Contribution from the Department of Chemistry,
University of California, Los Angeles, California 90024

Reactions of $(CO)_5MnSi(CH_3)_3$ with Organic Carbonyl Compounds

DENNIS LEE JOHNSON and J. A. GLADYSZ*

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Reactions of $(CO)_5MnSi(CH_3)_3$ (**1**) with organic carbonyl compounds have been investigated as a means of developing new metal–carbon bond-forming reactions. Benzaldehyde and **1** react over 2 weeks at 5 °C to give the silyloxyalkyl complex $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$ (**2**) in 65–90% yield, depending upon conditions. Complex **2** undergoes rapid homolysis at 80 °C to $[(CO)_5Mn]_2$ and the diastereomeric pinacol ethers $[-CH(C_6H_5)OSi(CH_3)_3]_2$ (**3a**, **3b**). Reactions of **1** with *p*-methoxybenzaldehyde and *p*-(dimethylamino)benzaldehyde are much faster but yield organometallic products which are much less stable toward homolysis. Compound **1** and butyraldehyde react to yield $(CO)_5MnH$ and the *E* and *Z* isomers (3:2 ratio) of butyraldehyde trimethylsilyl enol ether (**8**, **9**). The isolation of $(CO)_5MnCOCH(n\text{-}C_3H_7)OSi(CH_3)_3$ (**14**) when this reaction is conducted under 10 atm of CO provides good evidence for the intermediacy of $(CO)_5MnCH(n\text{-}C_3H_7)OSi(CH_3)_3$. Acetone, cyclohexanone, and 2-methylcyclohexanone similarly react with **1** to yield $(CO)_5MnH$ and trimethylsilyl enol ethers. In the latter case, a mixture of regioisomers is formed which equilibrate due to the $(CO)_5MnH$ present. These reactions are suggested to proceed via rate-determining formation of ion pairs $(CO)_5Mn^{-}\,{}^{+}CR(R')OSi(CH_3)_3$. The thermodynamics and relevance of these reactions to catalytic hydrosilylation processes are discussed.

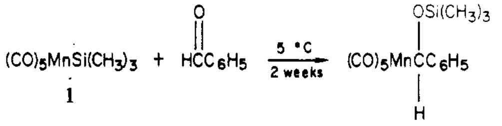
Introduction

An ongoing interest in our laboratory has been the synthesis of stable homogeneous transition-metal complexes containing ligand types believed to be related to catalyst-bound intermediates in CO reduction[1-4] and hydrosilylation[4,5] processes. Since α-hydroxyalkyl intermediates have been postulated to play pivotal roles in the metal-catalyzed synthesis of alcohols, glycols, and formate esters from CO/H_2 gas mixtures,[6] numerous research groups have sought means for the preparation of stable $L_nMCH(R)OH$ and $L_nMCH(R)OR'$ complexes.[4,7,8] Since many conventional methods of metal–carbon bond formation cannot be applied to such species (instability or unavailability of required precursors; product destruction under reaction conditions), we sought to investigate new methodology for their synthesis.

Our attention was drawn to targets of the $L_nMCH(R)OSiR_3$-type for two reasons: (1) a number of low-temperature methods exist for converting $OSiR_3$ to OH groups[9] and (2) this type of species is believed to be a key intermediate in the catalytic hydrosilylation of aldehydes and ketones.[10] Recently many *main-group* element trimethylsilanes, $(CH_3)_3Si\text{–}X$, have been shown to be extremely useful for the preparation of carbon–X-bonded species from oxygen-containing organic compounds.[11,12] We therefore initiated an exploratory program to determine if transition-metal–$Si(CH_3)_3$ compounds[13] could be used to effect similar transition-metal–carbon bond-forming reactions (or other useful or novel transformations). In this paper, we describe the reactions of $(CO)_5MnSi(CH_3)_3$ (**1**)[14,15] with a variety of organic carbonyl compounds.[16]

Results

Benzaldehyde was reacted with an equimolar amount of $(CO)_5MnSi(CH_3)_3$ (**1**) at 5 °C in the absence of solvent. After 2 weeks, the insertion product **2** had formed in 65% yield (eq 1). When the same reaction was conducted with a twofold excess of benzaldehyde under otherwise identical conditions, **2** formed in 90% yield. The identity of **2** was confirmed by independent synthesis via a lengthier and entirely different route (vide infra).[3] Its ^1H NMR spectrum contained a distinguishing low-field methine resonance (δ 6.07) which was used to monitor its formation and/or disappearance.[8b]



$$(CO)_5MnSi(CH_3)_3 + H\overset{\overset{O}{\|}}{C}C_6H_5 \xrightarrow[\text{2 weeks}]{5\ ^\circ C} (CO)_5Mn\underset{\underset{H}{|}}{\overset{\overset{OSi(CH_3)_3}{|}}{C}}C_6H_5 \qquad (1)$$

1

2 (65–90%)

In benzene, hexane, and dichloromethane, the reaction of **1** with benzaldehyde was dramatically slower than in the absence of solvent, presumably due to decreased reactant concentrations. Experiments were not conducted in THF since it independently reacted with **1**.[17] However, the formation

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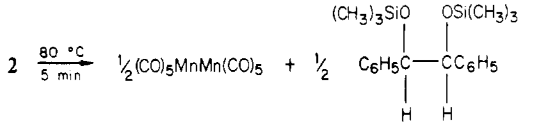
of **2** was somewhat faster when acetonitrile was used as solvent. After 1 hr at 35 °C, a CD_3CN solution which was initially 0.93 M in **1** and 2.50 M in benzaldehyde contained **2** in 70% yield. Under identical conditions without solvent, disappearance of **1** required ca. 1 day. The rate of formation of **2** was not accelerated by the presence of nucleophiles such as $[(C_6H_5)_3P]_2N^+(CO)_5Mn^-$ or Lewis acids such as $AlCl_3$ or ZnI_2.

Related manganese complexes were treated with benzaldehyde. No reaction was observed with $(CO)_5MnH$ in the absence of solvent (2 months, 10 °C, or 2 days, 65 °C). Anions $[(C_6H_5)_3P]_2N^+(CO)_5Mn^-$ (neat, 25 °C) and $Li^+(CO)_5Mn^-$ (THF solution, 25 °C) similarly did not react with benzaldehyde.

Due to its thermal instability, **2** could not be isolated in analytically pure form. Over the course of several hours at 25 °C or 5 min at 80 °C, **2** decomposed smoothly to $[(CO)_5Mn]_2$ and the pinacol ether $[-CH(C_6H_5)OSi(CH_3)_3]_2$ (**3a**, **3b**),[18] as shown in eq 2. The latter product was obtained in 85–95% yield as a 1:1 mixture of diastereomers. When excess benzaldehyde was present from the preparation of **2**, small amounts (5–15%) of $C_6H_5CH_2OSi(CH_3)_3$ (**4**) were also formed. The decomposition of **2** was observed to follow the rate law $-d[\mathbf{2}]/dt = k_{obsd}[\mathbf{2}]$. At 38 °C, k_{obsd} was found to be $(9.6 \pm 0.5) \times 10^{-5}$ s^{-1}, which corresponds to a half-life of 2.9 h.



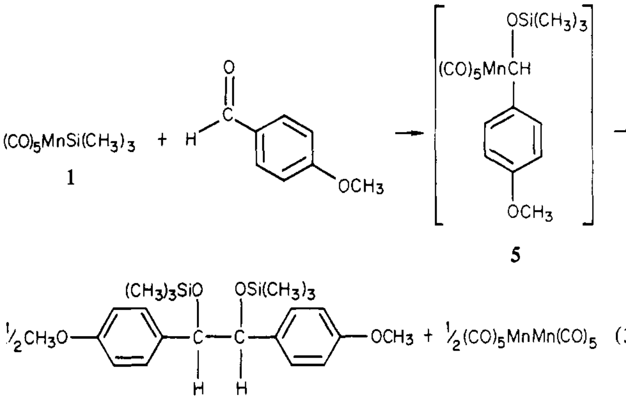
(2)

3a, **3b** (85–95%)
a = erythro
b = threo

When a 2:1 ratio of benzaldehyde and **1** was reacted at 80 °C (under which conditions **2** is rapidly decomposing), $C_6H_5CH_2OSi(CH_3)_3$ (**4**) formed in 5% yield. This yield increased as more benzaldehyde was employed and reached 15% when the ratio was 15:1. When benzaldehyde, $(CO)_5MnSi(CH_3)_3$, and $(CO)_5MnH$ were reacted in a 1:1:1 ratio at 80 °C, **4** and $[(CO)_5Mn]_2$ were the exclusive organic and inorganic products, respectively.

When the reaction (neat) of benzaldehyde with **1** at 80 °C was ^1H NMR monitored, CIDNP[19] emission was observed at δ 6.07, as shown in Figure 1 (see paragraph on supplementary material). No CIDNP was detected, however, when preformed **2a** was decomposed at 80 °C. Under optimum conditions, the most generous estimate indicated the enhancement factor associated with the emission to be less than 10. When benzaldehyde and **1** were reacted at 80 °C in the presence of O_2, all ^1H NMR resonances broadened, but the rate of the reaction and magnitude of the emission were not influenced. Other reactions of **1** and benzaldehyde were conducted under dry air; in all cases, reaction rates did not significantly differ from analogous experiments under argon.

Experiments utilizing substituted benzaldehydes followed similar courses. *p*-Methoxybenzaldehyde underwent a much faster reaction with **1** (vide infra), but the corresponding organometallic product, **5** (eq 3), was less stable than **2**. At room temperature in the absence of solvent, **5** could be generated in up to 60% yield; continued reaction led to pinacol ethers **6a** and **6b**[18] in 90% combined yield. Similarly, *p*-(dimethylamino)benzaldehyde reacted at an even faster rate, but an organometallic product was not detected by ^1H NMR under the conditions employed (C_6D_6, 5 °C and 40 °C). Pinacol ethers $[-CH(p\text{-}C_6H_4N(CH_3)_2)OSi(CH_3)_3]_2$ (**7a**, **7b**; 1:1 mixture of diastereomers)[18] formed in 90% yield, and $[(CO)_5Mn]_2$ was the only inorganic product.



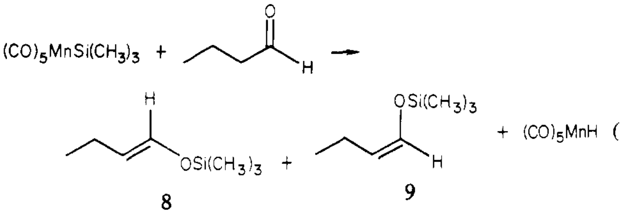
1

5

6a, **6b**

(3)

Reactions of **1** with aliphatic aldehydes and ketones were investigated. Butyraldehyde was found to react very slowly with **1** (1.2:1.0 ratio, neat); after 4 weeks at 5 °C, only 25% of **1** had been consumed. Enol ethers **8** and **9** (25%, 3:2 ratio; eq 4) and $(CO)_5MnH$ (25%) constituted the exclusive organic and inorganic products, respectively. At no point could an organometallic intermediate be detected by ^1H NMR.

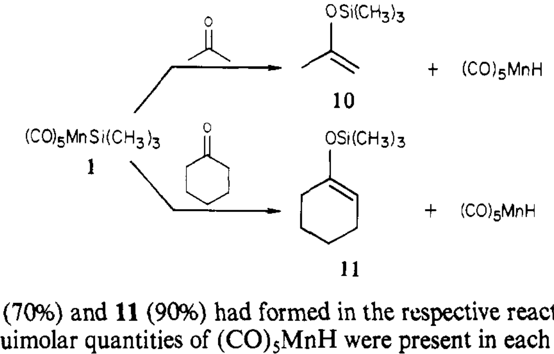


(4)

8 **9**

3:2

Acetone and cyclohexanone were reacted neat with **1** at 25 °C in ca. 2:1 molar ratios (eq 5). After 1 week, enol ethers **10** (70%) and **11** (90%) had formed in the respective reactions. Equimolar quantities of $(CO)_5MnH$ were present in each case, and no ^1H NMR evidence[8b] was observed for organometallic intermediates.



10

1

11

(5)

When equimolar quantities of **1** and 2-methylcyclohexanone were reacted neat at room temperature, $(CO)_5MnH$ and the regioisomeric enol ethers **12** and **13** formed. The product distribution was time dependent. At 10% conversion (ca. 1 day), the ratio of **12**:**13** was 2:1. At 90% conversion (4 weeks), the ratio of **12**:**13** was 9:1. Under identical conditions, $(CO)_5MnH$ was found to catalyze the isomerization of independently prepared[20] **13** to **12**. Control experiments showed

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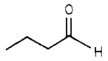
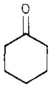
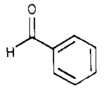
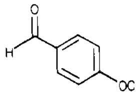
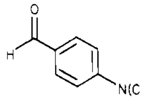
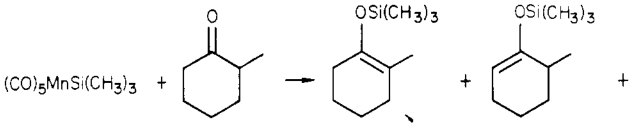
Table I. Time Required for Consumption of $(CO)_5MnSi(CH_3)_3$ (1) by Aldehydes and Ketones in CD_3CN at 49 °C[a]

CO compd	$t_{50\%}$, min	$t_{90\%}$, min
	20	40
	12	30
	9	30
	7	24
	4	15

[a] $[\text{Organic}]_0 = [1]_0$ = ca. 0.9 M.

that neither 1 nor 2-methylcyclohexanone was able to isomerize **13** to **12**. When $(CO)_5MnD$ was added to a 9:1 mixture of **12**:**13** $(CO)_5MnH$ formed and deuterium was incorporated into **12** and **13**.



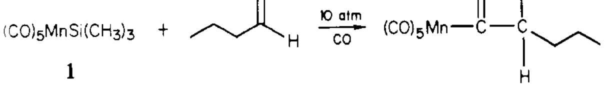
12 **13**

10% conversion, 2:1
90% conversion, 9:1

$(CO)_5MnH$ (6)

So that more accurate reactivity comparisons could be made, the rates of the reactions of **1** with butyraldehyde, cyclohexanone, benzaldehyde, *p*-methoxybenzaldehyde, and *p*-(dimethylamino)benzaldehyde were monitored under identical conditions. The data are compiled in Table I.

The course of the reaction of **1** with either benzaldehyde or cyclohexanone was not altered when conducted in CD_3CN under 10 atm of CO. However, when butyraldehyde (2.25 equiv) was reacted with **1** in CD_3CN under 10 atm of CO, a new product was formed in ca. 75% spectroscopic yield after 2 h. Removal of the volatiles under vacuum resulted in a yellow oil, from which the product was extracted with heptane. Although the product could not be obtained in analytically pure form (primarily because of its lack of crystallinity), its ^1H NMR, ^{13}C NMR, and IR spectra convincingly indicated it to be the manganese acyl **14** (eq 7). When this reaction



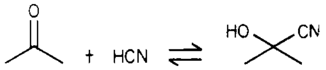
1 **14** (7)

was conducted under 10 atm of ^{13}CO, the ^{13}C NMR spectrum of **14** indicated a 31 ± 5% enrichment of the CO's cis to the acyl ligand but only a 10 ± 2% enrichment of the acyl carbon. A control experiment under identical conditions but without butyraldehyde indicated only a 10 ± 2% enrichment of the carbonyls in **1**. From these data, it can be calculated (Experimental Section) that ^{13}CO is incorporated into the carbonyl ligands of **14** about 1 order of magnitude more frequently than the acyl ligand.

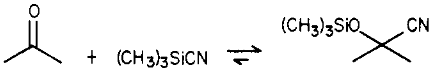
Other types of carbonyl-containing compounds were found to be less reactive than aldehydes and ketones toward **1**. Ethyl acetate, methyl benzoate, and benzoic anhydride did not react with **1** upon heating in CH_3CN. When **1** was reacted with benzoyl chloride in CH_3CN, $(CO)_5MnCOC_6H_5$ was detected by IR; however, this product was not stable under the reaction conditions, and after 1 day $(CH_3CN)Mn_2(CO)_9$ was the principal manganese-containing product. An independent experiment showed that mixing $(CO)_5MnCOC_6H_5$ with $(CH_3)_3SiCl$ in CH_3CN resulted in the formation of $(CH_3CN)Mn_2(CO)_9$.

Discussion

Reaction Thermodynamics. The addition of HCN to aldehydes and ketones (eq 8) is a reversible, and in some cases endothermic, reaction. In 1973, Evans reported that the addition of $(CH_3)_3SiCN$ to aldehydes and ketones (eq 9) was



(8)

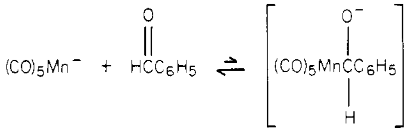


(9)

much more favorable thermodynamically.[11a,b] The formation of a strong silicon–oxygen bond (for which current estimates are 106–112 kcal/mol)[21] in the latter reaction is undoubtedly a major factor in this difference. Similarly, α-iodo alcohols are thermodynamically unstable with respect to HI loss and carbonyl compound formation. However, Jung has shown that silylated α-iodo alcohols can be prepared from aldehydes and $(CH_3)_3SiI$.[12b] Related carbonyl group additions have been observed with other $(CH_3)_3SiX$ species.[11c–e]

Similar strategies have not previously to our knowledge been applied in a designed fashion to transition-metal–carbon bond formation. Equation 1 represented an ideal test case, since we had previously prepared **2** by $(CH_3)_3N^+O^-$ decarbonylation of the acyl $(CO)_5MnCOCH(C_6H_5)OSi(CH_3)_3$ (which was in turn synthesized via sequential treatment of $(CO)_5MnCOCOC_6H_5$ with $Li(C_2H_5)_3BH$ and $(CH_3)_3SiCl$).[3]

So that eq 1 can be viewed in appropriate perspective, two additional equilibria should be considered (eq 10, 11). Experiments reported in this paper indicate that preparatively, eq 10 and 11 do not proceed in the forward direcion. Previous



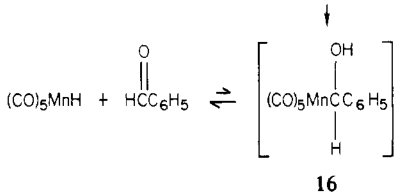
(10)

15

↑

2 and other
precursors

↓



(11)

16

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[21] Ebsworth, E. A. V. In "Organometallic Compounds of the Group IV Elements"; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1, Part 1, pp 46–50.

attempts by us to generate **15** and **16** (such as by F^- attack upon or protodesilylation of **2**) resulted only in the observations of products on the left-hand sides of eq 10 and 11.[3] These data strongly suggest that eq 10 and 11 are endothermic from left to right. Thus the presence of the oxygenophilic $(CH_3)_3Si$ group in **1** is critical to the success of eq 1.

Interestingly, the manganese–carbon bond dissociation energy in $(CO)_5MnCH_2C_6H_5$ is only 20–25 kcal/mol.[22a] Since the corresponding bond in **2** must be weaker, it provides only a small portion of the driving force for eq 1. While direct measurements of metal–tri*alkyl*silyl bond strengths have not been made, the iron–silicon bond in $(\eta\text{-}C_5H_5)(CO)_2FeSi(CH_3)_2CH_2Br$ has been shown to be no more than 5–7 kcal/mol stronger than the iron–carbon bond in $(\eta\text{-}C_5H_5)(CO)_2FeCH_2Si(CH_3)_2Br$.[23] Therefore the manganese–silicon bond $(CO)_5MnSi(CH_3)_3$ is probably significantly weaker than the manganese–hydrogen bond in $(CO)_5MnH$, which has been estimated to be as high as 64 kcal/mol.[6d] This would also contribute toward making eq 1 thermodynamically more favorable than eq 11.

The closest existing analogy to eq 1 and 2 is the reaction of $Hg[Si(CH_3)_3]_2$ with benzaldehyde. Pinacol ethers **3a** and **3b** form in 74% yield without the formation of detectable organometallic intermediates;[18] a fundamentally different mechanism is not unlikely.

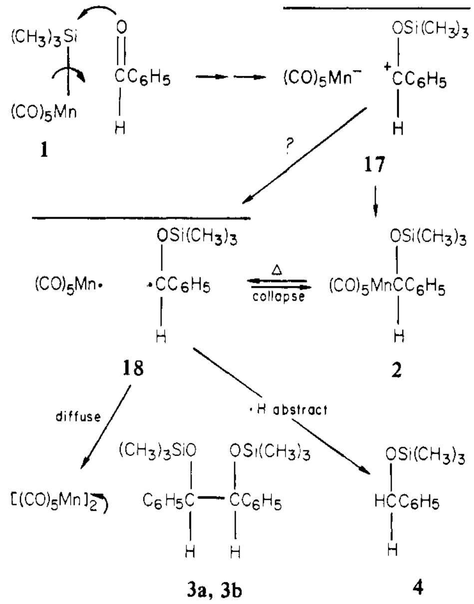
Reaction Mechanisms. Evans reported that the reaction of $(CH_3)_3SiCN$ with aldehydes and ketones could be catalyzed by both nucleophiles and Lewis acids.[11b] Chain mechanisms were proposed. In the former case, chain-carrying ^-CN was suggested to add to the carbonyl group to generate an alkoxide intermediate which underwent rapid silylation by $(CH_3)_3SiCN$. In the latter case, Lewis acids were suggested to activate the carbonyl group toward attack by carbonyl oxygen complexation. Our unsuccessful attempts to similarly catalyze eq 1 indicate that neither of these mechanisms are followed. Also, the rate of eq 1 was not affected by O_2, which is contrary to what would be expected of a radical chain mechanism.

$(CO)_5MnSi(CH_3)_3$ is thermally quite stable (93% recovery after heating 48 h at 160 °C in vacuo),[14a] and our ^{13}CO-exchange experiments indicate that CO does not significantly dissociate on the time scale of the more rapid (eq 3, 7) carbonyl addition reactions. Since the polar solvent acetonitrile accelerated the rate of eq 1, and substitution of electron-releasing substituents (OCH_3, $N(CH_3)_2$) for the para hydrogen of benzaldehyde resulted in much faster reactions, we propose that the initial and rate-determining step of eq 1 is the formation of the ion pair **17** (Scheme I).

In support of this suggestion, $(CH_3)_3N$ has been reported to react with **1** to form the *isolable* ion pair $(CH_3)_3N^+Si(CH_3)_3(CO)_5Mn^-$.[14a] Since the oxygen-silicon bond is by far the strongest formed in eq 1, it is reasonable to expect its formation early in the reaction.

At least two routes are possible by which product **2** can be formed from ion pair **17** (Scheme I): (a) by direct collapse, or (b) via electron transfer to yield the radical pair **18**, followed by collapse. The CIDNP observed when eq 1 is carried out at elevated temperatures (where **2** is also rapidly decomposing) does require the presence of geminate radical pairs. According to currently accepted theory,[19] emission from the methine proton of **2** is consistent with its formation from the collapse of a singlet born geminate radical pair in which the *g* value for $(CO)_5Mn\cdot$ is greater than the *g* value for $\cdot CH(C_6H_5)OSi(CH_3)_3$. Although these have not been directly measured, the recent *g* value ordering of $(CO)_5Mn\cdot > \cdot C(CH_3)_2C_6H_5$,[22] together with literature values for $\cdot CH(C_6H_5)OH$[24] and $\cdot C(C_6H_5)_2OSi(CH_3)_3$,[25] put this assignment on firm ground. Such a rationale, however, also predicts that CIDNP should be observed upon similar heating of preformed **2**, which we repeatedly failed to note. Another caveat is provided by the low (<10) enhancement factor of the emission. Considering the great sensitivity of CIDNP (and previous overzealous interpretations), we believe that the observed polarization likely results from some minor reaction pathway not represented in Scheme I.

Scheme I. Proposed Mechanism for the Reaction of 1 with Benzaldehyde



The formation of radical pair **18** upon thermolysis of **2** (Scheme I) is strongly supported by several pieces of data. First, the decomposition kinetics allow for only one molecule of **2** in the rate-determining step. Second, the formation of dimeric decomposition products $[(CO)_5Mn]_2$ and **3a** and **3b** (Scheme I) is suggestive of radical precursors, and other manganese alkyls behave similarly.[22] Finally, the formation and decomposition of **2** in the presence of hydrogen atom donors such as benzaldehyde and $(CO)_5MnH$[22] affords appreciable quantities of the hydrogen abstraction product $C_6H_5CH_2OSi(CH_3)_3$ (**4**, Scheme I). Halpern has previously shown $(CO)_5MnH$ to be a particularly good hydrogen atom donor to benzylic radicals.[22]

Since the reaction of **1** with enolizeable aldehydes and ketones did not result in organometallic products, the possibility of organometallic intermediates must be addressed. Potential precursors to the trimethylsilyl enol ether products include ion pairs, radical pairs, and manganese alkyls (or combinations thereof), as shown in Scheme II. For instance, $(CO)_5MnH$ is a weak acid ($pK_a \sim 7$);[26] therefore, $(CO)_5Mn^-$ should be a sufficiently strong base to effect H^+ transfer (and product formation) in the ion pair **19**. Alternatively, ion pair **19** could collapse to the organometallic **20**; manganese alkyls with β C–H bonds have been previously shown to eliminate olefins.[27] Such decomposition routes are not available to the corresponding species **2** in Scheme I.

Many $(CO)_5MnR$ complexes have been shown to carbonylate to $(CO)_5MnCOR$ complexes under mild conditions.[28]

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[22] (a) Halpern, J. *Pure Appl. Chem.* **1979**, *51*, 2171. (b) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335.

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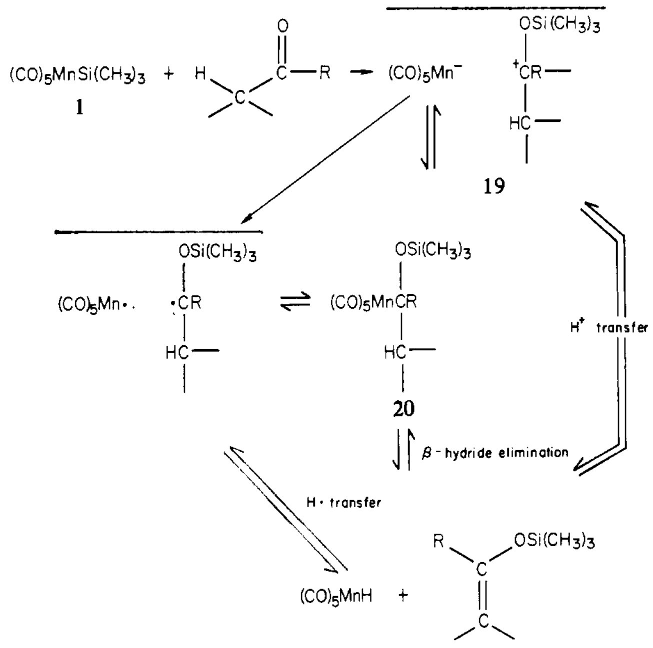
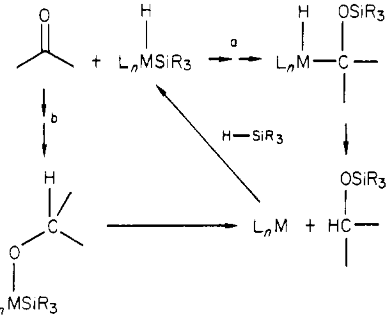
[28] Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

Scheme II. Possible Pathways for Trimethylsilyl Enol Ether Formation from 1



Scheme III. Some Previously Considered Pathways for the Catalytic Hydrosilylation of Carbonyl Compounds

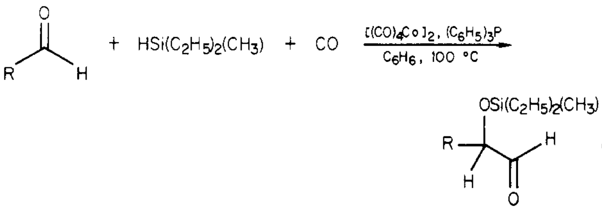


Labeling studies by Calderazzo have shown that the alkyl group migrates to an adjacent CO ligand and that incoming CO fills the resulting vacant coordination site. Therefore our isolation of manganese acyl **14** (eq 7) from the reaction of **1** and butyraldehyde under CO strongly suggests that the organometallic intermediate $(CO)_5MnCH(n\text{-}C_3H_7)OSi(CH_3)_3$ is formed under the conditions of eq 4. However, since carbonium ions have been observed to react with CO,[29] the possibility that **14** might arise from carbonylation of ion pair **19** must be considered. This would result in incorporation of the incoming CO into the acyl ligand. The experiment with ^{13}CO indicates this to be at best a minor reaction pathway, and that **14** is formed by the conventional Calderazzo carbonylation mechanism.[28]

The failure to obtain a manganese acyl product from the reaction of **1** with cyclohexanone under CO might be due to a change of mechanism (Scheme II) or decreased stability of the corresponding manganese alkyl **20**. A priori, the equilibration of the trimethylsilyl enol ethers of 2-methylcyclohexanone by $(CO)_5MnH$ could take place by the microscopic reverse of any of the three enol ether forming steps in Scheme II (or combinations thereof).

Overview. Although this study has shown that $(CO)_5MnCH(R)OSi(CH_3)_3$ complexes are accessible from $(CO)_5MnSi(CH_3)_3$ and aldehydes, preparative utility is limited by the instability of these adducts toward homolysis (Scheme I) and/or trimethylsilyl enol ether formation (Scheme II). However, these transformations do provide important precedent for the initial step in the catalytic hydrosilylation of aldehydes and ketones. The two reaction modes which have been most frequently considered are given as paths a and b in Scheme III. Our observations establish, for the first time, path a as a viable reaction type. Recently, other researchers have cited evidence suggesting path a to be the dominant catalyst mechanism.[10] Our data further suggest that prior carbonyl group coordination to the metal is not ***required*** for metal–carbon bond formation; however, this may change with the Rh(I) catalyst precursors commonly employed.

Murai has used $[(CO)_4Co]_2$ as a catalyst for effecting a number of elegant reactions of $HSi(C_2H_5)_2(CH_3)$, CO, and organic molecules.[30] One example is given in eq 12. Under



(12)

21 (49–54%)

the reaction conditions, a $(CO)_3LCoSiR_3$ catalyst is believed to be generated. Our observations provide direct precedent for the subsequent aldehyde insertion and carbonylation steps which Murai has postulated to occur. Product **21** (compare to **14**, eq 7) would then arise from reduction of an intermediate cobalt acyl.

Silane **1** may find occasional use as a reagent for trimethylsilyl enol ether formation (eq 4–6). Although **1** does not offer any improvement over existing methods[20,31] in terms of regiocontrol, it effects enol ether formation without the addition of exogeneous acids or bases. Good preparative conditions would be similar to those employed for the experiments in Table I.

Other transition-metal trimethylsilanes are under study in our laboratory,[4,5,17,32] and the rate-determining formation of ion pairs which we have postulated (Scheme I, II) for the reactions in this paper provides a convenient means of rationalizing their relative reactivity. Simplistically, metal trimethylsilanes in which the metals (L_nM) are good leaving groups should react faster. Hence there should be a ***roughly*** inverse correlation with metal nucleophilicity scales.[34] Thus $L_n(CO)_mCoSi(CH_3)_3$ species are expected to react with oxygen-containing organic molecules faster than **1**, and have better prospects for incorporation into catalytic cycles,[30,31c] as shown by Murai. Conversely, silanes such as $(\eta\text{-}C_5H_5)Fe(CO)_2Si(CH_3)_3$ and $(CO)_5ReSi(CH_3)_3$ are expected to have greatly diminished reactivity. As a corollary, transition-metal silanes which are bulky ($Si(C_6H_5)_3$) or superior π acceptors ($SiCl_3$) should be less reactive than trimethylsilanes.

In summary, transition-metal trimethylsilanes such as **1** have heretofore untapped potential for the synthesis of organometallic compounds and effecting organic functionality transformations via organometallic intermediates. Additional applications utilizing different metal–$Si(CH_3)_3$ systems and/or

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organic substrates will be forthcoming from this laboratory.

Experimental Section

Chemicals. $(CO)_5MnSi(CH_3)_3$ (**1**) was synthesized by either Malisch's procedure[14b] or one previously described by us.[15] $[(CO)_5Mn]_2$ was obtained from Strem and was sublimed before use. $(CO)_5MnCOC_6H_5$ and $[(C_6H_5)_3P]_2N^+(CO)_5Mn^-$ were prepared by previously described procedures.[16,15]

Benzaldehyde, *p*-methoxybenzaldehyde, acetone, cyclohexanone, 2-methylcyclohexanone, butyraldehyde, and benzoyl chloride were obtained from Aldrich and/or Eastman and were twice distilled under vacuum immediately before use. *p*-(Dimethylamino)benzaldehyde, *trans*-stilbene, and benzoic anhydride were obtained from Eastman and were used without purification. Ethyl acetate and methyl benzoate were obtained from Aldrich and used without purification. $(CH_3)_3SiCl$ was obtained from Aldrich and distilled from CaH_2 before use. $Li(C_2H_5)_3BH$ was purchased from Aldrich as a 1 M THF solution and used without standardization. ZnI_2 (Alfa) and $AlCl_3$ (Mallinckrodt) were used without purification.

C_6H_6 and C_6D_6 were distilled from potassium and freeze–pump–thaw degassed before use. CH_3CN, CD_3CN, and $CDCl_3$ were distilled from P_2O_5 and freeze–pump–thaw degassed before use. Hexane (Eastman) was saturated with N_2 (via prolonged purging) prior to use. CH_3OH and CH_3OD were employed without purification.

^{12}CO was obtained from Air Products and was used without purification; ^{13}CO (90.7% isotopic purity) was obtained from Prochem and used without purification or analysis.

Instruments. ^1H NMR spectra were recorded on either Varian A-60 or Bruker WP-200 spectrometers. ^{13}C NMR spectra were recorded at 50 MHz on a Bruker WP-200 spectrometer. IR and mass spectra were obtained on a Perkin-Elmer 521 and AEI-MS9 spectrometers, respectively. GLC analysis was performed on a Hewlett-Packard 5720A chromatograph equipped with a flame ionization detector.

Organic Product Analysis. All organic products were identified by comparison of ^1H NMR spectra *and* GLC retention times (including coinjection) with those of commercially available or independently prepared samples. Preparations of authentic samples are referenced in the individual experimentals.

For GLC yields of reactions conducted in NMR tubes, reactions were diluted to 0.50 mL with C_6D_6 or C_6H_6. Aliquots of 2.0 μL were withdrawn by syringe and chromatographed on a $^1/_8$ in. diameter column (4-ft. or 10-ft. length) packed with 10% DC 710 on Chromosorb W. N_2 was used as the carrier gas at a flow rate of 20 mL/min. Peak areas were measured by the "cut and weigh" or "height × width at half-height" methods. Reproducible results (±5%) were obtained from repeated injections. The two methods of area measurement gave identical results within ±3%; the latter method was used most frequently. Yields were calculated after conducting identical GLC analyses of known quantities of standards (commercial or independently prepared) which had been diluted to 0.50-mL volumes with C_6D_6 or C_6H_6. In all cases, yields were based upon the limiting reactant; those determined by ^1H NMR agreed well (±5%) with those determined by GLC.

General Procedure. Synthesis of $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$ (2). To a 5-mm NMR tube was added 270 mg (1.01 mmol) of $(CO)_5MnSi(CH_3)_3$ (**1**). The tube was sealed with a latex septum and evacuated/refilled with argon five times. Benzaldehyde (100 μL, 106 mg, 1.00 mmol) was then added by syringe, and the mixture was agitated until homogeneous. The tube was placed in a refrigerator at 5 °C and the formation of **2**[3] followed by ^1H NMR (δ 7.2 (m, 5 H), 6.07 (s, 1 H), 0.15 (s, 9 H)). After 14 days, integration of the resonance at δ 6.07 vs. either total C_6H_5 or total $Si(CH_3)_3$ as internal standard showed the yield of **2** to be 65 ± 5%.

For an improved yield of **2**, the general procedure was followed except that 343 mg (1.28 mmol) of **2** and 243 μL (258 mg, 2.43 mmol) of benzaldehyde were used. After 14 days at 5 °C, **2** had been formed in 90 ± 5% yield based on total $Si(CH_3)_3$ as internal standard.

Effect of Acetonitrile as Solvent and ZnI_2 as Catalyst upon the Rate of Formation of 2. The above general procedure was followed for two experiments using 100 mg (0.37 mmol) of **1** and 100 μL (106 mg, 1.00 mmol) of benzaldehyde, except that in both cases 0.40 mL of CD_3CN was used as solvent and in one tube 5 mg (0.02 mmol) of ZnI_2 was added. The rate of formation of **2** was followed at 35 °C by ^1H NMR and found to be identical (70 ± 5% after 1.0 h) in each case. The reaction containing ZnI_2 turned slightly orange over the course of the experiment; an IR spectrum in THF showed bands attributable to $(CO)_5MnI$ (2130 m, 2048 vs, 2017 m, 2005 s cm^{-1}).

Effect of $[(C_6H_5)_3P]_2N^+(CO)_5Mn^-$ upon the Rate of Formation of 2. The above general procedure was followed except that 231 mg (0.86 mmol) of **1** and 175 μL (185 mg, 1.75 mmol) of benzaldehyde were mixed in the presence of 76 mg (0.105 mmol) of $[(C_6H_5)_3P]_2N^+(CO)_5Mn^-$. The rate of formation of **2** was followed by ^1H NMR and found to be no faster than in an identical experiment conducted without $[(C_6H_5)_3P]_2N^+(CO)_5Mn^-$.

Attemped Reaction of $(CO)_5MnH$ and Benzaldehyde. To a 5-mm NMR tube was added 282 mg (1.05 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled with argon 5 times. Methanol (40 μL, 33.6 mg, 1.05 mmol) was added by syringe and the solution was heated to 50 °C for 2 h. A ^1H NMR showed the previously reported[34] conversion to $(CO)_5MnH$ and $CH_3OSi(CH_3)_3$ to be complete. Benzaldehyde (110 μL, 117 mg, 1.10 mmol) was then added by syringe, and the mixture was agitated until homogeneous. No change was observed in the ^1H NMR spectrum after 2 months at 5 °C or 2 days at 65 °C.

Attempted Reaction of $[(C_6H_5)_3P]_2N^+(CO)_5Mn^-$ with Benzaldehyde. To a 5-mL round-bottom flask equipped with a magnetic stir bar was added 321 mg (0.44 mmol) of $[(C_6H_5)_3P]_2N^+(CO)_5Mn^-$. The flask was flushed with argon and sealed with a Latex septum. Benzaldehyde (2.0 ml, 20 mmol) was added by syringe, and the mixture was stirred. A small amount was withdrawn by syringe and diluted with THF. An IR spectrum showed only absorbances due to starting materials. An identical spectrum was obtained after 24 h at room temperature.

Attempted Reaction of $Li^+(CO)_5Mn^-$ with Benzaldehyde. To a 50-mL round-bottom Schlenk flask equipped with a magnetic stir bar was added 195 mg (0.50 mmol) of $[(CO)_5Mn]_2$. The flask was flushed with argon and sealed with a rubber septum. THF (25 mL) was added by syringe followed by 1.0 mL of a 1.0 M solution of $Li(C_2H_5)_3BH$ in THF. After 1 h, IR showed the previously reported[15] conversion to $Li^+(CO)_5Mn^-$ to be complete. Benzaldehyde (2.0 mL, 2.1 g, 20 mmol) was added by syringe. No change was observed in the IR spectrum after 1 day at 25 °C.

Thermal Decomposition of 2. A NMR tube containing **2** which had formed in 90% yield from **1** (343 mg, 1.28 mmol) and benzaldehyde (243 μL, 258 mg, 2.43 mmol) was heated to 80 °C for 2 h. The contents solidified upon cooling and were redissolved in C_6D_6. Analysis by ^1H NMR and GLC (see above) showed equal amounts of pinacol ethers **3a** and **3b** (δ 4.57/4.77 (s, 2 H), 0.07/−0.24 (s, 18 H))[18] in 95% yield and $C_6H_5CH_2OSi(CH_3)_3$ (**4**) (δ 4.50 (s, 2 H), 0.05 (s, 9 H)) in 5% yield. An IR Spectrum showed $[(CO)_5Mn]_2$ to be the only inorganic product.

Rate of Decomposition of 2. A sample of **2** was synthesized from 288 mg (1.07 mmol) of **1** and 214 μL (227 mg, 2.14 mmol) of benzaldehyde by the standard procedure except that the reaction was allowed to proceed 4 weeks. The reaction was then diluted with 0.5 mL of C_6D_6. A ^1H NMR spectrum showed the absence of **1** and the presence of **2** in 95% yield (and **3a** and **3b** in 5% combined yield). The sample was allowed to decompose at 38 °C in the spectrometer probe. A plot of log [**2**] vs. time was linear over three half-lives ($t_{1/2} = 2.9$ h, $r^2 = 0.99$), and gave $k_{obsd} = (9.6 \pm 0.5) \times 10^{-5}\ s^{-1}$.

Reaction of 1 with Benzaldehyde at 80 °C. Effect of Reactant Ratios on Product Distribution. To a 5-mm NMR tube was added 243 mg (0.90 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled with argon five times. Benzaldehyde (180 μL, 190 mg, 1.80 mmol) was then added by syringe. The contents were agitated until homogeneous and then heated to 80 °C for 2 h. GLC analysis showed **4** to be present in 5% yield and equal amounts of pinacol ethers **3a** and **3b** in 95% yield. An IR spectrum in hexane showed $[(CO)_5Mn]_2$ to be the only inorganic product.

An experiment identical with the previous one was conducted with 174 mg (0.65 mmol) of **1** and 200 μL (2.00 mmol) of benzaldehyde. GLC analysis showed **4** to be present in 8% yield and **3a** and **3b** in 87% yield.

An experiment identical with the previous one was conducted with 55 mg (0.20 mmol) of **1** and 200 μL (3.00 mmol) of benzaldehyde. GLC analysis showed **4** to be present in 15% yield and **3a** and **3b** in 75% yield.

Reaction of 1 with Benzaldehyde in the Presence of $(CO)_5MnH$. To a 5-mm NMR tube containing 229 mg (0.85 mmol) of **1** was added (after standard flushing and capping) 19 μL (0.45 mmol) of CH_3OH. This mixture was heated at 60 °C until the NMR spectrum showed equal amounts of $(CO)_5MnH$ and **1** to be present.[34] Benzaldehyde (45 μL, 0.45 mmol) was then added and the reaction heated to 80

°C for 2 h. After the reaction was cooled and dissolved in C_6D_6, ^{1}H NMR spectra showed the absence of $(CO)_5MnH$. GLC indicated $C_6H_5CH_2OSi(CH_3)_3$ (100%) to be the only organic product, and an IR spectrum showed $[(CO)_5Mn]_2$ to be the only inorganic product.

Reaction of 1 with *p*-Methoxybenzaldehyde. To a 5-mm NMR tube was added 107 mg (0.40 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled with argon five times. C_6D_6 (0.25 mL) and then *p*-methoxybenzaldehyde (48 μL, 54.4 mg, 0.40 mmol) were added by syringe. The tube was shaken until homogeneous and held at 40 °C in a Varian A-60 probe. After 2 h, adduct **5** (δ 6.12 (s, 1 H), 3.43 (s, 3 H), 0.10 (s, 9 H)) had formed in 30 ± 5% yield. Pinacol ethers **6a** and **6b** (δ 4.79/4.65 (s, 2 H), 3.39/3.47 (s, 6 H), −0.14/0.07 (s, 18 H))[18] were present in a ca. 1:1 ratio and a combined yield of 10 ± 5%. After 24 h, the ^{1}H NMR indicated **5** to be absent and **6a** and **6b** to be present in 85 ± 5% combined yield. GLC analysis indicated a 90% combined yield of **6a** and **6b**. An IR spectrum in hexane indicated $[(CO)_5Mn]_2$ to be the only inorganic product.

In a related experiment, 10 mg (0.04 mmol) of **1** and 5 μL (5 mg, 0.04 mmol) of *p*-methoxybenzaldehyde were stirred without solvent under argon for 1 h at 25 °C. An IR spectrum in hexane showed **5** (2108 m, 2012 vs, 1995 vs cm^{-1}) to be present in ca. 60% yield.

Reaction of 1 with *p*-(Dimethylamino)benzaldehyde. To a 5-mm NMR tube was added 115 mg (0.43 mmol) of **1** and 63 mg (0.43 mmol) of *p*-(dimethylamino)benzaldehyde. The tube was sealed with a latex septum and evacuated/refilled with argon five times. Benzene-d_6 (0.25 mL) was added by syringe, and the tube was shaken to effect dissolution.

The reaction was held at 40 °C in the probe of a Varian A-60 NMR spectrometer. Formation of pinacol ethers **7a,b** (δ 4.83/4.72 (s, 2 H), 2.53/2.62 (s, 12 H), 0.01/−0.19 (s, 18 H))[18] was monitored by ^{1}H NMR. No resonances attributable[8b] to an organometallic product could be detected at any time. After 4 h, **7a,b** (ratio ca. 1:1) had formed in 90 ± 5% yield according to ^{1}H NMR and GLC analysis. An IR spectrum in hexane showed $[(CO)_5Mn]_2$ to be the only inorganic product. An identical experiment conducted at 5 °C proceeded similarly without the formation of detectable organometallic intermediates.

Reaction of 1 with Butyraldehyde. To a 5-mm NMR tube was added 253 mg (0.94 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled with argon five times. Butyraldehyde (100 μL, 71 mg, 1.13 mmol) was then added by syringe, and the mixture was shaken until homogeneous. After 4 weeks at 5 °C, the reaction was diluted to 0.50 mL with C_6D_6. GLC and ^{1}H NMR analysis showed considerable unreacted **1** and butyraldehyde. The only organic products were enol ethers **8** (δ 4.35 (m, 1 H), 5.97 (m, 1 H), 0.10 (s, 9 H)) and **9** (δ 4.90 (m, 1 H), 6.12 (m, 1 H), 0.10 (s, 9 H))[20] in a ratio of ca. 3:2 and a combined yield of 25% (based upon **1**). The ^{1}H NMR spectrum also showed $(CO)_5MnH$ (δ −7.9 (s, 1 H))[34] to be present in 25% yield.

Reaction of 1 with Acetone. To a 5-mm NMR tube was added 300 mg (1.12 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled with argon five times. Acetone (150 μL, 118 mg, 2.02 mmol) was added by syringe. After 1 week at room temperature, a ^{1}H NMR spectrum showed that roughly half of the **1** had been consumed and an IR spectrum in hexane showed no evidence of an organometallic complex. After 2 weeks at room temperature, analysis by ^{1}H NMR (C_6D_6) and GLC showed $(CO)_5MnH$ and enol ether **10** (δ 4.55 (m, 2 H), 1.95 (s, 3 H), 0.15 (s, 9 H))[20] to be the only products in 70% yield.

Reaction of 1 with Cyclohexanone. To a 5-mm NMR tube was added 142 mg (0.53 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled with argon five times. Cyclohexanone (110 μL, 104 mg, 1.06 mmol) was then added by syringe and the mixture shaken until homogeneous. After 1 week at room temperature, the reaction was diluted to 0.50 mL with C_6D_6. A ^{1}H NMR spectrum showed that no **1** remained and that **11** (δ 4.73 (m, 1 H), 0.10 (s, 9 H))[20] and $(CO)_5MnH$ (δ −7.9 (s, 1 H)[34] were present in 90 ± 5% yield. GLC analysis showed 0.51 mmol of cyclohexanone and 0.50 mmol of **11** (94% based upon **1**) to be present.

Reaction of 1 with 2-Methylcyclohexanone. To a 5-mm NMR tube was added 282 mg (1.05 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled with argon five times. 2-Methylcyclohexanone (130 μL, 120 mg, 1.07 mmol) was then added by syringe, and the mixture was shaken until homogeneous. The reaction was held at room temperature and was monitored by ^{1}H NMR and GLC. At 10% conversion (ca. 1 day), the ratio of **13** (δ 0.15 (s, 9 H)) to **12** (δ 4.75 (t, 1 H), 0.10 (s, 9 H))[20] was 2:1. This ratio grew steadily as the reaction proceeded; after 4 weeks, $(CO)_5MnH$ was present in 85 ± 5% yield. Compounds **13** and **12** were present in a 9:1 ratio and a 90% combined yield.

Attempted Isomerization of 12 to 13 in the Presence of 1. To a 5-mm NMR tube was added 145 mg (0.54 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled five times with argon. Enol ether **12**[20] was then added by syringe and the mixture shaken until homogeneous. After 4 weeks at room temperature, a ^{1}H NMR spectrum and GLC analysis showed no isomerization had occurred.

Isomerization of 12 to 13 in the Presence of $(CO)_5MnH$. To a 5-mm NMR tube was added 124 mg (0.46 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled with argon five times. Methanol (19 μL, 15 mg, 0.47 mmol) was added by syringe. The tube was held at ca. 50 °C for 1 h after which a ^{1}H NMR spectrum showed $(CO)_5MnH$ formation to be complete.[34] Enol ether **12**[20] (90 μL, 81 mg, 0.47 mmol) was added by syringe. GLC and ^{1}H NMR analysis showed that **12** was converted to a 9:1 mixture of **13** and **12** after 3 weeks at room temperature. A ^{1}H NMR spectrum showed that all $(CO)_5MnH$ remained.

Reaction of 12 and 13 with $(CO)_5MnD$. A 5-mm NMR tube containing 247 mg (0.92 mmol) of **1** was sealed with a Latex septum and evacuated/refilled with argon five times. CH_3OD (37 μL, 30 mg, 0.92 mmol) was added by syringe, and the tube was kept at 50 °C for 1 h. a ^{1}H NMR spectrum showed $CH_3OSi(CH_3)_3$ formation to be complete[34] and the absence of $(CO)_5MnH$. A 9:1 mixture of **13**:**12** (80 μL, 72 mg, 0.40 mmol)[20] was added by syringe. After 4 weeks at room temperature, the ^{1}H NMR spectrum showed (with use of $CH_3OSi(CH_3)_3$ as standard) that ca. 40% of the $(CO)_5MnD$ had been converted to $(CO)_5MnH$ (46% theoretical).

Reaction of 1 with Cyclohexanone under Carbon Monoxide. To the tube of a Fischer-Porter bottle was added a magnetic stir bar and 380 mg (1.41 mmol) of **1**. The apparatus was assembled and evacuated/refilled with argon three times and then flushed with CO (10 atm) twice. A solution of cyclohexanone (300 μL, 283 mg, 2.88 mmol) in CD_3CN (0.50 mL) was added by syringe. The reaction was pressurized to 10 atm with CO and stirred at room temperature.

After 2 h the reaction was vented and the contents transferred by syringe to a 5-mm NMR tube. A 60-MHz ^{1}H NMR spectrum showed $(CO)_5MnH$ and enol ether **11** to be present in 90% yield. An IR spectrum in heptane showed no bands attributable to an acyl complex.

Reaction of 1 with Butyraldehyde under CO. Synthesis of $(CO)_5MnCOCH(n\text{-}C_3H_7)OSi(CH_3)_3$ (14). To the glass tube of a Fischer-Porter bottle was added a magnetic stir bar and 268 mg (1.00 mmol) of **1**. The apparatus was assembled, evacuated/refilled with argon three times, and flushed with 10 atm of CO twice. A solution of butyraldehyde (200 μL, 158 mg, 2.25 mmol) in CD_3CN (0.50 mL) was added by syringe and the apparatus pressurized with 10 atm of CO and stirred at room temperature.

After 2 h the reaction was vented and the solution was transferred by syringe to a 5-mm NMR tube. A 60-MHz ^{1}H NMR spectrum (CD_3CN) showed resonances, (δ 3.65 (t, 2 H), 1.50 (m, 4 H), 0.95 (t, 3 H), 0.15 (s, 9 H)) assignable to **14** (yield 75 ± 5%) in addition to butyraldehyde. The solution was transferred to a Schlenk flash where solvent and excess butyraldehyde were removed under vacuum. A yellow oil remained which was dissolved in heptane. Its IR spectrum showed the presence of **14** (2117 m, 2048 m, 2018 vs, 1998 s, 1636 w cm^{-1}) and a small amount of $(CD_3CN)Mn_2(CO)_9$.[35] Upon cooling the solution to −78 °C, the $(CD_3CN)Mn_2(CO)_9$ (IR(hexane) (cm^{-1}): 2094 w, 2026 s, 2005 s, 1989 vs, 1964 m, 1947 m) precipitated. The cold solution was filtered and the heptane removed in vacuo to give **14** as a yellow oil. All attempts to crystallize **14** were unsuccessful: 200-MHz ^{1}H NMR (C_6D_6) δ 3.67 (t, *J* = 6 Hz, 2 H), 1.56 (m, 2 H), 1.42 (m, 2 H), 0.90 (t, *J* = 7 Hz, 3 H), 0.17 (s, 9 H); mass spectrum (*m/e*, 16 eV) 223 (6%, $Mn(CO)_6^+$), 145 (29% $^+CH(C_3H_7)OSi(CH_3)_3$), 144 (31%), 129 (42%), 75 (100%); ^{13}C NMR see below.

^{13}C NMR Spectrum of 14. A 10-mm NMR tube containing a magnetic stir bar and 300 mg (1.12 mmol) of **1** was placed in the tube of a Fischer-Porter bottle. The space surrounding the NMR tube was filled with Nujol to minimize the dead volume of the ap-

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(35) Ziegler, M. L.; Haas, H.; Sheline, R. K. *Chem. Ber.* **1965**, *98*, 2454.

paratus. The tube was assembled and evacuated/refilled with argon three times. A solution of butyraldehyde (100 μL, 82 mg, 1.14 mmol) in CD_3CN (0.40 mL) was added by syringe. The reaction was pressurized to 10 atm with CO and stirred at room temperature. After 2 h, the reaction was vented, the NMR tube was removed from the vessel, and the stirring bar was removed. CD_3CN (2.0 mL) was added, and the tube was capped and was rinsed with heptane to remove Nujol. A 50-MHz ^{13}C NMR spectrum at −23 °C showed resonances assignable to $(CO)_5MnSi(CH_3)_3$ (δ 214.0, 212.4, 6.4), butyraldehyde (δ 204.3, 46.3, 16.2, 14.0) and **14** (δ 270.7 (acyl carbon); 211.3; 210.1 (carbonyl carbons); 88.3 (ether carbon); 36.1, 14.5, 14.2 (alkyl carbons); and 0.05 ($Si(CH_3)_3$ carbons)). This spectrum served as an important reference for the following experiment.

Reaction of 1 with Butyraldehyde under ^{13}CO. ^{13}C NMR Spectrum of Enriched 14. An experiment identical with the previous one was conducted, except that ^{13}CO (90.7% isotopic purity) was used.

Integration of the ^{13}C NMR spectrum relative to the natural-abundance spectrum obtained in the previous experiment showed enrichment factors of 10 ± 2 in the acyl carbon resonance (δ 270.7) and 31 ± 5 in the cis carbonyl carbon resonances (δ 211.3), while the two spectra were identical in the alkyl region. The IR spectrum in heptane showed new bands (cm^{-1}) at 2108 m, 2038 m, 1981 sh, and 1948 w, while the band at 1636 did not change.

In a control experiment, a solution of **1** (300 mg, 1.12 mmol) in CD_3CN (2.50 mL) was stirred under ^{13}CO under identical conditions. A ^{13}C NMR spectrum indicated an enrichment factor of 10 ± 2 with use of the $Si(CH_3)_3$ resonance for calibration.

The control experiment indicates an average background enrichment of ca. 2% in each CO of **1**. Thus the enrichment factor for the four carbonyls of **14** cis to the acyl ligand was corrected to 23 ± 5; that for the acyl carbon was corrected to 8 ± 2. Multiplication of the former value by 4 yields 92 ± 20. The carbonyl trans to the acyl ligand was also enriched, but its less intense, broad δ 210.1 ^{13}C resonance could not as accurately be quantified. The data indicate that the ^{13}CO is incorporated into the carbonyl ligands of **14** about an order of magnitude more frequently than the acyl ligand.

Reaction of 1 with Benzoyl Chloride in Acetonitrile. To a 25-mL round-bottom Schlenk flask equipped with a magnetic stir bar was added 134 mg (0.50 mmol) of **1**. The flask was sealed with a rubber septum and evacuated/refilled with argon three times. CH_3CN (10 mL) was added by syringe, followed by benzoyl chloride (60 mL, 73 mg, 0.52 mmol). The reaction was stirred at room temperature and was monitored by withdrawing small aliquots by syringe, diluting them with CH_3CN, and recording their IR spectra. After 4 h, the formation of a low yield of $(CO)_5Mn(COC_6H_5)$ was evidenced by IR bands at 2120 and 1660 cm^{-1} (other bands were obscured by the presence of unreacted **1**).[36] After 1 day all starting material had been consumed, but $(CO)_5Mn(COC_6H_5)$ could no longer be detected. The IR spectrum showed $(CH_3CN)Mn_2(CO)_9$ to be the principal manganese-containing product.

In a related experiment, 40 mg (0.13 mmol) of $(CO)_5Mn(COC_6H_5)$ and 16 μL (14 mg, 0.13 mmol) of $(CH_3)_3SiCl$ were stirred in CH_3CN (1 mL) under argon for 1 day at room temperature. An identical IR spectrum was obtained.

Relative Reaction Rates in Acetonitrile (Table I). Butyraldehyde. To a 5-mm NMR tube was added 134 mg (0.50 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled with argon five times. CD_3CN (0.50 mL) was then added by syringe, and a ^1H NMR spectrum was recorded. Butyraldehyde (44 μL, 36 mg, 0.50 mmol) was added by syringe, and the tube was shaken to effect dissolution. The reaction was monitored by recording ^1H NMR spectra of the $Si(CH_3)_3$ region every 2 min at 39 °C.

Cyclohexanone. An experiment identical with the previous one was conducted, except that cyclohexanone (52 μL, 49 mg, 0.50 mmol) was used.

Benzaldehyde. An experiment identical with the previous one was conducted, except that benzaldehyde (51 μL, 53 mg, 0.50 mmol) was used.

***p*-Methoxybenzaldehyde.** An experiment identical with the previous one was conducted, except that *p*-methoxybenzaldehyde (61 μL, 68 mg, 0.50 mmol) was used.

***p*-(Dimethylamino)benzaldehyde.** To a 5-mm NMR tube was added 134 mg (0.50 mmol) of **1**. The tube was sealed with a Latex septum and evacuated/refilled with argon five times. CD_3CN (0.25 mL) was then added by syringe. The tube was shaken until homogeneous and a ^1H NMR spectrum was recorded. A solution of *p*-(dimethylamino)benzaldehyde (75 mg, 0.50 mmol) in CD_3CN (0.25 mL) was then added by syringe, and the contents were mixed by shaking the tube rapidly. The reaction was monitored as above.

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Registry No. **1**, 26500-16-3; **2**, 6186-14-7; **3a**, 6186-15-8; **3b**, 6186-14-7; **4**, 14642-79-6; **5**, 77589-68-5; **6a**, 30412-84-1; **6b**, 30412-82-9; **7a**, 30412-85-2; **7b**, 30412-83-0; **8**, 19980-23-5; **9**, 19980-22-4; **10**, 1833-53-0; **11**, 6651-36-1; **12**, 19980-35-9; **13**, 19980-33-7; **14**, 77589-69-6; benzaldehyde, 100-52-7; *p*-methoxybenzaldehyde, 123-11-5; *p*-(dimethylamino)benzaldehyde, 100-10-7; butyraldehyde, 123-72-8; acetone, 67-64-1; cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; $(CO)_5MnH$, 16972-33-1; benzoyl chloride, 98-88-4; $[(CO)_5Mn]_2$, 10170-69-1; $(CO)_5Mn(COC_6H_5)$, 15612-92-7; $(CH_3CN)Mn_2(CO)_9$, 26595-04-0.

Supplementary Material Available: Figure 1, CIDNP arising from the reaction of **1** with benzaldehyde (with experimental), and experimental procedures for some unsuccessful reactions (3 pages). Ordering information is given on any current masthead page.

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[36] Coffield, T. H.; Kozikowski, J.; Closson, R. D. *J. Org. Chem.* **1957**, *22*, 598.