Fluxional Behaviour of the Carbonyls $[M_3(CO)_{12}]$ (M = Fe, Ru or Os)

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A study of the crystal structures of the carbonyls $[M_3(CO)_{12}]$ (M = Fe, Ru or Os) and a series of their derivatives $[M_3(CO)_{12-n}L_n]$ has revealed good evidence in support of the hypothesis that the mechanism of ligand fluxionality goes *via* the intermediacy of an anticubeoctahedral complementary geometry. Several examples of systems with an icosahedral distribution of ligands and quasi-D_3 symmetry have been identified providing additional support for our earlier suggestion that a second isomer of $[Fe_3(CO)_{12}]$, which exists in solution, adopts a similar D_3 structure.

In 1976 we first suggested[1] that the structures of the cluster carbonyls of generic formula $M_m(CO)_n$ could be most conveniently explained by the Ligand Polyhedral Model (LPM) which views the molecular structures of these often apparently complicated species as a consequence of packing one polyhedron or polygon (the M_m metal unit) within another [the $(CO)_n$ carbonyl ligand polyhedron]. In subsequent papers[2,3] we demonstrated that this model works remarkably well for a comprehensive range of neutral and anionic carbonyl clusters, permitting for the very first time a clear understanding of the *apparently* anomalous structures of, for example $[Fe_3(CO)_{12}]$[4] and $[Co_4(CO)_{12}]$.[5] The LPM also provided a perfectly satisfactory explanation for the change in carbonyl bonding modes from bridging to terminal on descending a given transition-metal triad, *e.g.* $[Fe_3(CO)_{12}]$[2] with two μ-bridges along one Fe–Fe edge and C_{2v} symmetry, and $[M_3(CO)_{12}]$[6] (M = Ru or Os) with no CO bridges and D_{3h} symmetry. It also accounts for the presence of μ_3 face bridges in $[Rh_6(CO)_{16}]$ and for the occurrence of two isomers of $[Ir_6(CO)_{16}]$, one with four μ bridges and one with four μ_3 bridges.[7] More recently, Lauher,[8] in a detailed analysis of the same compounds, used the same polyhedral view of their molecular structures as the basis of his investigation of their molecular mechanics. He was able to calculate the relative stabilities of the various structural possibilities of a series of molecules of type $M_m(CO)_n$.

In a subsequent communication[9] we argued further that the existence of additional isomeric forms of $[Fe_3(CO)_{12}]$ which are observed in solution[10] could also be readily explained in terms of the LPM. We recognised that there were three *idealised* orientations of the Fe_3 triangle within the icosahedron of carbonyl groups, giving rise to three different structures for the molecule, two of symmetry C_{2v} and one of D_3.

This suggestion provided for the first time a satisfactory explanation of the observed infrared spectra for mixtures of the isomeric forms in solution. We also recognised that interconversion between these isomers could occur by the simple libration of the Fe_3 triangle within the icosahedron of carbonyls. This led in turn to an understanding of the detailed mechanism[11] for the fluxionality exhibited by $[Fe_3(CO)_{12}]$ in solution,[10] and as a solid.[12] Essentially, we argued that carbonyl fluxionality takes place by a process which involves both the libration of the metal triangle in the ligand envelope, and the flexing and ultimate polyhedral rearrangement of the carbonyl polyhedron. Libration of the metal triangle must be dominant in the solid and, as outlined above, brings about the interconversion of C_{2v} and D_3 forms (Fig. 1). During this process some flexing of the carbonyl polyhedron must also occur. However, the extent of this flexing will be constrained by the demands of the crystallographic lattice. It must be emphasised that by this process equilibration of CO groups can occur without the interchange of positions within the carbonyl icosahedron. In solution, however, when the constraints of the rigid crystallographic lattice are removed, carbonyl interchange may occur. We concluded that this process would correspond to a genuine polyhedral interconversion in which CO ligands interchange positions, probably involving an anticubeoctahedron transition state [Fig. 2(*a*)] and embracing all isomeric forms of the molecule with symmetries C_{2v}, D_3 and D_{3h}. This is entirely analogous to the mechanism of fluxional rearrangement commonly accepted for simple co-ordination compounds, *e.g.* as in the Berry pseudo-rotation for five-co-ordinate systems.

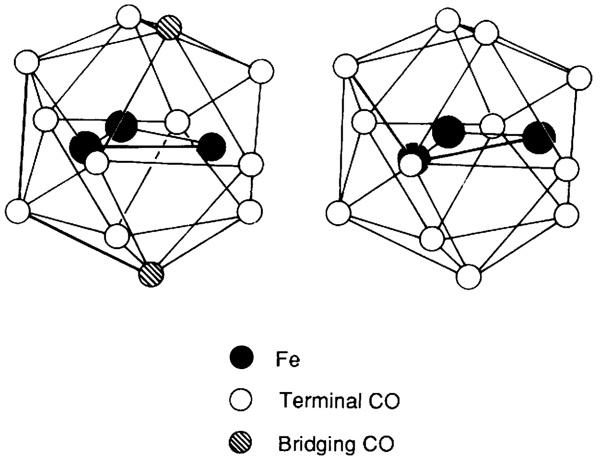


Fig. 1 The possible structures of the isomeric forms of $[Fe_3(CO)_{12}]$

We regard this behaviour as general and applicable to all carbonyl clusters, the only essential difference between one cluster and another being the overall cluster geometry and the symmetry of the ligand polyhedron. Thus, we proposed[2] that the apparently different patterns of carbonyl scrambling observed in the tetrameric carbonyls $[M_4(CO)_{12}]$ (M_4 = Co_4, Rh_4 or $RhCo_3$) or $[Ir_4(CO)_{11}(PPh_2Me)]$ and other related derivatives may all be described in terms of a concerted ligand-polyhedral rearrangement derived from the overall molecular symmetry. We suggested that the initial icosahedral envelope of CO ligands undergoes concerted distortion *via* a suitable intermediate or transition state (complementary geometry), which we *chose* to be an anticubeoctahedron, as in the case of $[Fe_3(CO)_{12}]$ or cubeoctahedron, as with $[M_4(CO)_{12}]$, to affect

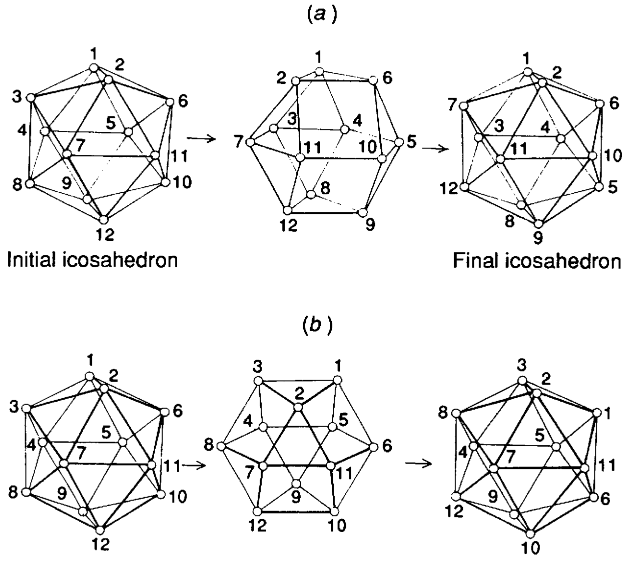
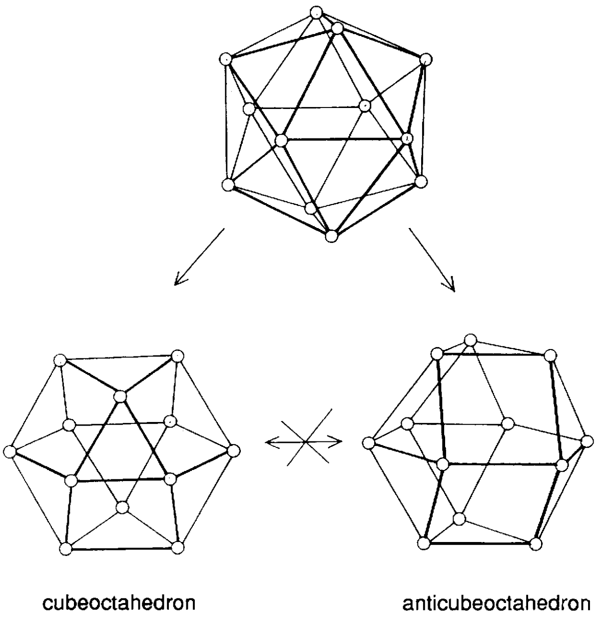


Fig. 2 Rearrangement of the icosahedron *via* (*a*) an anticubeoctahedral transition state, (*b*) a cubeoctahedral transition state



the pattern of ligand permutations. There is often confusion between these two polyhedra. For convenience, the cubeoctahedron and the anticubeoctahedron are illustrated. Both may be derived from the icosahedron by the cleavage of six edges, but differ in the distribution of the edges cleaved. The cubeoctahedron is closely related to cubic close packing with a 3:6:3′ distribution of vertices, whereas the anticubeoctahedron is related to hexagonal close packing with a 3:6:3 relationship of vertices. This difference is extremely important, for whereas the rearrangement through the former does *not* permit complete interchange of vertices (all antipodal relationships are retained), the latter does allow full permutation of the twelve vertices.

An essential feature of this proposal was the recognition of the role of both metal and ligand substitution and their ability to affect those permutations by changing the symmetry of the cluster. In the isolated icosahedron, rearrangement to the cubeoctahedron may occur *via* one of the five symmetry-equivalent ways, but when, for example, there is an M_4 tetrahedron within the icosahedron {to give the C_{3v} $[Rh_4(CO)_{12}]$ structure} this degeneracy is lifted. The degeneracy may be lifted further by the incorporation of a C_{3v} M_3M' metal unit, or by substitution of one or more CO groups in the ligand envelope by a different ligand, such as R_3P or CNR. Eventually, it is possible completely to remove the five-fold degeneracy of the original icosahedron. These lower-symmetry 'modes' give rise to different scrambling patterns. The same argument has been extended to $[Fe_3(CO)_{12}]$ and its derivatives.

The most important feature of this approach is that, rather than invoke an individual *ad hoc* mechanism to rationalise *each* observed fluxional process, there is a *single* type of carbonyl-scrambling pathway involving the concerted motion of all the carbonyl ligands in ways that are well defined in terms of molecular symmetry. As mentioned above, this single type of interconversion corresponds to the ligand permutation processes so commonly encountered for mononuclear co-ordination complexes, and will be dependent on the number of ligands present and the polygon or polyhedron they define. These may not necessarily conform to an idealised form and some distortion may be observed; this distortion will be expected to occur along that vector corresponding to the reaction pathway.

The problem with our system, just as with the more simple co-ordination compounds, is to spot the correct complementary geometry.[13] In the discussion above we assumed it to be an anticubeoctahedron for $[Fe_3(CO)_{12}]$ or cubeoctahedron for $[M_4(CO)_{12}]$ because these particular geometries have been observed for the carbonyl ligands in the compounds $[Ru_3(CO)_{12}]$ and $[Ir_4(CO)_{12}]$ respectively. Although this proposed unified mechanism of carbonyl fluxionality is attractive and apparently fits extremely well all the available experimental data and all the mechanistic pathways based on spectroscopic data, definitive proof is lacking. Therefore, although we favour, for example, the icosahedral $\longrightarrow$ anticubeoctahedral $\longrightarrow$ icosahedral interconversion (Fig. 2) in our above arguments, the alternative possibility *viz* icosahedron (bicapped pentagonal antiprism) $\longrightarrow$ bicapped pentagonal prism $\longrightarrow$ icosahedron, or any other, cannot be ruled out solely on the basis of the available spectroscopic data. In this paper we provide evidence to support the supposition that carbonyl fluxionality in $[Fe_3(CO)_{12}]$ does occur *via* an anticubeoctahedral complementary geometry.

Method

The fractional coordinate data for the structures[14–48] were retrieved from the Cambridge Structural Database *via* the Crystal Structure Search Retrieval program at Daresbury Laboratory.[49] Pictures of the ligand polyhedra and graphical data were generated using the program PLUTO[50] and EASYGRAPH respectively. Molecular geometry calculations utilised CALC.[51] The calculated parameters which were generated used as their basis an idealised anticubeoctahedral ligand polygon; each vertex describing the position of an O and P atom [Fig. 3(*b*)]. The O atoms are used to describe the polyhedron because M–O distances are more comparable with M–P than are M–C. The M_3 triangle sits in the plane described by the six shaded central atoms. A projected view of the polyhedron from the top face [Fig. 3(*a*)] shows the triangular polygon faces and the M_3 triangle perfectly aligned with each other. As distortion towards icosahedral occurs these triangular faces become rotated (α) with respect to each other [Fig. 3(*c*)] and the six shaded atoms deviate from planarity [Fig. 3(*d*)]. A similar comparison can be made between the M_3 triangle and either of the top or bottom triangular faces (β and γ respectively). In the most extreme case, *i.e.* icosahedral, the triangular faces are fully staggered [Fig. 3(*e*)] and the six shaded atoms adopt the 'chair' conformation [Fig. 3(*f*)]. The deviation from planarity of the six shaded atoms is given as their average deviation (σ) from the calculated, best-fit plane of all six.

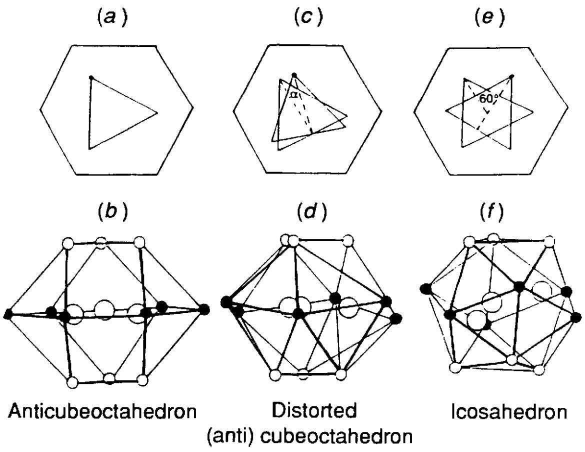


Fig. 3 Assignment of polyhedral parameters

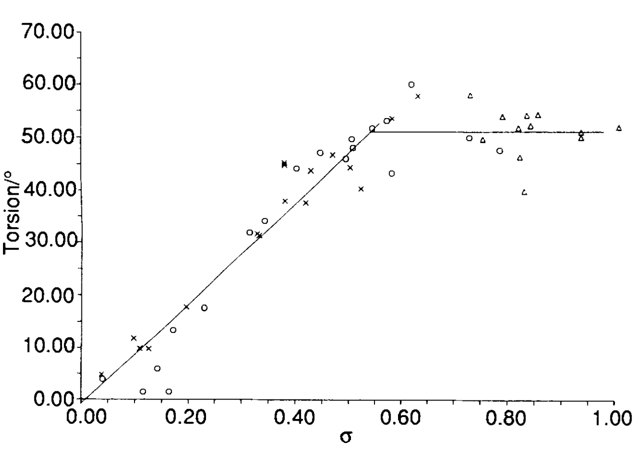


Fig. 4 Distortion from cubeoctahedral to icosahedral ligand arrangements in compounds of the type $[M_3(CO)_{12-n}L_n]$; (M = Ru (○), Os (×) or Fe (△))

However, the above description is of an idealised situation; substitution of CO by nPR_3 causes some distortion of the ligand polyhedron. Reasons for the distortion include: (*a*) shortening of M–L bonds (for Ru, Ru–O is typically 3.05 Å, compared with 2.25 Å for Ru–P); (*b*) steric effects, the cone angle of CO is approximately 95° compared with, for example, 145° for PPh_3; (*c*) different electronic properties of the various PR_3 ligands compared with CO and each other; and (*d*) extra constraints such as chelate 'bite' angles.

Hence, the 'normalised' situation for a given $[M_3(CO)_{12-n}L_n]$ compound is that no one plane, as described above, is parallel to another. This is seen in pictures of the compound's ligand polyhedron as 'missing' edges and an overall irregularity of shape. We have quantified, to some extent, this deviation by calculating the dihedral angles between given planes of the polyhedra, again based on anticubeoctahedral geometry. These are as follows: ρ = the angle formed by the top triangular face with the bottom triangular face; φ = the angle formed by the top triangular face with the M_3 triangle; π = the angle formed by the bottom triangular face with the M_3 triangle; τ = the angle formed by the best-fit plane of the six shaded atoms with the M_3 triangle. As a general rule, the values for these angles increase as the transition from anticubeoctahedral to icosahedral progresses.

Results and Discussion

Several years ago Dunitz and Burgi[52] proposed that crystallography can provide important information about the dynamic aspects of molecular structure of the sort described above. Molecules are not rigid and, as a consequence, their molecular geometry depends to some extent on their environment. This means that if a range of crystal structures of a series of similar molecules is examined a variation in the structural parameters will be found. If a species has a low-frequency vibrational mode (*i.e.* one with a large amplitude) it is likely that the structure will vary most along the pathway followed by that vibration. Studies of crystal structures can therefore reveal information about such vibrational modes, which may be reaction pathways leading to transition states or complementary geometries. For example, if five-co-ordinate phosphorus compounds are considered, most will be trigonal bipyramidal, a few will be square pyramidal and many will lie along the pathway linking these two configurations. Thus, the crystal structures of many different phosphorus compounds with co-ordination number five yield information about the Berry pseudo-rotation.

In this work we have used the Cambridge Database of crystal structures to study the structures and ligand polyhedra of a range of $[M_3(CO)_{12-n}L_n]$ (M = Fe, Ru or Os) cluster compounds. According to the views outlined above, if our suggestions for the mechanism of ligand fluxionality in these systems are correct then we should see some structures with an icosahedral distribution of ligands and with symmetry either of C_{2v} or D_3, some structures with an anticubeoctahedral distribution of ligands with symmetry D_{3h} and, most importantly, structures along the pathway between the two extremes of symmetries C_{2v} and D_{3h}. In a previous paper in this series we showed, from an analysis of the atomic displacement thermal parameters (a.d.p.s.), that the iron atoms of $[Fe_3(CO)_{12-n}L_n]$ show preferential motion of the triangle about the proposed C_2 axis as predicted for the $C_{2v} \longrightarrow D_3$ interconversion, and we anticipated that the work reported here would provide additional and conclusive support for this process and for the next stage of the interconversion process from D_3 to D_{3h}.

The results of our examination of these compounds are presented in Tables 1–3. The methods of investigation and tabulation are given in Method. It was important to determine whether or not the transition from anticubeoctahedral to icosahedral is a single, smooth continuous process. In order to illustrate the changes in ligand polyhedral geometry *actually* taking place, a plot of α (the rotation angle between the top and bottom triangular faces of the polyhedron) against σ (the deviation from planarity of the middle six atoms of the polyhedron (see Method) was drawn. A straight-line relationship would indicate a single, smooth transition, whereas a two-stage process would show a non-linear relationship. From a plot of all the structures examined, embracing all metals, Fe, Ru and Os (Fig. 4), it is clear that a smooth transition from the two extremes, C_{2v} bridged form and D_{3h} non-bridged form, is observed. In general, and as expected, the icosahedral carbonyl polyhedron is most frequently observed for the iron series, with less-frequent examples for ruthenium and fewer still for osmium. However, there are relatively few examples of these compounds with exactly the same chemical composition for these metals, making direct comparisons difficult. We shall comment on this later. As predicted in an earlier report, in general, substitution of carbonyl ligands by bulkier ligands such as tertiary phosphines or phosphites generally causes the ligand polyhedron to move away from anticubeoctahedral towards the icosahedral form.

The prototype for the C_{2v} form is clearly $[Fe_3(CO)_{12}]$,[4] although in the solid even this compound shows a slight deviation towards the D_3 form. The mixed-metal cluster $[Fe_2Os(CO)_{12}]$,[47] which has recently been the subject of an X-ray diffraction analysis, essentially retains the same C_2 structure with an icosahedral ligand polyhedron. Neither is significant deviation from the C_{2v} structure afforded by phosphine or phosphite derivatives of $[Fe_3(CO)_{12}]$. Only one ruthenium cluster, the tetraphosphine-substituted $[Ru_3(CO)_8\{PPh(OMe)_2\}_4]$,[14] has a C_{2v}-bridged structure similar to that of $[Fe_3(CO)_{12}]$ (see Fig. 5). In the mixed-metal carbonyl compound [FeRu$_2$-

Table 1 Polyhedral parameters for $[Ru_3(CO)_{12-n}L_n]$ (n = 1–4)

Compound	α	β	γ	ρ	φ	π	τ	σ	Ref.
$[Ru_3(CO)_{12}]$	3.86	2.41	1.45	0.23	0.16	0.14	0.32	0.039 85	32
$[Ru_3(CO)_{11}\{PPh(OMe)_2\}]$	46.04	34.79	21.70	3.55	1.56	2.08	3.01	0.496 21	30
$[Ru_3(CO)_{11}\{P(OCH_2CF_3)_3\}]$	31.87	41.11	13.79	1.91	1.35	0.82	2.10	0.313 93	30
$[Ru_3(CO)_{11}(PPh_3)]$	17.59	13.58	4.00	0.97	0.51	0.56	2.07	0.228 93	33
$[Ru_3(CO)_{11}\{P(C_6H_{11})_3\}]$	5.94	4.79	1.14	0.29	0.36	0.10	1.80	0.141 80	34
	13.38	8.78	4.60	1.38	0.76	0.74	1.36	0.169 87	
$[Ru_3(CO)_{10}\{PPh(OMe)_2\}_2]$	47.16	21.79	36.17	1.94	1.78	1.17	2.93	0.447 88	37
$[Ru_3(CO)_{10}\{P(OCH_2CF_3)_3\}_2]$	34.17	40.70	16.79	1.68	1.29	0.71	0.98	0.342 30	37
$[Ru_3(CO)_9\{P(OCH_2CF_3)_3\}_3]$	49.67	33.06	10.04	1.97	0.97	1.05	0.23	0.507 21	38
$[Ru_3(CO)_8\{PPh(OMe)_2\}_4]$	47.55	37.27	29.33	10.56	9.24	8.67	17.11	0.787 12	14
$[Ru_3(CO)_{11}(CNBu^t)]$	43.32	33.61	17.54	5.11	1.37	4.20	2.24	0.583 66	28
$[Ru_3(CO)_{11}\{P(OCH_2)_3CEt\}]$	48.06	35.29	23.28	2.54	1.16	1.43	0.29	0.509 67	30
$[Ru_3(CO)_8\{Me_2AsC{=}CAs(Me)_2C_2F_4\}_2]$	49.94	24.85	33.70	1.98	1.23	1.23	3.61	0.730 62	25
$[Ru_3(CO)_8(dpam)_2]$*	44.18	18.47	34.48	0.77	1.35	0.89	0.37	0.403 01	26
$[Ru_3(CO)_{10}(dppe)]$	59.94	30.85	32.12	3.73	1.33	2.56	2.44	0.620 86	27
$[Ru_3(CO)_{10}(dpam)]$*	51.72	25.44	32.43	3.49	0.93	2.57	1.12	0.545 94	29
$[Ru_3(CO)_{10}(dppm)]$	53.14	36.63	32.51	3.33	1.63	1.92	0.95	0.574 48	31
$[Ru_3(CO)_9\{\mu_3\text{-}(Bu_2P)_3SiMe\}]$	1.50	45.1	3.59	0.20	0.04	0.19	0.77	0.163 33	35
$[Ru_3(CO)_9\{Ph_2PCHP(Ph)C_6H_4PPh\}]$	1.43	1.14	2.59	0.64	0.33	0.97	1.60	0.115 18	36

* dpam = bis(diphenylarsino)methane.

Table 2 Polyhedral parameters for $[Os_3(CO)_{12-n}L_n]$ (n = 1–6)

Compound	α	β	γ	ρ	φ	π	τ	σ	Ref.
$[Os_3(CO)_{12}]$	4.76	4.10	0.67	0.21	0.12	0.30	0.21	0.378 6	35
$[Os_3(CO)_{11}(H_2NPBu^t_2)]$	9.79	5.12	4.65	1.43	1.11	0.51	2.08	0.108 36	40
	11.73	7.29	4.45	0.21	0.75	0.66	1.61	0.096 92	
$[Os_3(CO)_{11}(PPh_3)]$	17.75	3.60	14.14	0.55	0.27	0.50	1.77	0.194 58	30
$[Os_3(CO)_{11}\{PPh(OMe)_2\}]$	31.66	14.67	17.00	1.17	0.41	0.81	0.53	0.327 84	30
$[Os_3(CO)_{11}\{P(OMe)_3\}]$	9.72	8.99	0.71	0.28	0.32	0.29	1.30	0.125 02	30
$[Os_3(CO)_{11}\{P(NHPh)Ph_2\}]$	53.53	36.12	28.18	1.10	1.00	0.50	0.99	0.584 53	41
$[Os_3(CO)_{11}\{P(C_6F_5)_3\}]$	31.34	11.15	40.06	1.70	0.98	0.85	1.93	0.332 10	48
$[Os_3(CO)_{10}(PPh_3)_2]$	57.79	25.46	26.24	0.42	1.10	1.51	5.19	0.633 44	37
	44.34	36.81	7.25	1.64	1.05	2.34	2.43	0.504 22	
$[Os_3(CO)_{10}\{PPh(OMe_2)\}_2]$	43.80	21.36	30.21	1.80	1.22	0.76	2.63	0.429 98	37
$[Os_3(CO)_{10}\{P(OMe)_3\}_2]$	38.00	18.49	40.81	0.27	0.69	0.78	1.94	0.380 20	30
$[Os_3(CO)_9(PPh_3)_3]$	40.31	14.48	33.93	2.56	2.64	1.44	0.38	0.523 93	38
$[Os_3(CO)_{11}(CNBu^t)]$	37.61	35.66	13.77	3.12	0.27	3.02	4.03	0.419 34	43
$[Os_3(CO)_6\{P(OMe)_3\}_6]$	44.81	17.22	32.70	0.00	0.00	0.00	0.00	0.380 31	37
	45.24	17.65	32.70	0.00	0.00	0.00	0.00	0.380 30	
$[Os_3(CO)_{10}(dppe)]$	46.75	36.23	23.37	2.58	0.27	2.58	0.44	0.471 49	38

Table 3 Polyhedral parameters $[Fe_{3-x}M_x(CO)_{12-n}L_n]$ (n = 1–3, x = 1 or 2, M = Ru or Os)

Compound	α	β	γ	ρ	φ	π	τ	σ	Ref.
$[Fe_3(CO)_{12}]$	51.89	23.51	30.34	13.37	12.29	13.50	16.63	1.010 09	21
$[Fe_3(CO)_{11}(CNCF_3)]$	51.78	29.51	22.67	18.20	12.50	19.85	22.04	0.822 32	19
	58.02	29.91	25.38	14.33	11.70	13.07	20.29	0.732 79	
$[Fe_3(CO)_{11}(PPh_3)]$	49.65	23.91	31.68	14.06	9.67	9.98	16.24	0.756 48	19
	54.28	23.78	31.35	11.19	8.97	9.87	18.23	0.858 33	
$[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$	51.01	18.95	26.99	12.33	13.41	12.20	19.98	0.938 68	22
$[Fe_3(CO)_{11}(CNBu^t)]$	50.01	30.91	21.67	16.57	13.82	19.33	19.24	0.938 63	18
$[Fe_3(CO)_{10}(CNBu^t)_2]$	54.14	32.86	25.00	15.42	12.00	14.51	19.23	0.837 83	23
$[Fe_3(CO)_9(PPhMe_2)_3]$	52.18	36.17	26.03	14.35	11.46	13.36	21.25	0.844 86	20
$[Fe_3(CO)_{10}\{Me_2AsC{=}CAs(Me)_2C_2F_4\}]$	53.94	34.90	26.62	15.09	15.98	14.09	22.08	0.792 16	24
	46.31	36.20	22.34	16.48	14.65	9.27	21.12	0.825 07	
$[Fe_3(CO)_{10}\{o\text{-}C_6H_4(AsMe_2)_2\}]$	39.85	19.42	39.43	21.58	12.26	12.39	12.27	0.831 87	17
$[Fe_2Ru(CO)_{11}(PPh_3)]$	54.43	23.38	31.89	18.58	14.12	14.25	19.27	0.878 45	46
$[Fe_2Ru(CO)_{11}\{P(OMe)_3\}]$	56.75	24.50	30.89	19.51	16.51	15.27	21.81	0.784 26	46
$[Fe_2Os(CO)_{12}]$	56.31	33.34	34.02	17.00	18.53	18.74	26.28	0.775 52	47
	53.11	24.23	34.02	17.12	13.61	14.63	19.32	0.812 68	
$[FeRu_2(CO)_{11}(PPh_3)]$	54.81	29.25	31.36	13.33	6.24	7.49	7.91	0.691 41	15
$[FeRu_2(CO)_{10}(PPh_3)_2]$	49.59	25.18	32.42	12.86	8.53	8.53	14.67	1.020 90	15

$(CO)_{10}(PPh_3)_2]$[46] (see Fig. 6) the two axial carbonyls on the iron atom are bridging and the structure has C_{2v} symmetry.

There is no example of the idealised D_3 structure for any simple binary carbonyl. However, various phosphine or phosphite derivatives of $[Ru_3(CO)_{12}]$ have been found to possess the D_3 structure very similar to that produced during the libration of the Fe_3 triangle within the carbonyl icosahedron. In particular, in a number of substituted derivatives of

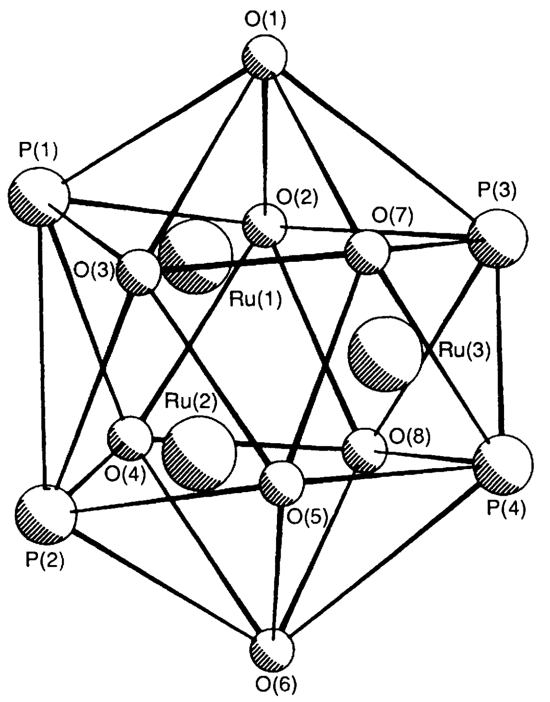


Fig. 5 The ligand polyhedron described by $[Ru_3(CO)_8\{PPh(OMe)_2\}_4]$

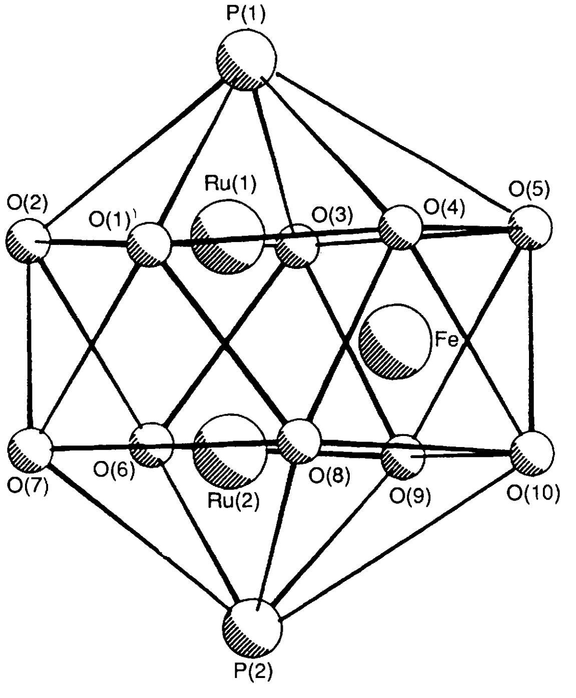
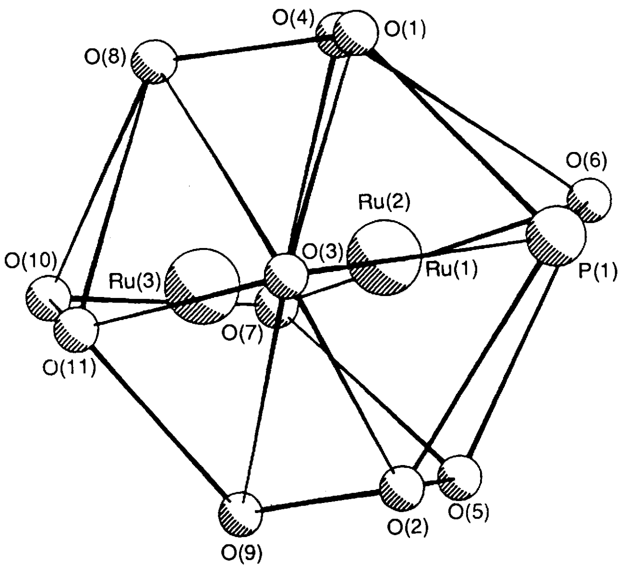


Fig. 6 The ligand polyhedron described by $[FeRu_2(CO)_{10}(PPh_3)_2]$



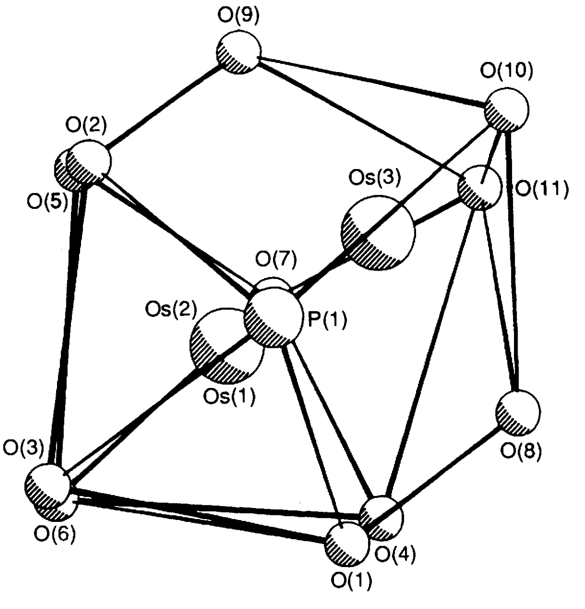


Fig. 7 The ligand polyhedra described by $[Ru_3(CO)_{11}(PPh_3)]$ and $[Os_3(CO)_{11}(PPh_3)]$

both ruthenium and osmium of the type $[M_3(CO)_{10}(L-L)]$ [M = Ru, L-L = $Ph_2P(CH_2)_nPPh_2$, $n = 1$ = dppm; M = Os, $n = 1$ = dppm; $n = 2$ = dppe; $n = 3$ = dppp; or $n = 4$ = dppb] the twelve donor atoms adopt an icosahedral arrangement with the metal triangle inserted so as to produce a derivative with a quasi-D_3 symmetry. Thus, the progressive movement from the C_{2v} to the D_3 icosahedral form is observed in keeping with prediction, and the proposal that $[Fe_3(CO)_{12}]$ can exist in an alternative D_3 form is well supported by these additional observations.

We find numerous examples of anticubeoctahedra. None is observed for iron but they are clearly the preferred arrangement for osmium. Lauher[8] did not comment on compounds of osmium, but reports that according to his calculations the C_{2v} and D_3 isomers with pseudo-icosahedral packing are the lowest in energy for both iron and ruthenium. The D_{3h} isomer, with its anticubeoctahedral packing of carbonyls, is apparently the least stable in each case. He argues that with the ruthenium case the need to attain a favourable metal–metal interaction brings about the less-favourable distribution of carbonyl ligands, whereas with $[Fe_3(CO)_{12}]$ the steric constraints of the twelve carbonyl ligands dominate. We prefer our original argument based on the radii of the metal atoms concerned, since in our opinion this allows a direct 'measurable' contribution and permits a fair prediction of the structure adopted. In reality, since 'bond strength' is dependent on 'the radius of the atom', we and Lauher are saying more or less the same thing. Nevertheless, it is important to note (see below) that, although ruthenium and osmium are basically similar and different from iron, they do not behave in precisely the same way even though they have the same effective radius.

As commented on above, there are relatively few examples of exactly the same type of compound for both ruthenium and osmium. Examples include $[M_3(CO)_{11}L]$ [L = PPh_3,[30,33]

$P(OMe)_2Ph$[30] or $CnBu^t$[28,43]] and $[M_3(CO)_{10}(dppe)]$.[27,45] As a consequence, it is difficult to draw any meaningful conclusions from a comparison of the two species, except to say that, apart from the compounds $[Ru_3(CO)_{11}(PPh_3)]$ and $[Os_3(CO)_{11}(PPh_3)]$ which have virtually identical structures (see Fig. 7), there is a tendency for the ruthenium derivatives to show a more pronounced distortion towards the icosahedral form. This would be in keeping with Lauher's comments about the relative contributions to the structure from metal–metal bond strength and ligand-repulsion terms (see above), given that the metal–metal bond strengths are in the order Os > Ru > Fe.

Conclusion

Good evidence has been found from the study of the crystal structures of $[M_3(CO)_{12}]$ carbonyls and a range of their derivatives to support the hypothesis that ligand rearrangement proceeds *via* the intermediacy of an anticubeoctahedral complementary geometry. Several examples of systems with an icosahedral distribution of ligands and quasi-D_3 symmetry have been identified, providing additional support for the earlier suggestion that a second isomer of $[Fe_3(CO)_{12}]$, which exists in solution, adopts a similar structure.

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