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The Mechanism of Carbonyl Substitution in the Trimetal Clusters $M_3(CO)_{12}$ (M = Fe, Ru or Os)

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An alternative mechanism for CO substitution reactions in the series of cluster carbonyls $M_3(CO)_{12}$ (M = Fe, Ru or Os) is presented; the important step being the heterolytic fission of an M–M bond in the trimetal unit.

The reactions of the trimetal carbonyls, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ with group Va donors (L) appear complicated leading not only to simple substitution products of the type $M_3(CO)_{12-n}L_n$ (where $n = 1$–3 and, very occasionally 4 or more) but also the products of fragmentation such as $M(CO)_4L$ and $M(CO)_3L_2$ [1–3].

The mechanism(s) by which these reactions occur remain(s) unclear. The reaction of $Fe_3(CO)_{12}$ with a pseudo-first order excess PPh_3 showed an apparent induction period lasting several hours at 30–40 °C before fragmentation to $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ occurred [1]. The rate seemed to be independent of PPh_3 concentration. In contrast, reaction with phosphites, $P(OR)_3$, usually leads to trisubstituted complexes $Fe_3(CO)_9L_3$. In the reaction of $Ru_3(CO)_{12}$ with $P(OPh)_3$ or $[P(OCH_2)]_3CEt$ the formation and decay of intermediates $Ru_3(CO)_{11}L$ and $Ru_3(CO)_{10}L_2$ were observed before the formation of the final product $Ru_3(CO)_9L_3$. In contrast, reaction with PPh_3 shows no evidence for similar intermediates, and with $P(OEt)_3$ and $PBu_3{}^n$ showed the formation of both trisubstituted clusters together with the products of fragmentation $Ru(CO)_4L$ and $Ru(CO)_3L_2$. Initial studies on reactions of $Ru_3(CO)_{12}$ [4, 5] showed that more basic ligands (L) reacted according to the rate eqn.

$$k_{obs} = k_1 + k_2[L]$$

At very high concentrations of L even weak nucleophiles such as $AsPh_3$, $P(OPh)_3$ and PPh_3 showed a detectable k_2 term in the rate eqn.; the value of k_2 increasing with ligand basicity. Very recent work on $Os_3(CO)_{12}$ has shown that in the reaction on $Os_3(CO)_{12}$ with PPh_3 the k_2 term is negligible and a simple dissociation process was preferred.

$$Os_3(CO)_{12} \rightleftharpoons Os_3(CO)_{11} + CO$$

$$Os_3(CO)_{11} + L \rightleftharpoons Os_3(CO)_{11}L \text{ etc.}$$

It was originally proposed that the reaction of $Ru_3(CO)_{12}$ with $PBu_3{}^n$ takes place via a radical pathway in which the trimetal unit undergoes homolytic rupture to produce $\dot{Ru}(CO)_4$ radicals.

$$Ru_3(CO)_{12} \rightleftharpoons 3\dot{Ru}(CO)_4$$

These rapidly undergo CO exchange with L to produce the substituted radical $Ru(CO)_4L$

$$\dot{Ru}(CO)_4 + L \rightleftharpoons \dot{Ru}(CO)_3L + CO$$

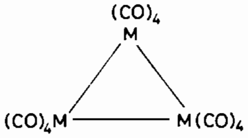
Recombination of the appropriate radical species then leads to the required products

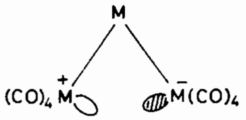
$$\dot{Ru}(CO)_3L + 2\dot{Ru}(CO)_4 \rightleftharpoons Ru_3(CO)_{11}L$$

$$2\dot{Ru}(CO)_3L + \dot{Ru}(CO)_4 \rightleftharpoons Ru_3(CO)_{10}L_2$$

$$3\dot{Ru}(CO)_3L \rightleftharpoons Ru_3(CO)_9L_3$$

This idea of complete dissociation into three radicals followed, at a later stage, by the combination of three radicals to produce a trimetal unit is not appealing. First, and more importantly, it requires an unlikely trimolecular transition state and, second, in reactions known to produce radical intermediates, e.g. substitution of $Mn_2(CO)_{10}$, the products of radical scavenging reactions are invariably found, this is not the case with $Ru_3(CO)_{12}$ except at elevated temperatures. The alternative suggestion that these reactions proceed with CO-dissociation as the primary step is attractive. However, we wish to propose a simple alternative which has the advantage of not only providing a satisfactory explanation of the complex data available but also of being applicable to polymetal carbonyls in general. In this new mechanism the primary – although not necessarily the rate determining step – involves the heterolytic fission of a metal–metal bond to generate a trimetal unit containing one eighteen electron, saturated metal atom and one sixteen electron, unsaturated metal atom





Intermediate I

0020-1693/86/$3.50

Substitution thus proceeds according to Scheme 1.

$M_3(CO)_{12} \rightleftharpoons (CO)_4\overset{\circ}{M}-M(CO)_4-\overset{\bullet}{M}(CO)_4$ step (i)

$(CO)_4M-M(CO)_4-M(CO)_4 \rightleftharpoons L(CO)_4M-M(CO)_4-M(CO)_4$ step (ii)

Formation of $M(CO)_4L$

$L(CO)_4M-M(CO)_4-M(CO)_4 \rightleftharpoons M(CO)_4L + M_2(CO)_8$ step (iii)

$M_2(CO)_8 + 2L \rightleftharpoons M(CO)_4L$

Formation of $M_3(CO)_{11}L$

$L(CO)_4M-M(CO)_4-M(CO)_4 \rightleftharpoons M_3(CO)_{11}L + CO$ step (iv)

Route A: Formation of $M(CO)_4L$ and $M(CO)_3L_2$

$M_3(CO)_{11}L \rightleftharpoons L(CO)_3M-M(CO)_4-M(CO)_4$ step (va)

$L(CO)_3M-M(CO)_4-M(CO)_4 \rightleftharpoons L_2(CO)_3M-M(CO)_4-M(CO)_4$ step (via)

$L_2(CO)_3M-M(CO)_4-M(CO)_4 \rightleftharpoons M(CO)_3L_2 + M_2(CO)_8$ step (viia)

Route B: Formation of $M_3(CO)_{10}L_2$

$L(CO)_3M-M(CO)_4-M(CO)_4 \rightleftharpoons L(CO)_3M-M(CO)_4-M(CO)_3L$ step (vib)

$L(CO)_3M-M(CO)_4-M(CO)_3L \rightleftharpoons M_3(CO)_{10}L_2 + CO$ step (viib)

Scheme 1. Proposed mechanism for the substitution of $M_3(CO)_{12}$ (M = Fe, Ru or Os).

Step (i), the heterolytic fission step is independent of [L]. Step (ii), in which L addition takes place is dependent on L and also the standing concentration of intermediate I. There are then two possible pathways. First (step (iii)), fragmentation to produce the stable $Ru(CO)_4L$ and the highly unstable, unsaturated dimetallic, $Ru_2(CO)_8$, which is expected to react rapidly with ligand L to produce 2 mol of $Ru(CO)_4L$. Second, (step iv), CO-dissociation followed by ring closure to generate $Ru_3(CO)_{11}L$. Further substitution to produce $Ru_3(CO)_{10}L_2$ may then occur by a similar route (steps va, vib, viib). Except that, because of the more polar nature of the $\bar{Ru}-Ru$ bonds arising from the introduction of L into the Ru_3 unit, heterolytic bond dissociation might reasonably be expected to occur with greater ease. Further, since L is, in general, a better base than CO, bond cleavage to generate $L(CO)_3\bar{Ru}-Ru(CO)_4-\bar{Ru}(CO)_4$ might be expected to occur in preference to the alternative $L(CO)_3\bar{Ru}-Ru(CO)_4-\overset{+}{Ru}(CO)_4$ leading to further addition of L to the same Ru atom and the formation of $Ru(CO)_3L_2$ (steps va, via and viia). The alternative reaction pathway is not, of course, excluded but the basicity of the coordinated substrate L will clearly affect the course of the reaction (A or B). The more basic ligands tending to favour route A.

Final substitution or fragmentation to generate $Ru_3(CO)_9L_3$ or $Ru(CO)_4L$ and $Ru(CO)_3L_2$ may be considered to occur similarly except that as with $Ru_3(CO)_{11}L$ the Ru–Ru bonds will be expected to more easily undergo heterolytic cissociation because of the additional bond polarity introduced by the presence of two L ligands. Enhanced fragmentation is thus expected (Scheme 2).

Further substitution to generate $Ru_3(CO)_8L_4$ is expected to be inhibited for two reasons:

(i) In $Ru_3(CO)_3L_3$ (as in $Ru_3(CO)_{12}$) the three Ru–Ru bonds are equivalent (they may vary slightly according to the position of L on each Ru – axial or equatorial); hence the bond polarity is zero.

(ii) In the intermediate $L(CO)_3\overset{+}{Ru}-Ru(CO)_3L-\bar{Ru}(CO)_3L$ the steric bulk of L will control further addition.

The difference in the rate of introduction of the 1st, 2nd and 3rd ligands into $Ru_3(CO)_{12}$ will be, in part, controlled by the ease with which Ru–Ru bond cleavage occurs. In Scheme 3 is illustrated the relationship between the three Ru–Ru bonds in $Ru_3(CO)_{12}$, $Ru_3(CO)_{11}L$, $Ru_3(CO)_{10}L_2$ and $Ru_3(CO)_9L_3$. The bond polarity in these molecules will fall in the order $Ru_3(CO)_{11}L \sim Ru_3(CO)_{10}L_2 > Ru_3(CO)_9L_3 \sim Ru_3(CO)_{12}$. For $Ru_3(CO)_{11}L$ there will be a statistical advantage for substitution, since there are two $Ru(CO)_4$ units available for attack (compared to one in $Ru_3(CO)_{10}L_2$). Steric effects (see above) will also exert an influence leading to a probable sequence of substitution rates although

$$M_3(CO)_{10}L_2 \rightleftharpoons L(CO)_3M{-}M(CO)_4{-}M(CO)_3L$$

$$L(CO)_3M{-}M(CO)_4{-}M(CO)_3L + L \rightleftharpoons L_2(CO)_3M{-}M(CO)_4{-}M(CO)_3L$$

$$L_2(CO)_3M{-}M(CO)_4{-}M(CO)_3L \rightleftharpoons M(CO)_3L_2 + M_2(CO)_7L$$

$$M_2(CO)_7L + 2L \rightleftharpoons M(CO)_3L_2 + M(CO)_4L$$

$$M_3(CO)_{10}L_2 \rightleftharpoons (CO)_4M{-}M(CO)_3L{-}M(CO)_3L$$

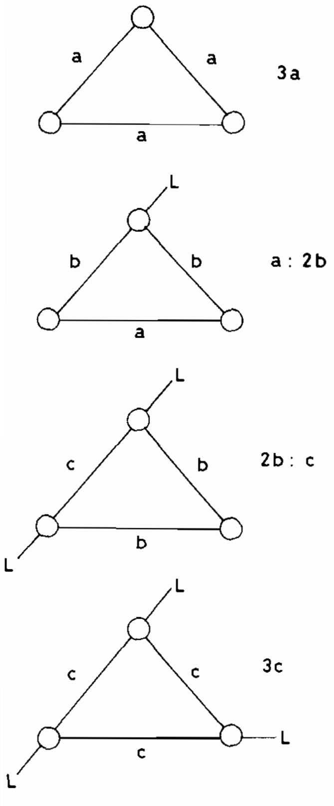
$$(CO)_4M{-}M(CO)_3L{-}M(CO)_3L + L \rightleftharpoons L(CO)_4M{-}M(CO)_3L{-}M(CO)_3L$$

$$L(CO)_4M{-}M(CO)_3L{-}M(CO)_3L \rightleftharpoons M_3(CO)_9L_3 + CO$$

$$L(CO)_4M{-}M(CO)_3L{-}M(CO)_3L \rightleftharpoons M(CO)_4L + M_2(CO)_6L_2$$

$$M_2(CO)_6L_2 + 2L \rightleftharpoons 2M(CO)_3L_2$$

Scheme 2. Substitution reactions of $M_3(CO)_{10}L_2$.



Scheme 3. Bond polarities in $Ru_3(CO)_{12-n}L_n$.

$$Ru_3(CO)_{11}L > Ru_3(CO)_{10}L_2 > Ru_3(CO)_{12} > Ru_3(CO)_9L_3$$

of course the precise order will depend on the nature of L.

Scheme 3 offers a simple explanation of much of the data currently available on the substitution reactions of the trimetal carbonyls $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, e.g.:

(i) that substitution occurs according to the rate eqn.

$$k_{obs} = k_1 + k_2[L]$$

(ii) the k_2 term increases with ligand basicity;

(iii) the formation and decay of intermediates $Ru_3(CO)_{11}L$ and $Ru_3(CO)_{10}L_2$ are observed before final formation of $Ru_3(CO)_9L_3$;

(iv) that in the reaction of $Ru_3(CO)_{12}$ with PBu_3 the ratio of $Ru(CO)_3L_2$:$Ru(CO)_4L$ in the product mixture is 1:2;

(v) the introduction of the 1st ligand L into the cluster increases the rate of CO-dissociation but the introduction of the second or third ligand leads to a somewhat lower CO loss (at least for $L = PPh_3$);

(vi) there is an induction period during the substitution of $Fe_3(CO)_{12}$ (since the rate of substitution will depend on an active concentration of intermediate I);

(vii) that $M_3(CO)_{12}$ and $M_3(CO)_9L_3$ resist substitution to a greater degree than $M_3(CO)_{11}L$ and $M_3(CO)_{10}L_2$;

(viii) the rate determining step need not necessarily be the same for every L or compound $M_3(CO)_{12-n}L_n$.

Finally, this mechanism which involves heterolytic fission of the M–M bond in polymetal carbonyls is not restricted to the compounds discussed here. It may also apply to higher nuclearity clusters, especially those of low symmetry such as $Os_6(CO)_{18}$ [10]. It may also be applied to the dimetal carbonyls $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ although in these cases a slightly modified view of the essential intermediate is required [10].

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