Reactions of (CO)5MnSiMe3 and CO with aldehydes and cyclic ethers. Syntheses of functionalized pentacarbonylmanganese acyls and homologated organic compounds

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Organometallics **1984**, *3*, 147–155 147

A mixture of t-Bu_2SiCl_2 (1.1 g, 5 mmol), lithium (0.14 g, 20 mmol) and biphenyl (0.25 mmol, 5 mol % relative to the dichlorosilane used) in THF (10 mL) was stirred for 4 h and then refluxed for 3 h under Ar. The resulting wine red solution was worked up to give a viscous light yellow liquid. GLC analysis for the liquid showed that it was a mixture containing many products from which three products were isolated by a preparative GLC. The first eluted product was identified by the usual manner to be tetra-*tert*-butyldisilane, [H-t-Bu_2SiSi-t-Bu_2H]:[13,24] IR (neat, cm^{-1}) 2070 (SiH); NMr (δ) 1.03 (s), 1.17 (s, t-Bu, 36 H), 3.58 (s, SiH, 2 H); MW 286 (M^+ by MS). The other higher molecular weight products were found by IR and NMR to contain both SiH and *tert*-butyl groups, respectively, but the structures remain unclear.

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Reactions of $(CO)_5MnSi(CH_3)_3$ and CO with Aldehydes and Cyclic Ethers. Syntheses of Functionalized Pentacarbonylmanganese Acyls and Homologated Organic Compounds

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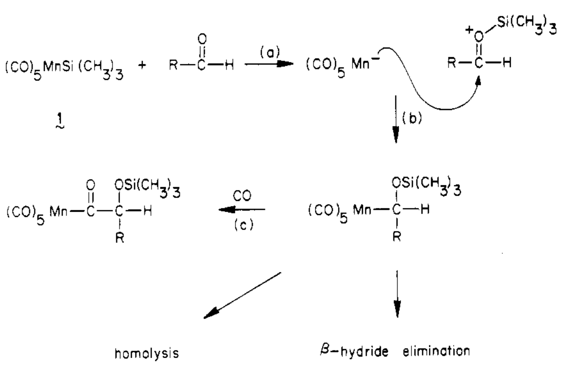
Reactions of $(CO)_5MnSi(CH_3)_3$ (**1**) and CO with aldehydes RCHO and cyclic ethers $\overline{OCH_2(CH_2)_nCH_2}$ (n = 0–2) give manganese acyls $(CO)_5MnCOCH(R)OSi(CH_3)_3$ and $(CO)_5MnCOCH_2(CH_2)_nCH_2OSi(CH_3)_3$ (n = 0, **6**; n = 1, **9**; n = 2, **10**) in 26–72% and 54–87% yields, respectively. Experiments conducted in the absence of CO show that these transformations proceed via labile alkyl intermediates $(CO)_5MnCH(R)OSi(CH_3)_3$ and $(CO)_5MnCH_2(CH_2)_nCH_2OSi(CH_3)_3$. Reactions of propylene oxide and cyclohexene oxide with **1** and CO give the manganese acyls expected from S_N2 ring opening. When the reaction of **1** with aldehydes is conducted in the presence of $(CO)_5MnH$ under careful conditions, homologated aldehydes $(CH_3)_3SiOCHRCHO$ form in 55–78% yields. Reaction of **1** and $(CO)_5MnH$ with oxetane gives $(CH_3)_3SiOCH_2CH_2CH_2CHO$ (**13**, 38%) and $(CH_3)_3SiO\overline{CHCH_2CH_2CH_2O}$ (**14**, 59%). Reaction of **9** and **10** with $[(CH_3CH_2)_2N]_3S^+Si(CH_3)_3F_2^-$ yields γ-butyrolactone (84–95%) and δ-valerolactone (60–85%), respectively. The mechanisms of these transformations, and their utility in organic and organometallic synthesis, are discussed.

Introduction

For some time, we have been engaged in the development of new stoichiometric reactions of transition-metal trialkylsilanes[2] which are of potential use in organic and organometallic synthesis.[3-8] Many of these reactions employ oxygen-containing organic substrates. The subsequent formation of a strong silicon–oxygen bond (106–127 kcal/mol)[9] provides a driving force for the formation of a weak[10] metal–carbon bond. The organometallic product may be isolable or trappable or may readily convert to organic and inorganic products.

Scheme I. Proposed Mechanism for the Formation of Manganese Acyls $(CO)_5MnCOCH(R)OSi(CH_3)_3$ from Aldehydes, 1, and CO



In this paper, we give a full account of our investigation of the reactions of $(CO)_5MnSi(CH_3)_3$ (**1**)[11] with aldehydes

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and cyclic ethers. With both types of substrates, carbon–oxygen bond cleavage occurs to give labile manganese alkyls which can be trapped under CO as stable manganese acyls. We also describe further transformations of these manganese acyls which afford lactones and functionalized aldehydes. A portion of this study has been communicated.[4]

Results

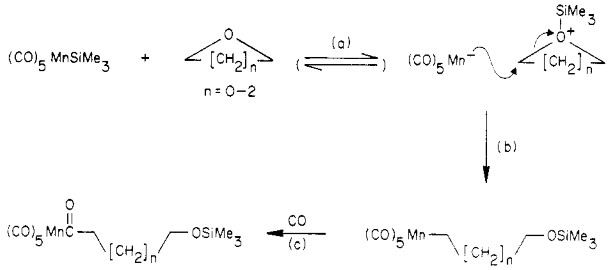
1. Syntheses of Organometallic Compounds. Silane $(CO)_5MnSi(CH_3)_3$ (**1**) was treated with 1.4 equiv of hydrocinnamaldehyde in CH_3CN under 350 psi of CO. The reaction was worked up after 36 h to give manganese acyl $(CO)_5MnCOCH(CH_2CH_2C_6H_5)OSi(CH_3)_3$ (**3**; entry 2, Table I) in 72% yield[12] as an analytically pure white powder. Similar reactions were conducted with **1** and acetaldehyde, cyclohexanecarboxaldehyde, and benzaldehyde under 200–350 psi of CO. Acyls of the formula $(CO)_5MnCOCH(R)OSi(CH_3)_3$ were isolated in fair to good yield (**2**, **4**, **5**; entries 1, 3, 4, Table I). Adducts **2**–**5** were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy, as summarized in Table I. One complex, **5**, has been synthesized by us previously by a completely different route.[13] The formation of **2**–**5** will be interpreted (Discussion) as involving the sequence of intermediates shown in Scheme I.

Several qualitative observations of relevance to Scheme I were made. Acetaldehyde reacted distinctly faster than the other aldehydes. Analysis of the reaction of **1** and CO with cyclohexanecarboxaldehyde by ^1H NMR (CD_3CN) showed the presence of cyclohexanecarboxaldehyde trimethylsilyl enol ether (δ 5.75 (s)), α-((trimethylsilyl)oxy)-α-cyclohexylacetaldehyde (δ 3.50 (d of d); **12c**, Table II below), and **4** in a ca. 1:2:2 ratio. Acrolein and **1** reacted, but manganese acyls were not obtained under conditions which led to **2**–**5**.

Silane **1** was treated with 1.9 equiv of oxetane in ether under 320 psi of CO. The reaction was worked up after 3 h to give manganese acyl $(CO)_5MnCOCH_2CH_2CH_2OSi(CH_3)_3$ (**9**; entry 8, Table I) in 83% yield as an analytically pure waxy white solid. Adduct **9** was characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy, as summarized in Table I.

Similar reactions were conducted with **1** and other cyclic ethers under 200–250 psi of CO. Epoxides ethylene oxide, propylene oxide, and cyclohexene oxide reacted to give acyls **6**–**8** (entries 5–7, Table I) in good yield. These substrates were somewhat less reactive than oxetane, so they were used in greater excess.[12] The propylene oxide adduct was principally one regioisomer, $(CO)_5MnCOCH_2CH(CH_3)OSi(CH_3)_3$ (**7**). However, a ca. 5% impurity, believed to be $(CO_5)MnCOCH(CH_3)CH_2OSi(CH_3)_3$, was detectable by ^{13}C NMR (69.9, 65.3, 12.3 ppm). The cyclohexene oxide adduct **8** was assigned trans stereochemistry on the basis of the characteristic[14] vicinal coupling, 9.5 Hz, of the two methine hydrogens. The reaction of **1** with isobutylene oxide under CO afforded a solid, presumably polymeric, product from which no organometallic complexes could be extracted.

Scheme II. Proposed Mechanism for the Formation of Manganese Acyls $(CO)_5MnCO(CH_2)_nCH_2OSi(CH_3)_3$ from Cyclic Ethers, 1, and CO



Reaction of **1** with neat THF under 250 psi of CO gave the acyl $(CO)_5MnCOCH_2CH_2CH_2CH_2OSi(CH_3)_3$ (**10**; entry 9, Table I) in 54% yield. This reaction was markedly slower than the previous ones and gave more byproducts. When THF was treated first with $(CH_3)_3SiI$ to generate alkyl iodide $ICH_2CH_2CH_2CH_2OSi(CH_3)_3$[15] and then $(CO)_5Mn^- K^+$/CO, acyl **10** was obtained in 81% yield. No reaction was observed between **1** and neat tetrahydropyran under 150 psi of CO. When this mixture was heated to 80 °C, a reaction occurred, but no manganese acyl product was found by IR spectroscopy.

The reaction of **1** and oxetane in the *absence* of CO was ^1H NMR monitored at 2 °C in CD_3CN. A new complex, **11**, with resonances at δ 3.53 (t, J = 7 Hz, 2 H), 2.94 (t, J = 7 Hz, 2 H), 1.64 (m, 2 H), and 0.07 (s, 9 H) formed in 55–80% spectroscopic yield over the course of 0.5 h. A nonvolatile, presumably polymeric product (δ 3.3–3.9 (m)), was also detected in some reactions. An IR spectrum of an aliquot (hexanes) showed absorptions at 2107 (w), 2010 (s), and 1990 (m) cm^{-1}. The CD_3CN solution of **11** was then treated with 250 psi of CO. Conversion of **11** to acyl **9** was observed by IR. When a separate solution of **11** was heated to 45 °C, rapid decomposition occurred. On the basis of these data, **11** was assigned the structure $(CO)_5MnCH_2CH_2CH_2OSi(CH_3)_3$. Hence, the formation of **6**–**10** will be interpreted (Discussion) as involving the sequence of intermediates shown in Scheme II.

2. Syntheses of Functionalized Aldehydes. Manganese acyls have been shown to be reduced by $(CO)_5MnH$ to the corresponding aldehydes.[16] However, when α-(silyloxy)acyls **2**–**5** were treated with $(CO)_5MnH$ at room temperature, only a very slow reaction took place. Upon heating, many byproducts formed in addition to the desired α-silyloxy aldehydes.

Interestingly, optimum yields of α-silyloxy aldehydes were obtained when **1** and the precursor aldehydes were reacted in the presence of $(CO)_5MnH$, as shown in eq 1. Identical yields were obtained in both the presence and absence of CO. Hence, reactions were conducted under a nitrogen atmosphere. The **1**/$(CO)_5MnH$ mixture could be conveniently generated, if desired, by the partial alcoholysis of **1**.[16a]

Considerable effort was invested in optimizing the conditions for eq 1. The reaction of acetaldehyde was complete within 0.5 h at room temperature and afforded **12a** (eq 1) in 76% yield. The other reactions were conducted at 5–13 °C for 1.5–10 days to minimize $HMn(CO)_5$ reduction of the starting aldehydes to alcohols and other

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(12) Unless noted otherwise, all yields are based upon the limiting reactant.

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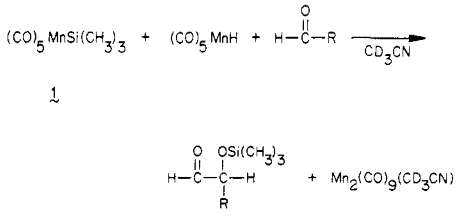


$$(CO)_5MnSi(CH_3)_3 + (CO)_5MnH + H{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow[CD_3CN]{} H{-}\overset{O}{\overset{\|}{C}}{-}\underset{R}{\underset{|}{\overset{OSi(CH_3)_3}{\overset{|}{C}}}}{-}H + Mn_2(CO)_9(CD_3CN) \quad (1)$$

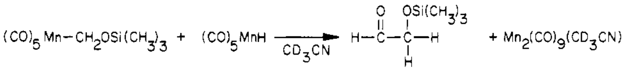
1

12a, R = CH_3; 76%
b R = $CH_2CH_2C_6H_5$; 78%
c R = cyclo—C_6H_{11}; 55%
d R = C_6H_5; 60%

side reactions. Because of the water and slight air sensitivity of aldehydes **12a–d**, yields were determined in situ by ^1H NMR (Experimental Section). Product identities were confirmed, following preparative GLC isolation, by ^1H NMR, ^{13}C NMR, IR, and mass spectroscopy (Table II).

The manganese-containing products were isolated from a preparative-scale synthesis of **12a** by column chromatography. Thus obtained were $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(CD_3CN)$[3b,17] (IR (cm^{-1}, hexanes): 2092 (w), 2025 (s), 2005 (s), 1989 (vs), 1965 (s), 1948 (m)) in 8% and 88% yields, respectively.

In order to test a logical mechanism for eq 1, the isolable manganese α-(silyloxy)alkyl $(CO)_5MnCH_2OSi(CH_3)_3$[18] was treated with $(CO)_5MnH$ (eq 2). The reaction was complete within 4.5 h at room temperature. Analysis by ^1H NMR indicated a 98% yield of aldehyde $(CH_3)_3SiOCH_2CHO$ (**12e**).[19] Product **12e** was subsequently isolated by preparative GLC and characterized as summarized in Table II.



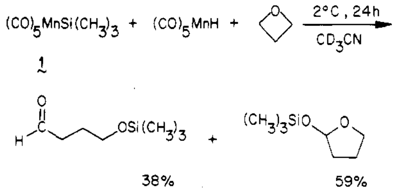
$$(CO)_5Mn{-}CH_2OSi(CH_3)_3 + (CO)_5MnH \xrightarrow[CD_3CN]{} H{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\underset{|}{\overset{OSi(CH_3)_3}{\overset{|}{C}}}}{-}H + Mn_2(CO)_9(CD_3CN) \quad (2)$$

12e (2)

Since eq 1 homologates an aldehyde to a new, α-silyloxy, aldehyde containing one additional carbon, we considered the possibility that additional, possibly catalytic, iterations might convert simple aldehydes into silylated carbohydrates. Unfortunately, all attempts to homologate α-silyloxy aldehydes such as **12a** or **12e** gave a myriad of organic products, as assayed by GLC and ^1H NMR, of which aldehydes were a very minor component.

A reaction analogous to eq 1 was attempted with oxetane as the organic substrate (eq 3). As shown, γ-silyloxy aldehyde **13** and the corresponding cyclic acetal **14** formed in a combined yield of 97%. When a possible intermediate in eq 3, alkyl **11**, was treated with $(CO)_5MnH$, **13** formed in 96% yield (eq 4).[12] This reaction mixture was allowed to stand several days before workup. During this period, **13** remained unchanged. No reaction took place between $(CO)_5MnH$ and oxetane over the course of 12 h at 5 °C or 6 h at room temperature.

Finally, attempts were made to convert the manganese acyls derived from cyclic ethers (**6–10**) into lactones. Treatment of **9** with the fluoride ion source[20,21] $[(CH_3CH_2)_2N]_3S^+Si(CH_3)_3F_2^-$ in THF gave γ-butyrolactone in 84–95% yields. A similar reaction of **10** in THF or



(3)

13 **14**

$$(CO)_5Mn{-}CH_2CH_2CH_2OSi(CH_3)_3 + (CO)_5MnH \xrightarrow[CD_3CN]{5°C,\ 0.5h} \mathbf{13}\quad 96\% \quad (4)$$

11

CH_3CN gave δ-valerolactone in 60–85% yields. IR spectra of both of these reactions showed characteristic lactone and $(CO)_5Mn^-$ absorptions. These transformations will be interpreted (Discussion) as involving the sequence of intermediates shown in Scheme III. Little or no β-lactone was obtained when acyls **6** and **7** were reacted under comparable conditions. Other commonly utilized fluoride ion sources gave lower lactone yields.

Discussion

The reactions summarized in Table I establish that $(CO)_5MnSi(CH_3)_3$ (**1**) is a versatile and useful reagent for the synthesis of manganese acyls from aldehydes and CO and cyclic ethers and CO. As discussed in our previous full papers,[3,5,6] it is highly probable that both types of reactions proceed via initial attack of the organic substrate oxygen upon the trimethylsilyl group of **1**. As shown in step a of Schemes I and II, this generates ion pairs which contain strong[9] silicon oxygen bonds. Such transformations are precedented: the reaction of **1** with $(CH_3)_3N$ yields the *isolable* ion pair $[(CH_3)_3NSi(CH_3)_3]^+(CO)Mn^-$.[11a]

We have previously studied the reaction of **1** with aldehydes in the *absence* of CO.[3,18] Aromatic aldehydes ArCHO are converted, in most cases, to detectable manganese alkyls $(CO)_5MnCH(Ar)OSi(CH_3)_3$ which homolyze at or below room temperature (Scheme I). Aliphatic aldehydes RCHO give, as the first detectable product, trimethylsilyl enol ethers which are net β-hydride elimination products of manganese alkyls $(CO)_5MnCH(R)OSi(CH_3)_3$. The trapping of these alkyls as acyls $(CO)_5MnCOCH(R)OSi(CH_3)_3$ (Scheme I, step c) constitutes important evidence for their intermediacy. The reaction of **1**, butyraldehyde, and ^{13}CO gives the acyl *cis*-$(CO)_4(^{13}CO)MnCOCH(CH_2CH_2CH_3)OSi(CH_3)_3$.[3] Hence, acyls **2–5** are likely formed via a conventional Calderazzo[22] mechanism (see Scheme IV).

In Scheme I, the best yields of manganese acyls would be expected from aldehydes which (1) undergo facile carbonyl addition reactions (steps a and b) and (2) do not contain alkyl groups –R which would retard the CO insertion step c. Accordingly, acetaldehyde, which hydrates more readily than other aliphatic aldehydes,[23] is converted to acyl **2** in good yield. Phenyl substituents at C_α have been shown to retard the rate of carbonylation of manganese and other metal alkyls.[24] Hence, benzaldehyde gives acyl **5** in only fair yield. It should be also noted that, with a single exception,[13] α-silyloxy, α-alkoxy, and other electron-withdrawing substituents have been found to retard the carbonylation rate of manganese alkyls.[18,24]

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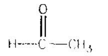
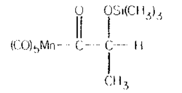
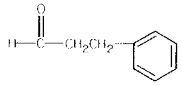
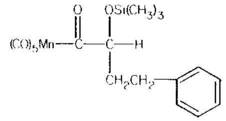
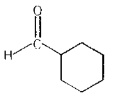
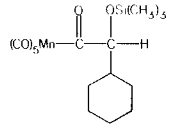
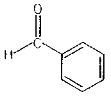
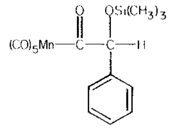
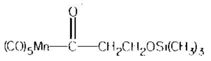
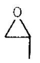
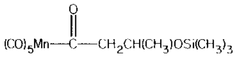
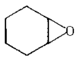
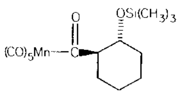
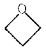
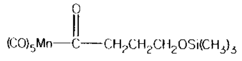
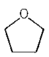
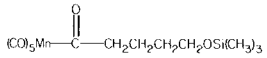
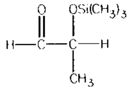
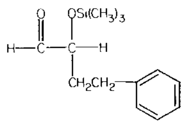
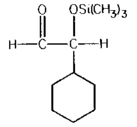
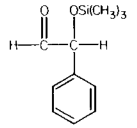
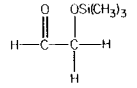
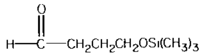
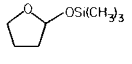
Table I. Spectroscopic Characterization of New $(CO)_5MnCOR$ Complexes Prepared from $(CO)_5MnSi(CH_3)_3$ (1) and Aldehydes and Cyclic Ethers under CO

entry	organic substrate	product	yield, %	IR,[a] cm^{-1}	^1H NMR,[b,c] δ	^{13}C NMR,[d] ppm
1		 **2**	68	2119 (w), 2052 (w), 2027 (s), 2015 (s), 2005 (m, sh), 1647 (m)	3.64 (q, J = 7 Hz, 1 H), 1.07 (d, J = 7 Hz, 3 H), 0.16 (s, 9 H)	271.1 (C=O), 209.6 (C≡O), 82.8 (CH), 18.9 (CCH_3), −0.7 $(SiCH_3)^{e-g}$
2		 **3**	72	2118 (w), 2049 (w), 2029 (s), 2013 (s), 2006 (m, sh), 1643 (m)	7.3–7.1 (m, 5 H), 3.57 (d of d, J = 6, 7 Hz, 1 H), 2.58 (m, 2 H), 1.82 (m, 2 H), 0.15 (s, 9 H)	269.9 (C=O), 209.5 (cis C≡O), 209.0 (trans C≡O), 141.2 (ipso C_6H_5), 2 × 128.0, 125.5 (C_6H_5), 86.2 (CH), 35.0, 30.0 (CH_2), −0.7 $(SiCH_3)^{e-g}$
3		 **4**	26	2118 (w), 2051 (w, sh), 2029 (s), 2010 (s), 2004 (m, sh), 1649 (w)	3.23 (d, J = 8 Hz, 1 H), 1.95–1.50 (m, 6 H), 1.3–0.8 (m, 5 H), 0.16 (s, 9 H)	267.1 (C=O), 209.5 (cis C≡O), 208.7 (trans C≡O), 92.1 (CHOSi), 37.6 (CHCC′C″), 27.9, 27.5, 2 × 25.6, 25.1 (ring), −0.8 $(SiCH_3)^{e-g}$
4		 **5**	39	2114 (w), 2050 (w), 2022 (s), 2014 (vs), 2001 (s), 1644 (w)	7.4–7.3 (m, 5 H), 4.69 (s, 1 H), 0.13 (s, 9 H)[h,i]	268.4 (C=O), 211.7 (C≡O), 139.4 (ipso C_6H_5), 129.8, 129.1, 128.1 (C_6H_5), 91.0 (CH) −0.2 $(SiCH_3)^{i,j}$
5		 **6**	85	2117 (m), 2054 (m), 2015 (vs), 2005 (s, sh), 1649 (mw)	3.70 (t, J = 6 Hz, 2 H), 3.13 (t, J = 6 Hz, 2 H), 0.16 (s, 9 H)	258.6 (C=O), 209.3 (cis C≡O), 208.2 (trans C≡O), 68.4, 58.5 (CH_2), −0.6 $(SiCH_3)^{b,e}$
6		 **7**	85	2118 (m), 2053 (m), 2017 (vs), 2006 (s, sh), 1652 (m)	4.19 (m, 1 H), 3.23 (d of d, J = 7, 16 Hz, 1 H), 2.88 (d of d, J = 5, 16 Hz, 1 H), 1.07 (d, J = 6 Hz, 3 H), 0.06 (s, 9 H)	257.2 (C=O), 209.1 (cis C≡O), 208.0 (trans C≡O), 75.6 (CH), 64.6 (CH_2), 23.5 (CCH_3), −0.1 $(SiCH_3)^{b}$
7		 **8**	87	2115 (m), 2053 (m), 2011 (s), 1997 (s), 1982 (m), 1650 (m)	3.74 (m, 1 H),[k] 3.12 (m, 1 H), 2.0–1.6 (m, 4 H), 1.3–0.8 (m, 4 H), 0.04 (s, 9 H)	262.2 (C=O), 209.7 (cis C≡O), 208.7 (trans C≡O), 80.7 (COSi), 72.6 (CCOMn), 35.4, 26.9, 24.9, 24.5 (CH_2), 0.0 $(SiCH_3)^{e,f,l}$
8		 **9**	83	2116 (m), 2051 (m), 2010 (vs), 2003 (s, sh), 1650 (m)	3.50 (t, J = 7 Hz, 2 H), 3.00 (t, J = 7 Hz, 2 H), 1.67 (pentet, J = 7 Hz, 2 H), 0.06 (s, 9 H)	256.5 (C=O), 209.8 (cis C≡O), 208.5 (trans C≡O), 63.8, 61.7, 27.7 (CH_2), −0.3 $(SiCH_3)^{e-g}$
9		 **10**	54	2117 (m), 2052 (m), 2010 (vs), 2003 (s, sh), 1646 (m)	3.52 (t, J = 6 Hz, 2 H), 2.94 (t, J = 6 Hz, 2 H), 1.65–1.35 (m, 4 H), 0.07 (s, 9 H)	256.2 (C=O), 209.8 (C≡O), 67.1, 62.1, 31.7, 20.9 (CH_2), −0.9 $(SiCH_3)^{e,f,l}$

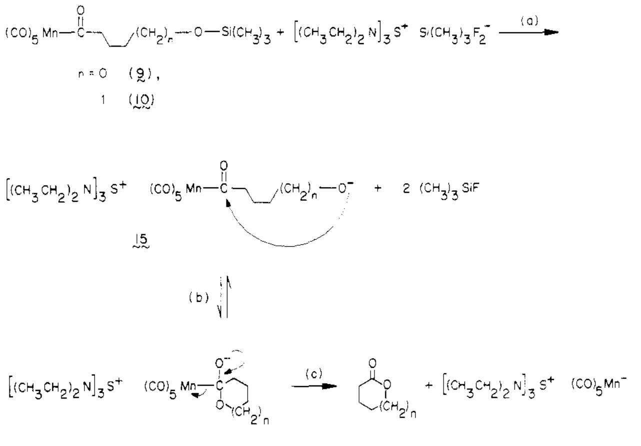
[a] In hexanes. [b] In $CDCl_3$. [c] At 200 MHz and ambient probe temperature unless noted. [d] At 50 MHz and ambient probe temperature unless noted. [e] $Cr(acac)_3$ added. [f] In CD_2Cl_2. [g] At −50 °C. [h] At 300 MHz. [i] In CD_3CN. [j] At 75 MHz. [k] A 300 MHz decoupling experiment in C_6D_6 showed the methine resonances at δ 3.85 (ddd) and 3.09 (m) with $^3J_{HH}$ = 9.5 Hz. Other data: δ 1.85 (m, 1 H), 1.71 (m, 1 H), 1.37 (m, 2 H), 1.17 (m, 1 H), 0.91 (m, 3 H), 0.15 (s, 9 H). [l] At 10 °C.

Table II. Spectroscopic Characterization of Silyloxy Aldehydes and Related Compounds

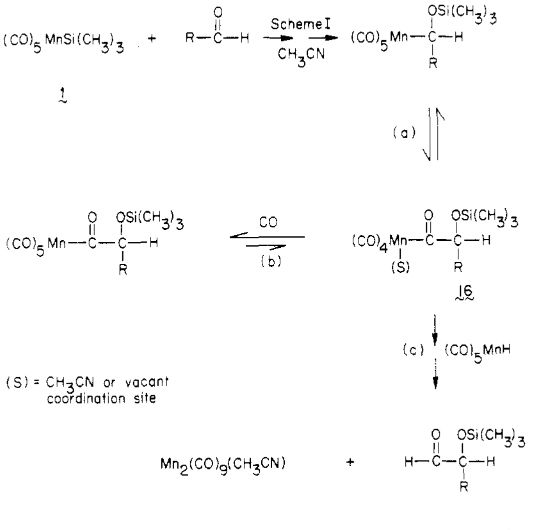
compd	IR (neat, cm^{-1}), $\nu_{C=O}$	^{1}H NMR,[a] δ	^{13}C NMR,[b] ppm	mass spectrum, *m/e* (70 eV)
 **12a**	1741	9.53 (s, 1 H), 4.18 (q, J = 7 Hz, 1 H), 1.21 (d, J = 7 Hz, 3 H), 0.12 (s, 9 H)[c]	205.4 (C=O), 74.5 (Cα), 18.5 (Cβ), 0.1 (SiCH$_3$)[c]	131 (M$^+$ − 15, 21%), 117 (M$^+$ − 29, 40%), 73 ((CH$_3$)$_3$Si$^+$, 100%)
 **12b**	1738	9.54 (s, 1 H), 7.4–7.1 (m, 5 H), 4.10 (t, J = 5 Hz, 1 H), 2.8–2.6 (m, 2 H), 2.0–1.8 (m, 2 H), 0.13 (s, 9 H)[d]	205.0 (C=O), 143.1 (ipso C$_6$H$_5$), 129.8, 129.7, 127.3 (C$_6$H$_5$), 78.0 (Cα), 34.7, 31.7 (Cβ, Cγ), 0.7 (SiCH$_3$)[d]	236 (M$^+$, 1%), 221 (M$^+$ − 15, 18%), 207 (M$^+$ − 29, 100%), 91 (C$_7$H$_7$$^+$, 100%)
 **12c**	1733	9.44 (d, J = 2 Hz, 1 H), 3.50 (dd, J = 2, 5 Hz, 1 H), 1.60–1.44 (m, 6 H), 1.19–0.96 (m, 5 H), 0.03 (s, 9 H)[e]	203.2 (C=O), 81.7 (Cα), 40.5 (Cβ), 28.8, 27.2, 26.1, 26.0, 25.9 (ring), −0.4 (SiCH$_3$)[e]	199 (M$^+$ − 15, 10%), 185 (M$^+$ − 29, 79%), 73 ((CH$_3$)$_3$Si$^+$, 100%)
 **12d**	1737	9.55 (s, 1 H), 7.40–7.25 (m, 5 H), 5.17 (s, 1 H), 0.12 (s, 9 H)[c]	201.3 (C=O), 138.5 (ipso C$_6$H$_5$), 130.1, 129.7, 128.3 (C$_6$H$_5$), 80.8 (Cα), 0.1 (SiCH$_3$)[c]	193 (M$^+$ − 15, 10%), 179 (M$^+$ − 29, 38%), 73 ((CH$_3$)$_3$Si$^+$, 100%)
 **12e**	1738	9.59 (s, 1 H), 4.26 (s, 1 H), 0.11 (s, 9 H)[c]	202.5 (C=O), 69.8 (Cα), −0.6 (SiCH$_3$)[c]	117 (M$^+$ − 15, 44%), 103 (M$^+$ − 29, 47%), 73 ((CH$_3$)$_3$Si$^+$, 100%)
 $H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2CH_2CH_2OSi(CH_3)_3$ **13**	1727	9.71 (t, J = 1 Hz, 1 H), 3.61 (t, J = 7 Hz, 2 H), 2.44 (dt, J = 1, 6 Hz, 2 H), 1.79 (pseudopentet, J = 6.5 Hz, 2 H), 0.08 (s, 9 H)[c]	204.5 (C=O), 62.5 (Cγ), 41.3 (Cα), 26.2 (Cβ), −0.6 (SiCH$_3$)[c]	145 (M$^+$ − 15, 26%), 75 ((CH$_3$)$_2$SiOH$^+$, 100%)[f]
 **14**		5.57–5.47 (m, 1 H), 4.02–3.60 (m, 2 H), 2.03–1.67 (m, 4 H), 0.12 (s, 9 H)[c]	99.6 (OCO), 67.7 (OCH$_2$), 35.6 (OCH$_2$CH$_2$CH$_2$), 23.9 (OCH$_2$CH$_2$), 0.2 (SiCH$_3$)[c]	159 (M$^+$ − 1, 4%), 145 (M$^+$ − 15, 49%), 75 ((CH$_3$)$_2$SiOH$^+$, 100%)[f]

[a] At 300 MHz and ambient probe temperature. [b] At 75 MHz and ambient probe temperature. [c] In CD$_3$CN. [d] In CDCl$_3$. [e] In benzene-d_6. [f] See: Sharkey, A. G.; Friedel, R. A.; Langer, S. H. *Anal. Chem.* **1957**, *29*, 770.

Scheme III. Proposed Mechanism of Lactone Formation



Scheme IV. Proposed Mechanism of Aldehyde Homologation



Thus the α-silyloxy substituents adversely affect the rate of step c in Scheme I.

The formation of alkyl $(CO)_5MnCH_2CH_2CH_2OSi(CH_3)_3$ (**11**) from **1** and oxetane, and its subsequent conversion to acyl **9**, constitutes excellent evidence for the intermediacy of manganese alkyls in Scheme II. The ring opening step b has abundant precedent in the reaction of other $(CH_3)_3Si$–X (X = I, Br, CF_3SO_3, CN) reagents with cyclic ethers.[14,25] Since the resulting manganese alkyls have α-silyloxy substituents at positions more remote from the metal (β, γ, δ) than in Scheme I, the carbonylation step c should not be significantly retarded.

The superior reactivity of oxetane in Scheme II can be rationalized. Oxetane has the greatest *solution* basicity of the simple cyclic ethers,[26] and its strain energy is comparable to that of ethylene oxide.[27] Hence steps a and b of Scheme II should occur rapidly. Tetrahydrofuran is more basic than ethylene oxide.[26] Its lower reactivity is likely attributable to a less rapid ring opening step b. The regiochemistry observed in the reaction with propylene oxide (Table I, entry 6), and the trans ring opening of cyclohexene oxide, indicate that step b generally follows a S_N2 mechanism.

Together, **1** and $(CO)_5MnH$ effect the novel reductive aldehyde homologation show in eq 1. Normally several steps, utilizing an "acyl anion" equivalent,[28] would be needed to accomplish this transformation. The reaction of $(CO)_5MnCH_2OSi(CH_3)_3$ and $(CO)_5MnH$ to give $(CH_3)_3SiOCH_2CHO$ (eq 2) provides good evidence that eq 1 proceeds via initial formation of an α-silyloxy manganese alkyl.

The question remains as to why homologated aldehydes are obtained in lower yields and at reduced rates from the reactions of acyls **2–5** with $(CO)_5MnH$. We rationalize these results as outlined in Scheme IV. Studies of Norton, Bergman, and Halpern have shown that metal hydrides are exceptionally reactive toward transition-metal alkyls and acyls with vacant or weakly solvated coordination sites.[16c,29] For instance, evidence has been obtained that the binuclear reductive elimination of aldehydes RCHO from $(\eta\text{-}C_5H_5)Mo(CO)_3R$ and $(\eta\text{-}C_5H_5)Mo(CO)_3H$ involves initial formation of the coordinatively unsaturated acyl $(\eta\text{-}C_5H_5)Mo(CO)_2(COR)$.[29b] A mechanistically similar reaction occurs between $(CO)_5MnCH_2\text{-}p\text{-}C_6H_4OCH_3$ and $(CO)_5MnH$ in CH_3CN.[16c] We therefore suggest that alkyls $(CO)_5MnCH(R)OSi(CH_3)_3$ are likewise in equilibrium with coordinatively unsaturated manganese acyls (**16**, Scheme IV) and that subsequent rapid aldehyde elimination occurs in the presence of $(CO)_5MnH$. Our data further indicate that the vacant (or weakly solvated) coordination site in **16** is more rapidly scavanged by $(CO)_5MnH$ than the CO dissolved under 300 psi in CH_3CN. When **16** is generated in the presence of CO alone, manganese acyls form as in Scheme I. However, these acyls apparently do not readily dissociate CO. Their reaction with $(CO)_5MnH$ is therefore sluggish, and side reactions have a greater opportunity to occur.

We attribute the reluctance of α-silyloxy aldehydes to undergo further homologation to the combined inhibiting effect of both α- and β-silyloxy groups on the rate of step a of Scheme IV. Precedented types of side reactions which can then compete include manganese–carbon bond homolysis,[3,16] CO dissociation from the intermediate manganese alkyl,[16c] and reduction of the aldehyde starting material or product by $(CO)_5MnH$ to the corresponding alcohol.[30]

The reactions of **1** and $(CO)_5MnH$ with oxetane (eq 3) gives a high overall yield of the acyclic (**13**) and hemiacetal (**14**) forms of silylated γ-hydroxybutanal. The control experiment in eq 4 shows that **14** does not arise from alkyl **11** and that **13** does not equilibrate with **14**. Since $(CO)_5MnH$ is a strong enough acid to open aziridine rings[31] and $(CO)_4CoH$ has been shown cleave epoxide carbon–oxygen bonds,[32] we had thought that **14** might arise via the initial reaction of $(CO)_5MnH$ with oxetane. However, $(CO)_5MnH$ and oxetane do not react under the conditions of eq 3, so we are at present unable to mechanistically account for the formation of **14**.

The conversion of acyls **9** and **10** to lactones (Scheme III) constitutes, when combined with Scheme II, a net ring expansion/carbonylation of cyclic ethers. Similar overall transformations, including the $Rh(Cl)(CO)(PPh_3)_2$-cata-

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[25] (a) Sakurai, H.; Sasaki, K.; Hosomi, A. *Tetrahedron Lett.* **1980**, *21*, 2329. (b) Detty, M. R.; Seidler, M. D. *Ibid.* **1982**, *23*, 2543. (c) Mullis, J. C.; Weber, W. P. *J. Org. Chem.* **1982**, *47*, 2873.

[26] Gritter, R. J. In "Chemistry of the Ether Linkage"; Patai, S., Ed.; Interscience: New York, 1967; pp 378–380.

[27] Eigenmann, H. K.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1973**, *77*, 1687.

[28] Hase, T. A.; Koskimies, J. K. *Aldrichim. Acta* **1982**, *15*, 35.

[29] (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (b) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447.

[30] Vaughn, G. D., unpublished results, UCLA and University of Utah; corresponding reduction with $(CO)_4CoH$: Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259.

[31] Beck, W.; Danzer, W.; Höfer, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 77.

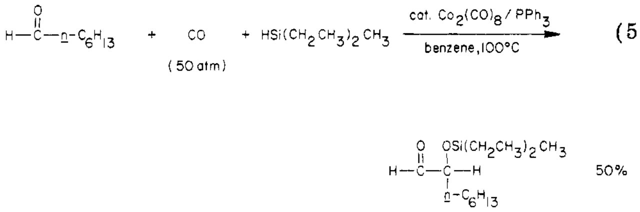
[32] Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 1460.

[33] Kamiya, Y.; Kawato, K.; Ohta, H. *Chem. Lett.* **1980**, 1549.

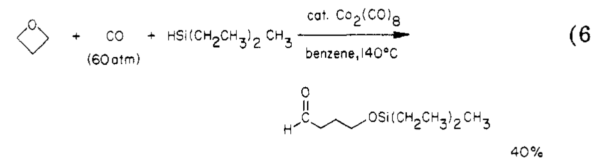
lyzed carbonylation of epoxides to β-lactones,[31] have been previously reported. We suggest that the reagent $[(CH_3CH_2)_2N]_3S^+Si(CH_3)_3F_2^-$ first effects the precedented[20] conversion of **9** and **10** to alkoxides **15** as shown in step a of Scheme III. Alkoxides $R'O^-$ have been previously shown to react with acyls $(CO)_5MnCOR$ to give esters RCO_2R'.[34] Hence, we propose that lactones are generated via the subsequent addition–elimination steps b and c.

Several observations of other researchers are particularly relevant to this study. First, Orchin has shown that formaldehyde reacts with $(CO)_4CoH$ and CO at 0 °C to give $HOCH_2CHO$ in 60–90% yields based upon $(CO)_4CoH$ consumed.[35] This transformation was proposed to occur via a Scheme IV type mechanism. However, most aldehydes are reduced to the corresponding alcohols when treated with $(CO)_4CoH$.[30] Second, Heck has reported that ethylene oxide and oxetane react with $(CO)_4CoH$ and CO at 0 °C to give labile hydroxyacyls $(CO)_4CoCOCH_2(CH_2)_nCH_2OH$ (n = 0, 1).[32] These reactions are logically interpreted as proceeding via a Scheme II type mechanism. Our methodology has the advantages of utilizing an easily handled, shelf-stable reagent which gives, under CO, readily isolated organometallic products.

Finally, elegant $Co_2(CO)_8$-catalyzed reactions of aldehydes and cyclic ethers with CO and $HSi(CH_2CH_3)_2CH_3$ have been developed by Murai.[36] Two representative transformations are given in eq 5 and 6. Although the reaction conditions are harsher than those employed in this study, obvious benefits accrue from the *catalytic* use of metal. The stoichiometric reactions described above provide excellent precedent for the mechanisms which have been proposed[36] for eq 5 and 6.



(5)



(6)

Conclusion

The reactions of 1 and CO with aldehydes and cyclic ethers provide, respectively, new and improved methodologies for the incorporation of these organic substrates into organometallic molecules. To our knowledge, there exists only one other *general* means for synthesizing organometalic complexes from aldehydes.[7] The functionalized manganese acyls which are obtained from 1 can be further transformed into useful homologated organic molecules. Additional applications of metal silane reagents in organic and organometallic synthesis are under active investigation.

Experimental Section

General Data. All reactions and manipulations were carried out under an atmosphere of dry N_2 or CO. THF and ether were purified by distillation from benzophenone ketyl. Hexane, CH_3CN and CD_3CN, and ethyl acetate were distilled from potassium, CaH_2, and $CaSO_4$, respectively. Other deuterated solvents and CO were used without purification. Silica gel and florisil were flame heated and vacuum dried before use.

IR spectra were recorded on a Perkin-Elmer Model 521 or 1500 (FT) spectrometer. ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Brüker WP-200 spectrometer or at 300 and 75 MHz, respectively, on a Varian SC 300 spectrometer. They were referenced to the deuterated solvent employed. Mass spectra were obtained on AEI MS-9, MS-25, or VG Micromass 7070 spectrometer. Analytical gas chromatography was conducted with a Hewlett-Packard 5720A chromatograph and 3380A integrator. Microanalyses were conducted by Galbraith Laboratories or Schwarzkopf Microanalytical Laboratories.

Starting Materials. Silane $(CO)_5MnSi(CH_3)_3$ (**1**) was prepared as previously described.[6,11b,c] Hydride $(CO)_5MnH$ was synthesized from $(CO)_5Mn^-K^+$ ($Mn_2(CO)_{10}$/NaK/ether)[37] and 85% H_3PO_4[38] or generated in situ in CH_3CN from $(CO)_5MnSi(CH_3)_3$ and t-C_4H_9OH.[16a] Alkyl $(CO)_5MnCH_2OSi(CH_3)_3$ and $[(CH_3CH_2)_2N]_3S^+Si(CH_3)_3F_2^-$ were prepared by literature methods.[18,20] Silane $(CH_3)_3SiI$ was obtained from Petrarch Systems and was distilled from CaH_2 and stored over fine granular copper under N_2.

Ethylene oxide, propylene oxide, isobutylene oxide, cyclohexene oxide, and oxetane were stirred with lithium wire and distilled prior to use. Tetrahydropyran, acrolein, and benzaldehyde were stirred with and (vacuum) distilled from CaH_2. Hydrocinnamaldehyde and cyclohexane carboxaldehyde were vacuum distilled from anhydrous $CaSO_4$. Acetaldehyde was twice distilled from $CaSO_4$. 2-Methyltetrahydrofuran was distilled from benzophenone ketyl.

Standards $(C_6H_5)_3CH$, biphenyl, and 2-methylnaphthalene were obtained from Aldrich and recrystallized from methanol before use. In addition, the latter compound was sublimed. Silane $(C_6H_5)_3SiCH_3$ was prepared from $(C_6H_5)_3SiCl$ and CH_3MgBr analogously to the literature procedure.[39]

Reaction of 1 with Acetaldehyde and CO. A mixture of 0.11 mL (2.0 mmol) of acetaldehyde and 0.90 mL of CH_3CN was syringed into a Fischer-Porter bottle which had been charged with a stir bar and 134 mg (0.50 mmol) of **1**. The bottle was pressurized with 200 psi of CO, and the reaction was stirred for 12 h. The volatiles were removed under vacuum. The resulting yellow oil was chromatographed on silica gel in hexane (to remove $Mn_2(CO)_{10}$) followed by 90:10 hexane/ethyl acetate. This gave 115 mg (0.34 mmol, 68%) of $(CO)_5MnCOCH(CH_3)OSi(CH_3)_3$ (**2**) as a colorless liquid which solidified upon cooling (mp 16.5–18 °C). Anal. Calcd for $C_{11}H_{12}O_7MnSi$: C, 38.95; H, 3.57. Found: C, 39.00; H, 3.69.

Reaction of 1 with Hydrocinnamaldehyde and CO. A mixture of 0.240 mL (1.83 mmol) of hydrocinnamaldehyde and 0.70 mL of CH_3CN was syringed into a Fischer-Porter bottle which had been charged with a stir bar and 350 mg (1.31 mmol) of **1**. The bottle was pressurized with 350 psi of CO, and the reaction was stirred for 36 h; an IR specltrum of an aliquot taken after 12 h showed the reaction to be not quite complete. The solvent was removed under vacuum. The resulting yellow oil was chromatographed on Florisil in hexane followed by 90:10 hexane/ethyl acetate. This gave 402 mg (0.94 mmol, 72%) of $(CO)_5MnCOCH(CH_2CH_2C_6H_5)OSi(CH_3)_3$ (**3**) as a white powoder, mp 58.5–62 °C. Anal. Calcd for $C_{18}H_{19}MnO_2Si$: C, 50.26; H, 4.45; Mn, 12.76, Si, 6.53. Found: C, 50.37, H, 4.53; Mn, 12.68; Si, 6.65.

Reaction of 1 with Cyclohexanecarboxaldehyde and CO. A solution of 112 mg (1.00 mmol) of cyclohexanecarboxaldehyde in 0.30 mL of CD_3CN was syringed into a Fischer-Porter bottle which had been charged with a stir bar and 268 mg (1.00 mmol) of **1**. The bottle was pressurized with 350 psi of CO, and the reaction was stirred for 20 h. The reaction was then transferred to a NMR tube, and a ^1H NMR spectrum was recorded (data and analysis: see text). The solvent was removed under vacuum. The resulting residue was chromatographed on silica gel in hexane

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followed by 90:10 hexane/ethyl acetate. This gave 107 mg (0.26 mmol, 26%) of $(CO)_5MnCOCH(\overline{CH(CH_2)_4CH_2})OSi(CH_3)_3$ (**4**) as a white powder, mp 75–77 °C. Anal. Calcd for $C_{16}H_{21}MnO_7Si$: C, 47.06; H, 5.18. Found: C, 47.44; H, 5.27.

Reaction of 1 with Benzaldehyde and CO. Benzaldehyde (53 mg, 0.50 mmol) was added to a Fischer-Porter bottle which had been charged with a stir bar, 134 mg (0.50 mmol) of **1**, and 0.5 mL of CH_3CN. The bottle was pressurized to 300 psi of CO, and the reaction was stirred for 20 h. The solvent was removed under vacuum. The resulting yellow oil was flash chromatographed on silica gel in hexane followed by 90:10 hexane/ethyl acetate. This gave 73 mg (0.18 mmol, 39%) of $(CO)_5MnCOCH(C_6H_5)OSi(CH_3)_3$ (**5**) as a white powder, mp 55–56 °C.[13]

Reaction of 1 with Ethylene Oxide and CO. Dry ethylene oxide (3.0 mL, 60 mmol) was vacuum transferred into a Fischer-Porter bottle which had been charged wth a stir bar and 500 mg (1.87 mmol) of **1**. The bottle was pressurized with 250 psi of CO, and the reaction was stirred for 20 h. The excess ethylene oxide was then evaporated leaving 620 mg of a light yellow powder. The powder was chromatographed on silica gel in 95:5 hexane-/ethyl acetate and vacuum sublimed to give 487 mg (1.43 mmol, 77%) of $(CO)_5MnCOCH_2CH_2OSi(CH_3)_3$ (**6**) as a white powder, mp 53–57 °C.

Reaction of 1 with Propylene Oxide and CO. A mixture of 1.0 mL (15 mmol) of propylene oxide and 1 mL of ether was vacuum transferred into a Fischer-Porter bottle which had been charged with a stir bar and 400 mg (1.49 mmol) of **1**. The bottle was pressurized with 250 psi of CO, and the reaction was stirred for 18 h. The volatiles were evaporated, and the light yellow oily residue was chromatographed on silica gel in 95:5 hexane/ethyl acetate. The product was collected and vacuum sublimed to give 449 mg (1.27 mmol, 85%) of $(CO)_5MnCOCH_2CH(CH_3)OSi(CH_3)_3$ (**7**) as a white powder, mp 48–50 °C. A manganese acyl byproduct (ca. 5%) was observed in the sublimate by ^1H and ^{13}C NMR; see text.

Reaction of 1 with Cyclohexene Oxide and CO. A mixture of cyclohexene oxide (0.220 mL, 2.17 mmol) and ether (1.5 mL) was syringed into a Fischer-Porter bottle which had been charged with a stir bar and 250 mg (0.93 mmol) of **1**. The bottle was pressurized with 200 psi of CO, and the reaction was stirred for 22 h. The volatiles were then removed under vacuum, and the residue was taken up in heptane and the crude yellow product precipitated at −78 °C. After a second heptane extraction/precipitation, the residue was vacuum sublimed to give 318 mg (0.81 mmol, 87%) of *trans*-$(CO)_5MnCO\overline{CHCH_2CH_2CH_2CH_2CH}OSi(CH_3)_3$ (**8**) as a white powder, mp 47–48 °C.

Reaction of 1 with Oxetane and CO. A mixture of oxetane (0.270 mL, 4.15 mmol) and ether (1.73 mL) was syringed into a Fischer-Porter bottle which had been charged with a stir bar and 600 mg (2.24 mmol) of **1**. The bottle was pressurized with 320 psi of CO, and the reaction was stirred for 3 h. The volatiles were evaporated to give a light yellow solid. The solid was taken up in heptane and precipitated at −29 °C (CH_3NO_2/liquid N_2 bath). After two additional heptane extractions/precipitations, the residue was vacuum sublimed to give 658 mg (1.86 mmol, 83%) of $(CO)_5MnCOCH_2CH_2CH_2OSi(CH_3)_3$ (**9**) as a waxy white solid, mp 31–33 °C. Anal. Calcd for $C_{12}H_{15}MnO_2Si$: C, 40.68; H, 4.27; Mn, 15.51. Found: C, 40.69; H, 4.52; Mn, 15.76.

Reaction of 1 with THF and CO. THF (5.0 mL, 62 mmol) was syringed into a Fischer-Porter bottle which had been charged with a stir bar and 250 mg (0.93 mmol) of **1**. The bottle was pressurized with 250 psi of CO, and the reaction was stirred for 21 h. The volatiles were evaporated to give a yellow oil. The oil was taken up in heptane and cooled to −29 °C; a solid precipitated. The solid was collected, and the heptane precipitation was repeated. The solid was vacuum sublimed to give 195 mg (0.50 mmol, 54%) of $(CO)_5MnCOCH_2CH_2CH_2CH_2OSi(CH_3)_3$ (**10**) as an off-white powder, mp 46–48 °C. Anal. Calcd for $C_{13}H_{17}MnO_7Si$: C, 42.40; H, 4.67. Found: C, 42.44; H, 4.58.

Reaction of THF with $(CH_3)_3SiI$, $(CO)_5Mn^-K^+$, and CO. A Fischer-Porter bottle was charged with 3 mL of THF and a stir bar and was cooled to −78 °C. Then 0.40 mL (2.94 mmol) of $(CH_3)_3SiI$ was added by syringe, and the solution was stirred and allowed to warm to room temperature over the course of 20 min. The solution was cooled to −78 °C and 468 mg (2.00 mmol) of $(CO)_5Mn^-K^+$ in 4.0 mL of THF was added via cannula. The bottle was pressurized with 240 psi of CO. The reaction was stirred as it was allowed to warm to room temperature. After 10 h, the reaction was filtered. Solvent was removed from the filtrate to give an orange solid. The solid was taken up in heptane and cooled to −78 °C, whereupon **10** precipitated as a light yellow powoder which was collected and dried (593 mg, 1.61 mmol, 81%).

Reaction of 1 with Oxetane. A 5-mm NMR tube was charged with 27 mg (0.10 mmol) of **1** and cooled to −196 °C (liquid nitrogen). Then 12 mg (0.21 mmol) of oxetane in 0.4 mL of CD_3CN was vacuum transferred into the tube. The tube was capped with a septum, and the reaction was allowed to proceed for 0.5 h at 2 °C, whereupon ^1H NMR and IR spectra indicated the presence of **11** as described in the results section. An analogous experiment with an internal standard is described below (reaction of $(CO)_5MnCH_2CH_2CH_2OSi(CH_3)_3$ with $(CO)_5MnH$). The contents of the tube were transferred to a Fischer-Porter bottle containing a stir bar. The bottle was pressurized with 250 psi of CO, and the reaction was stirred for 4 h. The solvent was removed under vacuum. An IR spectrum of the residue (hexanes) showed characteristic absorptions of **9** (Table I) at 2114 (w), 2049 (w), 2011 (vs), 2002 (s, sh), 1657 (m, br).

Reaction of 1 and $(CO)_5MnH$ with Acetaldehyde. A 5-mm septum-capped NMR tube was charged with 268 mg (1.00 mmol) of **1**, 196 mg (1.00 mmol) of $(CO)_5MnH$, and 1.0 mL of CD_3CN. Then 57 μL (45 mg, 1.02 mmol) of cold acetaldehyde was added via syringe. The tube was allowed to stand at room temperature for 0.5 h, after which time ^1H NMR analysis showed the reaction to be complete. The volatiles were vacuum transferred to a second NMR tube containing 49 mg (0.20 mmol) of $(C_6H_5)_3CH$ standard. Integration of the methine proton resonance of $(C_6H_5)_3CH$ (δ 5.63) vs. the methine proton resonance of **12a** (δ 4.18) indicated a 76% yield of **12a**. A sample of **12a** was isolated by prepraration GLC for additional characterization (Table II).

Reaction of 1 and $(CO)_5MnH$ with Hydrocinnamaldehyde. A 5-mm septum-capped NMR tube was charged with 268 mg (1.00 mmol) of **1**, 37 mg (0.50 mmol) of *tert*-butyl alcohol, 28 mg (0.10 mmol) of $(C_6H_5)_3SiCH_3$ standard, and 1.0 mL of CD_3CN. The tube was allowed to stand at room temperature for 0.5 h, after which time ^1H NMR analysis showed the formation of 0.50 mmol of $(CO)_5MnH$.[13a] Then 66 μL (68 mg, 0.51 mmol) of hydrocinnamaldehyde was syringed in, and the tube was placed in a 5 °C refrigerator for 1 week. Subsequent integration of the methyl ^1H NMR resonance of $(C_6H_5)_3SiCH_3$ (δ 0.81) vs. the methine proton resonance of **12b** (δ 4.10) indicated a 78% yield of **12b**. A sample of **12b** was isolated by preparative GLC for additional characterization (Table II).

Reaction of 1 and $(CO)_5MnH$ with Cyclohexanecarboxaldehyde. A 5-mm septum-capped NMR tube was charged with 54 mg (0.20 mmol) of **1**, 40 mg (0.20 mmol) of $(CO)_5MnH$, 24 mg (0.21 mmol) of cyclohexanecarboxaldehyde, 14 mg (0.10 mmol) of 2-methylnaphthalene standard, and 0.5 mL of CD_3CN. The tube was kept in a 13 °C water bath for 35 h. Subsequent integration of the methyl ^1H NMR resonance of 2-methylnaphthalene (δ 2.46) and the C_α methine proton resonance of **12c** (δ 3.50) indicated a 55% yield of **12c**. A sample of **12c** was isolated by preparative GLC for additional characterization (Table II).

Reaction of 1 and $(CO)_5MnH$ with Benzaldehyde. A 5-mm septum-capped NMR tube was charged with 255 mg (0.95 mmol) of **1**, 186 mg (0.95 mmol) of $(CO)_5MnH$, 106 mg (1.00 mmol) of benzaldehyde, 28 mg (0.20 mmol) of 2-methylnaphthalene standard, and 0.6 mL of CD_3CN. The tube was placed in a 5 °C refrigerator. After 2 days, ^1H NMR analysis showed $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$[3,12] to be the major species present (δ 6.07). Over an additional 10 days at 5 °C, **12d** (δ 9.50 (s), 5.09 (s)) formed in 60% yield vs. the standard. Two additional products appeared in 21% (δ 4.67) and 6% (δ 4.71 (t, 1 H), 3.60 (d, 2 H)) yields. On the basis of GLC comparison with an authentic sample, the former was identified as $C_6H_5CH_2OSi(CH_3)_3$. Also, 14% of benzaldehyde remained. A sample of **12d** was isolated by preprarative GLC for additional characterization (Table II).

Reaction of $(CO)_5MnCH_2OSi(CH_3)_3$ with $(CO)_5MnH$. A 5-mm septum-capped NMR tube was charged with 106 mg (0.36 mmol) of $(CO)_5MnCH_2OSi(CH_3)_3$, 77 mg (0.39 mmol) of $(CO)_5MnH$, 26 mg (0.18 mmol) of 2-methylnaphthalene standard, and

0.7 mL of CD_3CN. The tube was allowed to stand at room temperature for 0.5 h, after which time ^1H NMR analysis showed the reaction to be 80% complete. After 4.5 h, **2e** was present in 97% yield as determined by integrating its aldehydic proton (δ 9.59) vs. the methyl resonance of the standard (δ 2.46). A sample of **12e** was isolated by preparative GLC for additional characterization (Table II).[19]

Reaction of 1 and $(CO)_5MnH$ with Oxetane. A 5-mm NMR tube was charged with 134 mg (0.50 mmol) of **1**, 98 mg (0.50 mmol) of $(CO)_5MnH$, and 8 mg (0.05 mmol) of biphenyl internal standard. Then 70 mg (1.21 mmol) of oxetane in 0.40 mL of CD_3CN was vacuum transferred into the tube. The tube was capped with a septum and stored at 2 °C for 24 h. Subsequent ^1H NMR analysis showed **13** (δ 9.71 (t, J = 2 Hz, 1 H)) and **14** (δ 5.52 (m, 1 H)) to be present in 38% and 59% yields relative to the standard. Samples of **13**[40] and **14** were isolated by preparative GLC for additional characterization (Table II).

Reaction of $(CO)_5MnCH_2CH_2CH_2OSi(CH_3)_3$ (11) with $(CO)_5MnH$. A 5-mm NMR tube was charged with 134 mg (0.50 mmol) of **1** and 9.2 mg (0.060 mmol) of biphenyl internal standard and cooled to −196 °C (liquid nitrogen). Then 49 mg (0.84 mmol) of oxetane in 0.40 mL of CD_3CN was vacuum transferred into the tube. The reaction was allowed to stand for 2 h at 0 °C. Subsequent ^1H NMR analysis indicated a 56% yield of **11**. Then 98 mg (0.50 mmol) of $(CO)_5MnH$ was vacuum transferred into the tube. The reaction was allowed to stand for 0.5 h at 5 °C. Subsequent ^1H NMR analysis showed **13** (δ 9.71) to be present in 54% yield based upon **1** (96% based upon **11**). This yield remained constant over a 3-day period. Vacuum distillation afforded a CD_3CN solution of **13** and oxetane.

Reaction of 9 with $[(CH_3CH_2)_2N]_3{}^+Si(CH_3)_3F_2{}^-$. A 10-mL Schlenk flask was charged with 36 mg (0.10 mmol) of **9**, 43 mg (0.12 mmol) of $[(CH_3CH_2)_2N]_3S^+Si(CH_3)_3F_2{}^-$, 5.2 mg (ca. 7 μL, 0.023 mmol) of n-$C_{16}H_{34}$ standard, and a stir bar. The reaction was stirred for 10 min. Subsequent GLC analysis, including coinjection with an authentic sample, indicated a 93% yield of γ-butyrolactone. An IR spectrum of the reaction mixture showed the lactone $\nu_{C=O}$ at 1783 cm^{-1} (w).

Reaction of 10 with $[(CH_3CH_2)_2N]_3S^+Si(CH_3)_3F_2{}^-$. A 10-mL Schlenk flask was charged with 36 mg (0.10 mmol) of $[(CH_3CH_2)_2N]_3S^+Si(CH_3)_3F_2{}^-$, 5.7 mg (0.037 mmol) of biphenyl standard, 2.0 mL of THF, and a stir bar. Then 24.5 mg (0.067 mmol) of **10** in 0.65 mL of THF was added dropwise over 0.5 h with vigorous stirring. The reaction was stirred for an additional 2 h. Subsequent GLC analysis, including coinjection with an authentic sample, indicated an 85% yield of δ-valerolactone. An IR spectrum of the reaction mixture showed $(CO)_5Mn^-[(CH_3CH_2)_2N]_3S^+$ (1896 (s), 1864 (vs) cm^{-1}) and δ-valerolactone (1741 (w) cm^{-1}).

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Registry No. **1**, 26500-16-3; **2**, 87682-23-3; **3**, 87682-24-4; **4**, 87682-25-5; **5**, 68433-32-9; **6**, 77023-76-8; **7**, 77023-77-9; **8**, 77036-21-6; **9**, 77023-78-0; **10**, 77023-79-1; **11**, 87682-26-6; **12a**, 87682-27-7; **12b**, 87682-29-9; **12c**, 87682-30-2; **12d**, 87682-28-8; **12e**, 18147-36-9; **13**, 72157-18-7; **14**, 65769-92-8; $(CO)_5Mn^-K^+$, 15693-51-3; $(CO)_5MnH$, 16972-33-1; $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$, 68433-34-1; $(CO)_5MnCH_2OSi(CH_3)_3$, 81831-11-0; $[(CH_3CH_2)_2N]_3S^+Si(CH_3)_3F_2{}^-$, 59201-86-4; $(CO)_5Mn^-[(CH_3CH_2)_2N]_3S^+$, 542-28-9; $(CH_3)_3SiI$, 16029-98-4; THF, 109-99-9; acetaldehyde, 75-07-0; hydrocinnamaldehyde, 104-53-0; cyclohexanecarboxaldehyde, 2043-61-0; benzaldehyde, 100-52-7; ethylene oxide, 75-21-8; propylene oxide, 75-56-9; cyclohexene oxide, 286-20-4; oxetane, 503-30-0; γ-butyrolactone, 96-48-0; δ-valerolactone, 542-28-9.

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