Special Topic F: Metal Carbonyl Clusters

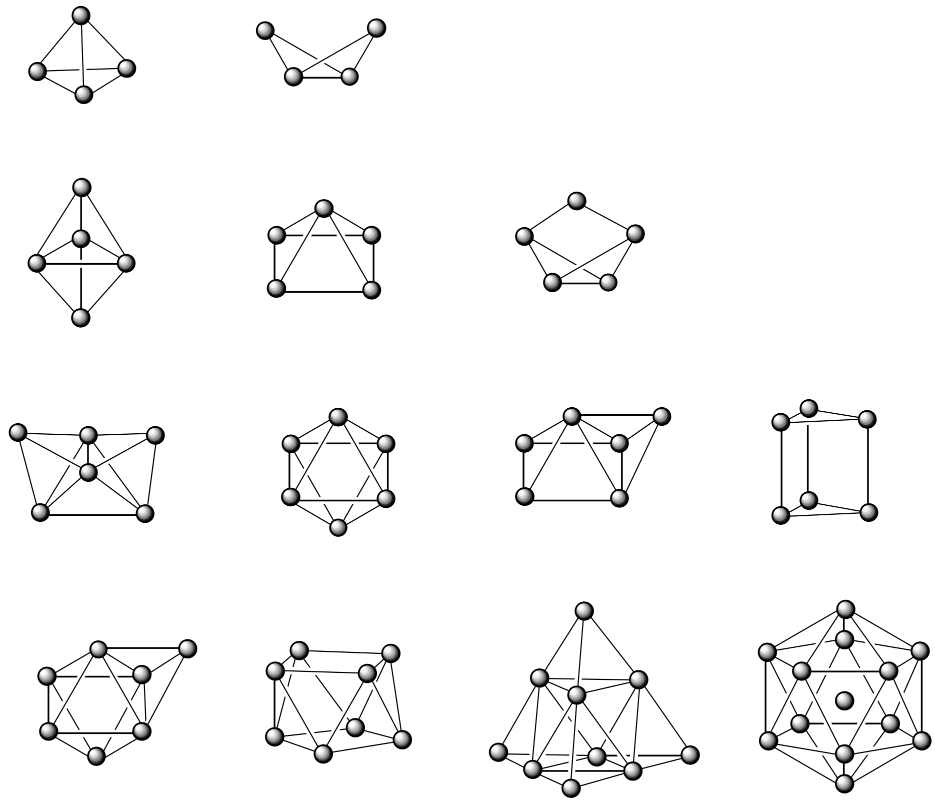

Figure F.1 Some metal core geometries

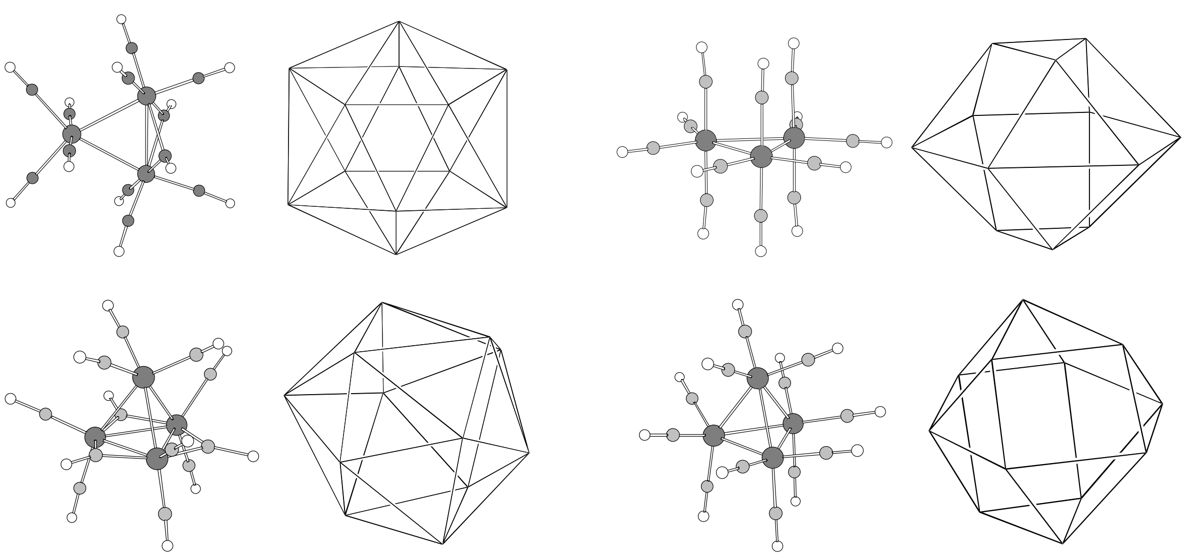

Figure F.2 Some dodecacarbonyl clusters and their ligand polyhedra; $Fe_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_4(CO)_{12}$, $Ir_4(CO)_{12}$

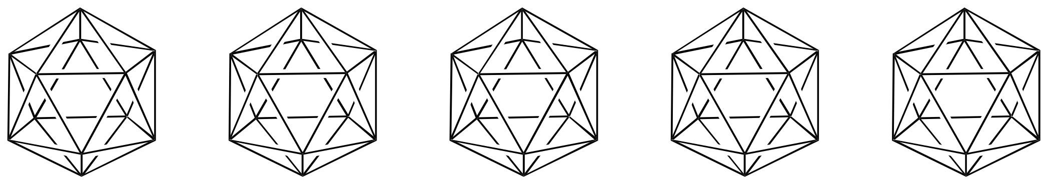

Figure F.3 Possible isomers of $M_x(CO)_9(PR_3)_3$.

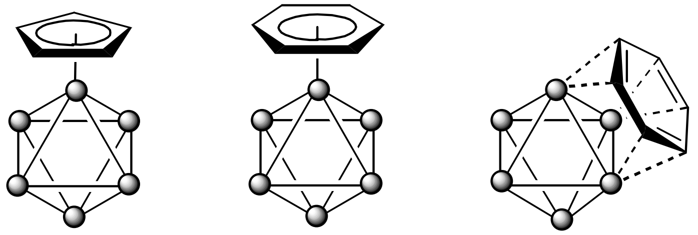

Figure F.4 Cyclopentadienyl and arene binding modes to clusters

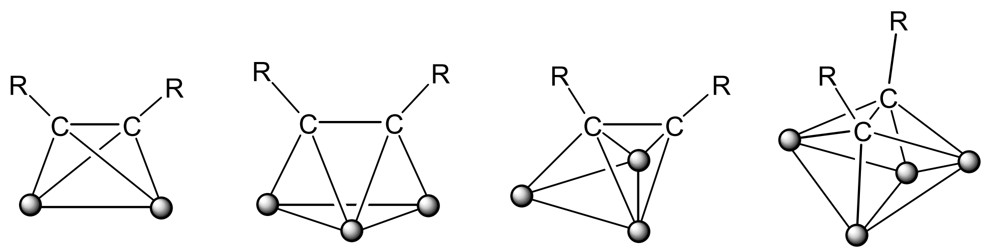

Figure F.5 Some binding modes of alkynes to clusters

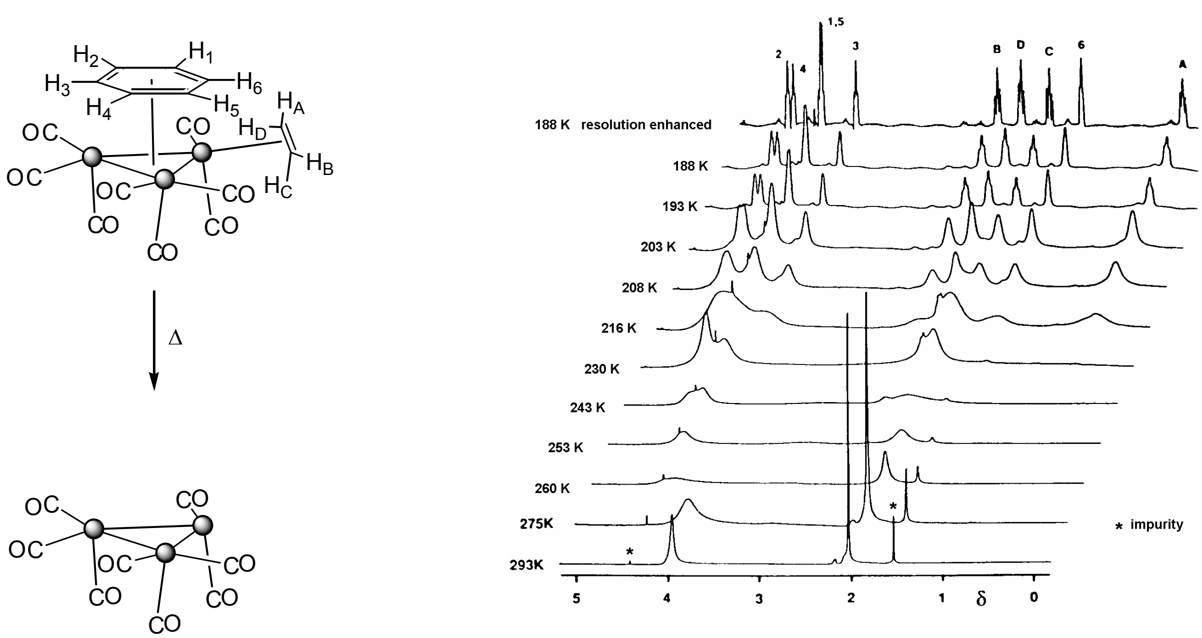

Figure F.6 An example of fluxional processes in organic ligands

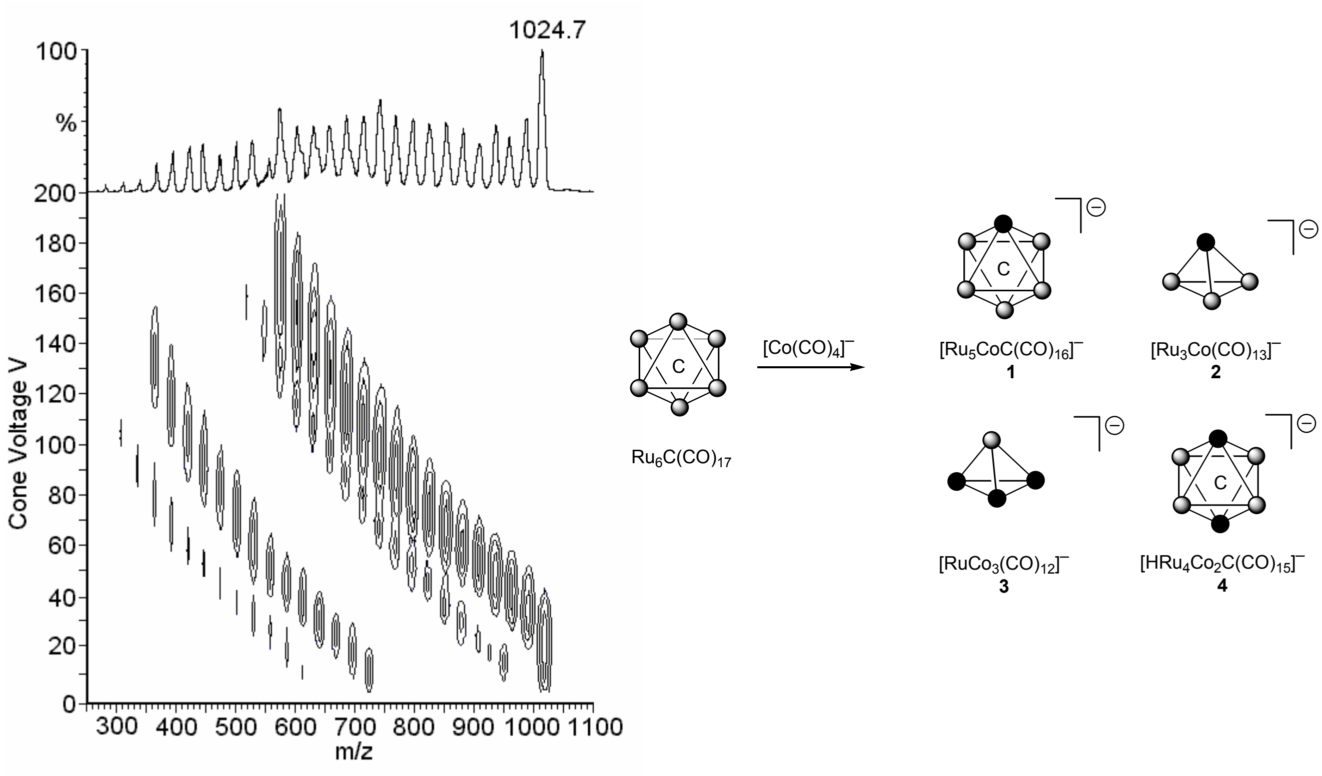

Figure F.7 Energy-dependent ESI-MS of a mixture of mixed-metal carbonyl cluster anions.

Table F.1 Bonding modes and number of electrons donated by ligands

No. of electrons	**Terminal** μ_1**-**	**Bridging** μ_2**-**	**Face-capping** μ_3**- or** μ_4**-**	**Interstitial**
1	H, F, Cl, Br, I, CR_3, CN	H, $AuPR_3$	H, $AuPR_3$	H
2	CO, CNR, NCR, NR_3, PR_3, SR_2, (η-C_2R_4)	CO, CNR, CR_2	CO, CNR	
3	(η^3-C_3R_3), NO	F, Cl, Br, I, PR_2, OR, SR, NO	CR, NO	B
4	(η^4-C_4R_4)	(η-C_2R_2)	O, S	C
5	(η^5-C_5R_5)		F, Cl, Br, I	N, P
6	(η^6-C_6R_6)		(η^2: η^2: η^2-C_6R_6)	O, S

The Si, Ge and Sn equivalents of C based ligands donate the same number of electrons. The same rule applies to Se and Te variants of O and S donor ligands, and As and Sb variants of P donor ligands.

18-electron rule

1. Always consider the metal atom (and all the ligands) to have an oxidation state of zero.
2. Add together the valence electrons of the metal atoms and the electrons donated by all the ligands.
3. Account for any overall charge on the complex by adding (negative charge) or subtracting (positive charge) the appropriate number of electrons.
4. Consider a metal-metal single bond to provide one electron to each metal, a double bond to provide two electrons to each metal, etc. (as the number of metal atoms increases the metal-metal bonds cannot always be treated in this way - see below).
5. Consider bridging ligands to provide an equal share of their electrons to each metal it interacts with.

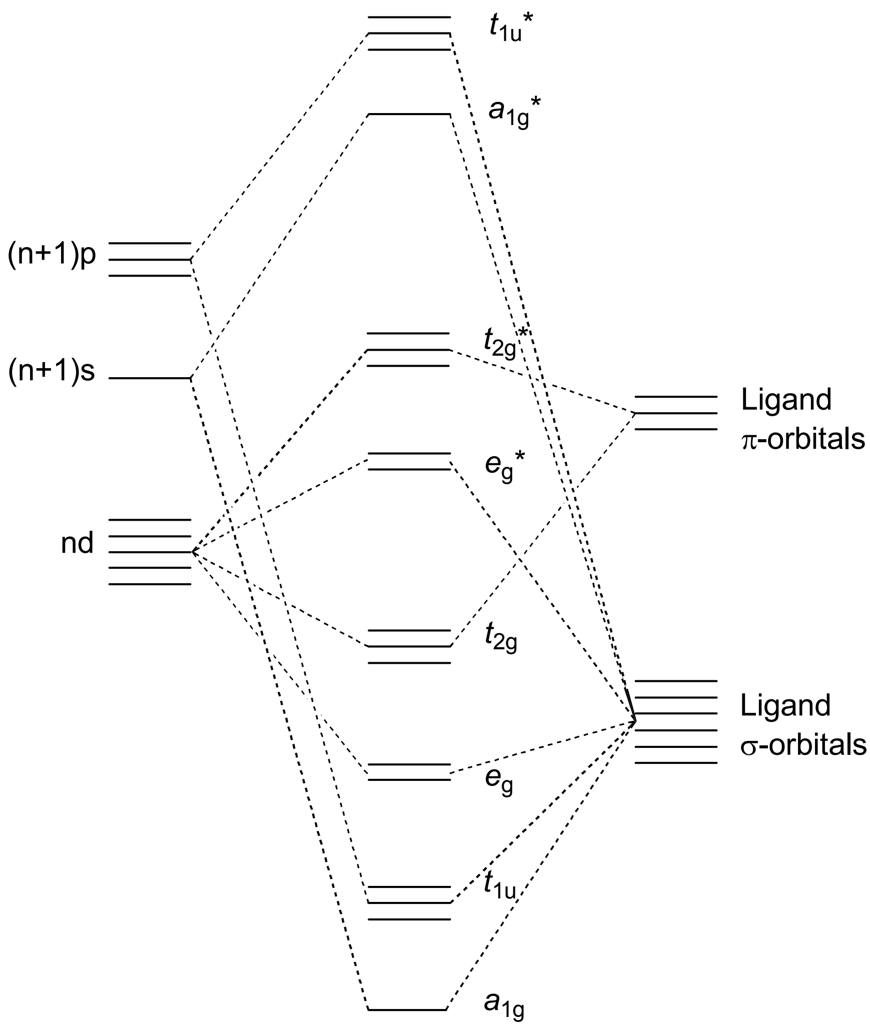

Figure F.8 The MO energy level diagram for $Cr(CO)_6$; note that the a_{1g}, t_{1u}, e_g and t_{2g} must be full for a stable complex.

Table F.2 The electron counts characteristic of the various polyhedra are listed below (*E* is the number of polyhedral edges, *k* the total electron count and *m* the number of M-M bonds)

Structure	***E***	***k***	***M***
Triangle	3	48	3
Linear / bent	2	50	2
Tetrahedron	6	60	6
Butterfly	5	62	5
Trigonal bipyramid	9	72	9
Square based pyramid	8	74	8
Bridged butterfly	7	76	7
Bicapped tetrahedron	12	84	12
Octahedron	12	86	11
Trigonal prism	9	90	9
Monocapped octahedron	15	98	14
Bicapped octahedron	18	110	17
Square antiprism	16	114	15
Tetracapped octahedron	24	134	23
Icosahedron	30	170	23

Table F.3 Characteristic electron counts of units common to both polyhedra.

Shared unit	***Subtract***
Vertex	18e
Edge	34e
Triangular face	48e
Triangular face [a]	50e
Square face	62e
Square face [b]	64e
Butterfly face	62e

[a] *When both parent polyhedra are deltahedra and have nuclearities of six or greater.*
[b] *When both parent polyhedra are three connected polyhedra, i.e. have M-M connectivities of three.*