LEVEL-3
Organo-transition metal chemistry
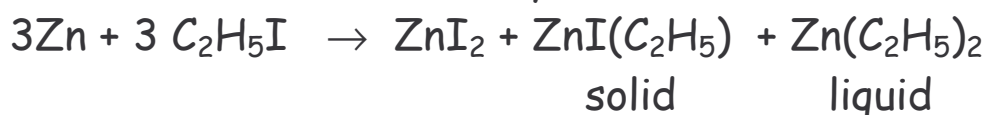
TEXTBOOK REFERENCES:

1. Housecroft & Sharpe *Inorganic Chemistry* Ch 23

2. Shriver & Atkins *Inorganic Chemistry* Ch 16

3. Elschenbroich & Salzer *Organometallics - a concise introduction*   Chs 13, 14 & 15

4. Cotton & Wilkinson *Advanced Inorganic Chemistry*
5th Edition   Chs 22-27

Level-3 Organometallics L1a

Brief history :

1825 - W. C. Zeise (Denmark) reacts Pt(2+) salts with ethanol. Originally formulated as $KCl.PtCl_2.EtOH$. In 1950's this was shown to be an **olefin** complex $K^+ [PtCl_3(CH_2=CH_2)]^- .H_2O$
(see *Organometallics* (2001) **20** 2)

1849 - E. Frankland (UK) synthesised first **metal alkyl**
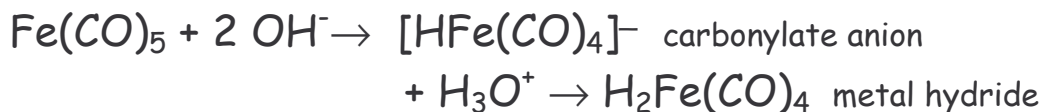$$3Zn + 3\ C_2H_5I \rightarrow ZnI_2 + ZnI(C_2H_5) + Zn(C_2H_5)_2$$
$$\text{solid} \qquad \text{liquid}$$
$ZnEt_2$ is **pyrophoric** - inert atmosphere required

1890 - L. Mond (Germany/UK) discovered **metal carbonyls**
$$Ni + 4CO \Leftrightarrow Ni(CO)_4$$
Soon after $Fe(CO)_5$ and $Cr(CO)_6$ sythesised

1930's - W. Hieber (Germany) worked on carbonyl chemistry of Fe
$Fe(CO)_5$ + en (ethylene diammine) $\rightarrow$ $Fe(CO)_3(en)$ carbonyl substitution

$Fe(CO)_5 + 2\ OH^- \rightarrow [HFe(CO)_4]^-$ carbonylate anion
$$+\ H_3O^+ \rightarrow H_2Fe(CO)_4 \text{ metal hydride}$$

1951 - Pauson synthesises ferrocene $(C_5H_5)_2Fe$ - "sandwich"
1955 - E.O. Fischer $(C_6H_6)_2Cr$ dibenzene chromium
1961 - Vaska shows $Ir(CO)Cl(PPh_3)_2$ *reversibly* binds dioxygen
1964 - E.O. Fischer makes first **carbene** $(CO)_5W=C(OMe)Me$
1973 - E.O. Fischer makes first **carbyne** $(C_5H_5)(CO)_2W\equiv CPh$

Level-3 Organometallics L1b

DEFINITION :
Organometallic compound contains a bond between a *transition metal* and an *organic* carbon

Nowadays **vast** numbers of different organometallics are known

Need to **organise** all this information in order to understand and process

One way is by considering by *ligands* rather than by *metals*

Two major classes of ligands
(a) sigma-bonded

Examples   alkyls $M-CH_3$ $M-C_2H_5$
             aryls $M-C_6H_5$ (phenyl)
             acyls $M-C(O)-R$ e.g. acetyl
             vinyls $M-CH=CH_2$
(b) pi-bonded
             carbonyls $M-CO$
             carbenes $M=CR_2$
             olefins $M(CR_2=CR_2)$
             cyclic olefins $M(C_5H_5)$

"Honary" organometallic compounds $Pt(PPh_3)_4$

Level-3 Organometallics L1c

Metal - sigma bonded compounds (metal alkyls)

Main group alkyls known from beginning $ZnEt_2$ $PbEt_4$ Quite stable (thermodynamically !) but it was found that synthesis of *transition metal* alkyls was difficult - i.e. didn't work

Some exceptions   Pope & Peachy (1901)

$$PtCl_4 + 3CH_3MgI \rightarrow [(CH_3)_3PtI]_4 \text{ "cubane"}$$

$$(C_5H_5)Fe(CO)_2(CH_3)$$

The latter type had π-acceptor ligands and it was thought that these might stabilise TM-C(alkyl) bonds

In 1950's several theoretical (MO) calculations showed that TM-C(alkyl) bonds were especially weak due to poor overlap between sp^3 C and metal $s\,p\,d$ orbitals. π-acceptor ligands were "shown" to increase overlap and so stabilise these compounds.

However, all these calculations were incorrect. In fact TM-C(alkyl) bonds have similar strength to Main-group- C(alkyl) bonds

compare	$TiEt_4$	v unstable decomposes at -80°C
	$PbEt_4$	stable to 200°C
BUT	Ti-C	~ 260 kJ mol^{-1}
	Pb-C	~ 170 kJ mol^{-1}

Confusion between *thermodyamic* stability and *kinetic* stability

Level-3 Organometallics L1c
The general β-elimination mechanism

One general decomposition mechanism involves *β-elimination*, resulting in a metal hydride and an olefin:

Level-3 Organometallics L2a

β-Elimination Mechanism

H/S p 603   E/S page 198   S/A 510 & 558

The β-elimination mechanism is the *primary route* for the decomposition of TM-alkyls where the alkyl group contains a β-H atom. It has a very low activation barrier if the transition state is easily attained and means that most such TM-alkyls will *spontaneously* decompose.

The mechanism has four major requirements or consequences
- presence of β-H
- *planar* four-membered transition state
- *vacant coordination site* (more strictly vacant orbital on TM)
- *alkene* is formed as by-product

These features lead to ways in which this mechanism can be circumvented and lead to designed synthesis of *stable* TM-alkyls

Level-3 Organometallics L2b

β-Elimination Mechanism

(1) Use alkyls without β-Hydrogens

Alkyls with no β-hydrogens *cannot* decompose by this mechanism and are found to be much more stable

Common examples of such alkyls are :

-CH_3 (methyl)   -CH_2Ph (benzyl)   -CH_2CMe_3 (neopentyl)

-CH_2SiMe_3 (trimethylsilyl)   perfluoroalkyls e.g.   -C_2F_5

For instance $Ti(CH_2CMe_3)_4$ is stable above its boiling point of 90°C compared with $TiEt_4$ decomp above -80°C

Perfluroalkyl complexes are particularly stable, in part due to the strength of the C-F bonds

Level-3 Organometallics L2c

β-Elimination Mechanism

(2) Absence of free coordination site

18-electron TM complexes do not have a suitable vacant orbital. To generate one, it is necessary to *lose* one or more ligands.

Mechanistic studies show that in general, prior ligand dissociation is a *requirement* for an 18-electron compound to undergo β-elimination.

If ligands are strongly bonded, this may not be easy

EXAMPLE : $CpFe(CO)_2(C_2H_5)$ Cp (cyclopentadienyl C_5H_5)

Both the Cp and CO ligands are strongly bonded and this compound is reasonably stable - will decompose through loss of CO though at elevated temperatures.

EXAMPLE :
compare $Rh(C_2H_5)(CO)_2(PPh_3)_2$ unstable - Rh(1+) is *5 coordinate*
          $[Rh(C_2H_5)(H_2O)_5]^{2+}$ stable - Rh(2+) is *6-coordinate*

Stability as used here is *relative* stability.

Level-3 Organometallics L2d

β-Elimination Mechanism

(3) β-Hydrogens cannot become syn-coplanar

With bulky alkyl groups, it may not be sterically possible for the β-H to get close to the metal

EXAMPLE - $Cr(CMe_3)_4$ is a reasonably stable *tetrahedral* metal alkyl. Although the tert-butyl group *does* contain β-H's, the bulkiness prevents these H-atoms from getting too close to the metal
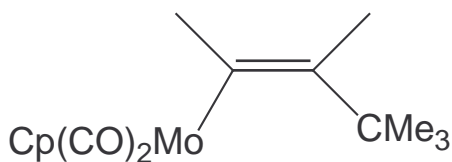
EXAMPLE -
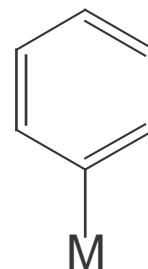
metal vinyl   metal aryl

In both these examples, the sp^2 carbon requires 120° angles and the β-H cannot approach the metal.

EXAMPLE - here the transition state cannot become syn-coplanar because atoms are fixed in ring system.
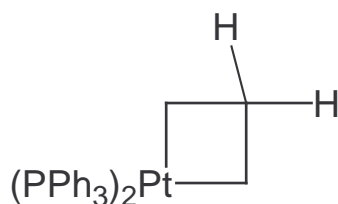
Level-3 Organometallics L2e

β-Elimination Mechanism

(4) Absence of suitable alkene

Bredt's rule states that double bonds to bridgehead carbon atoms are *highly unfavorable* because of ring-strain. Since such alkenes are either unknown or unstable, their formation in a β-elimination is unfavorable. This gives high kinetic stability to alkyl groups such as 1-norbornyl

$$L_3Cr$$

$$L =$$
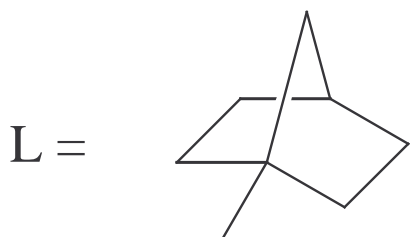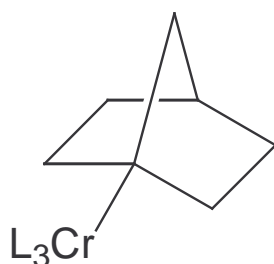
Tetrahedral complexes ML_4 These are known for Cr, Mn, Fe & Co - metals in +4 oxidation state which is very unusual for these metals.

Another reason why metal aryls cannot β-eliminate is that the corresponding alkene is in fact benzyne - a highly strained internal alkyne.

Level-3 Organometallics L2f

Synthesis of stable metal alkyl compounds

The ideas just given can be used to devise syntheses of stable TM-alkyls and other complexes containing TM-σ(C) bonds. The examples given also illustrate some important chemistry of organo-transition metal compounds.

(1) Metal halide plus Main group organoreagent

Best organoreagents (most reactive) are Lithium reagents LiR or Grignard reagents RMgX

EXAMPLE

$\quad$ $ZrCl_4$ + 4 $PhCH_2MgCl$ $\rightarrow$ $Zr(CH_2Ph)_4$ - tetrahedral complex

Also can use milder reagents such as R_2Zn or R_2Hg (note Me_2Hg is *extremely* poisonous) or R_4Sn

These will generally not replace all halides

EXAMPLE

$\quad\quad\quad\quad$ $NbCl_5$ + (excess) Me_2Zn $\rightarrow$ Me_2NbCl_3

These may be useful to prepare mixed-alkyl complexes

Level-3 Organometallics L3a

Synthesis of stable metal alkyl compounds

(2) Metal hydride plus alkene

This is the *reverse* of the β-elimination reaction and is an example of the general *insertion* reaction. These involve insertion of small molecules into transition metal-X bonds. In this case that of an alkene into a TM-H (hydride) bond.

EXAMPLE

$$trans\text{-}(Et_3P)_2PtHCl + C_2H_4 \rightarrow trans\text{-}(Et_3P)_2PtCl(C_2H_5)$$
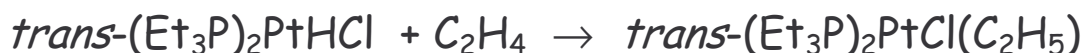
In this example the resulting ethyl complex is stable because the d^8 platinum Pt(2+) atom *strongly* prefers square-planar geometry.

A related route is insertion of a carbene into a TM-H bond

EXAMPLE

$$CpMo(CO)_3H + CH_2N_2 \rightarrow CpMo(CO)_3(CH_3)$$

CH_2N_2 is diazo-methane - an unstable molecule which acts as a source of the reactive intermediate "CH_2"

Level-3 Organometallics L3b

Synthesis of stable metal alkyl compounds

(3) Metal based nucleophile plus alkyl/acyl halide

This is closely related to the nucleophilic displacement reaction in organic chemistry

$$Nu^- + RX \rightarrow NuR + X^-$$
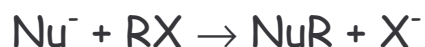
The nucleophile used are *metal centered* nucleophiles and are electron rich TM compounds. The most commonly used are *metal carbonylate anions.* Made with strong reducing agents such as sodium amalgam (Na/Hg)

EXAMPLE

$$Mn_2(CO)_{10} + Na/Hg \rightarrow 2 \ Na^+ [Mn(CO)_5]^-$$

Cleave Mn-Mn bond and reduce Mn to Mn(-1)

$$Na^+ [Mn(CO)_5]^- + CH_3I \rightarrow CH_3Mn(CO)_5$$

EXAMPLE

$$[CpFe(CO)_2]_2 + Na/Hg \rightarrow Na^+ [CpFe(CO)_2]^-$$

$$C_2H_5I \rightarrow CpFe(CO)_2(C_2H_5)$$
$$CH_3COCl \rightarrow CpFe(CO)_2C(O)CH_3$$
acyl complex

Level-3 Organometallics L3c

Synthesis of stable metal alkyl compounds

(4) Oxidative addition of alkyl halide to 16 e⁻ complex

Many 16 e^- compounds with a d^8 or d^{10} configuration react with alkyl halides

| 16 VE | 18 VE | 18 VE |

Metals undergo change of +2 in oxidation level. Very common for square-planar d^8 complexes

	square-planar	Rh(+1)	Pd(+2)	Pt(+2)
goes to	octahedral	Rh(+3)	Pd(+4)	Pt(+4)

Oxidative addition requires :
- metal has two accessible oxidation states differing by +2
- metal has vacant coordination sites

Also possible for zerovalent d^{10} compounds

| 16 VE | 18 VE | 16 VE |

Level-3 Organometallics L3d

Reactions of metal alkyls

(1) Decomposition

Main route is by β-elimination. Experimental evidence to support mechanism :

- from labelling studies it is proved that β-hydrogen is transferred

$(Bu_3P)CuCH_2CD_2Et$ $\rightarrow$ "$(Bu_3P)CuD$" + $CH_2=CDEt$

not detected

CH_2DCD_2Et
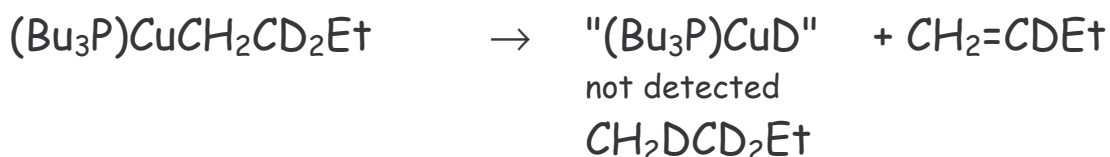
- necessity of vacant coordination site shown by inhibition of reaction with added PPh_3

$CpFe(alkyl)(CO)(PPh_3)$ $\rightarrow$ $CpFeH(CO)(PPh_3)$ + alkene
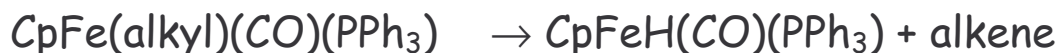
- best evidence comes from structures of alkyl complexes which show "agostic" interactions
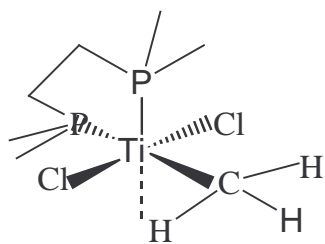
$Ti(dppm)Cl_2(CH_3)$
agostic methyl
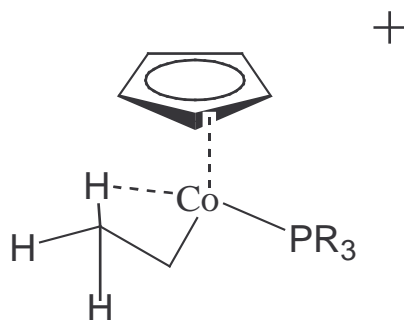
$[CpCo(PR_3)(C_2H_5)]^+$
agostic ethyl

Level-3 Organometallics L3e

Reactions of metal alkyls

(1) Decomposition ......

Other routes are by α-elimination

EXAMPLE : $WMe_6 \rightarrow 3CH_4 + 3"W(CH_2)_3"$ (unknown polymer)

or by *reductive* elimination - reverse of oxidative addition
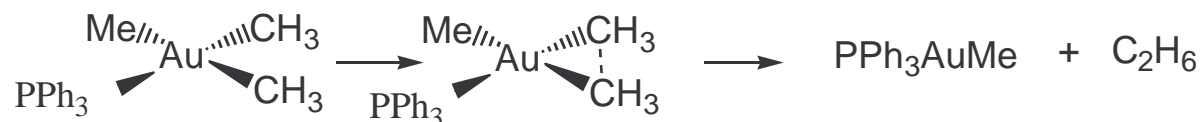
requires that groups eliminated are *cis*

(2) Insertion reaction

Many small molecules with multiple bonds (e.g. CO_2, CS_2, NO) will insert into M-C bonds. Most important is CO

EXAMPLE : $(CO)_5MnCH_3 + CO \rightarrow (CO)_5MnC(O)CH_3$ new acyl bond

Mechanistic studies show that
- the CO in the acyl groups comes from already coordinated CO
- incoming CO is *cis* to the acyl group

Level-3 Organometallics L3e

Reactions of metal alkyls

(1) Decomposition ......

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16 e intermediate

Level-3 Organometallics L4a

Complexes with unsaturated alkyl groups

Some alkyl groups have unsaturated functionality next at the α-C atom

metal alkenyl

metal aryl

metal alkynyl
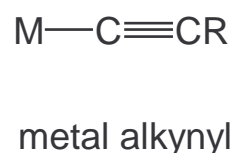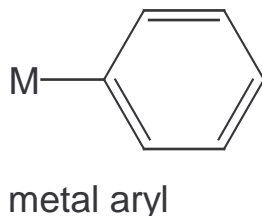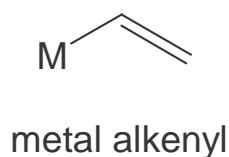
These have *possibility* for π-bonding to metal atom. Structural evidence suggests this is not happening.

EXAMPLE   *trans*-PtCl(PPhMe$_2$)$_2$R

	obs Pt-C (Å)	calc Pt-C (Å)
CH$_2$SiMe$_3$	2.08	2.01
CH=CH$_2$	2.03	1.98
C≡CPh	1.98	1.91

Unsaturated functionality *can* be bonded to another metal. example below is a bridging vinyl group
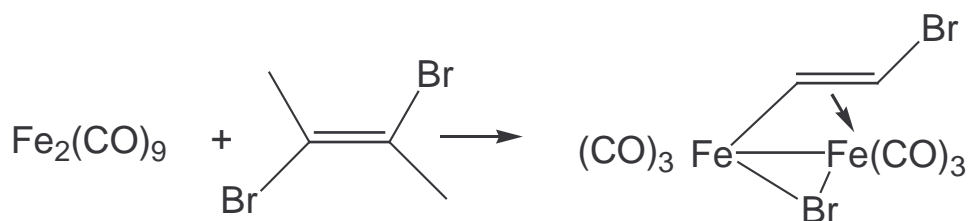
Level-3 Organometallics L4b

Complexes with π-acceptor ligands

There are many of these type of ligand (E/S Ch 15 S/A Ch 16) Some bond to metal through *one* atom - described as η^1 (eta-one) ligands, while others (described later) bind through more than one.

Examples of η^1 ligands

M-CO	M-PR$_3$	M-CNR	M=CR$_2$	M≡CR	M-CS	M-NO
carbonyl	phosphine	isocyanide	carbene	carbyne	thiocarbonyl	nitrosyl
		isonitrile	alkylidene	alkylidyne		

Conveniently classed together because bonding to TM is very similar in all cases - involves *synergic* bonding also called *back-bonding*

Evidence for back-bonding (E/Salzer pp 226-231)
- **bond lengths** *increases* the strength, hence *reduces* the length of M-C bond but *decreases* the strength, hence *increases* the length of the C-O bond. Not easy to see latter.
- **C-O stretching frequencies** - this is very sensitive to extent of backbonding. For *neutral (i.e. uncharged)* complexes the range of frequencies allows distinction between *terminal bridging and triply-bridging* bonding

Level-3 Organometallics L4c

energy-level diagram for CO
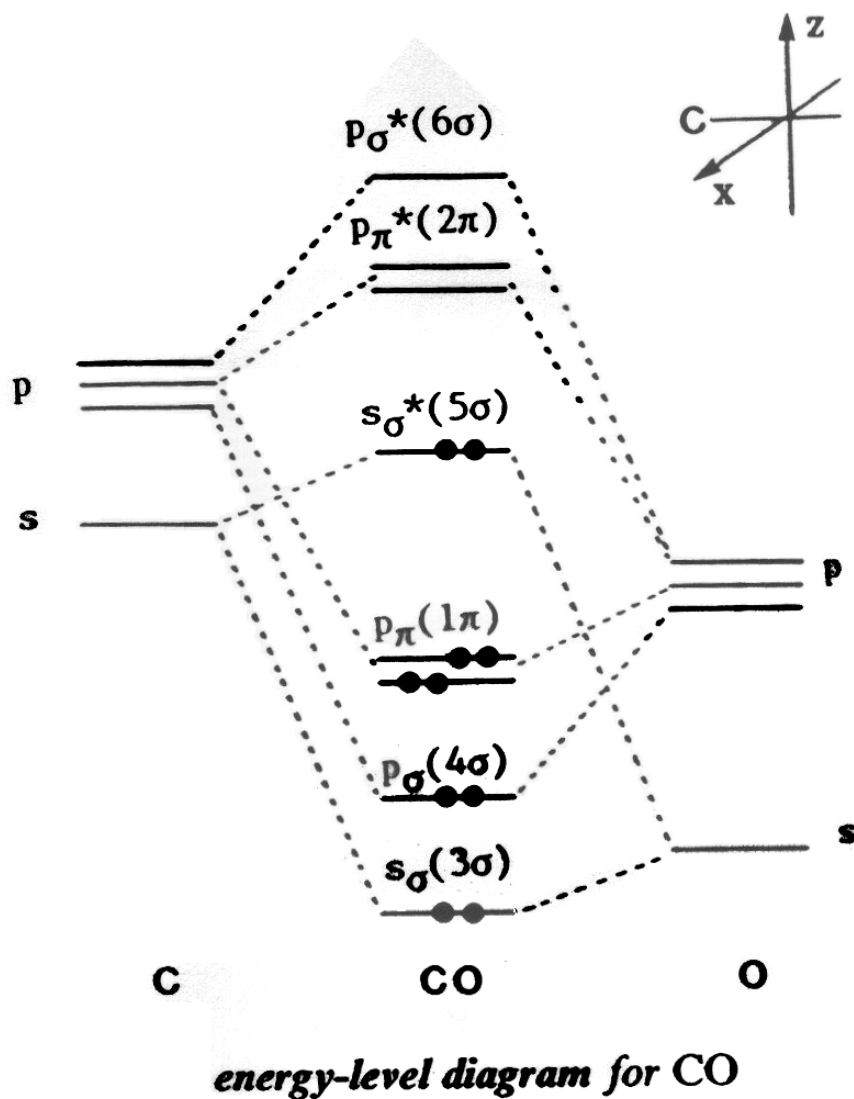
(a) Bonding modes of the carbonyl group

The change in vibrational stretching frequencies ν_{CO} is quite characteristic

	Free	Terminal	μ_2-CO	μ_3-CO
	$\overline{O} \equiv \underline{C}$	$\begin{matrix} O \\ \| \\ C \\ \| \\ M \end{matrix}$	$\begin{matrix} O \\ C \\ M \quad M \end{matrix}$	$\begin{matrix} O \\ C \\ M \quad M \quad M \end{matrix}$
ν_{CO} (cm^{-1})	2143	1850–2120	1750–1850	1620–1730

Level-3 Organometallics L4d

M-C bonding in CO complexes

There are *three* components to the bonding between CO and TM

(i) σ-donation *from* CO σ* level (5σ)

empty   filled

$$M(\sigma) \leftarrow CO(5\sigma)$$

(ii) π-donation *from* CO 1π

empty   filled
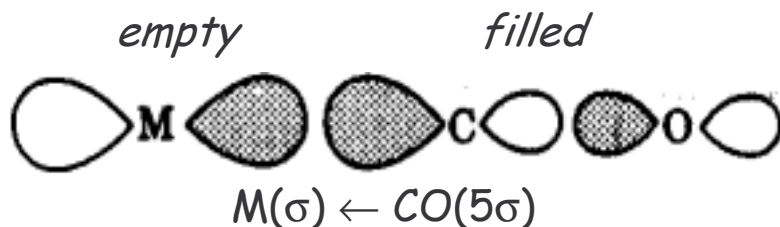
$$M(\pi) \leftarrow CO(1\pi)$$
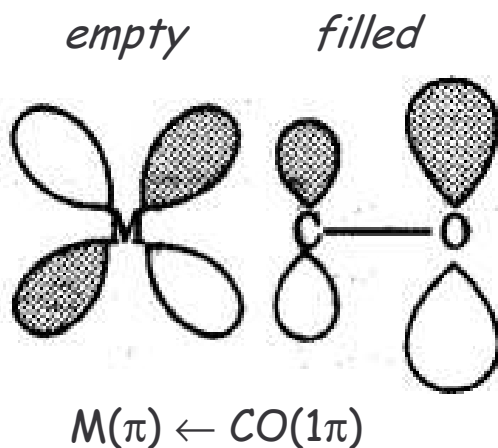
(iii) π-acceptor *from* metal *to* CO 2π*

filled   empty

$$M(\pi) \rightarrow CO(2\pi^*)$$
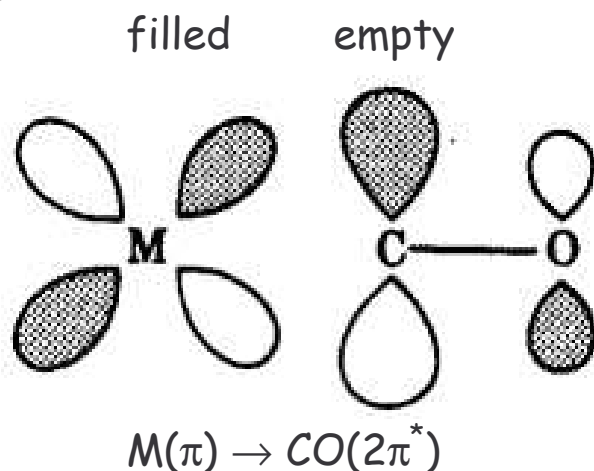
Level-3 Organometallics L4e

M-C bonding in CO complexes – the actual orbitals

2π

5σ

1π

4σ
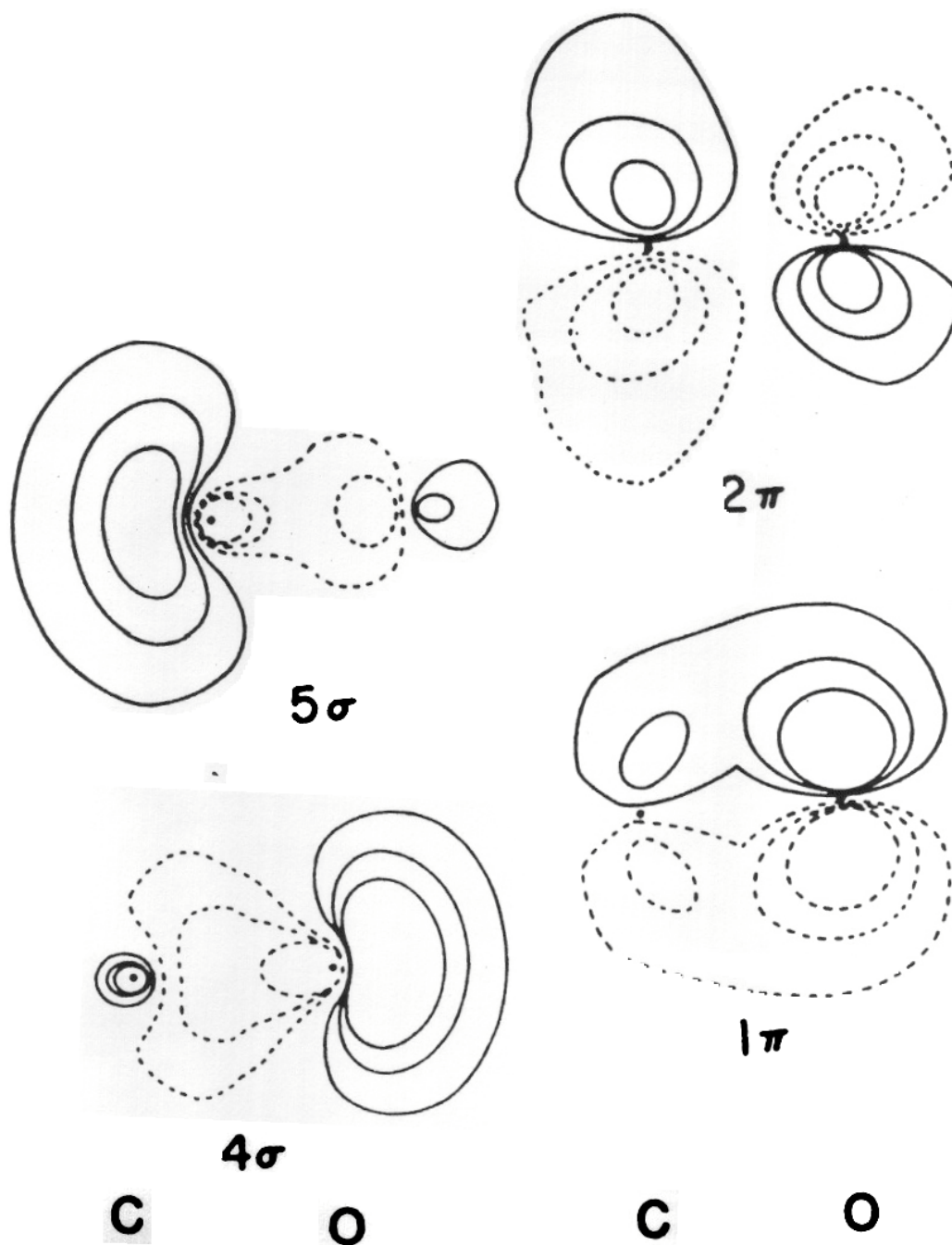
C   O   C   O

Level-3 Organometallics L5a
M-C bonding in CO complexes

All these interactions result in *strengthening* of the M-C bond.

Much evidence that this is case, e.g. for W-C distances
$W(CO)_6$ 2.06 Å WMe_6 2.15 Å $W(=CH_2)$ 1.94 Å

Difficult to separate effects of 3 components in metal complexes.

Evidence for σ-donor orbital (cases where *no* π-bonding is possible)
- Lewis adduct $H_3B{\leftarrow}CO$. Complex has $\nu(CO)$ at 2164cm^{-1} , free CO at 2143cm^{-1} therefore C-O bond order is *increased* with σ-donation, as predicted.
- Same for *cationic* metal carbonyls e.g. linear $[Hg(CO)_2]^{2+}$ $\nu(CO)$ 2164cm^{-1} - only stable in highly acid solvents (CO is very poor σ-donor)

Back-bonding is *very* effective in reducing formal charge on a transition metal. Therefore CO is a very good ligand for stabilising metals in electron rich LOW oxidation states.

Charge on a complex has great effect on $\nu(CO)$

complex	$[V(CO)_6]^-$	$Cr(CO)_6$	$[Mn(CO)_6]^+$
$\nu(CO)$ cm^{-1}	1860	2000	2090

Due to differing degrees of back-bonding.

Level-3 Organometallics L5b

Super-reduced carbonylate anions

CO can stabilise TM's in unusually low oxidation levels

EXAMPLE $Mn_2(CO)_{10}$ Mn(0)

$Mn_2(CO)_{10}$ + Na/Hg $\rightarrow$ $[Mn(CO)_5]^-$ Mn(-1)
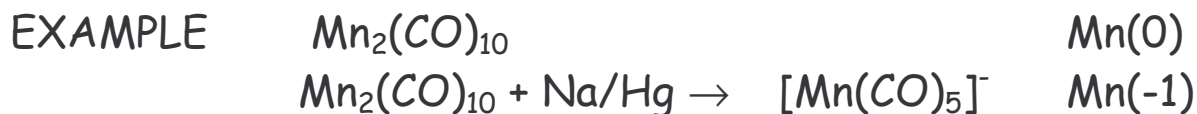
with stronger reducing agents (e.g. $Na^+ C_{10}H_8^-$) possible to get lower - *super reduced carbonylate anions*

$Na^+_3 [Mn(CO)_4]^{3-}$ Mn(-3) !!

Tetrahedral - unstable explosive

Other examples made in a similar fashion. Strong back donation shows in $\nu(CO)$ for series $[M(CO)_4]^{n-}$

	Ni	Co	Fe	Mn	Cr
charge n	0	-1	-2	-3	-4
$\nu(CO)$ cm^{-1}	2040	1890	1729	1670	1462

In -3 oxidation state $M(CO)_5^{3-}$ V, Nb, Ta

$\qquad\qquad\qquad\qquad\qquad\qquad$ $M(CO)_4^{3-}$ Mn, Re

$\qquad\qquad\qquad\qquad\qquad\qquad$ $M(CO)_3^{3-}$ Co, Rh, Ir

In -4 oxidation state $M(CO)_4^{4-}$ Cr, Mo, W

Level-3 Organometallics L5c

Super-reduced carbonylate anions

High negative charge is delocalised by carbonyl ligands

The formal high negative charge on the metals makes these ions extremely powerful metal-centered nucleophiles

EXAMPLES

$[Mn(CO)_4]^{3-}$ + $2Ph_3SnCl$ $\rightarrow$ $[Mn(CO)_4(SnPh_3)_2]^-$ (mono-anion)

$[Mn(CO)_4]^{3-}$ + $3Ph_3PAuCl$ $\rightarrow$ $Mn(CO)_4(AuPPh_3)_3$
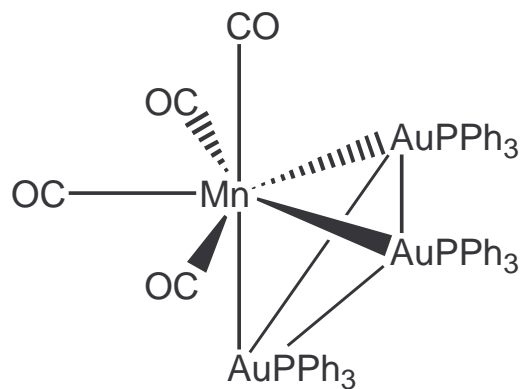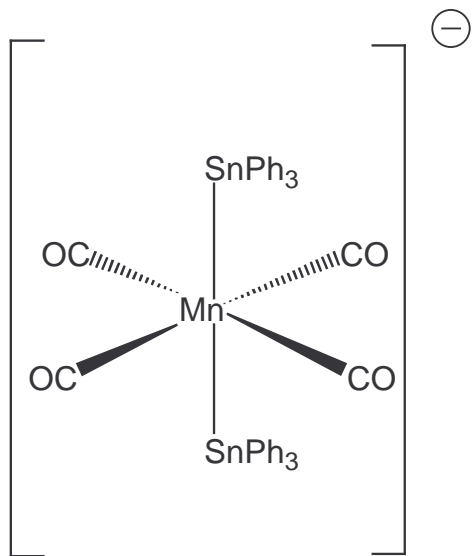
Level-3 Organometallics L5d

Other pi-acceptor ligands

The principles of bonding of CO to TM's applies in a very similar way to other π-acceptor ligands. However, there are always some differences/idiosyncracies

Dinitrogen (N_2)
Isoelectronic with CO, but not charge-polarised. Much poorer σ-donor and π-acceptor than CO.
Can bind in η^1-mode as M-N_2 but also bridging M-N≡N-M

Nitrosyl (NO)
Binds either terminal or bridging as CO.
Linear M-N-O angle 180-160° this is formal 3-electron donor
Bridging also 3-electron donor
Bent M-N-O angle 140-120° formal 1-electron donor

Isocyanide (RNC)
Isoelectronic with CO. Generally better σ-donor and poorer π-acceptor then CO, but this is a "tunable" ligand. Varying R-group changes properties, i.e. electron donating R group e.g. CMe_3 make for better σ-donor, while electron withdrawing R-group e.g. CF_3 make for better π-acceptor

σ-donor and π-acceptor properties are synergic

Level-3 Organometallics L5e

Other pi-acceptor ligands

Phosphine/phosphite PR_3 $P(OR)_3$

Also AsR_3 (arsines) SbR_3 (stibines) SR_2 (thio-ethers)

Generally better σ-donor and poorer π-acceptor then CO, but again these are "tunable" ligand. Varying R-group changes properties.

How to separate σ-donor and π-acceptor properties ?

Not easy - use $\nu(CO)$ in compounds such as $Mo(CO)_3(L)_3$ as "indicator" of backbonding

$L_3Mo(CO)_3$	$\nu(CO)$ cm^{-1}	
L = PF_3	2055, 2090	L very strong π-acceptor
L = PPh_3	1835, 1934	
L = pyridine	1746, 1888	L is "pure" σ-donor

Note values of $\nu(CO)$!!!

Using this, it is possible to "rank" ligands in order of π-acceptor strength

$$NO > CO > RNC > PF_3 > P(OR)_3 > PR_3$$

Level-3 Organometallics L6a
Alkene complexes - Dewar/Chatt/Duncanson model
H/S 587-590   S/A 561-570 E/S 256-265
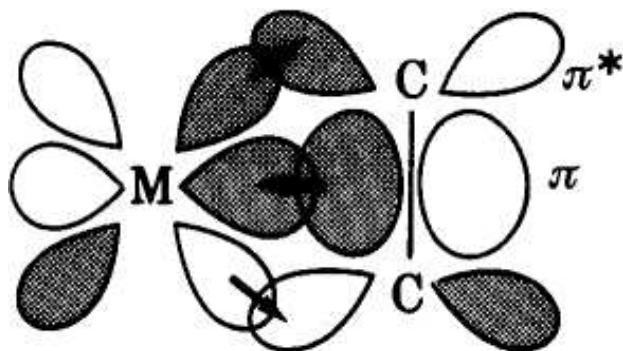
Two components
- σ-donation *from* alkene π-orbital *to* metal σ-orbital (s, p_z or d_{z2})
- π-donation *from* metal d-orbital *to* alkene π^* orbital

Evidence for this model ?

1. Structural data
(a) bond distances

Zeise's salt $[PtCl_3(C_2H_4)]^-$
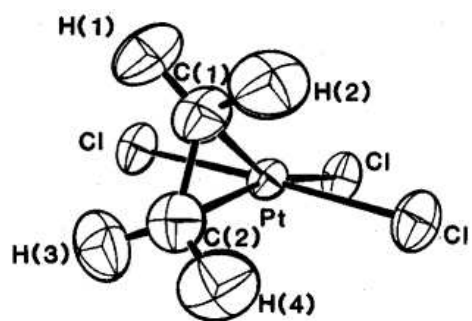
C-C distance = 1.37Å
C-C distance in free ligand = 1.35Å

Conclusion : in this complex most of bonding is ligand → M σ-donation

Both components *strengthen* M-C bonds and *weaken* C-C bonds, but π-donation has greatest effect in weakening C-C bond

Level-3 Organometallics L6b
Alkene complexes - Dewar/Chatt/Duncanson model
(b) bond angles

When backbonding occurs, hybridisation of alkene C- atoms changes from sp^2 to approaching sp^3. This has an implication for the bond angles (sp^2 C-atom is planar sp^3 C-atom is pyramidal)

So - substituents "bend-back" from the metal - the greater the π-donation the greater the bend-back.
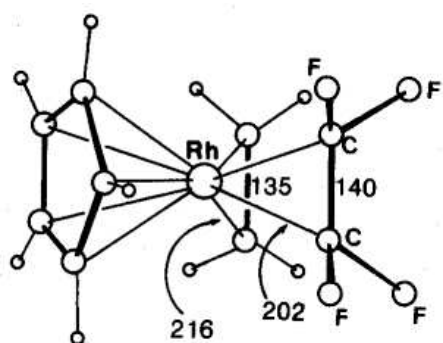
C-C distances C_2H_4 = 1.35 Å
                   C_2F_4 = 1.40 Å
Rh-C distances C_2H_4 = 2.16 Å
                   C_2F_4 = 2.02 Å

More π-donation in C_2F_4 ligand because F atoms are electron withdrawing.
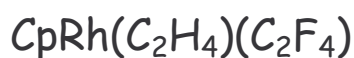
$CpRh(C_2H_4)(C_2F_4)$
"Bend-back" angle C_2H_4 = 17° C_2F_4 = 37°
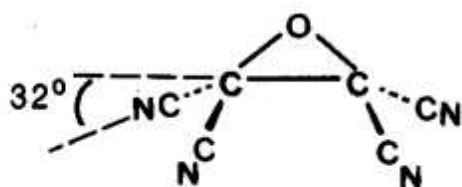
Epoxide
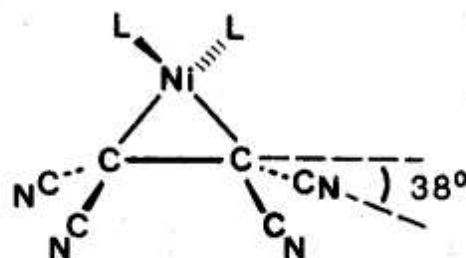
(η^2-Tetracyanoethylene)Ni complex
(nickelacyclopropane)

Alkene complexes can also be thought of as *metallacyclopropanes*
Two approaches are complementary.

Level-3 Organometallics L6c
Alkene complexes - Dewar/Chatt/Duncanson model

Localized orbitals	Linear combination	Delocalized orbitals

metallacyclopropane   Dewar/Chatt/Duncanson
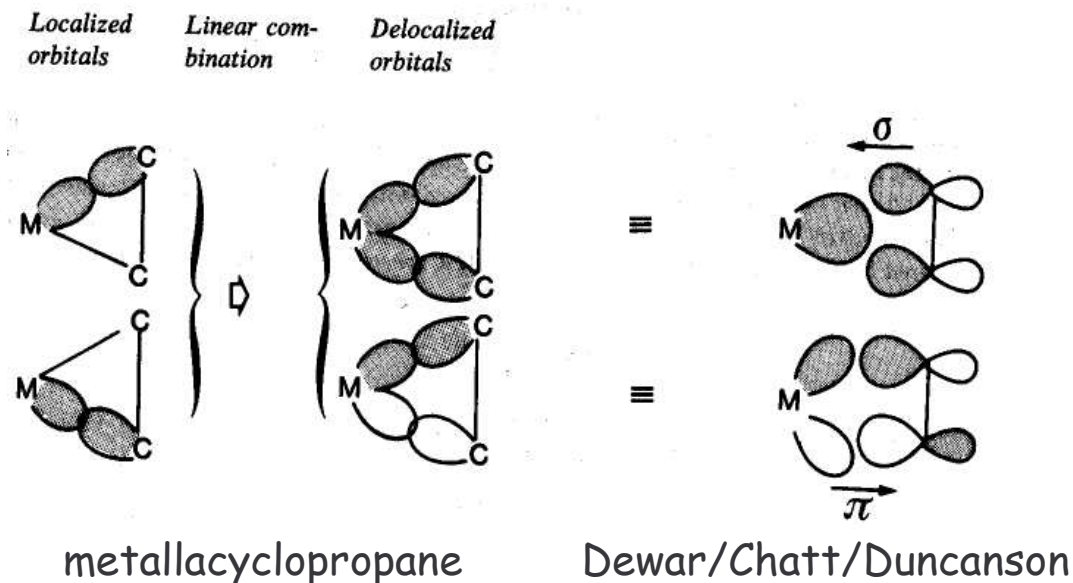
(2) Hindered rotation of coordinated alkenes

Alkenes can rotate about M-C=C axis
- M - alkene σ-bond is *invariant* to rotation (does not affect overlap)
- M - alkene π-bond is *strongly* dependent on rotation angle

Thus there is a energy cost (and hence a *energy barrier*) to this rotation. Barrier is of the size which can be detected by variable temperature NMR spectroscopy

Level-3 Organometallics L6d
Alkene complexes - Dewar/Chatt/Duncanson model

H-NMR spectrum of $C_5H_5Rh(C_2H_4)_2$ (200 MHz).

A.4   373K

^{1}H NMR   333K

313K

283K

AA'BB'   233K
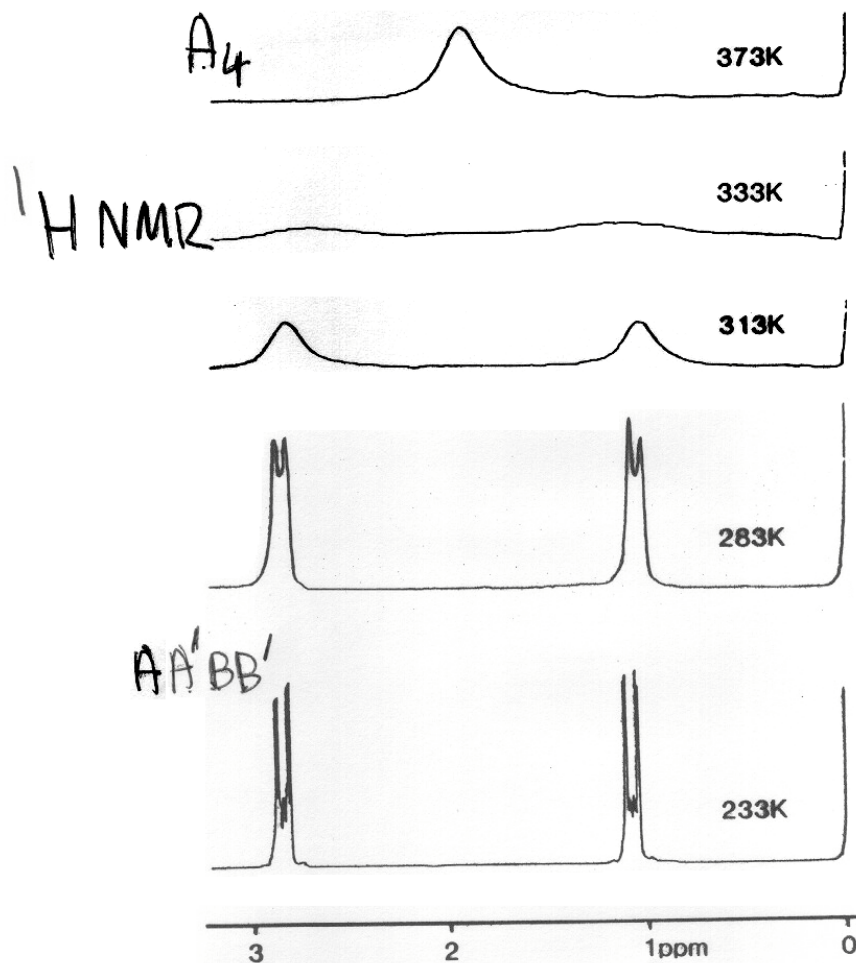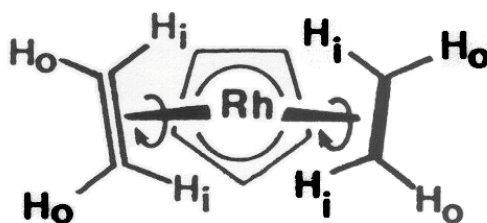
low T ABCD

↓

highT AA'BB'
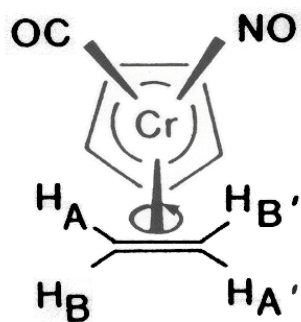
Level-3 Organometallics L6e
Alkene complexes - Dewar/Chatt/Duncanson model
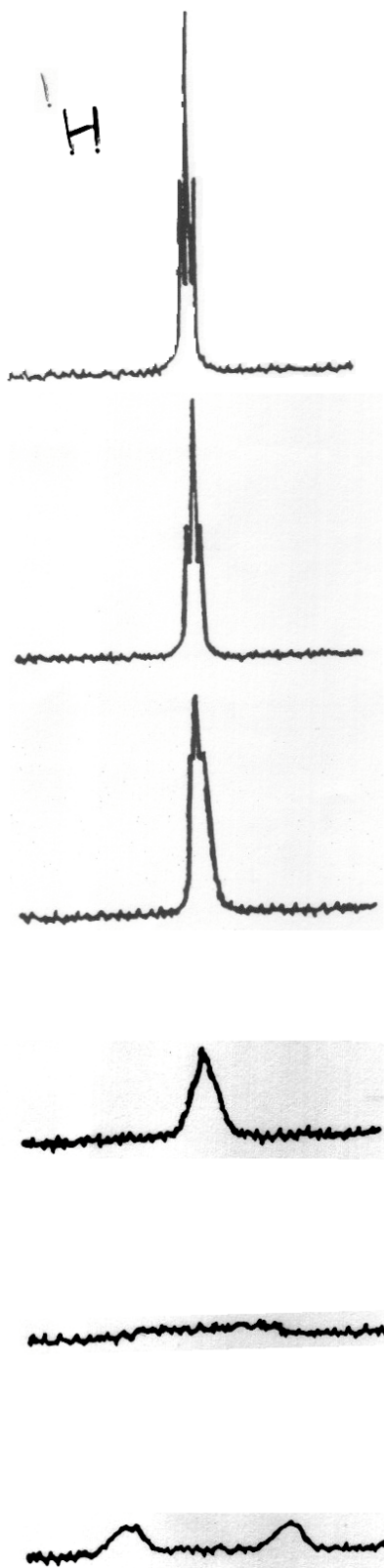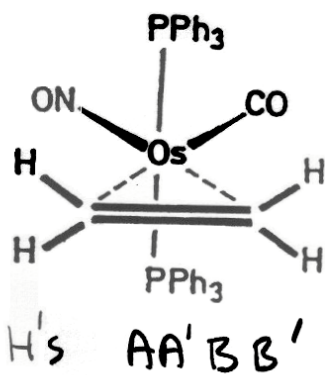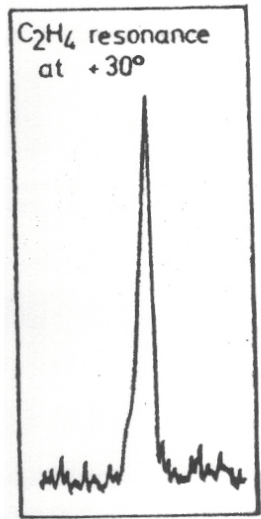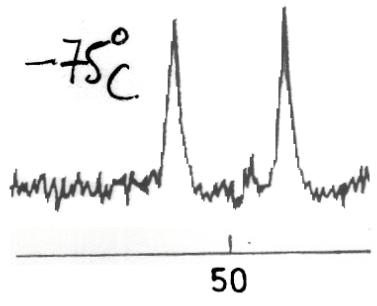
Level-3 Organometallics L7a
Metal hydride complexes

$KReO_4$ + K/EtOH → "K_2Re" white crystalline solid

Modern techniques X-ray, NMR not available. Compound actually contains the anion $[ReH_9]^{2-}$ - an 18 electron complex !!
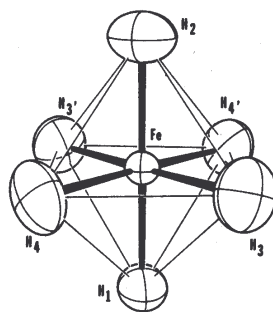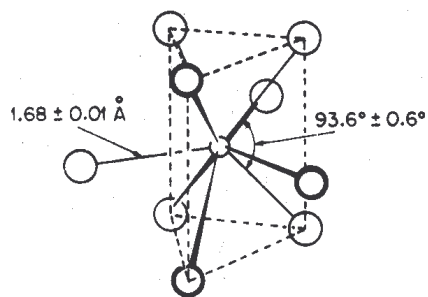
Only other well characterised *pure* hydride complex is Mg_2FeH_6 contains octahedral $[FeH_6]^{4-}$ also 18 electron compound

Most hydride complexes contain other ligands, usually π-acceptor ligands like CO, C_5H_5 or phosphine PR_3

Earliest examples made by protonation of metal carbonylate anion. Commonest way of making hydrides.

EXAMPLES

$[Mn(CO)_5]^-$ + H^+ → $HMn(CO)_5$ volatile yellow liquid $\delta(^1H)$ -7.5
                                      stable at 0°C

$[Fe(CO)_4]^{2-}$ + $2H^+$ → $H_2Fe(CO)_4$ decomp -10°C $\delta(^1H)$ –11.1
                                      ↓
                                $Fe_3(CO)_{12}$
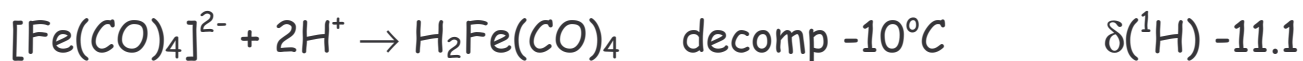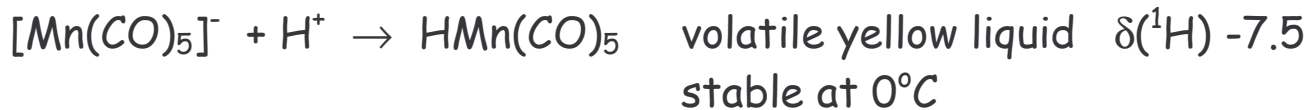
Level-3 Organometallics L7b
Metal hydride complexes

How to detect metal-hydrides ?

1. The *negative* chemical shifts in ^{1}H NMR are very diagnostic - no other type of H found here. Shielding due to non-local paramagnetic contribution from metal.

   Terminal M-H δ -5 $\rightarrow$ -15 ppm
   Bridging M-H-M δ -10 $\rightarrow$ -30 ppm

2. M-H stretch in IR at ~ 2000 cm^{-1} . Only CO stretches found in this region. M-H stretch first detected in Cp_2ReH.

   For bridging hydrides M-H-M stretch is ~ 1600 cm^{-1} and very weak and broad.

3. Diffraction. X-ray not a lot of good since H atoms do not have much electron density.
   Neutron diffraction much better - but serious drawbacks
   (i) need neutron source - nuclear reactor
   (ii) need very large crystals - difficult to grow

Level-3 Organometallics L7c
Metal hydride complexes

How are hydrides coordinated to metals ?

1. Terminal hydrides - normal coordination geometries

$HMn(CO)_5$

97 degrees
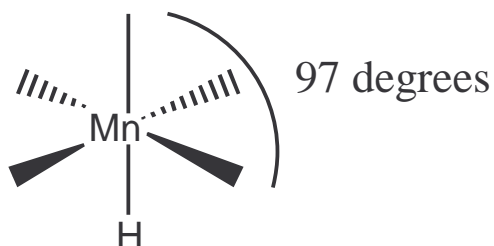
2. Bridging hydrides - very common in bimetallic and cluster compounds
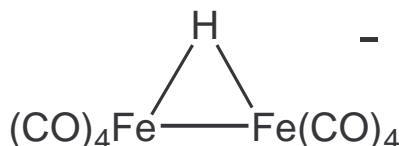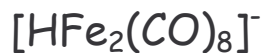
$[HFe_2(CO)_8]^-$

Has 3c-2e bond like B-H-B bond in boranes. This type of bonding has the effect of
- weakening Fe-Fe bond - longer than in $[Fe_2(CO)_8]^{2-}$
- lowers metal-H stretch to ~ 1700 - 1500 cm^{-1}

3. Encapsulated hydrides - completely inside metal cage
  $[HCo_6(CO)_{15}]^-$ CW/5 p 1111   E/S p 408

$\delta(^1H)$ +23 ppm

Level-3 Organometallics L7d
Metal hydride complexes

$$Co_2(CO)_8 \xrightarrow[\text{EtOH}]{\Delta T} [Co_6(CO)_{15}]^{2-} \xrightleftharpoons[\text{H}_2\text{O}]{\text{conc. HCl}} [HCo_6(CO)_{15}]^-$$

$d(Co-Co)$

251 pm

$d(Co-Co)$

258 pm

86 VE

[HCo$_6$(CO)$_{16}$]$^-$
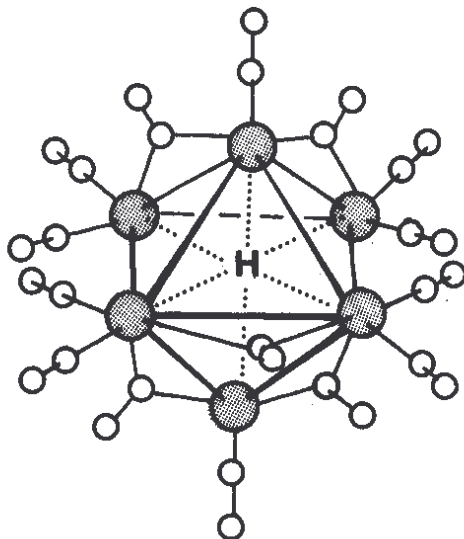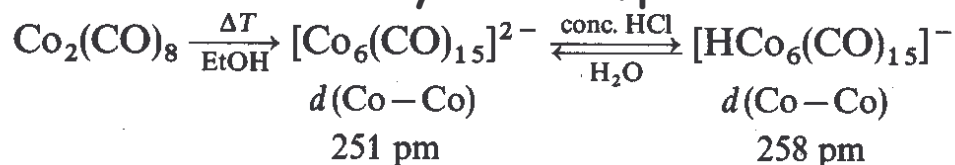
4. Polyhydrides - many examples with Mo and W. Have unusual properties - very fluxional

e.g. WH$_6$(PR$_3$)$_3$ RuH$_4$(PR$_3$)$_3$
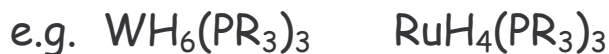
Because of small size, it is possible to pack several hydrides round metals in bimetallic polyhydrides

Cp$_2$Ru$_2$H$_4$

Ru≡R triple bond
Ru-Ru = 2.46 Å
normal Ru-Ru = ~ 2.9 Å
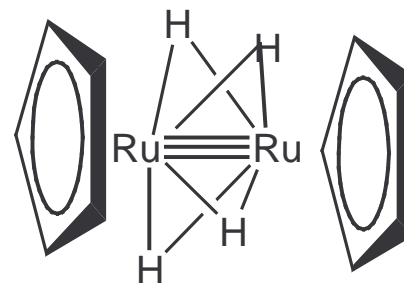
Some polyhydrides contains dihydrogen ligands

Level-3 Organometallics L7e
Metal dihydrogen complexes

$RuH_4(PR_3)_3$ is actually
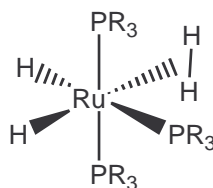
most examples of dihydrogen compounds are *octahedral*

Bonding has σ-donation and π-backdonation components. Most important is σ-donation. Too much π-backdonation leads to breaking of H-H bond giving *cis* dihydride
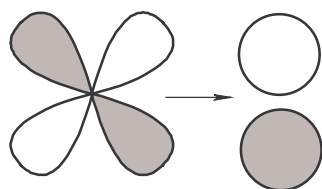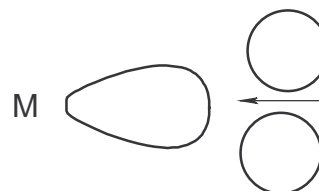
pi back donation   sigma donation

How to characterise dihydrogen ligands ?

1. Diffraction
Neutron diffraction is definitive way - but not always possible to get suitable crystals

Level-3 Organometallics L7f
Metal dihydrogen complexes

2. Spectroscopic characterisation

In IR, the H-H stretch should give weak absorption at ~2400cm^{-1}

$FeH_4(PEtPh_2)_3$	has H-H	2380 cm^{-1}
	and Fe-H	1880 cm^{-1}
but in $RuH_4(PPh_3)_3$	Ru-H	1942 cm^{-1}
	H-H	obscured

^{1}H NMR spectroscopy is better. Due to fluxionality it is NOT possible to see separate signals for H_2 and hydride ligands

Use the T_1 (relaxation time) criterion.
For hydrogen nuclei, relaxation is solely by dipole-dipole interactions with other H atoms

$$T_1 \propto r^6 \quad \text{(r is } average \text{ H-H distance)}$$

This is shorter for H_2 ligands   H-H ~ 1.0Å
than for cis - dihydrides where H-H $\geq$ 1.6 Å

EXAMPLE for $MH_4(PPh_3)_3$ complexes (M=Fe, Ru, Os)

	Fe	Ru	Os
T_1 (ms)	24	38	820

Conclusion : Osmium compound contains *classical* hydrides, other two contain dihydrogen ligands.

Level-3 Organometallics L8a
Metal-metal bonded cage compounds

References : S/A pp 302-307 & 572-579
               H/S pp 592-601 E/S Ch 16

Transition metals form three main classes of metal-metal bonded compounds

- Multiple bonded dimetal complexes (Dr Murrie)
- Halide/oxide clusters
- Carbonyl clusters

Halide/oxide clusters formed by early transition metals Nb, Ta, Mo, W, Re. Have halides and/or oxides as main (often only) ligands.

Examples of earliest known cluster compounds
EXAMPLES

"ReCl$_3$" is really Re$_3$Cl$_9$
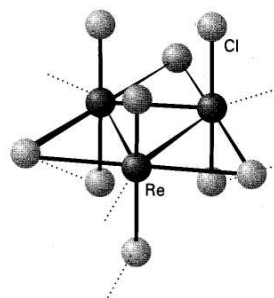
"NbCl$_2$" really contains [Nb$_6$Cl$_{12}$]$^{2+}$
(chlorides bridge all edges)
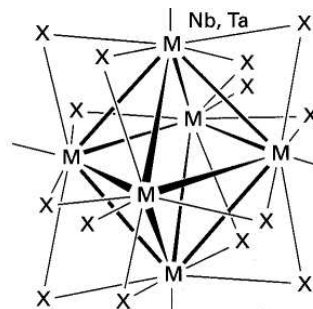
"MoCl$_2$" really contains [Mo$_6$Cl$_8$]$^{4+}$
(chlorides bridge all faces)
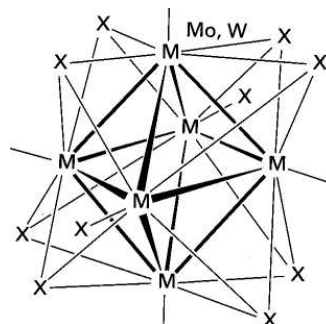
Level-3 Organometallics L8b
Metal-metal bonded cage compounds

Carbonyl clusters

Many thousands of examples known. Contain metal atoms in *low* oxidation states (zero or below). Ligands are invariably π-accpetor ligands CO, PR_3, NO C_5H_5 etc.

Compounds are either neutral molecules or anionic. Virtually NO examples of cationic clusters

Number of metal atoms range from two upwards .....

$[Ni_{38}Pt_6(CO)_{44}H_n]^{4-}$ (CO ligands not shown)
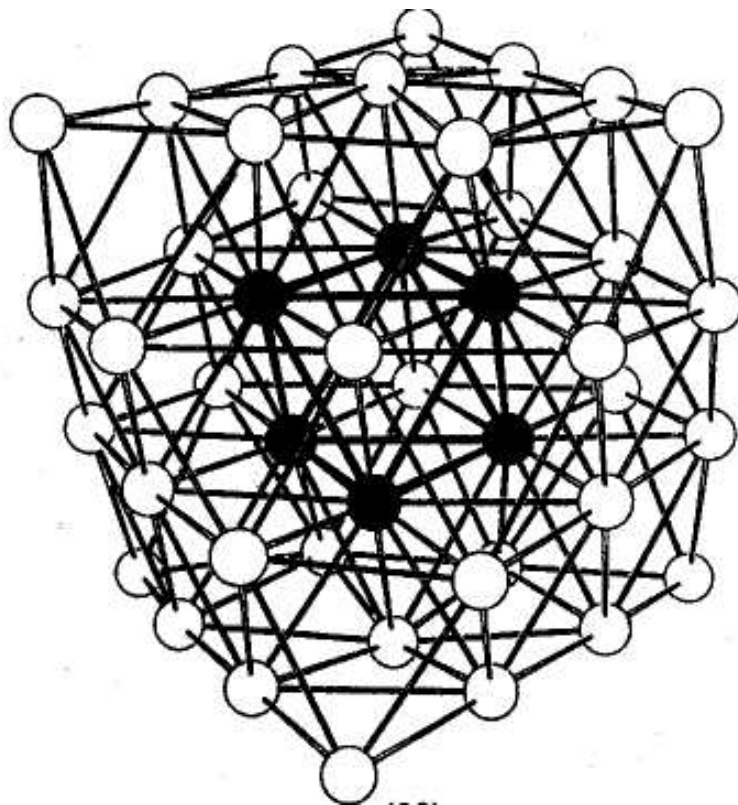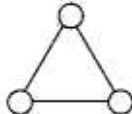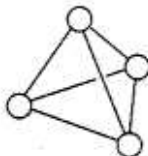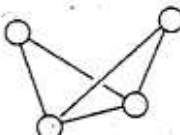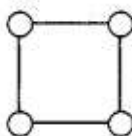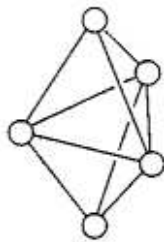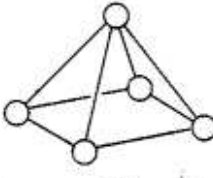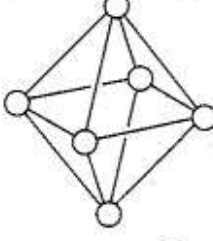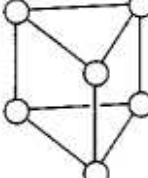
This "cherry cluster" models a small metal particle with chemisorbed ligands - useful in understanding mechanisms of heterogeneous catalysis

Level-3 Organometallics L8c
Metal-metal bonded cage compounds

Number of metal atoms	Structure of metal framework	Cluster valence electron count	Example
1 Single metal		18	$Ni(CO)_4$ (2)
2 Linear		34	$Mn_2(CO)_{10}$†
3 Closed triangle		48	$Co_3(CO)_9CH$ (59
4 Tetrahedron		60	$Co_4(CO)_{12}$ (57)
Butterfly		62	$[Fe_4(CO)_{12}C]^{2-}$
Square		64	$Os_4(CO)_{16}$
5 Trigonal bipyramid		72	$Os_5(CO)_{16}$
Square pyramid		74	$Fe_5C(CO)_{15}$
6 Octahedron		86	$Ru_6C(CO)_{17}$
Trigonal prism		90	$[Rh_6C(CO)_{15}]^{2-}$

Level-3 Organometallics L8d
Electron counting rules

The "magic numbers" seen in previous overhead can be rationalised through Molecular Orbital theory in several ways

Leads to "electron counting rules" which relate the *number of valence electrons* to the *skeleton structure of metals*. e.g Wades rules

Compare $[B_6H_6]^{2-}$ octahedron of BH units
with $[Os_6(CO)_{18}]^{2-}$ octahedron of $Os(CO)_3$ units

Why related ? : both fragments have *three* orbitals for skeletal bonding.

$[B_6H_6]^{2-}$ has $6\times3 + 6 + 2$ = 26 valence electrons
     needs 6×2 = 12 for B-H bonds
     leaves   14 electrons for B-B
bonds

     7 pairs (n+1) ≡ *closo*

$[Os_6(CO)_{18}]^{2-}$ has $6\times8 + 18\times2 +2$ = 86 valence electrons
     needs 6×12 = 72 for Os-ligand bonds
     leaves   14 electrons for Os-Os
bonds

     7 pairs (n+1) ≡ *closo*

Transition metals have 9 orbitals   - 6 NOT used for cage bonds
Main group elements have 4 orbitals - 1 NOT used for cage bonds

Level-3 Organometallics L8e
Metal-metal bonded cage compounds
Electron counting rules

The polyhedra which Wades rules are based on are the so-called *deltahedral* polyhedra - with triangulated faces

n = 4   Tetrahedron

n = 5   Trigonal bipyramid

n = 6   Octahedron

n = 7   Pentagonal bipyramid

.

n = 12   Icosahedron

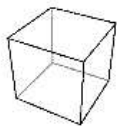These have the most number of nearest neighbour contacts and are the *most favourable polyhedra* (hence most stable).

        http://mathworld.wolfram.com/Deltahedron.html

Some of these are also the *Platonic solids* (each face a regular polygon)

TETRAHEDRON
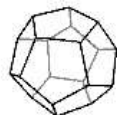Four triangular faces, four vertices, and six edges.

CUBE
Six square faces, eight vertices, and twelve edges.

OCTAHEDRON
Eight triangular faces, six vertices, and twelve edges.

DODECAHEDRON
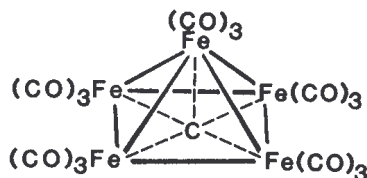Twelve pentagonal faces, twenty vertices, and thirty edges.

ICOSAHEDRON
Twenty triangular faces, twelve vertices, and thirty edges.

Level-3 Organometallics L8f
Electron counting rules

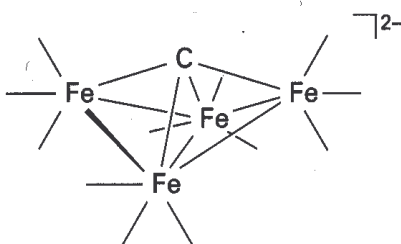Example of *nido* cluster is $Fe_5C(CO)_{15}$

C atom is encapsulated - uses *all* its valence electrons and an acts as 4 electron donor

Organic chemists - note the 5-coordinated carbon atom !!!

$Fe_5C(CO)_{15}$ has $5\times8 + 15\times2 + 4 = 74$ valence electrons

needs 5×12 $= 60$ for Fe-ligand bonds

leaves   14 electrons for Fe-Fe bonds

                                    7 pairs (n+2) ≡ *nido*

                                    octahedron - one vertex

Example of *arachno* cluster is $[Fe_4C(CO)_{12}]^{2-}$

$Fe_4C(CO)_{12}]^{2-}$ has $4\times8 + 12\times2 + 6 = 62$ valence electrons

needs 4×12 $= 48$ for Fe-ligand bonds

leaves   14 electrons for Fe-Fe bonds

                                    7 pairs (n+3) ≡ *arachno*

                                    octahedron - two vertices

also known as a "butterfly" cluster