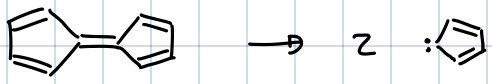
15.11.

Metallocenes

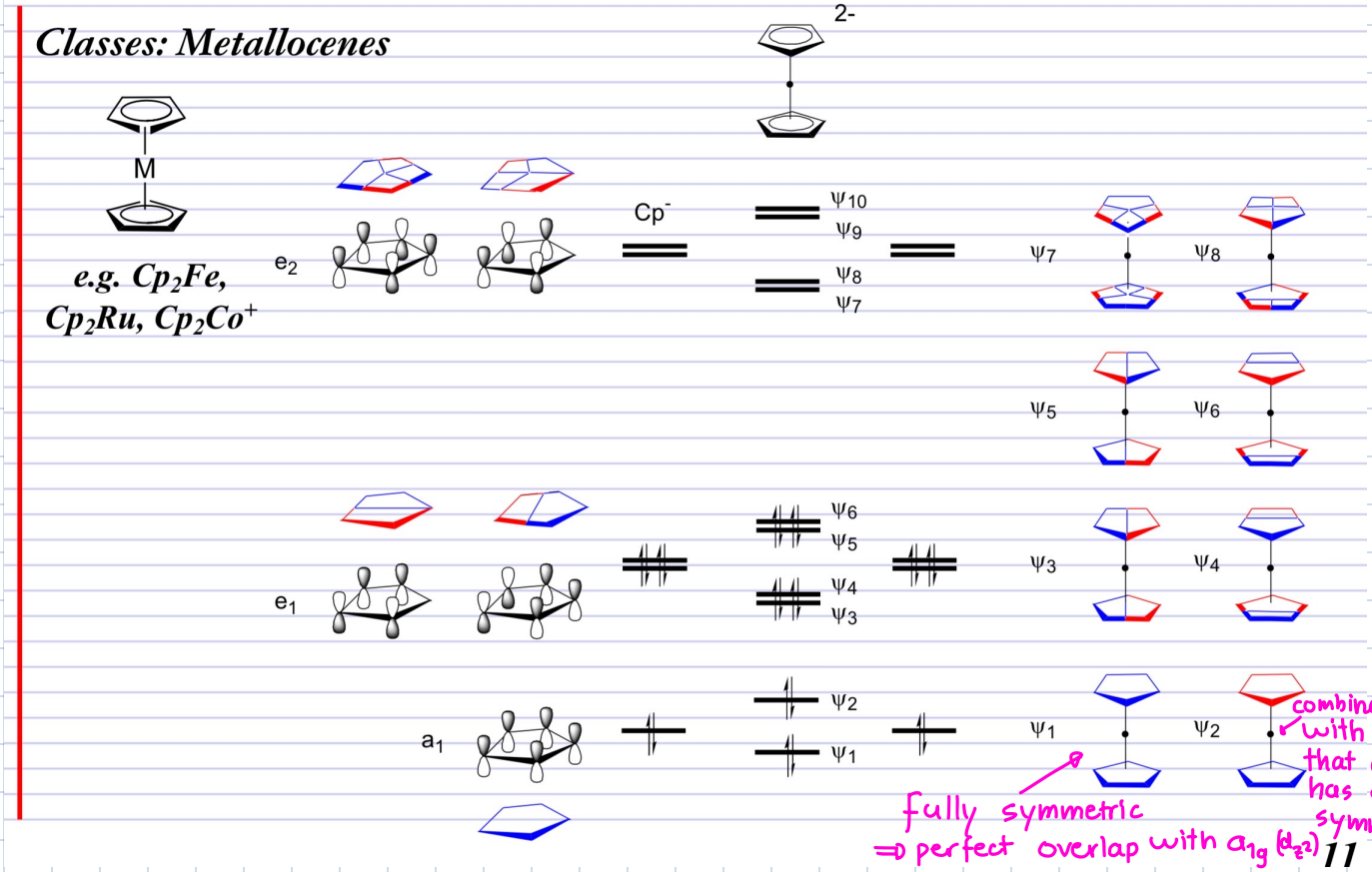
History : Discovered by Wilkinson

↝ Took infamous Cyclopentadiene (Cp), prep. from dicyclopentadiene:



↝ Ferrocene:

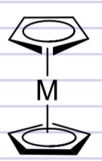
MO diagram for MCp_2 ⇒ "Superligand" Cp_2



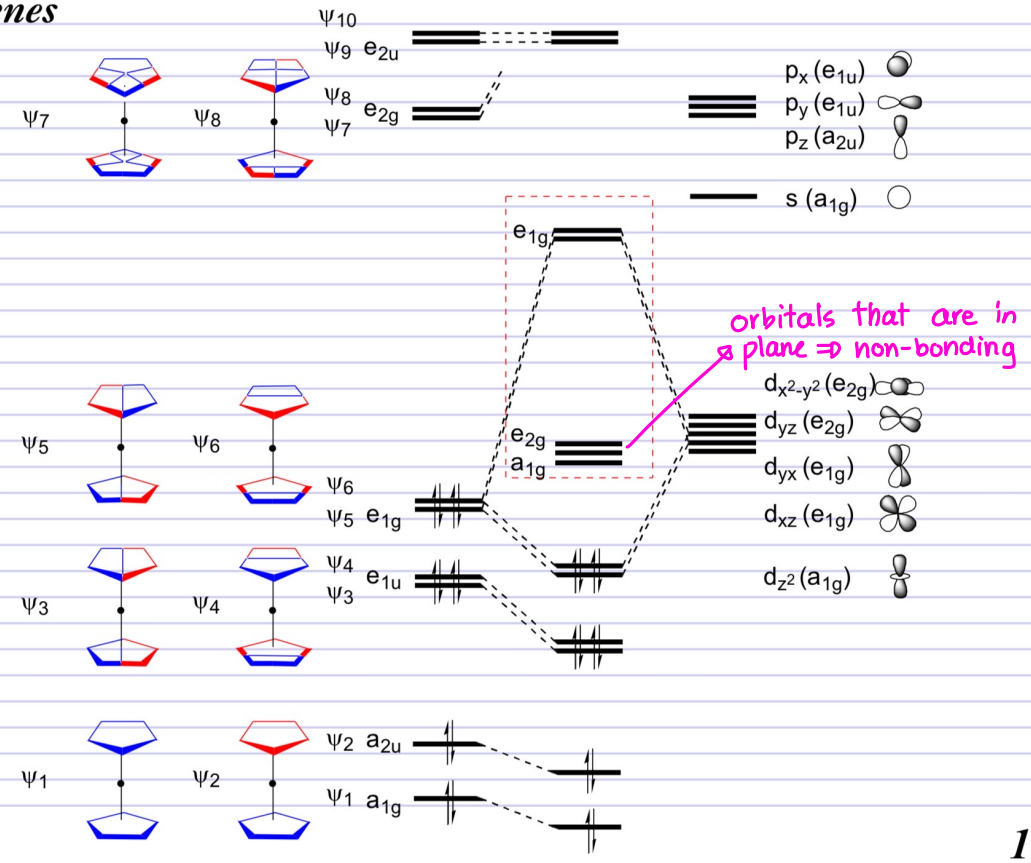
↳ Fe^{II}, Ru^{II}, Co^{III} all have d^6 ⇒ Octahedral coord. stable

↳ fulfilled, as each Cp is L_2X-type

Classes: Metallocenes

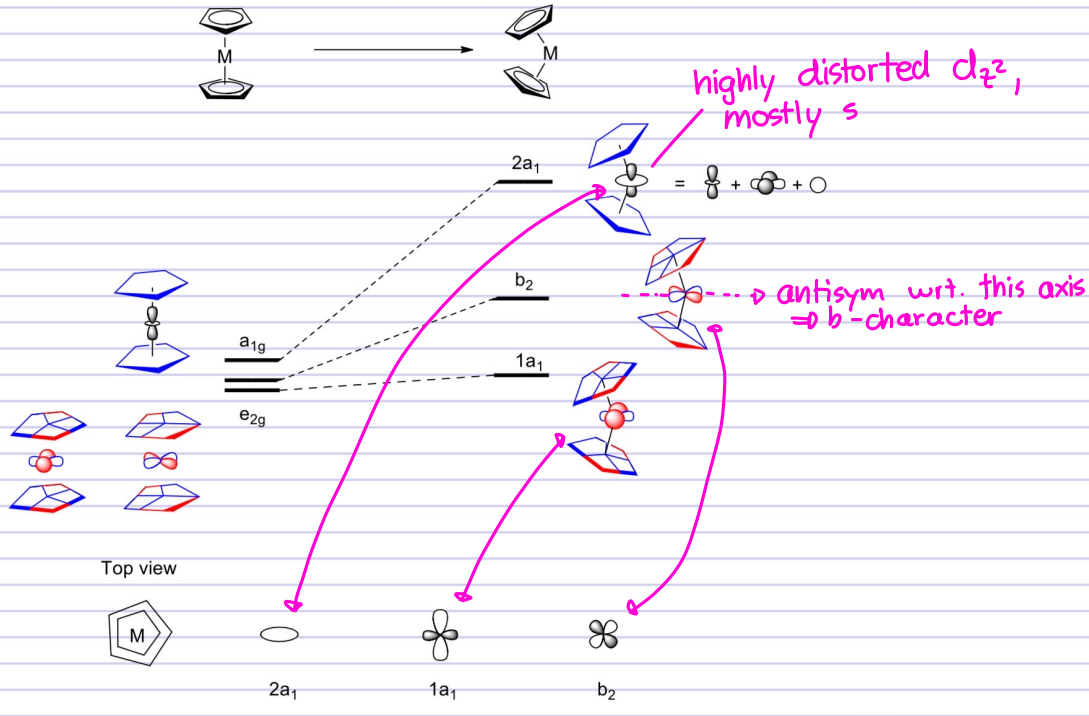


e.g. Cp_2Fe, Cp_2Ru, Cp_2Co^+



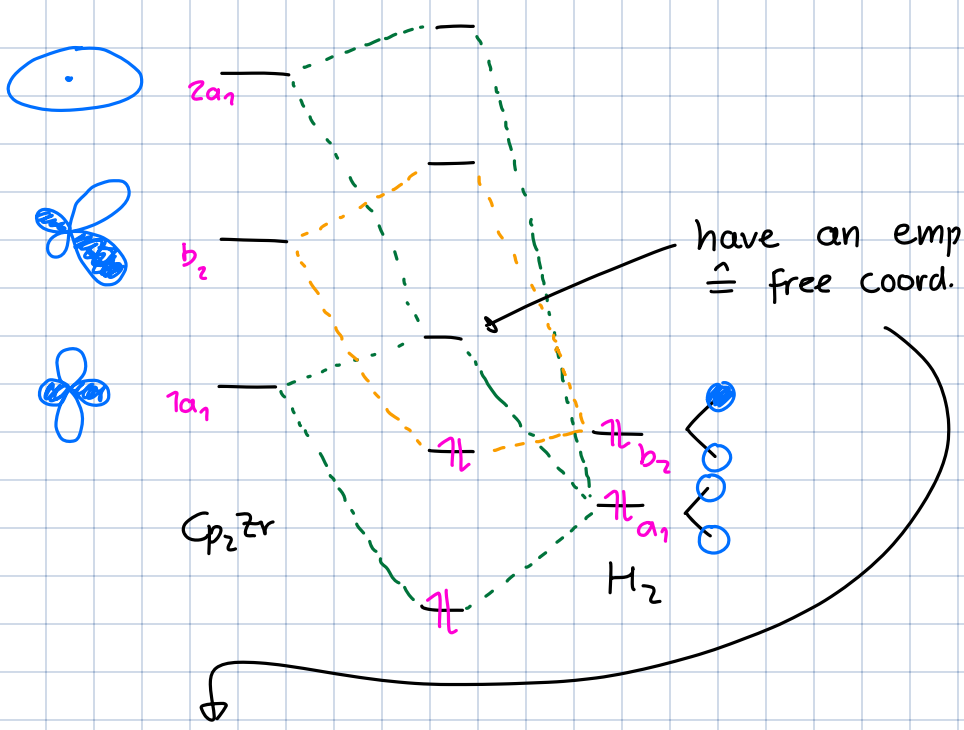
What happens when the Metallocene is distorted from linear Cp-M-Cp to bent Cp-M-Cp ?

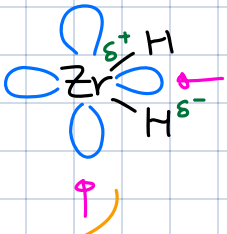
Classes: Electronic Structure of Bent Metallocenes



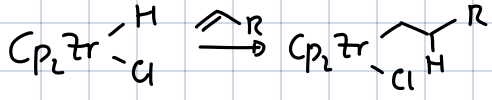
Lets consider an example Cp_2MX_2 with M= Zr, X=H

↑ pure σ-donor



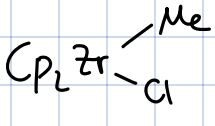


⇒ looks like BH_3
(that can do hydroboration)
⇒ Can also do hydrozirconiation:



But going across the PTE to $Cp_2Re^{\delta-}H_2^{\delta+}$ ⇒ get an acid
↝ But can also be in between (homolytic cleavage → H•)

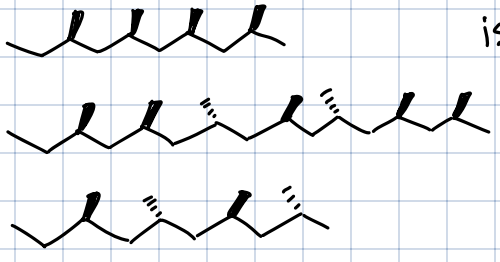
⇒ Back to MH → $M^+ + H^-$ / $M^\bullet + H^\bullet$ / $M^- + H^+$

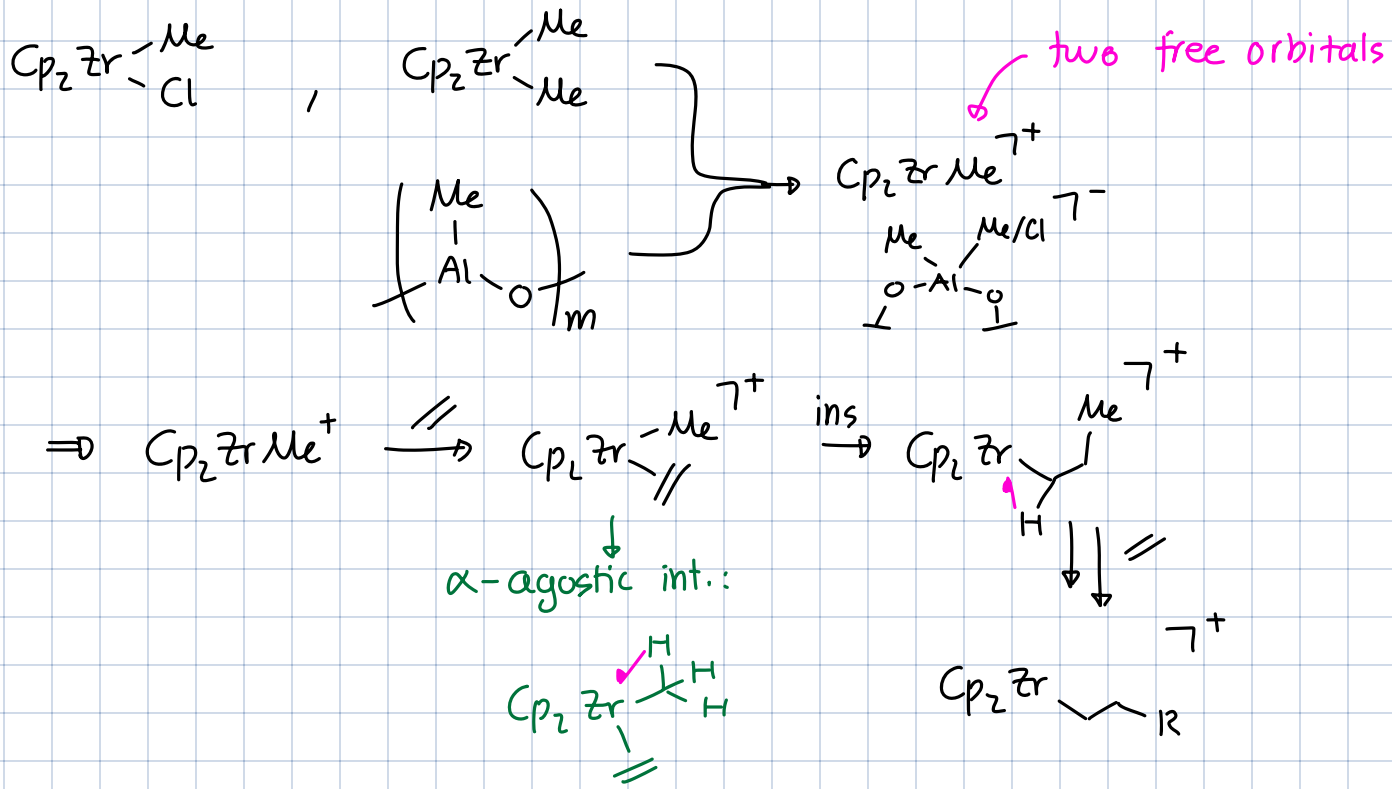


↝ Methyl group can be a π-donor with its C-H bonds !

Metallocenes in Polymerization

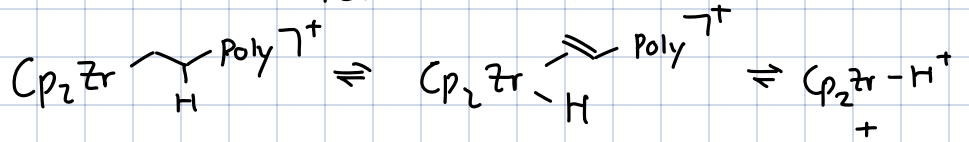
↝ Typical nomenclature of polymers (polypropylene)



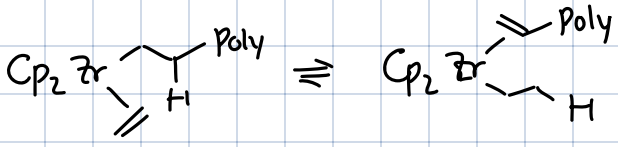


How to get back polymer (Termination):

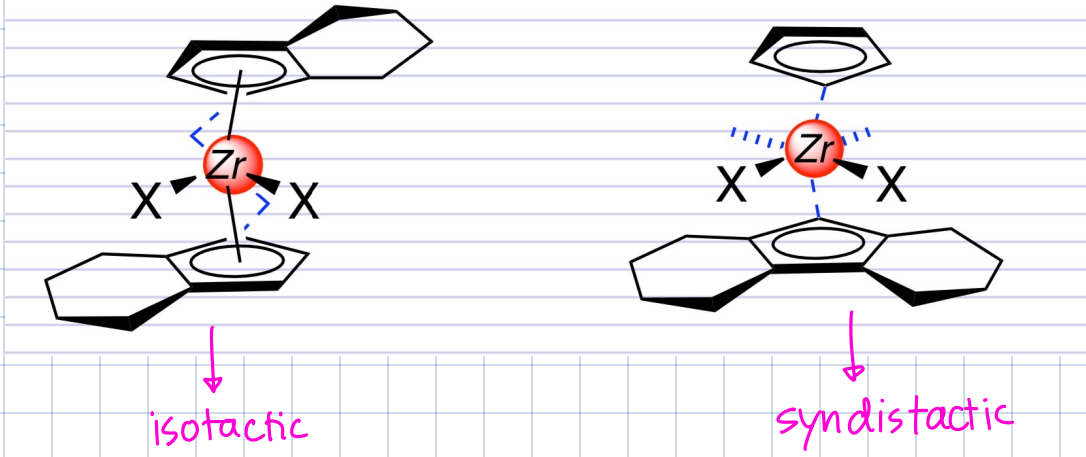
- Transmetalation → Cp_2ZrR^+ + M Polym.
- Quench with water or so
  → alcohols
  Problem: not catalytic in [Zr]!
- Add H_2
- β-H elim. ⇒ terminal olefin



- Proton transfer:



Can control tacticity by alternating structure of metallocene

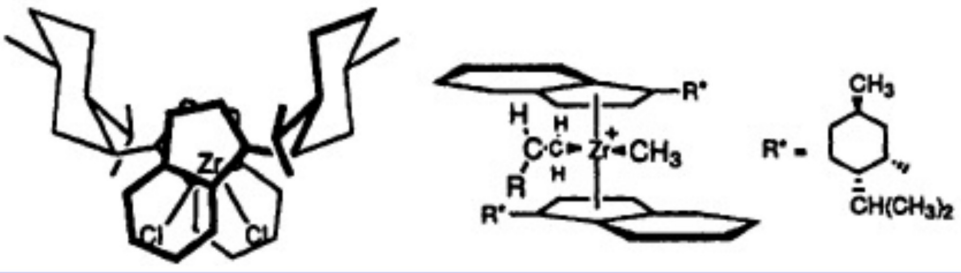


isotactic

syndistactic

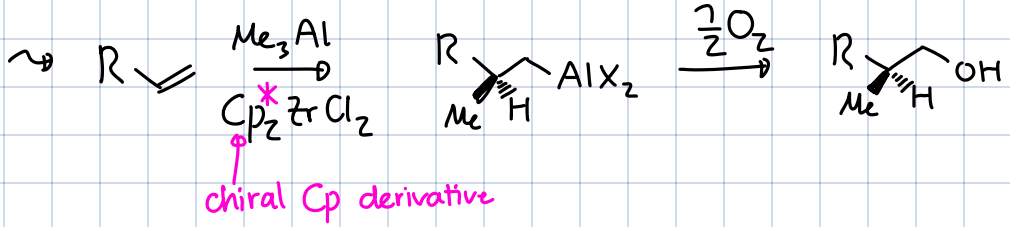
↳ but out of scope for this class

Beyond Olefin Polymerization

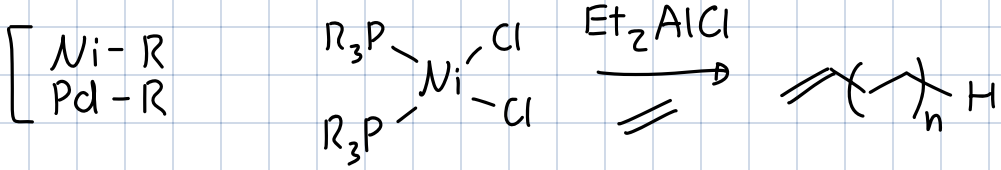


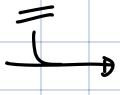
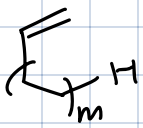
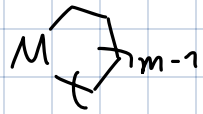
Negishi et al. Chem. Soc. Rev. 1996, 25, 417-426.

↳ Can make Vitamin A

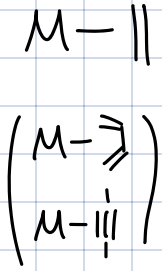


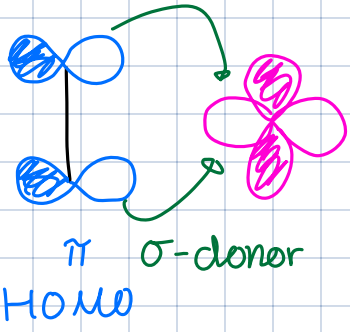
Can also use other TM than Zr to make olefins:

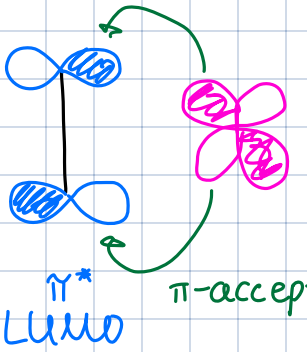


Ti, Cr   from 

How does an olefin bind to a metal center?

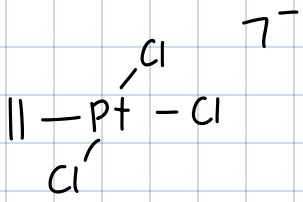
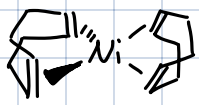




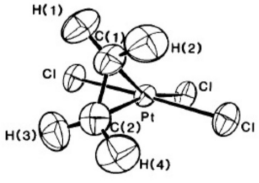


↝ Very similar to a CO

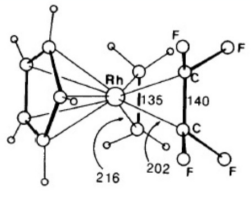
Historic:

- Zeise Salt: 
- $Ni(COD)_2$: 
- $Cp_2Zr(-\|)(PMe_3)$

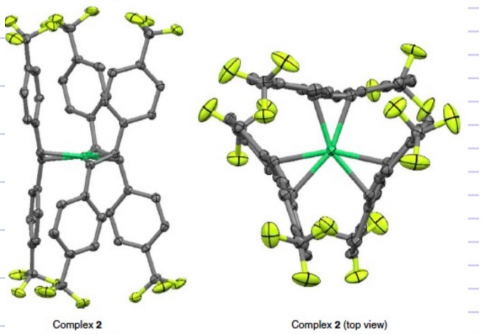
↝ Some X-Ray derived str.:



Structure (neutron diffraction) of $K[PtCl_3(C_2H_4)]$. *The C–C bond length is* 137 pm, *similar to the uncomplexed olefin* (135 pm). *The olefin is oriented perpendicular to the* $PtCl_3$*-plane. The Pt–Cl bond trans to the olefin is slightly elongated. The atoms* H(1)–H(4), C(1) *and* C(2) *are not coplanar. The dihedral angle between the* CH_2 *planes is* 146° (*Bau*, 1975).



Struture (X-ray diffraction) of $(C_8H_8)Rh(C_2H_4)(C_2F_4)$. *The carbon atoms of* C_2F_4 *are closer to the metal than those of* C_2H_4. *The dihedral angle between the two* CH_2*-planes in* C_2H_4 *is* 138°, *that of the* CF_2*-planes in* C_2F_4 *is* 106° (*Guggenberger*, 1972).



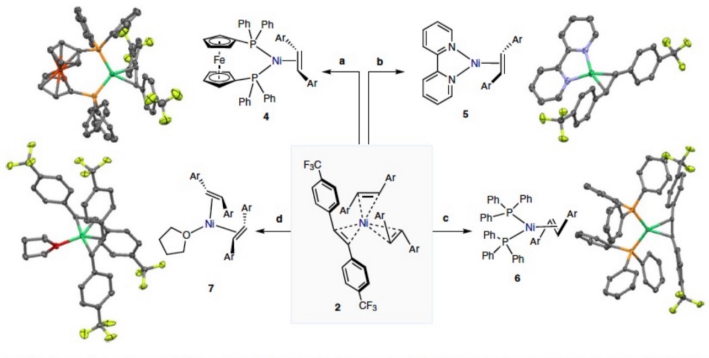


Fig. 3 | Ligand exchange of complex 2 with different ligands. a, Complex **2** (1 equiv.) and dppf (1 equiv.) in d_8-THF at 25 °C. One molecule of PhMe was present in the solid state and is omitted for clarity. **b**, Complex **2** (1 equiv.) and bipy (1 equiv.) in d_8-THF at 25 °C. One molecule of **3** crystallizes in the unit cell and is omitted for clarity. **c**, Complex **2** (1 equiv.) and PPh_3 (2 equiv.) in d_8-THF at 25 °C. **d**, Slow crystallization of **2** in THF from –20 °C to –78 °C. Ar, *p*-CF_3-C_6H_4; green, Ni; black, C; yellow, F; orange, P; deep orange, Fe; red, O; hydrogen atoms omitted for clarity (see the Supplementary Information for procedures).

Nature Catal. 2020, *3*, 6-13.

still a hot topic

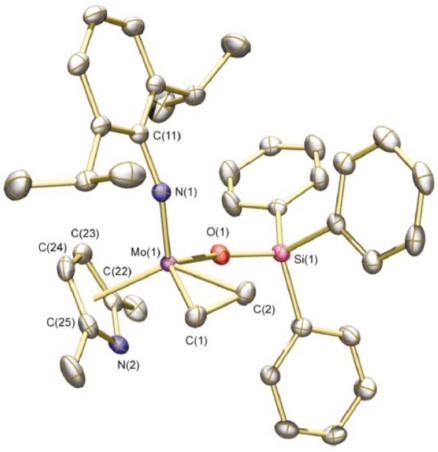


Figure 1. POV-ray drawing of **2c**. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted. Selected distances (Å) and angles (deg): Mo(1)−C(1) = 2.190(2) Å, Mo(1)−C(2) = 2.182(2) Å, Mo(1)−N(1) = 1.7353(18) Å, Mo(1)−O(1) = 2.0080(15) Å, C(1)−C(2) = 1.420(3) Å, Mo(1)−N(2) = 2.3588(18) Å, Mo(1)−C(22) = 2.458(2) Å, Mo(1)−C(23) = 2.506(2) Å, Mo(1)−C(24) = 2.441(2) Å, Mo(1)−C(25) = 2.355(2) Å, Mo(1)−N(1)−C(11) = 163.09(15)°, Mo(1)−O(1)−Si(1) = 149.06(9)°, N(1)−Mo(1)−C(1) = 98.75(9)°, N(1)−Mo(1)−C(2) = 97.89(8)°.

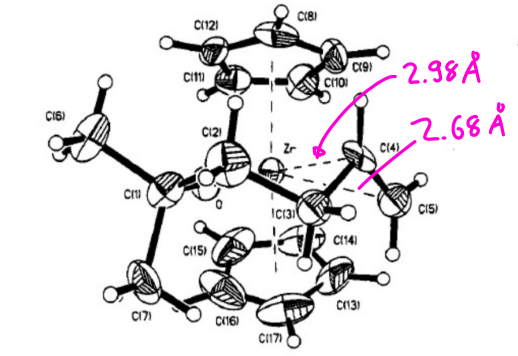


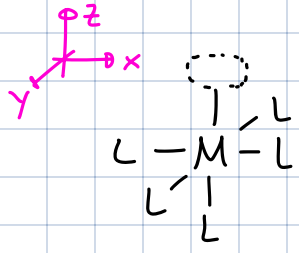
Figure 1. ORTEP view of the $Cp_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)^+$ cation of **9**.

Cp_2Zr short longer

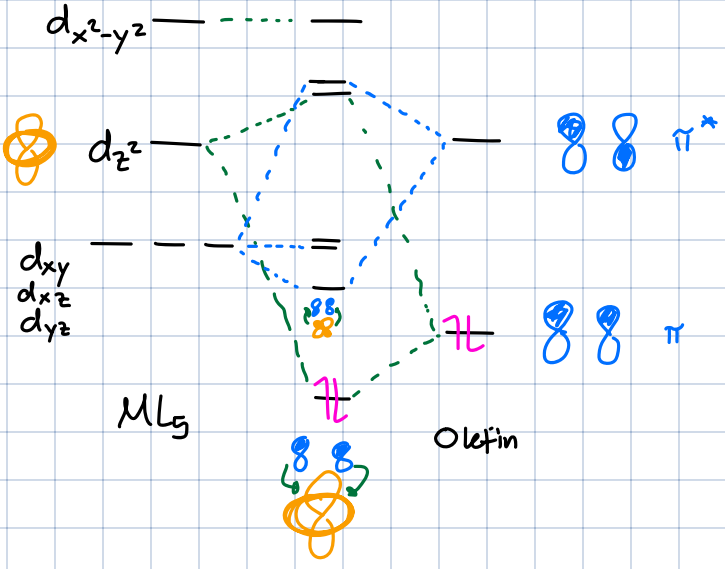
J. Am. Chem. Soc. 1995, *117*, 5867.

Organometallics 2010, *29*, 6816-6828.

Electronic Structure M-||



L_5M



↝ Inserting e^- into π* makes C=C → C−C

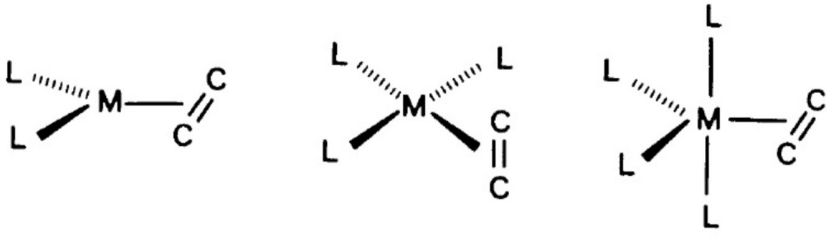
⇒ Olefin complex between the extremes

M−|| ⟷ M□

late TM like Pt

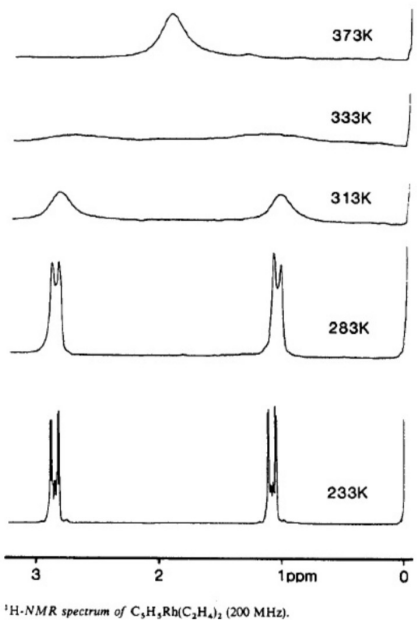
early TM like Zr more here (if $d^n > 0$)

El. structure of coord. determines alignment of olefin:



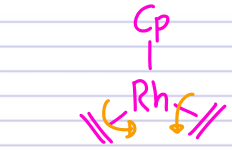
C.N. 3, 16 VE	C.N. 4, 16 VE	C.N. 5, 18 VE
L_2M (*alkene*)	L_3M (*alkene*)	L_4M (*alkene*)
L_2M (*alkyne*)		
Examples: $(PPh_3)_2NiC_2H_4$	$K[PtCl_3(C_2H_4)]$	$(PPh_3)_2IrBr(CO)TCNE$
$Pt(C_2H_4)_3$		TCNE = *tetracyanoethylene*

Spectroscopic Features and Information about Electronic Structure/Bonding



^{1}H-*NMR spectrum of* $C_5H_5Rb(C_2H_4)_2$ (200 MHz).

→ rotation smooths out @ high T

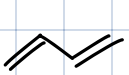
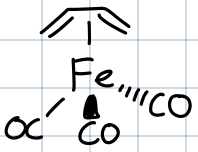


→ frozen @ low T

Synthesis

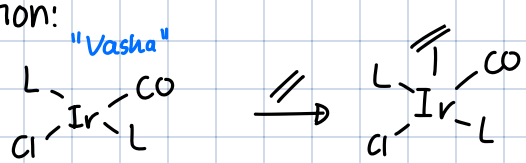
→ Start with Zeise salt: (Subst. rxn)

$$K_2PtCl_4 + = \xrightarrow[(60\ bar)]{H_2O} PtCl_3(II)^-\ K^+\ (H_2O)$$

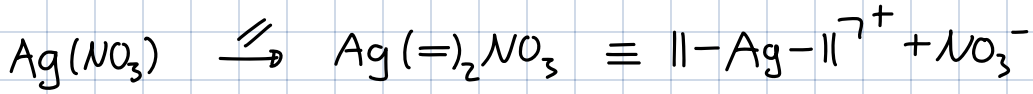
or $Fe(CO)_5$ +  $\xrightarrow[20\ bar]{135^\circ C}$  + CO

Addition:

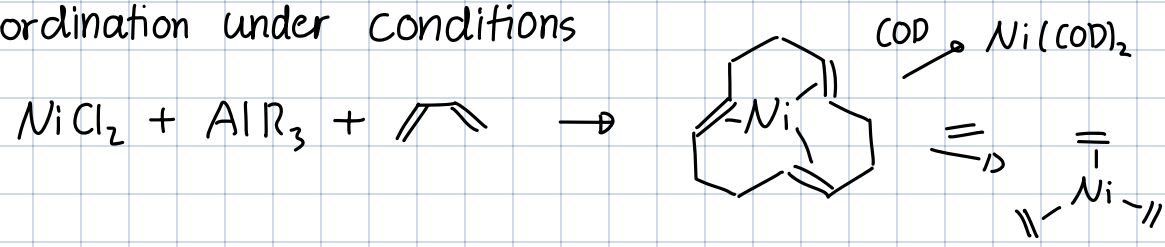
"Vasha"



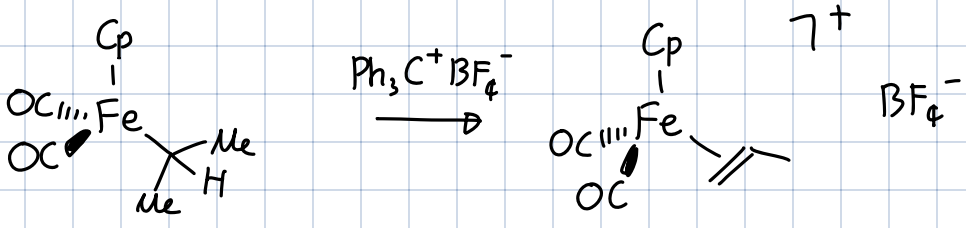
L = PPh_3

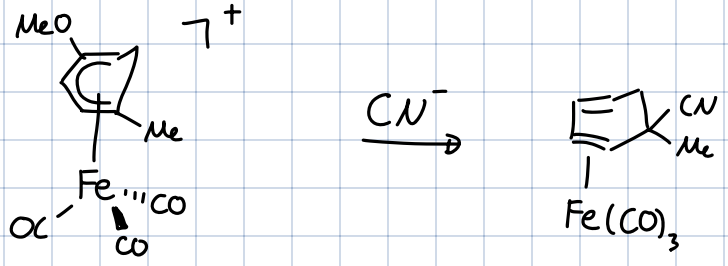


Coordination under conditions



H-abstraction





El. structure continued → Quantification of σ-donation & π-acceptance

Atom or Ion	Ground State	Promotion Energy $d^{10} \rightarrow d^9s^1$ or $d^8 \rightarrow d^7s^1$	Promotion Energy $d^{10} \rightarrow d^9p^1$ or $d^8 \rightarrow d^7p^1$	Electron Affinity $d^{10} \rightarrow d^{10}s^1$ or $d^8 \rightarrow d^8s^1$	π-Donor Character	σ-Acceptor Character
Ni(0)	d^8s^2 *	–1.80	1.72	1.2	very good	poor
Pd(0)	d^{10}	0.81	4.23	1.3	good	poor
Pt(0)	d^9s^1	–0.76	3.28	2.4	good	poor
Rh(I)	d^8		1.6	7.31	very good	good
Ir(I)	d^8		2.4	7.95	very good	good
Pd(II)	d^8		3.05	18.56	good	very good
Pt(II)	d^8		3.39	19.42	good	very good
Cu(I)	d^{10}	2.72	8.25	7.72	moderate	good
Ag(I)	d^{10}	4.87	9.94	7.59	moderate	good
Au(I)	d^{10}	1.87	7.83	9.22	poor	good
Zn(II)	d^{10}	9.65	17.1	17.96	poor	very good
Cd(II)	d^{10}	10.0	16.6	16.90	poor	very good
Hg(II)	d^{10}	5.31	12.8	18.75	poor	very good

like to make olefins

$M^{\delta-}-\|^{\delta+}$

* Energy of d^{10}-configuration above ground state is 1.80 eV for Ni(0) and 0.76 eV for Pt(0).

How do we know if we made an olefin complex? → IR

ν(C=C) Vibrational Frequencies

	ν(C=C) / cm^{-1}
free $H_2C=CH_2$	**1623**
$[Ag(C_2H_4)_2]BF_4$	1584
$[Fe(C_2H_4)_2(CO)_4]$	1551
$[Re(C_2H_4)_2(CO)_4]PF_6$	1539
$[Fe(Cp)(C_2H_4)(CO)_2]PF_6$	1527
$[PdCl_2(C_2H_4)]_2$	1525
$K[PtCl_3(C_2H_4)] \cdot H_2O$	1516
$[Mn(Cp)(C_2H_4)(CO)_2]$	1508
$[PtCl_2(C_2H_4)]_2$	1506
$[Rh(Cp)(C_2H_4)_2]$	1493

↝ But doesn't tell us if σ- donation or π- acceptance ⇒ NMR!

Compound	$\delta(^{13}C)$/ppm*	Compound	$\delta(^{13}C)$/ppm
C_2H_4	132	1,5-COD	128.6
NHC-$Ag(C_2H_4)^+$	127	$(COD)PdCl_2$	117.2
$Cl_3Pt(C_2H_4)^-$	40	$(COD)PtCl_2$	100.6
$Cp^*_2Ta(C_2H_4)(H)$	12	$[(COD)RhCl]_2$	78.0
		$[(COD)IrCl]_2$	62.1