R_w = 0.058 was obtained. The esd's for the atomic coordinates of the metallacyclic hydrogen were obtained from the last refinement cycle which used a sin θ/λ cutoff. The other hydrogens were not refined. The temperature factors of the hydrogen atoms were based on the temperature factors of the carbons to which they were bonded.

Acknowledgment. We are grateful to the Department of Energy for support of this project. FT NMR spectrometers utilized were provided by NSF departmental instrumentation grants.

Supplementary Material Available: Additional crystallographic data for **22** and preparations of $(C_2H_5)_4N^+F^-\cdot(H_2O)_{2.6}$ and $(C_6H_5)_2P(o\text{-}C_6H_4X)$ where X = CHO (**18**), CH_2OH (**19**), $CH_2OSi(CH_3)_3$, $CH(CN)OSi(CH_3)_3$, and $CH{=}N(t\text{-}C_4H_9)$ (29 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Metallacyclic Manganese α-Hydroxyalkyl Complexes Containing Aliphatic Bridges and Phosphorus and Nitrogen Donor Atoms; First Carbonylation of an Isolable α-Hydroxyalkyl Complex

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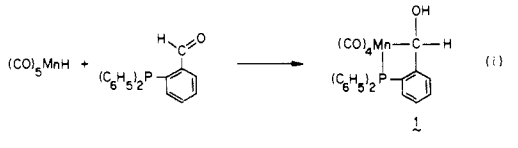
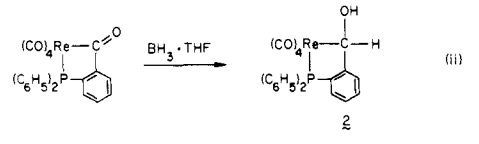
Abstract: Reaction of $(CO)_5MnH$ with $(C_6H_5)_2PCH_2CH_2CHO$ (**3**) gives *cis*-$(CO)_4Mn(H)P(C_6H_5)_2CH_2CH_2CHO$ (**4**, 97%), which cannot be induced to cyclize to α-hydroxyalkyl complex $(CO)_4MnP(C_6H_5)_2CH_2CH_2CHOH$ (**5**). Two other attempted syntheses of **5**—the photochemical decarbonylation of hydroxyacyl complex $(CO)_4MnP(C_6H_5)_2CH_2CH_2CH(OH)\text{—}C{=}O$ (**7**) and the BH_3·THF reduction of acyl complex $(CO)_4MnP(C_6H_5)_2CH_2CH_2C{=}O$ (**8**)—also give **4**. However, analogues of **5** in which the phosphorus is replaced by nitrogen are stable. Complexes $(CO)_4MnNH_2CHRCHR'CHOH$ (**10a**, R = R' = H; **10b**, R = CH_3, R' = H; **10c**, R = R' = $-(CH_2)_4-$) are prepared in ≥90% yields via BH_3 reduction of the corresponding acyl complexes $(CO)_4MnNH_2CHRCHR'\text{—}C{=}O$ (**9a-c**). Treatment of **10c** with $(CH_3)_3SiCl/[(CH_3)_3Si]_2NH$ gives α-(silyloxy)alkyl complex $(CO)_4MnNH_2CHRCHR'CHOSi(CH_3)_3$ (**12**, R = R' = $-(CH_2)_4-$, 52%). Under 250-360 psi of CO in CH_3NO_2 at -3 °C, **10c** and **12** carbonylate to acyl complexes $(CO)_4MnNH_2CHRCHR'CH(OH)\text{—}C{=}O$ (**11**) and $(CO)_4MnNH_2CHRCHR'CH(OSi(CH_3)_3)\text{—}C{=}O$ (**13**), respectively. The former reaction is ca. 16 times faster. IR (ν_{O-H}, $\nu_{C=O}$) and ^{13}C NMR spectra show the presence of a hydrogen bond between the hydroxyl and acyl oxygen in **11**. This is proposed to account, at least in part, for the faster carbonylation of **10c**. The possible relevance of these data to the metal-catalyzed conversion of CO/H_2 to oxygenates is discussed.

In the preceding papers,[1,2] we established that the stability of α-hydroxyalkyl complexes could be dramatically enhanced by incorporating the α-hydroxyalkyl ligand into a chelate ring. For example, we were able to prepare the metallacyclic manganese α-hydroxyalkyl complex $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CHOH)$ (**1**, eq i) from aldehyde and $(CO)_5MnH$ precursors.[2] Complex $(CO)_5MnCH(C_6H_5)OH$, which lacks the chelate ring of **1**, was too unstable to detect at -50 °C.[1] Rhenium α-hydroxyalkyl complex $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CHOH)$ (**2**) was prepared by two routes, one being the BH_3·THF reduction shown in eq ii. Unfortunately, **1** and **2** proved unreactive toward CO and other reagents, such as $P(CH_3)_3$, that can effect "CO insertion" into metal-alkyl bonds. Carbonylation of an α-hydroxymethyl intermediate is believed to be a key step in the metal-catalyzed conversion of CO/H_2 to dioxygenated C_2 molecules such as ethylene glycol[3] and in formaldehyde homologation.[4] Hence, we sought α-hydroxyalkyl complexes that could be converted to hydroxy*acyl* complexes.





In this paper, we explore the scope of aldehyde/$(CO)_5MnH$ (eq i) and BH_3·THF (eq ii) routes to metallacyclic α-hydroxyalkyl complexes. We find significant and surprising differences when the aryl linkage in metallacycle **1** is replaced with an aliphatic linkage and when the phosphorus donor atom is replaced with a nitrogen donor atom. We also report the first, and remarkably

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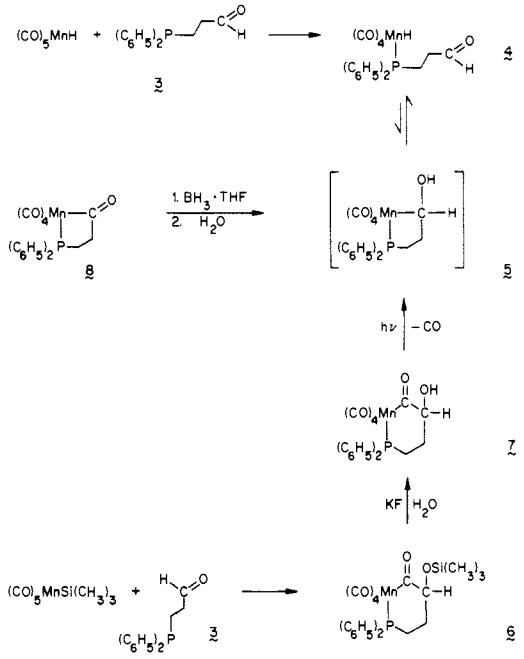
Scheme I. Attempted Syntheses of α-Hydroxyalkyl Complex $(CO)_4MnP(C_6H_5)_2CH_2CH_2CHOH$ (**5**)



facile, carbonylation of an isolable α-hydroxyalkyl complex. A portion of this study has been communicated.[5]

Results

I. Phosphorus-Containing Metallacycles. In order to probe the scope of eq i, we sought other phosphine aldehydes. The compound $(C_6H_5)_2PCH_2CHO$ had been described in the literature,[6] but it rapidly equilibrated with a mixture of enol tautomers. We were unable to prepare significant quantities of $(C_6H_5)_2PCH_2CHO$ in pure form. Hence, we synthesized the new phosphine $(C_6H_5)_2PCH_2CH_2CHO$ (**3**) by reaction of $(C_6H_5)_2PLi$ with $ClCH_2CH_2CH(OCH_3)_2$, followed by hydrolysis. Phosphine **3** was a thermally sensitive oil.

Reaction of **3** with $(CO)_5MnH$ in hexanes (1 h, 25 °C) gave the labile substitution product *cis*-$(CO)_4Mn(H)P(C_6H_5)_2CH_2CH_2CHO$ (**4**, 97%, Scheme I). The aldehyde functionality in **4** was apparent from ^1H NMR (δ 9.59) and IR (1726 cm^{-1}) spectra (Tables I and II). The chemical shift and $^2J_{HP}$ of the Mn–H ^1H NMR resonance (δ −7.68, 37.3 Hz) were also characteristic[7] of a *cis*-$(CO)_4Mn(H)PX_3$ complex. The three CO resonances observed in the ^{13}C NMR spectrum precluded a trans geometry. Hydride complex **4** could not be induced to cyclize to the desired α-hydroxyalkyl complex $(CO)_4MnP(C_6H_5)_2CH_2CH_2CHOH$ (**5**). This was in striking contrast to eq i, where cyclization was spontaneous. Hence, to probe the direction of the equilibrium **4** ⇌ **5**, other syntheses of **5** were attempted.

Reaction of **3** with $(CO)_5MnSi(CH_3)_3$ in benzene (29 h, 25 °C) gave, after workup, the oily metallacyclic (silyloxy)acyl complex $(CO)_4MnP(C_6H_5)_2CH_2CH_2CH(OSi(CH_3)_3)—C{=}O$ (**6**) in 30% yield (Scheme I). When this reaction was monitored by ^1H NMR, a *cis*-$(CO)_4Mn(H)PX_3$ byproduct with a resonance at δ −7.2 (d, J_{HP} = 37 Hz) was noted.

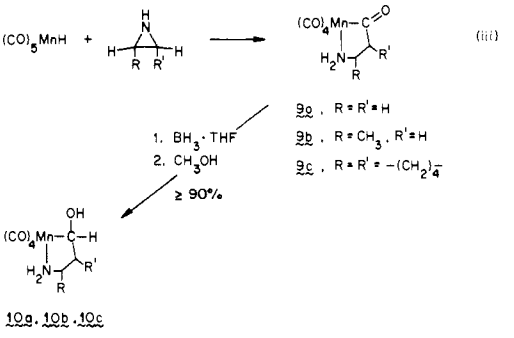
The trimethylsilyl group in **6** was removed with aqueous KF to give, after workup, the crystalline hydroxyacyl complex $(CO)_4MnP(C_6H_5)_2CH_2CH_2CH(OH)—C{=}O$ (**7**, Scheme I) in 85% yield. A number of attempts were made to thermally and photochemically decarbonylate **7** to **5**. Small amounts of **4** were usually produced, as assayed by ^1H NMR and IR spectroscopy. In no case was a compound with the spectroscopic features expected for **5** detected. In the most diagnostic experiment, a sample of **7** in a cavity IR cell (KBr, THF) was irradiated (Rayonet reactor, room temperature). After 65 s, **7** (2072 cm^{-1}) and **4** (2062, 1726 cm^{-1}) were present in approximately equal amounts. With continued irradiation (15 s), a third minor component (2046 cm^{-1}) appeared. However, complete photolysis of **7** could not be effected under these conditions. In a control experiment, it was shown that the 2046-cm^{-1} species did not arise from the photolysis of **4**.

We also attempted to generate **5** by a route analogous to eq ii. Metallacycle $(CO)_4MnP(C_6H_5)_2CH_2CH_2—C{=}O$ (**8**), previously prepared by Lindner,[8] was treated with BH_3·THF (0.75 equiv) in the presence of an internal standard. A ^1H NMR spectrum showed a new multiplet at δ 5.6. Water was then added. The δ 5.6 resonance disappeared, and **4** (20%) and an unidentified *cis*-$(CO)_4Mn(H)PX_3$ compound (δ −7.5, d, J_{HP} = 36 Hz, 46%) formed.

The above experiments provide excellent evidence that the equilibrium **4** ⇌ **5** lies strongly to the left. We wondered if small equilibrium quantities of **5** could be trapped by carbonylation. Hence, **4** was treated with 360 psi of CO in CH_3NO_2 at −3 ± 1 °C. Although some **4** decomposed, no **7** (which was shown to be stable to these conditions) was detected.

II. Nitrogen-Containing Metallacycles. We were surprised that five-membered metallacycle **1** was stable with respect to a ring-opened manganese phosphine aldehyde complex, but 5-membered metallacycle **5** was not. Additions to aliphatic aldehydes are usually thermodynamically more favorable than additions to aromatic aldehydes,[9] so we speculate that the ring size in **5**, which contains an aliphatic bridge, might not be optimal. Nitrogen makes substantially shorter bonds than phosphorus,[10] so we set out to make nitrogen analogues of **5**.

Manganese acyl complexes, $(CO)_4MnNH_2CHRCHR'—C{=}O$, **9a–c**, were prepared from $(CO)_5MnH$ and aziridines via procedures closely related to those reported by Beck (eq iii).[11] These were subsequently treated with



BH_3·THF (2 equiv) and CH_3OH. Workup gave α-hydroxyalkyl complexes $(CO)_4MnNH_2CHRCHR'CHOH$, **10a–c**, as thermally sensitive yellow powders in ≥90% yields. Complexes **10a–c** exhibited characteristic IR ν_{O-H} (Table II) and MnCH ^{13}C NMR (Table I) resonances. Their ^1H NMR spectral resonances were broadened, presumably due to paramagnetic impurities. Complex

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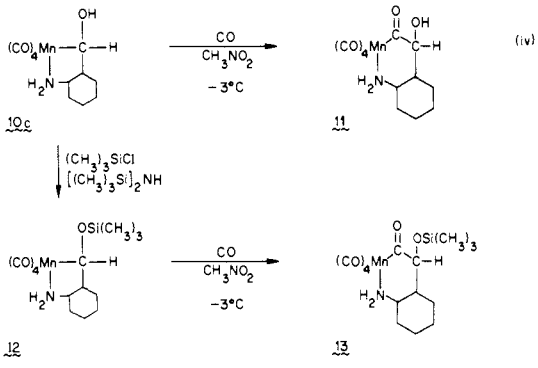
(9) Hine, J. "Structural Effects in Equilibria in Organic Chemistry"; John Wiley and Sons: New York, 1975; pp 257–265.
(10) (a) Compare, for example, $N(CH_3)_3$[10b] and $N(C_6H_5)_3$[10c] (1.42–1.45 Å) to $P(CH_3)_3$[10d] and $P(C_6H_5)_3$[10e] (1.83–1.85 Å). (b) Beagley, B.; Hewitt, T. G. *J. Chem. Soc., Faraday Trans.* **1968**, *64*, 2561. (c) Sasaki, Y.; Kimura, K.; Kubo, M. *J. Chem. Phys.* **1959**, *31*, 477. (d) Bartell, L. S.; Brockway, L. O. *Ibid.* **1960**, *32*, 512. (e) Daly, J. J. *J. Chem. Soc.* **1964**, 3799. (f) Compare also data in any recent issue of "Bond Index to the Determinations of Inorganic Crystal Structures", compiled by Brown, I. D.; Brown, M. C.; Hawthorne, F. C. Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada.
(11) Danzer, W.; Höfer, R.; Menzel, H.; Olgemöller, B.; Beck, W. *Z. Naturforsch.* **1984**, *39b*, 167.

10c was further characterized by microanalysis. Each complex underwent rapid OH/OD exchange in CD_3NO_2. Whereas **10c** was ≥95% diastereomerically pure, **10b** was a mixture of epimers.

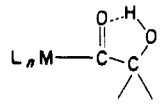
With the stability of nitrogen analogues of **5** established, we next sought to determine their reactivity toward CO. When α-hydroxyalkyl complex **10c** was treated with 350–360 psi of CO at −3 ± 1 °C in CH_3NO_2 for 44 h, the hydroxyacyl complex $(CO)_4MnNH_2CHCH(CH(OH)—C{=}O)CH_2CH_2CH_2CH_2$ (**11**) formed and was subsequently isolated in 74% yield (eq ii). For comparison purposes, α-((trimethylsilyl)oxy)alkyl $(CO)_4MnNH_2CHCH(CHOSi(CH_3)_3)CH_2CH_2CH_2CH_2$ (**12**) was prepared in 52% yield from **10c** and $(CH_3)_3SiCl/HN(Si(CH_3)_3)_2$. Complex **12** similarly carbonylated (350–360 psi of CO, −3 ± 1 °C, CH_3NO_2) to (silyloxy)acyl complex $(CO)_4MnNH_2CHCH(CH(OSi(CH_3)_3)—C{=}O)CH_2CH_2CH_2CH_2$ (**13**, eq ii). However, this reaction was considerably slower, and product **13** always partially decarbonylated upon workup.



The carbonylation rates of **10c** and **12** were monitored by IR spectroscopy at −3 ± 1 °C for 14 and 73 h, respectively, and found to be (k_{obsd}, 350–360 psi) 125 ± 5 × 10^{-7} and 7.5 ± 0.4 × 10^{-7} s^{-1}. Under 250–260 psi of CO, k_{obsd} of 66.0 ± 3.2 × 10^{-7} s^{-1} (**10c**, 14 h) and 4.0 ± 0.2 × 10^{-7} s^{-1} (**12**, 102 h) were measured. Hence, at −3 °C and 250–360 psi of CO in CH_3NO_2, *α-hydroxyalkyl complex **10c** carbonylates over 16 times faster than its α-((trimethyl)silyl)oxy analogue **12**.*

Carbonylation rates were also measured in CD_3NO_2 (350–360 psi), in which **10c** is converted to **10c**-d_1. Under these conditions, k_{obsd} of 81 ± 4 × 10^{-7} s^{-1} (**10c**, 24 h) and 5.5 ± 0.3 × 10^{-7} s^{-1} (**12**, 73 h) were measured. These give k_H/k_D of 1.54 (**10c**) and 1.36 (**12**), which are identical within experimental error.

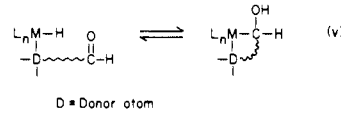
In order to help rationalize the faster carbonylation of **10c**, a detailed IR analysis of the starting materials and products in eq iv was undertaken. IR spectra of **10c** and **11** in CH_2Cl_2 were found to be concentration independent (±1 cm^{-1}) over the range 0.016–0.16 M. Key spectral regions are shown in Figure 1. Differences in the ν_{O-H} of **11** and **10c**, and the $\nu_{C=O}$ of **11** and **13**, clearly established the presence of an intramolecular hydrogen bond in **11**,[12] as depicted schematically in **14**. Furthermore, the ^{13}C NMR spectra of **11** and **13** (Table I) were virtually superimposable, except that the acyl resonance of **11** was 11 ppm downfield of that in **13**.



14

Discussion

I. Syntheses of α-Hydroxyalkyl Complexes. A generalized equilibrium for the formation of metallacyclic α-hydroxyalkyl complexes from aldehydic metal hydride precursors is shown in eq v. The above data indicate that the direction of this equilibrium



is highly dependent upon the nature of the metallacycle bridge. Nitrogen-containing α-hydroxyalkyl complexes **10a–c** show no tendency to decompose to $(CO)_4Mn(H)NH_2CHRCHR'CHO$ species, so we presume that for **10a–c** the equilibrium in eq v lies to the right. However, phosphorus-containing α-hydroxyalkyl complex **5** (Scheme I) is clearly unstable with respect to **4**. Hence, in this case the equilibrium in eq v lies to the left. We suggest that this difference is due to the shorter bond lengths in **10a–c** (Mn-N and N-C vs Mn-P and P-C) and consequently smaller metallacycle size.

To probe the influence of metallacycle ring size on α-hydroxyalkyl complex stability, we attempted to synthesize four-membered analogues of **5**. Unfortunately, we were unable to prepare the acyl complex $(CO)_4MnP(C_6H_5)_2CH_2—C{=}O$, which would have been an attractive substrate for BH_3·THF reduction. In a single run experiment, we treated $(CO)_5MnH$ with phosphine ketone $(C_6H_5)_2PCH_2COCH_3$.[13] Only CO subsitution occurred, as assayed by ^1H NMR spectroscopy. Reaction of $(CO)_5MnH$ with $(C_6H_5)_2PC(CH_3)_2CHO$[14] gave numerous products, and that of $(CO)_5MnSi(CH_3)_3$ with $(C_6H_5)_2PC(CH_3)_2CHO$ cleanly gave silyl enol ether $(CH_3)_2C{=}CHOSi(CH_3)_3$, as reported elsewhere.[14]

As described separately, we have been able to prepare silylated three-membered analogues of **5**, $(CO)_4MnP(C_6H_5)_2C(R)OSi(CH_3)_3$.[15] Upon attempted hydrolytic generation of α-hydroxyalkyl complexes $(CO)_4MnP(C_6H_5)_2C(R)OH$, acyclic *acyl* com-

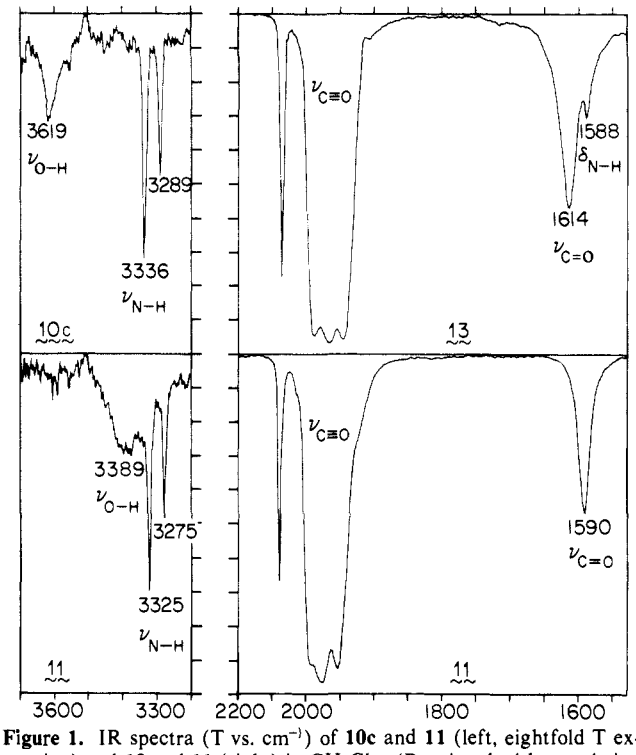


Figure 1. IR spectra (T vs. cm^{-1}) of **10c** and **11** (left, eightfold T expansion) and **13** and **11** (right) in CH_2Cl_2. (Reprinted with permission from ref 5. Copyright 1984, American Chemical Society.)

(12) See: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; John Wiley & Sons: New York, 1981: pp 112–115, 118.

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Table I. ^{1}H and ^{13}C NMR Data for Organometallic Compounds

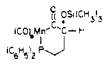
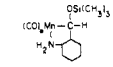
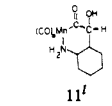
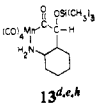
compound	^{1}H NMR (δ)[a]	^{13}C NMR (ppm)[a,b]		
		CO	CHOH or CHOSi	other
 **4**[c]	9.59 (br d, J_{HH} = 2.3 Hz, 1 H) 7.78–7.18 (m, 10 H) 2.81–2.66 (m, 2 H) 2.62–2.48 (m, 2 H) −7.68 (d, J_{HP} = 37.3 Hz, 1 H)	220.1 (s, C≡O) 218.7 (d, J = 19.6 Hz, 2 C≡O) 217.9 (d, J = 14.7 Hz, C≡O) 201.8 (d, J = 14.6 Hz, C═O)		136.0 (d, J = 41.6 Hz, ipso) 133.2 (d, J = 9.8 Hz) 132.0 (s, p) 130.3 (d, J = 9.7 Hz) 38.7 (s, PCH_2CH_2) 24.8 (d, J = 29.5 Hz, PCH_2)
 **6**[d,e]	7.65–7.36 (m, 10 H) 3.78 (dd, J = 6.6, 2.6 Hz, 1 H) 3.00–2.89 (m, 1 H) 2.52–2.40 (m, 1 H) 2.18–1.94 (m, 2 H) 0.19 (s, 9 H)	279.1 (d, J = 23.9 Hz, C═O) 216.2 (s, C≡O) 215.8, 215.5, 215.4, 215.1 (3 C≡O, ^{31}P couplings unassigned)	84.9 (s)[f]	135.8 (d, J = 42.2 Hz, ipso) 134.8 (d, J = 40.6 Hz, ipso) 132.4 (d, J = 10.3 Hz) 131.9 (d, J = 9.2 Hz) 131.1 (s, p), 131.0 (s, p) 129.3_2 (d, J = 9.0 Hz) 129.2_6 (d, J = 9.0 Hz) 28.7 (s, PCH_2CH_2) 23.7 (d, J = 28.3 Hz, PCH_2) −0.40 (s, SiC)[f,g]
 **7**[d]	7.68–7.35 (m, 10 H) 4.47 (br s, OH) 4.19 (br s, 1 H) 2.67–2.62 (m, 3 H) 1.76–1.74 (m, 1 H)	274.6 (d, J = 19.7 Hz, C═O) 216.7 (d, J = 19.8 Hz, C≡O) 215.7 (d, J = 16.8 Hz, C≡O) 215.4 (s, C≡O) 213.2 (d, J = 19.5 Hz, C≡O)[f]	86.5 (s)[f]	135.0 (d, J = 42.5 Hz, 2 ipso) 132.9 (d, J = 8.6 Hz) 132.1 (d, J = 8.8 Hz) 132.0 (s, p), 131.7 (s, p) 130.0 (d, J = 8.6 Hz) 129.9 (d, J = 10.8 Hz) 29.6 (s, PCH_2CH_2) 26.9 (d, J = 28.0 Hz, PCH_2)[f,g]
 **9a**[c]	3.70 (br s, NH_2) 2.77 (pseudo quintet, J_{HH} = 7.0 Hz, 2 H) 2.14 (t, J_{HH} = 7.0 Hz, 2 H)	286.5 (C═O) 219.8 (C≡O) 217.6 (C≡O) 215.1 (2 C≡O)[h]		57.2 (NCH_2CH_2) 42.7 (NCH_2)[h]
 **9b**	4.28 (br d, J_{HH} = 10.7 Hz, NH) 3.63 (pseudo t, J_{HH} = 10.7 Hz, NH) 2.85 (m, 1 H) 2.31 (ddd, J_{HH} = 15.4, 4.6, 2.1 Hz, 1 H) 1.94 (dd, J_{HH} = 15.4, 12.6 Hz, 1 H) 1.33 (d, J_{HH} = 6.2 Hz, 3 H)[i]	285.5 (C═O) 219.6 (C≡O) 217.2 (C≡O) 215.7 (C≡O) 215.0 (C≡O)[c,h]		64.7 (CH_2) 52.4 (CH) 22.1 (CH_3)[c,h]
 **9c**	4.60 (br s, NH) 4.05 (br s, NH) 2.27–2.00 (m, 3 H) 1.81–1.41 (m, 4 H) 1.27–0.84 (m, 3 H)[j]	280.2 (C═O) 219.6 (C≡O) 217.9 (C≡O) 216.5 (C≡O) 215.8 (C≡O)[k]		70.8 (CHCO) 59.8 ($CHNH_2$) 36.9 (CH_2) 27.2 (CH_2) 26.0 (CH_2) 25.1 (CH_2)[k]
 **10a**[l]	5.30 (br t, J_{HH} = 4.4 Hz, CHOH) 3.82 (br m, NH) 3.61 (br m, NH) 2.66 (br m, 1H) 2.51 (br m, 1H) 1.86 (br d, J_{HH} = 4.4 Hz, 2 H)[m]	222.8 (C≡O) 219.7 (C≡O) 218.1 (C≡O) 215.8 (C≡O)	86.9	46.5 (CH_2) 44.7 (CH_2)
 **10b**[l]	*m*	222.9, 222.0 (C≡O) 220.5, 219.4 (C≡O) 218.6, 218.1 (C≡O) 215.7, 215.4 (C≡O)[n]	85.5, 82.6[n]	56.5, 54.3 (CH) 53.0, 52.4 (CH_2) 22.3, 22.0 (CH_3)[n]
 **10c**[l]	4.82 (br d, J_{HH} = 5.9 Hz, CHOH)[m]	222.1 (C≡O) 220.7 (C≡O) 218.7 (C≡O) 216.0 (C≡O)	89.0	61.0 (CH) 58.7 (CH) 37.3 (CH_2) 34.3 (CH_2) 26.5 (CH_2) 26.2 (CH_2)
 **12**[d,e,h]	4.93 (d, J_{HH} = 9.6 Hz, CHOSi) 2.37–2.27 (br m, NH_2) 2.26–1.54 (m, 5H) 1.29 (pseudo quartet of d, J_{HH} = 9.6, 3.7 Hz, 1 H) 1.14–0.92 (m, 3 H) 0.84–0.71 (m, 1 H) 0.13 (s, 9 H)	221.0 (C≡O) 219.3 (C≡O) 217.0 (C≡O) 214.5 (C≡O)	88.8	59.6 (CH) 57.5 (CH) 37.4 (CH_2) 33.6 (CH_2) 25.4 (CH_2) 25.0 (CH_2) 0.00 (SiC)
 **11**[l]	4.01 (br d, J_{HH} = 11.7 Hz CHOH)[m]	282.1 (C═O) 217.9 (C≡O) 216.8 (C≡O) 214.0 (C≡O) 213.5 (C≡O)	91.4	59.8 (CH)[o] 37.9 (CH_2) 31.0 (CH_2) 26.1 (CH_2) 25.7 (CH_2)

Table I (Continued)

compound	^{1}H NMR (δ)[a]	^{13}C NMR (ppm)[a,b] CO	CHOH or CHOSi	other
 **13**[d,e,h]	3.90 (d, J_{HH} = 9.5 Hz, CHOSi)	270.9 (C=O)	92.5	61.3 (CH)
	2.78–2.52 (br m, NH_2)	217.2 (C=O)		47.4 (CH)
	2.22–2.16 (m, 1 H)	216.1 (C=O)		39.0 (CH_2)
	2.01–1.94 (m, 1 H)	213.0 (C=O)		30.0 (CH_2)
	1.80–1.53 (m, 3 H)	212.6 (C≡O)		25.0 (CH_2)
	1.40–0.73 (br m, 5 H)			24.7 (CH_2)
	0.07 (s, 9 H)			−0.18 (SiC)

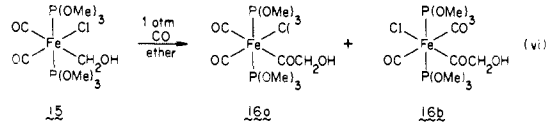
[a] At 300 MHz (^{1}H) or 75 MHz (^{13}C), ambient probe temperature, and referenced to $(CH_3)_4Si$ unless noted. [b] All couplings are to phosphorus. [c] Spectra in CD_3CN. [d] Spectra in CD_2Cl_2. [e] Referenced to $CHDCl_2$ (δ 5.32) or CD_2Cl_2 (53.2 ppm). [f] Spectrum at −20 °C. [g] Note that the two phosphorus-bound phenyls are diastereotopic. [h] Spectrum at 0 °C. [i] Spectrum in dioxane-d_8. [j] Spectrum in acetone-d_6. [k] Spectrum in pyridine at 0 °C. [l] Spectra in CD_3OD at 0 °C and referenced to CD_2HOD (δ 3.30) or CD_3OD (49.0 ppm). [m] This ^{1}H NMR spectrum exhibited severe broadening (see text) and a complete assignment of resonances was not possible. [n] A mixture of two diastereomers. [o] One cyclohexane ring resonance (~47 ppm) is likely obscured by solvent.

plexes *cis*-$(CO)_4Mn(COR)P(C_6H_5)_2H$ form. Hence, for this class of compounds, equilibrium also favors ring opening.

The sequence of reactions $(CO)_5MnSi(CH_3)_3 + (C_6H_5)_2PCH_2CH_2CHO \rightarrow$ **6** $\rightarrow$ **7** $\rightarrow$ **5** $\rightarrow$ **4** (Scheme I) has close analogy with reactions described in the previous two papers.[1,2] In earlier work, we have reported that $(CO)_5MnSi(CH_3)_3$ reacts with many aliphatic carbonyl compounds to give $(CO)_5MnH$ and trimethylsilyl enol ethers.[14,16] This could account for the $(CO)_4Mn(H)PX_3$ byproduct which accompanies **6**.

Equation iii and Scheme I show that the BH_3·THF reduction of metallacyclic acyl complexes to α-hydroxyalkyl complexes is of considerable generality. We speculate that the δ 5.6 (^{1}H NMR) intermediate observed in the conversion **8** $\rightarrow$ **4** prior to H_2O addition (Scheme I) is due to a $(CO)_4MnP(C_6H_5)_2CH_2CH_2CHOBX_2$ species. Masters and others have reported numerous cases where acyclic metal acyl complexes L_nMCOR are reduced to metal *alkyl* complexes L_nMCH_2R.[17] Hence, it appears that acyclic $L_nMCH(R)OBX_2$ intermediates are reduced more readily, possibly for conformational reasons. A plausible structure for the manganese hydride byproduct generated in the conversion **8** $\rightarrow$ **4** would be *cis*-$(CO)_4Mn(H)P(C_6H_5)_2CH_2CH_2CH_2OH$.

II. Reactivity of α-Hydroxyalkyl Complexes. Berke has reported that the α-hydroxyalkyl complex $((CH_3O)_3P)_2(CO)_2(Cl)FeCH_2OH$ (**15**), which is unstable above 0 °C, undergoes carbonylation (1 atm CO, ether) to a mixture of isomeric α-hydroxyacyl complexes (**16**, eq vi).[18] The reaction of $(CO)_4CoH$, $H_2C{=}O$, and CO to give glycolaldehyde is believed to involve the carbonylation of intermediate $(CO)_4CoCH_2OH$.[4b] However, eq iv constitutes the first example of the carbonylation of an *isolable* α-hydroxyalkyl complex. This greatly facilitates the mechanistic study of this process, which is believed to be a key step in several homogeneously catalyzed CO/H_2 reactions.[3,4]

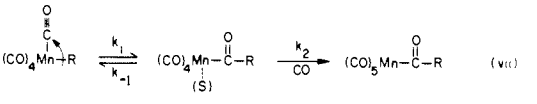


15 16a 16b

The carbonylation of manganese alkyl complexes $(CO)_5MnR$ has, in all cases examined to date,[19] been shown to occur by the two-stage mechanism shown in eq vii. The resulting rate expression

$$d[(CO)_5MnR]/dt = \frac{-k_1k_2[CO][(CO)_5MnR]}{k_{-1} + k_2[CO]}$$

has two limiting cases. When $k_{-1} \gg k_2[CO]$, $d[(CO)_5MnR]/dt = -(k_1k_2/k_{-1})[CO][(CO)_5MnR]$. When $k_2[CO] \gg k_{-1}$, $d[(CO)_5MnR]/dt = -k_1[(CO)_5MnR]$. For one study in an unspecified solvent (R = CH_3), the latter limit was realized at CO pressures of ≥225 psi.[19b,20] Since our k_{obsd} (−3 °C, CH_3NO_2, 250–360 psi of CO) for the carbonylation of **10c** and **12** are a nonlinear function of CO pressure, $k_2[CO]$ and k_{-1} are presumably of the same approximate magnitude.



(S) = solvent or vacant coordination site

The rate of eq vii is accelerated by polar, coordinating solvents.[19,21] From the rate data of Mawby, Basolo, and Pearson[21] for the reaction of $(CO)_5MnCH_3$ and *c*-$C_6H_{11}NH_2$ and Flood[22] for the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(PX_3)(CH_3)$ and CO, our attention was drawn to CH_3NO_2 as a particularly favorable carbonylation solvent. We speculate that complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2OH$, $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_2OH$, and $(\eta^5\text{-}C_5Me_5)Ru(CO)_2CH_2OH$, which are reported as inert to 4000–5000 psi of CO at 80 °C in medium polarity solvents such as THF,[23] might in fact react with CO in CH_3NO_2.

We had hoped to compare the carbonylation rate of **10c** to that of alkyl complex $(CO)_4MnNH_2CHCH(CH_2)CH_2CH_2CH_2CH_2$. However, we were unable to prepare this compound by reduction of **10c** or α-(silyloxy)alkyl complex **12**. Consequently **12** was used as a reference compound. Previously, we reported that α-(silyloxy)alkyl complex $(CO)_5MnCH_2OSi(CH_3)_3$ carbonylates ca. 3.5 times faster (24 °C, CD_3CN, 750–1500 psi CO) than α-methoxyalkyl complex $(CO)_5MnCH_2OCH_3$ and ca. 10 times

(16) (a) Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508. (b) Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147.

(17) (a) Van Doorn, J. A.; Master, C.; Volger, H. C. *J. Organomet. Chem.* **1976**, *105*, 245. (b) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927. (c) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *Ibid.* **1982**, *104*, 141. (d) Sweet, J. R.; Graham, W. A. G. *Ibid.* **1982**, *104*, 2811. (e) Thorn, D. L. *Organometallics* **1982**, *1*, 197. (f) Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. G.; Gladysz, J. A. *Ibid.* **1983**, *2*, 1852.

(18) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353.

(19) (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (c) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405. (d) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.

(20) Noack, K.; Ruch, M.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 345, see p 348.

(21) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994.

(22) Flood, T. C.; Campbell, K. D. *J. Am. Chem. Soc.* **1984**, *106*, 2853.

(23) (a) Lin, Y. C.; Milstein, D.; Wreford, S. S. *Organometallics* **1983**, *2*, 1461. (b) Nelson, G. O. *Ibid.* **1983**, *2*, 1474.

Table II. Summary of Key IR Data for Organometallic Compounds (cm^{-1})

compound (solvent)	$\nu_{C\equiv O}$	$\nu_{C=O}$	ν_{O-H}	ν_{N-H} (stretch)[a]	δ_{N-H} (bend)
4	2061 m	1726 mw			
(THF)	1978 s sh				
	1963 vs				
	1950 s sh				
(hexane)	2064 m	1731 w			
	1989 ms				
	1968 vs				
	1958 ms				
6	2070 ms	1607 m			
(hexane)	2006 ms				
	1998 s				
	1977 vs				
	1964 s				
	1956 s				
7	2072 ms	1592 m	3413 w		
(THF)	2003 s				
	1974 vs				
	1962 s sh				
(hexane)	2070 ms	1599 m	3430 w		
	2013 s				
	1979 vs				
	1962 s				
9a	2069 m	1643 m		3349 w	1601 w
(CH_2Cl_2)	1981 s sh			3302 w	
	1966 vs				
	1948 s				
9b	2069 m	1640 m		3335 w	1594 w
(CH_2Cl_2)	1981 s sh			3286 w	
	1966 vs				
	1948 s				
9c	2067 m	1649 m		3336 w	1595 w
(CH_2Cl_2)	1978 s sh	1639 m		3280 w	
	1963 vs				
	1946 s				
10a	2064 m		3612 vw	3351 w	1597 w
(CH_2Cl_2)	1968 vs			3305 w	
	1920 s				
10b	2063 m		3622 w	3337 w	1593 w
(CH_2Cl_2)	1966 vs			3289 w	
	1920 s				
10c	2061 m		3619 vw	3336 w	1596 w
(CH_2Cl_2)	1965 vs			3289 w	
	1919 s				
11	2078 ms	1590 m	3389 vw	3320 w	b
(CH_2Cl_2)	1992 s			3275 w	
	1976 vs				
	1954 s				
12	2059 ms			3338 w	1595 w
(CH_2Cl_2)	1965 vs			3290 w	
	1957 vs sh				
	1917 s				
13	2072 ms	1614 m		3321 w	1588 w
(CH_2Cl_2)	1987 s			3276 w	
	1966 vs				
	1947 s				

[a] The higher frequency band is always more intense. [b] Obscured by $\nu_{C=O}$.

slower than methyl complex $(CO)_5MnCH_3$ (24 °C, acetone-d_6, 1000 psi of CO).[24] Others have reported that $(CO)_5MnCH_2OCH_3$ carbonylates ca. 48 times slower than $(CO)_5MnCH_3$ (30 °C, $CH_3CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_3$).[19c] Hence, an α-$OSi(CH_3)_3$ substituent generally retards carbonylation analogously to other electron-withdrawing α-substituents.[25]

We propose that the 16-fold difference in carbonylation rates of **10c** and **12** (−3 °C, 250–350 psi CO) is too large to be attributed to a difference in $-OH/-OSi(CH_3)_3$ inductive effects. Indeed, available σ_m and σ_p values for these substituents (−OH: 0.02–0.13 and −(0.12–0.38); $-OSi(CH_3)_3$: 0.13 and −0.27) suggest a close inductive similarity.[26] Our provisional interpretation of the enhanced carbonylation rate of **10c** is therefore derived from the IR spectra shown in Figure 1. The product of the carbonylation of **10c**, α-hydroxyacyl complex **11**, clearly contains an intramolecular hydrogen bond of the type shown in **14**. *We propose that intramolecular hydrogen bonding can enhance the rate of eq vii.*

There are two distinct ways in which eq vii can be accelerated by intramolecular hydrogen bonding: (1) by stabilization of the k_1 transition state when k_1 is rate-limiting ($k_2[CO] \gg k_{-1}$), or (2) by stabilization of intermediate $(CO)_4Mn(S)COR$ and hence the k_1/k_{-1} preequilibrium when k_2 is rate-limiting ($k_{-1} \gg k_2[CO]$). Since under our conditions the carbonylation rates of **10c** and **12** are still dependent upon CO, we suggest that the latter is dominant. At first glance, it would seemingly strain the transition state to invoke hydrogen bonding during the k_1 step. However, C≡O ligands are capable of side-on (η^2) bonding with electrophilic metal centers.[27] Hence, side-on hydrogen bonding may also provide some stabilization.[28]

Hoffmann and Berke have in fact predicted that the k_1 transition state in eq vii (R = CH_3) will be stabilized by ca. 3 kcal/mol when a proton is attached to the C≡O oxygen with a C–O–H angle of 120–180°.[29] We also note that the overall K_{eq} for eq vii, $(CO)_5MnR + CO \rightleftharpoons (CO)_5MnCOR$, may be enhanced by hydrogen bonding in the acyl product.

In important related work, Shriver has shown that the rate of eq vii (R = CH_3) can be accelerated 2.4–9.4-fold by proton acids such as CH_2ClCO_2H, $CHCl_2CO_2H$, and CF_3CO_2H (pK_a's 2.86–0.23).[30] He has attributed this to intermolecular hydrogen bond stabilization of the k_1 transition state. Interestingly, IR spectra of mixtures of $(CO)_5MnCOCH_3$ and $CHCl_2CO_2H$ or CF_3CO_2H show, in addition to the $\nu_{C=O}$ of $(CO)_5MnCOCH_3$ (1653 cm^{-1}), strong absorptions at 1591 and 1581 cm^{-1}, respectively.[30] These were assigned to hydrogen-bonded acetyl ligands and are remarkably close to the $\nu_{C=O}$ of hydrogen-bonded hydroxyacyl complex **11** (Table II). Recently, Cutler has made similar observations with iron complexes.[31] Shriver has also shown that the k_1 step of eq vii is greatly accelerated by Lewis acids such as $AlCl_3$ and $AlBr_3$.[32]

The observation of a lower IR $\nu_{C=O}$ in hydroxyacyl complex **7** than in (silyloxy)acyl complex **6** (Table II) is suggestive of hydrogen bonding in the former. However, the difference in frequencies is not as great as with **11** and **13**. In the previous paper, the IR $\nu_{C=O}$ of hydroxyacyl complex $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OH)—C=O)$ was noted to be distinctly lower than that of the corresponding (silyloxy)acyl complex $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OSi(CH_3)_3)—C=O)$. Berke reported IR $\nu_{C=O}$ of 1598 and 1610 cm^{-1} for hydroxyacyl complexes **16a** and **16b**, respectively (eq vi). The *methoxy*acyl analogue of **16b** with an iodide in place of chloride[33] exhibited an IR

(24) Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056.

(25) For a possible exception, see ref 1.

(26) "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; pp 471–472.

(27) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 217 (see pp 268–279).

(28) There is an interesting probe of the importance of hydrogen bonding in the k_1 step of the conversion **10c** → **11**. Note that all c≡O ligands in **10c** are inequivalent. Hence, hydrogen bonding should direct alkyl migration to the CO cis to the OH group. However, it appears at present impractical to synthesize **10c** with this CO labeled.

(29) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

(30) Butts, S. B.; Richmond, T. G.; Shriver, D. F. *Inorg. Chem.* **1981**, *20*, 278.

(31) Forschner, T. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1247.

(32) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272.

$\nu_{C=O}$ of 1643 cm^{-1}.[18] Hence, hydrogen bonding is likely a general feature of α-hydroxyacyl ligands.

The carbonylation of α-hydroxyalkyl complex $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CHOH)$ could not be effected under the conditions of eq iv.[2] In this compound the α-hydroxyalkyl carbon is benzylic, and benzyl ligands carbonylate much more slowly than alkyl ligands.[19,24] Importantly, the corresponding α-hydroxyacyl complex $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OH)\text{—}C{=}O)$ is a stable compound.[2]

Finally, we note that when the carbonylations in eq iv are conducted in CD_3NO_2, significant isotope effects ($k_{CH_3NO_2}/k_{CD_3NO_2}$ = 1.36–1.54) are observed. We believe that these are primarily *solvent* isotope effects, although the -OD in **10c**-d_1 (generated by exchange with CD_3NO_2) will enter into hydrogen bonding at some point in the reaction coordinate. While some interesting organometallic reactions involving CD_3NO_2 have been previously reported,[34] we have not been able to find a precedent for, or for that matter any previous mention of, a CD_3NO_2 solvent isotope effect. In view of the established role of solvent in carbonylation reactions,[19,35] the isotope effect might arise from a change in basicity or coordinating ability.

III. Summary and Relevance to Catalysis. We conclude from this study that the stability of metallacyclic α-hydroxyalkyl complexes with respect to eq v is a sensitive function of donor atom, linkage type, and metallacycle size. These observations provide additional support for the "hemiacetal analogy" for α-hydroxyalkyl complex stability put forth in the previous paper.[2]

We also conclude that the BH_3·THF reduction of metallacyclic acyl complexes is the present method of choice for the synthesis of metallacyclic manganese and rhenium α-hydroxyalkyl complexes. Survey experiments have shown that reactions of $(CO)_5MnH$ with a variety of >D⁓CHO substrates are often complicated by aldehyde reduction reactions.

We have established the viability of intramolecular hydrogen bonding in metal α-hydroxyacyl complexes. We correspondingly interpret the relative carbonylation rates **10c** > **12** as providing *the first significant intramolecular hydrogen bond induced rate acceleration in an organometallic reaction.* This in turn suggests some possible, previously unrecognized, controlling factors in the conversion of CO/H_2 to ethylene glycol. It will be desirable to synthesize additional examples of α-hydroxyalkyl and α-(silyloxy)alkyl or α-alkoxyalkyl complexes which can be carbonylated so that the generality of our rate observations can be tested. However, on the basis of the present study, we believe it is highly probable that hydrogen bonding plays a key role in the homogeneously catalyzed formation of many oxygenated organic compounds from CO/H_2.

Experimental Section

General. General procedures employed were identical with those given in the previous paper.[2]

Solvents. Methanol-d_4 and CD_3NO_2 were purchased from Aldrich; the latter was purified by bulb-to-bulb distillation from P_2O_5 under static vacuum. Pyridine was stored over KOH and decanted and distilled from CaH_2. All other solvents were purified as described in the previous paper.

Reagents. Acetal $ClCH_2CH_2CH(OCH_2CH_3)_2$ was used as received from Aldrich. Aziridine (Chem Service) and 2-methylaziridine (Fluka) were distilled from CaH_2 and KOH, respectively. Aziridine 7-azabicyclo[4.1.0]heptane was synthesized from *trans*-1-azido-2-iodocyclohexane[36] via a literature procedure.[37] It was dried (neat, by bulb-to-bulb distillation under static vacuum) first over KOH/K_2CO_3 and then (twice) over CaH_2 and fractionally distilled (1 atm). Amine $HN(Si(CH_3)_3)_2$ and $i\text{-}C_3H_7OSi(CH_3)_3$ were obtained from Petrarch and were distilled from CaH_2.

Acyl complex $(CO)_4MnP(C_6H_5)_2CH_2CH_2\text{—}C{=}O$ (**8**) was prepared by the route of Lindner.[8] All other reagents were obtained as described in the previous paper.[2]

Synthesis of $(C_6H_5)_2PCH_2CH_2CHO$ (3). A 200-mL Schlenk flask was charged with Li wire (≥0.2 g, 29 mmol), THF (50 mL), $(C_6H_5)_2PCl$ (2.0 mL, 11 mmol), and a stir bar. The reaction was stirred for 12 h and then the excess wire was removed with forceps. The solution was cooled to −78 °C and $ClCH_2CH_2CH(OCH_2CH_3)_2$ (2.1 mL, 13 mmol) was added. The solution was stirred at −78 °C for 15 min and was then allowed to warm slowly to room temperature. After 3 h, solvent was removed under oil pump vacuum. The residue was treated with acetone (50 mL) and H_2O (8 mL), and CF_3CO_2H was added until Hydrion paper showed the solution to be acidic. The reaction was refluxed for 23 h. Solvents were then removed by rotary evaporation. The residue was taken up (in air) in CH_2Cl_2, extracted with $KHCO_3$ and saturated aqueous salt solutions, and dried over anhydrous K_2CO_3. The CH_2Cl_2 solution was then filtered through a plug of silica gel on a 30-mL fritted (M) funnel. The plug was eluted with additional CH_2Cl_2 (ca. 250 mL). Solvent was removed from the filtrate by rotary evaporation. The residue was taken up in a minimum of CH_2Cl_2 and applied to the top of a 3 × 40 cm silica gel column which had been packed in 90:10 (v/v) hexanes/ethyl acetate. The column was eluted with hexanes/ethyl acetate, and the product-containing fractions were taken to dryness by rotary evaporation (oil pump vacuum) in a glovebox. This gave **3** (0.881 g, 3.64 mmol, 33%) as an off-white cloudy oil which must be stored cold. IR (cm^{-1}, Fluorolube): $\nu_{H\text{-}CO}$ 2823 m, 2726 m; $\nu_{C=O}$ 1724 s. ^1H NMR (δ, CD_3CN): 9.64 (pseudoquintet, 1 H), 7.58–7.16 (m, 10 H), 2.54–2.24 (m, 4 H). $^{31}P\{^1H\}$ NMR (ppm, CD_3CN): −14.6.

Synthesis of *cis*-$(CO)_4Mn(H)P(C_6H_5)_2CH_2CH_2CHO$ (4). In a typical experiment, a 25-mL round-bottomed flask was charged with **3** (0.085 g, 0.35 mmol), $(CO)_5MnH$ (0.078 g, 0.40 mmol), hexanes (10 mL), and a stir bar. The reaction was stirred for 1 h and then the hexanes were removed by rotary evaporation. More hexanes were added and the rotary evaporation was again performed. This step was repeated three times to ensure volatilization of $(CO)_5MnH$. Finally, petroleum ether (bp 35–60 °C) was added and the mixture was filtered through a small plug of glass fiber filter paper. Solvent was removed from the filtrate by rotary evaporation. The residue was dried under oil pump vacuum to give 0.139 g (0.339 mmol, 97%) of **4** as a mixture of white crystals and a yellow oil. Complex **4** slowly decomposed at room temperature and showed an impurity by ^{31}P NMR which was not detectable by ^1H or ^{13}C NMR. ^{31}P NMR (ppm, CD_3CN): 57.6 (major), 56.8 (minor).

Synthesis of $(CO)_4MnP(C_6H_5)_2CH_2CH_2CH(OSi(CH_3)_3)\text{—}C{=}O$ (6). A 5-mm NMR tube was charged with **2** (0.202 g, 0.834 mmol), $(CO)_5MnSi(CH_3)_3$ (0.258 g, 0.940 mmol), and benzene (1 mL). The tube was fitted with a septum and shaken. A small needle was inserted into the septum to vent the CO. After 29 h, the tube was taken into a glovebox and the contents were rinsed with toluene into a round-bottomed flask. Solvent was removed by rotary evaporation. Toluene was added to the residue, and the rotary evaporation was repeated to complete the volatilization of $(CO)_5MnSi(CH_3)_3$. A 3 × 39 cm florisil (flame dried) precolumn was packed in 90:10 (v/v) hexanes/ethyl acetate. The reaction residue was taken up in acetone and applied to the column. The product fraction (which contained impurities) was collected under a N_2 purge. The solvent was removed by rotary evaporation and the residue was taken up in acetone. This was chromatographed on an identical column with 90:10 (v/v) hexanes/ethyl acetate. When the colorless product started to elute, the solvent was changed to 75:25 hexanes/ethyl acetate. The product was collected under a N_2 purge. Solvents were removed by rotary evaporation. The residue was dried under oil pump vacuum to give 0.129 g (0.253 mmol, 30%) of **6** as a light yellow oil. $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2): 42.1.

Synthesis of $(CO)_4MnP(C_6H_5)_2CH_2CH_2CH(OH)\text{—}C{=}O$ (7). A Schlenk flask was charged with **6** (0.145 g, 0.284 mmol), THF (5 mL), CH_3OH (4 mL), aqueous KF (5.2 M, 0.20 mL), and a stir bar. The reaction was stirred in subdued light for 75 min. Solvents were then removed via oil pump vacuum. The residue was transferred to a glovebox and taken up in a minimum of THF. This was applied to the top of a Pasteur pipet which had been loaded with silica gel. The pipet was eluted with ether. Solvent was removed from the colorless filtrate by rotary evaporation. The white residue was dried under oil pump vacuum to give 0.103 g (0.24 mmol, 85%) of **7**. An analytical sample was prepared by first taking **7** up in a minimum of THF. Then excess hexanes were added and the solution was cooled to −30 °C. Yellow-white needles of **7** formed. After ca. 4 h, these were collected on a cold frit and washed with cold petroleum ether. The recrystallization was repeated in subdued light to

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give white needles of **7**, decomposition point 124.5–131 °C (capillary sealed under N_2). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2): 47.7. Anal. Calcd for $C_{20}H_{16}MnO_6P$: C, 54.81; H, 3.68. Found: C, 54.98; H, 3.63.

Attempted Carbonylation of 4 to 7. A Fischer-Porter bottle was charged with **2** (0.068 g, 0.17 mmol) and CH_3NO_2 (6 mL) and was cooled to −3 ± 1 °C. Then 360 psi of CO was introduced. The reaction was monitored by IR over the course of 51 h. During this period, the color changed from light yellow to orange-yellow, and ca. 75% of the **4** was consumed. However, no **7** was present. In a separate experiment, **7** was shown to be stable to the reaction conditions (84 h, room temperature).

Reaction of $(CO)_4MnP(C_6H_5)_2CH_2CH_2$—C=O (8) and BH_3. A 5-mm NMR tube was charged with **8** (0.067 g, 0.16 mmol), i-$C_3H_7OSi(CH_3)_3$ (0.020 g, 0.15 mmol) standard, and THF (0.5 mL) and was capped with a septum. The tube was shaken, and then 1 M BH_3·THF in THF (120 μL, 0.120 mmol) was added. After 1.5 h a ^1H NMR spectrum showed a new multiplet at δ 5.6 (relative to i-$C_3H_7OSi(CH_3)_3$ at δ 0.07; 70% if 1 H). Then 10 μL (0.56 mmol) of H_2O was added. An aldehyde resonance at δ 9.5 (20% after 0.5 h) appeared and was assigned to **4**. Two principal manganese hydride resonances were present (δ −7.5, d, J_{HP} = 36 Hz, 46%; δ −7.6, d, J_{HP} = 36 Hz, **4**, 20%).

Synthesis of $(CO)_4MnNH_2CH_2CH_2$—C=O (9a). A 25-mL round-bottomed flask was charged with a solution of $(CO)_5MnH$ (0.696 g, 3.55 mmol) in benzene (3 mL) and a stir bar. The mixture was stirred vigorously and a solution of aziridine (0.140 g, 3.25 mmol) in benzene (2 mL) was quickly added. After 2 h, solvent and excess $(CO)_5MnH$ were removed by rotary evaporation. Toluene was added to the oily residue and (to volatilize residual $(CO)_5MnH$) was subsequently removed by rotary evaporation. The residue was applied (in air) to a 3 × 40 cm silica gel column with 90:10 (v/v) hexanes/ethyl acetate. A dark yellow-orange band eluted first which was immediately followed by a yellow product fraction. The latter was collected under a N_2 purge and taken into a glovebox. Solvent was removed by rotary evaporation. The residue was taken up in THF, and heptane was added. Rotary evaporation gave 0.532 g (2.23 mmol, 69%) of **9a** as a light yellow powder, decomposition point 147–159 °C (capillary sealed under N_2) (lit.[11] mp 156–160 °C).

Synthesis of $(CO)_4MnNH_2CH(CH_3)CH_2$—C=O (9b). A 25-mL round-bottomed flask was charged with a solution of $(CO)_5MnH$ (0.281 g, 1.43 mmol) in benzene (2 mL). The mixture was stirred vigorously and a solution of 2-methylaziridine (0.076 g, 1.33 mmol) in benzene (1 mL) was quickly added. The product started to precipitate after ca. 1 min. The reaction was stirred for 2 h. The product was then collected by filtration and rinsed with ether. This gave 0.237 g (0.936 mmol, 70%) of **9b** as a lemon yellow powder, decomposition point 153.5–162 °C (capillary sealed under N_2) (lit.[11] mp 156 °C).

Synthesis of $(CO)_4MnNH_2CHCH(—C=O)CH_2CH_2CH_2CH_2$ (9c). This compound was prepared in an identical manner to **9b** with use of 0.359 g (1.83 mmol) of $(CO)_5MnH$ and 0.166 g (1.71 mmol) of 7-azabicyclo[4.1.0]heptane. This gave 0.250 g (0.853 mmol, 50%) of **9c** as a lemon yellow powder, decomposition point 180–189 °C (capillary sealed under N_2). Anal. Calcd for $C_{11}H_{12}MnNO_5$: C, 45.07; H, 4.13. Found: C, 45.03; H, 4.24.

Syntheses of $(CO)_4MnNH_2CHRCHR'CHOH$ Complexes. A Schlenk flask was charged with the corresponding acyl complex (**9a**, **9b**, or **9c**; 0.330 mmol) and THF (50 mL). Then 1 M BH_3·THF in THF (660 μL; 2 equiv) was added. After 35–40 min, the reaction was cooled in an ice bath and CH_3OH (2 mL) was added. After 1 h solvents were removed under oil pump vacuum while the flask was maintained in the ice bath.

$(CO)_4MnNH_2CH_2CH_2CHOH$ (10a). The Schlenk flask was transferred to a glovebag in a 3 °C cold room. The residue was taken up in ether and filtered through a pipet loaded with dry silica gel. Heptane and 2 mL of CH_3OH were added to the filtrate. The filtrate was cooled in ice and solvents were removed under oil pump vacuum. This gave **10a** (93%) as a light yellow powder, decomposition point 122 °C and up (capillary sealed under N_2); several color changes occurred below 122 °C, and then gas slowly evolved with increasing temperature. **$(CO)_4MnNH_2CH(CH_3)CH_2CHOH$ (10b).** The residue was transferred to a glovebox, taken up in ether, and filtered through a pipet loaded with dry silica gel. The filtrate was collected in a Schlenk flask which had been charged with heptane (10 mL) and cooled to −30 °C. The flask was transferred to an ice bath outside of the box, and CH_3OH (2 mL) was added. Solvents were removed under oil pump vacuum to give a light yellow powder. This was dried for 2 h in vacuo to give a nearly quantitative yield of **10b**, which was stored at 3 °C. **$(CO)_4MnNH_2CHCH(CHOH)CH_2CH_2CH_2CH_2$ (10c).** This compound was isolated in near-quantitative yield in a manner identical with **10b**, decomposition point 174–183 °C (capillary sealed under N_2); color changes at >95 °C. Mass spectrum (m/e, 15 eV): 267 (M^+ − CO, 40%), 239 (M^+ − 2CO, 34%), 211 (M^+ − 3CO, 49%), 183 (M^+ − 4CO, 100%), 165 (M^+ − 4CO − H_2O, 42%). Anal. Calcd for $C_{11}H_{14}MnNO_5$: C, 44.76; H, 4.78; N, 4.75. Found: C, 45.00; H, 5.05; N, 4.94.

Synthesis of $(CO)_4MnNH_2CHCH(CH(OH)$—C=O)$CH_2CH_2CH_2CH_2$ (11). A Fischer-Porter bottle was cooled in a −3 °C bath and then charged with a −3 °C solution of **10c** (0.101 g, 0.345 mmol) in CH_3NO_2 (4 mL). The bottle was pressurized with 360 psi of CO. Pressure was maintained in the 350–370 psi range for 44 h, after which time CH_3NO_2 was removed under oil pump vacuum. The residue was taken up in THF and filtered (in air) through a pipet that had been loaded with silica gel. The THF was removed by rotary evaporation, and the residue was taken into a glovebox, where the silica gel filtration was repeated with ether. Hexanes were added to the filtrate and the solvents were removed by rotary evaporation. The resulting light yellow powder was dried under oil pump vacuum for 2 h at 0 °C. This gave 0.082 g (0.25 mmol, 72%) of **11**, decomposition point 76–89 °C (capillary sealed under N_2).

Synthesis of $(CO)_4MnNH_2CHCH(CHOSi(CH_3)_3)CH_2CH_2CH_2CH_2$ (12). A 50-mL Schlenk flask was sequentially charged with **9c** (0.084 g, 0.29 mmol), THF (5 mL), and 1 M BH_3·THF in THF (570 μL; 2 equiv). After 40 min the reaction was cooled with an ice bath and CH_3OH (2 mL) was added. Solvents were removed under oil pump vacuum while maintaining ice bath temperature. Then THF (4 mL) and $HN(Si(CH_3)_3)_2$ (0.24 mL, 1.1 mmol) were added. The flask was transferred to a glovebox where $(CH_3)_3SiCl$ (70 μL, 0.55 mmol) was added. After 2 h the volatiles were removed by rotary evaporation. Hexane was added to the residue and the mixture was filtered (removing a salt). The filtrate was then eluted through a Pasteur pipet charged with flame dried silica gel with 94:6 (v/v) hexanes/ether (ca. 40 mL). Solvent was removed from the filtrate by rotary evaporation. After 24 h (during which time a thermally unstable impurity decomposed), the silica gel filtration was repeated. Rotary evaporation of the filtrate gave 0.056 g (0.15 mmol, 52%) of **12** as a light yellow powder, decomposition point starting at 112 °C (capillary sealed under N_2). Anal. Calcd for $C_{14}H_{22}MnNO_5Si$: C, 45.77; H, 6.04. Found: C, 46.04; H, 6.06.

Synthesis of $(CO)_4MnNH_2CHCH(CH(OSi(CH_3)_3)$—C=O)$CH_2CH_2CH_2$ (13). A Fischer-Porter bottle was charged with **12** (0.059 g, 0.16 mmol) and CH_3NO_2 (4 mL) and was pressurized with CO (ca. 300 psi) for 138 h. The course of the reaction was periodically monitored by TLC, which suggested that an equilibrium had been reached. The reaction was cooled to 0 °C and the CH_3NO_2 was removed under oil pump vacuum. The residue was applied to a 3 × 40 cm silica gel column and eluted with 80:20 (v/v) hexanes/ethyl acetate. The product fraction was collected in a −78 °C Schlenk flask under a N_2 purge. A TLC of this solution showed only **13** to be present. Solvents were then removed via oil pump vacuum while the flask was kept in an ice water bath. This gave 0.0349 g (0.088 mmol, 55%) of **13** which TLC, IR, and NMR analysis showed to be contaminated with some **12**.

Rates of Carbonylation of 10c and 12. Rate data were obtained from reactions conducted in Fischer-Porter bottles. Aliquots were periodically removed and transferred to an IR cell under an inert atmosphere. Bands at 2060 cm^{-1} (**10c**) and 2058 cm^{-1} (**12**) were monitored. Solvent subtraction was performed with use of standard programs. All k_{obsd} were calculated by the least-squares method with use of ln (A_0/A_t) vs. time as input. These data are compiled elsewhere.[38] Absorbances ranged from 0.677 to 0.250.

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Registry No. 2, 79452-33-8; **3**, 100244-17-5; **4**, 100244-14-2; **6**, 100244-15-3; **7**, 100244-16-4; **8**, 79948-33-7; **9a**, 41742-59-0; **9b**, 41742-60-3; **9c**, 41742-59-0; **10a**, 91743-30-5; **10b**, 91743-31-6; **10c**, 91743-32-7; **11**, 91743-34-9; **12**, 91743-33-8; **13**, 91759-05-6; $(CO)_5MnH$, 16972-33-1; $(CO)_5MnSi(CH_3)_3$, 26500-16-3; $(C_6H_5)_2PCl$, 1079-66-9; $ClCH_2CH_2CH(OCH_2CH_3)_2$, 35573-93-4; i-$C_3H_7OSi(CH_3)_3$, 1825-64-5; BH_3·THF, 14044-65-6; $HN(Si(CH_3)_3)_2$, 999-97-3; $(CH_3)_3SiCl$, 75-77-4; aziridine, 151-56-4; 2-methylaziridine, 75-55-8; 7-azabicyclo[4.1.0]heptane, 286-18-0.

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