26.09.

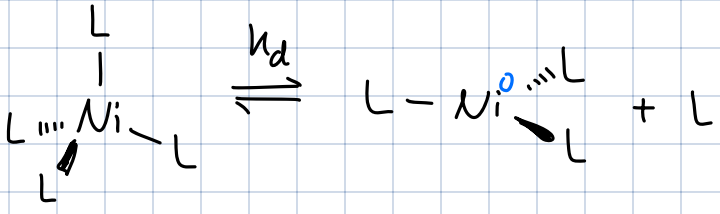
Dissociative LS: $L_nM \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} L_{n-1}M + L \xrightarrow[k_2]{L'} L_{n-1}ML$

Case study

$Ni(CO)_4 + L \longrightarrow Ni(CO)_3L + CO$

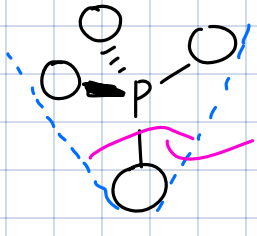
$Ni(0)$, d^{10}, $18e^-$ $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ $[Ni(CO)_3]$ $+ CO$ $\xrightarrow[k_2 \text{ (fast)}]{+L}$

Steric effects



$\rightsquigarrow$ Try out diff. ligands with diff. steric bulk

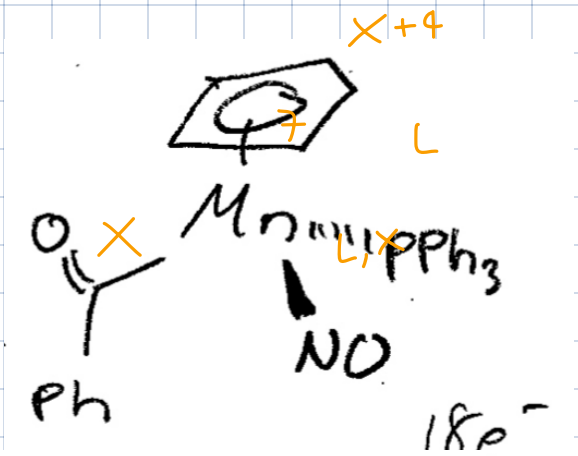
L	$P(OEt)_3$	$P(O\text{-}p\text{-tolyl})_3$	$P(O^iPr)_3$	PPh_3
K_d	too small to meas.	$6 \cdot 10^{-10}$	$2.7 \cdot 10^{-5}$	No NiL_4
TCA	109	128	130	145



angle of smallest cone = TCA

$\Rightarrow$ small TCA $\hat{=}$ small ligand

S_N1-like scrambling:



Cp X

~~7+4+3+2 = 16 ??~~

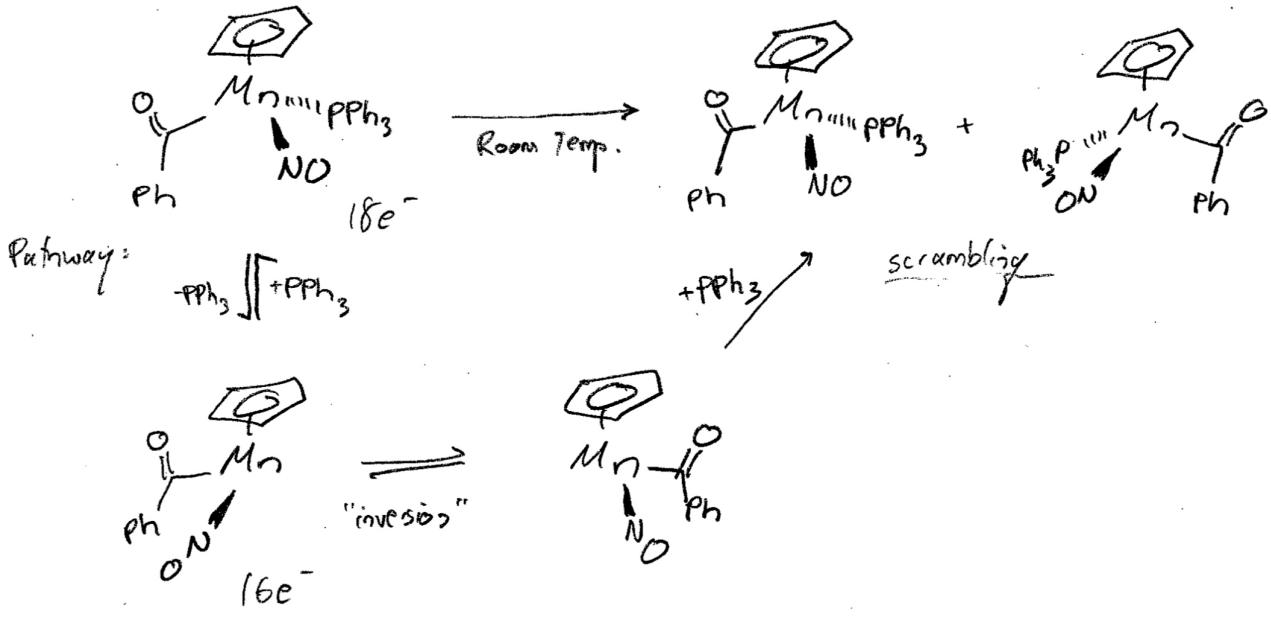
NO^- ligand:

$\leftarrow \bar{N}\equiv O$ vs. $\leftarrow N=O$

$\Rightarrow$ We have linear $\Rightarrow$ 4 e^-

$\Rightarrow$ 7+1 + 5 + 4 + 1 = 18

Cp L



M-L bonding

$M-H \rightsquigarrow L_nM^{\delta+}-H^{\delta-}$

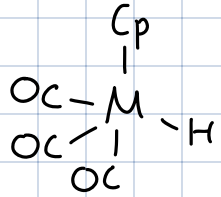
they're like hydrides? H^- sources? Not actually, many acidic!

$L_nM^{\delta+}-H^{\delta-}$ → H^+ (pK_a)

→ $H^\cdot$ (BDE)

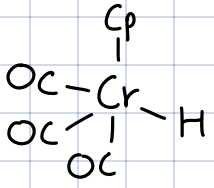
→ H^- (Hydricity)

a. Trends in M-H pK_a

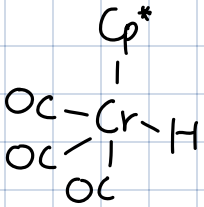


M	pK_a (CH_3CN)
Cr	13.3
Mo	13.9
W	16.1

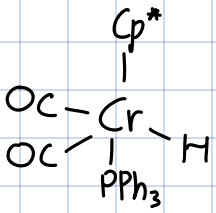
b. Effect of L



pK_a 13.3

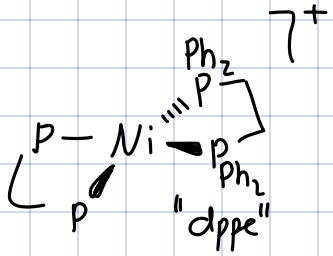


17.0



21.8

c. Effect of charge



→ $pK_a = 12.3$

"dppe"

pK_a measurements

$$L_nM-H + B: \rightleftharpoons L_nM^{\ominus} + B-H^{\oplus}$$

$$\rightarrow \Delta G^\circ = -RT \ln(K_{eq}) \approx 1.30\ pK_a \text{ units per } 1\ \frac{kcal}{mol}\ \Delta G^\circ$$

$\Delta G^\circ \left(\frac{kcal}{mol}\right)$	[SM]:[Prod]
-1.4	1:10
-2.8	1:100
-4.2	1:1000

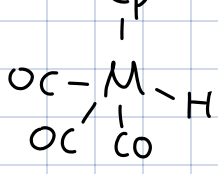
M-H Bond Strengths

	H-H	Ph-H	L_nM-H
BDE $\frac{kcal}{mol}$	104	113	(?)

a. Trends effect of M:

M	BDE
Cr	62
Mo	70
W	73

for



↝ How to measure a BDFE?

$$L_nM-H \longrightarrow L_nM^{\bullet} + H^{\bullet} \Rightarrow \Delta G^{\circ} = BDFE$$

$$\rightarrow L_nM-H \rightleftharpoons L_nM^{\ominus} + H^{\oplus} \qquad pK_a$$

$$e^- \uparrow\downarrow -e^- \qquad -e^- \uparrow\downarrow e^-$$

$$L_nM^{\bullet} + H^{\bullet}$$

from redox reaction, Nernst

solvent dep. constant

$$\Rightarrow BDFE = 1.37\, pK_a + 23.06\,(E^{\circ}) + C_G$$

pK_a cleavage