

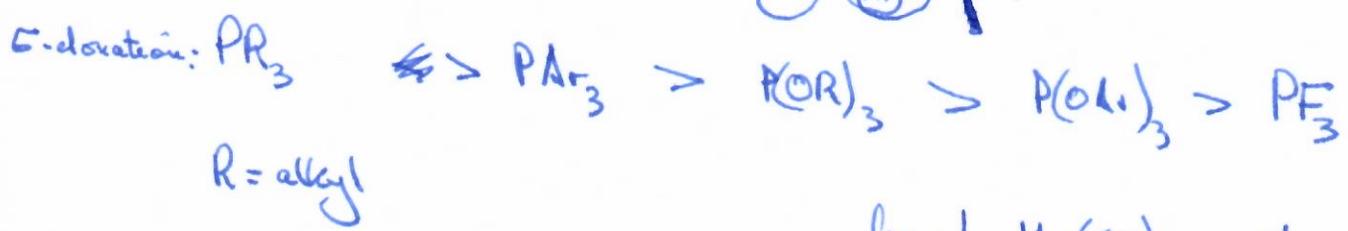
phosphines

lecture 8

Read: Chs 4,5

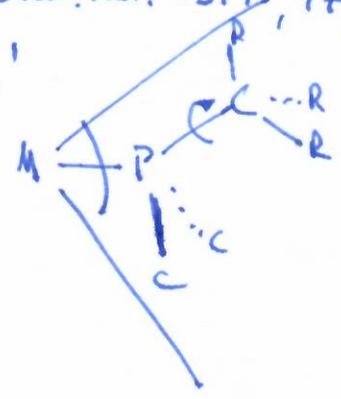
$M \leftarrow PR_3$ versatile spectator ligands

mostly σ -donation, but also back bonding



steric:

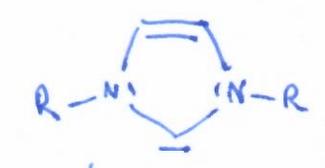
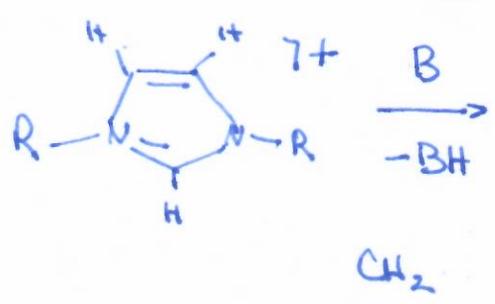
C. Tolman: Chem. Rev. 1977, 77, 313
'cone angle'



fac-L ₃ Mo(CO) ₃	ν_{CO}
L = PMe ₃	1928, 1830
PPh ₃	1934, 1835
P(OMe) ₃	1977, 1888
P(OAr) ₃	1992, 1917
PF ₃	2030, 2055
(CO)	2004

PF ₃	P(OAr) ₃	PMe ₃	PPh ₃	P ⁺ (Bu) ₃
104°	107°	118°	145°	<u>182°</u>

NHC's: 'N-heterocyclic carbenes'



a stable carbene! Nature 2014, 510, 485

B. Arduengo 1991 (JACS)

strong σ donors!

M.V. Hopkinson

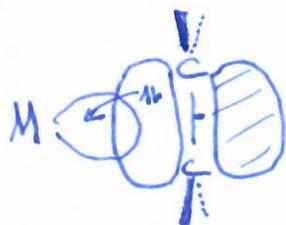
Olefin (π alkyne) Complexes

bonding: 'Dewar-Chatt-Duncanson' model

only π -system of ethene is involved \rightarrow π -complexes

a) σ -donation

b) π -backbonding



axis of ethylene
 π !
always side-on



LUMO, π^* of ethylene



'metalla cyclopropane'

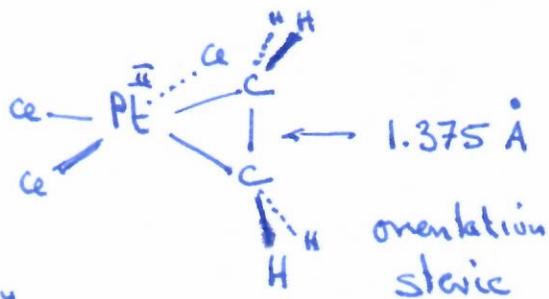
Spectroscopy

upfield shift in 1H & ^{13}C -NMR, IR:

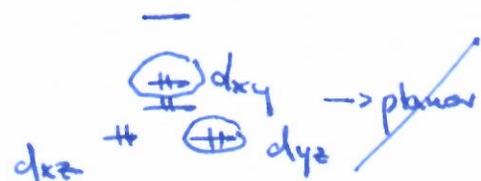
$\nu_{C=C}$ [cm^{-1}]

free C_2H_4	1623
$[PtCl_3(C_2H_4)]^-$	1516
$(C_2H_4)_2Fe(CO)_4$	1551
$CpRh(C_2H_4)_2$	1493

structures



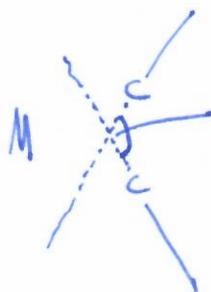
$\alpha = 146^\circ$



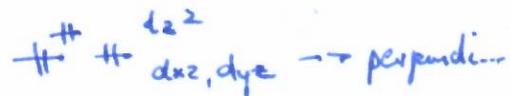
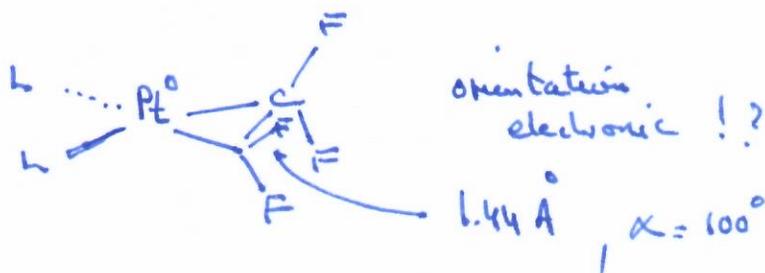
free C_2H_4

$C=C: 1.34 \text{ \AA}$

$\alpha = 180$



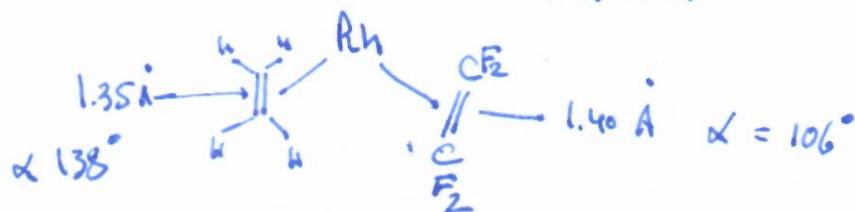
but:



Rh-C: 2.16 Å



Rh-C: 2.02 Å



free C_2F_4 1.31 Å