Hydrosilation of the Manganese Acetyl $(CO)_5MnC(O)CH_3$ with Monohydrosilanes

Brian T. Gregg and Alan R. Cutler*

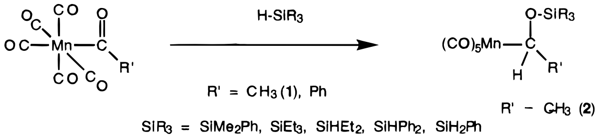
Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180

Received August 21, 1995[⊗]

Abstract: Treatment of the manganese acetyl $(CO)_5MnC(O)CH_3$ (**1**) with 1−2 equiv of a monohydrosilane furnished mixtures of α-siloxyethyl $(CO)_5MnCH(OSiR_3)CH_3$ (**2**) and α-siloxyvinyl $(CO)_5MnC(OSiR_3){=}CH_2$ (**3**) complexes. Relative yields of **2** and **3** varied from 80% and 6% for $HSiMe_2Ph$ to 28% and 59% for $HSiEt_3$. One of the latter compounds, $(CO)_5MnC(OSiEt_3){=}CH_2$ (**3j**), was fully characterized, and seven examples of **2** were isolated in moderate yields. Four α-siloxyethyl complexes **2** were further characterized as stable derivatives $(CO)_5MnC(O)CH(OSiR_3)CH_3$ after carbonylation. Mechanistic studies on the $HSiMe_2Ph$ and $HSiEt_3$ hydrosilation of **1** are noteworthy for (1) the absence of $(R_3SiO)CH{=}CH_2$ and $CH_3CH_2OSiR_3$ byproducts, (2) the presence of **3** but not $(CO)_5MnSiR_3$, (3) inhibition by CO, phosphine, or acetonitrile, but neither air nor light, (4) competitive hydrosilation of other substrates (e.g., acetone or $Cp(CO)_2FeC(O)R$) for which **1** is a precatalyst, (5) degradation of **2** by excess $HSiR_3$, giving $Mn_2(CO)_{10}$ and $(R_3Si)_2O$ as the final products, (6) the fact that this degradation results in autocatalysis by generating the transient active catalyst $(CO)_4MnSiR_3$ (**15**), and (7) the fact that the hydrosilation induction period can be removed by independently generating the putative **15**. These observations are consistent with an autocatalytic hydrosilation mechanism in which silane degradation of product **2** (or of other manganese complexes) generates the active catalyst **15**, which binds **1** and rearranges to the unsaturated bimetallic *μ*-siloxyethylidene $(CO)_5MnC(CH_3)(OSiMe_2Ph)Mn(CO)_4$ as the key catalysis intermediate: silane addition affords **2** whereas *β*-deinsertion produces **3**.

Introduction

The manganese acyl complexes $(CO)_5MnC(O)R'$ ($R' = CH_3$, Ph) represent intriguing substrates for reactions with hydrosilanes.[1] These thermally labile acyl complexes[2] undergo hydrosilation at room temperature: the manganese acetyl compound **1** ($R' = CH_3$), for example, when treated with monohydrosilanes affords isolable α-siloxyethyl complexes $(CO)_5MnCH(OSiR_3)CH_3$ (**2**). Several related hydrosilation products $(CO)_5MnCH(OSiR_3)R'$ ($R' = CH_3$, Ph) prepared using mono-, di-, and trihydrosilanes (eq 1) have been isolated or unambiguously characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. On the other hand, these labile manganese acyl complexes also function as extremely reactive catalyst precursors[3] for the hydrosilation of nonlabile iron acyls $Cp(CO)(L)FeC(O)R'$.[1b,d]



(1)

Hydrosilation reactions involving these manganese acyl complexes are of interest for three reasons. First, hydrosilation of labile or coordinatively unsaturated acyl complexes (as substrates) resembles the catalytically relevant reduction of acyl ligands with molecular hydrogen[4] or metal hydride complexes.[5] Second, acyl ligand hydrosilation chemistry engenders other novel ligand reactions. Examples include transforming acetyl ligands $L_xMC({=}O)CH_3$ plus hydrosilane to α-siloxyvinyl $L_xMC(OSiR_3){=}CH_2$,[6] vinyl $L_xMCH{=}CH_2$,[7] and fully reduced alkyl $L_xMCH_2CH_3$ groups.[7,8] Third, these manganese acyl/hydrosilane systems afford extremely active catalysts for, thus

---

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1996.

(1) (a) Gregg, B. T.; Hanna, P. K.; Crawford, E. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1991**, *113*, 384. (b) Hanna, P. K.; Gregg, B. T.; Cutler, A. R. *Organometallics* **1991**, *10*, 31. (c) Hanna, P. K.; Gregg, B. T.; Tarazano, D. L.; Pinkes, J. R.; Cutler, A. R. In *Homogeneous Transition Metal Catalyzed Reactions*; Advances in Chemistry Series No. 230; Moser, W. R., Slocum, D. W., Eds.; American Chemical Society: Washington, DC, 1992; p 491. (d) Gregg, B. T.; Cutler, A. R. Manuscript in preparation.

(2) Reversible carbonyl ligand dissociation for **1**: (a) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101. (b) Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* **1968**, *7*, 1806. (c) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4411. (d) McHugh, T. M.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 2323. (e) Ziegler, T.; Verslius, L.; Tschinke, V. *J. Am. Chem. Soc.* **1986**, *108*, 612. (f) Axe, F. U.; Marynick, D. S. *Organometallics* **1987**, *6*, 572. (g) Photochemical studies, Boese, W. T.; Ford, P. C. *Organometallics* **1994**, *13*, 3525. Boese, W. T.; Lee, B.; Ryba, D. W.; Belt, S. T.; Ford, P. C. *Organometallics* **1993**, *12*, 4739 and references cited therein.

(3) (a) Gregg, B. T.; Cutler, A. R. *Organometallics* **1993**, *12*, 2006. (b) Manganese alkyl and halide complexes $XMn(CO)_4(L)$ [$X = CH_3$, Ph, $CH_3CH(OSiR_3)$, Br; L = CO, PPh_3, PEt_3] also serve as effective precatalysts for the hydrosilation of a variety of organic and organometallic acyl compounds. Significantly, neither $R_3SiMn(CO)_5$ ($R_3Si = Me_2Ph$, $SiHPh_2$) nor $Mn_2(CO)_{10}$ is an effective precatalysts. Gregg, B. T.; Cutler, A. R. Manuscript in preparation.[1d]

(4) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 10.10. (b) Ungváry, F.; Markó, L. *Organometallics* **1983**, *2*, 1608. (c) Kovács, I.; Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 209. (d) Martin, J. T.; Baird, M. C. *Organometallic* **1983**, *2*, 1073.

(5) (a) Gladysz, J. A.; Tam, W.; Williams, G. M.; Johnson, D. L.; Parker, D. W. *Inorg. Chem.* **1979**, *18*, 1163. Tam, W.; Wong, W.-K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589. (b) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34. Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345. (c) Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150. Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33. (d) Kovács, I.; Hoff, C. D.; Ungvary, F.; Marko, L. *Organometallics* **1985**, *4*, 1347. (e) Ruszczyk, R. J.; Huang, B. - L.; Atwood, J. D. *J. Organomet. Chem.* **1986**, *299*, 205. (f) Bullock, R. M.; Rappoli, B. J. *J. Am. Chem. Soc.* **1991**, *113*, 1659.

(6) Gregg, B. T.; Cutler, A. R. Manuscript in preparation.

(7) (a) Crawford, E. J.; Hanna, P. K.; Cutler, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 6891. (b) Pinkes, J. R.; Mao, Z.; Cutler, A. R. Manuscript submitted for publication.

(8) (a) Akita, M.; Mitani, O.; Moro-Oka, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 527. (b) Akita, M.; Mitani, O.; Sayama, M.; Moro-Oka, Y. *Organometallics* **1991**, *10*, 1394.

S0002-7863(95)02880-0 CCC: $12.00

far, SiH/SiD isotope exchange,[3a] hydrosilane alcoholysis,[9a] hydrosilation of organic aldehydes and ketones,[9b,10] hydrosilation−reduction of esters,[9c] and silation of carboxylic acids.[9d]

Previously, Gladysz and co-workers[11] reported that treating aldehydes with $(CO)_5MnSiMe_3$ produced α-(trimethylsiloxy)-alkyl compounds $(CO)_5MnCH(OSiMe_3)R$. Although reported to be unstable, these compounds were carbonylated and derivatized as their acyl complexes. Akita, Moro-oka, and co-workers[8] generated examples of $(CO)_5MnCH(OSiHPh_2)R$ in C_6D_6 or THF by hydrosilation of $(CO)_5MnC(O)R$ (eq 1) with excess H_2SiPh_2 and 1% $(PPh_3)_3RhCl$. The rhodium catalyst, however, is unnecessary.[1a,c] In an earlier study on the reaction of triethylsilane and **1** in THF, Wegman[12a] reported that a 10-fold excess of this silane and 1 atm of CO (at 25°C) exclusively gave acetaldehyde and $(CO)_5MnSiEt_3$.

We now report the hydrosilation chemistry involving **1** and 13 monohydrosilanes. Ten α-siloxyethyl complexes $(CO)_5MnCH(OSiR_3)CH_3$ (**2**) were generated, seven of which were isolated in 46−70% yields after column chromatography and five of which were carbonylated to give their α-siloxypropionyl derivatives $(CO)_5MnC(O)CH(OSiR_3)CH_3$ (**4**). In six of the hydrosilation reactions, α-siloxyvinyl byproducts $(CO)_5MnC(OSiR_3){=}CH_2$ (**3**) were detected, with triethylsilane producing $(CO)_5MnC(OSiEt_3){=}CH_2$ (**3j**) as the major product. We account for the formation of both products **2** and **3** by an autocatalytic pathway in which silane-induced degradation of the initially formed **2** provides the active catalyst. Observations on forming and subsequently degrading $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (**2a**), $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**), and other manganese complexes with excess monohydrosilanes accordingly are discussed.

Experimental Section

Synthetic manipulations were performed in a nitrogen atmosphere using a combination of standard Schlenk line, glovebox, and vacuum line procedures.[13] Infrared spectra were recorded on a Perkin-Elmer Model 1600 FT spectrophotometer. NMR spectral data were obtained in C_6D_6 and were reported as δ values relative to residual C_6D_5H (^1H, 7.15 ppm), C_6D_6 (^{13}C, 128.00 ppm), and external $SiMe_4$ (^{29}Si, 0 ppm) using Varian Model XL-200, Unity 500, and IBM-WP100 spectrometers. $^{29}Si\{^1H\}$ NMR spectra of concentrated C_6D_6 solutions containing $Cr(acac)_3$ (0.5 mol %) were recorded using inverse gated decoupling for ~500 transients (<1 h) using a 90° pulse angle and a 1 s delay time. Combustion microanalyses were done by Quantitative Technologies, Bound Brook, NJ.

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; acetonitrile was purged with nitrogen and stored over activated 4 Å molecular sieves. Triethylsilane was dried over freshly activated 4 Å molecular sieves and fractionally distilled. Only the fraction that was collected over the boiling point range 107−108 °C was used; its NMR spectral data, ^1H δ 3.87 (sept, $J = 3.1$ Hz, SiH), 0.97 (t, $J = 6.8$, $SiCH_2CH_3$), 0.54 (m, $SiCH_2CH_3$); $^{13}C\{^1H\}$ δ 8.3 ($SiCH_2CH_3$), 2.9 ($SiCH_2CH_3$); $^{29}Si\{^1H\}$ δ 0.42, are consistent with the absence of the disiloxane $(Et_3Si)_2O$ [$^{13}C\{^1H\}$ δ 7.0 ($SiCH_2CH_3$), 6.8 ($SiCH_2CH_3$); $^{29}Si\{^1H\}$ δ 9.29] or detectable concentrations of other triethylsilyl derivatives.

Manganese complexes $(CO)_5MnC(O)CH_3$ (**1**) and $(CO)_5MnCH_3$[14] were prepared by treating $Mn(CO)_5^-K^+$ [15] in THF with acetyl chloride or methyl iodide. The acetyl **1** was isolated as a pale yellow solid (86% yield) after column chromatography on flash-grade silica gel/hexane, before it was sublimed to a cooled probe (−78 °C) at 10^{-1} Torr. The *p*-toluoyl complex $(CO)_5MnC(O)$-*p*-$C_6H_4CH_3$[16] was prepared by a similar procedure and was purified by column chromatography on flash-grade silica gel/hexane. Samples of $(CO)_5MnCH_2CH_3$,[17] $(CO)_5MnSi(CH_3)_2Ph$ (**5a**),[1a] $(PPh_3)(CO)_4MnC(O)CH_3$,[18] $CH_3CH_2OSiMe_2Ph$ (**7a**), and $CH_3CH_2OSiEt_3$ (**7j**)[9a,19] were prepared by literature procedures and judged pure by IR and ^1H NMR spectroscopy.

Hydrosilation of $(CO)_5MnC(O)CH_3$ (1) with Monohydrosilanes. Dimethylphenylsilane. A pale yellow solution of **1** (300 mg, 1.26 mmol) in 600 mg of C_6D_6 was treated with $HSiMe_2Ph$ (172 mg, 1.26 mmol) before it was transferred to a NMR tube and securely stoppered with a rubber septum. The solution turned dark orange within 25 min as **1** was depleted (^1H NMR spectral monitoring). This solution was chromatographed on a 1 × 4 cm column of deactivated silica gel (60−200 mesh) with hexane; an orange band was eluted (30 mL), leaving the column pale orange. The first five drops of the eluate, which retained contaminating $(PhMe_2Si)_2O$ (^1H NMR, δ 0.31, SiMe), were discarded. Evaporation of solvent from the remaining eluate left an orange oil (258 mg) that was identified as $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (**2a**) (55% yield). Anal. Calcd for $C_{15}H_{15}O_6SiMn$: C, 48.13; H, 4.04. Found: C, 48.06; H, 4.04.

Monohydrosilanes. Analogous experimental conditions were used for the other monohydrosilanes; α-siloxyethyl complexes **2b**−**2h** were isolated as spectroscopically pure orange oils (Table 1). For $(CO)_5MnCH(OSiMe_2OSiMe_3)CH_3$ (**2d**), Anal. Calcd for $C_{12}H_{19}O_7Si_2Mn$: C, 37.30; H, 4.96. Found: C, 36.99; H, 4.61. Spectral data are in Table 2.

Hydrosilation of $(CO)_5MnC(O)CH_3$ (1) with Triethylsilane. Reaction Profile. Manganese acetyl **1** (112 mg, 0.47 mmol), $HSiEt_3$ (100 mg, 0.87 mmol), and anisole (33 mg, 0.31 mmol) were dissolved in 600 mg of C_6D_6 and then transferred to a 5-mm NMR tube that was fitted with a rubber septum. ^1H NMR spectra were recorded within 10 min using spectrometer parameters that had been optimized with a 38° pulse angle for quantitative analyses of known concentrations of **1** and anisole. As a result, integration traces are believed to be accurate to within ±5%. The spectrometer pulse delay time of 10 s coincided with measurements of spin−lattice (T_1) relaxation times by a standard inversion−recovery experiment: **1** (δ 2.22, $T_1 = 0.11$ s), $(CO)_5MnC(OSiEt_3){=}CH_2$ (**3j**) ($T_1 = 1.21$ and 1.27 s), and $PhOCH_3$ (δ 3.31, $T_1 = 2.58$ s).

NMR spectral scans, recorded every 10 min, were integrated vs the anisole internal standard signal, δ 3.31 (s, $PhOCH_3$). The following

---

(9) (a) Gregg, B. T.; Cutler, A. R. *Organometallics* **1994**, *13*, 1039. (b) DiBiase-Cavanaugh, M.; Gregg, B. T.; Cutler, A. R. Manuscript submitted. (c) Mao, Z.; Gregg, B. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 10139. (d) Mao, Z.; Gregg, B. T.; Cutler, A. R. Manuscript in preparation.

(10) Reviews: (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 25. (b) Chaloner, P. A. *Handbook of Coordination Catalysis in Organic Chemistry*; Butterworths: Boston, 1986; Chapter 7.2. (c) Marciniec, B.; Guliñski, J. *J. Organomet. Chem.* **1993**, *446*, 15.

(11) (a) Gladysz, J. A. *Acc. Chem. Res.* **1984**, *17*, 326. (b) Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508. (c) Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147. (d) Selover, J. C.; Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1455. (e) Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1462. Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem.. Soc.* **1986**, *108*, 1473. Vaughn, G. D.; Krein, K. A.; Gladysz, J. A. *Organometallics* **1986**, *5*, 936. (f) Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056.

(12) (a) Wegman, R. W. *Organometallics* **1986**, *5*, 707. (b) Kovacs, I.; Sisak, A.; Ungvary, F.; Marko, L. *Organometallics* **1988**, *7*, 1025.

(13) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(14) (a) Closson, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598. (b) King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Part I, Vol. 1, p 147. (c) Mckinney, R. J.; Crawford, S. S. *Inorg. Synth.* **1989**, *26*, 155. (c) Anderson,J. M.; Moss, J. R. *Organometallics* **1994**, *13*, 5013.

(15) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

(16) (a) Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *Inorg. Synth.* **1978**, *18*, 56. (b) Motz, P. L.; Sheeran, D. J.; Orchin, M. *J. Organomet. Chem.* **1990**, *383*, 201.

(17) (a) Hieber, W.; Wagner, G. *Justus Liebigs Ann. Chem.* **1958**, *618*, 24. (b) Hieber, W.; Braun, G.; Beck, W. *Chem. Ber.* **1960**, *93*, 901. (c) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58.

(18) (a) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 5043. (b) Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* **1968**, *7*, 1806. (c) Noack, K.; Ruch, M.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 345.

(19) Caseri, W.; Pregosin, P. S. *Organometallics* **1988**, *7*, 1373.

(20) Messerle, L. In *Experimental Organometallic Chemistry*; ACS Symposium Series No. 357; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 7, p 198.

signals were used in establishing the materials balance: **1**, δ 2.22; **3j**, δ 4.29 (d, $MnC(OSiEt_3)=CHH$); **2j**, δ 1.83 (d, Mn-$CH(OSiEt_3)CH_3$); and $HSiEt_3$, δ 3.87 (heptet, SiH). Concentrations of these compounds are reported as a reaction profile–time plot, Figure 2, over 110 min. Within 70 min, **1** had transformed completely into a mixture containing 59% **3j** and 28% **2j**.

Two practical aspects of these triethylsilane reactions should be noted. First, results were independent of whether the $HSiEt_3$ was used "as received" or distilled. Second, reaction times and product distributions also were independent of whether the NMR tubes were securely sealed (e.g., with a torch after several freeze–pump–thaw cycles) or vented through a pinhole in the septum. Unlike the reactions of other hydrosilanes and **1**, those involving $HSiEt_3$ generated considerable pressure (presumably H_2), which for larger-scale reactions could dislodge a new rubber septum on a thin-wall 5-mm NMR tube.

The reaction solution was chromatographed on a 1 × 10 cm column of 40 μm (flash-grade) silica gel/hexane, from which an orange hexane eluate (25 mL) was collected and evaporated. The resulting mixture of an orange oil and solid was washed with hexane (2 × 2.5 mL), and the hexane extracts were combined in a centrifuge tube, cooled to −78 °C (10 min), and centrifuged. The combined solid residues, a yellow-orange powder (39 mg) after drying in a stream of nitrogen, was identified by IR spectroscopy (and the absence of ^1H NMR signals) as $Mn_2(CO)_{10}$ (42% yield). Although all three dimer IR ν(CO) bands at 2045 (s), 2009 (vs, br), and 1980 (s, sh) cm^{-1} overlap absorptions for **2j** and **3j**, the first and third absorptions for $Mn_2(CO)_{10}$ are unusually intense and qualitatively indicate its presence. Evaporating the hexane supernatant solution afforded an orange oil (91 mg) that was identified as $(CO)_5MnC(OSiEt_3)=CH_2$ (**3j**), 55% yield. Anal. Calcd for $C_{13}H_{17}O_6SiMn$: C, 44.47; H, 5.17. Found: C, 44.32; H, 4.86.

Reaction of $(CO)_5MnC(O)CH_3$ (1) in THF-d_8 with $HSiEt_3$. ^1H NMR Spectral Monitoring. A 5-mm septum-stoppered NMR tube was charged with 91 mg (0.38 mmol) of **1**, 493 mg of THF-d_8, 43 mg (0.40 mmol) of anisole as the internal standard, and then 68 mg (0.58 mmol, 1.5 equiv) of freshly distilled $HSiEt_3$. ^1H NMR spectral monitoring of the light yellow solution showed that no **1** was consumed after 1 h. Within 2 h, the solution turned orange commensurate with slow gas evolution; 12% of **1** was converted to $(CO)_5MnC(OSiEt_3)=CH_2$ (**3j**), δ 4.97 (d, J = 1.2 Hz, $=CHH$), 4.19 (d, J = 1.2, $=CHH$). After 4 h, all of the **1** was gone; also absent were absorptions that could be attributed to $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**), $CH_3CH_2OSiEt_3$ (**7j**),[9a,19] or acetaldehyde. The **3j** was quantified in 69% yield by integration of its vinyl ^1H NMR resonance (δ 4.19) vs anisole, with 0.09 mmol of the $HSiEt_3$ (δ 3.66) remaining.

Reaction of $(CO)_5MnC(O)CH_3$ (1) with Triethylsilane. Precatalyst Study. Pretreatment of manganese toluoyl $(CO)_5MnC(O)$-*p*-C_6H_4-CH_3 (14 mg, 0.005 mmol) in 600 mg of C_6D_6 with $HSiEt_3$ (100 mg, 0.86 mmol) gave a somewhat darker yellow solution after 45 min. The precatalyst solution then was pipetted into a 5-mm NMR tube, and the substrate **1** (112 mg, 0.47 mmol) was added. Results of ^1H NMR spectral monitoring were consistent with all of the **1** converting within 15 min to a 58:42 mixture of **2j** and **3j**.

Reaction of $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (2a) with Triethylsilane. To a 5-mL vial in the glovebox were added **2a** (100 mg, 0.42 mmol), C_6D_6 (600 mg), and $HSiEt_3$ (692 mg, 5.95 mmol). The orange-brown solution then was transferred to a 5-mm NMR tube that was fitted with a rubber septum, and ^1H NMR spectra were recorded within 10 min. After 1 h, neither **2j** nor **3j** was evident, as judged by the absence of diagnostic absorptions at δ 1.83 and 4.29, respectively. Most of the starting **2a** remained, although peak broadening precluded further analysis. ^{29}Si NMR spectra were recorded, and major signals were assigned at δ 9.34 $(Et_3Si)_2O$, 3.74 (**2a**), and −0.83 $(PhMe_2Si)_2O$. Although the $HSiEt_3$ (δ 9.33) was consumed within 3 h, **2a** was still present and neither **2j** (δ 16.14) nor **3j** (δ 17.19) was detected. Also absent were $(CO)_5MnSiMe_2Ph$ (**5a**) (δ 13.03), $EtOSiMe_2Ph$ (**7a**) (δ −3.58), and $EtOSiEt_3$ (**7j**) (δ 17.32). Unassigned absorptions were observed at δ 20.40, 19.91, 18.62, 11.41, 5.36, and −2.68.

Reaction of $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (2a) with Dimethylphenylsilane. Manganese acetyl **1** (100 mg, 0.42 mmol), $HSiMe_2Ph$ (143 mg, 1.05 mmol), and anisole (45 mg, 0.42 mmol) were dissolved in 600 mg of C_6D_6. The orange solution was transferred to a 5-mm NMR tube that was fitted with a rubber septum, and the first ^1H NMR spectrum of the initially pale yellow solution was recorded within 10 min.

Within 25 min, **1** was consumed in the dark orange solution; both **2a** and $(CO)_5MnC(OMe_2Ph)=CH_2$ (**3a**) were quantified (76% and 3%) using their δ 1.73 and 4.33 doublet absorptions, respectively. Conspicuous absorptions at δ 0.31 ($(PhMe_2Si)_2O$), 0.55, and 0.45 also appeared as the yield of **2a** dropped to 69% (45 min) and then to 52% (100 min). The $HSiMe_2Ph$ concentration decreased to 70% and 40% of its initial value after 45 and 100 min (integration of its δ 4.61 heptet). Similar quantification of the disiloxane ^1H NMR absorption at δ 0.31 is not reliable, since it overlaps other aborptions in the δ 0.3 chemical shift region that is common to organic dimethylphenylsilyl derivatives. Relevant multinuclear NMR spectral data: **7a** [^{13}C, δ 58.65, 18.73, −1.52], **5a** [^1H, δ 0.68; ^{13}C, δ 4.01], and $(PhMe_2Si)_2O$ [^1H, δ 0.30; ^{13}C, δ 0.95; ^{29}Si, δ −0.80].

Combined ^1H and ^{13}C NMR spectral monitoring of this reaction mixture further revealed that neither $(CO)_5MnSiMe_2Ph$ (**5a**) nor CH_3-CH_2OSiMe_2Ph (**7a**) was present. Also not detected was the ethyl complex $(CO)_5MnCH_2CH_3$, [δ 1.28 (t, J = 7.1 Hz), 1.13 (q) (^1H)/ 7.96 ($MnCH_2$), 5.50 (^{13}C)]. Compounds present included $HSiMe_2Ph$ [^1H NMR δ 4.61 (hept), 0.22 (d); ^{13}C NMR δ −3.71], $(PhMe_2Si)_2O$, and **2a**. Unassigned absorptions: ^1H NMR δ 3.87 (m), 3.52 (m), 3.40 (m), 1.08 (d), 0.55 (s), 0.43, 0.32, 0.29; ^{13}C NMR δ 69.90, 68.93, 20.57, 3.63, −0.74, −0.85, −1.64. A ^{29}Si NMR spectrum of this reaction mixture after 3 h was consistent with $(PhMe_2Si)_2O$ (δ −0.83) as the major Si-containing species, although peaks at δ 7.38 and 5.38 and at least six other weaker absorptions were evident. ^{29}Si NMR resonances for $HSiMe_2Ph$ (δ −16.83), **2a** (δ 3.74), **5a**, and **7a** were absent.

Preparation of $CH_3CH(OSiMe_2Ph)CH(OSiMe_2Ph)CH_3$ (8a). The following was adapted from the procedure for the dehydrogenative coupling of 2,2-dimethyl-1,3-propanediol and 2 equiv of $HSiMe_2Ph$ to give the fully characterized bis(silyl ether).[9a] A solution consisting of 2,3-butanediol (50 mg, 0.56 mmol), $HSiMe_2Ph$ (159 mg, 1.17 mmol), and $(CO)_5MnBr$ (2 mg, 0.0056 mmol) was prepared in 600 mg of C_6D_6. After 1.5 h, the light orange solution had darkened, and the slow, steady gas bubbling had ceased. NMR spectral examination of the reaction mixture established that the diol had converted to $CH_3CH(OSiMe_2$-$Ph)CH(OSiMe_2Ph)CH_3$ (**8a**) (>90%), presumably as a mixture of meso and *RR,SS* diastereomers: ^1H NMR δ 7.63–7.61 (m, 2H, Ph), 7.25–7.48 (m, 3H, Ph), 3.71 (m, 2H, CH), 1.13 (d, J = 5.5 Hz), 0.39 (SiMe); $^{13}C\{^1H\}$ δ 138.77 (ipso C, Ph), 133.86, 129.65, 127.99 (Ph), 73.64 (CH), 19.58 (CH_3), −0.67, −0.94 (SiMe); $^{29}Si\{^1H\}$ δ 5.05. Small concentrations (<5%) of $HSiMe_2Ph$ and $Me_2PhSiOSiMe_2Ph$ were also observed.

Reaction Profiles for $(CO)_5MnC(O)CH_3$ (1) and Dimethylphenylsilane. Excess Monohydrosilane. Complex **1** (50 mg, 0.21 mmol), $HSiMe_2Ph$ (50 mg, 0.37 mmol), and anisole (22 mg, 0.20 mmol) were dissolved in 600 mg of C_6D_6. The solution was transferred to a 5-mm NMR tube that was fitted with a rubber septum, and the first ^1H NMR spectrum was recorded within 10 min. NMR spectra were recorded over 120 min and were integrated vs the anisole internal standard signal, δ 3.31 (s, $PhOCH_3$). The following signals were used in establishing the materials balance: **1**, δ 2.23 (s, $MnCOCH_3$); **2a**, δ 1.74 (d, $MnCH(OSiMe_2Ph)CH_3$); and $HSiMe_2Ph$, δ 4.61 (heptet, SiH). Concentrations of these compounds are reported as a reaction profile plot, Figure 1.

Autocatalysis Studies. To a pale yellow solution of **1** (100 mg, 0.42 mmol) in 600 mg of C_6D_6 were added $HSiMe_2Ph$ (65 mg, 0.48 mmol) and anisole (60 mg, 0.55 mmol) before it was transferred to a stoppered NMR tube. Product $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (**2a**) was quantified by integrating the ^1H NMR spectra that were recorded as a function of time. Four additional experimental runs were carried out under the same conditions, but in which small quantities (1–2%) of manganese complexes were included as potential catalysts.

Two of the experimental runs also contained $(CO)_5MnSiMe_2Ph$ (**5a**) (2 mg, 0.0063 mmol) or **2a** (3 mg, 0.008 mmol). Two other experiments involved pretreating pale yellow solutions of **1** (3 mg, 0.008 mmol) or $(CO)_5MnC(O)$-*p*-$C_6H_4CH_3$ (1 mg, 0.003 mmol) in 600 mg of C_6D_6 with the silane ($HSiMe_2Ph$, 65 mg) for 45 min. The $(CO)_5MnC(O)$-*p*-$C_6H_4CH_3$ precatalyst solution turned dark yellow-orange, whereas the **1** precatalyst solution turned dark yellow. To each precatalyst solution was added the reactant **1** (100 mg), and the ^{1}H NMR spectra were monitored. Results for all five experimental runs appear in Figure 4.

CO Inhibition of the Reactions between Monohydrosilanes and 1. With Dimethylphenylsilane. A 5-mm NMR tube with its attached J. Young valve was charged with 50 mg (0.21 mmol) of $(CO)_5MnC(O)CH_3$ (**1**), 26 mg (0.24 mmol) of anisole, and 600 mg of C_6D_6. The C_6D_6 had been dried over activated 4A molecular sieves for 20 h and purged with a gentle stream of carbon monoxide (in the NMR tube) for 5 min. The $HSiMe_2Ph$ (35 mg, 0.26 mmol) then was injected into the NMR tube by a microliter syringe, and the rubber septum was replaced by the top of the J. Young valve. The NMR tube and its pale yellow solution was rotated end-over-end at 10 revolutions/min, and the tube periodically was removed for ^{1}H NMR spectral monitoring.

After 1.5 h, only a trace of **2a** was evident; its concentration increased to a maximum of 8−10% after 2.5 h with 39% and 38% of **1** and $HSiMe_2Ph$ consumed, respectively. Nearly all of the silane had transformed to $(PhMe_2Si)_2O$, although several minor $SiMe_2$ resonances were noted near δ 0.3. Between 4 and 8 h, the ratio of disiloxane to silane increased from 2:3 to 3:2 with only trace concentrations of **2a**. The silane was consumed after 10.5 h, leaving 38% of the starting **1** and <5% **5a**. An IR spectrum of this solution confirmed the presence of **1** along with $Mn_2(CO)_{10}$ as a minor component. ^{13}C and ^{29}Si NMR spectra of the dark orange solution were consistent with the presence of $(PhMe_2Si)_2O$ as the only detectable silicon species.

Without rotation of the NMR tube, 85% of the **1** was consumed within 4.5 h, although only 5−8% yields of **2a** were realized. During this reaction, the top 1 cm of the solution in the static NMR tube remained pale yellow as the remaining solution turned dark orange.

With Triethylsilane. A 5-mm NMR tube with its attached J. Young valve was charged with 100 mg (0.42 mmol) of **1** and 600 mg of C_6D_6. A gentle stream of CO was gently bubbled through the solution for 5 min; then 68 mg (0.58 mmol) of $HSiEt_3$ was injected with a microliter syringe, and the NMR tube valve was closed. ^{1}H NMR spectral monitoring of the pale yellow solution indicated that 30% of **1** had been consumed within 5 h. This was accounted for by a 9:1:0.5 mixture of $(CO)_5MnC(OSiEt_3){=}CH_2$ (**3j**), $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**), and $CH_3CH_2OSiEt_3$ (**7j**).

NMR spectral data for **7j** were available from a previous study:[9a,19] ^{1}H NMR δ 3.55 (q, $J = 6.9$, OCH_2CH_3), 1.11 (t, $J = 7.0$, OCH_2CH_3), 0.96 (m, $SiCH_2CH_3$), 0.56 (m, $SiCH_2CH_3$); $^{13}C\{^1H\}$ NMR δ 58.4 (OCH_2CH_3), 18.5 (OCH_2CH_3), 6.9 ($SiCH_2CH_3$), 4.9 ($SiCH_2CH_3$); $^{29}Si\{^1H\}$ δ 17.32.

The reaction of **1** with $HSiEt_3$ in the presence of 1 atm of CO was repeated twice using 10 mg (0.042 mmol) of **1**, 50 mg (0.42 mmol) of $HSiEt_3$, and either 600 mg of C_6D_6 or 493 mg of THF-d_8. ^{1}H NMR analyses of the very pale yellow solutions after 5 h showed that <5% of **1** had been consumed and only a trace (<5%) of **3j** was evident. A control reaction in C_6D_6 was carried out under the same conditions except that 1 atm of nitrogen was substituted for the CO. Within 80 min, **1** was converted to the same 2:1 ratio of products **3j** and **2j** that had been documented in the reaction profile studies, irrespective of the obvious pressure buildup.

Inhibition of the $(CO)_5MnC(O)CH_3$ (1) Reaction with Dimethylphenylsilane. Acetone Competition. A C_6D_6 solution (600 mg) of **1** (50 mg, 0.21 mmol) was treated with $HSiMe_2Ph$ (57 mg, 0.42 mmol) and acetone (24 mg, 0.42 mmol). Within 40 min, all of the silane was converted to a mixture of $(CH_3)_2CH(OSiMe_2Ph)$[19] and $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (**2a**), as judged from their ^{1}H and ^{13}C NMR spectra. No other products were evident; 89% of the acetone was transformed to $(CH_3)_2CH(OSiMe_2Ph)$ and 24% of the **1** to **2a**, with the residual acetone and **1** also being quantitated by ^{1}H NMR spectroscopy.

Phosphine Inhibition. A clear solution containing C_6D_6 (600 mg), **1** (48 mg, 0.20 mmol), $HSiMe_2Ph$ (27 mg, 0.20 mmol), and PPh_3 (53 mg, 0.20 mmol) was prepared and transferred to a NMR tube. This solution remained pale yellow, and ^{1}H NMR spectral monitoring confirmed that 82% of the $HSiMe_2Ph$ remained intact, with the remainder as $(PhMe_2Si)_2O$. No hydrosilation of **1** was detected (3 h). The starting **1** was accounted for as a mixture of *trans*- and *cis*-$(PPh_3)(CO)_4MnC(O)CH_3$[18] (7% and 13%, respectively), **1** (69%), and $(CO)_5MnCH_3$ (10%).

Acetonitrile Inhibition. **1** (100 mg, 0.42 mmol) and $HSiMe_2Ph$ (65 mg, 0.48 mmol) were dissolved in 600 mg of C_6D_6, and the solution was monitored by ^{1}H NMR spectroscopy. After 15 min, **1** was 56% consumed; 40 mg of CD_3CN (0.90 mmol) then was injected into the reaction mixture. Continued monitoring was consistent with 61% conversion of **1** to **2a** after 18, 25, and 60 min.

Effect of $HSi(SiMe_3)_3$. To a solution of **1** (50 mg, 0.21 mmol) and $HSiMe_2Ph$ (29 mg, 0.21 mmol) in 600 mg of C_6D_6 was added $HSi(SiMe_3)_3$ (10 mg, 0.040 mmol). The acetyl complex **1** was consumed within 40 min and was replaced by **2a** (71%), as arrived at by ^{1}H NMR quantitative integration vs unreacted $HSi(SiMe_3)_3$.

Presence of Air. A pale yellow solution of **1** (100 mg, 0.42 mmol) in 600 mg of C_6D_6 was aerated by sucking it into a glass pipet and then expelling it back into the reaction vial. This operation was repeated six times before $HSiMe_2Ph$ (136 mg, 1.0 mmol) and anisole internal standard were added. Then the pale yellow solution was transferred to a NMR tube, again in the air. Within 30 min the starting **1** was depleted in the resulting dark orange solution, and a 76% yield of **2a** was realized.

Carbonylation of α-Siloxyethyl Complexes $(CO)_5MnCH(OSiR_3)CH_3$ (2). $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (2a). An orange acetonitrile solution (30 mL) containing 258 mg of **2a** (0.69 mmol) was transferred to the 100-mL glass bottle of a Fisher-Porter pressure apparatus,[19] which also had a magnetic stirring bar. The reactor was pressurized with carbon monoxide to 82 psig and then vented; this cycle was repeated six times before a final 82 psig CO pressure was maintained. After 1 h of vigorous stirring, the solution had turned light yellow. The pressure then was vented, and an IR spectrum of the solution showed that the $\nu(CO)$ absorptions of **2a** at 2106, 2044, 2005, and 1982 cm^{-1} had been replaced by terminal $\nu(CO)$ bands at 2113, 2047, and 2011 cm^{-1} and a medium intensity acyl $\nu(CO)$ band at 1635 cm^{-1}.

The solution was evaporated, and the resulting light yellow oil was chromatographed on flash-grade silica gel with hexane in a 2.5 × 5 cm quartz column. (The silica gel contained 1% zinc silicate phosphor.) Eluting with hexane removed any $Mn_2(CO)_{10}$ (typically <2%) as a faint yellow band; subsequent elution with 70:30 methylene chloride−hexane (40 mL) removed the product as a pale yellow, almost colorless, band (a UV lamp was used for detection). This fraction afforded 247 mg of $(CO)_5MnC(O)CH(OSiMe_2Ph)CH_3$ (**4a**) as a light yellow oil (89% yield). Anal. Calcd for $C_{16}H_{15}O_7SiMn$: C, 47.77; H, 3.76. Found: C, 47.93; H, 3.65. Spectral data are recorded in Table 2.

The same procedure was followed for carbonylating other α-siloxyethyl complexes **2**, and in all cases the acyl derivatives $(CO)_5MnC(O)CH(OSiR_3)CH_3$ (**4**) were isolated as stable, pale yellow oils after column chromatography. $(CO)_5MnC(O)CH(OSiMePh_2)CH_3$ (**4b**): isolated yield 82%. Anal. Calcd for $C_{21}H_{17}O_7SiMn$: C, 54.32; H, 3.69. Found: C, 54.65; H, 3.60. $(CO)_5MnC(O)CH(OSiMe_2OEt)CH_3$ (**4c**): isolated yield 87%. Anal. Calcd for $C_{12}H_{15}O_8SiMn$: C, 38.93; H, 4.08. Found: C, 38.95; H, 4.04. $(CO)_5MnC(O)CH(OSiMe_2OSiMe_3)CH_3$ (**4d**): isolated yield 91%. Anal. Calcd for $C_{13}H_{19}O_8Si_2Mn$: C, 37.68; H, 4.62. Found: C, 37.70; H, 4.61.

$(CO)_5MnCH(OSiMe_2Et)CH_3$ (2e). Dimethylethylsilane (111 mg, 1.26 mmol) was added to a solution of $(CO)_5MnC(O)CH_3$ (**1**) (300 mg, 1.26 mmol) in 600 mg of C_6D_6. After 1 h, the resulting dark orange solution was transferred to a Fisher-Porter bottle that had been charged with a magnetic stirring bar and acetonitrile (10 mL), and the reaction was stirred vigorously under 82 psig of CO for 1 h. This left a yellow solution, which was evaporated at room temperature to give an orange oil. It was chromatographed on indicator-grade silica gel, from which the following fractions were isolated: fraction 1, with 25 mL of hexane gave $Mn_2(CO)_{10}$ (22 mg); fraction 2 with 25 mL of 1:1 CH_2Cl_2−hexane eluted as a yellow-orange band that left a yellow-orange oil (286 mg); fraction 3 with 15 mL of 1:1 CH_2Cl_2 came down as a pale yellow band that contained **1** (33 mg, 11% recovery). Fraction 2, which contained substantial $Mn_2(CO)_9(CH_3CN)$[11c] in addition to the $(CO)_5MnC(O)CH(OSiMe_2Et)CH_3$ (**4e**), was rechromatographed using 8:1 CH_2Cl_2−hexane. This cleanly removed a pale yellow band, which afforded **4e** as a spectroscopically pure oil, 122 mg (29% yield).

Results

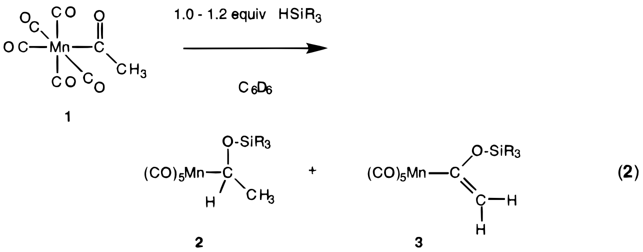
1. Reactions of $(CO)_5MnC(O)CH_3$ (1) with Monohydrosilanes that Afford Stable α-Siloxyethyl Complexes

Table 1. Reaction Products from $(CO)_5MnCOCH_3$ (**1**) and $HSiR_3$

entry	amt of $(CO)_5MnCOCH_3$ (mmol)[a]	silane reactant (equiv)	NMR yield (% **2**)[a]	NMR yield (% **3**)[b]	isolated yield[c] (% **2**)
1	1.26	$HSiMe_2Ph$ (1.0)	80, **2a**	6, **3a**	55
2	0.42	$HSiMe_2Ph$ (1.0)	76, **2a**	4, **3a**	
3	0.21	$HSiMe_2Ph$ (1.8)	76, **2a**	6, **3a**	
4	1.26	$HSiMePh_2$ (1.0)	81, **2b**	<2	54
5	1.26	$HSiMe_2(OEt)$ (1.1)	63, **2c**	5, **3c**	59
6	1.26	$HSiMe_2OSiMe_3$ (1.0)	69, **2d**	6, **3d**	70
7	0.84	$HSiMe_2Et$ (1.1)	63, **2e**	12, **3e**	60
8	0.84	$HSiMeEt_2$ (1.1)	47, **2f**	22, **3f**	46
9	0.84	$HSiMe(OSiMe_3)_2$ (1.2)	63, **2g**	<2	57
10	0.84	$HSiMe(OMe)_2$ (1.2)	50, **2h**	<2	*d*
11	0.42	$HSiMe_2Cl$ (2.0)	64, **2i**	<2	*d*
12	0.47	$HSiEt_3$ (1.9)	28, **2j**	59, **3j**[e]	*d*
13	0.44	$HSiEt_3$[f] (1.1)	23, **2j**	46, **3j**	*d*
14.	0.17	$HSiEt_3$[f] (1.2)	6, **2j**	38, **3j**	
15	0.17	$HSiEt_3$[f] (6.0)	17, **2j**	42, **3j**	d

[a] Reactions in 600 mg of C_6D_6 containing anisole or ferrocene internal standard; NMR yields determined by integration of ^1H NMR spectra. Starting **1** was consumed within 0.5–0.75 h under the conditions noted. [b] α-Siloxyvinyl complexes **3** characterized by ^1H and ^{13}C NMR spectra. [c] Orange oils after column chromatography on silica gel. α-Siloxyethyl complexes **2** were characterized by their ^1H and ^{13}C NMR spectra and by their α-siloxypropionyl derivatives $(CO)_5MnC(O)CH(OSiR_3)CH_3$. Acceptable microanalyses were obtained for $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (**2a**) and $(CO)_5MnCH(OSiMe_2OSiMe_3)CH_3$ (**2d**). [d] Product was unstable and decomposed upon attempted purification. [e] Isolated yield, 55%. [f] Reaction required 70 min to 2 h to consume **1**.

$(CO)_5MnCH(OSiR_3)CH_3$ (2). The manganese acetyl complex **1** at room temperature underwent rapid reactions with the monohydrosilanes in Table 1. Upon treatment with 1.0–1.2 equiv of these silanes, pale yellow C_6D_6 solutions of **1** turned dark orange-brown within 25–45 min. ^1H NMR spectral monitoring of these solutions indicated that for most of the monohydrosilanes studied **1** transformed to the α-siloxyethyl complexes $(CO)_5MnCH(OSiR_3)CH_3$ (**2a**–**2i**) as the major products (eq 2).



SiR_3 = (a) $SiMe_2Ph$, (b) $SiMePh_2$, (c) $SiMe_2Ph$, (d) $SiMe_2OSiMe_3$,
(e) $SiMe_2Et$, (f) $SiMeEt_2$, (g) $SiMe(OSiMe_3)_2$,
(h) $SiMe(OMe)_2$, (i) $SiMe_2Cl$, (j) $SiEt_3$

The α-siloxyethyl complexes **2a**–**2i** were isolated by rapid chromatography on short columns of deactivated silica gel in order to preclude their decomposition during prolonged chromatography. Some of each product nevertheless was sacrificed when its chromatography forerun, which also contained disiloxane contaminant, was discarded in order to render **2** spectroscopically pure. This was particularly noticeable for $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (**2a**), and in part accounts for its 25% drop in isolated yield from that quantified by NMR spectroscopy (Table 1).

We isolated seven α-siloxyethyl complexes **2** in 46–70% yields as thermally sensitive orange oils. Of these, **2a** and $(CO)_5MnC(O)CH(OSiMe_2OSiMe_3)CH_3$ (**2d**) (the most stable examples) were obtained analytically pure. Once isolated, **2a**–**2d** were stable in benzene solution for at least 6 h, which also holds if they are generated carefully using 1 equiv of monohydrosilane.

Structural assignment of the α-siloxyethyl complexes **2** follows from their NMR and IR spectra. Their ^1H NMR spectra, for example, exhibit diagnostic methine quartets at δ 5.0–5.2 ($J = 6.5$ Hz) and methyl doublets at δ 1.7–1.8 for the $MnCHCH_3$ spin systems. Their ^{13}C NMR spectral signals at δ 68–70 and 35 for the methine and methyl carbons, respectively, also agree with those reported for $(CO)_5MnCH(OSiPh_2H)CH_3$ (which was generated only in solution)[1a,c,8] and $CpFe(CO)_2$-α-siloxyethyl complexes (fully characterized).[1b,c,7,8] IR spectra of the complexes **2** in benzene show four terminal carbonyl ν(CO) bands between 2120 and 1980 cm^{-1} that characterize the $Mn(CO)_5R$ system with C_{4v} local symmetry.[21] These and other spectral assignments appear in Table 2. In addition, five examples of **2** were carbonylated and fully characterized as their more stable acyl derivatives, vide infra.

Triethylsilane differs from the other monohydrosilanes studied in that its reaction with **1** yielded the manganese α-(triethylsiloxy)ethyl **2j** only as a minor product. Instead, the major product proved to be $(CO)_5MnC(OSiEt_3){=}CH_2$ (**3j**), eq 2. In reactions involving 50–200 mg of **1** with 1.2–2.0 equiv of $HSiEt_3$ in C_6D_6 solutions, **1** was consumed within 0.75–1.5 h, and 79–87% of it was accounted for as 1.9–2.1:1.0 mixtures of **3j** and **2j**. Results of ^1H, ^{13}C, and ^{29}Si NMR spectral studies also were in accord with an optimal reaction stoichiometry of 1.5–1.8 equiv of $HSiEt_3$ for generating the α-(triethylsiloxy)vinyl complex **3j**.

Isolated yields of **3j** ranged from 55% to 64% after column chromatography, with the higher yields corresponding to preparations involving up to 4 g of **1**. The Experimental Section has further details on separating **3j** from the major contaminant $Mn_2(CO)_{10}$. The resulting stable **3j**, a yellow oil, was fully characterized. Its ^1H NMR spectrum shows two diagnostic vinylic doublets at δ 5.08 and 4.29 with a small geminal coupling ($^2J = 1.4$ Hz). IR spectra in benzene exhibit a three-band pattern for terminal carbonyl ν(CO) bands.[21]

The minor product was identified as the α-(triethylsiloxy)ethyl complex **2j** by its ^1H and ^{13}C NMR spectral data (Table 2). It proved to be more difficult to work with as it readily decomposed to $Mn_2(CO)_{10}$ and unidentified organic materials,

---

[21] These fundamental carbonyl ν(CO) stretching frequencies are assigned (in decreasing frequency) as having A_1, B_1, and $E + A_1$ symmetry. Many $(CO)_5MnR$ complexes reported herein have four terminal carbonyl ν(CO) bands due to the appearance of separate E (very intense, broad) and A_1 (medium intensity, 20–40 cm^{-1} lower in energy) fundamentals. This band splitting is associated with the presence of "less symmetrical" alkyl or acyl ligands R on $(CO)_5MnR$. Other complexes exhibit a three-band pattern for terminal carbonyl ν(CO) bands with relative intensities weak–medium–very strong/broad. (a) Cotton, F. A.; Musco, A.; Yagupsky, G. *Inorg. Chem.* **1967**, *6*, 1357. (b) Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844. (c) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975; pp 72, 223.

Table 2. Spectroscopic Characterization of Manganese Acetyl Hydrosilation Products

complex	IR (C$_6$H$_6$) ν(CO) (cm^{-1})	^{1}H NMR (C$_6$D$_6$) δ (ppm)	^{13}C{^{1}H} NMR (C$_6$D$_6$) δ (ppm)
(CO)$_5$MnCH(CH$_3$)OSiMe$_2$Ph (**2a**)	2107 (w)	7.56 (m, 2H, Ph)	133.8 (ipso-C, Ph)
	2044 (m)	7.21 (m, 2H, Ph)	69.6 (Mn*C*H)
	2005 (vs)	5.07 (q, *J* = 6.5 Hz, CH)	35.0 (MnCH*C*H$_3$)
	1982 (m,sh)	1.74 (d, *J* = 6.5 Hz, CH$_3$)	−1.1 (Si*C*H$_3$)
		0.33 (s, SiMe)	−1.6 (Si*C*H$_3$)
(CO)$_5$MnCH(CH$_3$)OSiPh$_2$Me (**2b**)	2107 (w)	7.71 (m, 4H, Ph)	210.3 (*C*≡O)
	2044 (m)	7.53 (m, 6H, Ph)	135.6 (ipso-C, Ph)
	2006 (vs)	5.20 (q, *J* = 6.5 Hz, MnCH)	70.1 (Mn*C*H)
	1983 (m, sh)	1.77 (d, *J* = 6.5 Hz, MnCH*CH$_3$*)	35.3 (MnCH*C*H$_3$)
		0.61 (s, SiCH$_3$)	−2.3 (Si*C*H$_3$)
(CO)$_5$MnCH(CH$_3$)OSiMe$_2$OEt (**2c**)	2107 (w)	5.17 (q, *J* = 6.4 Hz, MnCH)	213.1 (*C*≡O)
	2045 (m)	3.48 (q, *J* = 6.9 Hz, SiOCH$_2$)	68.7 (Mn*C*H)
	2007 (vs)	1.85 (d, *J* = 6.4 Hz, MnCH*CH$_3$*)	58.2 (SiO*C*H$_2$CH$_3$)
	1982 (m, sh)	1.11 (t, *J* = 6.9 Hz, SiOCH$_2$*CH$_3$*)	34.9 (MnCH*C*H$_3$)
		0.10 (s, SiCH$_3$)	18.5 (SiOCH$_2$*C*H$_3$)
		0.08 (s, SiCH$_3$)	−2.6 (Si*C*H$_3$)
			−2.9 (Si*C*H$_3$)
(CO)$_5$MnCH(CH$_3$)OSiMe$_2$OSiMe$_3$ (**2d**)	2107 (w)	5.21 (q, *J* = 6.3 Hz, CH)	213.4 (*C*≡O)
	2045 (m)	1.87 (d, *J* = 6.5 Hz, CH$_3$)	68.4 (Mn*C*H)
	2007 (vs)	0.14 (br s, SiCH$_3$)	34.9 (MnCH*C*H$_3$)
	1983 (m, sh)		−0.1 (Si*C*H$_3$)
			−0.6 (Si*C*H$_3$)
(CO)$_5$MnCH(CH$_3$)OSiMe$_2$Et (**2e**)	2106 (w)	4.98 (q, *J* = 6.5 Hz, CH)	214.2 (*C*≡O)
	2044 (m)	1.77 (d, *J* = 6.6 Hz, CH$_3$)	69.3 (Mn*C*H)
	2005 (vs)	0.96 (t, *J* = 7.9 Hz, SiCH$_2$*CH$_3$*)	35.1 (MnCH*C*H$_3$)
	1985 (m, sh)	0.57 (m, Si*CH$_2$*CH$_3$)	8.9 (Si*C*H$_2$CH$_3$)
		0.07 (s, SiCH$_3$)	6.9 (SiCH$_2$*C*H$_3$)
			−2.0 (Si*C*H$_3$)
			−2.4 (Si*C*H$_3$)
(CO)$_5$MnCH(CH$_3$)OSiEt$_2$Me (**2f**)	2106 (w)	5.09 (q, *J* = 6.4, CH)	212.9 (*C*≡O)
	2044 (m)	1.80 (d, *J* = 6.4 Hz, CH$_3$)	69.6 (Mn*C*H)
	2007 (vs)	0.99 (t, *J* = 7.3, SiCH$_2$*CH$_3$*)	35.3 (MnCH*C*H$_3$)
	1982 (m, sh)	0.49 (m, *J* = 7.3, Si*CH$_2$*CH$_3$)	8.6 (Si*C*H$_2$CH$_3$)
		0.06 (s, SiCH$_3$)	7.2 (SiCH$_2$*C*H$_3$)
			−2.3 (Si*C*H$_3$)
(CO)$_5$MnCH(CH$_3$)OSi(OSiMe$_3$)$_2$Me (**2g**)	2107 (w)	5.28 (q, *J* = 6.6 Hz, CH)	212.7 (*C*≡O)
	2044 (m)	1.90 (d, *J* = 6.6 Hz, CH$_3$)	68.2 (Mn*C*H)
	2007 (vs)	0.17 (s, CHOSi*CH$_3$*)	35.0 (MnCH*C*H$_3$)
	1983 (m, sh)	0.15 (s, SiOSiCH$_3$)	1.9 (SiOSi*C*H$_3$)
		0.14 (s, SiOSiCH$_3$)	1.8 (SiOSi*C*H$_3$)
			−1.9 (CHOSi*C*H$_3$)
			−2.9 (CHOSi*C*H$_3$)
(CO)$_5$MnCH(CH$_3$)OSi(OMe)$_2$Me (**2h**)	2108 (w)	5.26 (q, *J* = 6.0 Hz, CH)	212.6 (*C*≡O)
	2045 (m)	3.38 (s, SiOCH$_3$)	68.2 (Mn*C*H)
	2008 (vs)	1.87 (d, *J* = 6.0 Hz, CH$_3$)	49.9 (SiO*C*H$_3$)
	1982 (m, sh)	0.11 (s, SiCH$_3$)	34.8 (MnCH*C*H$_3$)
			−7.7 (Si*C*H$_3$)
			−8.5 (Si*C*H$_3$)
(CO)$_5$MnCH(CH$_3$)OSiMe$_2$Cl (**2i**[a])		5.19 (q, *J* = 6.4 Hz, CH)	
		1.79 (d, J=6.4, CH$_3$)	68.2 (Mn*C*H)
		0.29 (s, SiCH$_3$)	
(CO)$_5$MnCH(CH$_3$)OSiEt$_3$ (**2j**[a])		5.11 (q, *J* = 6.5 Hz, CH)	210.0 (*C*≡O)
		1.83 (d, *J* = 6.5 Hz, CH$_3$)	69.1 (Mn*C*H)
		1.00 (m, SiCH$_2$*CH$_3$*)	34.8 (MnCH*C*H$_3$)
		0.75 (m, Si*CH$_2$*CH$_3$))	6.8 (SiCH$_2$*C*H$_3$)
			5.3 (Si*C*H$_2$CH$_3$)
(CO)$_5$MnC(OSiMe$_2$Ph)═CH$_2$ (**3a**[b])		5.10 (d, *J* = 1.5 Hz, (*E*)-C*H*H)	
		4.33 (d, *J* = 1.5 Hz, (*Z*)-CH*H*)	
		0.43 (s, SiMe)	
(CO)$_5$MnCH(OSiMe$_2$OEt)═CH$_2$ (**3c**[b])		5.38 (d, *J* = 1.5 Hz, ═C*H*H)	
		4.43 (d, *J* = 1.5, ═CH*H*)	
		0.22 (s, SiMe)	
(CO)$_5$MnCH(OSiMe$_2$OSiMe$_3$)═CH$_2$ (**3d**[b])		5.31 (d, *J* = 1.5 Hz, ═C*H*H)	
		4.42 (d, *J* = 1.5 Hz, ═CH*H*)	
		0.24 (s, OSiMe$_2$O)	
		0.14 (s, OSiMe$_3$)	
(CO)$_5$MnCH(OSiMe$_2$Et)═CH$_2$ (**3e**[b])		5.07 (d, *J* = 1.5 Hz, ═C*H*H)	212.9 (*C*≡O)
		4.30 (d, *J* = 1.5 Hz, ═CH*H*)	173.7 (COSi)
		0.96 (m, SiCH$_2$*CH$_3$*)	109.6 (═*C*H$_2$)
		0.57 (m, Si*CH$_2$*CH$_3$)	9.1 (Si*C*H$_2$CH$_3$)
		0.18 (s, SiCH$_3$)	6.8 (SiCH$_2$*C*H$_3$)
			−1.9 (Si*C*H$_3$)

Table 2 (Continued)

complex	IR (C_6H_6) ν(CO) (cm^{-1})	^1H NMR (C_6D_6) δ (ppm)	$^{13}C\{^1H\}$ NMR (C_6D_6) δ (ppm)
$(CO)_5MnCH(OSiEt_2Me){=}CH_2$ (**3f**[b])		5.09 (d, J = 1.4 Hz, $=C\mathit{H}H$) 4.34 (d, J = 1.4 Hz, $=CH\mathit{H}$) 0.96 (m, $SiCH_2\mathit{CH_3}$) 0.54(m, $Si\mathit{CH_2}CH_3$) 0.17 (s, $SiCH_3$)	212.1 ($\mathit{C}{\equiv}O$) 174.2 (COSi) 109.1 ($=\mathit{C}H_2$) 7.1 ($Si\mathit{C}H_2CH_3$) 6.9 ($SiCH_2\mathit{C}H_3$) −4.5 ($Si\mathit{C}H_3$)
$(CO)_5MnCH(OSiEt_3){=}CH_2$ (**3j**)	2086 (w) 2045 (vs) 2017 (s sh)	5.08 (d, J = 1.4 Hz, (E)-$C\mathit{H}H$) 4.29 (d, J = 1.4, (Z)-$CH\mathit{H}$) 1.02 (m, $SiCH_2\mathit{CH_3}$) 0.71 (q, J = 7.9, $Si\mathit{CH_2}CH_3$)	210.9 ($\mathit{C}{\equiv}O$) 174.1 (COSi) 108.6 ($=\mathit{C}H_2$) 6.9 ($SiCH_2\mathit{C}H_3$) 5.6 ($Si\mathit{C}H_2CH_3$)
$(CO)_5MnC(O)CH(CH_3)OSiMe_2Ph$ (**4a**)	2114 (m) 2048 (w) 2011 (vs) 1635 (m) (C=O)	7.61 (m, 2H, Ph) 7.32 (m, 3H, Ph) 3.73 (q, J = 6.6 Hz, CH) 0.90 (d, J = 6.6, CH_3) 0.36 (s, $SiCH_3$) 0.33 (s, $SiCH_3$)	264.0 ($Mn\mathit{C}{=}O$) 210.1 ($\mathit{C}{\equiv}O$) 137.1 (ipso-C, Ph) 84.4 ($MnCO\mathit{C}H$) 19.2 ($COCH\mathit{C}H_3$) −1.2 ($Si\mathit{C}H_3$) −2.1 ($Si\mathit{C}H_3$)
$(CO)_5MnC(O)CH(CH_3)OSiPh_2Me$ (**4b**)	2114 (m) 2048 (w) 2013 (vs) 1634 (m)	7.65 (m, 4H, Ph) 7.22 (m, 6H, Ph) 3.95 (q, J = 6.8 Hz, COCH) 0.94 (d, J = 6.8 Hz, $CH\mathit{CH_3}$) 0.61 (s, $SiCH_3$)	263.8 ($Mn\mathit{C}{=}O$) 210.2 ($\mathit{C}{\equiv}O$) 135.7 (ipso-C, Ph) 135.3 (ipso-C, Ph) 85.3 ($MnCO\mathit{C}H$) 19.3 ($COCH\mathit{C}H_3$) −2.3 ($Si\mathit{C}H_3$)
$(CO)_5MnC(O)CH(CH_3)OSiMe_2OEt$ (**4c**)	21134 (w) 2048 (w) 2014 (vs) 1635 (w) (C=O)	3.82 (q, J = 6.8 Hz, COCH) 3.53 (q, J = 6.9 Hz, $SiOCH_2$) 1.08 (d, J = 6.8 Hz, $COCH\mathit{CH_3}$) 1.04 (t, J = 6.9 Hz, $SiOCH_2\mathit{CH_3}$) 0.12 (s, $SiCH_3$) 0.06 (s, $SiCH_3$)	264.3 ($Mn\mathit{C}{=}O$) 210.3 ($\mathit{C}{\equiv}O$) 83.9 ($MnCO\mathit{C}H$) 58.3 ($SiO\mathit{C}H_2CH_3$) 19.4 ($COCH\mathit{C}H_3$) 18.5 ($SiOCH_2\mathit{C}H_3$) −2.3 ($Si\mathit{C}H_3$) −3.2 ($Si\mathit{C}H_3$)
$(CO)_5MnC(O)CH(CH_3)OSiMe_2OSiMe_3$ (**4d**)	2114 (m) 2048 (w) 2016 (vs) 1634 (m) (C=O)	3.84 (q, J = 6.6 Hz, COCH) 1.09 (d, J = 6.6 Hz, $CH\mathit{CH_3}$) 0.12 (s, 3H, $Si(CH_3)_2$) 0.09 (s, 3H, $Si(CH_3)_2$) 0.06 (s, 9H, $Si(CH_3)_3$)	264.3 ($Mn\mathit{C}{=}O$) 210.4 ($\mathit{C}{\equiv}O$) 83.8 ($MnCO\mathit{C}H$) 19.5 ($COCH\mathit{C}H_3$) 1.7 ($Si(\mathit{C}H_3)_3$) 0.2 ($Si(\mathit{C}H_3)_2$) −0.9 ($Si(\mathit{C}H_3)_2$)
$(CO)_5MnC(O)CH(CH_3)OSiMe_2Et$ (**4e**)	2114 (m) 2047 (w) 2012 (vs) 1636 (m)	3.63 (q, J = 6.6 Hz, COCH) 0.97 (d, J = 6.6 Hz, $CH\mathit{CH_3}$) 0.88 (t, J = 7.8, $SiCH_2\mathit{CH_3}$) 0.51 (m, $Si\mathit{CH_2}CH_3$) 0.03 (s, $SiCH_3$) 0.01 (s, $SiCH_3$)	244.3 ($Mn\mathit{C}{=}O$) 210.4 ($\mathit{C}{\equiv}O$) 84.1($MnCO\mathit{C}H$) 19.5 $COCH\mathit{C}H_3$ 8.6 $Si\mathit{C}H_2CH_3$) 6.8 ($SiCH_2\mathit{C}H_3$) −2.3 ($Si\mathit{C}H_3$)

[a] Product unstable and mixed with $Mn_2(CO)_{10}$. [b] Minor component and not isolated.

especially in the presence of free $HSiEt_3$. Even under optimal reaction conditions, **2j** degraded slowly as it formed or upon attempts to chromatograph or concentrate the reaction mixtures.

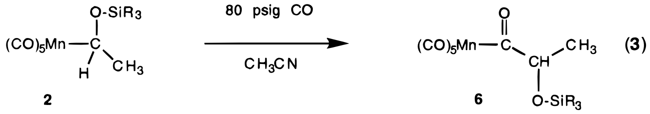
Other α-siloxyvinyl compounds analogous to **3j** evidently accumulate as byproducts during the hydrosilation of **1** with other monohydrosilanes. In five of these hydrosilation reactions (Table 2), ^1H NMR spectral monitoring also revealed vinyl CH doublets near δ 5.1−5.4 and 4.3−4.4 (J = 1.5 Hz) that were assigned to the α-siloxyvinyl compounds $(CO)_5MnC(OSiR_3){=}CH_2$ (**3**).

Three of these α-siloxyvinyl compounds—$(CO)_5MnC(OSiMe_2Ph){=}CH_2$ (**3a**), $(CO)_5MnC(OSiMe_2OEt){=}CH_2$ (**3c**), and $(CO)_5MnC(OSiMe_2OSiMe_3){=}CH_2$ (**3d**)—formed in 5−6% yields and were not further characterized. Two other examples—$(CO)_5MnC(OSiMe_2Et){=}CH_2$ (**3e**) and $(CO)_5MnC(OSiMeEt_2){=}CH_2$ (**3f**)—developed in moderate yields (12−22%); their ^{13}C NMR spectral assignments (δ 174 and 109 for the vinyl carbons) resemble those of **3j**. We did not attempt to isolate these siloxyvinyl compounds. Under our chromatography conditions, these siloxyvinyl compounds hydrolyzed to the starting acetyl complex **1**, which slowly eluted from the column and did not interfere with purifying the α-siloxyethyl products **2**.

Overall, the reactivity of monohydrosilanes toward **1** correlates with four groups of silane substituents. Monohydrosilanes bearing two methyl groups and one phenyl, alkoxy, or siloxy group ($HSiMe_2Ph$, $HSiMe_2OEt$, or $HSiMe_2OSiMe_3$) are extremely reactive and afforded the more stable α-siloxyethyl complexes **2a**, **2c**, and **2d**, but only low concentrations of their α-siloxyvinyl compounds **3**. Diphenylmethylsilane also fits into this category and gave **2b** but no **3b**. Trialkylsilanes, the second group of silanes, furnished significant concentrations of $(CO)_5MnC(OSiR_3){=}CH_2$ (**3**) in addition to diminished yields of less stable **2**. Interestingly, yields of **3** varied with the number of ethyl groups present: $HSiMe_2Et$ (12% yield of **3e**), $HSiMeEt_2$ (22% **3f**), $HSiEt_3$ (60% **3j**).

The remaining two monohydrosilane groups either produced unstable α-siloxyethyl complexes **2** or did not react. Thus, silanes that retain one chlorine ($HSiMe_2Cl$) or two alkoxy or siloxy substituents [$HSiMe(OMe)_2$ or $HSiMe(OSiMe_3)_2$], slowly generated unstable α-siloxyethyl products. Finally, the monohydrosilanes $HSiPh_2Cl$, $HSi(OMe)_3$, $HSiPh_3$, and $HSi(SiMe_3)_3$ are inert toward **1** under our reaction conditions.

2. Carbonylation of α-Siloxyethyl Complexes $(CO)_5MnCH(OSiR_3)CH_3$ (2). In order to further characterize the unstable (α-siloxyethyl)manganese complexes **2**, we prepared their acyl derivatives $(CO)_5MnC(O)CH(OSiR_3)CH_3$ (**4**). Carbonylation of **2** proved to be straightforward, in terms of both implementing the reactions and isolating the stable α-siloxypropionyl products **4**. These reactions (eq 3) were complete within 1 h at 82 psig of CO (22 °C) using either acetonitrile (0.02 M) or acetonitrile−benzene (1:1 to 3:1). Chromatography of the reaction mixtures then provided pale yellow oils; these exhibited a medium intensity IR ν(CO) band at 1635 cm^{-1} and a ^{13}C NMR spectral resonance near δ 264 that signal the presence of an acyl group. Further spectroscopic characterization of these analytically pure α-siloxypropionyl products **4** appears in Table 2.



SiR3 = (**a**) SiMe2Ph, (**b**) SiMePh2, (**c**) SiMe2OEt, (**d**) SiMe2OSiMe3, (**e**) SiMe2Et

Optimal yields of $(CO)_5MnC(O)CH(OSiMe_2Ph)CH_3$ (**4a**), $(CO)_5MnC(O)CH(OSiMePh_2)CH_3$ (**4b**), $(CO)_5MnC(O)CH(OSiMe_2OEt)CH_3$ (**4c**), and $(CO)_5MnC(O)CH(OSiMe_2OSiMe_3)CH_3$ (**4d**) (82−91%) required carbonylating the isolated α-siloxyethyl complexes **2a**−**2d** in acetonitrile. Attempted carbonylation of **2a** as the isolated material in THF or as the unpurified reaction mixture after diluting with acetonitrile dramatically reduced the yields of **4a**. Carbonylation of the hydrosilation reaction mixture containing $(CO)_5MnCH(OSiMe_2Et)CH_3$ (**2e**) (63%) after adding acetonitrile thus yielded only 29% $(CO)_5MnC(O)CH(OSiMe_2Et)CH_3$ (**4e**).

Our conditions for carbonylating purified (α-siloxyethyl)manganese complexes **2** were milder than those reported by Gladysz and coworkers for synthesizing $(CO)_5MnC(O)CH(OSiMe_3)CH_3$ (**4k**).[11a,c] They prepared **4k** by treating an acetonitrile solution of $(CO)_5MnSiMe_3$ (**5k**) with acetaldehyde and 250 psi of CO for 12 h. The extended reaction time in part also reflects the sluggish initial reaction between **5k** and acetaldehyde.[11b,c] Carbonylation of purified $(CO)_5MnCH_2(OSiMe_3)$ in acetonitrile nevertheless was reported to also require 200 psig CO (6 h).[11f] Spectral data for Gladysz's **4k** agrees with that presently reported for the α-siloxypropionyl compounds **4a**−**4e** in Table 2.

3. Reaction Profiles for $(CO)_5MnC(O)CH_3$ (1) with Monohydrosilanes. Reactivity of $(CO)_5MnCH(OSiR_3)CH_3$ (2) toward Excess Silane. Optimal conditions for the hydrosilation of **1** required 1.0−1.2 equiv of monohydrosilane, since the resulting $(CO)_5MnCH(OSiR_3)CH_3$ (**2**) degraded in the presence of excess hydrosilane. In order to study this silane-induced degradation of **2** by multinuclear NMR spectroscopy, we monitored reactions involving (a) **1** with excess $HSiMe_2Ph$ or $HSiEt_3$, (b) preformed $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (**2a**) with $HSiEt_3$, and (c) $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**) with $HSiMe_2Ph$.

The reaction between **2a** and $HSiMe_2Ph$ was conducted by treating **1** with 1.76 equiv of $HSiMe_2Ph$ (run 3, Table 1), and their concentrations were quantified by ^1H NMR spectroscopy. A reaction profile recording the time dependence of [**1**], [$HSiMe_2Ph$], and [**2a**] appears in Figure 1. The 5−10 min induction period preceeds the buildup to the $[\mathbf{2a}]_{max}$ (a 76% yield) within 40 min, although [**2a**] and [$HSiMe_2Ph$] subsequently decreased with time. After 120 min, [**2a**] and [$HSiMe_2Ph$] had dropped to 50% of the maximum and 6% of the initial values, respectively. Interestingly, $(CO)_5MnCH(OSiMe_2Ph)$=CH_2 (**3a**) maintained a constant concentration (4−6% yield) after 30 min.

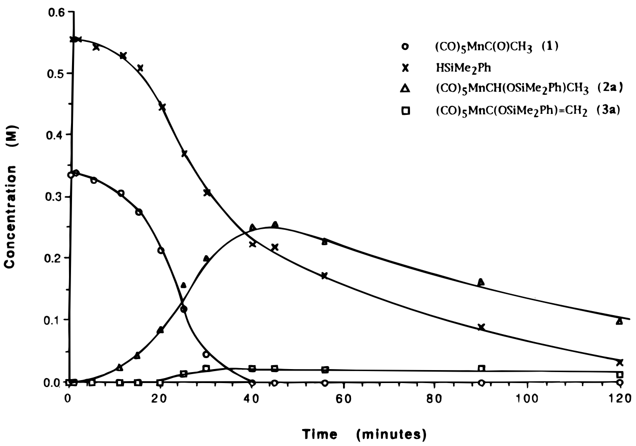


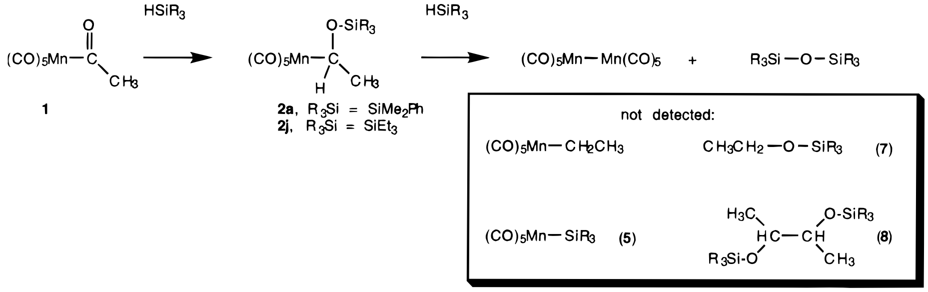
Figure 1. Reaction profile for the reaction between $(CO)_5MnC(O)CH_3$ (**1**) and dimethylphenylsilane. Conditions: $(CO)_5MnC(O)CH_3$ **(1)** (50 mg, 0.21 mmol), Me_2PhSiH (50 mg, 0.37 mmol, 1.75 equiv), and anisole (22 mg, 0.20 mmol) in 600 mg of C_6D_6 (25 °C). All concentrations were determined by quantative ^1H NMR spectroscopy (vs anisole).

Increasing the $[HSiMe_2Ph]_i$ to 2.5 equiv afforded the maximum yield of **2a** (76%) after 25−30 min, in addition to **3a** (3%) and low concentrations of $PhMe_2Si$-containing degradation materials, primarily $(PhMe_2Si)_2O$, Scheme 1. The yield of **2a** then dropped to 50% within 1.5 h as the silane decreased to 40% of its initial concentration. Again, the disiloxane accounted for ca. 80% of the silane residue, although NMR spectral data (experimental) also indicated low concentrations of several unidentified silicon-containing products. This silane degradation consumed all of the $HSiMe_2Ph$ and left $Mn_2(CO)_{10}$ as the final organomanganese product. In related studies, Akita, Moro-oka, and co-workers[8] established that treatment of **1** with excess H_2SiPh_2 produced mixtures of alkenes as the primary organic products.

Silane-induced degradation of **2a** also is noteworthy for several potential products that were absent (Scheme 1). For $HSiMe_2Ph$, manganese complexes not evident included $(CO)_5MnCH_2CH_3$[17] and $(CO)_5MnSiMe_2Ph$ (**5a**). Other potential organic byproducts that also were not detected by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy included CH_2=$CHOSiMe_2Ph$ (**6a**), $CH_3CH_2OSiMe_2Ph$ (**7a**),[9a,19] $Me_2PhSiSiMe_2Ph$, and $CH_3CH(OSiMe_2Ph)CH(OSiMe_2Ph)CH_3$ (**8a**). We previously had prepared the manganese silyl **5a**,[1a] and we now report generating **8a**, a mixture of diastereomers, by $(CO)_5MnBr$-catalyzed silation of its butane-2,3-diol.[9a] It was characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy.

Similar profiles for the reaction of **1** and $HSiEt_3$ probed the interdependency of $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**) and the more abundant $(CO)_5MnC(OSiEt_3)$=CH_2 (**3j**) (eq 2). A reaction profile for **1** and 1.9 equiv of $HSiEt_3$ appears in Figure 2, whereas Figure 3 illustrates a ^1H NMR spectrum of this reaction (after 60 min) from which [**2j**], [**3j**], [$HSiEt_3$], and [**1**] were measured. In this reaction, **1** transformed within 70 min to a mixture with [**3j**]/[**2j**] = 2.0 and a 59% NMR spectral yield of **3j**. After 2 h, the reaction was worked up as described in the Experimental Section to give **3j** (55%) and $Mn_2(CO)_{10}$ (42%), thus accounting for 97% of the manganese.

Scheme 1. $HSiR_3$-Induced Degradation of $(CO)_5MnCH(OSiR_3)CH_3$ (**2**).



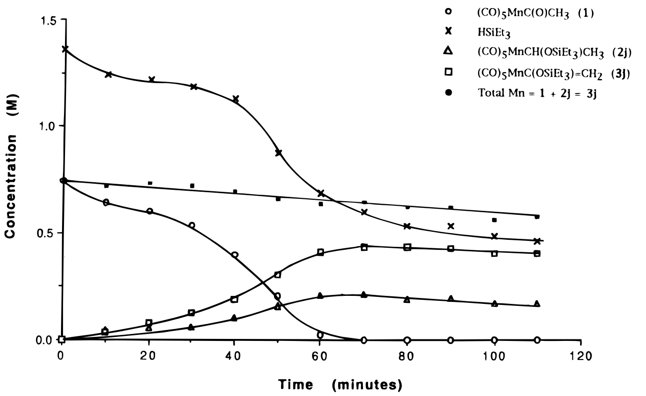


Figure 2. Reaction profile for the reaction between $(CO)_5MnC(O)CH_3$ (**1**) and triethylsilane. Conditions: $(CO)_5MnC(O)CH_3$ (**1**) (112 mg, 0.468 mmol), $HSiEt_3$ (100 mg, 1.84 equiv), and anisole (33 mg, 0.306 mmol) in 600 mg of C_6D_6 (25 °C). Total Mn refers to the sum of the concentrations of **1**, $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**), and $(CO)_5MnC(OSiEt_3){=}CH_2$ (**3j**). All concentrations were determined by quantitative ^1H NMR spectroscopy (vs anisole) at 10 min intervals.

This reaction profile illustrates that $(CO)_5MnC(OSiEt_3){=}CH_2$ (**3j**) forms independently of $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**). Both attained maximum concentrations at 70 min (when **1** was depleted); thereafter [**2j**] decreased by 19% as [**3j**] dropped 5%. Within a total of 270 min, **2j** was depleted although [**3j**] only decreased a total of 16%. We also plotted a "total manganese" concentration equal to [**1**] + [**2j**] + [**3j**], which diminished 13% (after 70 min) with respect to the $[\mathbf{1}]_i$, 24% (110 min, [**3j**]/[**2j**] = 2.4), and 43% (270 min, not illustrated). From inspection of Figure 2, it is apparent that the decreasing [**2j**] dominates the linear drop in our total Mn concentration concomitant with the buildup of $Mn_2(CO)_{10}$. Other experimental runs afforded similar results, although typically [**3j**] decreased only ca. 5%.

Degradation of **2j** requires a second equivalent of triethylsilane (Scheme 2). The first transformed **1** to **2j** or **3j**: after 70 min of reaction, the ratio of $[HSiEt_3]$ consumed to starting [**1**] was 1.03. The second equivalent of $HSiEt_3$ consumed (primarily) **2j**: even after 110 min of reaction, the ratio of the total $[HSiEt_3]$ used to $[\mathbf{1}]_i$ plus [**2j**] consumed was 1.09. (The [**2j**] consumed was ascribed to the difference of the $[\mathbf{1}]_i$ and the observed total Mn concentration.) Involvement of $HSiEt_3$ in degrading **2j** also is apparent from the parallel relationship (Figure 2) for attenuation of the $[HSiEt_3]$ and total Mn concentration (or [**2j**]) after 80 min.

Excess $HSiEt_3$ decomposed **2j** to $(Et_3Si)_2O$ and $Mn_2(CO)_{10}$ (and presumably alkene mixtures).[8] ^{29}Si NMR spectral monitoring during these reactions of $HSiEt_3$ with **1** established that concentrations of $(Et_3Si)_2O$ (δ 9.36) increased at the expense of **2j** (δ 16.17) with excess $HSiEt_3$ (δ 0.42), whereas the concentration of **3j** (δ 17.23) remained constant (in agreement with ^1H NMR spectral monitoring). Reaction times for completely degrading **2j** varied from 2 h (100 mg of **1** and 2.0 equiv of $HSiEt_3$/600 mg of C_6D_6) to 4.5 h (200 mg/600 mg of C_6D_6). The presence of $Mn_2(CO)_{10}$ was established by IR spectroscopy, and for some experimental runs was quantified (21−33%) after chromatography of the reaction mixture. Reliable materials balances for this degradation were precluded by the overlap of ^1H NMR spectral absorptions for $(Et_3Si)_2O$ and for smaller amounts of unidentified organosilanes.

Silane-induced degradation of **2j** was minimized by restricting the initial amount of $HSiEt_3$ to 1 equiv of the starting concentration of **1**, although at the expense of lower product yields and longer reaction times. Figure 2 has a reaction profile for 1.12 equiv of $HSiEt_3$ vs **1** (Table 1, entry 3): both [**3j**] and [**2j**] maximized (46% and 23% yields, respectively) just as **1** was consumed after 135 min. The curve tracking the drop in $[HSiEt_3]$ superimposes that for [**1**], and both [**2j**] and [**3j**] remained constant for at least an additional hour.

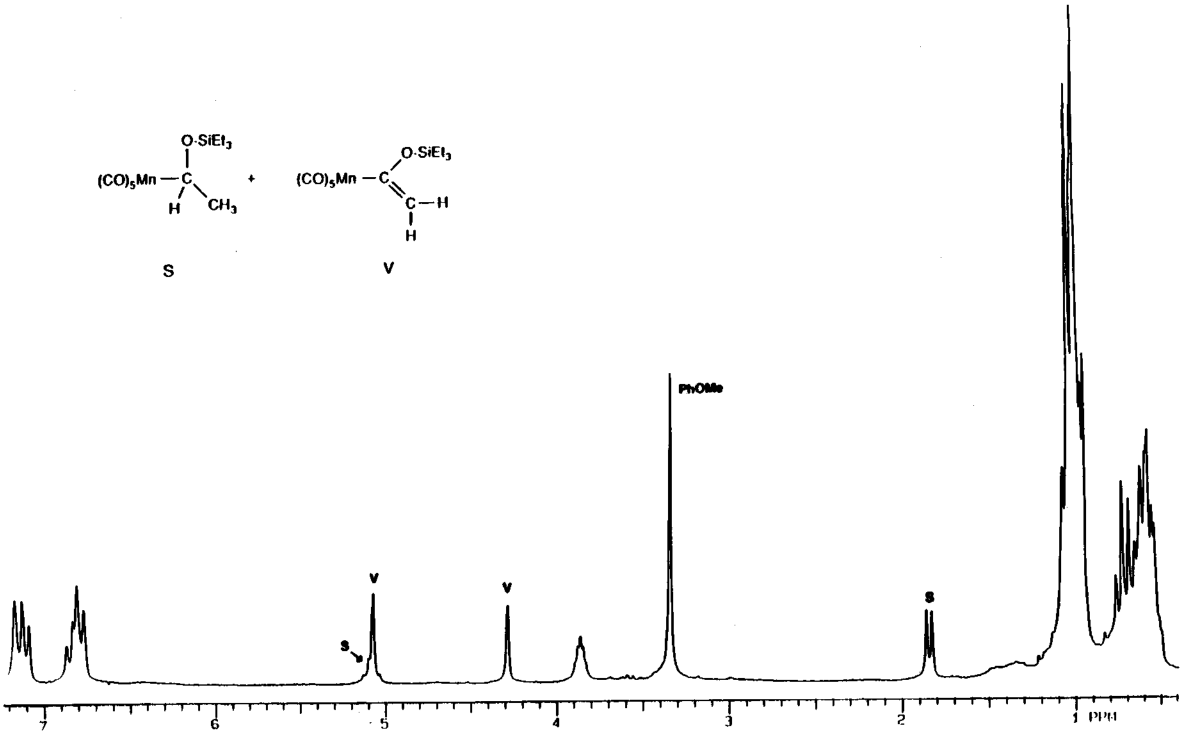
The $HSiEt_3$ reactions proved to be the slowest in terms of consuming **1**, 60−70 min vs 45 min with $HSiMeEt_2$ and 30 min with $HSiMe_2Et$ or $HSiMe_2Ph$ under comparable conditions, in addition to producing the highest yields of an α-siloxyvinyl complex **3j** as a 2:1 mixture with **2j**. We looked at the effect of increasing $HSiEt_3$ concentrations on the distribution of the products **2j** and **3j**, entries 14 and 15 in Table 1. In these parallel experiments, treatment of relatively dilute C_6D_6 solutions of **1** with either 1.2 or 6.0 equiv of $HSiEt_3$ afforded nearly the same amounts of **3j**. Yields of **2j**, however, increased from 6% to 17% upon increasing the $HSiEt_3$ from 1.2 to 6.0 equiv, in spite of its sensitivity toward excess $HSiEt_3$.

NMR spectral monitoring of the $HSiEt_3$ reaction with **1** also ruled out several potential byproducts (Scheme 1). As with the reaction of $HSiMe_2Ph$ and **1**, relevant organic compounds that were not detected include $CH_2{=}CHOSiEt_3$ (**6j**), $CH_3CH(OSiEt_3)CH(OSiEt_3)CH_3$ (**8j**), and acetaldehyde. Although $CH_3CH_2OSiEt_3$ (**7j**) was seen in small concentrations (<5%) during a few hydrosilation runs, the potential manganese carbonyl byproducts $(CO)_5MnH$, $(CO)_5MnCH_2CH_3$, and $(CO)_5MnCH{=}CH_2$ were not observed.

Ruling out $(CO)_5MnSiEt_3$ (**5j**) as a potential byproduct was more difficult. ^{29}Si and ^{13}C NMR spectra that were recorded during the reactions of **1** with $HSiEt_3$ were inconsistent with the presence of **5j**. On the other hand, we could not independently synthesize **5j**[22] using procedures that we had used for $(CO)_5MnSiMe_3$[15] and $(CO)_5MnSiMe_2Ph$ (**5a**).[1a] Treatment of Et_3SiCl with $Mn(CO)_5^-K^+$ or Na^+ provided a pale orange oil that could have contained **5j**, based on its IR spectrum, $\nu(CO)$ (hexane) 2050 (w), 2015 (m) 1980 (vs, br) cm^{-1}. Upon attempted purification, this material decomposed to a complex mixture that was dominated by $Mn_2(CO)_{10}$ and $(Et_3Si)_2O$. We have no reason to believe, however, that **5j** formed during hydrosilation of **1** by $HSiEt_3$, particularly since the analogous

---

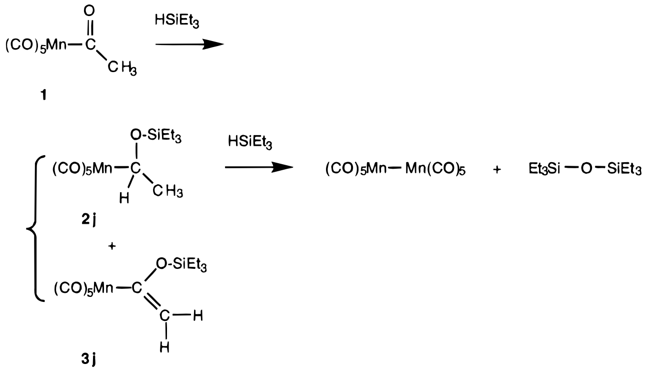
[22] Reviews on metal silyl complexes: (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; Part 2, Chapter 24. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1992; Chapter 10.



100 mg (0.42 mmol)(CO)5MnCOCH3 and 89 mg (0.84 mmol) Et3SiH in 600 mg C6D6 (80 min); PhOMe internal standard (33 mg, 0.31 mmol)

Figure 3. ^{1}H NMR spectrum of the reaction between $(CO)_5MnC(O)CH_3$ (**1**) and $HSiEt_3$. Conditions: See Figure 2. ^{1}H NMR spectrum after 60 min; S = $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**) and V = $(CO)_5MnC(OSiEt_3){=}CH_2$ (**3j**).

Scheme 2. $HSiEt_3$-Induced Degradation of $(CO)_5MnCh(OSiEt_3)CH_3$ (**2j**)



reactions with $HSiMe_2Ph$ cleanly provided **2a** without traces of **5a** or $CH_3CH_2OSiMe_2Ph$ (**7a**).[1a]

We also briefly studied the $HSiEt_3$-induced degradation of **2a**. During this reaction, $HSiEt_3$ (1.2 equiv) slowly degraded **2a** in C_6D_6 solutions to the expected disiloxanes without yielding either **2j** or **3j**. This result precludes **2a** regenerating **1** and $HSiMe_2Ph$. Since in independent studies we observed that mixtures of $HSiMe_2Ph$ and $HSiEt_3$ or $HSiEtMe_2$ containing a limited amount of **1** afforded **2a** and **2j** or **2e** with equal facility,[23] the reaction between **1** and $HSiMe_2Ph$ and presumably other monohydrosilanes must be irreversible. Similar results have been observed for the inverse reaction: treating **2j**, admixed with **3j**, with $HSiMe_2Ph$ did not produce **2a**.

4. Inhibition of the $HSiMe_2Ph$ and $HSiEt_3$ Reactions with $(CO)_5MnC(O)CH_3$ (1). We attempted to (selectively) inhibit the conversion of **1** plus hydrosilane to either α-siloxyethyl **2** or α-siloxyvinyl **3** complexes with carbon monoxide, PPh_3, air, acetone, acetonitrile, tris(trimethylsilyl)silane (a hydrogen atom donor),[24] and tetrahydrofuran (THF). Of these potential inhibitors, the influence of carbon monoxide proved to be the most intriguing. Maintaining 1 atm of CO over a properly agitated solution of **1** and $HSiMe_2Ph$ limited the hydrosilation product **2a** to a maximum 8−10% yield at 2.5 h. Nevertheless, **1** lost 39% (2.5 h) and then 68% (10 h) of its concentration commensurate with consuming 98% of the $HSiMe_2Ph$. Disiloxane $(PhMe_2Si)_2O$ remained the major product, along with lesser quantities of $(CO)_5MnSiMe_2Ph$ (**5a**) (<5%) and $Mn_2(CO)_{10}$, but no **3a**.

The presence of carbon monoxide likewise inhibited the formation of both products from **1** and $HSiEt_3$ in C_6D_6. After 1.5 h and under conditions that parallel reactions in the absence of CO had gone to completion, less that 5% of **1** was consumed. Although the amount of **1** decreased 30% after 5 h, 85% of its products corresponded to **3j**, with only small amounts of **2j** (10%) and $CH_3CH_2OSiEt_3$ (**7j**) (5%).

Somewhat different results were communicated by Akita, Moro-oka, and co-workers[8] for treating **1** with excess H_2SiPh_2. In these reactions, the presence of CO (1 atm) favored higher alkenes. Although these products presumably derived from the initially formed $(CO)_xMnCH(OSiHPh_2)CH_3$ ($x = 4, 5$), the fates of the manganese and silicon moieties were not reported.

Inhibition results for the $HSiMe_2Ph$ reaction with **1** proved to be more straightforward with other reagents. Neither the presence of air nor tris(trimethylsilyl)silane (0.19 equiv) had any noticeable effect on either the rate or outcome of this reaction. Similar results were obtained after treating **1** with $HSiMe_2Ph$ in the dark. In contrast, addition of PPh_3 (1.0 equiv) or CD_3CN (2.1 equiv) blocked the $HSiMe_2Ph$ reaction with **1**. With PPh_3, the starting **1** after 3 h was accounted for as *trans*-

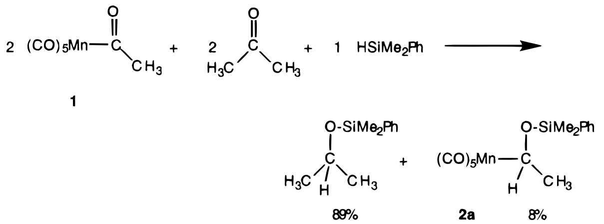
---

[23] (a) Gregg, B. T.; Cutler, A. R. Unpublished results. (b) Attempts to discern between intramolecular and intermolecular pathways via crossover experiments, thus far, have given ambiguous results. Interpretation of results from reactions involving **1** and $DSiMe_2Ph/HSiMe_2Et$ mixtures is complicated by independent **1**-catalyzed SiH/SiD exchange.[3a]

[24] Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188.

and *cis*-$(PPh_3)(CO)_4MnC(O)CH_3$[18] (7% and 13%, respectively), **1** (69%), and $(CO)_5MnCH_3$ (10%). These products represent the previously documented[2] (and independently confirmed) reaction of **1** with PPh_3 and its room temperature decarbonylation, respectively, in the absence of $HSiMe_2Ph$.

Acetone also blocked the hydrosilation of **1** by competing for the $HSiMe_2Ph$. A 2:2:1 mixture of $HSiMe_2Ph$/acetone/**1** accordingly yielded only 8% of the manganese acetyl-derived **2a** (along with 92% unreacted **1**), but 89% $(CH_3)_2CHOSiMe_2Ph$.[19] This acetone hydrosilation (eq 4) was consistent with our



(4)

previously established use of **1** as a precatalyst for the hydrosilation of ketones and aldehydes[9b] and of $Cp(CO)_2FeC(O)CH_3$.[1b,d] Similar results for the hydrosilation of $Cp(CO)_2FeC(O)CH_3$ were recorded when **2a** or $(CO)_5MnCH_3$ was used as a precatalyst.[1d]

Changing the solvent to THF-d_8 (at concentrations comparable to those of the C_6D_6 experiments) more than doubled the reaction time of **1** with $HSiEt_3$. During ^1H NMR monitoring of these THF-d_8 runs, moreover, we detected only $(CO)_5MnC(OSiEt_3){=}CH_2$ (**3j**) (69%). Although $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**) was not detected, its intermediacy and subsequent degradation cannot be ruled out. Thus, 31% of the starting **1** (0.12 mmol) that was unaccounted for matches the 0.23 mmol of unaccounted $HSiEt_3$, assuming that **1** uses 2 equiv of $HSiEt_3$ in the formation and subsequent degradation of **2j**.

An important issue that we must deal with is the discrepancy between our data and Wegman's observations[12a] on the $HSiEt_3$ reaction with **1**. He described the results of a kinetics study for **1** (0.05 M in THF) and a 10-fold excess of $HSiEt_3$ at 25 °C and under 1 atm of carbon monoxide. Under these conditions, acetaldehyde (identified by gas chromatography) and $(CO)_5MnSiEt_3$ (**5j**) (by IR spectroscopy) were reported as the primary products.

We never detected acetaldehyde during our studies on the reaction between $HSiEt_3$ and **1** in C_6D_6. A 2% yield of acetaldehyde easily would have been detected by ^1H NMR spectroscopy, as it was during a reaction between **1** and $HMo(CO)_3Cp$.[25] Acetaldehyde, moreover, represents an unlikely product, since we independently demonstrated that **1** efficiently catalyzes aldehyde and ketone hydrosilation.[9b] Indeed, the reaction between $HSiEt_3$ and **1** did produce small amounts of $CH_3CH_2OSiEt_3$ (**7j**) (<5%, typically in the presence of CO).

Most of our studies were carried out under conditions different from those used by Wegman.[12a] Our concentrations of **1** were much higher, 0.67 M in C_6D_6 and 0.84 in THF-d_8, and we used only 1.1−2.0 equiv of $HSiEt_3$. When our $HSiEt_3$ reactions were separately carried out under more dilute conditions in **1** (0.067 M in C_6D_6 and 0.084 M in THF-d_8) with 10 equiv of $HSiEt_3$ and 1 atm of CO—conditions comparable to those reported by Wegman—we observed <5% consumption of **1** over 5 h. The net effect of the carbon monoxide and to a lesser degree using THF in place of benzene was to dramatically reduce the reaction rate, while selectively producing **3j** (albeit in very low yields).

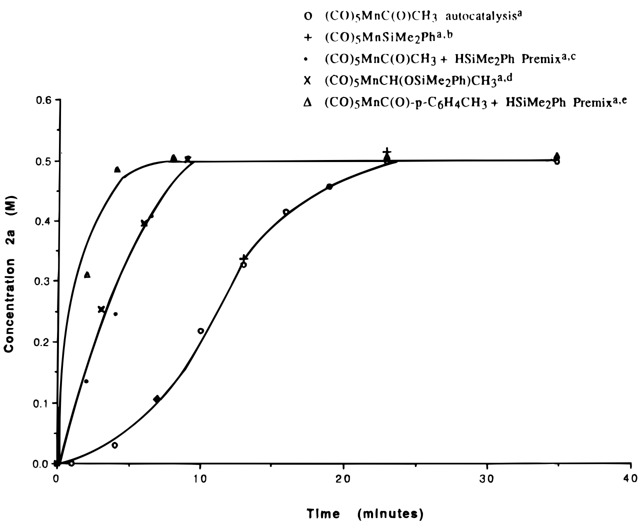
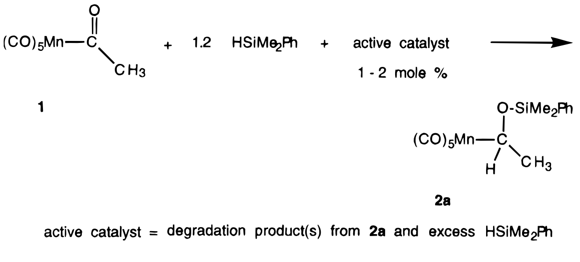


Figure 4. Reaction profiles: dimethyphenylsilane autocatalyzed hydrosilation of $(CO)_5MnC(O)CH_3$ (**1**). Conditions: (a) $(CO)_5MnC(O)CH_3$ (**1**) (100 mg, 0.42 mmol), Me_2PhSiH (65 mg, 0.48 mmol, 1.1 equiv), and anisole (60 mg, 0.55 mmol) in 600 mg of C_6D_6 (25 °C). All concentrations were determined by quantative ^1H NMR spectroscopy (vs anisole). (b) $(CO)_5MnSiMe_2Ph$ (**5a**) (2 mg, 0.0063 mmol, 1.5%) added. (c) Catalyst premix: $(CO)_5MnC(O)CH_3$ (**1**) (3 mg, 0.008 mmol, 1.9%) and Me_2PhSiH (65 mg, 0.48 mmol) in 600 mg of C_6D_6 reacted 45 min prior to addition of **1** (100 mg, 0.42 mmol). (d) $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (**2a**) (3 mg, 0.008 mmol, 1.9%) added. (e) Catalyst premix: $(CO)_5MnC(O)$-*p*-$C_6H_4CH_3$ (1 mg, 0.003 mmol, 0.9%) and $HSiMe_2Ph$ (65 mg, 0.48 mmol) in 600 mg of C_6D_6 reacted 45 min prior to addition of **1** (100 mg, 0.42 mmol).

5. Mechanistic Observations Concerning the Active Catalyst. If **1** plus hydrosilane affords low concentrations of an active catalyst for the hydrosilation of a variety of organic and organometallic acyl groups, then perhaps this same active catalyst promotes the hydrosilation of **1**. Under these conditions, the hydrosilation of **1** would be autocatalytic; either the initial hydrosilation product **2a** (e.g., with $HSiMe_2Ph$) or its silane-induced degradation product(s) would serve as the active catalyst(s) (eq 5).



(5)

Autocatalytic hydrosilation of **1** is consistent with the S-shaped reaction profile and the presence of an induction period[27] that could be eliminated by adding preformed active catalyst(s). Reaction profiles for **1** and $HSiMe_2Ph$ (1:1.1), plots of [**2a**] vs time, appear in Figure 4. The shorter 2 min induction period vs that recorded in Figure 1 is attributed to doubling the

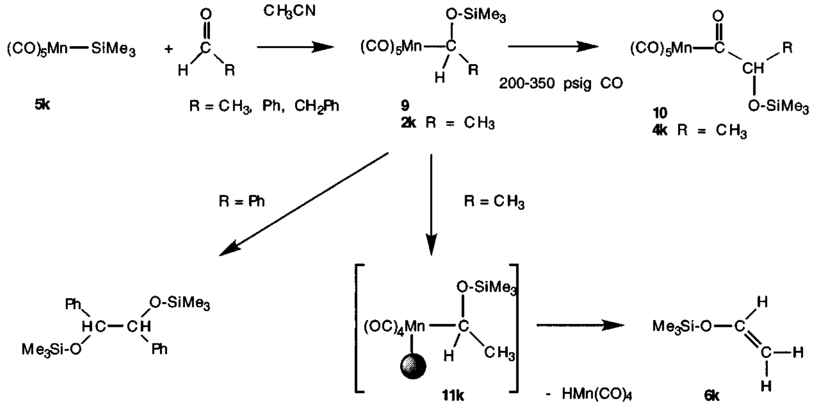
---

[25] Treatment of equimolar quantities of $HMo(CO)_3Cp$ and $(CO)_5MnC(O)CH_3$ (**1a**) (0.084 mmol in 600 mg of C_6D_6) afforded 4% acetaldehyde after 2 h and 23% after 8 h (^1H NMR spectral monitoring). Gregg, B. T.; Cutler, A. R. Unpublished observations. This bimolecular reductive elimination[26] occurs very slowly for $(CO)_5MnH$ and manganese acyl complexes, $(CO)_5MnC(O)R$.[5a,d−f]

[26] Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415. See also ref 5.

[27] (a) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; p 26. (b) Steinfeld, J. I; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: Engelwood Cliffs, NJ, 1989; p 182. (c) Schmid, R.; Sapunov, V. N. *Non-Formal Kinetics*; Verlag Chemie: Deerfield Beach, FL, 1982; p 54.

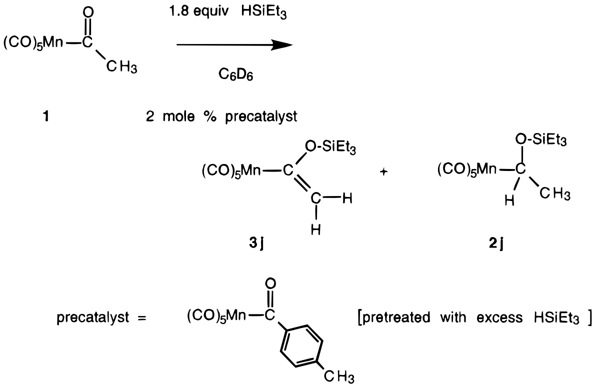
Scheme 3. $(CO)_5MnSiMe_3$−Aldehyde Chemistry[11]



initial concentration of **1**. Including the coordinatively saturated $(CO)_5MnSiMe_2Ph$ (**5a**) (1.5%) in this hydrosilation had no effect on its reaction profile; reactions still required 25 min to go to completion.

We eliminated the induction period and accelerated the reaction between **1** and $HSiMe_2Ph$ by including the product **2a** or other plausible precursors to the active catalyst in the initial reaction mixture. Under these conditions, **1** typically was consumed within 5−8 min (Figure 4). The proposed active catalyst(s) were generated by treating **1** (1.9%), **2a** (1.9%), or the manganese toluoyl $(CO)_5MnC(O)$-*p*-$C_6H_4CH_3$ (0.9%) in C_6D_6 with the full amount of silane (1.1 equiv with respect to substrate **1**) for 45 min prior to adding the substrate. This time for generating the active catalyst, signaled by the solution turning from pale yellow to dark orange, corresponded to consuming the starting manganese acetyl, methyl, or *p*-toluoyl precatalyst. The latter catalytic system, in particular, was that used in our previous kinetics study on the H/D isotope exchange between $HSiMe_2Et$ and $DSiMe_2Ph$.[3a]

We also used $(CO)_5MnC(O)$-*p*-$C_6H_4CH_3$ in the same catalyst premix procedure to accelerate the $HSiEt_3$ transformation of **1** (eq 6). Pretreating this manganese *p*-toluoyl precatalyst (2%) with the full amount of $HSiEt_3$ for 45 min prior to adding the substrate **1** transformed it into a 58:42 mixture of **3j** and **2j** within 10 min. The control reaction using 1.9 equiv of $HSiEt_3$ but without the manganese precatalyst required 70 min.



(6)

Discussion

1. Hydrosilation of $(CO)_5MnC(O)CH_3$ (1). General Observations. Of the 10 monohydrosilanes that reacted with $(CO)_5MnC(O)CH_3$ (**1**) in benzene at room temperature (eq 2), the $HSiMe_2Ph$- and $HSiEt_3$-derived reaction products exemplify the hydrosilation chemistry of **1**. Treatment of **1** with 1 equiv of $HSiMe_2Ph$, for example, cleanly yielded $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (**2a**) (76%), small amounts of $(CO)_5MnCH(OSiMe_2Ph){=}CH_2$ (**3a**) (6%), disiloxane $(PhMe_2Si)_2O$, and residual silane. Other monohydrosilanes in Table 1 showed similar reactivity toward **1**, although the relative proportion of the α-siloxyvinyl complexes **3** varied. The use of $HSiEt_3$ maximized the amounts of the α-siloxyvinyl complex: $(CO)_5MnCH(OSiEt_3){=}CH_2$ (**3j**) formed in over 50% yield and in approximately a 2:1 ratio with $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**).

A limited number of examples of $(CO)_5MnCH(OSiMe_3)R$ (**9**) that have been prepared include $(CO)_5MnCH_2OSiMe_3$, $(CO)_5MnCH(OSiMe_3)Ph$, and several chelated α-(trimethylsiloxy)alkyl compounds with another ligating heteroatom. These were synthesized by Gladysz and co-workers[11] using ligand reactions (Scheme 3) that are quite independent of those reported herein. They prepared $(CO)_5MnCH(OSiMe_3)Ph$, for example, by treating benzaldehyde with $(CO)_5MnSiMe_3$ (**5k**).[11b] Interestingly, $(CO)_5MnCH(OSiMe_3)Ph$ is unstable as it decomposes by homolytic cleavage and radical coupling to $PhCH(OSiMe_3)CH(OSiMe_3)Ph$ plus $Mn_2(CO)_{10}$. The stable rhenium analog $(CO)_5ReCH(OSiMe_3)Ph$, however, was prepared and fully characterized.[11d]

Of particular relevance to the present study is Gladysz's observation that treating enolizable aldehydes and ketones with $(CO)_5MnSiMe_3$ (**5k**) cleanly produces organic vinyl silyl ethers rather than manganese α-(trimethylsiloxy)alkyl complexes **9**. Although only a few examples of **9** had been detected, carbonylation of the reaction mixtures yielded their stable α-(trimethylsiloxy)acyl derivatives **10** (Scheme 3).[11c] For example, the reaction between acetaldehyde and **5k** gave $CH_2{=}CHOSiMe_3$ (**6k**) or in the presence of CO **4k**. The formation of **6k** was ascribed to intermediacy of coordinatively unsaturated $(CO)_4MnCH(OSiMe_3)CH_3$ (**11k**) (Scheme 3), which undergoes β-elimination.[11,28,29] Taken togeather, these observations suggest that the presence of a coordinatively unsaturated intermediate (e.g., **11**) in the hydrosilation pathway of an acyl ligand (and in the absence of exogenous CO) should furnish organic vinyl silyl ethers.

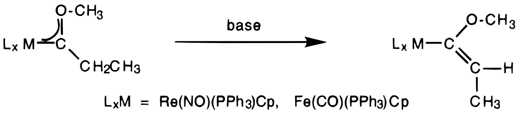
The α-siloxyethyl complexes **2** that we isolated from the hydrosilation of **1** were surprisingly stable at room temperature as long as excess hydrosilane was avoided. Starting with either purified or in situ generated **2a** (using 1.0 equiv of silane), for example, we noted the absence of organic products correspond-

---

[28] Similar intermediates have been proposed for the $Co_2(CO)_8/PPh_3$-catalyzed transformation of aldehyde (RCHO), $HSiR_3$, and CO to α-siloxyaldehydes $RCH(OSiR_3)CHO$ and for the hydrosilation of the cobalt acyl complex $(CO)_4CoC(O)CHMe_2$.[12b] (a) Chatani, N.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 1370. (b) Chatani, N.; Fugii, S.; Yamasaki, Y.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1986**, *108*, 7361. (c) Murai, S.; Seki, Y. *J. Mol. Catal.* **1987**, *41*, 197. (d) 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.

ing to (a) homolytic cleavage and generation of the bis(silyl) ether $CH_3CH(OSiMe_2Ph)CH(OSiMe_2Ph)CH_3$ (**8a**), (b) further reaction with hydrosilane and elimination of $CH_3CH_2OSiMe_2Ph$ (**7a**), or (c) β-deinsertion to form the silyl vinyl ether $CH_2{=}CH(OSiMe_2Ph)$ (**6a**).

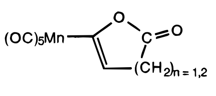
Although transformation of acyl complexes plus hydrosilane α-siloxyvinyl derivatives similar to **3** is unprecendented, a number of other mono- and bimetallic 1-oxyvinyl complexes had been characterized. Interest in these 1-oxyvinyl systems centers on (1) using nucleophilic α-(metaloxy)vinyl or α-alkoxyvinyl compounds $L_xMC(OR){=}CHR$ to form carbon−carbon bonds[30] and (2) transforming acyl ligands to bimetallic $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ ketene (or enolate) complexes.[31] α-Alkoxyvinyl compounds, for example, derive from deprotonating alkoxycarbene compounds (eq 7),[32] as exemplified by the (*Z*)-rhenium and iron alkoxy-1-propenyl compounds reported by the Gladysz[33] and Davies[34] groups, respectively.



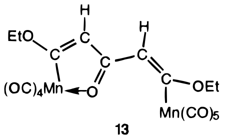
L_xM = Re(NO)(PPh$_3$)Cp, Fe(CO)(PPh$_3$)Cp

(7)

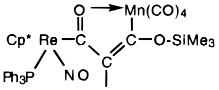
Organometallic 1-oxyvinyl enolates[35,36] $L_xMC(O^-){=}CHR$ are precursors to other 1-oxyvinyl compounds. Floriani accordingly trapped $Cp(PPh_3)(CO)FeC(O){=}CH_2^-$ as its titanoxy and zirconoxy derivatives $Cp(PPh_3)(CO)FeC(OMClCp_2){=}CH_2$.[37] Attempts to generate the corresponding α-siloxyvinyl complex $Cp(PPh_3)(CO)FeC(OSiMe_3){=}CH_2$ by silylating the same enolate instead gave $Cp(PPh_3)(CO)FeC(O)CH_2SiMe_3$.[35b,c] Gladysz converted the analogous rhenium α-silylacetyl to its α-siloxyvinyl tautomer $Cp(PPh_3)(NO)ReC(OSiMe_3)C{=}CH_2$.[35g] The extensive literature of $Mn(CO)_5$ chemistry[38] also includes several examples of 1-oxyvinyl complexes. Thus, 5-$(CO)_5$Mn-2(3*H*)-furanone and 6-$(CO)_5$Mn-3,4-dihydro-(2*H*)-pyran-2-one complexes **12**[39] and the recently reported $Mn_2(CO)_9\{\mu\text{-O}{=}C\text{-}[C(H){=}C(OEt)]_2\}$ (**13**)[40] contain 1-oxyvinyl functionalities. A particularly intriguing example is the trimethylsilyl enol ether derivative **14** of the bimetallic μ-malonyl compound Cp*(NO)(PPh$_3$)Re[μ-(COCH$_2$CO)-C^1,O^3:C^3]Mn(CO)$_4$,[41] which O'Connor used in establishing keto-enol tautomerization of a metal acyl system.



12



13



14

2. Hydrosilation of $CH_3C(O)Mn(CO)_5$ (1). Mechanistic Constraints. Any mechanism advanced for the reactions of $HSiMe_2Ph$, $HSiEt_3$, or other monohydrosilanes with $(CO)_5MnC(O)CH_3$ (**1**) must account for the following observations: (1) the absence of the organic byproducts $CH_2{=}CHOSiR_3$ (**6**) and $CH_3CH_2OSiR_3$ (**7**); (2) the presence of $(CO)_5MnCH(OSiR_3){=}CH_2$ (**3**) but not $(CO)_5MnSiMe_2Ph$ (**5**); (3) the formation of **3**, which needs just 1 equiv of hydrosilane, independent of $(CO)_5MnCH(OSiR_3)CH_3$ (**2**); (4) the inhibition by CO, phosphine, or acetonitrile, but neither air nor light; (5) the competitive hydrosilation of other substrates (e.g., acetone or $Cp(CO)_2FeC(O)R$) for which **1** is a precatalyst; (6) the autocatalysis during which product degradation affords the active catalyst; and, perhaps most informative, (7) the presence of an induction period that can be removed by independently generating the putative active catalyst.

Our working hypothesis for the mechanism of the reaction of $HSiR_3$with **1** accordingly engenders an intermolecular pathway in which a coordinatively unsaturated manganese silyl, $(CO)_4MnSiR_3$ (**15**), serves as the active catalyst (Scheme 4). According to this intermolecular, autocatalytic pathway, the active catalyst **15** ligates **1** as the bimetallic μ-acetyl **16** and rearranges to $(CO)_5MnC(CH_3)(OSiR_3)Mn(CO)_4$ (**17**). This unsaturated μ-siloxyethylidene serves as the key catalysis intermediate. It can coordinate silane to give **18**, which then reductively eliminates the α-siloxyethyl product **2**. Alternatively, **17** can competitively β-deinsert to give **19**, which then dissociates the α-siloxyvinyl product **3**.

Coordinatively unsaturated $(CO)_4MnSiR_3$ (**15**) previously had been implicated as the active catalyst for the SiH/Si′D isotope exchange between $HSiMe_2Et$ and $DSiMe_2Ph$ at room temperature (Scheme 5).[3a] In these reactions, $(CO)_5MnC(O)$-*p*-$C_6H_4CH_3$ was added as the precatalyst, and results of a kinetics study are consistent with it transforming into **15** during a reproducible induction period. The coordinatively unsaturated silyls **15a** and **15e** evidently function as the active catalysts in a ping-pong Bi

---

[29] The mechanism proposed for transforming **5k** and acetaldehyde to **6k** invokes **2k** as the initial product. Although **2k** was detected in unspecified concentrations by NMR spectroscopy, **6k** proved to be the isolable product. A more plausible pathway for this reaction would have the coordinatively unsaturated **11** as the common precursor to **6k** or **4k**. We do not know why **2k** should be less stable than $(CO)_5MnCH(OSiMe_2Et)CH_3$ (**2e**), for example, but we also cannot account for the limited stability of $(CO)_5MnCH(OSiEt_3)CH_3$ (**2j**). The salient difference between the reactivity of **5k** toward acetaldehyde and the hydrosilation of **1** is that the former process provides vinyl silyl ethers as a major product whereas the hydrosilation process yields isolable manganese α-siloxyalkyl complexes **2.**

[30] Blackburn, B. K.; Davies, S. G.; Whittaker, M. In *Stereochemistry of Organometallic an Inorganic Compounds*, Bernal; I., Ed.; Elsevier: Amsterdam, 1989; Vol. 3, Chapter 2.

[31] (a) Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1. (b) Ozawa, F.; Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Henling, L. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1319. (c) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427.

[32] (a) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

[33] Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.

[34] (a) Baird, G. J.; Davies, S. G.; Jones, R. H.; Prout, K.; Warner, P. *J. Chem. Soc., Chem. Commun.* **1984**, 745. Curtis, P. J.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1984**, 747. (b) Baird, G. J.; Davies, S. G.; Maberly, T. R. *Organometallics* **1984**, *3*, 1764.

[35] (a) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 5250. (b) Aktogu, N.; Felkin, H.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1982**, 1303. (c) Aktogu, N.; Felkin, H.; Baird, G. J.; Davies, S. G.; Watts, O. *J. Organomet. Chem.* **1984**, *262*, 49. (d) Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P.; Jones, R. H.; Prout, K. *J. Organomet. Chem.* **1985**, *285*, 213. (e) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194. (f) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (g) Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1185. (h) Ojima, I.; Kwon, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 5617.

[36] (a) Brinkman, K.; Helquist, P. *Tetrahedron Lett.* **1985**, *26*, 2845. (b) Akita, M.; Kondoh, A. *J. Organomet. Chem.* **1986**, *299*, 369.

[37] (a) Berno, I.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1990**, *9*, 1995. (b) Weinstock, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1986**, *108*, 8298.

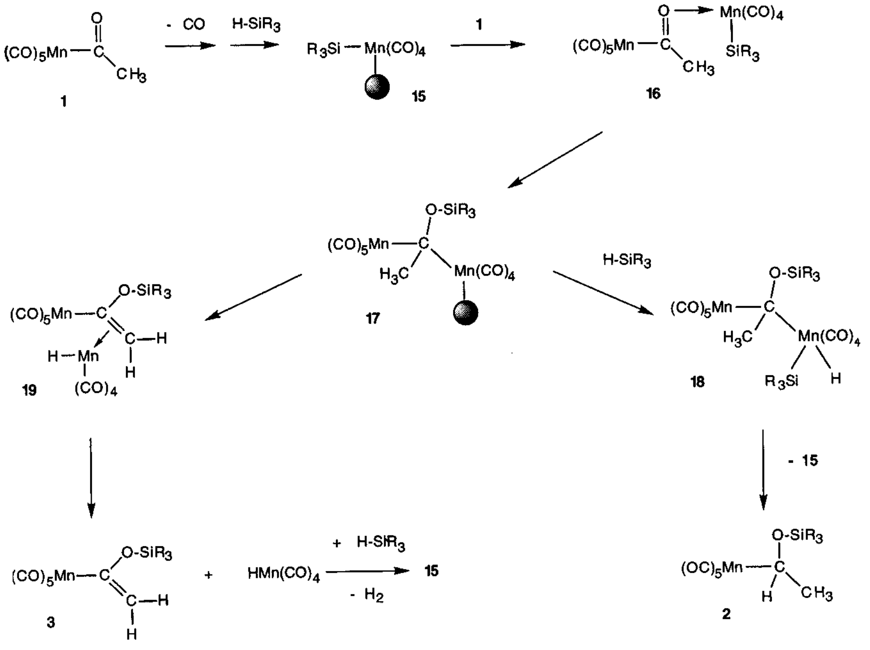
[38] Treichel, P. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 4, Chapter 29.

[39] Kraihanzel, C.; Herman, L. *J. Organomet. Chem.* **1986**, *15*, 397.

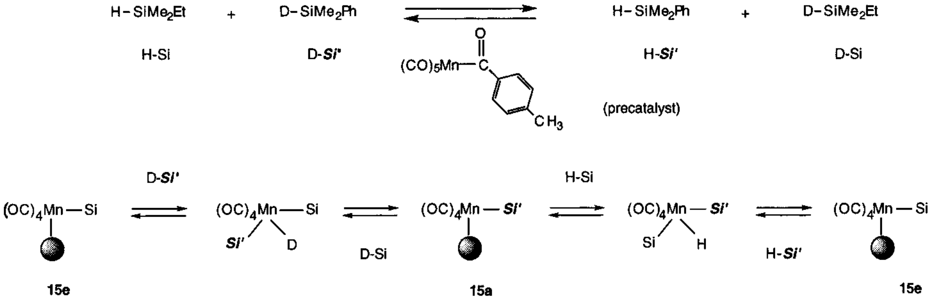
[40] Adams, R. D.; Chen, G.; Chen, L.; Wu, W.; Yin, J. *J. Am. Chem. Soc.* **1991**, *113*, 9406.

[41] O'Connor, J. M.; Uhrhammer, R.; Rheingold, A. L.; Roddick, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 4530. O'Connor, J. M.; Uhrhammer, R.; Rheingold, A. L.; Staley, D. L.; Chadha, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 7585.

Scheme 4. Intermolecular Pathways for $HSiR_3$ and $(CO)_5MnC(O)CH_3$ (**1**)



Scheme 5. $(CO)_5MnC(O)$-*p*-$C_6H_4CH_3$-Catalyzed SiH/Si′D Isotope Exchange



Bi mechanism that operates under rapid equilibrium conditions (Scheme 5). Silane SiH/Si′D isotope exchange thus interconverts **15a** and **15e** by sequentially adding one substrate silane and then releasing a product silane. The implicit silane oxidative-addition and reductive-elimination steps in this proposed mechanism, although precedented,[42] could be replaced by η^2-(H−Si) complexation[43] and σ-metathesis[44] steps.

A particularly salient observation is that the induction period common to both the manganese toluoyl-catalyzed SiH/Si′D isotope exchange and the reaction of $HSiR_3$ with **1** can be removed by a pretreatment procedure. This procedure involves treating the precatalyst, e.g., **1**, with excess hydrosilane prior to initiating the actual catalysis. Thus, the induction period for the SiH/Si′D isotope exchange can be eliminated by mixing the manganese toluoyl complex with excess of one hydrosilane. After 0.75 h, all of the precatalyst has been consumed, and catalysis immediately commences upon adding the other silane. The timing is critical since the active catalyst is short lived: productive catalysis of silane exchange stopped within 1.25 h.[45]

A similar pretreatment procedure also was used to demonstrate autocatalytic reactions of $HSiMe_2Ph$ and $HSiEt_3$ with **1**, Figure 4 and eq 6. Significantly, these reaction rates dramatically increased after pretreating catalytic quantities of $(CO)_5MnC(O)$-*p*-$C_6H_4CH_3$ (or even **1**) with excess $HSiMe_2Ph$ or $HSiEt_3$ (for 45 min) prior to adding the substrate **1**.

The unsaturated siloxyethylidene **17** intermediate in our proposed mechanism for the reaction of $HSiR_3$ with **1** (Scheme 4) serves as a common precursor to yielding either α-siloxyethyl **2** or α-siloxyvinyl **3** as products of competing pathways. Analogous dicobalt siloxyethylidene compounds $Co_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}R(COSiR'_3)\}$ have been fully characterized.[46] For the

---

[42] Isolobal examples (hydrido)(silyl)(alkyl)Co(III),[42a] (hydrido)(silyl)$_2$Co(III),[42b] (hydrido)(silyl)$_2$Fe(CO)Cp,[42c] $[(CO)_5Mn](CO)_4MnH(SnBu_3)$, and $(CO)_4MnH(SnBu_3)_2$[42d] have been characterized as the products of similar oxidative-addition/reductive-elimination sequences. Other examples of (hydrido)(silyl)(alkyl)metal complexes also have been reported/implicated as intermediates in hydrosilation catalysis.[42e] (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. (c) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366. (d) 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. (e) Brunner, H.; Fisch, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1131; *J. Organomet. Chem.* **1991**, *412*, C11. (f) Sullivan, R. J.; Brown, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 9155. (g) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527 and references therein.

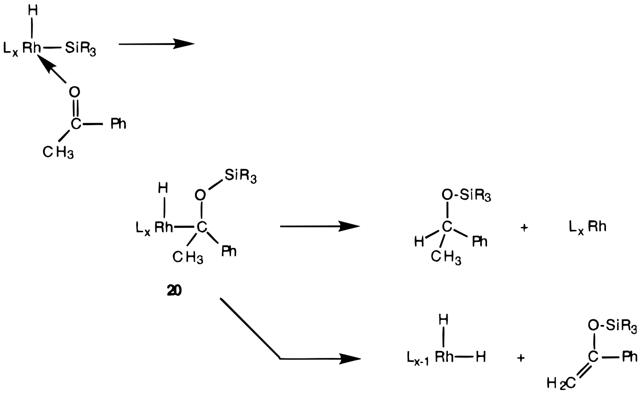
[43] (a) Luo, X. -L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527. (b) Lead reference for $(\eta^2\text{-H}-SiR_3)(CO)(L)MnCp$ complexes: Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.

[44] Woo, H. -G.; Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22.

[45] An alternative procedure of eliminating the induction period for the SiH/Si′D isotope exchange involved $(CO)_5MnSiMe_2Ph$ (**5a**) as the precatalyst under photochemical conditions.[3a] Under similar photochemical conditions **5a** also catalyzed the hydrosilation of ketones and esters.[9b,c] Photocatalysis of the hydrosilation of **1** using **5a**, however, was not pursued because of the photochemical lability of the substrate **1**. Under nonphotochemical conditions, **5a** does not promote these catalytic processes.

[46] Sisak, A.; Sironi, A.; Moret, M.; Zucchi, C.; Ghelfi, F.; Palyi, G. *J. Chem. Soc., Chem. Commun.* **1991**, 176.

Scheme 6. $(PPh_3)_3RhCl$-Catalyzed Hydrosilation of Acetophenone



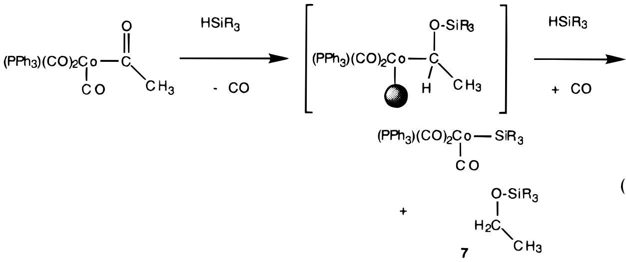
$HSiEt_3$-**1** reaction, its reaction profile (Figure 3) is in accord with **3j** forming independently of **2j**. Only 1 equiv of $HSiEt_3$ is required to generate **3j** and to eliminate presumably 1 equiv of H_2.

We anticipated that competition between branching pathways involving **17** should be sensitive to the hydrosilane concentration, with higher concentrations of hydrosilane favoring the production of **2**. For the $HSiEt_3$−**1** reaction, increasing the $HSiEt_3$ concentration from 1.2 to 6.0 equiv (Table 1) accordingly increased the yields of **2j** from 6% to 17%. The corresponding increase in yield of **3j** (from 38% to 42%), however, complicated further analysis, since a much greater increase in **2j** concentration conceivably could be masked by its sensitivity toward excess $HSiEt_3$.

It is the β-deinsertion step involving **17**, however, that distinguishes this mechanism. Assigning the β-elimination step to this bimetallic intermediate nicely accounts for generating an α-siloxyvinyl complex **3** instead of forming organic vinyl silyl ethers CH_2=$CH(OSiR_3)$ (**6**). Examples of **6** would be expected to form at least as byproducts via β-elimination on a mononuclear $(CO)_4MnCH(OSiR_3)CH_3$ (**11**), as discussed for Gladysz's trimethylsiloxy derivative **11k** (Scheme 3).

Organic vinyl silyl ethers also are byproducts of rhodium(I)-catalyzed hydrosilation of ketones.[10] With acetophenone, for example, a number of rhodium catalysts afford the CH_2=$C(OSiR_3)Ph$ as well as $CH_3CH(OSiR_3)Ph$ (Scheme 6).[47] The accepted mechanism[48] has a rhodium α-siloxyalkyl intermediate **20** that either reductively eliminates the silyl ether or deinserts across a β-hydrogen to give the silyl vinyl ether.[49]

Intermediacy of coordinatively unsaturated α-siloxyethyl complexes analogous to $(CO)_4MnCH(OSiR_3)CH_3$ (**11**) had been advanced in order to account for the noncatalytic hydrosilation of organometallic acyl compounds[50] such as $(PPh_3)(CO)_3CoC(O)CH_3$ (eq 8).[51] Treatment of this cobalt acetyl with 2 equiv of monohydrosilanes, including $HSiMe_2Ph$ and $HSiEt_3$, cleanly gives the saturated cobalt silyl, e.g., $(PPh_3)(CO)_3CoSiR_3$, plus the ethoxysilane **7**. Neither CH_2=$CHOSiR_3$ (**6**) nor $(PPh_3)(CO)_3CoCH(OSiR_3)CH_3$ was detected. This intramolecular hydrosilation mechanism appears in Scheme 7 as it might apply to **1**.[52]



(8)

This intramolecular mechanism also is consistent with the generation of **2** from **11** (via addition of CO), with the absence of air or light influence, and with the presence of CO and THF inhibition. We, however, would expect $(CO)_5MnSiR_3$ (**5**), **6** (cf. Scheme 3), and $CH_3CH_2OSiR_3$ (**7**) as byproducts. The absence of these byproducts,[53] even in the presence of excess hydrosilanes, precludes the transience of **11** and therefore operation of this mechanism. Competitive inhibition by acetone or $Cp(CO)_2FeC(O)R$—substrates for which **1** functions as a hydrosilation precatalyst[54] —however is consistent with the intermolecular pathway. These acyls compete with **1** as the substrate for the active catalyst **15**.

A surprising outcome of this study is that the reactions of $HSiR_3$ with **1** differ from those with $(PPh_3)(CO)_3CoC(O)CH_3$ (eq 8) or even $(CO)_5MnC(O)$-*p*-C_6H_4R (R = H, CH_3),[53] which afford the products anticipated for the intramolecular mechanism. With **1** as the substrate, a changeover to the intermolecular pathway (Scheme 4) occurs, and the unsaturated $(CO)_5MnC(CH_3)(OSiR_3)Mn(CO)_4$ (**17**) now functions as the bimetallic counterpart to the unsaturated α-siloxyethyl complex **11** in the intramolecular mechanism. Provided that $(CO)_4MnSiR_3$ (**15**), the proposed active catalyst, efficiently traps **1** and

---

[47] (a) Benes, J.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2264. (b) Sakurai, H.; Miyoshi, K.; Nakadaira, Y. *Tetrahedron Lett.* **1977**, 2671. (c) Matsumoto, H.; Hoshino, Y.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1279. (d) Payne, N. C.; Stephan, D. W. *Inorg. Chem.* **1982**, *21*, 182. (e) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217. (f) Brunner, H.; Becker, R.; Riepl, G. *Organometallics* **1984**, *3*, 1354. Brunner, H.; Kurzinger, A. *J. Organomet. Chem.* **1988**, *346*, 413. (g) Ojima, I.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 2606. (h) Wright, M. E.; Cochran, B. B. *J. Am. Chem. Soc.* **1993**, *115*, 2059.

[48] (a) Ojima, I.; Kogure, T; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, *122*, 83. Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671. Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390. (b) Hayashi, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1976**, *113*, 127. (c) Corriu, R. J. P.; Moreau, J. J. E. *Nouv. J. Chim.* **1977**, *1*, 71. (d) 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. (e) Kolb, I.; Hetflejs *Coll. Czech. Chem. Comm.* **1980**, *45*, 2224. (f) Zheng, G. Z.; Chan, T. H. *Organometallics* **1995**, *14*, 70 and references therein.

[49] We note however that **1**-catalyzed hydrosilation of enolizable ketones such as acetophenone does not provide the organic vinyl silyl ethers, e.g., $PhC(OSiR_3)$=CH_2. Using **1** as the precatalyst for the $HSiEt_3$ or $HSiMe_2Ph$ hydrosilation of acetophenone thus yields only its siloxybenzyls, $PhCH(OSiR_3)CH_3$.[9b]

[50] Hydrosilation of cobalt acyls,[12b] the $Co_2(CO)_8$-catalyzed siloxymethylation of aldehydes,[28] and the hydrosilation / reduction of the acyl ligand on $Cp(L)(CO)FeC(O)CH_2CH_2Ph$.[42d]

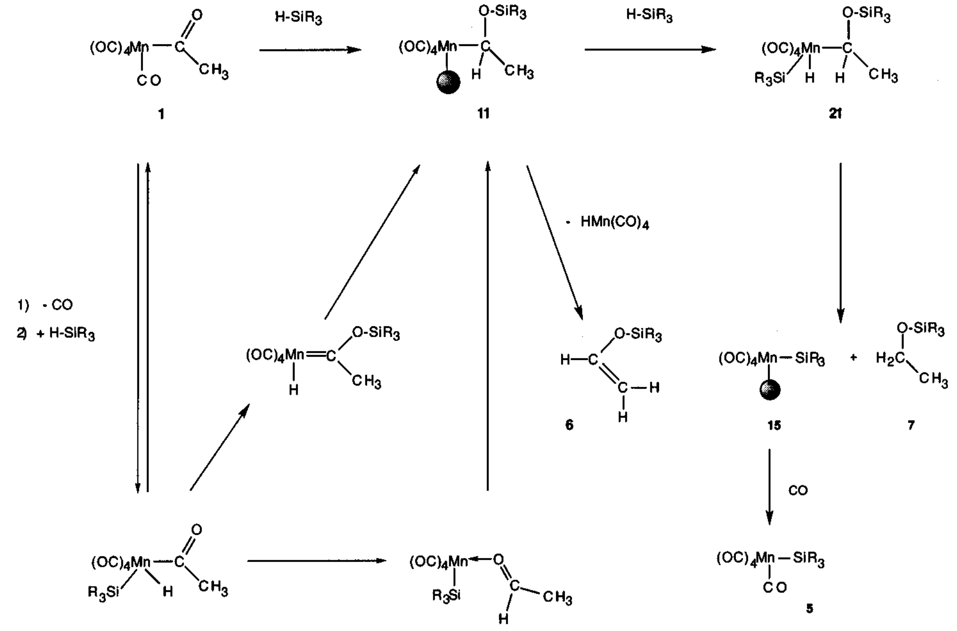
[51] Gregg, B. T.; Cutler, A. R. *Organometallics* **1992**, *11*, 4276.

[52] Intramolecular hydrosilation of **1** would require the coordinatively unsaturated **11** as the pivotal intermediate. This intermediate would originate via **1** dissociating carbon monoxide[2] and oxidatively adding $HSiR_3$ to give $(CO)_4Mn(H)(SiR_3)(COCH_3)$.[42] Rearrangement to **11** would occur either by reductive elimination and subsequent insertion involving ligated aldehyde[5f] or by a 1,3-silatropic shift[52a] and hydride migration. Association of CO at **11** would produce the observed α-siloxyalkyl product **2**. Alternatively, competing pathways for using **11** include β-elimination of CH_2=$CHOSiR_3$ and association of $HSiR_3$ and then reductive elimination of $CH_3CH_2OSiR_3$ (**7**). (a) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.

[53] This intramolecular pathway evidently is involved in the hydrosilation of manganese benzoyl and *p*-toluoyl complexes $(CO)_5MnC(O)$-*p*-C_6H_4R (R = H, CH_3).[1a,3a] These reactions provide the benzyl silyl ether (80−90%) plus the stable manganese silyl, e.g., $(CO)_5MnSiMe_2Ph$ (**5a**) (ca. 25−40%). Yields of **5a** increase with CO pressure, but decrease with increasing hydrosilane concentration. These and other observations (to be published) are consistent with the presence of a coordinatively unsaturated manganese silyl $(CO)_4MnSiMe_2Ph$ (**15a**) intermediate that degrades relatively slowly in the presence of excess silane.

[54] In work to be published we demonstrate that pretreating the manganese acetyl **1** or *p*-toluoyl complexes with excess $HSiMe_2Ph$ under the same conditions that were used in the silane exchange studies affords extremely active catalysts for the hydrosilation of $FpC(O)CH_3$,[9a] organic ketones,[9b] and esters.[9c]

Scheme 7. Intramolecular Pathways for $HSiR_3$ and $(CO)_5MnC(O)CH_3$ (**1**)



rearranges to **17**, subsequent *β*-deinsertion and dissociation of the fragment $(CO)_4MnH$ provide α-siloxyvinyl complexes **3** (vs an organic vinyl silyl ether **6** from **11**), whereas addition of hydrosilane to **17** yields **2** (vs an ethoxysilane from **10**).[33,34]

The absence of detectable $(CO)_5MnSiR_3$ (**5**) during the reactions between $HSiR_3$ and **1** may seem surprising given that unsaturated $(CO)_4MnSiR_3$ (**15**) is the proposed active catalyst and that CO dissociation is involved in generating **15** from **1**. The absence of **5** cannot be attributed to subsequent reaction chemistry: **5a** neither reacts with hydrosilanes under these reaction conditions nor serves as a precatalyst (Figure 4).[3] We believe that unstable **5** forms as a transient,[3a] promotes catalysis, and degrades in the presence of $HSiR_3$ to the observed disiloxanes.

A remaining issue concerns the origin of the purported active catalyst **15**. We hypothesize three plausible sources of **15**. First, silane-induced degradation of the product **2** could continuously replenish the low concentrations of the unstable catalyst **15** as it decomposed. Results of the reaction profiles for the $HSiMe_2Ph$−**1** hydrosilation (Figure 4) demonstrate that **2a** functions as an efficient precatalyst. Second, according to the intermolecular hydrosilation mechanism advanced in Scheme 4, the active hydrosilation catalyst **15** could be regenerated. Finally, the origin of **15** when **1** and $HSiR_3$ are mixed without the pretreatment procedure remains an unresolved issue. A possible explanation is that a few turnovers of the intramolecular mechanism or other unspecified hydrosilane-induced degradation of **1** could generate the initial **15.** Interestingly, $(CO)_5MnC(O)$-*p*-$C_6H_4CH_3$, perhaps the most effective reagent for the pretreatment procedure (Figure 4), evidently reacts by the intramolecular route and generates **15**/**5**.

Conclusions

Two significant results of this study are that (1) reactions between $(CO)_5MnC(O)CH_3$ (**1**) and monohydrosilanes afford isolable α-siloxyethyl complexes $(CO)_5MnCH(OSiR_3)CH_3$ (**2**) and (2) these reactions also provide an α-siloxyvinyl byproduct $(CO)_5MnC(OSiR_3){=}CH_2$ (**3**). These reactions readily occur at room temperature with 1−2 equiv of $HSiR_3$, all without adding a catalyst. In contrast, hydrosilation of the isolobal iron acetyl compounds $Cp(CO)(L)FeC(O)CH_3$ yields $Cp(CO)(L)FeCH(OSiR_3)CH_3$,[1] but these reactions require a catalyst; hydrosilation of the cobalt acetyl compounds $(PR_3)(CO)_3CoC(O)CH_3$[50] cleanly produces equimolar mixtures of $(CO)_3(PR_3)CoSiR_3$ plus $CH_3CH_2OSiR_3$ (**7**), although these reactions occur without benefit of a catalyst.

The formation of **3**, our second result, instead of $(CO)_5MnSiR_3$ (**5**) plus **7** [or $CH_2{=}CHOSiR_3$ (**6**)] forms the basis of our working hypothesis for an intermolecular catalysis pathway. This catalysis pathway features the coordinatively unsaturated $(CO)_4MnSiR_3$ (**15**) as the active catalyst. It binds the substrate **1** and rearranges to the *μ*-siloxyethylidene intermediate $(CO)_5MnC(CH_3)(OSiR_3)Mn(CO)_4$ (**17**) (Scheme 4), which transforms to **2** or **3**.

One postulated route to generate the unstable active catalyst **15** is autocatalysis that entails silane degradation of product **2** (but not **3**). This autocatalysis is consistent with the dramatic rate enhancements for the hydrosilation of **1** that attend pretreatment of catalytic quantities of **1**, $(CO)_5MnC(O)C_6H_4CH_3$, or even **2** with excess silane before adding the substrate **1**. Under these pretreatment conditions,[3,9] transient concentrations of **15** are believed to be generated, although further studies are required in order to elucidate the processes by which **15** derives from hydrosilane-induced degradation of manganese alkyl complexes.

Acknowledgment. We gratefully acknowledge receiving generous financial support from the Department of Energy, Office of Basic Energy Science. We also are indebted to Dr. Chongfu Xu for doing a key experiment and to Dr. Paul Hanna and Edward Crawford (RPI) for their preliminary observations.

JA9528801