Definition: "a finite group of metal atoms that are held together mainly, or at least to a significant extent, by bonds directly between metal atoms, even though some non-metal atoms may also be intimately associated with the cluster" – F.A. Cotton
Two extreme types of metal clusters:

- Molecular clusters are composed of 3 or more metal atoms stabilized by small molecules acting as ligands, and characterized by metal-metal bonds, either localized or delocalized over the metal framework.
• "Naked clusters" - have no ligands, electronically unsaturated, naked metal particles formed in atomic beams; are extremely reactive unless stabilized by a support or an inert matrix, e.g. [Pb5]2-.

In this part of the course, we focus on transition metal clusters with 2 or more M-M bonds, and, particularly, late TM clusters with CO ligands.
Importance:

(a)

Evolution of properties as cluster size increases (e.g. structure, magnetic behaviour, ionization potential):

**Transition from molecular → bulk metal domain.**

- metal-ligand charge transfer interactions are limited to the metal atoms which are at the surface of the metal cluster; inner-core metal atoms behave as a metal particle.
- properties of a solid gradually evolve as atoms are brought together to form increasingly larger units.
Interpretation of data obtained from metal surfaces which are active heterogeneous catalysis sites (cluster-surface analogy).

• models for chemi- and physi-sorption of small molecules onto metallic surfaces - e.g. fluxionality of the coordinated fragments, mechanism of hydrogen diffusion inside a metallic network, the distortions in metal close-packing induced by interstitial heteroatoms, etc.
• chemical reactivity of coordinated ligands in molecular metal clusters has been used for studying the reaction mechanisms at the metal centres, and for mimicking elementary processes relevant to homogeneous and heterogeneous catalysts.
c) Fascinating structures (!).

• first reports of organometallic transition metal clusters: Fe$_2$(CO)$_9$ (1905), Fe$_3$(CO)$_{12}$ (1907) and Co$_2$(CO)$_8$ (1910)

• computer analysis of X-ray crystallographic data → novel structural features
• variety of metal frame shapes, bonding modes for any given ligand and stereochemistry observed was only possible in the presence of several metal atoms

• solid state chemists and physicists also became interested – clusters as particulate metals enclosed in a ligand sphere.
• 1000s of examples of ligated metal clusters have been reported. Most common clusters are formed by:

- early transition metals stabilized by halide or oxygen atoms (aggregates)

- metals of group 6-10 stabilized by CO molecules

- transition or post-transition metals having halogen atoms, phosphine groups, and main group elements as ligands

• primary analytical tool is X-ray diffraction, bond lengths which are shorter than the sum of the covalent radii being a reliable indication of M-M bonding.
one of the first reported X-ray structural determinations of TMCCs was of Fe$_2$(CO)$_9$ (1939), revealed CO ligands bridging the M-M bond.
• historically, first unsupported M–M bonds were found in the analogous complexes Re$_2$(CO)$_{10}$ and Mn$_2$(CO)$_{10}$ (1957). Confirmed the existence of unsupported M-M bonds.
• also very early on, the structure of the pentacoordinate Fe$_5$(μ$_5$-C)(CO)$_{15}$ (1962) and [Re$_2$Cl$_8$]$_2$-

• Interesting structures stimulated research; lack of syntheses frustrated research. Recent systematic syntheses have led to the explosion in cluster chemistry.
STRUCTURE AND BONDING

(1) TYPES OF CLUSTERS

(i) π-Donor clusters: early transition metals (oxidation state +2 or +3) with π-donor ligands (O2–, S2–, Cl–, Br–, I–, OR–, etc.). Typically triangular or octahedral geometries.
Electron donating characteristics of common $\pi$-donor bridging ligands

**Edge-bridging ($\mu_2$)**
- Two electron donors: O, S, Se
- Three electron donors: SR, OR, PR2, AsR2, Cl, Br, I

**Face-bridging ($\mu_3$)**
- Four electron donors: O, S, Se, PR, AsR
- Five electron donors: Cl, Br, I
Examples:

[Nb6Cl12]2+, [Ta6Cl12]2+ octahedral M6, edge-bridging Cl (1)

[Mo6Cl8]4+, [W6Cl8]4+ octahedral M6, face-capping Cl (2)

[Re3Cl12]3- triangular Re3, 3 x μ-Cl, 9 x terminal Cl (3)
ii) **π-Acceptor clusters**: late transition metals (oxidation state 0, near 0) with π-acceptor ligands (CO, CNR, NO, PR₃, polyenes) and H⁻ - largest group of clusters.

**Electron donating characteristics of common π-acceptor ligands**

<table>
<thead>
<tr>
<th>Number of electrons</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H, X, R, SnR₃</td>
</tr>
<tr>
<td>2</td>
<td>CO, CNR, PR₃, R₂C=CR₂, CR₂, NCR</td>
</tr>
<tr>
<td>3</td>
<td>NO, allyl, PR₂, CR, μ-X, μ-C≡CR</td>
</tr>
<tr>
<td>4</td>
<td>cyclobutadiene, butadiene, RC≡CR, S, PR, C</td>
</tr>
<tr>
<td>5</td>
<td>cyclopentadienyl, μ₃-C≡CR, P, N</td>
</tr>
<tr>
<td>6</td>
<td>arenes</td>
</tr>
</tbody>
</table>
• COs frequency as a ligand for stabilizing low oxidation state clusters arises because of its flexibility - coordination as terminal, \( \mu \)- and \( \mu_3 \)- are all common and, because they are all 2e donors (unlike Cl), intramolecular exchange processes frequently have very low activation energies.

• H- is not a \( \pi \)-acceptor ligand, but there are many carbonyl clusters that also have H- as a ligand, so these clusters are usually considered together.
Ligand bonding modes

• see more extensive discussion on bonding modes of CO, hydrido and acetylenic ligands (later in course).

• Cl ligand is a 1 e donor when terminal, or uses a lone pair to become a 3e donor when edge-bridging, or a 5e donor using an additional lone pair when face bridging.
Bonding modes and electron count for some common ligands
(2) CLUSTER GEOMETRY –

• high symmetry - usually define regular polyhedra as triangle, tetrahedra, octahedra, etc

• metal positions usually define **deltahedra, i.e. Triangular** faces; other arrangements, e.g. square-planar, trigonal prismatic, square antiprisms occur to lesser extent
• many represent fragments of close-packed arrays of metal atoms, hcp ccp or bcc
• form interstitial complexes containing hydrogen, carbon, nitrogen, sulfur, phosphorus, and arsenic, as well as other metal atoms in the case of high-nuclearity clusters, in the interstices
3 metal atom clusters

• great majority are triangular. Structural differences require only small changes in total energies of molecules e.g. Fe$_3$(µ-CO)$_2$(CO)$_{10}$ and Ru$_3$(CO)$_{12}$.

• linear e.g [Mn$_3$(CO)$_{14}$]- or bent. Bond opening on a triangular cluster results in a linear geometry
4 metal atom clusters:

- many are tetrahedral with 6 M–M bonds, e.g. CpWIr₃(CO)₁₁
• butterflies can be regarded as resulting from a bond opening on the tetrahedron

e.g. CpWIr₃(CO)₈(F₃CC≡CCF₃)₂
• interplanar angle in butterflies can be near 180°, as in [Re4(CO)16]2-

• Fe4(μ4-C)(μ-CO)(CO)12 contains a carbide atom in the middle of the cluster, approximately colinear with the wing-tip atoms, providing an excellent model for a carbon atom on a metal surface.
• square-planar geometries - for carbonyl clusters, often contain a capping ligand

e.g. Fe$_4$(μ$_4$-NEt)(μ$_3$-η$_2$-ONEt)(μ-CO)$_3$(CO)$_8$
• bond rupture in a butterfly arrangement leads to a spiked triangle geometry, as in Re₄(μ-H)₃H(CO)₁₅
5 metal atom clusters

- trigonal bipyramidal forms largest group. e.g. Os$_5$(CO)$_{16}$

Lower symmetry arrays can be derived by M–M bond scission.
• breaking an equatorial bond produces a square pyramidal geometry. Most contain an interstitial or capping ligand such as C, N, S or PR groups, e.g. Fe₅(μ₅-C)(μ-CO)₂(CO)₁₂. The presence of these heteroatoms stabilizes the core, e.g. there is an extensive chemistry known for the Ru₅- and Os₅-carbido clusters.
• breaking an axial bond results in edge-bridged tetrahedral geometry, as in $\text{Os}_5(\mu-H)_2(\text{CO})_{16}$. Mostly osmium clusters.
• wing-tip bridged butterfly can be derived from the trigonal bipyramid by scission of two M–M bonds. Many have interstitial C, e.g. Os$_5$(μ$_5$-C)(CO)$_{16}$. 

\[ \text{Os}_5(\mu_5\text{-C})(\text{CO})_{16} \]
• edge-bridged butterfly or swallow, e.g. $\text{Ru}_5(\mu-\eta^2-\text{Bu}^t\text{NC})(\text{Bu}^t\text{NC})(\text{CO})_{14}$ and bow-tie e.g. $\text{Os}_5(\text{CO})_{19}$ can also be derived from the trigonal bipyramid by scission of 2 and 3 bonds respectively.
other less common geometries include edge-bridged square (e.g. Ru₅(μ₄-S)₂(CO)₁₄), spiked-square (Ru₅(μ₅-η²-C₂H)(μ₃-SPh)(μ-PPh₂)₂(CO)₁₂) or -butterfly,
...scorpion \([\text{Ru}_5(\mu_5-P)(\mu-P\text{Ph}_2)(\text{CO})_{16}]\), pentagon \([\text{Ru}_5(\mu_5-C_2)(\mu-\text{SMe})_2(\mu-P\text{Ph}_2)_2(\text{CO})_{11}]\) or chain \([\text{Ru}_5(\mu_5-\eta^3-C_2\text{PPh}_2)(\mu-\text{SMe})_2(\mu-P\text{Ph}_2)(\text{CO})_{13}]\) complexes.
6 metal atom clusters:

- octahedra are by far the largest group; many contain C and a few have H in the interstitial cavity, e.g. \([\text{Ru}_6(\mu_6-H)(\text{CO})_{18}]^-\).
• trigonal prism can also accommodate interstitial carbide e.g. \( \text{Rh}_6(\mu_6-\text{C})(\mu-\text{CO})_9(\text{CO})_6 \), or nitrido e.g. \([\text{Co}_6(\mu_6-\text{N})(\text{CO})_{15}]^-\) - only 1 example known which does not contain an interstitial atom, \( \text{Re}_6(\text{CO})_{18}(\text{PMe}_3) \).
Other geometries observed for hexanuclear carbonyl clusters can be derived from more simple arrangements by sharing of additional atoms to edges or faces of polyhedra of lower nuclearity:

• bicapped tetrahedra has 12 M–M bonds, as in the octahedral geometry e.g. Os₆(CO)₁₈.
• capped square pyramid is an open structure with 11 M–M bonds and frequently has the square face capped by a heteroatom, as in Os₆(μ₄-S)(CO)₁₇ although unsupported examples are also known e.g. Os₆(μ-H)₂(CO)₁₈.
raft clusters also provide good models for chemisorption of organic molecules onto metal surfaces e.g. Os₆(μ₃-O)(μ₃-CO)(CO)₁₈, Ru₆(μ₃-H)(μ-H)(μ₂-(O):μ₂-(C):η⁶-C₆H₄O)(μ-CO)(CO)₁₅.
• other geometries: bicapped butterfly and bi-edge-bridged tetrahedron \( \text{Os}_6(\mu-\text{H})_2(\mu_3-\text{SMe})_2(\mu-\text{CNMe}_2)_2(\text{CO})_{12} \) and \( \text{Ru}_6(\mu_4-\eta^2-\text{CO})_2(\mu-\text{CO})(\text{CO})_{12}(\eta-\text{C}_6\text{H}_3\text{Me}_3) \), respectively, are the only examples), biedge-bridged square, and a host of others...
Clusters with 7 or more metal atoms

- much rarer; structures mainly derived by condensation of structures of lower nuclearity by sharing edges and faces, as seen in the hexanuclear examples.
Examples of preparations

RuCl₃ → CO
50 atm, MeOH, 120 °C

Ru₃(CO)₁₂
80 %

Ru₃(μ-H)(μ-C₅H₄)CO₁₀
85 %

chlorobenzene → 132 °C

[Ru₂(μ-H)(μ-NC₅H₅)₂(NC₅H₅)₂(CO)₄][Ru₁₀(μ-H)(μ₆-C)(CO)₂₄]
90 %
\[ [\text{Ru}_{10}(\mu-H)_2(\text{CO})_{25}]^{2-} \quad \xrightarrow{n-\text{BuOH}} \quad [\text{Ru}_{10}(\mu_6-C)(\mu-H)(\text{CO})_{24}]^{+} \quad \text{n-BuOH} \quad 118^\circ \quad \sim 1 \text{ h} \]

\[ \text{Ru}_3(\mu-H)(\mu-\text{NC}_5\text{H}_4)(\text{CO})_{10} \quad \text{C}_6\text{H}_5\text{Cl} \quad 132^\circ \quad \sim 1 \text{ h} \]
Multiple capping of central octahedron (hexagonal close-packed)

$[H_2Ru_{10}(CO)_{25}]^{2-}$ 35%

$[Ru_8(\mu_8-P)(CO)_{22}]^{-}$ 30% square antiprism
Electron Counting in Clusters

Many approaches have been made to obtain some generalizations which may allow rationalization of the wide range of cluster geometry and reactivity observed. The most important are listed on the following slides.
<table>
<thead>
<tr>
<th><strong>Approach</strong></th>
<th><strong>Description</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective Atomic Number (EAN) or</td>
<td>The total number of cluster valence</td>
</tr>
<tr>
<td>Inert-Gas Rule</td>
<td>electrons (i.e. metal valence electrons plus those contributed by the ligands)</td>
</tr>
<tr>
<td></td>
<td>is such that each main group atom as well as each transition metal atom in the</td>
</tr>
<tr>
<td></td>
<td>cluster has 8 and 18 electrons, respectively. Clusters that follow this rule are</td>
</tr>
<tr>
<td></td>
<td>known as “electron precise” species.</td>
</tr>
<tr>
<td>Polyhedral Skeletal Electron</td>
<td>Bonding pattern in metal clusters is</td>
</tr>
<tr>
<td>Pair Theory</td>
<td>analogous to that in boranes (electron deficient species) where each atom</td>
</tr>
<tr>
<td></td>
<td>contributes 3 orbitals and 2 electrons to the skeletal bonding.</td>
</tr>
<tr>
<td>Isolobal Analogy</td>
<td>There are definite similarities between the number, energies, shapes, and nodal characteristics of both main group and transition metal carbonyl fragments. This analogy has proved to be useful in accounting for structural similarities between main group and transition metal clusters.</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Capping Principle</td>
<td>Capping a face by a ML$<em>3$ fragment or bridging an edge by a C$</em>{2v}$-ML$_4$ fragment on a given polyhedron leads to no change in the number of skeletal bonding MOs.</td>
</tr>
<tr>
<td>Polyhedral Fusion</td>
<td>Condensed clusters may be regarded as the result of two or more polyhedra sharing a vertex, an edge, or a face.</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Polyhedral Inclusion</td>
<td>High nuclearity clusters may be formally divided into an encapsulated, internal polyhedron and another, surface, polyhedron.</td>
</tr>
</tbody>
</table>

We will cover two methods of electronic rationalization of cluster types: the Effective Atomic Number (EAN) and the Polyhedral Skeletal Electron Pair (PSEPT) theories, briefly touching on the other concepts. The isolobal analogy was covered earlier in this course.
(i) **EAN** (Effective Atomic Number) or 18e rule. Based on some assumptions:

- that each metal atom will attain a noble gas configuration by forming the required number of M-M bonds.
- M–M bonds are localized on polyhedral edges, i.e. 2-electron 2-centre bonds, and although there is no requirement that each metal atom will be electronically correct, the cluster as a whole must satisfy the 18e rule.
• ligands serve as a source of electrons only, i.e. do not effect polyhedral shape whether the electrons are present as charge or through donation from ligands.
   e.g. Os₅(CO)₁₆ has 72 [(8 x 5) + (16 x 2)] cluster electrons, requires 90 (18 x 5) \therefore forms 9 M–M bonds, as in the trigonal bipyramidal geometry.

In this case, the cluster as a whole is satisfied, although the 2 Os atoms in the apical positions are formally 17e species, and the atom in the equatorial plane with 4 CO ligands is a 20e species.
### Other examples:

<table>
<thead>
<tr>
<th>Complex</th>
<th>Metal VE</th>
<th>Ligand VE</th>
<th>Total available</th>
<th>EAN requirement</th>
<th>M–M bonds possible</th>
<th>Observed Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃(CO)₁₂</td>
<td>24</td>
<td>24</td>
<td>48</td>
<td>54</td>
<td>3</td>
<td>Triangle</td>
</tr>
<tr>
<td>Cp₄Co₄H₄</td>
<td>36</td>
<td>24</td>
<td>60</td>
<td>72</td>
<td>6</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>Os₆(CO)₁₈</td>
<td>48</td>
<td>36</td>
<td>84</td>
<td>108</td>
<td>12</td>
<td>Bicapped tetrahedron</td>
</tr>
<tr>
<td>* [Rh₆(CO)₁₅I]⁻</td>
<td>54</td>
<td>32</td>
<td>86</td>
<td>108</td>
<td>11</td>
<td>Octahedral</td>
</tr>
<tr>
<td>Number of metal atoms</td>
<td>Structure of metal framework</td>
<td>CVE count</td>
<td>Example</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
<td>------------------------------</td>
<td>-----------</td>
<td>-------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Single metal</td>
<td>18</td>
<td>Ni(CO)$_4$ (2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Linear</td>
<td>34</td>
<td>Mn$<em>2$(CO)$</em>{10}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Closed triangle</td>
<td>48</td>
<td>[Co$_3$(CH)(CO)$_9$] (78)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedron</td>
<td>60</td>
<td>Co$<em>4$(CO)$</em>{12}$ (76)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Butterfly</td>
<td>62</td>
<td>[Fe$<em>4$(CO)$</em>{12}$C]$^{2-}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Square</td>
<td>64</td>
<td>Os$<em>4$(CO)$</em>{16}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of metal atoms</td>
<td>Structure of metal framework</td>
<td>CVE count</td>
<td>Example</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------------------------</td>
<td>-----------</td>
<td>-----------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramid</td>
<td>72</td>
<td>Os$<em>5$(CO)$</em>{16}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Square pyramid</td>
<td>74</td>
<td>Fe$<em>5$C(CO)$</em>{15}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Octahedron</td>
<td>86</td>
<td>Ru$<em>6$C(CO)$</em>{17}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trigonal prism</td>
<td>90</td>
<td>[Rh$<em>6$C(CO)$</em>{15}$]$^{2-}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
• Useful only for clusters having 5 or fewer atoms, and even here breaks down sometimes since polyhedral edges cannot be represented by formal 2-electron-2-centre bonds in the larger clusters - need a model which considers delocalization of electrons.

• * for hexanuclear clusters, deviations from the EAN rule are common - many octahedral clusters have 86 CVE, 2 more than required for the inert gas configuration for that geometry.
Relationship between structure and CVE according to the EAN

For a cluster of nuclearity $x$ ($M_x$) and having $y$ metal-metal bonds, the expected EAN electron count is given by:

$$\text{EAN count} = 18x - 2y.$$ 

e.g. an octahedral cluster: $x = 6$ and $y = 12$

expected EAN = 6(18) - 2(12) = 84
<table>
<thead>
<tr>
<th>Metal Cluster Structure</th>
<th>No. CVE predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triangle</td>
<td>48</td>
</tr>
<tr>
<td>Linear</td>
<td>50</td>
</tr>
<tr>
<td>Tetrahedron</td>
<td>60</td>
</tr>
<tr>
<td>Butterfly</td>
<td>62</td>
</tr>
<tr>
<td>Square planar</td>
<td>64</td>
</tr>
<tr>
<td>Trigonal bipyramid</td>
<td>72</td>
</tr>
<tr>
<td>Square pyramid</td>
<td>74</td>
</tr>
<tr>
<td>Edge-bridged tetrahedron</td>
<td>74</td>
</tr>
<tr>
<td>Edge-bridged butterfly</td>
<td>76</td>
</tr>
<tr>
<td>Swallow</td>
<td>76</td>
</tr>
<tr>
<td>Bow-tie</td>
<td>78</td>
</tr>
<tr>
<td>Octahedron</td>
<td>84</td>
</tr>
<tr>
<td>etc</td>
<td></td>
</tr>
</tbody>
</table>
trigonal bipyramid
edge-bridged tetrahedron
swallow
bow-tie
square pyramid
edge-bridged butterfly
spiked butterfly
scorpion
• in the case of electron-poor systems, the **electron deficit** must be compensated for by the formation of **M–M multiple bonds**.

   e.g. $\text{H}_2\text{Os}_3(\text{CO})_{10}$ has $[2 + 3(8) + 10(2)]$ 46 electrons, but forms a triangular cluster which has 48 CVE predicted by the EAN rule. \[ \therefore \] considered as having an Os=Os, since the EAN count for a system with 4 M–M bonds in a three-atom cluster is 46e.
• **electron excess** implies **bond breakage** and cluster opening, so that bonding orbitals become non-bonding. Triangular clusters with 49 (e.g. $\text{Ni}_3(\text{CO})_2\text{Cp}_3$) and 50 (e.g. $\text{Co}_3\text{S}_2\text{Cp}_3$) CVE exist - additional electrons occupy M–M orbitals which are, however, not antibonding enough to cause M–M rupture, but result in a slight lengthening of the M–M bonds.
• **d⁸ metal ions** have high-lying pz orbital which is non-bonding and remains empty, e.g. mononuclear Pt and Pd complexes have 16e. Clusters are similarly electron deficient e.g. generally form triangular clusters with 42 CVE, although some with 44 CVE are also known, the extra electrons being delocalized in a MO which is not strongly antibonding, leading to a slight lengthening of the M–M bonds similar to the Cp clusters above.

• **Group 1B** metals do not follow the EAN rule, e.g. gold(I) forms primarily 2-coordinate 14 electron complexes. Again, the p orbitals may not be fully utilized.
In summary

- can determine whether a molecule obeys the EAN rule if the number of M–M bonds is known,
- or can assume a complex is EAN precise and then determine the expected geometry

** Works well for clusters $M_n$ where $n \leq 5$ **
(ii) **PSEPT** (Polyhedral Skeletal Electron Pair Theory, also known as Wade's Rules)

Developed independently by Wade and Mingos in 1976-77 to rationalize the stoichiometries of boranes, which could not be explained by simple bonding schemes as found for hydrocarbons. There were insufficient electrons to allow classical 2-electron 2-centre bonds between adjacent pairs of atoms. With transition metal complexes, it is even more complicated since some complexes are electron precise, whereas others are electron deficient.
Wade's Rules consider only the electrons involved in the cluster framework, but they can be derived from transition metal or main group elements.

**PSEPT and transition metal complexes**

Uses analogy between metal clusters and the boranes, and is based on 2 assumptions:

1. the transition metal uses its 9 atomic orbitals: 3 are used to form the metal skeleton; the remaining 6 AOs are used for ligand bonding or for housing non-bonding electron pairs, and are the first to be filled.
2. the orbitals involved in the skeletal bonding have a similar form and symmetry to those of the \( sp \) and tangential \( p \) orbitals of the corresponding boranes and carboranes.

e.g. \( \text{Fe(CO)}_3 \) fragment is isolobal with the BH unit:

\[
\begin{align*}
\text{Fe} & \quad \text{dp} \quad \text{dp} \\
\text{OC} & \quad \text{d}_{z^2}\text{sp}_z \\
\text{OC} & \quad \text{dp} \\
\text{OC} & \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{p} \\
\text{B} & \quad \text{sp} \\
\end{align*}
\]

i.e. \( \text{Fe(CO)}_3 \) contributes the same no. of bonding electrons (2) and cluster orbitals (3) as the BH unit.
e.g. the \( n + 1 = 7 \) cluster bonding orbitals in \( \text{B}_6\text{H}_6^{2-} \) and its MO energy level diagram are as follows (not examinable):

![Diagram showing cluster bonding orbitals and MO energy level diagram](image)

**Figure 13-9**
Shriver & Atkins Inorganic Chemistry, Fourth Edition

**Figure 13-10**
Shriver & Atkins Inorganic Chemistry, Fourth Edition
e.g. $[\text{B}_6\text{H}_6]^{2-}$ is a *closo* octahedron - replacing each BH unit with Os(CO)$_3$ units gives $[\text{Os}_6(\text{CO})_{18}]^{2-}$, a known complex with octahedral geometry. Recall that this complex is an 86e cluster, and that CVE counting predicts 84e for the octahedral geometry, showing the utility of Wade's rules when applied to larger clusters.
Electron counting on transition metal cluster complexes:

\[
\text{no. SBE} = \text{total CVE} - 12n
\]

i.e. number of electrons available for cluster bonding = \((e \text{ from M}) + (e \text{ from L}) - (12e \text{ in remaining 6 orbitals of each transition metal})\)
Resulting geometries for $n$ skeletal atom cluster:

<table>
<thead>
<tr>
<th>No. skeletal</th>
<th>Geometry</th>
<th>bond</th>
<th>ing</th>
<th>electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2n$</td>
<td>$(n - 1)$ vertex polyhedron with cap</td>
<td></td>
<td></td>
<td>capped $closo$</td>
</tr>
<tr>
<td>$2n + 2$</td>
<td>$n$ vertex polyhedron</td>
<td></td>
<td></td>
<td>$closo$</td>
</tr>
<tr>
<td>$2n + 4$</td>
<td>$(n+1)$ vertex deltahedron less 1 vertex</td>
<td></td>
<td></td>
<td>$nido$</td>
</tr>
<tr>
<td>$2n + 6$</td>
<td>$(n+1)$ vertex deltahedron less 2 vertices</td>
<td></td>
<td></td>
<td>$arachno$</td>
</tr>
<tr>
<td>$2n + 8$</td>
<td>$(n+1)$ vertex deltahedron less 3 vertices</td>
<td></td>
<td></td>
<td>$hypho$</td>
</tr>
</tbody>
</table>
Some examples

no. SBE = total CVE - 12n

\[ H_2Ru_6(CO)_{18} \; n = 6 \]
\[ \text{no. CVE} = (6 \times 8) + (2 \times 18) + 2 = 86 \]
\[ \text{no. SBE} = 86 - (12 \times 6) = 14 \]
\[ \therefore \text{cluster has } (2n + 2) \]
\[ \Rightarrow 6 \text{ vertex } closo = \text{octahedron} \]

\[ Rh_6(CO)_{16} \; n = 6 \]
\[ \text{no. CVE} = (6 \times 9) + (2 \times 16) = 86 \]
\[ \text{no. SBE} = 86 - (12 \times 6) = 14 \]
\[ \therefore \text{cluster has } (2n + 2) \]
\[ \Rightarrow 6 \text{ vertex } closo = \text{octahedron} \]
Os$_6$(CO)$_{18}$  \[ n = 6 \]
\[ \text{no. CVE} = (6 \times 8) + (2 \times 18) = 84 \]
\[ \text{no. SBE} = 84 - (12 \times 6) = 12 \]
\[ \therefore \text{cluster has (2n) SBE} \]
\[ \Rightarrow \text{capped 5-vertex closo : (1 metal atom for cap) i.e. capped trigonal bipyramid} \]

Fe$_5$C(CO)$_{15}$  \[ n = 5 \]
\[ \text{no. CVE} = (5 \times 8) + (2 \times 15) + 4 = 74 \]
\[ \text{no. SBE} = 74 - (12 \times 5) = 14 \]
\[ \therefore \text{cluster has (2n + 4) SBE} \]
\[ \Rightarrow \text{5 vertex nido} \]

since the 6 vertex closo is the octahedron, this cluster must be an octahedron minus 1 apex = square pyramid
Polyhedral electron counting rules

- Rule 1: Ring cluster compounds are characterized by $16n$ valence electrons where $n$ is the number of cluster metal atoms.

  e.g. triangular ($n = 3$) and square ($n = 4$) clusters with 48 and 64 electrons respectively, with the metals contributing 2 orbitals for skeletal bonding.

  $\text{Fe}_3(\text{CO})_{12}$  \hspace{1cm}  $\text{Os}_3(\text{CO})_{12}$
• Rule 2: Three-connected polyhedral molecules are characterized by a total of 15m valence electrons.

  e.g. tetrahedron \((n = 4)\) and trigonal prism \((n = 6)\) clusters with 60e and 90e respectively, with the metals contributing 3 orbitals for skeletal bonding.

  \[
  \begin{align*}
  15 \times 4 &= 60 \text{ CVE} \\
  15 \times 6 &= 90 \text{ CVE} \\
  15 \times 8 &= 120 \text{ CVE}
  \end{align*}
  \]
• Rule 3: Four-connected polyhedral molecules are characterized by a total of $14n + 2$ valence electrons as long as the metal atoms lie approximately on a single spherical surface. 
e.g. octahedron ($n = 6$).

\[(14 \times 6) + 2 = 86 \text{ CVE}\]

Since metal carbonyls use only 3 orbitals for skeletal bonding, **cannot** describe bonding in 4-connected clusters in terms of localized edge bonds.
• Rule 4: **Closo-**, **Nido-** and **Arachno**-deltahedral clusters are characterized by $14m + 2$, $14m + 4$ and $14m + 6$ valence electrons, respectively, and have $m + 1$ skeletal bonding molecular orbitals.
<table>
<thead>
<tr>
<th>No. of M–M bonding e pairs ( (m + 1) )</th>
<th>Reference polyhedron</th>
<th>No. of vertices</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>closo</td>
</tr>
<tr>
<td>5</td>
<td>a tetrahedron</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>b trigonal bipyramid</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>c octahedron</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>d pentagonal bipyramid</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>e dodecahedron</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>f tricapped trigonal prism</td>
<td>9</td>
</tr>
<tr>
<td>11</td>
<td>g bicapped square antiprism</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>h octadecahebron</td>
<td>11</td>
</tr>
<tr>
<td>13</td>
<td>i icosahedron</td>
<td>12</td>
</tr>
</tbody>
</table>
• Rule 5: The total electron count for a *condensed polyhedron* is equal to the sum of the characteristic electron counts for the parent polyhedra (a) and (b) minus the electron count of the atom, pair of atoms, or face of atoms common to both polyhedra. **Characteristic electron counts are:**

  18 for a common vertex
  34 for a common edge
  48 for a common triangle
  64 for a common square
Polyhedron (A) \( n \) atoms

Polyhedron (B) \( m \) atoms

Electron count \( a \)

\[ (n+m-1) \text{ atoms} \]

Electron count \( c = a+b-18 \)

Face-shared polyhedron \( (n+m-3) \) atoms

Edge-shared polyhedron \( (n+m-2) \) atoms

Electron count \( c = a+b-48 \)

If \( n \) and \( m \) ≥ 6 and A and B deltahedra

\[ c = a+b-50 \]

Electron count \( b \)
# Common vertex

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ring cluster (16m)</strong></td>
<td><img src="#" alt="Diagram" /></td>
<td><img src="#" alt="Diagram" /></td>
<td>Os$<em>5$(CO)$</em>{19}$</td>
</tr>
<tr>
<td>p.e.c. 48</td>
<td>48</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td><strong>closo deltahedron</strong> (m = 5, 14m + 2)</td>
<td><img src="#" alt="Diagram" /></td>
<td><img src="#" alt="Diagram" /></td>
<td>H$_2$Os$<em>7$(CO)$</em>{22}$</td>
</tr>
<tr>
<td>p.e.c. 72</td>
<td>48</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td><strong>arachno deltahedron</strong> (m = 4, 14m + 6)</td>
<td><img src="#" alt="Diagram" /></td>
<td><img src="#" alt="Diagram" /></td>
<td></td>
</tr>
<tr>
<td>p.e.c. 62</td>
<td>62</td>
<td>106</td>
<td></td>
</tr>
</tbody>
</table>
# Common edge

<table>
<thead>
<tr>
<th>p.e.c. 60 + 48</th>
<th>$a + b - 34$</th>
<th>74</th>
<th>$\text{H}_2\text{Os}<em>5(\text{CO})</em>{16}$</th>
</tr>
</thead>
</table>

| p.e.c. 86 + 86 | $a + b - 34$ | 138 | $[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]^{2-}$ |
## Common triangular face

<table>
<thead>
<tr>
<th>3-connected polyhedra (15m)</th>
<th><img src="image" alt="Diagram" /></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Polyhedron" /> + <img src="image" alt="Polyhedron" /></td>
<td>a + b = 48</td>
</tr>
<tr>
<td>p.e.c. 60</td>
<td>60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><em>nido</em> deltahedron (14m + 4)</th>
<th><img src="image" alt="Diagram" /></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Polyhedron" /> + <img src="image" alt="Polyhedron" /></td>
<td>a + b = 48</td>
</tr>
<tr>
<td>p.e.c. 74</td>
<td>60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><em>closo</em> deltahedron (14m + 2)</th>
<th><img src="image" alt="Diagram" /></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Polyhedron" /> + <img src="image" alt="Polyhedron" /></td>
<td>a + b = 48</td>
</tr>
<tr>
<td>p.e.c. 86</td>
<td>60</td>
</tr>
</tbody>
</table>
Capping with a tetrahedron adds 12 e to the parent polyhedron

- e.g. application of rules 4-5 to a range of Os clusters
- columns show effect of successive capping on triangular faces
- capping increases electron count by 12

\[ \text{Os}_6(\text{CO})_{18} \]
closa → -12e → nido → -12e → arachno

OCTAHEDRON

[Os\(_6\)(CO)\(_{18}\)]^{2-} \rightarrow \text{not observed} \rightarrow \text{not observed} \rightarrow \text{not observed}

MONO-CAP

[Os\(_7\)(CO)\(_{21}\)] \(198\) \(e\) \(\rightarrow \) \(\rightarrow \) \(\rightarrow \) \(\rightarrow \)

BI-CAP

[Os\(_{8}\)(CO)\(_{22}\)]^{2-} \(110\) \(e\) \(\rightarrow \) \(\rightarrow \) \(\rightarrow \) \(\rightarrow \)

TRI-CAP

[Os\(_{9}\)(CO)\(_{23}\)] \(122\) \(e\) \(\rightarrow \) \(\rightarrow \) \(\rightarrow \) \(\rightarrow \)

TETRA-CAP

[Os\(_{10}\)(CO)\(_{24}\)]^{2-} \(134\) \(e\) \(\rightarrow \) \(\rightarrow \) \(\rightarrow \) \(\rightarrow \)
<table>
<thead>
<tr>
<th>n</th>
<th>EAN</th>
<th>PSPET</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$18 \times 3 = 54 - 6 = 48$</td>
<td>$48 - (12 \times 3) = 12 \rightarrow 6 \text{ pairs (arachno)}$</td>
</tr>
<tr>
<td>4</td>
<td>$18 \times 4 = 72 - 12 = 60$</td>
<td>$60 - (12 \times 4) = 12 \rightarrow 6 \text{ pairs (nido)}$</td>
</tr>
<tr>
<td>5</td>
<td>$18 \times 5 = 90 - 18 = 72$</td>
<td>$72 - (12 \times 5) = 12 \rightarrow 6 \text{ pairs (closo)}$</td>
</tr>
<tr>
<td>6</td>
<td>$18 \times 6 = 108 - 24 = 84$</td>
<td>$n + 2$</td>
</tr>
</tbody>
</table>

7
• Rule 6: If a transition metal atom occupying a vertex position is replaced by a main group atom then the polyhedral electron count is reduced by 10 (main group and transition metal fragments are related isolobally - see earlier lecture).
\[ \text{M}_6\text{A}_2 \text{ p.e.c. 82} \\
\text{e.g. Os}_5\text{S}_2(\text{CO})_{14}\text{H}_2 \]

\[ \text{M}_7\text{A}_2 \text{ p.e.c. 108} \\
\text{e.g. Os}_7\text{S}_2(\text{CO})_{20} \]

\[ \text{M}_4\text{A}_2 \text{ p.e.c. 66} \\
\text{e.g. Mo}_2\text{Fe}_2\text{S}_2(\text{Cp})_2(\text{CO})_8 \]

\[ \text{M}_3\text{A}_4 \text{ p.e.c. 58} \\
\text{e.g. Co}_3(\text{Cp})_3\text{B}_4\text{H}_4 \]

\[ \text{M}_3\text{A}_4 \text{ p.e.c. 60} \\
\text{e.g. Fe}_3(\text{CO})_8(\text{C}_2\text{Ph}_2)_2 \]

\[ \text{M}_4\text{A}_3 \text{ p.e.c. 66} \\
\text{e.g. Mo}_2\text{Co}_2\text{S}_3(\text{Cp})_2(\text{CO})_4 \]

\[ \text{M}_3\text{A}_2 \text{ p.e.c. 54} \\
\text{e.g. Mn}_3(\text{CO})_{10}\text{B}_2\text{H}_7 \]
$M_6A_2$ p.e.c. 82
e.g. $\text{Os}_5S_2(CO)_{14}H_2$

$M_7A_2$ p.e.c. 108
e.g. $\text{Os}_7S_2(CO)_{20}$

$M_4A_2$ p.e.c. 66
e.g. $\text{Mo}_2\text{Fe}_2S_2(Cp)_{2}(CO)_8$

$M_3A_4$ p.e.c. 58
e.g. $\text{Co}_3(Cp)_3B_4H_4$

$M_3A_4$ p.e.c. 60
e.g. $\text{Fe}_3(CO)_8(C_2\text{Ph})_2$

$M_4A_3$ p.e.c. 66
e.g. $\text{Mo}_2\text{Co}_2S_3(Cp)_2(CO)_4$

$M_3A_2$ p.e.c. 54
e.g. $\text{Mn}_3(CO)_{10}B_2H_7$
HYDRIDO CLUSTERS

- presence of hydride can be established using IR and \(^1\)H NMR:
  e.g.

<table>
<thead>
<tr>
<th>Bonding Mode</th>
<th>Compound</th>
<th>(\nu) (M-H), cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–H terminal</td>
<td>-</td>
<td>(~2000 - 1850)</td>
</tr>
<tr>
<td>(\text{M} \quad \overset{\text{H}}{\overset{\text{M}}{\nearrow}})</td>
<td>[HW(<em>2)(CO)(</em>{10})]^-</td>
<td>H: 1680, 71</td>
</tr>
<tr>
<td></td>
<td>H(_4)Ru(<em>4)(CO)(</em>{12})</td>
<td>H: 1605, 1272</td>
</tr>
<tr>
<td></td>
<td>H(_2)Os(<em>3)(CO)(</em>{10})</td>
<td>H: 1245, 73, 1922, 818</td>
</tr>
<tr>
<td></td>
<td>H(_2)Os(<em>3)(CO)(</em>{11})</td>
<td>D: 1220, 1095, 895</td>
</tr>
<tr>
<td></td>
<td>[HO(_8)Os(<em>6)(CO)(</em>{18})]^-</td>
<td>D: 905, 710, 1515, 777(^b)</td>
</tr>
<tr>
<td>M–M face-bridge</td>
<td>[H(_4)Re(<em>4)(CO)(</em>{12})]</td>
<td>H: 1250, 1023(^c)</td>
</tr>
<tr>
<td>[M(_6)H] interstitial</td>
<td>[HRu(<em>6)(CO)(</em>{18})]^-</td>
<td>D: 890</td>
</tr>
</tbody>
</table>

\(^a\) Terminal. \(^b\) Bridging. \(^c\) Band intensity temperature-dependent.
• **indirect methods** for location:
  - lengthening of the M—M bond.
  - distortion of the CO groups, angles or ligand orientations around a metal in order to accommodate the hydride (combined X-ray and neutron studies suggest overall radius of hydride ligand is only slightly less than a CO ligand).
- overall symmetry considerations of the hydride-containing molecule in relation to the symmetry of the molecule without the hydride e.g. if the X-ray data show high symmetry for a molecule, then would place the hydride in a position likely to maintain this symmetry, e.g.

Thus for instance in the draft of the equatorial plane of the anion \([\text{H}_2\text{Re}_3(\text{CO})_{12}]^-\) reproduced in Fig. 3.1 it can be observed that distance Re(2)–Re(3) is shorter than those to including Re(1). This feature, in addition to the distortion of the C-Re-Re-angles from their normal values of 105° indicating the equatorial Re(CO)\(_2\) groups on Re(2) and Re(3) are bending away from Re(1), point out to a location of the hydrogen atoms near the edges Re(1)–Re(2) and Re(1)–Re(3) of the triangle.

⇒ can lead to ambiguities or incorrect assignment.
Hydrogen Bonding Modes

- terminal hydrides are rare, usually in molecules where steric constraints impose a terminal rather than a bridging mode, e.g. the structure of $\text{H}_2\text{Os}_3(\text{CO})_{11}$. Both terminal and bridging H-ligands are attached to the same metal atom.
• bridging, face capping common (terminal $\equiv 2$ e 2-centre bond, $\mu$-$H \equiv 2$ e 3-centre bond, $\mu_3$-$H \equiv 2$-e 4-centre bond).
• few examples of interstitial hydrides,
  e.g. $\text{Co}_6(\mu_6$-$H)(\mu$-$\text{CO})_5(\text{CO})_{11}$. 
[H$_3$Rh$_{13}$(CO)$_{24}$]$^{2-}$ is thought to have three interstitial hydrides rapidly migrating inside the metal core, a fragment of a hexagonal close-packed lattice.
• prediction of hydride location is difficult - even isoelectronic clusters can differ in H location

e.g. $\text{H}_2\text{Ru}_6(\text{CO})_{18}$ - hydrides bridge faces on opposite sides of the octahedron

$\text{H}_2\text{Os}_6(\text{CO})_{18}$ - hydrides bridge opposite edges of capped square pyramid

$\text{H}_4\text{Co}_4\text{Cp}_4$ - tetrahedral with face-bridging hydrides

$\text{H}_4\text{Ru}_4(\text{CO})_{12}$ - tetrahedral with edge-bridging hydrides
Protonation of \([\text{M}_6(\text{CO})_{18}]^{2-}\) affords sequentially \([\text{HM}_6(\text{CO})_{18}]^-\) and \(\text{H}_2\text{M}_6(\text{CO})_{18}\) \((\text{M} = \text{Ru}^{165,166}, \text{Os}^{333})\); the ruthenium cluster \(\text{H}_2\text{Ru}_6(\text{CO})_{18}^{169,240}\) can also be obtained in low yields from the aforementioned reaction of \(\text{Ru}_3(\text{CO})_{12}\) with \([\text{Mn}(\text{CO})_5]^-\), after protic workup. The ruthenium clusters both adopt octahedral core geometries: \([\text{Ru}_6(\mu_5-\text{H})(\text{CO})_{18}]^-\) \((103)\) contains an interstitial hydrido ligand \(167,168\) (\(\delta\) \(\text{RuH}\) 16.41 ppm; \(167\) \(\nu(\text{RuH})\) 825 cm\(^{-1}\)\(^{341}\)), whereas \([\text{Ru}_6(\mu_3-\text{H})_2(\text{CO})_{18}]^-\) \((104)\) contains two face-capping hydrido ligands. \(169,170\) \([\text{Os}_6(\mu_3-\text{H})(\text{CO})_{18}]^-\) \((105)\) is octahedral with a face-capping hydride, and \(\text{Os}_6(\mu_2-\text{H})_2(\text{CO})_{18}\) \((106)\) has a monocapped square pyramidal core. \(164,171,333\) the hydrido ligands in the latter are calculated to occupy edge-bridging sites. \(342\) Thus, none of the Ru–Os pairs \([\text{M}_6(\text{CO})_{18}]^{2-}\), \([\text{HM}_6(\text{CO})_{18}]^-\) or \(\text{H}_2\text{M}_6(\text{CO})_{18}\) are isostructural.
Table 21.3 The influence of coordination and charge on CO stretching wavenumbers

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tilde{\nu}$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2143</td>
</tr>
<tr>
<td>[Mn(CO)$_6$]$^+$</td>
<td>2090</td>
</tr>
<tr>
<td>Cr(CO)$_6$</td>
<td>2000</td>
</tr>
<tr>
<td>[V(CO)$_6$]$^-$</td>
<td>1860</td>
</tr>
<tr>
<td>[Ti(CO)$_6$]$^{2-}$</td>
<td>1750</td>
</tr>
</tbody>
</table>
CO BONDING MODES

Schematic representation of some less usual bonding stereochemistries of carbon monoxide (blackened spheres).

(see also Prof Brian Mann's web site: http://brian-mann.staff.shef.ac.uk/Fe3CO12/Fe3-carbonyl-web.html)
Bürgi-Dunitz mapping: using statics (structural studies) to infer dynamics (fluxionality). The following is from the Cambridge Structural Database:

The CSD contains numerous crystal structure determinations of iron carbonyl derivatives. These structures contain either a terminal carbonyl (1), a carbonyl ligand that symmetrically bridges two Fe atoms (3) or a semi-bridging carbonyl where the ligand is bound asymmetrically (2). These bridged compounds (2,3) may be considered as snap-shots of the carbonyl exchange process:

The static distortions exhibited by these molecular fragments in a variety of crystalline environments are assumed to map the distortions the fragments would undergo during carbonyl exchange. Examination of a series of crystal structures can therefore enable a dynamic reaction pathway to be mapped. This principle is exemplified in *Structure Correlation* (Burgi & Dunitz, 1994), and application reviews have been presented by Klebe (*J. Mol. Struct.*, 308, 53, 1994) and Ferretti (*Cryst. Rev.*, 5, 3, 1996).
Rationalization:

(i) **electronic** - redistribution of electron density through either donation from the filled d orbital of a metal into a $\pi^*$ orbital of an adjacent metal atom’s CO group, or from an opposite flow of electron density from a filled $\pi$ orbital of a CO group into an empty d orbital of an adjacent, electronically unsaturated metal.

- bridging COs are better $\pi$-acids and more effective at removing electron density $\rightarrow$ mechanism for relieving an uneven charge distribution arising from uneven M-M or M-L bonds, or from bonds between different metals.
(ii) **steric** - assumes that the attractive interactions with the second (or third) metal atom are negligible, and the steric requirements of the whole ligand shell are responsible for the unsymmetric bridging in the solid state structure.

**eg.** $\text{Fe}_2(\mu\text{-CO})_3(\text{CO})_6$  
$\text{Fe-C} = 1.838 \text{ Å}$ terminal  
$2.016 \text{ Å}$ bridging

bridging CO is held further away from the cluster core
• in many cases, no obvious electronic or steric reason for bridging carbonyls, and there is some controversy as to the relative importance of electronic vs steric effects

e.g. \( \text{Fe}_3(\mu\text{-CO})_2(\text{CO})_{10} \quad \text{Ru}_3(\text{CO})_{12} \)
• bridging COs are common in 1st and 2nd row transition metal complexes, but are rare in neutral 3rd row clusters, occurring only when electron density on the metal atoms is increased through CO substitution by better donor ligands, or by developing a formal negative charge, e.g.

\[ \text{Co}_4(\mu-\text{CO})_3(\text{CO})_9 \quad \text{Rh}_4(\mu-\text{CO})_3(\text{CO})_9 \]

\[ \text{Ir}_4(\text{CO})_{12} \quad \text{Ir}_4(\mu-\text{CO})_3(\text{CO})_7(\text{PPh}_3)_2 \]

\[ [\text{Ir}_4\text{H}_2(\mu-\text{CO})_3(\text{CO})_7]^2^- \]
• increasing the donor strength of a ligand by permethylation favors bridging COs; the molecule at left has a plane of bridging COs, but the Cp analogue has the "all-terminal" CO arrangement.
The table shows that progression from terminal CO to $\mu_3$-CO to dihapto-CO bonding is associated with a lowering of the CO stretching frequency, indicating weakening of the C-O bond.

<table>
<thead>
<tr>
<th>CO Group</th>
<th>C–O Distance (Å)</th>
<th>$\nu$(CO) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>terminal</td>
<td>1.12 - 1.19</td>
<td>2150 - 1950</td>
</tr>
<tr>
<td>$\mu$-</td>
<td>1.165 - 1.20</td>
<td>1850 - 1750</td>
</tr>
<tr>
<td>$\mu_3$-</td>
<td>1.19 - 1.22</td>
<td>1700-1600</td>
</tr>
<tr>
<td>$\mu-\eta$2-</td>
<td></td>
<td>1560</td>
</tr>
<tr>
<td>$\mu_3-\eta$2-</td>
<td></td>
<td>1330</td>
</tr>
</tbody>
</table>
Alkyne coordination

I. Acetylene ligands - (RC≡CR)

• range from 1-metal to 4 or more metals interacting with a single acetylene unit.
• in all cases, the acetylene unit acts as a dihapto ligand.
• C≡C bond distance increases from ~ 1.20 Å in free alkyne to ~ 1.24 - 1.4 Å.
One metal atom interaction

- observed M–C, C=C bond lengths and R-C-C angle best fit the metallacycloprenone structure
- not common in clusters
Two metal atom interaction - $\mu_2$ bridging ligands

- $\sigma$ - bridging alkyne
- 2 e donor (1 to each M)
- acetylene ligand is parallel to M–M bond
- C≡C bond length $\sim 1.27\text{Å}$
Three metal atom interaction - $\mu_3$ alkynes

$\equiv$

$\mu_3, \eta^2 - C_2R_2$

- C≡C bond length $\sim 1.41 \text{ Å}$
Three metal atom interaction - $\mu_3$ alkynes

- C–C bond is perpendicular to M-M bond, with one C lying outside the metal triangle
- C≡C bond length $\sim 1.44$ Å
Four metal atom interaction - $\mu_4$ alkynes

$2\sigma, 2\pi$  \hspace{1cm}  $\mu_4, \eta^2 - \text{C}_2\text{R}_2$

- 4 metal atoms define a butterfly geometry
- acetylene is parallel to the M–M hinge bond, and perpendicular to the wing-tip M–M vector
- C≡C bond length $\sim 1.44$ Å
II. Acetylide ligands  \(-(\text{C}≡\text{CR})\)

- 1σ, 1π bond
- 3 electron donor

- 1σ, 2π bonds
- 5 electron donor
Note:
Many of the all-$\sigma$ representations show > 4 bonds to the C atoms, but as the number of alkyne-metal interactions increase, the C-C bond distance increases, suggesting that the alkyne ligand is either donating or backbonding more electron density than the alkyne ligands interacting with only 1 or 2 metal atoms

$\Rightarrow$ electron counts can lead to electron deficient clusters
solution: treat the acetylene unit as part of the framework where possible, and use Wade's rules for fused polyhedra.

e.g.

\[(\eta^5-C_5H_5)_2\text{Mo}_2\text{Ir}_2(\mu_4-\eta^2-\text{PhC}=\text{CH})(\mu-\text{CO})_4(\text{CO})_4\]
Consider: acetylene carbons as part of the framework. Then an octahedral cluster with 2 main group atoms: \((14 \times 6 + 2) - 2(10) = 66\) e.

Is this now electron precise? Count the electrons, treating the acetylene carbons as part of the core, and the acetylene substituents as "ligands":

no electrons = Me ("metal" valence electrons) + Le ("ligand" electrons)

\[= [ 2(6) + 2(9) + 2(4) ] + [ 2(5) + 8(2) + 1 + 1 ] = 66e \]

⇒ electron precise
How to characterize a cluster? Commonly use a combination of IR, NMR, MS, and X-ray diffraction.

**IR**

\[ \nu (\text{CO}) \quad 2100 - 1900 \text{ cm}^{-1} \]

\[ \nu (\mu_{\text{C}}\text{O}) \quad 1850 - 1750 \]

\[ \nu (\mu_{3}\text{C}O) \quad 1700 - 1600 \]

\[ \nu (\mu_{3}\eta^{2}\text{C}O) \quad 1330 \]

\[ \nu (\text{MH}) \quad 2000 - 1330 \]

\[ \nu (\text{MM}) \quad 200 - 100 \]


NMR

\begin{align*}
^{1}H & \text{ M–H} & \delta & \text{ -10 to -50 ppm} \\
& \text{ M–H(t)} & {\text{ -10 to -20}} \\
& \text{ M–H(b)} & {\text{ -20 to -40}} \\
& \text{ M}_6(\mu_6–H) & +15 \text{ to } +25 \\
^{13}C & \text{ M–CO (terminal)} & 180-200 \\
& \text{ M–CO (bridging)} & 200-250
\end{align*}
Mass spectra

EI for volatile compounds, e.g. $\text{Ru}_3(\text{CO})_{12}$

$[\text{M}]^+$, $[\text{M} - n\text{CO}]^+$, ..., $M_n$ core

FAB for non-volatile, salts

Electrospray for solutions

Note: characteristic isotope patterns.
X-ray (neutron) diffraction

Routine to determine crystal structures of reaction products.

\[
\begin{align*}
M-\text{M} & \pm 0.001 \ \text{Å} \\
M-\text{C} & \pm 0.01 \\
M-\text{H} & \pm 0.05
\end{align*}
\]

Neutron expensive, but sometimes essential, e.g. \text{Ru}_6(\mu_6-\text{H}), \text{Co}_6(\mu_6-\text{H}).
Cluster Reactivity

Low-nuclearity clusters

• Substitution, addition reactions, often under mild conditions.

Progression from monometallic complexes to clusters results in the possibility of:
  • associative mechanisms via transient M-M cleavage.
  • site-selectivity and metalloselectivity for substitution.
  • bond selectivity in mixed-metal clusters.
  • unusual multimetallic coordination/activation of ligands.
  • metal replacement.
Recall (S&A, pp 498-499): Monometallic complexes react via:

- associative mechanisms (below, left).
- dissociative mechanisms (below, middle).
- interchange mechanisms.

In an associative mechanism, an intermediate is formed with a higher coordination number than the original complex. In an interchange process, there is no evidence for an isolable intermediate.
• associative mechanisms via transient M-M cleavage.

Organometallics, 1995, 14, 1536

\[ \text{L} = \text{CO, PPh}_3 \]

Stepwise formation of mono- to tetrakis phosphine-substituted derivatives

This is a rare example of facile substitution via M-M cleavage at a high-nuclearity cluster. The Os\(_{10}\) analogue requires activation by \(X_2\) and refluxing xylene to react with phosphines.
Recall (S&A, pp 231-232): Monometallic complexes react to give 
trans and cis isomers after bis-substitution, and fac and mer isomers 
upon tris-substitution.
In almost all instances, multiple substitution at a cluster proceeds at differing vertices. A highly unusual example is shown below.

This was the first structurally characterized tetrahedral cluster with two terminal isocyanide groups ligated to the same metal vertex. A trinuclear precedent exists: [Fe$_3$($\mu$-CO)$_2$(CO)$_8$(CNBu')$_2$].

*J. Organomet. Chem.*, 1999, **579**, 75
site-selectivity and (for mixed-metal clusters)
metalloselectivity for substitution.

Consider tetrahedral clusters:

![Tetrahedral clusters diagram]

Figure 2.1.1. Solid-state structures of \([M_4(CO)_{12}]\) (M = Co, Rh, Ir)
All sites are equivalent in the all-terminal geometry. There are four distinct sites in the plane-of-bridging-COs geometry.

![Diagram](image)

(i) All terminal  (ii) Radial  (iii) Axial  (iv) Apical

(v) Bridging  (vi) Radial, axial chelating

**Figure 2.1.2.** Sites of substitution for derivatives of [Ir₄(CO)₁₂] (1)
site-selectivity and metalloselectivity for substitution. Note plane of bridging COs following ligand substitution.

\[ \text{diphosphines ligate diaxially at Ir} \]

*Organometallics, 1993, 12, 3468*
- site-selectivity and metalloselectivity for substitution.
Note plane of bridging COs following ligand substitution.

\[ \text{WIr}_3(\mu\text{-CO})_3(\text{CO})_{8-n}(L)_n(\eta\text{-C}_5\text{H}_5) \]

\[ L = \text{PPh}_3, \text{PMe}_3; n = 1 - 3 \]

*Organometallics, 1996, 15, 934*
unusual multimetallic coordination/activation of ligands.

Examples:

Bond cleavage(s)

\[
\begin{align*}
\text{PPh}_3 & \quad \rightarrow \quad \text{PPhC}_6\text{H}_4 + \text{C}_6\text{H}_6 \\
\text{PhC}≡\text{CPh} & \quad \rightarrow \quad \text{PhCC(Ph)}\text{CPh} + \text{CPh} \\
\text{PhC}≡\text{CPh} & \quad \rightarrow \quad \text{PhCC(Ph)C(Ph)CPh} + \text{CPh} + \text{CPh} \\
\text{RCH}_3 & \quad \rightarrow \quad \text{RCH} + \text{H} + \text{H} \\
\text{NC}_5\text{H}_5 + \text{Ph}_2\text{PCH}_2\text{PPh}_2 & \quad \rightarrow \quad \text{NC}_5\text{H}_4 + \text{Ph}_2\text{PCH}_2\text{PPh} + \text{C}_6\text{H}_6
\end{align*}
\]

Bond weakening

\[
\begin{align*}
\text{C=}\text{N} & \quad \rightarrow \quad \text{C····N}
\end{align*}
\]
• unusual multimetallic coordination/activation of ligands.

\[ \Delta, \text{toluene} \]

unusual multimetallic coordination/activation of ligands.

Scheme 4.2.1. Reactivity of [CpWIr$_3$(CO)$_{14}$] (2) and [Cp$_2$W$_2$Ir$_2$(CO)$_{16}$] (3) with diphenylacetylene.
unusual multimetallic coordination/activation of ligands.
Multiple oxidative addition of a methyl group.

Citation:
• unusual multimetallic coordination/activation of ligands.

Oxidative addition of pyridine.

(Chemical structures and reactions)

*J. Organomet. Chem., 1996, 513, 201*
unusual multimetallic coordination/activation of ligands.

Current challenge: to develop reliable routes to medium- and high-nuclearity clusters.

Problem: lack of general and reliable synthetic routes.

Possibility: extend chemistry developed with organic alkynes to "inorganic alkynes" (metal alkynyl complexes \([\text{M}]\text{C}=\text{CR}\), ethynylidyln complexes \([\text{M}]\text{C}=\text{C}[\text{M}]\)).