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A POSSIBLE MECHANISM FOR THE REACTIONS OF ELECTROPHILES WITH POLYNUCLEAR TRANSITION METAL CARBONYL AND RELATED COMPLEXES

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CONTENTS

A. INTRODUCTION

A common reaction of bi- and poly-nuclear metal carbonyl complexes is the two-electron oxidative cleavage of a metal–metal bond. It is the intention of this article to provide a mechanistic framework within which such

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reactions may be viewed. Although they may not always be correct in every detail, the proposed reaction pathways have accounted for the major and minor products of many of these reactions as well as for the effects of external variables. At the same time they are consistent, both internally and from one reaction to another.

These reactions are brought about by electrophilic reagents which may be regarded as oxidants, e.g. halogens, although this is not always the case, e.g. the halides of tin(II) or boron(III). Typically they give rise to a number of products whose relative yields are often dependent on factors such as the mole ratio of reactants and the reaction solvent. Furthermore, the products obtained from a particular metal carbonyl complex and a variety of electrophiles are usually similar and are often identical (i.e. are independent of the reagent). For example, $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ salts are important products from the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with $AgBF_4$ [1], $[Ph_3C]BF_4$ [2], and Cl_2 [3] in non-donor solvents such as CH_2Cl_2 or C_6H_6. This suggests that these reactions proceed via similar or, perhaps, identical intermediates.

Another characteristic reaction of polynuclear metal carbonyls containing μ-CO ligands is that with very strong Lewis acids such as $AlEt_3$ [4] or BF_3 [5]. Stable adducts are formed reversibly. In them the O atoms of the μ-CO ligands act as Lewis bases to give, for example $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CO \rightarrow AlEt_3\}_2]$ [4]. If one or two CO groups of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ are replaced by CNR ligands with their more basic N atoms, similar adducts having the general formulae $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CO)\{\mu\text{-}CN(R)E\}]$ (L = CO or CNR) may be isolated for a wide variety of even quite weak Lewis acids (or electrophiles) E including H^+ [6,7], Me^+ [8,9], $MeCO^+$ [10], $PhCO^+$ [10], MX_2 (M = Zn, Cd or Sn) [11], SnX_4 [11], AsX_3 [11], $AgNO_3$ [11] and $NiCl_2 \cdot 6H_2O$) [11] where X is generally a halogen. They possess N → E bonds, and spectroscopic data shows that all have structures (Fig. 1) similar to those determined by X-ray diffraction studies for $[cis\text{-}Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(Me)H\}][BF_4]$ [7] and $[cis\text{-}Fe_2(\eta\text{-}MeC_5H_4)_2(CO)_2(\mu\text{-}CO)[\mu\text{-}CNMe_2\}][BF_4]$ [8]. Although some of these adducts are quite stable, most decompose slowly to products which do not contain iron–iron bonds or bridging CO/CNR ligands [12]. These products are similar in

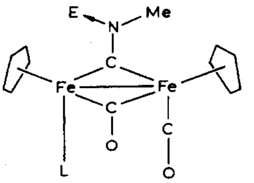


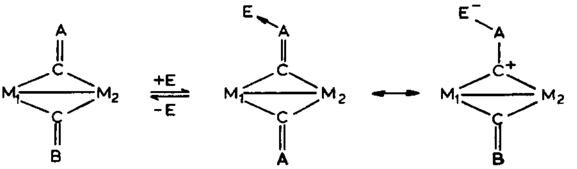
Fig. 1. Proposed structure of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CO)(\mu\text{-}CN(Me)E)]$ adducts (L = CO or CNMe). The corresponding *trans* isomer is also possible.

constitution and structure to those obtained from, for example, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and electrophilic oxidising agents. Furthermore, Lewis acids such as BF_3, CoI_2 and $CuCl_2 \cdot 2H_2O$) which would be expected to form adducts with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(L)(CNR)]$, instantly cleave them to mononuclear compounds [11,12].

These observations, when taken together, suggest that the cleavage and related reactions brought about by electrophiles, E, on transition metal complexes with μ-CO, μ-CNR, μ-CS or similar bridging ligands proceed via adducts containing μ-{CO → E}, μ-{CN(R) → E}, μ-{CS → E}, etc., groups. These may or may not be detected. On the basis of kinetic studies, Pöe and co-workers have suggested that interactions of this type take place during the initial stages of the reactions between halogens and a number of polynuclear metal carbonyl derivatives [13]. The envelope of relatively close-packed CO ligands [14] effectively shields the metal atoms and renders difficult direct attack on them. In the particular cases which are discussed here, the O, N, S, etc., atoms of the μ-ligands provide the most electron-rich sites on the periphery of the substrate molecules which are accessible to attack by electrophiles.

B. THE FORMATION AND BREAKDOWN OF ADDUCTS

A general equation (1) for reversible adduct formation is shown below. M_1 and M_2 are two metal atoms of the substrate joined by a metal–metal bond and two bridging ligands, CA and CB. The terminal ligands have been omitted for the sake of clarity.



(1)

The basic site of the substrate molecule which is attacked by the electrophile E is the atom A of the μ-ligand CA. The A → E bond of the adduct **A** lies in the M_1M_2CA plane but is not colinear with CA [4,8]. It is defined as being *cis* to the M_1–CA bond. **B** is a resonance form of **A** which is more convenient to use in subsequent discussions.

In many reactions these adducts break down, usually irreversibly, to products which may be accounted for if it is assumed that the electrophile is lost as E^{2-}. At the same time there is scission of one M–CA bond as shown below to give intermediates **C** or **D** which incorporate none (2), part (3), or all (4) of E^{2-} *. In (3) X^- is one fragment of E^{2-} and Y^- the other.

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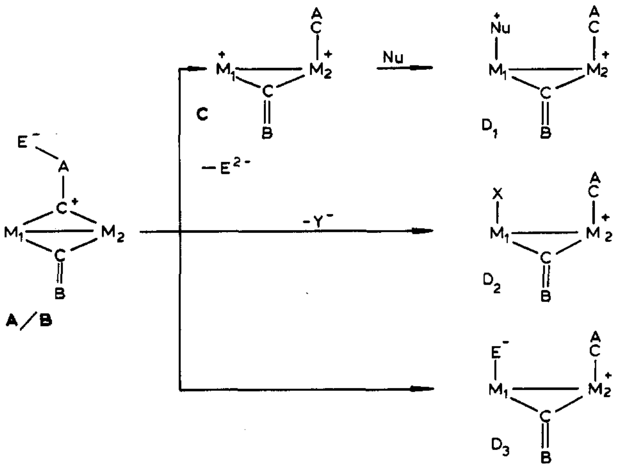
* Monobridged structures of the type proposed for intermediates $\mathbf{D}_1$, $\mathbf{D}_2$ and $\mathbf{D}_3$ have been observed for $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_3]$ [15], $[Os_2(CO)_9]$ [16], and $[FeCo(CO)_8]$ [17].



(2)

(3)

(4)

A number of conventions have been observed: (i) if either E^{2-} or X^- migrate from CA, they do so to the metal atom M_1 which is *cis* to the CA → E bond; (ii) the electron pair associated with the CA → E bond migrates with E as E^{2-}; (iii) the electron pair associated with the M_1–CA bond is retained by the ligand CA on cleavage of that bond; (iv) the M_x–CA bond which cleaves is *cis* to the CA → E bond, i.e., is to M_1, which facilitates the intramolecular migration of E^{2-} or X^- from A to M_1 in (3) and (4) whilst enabling the resultant intermediates $\mathbf{D}_2$ and $\mathbf{D}_3$ to obey the EAN (Effective Atomic Number) rule, and it is retained in (2) whilst not being strictly necessary. Pathways in which E remains bonded to CA will be mentioned in Section E.

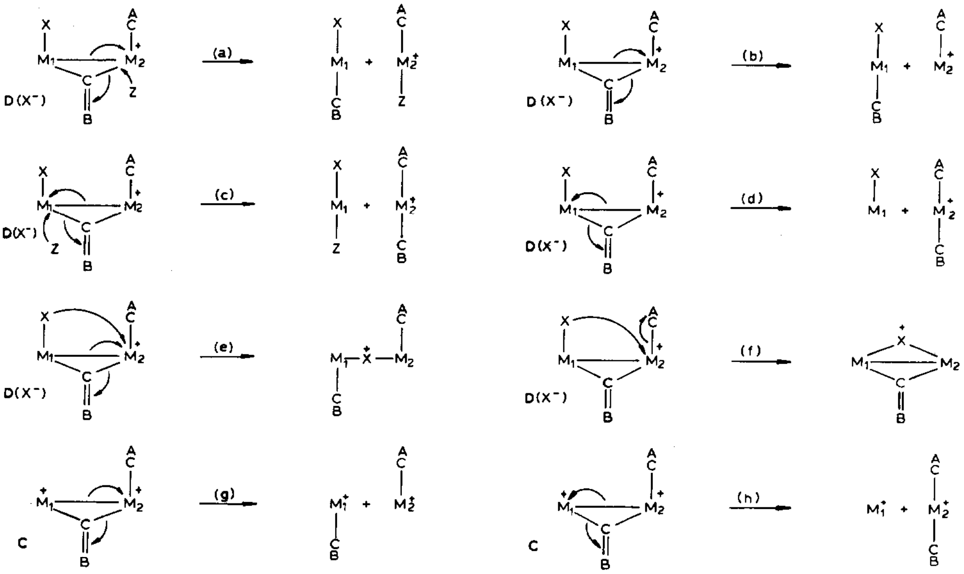
The total loss of E^{2-} via (2) gives an intermediate **C** in which M_1 is coordinatively unsaturated whilst formally positively charged. It would thus be a very powerful electrophile and very susceptible to attack at M_1 by a nucleophile Nu with formation of the intermediate $\mathbf{D}_1$. Nu may be a solvent molecule or a specially added nucleophile such as an anion, for example. It is possible that the overall reaction to give $\mathbf{D}_1$ may be initiated by attack of Nu at M_1 in the adduct.

The adduct breakdown pathway which is adopted will clearly be a function of the nature of E (or E^{2-}) and of the availability and efficacy of Nu. If E^{2-} is unable to form a bond with M_1 (as in pathway (4)) or give a fragment X^- which can migrate from A to M_1 (as in pathway (3)) then a reaction proceeding via **C** [pathway (2)] could become more important. This is most likely to happen if, for example, E^{2-} is extremely bulky and unable to form $\mathbf{D}_3$ or $\mathbf{D}_2$, or if E is a metal salt with non-coordinating anions which is reduced to the free metal during adduct breakdown. This would be possible in a non-coordinating reaction solvent, but a nucleophilic solvent would eliminate the possibility of subsequent reactions of **C** by converting it to $\mathbf{D}_1$ or by promoting the breakdown of **A/B** to $\mathbf{D}_1$ as discussed above. However such a solvent molecule may be associated with E during adduct formation and then the reaction to give $\mathbf{D}_1$ would be only a special case of pathway (3) with X^- = solvent molecule.

The intermediates $\mathbf{D}_1$–$\mathbf{D}_3$ are closely related species which differ only in the nature of the introduced ligands coordinated to M_1, and these are independent of the precise nature of E in $\mathbf{D}_1$ and $\mathbf{D}_2$. In subsequent discussions they will be referred to collectively as the intermediates **D** and if necessary the introduced ligand coordinated to M_1 will be shown e.g. **D**(Nu), **D**(X^-), **D**(E^{2-}), **D**(L), etc.

C. BREAKDOWN OF THE INTERMEDIATES C AND D

Reactions to give the final products or their obvious precursors are envisaged as taking place by one of six possible routes for **D**, (a)–(f), and two for **C**, (g) and (h). These are shown below for intermediate **D**(X^-).



Only (f) does not involve M_1–M_2 bond scission and is a consequence of internal nucleophilic attack by X on M_2 with displacement of CA or a related ligand. It results in replacement of one bridging ligand, CA, by another, X^+. Route (e) is related to it but results instead in M_1–M_2 and M_2–CB bond scission so that X^+ is inserted into the M_1–M_2 bond. To bring about either (e) or (f), X would have to possess a suitable lone pair of electrons. Routes (a) and (c) are a consequence of attack by an external nucleophile Z on M_2 and M_1 respectively. (b) and (d) are related to these but are intramolecular and spontaneous; (g) and (h) are the analogous reactions of **C**. These must be intramolecular as nucleophilic attack on **C** would first give **D**.

In the reactions summarised in routes (a)–(h) two conventions have been adhered to. One is related to (iii) in Section B in that it is assumed that the μ-ligand (here it is CB) retains the electron pair associated with the M_x–C bond on cleavage of that bond. Another convention (v) is a consequence of (iii) and states that at the same time M_x retains the electron pair associated with the M_1–M_2 bond on its cleavage ($x = 1$ or 2). Where applicable (routes (a), (c) and (e)) M_x is the metal atom in **D** which undergoes nucleophilic attack. As a desired result of these constraints, the products of routes (a), (c) and (e) obey the EAN rule whilst some of those from (b), (d), (g) and (h) are coordinatively unsaturated 16- or 14-electron species. None have odd numbers of electrons.

The nucleophile Z may be the fragment Y^- arising from E during reaction (3), the ligands CA, CB, etc., released into the reaction mixture on the decomposition of the more unstable products of routes (a)–(h) (see below), or the same as Nu (Section B), i.e., a solvent molecule or added reagent. However, it should be noted that although a nucleophile may be effective as Nu in the **A**/**B** → $\mathbf{D}_1$ reaction, it need not be effective as Z in the context of routes (a) and (c).

Many of the "final" products of routes (a)–(h) may undergo further reactions. It is unlikely that the coordinatively unsaturated $[M{-}Nu]^+$, $[M{-}CA]^+$, $[M{-}CB]^+$ and $[M]^+$ would be stable, but they may react with the solvent rather than simply decomposing with the release of Nu, CA, CB and other ligands into the reaction mixture, e.g., in C_6H_6 solution such species derived from $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ could give $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$ salts. Even coordinatively saturated products containing Nu or Z may have these replaced slowly by other stronger ligands, whilst species containing both of these are unlikely to be detected.

The route by which a particular intermediate **C** or **D** decomposes to the "final" products depends upon many factors including the availability and efficacy of external or internal nucleophiles Z or X, the metal atoms M_1 and M_2 and, very importantly, the steric and electronic effects of the other ligands coordinated to them, including X. However, a number of general points may be made. If suitable nucleophiles are absent from the reaction mixture, e.g., if the electrophile is a metal salt with non-coordinating anions in non-coordinating solvent, then the overall reaction could proceed via **C** and routes (g) or (h). Although one may feel that of these two alternatives (h) would be favoured because it gives an 18-electron species as one product, there is no unequivocal evidence to support this. Moreover, as mentioned in

Section B, such a situation may never arise as the electrophilicity of **C** may be so great that even very poor ligands would coordinate to M_1 to give **D**.

If Z is an effective nucleophile for a reaction proceeding via **D**, then routes (a) or (c) will be favoured. Which route depends on other factors. For example, a reduction in the electron-donor capability of X^- or an increase in the electronegativity of X will increase the $M(\delta+)$–$X(\delta-)$ polarity as shown, e.g., along the series $X = I < Br < Cl$. This will increase the probability of nucleophilic attack by Z on M_1 rather than M_2 and hence of a reaction proceeding via (c) rather than (a). Predictable consequences would also result if attack on one metal atom were hindered sterically by other ligands coordinated to it.

On the other hand if Z is not an effective nucleophile (b), (d), (e) and (f) will become increasingly important. Although the validity, if any, of the "spontaneous" routes (b) and (d) is difficult to assess it is clear that **D** can only break down via (e) or (f) if suitable electron pairs are available on X to enable it to act as a nucleophile. Furthermore severe steric constraints are imposed in (f) and it is probable that this would only be observed in favoured instances.

Other possible modes of breakdown of **D** have not been considered here. The most conspicuous omissions are those which involve attack on a ligand coordinated to M_2 (including CA) by an external or internal nucleophile Z or X respectively. They will be mentioned later.

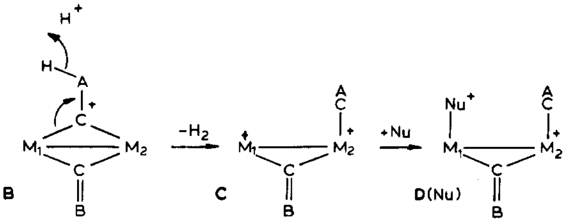
D. SPECIFIC EXAMPLES

The ideas outlined in Sections A–C will be applied to specific reactions.

(i) Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ *with anhydrous strong acids*

Although adducts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (**I**) with anhydrous strong acids (**A**/**B** with CA = CB = CO and $E = H^+$) have not been detected, the observed reactions are consistent with their formation. The sole, detectable initial products with anhydrous HCl [18] or H_2SO_4 [19], etc., are $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}H)]^+[Y]^-$ salts (**II**) of the type $[(BC)M_1\text{–}X\text{–}M_2(CA)]^+$ formed exclusively via **D**(H^-) and route (e). In this particular case the reactions are reversible so that the products are in equilibrium with the reagents and revert to them on the addition of water.

On standing in the presence of the anhydrous acids, $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}H)]^+$ salts of non-coordinating anions decompose by unsymmetrical cleavage to $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ salts. These are also formed in the absence of the acids together with approximately comparable amounts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [18]. This is entirely explicable. The adduct not only undergoes the fast, reversible insertion of H^+ into the Fe–Fe bond as discussed above, it also reacts irreversibly with excess protons which are present in the acid. This would give **C** if the acid anions cannot coordinate, or **D** if the anions can coordinate as Nu, albeit very weakly (5).



(5)

The intermediates then break down; **C** via (h), and **D**(Nu) via (d) or (c) with the acid anion as Z. This reaction is one of the few where it is reasonable to propose the formation of **C** or the decomposition of **D** via the "spontaneous" routes (c) or (d), and where the alternatives are not immediately more attractive.

In the absence of free acid, the extra protons for the cleavage of (**I**) must arise from (**II**) through the dissociation of the adduct **A**/**B** with the release of one mole of free (**I**) per mole of $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ formed.

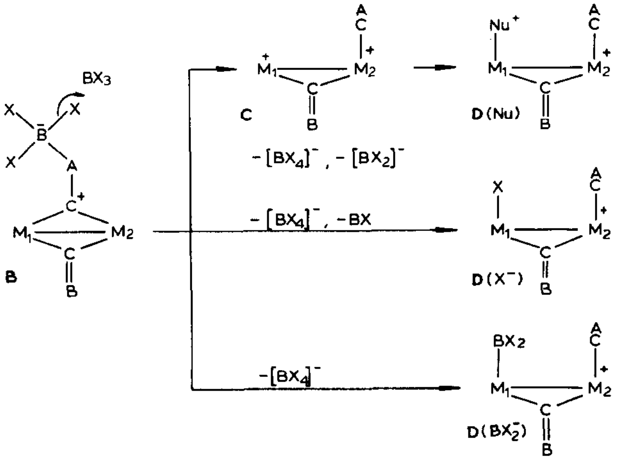
In this reaction the protons are acting as oxidising agents and free H_2 should be liberated under anaerobic conditions. This does not happen in the presence of more conventional oxidising agents such as O_2 [Section D (vii)]. The fate of the other products from routes (c), (d) or (h) is not known, but one presumes that they decompose with liberation of free CO which should also be detectable.

This scheme is also applicable to the reactions of the related $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{P(OMe)_3\}]$ [20], $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(Ph_2PCH_2CH_2PPh_2)]$ [21] and $[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [20] complexes with strong acids. All give products of type (**II**) with H^+ insertion into the metal–metal bonds, but their subsequent reactions have not been investigated.

The $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ complexes ($n = 1$ or 2) with their more basic N atoms react rapidly and reversibly with mineral acids to give isolable adducts of the type **A**/**B** (CA = CNMe and E = H^+). These are very stable and it is, perhaps, for this reason that they do not undergo any rapid, subsequent reactions. They decompose only slowly in solution when the counter ion is a poor nucleophile such as $[BF_4]^-$ or $[PF_6]^-$, but somewhat more rapidly when it is $[Cl]^-$ or $[I]^-$ [7]. However this breakdown reaction has not, as yet, been investigated in detail.

(ii) *Reactions of* $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ *(n = 0–2) with trihalides of boron and aluminium*

There are three ways in which the adducts **A/B** of these very powerful, non-protic Lewis acids may break down to the intermediates **C** or **D**. These are shown below for BX_3. The reactions may be BX_3-assisted, as shown, or they may not, in which case $[BX_4]^-$ should be replaced by X^-.



(6)

(7)

(8)

In (6) there is loss of $[BX_2]^-$ and $[BX_4]^-$ from **A/B** to give **C** which forms **D**(Nu) with an external nucleophile; in (7) there is migration of a halide ion from boron to M_1; and in (8) there is migration of $[BX_2]^-$ from A to M_1.

All intermediates **C** and **D** may undergo further reactions by routes (a)–(h) as outlined above, except that from (8). **D**(BX_2^-) is a derivative of boron(III). Therefore subsequent nucleophilic attack could be at boron, and also $[BX_2]^-$ is unlikely to act as an internal nucleophile in (e) or (f).

Unlike most other electrophiles, BX_3 and AlX_3 reversibly form isolable adducts with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$. That of BCl_3 decomposes to $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ (and other unidentified products) [5]. A possible course of this reaction would be via **D**(Cl^-) and the "spontaneous" route (b), but there are other alternatives.

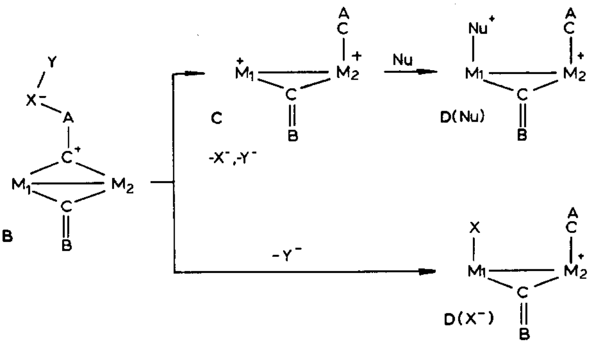
Surprisingly, adducts were not detected in the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ with $[BF_3 \cdot OEt_2]$. Instead, rapid cleavage gave $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$ [11]. This could come from an adduct of the type shown in Fig. 1, where $M_1 = Fe(\eta\text{-}C_5H_5)(CO)$, $M_2 = Fe(\eta\text{-}C_5H_5)(CNMe)$, CA = CNMe with its more basic N atom, and CB = CO. This may break down either via a BF_3-assisted reaction to **C** and then route (h) or via **D**(OEt_2) and then (d) or (c) ($Z = OEt_2$). Alternatively the adduct could have $M_1 = M_2 = Fe(\eta\text{-}C_5H_5)(CO)$ and CA = CB = CNMe (cf. $[Fe_2(\eta$-

$C_5H_5)_2(CO)_2\{\mu\text{-}CN(Me)H\}_2]^{2+}$ [7]). This could break down via **C** and (h) or **D**(OEt_2) and (d) or (c) ($Z = OEt_2$).

The adduct which could be detected in the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$ with $[BF_3 \cdot OEt_2]$ in ether at −25°C had $M_1 = Fe(\eta\text{-}C_5H_5)(CNMe)$, $M_2 = Fe(\eta\text{-}C_5H_5)(CO)$, and CA = CB = CNMe. It decomposed at 25°C to give $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$ [11]. This may have taken place via **C** and (h), **D**(OEt_2) and (c) ($Z = OEt_2$) or **D**(OEt_2) and (d). As the reaction was carried out in ether, the **D**/(c) route is the most probable.

(iii) Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$ *(L = CO,* PEt_3 *or* $P(OPh)_3$ *with halogens*

For a mixed halogen molecule of polarity X(δ +)–Y(δ −), it is X which would coordinate to CA to give the adduct. Steric interactions would orientate the coordinated halogen so that the X–Y bond points away from the substrate molecule and, more specifically, M_1. There is an alternative possibility, which is not illustrated, where loss of Y^- accompanies formation of the adduct rather than its subsequent reactions. These are shown below and involve loss of both X^- and Y^- to give **C** and then **D**(Nu) (9) as a consequence of subsequent attack by Nu, or loss of Y^- and migration of X^- from CA to M_1 giving **D**(X^-) (10).



(9)

(10)

Although **D** could be formed in pathway (10) by migration of the β-atom Y from CA to M_1, the steric effects mentioned above would tend to preclude it. Furthermore, the experimental evidence cited below indicates that the less electronegative halogen X is always involved in attack on M_1.

The intermediates **C** and **D** may react further by routes (a)–(h) as described in Section C.

Experiments have shown that the sole products of the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with IY (Y = Cl, Br or I) in benzene solution are the iodo-bridged cations $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}I)]^+$ which may undergo subsequent reactions [3]. Adducts **A/B** [$M_1 = M_2 = Fe(\eta\text{-}C_5H_5)(CO)$; CA = CB = CO] were not observed *, but it is suggested that the reactions take place through them, **D**(I^-) and then route (e) without the formation of **C**. On the other hand, in benzene solution Br_2 and Cl_2 also give increasing amounts of [$Fe(\eta\text{-}C_5H_5)(CO)_2X$] and the [$Fe(\eta\text{-}C_5H_5)(CO)_3$]$^+$ cation [3]. ** [$Fe(\eta\text{-}C_5H_5)(CO)_2X$] alone could be formed from [$\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}X)$]$^+$ on reaction with X^- [3], [$Fe(\eta\text{-}C_5H_5)(CO)_3$]$^+$ alone from **C**, and both of them from **D**(X^-). Routes involving **D**(Nu) need not be considered. As the reaction solvent was benzene the only nucleophile available to act as Nu in **C** → **D**(Nu) would be X^- and this would tend to be constrained with **C** in a solvent cage. Under such circumstances **D**(Nu) and **D**(X^-) are identical and differ only in their modes of formation. Furthermore, the constraints imposed by the solvent cage are likely to inhibit the formation of **C** even when $X^- = Cl^-$ and it is most unlikely to be formed. Consequently it seems probable that all three products are formed largely, if not entirely, by reactions which proceed through **D**(X^-) and routes (a)–(e). The solvent cage and ion pair formation effects may also inhibit the "spontaneous" routes (b) and (d) so that (a), (c) and (e) are likely to be the most important. However, the available data are not sufficient to allow an unequivocal decision.

Unlike mechanisms which invoke direct attact by the halogen on the metal atoms [3], the above offers a plausible and convincing explanation for unsymmetrical dimer cleavage to [$Fe(\eta\text{-}C_5H_5)(CO)_3$]$^+$ within the context of symmetrical cleavage to [$Fe(\eta\text{-}C_5H_5)(CO)_2X$] and X^+ insertion into the metal–metal bond. Furthermore it is able to account for the increasing importance of unsymmetrical cleavage along the series $XY = I_2 < Br_2 < Cl_2$. As the electronegativity of the halogen, X, increases, so too would the bond polarity M_1 ($\delta +$)–X($\delta -$) in **D**(X^-), the susceptibility of M_1 to nucleophilic attack by Z (route (c)) and hence the tendency towards unsymmetrical cleavage. These observations and conclusions also favour the **A/B** → **D**(X^-) over the **A/B** → **C** reaction.

Although the reaction of [$Fe_2(\eta\text{-}C_5H_5)_2(CO)_4$] with halogens appears to be solvent dependent, the published data are not clear. This is not the case for the reaction of [$Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(L)$] (L = Et_3P or $(PhO)_3P$) with iodine. Three products are obtained, [$Fe(\eta\text{-}C_5H_5)(CO)_2I$], [$Fe(\eta\text{-}C_5H_5(CO)(L)I$] and [$Fe(\eta\text{-}C_5H_5)(CO)_2(L)$]$^+$[I]$^-$. In dichloromethane solution they are formed in approximately equal amounts, but in toluene the last

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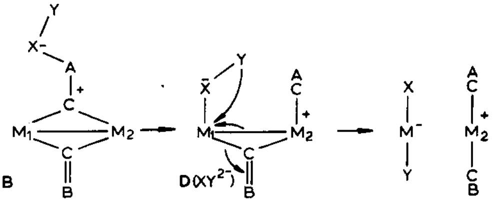
* An adduct of this type has been obtained, [$Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CSI)$]I [12].

** [$\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}Br)$]$^+$ has been isolated from these reactions in benzene, but it is not clear if [$\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}Cl)$]$^+$ is formed even though it has been isolated as its very unstable [BPh_4]$^-$ salt when a benzene–methanol–carbon tetrachloride mixture is used as the reaction solvent.

predominates and the others are obtained in trace amounts only [22]. There is no evidence for the formation of products of the type $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(L)(\mu\text{-}I)]^+$ which are overwhelmingly important when L = CO.

Steric arguments suggest that in the adduct **A/B** the CA → I bond would point away from the metal atoms containing the more bulky substituents so that $M_1 = Fe(\eta\text{-}C_5H_5)(CO)$, $M_2 = Fe(\eta\text{-}C_5H_5)(L)$ and CA = CB = CO. Fortunately this is the only adduct configuration which would allow the formation of $[Fe(\eta\text{-}C_5H_5)(CO)_2(L)]^+$. For the reasons discussed above **A/B** would be expected to break down to the intermediate $\mathbf{D}(I^-)$ rather than **C**, and from there via (a) and (c) to the final products. In both solvent systems attack at M_2 by internal or external nucleophiles (routes (e) or (a)) is very much less important and attack at M_2 is much more important than when L = CO. Possibly this is due to the combination of steric effects with the greater bulk of $L = (PhO)_3P$ or Et_3P inhibiting attack at M_2, and electronic effects. These phosphorus (III) ligands are relatively powerful σ-donors as compared with CO. This would tend to reduce both the effective positive charge on M_2 and its susceptibility to nucleophilic attack. Consequently attack on M_1 (route (c)) would become a relatively more attractive reaction pathway. The solvent effect is much more difficult to rationalise. It is possible that in toluene solution the solvent cage and the tendency towards tight ion-pair formation would restrict the mobility of I^- which is formed together with $\mathbf{D}(I^-)$ and, in the absence of other nucleophiles, encourage it to attack M_1 in $\mathbf{D}(I^-)$. However, an alternative possibility is that owing to the nature of the solvent the adduct **A/B** may not break down to $\mathbf{D}(X^-)$ with loss of Y^- (pathway (10)), but instead the molecule $XY(=I_2)$ would migrate intact together with two electrons from CA to M_1 to give $\mathbf{D}(XY^{2-})$ (eqn. (11)).



(11)

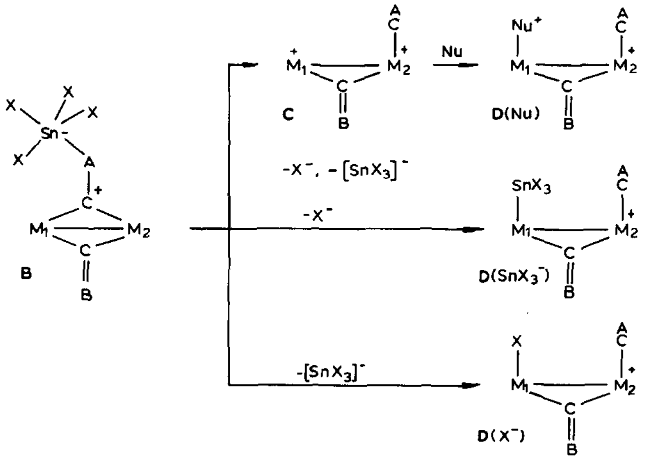
It is easy to see how this could decompose almost exclusively to $[Fe(\eta\text{-}C_5H_5)(CO)_2(L)]^+$ via route (d) which is an intramolecular rearrangement reaction in this case.

On the other hand, in dichloromethane the formation of $\mathbf{D}(X^-)$ and Y^-, and the mobility of Y^- would be encouraged. Consequently Y^- attack on either M_1 or M_2 would be possible and controlled by the factors discussed above.

(iv) Reactions of [$Fe_2(\eta$-$C_5H_5)_2(CO)_4$] and other binuclear metal carbonyl complexes with haloderivatives of tin(IV)

These reactions are superficially similar to the halogenations discussed earlier. The reagents include not only the tetrahalides of tin, SnX_4, but also $RSnX_3$, R_2SnX_2, and R_3SnX derivatives where R is an organo or transition metal based radical such as Me, Ph, $Fe(\eta$-$C_5H_5)(CO)_2$ or $Co(CO)_3(PBu_3)$ (Bu = n-butyl). The reaction schemes may also be extended to include related derivatives of the other group IV elements.

The adducts **A**/**B** in which the tin atom is the electrophilic centre may break down to give **C** (and hence **D**(Nu)) (12), **D**(SnX_3^-) (13), or **D**(X^-) (14) as shown in routes (12)–(14) below. X^- and SnX_3^- may act subsequently as Nu or Z.



(12)

(13)

(14)

As there is pentacoordination about Sn in **A**/**B**, it is unlikely that steric effects would discourage selectively the close approach of M_1 and the atom X which is β to CA as they may do in halogenation reactions. There is a possibility that adduct formation would be accompanied by loss of X^- from SnX_4. As this does not differ in its effects from (12) and (13), it will not be considered separately.

The four intermediates may undergo further reactions via routes (a)–(h). However (e) and (f) of **D**(SnX_3^-), which involve internal nucleophilic attack by tin in its 4+ oxidation state on M_2, are unlikely and will not be considered. Also it is possible that $[SnX_3]^-$, which may act as the nucleophile Z in these subsequent reactions, is unstable and could decompose to SnX_2 and X^-, the effective Z.

Although adducts have not been detected in the reactions of [$Fe_2(\eta$-$C_5H_5)_2(CO)_4$] [23] or [$Co_2(CO)_6(PBu_3)_2$] [24a] with tin(IV) halides they have been obtained from [$Fe_2(\eta$-$C_5H_5)_2(CO)_{4-n}(CNMe)_n$] ($n$ = 1–3) with their intrinsically more basic nitrogen atoms [11,12]. However they are probably intermediates in the reactions of SnX_4 with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (mole ratio 1 : 1; X = Cl, Br, or I) which give equimolar amounts of $[Fe(\eta\text{-}C_5H_5)(CO)_2SnX_3]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ in high yields [23]. The obvious reaction pathways from **A**/**B** are via **D**(X^-) and route (a) with Z = $[SnX_3]^-$ or **D**(SnX_3^-) and (a) with Z = X^-. It is not possible to rule out unequivocally the route via **D**(X^-) and (e), but there is no evidence for the formation of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}X)][SnX_3]$ [23], which might be expected to be quite stable when X = I.

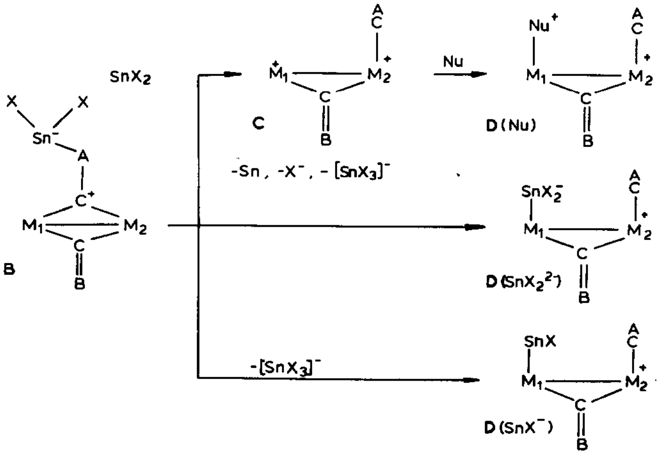
A related reaction is the second step of the "indirect"reaction of SnX_2 with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [23]. The $[Fe(\eta\text{-}C_5H_5)(CO)_2SnX_3]$ formed in the first step (see below) acts as the Sn(IV) electrophile which is less reactive than SnX_4. Perhaps replacement of a halogen radical, X, by a more bulky and poorer electron-withdrawing metal-based radical R makes $RSnX_3$ a less effective Lewis acid and/or $[RSnX_2]^-$ a poorer leaving group. Similar arguments apply when R is an organic radical and to a greater extent to R_2SnX_2 and R_3SnX. However this diminished reactivity has its advantages as reactions often become easier to study and the consequences of changes in reaction conditions are often accentuated. For example, whereas the reaction of $[Co_2(CO)_8]$ with $SnCl_4$ is rapid in either benzene or tetrahydrofuran solution, that with $[Fe(\eta\text{-}C_5H_5)(CO)_2SnCl_3]$ is complete in 10 min. in tetrahydrofuran but requires about 3 days in benzene [24a]. This is clearly consistent with the proposed mechanisms as the formation of ionic intermediates would be favoured by polar as opposed to non-polar solvents. As $[Co_2(CO)_8]$ does not react extensively with tetrahydrofuran during the 10 min. reaction time at room temperature, it is possible to rule out a metathetical pathway involving formation of $[Co(CO)_4]^-$ and its displacement of Cl^-.

In the preceding examples it is not possible to determine unambiguously whether the reactions proceed via **D**(X^-) or **D**(SnX_3^-). However some evidence is available from the reaction of $[Co_2(CO)_6(PBu_3)_2]$ with $SnCl_2$ (mole ratio 3 : 1) in refluxing ethanol. Its final products are a mixture of $[\{Co(CO)_3(PBu_3)\}_4Sn]$ and $[\{Co(CO)_3(PBu_3)\}_3SnH]$ [24a]. It proceeds via the tin(IV) Lewis acid $[\{Co(CO)_3(PBu_3)\}_2SnCl_2]$, formed by $SnCl_2$ insertion into the Co–Co bond (see next reaction), which with $[Co_2(CO)_6(PBu_3)_2]$ reacts via **D**(X^-) and (a) Z = $[SnX_3]^-$ or **D**(SnX_3^-) and (a) Z = X^- to give $[\{Co(CO)_3(PBu_3)\}_3SnCl]$. The reaction of this last with more $[Co_2(CO)_6(PBu_3)_2]$ probably proceeds at least in part via **D**(X^-) as the most obvious source of $[\{Co(CO)_3(PBu_3)\}_3SnH]$ is the leaving group $[\{Co(CO)_3\}_3Sn]^-$ ($[SnX_3]^-$ in (14)) which abstracts a proton from the solvent, ethanol. $[\{Co(CO)_3(PBu_3)\}_4Sn]$ may be formed via **D**(X^-) and route (a) with any surviving $[\{Co(CO)_3PBu_3\}_3Sn]^-$ acting as the nucleophile Z, or via **D**(SnX_3^-) and (a) with Z = Cl^-. It seems reasonable to suppose that as *n* increases for the $[R_nSnX_{3-n}]^-$ ion, reaction pathway (14) to **D**(X^-) which involves its formation would decline in importance with respect to pathway (13) where a free halide ion X^- is formed. Therefore, as pathway (14) is important in a case where $n = 3$, it is probable that it is always important. Further evidence for this proposal is available from the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ with $SnBr_4$ which proceeds via isolable adducts **A**/**B** ($M_1 = M_2 = Fe(\eta\text{-}C_5H_5)(CO)$; CA = CNMe and CB = CO) to give high yields of $[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnBr_3]$ but no $[Fe(\eta\text{-}C_5H_5)(CO)_2SnBr_3]$ or $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Br]$ [12]. It is a general feature of the mechanism that the group which migrates from either CA or E to M_1 during breakdown of the adduct cannot end up coordinated to the same metal atom as CA either in the intermediates **D** or in the final products except those formed via (e) and (f). Consequently the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3CNMe]/SnBr_4$ reaction can only proceed via **D**(X^-) with the leaving group $[SnX_3]^-$, which subsequently acts as Z.

(v) Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and other binuclear metal carbonyl complexes with tin(II) halides

These are extremely complicated and yield a wide variety of products which may be derivatives of tin(II) or tin(IV), or contain no tin at all. The course of the reactions is affected by the presence of impurities which are potential ligands to tin(II) and by the nature of X in SnX_2.

In those circumstances where the substrate is the only ligand to SnX_2 in the adduct **A**/**B** there will be pyramidal coordination about the tin atom. As a consequence of steric effects the Sn–X bonds would tend to point away from M_1–M_2 so that X · · · M_1 interactions would be unlikely. The adduct may break down (15) to **C** (and perhaps **D**(Nu)) with loss of Sn metal and



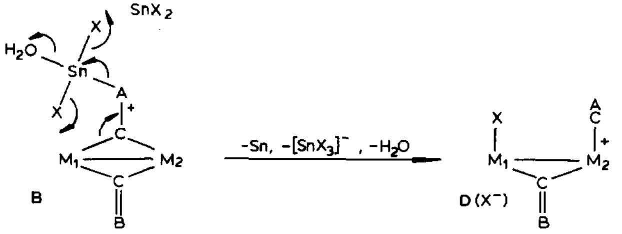
(15)

(16)

(17)

two X^- ligands if the reaction is not assisted by SnX_2 acting as a Lewis acid-halide ion abstractor and to Sn, X^- and SnX_3^- if it does (here and elsewhere the SnX_2-assisted reactions are illustrated); (16) with migration of SnX_2^{2-} from CA to M_1; or (17), as (16) but with loss of X^-, perhaps with SnX_2 assistance, so that SnX^- migrates from CA to M_1.

There is the possibility that the tin atom could take up a fourth ligand such as H_2O in the adduct so that the adduct may break down by a fourth pathway (18), as well as (15)–(17). In this there is migration of X from Sn to M_1 with the formation of **D**(X^-), X^- or $[SnX_3]^-$ ions, and tin metal.



(18)

The five intermediates **C** and **D** may undergo further reactions via routes (a)–(h) including those which involve internal nucleophilic attack, (e) and (f). The external nucleophiles Nu or Z may be X^-, $[SnX_3]^-$ or a solvent molecule.

As might be expected there have been no reports of adducts of tin(II) halides with metal carbonyls although they have been detected or isolated with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ when $n = 1$, 2, and 3. In all of them CA = CNMe [11]. However the products from the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with tin(II) halides [23] may be rationalised on the basis of adduct formation and breakdown. Thus both SnF_2 and $SnCl_2$ (mole ratio 1 : 1) gave only $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SnX_2]$ (the "direct" reaction product in ref. 23) which must have been formed via **D**(SnX_2^{2-}) and (e). Increasing the amounts of SnX_2 in the reaction mixtures has no effect when X = F, but when X = Cl increasing amounts of $[Fe(\eta\text{-}C_5H_5)(CO)_2SnCl_3]$ are formed. This is a clear indication that reactions are taking place via $SnCl_2$-assisted routes. The most likely is (18) to **D**(X^-) and then (a) with Z = $[SnX_3]^-$ but it is not possible to rule out **B** → **C** → **D**(Nu) and route (a) where Nu and/or Z may be the ions X^- or $[SnX_3]^-$ produced in (15) or they may be solvent molecules which are subsequently replaced. Any $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ would be converted rapidly to $[Fe(\eta\text{-}C_5H_5)(CO)_2SnCl_3]$ under the conditions of the reaction [25]. Similar sequences must be much more important in the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]/SnBr_2$ reaction (mole ratio 1 : 1) where no $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SnBr_2]$ is observed and there is rapid conversion of half of the dimer to an equimolar mixture of $[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2SnBr_3]$. If the reactant mole ratio is increased to 1 : 2, dimer scission is complete [23]. It has been suggested that this reaction is catalysed by traces of water [26], and in its absence does not take place. This is consistent with a reaction pathway such as (18) proceeding from an adduct with a four-coordinate tin atom **B′** via **D**(X^-) and route (a) with $Z = SnX_3^-$. In the absence of a water catalyst the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]/SnBr_2$ reaction is slow to give $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SnBr_2]$ only (**D**(SnX_2^{2-}) and (e)). The increased rate of the dimer scission reaction via **B′** and **D**(X^-) may be a consequence of the increased steric crowding about tin which would increase with increasing size of $X = F < Cl < Br$. At the same time the decreasing electronegativity of X along the same series would tend to destabilise **D**(SnX_2^{2-}) and hence render less favourable (and slower) reactions which proceed through it, i.e. the formation of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SnX_2]$.

In tetrahydrofuran or methanol solvents, the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]/SnI_2$ reaction (mole ratio 1 : 1) is similar to that of $SnBr_2$. On the other hand in benzene solution, scission is unimportant with respect to insertion and the only product is $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SnI_2]$ even when large amounts of SnI_2 are used [23]. Clearly the non-polar solvent increases the importance of the internal reaction via **D**(SnI_2^{2-}) and (e) whilst supressing those via **C** and **D**(I^-) which involve loss of $[SnI_3]^-$ or I^-. The differences in behaviour between SnI_2 and $SnBr_2$ may be a consequence of the former being a weaker Lewis acid and therefore less effective in promoting X^- loss as $[SnX_3]^-$ under relatively unfavourable conditions.

Only a few of the various possible routes appear to be utilised to any great extent in the reactions of SnX_2 (X = halogen) with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$. * In other systems, the reactions proceed via other routes. For example, $[Co_2(CO)_6(PBu_3)_2]$ reacts with tin(II) halides in much the same ways as does $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ so that $[\{Co(CO)_3(PBu_3)\}_2SnX_2]$ are the only products when X = F, Cl, or Br (formed via **D**(SnX_2^{2-}) and (e)), whilst SnI_2 in tetrahydrofuran also gives $[Co(CO)_3(PBu_3)SnI_3]$ via **D**(X^-) [24a]. On the other hand, one product of the $[Co_2(CO)_8]/SnX_2$ reaction is $[Co_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SnX_2)]$ when X = 4-phenylbutane-2,4-dionate, and "$[Co(CO)_4SnX]$" when X = pentane-2,4-dionate [24b]. The first may be formed via **D**(SnX_2^{2-}) and (f), and the second via **D**(SnX^-) and (a).

(vi) Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with haloderivatives of arsenic(III), antimony(III) or bismuth(III)

In the equations for adduct breakdown, (19)–(22), Lewis acids of the type MX_3 are used. However, it would be equally valid if they were replaced by

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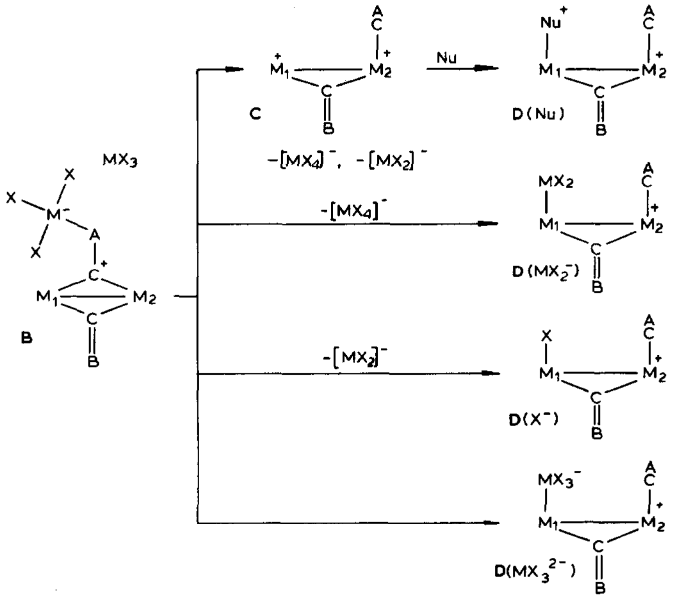
* It is possible that other pathways are employed and although they are not important they may give rise to small amounts of other products such as $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ or $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}X)]^+$ which have not yet been detected.

RMX_2 and R_2MX derivatives ($M = As$, Sb, or Bi; $X = F$, Cl, Br, or I; R = an organo or transition metal radical).

Detectable adducts **A/B** are formed with these reagents by $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ but not by $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [11]. However their formation as a transient intermediate is postulated. Such adducts may break down to four different intermediates in reactions which MX_3 may, or may not, assist by promoting the loss of X^- from the adduct as $[MX_4]^-$. The efficacy of MX_3 as a Lewis acid will determine which of these two courses is adopted, but eqs. (19)–(22) illustrate the MX_3-assisted alternatives where appropriate.



(19)

(20)

(21)

(22)

In (19) **C** and thence **D**(Nu) are formed from **A/B** by loss of X^- and $[MX_2]^-$ (perhaps as MX and X^-); in (20) X^- is lost from M (perhaps during adduct formation) and $[MX_2]^-$ migrates from CA to M_1; in (21) $[MX_2]^-$ (or MX and X^-) is lost whilst X^- migrates from CA to M_1; and in (22) $[MX_3]^{2-}$ migrates from CA to M_1. The third is possible because steric effects do not inhibit the approach of M_1 and X (cf. the $SnX_2/[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ reaction). The formation of derivatives of M(I) such as free MX or $[MX_2]^-$ seems to be inherently unlikely. Hence the reactions of which they are products, (19) and (21), are probably not going to be important.

The intermediates **C** and **D** may break down via routes (a)–(h) to the final products.

SbX_3 and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ ($X = Cl$, Br, or I; mole ratio 1 : 1) react in benzene solution giving $[Fe(\eta\text{-}C_5H_5)(CO)_2SbX_2]$ and $[Fe(\eta\text{-}$

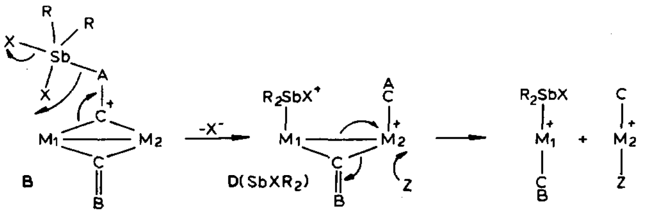
$C_5H_5)(CO)_2X]$ [27]. The most obvious course for such a reaction is via the non-SbX_3-assisted formation of **D**(SbX_2^-). One cannot rule out **C** (from reaction (19)) or **D**(X^-) (from reaction (21)) as intermediates except as a consequence of prejudice against the formation of free $[SbX_2]^-$ or SbX and their subsequent activity as nucleophiles. The further reactions of **D**(SbX_2^-) would be expected to be solvent dependent. In benzene solution it would probably remain as a reasonably tight ion-pair with X^- which would rapidly attack it via route (a) $Z = X^-$. However there is no evidence to rule out a route from **D**(SbX_2^-) via (e) followed by nucleophilic attack of X^- on the $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SbX_2]^+$ thus formed except that one would expect such a salt to be observable (see below).

If the above reactions are carried out in tetrahydrofuran (mole ratio 2 : 1) [27], the products are $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ and $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SbX]$. The most probable pathway has two separate stages each similar to that described above. First, the formation of $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2SbX_2]$ via **D**(SbX_2^-) and (a) $Z = X^-$, or tetrahydrofuran which is subsequently replaced by X^-; second, the formation of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SbX]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ in the same way but with the electrophile SbX_3 replaced by $[Fe(\eta\text{-}C_5H_5)(CO)_2SbX_2]$.

The principal products of the $SbX_3/[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ reaction in CH_2Cl_2 (mole ratio 1 : 1; X = Cl or Br) are salts of the $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SbX_2]^+$ cations [27,28]. The only possible route for their formation is via **D**(SbX_2^-) and (e) with SbX_3 assistance. The very small amounts of SbX_3 adducts of $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ probably arise by pathways similar to those suggested for other solvents. A possible explanation for the solvent effects is that whereas both CH_2Cl_2 and tetrahydrofuran, unlike benzene, allow solvation of **D**(SbX_2^-) and X^- (or SbX_4^-) and their separation, tetrahydrofuran is a sufficiently effective nucleophile to act as Z in the route (a) reaction of **D**(SbX_2^-). On the other hand, CH_2Cl_2 is not and consequently **D**(SbX_2^-) reacts via route (e) with internal nucleophilic attack by Sb on M_2.

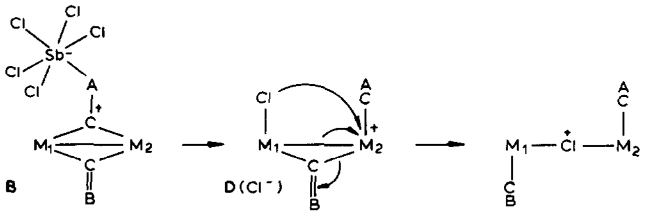
With SbI_3 in CH_2Cl_2 $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ does not give the ionic product, only a mixture of $[Fe(\eta\text{-}C_5H_5)(CO)_2SbI_2]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ [27,28]. This is probably a consequence of I^- being a poor leaving group and SbI_3 a weak Lewis acid so that nucleophilic attack by $Z = I^-$ on **D**(SbI_2^-) in route (a) is not hindered by solvent separation of ion pairs or formation of $[SbI_4]^-$. In contrast the substituted iodide $(CF_3)_2SbI$, which is probably a stronger Lewis acid than SbI_3, gives $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2Sb(CF_3)_2]^+$ $[(CF_3)_2SbI_2]^-$ [32,33], clear evidence for the formation of **D**($Sb(CF_3)_2^-$) by $(CF_3)_2SbI$-assisted loss of I^- and its further reaction via route (e).

Under more forcing conditions, SbX_3 (X = F, Cl, Br or I) and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ give $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_3SbX]^+$ salts [28,29], possibly via a series of reactions each similar to the above with the last step being formation of D(SbXR$^-$) from (21), and its breakdown via (e) (R = [Fe(η-C_5H_5)(CO)$_2$]). There is an alternative in which the [{Fe(η-C_5H_5)(CO)$_2$}$_2$ SbX$_2$]$^+$ cation, formed as outlined above, acts as a Lewis acid. Its adduct with [Fe$_2$(η-C_5H_5)$_2$(CO)$_4$] breaks down to an intermediate D(SbXR$_2$) (R = [Fe(η-C_5H_5)(CO)$_2$]) that undergoes nucleophilic attack by Z on M$_2$ (route (a)) to give [{Fe(η-C_5H_5)(CO)$_2$}$_3$SbX]$^+$ and [Fe(η-C_5H_5)(CO)$_2$Z]$^+$ (23).



(23)

In this series of reactions, the antimony is best regarded as being in the 5 + rather than 3 + oxidation state. With another such electrophile, SbCl$_5$, a different reaction pathway is adopted with the loss of [SbCl$_4$]$^-$ and the migration of Cl$^-$ from Sb to M$_1$ on breakdown of the adduct to D(Cl$^-$). As a consequence of the reaction conditions (absence of a suitable nucleophile and a non-nucleophile solvent) this undergoes internal nucleophilic attack via (e) to give [{Fe(η-C_5H_5)(CO)$_2$}$_2$Cl]$^+$ isolated as its [SbCl$_6$]$^-$ salt [28]. The [SbCl$_6$]$^-$ anion presumably arises from Cl$^-$ transfer from [SbCl$_4$]$^-$ to SbCl$_5$



(24)

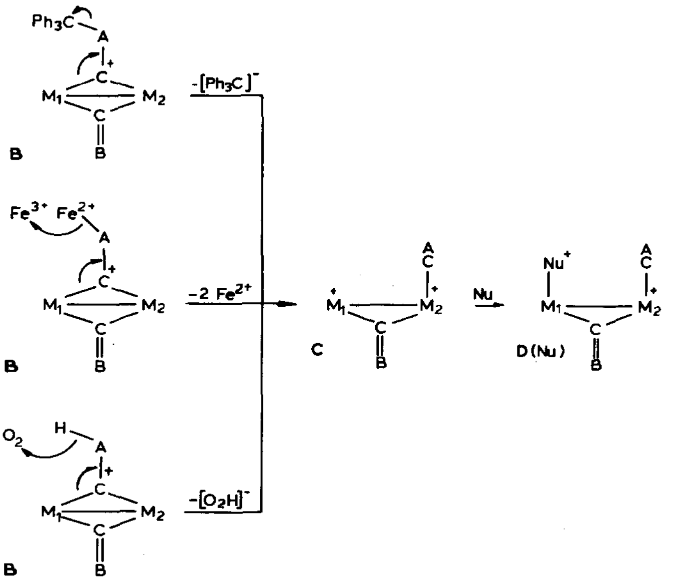
The reactions of [Fe$_2$(η-C_5H_5)$_2$(CO)$_4$] with AsX$_3$ (X = F, Cl, or Br) to give [Fe(η-C_5H_5)(CO)$_2$AsX$_2$] and [{Fe(η-C_5H_5)(CO)$_2$}$_2$AsX$_2$]$^+$ [27–29], RAsX$_2$ to give [{Fe(η-C_5H_5)(CO)$_2$}$_2$As(R)X]$^+$ [29], and R$_2$AsX to give [{Fe(η-C_5H_5)(CO)$_2$}$_2$AsR$_2$]$^+$ [29] probably proceed by the same routes as the relevant SbX$_3$ reactions discussed above. Here, R is an alkyl or aryl group.

BiX$_3$ (X = Cl, Br or I) react with [Fe$_2$(η-C_5H_5)$_2$(CO)$_4$] in much the same way as does SbI$_3$ [27,28]. This seems to be a consequence of BiX$_3$ being weak Lewis acids like SbI$_3$.

In many of these reactions, the product yields are low [27–29]. It is possible that other compounds have been formed, but have not been detected.

(vii) Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ *with* $[Ph_3C]BF_4$, $Fe[ClO_4]_3$ *and* O_2/HBF_4

As a class these reactions give intermediates which do not contain even a part of the electrophile E. As shown in eqs. (25)–(27), the adducts **A**/**B** breakdown to **C** and perhaps **D**(Nu) if a suitable nucleophile Nu is present, but it is possible, as suggested earlier, that adduct breakdown may be a consequence of attack on it by Nu and would proceed directly to **D**(Nu).



(25)

(26)

(27)

$[Ph_3C]^+$ may act as either a one electron oxidant (when it is converted to $Ph_3C^{\cdot}$) or as a two electron oxidant (when it is converted to $[Ph_3C]^-$), but only the latter is illustrated. O_2 (and also the $[O_2H]^-$ ion produced from it) is also a two-electron oxidant, but Fe(III) is a one electron oxidant. It is shown to act as a two electron reagent as a consequence of attack by a second cation upon the adduct. However it is possible that it reacts by two successive one electron oxidations, the first of which gives a radical cation. There is also the possibility that the nucleophile Nu (e.g. a donor solvent molecule) may be coordinated to Fe(III) in **A**/**B** and migrates from it to M_1 during adduct breakdown to **D**(Nu) without the prior formation of **C**.

The intermediates **C** and **D**(Nu) may themselves react further by routes (a)–(h).

Adducts of these reagents with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ have not been observed. However $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ forms unstable adducts with Fe(III) salts and with $[Ph_3C]BF_4$ but their decomposition products were not investigated in detail although it has been noted that they do not contain

μ-CO or μ-CNMe ligands [8,11]. However, $[Ph_3C]BF_4$ reacts with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ in CH_2Cl_2 solution in the presence of olefins to give $[Fe(\eta\text{-}C_5H_5)(CO)_2(\text{olefin})]^+$ salts as the major products via **D**(olefin) and (a) Z = olefin. However $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ is a minor product of this reaction. In the absence of an olefin it becomes the major product formed via **C** and (h), **D**(CH_2Cl_2) and (c) Z = CH_2Cl_2, or **D**(CH_2Cl_2) and (d). The reduction of $[Ph_3C]^+$ is to $[Ph_3C]^-$ (which on hydrolysis gives Ph_3CH) rather than the anticipated $[Ph_3C]^{\cdot}$ radical [2]. It is an important feature of the scheme that it accounts for this "surprising" observation [2] in a straightforward way.

The $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]/Fe[ClO_4]_3$ reaction in acetone or acetonitrile [30] gives $[Fe(\eta\text{-}C_5H_5)(CO)_2(\text{solvent})]^+$ salts via **D**(solvent) and (a) Z = solvent.

The third reaction to be discussed in this section is the oxidation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ by O_2 in the presence of acids. Here H^+ forms the adduct and O_2 is the oxidant. If the acid has a non-coordinating anion, e.g. $[BF_4]^-$, but coordinating solvent molecules are present, e.g. H_2O or acetone, then the reaction proceeds via **D**(solvent) and (a) Z = solvent to $[Fe(\eta\text{-}C_5H_5)(CO)_2(\text{solvent})]^+$ [31]. If the acid has a coordinating anion, e.g. Cl^-, then the only observed products are, e.g., $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ [32] which may be formed directly or by displacement of the relatively labile solvent molecules from $[Fe(\eta\text{-}C_5H_5)(CO)_2(\text{solvent})]^+$ ions.

E. GENERAL COMMENTS AND EXTENSIONS

(i) Relative importance of the proposed reaction pathways

It is clear that in the preceding examples certain of the proposed reaction pathways are utilised more extensively than others, and that some do not appear to be at all important. In particular, the formation of **C** and its subsequent reactions as well as the "spontaneous" reactions of **D** via routes (b) and (d) are rather doubtful. As mentioned earlier (Section C), it is possible that **C** would convert to **D** even with weak nucleophiles such as $[BF_4]^-$ because of the low coordination number and positive charge of M_1.

(ii) Alternative reaction intermediates

Although it has been assumed that the adducts **A**/**B** break down to **C** and **D**, alternative reaction intermediates can be envisaged. They have not been considered because they are not common. One which could be important under special circumstances is when the adduct breaks down without scission of the CA → E bond. The resultant intermediates are similar to **C** or **D** but have the $(CA)^+$ ligand replaced by the potential carbyne $(C{-}A{-}E)^-$ or a related group in which partial fragmentation of E has taken place.

(iii) Alternative modes of breakdown of the intermediates

An important possibility is that attack on the intermediates **D** by external nucleophiles Z (routes (a) and (c)) or the internal nucleophile X (routes (e) or (f)) may not be on M_2 or M_1 but on the terminal ligands (e.g. CO, CNR or CS) coordinated to them. The relatively electron-deficient nature of most **D** would tend to encourage such reactivity. It could be particularly important when one of the ligands is CS, as this appears to be particularly susceptible to nucleophilic attack, for example in $[Fe(\eta\text{-}C_5H_5)(CO)_2(CS)]^+$ [33]. It may be the intervention of such reaction pathways which prevents the formation of $[Fe(\eta\text{-}C_5H_5)(CO)(CS)X]$ from the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CS)]$ with halogens [34].

(iv) Extensions of the proposed mechanism

The mechanism may be extended to polymeric compounds which ostensibly do not contain the appropriate μ-ligands, but for which μ-isomers are accessible even if they lie at relatively high energies and are not present in the reaction mixtures in detectable amounts. For example, $[Co_2(CO)_2(L)_2]$ complexes (L = tertiary arsine, phosphine, phosphite, or stilbine) exist as non-bridged isomers only in the solid state, but their solutions contain mixtures of these in equilibrium with various bridged species. The isomer ratios are markedly dependent on L, but in most cases all of the isomers can be detected [35]. On the other hand only the non-bridged forms of $[M_2(\eta\text{-}C_5H_5)_2(CO)_6]$ (M = Mo, or W) have been detected in the solid state or in solution, but variable temperature NMR studies have shown that the closely related $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_5(CNMe)]$ is fluxional via μ_2-CNMe isomers which would not otherwise have been detected [36]. In this context it is possible that semi-bridging CO (or CNR, CS, etc.) ligands would provide sites for adduct formation or suggest potentially accessible μ-ligands.

Another extension is to compounds with multiple bonds between metal atoms. Breakdown of the intermediates via routes (a)–(e) would result in a reduction of the $M_1{-}M_2$ bond order but not in bond scission.

Transition metal clusters possessing the appropriate doubly or triply bridging ligands may also be susceptible to electrophilic attack by way of the proposed mechanism. However, the alternative reaction pathways within the scope of the mechanism which could be adopted may well be increased greatly. In particular it should be remembered that in such clusters the μ-ligand CB could be replaced by a more rigid bridging group such as a metal atom which does not allow a marked increase in the M_1–M_2 atom separation on bond scission or could itself become the site of nucleophilic attack in the subsequent reactions of the intermediates. Consequently reactions such as (f) may well be more common than for binuclear substrates.

A fundamental consequence of adduct formation is the appearance (actual or potential) of a positive charge on the bridging carbon atom of the μ-CA ligand of the substrate. If this positive charge can be induced on the bridging atom of other μ-ligands (e.g. carbenes) during a reaction, that reaction may well proceed along pathways similar to those outlined in Sections B and C. If that is the case, the applicability of the proposed mechanism may be increased greatly.

F. SUMMARY AND CONCLUSIONS

In Sections A–C a mechanistic scheme was proposed as a framework within which could be considered the reactions between electrophiles and polynuclear metal carbonyls. Although it is speculative and may not be an entirely accurate description of what actually happens, it does account very satisfactorily for various aspects of the reactions which have been surveyed in Section D. However it can be seen that most of the examples have been drawn from the chemistry of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ derivatives. Although this may be because these compounds have been studied carefully and in detail, it may also be because the proposed pathways are particularly favoured in these systems and that their more general applicability is limited.

There are a number of factors which could contribute to this limitation. They may be grouped under three headings: (a) μ-isomer inaccessibility; (b) limitations imposed by the Lewis acid and Lewis base centres involved; and (c) the availability of more attractive alternative reaction pathways.

The first of them refers to both steric and energetic limitations on μ-isomer accessibility and is self-evident. However the second is more subtle. It is well-known that the lowering of the frequency of the ν(CA) vibration of a bridging or terminal CA ligand is a consequence of increasing metal-to-ligand back bonding into its C–A π^*-orbital which results not only in a decrease of the C–A bond order but also an increase in the basicity of A. This is why, for example, the μ_2-CO/EtOH hydrogen bonding is extensive for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ but virtually non-existent for $[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$ ($\nu(CO_\mu) = 1787$ and 1800 cm^{-1}, and 1847 and 1892 cm^{-1} respectively in CS_2 solution) [37]. Therefore the former will probably more readily form adducts than the latter with a particular electrophile. Thus the metal atoms and ligands other than CA which are in the substrate will have their electronic consequences. However varying A is more directly important.

It will affect the π-acceptor capacity and hence basicity of CA (e.g. CA = CS > CO), change the intrinsic basicity of A (e.g. A = N > O), and affect the Lewis acid–Lewis base compatibility of μ-CA with various electrophiles. As well as the electronic effects there are steric limitations to adduct formation. One is the bulk of the $M_1M_2(\mu\text{-CB})$ fragment of the substrate molecule, and the other is the bulk of the groups attached to A, particularly when CA = CNR. However this is not always a negative factor in the context of the overall reaction (see below). Similar considerations with respect to adduct formation also apply to the electrophile E, i.e., its strength as a Lewis acid, its compatibility with the Lewis base centre of the substrate, μ-CA, and the limitation imposed by its steric bulk. Finally, although the importance of adduct formation as a prerequisite to oxidative cleavage has been emphasised, it is as well to point out that if an adduct is too stable, its subsequent reactions become very slow. A good example of this is the formation of the inert $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(H)Me\}]^+$ salts from $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ and acids (cf. the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with H^+ in Section D) [7].

There are a number of alternative reaction pathways which provide the third limitation. It is possible that electrophilic attack could occur at other sites of high electron density within the molecule such as the metal–metal bond or the individual metal atoms. In general this would probably be hampered by the relatively close-packed ligands which shield the metal atom core (e.g. ref. 14), and it is only in certain favoured circumstances that they would be important. A possible example lies in the chemistry of $[Rh_2(\eta\text{-}C_5R_5)_2(CO)_2]$ (R = Me or H) complexes [38] where attack on the Rh–Rh multiple bond from above or below the $Rh_2(\mu\text{-}CO)_2$ plane would clearly be an attractive option reminiscent of electrophilic attack on C_2H_4. However, the most obvious of the alternative reaction pathways involves homolytic scission of the M_1–M_2 bond. It would be expected to be common as many dinuclear metal carbonyl derivatives undergo readily and reversibly such scission reactions to give transition metal centred radicals such as $[Fe(\eta\text{-}C_5H_5)(CO)_2]^\cdot$ [39]. However there is considerable evidence to suggest that such pathways are not important for the reactions discussed in Section D. The formation of asymmetric scission products such as $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ and the factors which affect it, e.g. non-coordinating solvents and anions, would be difficult to rationalise on the basis of a radical mechanism. Furthermore, oxidation of the dimers is almost always a two-electron process even with electrophiles for which a one-electron mechanism would seem particularly appropriate; for example $[Ph_3C]^+$ is reduced to $[Ph_3C]^-$ and not to the well-known, stable $[Ph_3C]^\cdot$ radical [2]. Finally solvent effects are often more consistent with ionic rather than free radical processes, e.g. the $[Co_2(CO)_8]/[Fe(\eta\text{-}C_5H_5)(CO)_2SnCl_3]$ reaction. However, there are some instances where radical pathways appear to be particularly important. This may well be the case for the reactions of $[M_2(\eta\text{-}C_5H_5)_2(CO)_6]$ (M = Cr, Mo, W) with SnX_2 where the product distributions and the effects of light imply strongly that the free radicals $[M(\eta\text{-}C_5H_5)(CO)_3]^{\cdot}$ are involved at least to some extent to give $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2SnX_2]$ rather than alternative products [40]. Furthermore there is evidence to suggest that when M = Cr both monomer and dimer co-exist in solution [41]. In general, the importance of radical pathways can be expected to increase with decreasing metal–metal bond strengths.

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