description is likely appropriate for all our systems.

At present, we are not aware of any other reasonable mechanistic alternatives to the proposed superexchange mechanism that can account for the observed decay behavior of $H_2{}^*\frown$Zn–Q and $H_2{}^*$–Zn–Q. Superexchange involving the bridge linking the donor and acceptor has been proposed for a number of systems.[7,11b–d] The observed time constant of 55–110 ps is significantly faster than expected for a 12–14-Å edge-to-edge distance if ET proceeds through the solvent, as discussed on the basis of the fluorescence data.[13] Additionally, in our monometalated dimers, the 55–110-ps time constant is much faster than that observed for ET over about the same distance (and with about the same driving force) from an excited porphyrin to a benzoquinone linked by a bisbicyclooctyl spacer.[6l] This suggests that the mediating Zn–porphyrin subunit provides an excellent superexchange bridge, perhaps due to the conjugated π-electron system or to the energies of the relevant orbitals. In any case, we have presented here a key, and we believe clear, example, which demonstrates that a porphyrin can serve very effectively as a superexchange mediator in well-defined complexes containing close electronic and structural relatives of the cofactors in the bacterial reaction center.

Aside from the specific question of superexchange, the observation of highly efficient low-temperature charge separation is of interest in its own right. There are only a few other examples of porphyrin-based photosynthetic model systems in which this has been observed.[8] Indeed, there has been considerable discussion as to whether low-temperature charge separation can be effected in model systems without the benefit of unusual structure or energetics (i.e., driving force).[8c] Both the time-resolved results reported here and the supporting low-temperature fluorescence emission studies[13] indicate, in fact, that ET in covalently linked porphyrin–quinone systems can take place efficiently at low temperature (and in nonpolar solvents), as it does in the reaction center.[28] Apparently, one of the factors that is needed is a rigid, temperature-independent structure: If the model system is floppy, then at room temperature ET may occur efficiently only in geometries where the donor and acceptor subunits closely approach. These favorable geometries may not be accessible in a frozen solvent and the ET efficiency would be expected to decrease. To the extent that ET occurs predominantly through the bonds in the bridge separating the donor and acceptor, one would expect to observe efficient low-temperature photoinduced ET in a wide variety of model systems. Our results on structurally rigid and well-defined quinone-substituted porphyrin complexes are consistent with this point of view.

Acknowledgment. This work was supported by a grant from the Robert A. Welch Foundation (F-1018 to J.L.S., the Dreyfus Foundation (New Faculty Grant 1984 and Teacher–Scholar Award 1988–1992 to J.L.S.; Teacher–Scholar Award 1987–1991 to R.A.F.), the National Science Foundation (PYI Award 1986 to J.L.S.), and National Institutes of Health Grants (GM 34685 to D.H. and GM 41657 to J.L.S.). R.A.F. also acknowledges receipt of a Research Career Development Award from the NIH, Institute of General Medical Sciences.

---

[28] Temperature-insensitive electron transfer in the bacterial reaction center is discussed in refs 2a,b,e,4c,25,26b, and 27.

Preparation and Reactions of $Mn_2(CO)_9(\eta^1$-aldehyde) Complexes

R. Morris Bullock* and Brian J. Rappoli

Contribution from the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973. Received July 24, 1990

Abstract: The reaction of $HMn(CO)_5$ with $RMn(CO)_5$ (R = CH_3, p-$CH_3C_6H_4$, or $CH_2CH_2CH{=}C(Ph)CH_3$) gives $Mn_2(CO)_9(\eta^1\text{-RCHO})$ complexes. It is suggested that these $Mn_2(CO)_9(\eta^1$-aldehyde) complexes may provide a model for a previously unobserved intermediate in the formation of aldehydes from the hydroformylation of olefins. The η^1-aldehyde ligand is weakly bound to the manganese, as evidenced by its facile displacement by ligands such as CO, PPh_3, and CH_3CN. The kinetics of the reaction of $HMn(CO)_5$ with $(CO)_5Mn(CH_2CH_2CH{=}C(Ph)CH_3)$ were studied by ^1H NMR at 25 °C in C_6D_6. The reaction is first-order in the manganese alkyl complex, and the rate of the reaction decreases slightly with increasing concentration of $HMn(CO)_5$. A negligible isotope effect ($k_H/k_D = 1.04 \pm 0.09$) was found for the reaction of $(CO)_5Mn(CH_2CH_2CH{=}C(Ph)CH_3)$ with $DMn(CO)_5$. The reaction of $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$ with excess $HMn(CO)_5$ takes several days at room temperature and produces ethanol and the manganese cluster complex $Mn_3(CO)_9(\mu_3\text{-OEt})_2(\mu_2\text{-OEt})$.

Aldehyde and ketone complexes of transition metals have been known for many years, but detailed studies of the formation and reactions of such complexes have only recently been reported.[1] Both aldehydes and ketones can bond to metal centers by either η^1- or η^2-bonding modes (Figure 1), and several examples of both of these have been crystallographically characterized.

In a few cases, isolable aldehyde and ketone complexes have been utilized in organic synthesis. Gladysz and co-workers have prepared optically active η^2-aldehyde complexes of Re and have converted them into optically active alcohols.[2] Hersh and co-workers have structurally characterized a cationic W η^1-aldehyde complex and have demonstrated that it is an excellent catalyst for the Diels–Alder reaction between dienes and α,β-unsaturated enones.[3] In other cases, aldehyde complexes are not directly observed but have been postulated as key intermediates in metal-mediated organic syntheses. For example, Faller and co-workers

---

[1] (a) For a review of aldehyde and ketone complexes of transition metals, see: Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298–303. (b) For a review treating both transition-metal and main-group Lewis acid complexes of aldehydes, ketones, etc., see: Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256–272.

[2] (a) Fernández, J. M.; Emerson, K.; Larsen, R. H.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8268–8270. (b) Garner, C. M.; Quirós Méndez, N.; Kowalczyk, J. J.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146–5160.

[3] Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070–6081. (b) Honeychuck, R. V.; Bonnesen, P. V.; Farahi, J.; Hersh, W. H. *J. Org. Chem.* **1987**, *52*, 5293–5296.

0002-7863/91/1513-1659$02.50/0 © 1991 American Chemical Society

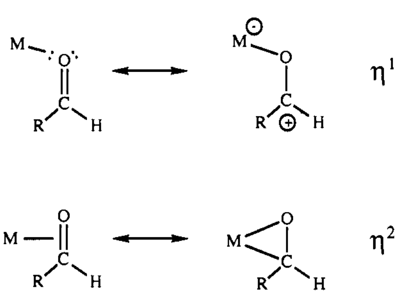


Figure 1. Resonance forms of η^1- and η^2-aldehyde complexes.

suggested that a Mo η^1-aldehyde complex was a crucial intermediate in their synthesis of optically active homoallylic alcohols.[4] Burkhardt, Bergman, and Heathcock proposed a Ni η^1-aldehyde intermediate in the reaction of a Ni enolate complex with benzaldehyde.[5] Pedersen and co-workers proposed an η^1-aldehyde intermediate in the V(II)-mediated cross-coupling of aldehydes to produce 1,2-diols.[6]

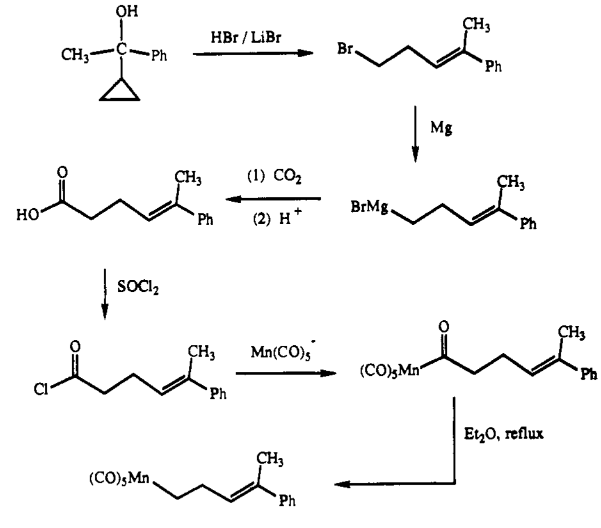
One of the most thoroughly investigated methods for synthesis of aldehydes is the metal-catalyzed hydroformylation of olefins.[7] In view of the recent interest in aldehyde complexes as well as the long-standing interest in mechanistic details of the hydroformylation reaction, the possible intermediacy of complexes containing aldehydes *directly bonded* to transition metals during the hydroformylation reaction is of substantial mechanistic importance.

In several studies of the aldehyde-forming step of the hydroformylation reaction, free aldehydes have been shown to result from a dinuclear elimination reaction between a metal hydride and a metal alkyl complex.[8] We recently discovered that $Mn_2(CO)_9(\eta^1$-aldehyde) complexes can be prepared from reaction of $(CO)_5MnR$ (R = alkyl or aryl) and $HMn(CO)_5$.[9] These complexes differ significantly from the aldehyde complexes mentioned above. In nearly all examples of isolable organometallic aldehyde complexes reported to date, η^2-bonding is found for neutral complexes. In contrast, cationic aldehyde complexes typically exhibit η^1-bonding. The $Mn_2(CO)_9(\eta^1$-aldehyde) complexes reported herein provide rare examples of isolable, neutral, η^1-aldehyde complexes. Furthermore, nearly all previously reported aldehyde complexes were prepared by adding a free aldehyde to a metal complex containing a weakly bound ligand. In our synthetic method, the aldehyde is formed during the reaction, with the R group and carbonyl being supplied from $(CO)_5MnR$ and the aldehyde H coming from the hydride of $HMn(CO)_5$. In this paper, we report the synthesis, characterization, and reactions of these $Mn_2(CO)_9(\eta^1$-aldehyde) complexes.

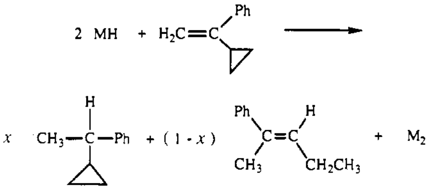
Results

Synthesis of $Mn_2(CO)_9(\eta^1$-aldehyde) Complexes. We discovered the first $Mn_2(CO)_9(\eta^1$-aldehyde) complex while carrying out a kinetic and mechanistic study of the hydrogenation of α-cyclopropylstyrene by a series of transition-metal hydrides.[10] This

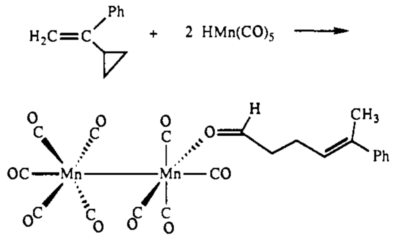
Scheme I

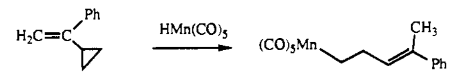


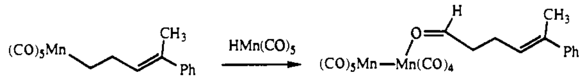
hydrogenation proceeds by sequential hydrogen atom transfers from the metal hydride to the organic substrate; metal hydrides that hydrogenate α-cyclopropylstyrene as shown in eq 1 include


(1)

$HM(CO)_3Cp$ (M = Cr, Mo, or W), $HFe(CO)_2Cp$, $HMn(CO)_4(PPh_3)$, etc. While rigorously purified $HMn(CO)_5$ behaved similarly to the other metal hydrides, we were surprised to find that samples of $HMn(CO)_5$, which were not thoroughly dried with P_2O_5, resulted in the unexpected ring-opening hydroformylation reaction shown in eq 2. A spectroscopically observable intermediate in this reaction was identified as the manganese alkyl complex $(CO)_5Mn(CH_2CH_2CH{=}C(Ph)CH_3)$ (hereafter this alkyl group will be abbreviated as $R' = CH_2CH_2CH{=}C(Ph)CH_3$). This manganese alkyl complex, which had formed from the reaction of α-cyclopropylstyrene with 1 equiv of $HMn(CO)_5$ (eq 3), was reacting with 1 equiv of $HMn(CO)_5$ (eq 4) to produce


(2)


(3)


(4)

$Mn_2(CO)_9(\eta^1$-R'CHO). The formation of $(CO)_5MnR'$ from α-cyclopropylstyrene and $HMn(CO)_5$ is a perplexing reaction, which has an induction period; an impurity (not yet conclusively identified) present in the $HMn(CO)_5$ appears to be necessary for this reaction. The fact that $(CO)_5MnR'$ was being concurrently

---

(4) Faller, J. W.; John, J. A.; Mazzieri, M. R. *Tetrahedron Lett.* **1989**, *30*, 1769–1772.

(5) Burkhardt, E. R.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 30–44.

(6) Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 8014–8016.

(7) For reviews of hydroformylation, see: (a) Pruett, R. L. *Acc. Chem. Res.* **1979**, *17*, 1–60. (b) Cornils, B. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: New York, 1980. (c) Pruett, R. L. *J. Chem. Educ.* **1986**, *63*, 196–198.

(8) (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332–338. (b) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34–41. (c) Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150–2160. (d) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33–39. (e) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447–5449. (f) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415–4423.

(9) For a preliminary account of part of this work, see: Bullock, R. M.; Rappoli, B. J.; Samsel, E. G.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 261–263.

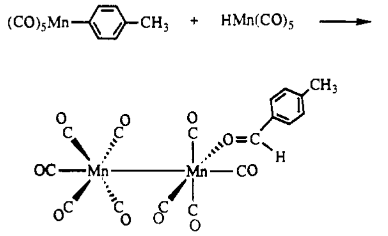
(10) Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1987**, *109*, 6542–6544; *J. Am. Chem. Soc.* **1990**, *112*, 6886–6898.

formed (eq 3) and consumed (eq 4) complicated the study of the latter. Details of the reaction shown in eq 3 will be published separately.

We recognized, however, that the formation of $Mn_2(CO)_9(\eta^1$-aldehyde) complexes was probably not limited to the specific example that we discovered and furthermore that such reactions could be studied separately by reaction of appropriate $(CO)_5MnR$ (R = alkyl or aryl) complexes with $HMn(CO)_5$. The independent synthesis of $(CO)_5MnR'$ was accomplished by the straightforward route shown in Scheme I and produces the alkyl complex as a reasonably air-stable solid that could be purified by crystallization and/or sublimation.

The ^1H NMR spectrum of this independently prepared $(CO)_5MnR'$ complex was identical with that observed as an intermediate in reaction 3. However, the appearance of the ^1H NMR peaks was clearly not a simple first-order pattern. For example, the $MnCH_2$ resonance was not a triplet as might have been expected from coupling of equivalent protons of $MnCH_2$ to the vicinal allylic CH_2 protons. The chemical shifts and coupling constants were determined by computer simulation of the ^1H NMR spectrum of $(CO)_5MnR'$. Figure 2 shows the calculated and experimental spectra for the $MnCH_2CH_2$, $MnCH_2CH_2$, vinyl, and methyl resonances. A Newman projection of the most stable conformation of $(CO)_5MnR'$ is shown in Figure 3. The diastereotopic protons H_A and H_B of $MnCH_2$ are strongly coupled to each other (J = 15.4 Hz), as are the geminal allylic protons H_C and H_D (J = 11.5 Hz). The inequivalence of these protons does *not* require restricted rotation about the Mn-C or C-C bonds.[11] The experimental spectrum shown in Figure 2 was recorded at 23 °C, but no change in the spectrum was observed at −70 °C. A complete listing of coupling constants and chemical shifts is given in the Experimental Section.

The successful synthesis of $Mn_2(CO)_9(\eta^1$-R'CHO) by reaction of a manganese alkyl complex with $HMn(CO)_5$ suggested that similar aldehyde complexes should be available from other manganese alkyl or aryl precursors. The reaction of $(CO)_5Mn(p\text{-}CH_3C_6H_4)$ with $HMn(CO)_5$ in hexane gave $Mn_2(CO)_9(\eta^1\text{-}CH_3C_6H_4CHO)$ (eq 5) in 80% isolated yield. Toluene (about 2% yield) was a minor component of this reaction. A similar reaction between $CH_3Mn(CO)_5$ and $HMn(CO)_5$ produced $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$.



(5)

Physical Properties and Spectral Data of $Mn_2(CO)_9(\eta^1$-aldehyde) Complexes. Both $Mn_2(CO)_9(\eta^1$-R'CHO) and $Mn_2(CO)_9(\eta^1\text{-}CH_3C_6H_4CHO)$ can be crystallized from hexane to give air-sensitive orange crystals, which are stable for >1 year when stored at −20 °C under argon. The acetaldehyde complex $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$ was obtained as an orange powder; qualitative observations indicate that the thermal stability of this complex in solution is somewhat lower than those for the other two η^1-aldehyde complexes. The acetaldehyde complex also decomposes when left under high vacuum for several hours, presumably due to the lability of the acetaldehyde ligand. The X-ray crystal structure[9] of $Mn_2(CO)_9(\eta^1$-R'CHO) verified the η^1-bonding, which had been assigned on the basis of spectroscopic data. The C=O bond length of the aldehyde is 1.216 (9) Å. This is only slightly longer than a typical C=O bond distance (~1.20 Å) for a free aldehyde. Little structural data on other η^1-aldehyde complexes are available for comparison, but the slight elongation of the C=O bond of aldehydes upon η^1-coordination is also observed in cationic η^1-ketone complexes.[1] In contrast, C=O bond lengths of η^2-aldehyde complexes are generally >1.3 Å.[1] This suggests that the resonance form in the upper left of Figure 1 (with a C=O double bond) is the predominant contributor for η^1-aldehyde complexes, while the metallaoxirane structure at the lower right of Figure 1 (with a C—O single bond) is the predominant resonance contributor for η^2-aldehyde complexes.

The pattern and intensities of the IR bands of the carbonyl ligands bonded to Mn indicate an equatorially substituted $Mn_2(CO)_9$ moiety, and this was also confirmed by the crystal structure[9] of $Mn_2(CO)_9(\eta^1$-R'CHO). The aldehyde C=O stretch is observed as a weak band at 1640 cm^{-1} for $Mn_2(CO)_9(\eta^1\text{-}CH_3C_6H_4CHO)$. This band is only 72 cm^{-1} lower than the C=O band in free *p*-tolualdehyde (1712 cm^{-1}), which is also in agreement with only a slight weakening of the C=O bond. In contrast, IR bands of aldehyde C=O stretches for η^2-aldehyde complexes are typically found at much lower energy (~1200 cm^{-1} or lower).[1] The aldehyde ^1H NMR resonance is observed at δ 7.91 (in C_6D_6) for $Mn_2(CO)_9(\eta^1\text{-}CH_3C_6H_4CHO)$ (compared to δ 9.68 for free tolualdehyde in C_6D_6). These spectroscopic criteria all confirm that the η^1-bonding of the aldehyde found in the crystal structure is maintained in solution.

The orange color of the $Mn_2(CO)_9(\eta^1$-aldehyde) complexes is due to a visible absorption band [e.g., λ_{max} = 470 nm for $Mn_2(CO)_9(\eta^1\text{-}CH_3C_6H_4CHO)$]. The electronic absorption spectra of $Mn_2(CO)_{10}$ and substituted derivatives such as $Mn_2(CO)_9(PPh_3)$ have been assigned by Levenson and Gray.[12]

Aldehyde Displacement Reactions of $Mn_2(CO)_9(\eta^1$-aldehyde) Complexes. The weak bond between the aldehyde and the manganese is readily broken by reaction with donor ligands. Exposure of an orange solution of $Mn_2(CO)_9(\eta^1\text{-}CH_3C_6H_4CHO)$ to CO (1 atm) causes release of free tolualdehyde and fading of the solution to the yellow color of $Mn_2(CO)_{10}$ within 30 s. Similar reactions are observed with CH_3CN and PPh_3, giving previously reported compounds $Mn_2(CO)_9(CH_3CN)$[13] and $Mn_2(CO)_9(PPh_3)$.[13] A qualitative indication of the mild conditions under which the aldehyde can be displaced comes from an experiment in which the reaction of $Mn_2(CO)_9(\eta^1$-R'CHO) (~0.04 M) with CH_3CN (~0.3 M) was complete within a few minutes at −30 °C in toluene-d_8. The acetaldehyde complex $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$ was further characterized by its reaction with CO to give CH_3CHO and $Mn_2(CO)_{10}$ and by its reaction with tolualdehyde to give $Mn_2(CO)_9(\eta^1\text{-}CH_3C_6H_4CHO)$ and free CH_3CHO. Preliminary experiments indicate that the aldehyde ligand in these complexes is readily displaced by an excess of acetone, dimethylformamide, dimethyl sulfoxide, triphenylphosphine oxide, and other donors. Quantitative experiments to assess the kinetics and thermodynamics of aldehyde displacement will be reported later.

Kinetics of the Reaction of $(CO)_5MnR'$ with $HMn(CO)_5$. The kinetics of reaction 4 were studied by ^1H NMR in C_6D_6 at 25 °C. The rate of disappearance of $(CO)_5MnR'$ (0.05–0.07 M) was determined as a function of excess $HMn(CO)_5$ concentration. The observed pseudo-first-order rate constants are listed in Table I. The reaction of $(CO)_5MnR'$ with a mixture of $HMn(CO)_5$ and $DMn(CO)_5$ at 22 °C had a negligible isotope effect of k_H/k_D = 1.04 ± 0.09. A pseudo-first-order plot for disappearance of $(CO)_5MnR'$ over the first 3 half-lives of the reaction is shown in Figure 4. The rate of disappearance of $(CO)_5MnR'$ is cleanly first-order, but the relative amounts of free and complexed aldehyde change as the reaction proceeds. More of the free aldehyde is observed at early reaction times, whereas the product ratio levels out at longer times. Figure 5 shows a plot of $[Mn_2(CO)_9(\eta^1\text{-R'CHO})]/[\text{total aldehyde}]$ as a function of time.

The reaction between $(CO)_5MnR'$ and $HMn(CO)_5$ is much faster in CD_3CN than in C_6D_6. A frozen solution of $(CO)_5MnR'$

---

(11) (a) Becker, E. D. *High Resolution NMR*; Academic Press: New York, 1969; pp 224–228. (b) Waugh, J. S.; Cotton, F. A. *J. Phys. Chem.* **1961**, *65*, 562–563. (c) Sanders, J. K.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: Oxford, 1987; pp 299–302.

(12) Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042–6047.

(13) Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53–62.

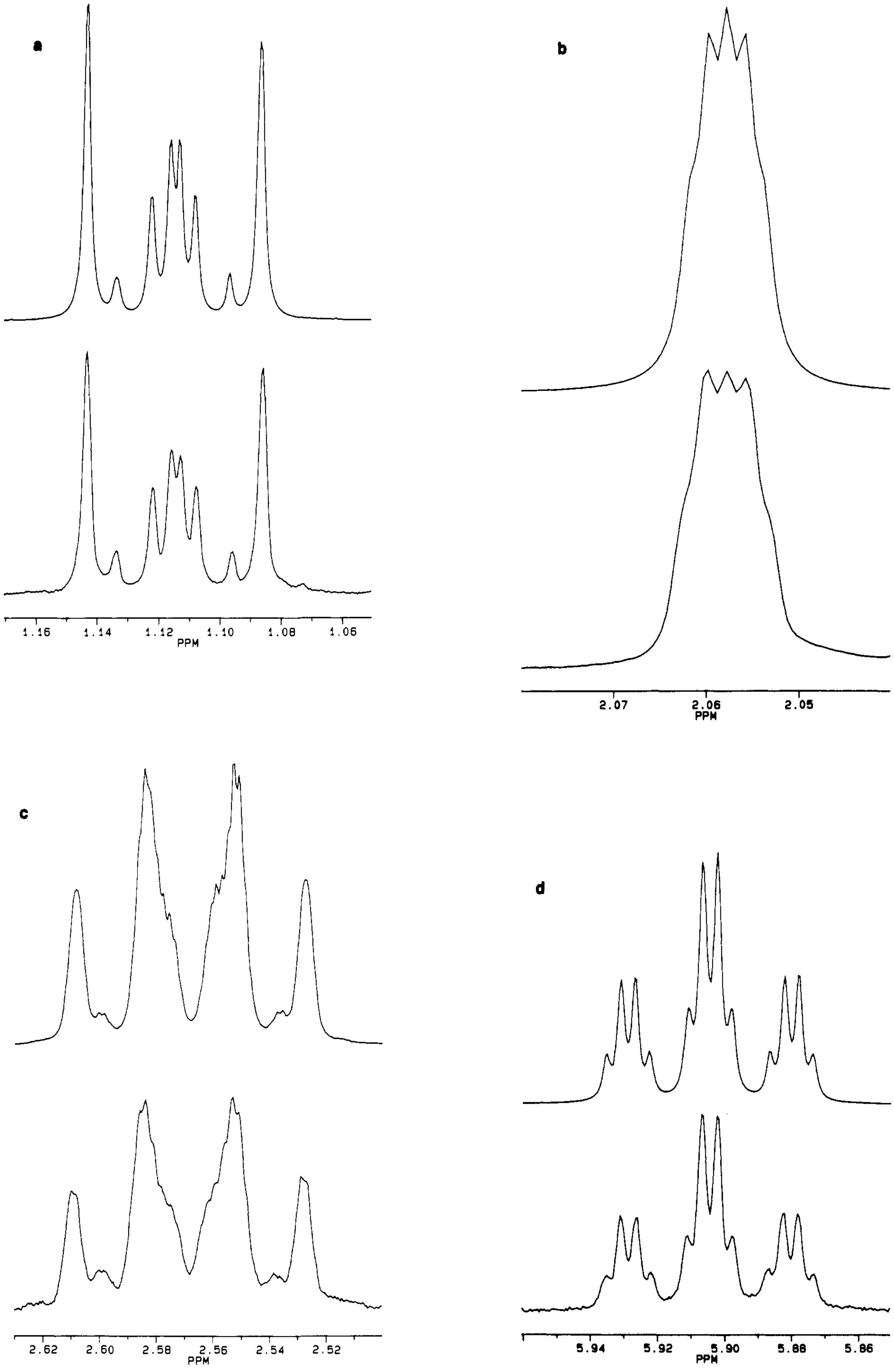


Figure 2. Calculated (upper) and experimental (lower) ^{1}H NMR spectra of $(CO)_5MnCH_2CH_2CH{=}C(Ph)CH_3$: (a) $MnC\mathit{H}_2$, (b) $C\mathit{H}_3$, (c) $MnCH_2C\mathit{H}_2$, and (d) $C{=}C\mathit{H}$.

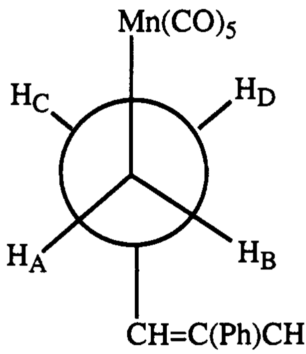


Figure 3. Newman projection of $(CO)_5MnCH_2CH_2CH{=}C(Ph)CH_3$.

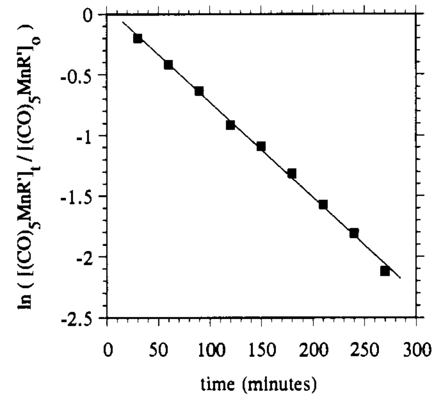


Figure 4. First-order plot of the rate of disappearance of $(CO)_5MnR'$ (0.06 M) in its reaction with $HMn(CO)_5$ (0.95 M) in C_6D_6 at 25 °C.

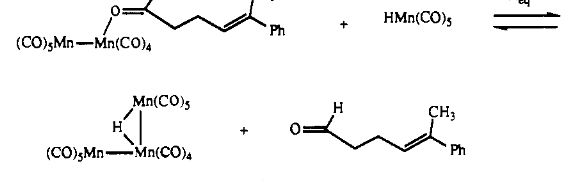
Table I. Observed Pseudo-First-Order Rate Constants for Disappearance of $(CO)_5MnR'$ in Reaction with Excess $HMn(CO)_5$ at 25 °C in C_6D_6

$[HMn(CO)_5]$, M	10^4k_{obs},[a] s^{-1}
0.54	1.9
0.95	1.3
2.0	1.1
2.6	1.0

[a] Estimated error ± 10% on all rate constants.

(0.06 M) and excess $HMn(CO)_5$ (1.7 M) in CD_3CN turned yellow immediately upon thawing to room temperature. A ^1H NMR spectrum taken within 4 min of thawing showed complete reaction, and only resonances due to the free aldehyde were observed. The yellow organometallic product was identified as $Mn_2(CO)_9(CD_3CN)$ by comparison of its IR spectrum to that of an authentic sample.[13] The free aldehyde was also produced in a slow reaction between the acyl complex $(CO)_5Mn(COR')$ (0.17 M) and $HMn(CO)_5$ (2.6 M) in C_6D_6 (89% yield after 6 days at room temperature).

$HMn(CO)_5$ vs η^1-Aldehyde as a Ligand on $Mn_2(CO)_9$. It was mentioned above that relatively weak nucleophiles such as CH_3CN can displace the η^1-aldehyde ligand. The change in the free aldehyde to complexed aldehyde ratio observed (Figure 5) in the study of the kinetics of formation of $Mn_2(CO)_9(\eta^1\text{-}R'CHO)$ suggested an equilibrium in which $HMn(CO)_5$ displaced the aldehyde ligand. Direct observation of the equilibrium shown in eq 6 was accomplished by adding an excess of $HMn(CO)_5$ to a C_6D_6 solution of $Mn_2(CO)_9(\eta^1\text{-}R'CHO)$. When a frozen solution containing $HMn(CO)_5$ and the aldehyde complex was warmed to room temperature, the color of the solution immediatetely changed from orange to a darker orange. In addition to resonances in the ^1H NMR spectrum for the free aldehyde, a broad (~80-Hz line width at half-height) resonance was observed at δ -22.1. This resonance is assigned to $HMn_3(CO)_{14}$. The chemical shift of $HMn_3(CO)_{14}$ is similar to the bridging hydride resonance of $H_3Mn_3(CO)_{12}$,[14] which we have found to be at δ -23.9 in C_6D_6. The formation of $HMn_3(CO)_{14}$ was also observed in experiments involving the other two aldehyde complexes.



(6)

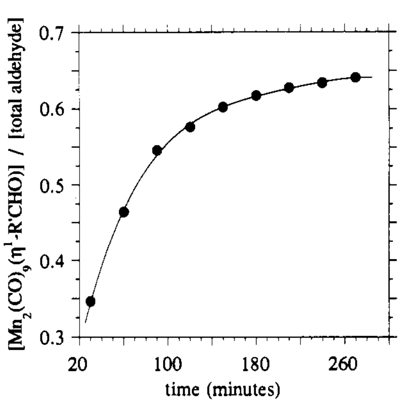
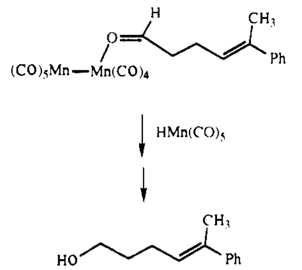


Figure 5. $[Mn_2(CO)_9(\eta^1\text{-}R'CHO)]/[\text{total aldehyde}]$ as a function of time.

The concentrations of $HMn(CO)_5$, free aldehyde, and complexed aldehyde determined in the kinetics experiments also provide a measure of the equilibrium constant for eq 6 over the course of the reaction. The equilibrium constant determined at 22 °C for eq 6 was $K_{eq} = (1.2 \pm 0.1) \times 10^{-2}$. In a related experiment, K_{eq} for eq 6 was determined from the reaction of $(CO)_5MnR'$ and $HMn(CO)_5$ at 8 °C in C_6D_6. The equilibrium constant determined in this experiment from data points taken during the first half-life of the reaction did not differ appreciably from the equilibrium constant determined at the end of the reaction. This indicates that, under our experimental conditions, the equilibrium in eq 6 is rapidly established, compared to the rate of the reaction of $(CO)_5MnR'$ with $HMn(CO)_5$. The equilibrium constant determined at 8 °C was $K_{eq} = (1.1 \pm 0.2) \times 10^{-2}$. The small value of the equilibrium constant indicates that $HMn(CO)_5$ is even more weakly bound to $Mn_2(CO)_9$ than is the η^1-aldehyde ligand ($\Delta G° \approx 2.5$ kcal/mol for eq 6).

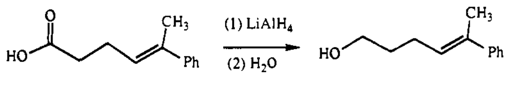
Reduction of $Mn_2(CO)_9(\eta^1\text{-aldehyde})$ Complexes to Alcohols and Related Products. In our studies of the kinetics of reaction 4, the combined yield of free and complexed aldehyde was >95% and the solutions were dark wine red when the consumption of the alkyl complex was complete after several hours. However, when these solutions (which still contaion an excess of $HMn(CO)_5$) are left at room temperature in the dark for 3-5 days, the wine red color of the solution fades to a somewhat lighter orange color. During this time, the resonances for both the free aldehyde and $Mn_2(CO)_9(\eta^1\text{-}R'CHO)$ decrease in intensity and are replaced by new peaks due to the formation of the alcohol $R'CH_2OH$ (60-80% yield) (eq 7). Confirmation of the identity of this alcohol was obtained by comparison of its ^1H NMR spectrum with that of an authentic sample prepared as shown in eq 8.



(7)

---

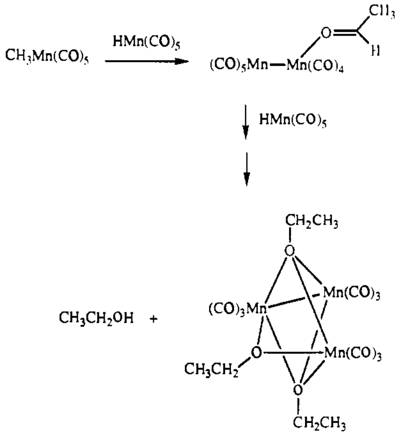
(14) Johnson, B. F. G.; Johnston, R. D.; Lewis, J.; Robinson, B. H.; Olazagasti, M.; Muetterties, E. *Inorg. Synth.* **1970**, *12*, 43-45.



(8)

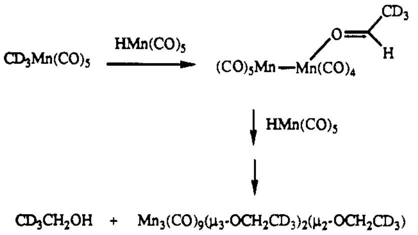
An analogous reduction of acetaldehyde to ethanol was also observed with $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$. A C_6D_6 solution of $(CH_3)Mn(CO)_5$ (0.35 M) and $HMn(CO)_5$ (1.8 M) had turned dark wine red after 21 h at room temperature, giving $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$ (72%) and free CH_3CHO (21%). The free and complexed aldehydes were nearly completely consumed after 7 days. Along with other peaks to be discussed later, two very broad, overlapping resonances were observed at δ 3.62 and δ 3.33. Addition of CH_3CN resulted in the coalescence of these resonances to a broad[15] singlet at δ 3.42. This resonance is assigned as the CH_2 group of ethanol; the yield of ethanol was 41% based on ^1H NMR integration vs an internal standard. Further spectroscopic data supporting this assignment are given in the Experimental Section. We suggest that an ethanol complex ($Mn_2(CO)_9(EtOH)$) is formed initially and that the addition of CH_3CN displaces the weakly coordinated alcohol ligand to give free EtOH. Further evidence in support of $Mn_2(CO)_9(EtOH)$ is presented below.

Along with the braod peaks discussed above and assigned to free and coordinated ethanol, two well-resolved quartets and accompanying triplets were also observed in the reaction of $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$ with $HMn(CO)_5$. These resonances are due to $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$. This assignment was confirmed by comparison of the IR and ^1H NMR spectra of $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$ from reaction 9 with those of an authentic sample.[16] The 44% yield of this Mn_3 cluster, together with the 41% yield of EtOH mentioned above, accounts for an 85% combined yield based on $CH_3Mn(CO)_5$.

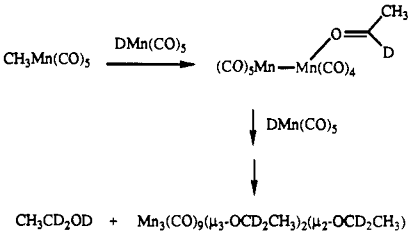


(9)

Deuterium-labeling experiments provided further confirmation of the formation of ethanol in the reaction of $CH_3Mn(CO)_5$ with $HMn(CO)_5$. The reaction of $CH_3Mn(CO)_5$ (0.20 M) with $DMn(CO)_5$ (1.0 M) in C_6D_6 gave $Mn_2(CO)_9(\eta^1\text{-}CH_3CDO)$ (61%) and free CH_3CDO (19%) along with unreacted $CH_3Mn(CO)_5$ (8%) after 24 h at room temperature. After 5.5 days, CH_3CN was added to displace coordinated aldehyde and alcohol. The organic products CH_3CDO and CH_3CD_2OD/CH_3CD_2OH were verified by ^1H NMR and by GC/MS. A complementary experiment was carried out with D labels in the methyl group: The reaction of $CD_3Mn(CO)_5$ (0.16 M, >99% D) and $HMn(CO)_5$ (1.0 M) was carried out for 5.5 days at room temperature, and the solution was then treated with CH_3CN. The volatile products CD_3CHO and CD_3CH_2OH were identified by ^1H NMR and by GC/MS. In both of these deuterium-labeling experiments, the ^1H NMR spectra verified the expected deuterium incorporation into the ethoxy groups of $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$, as shown in eq 10 and 11.

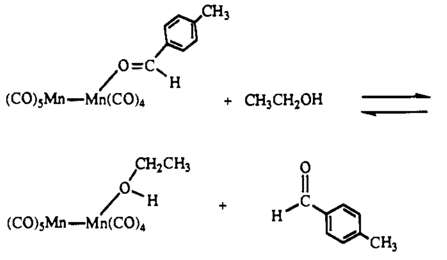


(10)



(11)

The data presented above provide evidence for an ethanol complex $Mn_2(CO)_9(EtOH)$ as one of the products from the reaction of $CH_3Mn(CO)_5$ with $HMn(CO)_5$. Additional supporting evidence for this alcohol complex comes from direct observation of the reversible reaction shown in eq 12. When EtOH was added to a C_6D_6 solution of $Mn_2(CO)_9(\eta^1\text{-tolualdehyde})$, the color of the solution turned from dark wine red to a lighter red-orange and resonances due to free tolualdehyde and coordinated CH_3CH_2OH were observed. The OH resonance of coordinated EtOH, which appeared as a triplet at δ 4.41, was absent in an analogous experiment carried out with CH_3CH_2OD. When the volatile components were evaporated on a vacuum line and C_6D_6 was readded, all of the peaks assigned to $Mn_2(CO)_9(EtOH)$ disappeared but the resonances for $Mn_2(CO)_9(\eta^1\text{-tolualdehyde})$ remained. This verifies that the reaction is reversible, since EtOH (bp 78 °C) is readily evaporated on the vacuum line along with the C_6D_6 solvent, whereas less volatile tolualdehyde (bp 204 °C) was not pumped off, but recoordinated to the manganese. A $K_{eq} \approx 0.4$ was determined for eq 12, indicating that the alcohol is even more weakly bound to the $Mn_2(CO)_9$ moiety than is the aldehyde. A stronger binding constant of aldehydes compared to alcohols was also found in cationic Re complexes studied by Gladysz and co-workers.[17] They recently reported that the benzyl alcohol ligand of $(Cp)Re(NO)(PPh_3)(PhCH_2OH)^+BF_4^-$ is displaced by benzaldehyde to produce $(Cp)Re(NO)(PPh_3)(\eta^2\text{-}PhCHO)^+BF_4^-$. Organometallic complexes with alcohol ligands are relatively rare, but there are a few examples of well-characterized cationic organometallic complexes with alcohol ligands.[18]



(12)

---

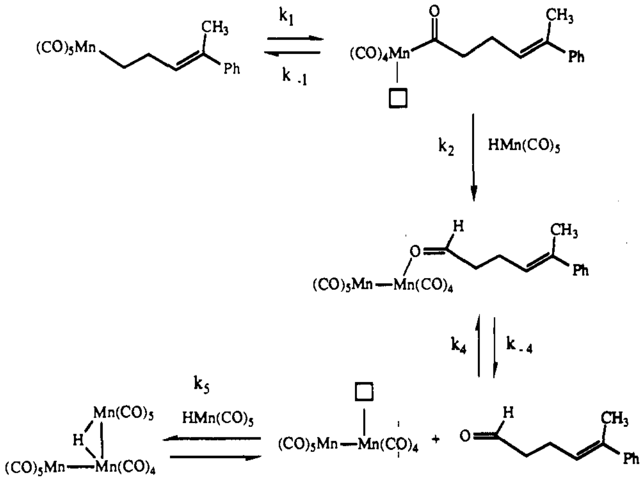
[15] It is not clear why the resonances for free ethanol are broadened, but rapid exchange of free and coordinated ethanol is ruled out by the fact that the coordinated ethanol resonances are well-resolved. We note that the resonances due to free aldehyde are also broadened compared to complexed aldehyde in these experiments. We considered the possibility that the alcohol and aldehyde were in rapid equilibrium with the hemiacetal, but this does not appear to be responsible for the broadening, since a C_6D_6 solution of *p*-tolulaldehyde and ethanol exhibited sharp resonances (in the absence of any Mn complexes), even in the presence of a trace of acid.

[16] (a) Abel, E. W.; Farrow, G.; Towle, I. D. H. *J. Chem. Soc., Dalton Trans.* **1979**, 71-73. (b) Abel, E. W.; Towle, I. D. H.; Cameron, T. S.; Cordes, R. E. *J. Chem. Soc., Dalton Trans.* **1979**, 1943-1949.

[17] Agbossou, S. K.; Smith, W. W.; Gladysz, J. A. *Chem. Ber.* **1990**, *123*, 1293-1299.

[18] Sünkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 231-240. (b) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994-7001. (c) Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1985**, *24*, 3898-3903.

Scheme II



In a control experiment, no hydrogenation of free acetaldehyde to ethanol was observed when a solution of CH_3CHO and a large excess of $HMn(CO)_5$ was kept at room temperature for 6 weeks.

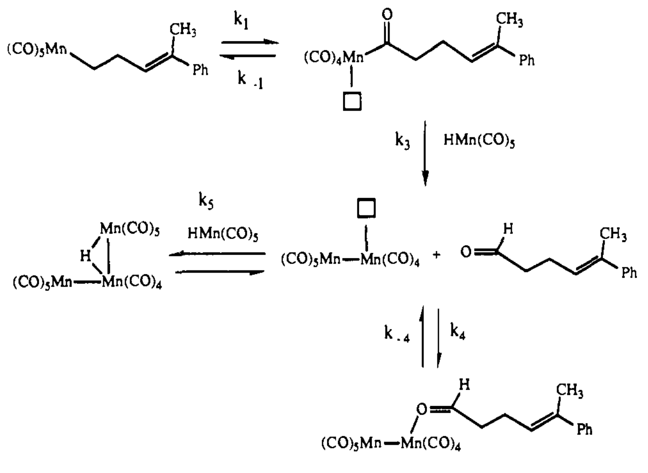
Discussion

Formation of η^1-Aldehyde Complexes in Dinuclear Elimination Reactions. The isolation of these $Mn_2(CO)_9(\eta^1$-aldehyde) complexes stands in marked contrast with several closely related reactions of metal alkyls and metal hydrides which give *free* aldehydes. Bergman and co-workers reported the formation of CH_3CHO from reaction of $CH_3Mo(CO)_3(C_5H_5)$ with $HMo(CO)_3(C_5H_5)$.[8e,f] Halpern and co-workers found that the reaction of (p-$CH_3OC_6H_4CH_2)Mn(CO)_5$ with $HMn(CO)_5$ in CH_3CN produced p-$CH_3OC_6H_4CH_2CHO$ and $Mn_2(CO)_9(CH_3CN)$.[8a,b] In both of these cases, kinetic and mechanistic evidence indicated that alkyl migration generated a coordinatively unsaturated acyl complex, which then formed the free aldehyde by reaction with the metal hydride. In the latter study, however, reactions of other closely related benzylmanganese complexes with manganese hydrides gave alkanes instead of aldehydes and several different mechanistic pathways were identified. Halpern called attention to the diversity of these reactions and noted that "relatively modest changes in ligands, solvent, or CO concentration may result in essentially complete crossover from one pathway to another."[8b] Our results provide additional support for this statement, since we observe $Mn_2(CO)_9(\eta^1$-aldehyde) complexes only when the reactions are carried out in nondonor solvents in the absence of CO. If the reactions are carried out in CH_3CN, or in benzene or hexane under CO, then only the free aldehyde is observed. In view of the considerable amount of previous work on reactions of metal alkyls with metal hydrides (and especially the seminal role that studies of alkyl migration reactions of $(CO)_5MnR$ complexes have played in the development of a detailed understanding of migratory insertion reactions), it is perhaps surprising that these $Mn_2(CO)_9(\eta^1$-aldehyde) complexes were discovered from the straightforward reaction of $(CO)_5MnR$ with $HMn(CO)_5$.

Norton and co-workers have found that rate constants for reaction of $EtRe(CO)_5$ with $HW(CO)_3Cp$, $HMn(CO)_5$, or $HRe(CO)_5$ (all of which give EtCHO) are the same and furthermore that the rate of these reactions is equal to the rate of migration of the ethyl group to form a Re acyl complex.[8d] A study of the kinetics of the reactions of several metal hydrides with the spectroscopically observable metal acyl complex $Et(C{=}O)Re(CO)_4(CH_3CN)$ indicated that the metal hydrides reacted as nucleophiles toward the solvated acyl intermediate. A quantitative scale of relative nucleophilicity of several metal hydrides was established from this work.

Formation of a coordinatively unsaturated metal acyl intermediate has been established as the initial step for the formation of *free* aldehydes in the reactions cited above. We propose that the mechanism of formation of the $Mn_2(CO)_9(\eta^1$-aldehyde) complexes involves migration[19] of the alkyl (or aryl) group to produce a coordinatively unsaturated manganese acyl intermediate, which then reacts with $HMn(CO)_5$ to produce the aldehyde complex (Schemes II and III; the empty square is used to represent a vacant coordination site). Applying the steady-state approximation to the intermediate acyl complex gives the rate law shown in eq 13. This rate law can give overall first-order, second-order,

Scheme III



$$\frac{d[Mn_2(ald)]}{dt} = \frac{k_1k_2[MR][MH]}{k_{-1} + k_2[MH]} = k_{obs}[MR] \qquad (13)$$

$$\text{where } k_{obs} = \frac{k_1k_2[MH]}{k_{-1} + k_2[MH]} \qquad (14)$$

or mixed kinetics depending on the relative magnitudes of the rate constants. In cases where $k_{-1} \gg k_2[MH]$, then $k_{obs} = (k_1k_2/k_{-1})[MH]$; the reaction rate will increase with increasing [MH], and the reaction will obey second-order kinetics. On the other hand, when $k_2[MH] \gg k_{-1}$, then $k_{obs} = k_1$, so the overall reaction is determined by the rate of alkyl migration and will be independent of [MH]. We suggest that the kinetic data summarized in Table I indicate that $k_2[MH] \gg k_{-1}$ in our reactions. However, the data in Table I show that the rate *increased* slightly with *decreasing* $[HMn(CO)_5]$. This unusual result is not predicted by the rate law and requires an additional explanation. We propose that, in each of our kinetic experiments, $k_{obs} \approx k_1$ but that the value of k_1 decreases slightly at higher $[HMn(CO)_5]$ due to a solvent effect. The high concentrations of $[HMn(CO)_5]$ used in these kinetics experiments cause the nature of the medium to vary considerably as $[HMn(CO)_5]$ is changed. For example, in the kinetics experiment with $[HMn(CO)_5] = 2.6$ M, the solution was 39% $HMn(CO)_5$ by volume. At the lower end of the concentrations used for the kinetics study ($[HMn(CO)_5] = 0.54$ M), the solution was only 9% $HMn(CO)_5$ by volume. As discussed below, large solvent effects on other migration reactions are commonly observed. The negligible isotope effect that we found from reaction of $(CO)_5MnR'$ with $HMn(CO)_5/DMn(CO)_5$ is also consistent with the interpretation that $k_{obs} \approx k_1$. The step involving M–H (D) bond cleavage (k_2 in Scheme II or k_3 in Scheme III) occurs after the rate-determining step, so any isotope effect on this step would not affect the observed kinetics.

The rate constant of $k_1 = (1-2) \times 10^{-4}$ s^{-1}, which we found in the reactions of $(CO)_5MnR'$, is significantly larger than the rate constant for methyl migration of $CH_3Mn(CO)_5$, which was reported to be $k = 2.18 \times 10^{-6}$ s^{-1} at 25.5 °C in mesitylene.[20] These relative rates conform to the general trend that ethyl and

---

[19] For reviews of CO insertion reactions, see: (a) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299–311. (b) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195–225. (c) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87–145. (d) Alexander, J. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds; John Wiley and Sons: New York, 1985; Vol. 2, pp 339–400.

[20] Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994–3999.

longer chain alkyl groups undergo alkyl migration reactions faster than methyl. For example, Calderazzo and Cotton found that the rate of migration for $EtMn(CO)_5$ was 13 times faster than that for $CH_3Mn(CO)_5$ (at 30 °C in 2,2'-dimethoxydiethyl ether).[21]

A common feature of alkyl migration reactions is that they proceed much faster in donor solvents. The rate of methyl migration of $CH_3Mn(CO)_5$ is $\sim 10^4$ times faster in dimethylformamide compared to mesitylene.[20] We find that the reaction of $(CO)_5MnR'$ with $HMn(CO)_5$ is markedly accelerated in acetonitrile compared to that in benzene. Wax and Bergman have studied the kinetics of the formation of $Cp(CO)_2(PMePh_2)MoCOCH_3$ from $Cp(CO)_3MoCH_3$ and $PMePh_2$ in THF and in several methyl-substituted THF solvents (i.e., solvents of comparable polarity but significantly different donor abilities).[22] The results of their study established that the solvent coordinates to the metal and assists the migratory CO insertion. Further clarification of the role of donor solvents in the promotion of migratory insertions was provided by Halpern and co-workers, who found that nucleophilic solvents not only catalyze the formation of coordinatively unsaturated acyl complexes but also dissociate prior to trapping by the metal hydride.[23]

It is possible that aldehyde complexes are unobserved intermediates in *all* of the reactions discussed above in which aldehydes are formed from metal alkyls and metal hydrides but that their high reactivity precludes their observation in the presence of sufficiently reactive nucleophiles. Aldehyde complexes may also be unobserved intermediates in the formation of free aldehydes in catalytic hydroformylations. Note that these manganese aldehyde complexes react rapidly with 1 atm of CO. Considering the generally higher reactivity observed for $(CO)_4CoR$ complexes compared to those for related $(CO)_5MnR$ compounds, it seems unlikely that analogous $Co_2(CO)_7(\eta^1\text{-aldehyde})$ complexes could be directly observable under the high pressures of CO typically utilized in catalytic hydroformylations.

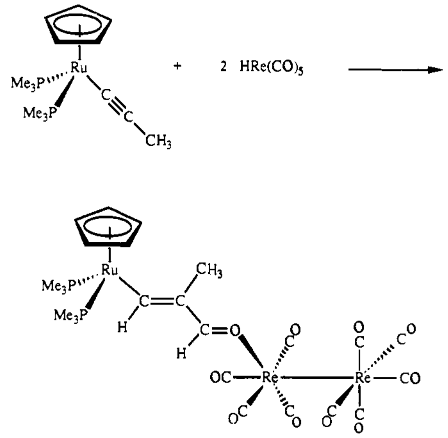
Although our results suggest that an aldehyde complex is the initially formed product, we cannot rigorously distinguish between the closely related mechanisms shown in Schemes II and III. In Scheme II, $Mn_2(CO)_9(\eta^1\text{-R'CHO})$ is formed directly in the step with rate constant k_2. The initially formed products in Scheme III are the free aldehyde and the coordinatively unsaturated intermediate $Mn_2(CO)_9$ (k_3, Scheme III). Both schemes have the alkyl migration (k_1) as the first step; similarly the steps with rate constants k_4 and k_5, which establish the equilibrium of eq 6, are the same in the two mechanisms. In principle, the mechansisms of Schemes II and III could be distinguished if the direction from which the equilibrium of eq 6 is approached could be determined, but experiments to distinguish between these possibilities are thwarted by the fact that the equilibrium of eq 6 is rapidly established under the experimental conditions. The rate of reaction of $Mn_2(CO)_9(\eta^1\text{-R'CHO})$ with CH_3CN is much faster than the rate of formation of the aldehyde complex. Since this aldehyde displacement probably proceeds by a dissociative mechanism involving the intermediacy of coordinatively unsaturated $Mn_2(CO)_9$, this implies that the k_4/k_{-4} equilibrium of Schemes II and III (as well as the overall equilibrium of eq 6) is rapidly established. The fact that K_{eq} for eq 6 (measured directly by NMR) remained constant over the course of the reaction also verifies that the equilibrium of eq 6 was rapidly established in all of our experiments. The data are therefore consistent with either direct formation of the aldehyde complex (k_2, Scheme II) or formation of the free aldehyde, which then coordinates to $Mn_2(CO)_9$ (k_4, Scheme III).

The change in the free to complexed aldehyde ratio (Figure 5) is explained by the equilibrium of eq 6. The increase in $[HMn_3(CO)_{14}]$ as the reaction proceeds drives the equilibrium of eq 6 to the left, resulting in a larger amount of complexed aldehyde at the end of the reaction compared to that at early reaction times.

Regardless of the detailed mechanism of formation of the $Mn_2(CO)_9(\eta^1\text{-aldehyde})$ complexes, our observation of facile displacement of the aldehyde ligand of the $Mn_2(CO)_9(\eta^1\text{-aldehyde})$ complexes by CH_3CN and other nucleophiles provides a plausible explanation of why these aldehyde complexes are isolable, whereas closely related experiments have led to the observation of only free aldehydes. A crucial factor in the successful isolation of the $Mn_2(CO)_9(\eta^1\text{-aldehyde})$ complexes is the lack of donors (such as CH_3CN), which bond to the coordinatively unsaturated intermediate $Mn_2(CO)_9$ more strongly than the aldehydes.

The trinuclear cluster complex $HMn_3(CO)_{14}$ can be considered to be comprised of $Mn_2(CO)_9$ with $HMn(CO)_5$ as a ligand. The bonding in the $Mn(\mu\text{-H})Mn$ bridge involves a 3-center, 2-electron interaction. The L-shaped geometry of the three Mn atoms depicted for $HMn_3(CO)_{14}$ is analogous to the structures of $HRe_2Mn(CO)_{14}$[24] and $HReMn_2(CO)_{14}$,[25] which have been established by crystallography. Warner and Norton reported that $HMnRe_2(CO)_{14}$ and CH_3CHO resulted from the reaction of $CH_3Mn(CO)_5$ with $HRe(CO)_5$ in benzene, whereas the same reaction in CH_3CN gave the free aldehyde and $(CO)_5ReMn(CO)_4(CH_3CN)$.[8c] We have found that $HRe(CO)_5$ reacts with $Mn_2(CO)_9(\eta^1\text{-}CH_3C_6H_4CHO)$ to produce $HReMn_2(CO)_{14}$ and free tolualdehyde.[25] The displacement of the η^1-aldehyde ligand by $HRe(CO)_5$ clearly indicates the thermodynamic preference of $HRe(CO)_5$ over an aldehyde, as a ligand on $Mn_2(CO)_9$. Since the value of $\Delta G° \approx 2.5$ kcal/mol for eq 6 indicates that the aldehyde bonds more strongly to $Mn_2(CO)_9$ than does $HMn(CO)_5$, the order of binding preference to the unsaturated $Mn_2(CO)_9$ moiety is established as $HRe(CO)_5 > \eta^1\text{-}CH_3C_6H_4CHO > HMn(CO)_5$.

We have recently reported the preparation of X-ray crystal structure of an unusual $Re_2(CO)_9(\eta^1\text{-aldehyde})$ complex, which was prepared by hydroformylation of the C≡C bond of $(C_5H_5)(PMe_3)_2Ru(C{\equiv}CCH_3)$ by $HRe(CO)_5$[26] (eq 15). In spite of the completely different synthetic procedures used to prepare them, there are some striking similarities between the Mn_2 and Re_2 aldehyde complexes. Both complexes contain an aldehyde η^1-bonded to a group 7 metal, and both are proposed to form by reaction of a metal hydride with a coordinatively unsaturated metal acyl intermediate.



(15)

Comparison of $Mn_2(CO)_9(\eta^1$-aldehyde) Complexes with Other Aldehyde Complexes. These $Mn_2(CO)_9(\eta^1\text{-aldehyde})$ complexes are rare examples of η^1-bonding of an aldehyde in a neutral organometallic complex, since most of the previously reported neutral aldehyde complexes of transition metals exhibit η^2-bonding.[1] In contrast, most of the previously reported cationic organometallic aldehyde complexes are η^1-bonded; examples in-

---

[21] Calderazzo, F.; Cotton, F. A. *Abstr. Int. Conf. Coord. Chem.* Stockholm, 1962; Paper 6H7 (cited on page 101 of ref 19c).

[22] Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028-7030.

[23] Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345-347.

[24] Churchill, M. R.; Bau, R. *Inorg. Chem.* **1967**, *6*, 2086-2092.

[25] Albinati, A.; Bullock, R. M.; Rappoli, B. J.; Koetzle, T. F. *Inorg. Chem.*, in press.

[26] Bullock, R. M.; Ricci, J. S.; Szalda, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 2741-2743.

clude $(Cp)(CO)_3Mo(\eta^1\text{-}PhCHO)^+$,[27] $(CO)_5Re(\eta^1\text{-}CH_3CHO)^+$,[27] $(NO)(PMe_3)(CO)_3W(\eta^1\text{-}CH_2{=}CHCHO)^+$,[3] $(PPh_3)_2(CO)Ir(\eta^1\text{-}CH_3CH{=}CHCHO)^+$,[28] and several $Cp(CO)_2Fe(\eta^1$-aldehyde$)^+$ complexes.[3,29] Since the choice of bonding mode is influenced by a metal's oxidation state and ligands as well as the overall charge, the trend of η^1-bonding for cationic aldehyde complexes vs η^2-bonding for neutral complexes is not an infallible rule but only a generalization based on the low oxidation state organometallic complexes studied to date. In contrast to the tendency of neutral metal carbonyl complexes in low oxidation states to favor η^2-bonding, aldehyde complexes of $TiCl_4$ and other "hard" metal centers in high oxidation states normally exhibit η^1-bonding for aldehydes.[1]

Recent studies have provided some insight into interconversions between η^2- and η^1-bonding modes of aldehydes and ketones. Gladysz and co-workers recently reported the equilibration of η^2- and η^1-isomers of the aromatic aldehyde complexes $(Cp)(NO)(PPh_3)Re(RCHO)^+$.[30] Taube and co-workers found that $(NH_3)_5Os(\eta^1\text{-}CH_3C({=}O)CH_3)^{3+}$ undergoes an $\eta^1 \rightarrow \eta^2$ isomerization upon one-electron reduction; the kinetics of the oxidatively induced $\eta^2 \rightarrow \eta^1$ isomerization of $(NH_3)_5Os(\eta^2\text{-}CH_3C({=}O)CH_3{}^{2+}$ were also reported.[31]

Hydrogenation of Aldehydes to Alcohols. The predominant reaction observed with the $Mn_2(CO)_9(\eta^1$-aldehyde) complexes is displacement of the weakly bound aldehyde ligand by CO, PPh_3, and nucleophilic solvents such as CH_3CN. In all of these cases, the free aldehyde is formed. These reactions contrast with the hydrogenation of the aldehyde ligand observed when $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$ or $Mn_2(CO)_9(\eta^1\text{-}R'CHO)$ undergoes further reaction with $HMn(CO)_5$. Hydrogenation of aldehydes to alcohols is commonly observed in catalytic hydroformylations.[7] The amount of aldehyde hydrogenation observed under catalytic conditions is a sensitive function of temperature, pressures of CO and H_2, etc. Alcohol formation is sometimes an undesired side reaction, but in other cases reaction conditions have been optimized to maximize the yield of alcohols. As clearly as 1962, an η^2-aldehyde complex $(HCo(CO)_3(\eta^2\text{-}RCHO))$ was proposed as an intermediate in the hydrogenation of aldehydes to alcohols catalyzed by $Co_2(CO)_8$.[32]

Bonding of an aldehyde to a transition metal (or main-group Lewis acid) activates the carbonyl group toward attack by hydride. Reetz and co-workers calculated a higher positive charge density on the carbonyl carbon of BF_3 adduct of acetaldehyde, compared to free acetaldehyde.[33] Gladysz and co-workers have demonstrated that hydride donation (from the formyl complex $(Cp)Re(NO)(PPh_3)CHO$) to optically active aldehyde complexes $(Cp)Re(NO)(PPh_3)(\eta^2\text{-}RCHO)^+$ results in clean conversion to optically active alkoxide complexes.[2] It is possible that the alcohol formed in our reactions of $Mn_2(CO)_9(\eta^1$-aldehyde) complexes results from initial hydride donation from $HMn(CO)_5$ to the η^1-aldehyde, giving an alkoxide complex that could be subsequently cleaved by 1 equiv of $HMn(CO)_5$ (acting in this case as a proton source) to produce the alcohol. We have shown that $HMn(CO)_5$ and other metal hydrides can function as efficient stoichiometric hydride donors to carbocations formed by protonation of certain hindered olefins.[34] However, this mechanistic probability is speculative, since we do not presently understand the details of the formation of the alcohols or of the cluster complex $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$. The formation of alcohol (and alkoxide) products from $Mn_2(CO)_9(\eta^1$-aldehyde) complexes is very slow, even in the presence of a large excess of $HMn(CO)_5$. The primary importance of the aldehyde hydrogenation in our system is due to its relevance to the formation of alcohols in the hydroformylation reaction, since it is not attractive or feasible as a method for synthesis of alcohols, especially in comparison to more efficient and widely applicable methods developed by others.

Summary and Conclusions

The reaction of $(CO)_5MnR$ (R = alkyl or aryl) with $HMn(CO)_5$ in noncoordinating solvents produces $Mn_2(CO)_9(\eta^1$-aldehyde) complexes. The aldehyde ligand is weakly bonded to the manganese, as evidenced by facile displacement by CO, PPh_3, CH_3CN, etc. The isolation of the aldehyde complexes in these reactions contrasts with previously reported reactions in which a dinuclear elimination reaction between metal alkyls and metal hydrides resulted in free aldehydes. It is suggested that the $Mn_2(CO)_9(\eta^1$-aldehyde) complexes may provide a model for previously unobserved intermediates in the formation of aldehydes from the hydroformylation of olefins.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of nitrogen or argon with use of Schlenk or vacuum-line techniques or in a Vacuum Atmospheres drybox. NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz for ^1H). IR spectra were recorded on a Mattson Polaris FT-IR spectrometer or a Nicolet MX-1 spectrometer with CaF_2 cells. Toluene, THF, Et_2O, and hexane were distilled under nitrogen from Na/benzophenone. C_6D_6 was dried over NaK, stored over $(Cp_2TiCl)_2Zn(Cl)_2$,[35] and vacuum-transferred into the NMR tubes. $Ph(CH_3)C{=}CHCH_2CH_2Br$ was prepared as reported previously.[10] $(p\text{-}CH_3C_6H_4)Mn(CO)_5$[36a] was prepared according to the general procedure reported by Stewart and Treichel[36b] for $(p\text{-}XC_6H_4)Mn(CO)_5$ compounds. Elemental analyses were carried out by Galbraith or Schwarzkopf Laboratories. $HMn(CO)_5$ was prepared by a published procedure[8c] and purified by vacuum transfer from P_2O_5 several times. This hydride was stored under vacuum at −20 °C in the dark and vacuum-transferred immediately prior to each use. $CH_3Mn(CO)_5$ and $CD_3Mn(CO)_5$ were prepared by M. A. Andrews for an earlier work.[37] $Cr(acac)_3$ (0.07 M) was used in ^{13}C NMR spectra as a relaxation agent.[38] ^{13}C NMR spectra of Mn carbonyl complexes were carried out at low temperature ("thermal decoupling")[39] in order to minimize line-broadening effects from the ^{55}Mn ($I = {}^5/_2$) quadrupole. EtOD (Aldrich) was used as received.

$Ph(CH_3)C{=}CHCH_2CH_2CO_2H$. A solution of $Ph(CH_3)C{=}CHCH_2CH_2Br$ (6.0 g, 0.027 mol) in Et_2O (60 mL) was added dropwise to a flask containing Mg (0.94 g, 0.039 mol). The mixture was refluxed for 1 h and then treated with an excess of gaseous CO_2. A saturated aqueous solution (10 mL) of NH_4Cl was added, followed by addition of dilute aqueous HCl (30 mL). The product was extracted into Et_2O. This organic solution was then extracted with aqueous NaOH, and the basic solution was neutralized with HCl. This aqueous solution was extracted with Et_2O, and the Et_2O solution was dried ($MgSO_4$). The Et_2O was removed by evaporation, and recrystallization from hexane gave $Ph(CH_3)C{=}CHCH_2CH_2CO_2H$ as a white solid. Yield: 2.78 g (0.0146 mol, 55% unoptimized). ^1H NMR (C_6D_6): δ 11.5 (br s, 1 H, CO_2H), 7.3–7.1 (m, 5 H, aromatic), 5.58 (tq, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 1.3$ Hz, 1 H, $C{=}CH$), 2.28 (q, $J = 7$ Hz, 2 H, $C{=}CHCH_2$), 2.13 (m, 2 H, CH_2CO_2H), 1.81 (m, 3 H, CH_3).

$ClCOCH_2CH_2CH{=}C(Ph)CH_3$. $SOCl_2$ (2.6 mL, 0.069 mol) was added to $Ph(CH_3)C{=}CHCH_2CH_2CO_2H$ (1.27 g, 6.68×10^{-3} mol). No solvent (other than $SOCl_2$) was used, and throughout this reaction N_2 was bubbled through the reaction mixture in order to remove the HCl that is formed. (If the HCl is not removed, it adds to the C=C bond and the saturated acyl chloride $ClCO(CH_2)_3C(Cl)(Ph)CH_3$ results.) After the solution was stirred at room temperature for 30 min, additional

---

[27] Appel, M.; Sacher, W.; Beck, W. *J. Organomet. Chem.* **1987**, *322*, 351–356.

[28] Yang, K. J.; Chin, C. S. *Inorg. Chen.* **1987**, *26*, 2732–2733.

[29] (a) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253–265. (b) Schmidt, E. K. G.; Thiel, C. H. *J. Organomet. Chem.* **1981**, *209*, 373–384.

[30] Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A., submitted for publication. We thank Prof. Gladysz for a preprint of this paper.

[31] Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439–2445.

[32] (a) Markó, L. *Proc. Chem. Soc.* **1962**, 67–68. (b) Aldridge, C. L.; Jonassen, H. B. *J. Am. Chem. Soc.* **1963**, *85*, 886–891.

[33] Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405–2408.

[34] Bullock, R. M.; Rappoli, B. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1447–1448.

[35] Sekutowski, D. G.; Stucky, G. D. *Inorg. Chem.* **1975**, *9*, 2192–2199.

[36] (a) Beck, W.; Hieber, W.; Tengler, H. *Chem. Ber.* **1961**, *94*, 862–872. (b) Stewart, R. P.; Treichel, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2710–2718.

[37] Andrews, M. A.; Eckert, J.; Goldstone, J. A.; Passell, L.; Swanson, B. *J. Am. Chem. Soc.* **1983**, *105*, 2262–2269.

[38] (a) Gansow, O. A.; Burke, A. R.; LaMar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456–457. (b) Levy, G. C.; Cargioli, J. D. *J. Magn. Reson.* **1973**, *10*, 231–234.

[39] Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *80*, C31–C34.

$SOCl_2$ (2.4 mL) was added. After the solution was stirred for an additional 1 h, the volatiles were removed by evaporation, leaving $ClCOCH_2CH_2CH{=}C(Ph)CH_3$ as an amber liquid (1.42 g, ~100% crude yield). Further purification can be accomplished by distillation (95 °C, 0.1 mmHg) to give the product as a clear liquid. ^1H NMR ($CDCl_3$): δ 7.4–7.2 (m, 5 H, aromatic), 5.66 (tq, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.3$ Hz, 1 H, $C{=}CH$), 3.02 (t, $J = 7.3$ Hz, 2 H, $ClCOCH_2$), 2.59 (q, $J = 7.3$ Hz, 2 H, $ClCOCH_2CH_2$), 2.06 (singlet with some unresolved fine structure, 3 H, CH_3).

$(CO)_5Mn(COCH_2CH_2CH{=}C(Ph)CH_3)$. A solution of $Mn_2(CO)_{10}$ (1.29 g, 3.31×10^{-3} mol) in THF (15 mL) was treated with NaK (0.4 g) and stirred at room temperature for 90 min to give $[Mn(CO)_5]^-$. The solution was filtered through Celite, and the volume was reduced to about 2 mL by evaporation of the THF. Et_2O (20 mL) was added, and the solution was cooled to −78 °C and treated with a solution of $ClCOCH_2CH_2CH{=}C(Ph)CH_3$ (1.29 g, 6.18×10^{-3} mol) in Et_2O (2 mL). This solution was stirred at −78 °C for 30 min, followed by warming to −15 °C and stirring for 1 h more to give a yellow suspension. The solvent was evaporated, and the yellow-orange solid was crystallized from CH_2Cl_2/hexane to give a pale yellow solid (2.048 g, 90% yield). Further purification can be carried out by flash chromatography on silica gel with 1:2 CH_2Cl_2/hexane. ^1H NMR (C_6D_6): δ 7.3–7.1 (m, 5 H, aromatic), 5.64 (t, $J = 7$ Hz, 1 H, $C{=}CH$), 2.77 (t, $J = 7.1$ Hz, 2 H, $MnCOCH_2$), 2.31 (q, $J = 7.1$ Hz, 2 H, $MnCOCH_2CH_2$), 1.86 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −43 °C): δ 247.4 (s, acyl CO), 209.2 (s, equatorial $Mn(CO)_4$), 208.0 (s, axial $Mn(CO)$), 142.9, 134.8, 126.3, 126.1 (s, ipso and para and both $C{=}C$), 127.8, 125.0 (ortho and meta), 66.2 (s, $MnCOCH_2$), 23.6 (s, $MnCOCH_2CH_2$), 15.1 (s, CH_3). IR (CH_2Cl_2): 2115 w, 2051 w, 2011 s, 1642 w (acyl) cm^{-1}. Anal. Calcd for $C_{17}H_{13}MnO_6$: C, 55.45; H, 3.56. Found: C, 55.42; H, 3.58.

$(CO)_5Mn(CH_2CH_2CH{=}C(Ph)CH_3)$. A solution of $(CO)_5Mn(COCH_2CH_2CH{=}C(Ph)CH_3)$ (0.503 g, 1.37×10^{-3} mol) in Et_2O (25 mL) was refluxed for 5.5 h. The solvent was evaporated, and the residue was extracted with hexane and filtered. The hexane was evaporated to give a yellow-white solid (0.420 g, 90% yield). Sublimation (50 °C, 10^{-5} Torr) gave a white solid. ^1H NMR (CD_2Cl_2) δ 7.5–7.1 (m, 5 H, aromatic), 5.90 (1 H, $C{=}CH$), 2.57 (2 H, $MnCH_2CH_2$), 2.06 (3 H, CH_3), 1.11 (2 H, $MnCH_2$); see Figure 2 for spectra. $^{13}C\{^1H\}$ NMR (toluene-d_8, −40 °C): δ 213.8 (s, equatorial $Mn(CO)_4$), 210.2 (s, axial $Mn(CO)$), 35.7 (s, $MnCH_2CH_2$), 15.5 (s, CH_3), 5.8 (s, $MnCH_2$), aromatic and $C{=}C$ resonances obscured by the toluene solvent peaks. IR (cyclohexane): 2105 w, 2006 s, 1989 m cm^{-1}. Anal. Calcd for $C_{16}H_{13}MnO_5$: C, 56.49; H, 3.85. Found: C, 56.59; H, 3.80.

$Mn_2(CO)_9(\eta^1\text{-}HCOC_6H_4CH_3)$. ($p$-$CH_3C_6H_4)Mn(CO)_5$ (0.930 g, 3.25×10^{-3} mol) was dissolved in methylcyclopentane (10 mL), and $HMn(CO)_5$ (0.676 g, 3.45×10^{-3} mol) was added by vacuum transfer. After 32 h at room temperature, the solution was dark wine red with a small amount of orange precipitate. Cooling to −35 °C produced red-orange crystals, which were collected by filtration and dried under vacuum. Yield: 1.25 g (2.59×10^{-3} mol, 80%). ^1H NMR (C_6D_6): δ 8.91 (s, CHO), 6.93, 6.56 (AA′XX′, J(apparent) = 8.0 Hz, 4 H, ortho and meta), 1.77 (s, CH_3). $^{13}C\{^1H\}$ NMR (toluene-d_8, −40 °C): δ 226.4 (s, 2 $Mn(CO)$), 223.0 (5 $Mn(CO)$), 216.0 (2 $Mn(CO)$), 204.5 (aldehyde CO), 148.6 (s, ipso), 131.8, 130.0 (s, ortho and meta), other aromatic C obscured by toluene solvent resonances, 21.9 (s, CH_3). IR (hexane): 2089 w, 2023 s, 2003 m, 1992 s, 1981 s, 1974 m, 1974 m, 1966 m, 1939 w, 1635 w cm^{-1}. UV–vis (cyclohexane): λ_{max} 340 nm ($\epsilon = 1.5 \times 10^4$ M^{-1} cm^{-1}), 470 (5.5×10^3). Anal. Calcd for $C_{17}H_8Mn_2O_{10}$: C. 42.35; H, 1.67; Mn, 22.8. Found: C, 42.24; H, 1.60; Mn, 22.5.

$Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$. $CH_3Mn(CO)_5$ (0.673 g, 3.20×10^{-3} mol) was dissolved in hexane (18 mL), and $HMn(CO)_5$ (0.617 g, 3.15×10^{-3} mol) was added by vacuum transfer. After 50 h at room temperature, the solution was dark wine red with a light orange precipitate. The volatiles were removed by evaporation, and the light orange product was washed with hexane (2 × 5 mL) and dried under vacuum to give an orange powder. Yield: 0.635 g (1.56×10^{-3} mol, 50%). ^1H NMR (C_6D_6): δ 7.91 (br s, 1 H, CHO), 0.84 (br s, 3 H, CH_3). The ^1H NMR resonances appear at slightly different chemical shifts for the isolated aldehyde complex compared to those of the same complex prepared in an NMR tube from $(CH_3)Mn(CO)_5$ (~0.3 M) and excess $HMn(CO)_5$. When prepared in the NMR tube in concentrated solutions, the resonances appear at δ 8.18 and δ 1.06. IR (hexane): 2092 w, 2024 s, 2005 m, 1995 s, 1982 s. 1974 m, 1970 m, 1946 sh w, 1940 w, 1678 w cm^{-1}. Anal. Calcd for $C_{11}H_4Mn_2O_{10}$: C. 32.54; H, 0.99. Found: C, 32.90; H, 1.46.

$Mn_2(CO)_9(\eta^1\text{-}HCOCH_2CH_2CH{=}C(Ph)CH_3)$. This aldehyde complex was isolated in 50–70% yield from the ring-opening hydroformylation reaction (eq 2) carried out in hexane at 7 °C. Details of this preparation will be published separately, including the precise procedures required for $HMn(CO)_5$ in order to ensure the reproducibility of the ring-opening hydroformylation reaction. Spectroscopic data are provided here for comparison with the other aldehyde complexes. ^1H NMR (C_6D_6): δ 8.47 (s, 1 H, CHO), 5.13 (t, $J = 7$ Hz, 1 H, $C{=}CH$), 1.75 (q, partially overlapped with methyl singlet at δ 1.72, $J = 7$ Hz, 2 H, $C{=}CHCH_2$), 1.72 (s, CH_3), 1.54 (t, $J = 7$ Hz, 2 H, CH_2CHO). $^{13}C\{^1H\}$ NMR (toluene-d_8, −40 °C): δ 226.8 (s, 2 $Mn(CO)$), 222.9 (s, 5 $Mn(CO)$), 219.4 (s, 1 $Mn(CO)$), 216.2 (s, 1 $Mn(CO)$), 215.7 (s, CHO), 142.9 (s, ipso), 124.0 (aromatic or alkene carbon, remainder of the aromatic and alkene carbons obscured by the solvent resonances), 44.8 (s, CH_2CHO), 25.3 (s, $C{=}CHCH_2$), 15.6 (s, CH_3). IR (hexane): 2091 w, 2024 s, 2005 m, 1993 s, 1982 s, 1974 m, 1974 m, 1968 m, 1945 w sh, 1939 w, 1675 w cm^{-1}. UV–vis (cyclohexane): λ_{max} 340 nm ($\epsilon = 1.1 \times 10^4$ M^{-1} cm^{-1}), 462 (2.2×10^3). Anal. Calcd for $C_{21}H_{14}Mn_2O_{10}$: C, 47.04; H, 2.63. Found: C, 46.82; H, 2.80.

$Ph(CH_3)C{=}CHCH_2CH_2CH_2OH$. Et_2O (20 mL) and $LiAlH_4$ (6.0 mL of a 1.0 M THF solution, Aldrich) were added to a three-neck flask, which was fitted with a reflux condenser and a dropping funnel containing $Ph(CH_3)C{=}CHCH_2CH_2CO_2H$ (1.07 g, 5.6×10^{-3} mol) in Et_2O (20 mL). The solution of the carboxylic acid was added dropwise to the $LiAlH_4$ over 10 min, at a rate that maintained the solution at reflux. After the solution was stirred for an additional 2 h, the reaction was quenched with EtOAc (2 mL) followed by isopropyl alcohol (2 mL). Water (50 mL) was added, and the reaction mixture was extracted with Et_2O (3 × 30 mL). The organic layer was separated, dried ($MgSO_4$), and evaporated to give a colorless liquid (0.913 g, 93% crude yield). The alcohol was further purified by thin-layer radial chromatography (Chromatotron Model 7924, Harrison Research, Inc.) with CH_2Cl_2 on silica gel. Yield: 0.615 g (3.49×10^{-3} mol, 62%). ^1H NMR (C_6D_6): δ 7.34–7.07 (m, 5 H, aromatic), 5.73 (tq, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 1.3$ Hz, 1 H, $C{=}CH$), 3.34 (t, $J = 6.4$ Hz, 2 H, CH_2OH), 2.12 (q, $J = 7$ Hz, 2 H, $C{=}CHCH_2$), 1.90 (d, $J \approx 1$ Hz, 3 H, CH_3), 1.47 (apparent quintet, $J \approx 7$ Hz, 2 H, $CH_2CH_2CH_2$), 0.72 (br s, 1 H, OH).

NMR Line Simulation. Line-simulation calculations were carried out on the Aspect 3000 computer of the Bruker NMR spectrometer with use of the iterative line-simulation program PANIC. Proton labels are as follows: $MnCH_AH_BCH_CH_DCH_E{=}C[C(H_F)_3]Ph$. Chemical shifts (Hz) are the following: $\delta(H_A)$ 333.7, $\delta(H_B)$ 334.7, $\delta(H_C)$ 772.2, $\delta(H_D)$ 769.3, $\delta(H_E)$ 1772.2, and $\delta(H_F)$ 617.7. J_{HH} values (Hz) are the following: $^2J(A,B) = 15.4$, $^3J(A,C) = {}^3J(B,D) = 5.1$, $^3J(A,D) = {}^3J(B,C) = 12.0$, $^4J(A,E) = 0.3$, $^4J(B,E) = 0.5$, $^2J(C,D) = 11.5$, $^3J(C,E) = 7.0$, $^5J(C,F) = {}^5J(D,F) = 0.6$, $^3J(D,E) = 7.6$, and $^4J(E,F) = 1.3$.

General Procedure for Reactions Carried Out in NMR Tubes. Reactions between $(CO)_5MnR$ and $HMn(CO)_5$, which were carried out in NMR tubes, were prepared by adding a measured quantity of $(CO)_5MnR$ and an internal NMR integration standard (bibenzyl or 1,4-bis(trimethylsilyl)benzene) to an NMR tube in the glovebox. The NMR tubes were either joined to a stopcock so that they could be sealed off with a flame on the vacuum line or connected to a Teflon valve directly on the top of the tube (NMR tubes with J. Young valves purchased from Wilmad Glass Co.). The NMR tube was then removed from the glovebox and attached to a high-vacuum line, and C_6D_6 was added by vacuum transfer. In some experiments, the height of the solution was measured at this point (i.e., prior to addition of $HMn(CO)_5$) so that the percent volume of $HMn(CO)_5$ could be subsequently determined. The volume of the solution was calculated from the height of the solution in the NMR tube with a published formula.[40] The $HMn(CO)_5$ was then added by vacuum transfer, and the tube was either flame-sealed or sealed by closing the Teflon valve. Tubes were generally kept at −196 °C and thawed immediately prior to measuring the initial NMR spectrum. Spectra were measured over the couse of the reaction and integrated vs the internal standard.

Kinetics of the Reaction of $(CO)_5MnR'$ with $HMn(CO)_5$. NMR tubes were prepared as described above, with 10–11 mg of $(CO)_5MnR'$ in each experiment. The percent volume of $HMn(CO)_5$ varied from 9% for $[HMn(CO)_5] = 0.535$ M to 39% by volume for the kinetic run at $[HMn(CO)_5] = 2.6$ M. The reactions were monitored by ^1H NMR at 25 °C. Pseudo-first-order rate constants were determined from the slope of plots of ln $([(CO)_5MnR']_t/[(CO)_5MnR']_0)$ vs time. A sample plot is shown in Figure 4. The ratio of free to complexed aldehyde changed as the reaction proceeded (see Figure 5). After the completion of the kinetics experiments, the tubes were removed from the NMR spectrometer and kept at room temperature in the dark for 3–5 days. Another ^1H NMR spectrum was then taken to determine the yield of $Ph(CH_3)C{=}CHCH_2CH_2CH_2OH$.

Determination of K_{eq} for Eq 6. With use of the general procedure outlined above, $(CO)_5MnR'$ (10.9 mg, 3.2×10^{-5} mol) and an internal integration standard (1,4-bis(trimethylsilyl)benzene) were added to an

---

(40) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805–4813.

NMR tube. C_6D_6 and $HMn(CO)_5$ (77 mg, 3.9×10^{-4} mol) were added by vacuum transfer, giving a solution that had a total volume of 0.49 mL and initial concentrations of $[(CO)_5MnR'] = 0.065$ M and $[HMn(CO)_5] = 0.80$ M. The tube was frozen at −196 °C and then thawed and placed in an NMR probe at 8 °C. The approximate pseudo-first-order rate constant for the reaction was $k = 2.1 \times 10^{-5}\ s^{-1}$. A plot of $[Mn_2(CO)_9(\eta^1\text{-}R'CHO)]$/[total aldehyde] similar to that shown in Figure 5 was obtained. The equilibrium constant for eq 6 is $K_{eq} = ([R'CHO][HMn_3(CO)_{14}])/([Mn_2(CO)_9(\eta^1\text{-}R'CHO)][HMn(CO)_5])$. Since the stoichiometry of eq 6 requires that $[HMn_3(CO)_{14}] = [R'CHO]$ at all times, it proved more convenient (and accurate) experimentally to measure the equilibrium constant as $K_{eq} = [R'CHO]^2/([Mn_2(CO)_9(\eta^1\text{-}R'CHO)][HMn(CO)_5])$. (Separate measurements with integrated values for $[HMn_3(CO)_{14}]$ gave similar values of K_{eq}. In most experiments, a large excess of $HMn(CO)_5$ was used so $[HMn(CO)_5]$ did not change appreciably during the course of the reaction and the concentrations of free and complexed aldehydes were readily measured by ^1H NMR integration). In this experiment, the K_{eq} determined from 12 data points collected during the first half-life of the reaction was equal within experimental error to the K_{eq} determined from data points taken after 3–5 half-lives. The average K_{eq} determined at 8 °C was $K_{eq} = 1.1\ (\pm 0.2) \times 10^{-2}$.

Isotope Effect Determination for the Reaction of $(CO)_5MnR'$ with $HMn(CO)_5/DMn(CO)_5$. With use of the general procedure outlined above, $(CO)_5MnR'$ (9.1 mg, 2.7×10^{-5} mol) and an internal integration standard (1,4-bis(trimethylsilyl)benzene) were added to an NMR tube. C_6D_6, $HMn(CO)_5$ (72 mg, 3.7×10^{-4} mol), and $DMn(CO)_5$ (69 mg, 84% D) were added by vacuum transfer. Taking account of the percent D in the $DMn(CO)_5$ and the volume of the the solution, the initial concentrations were determined to be $[(CO)_5MnR']_0 = 0.05$ M, $[HMn(CO)_5]_0 = 0.81$ M, and $[DMn(CO)_5]_0 = 0.56$ M. Three spectra were taken over the course of the reaction (when the reaction was 54, 85, and 100% complete). From each of these spectra, the amount of H in the aldehyde C*H*O position was determined (vs the vinyl H of the aldehyde) for both the free and complexed aldehyde. This gave six separate measurements of the isotope effect. The average of these six determinations indicated that $k_H/k_D = 1.04 \pm 0.09$.

Reaction of $CH_3Mn(CO)_5$ with $HMn(CO)_5$. With use the general procedure outlined above, $CH_3Mn(CO)_5$ (37.7 mg, 1.79×10^{-4} mol) and bibenzyl (9.8 mg, internal migration standard) were added to an NMR tube. C_6D_6 and $HMn(CO)_5$ were added by vacuum transfer. Initial concentrations were $[CH_3Mn(CO)_5] = 0.35$ M and $[HMn(CO)_5] = 1.8$ M. Comparison of the volume of the tube before and after addition of $HMn(CO)_5$ indicated that the solution was 33% $HMn(CO)_5$ by volume. After 21 h at room temperature, the solution was dark wine red and ^1H NMR integration indicated $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$ (72% yield), free CH_3CDO (21% yield), and unreacted $CH_3Mn(CO)_5$ (~1%). After 70 h, the yields had decreased to 36% $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$ and 13% free CH_3CHO. After 7 days, both of these compounds were nearly completely consumed and two very broad, overlapping resonances were observed at δ 3.62 and 3.33 in about a 1:3 intensity ratio. Addition of CH_3CN (10 μL, 0.4 M) resulted in the coalescence of these resonances to a single broad resonance at δ 3.42. This resonance is assigned to the CH_2 group of ethanol; the yield of ethanol was 41%. Further support for this assignment comes from the increase in the intensity of this peak (as well as the peak at δ 1.01 assigned to the methyl group of ethanol) when ethanol (15 μL) was added. Along with the broad peaks noted above and assigned to free and coordinated ethanol, two quartets (δ 4.25, 3.04, J = 6.8 Hz) and accompanying triplets (δ 1.43, 1.16) were also observed in the reaction of $Mn_2(CO)_9(\eta^1\text{-}CH_3CHO)$ with $HMn(CO)_5$. These resonances are due to $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$. This assignment was confirmed by comparison of the IR and ^1H NMR spectra of $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$ from reaction 9 with those of this compound prepared by a known route.[16] The 44% yield of this Mn_3 cluster, together with the 41% yield of EtOH mentioned above, accounts for an 85% combined yield based on $CH_3Mn(CO)_5$.

Reaction of $CH_3Mn(CO)_5$ with $DMn(CO)_5$. With use of the general procedure outlined above, $CH_3Mn(CO)_5$ (23.5 mg, 1.12×10^{-4} mol) and 1,4-bis(trimethylsilyl)benzene (3.4 mg) were added to an NMR tube. C_6D_6 and $DMn(CO)_5$ (84% D) were added by vacuum transfer. Initial concentrations were $[CH_3Mn(CO)_5] = 0.20$ M and $[DMn(CO)_5] = 1.0$ M. Comparison of the volume of the tube before and after addition of $DMn(CO)_5$ indicated that the solution was 20% $DMn(CO)_5$ by volume. After 24 h at room temperature, the solution was dark wine red and ^1H NMR integration of the methyl groups (vs the 1,4-bis(trimethylsilyl)benzene internal standard) indicated $Mn_2(CO)_9(\eta^1\text{-}CH_3CDO)$ (δ 0.95, 61% yield), free CH_3CDO (δ 1.40, 19% yield), and unreacted $CH_3Mn(CO)_5$ (δ 0.21, 8%). At t = 5.5 days, the color of the solution was orange; CH_3CN (7 μL) was added to displace coordinated aldehyde and alcohol, and the solution turned lighter orange. The methyl resonance of CH_3CDO was observed at δ 1.40, and that of CH_3CD_2OD was observed at δ 0.95. Singlets at δ 1.43 and 1.12 were observed for the CH_3 groups of $Mn_3(CO)_9(\mu_3\text{-}OCD_2CH_3)_2(\mu_2\text{-}OCD_2CH_3)$. The CH_3CDO and CH_3CD_2OD/CH_3CD_2OH were also identified by GC/MS.

Reaction of $CD_3Mn(CO)_5$ with $HMn(CO)_5$. With use of a procedure analogous to that described above, a C_6D_6 solution of $CD_3Mn(CO)_5$ (20.6 mg, 9.67×10^{-5} mol; >99% D; initial concentration 0.16 M) and $HMn(CO)_5$ (initial concentration 1.0 M) was prepared in an NMR tube. After 24 h, an NMR spectrum of the dark wine red solution indicated a 1:2.7 ratio of free CD_3CHO (δ 9.20, br) to $Mn_2(CO)_9(\eta^1\text{-}CD_3CHO)$ (δ 8.05). After a total of 5.5 days at room temperature in the dark, the intensity of the resonances due to CD_3CHO and $Mn_2(CO)_9(\eta^1\text{-}CD_3CHO)$ had decreased; singlets observed at δ 4.22 and 3.00 are assigned to $Mn_3(CO)_9(\mu_3\text{-}OCH_2CD_3)_2(\mu_2\text{-}OCH_2CD_3)$. Addition of CH_3CN (7 μL) caused a slight color change from medium orange to a lighter orange. The volatile components were vacuum-transferred to another NMR tube, and the ^1H NMR spectrum exhibited resonances for $CD_3C\mathit{H}O$ (δ 9.17) and $CD_3C\mathit{H}_2OH$ (δ 3.33, s). The presence of CD_3CHO and CD_3CH_2OH was also confirmed by GC/MS.

Reaction of $Mn_2(CO)_9(\eta^1\text{-}HCOC_6H_4CH_3)$ with EtOH and EtOD. $Mn_2(CO)_9(\eta^1\text{-}HCOC_6H_4CH_3)$ (13.5 mg, 2.80×10^{-5} mol), internal standard (1,4-bis(trimethylsilyl)benzene), and C_6D_6 were added to a screw-cap NMR tube. When EtOH (~5.5 equiv) was added, the dark wine red solution of the aldehyde complex turned to a lighter red-orange color and integration of free and complexed alcohol and aldehyde indicated $K_{eq} \approx 0.4$. Resonances for $Mn_2(CO)_9(CH_3CH_2OH)$ are as follows: δ 4.14 (t, J = 5.3 Hz, 1 H, OH), 3.00 (apparent quintet, $J \approx 6.6$ Hz, 2 H, CH_2), 0.70 (t, J = 6.9 Hz, 3 H, CH_3). In a similar experiment with CH_3CH_2OD, resonances assigned to coordinated CH_3CH_2OD were observed at δ 3.05 (q, J = 7 Hz, 2 H, CH_2), 0.76 (t, J = 7 Hz, 3 H, CH_3).

Preparation of $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$. This Mn_3 cluster was prepared in 53% yield from the reaction of $BrMn(CO)_5$ with EtOH and NEt_3 via the published procedure.[16] ^1H NMR (C_6D_6): δ 4.20 (q, J = 6.8 Hz, 2 H, $\mu_2\text{-}OC\mathit{H}_2CH_3$), 2.95 (q, J = 6.8 Hz, 4 H, $\mu_3\text{-}OC\mathit{H}_2CH_3$), 1.37 (t, J = 6.8 Hz, 3 H, $\mu_2\text{-}OCH_2C\mathit{H}_3$), 1.07 (t, J = 6.8 Hz, 6 H, $\mu_3\text{-}OCH_2C\mathit{H}_3$). ^1H NMR ($CDCl_3$): δ 4.53 (q, J = 6.9 Hz, 2 H, $\mu_2\text{-}OC\mathit{H}_2CH_3$), 3.47 (q, J = 6.9 Hz, 4 H, $\mu_3\text{-}OC\mathit{H}_2CH_3$), 1.61 (t, J = 6.9 Hz, 3 H, $\mu_2\text{-}OCH_2C\mathit{H}_3$), 1.47 (t, J = 6.9 Hz, 6 H, $\mu_3\text{-}OCH_2C\mathit{H}_3$). The IR spectrum (hexane) of this authentic material was identical with the spectrum of $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$ that was prepared from the reaction of $CH_3Mn(CO)_5$ with $HMn(CO)_5$; these observed IR bands agree (±2 cm^{-1}) with those reported previously.[16]

Acknowledgment. This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH0016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. We gratefully acknowledge Dr. Edward Samsel for preparation of the $Ph(CH_3)C{=}CHCH_2CH_2CO_2H$ and for other preliminary experiments on this project. We thank Drs. Mark Andrews, George Gould, and Frederick Lemke for helpful suggestions.