Ca(II)-dependent ATPase proceeds at the same rate with ATP and ATPβS (*R* and *S*) as substrates but the Ca(II)-independent ATPase is not detectable with ATPβS as substrate. (4) The metal dependence of stereoselectivity of ATPαS and of ATPβS has contributed significantly to the elucidation of the metal chelate structures of the nucleotide but has often raised as many questions as it has answered. Again, the variability of the patterns among the phosphoryl-transfer reactions is striking. (5) The use of the difference in free energy change between the nucleoside di- and triphosphate pairs of the β-S analogues relative to the oxynucleotide as a probe in energy transduction systems has only begun. In addition to studies of equilibria and coupling mechanisms, the ability to manipulate concentrations of products in metabolic and biosynthetic pathways by replacement of ATP by ATPβS may yet prove the most valuable property of the thionucleotide.

Formation of Carbon–Hydrogen Bonds by Reductive Elimination

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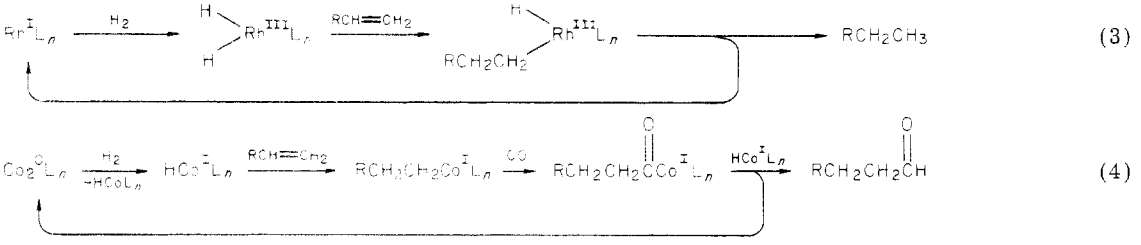
Formation of a C–H bond by coupling of a metal-bonded alkyl, aryl, or acyl ligand with a hydride ligand constitutes an important and widespread class of reactions in organometallic chemistry. Such reactions commonly are referred to as *reductive eliminations* because they typically are accompanied by a decrease in the formal oxidation states of the metal complexes. Reductive elimination reactions may be either intramolecular or intermolecular, specific examples being

$$\underset{\mathbf{1}}{cis\text{-}[Pt^{II}H(CH_3)(PPh_3)_2]} \rightarrow CH_4 + [Pt^0(PPh_3)_2] \quad (1)$$

$$\underset{\mathbf{2}}{[C_6H_5CH_2Mn^I(CO)_5]} + [HMn^I(CO)_5] \rightarrow C_6H_5CH_3 + [Mn_2^0(CO)_{10}] \quad (2)$$

Such reactions commonly constitute the product-forming steps in catalytic processes such as hydrogenation[1] and hydroformylation[2] as exemplified by the simplified mechanistic schemes of eq 3 and 4 (where $RhL_n = [Rh^ICl(PPh_3)_3]$ and $CoL_n = [Co(CO)_4]$).

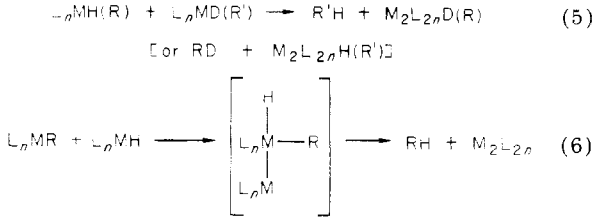


(3)

(4)

While the distinction between intramolecular and intermolecular reductive elimination reactions, exemplified by eq 1 and 2, is readily apparent from a stoichiometric standpoint, the mechanistic implications of the distinction are less clear. For example, mononuclear hydridoalkyl complexes may undergo reductive elimination through intermolecular mechanisms (demonstrable by double labeling)[3,4] as in the schematic example of eq 5. On the other hand, apparently intermolecular reductive elimination may proceed through an intramolecular step (eq 6).

This Account is concerned with the scope of such reductive elimination reactions, with their kinetic and mechanistic aspects, and with the factors that influence their rates and reactivity patterns. The study of such reactions also is of obvious relevance to an understanding of the reverse process, i.e., the oxidative addition of C–H bonds, a topic of considerable current



(5)

(6)

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interest from the standpoint of activation of hydrocarbons.[5]

Two other recent reviews, by Norton[4] and by Bergman,[6] also have dealt with aspects of the mechanisms of reductive elimination reactions that are relevant to the subject of this Account.

Intramolecular Reductive Elimination

Intramolecular alkyl–hydride reductive elimination reactions such as reaction 1 tend to very rapid, especially when R and H are cis related. Accordingly, few documented examples of stable hydridoalkyl complexes exist. Known examples include (a) several *trans*-hydridoalkyl complexes, in some cases apparently constrained to be so by bulky ligands, e.g., *trans*-$NiH(CH_3)[P(C_6H_{11})_3]_2$ (C_6H_{11} = cyclohexyl),[7] (b) several complexes containing *substituted* alkyl groups with stabilizing substituents, e.g., $PtH(CH_2CN)(PPh_3)_2$,[8] and (c) complexes such as *cis*-$OsH(CH_3)(CO)_4$[3,9,10] that apparently would yield highly unstable residues [e.g., $Os(CO)_4$] on reductive elimination. Recently several general methods for preparing a variety of *trans*-hydridoalkyl metal complexes have been reported.[11,12]

In certain cases the use of low temperatures permits reactive *cis*-hydridoalkylmetal complexes to be prepared under conditions where they are sufficiently stable and long-lived to be directly observed and characterized.[13] Using this approach we have synthesized a series of *cis*-hydridoalkylplatinum(II) compounds of the composition *cis*-$PtH(R)(PR'_3)_2$ (where R = alkyl or aryl and R′ = aryl) by the reaction

$$\textit{trans}\text{-}PtHCl(PR'_3)_2 + RMgBr \xrightarrow[\text{toluene}]{-78\ ^\circ C} \textit{cis}\text{-}PtH(R)(PR'_3)_2 + MgClBr \quad (7)$$

The *cis*-$PtHR(PR'_3)_2$ complexes prepared in this way typically were stable in solution for at least several days at temperatures below −50 °C and were fully characterized by ^1H and ^{31}P NMR spectroscopy. Their chemical behavior at higher temperatures is exemplified by the following account of the chemistry of *cis*-$PtH(CH_3)(PPh_3)_2$ (1).

When a toluene solution of *cis*-$PtH(CH_3)(PPh_3)_2$ (1) was warmed to −25 °C, decomposition occurred at a conveniently measurable rate to yield $Pt(PPh_3)_3$ and CH_4 according to eq 8. In the presence of added lig-

$$3\textit{cis}\text{-}PtH(CH_3)(PPh_3)_2 \rightarrow 3CH_4 + 2Pt(PPh_3)_3 + Pt \quad (8)$$

ands (L = PPh_3 or PhC≡CPh) *the rate of decomposition was unaffected* but the stoichiometry was altered to that of eq 9. Kinetic measurements yielded the

$$\textit{cis}\text{-}PtH(CH_3)(PPh_3)_2 + L \rightarrow CH_4 + Pt(PPh_3)_2L \quad (9)$$

first-order rate law, $-d[1]/dt = k_1[1]$, with $k_1 = 4.5 \times 10^{-4}$ s^{-1}, independent of the nature or concentration of added L. Deuterium labeling experiments confirmed that the reductive elimination was *intramolecular*. Thus, decomposition of an equimolar mixture of $PtH(CH_3)(PPh_3)_2$ and $PtD(CD_3)(PPh_3)_2$ yielded almost exclusively CH_4 and CD_4, while an equimolar mixture of $PtH(CD_3)(PPh_3)_2$ and $PtD(CH_3)(PPh_3)_2$ yielded almost exclusively CH_3D and CD_3H. Comparison of the rates of decomposition of $PtH(CH_3)(PPh_3)_2$ and $PtD(CH_3)(PPh_3)_2$ revealed an appreciable normal primary kinetic isotope effect with $k_1^H/k_1^D = 3.3 \pm 0.3$.[13]

These observations are most plausibly interpreted in terms of a mechanistic scheme comprising the rate-determining step (eq 1), followed by

$$3Pt(PPh_3)_2 \xrightarrow{\text{fast}} 2Pt(PPh_3)_3 + Pt \quad (10)$$

or, in the presence of an added ligand, L,

$$Pt(PPh_3)_2 + L \xrightarrow{\text{fast}} Pt(PPh_3)_2L \quad (11)$$

Similar results were obtained for corresponding complexes of several parasubstituted triarylphosphines, *cis*-$PtH(CH_3)(PR'_3)_2$, where R′ = *p*-XC_6H_4. The rates of reaction decreased along the sequence R′ = *p*-ClC_6H_4 (9.2) > C_6H_5 (4.5) > *p*-$CH_3C_6H_4$ (1.4) > *p*-$CH_3OC_6H_4$ (0.47), where the values in parentheses are 10^4k (s^{-1}) at −25 °C. This sequence is consistent with the expected increasing tendency of electron-withdrawing substituents on the phosphine ligands to stabilize Pt(0) and, hence, to increase the driving force for the reductive elimination reaction (eq 1).[13]

Similar experiments on *cis*-$PtH(C_2H_5)(PPh_3)_2$ demonstrated the analogous reductive elimination of C_2H_6 (rather than β elimination of C_2H_4) with $k_1 = 9 \times 10^{-4}$ s^{-1}, i.e., about twice the corresponding rate for the methyl compound. Only a few other $PtH(R)(PPh_3)_2$ compounds have been examined, revealing the reactivity sequence, R = $C_6H_5 > C_2H_5 > CH_3 > CH_2CH{=}CH_2$.[13] Unfortunately, attempts to extend these studies to a wider range of compounds have been constrained by the limited applicability of the synthetic approach. The reason that reaction 7 yields the cis compounds in the cases cited is unclear. Attempts to extend this reaction to other starting *trans*-$MHCl(PR'_3)_2$ compounds, notably when M = Pd instead of Pt or when R′ = alkyl instead of aryl, generally yielded *trans*-$MH(R)(PR'_3)_2$ compounds.[11] As expected, such trans compounds are rather stable with respect to reductive elimination of RH.

A noteworthy feature of the behavior exhibited by reactions 8 and 9 is that the rate is not enhanced by the addition of L, i.e., of ligands such as phosphines, acetylenes, or olefins. This is surprising since *cis*-$PtH(CH_3)(PPh_3)_2$, a 16-electron complex, is coordinatively unsaturated and since $Pt(PPh_3)_2$ is relatively unstable (compared with $Pt(PPh_3)_3$, $Pt(PPh_3)_2(C_2H_4)$, etc.). Accordingly, the addition of such ligands might have been expected to enhance the driving force for reductive elimination through a mechanism, depicted by eq 12

$$PtH(CH_3)(PPh_3)_2 \xrightarrow{L} [PtH(CH_3)(PPh_3)_2L] \rightarrow CH_4 + Pt(PPh_3)_2L \quad (12)$$

(4) J. R. Norton, *Acc. Chem. Res.*, **12**, 139 (1979).
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(13) L. Abis, A. Sen, and J. Halpern, *J. Am. Chem. Soc.*, **100**, 2915 (1978).

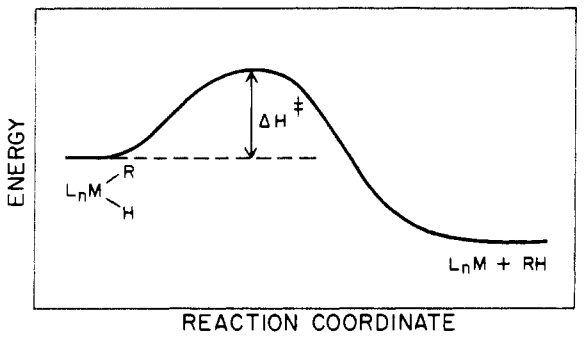


Figure 1. Schematic energy vs. reaction coordinate profile for the reductive elimination of an alkane from a *cis*-hydridoalkyl metal complex.

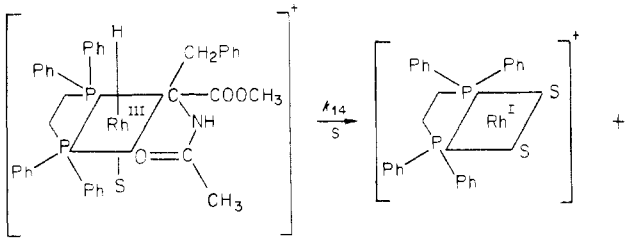
involving *prior* coordination of L. Such ligand-promoted reductive elimination has been reported in other systems, for example, the reductive elimination of R_2 from $NiR_2(bpy)$ (R = CH_3, C_2H_5, etc.).[14]

The initial product of the reductive elimination reaction 1, i.e., $Pt(PPh_3)_2$, has previously been identified as an intermediate in substitution and oxidative addition reactions of Pt(0) complexes, for example, reaction 13.[15] The facile intramolecular reductive elimination

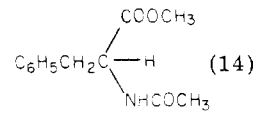
$$Pt(PPh_3)_3 \overset{-PPh_3}{\rightleftharpoons} [Pt(PPh_3)_2] \xrightarrow{RC\equiv CR} Pt(PPh_3)_2(RC\equiv CR) \quad (13)$$

of CH_4 from $PtH(CH_3)(PPh_3)_2$ at temperatures as low as −25 °C clearly demonstrates not only that the process is thermodynamically favorable but also that the kinetic barrier is fairly low ($\Delta G^{\ddagger}$ = 18.2 kcal/mol at −25 °C). The reverse process, i.e., the oxidative addition of CH_4 to $Pt(PPh_3)_2$, accordingly, *must be precluded on thermodynamic rather than on kinetic grounds* and the reaction profile must resemble that depicted in Figure 1. This conclusion is consistent with recent estimates of transition-metal–hydrogen-bond dissociation energies (of the order of 60 kcal/mol)[16] and of transition-metal–alkyl-bond dissociation energies (20–30 kcal/mol).[17] When these values are used, the oxidative addition of CH_4 (D_{CH_3-H} = 103 kcal/mol) is estimated to be endothermic by at least 10 kcal/mol. This conclusion is of some significance in the context of the widespread current interest in the catalytic activation of saturated hydrocarbons and suggests that oxidative addition (at least with such relatively stable mononuclear complexes), while not precluded, is not a promising approach.[18]

Intramolecular reductive elimination reactions of intermediate *cis*-hydridoalkyl complexes analogous to **1** frequently have been postulated as the product-forming steps in catalytic hydrogenation and related processes (e.g., eq 3).[1] However, only recently has the first example of such an intermediate in a catalytic hydrogenation reaction been intercepted and characterized and the product-forming reductive elimination step directly observed.[19] When the hydrogenation of methyl (*Z*)-α-acetamidocinnamate in methanol solution, catalyzed by $[Rh(diphos)(CH_3OH)_2]^+$ (diphos = 1,2-bis(diphenylphosphino)ethane), is conducted at low temperatures (< −40 °C), the intermediate **3** is observed to accumulate. The rate-determining step of the reaction under these conditions is the product-forming intramolecular reductive elimination process corresponding to eq 14. This reaction was observed directly to proceed according to a first-order rate law with the activation parameters $\Delta H_{14}^{\ddagger}$ = 17.0 kcal/mol and $\Delta S_{14}^{\ddagger}$ = 6 cal/(mol K).[19] These values yield $\Delta G_{14}^{\ddagger}$ = 15.5 kcal/mol at −25°, compared with $\Delta G_1^{\ddagger}$ = 18.2 kcal/mol for reaction 1. It is the remarkably high activity of this particular catalyst system (notably the high rate of the migratory olefin insertion step leading to the formation of the hydridoalkyl complex, **3**) that permits the reaction to be conducted at sufficiently low temperatures for the hydridoalkyl intermediate to be intercepted and the product-forming reductive elmination reaction to be observed directly. Unfortunately, most hydrogenation catalysts are not sufficiently active to permit this.



3 (S = solvent)



(14)

A recent report[20] describes the formation of analogous relatively stable hydridoalkyliridium complexes by insertion of activated olefins into one of the Ir–H bonds of *cis*-dihydridoiridium complexes and concludes that such hydridoalkyl complexes are intermediates in catalytic hydrogenation reactions.

Intermolecular Reductive Elimination

Although, in principle, intermolecular reductive elimination reactions such as (2) are readily susceptible to direct observation and study, only recently has the investigation of such reactions received serious attention.[3,4,21-23] One such study, which is the principal theme of this section, encompasses reaction 2 and some closely related reactions involving substituted benzyl-

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(17) (a) J. Halpern, F. T. T. Ng, and G. L. Rempel, *J. Am. Chem. Soc.*, **101**, 7124 (1979); (b) F. T. T. Ng, G. L. Rempel, and J. Halpern, *ibid.*, **104**, 621, (1982); (c) T. T. Tsou, M. Loots, and J. Halpern, *ibid.* **104**, 623 (1982); (d) J. Halpern, *Acc. Chem. Res.*, **15**, 238 (1982).

(18) Only with highly unstable and reactive species, for example, the coordinately unsaturated complex $[Ir(C_5Me_5)(PMe_3)]$ (generated by the *photochemical* reductive elimination of H_2 from $[IrH_2(C_5Me_5)(PMe_3)]$), have such *intermolecular* oxidative addition reactions of saturated hydrocarbons very recently been observed (A. H. Janowicz and R. G Bergman, *J. Am. Chem. Soc.*, **104**, 352 (1982); see also J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, **104**, 3723 (1982). The oxidative addition of *aromatic* C–H bonds appears to be a more facile reaction[5] probably for kinetic, as well as thermodynamic, reasons. Unsaturation at the C–H site is expected to enhance reactivity while, at the same time, transition-metal–aryl bonds probably are stronger than the corresponding metal–alkyl bonds.

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manganese carbonyls (**4a**, **4b**, abbreviated $Bz'Mn(CO)_5$

$$\underset{\mathbf{4}}{cis\text{-}p\text{-}CH_3OC_6H_4Mn(CO)_4L} \qquad \underset{\mathbf{5}}{cis\text{-}HMn(CO)_4L} \tag{8}$$

a, L = CO; **b**, L = $(p\text{-}CH_3OC_6H_4)_3P$

and $Bz'Mn(CO)_4P$, respectively) and hydridomanganese carbonyls (**5a**, **5b**, i.e., $HMn(CO)_5$ and $HMn(CO)_4P$).[23,24]

The original objective that prompted us to undertake a study of reaction 2 was the determination of the Mn–C bond dissociation energy of **2**. Extrapolation from earlier estimates of other Mn–C bond dissociation energies [e.g., ca. 30 kcal/mol for CH_3–$Mn(CO)_5$][25] suggested to us that the manganese–benzyl bond dissociation energy of **2** should be about 25 kcal/mol. Accordingly, we anticipated that this bond should undergo homolysis under mild conditions, generating a benzyl radical that should readily be trapped by $HMn(CO)_5$, resulting in the overall reaction 2 through the scheme of eq 15–17. According to this scheme, the

$$\underset{\mathbf{2}}{C_6H_5CH_2Mn(CO)_5} \xrightarrow{k_{15}} C_6H_5CH_2\cdot + \cdot Mn(CO)_5 \tag{15}$$

$$C_6H_5CH_2\cdot + HMn(CO)_5 \xrightarrow{\text{fast}} C_6H_5CH_3 + \cdot Mn(CO)_5 \tag{16}$$

$$2\cdot Mn(CO)_5 \xrightarrow{\text{fast}} Mn_2(CO)_{10} \tag{17}$$

activation enthalpy of the rate-determining step 15 should approximate the $C_6H_5CH_2$–$Mn(CO)_5$ bond dissociation energy (since the reverse reaction is expected to be diffusion controlled).[26,27]

Our initial studies did reveal that reaction 2 proceeds readily under mild conditions (ca. 50 °C) in the absence of CO, in solvents such as benzene, with a first-order rate law, $-d[C_6H_5CH_2Mn(CO)_5]/dt = k[C_6H_5CH_2Mn(CO)_5]$ (rate independent of $[HMn(CO)_5]$, $\Delta H^{\ddagger} = 25$ kcal/mol; $\Delta S^{\ddagger} = 0$).[28] This behavior did appear to be consistent with the kinetics expected for the scheme of eq 15–17, but ultimately could not be reconciled with such an interpretation. In particular, it was found that thermal decomposition of $C_6H_5CH_2Mn(CO)_5$ in the absence of $HMn(CO)_5$ [to yield predominantly $(C_6H_5CH_2)_2$ and $Mn_2(CO)_{10}$], which is expected to proceed at the same rate as reaction 15, was in fact some 10^3 times slower than reaction 2. This made it unlikely that reaction 15 was the rate-determining step of reaction 2.

Further studies, particularly on the related reactions of the substituted benzylmanganese carbonyls **4a** and **4b**, did reveal conditions under which reductive elimination of toluene occurred by a scheme analogous to that of eq 15–17 but also demonstrated that the overall pattern of reactions between benzylmanganese carbonyls and the corresponding hydrides was considerably more complex.[23] Four distinct reaction pathways, depicted schematically by eq 18a–18d (where R = C_6H_5-CH_2 or p-$CH_3OC_6H_4CH_2$, L = CO or a phosphine ligand, and S = solvent), were identified. The choice of reaction pathway was found to depend upon the nature of the ligand L, the solvent, and the CO concentration. The following account summarizes some of the evidence upon which these mechanistic conclusions rest and discusses some of the factors that influence the choice of reaction pathway in this relatively simple system which, nevertheless, exhibits such remarkably diverse chemistry.[23]

$$RMn(CO)_4L \xrightarrow{-CO} RMn(CO)_3L \xrightarrow{HMn(CO)_4L} RH + Mn_2(CO)_7L_2 \ (\xrightarrow{CO} Mn_2(CO)_8L_2) \tag{18a}$$

$$RMn(CO)_4L \xrightarrow{S} RC(=O)Mn(CO)_3LS \xrightarrow{HMn(CO)_4L} RCHO + Mn_2(CO)_7L_2S \tag{18b}$$

$$RMn(CO)_4L \rightarrow R\cdot + \cdot Mn(CO)_4L \xrightarrow{HMn(CO)_4L} RH + 2\cdot Mn(CO)_4L \ (\rightarrow Mn_2(CO)_8L_2) \tag{18c}$$

$$RMn(CO)_4L \xrightarrow{CO} RC(=O)Mn(CO)_4L \xrightarrow{HMn(CO)_4L} RCHO + Mn_2(CO)_8L_2 \tag{18d}$$

Reaction 18a. This pathway was identified for the reaction of $Bz'Mn(CO)_5$ [or $C_6H_5CH_2Mn(CO)_5$] with $HMn(CO)_5$ in nonpolar solvents such as benzene. This reaction exhibited the stoichiometry of eq 19 (or eq 2)

$$Bz'Mn(CO)_5 + HMn(CO)_5 \rightarrow p\text{-}CH_3OC_6H_4CH_3 + Mn_2(CO)_{10} \tag{19}$$

$$-d[Bz'Mn(CO)_5]/dt = \frac{k_{21}k_{22}[Bz'Mn(CO)_5][HMn(CO)_5]}{k_{-21}[CO] + k_{22}[HMn(CO)_5]} \tag{20}$$

$$Bz'Mn(CO)_5 \underset{k_{-21}}{\overset{k_{21}}{\rightleftharpoons}} \underset{\mathbf{6}}{p\text{-}CH_3OC_6H_4CH_2Mn(CO)_4} + CO \tag{21}$$

$$\mathbf{6} + HMn(CO)_5 \xrightarrow{k_{22}} p\text{-}CH_3OC_6H_4CH_3 + Mn_2(CO)_9 \ [\xrightarrow[\text{fast}]{CO} Mn_2(CO)_{10}] \tag{22}$$

and, under a CO-containing atmosphere, the rate law corresponding to eq 20, where k_{21} (65 °C) = 6.0×10^{-4} s^{-1}, k_{-21}/k_{22} (65 °C) = 8.5, $\Delta H_{21}^{\ddagger} = 23.2$ kcal/mol, and $\Delta S_{21}^{\ddagger} = -4.8$ cal/(mol K) (in benzene).[23] This behavior in consistent with, and strongly supportive of, the mechanistic scheme of eq 21 and 22. A plausible mechanism of step 22 is that depicted by eq 6, i.e., oxidative addition of $HMn(CO)_5$ to the coordinatively unsaturated intermediate **6** to form $[p\text{-}CH_3OC_6H_4CH_2\overline{MnH(CO)_4Mn}(CO)_5]$, followed by the *one-center* reductive elimination of $p\text{-}CH_3OC_6H_4CH_3$. The first-order rate law originally observed for reaction 2 thus corresponds to the limiting form of eq 20 at low CO concentrations, i.e., to the rate-determining loss of CO according to eq 21.

Reaction 18b. The reaction of $Bz'Mn(CO)_5$ with $HMn(CO)_5$ in polar (coordinating) solvents such as acetone or acetonitrile (S) followed a quite different course, yielding the aldehyde, $p\text{-}CH_3OC_6H_4CH_2CHO$, and $cis\text{-}Mn_2(CO)_9S$ in accord with eq 23 and with the

(24) The p-CH_3O-substituted derivatives, **4a**, **4b**, and **5b**, were used in most of these studies because of their higher solubilities and because of the convenience of the OCH_3 ^1H NMR signal. Apart from modest rate variations no significant differences were noted between the behavior of **4a** and **2**.

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(26) The recombination of $\cdot Mn(CO)_5$ radicals according to eq 17 also has been shown to be diffusion controlled.[27]

(27) (a) J. L. Hughey IV, C. P. Anderson, and T. J. Meyer, *J. Organomet. Chem.*, 125, C49 (1977); (b) W. L. Waltz, O. Hackelberg, L. M. Dorfman, and A. Wojcicki, *J. Am. Chem. Soc.*, 100, 7260 (1978).

(28) J. Halpern, R. L. Sweany, and M. J. Russell, unpublished results.

$$Bz'Mn(CO)_5 + HMn(CO)_5 + S \rightarrow p\text{-}CH_3OC_6H_4CH_2CHO + Mn_2(CO)_9S \quad (23)$$

$$\frac{-d[Bz'Mn(CO)_5]}{dt} = \frac{k_{25}k_{26}[Bz'Mn(CO)_5][HMn(CO)_5]}{k_{-25} + k_{26}[HMn(CO)_5]} \quad (24)$$

$$Bz'Mn(CO)_5 + S \underset{k_{-25}}{\overset{k_{25}}{\rightleftharpoons}} \underset{7}{p\text{-}CH_3OC_6H_4CH_2C(=O)Mn(CO)_4S} \quad (25)$$

$$7 + HMn(CO)_5 \xrightarrow{k_{26}} p\text{-}CH_3OC_6H_4CH_2CHO + Mn_2(CO)_9S \quad (26)$$

rate law of eq 24, where k_{25} (25 °C) = 4.8×10^{-4} s^{-1}, $k_{-25}/k_{26} = 2.8 \times 10^{-2}$, $\Delta H_{25}^{\ddagger} = 16.7$ kcal/mol and $\Delta S_{25}^{\ddagger} = -18$ cal/(mol K).[23] This is consistent with the mechanistic scheme of eq 25 and 26. The value of k_{25} was found to be identical with that determined for the reaction of $Bz'Mn(CO)_5$ with PMe_2Ph to form $p\text{-}CH_3OC_6H_4CH_2C(=O)Mn(CO)_4PMe_2Ph$, presumably by the rate-determining step 25, followed by rapid trapping of 7 with PMe_2Ph. The difference in behavior between nonpolar and polar solvents is consistent with, and expected from, the known enhancement of the rates of other CO migratory insertion reactions [e.g., that of $CH_3Mn(CO)_5$] by polar (coordinating) solvents.[29]

Reaction 18c. While the stoichiometry depicted by eq 27 paralleled that of reaction 19, the reaction of

$$Bz'Mn(CO)_4P + HMn(CO)_4P \rightarrow p\text{-}CH_3OC_6H_4CH_3 + Mn_2(CO)_8P_2 \quad (27)$$

$$\frac{-d[Bz'Mn(CO)_4P]}{dt} = \frac{k_{29}k_{30}[Bz'Mn(CO)_4P][HMn(CO)_4P]}{k_{-29}\left(\frac{k_{-31}}{k_{31}}\right)^{1/2}[Mn_2(CO)_8P_2]^{1/2} + k_{30}[HMn(CO)_4P]} \quad (28)$$

$$Bz'Mn(CO)_4P \underset{k_{-29}}{\overset{k_{29}}{\rightleftharpoons}} p\text{-}CH_3OC_6H_4CH_2\cdot + \cdot Mn(CO)_4P \quad (29)$$

$$p\text{-}CH_3OC_6H_4CH_2\cdot + HMn(CO)_4P \xrightarrow{k_{30}} p\text{-}CH_3OC_6H_4CH_3 + \cdot Mn(CO)_4P \quad (30)$$

$$2\cdot Mn(CO)_4P \underset{k_{-31}}{\overset{k_{31}}{\rightleftharpoons}} Mn_2(CO)_8P_2 \quad (31)$$

$Bz'Mn(CO)_4P$ with $HMn(CO)_4P$ in benzene exhibited a distinctly different rate law corresponding to eq 28, where k_{29} (75 °C) = 5.5×10^{-4} s^{-1}, $k_{-29}/k_{30}(k_{31}/k_{-31})^{1/2} = 3.1 \times 10^{-2}$ $M^{-1/2}$, $\Delta H_{29}^{\ddagger} = 27.5$ kcal/mol, and $\Delta S_{29}^{\ddagger} = 4.5$ cal/(mol K).[23] This is consistent with the mechanism of eq 29–31, where P = $(p\text{-}CH_3OC_6H_4)_3P$.

Further confirmation of this mechanistic scheme was provided by experiments in which the $\cdot Mn(CO)_4P$ radical, generated in step 29, was intercepted and trapped by reaction with $HMn(CO)_5$ or CO according to eq 32 and 33, respectively.[23]

$$\cdot Mn(CO)_4P + HMn(CO)_5 \rightarrow HMn(CO)_4P + \cdot Mn(CO)_5 \quad (32)$$

$$\cdot Mn(CO)_4P + CO \rightarrow \cdot Mn(CO)_5 + P \quad (33)$$

The change in mechanism in going from reaction 19 to 27 presumably reflects the familar influence of phosphine ligand substitution in inhibiting the dissociation of CO from carbonyl complexes,[30] thus disfavoring the step corresponding to eq 21. The observation of the full rate law 28 also is favored by the lowering of the Mn–Mn bond dissociation energy in going from $Mn_2(CO)_{10}$ to $Mn_2(CO)_8P_2$.[31] This enhances the steady-state concentration of $\cdot Mn(CO)_4P$ and the resulting competition from the k_{-29} step.

Reaction 18d. Reaction of $Bz'Mn(CO)_4P$ with $HMn(CO)_5$ in benzene under N_2 resulted in the formation of $p\text{-}CH_3OC_6H_4CH_3$, with a rate law consistent with the rate-determining step 29, followed by rapid abstraction of a H atom from $HMn(CO)_5$ by the $p\text{-}CH_3OC_6H_4CH_2\cdot$ radical. Replacement of the N_2 atmosphere by CO resulted in enhancement of the rate of reaction as reflected in the second term of the rate law corresponding to eq 34 where k_{35} (75 °C) = 5.8×10^{-2}

$$-d[Bz'Mn(CO)_4P]/dt = (k_{29} + k_{35}[CO])[Bz'Mn(CO)_4P] \quad (34)$$

$$Bz'Mn(CO)_4P + CO \xrightarrow{k_{35}} [p\text{-}CH_3OC_6H_4CH_2C(=O)Mn(CO)_4P] \xrightarrow{HMn(CO)_5} \underset{8}{} p\text{-}CH_3OC_6H_4CH_2CHO \quad (35)$$

$$8 \rightarrow \cdot Mn(CO)_4P + p\text{-}CH_3OC_6H_4CH_2C(=O)\cdot \xrightarrow{HMn(CO)_5} p\text{-}CH_3OC_6H_4CH_2CHO \quad (36)$$

M^{-1} s^{-1}.[23] This *additional* contribution to the rate was reflected in the formation of a different product, namely the aldehyde $p\text{-}CH_3OC_6H_4CHO$, presumably by the reaction sequence of eq 35. Consistent with this interpretation, the product distribution was found to obey the relation $[p\text{-}CH_3OC_6H_4CH_2CHO]/[p\text{-}CH_3OC_6H_4CH_3] = k_{35}[CO]/k_{29}$. Since the intermediate 8 in reaction 35 hardly can contain a vacant coordination site, direct reaction with $HMn(CO)_5$ seems unlikely. Accordingly, the free-radical mechanism corresponding to eq 36 (i.e., analogous to that of eq 29–31) is favored. This suggests that the Mn-C(=O)R bond dissociation energy is relatively low, probably not in excess of 25 kcal/mol. Reaction 36 may be considered another model of the aldehyde-forming step in cobalt carbonyl catalyzed hydroformylation according to the mechanism depicted by eq 4.[2,21]

Comparisons with Other Intermolecular Reductive Elimination Reactions. The mechanistic features of at least two other systems involving intermolecular carbon–hydrogen bond forming reactions, namely those depicted by eq 37[21] and 38[3,4] (Cp = η^5-C_5H_5), have recently been investigated in some detail.[32]

$$CH_3Mo(CO)_3Cp + HMo(CO)_3Cp \rightarrow CH_3CHO + {}^1/_2[Mo_2(CO)_4(Cp)_2 + Mo_2(CO)_6(Cp)_2] \quad (37)$$

$$2cis\text{-}OsH(CH_3)(CO)_4 \rightarrow CH_4 + \overline{OsH(CO)_4Os(CH_3)(CO)_4} \quad (38)$$

(29) (a) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964); (b) M. J. Wax and R. G. Bergman, *ibid.*, **103**, 7028 (1981).

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

(31) (a) R. A. Jackson and A. J. Poe, *Inorg. Chem.*, **17**, 997 (1978); (b) R. A. Jackson and A. J. Poe, *ibid.*, **18**, 33 (1979).

(32) Several other apparently intermolecular reductive elimination have been described whose mechanisms have not been elucidated or which appear to proceed through indirect mechanisms.[21,22]

Reaction 37, which exhibited the second-order rate law $-d[CH_3Mo(CO)_3Cp]/[dt = k_{37}[CH_3Mo(CO)_3Cp][HMo(CO)_3Cp]$, was interpreted in terms of the mechanism depicted by eq 39 which corresponds to the

$$CH_3Mo(CO)_3Cp \rightleftarrows CH_3C(=O)Mo(CO)_2Cp \xrightarrow{HMo(CO)_3Cp} CH_3CHO + {}^1/_2[Mo_2(CO)_4(Cp)_2 + Mo_2(CO)_6(Cp)_2] \quad (39)$$

pathway 18b in our system. The corresponding reaction of $C_2H_5Mo(CO)_3Cp$ to yield C_2H_5CHO apparently proceeds through a similar mechanism. However, the reaction of $C_6H_5CH_2Mo(CO)_3Cp$ was more complicated and yielded some toluene as well as aldehyde, suggesting some contribution from a path analogous to (18c).

In the absence of added ligands, the reductive elimination of CH_4 from *cis*-$OsH(CH_3)(CO)_4$ was demonstrated to be binuclear, in accord with eq 38, by double labeling experiments [e.g., a mixture of $OsH(CD_3)(CO)_4$ + $OsD(CH_3)(CO)_4$ yields a mixture of CH_4, CH_3D, CD_3H, and CH_4]. Nevertheless, the reaction exhibited a *first-order* rate law. In the presence of an added ligand, L (such as PPh_3, PEt_3, pyridine, or ethylene), the reductive elimination of CH_4 (together with formation of $Os(CO)_4L$) exhibited the same rate law but was *intramolecular*. These observations were interpreted in terms of the mechanistic scheme of eq 40 and 41.[3,4]

$$OsH(CH_3)(CO)_4 \xrightarrow{\text{rate determining}} [CH_3COsH(CO)_3] \quad (40)$$

$$[CH_3COsH(CO)_3] \xrightarrow{\text{fast}} \begin{cases} \xrightarrow{OsH(CH_3)(CO)_4} CH_4 + OsH(CO)_4Os(CH_3)(CO)_4 \\ \xrightarrow{L} [CH_3COsH(CO)_3L] \longrightarrow CH_4 + Os(CO)_4L \end{cases} \quad (41a, 41b)$$

Two features of this system warrant comment in relation to the systems discussed earlier, namely:

(a) While the rate-determining step of the reactions encompassed by eq 40 and 41 parallels the initial steps of (18b) and (39), the formation of CH_4 instead of aldehyde from the intermediate acyl complex contrasts to the latter two reactions and seems surprising. The reasons for this distinction are unclear and warrant further investigation.

(b) *cis*-$OsH(CH_3)(CO)_4$ does not appear to undergo a simple *unassisted intramolecular* CH_4 reductive elimination reaction, i.e., analogous to eq 1. The reason for this probably is the instability of the fragment, i.e., $Os(CO)_4$, that would result from such a reductive elimination. This emphasizes the importance of thermodynamic, in addition to mechanistic, factors in influencing the course of such reductive elimination reactions. In the cases considered, intramolecular reductive elimination pathways leading to bimolecular products presumably are favored by the additional thermodynamic driving force derived from metal–metal bond formation.

A closely related reaction, the reductive elimination of H_2 from *cis*-$OsH_2(CO)_4$ [to form $Os_2H_2(CO)_8$], also has been demonstrated to be intermolecular and probably proceeds by a mechanism analogous to eq 18a.[33]

Application to the Determination of Transition-Metal–Alkyl Bond Dissociation Energies

The identification of the reductive elimination pathway corresponding to eq 18c (exemplified by reaction 27) opens up the possibility of utilizing kinetic measurements on such reductive elimination reactions to estimate transition-metal–alkyl bond dissociation energies, only a few of which are presently known reliably. If, as seems highly likely (and consistent with the available evidence),[16] the recombination of alkyl radicals with 17-electron metal radicals such as $Mn(CO)_5$ is diffusion-controlled, the activation enthalpy for homolytic metal–alkyl bond dissociation should approximate closely to the corresponding bond dissociation energy (exceeding the latter by about 2 kcal/mol). On this basis, a value of about 25 kcal/mol can be deduced for the Mn–C bond dissociation energy of *p*-$CH_3OC_6H_4CH_2Mn(CO)_4P$, from the value of $\Delta H_{29}^{\ddagger}$ (27.5 kcal/mol) derived from the kinetic measurements on reaction 27. (In any event, $\Delta H_{27}^{\ddagger}$ *must* constitute an *upper limit* for the corresponding bond dissociation energy.)

Relevance to Homologation Processes

Homologation reactions such as hydroformylation[34] and methanol homologation[35] currently are of great interest from the standpoints both of their chemistry and of the objective of utilizing synthesis gas (CO/H_2). Such reactions commonly proceed by a sequence of steps involving CO insertion into a metal–carbon bond followed by a C–H bond-forming reductive elimination step of the resulting acyl complex, yielding aldehyde. The efficiency of homologation in such systems may be constrained by competing hydrogenation resulting from a C–H bond-forming reductive elimination reaction of the alkylmetal complex prior *to CO insertion*. Such a situation is exemplified by the recently reported rhodium complex catalyzed hydroformylation of formaldehyde, which yields a mixture of glycolaldehyde and methanol, probably through a mechanistic scheme of the following type.[36]

$$CH_2{=}O \xrightarrow{Rh(CO)H_n} HOCH_2Rh(CO)H_{n-1} \begin{cases} \longrightarrow HOCH_2C(=O)RhH_{n-1} \longrightarrow HOCH_2CH(=O) & (42a) \\ \longrightarrow CH_3OH & (42b) \end{cases}$$

According to this scheme, the yield of $HOCH_2CHO$ relative to CH_3OH should be determined by the relative rates of migratory CO insertion and reductive elimination (i.e., of eq 42a and 42b). Studies such as those on reactions 19 and 23 suggest that the rate of migratory CO insertion, and hence the yield of $HOCH_2CHO$ ho-

(33) J. Evans and J. R. Norton, *J. Am. Chem. Soc.*, **96**, 7577 (1974).
(34) P. Pino, F. Piacenti, and M. Bianchi in "Organic Syntheses via Metal Carbonyls", Vol. 2, I. Wender and P. Pino, Eds., Wiley, New York, 1977, p 43, and references therein.
(35) (a) W. R. Pretzer and T. P. Koblynski, *Ann. N.Y. Acad. Sci.*, **333**, 58 (1980); (b) D. Slocum, in "Catalysis in Organic Synthesis", Academic Press, New York, 1980, p 245.
(36) A. Spencer, *J. Organomet. Chem.*, **194**, 113 (1980).

mologation product, should be enhanced by coordinating solvents. The marked increase in $HOCH_2CH$-O:CH_3OH product ratio in going from less coordinating solvents (e.g., 1:35 in tetrahydrofuran) to dimethylformamide (2.6:1) or pyridine (1:1.6) is consistent with this.[36]

Concluding Remarks

Although both intramolecular and intermolecular C–H bond-forming reductive elimination reactions are believed to be of widespread occurrence in the context of a variety of catalytic and stoichiometric processes, only a few such reactions, notably those that have been cited in this Account, have been subjected to detailed kinetic and mechanistic studies. The scope of intramolecular C–H bond-forming reductive elimination reactions that are susceptible to direct observation and study appears to be constrained by the accessibility and stability of the *cis*-hydridoalkyl starting compounds. The available information governing the mechanisms and reactivity patterns of such reactions, accordingly, is very limited.

The scope for directly observing and studying intermolecular C–H bond-forming reductive elimination reactions is considerably more extensive. Indeed, such processes appear to be widespread and to occur even for compounds, for example *cis*-$OsH(CH_3)(CO)_4$, that can, in principle, undergo intramolecular reductive elimination. Our studies on the reductive elimination reactions of benzylmanganese carbonyls with hydridomanganese carbonyls have been particularly revealing and have resulted in the identification of four distinct pathways of binuclear reductive elimination, depicted by eq 18a–18d, in closely related systems.[23] 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 mechanisms of such reductive elimination reactions without appropriate diagnostic evidence, or of extrapolating from one system or set of conditions to another (even closely related) one. While some of the factors influencing the rate and choice of pathway in such reactions have been identified, unresolved questions remain and further studies on a wider range of systems clearly are warranted.

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