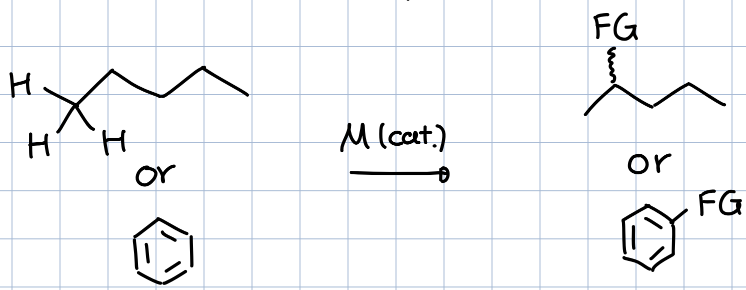
10.10.

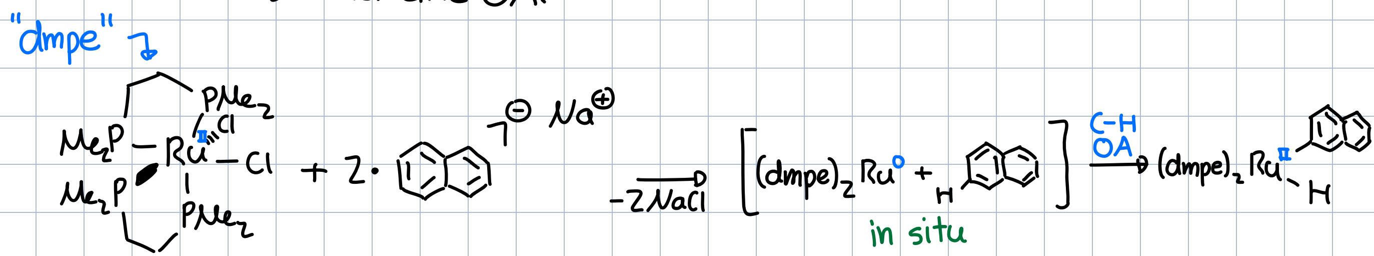
C-H bonds: OA continued

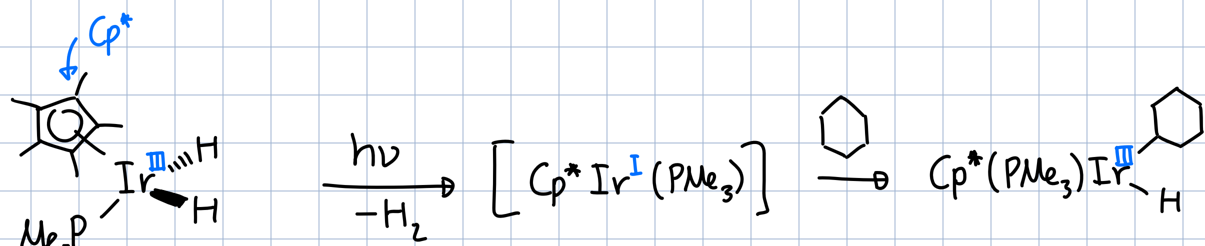
Want to convert feedstock chemicals:



Examples:

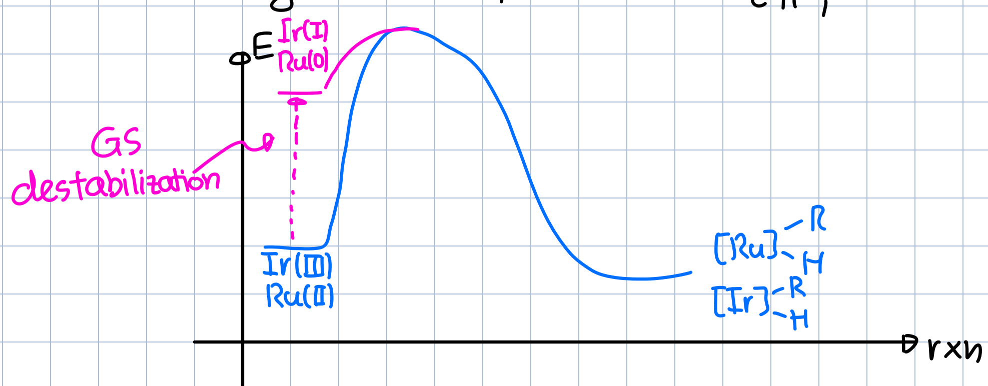
Stoichiometric OA:





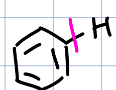
→ Why do we need hν/Reductant?

To get e⁻-density into the σ^*_{C-H}, as ΔE very high:



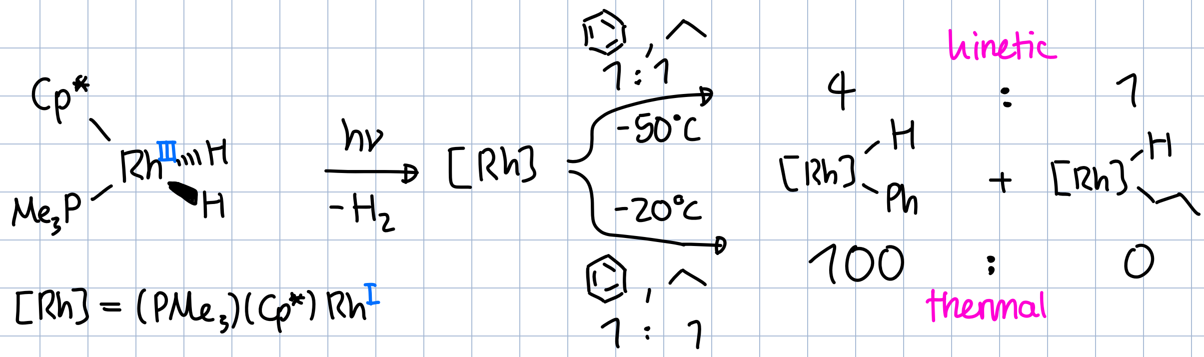
Selectivity:

- C(sp²) vs. C(sp³) ?



113 kcal/mol

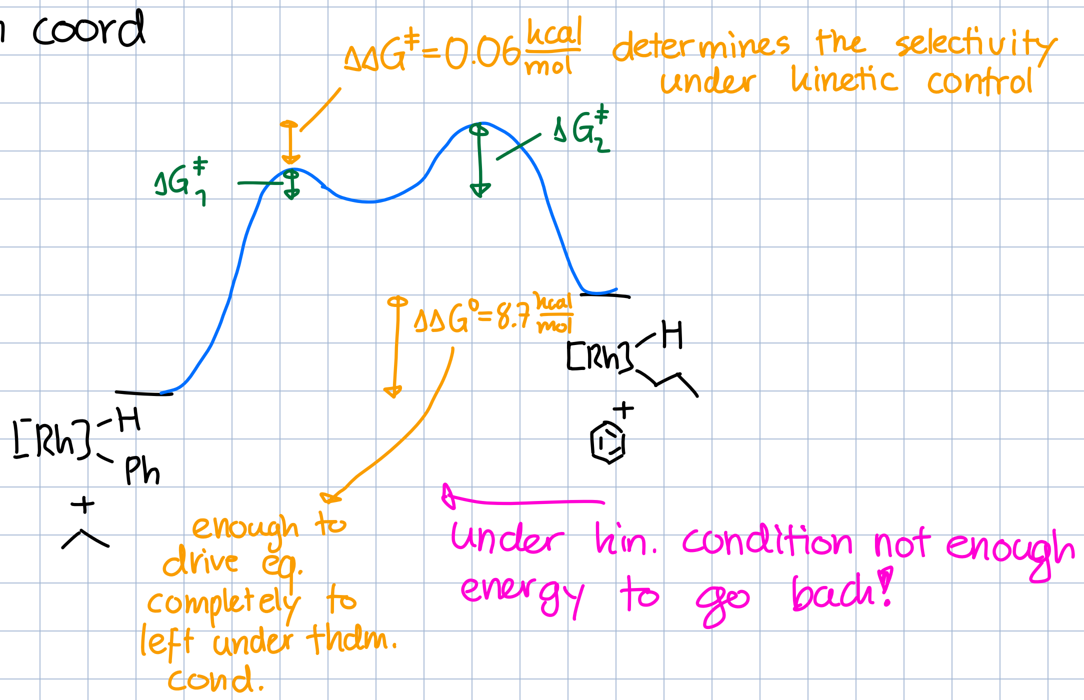
BDEs: H_3C–H 105 kcal/mol



$[Rh] = (PMe_3)(Cp^*)Rh^{I}$

↓

Rxn coord



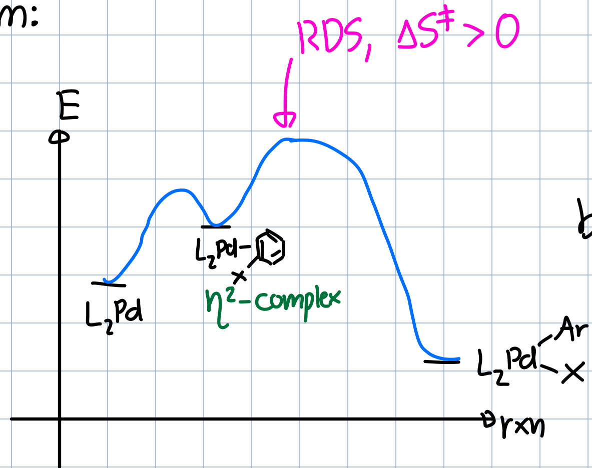
→ $\Delta\Delta G^\circ$ is $\Delta BDFE_{R-C}$ between [Rh](H)(Ph) vs. [Rh](H)(alkyl)

⇒ Selectivity OA_{CH} det. by $BDFE_{M-X}$

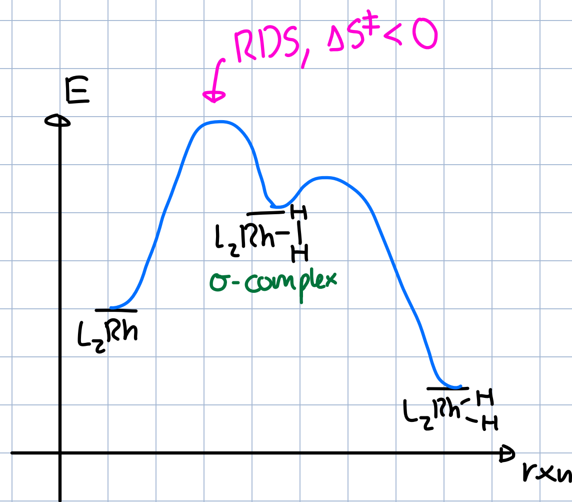
→ Order of selectivity: M–C(aryl) >> M–C(1°) > M–C(2°) > M–C(3°)

Mechanism:

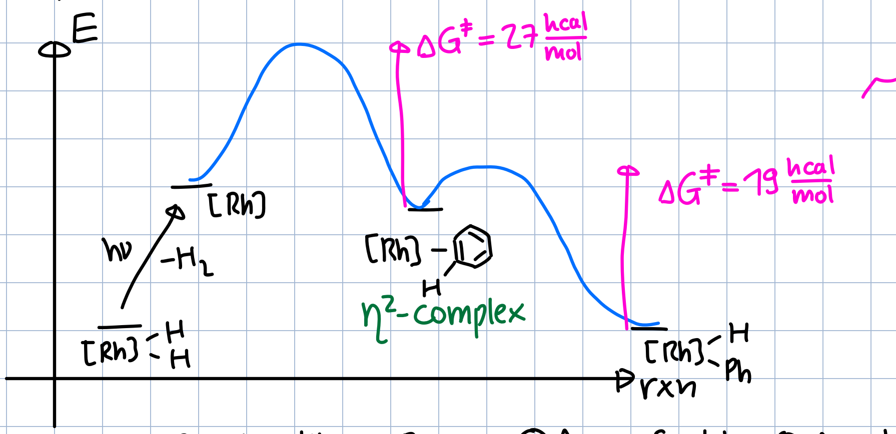
Recall:



but



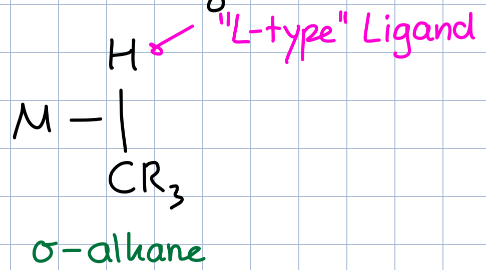
Now for C–H: [Rh] = (Cp*)(PMe_3)Rh



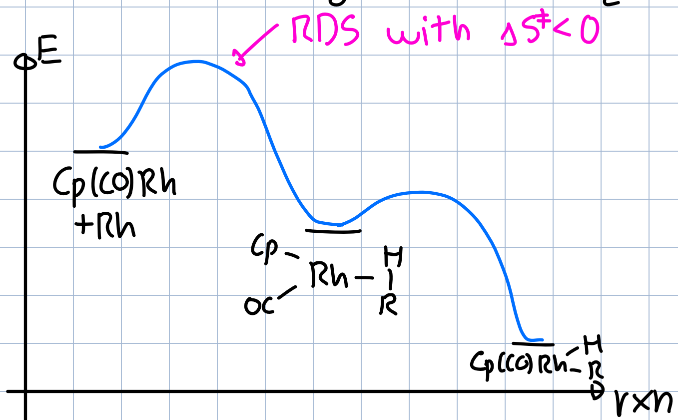
⇒ Just like for OA of H_2 OA, the RDS is the coordination!
This is because metal-d-orbitals have to donate into high-E π* orbitals

What about C(sp^3)–H?

Would have to go over intermediate:



↳ unfav. because high E σ* orbitals and symmetry not as welcoming as in H_2



Bonding picture:

Key interactions are filled-unfilled: