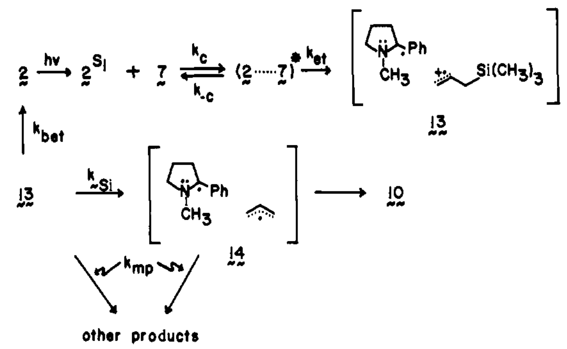
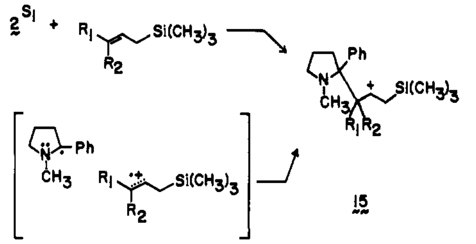
Scheme II



Scheme III



$\infty)\phi_{dis}$ and rate constant for disappearance of **2** are represented by $\alpha = k_{Si} + k_{mp})/(k_{bet} + k_{Si} + k_{mp})$ and k_{dis}, respectively. Thus, the ratio of the intercept to slope from a plot of ϕ_{dis}^{-1} vs. $[7]^{-1}$ found to be 3.4 ± 0.6 M^{-1} is equal to $k_{dis}\tau_0/\alpha$. The slope of $k_q\tau_0$ obtained from the Stern–Volmer plot of fluorescence quenching data is experimentally 3.8 ± 0.1 M^{-1} and mathematically $k_{dis}\tau_0/\alpha$. Thus, the close agreement of the quantities obtained from these separate experiments suggests that fluoresence quenching and photoreaction are kinetically coupled and, thus, that photoaddition is a singlet excited-state process of **2**. ϕ_{dis} is twice as great as ϕ_r at equal [7], suggesting that alternative, as yet unidentified, reaction pathways are available to this system (k_{mp}). If the products of these alternate pathways arise via the cation radical pair **13** or an ensuing intermediate such as **14**, we can estimate that $k_{Si} \sim k_{mp}$ and $k_{bet} \sim 34k_{Si}$. Therefore, the quantum inefficiency of the photoadditions ($\phi_r = 0.01$ at [7] = 0.2 M) is due mainly to back-electron-transfer from **13**, a process expected to be rapid.

The allylsilane pyrrolinium salt photoadditions represent a potentially interesting class of carbon–carbon bond-forming reactions. Their regio- and stereochemical courses can be understood in terms of pathways involving nucleophile-induced desilylation[11] of initially formed cation radicals followed by coupling at the least substituted allyl radical terminus.[12] Importantly, the regiochemistry observed is inconsistent with alternate mechanisms for these additions in which either attack of the electron-rich allylsilane occurs on the high-energy iminium cation, or cation radical pair coupling occurs prior to desilylation. Both of these routes would produce intermediate **15**, and thus, conjugate addition[13] analogous to that seen in reaction of allyl silanes with electrophiles should predominate due to the efficient σ–π stabilization of cations by adjacent C–Si bonds.[14,8a] Further mechanistic and synthetic aspects of these processes should be uncovered in our continuing studies in this area.[16]

Registry No. 1, 69105-60-8; **2**, 2826-88-2; **7**, 762-7 **8**, 18293-99-7; **9**, 17891-78-0; **10**, 80326-41-6; **11**, 80326-42-7; **12**, 80326-43-8; cyclohexene, 110-83-8; 1-octene, 111-66-0; $PhCH_2Si(CH_3)_3$, 770-09-2; $CH_2{=}CHSi(CH_3)_3$, 754-05-2.

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[11] Weak nucleophiles such as CH_3CN are apparently sufficient for desilylation of the allylsilane-derived cation radicals. Desilylation by this nucleophile follows Ritter-reaction-type pathways leading most probably to acetamide and polysiloxanes upon workup. The low mass balances obtained from irradiations of **2** in the presence of allylsilanes **7** and **8** are most probably due to losses incurred during product purification and to alternate reaction pathways followed by the radical components of the pairs **14** (Scheme II). The alternate pathways must produce volatile products since NMR spectroscopic analyses of the crude photolysates demonstrate the absence of other major components. This speculation is supported by recent, unpublised observations which show that intramolecular counterparts of the reactions described here are exceptionally efficient. Accordingly, photocyclizations of *N*-(trimethylsilylallyl) iminium salts take place in near quantitative yields due to the prohibition of radical cage escape pathways.

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[16] Support for this research by the National Science Foundation (CHE-09813) and National Institutes of Health (GM-27251) is gratefully acknowledged. Support for the purchase of the 200-MHz NMR spectrometer used in this work was provided by NSF (CHE-26025).

Diverse Mechanisms of Carbon–Hydrogen Bond Formation through Binuclear Reductive Elimination Reactions

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Although binuclear reductive elimination reactions between transition-metal alkyls and hydrides constitute important steps in a variety of stoichiometric and catalytic processes (for example, the product-forming steps in olefin hydrogenation and hydroformylation[1]), only recently have such reactions received direct attention.[2-5] Several recent studies of such reactions have revealed puzzlingly diverse reactivity patterns and yielded disparate mechanistic conclusions.[2-4] We describe here some results of an ongoing study of reactions between several benzylmanganese carbonyls (**1**) and the corresponding hydridomanganese carbonyl complexes (**2**) which reveal clearly the accessibility of several distinct mechanisms for such bimolecular reductive elimination (including a free radical mechanism involving metal–carbon bond homolysis) and identify some of the factors that influence the choice among these mechanisms.

$p\text{-X-}C_6H_4CH_2Mn(CO)_4L(cis)$	$HMn(CO)_4L(cis)$
1a, X = CH_3O; L = CO	**2a**, L = CO
1b, X = CH_3O; L = $(p\text{-}CH_3OC_6H_4)_3P$	**2b**, L = $(p\text{-}CH_3OC_6H_4)_3P$
1c, X = H; L = CO	

Reaction of 1a with 2a in Nonpolar Solvents. The reaction of **1a** (or **1c**)[6] with **2a** in nonpolar solvents such as benzene yielded the corresponding toluene in accord with eq 1 and with the rate law (eq 2) where k_3(65 °C) = (6.0 ± 0.5) × 10^{-4} s^{-1}, k_{-3}/k_4(65 °C) = 8.5 ± 1.0, $\Delta H_3^{\ddagger}$ = 23.2 ± 0.3 kcal/mol and $\Delta S_3^{\ddagger}$ = −4.8

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[1] Alemdaroglu, N. H.; Penninger, J. M. L.; Oltay, E. *Monatsh. Chem.* **1976**, *107*, 1043.

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[6] The $p\text{-}CH_3O$-substituted derivatives, **1a**, **1b**, and **2b**, were used because of their higher solubilities and because of the convenience of the OCH_3 ^1H NMR signal. Apart from modest rate variations (e.g., k_3 for **1a** ca. 3 times higher than for **1c**), no significant differences were noted between the behavior of **1a** and **1c**.

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± 1.1 cal/mol·K (all in benzene).[7] This behavior is consistent with and strongly supports the mechanistic scheme of eq 3 and 4. A plausible mechanism for eq 4 involves the oxidative addition of **2a** to the coordinatively unsaturated intermediate **3a** to form $[p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\overline{\text{MnH(CO)}_4\text{Mn}}\text{(CO)}_5]$, followed by reductive elimination of $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_3$.

$$\mathbf{1a} + \mathbf{2a} \rightarrow p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_3 + \text{Mn}_2(\text{CO})_{10} \quad (1)$$

$$-\text{d}[\mathbf{1a}]/\text{d}t = k_3k_4[\mathbf{1a}][\mathbf{2a}]/(k_{-3}[\text{CO}] + k_4[\mathbf{2a}]) \quad (2)$$

$$\mathbf{1a} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\mathbf{3a}}{p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{Mn(CO)}_4} + \text{CO} \quad (3)$$

$$\mathbf{3a} + \mathbf{2a} \xrightarrow{k_4} p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_3 + \text{Mn}_2(\text{CO})_9 \quad [\xrightarrow{\text{CO}} \text{Mn}_2(\text{CO})_{10}] \quad (4)$$

Reaction of 1a with 2a in Polar Solvents. The reaction of **1a** with **2a** in polar (coordinating) solvents such as acetone or acetonitrile (S) followed a different course, yielding the aldehyde $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CHO}$ and *cis*-$\text{Mn}_2(\text{CO})_9\text{S}$ (identified by NMR and IR[8] spectroscopy) in accord with eq 5 and with the rate-law, eq 6 [where k_7(25 °C) = 4.8×10^{-4} s^{-1}, $k_{-7}/k_8 = 2.8 \times 10^{-2}$ M, $\Delta H^{\ddagger}_7 = 16.7 \pm 1.3$ kcal/mol and $\Delta S^{\ddagger}_7 = -18 \pm 4$ cal/mol·K (all in acetone)],[9] consistent with the mechanism of eq 7 and 8. The value of k_7 was identical with that determined for the reaction of **1a** with PMe$_2$Ph to form $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{COMn(CO)}_4\text{PMe}_2\text{Ph}$, presumably by the rate-determining step 7, followed by the rapid trapping of **4a** with PMe$_2$Ph. The difference in behavior between nonpolar and polar solvents is consistent with, and expected from, the known enhancement of the rate of migratory insertion [e.g., for $\text{CH}_3\text{Mn(CO)}_5$][10] by polar solvents.

$$\mathbf{1a} + \mathbf{2a} + \text{S} \rightarrow p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{C}(=\text{O})\text{H} + \text{Mn}_2(\text{CO})_9\text{S} \quad (5)$$

$$-\text{d}[\mathbf{1a}]/\text{d}t = k_7k_8[\mathbf{1a}]/(k_{-7} + k_8[\mathbf{2a}]) \quad (6)$$

$$\mathbf{1a} + \text{S} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \underset{\mathbf{4a}}{p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{C}(=\text{O})\text{Mn(CO)}_4(\text{S})} \quad (7)$$

$$\mathbf{4a} + \mathbf{2a} \xrightarrow{k_8} p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{C}(=\text{O})\text{H} + \text{Mn}_2(\text{CO})_9\text{S} \quad (8)$$

Reaction of *cis*-1b with *cis*-2b in Benzene. While the stoichiometry depicted by eq 9 paralleled that of reaction 1, the reaction of *cis*-**1b** with *cis*-**2b** in benzene exhibited a distinctly different rate law corresponding to eq 10 [where k_{11} (75 °C) = $(5.5 \pm 0.5) \times 10^{-4}$ s^{-1}, $k_{-11}/k_{12}(k_{13}/k_{-13})^{1/2} = 3.1 \times 10^{-2}$ M$^{-1/2}$, $\Delta H^{\ddagger}_{11} = 27.5 \pm 0.5$ kcal/mol, and $\Delta S^{\ddagger}_{11} = +4.5 \pm 1.5$ cal/mol·K],[11] consistent with the mechanism of eq 11–13 [P = $(p\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}$].[12]

$$\mathbf{1b} + \mathbf{2b} \rightarrow p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_3 + \text{Mn}_2(\text{CO})_8\text{P}_2 \quad (9)$$

$$\frac{-\text{d}[\mathbf{1b}]}{\text{d}t} = \frac{k_{11}k_{12}[\mathbf{1b}][\mathbf{2b}]}{k_{-11}(k_{-13}/k_{13})^{1/2}[\text{Mn}_2(\text{CO})_8\text{P}_2]^{1/2} + k_{12}[\mathbf{2b}]} \quad (10)$$

$$\mathbf{1b} \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\cdot + \cdot\text{Mn(CO)}_4\text{P} \quad (11)$$

$$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\cdot + \mathbf{2b} \xrightarrow{k_{12}} p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_3 + \cdot\text{Mn(CO)}_4\text{P} \quad (12)$$

$$2\cdot\text{Mn(CO)}_4\text{P} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} \text{Mn}_2(\text{CO})_8\text{P}_2 \quad (13)$$

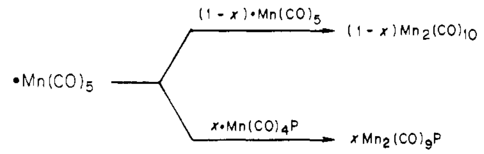
The change in mechanism in going from reaction 1 to 9 presumably reflects the familiar influence of phosphine substitution in inhibiting the dissociation of CO from carbonyl complexes,[14] thus disfavoring the step corresponding to eq 3. The observation of the full rate law (eq 10) also is favored by the lowering of the Mn–Mn bond dissociation energy[15] in going from $\text{Mn}_2(\text{CO})_{10}$ to $\text{Mn}_2(\text{CO})_8\text{P}_2$, thereby increasing the steady-state concentration of $\cdot\text{Mn(CO)}_4\text{P}$ and the resulting competition from the k_{-11} step.[16]

Reaction of 1b with 2a in Benzene. Trapping of ·Mn(CO)$_4$P. Further evidence for the free radical mechanism depicted by eq 11–13 was obtained through experiments involving the trapping of $\cdot\text{Mn(CO)}_4\text{P}$.[18] The reaction of **1b** with **2a** in C$_6$D$_6$ (under N$_2$) exhibited the stoichiometry of eq 14 ($0 < x < 1$) and the rate law, $-\text{d}[\mathbf{1b}]/\text{d}t = k_{11}[\mathbf{1b}]$, consistent with the mechanistic scheme of the rate-determining step (eq 11) followed by eq 15–17. Consistent with the role of reaction 16 in this scheme, the yield of $\text{HMn(CO)}_4\text{P}$ increased (approximately linearly) from 77 to 94% of the initial **1b** concentration when the **2a** concentration increased from 0.3 to 1.2 M. The occurrence of reaction 16 demonstrates that the Mn–H bond dissociation energy increases when a CO ligand is replaced by phosphine (i.e., in going from **2a** to **2b**) and that H atom transfer from HMn(CO)_5 to $\cdot\text{Mn(CO)}_4\text{P}$ is fast.[19]

$$\mathbf{1b} + (2 - x)\mathbf{2a} \rightarrow p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_3 + (1 - x)\text{HMn(CO)}_4\text{P} + x\text{Mn}_2(\text{CO})_9\text{P} + (1 - x)\text{Mn}_2(\text{CO})_{10} \quad (14)$$

$$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\cdot + \mathbf{2a} \rightarrow p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_3 + \cdot\text{Mn(CO)}_5 \quad (15)$$

$$(1 - x)\cdot\text{Mn(CO)}_4\text{P} + (1 - x)\mathbf{2a} \rightarrow (1 - x)\text{HMn(CO)}_4\text{P} + (1 - x)\cdot\text{Mn(CO)}_5 \quad (16)$$



(17a)

(17b)

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(7) Two series of kinetic experiments were performed, the first (at 65 °C) encompassing the initial concentration ranges 2.5×10^{-3}–5.4×10^{-3} M **1a**, 2.5×10^{-2}–7.4×10^{-2} M **2a**, and 0–8.3×10^{-3} M (0–1.0 atm) CO and the second (at temperatures ranging from 55 to 75 °C) ca. 6×10^{-2} M **1a** and ca. 0.5 M **2a**. In the first case the reaction rates were monitored by IR spectroscopy, and in the second case by ^{1}H NMR spectroscopy. Excellent agreement was obtained between the two series.

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

(9) These kinetic measurements encompassed the temperature range 20–35 °C and the initial concentration ranges ca. 10^{-3} M **1a** and 2.4×10^{-2}–1.5×10^{-1} M **2a**.

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

(11) These kinetic measurements encompassed the temperature range 68.5–83.4 °C and the initial concentration ranges 7.1×10^{-3}–3.3×10^{-2} M **1b**, 1.1×10^{-2}–3.3×10^{-1} M **2b**, and 0–4.0×10^{-2} M $\text{Mn}_2(\text{CO})_8\text{P}_2$.

(12) The value of $\Delta H^{\ddagger}_{11}$ (27.5 kcal/mol) represents an upper limit of the Mn–C bond dissociation energy of **1b**. Assuming k_{-11} to be diffusion controlled yields ca. 25 kcal/mol for this bond dissociation energy, a value that is reasonable in the light of the previously reported value of ca. 30 kcal/mol for the Mn–C bond dissociation energy of $\text{CH}_3\text{Mn(CO)}_5$.[13]

(13) Brown, D. L. S.; Connor, J. A.; Skinner, H. A. *J. Organomet. Chem.* **1974**, *81*, 403.

(14) Basolo, F.; Wojcicki, A. *J. Am. Chem. Soc.* **1961**, *83*, 520.

(15) (a) Jackson, R. A.; Poe, A. *Inorg. Chem.* **1978**, *17*, 997. (b) Jackson, R. A.; Poe, A. *Inorg. Chem.* **1979**, *18*, 3331.

(16) The reaction, $2\,\text{Mn(CO)}_5 \rightarrow \text{Mn}_2(\text{CO})_{10}$, has been shown to be diffusion controlled.[17] Assuming diffusion-controlled values (ca. 10^{10} M^{-1} s^{-1} at 75 °C), the corresponding rate-constant k_{-13} as well as for the rate-constant k_{-11} of the other radical-coupling step, and using the previously determined[15] value of k_{-13} (ca. 1×10^{-1} s^{-1}), yields $k_{12} \sim 10^6$ M^{-1} s^{-1}, a value consistent with the expectedly facile highly exothermic abstraction of a H atom from a metal hydride by a carbon radical.

(17) (a) Hughey, J. L., IV; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49. (b) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259.

(18) $\cdot\text{M(CO)}_4\text{P}$, formed in reaction 11, also could be trapped by exchange with CO, resulting in the overall substitution reaction, **1b** + CO → **1a** + P, proceeding by the rate-determining step (eq 11) followed by the fast reactions, $\cdot\text{Mn(CO)}_4\text{P} + \text{CO} \rightarrow \cdot\text{Mn(CO)}_5 + \text{P}$; $\cdot\text{Mn(CO)}_5 + p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\cdot \rightarrow$ **1a**.

(19) The possibility that $\text{HMn(CO)}_4\text{P}$ arises from the secondary scrambling reaction, $\text{Mn}_2(\text{CO})_9\text{P} + \text{HMn(CO)}_5 \rightarrow \text{Mn}_2(\text{CO})_{10} + \text{HMn(CO)}_4\text{P}$, was ruled out by direct demonstration that the rate of this reaction was too slow, by a factor of ca. 12, to account for the formation of $\text{HMn(CO)}_4\text{P}$ under the conditions of reaction 14. The mechanism of this reaction, which exhibits the rate law, $-\text{dln}\,[\text{Mn}_2(\text{CO})_9\text{P}]/\text{d}t = 4.1 \times 10^{-5}$ s^{-1} at 75 °C ($\Delta H^{\ddagger} = 30$ kcal/mol, $\Delta S^{\ddagger} = 7$ cal/mol·K), apparently is $\text{Mn}_2(\text{CO})_9\text{P} \rightarrow \text{Mn(CO)}_5 + \text{Mn(CO)}_4\text{P}$ (rate determining); $\text{Mn(CO)}_4\text{P} + \text{HMn(CO)}_5 \rightarrow \text{HMn(CO)}_4\text{P} + \text{Mn(CO)}_5$; $2\text{Mn(CO)}_5 \rightarrow \text{Mn}_2(\text{CO})_{10}$.

Reaction of 1b with 2a in Benzene under CO. Replacement of the N_2 atmosphere by CO resulted in enhancement of the rate of reaction between **1b** and **2a** (i.e., beyond that corresponding to reaction 14) as reflected in the *additional* term in the rate law corresponding to eq 18 where $k_{19}(75\ °\mathrm{C}) = 5.8 \times 10^{-2}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.

$$-\mathrm{d}[\mathbf{1b}]/\mathrm{d}t = (k_{11} + k_{19}[\mathrm{CO}])[\mathbf{1b}] \qquad (18)$$

$$\mathbf{1b} + \mathrm{CO} \xrightarrow{k_{19}} \underset{\mathbf{5b}}{[p\text{-}\mathrm{CH_3OC_6H_4CH_2C({=}O)Mn(CO)_4P}]} \xrightarrow{\mathbf{2a}} \underset{\mathbf{7}}{p\text{-}\mathrm{CH_3OC_6H_4CH_2CHO}} \qquad (19)$$

$$\mathbf{5b} \rightarrow \cdot\mathrm{Mn(CO)_4P} + \underset{\mathbf{6}}{p\text{-}\mathrm{CH_3OC_6H_4CH_2C({=}O)}\cdot} \xrightarrow[k_{20}]{\mathbf{2a}} \underset{\mathbf{7}}{p\text{-}\mathrm{CH_3OC_6H_4CH_2CHO}} \qquad (20)$$

This additional contribution to the rate was reflected in the formation of a different product, namely, the aldehyde p-$CH_3OC_6H_4CH_2CHO$, presumably by the reaction sequence of eq 19. Consistent with this interpretation, the product distribution was found to obey the relation $[p\text{-}CH_3OC_6H_4CH_2CHO]/[p\text{-}CH_3OC_6H_4CH_3] = k_{19}[CO]/k_{11}$, the aldehyde fraction increasing from 0 to 46% when the CO partial pressure was increased from 0 to 1 atm. Since the intermediate **5b** in reaction 19 hardly can contain a vacant coordination site, direct reaction with **2a** seems unlikely, and the free radical mechanism corresponding to eq 20 (i.e., analogous to that of eq 11–13) is favored.[20] This suggests that the Mn—C(=O)R bond dissociation energy is relatively low, probably not exceeding 25 kcal/mol. Attempts to establish this directly by experiments on acylmanganese carbonyl complexes are in progress. Reaction 20 may be considered another[3] model of the aldehyde-forming step in cobalt-carbonyl-catalyzed hydroformylation.[1]

Four distinct pathways, corresponding to the schemes of eq 3 and 4; 7 and 8; 11–13; and 19, respectively, have been identified for binuclear reductive elimination reactions of benzylmanganese carbonyls with hydridomanganese carbonyls. Relatively modest changes in ligands, solvent, or CO concentration may result in essentially complete crossover from one pathway to another. This underlines the danger of assuming the mechanism of such binuclear reductive elimination reactions, the occurrence of which is widespread, without appropriate diagnostic evidence, or of extrapolating from one system or set of conditions to another. While some of the factors influencing the choice of pathway in such reactions have been identified, further elucidation of these factors clearly is called for and our studies designed to achieve this are continuing.

Finally, it is of interest to compare the behavior of these systems with others that have been investigated. The reaction of $HMo(CO)_3Cp$ with $CH_3Mo(CO)_3Cp$ to form CH_3CHO has been shown to follow a pathway analogous to that of eq 7 and 8, while the corresponding reaction with $C_6H_5CH_2Mo(CO)_3Cp$ appears to proceed, in part, through a free radical pathway analogous to eq 11–13, yielding toluene.[9] On the other hand, the *binuclear* reaction of *cis*-$OsH(CH_3)(CO)_4$ to form CH_4 appears to proceed through a variant of the mechanistic scheme of eq 7 and 8 in which migratory insertion of CO into the Os–CH_3 bond is followed (for reasons that are puzzling) by reductive elimination of alkane rather than of aldehyde.[2] The mechanism encompassed by eq 3 and 4 finds a parallel in that proposed for the binuclear reductive elimination of H_2 from *cis*-$Os(CO)_4H_2$.[22]

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(20) The formation of aldehyde **7** according to route 20 requires that the hydrogen abstraction step, $\mathbf{6} + \mathbf{2a} \xrightarrow{k_{20}} \mathbf{7} + \mathrm{Mn(CO)_5}$, be fast compared with the decarbonylation of **6**, i.e., $\mathbf{6} \rightarrow p\text{-}\mathrm{CH_3OC_6H_4CH_2}\cdot + \mathrm{CO}$. The rate constant of the corresponding decarbonylation of $C_6H_5CH_2(CO)\cdot$ to $C_6H_5CH_2\cdot$ + CO has been estimated to be ca. $5 \times 10^7\ \mathrm{s}^{-1}$ at room temperature.[21] A similar decarbonylation rate constant for **6** would require that $k_{20} > 5 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. This is significantly higher than our estimate[16] of ca. $10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ for k_{12} but is not considered incompatible with the latter since $HMn(CO)_5$ is expected to be a much better H donor than $HMn(CO)_4P$.

(21) Brunton, G.; McBay, H. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 4447.

(22) Evans, J.; Norton, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 7577.

Acknowledgment. Pertinent preliminary studies on these and related systems were performed in this laboratory by R. L. Sweany (who first identified reaction 1) and M. J. Russell. Support through grants from the National Science Foundation and the National Institutes of Health is gratefully acknowledged. R.S. thanks the Montedison Donegani Institute for a leave of absence.

Registry No. 1a, 80105-78-8; **1b**, 80105-79-9; **1c**, 14049-86-6; **2a**, 16972-33-1; **2b**, 80105-80-2.

Ligand Effects on Transition-Metal-Alkyl Bond Dissociation Energies

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The importance of transition-metal–alkyl bond dissociation energies in various organometallic, biochemical, and catalytic contexts has been widely recognized.[1] Notwithstanding this, few such bond energies have been determined reliably,[2] and the factors that influence the strengths of such bonds and the stabilities of transition-metal–alkyl compounds still are unclear and controversial.[3] We report here the first systematic determinations of the influence of ligand variation on transition-metal–carbon bond dissociation energies. Our results, which relate to a series of organocobalt compounds, are of particular interest in view of the relevance of such compounds as vitamin B_{12} coenzyme models and of the role widely accorded to cobalt–carbon bond homolysis in coenzyme B_{12}-promoted reactions.[4–6] Our results also bear on the mechanism of olefin elimination from organocobalt compounds for which alternative interpretations have been advanced.[7,8]

Our studies involve determination of the cobalt–carbon bond dissociation energies, using a procedure that we previously described,[9] of a series of (α-phenylethyl)cobalt compounds, $[L(DH)_2Co\text{-}CH(CH_3)C_6H_5]$ (where DH_2 = dimethylglyoxime and L is an axial ligand such as pyridine, a 4-substituted pyridine, or imidazole). This involves determination of the equilibrium constant (K_1) and enthalpy ($\Delta H_1°$) of the reversible reaction corresponding to reaction 1. In combination with available data for

$$[\mathrm{L(DH)_2Co^{III}CH(CH_3)C_6H_5}] \rightleftarrows [\mathrm{L(DH)_2Co^{II}}] + \mathrm{C_6H_5CH{=}CH_2} + {}^1/_2\mathrm{H_2}\ (\Delta H_1°) \qquad (1)$$

$$\mathrm{C_6H_5CH{=}CH_2} + {}^1/_2\mathrm{H_2} \rightleftarrows \mathrm{C_6H_5\dot{C}HCH_3}\ (\Delta \mathrm{H_2}°) \qquad (2)$$

$$[\mathrm{L(DH)_2Co^{III}CH(CH_3)C_6H_5}] \rightleftarrows [\mathrm{L(DH)_2Co^{II}}] + \mathrm{C_6H_5\dot{C}HCH_3}\ (\Delta H_3° \sim D_{\mathrm{Co–R}}) \qquad (3)$$

the heats of formation of $C_6H_5CH{=}CH_2$ ($\Delta H_f° = 35.2$ kcal/mol)[10] and the $C_6H_5\dot{C}HCH_3$ radical ($\Delta H_f° = 33$ kcal/mol)[11] (yielding $\Delta H_2° = -2.2$ kcal/mol for reaction 2), the cobalt–carbon

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