spectra were monitored. The extent of reaction (Table 1) was quantified by ^1H NMR integration of the acetone and **3** methyl absorptions at δ 1.63 and 1.07, respectively.

2. $PhMe_2SiH$ or Ph_2SiH_2 and Ketones: Pretreatment of $(PPh_3)(CO)_4MnC(O)CH_3$ (1). A pale yellow solution of the precatalyst **1** (5 mg, 0.011 mmol) in C_6D_6 (300 mg) was treated with 0.50 mmol of either $PhMe_2SiH$ or Ph_2SiH_2. The resulting solution darkened to golden yellow over 20 min. To this solution then was added a second C_6D_6 solution (300 mg) containing 0.45 mmol of the ketone (Table 2) and anisole (49 mg, 0.45 mmol) as the internal standard. Quantitative ^1H NMR measurements were accurate to within 5%, based upon the results of integrating examples of the second C_6D_6 reactant solution. Similar reactions were carried out using $Rh(PPh_3)_3Cl$ (10 mg, 0.011 mmol) as the catalyst, although the ketone substrate, hydrosilane, and rhodium catalyst were mixed in 600 mg of C_6D_6 and transferred to an NMR tube. $(CH_3)_2CH(OSiHPh_2)$ (**6**): ^1H NMR δ 7.70 (m, 4H, Ph), 7.20 (m, 6H, Ph), 5.69 (s, SiH), 4.08 (sept, $J = 6.1$, CH), 1.15 (d, $J = 6.1$, CH_3); ^{13}C NMR δ 135.15 (ipso C, Ph), 134.96, 130.44, 128.27 (Ph), 67.39 (CH), 25.42 (CH_3). $(CH_3)PhCH(OSiHPh_2)$ (**7**): ^1H NMR δ 7.68 (m, 4H, SiPh), 7.31 (m, 2H, Ph), 7.17 (m, 9H, SiPh + Ph), 5.71 (s, SiH), 5.00 (q, $J = 6.2$, CH), 1.46 (d, $J = 6.2$, CH_3); ^{13}C NMR δ 145.65 (ipso C, Ph), 134.72, 134.46 (ipso C, SiPh), 73.04 (CH), 26.48 (CH_3). $\overline{CH_2(CH_2)_4C}H(OSiHPh_2)$ (**8**): ^1H NMR δ 7.71 (m, 4H, Ph), 7.18 (m, 6H, Ph), 5.74 (s, SiH), 3.84 (m, 1H, CHOSi), 1.83 (m, 2H, Cα-eq H), 1.61 (m, 2H, Cβ-eq H), 1.50 (m, 2H, Cα-ax H), 1.27 (m, 1H, Cγ-ax H), 1.07 (m, 3H, Cγ-eq + Cβ-axH); ^{13}C NMR δ 134.68 (ipso C, Ph), 130.52 (ipso C, Ph), 72.89 (CHOSi), 35.50 (α-CH_2), 25.75 (γ-CH_2), 23.96 (β-CH_2).[21]

$(PPh_3)(CO)_4MnC(O)CH_3$ (1)-Catalyzed Hydrosilation of Ketones: Preparative-Scale Reactions. 1. Cyclohexanone Hydrosilation with $PhMe_2SiH$. A 10-mL round-bottom flask was charged with 3.0 g (3.4 mL) of C_6H_6, 28 mg of **1** (0.060 mmol, 2.4 mol %), and 375 mg of $PhMe_2SiH$ (2.75 mmol, 1.1 equiv). After 20 min, 245 mg of cyclohexanone (2.50 mmol, 1.0 equiv) was added, and the reaction mixture was removed from the glovebox. The reaction, which was exother-

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(21) NMR spectral assignments are consistent with the results of ^1H NMR spin decoupling, and with COSY and HMQC experiments.

mic, was run under a nitrogen atmosphere for 45 min; the solvent was evaporated from the lemon yellow solution, and the residue was distilled through a short-path distillation apparatus (0.30 mmHg, >210 °C). This afforded 540 mg of a clear, colorless fluid that was identified as spoectroscopically pure $\overline{CH_2(CH_2)_4C}H(OSiMe_2Ph)$ (**5**),[4b,5b] 92% yield: ^1H NMR δ 7.62 (m, 2H, Ph), 7.22 (m, 3H, Ph), 3.64 (m, 1H, CHOSi), 1.72 (m, 2H, Cα-eq H), 1.61 (m, 2H, Cβ-eq H), 1.41 (m, 2H, Cα-ax H), 1.32 (m, 2H, Cγ H), 1.10 (m, 3H, Cβ-ax + Cα-eqH), 0.27 (s, SiMe); ^{13}C NMR δ 139.21 (ipso C, Ph), 71.07 (CHOSi), 36.12 (α-CH_2), 25.89 (γ-CH_2), 24.15 (β-CH_2), −0.77 (SiMe).[21]

2. Hydrosilations of Acetone and Acetophenone with $PhMe_2SiH$ and 2-Cyclohexen-1-one with Ph_2SiH_2. Hydrosilation of acetone (290 mg, 5.00 mmol) and acetophenone (300 mg, 2.50 mmol) was carried out with 1.1 equiv of $PhMe_2SiH$ (749 mg, 5.50 mmol and 375 mg, respectively) with 2.4 mol % of **1** (57 mg, 0.12 mmol, and 28 mg). Both $(CH_3)_2CHOSiMe_2Ph$[22] (**3**) and $Ph(CH_3)CHOSiMe_2Ph$[3] (**4**) were isolated (91% and 95% yields) as spectroscopically pure, colorless fluids after short-path distillations at 210 °C. **3**: ^1H NMR (C_6D_6) δ 7.58 (m, 2H, Ph), 7.22 (m, 3H, Ph), 3.87 (sept, $J = 6.1$ Hz, CH), 1.07 (d, $J = 6.1$, CH_3), 0.32 (s, SiMe); ^{13}C NMR δ 139.00 (ipso C, Ph), 133.79, 128.05, 129.66 (Ph), 65.33 (CH), 25.93 (CH_3), −0.93 (SiMe). **4**: ^1H NMR δ 7.57 (m, 2H, SiPh), 7.27 (m, 2H, Ph), 7.20 (m, 3H, SiPh), 7.15 (m, 2H, Ph), 7.06 (m, 1H, Ph), 4.78 (q, $J = 6.3$, CH), 1.37 (d, $J = 6.3$, CH_3), 0.30, 0.25 (s's, SiMe); ^{13}C NMR δ 146.75 (ipso C, Ph), 138.46 (ipso C, SiPh), 71.46 (CH), 27.17 (CH_3), −0.76 (SiMe), −1.26 (SiMe).

To a solution of **1** (28 mg, 0.06 mmol) in 3.0 g of C_6H_6 was added 507 mg of Ph_2SiH_2 (2.75 mmol), and after 20 min the resulting lemon yellow solution was treated with 2-cyclohexen-1-one (240 mg, 2.50 mmol). After 5 h, the reaction was chromatographed on a 10 × 1 cm of flash-grade silica gel containing zinc silicate phosphor. A UV lamp was used to detect the colorless band that initially was eluted; this afforded 564 mg of a pale yellow oil that was identified as spectroscopically pure $\overline{CH_2(CH_2)_2CH{=}CHC}H(OSiHPh_2)$ (**9**),[5b,23] 81% yield: ^1H NMR δ 7.71 (m, 4H, Ph), 7.17 (m, 6H, Ph), 5.84, 5.82 (dm, 1H, =CHCOSi), 5.75 (s, SiH), 5.62, 5.60 (dm, 1H, *CH*=CHCOSi), 4.43 (m, 1H, CHOSi), 1.75 (3H, α-*CH*$_2$CHOSi + γ-*CH*$_2$CH=), 1.65 (2H, γ-*CH*$_2$CH= + β-C*H*H), 1.27 (1H, β-CH*H*); ^{13}C NMR δ 135.05 (ipso C, Ph), 135.04 (ipso C, Ph), 130.38 (β-CH=), 129.80 (α-CH=), 68.62 (CHOSi), 32.16 (α-*CH*$_2$-CHOSi), 25.13 (γ-*CH*$_2$CH=), 19.41 (β-CH_2).[21]

Turnover Frequency for the $(PPh_3)(CO)_4MnC(O)CH_3$ (1)-Catalyzed $PhMe_2SiH$ Hydrosilation of Acetone. A 1.00-mL aliquot from a stock solution of **1** (36 mg, 0.080 mmol) in 4.00 mL of C_6H_6 and $PhMe_2SiH$ (327 mg, 2.40 mmol) was transferred to a stoppered vial. A 25-mL flask was charged with C_6H_6 (11.00 g, 12.60 mL) and acetone (116 mg, 2.00 mmol) before it also was stoppered. Both the vial and flask were removed from the glovebox; after the precatalyst solution turned yellow-brown (20 min), it was transferred via cannula to the flask containing the acetone. Every 2 min an aliquot was removed, and its IR spectrum was recorded.

The absorbancy values for the acetone ν(CO) 1716 cm^{-1} absorption band were converted via a (linear) Beer's law plot to concentrations, which were plotted vs time (the reaction rates leveled off within 12 min). From these plots, initial values (slopes) for the reaction velocity (v_i) were obtained. Values for the turnover frequency, $N_t = v_i/(\text{precatalyst})$,[24] were determined: $N_t = 27.2 \pm 5.0$ min^{-1} (2σ for 5 replicate runs). Erratic results and lower turnover frequencies (<10 min^{-1}) were observed when the precatalyst stock solution was prepared more than 4 h before use or when the catalysis experiments—after the active catalyst was generated—were run in air.

Table 1. Catalyst Screening for Hydrosilation of Acetone with $HSiMe_2Ph$

precatalyst[a]	time (h)	extent of reacn[b] (%)
$(PPh_3)(CO)_4MnC(O)CH_3$ (**1**)	0.45	>95[b]
$(PPh_3)(CO)_4MnC(O)CH_3$[c]	<5 min	>95[b]
$(CO)_5MnC(O)Ph$	1.5	90+[b]
$(CO)_5MnC(O)CH_3$	4.5	>95[b]
$(CO)_5MnCH_3$	5.0	80−90[b]
$(CO)_5MnBr$	6.0	70[b]
$(PPh_3)(CO)_4MnBr$	6.0	0
$(CO)_5MnSiMe_2Ph$ (**2**)	6.0	0
$Mn_2(CO)_{10}$	6.0	0
$(CO)_4CoSiMe_2Ph$ (**11**)	4.0	5[d]
$Co_2(CO)_8$	4.0	16[d]

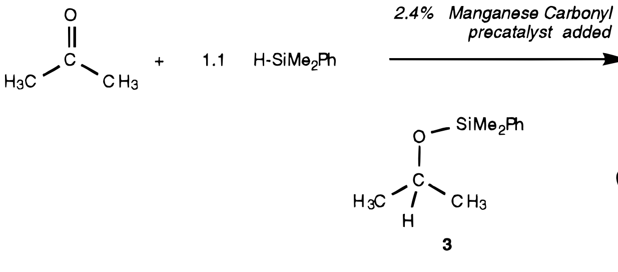
[a] Reaction conditions: precatalyst (0.011 mmol, 2.4 mol %), $CH_3C(O)CH_3$ (0.45 mmol), $HSiMe_2Ph$ (0.50 mmol), and 0.45 mmol anisole (internal standard) in 600 mg of C_6D_6. [b] Reaction was monitored by ^1H NMR spectroscopy; only starting materials and $(CH_3)_2CH(OSiMe_2Ph)$ (**3**) were detected in the yellow solutions, along with occassional traces of $(PhMe_2Si)_2O$ (^1H NMR, δ 0.31). [c] Precatalyst treated with full amount of $HSiMe_2Ph$ for 20 min prior to adding the acetone. [d] Refers to % **3** formed in dark brown solutions with black sediments; amounts of acetone consumed, 17% and 12%, respectively.

Photochemical Activation of $(CO)_5MnSiMe_2Ph$ (2) as a Hydrosilation Catalyst. A C_6D_6 solution (600 mg, 0.63 mL) with acetone (26 mg, 0.45 mmol), **2** (4 mg, 0.011 mmol), and $PhMe_2SiH$ (68 mg, 0.50 mmol) was transferred to an NMR tube. This NMR tube, sealed with a rubber septum, was immersed in a 50-mL Erlenmeyer flask filled with cold water, which was centered in a Rayonet photochemical reactor (3500 Å). The sample was photolyzed at room temperature, with changing of the water every 30 min. After 20 min, the colorless reaction mixture had turned light yellow, and after 1 h of photolysis, this color had darkened to lemon yellow. ^1H NMR spectral monitoring was consistent with 27% conversion of acetone to $(CH_3)_2CHOSiMe_2Ph$ (**3**)[22] after 1 h. This concentration remained constant after stopping the photolysis for another 2 h. The lemon yellow solution, however, had faded to pale yellow within 5 min after removing the sample from the photochemical reactor. Continued photolysis of the reaction mixture for a total of 3 h afforded a 63% yield of **3**, which increased to 73% after a total of 5 h of photolysis.

This reaction was repeated using a Hanovia Hg vapor high-pressure lamp; the NMR tube containing the reaction mixture was strapped to the quartz, water-cooled photochemical probe, which was immersed in an ice water bath. After 30 min of photolysis, the NMR tube was removed and the ^1H NMR spectrum was consistent with 35% conversion of acetone to **3**, which increased to 72% after a total of 2 h of photolysis.

Results and Discussion

1. Acetone Hydrosilation: $(PPh_3)(CO)_4MnC(O)CH_3$ (1) as an Optimal Precatalyst. We surveyed the manganese carbonyl complexes in Table 1 as prospective catalysts for the hydrosilation of acetone, eq 3. Under



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[22] Caseri, W.; Pregosin, P. S. *Organometallics* **1988**, *7*, 1373.

[23] (a) Chan, T. H.; Zheng, G. Z. *Tetrahedron Lett.* **1993**, *34*, 3095. (b) Zheng, G. Z.; Chan, T. H. *Organometallics* **1995**, *14*, 70 and references therein.

[24] Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; W. H. Freeman: New York, 1990; p 543.

the conditions noted, acetone smoothly transformed to the previously characterized $(CH_3)_2CH(OSiMe_2Ph)$ (**3**),[22] which formed in over 90% yields with the manganese acetyl, benzoyl, and methyl precatalysts. Traces of $(PhMe_2Si)_2O$, the only byproduct, were detected by ^1H and ^{13}C NMR spectral monitoring.

The relative activity of the manganese carbonyl precatalysts corresponds to the time judged (^1H NMR spectral monitoring) for consuming the acetone substrate:

$$(PPh_3)(CO)_4MnC(O)CH_3\ (\mathbf{1})\ (<5\ \text{min}) \gg (CO)_5MnC(O)\text{-}p\text{-}C_6H_4CH_3 > (CO)_5MnC(O)CH_3 > (CO)_5MnCH_3 > (CO)_5MnBr\ (6.0\ \text{h}) \gg Mn_2(CO)_{10} \approx (PPh_3)(CO)_4MnBr \approx (CO)_5MnSiMe_2Ph\ (\mathbf{2})$$

The inactivity of a manganese silyl **2** and $Mn_2(CO)_{10}$ agrees with our previous results on the catalytic dehydrogenative silation of alcohols,[25] the SiH/SiD isotope exchange,[9] and the hydrosilation of organometallic acyls[6,8] and organic esters.[10]

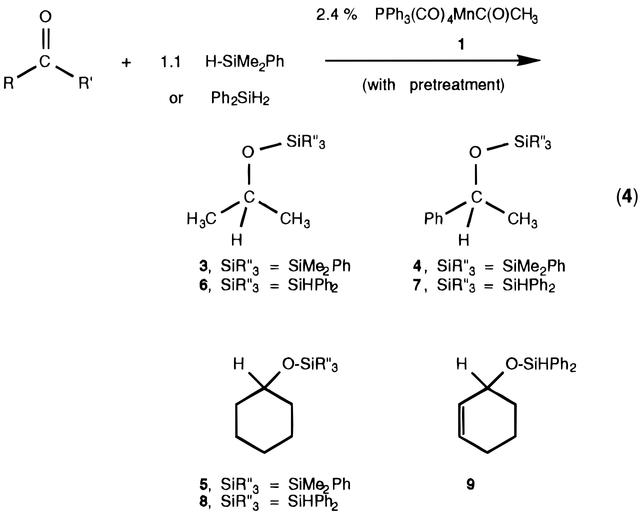
Acetone hydrosilation catalysis involving $(PPh_3)(CO)_4MnC(O)CH_3$ (**1**) is unique in that this precatalyst is both the most active as well as the only one that shows enhanced reactivity after the pretreatment procedure. This procedure entails treating the precatalyst with the full amount of $PhMe_2SiH$ for 20 min, which degrades **1**[8−10] and affords the presumed active catalyst(s). As a result of this pretreatment, the catalysis time dropped from 45 min to less than 5 min. We used this pretreatment procedure in all subsequent experiments involving **1**.

Our use of 2.4% precatalyst **1**, although convenient for running the acetone hydrosilation reactions, does not convey the activity of the catalyst. In order to measure turnover frequencies, N_t, from initial reaction velocities, we reduced both the **1**:acetone substrate ratio, from 1:42 to 1:100, and the acetone concentration, from 0.71 to 0.15 M. Acetone concentrations during catalytic runs (which took ca. 12 min) then were determined by IR spectroscopy. The initial reaction velocities, $-(d[\text{acetone}]/dt)_i$, were converted to turnover frequencies, $N_t = v_i/(\text{precatalyst})$,[24] of $27.2 \pm 5.0\ \text{min}^{-1}$.

This value for the turnover frequency N_t surely represents a lower limit, since we assumed that the concentration of the active catalyst equaled the starting concentration of the precatalyst. The pretreatment procedure consumes **1**, but the resulting active catalyst also readily degrades.[8−10] Therefore, accurate values for the active catalyst concentration (even its initial value) during ongoing catalysis are not available.

Reducing the concentration of the precatalyst **1** below 2% slowed the hydrosilation catalysis. For example, hydrosilation of acetone on a 0.5 mmol scale with 1.0% **1** required 2.5 h to go to completion. Further reducing the precatalyst concentration to 0.1% of the acetone, while maintaining the 1:1.1 ratio between substrate and $PhMe_2SiH$, afforded 60% hydrosilation after 2 h. Attempts to determine turnover frequencies with less than 0.5% precatalyst **1** gave erratic results.

2. Ketone Hydrosilation: $(PPh_3)(CO)_4MnC(O)CH_3$ (1) Compared to $Rh(PPh_3)_3Cl$ as Precatalysts with $PhMe_2SiH$ and Ph_2SiH_2. Table 2 summarizes the results of using **1** or $Rh(PPh_3)_3Cl$ as catalysts with $PhMe_2SiH$ and Ph_2SiH_2 to hydrosilate acetone, acetophenone, cyclohexanone, and 2-cyclohexen-1-one (eq 4).



(**4**)

The catalysis conditions match those reported in the survey reactions of Table 1 (2.4 mol % of precatalyst and 1:1.1 ketone substrate/hydrosilane in C_6D_6), and the reaction times designate essentially quantitative conversion of ketones to alkoxysilane products.

With $PhMe_2SiH$, **1** immediately and cleanly transformed acetone, acetophenone, and cyclohexanone to their (previously characterized) alkoxysilanes $(CH_3)_2CH(OSiMe_2Ph)$ (**3**),[22] $(CH_3)PhCH(OSiMe_2Ph)$ (**4**),[3] and $\overline{CH_2(CH_2)_4C}H(OSiMe_2Ph)$ (**5**).[4b,5b] We found no traces of vinyl silyl ethers, e.g., $PhC(OSiMe_2Ph){=}CH_2$,[4] which result from competing dehydrogenative silation reactions during catalytic ketone hydrosilation.[5]

We also found that **1** is a much more active ketone hydrosilation catalyst than is $Rh(PPh_3)_3Cl$, at least with $PhMe_2SiH$ (and presumably other monohydrosilanes). Under our reaction conditions, $Rh(PPh_3)_3Cl$ did not catalyze the $PhMe_2SiH$ hydrosilation of acetone, acetophenone, or cyclohexanone. When preparative-scale hydrosilation reactions with 2.4 mol % of **1** as the precatalyst were run on with 2.5−5.0 mmol of ketone, the alkoxysilane products **3**−**5** were isolated spectroscopically pure in over 90% yields (Table 2).

With Ph_2SiH_2 and under the same conditions, both **1** and $Rh(PPh_3)_3Cl$ exhibited similar hydrosilation reactivity in yielding $(CH_3)_2CH(OSiHPh_2)$ (**6**),[3] $(CH_3)PhCH(OSiHPh_2)$ (**7**),[3b,5d] and $\overline{CH_2(CH_2)_4C}H(OSiHPh_2)$ (**8**).[3] These alkoxysilanes, which rapidly and quantitatively formed, were characterized by their ^1H and ^{13}C NMR spectra. Surprisingly, bis(alkoxy)silane byproducts $[(R)R'CHO]_2SiPh_2$ (**6′**−**8′**) were not detected.[3,26]

The catalytic hydrosilation of 2-cyclohexen-1-one proved to be more demanding, since **1** proved to be ineffective with $PhMe_2SiH$, even in the absence of solvent. In

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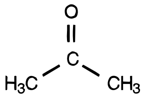
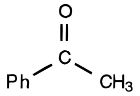
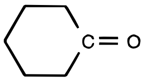
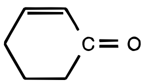
[25] Gregg, B. T.; Cutler, A. R. *Organometallics* **1994**, *13*, 1039.

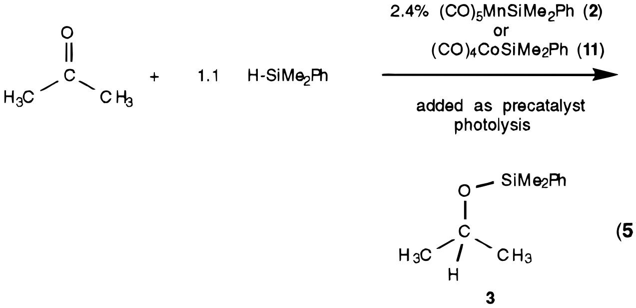
[26] Significant concentrations of **6′**−**8′** (up to 35% yields after reaction times of 0.5−1.5 h) were observed during preliminary studies with $(CO)_5MnC(O)Ph$ as the precatalyst. These byproducts exhibit diagnostic upfield shifts of their ^{13}C NMR methine absorptions, e.g., δ 71.74, 71.70 for the diastereotopic sites on $[PhCH(CH_3)O]_2(SiPh_2)$ (**7′**). We previously reported similar product selectivity for the hydrosilation of $FpC(O)CH_3$ with R_2SiH_2 (R = Et, Ph):[6a] use of **1** as the precatalyst exclusively afforded $FpCH(OSiHR_2)CH_3$, whereas $(CO)_5MnC(O)R$ (R = CH_3, Ph) gave $FpCH(OSiHR_2)CH_3$ and $[FpCH(CH_3)O]_2SiR_2$, which were separated by size-exclusion chromatography and fully characterized.[6c]

Table 2. $(PPh_3)(CO)_4MnC(O)CH_3$-Catalyzed Hydrosilation of Ketones with $PhMe_2SiH$ and Ph_2SiH_2

Ketone	Silane	Precatalyst	Reaction Time (min)[a]	Product	NMR Yield[a]	Isolated Yield[b]
	$PhMe_2SiH$	$(PPh_3)(CO)_4MnC(O)CH_3$	< 4 min	$(CH_3)_2CH(OSiMe_2Ph)$ **3**	> 95%	90%
		$(PPh_3)_3RhCl$	> 6 hours		none	
	Ph_2SiH_2	$(PPh_3)(CO)_4MnC(O)CH_3$	< 4 min	$(CH_3)_2CH(OSiHPh_2)$ **6**	> 95%	
		$(PPh_3)_3RhCl$	< 4 min		> 90%	
	$PhMe_2SiH$	$(PPh_3)(CO)_4MnC(O)CH_3$	< 4 min	$Ph(CH_3)CH(OSiMe_2Ph)$ **4**	> 95%	95%
		$Rh(PPh_3)_3Cl$	> 6 hours		none	
	Ph_2SiH_2	$(PPh_3)(CO)_4MnC(O)CH_3$	< 4 min	$Ph(CH_3)CH(OSiHPh_2)$ **7**	> 95%	
		$(PPh_3)_3RhCl$	< 4 min		> 90%	
	$PhMe_2SiH$	$(PPh_3)(CO)_4MnC(O)CH_3$	< 4 min	$C_6H_{11}(OSiMe_2Ph)$ **5**	> 94%	92%
		$(PPh_3)_3RhCl$	> 6 hours		none	
	Ph_2SiH_2	$(PPh_3)(CO)_4MnC(O)CH_3$	< 4 min	$C_6H_{11}(OSiHPh_2)$ **8**	91%	
		$(PPh_3)_3RhCl$	< 4 min		> 90%	
	$PhMe_2SiH$	$(PPh_3)(CO)_4MnC(O)CH_3$	> 6 hours		none	
		$(PPh_3)_3RhCl$	3 hours		80%	
	Ph_2SiH_2	$(PPh_3)(CO)_4MnC(O)CH_3$	4 hours	$C_6H_9(OSiHPh_2)$ **9**	85%	80%
		$(PPh_3)_3RhCl$	< 4 min		90%	

[a] Reaction conditions: 0.011 mmol of precatalyst (2.4 mol %), 0.45 mmol of ketone, 0.50 mmol of $PhMe_2SiH$ or Ph_2SiH_2, and 0.45 mmol of anisole (internal standard) in 600 mg of C_6D_6. $(PPh_3)(CO)_4MnC(O)CH_3$ (**1**) precatalyst was treated with the hydrosilane for 20 min before adding the ketone; reaction was monitored by ^1H NMR spectroscopy. [b] Preparative-scale reactions with 2.5−5.0 mmol of ketone, 1.1 equiv of hydrosilane, and 2.4 mol % **1** (pretreated with hydrosilane for 20 min) in 3.00 g of benzene. [c] (Cyclohex-2-en-1-yloxy)diphenylsilane (**9**), $CH_2(CH_2)_2CH{=}CHCH(OSiHPh_2)$; (cyclohex-1-en-1-yloxy)dimethylphenylsilane (**10**), $CH_2(CH_2)_2CH{=}C(OSiMe_2Ph)$.

contrast, switching to $Rh(PPh_3)_3Cl$ as the precatalyst yielded the 1,4 addition product $CH_2(CH_2)_2CH{=}C(OSiMe_2Ph)$ (**10**).[23] With the more reactive Ph_2SiH_2, both catalysts selectively generated the 1,2-addition product (cyclohex-2-en-1-yloxy)diphenylsilane **9**, as expected,[3,23] although the rhodium catalyst proved to be more active. We isolated **9** in 80% yield from a 2.50 mmol scale reaction with 2.4% **1** as the precatalyst; the resulting clear fluid was free of the 1,4-addition byproduct, $CH_2(CH_2)_2CH{=}C(OSiHPh_2)$.[2]



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3. Acetone Hydrosilation with $(CO)_5MnSiMe_2Ph$ (2) under Photochemical Conditions: Comparison with $(CO)_4CoSiR_3$ Activity. Although $(CO)_5MnSiMe_2Ph$ (**2**) did not catalyze acetone hydrosilation between 22 and 45 °C, photolysis of these reactions at room temperature initiated productive hydrosilation catalysis. Continuous irradiation of C_6D_6 solutions containing 1.1 equiv of $PhMe_2SiH$ and 2.4% **2** for 2 h afforded **3** in 70% spectroscopic yields (eq 5). This photocatalysis closely resembles that already established for the **2**-catalyzed hydrosilation of ethyl acetate to yield $CH_3CH(OSiMe_2Ph)(OEt)$.[10] Under identical conditions, both reactions converted acetone or ethyl acetate after 1 h of photolysis to their respective alkoxysilane products in 35% yields.

We extended our hydrosilation studies involving the manganese silyl **2** to its potentially more labile cobalt analog[19] $(CO)_4CoSiMe_2Ph$ (**11**). Isolobal $Mn(CO)_5$ and $Co(CO)_4$ complexes generally exhibit similar chemical reactivity, although the cobalt complexes typically are much more labile or reactive.[27]

Cobalt silyl complexes $(CO)_4CoSiR_3$,[28b] which are easily available by treating $Co_2(CO)_8$ with 2 equiv of

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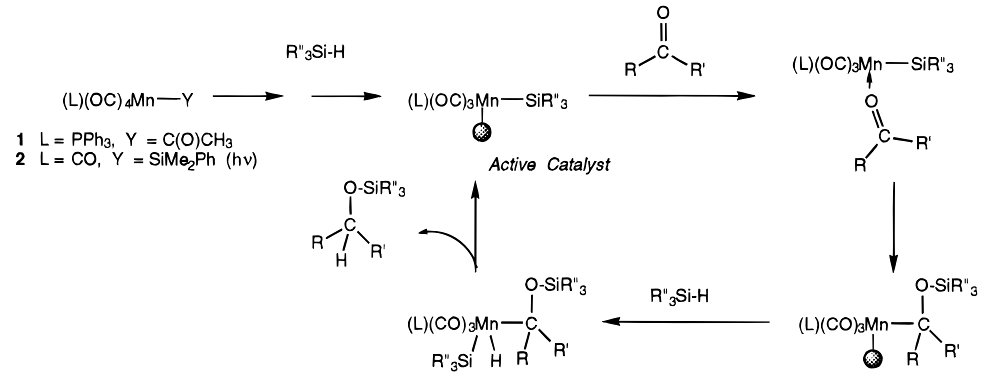
[27] (a) Galamb, V.; Pályi, G. *Coord. Chem. Rev.* **1984**, *59*, 203. (b) Kovács, I.; Hoff, C. D.; Ungváry, F.; Markó, L. *Organometallics* **1985**, *4*, 1347.

Scheme 1



hydrosilane,[20] serve as precatalysts for the hydrosilation of alkenes[28] and for the siloxymethylenylation of alkenes and aldehydes.[29] Recently, Ojima and co-workers[5b] reported that $Co_2(CO)_8$ in the presence of excess R_3SiH slowly catalyzed the hydrosilation of cyclohexanone, albeit with formation of the (cyclohex-1-en-1-yloxy)-dimethylethylsilane dehydrogenative silation by-product.[4b,f,5b] Plausible intermediates for this catalysis include (hydrido)(silyl)(alkyl)Co^{III}, for which (hydrido)-(silyl)$_2Co^{III}$ [30] analogs have been generated independently via photolysis of $(CO)_4CoSiR_3$ and trapping the resulting coordinatively unsaturated $(CO)_3CoSiR_3$ systems with excess hydrosilane.[31]

Table 1 also records results of using $(CO)_4CoSiMe_2$-Ph (**11**) or $Co_2(CO)_8$ plus excess $HSiMe_2Ph$ to catalyze the hydrosilation of acetone, eq 5. Reaction conditions parallel those used in exploratory experiments with manganese carbonyl complexes. Even upon photochemical activation, **11** was an ineffective catalyst that consumed up to 12% more substrate than could be accounted for by the alkoxysilane product **3** ($<$20% over 8 h). These numbers are only approximate due to the difficulty in obtaining reproducible integrations for the broadened ^1H NMR spectral scans.

The photochemical activation of **2** and the pretreatment of **1** with excess hydrosilane to advance hydrosilation catalysis of ketones is consistent with a reaction pathway involving coordinatively unsaturated manganese silyl intermediates, $(L)(CO)MnSiR''_3$ as the active catalysts.[4,5] A plausible pathway, a working hypothesis, appears in Scheme 1; it essentially resembles that commonly accepted for the rhodium(I)-catalyzed hydrosilation of ketones.[3,5c,23b,32]

This mechanism also corresponds closely to those that we advanced for manganese carbonyl-catalyzed hydrosilation of $FpC(O)CH_3$[6] and organic esters,[10] as well as the autocatalytic hydrosilation of $(CO)_5MnC(O)CH_3$[8] [Scheme 1, $R' = Mn(CO)_5$]. In these latter studies, we established procedural details and some mechanistic evidence for transforming **2** (photochemical conditions) or manganese alkyl and acyl complexes (including **1**) plus excess hydrosilanes to the postulated active hydrosilation catalysts.

Conclusions

Perhaps the most surprising result of these studies is that easily available manganese carbonyl complexes afford powerful ketone hydrosilation precatalysts. This chemistry, while unexpected in terms of published manganese carbonyl chemistry, is consistent with results of our ongoing studies on the reactions of hydrosilanes with labile metal carbonyl alkyl/acyl compounds. The resulting reaction mixtures function as hydrosilation catalysts toward a variety of organometallic and organic acyls or as dehydrogenative silation catalysts toward alcohols and carboxylic acids.

Although we have not yet developed the optimal precatalyst or catalysis conditions involving these manganese hydrosilation systems, those available already eclipse the activity of the standard $Co_2(CO)_8/(CO)_4CoSiR_3$ and $RhCl(PPh_3)_3$ catalytic systems. Use of $(PPh_3)(CO)_4MnC(O)CH_3$ (**1**) as the precatalyst, after pretreatment with the hydrosilane, affords a particularly active ketone hydrosilation catalyst. Distinguishing attributes of this catalytic system are that it operates with monohydrosilanes and apparently it is not prone to undergo competing dehydrogenative silation to give vinyl silyl ethers.

Acknowledgment. We gratefully acknowledge receiving generous financial support from the Department of Energy, Office of Basic Energy Science.

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[28] (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 1133. (b) Reviews on the reactivity of metal silyl complexes: Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley Interscience: New York, 1989; Part 2, Chapter 24. Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1992; Chapter 10.

[29] (a) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837. (b) Murai, S.; Seki, Y. *J. Mol. Catal.* **1987**, *41*, 197. (c) Murai, T.; Yasui, E.; Kato, S.; Hatayama, Y.; Suzuki, S.; Yamasaki, Y.; Sonoda, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *J. Am. Chem. Soc.* **1989**, *111*, 7938. (d) Kovács, I.; Sisak, A.; Ungváry, F.; Markó, L. *Organometallics* **1988**, *7*, 1025.

[30] (a) Wrighton, M. S.; Seitz, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289. Hardin, S.; Turney, T. W. *J. Mol. Catal.* **1987**, *39*, 237. Archer, N. J.; Haszeldine, R. N.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1979**, 695. (b) Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* **1980**, *19*, 3858. Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 995.

[31] Examples of (hydrido)(silyl)(alkyl)metal complexes have been reported or implicated as intermediates in hydrosilation catalysis.[2,28b] (a) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366. Brunner, H.; Fisch, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1131; *J. Organomet. Chem.* **1991**, *412*, C11. Akita, M.; Oku, T.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1991**, *10*, 3080. (b) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527 and references therein.

[32] (a) Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671. Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390. (b) Corriu, R. J. P.; Moreau, J. J. E. *Nouv. J. Chim.* **1977**, *1*, 71. (c) Peyronel, J. F.; Kagan, H. B. *Nouv. J. Chim.* **1978**, *2*, 211. Kagan, H. B.; Peyronel, J. F.; Yamagishi, T. In *Advances in Chemistry Series No. 173*; King, R. B., Ed.; American Chemical Society: Washington, DC, 1979; p 50. (d) Kolb, I.; Hetflejs, J. *Coll. Czech. Chem. Commun.* **1980**, *45*, 2224. (e) Nagashima, H.; Tatebe, K.; Ishibashi, T.; Nakaoka, A.; Sakakibara, J.; Itoh, K. *Organometallics* **1995**, *14*, 2868.