Reactivity

Brief Survey of the Transition Metals

Early Transition Metals
Groups 3, 4

1. Strongly electrophilic and oxophilic
2. Few redox reactions (exception: Ti)
3. Nearly always < 18e
4. Polar and very reactive M-C bonds
   (to alkyl and aryl)
5. Few d-electrons:
   1. preference for "hard" $\sigma$-donors
   2. weak complexation of $\pi$-acceptors

http://home.cc.umanitoba.ca/~budzelaa/CHEM4680/Lectures/TransitionMetals.ppt
Reactivity

Early Transition Metals
Groups 3,4

Typical catalysis: Polymerization

http://home.cc.umanitoba.ca/~budzelaa/CHEM4680/Lectures/TransitionMetals.ppt
"Middle" Transition Metals
Groups 5-7

1. Many accessible oxidation states
2. Mostly 18e
3. Ligands strongly bound
4. Strong, not very reactive M-C bonds
5. Preference for $\sigma$-donor/$\pi$-acceptor combinations (CO!)

http://home.cc.umanitoba.ca/~budzelaa/CHEM4680/Lectures/TransitionMetals.ppt
"Middle" Transition Metals
Groups 5-7

Typical catalysis: Alkene and alkyne metathesis

http://home.cc.umanitoba.ca/~budzelaa/CHEM4680/Lectures/TransitionMetals.ppt
Late Transition Metals
Groups 8, 9 (and 10)

1. Many accessible oxidation states
2. Mostly 18e or 16e
   16e common for square-planar complexes
3. Easy ligand association/dissociation
4. Weak, not very reactive M-C bonds
5. Even weaker, reactive M-O/M-N bonds
6. Preference for $\sigma$-donor/weak $\pi$-acceptor ligands (phosphines)
Late Transition Metals
Groups 8, 9 (and 10)

Typical catalysis: Hydroformylation

Reactivity
Reactivity

3d metals can be contrasted with 4d and 5d metals

1\textsuperscript{st} row:
1. often unpaired electrons
2. different spin states (HS/LS) accessible
3. highest oxidation states not very stable

2\textsuperscript{nd}/3\textsuperscript{rd} row:
1. nearly always "closed shell"
2. highest oxidation states fairly stable
3. 2\textsuperscript{nd} row often more reactive than 3\textsuperscript{rd}
Reactivity

Certain groups of metals have specific names

![Chemical Elements Diagram](image-url)
The mode of attachment of the donor ligand is described by denoting the number of atoms (together with positions if necessary) attached to the metal atom by $\eta^n$. This formalism contains no implications regarding the type of bonding.

e.g. pentacarbonyl($\eta^1$-methyl)manganese(I), MnMe(CO)$_5$
($\eta^1$-allyl)pentacarbonylmanganese(I), Mn($\eta^1$-CH$_2$CH=CH$_2$)(CO)$_5$
($\eta^3$–allyl)tetracarbonylmanganese(I), Mn(CO)$_4$(\eta^3-C$_3$H$_5$)
tricarbonyl($\eta^5$-cyclopentadienyl)manganese(I), Mn(CO)$_3$(\eta^5-C$_5$H$_5$)
Effective Atomic Number or 18 Electron Rule

Transition Metals have the following numbers of electrons:

<table>
<thead>
<tr>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
</tr>
<tr>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
</tr>
<tr>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
</tr>
</tbody>
</table>

and require the following numbers of electrons to achieve the 18e configuration:

| 14 | 13 | 12 | 11 | 10 | 9 | 8 |

These ligands donate the following numbers of electrons:

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>H, X</td>
<td>CO</td>
<td>NO (bent) CNR</td>
<td>NO (linear)</td>
<td>R</td>
<td>PR₃</td>
<td>SnR₃</td>
<td>R₂C ≡ CR₂</td>
</tr>
</tbody>
</table>

When π-acceptor ligands are present, bonding combinations with otherwise non-bonding orbitals at the metal (octahedral: t₂g set) result in 9 bonding MOs, and a stable 18 electron configuration.
Effective Atomic Number or 18 Electron Rule


### Table 21.2 Typical ligands and their electron counts

(a) **Neutral-ligand method**

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Formula</th>
<th>Designation*</th>
<th>Electrons donated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl</td>
<td>CO</td>
<td>L</td>
<td>2</td>
</tr>
<tr>
<td>Phosphine</td>
<td>PR₃</td>
<td>L</td>
<td>2</td>
</tr>
<tr>
<td>Hydride</td>
<td>H</td>
<td>X</td>
<td>1</td>
</tr>
<tr>
<td>Dihydrogen</td>
<td>H₂</td>
<td>L</td>
<td>2</td>
</tr>
<tr>
<td>η²-Alkyl, -alkenyl, alkynyl, and -aryl groups</td>
<td>R</td>
<td>X</td>
<td>1</td>
</tr>
<tr>
<td>η²-Alkene</td>
<td>CH₂=CH₂</td>
<td>L</td>
<td>2</td>
</tr>
<tr>
<td>η²-Alkyne</td>
<td>RCCR</td>
<td>L</td>
<td>2</td>
</tr>
<tr>
<td>Dinitrogen</td>
<td>N₂</td>
<td>L</td>
<td>2</td>
</tr>
<tr>
<td>Butadiene</td>
<td>CH₂=CH—CH=CH₂</td>
<td>L₂</td>
<td>4</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>L₃</td>
<td>6</td>
</tr>
<tr>
<td>η²-Allyl</td>
<td>CH₃CH₂H₂</td>
<td>LX</td>
<td>3</td>
</tr>
<tr>
<td>η⁵-Cyclopentadienyl</td>
<td>C₅H₅</td>
<td>L₂X</td>
<td>5</td>
</tr>
</tbody>
</table>

* Ligands are defined as **L type** if they are neutral two-electron donors (such as CO, PMe₃), and **X type** if, when they are considered to be neutral, they are one-electron radical donors (such as halogen atoms, H, CH₃).

(b) **Donor-pair method***

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Formula</th>
<th>Electrons donated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl</td>
<td>CO</td>
<td>2</td>
</tr>
<tr>
<td>Phosphine</td>
<td>PR₃</td>
<td>2</td>
</tr>
<tr>
<td>Hydride</td>
<td>H⁻</td>
<td>2</td>
</tr>
<tr>
<td>Dihydrogen</td>
<td>H₂</td>
<td>2</td>
</tr>
<tr>
<td>η²-Alkene</td>
<td>CH₂=CH₂</td>
<td>2</td>
</tr>
<tr>
<td>η²-Alkyne</td>
<td>RCCR</td>
<td>2</td>
</tr>
<tr>
<td>Dinitrogen</td>
<td>N₂</td>
<td>2</td>
</tr>
<tr>
<td>Butadiene</td>
<td>CH₂=CH—CH=CH₂</td>
<td>4</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>6</td>
</tr>
<tr>
<td>η²-Allyl</td>
<td>CH₃CH₂H₂</td>
<td>4</td>
</tr>
<tr>
<td>η⁵-Cyclopentadienyl</td>
<td>C₅H₅⁻</td>
<td>6</td>
</tr>
</tbody>
</table>

* We use this method throughout this book.

---

Table 21.2a
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Table 21.2b
Shriver & Atkins Inorganic Chemistry, Fourth Edition
### Table 21.1 Validity of the 16/18-electron rule for d-metal organometallic compounds

<table>
<thead>
<tr>
<th>Usually less than 18 electrons</th>
<th>Usually 18 electrons</th>
<th>16 or 18 electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
</tr>
<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
</tr>
<tr>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tc</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ru</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rh</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd</td>
</tr>
<tr>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Re</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Os</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ir</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
</tr>
</tbody>
</table>

*Shriver & Atkins Inorganic Chemistry, Fourth Edition*

**EAN Rule**

**Electron Precise Complexes**

- \( \text{Ni}(\text{CO})_4 \quad \text{Ni}(10) + 4 \times \text{CO}(2) \quad = 18 \)
- \( \text{Mn}_2(\text{CO})_{10} \quad \text{Mn}(7) + 5 \times \text{CO}(2) + \text{M–M}(1) \quad = 18 \)
- \( \text{V}(\text{CO})_4(\text{C}_5\text{H}_5) \quad \text{V}(5) + 4 \times \text{CO}(2) + \text{C}_5\text{H}_5(5) \quad = 18 \)
- \( \text{FeMe}(\text{CO})_2(\text{C}_5\text{H}_5) \quad \text{Fe}(8) + 2 \times \text{CO}(2) + \text{Me}(1) + \text{C}_5\text{H}_5(5) \quad = 18 \)
EAN Rule

Exceptions to the EAN Rule

(S&A, p 528) (D,M&A, p 569)

Four main types:
Early transition metals  Full coordination
Bulky ligands  Square planar (d⁸)

e.g.

ZrCl₂(C₅H₅)₂  Zr(4) + 2 x Cl(1) + 2 x C₅H₅(5)  = 16
TaCl₂Me₃  Ta(5) + 2 x Cl(1) + 3 x Me(1)  = 10
WMe₆  W(6) + 6 x Me(1)  = 12
Pt(PPh₃)₃  Pt(10) + 3 x PPh₃(2)  = 16
IrCl(CO)(PPh₃)₂  Ir(9) + Cl(1) + CO(2) + 2 x PPh₃(2)  = 16
EAN Rule

\[ \begin{align*}
\Delta_{SP} & \\
d_{x^2-y^2} & \\
d_{xy} & \\
d_{z^2} & \\
d_{yz}, d_{zx} & \\
\end{align*} \]

6 \textit{trans-}[\text{IrCl(CO)(PPh}_3\text{)}_2]
A large number of metal carbonyls exist. They are usually EAN precise. Metal carbonyls are often the entry point into organometallic chemistry. Some representative examples:

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(CO)₆</td>
<td>dark blue</td>
<td>liquid</td>
</tr>
<tr>
<td>Cr(CO)₆</td>
<td>white</td>
<td></td>
</tr>
<tr>
<td>Mn₂(CO)₁₀</td>
<td>yellow</td>
<td>liquid</td>
</tr>
<tr>
<td>Fe(CO)₅</td>
<td>yellow</td>
<td>liquid</td>
</tr>
<tr>
<td>Co₂(CO)₈</td>
<td>orange</td>
<td></td>
</tr>
<tr>
<td>Ni(CO)₄</td>
<td>colourless</td>
<td>liquid</td>
</tr>
<tr>
<td>Mo(CO)₆</td>
<td>white</td>
<td>liquid</td>
</tr>
<tr>
<td>Tc₂(CO)₁₀</td>
<td>white</td>
<td></td>
</tr>
<tr>
<td>Ru(CO)₅</td>
<td>yellow</td>
<td></td>
</tr>
<tr>
<td>Rh₄(CO)₁₂</td>
<td>orange</td>
<td></td>
</tr>
<tr>
<td>Pd(CO)₄</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>W(CO)₆</td>
<td>white</td>
<td>liquid</td>
</tr>
<tr>
<td>Re₂(CO)₁₀</td>
<td>white</td>
<td></td>
</tr>
<tr>
<td>Os(CO)₅</td>
<td>colourless</td>
<td>liquid</td>
</tr>
<tr>
<td>Ir₄(CO)₁₂</td>
<td>yellow</td>
<td></td>
</tr>
<tr>
<td>Pt(CO)₄</td>
<td>colourless</td>
<td>liquid</td>
</tr>
</tbody>
</table>
Binary Metal Carbonyl Complexes

Structures usually correspond to the COs minimizing repulsion.

Table 21.5 Formulas and electron count for some 3d-series carbonyls

<table>
<thead>
<tr>
<th>Group</th>
<th>Formula</th>
<th>Valence electrons</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Cr(CO)₆</td>
<td>Cr 6</td>
<td>![Cr(CO)₆ structure]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6(CO) 12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Mn₂(CO)₁₀</td>
<td>Mn 7</td>
<td>![Mn₂(CO)₁₀ structure]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5(CO) 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>M—M 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Fe(CO)₅</td>
<td>Fe 8</td>
<td>![Fe(CO)₅ structure]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5(CO) 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Co₃(CO)₈</td>
<td>Co 9</td>
<td>![Co₃(CO)₈ structure]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4(CO) 8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>M—M 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Ni(CO)₄</td>
<td>Ni 10</td>
<td>![Ni(CO)₄ structure]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4(CO) 8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

Structure 8-1
Shriver & Atkins Inorganic Chemistry, Fourth Edition
Tendency to bridge (µ-CO) decreases going down the periodic table.
Binary Metal Carbonyl Complexes

\[ \text{3 } \left[ \text{Fe}_4\text{(CO)}_{13} \right]^{2-} \]

\[ \text{76 } \left[ \text{Co}_4\text{(CO)}_{12} \right] \]
Energy levels that arise from bonding of a strong-field ligand (e.g. CO) to a 3d metal atom. There are 6 bonding MOs from $\sigma$ interactions and 3 bonding MOs from $\pi$ interactions. Filling all 9 bonding MOs gives an 18 electron configuration.
A pictorial orbital description of M–CO bonding.

$\sigma$-bonding + $\pi$-back-bonding $\rightarrow$ stronger M–CO bond (synergistic)

MO scheme for CO: the HOMO has $\sigma$ symmetry and the LUMO has $\pi$ symmetry.
Binary Metal Carbonyl Complexes

Physical evidence for this bonding: IR data

\( \nu(\text{CO}) \)

<table>
<thead>
<tr>
<th></th>
<th>( \nu(\text{CO}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free CO</td>
<td>2143 cm(^{-1})</td>
</tr>
<tr>
<td>( \text{Cr(CO)}_6 )</td>
<td>2000</td>
</tr>
<tr>
<td>In general</td>
<td>1850-2120</td>
</tr>
</tbody>
</table>

Effect of charge

<table>
<thead>
<tr>
<th>([\text{Ti(CO)}_6]^2-)</th>
<th>([\text{V(CO)}_6]^-)</th>
<th>(\text{Cr(CO)}_6)</th>
<th>([\text{Mn(CO)}_6]^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1748</td>
<td>1858</td>
<td>2000</td>
<td>2095</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_4]^3-)</td>
<td>([\text{Fe(CO)}_4]^2-)</td>
<td>([\text{Co(CO)}_4]^-)</td>
<td>(\text{Ni(CO)}_4)</td>
</tr>
<tr>
<td>1670</td>
<td>1790</td>
<td>1883</td>
<td>2046 cm(^{-1})</td>
</tr>
</tbody>
</table>
Binary Metal Carbonyl Complexes

CO stretching frequencies: $\text{MCO} > \text{M}_2\text{CO} > \text{M}_3\text{CO}$
## Binary Metal Carbonyl Complexes

The number of CO bands assists structural assignment

<table>
<thead>
<tr>
<th>Complex</th>
<th>Isomer</th>
<th>Structure</th>
<th>Point group</th>
<th>Number of bands*</th>
<th>Complex</th>
<th>Isomer</th>
<th>Structure</th>
<th>Point group</th>
<th>Number of bands*</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(CO)$_4$</td>
<td></td>
<td></td>
<td>$O_h$</td>
<td>1</td>
<td>M(CO)$_5$</td>
<td></td>
<td></td>
<td>$D_{3h}$</td>
<td>2</td>
</tr>
<tr>
<td>M(CO)$_3$L</td>
<td></td>
<td></td>
<td>$C_{3v}$</td>
<td>3$^\dagger$</td>
<td>M(CO)$_3$, $\alpha$</td>
<td></td>
<td>$C_{3v}$</td>
<td>3$^\ddagger$</td>
<td></td>
</tr>
<tr>
<td>M(CO)$_4$L$_2$</td>
<td>trans</td>
<td></td>
<td>$D_{4h}$</td>
<td>1</td>
<td>M(CO)$_4$L</td>
<td></td>
<td></td>
<td>$C_{2v}$</td>
<td>4</td>
</tr>
<tr>
<td>M(CO)$_4$L$_2$</td>
<td>cis</td>
<td></td>
<td>$C_{2v}$</td>
<td>4$^\ddagger$</td>
<td>M(CO)$_4$L$_2$, trans</td>
<td></td>
<td>$D_{3h}$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>M(CO)$_3$L$_3$</td>
<td>mer</td>
<td></td>
<td>$C_{2v}$</td>
<td>3$^\ddagger$</td>
<td>M(CO)$_3$L$_2$, cis</td>
<td></td>
<td>$C_{2v}$</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>M(CO)$_3$L$_3$</td>
<td>fac</td>
<td></td>
<td>$C_{3v}$</td>
<td>2</td>
<td>M(CO)$_4$</td>
<td></td>
<td></td>
<td>$T_{d}$</td>
<td>1</td>
</tr>
</tbody>
</table>

* The number of IR bands expected in the CO stretching region is based on formal selection rules, and in some cases fewer bands are observed, as explained below.

$^\dagger$ If the fourfold array of CO ligands lies in the same plane as the metal atom, two bands will be observed.

$^\ddagger$ If the trans CO ligands are nearly collinear, one fewer band will be observed.

$^\ddagger\ddagger$ If the threefold array of CO ligands is nearly planar, only two bands will be observed.

---

Binary Metal Carbonyl Complexes

Other bonding modes are possible and are important in CO activation (see later).

The complex above was made at the ANU and has the longest CO bond thus far. Its IR spectrum contains a band assigned to $\nu$(CO) at 1424 cm$^{-1}$. 
Binary Metal Carbonyl Complexes

Some metal carbonyls are formed by direct reaction - most of these require high P and T.

\[
\text{Ni} + 4\text{CO} \rightarrow \text{Ni(CO)}_4 \\
303\text{K, 1 atm}
\]

\[
\text{Fe} + 5\text{CO} \rightarrow \text{Fe(CO)}_5 \\
473\text{K, 200 atm}
\]

Other metal carbonyls are formed by reductive carbonylation.

High-pressure reaction vessel for synthesis of metal carbonyls
Organometallic Synthesis
Phosphine Complexes

Replacement of CO by PR$_3$ can be effected by:
1. Heating
2. Photodissociation of CO
3. Use of trimethylamine $N$-oxide
4. Electron transfer chain catalysis

Apparatus for photochemical ligand substitution of metal carbonyls
Phosphine Complexes

Electron transfer catalyzed substitution of a metal carbonyl. This process uses a catalytic amount of a reducing initiator.
Revision: *cis* and *trans* isomers exist for octahedral complexes of formula MA$_4$B$_2$, and *mer* and *fac* isomers are possible for complexes of formula MA$_3$B$_3$. 

Phosphine substitution of metal carbonyls can afford isomers.
Phosphine Complexes

Three common monodentate phosphines with varying electronic and steric properties. The diversity of available phosphines can be used to tune the electronic and steric environment at the metal centres.
Two important bidentate diphosphines - these form particularly stable complexes because of the chelate effect.

21 $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2, \text{dppe}$

23 $2,2^{\prime}-\text{bis(diphenylphosphino)}$-$1,1^{\prime}$-$\text{binaphthyl}, \text{BINAP}$
Phosphine Complexes

The $\sigma$-donating and $\pi$-accepting ability of phosphines are inversely correlated: good donors are poor acceptors and vice versa.

Alteration of electron density on metal atom (S&A, p 534): $\nu$(CO) vs ligand gives a measure of the $\pi$-acceptor ability.

$\text{fac-Mo(CO)}_3(L)_3$

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\nu$(CO) (cm$^{-1}$)</th>
<th>weighted average (1:2) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>py</td>
<td>1888, 1746</td>
<td>1793</td>
</tr>
<tr>
<td>MeCN</td>
<td>1915, 1783</td>
<td>1827</td>
</tr>
<tr>
<td>PPh$_3$</td>
<td>1934, 1835</td>
<td>1868</td>
</tr>
<tr>
<td>PMe$_3$</td>
<td>1945, 1854</td>
<td>1884</td>
</tr>
<tr>
<td>P(OMe)$_3$</td>
<td>1977, 1888</td>
<td>1918</td>
</tr>
<tr>
<td>P(OPh)$_3$</td>
<td>1994, 1922</td>
<td>1946</td>
</tr>
<tr>
<td>PCl$_3$</td>
<td>2040, 1991</td>
<td>2007</td>
</tr>
<tr>
<td>PF$_3$</td>
<td>2090, 2055</td>
<td>2067</td>
</tr>
</tbody>
</table>

Positions of carbonyl bands in IR spectra provide important clues to the electronic environment of the metal.
Phosphine Complexes

Cone angle is a useful measure of the steric bulk of a ligand (cf. C.A. Tolman, Chem. Rev., 1977, 77, 313).

**Table 21.4** Tolman cone angles (in degrees) for selected phosphines

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Cone Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF₃</td>
<td>104</td>
</tr>
<tr>
<td>P(OMe)₃</td>
<td>107</td>
</tr>
<tr>
<td>PMe₃</td>
<td>118</td>
</tr>
<tr>
<td>PCl₃</td>
<td>125</td>
</tr>
<tr>
<td>P(OPh)₃</td>
<td>127</td>
</tr>
<tr>
<td>PEt₃</td>
<td>132</td>
</tr>
<tr>
<td>PPPh₃</td>
<td>145</td>
</tr>
<tr>
<td>PCy₃</td>
<td>169</td>
</tr>
<tr>
<td>PᵗBu₃</td>
<td>182</td>
</tr>
<tr>
<td>P(o-tol)₃</td>
<td>193</td>
</tr>
</tbody>
</table>

(θ = 118°)

(image from Wikipedia Commons)
Phosphine Complexes

Dissociation of tertiary phosphines can be related to their size (cone angle).

**Table 21.11** Cone angles and dissociation constants for some Ni complexes

<table>
<thead>
<tr>
<th>L</th>
<th>$\theta$/°</th>
<th>$K_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMe$_3$</td>
<td>118</td>
<td>$&lt;10^{-9}$</td>
</tr>
<tr>
<td>PEt$_3$</td>
<td>137</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>PMePh$_2$</td>
<td>136</td>
<td>$5.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>PPh$_3$</td>
<td>145</td>
<td>Large</td>
</tr>
<tr>
<td>PrBu$_3$</td>
<td>182</td>
<td>Large</td>
</tr>
</tbody>
</table>

Data are for NiL$_4$$\rightleftharpoons$NiL$_3$ + L in benzene at 25°C.
Phosphine Complexes

Bulky ligands can result in coordinative unsaturation. The complexes below are 3 and 5 coordinate, respectively, and possess 16 valence electrons.

4 \([\text{Pt(Pcy}_3\text{)}], \text{cy=cyclo-C}_6\text{H}_{11}\)

2 \([\text{Ru(Cl)}_2\text{(PPh}_3\text{)}_3]\)
Bridging diphosphines can stabilize dinuclear complexes and prevent fragmentation during reaction. The complex at right is formed from the complex at left on reaction with diazomethane.
Carbocycles are important co-ligands in organometallic chemistry. The most important is the five-membered example, the cyclopentadienyl ligand. It can coordinate in mono-hapto, tri-hapto (rare), and penta-hapto (most common) modes.
\(\eta^5\)-Cyclopentadienyl rings can undergo ring "slippage" to \(\eta^3\)-coordination, at which time the metal centre has lost two electrons and is susceptible to nucleophilic attack. Following coordination of the incoming ligand, the ring can revert to \(\eta^5\)-coordination, with loss of a ligand.
This can be seen in comparing reaction rates for ligand substitution in 83 with 84. The indenyl complex 84 reacts much faster than the cyclopentadienyln complex 83. This outcome is sufficiently well-known and widespread that it has gained a name: the "indenyl effect". This is supposedly because the non-coordinated ring gains aromaticity (see 85) (S&A, p 563). In contrast, recent theoretical studies suggest it is due to differing Cp'-M bond strengths (M.J. Calhorda et al, Chem. Eur. J. 2002, 8, 868).
Cyclopentadienyl Complexes

Fluorenyl complexes are even more reactive than indenyl complexes.

A range of cyclopentadienyl ligands exist, and many have "trivial" names or abbreviations. Some important ones are cyclopentadienyl (Cp), methylcyclopentadienyl (Cp'), and pentamethylcyclopentadienyl (Cp*). The methyl group is more electron donating and larger than H, so increasing alkylation makes the corresponding metal complex increasingly electron rich at the metal centre, and more sterically crowded.
The cyclopentadienide anion is a six-electron donor. The $a_1$ ($\sigma$ bonding) and $e_1$ ($\pi$ bonding) MOs have appropriate symmetry to form bonding interactions with the $d_{z^2}$ and $d_{xz}$, $d_{yz}$, respectively.
Complexes of formula M(η⁵-C₅H₅)₂ are called metallocenes ("sandwich" complexes). Most first-row transition metals form metallocenes.

<table>
<thead>
<tr>
<th></th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>16</td>
<td>17</td>
<td>18</td>
<td>19</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

electrons  
unpaired elections

In general, metallocenes with non-18 electron counts react to attain an 18 electron count. Ferrocene reacts to preserve its 18 electron count.

The synthesis and structure elucidation of ferrocene lead to enormous subsequent research effort in organometallic chemistry.
Cyclopentadienyl Complexes

The stability of the non-18 electron metallocenes is because the frontier orbitals (boxed) are neither strongly bonding nor strongly antibonding.

Table 21.8 Electronic configuration and M—C bond length in \([\text{M}(\eta^5\text{-Cp})_2]\) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Valence electrons</th>
<th>Electron configuration</th>
<th>M—C bond length/pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{V}(\eta^5\text{-Cp})_2])</td>
<td>15</td>
<td>(e_2^2d_{1}^1)</td>
<td>228</td>
</tr>
<tr>
<td>([\text{Cr}(\eta^5\text{-Cp})_2])</td>
<td>16</td>
<td>(e_2^3d_{1}^1)</td>
<td>217</td>
</tr>
<tr>
<td>([\text{Mn}(\eta^5\text{-Me-C}_5\text{H}_4)_2])*</td>
<td>17</td>
<td>(e_2^3d_{1}^2)</td>
<td>211</td>
</tr>
<tr>
<td>([\text{Fe}(\eta^5\text{-Cp})_2])</td>
<td>18</td>
<td>(e_2^4d_{1}^2)</td>
<td>206</td>
</tr>
<tr>
<td>([\text{Co}(\eta^5\text{-Cp})_2])</td>
<td>19</td>
<td>(e_2^4e_1^m1d_{1}^2)</td>
<td>212</td>
</tr>
<tr>
<td>([\text{Ni}(\eta^5\text{-Cp})_2])</td>
<td>20</td>
<td>(e_2^4e_1^m2d_{1}^2)</td>
<td>220</td>
</tr>
</tbody>
</table>

*Data are quoted for this complex because \([\text{Mn}(\eta^5\text{-Cp})_2]\) has a high-spin configuration and hence an anomalously long M—C bond (238 pm).
Cyclopentadienyl Complexes

With the exception of oxidation (which is more difficult at ferrocene than cobaltocene), all other reactions preserve an 18 electron count at iron. The cyclopentadienyl rings in ferrocene undergo typical aromatic reactivity.

• No direct nitration, halogenation, sulfonation.
Cyclopentadienyl Complexes

Bent metallocenes also exist (including those with an intramolecular bridge between the rings: ansa-metallocenes). Three metal atom orbitals project from the metal and can be used for bonding.
Cyclopentadienyl Complexes

Cyclopentadienyl metal carbonyls with d^{odd} transition metals are known as "piano stool" complexes (D,M&A, pp 589-590) (H p 676) (M&T, pp 491-492) (H&S, pp 613-614). They usually observe the EAN Rule, so with d^{even} transition metals they possess M-M bonds.

cis isomer also
Cyclopentadienyl Complexes

Other aspects of cyclopentadienyl complex chemistry:

The compound at right is the most well-known example of the "triple-decker sandwich" complexes.

The cyclopentadienyl ligand at right contains a chiral substituent (neo-menthyl group). Chiral cyclopentadienyl ligands are employed in stereoselective reactions.
The cyclopentadienyl ligand is the most important carbocycle in organometallic chemistry. There are many other carbocyclic ligands that coordinate as $\eta^3$-$C_nH_n$.

$n = 3$ (cyclopropenyls)

$$[C_3Ph_3]Br + Ni(\text{CO})_4 \rightarrow NiBr(\text{CO})_2(\eta-C_3Ph_3)$$

\[\text{Ni} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \]
Cyclobutadiene is rectangular and unstable as a free molecule (MO diagram left), but square and stable when coordinated (MO diagram right). The complexed form has a 6 electron aromatic configuration.
Complexes with other Carbocyclic Ligands

$n = 4$ (cyclobutadienes)
Because cyclobutadiene is unstable, it must be generated in the presence of the metal. Two possibilities are dimerization of alkynes (first reaction), or halogen abstraction from dihalocyclobutenes (lower three reactions).

\[ \text{C}_2\text{Ph}_2 \quad \text{Fe}(	ext{CO})_5 \quad \text{Fe}(	ext{CO})_3(\eta^1\text{C}_4\text{Ph}_4) \]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[ \text{Fe}_2(\text{CO})_9 \quad \text{Fe}(	ext{CO})_3 \quad \text{Fe}(	ext{CO})_3 \]

\[ \text{M(CO)}_6 \quad \text{M(CO)}_4 \quad \text{Hg/Na} \]

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[ \text{Fe}_2(\text{CO})_9 \quad \text{Fe}(	ext{CO})_3 \quad \text{Fe}(	ext{CO})_3 \]

\[ \text{FeBr}_2 \quad \text{FeBr}_2 \]

\[ \text{Fe}(	ext{CO})_3 \quad \text{Fe}(	ext{CO})_3 \]

\[ \text{Fe}(	ext{CO})_3 \quad \text{Fe}(	ext{CO})_3 \]
Complexes with other Carbocyclic Ligands

\( n = 6 \) (arenes)

Both "piano stool" (left) and "sandwich" (centre) complexes exist. There are three bonding and three antibonding orbitals in benzene, the former forming a \( \sigma \) bond with \( d_{z^2} \) and two \( \pi \) bonds with \( d_{xz} \) and \( d_{yz} \) orbitals of the metal atom (MO diagram at right).
n = 6 (arenes)

Arene complexes are usually formed from reactions between arenes and \( \text{M(CO)}_n \).

\[
\text{Cr(CO)}_6 + \text{C}_6\text{H}_5\text{R} \rightarrow \text{Cr(CO)}_3(\eta-\text{C}_6\text{H}_5\text{R})
\]

Reactions are facilitated by using precursors with weakly-bound ligands, e.g. \( \text{Cr(CO)}_3(\text{NH}_3)_3 \), \( \text{Mo(CO)}_3(\eta^6-\text{C}_7\text{H}_8) \).

\( \text{C}_6\text{H}_6 \) is not a good ligand; the extra donor power of mesitylene \((1,3,5-\text{C}_6\text{H}_3\text{Me}_3)\) or \( \text{C}_6\text{Me}_6 \) gives more stable complexes.
Complexes with other Carbocyclic Ligands

\( n = 7 \) (cycloheptatrienyl)

\( \text{C}_7\text{H}_7^+ \) (left) is aromatic (and known as tropylium). This is available commercially. It can also be prepared \textit{in situ} by deprotonation of a cycloheptatriene complex to give complexes such as that at right.
Complexes with other Carbocyclic Ligands

\( n = 8 \) (cyclooctatetraenes)

Cyclooctatetraene (left) is antiaromatic (S&A) (note: this is arguable, because it is not planar in the free state). It forms \( \eta^2 \), \( \eta^4 \) (right) or \( \eta^6 \) complexes to many metals.
Complexes with other Carbocyclic Ligands

$n = 8$ (cyclooctatetraenes)

Cyclooctatetraene can also bridge two metal centres, frequently in a $2\eta^4$ coordination mode (right).

The cyclooctatetraenide dianion is aromatic and planar, but very few metals are large enough to permit $\eta^8$ coordination (below).

$$\text{UCl}_4 + \text{K}_2[\text{C}_8\text{H}_8] \rightarrow \text{U} - \text{U}$$
Alkene Complexes


Importance: alkene complexes are involved in the organotransition metal-catalyzed hydrogenation, oligomerization, polymerization, cyclization, hydroformylation, isomerization and oxidation of alkenes.
Alkene Complexes

A qualitative orbital description of metal-alkene bonding. This is known as the Dewar-Chatt-Duncanson model.

The bonding can be considered to arise from a $\sigma$ interaction from the alkene multiple bond to the metal atom (a) and a $\pi$ backbonding interaction from the metal atom to the $\pi^*$ antibonding orbital on the alkene (b), which together give the bonding model above.
**Alkene Complexes**

Mono-ene (left), diene (centre) and triene (right) complexes exist. Certain alkenes have acquired abbreviations (cod, cycloocta-1,5-diene; nbd, norbornadiene).

The $[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]^-$ anion of Zeise’s salt.
Alkene Complexes

Syntheses - Ligand Substitution
(AlCl₃ and Ag⁺ are functioning as halide abstracting agents)

\[
\text{Re(CO)₅Cl} + \text{C}_2\text{H}_4 \xrightarrow{\text{AlCl}_3} [\text{Re(CO)₅(C}_2\text{H}_4)]\text{AlCl}_4
\]

\[
\text{CpFe(CO)₂I} + \text{C}_2\text{H}_4 + \text{AgBF}_4 \rightarrow [\text{CpFe(CO)₂(C}_2\text{H}_4)]\text{BF}_4 + \text{AgI}
\]

\[
\text{Fe(CO)₅} + \text{buta–}1,3\text{-diene} \xrightarrow{135^\circ \text{C}, 20 \text{ bar}} \text{Fe(CO)₃} + 2\text{CO}
\]

\[
\text{CpMn(CO)₃} + \text{CHO} \xrightarrow{\text{hv}} \text{Mn(OH)}_2 + 2\text{OC} + \text{CHO}
\]
Syntheses - Hydride Abstraction from Alkyl Complexes

\[
\text{Fe(C}_2\text{H}_5\text{)(CO)}_2(\text{C}_5\text{H}_5) + [\text{CPh}_3]^+ \rightarrow [\text{Fe}(\text{C}_2\text{H}_4\text{)(CO)}_2(\text{C}_5\text{H}_5)]^+ \\
+ \text{CPh}_3
\]

([CPh₃]⁺ is a hydride abstracting agent)

Coordination of an alkene to a metal alters its reactivity. Free alkenes undergo electrophilic reactions. Alkene-Pd complexes are attacked by nucleophiles. Some of these reactions form the basis for transition metal-catalyzed reactions of alkene feedstocks which are important industrial processes (see later).
Alkene Complexes

Hydride abstraction from a coordinated cycloheptatriene ligand gives a coordinated cycloheptatrienyl ligand.

\[
\text{Mo(CO)}_6 + \text{C}_7\text{H}_8 \rightarrow \begin{array}{c}
\text{Mo(CO)}_3 \\
\text{Mo(CO)}_3
\end{array}
\]

\[
[\text{CPh}_3]^+ \rightarrow \begin{array}{c}
\text{Mo(CO)}_3 \\
\text{Mo(CO)}_3
\end{array}
\]

54 Cycloheptatriene

55

56

57
Alkene Complexes

The coordinated linkage is lengthened compared to the corresponding linkage in the free state.

Bonding can be understood by considering the Dewar-Chatt-Duncanson model.
Alkyne Complexes


Alkynes have two filled mutually orthogonal $\pi$ molecular orbitals. They can bond similar to alkenes by using one electron pair or can use both $\pi$-bonds to coordinate to 2 (bottom right and next slide), 3 or 4 metal atoms.

There are two representations of metal-alkyne bonding:

$\pi$-alkyne  metallacyclopropene
Alkynes form stable polymetallic complexes - each of the two $\pi$-bonds donates two electrons to a metal atom.

These complexes are considered further in Second Semester.
Alkyne Complexes

Syntheses - Ligand Substitution

\[
\text{(η}^5\text{–C}_5\text{H}_5)\text{Mn(CO)}_3 + \text{C}_2\text{Ph}_2 \xrightarrow{\text{hv}} \text{hexane} \rightarrow \text{(η}^5\text{–C}_5\text{H}_5)\text{Mn(CO)}_2(\text{η}^2\text{–C}_2\text{Ph}_2) + \text{CO}
\]

\[
\text{(η}^5\text{–C}_5\text{H}_5)\text{2Ti(CO)}_2 + \text{C}_2\text{Ph}_2 \xrightarrow{\text{heptane}} \xrightarrow{25C \ 3h} \text{(η}^5\text{–C}_5\text{H}_5)\text{2Ti(CO)(η}^2\text{–C}_2\text{Ph}_2) + \text{CO}
\]

Syntheses - Coordinatively Unsaturated Metal + Alkyne
(note Ag⁺ as halide abstracting agent)

\[
\text{FeI(CO)}_2(\text{η}^5\text{–C}_5\text{H}_5) + \text{C}_2\text{R}_2 \xrightarrow{\text{Ag}^+} \rightarrow [\text{Fe(η}^2\text{–C}_2\text{R}_2)(\text{CO})_2(\text{η–C}_5\text{H}_5)]^+
\]
Alkyne Complexes

Metal-promoted dimerization and oligomerization of alkynes (templated in the metal coordination sphere)

\[ \text{Fe(CO)}_3 \]

\[ \text{(OC)}_3\text{Fe} \]

\[ \text{C}_2\text{R}_2 \]
π-Enyl ligands are unsaturated hydrocarbons $C_nH_{n+2}$ with odd numbers of carbon atoms; they can be regarded as neutral ligands with an odd number of π-electrons or as anionic or cationic ligands possessing an even number of valence electrons:
Neutral radicals are highly reactive, and anions as Li$^+$, K$^+$ or Mg$^{2+}$ salts are air and moisture sensitive, but transition metal complexes are thermally robust and stable toward hydrolysis.
Allyl Complexes


The allyl ligand can bind in either a \( \eta^1 \)-manner (left) or as a \( \eta^3 \)-ligand (centre). The \( \eta^3 \)-coordination can be considered as a resonance hybrid of two \( \eta^1, \eta^2 \)-ligated forms (right). C-C bond lengths in the \( \eta^3 \)-ligand are equivalent.
Allyl Complexes

MO diagram for the allyl ligand, and appropriate metal-based orbitals to form bonding interactions. Note that the precise electron distribution is markedly dependent on the ancillary ligands on the metal, so that electron density may flow from $M \rightarrow 2\pi$ or $2\pi \rightarrow M$ (the latter with electronegative ligands, e.g. Cl). Since the $2\pi$ orbital is localized on the terminal carbons, reaction will occur at this location (electrophilic or nucleophilic, respectively).
Allyl Complexes

Syntheses - Metal Complex + Allyl Grignard/Halide/Alcohol

\[
\text{NiCl}_2 + \text{C}_3\text{H}_5\text{MgBr} \rightarrow \text{Ni}(\eta^2\text{C}_3\text{H}_5)_2
\]

\[
\text{Na}[	ext{Mn}(\text{CO})_5] + \text{ClCH}_2\text{CH}==\text{CH}_2 \xrightarrow{\text{thf}}_{25^\circ C} (\text{OC})_5\text{MnCH}_2\text{CH}==\text{CH}_2
\]

\[
\downarrow \text{86}^\circ \text{C}
\]

\[
(\text{OC})_4\text{Mn}(\eta^3\text{C}_3\text{H}_5) + \text{CO}
\]
Allyl Complexes

Syntheses - Hydride Abstraction from Alkene Ligands or Protonation of Butadiene Ligands

\[
\text{Fe(CO)}_3 + \text{HCl} \xrightarrow{\text{hexane}} \text{Fe(CO)}_3\text{Cl}
\]
**Allyl Complexes**

Substituents at the terminal carbon atoms are either *syn* or *anti* with respect to the central hydrogen.

These isomers can interconvert by dissociation to $\eta^1$–allyl complexes. If this process is fast on the NMR time scale, only two resonances will be observed: doublet (H^a, H^b), quintet (H^i)
Allyl Complexes

Isomerization of alkenes may proceed via allyl-hydrido-metal complexes (see later)

\[
\begin{align*}
&\text{oxidative addition} \\
&M^0 & \text{M}^2+ & \text{reductive elimination} & \text{M}^0
\end{align*}
\]
Hydrido Complexes

(S&A, p 535) (H pp 641-647) (H&S, pp 586-587)

Hydrogen may be bonded to one or more metal atoms. Some examples:

- $\text{HZrCl(}\eta-\text{C}_5\text{H}_5\text{)}_2$
- $\text{HIr(CO)(PPh}_3\text{)}_3$
- $[\text{HNi}\{\text{P(OEt)}_3\}_4]^{-}$
- $[\text{HOs(CO)}_4]^{-}$
- $[(\text{OC})_5\text{Cr–H–Cr(CO)}_5]^{-}$
- $\text{H}_6\text{W(PMePh}_2\text{)}_3$
Properties of Hydrido Ligands

• Occupies one coordination site.
• M–H bond strength generally > M–C bond strength.
• IR: Weak to medium intensity band 1900-2300 cm\(^{-1}\)
  H/D exchange gives band at lower wavenumber
  \(\nu(MH)/\nu(MD) = \sqrt{2}\)
• NMR: High field chemical shifts in the range \(\delta\) -7 to -24.
  Often show coupling to metal nuclei (\(^{103}\)Rh, \(^{183}\)W, \(^{187}\)Os, \(^{195}\)Pt) with \(J(HM)\) 30-1500 Hz, as well as to \(^{31}\)P through metal.

Structural characterization by X-ray not always possible, although in favourable cases, the M–H bond-length (1.6-1.9 Å) can be determined to \(\pm 0.05\) Å. Accurate studies require neutron diffraction.
Hydrido Complexes

Preparation

1. Protonation of Metal Carbonyl Anion
e.g. Na$_2$[Fe(CO)$_4$] + H$^+$ $\rightarrow$ Na[FeH(CO)$_4$] + H$^+$ $\rightarrow$ FeH$_2$(CO)$_4$

2. Reaction of Metal Complex with Molecular Hydrogen
e.g. IrCl(PPh$_3$)$_3$ + H$_2$ $\rightarrow$ Ir(H)$_2$Cl(PPh$_3$)$_3$

3. Replacement of Halide by Hydride (from NaBH$_4$, etc.)
e.g. Zr(Cl)$_2$(η–C$_5$H$_5$)$_2$ + LiAlH$_4$ $\rightarrow$ Zr(H)(Cl)(η–C$_5$H$_5$)$_2$

4. Reaction of Metal Carbonyl with Hydroxide
e.g. Cr(CO)$_6$ + KOH $\rightarrow$ K[Cr(H)(CO)$_5$] + CO$_2$ ($\beta$-elimination)
Reactivity

(a) Acidity

<table>
<thead>
<tr>
<th>Hydride</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CoH(CO)₄]</td>
<td>8.3</td>
</tr>
<tr>
<td>[CoH(CO)₃P(OPh)₃]</td>
<td>11.3</td>
</tr>
<tr>
<td>[Fe(H)₂(CO)₄]</td>
<td>11.4</td>
</tr>
<tr>
<td>[CrH(Cp)(CO)₃]</td>
<td>13.3</td>
</tr>
<tr>
<td>[MoH(Cp)(CO)₃]</td>
<td>13.9</td>
</tr>
<tr>
<td>[MnH(CO)₅]</td>
<td>15.1</td>
</tr>
<tr>
<td>[CoH(CO)₃PPh₃]</td>
<td>15.4</td>
</tr>
<tr>
<td>[WH(Cp)(CO)₃]</td>
<td>16.1</td>
</tr>
<tr>
<td>[MoH(Cp*)(CO)₃]</td>
<td>17.1</td>
</tr>
<tr>
<td>[Ru(H)₂(CO)₄]</td>
<td>18.7</td>
</tr>
<tr>
<td>[FeH(Cp)(CO)₂]</td>
<td>19.4</td>
</tr>
<tr>
<td>[RuH(Cp)(CO)₂]</td>
<td>20.2</td>
</tr>
<tr>
<td>[Os(H)₂(CO)₄]</td>
<td>20.8</td>
</tr>
<tr>
<td>[ReH(CO)₅]</td>
<td>21.1</td>
</tr>
<tr>
<td>[FeH(Cp*)(CO)₂]</td>
<td>26.3</td>
</tr>
<tr>
<td>[WH(Cp)(CO)₃PMe₃]</td>
<td>26.6</td>
</tr>
</tbody>
</table>

Table 21.6 Acidity constants of d-metal hydrides in acetonitrile at 25°C

Shriver & Atkins Inorganic Chemistry, Fourth Edition
Hydrido Complexes

Reactivity

(b) Replacement of hydride by halide, often with halogenated solvents:
\[ \text{HMn(CO)}_5 + \text{CCl}_4 \rightarrow \text{ClMn(CO)}_5 + \text{CHCl}_3 \]

(c) Hydridic properties (i.e. basic) in reactions with acids:
\[ \text{HFe(CO)}_2(\eta–\text{C}_5\text{H}_5) + \text{HCl} \rightarrow \text{FeCl(CO)}_2(\eta–\text{C}_5\text{H}_5) + \text{H}_2 \]

(d) Insertion reactions (see later discussion):
\[ \text{HW(CO)}_3(\eta–\text{C}_5\text{H}_5) + \text{CF}_2=\text{CF}_2 \rightarrow \text{HCF}_2\text{CF}_2\text{W(CO)}_3(\eta–\text{C}_5\text{H}_5) \]
Dihydrogen complexes have been isolated
e.g. \[ M(H_2)(CO)_3(PR_3) \quad \text{and} \quad [M(H_2)(H)(dppe)_2]^{+} \]
\( (M = Mo, W; R = Pr, Cy) \quad \text{and} \quad (M = Fe, Ru) \)
Hydrido Complexes

The H–H separation is \(~0.84 \text{ Å} \) (cf. \(0.74 \text{ Å}\) in free \(\text{H}_2\)).

The bonding of \(\text{H}_2\) to a transition metal is a combination of \(\sigma\) donation from the \(\text{H}_2\) bond to the metal atom and \(\pi\) backdonation from the metal to the \(\sigma^*\) \(\text{H}-\text{H}\) antibonding orbital. Increasing backbonding eventually leads to \(\text{H}-\text{H}\) cleavage and two hydrido ligands.
Alkyl and Aryl Complexes


Long believed that binary transition metal alkyls or aryls could not be made under laboratory conditions. Known compounds invariably contained other ligands (e.g. $\eta^5$-C$_5$H$_5$, CO, PR$_3$, halides).

Now known that difficulty is not due to low thermodynamic stability, but rather kinetic lability. Can prepare such complexes by blocking decomposition pathways.
Stabilization of metal alkyls

1. Thermal stability increases with lack of $\beta$-hydrogens
   \[ \text{WMe}_6, \text{Cr(CH}_2\text{SiMe}_3)_4 \]

2. Coordinatively saturated complexes are more stable
   \[ \text{TiMe}_4(\text{bipy}) > \text{TiMe}_4 \]
   \[ \text{MnEt(CO)}_5 > \text{MnEt}_2 \]

3. Complexes may be kinetically inert to substitution:
   octahedral Cr$^{III}$, Co$^{III}$, Rh$^{III}$ -> stable alkyls e.g.
   \[ [\text{Rh(NH}_3)_5\text{Et}]^{2+} \]. Vitamin B$_{12}$ coenzyme Co$^{III}$–alkyl.
Alkyl and Aryl Complexes

Preparation of Metal Alkyl or Aryl Complexes

1. Metal Carbonyl Anion + Organic Halide
e.g. \[[\text{Fe}(\text{CO})_2(\eta–\text{C}_5\text{H}_5)]^- + \text{MeI} \rightarrow \text{FeMe}(\text{CO})_2(\eta–\text{C}_5\text{H}_5) + \text{I}^-\]

2. Alkyl (or Aryl) Lithium + Metal Halide
e.g. \[\text{ZrCl}_2(\eta–\text{C}_5\text{H}_5)_2 + 2\text{LiPh} \rightarrow \text{ZrPh}_2(\eta–\text{C}_5\text{H}_5)_2 + 2\text{LiCl}\]

3. Addition of M–H or M–C Bond Across Alkenes:
   \[\text{HCo(CO)}_4 + \text{F}_2\text{C}=\text{CF}_2 \rightarrow \text{HCF}_2\text{CF}_2\text{Co(CO)}_4\]
   \[\text{MeRe(CO)}_5 + \text{F}_2\text{C}=\text{CF}_2 \rightarrow \text{MeCF}_2\text{CF}_2\text{Re(CO)}_5\]

4. Reduction of Alkene Complexes:
   \[[\text{Fe}(\eta–\text{C}_2\text{H}_4)(\text{CO})_2(\eta–\text{C}_5\text{H}_5)]^+ + \text{H}^- \rightarrow \text{Fe(C}_2\text{H}_5)(\text{CO})_2(\eta–\text{C}_5\text{H}_5)\]

5. Oxidative Addition Reactions: see later.
Acyl Complexes

Syntheses

1. Metal Carbonyl Anion + Acyl Halide
e.g. \([\text{Mn(CO)}_5]^– + \text{MeCOCl} \rightarrow \text{MeC(=O)Mn(CO)}_5\)
\[\text{↓Δ}\]
\[\text{MeMn(CO)}_5\]

2. (Apparent) Insertion of CO into M–C Bond
e.g. \([\text{FeMe(CO)}_2(\eta–\text{C}_5\text{H}_5)] + \text{CO} \rightarrow \text{Fe[C(=O)Me](CO)}_2(\eta–\text{C}_5\text{H}_5)\)
Alkenyl Complexes

Syntheses

1. Metal Halide + Vinyl Lithium
e.g. $\text{ZrCl}_4 + 4 \text{Li(CPh} = \text{CMe}_2) \rightarrow \text{Zr(CPh} = \text{CMe}_2)_4 + 4 \text{LiCl}$

2. Oxidative Addition (see later) of $\text{HX}$ to $\pi$-Alkyne Complex:
e.g. $\text{(R}_3\text{P})_2\text{Pt} \rightarrow \text{(R}_3\text{P})_2\text{ClPt}$

cis-stereochemistry
3. Nucleophilic Addition (see later) at Cationic Alkyne Complexes

Fe(CO)(PPh₃)Cp unit “protects” one face of the alkyne
Alkynyl Complexes

Syntheses

1. Metal Halide + Alkali Metal Acetylide
e.g. CuI + KC≡CH → CuC≡CH + KI

2. Deprotonation of Metal Vinylidene Complexes
Alkynyl Complexes

62 \textit{fac}-[\text{RhH(C}≡\text{CR)}_2(\text{PMe}_3)_3]

63 \textit{mer-trans}-[\text{RhH(C}≡\text{CR)}_2(\text{PMe}_3)_3]

64 \textit{mer-cis}-[\text{RhH(C}≡\text{CR)}_2(\text{PMe}_3)_3]
σ-Bound Ligands

Summary

1. Alkyl \((M \rightarrow R)\)

2. Acyl \((M \rightarrow \text{C} \rightarrow \text{C})\)

3. Alkenyl

4. Alkynyl \((M-\text{C} \equiv \text{C}-\text{R})\)
Aryl, acyl, alkenyl and alkynyl can in principle interact with occupied metal d orbitals. In practice, though, little if any \( \pi \)- (double bond) character in M–C bond.

\[
\begin{array}{cccc}
\text{Pt–C} & r_{\text{cov} \text{Pt}^{\text{II}}} & r_{\text{cov} \text{C}} \text{ (pm)} \\
\text{trans–PtCl(CH}_2\text{SiMe}_3)(\text{PPhMe}_2)_2 & 208 & 131 & 77 \text{ (sp}^3) \\
\text{trans–PtCl(CH=CH}_2)(\text{PPhMe}_2)_2 & 203 & 131 & 67 \text{ (sp}^2) \\
\text{trans–PtCl(C=CPPh)(PPhMe}_2)_2 & 198 & 131 & 60 \text{ (sp)} \\
\end{array}
\]

Pt–C not shorter than \( r_{\text{cov} \text{Pt}^{\text{II}}} + r_{\text{cov} \text{C}} \) \( \therefore \) no indication of \( \pi \)-bonding.
Reactivity of Organometallic Complexes

A. At the metal centre
   2. Ligand dissociation (S&A, pp 561-563) (M&T, pp 521-523)

B. At the ligand
   1. Electrophilic attack (S&A, p 550) (H, pp 700-703)
Reactivity of Organometallic Complexes

The 16-18 Electron Rule (D,M&A, pp 696-697)

1. Diamagnetic organometallic complexes of transition metals may exist in a significant concentration at moderate temperatures only if the metal valence shell contains 16 or 18 electrons. (A significant concentration is one that may be detected spectroscopically or kinetically and may be in the gaseous, liquid or solid state).

2. Organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons.

Tolman, Chem Soc. Rev. 1972, 1, 337.
## Reactivity of Organometallic Complexes

### Characteristics of organometallic reactions

- $\Delta VE$: change in valence electrons
- $\Delta OS$: change in oxidation state
- $\Delta N$: change in coordination number

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta VE$</th>
<th>$\Delta OS$</th>
<th>$\Delta N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand dissociation</td>
<td>$-2$</td>
<td>$0$</td>
<td>$-1$</td>
</tr>
<tr>
<td>Ligand association</td>
<td>$+2$</td>
<td>$0$</td>
<td>$+1$</td>
</tr>
<tr>
<td>Insertion</td>
<td>$-2$</td>
<td>$0$</td>
<td>$-1$</td>
</tr>
<tr>
<td>Deinsertion</td>
<td>$+2$</td>
<td>$0$</td>
<td>$+1$</td>
</tr>
<tr>
<td>Oxidative addition</td>
<td>$+2$</td>
<td>$+2$</td>
<td>$+2$</td>
</tr>
<tr>
<td>Reductive elimination</td>
<td>$-2$</td>
<td>$-2$</td>
<td>$-2$</td>
</tr>
</tbody>
</table>
**Oxidative Addition**

(D,M&A, pp 668-675)

\[ \Delta \text{VE} \quad 2 \]

\[ \Delta \text{OS} \quad 2 \]

\[ \Delta \text{N} \quad 2 \]

$L_nM + X-Y \rightleftharpoons L_nM \overset{X}{\underset{Y}{\leftrightarrow}}$

X–Y may be

- H–H
- H–X (X = Cl, Br, I)
- H–R (R = aryl)
- H–OR (R = H, Me, Ph)
- H–SR
- H–SiR$_3$
- X–X (X = Cl, Br, I)
- X–R (R = alkyl, aryl)
- X–M (M = SiR$_3$, GeR$_3$, SnR$_3$, HgR)
- X–C(O)R
Oxidative Addition

Four-coordinate $d^8$ complexes
RhCl($PPh_3)_3$ (Wilkinson’s complex), IrCl(CO)(PPh$_3)_2$ (Vaska’s complex)

Reactivity for

\[ L_4M + X-Y \rightleftharpoons L_4M(X-Y) \]

\[ M = Os^+ > Ru^+ > Fe^+ >> Ir^I > Rh^I > Co^I >> Pt^{II} > Pd^{II} >> Ni^{II}, Au^{III} \]

ease of oxidation
Reductive Elimination

(D, M & A, pp 675-676)

The reverse of oxidative addition, important for removing organic parts of complexes after reaction within the coordination sphere.

\[
\begin{align*}
\text{L}_2\text{M} \quad \text{A} & \quad \rightarrow \quad \text{L}_2\text{M} \quad + \quad \text{A} - \text{B} \\
\Delta \text{VE} & \quad -2 \\
\Delta \text{OS} & \quad -2 \\
\Delta \text{N} & \quad -2
\end{align*}
\]

Requirements are/favoured by:

(i) mutually cis arrangement of A and B
(ii) relative stability of lower oxidation state of metal
(iii) presence of bulky ligands

The reaction is both thermodynamically and kinetically favourable: whereas cis–PtHMe(PPh\textsubscript{3})\textsubscript{2} rapidly eliminates CH\textsubscript{4} at –25°C, trans–NiHMe(PCy\textsubscript{3})\textsubscript{2} is kinetically stable.
Insertion and Deinsertion

(D,M&A, pp 662-668)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta V E$</th>
<th>$\Delta OS$</th>
<th>$\Delta N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insertion</td>
<td>$-2$</td>
<td>$0$</td>
<td>$-1$</td>
</tr>
<tr>
<td>Deinsertion</td>
<td>$+2$</td>
<td>$0$</td>
<td>$+1$</td>
</tr>
</tbody>
</table>

The CO insertion reaction in detail:
(S&A, pp 566-567) (M&T, pp 528-532)

$$\text{MeMn(CO)}_5 + \text{PPh}_3 \rightarrow \text{MeMn(CO)}_4(\text{PPh}_3)$$

Reaction proceeds via formation of $\text{MeC(O)Mn(CO)}_4$ (16e), with dissociation of CO being the rate-determining step.
Let us examine the reaction between CO and MeMn(CO)$_5$. Three mechanisms could be considered:

A. Direct insertion

\[
\begin{align*}
&\text{Mn} \quad \text{CO} \quad \text{CH}_3 \\
&\text{Mn} \quad \text{CO} \quad \text{CH}_3
\end{align*}
\]

B. Intramolecular direct insertion

\[
\begin{align*}
&\text{Mn} \quad \text{CO} \quad \text{CO} \quad \text{H}_3\text{C} \\
&\text{Mn} \quad \text{CO} \quad \text{CO} \quad \text{CH}_3
\end{align*}
\]
C. Methyl migration on to adjacent CO

Add labelled CO (*CO)

This gives

as the only product

i.e. rules out A
Microscopic reversibility: study decarbonylation of labelled acetyl complex

Now decarbonylate complex with labelled CO cis to acetyl

+ unlabelled complex
Insertion and Deinsertion

Mechanism C

Reaction more correctly described as alkyl migration.
Insertion and Deinsertion

In summary,

\[ \Delta \text{VE} = -2 \]
\[ \Delta \text{OS} = 0 \]
\[ \Delta \text{N} = -1 \]
Insertion and Deinsertion

Fundamentally important reactions:

\[
\begin{align*}
M - H & \quad + \quad C = C \\
M - R & \quad \rightarrow \quad M - C - C - H \\
& \quad + \quad M - C - C - R
\end{align*}
\]

Similarly, alkynes \( \rightarrow \) vinyls

\[
\begin{align*}
M - H & \quad + \quad C \equiv C \\
M - R & \quad \rightarrow \quad M - C \equiv C - H \\
& \quad + \quad M - C \equiv C - R
\end{align*}
\]

Kinetic studies show:

\[
\begin{align*}
L_N M - H & \quad + \quad C = C \\
& \quad \rightarrow \quad L_{N-1} M \\
& \quad + L \quad \rightarrow \quad L_N M - C - C - H
\end{align*}
\]

There is \( cis \) migration of H or R on to complexed hydrocarbon.
The $\beta$-elimination is the reverse of the alkene insertion reaction and is important in the decomposition of metal alkyls. An increase in coordination number occurs, so that if we increase coordinative saturation (or fill vacant coordination sites), stability is increased.
Insertion and Deinsertion

Mechanism

\[
\begin{align*}
L_NM & \quad \text{CH}_2\text{CH}_2\text{R} \\
\text{L}_N\text{M} & \quad \text{CH}_2 \\
\text{L}_N\text{M} & \quad \text{CHR} \\
\text{H} & \quad \text{CHR} \\
\text{H} & \quad \text{L}_N\text{M} \\
\text{L}_N\text{MH} & + \quad \text{H}_2\text{C} = \text{CHR}
\end{align*}
\]

In summary,

\[
\begin{align*}
\Delta \text{VE} & \quad +2 \\
\Delta \text{OS} & \quad 0 \\
\Delta \text{N} & \quad +1
\end{align*}
\]
Reactions of Coordinated Ligands

(D,M&A, pp 680-685)

These reactions occur without prior coordination of nucleophile to the metal centre. Three conditions favour these direct reactions:

(i) Reactivity of nucleophile;
(ii) Coordinative saturation of the metal complex;
(iii) Formal positive charge on the metal complex.

Known for most unsaturated ligands; in general, oxidation states do not change.
Reactions of Coordinated Ligands

(a) Carbon monoxide

Complexation activates CO to nucleophilic attack
Reactions of Coordinated Ligands

(b) Alkyne complexes

\[ [\text{Fe}] = \text{Fe(CO)}(\text{PPh}_3)(\eta^5-\text{C}_5\text{H}_5) \] ensures stereoselectivity
Homogeneous catalysis proceeds via a series of organometallic reaction steps, coupled to each other in such a way that they form a loop.

It should be born in mind that the actual catalyst of a reaction is not always known, and that the term catalyst often refers to a “precatalyst”. 
Alkene Isomerization

(S&A, pp 681-682)

The hydride mechanism of alkene isomerization.

A→B ligand association
B→C migratory insertion
C→D deinsertion
D→A ligand dissociation

The catalyst requires a hydride ligand and a vacant coordination site.
Alkene Isomerization

The allyl mechanism of alkene isomerization. The catalyst requires two vacant coordination sites.

\[ \text{oxidative addition} \quad \text{M}^0 \quad \text{M}^2+ \quad \text{reductive elimination} \quad \text{M}^0 \]
Alkene Hydrogenation

\[ \text{CH}_2=\text{CHR} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{R} \]

RhCl\((\text{PPh}_3)_3\) (A) (Wilkinson’s catalyst)

A\(\rightarrow\)B oxidative addition

B\(\rightarrow\)C ligand dissociation

C\(\rightarrow\)D ligand association

D\(\rightarrow\)E migratory insertion

E\(\rightarrow\)F ligand association

F\(\rightarrow\)A reductive elimination

A slower cycle (in which the order of addition of \(\text{H}_2\) and alkene is reversed) and

a faster cycle (in which the catalyst is RhCl\((\text{PPh}_3)_2\)) are also possible.
Alkene Hydrogenation

1. Oxidative addition
2. Ligand association
3. Migratory insertion (RDS)
4. trans to cis isomerization
5. Reductive elimination

[Rh(PPh₃)₃(H)₂Cl], [Rh(PPh₃)₃Cl], [Rh(PPh₃)₂(alkene)Cl], [Rh(PPh₃)₂Cl]₂, [Rh(PPh₃)₂(H)Cl]₂ have been observed.

(1) Hydrogen added in syn fashion
e.g.

\[
\begin{array}{c}
\text{RhCl(PPh}_3\text{)}_3 \\
\end{array}
\]

(2) Loss of alkane is irreversible.
For enantioselective reactions, alkene must be prochiral (complexation must result in R or S chirality). The resulting diastereomers (see above) can react at different rates, resulting in enantioselectivity.
Alkene Hydrogenation

DiPAMP (left) is used by Monsanto to synthesize L-Dopa (centre). The minor isomer leads to the major product because of a lower activation barrier (right).

\[
\text{Ar = 3, 4-C}_6\text{H}_3(\text{OH})_2
\]
BiNAP complexes are used in enantioselective transformations

4. Ru(BiNAP)Br₂, X=PPh₂

DIOP


CHIRAPHOS

Bosnich J. Am. Chem. Soc. 1977, 94, 6262

NORPHOS

Brunner Angew Chem Int Ed Engl. 1979, 18, 620
Alkene Hydrogenation

Synthesis of naproxen: Noyori catalyst

\[
\text{MeO} \quad \text{MeO} \\
\text{CO}_2\text{H} \quad \text{CO}_2\text{H} \\
\text{H}_2 \quad \text{H}_2 \\
\{(S)\text{-BINAP}\}\text{-Ru(OCOR)}_2 \quad \{(S)\text{-BINAP}\}\text{-Ru(OCOR)}_2 \\
\text{Inorg. Chem. 1988, 27, 629}
\]
Alkene Hydrogenation

Noyori catalyst

\[ \text{[(R-BINAP)RuX(sol)]}^+ \xrightarrow{\text{EtOH, } H_2, 50-100 \text{ bar}} \text{R} \overset{\text{O}}{\text{Cn}} \text{Y} \]

\[ \text{[(S-BINAP)RuX(sol)]}^+ \xrightarrow{\text{EtOH, } H_2, 50-100 \text{ bar}} \text{OH} \overset{\text{Cn}}{\text{Y}} \text{H} \]

\( X = \text{halogen}; \; Y = \text{heteroatom}; \; C_n = \text{sp}^2 \text{ or sp}^3 \text{ carbon, } n = 1-3 \)

\[ \text{[(R)-BINAP]RuCl}_2 \]

\[ \text{[(BINAP)RuX}_2] \]

\( \text{OR} \overset{\text{H}_2, 70 \text{ bar}}{\xrightarrow{\text{H}_2}} \text{(R)} \overset{\text{OH}}{\text{O}} \)

99% ee

at 10% conversion

100% ee

meso

99 : 1

\[ \text{OH} \overset{\text{OH}}{\text{O}} \]

> 99% ee

> 95% yield

\[ \text{[BINAP]RuX}_2 \]

\[ \text{OR} \overset{\text{H}_2, 80-100 \text{ bar}}{\xrightarrow{\text{H}_2}} \text{OR} \]

92% ee

97% yield
Alkene Hydroformylation


\[ \text{CH}_2\text{=}\text{CHR} + \text{H}_2 + \text{CO} \rightarrow \text{RCH}_2\text{CH}_2\text{CHO} \]
Linear aldehydes are desirable but branched aldehydes can also be formed. The migratory insertion step at C->D can afford a secondary alkyl. This has a larger cone angle than the corresponding primary alkyl.
Formation of linear aldehydes is favoured when bulky phosphines (PBu$_3$) are used with the cobalt catalyst.

The complex at left is an efficient precatalyst (it loses PPh$_3$ in situ). Hydroformylation occurs under mild conditions of the Co catalyst, and the PPh$_3$ ligands favour linear aldehyde products.
Methanol Carbonylation

\[ \text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH} \]

A→B oxidative addition
B→C migratory insertion
C→D ligand association
D→A reductive elimination

Rh and Ir catalysts are preferred to Co.
Alkene Oxidation

(D,M&A, p 695) (S&A, pp 689-690) (M&T, p 541)

A->B ligand association
B->C nucleophilic attack on coordinated substrate
C->D deinsertion
D->E migratory insertion
E->F elimination
F->A redox cycling
Alkene Oxidation

\[ [\text{PdCl}_4]^{2-} + \text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO} + \text{Pd}^\circ + 2\text{HCl} + 2\text{Cl}^- \]

\[ \text{Pd}^\circ + 2\text{CuCl}_2 + 2\text{Cl}^- \rightarrow [\text{PdCl}_4]^{2-} + 2\text{CuCl} \]

\[ 2\text{CuCl} + 1/2 \text{O}_2 + 2\text{HCl} \rightarrow 2\text{CuCl}_2 + \text{H}_2\text{O} \]

\[ \text{C}_2\text{H}_4 + 1/2 \text{O}_2 \rightarrow \text{CH}_3\text{CHO} \]

Specific Pd catalyst is unknown, but redox cycling with Cu is important.
We have already examined alkyl complexes $L_nM-\text{CR}_3$. Carbene complexes $L_nM=\text{CR}_2$ and carbyne complexes $L_nM≡\text{CR}$ also exist and are important in metathesis chemistry.

Two electronic configurations for carbene: triplet (left), and singlet (right). The latter can bond to metals using its electron pair.
Carbene Complexes

The empty p-orbital on C can accept electron density from the metal (left). This is a Fischer-type carbene complex. These are characterized by \( \pi \)-donor substituents on the C (e.g. – OMe, –NMe\(_2\)), low oxidation state, late transition metals, and \( \pi \)-acceptor ligands. The carbene ligand is electrophilic.

A second type of carbene complex is the Schrock-type carbene. These involve high oxidation state, early transition metals with non \( \pi \)-acceptor ligands. The carbene ligand is nucleophilic.
Carbene Complexes

The relative energies of the M(d$_{\pi}$) and the C(p$_z$) orbitals control the electrophilic or nucleophilic character of the carbene. (a) The orbitals of free CH$_2$. (b) If the M(d$_{\pi}$) levels are lower in energy, a Fischer carbene will result. (c) If the M (d$_{\pi}$) levels are higher in energy, a Schrock carbene will result. Shading represents occupied orbitals.
Recently N-heterocyclic carbenes have been reported. These have two N atoms adjacent to the carbene C (below left). They can be stabilized by linking the N atoms via a ring (below centre). Optimal stability results when the linking bridge is unsaturated (below right).
Carbene Complexes

Preparation of Metal Carbene Complexes

1. (Fischer-type Carbene Complexes)
   Addition of Alkyl Lithium to M–CO or M–CNR

   e.g.

   \[
   \text{Cr(CO)}_6 + \text{LiR} \rightarrow \text{Li}^+ \left[ \text{(OC)}_5\text{Cr} \cdots \text{C}_R^O \right]^- \]

   \[
   \downarrow [\text{Me}_3\text{O}]\text{BF}_4
   \]

   \[
   (\text{OC})_5\text{Cr} = \text{C}_R^\text{OCH}_3
   \]
Preparation of Metal Carbene Complexes

2. (Schrock-type Carbene Complexes) 
\( \alpha \)-Deprotonation of an M–alkyl Group

e.g.

\[
\begin{array}{c}
\text{Cp}_2\text{Ta} \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\quad +
\quad \text{NaOMe}
\quad \text{-MeOH}
\quad \rightarrow
\begin{array}{c}
\text{Cp}_2\text{Ta} \\
\text{CH}_2 \\
\text{CH}_3 \\
\end{array}
\]
Preparation of Metal Carbyne Complexes

1. (Fischer-type carbyne complexes).
Electrophilic Abstraction of Methoxide from a Methoxy Carbene

e.g. \(L(CO)_4M=\text{C(OMe)}\text{Me} + BX_3 \rightarrow [L(CO)_4M\equiv\text{CMe}]^+BX_4^-\)
\(+ BX_2(\text{OMe}) \rightarrow X(CO)_4M\equiv\text{CMe}\)
Preparation of Metal Carbyne Complexes

2. **(Schrock-type Carbyne Complexes)**
   \( \alpha \)-Deprotonation of a Carbene Ligand

   (i) \( \text{PMe}_3 \)
   \((\eta-C_5H_5)(\text{Cl})_2\text{Ta}(\equiv\text{CHR}) \rightarrow (\text{Cl})(\text{PMe}_3)(\eta-C_5H_5)\text{Ta}(\equiv\text{CR}) \)
   (ii) \( \text{Ph}_3\text{P}=\text{CH}_2 \)

3. **(Schrock-type Carbyne Complexes)**

   \((t\text{BuO})_3\text{W}=\text{W}(t\text{BuO})_3 + \text{RC}=\text{CR} \rightarrow 2(t\text{BuO})_3\text{W}=\text{CR} \)
   (Metathesis reaction)
CH₂ can be terminal or bridging (c.f. CO). When bridging, there is usually a metal-metal bond present.

**Preparation:** best method employs diazomethane

\[
\text{CpMn(CO)_2(thf)} + (\text{CH}_2\text{N}_2) \rightarrow \text{Cp(CO)_2Mn} + \text{Mn(CO)_2Cp}
\]
Importance of Metal Carbenes and Carbynes

• In the free state, unstable short-lived species.
• Metal-carbon multiple bonding of intrinsic interest (unique bonding type, structural diversity).
• Proposed intermediates in catalytic processes.
• Applications in organic synthesis.
Alkene Metathesis

(C,G,W&W pp 1074-1076)

\[
\text{CH}_2 \equiv \text{CHR} + \text{CH}_2 \equiv \text{CHR} \quad \text{CH}_2 + \text{CHR} \quad \text{CH}_2 + \text{CHR}
\]

Catalyst: \( \text{WO}_3 \) at 150-500° (heterogeneous)
\( \text{WCl}_6 + \text{CIAlMe}_2 \) in solution
Alkene Metathesis

Generation of solution catalyst:

\[
\begin{align*}
WCl_6 + (CH_3)_2AlCl & \rightarrow Cl-W-CH_3 \quad \text{EtOH} \quad Cl-W=CH_2 \rightarrow Cl-W=CH_2 + CH_4 \\
\end{align*}
\]

Generation of heterogeneous catalyst:

precatalyst $\rightarrow$ cat. $\rightarrow$ $O=CR_2$
Heterogeneously catalyzed Shell Higher Olefin Process (SHOP)

\[ \text{C}_4 + \text{C}_{22} \xrightarrow{\text{cat. MoO}_3/\text{Al}_2\text{O}_3} 2 \text{C}_{13} \]

\( \text{C}_4 \) to \( \text{C}_{30+} \) \( \alpha \)-olefins are produced from \( \text{C}_2\text{H}_4 \), and then the \( \text{C}_8 \) - \( \text{C}_{18} \) fraction is enriched by catalysis.
**Alkene Metathesis**

**Mechanism:** via carbene, possibly metallacyclobutane, complexes.

![Chemical diagram for alkene metathesis](image)

Similarly, alkynes are metathesized by the carbyne complex \((^t\text{BuO})_3 W(≡\text{CBu})\), apparently via a tungstenacyclobutadiene intermediate.

![Chemical diagram for alkyn metathesis](image)
Alkene Metathesis

Alkene Metathesis

Schrock catalyst

1st Generation Grubbs catalyst

Ar = 2,6-(i-Pr)₂C₆H₃
R = (F₃C)₂(CH₃)C


- highly reactive - poorly tolerant of functional groups
- catalytic activity increases with increasing electron withdrawing nature of R
- metathesis of tri, tetra substituted alkenes
- tolerant of functional groups CO, OH, NH₂
- selectivity to unhindered alkenes and strained alkenes
- tri, tetra substituted alkenes not attacked
First (left) and second (right) generation Grubbs catalysts catalyze alkene metathesis.
Alkene Metathesis

Alkene metathesis can be used to afford a wide range of products

<table>
<thead>
<tr>
<th>Table 25.2</th>
<th>The scope of the alkene metathesis reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n \begin{array}{c} X \ \end{array} \rightarrow \begin{array}{c} \left( X \right) \ \end{array} \end{array} )</td>
<td>Ring-opening metathesis polymerization (ROMP)</td>
</tr>
<tr>
<td>( n \begin{array}{c} X \ \end{array} \rightarrow \begin{array}{c} \left( X \right) \ \end{array} )</td>
<td>Acyclic diene metathesis polymerization (ADMET)</td>
</tr>
<tr>
<td>( X \begin{array}{c} \end{array} \rightarrow \begin{array}{c} X \ \end{array} )</td>
<td>Ring-closing metathesis (RCM)</td>
</tr>
<tr>
<td>( X \begin{array}{c} \end{array} \rightarrow \begin{array}{c} X \ R \ \end{array} )</td>
<td>Ring-opening metathesis (ROM)</td>
</tr>
<tr>
<td>( \begin{array}{c} R_1 \ \end{array} \rightarrow \begin{array}{c} \end{array} \end{array} )</td>
<td>Cross-metathesis (CM or XMET)</td>
</tr>
</tbody>
</table>
Cross metathesis has limited utility in the lab:

For practical use, one needs high product and $E/Z$ selectivity.

*J. Am. Chem. Soc.* 2000, 122, 58 has many examples
Alkene Metathesis

Ring closing metathesis:

\[ \text{WCl}_6, \text{Cp}_2\text{TiMe}_2 \]

\[ \text{18\%} \]

Alkene Metathesis

Asymmetric ring closing metathesis:

Chem. Eur. J. 2001, 7, 945 reviews early work in this area
Alkene Metathesis

Ring opening metathesis (ROM) (favoured by ring strain in the precursor):

- **BOC** = tert-butoxycarbonyl

![Chemical reaction diagram]

- **89%**  \( E/Z = 1 : 3.2 \)
- **83%**  \( E/Z = 2 : 1 \)
Alkene Metathesis

Ring opening metathesis polymerization (ROMP):

\[
\text{poly(norbornene)} - \text{artificial leather, body armour}
\]

\[
\text{poly(dicyclopentadiene)} - \text{body panels for trucks, waste water units}
\]

\[
\text{poly(cyclooctene)} - \text{used in tyres}
\]
Alkyne Metathesis

Alkene metathesis gives a mixture of Z and E isomers. Alkyne metathesis followed by stereoselective reduction can give the desired stereochemistry.

Alkyne Metathesis

Alkene metathesis followed by alkyne metathesis and stereoselective reduction

Alkene Alkyne Metathesis
Alkene Alkyne Metathesis

(Trost, 1991)

EtOOC
EtOOC
E/Z = 80 : 20

[Ru(CO)3Cl2]2
toluene, CO
100 °C, 4h

86%
(>98% E)
C-C bond formation is the primary task of synthetic chemists. The most useful procedures involve Pd catalysis: Pd is able to promote all the mechanisms necessary for catalysis as well as possessing:

- Tolerance of numerous functional groups
- Relative unreactivity towards air and water
- Low toxicity
- Economic advantages relative to Rh, Ir and Pt

Pd catalyzes many C-C bond forming processes (Kumada, Heck, Suzuki, Stille, Sonogashira).
Chemistry of Palladium

- bonding of nucleophiles to the organic residues with concomitant reductive elimination and reformation of Pd(0)
Pd-catalyzed C-C Coupling

In Pd-catalyzed coupling, organic fragments need to be cis for reductive elimination. To facilitate this, bidentate diphosphines (see below) are employed.
Grignard Aryl Halide Coupling

First Pd-catalyzed C-C coupling? Kumada coupling

\[
\text{cat. } [\text{MCl}_2(\text{PPh}_3)_2] \\
\text{RMgX} + \text{R}'\text{X} \quad \longrightarrow \quad \text{R-R'} + \text{MgX}_2
\]

M = Ni, Pd

Grignard Aryl Halide Coupling

Key step: second organic group introduced into the transition metal coordination sphere via the nucleophilic Grignard reagent.
Heck Coupling

Palladium Catalyzed Coupling of Aryl/Alkenyl Halides to Alkenes

\[ \text{R}_1-\text{X} + \text{R}_2 \xrightarrow{\text{Pd}} \text{R}_1\text{R}_2 \]

\( R_1 = \) alkenyl, aryl, allyl, alkynyl, benzyl, alkoxy carbonylmethyl
\( R_2 = \) alkyl, alkenyl, aryl, CO\(_2\)R, OR, SiR\(_3\)

\( R_1 \) can’t have an H attached to an sp\(^3\) C in the \( \beta \) position or \( \beta \)-elimination will occur after oxidative addition to Pd.
Heck Coupling

Alkene + Aryl/Heteroaryl/Vinyl/Benzyl Halide/Triflate -> Alkene

A->B oxidative addition
B->C ligand dissociation and ligand association
C->D migratory insertion
D->E deinsertion and reductive elimination
E->A ligand dissociation and ligand association
Heck Coupling

A large variety of Pd catalysts have been employed.

<table>
<thead>
<tr>
<th>Palladium catalyst</th>
<th>Application</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(OAc)$_2$</td>
<td>All systems</td>
<td>Most frequently employed, inexpensive</td>
</tr>
<tr>
<td>Pd(OTf)$_2$</td>
<td></td>
<td>Air-stable</td>
</tr>
<tr>
<td>PdCl$_2$</td>
<td></td>
<td>Least expensive Pd salt</td>
</tr>
<tr>
<td>[Pd(acac)$_2$]</td>
<td>Aryl iodides</td>
<td>Air-stable</td>
</tr>
<tr>
<td>[Pd(db)$_2$]</td>
<td>Alkenyl triflates</td>
<td>Limited air stability</td>
</tr>
<tr>
<td>[Pd(dppb)]</td>
<td>Aryl iodides</td>
<td>From [Pd$_2$(dba)$_2$] and dppb</td>
</tr>
<tr>
<td>Palladacycles 1</td>
<td>Chloride as leaving group</td>
<td>Air-stable</td>
</tr>
<tr>
<td>Palladium on charcoal</td>
<td>Aryl chloride as leaving group</td>
<td>Inexpensive</td>
</tr>
<tr>
<td>Palladium on other solids (SiO$_2$)</td>
<td>Aryl iodides</td>
<td>Inexpensive</td>
</tr>
<tr>
<td>Palladium black</td>
<td>Aryl iodides</td>
<td>Air-stable</td>
</tr>
<tr>
<td>[Pd(PPh)$_3$]$_2$</td>
<td>Alkenyl triflates</td>
<td>Air-sensitive</td>
</tr>
<tr>
<td><a href="OTf">Pd(PPh)$_3$</a>$_2$</td>
<td>Aryl iodides</td>
<td>Air-sensitive</td>
</tr>
<tr>
<td>[Pd(PPh)$_3$]Cl$_2$</td>
<td>Aryl triflates</td>
<td>Air-stable</td>
</tr>
<tr>
<td>[Pd(PhCN)$_2$]Cl$_2$</td>
<td>Arenesulfonyl chlorides</td>
<td>Air-stable, soluble form of PdCl$_2$</td>
</tr>
<tr>
<td>[Pd(MeCN)$_2$]Cl$_2$</td>
<td>Alkenyl triflates</td>
<td>Soluble form of PdCl$_2$</td>
</tr>
<tr>
<td>Pd clusters</td>
<td>Aryl iodides, bromides, chlorides</td>
<td>Air-stable</td>
</tr>
<tr>
<td>Pd colloids</td>
<td>Activated aryl bromides</td>
<td>Air-stable</td>
</tr>
<tr>
<td>Pd graphite$^{(b)}$</td>
<td>Aryl iodides, polycondensation [36c]</td>
<td>Air-stable</td>
</tr>
<tr>
<td>Pd on derivatized polystyrenes</td>
<td>Aryl halides</td>
<td>Air-stable</td>
</tr>
<tr>
<td>Pd on derivatized clay</td>
<td>Aryl halides</td>
<td>Air-stable</td>
</tr>
<tr>
<td>Pd on controlled-pore glass beads</td>
<td>Aryl halides</td>
<td>Air-stable</td>
</tr>
</tbody>
</table>
The large variety of Pd catalysts is complemented by a large variety of possible solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Remarks</th>
<th>Example of catalytic system</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>Standard solvent</td>
<td>Pd(OAc)$_2$, NEt$_3$, PPh$_3$, Ia, base (aryl chloride)</td>
</tr>
<tr>
<td>DMA</td>
<td>Higher boiling point than DMF</td>
<td>$[\text{Pd}(\text{PPh}_3)_4]$, NEt$_3$, (aryl iodide)</td>
</tr>
<tr>
<td>NMP</td>
<td>More stable at elevated temp.</td>
<td>$\text{Pd(OAc)}_2$, (S)-BINAP, Bu$_3$NOAc</td>
</tr>
<tr>
<td>MeCN</td>
<td>Common solvent</td>
<td>$\text{Pd/C, 60}^\circ\text{C, 12 h}$</td>
</tr>
<tr>
<td>DMSO</td>
<td>For diazonium salts</td>
<td>$[\text{Pd(dba)}_3]$, BINAP, K$_2$CO$_3$, (for alkenyl triflates)</td>
</tr>
<tr>
<td>MeOH or EtOH</td>
<td></td>
<td>$[\text{Pd(PPh}_3)_4]$, LiCl, Li$_2$CO$_3$, 163 h (aryl iodide)</td>
</tr>
<tr>
<td>tBuOH</td>
<td></td>
<td>$\text{Pd(OAc)}_2$, BINAP, K$_2$CO$_3$, 163 h (aryl iodide)</td>
</tr>
<tr>
<td>THF</td>
<td></td>
<td>$\text{Pd(OAc)}_2$, NEt$_3$, Bu$_3$NBr, rt, 163 h (aryl iodide)</td>
</tr>
<tr>
<td>Dioxane</td>
<td></td>
<td>$[\text{Pd(PPh}_3)_4]$/OTf$_2$, pentamethylpiperidine (PMP), 110$^\circ$C</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td>$[\text{Pd(PPh}_3)_4]$Cl$_2$, K$_2$CO$_3$, BnOct$_2$NCl, 140$^\circ$C, 4 h (aryl sulfonyl chloride)</td>
</tr>
<tr>
<td>Toluene</td>
<td>High-boiling, nonpolar</td>
<td>$\text{Pd(OAc)}_2$, BINAP, K$_2$CO$_3$, $[\text{Pd(PPh}_3)_4]$KOBu</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>High-boiling, nonpolar</td>
<td>$\text{Pd(OAc)}_2$, BINAP, K$_2$CO$_3$, $[\text{Pd(PPh}_3)_4]$KOBu</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>High-boiling, nonpolar</td>
<td>$\text{Pd(OAc)}_2$, BINAP, K$_2$CO$_3$, $[\text{Pd(PPh}_3)_4]$KOBu</td>
</tr>
<tr>
<td>Anisole</td>
<td></td>
<td>$\text{Pd(OAc)}_2$, BINAP, K$_2$CO$_3$, $[\text{Pd(PPh}_3)_4]$KOBu</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td></td>
<td>$\text{Pd(OAc)}_2$, BINAP, K$_2$CO$_3$, $[\text{Pd(PPh}_3)_4]$KOBu</td>
</tr>
<tr>
<td>ClICH$_2$CH$_2$Cl</td>
<td></td>
<td>$\text{Pd(OAc)}_2$, BINAP, K$_2$CO$_3$, $[\text{Pd(PPh}_3)_4]$KOBu</td>
</tr>
<tr>
<td>NEt$_3$</td>
<td></td>
<td>Pd(OAc)$_2$, PPh$_3$, reflux (aryl iodides)</td>
</tr>
<tr>
<td>tPrCN</td>
<td></td>
<td>Pd(OAc)$_2$, BuEt$_3$NBr, KOAc, 90$^\circ$C (aryl iodides)</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Neat [46] or in mixtures with,</td>
<td>Pd(OAc)$_2$, TPPTS, K$_2$CO$_3$, DMF/H$_2$O</td>
</tr>
<tr>
<td>HMPA [17c],</td>
<td>e.g., HMPA [17c], DMF [18] or</td>
<td>Pd(OAc)$_2$, TBABr, K$_2$CO$_3$, (acylates)</td>
</tr>
<tr>
<td>MeCN [17d]</td>
<td>MeCN [17d]</td>
<td>Pd(OAc)$_2$, TBABr, K$_2$CO$_3$, (acylates)</td>
</tr>
<tr>
<td>No solvent</td>
<td>Alkene acts as solvent</td>
<td>Pd(OAc)$_2$, TBABr, K$_2$CO$_3$, (acylates)</td>
</tr>
<tr>
<td>Molten salts</td>
<td>Equivalent to conditions without solvents</td>
<td>Pd(PPh$_3$)$_2$Cl$_2$, TBABr, 100$^\circ$C, 6–43 h (aryl halides, acrylates)</td>
</tr>
</tbody>
</table>
Heck Coupling

Solvent polarity affects the reaction mechanism.

Chem. Rev. 2000, 100, 3009.
Heck Coupling

Solvent and counterion can affect structural isomer regioselectivity.

\[
\begin{align*}
(d\text{ppe})\text{PhPdX} + \text{Ph} & \rightarrow \text{Ph} + \text{Ph} \\
\text{X}^- & \text{ solvent} & \% & \%
\end{align*}
\]

<table>
<thead>
<tr>
<th>(X^-)</th>
<th>solvent</th>
<th>%</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTf(^-)</td>
<td>DMF/H(_2)O (9:1)</td>
<td>42</td>
<td>58</td>
</tr>
<tr>
<td>PF(_6)(^-)</td>
<td>DMF</td>
<td>43</td>
<td>57</td>
</tr>
<tr>
<td>I(^-)</td>
<td>DMF</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>OTf(^-)</td>
<td>THF</td>
<td>8</td>
<td>92</td>
</tr>
</tbody>
</table>

*Organometallics, 1999, 18, 970.*
The insertion product undergo deinsertion by $\beta$-elimination at $sp^3 \beta$-CHs.

This reaction can be enantioselective when using chiral chelating ligands such as (R)-BINAP
Palladium-catalyzed reaction of an organoboron compound with an alkenyl, alkynyl or aryl halide

\[ \text{RB(OH)}_2 + \text{R'}X \xrightarrow{\text{L}_n\text{Pd}(0) \text{ base}} \text{R-R'} + \text{BX(OH)}_2 \]

Suzuki showed that aryl halides could couple with alkenylboranes; the bromides and iodides reacted readily but the chlorides did not.
Suzuki(-Miyaura) Coupling

R = allyl, benzyl, aryl, alkenyl, alkynyl

A oxidative addition
B transmetallation
C isomerization
D reductive elimination
The Mechanism
A base is required. In the transmetallation step, absence of base gives tri-valent boron, whose R groups are not nucleophilic enough for transmetallation.
Solution: Use tetravalent boron. The methyl group in \([\text{BMe}_4]^{-}\) is much more electronegative than \(\text{BMe}_3\).

<table>
<thead>
<tr>
<th></th>
<th>Base</th>
<th>Solvent</th>
<th>time</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>b</td>
<td>thf</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>b</td>
<td>C(_6)H(_6)</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>a</td>
<td>NaOEt</td>
<td>thf</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>b</td>
<td>NaOEt</td>
<td>C(_6)H(_6)</td>
<td>2</td>
</tr>
</tbody>
</table>

If starting materials are stereodefined their three dimensional configurations are retained at greater than 98%.
Suzuki(-Miyaura) Coupling

Steric hindrance is not a major factor in reactions of aryl halides with one ortho group, but when two ortho groups are present the yields drop. Improvements – use:

- Longer reaction times
- Stronger bases

\[
\text{B(OH)}_2 + \text{I}^- \xrightleftharpoons{\text{Pd(PPh}_3)_4}{\text{solvent}} \rightarrow \text{phenyl-phenyl}
\]

<table>
<thead>
<tr>
<th>Base</th>
<th>Solv.</th>
<th>T</th>
<th>Yield 8 h</th>
<th>Yield 24 h</th>
<th>Yield 48 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$CO$_3$,</td>
<td>C$_6$H$_6$</td>
<td>80</td>
<td>25(6)</td>
<td>77(12)</td>
<td>84(25)</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>dme</td>
<td>80</td>
<td>50(1)</td>
<td>66(2)</td>
<td>83(7)</td>
</tr>
<tr>
<td>K$_3$PO$_4$</td>
<td>dme</td>
<td>80</td>
<td>70(0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>dme</td>
<td>80</td>
<td>95(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba(OH)$_2$</td>
<td>dme</td>
<td>80</td>
<td>99(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Stille Coupling

Palladium-catalyzed coupling of organotin reagents with organic halides

\[ R^1X + R^2SnR_3^3 \xrightarrow{\text{Pd}^0L_n} R^1-R^2 + XSnR_3^3 \]

\( X = \text{Br, I, OSO}_2\text{CF}_3 \)

Note that:

- the use of bulky phosphines and basic additives have made the use of chlorides possible.
- no \( \beta \)-hydrogens should be present
- the reactivity of \( R^1SnR''_3 \) increases according to:

\( R^1 = \text{alkyl} < \text{benzyl} \sim \text{allyl} < \text{aryl} < \text{alkenyl} < \text{alkynyl} \)
Stille Coupling

One pathway is:

1. Oxidative addition
2. Isomerization
3. Transmetallation
4. Reductive elimination

Stille reaction

(note bridging halide)

Stille Coupling

Stille coupling may be combined with carboxylation in two ways.

1. Coupling of acid chlorides

\[ R^1\text{COCl} + \text{Me}_3\text{SnR}^2 \xrightarrow{\text{PdL}_n} R^1\text{COR}^2 + \text{Me}_3\text{SnCl} \]

2. “Normal” coupling in the presence of CO

\[ R^1\text{X} + R^2\text{SnR}_3^3 \xrightarrow{\text{Pd}^0\text{L}_n/\text{CO}} R^1\text{-CO-R}^2 + X\text{SnR}_3^3 \]

In the latter, CO exchanges for a PR$_3$ ligand, and inserts to form an acyl Pd complex.
Sonogashira Coupling

General reaction:

\[
R^1X + HCCR^2 \xrightarrow{\text{Et}_3\text{N}} \xrightarrow{\text{PdL}_n, \text{Cul}} \xrightarrow{-[\text{Et}_3\text{N}]X} R^1-\underline{\text{C=\text{C}}}-R^2
\]

Catalysis proceeds via CuC\textsubscript{2}R\textsuperscript{2} transfer

Alkene stereochemistry is usually preserved:
Sonogashira Coupling

(http://www.organic-chemistry.org/namedreactions/sonogashira-coupling.shtm)
Sonogashira Coupling

[Ru] = trans-[Ru(dppe)$_2$]. 1. a. cis-[RuCl$_2$(dppe)$_2$], NH$_4$PF$_6$; b. NEt$_3$; 2. NH$_4$PF$_6$, NEt$_3$; 3. Pd(PPh$_3$)$_4$, NEt$_3$; 4. NBu$_4$F.
Sonogashira Coupling

Molecular modelling
SPARTAN model of 5b.

Electron microscopy
TEM image of 5b.

Sonogashira Coupling

Organometallics, 2003, 22, 1402.
Sharpless Epoxidation

Oxidation of prochiral alkenes (e.g. allyl alcohols) to produce chiral epoxides.

Catalyst is a Ti complex with diethyl tartrate ligands. The dimeric complex at left is a suggested intermediate.
Jacobsen Epoxidation


Another procedure for conversion of prochiral alkenes to chiral epoxides (but with a broader substrate scope). The catalyst is a Mn(V) oxide, but the mechanism has not been defined (there are several suggestions).
The intermediacy of manganaoxetanes (bottom pathway – an organometallic complex) has received theoretical support.
Small Molecule Activation

Organometallic compounds bind and activate small molecules (previous lectures: example of ethene). Other important molecules to be activated: CO, alkanes.

Goal: Relatively common carbon compounds (coal?)

↓ how?

Useful organic chemicals

Coal $\xrightarrow{\Delta} O_{2\text{steam}}$ Synthesis gas (CO: H$_2$ mixture)
CO Activation

Water-Gas Shift Reaction

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

Changes CO: H\(_2\) ratio

(H pp 709-710) (M&T, pp 550-551)

The \(\text{Fe(CO)}_5\) catalyzed water-gas shift reaction
# CO Activation

<table>
<thead>
<tr>
<th>BONDING MODE</th>
<th>EXAMPLE</th>
<th>ν(CO) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td></td>
<td>2143</td>
</tr>
<tr>
<td>M–C≡O</td>
<td>Cr(CO)₆</td>
<td>2000</td>
</tr>
<tr>
<td>+M–C≡O</td>
<td>[Mn(CO)₆]⁺</td>
<td>2100</td>
</tr>
<tr>
<td>−M–C≡O</td>
<td>[V(CO)₆]⁻</td>
<td>1860</td>
</tr>
<tr>
<td>(OC)₃Co(µ–CO)₂Co(CO)₃</td>
<td></td>
<td>1700</td>
</tr>
</tbody>
</table>
## CO Activation

<table>
<thead>
<tr>
<th>BONDING MODE</th>
<th>EXAMPLE</th>
<th>$\nu$(CO) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–C–O–M</td>
<td>$\text{Mn}_2(\text{CO})_5(\text{dppm})_2$</td>
<td>1645</td>
</tr>
<tr>
<td></td>
<td>$(\eta–\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo}(\mu–\text{CO})$-ZrMe($\eta–\text{C}_5\text{H}_5$)$_2$</td>
<td>1545</td>
</tr>
<tr>
<td></td>
<td>$[\text{Fe}(\text{CO})(\eta–\text{C}_5\text{H}_5)]_4$</td>
<td>1600</td>
</tr>
<tr>
<td></td>
<td>$(\mu_3–\text{CO})[\text{Nb}(\text{CO})_2(\eta–\text{C}_5\text{H}_5)]_3$</td>
<td>1330</td>
</tr>
</tbody>
</table>
Catalytic processes involving CO
Mentioned thus far:

Alkene hydroformylation (“oxo” process).
\[
\text{CH}_2 = \text{CHR} + \text{H}_2 + \text{CO} \overset{\text{Co or Rh}}{\rightarrow} \text{RCH}_2\text{CH}_2\text{CHO}
\]

Monsanto acetic acid process
\[
\text{CH}_3\text{OH} + \text{CO} \overset{\text{Rh}}{\rightarrow} \text{CH}_3\text{CO}_2\text{H}
\]
Fischer-Tropsch Synthesis

(H pp 715-717) (H&S, pp 676-677)
Non-selective:

\[
\text{CO} + \text{H}_2 \xrightarrow{\text{Fe oxide cat.} \atop 320-340 \, ^\circ\text{C} / 25 \, \text{bar}} \text{gasoline} + \text{diesel oil, waxes, etc.}
\]

\[1 : 3.5\]

70% (Sasol plant)

Selective formation of products required:

\[
2\text{CO} + 3\text{H}_2 \xrightarrow{[\text{Rh}_{12}(\text{CO})_{34}]^{2-} \atop 250 \, ^\circ\text{C} / 3000 \, \text{bar}} \text{HOCH}_2\text{CH}_2\text{OH}
\]

(Union Carbide - Pruett, 1974)
Heterogeneous Catalysis

The mechanism is unknown: the following surface species have been postulated as important intermediates.

\[ \begin{align*}
M & \equiv C & \text{carbide} \\
M & \equiv C - H & \text{methylenecarbide} \\
M & \equiv C - H & \text{\(\mu_2\)-methylenecarbide} \\
M & \equiv C - OH & \text{hydroxymethylene} \\
M & \equiv C - CH_2 - OH & \text{hydroxyalkyl} \\
M & \equiv C - H & \text{formyl} \\
M & \equiv C - H & \text{\(\eta^2\)-formaldehyde}
\end{align*} \]
Currently favoured mechanism for the F–T reaction is:

These species (“ligands”) are also found coordinated to transition metal clusters, which thus serve as models.
Hydrogenation of ethene by deuterium on a metal surface. The individual steps are similar to those seen with monometallic complexes in solution.
C-H Activation

Small Molecule Activation: Alkanes
Goal: selective activation of C–H bonds.
Cyclometallation and activation of hydrocarbons

![Diagram of cyclometallation and activation of hydrocarbons]
C-H Activation

Commonly found with PPh$_3$, P(OPh)$_3$ and related ligands.
Useful for catalytic H/D exchange.

Cyclometallation reaction is activation of C–H bond.
Olefins are versatile feedstocks (polymerization, hydroformylation, etc) but alkanes are more plentiful, less reactive. Can we use transition metals to activate alkane C–H bonds, i.e. insertion of $\text{ML}_n$ into C–H bond?

Tertiary phosphines with bulky groups can be metallated.

\[ \text{Bu}^t_2\text{PCH}_2\text{CMe}_3 \xrightarrow{\text{PtCl}_2(\text{NCPh})_2} \]

\[ \begin{array}{c}
\text{Pt} \\
\text{P} \\
\text{Bu}^t_2 \\
\text{Cl} \\
2
\end{array} \]
C-H Activation

Usually thermodynamically unfavourable:

\[ \text{L}_n\text{M} + \text{H}_2 \rightarrow \text{L}_n\text{M} \text{H} \quad \Delta H < 0 \]

\[ \text{L}_n\text{M} + \text{C}_\text{H}_4 \rightarrow \text{L}_n\text{M} \text{C}_\text{H}_2 \quad \Delta H > 0 \]

Reason: M–C bond much weaker than M–H bond.

Widespread occurrence of cyclometallation is due to their neutral entropic character; a prerequisite is that the C–H bonds are located so as to allow close approach to the metal atom.
C-H Activation

Alkane coordination can arise from donation of electron density from a C-H σ bond to the metal atom (left), and back-donation of electron density from the metal atom to the C-H σ* orbital (centre). Alkane complexes have been recently isolated (right).
Interest in obtaining evidence for M ... H–C interaction in ground-state structures - see D,M&A, pp 608-609. 2e 3 centre bonds between C–H and M are termed “agostic”. The existence of agostic interactions can be deduced from
- structural data (especially neutron diffraction)
- chemical shifts to high field in $^1$H NMR ($\delta = – 5$ to $– 15$ ppm)
- reduced coupling constants [$^1$J(C,H) = 75-100 Hz]
- vibrational frequencies at low cm$^{-1}$ ($\nu$CH = 2100 - 2300 cm$^{-1}$)
C-H Activation

Typical examples of agostic interactions.
**C-H Activation**

**Strategy:** generate unstable 16e moiety which can then undergo oxidative addition. Examples:
C-H Activation

Methodology: make transition metal electron rich
(a) use C₅Me₅ instead of C₅H₅
(b) use PMe₃ instead of PPh₃