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Binuclear Oxidative Addition–Reductive Elimination Reactions*

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Summary

The mechanistic aspects of oxidative addition and reductive elimination reactions in systems involving binuclear complexes are discussed. A variety of mechanisms are identified. In some cases the reactive species are mononuclear complexes. In others, binuclear species are directly involved but the oxidative addition or reductive elimination step itself occurs at a single metal atom site. The systems examined fail to reveal distinctive reactivity patterns or roles for binuclear complexes in such oxidative addition or reductive elimination reactions beyond those of thermodynamically stable reactant or product reservoirs.

Introduction

The study of binuclear and polynuclear complexes, especially of transition metals, has attracted extensive interest in recent years [1]. Many such complexes, often exhibiting distinctive compositions and bonding arrangements, now have been synthesized and structurally characterized. At the same time, relatively little progress has been made toward the elucidation of the chemical behavior of such systems and toward the realization of distinctive reactivity patterns and catalytic properties on the part of polynuclear complexes, compared with their mononuclear counterparts [1].

This article addresses some fairly elementary aspects of the chemistry of such systems, notably relating to oxidative addition [2] and reductive elimination reactions involving two metal centers, such as those depicted by eqns. 1–3. The kinetic and mechanistic features of such reactions are discussed with particular reference to the roles of 'binuclear' *vs.* 'mononuclear' species and reactions steps.

The clear recognition of the roles of binuclear complexes in such reactions tends to be complicated by the following considerations:

(a) The formation and dissociation of binuclear complexes often are fast compared with the reactions of interest. Hence, both mononuclear and binuclear complexes are present and accessible as reactants. The recognition of binuclear complexes as the *initial* reactants or *final* products does not necessarily identify such species as being directly involved in the actual oxidative addition or reductive elimination step.

(b) The oxidative addition–reductive elimination reactions typically observed in binuclear systems often are exhibited also by mononuclear complexes, so that the roles of binuclear complexes are not readily identified by their distinctive chemistry. Indeed, very little distinctive chemistry, including chemistry relevant to catalysis, has thus far been identified for binuclear and polynuclear complexes.

$$M_2L_{2n}\ (\text{or } 2ML_n) + H_2 \rightleftarrows 2H{-}ML_n \qquad (1)$$

$$M_2L_{2n}\ (\text{or } 2ML_n) + O_2 \rightleftarrows L_nM{-}O{-}O{-}ML_n \text{ or } L_nM{-}ML_n(O_2) \qquad (2)$$

$$R{-}ML_n + H{-}ML_n \rightarrow R{-}H + M_2L_{2n}\ (\text{or } 2ML_n) \qquad (3)$$

Oxidative Addition of H_2

The possible involvement of binuclear species or reactions in the catalytic activation of H_2 was recognized early in the study of such systems [3, 4]. Among the earliest samples of a homogeneously catalyzed hydrogenation reaction to be identified was the catalysis by copper(I) acetate in quinoline solution of the reduction by H_2 of substrates such as copper(II) or quinone (Q). The rate-law for these reactions, represented by eqn. 4, originally was interpreted [3] in terms of catalysis by a binuclear $(Cu^I)_2$ complex according to eqn. 5 but this interpretation was subsequently questioned and an alternative mechanism involving a termolecular rate-determining step (eqn. 6) was favored [4]. Since the equilibrium for formation of the alleged binuclear complex (eqn. 7) presumably is rapidly established, the two alternative interpretations are kinetically indistinguishable and the role, if any, of binuclear complexes in this system remains uncertain.

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$$\text{Rate} = k_4[H_2][(Cu^I)_2] \quad OR \quad k_4'[H_2][Cu^I]^2 \qquad (4)$$

$$(Cu^I)_2 \xrightarrow[k_4]{[H_2]} [(Cu^I)_2\cdot H_2] \xrightarrow[\text{fast}]{Q} QH_2 + (Cu^I)_2 \qquad (5)$$

$$2Cu^I \xrightarrow[k_4']{H_2} 2[Cu^I\cdot H] \xrightarrow[\text{fast}]{Q} QH_2 + 2Cu^I \qquad (6)$$

$$2Cu^I \rightleftarrows (Cu^I)_2 \qquad (7)$$

An interesting sequel to this situation was our finding, in a closely related system, that copper(I) heptanoate in heptanoic acid solution also catalyzes the oxidation of H_2, for example by copper(II) [5]. In this case the reversible dimerization of Cu^I to form a binuclear complex as depicted by eqn. 7 was unequivocally demonstrated by spectroscopic and kinetic measurements. However, the binuclear complex was found to be completely inactive, the catalytic mechanism involving the *heterolytic* splitting of H_2 by mononuclear Cu^I according to eqn. 8.

$$Cu^I \xrightarrow[-H^+]{H_2} CuH \xrightarrow[-H^+]{2Cu^{II}} 3Cu^I \qquad (8)$$

Another early example of the homogeneous activation of H_2 involves the hydroformylation of olefins and related hydrogenation reactions catalyzed by cobalt carbonyl complexes [6]. In this case also a binuclear complex, $[Co_2(CO)_8]$, was identified, at least as a catalyst precursor. However, it is now clear that this complex is converted through dissociative reactions to mononuclear reaction intermediates, notably $HCo(CO)_4$, and the role, *if any*, of binuclear complexes in this system still remains uncertain. The absence of evidence for a definitive role for binuclear complexes extends to virtually all of the many homogeneously catalyzed hydrogenation reactions that have now been identified including those in which two metal centers clearly are involved as in the examples of eqn. 9 [7] and 10 [8].

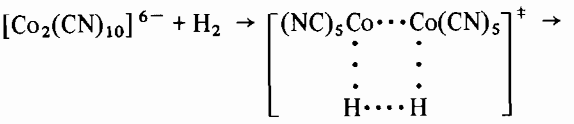
$$2Ag^+ + H_2 \rightleftarrows 2AgH^+ \qquad (9)$$

$$2[Co(CN)_5]^{3-} + H_2 \rightleftarrows 2[HCo(CN)_5]^{3-} \qquad (10)$$

Even where binuclear complex formation is detected, *e.g.*, for $[Co(CN)_5]^{3-}$ (eqn. 11), such formation is rapid compared with the reaction with H_2 so that the alternative bimolecular and termolecular reaction pathways corresponding to eqns. 12a and 12b are kinetically indistinguishable.

$$2[Co(CN)_5]^{3-} \rightleftarrows [Co_2(CN)_{10}]^{6-} \qquad (11)$$

$$2[Co(CN)_5]^{3-} + H_2 \rightarrow [(NC)_5Co\cdots H\cdots H\cdots Co(CN)_5]^{\ddagger} \rightarrow 2[HCo(CN)_5]^{3-} \qquad (12a)$$

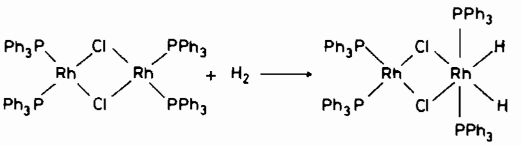


$$[Co_2(CN)_{10}]^{6-} + H_2 \rightarrow \left[\begin{array}{ccc} (NC)_5Co & \cdots & Co(CN)_5 \\ \vdots & & \vdots \\ H & \cdots & H \end{array}\right]^{\ddagger} \rightarrow 2[HCo(CN)_5]^{3-} \qquad (12b)$$

Notwithstanding a widespread prejudice to favor bimolecular reaction pathways over alternative termolecular ones, it seems likely that the four-center transition state in eqn. 12b is disfavored on orbital symmetry grounds, and the termolecular mechanism corresponding to eqn. 12a, *which does not involve the binuclear* $[Co_2(CN)_{10}]^{6-}$ *complex*, is preferred. This situation finds a close parallel in the reaction between H_2 and I_2 which has now been demonstrated to proceed through $I^\bullet$ atoms formed by reversible dissociation of I_2, the latter itself being unreactive toward H_2 (eqn. 13) [9].

$$I_2 \rightleftarrows 2I^\bullet \xrightleftharpoons{H_2} 2HI \qquad (13)$$

One documented example of the oxidative addition of H_2 to a binuclear complex is depicted by eqn. 14 [10, 11]. In this case, the oxidative addition reaction is *mononuclear*, involving only one of the Rh centers. Remarkably, the rate constant of reaction 14 ($5\ M^{-1}\ sec^{-1}$ at 25 °C) is virtually identical to that for the oxidative addition of H_2 to the closely related mononuclear complex, $[RhCl(PPh_3)_3]$ [10]. On the other hand, addition of H_2 to one of the Rh atoms of the binuclear complex $[Rh_2Cl_2(PPh_3)_4]$ (eqn. 14) apparently deactivates the other Rh^I center toward oxidative addition of a second H_2 molecule. It is unclear whether the reasons for this are steric or electronic. In any event, the reactivity of this binuclear Rh^I complex toward oxidative addition of H_2 does not appear to be in any way distinctive from that of related mononuclear complexes.



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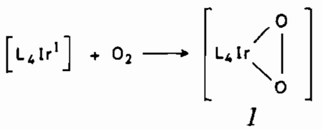
In closely related systems, the reaction of H_2 with the thiolato-bridged binuclear complexes, $[Ir(\mu\text{-S-t-Bu})(CO)(PR_3)]_2$ (R = Me, Ph, OMe, etc.) to form dihydrides $[IrH(\mu\text{-S-t-Bu})(CO)(PR_3)]_2$ in which one H atom is bound to each Ir, also has been postulated to proceed *via* initial oxidative addition of H_2 to *one* of the Ir atoms followed by migration of one of the H atoms to the other Ir atom [12]. Initial oxidative addition to one Rh atom also has been proposed for the reactions of CH_3I and CH_3Br with a related binuclear Rh complex, $[Rh(S\text{-t-Bu})(CO)(PMe_2Ph)]_2$ [13].

Oxidative Addition of O_2

Two general modes of binding of O_2 to metal complexes, exemplified by eqns. 15 and 16, now are well recognized [14].



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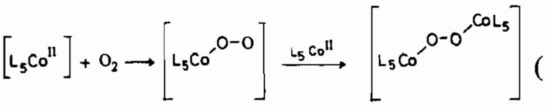

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Such reactions are accompanied by increases in the formal oxidation state of the metals (*e.g.*, $Ir^I \rightarrow Ir^{III}$; $Co^{II} \rightarrow Co^{III}$, *etc.*) and thus can be described as oxidative addition reactions. The symmetrical ('side on') bonding of O_2 corresponding to *1* is characteristic of two electron donor metal complexes, *e.g.*, those of Pt^0, Co^I, Rh^I, Ir^I, *etc.* while the 'end on' bonding corresponding to *2* and *3* is characteristic of one electron donor complexes such as those of Co^{II} and Fe^{II}. Such one electron donors may form either mononuclear or dinuclear adducts of O_2, exemplified by *2* and *3*, respectively, but the formation of the latter is believed to result from sequential reactions of mononuclear complexes as depicted by eqn. 16. Such adducts, notably of Fe^{II}, have received considerable attention in view of their roles as biological oxygen carriers (*e.g.*, myoglobin and hemoglobin) [15] and as oxygen-activating enzymes such as cytochrome P_{450} [16].

While examples of type *3 binuclear binding* of O_2 to Co^{II} complexes are well documented, departures from this mode also have been identified. We have found that $[Co^{II}(CN)_2(PMe_2Ph)_3]$ reacts with O_2 according to the usual 2:1 stoichiometry, (eqn. 17) but the resulting binuclear adduct has the structure depicted by *4* in which O_2 is coordinated symmetrically to *one* Co atom in a manner similar to that of *1* [17]. The two Co^{III} ions thus are connected by a CN^-, rather than by an O_2, bridge.

$$2[Co(CN)_2(PMe_2Ph)_3] + O_2 \rightarrow [Co_2(CN)_4(PMe_2Ph)_5(O_2)] + PMe_2Ph \qquad (17)$$

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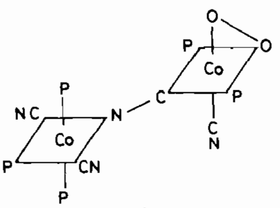

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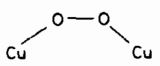
The rate-law for reaction 17 (eqn. 18a) [17] is consistent with the mechanism depicted by eqn. 18b. According to this mechanism, the coupling of two Co^{II} ions to form the binuclear unit *5* (Co_2^{II} or Co^{III}–Co^I) serves the purpose of generating a two electron reservoir (*i.e.*, an effective Co^I complex) rather than providing two Co^{II} sites for binuclear O_2 binding.

$$\text{Rate} = k[Co(CN)_2P_3]^2[O_2][CN^-]^{-1} \qquad (18a)$$

$$2[Co^{II}(CN)_2P_3] \overset{-P}{\rightleftharpoons} \underset{5}{[P_3(NC)_2Co^{III}\text{–NC–}Co^I(CN)_2P_2]} \xrightarrow{O_2} \underset{4}{[P_3(NC)_2Co^{III}\text{–NC–}Co^{III}(CN)_2P_2(O_2)]} \qquad (18b)$$

The unprecedented structure of *4* suggests that reexamination is warranted of the structures assumed for other binuclear O_2 adducts, for example the closely related 1:2 adduct of O_2 with $[Co^{II}(CN)_2(Ph_2PCH_2PPh_2)_2]$ which has been formulated as an O_2-bridged complex [18]. At issue also is the mode of binding of O_2 to binuclear metalloproteins such as hemocyanin and hemerythrin, in which binding of O_2 is associated with two Cu^I and two Fe^{II} ions, respectively. While the binding of O_2 to these proteins usually is assumed to be binuclear as in *6* [19, 20] the alternative possibility of mononuclear binding (*7*), by analogy with *4*, obviously also warrants consideration.



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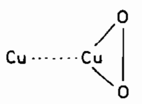

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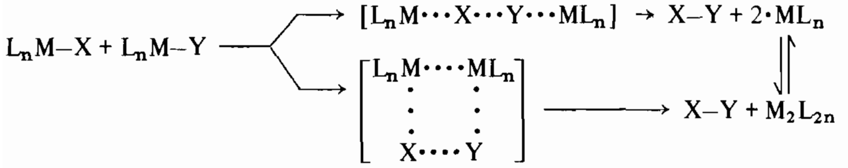
Binuclear Reductive Elimination Reactions

Binuclear reductive elimination reactions conform to the general overall stoichiometry of eqn. 19. Known variants include those for which: X = Y = H; X = alkyl or acyl, Y = H; X, Y = alkyl or acyl.

$$L_nM\text{–}X + L_nM\text{–}Y \rightarrow X\text{–}Y + M_2L_{2n} \text{ (or } 2ML_n) \qquad (19)$$

Several plausible alternative mechanisms may be envisioned for such reactions, namely:

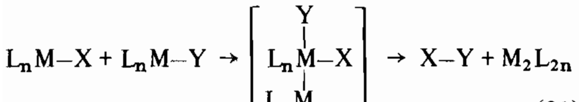
(a) *Concerted (2-Center)*



$$L_nM\text{–}X + L_nM\text{–}Y \rightarrow [L_nM\cdots X\cdots Y\cdots ML_n] \rightarrow X\text{–}Y + 2{\cdot}ML_n \qquad (20a)$$

$$L_nM\text{–}X + L_nM\text{–}Y \rightarrow \left[\begin{matrix} L_nM\cdots ML_n \\ \vdots \quad\quad \vdots \\ X\cdots Y \end{matrix}\right] \longrightarrow X\text{–}Y + M_2L_{2n} \qquad (20b)$$

(b) *Concerted (1-Center)*



$$L_nM\text{–}X + L_nM\text{–}Y \rightarrow \left[\begin{matrix} Y \\ | \\ L_nM\text{–}X \\ | \\ L_nM \end{matrix}\right] \rightarrow X\text{–}Y + M_2L_{2n}$$

(21)

(c) *Stepwise (Free Radical)*

$$L_nM\text{–}X \rightarrow X{\cdot} + {\cdot}ML_n \qquad (22a)$$

$$X{\cdot} + L_nM\text{–}Y \rightarrow X\text{–}Y + {\cdot}ML_n \qquad (22b)$$

$$2{\cdot}ML_n \rightarrow M_2L_{2n} \qquad (22c)$$

Reactions 20a and 20b correspond to the reverse of the oxidative addition reactions 12a and 12b, respectively. Thus, from considerations of microscopic reversibility, it may be concluded that the reductive elimination of H_2 from $[HCo(CN)_5]^{3-}$ proceeds through such a mechanism (probably 20a) [8]. The reverse of the mechanism corresponding to eqn. 22 has been identified for the oxidative addition of alkyl halides and H_2O_2 to Co^{II} complexes (*e.g.*, eqn. 23) [21–23]. Clear evidence for oxidative addition by the reverse of reaction 21 is lacking but a *possible* instance is the reaction of H_2 with $[Co_2(CO)_8]$ to form $[HCo(CO)_4]$.

$$[Co(CN)_5]^{3-} + RX \rightarrow [XCo(CN)_5]^{3-} + R{\cdot} \qquad (23a)$$

$$[Co(CN)_5]^{3-} + R{\cdot} \rightarrow [RCo(CN)_5]^{3-} \qquad (23b)$$

It should be noted that only in the mechanism corresponding to eqn. 20, can the reductive elimination step itself be described as binuclear. In the case of eqn. 21 the formation of the binuclear intermediate presumably enhances the driving force for the overall reaction by virtue of the metal–metal bond, but the reductive elimination step itself involves only one metal atom site. In the case of mechanism 22, binuclear species play no role whatsoever in the reaction.

In the present paper we shall examine particularly the mechanistic aspects of binuclear reductive elimination reactions such as those depicted by eqn. 3 where R = alkyl or acyl. Such reactions are believed to be of widespread occurrence and of considerable importance in various catalytic processes, for example the product forming steps in $[HCo(CN)_5]^{3-}$-catalyzed hydrogenation [24] and $[HCo(CO)_4]$-catalyzed hydroformylation of olefins [25].

Notwithstanding their widespread occurrence and importance, only recently have such C–H bond-forming reductive elimination reactions been directly examined and some features of their mechanisms identified. The most extensive and detailed investigations reported thus far relate to the reactions of benzylmanganese complexes (*8*) with the corresponding manganese carbonyl hydrides (*9*) [26]. The results of our studies on these systems are summarized below.

Cis-$RMn(CO)_4L$	*Cis*-$HMn(CO)_4L$
8a R = *p*-$CH_3OC_6H_4CH_2$, L = CO	*9a* L = CO
8b R = *p*-$CH_3OC_6H_4CH_2$, L = (*p*-$CH_3OC_6H_4)_3P$	*9b* L = (*p*-$CH_3OC_6H_4)_3P$

Reaction of 8a with 9a in Non-polar Solvents

The reaction of *8a* with *9a* in non-polar solvents such as benzene yields the corresponding toluene in accord with eqn. 24, and with the rate law depicted by eqn. 25, supporting the mechanistic scheme of eqn. 26–27. A plausible mechanism for step 27 involves the oxidative addition of *9a* to the coordinatively unsaturated intermediate *10* to form $[\overline{RMnH(CO)_4Mn}(CO)_5]$, followed by reductive elimination of *p*-$CH_3OC_6H_4CH_3$ (RH). *This mechanism corresponds to that of eqn. 21.*

$$8a + 9a \rightarrow RH + Mn_2(CO)_{10} \qquad (24)$$

$$-d[8a]/dt = k_{26}k_{27}[8a]\,[9a]/(k_{-26}[CO] + k_{27}[9a]) \qquad (25)$$

$$8a \underset{k_{-26}}{\overset{k_{26}}{\rightleftharpoons}} \underset{10}{RMn(CO)_4} + CO \qquad (26)$$

$$10 + 9a \xrightarrow{k_{27}} RH + Mn_2(CO)_9 \quad [\xrightarrow{CO} Mn_2(CO)_{10}] \qquad (27)$$

Reaction of 8a with 9a in Polar Solvents

The reaction *8a* with *9a* in polar solvents such as acetone or acetonitrile (S) follows a different course, yielding the aldehyde p-$CH_3OC_6H_4CH_2CHO$ (RCHO) and *cis*-$Mn_2(CO)_9S$ in accord with eqn. 28 and with the rate-law, eqn. 29, consistent with the mechanism of eqns. 30–31. The value of k_{30} (4.8×10^{-4} sec^{-1} at 25 °C) is identical with that determined for reaction of *8a* with PMe_2Ph to form $RCOMn(CO)_4PMe_2Ph$, presumably by the rate determining step 20, followed by rapid trapping of *11* with PMe_2Ph. The difference in behavior between non-polar and polar solvents is consistent with, and expected from, the known enhancement of the rate of migratory insertion [*e.g.*, for $CH_3Mn(CO)_5$] by polar solvents [27].

$$8a + 9a + S \rightarrow RHCO + Mn_2(CO)_9S \qquad (28)$$

$$-d[8a]/dt = k_{30}k_{31}[8a]/(k_{-30} + k_{31}[9a]) \qquad (29)$$

$$8a + S \underset{k_{-30}}{\overset{k_{30}}{\rightleftharpoons}} \underset{11}{R\overset{\overset{O}{\|}}{C}Mn(CO)_4S} \qquad (30)$$

$$11 + 9a \xrightarrow{k_{31}} RCHO + Mn_2(CO)_9S \qquad (31)$$

Reaction of 8b with 9b

While the stoichiometry depicted by eqn. 32 parallels that of reaction 24, the reaction of *8b* with *9b* in benzene exhibits a distinctly different rate-law corresponding to eqn. 33, consistent with the mechanism of eqns. 34–36. The change in mechanism in going from reaction 24 to 32 presumably reflects the familiar influence of phosphine substitution in inhibiting the dissociation of CO from carbonyl complexes [28], thus disfavoring the step corresponding to eqn. 26. Further evidence for the proposed mechanism also is provided by the trapping of $\cdot Mn(CO)_4P$ (by H-abstraction from $HMn(CO)_5$ or by reaction with CO) to form $Mn(CO)_5$ [26]. The measured value of $\Delta H^{\neq}_{34}$ (27 kcal/mol) can be identified with the R–Mn bond dissociation energy of *8b*. This illustrates the potential utility of the study of such reductive elimination reactions for the determination of transition metal–alkyl bond dissociation energies, only few of which have been reliably measured to date. *The mechanism depicted by eqns. 34–36 corresponds to that of eqn. 22.*

$$8b + 9b \rightarrow RH + Mn_2(CO)_8P_2 \qquad (32)$$

$$\frac{-d[8b]}{dt} = \frac{k_{34}k_{35}[8b]\,[9b]}{k_{-34}(k_{-36}/k_{36})^{1/2}\,[Mn_2(CO)_8P_2]^{1/2} + k_{35}[9b]} \qquad (33)$$

$$8b \underset{k_{-34}}{\overset{k_{34}}{\rightleftharpoons}} R\cdot + \cdot Mn(CO)_4P \qquad (34)$$

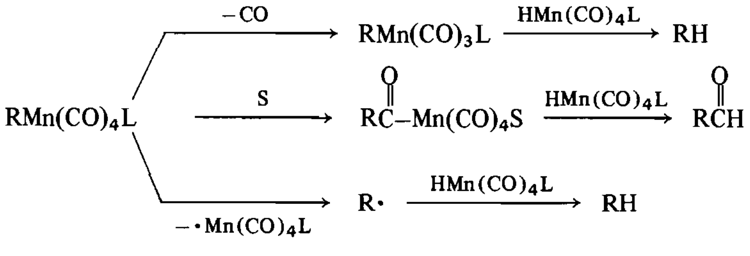
$$R\cdot + 9b \xrightarrow{k_{35}} RH + \cdot Mn(CO)_4P \qquad (35)$$

$$2\cdot Mn(CO)_4P \underset{k_{-36}}{\overset{k_{36}}{\rightleftharpoons}} Mn_2(CO)_8P_2 \qquad (36)$$

Thus, three distinct pathways, corresponding to the schemes of eqns. 37a, 37b and 37c, respectively, have been identified for binuclear reductive elimination reactions of benzylmanganese carbonyls with hydridomanganese carbonyls [26].

(See eqns. 37a,b,c below.)

Relatively modest changes in ligands or solvent may result in essentially complete crossover from one pathway to another. This underlines the danger of assuming the mechanisms of such binuclear reductive elimination reactions without appropriate diagnostic evidence or of extrapolating from one system or set of condition to another.



(37a)

(37b)

(37c)

It is significant that none of the C–H bond-forming reductive elimination pathways identified actually involves concerted 2-center binuclear reductive elimination (*i.e.*, according to eqn. 20).

Comparisons with other Reductive Elimination Reactions

The mechanistic features of two other systems involving intermolecular C–H bond-forming reductive elimination reactions, namely those depicted by eqn. 38 [29] and 39 [30, 31] ($Cp = \eta^5\text{-}C_5H_5$) have recently been examined in some detail.

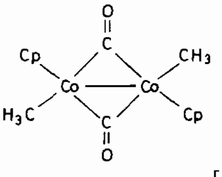
$$[CH_3Mo(CO)_3Cp] + [HMo(CO)_3Cp] \rightarrow CH_3\overset{O}{\overset{\|}{C}}H + 1/2[Mo_2(CO)_4(Cp)_2] + 1/2[Mo_2(CO)_6(Cp)_2] \quad (38)$$

$$2\,cis\text{-}[OsH(CH_3)(CO)_4] \rightarrow CH_4 + [\overline{OsH(CO)_4Os}(CH_3)(CO)_4] \quad (39)$$

Reaction (38) has been shown to follow a pathway analogous to that of eqn. 37a, while the corresponding reaction of $[C_6H_5CH_2Mo(CO)_3Cp]$ with $[HMo(CO)_3Cp]$, which yields toluene, appears to proceed, at least in part, through a free radical pathway analogous to eqn. 37c [29]. On the other hand reaction 39 appears to proceed through a variant of eqn. 37b, in which migratory insertion of CO in the Os–CH_3 bond to form $[OsH(COCH_3)(CO)_3]$, followed by reaction with $[OsH(CH_3)(CO)_4]$, results in reductive elimination of CH_4 rather than of CH_3CHO [30, 31]; the reasons for this disparity are unclear. The mechanism encompassed by eqn. 37a also finds a parallel in that proposed for the ***binuclear*** reductive elimination of H_2 from *cis*-$[OsH_2(CO)_4]$ [32].

It is of interest that *cis*-$[OsH(CH_3)(CO)_4]$ and *cis*-$[OsH_2(CO)_4]$ do not appear to undergo simple ***unassisted intramolecular*** reductive elimination reactions, *i.e.*, to yield CH_4 and H_2, respectively. The reason for this probably is the instability of the mononuclear fragment, *i.e.*, $[Os(CO)_4]$, that would result from such a process. This emphasizes the importance of thermodynamic, in addition to mechanistic, factors in influencing the course of such reductive elimination reactions. In the cases considered, intermolecular reductive elimination pathways leading to binuclear products presumably are favored by the additional thermodynamic driving force derived from metal–metal bond formation.

An example of C–C bond-forming reductive elimination reaction of a binuclear complex (*12*) is depicted by eqn. 40 [33]. The mechanism deduced for this reaction is depicted by eqn. 41. Significantly, it is concluded that the reductive elimination process itself (eqn. 41b) involves a mononuclear species, *i.e.*, *13*. The role of the binuclear complex *12* in this system apparently is only that of a thermodynamically stable 'reservoir'.



12

$$\rightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 + [Co_x(Cp)_y(CO)_z]\ \text{clusters} \quad (40)$$

$$\mathit{12} \rightleftarrows 2[CpCo(CO)CH_3] \rightarrow \underset{\mathit{13}}{[CpCo(CO)(CH_3)_2]} + [\text{“CpCoCO”}] \quad (41a)$$

$$\mathit{13} \rightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 + [\text{“CpCo”}] \quad (41b)$$

$$[\text{‘CpCoCO”}] + [\text{“CpCO”}] \rightarrow [Co_x(Cp)_y(CO)_z]\ \text{clusters} \quad (41c)$$

Concluding Remarks

Only a few oxidative addition and reductive elimination reactions involving binuclear complexes have been mechanistically characterized. A variety of mechanisms have been identified for such systems. In some cases, the reactions proceed through mononuclear intermediates with no recognizable role for the binuclear species other than that of thermodynamically stable reaction or product reservoirs. In other instances binuclear species are directly involved in the reaction but even in such cases the oxidative addition or reductive elimination step itself may occur at a single metal atom site. The systems thus far examined and discussed in this article fail to reveal distinctive reactivity patterns for binuclear complexes in oxidative addition–reductive elimination reactions.

Acknowledgement

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