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A new mechanism for the substitution reactions of metal carbonyl dimers

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Abstract

A new mechanism in which the heterolytic fission of the metal–metal bond is considered to be the key initial step in the substitution reactions of the metal carbonyl dimers $MM'(CO)_{10}$ ($M = M' =$ Mn or Re; $M =$ Mn, $M' =$ Re) and $Co_2(CO)_8$ is described.

The substitution reactions of the metal carbonyl dimers of manganese, rhenium and cobalt are amongst the most widely studied reactions in carbonyl chemistry and recently have been discussed in considerable detail in a standard text [1]. They are not simple and depending on the nature of the incoming nucleophile, the solvent, and the reaction conditions, neutral substitution products or ionic materials may result.

Reactions of the metal carbonyl dimer $M_2(CO)_{10}$ ($M_2 = Mn_2$, Re_2 or MnRe) with nucleophiles such as ER_3 (E = P or As) usually lead to either mono- or bis-substituted products depending on the metal and the reaction conditions employed and, in general, substitution occurs in the axial positions. The mechanism(s) by which these reactions occur has been a subject of considerable debate. Two possibilities have been considered. The first, which follows naturally from our understanding of the substitution reactions of the mononuclear carbonyls such as $Cr(CO)_6$, involves CO dissociation to give an active unsaturated intermediate as the primary step [see eq. (a)]. The second, more controversial mechanism, involves the initial homolytic fission of the metal bond to produce the highly reactive radical species $M(CO)_5$ [see eq. (b)]. It has been argued [2], on the basis of the now considerable information available from detailed studies of the reactions of the mixed dimer $MnRe(CO)_{10}$ and various isotopically enriched samples of the homonuclear dimers, that the homolytic fission of the metal–metal bond [eq. (b)] is not a viable process—at least for straightforward CO substitution—and that mechanism (a), involving CO dissociation, is the more likely.

The two possible mechanisms for substitution in $M_2(CO)_{10}$:

$$M_2(CO)_{10} \overset{-CO}{\rightleftharpoons} M_2(CO)_9 \overset{+L}{\rightleftharpoons} M_2(CO)_9L \tag{a}$$

$$\begin{aligned} M_2(CO)_{10} &\rightleftharpoons 2\dot{M}(CO)_5 \\ \dot{M}(CO)_5 + L &\rightleftharpoons \dot{M}(CO)_4L \\ \dot{M}(CO)_5 + \dot{M}(CO)_4L &\rightleftharpoons M_2(CO)_9L \\ 2\dot{M}(CO)_4L &\rightleftharpoons M_2(CO)L_2 \end{aligned} \tag{b}$$

This mechanism [eq. (a)] is clearly attractive but does not easily explain all of the available data. For example, the reaction of the mixed metal dimer, $MnRe(CO)_{10}$, with a tertiary phosphine ligand L leads to mainly the rhenium substituted isomer $(CO)_5MnRe(CO)_4L$. Given that substitution reactions on $Mn_2(CO)_{10}$ occur in the temperature range 90 to 110 °C and on $Re_2(CO)_{10}$ from 130 to 150 °C—which means that CO dissociation from manganese will occur at a rate about a hundred times greater than from rhenium—such a result is surprising and not readily compatible with the dissociative mechanism. One possible explanation of this behaviour is that the CO ligand dissociates initially from the manganese and that the reaction intermediate contains a bridging CO group such that unsaturation on the manganese is transferred to the rhenium. In addition, mechanism (a) gives no clue to the method of formation of ionic products.

Reactions with more basic ligands such as pyridine (L) cause the carbonyl dimer to undergo heterolytic cleavage to produce salts of the type $[MnL_6][Mn(CO)_6]_2$. Such behaviour is also commonly observed with other higher nuclearity clusters such as $Fe_3(CO)_{12}$ but, as far as we can judge, no kinetic studies of this reaction have been reported and no mechanism for the process proposed. Whatever the mechanism, both heterolytic fission of the metal-metal bond and complete replacement of CO from one metal atom (to form $[ML_6]^{2+}$) are required at some stage.

The substitution reactions of $Co_2(CO)_8$ appear, at least at first sight, to be far more complicated. In non-polar solvents reactions with mild nucleophiles such as $AsPh_3$ show a rate law which is independent of the concentration of the incoming nucleophile—^{13}CO, PR_3 or $AsPh_3$—at temperatures from −15 to 30 °C. The activation parameters ($\Delta H^\star = 22$ kcal and $\Delta S^\star = 10$ e.u.) and the apparent lack of dependence on L are regarded as being consistent with a CO dissociative mechanism [eq. (c)].

$$\begin{aligned} Co_2(CO)_8 &\rightleftharpoons Co_2(CO)_7 + CO \\ Co_2(CO)_7 + AsPh_3 &\rightleftharpoons Co_2(CO)_7AsPh_3 \end{aligned} \tag{c}$$

Reaction of $Co_2(CO)_7AsPh_3$ with further mole of $AsPh_3$ leads to the disubstituted complex $Co_2(CO)_6(AsPh_3)_2$ at a much slower rate indicating that the $AsPh_3$ ligand already present in $Co_2(CO)_7AsPh_3$ affects the reactivity. These simple substitution reactions clearly parallel the reaction of manganese and rhenium. However, it is interesting to note that the alternative, dissociative radical mechanism for these substitutions similar to that proposed for manganese and rhenium has not been postulated.

In contrast, the substitution pattern of $Co_2(CO)_8$ with tertiary phosphines or arsines in polar solvents is quite different and leads to the ionic products $[Co(CO)_3(MR_3)_2][Co(CO)_4]$ [eq. (d)] at rates that are more rapid than CO dissociation and that depend on the concentration and the nucleophilicity of the entering ligand. Here it is pertinent to note that a radical chain pathway has been suggested to account for these observations. Further substitution of the cationic species $[Co(CO)_3(PR_3)_2]^+$ to give $[CoL_5][Co(CO)_4]$ is observed when $L = P(OR)_3$ or CNR [eq. (e)].

$$Co_2(CO)_8 + PR_3 \rightarrow [Co(CO)_3(PR_3)_2][Co(CO)_4] + CO \qquad (d)$$

$$Co_2(CO)_8 + L \rightarrow [CoL_5][Co(CO)_4] + 4CO \qquad (e)$$

Reaction with stronger bases such as pyridine are apparently similar and these reactions are at least superficially similar to those of manganese and rhenium. Thus, two distinct mechanisms have been put forward to explain the substitution patterns observed for $Co_2(CO)_8$ and $Co_2(CO)_7AsPh_3$. For reaction with weak nucleophiles to produce simple substituted derivatives, a CO dissociative route is preferred whereas for stronger nucleophiles a radical chain pathway is preferred to account for the formation of ionic products.

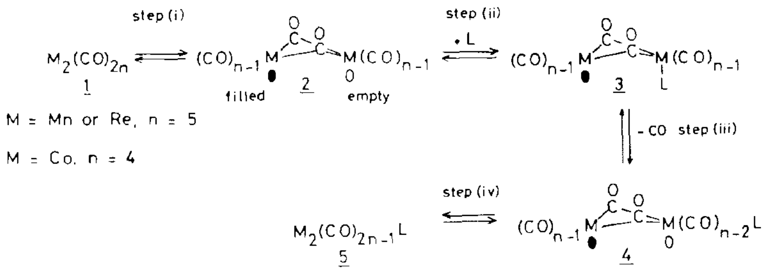
Although we do not disagree with these suggested mechanistic pathways for these substitution reactions of either $Co_2(CO)_8$ or $M_2(CO)_{10}$, we wish to propose a simple alternative mechanism which has the advantage that it not only readily explains most, if not all, of the current data available for both simple substitution and the apparently more complicated disproportionation reactions of these carbonyl dimers, but is also more generally applicable to other cluster carbonyls containing metal–metal bonds. In putting forward this proposal we recognise that it is not possible to conclusively prove any mechanism but would argue that the main function of any proposal is to offer a realistic explanation of the available data and at the same time provide a clear indication of possible ways forward. We believe this new alternative satisfies these criteria [3].

In this new alternative pathway the primary step in the substitution reaction of the dimeric carbonyls, $M_2(CO)_{10}$, involves the formation of an intermediate with (probably) two CO-bridges and the concerted heterolytic fission of the metal–metal bond to generate one eighteen-electron, saturated metal centre and one sixteen-electron, unsaturated metal centre. According to this approach substitution of the dimeric carbonyls of manganese, and rhenium then proceeds by the addition of L to the unsaturated 16-electron centre followed by CO loss from the same metal atom. Thus, the overall process may be visualised as proceeding via the following reaction sequence (Scheme 1).

Step (i). The formation of (probably two) CO-bridges [4] and the concerted heterolytic fission of the M–M bond to form intermediate **2** which contains one 18-electron centre and one 16-electron centre. This step is clearly independent of L.

Step (ii). The addition of L to the unsaturated 16-electron metal atom to give adduct **3**. This will depend both on L and the active intermediate **2** produced in step (i).

Step (iii). CO dissociation from the adduct **3** produced in step (ii) to produce the new intermediate **4**.



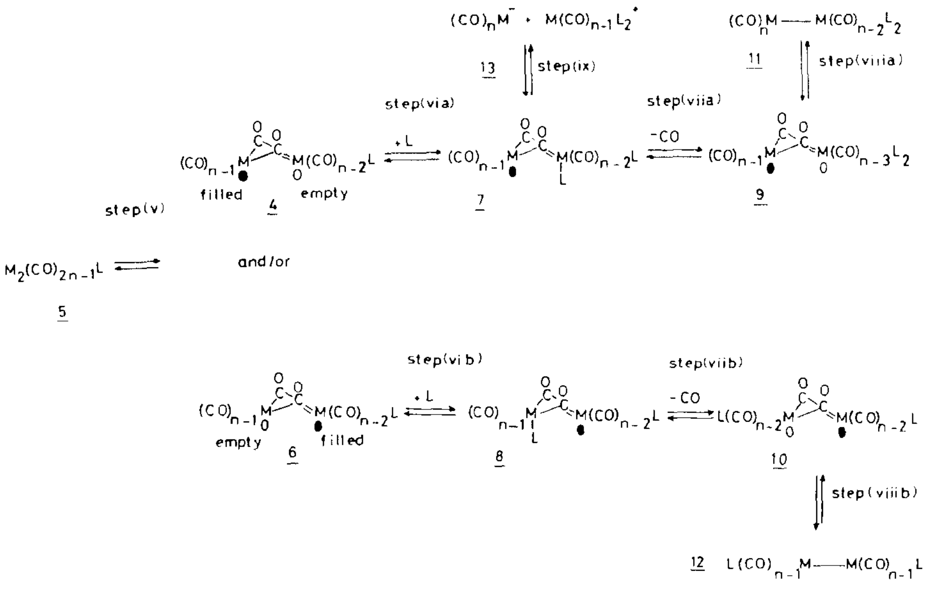
Scheme 1.

Step (iv). The final step in which the intermediate **4** undergoes conversion by both bridge opening and concerted M–M bond formation to produce the final product $M_2(CO)_9L$ (**5**).

The difference in the rate of substitution for $M_2 = Mn_2$, MnRe, or Re_2 will thus be controlled, to a large part, by the ease with which heterolytic M–M heterolytic bond cleavage occurs. The formation of the substitution site will be controlled by the ability of the metal atom to stabilise 16-electron unsaturated centre and by the size of that metal atom. Thus, for the mixed metal system, $MnRe(CO)_{10}$, substitution will be preferred on the third row metal since this is better able to stabilise a 16-electron count and is also the larger metal atom, and hence the less sterically hindered centre.

Further substitution to produce $M_2(CO)_8L_2$ may then occur by a similar route, as shown in Scheme 2.

Step (v). The formation of (probably two) CO-bridges and the concerted heterolytic fission of the M–M bond to form either intermediate **4** or **6**, each of which contains one 18-electron centre and one 16-electron centre.



Scheme 2.

Step (vi). The addition of L to the unsaturated 16-electron metal atom to give either adduct **7** [step (via)] or **8** [step (vib)]. This will depend both on the nature of the already bonded L and that of the incoming L together with the nature of the active intermediates **4** or **6** produced in step (v).

Step (vii). CO dissociation from the adduct **7** produced in step (vi) to produce the new intermediate **9** [step (viia)] or from the adduct **8** to give intermediate **10**.

Step (viii). The final step in which the intermediates **9** and **10** undergo conversion by both bridge opening and concerted M–M bond formation to produce the products **11** and **12**.

Step (ix). This is an alternative to step (viii). The CO-bridges open and the dimeric intermediate **7** undergoes cleavage to produce the two ions **13**.

This mechanistic pathway is, in large part, similar to that outlined in Scheme 1. Here, however, the first step (v) can lead to two possible intermediates **4** or **6** (Scheme 2). In **6**, heterolytic fission of the M–M bond leads to unsaturation on the unsubstituted M atom, whereas in **4** fission leads to unsaturation on the already substituted M atom. The tendency to form either intermediate **4** or **6** will be dependent on the nature of the bonded ligand L. The presence of a more basic ligand L will tend to stabilise the 16-electron site on the already substituted metal atom thereby favouring the formation of intermediate **4**. In addition to the basicity of L its steric bulk will be critically important. The larger the cone angle of the bonded L the greater the tendency will be for the incoming ligand L to be directed towards the unsubstituted metal atom M and to form intermediate **8**. Thus, in step (vi) the nature of the product will depend on both the basicity and cone angle of L, the smaller more basic ligands clearly favouring the formation of intermediate **4**, and hence **7** and **9** [steps (via), and (viia)] and the larger less basic ligands favouring substitution on the second metal atom and the formation of intermediate **6**, and hence **8** and **10** [steps (vib), and (viib)]. The role of the solvent will also be important in governing the direction of this second attack (see below). Finally, either CO bridge opening with the concerted formation of the metal–metal bond will give the substitution product **11** or **12** [step (viii)], or CO bridge opening without the formation of a metal–metal bond leading to dissociation and the formation of the ionic product **13** [step (ix)]. The dependency of the second (or even further) subsequent substitution on the nature of L is thus apparent.

It is worth commenting on the alternative pathway to intermediate **7**. The ability of this intermediate to close up and ultimately form the derivative **11** [step (viii)] will depend on the steric constraints imposed by the bonded ligands L [4]. This follows naturally from a consideration of the Ligand Polyhedral Model in its application to the metal carbonyls [5]. If such closure [step (viiia)] is not desirable because the presence of bulky ligands L (especially on one metal atom) would lead to the formation of a long and hence weak metal–metal bond in **12** then intermediate **7** will preferentially undergo the alternative ionic dissociation pathway to give the ionic product **13** simply by CO-bridge opening without the concerted formation of a metal–metal bond. The formation of ionic products is thus a natural consequence of the proposed mechanism. Clearly the greater the degree of substitution of CO by L on the same metal atom within the dimeric unit the higher the probability that ionic dissociation will take place. The formation of the more highly substituted cationic complexes may follow a similar route but we would expect that complete substitution to produce cations of the type $[ML_n]^{n+}$ will occur by direct substitution on the preformed cation of the type $[M(CO)_3L_2]^{n+}$.

Clearly, the reaction sequences may also operate for $[Co_2(CO)_8]$ except that in this case the first step requires only the heterolytic scission of the Co–Co bond since two CO-bridges are already present. However, a major difference in the reactions shown by the cobalt system and those of manganese and rhenium lies in the enhanced tendency of the cobalt compound to undergo disproportionation with, for example, tertiary phosphines to give ionic products. This is almost certainly due to the difference in the steric constraints placed on the two systems. For the more sterically restricted systems of manganese and rhenium with five ligands about each metal atom there is expected to be a greater dependence on the steric bulk of the incoming substrate. Thus, the manganese or rhenium atom is six-coordinated in the intermediate [5] **2** or **4** whereas the cobalt atom is only five coordinated. Attack at a metal atom within the dimeric unit is thus expected to occur preferentially at the less sterically hindered metal with manganese leading to a bis-substituted system whereas for cobalt, where there is a less demanding steric constraint, attack can more easily occur at the same metal atom within the dimeric unit leading eventually to ionic products.

$$Co_2(CO)_8 + PR_3 \rightarrow [Co(CO)_3(PR_3)_2][Co(CO)_4] + CO$$

The role of the solvent in these reactions is also clearly understood. The possible formation of a solvent stabilised intermediate, $M_2(CO)_{2n-1}S$, in step (ii) ($L = S$) of the proposed new scheme, although not strictly necessary, would lead to the same conclusions. Polar solvents such as MeCN will tend to favour the initial formation of the moderately stable adduct, $M_2(CO)_{2n-1}S$, and the reaction sequence in which successive attack of the relatively small but strongly nucleophilic solvent molecule occurs on the same metal atom leading to the formation of ionic products will be favoured. In this sequence the intermediate **3** ($L = S$) and subsequent more highly substituted intermediate **7** ($L = S$) will be preferentially stabilised by the strongly donating ability of the polar solvent molecule (S). At any stage during the reaction sequence solvent S may be displaced from the coordination sphere by the incoming nucleophile L leading to the observed products. In these reactions the prior coordination of the more labile and smaller solvent molecule S will have the effect of directing L (more-or-less irrespective of the nature of L) to the same metal atom; as a consequence the tendency to form intermediates of type **8** will be decreased and the tendency to form ionic products increased.

The mechanisms outlined in Schemes 1 and 2 offer a simple, alternative explanation of much of the data currently available on the substitution reactions of the dimeric carbonyls of cobalt, manganese, technetium and rhenium. Contrary to current opinion, we believe that basically one mechanism may be dominant, i.e. the heterolytic fission of the metal–metal bond. The proposition that these reactions follow a CO dissociation pathway is based primarily on the basis that the rate equation is similar to that found for $Cr(CO)_6$. For this new mechanism the rate law

$$\text{rate} = k_1[M_2(CO)_{2n}] + k_2[L][M_2(CO)_{2n}]$$

is expected, with $k_1 \gg k_2$ (usually but not necessarily always).

In conclusion, we would argue that the substitution reactions of the dimeric carbonyls of manganese, rhenium or cobalt to give either simple substitution products, or, by disproportionation, ionic materials, may be viewed as taking place by essentially the same initial heterolytic metal–metal bond cleavage step. Furthermore, the mechanism is governed by the same factors whether or not an ionic or simple substitution product is produced. Importantly, this new mechanistic pathway provides satisfactory explanations for: (i) the observed rate equation; (ii) the formation of neutral substitution derivatives or ionic products as a function of the type and number of ligands, L; (iii) the observed solvent dependence of these reactions; (iv) the preferential substitution at the rhenium atom in the mixed dimer $MnRe(CO)_{10}$; (v) the enhanced tendency of cobalt to produce ionic derivatives.

Clearly, the application of this mechanism is not restricted to these dimeric carbonyls but may be extended to other highly nuclearity carbonyl clusters with equal success.

References

1 J.D. Atwood, Inorganic and Organometallic Reaction Mechanisms, Brooks/Cole, New York, USA, 1985.

2 N.J. Colville, A.M. Stolzenberg and E.L. Muetterties, J. Am. Chem. Soc., 105 (1983) 2499.

3 B.F.G. Johnson, Inorg. Chim. Acta, 115 (1986) L39.

4 This follows from a consideration of $Mn_2(CO)_{10}$ on the basis of the Ligand Polyhedral Model, B.F.G. Johnson, to be reported.

5 B.F.G. Johnson, J. Chem. Soc., Chem. Commun., (1976) 211; B.F.G. Johnson, J. Chem. Soc., Chem. Commun., (1976) 703; R.E. Benfield and B.F.G. Johnson, Transition Met. Chem., 6 (1981) 131; C.E. Anson, R.E. Benfield, A.W. Bott, B.F.G. Johnson, D. Braga and E.A. Marseglia, J. Chem. Soc., Chem. Commun., (1988) 889; A. Bott and B.F.G. Johnson, J. Chem. Soc., Dalton Trans., (1990) 2437.