MAX-PLANCK-INSTITUT
FÜR KOLLOID- UND
GRENZFLÄCHENFORSCHUNG

11. CATALYTIC C-H FUNCTIONALIZATION

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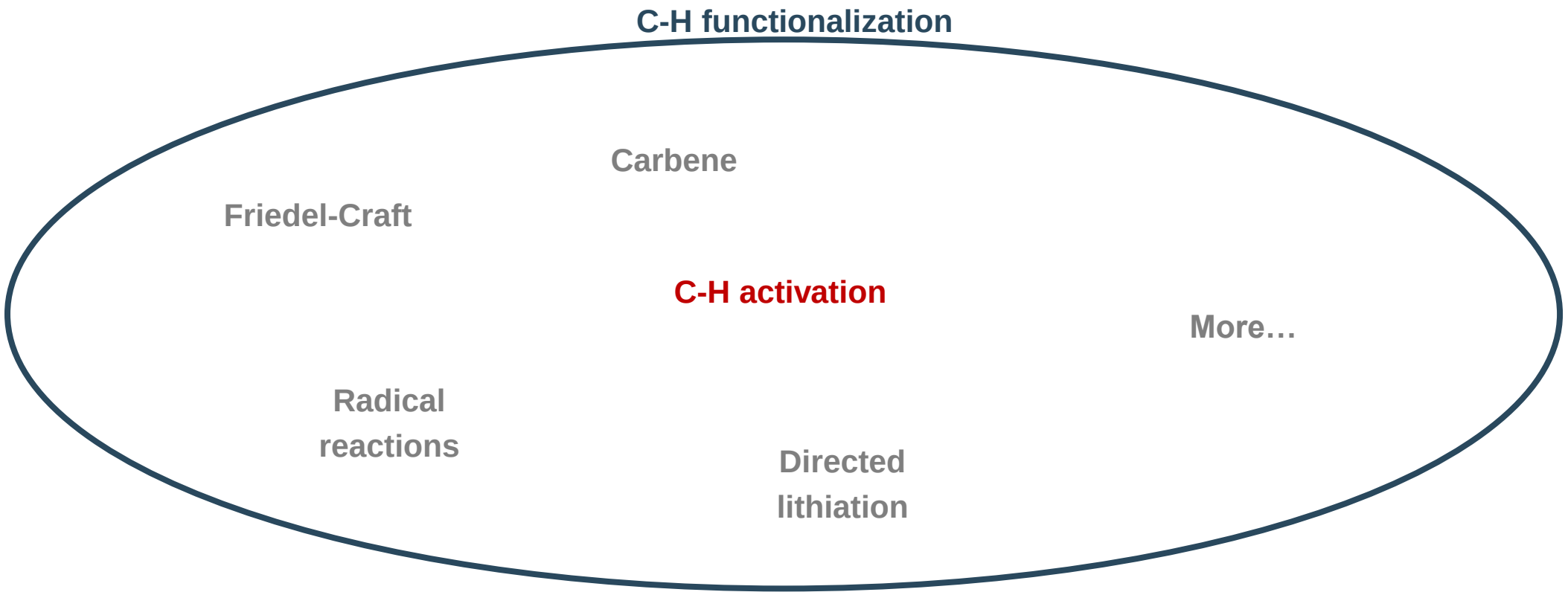
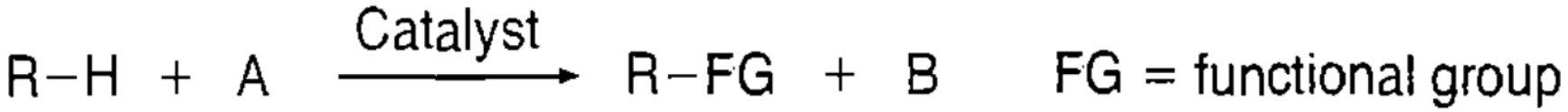
11.1.1 C-H ACTIVATION AND C-H FUNCTIONALIZATION



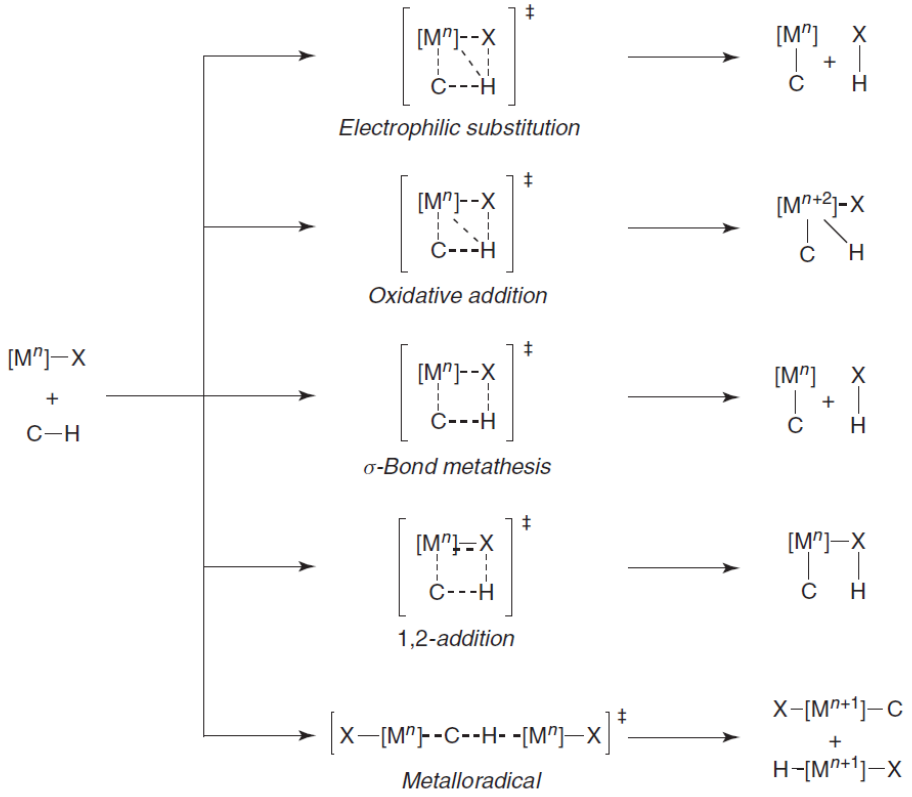
11.1.2 C-H ACTIVATION



Inert C-H bonds:

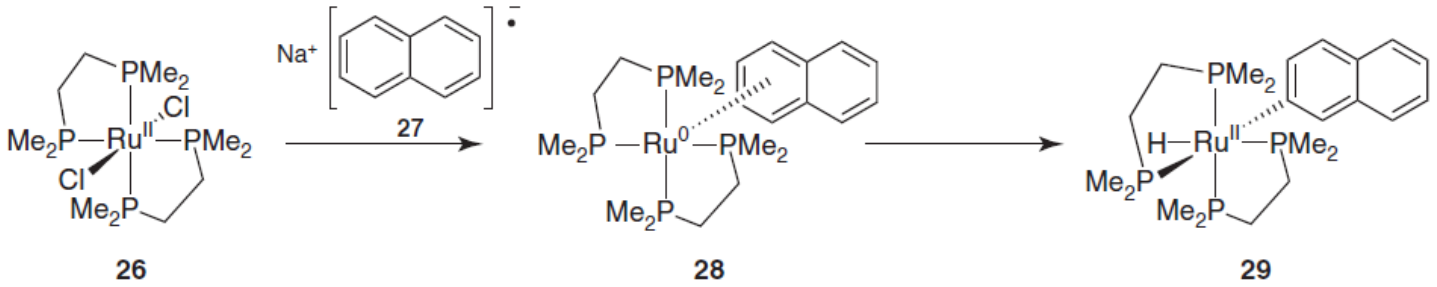
- **High BDE**
- **High pKa**
- **HOMO/LUMO inaccessible**

11.1.3 MECHANISTIC OVERVIEW



Labinger *Nature* **2002** 417, 507. DOI: 10.1038/417507a
Transition Metal-Catalyzed CH Functionalization, Wiley **2012** DOI: 10.1002/9783527664801.ch8

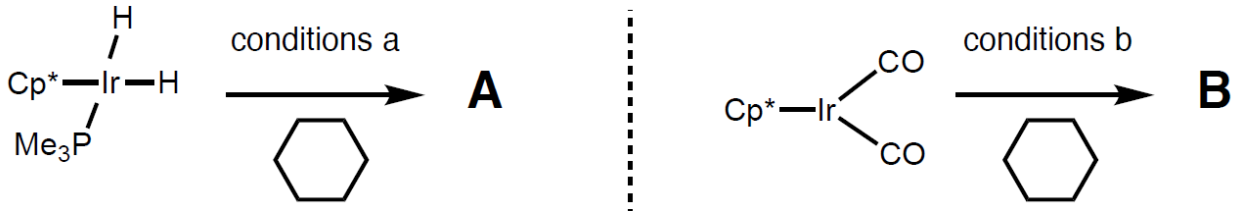
11.2.1 OXIDATIVE ADDITION



Chatt and Dowison *J Chem Soc* **1965** 843. DOI: 10.1039/JR9650000843

POD 1

The two reactions below are among the earliest well-defined C–H activation processes.

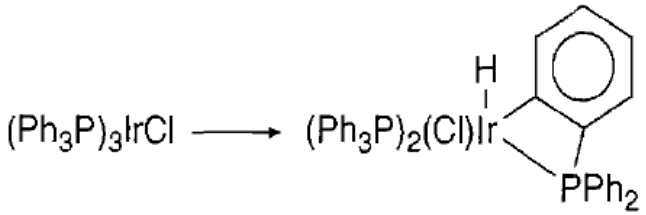


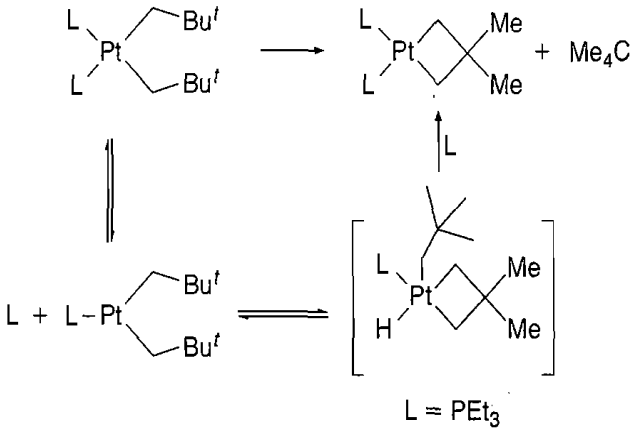
a) Provide the oxidation state, electron count, and coordination number for the two starting complexes.

b) Predict the products and provide reasonable reaction conditions (i.e., activation mode).

Bergman *JACS* **1982** 104, 352. DOI: 10.1021/ja00365a091
Graham *JACS* **1983** 105, 7190. DOI: 10.1021/ja00362a039

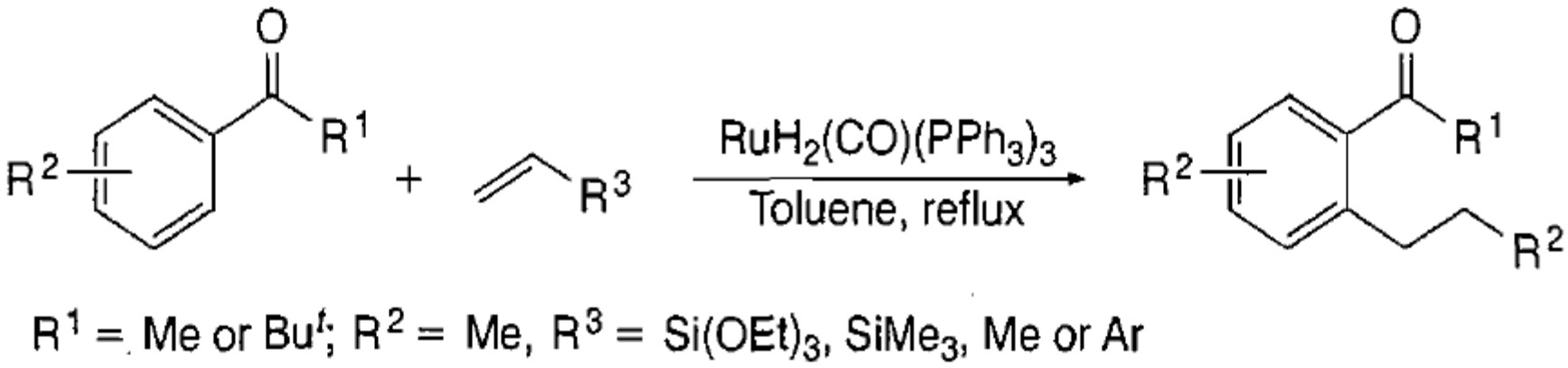
10.2.2 CYCLOMETALATION





Bennett *JACS* **1969** 91, 6983. DOI: 10.1021/ja01053a016
Whitesides *OM* **1982** 1,13. DOI: 10.1021/om00061a004

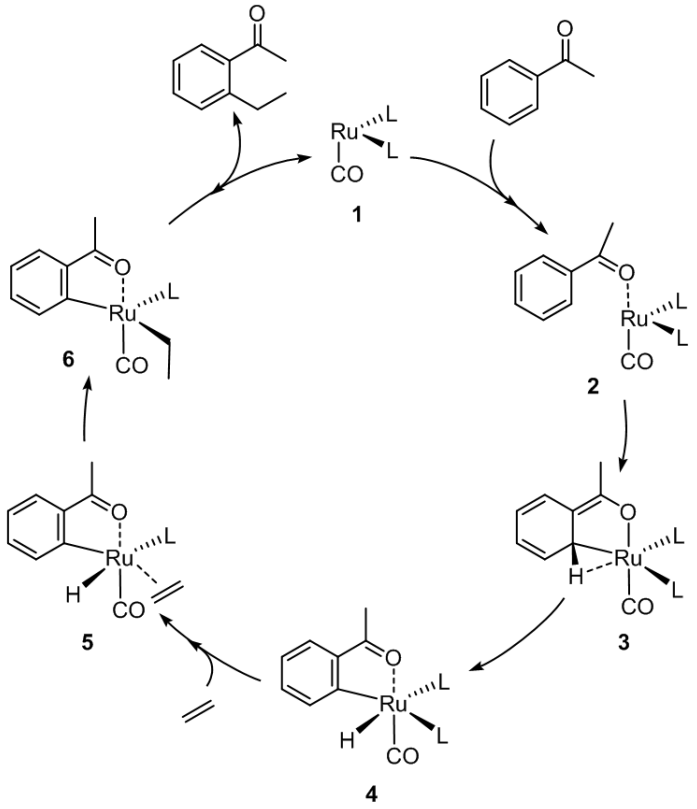
10.2.3 MURAI REACTION



R^1 = Me or Bu^t; R^2 = Me, R^3 = $Si(OEt)_3$, $SiMe_3$, Me or Ar

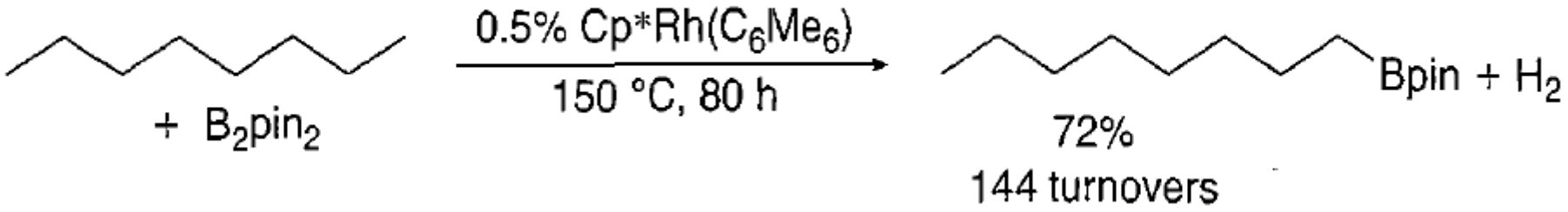
Murai *Nature* **1993** 366, 529. DOI: 10.1038/366529a0

10.2.3 MURAI REACTION



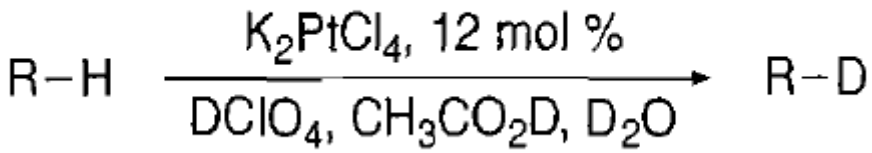
10.2.4 ALKANE BORYLATION

See seminar presentation!



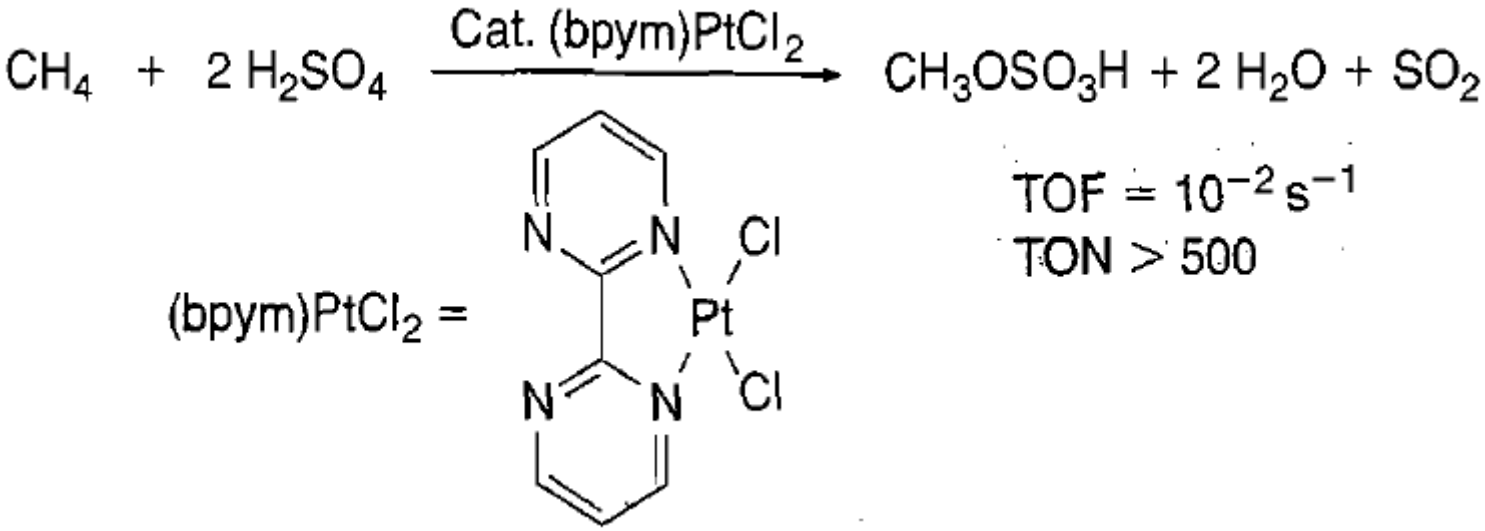
Hartwig *Science* **1997** + follow-up

10.3.1 ELECTROPHILIC ACTIVATION – SHILOV SYSTEM



Shilov *Coord. Chem. Rev.* **1977** 24 97. DOI: 10.1016/S0010-8545(00)80336-7

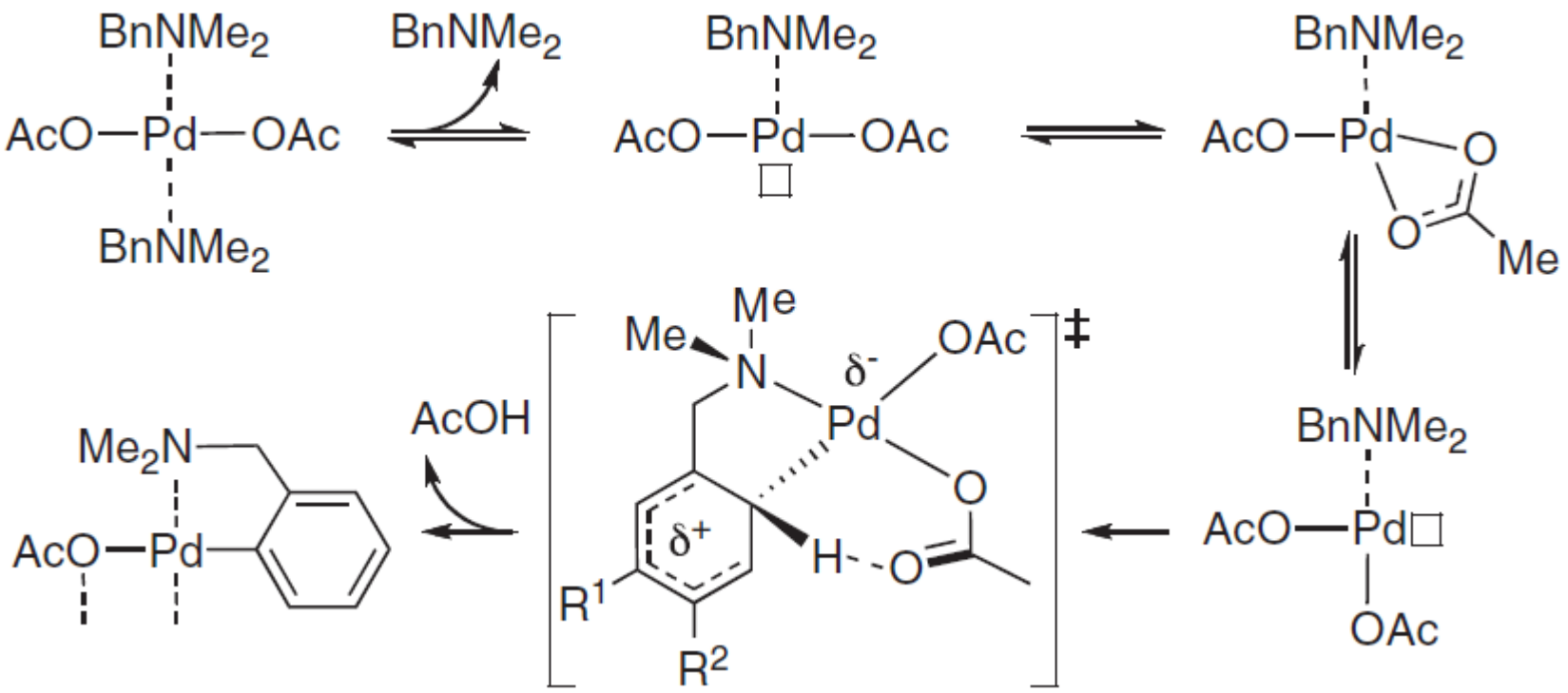
10.3.2 Pt-CATALYZED ALKANE OXIDATION



Periana *Science* **1993** 259, 340. DOI: 10.1126/science.259.5093.340
Periana *Science* **1998** 280, 560. DOI: 10.1126/science.280.5363.560

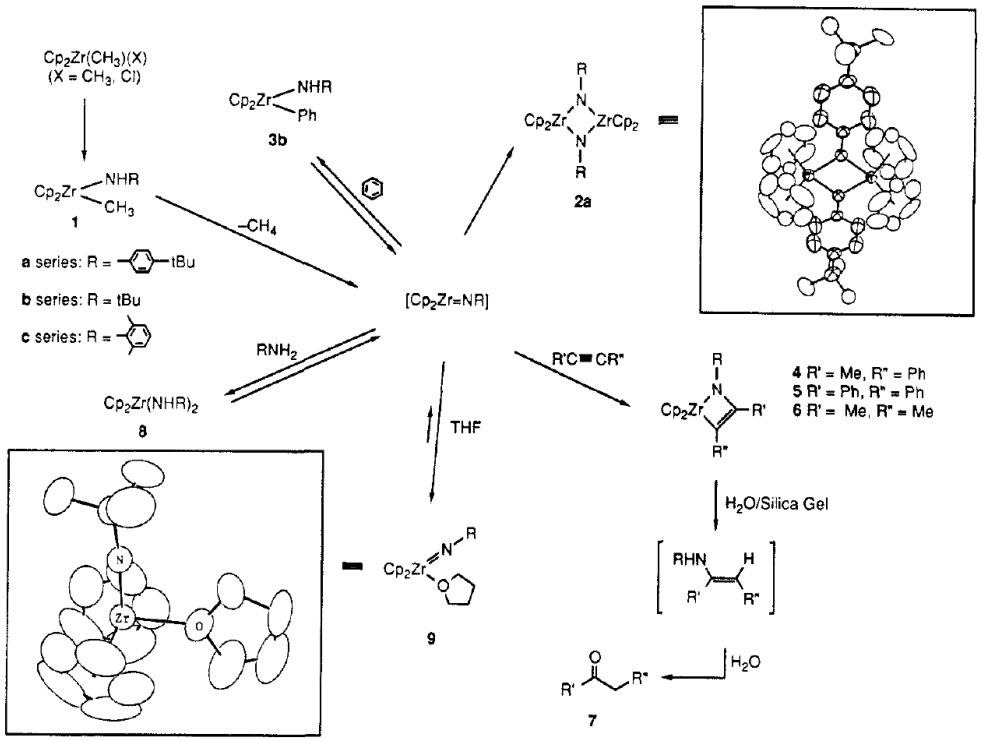
10.3.3 FUIJWARA MORITANI VS. CMD

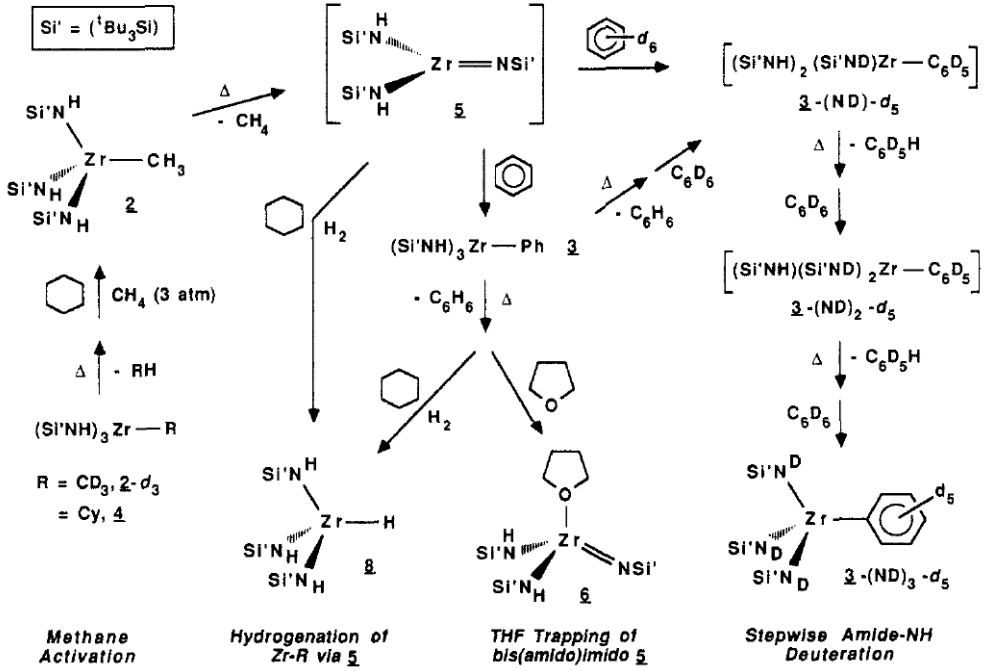
10.4 CONCERTED METALATION DEPROTONATION (CMD)



Fagnou *Chem Lett* **2010** 39, 1118. DOI: 10.1246/cl.2010.1118

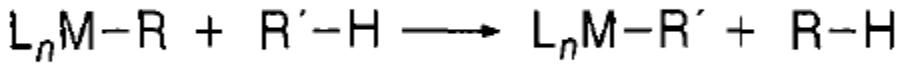
10.5 1,2 ADDITION



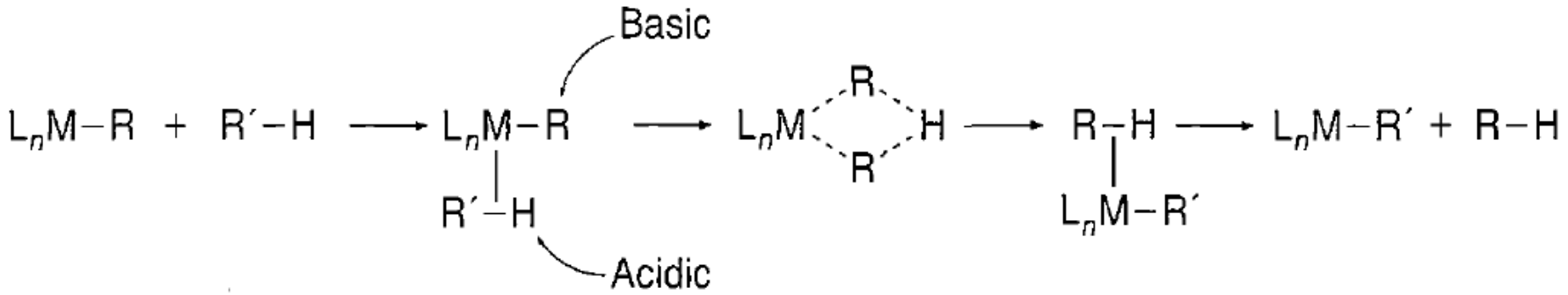


Bergman *JACS* **1988** 110, 8729. DOI: 10.1021/ja00234a043
Wolczanski *JACS* **1988** 110, 8731. DOI: 10.1021/ja00234a044

10.6.1 σ-BOND METATHESIS

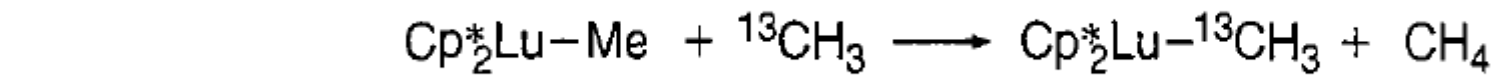


- Late TM-alkyl w/ d electrons reacting with H_2 or C_nH_{n+2} -> O.A. + R.E.
- Early TM, d^0 complexes -> **σ-bond metathesis**
- Unsaturation site needed and max $16ve^-$

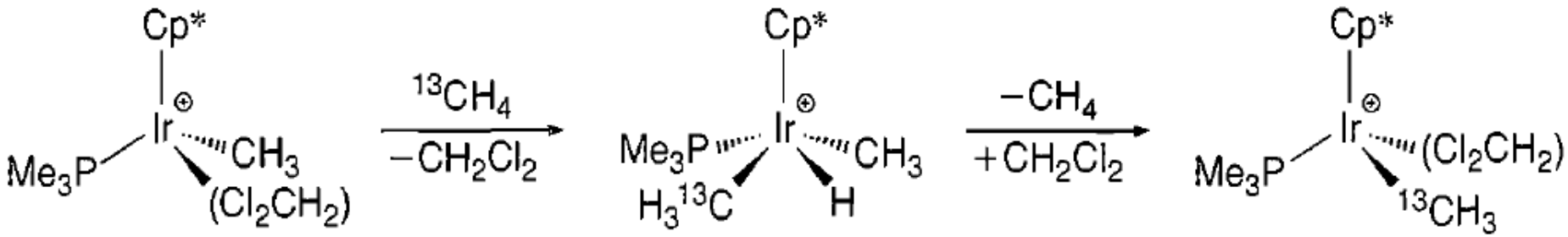


10.6.1 σ-BOND METATHESIS

e.g.



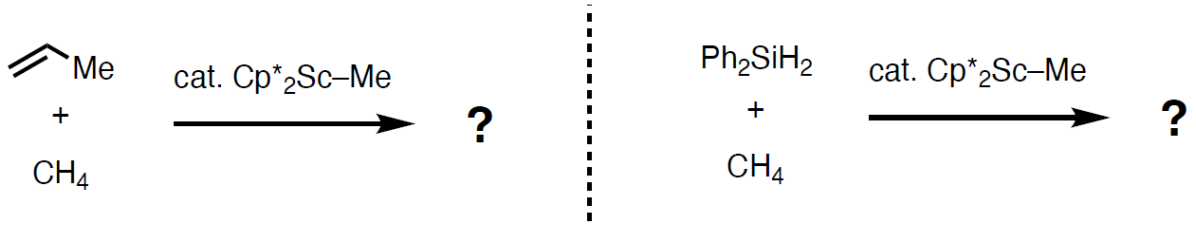
However,



Watson *JACS* **1983** 105, 6491. DOI: 10.1021/ja00359a023

POD #2

For the two Sc-catalyzed reactions below, provide the products and propose a reasonable catalytic cycle.



Tilley *ACIE* **2003** 42, 803. DOI: 10.1002/anie.200390213