Catalytic Hydrosilation of Organic Esters Using Manganese Carbonyl Acetyl Complexes, $(L)(CO)_4MnC(O)CH_3$ (L = CO, PPh_3)

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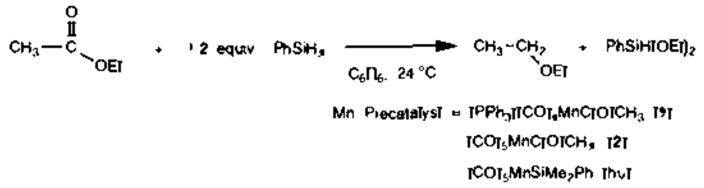
Although the hydrosilation of ketones is catalyzed readily by a number of transition-metal compounds,[1] organic esters have previously been regarded as inert.[2] Recently, Buchwald and co-workers established that catalytic quantities of the titanium complexes Cp_2TiCl_2/*n*-BuLi or $Ti(O\text{-}i\text{-}Pr)_4$ and $(EtO)_3SiH$ reduce esters to alcohols (after aqueous workup).[3] We now report that manganese acetyl complexes $(L)(CO)_4MnC(O)CH_3$ [L = PPh_3, (**1**); CO, (**2**)] catalyze the hydrosilation of esters RC(=O)OR′ to give successively silyl acetal $RCH(OSiR''_3)OR'$, then ether RCH_2OR' [4] or alkoxysilane products $RCH_2OSiR''_3$ and $R'OSiR''_3$.[5]

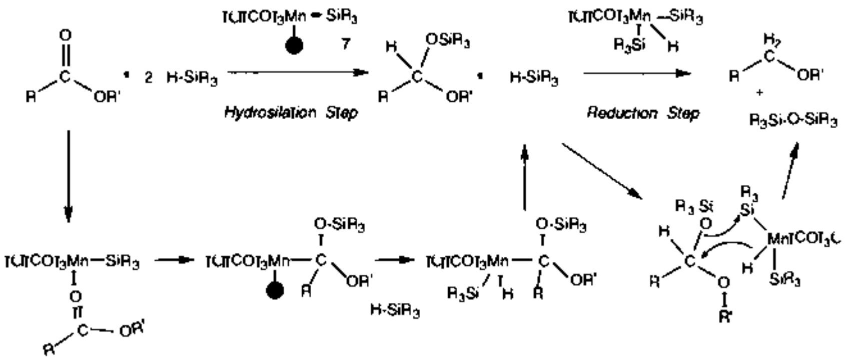
Addition of 1.5−3.0 mol % of **1** to a C_6D_6 solution containing ethyl acetate and $PhSiH_3$ exothermically transformed this ester within 15 min to ethyl ether (85%) and $PhSiH(OEt)_2$ (eq 1).[6]



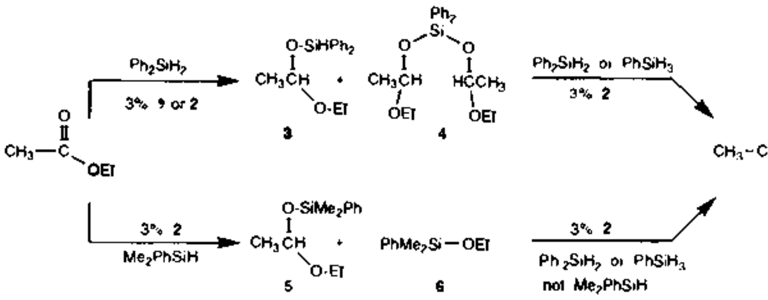
$$CH_3C(O)OEt + 1.2\ \text{equiv}\ PhSiH_3 \xrightarrow[C_6D_6,\ 24\ °C]{} CH_3CH_2OEt + PhSiH(OEt)_2 \qquad (1)$$

With the precatalyst **2**, the slower reactions quantitatively gave Et_2O after 1.5 h. Under similar conditions, the less effective $Mn(CO)_5CH_3$ and $Mn(CO)_5Br$ catalysts converted CH_3CO_2Et over 4 h to Et_2O (85 and 55%), in addition to the silyl acetals $PhSiH_{3-x}[OCH(CH_3)OEt]_x$ ($x = 1, 2$). In contrast, $Mn(CO)_5(SiMe_2Ph)$, $Mn(CO)_5(SiHPh_2)$, and $Mn_2(CO)_{10}$ were inactive.

Scheme 1



The role of silyl acetal intermediates during catalytic ester hydrosilation was probed by switching to Ph_2SiH_2 and $PhMe_2SiH$ (eqs 2 and 3). Hydrosilation of CH_3CO_2Et by Ph_2SiH_2 (1.2 equiv) and 3% **1** (30 min) gave $Ph_2SiH[OCH(CH_3)OEt]$ (**3**) (95% NMR yield; isolated, 81%) and $Ph_2SiH(OEt)$ (5%).[6] With 2.2 equiv of Ph_2SiH_2, however, **3** smoothly converted to ether and $(Ph_2HSi)_2O$. Using **2** as the catalyst (1.2 equiv of Ph_2SiH_2) again slowed the reaction (2.5 h to consume the ester) but also yielded a 2:1 mixture of **3** and $Ph_2Si[OCH(CH_3)OEt]_2$ (**4**) (eq 2). Reaction of this mixture with 1.2 equiv of $PhSiH_3$ and fresh **2** for 2 h produced Et_2O (88%) and the alkoxysilanes $Ph_2SiH(OEt)$ and $PhSiH(OEt)_2$.

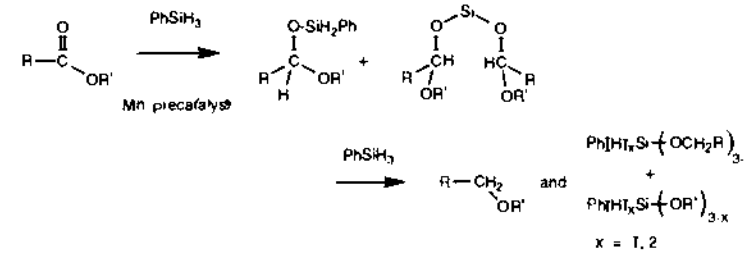


(2)

(3)

Treatment of CH_3CO_2Et with 1.2 equiv of $PhMe_2SiH$ and 3% **2** (eq 3) for 1.75 h gave $PhMe_2SiOCH(CH_3)OEt$ (**5**) (89% NMR yield; isolated, 84%) plus 12% $PhMe_2SiOCH_2CH_3$ (**6**). Using excess $PhMe_2SiH$ (2.2 equiv) in this reaction afforded a 2:1 mixture of **5** and **6** but no Et_2O. In contrast, Ph_2SiH_2 plus 3% **2** converted **5** over 2 h to Et_2O (68%), $PhMe_2SiOSiHPh_2$, and a 1:1 mixture of the alkoxysilanes $Ph_2SiH(OCH_2CH_3)$ and **6**. The yield of ether increased to 84% when 1.1 equiv of $PhSiH_3$ was used to reduce **5**.

The results of treating a variety of esters with $PhSiH_3$ and 3% **1** appear in Table 1. All esters were consumed within 1 h [the faster reactions (<0.5 h) were exothermic], although only the straight-chain esters cleanly yielded their ethers. The other esters gave mixtures of their ether and the alkoxysilanes $Ph(H)_xSi(OCH_2R)_{3-x}/Ph(H)_xSi(OR')_{3-x}$ ($x = 1, 2$), which resulted from further reduction of silyl acetal intermediates $PhH_xSi(OCHROR')_{3-x}$ (eq 4). In a few reactions, these alkoxysilanes predominated; methyl pivalate- and *p*-tolyl acetate-derived silyl acetals,[7] for example (Table 1, entries 9 and 10), slowly transformed into their alkoxysilane major products.



(4)

Silyl acetals are observable intermediates as **1** or **2** catalyze the hydrosilation then reduction of organic esters with hydrosilanes. Although detailed mechanistic studies are required, we offer the following working hypothesis for this two-stage process (Scheme 1). The precatalyst **1** or **2** first transforms to a

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[1] Reviews: (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley Interscience: New York, 1989; Part 2, Chapter 25. (b) Marciniec, B.; Guliñski, J. *J. Organomet. Chem.* **1993**, *446*, 15.

[2] (a) Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* **1976**, *111*, 43. Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671. (b) Metal halides under harsh or noncatalytic reaction conditions promote the hydrosilation of esters: Corriu, R. J. P.; Perz, R.; Reyé, C. *Tetrahedron* **1983**, *39*, 999. Calas, R. *Pure Appl. Chem.* **1966**, *13*, 61 and references therein. (c) For intramolecular hydrosilation of *β*-siloxyesters, see: Davis, A. P.; Hegarty, S. C. *J. Am. Chem. Soc.* **1992**, *114*, 2745 and references therein.

[3] (a) Berk, S. C.; Kreutzer, K. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 5093. (b) Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 3751. (c) Barr, K. J.; Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1994**, *59*, 4323. (d) Breeden, S. W.; Lawrence, N. J. *Synlett* **1994**, 833.

[4] Documented procedures for the reduction of esters give aldehydes and alcohols, RCH_2OH,[3] or less commonly ethers, RCH_2OR'. Hudlicky, M. *Reductions in Organic Chemistry*; Wiley: New York, 1984. Larock, R. C. *Comprehensive Organic Transformations*; VCH Publishers: New York, 1989; p 471.

[5] These readily available and stable manganese complexes also catalyze the alcoholysis of hydrosilanes[5a] and the hydrosilation of ketones[5b] and $CpFe(CO)_2C(O)R$.[5c,d] (a) Gregg, B. T.; Cutler, A. R. *Organometallics* **1994**, *13*, 1039. (b) DeBiase-Cavanaugh, M.; Gregg, B. T.; Cutler, A. R., manuscript submitted. (c) Gregg, B. T.; Hanna, P. K.; Crawford, E. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1991**, *113*, 384. (d) Hanna, P. K.; Gregg, B. T.; Tarazano, D. L.; Pinkes, J. R.; Cutler, A. R. In *Homogeneous Transition Metal Catalyzed Reactions*; Moser, W. R., Slocum, D. W., Eds.; Advances in Chemistry Series 230; American Chemical Society: Washington, DC, 1992; p 491.

[6] Typical reaction conditions: 0.50−1.00 mmol of ester, 1.0−1.2 molar equiv of hydrosilane, 1.5−3.0% of **1** or **2**, and $(Me_3Si)_2O$ internal standard were mixed in C_6D_6 (600 mg) and transferred to a NMR tube. Products were identified by their ^1H and $^{13}C\{^1H\}$ NMR spectra; reaction yields were quantified (± 5%) from their ^1H NMR spectra.

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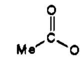
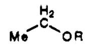
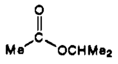
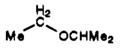
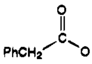
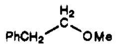
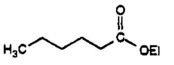
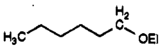
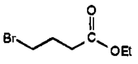
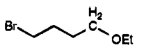
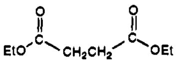
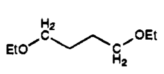
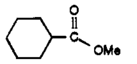
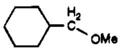
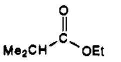
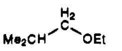
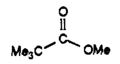
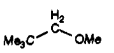
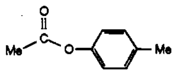
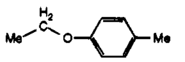
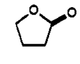
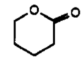
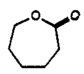
Table 1. $(PPh_3)(CO)_4MnC(O)CH_3$ (**1**)-Catalyzed Ester Hydrosilation with $PhSiH_3$

Entry	Ester	Consume Ester (min)[a]	Ether	NMR yield (%)[a]	Isolated yield (%)[a]
1.	 R = Me, Et	≤ 15		85[b]	
2.		≤ 30		95	
3.		25		92[b]	83[c]
4.		30		96	81[d]
5.		35		92	72[c]
6.		20		83	68[d]
7.		≤ 25		81	70[c]
8.		≤ 30		69	61[d]
9.		30 12 h		10[b,e] 34[f]	
10.		15 10 h		5[b,g] 12[h]	
11.		30		40[i]	35[d]
12.		30		43[i]	40[d]
13.		≤30		69[i]	65[d]

[a] Reaction conditions: see footnote 6. Reaction times: ester replaced by mixtures of silyl acetal, ether, and in some reactions alkoxysilanes. NMR yields obtained after 1 h; isolated yields for 20 mmol scale reactions after 2 h. [b] Analogous silyl acetals $Ph_2HSi[OCH(OR')R]$ were independently synthesized from RC(O)OR′. [c] 2.0 mmol scale reaction in 2.0 g C_6H_6; product was isolated by flash chromatography. [d] 20.0 mmol scale in 10 mL C_6H_6; product was distilled. [e] 40% silyl acetals, mostly $PhSiH[OCH(OMe)CMe_3]_2$, and 46% alkoxysilanes, mostly $PhSiH(OCH_2CMe_3)_2$ and $PhSiH(OMe)_2$. [f] Silyl acetals and alkoxysilanes: 16% and 50%, respectively. [g] Silyl acetals, $PhSiH[OCH(CH_3)(p\text{-}OC_6H_4Me)]_2$ (49%), and alkoxysilanes, $PhSiH(p\text{-}OCH_2C_6H_4Me)_2$/$PhSiH(OEt)_2$ (46%). [h] Silyl acetals and alkoxysilanes: 8% and 76%, respectively. [i] Integrations approximate; partial overlap with broadened absorptions due to ring-opening polymerization.

coordinatively unsaturated manganese silyl $(L)(CO)_3MnSiR_3$ (**7**), the active catalyst.[8] Catalyst **7** ligates and then inserts[1] the ester to give $(L)(CO)_3Mn[CR(OSiR_3)(OR')]$, coordinates $HSiR_3$, and reductively eliminates the silyl acetal $RCH(OSiR_3)OR'$ plus **7**. In the second stage, $(L)(CO)_3MnH(SiR_3)_2$ (i.e., **7** plus $HSiR_3$)[10] transfers hydride to the silyl acetal commensurate with release of disiloxane, $R_3SiOSiR_3$.[11]

The proposed activated catalyst **7** (L = CO) apparently can be generated by photolysis of $(CO)_5MnSiMe_2Ph$ in the presence of excess $PhSiH_3$ (eq 1). Irradiation of a C_6D_6 solution containing $CH_3C(O)OEt$, $PhSiH_3$ (0.50 mmol scale/1.2 equiv), and 3% $(CO)_5MnSiMe_2Ph$ at 350 nm (20 °C) thus quantitatively yielded Et_2O within 35 min. Presumably, the photochemically generated $(CO)_4MnSiMe_2Ph$[10c] transformed to **7** (L = CO) via established silane exchange.[8a]

Whether photochemically or thermally generated (from **1** or **2**), these manganese carbonyl active catalysts in the presence of $PhSiH_3$ clearly engender a powerful catalytic system for the hydrosilation then reduction of esters. Studies in progress address harnessing this reactivity through a second generation of catalytic systems that more efficiently couple ester hydrosilation with selective reduction to ethers or alkoxysilanes.

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

Supporting Information Available: Experimental details, NMR spectral data (Table 2), and elemental analyses of organosilicon products (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(7) Their NMR spectra resemble those of analogous Ph_2SiH_2-derived silyl acetals, $Ph_2SiH[OCH(OR')R]$ (Table 2, supporting information). Authentic samples of alkoxysilanes $PhSiH_{3-x}[OCH_2R]_x$ (x = 1−3; R = Me, Et, and CMe_3) and $PhSiH_{3-x}[p\text{-}OC_6H_4Me]_x$ (x = 1,2) were generated by **1**-catalyzed dehydrogenative silation of the requisite alcohol and $PhSiH_3$.[5a]

(8) Similar active catalysts have been implicated for SiH/SiD isotope exchange between $EtMe_2SiH$ and $PhMe_2SiD$,[8a] for autocatalytic hydrosilation of manganese acyl complexes,[8b,c] and for **1**- or **2**-catalyzed hydrosilation of FpC(O)R complexes or of aldehydes and ketones.[5b−d,9] (a) Gregg, B. T.; Cutler, A. R. *Organometallics* **1993**, *12*, 2006. (b) Hanna, P. K.; Gregg, B. T.; Cutler, A. R. *Organometallics* **1991**, *10*, 31. (c) Gregg, B. T.; Cutler, A. R., manuscript submitted.

(9) CO (1 atm) inhibits the hydrosilation of the manganese acetyl precatalysts.[8c] Adding the CO after they transformed to active catalysts also blocked catalytic hydrosilation of organometallic acyl complexes and ketones.[8a−c] Cyclopentene (1 equiv) has no effect on the ethyl acetate reaction with 3% **1**-$PhSiH_3$.

(10) Isolobal examples, e.g., $(H)(R_3Si)_2Co(CO)_3$ and $(H)(R_3Si)(R'_3Si)Co(CO)_3$, are characterized intermediates of similar oxidative addition/reductive elimination sequences.[1] (a) Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 995. Wrighton, M. S.; Seitz, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289. (b) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527 and references cited. (c) Examples of coordinatively unsaturated $(CO)_4MnSiR_3$ have been generated photochemically: Sullivan, R. J.; Brown, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 9155.

(11) A similar pathway evidently operates during the $RhCl(PPh_3)_3$-catalyzed reduction of $Cp(L)(CO)FeC(O)CH_3$ to $Cp(L)(CO)FeCH_2CH_3$ with Ph_2SiH_2 or $PhSiH_3$. In these reactions, hydride transfer from $(PPh_3)_2(Cl)RhH(SiR_3)$ to $Cp(L)(CO)FeCH(OSiR_3)CH_3$ is presumed to be concerted with respect to disiloxane loss. (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 in preparation.