

The mechanism of carbonyl substitution reactions of $\text{Ir}_4(\text{CO})_{12-n}\text{L}_n$ ($n = 0-3$)

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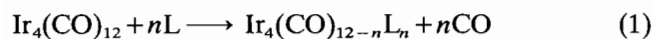
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Abstract

A 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 tetranuclear clusters $\text{Ir}_4(\text{CO})_{12-n}\text{L}_n$ ($n = 0-3$) is described.

There have been relatively few kinetic studies of transition metal carbonyl clusters. In the main, information has tended to be restricted to the substitution reactions of the dimeric carbonyls $\text{Co}_2(\text{CO})_8$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$ and $\text{MnRe}(\text{CO})_{10}$, the trimeric carbonyls $\text{Fe}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ and the tetrameric carbonyl $\text{Ir}_4(\text{CO})_{12}$ [1]. In two earlier reports [2, 3] we discussed a possible new mechanism of carbonyl substitution which we applied to both the dimeric and trimeric series of compounds mentioned above. We argued that most of the kinetic data could be readily explained by a simple mechanism which considers the heteronuclear fission of the metal–metal bond to generate one unsaturated, 16-electron metal centre and one saturated 18-electron metal centre to be the key initial step. In this communication we wish to report the application of the same mechanistic approach to the substitution reactions of $\text{Ir}_4(\text{CO})_{12}$ and its derivatives $\text{Ir}_4(\text{CO})_{12-n}\text{L}_n$ ($n = 1-3$).

The substitution reactions of $\text{Ir}_4(\text{CO})_{12}$ (eqn. (1)) have been studied in detail [4–7] and have been summarised in a standard text [1].



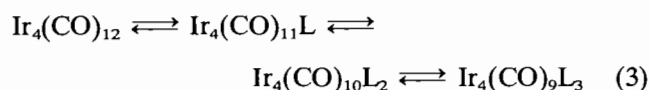
These reactions apparently conform to the rate law given in eqn. (2)

$$\text{rate} = (k_1 + k_2[\text{L}])[\text{Ir}_4(\text{CO})_{12}] \quad (2)$$

and are thus similar to those observed for other, related cluster systems [1]. The ligand independent term k_1 ,

has been interpreted as a CO dissociative step and the ligand dependent term k_2 appears to dominate for good nucleophilic ligands such as CNR, PBU_3 , PPh_3 and P(OR)_3 [5, 8].

This behaviour is somewhat different from that recorded for the monosubstituted compound $\text{Ir}_4(\text{CO})_{11}\text{L}$ ($\text{L} = \text{PPh}_3$, P(OPh)_3 and AsPh_3), for which the k_1 term apparently dominates [6, 7]. Again, this has been interpreted as indicating CO dissociation as the primary step. For this reaction an acceleration in the substitution rate is observed and this acceleration is even more apparent in the successive formation of $\text{Ir}_4(\text{CO})_{10}\text{L}_2$ and $\text{Ir}_4(\text{CO})_9\text{L}_3$. A dependence of the substitution rate on the ligands L already present has been taken to indicate that the donor capability of the ligand is important in stabilising the unsaturated intermediate formed by ligand loss. We shall comment on this again later. The rate of further substitution of $\text{Ir}_4(\text{CO})_9\text{L}_3$ to produce $\text{Ir}_4(\text{CO})_8\text{L}_4$ falls substantially. We have previously suggested [9] that this is possible due to the highly symmetric tris-substituted icosahedral ligand shell in $\text{Ir}_4(\text{CO})_9\text{L}_3$ (see below).



Throughout this sequence of substitution reactions (3), a change in the coordination geometry of the ligand shell is observed (see Figs. 1 and 2). In $\text{Ir}_4(\text{CO})_{12}$, the ligand envelope adopts a cubeoctahedral arrangement (Fig. 2(a)). On replacement of CO by PPh_3 , this geometry changes to the more compact icosahedral arrangement,

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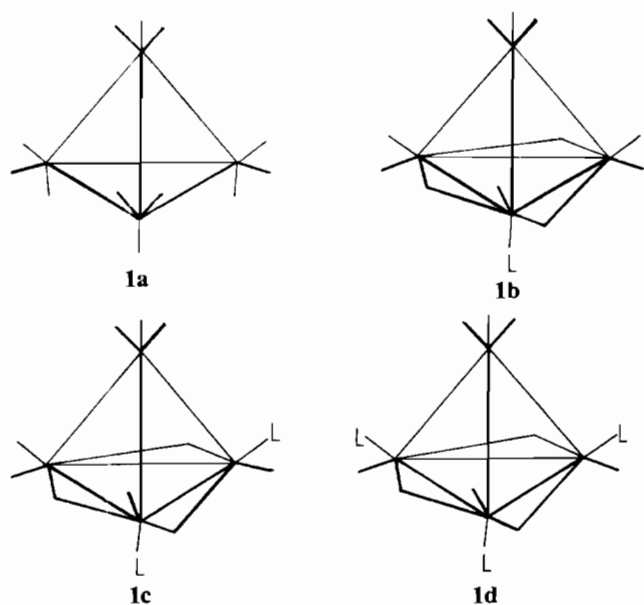


Fig. 1. The molecular structures of $\text{Ir}_4(\text{CO})_{12}$ (**1a**), $\text{Ir}_4(\text{CO})_{11}\text{L}$ (**1b**), $\text{Ir}_4(\text{CO})_{10}\text{L}_2$ (**1c**) and $\text{Ir}_4(\text{CO})_9\text{L}_3$ (**1d**).

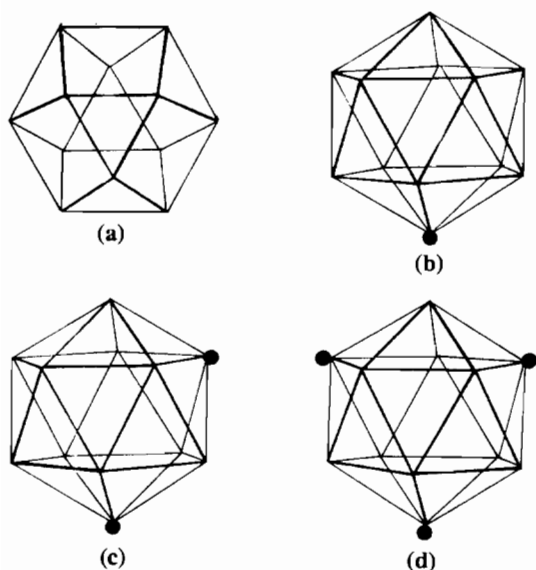


Fig. 2. The ligand polyhedra found for **1a**, **1b**, **1c** and **1d**: (a) cubeoctahedron; (b) 1-substituted icosahedron; (c) 1,7-disubstituted icosahedron; (d) 1,7,9-trisubstituted icosahedron, respectively.

leading to structures based on the quasi- C_{3v} structure with three CO bridges as is found for $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}^*$.

In the first PPh_3 substitution the incoming ligand occupies an axial site on a basal iridium atom [10] (**1b**). When two PPh_3 ligands are substituted into the system, one occupies an axial site and the second an

*Although this is not the case for $\text{Ir}_4(\text{CO})_{11}(\text{CNBu}^t)$ where no kinetic data is available.

equatorial site, both on basal iridium atoms (**1c**). Final substitution gives $\text{Ir}_4(\text{CO})_9(\text{PPh}_3)_3$, with phosphine incorporation at two equatorial sites and one axial site (**1d**), again on basal iridium atoms.

According to the ligand polyhedral model (LPM) [9, 11], the ligand polyhedra in **1b**, **1c** and **1d** correspond to the 1-substituted icosahedron (Fig. 2(b)), the 1,7-disubstituted icosahedron (Fig. 2(c)) and the 1,7,9-trisubstituted icosahedron (Fig. 2(d)), respectively**. In Fig. 2(d) the three PPh_3 ligands are distributed equally within the icosahedral framework; this is more easily seen from the alternative view of the ligand icosahedron given in Fig. 3. It follows that for the 'empty' ligand shell all nine carbonyl ligands are equivalent. Insertion of the Ir_4 tetrahedron into the various substituted ligand shells (Fig. 2(b)–(d)) gives the observed structures (Fig. 1).

An important feature of the 1,7,9-trisubstituted icosahedron (Fig. 2(d)) is that, because of the highly symmetric arrangement of ligands, rearrangement is required before insertion of a fourth ligand grouping if the ligand–ligand interaction is to be minimised. It is this requirement which presumably provides the discontinuity in the substitution process and is a direct result of the tendency of the ligand polyhedron to adopt an icosahedral ligand envelope rather than the cubeoctahedral arrangement observed in the parent $\text{Ir}_4(\text{CO})_{12}$ (**1a**) [9]. Thus, the stereochemical demands of the ligand envelope change as we progress across the series $\text{Ir}_4(\text{CO})_{12} \rightarrow \text{Ir}_4(\text{CO})_{11}\text{L} \rightarrow \text{Ir}_4(\text{CO})_{10}\text{L}_2 \rightarrow \text{Ir}_4(\text{CO})_9\text{L}_3$. Originally, substitution into a cubeoctahedral geometry is required, whereas later, substitution into a quasi-icosahedron has to be considered. This is true irrespective of the reaction mechanism involved, whether it be via a dissociative or associative process.

We have previously proposed [2, 3] that the important, primary step in the mechanism of CO substitution in $\text{Co}_2(\text{CO})_8$, $\text{M}_2(\text{CO})_{10}$ and $\text{M}_3(\text{CO})_{12}$ systems is the heteronuclear cleavage of a metal–metal bond. We believe

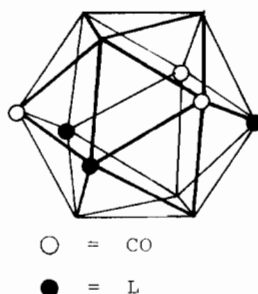


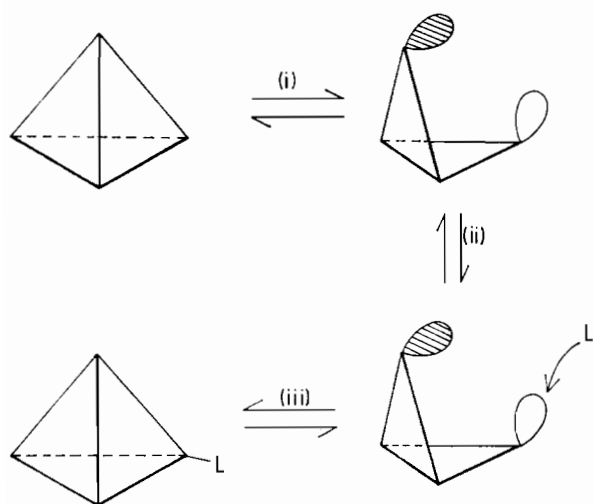
Fig. 3. The tri-substituted icosahedral ligand polyhedron in $\text{Ir}_4(\text{CO})_9\text{L}_3$.

**The application of the LPM to $\text{Ir}_4(\text{CO})_{12}$ and its derivatives will be discussed fully in a forthcoming paper.

that such a step is consistent with most, if not all, available data and may be general to all metal cluster systems.

Application to $\text{Ir}_4(\text{CO})_{12}$ is comparatively straightforward. Opening of one of the Ir_4 tetrahedral edges would produce a quasi-butterfly structure with one 18-electron, saturated metal centre and one 16-electron, unsaturated metal centre. Given that in the parent molecule there are six identical edges, this process can occur in twelve ways, all of which are equivalent (step (i)). In step (ii) the incoming ligand donates into the vacant orbital on the unsaturated metal atom. This is followed by step (iii), CO ejection and the reformation of an Ir–Ir bond (see Scheme 1). Step (i) will be ligand independent, but step (ii) will clearly be favoured for good donors.

For $\text{Ir}_4(\text{CO})_{11}\text{L}$, substitution will be considerably more complex. The symmetry of the compound is lowered and four different tetrahedral edges (a–d) will now be present in the Ir_4 unit (Fig. 4). Heterometallic edge-



Scheme 1. Mechanism of CO substitution for $\text{Ir}_4(\text{CO})_{12}$. Step (i): heteronuclear metal–metal bond cleavage. Step (ii): donation from the incoming substrate L to generate a new M–L bond. Step (iii): CO ejection, followed by M–M bond formation to produce monosubstituted derivative $\text{Ir}_4(\text{CO})_{11}\text{L}$.

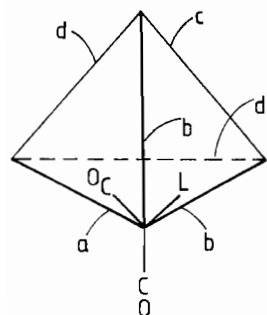


Fig. 4. Tetrahedral edge types in $\text{Ir}_4(\text{CO})_{11}\text{L}$.

cleavage may now produce a range of possible intermediates, depending on the edge-cleavage involved and the site of unsaturation (Scheme 2, (I)–(V)). Cleavage of edges a or d may lead to two different sites of unsaturation, viz. on the $\text{Ir}(\text{CO})_2\text{L}$ unit or on the $\text{Ir}(\text{CO})_3$ unit. For good donors (L) already present in the complex the former would be preferred [2]. The better donors would also tend to stabilise the reaction intermediate, e.g. (I), in line with the observation (see above). Attack at the $\text{Ir}(\text{CO})_2\text{L}$ site would, however, be hindered by the steric bulk of both the ligand L already present in the complex and that of the incoming nucleophile.

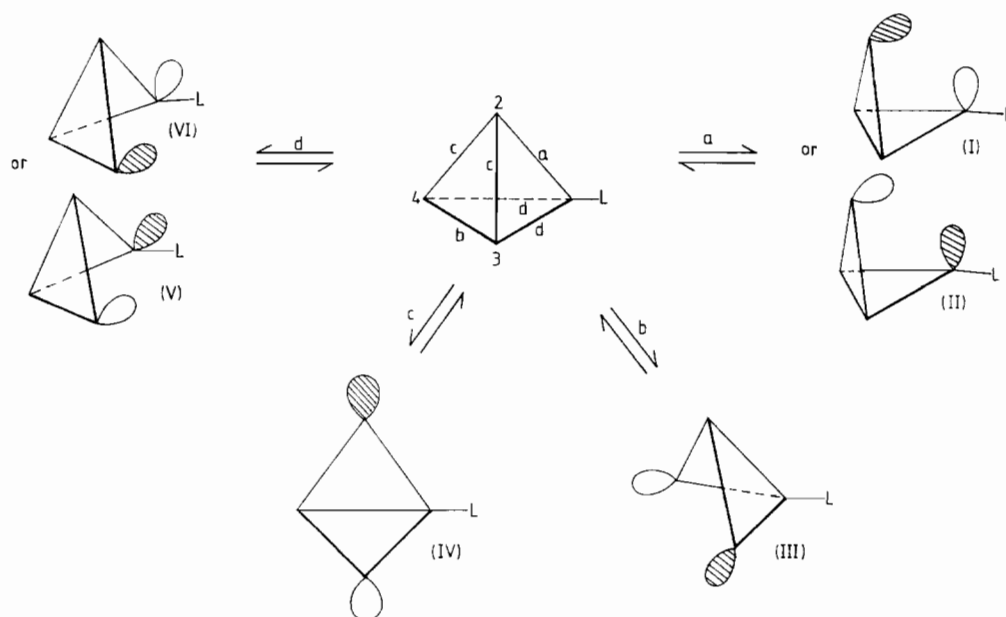
Should attack occur at this site, however, then the highly unfavourable* 1,2-disubstituted icosahedral distribution of ligands would result. It is conceivable that the 1,2-isomer is formed and that interconversion to the observed 1,7-isomer takes place via the anticuboctahedral complementary geometry, but we regard this as less likely than the alternative, viz. attack on Ir(2) or Ir(3).

Heteronuclear fission of edges Ir(2)–Ir(3), Ir(2)–Ir(4) or Ir(3)–Ir(4) (b, c or d) can also occur. This, for reasons we outlined previously [2], we regard as less likely. Formation of the 1,7-isomer automatically leads to axial and equatorial substitution (Fig. 2). Isomerisation to the 1,12-form would generate a structure in which the ligands L would occupy a bridging site and equatorial position of a basal iridium atom (and is therefore excluded for PR_3 ligands) or alternatively, one axial position on a basal iridium atom and one coordination site on the apical iridium atom. Such an isomerisation from the 1,7- to the 1,12-form would almost certainly be a higher energy process, but is known to occur in $\text{Fe}_3(\text{CO})_{10}\text{L}_2$ [12], which also contains a quasi-icosahedral array of ligands.

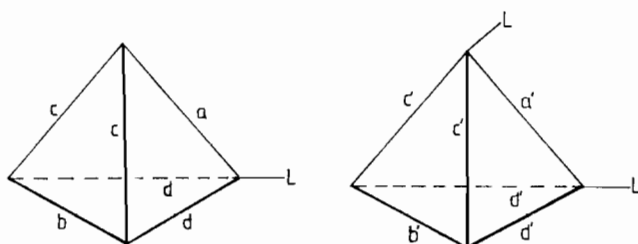
The difference in rate of introduction of 1st, 2nd and 3rd ligands into $\text{Ir}_4(\text{CO})_{12}$ will, in part, be controlled by the ease with which Ir–Ir cleavage occurs. As further L is introduced, the bond polarity is expected to change (Fig. 5) and heteronuclear bond dissociation might reasonably be expected to occur with greater ease [2].

Substitution into $\text{Ir}_4(\text{CO})_{10}\text{L}_2$ apparently yields a 1,7,9-ligand icosahedron. In this arrangement (see above) the L–L interaction is clearly minimised (Fig. 3). This is especially important for larger ligands L. More than one form of $\text{Ir}_4(\text{CO})_9\text{L}_3$ is possible, but the observation that the three ligands occupy two equatorial sites and one axial site on basal iridium atoms is a direct result of the insertion of the Ir_4 tetrahedron into the 1,7,9-icosahedron (Fig. 2(d)). Interestingly, an alternative site occupancy, leading to one equatorial and two axial site occupancy, is also possible. It might be reasonably argued that 1,7,9-distribution of L is a genuine result

*The two L ligands would be adjacent to each other.



Scheme 2.

Fig. 5. Tetrahedral edge types in $\text{Ir}_4(\text{CO})_{10}\text{L}_2$.

of steric constraints, but that the formation of the two equatorial/one axial rather than the one equatorial/two axial is a result of some electronic influence.

Further substitution to give $\text{Ir}_4(\text{CO})_8\text{L}_4$ might be expected to occur easily, given the enhanced activation of the Ir_4 cage by increased bond polarity generated by three ligands L. However, given the fact that it is not possible to arrange four ligands L in equivalent positions within the icosahedron, an additional steric barrier will exist. Additional incorporation of four or more ligands will thus be less problematic for small ligands.

Within this new proposition, solvent effects are difficult to quantify. On first impression there is a tendency to assume that heterolytic metal-metal bond cleavage will produce a dipole and hence be favoured by solvents which favour the separation of charges. This is not necessarily the case. Ligand loss to generate a 16-electron intermediate as with, for example, $\text{Fe}(\text{CO})_5 \rightleftharpoons \text{Fe}(\text{CO})_4 + \text{CO}$, is not taken as producing a $\delta+$ species and the mechanism suggested here is similar. Nevertheless, good donor solvents such as MeCN might be expected to stabilise the reaction intermediate and

influence the direction of the reaction. This aspect has been covered in earlier work [3] and is currently under further investigation.

In summary, we suggest that the reaction schemes outlined in this paper for the substitution reactions of $\text{Ir}_4(\text{CO})_{12-n}\text{L}_n$ provide a totally reasonable explanation of the currently available data. It is exactly the same approach as that described for $\text{Co}(\text{CO})_8$, $\text{M}_2(\text{CO})_{10}$ and $\text{M}_3(\text{CO})_{12}$ systems, accounting for:

- (i) substitution occurring according to the rate equation: $k_{\text{obs}} = (k_1 + k_2[\text{L}])[\text{Ir}_4(\text{CO})_{12-n}\text{L}_n]$;
- (ii) the k_2 term increasing with ligand basicity;
- (iii) substitution reactions of $\text{Ir}_4(\text{CO})_{11}\text{L}$ or $\text{Ir}_4(\text{CO})_{10}\text{L}_2$ being dependent on the basicity (stabilisation of intermediate) and bulk of L, and k_1 becoming increasingly important;
- (iv) further substitution of $\text{Ir}_4(\text{CO})_9\text{L}_3$ being inhibited;
- (v) the distribution of L within $\text{Ir}_4(\text{CO})_{10}\text{L}_2$ and $\text{Ir}_4(\text{CO})_9\text{L}_3$, giving both equatorial and axial distributions of L on basal iridium atoms;
- (vi) some distortion of the Ir_4 metal unit towards a butterfly arrangement [13, 14].

Acknowledgements

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