phenyl rings were refined as rigid groups (C-C = 1.29 Å; C-H = 1.00 Å).[46] The manganese and phosphorus atoms were refined anisotropically, while the carbon, oxygen, and nitrogen atoms were refined isotropically. No absorption corrections were applied. The methine hydrogen was located on a difference Fourier map after complete refinement of the structure. The inclusion of this hydrogen (with a fixed thermal paremeter $B_{iso} = 4.0$) in two additional refinements did not affect the R values,[47] which converged to $R = 0.055$, $R_w = 0.058$.

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(47) All least-squares refinements computed the agreement factors R and R_w according to $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum\omega_i||F_o| - |F_c||^2/\sum\omega_i|F_o|^2]^{1/2}$, where F_o and F_c are the observed and calculated structure factors, respectively, and $\omega_i^{1/2} = 1/\sigma(F_o)$. The function minimized in all least-squares refinements was $\sum\omega_i||F_o| - |F_c||^2$.

Synthesis and Reactivity of Stable Metallacyclic Manganese and Rhenium α-Hydroxyalkyl Complexes of the Formula $(CO)_4MP(C_6H_5)_2(o\text{-}C_6H_4CHOH)$

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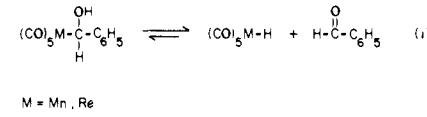
Abstract: Reaction of $(CO)_5ReCH_2C_6H_5$ with $(C_6H_5)_2P(o\text{-}C_6H_4OSi(CH_3)_2(t\text{-}C_4H_9))$ in octane (100–126 °C) gives the metallacycle $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CHOSi(CH_3)_2(t\text{-}C_4H_9))$ (**21**, 46%). Reaction of **21** with $(C_2H_5)_4N^+F^-\cdot(H_2O)_{2.6}$, followed by silica gel filtration, gives the stable α-hydroxyalkyl complex $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CHOH)$ (**5**, 77%). When this reaction is worked up prior to silica gel filtration, crystalline metallabicycle $(C_2H_5)_4N^+$-*fac*-$[(CO)_3ReP(C_6H_5)_2(o\text{-}C_6H_4C(H)OC{=}O)]^-$ (**22**, 94%) is isolated. The structure of **22** is established by X-ray crystallography. Complex **5** can also be prepared by reduction of $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4C{=}O)$ (**24**) with $BH_3\cdot THF$ (93%). Depending upon conditions, CF_3SO_3H converts **5** either to the ether $[(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CH)\text{-}]_2O$ (**23**) or an ca. 1:1 mixture of **24** and $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CH_2)$ (**25**). Reaction of $(CO)_5MH$, M = Re, with $(C_6H_5)_2P(o\text{-}C_6H_4CHO)$ (**18**) does not give **5**, but when M = Mn, $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CHOH)$ (**4**, 75–84%) is obtained. On the basis of these data and results of other researchers, it is suggested that many of the factors that influence the stability of organic XCH(R)OH compounds (e.g., hemiacetals) also influence the stability of $L_nMCH(R)OH$ complexes. Complexes **4** and **5** do not carbonylate under 300 psi of CO. Reaction of $(CO)_5MnSi(CH_3)_3$ with **18** gives $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OSi(CH_3)_3)\text{—}C{=}O)$ (**29**, 52%), which upon subsequent treatment with KF gives an authentic sample of carbonylated **4**, hydroxyacyl complex $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OH)\text{—}C{=}O)$ (**30**, 93%).

In the preceding paper, we described the generation of manganese and rhenium α-hydroxyalkyl complexes of the formula $(CO)_5MCH(C_6H_5)OH$ that were unstable with respect to metal hydride $(CO)_5MH$ and benzaldehyde (eq 1).[3] Since metal α-hydroxyalkyl complexes are a scarce class of compounds,[4-16] and are involved in several important catalytic processes, we sought a means to block this decomposition mode.



(1)

A survey of stable metal α-hydroxyalkyl complexes that had been reported by others in the literature at that time (**1–3**, Figure 1)[4-7] and since (**6–17**)[9-15] suggested to us that these compounds might closely parallel the behavior of hemiacetals, R'OCH(R)OH, and other XCH(R)OH species. In general, XCH(R)OH com-

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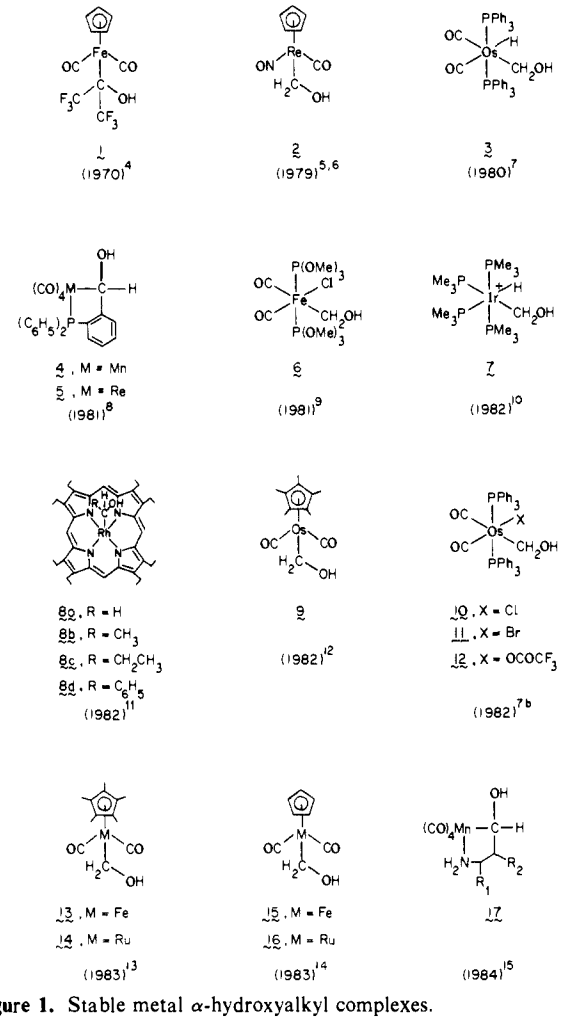


Figure 1. Stable metal α-hydroxyalkyl complexes.

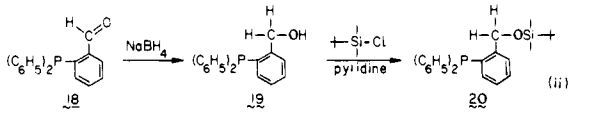
pounds rapidly decompose to aldehydes RCH=O and HX unless (a) X is a very poor leaving group (e.g., CN),[17] (b) R is a very electronegative group (CCl_3, CF_3), which weakens the RCH=O carbon–oxygen bond[17-20] and renders the 1,2-addition of HX thermodynamically more favorable, or (c) X and R are incorporated into a ring, as in certain naturally occurring hemiacetals.[21] Hence, XCH(R)OH compounds may be stabilized (a) kinetically, (b) enthalpically, or (c) entropically.

In this paper, we describe the use of strategy c—implemented by constructing a second link of the α-hydroxyalkyl carbon to the metal—to reverse the direction of the equilibrium in eq i. Complexes $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CHOH)$ (**4**, Figure 1) and $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CHOH)$ (**5**) are isolated in high yields via three distinct synthetic approaches. We also describe the properties of some novel intermediates encountered in these syntheses, including an X-ray crystal structure of the anionic metallabicycle $(C_2H_5)_4N^+$-*fac*-$[(CO)_3ReP(C_6H_5)_2(o\text{-}C_6H_4C(H)OC{=}O)]^-$. A portion of this study has been communicated.[8]

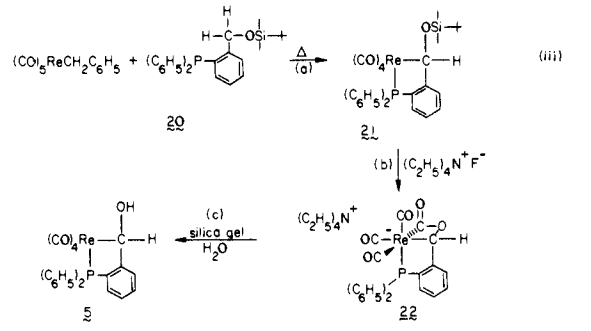
Results

I. Synthesis of Rhenium α-Hydroxyalkyl Complex 5 via Cyclometalation. Kaesz and McKinney have shown that the reaction of methyl complex $(CO)_5MnCH_3$ and $P(o\text{-}C_6H_4CH_3)_3$ in refluxing THF gives cyclometalated product $(CO)_4MnP(o\text{-}C_6H_4CH_3)_2(o\text{-}C_6H_4CH_2)$.[22] Subsequently, Bennet, Bruce, and Stone found benzyl complex $(CO)_5MnCH_2C_6H_5$ to be more reactive than $(CO)_5MnCH_3$.[23] Hence, we decided to attempt the preparation of our target complexes via the cyclometalation of suitably functionalized phosphines with $(CO)_5MCH_2C_6H_5$. Since rhenium complexes often exhibit greater kinetic stability than manganese analogues,[24] we first investigated the synthesis of $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CHOH)$ (**5**).

Reaction of phosphine aldehyde $(C_6H_5)_2P(o\text{-}C_6H_4CHO)$ (**18**)[25] with $NaBH_4$ gave alcohol $(C_6H_5)_2P(o\text{-}C_6H_4CH_2OH)$ (**19**, eq ii; 96%).[26] Treatment of **19** with $(t\text{-}C_4H_9)(CH_3)_2SiCl$/pyridine gave $(C_6H_5)_2P(o\text{-}C_6H_4CH_2OSi(CH_3)_2(t\text{-}C_4H_9))$ (**20**) in 95% yield. Trimethylsilyl compound $(C_6H_5)_2P(o\text{-}C_6H_4CH_2OSi(CH_3)_3)$ was similarly prepared.



When **20** and $(CO)_5ReCH_2C_6H_5$[27] were heated in octane on a steam bath (3 h) and then at reflux (2 h), substitution of CO, rhenium–carbon bond formation, and toluene elimination were accomplished in a single step, giving after workup analytically pure $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CHOSi(CH_3)_2(t\text{-}C_4H_9))$ (**21**) in 46% yield (eq iii, step a). Complex **21** exhibited two ^1H and ^{13}C



NMR resonances for the diastereotopic $Si(CH_3)_2$ methyl groups, as summarized in Table I. The methine ^1H NMR resonance, δ 6.11, was a doublet of doublets with J_{HP} = 2.1 Hz and J_{HH} = 1.0 Hz. Decoupling experiments showed the latter coupling to be due to a long-range interaction with an aryl proton. Complex **21** also exhibited the expected methine carbon ^{13}C NMR resonance (65.1 ppm), and its IR $\nu_{C\equiv O}$ pattern (Table II) was characteristic of cis-disubstituted rhenium tetracarbonyls.[3,28]

When phosphine **20** and $(CO)_5ReCH_2C_6H_5$ were reacted for 1.5 h in refluxing heptane, a precursor to metallacycle **21** could be isolated in good yield. On the basis of IR [(cm^{-1}, CCl_4) 2077 m, 1993 s, 1969 vs, 1933 s)] and ^1H NMR data, this material was assigned as the substitution product *cis*-$(CO)_4Re(CH_2C_6H_5)P(C_6H_5)_2(o\text{-}C_6H_4CH_2OSi(CH_3)_2(t\text{-}C_4H_9))$. Subsequent thermolysis in refluxing octane gave **21**.

Reactions of phosphine alcohol **19** with $(CO)_5ReCH_2C_6H_5$ (refluxing toluene, heptane) and $(CO)_5MnCH_2C_6H_5$ (refluxing hexane) were attempted. By analogy to step a of eq iii, it was

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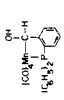
Table I. ^1H and ^{13}C NMR Data for New Organometallic Compounds

	^1H NMR (δ)[a]			^{13}C NMR (ppm)[b,c]			
compound	phenyl	ortho methine or methylene	other	CO	phenyl	methine or methylene	other
21	7.63–7.55 (m, 1 H), 7.53–7.31 (m, 11 H), 7.08–6.97 (m, 2 H)	6.11 (d of d, J_{HP} = 2.1 Hz, $J_{HH_{aryl}}$ = 1.0 Hz, 1 H)	0.92 (s, 9 H, $C(CH_3)_3$), 0.15 (s, 3 H, $SiCH_3$), 0.07 (s, 3 H, $SiCH_3'$)	191.7, 191.1 (2 C≡O), 189.8	166.6, 133.8, 132.9, 132.6, 131.5, 131.3, 131.1, 129.3, 129.1, 126.0, 125.5[e]	65.1	26.3 ($C(CH_3)_3$), 18.6 ($C(CH_3)_3$), −4.9 ($SiCH_3$), −5.1 ($SiCH_3'$)
5	7.82–7.72 (m, 1 H), 7.65–7.07 (m, 13 H)	6.08 (d, J_{HH} = 5.6 Hz, 1 H)	3.30 (d, J_{HH} = 5.6 Hz, 1 H, OH)	192.2, 191.6 (2 C≡O), 190.8	167.5, 134.2, 132.8, 132.4, 132.2, 132.1, 131.8, 130.0, 127.5, 126.8[e]	65.6	
22	8.02–7.87 (m, 2 H), 7.61 (t, J_{HH} = 7.4 Hz, 1 H), 7.47–7.10 (m, 11 H)	5.51 (d, J_{HP} = 5.4 Hz, 1 H)	3.04 (q, J_{HH} = 7.3 Hz, 8 H, NCH_2), 1.08 (tt, J_{HH} = 7.3 Hz, J_{HN} = 1.8 Hz, 12 H, CH_3)	204.5 (d, J_{CP} = 53.6 Hz, C≡O trans to P),[g] 203.2 (d, J_{CP} = 7.4 Hz, C≡O cis to P), 203.1 (d, J_{CP} = 7.4 Hz, C≡O cis to P), 188.6 (d, J_{CP} = 14.9 Hz, C=O)	162.2, 135.5, 134.1, 132.5, 131.8, 131.2, 130.8, 130.2, 129.2, 129.0, 127.7[e]	65.9	53.0 (t, J_{CN} = 3.0 Hz, NCH_2), 7.7 (CH_3)
23	7.95–7.84 (m, 2 H), 7.70–7.05 (m, 22 H), 7.05–6.92 (m, 4 H)	6.21 (s, 2 H)		193.4, 191.9, 191.4, 189.8	165.8, 135.9, 134.9, 133.8, 133.7, 132.3, 132.1, 131.4, 131.3, 129.8, 129.7, 129.5, 127.9, 126.0[e]	75.8	
25	7.62–6.94 (m, 14 H)	2.64 (d, J_{HP} = 4.2 Hz, 2 H)		190.9, 190.4 (2 C≡O), 189.3	162.7, 135.0, 134.2, 132.4, 131.7, 131.3, 130.5, 130.4, 128.7, 124.4	2.6	
26	7.81–7.72 (m, 5 H), 7.57–7.52 (m, 7 H), 7.40–7.34 (m, 1 H), 6.87–6.80 (m, 1 H)	5.83 (s, 1 H)	3.83 (m, AA'BB', 4 H, CH_2), −4.97 (d, J_{HP} = 21.7 Hz, 1 H, ReH)	191.8 (d, J_{CP} = 6.8 Hz), 191.1 (d, J_{CP} = 9.3 Hz, 2 C≡O), 190.3 (d, J_{CP} = 42.0 Hz)	PC_6H_4C: 141.5 (d, J_{CP} = 9.0 Hz, o),[k] portion of obscured d at 135.3 (ipso), 132.3 (d, J_{CP} = 7.1 Hz, o'), 132.2 (s, p), 131.2 (d, J_{CP} = 7.0 Hz, m), 130.6 (d, J_{CP} = 9.1 Hz, m). C_6H_5: 135.7 (d, J_{CP} = 11.6 Hz), 133.8 (d, J_{CP} = 48.7 Hz, ipso), 132.4 (s, p), 130.1 (d, J_{CP} = 9.4 Hz)	101.2 (d, J_{CP} = 11.1 Hz, CH)	66.2 (s, CH_2)
27	7.80–7.72 (m, 5 H), 7.58–7.53 (m, 7 H), 7.42–7.36 (m, 1 H), 7.18–7.11 (m, 1 H)	5.47 (s, 1 H)	3.01 (s, 6 H, OCH_3), −4.91 (d, J = 21.9 Hz, 1 H, ReH)	191.8 (d, J_{CP} = 6.9 Hz), 191.3 (d, J_{CP} = 9.5 Hz, 2 C≡O), 190.3 (d, J_{CP} = 42.0 Hz)	PC_6H_4C: 142.1 (d, J_{CP} = 9.0 Hz, o),[k] 133.7 (d, J_{CP} = 11.2 Hz, o'), 133.1 (d, J_{CP} = 44.0 Hz, ipso), 131.8 (s, p), 130.2 (d, J_{CP} = 9.2 Hz, m), 129.7 (d, J_{CP} = 9.2 Hz, m). C_6H_5: 135.7 (d, J_{CP} = 11.6 Hz), 134.4 (d, J_{CP} = 48.6 Hz, ipso), 132.4 (s, p), 130.0 (d, J_{CP} = 11.4 Hz)	101.8 (d, J_{CP} = 7.1 Hz, CH)	54.5 (s, CH_3)
28	7.84–7.75 (m, 4 H), 7.71–7.66 (m, 1 H), 7.54–7.33 (m, 9 H)	4.17 (s, 2 H)	3.01 (s, 3 H, OCH_3)	183.9 (d, J_{CP} = 8.5 Hz, 2 C≡O), 182.5 (d, J_{CP} = 6.2 Hz), 180.9 (d, J_{CP} = 54.1 Hz)[l]	PC_6H_4C: 141.0 (d, J_{CP} = 8.2 Hz, o),[k] 133.6 (d, J_{CP} = 10.4 Hz, o'), 128.4 (d, J_{CP} = 10.2 Hz, m). C_6H_5: 134.3 (d, J_{CP} = 10.4 Hz), 129.1 (d, J_{CP} = 10.4 Hz). Unassigned: 132.2, 131.8, 131.6, 131.5, 130.9, 130.5, 130.5[l]	72.8 (d, J_{CP} = 6.0 Hz, CH_2)[l]	58.7 (s, CH_3)[l]

 **4'**	7.82–7.73 (m, 1 H), 7.64–7.12 (m, 13 H)	6.28 (br s, 1 H)	3.73 (br s, 1 H, OH)	219.0 (br), 218.6 (br), 217.3 (br)[f]	165.3, 135.8, 134.2, 133.9, 132.4, 132.1, 131.9, 131.6, 131.4, 130.0, 126.9, 126.8[e,f]	78.6[f]
29'	7.68–7.29 (m, 13 H), 6.91–6.84 (m, 1 H)	4.85 (s, 1 H)	–0.14 (s, 9 H, $SiCH_3$)	268.1 (d, J_{CP} = 16.4 Hz, C≡O), 216.3 (d, J_{CP} = 17.9 Hz, C≡O), 215.9 (d, J_{CP} = 14.0 Hz, C≡O), 215.8 (s), 215.2 (d, J = 20.8 Hz, C≡O)[f]	PC_6H_4C: 143.4 (d, J_{CP} = 13.7 Hz, o).[k] C_6H_5: 133.8 (d, J = 10.5 Hz), 132.6 (d, J = 9.0 Hz), 131.5 (s, p), 131.2 (s, p), 129.4 (d, J_{CP} = 9.0 Hz), 129.3 (d, J_{CP} = 9.0 Hz). Unassigned: 133.1, 132.3, 132.0, 128.4, 128.3, 128.2, 128.1, 127.7[e,f]	89.5 (d, J_{CP} = 7.4 Hz)[f]	–0.99 (s, SiC)[f]
30'	7.91–7.86 (m, 1 H), 7.62–7.22 (m, 12 H), 6.69–6.62 (m, 1 H)	4.83 (d, J = 4.0 Hz, 1 H (s, after D_2O addition))	4.95 (d, J = 4.1 Hz, 1 H, OH)	266.2 (d, J_{CP} = 15.4 Hz, C≡O), 217.0 (d, J_{CP} = 18.2 Hz, C≡O), 216.1 (s), 215.9 (d, J_{CP} = 11.2 Hz, C≡O), 215.8 (d, J_{CP} = 16.9 Hz, C≡O)[f]	PC_6H_4C: 143.9 (d, J_{CP} = 12.9 Hz, o),[k] 132.9 (d, J_{CP} = 7.0 Hz, o'), 128.5 (d, J_{CP} = 7.2 Hz, m), 128.4 (d, J_{CP} = 40.7 Hz, ipso), 126.7 (d, J_{CP} = 9.8 Hz, m). C_6H_5: 135.6 (d, J_{CP} = 11.1 Hz), 133.7 (d, J_{CP} = 11.1 Hz), 133.2 (s, p), 132.4 (d, J_{CP} = 48.9 Hz, ipso), 132.2 (d, J_{CP} = 43.6 Hz, ipso), 131.9 (s, p), 130.9 (d, J_{CP} = 7.0 Hz), 130.7 (d, J_{CP} = 7.2 Hz)[e,f]	90.4 (d, J_{CP} = 10.1 Hz)[f]	

[a] At 200 or 300 MHz, ambient probe temperature, and referenced to $(CH_3)_4Si$ unless noted. [b] At ambient probe temperature and referenced to $(CH_3)_4Si$ unless noted. [c] Spectra of **4**, **5**, and **21**–**24** are at 50 MHz and ^1H and ^{31}P decoupled; resonances are singlets unless noted. Spectra of **26**–**30** are at 75 MHz and ^1H decoupled. Assignments are discussed in greater detail in ref 56. [d] Spectra in CD_2Cl_2. [e] Note that the two phosphorus-bound phenyls are diastereotopic. [f] Spectra in CD_3CN. [g] Coupling constants were obtained from a separate $^{13}C\{^1H\}$ spectrum. [h] Spectra in THF-d_8. [i] Spectra in $CDCl_3$. [j] Spectra in acetone-d_6 (^{13}C NMR at 0 °C). [k] Carbons in the disubstituted aryl ring are designated as follows: ipso, P–C; o, metallacyclic carbon ortho to phosphorus; o', C–H carbon ortho to phosphorus; p, carbon para to phosphorus. [l] Spectrum at –20 °C. [m] Referenced to $CHDCl_2$ (δ 5.32) or CD_2Cl_2 (53.2 ppm).

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

compound (solvent)	$\nu_{C\equiv O}$	other
21 (THF)	2081 m, 1988 s, sh, 1980 vs, 1943 s	
5 (CH_3CN)	2082 m, 1986 sh, 1939 s	ν_{O-H} 3520 w, br
22 (CH_3CN)	1976 vs, 1940 s, 1861 s	$\nu_{C=O}$ 1640 m
23 (THF)	2073 m, 1992 vs, 1980 s, 1939 vs	
25 (THF)	2080 m, 1977 vs, 1937 s	
26 (hexanes)	2085 m, 1999 s, 1990 mw, 1977 vs, 1959 s[a]	
27 (hexanes)	2083 ms, 1996 s, 1979 s, 1974 vs, 1966 s, 1959 sh	
28 (hexanes)	2101 ms, 2020 s, 2003 vs, 1949 s	
4 (CH_3CN)	2059 ms, 1967 vs, 1941 s	ν_{O-H} 3496 w, br
29 (THF)	2064 s, 1992 ms, 1971 vs	$\nu_{C=O}$ 1657 w, 1629 m
30 (THF)	2069 s, 1999 ms, 1976 vs	$\nu_{C=O}$ 1624 sh, 1613 m, ν_{O-H} 3394 vw, br

[a] This absorption shifted to 1948 cm^{-1} in the corresponding rhenium deuteride; the other absorptions were unchanged; see ref 57 for a similar trans effect.

hoped that target α-hydroxyalkyl complexes **4** and **5** might be obtained directly. Starting materials were consumed, but no trace of the desired products was found by IR or ^1H NMR spectroscopy. On the basis of the thermal stabilities of **4** and **5** (vide infra), some decomposition would be expected under the reaction conditions. Also, the reaction of $(C_6H_5)_2P(o\text{-}C_6H_4CH_2OSi(CH_3)_3)$ with $(CO)_5ReCH_2C_6H_5$ was briefly examined. This phosphine appeared much less reactive than **20** toward cyclometalation.

Attention was next turned to the conversion of **21** to the desired α-hydroxyalkyl complex **5**. Treatment of **21** with $(C_2H_5)_4N^+F^-\cdot(H_2O)_{2.6}$ in acetone/CH_3CN, followed by addition of H_2O and silica gel filtration, removed the trialkylsilyl protecting group and gave, after preparative HPLC, analytically pure **5** in 77% yield (eq iii, steps b and c). Complex **5** exhibited an OH ^1H NMR resonance (CD_3CN) at δ 3.30 (d, J_{HH} = 5.6 Hz; Table I). When **5** was dissolved in $CDCl_3/D_2O$ or acetone-d_6, the OH resonance disappeared. The 70-eV mass spectrum of **5** showed a molecular ion. The IR spectrum of **5** (CH_3CN, Table II) indicated ν_{O-H} (3517 cm^{-1}) to be weak relative to $\nu_{C\equiv O}$ (2081 m, 1975 vs, 1939 s). In **5**-d_1 (prepared by D_2O exchange), ν_{O-D} was observed at 2603 cm^{-1}.

II. Synthesis and X-ray Structure of Metallabicycle 22. When the reaction of **21** with $(C_2H_5)_4N^+F^-$ was worked up prior to silica gel filtration (eq iii, step b), a crystalline compound was obtained in 94% yield whose microanalysis suggested the possible *alkoxide* structure $(C_2H_5)_4N^+(CO)_4Re\overline{P(C_6H_5)_2(o\text{-}C_6H_5CHO^-)}$. However, the IR spectrum showed a medium acyl absorbance, $\nu_{C=O}$ 1640 cm^{-1}, and a $\nu_{C\equiv O}$ pattern (1983 s, 1885 s, 1861 s) characteristic[28b] of a *fac*-substituted LL'L''$M(CO)_3$ complex. This suggested the bicyclic "lactone" structure **22** (eq iii), or possibly a dimer containing an eight-membered ring. Since we were unaware of any structurally related complexes, and wished to unambiguously determine the ring size,[29] an X-ray crystal structure was executed.

Single-crystal X-ray data were obtained under the conditions summarized in Table III. The unit cell was found to be monoclinic, with the lattice parameters listed in Table III. Refinement, described in the Experimental Section, included location of the

(29) For instance, examples of four-membered metallacycles in equilibrium with eight-membered dimetallacycles are known: Webb, M. J.; Bennett, M. J.; Chan, L. Y. Y.; Graham, W. A. G. *J. Am. Chem. Soc.* **1974**, *96*, 5931.

Table III. Summary of Crystallographic Data for **22**

formula	$C_{31}H_{35}NO_5PRe$
formula wt	718.80
crystal system	monoclinic
systematic absences	hkl, $k + l \neq 2n$ and $h0l$, $h \neq 2n$
space group	$A2/a$
cell dimensions (−158 °C)	
a, Å	18.538 (7)
b, Å	10.474 (4)
c, Å	32.24 (1)
β, deg	91.89 (3)
V, Å^3	6257 (4)
Z	8
d_{obsd}, g/cm^3 (20 °C)	1.54
d_{calcd}, g/cm^3 (−158 °C)	1.53
crystal dimensions, mm	0.25 × 0.20 × 0.35
radiation, Å	Mo Kα (λ 0.71069)
temp of collection, °C	−158
data collection method	θ–2θ
scan speed, deg/min	8.0
scan range, deg	$K\alpha_1$ −1.0 to $K\alpha_2$ +1.25
no. of reflections between std.	97
total unique data	5557
obsd data, $I > 3\sigma(I)$	4724
abs. coeff. (μ), cm^{-1}	40.22
no. of variables	352
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.035
$R_w = [\sum\omega_i\|\|F_o\| - \|F_c\|\|^2/\sum\omega_i\|F_o\|^2]^{1/2}$	0.058
goodness of fit	2.04
max absorption corr	0.7388
min absorption corr	0.6593
av absorption corr	0.7177

Table IV. Positional Parameters of Atoms in **22** and Their Estimated Standard Deviations[a]

atom	x	y	z
Re	0.45050 (1)	0.07140 (2)	0.14440 (1)
P	0.4160 (1)	0.2548 (2)	0.1029 (1)
C1	0.5366 (4)	0.0535 (7)	0.1112 (2)
C2	0.4873 (4)	−0.0496 (7)	0.1860 (2)
C3	0.3930 (4)	−0.0485 (7)	0.1117 (2)
C4	0.4781 (4)	0.2287 (7)	0.1885 (2)
C5	0.3724 (4)	0.1244 (7)	0.1898 (2)
O1	0.5893 (3)	0.0445 (5)	0.0932 (2)
O2	0.5099 (3)	−0.1169 (5)	0.2116 (2)
O3	0.3544 (3)	−0.1166 (6)	0.0929 (2)
O4	0.4087 (2)	0.2200 (5)	0.2114 (1)
O5	0.3126 (3)	0.0951 (5)	0.2020 (2)
N	0.7387 (3)	0.2928 (6)	0.1850 (2)
C(1A)	0.3207 (4)	0.2877 (7)	0.0893 (2)
C(1B)	0.4500 (4)	0.3923 (7)	0.1321 (2)
C(1C)	0.4590 (4)	0.2657 (7)	0.0522 (2)
C(2A)	0.3009 (4)	0.3853 (8)	0.0616 (2)
C(2B)	0.4810 (4)	0.3634 (7)	0.1714 (2)
C(2C)	0.5147 (4)	0.3451 (8)	0.0440 (2)
C(3A)	0.2665 (4)	0.2146 (8)	0.1069 (3)
C(3B)	0.4485 (4)	0.5201 (7)	0.1178 (2)
C(3C)	0.4372 (5)	0.1757 (8)	0.0223 (3)
C(4A)	0.2281 (5)	0.4105 (9)	0.0535 (3)
C(4B)	0.5117 (4)	0.4618 (7)	0.1956 (2)
C(4C)	0.5502 (5)	0.3377 (10)	0.0065 (3)
C(5A)	0.1753 (5)	0.3394 (9)	0.0716 (3)
C(5B)	0.5117 (4)	0.5864 (7)	0.1807 (3)
C(5C)	0.5289 (6)	0.2492 (9)	−0.0224 (3)
C(6A)	0.1961 (5)	0.2405 (9)	0.0981 (3)
C(6B)	0.4799 (5)	0.6160 (7)	0.1418 (2)
C(6C)	0.4729 (6)	0.1684 (9)	−0.0149 (3)
C(N1)	0.8098 (4)	0.2307 (8)	0.1965 (2)
C(N2)	0.8326 (4)	0.2399 (8)	0.2429 (2)
C(N3)	0.6778 (4)	0.2288 (7)	0.2075 (2)
C(N4)	0.6681 (5)	0.0873 (7)	0.1997 (3)
C(N5)	0.7288 (4)	0.2779 (8)	0.1380 (2)
C(N6)	0.6586 (5)	0.3327 (8)	0.1190 (2)
C(N7)	0.7363 (4)	0.4323 (7)	0.1982 (2)
C(N8)	0.7959 (5)	0.5156 (8)	0.1806 (3)
H	0.523 (10)	0.213 (19)	0.213 (6)

[a] Atoms are numbered as indicated in Figure 2.

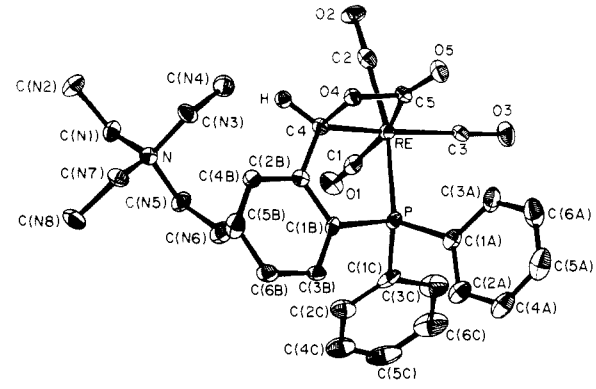


Figure 2. Molecular structure of $(C_2H_5)_4N^+$-*fac*-$[(CO)_3ReP(C_6H_5)_2$-$(o$-$C_6H_4C(H)OC{=}O)]^-$ (**22**). The H atom is drawn with an arbitrary isotropic thermal parameter.

Table V. Bond Distances in **22**[a]

from	to	distance (Å)
C1	O1	1.156 (9)
C1	Re	1.960 (7)
C2	O2	1.151 (9)
C2	Re	1.953 (8)
C3	O3	1.168 (9)
C3	Re	1.935 (7)
C4	H	1.130
C4	O4	1.506 (8)
C4	Re	2.225 (7)
C5	O5	1.226 (9)
C5	O4	1.382 (8)
C5	Re	2.165 (7)
P	Re	2.416 (2)
C(1A)	C(3A)	1.397 (12)
C(1A)	C(2A)	1.398 (11)
C(1A)	P	1.837 (7)
C(1B)	C(2B)	1.406 (10)
C(1B)	C(3B)	1.415 (10)
C(1B)	P	1.822 (7)
C(1C)	C(2C)	1.358 (11)
C(1C)	C(3C)	1.399 (11)
C(1C)	P	1.844 (7)
C(2A)	C(4A)	1.392 (12)
C(2B)	C(4B)	1.402 (10)
C(2B)	C4	1.516 (10)
C(2C)	C(4C)	1.397 (11)
C(3A)	C(6A)	1.355 (12)
C(3B)	C(6B)	1.385 (11)
C(3C)	C(6C)	1.393 (12)
C(4A)	C(5A)	1.374 (14)
C(4B)	C(5B)	1.390 (10)
C(4C)	C(5C)	1.364 (13)
C(5A)	C(6A)	1.388 (13)
C(5B)	C(6B)	1.404 (11)
C(5C)	C(6C)	1.367 (14)
C(N1)	N	1.506 (9)
C(N1)	C(N2)	1.547 (10)
C(N3)	C(N4)	1.513 (11)
C(N3)	N	1.518 (9)
C(N5)	N	1.526 (9)
C(N5)	C(N6)	1.533 (11)
C(N7)	N	1.523 (9)
C(N7)	C(N8)	1.530 (10)

[a] Atoms are numbered as indicated in Figure 2.

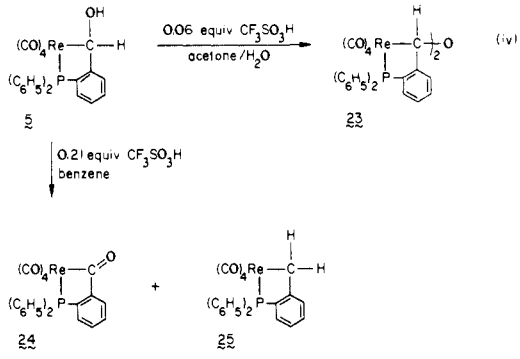
metallacyclic methine hydrogen from an electron difference map. All other hydrogens were geometrically located and assigned C–H bond distances of 1.0 Å.

The molecular structure of **22** is given in Figure 2. Positional parameters are summarized in Table IV. Bond distances and angles are compiled in Tables V and VI.

When CD_3CN solutions of **22** were treated with CF_3CO_2H (1.0 equiv), α-hydroxyalkyl complex **5** formed in 74% spectroscopic yield.

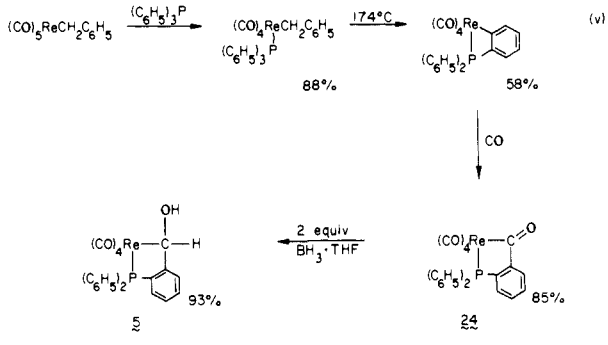
III. Chemistry of and Other Synthetic Approaches to Rhenium α-Hydroxyalkyl Complex 5. Attempts to insert CO into the rhenium–hydroxyalkyl carbon bond of **5** were unsuccessful. For example, no reaction was observed when **5** was treated with 3 equiv of $P(CH_3)_3$ in refluxing acetone (11 h).

Complex **5** underwent facile and highly condition dependent reactions with acids (eq iv). For instance, treatment of **5** with



0.06 equiv of CF_3SO_3H in acetone/H_2O gave the symmetrical ether $[(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CH)\text{-}]_2O$ (**23**; 28–36% of theory). The same product was obtained (84% of theory) when (silyloxy)alkyl complex **21** was treated with CF_3SO_3H in acetone/H_2O. In both cases, NMR data (Table I) indicated **23**, which contains two chiral centers, to be comprised of a single diastereomer.

When **5** was treated with CF_3SO_3H (0.21 equiv) in benzene (eq iv), hydride transfer disproportionation occurred to give acyl complex $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4C{=}O)$ (**24**, 79% of theory) and alkyl complex $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CH_2)$ (**25**, 75% of theory). Acyl complex **24** had been previously reported,[30] and an authentic sample was synthesized by a modified procedure (eq v). However, **25** was a new compound and was independently prepared by the reaction of $(CO)_5ReCH_2C_6H_5$ and $(C_6H_5)_2P(o\text{-}C_6H_4CH_3)$ in refluxing heptane (13 h; 56%).

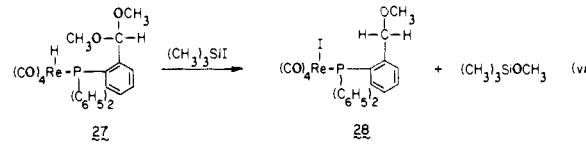


In the process of characterizing complexes **24** and **25**, we reacted **24** and BH_3·THF. On the basis of literature precedent,[31] the expected product was **25**. However, substantial amounts of α-hydroxyalkyl complex **5** formed, and by optimization of conditions we were able to isolate **5** in 93% yield (eq v). The sequence of reactions shown in eq v therefore constitutes the most direct route to **5**. Acyl complex **24** was inert to 2000 psi of H_2 in acetone (25 °C, 7 days).

Although we were pleased that **5** was an isolable complex, we had not yet demonstrated that the direction of the equilibrium in eq i could be reversed entropically. Hence, we attempted to prepare **5** from $(CO)_5ReH$ via the substitution product *cis*-$(CO)_4Re(H)P(C_6H_5)_2(o\text{-}C_6H_4CHO)$. Substitution of CO in $(CO)_5ReH$ by phosphines is known to occur at erratic rates by free radical chain mechanisms,[32] and we obtained widely diverging results depending upon the phosphine employed.

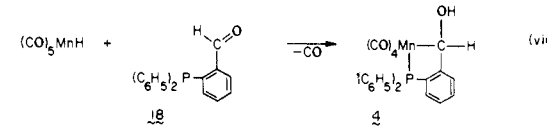
First, $(CO)_5ReH$ and $(C_6H_5)_2P(o\text{-}C_6H_4CHO)$ (**18**) did not react at room temperature (C_6D_6, 7.5 days). A reaction occurred upon reflux, but α-hydroxyalkyl complex **5** was not produced. The aldehyde functionality in **18** was then protected. Silylated cyanohydrin $(C_6H_5)_2P(o\text{-}C_6H_4CH(CN)OSi(CH_3)_3)$ was prepared from **18** and $(CH_3)_3SiCN$,[33] but failed to react with $(CO)_5ReH$ in C_6D_6 at 40 °C (6 h). However, room-temperature reactions of $(CO)_5ReH$ with phosphine acetals $(C_6H_5)_2P(o\text{-}C_6H_4CHOCH_2CH_2O)$[25] and $(C_6H_5)_2P(o\text{-}C_6H_4CH(OCH_3)_2)$ readily gave *cis*-$(CO)_4Re(H)P(C_6H_5)_2(o\text{-}C_6H_4CHOCH_2CH_2O)$ (**26**, 92%) and *cis*-$(CO)_4Re(H)P(C_6H_5)_2(o\text{-}C_6H_4CH(OCH_3)_2)$ (**27**, 83%), respectively.

Unfortunately, we were subsequently unable to remove the aldehyde protecting groups in **26** and **27**, even under conditions that deblocked the free phosphine acetals.[34] In some cases, well-defined alternative reactions were observed. For example, attempted use of $(CH_3)_3SiI$ as a deprotecting agent[35] for **27** gave iodide complex *cis*-$(CO)_4Re(I)P(C_6H_5)_2(o\text{-}C_6H_4CH_2OCH_3)$ (**28**, eq vi) in 98% yield.



IV. Synthesis of Manganese α-Hydroxyalkyl Complex 4 and Related Compounds. In order to circumvent some of the problems encountered with $(CO)_5ReH$ above, we next investigated reactions of a more acidic[36] and substitution labile[32,37] hydride, $(CO)_5MnH$, with functionalized phosphines.

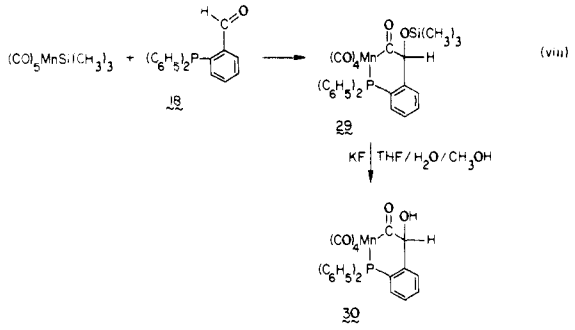
The first reaction attempted, that of $(CO)_5MnH$ with phosphine aldehyde **18** in benzene (eq vii), gave α-hydroxyalkyl complex **4** in quantitative yield as assayed by ^1H NMR spectroscopy. The



product was isolated as a light yellow oil in 75–84% yields following column chromatography; lemon yellow crystals were obtained from ether/hexanes. Complex **4** exhibited an OH ^1H NMR resonance (CD_3CN) at δ 3.73 (br s) and a weak molecular ion in a 15 eV mass spectrum. Its IR spectrum (Table II) showed ν_{O-H} at 3503 cm^{-1} (w, br).

Manganese silane complex $(CO)_5MnSi(CH_3)_3$ has been shown to undergo facile 1,2-addition to aldehydes.[38] Hence, it was treated with phosphine aldehyde **18** (eq viii). Subsequently isolated was (silyloxy)*acyl* complex $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OSi(CH_3)_3)\text{—}C{=}O)$ (**29**, 52%). Reaction of **29** with KF in $THF/CH_3OH/H_2O$ gave hydroxyacyl complex $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OH)\text{—}C{=}O)$ (**30**, 93%; eq viii), thus providing an authentic sample of the carbonylation product of **4**. Complex **30** showed no tendency to decarbonylate on routine handling and was stable to the conditions of eq vii.

(30) McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3066.
(31) (a) Van Doorn, J. A.; Masters, C.; Volger, H. C. *J. Organomet. Chem.* **1976**, *105*, 245. (b) Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. G.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852.
(32) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527.
(33) (a) Evans, D. A.; Truesdale, L. K.; Carroll, G. L. *J. Chem. Soc., Chem. Commun.* **1973**, 55. (b) Evans, D. A.; Truesdale, L. K. *Tetrahedron Lett.* **1973**, 4929.
(34) This suggests that the phosphorus lone pair assists the hydrolysis of the uncomplexed phosphine acetals.
(35) Jung, M. E.; Andrus, W. A.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, 4175.
(36) (a) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 321. (b) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.
(37) Byers, B. H.; Brown, T. L. *J. Organomet. Chem.* **1977**, *127*, 181.
(38) (a) Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508. (b) Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147.

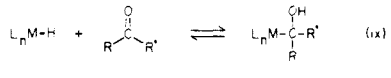


The carbonylation of **4** was attempted under a variety of conditions. No reaction was observed in benzene under 300 psi of CO. In CD_3CN (310–360 psi of CO) and CH_3NO_2 (350–360 psi of CO) decomposition occurred. In no case was any **30** observed. Complex **30** was independently shown to be stable in CH_3NO_2/THF (1.0:1.3) under 350–360 psi of CO.

Discussion

I. Syntheses and Factors Influencing the Stability of Metal α-Hydroxyalkyl Complexes. Three strategies are utilized above for the synthesis of metallacyclic α-hydroxyalkyl complexes **4** and **5**: cyclometalation/deprotection (eq iii), metallacyclic acyl complex reduction (eq v), and aldehyde addition (eq vii). Each employs readily available ortho-functionalized aryl phosphines, some of which have been independently prepared by Rauchfuss. In this section, we analyze selected thermodynamic and mechanistic aspects of these syntheses and related chemistry of other α-hydroxyalkyl complexes.

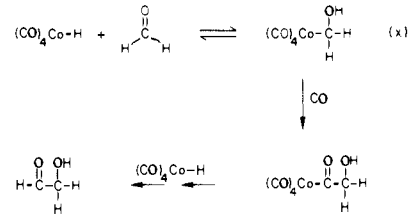
Consider the generalized equilibrium shown in eq ix for the formation of a metal α-hydroxyalkyl complex from a metal hydride and an aldehyde or ketone. In the previous paper, we found that complexes of the type $(CO)_5MCH(C_6H_5)OH$ (M = Mn, Re) rapidly decomposed to $(CO)_5MH$ and benzaldehyde (eq i). We presume that similar results would be obtained with phosphine-substituted analgoues $(CO)_4(L)MnCH(C_6H_5)OH$. The successful synthesis of **4** (eq vii) can then be directly attributed to the presence of a chelate ring—ΔS is no longer favorable (positive) for metal hydride formation. There are abundant examples of carbonyl addition reactions which are entropically driven,[21] the most familiar of which is the cyclization of glucose to its hemiacetal forms.



Contrast the formation of α-hydroxy*alkyl* complex **4** from $(CO)_5MnH$ and **18** (eq vii) with that of (silyloxy)*acyl* complex **29** from $(CO)_5MnSi(CH_3)_3$ and **18** (eq viii). Carbon monoxide is lost in the former but retained (as acyl C=O) in the latter. Accordingly, we propose initial phosphine substitution for CO in eq vii but initial aldehyde addition (by Mn–Si) in eq viii.

Regardless of the exact sequence of steps, there are at least two possible mechanisms for manganese–hydrogen bond addition to the aldehyde moiety in eq vii. First, since $(CO)_5MnH$ is a moderate acid ($pK_a \sim 7$),[36] the manganese–hydrogen bond should be capable of uncatalyzed ionic addition. Alternatively, $(CO)_5MnH$ can also undergo nonchain radical additions to unsaturated organic substrates.[39]

Metal hydrides that are acidic and/or good H· donors would seem to be kinetically the most suited for reacting as in eq ix, regardless of the position of equilibrium. Accordingly, Orchin has found that $(CO)_4CoH$, which is both a good acid ($pK_a \sim 1$)[36] and H· donor,[40] and CO convert formaldehyde to glycolaldehyde (eq x).[41] As shown, the best precendented mechanism would involve initial formation of α-hydroxyalkyl complex $(CO)_4CoCH_2OH$. Metal hydrides that are hydridic and reduce aldehydes and ketones to alkoxides[42] should be considerably poorer prospects for reacting as in eq ix.



Of the other α-hydroxyalkyl species in Figure 1, only Wayland's rhodium octaethylporphyrin complexes **8a–d** have been unambiguously prepared from the corresponding metal hydride and aldehydes. Rhodium octaethylporphyrin hydride is of unknown acidity, but it has recently been shown to be a good H· donor.[43]

Equation ix will also be favored with organic substrates containing weaker C=O bonds. Formaldehyde has a weaker C=O bond than other aldehydes.[19] Hence, it is probably not a coincidence that $L_nM–CH_2OH$ complexes are more common than $L_nM–CHROH$ complexes.

Electron-withdrawing substituents (CCl_3, CF_3, etc.) also weaken C=O bonds.[19,20] This is likely a major factor in the stability of $C(CF_3)_2OH$ complex **1** (Figure 1). Since **1** was prepared by the addition of acid to a $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-/(CF_3)_2C{=}O$ reaction mixture, it may have formed via an eq ix type route. Analogous reactions of $(CF_3)(CF_2H)C{=}O$ and $(CF_3)(CF_2Cl)C{=}O$ gave only traces of possible α-hydroxyalkyl complexes.[4]

Electron-withdrawing substituents can also provide kinetic stabilization of α-hydroxyalkyl complexes. For example, fluorine substitution increases the homolytic metal–carbon bond dissociation energy in transition-metal alkyls.[44] Bakač and Espenson have characterized a number of labile α-hydroxyalkyl complexes of formula $(H_2O)_5CrCH(R)OH^{2+}$ in aqueous solution.[16a,b] These decompose by protonolysis and homolysis, as opposed to an eq ix type reaction. The species with R = CF_3 is by far the most stable with respect to both decomposition modes.

Finally, the metal hydride $L_nM–H$ can also influence the equilibrium in eq ix. Metal–hydrogen bonds are 20–30 kcal/mol stronger than corresponding metal–alkyl bonds.[44] As has been previously noted by Wayland,[11] L_nM systems that minimize this difference (i.e., have a stronger "carbon basicity"[17]) will favor formation of the α-hydroxyalkyl complex.

Even when α-hydroxyalkyl complexes are thermodynamically unstable with respect to eq ix, they may possess sufficient kinetic stability to be prepared by other routes. Greater kinetic stability would be realized with L_nM moieties that are poor heterolytic and homolytic leaving groups. Hence, complexes with good donor ligands and/or of third-row metals are optimal. In other cases, eq ix might be thermodynamically favorable, but the metal hydride may undergo other types of reactions with the aldehydic substrate at a lower temperature. Alternatively, high temperatures might be required to establish equilibrium, which could destroy the α-hydroxyalkyl product.

Substrates and conditions for the cyclometalation/deprotection route to rhenium α-hydroxyalkyl complex **5** (eq iii) have been carefully optimized. Reactions of additional ortho-substituted phosphines, $(C_6H_5)_2P(o\text{-}C_6H_4CH_2OR)$, with $(CO)_5ReCH_2C_6H_5$

(39) (a) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335. (b) Sweany, R.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487.

(40) (a) Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259. (b) Nalesnik, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222.

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(42) (a) Labinger, J. A.; Komadina, K. H. *J. Organomet. Chem.* **1978**, *155*, C25. (b) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. *J. Am. Chem. Soc.* **1985**, *107*, 2428.

(43) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

(44) (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238. (b) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Takhin, G. A.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166. (c) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824. (d) Beauchamp, J. L.; Martinho Simões, J. A. *Chem. Rev.*, in press.

Table VI. Bond Angles in **22**[a]

from	thru	to	angle (deg)	from	thru	to	angle (deg)
O1	C1	Re	176.84 (65)	C(3A)	C(1A)	C(2A)	118.77 (71)
O2	C2	Re	177.20 (63)	C(3A)	C(1A)	P	119.98 (60)
O3	C3	Re	175.54 (64)	C(2A)	C(1A)	P	121.25 (60)
H	C4	O4	106.15	C(2B)	C(1B)	C(3B)	119.99 (63)
H	C4	C(2B)	110.20	C(2B)	C(1B)	P	114.84 (52)
H	C4	Re	118.89	C(3B)	C(1B)	P	125.15 (53)
O4	C4	C(2B)	105.99 (51)	C(2C)	C(1C)	C(3C)	118.83 (72)
O4	C4	Re	94.93 (37)	C(2C)	C(1C)	P	124.42 (58)
C(2B)	C4	Re	117.85 (44)	C(3C)	C(1C)	P	116.37 (63)
O5	C5	O4	116.77 (62)	C(4A)	C(2A)	C(1A)	119.41 (81)
O5	C5	Re	141.61 (56)	C(4B)	C(2B)	C(1B)	119.28 (64)
O4	C5	Re	101.55 (41)	C(4B)	C(2B)	C4	120.04 (63)
C5	O4	C4	101.97 (47)	C(1B)	C(2B)	C4	120.61 (61)
C(1B)	P	C(1A)	106.76 (32)	C(1C)	C(2C)	C(4C)	121.21 (80)
C(1B)	P	C(1C)	104.87 (34)	C(6A)	C(3A)	C(1A)	120.47 (81)
C(1B)	P	Re	105.11 (24)	C(6B)	C(3B)	C(1B)	120.02 (66)
C(1A)	P	C(1C)	102.64 (33)	C(6C)	C(3C)	C(1C)	119.74 (88)
C(1A)	P	Re	121.02 (26)	C(5A)	C(4A)	C(2A)	121.15 (85)
C(1C)	P	Re	115.19 (24)	C(5B)	C(4B)	C(2B)	120.26 (68)
C3	Re	C2	97.24 (31)	C(5C)	C(4C)	C(2C)	119.68 (89)
C3	Re	C1	94.85 (30)	C(4A)	C(5A)	C(6A)	118.56 (81)
C3	Re	C5	99.53 (28)	C(4B)	C(5B)	C(6B)	120.64 (69)
C3	Re	C4	159.87 (28)	C(4C)	C(5C)	C(6C)	120.28 (79)
C3	Re	P	94.79 (22)	C(3A)	C(6A)	C(5A)	121.58 (87)
C2	Re	C1	92.34 (31)	C(3B)	C(6B)	C(5B)	119.77 (69)
C2	Re	C5	85.89 (29)	C(5C)	C(6C)	C(3C)	120.25 (85)
C2	Re	C4	88.52 (28)	N	C(N1)	C(N2)	114.85 (61)
C2	Re	P	167.78 (21)	C(N4)	C(N3)	N	116.01 (64)
C1	Re	C5	165.62 (28)	N	C(N5)	C(N6)	115.56 (61)
C1	Re	C4	104.22 (27)	N	C(N7)	C(N8)	114.56 (61)
C1	Re	P	88.80 (22)	C(N1)	N	C(N3)	110.54 (56)
C5	Re	C4	61.51 (26)	C(N1)	N	C(N7)	112.27 (57)
C5	Re	P	90.00 (20)	C(N1)	N	C(N5)	105.95 (54)
C4	Re	P	79.42 (19)	C(N3)	N	C(N7)	105.12 (54)
				C(N3)	N	C(N5)	111.29 (56)
				C(N7)	N	C(N5)	111.80 (56)

[a] Atoms are numbered as indicated in Figure 2.

were briefly examined, and cyclometalation yields were found to qualitatively correlate with ligand bulk. In all cases, initial phosphine substitution occurred. We note in passing that major mechanistic questions attend the subsequent cyclometalation steps.[23]

Since cyclometalation is a very general reaction of transition-metal complexes,[45] variations of eq iii might have broad applicability for the synthesis of α-hydroxyalkyl complexes. The final deprotection sequence, the O-desilylation **21** →→ **5**, has some analogy in one synthesis of **2** (O-demethylation)[5] and **7** (O-desilylation).[10b]

Most of the remaining α-hydroxyalkyl complexes in Figure 1 were synthesized by the carefully controlled hydride reduction of the corresponding carbonyl or formyl complexes (**2**, **7**, **9**, **13**–**17**). The surprisingly successful BH_3·THF acyl reduction route[31] to rhenium α-hydroxyalkyl complex **5** (eq v) belongs to this category. The scope of this reaction is expanded and discussed in the following paper.[15b]

II. Properties of α-Hydroxyalkyl Complexes. The conversions of α-hydroxyalkyl complexes to symmetrical ethers (eq iv), and hydride transfer disproportionation products (eq v), are emerging as transformations of considerable generality. For example, Casey has reported that **2** (Figure 1) can, in the presence of acid, undergo dimerization to ether $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)CH_2\text{–}]_2O$ or disproportionate to a 2:1 mixture of $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(CH_3)$ and $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+$.[5b,c] Wayland has reported that **8b** slowly dimerizes in benzene to an ether, which subsequently disproportionates to rhodium octaethylporphyrin acetyl and ethyl complexes.[11] These results suggest that α-hydroxyalkyl complexes are readily ionized to ^-OH and cationic alkylidene complexes. Such α-ionizations are common in organometallic chemistry—e.g., with L_nMCOOH and L_nMCH_2Cl complexes.[46]

The reluctance of α-hydroxyalkyl complexes **4** and **5** to carbonylate to six-membered hydroxyacyl complexes (e.g., **30**) can be attributed to several factors. First, both α-oxy (OR, $OSiR_3$, etc.) substituents and α-benzyl substituents commonly retard the rates of alkyl migration to coordinated CO.[47] Second, Lindner has observed that with metallacycles of formula $(CO)_4Mn\text{-}(CH_2)_nP(C_6H_5)_2$, carbonylative ring expansion to acyl complexes $(CO)_4MnCO(CH_2)_nP(C_6H_5)_2$ is considerably more facile, both kinetically and thermodynamically, for $n = 2$ (4- → 5-membered ring) than for $n = 3$ (5- → 6-membered ring).[48] Note that the $\nu_{C=O}$ in the IR spectrum of the hydroxyacyl complex **30** (Table II) is somewhat lower than the $\nu_{C=O}$ in silyloxyacyl complex **29**. Coupled with the low ν_{O-H} in **30**, an intramolecular hydrogen bond, $L_nMC(=O)CH(R)OH$, is suggested. This observation is relevant to the successful carbonylation of **17** (Figure 1) described in the following paper.

The ν_{O-H} of α-hydroxyalkyl complexes **4** and **5** (Table II) are in a normal range. However, they are weak in intensity compared to $\nu_{C=O}$. The hydroxyl proton in **5** is evidently slow to exchange in CD_3CN, as coupling to the methine proton occurs (Table I). Analogous couplings have been observed with a number of other α-hydroxyalkyl complexes (**2** (Me_2SO-d_6),[6d] **8** (toluene-d_8),[11] **9** (Me_2SO-d_6),[12] **13** (acetone-d_6),[13a] **14** (C_6D_6),[13b] **15** and **16** (acetone-d_6)[14a]).

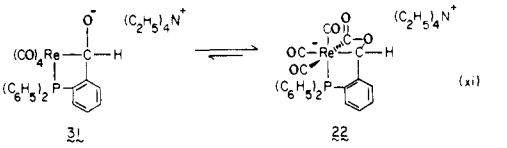
(45) (a) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (b) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. (c) Omae, I. *Chem. Rev.* **1979**, *79*, 287.

(46) (a) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627. (b) Pelling, S.; Botha, C.; Moss, J. R. *J. Chem. Soc., Dalton Trans.* **1983**, 1495. (c) Richmond, T. G.; Shriver, D. F. *Organometallics* **1984**, *3*, 305.

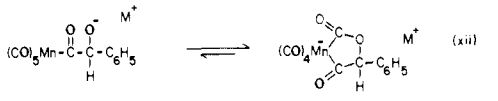
(47) (a) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *Organomet. Chem.* **1979**, *172*, 405. (b) Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056.

(48) Lindner, E.; Funk, G. *J. Organomet. Chem.* **1981**, *216*, 393.

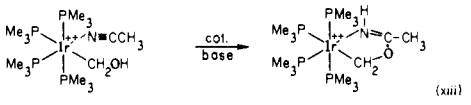
III. The Metallabicycle 22. The mode of formation of **22**, and its subsequent protonolysis to **5** (eq iii), suggests that **22** is in equilibrium with the alkoxide **31** (eq xi). A similar equilibrium, **32** ⇌ **33** (eq xii), involving an alkoxide on a carbon β to a metal, was described in the preceding paper.[3] To our knowledge, α-metallated alkoxides have not been isolated, but they have been suggested as reaction intermediates.[10c,49] Of particular relevance is the finding by Thorn that the labile hydroxymethyl complex **34** undergoes the base-catalyzed cyclization shown in eq xiii.[10c] This reaction likely proceeds via alkoxide attack upon coordinated CH_3CN.



(xi)



(xii)



(xiii)

We are unaware of any close structural relatives of the metallabicycle **22**.[49b] One may view the rhenium as occupying a "bridgehead" position and the four-membered ring as an adduct of CO_2 with an alkylidene complex. In the four-membered ring, the C4–Re–C5 angle (61.5°) is markedly compressed from theory (octahedral, 90°). The O4–C4 bond (1.506 (8) Å) is elongated relative to normal carbon–oxygen single bonds (e.g., 1.437 Å in H_3C–OCH_3)[50] and the corresponding bond in the related metallacycle **33** (1.418 (7) Å).[3] However, such carbon–oxygen bond lengths are not uncommon.[51] The Re–C5 bond length (2.165 (7) Å) in **22** is comparable to the rhenium–acyl bond length in *cis*-$(CO)_4Re(H_2NC_6H_5)(COCH_3)$ (2.211 (6) Å),[52] and the Re–C4 bond length (2.225 (7) Å) shows no lengthening over that of other octahedral rhenium alkyl complexes.[53]

IV. Summary and Relevance to Catalysis. In the preceding discussion, we have intermingled thermodynamic and kinetic facets of the stability of α-hydroxyalkyl complexes. To summarize, the thermodynamic stability of α-hydroxyalkyl complexes with respect to eq ix will be (1) lowered by α-alkyl substituents and enhanced by electron-withdrawing substituents, (2) enhanced with L_nM systems for which metal–carbon bonds are as close as possible in strength to metal–hydrogen bonds, and (3) enhanced by chelation. Both (1) and (2) are enthalpic, whereas (3) is entropic. Importantly, however, the above points also have kinetic counterparts. For example, α-alkyl substituents lower metal–carbon bond-dissociation energies (and therefore increase homolysis rates), whereas electron-withdrawing substituents generally raise metal–carbon bond-dissociation energies.[16b,44] Hence, factors affecting thermodynamic and kinetic stability of α-hydroxyalkyl complexes are intertwined. Regardless, a reasonably detailed model is now available (the "hemiacetal analogy") which accounts for many properties of this catalytically important class of compounds.

In catalysis, α-hydroxyalkyl complex stability is secondary to reactivity. For example, in the catalytic hydroformylation of formaldehyde, eq ix is a necessary step. However, only small equilibrium concentrations of α-hydroxyalkyl intermediates need to be generated for subsequent carbonylation to occur. Nonetheless, in both this process and in the synthesis of ≥ C_2 oxygenates from CO/H_2, it would appear optimal to employ a L_nM catalyst whose hydride reacted with carbonyl compounds as in eq ix, as opposed to one whose hydride would give an alkoxide.

In the following paper,[15b] we continue to examine the effect of chelation upon the stability of metal α-hydroxyalkyl complexes. By this strategy, we are able to synthesize the first isolable α-hydroxyalkyl complex that carbonylates to a hydroxyacyl complex. This reactivity is examined in detail.

Experimental Section

General. All reactions and filtrations were carried out under a dry N_2 atmosphere unless noted. IR spectra were recorded either on Perkin-Elmer Model 521 or 1500 (FT) spectrometers. All NMR data were acquired either on a Bruker WP 200 or a Varian SC 300 spectrometer. ^{31}P NMR chemical shifts were referenced to external 85% H_3PO_4; positive values indicate downfield shifts. For other information, see Table I. Mass spectra were obtained on an AEI MS-9 spectrometer. Microanalyses were conducted by Galbraith and Schwarzkopf Laboratories.

Solvents. All solvents were distilled under N_2. Benzene, toluene, THF, and dioxane were distilled from Na/benzophenone. Acetonitrile was distilled from CaH_2. Nitromethane, CH_2Cl_2, and $CHCl_3$ were distilled from P_2O_5. Acetone was distilled from anhydrous $CaSO_4$ (Drierite). Hexanes, heptane, and octane were distilled from sodium. Decane was vacuum distilled from sodium. The above solvents were purged with N_2 for at least 0.5 h before use. Ether was distilled from Na/benzophenone and freeze–pump–thaw degassed before use. Petroleum ether (bp 37–58 °C) was distilled from $LiAlH_4$ and was also freeze–pump–thaw degassed before use.

Ethyl acetate and methanol were reagent grade and used as received. Pyridine was stored over KOH and used without distillation.

NMR solvents were dried over the following drying agents and then transferred by bulb-to-bulb distillation to a dry container. C_6D_6 and CD_3CN: CaH_2. $CDCl_3$: P_2O_5. CD_2Cl_2: either P_2O_5 or CaH_2. Acetone-d_6: 4A molecular sieves. THF-d_8: $LiAlH_4$.

Reagents. Silanes $(CH_3)_3SiBr$, $(CH_3)_3SiI$, $(CH_3)_3SiCN$, and $(t\text{-}C_4H_9)(CH_3)_2SiCl$ were obtained from Petrarch. The first three were distilled from CaH_2. With $(CH_3)_3SiCN$, the first fraction was discarded. Technical grade $(C_6H_5)_2PCl$ (Aldrich) was distilled under vacuum; the first fraction was discarded. Phosphines $(C_6H_5)_3P$ and $(C_6H_5)_2P(o\text{-}C_6H_4CH_3)$ were used as received from Aldrich and Strem, respectively.

Ortho ester $HC(OCH_3)_3$ (Aldrich) was distilled from CaH_2. Standard $(C_6H_5)_3CH$ (Aldrich) was recrystallized from ethanol. Standard $(C_6H_5)_3SiCH_3$ was prepared from sublimed $(C_6H_5)_3SiCl$ (Petrarch) and CH_3MgBr in THF by a slight modification of the literature procedure[54] and was subsequently sublimed.

The following were used as received: BH_3·THF, 1 M in THF (Aldrich); $p\text{-}CH_3C_6H_4SO_3H\cdot H_2O$ (Matheson Coleman and Bell); $(n\text{-}C_4H_9)_4N^+F^-\cdot(H_2O)_3$ (Fluka); CF_3CO_2H (Fischer); CF_3SO_3H (Aldrich); CO (Matheson).

Hydrides $(CO)_5MnH$[55,56] and $(CO)_5ReH$[57] were prepared from $(CO)_5M^-$ by modifications of the literature procedures. Yields improved somewhat when $K^+(CO)_5M^-$ were used[58] instead of $Na^+(CO)_5M^-$. Silane $(CO)_5MnSi(CH_3)_3$ was prepared as previously described[59] except that isolated $K^+(CO)_5Mn^-$ was used.[58] Carbonyl $Mn_2(CO)_{10}$ was purchased from Strem and sublimed before use. Complex $(CO)_5ReCH_2$-

(49) (a) Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *162*, C11. (b) A carborane complex with a Mo–C–O–C=O linkage (generated by alkoxide cyclization) recently has been called to our attention: Wegner, P. A.; Guggenberger, L. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1970**, *92*, 3473.

(50) Reference 19, p 527.

(51) For leading references, see: Allen, F. H.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6197 and immediately following papers.

(52) Lukehart, C. M.; Zeile, J. V. *J. Organomet. Chem.* **1977**, *140*, 309.

(53) (a) $(CO)_5ReCH_3$, 2.308 (17) Å: Rankin, D. W. H.; Robertson, A. *J. Organomet. Chem.* **1976**, *105*, 331. (b) (−)-(*R*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$, 2.203 (8) Å: Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(54) Marsden, H.; Kipping, F. S. *J. Chem. Soc.* **1908**, *93*, 198.

(55) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 196.

(56) Vaughn, G. D. Ph.D. Thesis, UCLA, 1984.

(57) Braterman, P. S.; Harrill, R. W.; Kaesz, H. D. *J. Am. Chem. Soc.* **1967**, *89*, 2851.

(58) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263.

(59) (a) Marsi, M.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1467. (b) Malisch, W.; Kuhn, M. *Chem. Ber.* **1974**, *107*, 979. (c) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

C_6H_5 was prepared by a literature procedure.[27] Phosphines not given below and $(C_2H_5)_4N^+F^-\cdot(H_2O)_{2.6}$[60] were prepared as described in the supplementary material.

Synthesis of $(C_6H_5)_2P(o\text{-}C_6H_4CH_2OSi(CH_3)_2(t\text{-}C_4H_9))$ (20). This preparation was conducted in air. A round-bottomed flask was fitted with a reflux condenser and a drying tube and was charged with $(C_6H_5)_2P(o\text{-}C_6H_4CH_2OH)$ (**19**, 2.81 g, 9.61 mmol),[26] CH_2Cl_2 (50 mL), $(t\text{-}C_4H_9)(CH_3)_2SiCl$ (2.05 g, 13.6 mmol), and pyridine (0.9 mL, 11 mmol). The reaction was refluxed for 32 h. Then hexanes (50 mL) were added. The precipitated salts were removed by filtration and rinsed with hexanes. Solvent was removed from the filtrate by rotary evaporation, and the residue was chromatographed on silica gel with 90:10 hexanes/ethyl acetate. Solvent was removed from the product-containing fractions and the residue was dried under vacuum for 3 days to give 3.71 g (9.12 mmol, 95%) of **20** as a white solid, mp 52.5–53.5 °C. This preparation frequently gave **20** as a colorless oil. ^1H NMR (δ, $CDCl_3$): 7.68–7.59 (m, 1 H), 7.40–7.19 (m, 11 H), 7.18–7.07 (m, 1 H), 6.88–6.79 (m, 1 H), 4.88 (d, J_{HP} = 1.8 Hz, 2 H), 0.88 (s, 9 H), −0.01 (s, 6 H). $^{13}C\{^1H, ^{31}P\}$ NMR (ppm, $CDCl_3$): 145.3, 136.1, 133.9, 133.3, 132.7, 128.8, 128.7, 128.5, 126.8, 125.9, 63.0, 25.9, 18.3, −5.4. $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): −15.9. Anal. Calcd for $C_{25}H_{31}OPSi$: C, 73.85; H, 7.68. Found: C, 73.64; H, 8.04.

Synthesis of $(C_6H_5)_2P(o\text{-}C_6H_4CH(OCH_3)_2)$. A Schlenk flask was charged with N_2-purged methanol (40 mL), $(C_6H_5)_2P(o\text{-}C_6H_4CHO)$ (**18**, 0.296 g, 1.02 mmol),[25] $HC(OCH_3)_3$ (0.2 mL, 1.8 mmol), and about 10 mg of $p\text{-}CH_3C_6H_4SO_3H\cdot H_2O$. The reaction was stirred for 14 h, during which time it decolorized. Then K_2CO_3 was added. The mixture was filtered, and solvent was removed from the filtrate by rotary evaporation. The resulting residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on a silica gel column (2 × 15 cm) with 3:1 hexanes/ethyl acetate. The eluant was collected under a N_2 purge. Subsequent solvent removal gave 0.294 g (0.874 mmol, 86%) of product as a white powder, mp 84.5–86 °C. ^1H NMR (δ, $CDCl_3$): 7.75–7.62 (m, 1 H), 7.47–7.06 (m, 12 H), 7.04–6.90 (m, 1 H), 6.00 (d, J_{HP} = 5.2 Hz, 1 H), 3.14 (s, 6 H). $^{13}C\{^1H, ^{31}P\}$ NMR (ppm, $CDCl_3$): 142.8, 136.9, 135.7, 134.1, 133.9, 128.8, 128.5, 128.4, 126.4, 101.7, 53.4. $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): −15.9. Anal. Calcd for $C_{21}H_{21}O_2P$: C, 74.99; H, 6.29; P, 9.21. Found: C, 75.02; H, 6.32; P, 9.32.

Synthesis of $(CO)_4\overline{ReP(C_6H_5)_2(o\text{-}C_6H_4CHOSi(CH_3)_2(t\text{-}C_4H_9))}$ (21). A Schlenk flask was charged with $(CO)_5ReCH_2C_6H_5$ (1.69 g, 4.05 mmol), **20** (1.48 g, 3.65 mmol), and octane (100 mL) which had been purged with N_2. The resulting soltuion was heated on a steam bath for 3 h and then refluxed for 2 h. The solvent was then removed under oil pump vacuum and the residue chromatographed on a 4 × 50 cm silica gel column with 9:1 hexanes/ethyl acetate. The product-containing fractions were collected under N_2. Solvent was removed by rotary evaporation and the residue taken up in toluene and filtered through a Pasteur pipet filled with dry silica gel. The toluene was removed by rotary evaporation, and the residue was recrystallized from CH_3CN to give 1.19 g (1.69 mmol, 46%) of white crystalline **21**, decomposition point (unsealed capillary) 130–135 °C. Mass spectrum (*m/e*, 16 eV, ^{187}Re): 704 (M^+, 1%), 620 (M^+ − 3 CO, 62%), 75 ($OSi(CH_3)_2H^+$, 100%). Anal. Calcd for $C_{29}H_{30}O_5PReSi$: C, 49.49; H, 4.30; P, 4.40; Re, 26.46. Found: C, 49.39; H, 4.41; P, 4.50; Re, 26.32.

Synthesis of $(CO)_4\overline{ReP(C_6H_5)_2(o\text{-}C_6H_4CHOH)}$ (5) from 21. To a stirred solution of **21** (0.263 g, 0.374 mmol) in acetone (5 mL) was added a solution of $(C_2H_5)_4N^+F^-\cdot(H_2O)_{2.6}$ (0.483 g, 2.5 mmol) in CH_3CN (6 mL). After 3 h, 10 mL of 90:10 (v/v) acetone/H_2O was added, followed by 10 mL of acetone. The following manipulations were conducted in air. The reaction mixture was filtered through silica gel, and the silica gel was eluted with additional acetone. Solvent was removed from the filtrate, the resulting residue was taken up in ether, and a second silica gel filtration was performed. Solvent was again removed from the filtrate and the residue was taken up in CH_3CN and filtered through glass fiber filter paper (total filtrate volume: 1.5 mL). The remaining workup was performed under N_2. The filtrate was added in 0.3-mL aliquots to a preparative reverse-phase HPLC system (Altex 10 × 250 mm Ultrasphere-ODS 5 μm, 80:20 (v/v) CH_3OH/H_2O, flow rate 5 mL/min, UV detection at 370 nm). Solvent was removed from the combined product-containing fractions to give 0.170 g (0.288 mmol, 77%) of **5** as a fine white powder, mp 64–66 °C (evacuated capillary). $^{31}P\{^1H\}$ NMR (ppm, CD_3CN): 26.6. Mass spectrum (*m/e*, 70 eV, ^{187}Re): 590 (M^+, 26%), 562 (M^+ - CO, 4%), 534 (M^+ - 2CO, 30%), 506 (M^+ - 3CO, 100%), 478 (M^+ -4CO, 35%). Anal. Calcd for $C_{23}H_{16}O_5PRe$: C, 46.86; H, 2.74; P, 5.25; Re, 31.58. Found: C, 46.99; H, 2.94; P, 5.09; Re, 31.67.

(60) This synthesis combines aspects of earlier preparations: Clark, J. H.; Miller, J. M. *J. Chem. Soc., Perkin Trans 1* **1977**, *15*, 1743. Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

Synthesis of $(C_2H_5)_4N^+$-*fac*-$[(CO)_3\overline{ReP(C_6H_5)_2(o\text{-}C_6H_4C(H)OC{=}O)}]^-$ (22). To a stirred solution of **21** (0.222 g 0.315 mmol) in acetone (2 mL) was added a solution of $(C_2H_5)_4N^+F^-\cdot(H_2O)_{2.6}$ (0.082 g, ca. 0.4 mmol) in CH_3CN (3.8 mL). After 40 h, the solvents were removed by rotary evaporation. The residue was extracted with CH_3CN. Ether was slowly added to the extract until a persistent cloud point was reached. After 2–3 days, colorless crystals of **22** (0.212 g, 0.295 mmol, 94%) were collected by filtration and dried under oil pump vacuum, decomposition point 144–146 °C (evacuated capillary). Repeated recrystallizations were necessary to achieve analytical purity. Anal. Calcd for $C_{31}H_{35}NO_5PRe$: C, 51.80; H, 4.91; N, 1.95; P, 4.31; Re, 25.90. Found: C, 52.09; H, 5.09; N, 2.24; P, 3.92; Re, 25.68.

Synthesis of 5 from 22. A 5-mm NMR tube was charged with **22** (0.0892 g, 0.124 mmol), Ph_3CH (0.0294 g, 0.120 mmol) standard, and CD_3CN (0.45 mL) and capped with a septum. To the resulting suspension was added 10 μL (0.13 mmol, 1.0 equiv) of CF_3CO_2H. The tube was shaken and the reaction immediately became homogeneous. Analysis by ^1H NMR after 15 min showed **22** to be consumed and the presence of **5** in 74% yield, as assayed by the integration of its δ 6.1 resonance vs. the standard. A second experiment with Ph_3SiCH_3 standard also gave a 74% spectroscopic yield of **5**.

Synthesis of $[(CO)_4\overline{ReP(C_6H_5)_2(o\text{-}C_6H_4CH)}\text{-}]_2O$ (23) from 21. A 5-mm NMR tube was charged with **21** (0.087 g, 0.124 mmol), acetone (1.1 mL), H_2O (65 μL), and CF_3SO_3H (ca. 0.5 μL, 0.006 mmol, 0.05 equiv) and capped with a septum. The tube was vigorously shaken for ca. 1 min and then allowed to stand. After 15 min, the formation of yellow crystals was observed. After 36 h, these were collected by filtration and dried under vacuum. Thus obtained was 0.0604 g (0.052 mmol, 84% of theory) of **23**. An analytical sample was recrystallized from THF/CH_3CN, decomposition point 212–216 °C (unsealed capillary). Mass spectrum (*m/e*, 16 eV, $^{187}Re^{187}Re$): 1162 (M^+, 8%), 1106 (M^+ - 2CO, 100%), 1062 (M^+ - 3CO - O, 20%), 1034 (M^+ - 4CO - O, 62%), 1006 (M^+ - 5CO - O, 97%), 994 (M^+ - 6CO, 8%), 978 (M^+ - 6CO - O, 54%), 966 (M^+ - 7CO, 11%), 950 (M^+ - 7CO - O, 18%), 922 (M^+ - 8CO - O, 21%). Anal. Calcd for $C_{46}H_{30}O_9P_2Re_2$: C, 47.59; H, 2.60; P, 5.34; Re, 32.07. Found: C, 47.78; H, 2.70; P, 5.34; Re, 31.59.

Synthesis of 23 from 5. A 5-mm NMR tube was charged with **5** (0.055 g, 0.093 mmol), acetone (0.6 mL), H_2O (30 μL), and CF_3SO_3H (ca. 0.5 μL, 0.006 mmol, 0.06 equiv) and capped with a septum. The tube was vigorously shaken for ca. 1 min and then kept at room temperature. Yellow crystals of **23** formed and were collected by filtration (0.015 g, 0.013 mmol, 28% of theory). Silica gel TLC analysis of the filtrate showed at least six other products.

Synthesis of $(CO)_4\overline{ReP(C_6H_5)_2(o\text{-}C_6H_4C{=}O)}$ (24) from $(CO)_5ReCH_2C_6H_5$. A Schlenk flask was charged with $(CO)_5ReCH_2C_6H_5$ (1.752 g, 4.20 mmol), $(C_6H_5)_3P$ (1.087 g, 4.14 mmol), and toluene (175 mL). The reaction was refluxed for 2 h, allowed to cool, and filtered through a plug of silica gel. The silica gel was further eluted with CH_2Cl_2. Solvents were removed from the filtrate by rotary evaporation. The resulting residue gave white crystals of *cis*-$(CO)_4Re(CH_2C_6H_5)(P(C_6H_5)_3)$ (2.363 g, 3.63 mmol, 88%) from THF/hexanes. IR (cm^{-1}, hexanes): 2080 m, 1999 s, 1975 vs, 1942 s.

A Schlenk flask was charged with *cis*-$(CO)_4Re(CH_2C_6H_5)(P(C_6H_5)_3)$ (0.324 g, 0.497 mmol) and decane (200 mL). The reaction was refluxed for 2 h. The solvent was then removed at 55 °C under oil pump vacuum. The residue was taken up in CH_2Cl_2 and filtered through a plug of silica gel. Solvent was removed from the filtrate by rotary evaporation. The resulting yellow residue was chromatographed on a silica gel column with 95:5 (v/v) hexanes/ethyl acetate. Solvent was removed from the product-containing fractions by rotary evaporation. Subsequent vacuum drying gave 0.162 g (0.290 mmol, 58%) of $(CO)_4\overline{ReP(C_6H_5)_2(o\text{-}C_6H_4)}$.[30]

A Fischer-Porter bottle was charged with $(CO)_4\overline{ReP(C_6H_5)_2(o\text{-}C_6H_4)}$ (0.447 g, 0.800 mmol) and dioxane (15 mL). The bottle was pressurized with 360 psi of CO and the bottom portion was immersed in a 105 °C bath. Gas was vented to maintain the 360-psi internal pressure. After 44 h, the CO was vented and solvent was removed by rotary evaporation. The residue was chromatographed on a silica gel column. A yellow impurity eluted with 90:10 (v/v) hexanes/ethyl acetate. The yellow product eluted with 75:25 (v/v) hexanes/ethyl acetate. Rotary evaporation and subsequent vacuum drying gave 0.397 g (0.676 mmol, 85%) of **24**.[30]

Synthesis of $(CO)_4\overline{ReP(C_6H_5)_2(o\text{-}C_6H_4CH_2)}$ (25) from $(CO)_5ReC$-

$H_2C_6H_5$. A Schlenk flask was charged with $(CO)_5ReCH_2C_6H_5$ (0.504 g, 1.21 mmol), $(C_6H_5)_2P(o\text{-}C_6H_4CH_3)$ (0.313 g, 1.13 mmol), and heptane (25 mL). This mixture was refluxed for 13 h. The following manipulations were performed in air. The reaction mixture was filtered through a plug of silica gel in a 15-mL fritted (M) funnel. The plug was further washed with ca. 250 mL of benzene. Solvents were removed from the filtrate by rotary evaporation at room temperature. A CH_2Cl_2 solution of the residue was adsorbed onto Celite. A 3 × 36 cm silica gel column was packed in hexanes. The Celite was loaded on top of the column and the column was eluted with hexanes. The product-containing fractions were collected under a N_2 purge. In a glovebox, solvents were removed by rotary evaporation to give white crystals of **25** which were dried under vacuum (0.364 g, 0.635 mmol, 56%), mp 144–146 °C (capillary sealed under N_2). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): 30.7. Anal. Calcd for $C_{23}H_{16}O_4PRe$: C, 48.16; H, 2.81. Found: C, 47.96; H, 2.76.

Syntheses of 24 and 25 from 5. A 5-mm NMR tube was charged with **5** (0.0578 g, 0.0980 mmol) and C_6D_6 (0.8 mL) and was then capped with a septum. Then CF_3SO_3H (1.8 μL, 0.020 mmol, 0.2 equiv) was added and the tube was shaken. The reaction immediately turned yellow. The only detectable ReCH ^1H NMR resonance was that of **25**. The reaction was applied (in air) to a 10 × 20 cm preparative TLC plate. Development with 90:10 (v/v) hexanes/ethyl acetate gave two product bands which were extracted to give yellow **24** (0.0228 g, 0.0388 mmol, 79%) and white **25** (higher R_f, 0.0210 g, 0.0366 mmol, 75%).

Synthesis of 5 from 24. A 50-mL Schlenk flask was charged with **24** (0.0756 g, 0.129 mmol), THF (5 mL), and a magnetic stir bar. Then a 1 M THF solution of BH_3·THF (260 μL, 0.260 mmol) was added and the reaction was stirred. Over the course of 15 min the yellow reaction decolorized. After an additional 15 min, CH_3OH (2 mL) was added, and stirring was continued (30 min). Solvents were then removed under oil pump vacuum. The residue was taken into a glovebox and extracted with ether. The extract was filtered through a Pasteur pipet containing dry silica gel. Hexanes were added to the filtrate. Subsequent solvent removal by rotary evaporation gave **5** (0.073 g, 0.12 mmol, 93%) as a white bubble-up solid.

Synthesis of *cis*-$(CO)_4Re(H)P(C_6H_5)_2(o\text{-}C_6H_4\overline{CHOCH_2CH_2O})$ (26). A 5-mm NMR tube was charged with $(CO)_5ReH$ (0.126 g, 0.385 mmol), $(C_6H_5)_2P(o\text{-}C_6H_4\overline{CHOCH_2CH_2O})$ (0.116 g, 0.347 mmol), and benzene (0.5 mL) and was capped with a septum. After 19 h (times required for complete reaction, as assayed by ^1H NMR spectra of the Re–H region, varied widely), the reaction was filtered through a Pasteur pipet containing dry silica gel. The silica gel was washed with additional benzene. The filtrate was concentrated by rotary evaporation. Heptane was added, and solvent was removed by rotary evaporation to give off-white air-stable crystals of **26** which were collected by filtration and vacuum dried (0.202 g, 0.319 mmol, 92%), decomposition point 159–164 °C (capillary sealed under N_2). $^{31}P\{^1H\}$ NMR (ppm, acetone-d_6): 13.3. Anal. Calcd for $C_{25}H_{20}O_6PRe$: C, 47.39; H, 3.18. Found: C, 47.40; H, 3.27.

Synthesis of *cis*-$(CO)_4Re(H)P(C_6H_5)_2(o\text{-}C_6H_4CH(OCH_3)_2)$ (27). This compound was prepared analogously to **26** from $(CO)_5ReH$ (0.070 g, 0.21 mmol) and $(C_6H_5)_2P(o\text{-}C_6H_4CH(OCH_3)_2)$ (0.0643 g, 0.191 mmol). After 38 h, workup gave beige, air-stable crystalline **27** (0.101 g, 0.159 mmol, 83%). An analytical sample was prepared by taking **27** up in a minimum of petroleum ether at room temperature; white crystals, mp 143–144.5 °C (capillary sealed under N_2), subsequently formed. $^{31}P\{^1H\}$ NMR (ppm, acetone-d_6): 13.6. Anal. Calcd for $C_{25}H_{22}O_6PRe$: C, 47.24; H, 3.49. Found: C, 47.42; H, 3.61.

Synthesis of *cis*-$(CO)_4Re(I)P(C_6H_5)_2(o\text{-}C_6H_4CH_2OCH_3)$ (28). A 5-mm NMR tube was charged with **27** (0.0830 g, 0.131 mmol), C_6D_6 (0.45 mL), and $(CH_3)_3SiI$ (0.028 g, 0.14 mmol). After 20 min, a ^1H NMR spectrum indicated that **27** had been consumed; characteristic resonances of $CH_3OSi(CH_3)_3$ (δ 3.30 and 0.11, referenced to C_6D_5H) were noted. In a glovebox, the contents of the tube were washed into a flask with toluene and concentrated to an oily residue by rotary evaporation. The residue was taken up in benzene and filtered through a Pasteur pipet containing dry silica gel. Toluene was added to the filtrate, which was subsequently concentrated to ca. 1 mL by rotary evaporation. Then 25 mL of hexanes was added. Solvent was removed by rotary evaporation to give **28** as a bubble-up foam (0.094 g, 0.129 mmol, 98%). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): −5.1. Anal. Calcd for $C_{24}H_{19}IO_5PRe$: C, 39.41; H, 2.62. Found: C, 39.62; H, 2.90.

Synthesis of $(CO)_4\overline{MnP(C_6H_5)_2(o\text{-}C_6H_4CHOH)}$ (4).[61] A 5-mm NMR tube was charged with **18** (0.211 g, 0.727 mmol). Then a solution of $(CO)_5MnH$ (0.153 g, 0.781 mmol) in 1.5 mL of benzene was added via syringe. The tube was fitted with a septum and shaken. A small needle connected to a hood-vented oil bubbler was inserted into the septum to vent the CO that vigorously evolved. After the CO evolution subsided, the disappearance of the aldehyde ^1H NMR doublet (J_{HP} = 5 Hz, ca. δ 10.5) was monitored. After 9 h, the aldehyde was consumed. A 3 × 37 cm silica gel column was packed in 85:15 (v/v) hexanes/ethyl acetate. The contents of the tube were directly applied to the top of the column. The tube was rinsed once with acetone. The reaction mixture was then eluted (under N_2) from the column with 85:15 hexanes/ethyl acetate. A yellow $Mn_2(CO)_{10}$ fraction eluted first, followed by a light yellow product fraction. Solvent was removed from the latter under oil pump vacuum to give **4** (0.279 g, 0.609 mmol, 84%) as a light yellow oil. The oil was taken up in a minimum of ether. Hexane was added and the mixture was concentrated under oil pump vacuum until a cloud point was reached. The mixture was allowed to stand for 1 h and was then placed in a −4 °C refrigerator for 12 h. Lemon yellow crystals of 4, mp 121.5–123.5 °C (capillary sealed under N_2), were subsequently collected by filtration. $^{31}P\{^1H\}$ NMR (ppm, CD_3CN): 77.4.[62] Mass spectrum (*m/e*, 15 eV): 458 (M^+, 0.4%), 430 (M^+ - CO, 9.4%), 402 (M^+ - 2CO, 1.0%), 374 (M^+ - 3CO, 22.2%), 346 (M^+ - 4CO, 100%), and 316 (M^+ - 4CO - CH_2O, 52.3%). Anal. Calcd for $C_{23}H_{16}MnO_5P$: C, 60.28; H, 3.52. Found: C, 60.35; H, 3.70.

Synthesis of $(CO)_4\overline{MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OSi(CH_3)_3)—C=O)}$ (29). A round-bottomed flask was charged with **18** (0.119 g, 0.410 mmol), CH_2Cl_2 (2 mL), and $(CO)_5MnSi(CH_3)_3$ (0.139 g, 0.518 mmol). The times needed for reaction varied from 5 to 8 h, as judged by monitoring the consumption of **18** by TLC. The reaction was concentrated by rotary evaporation. Hexanes were added and all solvents were then completely removed. The resulting residue was taken up in a small amount of CH_2Cl_2, added to the top of a 3 × 39 cm silica gel column, and then eluted with 90:10 (v/v) hexanes/ethyl acetate. The light yellow product band was collected under a N_2 purge. Solvent was removed by rotary evaporation to give, after vacuum drying, 0.119 g (0.213 mmol, 52%) of **29**. Lemon yellow crystals, decomposition point 156–157.5 °C (capillary sealed under N_2), were obtained from CH_2Cl_2/CH_3CN. $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2): 50.1.[62] Mass spectrum (*m/e*, 20 eV): 502 (M^+ - 2CO, 5%), 446 (M^+ - 4CO, 1%), 418 (M^+ - 5CO, 100%). Anal. Calcd for $C_{27}H_{24}MnO_6PSi$: C, 58.07; H, 4.33; Mn, 9.84; P, 5.55. Found: C, 58.00; H, 4.55; Mn, 9.90; P, 5.57.

Synthesis of $(CO)_4\overline{MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OH)—C=O)}$ (30). A Schlenk flask was charged with **29** (0.082 g, 0.15 mmol), THF (5 mL), CH_3OH (4 mL), and aqueous KF (5.2 M, 0.150 mL). The reaction was stirred for 45 min and the solvents were removed by oil pump vacuum. The residue was extracted with benzene and then filtered through a Pasteur pipet containing dry silica gel. The silica gel was eluted with ca. 50 additional mL of benzene. Solvent was removed from the filtrate to give, after vacuum drying, 0.067 g (0.14 mmol, 93%) of **30** as a white powder, decomposition point 152–158 °C (capillary sealed under N_2). $^{31}P\{^1H\}$ NMR (ppm, THF-d_8): 47.0.[62] Anal. Calcd for $C_{24}H_{16}MnO_6P$: C, 59.28; H, 3.32. Found C, 59.27; H, 3.15.

X-ray Crystal Structure of 22. A suitable single crystal was grown by layering a CH_3CN solution of **22** with ether. Data were collected on a Syntex PĪ automatic diffractometer as outlined in Table III. Of 5557 reflections with $2\theta < 50°$ collected, 4724 with $I \geq 3\sigma(I)$ were used in the final refinement.[63]

The rhenium position was obtained from a three-dimensional Patterson map. Several cycles of Fourier synthesis and least-squares refinement yielded positions of all non-hydrogen atoms. Absorption corrections were then applied. After refinement to convergence at R = 0.042, R_w = 0.068,[64] the position of the metallacyclic hydrogen atom was located from an electron difference map. All the other hydrogens were geometrically located and assigned C–H bond distances of 1.00 Å. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positional parameters for the hydrogen atom H were refined with use of a maximum sin θ/λ cutoff value of 0.35 while the other atomic positions and thermal parameters were kept constant. In the final refinement cycle, only the non-hydrogen atoms were refined. A final R index of 0.035 with

(61) A more detailed preparation is available: Vaughn, G. D.; Gladysz, J. A. *Inorg. Synth.*, in press.

(62) The ^{31}P NMR chemical shifts of 4, **29**, and **30** exhibit ring size effects previously noted by Garrou and Lindner: Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. Lindner, E.; Funk, G.; Hoehne, S. *Chem. Ber.* **1981**, *114*, 2465.

(63) In-house programs (UCLA) were used for data refinement. One of these incorporated modifications of the programs CARESS by R. W. Broach (University of Wisconsin) and PROFILE by P. Coppens, P. Becker, and R. H. Blessing (SUNY, Buffalo).

(64) All least-squares refinements computed the agreement factors R and R_w according to $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w_i||F_o| - |F_c||^2/\sum\omega_i|F_o|^2]^{1/2}$, where F_o and F_c are the observed and calculated structure factors, respectively, and $\omega_i^{1/2} = 1/\sigma(F_o)$. The function minimized in all least-squares refinements was $\sum\omega_i||F_o| - |F_c||^2$.

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.

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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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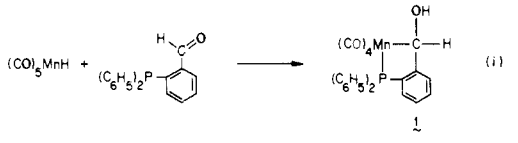
Abstract: Reaction of $(CO)_5MnH$ with $(C_6H_5)_2PCH_2CH_2CHO$ (**3**) gives *cis*-$(CO)_4Mn(H)P(C_6H_5)_2CH_2CH_2CHO$ (**4**, 97%), which cannot be induced to cyclize to α-hydroxyalkyl complex $(CO)_4MnP(C_6H_5)_2CH_2CH_2CHOH$ (**5**). Two other attempted syntheses of **5**—the photochemical decarbonylation 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.



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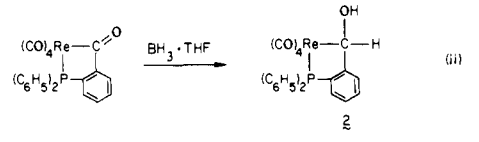

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In this paper, we explore the scope of aldehyde/$(CO)_5MnH$ (eq i) and BH_3·THF (eq ii) routes to metallacyclic α-hydroxyalkyl complexes. We find significant and surprising differences when the aryl linkage in metallacycle **1** is replaced with an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