Organometallic Elimination Mechanisms: Studies on Osmium Alkyls and Hydrides

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Received June 23, 1978

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-

$$M—CH_2CH_2R \rightarrow M—H + CH_2{=}CHR \quad (1)$$

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

$$ML_n + X—Y \rightarrow ML_nXY \quad (2)$$

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

$$ML_nXY \rightarrow ML_n + X—Y \quad (3)$$

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 polyhydrides[13] 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. There are now respectable arguments[14] 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 $\Delta H^{\ddagger}$ as well as ΔH would be lowest for R–H elimination. If $\Delta H^{\ddagger}$ 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 °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

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(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, $Me_2PCH_2CH_2PMe_2$.

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

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(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).

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hydrogen ligands outweighs bond strength considerations. If *cis*-$Pt(Ph_3P)_2H_2$ proves more stable than *cis*-$Pt(Ph_3P)_2(H)CH_3$, it will imply that the transition state for R–H elimination from the latter strongly resembles the products. Similarly, Cp_2WH_2 and $Cp_2W(CH_3)_2$ are more stable than $Cp_2W(H)CH_3$;[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] $(\pi\text{-}C_5H_5)Pt(CH_3)_3$ 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 "$C_5H_5PtCH_3$".

Eliminations from Mononuclear Osmium Complexes

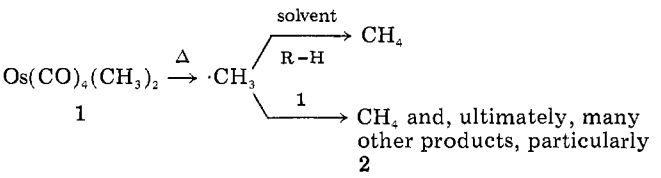
Our attention was attracted by the series of complexes of general formula *cis*-$Os(CO)_4(R^1)(R^2)$, several

$$Os(CO)_4(R^1)(R^2) \rightarrow Os(CO)_4 + R^1{-}R^2$$

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 discovery[24] 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 $R^1{-}R^2$ is a very high-energy elimination process indeed, and that it is very unlikely to occur for any R^1 and R^2.

Simple intramolecular reductive elimination certainly does not occur for *cis*-$Os(CO)_4(CH_3)_2$ (**1**). This extraordinarily stable organometallic compound decomposes slowly even at 162.5 °C.[25] The principal

Scheme I



$$cis\text{-}Os(CO)_4(CH_3)_2 \xrightarrow[\mathbf{1}]{162.5\ ^\circ C} 0.8\text{–}1.2CH_4 + \text{some } (CH_3)_2C{=}O$$

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 $Os_4(CO)_{14}(CH_2)_2$ (**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 $(\pi\text{-}C_5H_5)Pt(CH_3)_3$, 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,[2c,d] recently suggested as a mechanism for the formation of methane from $(CH_3)_2Co[P(OCH_3)_3]_4^+$.[26]

It is easy to rule out reversible α elimination or, for that matter, any other reversible process. The rate of

$$Os(CO)_4(CH_3)_2 \rightleftarrows Os(CH_3)H(CO)_4{=}CH_2 \rightleftarrows CH_4 + Os(CO)_4{=}CH_2$$

decomposition in the gas phase is not significantly affected by the presence of 0.2 atm of CH_4, nor is any H found in $Os(CO)_4(CD_3)_2$ recovered after partial decomposition in the presence of 1 equiv of CH_4.[25]

It is harder to rule out irreversible α elimination. If this were the only reaction occurring, thermolysis of a mixture of $Os(CO)_4(CH_3)_2$ and $Os(CO)_4(CD_3)_2$ in the gas phase would yield only CH_4 and CD_4. Instead, a mixture of all possible isotopically substituted methanes (CH_4, CH_3D, CH_2D_2, CHD_3, CD_4) is formed. However, the observation that CH_2D_2 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, CD_3H is found when $Os(CO)_4(CD_3)_2$ 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

(16) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2969 (1969).
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(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).
(25) J. Evans, S. J. Okrasinski, A. J. Pribula, and J. R. Norton, *J. Am. Chem. Soc.*, **99**, 5835 (1977).
(26) E. L. Muetterties 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.

expected to display at this temperature.[28,29]

Some CD_4 is formed as a byproduct even in nondeuterated solvents, especially at high concentrations. It presumably arises from the attack of $\cdot CD_3$ on the starting material, $Os(CO)_4(CD_3)_2$. This reaction probably leads to the formation of **2**; yields of the latter are greatly increased when the reaction is run in fluorocarbon solvents, inert toward radical attack.[27]

Scheme I summarizes the known events in a reaction of considerable complexity. The most important result is the complete absence of simple intramolecular reductive elimination of ethane.

It is not immediately obvious what alternatives there might be to intramolecular reductive elimination in the case of the simplest member of our series, *cis*-$Os(CO)_4H_2$ (**3**). The cis structure has been confirmed by an electron diffraction study in the gas phase.[30] Complex **3** evolves hydrogen readily at 125 °C, but, in view of the strength of transition-metal–hydrogen bonds,[14] Os–H bond cleavage is not a reasonable mechanism. The primary thermolysis reaction[31,32] gives the dinuclear product **4**[33] and suggests another possi-

$$\underset{\mathbf{3}}{2Os(CO)_4H_2} \rightarrow \underset{\mathbf{4}}{H_2Os_2(CO)_8} + H_2$$

bility which we shall call dinuclear elimination, defined by eq 4.

$$M{-}R^1 + M{-}R^2 \rightarrow R^1{-}R^2 + M{-}M \qquad (4)$$

In a complex $ML_n(R^1)(R^2)$ such as **3**, it is only possible to distinguish dinuclear elimination from simple intramolecular reductive elimination by an appropriate isotope labeling study. Reaction of $Os(CO)_4H_2$ and $Os(CO)_4D_2$ gives the crossover product HD,[32] whereas

$$Os(CO)_4H_2 + Os(CO)_4D_2 \rightarrow H_2, D_2, \text{ and } HD + \mathbf{4}$$

a simple intramolecular reductive elimination, which could give **4** by subsequent insertion in an Os–H bond, would produce only H_2 and D_2. The possibility that

$$Os(CO)_4H_2 \rightarrow Os(CO)_4 + H_2$$

$$Os(CO)_4D_2 \rightarrow Os(CO)_4 + D_2$$

$$Os(CO)_4 + Os(CO)_4H_2 \rightarrow \mathbf{4}$$

HD is produced, not in the elimination reaction, but by H_2/D_2 scrambling catalyzed by the secondary product system,[31] can be ruled out by carrying out the reaction under D_2.

$$Os(CO)_4H_2 \xrightarrow{D_2} \mathbf{4} + H_2 + D_2$$

Hydrogen elimination from $Os(CO)_4H_2$ is thus dinuclear. It is not kinetically bimolecular: the rate is first order in **3**, with k_1 being 6.1×10^{-5} s^{-1} at 125.8 °C.

$$d[Os(CO)_4H_2]/dt = -k_1[Os(CO)_4H_2]$$

The rate law and activation parameters suggest a rate-determining step involving carbon monoxide dissociation followed by fast dinuclear elimination of hydrogen and recoordination of CO (Scheme II).

Scheme II

$$Os(CO)_4H_2 \xrightarrow{k_1/2} Os(CO)_3H_2 + CO \qquad (5)$$

$$Os(CO)_3H_2 + Os(CO)_4H_2 \xrightarrow{\text{fast}} H_2Os_2(CO)_7 + H_2 \qquad (6)$$

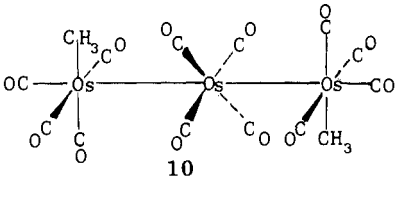
$$H_2Os_2(CO)_7 + CO \xrightarrow{\text{fast}} H_2Os_2(CO)_8 \qquad (7)$$

In this mechanism the hydride starting material successfully competes with CO for a vacant coordination site on $Os(CO)_3H_2$.[34-36] As a result, when the reaction is carried out under ^{13}CO and stopped after one half-life, negligible label is incorporated into recovered $Os(CO)_4H_2$, whereas considerable labeled carbon is found in the dinuclear product **4**.[32] As the rate of dissociative CO exchange per $Os(CO)_4$ unit in $Os_3(CO)_{12}$,[37] extrapolated to 125.8 °C, is 25×10^{-5} s^{-1}, very close to the rate of decomposition of $Os(CO)_4H_2$, it is not surprising that carbonyl dissociation is occurring thermally from the latter at 125.8 °C and is rate determining.

Before we could explore the elimination mechanisms of the most interesting case, the mixed hydridoalkyls (R^1 = H, R^2 = alkyl), it was necessary to devise a practical method for their preparation. (Only *cis*-$Os(CO)_4(H)CH_3$, **5**, had been reported, as a minor byproduct of several reactions.[20,22]) The reaction of $HOs(CO)_4^-$ with the powerful methylating agent CH_3OSO_2F consumes all the $HOs(CO)_4^-$ before it can engage in proton transfer side reactions and permits the preparation of 99% pure **5** in yields of up to 90%.[38] $Os(CO)_4(H)CH_3$ is quite unstable compared with **1** and **3**, offering evidence for the general statement above that dialkyls and dihydrides are more stable than alkyl hydrides.

The initial decomposition reaction is elimination of methane to form the dinuclear methyl hydride complex **6**. The appropriate labeling experiments indicate that

$$\underset{\mathbf{5}}{2Os(CO)_4(H)CH_3} \xrightarrow[49\ °C]{} CH_4 + \underset{\mathbf{6}}{OsH(CO)_4Os(CO)_4(CH_3)}$$



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the above elimination is dinuclear.[39] The conclusion

(28) J. R. McNesby, *J. Phys. Chem.*, **64**, 1671 (1960), and references therein.

(29) W. M. Jackson, J. R. McNesby, and B. deB. Darwent, *J. Chem. Phys.*, **37**, 1610 (1962).

(30) A. G. Robiette and K. Hedberg, unpublished work.

(31) $Os_3(CO)_{12}$ and various polynuclear hydride carbonyls are produced as *secondary* products; they arise from further reaction of primary product **4**.

(32) J. Evans and J. R. Norton, *J. Am. Chem. Soc.*, **96**, 7577 (1974).

(33) J. R. Moss and W. A. G. Graham, *Chem. Commun.*, 800 (1969); *J. Chem. Soc., Dalton Trans.*, 89 (1977).

(34) This is not very surprising when one considers the conditions under which these experiments were performed.[32] To enable accurate ^1H NMR determination of **3** in aliquots, its concentration had to be kept over 0.4 M, whereas the concentration of CO in solution was $< 10^{-3}$ M. We have more recently[27] shown that, with dilute solutions of **3**, 40 psi of CO retards the rate of its disappearance by a factor of 2.5—reflecting the operation of the reverse of reaction 5.

(35) Moss and Graham[36] have offered a number of mechanisms, including one involving our eq 5–7, for the formation of **4** from OsO_4, CO, and H_2. We do not insist on the primacy of our mechanism under the drastic conditions (180 atm, 170 °C) employed by those workers.

(36) J. R. Moss and W. A. G. Graham, *Inorg. Chem.*, **16**, 75 (1977).

(37) G. Cetini, O. Gambino, E. Sappa, and G. A. Vaglio, *Atti Accad. Sci. Torino*, **101**, 855 (1967).

(38) J. Evans, S. J. Okrasinski, A. J. Pribula, and J. R. Norton, *J. Am. Chem. Soc.*, **98**, 4000 (1976).

$$Os(CO)_4(H)CD_3 + Os(CO)_4(D)CH_3 \rightarrow 6 + CH_4, CH_3D, CD_3H, CD_4$$

$$Os(CO)_4(H)CH_3 \xrightarrow{CD_4} 6 + CH_4 \text{ and } CD_4 \textit{ only}$$

is confirmed by an appropriate control experiment showing that isotopically labeled alkane is not affected under the reaction conditions. (It will be demonstrated later that no scrambling of isotope labels occurs prior to the rate-determining step in the elimination process.)

The rate of the dinuclear elimination of methane from $Os(CO)_4(H)CH_3$ is, as with the dihydride **3**, kinetically first order, with $k_2 = 1.38 \times 10^{-4}$ s^{-1} at 49 °C

$$d[Os(CO)_4(H)CH_3]/dt = -k_2[Os(CO)_4(H)CH_3]$$

in methylcyclohexane (it varies only slightly with solvent).[39] The hydridoethyl complex $Os(CO)_4(H)C_2H_5$ (**7**) decomposes by an analogous dinuclear elimination of ethane, but more rapidly.[27,40]

The creation of a vacant coordination site in the rate-determining step for dinuclear elimination of methane from $Os(CO)_4(H)CH_3$ is clearly indicated, but it cannot reasonably be carbonyl dissociation as with **3**; the rate of CO loss would have to be much faster for the methyl hydride **5** than it is for either the dimethyl **1** or the dihydride **3**. Indeed, $\Delta S^{\ddagger}$ is −8 eu, and when the reaction is carried out under ^{13}CO no label is incorporated into either product or recovered starting material.[39]

Our presumption that the rate-determining step must somehow produce a vacant coordination site led to our carrying out the reaction in the presence of added nucleophilic ligands L (such as Et_3P, Ph_3P, $(MeO)_3P$, pyridine, and ethylene).[39,40] The reaction products

$$\underset{\mathbf{5}}{Os(CO)_4(H)CH_3} + L \rightarrow \underset{\mathbf{8}}{Os(CO)_4L} + CH_4$$

suggest acceleration of alkane elimination by the entering nucleophile, a phenomenon predicted on theoretical grounds,[2a] but the kinetics prove otherwise. The rate of disappearance of **5** and **6** is not accelerated by even 110 equiv of Et_3P.[39]

$$d[Os(CO)_4(H)CH_3]/dt = -k_3[Os(CO)_4(H)CH_3]$$

The rate constant k_3 is half its counterpart k_2 in the absence of Et_3P, i.e., the addition of excess Et_3P *decreases* the rate of disappearance of **5**. Furthermore, the alkane produced results from a *mononuclear* process. These observations require the mechanism

$$Os(CO)_4(H)CD_3 + Os(CO)_4(D)CH_3 + \text{excess } Et_3P \rightarrow Os(CO)_4(PEt_3) + CD_3H + CH_3D \textit{ only}$$

shown in Scheme III, where k_4 is rate-determining and much slower than k_5 or k_6, and **9** is an isomerized, reactive form of the initial alkyl hydride. Assuming that **9** has a vacant coordination site, the only structure it can reasonably be assigned is that of the five-coordinate acyl hydride $Os(CO)_3(H)(C(O)R)$.[27]

The course of the reaction reflects the outcome of the competition for the intermediate **9** between added nucleophilic ligands L and the original hydridoalkyl complex. If L wins, alkane arises from an intramolecular process, and starting material disappears at the rate of k_4; if $Os(CO)_4(H)R$ wins, alkane arises from an

(39) S. J. Okrasinski and J. R. Norton, *J. Am. Chem. Soc.*, **99**, 295 (1977).
(40) J. R. Norton, W. J. Carter, J. W. Kelland, and S. J. Okrasinski, *Adv. Chem. Ser.*, **No. 167**, 170 (1978).

Scheme III

$$Os(CO)_4(H)R \xrightarrow[\text{rate determining}]{k_4} \underset{\mathbf{9}}{Os(CO)_3(H)(C(O)R)} \quad (8)$$

$$\underset{\mathbf{9}}{Os(CO)_3(H)(C(O)R)} \xrightarrow{k_5, L} Os(CO)_3L(H)(C(O)R) \xrightarrow{\text{fast}} Os(CO)_4L + R{-}H \quad (9)$$

$$\underset{\mathbf{9}}{Os(CO)_3(H)(C(O)R)} \xrightarrow{k_6} \underset{(H)R}{Os(CO)_4} HOs(CO)_4Os(CO)_4R + R{-}H \quad (10)$$

intermolecular process (*dinuclear elimination*), and starting material disappears at a rate of $2k_4$, as reaction 10 consumes another equivalent of $Os(CO)_4(H)R$ for every one that disappears in the rate-determining step.

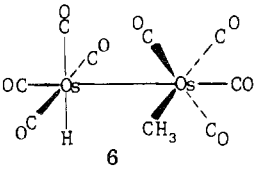
The rate-determining step, reaction 8, is thus the same whether or not added nucleophilic ligand is present. As reaction 9, involving added ligand, produces alkane intramolecularly, it is apparent that there is no scrambling of labeled ligands prior to reaction 8. The inference of dinuclear elimination from the formation of CD_4 from $Os(CO)_4(H)CD_3$ and $Os(CO)_4(D)CH_3$ is thus valid.[39]

Formation and Decomposition of Polynuclear Osmium Alkyls and Hydrides

The dinuclear hydridomethyl complex **6** reacts with the mononuclear hydridomethyl complex **5** to eliminate

$$\underset{\mathbf{6}}{OsH(CO)_4Os(CH_3)(CO)_4} + \underset{\mathbf{5}}{Os(CO)_4(H)CH_3} \rightarrow H_2 + \underset{\mathbf{10}}{Os_3(CO)_{12}(CH_3)_2}$$

hydrogen and form the trinuclear dialkyl **10**. The



6

structure shown is that found in the solid state by X-ray crystallography. It is centrosymmetric, with the Os–Os distance 2.909 Å.[41] As the formation of the trinuclear dimethyl complex from **6** is only a bit slower than formation of the latter from $Os(CO)_4(H)CH_3$, **10** is a major product (24% yield) of the thermal decomposition of $Os(CO)_4(H)CH_3$ (**5**) when that process is allowed to go to completion.[38]

Comparatively minor amounts are found of the product **11** that one would naively expect to result from

$$\underset{\mathbf{11}}{OsH(CO)_4Os(CO)_4OsR(CO)_4}$$

two successive dinuclear eliminations of the type described above. It thus appears that the hydride end of the dinuclear hydridomethyl complex **6** is more reactive than its mononuclear counterpart **5**. The hydride end of **6** also reacts with ethylene to give the dinuclear ethyl

$$\underset{\mathbf{6}}{OsH(CO)_4Os(CH_3)(CO)_4} \xrightarrow[75\ °C]{C_2H_4} \underset{\mathbf{12}}{Os(C_2H_5)(CO)_4Os(CH_3)(CO)_4}$$

(41) M. R. Churchill, personal communication.

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

$$\underset{\mathbf{5}}{Os(CO)_4(H)CH_3} + C_2H_4 \rightarrow Os(CO)_4(C_2H_4) + CH_4$$

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

$$\underset{\mathbf{6}}{OsH(CO)_4Os(CH_3)(CO)_4} + Ph_3P \rightarrow \underset{\mathbf{13}}{OsH(PPh_3)(CO)_3Os(CH_3)(CO)_4}$$

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 hydridocarbonyls.[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

$$I\cdot + \mathbf{6} \rightarrow I{-}H + \cdot\underset{\mathbf{14}}{Os(CO)_4Os(CO)_4CH_3}$$

$$\mathbf{14} + PPh_3 \rightarrow \cdot\underset{\mathbf{15}}{Os(PPh_3)(CO)_3Os(CO)_4CH_3} + CO$$

$$\mathbf{15} + \mathbf{6} \rightarrow \underset{\mathbf{13}}{OsH(PPh_3)(CO)_3Os(CH_3)(CO)_4} + \cdot\underset{\mathbf{14}}{Os(CO)_4Os(CO)_4CH_3}$$

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

$$\underset{\mathbf{16}}{\overset{R\ \ R}{M{-}M}} \rightarrow M{=}M + R{-}R \qquad (11)$$

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

$$\left.\begin{array}{l} Os(CO)_4(D)CH_3 \rightarrow \underset{D}{Os(CO)_4}\underset{CH_3}{Os(CO)_4} \\ Os(CO)_4(H)CD_3 \rightarrow \underset{H}{Os(CO)_4}\underset{CD_3}{Os(CO)_4} \end{array}\right\} \xrightarrow{\Delta \text{ or } h\nu} \begin{array}{l} CH_4,\ CH_3D, \\ CD_3H,\ CD_4 \end{array}$$

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 Hoffmann[54] 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

(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.
(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).

complex such as **5** or **7** has both elements present and is thus uniquely unstable with regard to dinuclear elimination.

We view dinuclear elimination as proceeding via **19**,

$$L_nM{-}H + ML_{n-1}{-}R \rightarrow L_nM\!\!<\!\!\begin{matrix}H\\R\end{matrix}\!\!>ML_{n-1}$$

17 **18** **19**

where **18** possesses a vacant coordination site and R can be hydride, alkyl, or acyl.[55] One can thus divide dinuclear eliminations into three classes.

(1) R may be alkyl or hydrogen, R–H is to be eliminated, and the vacant coordination site is present without any need for acyl formation. An example is, of course, the decomposition of **3**, where R = H and the vacant site is created by carbonyl dissociation. Examples involving $Au(PPh_3)Me$, coordinatively unsaturated to begin with, can be found in the literature.[56]

$$HMn(CO)_5 + CH_3AuPPh_3 \rightarrow Au(PPh_3)Mn(CO)_5 + CH_4$$

$$HOs(CO)_4SiMe_3 + CH_3AuPPh_3 \rightarrow Au(PPh_3)Os(CO)_4SiMe_3 + CH_4$$

Where coordinatively unsaturated alkyls are available, as with Au, Pt, Ir, and their periodic analogues, this type of dinuclear elimination should offer a general synthesis of heterometallic metal–metal bonded compounds.

(2) R may be acyl and an alkane R–H is to be eliminated. This process will leave a coordinatively saturated, in general stable, dinuclear fragment behind.

(3) R may be acyl and an aldehyde RCHO is to be eliminated. This process will leave a coordinatively unsaturated dinuclear fragment.

It is clear that thermodynamic arguments (fragment-stability considerations) favor process 2 over process 3, and process 2 generally occurs in the osmium systems we have investigated. Process 3 is, however, more straightforward mechanistically, and it is not surprising to find that it sometimes occurs. For example, some acetaldehyde is formed as a byproduct in the reaction of the osmium dimethyl complex with the dihydride.

$$\underset{\mathbf{1}}{Os(CO)_4(CH_3)_2} + \underset{\mathbf{3}}{Os(CO)_4H_2} \xrightarrow{\Delta} \underset{\mathbf{6}}{Os(CO)_4(H)Os(CO)_4(CH_3)} + CH_4 + \textit{some}\ CH_3CHO$$

Process 2, in the systems we have studied, proceeds without carbonyl dissociation, so loss of alkane must occur through either alkyl migration onto the metal, producing a 36-electron transition state,[57] or direct migration of alkyl onto the bridging hydride. A similar situation occurs in the second step of reaction 9, Scheme III, where alkane evolves rapidly and intramolecularly after the coordination of the added nucleophile L. The

$$Os(CO)_3L(H)(C(O)R) \rightarrow Os(CO)_4L + R{-}H$$

distinction between migration via the metal and direct migration is more formal than real, and we consider either description a reasonable possibility.

Such reactions may account for the rarity of stable acyl hydrides. They are believed intermediate in the decarbonylation of aldehydes—resulting, of course, in alkane elimination.[58] When they eliminate aldehydes (as $Ir(C(O)Et)HCl(CO)(PPh_3)_2$ does[59]), the resulting fragment (e.g., $IrCl(CO)(PPh_3)_2$) is an extremely stable complex, in contrast to the unstable $Os(CO)_3L$ that would result if $Os(CO)_3L(H)(C(O)R)$ gave aldehyde elimination.[60-64]

A number of recent experiments offer additional insight into dinuclear elimination via process 2. First, one would predict that other alkyl carbonyls and other hydrides would undergo similar dinuclear elimination,

$$\underset{\mathbf{5}}{Os(CO)_4(H)CH_3} + \underset{\mathbf{3}}{Os(CO)_4H_2} \rightarrow \underset{\mathbf{4}}{H_2Os_2(CO)_8} + CH_4$$

$$\underset{\mathbf{5}}{Os(CO)_4(H)CH_3} + HRe(CO)_5 \rightarrow HOs(CO)_4Re(CO)_5 + CH_4$$

and we have confirmed this prediction.[27] Another case is the reaction of $Os(CO)_4(CH_3)_2$ and $Os(CO)_4H_2$ to give the dinuclear hydridomethyl complex **6**. This reaction offers a general synthesis of heterometallic metal–metal-bonded compounds from methyl metal carbonyls and hydrides.

Second, we have examined quantitatively the competition between various added nucleophiles L and the hydride on **5** for the reactive acyl intermediate **9**, i.e., the relative rates k_5/k_6 of the fast reactions 9 and 10 for a series of different L. Despite the fact that the relative concentrations of L and **5** vary during the course of the reaction, the ratio k_5/k_6 may be obtained from

Table I
Relative Reactivities k_5/k_6 of 9 toward Other Nucleophiles vs. the Hydride of 5

nucleophile	k_5/k_6
Et_3P	0.35 ± 0.03
Ph_3P	0.15 ± 0.03
$(MeO)_3P$	0.050 ± 0.006
pyridine	<0.02

(55) In discussing our work in their review, Humphries and Kaesz[45] have written **19** as though it involved the complete oxidative addition of the metal hydride to **18**, giving an intermediate which is formally Os(IV). While this suggestion is not fundamentally different from ours, being merely one extreme of the possibilities encompassed by **19**, we prefer to emphasize the importance of the bridging ability of hydride by writing **19** as is.

(56) C. M. Mitchell and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 102 (1972).

(57) These are not uncommon in dinuclear systems; for an example, see J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, R. G. Komoto, and J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 1119 (1978).

(58) For comments and an example of an acyl hydride stabilized by chelation, see J. W. Suggs, *J. Am. Chem. Soc.*, **100**, 640 (1978), and references and notes therein.

(59) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).

(60) Although the iron acyl anion $[Fe(CO)_3(PPh_3)(C(O)R)]^-$ does yield aldehyde on acidification,[61,62] there is no evidence that protonation occurs on iron to give $Fe(CO)_3(PPh_3)(H)(C(O)R)$. Analogous Cr, Mo, and W acyls also give aldehydes upon acidification, but hydroxycarbene complexes are observed as unstable intermediates after protonation *on oxygen*.[63] Other acyls are known which yield alkane rather than aldehyde on acidification.[64] It is always dangerous to draw conclusions about hydride chemistry from acidification experiments unless the intermediacy of a hydride can be spectroscopically verified.

(61) M. P. Cooke, Jr., *J. Am. Chem. Soc.*, **92**, 6080 (1970).

(62) J. P. Collman, *Acc. Chem. Res.*, **8**, 342 (1975).

(63) E. O. Fischer and A. Maasböl, *Chem. Ber.*, **100**, 2445 (1967); E. O. Fischer, G. Kreis, and F. R. Kreisl, *J. Organomet. Chem.*, **56**, C37 (1973).

(64) H. F. Klein and H. H. Karsch, *Chem. Ber.*, **109**, 2524 (1976).

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

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

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 $[RhI_3(CO)(C(O)CH_3)]^-$[66] and $Ir(CO)Cl_2(AsPh_3)(C(O)CH_3)$.[53a] The second acyl is generated in situ at a known rate from $Ir(CO)_2Cl_2(AsPh_3)CH_3$, and $Os(CO)_4H_2$ 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. $HCo(CO)_4$ can produce aldehydes from acylcobalt tetracarbonyls stoichiometrically. The reaction is inhibited by CO,[67] suggesting that it proceeds via $RC(O)Co(CO)_3$.

$$RC(O)Co(CO)_3 + HCo(CO)_4 \rightarrow RCHO + Co_2(CO)_7$$

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 $HCo(CO)_4$ should be very low". We can now see that 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 $HCo(CO)_4$ as an acyl cleavage reagent *under catalytic conditions* has recently been reported by Alemdaroglu, Penninger, and Oltay.[68] They measured the ratio of $Co_2(CO)_8$ to $HCo(CO)_4$ 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.

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