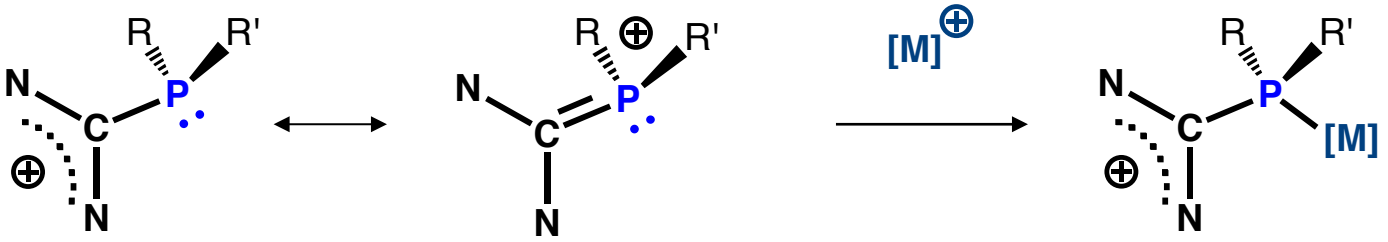
Theoretical studies of the metal-phenylene interaction in a P(CH)P pincer rhodium(I) complex

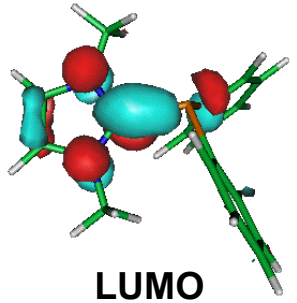
Christine Lepetit, Jordi Poater, Julia Contreras-Garcia,
Yves Canac, Remi Chauvin

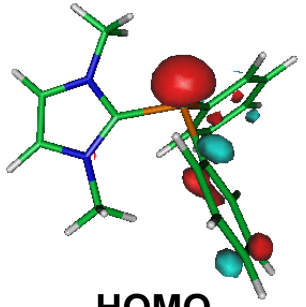
Laboratoire de Chimie de Coordination – UPR 8241 CNRS
Toulouse - France

Amidiniophosphines

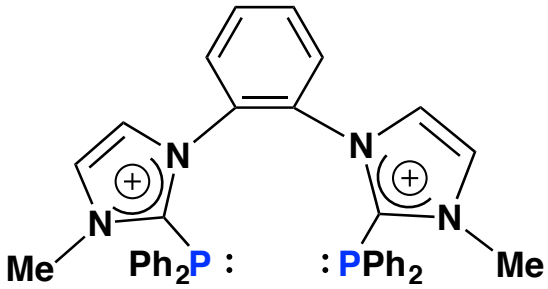
Cationic phosphorus ligands of L type





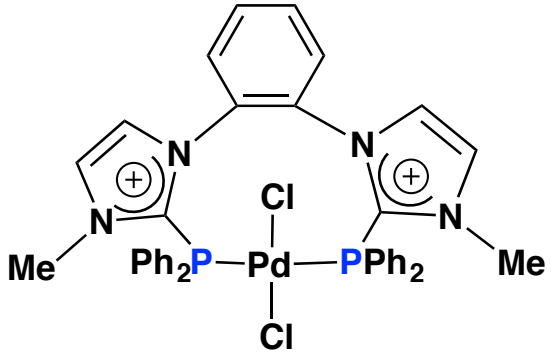


Experimental representatives



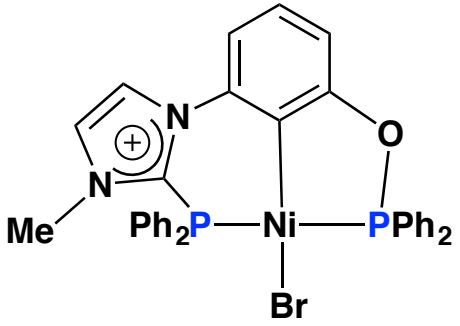
Bis - amidiniophosphine

Inorg. Chem. **2009**, *48*, 5562.



Trans-chelated dicationic complex

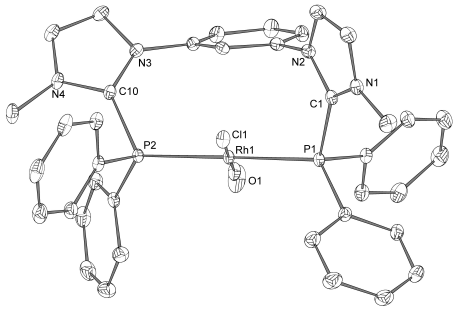
Inorg. Chem. **2011**, *50*, 10810.



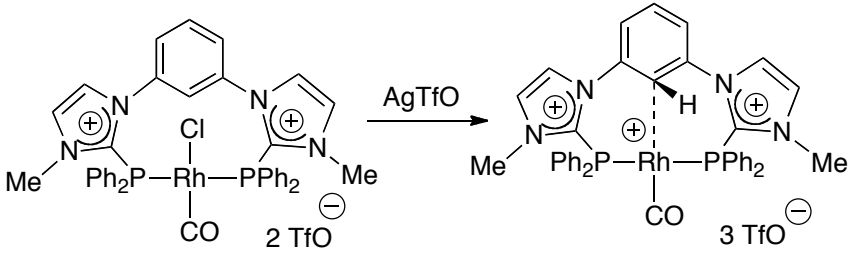
Dipolar pincer Ni complex

Chem. Commun. **2012**, *48*, 10446.

Unexpected P(CH)P pincer rhodium(I) complex

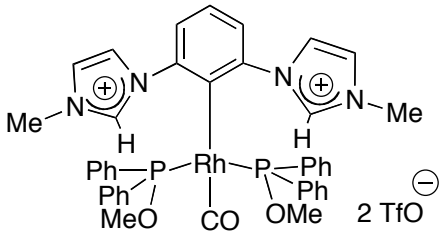


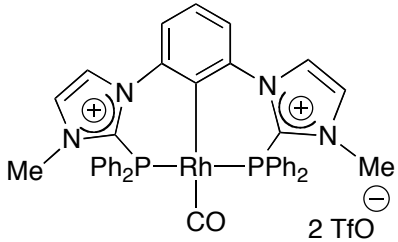
P(CH)P pincer



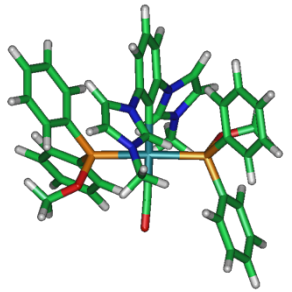
MeOH

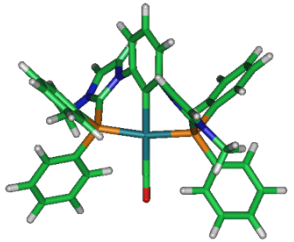
Base



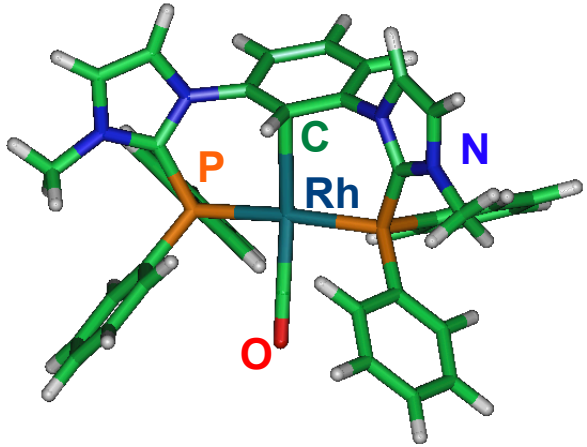


« Open » pincer





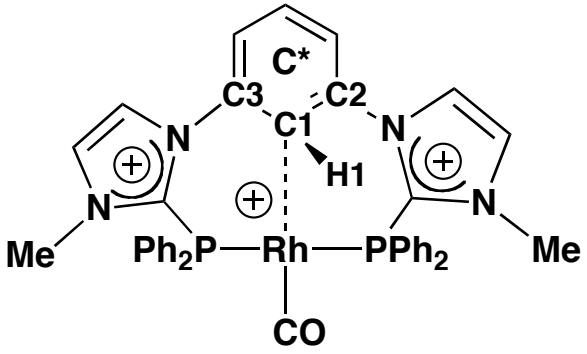
PCP pincer



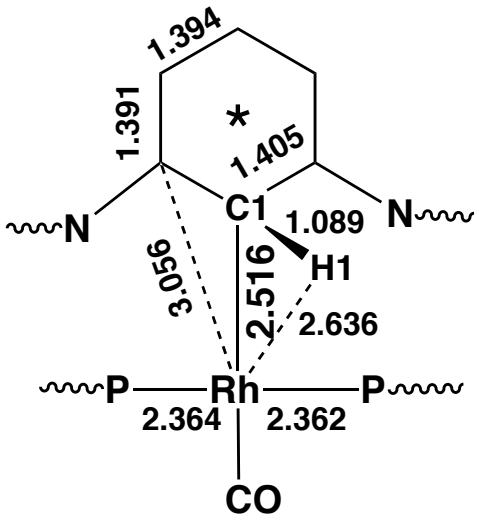
PCM - B3PW91/6-31G/LANL2DZ*(Rh)**

Inorg. Chem. **2013**, *52*, 48.

Calculated structure of the P(CH)P pincer



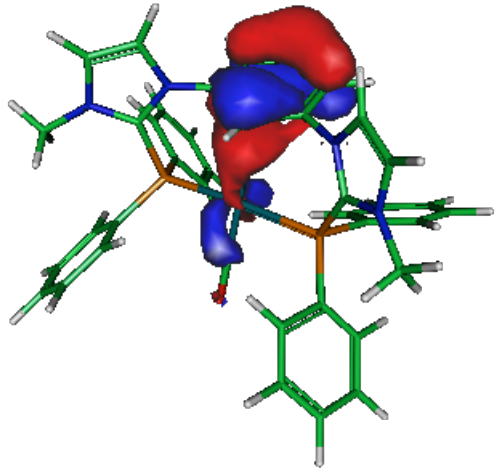
Geometry



Quasi-C_s symmetry

Bond lengths in Å

Molecular orbital analysis



HOMO-14

Rh-C and Rh-H bond lengths

Shorter than the sum of vdW radii :

Rh = 2.00 Å C = 1.70 Å, H = 1.10 Å

Sum of covalent radii of Rh and C = 2.10 Å

Out-of-plane C1-H1 bending

C*-C1-H1 = 169.7°

NBO analysis

Donor-acceptor interactions :

$\sigma_{C1\text{-}H1}$ –> LP*(Rh) : $E^{(2)}$ = 1.8 kcal/mol

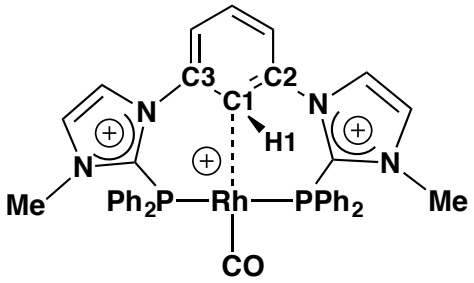
$\pi_{C1\text{-}C3}$ –> LP*(Rh) : $E^{(2)}$ = 5.5 kcal/mol

–> Weak Rh-phenylene interaction

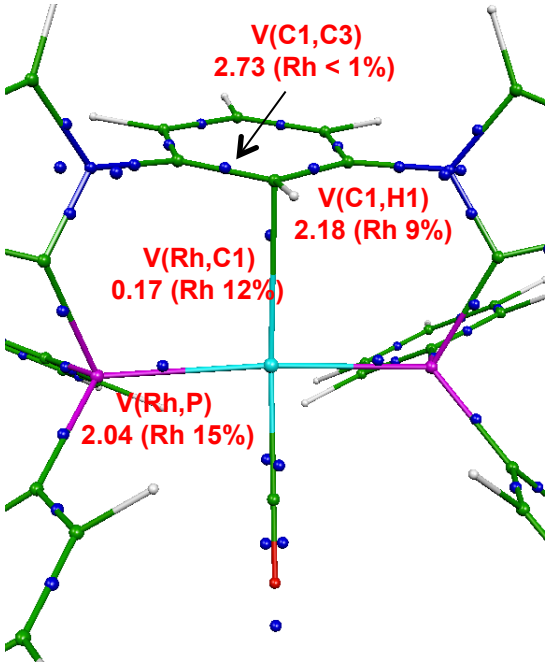
PCM - B3PW91/6-31G**/LANL2DZ*(Rh)

Inorg. Chem. **2013**, *52*, 48.

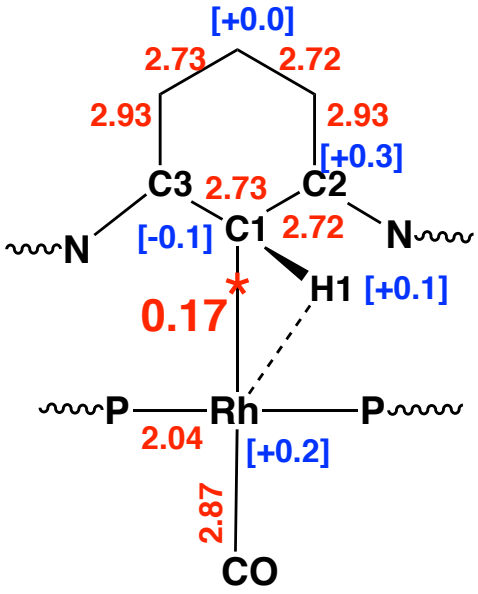
ELF topological analysis of the P(CH)P pincer



Disynaptic V(Rh,C1) basin of low population



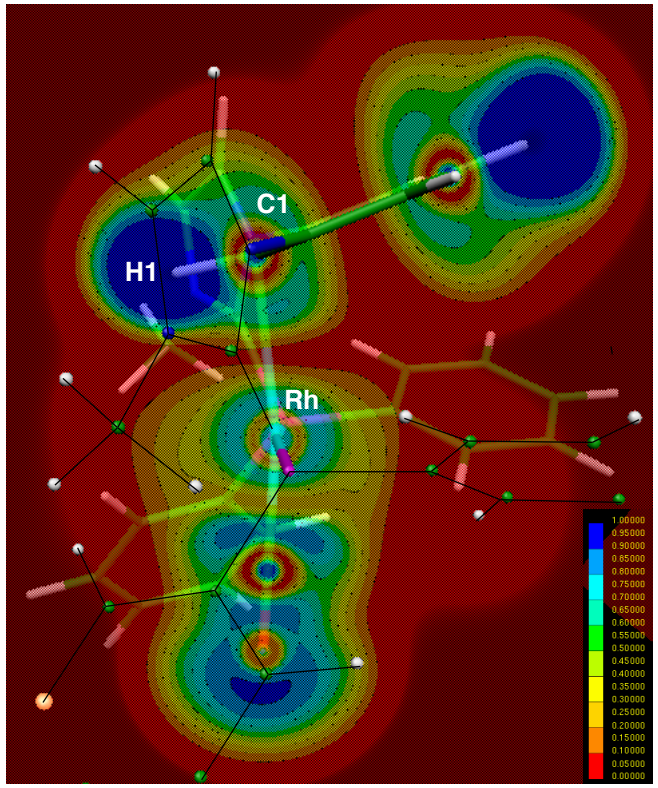
Valence attractors in blue



ELF populations

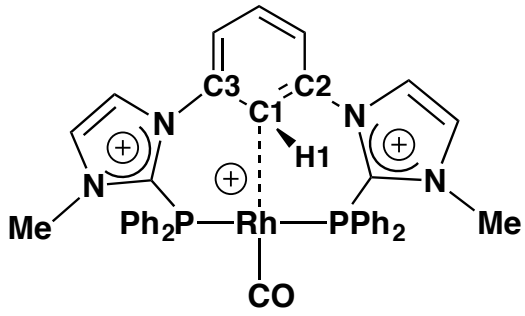
AIM charges

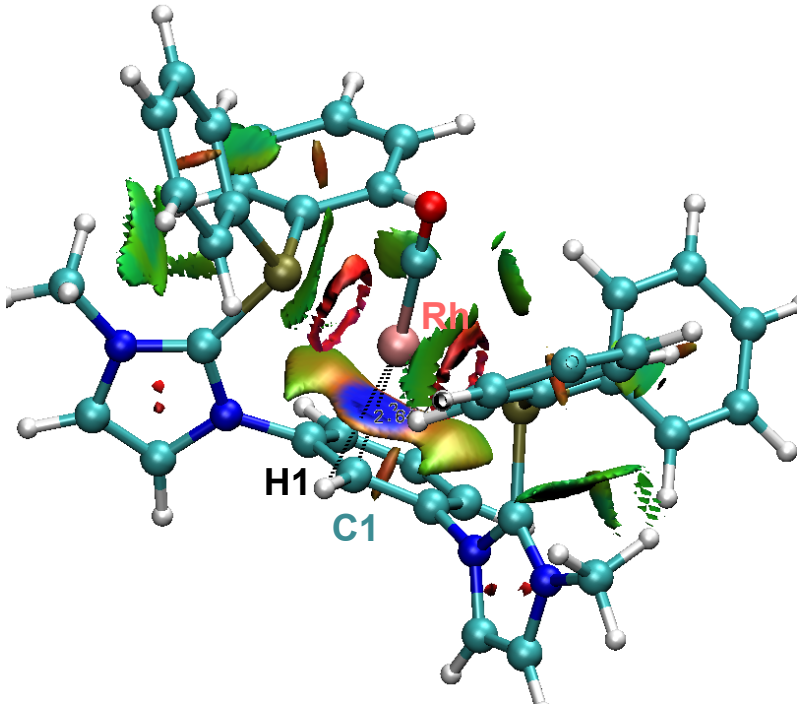
ELF map in the Rh-C1-H1 plane

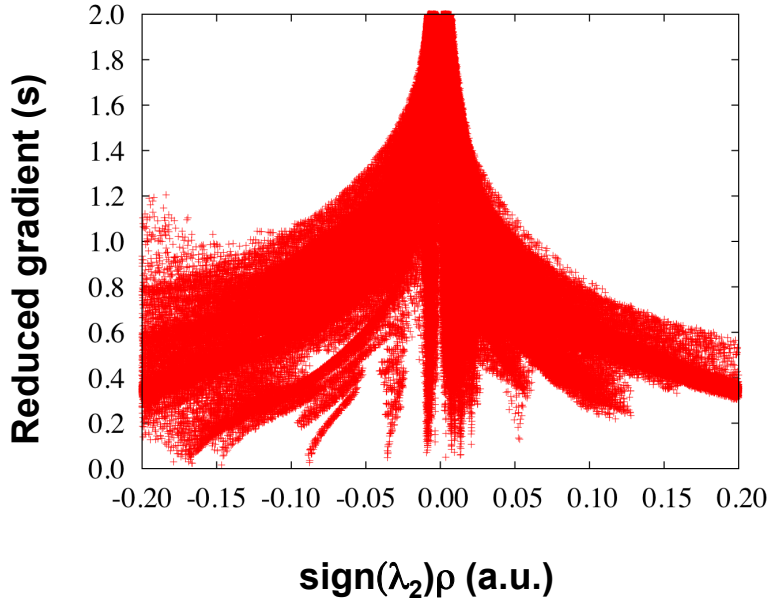


B3PW91/6-31G**/LANL2DZ*(Rh)//PBE-D3/6-31G**/LANL2DZ*(Rh)

NCI analysis of the P(CH)P pincer







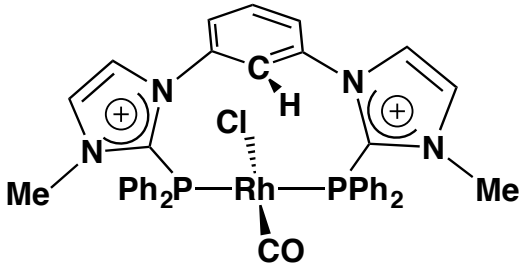
η^1-C or η^2-C,H agostic?

B3PW91/6-31G**/DGDZVP(Rh)//PCM - B3PW91/6-31G**/LANL2DZ*(Rh)

Julia Contreras-Garcia

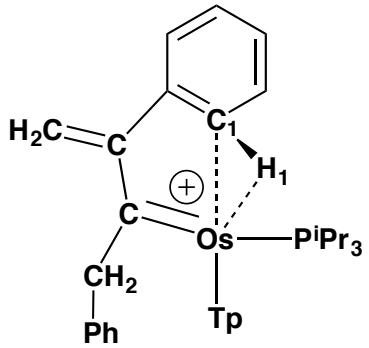
Series of related complexes

Chlorinated precursor : no interaction?



X-ray structure

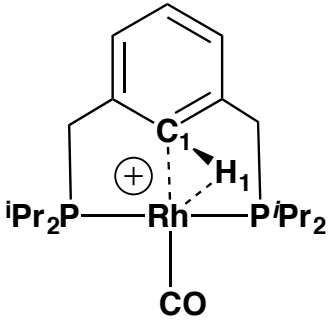
Strong η^2-C,H agostic interaction



X-ray structure

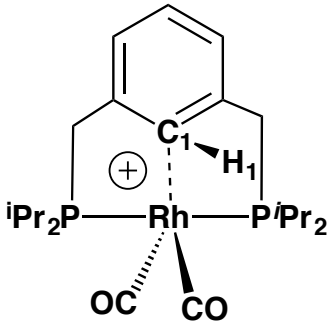
Lopez *et al*. *Organometallics* **2008**, *27*, 3547.

A : η^2-C,H agostic interaction



X-ray structure

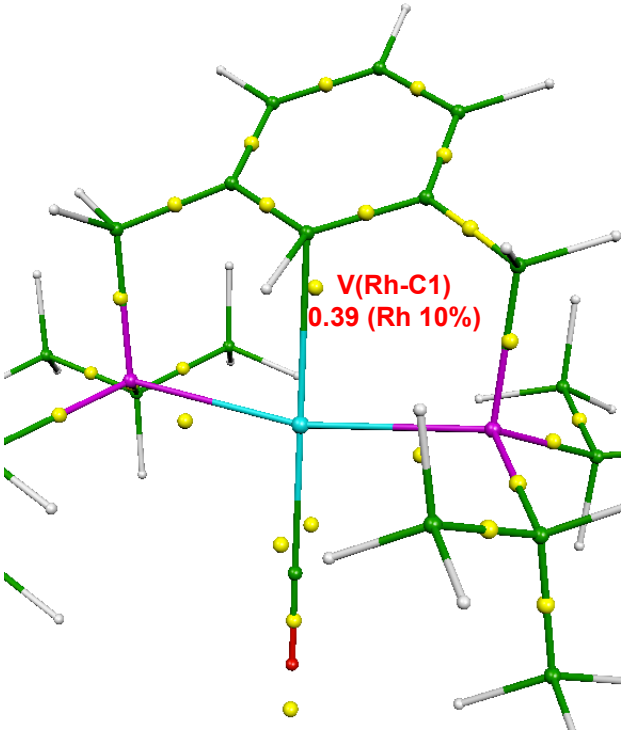
B : weak η^1-C interaction



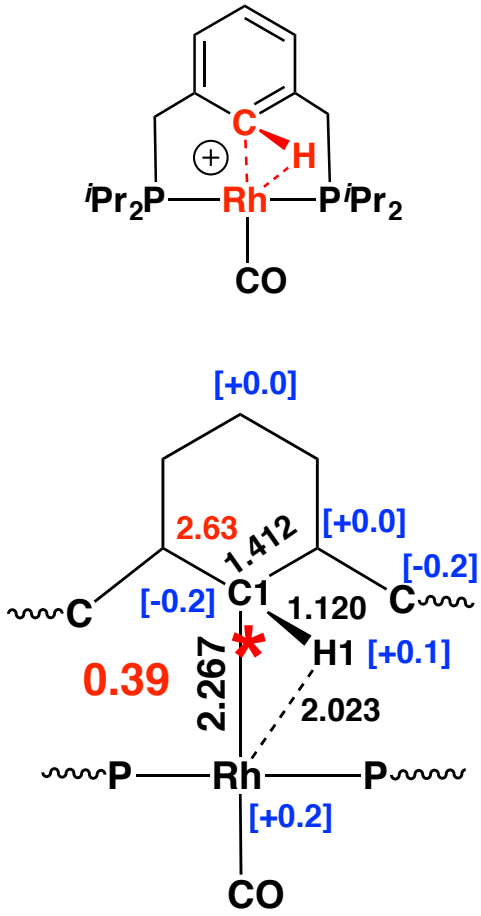
Calculated structure

Milstein *et al*. *Chem*. *Eur*. *J*. **2010**, *16*, 328.

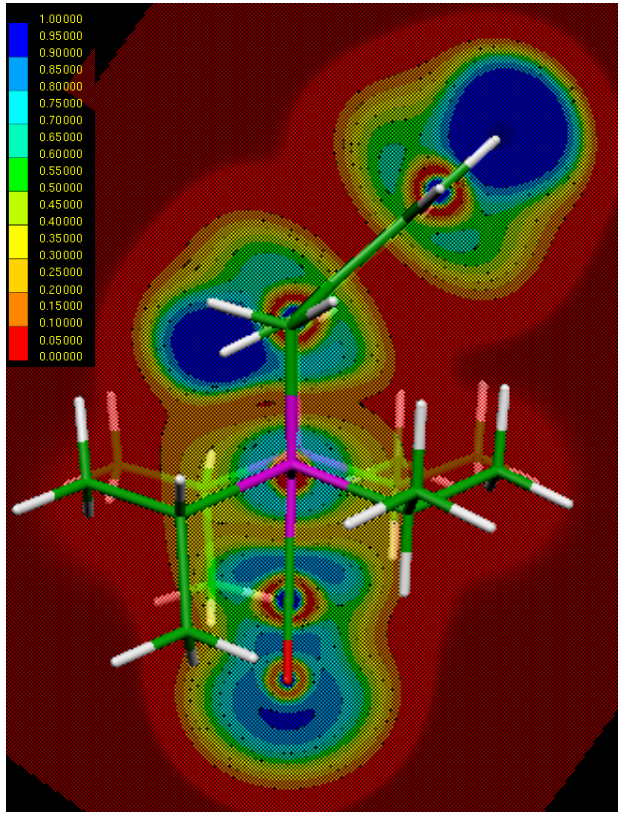
ELF analysis of P(CH)P pincer A



Valence attractors in yellow



Distances in Å
ELF populations
AIM charges

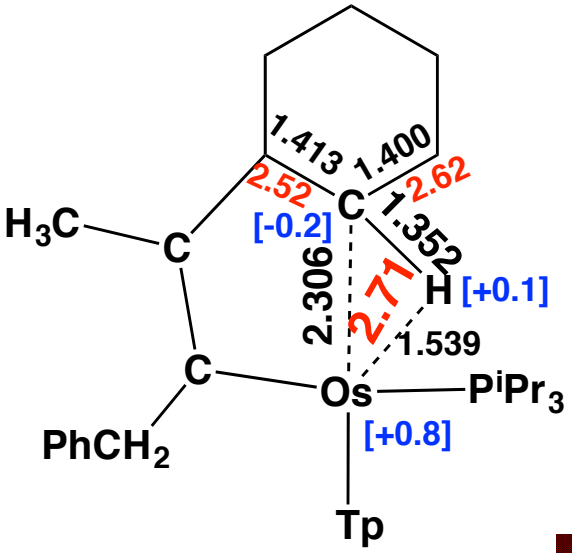


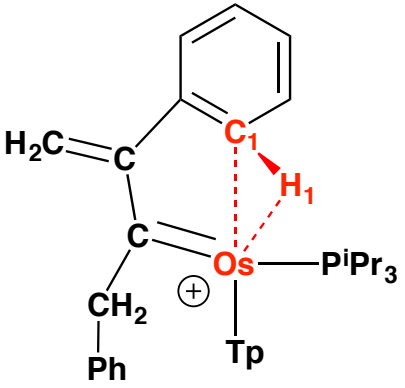
ELF map in the Rh-C1-H1 plane

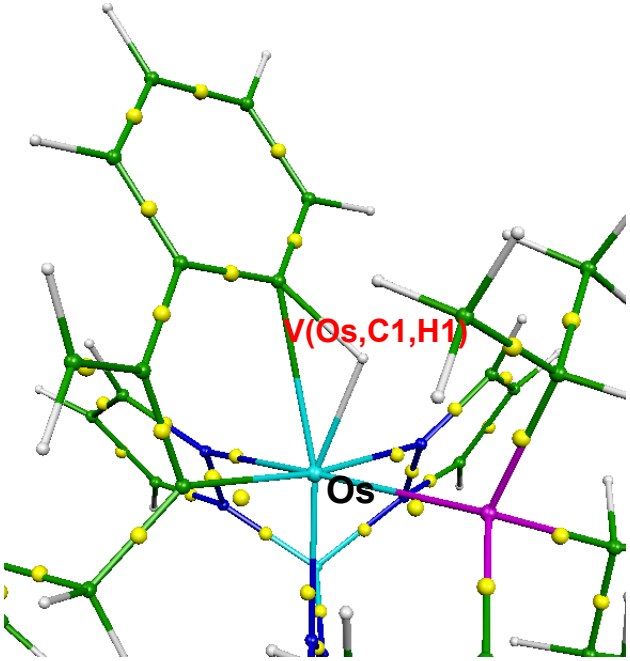
B3PW91/6-31G**/LANL2DZ*(Rh)//PBE-D3/6-31G**/LANL2DZ*(Rh)

ELF analysis of osmium complex

Distances in Å
ELF populations
AIM charges

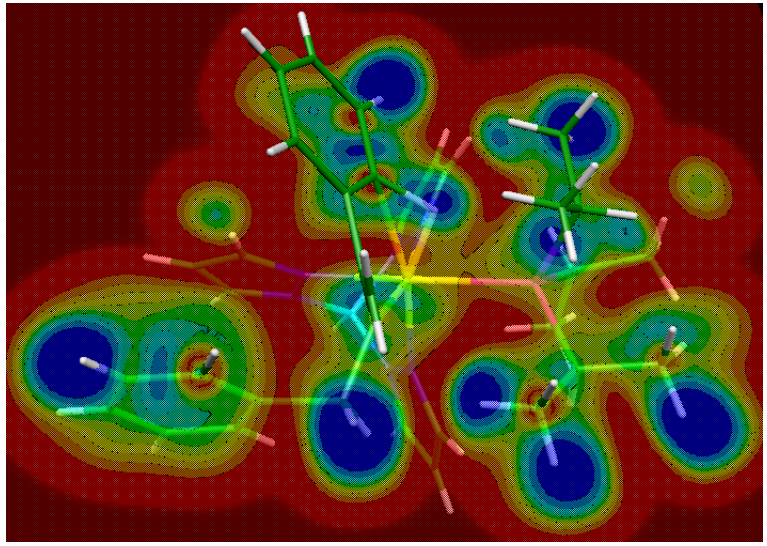






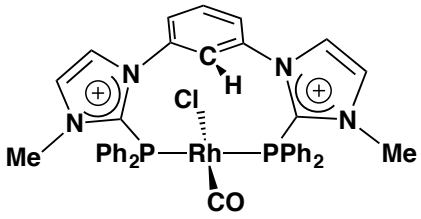
Trisynaptic basin
V(Os,C1,H1)
2.71
Os(13%)
C(44%) H(43%)

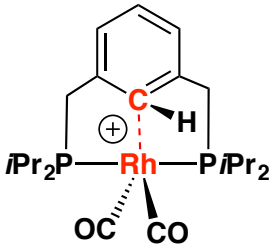
Attractor ≈ H1

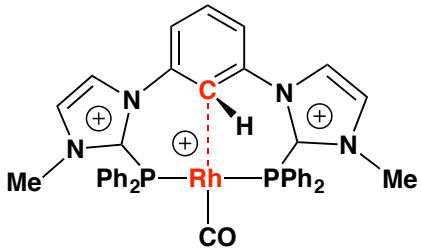


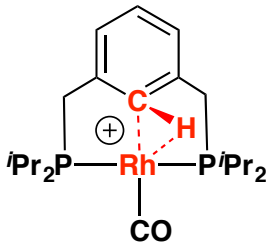
B3PW91/6-31G**/LANL2DZ*(Os)

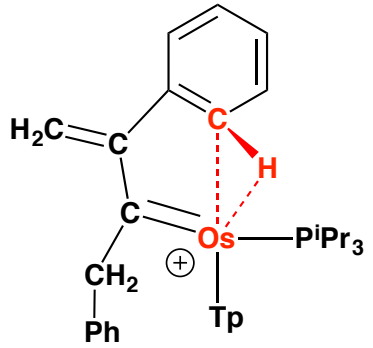
ELF analysis



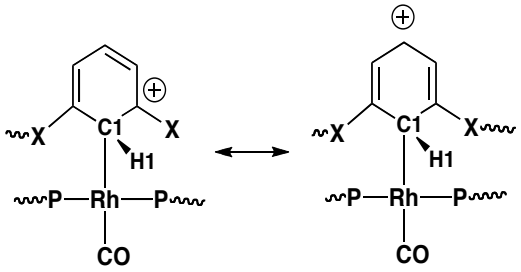


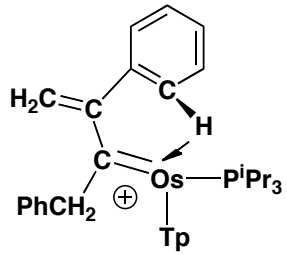






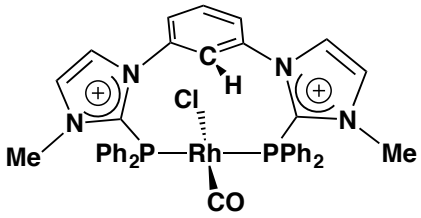
2.755	2.599	2.508	2.267	2.306	M-C
1.088	1.100	1.095	1.143	1.352	C-H
5.5°	6.4°	10.9°	18.5°	19.9°	bending
-	-	V(Rh,C) 0.17	V(Rh,C) 0.39	V(Os,C,H) 2.71	ELF
No interaction	No interaction	η1-C	η1-C	η2-(C,H)	

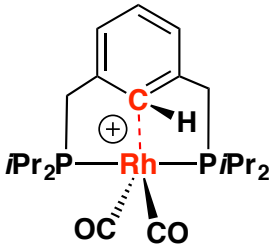


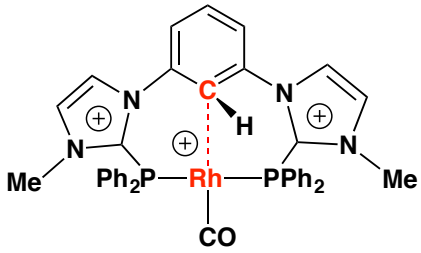


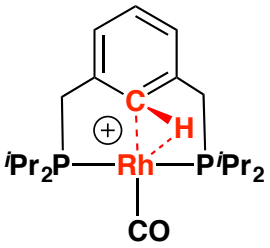
B3PW91/6-31G**/LANL2DZ*(Rh)//PBE-D3/6-31G**/LANL2DZ*(Rh)

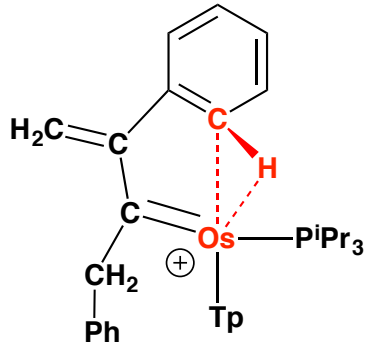
MCIs and AIM analysis











0.008 0.013	0.019 0.022	0.033 0.020	0.031 0.067	0.013 0.088	C-C-M H-C-M

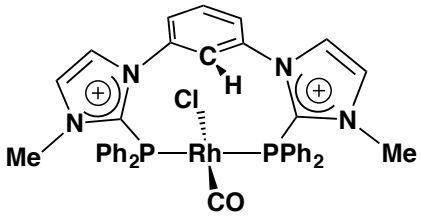
Increasing interaction

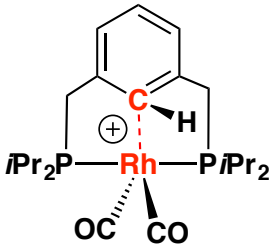
					M-C BCP
0.028 (-0.017)	0.036 (-0.023)	0.036 (-0.028)	0.067 (-0.065)	0.283 (-0.054)	ρ (Δρ)

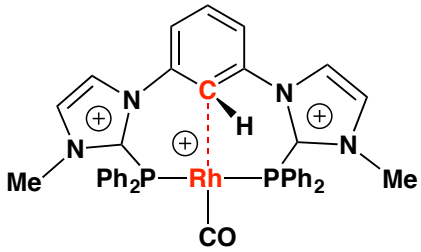
B3PW91/6-31G**/LANL2DZ*(Rh)//PBE-D3/6-31G**/LANL2DZ*(Rh)

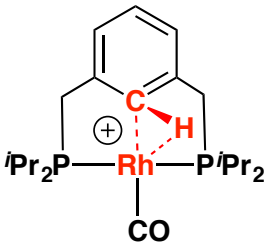
Jordi Poater

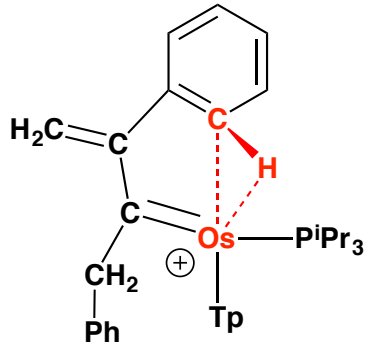
Comparison with NBO











0.008	0.019	0.033	0.031	0.013	C-C-M
0.013	0.022	0.020	0.067	0.088	H-C-M
0.028	0.036	0.036	0.067	0.283	AIM
(-0.017)	(-0.023)	(-0.028)	(-0.065)	(-0.054)	

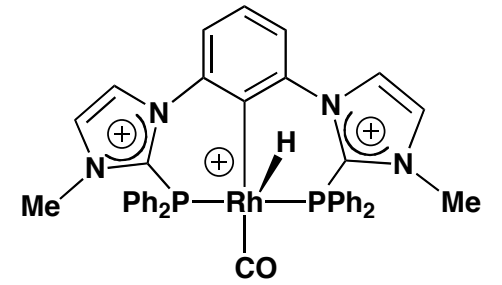
Increasing interaction

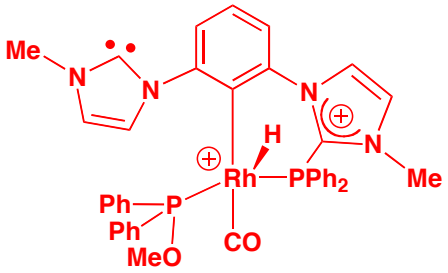
NBO : $E^{(2)}$ (kcal/mol)

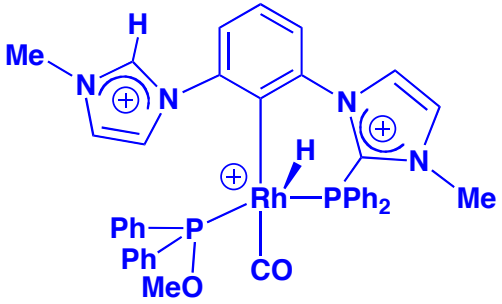
-	σ_{C-H} –> LP*(Rh) : 4.0	σ_{C-H} –> LP*(Rh) : 1.8	σ_{C-H} –> BD*(Rh-CO)	σ_{C-H} –> LP*(Os)
	π_{C-C} –> LP*(Rh) : 6.0	π_{C-C} –> LP*(Rh) : 5.5	27.6	112.6

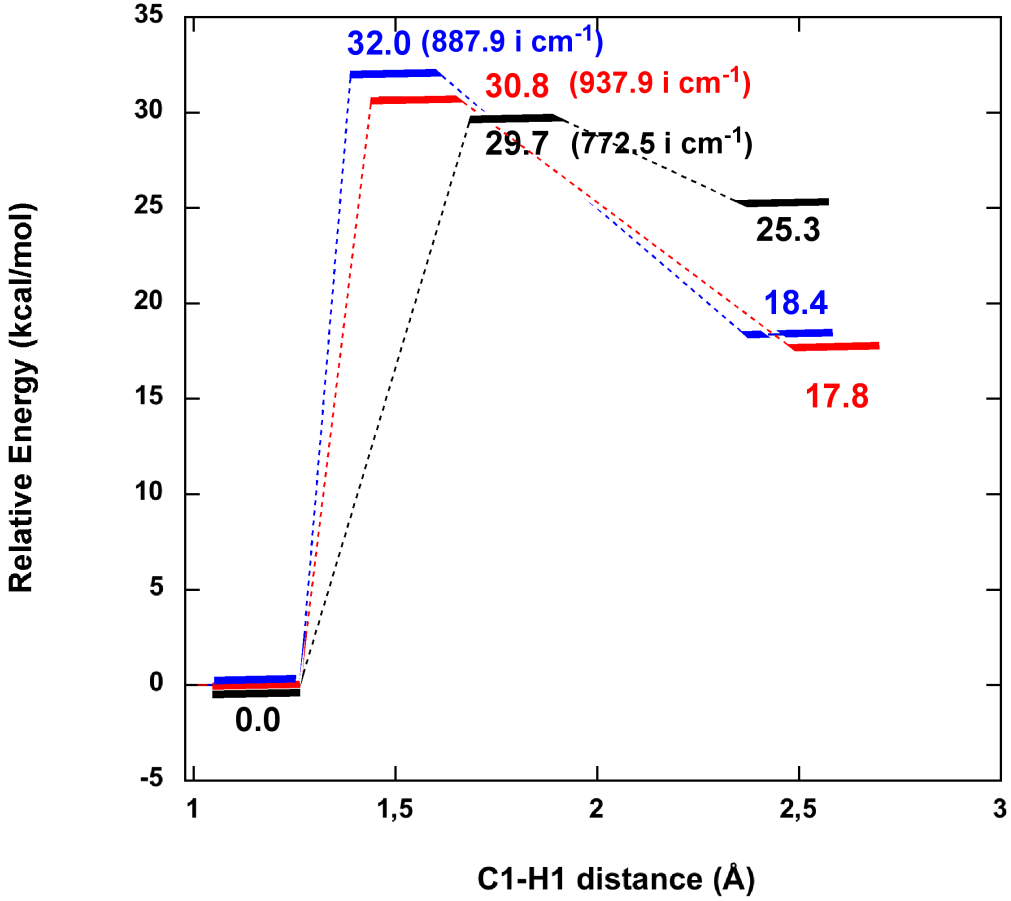
B3PW91/6-31G**/LANL2DZ*(Rh)//PBE-D3/6-31G**/LANL2DZ*(Rh)

Arrested C-H oxidative addition intermediate ?









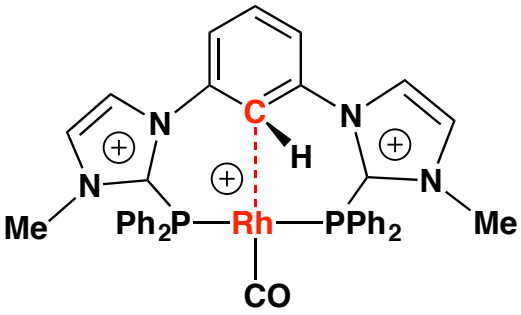
High C-H oxidative addition barriers

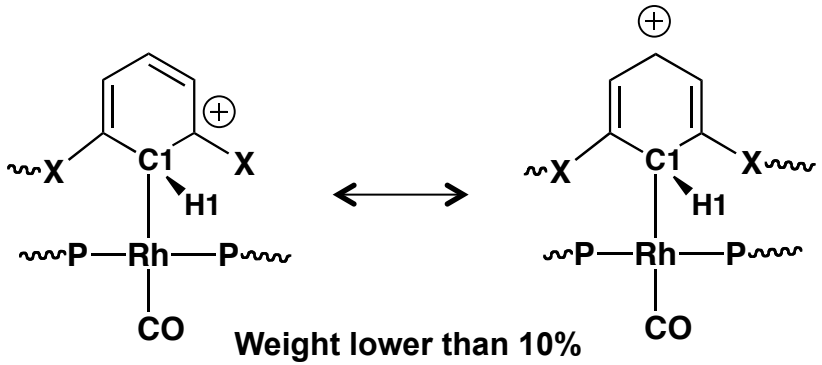
PCM - B3PW91/6-31G/LANL2DZ*(Rh)**

Inorg. Chem. **2013**, *52*, 48.

Conclusions

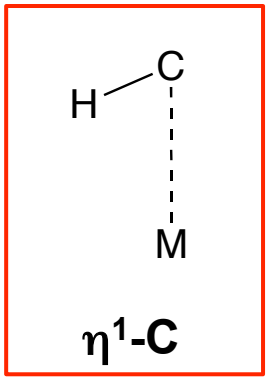
- $\eta 1$-C interaction in the P(CH)P pincer complex



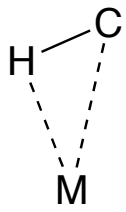


Weight lower than 10%

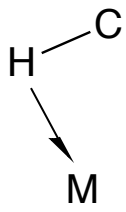
- **Missing entry in the agostic - anagostic series**

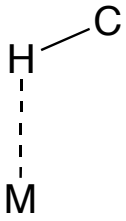


η^1-C



Agostic



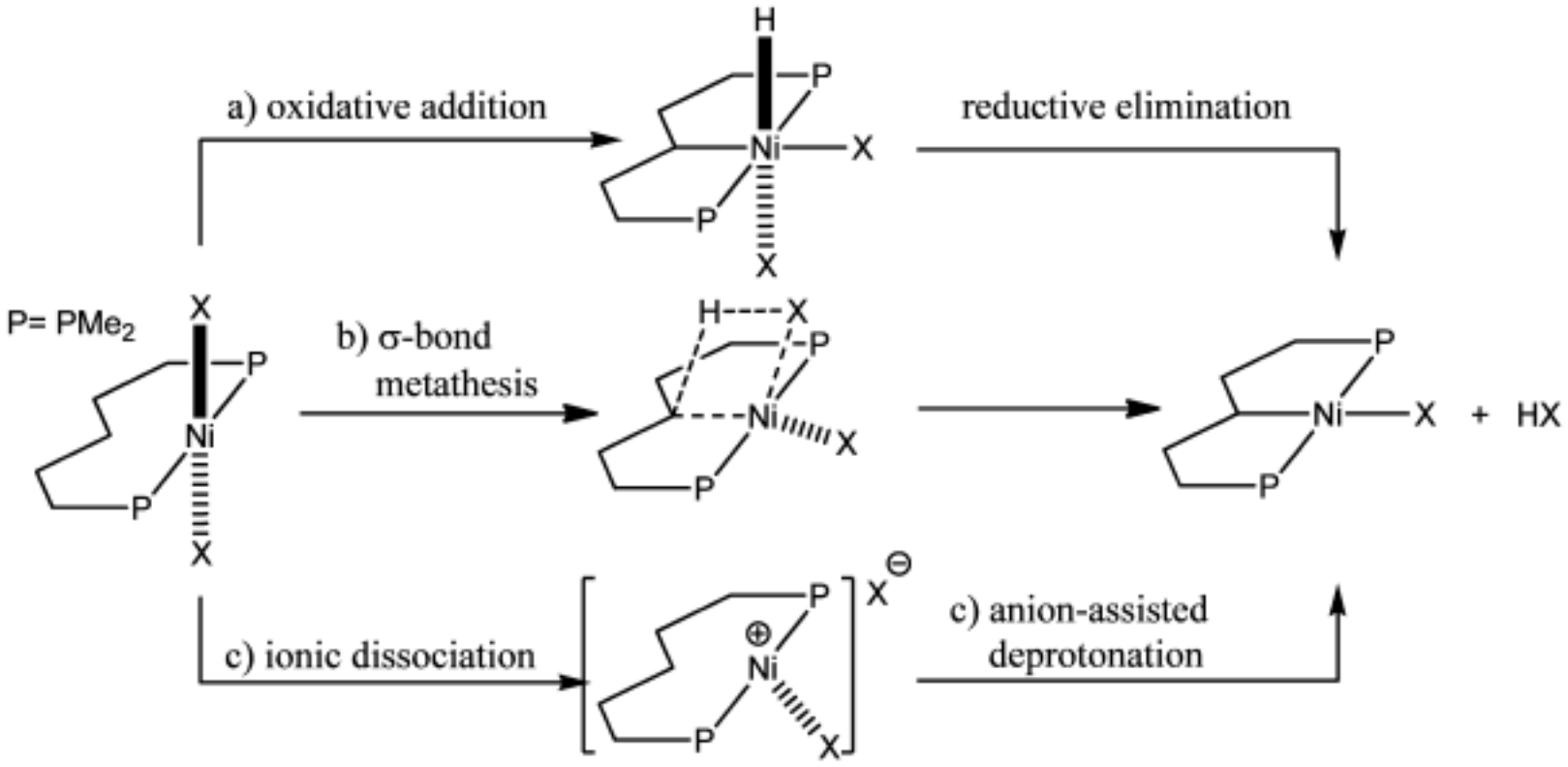


Anagostic

Brookhart *et al*. *PNAS* **2007**, *104*, 6908.

Conclusions

- **Arrested C-H oxidative addition or alternative pathway?**



Zargarian *et al*. *Organometallics* **2012**, *31*, 6041.

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Remi Chauvin

Yves Canac

Davit Zargarian (Montréal)

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Jordi Poater (Girona)

Miquel Solà (Girona)

Julia Contreras-Garcia

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