

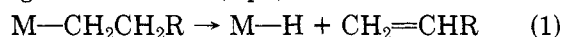
Organometallic Elimination Mechanisms: Studies on Osmium Alkyls and Hydrides

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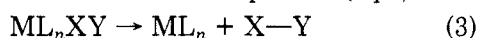
Any application of transition-metal reagents to organic synthesis, whether stoichiometric or catalytic, requires the removal of the product from the metal at the end of the reaction. An understanding of elimination processes is thus essential. Unfortunately, only β -hydrogen elimination (eq 1) can be said to be well-



established and understood (at least for group 8 metals).^{1,2} Since oxidative addition (eq 2) is an important



way of forming metal-carbon bonds,³ conventional wisdom has been that the reverse process (eq 3) must



be an important way of breaking them. Although this process is usually called "reductive elimination", we shall use the more specific "simple intramolecular reductive elimination" for the process shown in eq 3, leaving "reductive elimination" as a general term for all processes, regardless of the number of metals involved, where formal oxidation states decrease after elimination.

There are, however, a number of observations which are difficult to explain if β -hydrogen elimination and simple intramolecular reductive elimination are the only processes involved. One observation is the near-total absence of stable alkyl hydrides,⁴⁻¹¹ despite the fact that they appear to be intermediates in many reactions. (For example, $Rh(PPh_3)_3Cl$ ¹² and other homogeneous catalysts for olefin hydrogenation have as the final step in their mechanism of action the elimination of alkane from an alkyl hydride complex.)

While the rarity of alkyl hydrides does not logically imply instability, it does suggest it, particularly as large numbers of stable dialkyls, dihydrides, and indeed polyalkyls^{2c,d} and polyhydrides¹³ are known. One thus inquires whether the simple intramolecular reductive elimination of R-H can be faster than that of R-R or H-H. Construction of an orbital correlation diagram for *cis*- ML_4R_2 discloses that concerted *cis* elimination of R-R is not forbidden by any symmetry considerations,^{2a} and the unsymmetric R-H elimination thus has no advantage over the symmetric eliminations R-R and H-H.

If one analyzes the reaction thermodynamically, it turns out to be possible for ΔH to be lower and more favorable for R-H elimination than for R-R or H-H.

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There are now respectable arguments¹⁴ for the proposition that M-H bond strengths are greater than M-C bond strengths. If for a given system one assumes a constant M-H bond strength X greater than a constant M-C bond strength Y , and takes C-H, C-C, and H-H bond strengths at 99, 83, and 104 kcal/mol, respectively, then ΔH for R-R elimination is $(2Y - 83)$ and for H-H elimination is $(2X - 104)$. If $16 > (X - Y) > 5$, ΔH is lowest for R-H elimination.

The rate of elimination, however, could only be affected if the transition state strongly resembled the products, so that ΔH^\ddagger as well as ΔH would be lowest for R-H elimination. If ΔH^\ddagger is largely a function of the energies of the bonds being broken, then R-H elimination obviously cannot be faster than both R-R and H-H elimination. Unfortunately, an homologous series ML_nR_2 , $ML_n(R)(H)$, ML_nH_2 , all of the members of which undergo simple intramolecular reductive elimination, is unknown.

Facile simple intramolecular reductive elimination at $-25^\circ C$ has, however, recently been demonstrated for *cis*- $Pt(PPh_3)_2(H)CH_3$.¹⁵ The corresponding dialkyls are more stable. If the intramolecular reductive elimination of H_2 from the hypothetical *cis*- $Pt(Ph_3P)_2H_2$ proves fastest of all, it will imply either that the Pt-H bond is weaker than the Pt-C bond, contrary to the general trend noted above, or that the greater mobility of

(1) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Am. Chem. Soc.*, **94**, 5258 (1972); J. X. McDermott, J. F. White, and G. M. Whitesides, *ibid.*, **98**, 6521 (1976).

(2) For reviews of general decomposition modes for the M-R bond see (a) P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, **2**, 271 (1973); (b) M. C. Baird, *J. Organomet. Chem.*, **64**, 289 (1974); (c) R. R. Schrock and G. W. Parshall, *Chem. Rev.*, **76**, 243 (1976); (d) P. J. Davidson, M. R. Lappert, and R. Pearce, *ibid.*, **76**, 219 (1976).

(3) (a) J. P. Collman, *Adv. Organomet. Chem.*, **7**, 53 (1968); (b) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1970); (c) J. Halpern, *ibid.*, **3**, 386 (1970).

(4) The only hydridomethyl complexes known to us other than the ones discussed in this paper are *cis*- $RuH(CH_3)(Ph_2PCH_2CH_2PPh_2)_2$,⁵ *trans*- $Ni(H)CH_3(PCy_3)_2$,⁶ $Cp_2Zr(H)CH_3$,⁷ $[Cp_2MoH_2(CH_3)]^+$,⁸ $RuH(CH_3)(PPh_3)_2(Et_2O)_2$,⁹ and $Cp_2WH(CH_3)$.¹⁰ There are also a few hydride complexes with alkyl ligands stabilized by substitution or chelation, e.g., $[Ru(dmpe)(H)(Me_2PCH_2CH_2P(CH_3)CH_2)]_2$.¹¹ Abbreviations used: Cy, cyclohexyl; Cp, π -cyclopentadienyl; dmpe, $Me_2PCH_2CH_2PMe_2$.

(5) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 6017 (1963).

(6) K. Jonas and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **8**, 519 (1969).

(7) P. C. Wailles and H. Wiegold, *J. Organomet. Chem.*, **24**, 405 (1970).

(8) D. Stroppe and D. F. Shriver, *J. Am. Chem. Soc.*, **95**, 8197 (1973).

(9) D. J. Cole-Hamilton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 797 (1977).

(10) M. Berry, S. G. Davies, and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 99 (1978).

(11) F. A. Cotton, D. L. Hunter, and B. A. Frenz, *Inorg. Chim. Acta*, **15**, 155 (1975).

(12) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(13) "Transition Metal Hydrides", E. L. Muetterties, Ed., Marcel Dekker, Inc., New York, 1971.

(14) See J. A. Connor, *Top. Current Chem.*, **71**, 71 (1977), especially p 87.

(15) L. Abis, A. Sen, and J. Halpern, *J. Am. Chem. Soc.*, **100**, 2915 (1978).

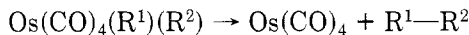
hydrogen ligands outweighs bond strength considerations. If *cis*-Pt(Ph₃P)₂H₂ proves more stable than *cis*-Pt(Ph₃P)₂(H)CH₃, it will imply that the transition state for R-H elimination from the latter strongly resembles the products. Similarly, Cp₂WH₂ and Cp₂W(CH₃)₂ are more stable than Cp₂W(H)CH₃,¹⁰ if the latter proves to decompose by simple intramolecular reductive elimination, the transition state will probably resemble the products.

The search for a satisfactory explanation of the apparently unique instability of alkyl hydrides requires that we consider alternatives to simple intramolecular reductive elimination. A look at eq 3 tells us when we might expect to find them. Although little attention has been paid to this point, it is obvious that the higher the energy of the fragment ML_n, the more difficult simple intramolecular reductive elimination will become, regardless of what is being eliminated. The only questions are whether or not there are ML_n of such high energy that the complexes ML_n(X)(Y) (X and Y = R or H) are in fact forced to find alternative decomposition modes, and what these alternatives are.

The chemistry of octahedral organometallic Pt(IV) complexes suggests one alternative decomposition mode. While intramolecular elimination of methyl ligands to form ethane occurs readily when a stable Pt(II) complex can be formed,^{16,17} (π-C₅H₅)Pt(CH₃)₃ gives no ethane but does form methane at 165 °C, apparently through intermediate methyl radicals.¹⁸ The difference is reasonably explained as a consequence of the high energy of the hypothetical "C₅H₅PtCH₃".

Eliminations from Mononuclear Osmium Complexes

Our attention was attracted by the series of complexes of general formula *cis*-Os(CO)₄(R¹)(R²), several



members of which had been reported or observed spectroscopically.^{19–22} Matrix isolation experiments, on Os(CO)₄ and on its more extensively studied periodic analogue Fe(CO)₄,²³ suggested that Os(CO)₄ would be a particularly unstable fragment. One's estimate of the energy required for simple intramolecular reductive elimination is raised even further by the recent discovery²⁴ that Fe(CO)₄ is paramagnetic. If one assumes that matrix-isolated Os(CO)₄ is also a triplet, that there is a singlet state of higher energy, and that this singlet Os(CO)₄ would probably be formed in such a reaction, one concludes that the intramolecular elimination of R¹–R² is a very high-energy elimination process indeed, and that it is very unlikely to occur for any R¹ and R².

Simple intramolecular reductive elimination certainly does not occur for *cis*-Os(CO)₄(CH₃)₂ (1). This ex-

(16) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2969 (1969).

(17) M. P. Brown, R. J. Puddephatt and C. E. E. Upton, *J. Chem. Soc., Dalton Trans.*, 2457 (1974).

(18) K. W. Egger, *J. Organomet. Chem.*, **24**, 501 (1970).

(19) F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, **6**, 2092 (1967).

(20) F. L'Eplattenier, *Inorg. Chem.*, **8**, 965 (1969).

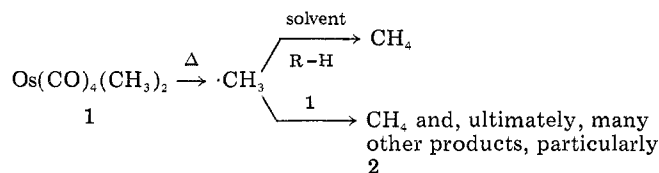
(21) F. L'Eplattenier and C. Pelichet, *Helv. Chim. Acta*, **53**, 1091 (1970).

(22) R. D. George, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 972 (1973).

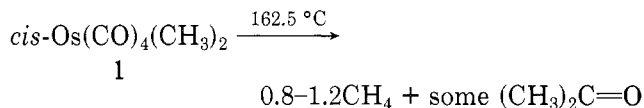
(23) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1351 (1973); M. Poliakoff and J. J. Turner, *ibid.*, 2276 (1974).

(24) T. J. Barton, R. Grinter, A. J. Thompson, B. Davies, and M. Poliakoff, *J. Chem. Soc., Chem. Commun.*, 841 (1977).

Scheme I



traordinarily stable organometallic compound decomposes slowly even at 162.5 °C.²⁵ The principal



gaseous product is methane, with small amounts of acetone being formed under most conditions. The osmium-containing residue is a complex mixture; one component has been tentatively identified as Os₄(CO)₁₄(CH₂)₂ (2).

We have concluded that Os–C bond homolysis and formation of methyl radicals is the primary mode of decomposition. As the temperature required for the thermolysis of 1 is comparable to that required for (π-C₅H₅)Pt(CH₃)₃, and as this temperature and activation energy are compatible with known third-row metal–carbon bond strengths,¹⁴ the conclusion is reasonable. There were, however, viable alternative mechanisms for the formation of methane which had to be eliminated. Chief among them was α elimination,^{26,27} recently suggested as a mechanism for the formation of methane from (CH₃)₂Co[P(OCH₃)₃]₄⁺.²⁶

It is easy to rule out reversible α elimination or, for that matter, any other reversible process. The rate of $\text{Os}(\text{CO})_4(\text{CH}_3)_2 \rightleftharpoons \text{Os}(\text{CH}_3)\text{H}(\text{CO})_4=\text{CH}_2 \rightleftharpoons \text{CH}_4 + \text{Os}(\text{CO})_4=\text{CH}_2$

decomposition in the gas phase is not significantly affected by the presence of 0.2 atm of CH₄, nor is any H found in Os(CO)₄(CD₃)₂ recovered after partial decomposition in the presence of 1 equiv of CH₄.²⁵

It is harder to rule out irreversible α elimination. If this were the only reaction occurring, thermolysis of a mixture of Os(CO)₄(CH₃)₂ and Os(CO)₄(CD₃)₂ in the gas phase would yield only CH₄ and CD₄. Instead, a mixture of all possible isotopically substituted methanes (CH₄, CH₃D, CH₂D₂, CHD₃, CD₄) is formed. However, the observation that CH₂D₂ is formed shows that methane is being attacked after its formation, so that the methane mixture does not necessarily reflect the outcome of the primary gas-phase thermolysis process.

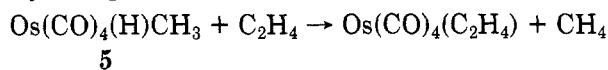
These gas-phase results require the irreversible formation of methane via a species capable of reacting with it and suggest the intermediacy of methyl radicals. Solvent attack is thus expected when the thermolysis of 1 is run in solution. Indeed, CD₃H is found when Os(CO)₄(CD₃)₂ is decomposed in a wide variety of solvents (e.g., mesitylene, dodecane, di-*n*-pentyl ether, and acetophenone), and a value of *k*_H/*k*_D of 5–6 is observed in mixtures of deuterated and undeuterated dodecanes,^{25,27} the selectivity methyl radicals would be

(25) J. Evans, S. J. Okrasinski, A. J. Pribula, and J. R. Norton, *J. Am. Chem. Soc.*, **99**, 5835 (1977).

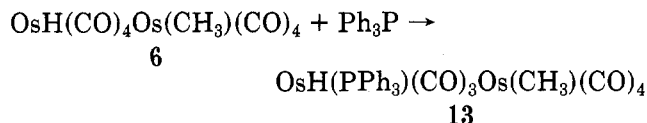
(26) E. L. Muettterties and P. L. Watson, *J. Am. Chem. Soc.*, **98**, 4665 (1976).

(27) W. J. Carter, S. J. Okrasinski, and J. R. Norton, manuscript in preparation.

methyl complex 12, whereas 5 gives no mononuclear ethyl complex.⁴⁰

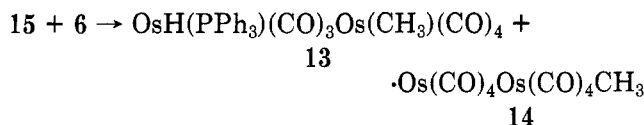
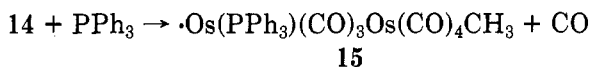
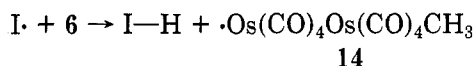


Phosphine substitution also proceeds exclusively at the hydride end of the dinuclear hydridomethyl complex 6,⁴² and in this case the explanation is clear.



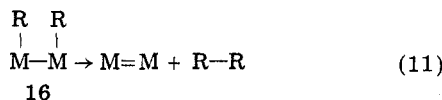
The reaction shows all of the symptoms (induction periods of varying length, acceleration by the addition of dibenzoyl peroxide, and inhibition by radical scavengers such as air^{42b}) of the radical chain substitution processes well-established for mononuclear hydrido-carbonyls.⁴³ The mechanism is thus Scheme IV, where I· is an initiator. The availability of 14 is probably of general importance in explaining the high reactivity of the hydride end of the dinuclear hydridomethyl complex 6.

Scheme IV



It is not surprising that the Os-H bonds are more readily broken in reactions of polynuclear complexes than of mononuclear ones, as in the former case the remaining unpaired electron is delocalized over more than one transition metal. It is similarly not surprising that the trinuclear dimethyl complex 10 decomposes much more readily (100 °C lower temperature) than the mononuclear dimethyl complex 1, apparently by loss of methyl radicals and subsequent solvent attack. The methyl groups of 12 are also easily removed by acid, whereas halogens preferentially cleave Os-Os bonds.⁴²

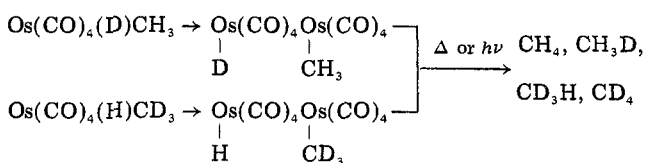
The elimination of the organic ligands from dinuclear alkyl hydrides such as 6 is of even more interest. In a symmetric dialkyl metal fragment such as 16, the concerted elimination of R-R via a C_{2v} transition state (reaction 11) is forbidden by symmetry considerations, just as is the suprafacial elimination of hydrogen from ethane.⁴⁴ However, in 6 the methyl and hydrogen



ligands differ, and thus concerted 1,2 methane elimination is no longer rigorously forbidden.

Methane is indeed eliminated from 6, both upon heating (74 °C) and upon photolysis at room temper-

ature. However, in both cases there is *no evidence that*



the elimination is intramolecular (although it is impossible to say whether crossover occurs before or during elimination).^{40,42}

Explanation for the Instability of Alkyl Hydrides and General Implications of Dinuclear Elimination

Dinuclear elimination occurs from 3, 5, and 7, all of which have hydride ligands. It does not occur from 1, where hydride is neither present nor available. We thus conclude that *dinuclear elimination is only possible when at least one of the ligands to be eliminated is hydride*. This requirement is reasonably explained by the unique ability of hydride ligands to bridge pairs of transition-metal atoms. Examples of hydride bridges among stable compounds are legion,⁴⁵ whereas alkyl bridges are exceedingly rare.⁴⁶⁻⁴⁹

The second requirement for dinuclear elimination appears to be a *vacant coordination site*. This site can be created far more readily by alkyl carbonyl complexes than by hydride carbonyl complexes. Although the formation of formyl complexes as reactive intermediates via intramolecular hydride migration has been suggested,⁵⁰ no observable formyl complex has ever been made by this route.⁵¹ Alkyl migrations, on the other hand, are extremely common,⁵² and solvent-unassisted migrations (of the type that occurs in the formation of Os(CO)₃(H)(C(O)R) from Os(CO)₄(H)R in the rate-determining step 8 of Scheme III) are a well-recognized class.⁵³ (A recent theoretical analysis by Berke and Hoffmann⁵⁴ of alkyl migrations onto carbonyl ligands argues that these reactions generally occur without significant solvation of the transition state.)

We are now in a position to explain the unique instability of those alkyl hydrides containing carbonyls and incapable of simple intramolecular reductive elimination. An alkyl carbonyl, e.g., 1, has a vacant coordination site readily available from alkyl migration, but no hydride to make dinuclear elimination possible. A carbonyl hydride, e.g., 3, is capable of dinuclear elimination but must rely on the comparatively high-energy process of carbonyl dissociation in order to provide the necessary vacant site. A hydridoalkyl

(45) For a review with numerous examples, see A. P. Humphries and H. D. Kaesz, *Prog. Inorg. Chem.*, in press.

(46) See comments in J. Holton, M. F. Lappert, G. R. Scollary, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 425, 480 (1976).

(47) K. Fischer, K. Jonas, P. Misbach, R. Stabba, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 12, 943 (1973).

(48) A. F. Masters, K. Mertis, I. F. Gibson, and G. Wilkinson, *Nouv. J. Chim.*, 1, 389 (1977).

(49) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, 99, 5225 (1977).

(50) J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, 100, 2716 (1978).

(51) C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, 98, 5395 (1976).

(52) For reviews see A. Wojcicki, *Adv. Organomet. Chem.*, 11, 87 (1973); F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, 16, 299 (1977).

(53) (a) R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, 4, 331 (1970); (b) C. J. Wilson, M. Green, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1293 (1974).

(54) H. Berke and R. Hoffmann, *J. Am. Chem. Soc.*, 100, 7224 (1978).

(42) (a) J. W. Kelland and J. R. Norton, *J. Organometal. Chem.*, 149, 185 (1978); (b) J. W. Kelland and J. R. Norton, unpublished work.

(43) B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, 97, 947, 3260 (1975); 99, 2527 (1977).

(44) R. G. Pearson, "Symmetry Rules for Chemical Reactions", Wiley-Interscience, New York, 1976, p 69.

$$\frac{k_5}{k_6} = \frac{S_t - 2S_0e^C}{[L]e^C - [L]}$$

$$C \equiv 2k_4t + 2 \log (S_t/S_0)$$

where S_0 is the initial concentration of **5**, S_t is its concentration at time t , and C is given in terms of the known rate constant k_4 for the rate-determining step. The results are given in Table I.²⁷

The relative reactivities indicate that **9** is only moderately selective and are consistent with our characterization of it as a coordinatively unsaturated acyl hydride. The most interesting result, however, is that all of the ratios are less than one—the hydride ligand in **5** is considerably faster at filling the vacant site on **9** than even Et_3P . Analogous results have recently been obtained by Bergman and co-workers in a vanadium system.⁶⁵

Third, we have reacted our hydride, **3**, with known coordinatively unsaturated acetyl complexes. Methane is formed, as predicted, from the reaction of **3** with $[\text{RhI}_3(\text{CO})(\text{C}(\text{O})\text{CH}_3)]^-$ ⁶⁶ and $\text{Ir}(\text{CO})\text{Cl}_2(\text{AsPh}_3)(\text{C}(\text{O})\text{CH}_3)$.^{63a} The second acyl is generated in situ at a known rate from $\text{Ir}(\text{CO})_2\text{Cl}_2(\text{AsPh}_3)\text{CH}_3$, and $\text{Os}(\text{CO})_4\text{H}_2$ is consumed at that rate. The system thus models our dinuclear elimination mechanism, reactions 8 and 10 of Scheme III, but with a five-coordinate acyl known to be generated in the rate-determining step.

We close by noting that dinuclear elimination of aldehydes, process 3 above, is probably involved in the cobalt-catalyzed oxo reaction in which aldehydes are formed from olefins, CO, and H_2 . $\text{HCo}(\text{CO})_4$ can produce aldehydes from acylcobalt tetracarbonyls stoichiometrically. The reaction is inhibited by CO,⁶⁷ suggesting that it proceeds via $\text{RC}(\text{O})\text{Co}(\text{CO})_3$.



However, Heck has argued^{67c} that "It is unlikely that this reaction occurs to a significant extent under [catalytic] hydroformylation conditions because it is second-order in cobalt complexes and the concentration of $\text{HCo}(\text{CO})_4$ should be very low". We can now see that

(65) R. J. Kinney, W. D. Jones, and R. G. Bergman, *J. Am. Chem. Soc.*, **100**, 7902 (1978).

(66) D. Forster, *J. Am. Chem. Soc.*, **98**, 846 (1976).

(67) (a) R. F. Heck and D. S. Breslow, *Chem. Ind. (London)*, 467 (1960), as quoted in (b) R. F. Heck, *Adv. Organomet. Chem.*, **4**, 243 (1966), and (c) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974, p 217.

this argument is weak: our dinuclear eliminations have been first order, with the rate-determining step involving the creation of a vacant coordination site, and the reactivity of a metal hydride toward such sites, once they exist, is very high.

Indeed, persuasive experimental evidence for the importance of $\text{HCo}(\text{CO})_4$ as an acyl cleavage reagent under catalytic conditions has recently been reported by Alemdaroglu, Penninger, and Oltay.⁶⁸ They measured the ratio of $\text{Co}_2(\text{CO})_8$ to $\text{HCo}(\text{CO})_4$ under catalytic conditions and observed that it initially increased upon the addition of substrate olefin—an observation which cannot be explained by the traditional mechanism (in which H_2 itself is responsible for acyl cleavage) and which can only result from the dinuclear elimination of aldehyde.

Concluding Remarks

We have found that simple intramolecular reductive elimination becomes disfavored as the energy of the remaining metal fragment increases and that eventually other elimination processes occur. These alternative processes are metal-carbon bond homolysis and dinuclear elimination. The latter requires (1) the presence or availability of a hydride ligand on one partner and (2) a vacant coordination site on the other.

Dinuclear elimination is thus uniquely rapid for hydridoalkylmetal carbonyls, as they both possess the necessary hydride ligand and are capable of generating a vacant coordination site by alkyl migration into a carbonyl ligand. These complexes are thus much less stable than their dihydride and dialkyl counterparts.

Dinuclear eliminations are probably much more common than has been realized. An important reason for their occurrence is the extraordinary ability of metal hydrides to fill vacant coordination sites on other metals. We expect dinuclear elimination, in addition to becoming recognized as mechanistically important, to be a generally applicable method for the synthesis of heterometallic metal-metal bonded compounds.

I wish to acknowledge the hard work of the postdoctoral research associates and graduate students named in the references and the financial support of the National Science Foundation, Chevron Research Co., and the Research Corporation.

(68) N. H. Alemdaroglu, J. L. M. Penninger, and E. Oltay, *Monatsh. Chem.*, **107**, 1153 (1976).