Hydrosilation of Manganese Acyls $(CO)_5MnCOR$ (R = CH_3, Ph)

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Thermally labile cobalt and manganese acyl compounds $L(CO)_3Co–COR$ (L = CO, PPh_3)[1] and $(CO)_5Mn–COR$[2] reportedly incorporate hydrosilanes and fragment to aldehyde RCHO plus metal silyl complex under mild conditions.[3] An alternative pathway in which Si–H adds across the acyl carbonyl and generates α-siloxyalkyl compounds has not been observed previously, even though such products are available by other pathways.

Cobalt examples, $L(CO)_3Co–CH(OSiR'_3)R$, that derive from silyl complexes and aldehydes are presumed intermediates during $Co_2(CO)_8$-catalyzed incorporation of CO and silane into alkenes and various organic oxygen-containing compounds.[4] Gladysz and co-workers[5] isolated several unstable manganese α-siloxyalkyl complexes after treating $(CO)_5Mn–SiMe_3$ with aldehydes. The resulting $(CO)_5Mn–CH(OSiMe_3)Ph$ slowly undergoes homolytic dissociation of the Mn–C bond,[6] and $(CO)_5Mn–CH(OSiMe_3)CH_3$ rapidly β-eliminates $(CO)_5MnH/CH_2{=}CHOSiMe_3$, although in the presence of CO it affords the α-siloxypropionyl derivative $(CO)_5Mn–COCH(OSiMe_3)CH_3$.[5b] Stable α-siloxyethyl complexes $Fp–CH(OSiHR'_2)CH_3$ (R'_2 = Et_2, Ph_2, MePh) are available through Rh(I)-catalyzed hydrosilation of $Cp(CO)_2Fe–COCH_3$[7] (and analogous thermally nonlabile acyl compounds)[8] with dihydrosilanes. We now report that acetyl and benzoyl manganese compounds $(CO)_5Mn–COR$ directly add dihydro- and monohydrosilanes under appropriate conditions and afford α-siloxyalkyl complexes.

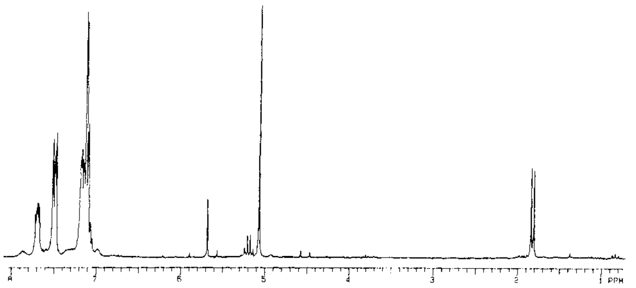
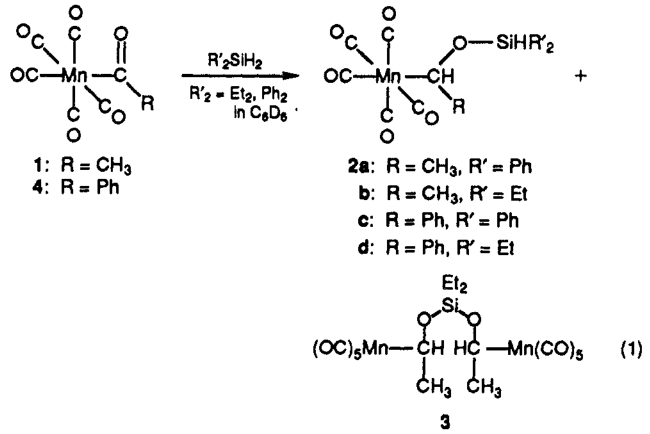


Figure 1. ^1H NMR spectrum (200 MHz) of $(CO)_5Mn–CH(OSiHPh_2)CH_3$ (**2a**): 50 mg (0.21 mmol) of $(CO)_5MnCOCH_3$ (**1**) and 116 mg (0.63 mmol) of Ph_2SiH_2 in 600 mg of C_6D_6 (15 min). Residual Ph_2SiH_2, δ 5.14.



1: R = CH_3
4: R = Ph

2a: R = CH_3, R' = Ph
b: R = CH_3, R' = Et
c: R = Ph, R' = Ph
d: R = Ph, R' = Et

3

(1)

Treatment of $(CO)_5Mn–COCH_3$ (**1**) in C_6D_6 with 1 to 3 equiv of Ph_2SiH_2 affords a light-orange solution within 5 min. Its ^1H and ^{13}C NMR and IR spectral data[9-11] are consistent with quantitative transformation of **1** to $(CO)_5Mn–CH(OSiHPh_2)(CH_3$ (**2a**) (91% yield ascertained by ^1H NMR spectroscopy with a Cp_2Fe internal standard). Figure 1, a ^1H NMR spectrum of this reaction mixture, illustrates the cleanliness of this reaction: no traces of acetaldehyde, its hydrosilated product $EtOSiHPh_2$, $(CO)_5Mn–SiHPh_2$,[12,13] a siloxyvinyl ether, or $Ph_2Si(H)Si(H)Ph_2$ (the anticipated dehydrogenative coupling product from excess Ph_2SiH_2[14]) are evident.

Instability of **2a** precludes its isolation. Solutions containing **2a** and excess Ph_2SiH_2 (2 equiv) slowly degrade over several hours

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[2] Dissociation of a terminal carbonyl from $(CO)_5MnCOCH_3$ (25 °C)[2a] is a prerequisite for subsequent reactions with PPh_3 and H_2,[2b] as well as for binuclear reductive elimination (of CH_3CHO) with metal hydride complexes.[2c] Analogous unsaturated acyl transient intermediates $(CO)_4Mn–COR$ bearing a vacant or weakly solvated coordination site also are implicated in binuclear reductive elimination between manganese alkyls $(CO)_5MnR$ and metal hydrides.[2d] (a) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101. Noack, K.; Ruch, M.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 345. Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166. Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405. (b) King, R. B.; King, A. D.; Iqbal, M. Z.; Frazier, C. C. *J. Am. Chem. Soc.* **1978**, *100*, 1687. Freudenberger, M. H.; Orchin, M. *Organometallics* **1982**, *1*, 1409. Sheeran, D. J.; Arenivar, J. D.; Orchin, M. *J. Organomet. Chem.* **1986**, *316*, 139. Chen, M. J.; Rathke, J. W. *Organometallics* **1987**, *6*, 1833. (c) Tam, W.; Wong, W.-K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589. Gladysz, J. A.; Tam, W.; Williams, G. M.; Johnson, D. L.; Parker, D. W. *Inorg. Chem.* **1979**, *18*, 1163. Ruszczyk, R. J.; Huang, B.-L.; Atwood, J. D. *J. Organomet. Chem.* **1986**, *299*, 205. (d) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. Nappa, M. J.; Santi, R.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *4*, 34. 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. Kovacs, I.; Hoff, C. D.; Ungvary, F.; Marko, L. *Organometallics* **1985**, *4*, 1347. Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466.

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

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[6] More stable $(CO)_5Re–CH(OSiMe_3)Ph$ and several chelated Mn and Re analogues have been fully characterized. (a) Selover, J. C.; Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1455. (b) 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. (c) $(CO)_5Mn–CH_2OSiMe_3$ has been prepared via other reaction chemistry. Brinkman, K. C; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056. For examples of other siloxymethyl complexes, see: Sisak, A.; Sampar-Szerencses, E.; Galamb, V.; Nemeth, L.; Ungvary, F.; Palyi, G. *Organometallics* **1989**, *8*, 1096 and references therein.

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[9] For **2a**: IR (C_6H_{12}) 2128 (br, SiH), 2108 (w), 2043 (w), 2011 (s), 1991 (s) cm^{-1} (CO); ^1H NMR (C_6D_6) δ 7.71 (m, 4 H, Ph), 7.20 (m, 6 H, Ph), 5.72 (s, SiH), 5.22 (q, *J* = 6.4 Hz, MnCH), 1.84 (d, *J* = 6.4 Hz, CH_3); ^{13}C NMR (C_6D_6) δ 212.4 (br s, CO), 71.1 (MnCH), 34.4 (MnCH*C*H_3).

[10] Our data for **2a** agree with that of Akita and co-workers.[7a] They generated **2a** by $Rh(PPh_3)_3Cl$-catalyzed hydrosilation of **1** in THF. We obtained identical results, clean production of **2a**, using 4.5% $Rh(PPh_3)_3Cl$ and 2 equiv of Ph_2SiH_2/**1**.

[11] NMR spectral data for **2a**, **2b**, and **3** closely resemble that of their stable Fp analogues, $Fp–CH(OSiHR'_2)CH_3$ and $[Fp–CH(CH_3)O]_2SiR'_2$ (R' = Ph or Et). All four mono- and bis(Fp–siloxyethyl) complexes were separated by size-exclusion chromatography and are fully characterized. Hanna, P. K.; Gregg, B. T.; Cutler, A. R. *Organometallics* **1990**, in press.

[12] Powell, J.; Sawyer, J. F.; Shiralian, M. *Organometallics* **1989**, *8*, 577.

[13] Spectral data are recorded in Table I (Supplementary Material).

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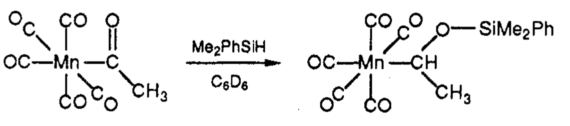
to dark red mixtures that exhibit paramagnetic broadening (and the presence of $Mn_2(CO)_{10}$ by IR spectroscopy). Excess silane stabilizes **2a**, since either adjusting the initial stoichiometry of **1**/Ph_2SiH_2 to 1:1 (even at 5 °C) or subsequently removing excess silane by size-exclusion chromatography (polystyrene beads) rapidly degrades **2a**. Conducting the reaction in the presence of CO (1 atm) slows formation of **2a** to 30 min without noticeably stabilizing the product.

Diethylsilane exhibits similar reactivity toward **1** (eq 1) except that the bis(manganese siloxyethyl) complex **3** also forms in a 1.5–2.0:1 ratio of **2b**/**3**. Structural assignments rest primarily on ^1H and ^{13}C NMR spectral data for their ethylidene groups.[11,13] Conducting the reaction in the presence of 4–5% $Rh(PPh_3)_3Cl$ as the catalyst selectively affords **2b**, although substantial amounts of $EtOSiHEt_2$ (up to 30%) and minor amounts of unidentified organics also form.[15] In the absence of $Rh(PPh_3)_3Cl$, neither $EtOSiHEt_2$ nor $(EtO)_2SiEt_2$ are detected by ^1H and ^{13}C NMR spectroscopy.

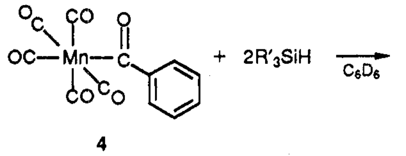
Using the monohydrosilane Me_2PhSiH permitted isolation and full characterization of the stable α-siloxyethyl complex $(CO)_5Mn-CH(OSiMe_2Ph)CH_3$ (**5**) (eq 2). NMR spectral monitoring of the orange solution within 15 min of mixing **1** and Me_2PhSiH (1:1) in C_6D_6 established the presence of **5** as the only organomanganese complex in at least 83% yield (vs Cp_2Fe) and the absence of CH_3CHO, $EtOSiMe_2Ph$, and $(CO)_5Mn-SiMe_2Ph$.[13] Column chromatography with hexane/silica gel afforded **5** as a brown oil (67% yield).[16]



(2)

1 5

Reactions between manganese benzoyl **4** and silanes are less straightforward. Ph_2SiH_2 rapidly and quantitatively consumes freshly recrystallized $(CO)_5MnCOPh$ (**4**) and gives the unstable siloxybenzyl complex **2c** (eq 1) (81% yield vs Cp_2Fe) and 5–8% of the silylether $PhCH_2OSiHPh_2$, but no detectable $(CO)_5Mn-SiHPh_2$. IR and ^1H, ^{13}C NMR spectral data for **2c**[13] closely match relevant absorptions for Gladysz's $(CO)_5Mn-CH(OSiMe_3)Ph$.[5a,6a] Et_2SiH_2 reacts analogously, except that the product $(CO)_5Mn-CH(OSiHEt_2)Ph$ (**2d**)[13] is less stable ($t_{1/2}$ = 1.5 h in the presence of 3 equiv of Et_2SiH_2). Both monohydrosilanes Me_2PhSiH and Et_3SiH cleanly transform **4** into their benzyl silyl ethers and manganese silyl complexes (eq 3). The observed yields (75–85%) under a variety of reaction conditions agree with the indicated stoichiometry. Although these reactions are slower (1–4 h), ^1H NMR spectral monitoring indicated the presence of at most trace concentrations of $(CO)_5Mn-CH(OSiR'_3)Ph$.



4

$PhCH_2OSiR'_3$ + $(OC)_5Mn-SiR'_3$ (3)

6a: $R'_3 = Me_2Ph$
b: $R'_3 = Et_3$

Directly hydrosilating an acyl ligand and forming the manganese α-siloxyalkyl complexes **2a–d** and **5** represents only one facet of manganese acyl/hydrosilane chemistry. Both **1** and **4** serve as extremely efficient aldehyde and ketone hydrosilation catalysts;[17,18] all silyl ethers noted were generated quantitatively with 2–4% **1** or **4** as catalyst and a 1:1 mixture of aldehyde plus hydrosilane.[19] Manganese acyls **1** and **4** also are more active and general catalysts than is $Rh(PPh_3)_3Cl$[7] toward hydrosilation of FpCOR with mono- and dihydrosilanes.[20] A straightforward albeit speculative mechanism for hydrosilation of $(CO)_5MnCOR$ (**1** and **4**) entails oxidative addition of hydrosilane at manganese;[3–5] the resulting transient $(CO)_4Mn(H)(SiR'_3)(COR)$ rearranges first to $(CO)_4(H)Mn{=}C(OSiR'_3)R$ (via a 1,3-silatropic shift)[21] and then to the coordinatively unsaturated α-siloxyalkyl intermediate $(CO)_4Mn-CH(OSiR'_3)R$. Studies in progress are concerned with further applications of manganese acyls as hydrosilation catalysts and with their mechanism(s) of action.

Acknowledgment. Support from the Department of Energy, Office of Basic Energy Science is gratefully acknowledged.

Supplementary Material Available: Table I containing ^1H and ^{13}C NMR and IR spectral assignments for **2a–d**, **3**, **5**, the silyl ethers, and the silylmanganese complexes $(CO)_5Mn-SiHPh_2$ and $(CO)_5Mn-SiMe_2Ph$ and microanalytical data (4 pages). Ordering information is given on any current masthead page.

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(15) Treatment of this reaction mixture with Fp^-Na^+ (−78 °C) and workup by silica gel chromatography affords the known[7b] $Fp-CH(OSiHEt_2)CH_3$ in 31% yield. Similar transmetalation[15a] of $(CO)_5MnCH_2OCH_3$ provides $FpCH_2OCH_3$ (65% yield). (a) Casey, C. P.; Cyr, C. R.; Anderson, R. L.; Martin, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053.

(16) For **5**: IR (C_6H_{12}) 2106 (w), 2044 (w), 2007 (s), 1987 (m) cm^{-1} (CO); ^1H NMR (C_6D_6) δ 7.56 (m, 2 H, Ph), 7.21 (m, 3 H, Ph), 5.07 (q, J = 6.5 Hz, MnCH), 1.74 (d, J = 6.5, MnCHCH_3), 0.33 (s, $SiMe_2$); ^{13}C NMR (C_6D_6) δ 133.8, 129.8, 128.0, 127.1 (Ph), 69.6 (MnCH), 35.0 (MnCHCH$_3$), −1.1, −1.6 ($SiMe_2$). Anal. Calcd for $C_{15}H_{15}O_6SiMn$: C, 48.13; H, 4.04. Found: C, 48.06; H, 4.03.

(17) (a) Both $Co_2(CO)_8$[4b] and $Co(CO)_4SiR_3$[3b] complexes induce catalytic hydrosilation of ketones,[17a] a sequence not previously documented with $(CO)_5Mn$ Complexes. Sakurai, H.; Miyoshi, K.; Nakadaira, Y. *Tetrahedron Lett.* **1977**, 2671. (b) $(CO)_5MnSiR_3/Mn_2(CO)_{10}$ systems catalytically hydrosilate alkenes and *O*-silate alcohols. Faltynek, R. A. *J. Organomet. Chem.* **1983**, *258*, C5. Hilal, H. S.; Abu-Eid, M.; Al-Subu, M.; Khalaf, S. *J. Mol. Catal.* **1987**, *39*, 1. Hilal, H. S.; Khalaf, S.; Al-Nouri, M.; Karmi, M. *Ibid.* **1986**, *35*, 137.

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(19) ^1H and ^{13}C NMR spectral data[13] agree with literature values or data obtained with commercially available samples.

(20) Aldehyde and FpCOR substrates inhibit hydrosilation at the manganese acyl catalyst (**1** or **4**) until all substrate is consumed. Results of ^1H and ^2H NMR spectral studies with **1** and **1**-d_3 (5–18% of reaction mixture) are particularly definitive. Reference 11 and unpublished observations.

(21) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.

π-Bond Energies in Protonated Schiff Bases

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The increased stretching frequency observed upon protonation of Schiff bases in the retinoids and other related systems is well documented.[2] Because the protonated Schiff base (PSB) has been thought to have a weaker π bond than its parent Schiff base (SB)

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(2) Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*; Academic Press: New York, 1963 and references cited therein.