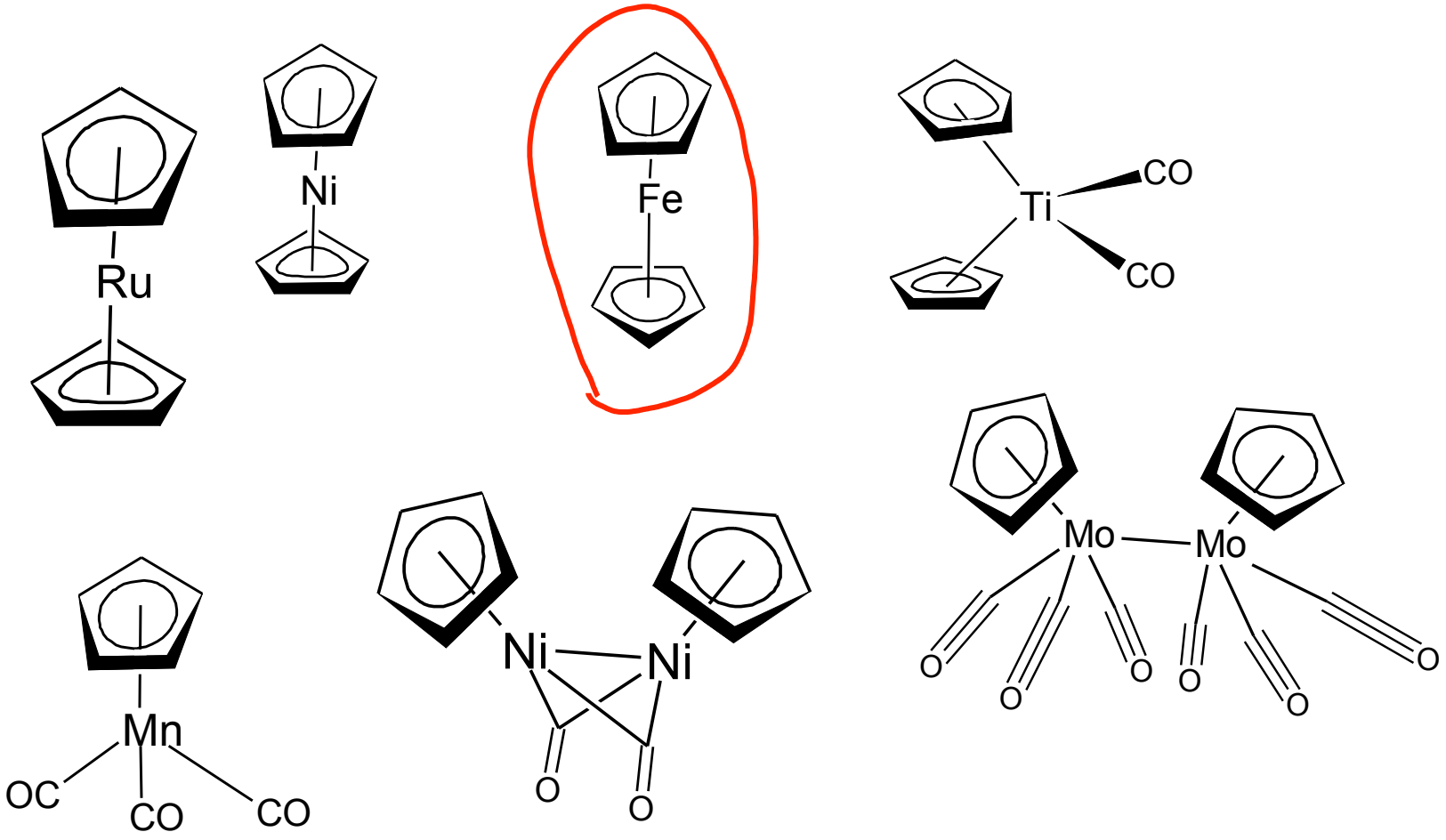
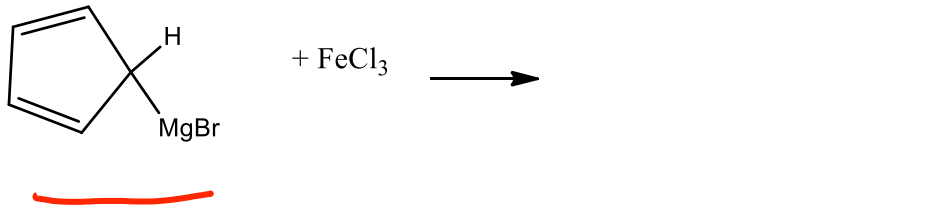
Cyclopentadienyl Complexes

Sandwich compounds

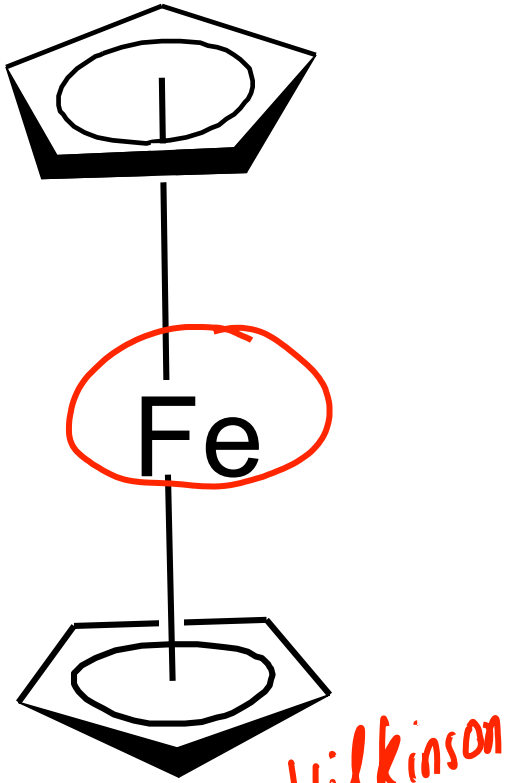
Structures



- Accidental discovery!
- Two groups in 1951
  - (a) Miller and
  - (b) Pauson and Kealy
- Properties don't match the properties of the expected cpd nor the properties of the structure proposed by Pauson and co..

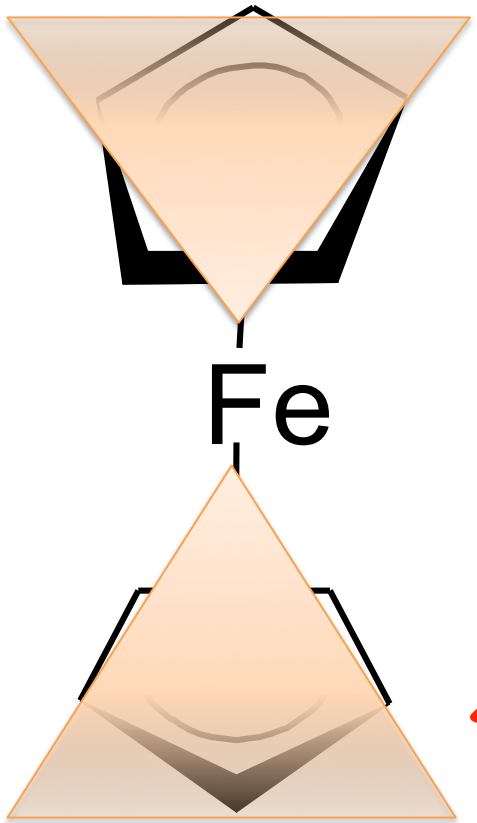


Proposed structures of Wilkinson / Woodward and Fischer



Wilkinson

Sandwich Structure

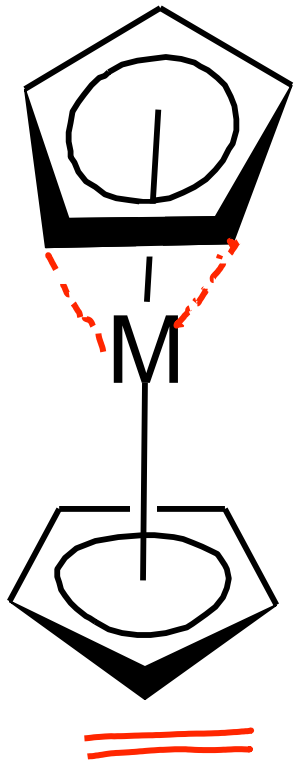


Fischer

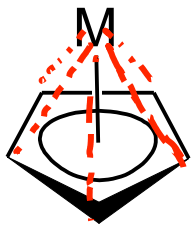
Double cone

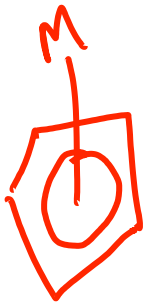
- Diamagnetism
- Chemical behaviour
- Xray analysis

- Fischer and Wilkinson enter a “historic race” to make the Periodic Table of metallocenes!
- It ends in a Nobel Prize in 1973 for both!!



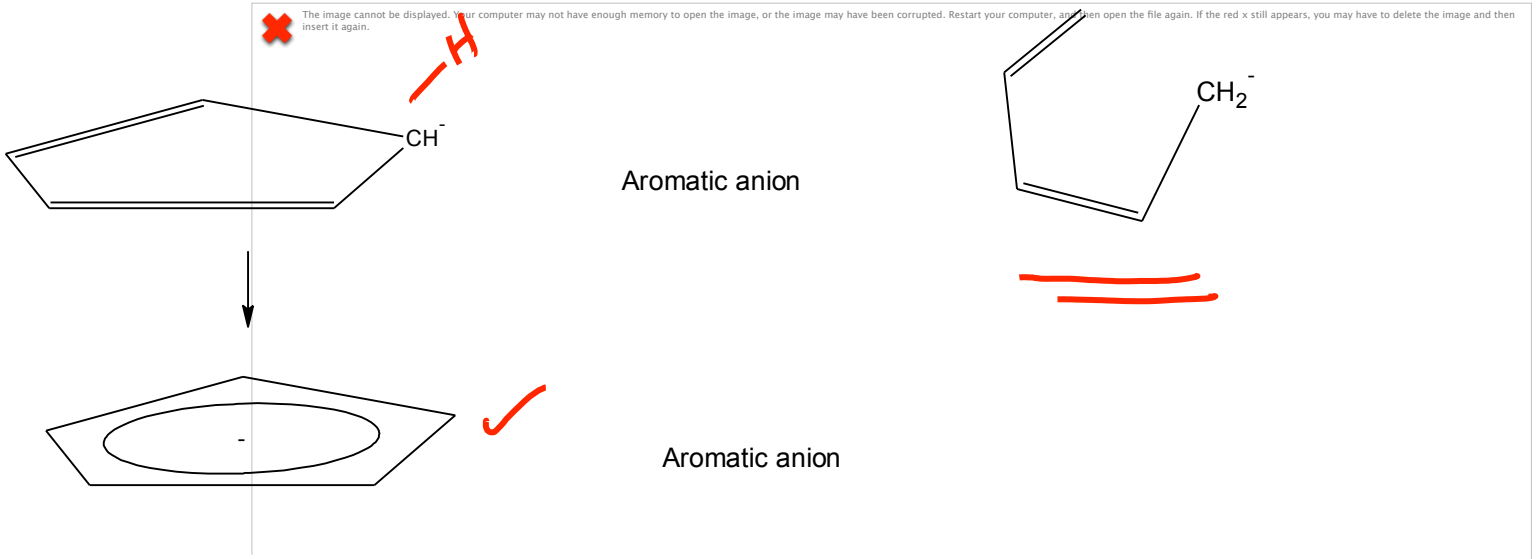
- Cp is $[C_5H_5]^-$ $4n+2$ $n=1$
- Pentamethyl cyclopentadienyl group is also popular $[C_5Me_5]^-$ = Cp*
- It is essentially an anionic group R^- but has the ability to coordinate multiple (5) C atoms to the metal.
  - Allyl had 3 C atoms
  - Cp has 5 C atoms





A line in the centre implies
All 5 C atoms are bonded!

Preparation of metallocenes



Transmetallation

- TlCp is easily made and can be stored. So it is considered a convenient source of cyclopentadienyl complexes!
- Tl is toxic and so should be handled with care!

- CpMgBr and CpLi can be used as well.

- CpLi can be made from CpH and Li sand.

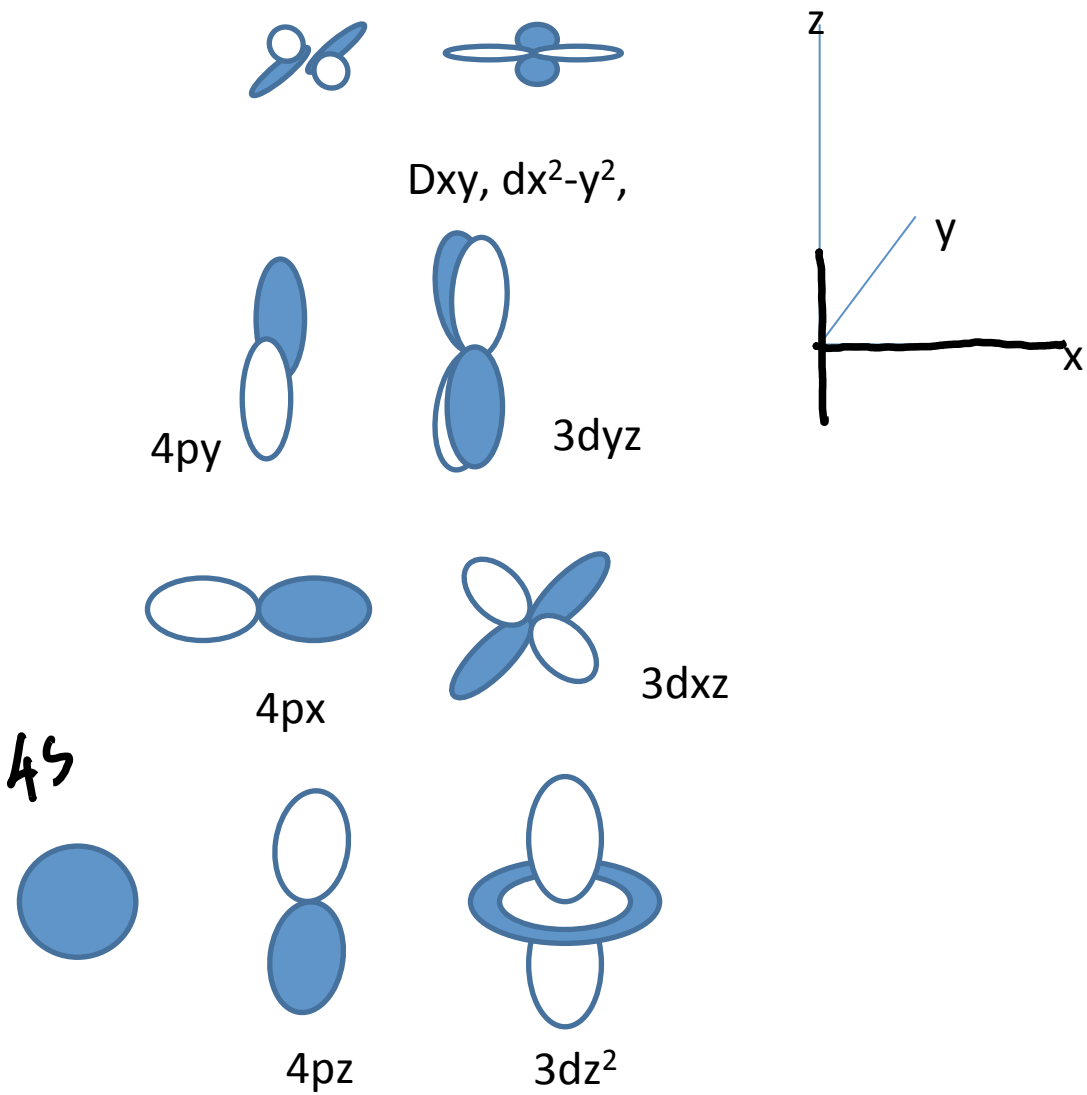
Direct Reaction

- Ferrocene can be made from $FeCl_3$ and Fe powder with Et_3N and CpH under reflux conditions.
- The amine removes the HCl that is generated!
- Fe reduces the Fe(III) to Fe(II)

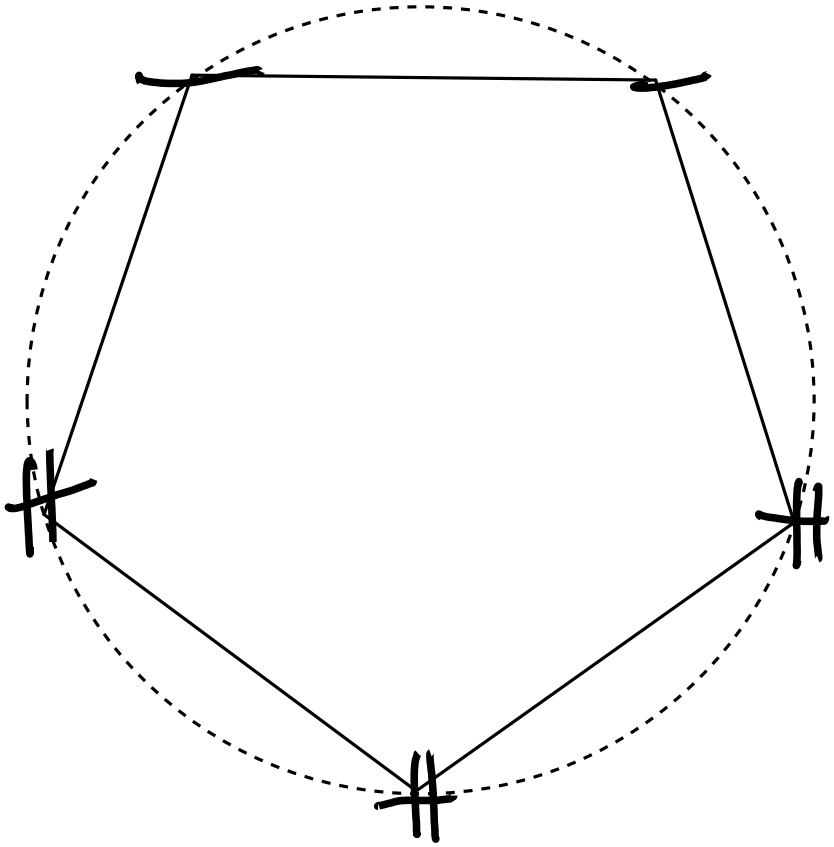
- Alt: Fe and $Et_3N{\cdot}HCl$ at a higher temp.

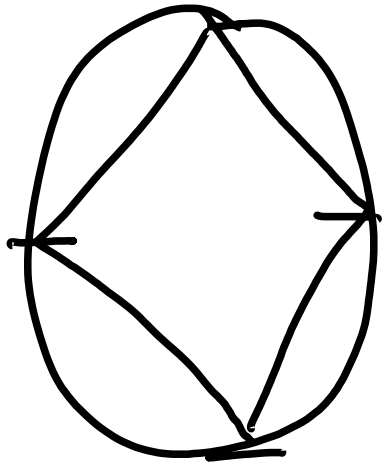
- Always, CpH is freshly prepared from cracking $C_{10}H_{12}$ $(CpH)_2$

Bonding

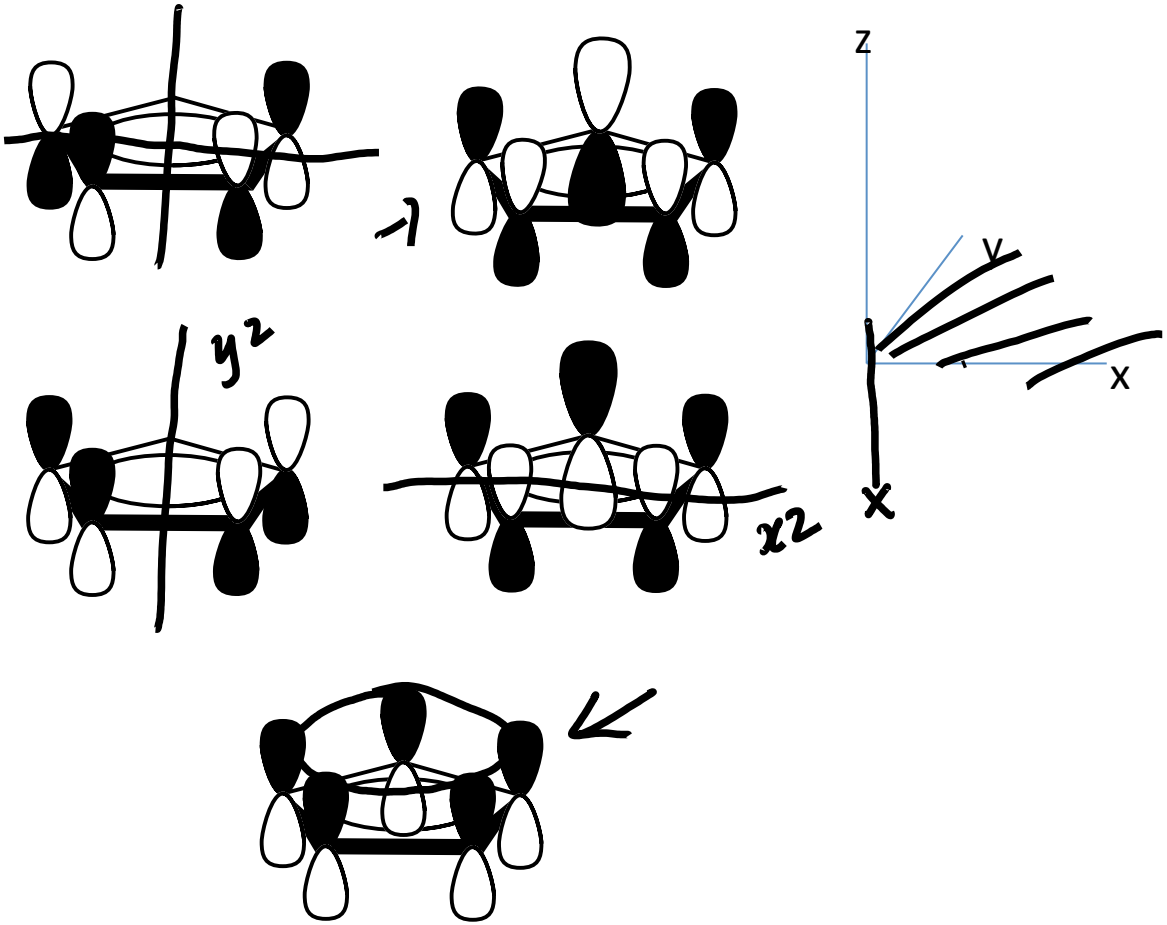


Energy Levels

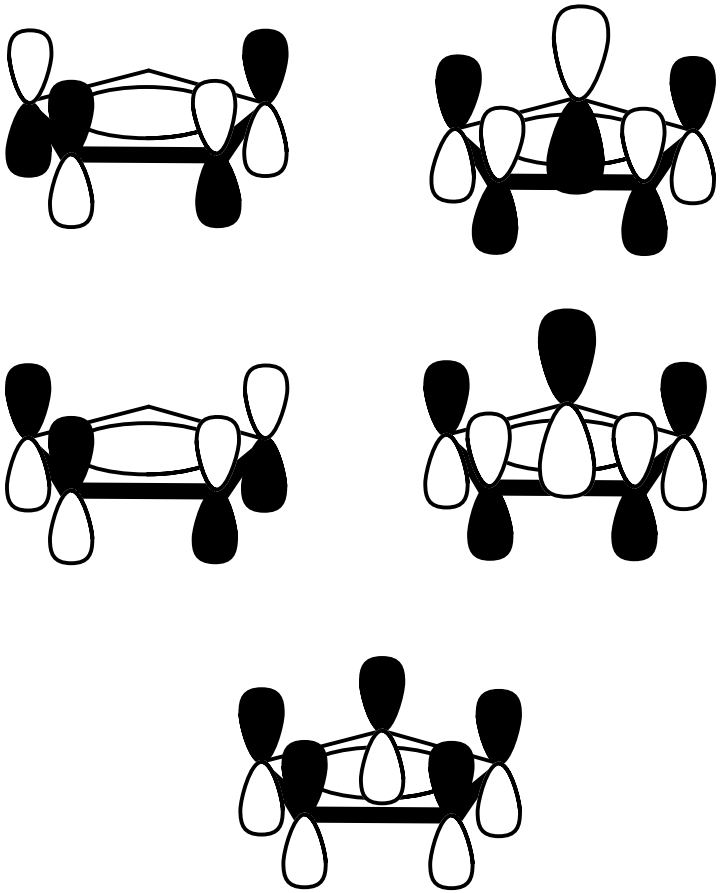


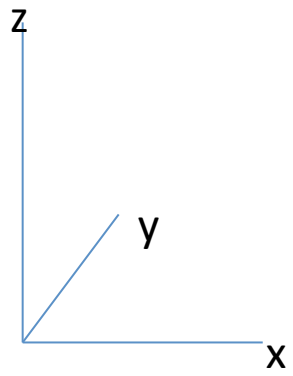


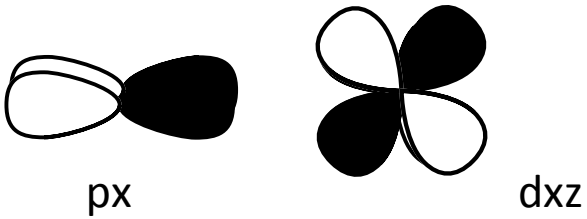
Cyclopentadienyl MO



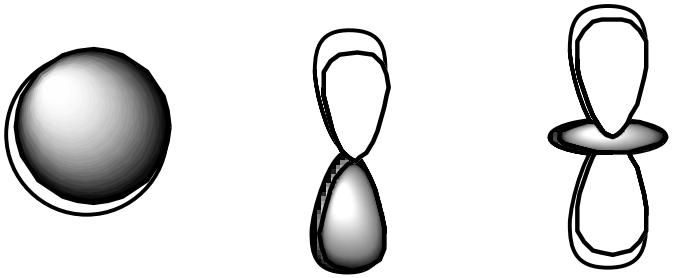
Mix and Match





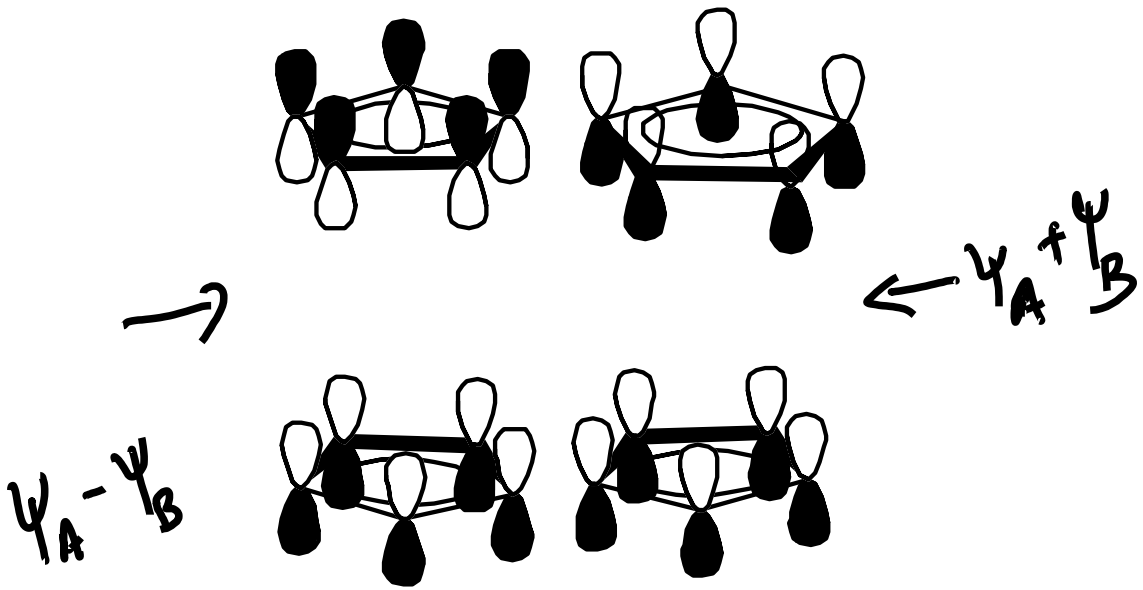


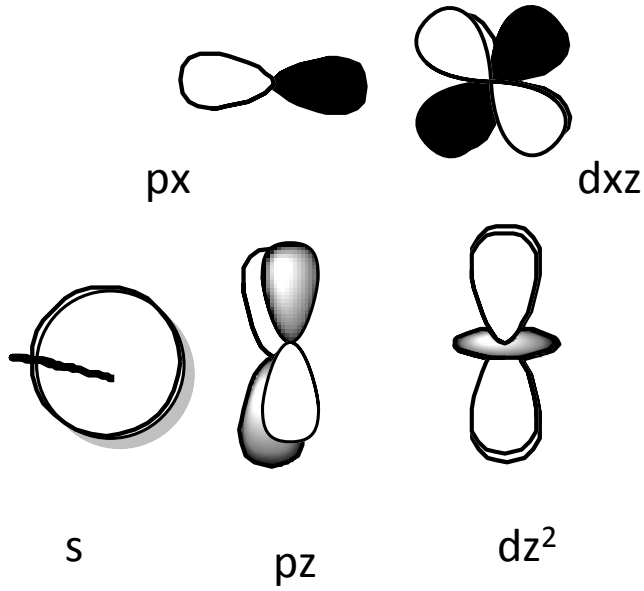
px dxz



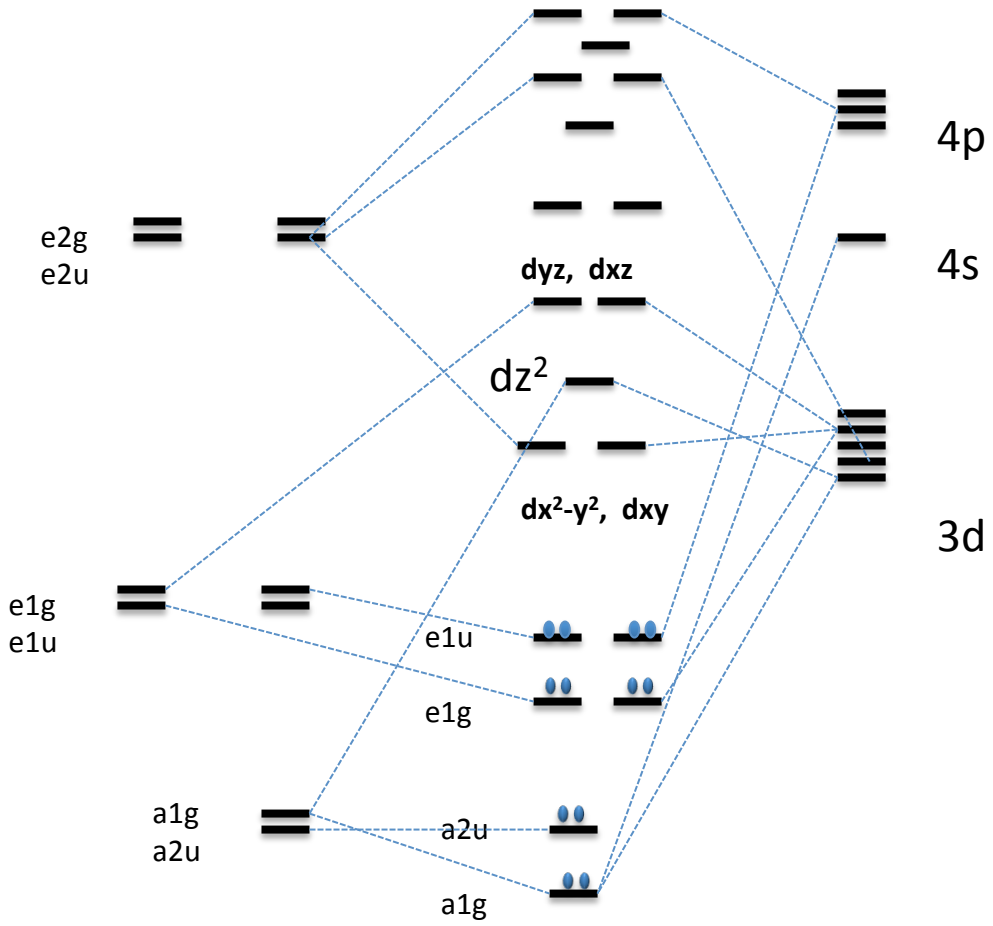
pz dz^2

Remember there are two Cp rings!

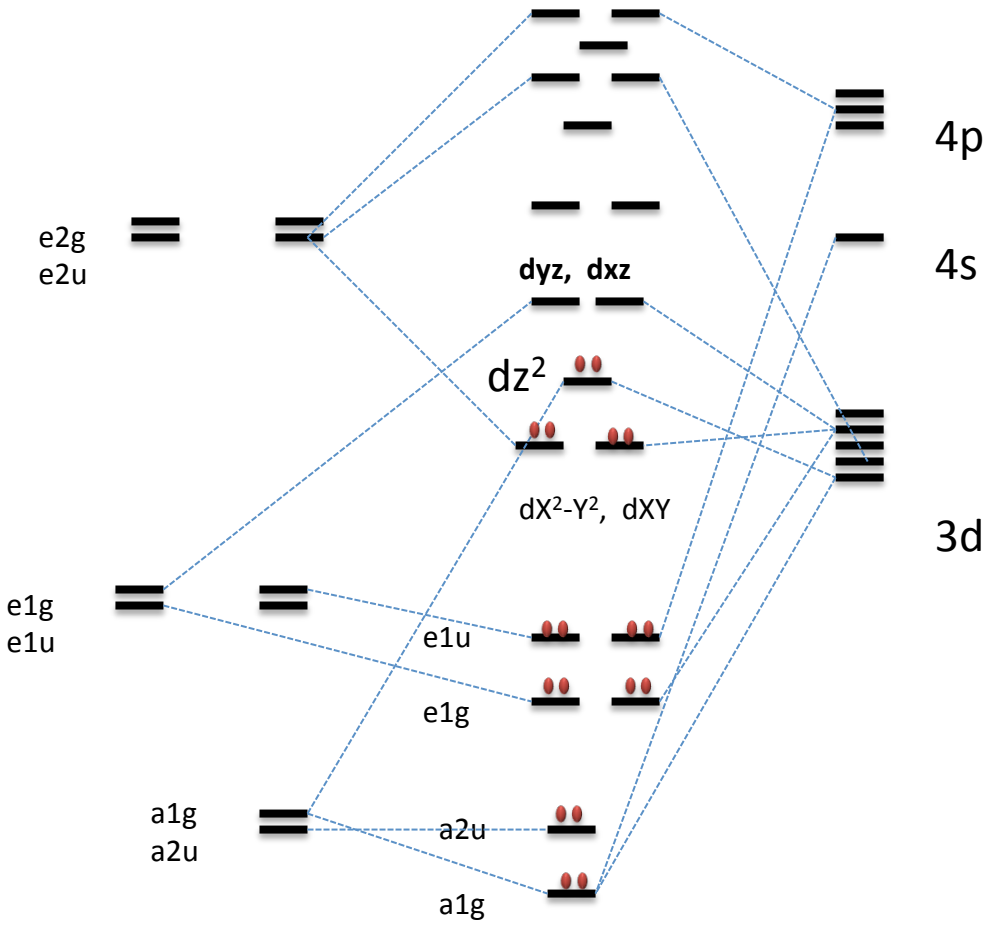




MO Energy diagram of Ferrocene

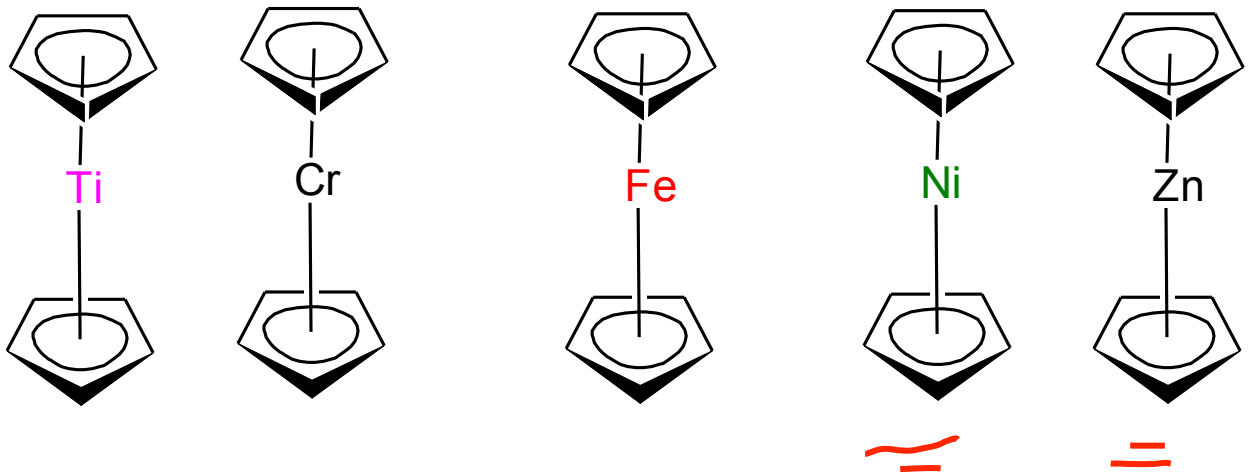


Electron Count! Iron is the best!



Properties!

Metallocene	Color	upe	Exper. B.M	Expected B.M	Interplanar distance (pm)
VCp_2	Purple	3	3.84	3.87	
$CrCp_2$	Red	2	3.2	2.83	361
$MnCp_2$	Amber	5	5.81	5.92	
$FeCp_2$	Orange	0	0.00	0	332
$CoCp_2$	Black	1	1.76	1.73	340
$NiCp_2$	green	2	2.86	2.83	360

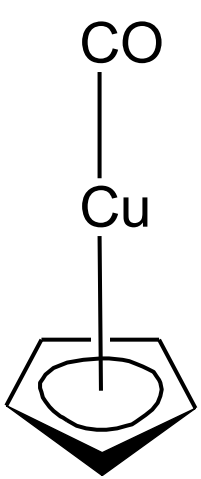


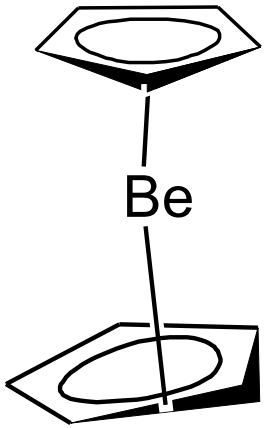
Ferrocene: Most stable, 300+ ^{o}C
Sublimes and is used for making carbon nanotubes!
Bond distance is shortest for Fe (18 electron system)
Magnetic properties are predictable!!

$[Co(Cp)_2]^+$ should be a very stable system! It is

$[Mn(Cp)_2]^-$ is not as stable as it should be because, Cp- is lost!
Look at the MO diagram.

- Bonding mode should depend on the electron count!

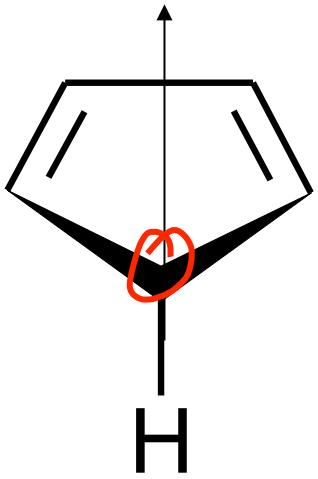




Many of the M^{2+} structures are slipped from the centre

- But most structures are fluxional.

Importantly, the Cp is a ligand which can adjust the electron donation
By sliding the metal along the line shown by the arrow



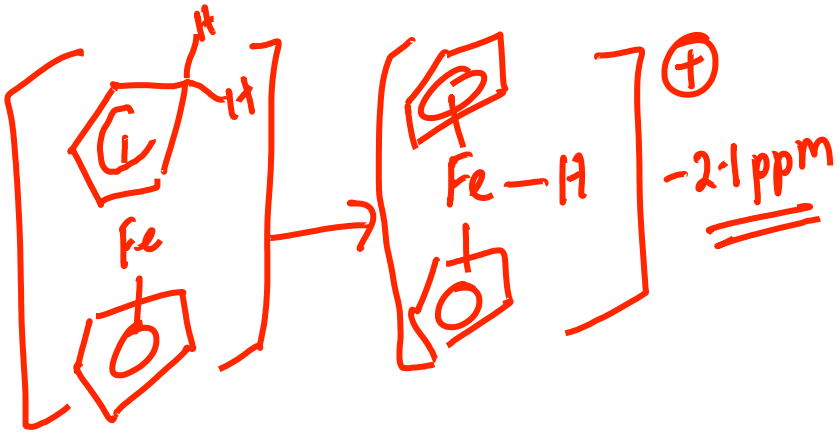
η^1

M

η^5

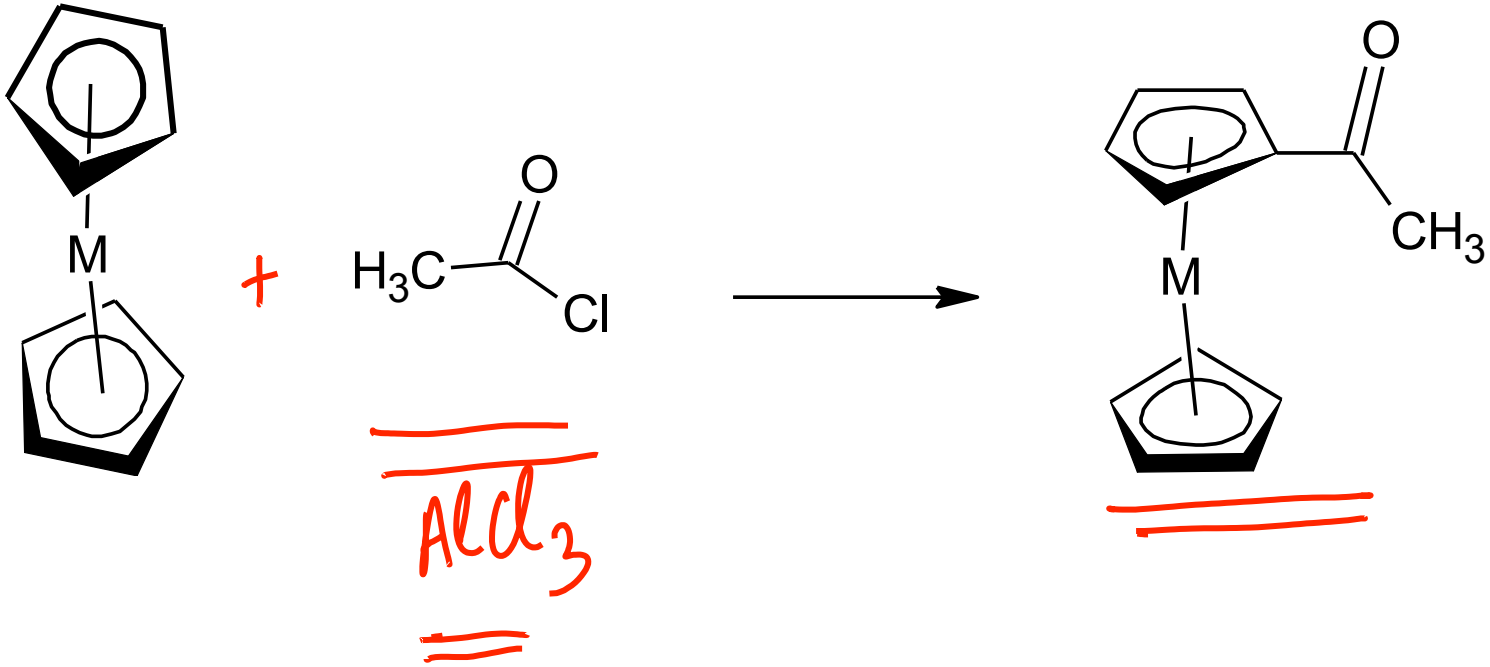
η^3

- Ferrocenes can be oxidized and protonated.
- $Fe(Cp)_2$ is oxidized with $AgBF_4$ to produce a $[Fe(Cp)_2]^+$ species. It leaves behind silver metal
- H^+ can be added to ferrocene to give $[Fe(Cp)_2]H^+$



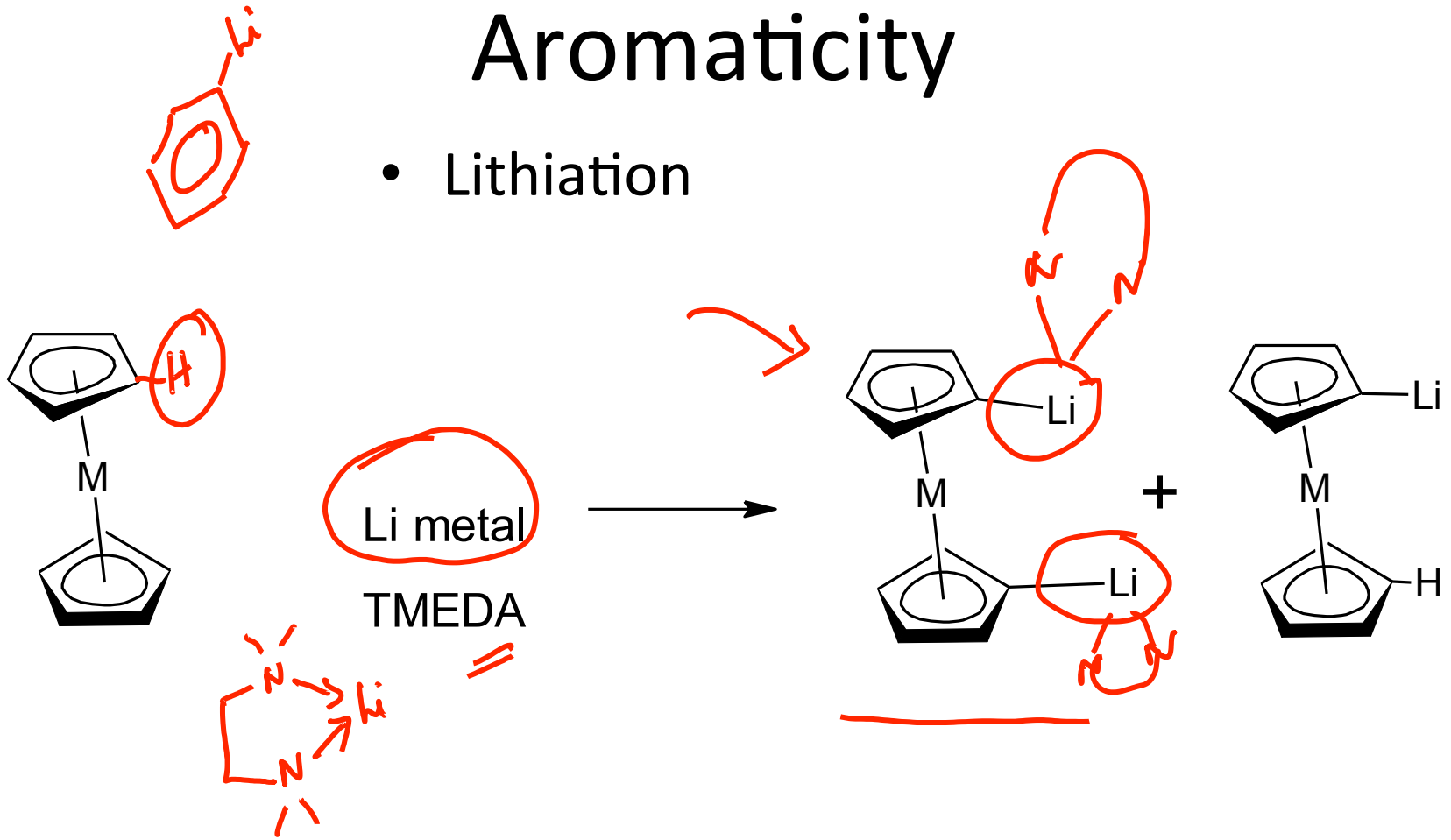
Aromaticity

- Acetyl chloride / $AlCl_3$



Aromaticity

- Lithiation



1500 *Organometallics* **2010,** *29,* 1500–1517
DOI: 10.1021/om100016p

ORGANOMETALLICS
Review

Group 4 Transition Metal Sandwich Complexes: Still Fresh after Almost 60 Years†

Paul J. Chirik*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853

Received January 6, 2010

$(C_5H_5)_2Ti$ The "mystery-cene"

1956 Wilkinson group reports formation of bright green paramagnetic solid. It transforms to a brown solid spontaneously!

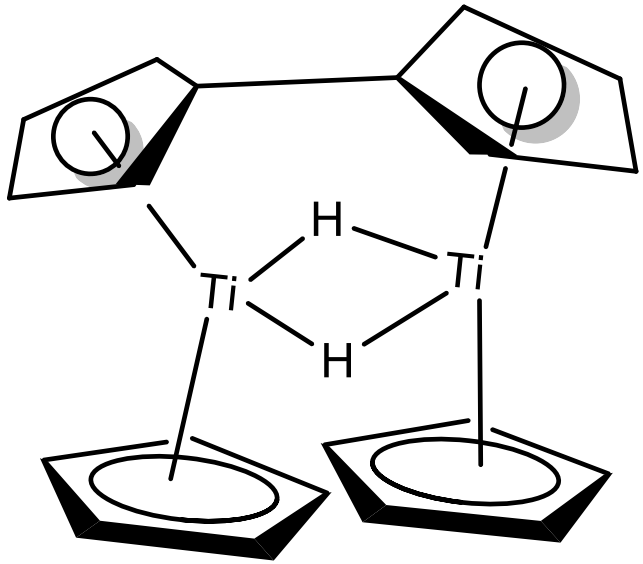
Much later, Watt, Baye and Drummond said that titanocene was diamagnetic and had a molecular weight of 346! Twice what is expected for $(C_5H_5)_2Ti$

14 years after Wilkinson, in 1970, a strong band at 1230 cm^{-1} is identified as a Ti-H bond in the titanocene. Britzinger and Bercaw suggest the structure:
((C5H5)-C5H4)TiH)2

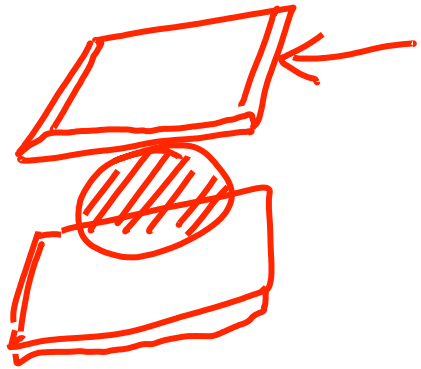
20 years later,1976:
LT NMR spectrum of the compound confirms the presence of Ti-H bond

Finally in 1992, the crystal structure of titanocene is confirmed. It is not what Wilkinson proposed, it was a dimer with a Ti-H bridge.

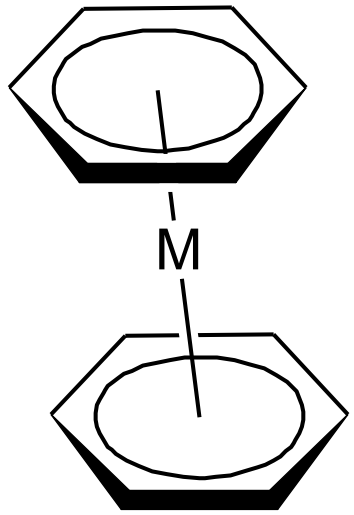
X-ray structure of titanocene



Arene Sandwich Complexes



Hein (1919) mixed ArMgX and Metal $CrCl_3$ to make $Cr(Ar)_3$ and accidentally made a compound that analyzed for $Cr(ArH)_2$



M is a chromium group metal

More rational approach
Fischer Hafner (1955) synthesis

- Mix Al (powder) + 3 $CrCl_3$ + 6ArH
- Forms 2 $[(ArH)_2Cr]^+$ + $AlCl_4^-$
- What is obtained is the Cr(+1) complex !!
- Used $AlCl_3$ and Al as catalysts! Later used $Na_2S_2O_8$ as a reductant to generate the Cr(0) species in good yield

Limitations of F-H synthesis

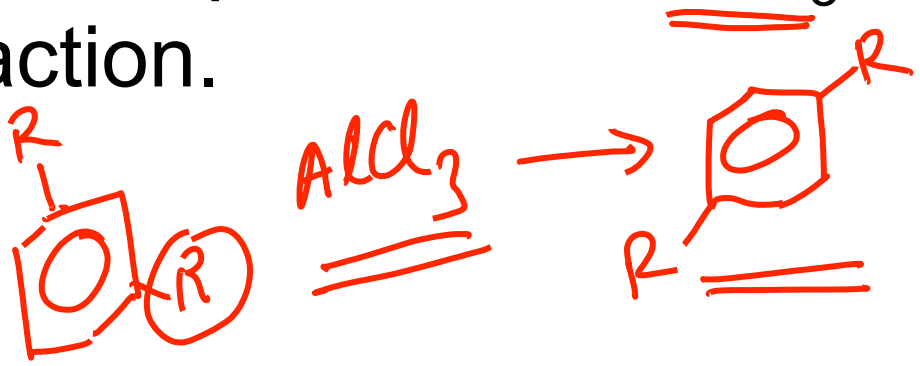
- Does not work with all metals

Cr	Mn	Fe	Co	Ni
Mo	Tc	Ru	Rh	Pd
W	Re	Os	Ir	Pt

$MX_n + Al + AlCl_3$

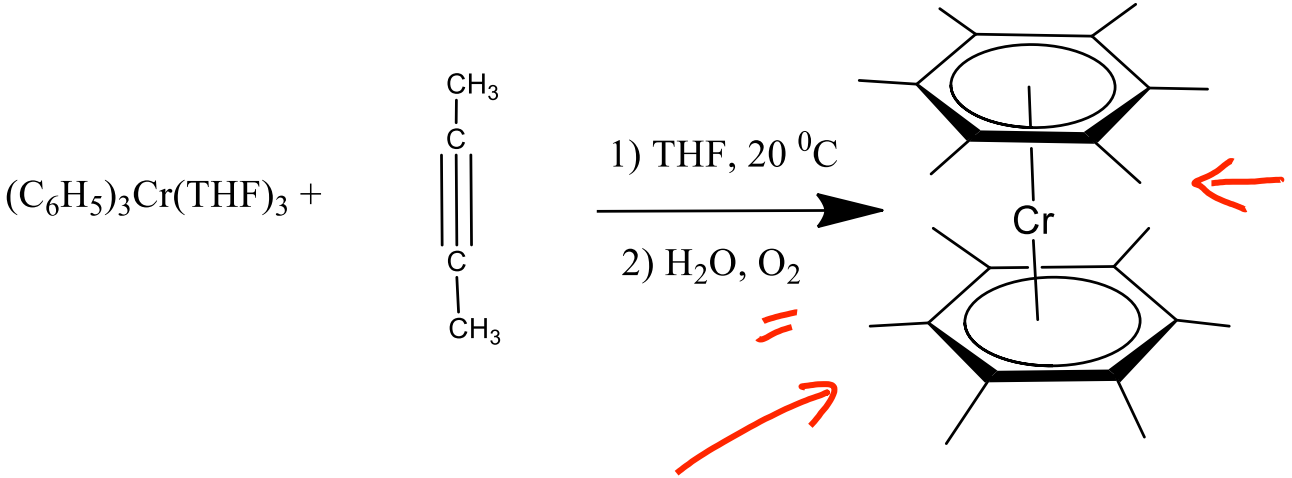
Limits on the aromatic rings

- Ar-X where X = any group with a lone pair of electrons -Cl -NR_2
- The lone pair complexes with $AlCl_3$ and stops the reaction.



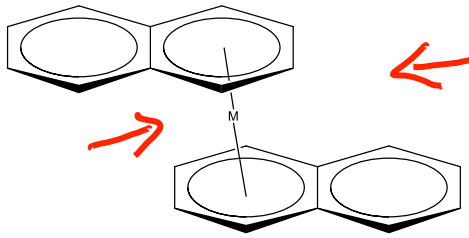
Cyclotrimerization of alkynes

- Me-C≡C-Me is trimerized with some metals in a template synthesis to give an arene:



Reduction and substitution

– $MCl_n(THF)_{6-n}$ + $nLiC_{10}H_8$



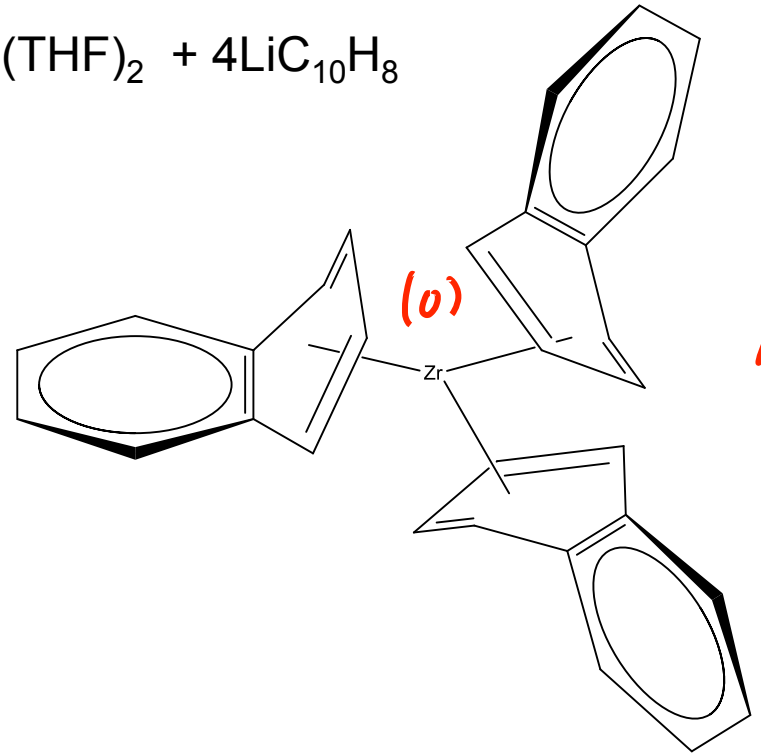
ArH + Li → Li(ArH)

'M"

– This METHOD WORKS for Cr, Mo, and V

Surprise! Surprise!

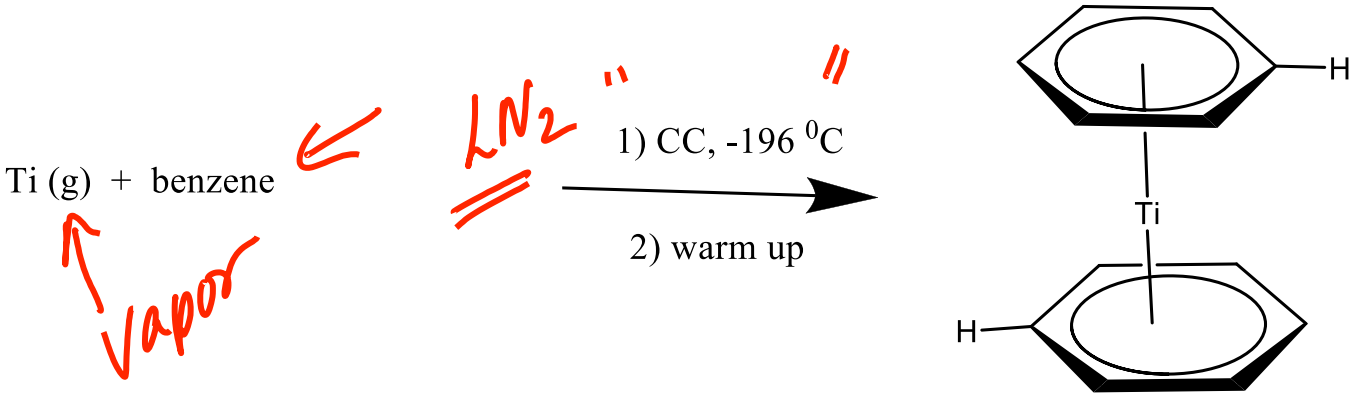
$ZrCl_4(THF)_2 + 4LiC_{10}H_8$



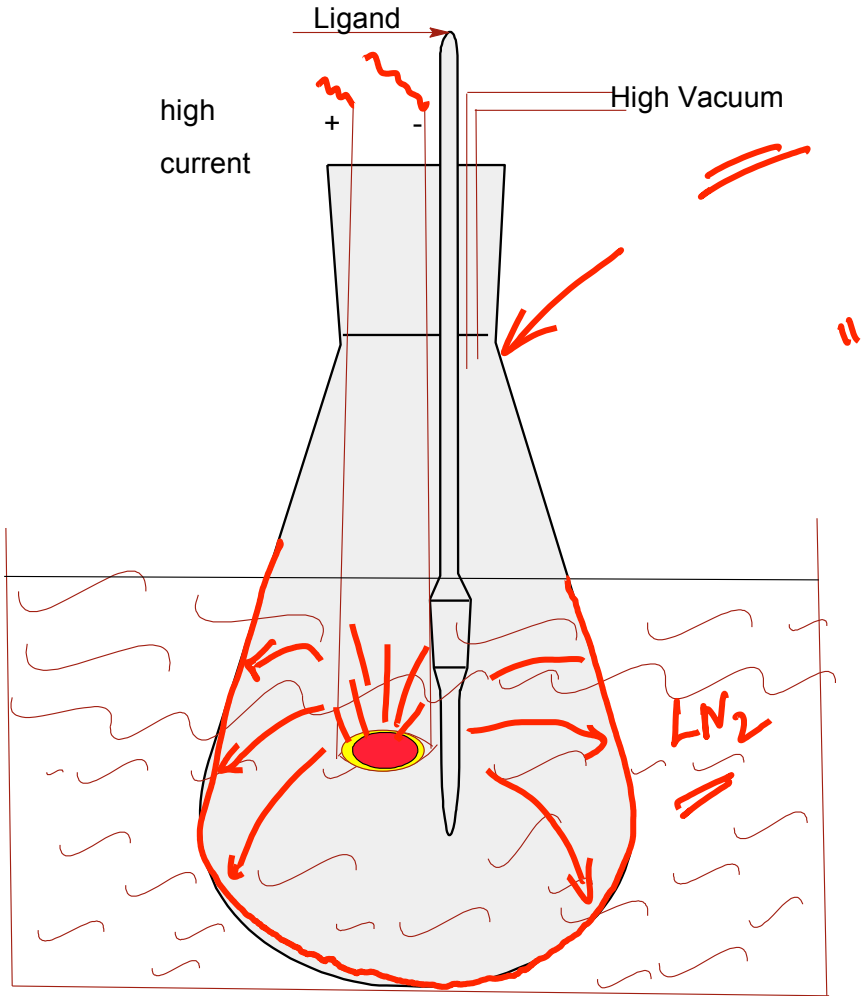
16 e⁻ Complex

Metal atom ligand vapor co-condensation

- Works even when the electron count is bad Cr, Ti, Zr, Hf, Nb, Y, Gd,
- Eg. Ti(g) + 2 C_6H_6

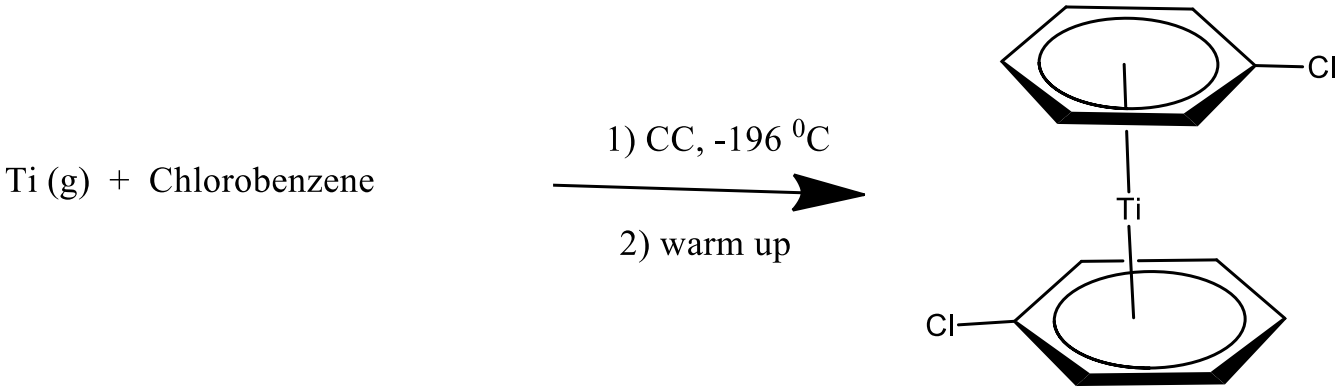


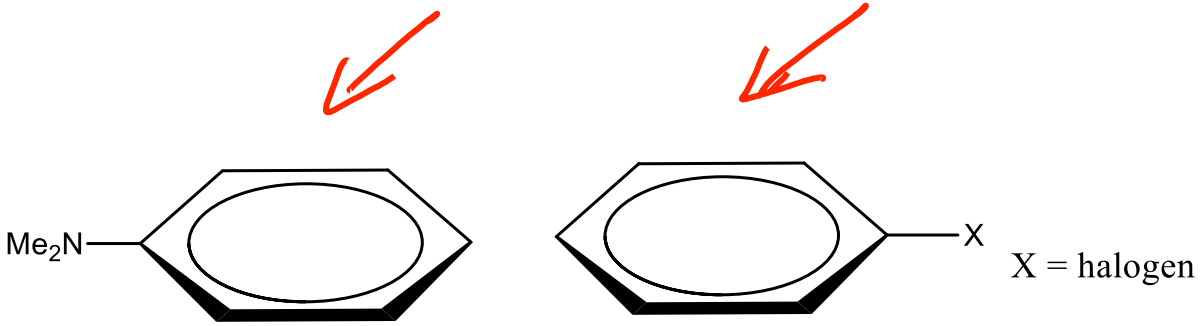
Schematic Representation of Metal Vapor Synthesis



Metal atom ligand vapor co-condensation CC

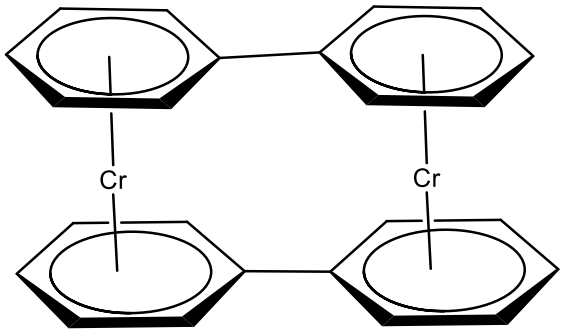
- Coordinating arenes: Chlorobenzene, dimethylamino benzene

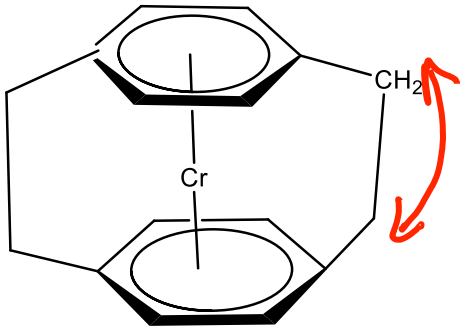


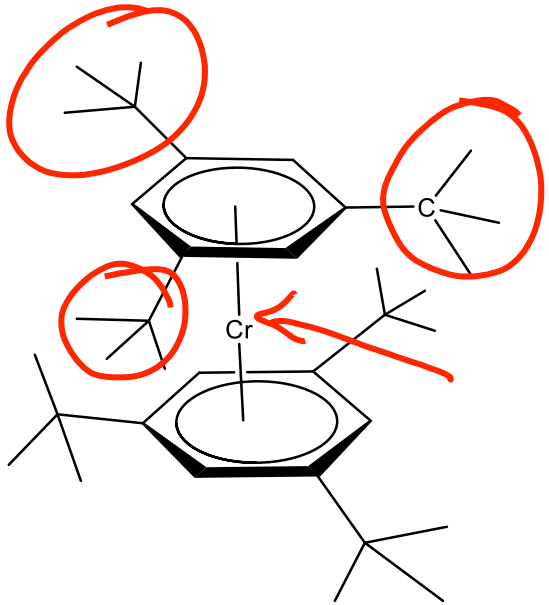


Metal atom ligand vapor co-condensation

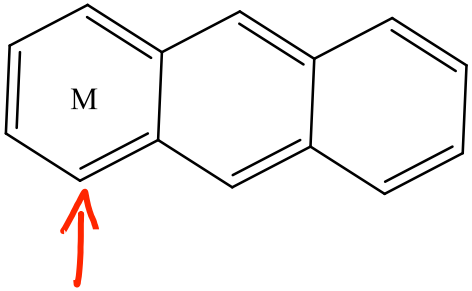
- Works even with sterically inaccessible phenyl groups: Biphenyl, *tri*-^{t}butylbenzene

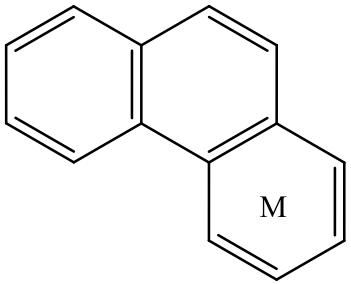


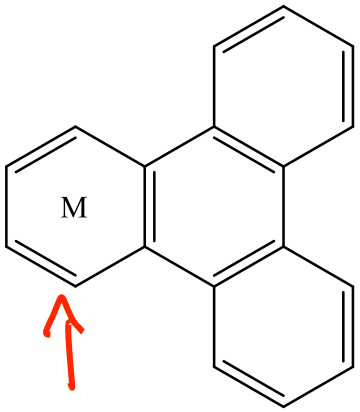


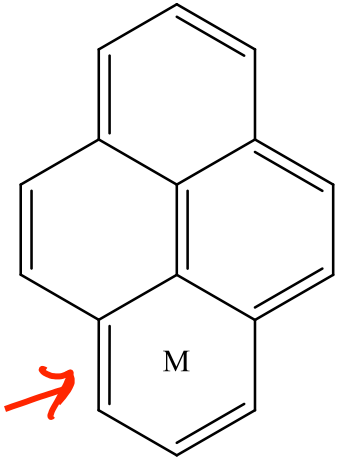


Metal prefers aromatic centers!



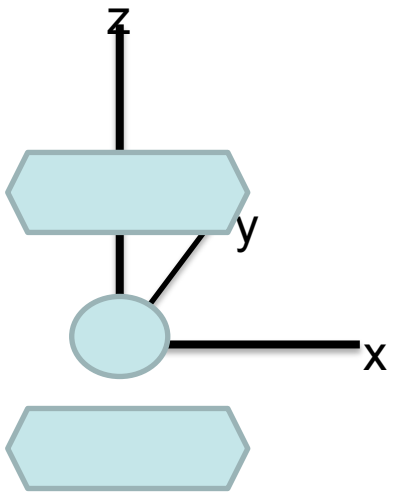




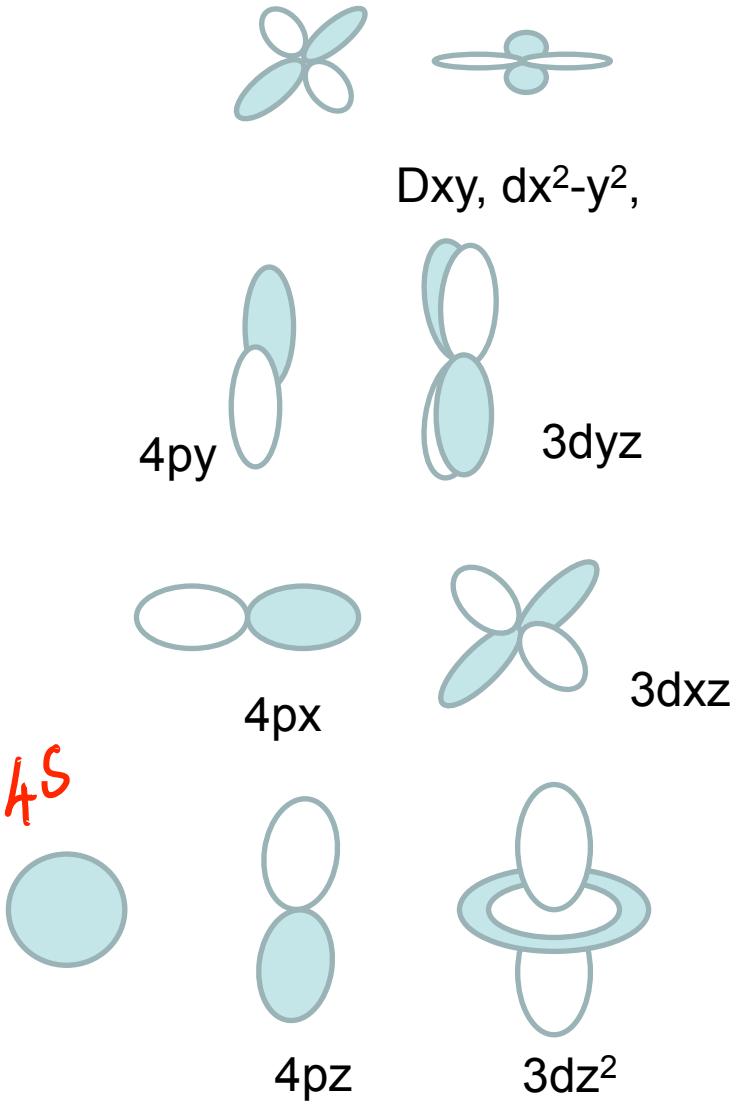


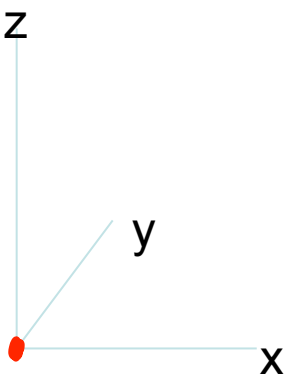
Bonding and Structure

MO treatment



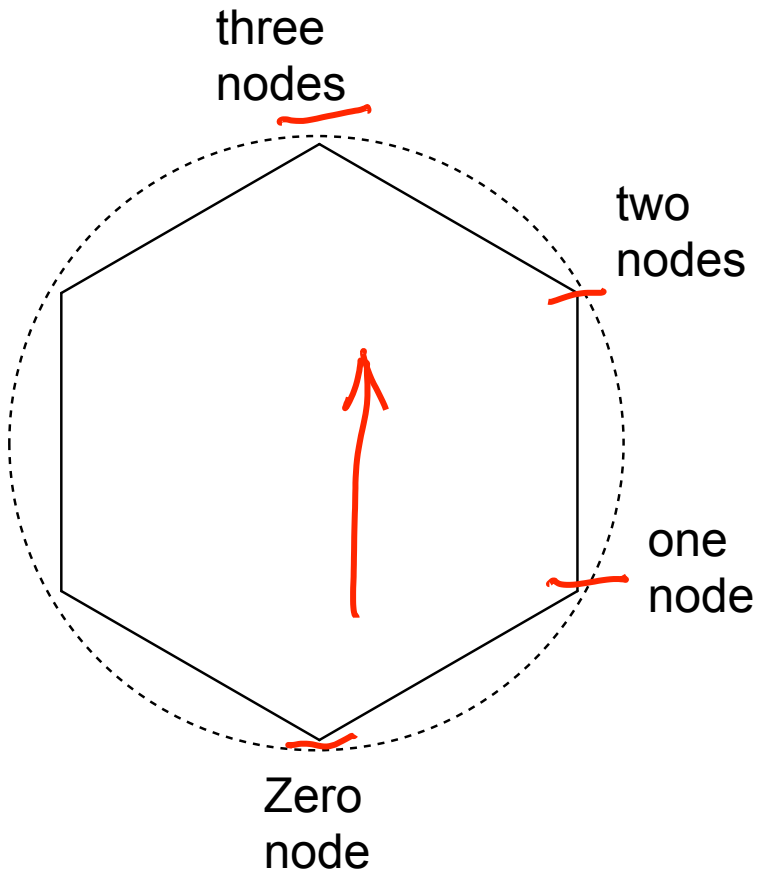
Bonding



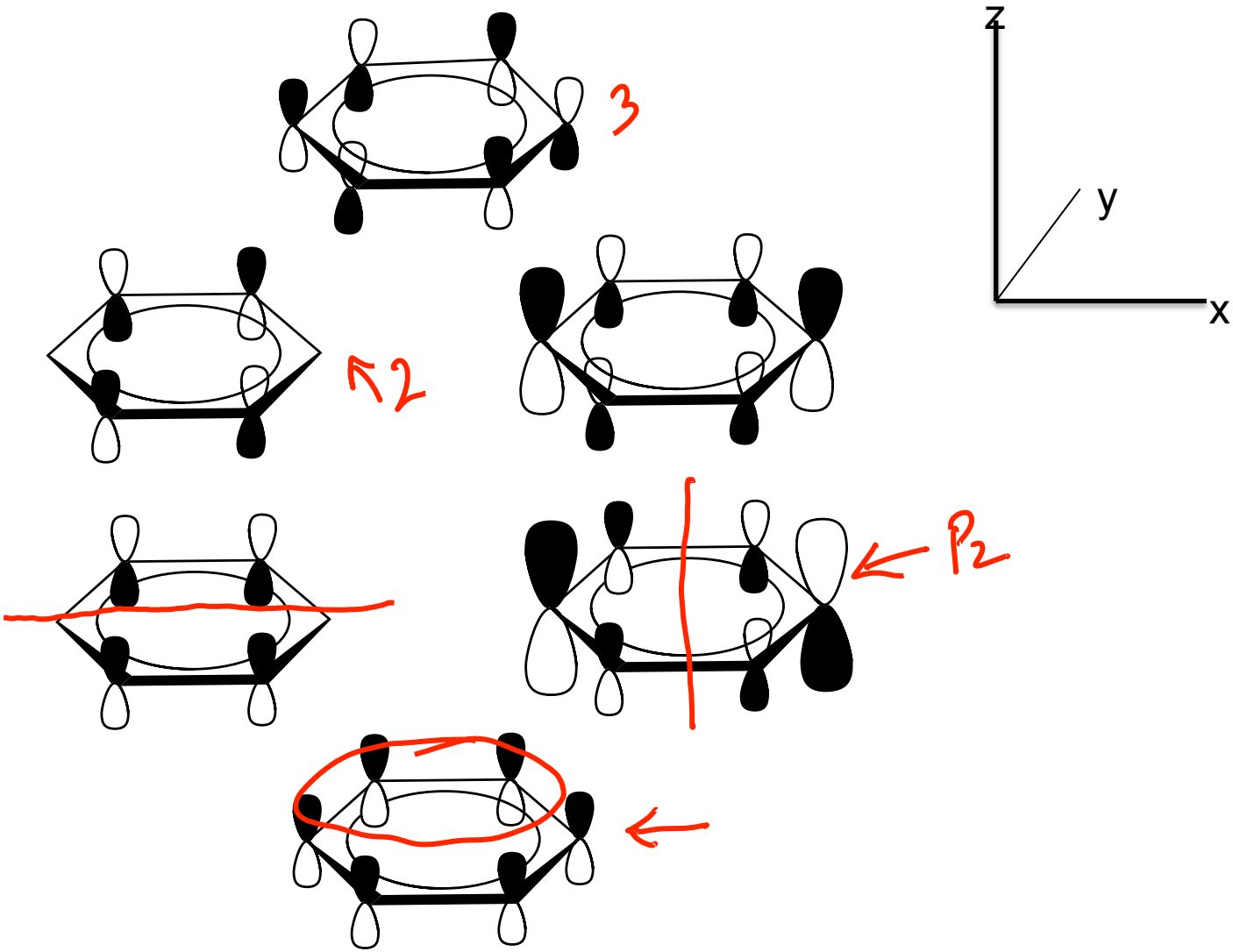


Metal along the z axis!

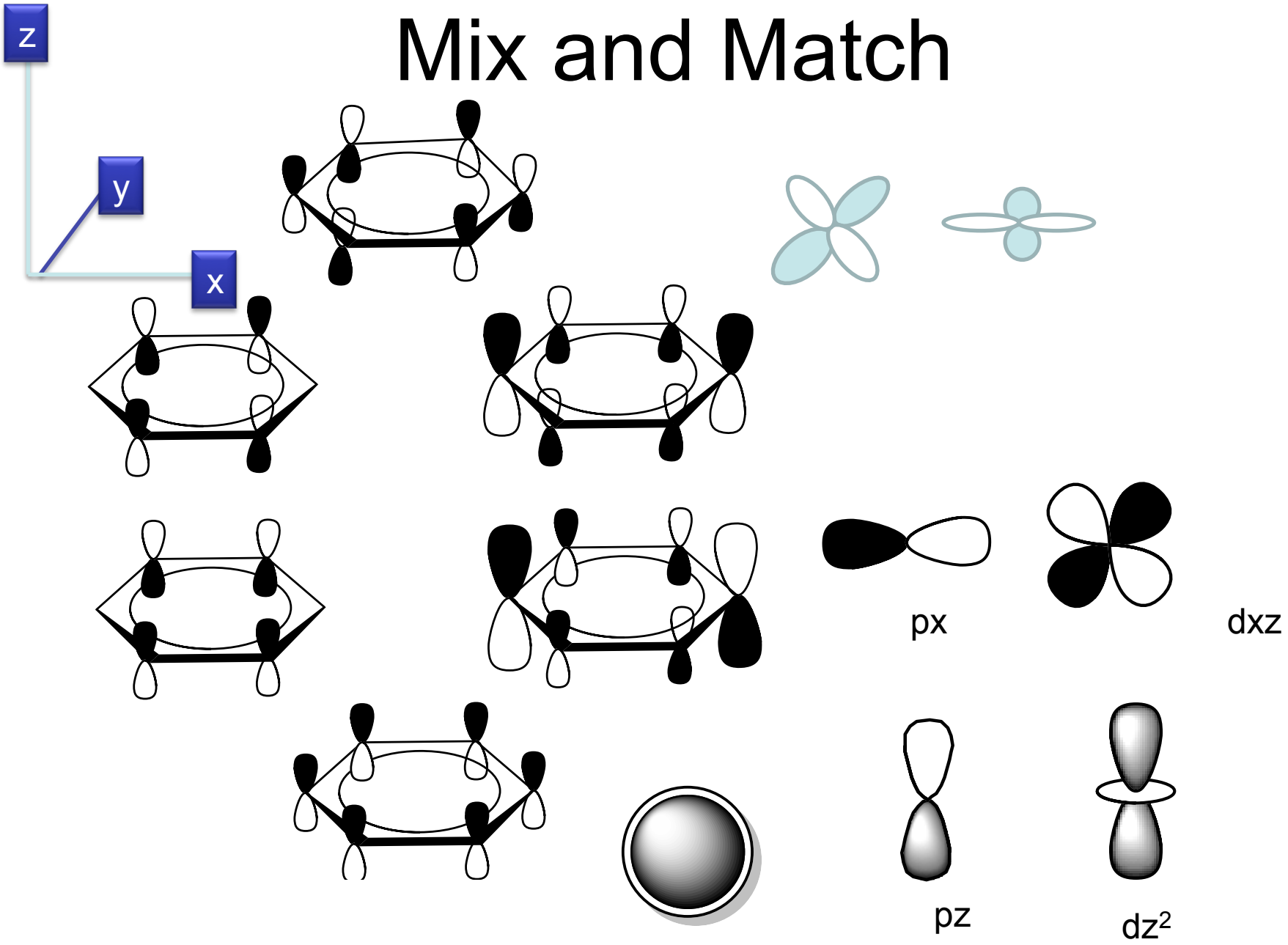
Frost's Energy level diagram



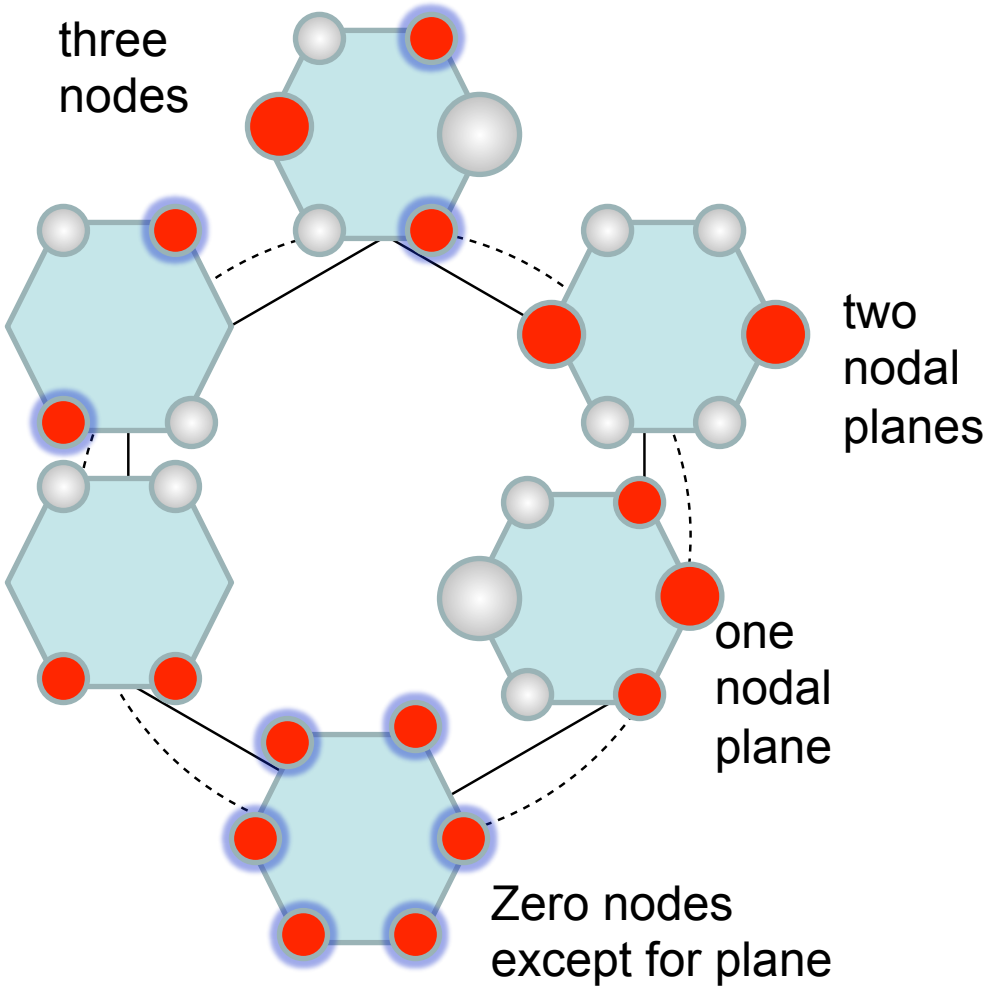
Benzene MO

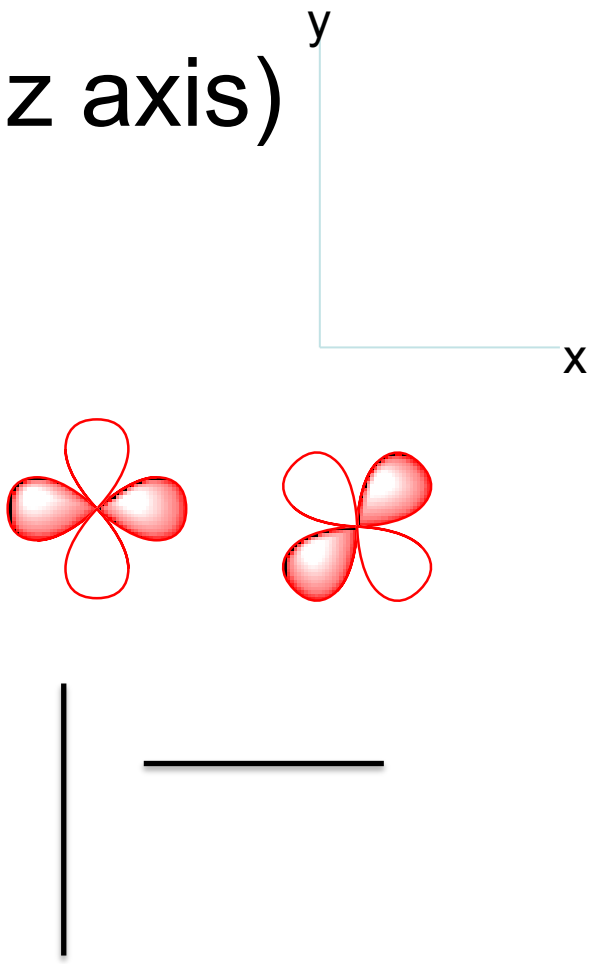


Mix and Match

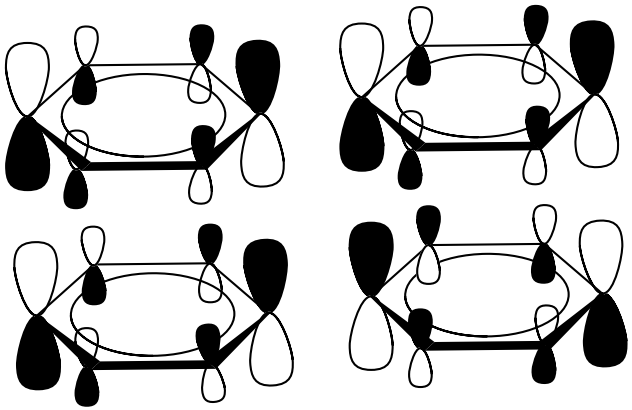


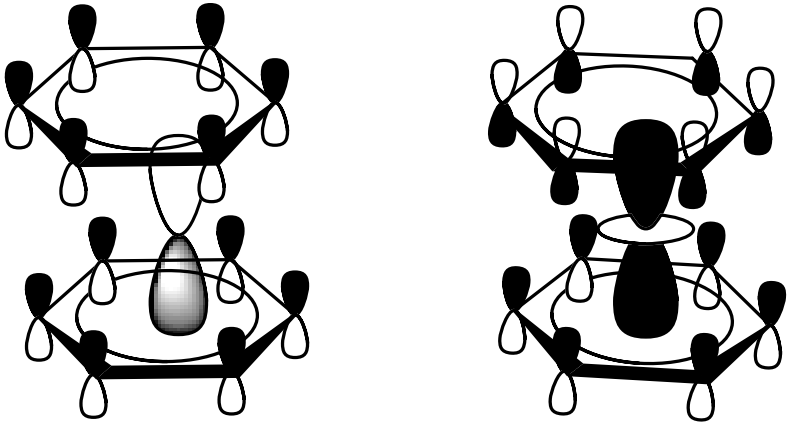
Top view of MO's (down z axis)

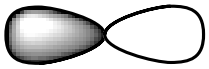




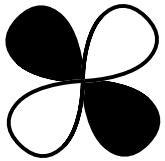
Remember there are two arene rings!



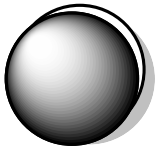




px



dxz

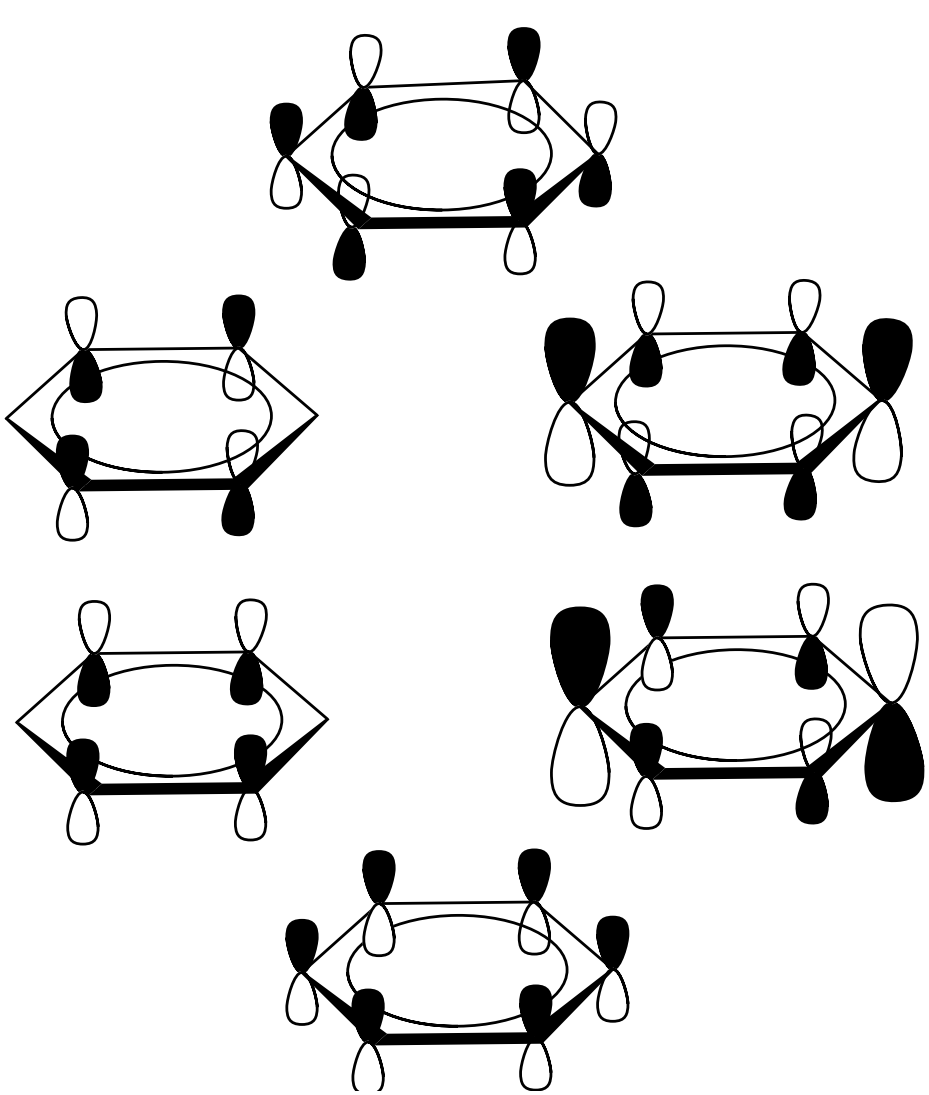


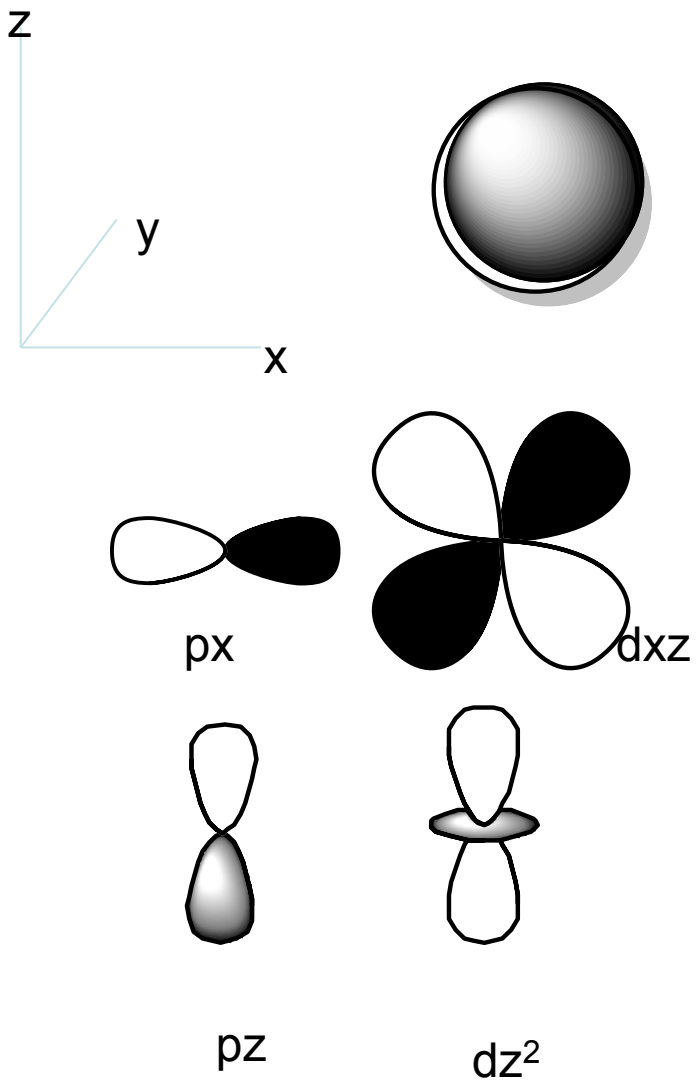
s

pz

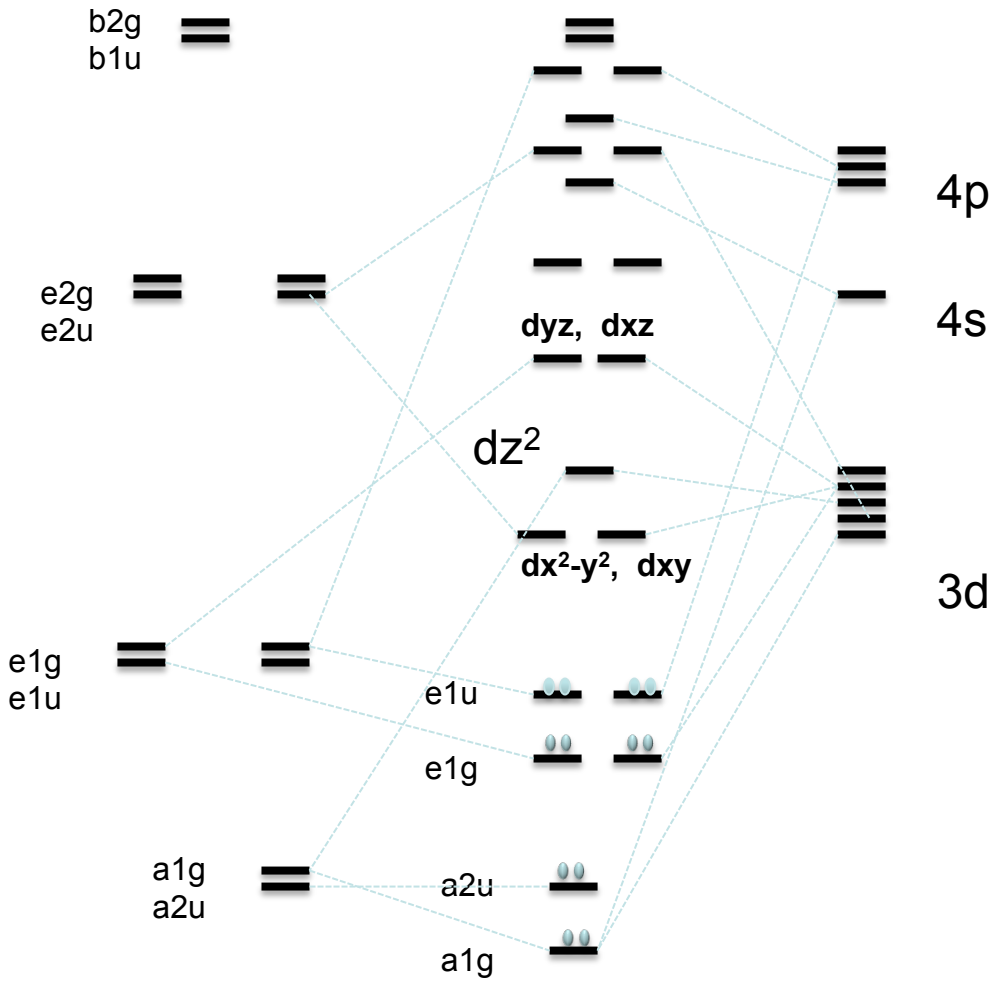
dz^2

Mix and Match

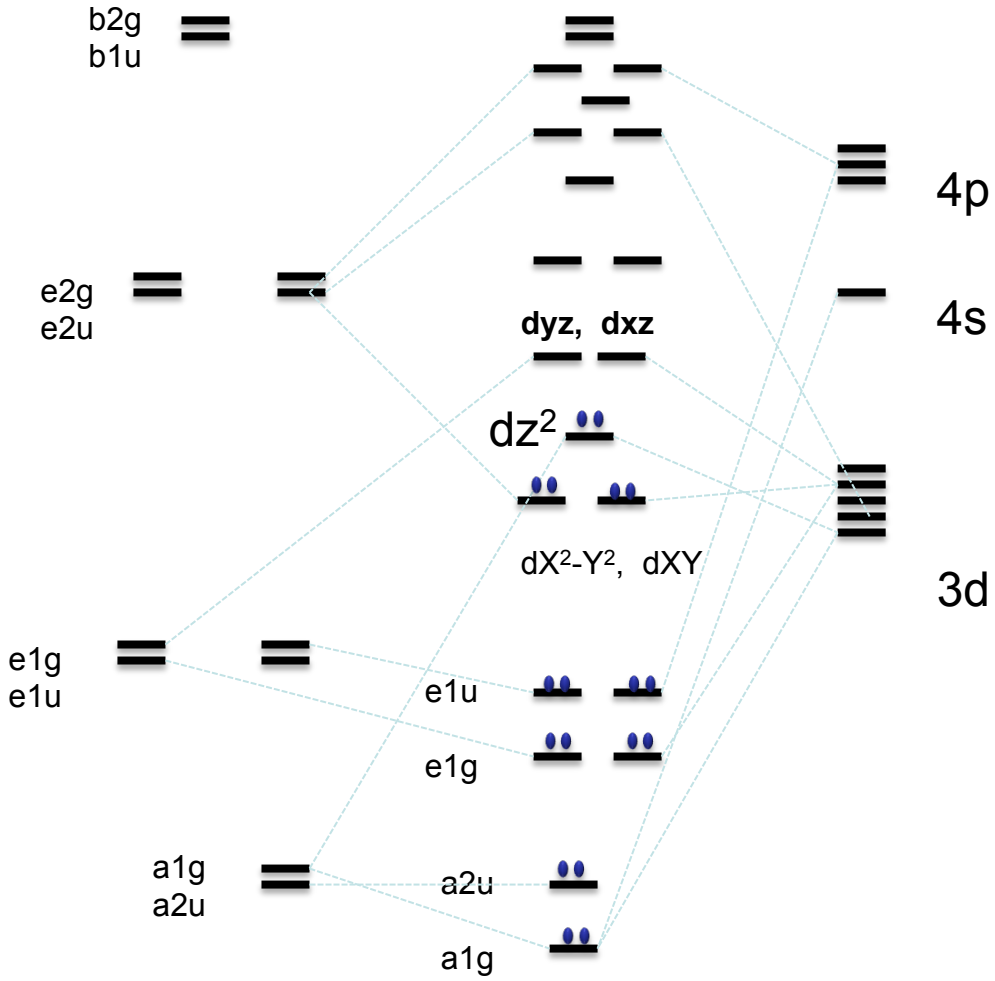




MO Interaction diagram of bis-benzene chromium (Eclipsed Geometry)



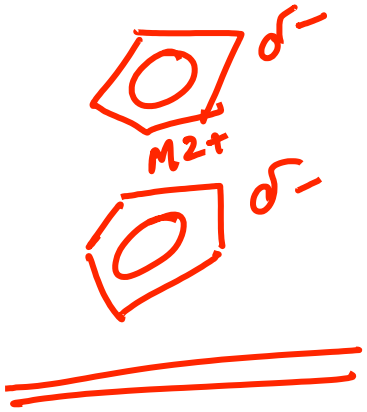
Electron Count!
Chromium is the Best!

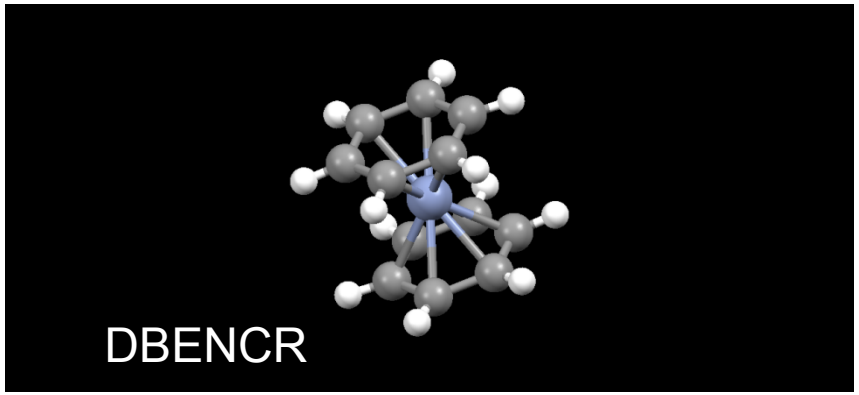


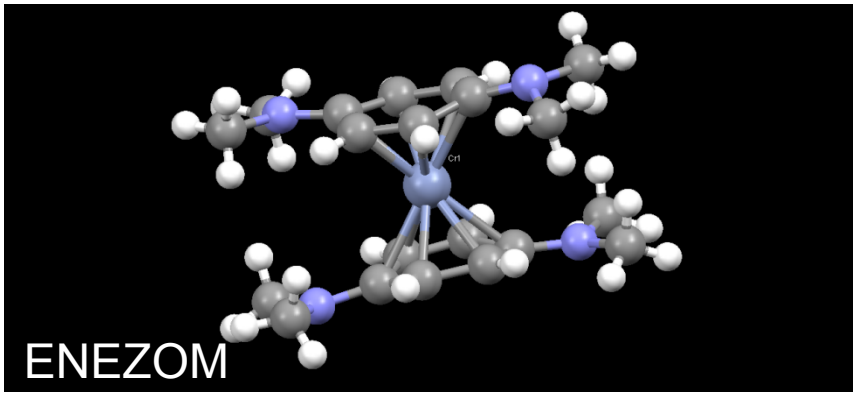
- Cr bears a +Ve charge of 0.7 e
- Benzene bears -0.35 e
- Attributed to Cr transferring electrons through δ bonding

- Bond energy of bis benzene chromium is 170 kJ mol^{-1}
- Ferrocene has a value of 260 kJ mol^{-1}

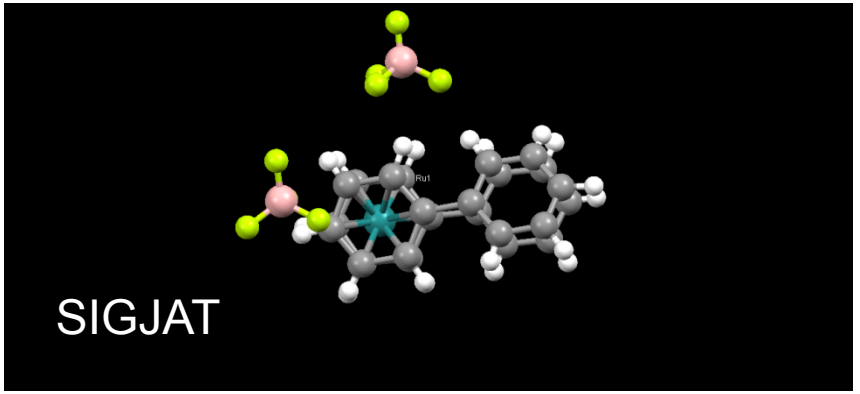
- Look at some structures of these molecules!







- Structures of a few arene complexes!

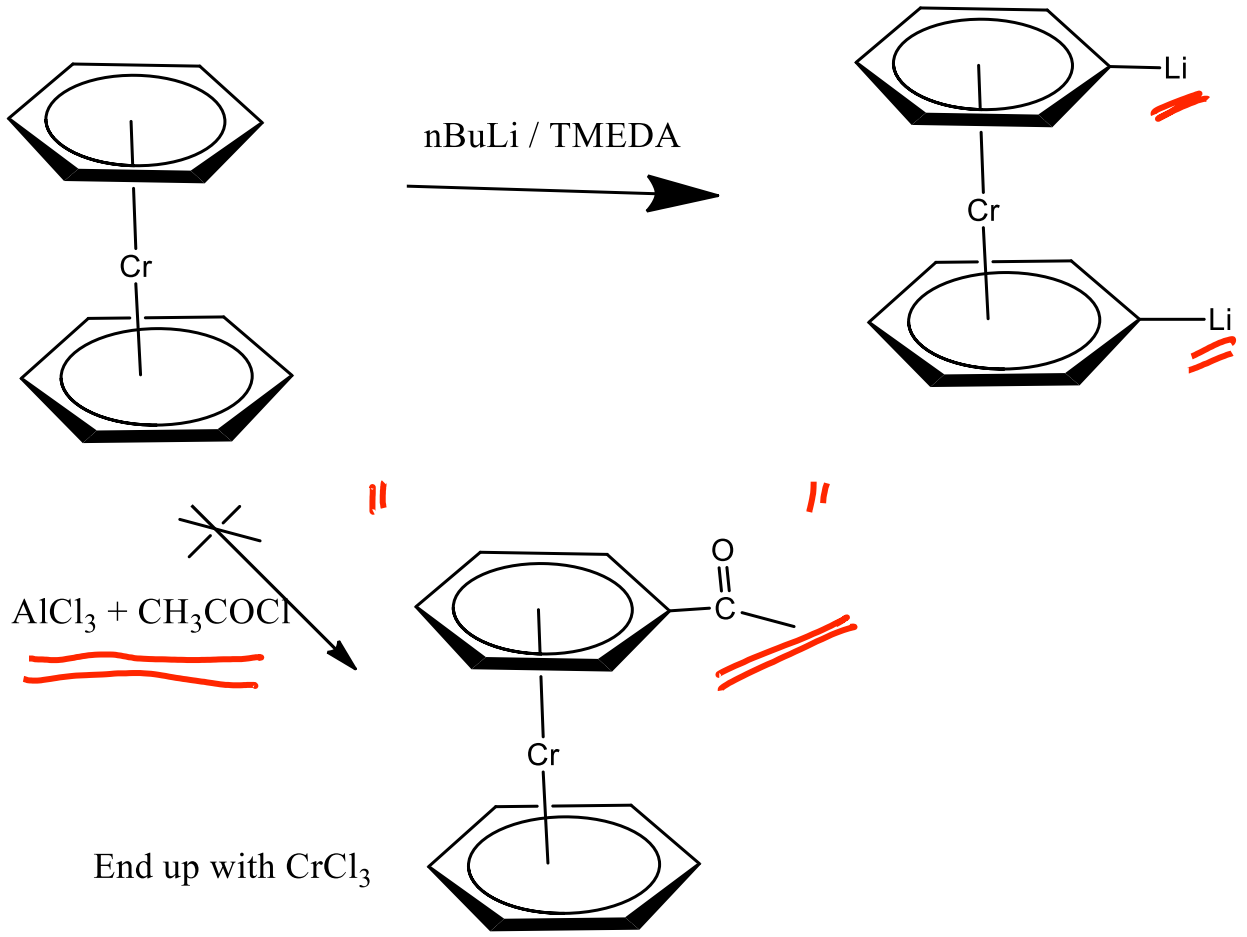


Properties!

Metallocene	Color	upe	Exper. B.M	Expected B.M	Interplanar distance (pm)
$(C_6H_6)_2Ti$	red	0	0	0	
$(C_6H_6)_2V$	Dark Red	1	1.68	1.73	
$(C_6H_6)_2Cr$	brown	0	0	0	322
$(C_6Me_6)_2Fe$		2	3.08	2.83	
$(C_6Me_6)_2Co$	Black	1	1.86	1.73	
$(C_6Me_6)_2Ni$		2	3.00	2.83	

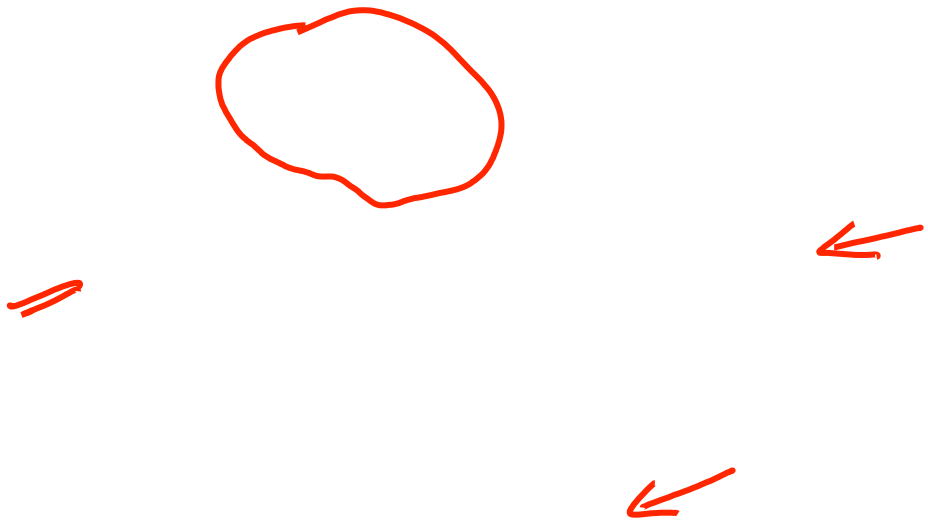
Reactions of arene complexes

Is the aromaticity retained?

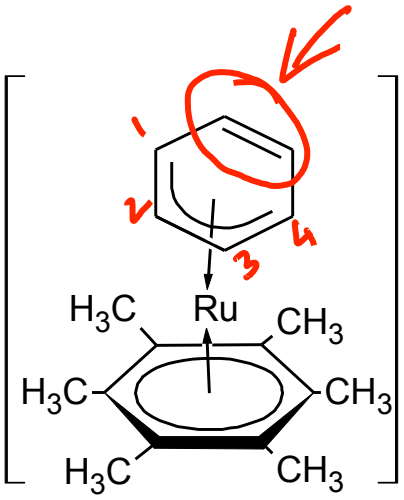


Ligand exchange

Benzene ring on $(C_6H_6)_2Cr$
is not labile
but annelated
rings exchange



η^4 complexes

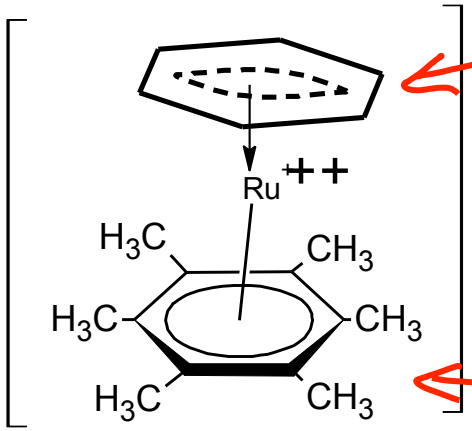


Ru(0) - 8
1Ar - 6

η4 and η6

- 2 electrons

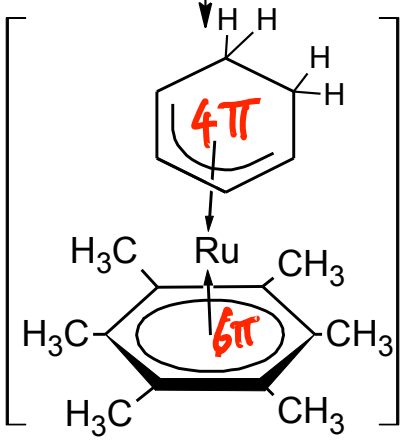
+2e⁻



η6 and η6

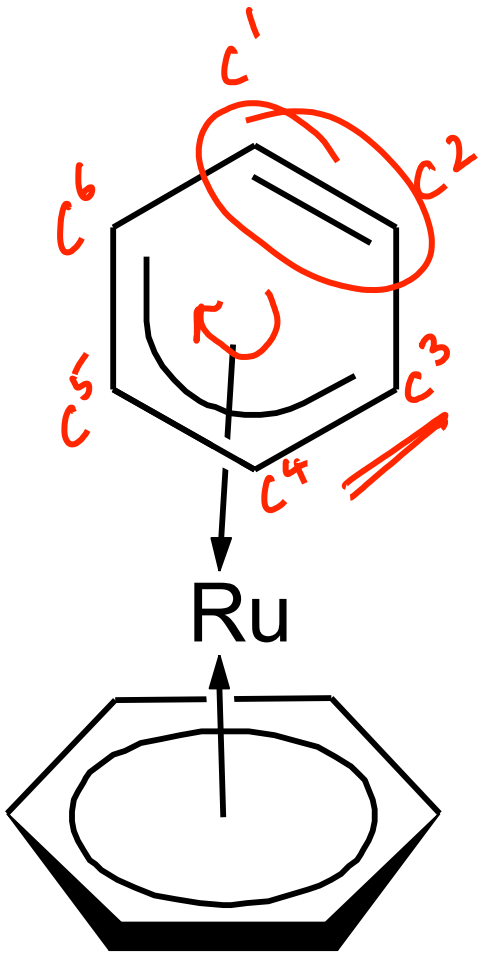
$NaBH_4$ / THF

$2H^-$ units are added



η4 and η6

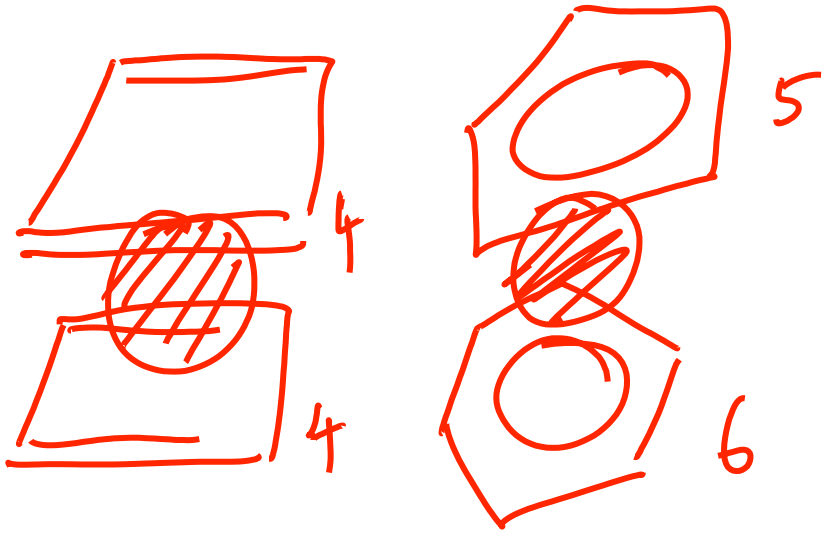
η^4 complexes



Neutral complexes can be made by reducing the Ru^{2+} cation which is a 18 electron complex with Na/ NH_3

X-ray reveals complete bond Localization and bending, NMR shows a dynamic structure!

Hetero-Sandwiches

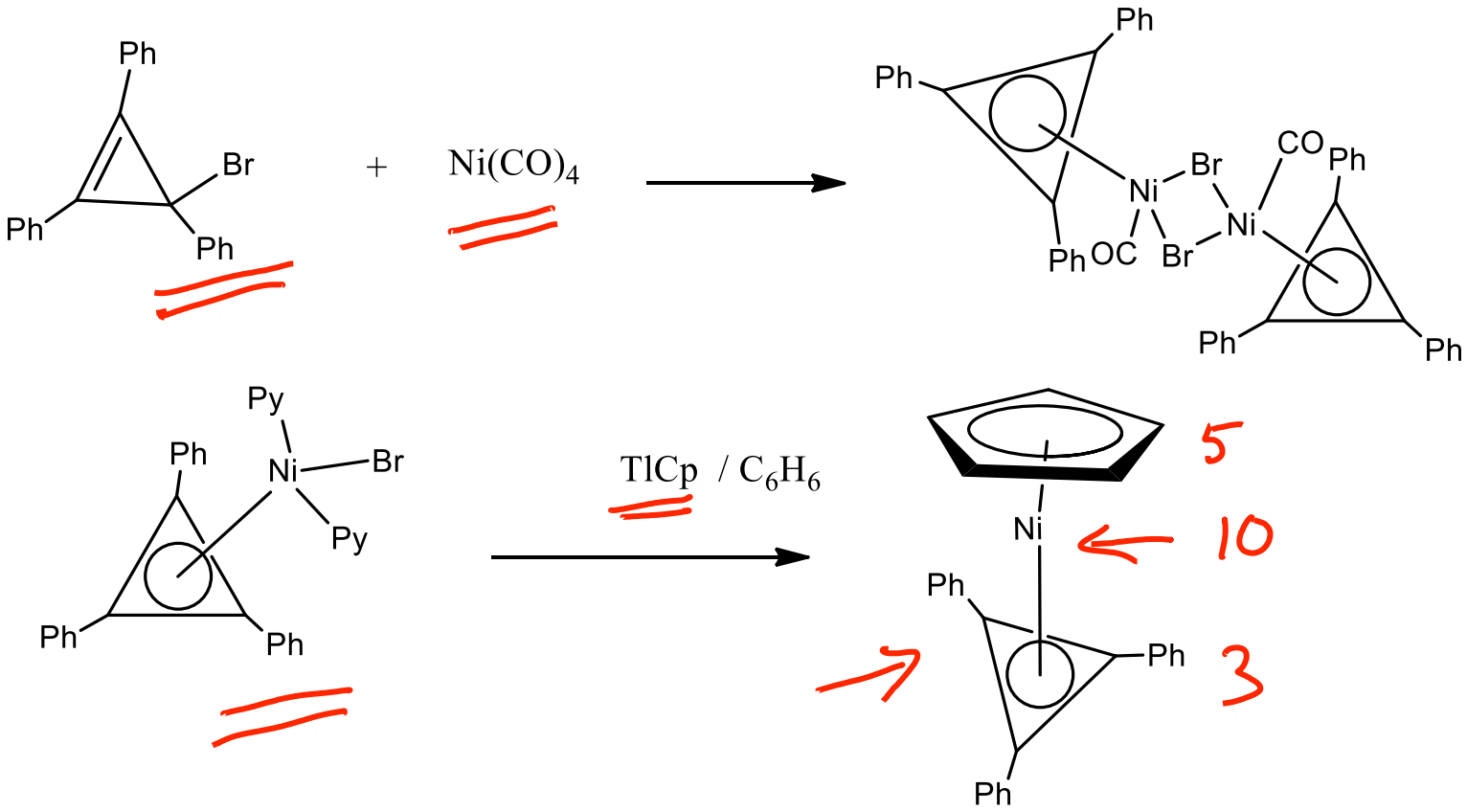


Electron Counting

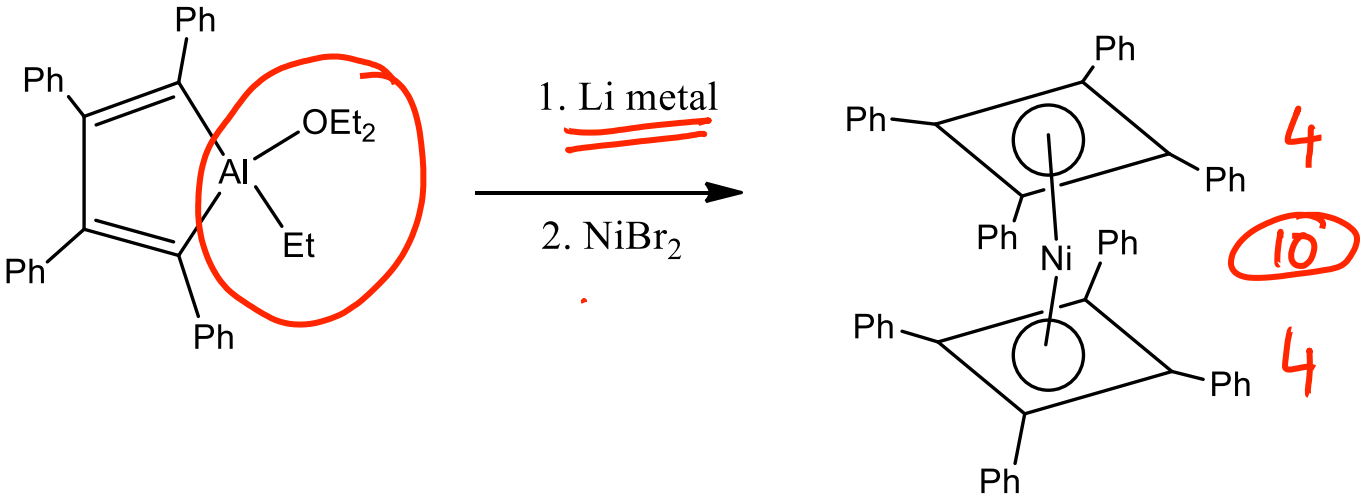
- $CpMC_6H_6$ what would be M ?
  - 6 electrons from the arene
  - 5 from the Cp (neutral method)
  - M has to give 7 electrons! M=Mn
- $CBDMC_6H_6$ What should be M
  - 4 from Cyclobutadiene CBD
  - 6 from Arene
  - 8 from metal! M= Fe

18

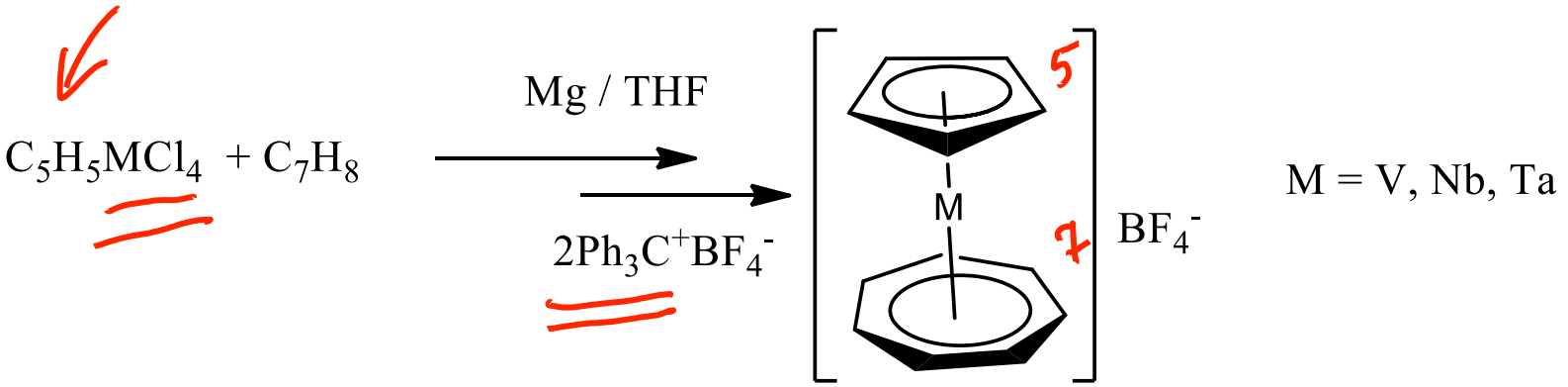
Cyclopropenyl rings

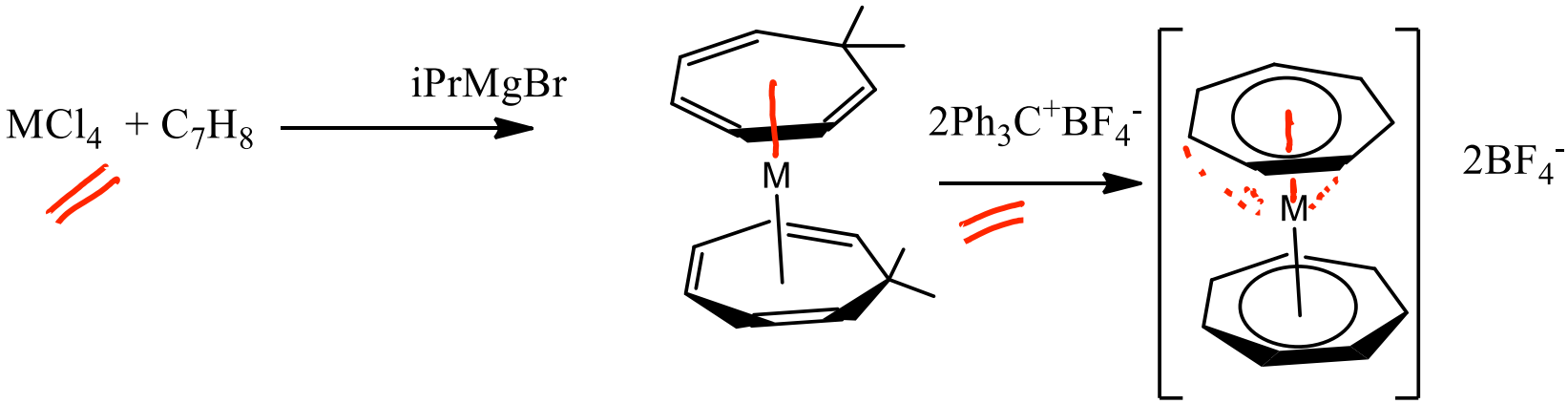


Cyclobutadiene sandwich!

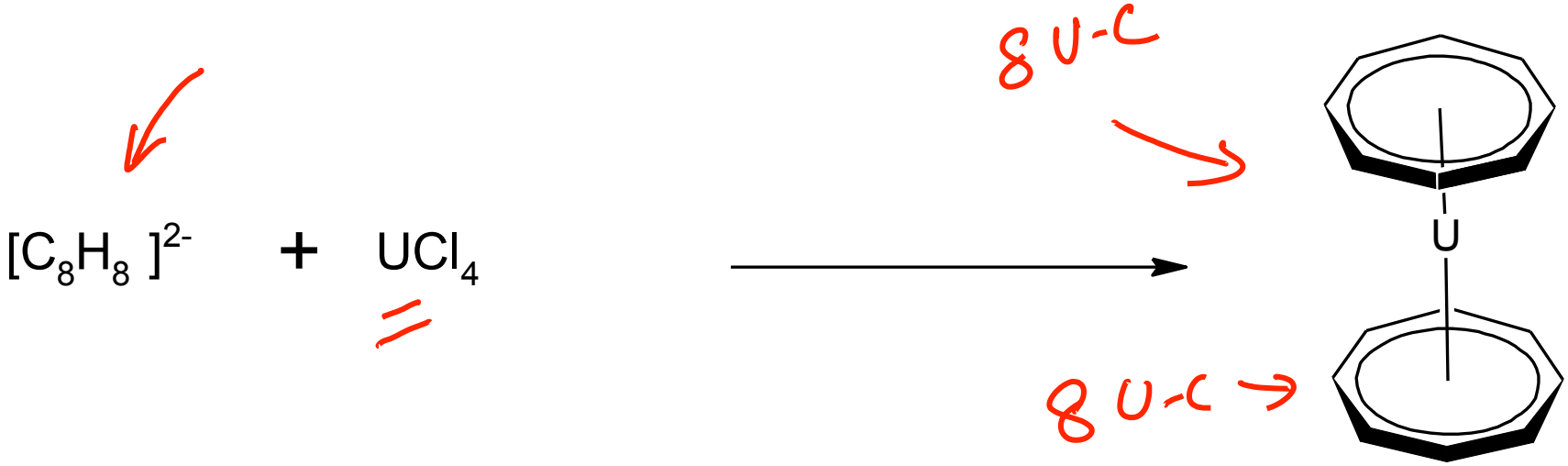


Cycloheptatrienyl





Beyond 7 it is difficult for d group metal ions but lanthanides and actinides like U can form complexes!



Summary

- 18 electron rule holds good!
- Possible to have some reactions of the benzene ring
- One can make hetereo sandwiches!

Sandwich Complexes

Half, Bent, Open and Multi

Journal of the Chemical Society (Resumed), 1956 p. 1969
doi:10.1039/JR9560001969

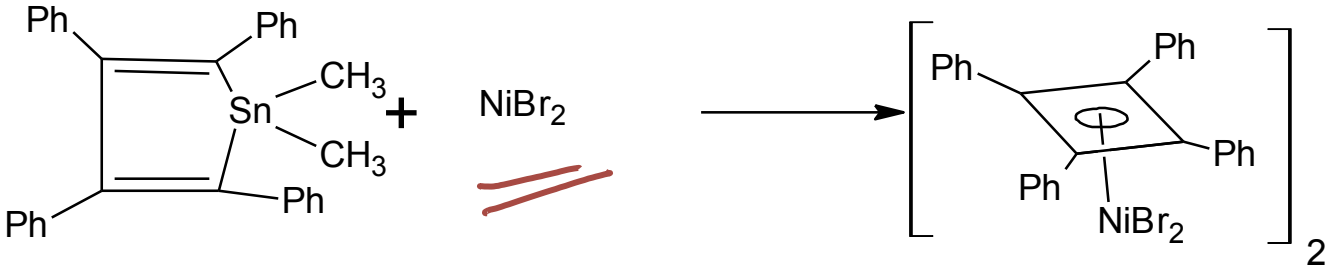
The Possible Existence of Transition-metal Complexes of *cyclo* Butadiene.

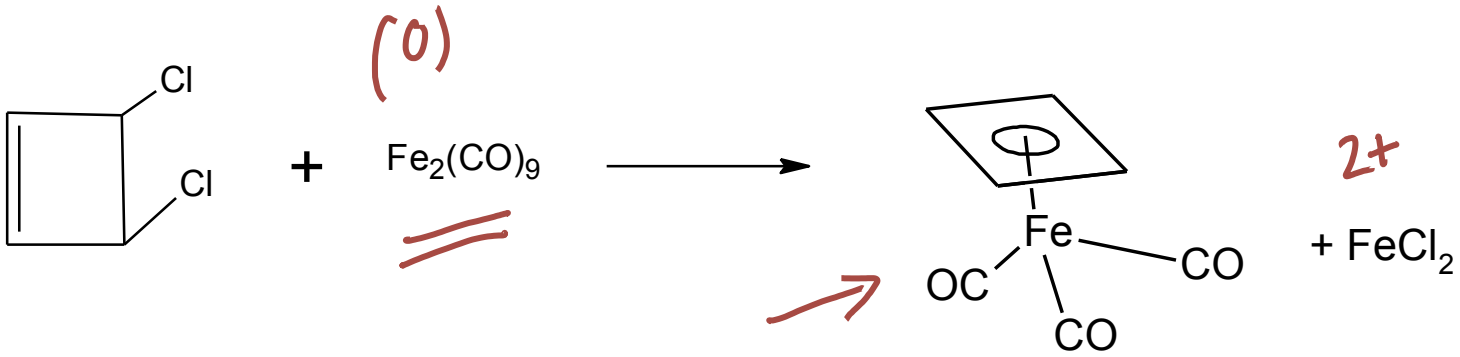
By
H. C. LONGUET-HIGGINS and L. E. ORGEL.

- "The possibility that the unstable cyclobutadiene molecule can be stabilised by combination with **a suitable transition-metal ion is investigated by use** of molecular-orbital theory."

- "complexes of the type $MnX_2(C_4H_4,)$, where M is nickel, palladium, or platinum and X is a univalent ligand, may be stable,"
- "$Ni(CN)_2(C_4H_4)$ is an intermediate in the Reppe synthesis of cyclooctatetraene."

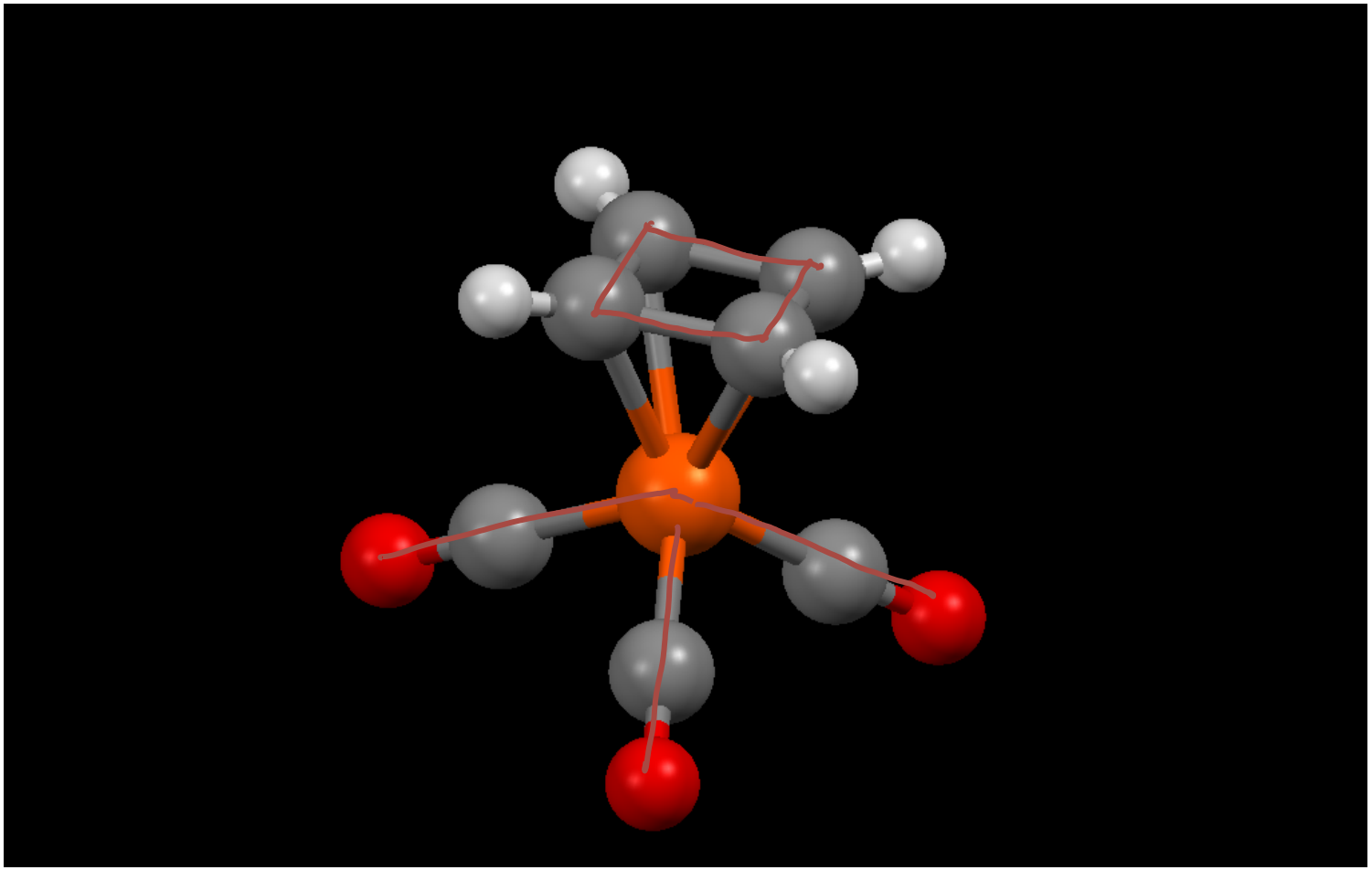
Synthesis of 4 membered rings …



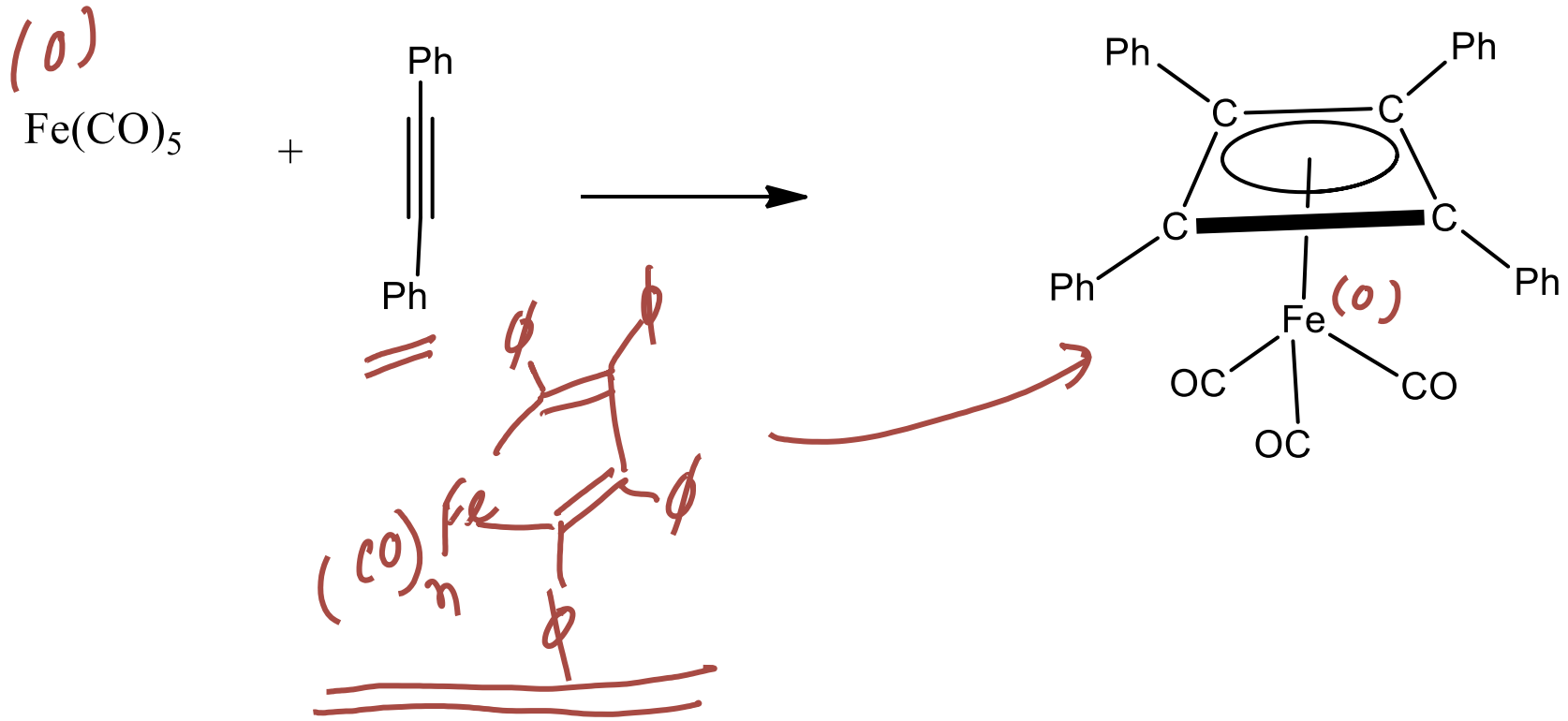


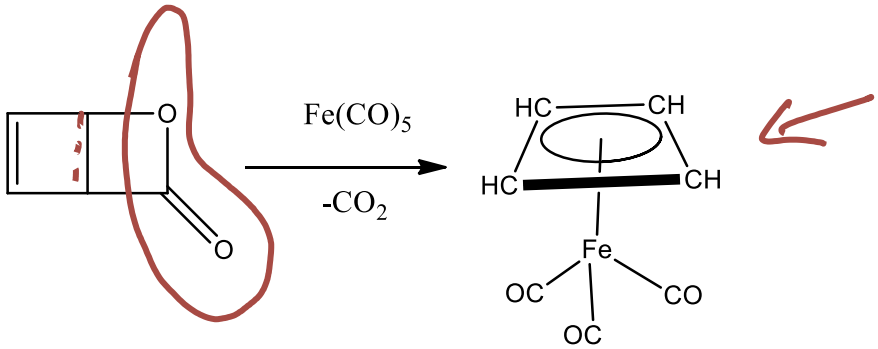
Crystal structure of a CBD complex

P.D.Harvey, W.P.Schaefer, H.B.Gray, D.F.R.Gilson, I.S.Butler, Inorg.Chem. (1988), 27, 57

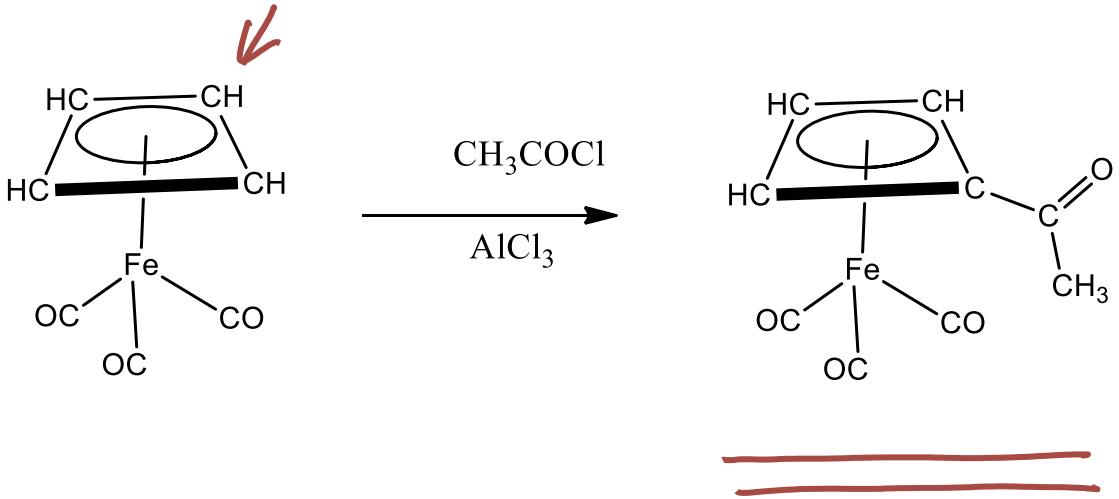


Synthetic routes

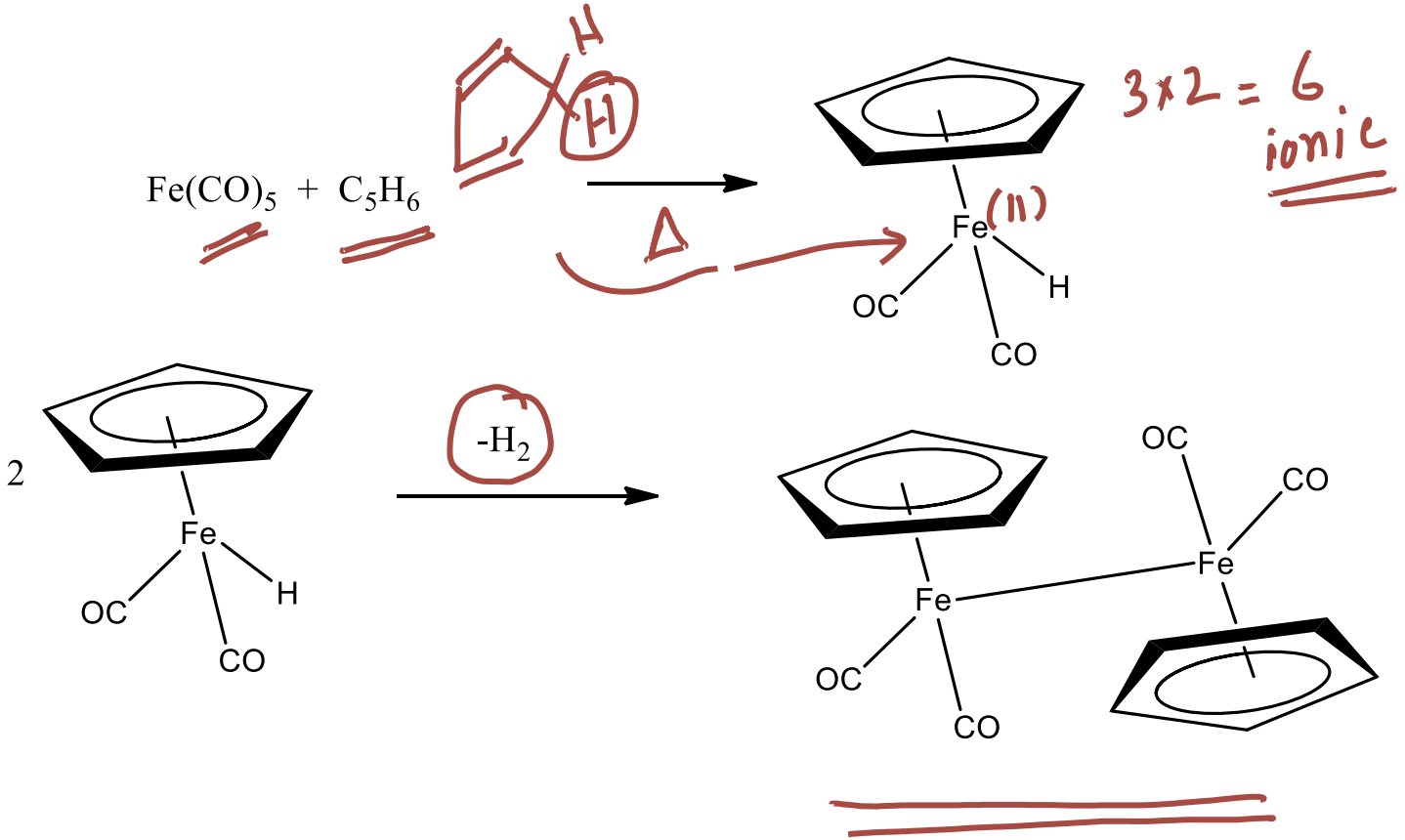



O
O
Fe(CO)5
-CO2
HC
CH
HC
CH
Fe
OC
CO
OC

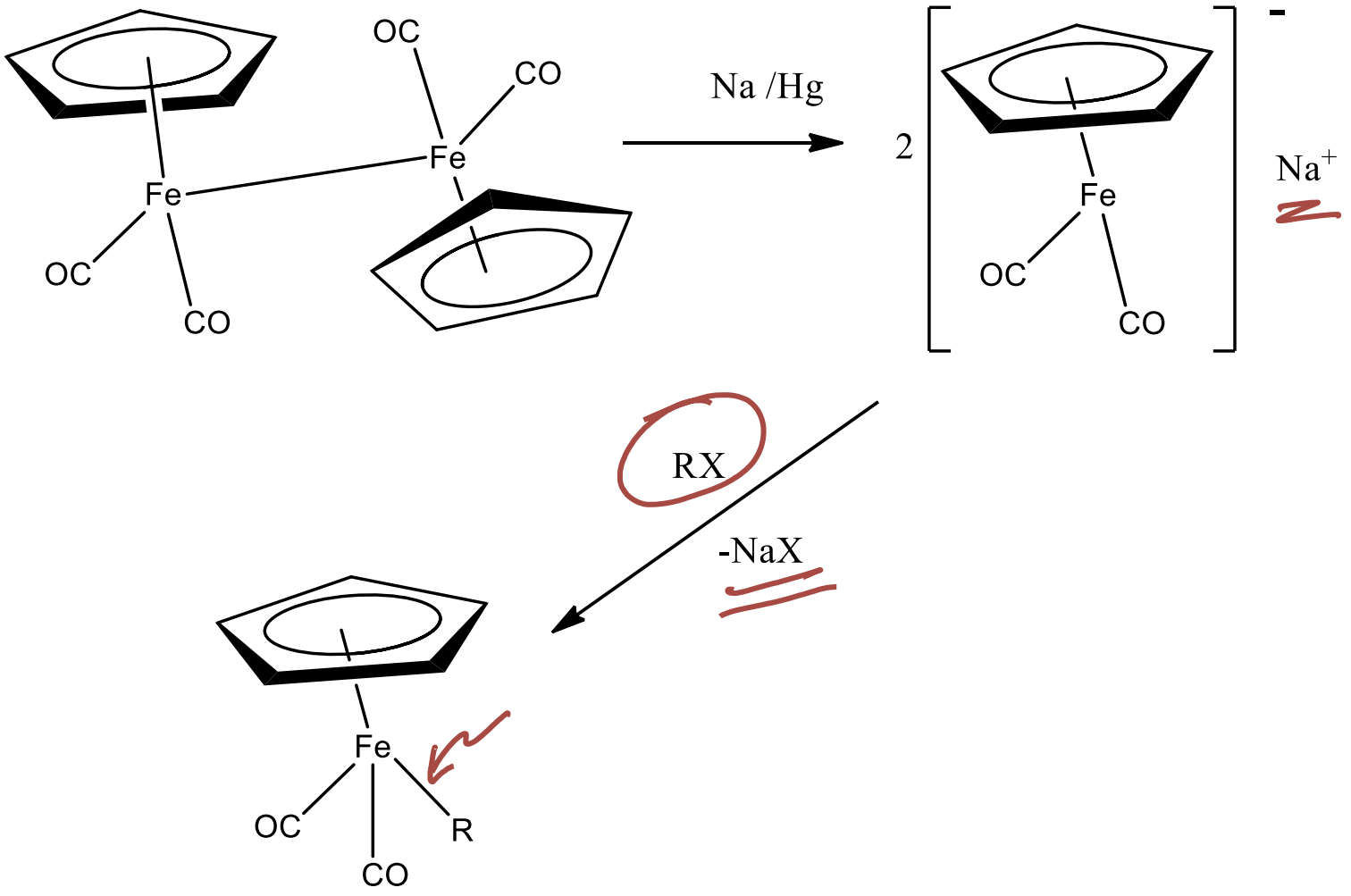
Reactivity
Aromatic Behavior!

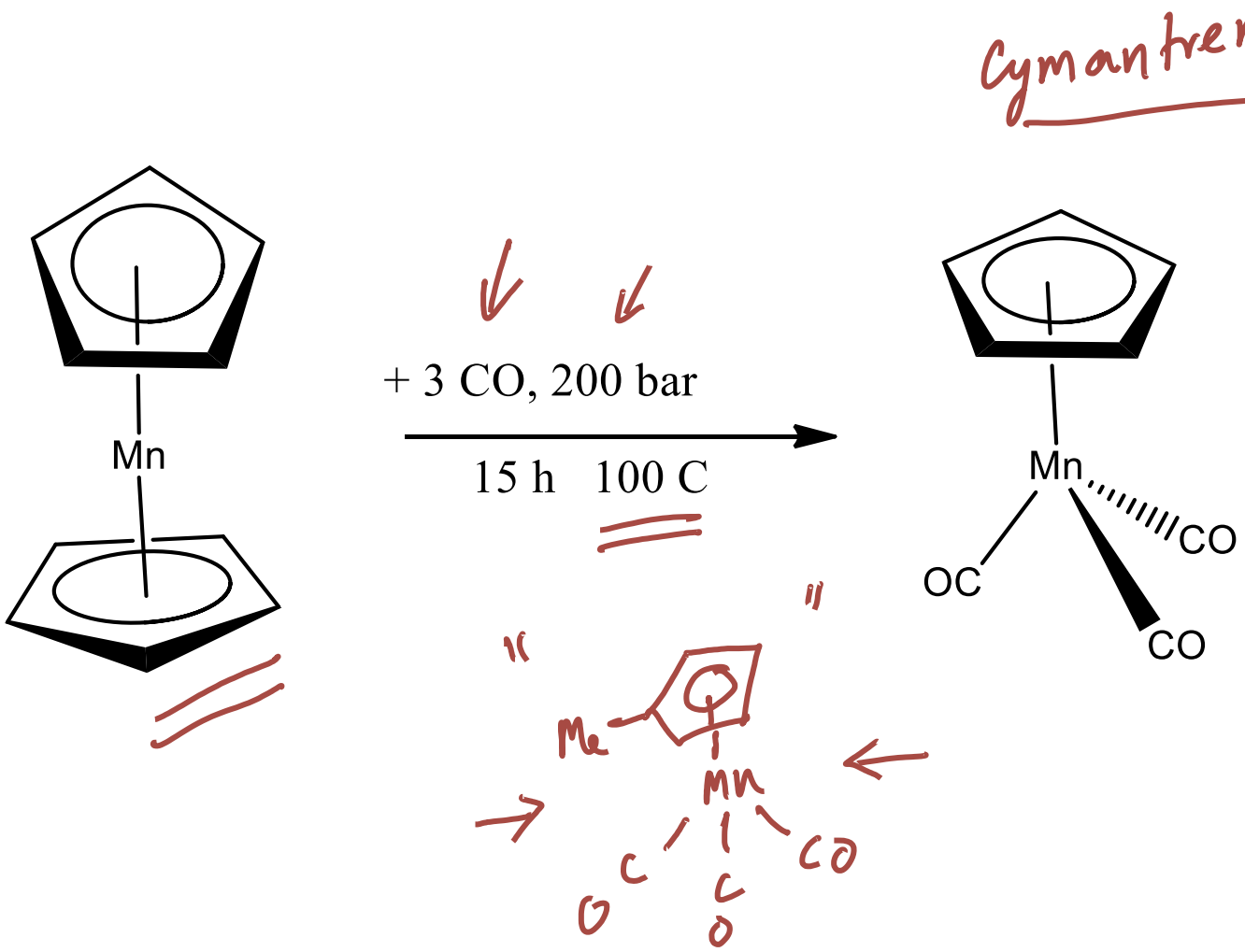


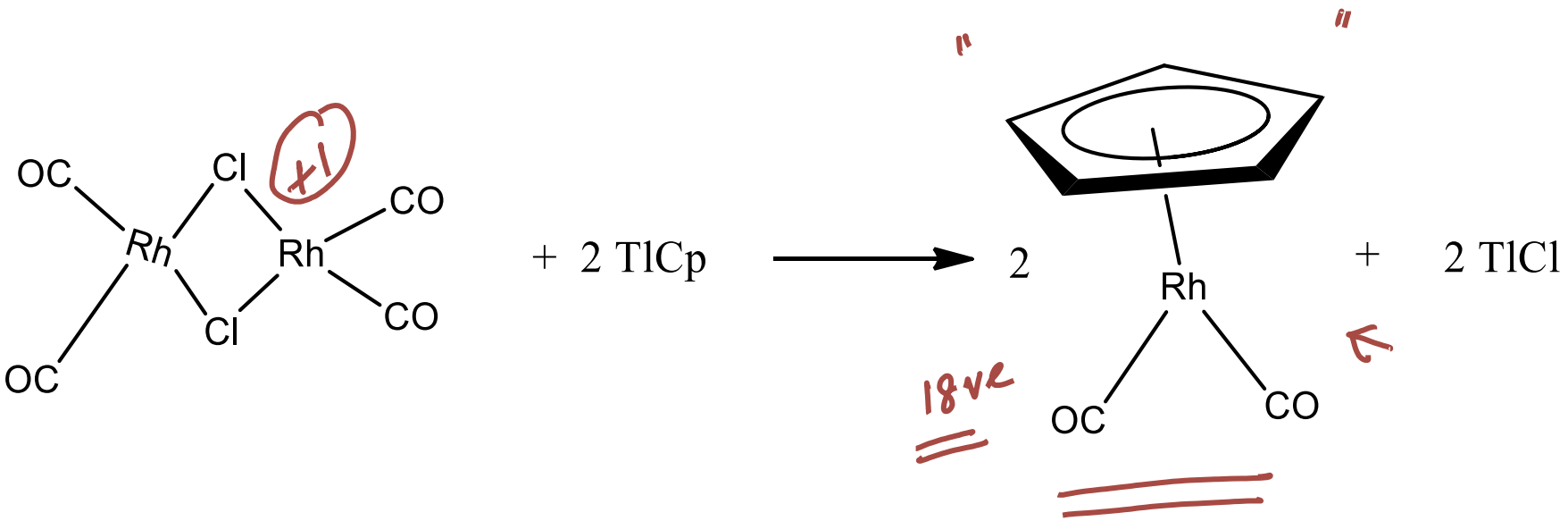
Other half sandwich complexes



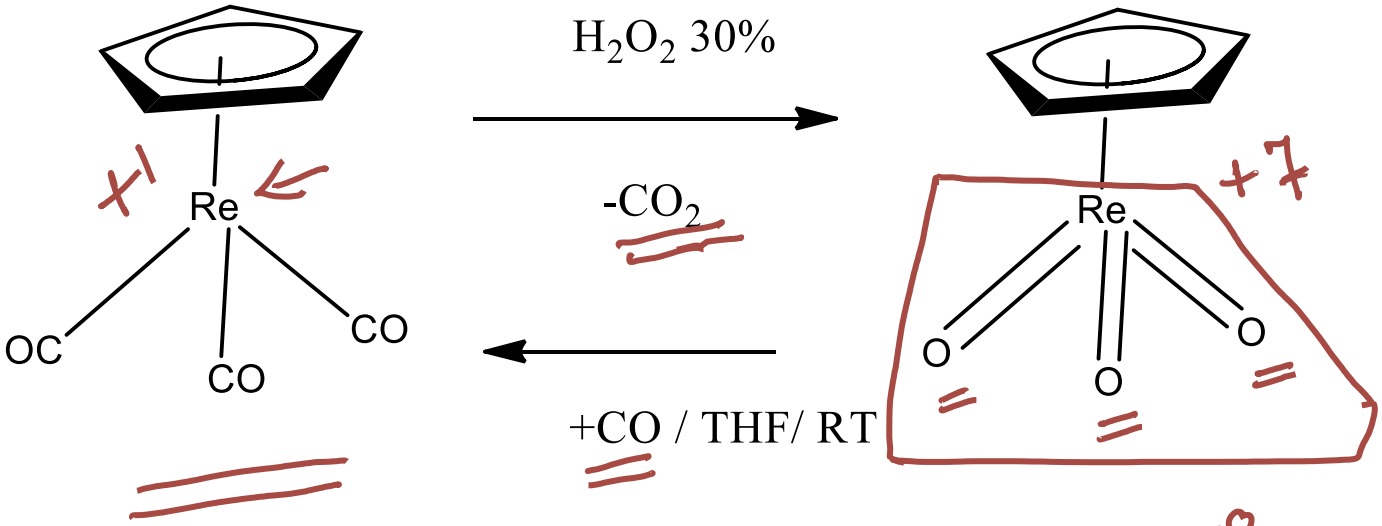
Mn – Mn Na/Hg



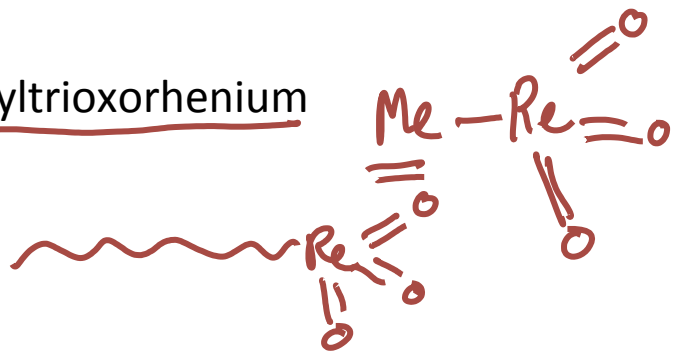

Cymantrene
Mn
+ 3 CO, 200 bar
15 h 100 C
Mn
CO
OC
CO
Me
Mn
CO
C
O
C
O


OC
Cl
Rh
Rh
CO
CO
Cl
OC
x1
+ 2 TlCp
2
Rh
OC
CO
+ 2 TlCl
18ve

CpTO!
The organic metal oxide!

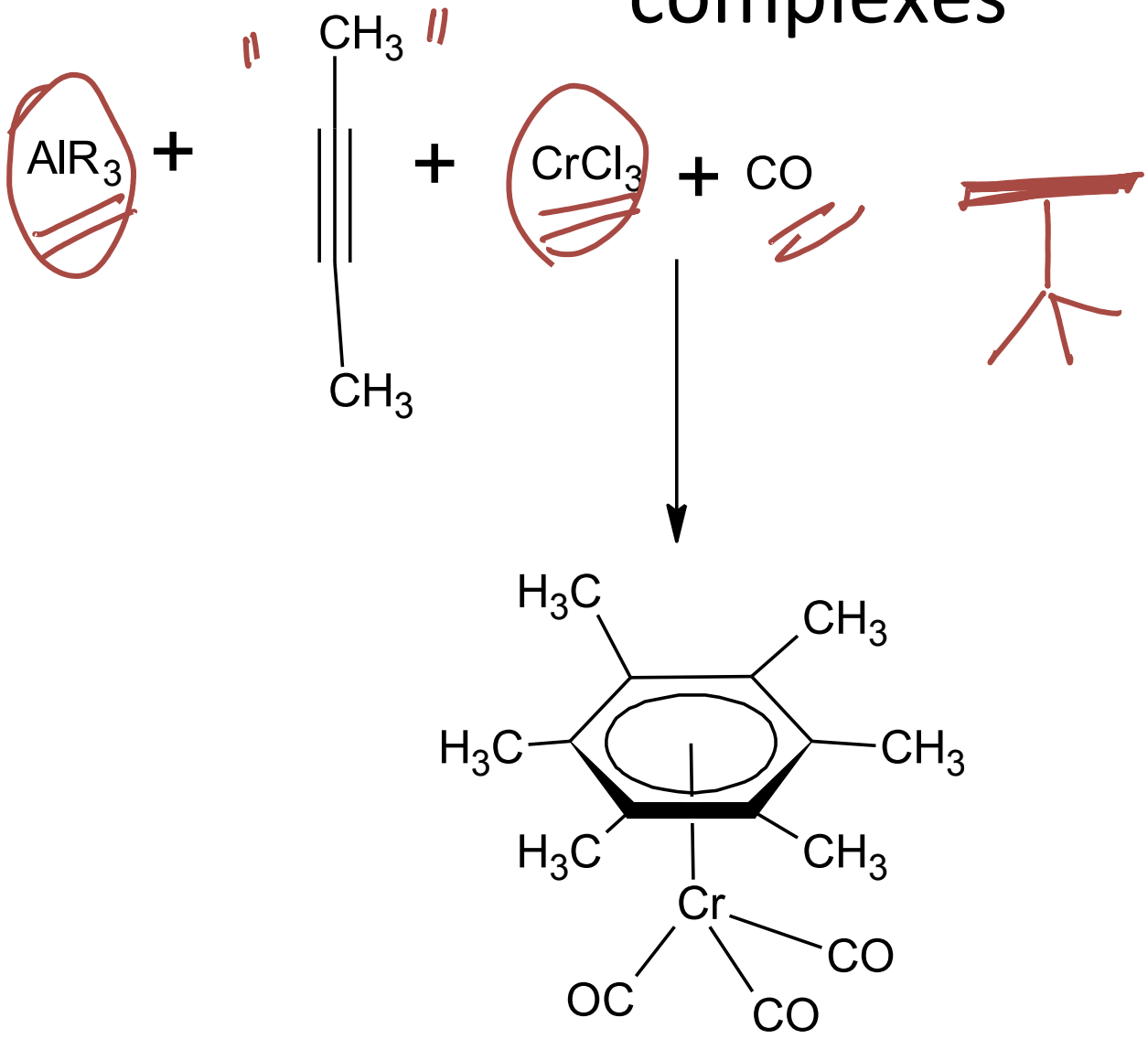


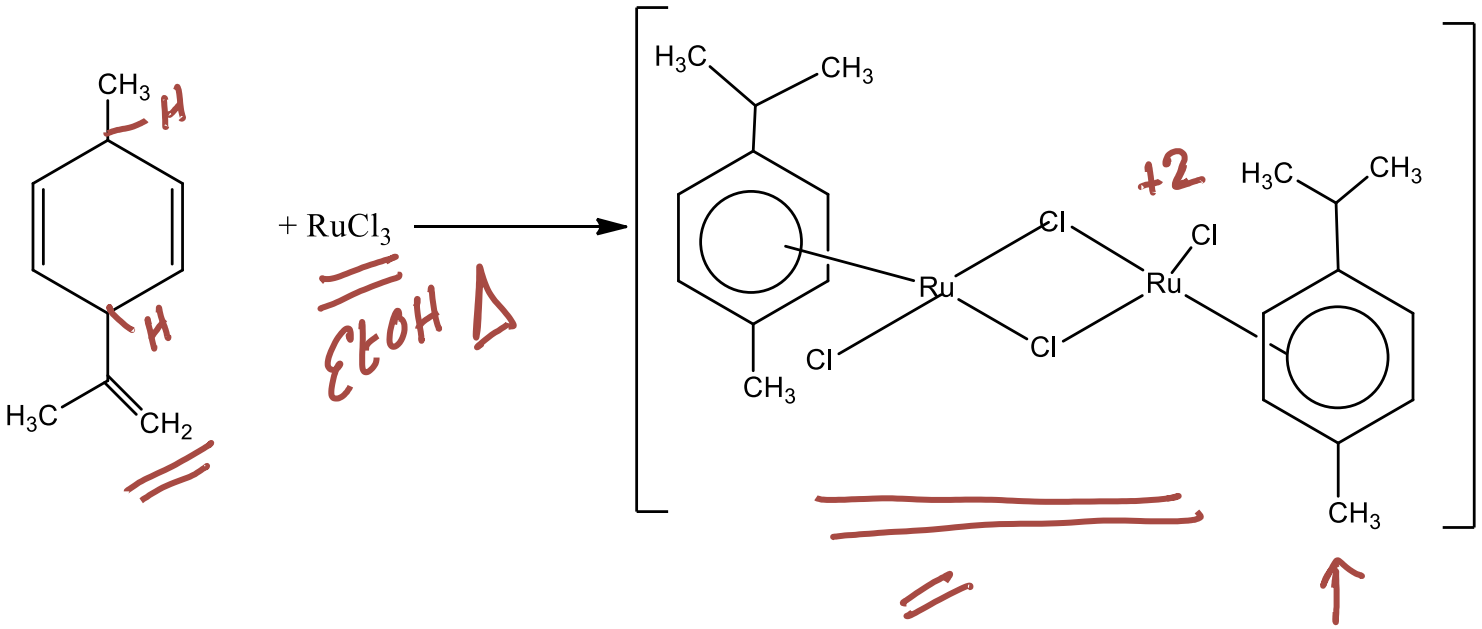
Methyltrioxorhenium



Arene half sandwiches

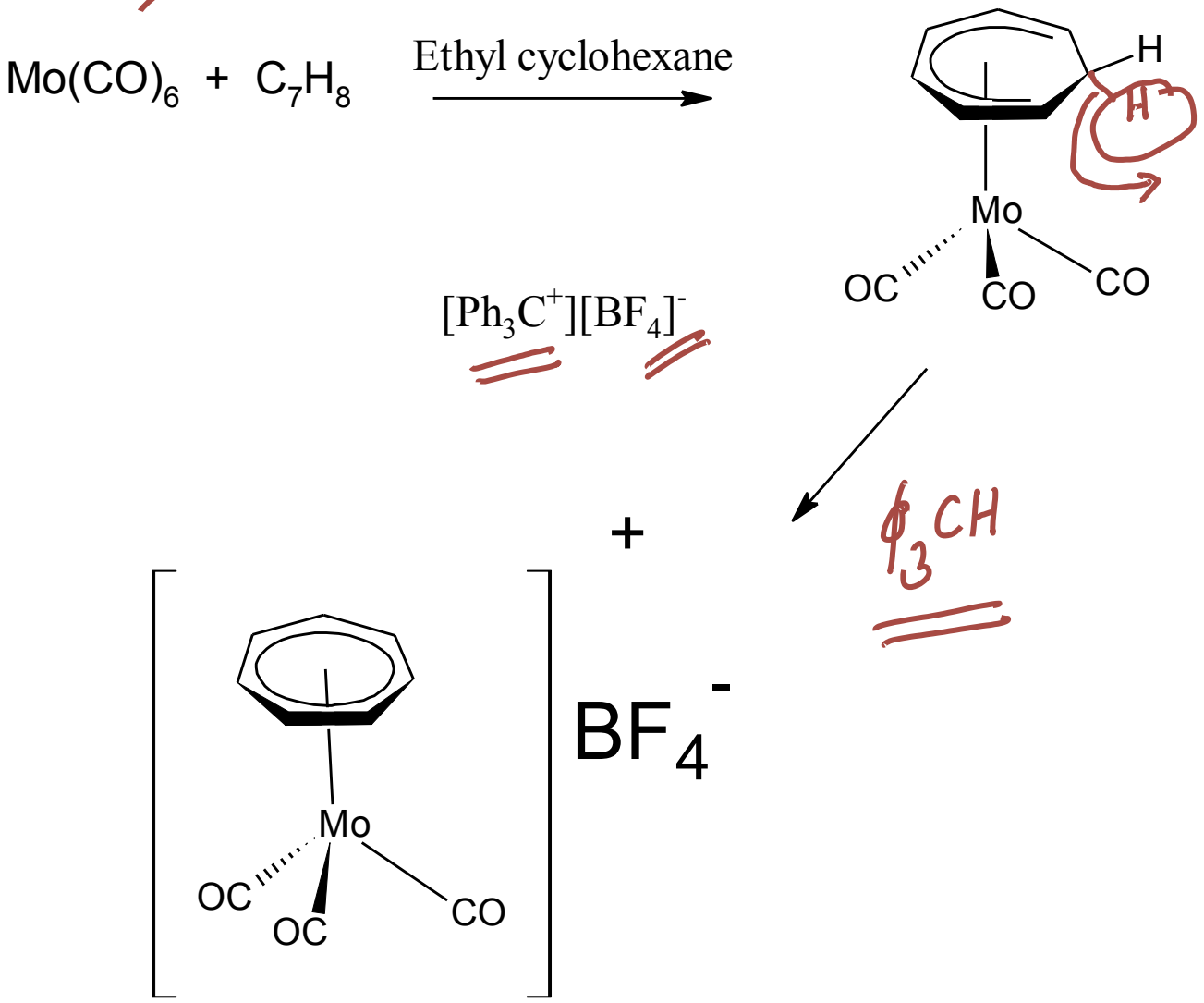
Templated synthesis of Piano stool complexes



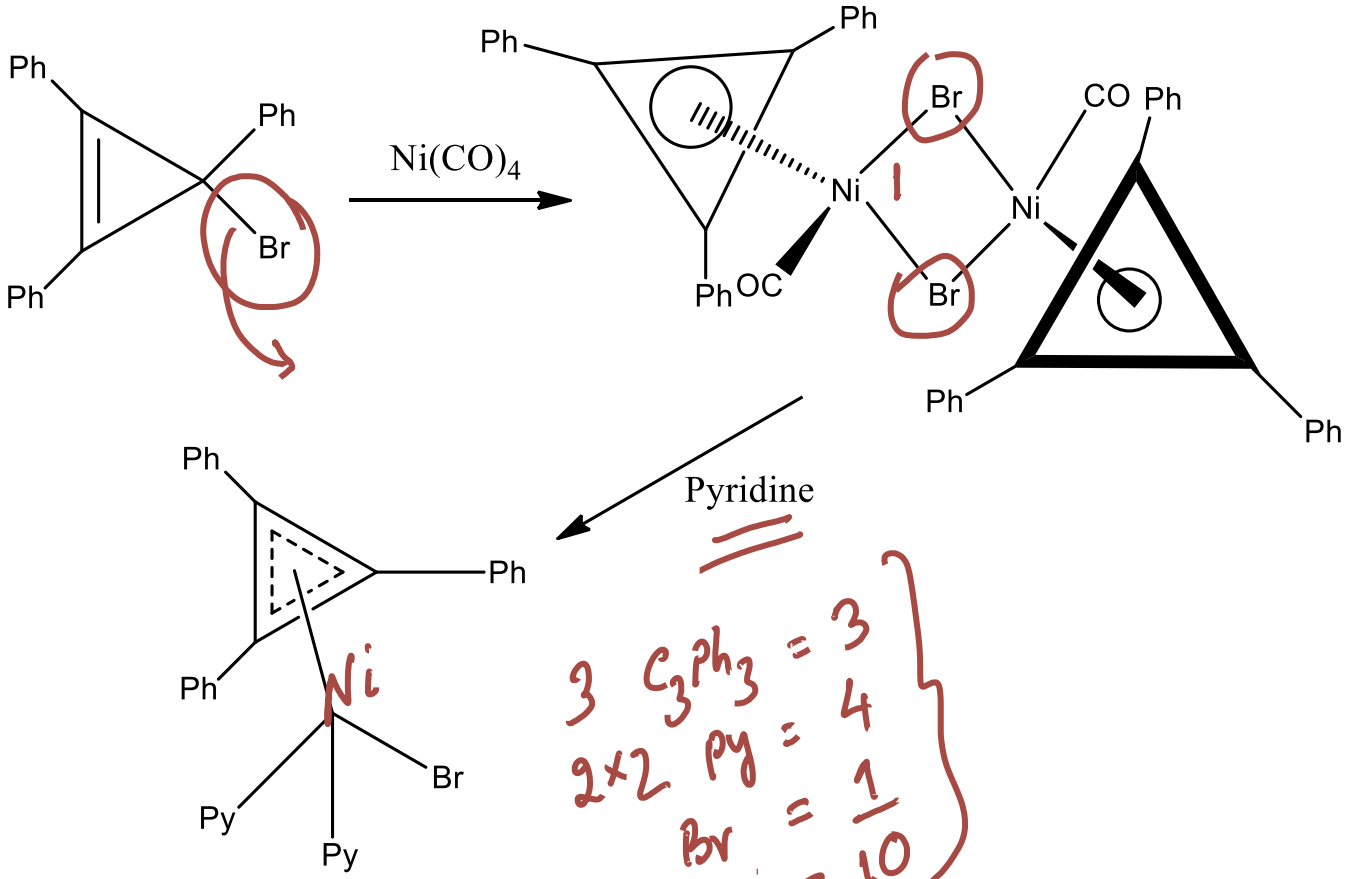

CH3
H
H
H3C
CH2
+ RuCl3
EtOH Δ
H3C
CH3
Ru
Cl
Cl
Cl
Ru
Cl
CH3
+2
H3C
CH3
CH3


Ru

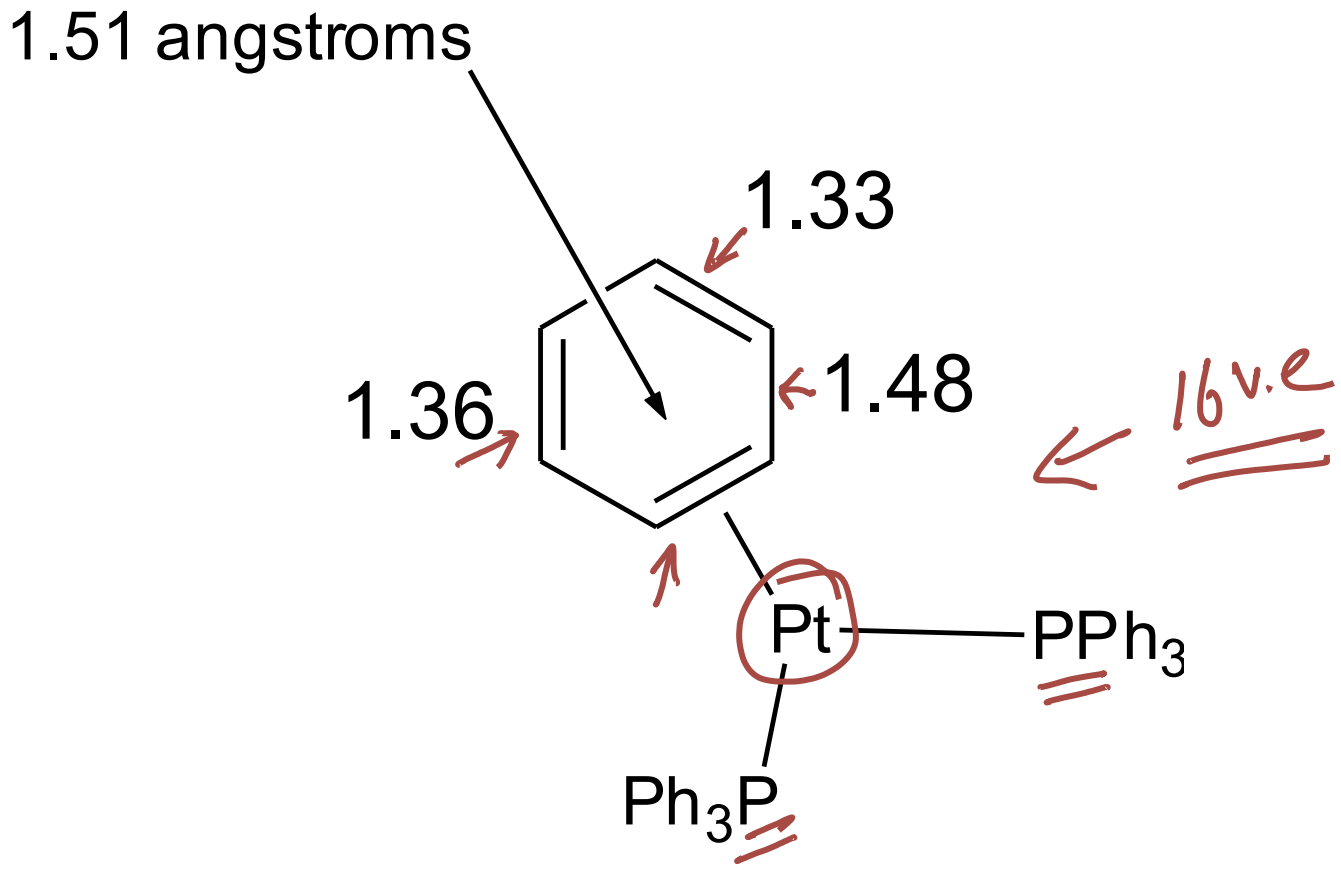
η^7 complexes are possible!



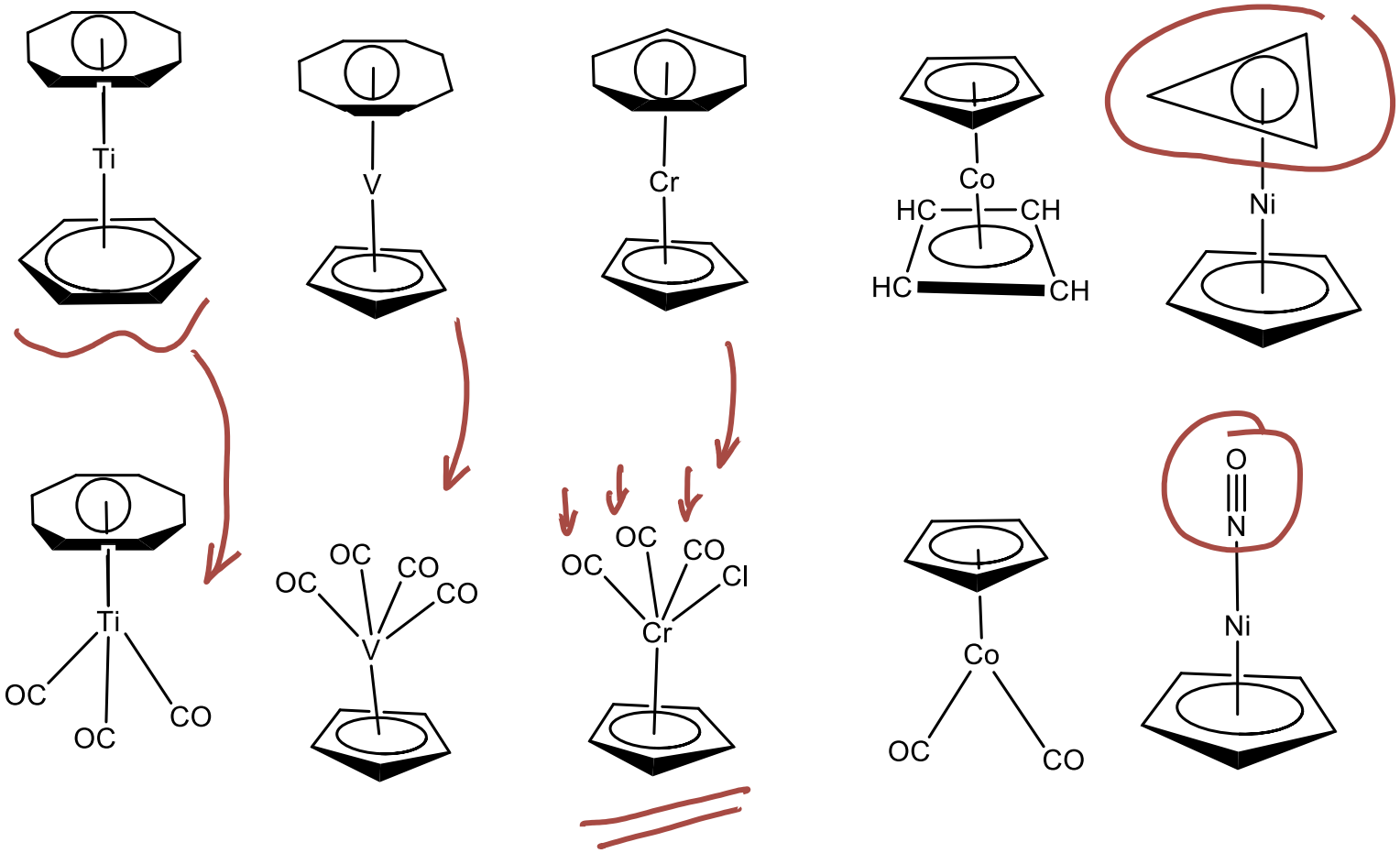
C_3H_3 half sandwiches



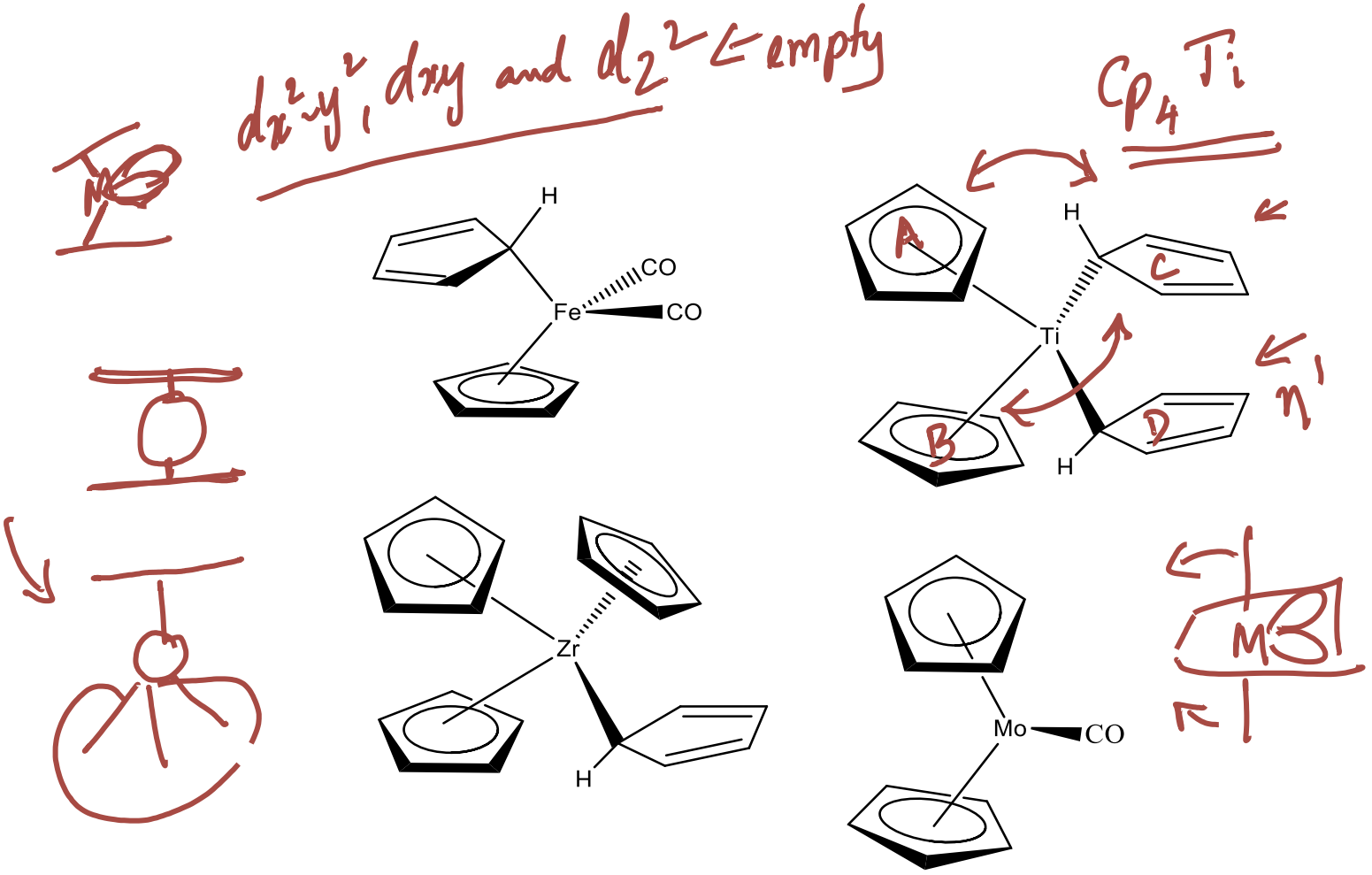
η^2 arene complexes



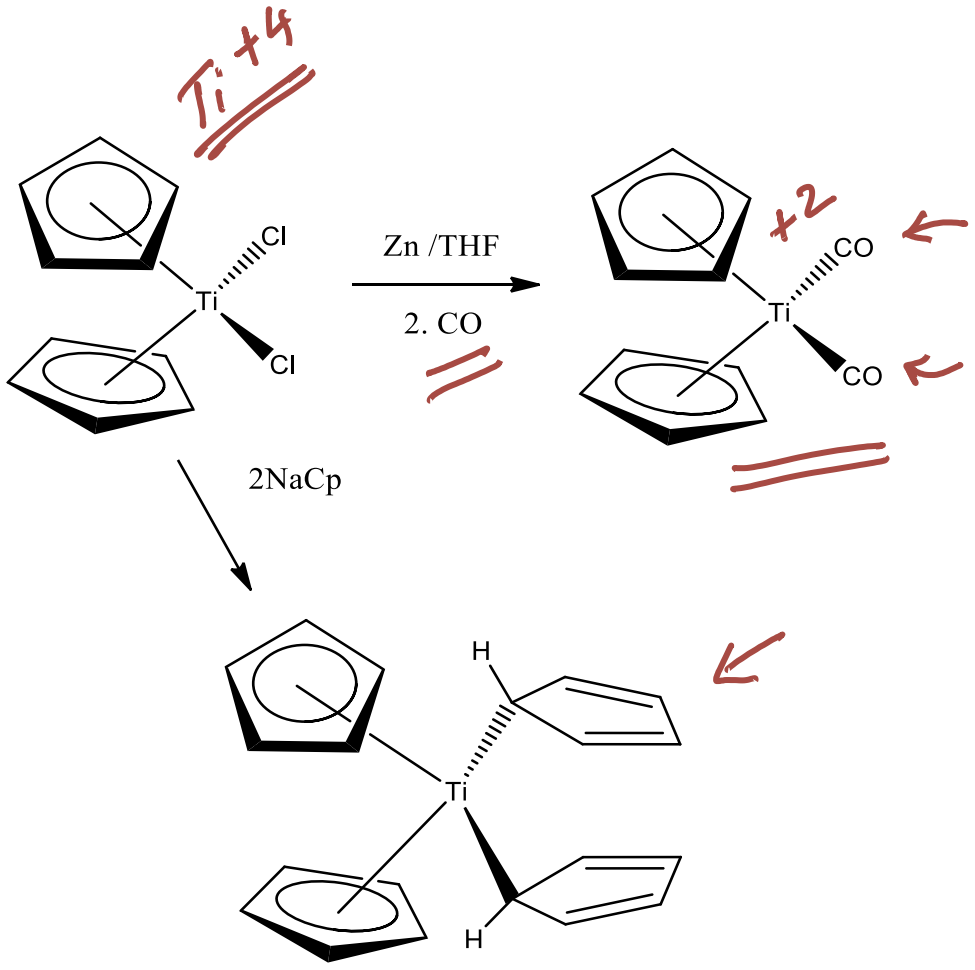
Mixed Sandwiches to half sandwiches!



Bent Metallocenes



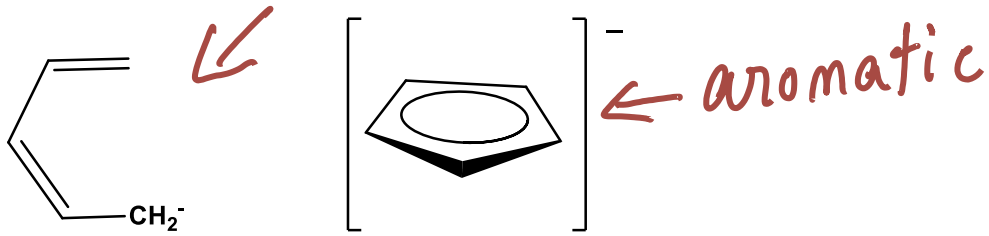
Bent titanocenes



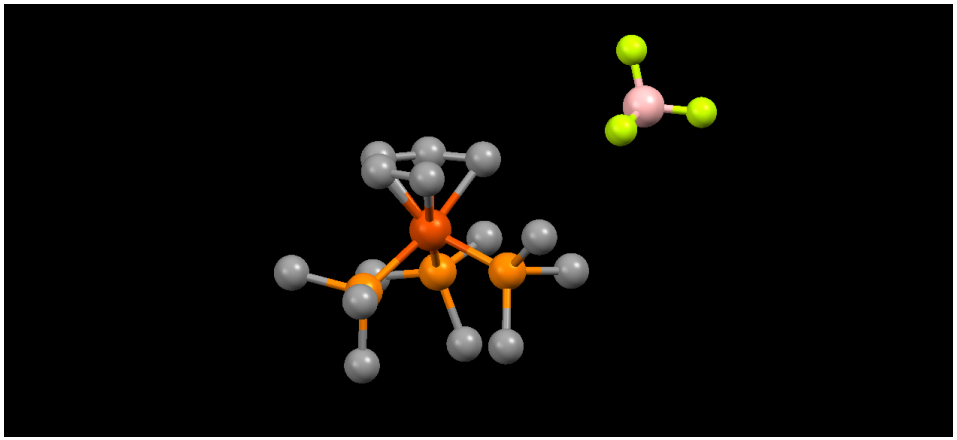
Catalysis, fluxional behaviour

Open Sandwiches

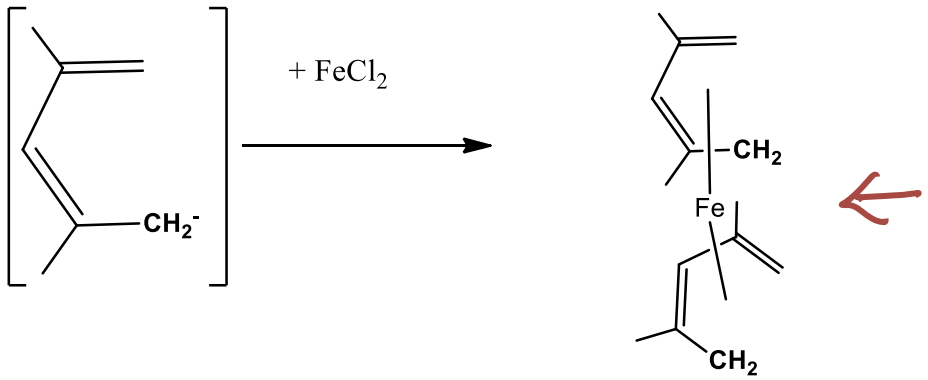
- Acyclic version of cp- is $C_5H_7^-$



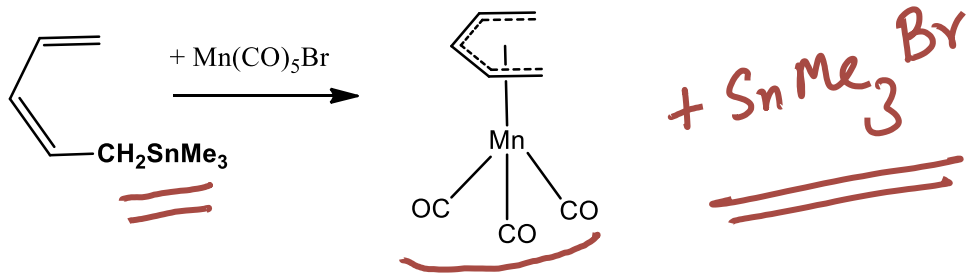
(η^5-Pentadienyl)-tris(trimethylphosphine)-iron tetrafluoroborate
GEVDOA from CSDS



Synthesis of Open Metallocene

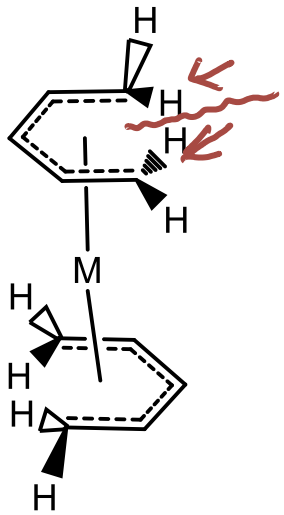


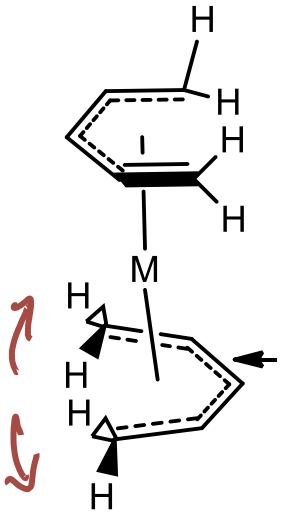
Synthesized in 1988 by Ernst



Structure of Open Metallocene

Ruthenium analog of the open metallocene



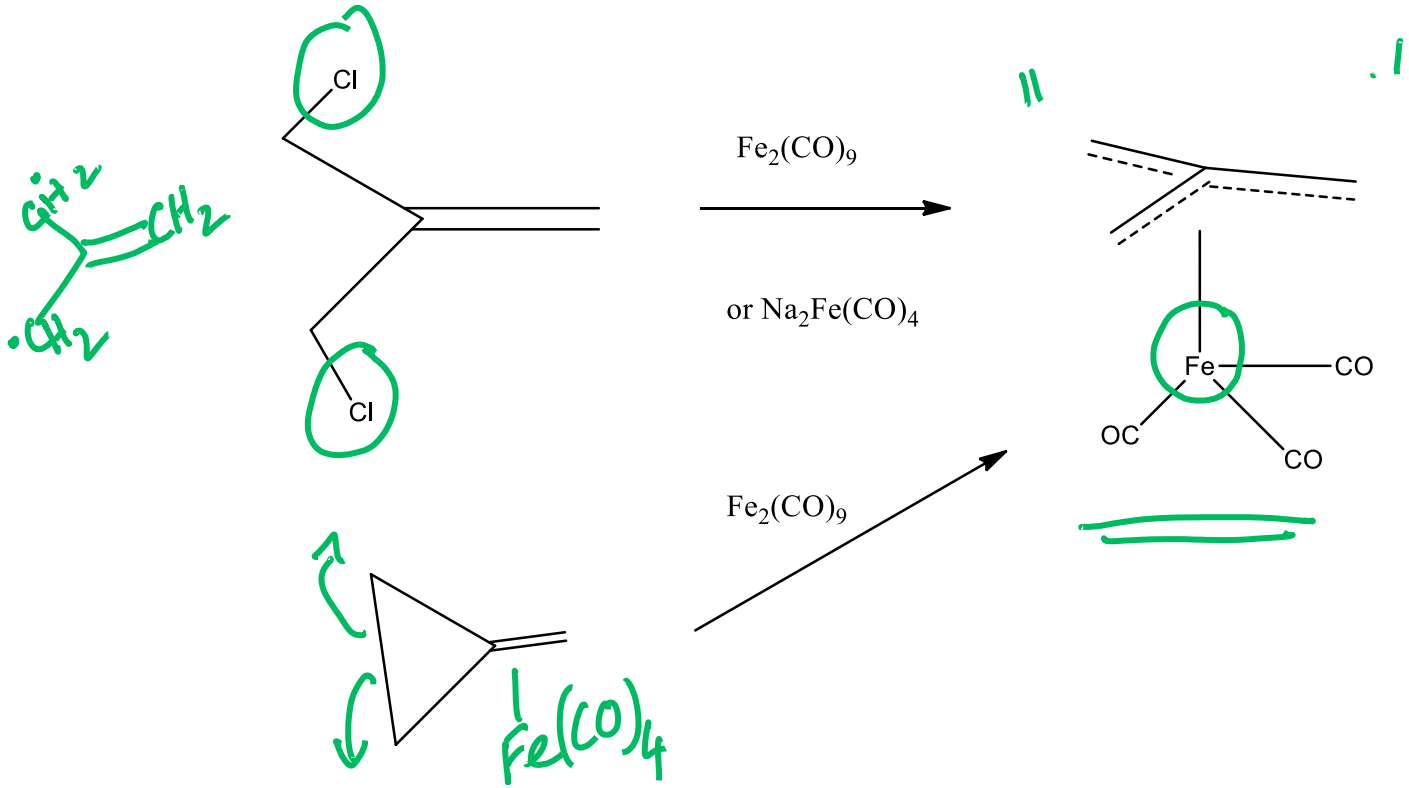


twisted CH_2

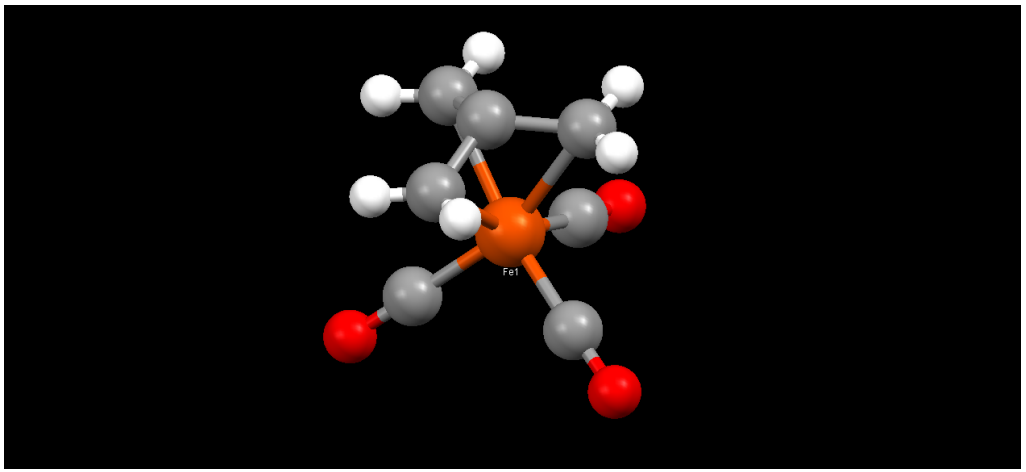
In plane / wide angle

Ruthenium vs. Iron
What is the difference?

Trimethylenemethane



Structure of TMM-$Fe(CO)_3$

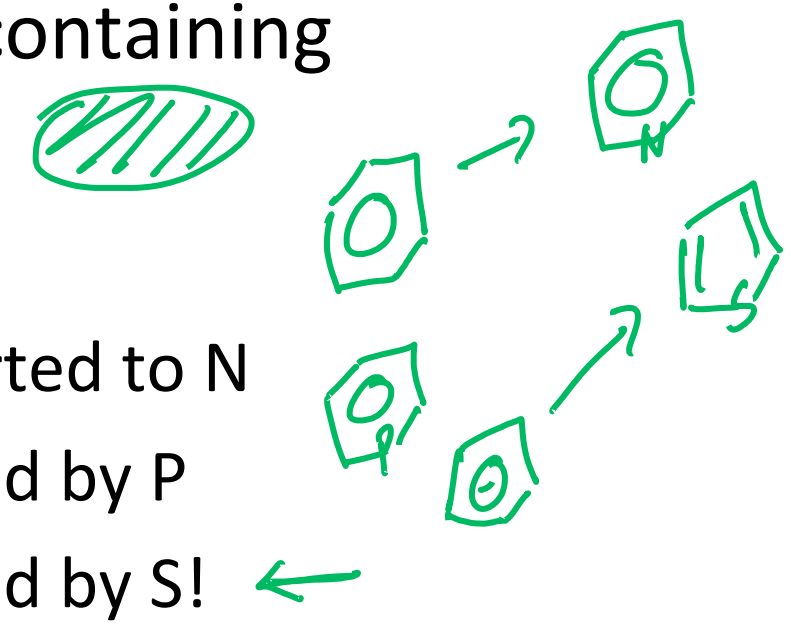


(η^4-Trimethylenemethane)-tricarbonyl-iron
REHZEK from CSDS

- Note Inverted umbrella structure
- Staggered orientation of tmm!

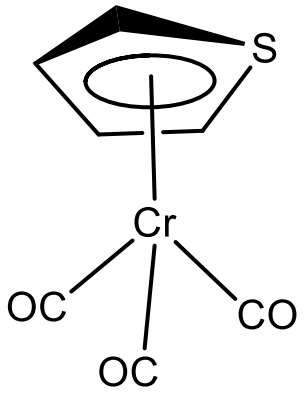
Exotic Sandwiches

- Hetero atom containing "bread"

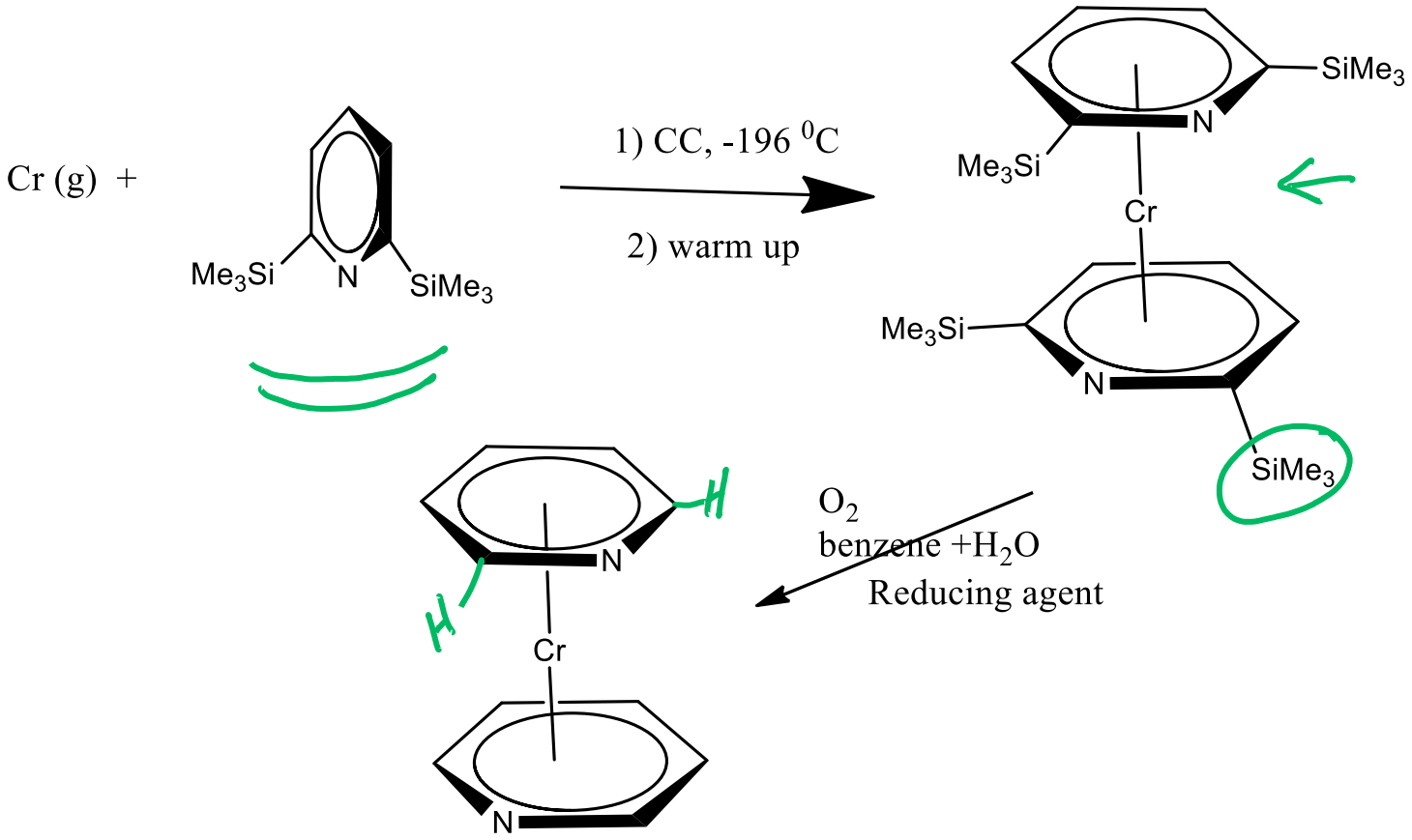


  - C-H is converted to N
  - C-H is replaced by P
  - CH- is replaced by S!

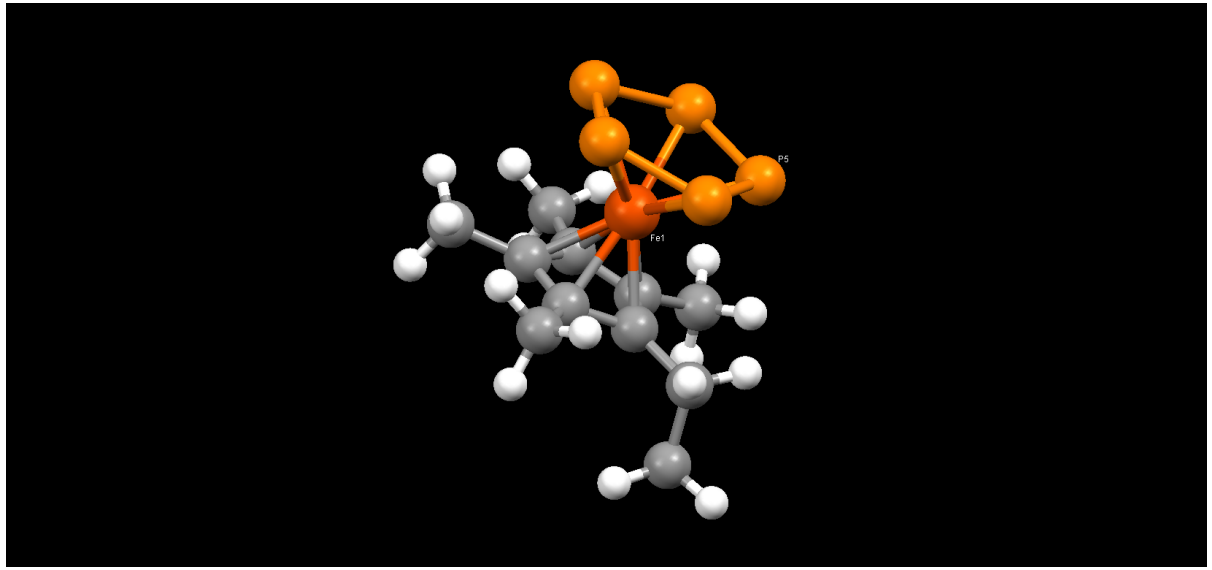
- Thiophene

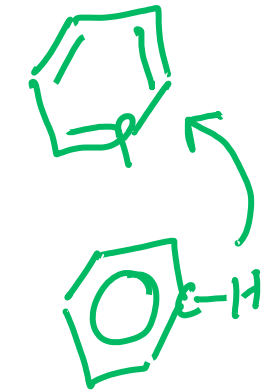


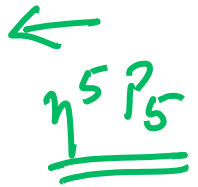
CC with pyridine!



P_5 Sandwich!



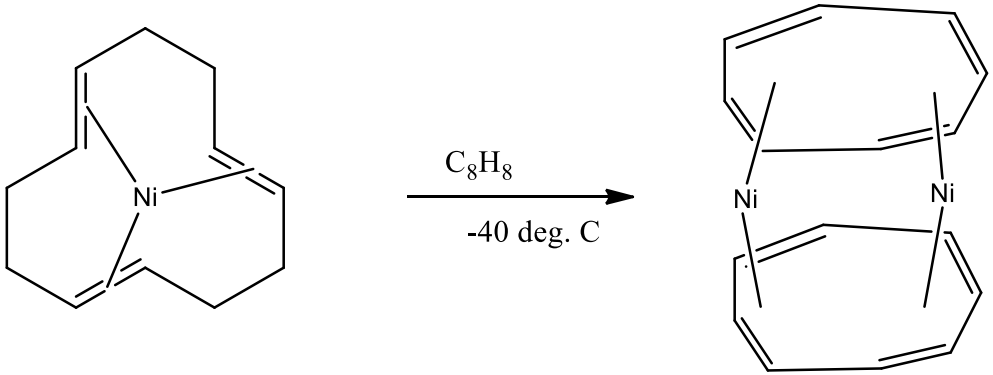




(η5-Ethyltetramethyl-cyclopentadienyl)-(h5-cyclopentaphosphorus)-iron

GEVRUU from CSDS

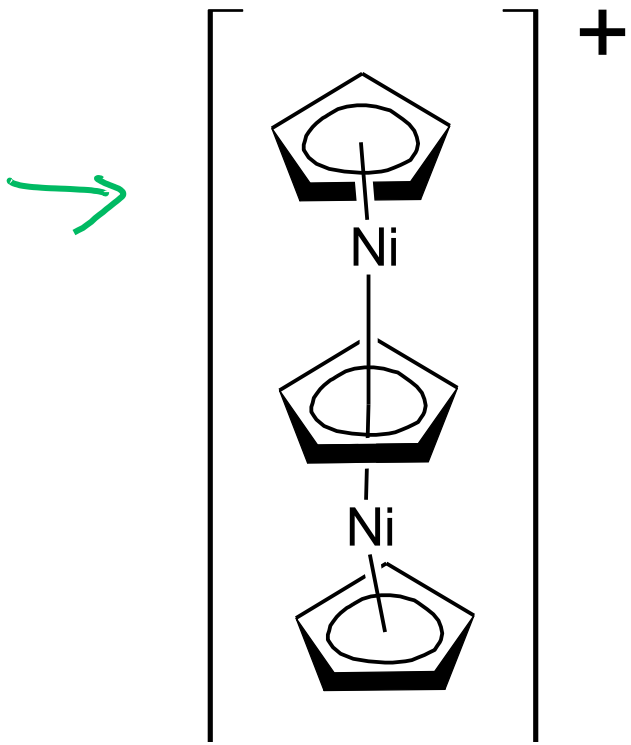
Multimetal Sandwich



Multidecker Sandwiches

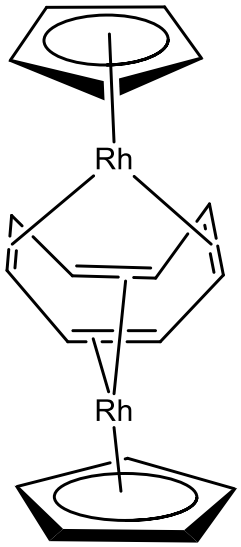
- What is the use of making sandwich complexes?

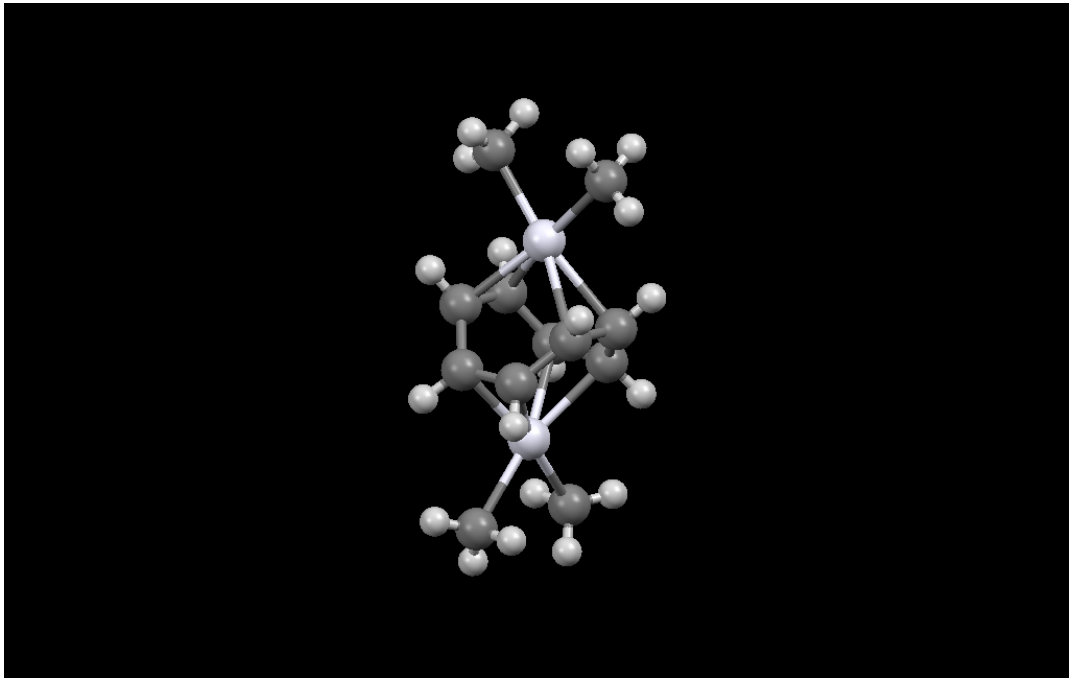
- Observed in the mass spectrometer and later synthesized.



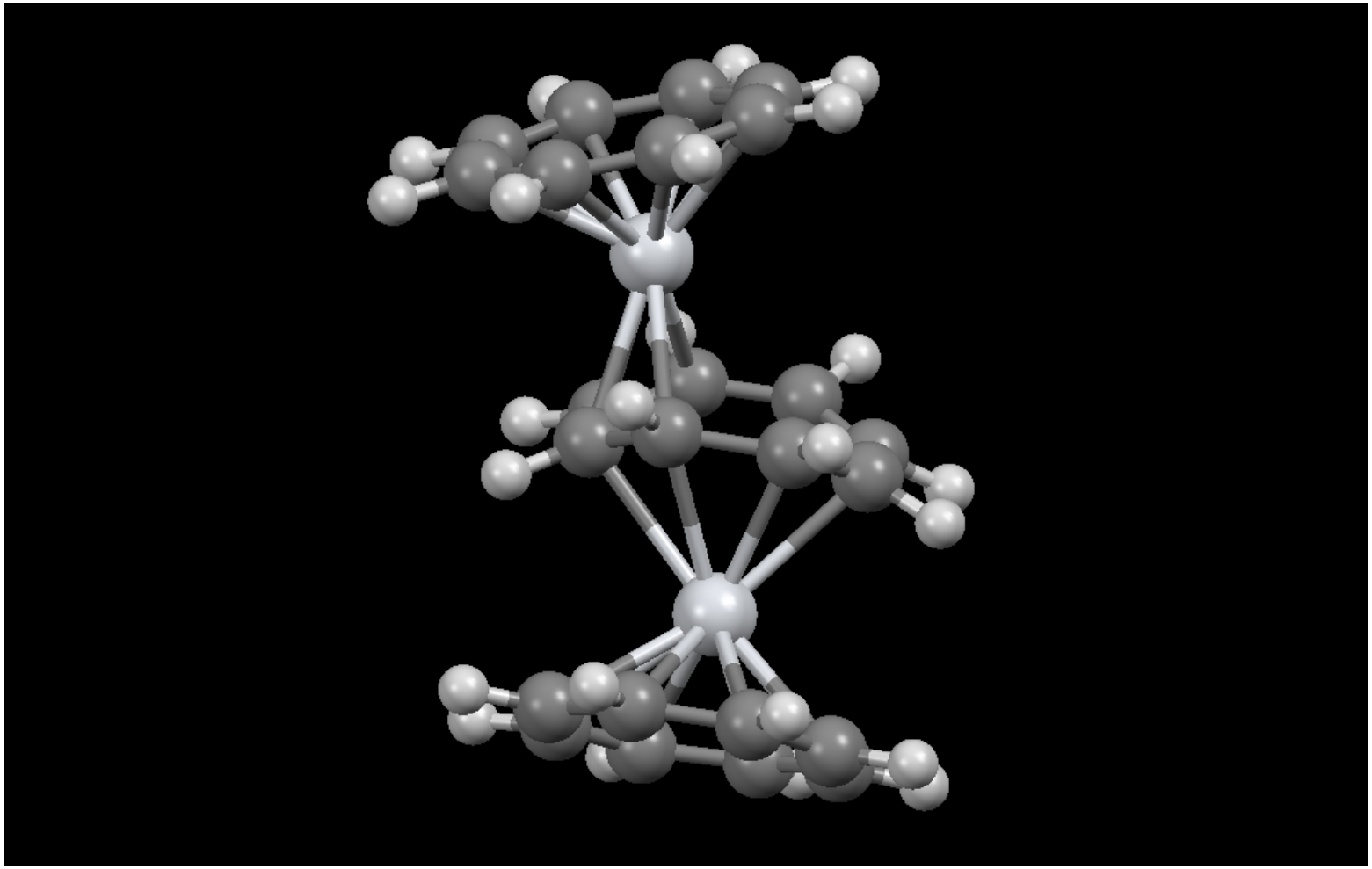
Inverse Sandwich

COT as an inverse sandwich synthon

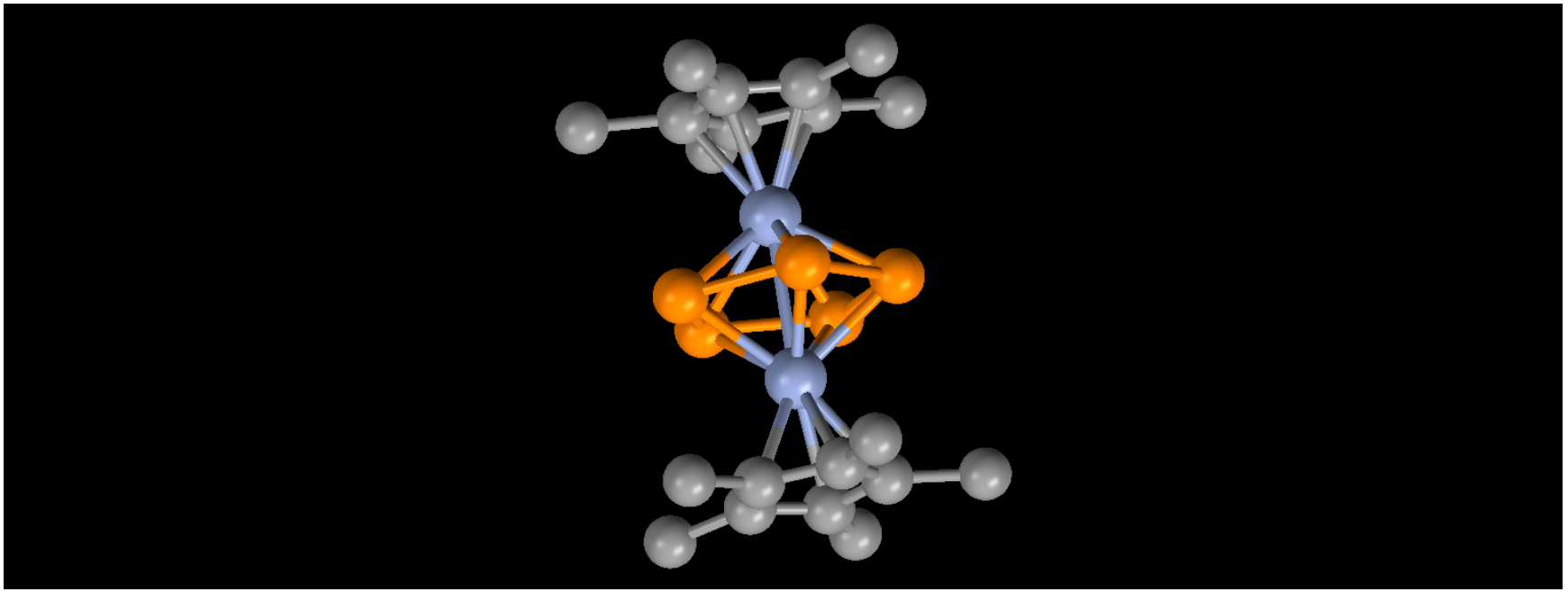




YUHRUO from CSDS



Inverse and Exotic!



(μ^2-(η^{10}-Cyclopentaphosphorus))-bis(η^5-pentamethyl-cyclopentadienyl)-di-chromium
DOMYAF from CSDS

Summary

- The sky is the limit!
- 18 electron rule is a great guiding principle
- The complexes are useful as catalysts as the "bread" is flexible and can change hapticity!

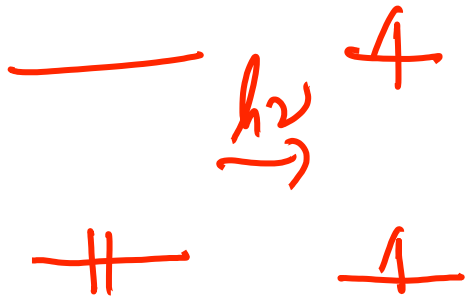
Reactivity Changes of Coordinated Ligands

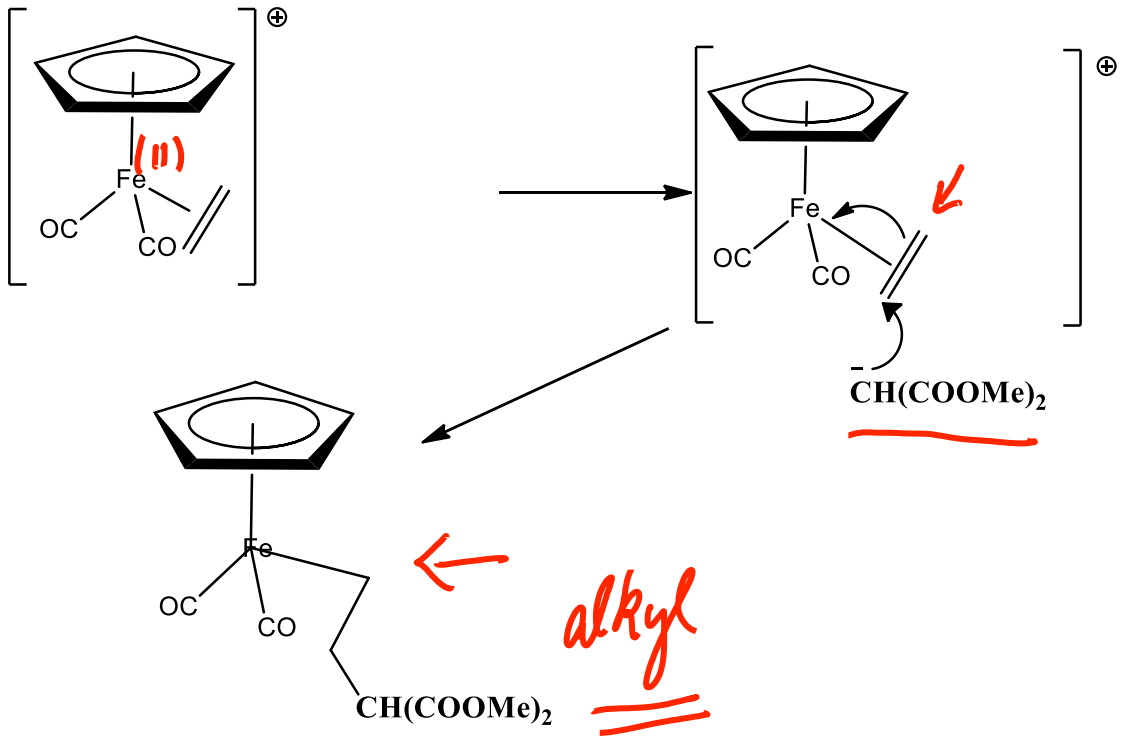
Modified Ligand Reactivity

General features of M-olefin bonding.

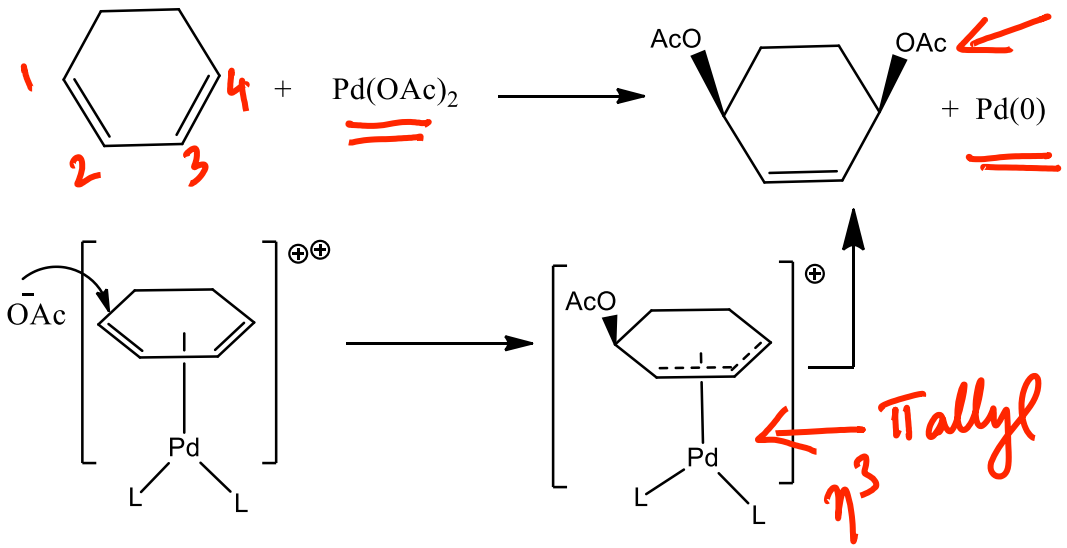
- Removal of electron density from olefin π by metal.
- Population of the π* orbital of the olefin/polyene by metal 'd' electrons.

- 1. Nucleophilic addition enhanced / Electrophilic reactions suppressed
- 2. Photochemical type of reactivity.




(II)
Fe
OC
CO
CH(COOMe)2
alkyl

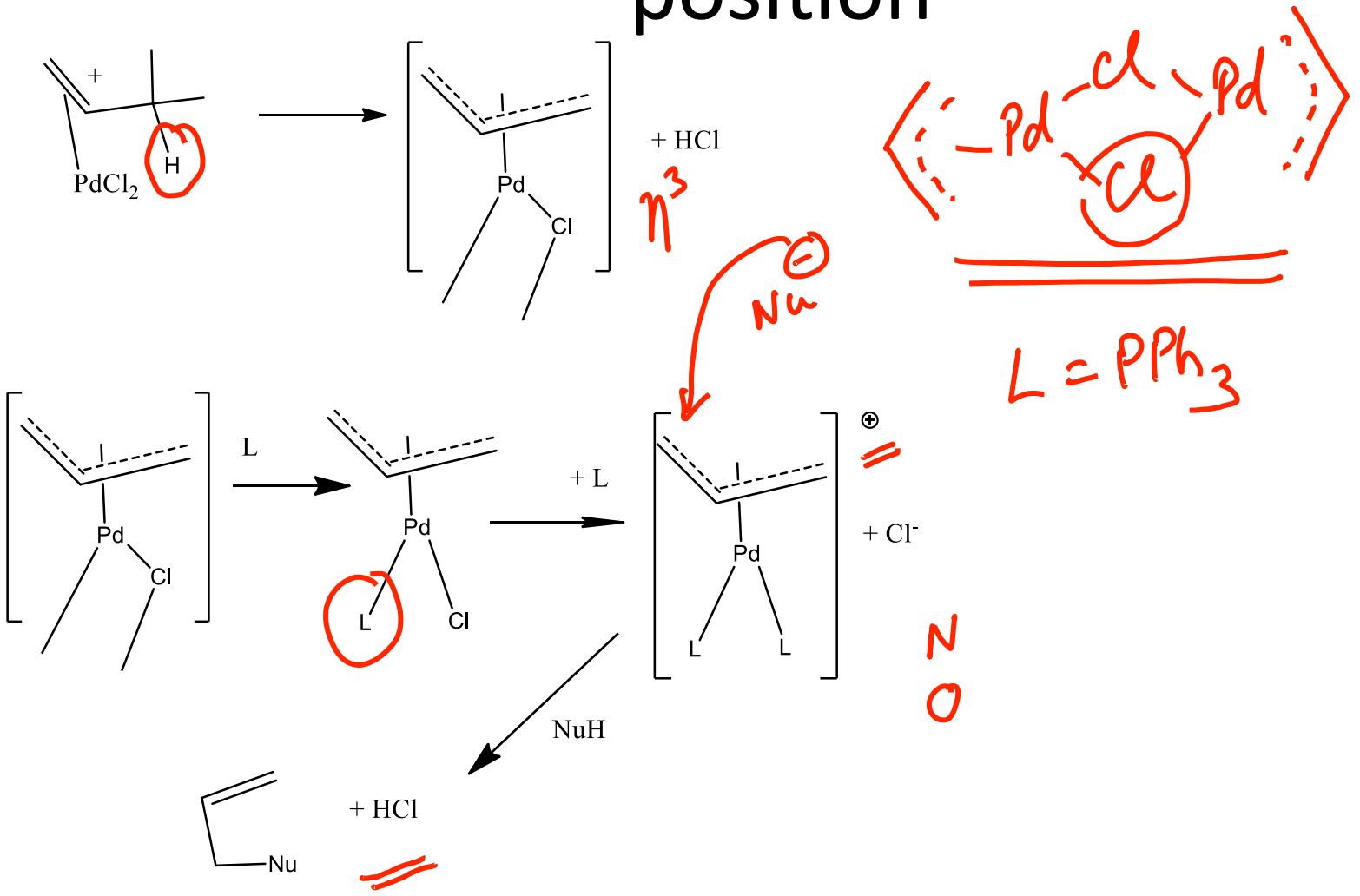
Oxidation of Dienes with Pd



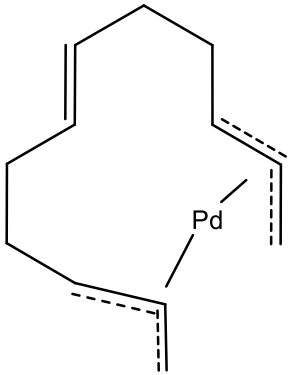
$Pd(0) + O_2 + HOAC \dashrightarrow Pd(OAC)_2 + H_2O$

Involves a nucleophilic attack on the coordinated olefin!!

Oxidation of alkenes at the allylic position



Allylic complex is a “chem”eleon

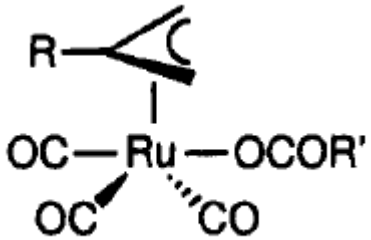


$CpFe(CO)_2CH_2\text{-}CH{=}CH_2$

Fe allyl complexes behaved as allyl anion

Ni(0) / Pd(0) based coupling is almost like allyl radical coupling

Ru(IV) allyl complexes behaved as if they were allyl cations



Ox. state metal

L on M

Modified Ligand Reactivity

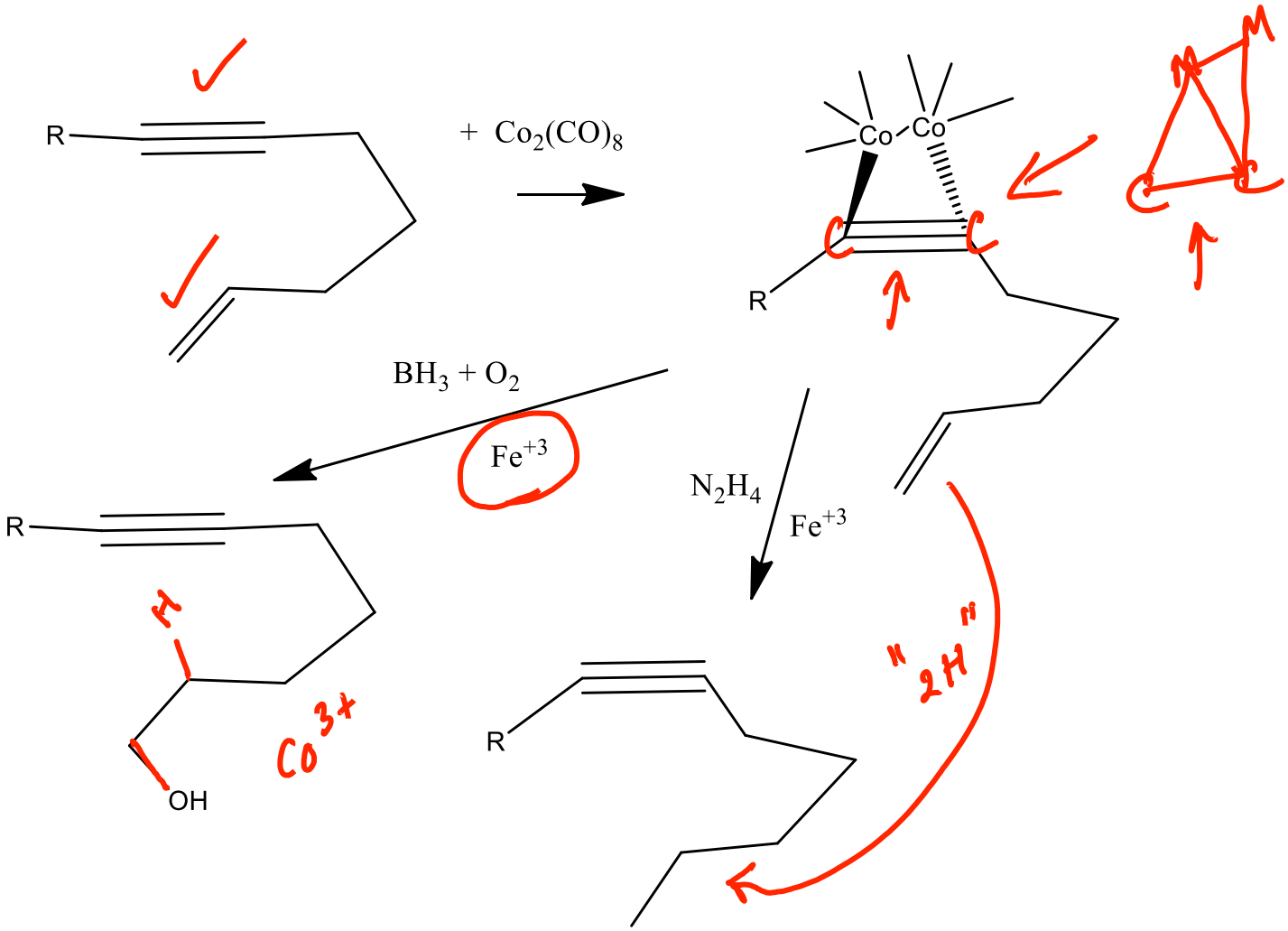
General features of M-olefin bonding.

- Unavailability for usual reactions common for double bonds.
- Loss of conjugation in a polyene.

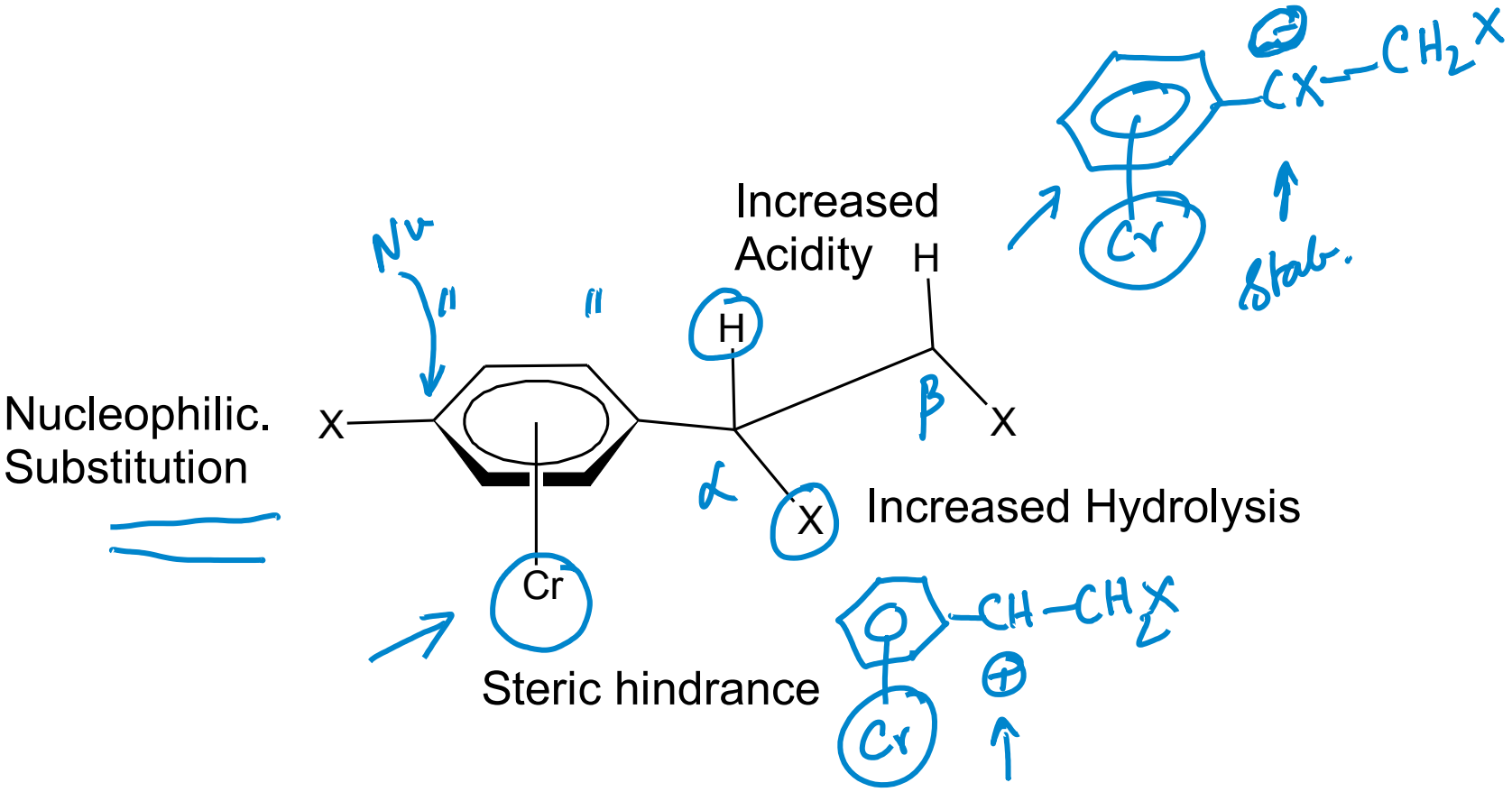
3. Protection from hydrogenation
or
Enhanced reactivity of other D.B.

4. Alternate reactions due to 1,2,3.

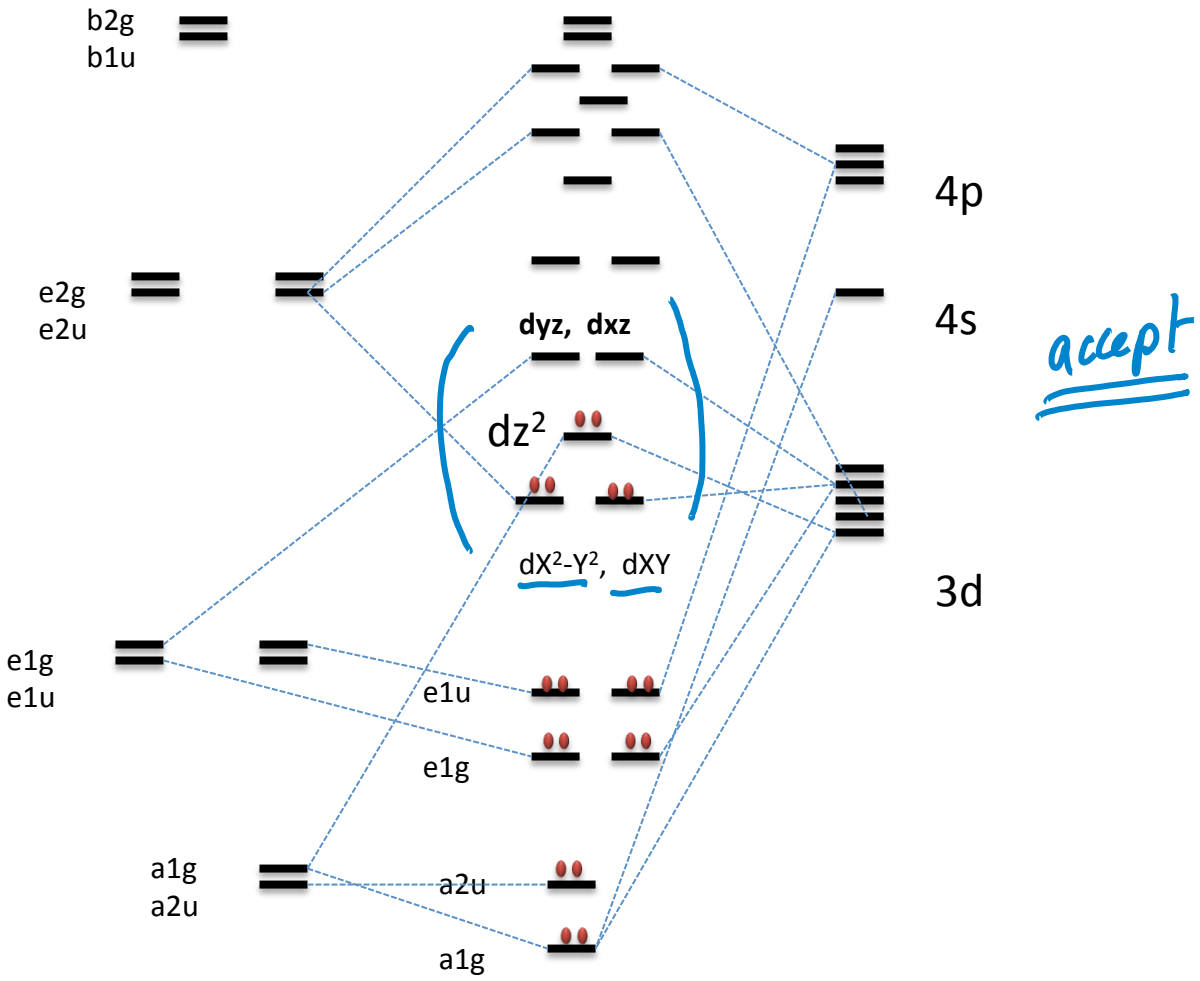
Protection of an alkyne!



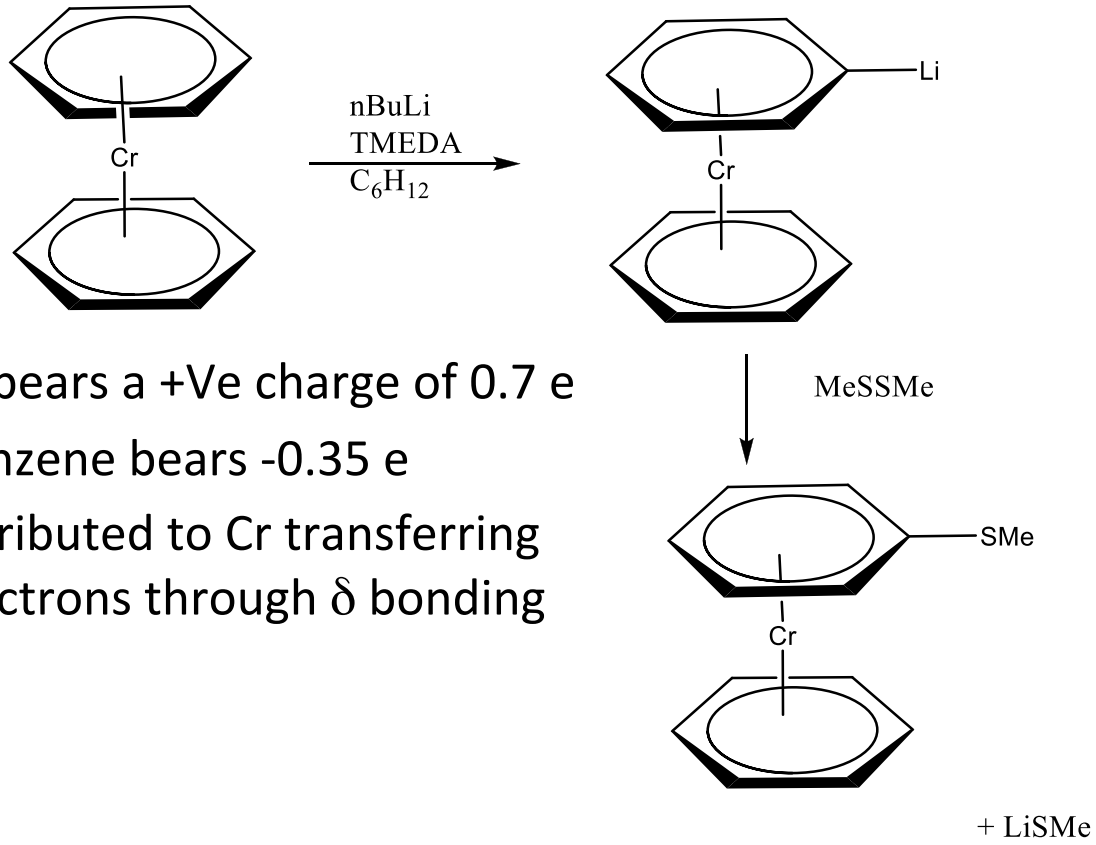
Different Reactivity for the arene



The source of anchimeric assistance



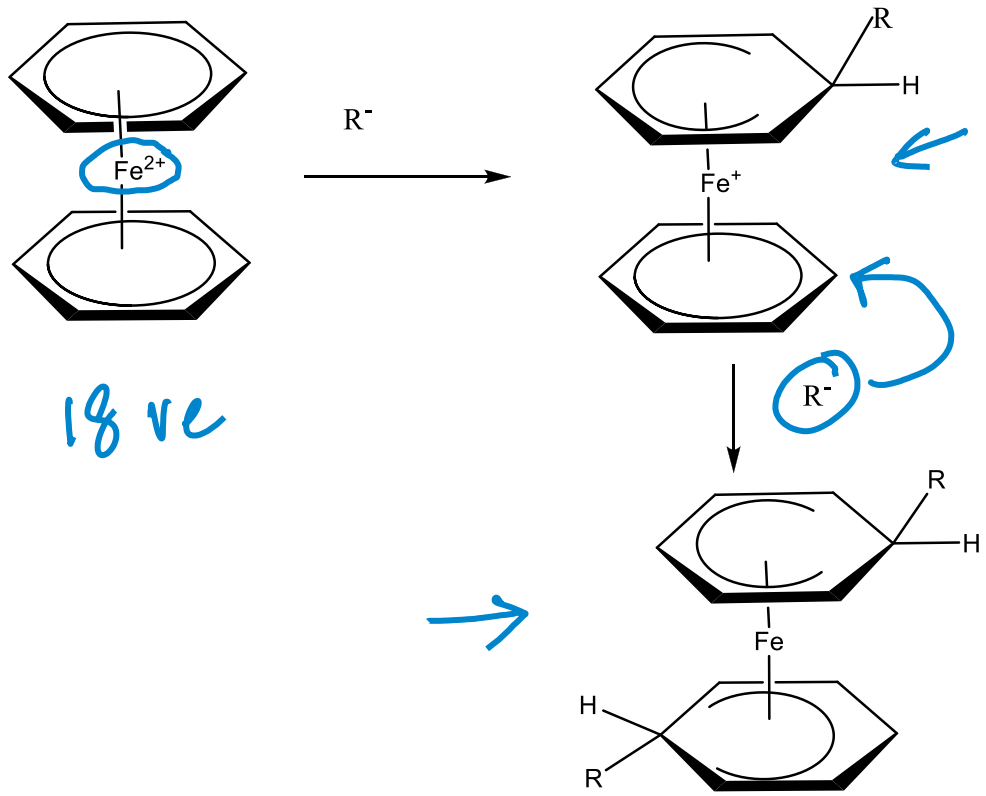
Reduced Nucleophilic Attack!



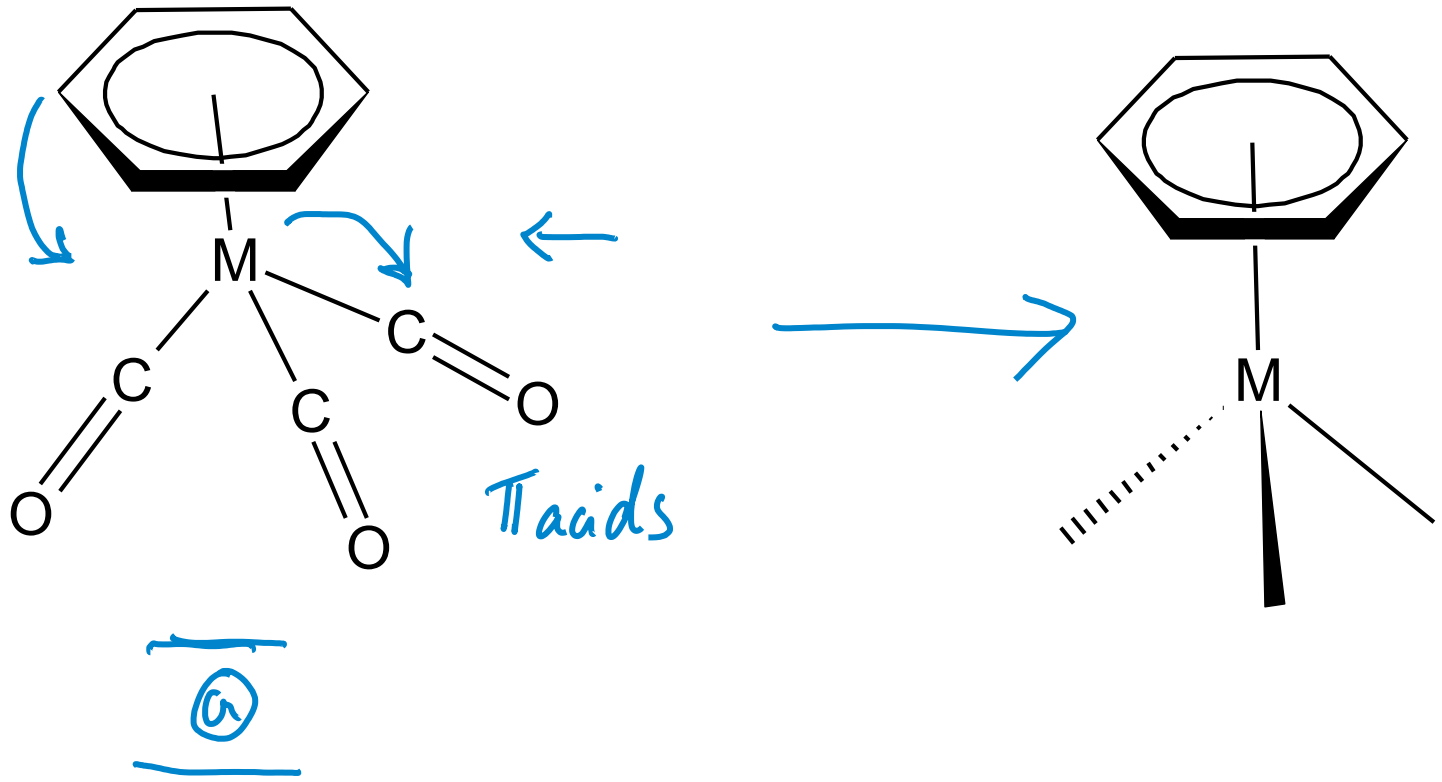
Dilithio and Monolithio Cpds are formed

- Cr bears a +Ve charge of 0.7 e
- Benzene bears -0.35 e
- Attributed to Cr transferring electrons through δ bonding

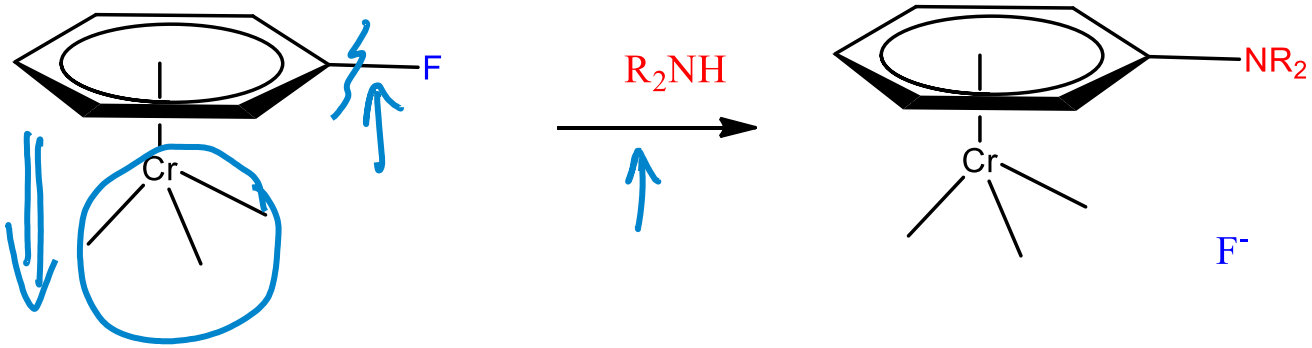
Enhancing nucleophilic attack
Metal effect



Half Sandwich complexes
Ligand effect

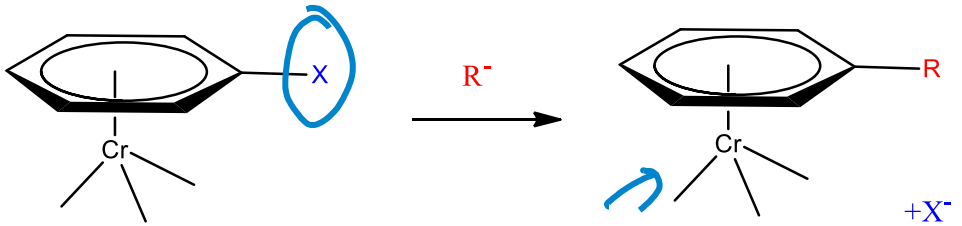


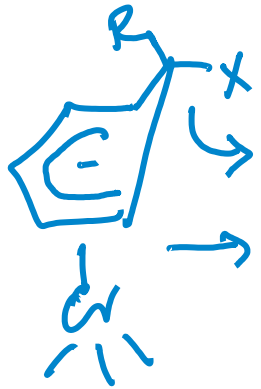
Nucleophilic substitution



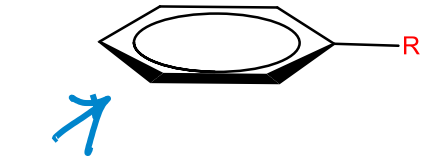
H+

Nucleophilic substitution





Oxidation
iodine/ CAN



- $CH(COOMe)_2$
- $CMe_2(COOEt)$
- $C(CN)(COOMe)_2$

CN^-

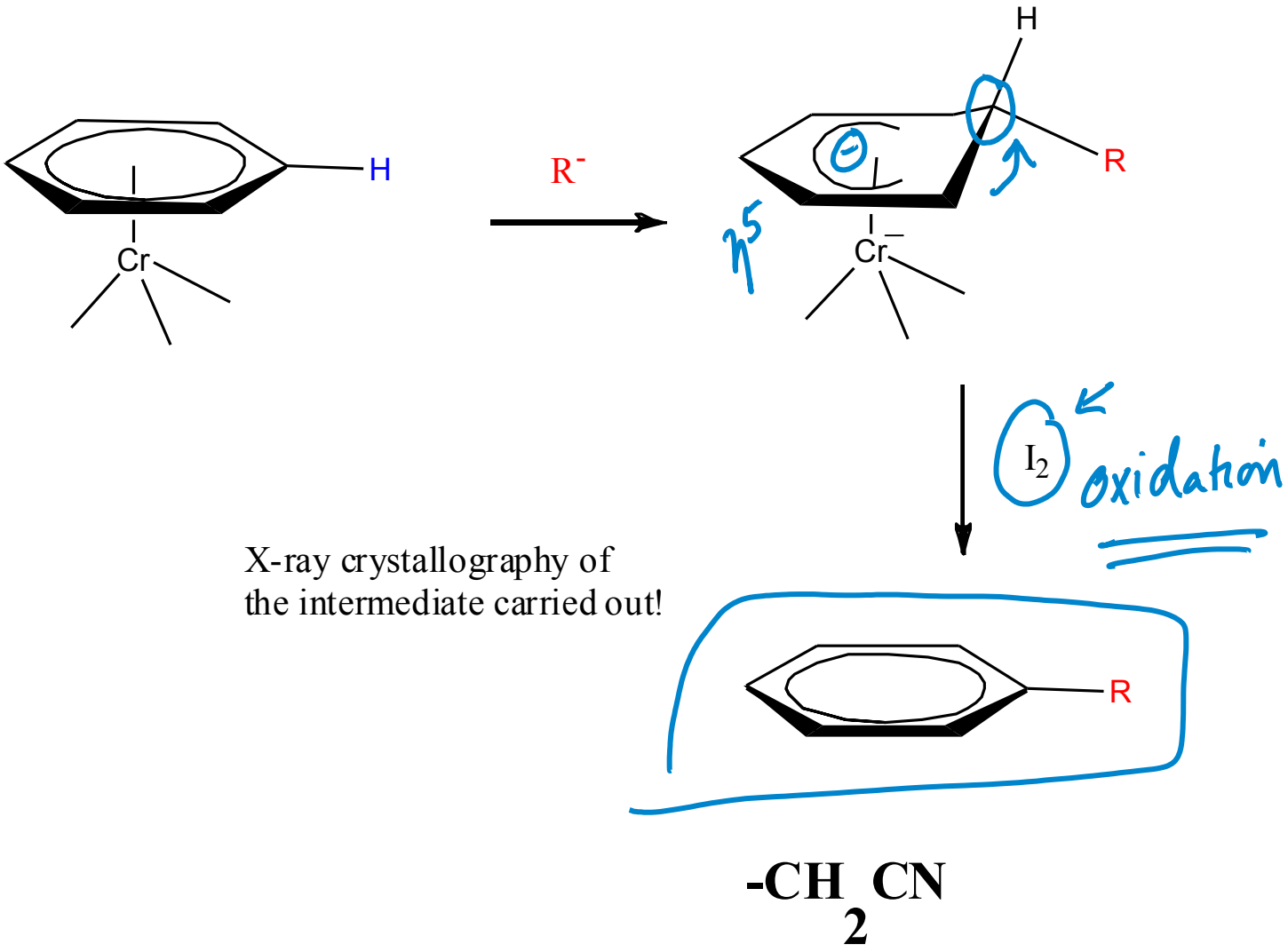
- $CPh(CN)(OMe)$
- $CMe_2(COOEt)$
- $C(CN)(CMe)_2$

Ce^{4+}

Two step addition elimination

Martin Semmelhack

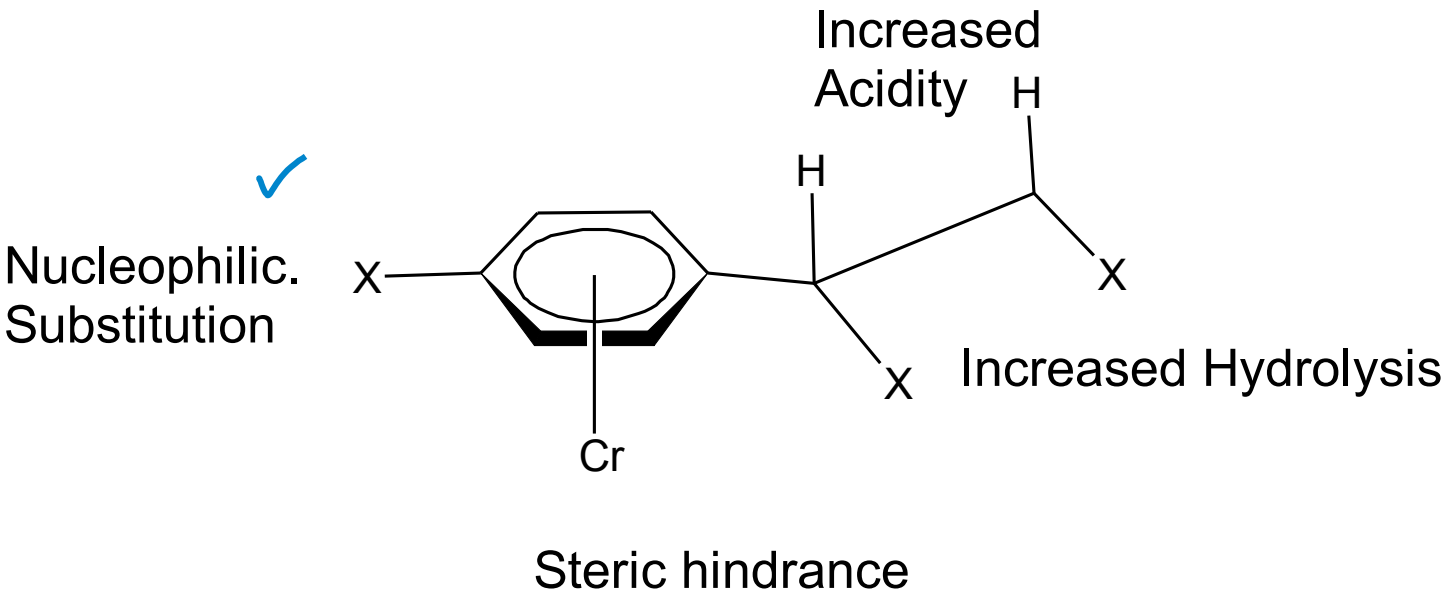
Nucleophilic substitution

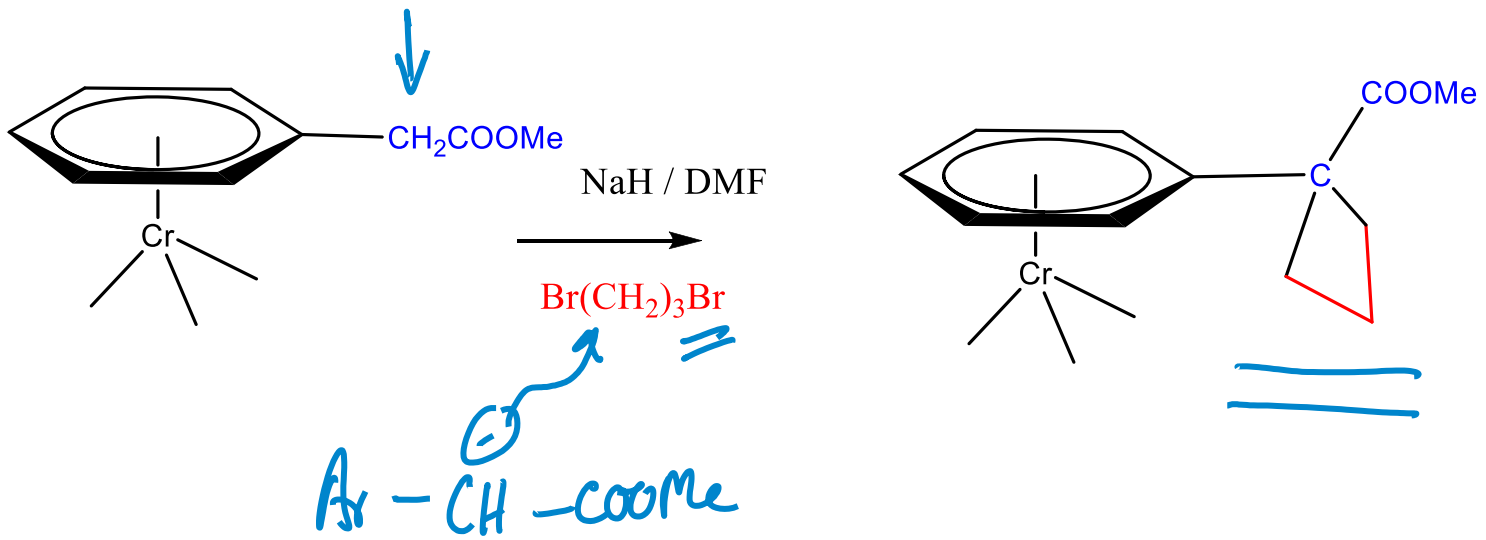


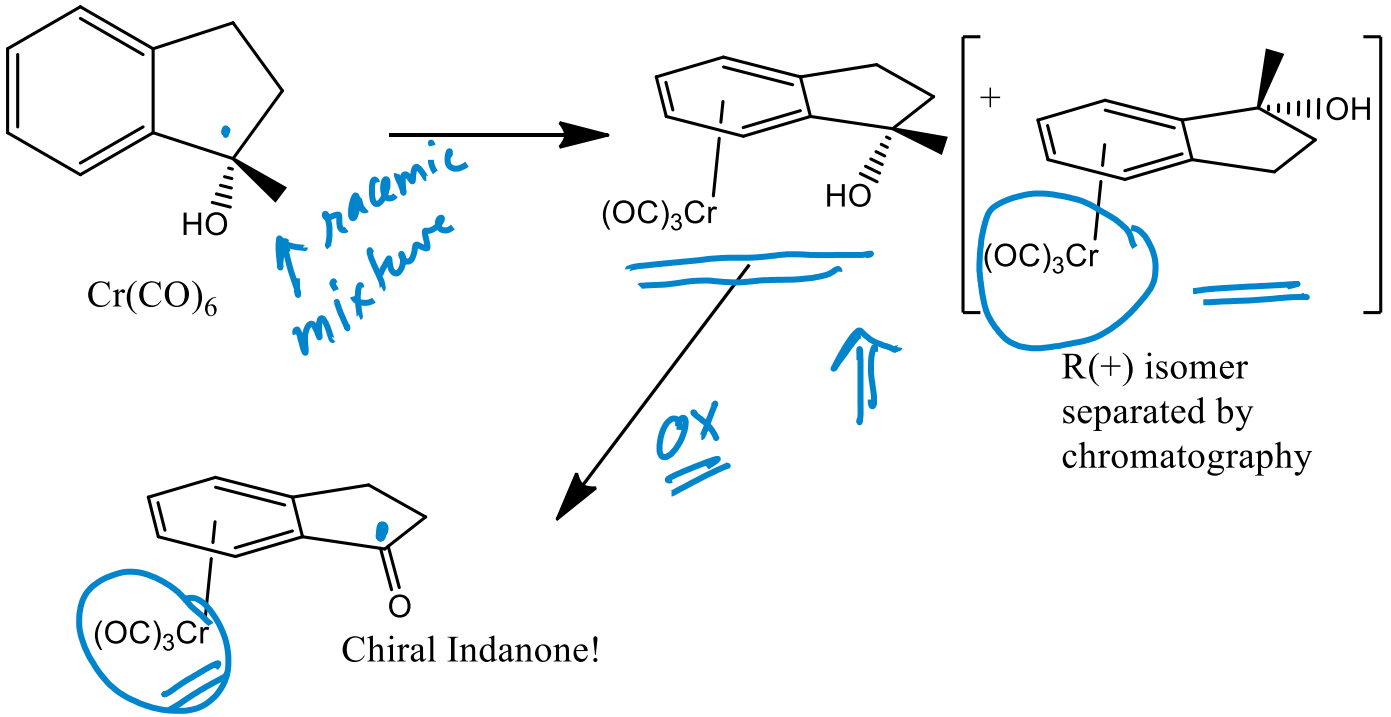
X-ray crystallography of
the intermediate carried out!

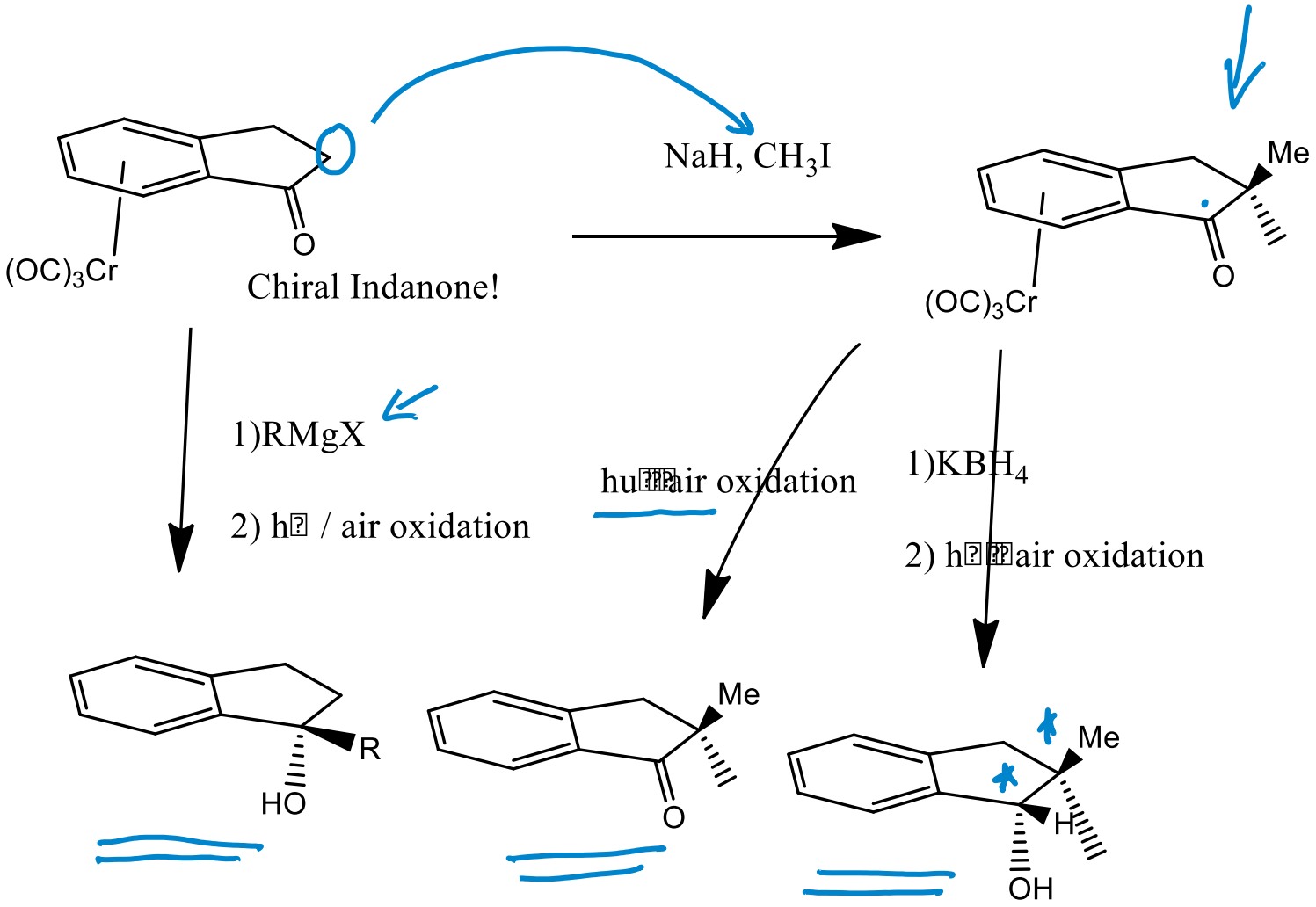
-CH$_2$CN

Different Reactivity for the arene

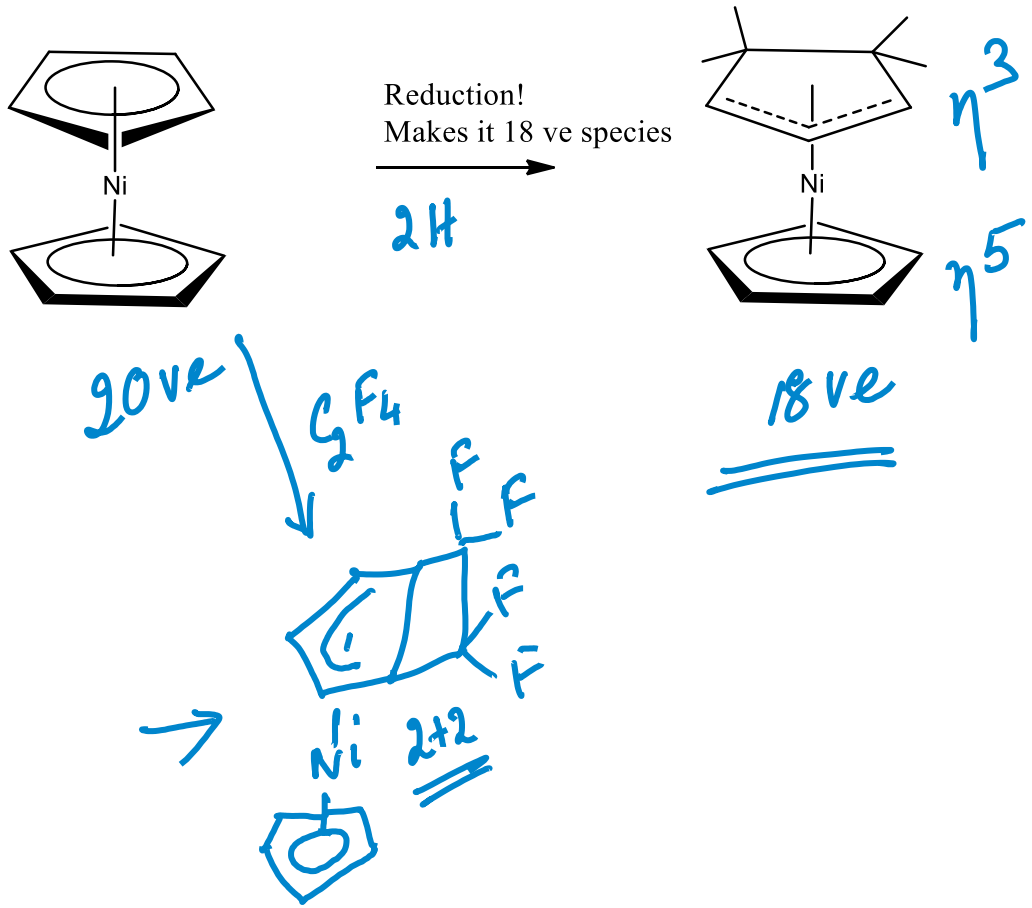



CH2COOMe
Cr
NaH / DMF
Br(CH2)3Br
Ar – CH – COOMe
COOMe
C
Cr


HO
Cr(CO)6
racemic mixture
(OC)3Cr
HO
+
OH
(OC)3Cr
R(+) isomer separated by chromatography
ox
(OC)3Cr
O
Chiral Indanone!


NaH, CH_3I
$(OC)_3Cr$
O
Chiral Indanone!
Me
1)RMgX
2) h / air oxidation
hu air oxidation
1)KBH_4
2) h air oxidation
R
HO
Me
O
Me
H
OH

Reduced aromaticity



Electrophilicity reactivity index

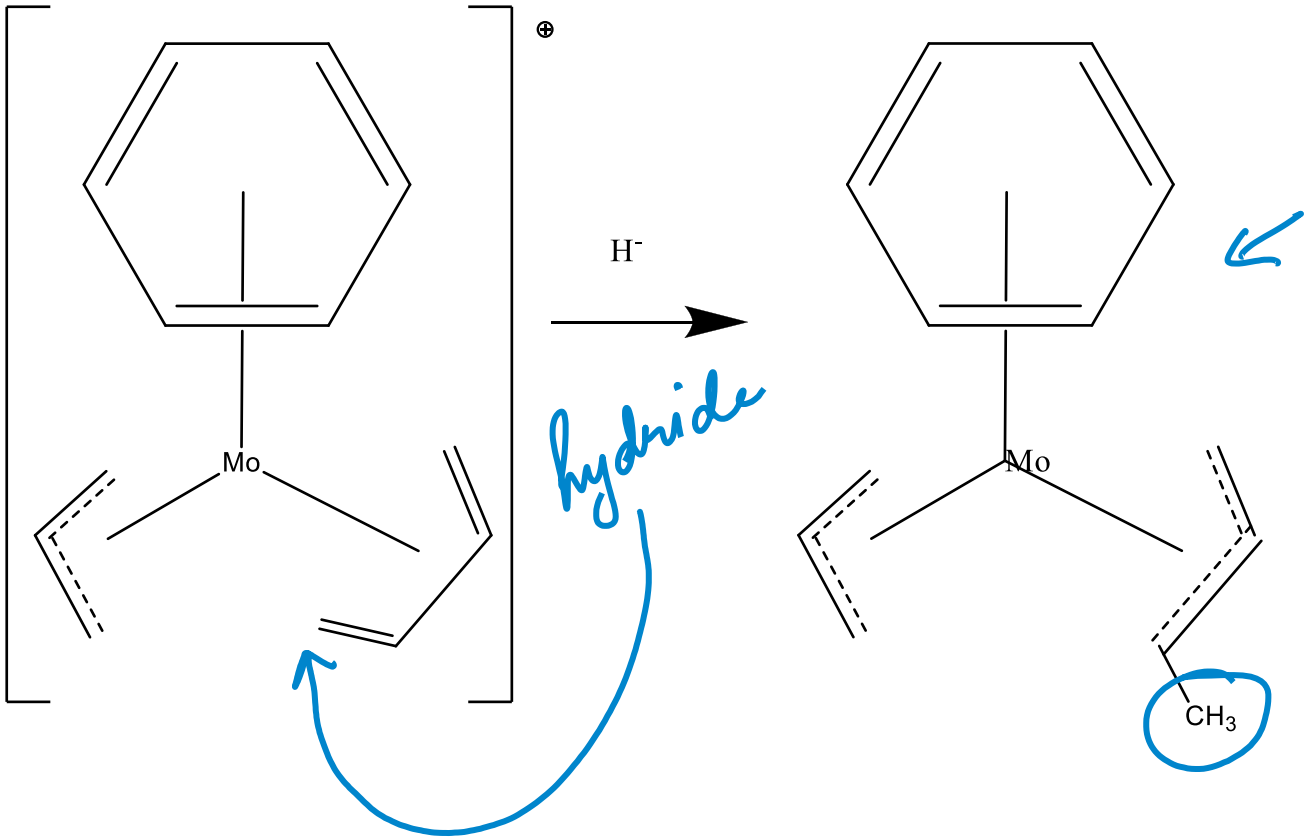
Davies Mingos and Green

DMG

- Nucleophilic attack occurs preferentially at **even** coordinated polyenes
- Nucleophilic addition to **open** coordinated polyenes is prefered over closed polyene ligands
- In the case of even polyenes, nucleophilic attack always occurs at the terminal carbon atom.

DMG rules

Even and odd polyenes are present. Rule 1 says that the even polyene will be attacked by the nucleophile. Rule 2 says it will be the open polyene.

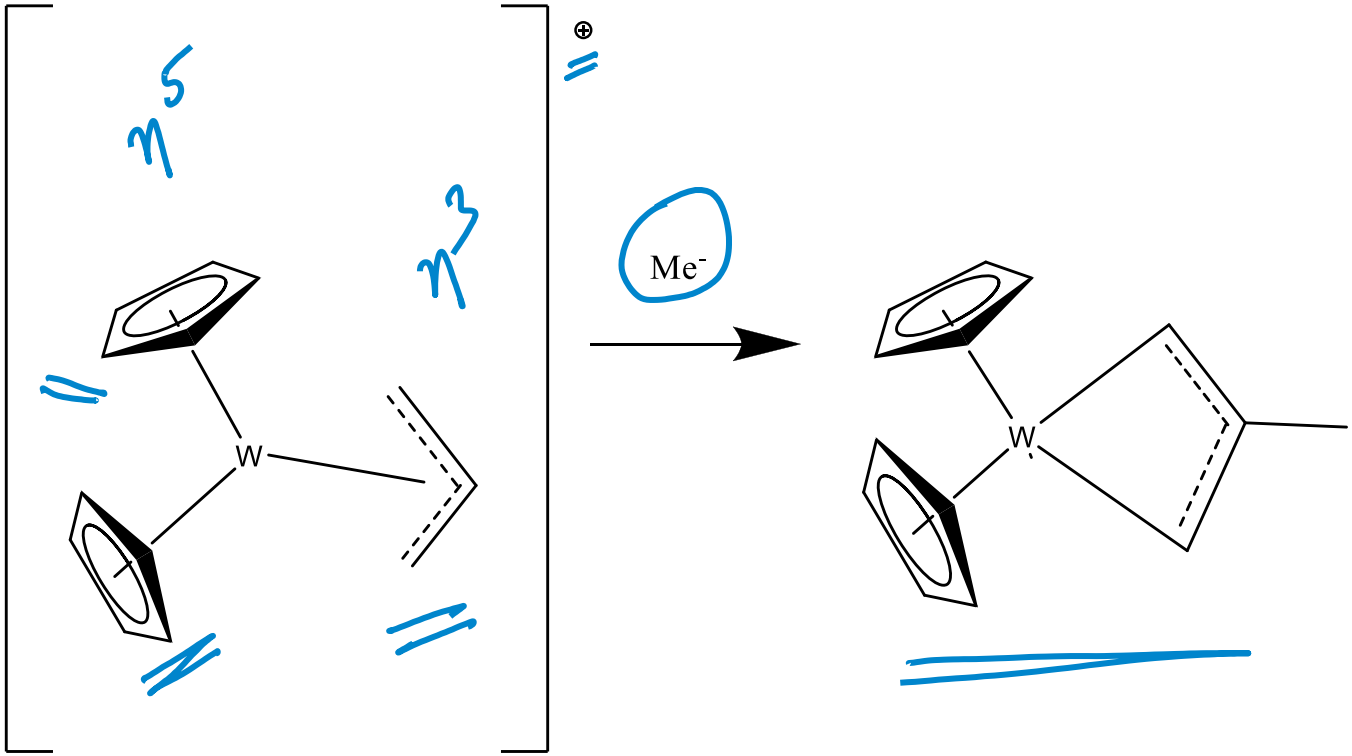


Davies Mingos and Green

- For odd polyenyls, attack at the terminal carbon atom occurs only if the metal is a relatively strong electron withdrawing fragment

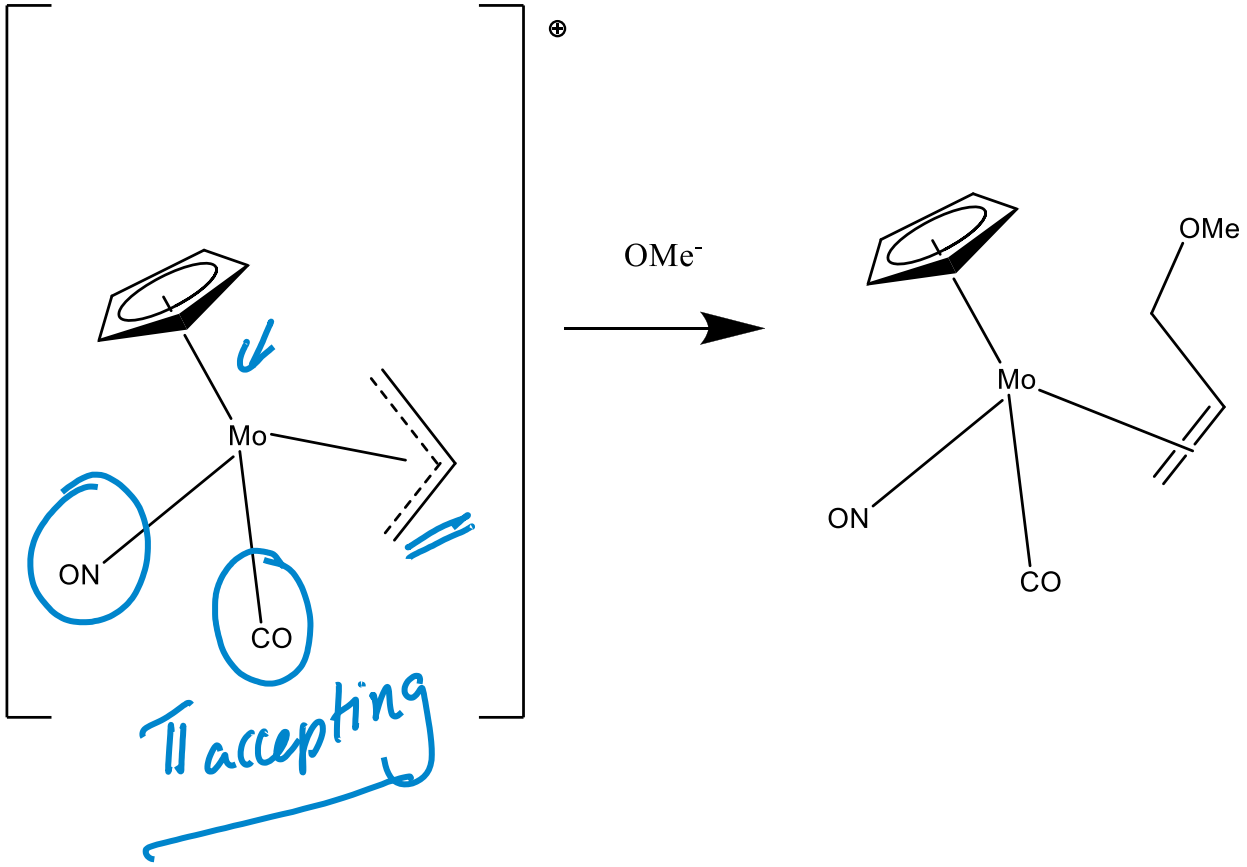
DMG rules

Only odd polyenes are present. Rule 3 says that the odd open polyene will be attacked by the nucleophile. Rule 4 says it will be at the center position.

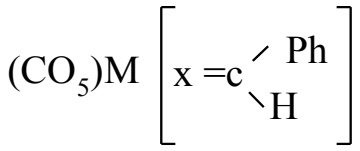


DMG rules

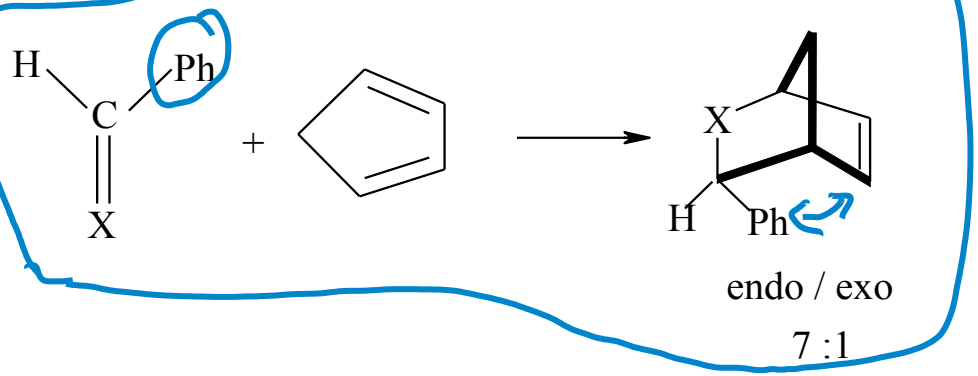
Odd polyenes are present. Open is to be attacked but it is attacked on the terminal



Altered Reactivity of coordinated ligands

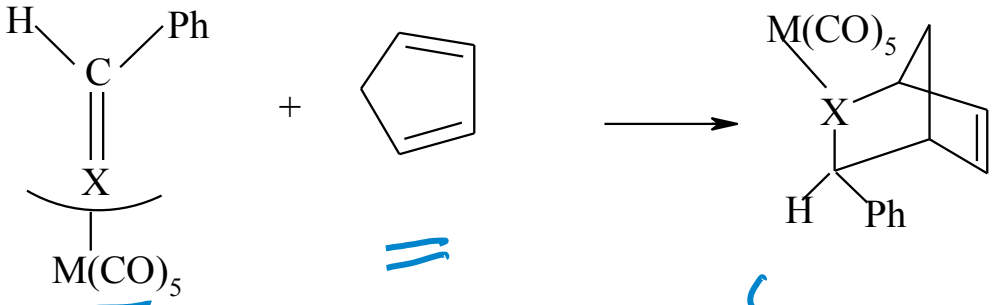


x = S,Se
M = Cr,W



endo / exo

7 :1



exo

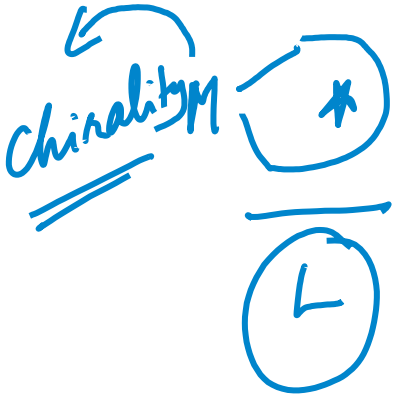
= W 1:7

How does the reactivity change ?

a. Change in selectivity.
b. Rate of reaction decreases.

]

Asymmetric Catalysis



Summary

- Altered reactivity: primarily enhanced and directed nucleophilic attacks!
- Metal oxidation state makes a difference
- Ligands like CO enhance reactivity NO
- Protection of triple / double bonds
- Reduction of aromaticity / conjugation
- Steric effects that introduce “facial” selectivity