Agostic Interactions

Reviews: Brookhart, M.; Green, M. L. H. *J. Organometall. Chem*. **1983**, *250*, 395.
Crabtree, R. H. *Angew. Chem., Int. Ed. Engl*. **1993**, *32*, 789.
Schneider, J. J. *Angew. Chem., Int. Ed. Engl*. **1996**, *35*, 1068.
Scherer, W.; McGrady, G. S. *Angew. Chem., Int. Ed. Engl*. **2004**, *43*, 1782.

Outline

1. Definition
2. Conceptualization
3. Significance
4. σ bond complexation
5. Catalysis
6. σ bond metathesis
7. Some synthesis
8. Conclusion

αγοστϖ

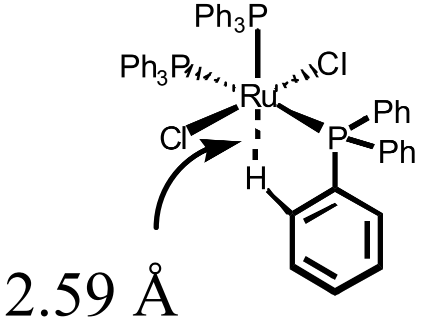
“ to clasp or hold to oneself”
- Coined into chemistry as a term by Malcolm Green.

Original definition: “to refer specifically to situations in which a **hydrogen atom** is *covalently* bonded to both a **carbon** and to a **transition metal** atom.”
Brookhart, M.; Green, M. L. H. *J. Organometall. Chem*. **1983**, *250*, 395

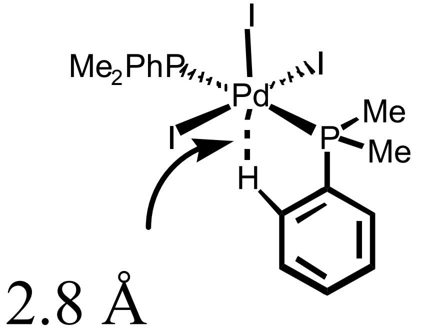
Redefined definition : “distortion of an **organometallic moiety** which brings an appended **C-H bond** into **close proximity** with the metal center
Scherer, W.; McGrady, G. S. *Angew. Chem., Int. Ed. Engl*. **2004**, *43*, 1782

Development of the concept

1. Early Indications



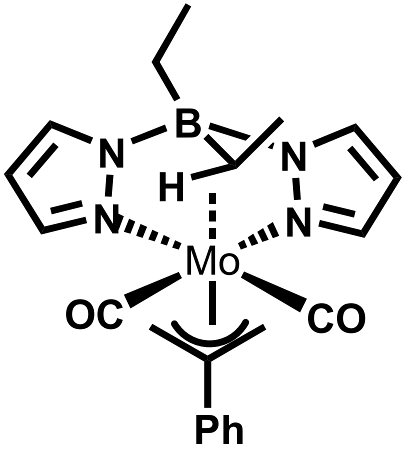
La Place S. J.; Ibers, J. A. *Inorg Chem*. **1965**, *4*, 778.
-“ is about what is expected from van der Waals radii”
-Considered it to be a five coordinated species.



Bailey, N. A.; Jenkins, J. M.; Mason, R.; Shaw, B. L. *J. Chem. Soc. Chem. Commun*. **1965**, 237.
-“ a distorted octahedron, the sixth coordination being ocupied by a hydrogen”

Development of the concept

2. Mounting Evidence

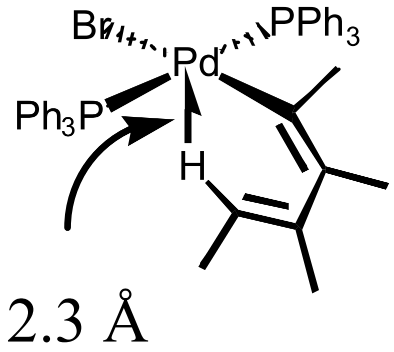


Trofimenko, S. *J. Am. Chem. Soc*. **1968**, *90*, 4754.
Inorg. Chem.**1970**, *9*, 2493.
-Observation “Hydridic” character in the NMR
“hydrogens are intruding into a suitable empty metal orbital.”

Cotton, F. A.; LaCour, T.; Stanislowski, A. G.
J. Am. Chem. Soc. **1974**, *96*, 754.
-studied by single-crystal X-ray diffraction
“ a three center, two-electron bond encompassing the C-H-Mo atoms

Development of the concept

2. Mounting evidence

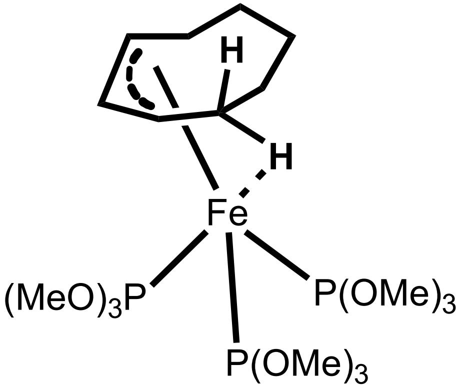


Less than the sum of the van der Waals radii

Roe, D. M.; Bailey, P. M.; Moseley, K.; Maitlis, P.M..
J. Chem.Soc. Chem. Commun. **1972**, 1237.
-“ This type of interaction has not been observed before,
though Trofimenko noted that the …”

Development of the concept

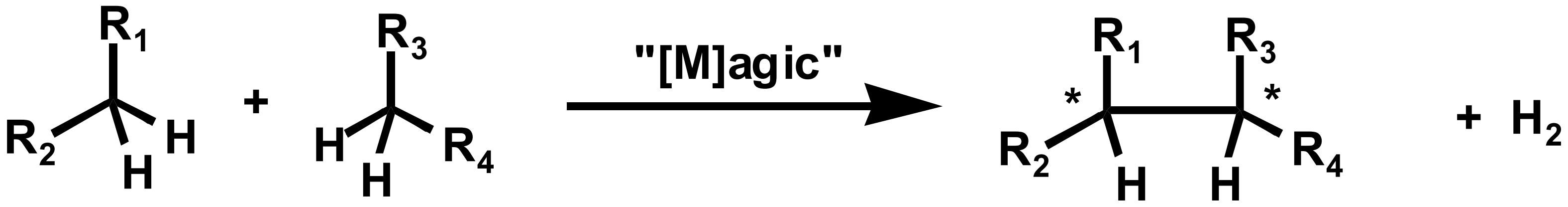
3. Conclusive Evidence: Neutron diffraction Studies



Brown, R. K.; Williams, J. M.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 981.

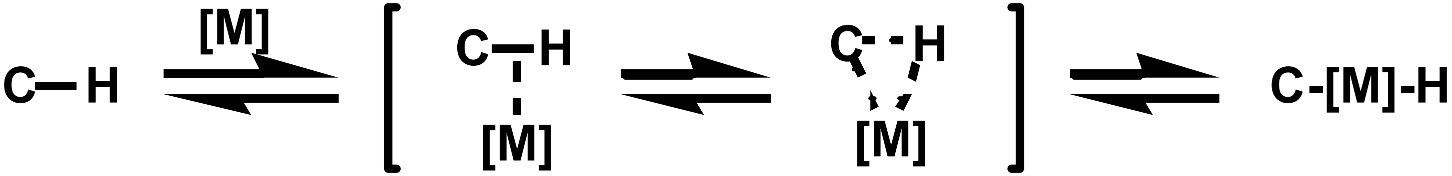
Why do we care?

“Ideal” synthetic chemistry

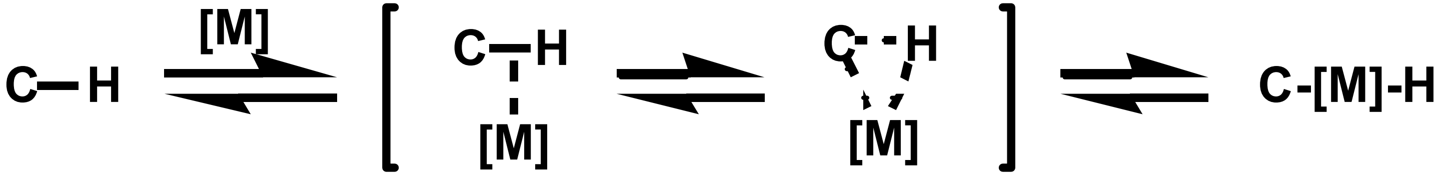


Need to find method(s) to “selectively” functionalize
the desired C-H bond(s) for transformation
(in catalytic fashion).

Mechanistic Pathway on C-H activation: Agostic interaction



Importance of transition metal complex of σ bonds



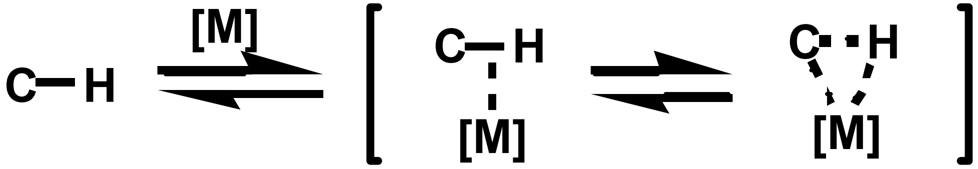
Metal is on way to :

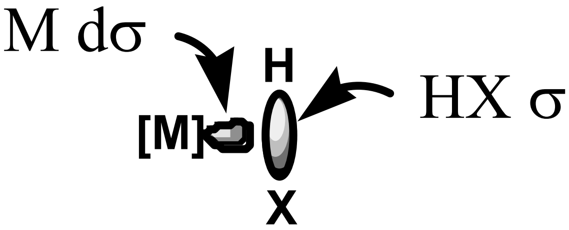
1. Change in oxidation state: n to n+2
2. Increase in number of coordination

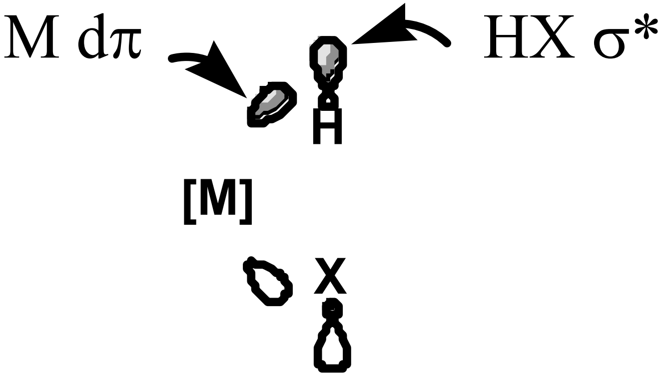
Metal should be able to:

1. Accommodate two additional electrons.
2. Have geometrically accessible empty coordination site(s)

Transition Metal Complexation of σ bonds





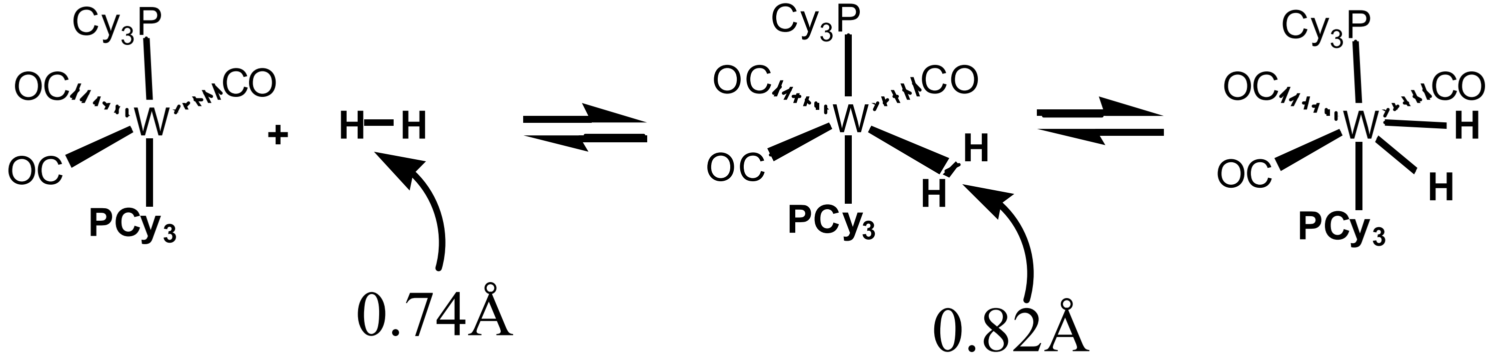


Electron are donated
from HX σ to M dσ

Electron are donated
from M dπ to HX σ*

∴ Metal character needed for a strong complexation to a σ bond:
σ acid, π base

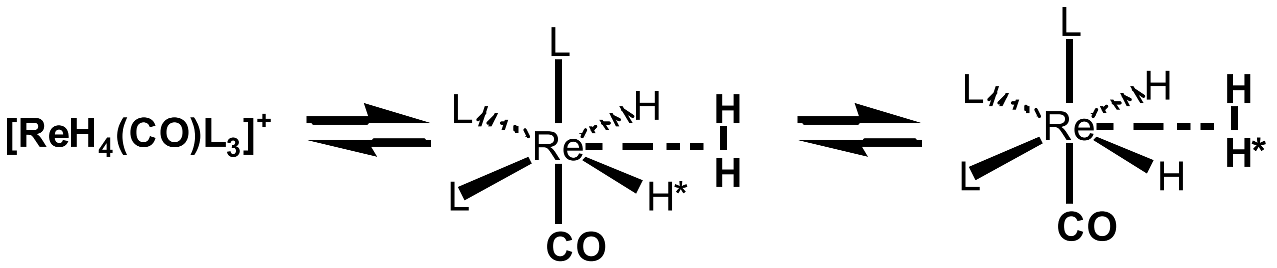
Transition Metal Complexation of σ bonds



Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P.J.; Wasserman, H. J.
J. Am. Chem. Soc. **1984**, *100*, 451.

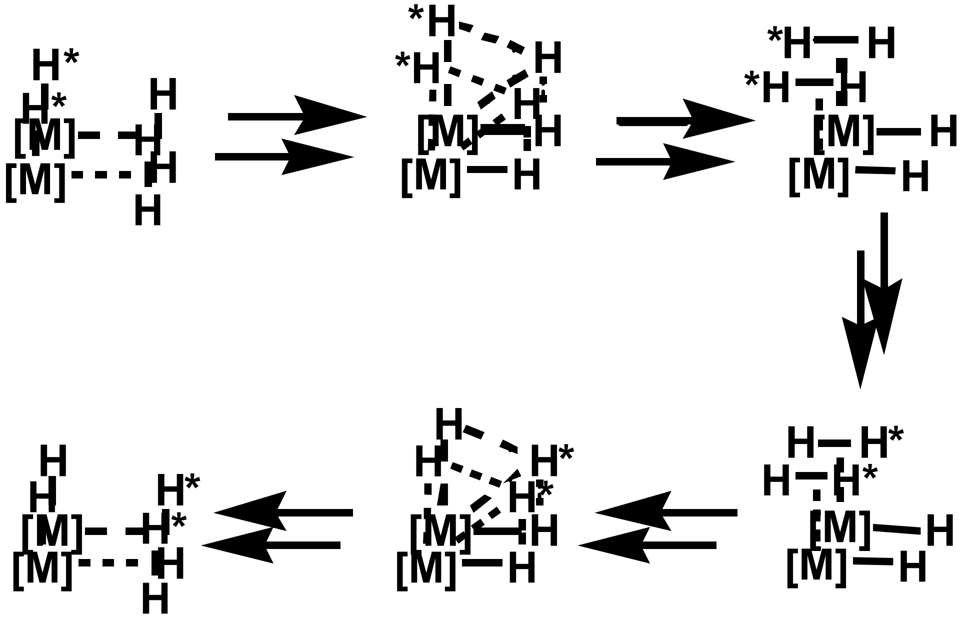
The fact that above structures could exists in equilibrium suggests possibility of **catalysis**

Scrambling of H* within the coordination sphere of the metal via agostic intermediate

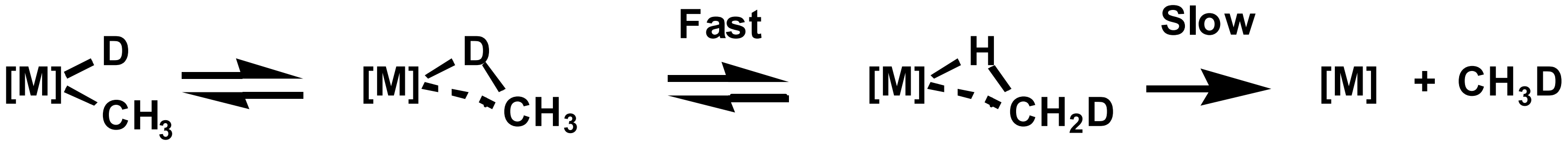


Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912.

Proposed mechanism of isomerization of H*



Isomerization via
agostic interaction / σ bond metathesis

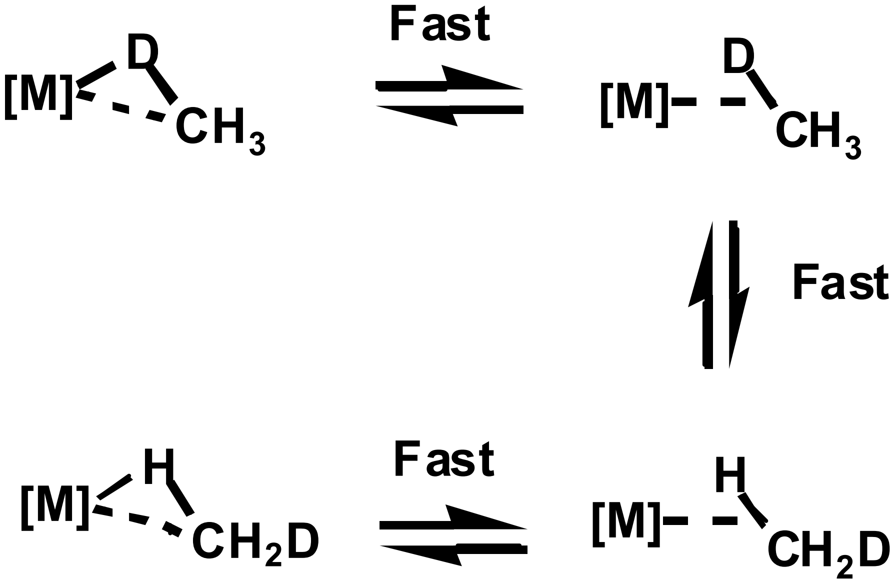


[M] = $Cp^*Ir(PMe_3)_3$, Cp_2W, Cp_2Re^+

Ir: Periana, R.A.; Bergman, R. G. *J. Am. Chem. Soc*. **1986**, *108*, 7332.

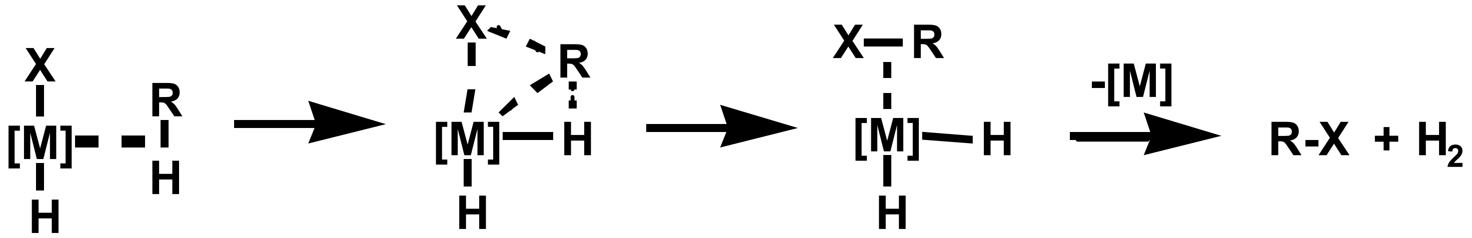
W: Bullock, R. M.; Headford, C. E. L; Kegley, S. E.; Norton, J. R.
J. Am.Chem. Soc. **1985**, *107*, 727.

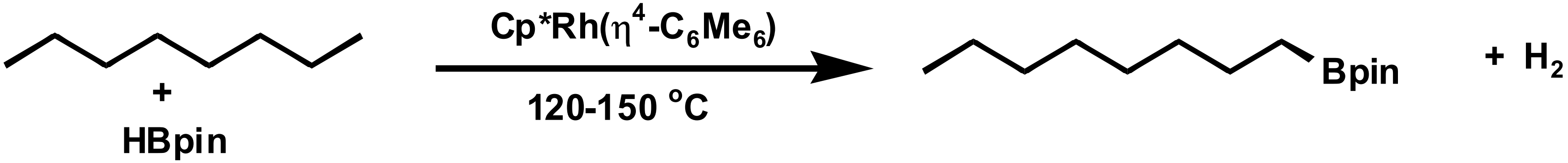
Re: Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc*. **1989**, *111*, 5502.



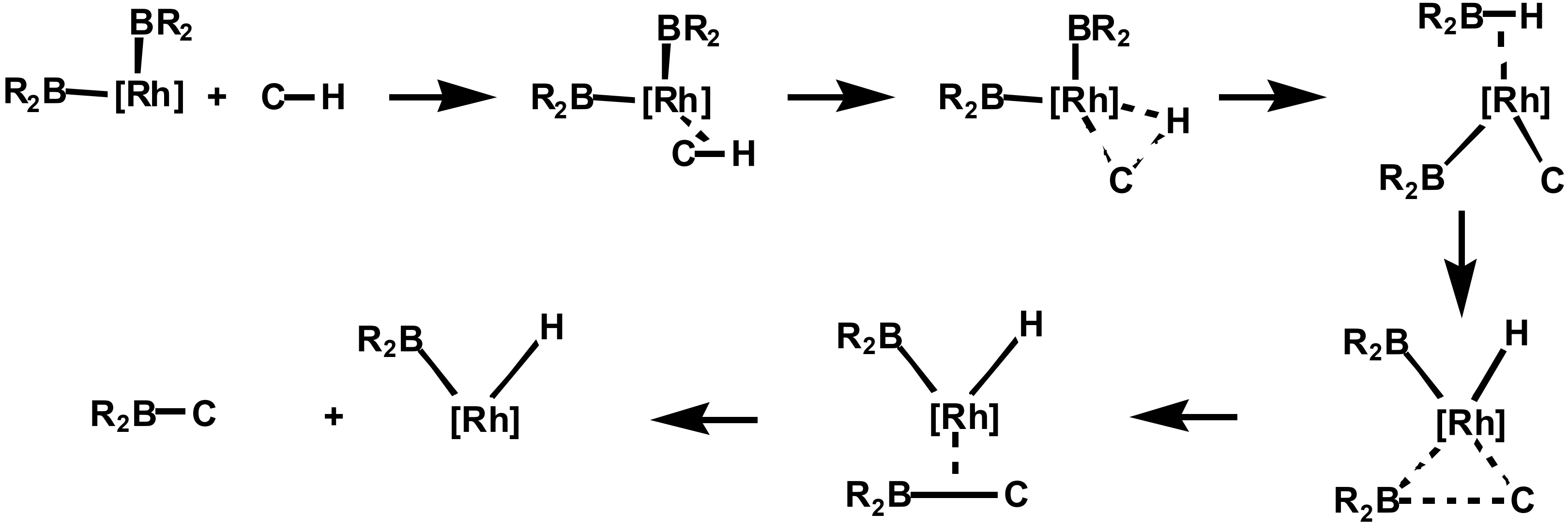
Isotope exchange faster than reductive elimination of alkyl group
: Involvement of alkane σ complex

Hypothetical(?) reaction conceivable based on previous reaction





Chen, H.; Schelecht, S.; Semple, T.C.; Hartwig, J. F. *Science* **2000**, *287*, 1995.

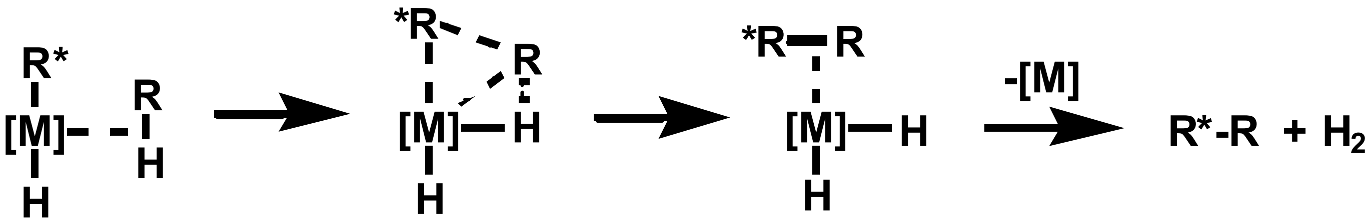


Hartwig, J.F.; Cook, K. S.; Hapke, M.; Incarvito, C.D.; Fan, Y.; Webster, C. E.; Hall, M. B. *J. Am. Chem. Soc*. **2005**, *127*, 2538.

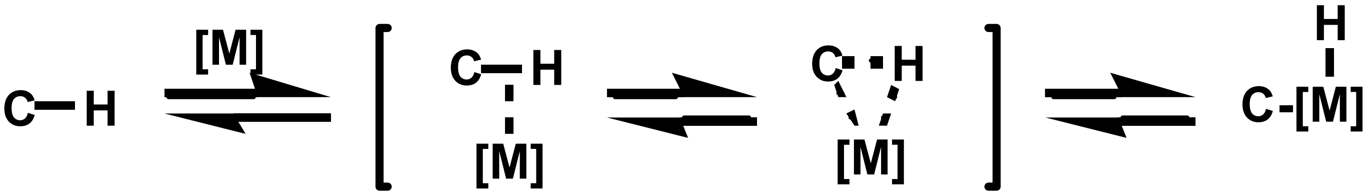
-Oxidation state of Rh does not change
-Empty p orbital in Boron is essential to success of this chemistry

What is the role of empty p orbital on boron?

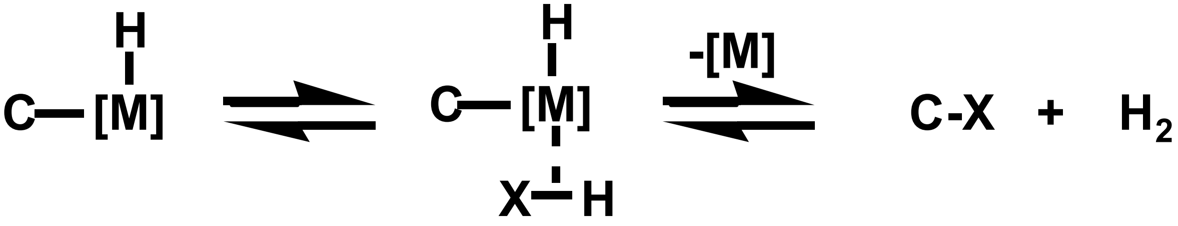
Would it possible?



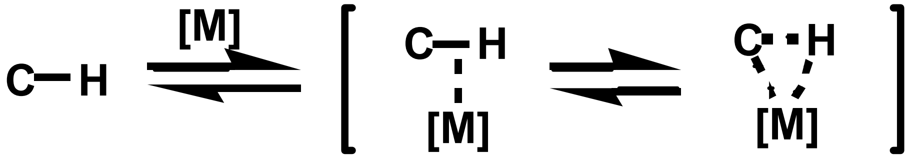
Assuming the first agostic interaction leads to C-H activation By oxidative addition

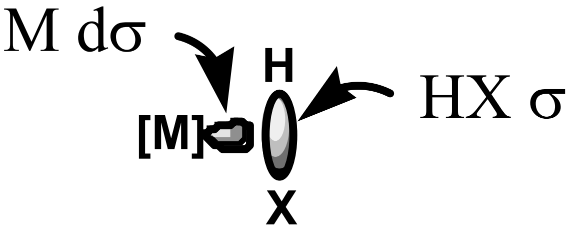


What about the second agostic interaction that actually leads to C-C bond formation?

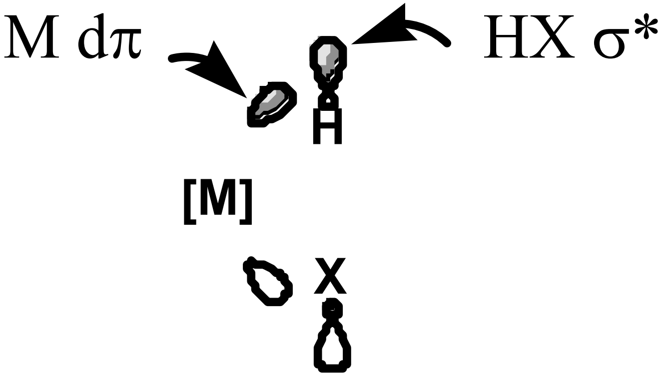


Transition Metal Complexation of σ bonds



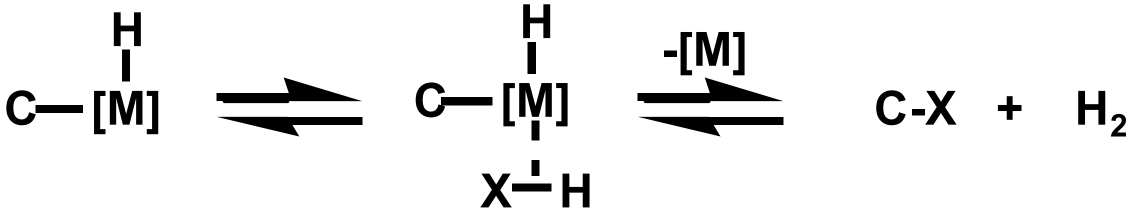


Electron are donated
from HX σ to M dσ



Electron are donated
from M dπ to HX σ*

∴ Metal character needed for a strong complexation to a σ bond:
σ acid, π base



The two acquired ligands via C-H activation:
Are they beneficial to the second necessary agostic interaction?
-alkyl ligands : good σ donating, weak π acid / base.

Sterics?
Geometry?

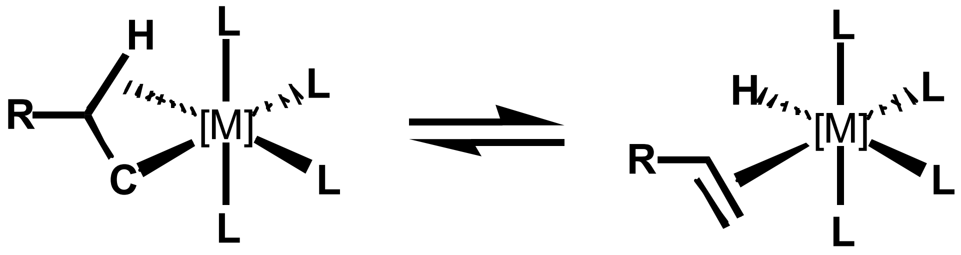
σ bond metathesis vs. oxidative addition

σ bond metathesis vs. oxidative addition

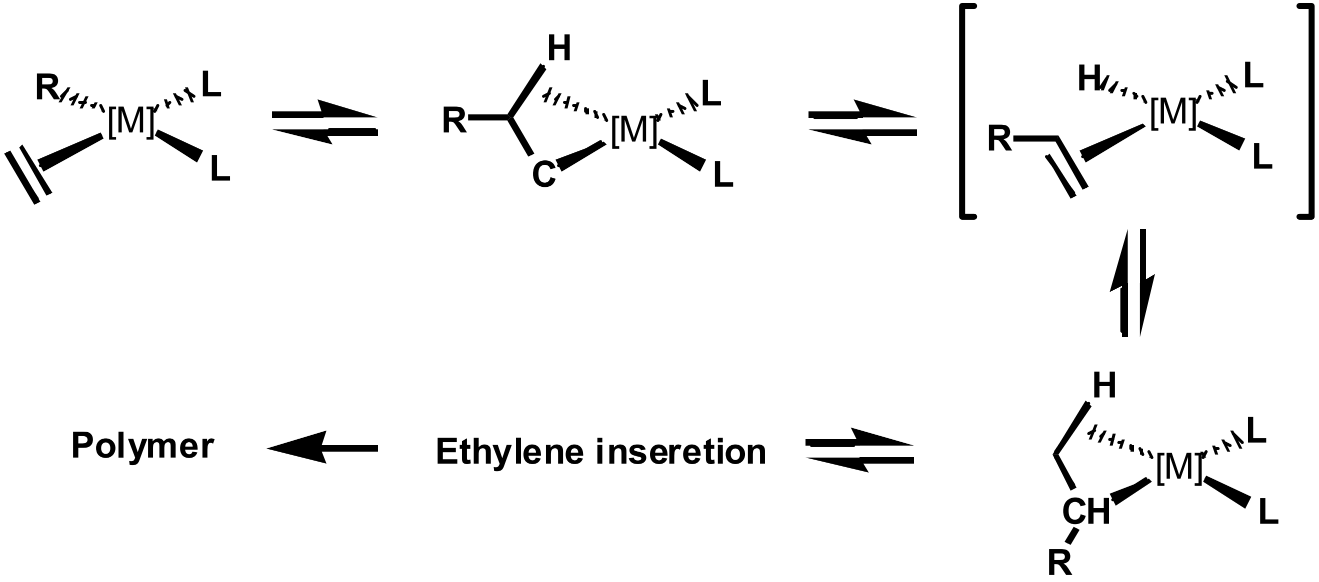
Intermediate for σ bond metathesis

Intermediate via oxidative addition

Potential pitfall (opportunity) after the initial oxidative addition: β-H elimination (Alkene insertion)



Early → **Late**

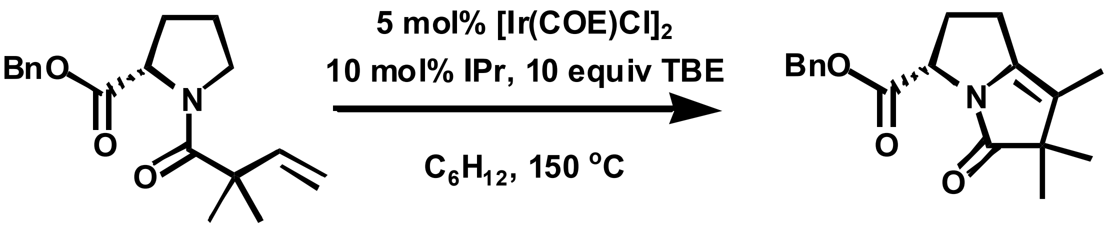


M: Pd, Ni , L: di-imine ligands

Leatherman, M.D.; Svedja, S. A.; Johnson, L. K.; Brookhart, M
J. Am. Chem. Soc. **2003**, *125*, 3068.

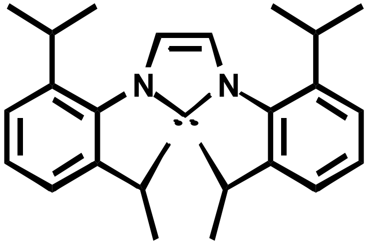
Polymer structure controlled by agostic interaction

Synthetic application



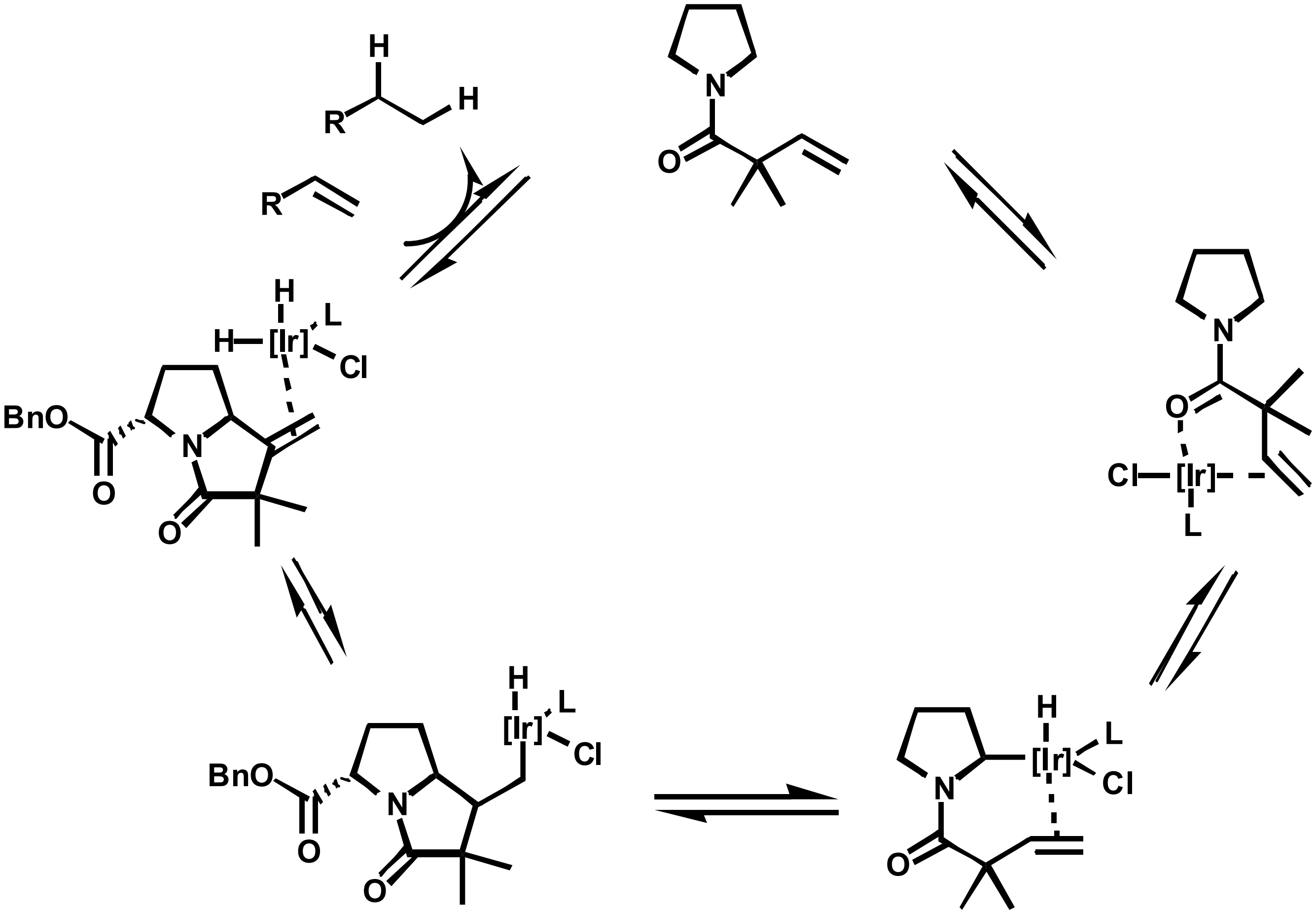
46% isolated yield
>99% ee

IPr=



DeBoef, B.; Pastine, S. J.; Sames, D.
J. Am. Chem. Soc. **2004**, *126*, 6556.

Proposed mechanism



What have we learned ?

- Agostic interaction is involved in all the critical steps of our “ideal” reaction.

- We are “yet” still a long ways from knowing how to execute.