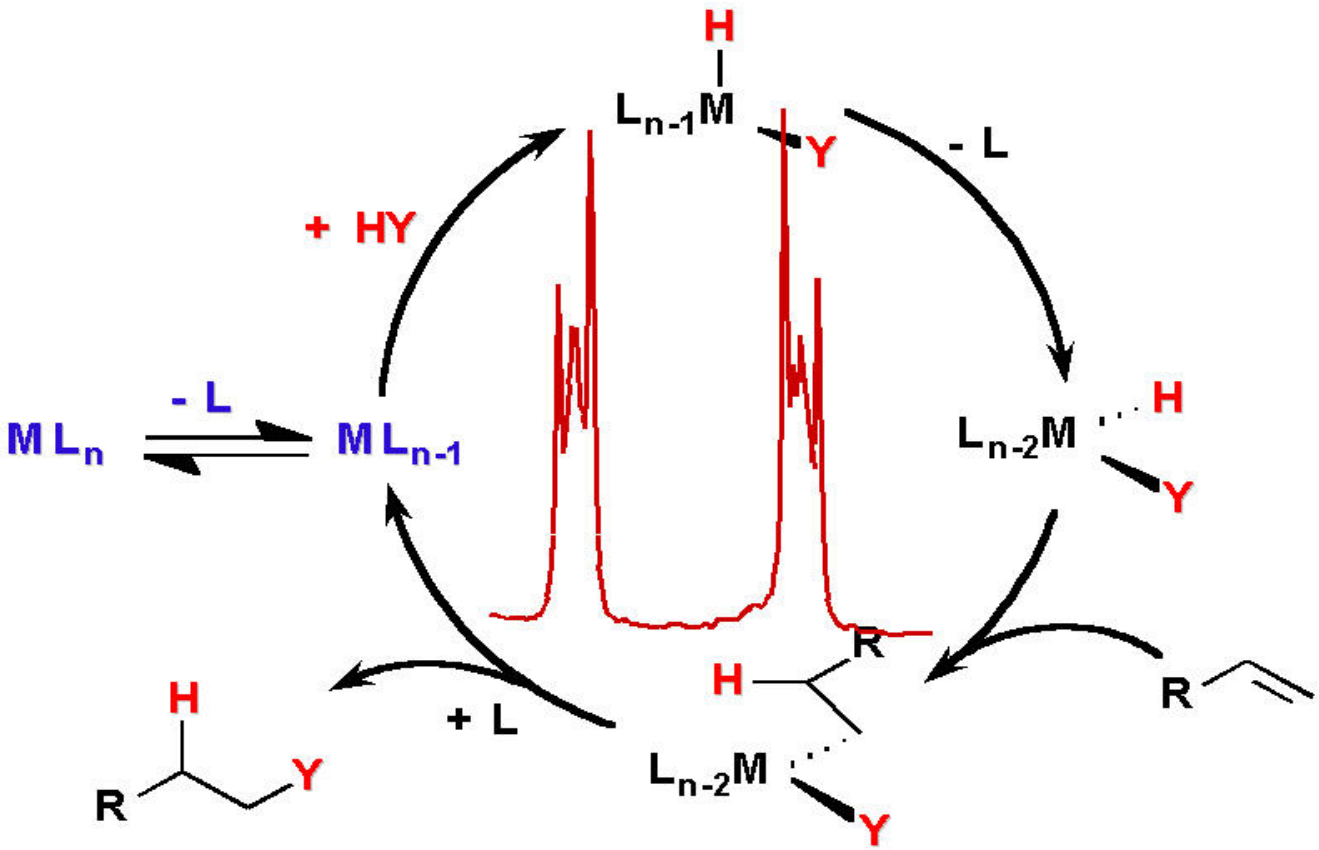
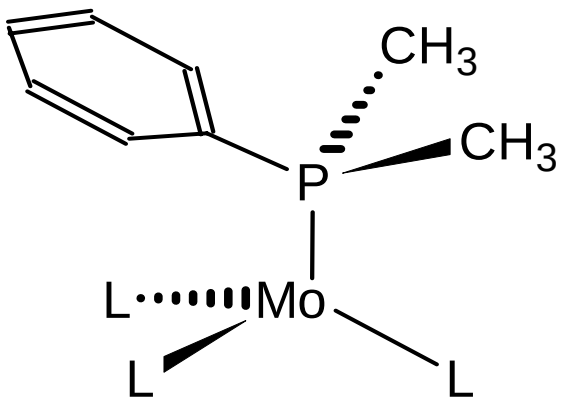
Inorganic Chemistry
6BA40



Organometallic Compounds, d-Block
Woe, 29-10-2008 (H24 Selected Topics)

The 18 electron rule & catalysis

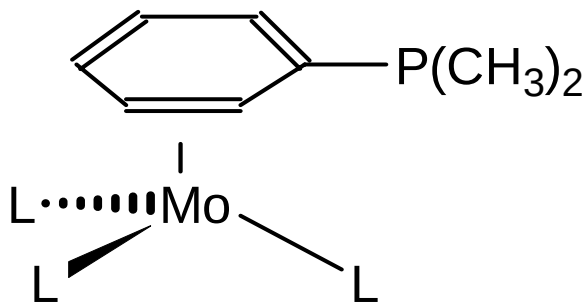
- **18 e complexes are unwanted in catalysis**
- **They are either catalyst precursors, resting states in a catalytic cycle or just a bad proposal**
- **<<18 e complexes should be closer examined (except for early transition metals).**



presumed 14-e complex

– **Chatt, 1971 (Mo, 6e)**

versus



18-e complex with unexpected η^6-arene coordination

Types of M-C Bonds in the Periodic Table

Key: element name / atomic number / symbol / 1997 atomic weight (mean relative mass)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 H 1.00794(7)																	helium 2 He 4.002602(2)
lithium 3 Li 6.941(2)	beryllium 4 Be 9.012182(3)											boron 5 B 10.811(7)	carbon 6 C 12.0107(8)	nitrogen 7 N 14.00674(7)	oxygen 8 O 15.9994(3)	fluorine 9 F 18.9984032(5)	neon 10 Ne 20.1797(6)
sodium 11 Na 22.989770(2)	magnesium 12 Mg 24.3050(6)											aluminium 13 Al 26.981538(2)	silicon 14 Si 28.0855(3)	phosphorus 15 P 30.973761(2)	sulfur 16 S 32.066(6)	chlorine 17 Cl 35.4527(9)	argon 18 Ar 39.948(1)
potassium 19 K 39.0983(1)	calcium 20 Ca 40.078(4)		scandium 21 Sc 44.955910(8)	titanium 22 Ti 47.867(1)	vanadium 23 V 50.9415(1)	chromium 24 Cr 51.9961(6)	manganese 25 Mn 54.938049(9)	iron 26 Fe 55.845(2)	cobalt 27 Co 58.933200(9)	nickel 28 Ni 58.6934(2)	copper 29 Cu 63.546(3)	zinc 30 Zn 65.39(2)	gallium 31 Ga 69.723(1)	germanium 32 Ge 72.61(2)	arsenic 33 As 74.92160(2)	selenium 34 Se 78.96(3)	bromine 35 Br 79.904(1)	krypton 36 Kr 83.80(1)
rubidium 37 Rb 85.4678(3)	strontium 38 Sr 87.62(1)		yttrium 39 Y 88.905850(7)	zirconium 40 Zr 91.224(2)	niobium 41 Nb 92.906380(7)	molybdenum 42 Mo 95.94(1)	technetium 43 Tc [97.9072]	ruthenium 44 Ru 101.07(2)	rhodium 45 Rh 102.905500(9)	palladium 46 Pd 106.42(1)	silver 47 Ag 107.8682(2)	cadmium 48 Cd 112.411(8)	indium 49 In 114.818(3)	tin 50 Sn 118.710(7)	antimony 51 Sb 121.760(1)	tellurium 52 Te 127.60(3)	iodine 53 I 126.90447(3)	xenon 54 Xe 131.29(2)
caesium 55 Cs 132.90545(2)	barium 56 Ba 137.327(7)	57-70 *	lutetium 71 Lu 174.967(1)	hafnium 72 Hf 178.49(2)	tantalum 73 Ta 180.94788(2)	tungsten 74 W 183.84(1)	rhenium 75 Re 186.207(1)	osmium 76 Os 190.23(3)	iridium 77 Ir 192.217(3)	platinum 78 Pt 195.078(2)	gold 79 Au 196.96655(2)	mercury 80 Hg 200.59(2)	thallium 81 Tl 204.3833(2)	lead 82 Pb 207.2(1)	bismuth 83 Bi 208.98038(2)	polonium 84 Po [208.9824]	astatine 85 At [209.9871]	radon 86 Rn [222.0176]
francium 87 Fr [223.0197]	radium 88 Ra [226.0254]	89-102 **	lawrencium 103 Lr [262.110]	rutherfordium 104 Rf [261.1108]	dubnium 105 Db [262.1144]	seaborgium 106 Sg [263.1213]	bohrium 107 Bh [264.1247]	hassium 108 Hs [265.1301]	meitnerium 109 Mt [268.1388]	ununnilium 110 Uun [269.1451]	unununium 111 Uuu [272.1535]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]		ununhexium 116 Uuh [289]		ununoctium 118 Uuo [293]

*lanthanoids	lanthanum 57 La 138.90550(2)	cerium 58 Ce 140.116(1)	praseodymium 59 Pr 140.90765(2)	neodymium 60 Nd 144.24(3)	promethium 61 Pm [145.9127]	samarium 62 Sm 150.36(3)	europium 63 Eu 151.964(1)	gadolinium 64 Gd 157.25(3)	terbium 65 Tb 158.92534(2)	dysprosium 66 Dy 162.50(3)	holmium 67 Ho 164.93032(2)	erbium 68 Er 167.26(3)	thulium 69 Tm 168.93421(2)	ytterbium 70 Yb 173.04(3)
**actinoids	actinium 89 Ac [227.0277]	thorium 90 Th 232.03806(2)	protactinium 91 Pa 231.03588(2)	uranium 92 U 238.02891(3)	neptunium 93 Np [237.0482]	plutonium 94 Pu [244.0642]	americium 95 Am [243.0614]	curium 96 Cm [247.0703]	berkelium 97 Bk [247.0703]	californium 98 Cf [251.0796]	einsteinium 99 Es [252.0830]	fermium 100 Fm [257.0951]	mendelevium 101 Md [258.0986]	nobelium 102 No [259.1011]

- electron deficiency compounds
- ionic compounds
- d-metals, M-C σ-bonding and π-bonding
- covalent M-C σ-bonding
- metalloids
- non-metals

Early transition metals
Groups 3-4

Sc	Ti	
Y	Zr	
La	Hf	
Ac		

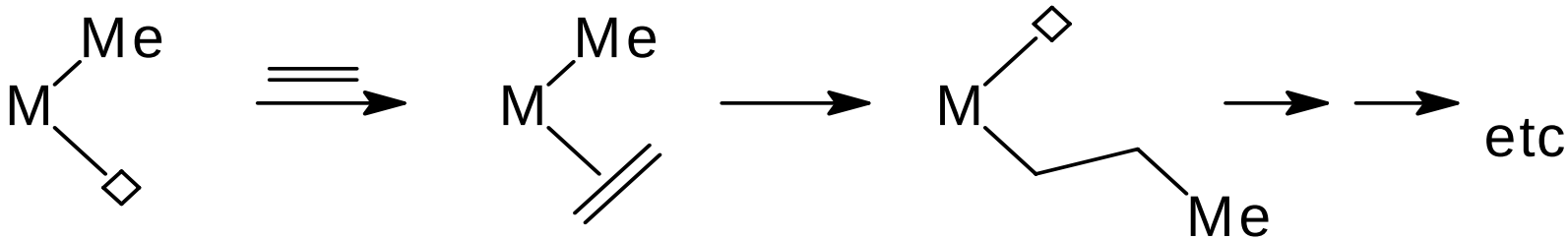
- **Strongly electrophilic and oxophilic**
- **Little redox chemistry (exception: Ti)**
- **Virtually always < 18*e* complexes**
- **Polar and very reactive M-C bonds**
- **Little *d*-electrons:**
  - **preference for "hard" s-donors**
  - **weak coordination to p-acceptors**

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

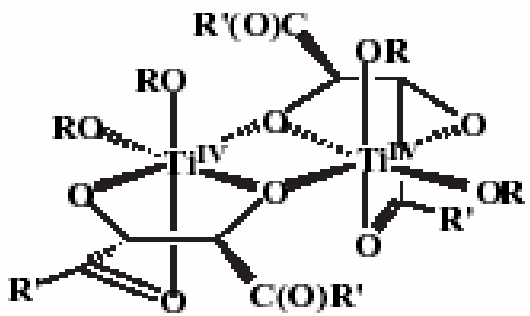
Early transition metals
Groups 3-4

Sc	Ti	
Y	Zr	
La	Hf	
Ac		

- **Typical catalysis: polymerization:**



Epoxidation:



Sharpless titanium-tartrate epoxidation catalyst

t-BuOOH, 4Å MS
CH_2Cl_2, -20°C

70-90% yield
94->98% *ee*

Sharpless *JACS* **1987** (109) 5765.

Middle transition metals
Groups 5-7

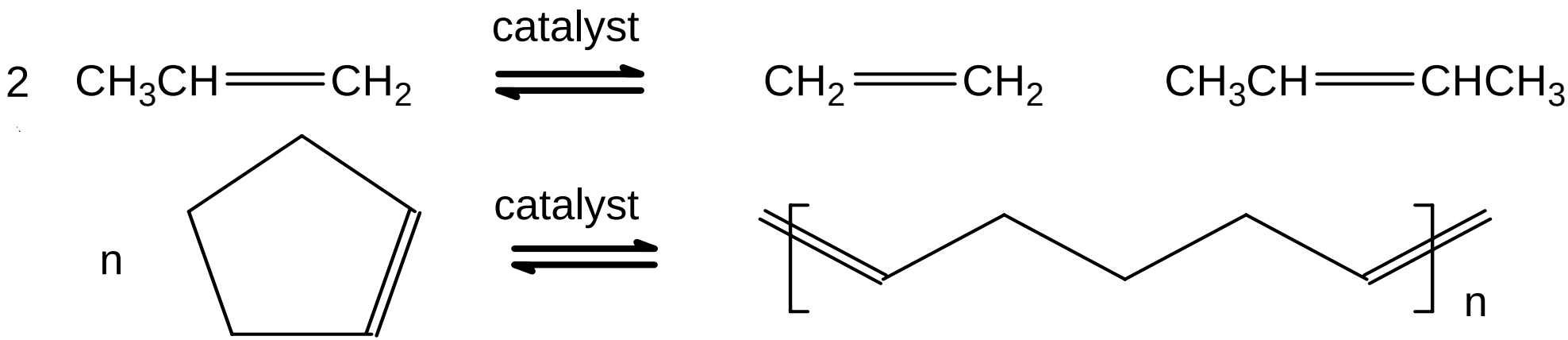
V	Cr	Mn
Nb	Mo	Tc
Ta	W	Re

- **Many oxidation states are accessible**
- **Mostly 18*e* complexes**
- **Ligands are strongly bound**
- **Strong, rather unreactive M-C bonds**
- **Preference for s-donor/p-acceptor combinations (CO!)**

Middle transition metals
Groups 5-7

V	Cr	Mn
Nb	Mo	Tc
Ta	W	Re

- **Typical catalysis: alkene and alkyne metathesis**



Late transition metals
Groups 8,9,10

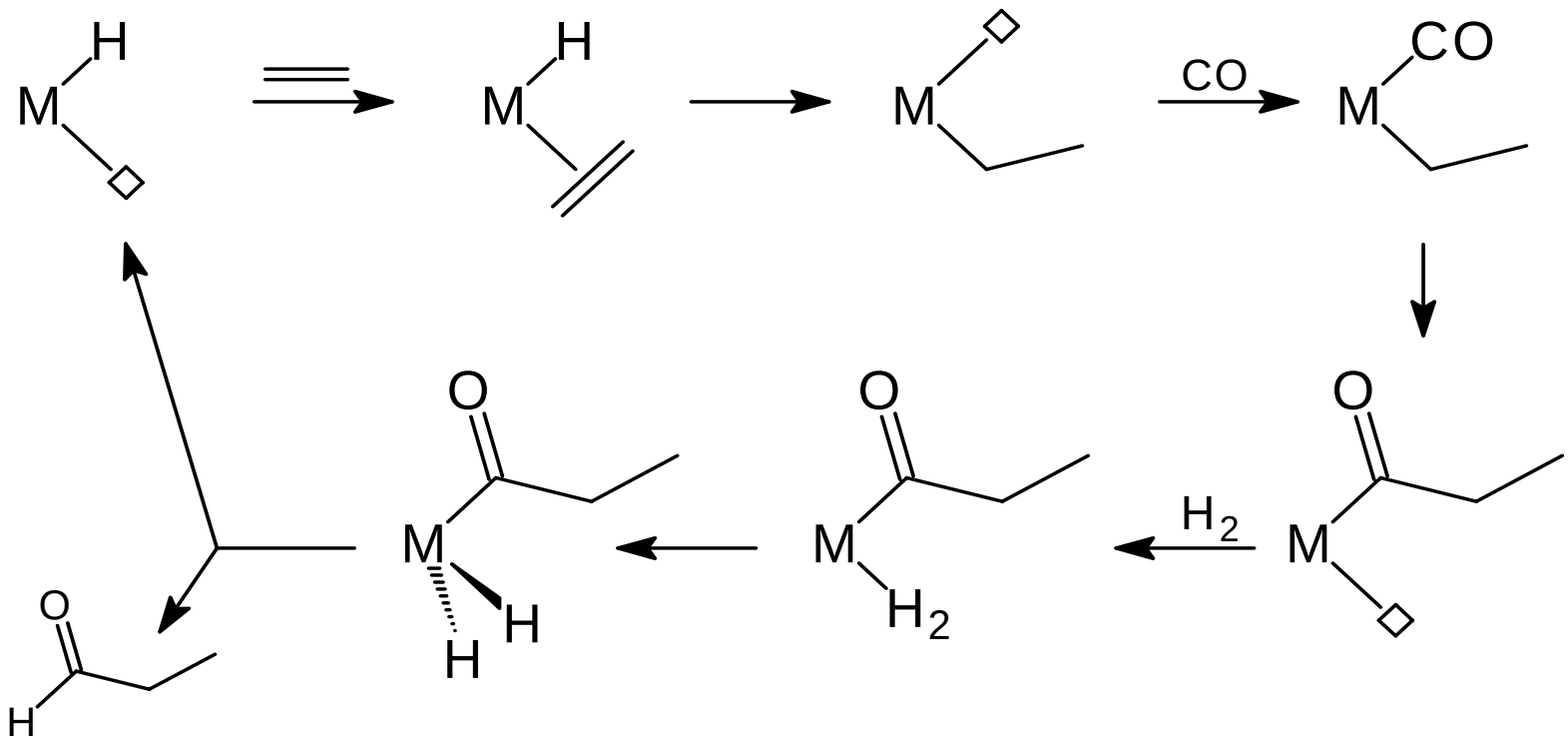
Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

- **Multiple oxidation states**
- **Mostly 18*e* of 16*e* complexes**
  - **16*e* typically square planar coordination**
- **Easy ligand association/dissociation**
- **Weak, not too reactive M-C bonds**
- **Even weaker, and reactive M-O/M-N bonds**
- **Preference for s-donor/(weak) p-acceptor bonding (Phosphines)**

Late transition metals
Groups 8,9,10

Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

- **Typical catalysis: hydroformylation (-silylation, -amination, -cyanation), hydrogenation, etc.**



Periodic trends

1st row:

- often unpaired electrons (paramagnetic)
- Several spin states accessible (HS/LS)
- Highest oxidation state less stable

$2^{nd}/3^{rd}$ row:

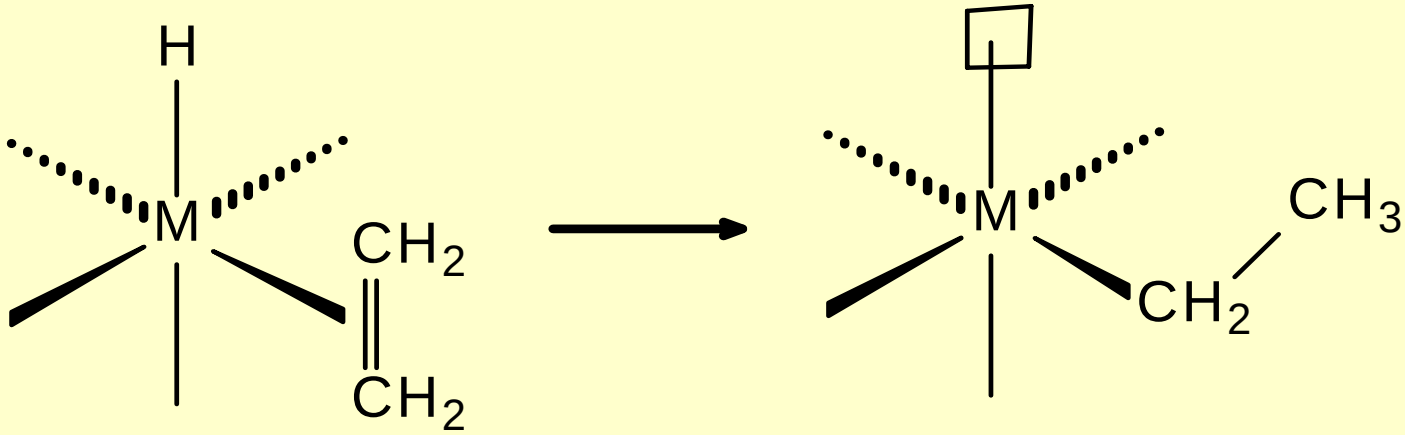
- "closed shell"
- Higher oxidation states relatively stable
- 2nd row often more reactive than 3rd

…Very bold generalizations for your research

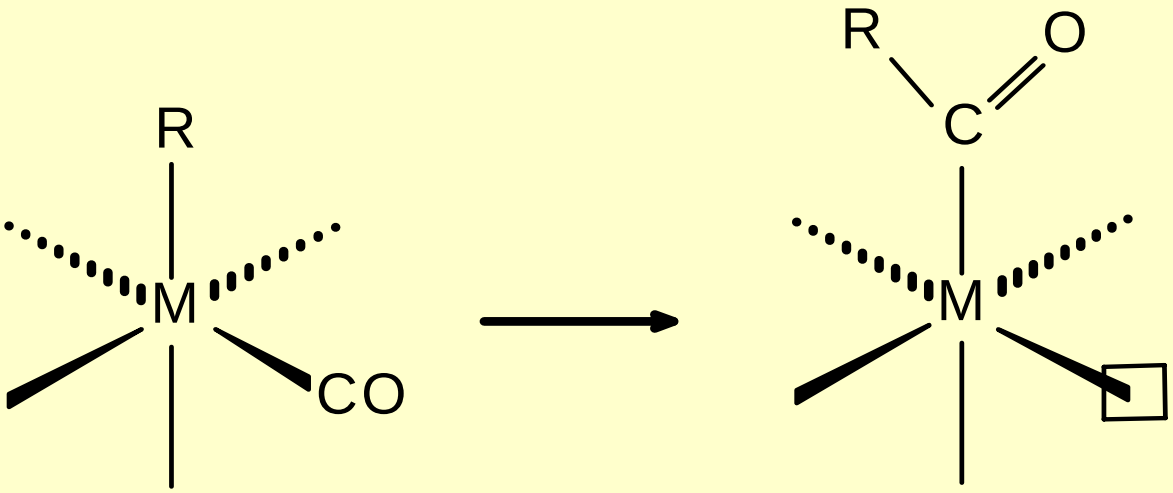
- **Working with 1st row elements:**
  - difficult, you probably can't use NMR
- **Working with 2nd row elements**
  - You'll find exiting catalysts…
  - …they will be to active to be studied in detail
  - Nice for industry, less for academia
- **Working with 3rd row elements**
  - you'll make beautiful complexes and can study their reactivity in detail
  - Nice for academia, less for industry

Synthesis of Metal Alkyls / Acyls

- **Insertions**



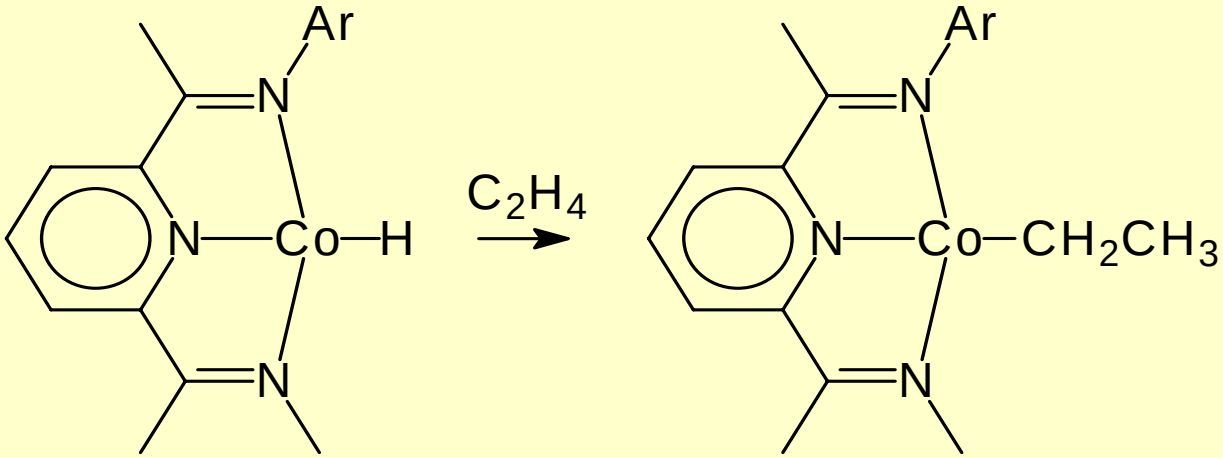
alkyl generation

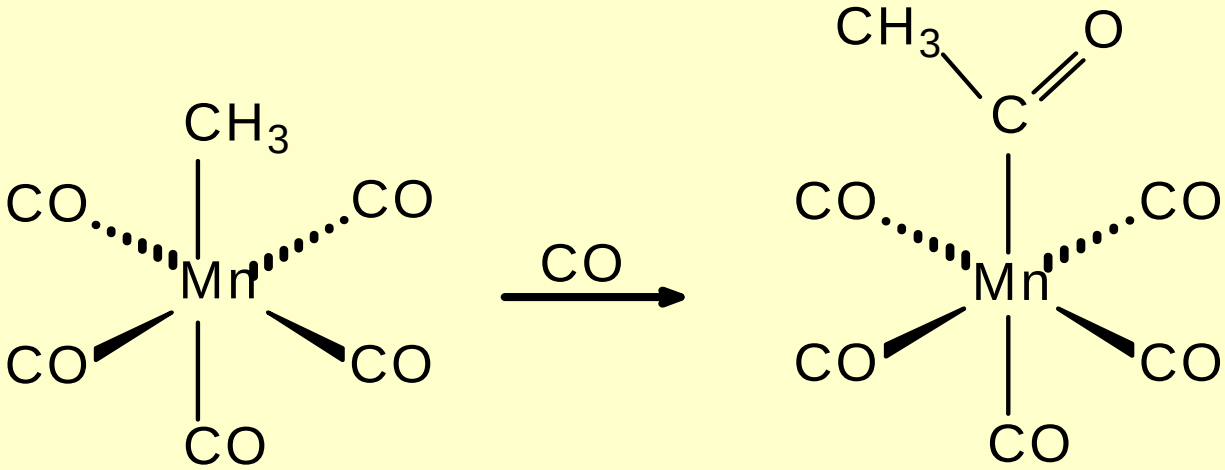


acyl formation

Synthesis of Metal Alkyls / Acyls

- **Insertions**

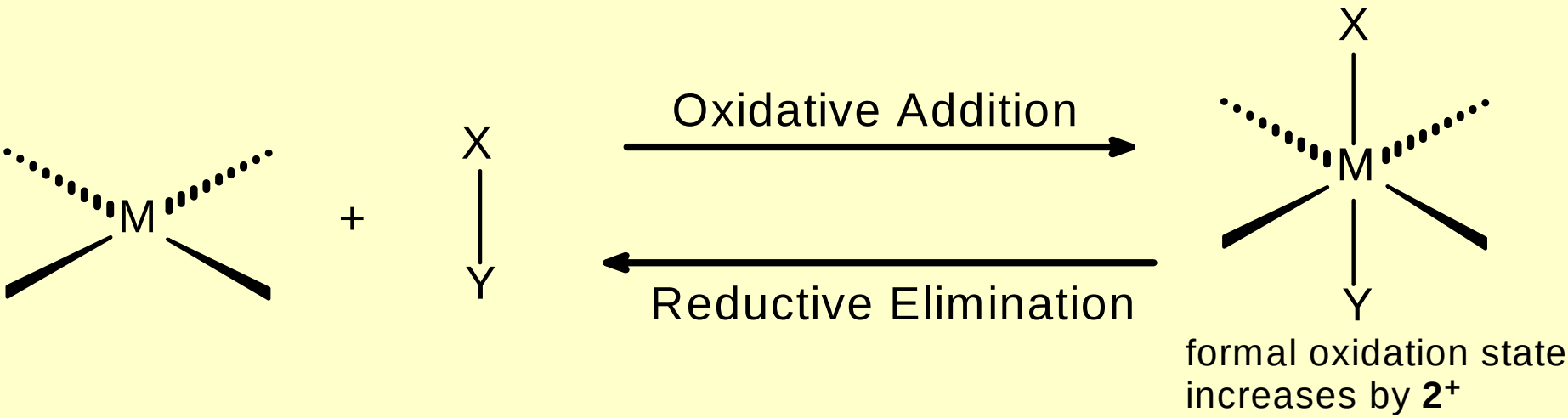


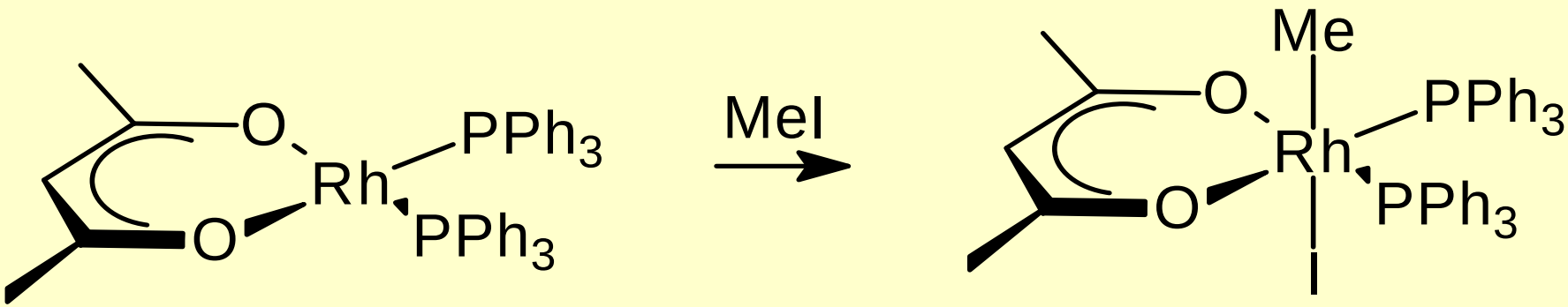


E_a = 61.9 kJ/mol, ΔH^* = 59.4 kJ/mol,
ΔS^* = -88.3 J/mol.K en ΔF^* = 86.2 kJ/mol

Synthesis of Metal Alkyls

- **Oxidative Addition**



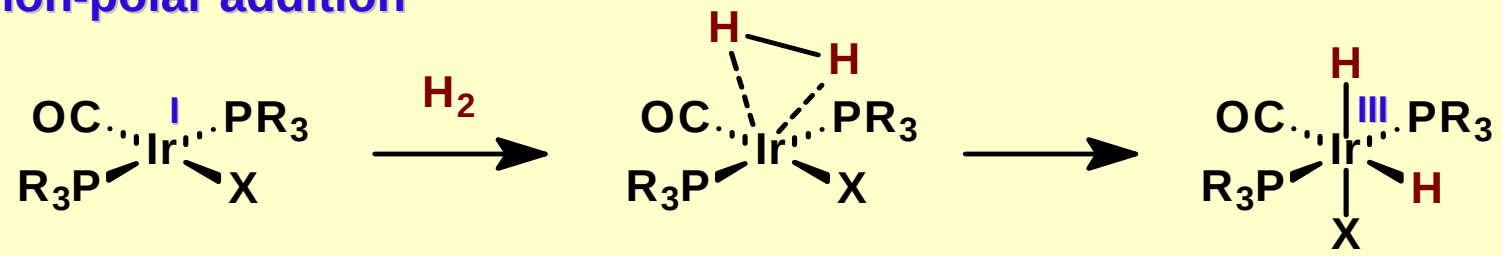


Oxidative Addition

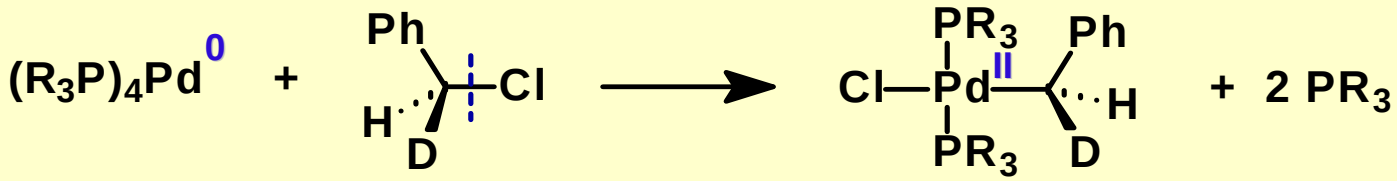
- Usually both, coordination number and oxidation state increase by two!

➔ Three important mechanisms for oxidative addition:

- non-polar addition

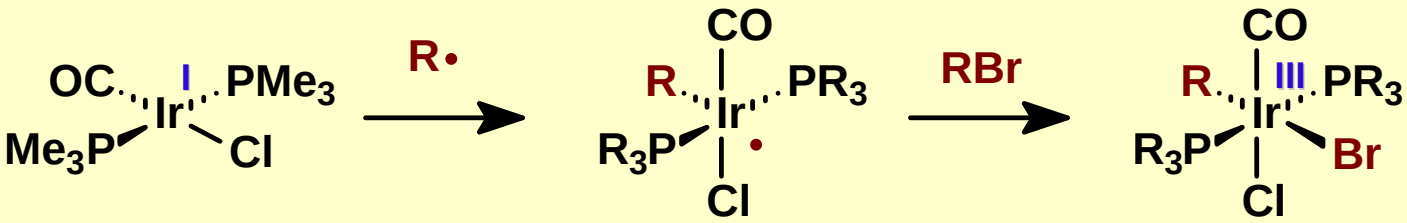


- nucleophilic attack on a carbon atom by the lone pairs of the metal



$CH_3X > CH_3CH_2X > CHR_2X > CyX$ X = halogen

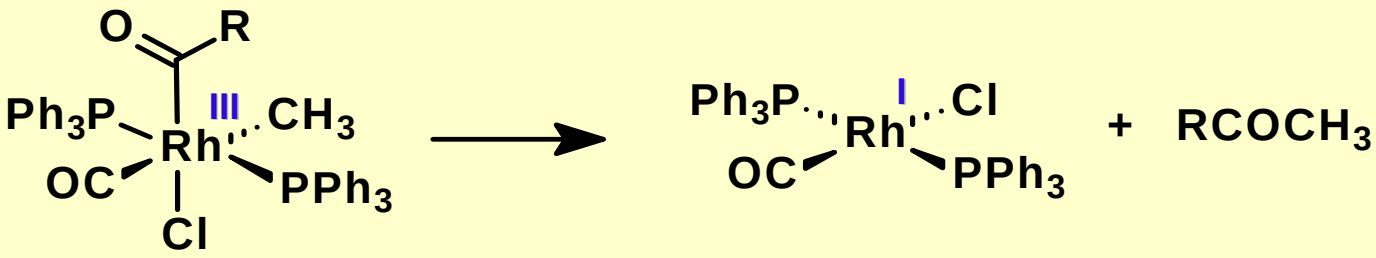
- radical addition in a stepwise reaction



Reductive Elimination

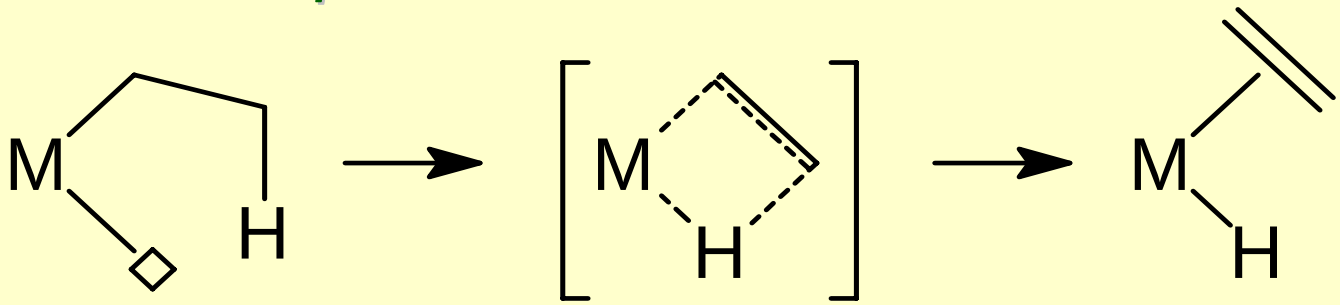
- Usually both, coordination number and oxidation state decrease by two!

➔ Reductive elimination is the reverse mechanism of oxidative addition

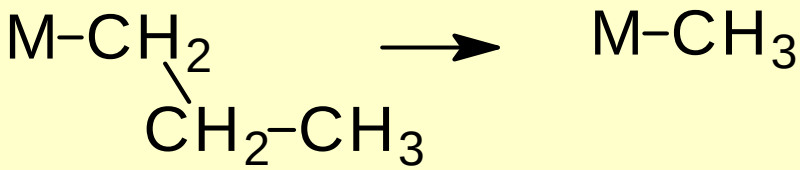


Decomposition pathways for Metal Alkyls

- **Most common: β-H elimination**



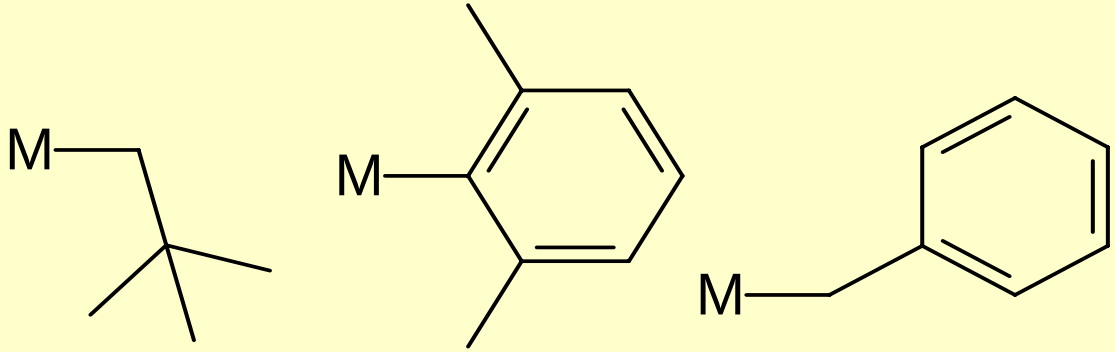
- **Other:**
  - **homolysis**
  - **α/γ/δ-eliminations**



  - **reductive elimination (often with hydride or other alkyl)**
  - **Ligand Metallation (e.g. cyclometallation)**

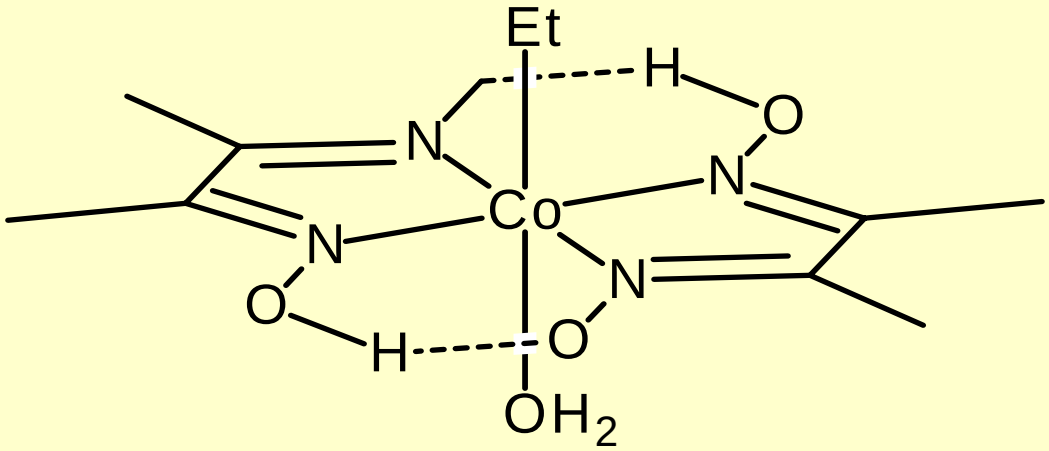
How to prevent β-H elimination ?

- **"Don't have β-H"**

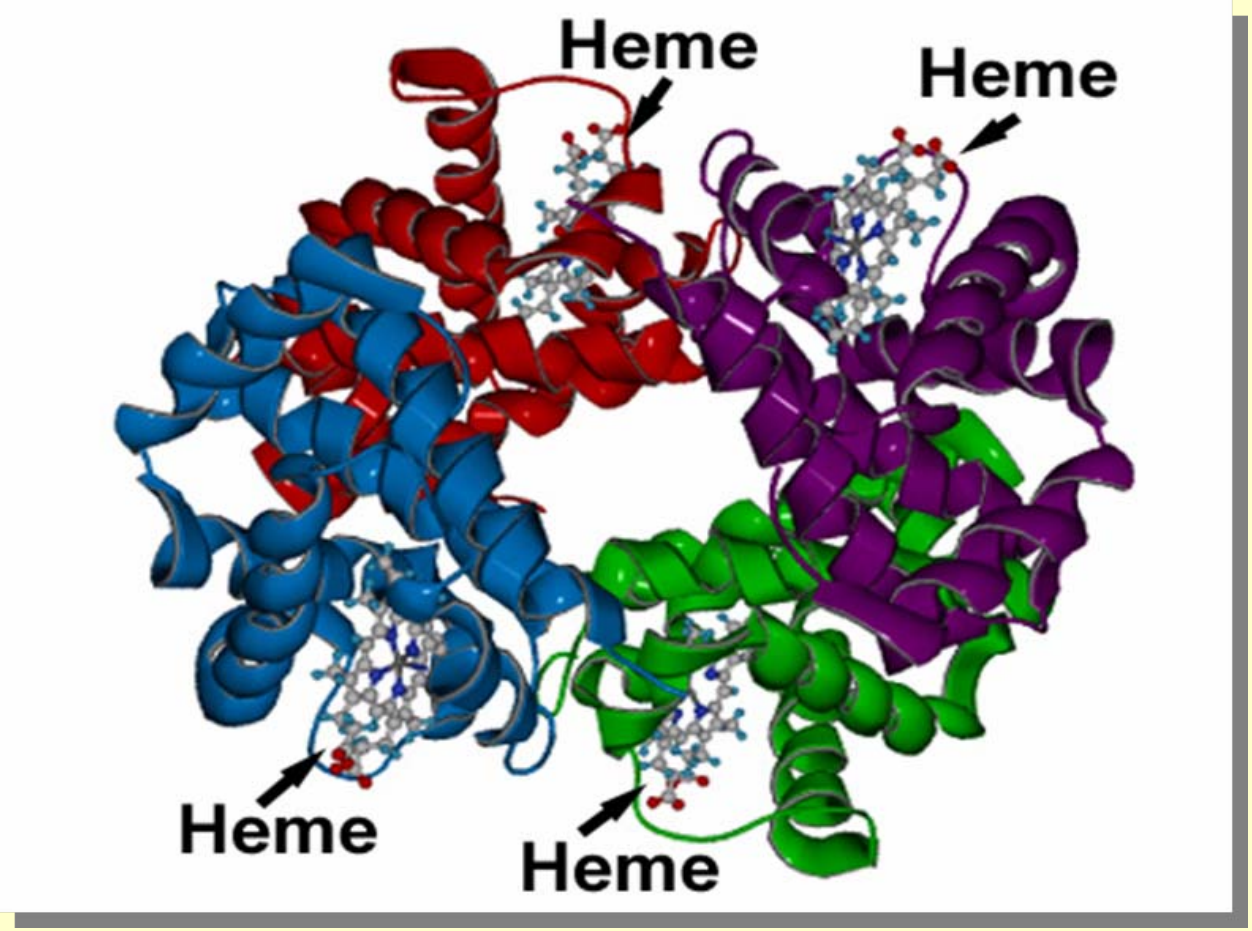


neopentyl xylyl benzyl

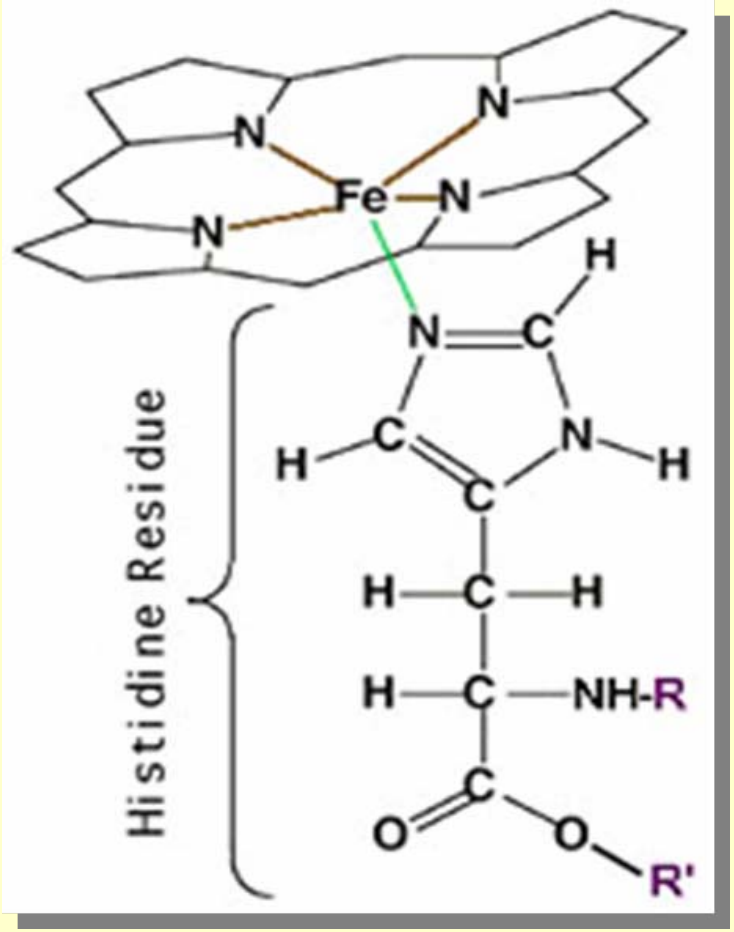
- **"Don't have a vacant coordination site *cis* to the alkyl**



Toxicity of Carbon Monoxide (CO)

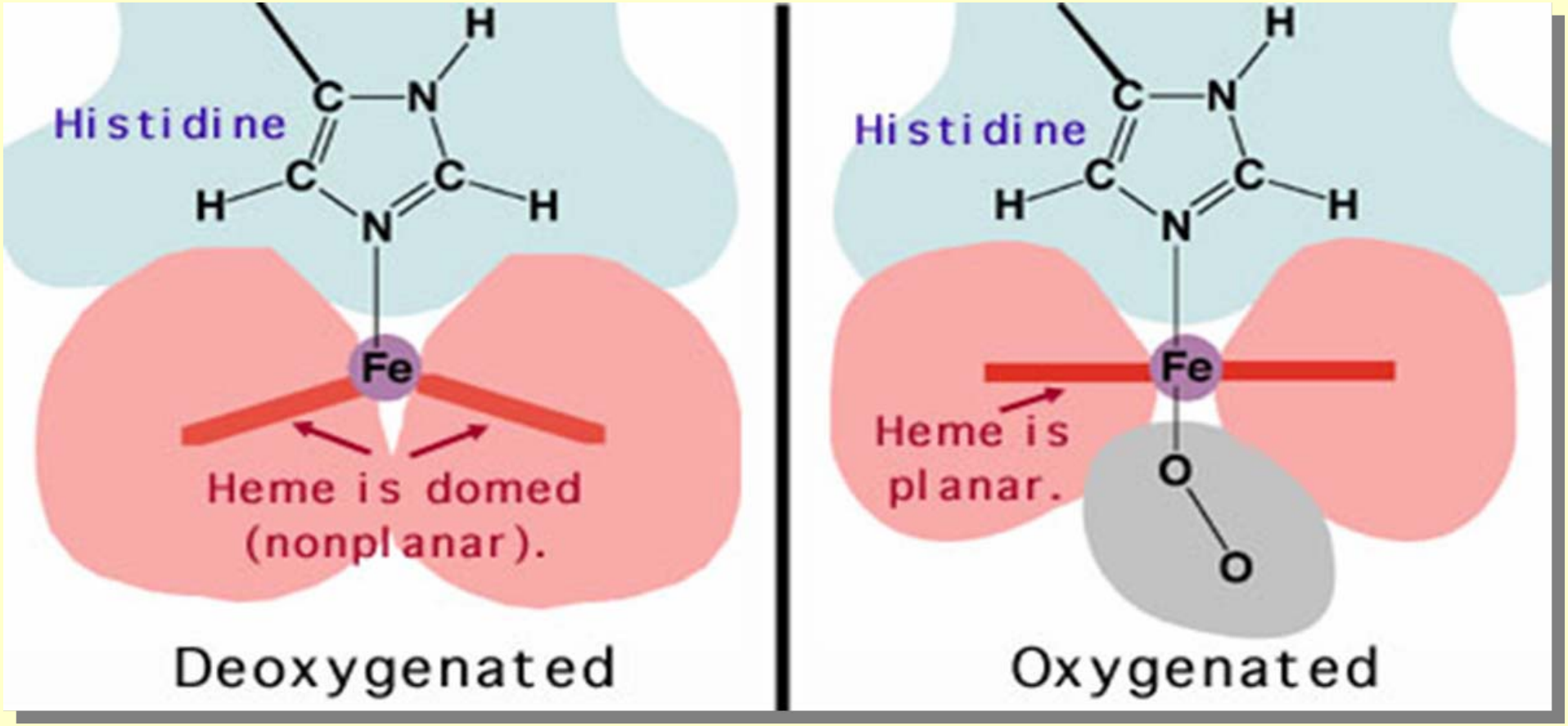


Hemoglobin: The O_2-carrier



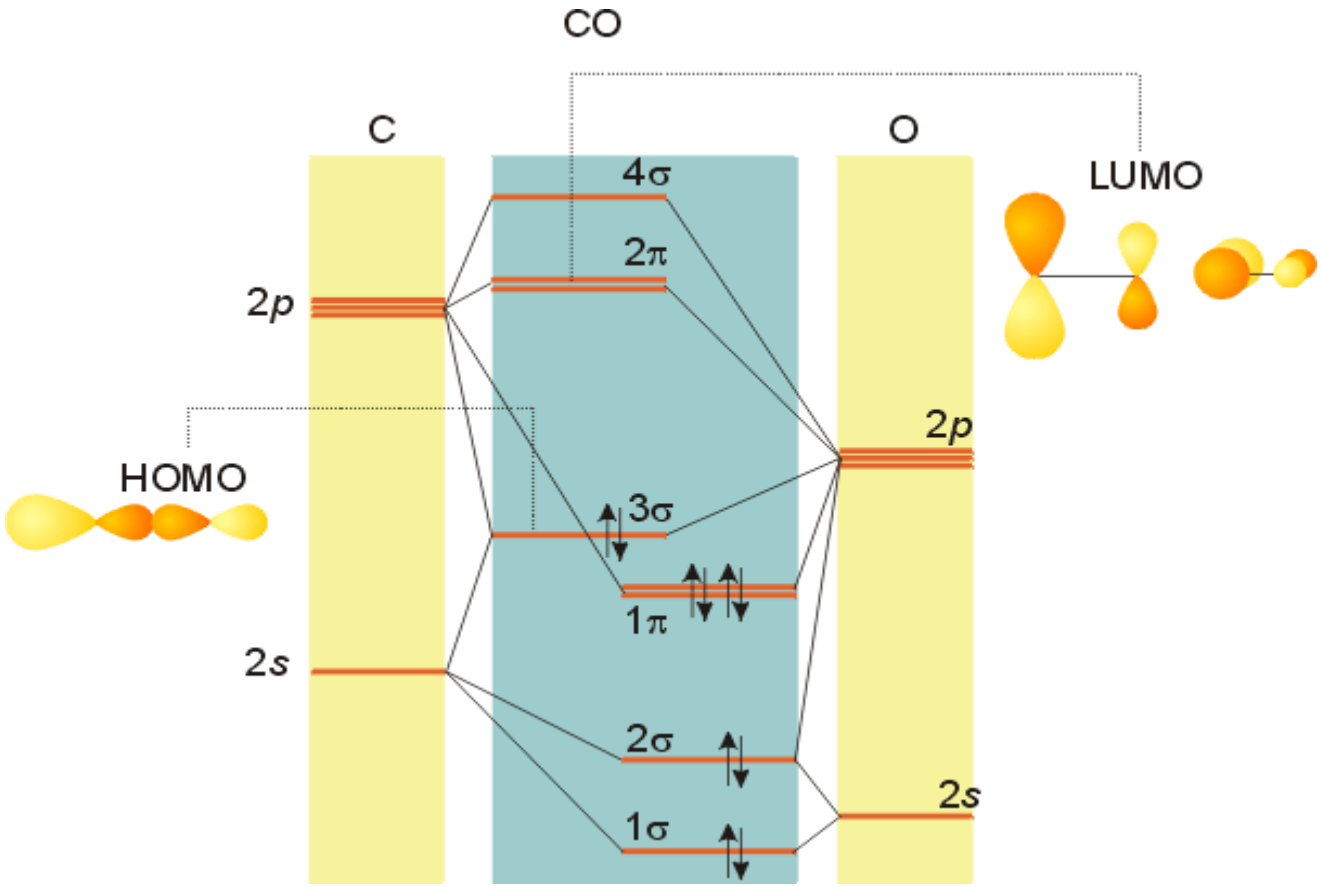
Heme-unit

Toxicity of Carbon Monoxide (CO)



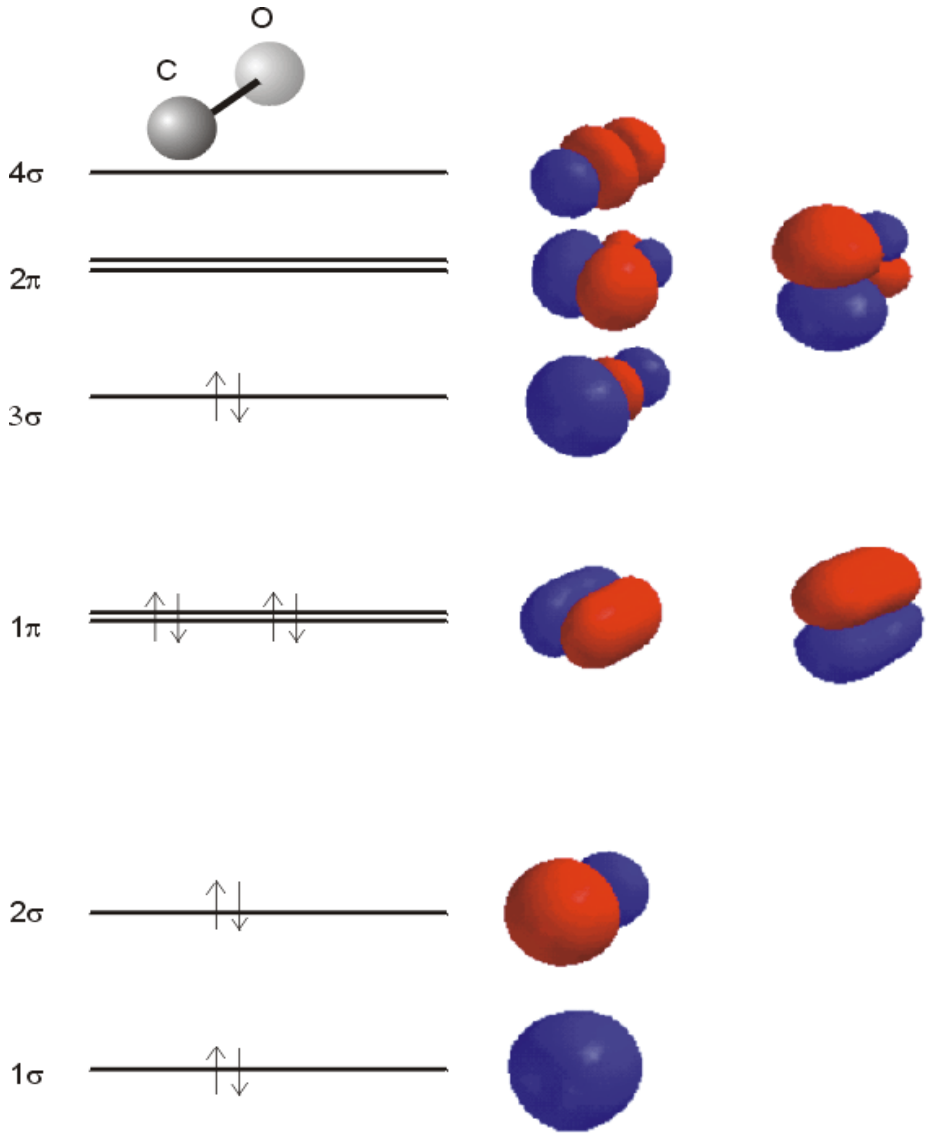
CO binds ca. 250 times better than O_2!

MO's of Carbon Monoxide

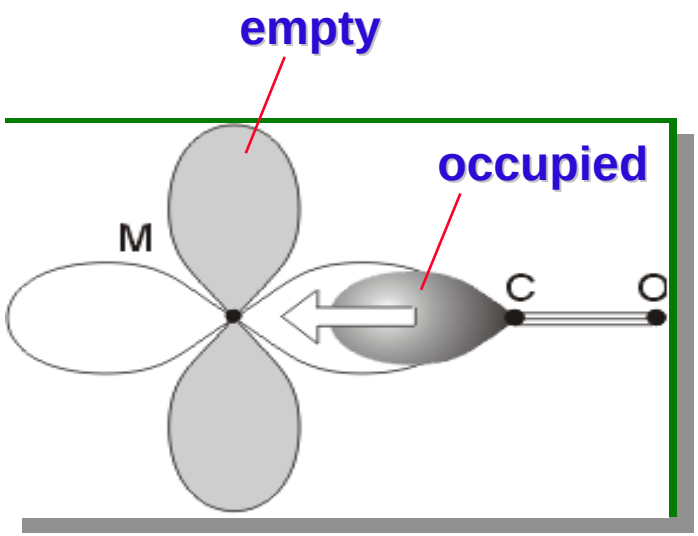


- HOMO has σ symmetry and point away from C in the CO-axis
  => forms σ-donor bonds with the metal
- LUMO's are π* orbitals which play a crucial role in overlap with t_{2g} metal orbitals
  => CO acts as strong π-acceptor

MO's of Carbon Monoxide

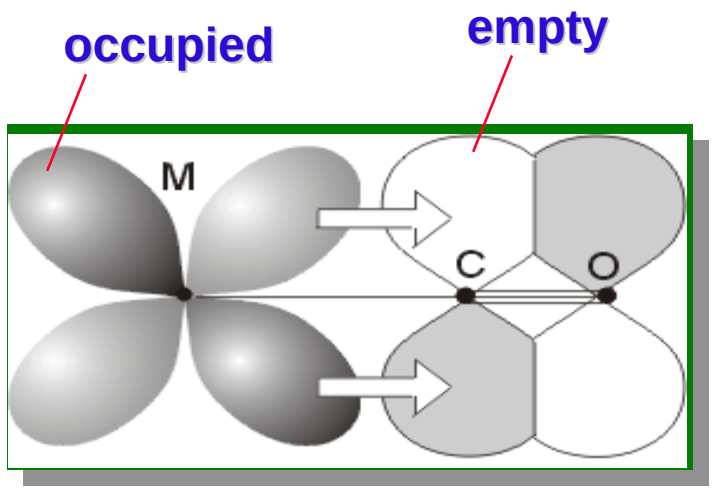


IR Spectroscopy on M-CO compounds



σ-donor

$$M(\sigma) \longleftarrow CO(\sigma)$$

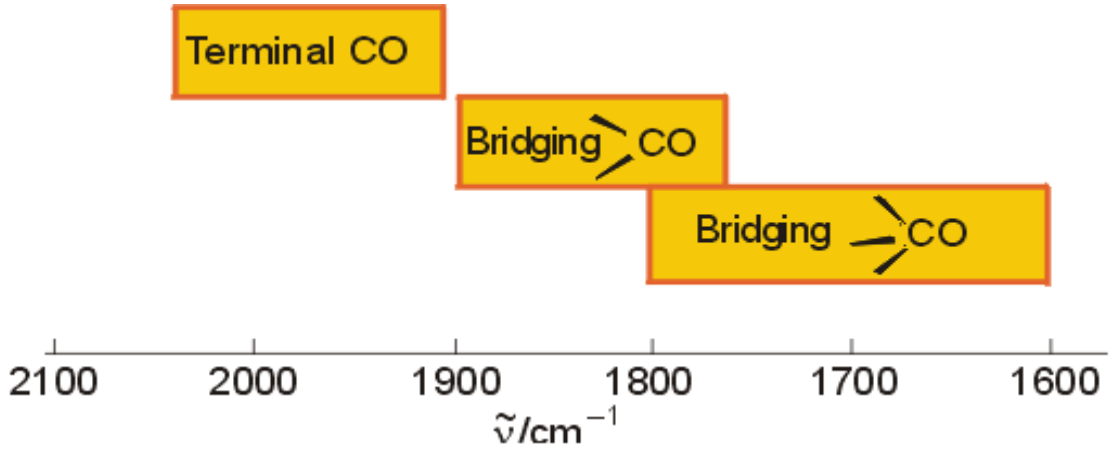


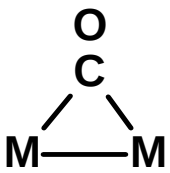
π-acceptor

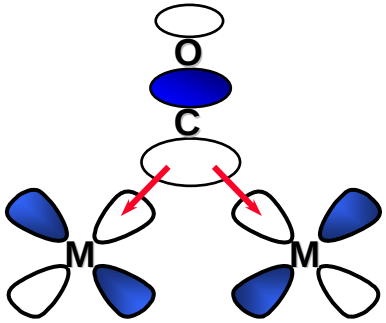
$$M(\pi) \longrightarrow CO(\pi)$$

Stretching frequency ν (CO)	increases	decreases

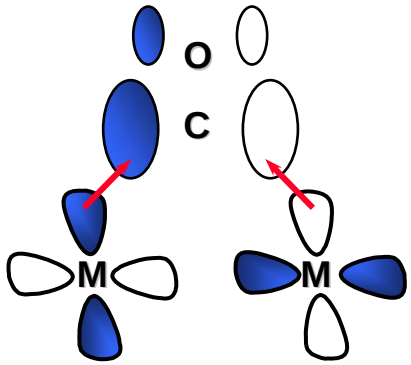
Types of CO Binding Modes







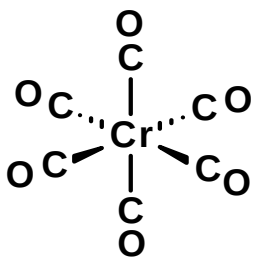
σ-donor



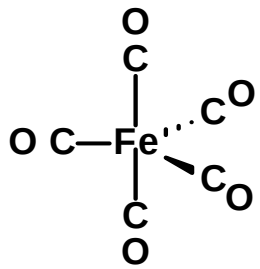
π-acceptor

Structure

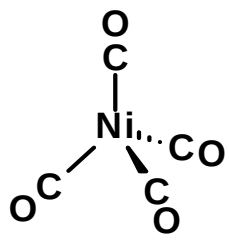
- The simple metal carbonyl compounds show a symmetrical structure with the CO ligands in the most distant positions



O_h



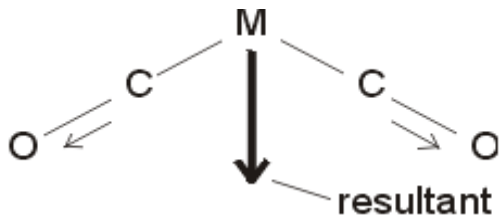
D_{3h}



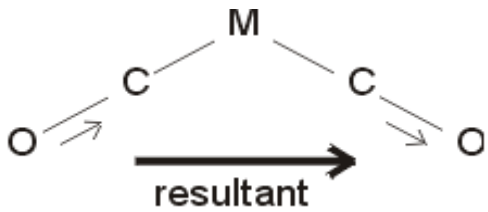
T_d

- ^{13}C NMR and IR spectroscopy provide structural information

- Non symmetrical compounds bearing N CO ligands will show N ν_{CO} (see slide Organomet_25)



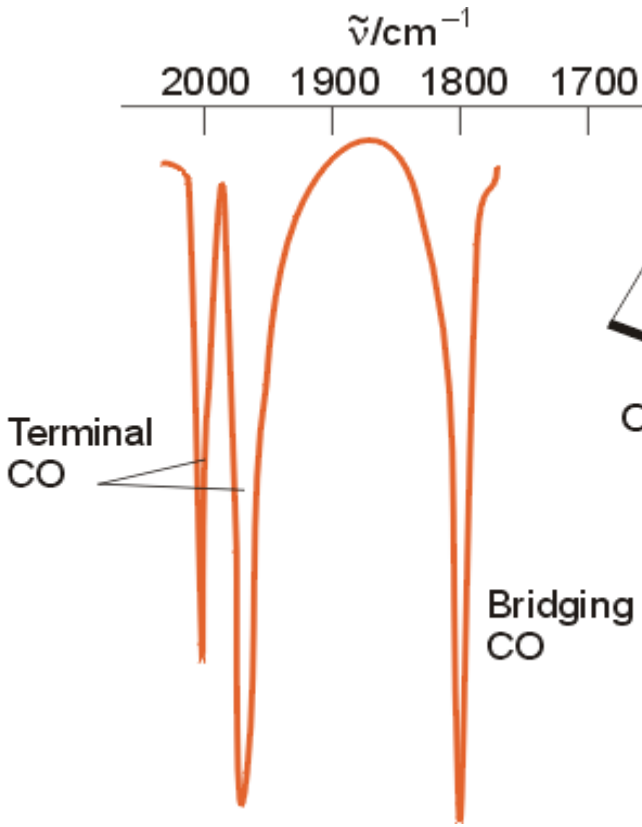
symmetric

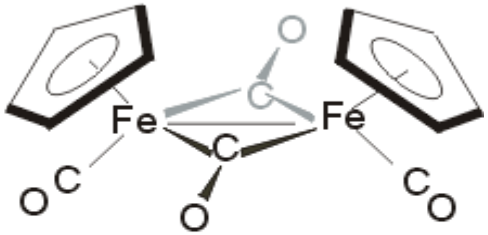


anti-symmetric

Structure

- **If the positions of the CO ligands are more symmetrical arranged than the point group of the whole compound suggests, fewer ν_{CO} will be observed! (see slide Organomet_25)**



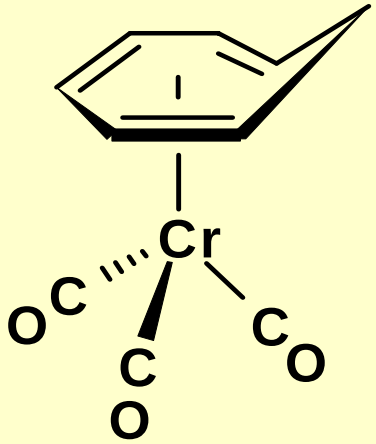


nearly co-linear bridging CO ligands

Reactions of M-CO

1) Ligand substitution

$$Cr(CO)_6 \xrightarrow[\text{reflux}]{CH_3CN} Cr(CO)_3(CH_3CN)_3 \xrightarrow{C_7H_8}$$

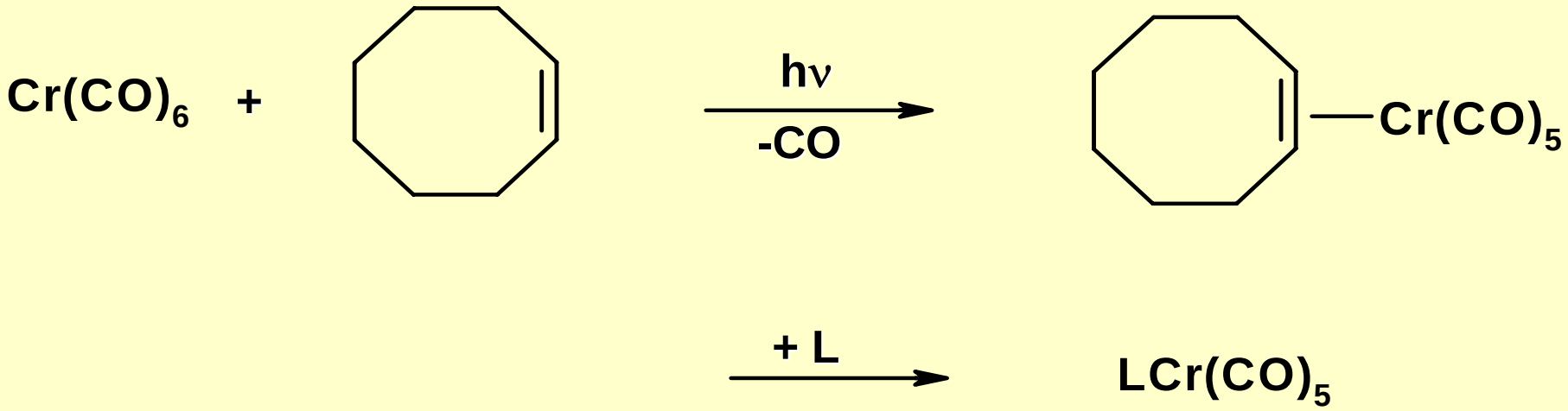


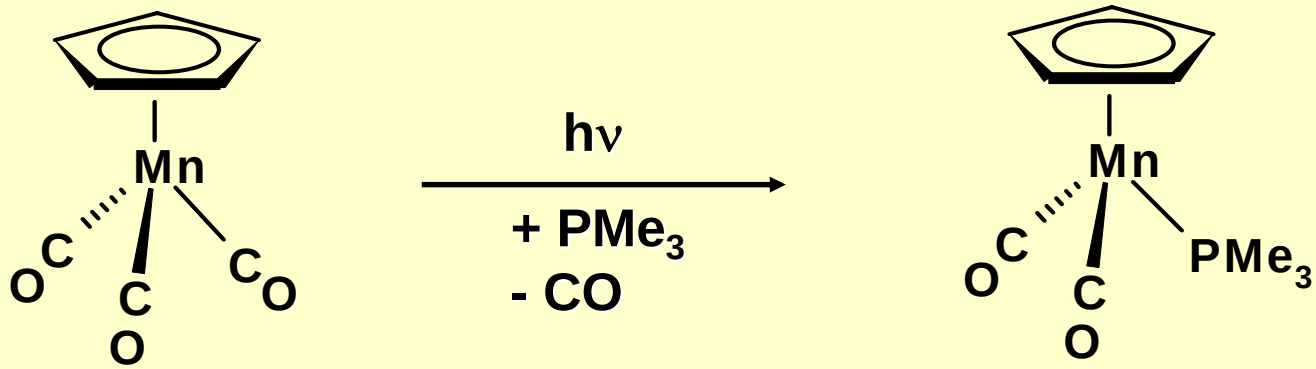
Introduction of the labile ligand CH_3CN

→ Substitution by other ligands possible

Reactions of M-CO

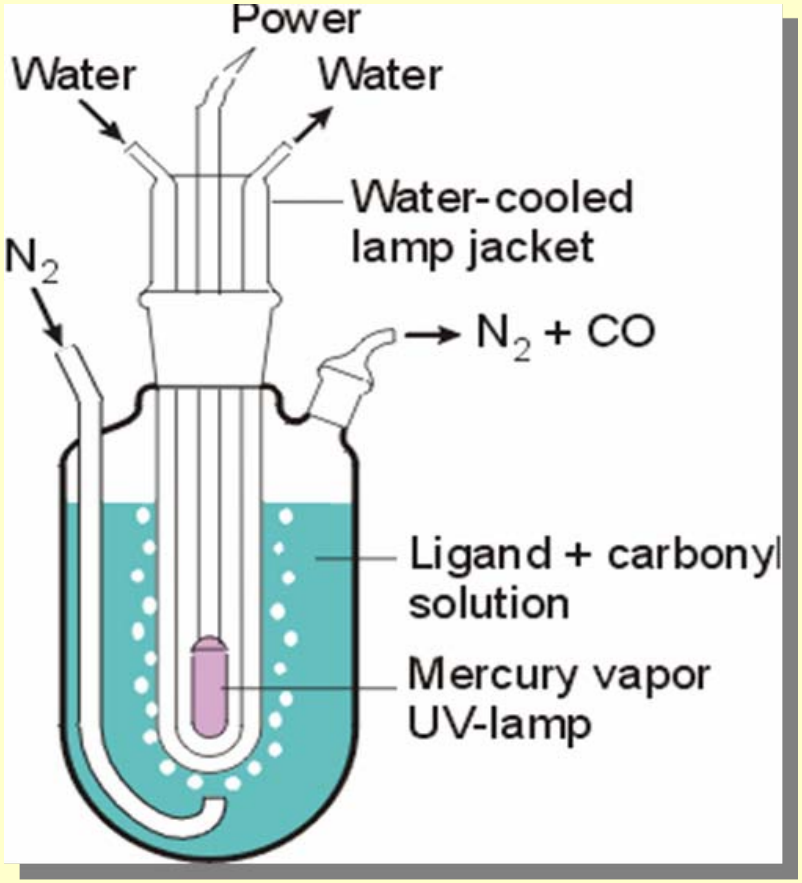
2) Photochemical ligand substitution





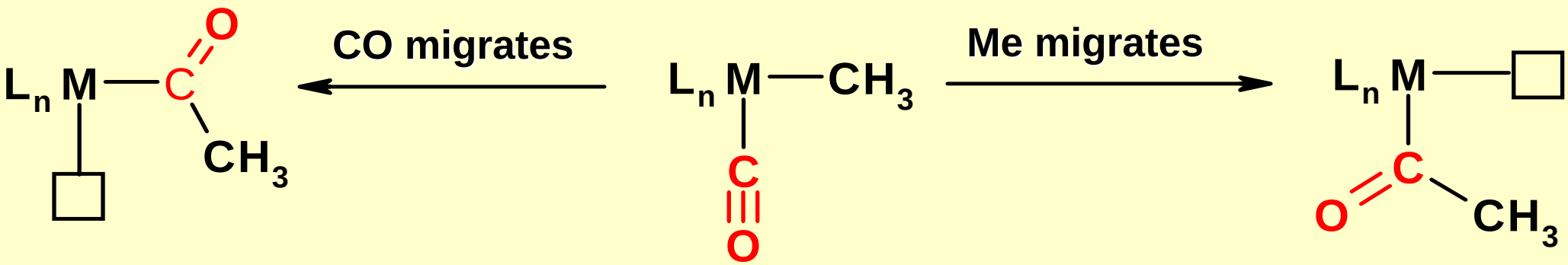
Reactions of M-CO

Photochemical ligand substitution



Reactions of M-CO

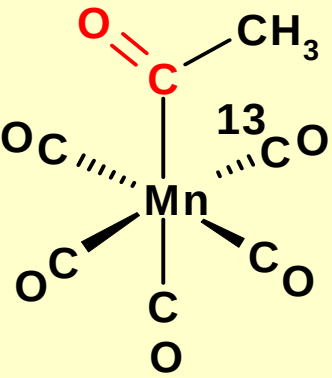
3) Migratory insertion



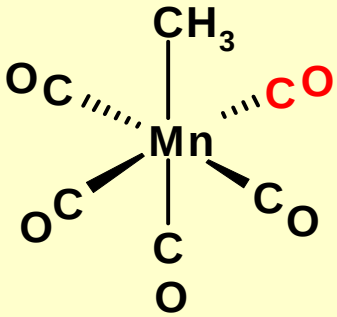
Reversible reaction: de-insertion: same mechanism (principle of Microscopic Reversibility)

Reactions of M-CO

Migratory insertion

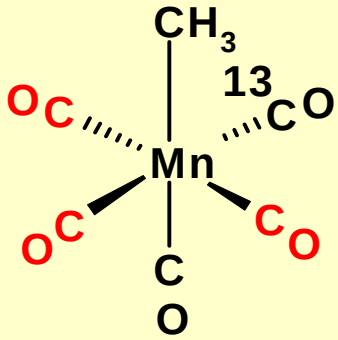


If CO moves



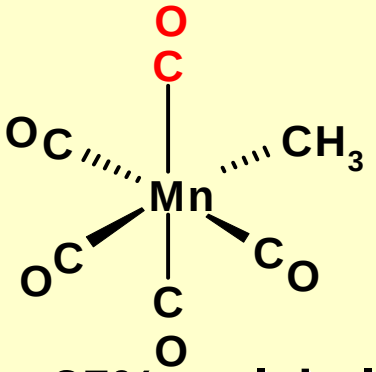
25% no label

+

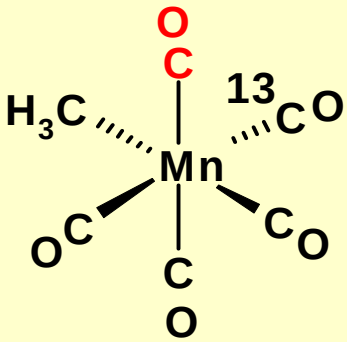


75%

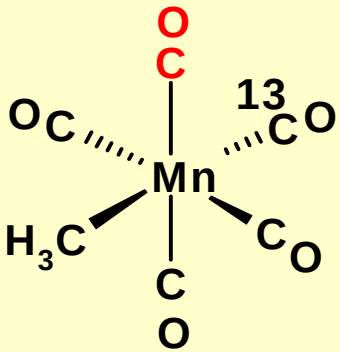
If Me moves



25% no label



50% *cis*

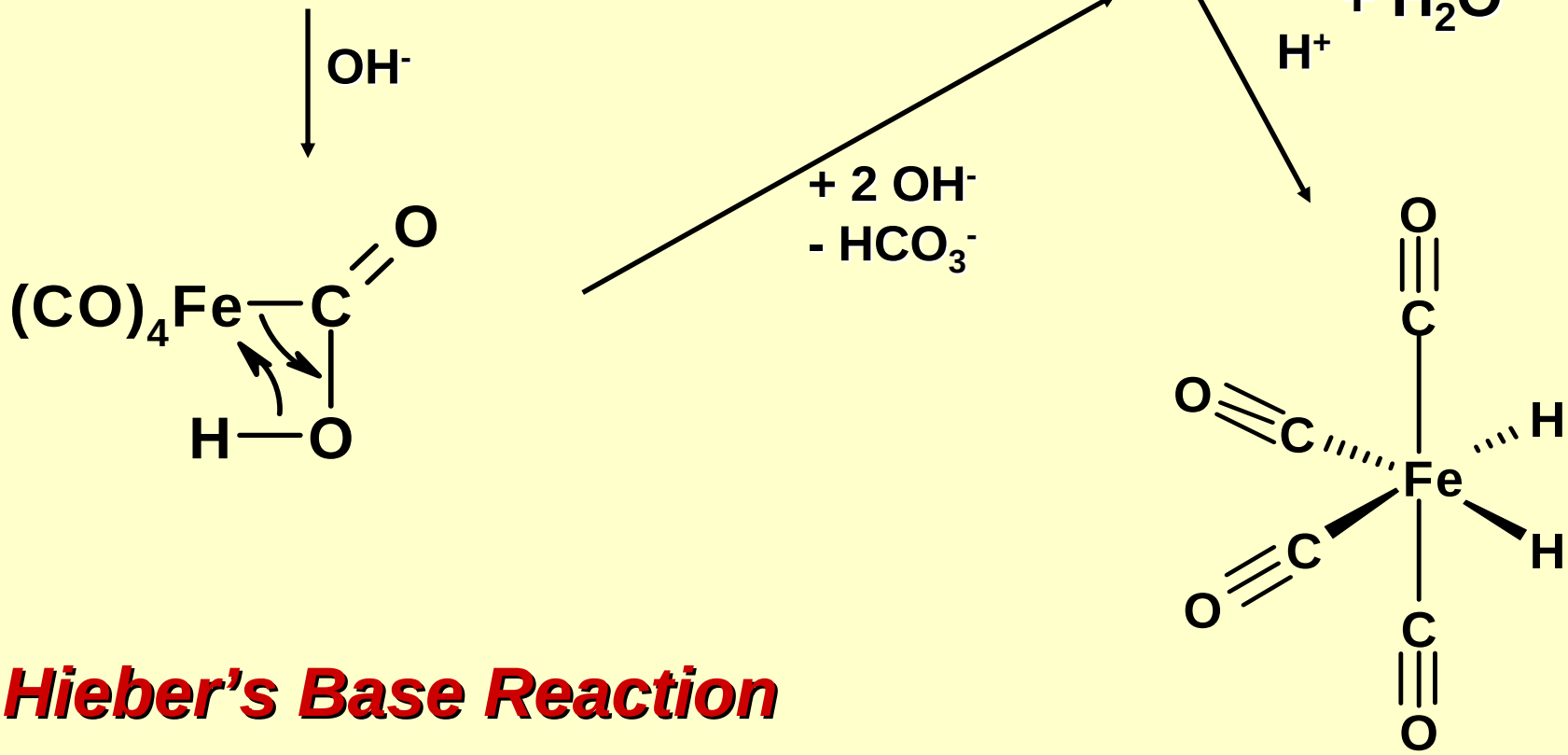


25% *trans*

Reactions of M-CO

4) Reaction of M-CO with strong bases

$$Fe(CO)_5 + 3\ NaOH\ (aq) \longrightarrow Na^+[HFe(CO)_4]^- + Na_2CO_3 + H_2O$$



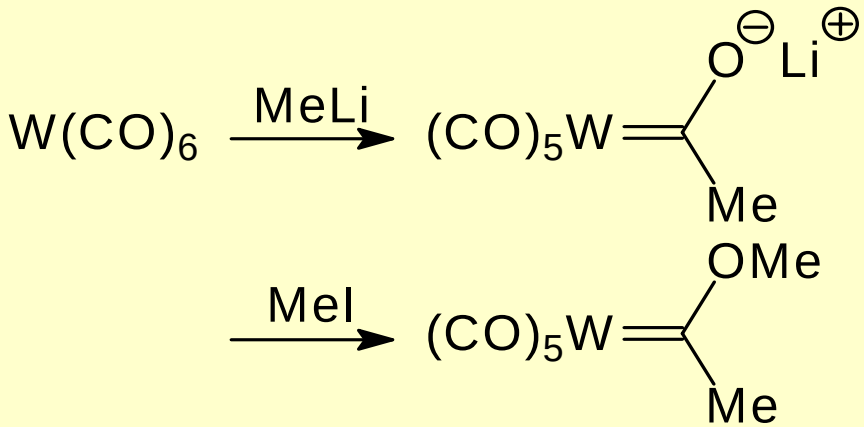
Hieber's Base Reaction

Synthesis of Fischer Carbenes

Mostly from CO complexes through:

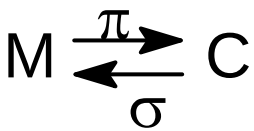
1) Nucleophilic attack at CO

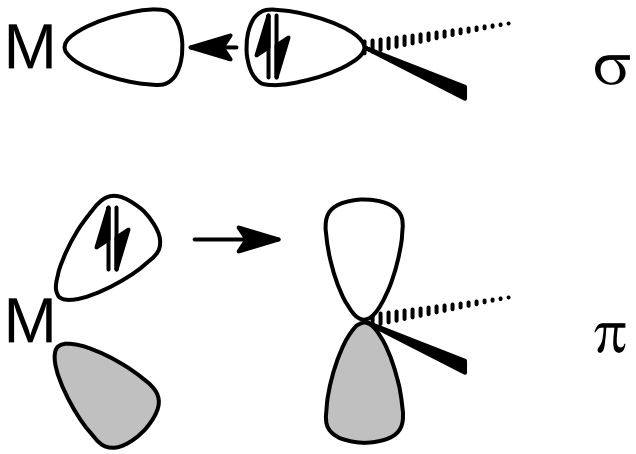
2) Electrophilic attack at O



Also spontaneous isomerization of vinyl, alkene or acetylene complexes (Ru)

Fischer carbenes

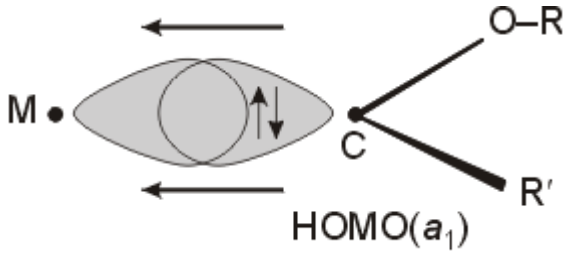




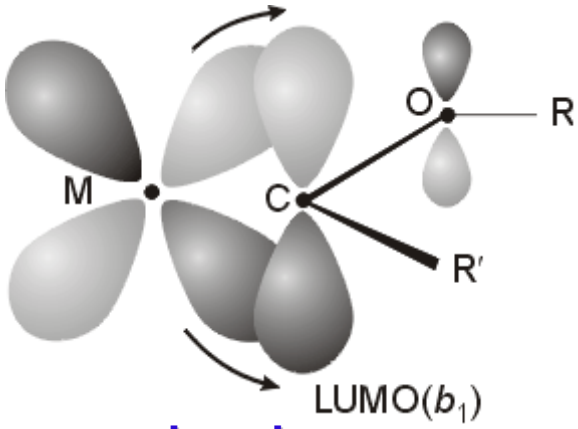
- **singlet ground state (Heteroatoms)**
- **Late(r) transition metals with lower oxidation states (donation of electrons)**
  - **carbene is considered neutral**

Metal Alkylidene Bonds

- η^1- bound $2e^-$ ligands CH_2, CHR, CR_2
- metal - C double bond



σ-bond

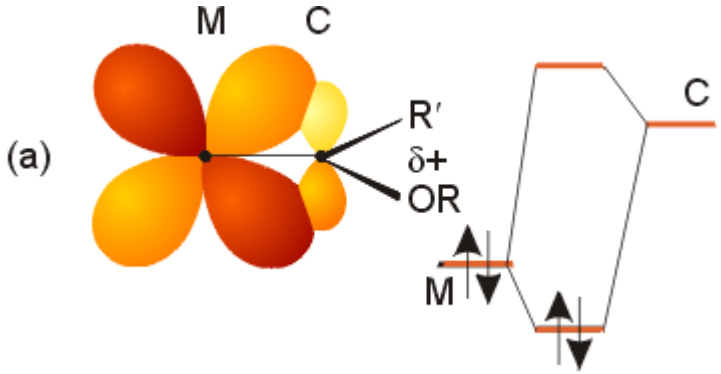


π-bond

Fischer Carbenes

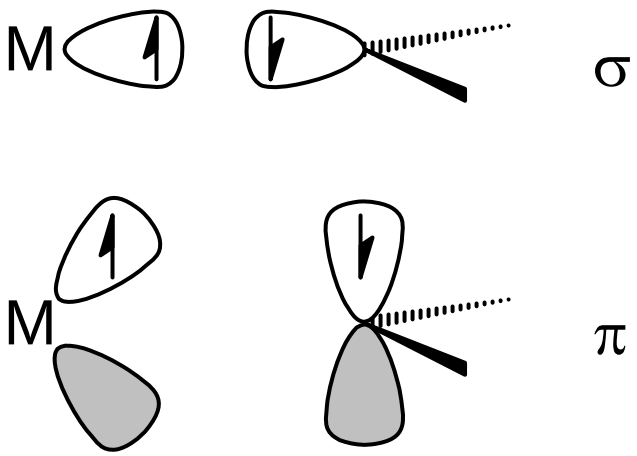
- Middle to late transition metal carbenes
- vacant carbon p_z orbital higher in energy than d-π orbitals

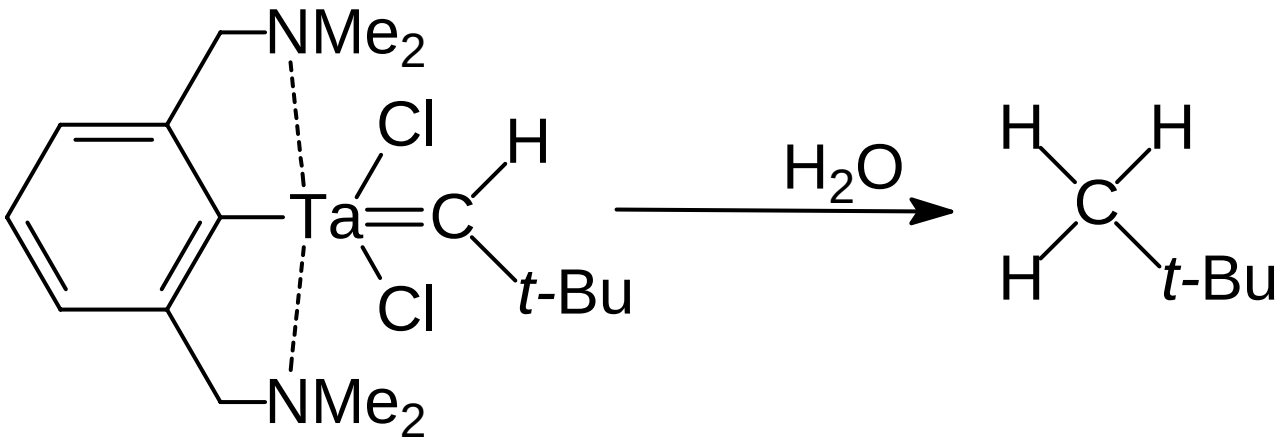
=> Fischer carbene C is electrophilic



Schrock Carbenes (Alkylidenes)

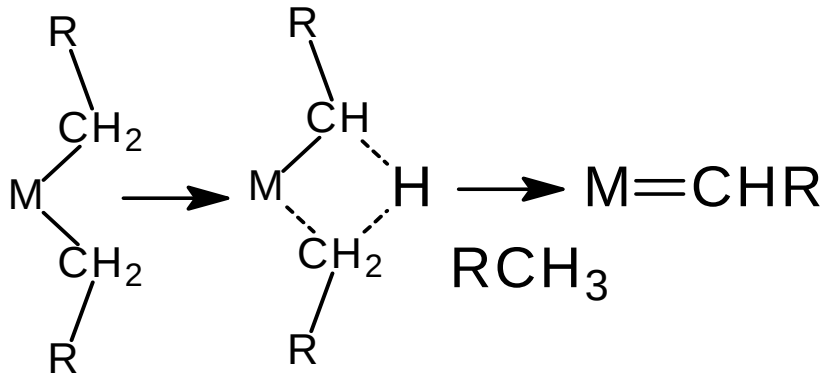
- ”Conventional" M=C bond:
  - both σ en π are covalent, expected polarization M^{d+}-C^{d-}
- Triplet ground state
- Early transition metals with high oxidation states
  - Carbene is formally C^{2-}
- Carbene C is nucleophilic



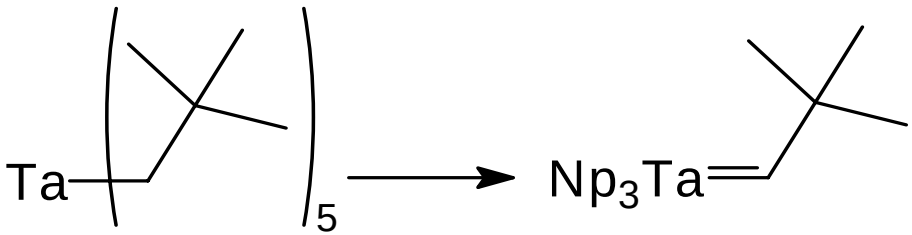


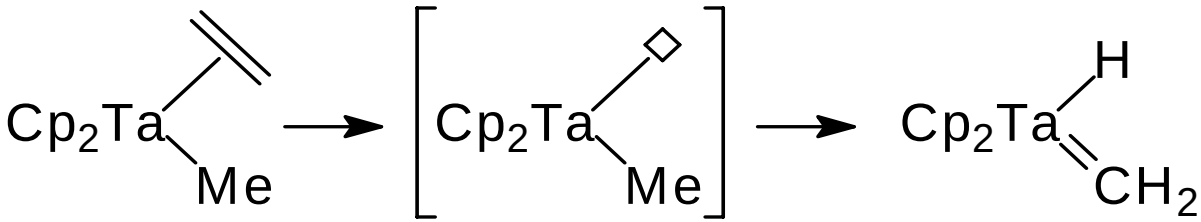
Synthesis of Schrock alkylidens

Decomposition of metal alkyls (α-eliminatie)



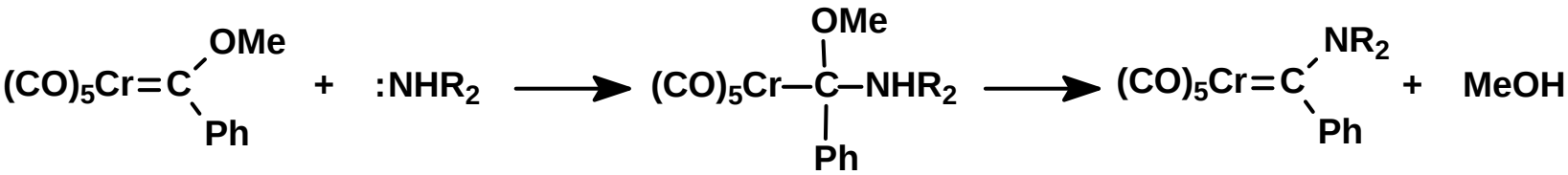
Examples:





Metal Alkylidene Bonds

- electrophilic Fischer carbenes react with a nucleophiles

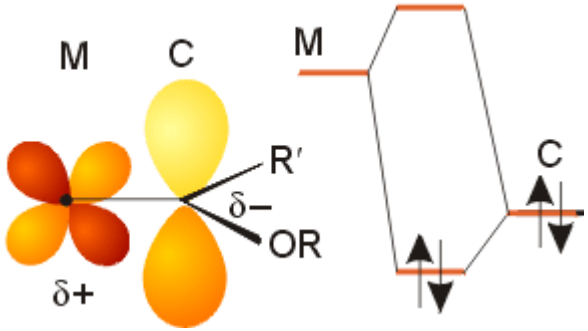


Schrock Carbenes

(b)

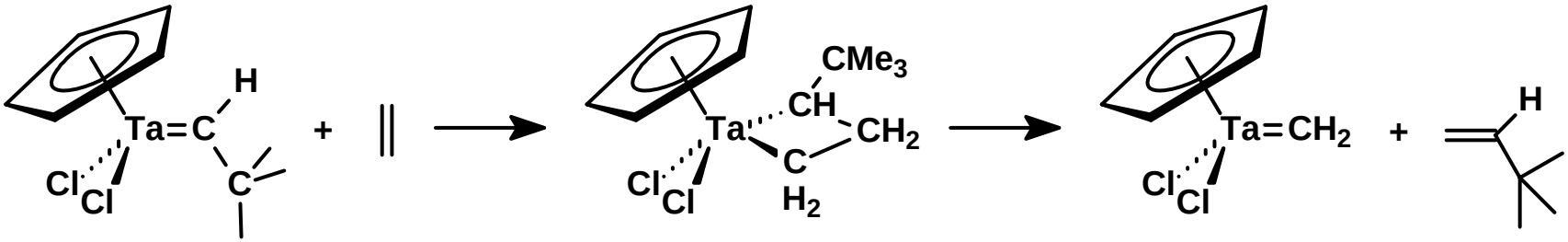
- Early transition metal carbenes
- filled carbon p_z orbital lower in energy than d-π orbitals

=> Schrock carbene C is nucleophilic

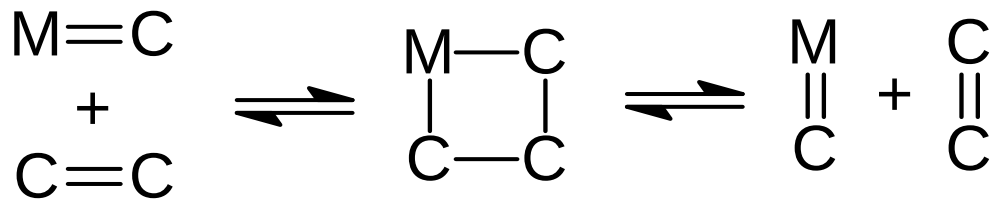


Wrong picture!

- Schrock carbenes are catalysts for the alkene metathesis reaction

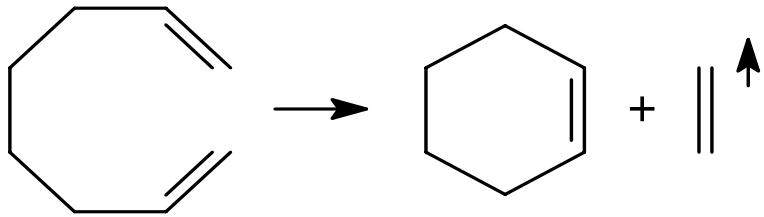


Catalytic Alkene Metathesis

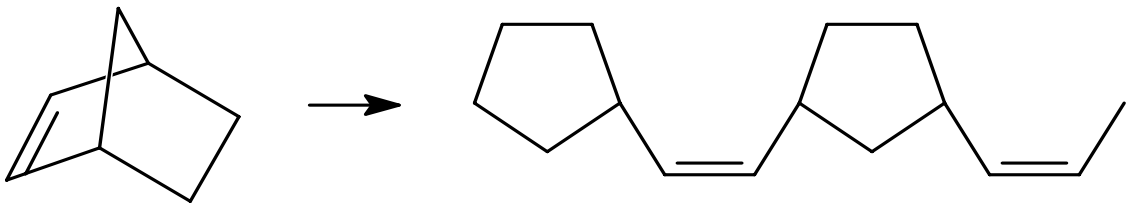


Driving forces:

- **Liberation of volatile reactants**



- **Reduction of Ring strain**



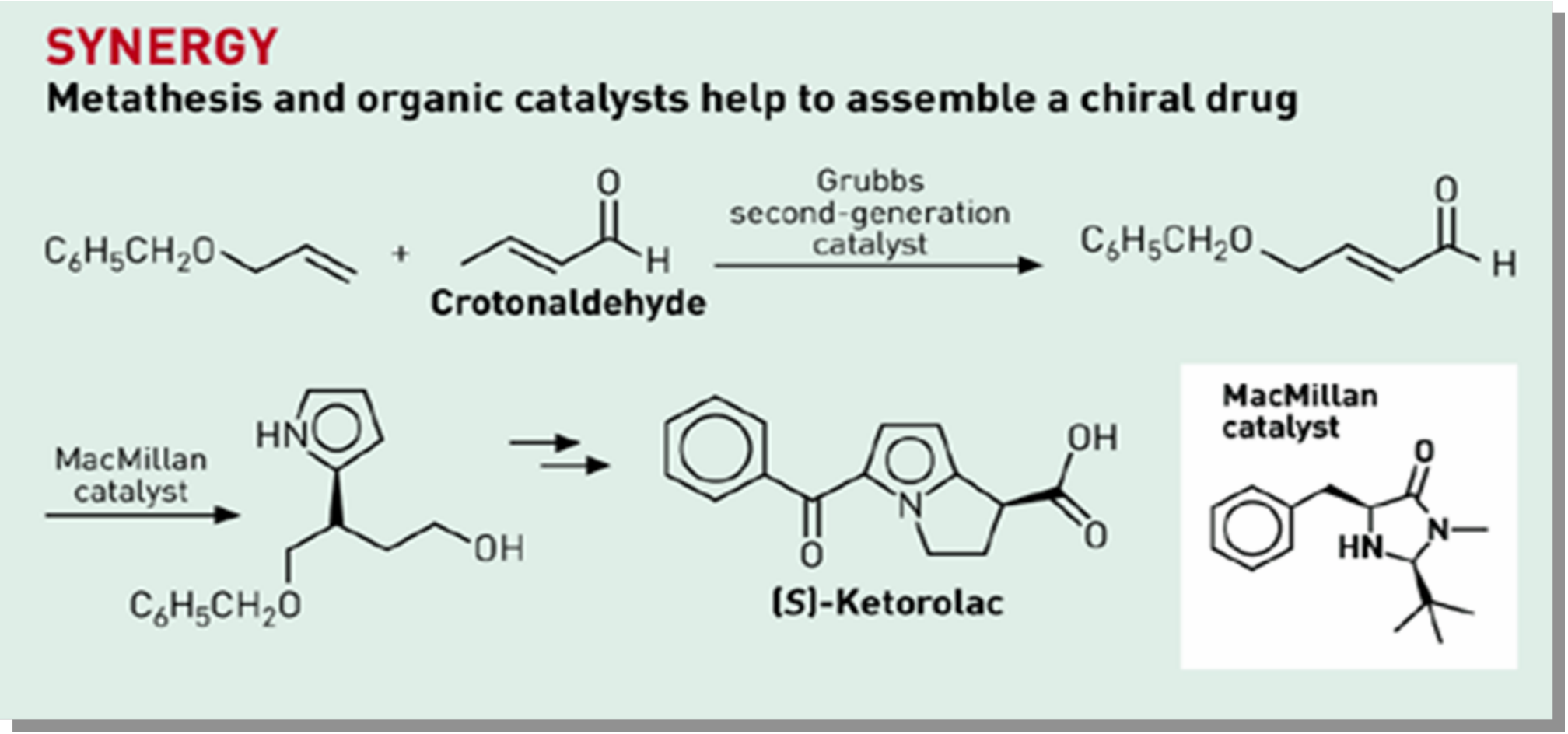
Olefin metathesis is key in the production of linear olefins at the Geismar, La., facilities of Shell Chemicals.

Application example of ROMP

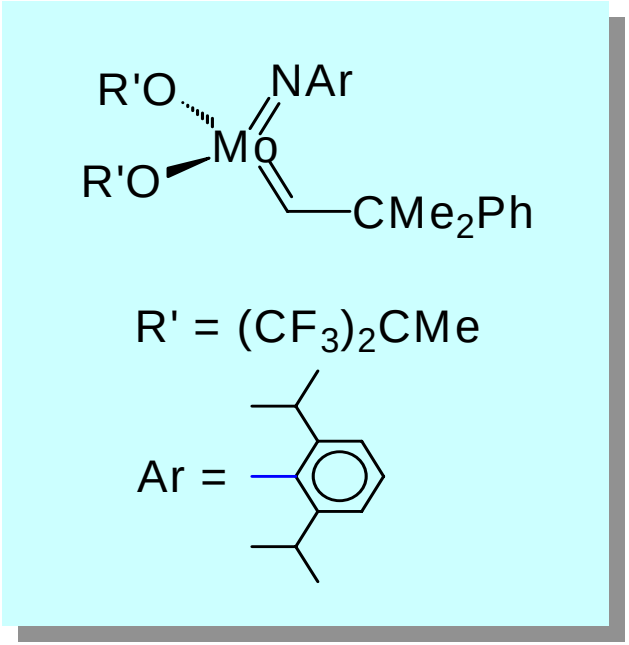
-

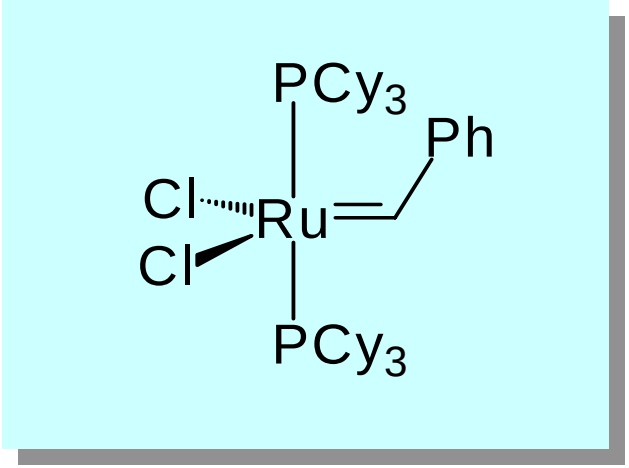
A 1.5-inch-thick polydicyclopentadiene resin prepared with ruthenium technology is impenetrableto 9-mm bullets.

Alkene metathesis & Fine Chemicals



Development of Metathesis Catalysts

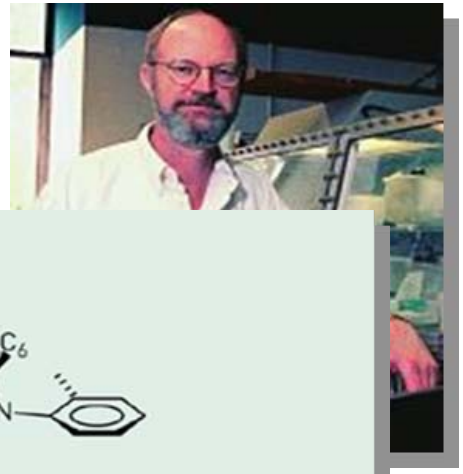




Schrock catalyst.
Very active but sensitive for functional groups

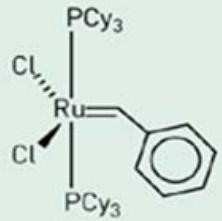
Grubbs catalyst.
Stable, tolerates functional groups but PCy_3 has to dissociate prior to reaction.

Schrock and Grubbs Catalysts

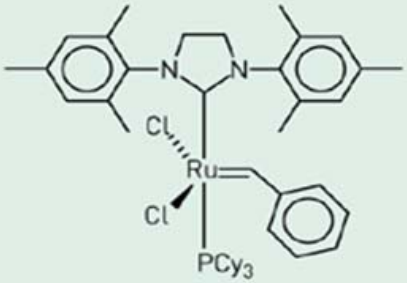


NO SWEAT

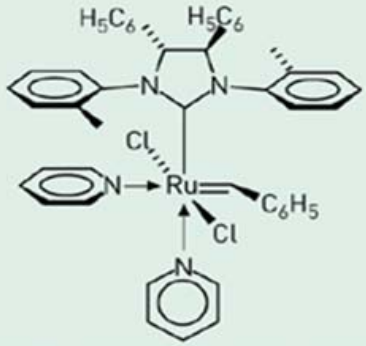
Metal carbenes have made reactions easy to run



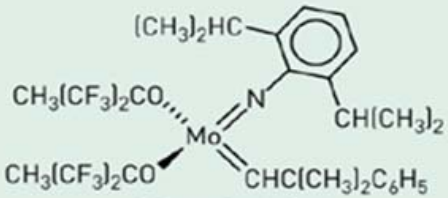
Grubbs catalyst



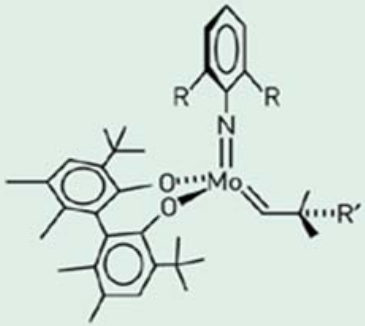
Grubbs second-generation catalyst

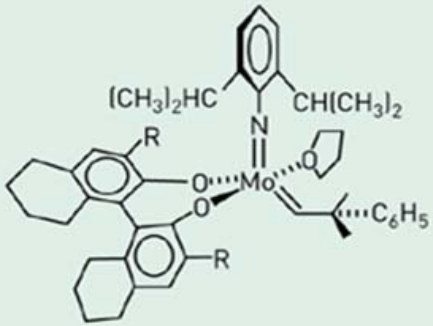


Grubbs chiral ruthenium catalyst



Schrock catalyst





Schrock-Hoveyda chiral molybdenum catalysts

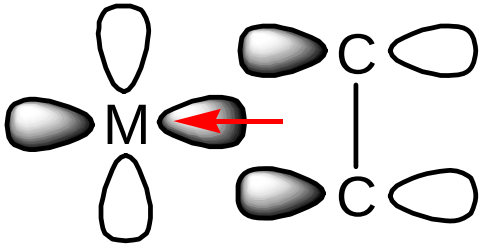
Cy = cyclohexyl

Transition Metal - Alkene Complexes

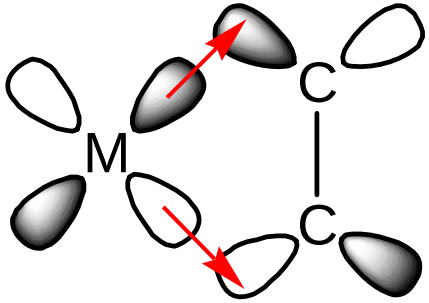
Bonding Situation

Dewar-Chatt-Duncanson Model

σ-bond



π-backbond

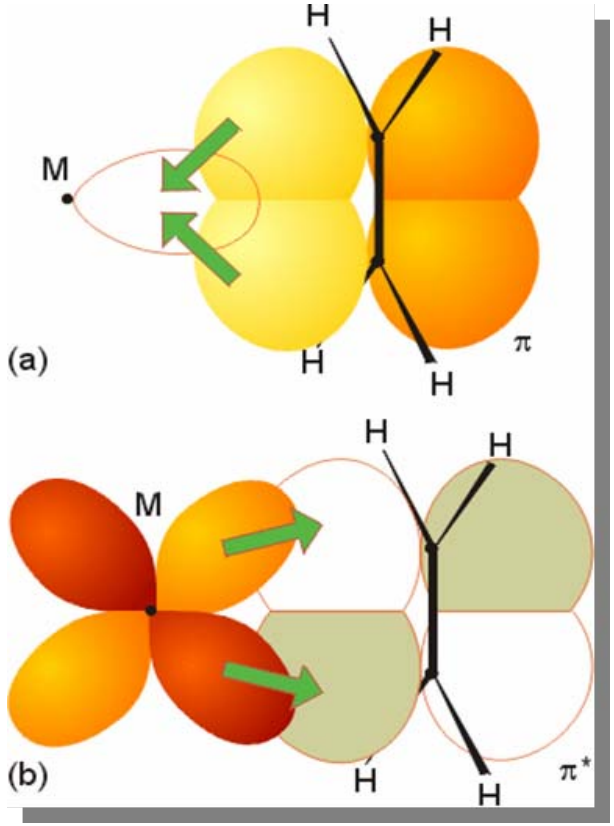


empty d-orbital

filled ethylene π-orbital

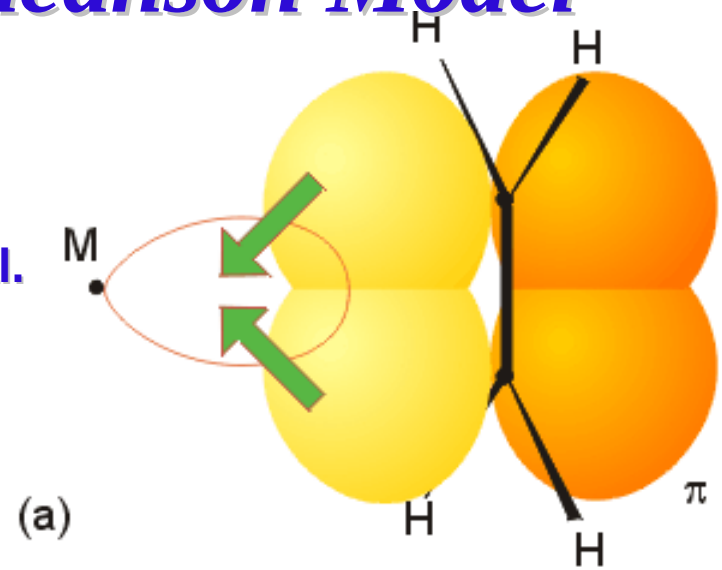
filled d-orbital

empty ethylene π* orbital

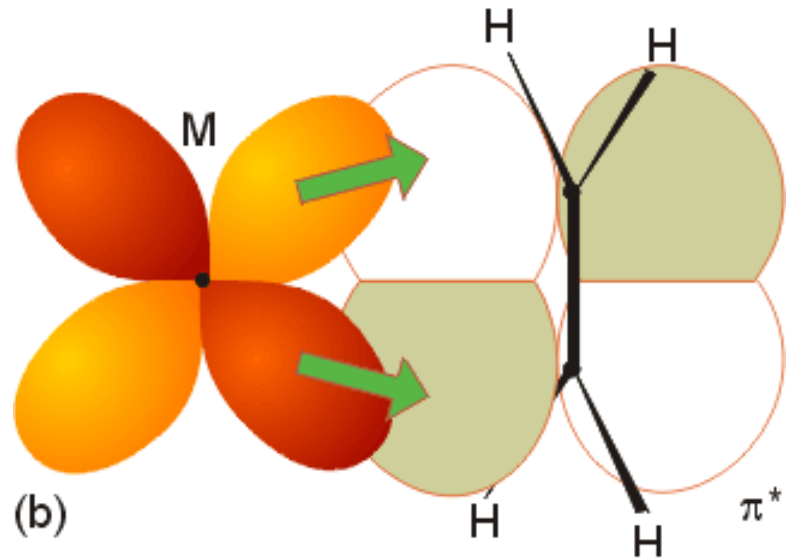


Metal Alkene Bonds
Dewar-Chatt-Duncanson Model

- **Donation of e⁻ density from a filled π-MO of the alkene into a vacant metal σ-orbital.**

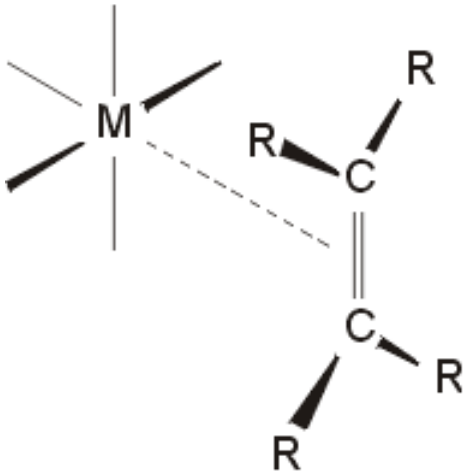


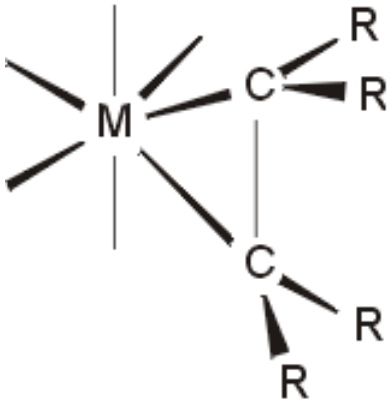
- **Acceptance of e⁻ density from a filled metal dπ orbital into the vacant π*-MO of the alkene.**



Metal Alkene Bonds
Bonding Modes

- **Depending on the electron density in both, the metal and the alkene, the actual situation will lie between two extremes**



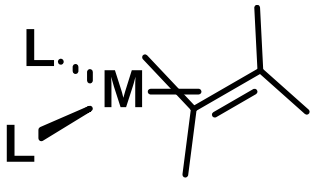


- **normal situation for most alkenes**

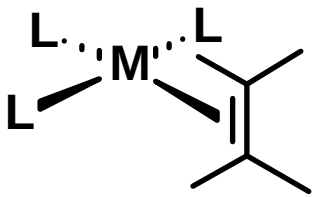
- **very e^- rich metal fragments**
- **strongly e^- withdrawing substituents on the alkene**

Metal Alkene Bonds
Bonding Modes

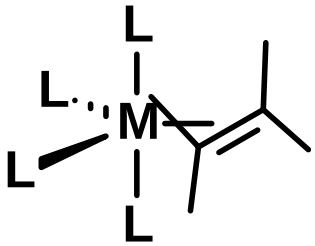
- **The conformation with respect to the metal-alkene bond depends on the metal fragment**



coordination no.: 3
16 valence e$^-$
L_2M(alkene)



coordination no.: 4
16 valence e$^-$
L_3M(alkene)



coordination no.: 5
18 valence e$^-$
L_4M(alkene)

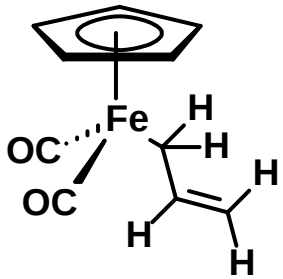
- **Examples**

$(PPh_3)_2Ni(C_2H_4)$
$Pt(C_2H_4)_3$

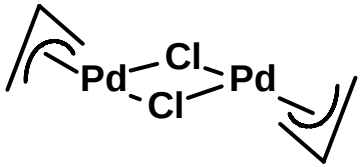
$K[PtCl_3(C_2H_4)]$

$(PPh_3)_2IrBr(CO)TCNE$
TCNE = tetracyanoethene

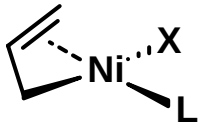
Metal Allyl Bonds
Bonding Modes



η^1- coordination

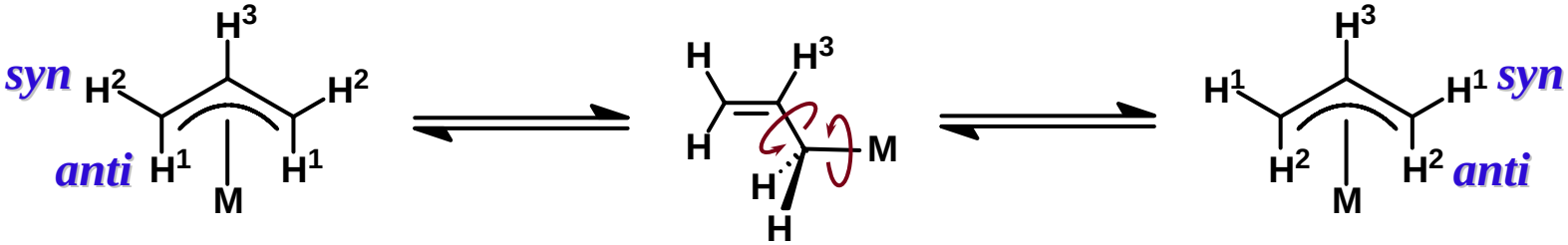


η^3- coordination



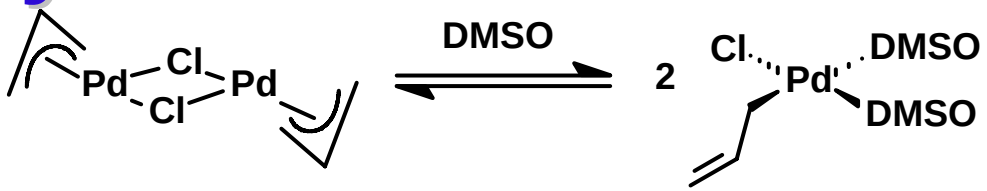
η^1- η^2- coordination

- ***Syn* and *anti* protons can be distinguished in ^{1}H-NMR spectrum**
- ***Dynamic behaviour (isomerization) on the NMR time-scale often leads to averaged signals***



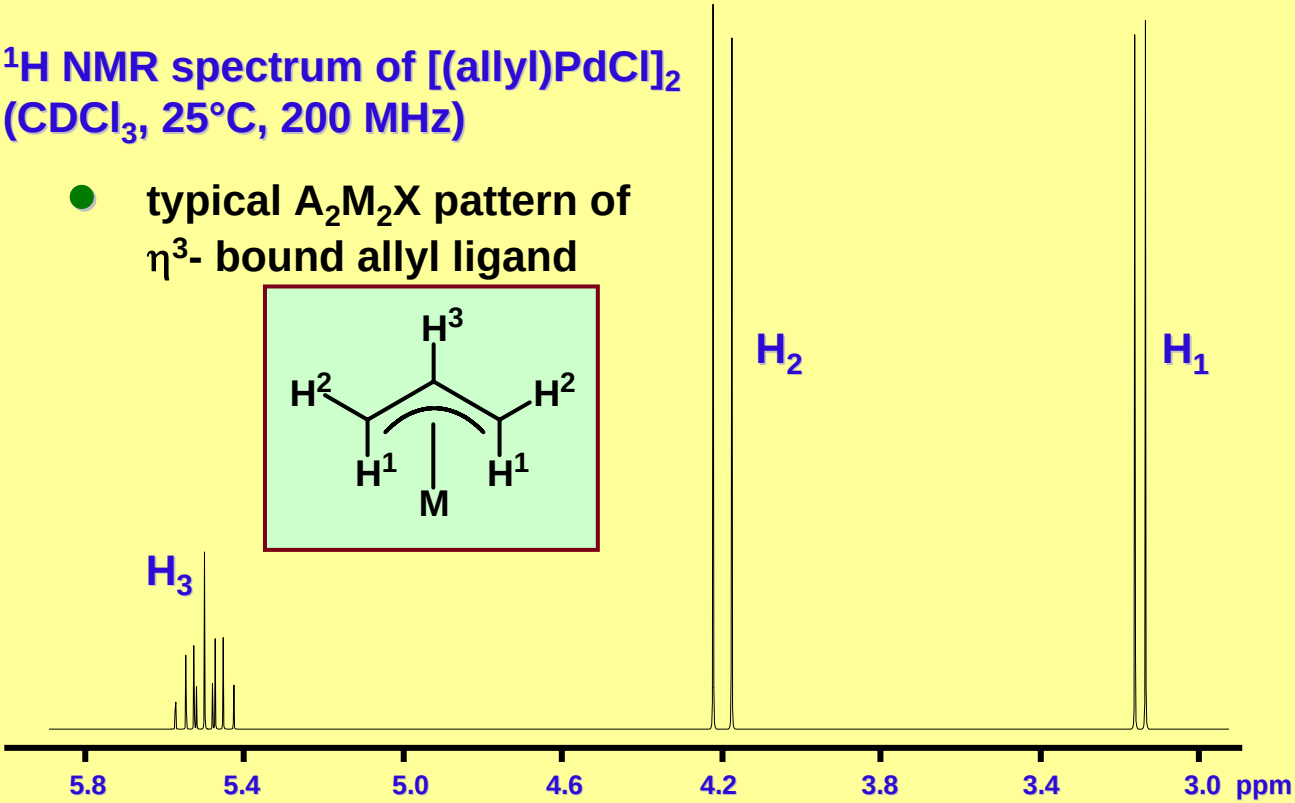
- **Allyl metal complexes are important intermediates and metal-precursors in catalytic reactions**

Dynamic NMR Behavior



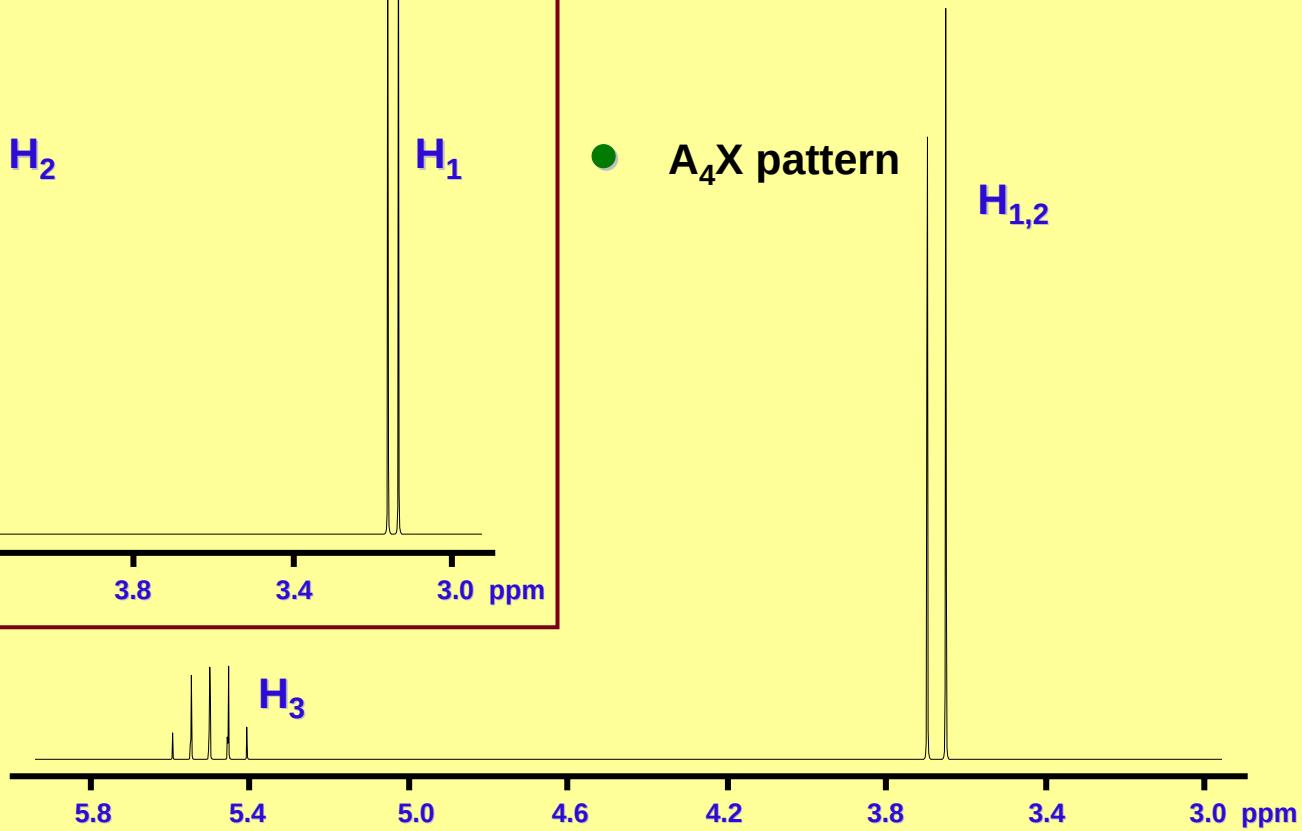
^{1}H NMR spectrum of [(allyl)PdCl]$_2$ ($CDCl_3$, 25°C, 200 MHz)

- typical A_2M_2X pattern of η^3- bound allyl ligand



^{1}H NMR spectrum of [(allyl)PdCl]$_2$ (d^6-DMSO, 140°C, 200 MHz)

- A_4X pattern

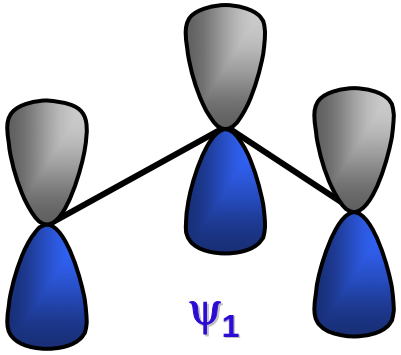


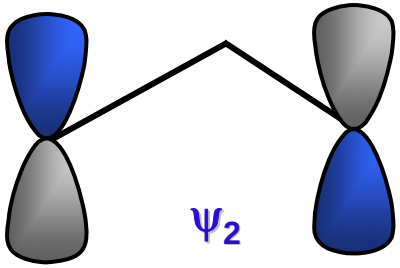
Metal Allyl Binding

σ-bonds

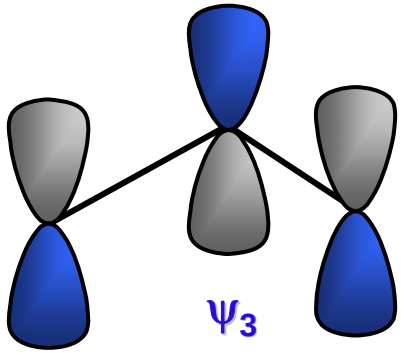
π-bonds

ligand A_2

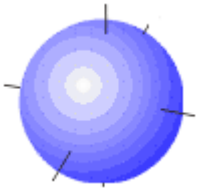




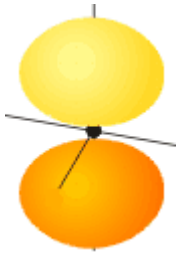
B_1



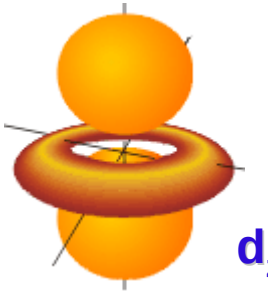
metal



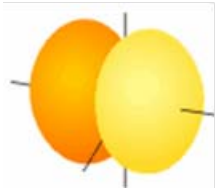
s



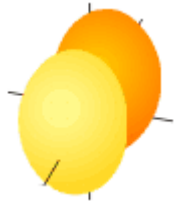
p_z



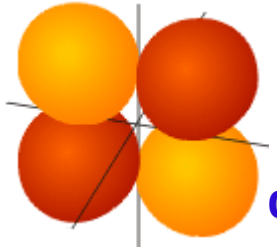
d_{z^2}



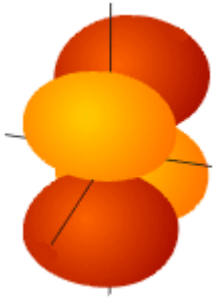
p_y



p_x



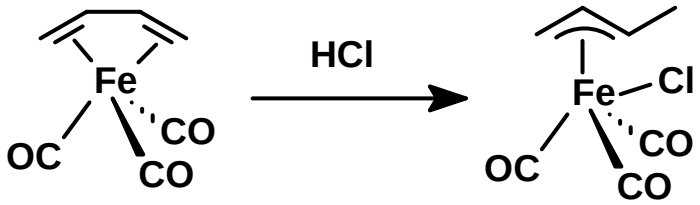
d_{yz}



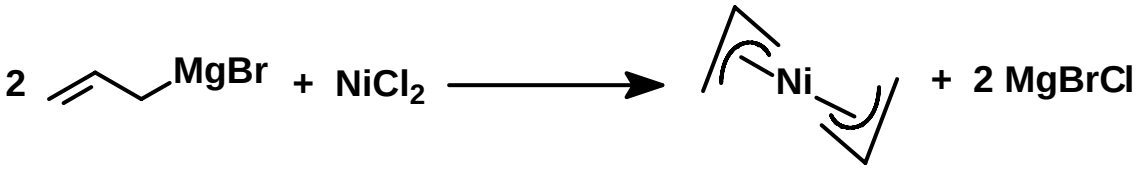
d_{xz}

Metal Allyl Bonds
Synthesis

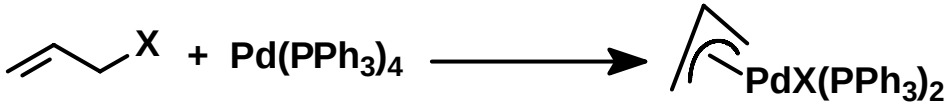
- **protonation of 1,3-diene complexes**

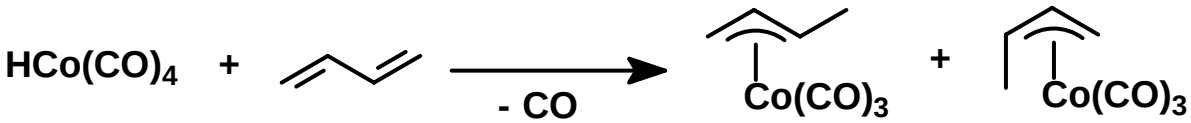


- **reaction of metal halides with an allyl-Grignard reagent**



- **allylic substitution reactions**



X = OAc, OC(=O)R

- **reaction of a metal-hydride with a 1,3-diene**