

## (chemistry of metals in low oxidation states)

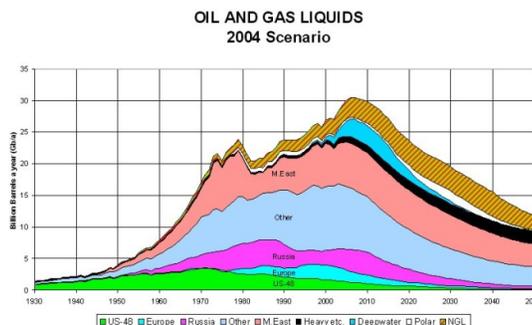
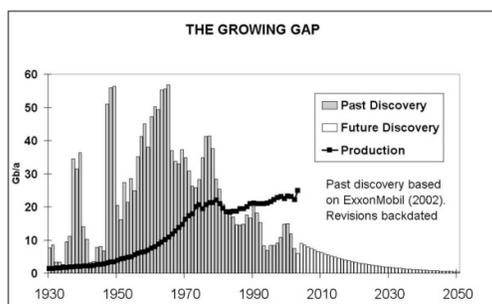
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This course deals with complexes in which the metals are in low oxidation states.  
Compare the compounds in Housecroft chapters 20-23 with those in chapter 24.

These handouts are not a full set of notes! Most of the important diagrams are included but it is up to you to create your own notes.

These are useful sources but use the library as well please:

- A.F. Hill, *Organotransition Metal Chemistry*, RSC. Tutorial Chemistry Text, 2002.
- G.L. Miessler, P.J. Fischer, and D.A. Tarr, *Inorganic Chemistry*, 5th ed., Pearson, 2014.
- F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., chapters 2, 22-27, John Wiley & Sons, 1988.



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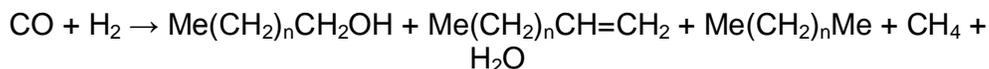
## Some industrial processes

### Synthesis gas [Housecroft]

Mixtures of CO and H<sub>2</sub> are referred to as synthesis gas ('syngas'). The second reaction is the water gas shift reaction. The reaction does not go to completion and the CO<sub>2</sub> is a removable byproduct.

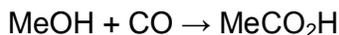


## Fischer Tropsch (FT) reactions [Housecroft, Bochmann]



The Fischer Tropsch reaction class. This requires heat, pressure, and a catalyst.

## Acetic acid process [Housecroft, Bochmann]



This reaction is catalysed by cobalt-, rhodium-, or iridium-based compounds. Look up the BP-Monsanto and the Cativa processes for additional information.

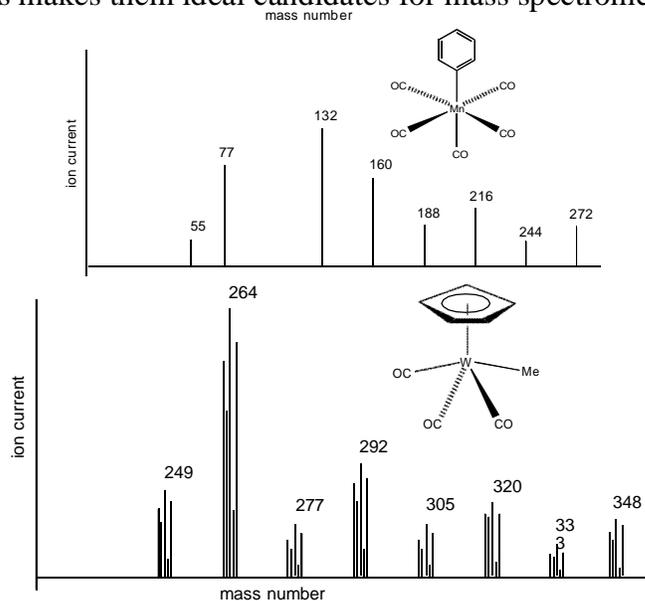
## Properties and characterisation of low oxidation state complexes

The principles of coordination chemistry you learned last year (crystal field theory, etc.) are equally applicable to the chemistry of this course. You have had a number of courses on characterisation from which knowledge will be assumed:

- IR spectroscopy (including group theory)
- NMR spectroscopy: in particular  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$
- X-ray crystallography

## Mass spectrometry

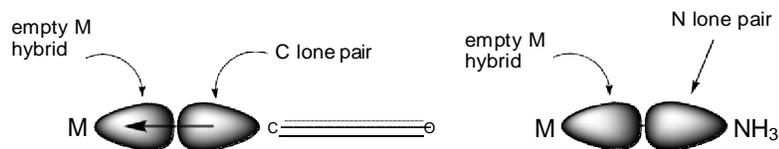
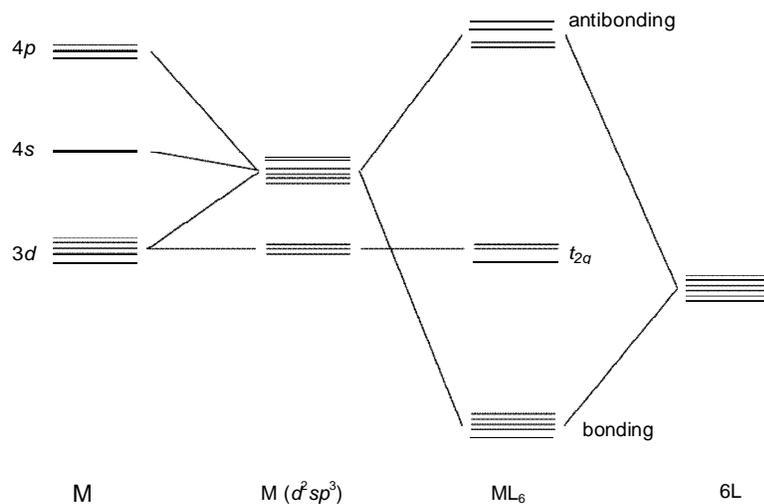
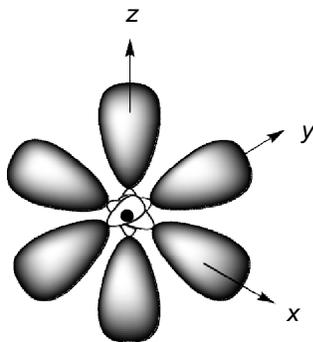
When low oxidation state complexes are neutral, they tend to be rather volatile. This makes them ideal candidates for mass spectrometry.



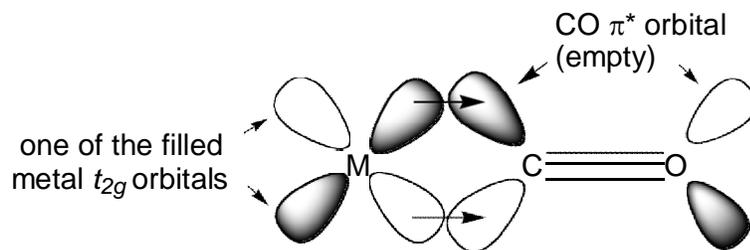
Schematic mass spectra of  $\text{MnPh}(\text{CO})_5$  (left) and  $\text{CpWMe}(\text{CO})_3$ .

**Exercise:** The relative abundances of tungsten isotopes are 180 (0.135%), 182 (26.4%), 183 (14.4%), 184 (30.6%), and 186 (28.4%). Sketch a graph of relative abundance against mass number for tungsten. Using the appearance of this sketch, assign the peaks in the spectrum above to fragments of the molecule  $\text{CpWMe}(\text{CO})_3$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ).

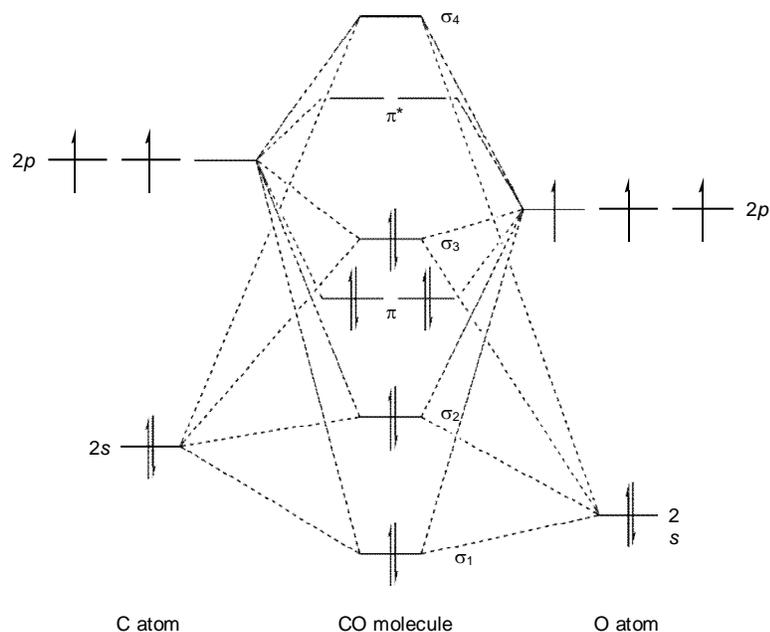
The nature of M-CO bonding [Housecroft p807; Bochmann p10]



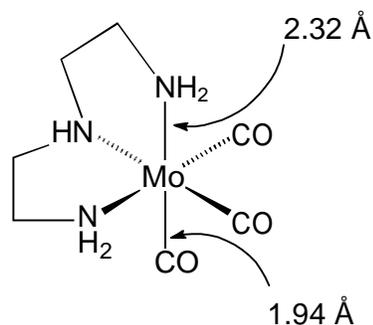
The  $\sigma$ -component



The  $\pi$ -component



### Bond length evidence: Mo(CO)<sub>3</sub>(dien)



The covalent radii of N(*sp*<sup>3</sup>) and C(*sp*) are both 0.7 Å. Therefore the Mo—C and Mo—N bond lengths should both be equal if there is no back bonding.

### Infrared spectroscopic evidence

The CO stretches for metal carbonyls are particularly strong and occur in regions of the spectrum uncluttered by other bands. The CO stretching frequency for CO gas is 2143 cm<sup>-1</sup>. There is no back bonding in the adduct OC:BH<sub>3</sub>. For this species  $\nu_{\text{CO}}$  is 2164 cm<sup>-1</sup>.

#### Infrared $\nu_{\text{CO}}$ and $\nu_{\text{MC}}$ stretching data (values in cm<sup>-1</sup>)

complex	[Mn(CO) <sub>6</sub> ] <sup>+</sup>	Cr(CO) <sub>6</sub>	[V(CO) <sub>6</sub> ] <sup>-</sup>
$\nu_{\text{CO}}$	2096	2000	1859
$\nu_{\text{MC}}$	416	441	460

#### Infrared $\nu_{\text{CO}}$ stretching data (values in cm<sup>-1</sup>)

complex	Ni(CO) <sub>4</sub>	[Co(CO) <sub>4</sub> ] <sup>-</sup>	[Fe(CO) <sub>4</sub> ] <sup>2-</sup>	[Mn(CO) <sub>4</sub> ] <sup>3-</sup>
$\nu_{\text{CO}}$	2046	1883	1789	1670

## Carbonyl complexes and their structures

The most stable neutral homoleptic carbonyl complexes (homoleptic: means all ligands in a complex are identical)

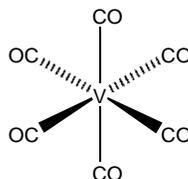
5	6	7	8	9	10
V(CO) <sub>6</sub>	Cr(CO) <sub>6</sub>	Mn <sub>2</sub> (CO) <sub>10</sub>	Fe(CO) <sub>5</sub> Fe <sub>2</sub> (CO) <sub>9</sub> Fe <sub>3</sub> (CO) <sub>12</sub>	Co <sub>2</sub> (CO) <sub>18</sub> Co <sub>4</sub> (CO) <sub>12</sub> Co <sub>6</sub> (CO) <sub>16</sub>	Ni(CO) <sub>4</sub>
	Mo(CO) <sub>6</sub>	Tc <sub>2</sub> (CO) <sub>10</sub>	Ru(CO) <sub>5</sub> Ru <sub>3</sub> (CO) <sub>12</sub>	Rh <sub>4</sub> (CO) <sub>12</sub> Rh <sub>6</sub> (CO) <sub>16</sub>	
	W(CO) <sub>6</sub>	Re <sub>2</sub> (CO) <sub>10</sub>	Os(CO) <sub>5</sub> Os <sub>3</sub> (CO) <sub>12</sub>	Ir <sub>4</sub> (CO) <sub>12</sub> Ir <sub>6</sub> (CO) <sub>16</sub>	

Titanium group (Ti, Zr, Hf;  $d^4$ )

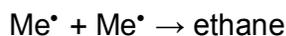
The  $d^4$  configuration requires that seven carbonyls ( $4 + 2 \times 7 = 18$ ) arrange themselves around the central atom. None known.

Vanadium group (V, Nb, Ta;  $d^5$ )

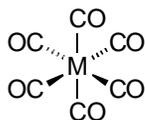
For this group thirteen electrons are required to attain the 18-electron configuration.



Consider, in a formal sense, the reaction of two *seven*-electron methyl radicals:



A carbon—carbon bond results and the octet configuration required for carbon is attained. In analogous fashion, if one were to react two 17-electron  $\text{V}(\text{CO})_6$  units, one might expect a dimeric species which obeys the 18-electron rule:

Chromium group (Cr, Mo, W;  $d^6$ )

M = Cr, Mo, W

One only:  $[\text{M}(\text{CO})_6]$ , all known.