# 04.10.

Pd-cat. cross coupling: OA continued

## Ligand effects

↳ Recall that $L_4Pd$ ($L = PPh_3$) not the active species, but

$$L_4Pd \rightleftharpoons L_3Pd \rightleftharpoons L_2Pd \xrightarrow[OA]{Ph-X} L_2Pd(Ph)(X)$$

18e⁻ 16e⁻ 14e⁻

## How to drive OA

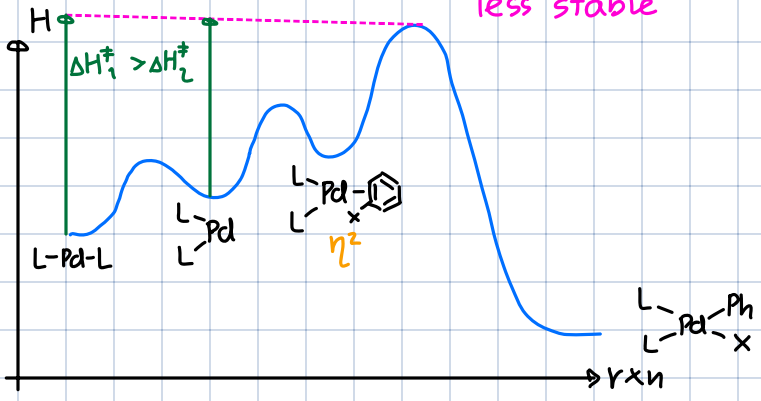
### 1. Bidentate vs. monodentate

Recall that the OA occurs in cis conf. ⇒ need to rearr.:

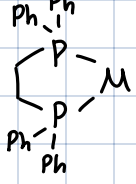
$$L-Pd-L \rightleftharpoons \underset{L}{\overset{L}{Pd}} \xrightarrow[OA]{Ph-X} L_2Pd(Ph)(X)$$

OA

cis $L_2Pd$, thdm less stable




⇒ If we use a bidentate ligand such as

dppe: 

that is already locked in cis conformation, we can lower $\Delta H^{\ddagger}$ ⇒ faster reaction

### 2. Sterics: Bulkier ligands favor L dissociation ⇒ lower VEC

↳ Example: $R_3P-Pd-PR_3 \rightleftharpoons R_3P-Pd \xrightarrow[OA]{Ph-X} R_3P-Pd(Ph)(X)$

14e⁻ 12e⁻

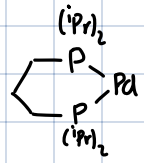
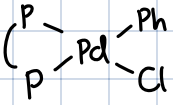
with R = O-tolyl or $^tBu$ ⇒ $k_{OA,\text{large R}} > k_{OA,\text{small R}}$

3. Electronics: $e^-$ rich vs. $e^-$ poor

Recall: Ar-I > Ar-Br > Ar-Cl, due to $E(\sigma^*)$ ↗

Now if we make the metal more electron rich, we increase the E(d-orbitals) ⇒ tackle effect from other side:

$Pd(dppe)_2$ —Ph-Cl→ No rxn

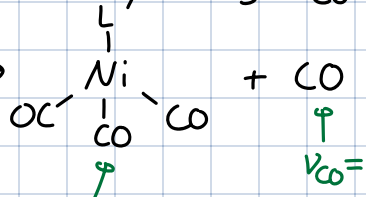
$Pd(dippp)_2$ ⇌  —Ph-Cl→ 

"dippp" → more electron rich

## Quantify Ligand sterics & electronics

- Electronics: Tolman Electronic Parameter (TEP)

↳ Quantifies the $e^-$ richness of M, using $\nu_{CO}$ in IR in

$Ni(CO)_4 + L \longrightarrow$ 

$\nu_{CO}$ = 2743 $cm^{-1}$

$\nu_{CO}$ = ? → typically lower than free CO due to backbonding filling $\pi^*$

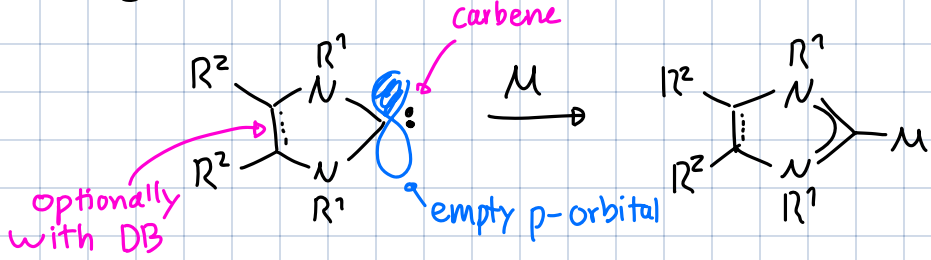
Examples:

| L | TEP/$cm^{-1}$ | $pK_a$ in DCM |
|---|---|---|
| $F_3P$ | 2110 | |
| $Ph_3P$ | 2069 | 2.7 |
| $Me_3P$ | 2064 | 8.7 |
| $^tBu_3P$ | 2056 | 11.4 |

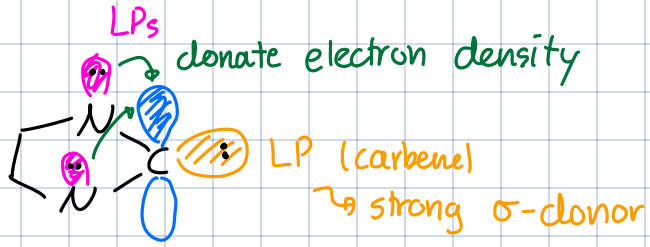
some what correlated

$e^-$ richness ↓

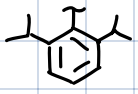
- Strong σ-donors: NHCs



Why stable?

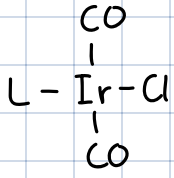



How electron donating?

| R | TEP/cm$^{-1}$ |
|---|---|
|  | 2051 |
|  "Ad" | 2046 |

⇒ Already much stronger than the phosphenes above

Another series (not TEP, stands on its own)



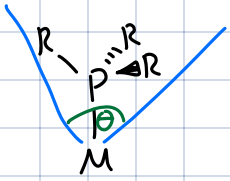
| L | ν(CO) /cm$^{-1}$ |
|---|---|
| $PPh_3$ | 2043 |
| $P^tBu_3$ | 2037 |
| py | 2038 |

⇒ σ-donation trend

NHC > $PR_3$ > py > imines, ect.

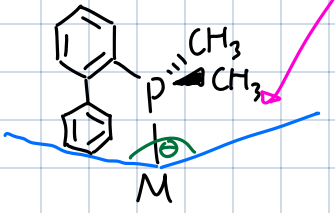
- L-sterics: How big is L?

Recall TCA:



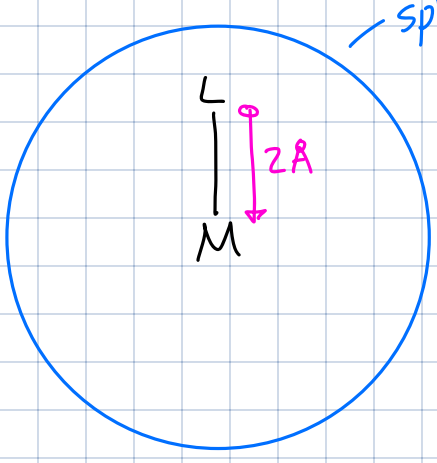
| L | θ |
|---|---|
| $Me_3P$ | 118° |
| $^tBu_3P$ | 182° |

Problem:




⇝ get a huge θ, even though there's a lot of empty space

Improvement: % Buried Volume:

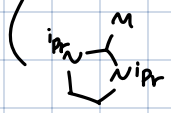



⇒ Calc. fraction of space taken by L

Examples:

Cy = 

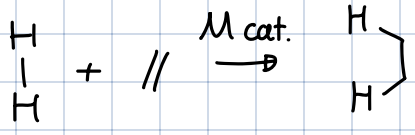
| L | % $V_{bur}$ |
|---|---|
| $Me_3P$ | 26.1 |
| $Cy_3P$ | 37.1 |
| X-Phos | 57.1 |
| NHC | 44.5 |




OA of $H_2$

$$L_nM^{m+} + H-H \longrightarrow L_nM^{(m+2)+}\begin{matrix}H\\H\end{matrix}$$

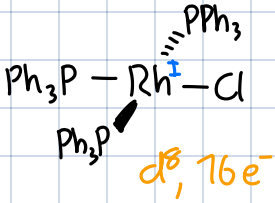
Why needed? Because can now:

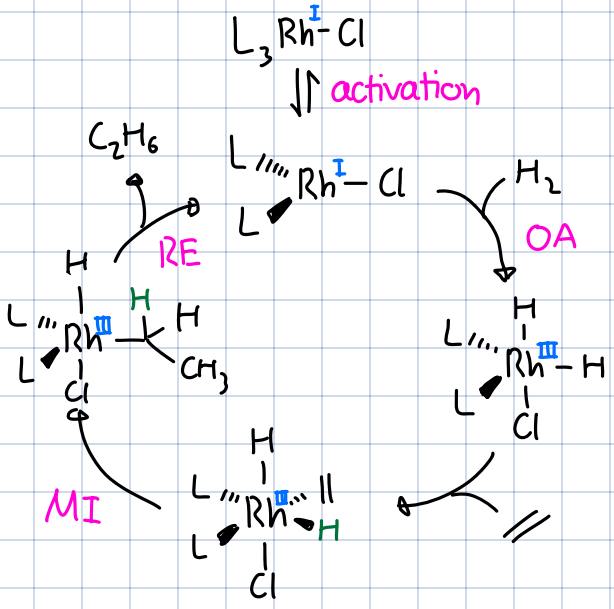



[s(2s) + π (2s)]

Classic: Wilkinson cat.

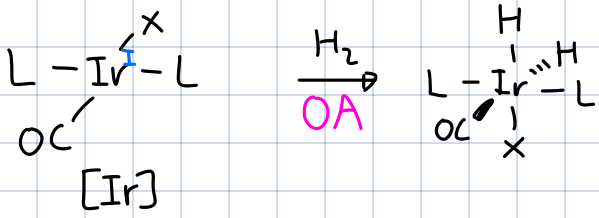
L = $PPh_3$



# Closer Look Vaskas Complex

L = $PPh_3$, X = Cl



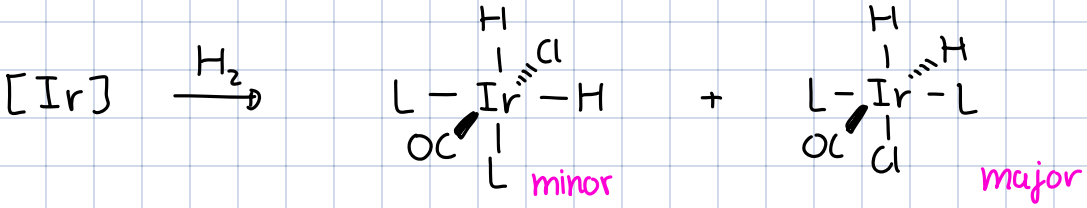

Lets compare diff. halogens:

| X | $\nu_{CO}/cm^{-1}$ | $k_{rel}(H_2OA)$ |
|---|---|---|
| Cl | 1950 | 0.67 |
| Br | 1955 | 10.5 |
| I | 1975 | >100 |

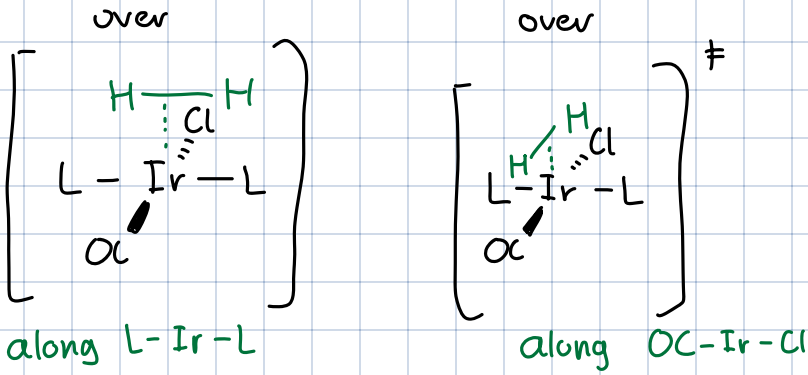
$e^-$ rich

because better $\pi$-donors (LPs)

## Stereochem. considerations:




minor prod. is thdm. fav.
⇒ Kinetic cont.
⇒ Analyze TS




## Orbital view:

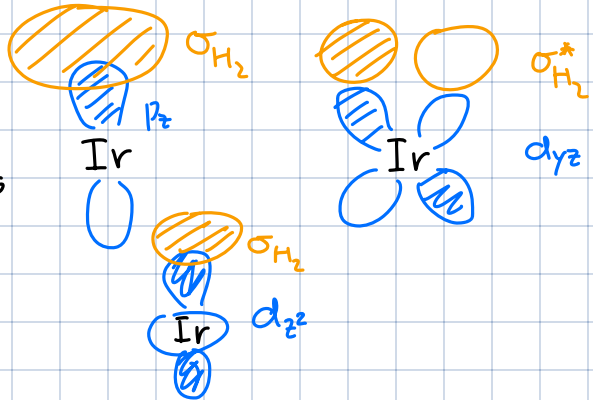
Recall for SQP

— $d_{x^2-y^2}$ ← sterically blocked ⇒ donate into $p_z$

≠ $d_{xy}$

≠ $d_{z^2}$

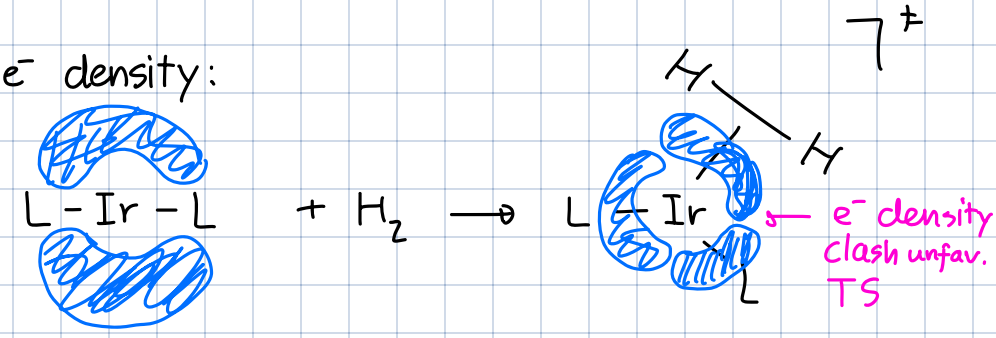
$d_{xz}$ ≠ ≠ $d_{yz}$




"good" filled-empty interactions

but also "bad" filled$^2$

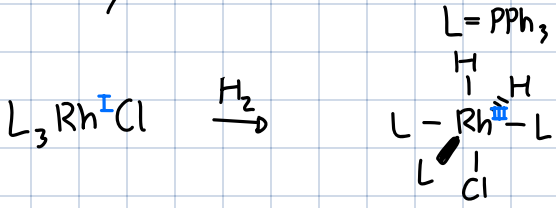
DFT for $e^-$ density:




High E: σ-donors / π-donors ⇒ unfav.
Low E: π-acceptors

⇒ Cl < Br < I

Case Study with data:




$\Delta H^{\ddagger} = 10 \frac{kcal}{mol}$, $\Delta S^{\ddagger} = -20$ e.u.
Slower with more $PPh_3$

⇒ 2 Parallel mech.:

A) Direct OA: $L_3RhCl + H_2 \xrightarrow{k_1} L_3RhCl(H)_2$

B) L-dissoc.: $L_3RhCl \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} L_2RhCl + L$

$L_2RhCl + H_2 \xrightarrow{k_3} L_2RhCl(H)_2$

$L_2RhCl(H)_2 + L \xrightarrow{fast} L_3RhCl(H)_2$

Giving

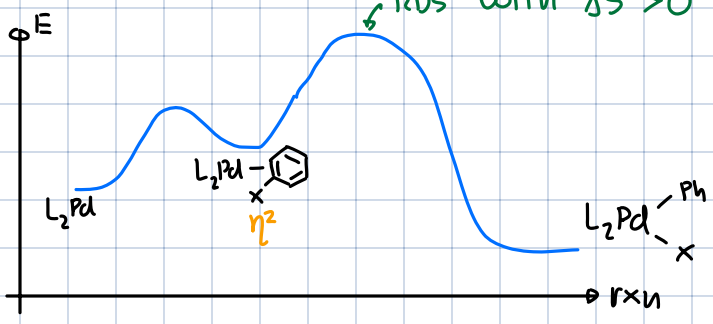
$$rate = k_1[Rh][H_2] + \frac{k_1k_3[H_2][Rh]}{k_{-2}[L] + k_3[H_2]}$$

A) B)

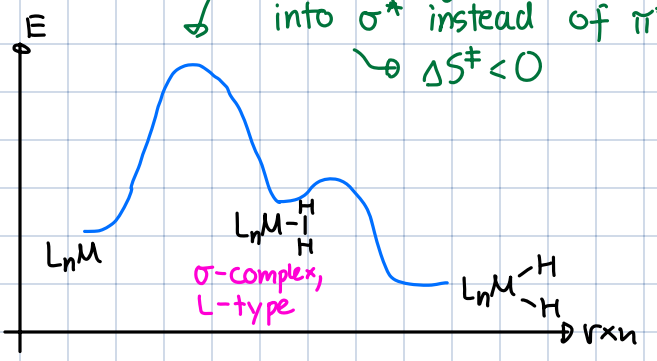
$k_1 = 4.8\ M^{-1}s^{-1}$
$k_2 = 0.71\ s^{-1}$
$k_3 = 7 \cdot 10^4\ M^{-1}s^{-1}$ → OA a lot faster with dissoc. a ligand!

Why $\Delta S^{\ddagger} < 0$?

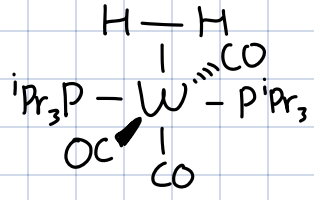
Recall



But now




↳ first one isolated (big deal, because disagreements about the mechanism)




$H_2$ σ-complex