Reaction of O_2 with [(–)-Sparteine]Pd(H)Cl: Evidence for an Intramolecular $[H–L]^+$ "Reductive Elimination" Pathway

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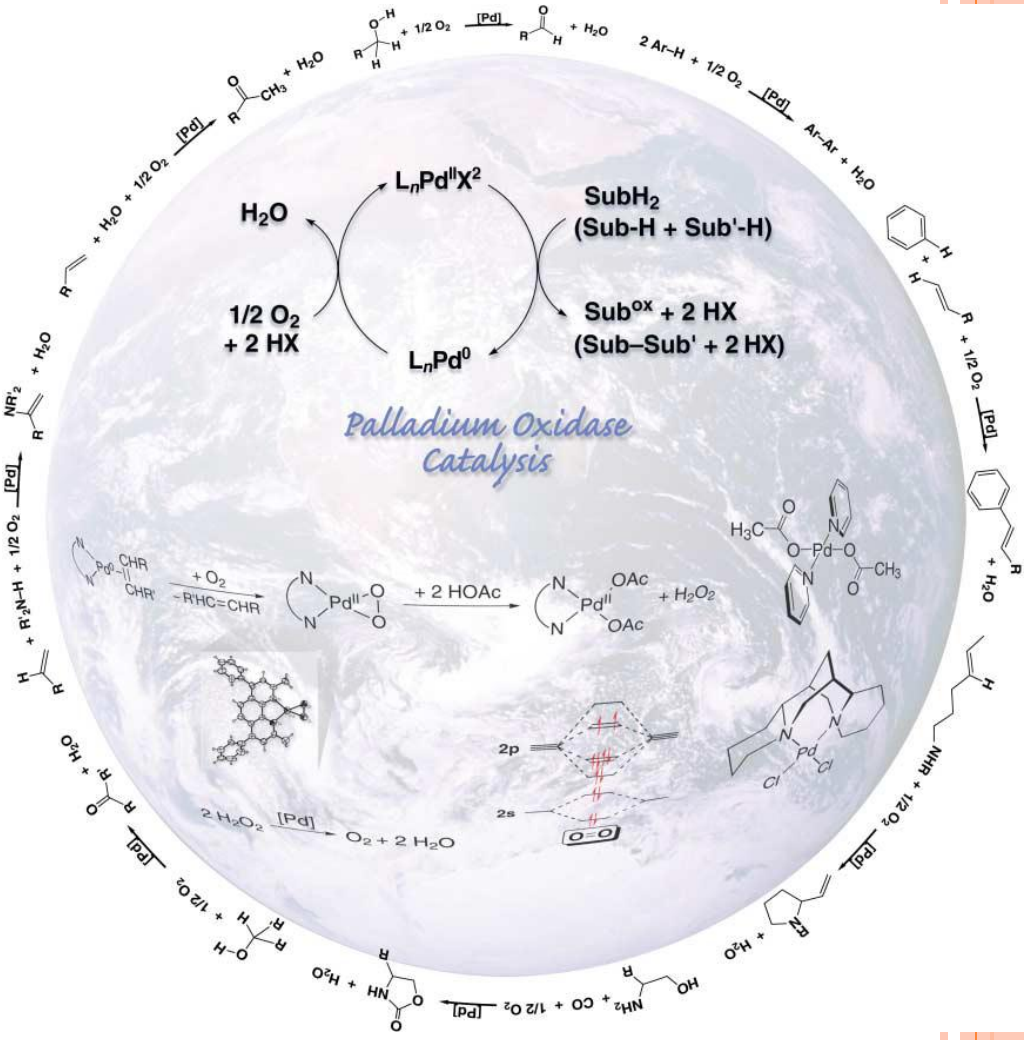
Presented by Ariana Hall and Alex Gaudette

Pd Catalyzed aerobic oxidation reactions

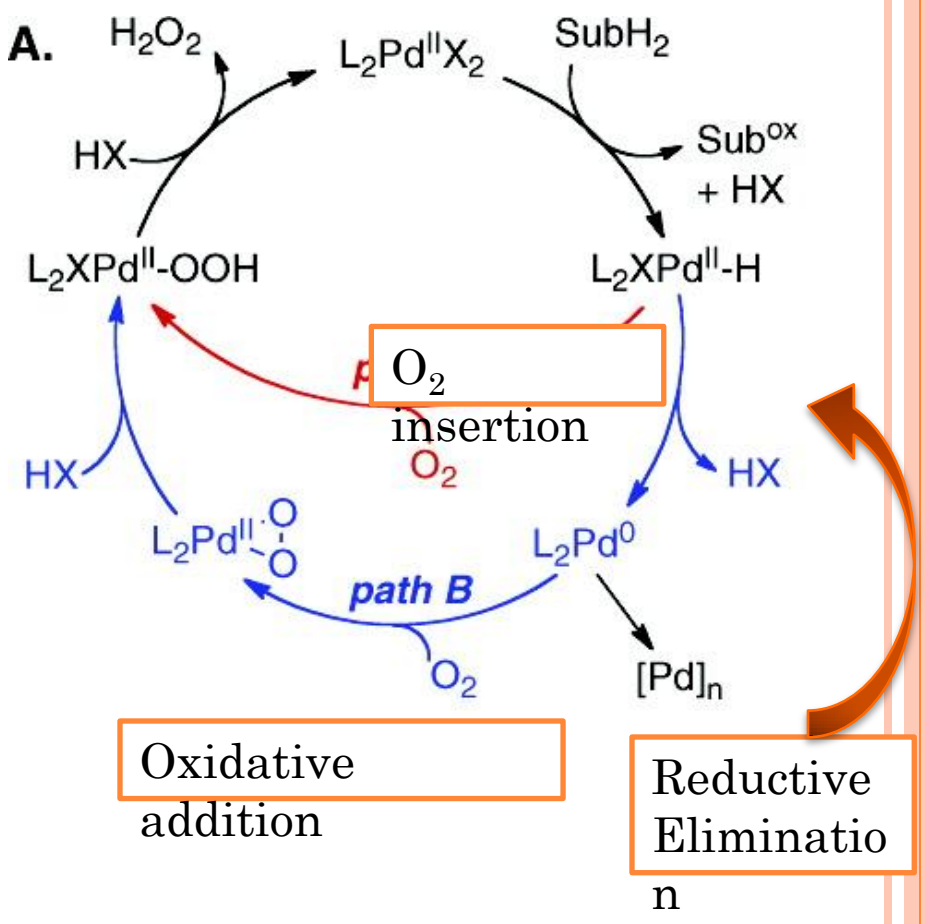
- Pd catalysts widely used for oxidation reactions
  - Alcohol→ketone
  - Oxidative coupling

- What is the mechanism of Pd oxidation?

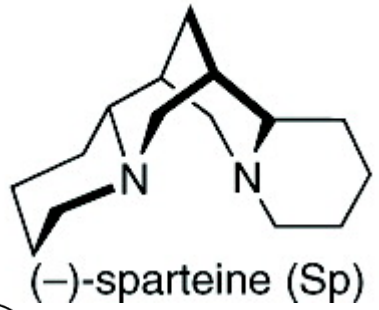


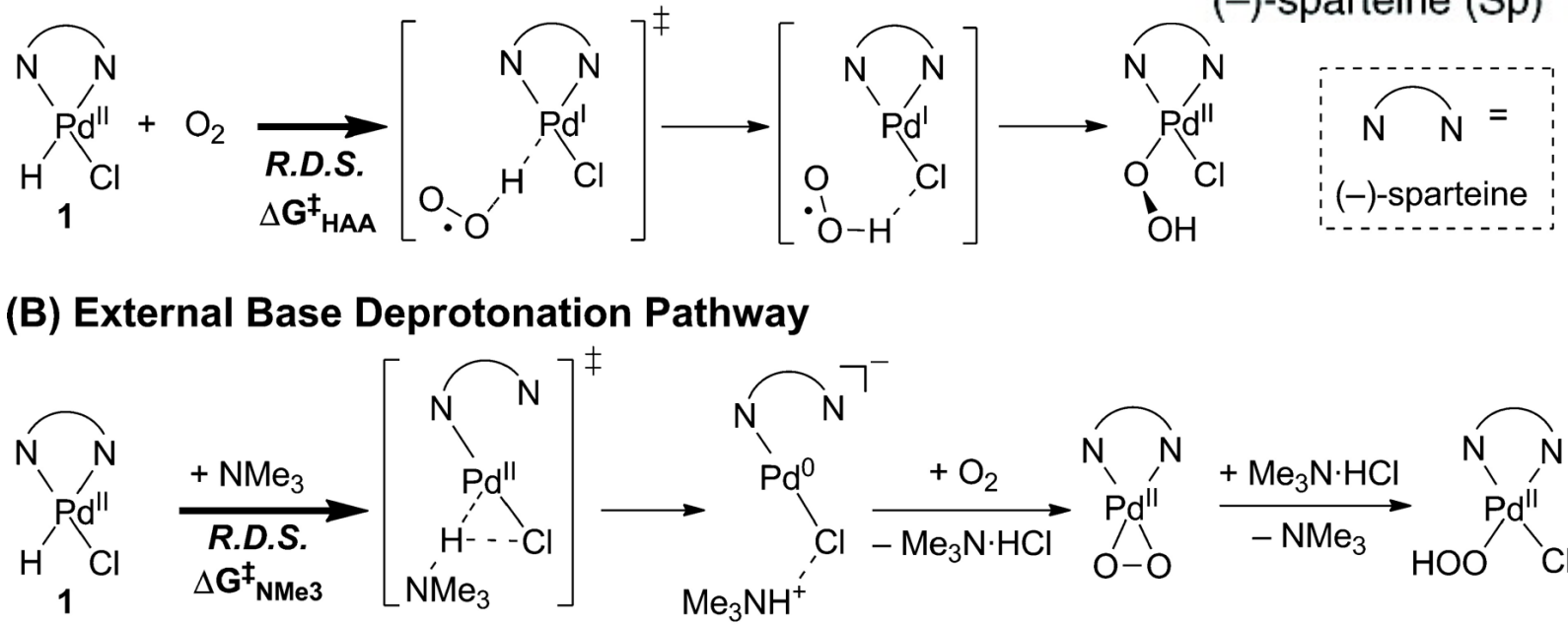
Previous studies of Pd-H Oxidation

- Path A (HAA)
  - H atom abstraction by O_2
- Path B (HXRE)
  - H-X Reductive elimination
- Experimental evidence for HXRE but not for HAA.
- Is HAA actually viable?



Specifically Sparteine

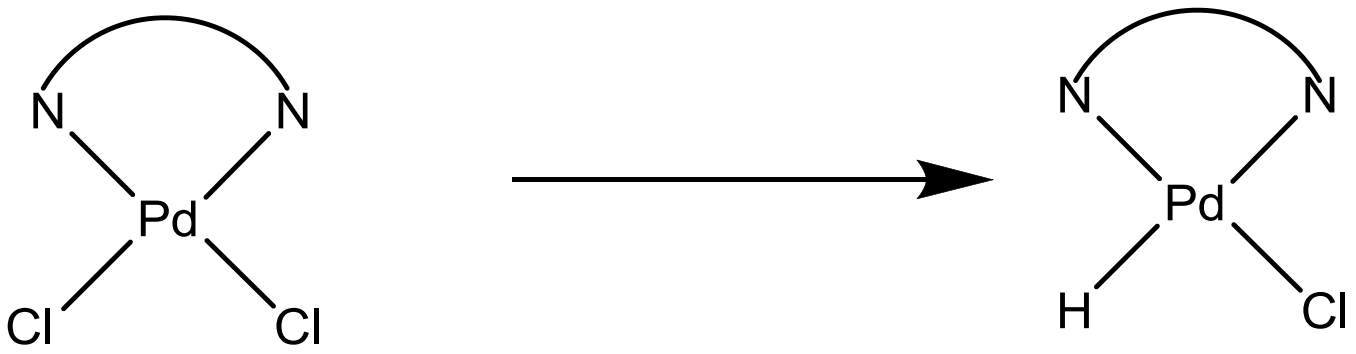




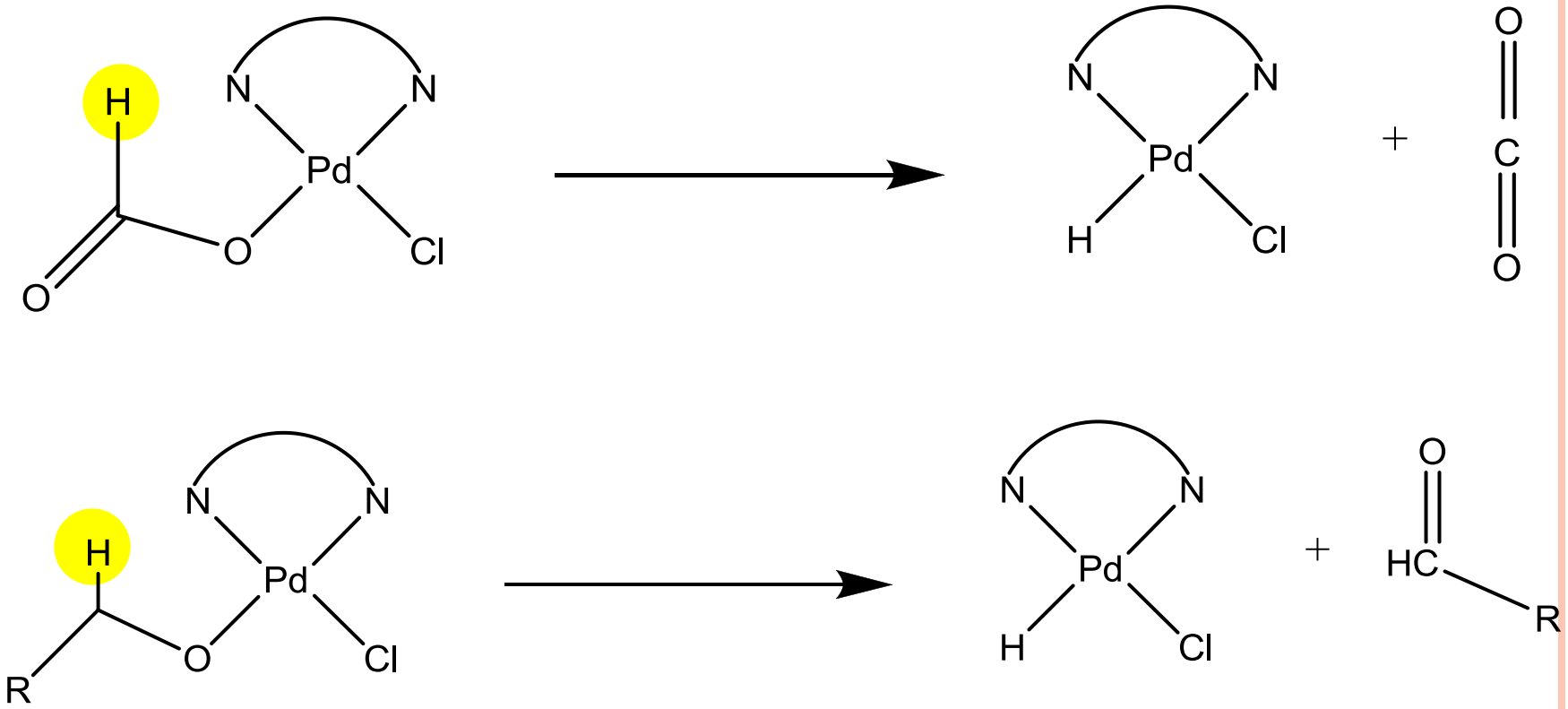
- External base higher energy than HAA
- Determine mechanism based on rate dependence on $[O_2]$

Synthesis:

Goal: Conversion to (Sp)Pd(H)Cl

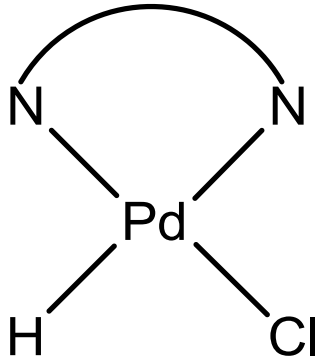


B-ELIMINATION:



Oxidative Addition

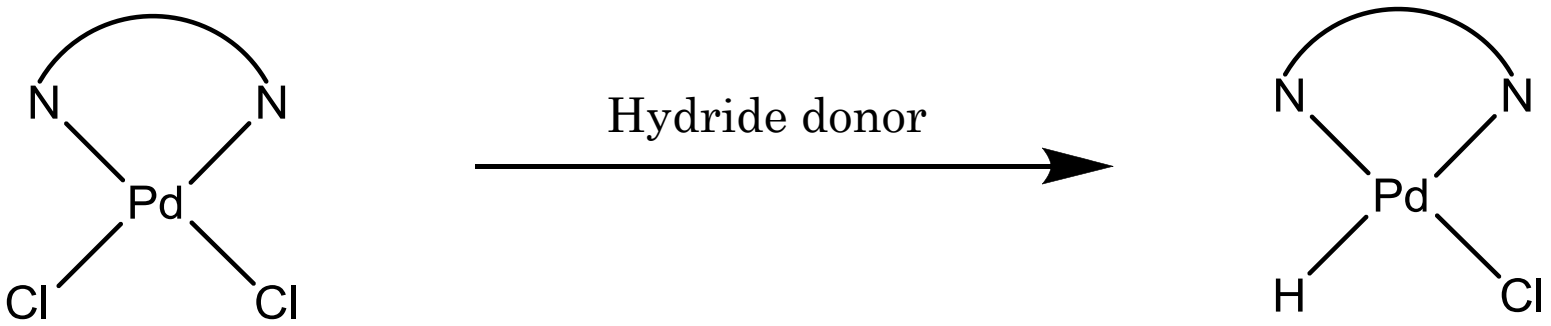
$L_nPd + HCl + (-)\text{-sparteine} \longrightarrow$



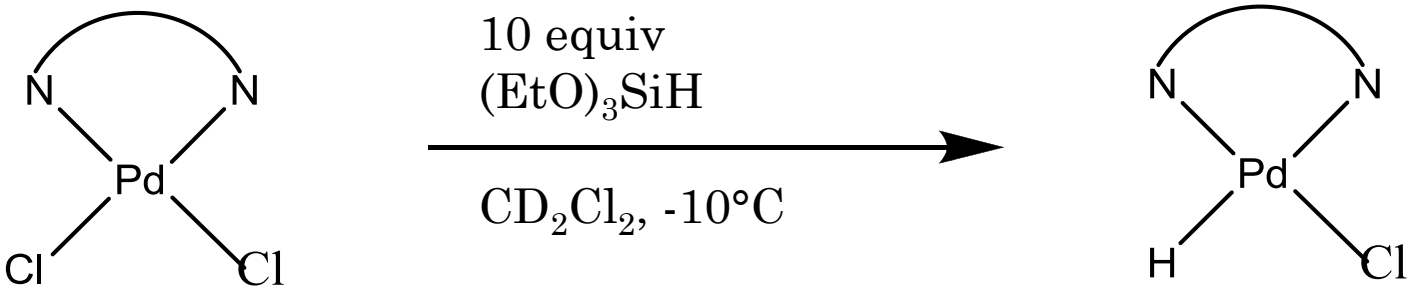
- Pd^0 oxidized to Pd^{+2}
- Alkene and phosphine ligands

Hydride Donors

- Sn, Si and B reagents

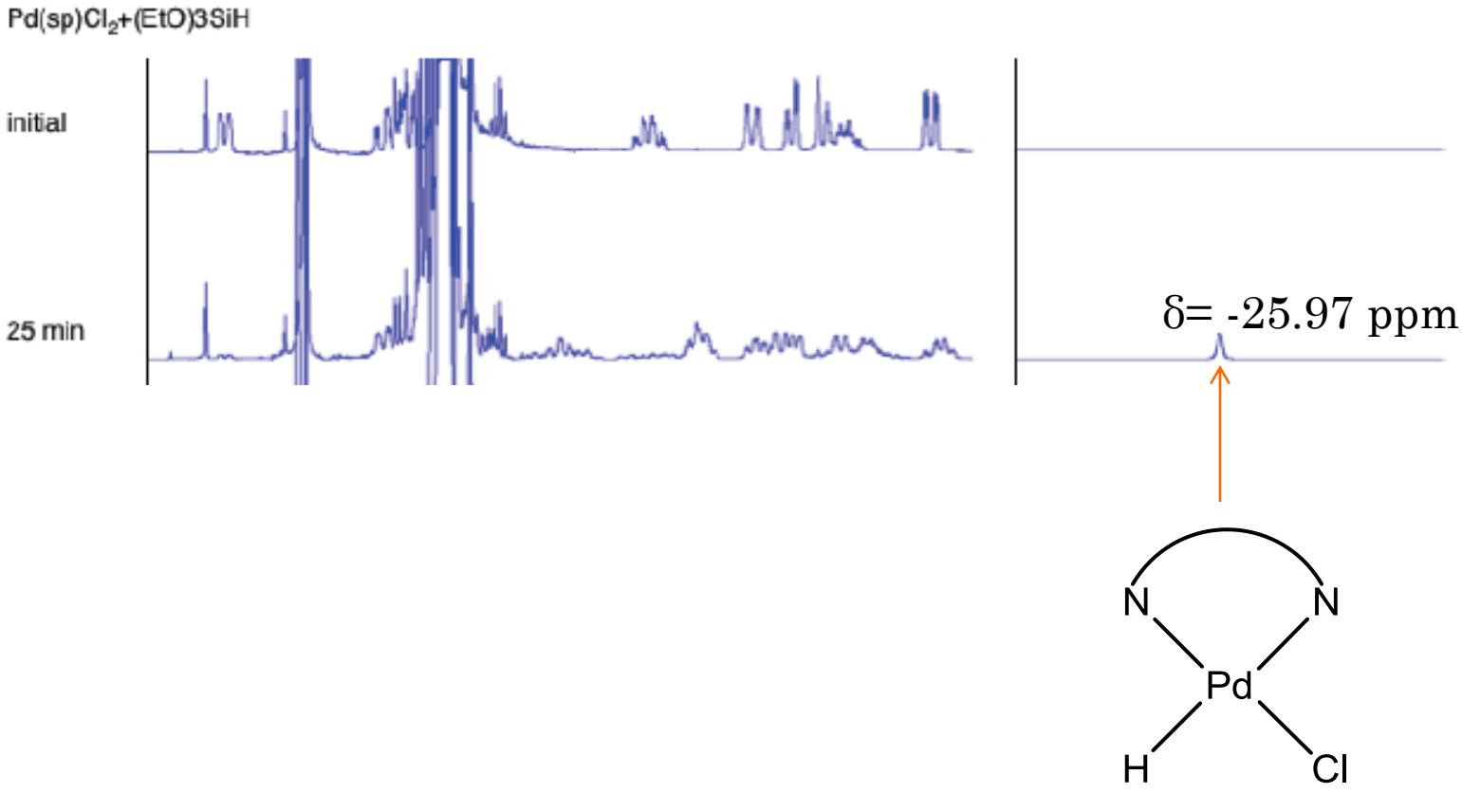


$(EtO)_3SiH$ works best

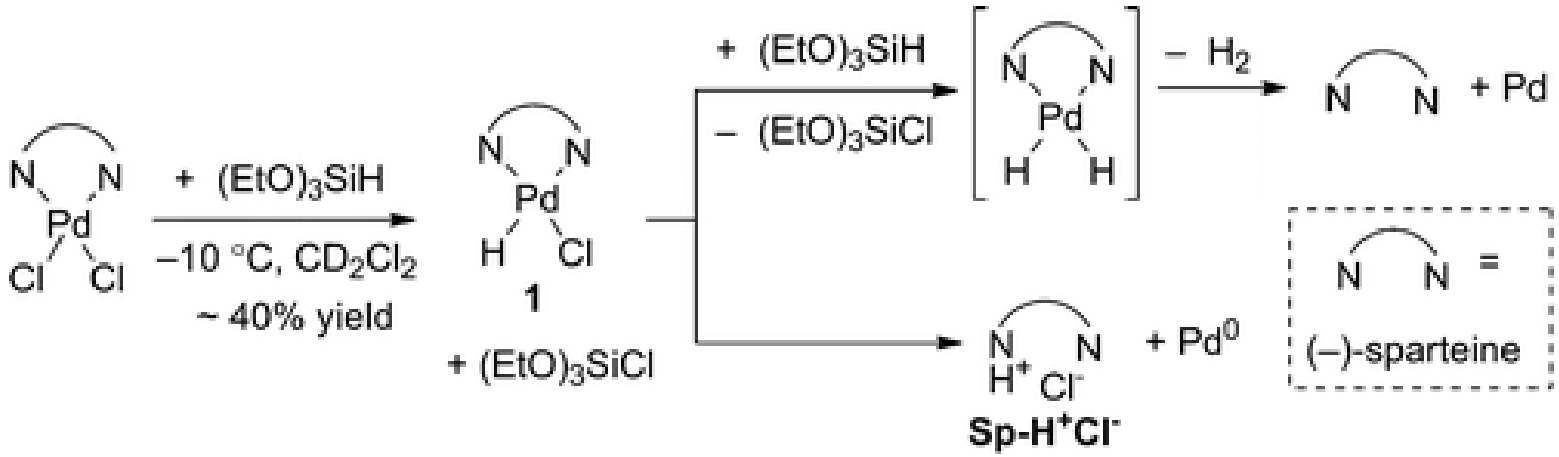


- Dark brown product
- 40% yield

NMR Evidence



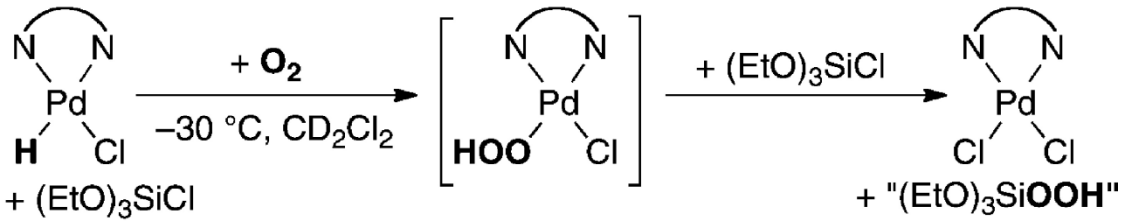
Degradation:



Kinetic studies

- Need rate dependence of [O_2] to determine mechanism
- Caveats:
  - Cant be purified
  - Catalyst not characterized
- Follow reaction by NMR (-30°C)
- Vary [O_2]

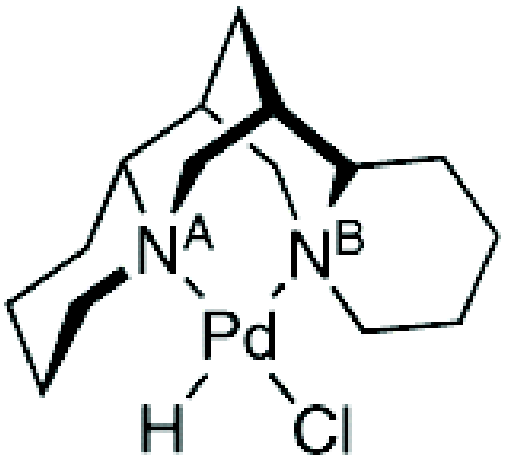
A.



Thermodynamic calculations:

- Calculate energy of intermediates
- Density functional theory
  - Use for calculations of many-body systems
  - Use particle density to get wavefunction
  - Alternative to Slater determinants
  - Calculations done with Gaussian

- Pd-N^B bond is longer than Pd-N^A
- Weaker bond is more easily broken



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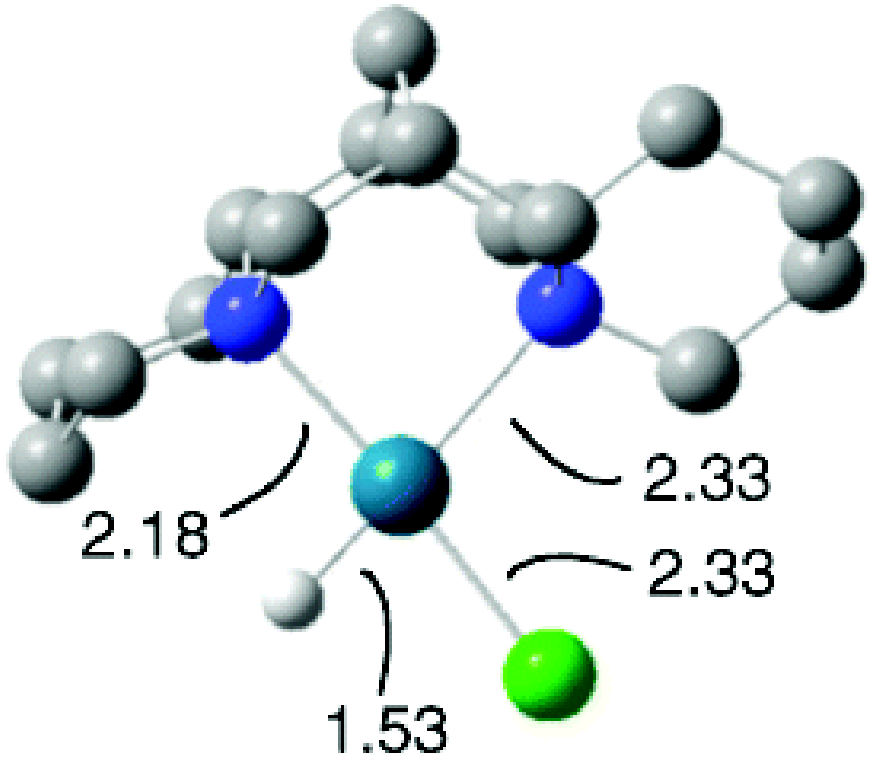
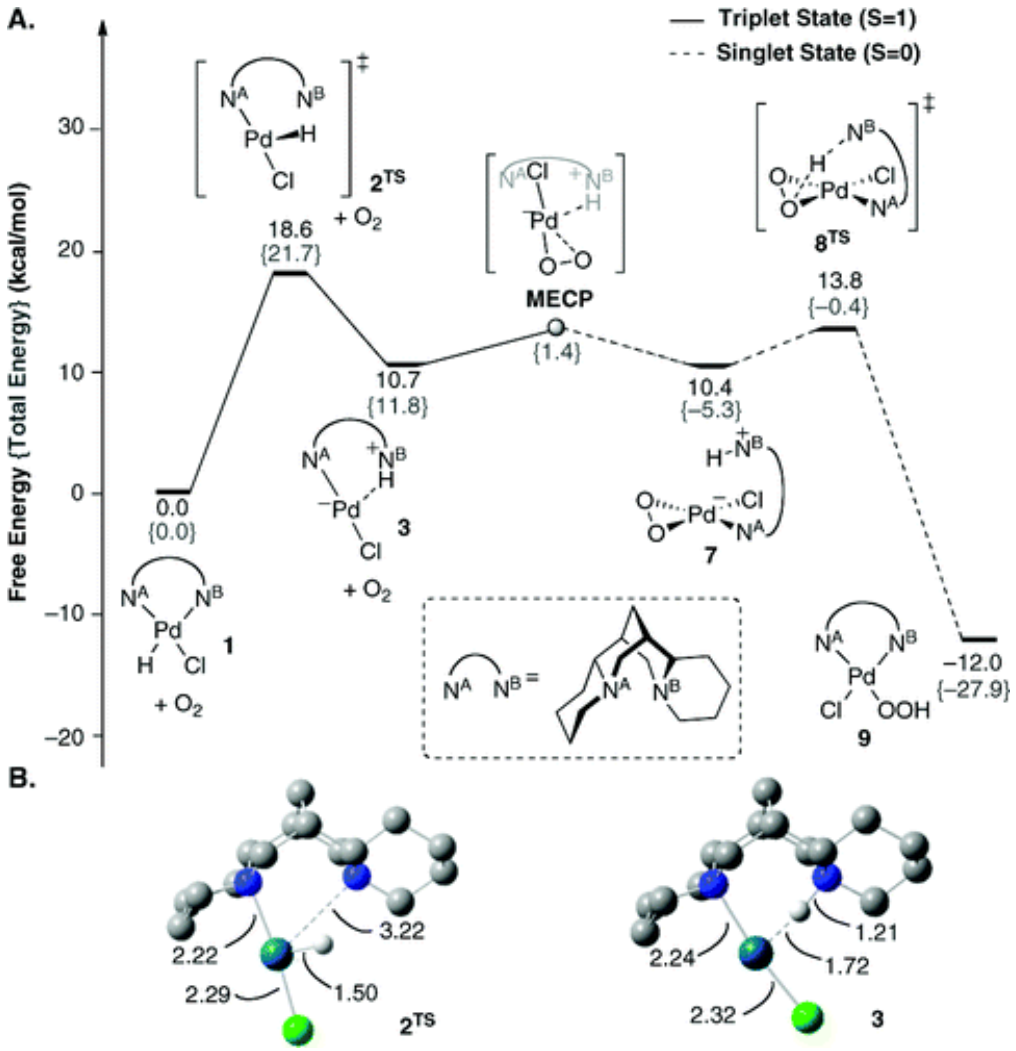
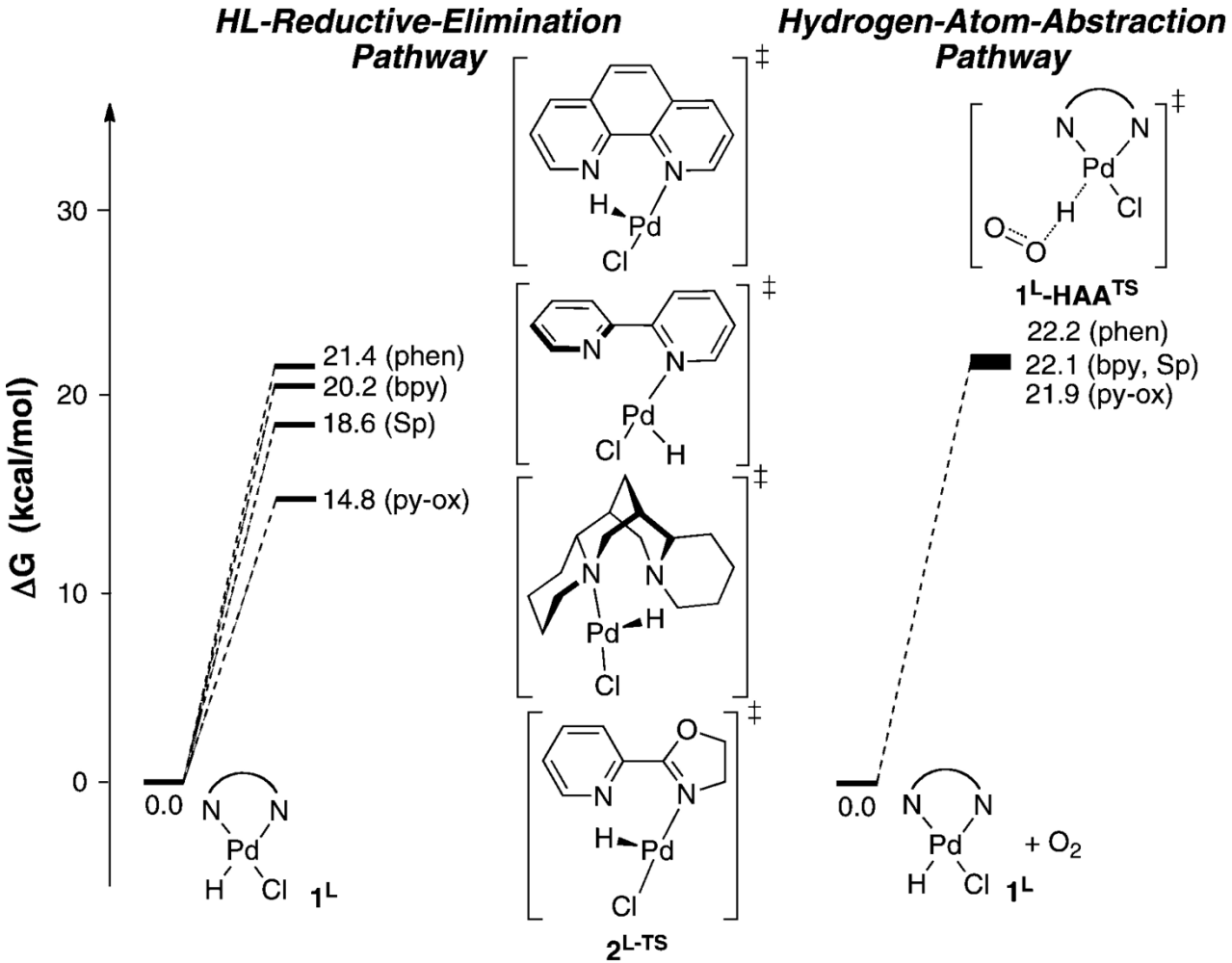
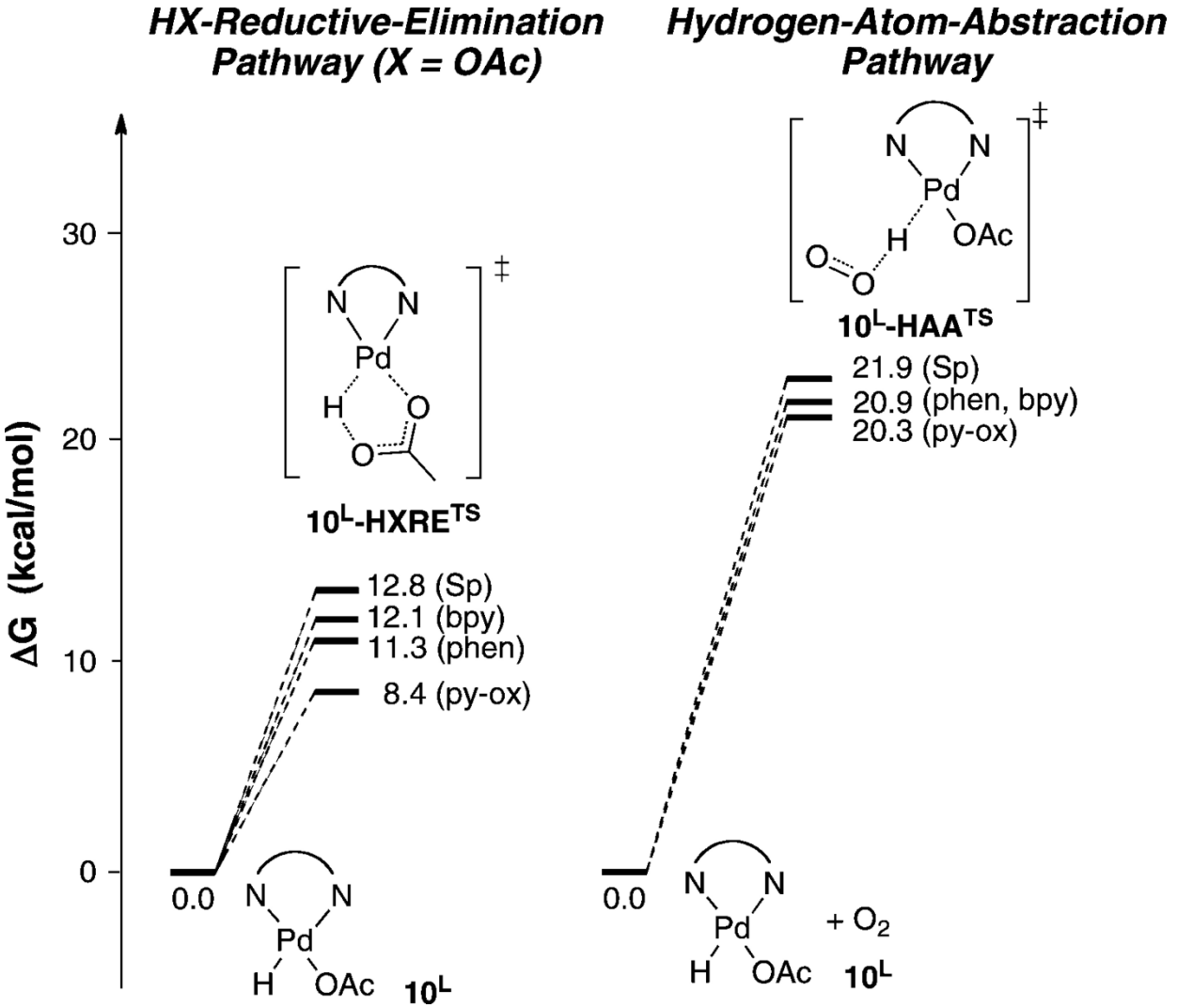


HLRE

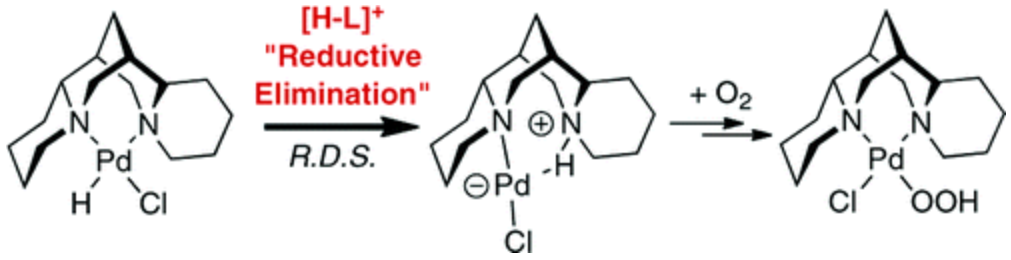

A.
Triplet State (S=1)
Singlet State (S=0)
Free Energy {Total Energy} (kcal/mol)
30
20
10
0
−10
−20
0.0
{0.0}
18.6
{21.7}
10.7
{11.8}
{1.4}
10.4
{−5.3}
13.8
{−0.4}
−12.0
{−27.9}
MECP
+ O2
1
2TS
3
7
8TS
9
B.
2.22
2.29
3.22
1.50
2.24
2.32
1.21
1.72

Does it work with other Ligands?




HX-Reductive-Elimination Pathway (X = OAc)
Hydrogen-Atom-Abstraction Pathway
ΔG (kcal/mol)
30
20
10
0
N
N
Pd
H
O
O
‡
10L-HXRETS
12.8 (Sp)
12.1 (bpy)
11.3 (phen)
8.4 (py-ox)
0.0
OAc
10L
10L-HAATS
21.9 (Sp)
20.9 (phen, bpy)
20.3 (py-ox)
+ O2

Conclusion



- Kinetic studies show that HAA mechanism does not occur
- HLRE has zero-order rate dependence on oxygen and is thermodynamically favorable over HAA
- “Ancillary” ligands aren’t really ancillary!