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The Ligand Polyhedral Model (LPM).

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According to the LPM, different types of carbonyl scrambling within the same molecule (bridge-terminal exchange, rotation, *etc.*) may be explained by a single overall method rather than using an *ad hoc* localised mechanism to account for each process¹⁻³. It does not disagree with the localised process but offers alternative pathways involving the concerted motion of all carbonyl ligands in ways which are well defined in terms of molecular symmetry and based on the polygon or polyhedron defined by the carbonyl ligands. Because it is symmetry governed the number of potential mechanistic pathways may be predicted, and since the mechanism of these fluxional processes tallies exactly with the localised picture, it follows that they are consistent with the spectroscopic data. It should also be noted that the LPM view of cluster carbonyls is commonly used in the description of these compounds even by those who are opposed the model. Mann⁴, for example, uses the LPM to account for the fluxional behaviour of $[\text{Fe}_3(\text{CO})_{12}]$ and describes the rotation of the Fe_3 triangle within the CO icosahedron (or the reverse) *albeit* about a C_5 rather than our preferred C_2 axis. This is very close to our initial postulate.

Concern has been expressed about the minimum energies calculated for $[\text{Fe}_3(\text{CO})_{12}]$ and $[\text{Rh}_4(\text{CO})_{12}]$. Mention has been made that King⁵ has calculated that the C_{2v} isomer of $[\text{Fe}_3(\text{CO})_{12}]$ has a global minimum energy below that of the all-terminal D_{3h} -form. That is totally consistent with the LPM which clearly recognises that the icosahedral C_{2v} form is of lower energy than the anti-cube-octahedral D_{3h} form. No reference was made of the all-important D_3 (fully terminal icosahedral) form which has been shown to have an energy similar to that of the C_{2v} form and which is the essence of the librational component of the LPM. This D_3 form has now been observed experimentally in the mixed carbonyl $[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$ and in other compounds⁶. Reference has also been made to the 'DFT calculations on $[\text{Rh}_4(\text{CO})_{12}]$ which correctly predict that the lowest energy structure to be the C_{3v} form found in the solid state, with the Rh_4 tetrahedron enveloped in a $(\text{CO})_{12}$ icosahedron'. No mention is made of calculations on the postulated T isomer but nevertheless it is rejected. In this connection we refer to Lauher⁷ who said 'The global minimum in the $[\text{M}_4(\text{CO})_{12}]$ systems appears to correspond to a third isomer that has not yet been observed experimentally. This isomer has T symmetry and is analogous to the D_3 isomer in the $[\text{M}_3(\text{CO})_{12}]$ system. The carbonyl packing in the calculated T isomer corresponds to a distorted icosahedron. The C_{3v} bridged isomer also has a distorted icosahedral packing of the carbonyls and can be converted into the T isomer by rotation of about 12° of the M_4 metal core within the carbonyl polyhedron'. This is entirely consistent with our view. We would emphasise that throughout these calculations workers use the LPM description of the molecules under investigation.

The LPM consists of two parts. First, there is the libration of the metal unit within a fixed carbonyl polytope or polyhedron (or the reverse). This is a well-established physical phenomenon. Second, there is a polyhedral re-arrangement of the carbonyl envelope which takes place through a

'complementary geometry' *via* the classic diamond-square-diamond process. This is based firmly on the views of rearrangement in mononuclear systems, e.g. rearrangement of the vertices of an octahedral complex *via* a trigonal prismatic complementary geometry. Both libration and polyhedral rearrangement will always be available to carbonyl systems and they are expected to act in concert. Libration is regarded as the lower energy process. It would seem that only libration has been considered and there is no mention polyhedral rearrangement which is an essential component of LPM and a major part of our discussion of $[\text{Rh}_6(\text{CO})_{15}\text{L}]$.

In related work, Garland⁸ identified a new C_{3v} isomeric form of $[\text{Rh}_4(\text{CO})_{12}]$ with an anti-cube-octahedral carbonyl shell and states 'The C_{3v} anti-cube-octahedral symmetry was suggested by Johnson as the most appropriate intermediate that can explain the total coalescence of the NMR signal at $T=-5\text{K}$ '. Significantly, this polyhedral interchange requires the CO polyhedron to rearrange from an icosahedron to an anti-cube-octahedron in concert with the movement of the internal metal unit'. This is exactly in accord with our view. The transition from icosahedron to anti-cube-octahedron must go through an intermediate or complementary geometry and the possibility of an intermediate with T-symmetry in this process cannot be excluded and must remain a distinct possibility.

For $[\text{Rh}_4(\text{CO})_8\text{L}_4]$ a mechanism involving the initial formation of an all terminal isomer has been proposed. This exactly parallels our proposed route for $[\text{Rh}_4(\text{CO})_{12}]$. Whether the CO ligands are adjusted by bridge-opening or by the movement of the metal unit within the carbonyl envelope is immaterial. No comment about the polyhedral arrangement of the twelve ligands in this all terminal intermediate was made but in the ground-state structure it is known to be an icosahedron. The mechanism is then said to continue *via* the rapid rotation of each $\text{Rh}(\text{CO})_2\text{L}$ group about the *pseudo*- C_3 axis'. Rotation about this axis converts the ligand polyhedron into its complementary geometry (this is the clearly understood method of going from an icosahedron to a cube-octahedron!). This corresponds precisely to the LPM approach⁹.

It has been said that the inability of phosphine ligands to form bridge bonds puts them outside the scope of the LPM. Yes, they cannot bridge but, as we have demonstrated elsewhere, clusters containing these ligands are most definitely included. In fact, the loss of symmetry they introduce can be an aid. In our paper we apply the LPM to $[\text{Rh}_6(\text{CO})_{15}\text{L}]$ and comment 'For substituted derivatives e.g. $[\text{Rh}_6(\text{CO})_{15}\text{L}]$, the emergence of a second process follows naturally from the reduction in symmetry and because the ligand L cannot occupy a bridging position'.

Using examples of other Rh compounds it has been said 'all these CO-migrations cannot arise from localised librations of the metal polyhedron within a CO polyhedron using the LPM'. No evidence to support this view has been provided and we have not published our work on these compounds. Having said that, looking at $\{\text{Rh}_{13}\text{H}_n(\text{CO})_{24}\}^{(5-n)-}$ ($n = 2$ or 3) for example, application of the LPM reveals three pathways which arise by libration about each of the three C_2 axes of the Rh_{13} anti-cube-octahedron. Two are equivalent. A fourth libration axis falls through the principal C_3 axis. This corresponds exactly with the recorded behaviour. Similarly, libration about the principal C_2 axis through the A-A vector in the Rh_6 compound, and through the principal C_3 axis in the Rh_7 compound, would appear to support the LPM approach. We would respectively suggest that a full discussion of this work awaits our full report⁹.

We would emphasise that the LPM approach to $[\text{Rh}_6(\text{CO})_{15}\text{L}]$ ($\text{L} = \text{CO}$ or PR_3), predicts the same number of mechanistic pathways as the localised approach and therefore does not, as suggested, predict a single rate constant.

In conclusion, to reject the whole (LPM) approach on the basis of one proposed intermediate, a view which itself can be questioned, is at the very least ill-considered. There can be little doubt that the LPM will have its limits but to suggest that it is inapplicable to certain molecules without exploring the possibility is unreasonable. For $[\text{Rh}_6(\text{CO})_{15}\text{L}]$, even if the LPM is rejected, the proposed mechanisms fit all the experimental data, are predictable and far simpler than those published. Again, despite their objections, it is highly significant that workers in the area including Heaton (*vide supra*) use the LPM description of the Rh_4 compounds.

We believe we have responded to all Heaton's objections.

Finally, we would add that the LPM was the first to explain the complex structure of the carbonyl clusters and the number and type of bridging carbonyl ligands they contain. It may also be used to rationalise the structure of isomers and the variation in fluxional behaviour and isomerisation processes they undergo, the disorder they frequently show in the solid state and the fluxionality in they undergo in the solid, the substitution behaviour they, *etc, etc*. Importantly, it also offers an explanation for the range of energies observed for the observed fluxional behaviour, and the reason why fluxionality occurs. The localised model offers no explanations. It is a model which serves as a basis for the whole of carbonyl cluster behaviour and is not reserved simply to fluxional mechanisms. To reject it on the basis of one minor component which is itself in doubt is totally unreasonable.

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