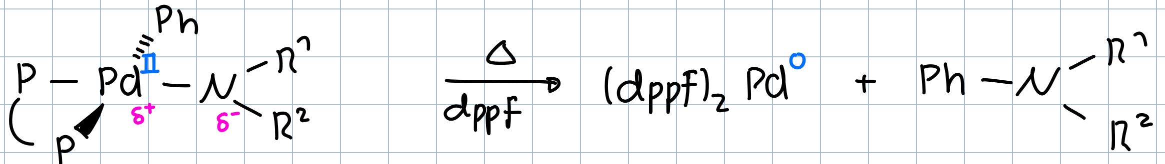
17.10.

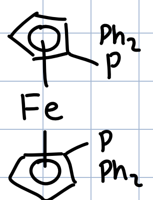
RE continued

Polar C–X

Electronics: Leaving ligands (A, B)



"dppf":



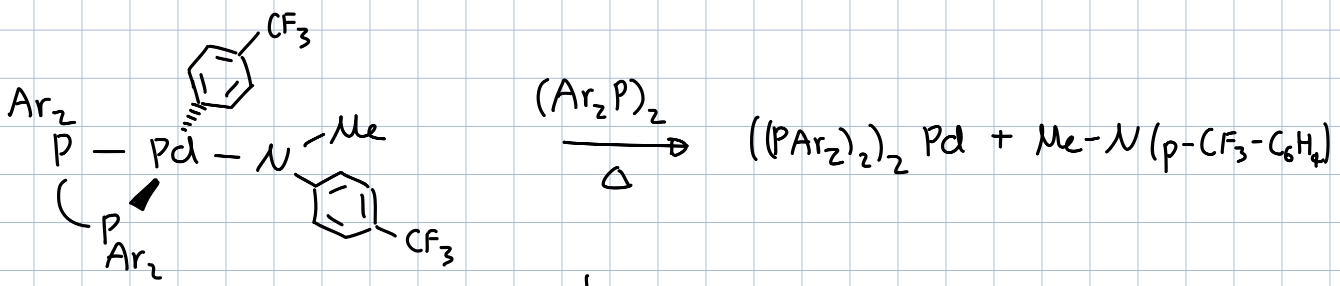
wide-angle, electron-withdrawing

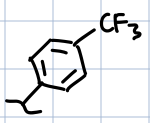
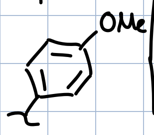
R^1	R^2	T required
p-tolyl	p-tolyl	80°C
H	Ph	25°C
H	^tBu	0°C

increasingly electron rich

⇒ leaving promotes RE

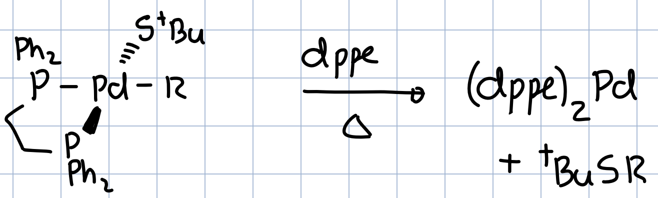
Spectator ("ancilliary") Ligands L

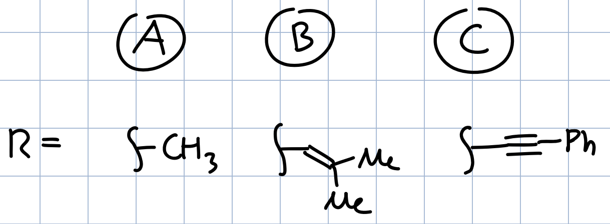


Ar	k_{obs}
	27
Ph	13
	4.2

increasingly electron rich

C–S RE





What would be k_{rel} if the following dictated rule:

① M-L BDE of starting [Pd]
② C-S BDE of organic prod.
③ R ligand sterics

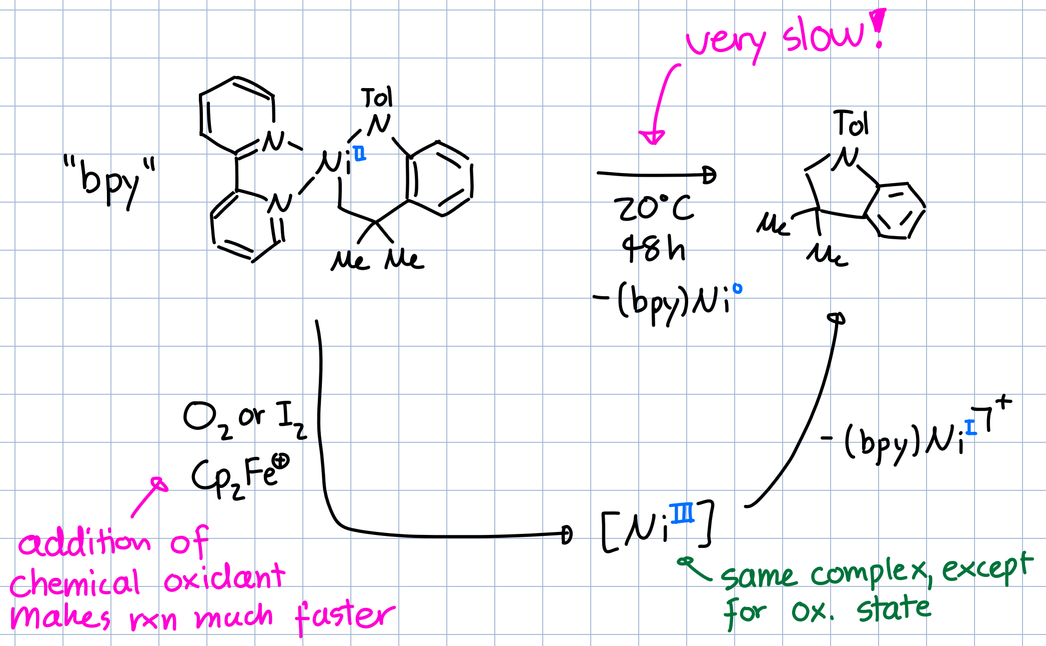
k_{rel}			
fastest	interm.	slowest	
A	B	C	↝ more s-char. ⇒ BDE ↗
C	B	A	↝ more stable product ⇒ faster
B	A	C	↝ the bulkier, the less stable the starting [Pd]

However, experimentally we obtain none of these, but:

fastest B > C > A slowest ⇒ Why?

which is also true for the reverse
↳ Reason revealed in ex. class

Oxidation induced RE

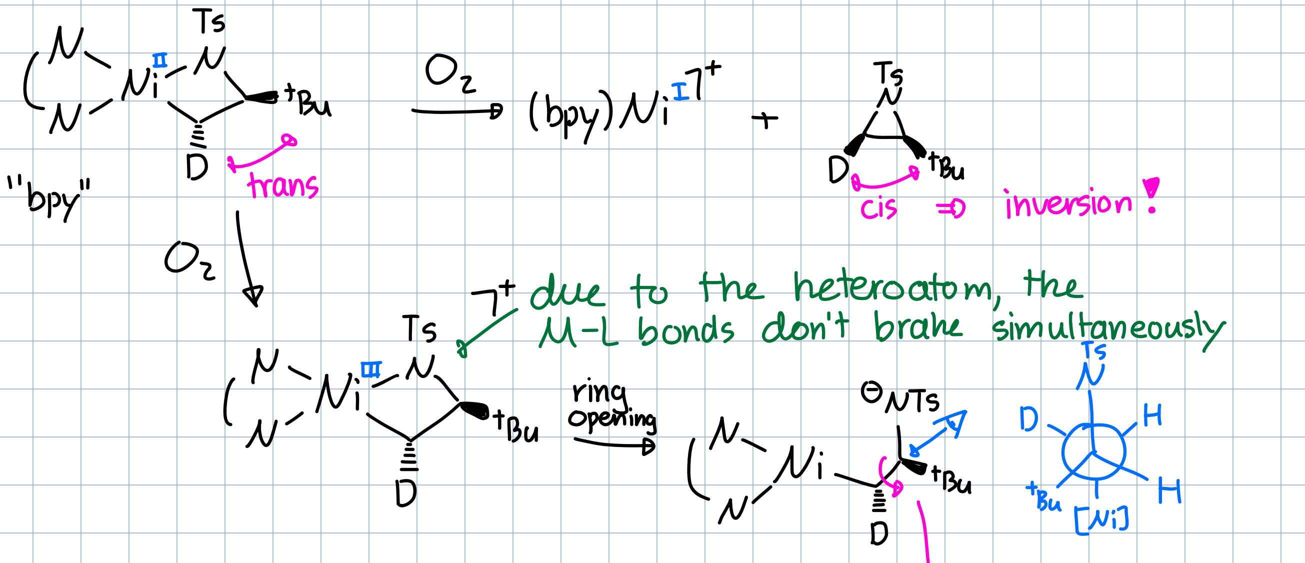


very slow!

addition of chemical oxidant makes rxn much faster

same complex, except for ox. state

Stereochemistry



trans

cis ⇒ inversion!

due to the heteroatom, the M-L bonds don't brake simultaneously

→ needs to be anti for S_N2!

As OA reverse of RE

→ Does OA of C-X bond invert?