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Synthesis and Reactivity of Metal α-Hydroxyalkyl Complexes; Generation of $(CO)_5MCH(C_6H_5)OH$ (M = Mn, Re)

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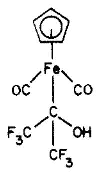
Abstract: Reaction of $(CO)_5MnCOCOC_6H_5$ with $Li(C_2H_5)_3BH$ gives the metallacycle $Li^+[(CO)_4\overline{MnCOCH(C_6H_5)OC}{=}O]^-$ (Li^+-**2**), which upon treatment with $[((C_6H_5)_3P)_2N]^+Cl^-(PPN^+Cl^-)$ gives PPN^+-**2**. The structure of PPN^+-**2** is established by X-ray crystallography. Reaction of PPN^+-**2** or Li^+-**2** with $(CH_3)_3SiCl$ and CF_3SO_3H yields acyl complexes $(CO)_5MnCOCH(C_6H_5)OSi(CH_3)_3$ (**4**) and $(CO)_5MnCOCH(C_6H_5)OH$ (**5**), respectively. Treatment of **4** with $(CH_3)_3N^+{-}O^-$ gives α-(silyloxy)alkyl complex $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$ (**6**). When **6** is treated with HCl (−78 to −50 °C, 3 min), H_2O (−10 °C, 2 h), or CH_3OH (10 °C, 3 h), or **5** is treated with $(CH_3)_3N^+{-}O^-$, $(CO)_5MnH$ and benzaldehyde form in a 1:1 ratio. These reactions are interpreted as proceeding via the α-hydroxyalkyl complex $(CO)_5MnCH(C_6H_5)OH$ (**8**). Similarly, reaction of $(CO)_5ReCOCOC_6H_5$ with $Li(C_2H_5)_3BH$ and then $(CH_3)_3SiCl$ gives acyl complex $(CO)_5ReCOCH(C_6H_5)OSi(CH_3)_3$ (**11**). Reaction of **11** with H_2O gives acyl complex $(CO)_5ReCOCH(C_6H_5)OH$ (**12**), and photolysis of **11** gives α-(silyloxy)alkyl complex $(CO)_5ReCH(C_6H_5)OSi(CH_3)_3$ (**13**). When **13** is treated with HF gas (−78 to −50 °C) or H_2O (25 °C), or when **12** is photolyzed (−78 to −50 °C), $(CO)_5ReH$ and benzaldehyde form in a 1:1 ratio. These reactions are interpreted as proceeding via the α-hydroxyalkyl complex $(CO)_5ReCH(C_6H_5)OH$ (**14**). When **13** is treated with HCl, $(CO)_5ReCH(C_6H_5)Cl$ (**15**) is obtained. Mechanisms for these transformations are proposed.

Homogeneous metal α-hydroxyalkyl complexes, $L_nMCH(R)OH$, have been proposed as key catalytic intermediates in a number of processes of industrial importance (Scheme I).[3–7] For instance, the conversion of CO/H_2 to oxygenated organic products, and in particular diol and glycolaldehyde derivatives, via homogeneous ruthenium, cobalt, and rhodium catalysts has been suggested to involve L_nMCH_2OH intermediates as shown in eq a, Scheme I.[3] Similar intermediates are undoubtedly generated when formaldehyde is hydroformylated to C_2 organic products, as illustrated in eq b, Scheme I.[4] In the aqueous Wacker oxidation of ethylene to acetaldehyde, all hydrogens of the ethylene starting material are retained in the product.[5] Hence, free acetaldehyde enol is excluded as an intermediate, and the α-hydroxyalkyl complex $L_nPdCH(CH_3)OH$ shown in eq c of Scheme I has been suggested as the acetaldehyde precursor.[5] Some catalytic hydrogenations of aldehydes and ketones to alcohols have been proposed to proceed via $L_nMCR(R')OH$ species.[6] Similarly, the hydroformylation of olefins $H_2C{=}CHR$ to oxo alcohols $HOCH_2CH_2CH_2R$ may take place, in part, via α-hydroxyalkyl intermediates $L_nMCH(CH_2CH_2R)OH$.[4b,7] Finally, 1,2-diol rearrangements catalyzed by the vitamin B_{12} coenzyme may occur via cobalt α-hydroxyalkyl intermediates, as shown in eq d of Scheme I.[8]

In view of the above, the preparation and study of homogeneous α-hydroxyalkyl complexes can be expected to provide significant insight into several important metal-catalyzed reactions. Hence, we have undertaken a program to systematically synthesize and examine the reactivity of α-hydroxyalkyl complexes. Surprisingly, when we began this study nearly a decade ago,[9] only two such complexes, I and II, had been reported in the literature.[10,11] Curiously, the originally claimed preparation of II was shown to be incorrect, but II was subsequently synthesized by Casey and Graham.[12] Since this time, additional stable α-hydroxyalkyl complexes have been prepared.[13–15] The factors that influence their stability are analyzed in detail in the following companion paper.[16] In this paper, we describe our attempts to synthesize α-hydroxyalkyl complexes $(CO)_5MCH(C_6H_5)OH$ where M = manganese and rhenium. Although these complexes are not isolable, good evidence is obtained for their intermediacy. Furthermore, the reactivity patterns suggested by their decomposition provide critical insight for the design of stable α-hydroxyalkyl complexes as described in the following paper.[16]



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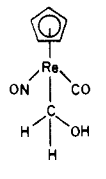

II

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(3) (a) Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325. (b) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136. (c) Rathke, J. W.; Feder, H. M. "Catalysis of Organic Reactions"; Moser, W. R., Ed.; Marcel Dekker: New York, 1981; p 209. (d) Keim, W.; Berger, M.; Schlupp, J. *J. Catal.* **1980**, *61*, 359. (e) Knifton, J. F.; Grigsby, R. A., Jr.; Lin, J. J. *Organometallics* **1984**, *3*, 62. (f) For a discussion of α-hydroxyalkyl intermediates in ***heterogeneous*** CO reduction, see: Henrici-Olivē, G.; Olivē, S. *J. Mol. Catal.* **1984**, *24*, 7.

(4) (a) Chan, A. S. C.; Carroll, W. E.; Willis, D. E. *J. Mol. Catal.* **1983**, *19*, 377. (b) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *173*, C9.

(5) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.

(6) (a) James, B. R.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1978**, 929. (b) Törōs, S.; Kollár, L.; Heil, G.; Markō, L. *J. Organomet. Chem.* **1983**, *253*, 375. (c) Okamoto, T.; Oka, S. *J. Mol. Catal.* **1984**, *23*, 107.

(7) (a) Pino, P.; Piacenti, F.; Bianchi, M. In "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, pp 43–231. (b) Masters, C. "Homogeneous Transition-metal Catalysis—A Gentle Art"; Chapman and Hall: London, New York, 1981; pp 110–112.

(8) Dolphin, D., Ed. "B_{12}"; Wiley: New York, 1982; Vol. I, Chapters 14 and 15; Vol. II, Chapter 9.

(9) Preliminary communication: Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766.

(10) Blackmore, T.; Bruce, M. I.; Davidson, P. J.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, *3153*.

(11) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Krasnoslobodskaya, L. L. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1970**, 807.

(12) (a) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927. (b) Sweet, J. R.; Graham, W. A. G. *Ibid.* **1982**, *104*, 2811.

(13) (a) Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5608. (b) Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1596.

(14) (a) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7. (b) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *Ibid.* **1982**, *231*, 335. (c) May, C. J.; Graham, W. A. G. *Ibid.* **1982**, *234*, C49. (d) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *Ibid.* **1981**, *219*, 353. (e) Thorn, D. L. *Organometallics* **1982**, *1*, 197. (f) Thorn, D. L.; Tulip, T. H. *Ibid.* **1982**, *1*, 1580. (g) Wayland, B. B.; Woods, B. A.; Minda, V. M. *J. Chem. Soc., Chem. Commun.* **1982**, 634. (h) Lapinte, C.; Astruc, D. *Ibid.* **1983**, 430. (i) Lin, Y. C.; Milstein, D.; Wreford, S. S. *Organometallics* **1983**, *2*, 1461. (j) Nelson, G. O. *Ibid.* **1983**, *2*, 1474. (k) Lapinte, C.; Astruc, D. *J. Organomet. Chem.* **1984**, *260*, C13.

(15) Kirker, G. W.; Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249 and references therein.

(16) Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.*, following paper in this issue.

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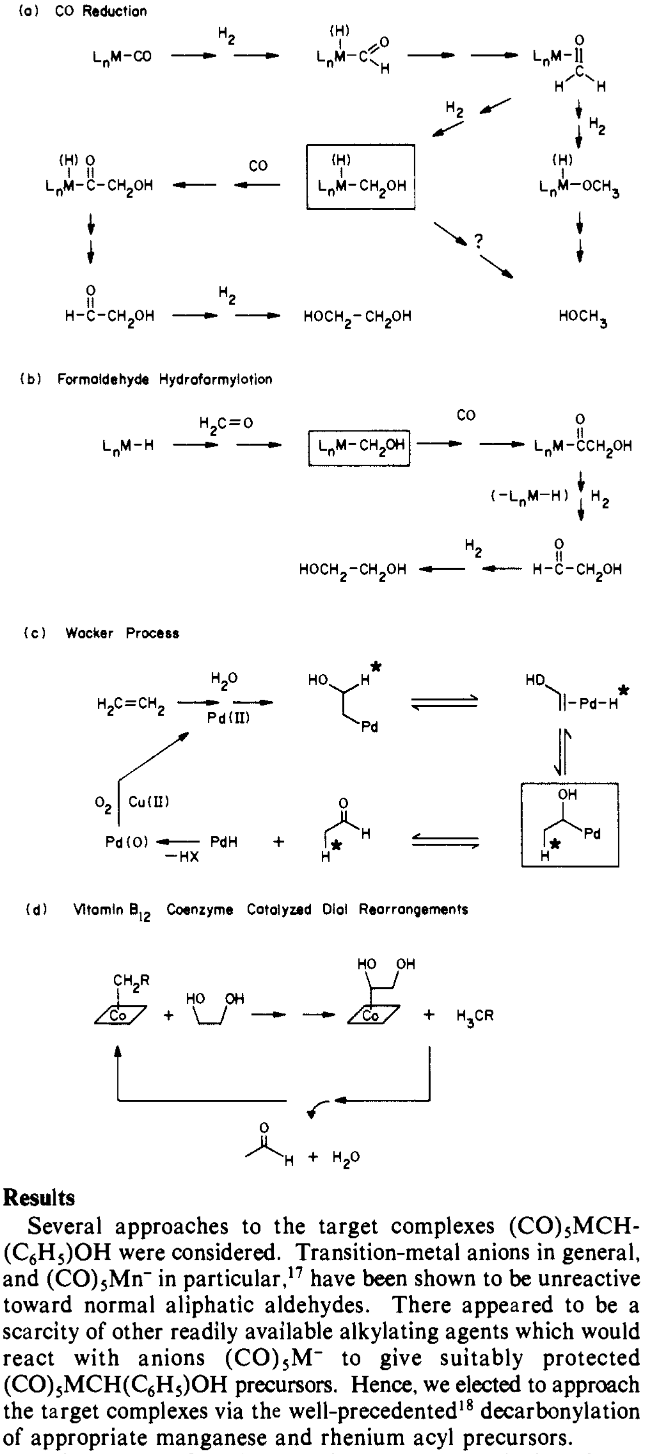
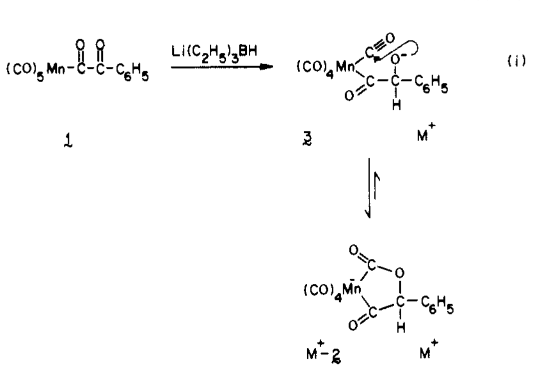
Scheme I. Some Metal-Catalyzed Processes that may Involve α-Hydroxyalkyl Intermediates



Results

Several approaches to the target complexes $(CO)_5MCH(C_6H_5)OH$ were considered. Transition-metal anions in general, and $(CO)_5Mn^-$ in particular,[17] have been shown to be unreactive toward normal aliphatic aldehydes. There appeared to be a scarcity of other readily available alkylating agents which would react with anions $(CO)_5M^-$ to give suitably protected $(CO)_5MCH(C_6H_5)OH$ precursors. Hence, we elected to approach the target complexes via the well-precedented[18] decarbonylation of appropriate manganese and rhenium acyl precursors.

I. Manganese Complexes. The manganese-substituted 1,2-diketone, $(CO)_5MnCOCOC_6H_5$ (**1**),[19] was treated with 1.2 equiv of $Li(C_2H_5)_3BH$ and then PPN^+Cl^- (eq i).[20] Workup gave the novel metallacycle $PPN^+[(CO)_4\overline{MnCOCH(C_6H_5)OC}{=}O]^-$ (PPN^+-**2**) in 66% yield. The structure of PPN^+-**2** was verified by X-ray crystallography,[9,21] as described below. This compound

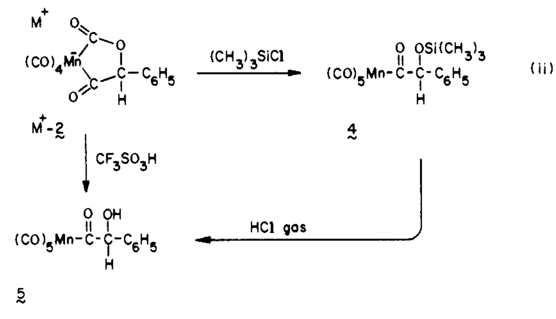


is visualized as arising via net hydride attack upon the acyl carbon β to the manganese. The resulting alkoxide $(CO)_5MnCOCH(C_6H_5)O^-$ (**3**) then cyclizes by attack upon a cis CO ligand, as shown in eq i. In THF, PPN^+-**2** exhibited two IR $\nu_{C=O}$ (1664 m br, 1636 m br cm^{-1}) and a $\nu_{C\equiv O}$ pattern (2043 ms, 1959 ms, 1940 vs, 1927 s cm^{-1}) characteristic of a cis-disubstituted manganese tetracarbonyl complex.[22] Hence, the metallacyclic structure of a crystalline PPN^+-**2** is retained in solution.

Several studies[22] have shown that alkyl lithium and hydride attack upon manganese acyl complexes $(CO)_5Mn(COR)$ and related compounds occurs preferentially upon coordinated CO. Hence, the reaction of $Li(C_2H_5)_3BH$ with **1** in THF was monitored by ^1H NMR at −50 °C. No characteristic low-field −CHO ^1H NMR resonance[23] was noted. In a separate experiment, the IR spectrum of the reaction mixture was recorded. Only absorbances ascribable to Li^+-**2** ($\nu_{C\equiv O}$ 2052 ms, 1972 ms, 1950 vs, 1941 sh; $\nu_{C=O}$ 1646 m, 1610 m, br cm^{-1}) and $Li^+[(CO)_5Mn]^-$ (1896 m, 1863 m cm^{-1})[19b] were present.

Metallacycle PPN^+-**2** was air sensitive in solution but was stable in air for 7 years in crystalline form. A sample of PPN^+-**2** was refluxed for 6 days in THF. Subsequently isolated were $PPN^+[(CO)_5Mn]^-$ (79%)[19b,24] and benzaldehyde (80%, as 2,4-dinitrophenylhydrazone).

Reactions of **2** with electrophiles were examined. Treatment of either PPN^+-**2** or Li^+-**2** (generated in situ) with $(CH_3)_3SiCl$ gave (silyloxy)acyl complex $(CO)_5MnCOCH(C_6H_5)OSi(CH_3)_3$ (**4**) in 70% and 95% yields, respectively (eq ii). This compound exhibited IR ($\nu_{C=O}$ 1638 cm^{-1}) and ^{13}C NMR (C=O, 285.6 ppm) spectra characteristic of $(CO)_5MnCOR$ complexes.[19,25] Similarly, reaction of PPN^+-**2** or Li^+-**2** with CF_3SO_3H gave hydroxyacyl complex $(CO)_5MnCOCH(C_6H_5)OH$ (**5**) as a labile oil in 61% and 79% yields (eq ii). This compound could not be rendered analytically pure, but it exhibited IR ν_{O-H} at 3610–3260 cm^{-1} and $\nu_{C=O}$ at 1639 cm^{-1} and cyclized to Li^+-**2** when deprotonated with $Li(C_2H_5)_3BH$. Hydroxyacyl complex **5** was also prepared by treating (silyloxy)acyl **4** with HCl gas.



No evidence was observed for the generation of any Fischer-type silyloxy or hydroxycarbene complexes in the reactions shown in eq ii. The formation of ring-opened products **4** and **5** suggests

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(17) Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508.

(18) (a) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (b) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87.

(19) (a) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166. (b) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

(20) PPN^+Cl^- = $[(C_6H_5)_3P{=}N{=}P(C_6H_5)_3]^+Cl^-$: Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.

(21) Selover, J. C. Ph.D. Thesis, UCLA, 1979.

(22) (a) Casey, C. P.; Bunnell, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 436. (b) Block, T. F.; Fenske, R. F.; Casey, C. P. *Ibid.* **1976**, *98*, 441. (c) Lukehart, C. M. *Acc. Chem. Res.* **1981**, *14*, 109. (d) Selover, J. C.; Marsi, M.; Parker, D. W.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *206*, 317.

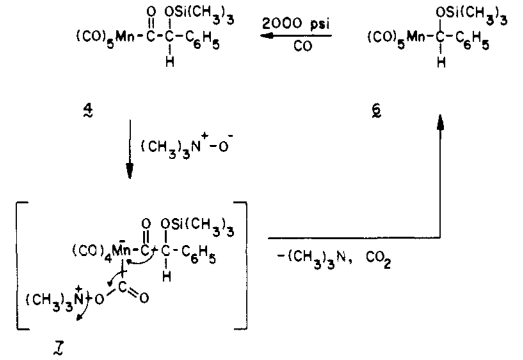
(23) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

(24) Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 2701.

(25) Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds"; Academic Press: New York, 1981; Table 2.7.

that PPN$^+$-**2** and Li$^+$-**2** are in equilibrium with the acylic alkoxide **3** (eq i).

The decarbonylation of (silyloxy)acyl complex **4** to α-(silyloxy)alkyl complex $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$ (**6**) was attempted next. Standard thermal and photochemical reactions[18] failed,[26] a result that in retrospect can be attributed to the lability of **6**. However, treatment of **4** in $CHCl_3$ at room temperature with 1.0–1.1 equiv of anhydrous $(CH_3)_3N^+$–O^- gave, over the course of 45 min, **6** in high yields (eq iii). On the basis of literature precedent,[18,27] this transformation likely proceeds via initial $(CH_3)_3N^+$–O^- attack upon coordinated CO to give intermediate **7** (eq iii). Complex **6** was thermally labile and exhibited the low-field methine resonance (δ 6.07) characteristic[9-14,28] of $L_nMCH(R)CR'$ complexes. It has since been prepared by the direct reaction of $(CO)_5MnSi(CH_3)_3$ with benzaldehyde.[17]



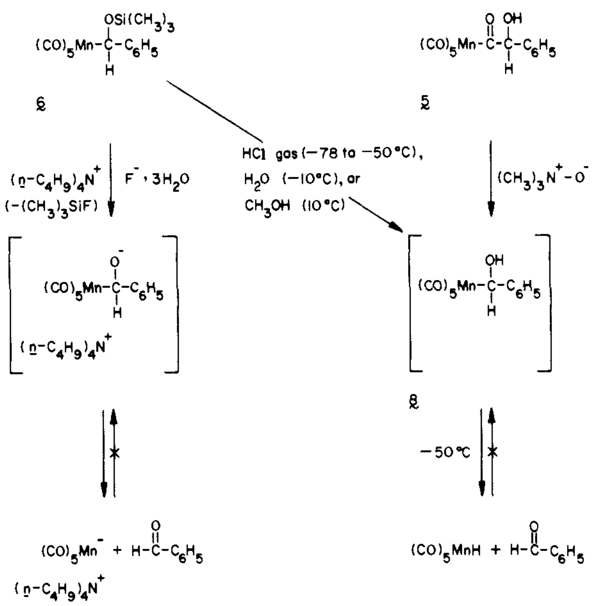
(iii)

In order to provide additional support for the structure of α-(silyloxy)alkyl complex **6**, carbonylation to (silyloxy)acyl complex **4** was attempted. For determination of the effect of the α-silyloxy substituent upon this "insertion" reaction, side-by-side experiments were conducted with $(CO)_5MnCH_2C_6H_5$, which has been reported as inert to carbonylation.[18a] In our hands, $(CO)_5MnCH_2C_6H_5$ remained unreacted after 1 h at 25 °C in THF under 2000 psi of CO. Under identical conditions, α-(silyloxy)alkyl complex **6** was 50% carbonylated to (silyloxy)acyl complex **4**, as assayed by IR spectroscopy. Some decomposition accompanied this carbonylation. Under 500 psi of CO, the conversion of **6** to **4** was 11%. Hence, at least in this case,[29] an α-silyloxy substituent promotes carbonylation.

Efforts were next directed at the protodesilylation of α-(silyloxy)alkyl complex **6** to α-hydroxyalkyl complex $(CO)_5MnCH(C_6H_5)OH$ (**8**). Reaction of **6** and $(n\text{-}C_4H_9)_4N^+F^-\cdot 3H_2O$ in THF at 25 °C instantly gave $(n\text{-}C_4H_9)_4N^+[(CO)_5Mn]^-$ and benzaldehyde, as assayed by IR spectroscopy (Scheme II). The anticipated intermediate alkoxide $(CO)_5MnCH(C_6H_5)O^-$ apparently fragmented rapidly. Consequently, neutral or acidic protodesilylating conditions were sought. Treatment of **6** with H_2O (−10 °C, 2 h), CH_3OH (10 °C, 3 h), or HCl (gas or aqueous, −10 °C, 3 min) gave, as assayed by ^1H NMR spectroscopy, equal quantities of $(CO)_5MnH$ and benzaldehyde. Finally, ca. 2 equiv of HCl gas was bubbled through a THF-d_8 solution of **6** at −78 °C. A subsequent ^1H NMR spectrum (3 min, −50 °C) showed that $(CO)_5MnH$ and benzaldeyde had formed cleanly and without observable intermediates. These products will be interpreted (Discussion Section) as arising from α-hydroxyalkyl complex **8**.

An independent generation of α-hydroxyalkyl complex **8** from hydroxyacyl complex **5** was attempted (Scheme II). Treatment of **5** with $(CH_3)_3N^+$–O^- under conditions that successfully decarbonylated (silyloxy)acyl complex **4** gave only $(CO)_5MnH$ and benzaldehyde.

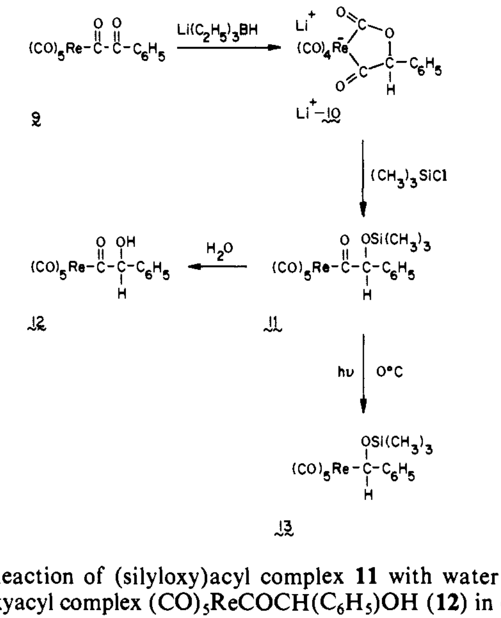
Scheme II. Attempted Syntheses of α-Hydroxyalkyl Complex $(CO)_5MnCH(C_6H_5)OH$ (**8**)



II. Rhenium Complexes.

Rhenium has been shown to make stronger metal–ligand bonds than manganese,[30] and organorhenium complexes are often kinetically more stable than corresponding manganese complexes.[31] Hence, we set out to synthesize rhenium complexes analogous to those in eq i–iii.

Reaction of $Na^+[(CO)_5Re]^-$ with acid chloride $C_6H_5COCOCl$ gave the rhenium-substituted 1,2-diketone $(CO)_5ReCOCOC_6H_5$ (**9**) in 58% yield. This compound was treated with $Li(C_2H_5)_3BH$ similarly to manganese analogue **1**. IR monitoring showed the clean formation of a complex with $\nu_{C\equiv O}$ at 2072 m, 1974 sh, 1960 s, br, and 1933 sh cm^{-1} and $\nu_{C=O}$ at 1611 m cm^{-1}. By analogy to **2**, the structure of this product was assigned as Li$^+$-$[(CO)_4\overline{ReCOCH(C_6H_5)OC}{=}O]^-$ (Li$^+$-**10**; eq iv). This compound was not characterized further but was instead treated with excess $(CH_3)_3SiCl$ to give (silyloxy)acyl complex $(CO)_5ReCOCH(C_6H_5)OSi(CH_3)_3$ (**11**, 54%), as shown in eq iv.



(iv)

Reaction of (silyloxy)acyl complex **11** with water gave hydroxyacyl complex $(CO)_5ReCOCH(C_6H_5)OH$ (**12**) in 68% yield (eq iv). Surprisingly, we were unable to obtain **12** from the

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(26) Additional details of these experiments are provided in ref 21.

(27) (a) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1975**, 829. (b) Blumer, D. J.; Barnett, K. W.; Brown, T. L. *J. Organomet. Chem.* **1979**, *173*, 71. (c) Davies, S. G. *Ibid.* **1979**, *179*, C5. (d) Albers, M. O. *Coord. Chem. Rev.* **1984**, *53*, 227. (e) Luh, T.-Y. *Ibid.* **1984**, *60*, 255.

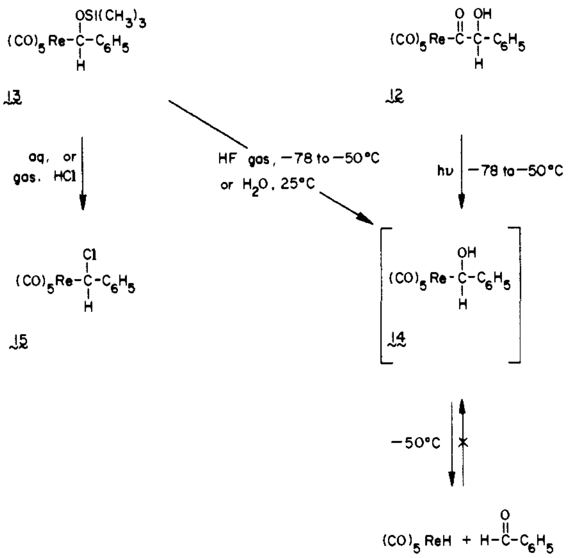
(28) Labinger, J. A. *J. Organomet. Chem.* **1980**, *187*, 287.

(29) This substituent effect (which a reviewer has suggested may be due to differences in K_{eq}) is reversed in other $(CO)_5MnR$ complexes: Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056.

(30) (a) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71. (b) Beauchamp, J. L.; Martinho Simões, J. A. *Chem. Rev.*, in press.

(31) (a) Tam, W.; Marsi, M.; Gladysz, J. A. *Inorg. Chem.* **1983**, *22*, 1413. (b) Tam, W.; Lin, G.-Y.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525. (c) Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2723, 2728.

Scheme III. Attempted Syntheses of α-Hydroxyalkyl Complex $(CO)_5ReCH(C_6H_5)OH$ (**14**)



reaction of Li^+-**10** with CF_3SO_3H.[26] Complex **12** exhibited IR ν_{O-H} at 3416 cm^{-1} and $\nu_{C=O}$ at 1618 vw, 1606 w, 1598 w, and 1586 vw cm^{-1}. The fact that some $\nu_{C=O}$ were considerably lower than that of **11** (1623 cm^{-1}) was attributed to hydrogen bonding.[13b,32]

The decarbonylation of (silyloxy)acyl complex **11** to α-(silyloxy)alkyl complex $(CO)_5ReCH(C_6H_5)OSi(CH_3)_3$ (**13**) was attempted next. When **11** was thermolyzed or treated with $(CH_3)_3N^+{-}O^-$,[26] numerous decomposition products were obtained. However, photolysis of **11** for 15 min at 0 °C gave, after chromatography, **13** in 25–57% yields (eq iv).

Attempts were next made to protodesilylate α-(silyloxy)alkyl complex **13** to α-hydroxyalkyl complex $(CO)_5ReCH(C_6H_5)OH$ (**14**). Reaction of an acetone-d_6 solution of **13** with water gave, over the course of 1 day, $(CO)_5ReH$ and benzaldehyde as the only products (Scheme III). Gaseous HF was bubbled through a −78 °C solution of **13** in THF-d_8. Subsequent ^1H NMR analysis at −50 °C showed only $(CO)_5ReH$ and benzaldehyde. Identical products were obtained when **13** was treated with $(n\text{-}C_4H_9)_4N^+F^-\cdot 3H_2O$. The formation of $(CO)_5ReH$ in this reaction, as compared with $[(CO)_5Mn]^-$ in the corresponding reaction of **6**, was ascribed to the greater basicity of $[(CO)_5Re]^-$.[33] Interestingly, reaction of **13** with aqueous or gaseous HCl gave α-chloroalkyl complex $(CO)_5ReCH(C_6H_5)Cl$ (**15**).

Other means of generating α-hydroxyalkyl complex **14** were attempted. Hydroxyacyl complex **12** was photolyzed in THF-d_8 at −78 °C for 15 min (Scheme III). These conditions successfully decarbonylated (silyloxy)acyl complex **11**. Subsequent ^1H NMR analysis at −50 °C indicated a 95% conversion to $(CO)_5ReH$ and benzaldehyde. Shorter irradiation times gave lower conversions. No reaction was observed when $(CO)_5ReH$ and benzaldehyde were heated neat for 20 min at 80 °C.

III. X-ray Crystal Structure of PPN⁺-2. Single-crystal X-ray data on PPN^+-**2** were obtained under the conditions summarized in Table I. The unit cell was found to be triclinic, with the lattice parameters listed in Table I. Refinement, described in the Experimental Section, utilized rigid groups for all seven phenyl rings and included location of the metallacyclic methine hydrogen from an electron difference map.

Table I. Summary of Crystallographic Data for PPN^+ $[(CO)_4\overline{MnCOCH(C_6H_5)OC}{=}O]^-$ (PPN^+-**2**)

formula	$C_{49}H_{36}NO_7P_2$
formula wt	867.71
crystal system	triclinic
systematic absences	none
space group	$P\bar{1}$
cell dimensions (−160 °C)	
a, Å	10.016 (4)
b, Å	15.772 (5)
c, Å	15.698 (5)
α, deg	86.55 (3)
β, deg	89.09 (3)
γ, deg	118.62 (3)
V, Å³	2170
Z	2
d_{obsd}, g/cm³ (20 °C)	1.283
d_{calcd}, g/cm³ (−160 °C)	1.304
crystal dimensions, mm	0.26 × 0.16 × 0.04
radiation, Å	Mo Kα (λ 0.71069)
temp of collection, °C	−160
data collection method	θ–2θ
scan speed, deg/min	2.0
scan range, deg	$K\alpha_1$ −1.0 to $K\alpha_2$ +1.0
no. of reflections between std.	97
total unique data	5697
obsd data, $I > 3\sigma(I)$	2994
abs. coeff. (μ), cm^{-1}	4.4
no. of variables	176
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.055
$R_w = [\sum\omega_i(\|F_o\| - \|F_c\|)^2/\sum\omega_i\|F_o\|^2]^{1/2}$	0.058
goodness of fit	1.28

Table II. Positional Parameters of Atoms and Rigid Phenyl Groups in PPN^+-**2**

atom[a]	*x*	*y*	*z*
Mn	1.0425 (13)	1.2306 (8)	0.2856 (7)
O1	0.8102 (61)	1.0644 (39)	0.3978 (34)
O2	1.1117 (57)	1.3831 (37)	0.4072 (32)
O3	1.0260 (54)	1.0766 (35)	0.1814 (30)
O4	0.8081 (53)	1.2938 (34)	0.2621 (30)
O5	1.2857 (61)	1.1839 (38)	0.3364 (33)
O6	1.2438 (57)	1.3765 (37)	0.1481 (32)
O7	0.7969 (53)	1.1935 (34)	0.1693 (30)
C1	0.9014 (86)	1.1307 (55)	0.3556 (47)
C2	1.0837 (82)	1.3229 (54)	0.3606 (46)
C3	0.9795 (79)	1.1334 (51)	0.1968 (44)
C4	0.8653 (79)	1.2457 (51)	0.2401 (44)
C5	1.1933 (90)	1.2039 (56)	0.3178 (49)
C6	1.1660 (83)	1.3207 (53)	0.2014 (47)
C7	0.8508 (84)	1.1313 (56)	0.1404 (45)
H	0.7727 (606)	1.0648 (397)	0.1504 (322)
N	0.4147 (62)	1.2296 (39)	−0.2410 (35)
P1	0.5430 (21)	1.2242 (14)	−0.1861 (12)
P2	0.3944 (21)	1.2825 (14)	−0.3240 (12)

phenyl group[b]	*X*[c]	*Y*[c]	*Z*[c]	φ[d]	θ[d]	ρ[d]
1	0.5039	1.2334	−0.0762	−1.1868	−2.9249	1.8047
2	0.5399	1.1110	−0.1980	1.7764	2.0020	−2.8090
3	0.7339	1.3189	−0.2151	0.7122	−2.6708	−0.3519
4	0.4222	1.4022	−0.3057	2.7281	−1.8210	0.7136
5	0.5180	1.2954	−0.4141	2.7263	2.7993	−2.2464
6	0.2007	1.2126	−0.3529	−2.7439	−2.3989	−0.2913
7	0.9043	1.1577	0.0474	−2.8513	3.0580	−1.8568

[a] Atoms are numbered as indicated in Figure 1. [b] Groups 1, 2, and 3 are bound to P1; groups 4, 5, and 6 are bound to P2; group 7 is bound to C7. [c] *X*, *Y*, and *Z* are the fractional coordinates of the centroid of the rigid group. [d] These parameters are defined in ref 46.

The structure of the metallacyclic portion of PPN^+-**2** is shown in Figure 1. Positional parameters are given in Table II, and bond distances and angles are compiled in Tables III and IV. Since thermal parameters and structure factors were included in the Supplementary Material of our communication[9] and elsewhere,[21] they are not republished here.

As is evident from Figure 1, the metallacycle is virtually planar. The atoms C7 and O7 deviate from the plane defined by C4, Mn, and C3 by 0,138 (13) and 0.119 (11) Å, respectively. The acyl oxygen atoms O3 and O4 are also only very slightly removed from this plane (−0.098 (12) and −0.059 (12) Å). A related anionic

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[32] 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.

[33] $pK_a((CO)_5MnH) \simeq 7$; $pK_a((CO)_5ReH) > 16$. Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231.

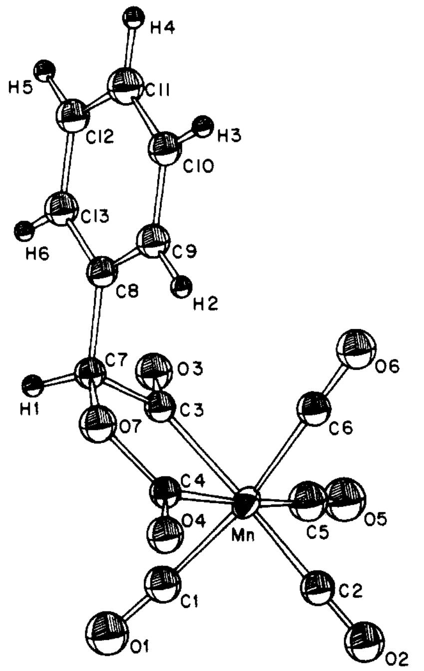
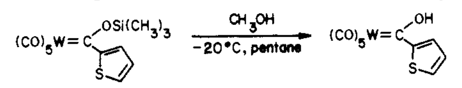


Figure 1. Structure of the metallacyclic portion of PPN$^+$-[(CO)$_4$MnCOCH(C$_6$H$_5$)OC=O]$^-$ (PPN$^+$-**2**). The atom H1 is drawn with an arbitrary isotropic thermal parameter.

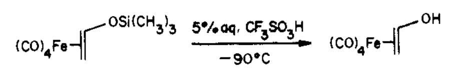
bis(acyl) complex, (C$_2$H$_5$)$_4$N$^+$ *cis*-[(CO)$_4$Mn(COCH$_3$)-(COC$_6$H$_5$)]$^-$, has been structurally characterized by Casey and Bunnell.[22a] It shows distortions from idealized octahedral geometry that are remarkably similar to those exhibited by PPN$^+$-**2** in Figure 1. These include an acyl-Mn-acyl angle of 81.2 (4)°, which compares to a C3-Mn-C4 angle of 81.4 (3)° in the metallacycle and a significant bending of one of the mutually trans C≡O's toward the acyl carbons.

Discussion

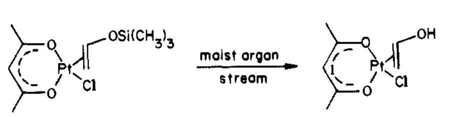
The aspect of this study that deserves the most critical examination is whether α-hydroxyalkyl complexes **8** and **14** are in fact generated under the conditions outlined in Schemes II and III. The literature precedents given in eq v-vii[34-36] are particularly relevant to this question. In each case, an extremely labile ligand is generated in high yield under neutral or acidic protodesilylating conditions. Under acidic conditions (HX), simple alkyl and aryl silyl ethers are cleaved via initial protonation of the ether oxygen, followed by X$^-$ attack upon silicon.[37] We note that in eq v and vi, if protonation at the *metal* had preceded silicon-oxygen bond cleavage, products *other* than those observed (likely organic aldehydes) would have been expected. Hence, we propose that the



(v)



(vi)



(vii)

Table III. Important Bond Distances in PPN$^+$-**2**[a]

from	to	distance (Å)
Mn	C1	1.816 (8)
Mn	C2	1.822 (8)
Mn	C5	1.823 (8)
Mn	C6	1.826 (8)
Mn	C3	2.012 (7)
Mn	C4	2.034 (7)
P1	N	1.591 (6)
P2	N	1.574 (6)
O1	C1	1.162 (8)
O2	C2	1.173 (8)
O3	C3	1.224 (8)
O4	C4	1.211 (8)
O5	C5	1.148 (8)
O6	C6	1.148 (8)
O7	C4	1.406 (8)
O7	C7	1.418 (8)
C3	C7	1.565 (10)
C7	H	0.963 (53)

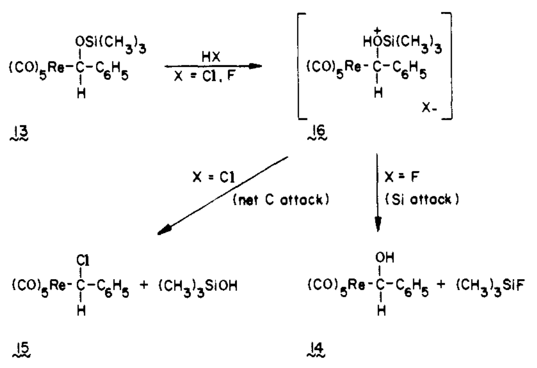
[a] Atoms are numbered as indicated in Figure 1.

Table IV. Important Bond Angles in PPN$^+$-**2**[a]

from	thru	to	angle (deg)
C1	Mn	C2	95.6 (3)
C1	Mn	C5	92.1 (3)
C1	Mn	C6	170.9 (3)
C1	Mn	C3	85.0 (3)
C1	Mn	C4	86.3 (3)
C2	Mn	C5	95.5 (3)
C2	Mn	C6	92.1 (3)
C2	Mn	C3	173.2 (3)
C2	Mn	C4	91.9 (3)
C5	Mn	C6	92.1 (3)
C5	Mn	C3	91.2 (3)
C5	Mn	C4	172.6 (3)
C6	Mn	C3	86.7 (3)
C6	Mn	C4	88.5 (3)
C3	Mn	C4	81.4 (3)
P2	N	P1	141.4 (4)
C4	O7	C7	117.3 (5)
O1	C1	Mn	177.4 (7)
O2	C2	Mn	178.7 (7)
O3	C3	C7	116.5 (6)
O3	C3	Mn	129.8 (6)
C7	C3	Mn	113.6 (5)
O4	C4	O7	112.6 (6)
O4	C4	Mn	131.4 (5)
O7	C4	Mn	116.0 (5)
O5	C5	Mn	177.3 (7)
O6	C6	Mn	179.3 (6)
H	C7	O7	109.9 (32)
H	C7	C3	101.7 (31)
O7	C7	C3	111.2 (6)

[a] Atoms are numbered as indicated in Figure 1.

Scheme IV. Comparison of the Reactions of HCl and HF with α-(Silyloxy)alkyl Complex (CO)ReCH(C$_6$H$_5$)OSi(CH$_3$)$_3$ (**13**)



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(34) Fischer, E. O.; Selmayr, T.; Kreissl, F. R.; Schubert, U. *Chem. Ber.* **1977**, *110*, 2574.

(35) Thyret, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 520.

(36) Hillis, J.; Francis, J.; Ori, M.; Tsutsui, M. *J. Am. Chem. Soc.* **1974**, *96*, 4800.

(37) (a) Åkerman, E. *Acta Chem. Scand.* **1956**, *10*, 298; **1957**, *11*, 373. (b) Novice, M. H.; Seikaly, H. R.; Seiz, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 5835.

reactions of HCl with manganese α-(silyloxy)alkyl complex **6** and HF with rhenium α-(silyloxy)alkyl complex **13** occur via initial *oxygen*, not metal, protonation and that subsequent X^- attack upon the $Si(CH_3)_3$ group affords α-hydroxyalkyl complexes **8** and **14**.

The formation of rhenium α-chloroalkyl complex **15** from the reaction of α-(silyloxy)alkyl complex **13** with HCl also likely proceeds via an oxygen-protonated intermediate, **16** (Scheme IV). However, carbon-oxygen bond cleavage, possibly via a $HOSi(CH_3)_3$ elimination/Cl^- addition mechanism, subsequently occurs. Fluorine makes a stronger bond to silicon (160–193 kcal/mol) than chlorine (ca. 113 kcal/mol),[38] so in the reaction of **13** with HF, **16** is cleaved at silicon. The differing reactivities of α-(silyloxy)alkyl complexes **6** and **13** towards HCl may be attributable to the generally greater basicity of rhenium complexes.[33]

The protodesilylations of **6** and **13** under neutral conditions (H_2O, CH_3OH) are considerably slower than under acidic conditions and therefore do not afford as good an opportunity for the observation of α-hydroxyalkyl intermediates. Nonetheless, the fact that $(CO)_5MH$ and benzaldehyde are formed as with HCl and HF suggests that α-hydroxyalkyl complexes **8** and **14** are again generated.

The same conclusion may be reached regarding the decarbonylations of manganese hydroxyacyl complex **5** ($(CH_3)_3N^+{-}O^-$) and rhenium hydroxyacyl complex **12** ($h\nu$, −50 °C), both of which give $(CO)_5MH$ and benzaldehyde. The former reaction requires room temperature and generates a byproduct, $(CH_3)_3N$, which likely can accelerate the decomposition of α-hydroxyalkyl complex **8**. The latter reaction would seem to offer an excellent opportunity for observing α-hydroxyalkyl complex **14**, were it to be stable at −50 °C.

The overall picture that emerges, then, is one of an unfavorable equilibrium, $(CO)_5MCH(C_6H_5)OH \rightleftharpoons (CO)_5MH + C_6H_5CHO$. It is understandable that alkoxide intermediates $(CO)_5MCH(C_6H_5)O^-$ should fragment (Scheme II), since a strong carbon-oxygen π bond is formed at the expense of a weak[30] metal–carbon bond. The reaction of $(CO)_5MnSi(CH_3)_3$ and benzaldehyde[17] to give α-(silyloxy)alkyl complex **6** is particularly instructive. Here, a strong oxygen–silicon bond (106–127 kcal/mol)[38] provides a driving force for breaking a carbon–oxygen π bond. Apparently, the oxygen–hydrogen bond strength in α-hydroxyalkyl complexes **8** and **14** is insufficient to drive a similar reaction.

The preceding rationale for the instability of **8** and **14** can be tested. Factors that influence K_{eq} for carbonyl group additions have been studied in detail and are summarized in the following paper.[16] We utilize these to predict, and subsequently synthesize, α-hydroxyalkyl complexes related to **8** and **14** that are stable at room temperature.

Experimental Section

General. All reactions and filtrations were carried out under a dry N_2 atmosphere. In chromatographic separations, the collection vessel was maintained under a N_2 atmosphere.

IR spectra were recorded either on a Beckman IR-4A spectrometer (those in cyclohexane) or Perkin Elmer Model 521 and 1500 spectrometers. All ^1H NMR spectra recorded below room temperature were obtained on a Varian A-60 spectrometer and calibrated against internal $(CH_3)_4Si$ (δ 0.00) or 1,2,4,5-tetrachlorobenzene (δ 7.52). Ambient temperature ^1H NMR spectra were recorded on a Varian T-60 spectrometer. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer and were calibrated against internal $(CH_3)_4Si$ unless noted. Mass spectra were obtained on an AEI MS-9 spectrometer. Microanalyses were conducted by Galbraith Laboratories.

Solvents and Starting Materials. Ether and THF were distilled from Na/benzophenone immediately prior to use. Hexane was distilled from $CaSO_4$ or Na/benzophenone. Benzene was distilled from potassium. Chlorocarbons $CHCl_3$ and CH_2Cl_2 were distilled from P_2O_5. THF-d_8 and toluene-d_8 were distilled from sodium. Other deuterated solvents were used without purification.

Starting materials **1**,[19b] PPN^+Cl^-,[20] and $C_6H_5COCOCl$[39] were synthesized by literature procedures. Commercial $(CH_3)_3N^+{-}O^-{\cdot}3H_2O$ was dehydrated by the method of Franzen.[40] $Li(C_2H_5)_3BH$ was obtained from Aldrich as a 1.0 M THF solution and was used without standardization. The following compounds were obtained from common commercial sources and were used without purification: $Re_2(CO)_{10}$, CF_3SO_3H, $(CH_3)_3SiCl$, $(n\text{-}C_4H_9)_4N^+F^-{\cdot}3H_2O$, HCl gas, HF gas.

Synthesis of $PPN^+[(CO)_4\overline{MnCOCH(C_6H_5)OC}{=}O]^-$ (PPN^+-2). To a stirred solution of $(CO)_5MnCOCOC_6H_5$ (**1**; 3.283 g, 10.0 mmol) in 30 mL of THF was added 12.0 mL of 1.0 M $Li(C_2H_5)_3BH$ in THF (12.0 mmol). After 15 min, a solution of 5.747 g (10.0 mmol) of PPN^+Cl^- in CH_2Cl_2 (50 mL) was added. The resulting solution was stirred for 10 min, and solvent was then removed by high-vacuum rotary evaporation at room temperature. The brown sludge which remained was extracted with 400 mL of ether. The extract was concentrated to 50 mL and cooled at 0 °C for 12 h. Product PPN^+-**2** formed as a yellow precipitate (5.73 g, 6.6 mmol, 66%). The precipitate was washed with cold ether and extracted into THF. The extract was filtered and the THF was slowly evaporated to give PPN^+-**2** as a gold powder (3.99 g, 4.6 mmol, 46%), mp 40–42 °C. IR (cm^{-1}, THF): $\nu_{C\equiv O}$ 2043 ms, 1959 ms, 1940 vs, 1927 s; $\nu_{C=O}$ 1664 m br, 1636 m br. ^1H NMR (δ, acetone-d_6): 7.60 and 7.23 (m, 35 H total), 4.57 (s, 1 H). ^{13}C NMR (ppm, $CDCl_3$, 75 MHz): 288.1 (C=O),[41] 229.0 (C=O), 218.9 (2 × C≡O),[41] 215.4 (2 × C≡O);[41] CC_6H_5 at 138.4 (ipso), 127.8, 126.7, 126.1; PC_6H_5 (assigned by comparison with ^{13}C NMR spectrum of PPN^+I^-) at 134.2 (s), 132.4 (t, J = 6 Hz), 129.9, (t, J = 7 Hz), 127.0 (d, J = 108 Hz, ipso); 94.2 (CC_6H_5). UV (nm, CH_3CN): 228 (pk, ε 60 500), 266 (sh, 5700), 274 (sh, 2800), 350 (sh, 476). Anal. Calcd for $C_{49}H_{36}MnNO_7P_2$: C, 67.80; H, 4.18; P, 7.14. Found: C, 67.76; H, 4.20; P, 7.08.

Thermolysis of PPN^+-2. A solution of 0.10 g (0.12 mmol) of PPN^+-**2** in 25 mL of THF was refluxed for 6 days. The solution was allowed to cool to room temperature and 20 mL of hexane was added. This solution was cooled at −20 °C for 2 h. Product $PPN^+[(CO)_5Mn]^-$ precipitated and was collected by filtration (0.047 g, 0.063 mmol, 79%).[19b,24] The solvent was removed from the filtrate by high-vacuum rotary evaporation at room temperature, and the residue was taken up in 4 mL of 95% ethanol. Then 0.03 g of 2,4-dinitrophenylhydrazine in acidified aqueous ethanol[42] was added. The 2,4-dinitrophenylhydrazone crystallized, was collected by filtration, and was recrystallized from ethanol (0.018 g, 0.096 mmol, 80%), mp 235 °C (lit.[42] mp 237 °C).

Synthesis of $(CO)_5MnCOCH(C_6H_5)OSi(CH_3)_3$ (4). (A) To a stirred solution of **1** (0.331 g, 1.01 mmol) in 30 mL of THF was added 1.2 mL of 1.0 M $Li(C_2H_5)_3BH$ in THF. After 30 min, 1.0 mL (7.9 mmol) of $(CH_3)_3SiCl$ was added. The reaction was stirred for 2 h, and solvent was removed by high-vacuum rotary evaporation at room temperature. The residue was chromatographed on 50 g of silica gel with 95:5 hexane/ethyl acetate. Product **4** eluted rapidly and crystallized upon solvent evaporation (0.386 g, 0.96 mmol, 95%), mp 51–53 °C.[43] IR (cm^{-1}, $CHCl_3$): $\nu_{C\equiv O}$ 2119 m, 2048 m, sh, 2020 vs; $\nu_{C=O}$ 1638 m. ^1H NMR (δ, CCl_4): 7.33 (m, 5 H), 4.68 (s, 1 H), 0.20 (s, 9 H). ^{13}C NMR and additional data: see ref 43. Mass spectrum (m/e, 70 eV): 223 ($Mn(CO)_6^+$, 19%), 179 ($CH(C_6H_5)OSi(CH_3)_3^+$, 68%), 106 ($C_6H_5CHO^+$, 91%), 105 ($C_6H_5CO^+$, 100%). Anal. Calcd for $C_{16}H_{15}MnO_7Si$: C, 47.77; H, 3.76; Mn, 13.66. Found: C, 47.59; H, 3.91; Mn, 13.49. (B) To a stirred solution of PPN^+-**2** (0.260 g, 0.30 mmol) in 5 mL of THF was added 0.05 mL (0.6 mmol) of $(CH_3)_3SiCl$. The solution was stirred for 4 h, during which time white needles of PPN^+Cl^- crystallized. The solvent was removed by high-vacuum rotary evaporation, and product **4** was isolated (0.084 g, 0.21 mmol, 70%) as described above.

Synthesis of $(CO)_5MnCOCH(C_6H_5)OH$ (5). (A) To a stirred solution of **1** (0.331 g, 1.01 mmol) in 25 mL of THF was added 1.3 mL of 1.0 M $Li(C_2H_5)_3BH$ in THF. After 30 min, 0.14 mL (1.6 mmol) of CF_3SO_3H was added. The reaction was stirred for 20 min, and the solvent was removed by high-vacuum rotary evaporation at room temperature. The residue was treated with 20 mL of $CHCl_3$. White crystals of $Li^+CF_3SO_3^-$ formed and were removed by filtration. Solvent was removed from the filtrate by high-vacuum rotary evaporation to give **5** as a labile yellow oil (0.264 g, 0.800 mmol, 79%) which decomposed over the course of 2 days under N_2 at −20 °C. IR (cm^{-1}, $CHCl_3$): ν_{O-H} 3610–3260 s, br; $\nu_{C\equiv O}$ 2116 m, 2052 m, sh, 2016 vs; $\nu_{C=O}$ 1639 m. ^1H NMR (δ, $CDCl_3$): δ 7.2 (m, 5 H), 6.2 (s, 1 H), 5.0 (s, 1 H). (B) To a stirred suspension of PPN^+-**2** (0.215 g, 0.25 mmol) in 20 mL of ether was added, dropwise, 0.025 mL (0.28 mmol) of CF_3SO_3H. During the addition, the solution became yellow, and white crystals of $PPN^+CF_3SO_3^-$ formed. The reaction was filtered and solvent was removed from the filtrate by

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[38] (a) Colvin, E. "Silicon in Organic Synthesis"; Butterworths: London, Boston, 1981; p 4. (b) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

[39] Ottenheijm, H. C. J.; De Man, J. H. M. *Synthesis* **1975**, 163.

[40] Franzen, V. *Org. Synth.* **1967**, *47*, 96.

[41] At optimal resolution, these resonances show small (3–7 Hz) splittings.

[42] Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds", 5th ed.; Wiley: New York, 1964; pp 253–254; p 320.

[43] Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147.

high-vacuum rotary evaporation. Product **5** (0.050 g, 0.151 mmol, 61%) was isolated as described above.

Synthesis of $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$ (6). To a stirred solution of **4** (0.117 g, 0.29 mmol) in 25 mL of $CHCl_3$ was added a solution of anhydrous $(CH_3)_3N^+{-}O^-$ (0.023 g, 0.30 mmol) in 2 mL of $CHCl_3$. The reaction was stirred for 45 min at room temperature. The solvent was then removed by high-vacuum rotary evaporation at room temperature. The residue was rapidly chromatographed on 10 g of silica gel with 99.5:0.5 hexane/ethyl acetate. Product **6** was obtained as a white oily, easily homolyzed[17] solid (0.094 g, 0.25 mmol, 86%), mp 27–29 °C. IR (cm^{-1}, hexane): $\nu_{C\equiv O}$ 2118 m, 2024 vs, 2005 s. ^1H NMR (δ, CD_2Cl_2): 7.30 (s, 5 H), 6.07 (s, 1 H), 0.71 (s, 9 H). ^{13}C NMR (ppm, CD_2Cl_2): 195.9 (C≡O); 129.9, 125.7, 123.0 (C_6H_5); 74.8 (CC_6H_5); 1.1 (CSi). Mass spectrum (*m/e*, 70 eV): 196 ($HMn(CO)_5^+$, 8%), 195 ($Mn(CO)_5^+$, 4%), 179 ($CH(C_6H_5)OSi(CH_3)_3^+$, 12%), 106 ($C_6H_5CHO^+$, 100%).

Attempted Syntheses of $(CO)_5MnCH(C_6H_5)OH$ (8). **(A)** A 5-mm septum-capped NMR tube was charged with **6** (0.047 g, 0.125 mmol) and THF-d_8 (0.5 mL). An initial ^1H NMR spectrum was recorded at −50 °C, and the tube was cooled to −78 °C. Then ca. 5.6 mL of HCl gas (ca. 0.25 mmol) was bubbled through the tube and the tube was quickly transferred to the −50 °C probe. A ^1H NMR spectrum was recorded immediately. Benzaldeyde and $(CO)_5MnH$ were present in a 1:1 ratio in >80% spectroscopic yield. **(B)** A 5-mm septum-capped NMR tube was charged with **6** (0.058 g, 0.145 mmol), THF-d_8 (0.5 mL), and 1,2,4,5-tetrachlorobenzene internal standard. The sample was cooled at −10 °C in a NMR probe. An initial ^1H NMR spectrum was recorded. Then water (0.03 mL) was injected into the tube. Reaction occurred over the course of 2 h to give benzaldehyde and $(CO)_5MnH$ in 97% and 92% spectroscopic yields, respectively. (C) Experiments identical with the previous one were conducted on 0.20-mmol scales with aqueous 37% HCl (0.03 mL, −10 °C) and CH_3OH/H_2O (0.03 mL, 1:1, 10 °C). Identical results were obtained. (D) A stream of HCl gas was bubbled through a sample of 4 (0.303 g, 0.75 mmol) in 15 mL of $CDCl_3$ for 2 min. The solution was then flushed with N_2. Analysis of aliquots by IR and ^1H NMR verified the spectroscopically quantitative formation of hydroxyacyl **5**. Solvent was removed in vacuo at −10 °C and the residue was taken up in CD_2Cl_2. Next 0.057 g (0.75 mmol) of solid anhydrous $(CH_3)_3N^+{-}O^-$ was added. The reaction was stirred for 10 min, during which time the $(CH_3)_3N^+{-}O^-$ dissolved and gas evolution occurred. Analysis by IR and ^1H NMR indicated the formation of benzaldehyde and $(CO)_5MnH$ in ≥75% spectroscopic yields.

Synthesis of $(CO)_5ReCOCOC_6H_5$ (9). By use of standard procedures,[44] a solution of $Na^+[(CO)_5Re]^-$ in 100 mL of THF was generated from Na/Hg amalgam (0.458 g, 20.0 mmol of Na in 25 mL of Hg) and $Re_2(CO)_{10}$ (5.870 g, 9.01 mmol). This solution was cooled to −78 °C, and 3.12 g (18.5 mmol) of $C_6H_5COCOCl$ in 10 mL of THF was added. The reaction was stirred for 30 min at −78 °C and was then allowed to warm to room temperature. The solvent was then removed by high-vacuum rotary evaporation at room temperature. The resulting reddish gum was chromatographed on 200 g of silica gel with 90:10 hexane/ethyl acetate. Product **9** was obtained upon solvent evaporation as orange crystals (4.789 g, 10.4 mmol, 58%), mp 74–76 °C. IR (cm^{-1}, THF): $\nu_{C\equiv O}$ 2138 w, 2068 w, 2025 vs; $\nu_{C=O}$ 1669 w, 1600 w. IR (cm^{-1}, cyclohexane): $\nu_{C\equiv O}$ 2139 m, 2068 m, 2045 w sh, 2028 s, 2008 s; $\nu_{C=O}$ 1672 w, 1609 m. ^1H NMR (δ, $CDCl_3$): 8.0 (m, 2 H), 7.6 (m, 3 H). ^{13}C NMR (ppm, $CDCl_3$): 252.0 ($ReCOCOC_6H_5$); 197.3 (COC_6H_5); 182.2, 181.3 (ca. 4:1, C≡O); 134.1, 130.6, 129.7, 129.0 (C_6H_5). Anal. Calcd for $C_{13}H_5O_7Re$: C, 33.99; H, 1.10; Re, 40.53. Found: C, 33.73; H, 1.22; Re, 40.72.

Synthesis of $(CO)_5ReCOCH(C_6H_5)OSi(CH_3)_3$ (11). To a stirred solution of **9** (1.847 g, 4.02 mmol) in 100 mL of THF was added 5.0 mL (5.0 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF. The reaction mixture was stirred for 20 min, after which time an IR assay[19b] indicated 9 to be consumed. Then 2.0 mL (16 mmol) of $(CH_3)_3SiCl$ was added. The reaction mixture was stirred for an additional 2 h, and the solvent was then removed by high-vacuum rotary evaporation at room temperature. The resulting crude yellow oil was chromatographed on 50 g of silica gel with 90:10 hexane/ethyl acetate. Solvent removal from a yellow fraction gave **11** as a pale yellow oil (1.157 g, 2.17 mmol, 54%) which when left in the freezer overnight solidified: mp 69–71 °C. IR (cm^{-1}, hexane): $\nu_{C\equiv O}$ 2132 w, 2059 w, 2026 vs, 2019 vs, 1998 s; $\nu_{C=O}$ 1623 w. ^1H NMR (δ, $CDCl_3$): 7.42 (s, 5 H), 4.50 (s, 1 H), 0.21 (s, 9 H). ^{13}C NMR (ppm, $CDCl_3$): 254.9 (C=O); 182.9, 181.7 (C≡O); 137.1, 128.2, 127.3, 126.1 (C_6H_5); 92.3 (CC_6H_5); −0.2 (CSi). Anal. Calcd for $C_{16}H_{15}O_7ReSi$: C, 36.01; H, 2.84; Re, 34.90; Si, 5.26. Found: C, 35.75; H, 2.93; Re, 35.12; Si, 5.01.

Synthesis of $(CO)_5ReCOCH(C_6H_5)OH$ (12). A stirred solution of **11** (0.159 g, 0.30 mmol) in 3 mL of acetone was treated with 0.1 mL (5.6 mmol) of distilled water. This mixture was stirred for 4 days at room temperature, after which TLC analysis showed **11** to be consumed, and **12** and $Re_2(CO)_{10}$ to be present. The solvents were removed by room-temperature rotary evaporation and the residue recrystallized from acetone/hexane at −20 °C. Yellow crystals of **12** (0.093 g, 0.20 mmol, 67%), mp 73–76 °C, dec, formed overnight. IR (cm^{-1}, hexane): ν_{O-H} 3416 vw; $\nu_{C\equiv O}$ 2138 w, 2070 w, 2032 vs, 2024 vs, 2006 s, 1998 sh; $\nu_{C=O}$ 1618 vw, 1606 w, 1598 w, 1586 vw. ^1H NMR (δ, $CDCl_3$): 7.13 (s, 5 H), 4.65 (s, 1 H), 3.4 (s, v br, 1 H). Mass spectrum (*m/e*, 70 eV, ^{187}Re): 355 ($Re(CO)_6^+$, 23%), 327 ($Re(CO)_5^+$, 9%), 107 ($C_6H_5CHOH^+$, 95%), 106 ($C_6H_5CHO^+$, 28%), 105 ($C_6H_5CO^+$, 100%). Anal. Calcd for $C_{13}H_7O_7Re$: C, 33.84; H, 1.53. Found: C, 33.79; H, 1.83.

Synthesis of $(CO)_5ReCH(C_6H_5)OSi(CH_3)_3$ (13). A Pyrex Schlenk tube was charged with **11** (0.156 g, 0.29 mmol), 10 mL of pentane, and a stir bar. This solution was kept under N_2, placed in an ice bath, and stirred. It was then irradiated for 15 min with a Hanovia 450 W medium-pressure mercury lamp. The solvent was then removed via high-vacuum rotary evaporation at room temperature. The resulting residue was chromatographed under N_2 on 10 g of silica gel with pentane. Product **13** was obtained as a pale yellow oil (0.071 g, 0.14 mmol, 48%) which solidified when kept overnight in the freezer, mp 27–29 °C. IR (cm^{-1}, hexane): $\nu_{C\equiv O}$ 2129 w, 2058 w, 2020 vs, 2014 vs, 1987 s. ^1H NMR (δ, $CDCl_3$): 7.24 (s, 5 H), 5.98 (s, 1 H), 0.12 (s, 9 H). Anal. Calcd for $C_{15}H_{15}O_6ReSi$: C, 35.63; H, 3.00. Found: C, 36.06; H, 2.83.

Attempted Syntheses of $(CO)_5ReCH(C_6H_5)OH$ (14). **(A)** A 5-mm septum-capped NMR tube was charged with **13** (0.099 g, 0.195 mmol) and THF-d_8 (0.6 mL). An initial ^1H NMR spectrum was recorded at −50 °C, and the tube was cooled to −78 °C. Then dry HF gas was slowly bubbled into the solution for a period of 0.5 min. The tube was quickly transferred to a −50 °C NMR probe. A ^1H NMR spectrum was immediately recorded and showed the formation of $(CO)_5ReH$ (δ −5.80, 90%) and benzaldehyde (δ 10.03, 84%). **(B)** A 5-mm septum-capped NMR tube was charged with **13** (0.058 g, 0.11 mmol) and acetone-d_6 (0.5 mL). Then 0.02 mL (1.1 mmol) of distilled H_2O was syringed into the tube, and the reaction was monitored by ^1H NMR. Reaction slowly occurred over the course of 24 h to give $(CO)_5ReH$ (δ −5.78, 90%) and benzaldehyde (δ 9.98, 90%) as the only products. (C) A 5-mm septum-capped NMR tube was charged with **13** (0.072 g, 0.23 mmol) and CD_2Cl_2 (0.5 mL). Then a solution of $(n\text{-}C_4H_9)_4N^+F^-\cdot 3H_2O$ (0.131 g, 0.26 mmol) in CD_2Cl_2 (0.2 mL) was added via syringe. The mixture was allowed to stand for 5 min and a ^1H NMR spectrum was recorded. Benzaldehyde (δ 9.98) and $(CO)_5ReH$ (δ −5.81) had formed in 94% and 67% yields, respectively, as determined by subsequent injection of a standard *p*-di(*tert*-butyl)benzene solution. **(D)** A 5-mm septum-capped NMR tube was charged with **13** (0.071 g, 0.14 mmol) and $CDCl_3$ (0.5 mL). Then 0.02 mL (~0.27 mmol) of 37% HCl was added via syringe. The tube was shaken and a ^1H NMR spectrum was immediately recorded. Starting material had been consumed, but $(CO)_5ReH$ and benzaldehyde were not present. Resonances at δ 5.30 (1 H) and 7.35 (5 H) were attributed to $(CO)_5ReCH(C_6H_5)Cl$ (**15**), which was subsequently isolated by ether/cyclohexane recrystallization, mp 81–84 °C dec. IR (cm^{-1}, cyclohexane): 2139 m, 2071 m, 2014 s, 1990 m sh. Mass spectrum (*m/e*, 70 eV, $^{187}Re/^{35}Cl$): 452 (M^+, 52%), 312 ($ReCH(C_6H_5)Cl^+$, 100%), 125 ($CH(C_6H_5)Cl^+$, 41%). The same compound formed when 0.15 g (0.30 mmol) of **13** in 0.6 mL of toluene-d_8 was treated with HCl gas at −78 °C in a manner analogous to experiment A. **(E)** A 5-mm septum-capped NMR tube was charged with **12** (0.1 g, 0.2 mmol) and acetone-d_6 (0.7 mL). An initial ^1H NMR spectrum was recorded at −50 °C. The tube was then immersed in a Pyrex dewar containing a CO_2/acetone bath. The sample was irradiated for 15 min at −78 °C with a Hanovia 450-W medium-pressure mercury lamp. The tube was quickly transferred back to the cold NMR probe, which was reequilibrated to −50 °C. Benzaldehyde (δ 10.00) and $(CO)_5ReH$ (δ −5.86) were present in ≥95% spectroscopic yield. This reaction was repeated with a 5-min irradiation time. Subsequent ^1H NMR analysis (immediate, −50 °C) showed some starting **12** as well as benzaldehyde and $(CO)_5ReH$.

X-ray Crystal Structure of PPN$^+$-2. Suitable single crystals (cream-colored plates) were grown by repeated crystallization from ether/hexane at −20 °C under N_2. Data were collected on a Syntex P$\bar{1}$ automatic diffractometer as outlined in Table I. Lattice parameters were determined from a least-squares fit of 15 automatically centered diffraction maxima. Of 5697 reflections with $2\theta < 40°$ collected, 2994 with $I \geq 3\sigma(I)$ were used in the final refinement.[45]

The data were analyzed by direct methods. The atomic parameters were refined via the block-diagonal least-squares method. All seven

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(44) King, R. B. "Organometallic Syntheses"; Eisch, J. J., King, R. B., Eds.; Wiley: New York, 1965; Vol. 1, pp 148–155.

(45) Programs utilized for data refinements (IBM 360/91 computer) included the following: JBPATT, JBFOUR, and PKLIST by Blount; ORFLS and ORFEE by Busing, Martin, and Levy; ORTEP by Johnson; PUBLIST by Hoel.

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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[46] Scheringer, C. *Acta. Crystallogr.* **1963**, *16*, 546.

[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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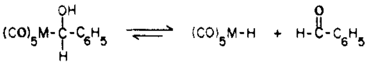
Abstract: Reaction of $(CO)_5ReCH_2C_6H_5$ with $(C_6H_5)_2P(o\text{-}C_6H_4OSi(CH_3)_2(t\text{-}C_4H_9))$ in octane (100–126 °C) gives the metallacycle $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CHOSi(CH_3)_2(t\text{-}C_4H_9))$ (**21**, 46%). Reaction of **21** with $(C_2H_5)_4N^+F^-\cdot(H_2O)_{2.6}$, followed 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 $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OSi(CH_3)_3){-}C{=}O)$ (**29**, 52%), which upon subsequent treatment with KF gives an authentic sample of carbonylated **4**, hydroxyacyl complex $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CH(OH){-}C{=}O)$ (**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.



$$(CO)_5M\text{-}\overset{OH}{\underset{H}{C}}\text{-}C_6H_5 \rightleftharpoons (CO)_5M\text{-}H + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_5 \quad (1)$$

M = Mn, Re

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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[3] Selover, J. C.; Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.*, preceding paper in this issue.

[4] Blackmore, T.; Bruce, M. I.; Davidson, P. J.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3153.

[5] (a) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741. (b) Casey, C. P; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *Ibid.* **1980**, *102*, 1927. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43.

[6] (a) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173* C9. (b) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811.

[7] (a) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7. (b) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *Ibid.* **1982**, *231*, 335.

[8] Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5608.

[9] Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353. This well-characterized α-hydroxyalkyl complex is unstable above 0 °C.

[10] (a) Thorn, D. L. *Organometallics* **1982**, *1*, 197. (b) Thorn, D. L.; Tulip, T. H. *Ibid.* **1982**, *1*, 1580. (c) See also: Thorn, D. L.; Calabrese, J. C. *J. Organomet. Chem.* **1984**, *272*, 283.

[11] (a) Wayland, B. B.; Woods, B. A.; Minda, V. M. *J. Chem. Soc., Chem. Commun.* **1982**, 634. (b) Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887.

[12] May, C. J.; Graham, W. A. G. *J. Organomet. Chem.* **1982**, *234*, C49.

[13] (a) Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1983**, 430. (b) Nelson, G. O. *Organometallics* **1983**, *2*, 1474. (c) Lapinte, C.; Astruc, D. *J. Organomet. Chem.* **1984**, *260*, C13.

[14] (a) Lin, Y. C.; Milstein, D.; Wreford, S. S. *Organometallics* **1983**, *2*, 1461. (b) See also Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275.

[15] (a) Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1596. (b) Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.*, following paper in this issue.

[16] (a) Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2721. (b) Kirker, G. W.; Bakač, A.; Espenson, J. H. *Ibid.* **1982**, *104*, 1249. (c) A metallabicyclic iridium α-hydroxyalkyl complex recently has been reported: Clark, G. R.; Greene, T. R.; Roper, W. R. *J. Organomet. Chem.* **1985**, *293*, C25.

0002-7863/86/1508-1462$01.50/0