Chem-2X-Organometallics

Metal-organo compounds can be conveniently divided into those containing

(a) Main group metals *s*-block (Na, Mg..) & *p*-block (Al, Sn, Bi .. & Zn)

(b) Transition metals Ti-Cu

All contain a *polar* $M^{\delta+}-C^{\delta-}$ bonds - some more polar than others ......

electronegativities
2.5   1.0

H
H—C—Li
H

C–Li σ bond polarized towards carbon

MeLi attacks electrophiles here

electronegativities
2.5   3.5

H
C=O
H

C=O π bond polarized towards oxygen

nucleophiles attack here
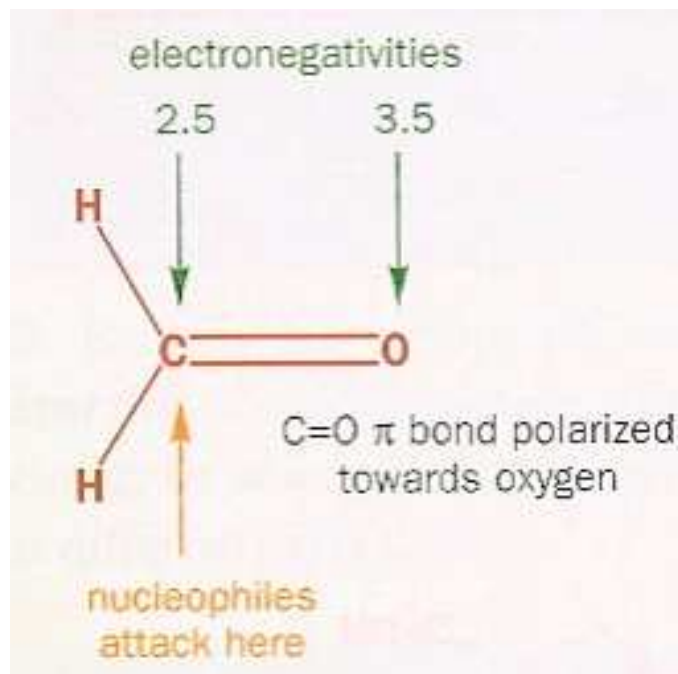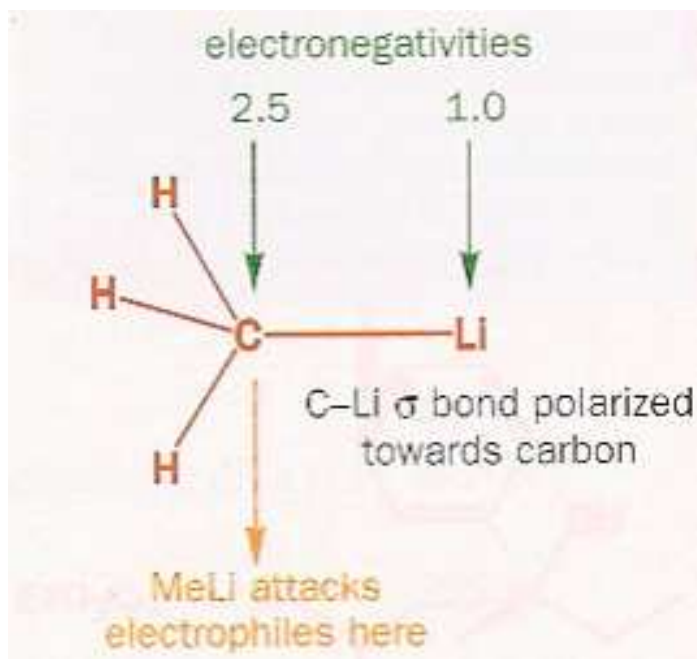
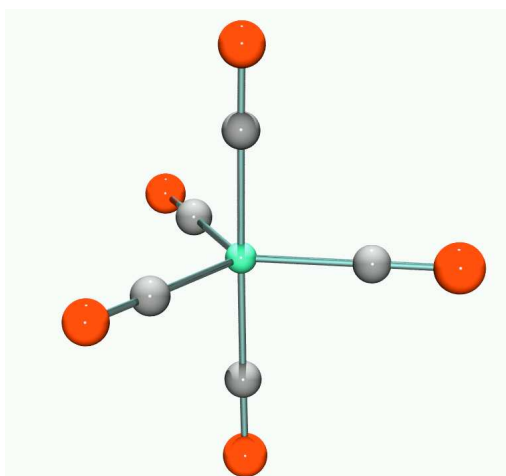This polarisation of the M-C bond is extremely useful in synthesis

$R_2C^{\delta+}=O^{\delta-}$ + $LiCH_3$ $\rightarrow$ $R_2MeC\text{-}OLi$ $\rightarrow$ $R_2MeC\text{-}OH$
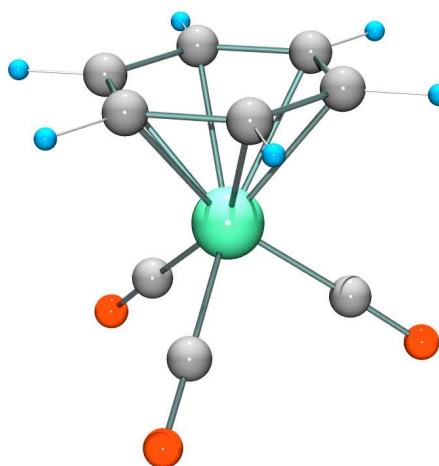
hydrolysis
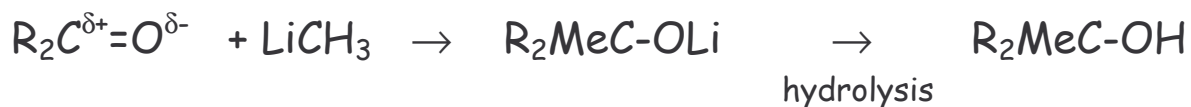
ketone/aldehyde $\rightarrow$ alcohol

A huge variety of organic molecules can be bonded to metals, especially transition metals.

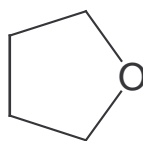Examples include : alkyl & aryl groups, alkenes, alkynes, CO (carbonyls)

$Fe(CO)_5$

$Cr(CO)_3(C_6H_5)$

First look at main group organometallics and how they are prepared ....

Synthesis

1. Metal and organic halide

$$RX + Mg \rightarrow RMgX \text{ (Grignard reagent)}$$

$$CH_3Cl + 2Li \rightarrow LiCH_3 + LiCl \text{ (organo-lithium reagent)}$$

Use donor solvents, e.g. ethers tetrahydrofuran (THF)

Aluminium (Al) and zinc (Zn) also work well, along with other active metals
Other metals may need more forcing conditions (e.g. higher temperatures, sonication)

$$CH_3Cl + Si \xrightarrow{\text{300 C / Cu catalyst}} (CH_3)_2SiCl_2$$

(plus others)
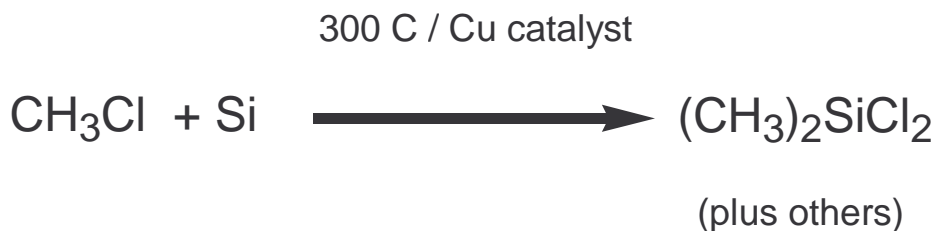
The formation of chloromethylsilanes has great commercial importance

While these reactions can look simple from the equations, they are in reality quite complex

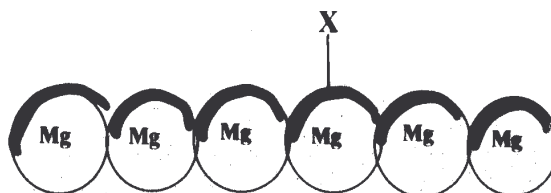# Formation of Grignard reagents

1.

R—X

2.

R•

X

3.

R

X

4.

R   X

Et$_2$O

R   X

Mg

Et$_2$O   OEt$_2$
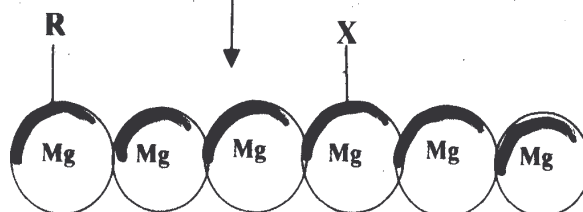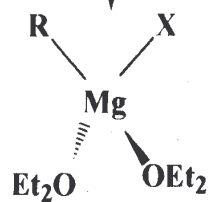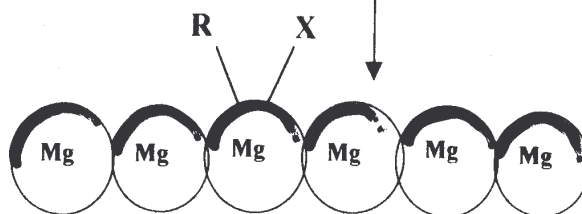
Synthesis

2. Metathesis reactions (exchange of partners)

$$4MeLi + SiCl_4 \longrightarrow SiMe_4 + 4LiCl$$

The electronegative halide ends up with the most electro-positive metal, so that the new organometallic compound has less polar M-C bonds and is less reactive.

e.g

$$2MeLi + CuI \xrightarrow{Et_2O} Me_2CuLi + LiI$$

"Gilman reagent"

carbonyl group unchanged
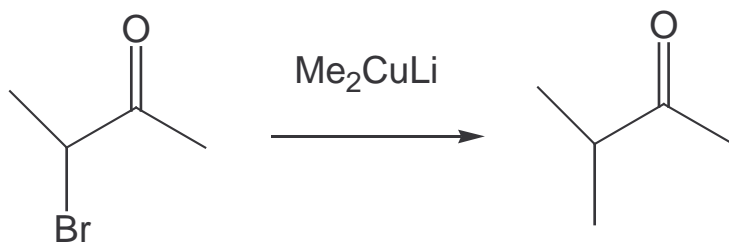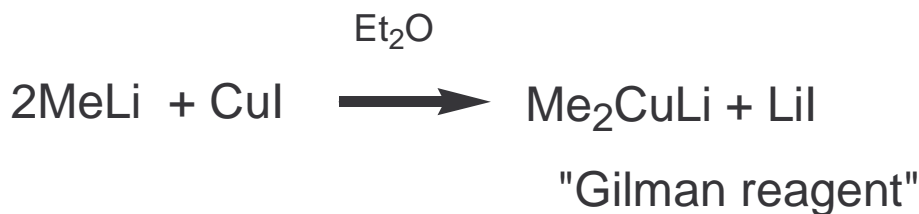
Special case of metathesis - *redistribution reactions*

$$SnPh_4 + SnCl_4 \longrightarrow SnPh_2Cl_2 \text{ (also } Ph_3SnCl, PhSnCl_3)$$

Synthesis

3. Hydrometallation

$$Et_2O\text{-}BH_3 + RCH{=}CH_2 \longrightarrow RCH_2CH_2BH_2 + Et_2O$$

This hydroboration reaction
is very important : it can be used
to achieve *anti*-Markownikow
addition to alkenes

H_2O_2

$$RCH_2CH_2OH$$
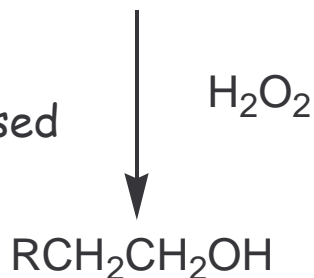
A metal hydride adds to an unsaturated link. This is a vital (and reversible) step in transition metal organometallic reactions and catalysis. Becoming important in main group chemistry also ....

4. Trans-metallation

Direct reaction can transfer an organic group to a more reactive metal

$$2Li + Hg(CH_2Ph)_2 \longrightarrow 2LiCH_2Ph + Hg$$

$$4Li + Sn(CH{=}CH_2)_4 \longrightarrow 4LiCH{=}CH_2 + Sn$$

(Neither benzyl-lithium nor vinyl-lithium can be made by direct reaction from the metal plus organic halide)

5. Metal-Hydrogen exchange

A carbanionic R group will combine with an acidic hydrogen on a hydrocarbon, forming a new reagent

$$RMgX + R'C{\equiv}CH \rightarrow R'C{\equiv}CMgX + RH$$
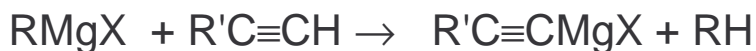
Compound types and reactivity

Group	1	2	12	13	14	15
Example	$LiCH_3$ (MeLi)	PhMgBr $MgMe_2$	$ZnEt_2$ $HgMe_2$	$AlMe_3$	$SiMe_4$	$AsPh_3$ $SbMe_3$
Element	Li	Be		B		
	Na	Mg		Al	Si	
	K	Ca	Zn	Ga	Ge	As
	Rb	Sr	Cd	In	Sn	Sb
	Cs	Ba	Hg	Tl	Pb	Bi

A	B	C

A. Ionic compounds with very electropositive metals e.g. NaC_6H_5
Behaves as $Na^+ \, C_6H_5^-$ - an insoluble and *pyrophoric* (i.e. spontaneously inflame in air) solid. Not much practical use due to its insolubility.

B. Polar covalent compounds e.g. Grignard reagents $CH_3^{\delta-}$-$Mg^{\delta+}$-X.
They are reactive and are often useful compounds. All react with air and moisture, and some are *pyrophoric*

C. Compounds of less electropositive metals - they are covalent and often quite unreactive

Reactivity relationships

Reactivity falls sharply as elements become less electropositive

Reagent	$MgMe_2$	$ZnMe_2$	$CdMe_2$	$HgMe_2$
O_2	inflames	inflames	oxidises	inert
H_2O	explodes	explodes	hydrolyses	inert
CO_2	reacts	reacts	inert	inert

Example of Main Group Organometallics – ZnEt$_2$

Varying reactivity means that main group organometallics can be used as specific reagents for specific purposes, e.g. Gilman reagent used to attack *C-Br* bond but not *C=O* bond.

Diethyl zinc was the *first* organo-metal compound made, by the British chemist Edward Frankland in 1850. Made from EtI and Zn and protected by a CO_2 or H_2 atmosphere - the compound is highly *pyrophoric*

ZnEt$_2$ is used nowadays to de-acidify the paper of important old books and documents (they become yellowed and brittle with time)

$$2H^+ + ZnEt_2 \rightarrow Zn^{2+} + 2\ C_2H_6 \uparrow$$

Any moisture in the paper reacts to give the white, basic oxide ZnO, which buffers further acidity

$$H_2O \text{ (in paper)} + ZnEt_2 \rightarrow ZnO + 2\ C_2H_6 \uparrow$$

However, difficult to use because it is so reactive and dangerous.

Nature of Grignard reagents

R-Mg-X - simple formula belies a complicated situation.
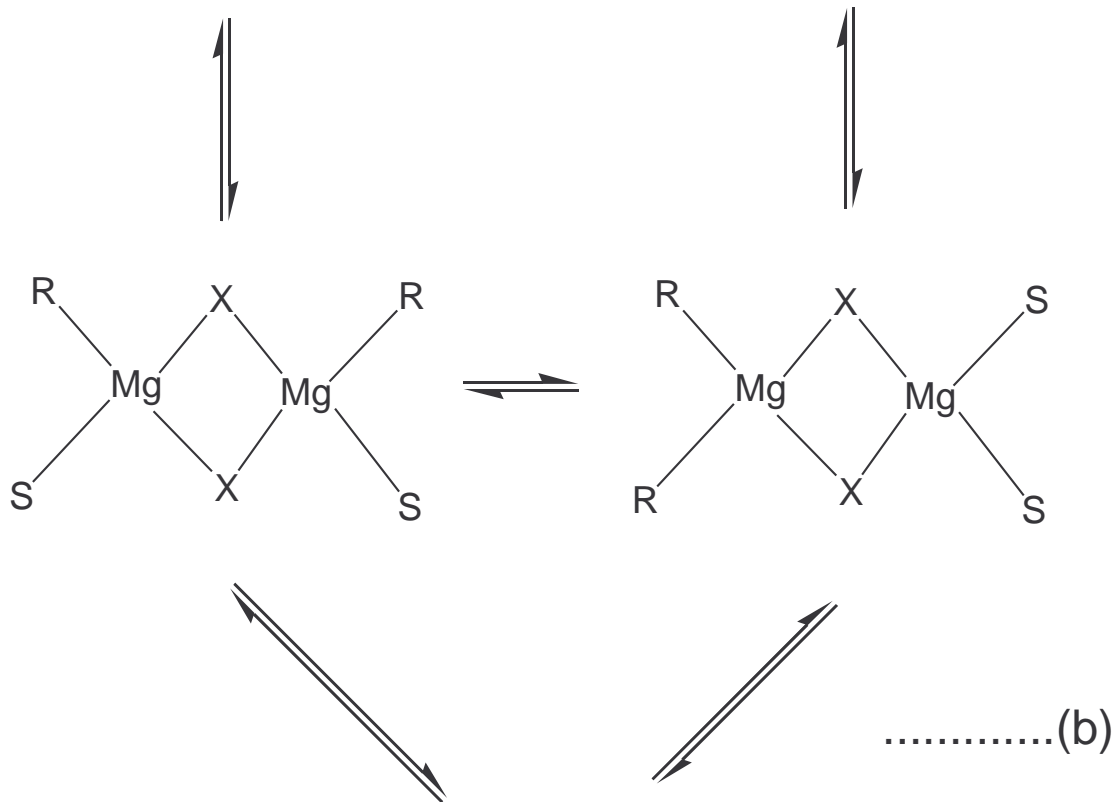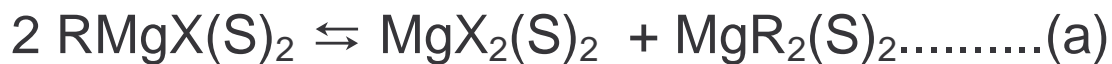Many species present in solution - known as Schlenk equilibria.

Evidence
 (a) RMgX when treated with dioxane gives MgX_2.dioxane
Also mixtures of solutions of $MgEt_2$ and $MgBr_2$ are indistinguisable from solutions of EtMgBr.

$$2RMgX + \text{[dioxane]} \longrightarrow MgX_2.\text{dioxane} + MgR_2$$

(b) Molecular weights in solution are too big - indicates oligomers are present with 1-4 units. Clusters have now been isolated.

(c) Grignard reagents conduct electricity, indicating that _ionic_ species are present in solution. Mg is deposited at _both_ the cathode _and_ anode.

Schlenk equilibria in Grignard reagents

$$2\,RMgX(S)_2 \leftrightharpoons MgX_2(S)_2 + MgR_2(S)_2 \ldots\ldots(a)$$

R   X   R   R   X   S

Mg   Mg   ⇌   Mg   Mg

S   X   S   R   X   S

$$\ldots\ldots\ldots(b)$$

$$[XMg(S)_3]^+,\ [RMg(S)_3]^+,\ [R_2MgX(S)]^-,\ [RMgX_2(S)]^- \ \ldots\ldots(c)$$

Here S is a solvent molecule (usually an ether molecule)

This horrible mixture is present in all Grignard solutions !!

Structure and bonding

Compounds of larger and less electropositive elements have structures just as the formulae suggest : $SiMe_4$ is tetrahedral and $HgPh_2$ is linear.

Some of the lighter and more electropositive metals tend to use their s and p orbitals to produce 4-coordination or greater, even when there are insufficient electrons to allow two electrons per bond.

Such molecules are called *electron deficient* and are quite common with Li, Be, Mg and Al
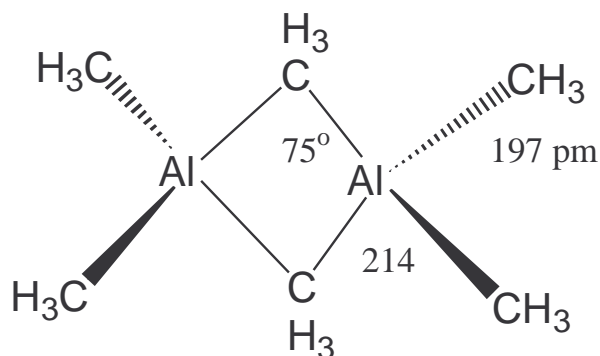
e.g "$AlMe_3$" is actually dimeric, Al_2Me_6 with *bridging* methyl groups

Al_2Me_6 is an excellent carbanionic methylating agent

$$SiO_2 + Al_2Me_6 \rightarrow SiMe_4$$

It can be made in the lab by trans-metallation

$$Al + HgMe_2 \rightarrow Al_2Me_6 + Hg$$

Structure and bonding

CH3

3-centre 2-electron bond

Each Al is sp^3 hybridised and is bonded to four C atoms, but there are not enough electrons to assign a pair of electrons per chemical bond.

This is common in aluminium alkyls and similar *electron deficient* bridges are found in other alkyls, e.g. $MgMe_2$ and $BeMe_2$ are *polymeric* through bridging methyl groups ...
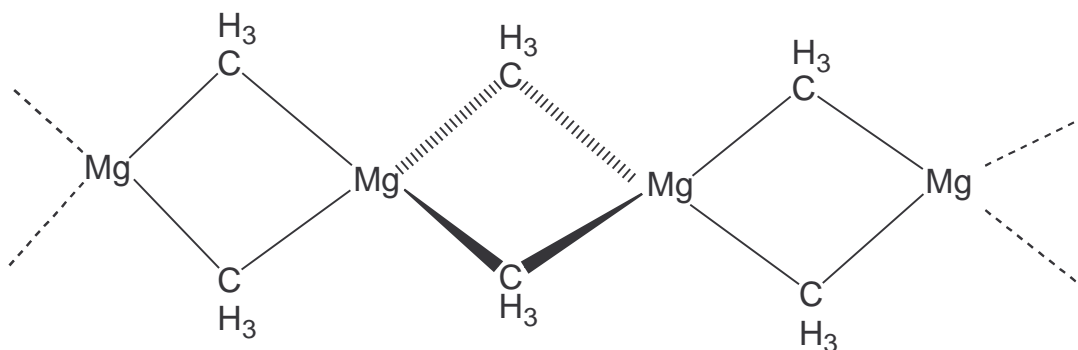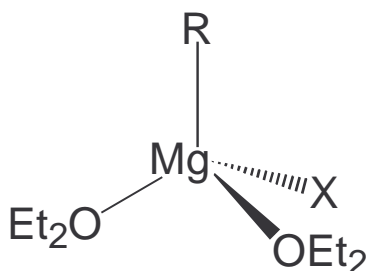

$Be(CMe_3)_2$ is a *linear* molecule because tertiary butyl group is large ! Lithium methyl is tetrameric $(LiMe)_4$ - *cubane* structure in solid and solution.

No bonds between Li atoms !
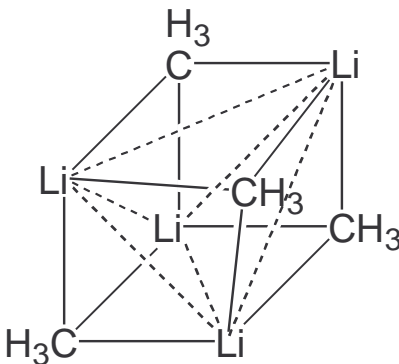
Solvation of organometallics

Compounds of the electropositive metals are energetically solvated, e.g. BeR_2 RMgX, ZnR_2, AlR_3

Complex formation prior to any reaction is almost certain to occur as part of the reaction sequence, e.g. hydrolysis of aluminium alkyls to give alkanes.

$$1/2\ Al_2R_6 + H_2O \rightarrow [H_2O \rightarrow AlR_3]\ \rightarrow\ AlR_2(OH) + RH$$

CdR_2 is less energetically solvated and reacts more slowly, while HgR_2 has practically no tendency to increase its coordination above two (and hence form complexes like Mg above).

This accounts for the inert behaviour of $HgMe_2$

$$HgMe_2 + H_2O\ \rightarrow\ HgO + 2CH_4\quad \Delta H^0 = \text{-8 kJ mol}^{-1}$$

Reactions doesn't go and $HgMe_2$ is *kinetically stable* because a solvated intermediate is not formed. This is why $HgMe_2$ and methyl mercury derivatives such as $MeHg^+$ are so dangerous in the environment.

Minamata disaster - methyl mercury poisoning
http://www.american.edu/TED/MINAMATA.HTM

From 1932 to 1968, the Chisso Corporation, a company located in Kumamoto Japan, dumped an estimated 27 tons of mercury compounds into Minamata Bay. The town consists of mostly farmers and fisherman.

Thousands of people whose normal diet included fish from the bay unexpectedly developed symptoms of methyl mercury poisoning. The illness became known as the "Minamata Disease" and over 3000 victims have been compensated in the Japanese courts.

The mercury compounds were absorbed by sea organisms and converted to methyl mercury derivatives and passed into the food chain.

Methyl mercury and derivatives are serious neurotoxins !

The phrase "Mad as a hatter" comes from a similar poisoning. In the 18th & 19th centuries, hatters utilised treatement of hat-felt with mercury compounds.

The story so far ....

1. Organometallic compounds of *electropositive* main group elements are very reactive. Those of less electropositive metals are less so (but react more selectively)

2. The compounds can be prepared by direct reaction of metals and organic halides, by adding a metal-hydrogen bond across a C=C bond, or by transfer of organic groups between metals.

3. Grignard reagents in solution involve many complex equilibria between several organometallic species

4. Organometallic compounds of the light elements (e.g. Li, Be, Mg, Al) are often *electron deficient*, with bridging R groups and 2-electron 3-centre bonds.

5. These electron deficient compounds tend to react readily with electron rich species, e.g. electron pair donors (solvent or multiple bonds)

Solvent effects on Grignard reagents

1. Powerful electron donors
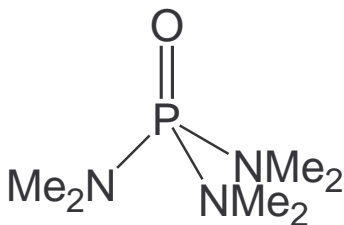
These confer *carbanion* behavior on RMgX, e.g. HMPA

This is a powerful solvent of high dielectric constant, high polarity and low reactivity (and is carcinogenic !)

$PhCH_2MgCl$ in HMPA has the characteristic red colour of $PhCH_2^-$ carbanion. This reagent is a better metallating reagent then normal (ether) Grignard reagents

$$PhCH_2^- + Ph_2CH_2 \rightarrow Ph_2CH^- + PhCH_3$$
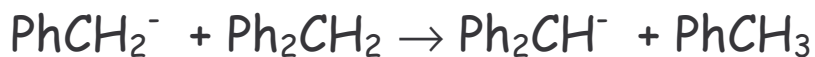
2. Chiral solvents

These allow Grignard reagents to be used in *enantioselective* syntheses.

$$RR'C=O \quad + \quad R''MgX \quad \rightarrow \quad RR'R''\,^*C\text{-}OH$$

prochiral ketone   *excess of one enantiomer*
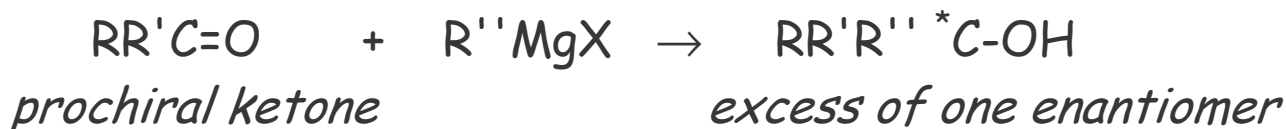
Example of chiral solvent (+)(S)-EtMeHC*-CH$_2$OEt

Now move onto transition metal organometallics ....

Metal carbonyls

$Ni(CO)_4$ nickel tetracarbonyl - Ludwig Mond (1889)

$$Ni + 4CO \underset{150\ ^oC}{\overset{30\ ^oC,\ 1\ atm}{\rightleftharpoons}} Ni(CO)_4$$
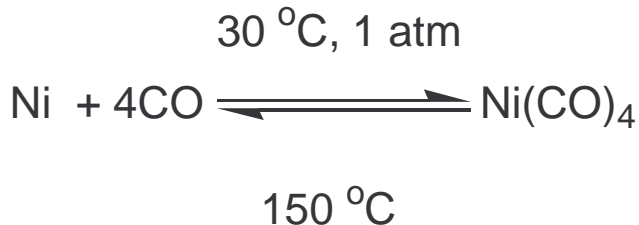
A toxic, colourless volatile liquid (b.pt 43 ^oC), is easily decomposed. It has a tetrahedral structure.

$Fe(CO)_5$ iron pentacarbonyl - Berthelot, Mond (1891)

Yellow liquid, trigonal bipyramidal structure. Made from Fe and CO at 200 ^oC and high pressure

$$CrCl_3 + Al + CO \xrightarrow{\text{benzene, high P}} Cr(CO)_6 + AlCl_3$$

These are the ONLY two carbonyls which can be made by direct reaction of metal and CO. Others require in-situ reduction and/or high pressure

$Cr(CO)_6$ a white crystalline solid - $Mo(CO)_6$, $W(CO)_6$ v. similar
Stability order $Cr(CO)_6$ > $Fe(CO)_5$ > $Ni(CO)_4$

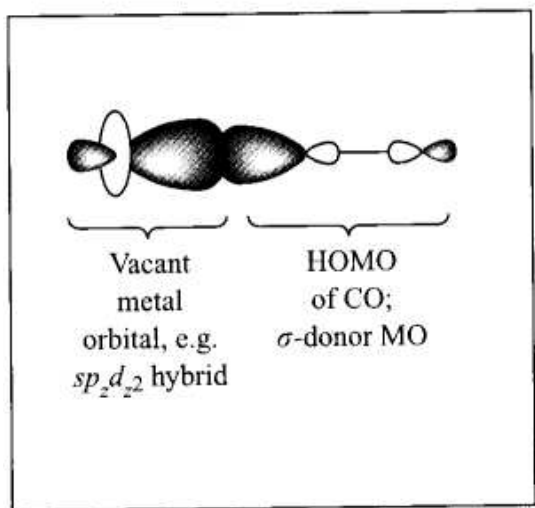$U(CO)_6$? possible volatile Uranium comp for nuclear industry
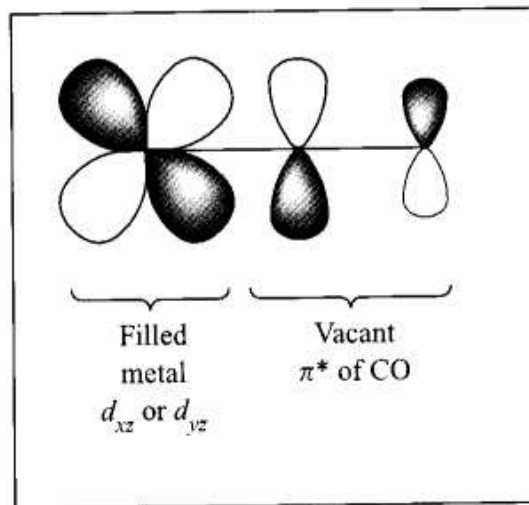
Metal carbonyls

Questions

- What holds these compounds together ? (metals have no charge)
- Why the different numbers of CO ligands ?

Need to understand the *molecular orbitals* of CO (Housecroft/Sharpe p42)

CO   has (a) filled sigma (σ) bonding orbital - the *donor* orbital

(b) empty pi(π^*) antibonding orbital - *acceptor* orbital

Vacant
metal
orbital, e.g.
$sp_z d_{z^2}$ hybrid

HOMO
of CO;
σ-donor MO

CO-to-M donation

Filled
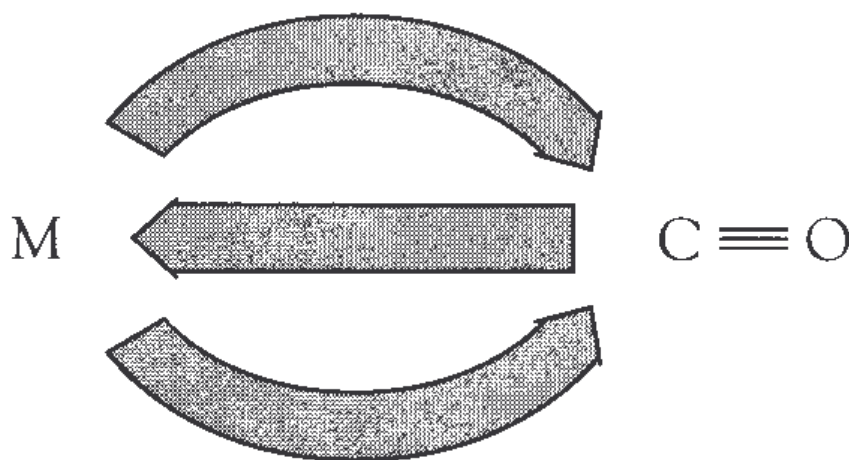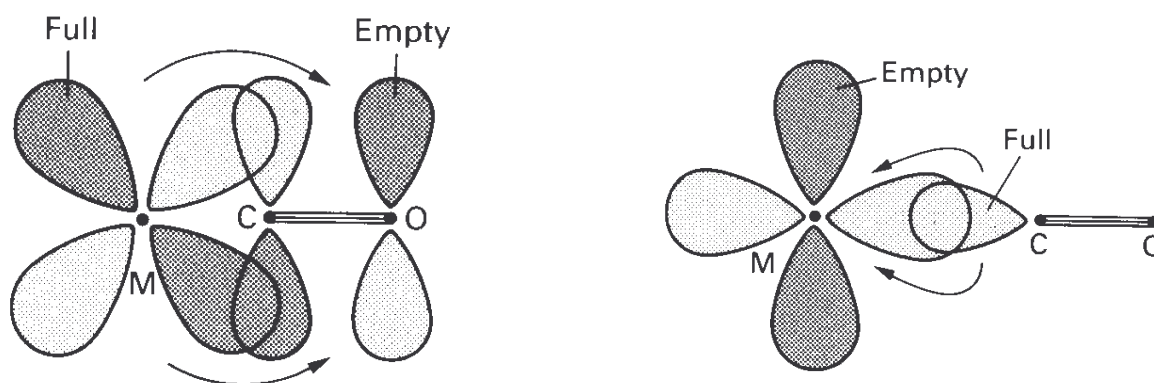metal
d_{xz} or d_{yz}

Vacant
π^* of CO

M-to-CO back-donation

Both these orbitals are used to make bonds with the *d*-orbitals on the transition metal. They both have the same *symmetry* and *similar energies* to the metal *d*-orbitals.

Housecroft/Sharpe diagram page 585

Metal carbonyls

The CO transfers electrons to the metal through the sigma-bond, but the metal transfers electrons to the CO through the pi-bond. This two-way flow of electrons is known as *back-bonding* or *synergic* bonding. It is self re-inforcing, so makes for strong bonds (M-CO bond strength is greater than a single bond).

Effects of π-bonding ligands

CO and related ligands are called π-acceptor ligands

1. Effect on the metals

Removal of electron density can stabilise metals in low oxidation levels (zero or below).

Fe(CO)$_5$ contains Fe(0)   zerovalent compound

Na$_2$Fe(CO)$_4$ contains Fe(-2)

2. Effect on the ligands

As the π^* (antibonding) orbitals are populated the C$\equiv$O bond order is reduced (from 3 to 2.something) and the bond is weakened.

The evidence for this comes from :

- X ray crystallography - there is a small increase in the C-O bond length
- IR spectroscopy - the ν(CO) stretch in free CO is 2148 cm^{-1} but in carbonyl complexes it is lower, ~ 2000 cm^{-1} (in organic ketones the ν(CO) stretch comes ~ 1750 cm^{-1})

18 electron rule

Second question : $Cr(CO)_6$ $Fe(CO)_5$ $Ni(CO)_4$
Why different number of CO ligands ?

Answer : 18 Electron Rule
Organometallic compounds will be most stable if they have 18 valence electrons in total.

This is an important *empirical rule*, i.e. the result of many observations and has no *really sound* justification in theory.

Best way to think of it is like the octet rule - the transition metal is trying to attain the rare gas configuration.

Transtion metals have 9 valence orbitals - for first row metals five 3*d*, one 4*s* and three 4*p*. Most stable if all are filled.

Electrons come from both the *metal* and *ligands*.

CAVEAT : 18 Electron Rule ONLY applies to transition metal organometallic compounds, generally with π-acceptor ligands.

18 electron rule

Using the 18 Electron Rule

Count all the valence (outer) electrons of the metal and those donated to the metal by the ligands (usually 2 per lone pair)

$Cr(CO)_6$ Cr has **six** valence electrons (e⁻) d^6 6

                       6 CO ligands $\rightarrow$ 6 x 2 = 12 e⁻   <u>12</u>

                                                                           18

$Ni(CO)_4$ Ni has **ten** valence electrons (e⁻) d^{10} 10

                       4 CO ligands $\rightarrow$ 4 x 2 = 8 e⁻   <u>8</u>

                                                                       18

When there are an ODD number of electrons, the species usually dimerises with the formation of metal-metal bonds.

Metal-metal bonds can be regarded as normal covalent bonds, using ONE electron from each metal.

To apply the 18-electron rule to these compounds, do the count at EACH metal and add one more electron from the other metal. Often both halves are the same so only need to do this once.

18 electron rule

$$Mn_2(CO)_{10}$$
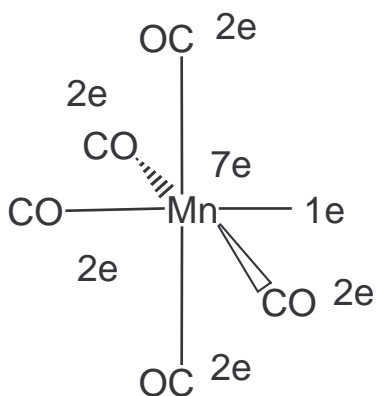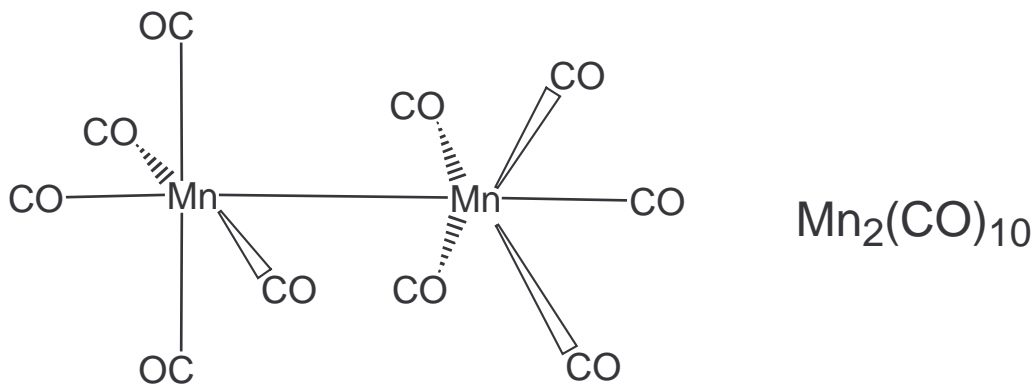
$Mn(CO)_5$ unit has 17 e

$Mn(CO)_6$ would have 19 electrons - so it is not stable and does not exist (but it can *lose an electron* to give the stable $[Mn(CO)_6]^+$ which now has 18 e)

18-electron rule is very useful as it gives us a clue as to which molecular structures will be stable. There are almost NO stable organometallic compounds where the metal has more than 18 electrons.

18 electron rule

Cobalt is similar to manganese and gives $Co_2(CO)_8$. This molecule has several structures.

$Co_2(CO)_8$
in the solid

Co	- 9
$3CO_{terminal}$	- 6
$2CO_{bridging}$	- 2
Co-Co bond	- $\underline{1}$
	18
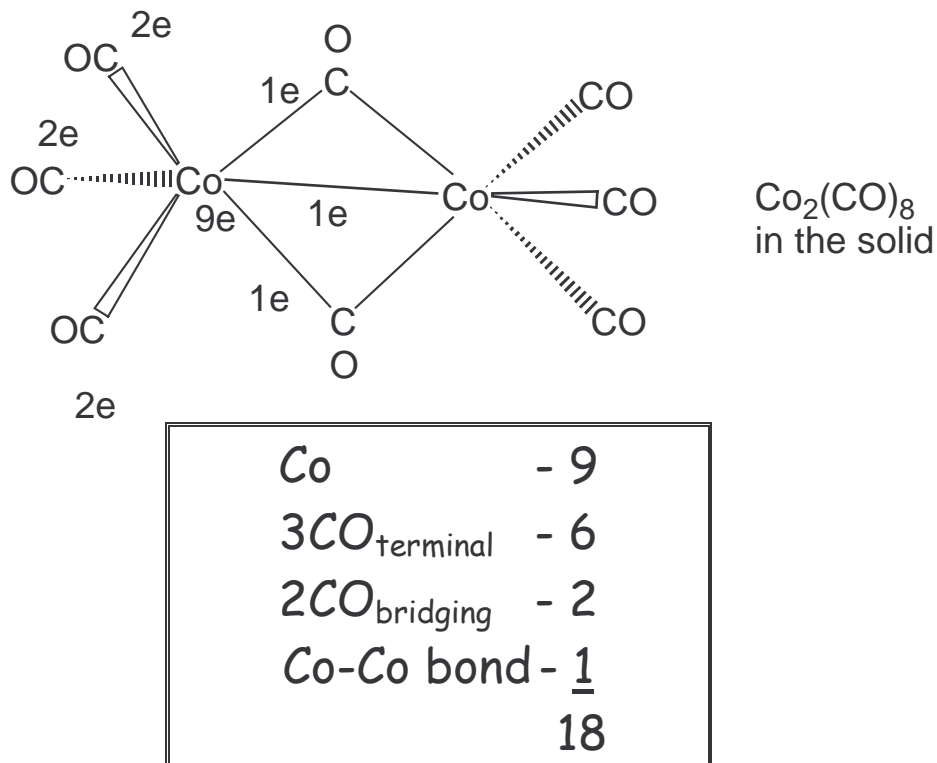
The bridging carbonyl has a $\nu(CO)$ stretch in the infra-red (IR) spectrum ~ 1800 cm^{-1} This is much lower than terminal carbonyls and more similar to an organic ketone $R_2C=O$ which has a $\nu(CO)$ stretch ~ 1750 cm^{-1}

In solution $Co_2(CO)_8$ also has a structure with only terminal carbonyls, i.e. four per Co atom (this is also 18 e). Terminal $\nu(CO)$ stretches ~ 1950-2000 cm^{-1}

In exams need to know (1) 18-e rule (2) use of IR spectra

18 electron rule

All the simple carbonyls of the 1st row transition metals

$Ni(CO)_4$ $Co_2(CO)_8$ $Fe(CO)_5$ $Mn_2(CO)_{10}$ $Cr(CO)_6$

have formulae which can be understood in terms of the 18-electron rule.

But $V(CO)_6$ is a stable 17-electron compound - doesn't dimerise. Why?

Answer is steric reasons : Cannot get 6 carbonyl ligands around the V atom AND also get a V-V bond with another $V(CO)_6$ molecule - not enough space. So......

$V(CO)_6$ is *paramagnetic* (i.e. has unpaired electron) and is very reactive. Will easily gain an electron by chemical reduction to give the anion $[V(CO)_6]^-$. This now satisfies the 18-e rule and is much more stable.

V   - 5
6CO   -12
-charge - <u>1</u>
           18

But CAN get a small ligand like H (hydride) - $HV(CO)_6$
This has a direct V-H bond

Other π-acceptor ligands

There are a multitude of other organic (and unsaturated) molecules which can bond to transition metals in a similar way to CO

1. Nitrosyls (NO)

NO is similar to CO, but has an extra electron, so donates THREE electrons to a metal, e.g. $Co(NO)(CO)_3$

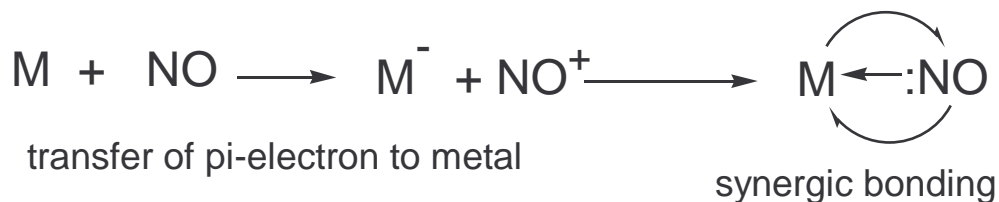|	
Co	9
NO	3
3CO	6
	18

Another example $Fe(CO)_2(NO)_2$

Fe=8 plus 2x2 CO plus 2x3 NO = 18

$Fe(CO)_3(NO)$ - this is 17e compound, so it dimerises to give an Fe-Fe bond (like $Mn_2(CO)_{10}$)

One way of viewing the bonding in nitrosyls

$$M \; + \; NO \longrightarrow M^- + NO^+ \longrightarrow M \longleftarrow :NO$$

transfer of pi-electron to metal   synergic bonding

NO is more strongly bound than CO
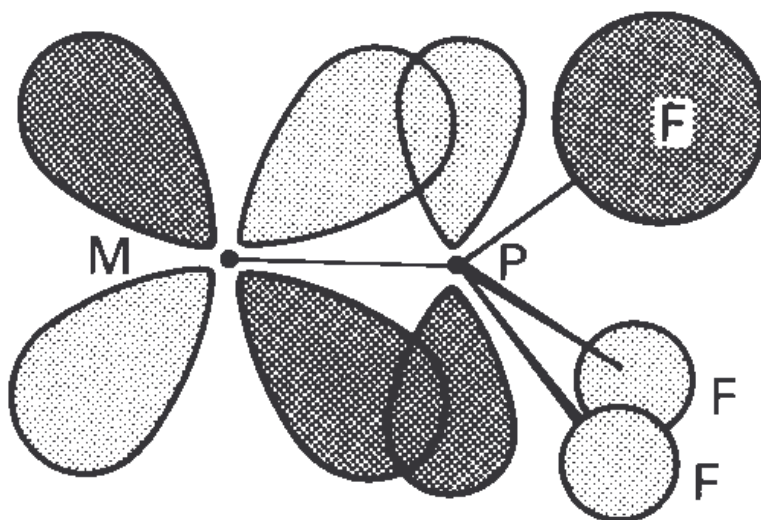
Other π-acceptor ligands

2. Phosphines PR$_3$

These are an extremely important class of ligands. The P atom can be both a σ-donor and a π-acceptor. Which is these is most important depends on the nature of the R group.

If the R group is electron donating (inductive) e.g. Me, CMe$_3$ then phosphine is good σ-donor.

If the R group is electron withdrawing, e.g. F then phosphine acts as a π-acceptor - PF$_3$ is as good a π-acceptor as CO.

Ligand always is terminal (bridging phosphines virtually unknown), and is a TWO electron donor - Ni(PF$_3$)$_4$ is 18-e
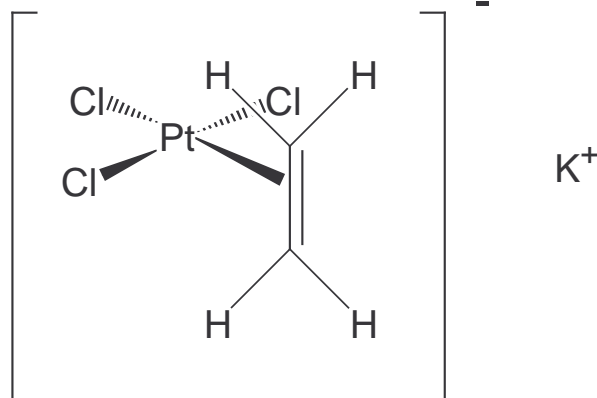
Other π-acceptor ligands

3. Alkenes

First organometallic compound made - Zeise's salt - 1827. Made by reaction of reaction of KCl, $PtCl_2$ in ethanol. Original formulation - a double salt $KCl.PtCl_2.EtOH$

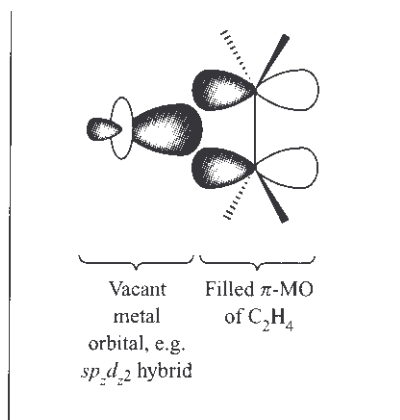Actually shown (1955) to be potassium salt of an anionic ethene-complex K^+ $[PtCl_3(C_2H_4)]^-.H_2O$ (same empirical formula)

X-ray structure shows a square-planar platinum(II)

The bonding in this compound has similarities with previous examples of π-acceptor ligands. The experimental evidence shows :
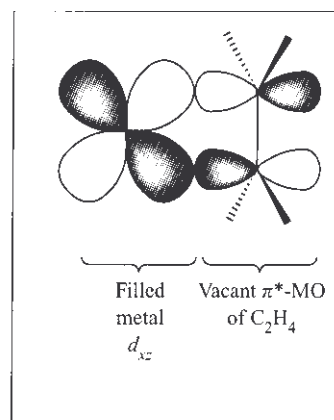
- The C=C bond is *weakened* when complexed with transition metal. In free ethene the C=C bond length is 1.34Å, in Zeise's salt it is 1.35Å

- IR stretching frequency of C=C bond drops also (but not as easily seen as in CO)

# Other π-acceptor ligands

Dewar-Chatt-Duncanson model

Vacant metal orbital, e.g. $sp_zd_{z^2}$ hybrid	Filled π-MO of C_2H_4

Alkene-to-M donation
(a)

Filled metal d_{xz}	Vacant π^*-MO of C_2H_4

M-to-alkene back-donation
(b)

Side-on π-bonding. Involves *donation* from C=C π-bond to empty metal *d*-orbitals and backdonation from filled metal *d*-orbitals to π^* orbitals - synergic bonding (H/S p 588)

Most stable alkene complexes are found with metals in *low oxidation states*, e.g. Ag(1), Cu(1), Fe(O)
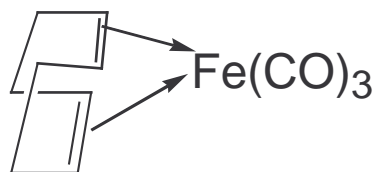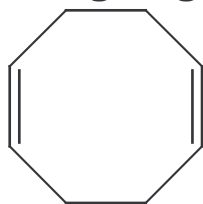
cyclo-octa-1,5-diene (cod)

Fe(CO)$_3$

Alkenes are TWO electron donors (like CO). In polyalkenes each double bond acts as a 2e-donor. For example cyclo-octa-1,5-diene has a pair of double bonds
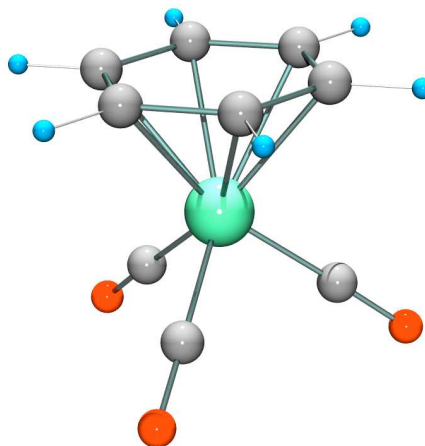
Each double bond in cod contributes 2e, so electron count is

4 (for cod) plus 8 (Fe) plus 6 (3CO) = 18 e

Other π-acceptor ligands

4. Conjugated cyclic polyenes
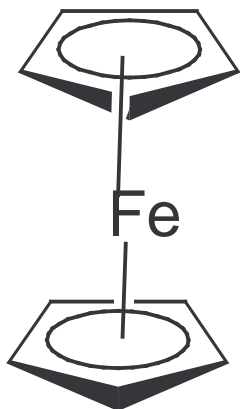
ferrocene

$(C_6H_6)Cr(CO)_3$

The commonest examples are cyclopentadienyl (C_5H_5) and benzenes . Here the transition metal binds to all the C atoms of the ring, giving the sandwich and half sandwich compounds

The rings are aromatic and fully conjugated (all atoms equivalent). The number of electrons donated to the metal usually is the same as the number of C atoms attached to the metal.
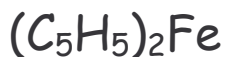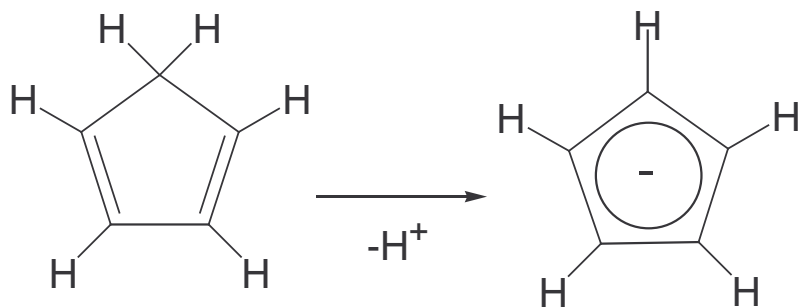
$(C_5H_5)_2Fe$ Fe(= 8) plus 2 x 5 (C_5H_5) = 18
$(C_6H_6)Cr(CO)_3$ Cr(=6) plus 6 (3CO) plus 6 (C_6H_6) = 18

Other π-acceptor ligands

Cyclopentadienyl complexes

cyclopentadiene
mildly acidic - loses H
quite easily

cyclopentadienyl anion

Of great historical importance - 1950's renaissance of Inorganic chemistry started by discovery of ferrocene

Ferrocene discovered simultaneously in 1951 by Wilkinson & Pauson (Wilkinson got Nobel prize for this work)

Structure by X-ray crystallography is a highly symmetrical "sandwich compound"

All 10 H's chemically identical (one signal in ^{1}H NMR spectrum)

All 10 C's also identical

$$FeCl_2 + C_5H_5MgCl$$
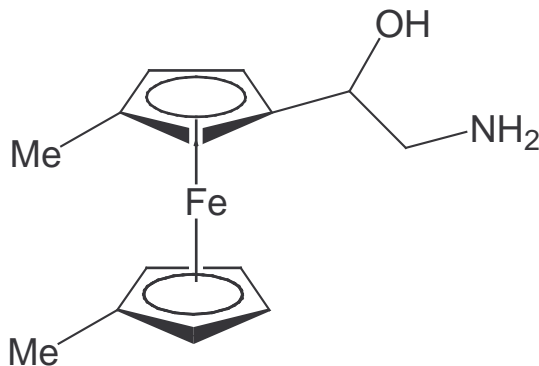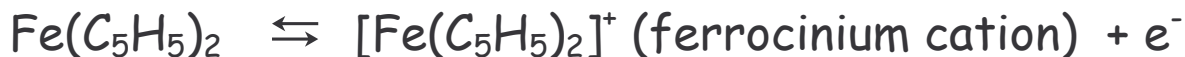
$$Fe + C_5H_6 \longrightarrow C_{10}H_{10}Fe$$

orange crystals m.pt 174 C
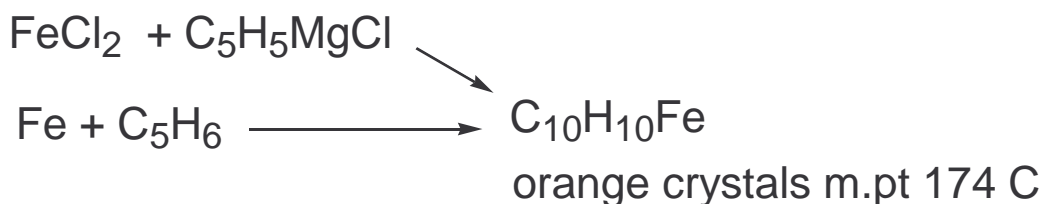
The $C_5H_5^-$ anion and ferrocene contain aromatic 6-π electron rings and the rings in ferrocene react easily by *electrophilic substitution* (like benzene).

Other π-acceptor ligands

Thousands of derivatives of ferrocene now known. Some have commercial uses, e.g. redox reaction

$$Fe(C_5H_5)_2 \; \leftrightharpoons \; [Fe(C_5H_5)_2]^+ \text{ (ferrocinium cation) } + e^-$$


The "ExacTech" pen meter is used to measure blood glucose levels. It uses a ferrocene derivative

The redox active ferrocene derivative facilitates electron transfer between glucose and glucose oxidase, and allows a quick measure of glucose concentration.
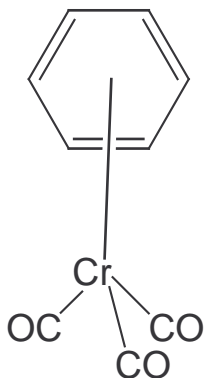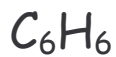
Easy to use - particularly for children suffering from diabetes

Other π-acceptor ligands

Other π-conjugated ring systems which act as ligands

$C_7H_7{}^+$ C_6H_6 C_4H_4 $C_3H_3{}^+$
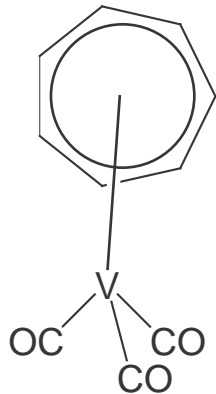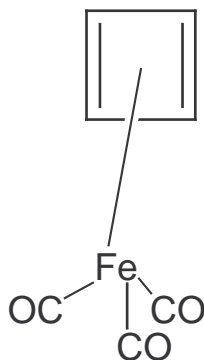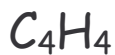
tropylium   benzene   cyclobutadiene   cyclopropenium
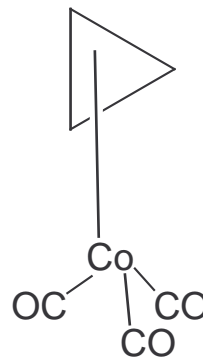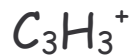
18 e- rule applies to all these compounds

V	5	Cr	6	Fe	8	Co	9
C_7H_7	7	C_6H_6	6	C_4H_4	4	C_3H_3	3
3CO	6	3CO	6	3CO	6	3CO	6
	18		18		18		18

Open conjugated ring systems also act the same
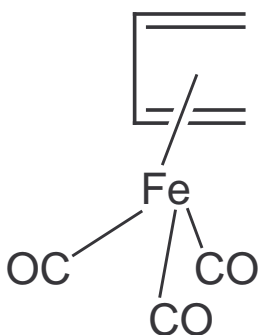
butadiene C_4H_6 allyl C_3H_5
4e donor   3e donor
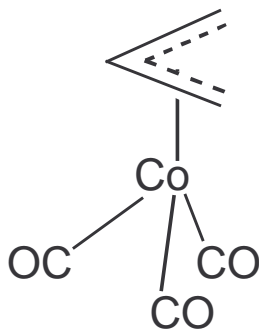
σ-bonded ligands

Like the main group metals, it is also possible for transition metals to form *sigma-bonds* (σ-bonds) to certain organo (and other) ligands.

Example 1.

$$0.5 \ Mn_2(CO)_{10} \xrightarrow{\ \ Na \ \ } Na^+ [Mn(CO)_5]^-$$

CH$_3$Cl

H$_2$O

Mn(CO)$_5$CH$_3$
+ NaCl

HMn(CO)$_5$ + NaOH

contains Mn-CH$_3$ bond

contains Mn-H bond

Example 2

PhLi

sigma-bond

phenyl group (not pi-benzene) !
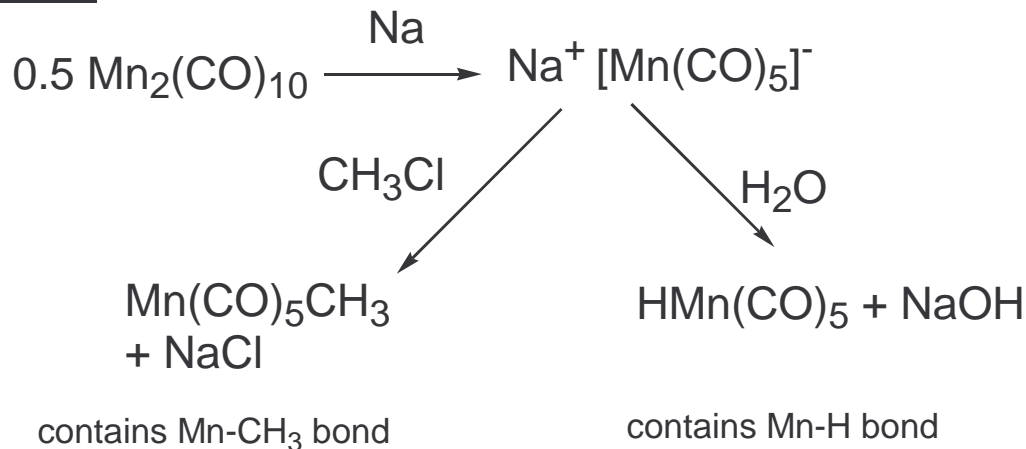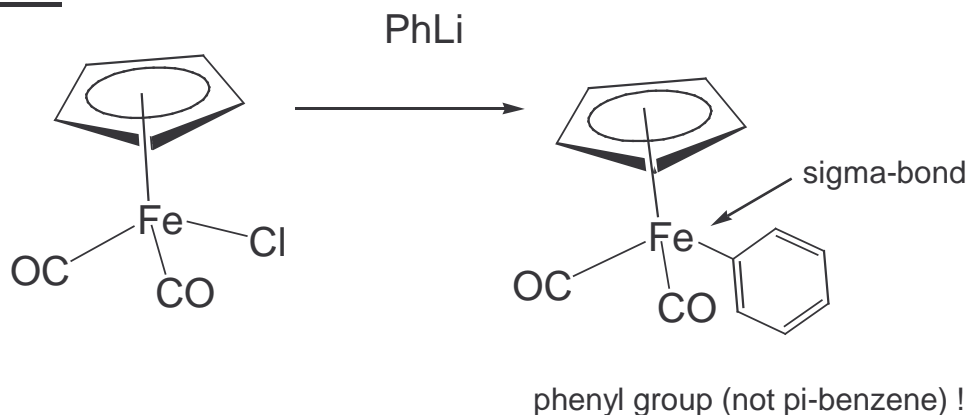
Each σ-bonded ligand CH$_3$, H (hydride), Cl or σ-C$_3$H$_5$ (allyl) counts ONE electron towards the 18 electron rule.

Each σ-bonded ligand behaves as an ANION with a single negative charge (need to know to work out oxidation no.)

Stability of organometallics

Many attempted reactions to form transition metal-organometallic compounds fail, e.g.

$$EtMgX + PtCl_2 \rightarrow \text{"black tar"}$$
$$but..... \quad EtMgX + (Ph_3P)_2PtCl_2 \rightarrow (Ph_3P)_2PtEt_2$$
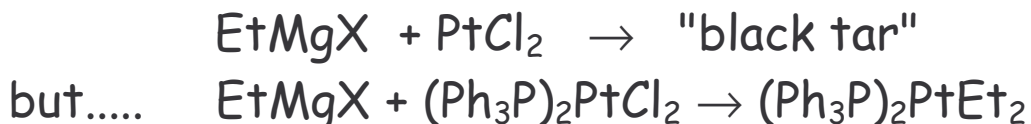
The presence of additional π-bonding ligands (in this case a phosphine ligand PPh_3 - triphenylphosphine) stabilises the organo-transition metal compound.

The ability of transition metals to easily change their *oxidation number* or *coordination number* means that these compounds have available *extra reaction pathways* which can lead to decomposition.

One such mechanism is the β-elimination process
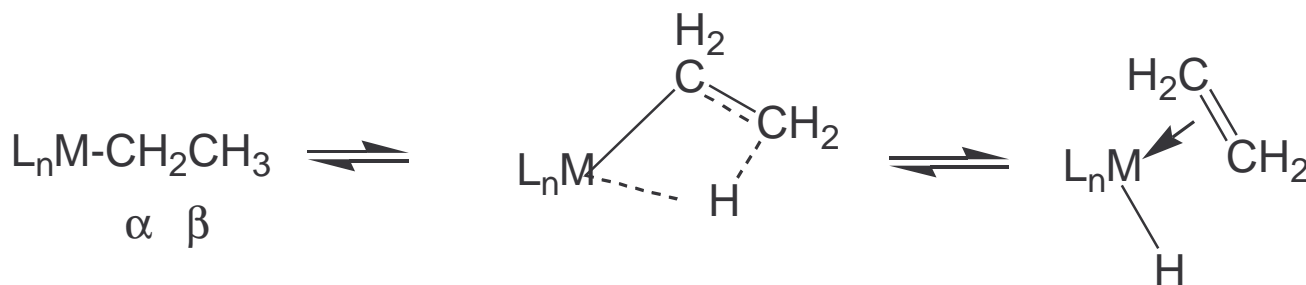
The β-H atom is transferred to the metal to give a metal hydride

β-elimination process

Example

$$[CoEt_2(acac)(PR_3)_2] \longrightarrow [CoEt(C_2H_4)H(acac)(PR_3)] + PR_3$$

Co(+3)

$$C_2H_6 + C_2H_4 + [Co(acac)(PR_3)_2]$$

Co(+1)

acac is 2,4-pentanedionato - a chelating anionic ligand

is lost and H replaces it
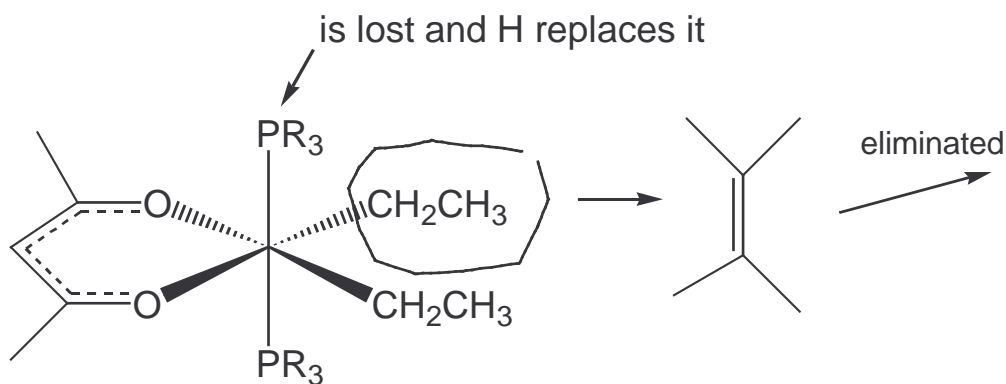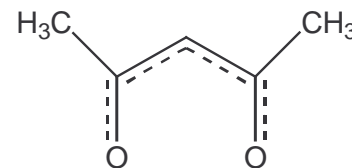
eliminated

The process requires
- a coordination site (made available by PR$_3$ loss)
- easy change from Co(+3) to Co(+1)
- transferred H is also eliminated by combining with the ethyl group to give ethane (reductive elimination)

oxidative addition & reductive elimination

$$L_nM \begin{array}{c} H \\ \diagdown \\ H \end{array}$$

$+H_2$ $\uparrow\downarrow$ $-H_2$

$$L_nM \xrightarrow{\text{+ X-Y oxidative addition}} L_nM \begin{array}{c} X \\ \diagdown \\ Y \end{array}$$

$-X-Y$ reductive elimination

$+HX$ $\uparrow\downarrow$ $-HX$

$$L_nM \begin{array}{c} X \\ \diagdown \\ H \end{array}$$
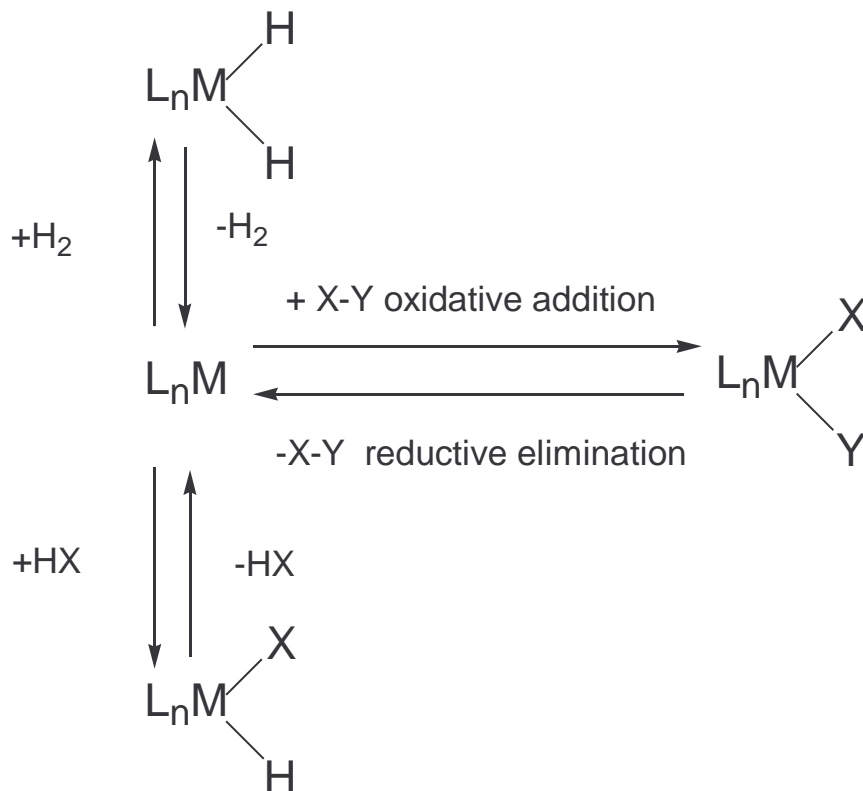
NOTE : *both* the *oxidation numbers* and the *coordination numbers* change by 2.

Examples of reductive elimination - here there are TWO possible products, eliminating C_2H_6 or CH_3Cl

C_2H_6 is v. unreactive so
process is *non-reversible*

$$\begin{array}{c} Cl \\ R_3P_{\prime\prime\prime\prime\prime}\ \ _{\prime\prime\prime\prime}CH_3 \\ Pt \\ R_3P \ \ \ \ CH_3 \\ Cl \end{array}$$

$\longrightarrow$ $(R_3P)_2PtCl_2$ + C_2H_6

$\rightleftharpoons$ $(R_3P)_2Pt(CH_3)Cl + CH_3Cl$

CH_3Cl is reactive so
process is *reversible*

insertion reactions

$$LnM-R \quad \xrightarrow{CO} \quad LnM-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

$$LnM-R \quad \xrightarrow{C_2H_4} \quad LnM-CH_2CH_2R$$
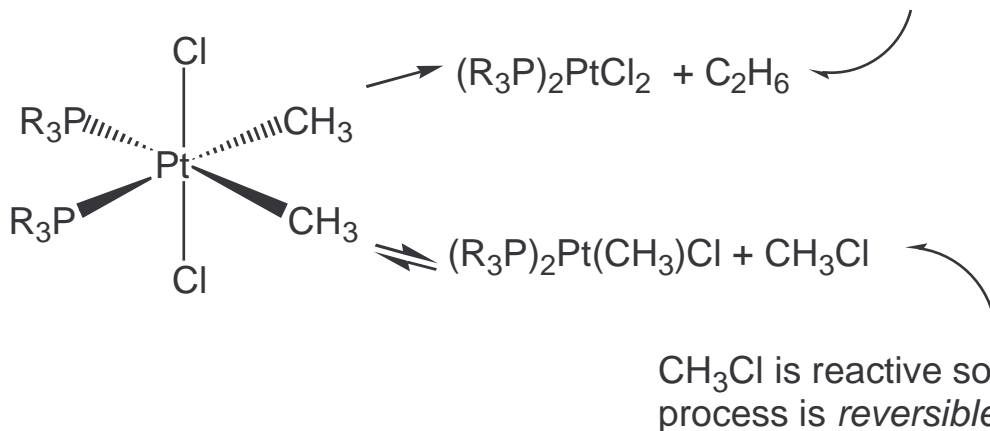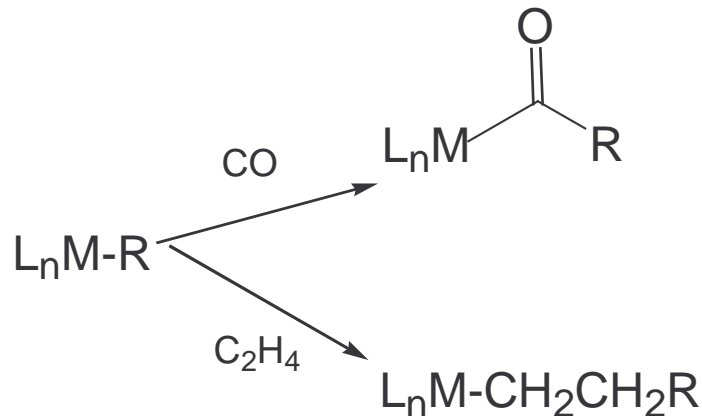
Small unsaturated molecules (CO, alkenes, etc) can "insert" into the M-C bond of transition metal alkyls.

Carbenyl "migratory insertions" of "CH_2" increase the chain length by one, and functionalise the R group.

Example

$(OC)_5MnCH_3 + L \rightarrow (OC)_4(L)Mn-C(O)-CH_3 \quad L = CO, PPh_3$

CO group is apparently inserted into the $Mn-CH_3$ bond

Example

Alkene insertions take place in the Ziegler-Natta catalysed polymerisations of ethene

$$C_2H_4 \quad \xrightarrow[\text{Ziegler/Natta catalyst}]{TiCl_4 \,/\, AlEt_3} \quad -CH_2-CH_2-CH_2-CH_2- \quad \text{(linear polythene)}$$
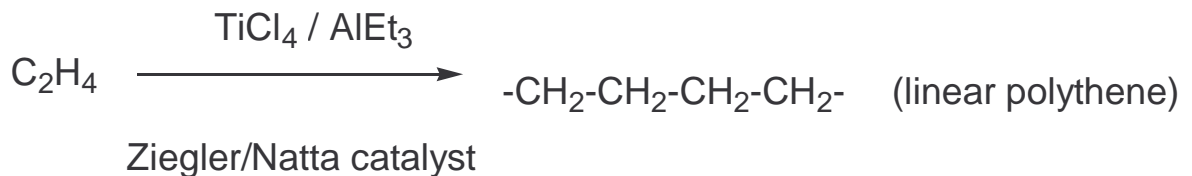
Conclusions

- All these reactions involves either a change in the *oxidation number* or the *coordination number* of the transition metal (or both).

- These are typical properties of transition metals.

- Ligands such as C_5H_5 and other strongly π-bonded ligands can control or supress these reactions and can thus be used to stabilise transition metal organometallic compounds.

- Many of these reactions are easily reversible (low activation barrier) and are consequently very important in catalytic reactions.

Transition metal organometallics - summary

π-bonded compounds

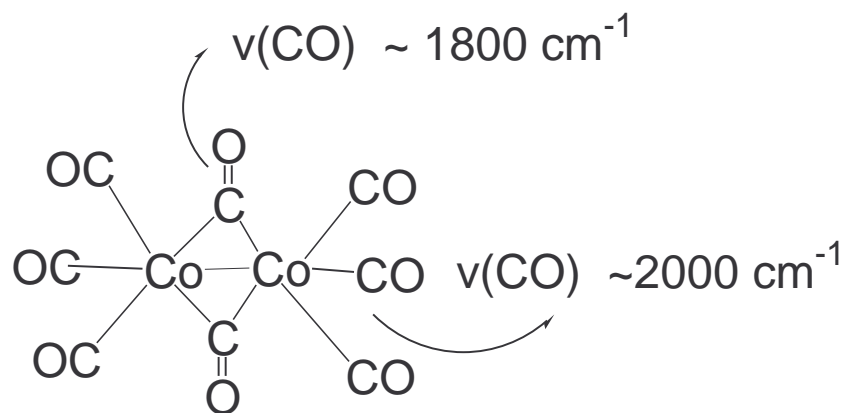- Ligands such as CO, NO and phosphines (PR_3) bind to low oxidation state transition metals by "synergic" π & σ bonds.
- Alkenes and other unsaturated organic molecules attach side-on to the metal atoms. They also are held in place by "synergic" π & σ bonds.
- low oxidation-state compounds of these types usually obey the 18-electron rule. CO, PR_3 are 2 e^- donors, NO is a 3 e^- donor and unsaturated organic molecules count 1 e^- for *each* C atom which is bonded to the metal.

σ-bonded compounds

- transition metal organometallics can undergo a variety of reactions not available to main-group compounds. These include β-elimination, reductive-elimination, oxidative-addition and insertion reactions.
- These above reactions can lead to decomposition of the compound, unless the coordination sites they need are firmly occupied by other ligands.

OXO or hydroformylation process

This is an example of a *homogeneously catalysed* process (all reactants in the same phase). The mechanism illustrates several of the reactions summarised above.

overall reaction $RCH=CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO$

$v(CO) \sim 1800 \text{ cm}^{-1}$

$v(CO) \sim 2000 \text{ cm}^{-1}$
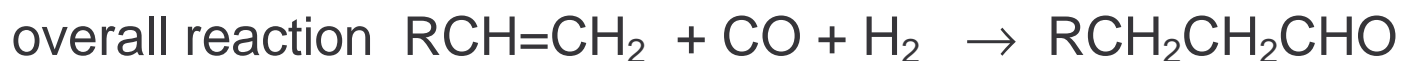
Catalyst is $Co_2(CO)_8$

There are TWO major commercial applications of this reaction

1. R = Me   i.e. propene $\rightarrow$ butanal   (~ 3m tonnes per year)

$2 \text{ CH}_3\text{CH}_2\text{CH}_2\text{CHO} \xrightarrow[\text{- H}_2\text{O}]{\text{base}}$
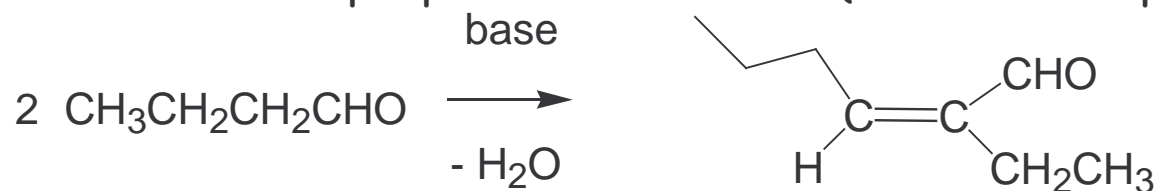
2-ethyl hex-2-ene-al used in phthalate plasticisers

2. R = hexyl i.e. 1-octene $\rightarrow$ nonanal (biodegradable detergents)

OXO or hydroformylation process -mechanism

product

$Co_2(CO)_8$

RCH$_2$CH$_2$CHO

1 $\downarrow$ H$_2$

HCo(CO)$_4$

CH$_2$=CHR

2

CO

5

H$_2$

$\begin{bmatrix} H\overset{\uparrow}{C}o(CO)_3 \\ RCH=CH_2 \end{bmatrix}$

RCH$_2$CH$_2$C(O)-Co(CO)$_4$

4

CO

3

CO

RCH$_2$CH$_2$-Co(CO)$_4$
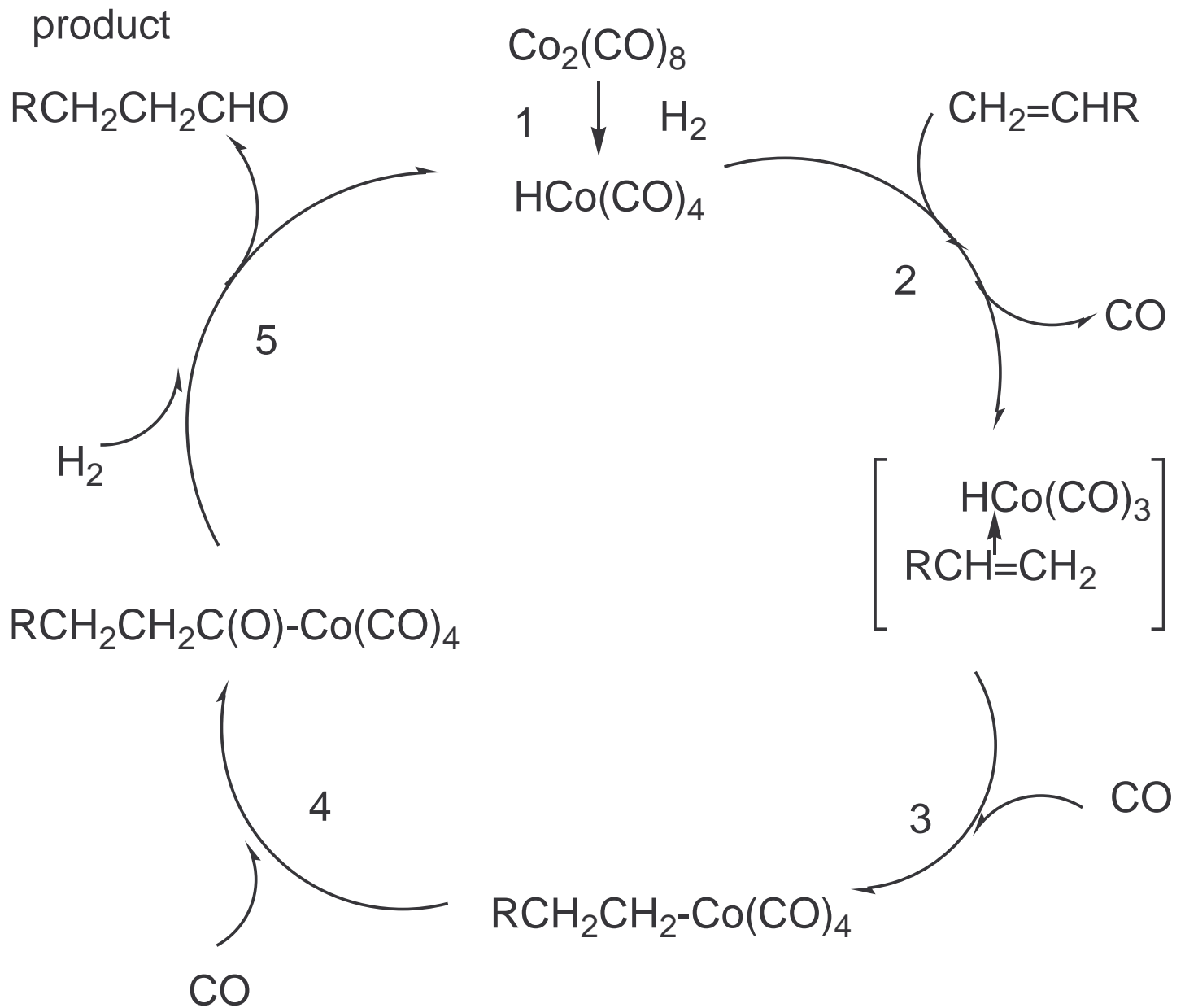
CoCl$_2$ added as a "pre-catalyst" - converted under reaction conditions

$$CoCl_2 + H_2 + CO \rightarrow Co_2(CO)_8$$

OXO or hydroformylation process -mechanism

Multi-stage "cyclical" reaction

Step 1. *Reduction*

$Co_2(CO)_8 + H_2 \rightarrow 2\ HCo(CO)_4$ "active catalyst" (18 e compd)

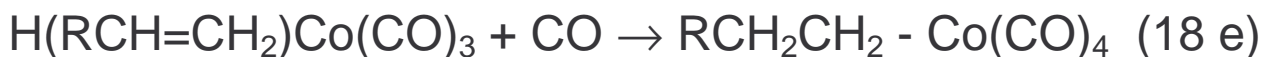## Step 2. *Ligand replacement*

CO is replaced by $RCH=CH_2$ $HCo(RHC=CH_2)(CO)_3$ (18 e)

The metal atom is "holding" the reactive species together.

Step 3. *Insertion of alkene into Co-H bond*

Hydride H atom adds to C atom of alkene

$H(RCH=CH_2)Co(CO)_3 + CO \rightarrow RCH_2CH_2 - Co(CO)_4$ (18 e)

Step 4. *Insertion of CO into Co-alkyl bond*

$RCH_2CH_2Co(CO)_4 + CO \rightarrow RCH_2CH_2 - C(O) - Co(CO)_4$ (18 e)
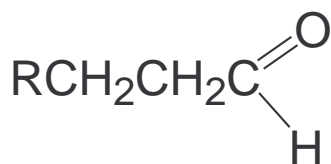
Step 5. *Reduction and product elimination*

H_2 *adds oxidatively* to metal complex and the product is then eliminated in *a reductive elimination* reaction
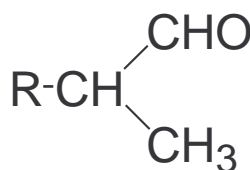
OXO or hydroformylation process

Process runs at 120°C and at 200 atm pressure of CO

High CO pressure prevents loss of CO from cobalt atom, which would lead to decomposition. Reaction only 80% specific.

$$RCH_2CH_2C\overset{\displaystyle O}{\underset{\displaystyle H}{\diagup}}$$

80% linear

$$R\text{-}CH\overset{\displaystyle CHO}{\underset{\displaystyle CH_3}{\diagdown}}$$

20% branched
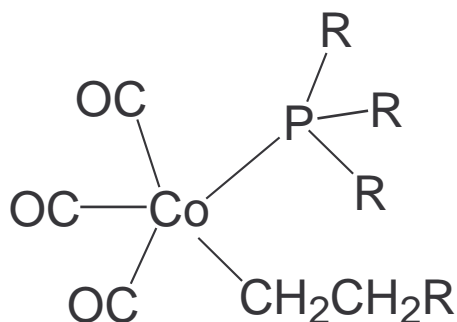
Divergence happens at stage 3. The H atom can add to the CH$_2$ group rather than the CHR group.

In commercial process one of the CO ligands on the cobalt is replaced by a bulky phosphine ligand PR$_3$

HCo(CO)$_4$ + PR$_3$ $\rightarrow$ HCo(CO)$_3$(PR$_3$) + CO   (18 e)

The steric crowding at the Co atom forces the H addition to make the *linear* rather than *branched chain* isomer.

OXO or hydroformylation process

This "trick" enables the efficiency of the reaction to go from 80% yield of linear chain product, up to nearly 100%

This is one very important advantage of homogeneous catalysis.

HIGH SELECTIVITY (commercially important)

Disadvantages

Catalyst is in same phase as products - how to separate the two ??

$$HCo(CO)_4 \ + NaHCO_3 \ \rightarrow \ Na^+ \ [Co(CO)_4]^- \ \ (water \ soluble)$$
$$+ \ H_2O + CO_2$$
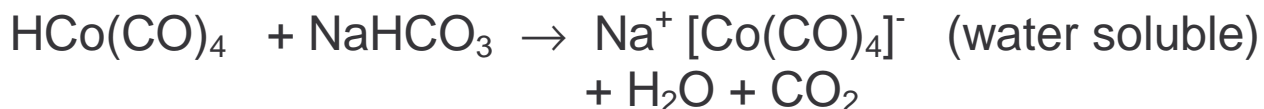
Catalyst can then be regenerated

$$Na[Co(CO)_4] + H_2SO_4 \rightarrow \ HCo(CO)_4$$

Chem2X Organometallics course : specimen questions

June 2000

1. Manganese chloride, $MnCl_2$, reacts with one mole equivalent of C_5H_5Na then of C_6H_5MgBr to produce, after hydrolysis, a deep red crystalline product, **A**, that analyses as C, 66.68; H, 5.56; Mn, 27.73% and has a molecular weight of 198.13. The ^1H NMR spectrum of **A** shows two singlets at 3.83ppm (5H) and 4.50ppm (6H). Its ^{13}C NMR spectrum similarly has two signals of relative intensities 5:6.

    Interpret these data to identify **A**, and use the 18 electron rule to rationalise its structure.
    [10]

    Relative atomic masses: C, 12.01; H, 1.008; Mn, 54.94

August 2000

(2) Use the reactions with H_2O, O_2 and CO_2 to illustrate how the reactivity of simple organometallic compounds of the main group elements varies with the electronegativity of the element.
    [7]

(3) The reaction of iodomethane and lithium in ether produces a crystalline, pyrophoric compound analysing as C, 54.66; H, 13.75; Li, 31.59% with a molecular weight of 87.90. Derive the formula of this compound and draw its likely structure. Describe the bonding within this molecule.
    [8]

    Relative atomic masses: C, 12.01; H, 1.008; Li, 6.94.

June 2002

(4) Phenylmagnesium bromide, PhMgBr, reacts with $(C_5H_5)Fe(CO)_2Cl$ to produce a yellow, crystalline compound (**A**) which analyses as C, 61.4; H, 3.9; O, 12.6; Fe, 22.0%. **A** has strong IR absorptions at $2021cm^{-1}$ and $1969cm^{-1}$. Its ^1H NMR spectrum consists of two resonances, at 7.1ppm (5H) and 4.97ppm (5H).
    Identify compound **A** and interpret its spectroscopic data.
    Show that both $(C_5H_5)Fe(CO)_2Cl$ and compound **A** conform to the 18 electron rule.
    [10]

    Relative atomic masses: C, 12.01; H, 1.008; Fe, 55.847.

August 2002

(5) Describe the working of the 18 electron rule, illustrating its application by reference to $Cr(CO)_6$ and $Mn_2(CO)_{10}$.
    [6]

(6) Nitric oxide, NO, is a paramagnetic gas. It readily displaces three of the carbonyl ligands of $Fe(CO)_5$ to give the diamagnetic compound $Fe(CO)_2(NO)_2$.
Explain why NO is paramagnetic, but its transition metal complexes are diamagnetic. Explain why NO so readily displaces CO.
Does $Fe(CO)_2(NO)_2$ obey the 18 electron rule ? Give your reasons.

[9]

August 1999

(7) Explain the 18 electron rule and show how the following compounds adhere to this rule : $Fe(C_5H_5)_2$ $Co_2(CO)_8$ and $Cr(CO)_3(C_6H_6)$.

June 1998

(8) Free CO gas has $\nu(CO)$ at 2140 cm^{-1} in its IR spectrum. Crystalline $Mn_2(CO)_{10}$ has $\nu(CO)$ values near 2000 cm^{-1} but crystalline $Co_2(CO)_8$ has IR carbonyl absorptions near both 2000 cm^{-1} and 1800 cm^{-1}. Relate these observations to the structure and bonding in the compounds.

(9) Aluminium chloride reacts with methyl-lithium to produce a volatile liquid **Y** which spontaneously ignite in air and explodes in contact with water. **Y** analyses as C, 49.99; H, 12.58; Al, 37.43% and has a molecular weight of 144.
(i) Identify **Y** and describe its structure and bonding
(ii) Predict how **Y** would react with (a) ether and (b) ethanol
Relative atomic masses, C, 12.011; H,1.008;, Al, 26.98

(10) Methyl-lithium (excess) reacts with $SiCl_4$ to produce a colourless volatile and unreactive liquid **X**, which analyses as $C_4H_{12}Si$. The NMR spectrum of **X** consists of a singlet at 0 ppm.
Identify **X** and suggest reasons for its inert behaviour.