Organo-transition-metal Complexes: Stability, Reactivity and Orbital Correlations

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1 Introduction

Much of the interest in organo-transition-metal (OTM) chemistry derives from the relative ease with which σ-bonds between a transition metal and carbon can be made or broken. Such behaviour is central both to organometallic catalysis and to the stoicheiometric uses of OTM species in organic synthesis. In addition, changing views on the nature of the bond-making and bond-breaking processes have led in recent years to dramatic extensions of the range of descriptive transition-metal chemistry, while spectroscopic studies of the new species formed, and mechanistic investigations of metal–carbon bond reactivity, continue to enrich our understanding of inorganic chemistry as a whole.

For many years it was widely believed[1] that metal–carbon σ-bonds in OTM complexes were inherently unstable unless a certain special condition was satisfied.[2] This condition was the presence of π-accepting ligands, which were thought to stabilize the bond to cleavage by increasing the energy separation between filled and empty d-orbitals on the metal. For many reasons, some of which the authors have summarized elsewhere,[3] this position can no longer be maintained. Instead, it has become apparent that metal–carbon bond cleavage must be discussed in terms of the mechanistic pathways open to the various complexes. The same is evidently true for processes in which metal–carbon σ-bonds are formed.

Evidence is rapidly accumulating that both the bond-making and bond-breaking reactions generally proceed by electron-pair processes, and that the conditions controlling such processes may be rationalized by reference to possible mechanisms. Consideration of these mechanisms leads us to suggest that many bond-making and bond-breaking processes have much in common with apparently rather different reactions involving, for example, rearrangement and insertion. It should then be a useful exercise to compare these apparently diverse reactions throughout the entire range of OTM complexes.

Such a comparison is the purpose of this review. In Section 2 we survey current views on metal–carbon bond lability in the light of the recent rapid extension of the range of one-electron-donor OTM complexes. The relationships between the bonding of these one-electron-donor complexes and many-electron-donor complexes are well understood and are alluded to in Section 3. There, formal similarities are used to compare various addition and elimination

[1] M. L. H. Green, 'Organometallic Compounds', Methuen, London, 1968.
[2] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705; 1960, 1718.
[3] P. S. Braterman and R. J. Cross, *J.C.S. Dalton*, 1972, 657.

reactions. Electrno-correlation diagrams are employed to show that such comparisons are real, and more precise than those derived simply from electron counting.[4] The use of such correlation diagrams in determining whether or not a given process is symmetry-allowed is demonstrated. Section 4 is devoted to a discussion, with many examples, of the factors controlling the reaction types reviewed. Variations in behaviour across the length and breadth of the Periodic Table are pointed out and explained. Finally, in Section 5, the relationships between bond-breaking and other processes, implicit throughout this review, are examined and discussed.

2 The Lability of Transition-metal–Carbon Bonds

A. Development of Organo-transition-metal Chemistry.—The early belief that transition-metal–carbon bonds were weak has had a profound and lasting (though not necessarily unhelpful) effect on the development of their chemistry. As far as one-electron carbon donors were concerned, the first complexes to be isolated contained other ligands (often with π-bonding properties) in the co-ordination sphere of the metal, and this led, not unnaturally, to the idea that these ligands were responsible for stabilizing the metal–carbon bonds.

The situation was rationalized thus. Bonds from transition metals to carbon were weak owing to the availability of high-energy d-electrons. Facile thermal promotion of one of these electrons to antibonding levels led to cleavage of M—C, and the reactive fragments produced (free radicals, carbanions, or carbonium ions) ensured rapid and irreversible decomposition. The operation of this process in, for example, halide or olefin complexes would result in stable dissociation products (ion-pairs or olefin) and the reaction could later reverse. Main-group elements, of course, lacked the high-energy d-electrons for facile promotion. After the isolation of compounds such as $(Et_3P)_2PtMeCl$,[2] it was proposed that π-bonding ligands stabilized the metal–carbon bonds by lowering the energies of the filled d-orbitals, thereby increasing the activation energy for decomposition. Numerous compounds have since been isolated which appeared to conform to this hypothesis.

The evidence available today renders this 'supporting π-ligand' theory untenable. In the first place, many organometallic species are now known which contain other ligands with no π-bonding properties, *e.g.* $[PhCH_2Cr(OH_2)_5]^{2+}$, $[EtRu(NH_3)_5]^{2+}$,[5,6] and the number of derivatives with no 'supporting ligand' of any kind is growing *e.g.* $(PhCH_2)_4Ti$,[7] Me_6W,[8] $(Ph_3C)_2Ni$.[9] Secondly, such spectroscopic and bond-length data as are available suggest that transition-metal–carbon bonds are of similar strength to main-group-metal–carbon bonds, and the presence of other ligands has little effect on these parameters. Thirdly, a

[4] C. A. Tolman, *Chem. Soc. Rev.*, 1972, **1**, 337.
[5] F. A. L. Anet and E. Leblanc, *J. Amer. Chem. Soc.*, 1957, **79**, 2649.
[6] K. Thomas, J. A. Osborn, A. R. Powell, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 1801.
[7] U. Giannini and U. Zucchini, *Chem. Comm.*, 1968, 940.
[8] A. Shortland and G. Wilkinson, *J.C.S. Chem. Comm.*, 1972, 378.
[9] G. Wilke and H. Schott, *Angew. Chem. Internat. Edn.*, 1966, **5**, 583.

consideration of the energies involved shows that the promotional mechanism originally proposed is unlikely to operate under thermal conditions. These arguments are expanded in a recent paper.[3]

Despite strong metal–carbon bonds, many transition-metal organometallics are thermally labile, however. The explanation of their lability lies in the characteristic transition-metal properties of variable oxidation states and co-ordination numbers. These allow several facile decomposition pathways to operate which are denied to their main-group analogues. They are usually concerted reactions: reactions involving other co-ordination sites as well as the metal–carbon bond under consideration. The reactions proceed by paired-electron processes. Evidence continues to accrue which suggests that the chemistry of transition-metal organometallic compounds is dominated by such processes.

B. Concerted Reactions.—We shall illustrate three such reaction types: reductive (1,1) and related (1,2 and 1,n) eliminations; β-eliminations of metal and, for example, hydrogen from a ligand; and dinuclear elimination. The relationship of these to other concerted processes and to their reverse reactions is discussed in subsequent sections. Simple nucleophilic or electrophilic displacement of metal from carbon may also be an important process, *e.g.* in transmetallations,[10] but is outside the scope of this review.

Both the oxidation number and the co-ordination number of the metal are reduced by two in reductive elimination reactions, *e.g.*[11]

$$(Ph_3P)AuMe_3 \rightarrow (Ph_3P)AuMe + C_2H_6$$

Bond-making accompanies bond-breaking, and no free-living high-energy intermediates such as free radicals, carbanions, or carbonium ions are involved. The concerted nature of reductive elimination has recently been confirmed[12] for the reaction

$$(PhMe_2P)_2PtMe_3I \rightarrow (PhMe_2P)_2PtMeI + C_2H_6$$
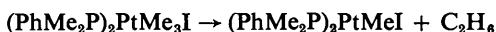
Specific labelling shows that this reaction is intramolecular and it follows first-order kinetics in dioxan between 335 and 365 K. The activation energy of 129 ± 5 kJ mol^{-1} is less than that for the thermolysis of $(h^5\text{-}C_5H_5)PtMe_3$,[13] the value for which might be taken (see below) as a plausible lower limit for the homolysis of a Pt^{IV}—CH_3 bond.

Reductive elimination frequently follows oxidative addition, and this combination of reactions is a common route to overall exchange. The similar nature of
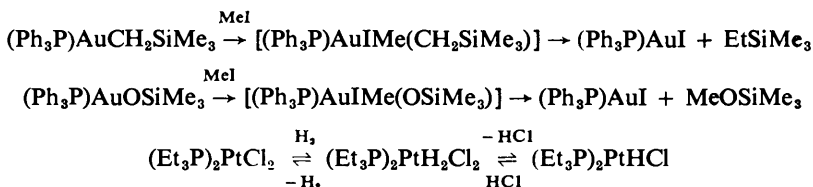
[10] See *e.g.*, G. Agnes, S. Bendle, H. A. O. Hill, F. R. Williams, and R. J. P. Williams, *Chem. Comm.*, 1971, 850.
[11] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.
[12] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton. *J. Organometallic Chem.*, 1973, **49**, C61.
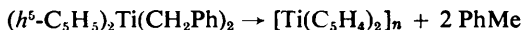[13] K. W. Eggar, *J. Organometallic Chem.*, 1970, **24**, 501.

metal–oxygen, metal–carbon, and metal–hydrogen bonds is illustrated by the following reactions:[14,15]

$$\underset{\text{MeI}}{(Ph_3P)AuCH_2SiMe_3 \rightarrow [(Ph_3P)AuIMe(CH_2SiMe_3)] \rightarrow (Ph_3P)AuI + EtSiMe_3}$$

$$\underset{\text{MeI}}{(Ph_3P)AuOSiMe_3 \rightarrow [(Ph_3P)AuIMe(OSiMe_3)] \rightarrow (Ph_3P)AuI + MeOSiMe_3}$$

$$(Et_3P)_2PtCl_2 \underset{-H_2}{\overset{H_2}{\rightleftharpoons}} (Et_3P)_2PtH_2Cl_2 \underset{HCl}{\overset{-HCl}{\rightleftharpoons}} (Et_3P)_2PtHCl$$
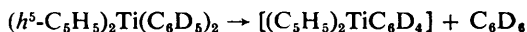
Reductive elimination is a well-established process of (1,1) elimination of two groups from the same metal centre. It has now recently become apparent that (1,2) and (1,n) eliminations are more common than had been supposed. Thus the thermolysis of tetramethyltitanium to give methane has been shown by labelling experiments not to involve hydrogen abstraction from solvent, and to lead to the production of titanium carbide rather than pure titanium metal.[16] A plausible first step in the reaction could then be

$$Ti(Me)_4 \rightarrow [Me_2Ti{=}CH_2] + CH_4$$

Related elimination processes include[17]

$$(h^5\text{-}C_5H_5)_2Ti(CH_2Ph)_2 \rightarrow [Ti(C_5H_4)_2]_n + 2\,PhMe$$

also a (1,2) elimination, and[18]

$$(h^5\text{-}C_5H_5)_2Ti(C_6D_5)_2 \rightarrow [(C_5H_5)_2TiC_6D_4] + C_6D_6$$
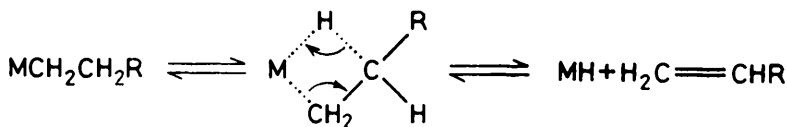
a (1,3) elimination.

β-Elimination is perhaps best documented of the elimination reactions and its importance as a decomposition route for organometallics has been emphasized.[19] It may be represented thus

Deuteriation studies have confirmed the steric course of the reaction[20]

[14] A. Shiotani and H. Schmidbaur, *J. Organometallic Chem.*, 1972, **37**, C24.
[15] E. H. Brooks, R. J. Cross, and F. Glockling, *Inorg. Chim. Acta*, 1968, **2**, 17.
[16] F. S. Dyachkovsky and N. E. Khrusch, *Zhur. obshchei Khim.*, 1971, **41**, 1779; A. S. Khachaturov, L. S. Breslov, and I. Yu. Paddubnyi, *J. Organometallic Chem.*, 1972, **42**, C18.
[17] G. Fachinetti and C. Floriani, *J.C.S. Chem. Comm.*, 1972, 654.
[18] I. Dvorak, R. J. O'Brien, and W. Santo, *Chem. Comm.*, 1970, 411.
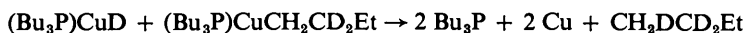[19] (a) W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533; (b) M. R. Collier, M. F. Lappert, and M. M. Truelock, *J. Organometallic Chem.*, 1970, **25**, C36.
[20] G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Fillipo, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 1426.

$$(Bu_3P)CuCH_2CD_2Et \rightarrow (Bu_3P)CuD + H_2C{=}CDEt$$
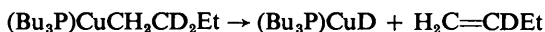
though when a fast reverse reaction operates, effective mixing of H and D results.[21] This process is featured in many reactions of great synthetic value, such as the formation of transition-metal hydrides from alkoxides. It also features prominently in such catalytic reactions as the isomerization of olefins, and is a frequently encountered terminator in polymerization reactions.

Dinuclear elimination, an intermolecular reaction, involves the formation of metal–metal bonds and/or metal alkyl (aryl) bridges in order to bring into proximity leaving groups from different metal atoms. Dinuclear or indeed poly-nuclear reactions are clearly indicated in the process[20]

$$(Bu_3P)CuD + (Bu_3P)CuCH_2CD_2Et \rightarrow 2\ Bu_3P + 2\ Cu + CH_2DCD_2Et$$

and in[11]

$$2\ (Ph_3P)AuMe \rightarrow 2\ Ph_3P + 2\ Au + C_2H_6$$

Similar dinuclear interactions probably operate in the recently reported exchange of alkyl groups between gold(I) and gold(III):[22]

$$(Ph_3P)AuMe_2I + (Ph_3P)AuMe \rightarrow (Ph_3P)AuMe_3 + (Ph_3P)AuI$$
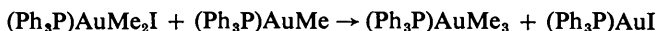
Bridging groups other than alkyls are clearly possible and an example of hexa-fluorobut-2-yne acting as bridging ligand in a dinuclear type of elimination has been reported (Scheme 1).[23] Interestingly, when tetrafluoroethylene replaces the
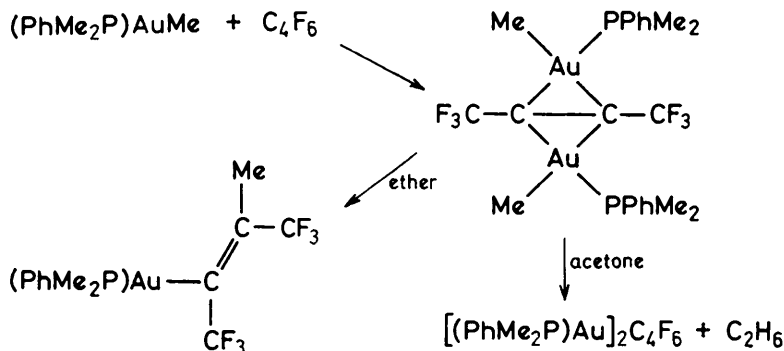
Scheme 1

alkyne, removing the possibility of alkyne bridges, insertion is the only subse-quent reaction.[24] Some dinuclear reactions appear to be preceded by processes that leave one of the component metal centres co-ordinatively unsaturated. A
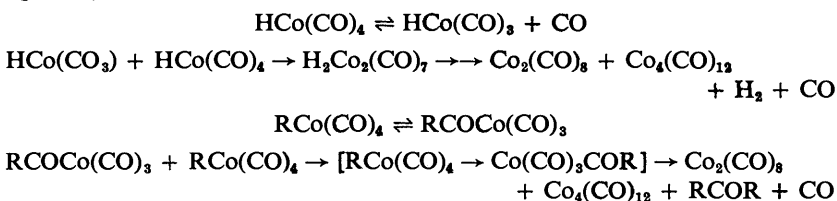
[21] G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 1972, **94**, 5258.
[22] A. Tamaki and J. K. Kochi, *J. Organometallic Chem.*, 1972, **40**, C81.
[23] A. Johnson, R. J. Puddephatt, and J. L. Quink, *J.C.S. Chem. Comm.*, 1972, 938.
[24] C. M. Mitchell and F. G. A. Stone, *J.C.S. Dalton*, 1972, 102.

dinuclear species can then be formed without necessarily involving bridging ligands (Scheme 2).[25,26]

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO$$

$$HCo(CO_3) + HCo(CO)_4 \rightarrow H_2Co_2(CO)_7 \rightarrow \rightarrow Co_2(CO)_8 + Co_4(CO)_{12}$$
$$+ H_2 + CO$$

$$RCo(CO)_4 \rightleftharpoons RCOCo(CO)_3$$

$$RCOCo(CO)_3 + RCo(CO)_4 \rightarrow [RCo(CO)_4 \rightarrow Co(CO)_3COR] \rightarrow Co_2(CO)_8$$
$$+ Co_4(CO)_{12} + RCOR + CO$$

Scheme 2

Acceptance of the importance of concerted reactions is already proving useful in the design of new compounds and the interpretation of reactions. The preparation of derivatives with no transferable β-groups confers stability in cases where the β-elimination is likely to operate. Thus a variety of compounds with trimethylsilylmethyl, neopentyl, and the like have been isolated lately.[19,27] The extra stability of methyls compared with higher alkyls is well known and lack of a β-migration pathway has been invoked to explain this.[19] The influence of transition-metal ions on the coupling of Grignard reagents continues to receive study: recently the complexity of products produced from copper(I)-catalysed reactions has been explained in terms of β-eliminations, whilst the operation of dinuclear eliminations is apparent in silver(I)-catalysed systems:[28a]

$$R^1Ag + R^2Ag \rightarrow R^1\!-\!R^1 + R^1\!-\!R^2 + R^2\!-\!R^2$$

Reductive elimination from silver is a critical step in the Ag^I-modified addition of benzyne to cyclic polyenes:[28b]
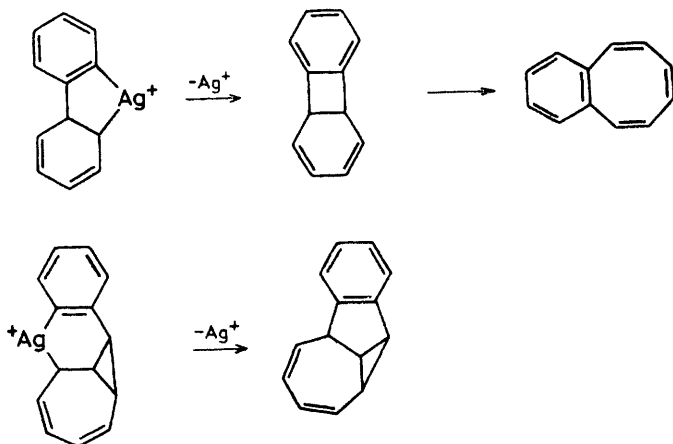
[25] F. Ungvary and L. Marko, *J. Organometallic Chem.*, 1969, **20**, 205.
[26] R. F. Heck, *Adv. Organometallic Chem.*, 1966, **4**, 243.
[27] W. Mowat and G. Wilkinson, *J. Organometallic Chem.*, 1971, **28**, C34.
[28] (*a*) M. Tamura and J. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 1483, 1485; (*b*) L. A. Paquette, *Chem. Comm.*, 1971, 1076.

C. The Role of Supporting Ligands.—The critical effect of other ligands in stabilizing organo-transition-metal compounds is not that of π-bonding, but that of firm occupation of the co-ordination site (π-bonding may, of course, help to achieve this). This denies the use of that co-ordination site for concerted decomposition routes. Thus with reference to β-eliminations the stability[6] of $[RhR(NH_3)_5]^{2+}$ has been contrasted with the lability of $[RhR(CO)(PPh_3)_3]$,[29] which easily eliminates Ph_3P to make available an extra co-ordination site.

A possible steric effect of other ligands is also implicit. Bulky ligands will prevent use of adjacent co-ordination sites as well as their own. This may account for the existence of certain highly co-ordinately-unsaturated molecules such as $(Ph_3C)_2Ni$,[9] and for the ready formation of $[Cr(tsm)_4]^-$ and $Cr(tsm)_4$ (tsm = trimethylsilylmethyl), whereas less bulky ligands (methyl or 1,4-butenyl)[30] or bulkier metals (molybdenum even with tsm as ligand) give rise to dinuclear products.[19a]

D. Free-radical Processes.—The dominance of paired-electron processes in organo-transition-metal chemistry is not complete. Indeed, it should not be expected to be. The similarity of transition-metal–carbon bonds to main-group-element–carbon bonds, the rupture of which to produce free radicals being both well recognized and exploited, is evident: thus some free-radical reactions of transition-element derivatives are probable. One example may be the thermolysis[13] of $(\pi\text{-}C_5H_5)PtMe_3$, referred to above, which decomposes according to first-order kinetics at 438 K in the vapour phase, with an activation energy of 163 kJ mol^{-1}. The main organic product identified was methane, but smaller amounts of ethane and dihydrogen were also formed. It may be that methane production in fact involves 1,2-elimination from the system H_3C—[Pt]—CH_2—H or even from one methyl group and a cyclopentadienyl ring, but in any case the steric impossibility of square-planar '$(\pi\text{-}C_5H_5)PtCH_3$' presumably precludes a simple concerted reductive elimination of two methyls.

Photochemical reactions of metal–carbon single bonds are expected to give radical products.[3] A recent example is the photolysis of methylcobalamin, in which excitation of the ring $\pi \rightarrow \pi^*$ transition leads to homolytic cleavage of the cobalt–methyl bond.[31]

Although electron promotion from a non-bonding to an antibonding orbital does not appear to be an important thermal process, the promotion under thermal conditions of a bonding electron into a non-bonding orbital[2] is feasible in compounds containing less than six d-electrons, and radical products would result. We have ourselves[3] (it would now seem erroneously) advanced this as an explanation for the high lability of $TiMe_4$ compared with $SnMe_4$. A consequence of such a mechanism would be that π-accepting ligands should *labilize* the

[29] G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. (A)*, 1970, 1392.
[30] (a) J. Krausse, G. Marx, and G. Schödl, *J. Organometallic Chem.*, 1970, **20**, 159; (b) J. Krausse and G. Schödl, *ibid.*, 1971, **27**, 59.
[31] J. M. Pratt and B. R. D. Whitear, *J. Chem. Soc. (A)*, 1971, 253.

metal–carbon bonds, and this feature was invoked by Cossee[32] to explain the apparent labilizing effect of olefins on titanium–alkyl bonds in certain Ziegler catalysts. More recently, thermolysis studies[33] of $(h^5\text{-}C_5H_5)_2\text{TiRCl}$ (R = Me, Et, Bu^i, Ph, CH$_2$Ph, or C$_2$H$_4$Ph) show first-order loss of R with an activation energy of bond-breaking of *ca.* 105 kJ mol^{-1}. The products were rationalized in terms of an initial electron promotion from a Ti—C σ-bond, leaving species with an activated neutral R group within the titanium co-ordination sphere. This undergoes reaction by migration to other centres or (with donor solvents) by free radical formation.
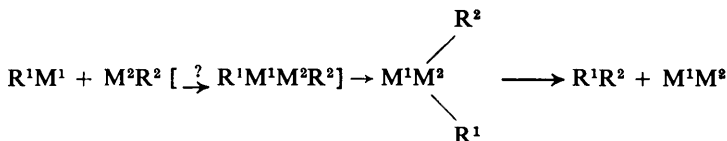
It must now be recognized, however, that even amongst elements at the beginning of the Periodic Group where this promotional mechanism could apply, concerted reaction paths are still able to operate.

3 Some Relationships among Bond-breaking Processes

A. Formal Analogies.—Dinuclear eliminations, although appearing to be quite different to the other (unimolecular) eliminations discussed in Section 2B, can in fact be regarded as intramolecular eliminations from the reaction intermediates, *e.g.*
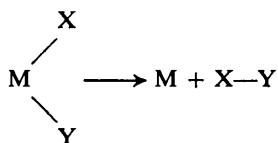
$$R^1M^1 + M^2R^2 \rightarrow R^1M^1M^2R^2 \rightarrow R^1R^2 + M^1\text{—}M^2$$

or

$$R^1M^1 + M^2R^2 \; [\underset{\rightarrow}{\overset{?}{}} R^1M^1M^2R^2] \rightarrow M^1M^2 \overset{\displaystyle R^2}{\underset{\displaystyle R^1}{\diagup \diagdown}} \longrightarrow R^1R^2 + M^1M^2$$

The former process is formally a 1,2-elimination of R^{1}R^2 across the metal–metal bond, whereas the latter is oxidative addition of R^1—M^1 to M^2, followed by reductive elimination of R^1—R^2.

Reductive eliminations for our purpose are processes of the type

$$M \overset{\displaystyle X}{\underset{\displaystyle Y}{\diagup \diagdown}} \longrightarrow M + X\text{—}Y$$

No free-radical or high-energy intermediates need be involved since, as we have seen, there is evidence that bond formation between X and Y can accompany the breaking of M—X and M—Y. The extreme valence-bond representation of olefin–metal complexes depicts them as metalla-cyclopropanes, and as such the two M—C bonds are analogous to M—X and M—Y. Elimination of the olefin

[32] P. Cossee, *J. Catalysis*, 1964, **3**, 80.
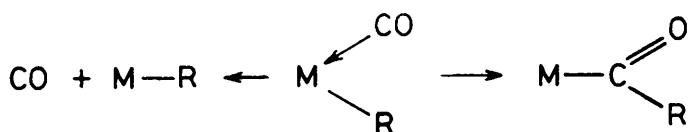[33] J. A. Waters, V. V. Vickroy, and G. A. Mortimer, *J. Organometallic Chem.*, 1971, **39**, 41.

from the metal co-ordination sphere is thus equivalent to reductive elimination of XY:

$$M \overset{\displaystyle C}{\underset{\displaystyle C}{\big|}} \longrightarrow M + C=C$$
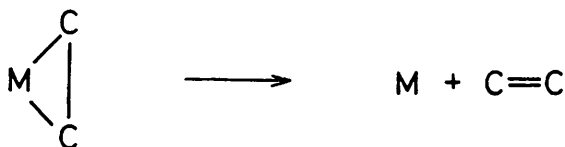
Acetylene derivatives, formally metalla-cyclopropenes, can be treated similarly, as can dimerizations, polymerizations, and ring-closure reactions:

$$\longrightarrow \qquad \longrightarrow \qquad M + \begin{matrix} C-C \\ | \quad | \\ C-C \end{matrix}$$
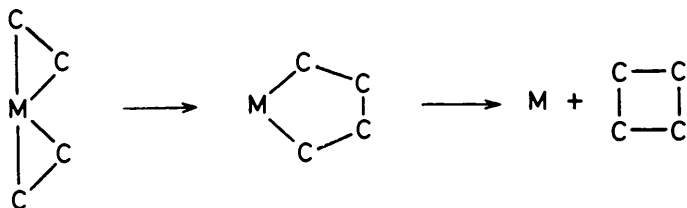
The number of electrons formally donated to the metal is reduced by two in each of the elimination steps mentioned. Other reactions that produce this result include the straightforward loss of two-electron unidentate ligands, and the insertion of co-ordinated CO into metal–carbon bonds:

$$CO + M-R \longleftarrow M\overset{\displaystyle CO}{\underset{\displaystyle R}{\big\langle}} \longrightarrow M-C\overset{\displaystyle O}{\underset{\displaystyle R}{\big\langle}}$$

The β-elimination and 1,3-elimination reactions are clearly related to each other, and may involve a common (internal) oxidative addition step [pathways (i) or (ii) of Scheme 3]. Pathway (iii) of Scheme 3 can only lead to 1,3-elimination, unless further steps intervene, probably involving changes in oxidation number at X and Y. The various pathways of Scheme 3 are, of course, idealizations, in which two-centre interactions are used to describe a many-centre process. They may, nonetheless, have some reality, which could cause differences in primary isotope effects, solvent effects, or chemical requirements.

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2
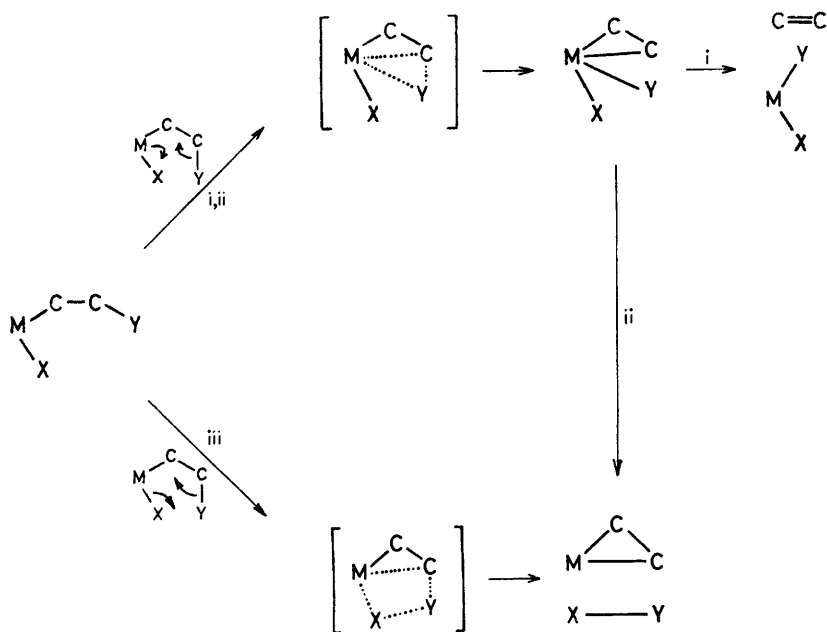
Scheme 3

B. Orbital Correlations in Bonding and Bond-breaking.—Figure 1 compares conventional bonding schemes for fragments of type M(alkene), ML, and MR^1R^2,
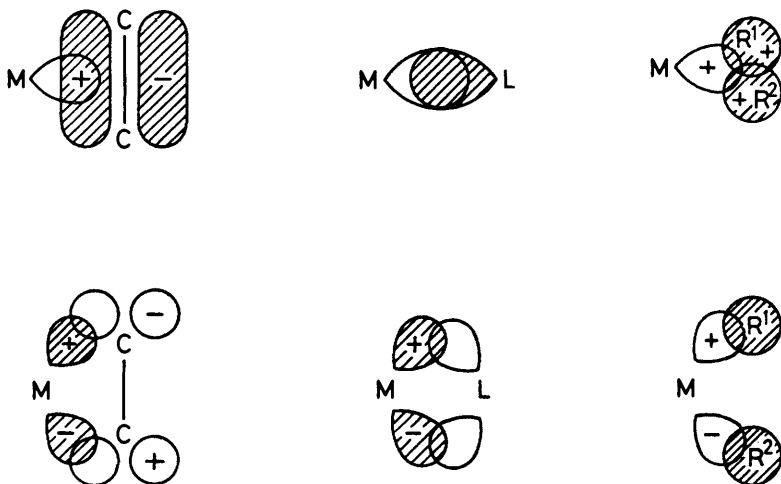

Figure 1 *Bonding in* M(*alkene*), ML, *and* MR^1R^2 *systems*

where L is a unidentate, more-or-less π-accepting, ligand and R^1, R^2 are two groups similarly σ-bonded to the metal. Figure 2 illustrates the fate of the
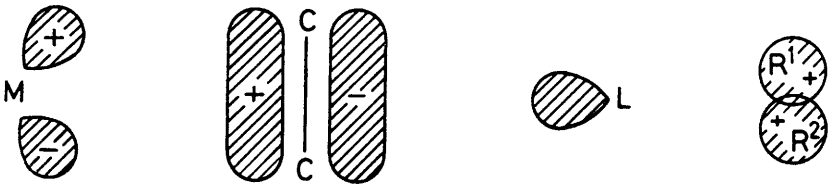

Figure 2 *Electron distribution in separated M and alkene, L, or R^1—R^2 fragments*

electrons involved in bonding on unimolecular loss of alkene, L, or R^1—R^2. In Figure 1 those orbitals formally regarded as filled[34] are shaded.* The assignment is, of course, artificial and would differ if the metalla-cyclopropane, $\overline{M—C—C}$, description were preferred for the alkene complex. The assignment of Figure 2 is, however, not formal but real.

In each case four electrons are involved in bonding and these are in a configuration $(a')^2(a'')^2$. In each case also, separating the fragments leaves the metal in the configuration $(a'')^2$ and the leaving group in the configuration $(a')^2$, so that there is a loss of two electrons from the co-ordination shell of the metal. Formally, there is no change in oxidation number on loss of L, whereas the oxidation number falls by two on loss of R^1—R^2. This is because in the former case the a'' electrons are regarded as localized mainly on the metal in both the bonded and separated states, whereas in the latter, the a'' electrons are formally assigned to the ligands in the bound state, although they are left at the metal on separation. Which of these cases the alkene resembles will depend on whether the metalla-cyclopropane description is preferred or, as here, the ligand alkene description.

A more rigorous test of the proposed correlation is given by Figure 3. Here, the loss of two mutually *cis* one-electron donors from an octahedral complex is compared with the loss of L or (in-plane) alkene from a trigonal-bipyramidal complex. The losses are regarded as taking place by way of C_{2v} transition states to give products of symmetry D_{4h}. This maximizes symmetry at all stages and thus provides the most rigorous test of the proposed correlations. The path discussed is likely to be that in fact preferred, since it minimizes ligand–ligand interactions, and these are presumably generally repulsive. (This is of course not so for the interaction between R^1 and R^2 themselves, nor for related interactions in insertion, migration, β-elimination, or ring-expansion processes.) Energy orderings within the broad groupings bonding < non-bonding < antibonding are uncertain and probably variable, but such is the effectiveness of the correla-

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* In- and out-of-phase combinations of R^1—M and R^2—M orbitals are chosen; within the single configuration approximation this description is equivalent to that using localized σ-bonded MOs.

34 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 3rd edn., Interscience. London, 1972.
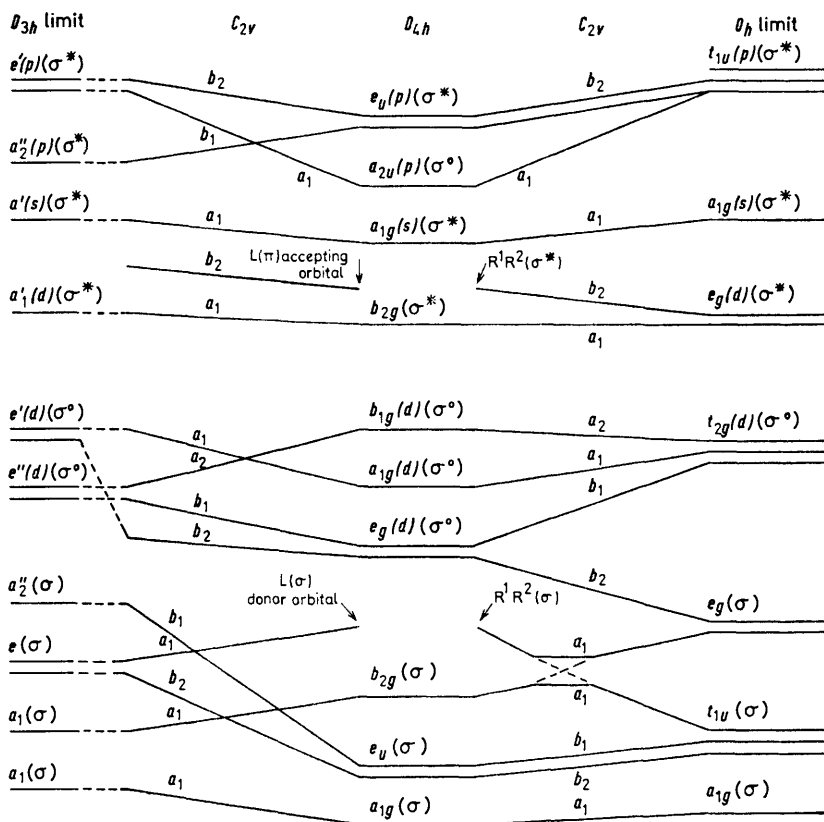
Figure 3 *Qualitative correlation diagrams for loss of a π-accepting equatorial ligand from a trigonal bipyramid, and reductive* cis *elimination of* R^1R^2 *from an octahedral complex. In the D_{3h} and O_h limits, all ligands are treated as equivalent. In the $C_{2v}(D_{3h} \rightarrow D_{4h})$ correlation, the effect of an in-plane π-acceptor orbital of the departing ligand is included*

tions of these broad groupings themselves that such variations are on the whole without chemical significance. [An obvious exception is the correlation of the b_2 component of σ^0 (e_g) in D_{4h} with a bonding orbital of $ML_4R^1R^2$; thus the formal selection rules for ground-state concerted oxidative addition to square-planar complexes could depend for electron-deficient species on the number and arrangement of non-bonding electrons present.] More relevant to the present discussion is the general similarity of the correlations involved in reductive eliminations and in ligand loss, and the general preservation in Figure 3 of the correlations implicit in the simplified Figures 1 and 2.

Contrary to the view of some authors,[35] concerted *trans* elimination of R^1—R^2 from an octahedral compound (and, relatedly, *trans* addition of R^1—R^2 to a square-planar complex) is not an allowed thermal process within this one-electron model. The ground state of the octahedral complex has the configuration $(a')^2(a'')^2$ (primes representing behaviour under reflection in the xy plane, choosing z to lie along the R^1—M—R^2 axis), but the separated fragments have the configuration $(d_{z^2})^2$, $\sigma(R^1$—$R^2)^2$, which is of type $(a')^2(a')^2$. Such processes have been claimed,[36] but may well be non-concerted.

4 Controlling Influences in Bond Cleavage

A. 1,2-Eliminations.—It is as yet too early to say much about factors controlling the 1,2-elimination reaction. The transition state for this reaction must be of low symmetry, precluding simple theoretical discussion, while from an experimental point of view the generality of this recently recognized process is completely unknown. It is worth pointing out, however, that the process is a reduction:

$$R^1M^{(N)}\text{—}CHR_2^2 \rightarrow R^1H + M^{(N-2)} \leftarrow :CR_2^2$$

This reduction is presumably real as well as formal, with two electrons entering a vacant metal d-orbital, of suitable symmetry for back-donation to the vacant carbene carbon p-orbital. As such, the process may be expected to operate in metals of high formal oxidation state with empty $d(\pi)$ orbitals. Moreover, the process alleviates steric crowding and is likely to be favoured when such crowding exists, both on thermodynamic and kinetic grounds. It is relevant that the reaction is established as yet only for Ti^{IV} species, which are either octahedrally co-ordinated ($TiMe_4$ in ether) or sterically crowded by large ($h^5\text{-}C_5H_5$) groups. It would be of interest to know whether this process applies to WMe_6.

The conditions for 1,2-elimination would appear to be similar to, but more restricted than, those suggested by us for promotional radical loss.[3] This latter process is available, as 1,2-elimination is not, for compounds in which the metals have *half-filled* d-orbitals, but no empty d-orbitals, of high electron-demand.

B. 1,1-Eliminations.—The situation with regard to 1,1-eliminations is more clear. The essential point of similarity between these eliminations and the ligand loss processes with which they are compared in Section 3 is that they reduce the orbital occupation at the metal by two electrons. Thus compounds in which this orbital occupation is higher than usual for the metal concerned will be more prone to undergo elimination reactions, and any reaction or change in conditions which increases orbital occupation is likely to be followed by a counter-balancing elimination.
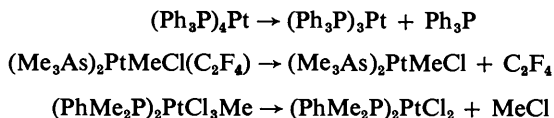
Such effects are most noticeable towards the end of the transition series, where reducing d-orbital energies and increasing $nd \rightarrow (n + 1)p$ promotion energies make full orbital occupation leading to 18-electron molecules energetically less favourable.[1,37] Thus where 18-electron species are common for iron,
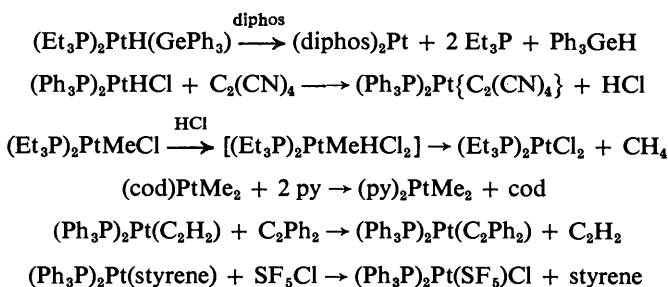
[35] R. G. Pearson, *Pure Appl. Chem.*, 1971, **21**, 145.
[36] R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 1970, **92**, 5519.
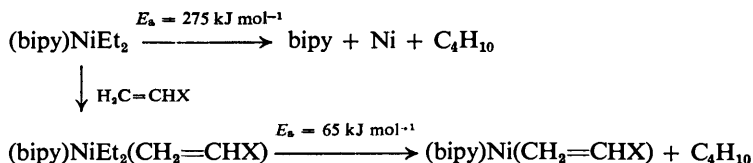[37] P. S. Braterman, *Structure and Bonding*, 1972, **10**, 57.

ruthenium, and osmium, 16-electron compounds are generally more stable for nickel, palladium, and platinum, and 18-electron molecules of these latter elements readily undergo elimination reactions:[38-40]

$$(Ph_3P)_4Pt \rightarrow (Ph_3P)_3Pt + Ph_3P$$

$$(Me_3As)_2PtMeCl(C_2F_4) \rightarrow (Me_3As)_2PtMeCl + C_2F_4$$

$$(PhMe_2P)_2PtCl_3Me \rightarrow (PhMe_2P)_2PtCl_2 + MeCl$$

It is apparent that the formal oxidation number (0, 2, and 4, respectively, in the above examples) is here less important than electron availability at the metal. Many similar reactions proceed without isolation of the 18-electron species. Examples of such addition–elimination reactions involving olefins, two-electron unidentate ligands, and two one-electron ligands are given below:[15,41-45]

$$(Et_3P)_2PtH(GePh_3) \xrightarrow{\text{diphos}} (diphos)_2Pt + 2\,Et_3P + Ph_3GeH$$

$$(Ph_3P)_2PtHCl + C_2(CN)_4 \longrightarrow (Ph_3P)_2Pt\{C_2(CN)_4\} + HCl$$

$$(Et_3P)_2PtMeCl \xrightarrow{\text{HCl}} [(Et_3P)_2PtMeHCl_2] \rightarrow (Et_3P)_2PtCl_2 + CH_4$$

$$(cod)PtMe_2 + 2\,py \rightarrow (py)_2PtMe_2 + cod$$

$$(Ph_3P)_2Pt(C_2H_2) + C_2Ph_2 \rightarrow (Ph_3P)_2Pt(C_2Ph_2) + C_2H_2$$

$$(Ph_3P)_2Pt(styrene) + SF_5Cl \rightarrow (Ph_3P)_2Pt(SF_5)Cl + styrene$$

The decomposition of (bipy)NiEt$_2$ to give butane illustrates the effect of increasing orbital occupation at nickel. The activation energy for decomposition in the solid state is 275 kJ mol^{-1}. In the presence of olefins, however, this parameter is reduced to *ca.* 65 kJ mol^{-1}, and 18-electron intermediates of the type Ni(bipy)Et$_2$(olefin) can be isolated:[46]

$$(bipy)NiEt_2 \xrightarrow{E_a\,=\,275\;kJ\;mol^{-1}} bipy + Ni + C_4H_{10}$$

$$\downarrow\; H_2C{=}CHX$$

$$(bipy)NiEt_2(CH_2{=}CHX) \xrightarrow{E_a\,=\,65\;kJ\;mol^{-1}} (bipy)Ni(CH_2{=}CHX) + C_4H_{10}$$

Labile, 18-electron intermediates are probably also involved in the selective cross-coupling of organic halides and Grignard reagents, catalysed by nickel(II)

[38] R. Ugo, *Coordination Chem. Rev.*, 1968, **3**, 319.
[39] H. C. Clark and R. Puddephatt, *Inorg. Chem.*, 1971, **10**, 18.
[40] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. (A)*, 1969, 2969.
[41] P. Uguagliati and W. H. Baddley, *J. Amer. Chem. Soc.*, 1968, **90**, 5446.
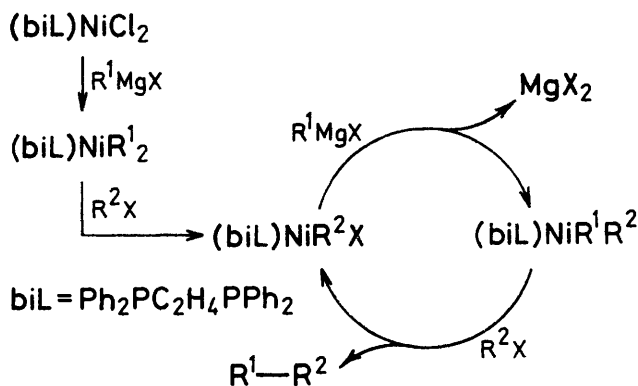[42] U. Belluco, M. Giustiniani, and M. Graziani, *J. Amer. Chem. Soc.*, 1967, **89**, 6494.
[43] C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, *Inorg. Chem.*, 1963, **2**, 1255.
[44] J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 1957, 208.
[45] R. D. W. Kemmitt, R. D. Peacock, and J. Stocks, *Chem. Comm.*, 1969, 554.
[46] T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1971, **93**, 3350, 3360.

and phosphine complexes (Scheme 4).[47] The key steps, which occur both in the formation of the 'active catalyst' and in the catalytic cycle, are the reactions of

$(biL)NiCl_2$

$\downarrow R^1MgX$

$(biL)NiR^1_2$

R^1MgX $\qquad$ MgX_2

$\downarrow R^2X$

$(biL)NiR^2X$ $\qquad$ $(biL)NiR^1R^2$

$biL = Ph_2PC_2H_4PPh_2$

$R^1\!-\!R^2$ $\qquad$ R^2X

Scheme 4

the organic halide with the diorgano-nickel complexes, and these most likely proceed *via* oxidative addition of R^2X to form 18-electron intermediates, followed by reductive elimination of R^1R^1 or R^1R^2, respectively.

An increase in orbital occupation through nucleophilic interactions might well account for the oft-encountered increase in lability when organometallic compounds are dissolved or melted. This effect has often been ascribed to lattice-stabilization effects. Evidence from the i.r. and electronic spectra of the $Cr(CO)_5$ fragment in hydrocarbon (as opposed to argon) matrices indicates that even these 'inert' solvents produce interactions.[48]
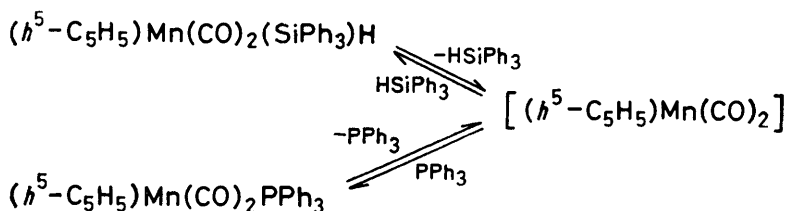
C. Effects of Varying the Metals and Ligands.—As the transition series is traversed left from the nickel group, 18-electron molecules become more stable. This is apparent even within the Group VIII triad: eliminations from $Fe(CO)_5$ usually require energy (either heat or u.v. irradiation – examples are given later), whereas the process is spontaneous in solution for $Ni(PPh_3)_4$.[38] In as much as oxidative addition is the reverse of concerted reductive elimination,† such reactions can be rationalized by converse arguments but show the effects of the same trends. Thus oxidative additions involving electron-saturated metals frequently require loss of a two-electron species as a first step. An example is in

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† This is generally true. Polar molecules in solvents of high dielectric constant may react by an ionic mechanism, however, and *trans* addition can result (see 'Correlations' section and ref. 49). The reverse of such reactions is more akin to loss of two-electron unidentate ligands.

[47] K. Tamao, K. Sumitnni, and M. Kumadb, *J. Amer. Chem. Soc.*, 1962, **94**, 4374.
[48] M. A. Graham, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Organometallic Chem.*, 1972, **34**, C34.
[49] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, **7**, 53.

$(h^5-C_5H_5)Mn(CO)_2(SiPh_3)H$

$-HSiPh_3$

$HSiPh_3$

$[(h^5-C_5H_5)Mn(CO)_2]$

$-PPh_3$

PPh_3

$(h^5-C_5H_5)Mn(CO)_2PPh_3$

Scheme 5

Scheme 5.[50] Similar elimination reactions are commonly encountered as the first step in ligand-exchange reactions involving 18-electron molecules, such as $Cr(CO)_6$,[51] $Mn(CO)_5Br$,[52] and $Ru(CO)_4(SiCl_3)_2$.[53] A mechanistic study of the polymerization of olefins catalysed by the 18-electron species $(bipy)_2FeEt_2$ indicates a preliminary dissociation of an Fe—N bond before the olefins can co-ordinate to iron.[54]

The trend from 18- to 16-electron molecules is continued past Group VIII to the coinage metals, where stable 14-electron molecules are common, and even 16-electron species undergo facile eliminations.

A consequence of the lanthanide contraction which is still noticeable in the Group VIII elements is that the change in the $nd \rightarrow (n+1)p$ promotion energy as the group is descended is not regular.[55] The trend towards lower orbital occupation as the group is descended is therefore also irregular, and the elements of the second row, Ru, Rh, and Pd, show the least tendency towards forming 18-electron molecules, followed by Os, Ir, and Pt. The first-row elements Fe, Co, and Ni are the elements of their groups most likely to be found in 18-electron molecules. The effect of this inversion can be seen in various systems and is particularly relevant to the elimination reactions under discussion.

Thus the $nd^{10} \rightarrow nd^9(n+1)p^1$ promotion energies for Ni, Pd, and Pt (1.72, 4.23, and 3.28 eV, respectively) follow the same order as λ_{max} for the lowest-energy absorptions in $M(PPh_3)_3$ (M = Ni, 393 nm; Pd, 322 nm; and Pt, 332 nm) and this reflects the trend Ni $\gg$ Pd $<$ Pt for $M(PPh_3)_3$ to add a further two-electron ligand.[56] Also, in the displacement of PF_3 by RNC in the complexes $(F_3P)_4M$ (M = Ni, Pd, or Pt), a reaction which follows the expected elimination-addition mechanism, the activation energies for breaking the first M—P bonds show the same irregular sequence.[57] Similar comparisons of the tendencies for

[50] A. J. Hart-Davies and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1971, **93**, 4388.
[51] For reviews see H. Werner, *Angew. Chem. Internat. Edn.*, 1968, **7**, 930; W. Strohmeier, *Fortschr. Chem. Forsch.*, 1968, **10**, 306.
[52] A. Berry and T. L. Brown, *Inorg. Chem.*, 1972, **11**, 1165.
[53] R. K. Pomeroy, R. S. Gay, G. O. Evans, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1972, **94**, 272.
[54] T. Yamamoto, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Japan*, 1972, **45**, 1104, 1111.
[55] C. E. Moore, 'Atomic Energy Levels', National Bureau of Standards, Circular 467, Washington, U.S. Printing Office, 1952, vol. 2; 1958, vol. 3.
[56] C. A. Tolman, W. C. Seidel, and D. H. Gerloch, *J. Amer. Chem. Soc.*, 1972, **94**, 2669.
[57] R. D. Johnston, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 77.

$M(biL)_2^+$ (M = Co, Rh, or Ir; biL = *cis*-$Ph_2PCH=CHPPh_2$) to add either O_2, CO, or H_2 reveal the same type of discontinuity; Co $\gg$ Rh < Ir.[58]

Although such comparisons of isostructural and isoelectronic complexes down an entire periodic group are rare, many effects of the inversion are apparent in compounds of the second- and third-row elements only. For example, several six-co-ordinate iridium(III) complexes, typified by $(Ph_3P)_2(CO)IrHCl(SiCl_3)$, are known, but five-co-ordinate 16-electron species such as $(Ph_3P)_2RhHCl(SiCl_3)$ are favoured by rhodium.[59] Addition of a further ligand leads to eliminations:

$$(Ph_3P)_2RhHCl(SiCl_3) \overset{CO}{\underset{-CO}{\rightleftharpoons}} (Ph_3P)_2(CO)RhHCl(SiCl_3)$$

$$\downarrow$$

$$(Ph_3P)_2(CO)RhCl + HSiCl_3$$
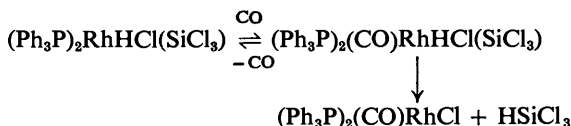
Also, the fact that $(PhMe_2P)_2(cod)Rh^IMe$ shows intermolecular phosphine exchange in solution whereas its iridium(I) analogue does not[60] reflects once again the more facile elimination from rhodium than iridium.

The nucleophilicity of the ligands can exert an influence on addition or elimination reactions in two ways which appear at first to be directly conflicting. Strong nucleophiles raise the energy of metal *d*-electrons, which should favour their formal loss in bond formation and thus favour oxidative additions, but also raise that of the *p*-orbitals, favouring eliminations. The latter effect is more directional in application however, and is related to the σ-bonding *trans* influence. These effects can be seen in the addition of molecular oxygen to $(R_3P)_2(CO)IrCl$. The affinity for oxygen generally increases[61] with increasing base strength of R_3P (though steric effects also exert an influence), and the structure of the adducts $(R_3P)_2(CO)IrCl(O_2)$ is such that the oxygen atoms lie *trans* to CO and Cl.[62] In keeping with the aforementioned trends, the affinity of analogous rhodium complexes for O_2 appears to be much less.[63]

It can be noted at this point that the structure of olefin adducts of d^8 molecules, like the O_2 adducts discussed above, can be described as octahedral (depicting the olefin as a bidentate ligand), though the angle subtended by the olefin at the metal is usually much less than 90° (several structures of this type can be found in ref. 1). This is in keeping with the general orbital correlations described herein.

The possibility of steric factors influencing elimination reactions cannot be ignored, but we believe their role to be secondary. For example, *cis*-$(Ph_3P)_2PtMe_2$ is stable to 235 °C, whereas the less-cluttered $(Ph_3P)AuMe_3$ loses ethane at

[58] L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, 1971, **93**, 6671.
[59] E. H. Brooks and R. J. Cross, *Organometallic Chem. Rev. (A)*, 1970, **6**, 227.
[60] D. P. Rice and J. A. Osborn, *J. Organometallic Chem.*, 1971, **30**, C84.
[61] G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *Chem. Comm.*, 1971, 758; L. Vaska and L. S. Chen, *ibid.*, p. 1080.
[62] S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 1965, **87**, 2581; M. S. Weininger, I. F. Taylor, jun., and E. L. Amma, *Chem. Comm.*, 1971, 1172.
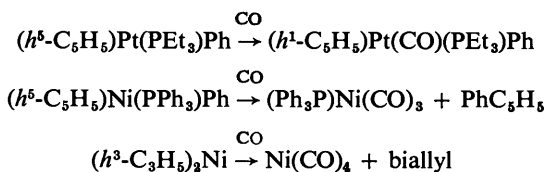[63] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1969, **91**, 6301.

120 °C.[11] This is compatible with the expected tendency to lower orbital occupation of gold compared with platinum. The geometrical arrangement of the ligands is important of course, as the leaving groups must be *cis*.

5 Related Processes

These include $\pi \rightarrow \sigma$ rearrangements of unsaturated ligands, oligomerizations, the β-interaction, and carbonyl insertions.

The conversion of π-allyls[64] or π-cyclopentadienyls[65] to σ-bonded groups by entering nucleophiles resembles olefin elimination and is not remarkable. It is not generally known whether the addition of the nucleophile is the first or second step, and comparison with the previously discussed eliminations would suggest that this will depend upon the degree of orbital occupation of the metal involved. Where some reactions convert 18-electron molecules into 16-electron species, others are followed by eliminations of the groups under consideration:[65-67]

$$(h^5\text{-}C_5H_5)Pt(PEt_3)Ph \xrightarrow{CO} (h^1\text{-}C_5H_5)Pt(CO)(PEt_3)Ph$$

$$(h^5\text{-}C_5H_5)Ni(PPh_3)Ph \xrightarrow{CO} (Ph_3P)Ni(CO)_3 + PhC_5H_5$$

$$(h^3\text{-}C_3H_5)_2Ni \xrightarrow{CO} Ni(CO)_4 + \text{biallyl}$$

Eliminations similar to the latter example are involved in the ring-closure steps in the cyclo-dimerization and -trimerization of butadiene at nickel atoms:[68]
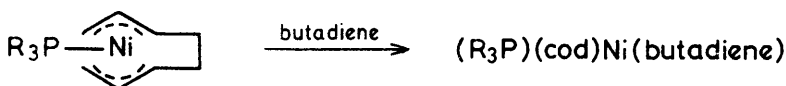
Related elimination reactions forming C—C bonds between neighbouring co-ordinated olefins or acetylenes lead to metalla-cyclopentanes or metalla-cyclopentadienes. Further ring expansions, ring closures, or other eliminations can lead to a variety of products. Many examples of such reactions can be found in refs. 1 and 68. Some recent examples shown in Scheme 6[69-72] serve to indicate the variety of unsaturated molecules which can participate in such oligomerizations.

[64] M. L. H. Green and P. L. I. Nagy, *Adv. Organometallic Chem.*, 1965, **2**, 325.
[65] R. J. Cross and R. Wardle, *J. Chem. Soc. (A)*, 1971, 2000.
[66] H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, and N. Hagihara, *J. Organometallic Chem.*, 1966, **6**, 86.
[67] G. Wilke, *Angew. Chem. Internat. Edn.*, 1963, **2**, 105.
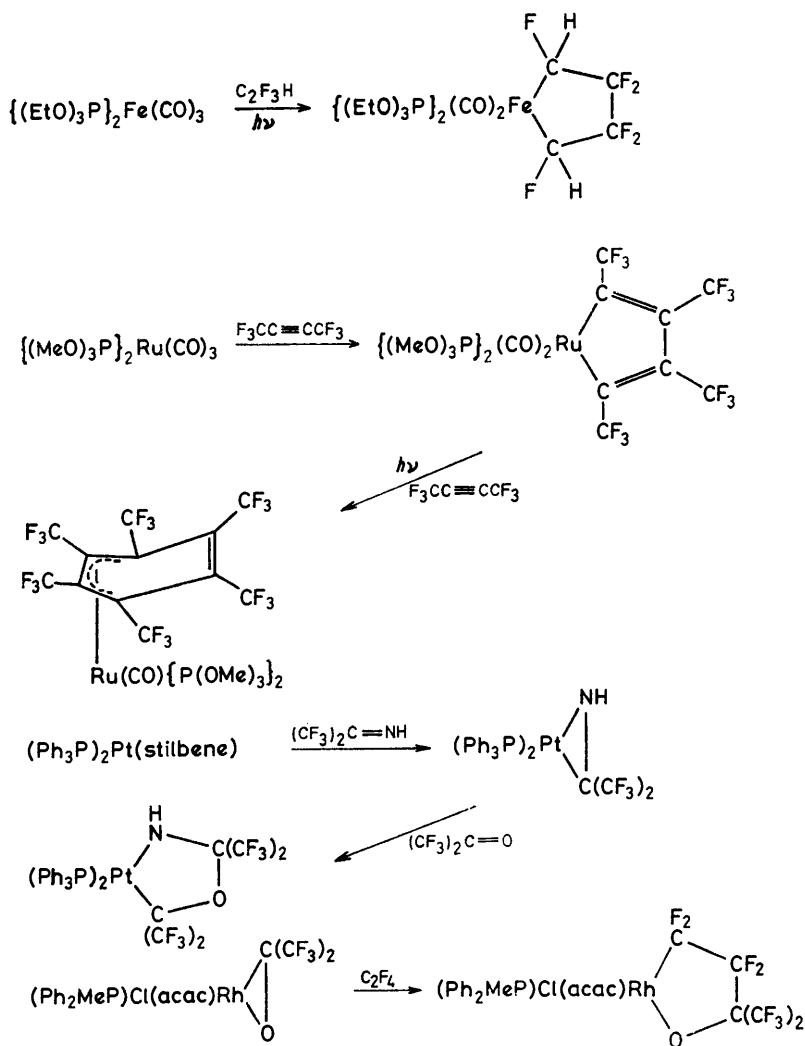[68] P. Heimbach, P. W. Jolly, and G. Wilke, *Adv. Organometallic Chem.*, 1970, **8**, 29.
[69] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. (A)*, 1970, 2975.
[70] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. (A)*, 1970, 2981.
[71] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1970, 3161.
[72] A. J. Mukhedkar, V. A. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1970, 3166.

$\{(EtO)_3P\}_2Fe(CO)_3 \xrightarrow[h\nu]{C_2F_3H} \{(EtO)_3P\}_2(CO)_2Fe$ (cyclic structure with F, H, CF$_2$, CF$_2$)

$\{(MeO)_3P\}_2Ru(CO)_3 \xrightarrow{F_3CC\equiv CCF_3} \{(MeO)_3P\}_2(CO)_2Ru$ (ring with CF$_3$ groups)

$\xleftarrow[F_3CC\equiv CCF_3]{h\nu}$

(structure) Ru(CO)$\{P(OMe)_3\}_2$ with CF$_3$ groups

$(Ph_3P)_2Pt(stilbene) \xrightarrow{(CF_3)_2C=NH} (Ph_3P)_2Pt\diagdown \overset{NH}{\underset{C(CF_3)_2}{|}}$

$(Ph_3P)_2Pt$ (ring with N, H, C(CF$_3$)$_2$, O, C(CF$_3$)$_2$) $\xleftarrow{(CF_3)_2C=O}$

$(Ph_2MeP)Cl(acac)Rh$ (ring with C(CF$_3$)$_2$, O) $\xrightarrow{C_2F_4} (Ph_2MeP)Cl(acac)Rh$ (ring with C$_2$F$_2$, CF$_2$, C(CF$_3$)$_2$, O)

Scheme 6

β-Eliminations are only one type of a general class of reactions which proceed *via* an internal oxidative addition step. Examples are given in Scheme 7.[73-76]
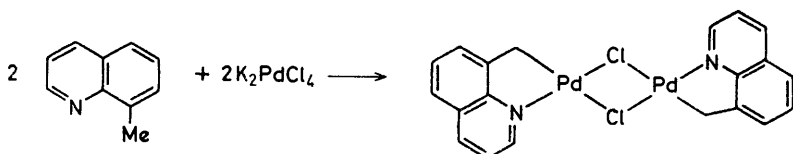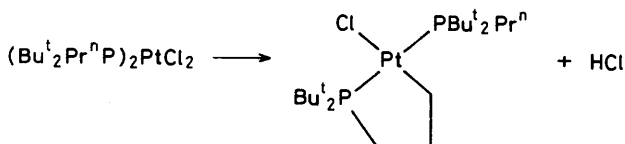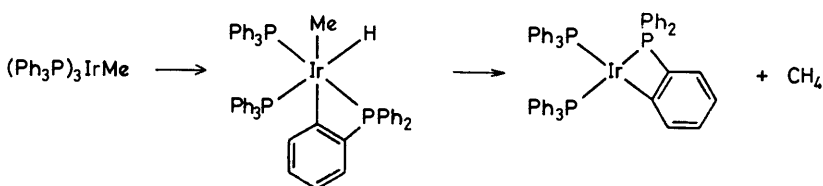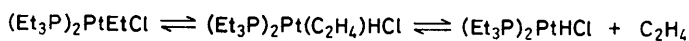
Most examples are found in the chemistry of the square-planar d^8 complexes of Rh, Ir, Pd, and Pt, so it is most likely that the reactions are governed by the

[73] J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. (A)*, 1968, 190.
[74] J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, 1972, 94, 6226.
[75] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176.
[76] G. E. Hartwell, R. V. Lawrence, and M. J. Smas, *Chem. Comm.*, 1970, 912.

$(Et_3P)_2PtEtCl \rightleftharpoons (Et_3P)_2Pt(C_2H_4)HCl \rightleftharpoons (Et_3P)_2PtHCl + C_2H_4$

$(Ph_3P)_3IrMe \longrightarrow$

$+ CH_4$

$(Bu^t_2Pr^nP)_2PtCl_2 \longrightarrow$

$+ HCl$

2 [quinoline structure with Me] $+ 2K_2PdCl_4 \longrightarrow$

Scheme 7

same factors as 'normal' oxidative additions and reductive eliminations. In general, however, the conditions for these reactions are poorly documented and the expected intermediates verified in only a few cases. A close approach of the transfer group to the metal is obviously required. Some structure determinations show such an interaction in molecules closely related to those which undergo these intramolecular rearrangements. An example is shown in (1).[77]
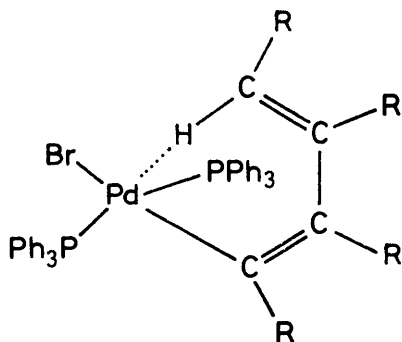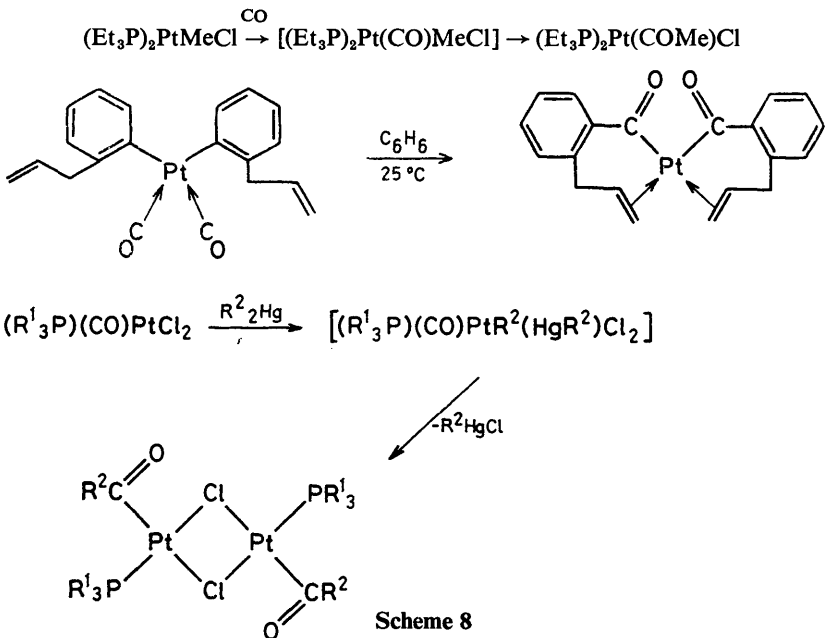

(1) $R = CO_2Me$

[77] D. M. Roe, P. M. Bailey, K. Moseley, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1972, 1273.

β-Interactions and related processes are often involved in homogeneous catalytic reactions such as olefin isomerization[1] and H–D exchange.[78] The same mechanisms (and controlling influences) probably operate in heterogeneous catalysis reactions by metals and supported metal atoms. The more drastic reactions often observed in heterogeneous processes (such as H–D exchange and C—C bond breaking in saturated hydrocarbons) may result from the high levels of electron unsaturation possible at the surface atoms, as well as from the more rigorous available operating conditions. (Similar processes for homogeneous systems have been reported in a few cases.[79])

The insertion of carbon monoxide into metal–carbon bonds is a common reaction, and one of some importance. Like many of the elimination reactions discussed above, the insertions are often initiated by an entering nucleophile, and this suggests that these reactions, also, may be controlled by the level of orbital occupation of the metal. The entering ligand can be the inserting group itself, but when CO is already in the metal co-ordination sphere, it is usually a 'resident' group which inserts. The examples in Scheme 8[80–82] demonstrate the similarity in effect of a two-electron unidentate ligand, an olefin, or two one-electron groups in increasing orbital occupation and thus causing CO insertion.

$$(Et_3P)_2PtMeCl \xrightarrow{CO} [(Et_3P)_2Pt(CO)MeCl] \rightarrow (Et_3P)_2Pt(COMe)Cl$$

$$(R^1_3P)(CO)PtCl_2 \xrightarrow{R^2_2Hg} [(R^1_3P)(CO)PtR^2(HgR^2)Cl_2]$$

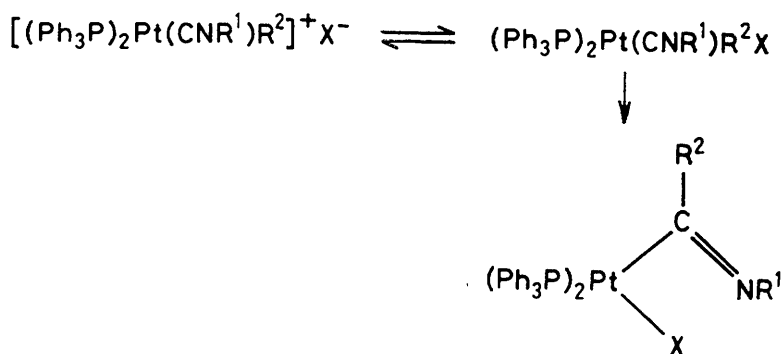**Scheme 8**

[78] C. Masters, *J.C.S. Chem. Comm.*, 1973, 191.
[79] C. Masters, *J.C.S. Chem. Comm.*, 1972, 1258; T. H. Whitesides and R. A. Budnik, *ibid.*, 1973, 87; R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, 1972, **11**, 2237.
[80] G. Booth and J. Chatt, *J. Chem. Soc. (A)*, 1966, 634.
[81] M. Aresta and R. S. Nyholm, *Chem. Comm.*, 1971, 1459.
[82] R. J. Cross and R. Wardle, *J. Chem. Soc. (A)*, 1970, 840.

Carbon monoxide can generally be eliminated from the acyls by heating in conditions which remove the gas from the reaction site. The equilibrium $RCo(CO)_4 \rightleftharpoons (RCO)Co(CO)_3$ exists in solution,[26] and might reflect the intermediate position of cobalt in its ability to accept full orbital occupation. Similar equilibria may exist with the 18-electron complex $(Ph_3As)(CO)_2IrMeCl$,[83] and, interestingly, with the 16-electron $(Ph_3As)(CO)PtMeCl$.[84] Insertion reactions of related molecules such as isocyanides[85] extend the synthetic value of this process, *e.g.*[85a]

$$[(Ph_3P)_2Pt(CNR^1)R^2]^+X^- \rightleftharpoons (Ph_3P)_2Pt(CNR^1)R^2X$$

In all of the processes discussed, the possibility of competing eliminations accompanying the desired reaction can lead to unpredictable products. In some cases this has led to unusual new compounds. The examples in Scheme 9[70,86-88] illustrate some results of competing processes operating alongside CO insertion.

Reactions of particular interest are the insertions of CO into Mn—R in the compounds $RMn(CO)_5$ and their substituted analogues. The insertion is initiated by an entering nucleophile such as CO, amine, phosphine, or, in polar solvents, a solvent molecule.[1] It has been established by isotopic labelling[89] that, at least where the entering nucleophile is CO, the key step of this reaction is migration of a methyl group to a neighbouring CO ligand. Such migration involves the movement of a ligand across a region of high electron density, and it is not immediately clear how this process is facilitated by the presence of the entering nucleophile. Relevant to this problem, however, is the probability that bimolecular nucleophilic attack on carbonyl complexes occurs initially at co-ordinated carbon.[90] The probable reaction scheme is shown in Scheme 10. The incoming carbonyl

[83] R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 331.
[84] R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, 1971, **10**, 854.
[85] (a) P. M. Treichel and R. W. Hess, *J. Amer. Chem. Soc.*, 1970, **92**, 4731. (b) B. Grociani, M. Nicolini, and T. Boschi, *J. Organometallic Chem.*, 1971, **33**, C81.
[86] B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. (A)*, 1970, 308.
[87] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1960, 989; E. Weiss, R. Merenyi, and W. Hubel, *Chem. Ber.*, 1962, **95**, 1170.
[88] R. Baker, B. N. Blackett, and R. C. Cookson, *J.C.S. Chem. Comm.*, 1972, 802.
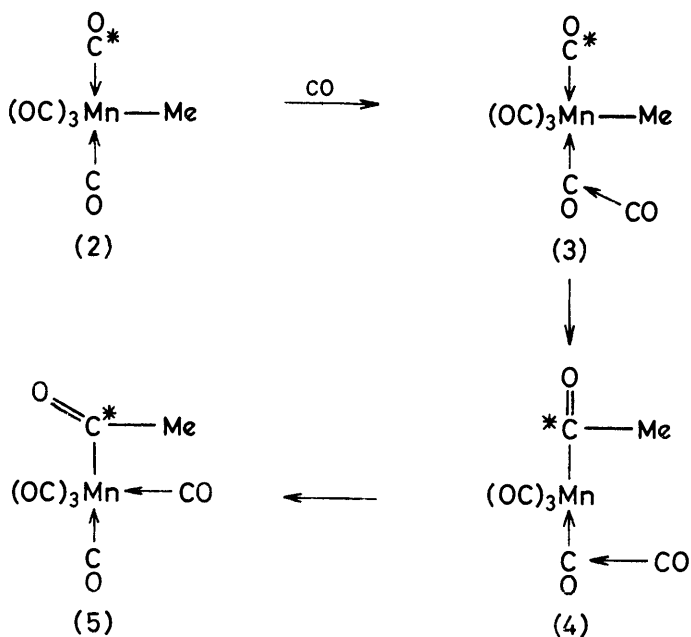[89] K. Noack and F. Calderazzo, *J. Organometallic Chem.*, 1967, **10**, 101.
[90] (a) K. Caulton and R. F. Fenske, *Inorg. Chem.*, 1968, **7**, 1273; (b) D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chim. Acta*, 1971, **5**, 247.
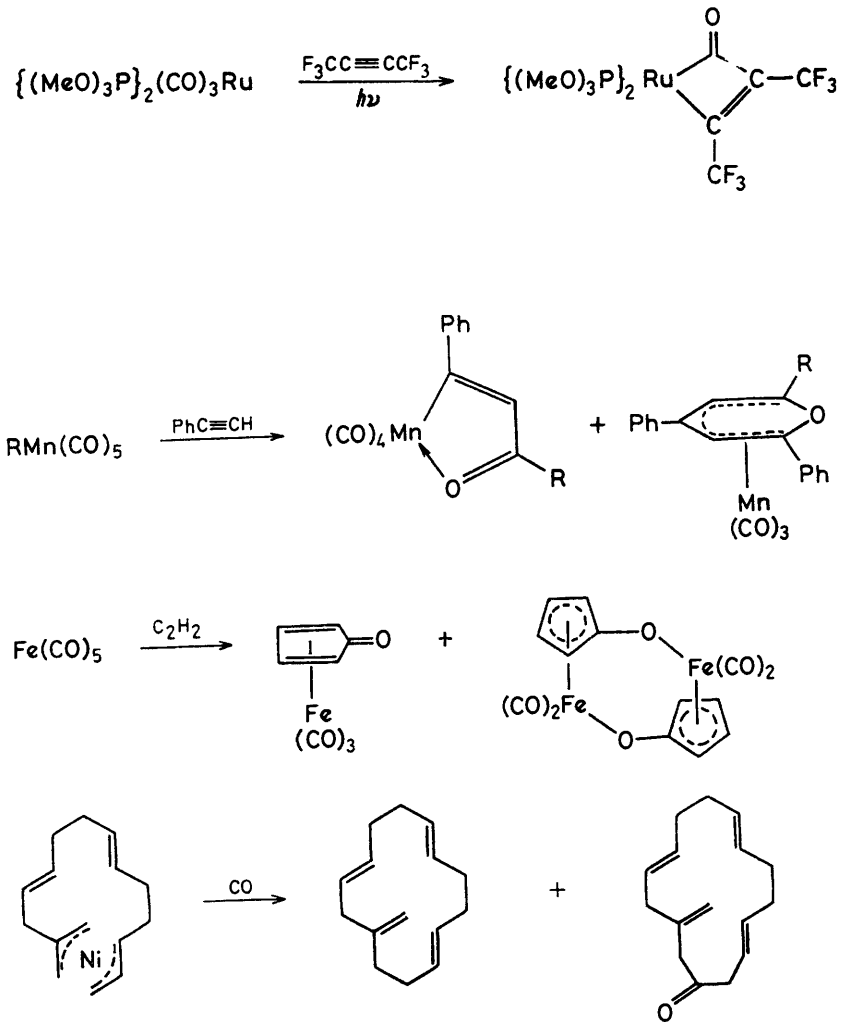
Scheme 9

group of (3) is correctly placed to accept charge from the d_{xy} orbital of the metal (labelling the initial Mn—CH$_3$ and Mn—$\overset{\bullet}{C}$O directions as x and y axes), thus reducing the barrier for the migration (3) → (4) [or (3) → (5) if methyl and entering carbonyl migration are synchronous]. Extreme valence-bond formulations of the process, such as (6) → (7), illustrate both the formal analogy between

$$
\begin{array}{ccc}
\begin{matrix} \overset{O}{\underset{\downarrow}{C}}\!* \\ (OC)_3Mn\!-\!Me \\ \uparrow \\ \underset{O}{C} \end{matrix} & \xrightarrow{\ CO\ } & \begin{matrix} \overset{O}{\underset{\downarrow}{C}}\!* \\ (OC)_3Mn\!-\!Me \\ \uparrow \\ \underset{O}{C}\!\nwarrow_{CO} \end{matrix} \\
(2) & & (3)
\end{array}
$$

(5) $O\!=\!\overset{*}{C}\!-\!Me$, $(OC)_3Mn\!\leftarrow\!CO$, C , O $\longleftarrow$ **(4)** $\overset{O}{*C}\!-\!Me$, $(OC)_3Mn$, $C\!\leftarrow\!CO$, O

Scheme 10

methyl (metal-to-ligand) migration and reductive elimination, and also that here
proposed between the concomitant reverse process, carbonyl (ligand-to-metal)
migration, and oxidative addition. Whether or not these detailed pathways are

$$
\begin{array}{ccc}
\begin{matrix} \overset{O}{\|} \\ \overset{C}{\underset{\|}{}}\!* \\ (OC)_3Mn\!-\!Me \\ | \\ C\!-\!C\!=\!O \\ \| \\ O \end{matrix} & \longrightarrow & \begin{matrix} \overset{O}{\|} \\ \overset{C}{\underset{\|}{}}\!*\!-\!Me \\ | \\ (OC)_3Mn\!=\!C\!=\!O \\ \| \\ C \\ \| \\ O \end{matrix} \\
(6) & & (7)
\end{array}
$$
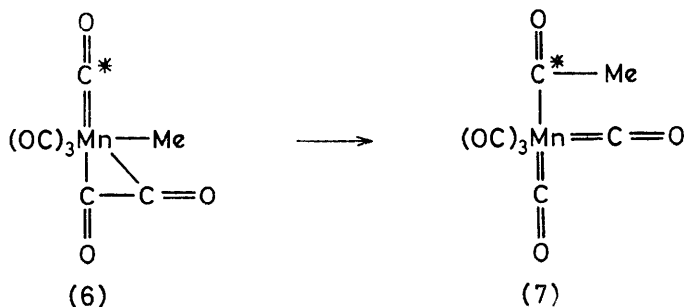
ultimately substantiated, it is already clear that such speculations can give a new
unity to organometallic chemistry, relating and combining both synthetic and
mechanistic aspects.