CHM 8302-B

General concepts
(crystal field ligand field and isolobality)
Coordination and back and pi-bonding

Nature of coordinative bond
Back-bonding
Bonding of metals to $\pi$-systems
Valence bond and hybridization
Valence Bond Theory

For a $d^5$ metal ion:
Inner orbital

\[
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
3d
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4s
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4p
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4d
\end{array}
\]

\[d^2sp^3\]

For a $d^7$ metal ion:
Inner orbital

\[
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
3d
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4s
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4p
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
5s\quad \text{(or} \quad 4d\text{)}
\end{array}
\]

\[d^2sp^3\]

For a $d^6$ metal ion:
Outer orbital

\[
\begin{array}{c}
\uparrow \uparrow \uparrow \uparrow \\
3d
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4s
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4p
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4d
\end{array}
\]

\[sp^3d^2\]

For a $d^7$ metal ion:
Outer orbital

\[
\begin{array}{c}
\uparrow \uparrow \uparrow \uparrow \\
3d
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4s
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4p
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4d
\end{array}
\]

\[sp^3d^2\]
Crystal Field

Basic Idea

\[ E \]

- Metal in the center of a charged sphere
- Metal in the center of an octahedral field

\[ E \text{ is a function of } n \text{ and } l \text{ quantum numbers and therefore the } d \text{ orbitals should be degenerate.} \]
Crystal Field and molecular geometry

The diagram shows the energy levels ($E_\text{cr}$) for different molecular geometries. The $d$-orbital levels are labeled as $d_{x^2-y^2}$, $d_{xz}$, $d_{yz}$, and $d_{xy}$, with corresponding degeneracies indicated by the number of horizontal lines above each level. The geometries include square planar, trigonal bipyramidal, square pyramidal, octahedral, pentagonal bipyramidal, and square antiprismatic.
Figure 9.19 Octahedral sigma overlap for first-row transition-metal orbitals.

No net overlap (sigma nonbonding)

Figure 9.20 Sigma-only MOs for octahedral overlap.
Figure 9.23 Square-planar sigma overlap for first-row transition-metal orbitals.
Figure 9.21 Tetrahedral sigma overlap for first-row transition-metal orbitals.

Figure 9.22 Sigma-only MOs for tetrahedral overlap.
Figure 9.26 Effect of pi bonding to pi-acceptor ligands on sigma-only O₅ energy levels.

Figure 9.28 Effect of pi bonding to pi-donor ligands on sigma-only O₅ energy levels.
Effect of pi-bonding on ligand field:

Figure 10.10 Octahedral MOs for varying degrees of sigma and pi interaction.
Analogy Organic-Inorganic

Overall:
Inorganic chemistry is richer (more complex, less well understood) than organic chemistry but parallels exist. Examine parallels, use understanding of organic chemistry to enhance understanding of inorganic, and of main group chemistry to enhance understanding of transition metals.
Electronic Equivalence

Organic versus Inorganic Reactivity Parallelism: the first idea

(J. Halpern C&En Oct 31-1966 pag. 68)

Saturated          Organic          Inorganic

Non bonding e-      0                4                6                6

coordination #      12 el            6 el

SN2 and SN1 reactions ligand replacement reactions

8 bonding el. (octect) anti-bond

non-bonding       18 el
### Electronic Equivalence (empirical approach)

<table>
<thead>
<tr>
<th></th>
<th>Organic</th>
<th></th>
<th>Inorganic</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-bonding el.</td>
<td>Coord. #</td>
<td>Non-bonding el.</td>
<td>Coord. #</td>
</tr>
<tr>
<td><strong>Saturated</strong> (substitutions)</td>
<td>0</td>
<td>4</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td><strong>Radical</strong> (atom abstractions &amp; addition)</td>
<td>1</td>
<td>3</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td><strong>Carbene</strong> (cyclopropanation, oxidative addition)</td>
<td>2</td>
<td>2</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td><strong>Carbanion</strong> (nucleophiles)</td>
<td>2</td>
<td>3</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td><strong>Carbocation</strong> (electrophiles, low spin)</td>
<td>0</td>
<td>3</td>
<td>6</td>
<td>5</td>
</tr>
</tbody>
</table>


**Electronic Equivalence**


<table>
<thead>
<tr>
<th>Electrons short of filled shells</th>
<th>Examples of electronically equivalent species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl, Br, I</td>
</tr>
<tr>
<td>2</td>
<td>S</td>
</tr>
<tr>
<td>3</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td><strong>Main group</strong></td>
</tr>
<tr>
<td></td>
<td>Cl, Br, I</td>
</tr>
<tr>
<td></td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>P</td>
</tr>
<tr>
<td></td>
<td><strong>Metal carbonyl</strong></td>
</tr>
<tr>
<td></td>
<td>Mn(CO)₅</td>
</tr>
<tr>
<td></td>
<td>Fe(CO)₄, Os(CO)₄</td>
</tr>
<tr>
<td></td>
<td>Co(CO)₃, Ir(CO)₃</td>
</tr>
</tbody>
</table>

octet rule \( \leftrightarrow \) 18 electron rule
7 e species \( \leftrightarrow \) 17 e species
6 e species \( \leftrightarrow \) 16 e species
5 e species \( \leftrightarrow \) 15 e species

Comparisons useful in cases where 18e rule holds (in transition metal chemistry this is organometallic chemistry).
Electronic Equivalence: is that meaningful?

Parallels between Cl and Co(CO)₄:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Examples</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion of 1- charge</td>
<td>Cl⁻</td>
<td>[Co(CO)₄]⁻</td>
</tr>
<tr>
<td>Neutral dimeric species</td>
<td>Cl₂</td>
<td>[Co(CO)₄]₂</td>
</tr>
<tr>
<td>Hydrohalic acid</td>
<td>HCl (strong acid in aq soln)</td>
<td>HCo(CO)₄ (strong acid in aq soln)</td>
</tr>
<tr>
<td>Formation of interhalogen compounds</td>
<td>Br₂ + Cl₂ → 2 BrCl</td>
<td>I₂ + [Co(CO)₄]₂ → 2 ICo(CO)₄ (unstable)</td>
</tr>
<tr>
<td>Formation of heavy metal salts of low solubility in water</td>
<td>AgCl</td>
<td>AgCo(CO)₄</td>
</tr>
<tr>
<td>Addition to unsaturated species</td>
<td>Cl₂ + H₂C=CH₂ → H–C–C–H</td>
<td>+ [Co(CO)₄]₂ + F₂C=CF₂ → Co–C–C–Co (CO)₄</td>
</tr>
<tr>
<td>Disproportionation by Lewis base</td>
<td>Cl₂ + NMe₃ → [ClNMe₃] Cl</td>
<td>[Co(CO)₄]₂ + C₅H₁₀NH → [(CO)₄Co(C₅H₁₀NH)][Co(CO)₄]</td>
</tr>
</tbody>
</table>
### Isolobal Analogy

**Parallels between S and Fe(CO)₄:**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Examples</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion of 2- charge</td>
<td>S²⁻</td>
<td>[Fe(CO)₄]²⁻</td>
</tr>
<tr>
<td>Neutral compound</td>
<td>S₈</td>
<td>Fe₂(CO)₉, Fe₃(CO)₁₂</td>
</tr>
<tr>
<td>Hydride</td>
<td>H₂S: ( pK₁ = 7.24 ) *</td>
<td>H₂Fe(CO)₄: ( pK₁ = 4.44 ) *</td>
</tr>
<tr>
<td></td>
<td>( pK₂ = 14.92 )</td>
<td>( pK₂ = 14 )</td>
</tr>
<tr>
<td>Phosphine adduct</td>
<td>Ph₃PS</td>
<td>Ph₃PFe(CO)₄</td>
</tr>
<tr>
<td>Polymeric mercury compound</td>
<td><img src="image" alt="Polymeric mercury compound" /></td>
<td><img src="image" alt="Polymeric mercury compound" /></td>
</tr>
<tr>
<td>Compound with ethylene</td>
<td><img src="image" alt="Compound with ethylene" /></td>
<td><img src="image" alt="Compound with ethylene" /></td>
</tr>
</tbody>
</table>

Note: *pK values in aq. solution at 25 °C.*
– *Electronic Equivalence*

**Limitations:**

*octet expansion (main group), reaction chemistry* (organometallic).

– Isolobal Analogy


**Definition:** two fragments are isolobal if the **number**, **symmetry** properties, approximate **energies** and **shape** of frontier orbitals, as well as the **number** of electrons occupying them, are similar (not identical).

Then:

- $d^6$–ML$_6$ ↔ CH$_4$ methane
- $d^7$–ML$_5$ ↔ CH$_3$· methyl
- $d^8$–ML$_4$ ↔ CH$_2$∶ methylene
- $d^9$–ML$_3$ ↔ CH∶ methylidyne
- Isolobal Analogy

Combine fragments into molecules:

\[
\cdot \text{CH}_3 \quad \overset{\sigma}{\leftrightarrow} \quad \cdot \text{Mn}(\text{CO})_5
\]

\[
\text{H}_3\text{CCH}_3 \quad \overset{\sigma}{\leftrightarrow} \quad \text{H}_3\text{CMn(\text{CO})}_5 \quad \overset{\sigma}{\leftrightarrow} \quad (\text{CO})_5\text{Mn} - \text{Mn(\text{CO})}_5
\]

(organic and organometallic parallels)
– Isolobal Analogy

Starting-point for the derivation of the lobal properties of organometallic fragments is the simplified MO scheme of an octahedral complex.

The removal of one ligand L converts a bonding $\sigma$-MO of the complex ML$_6$ into a nonbonding frontier orbital $\psi_{hy}$ of the fragment ML$_5$. 
– *Isolobal Analogy*

\[
\begin{align*}
\text{M} & \quad \text{d}^6-\text{ML}_6 & \quad 6L \\
\text{M} & \quad \text{d}^6-\text{ML}_5 & \quad 5L
\end{align*}
\]
– Isolobal Analogy

The removal of 2 L creates 2 new frontier orbitals

and the removal of 3 L creates 3 new frontier orbitals, ψhy:

- \( \text{Mn(CO)}_5 \)
  - \( d^7 – ML_5 \)

- \( \text{Fe(CO)}_4 \)
  - \( d^8 – ML_4 \)

- \( \text{Co(CO)}_3 \)
  - \( d^9 – ML_3 \)
– Isolobal Analogy

The frontier orbitals \( t_{2g} \) and \( \psi_{hy} \) are filled by \( n \) electrons of the central metal (configuration \( dn \)). This provides \( \text{Mn(CO)}_5 \) with one, \( \text{Fe(CO)}_4 \) with two, and \( \text{Co(CO)}_3 \) with three, singly occupied orbitals with distinct spatial orientation. These organometallic fragments are complementary to organic analogues:

\[
\begin{align*}
\text{d}^7-\text{ML}_5 & \quad \leftrightarrow \quad \cdot \text{CH}_3 \\
\text{d}^8-\text{ML}_4 & \quad \leftrightarrow \quad : \text{CH}_2 \\
\text{d}^9-\text{ML}_3 & \quad \leftrightarrow \quad : \text{CH} \\
\text{methyl} & \\
\text{methylene} & \\
\text{methylidyne} &
\end{align*}
\]
**Isolobal Analogy**

The isolobal connection allows a joint consideration of inorganic, organic and organometallic structures, the relationships being based on the isolobal nature of the respective molecular fragments.
– Isolobal Analogy

\[ d^8 - ML_4 \quad \leftrightarrow \quad CH_2 \]

- \( C_3H_6 \) (cyclopropane)
- \((C_2H_4)Fe(CO)_4\)
- \( C_5H_8 \) (spiropentane)

- \((\mu-CH_2)Fe_2(CO)_8\)
- \(Os_3(CO)_{12}\)
- \(Fe(CO)_4 \quad \leftrightarrow \quad CH_2\)
Isolobal Analogy

\[ d^9 - ML_3 \rightleftharpoons CH \]

\[
\begin{align*}
\text{RC} & \quad \text{RC} \\
\text{CR} & \quad \text{CR} \\
\text{RC} & \quad \text{RC} \\
\text{RC} & \quad \text{RC} \\
\text{(CO)}_3 & \quad \text{(CO)}_3 \\
\text{(OC)}_3\text{Co} & \quad \text{(OC)}_3\text{Ir} \\
\text{Co} & \quad \text{Ir} \\
\text{(CO)}_3 & \quad \text{(CO)}_3 \\
\text{(CO)}_3\text{Co} & \quad \text{(CO)}_3\text{Ir} \\
\text{Co} & \quad \text{Ir} \\
\text{(CO)}_3 & \quad \text{(CO)}_3
\end{align*}
\]
– Isolobal Analogy

Unnumbered figure pg 52a
*Shriver & Atkins Inorganic Chemistry, Fourth Edition*

Unnumbered figure pg 52b
*Shriver & Atkins Inorganic Chemistry, Fourth Edition*

Unnumbered figure pg 52c
*Shriver & Atkins Inorganic Chemistry, Fourth Edition*
– **Isolobal Analogy**

The concept of isolobality focuses on partly occupied orbitals only.
– Isolobal Analogy

Even the molecules P4, As4 and Sb4 may be included into a larger family:

\[ \text{d}^9 - \text{ML}_3 \quad \overset{\text{O}}{\longleftrightarrow} \quad \text{CH} \quad \overset{\text{O}}{\longleftrightarrow} \quad \text{As} \]

and hence the following tetrahedranes are analogous:
– *Isolobal Analogy*

Inclusion of the ligand $\eta$-$\text{C}_5\text{H}_5^-$ which, as a donor of 3 \( \pi \)-electron pairs formally occupies 3 coordination sites, yields the analogies:

$$\text{Fe(CO)}_4 \leftrightarrow \text{CpFe(CO)}^- \leftrightarrow \text{CpRh(CO)} \quad (\text{d}^8-\text{ML}_4)$$

The following molecules are related:
Another analogy is that between cyclopropane and μ-alkylidene complexes:
### Isolobal Analogy

Table 21.10  Selected isolobal fragments

![Isolobal Analogy Diagram](image)

Note that electrons can be added to or subtracted from each member of the isolobal group and still maintain isolobality. For example, $\text{CH}_3^+ \leftrightarrow \text{Mn(CO)}_5^+ \leftrightarrow \text{Co(CO)}_4^-$. 

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Table 21-10
*Shriver & Atkins Inorganic Chemistry, Fourth Edition*

- Isolobal Analogy

The cluster above is the metallocyclopropane version of the cluster at top right, which is isolobally connected to the complex at bottom right.
– **Isolobal Analogy**

The realm of isolobal connections is considerably extended if the mutual replacement of σ-donor ligands and metal electron pairs is introduced:

<table>
<thead>
<tr>
<th>Organic fragment</th>
<th>Coordination number of the metal on which derivation of the isolobal fragments is based</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9</td>
</tr>
<tr>
<td>CH₃</td>
<td>d¹-ML₈</td>
</tr>
<tr>
<td>CH₂</td>
<td>d²-ML₇</td>
</tr>
<tr>
<td>CH</td>
<td>d³-ML₆</td>
</tr>
</tbody>
</table>
– Isolobal Analogy

Analogy can be extended to:

(a) charged species

(b) ligands other than CO

(c) geometries other than octahedral
– Isolobal Analogy

**Charged species:**

(a) \( \text{CH}_3 \quad \leftrightarrow \quad \text{Mn(CO)}_5 \quad \leftrightarrow \quad [\text{Fe(CO)}_5]^+ , [\text{Cr(CO)}_5]^+ \quad \text{all } d^7-\text{ML}_5 \)

\( \text{CH}_3^+ \quad \leftrightarrow \quad [\text{Mn(CO)}_5]^+ , \text{Cr(CO)}_5 \)

- 6 electron
- 16 electron

\( \text{CH}_3^- \quad \leftrightarrow \quad [\text{Mn(CO)}_5]^-, \text{Fe(CO)}_5 \) (not trig. bipy., but squ. py.)

- 8 electron
- 18 electron
Isolobal Analogy

Ligands other than CO:

(b) \[ \text{Mn(CO)}_5 \leftrightarrow \text{Mn(PR}_3)_5 \leftrightarrow [\text{MnCl}_5]^{5-} \]

\[ \text{Mn(CO)}_5 \leftrightarrow [\text{Fe(CO)}_5]^+ \leftrightarrow \text{Fe(CO)}_2(\eta-C_5H_5) \]

\[ [\text{Mn(CO)}_5]^+ \leftrightarrow \text{Cr(CO)}_5 \leftrightarrow \text{Mn(CO)}_2(\eta-C_5H_5) \]

\[ (\eta-C_5H_5)^- \text{ occupies 3 coord sites and donates 6 electrons} \]
– Isolobal Analogy

Geometries other than octahedral:

(c) $d^{x-}ML_n \leftrightarrow d^{x+2}ML_{n-2}$

e.g. oct. $ML_5$ \hspace{2cm} sq. pl. $ML_3$

$d_z^2$ orbital changes from antibonding to nonbonding

$Cr(CO)_5 \leftrightarrow Fe(CO)_3 \leftrightarrow [PtCl_3]^-$

$d^6$ (oct) \hspace{2cm} $d^8$ (sq planar) \hspace{2cm} $d^8$

$Fe(CO)_4 \leftrightarrow Ni(PR_3)_2 \leftrightarrow Pt(PR_3)_2$

$d^8$ (oct) \hspace{2cm} $d^{10}$ (sq planar) \hspace{2cm} $d^{10}$
### Isolobal Analogy

**Examples of isolobal fragments:**

<table>
<thead>
<tr>
<th>Neutral hydrocarbon</th>
<th>( \text{CH}_4 )</th>
<th>( \text{CH}_3 )</th>
<th>( \text{CH}_2 )</th>
<th>( \text{CH} )</th>
<th>( \text{C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Isolobal organometallic fragments</strong></td>
<td>( \text{Cr(CO)}_6 )</td>
<td>( \text{Mn(CO)}_5 )</td>
<td>( \text{Fe(CO)}_4 )</td>
<td>( \text{Co(CO)}_3 )</td>
<td>( \text{Ni(CO)}_2 )</td>
</tr>
<tr>
<td></td>
<td>( \text{[Mn(CO)}_6^+ )</td>
<td>( \text{[Fe(CO)}_5^+ )</td>
<td>( \text{[Co(CO)}_4^+ )</td>
<td>( \text{[Ni(CO)}_3^+ )</td>
<td>( \text{[Cu(CO)}_2^+ )</td>
</tr>
<tr>
<td>( \text{CpMn(CO)}_3 )</td>
<td>( \text{CpFe(CO)}_2 )</td>
<td>( \text{CpCo(CO)} )</td>
<td>( \text{CpNi} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Anionic hydrocarbon fragments obtained by loss of ( \text{H}^+ )</strong></td>
<td>( \text{CH}_3^- )</td>
<td>( \text{CH}_2^- )</td>
<td>( \text{CH}^- )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Fe(CO)}_5 )</td>
<td>( \text{Co(CO)}_4 )</td>
<td>( \text{Ni(CO)}_3 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Isolobal OM fragments</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cationic hydrocarbon fragments obtained by gain of ( \text{H}^+ )</strong></td>
<td>( \text{CH}_4^+ )</td>
<td>( \text{CH}_3^+ )</td>
<td>( \text{CH}_2^+ )</td>
<td>( \text{CH}^+ )</td>
<td></td>
</tr>
<tr>
<td>( \text{V(CO)}_6 )</td>
<td>( \text{Cr(CO)}_5 )</td>
<td>( \text{Mn(CO)}_4 )</td>
<td>( \text{Fe(CO)}_3 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Isolobal OM fragments</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>