

Organometallic Chemistry and Homogeneous Catalysis

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Lecture N6

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Group VIB: Cr, Mo, W

- Oxidation states from -2 to +6
- While +2 and +3 for Cr are quite usual, compounds for Mo and W are rarely known
- Chromocenes (Cp_2Cr) are stable, but corresponding Mo and W complexes are known only as intermediates
- Ligands like CO, Cp – are very popular for the organometallic complexes of Cr, Mo, W

Synthesis:



Using Li, Mg, Al - organic compounds



WMe_6 – red crystals, stable below room temperature

IR: $\nu(\text{W-C}) = 482 \text{ cm}^{-1}$ NMR ^1H : $\delta(\text{CH}_3) = 1.62 \text{ ppm}$ – singlet with W-satellite ($^1J_{\text{WC}} = 3\text{Hz}$)



Anionic acyl-chromium complex can be used further for the synthesis of carbene complexes

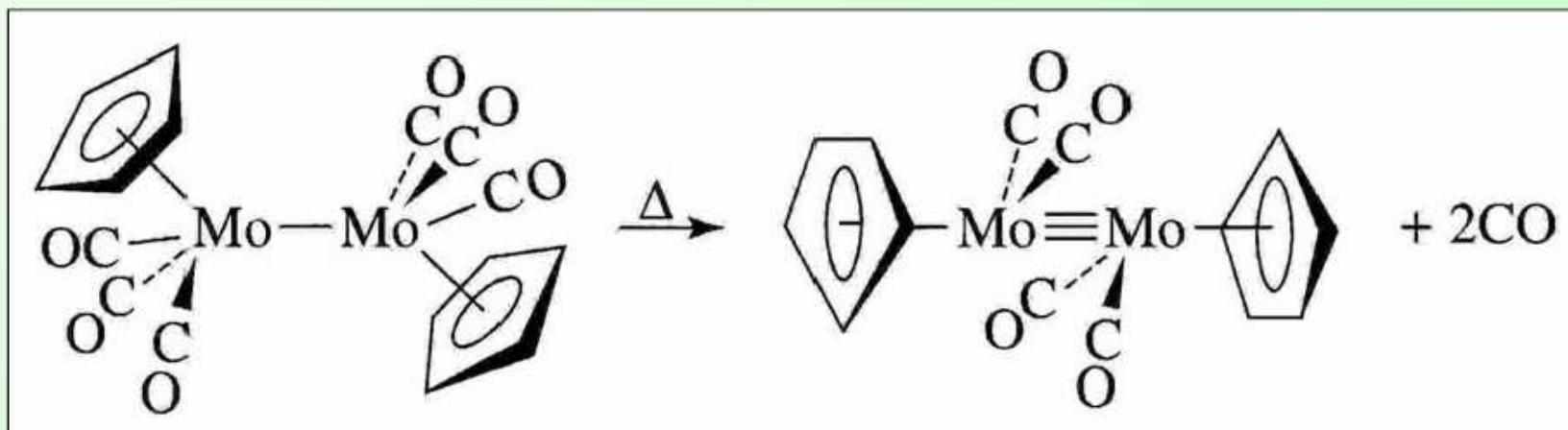


$\text{Cr}(\eta^3\text{-C}_3\text{H}_5)_3$ – dark-red crystals, stable below the melting point (78°C)

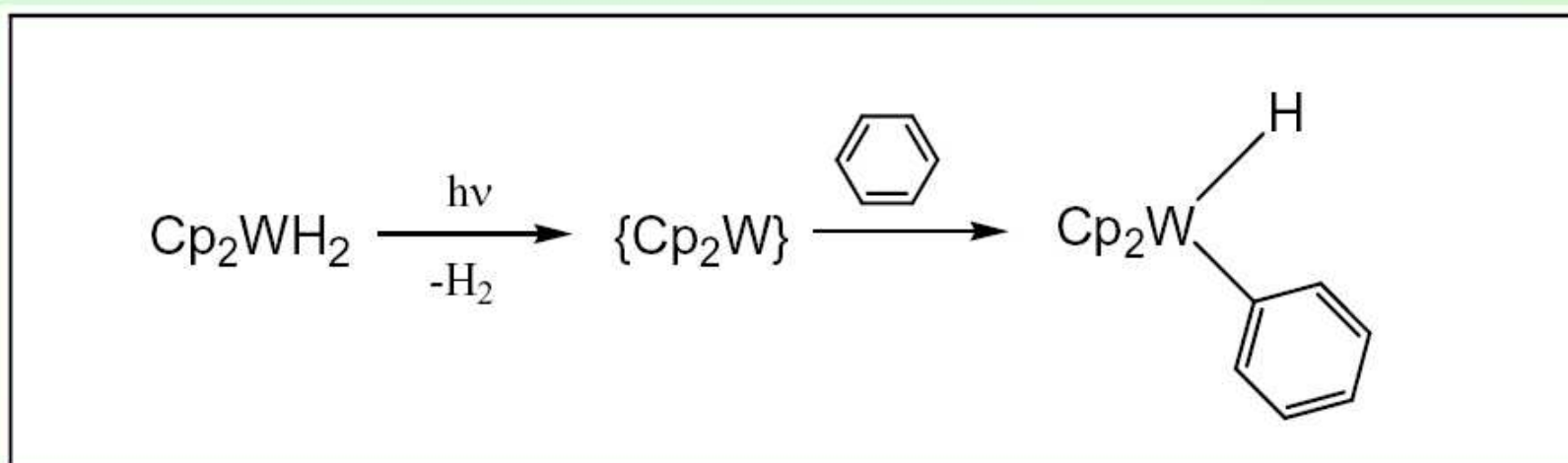
Reactivity:



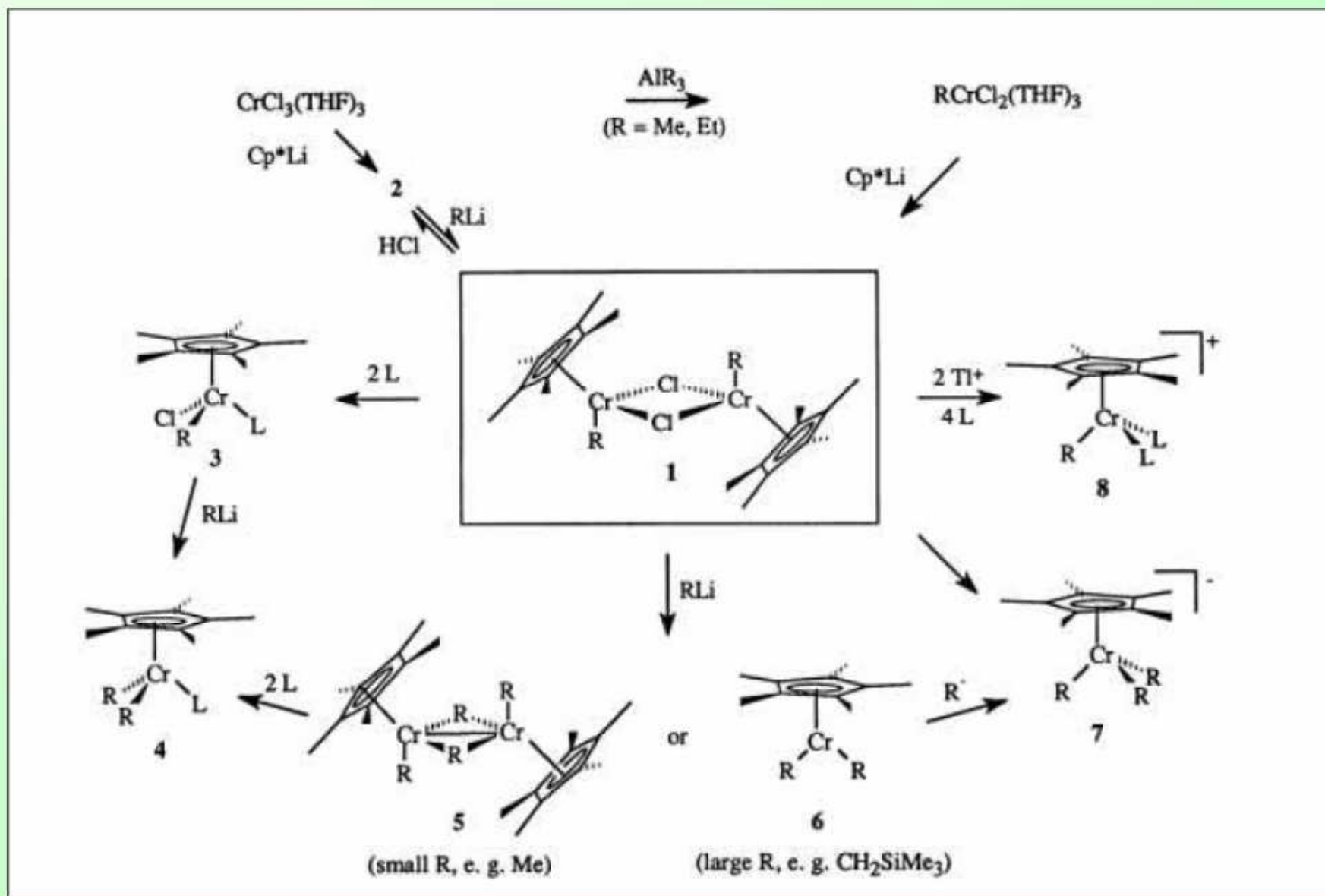
1. Tendency to form multiple M-M bonds:



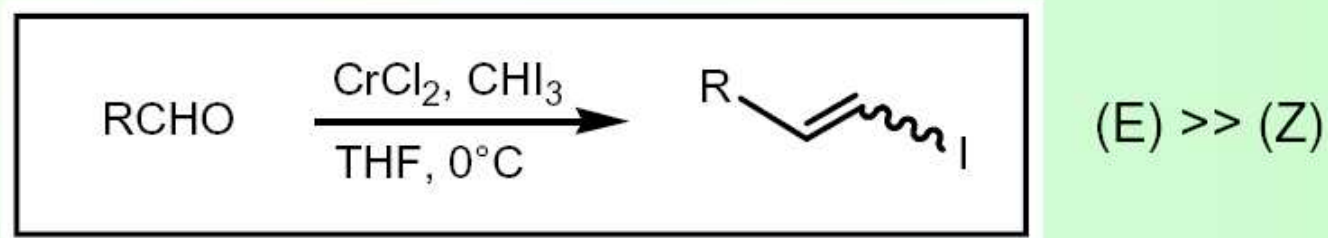
2. Reactive $\{\text{Cp}_2\text{W}\}$ intermediate can activate aromatic C-H bonds:



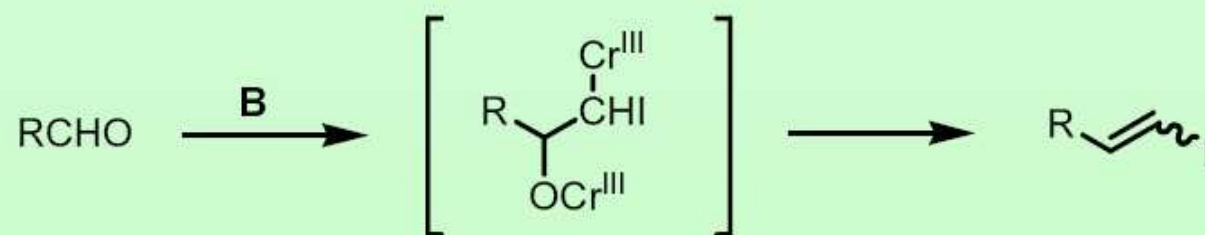
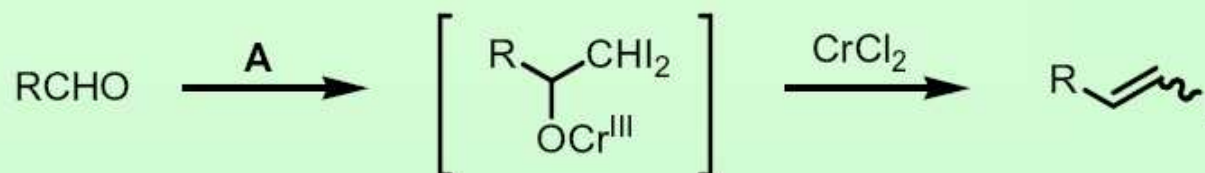
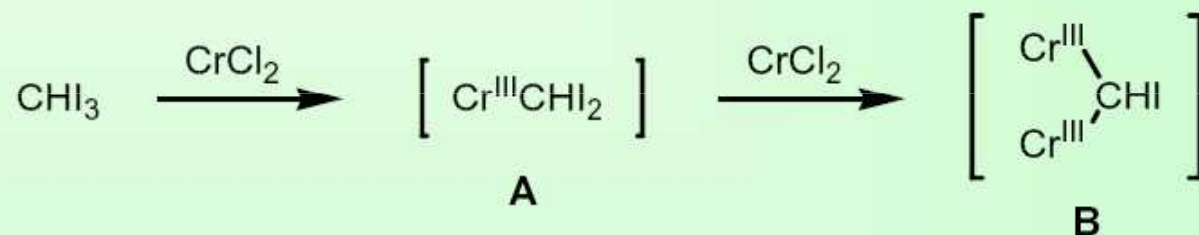
3. Cr (III) cyclopentadienyls can be synthesized starting from $\text{CrCl}_3 \cdot 3\text{H}_2\text{O}$. These compounds have very diverse chemistry:



4. Cr(III) organyl are important intermediates in iodoolefination (Takai Reaction)



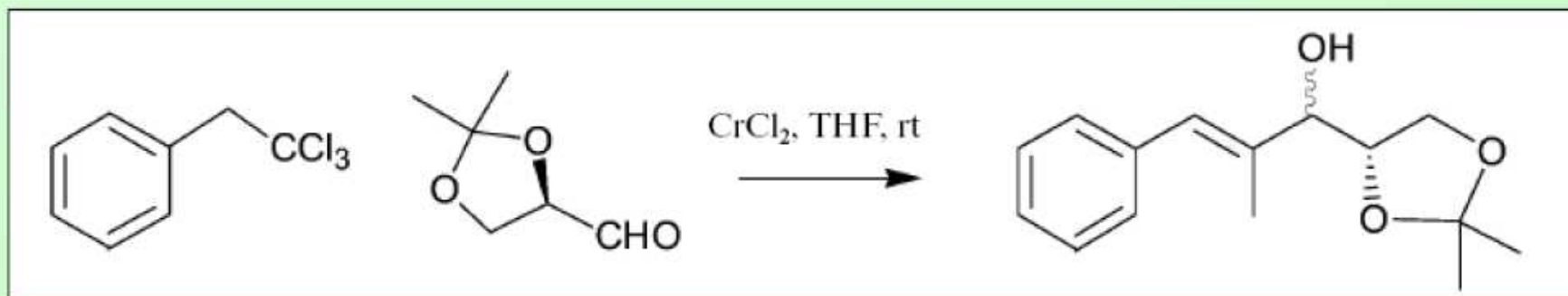
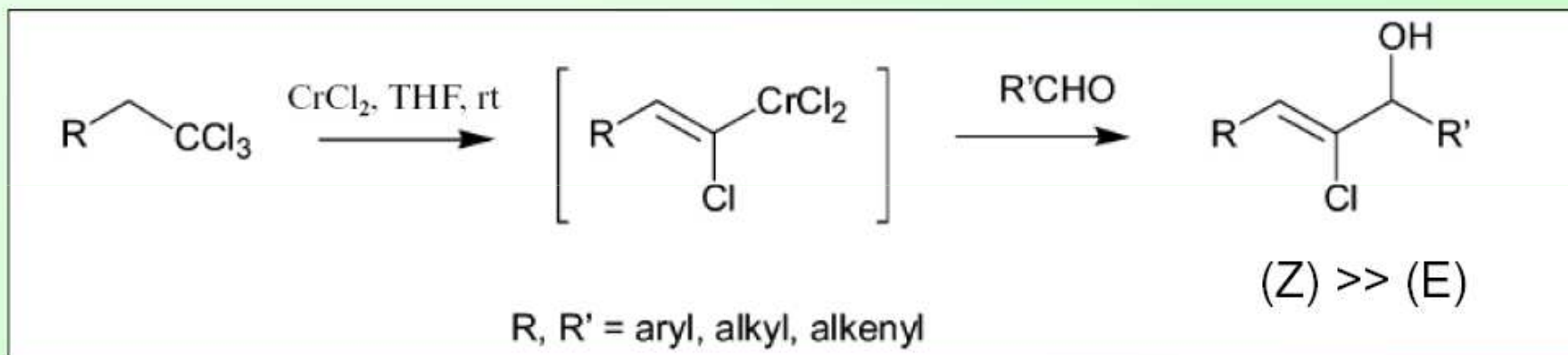
Mechanism:



5. Cr(III) organyl are important intermediates in the addition of $R\text{-CCl}_3$ to an aldehyde $\text{C}=\text{O}$ bond



Trichloroalkanes are stereoselectively transformed to (*E*)-chromium vinylidene carbenoids, which add smoothly to a variety of aldehydes to afford (*Z*)-2-chloroalk-2-en-1-ols:



2:1 mixture of *syn/anti*-isomers

Group VIIB: Mn, Tc, **Re**



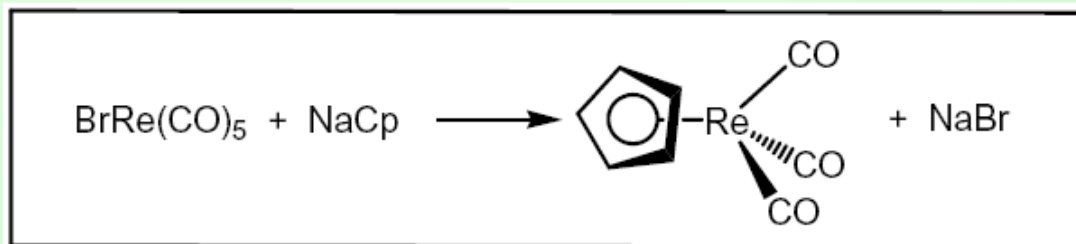
-Oxidation states from -3 to +7

- +1 and +2 for Mn are more typical than higher oxidative states

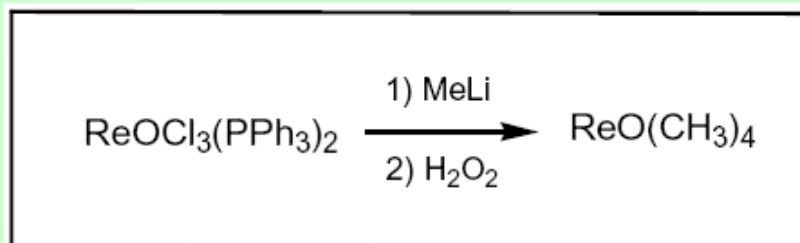
-Ligands like CO, Cp – are very popular for the organometallic complexes of Mn, Tc, Re

Synthesis:

Using Li, Na, Mg - organic compounds

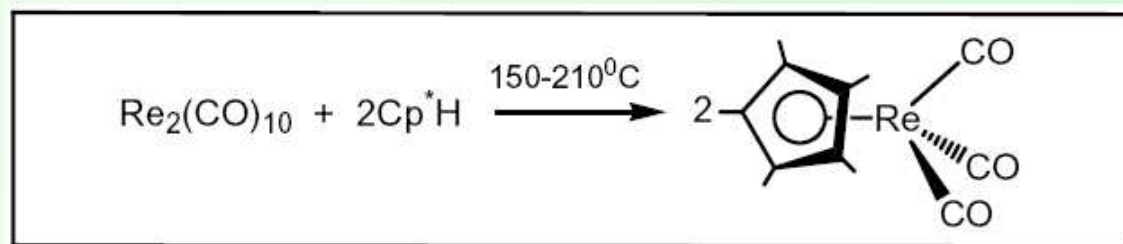


$\text{ORe}(\text{CH}_3)_4$ can be obtained as reddish-purple crystals using MeLi:

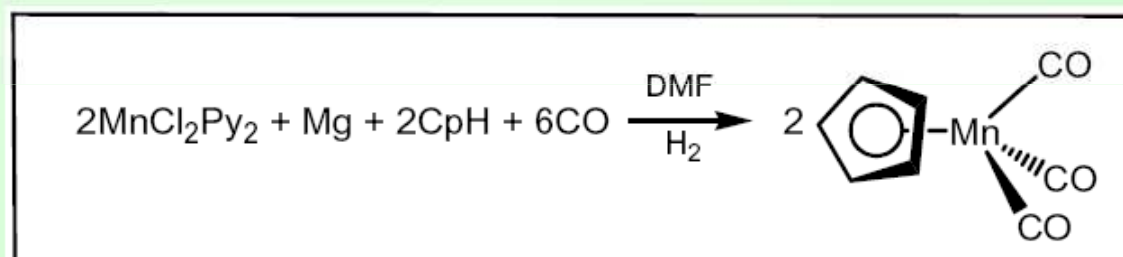


IR: $\nu(\text{Re}=\text{O}) = 1002 \text{ cm}^{-1}$

2. Metallation of hydrocarbons is also possible:



$\text{CpMn}(\text{CO})_3$ as an air-stable pale-yellow crystals also can be obtained via metallation of hydrocarbon:

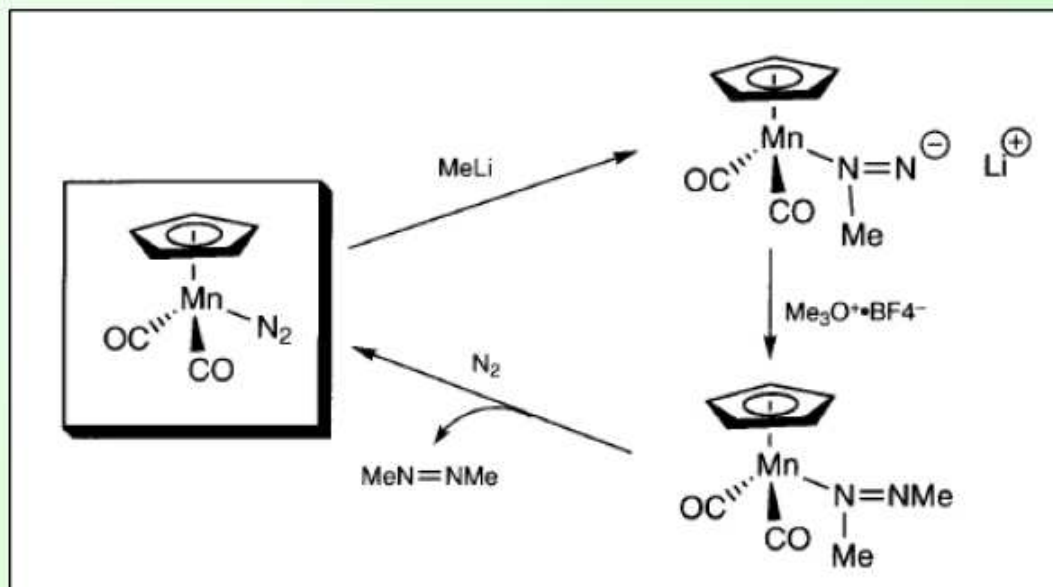


Application:

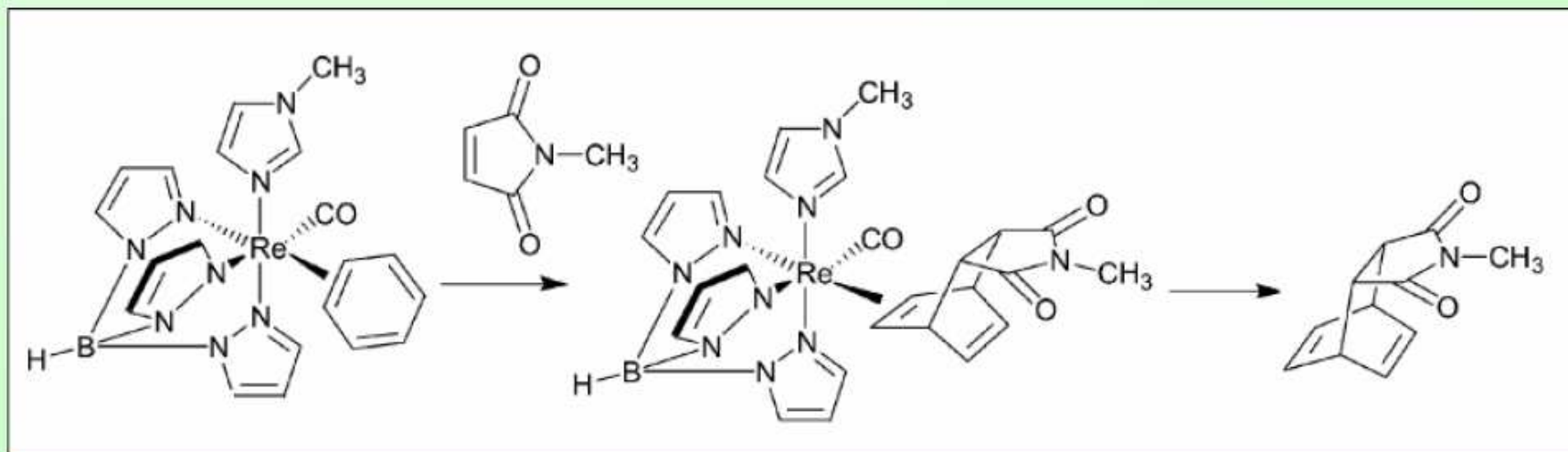
1. The analog of the above mentioned complex - $\eta^5\text{-(MeC}_5\text{H}_4\text{)Mn}(\text{CO})_3$ has been commercially produced by the same procedure since it is used as an antiknock agent in gasoline

2. Nitrogen activation

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3. Diels-Alder reaction



(benzene is usually inert in this reaction without metal catalyst)

Group VIIB: Fe, Ru, Os



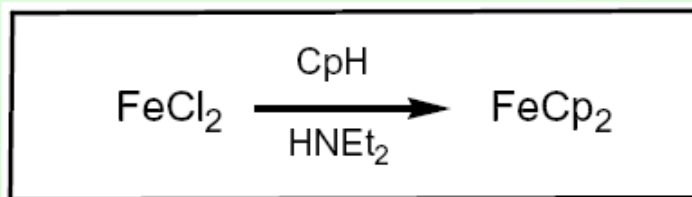
-Oxidation states from -2 to +4 for Fe and Ru and from -2 to +2 for Os

- 0 and +2 are more typical

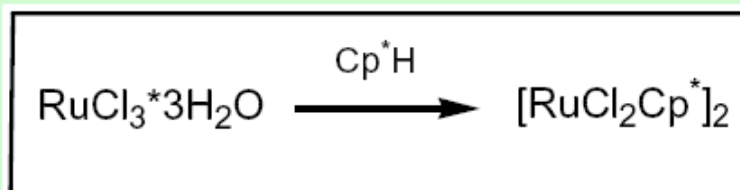
-Ligands like CO, phosphines – are very popular for the organometallic complexes of Fe, Ru, Os

Synthesis:

1. Metallation of hydrocarbons:

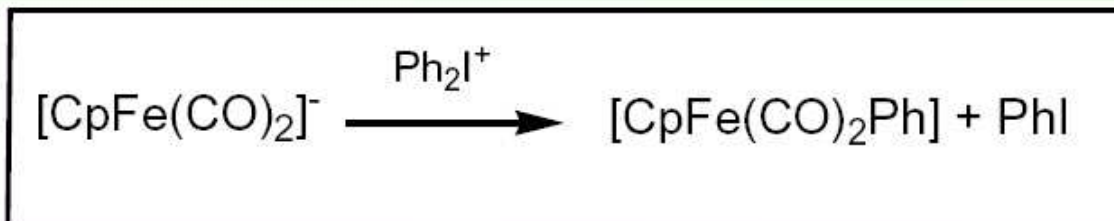


FeCp_2 – orange crystals, stable on air. NMR ^1H : $\delta(\text{C}_5\text{H}_5) = 4.01$ ppm



$[\text{RuCl}_2\text{Cp}^*]_2$ – dark-brown crystals. NMR ^1H : $\delta(\text{CH}_3) = 4.90$ ppm

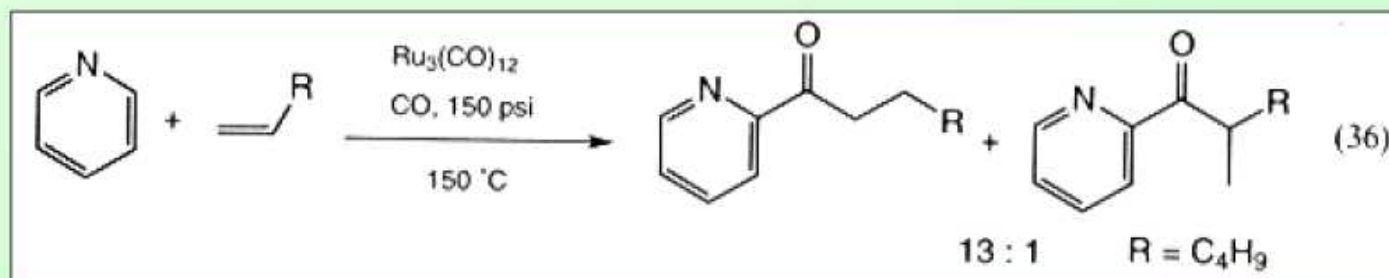
2. Electrophilic attack on the metal:



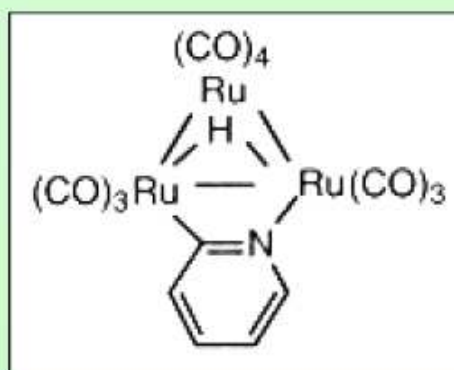
Application:

C-H bond activation

a) Aromatic C-H bonds:

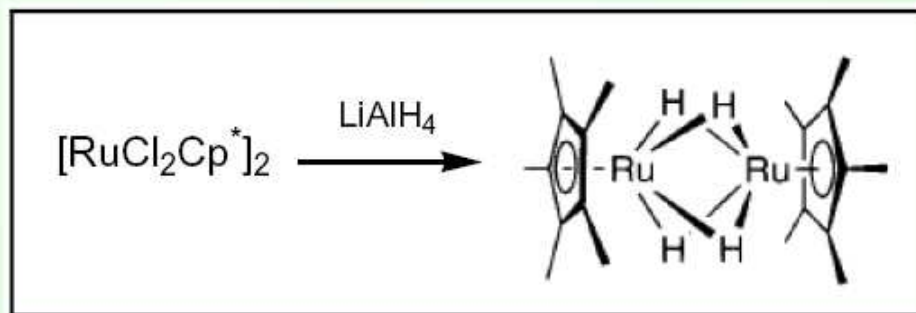


Intermediate:

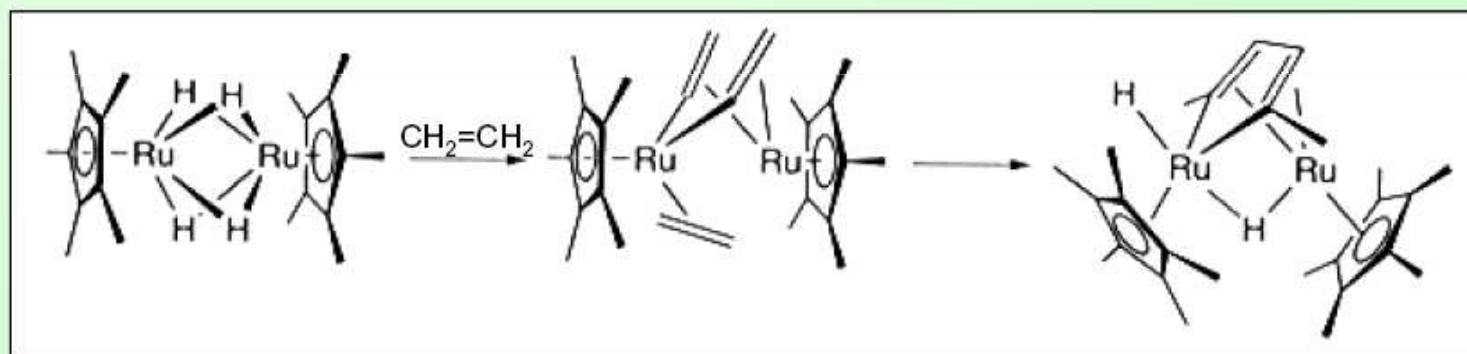


b) Vinylic C-H bonds:

Tetrahydride diruthenium complex, which can be obtained by the reaction:



can activate C-H bonds of ethylene:



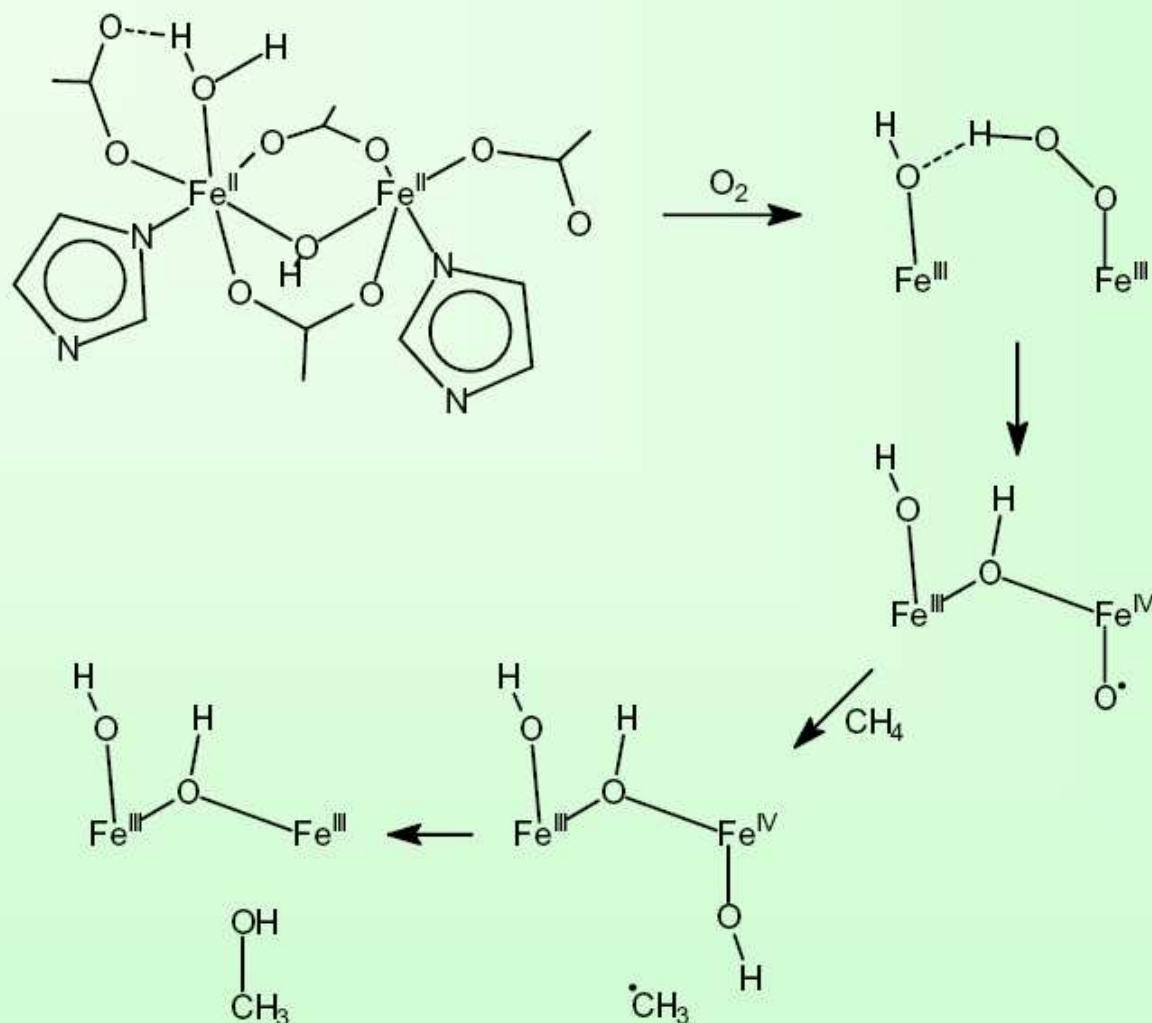
c) Aliphatic C-H bonds activation:

Certain metalloenzymes can break alkane C-H bonds via homolytic C-H bond breaking to give carbon radicals. Abstraction of an H atom from the alkane is effected by a high reactive oxo group coordinated to a high valent iron center in the enzyme.

CH₄ to CH₃OH:

enzyme MMO - methane mono-oxygenase

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Selectivity: 3^o > 2^o > 1^o

Gif-system: model has been developed which act in the same way: iron dipyridil complex



Selectivity: 2^o > 3^o > 1^o

Group VIII B: Co, Rh, Ir



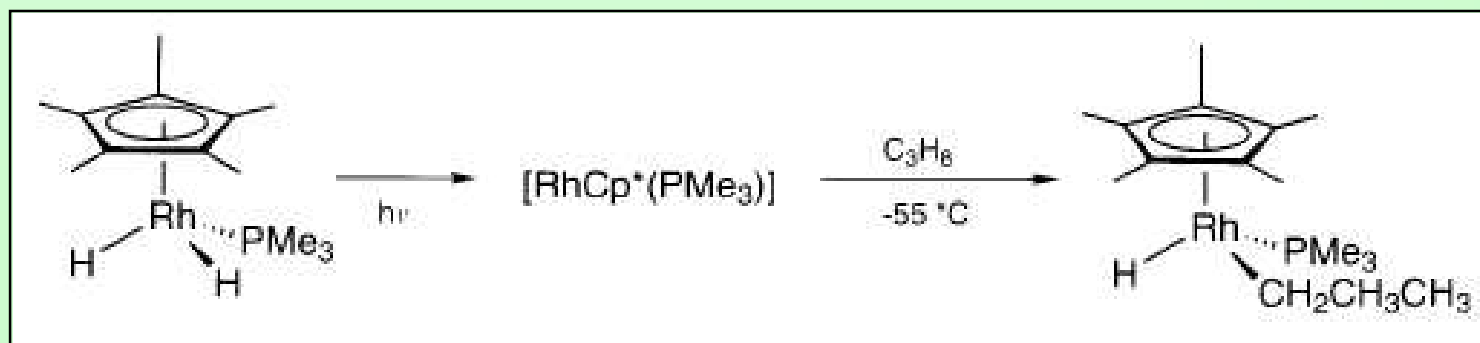
-Oxidation states from -3 to +4

- +1 and +3 are most stable

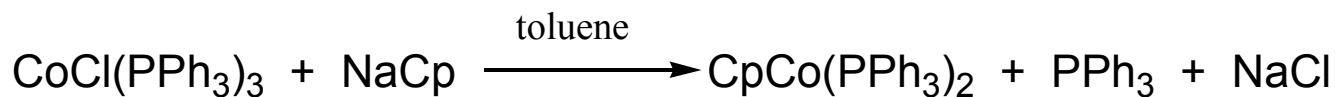
- π -acidic ligands like CO, phosphines, alkenes – are very popular for the organometallic complexes of Co, Rh, Ir

Synthesis:

Direct activation of the C-H bond:



2) Using Li, Na, Mg – organic compounds



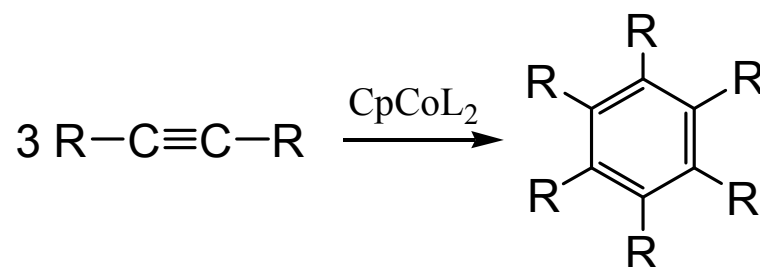
$\text{CpCo}(\text{PPh}_3)_2$ – black crystals (should be stored at low temperature under nitrogen, but short exposition to air at room temperature is possible)

$^1\text{H NMR}$: $\delta(\text{C}_5\text{H}_5) = 4.45 \text{ ppm}$



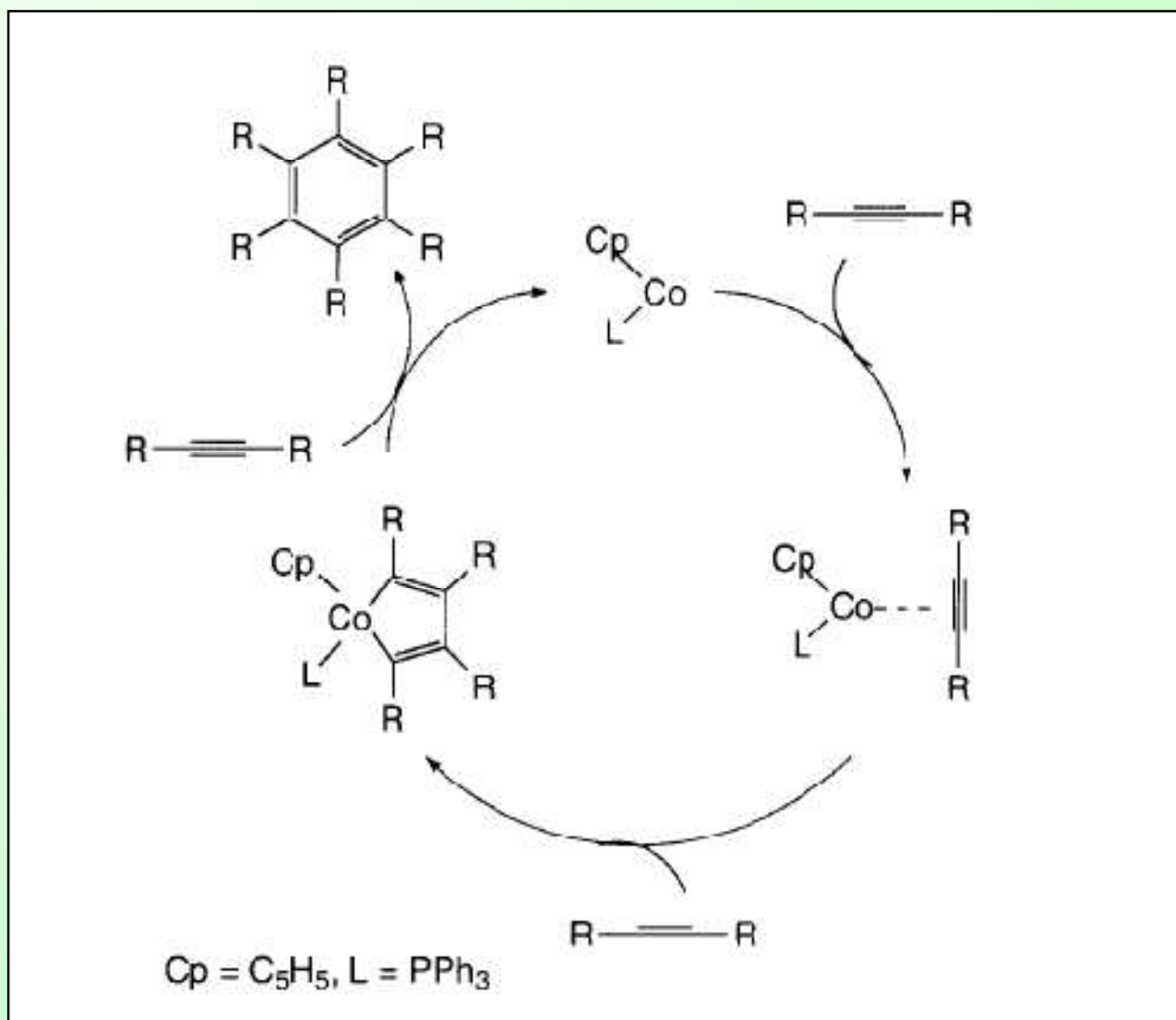
Reactivity:

1. Cyclotrimerization of alkynes with CoCpL_2 , $\text{L} = \text{PPh}_3, \text{CO}$, cyclooctadien (COD):

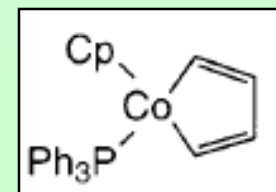


Mechanism:

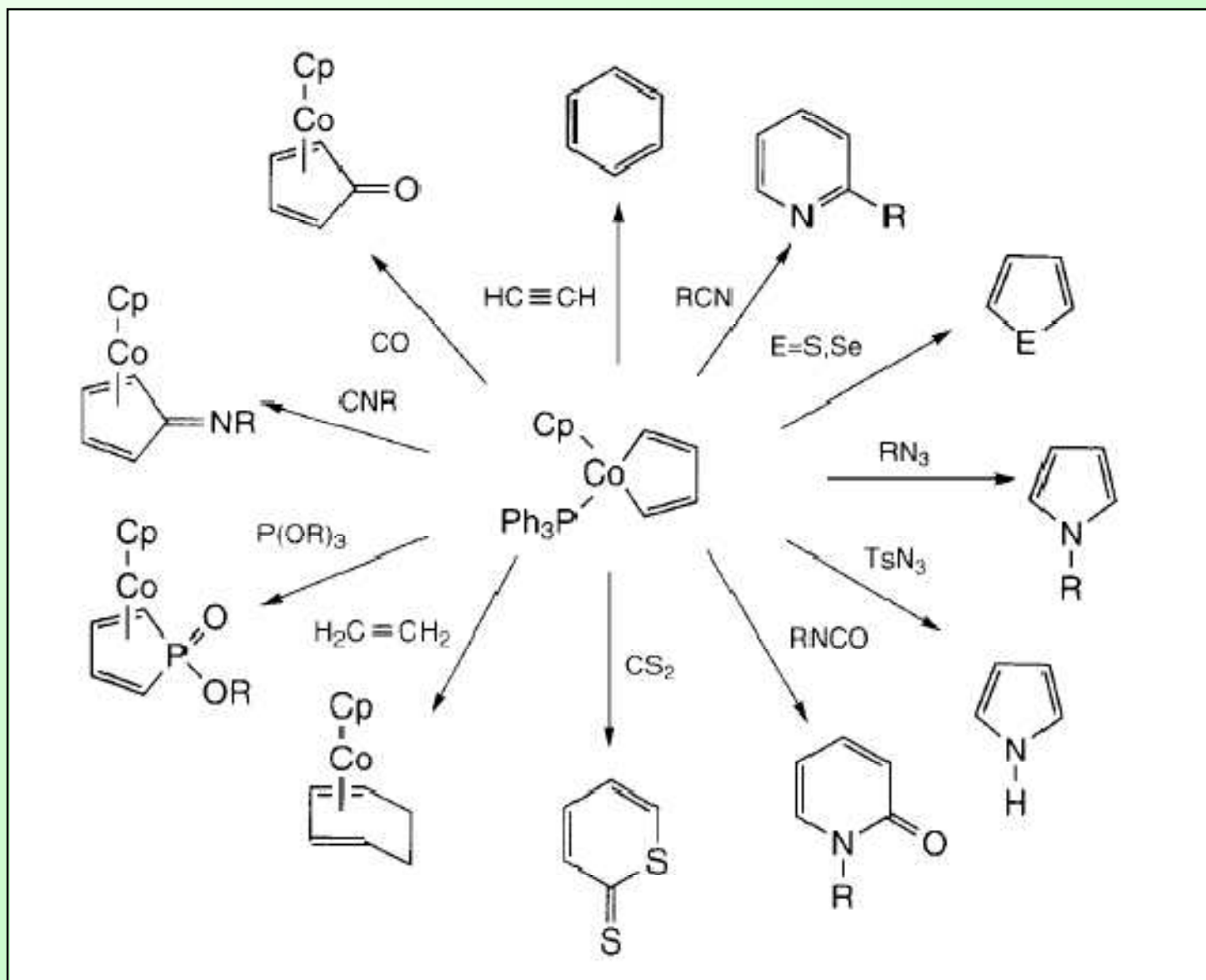
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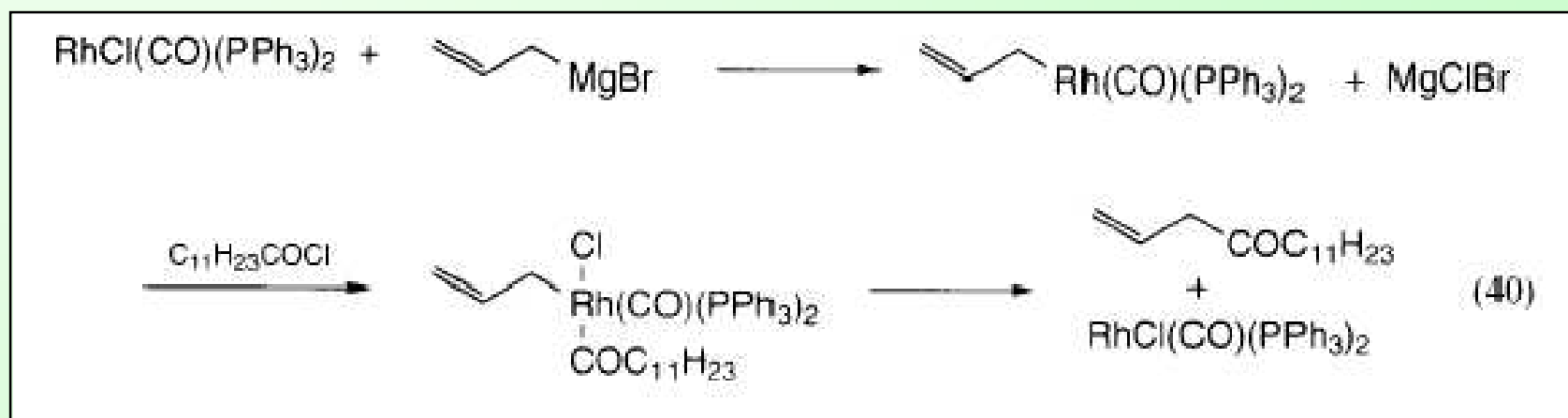
In the case of $CpCo(PPh_3)_2$ the catalytic intermediate cobaltocyclopentadiene complex can be isolated:



The cobaltocyclopentadiene can react with a variety of compounds containing multiple bonds to give cyclic products:



2. C-C bond formation using Rh-complexes:



In this cascade of 2 reactions $\text{RhCl(CO)(PPh}_3)_2$ can be recovered and reused.

Dimerization of terminal alkynes is promoted with $\text{RhCl(PPh}_3)_2$:



Group VIII B: Ni, Pd, Pt



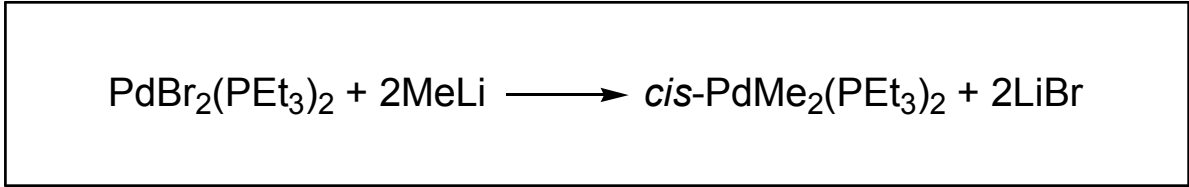
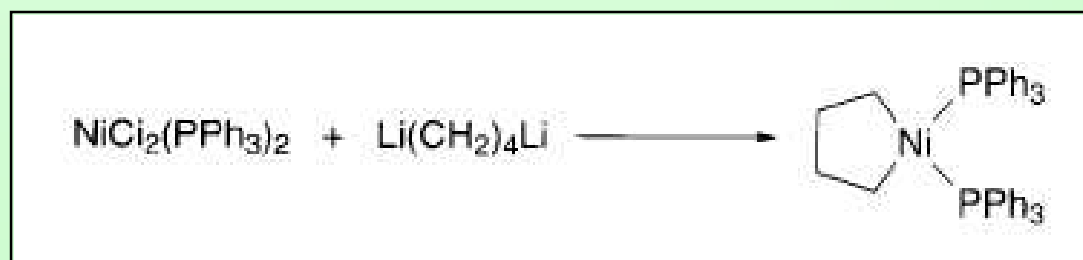
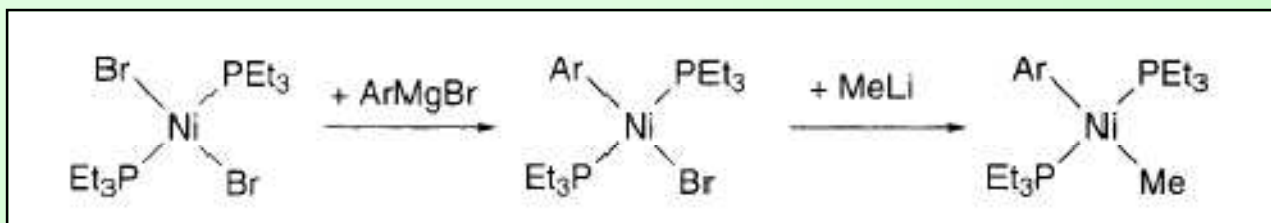
-Oxidation states from 0 to +4

- +2 is most stable

-Phosphines, alkenes – are very popular for the organometallic complexes of Ni, Pd, Pt

Synthesis:

1) Using Li, Mg, Al – organic compounds

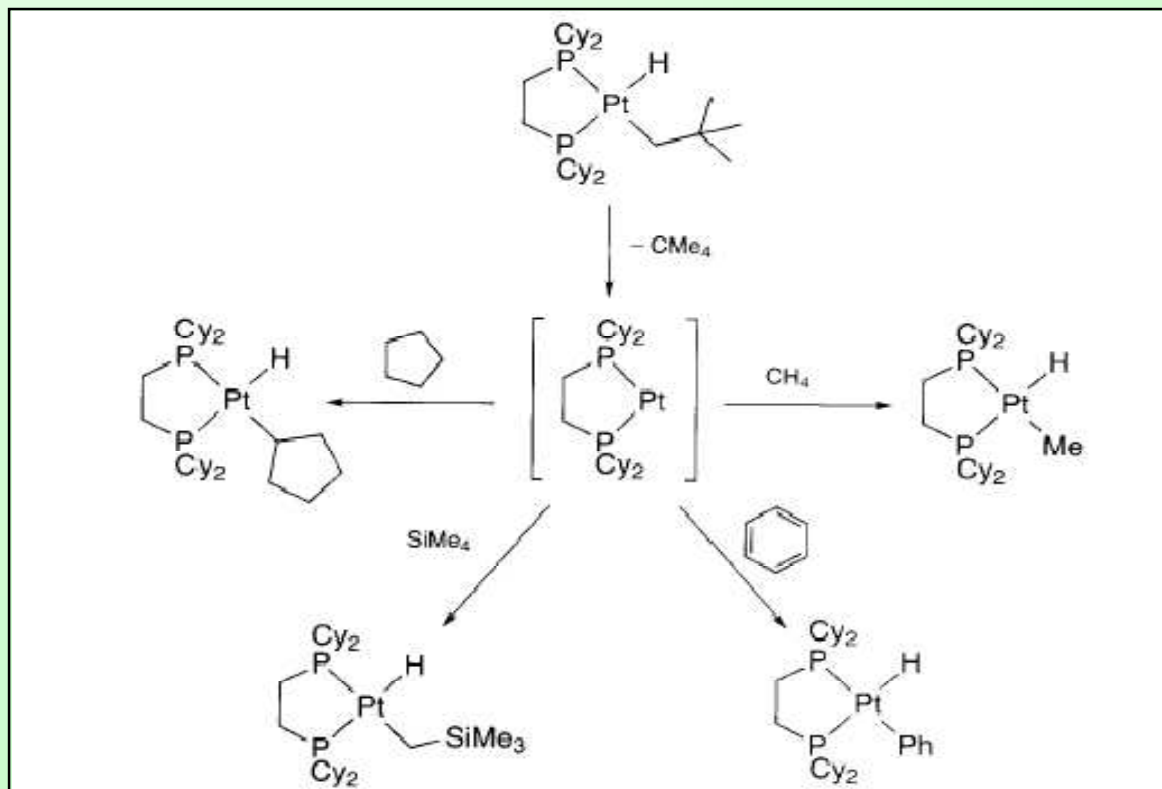
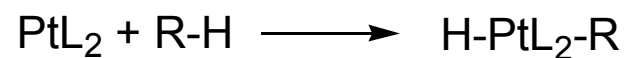


2) Oxidative addition of C-Halogen bond to Ni, Pd, Pt(0) compounds:



R = alkyl, aryl, alkenyl, benzyl; X = Cl, Br, I, OTf

3) Oxidative addition of C-H bond to Pd, Pt(0) compounds:



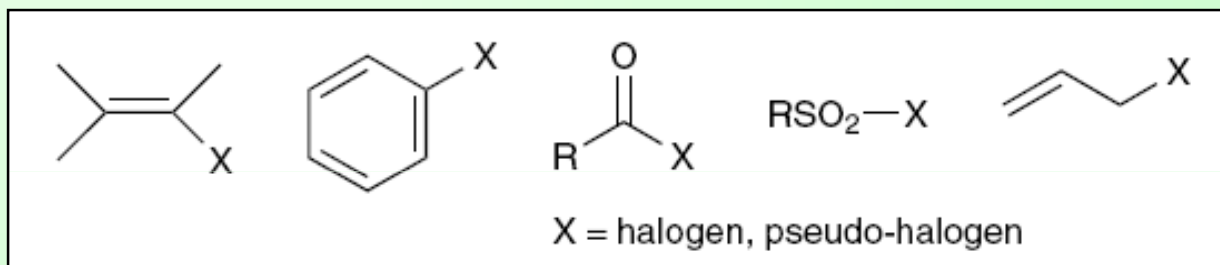
Reactivity:



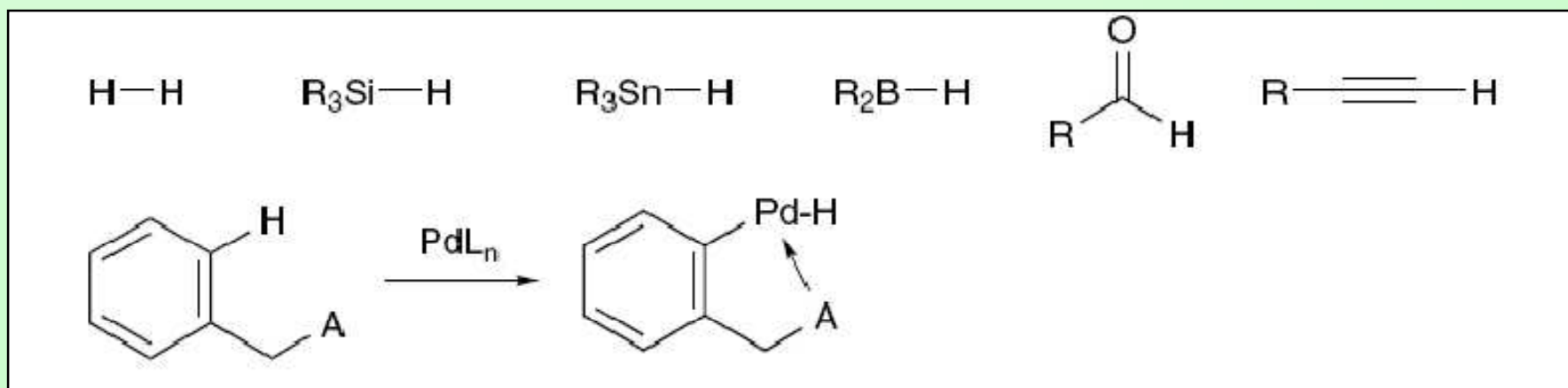
1. Oxidative addition to M(0). This is an important step in many catalytic processes.



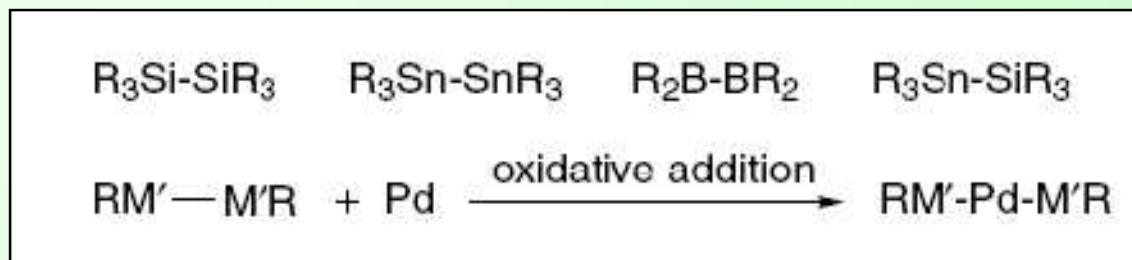
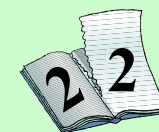
Not only acyl halides but also other compounds can undergo oxidative addition:



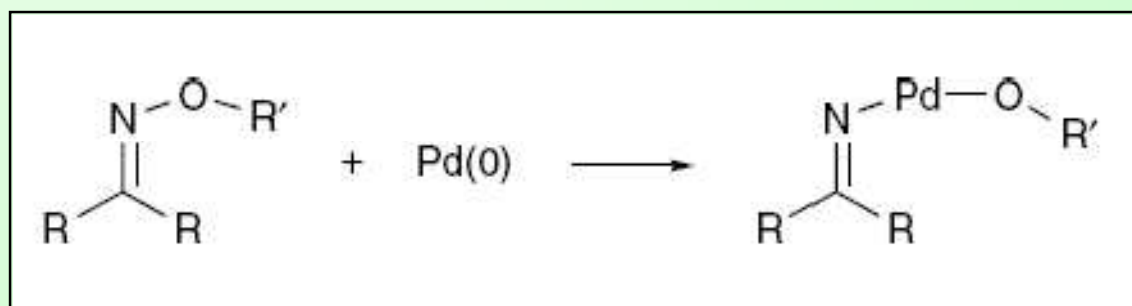
C-H substrates which can undergo oxidative addition to Pd(0):



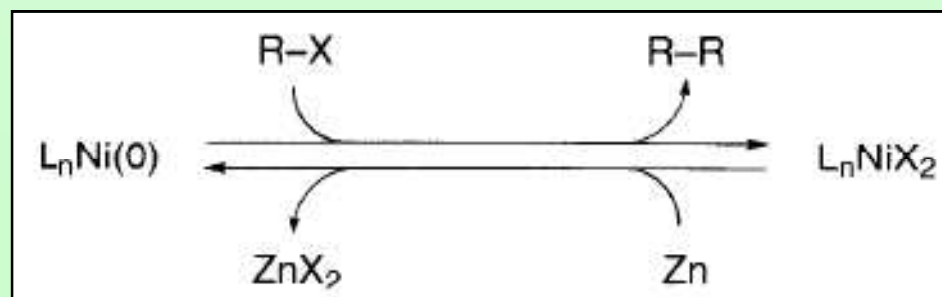
Substrates with element-element bond which can undergo oxidative addition to Pd(0):

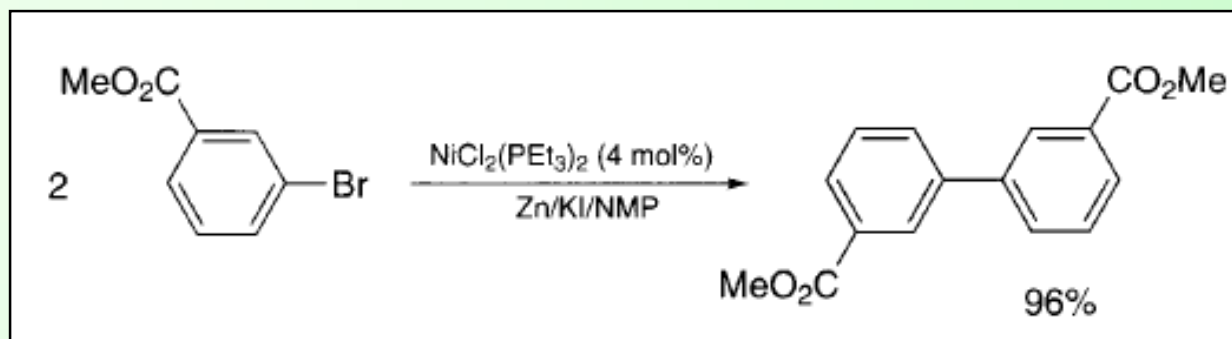


N-O bond in oximes can also undergo oxidative addition to Pd(0):



Ni^{II}/Zn⁰ system was elaborated for the C-C coupling which includes oxidative Addition to Ni⁰:

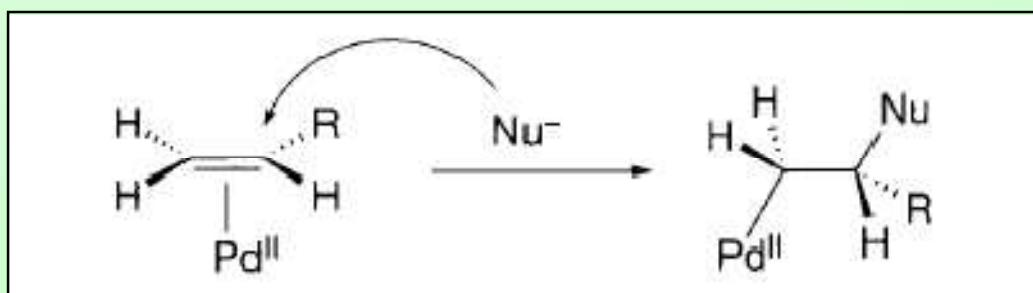




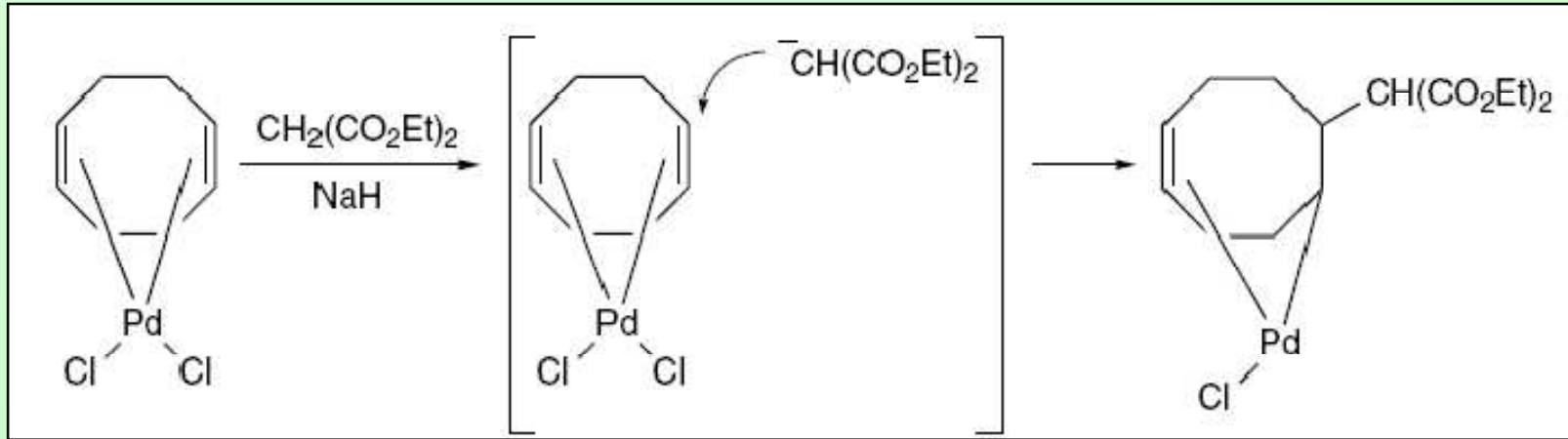
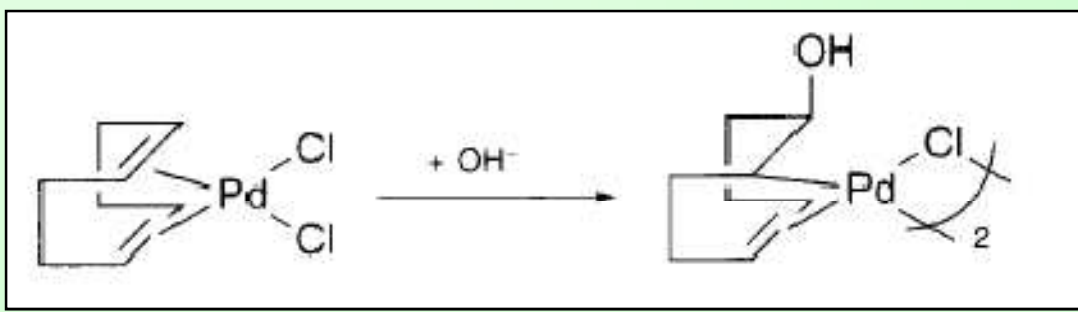
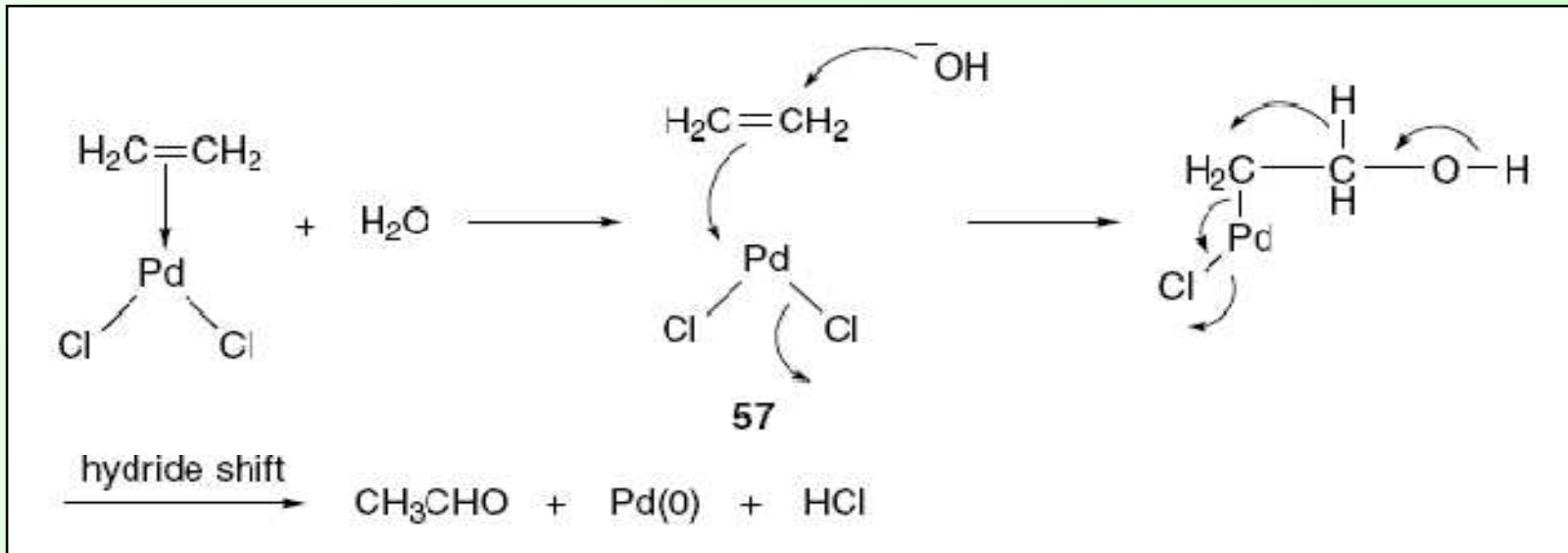
2. Reactions in the coordination sphere: organopalladium(II) species and nucleophiles

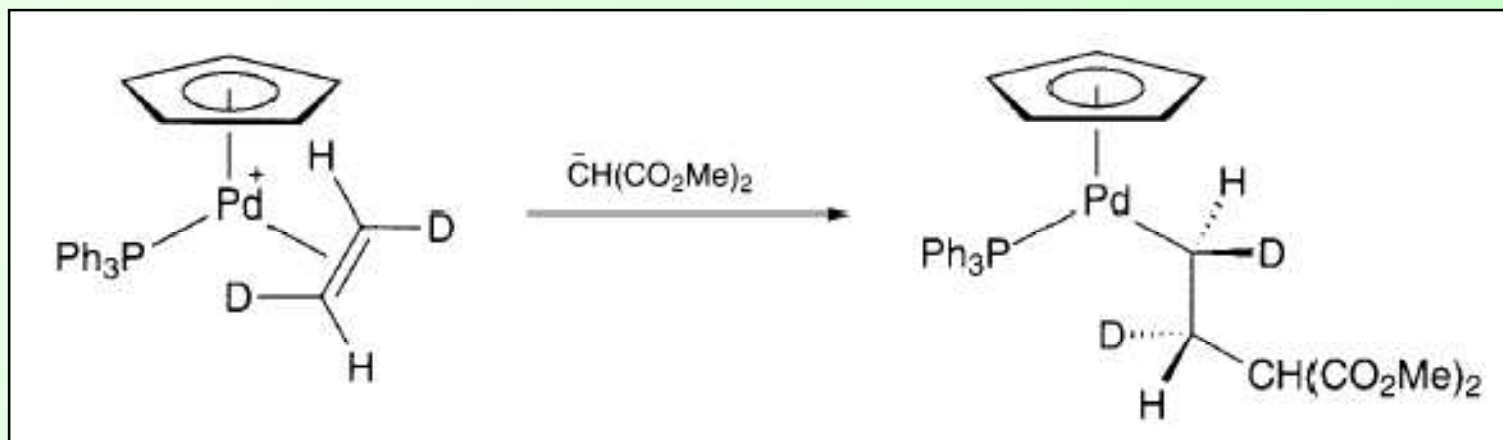
CO
alkenes
alkynes } are rather unreactive towards nucleophiles because they are electron rich

However, their reactivity is inverted when coordinate to electron deficient Pd(II)

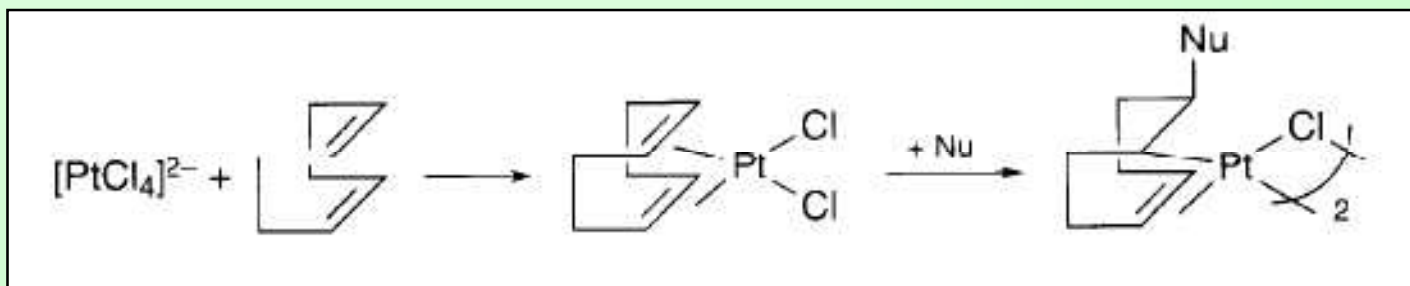


In the case of non-symmetrical alkenes the attack of a nucleophile takes place at the more substituted vinylic carbon atom





Coordination of alkenes to platinum(II) also facilitates a nucleophile attack:



Nu = alkoxides, amines, carboxilates.

Physical Methods in Organometallic Chemistry



NMR of organometallic Compounds

- The metal
- The organic groups (alkyl/aryl)
- The other ligands
- Coupling with heteronuclei



Metal complexes:



Diamagnetic:

Metal complexes with no unpaired electrons will behave similarly to organic materials.

Requires an **even** electron count and a low-spin configuration with no unpaired electrons.

Examples of diamagnetic metal centers:

d^0 , d^4 (low spin, tetrahedral), d^6 (low spin), d^8 (square planar), d^{10}

Paramagnetic:

Metal complexes with **odd** electron counts or high spin configurations with one or more unpaired electrons are paramagnetic.

The paramagnetic metal center will significantly affect the chemical shift (^1H chemical shifts of +200 to -200 are quite possible). In addition, the paramagnetic center will often **broaden** the peak, often to the point where it is practically unobservable.

Nucleus	Spin	Natural Abundance (%)	Frequency $^1\text{H} = 100 \text{ MHz}$	Receptivity $^{13}\text{C} = 1$
Ligands				
^1H	1/2	99.99	100	5870
^{13}C	1/2	1.1	25.15	1.00
^{19}F	1/2	100	94.1	4900
^{31}P	1/2	100	40.5	391
Metals				
^{103}Rh	1/2	100	4.9	0.68
^{107}Ag	1/2	51.8	4.05	0.20
^{109}Ag	1/2	48.2	4.65	0.28
^{195}Pt	1/2	33.8	21.4	20.1

The organic groups (alkyl/aryl)



Alkyl groups

- at main group metals:
 - shift to high field (compared to a H or CH₃ substituent):
0-4 ppm in ¹H, 0-15 ppm in ¹³C
 - the metal is a σ -donor!
- at transition metals:
 - larger high-field shift for metals with a partially filled *d* shell

Aryl groups

usually low-field shift of *ortho* H and *ipso* and *ortho* C

Hydrides

extreme high-field shift (up to 100 ppm) for metals with a partially filled *d* shell.

Example of hydride NMR signal description:

δ -10.44 (d, ²J(P,H) = 15.0 Hz, 1H, H_a)

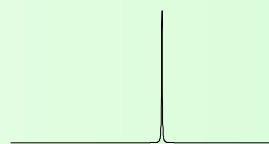
splitting J constant integration assignment

Coupling to heteronuclei



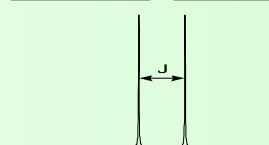
M-CH₃

M NMR-inactive



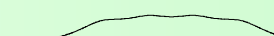
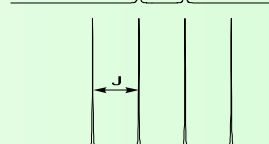
Pd-CH₃

M S = 1/2



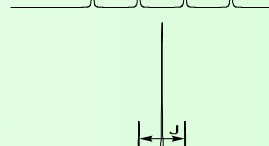
Rh-CH₃

M S = 3/2



Cu-CH₃

M 30% S = 1/2

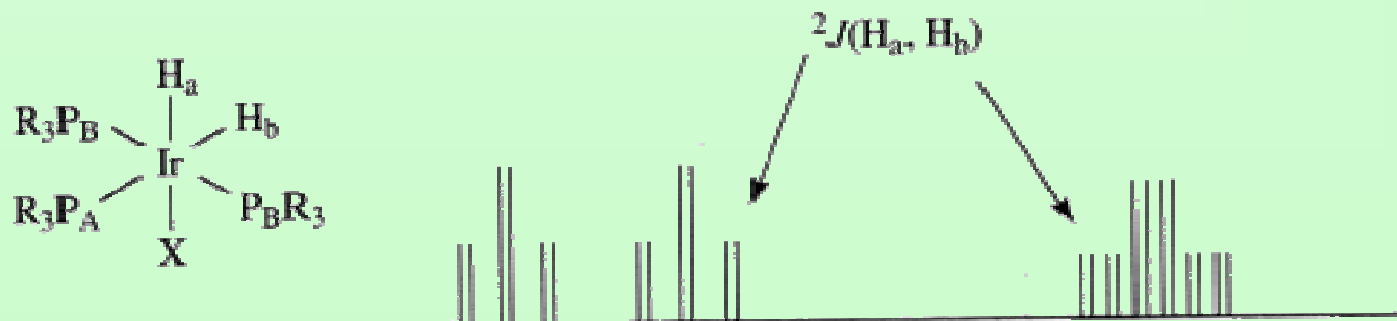
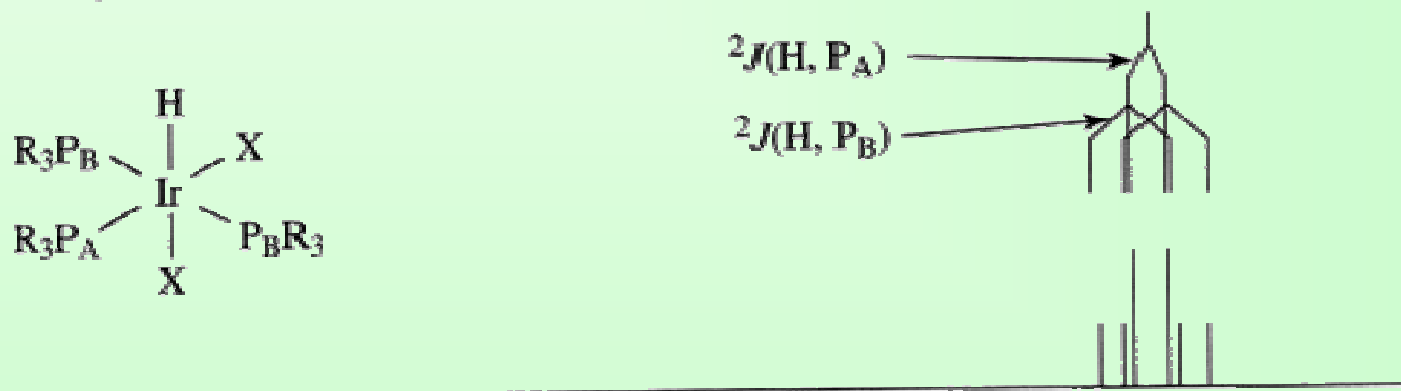
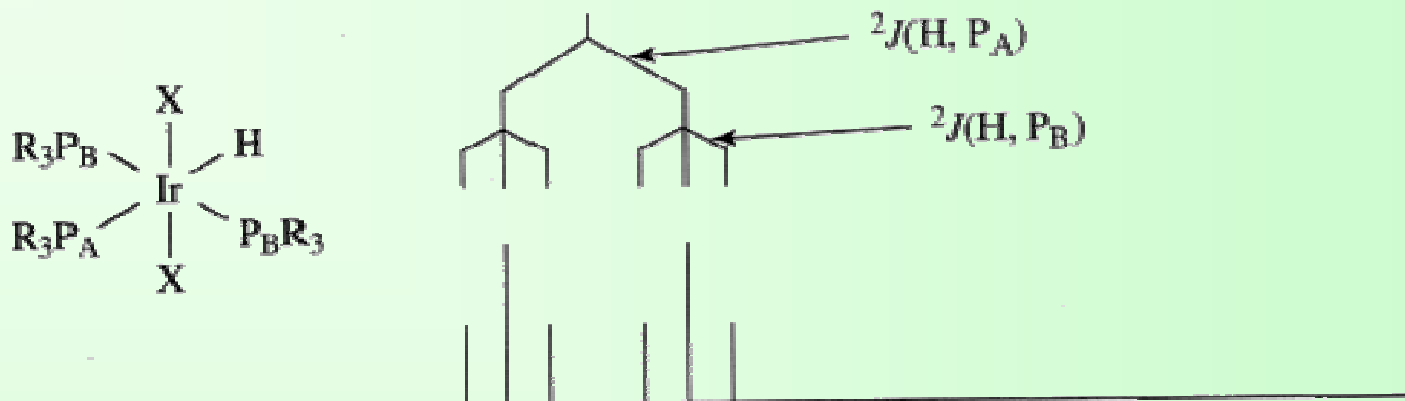


Pt-CH₃

¹⁹⁵ Pt Coupling	Typical Range (Hz)	¹⁰³ Rh Coupling	Typical Range (Hz)
¹ J(¹⁹⁵ Pt- ¹ H)	700-1370	¹ J(¹⁰³ Rh- ¹ H)	15-30
¹ J(¹⁹⁵ Pt- ¹³ C)	850-2500 (CO, CNR) 38-429 (alkyl, aryl)	¹ J(¹⁰³ Rh- ¹³ C)	55-85 (CO, CNR) 11-43 (alkyl, aryl)
¹ J(¹⁹⁵ Pt- ³¹ P)	1000-4000	¹ J(¹⁰³ Rh- ³¹ P)	74-194
¹ J(¹⁹⁵ Pt- ¹⁹ F)	200-2000	¹ J(¹⁰³ Rh- ¹⁹ F)	50

The ²J_{L-L} coupling constant is strongly dependent on the L-M-L angle. The coupling will be largest when the angle is 180° (trans) and will be at a minimum when the angle is 90°.

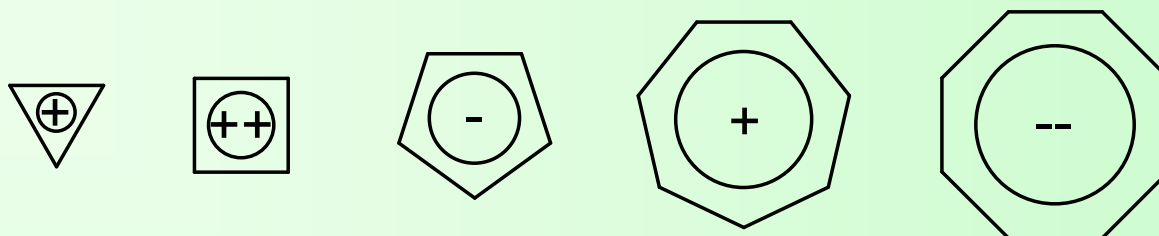
Trans coupling (90-160 Hz) / cis coupling (10-30 Hz)



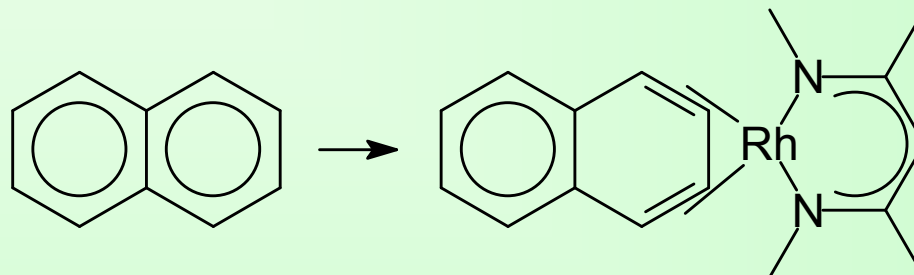
The other ligands



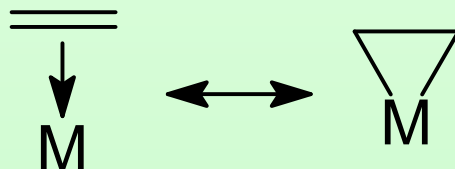
- Charged ligands usually become aromatic



- Arenes become less aromatic and sometimes more localized

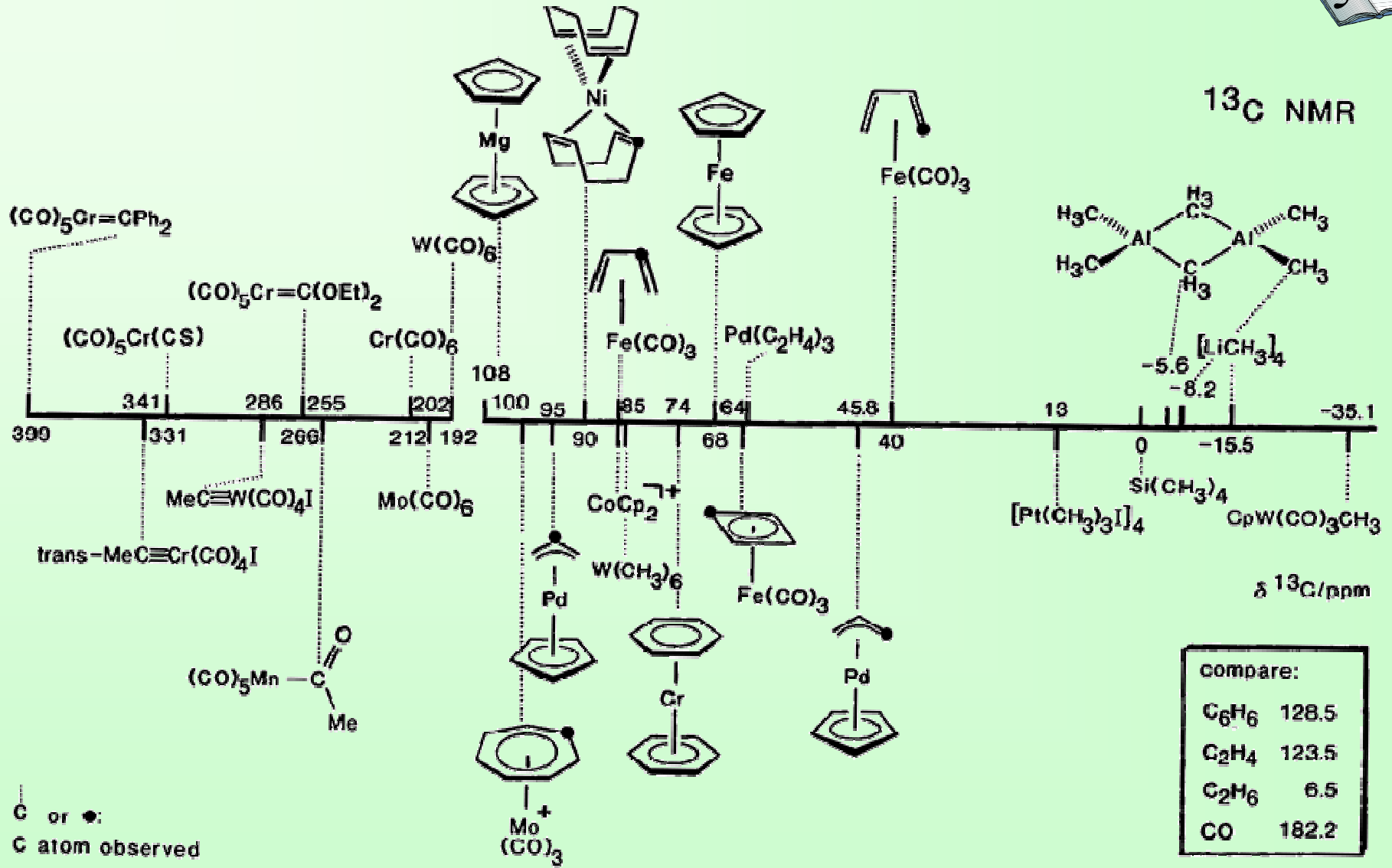


- Olefins shift to higher field (metallacyclopropane character!)

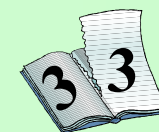


	free ethene	coordinated ethene	cyclopropane
^1H	5.2	1-3	0.2
^{13}C	122	40-90	-3

¹³C-NMR:

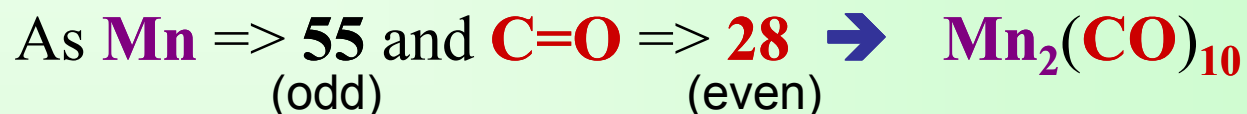


MS of organometallic Compounds



It is often possible to determine molecular weight of a compound by MS

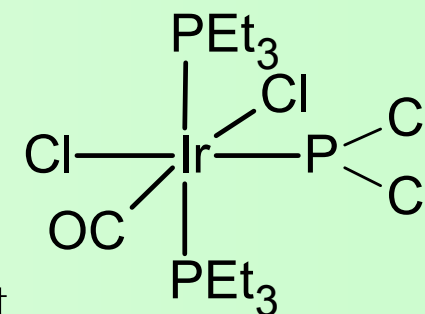
For example: **Manganese carbonyl** => **m/z 390**



Another example: Iridium complex

NMR and IR can give a lot of information but without MS it is very difficult to show the presence of Cl.

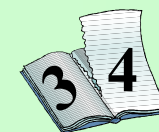
With MS, it is easy to show that 4 chlorine atoms are present



Molecular ion is usually present with Laser desorption. However, ions produced that way comes from condensed phase (solid/liquid) and structure in these phase might be very different from the one in gaz phase.

With FAB (Fast Atom Bombardment) most intense cation peak is the protonation ion (M+1) peak. Anion (M-1) can also be formed.

IR of organometallic Compounds



Bond Stretching Frequencies: Hydrogen

Hydrogen: all bond stretch occur in the range:

4000 to 1700 cm^{-1} (for H-F down to H-Pb)

Going down any main group in periodic table increase the mass
And decrease the bond strength \Rightarrow Lowering stretching Frequency

From Left to right along a row: the effect of increasing the mass is outweighed
by the increase in Bond strength \Rightarrow Frequency increase

Increase (cm^{-1})

Decrease (cm^{-1})

Typical M—H Bond Stretching Frequencies for *p*-block Elements

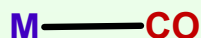
B	2300	C	3000	N	3400*	O	3700*	F	3962*
Al	1800	Si	2200	P	2350	S	2600	Cl	2836
Ga	1850	Ge	2100	As	2200	Se	2350	Br	2559
		Sn	1850	Sb	1900	Te	2070	I	2230

*Note: normally reduced considerably by hydrogen bonding in condensed phases.

Bond Stretching Frequencies: CO-ligand

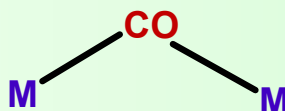


Terminal



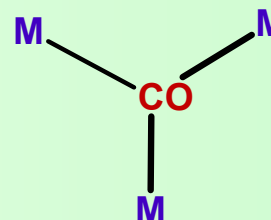
2130 – 1700 cm^{-1}

Bridging



1900 – 1780 cm^{-1}

Triple Bridge



1900 – 1780 cm^{-1}

We can therefore state: CO above 1900 => terminal CO

Below 1900 : Can be due to bridging CO or terminal CO with unusual reduction of CO strength (d -> π^* back bonding)

Isotopic substitution:

- A band at ~2000 cm^{-1} may be due to M-H or M-CO
- Changing H to D we can distinguish between these two situations

At about $2000/\sqrt{2} = 1414 \text{ cm}^{-1}$

$$\nu = \frac{1}{2\pi c} \left\{ \sqrt{\frac{k}{m_r}} \right\}$$

(where c = the velocity of light)

$$m_r = \frac{m_1 m_2}{m_1 + m_2}$$

Some IR bands of $\text{Co}(\text{CO})_4\text{H}$



$\text{Co}(\text{CO})_4\text{H}$	$\text{Co}(\text{CO})_4\text{D}$	Assignment
2121	2120	$\nu(\text{CO})$
2062	2058	
2043	2043	
1934	1396	$\nu(\text{CoH}, \text{D})$
703	600	deformations involving H-atom motion
505	482	
403	393	
331	296	

$1934/\sqrt{2} = 1367 \text{ cm}^{-1}$, close to experiment: **1396** cm^{-1}