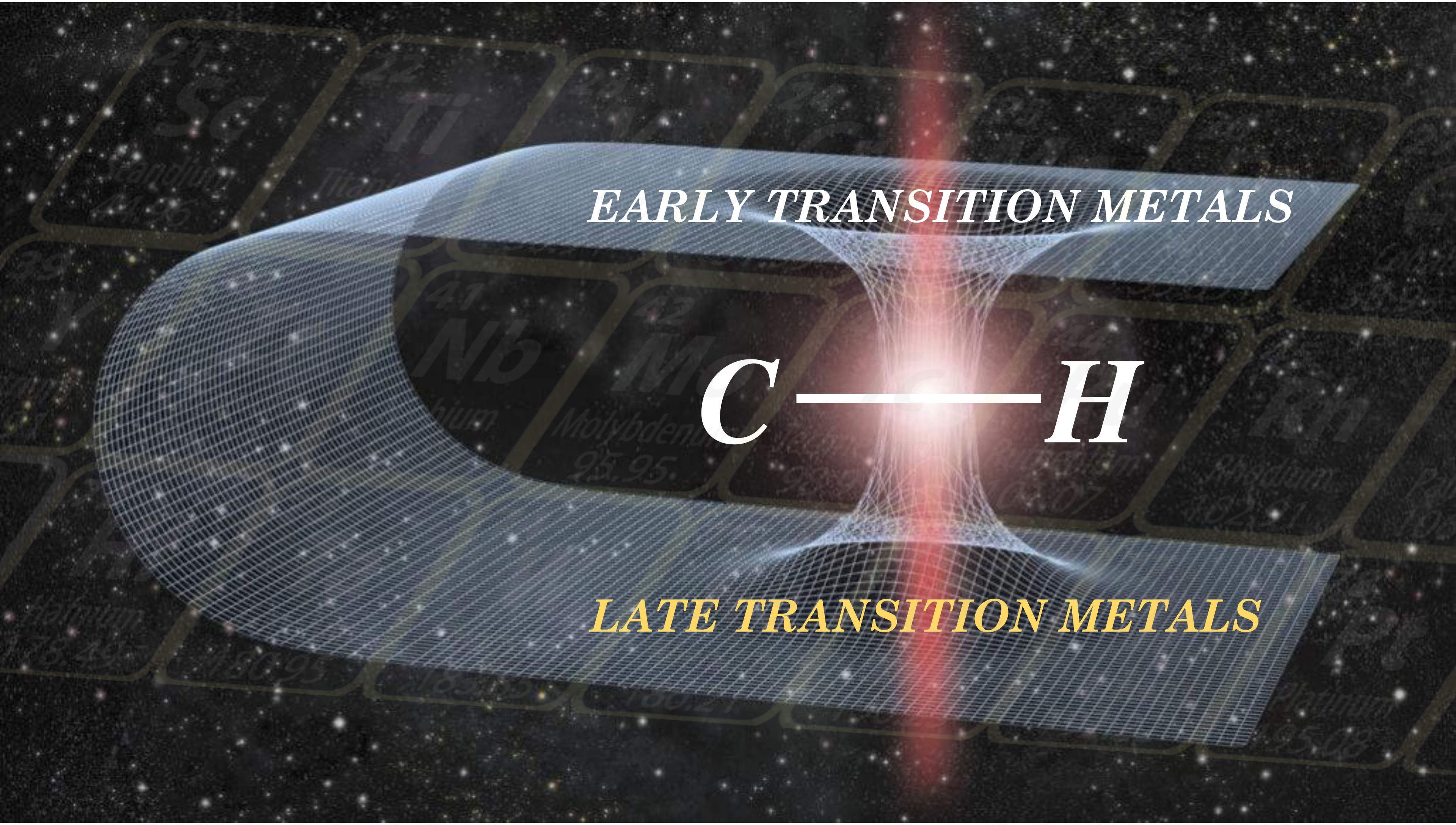
Myth or Reality?

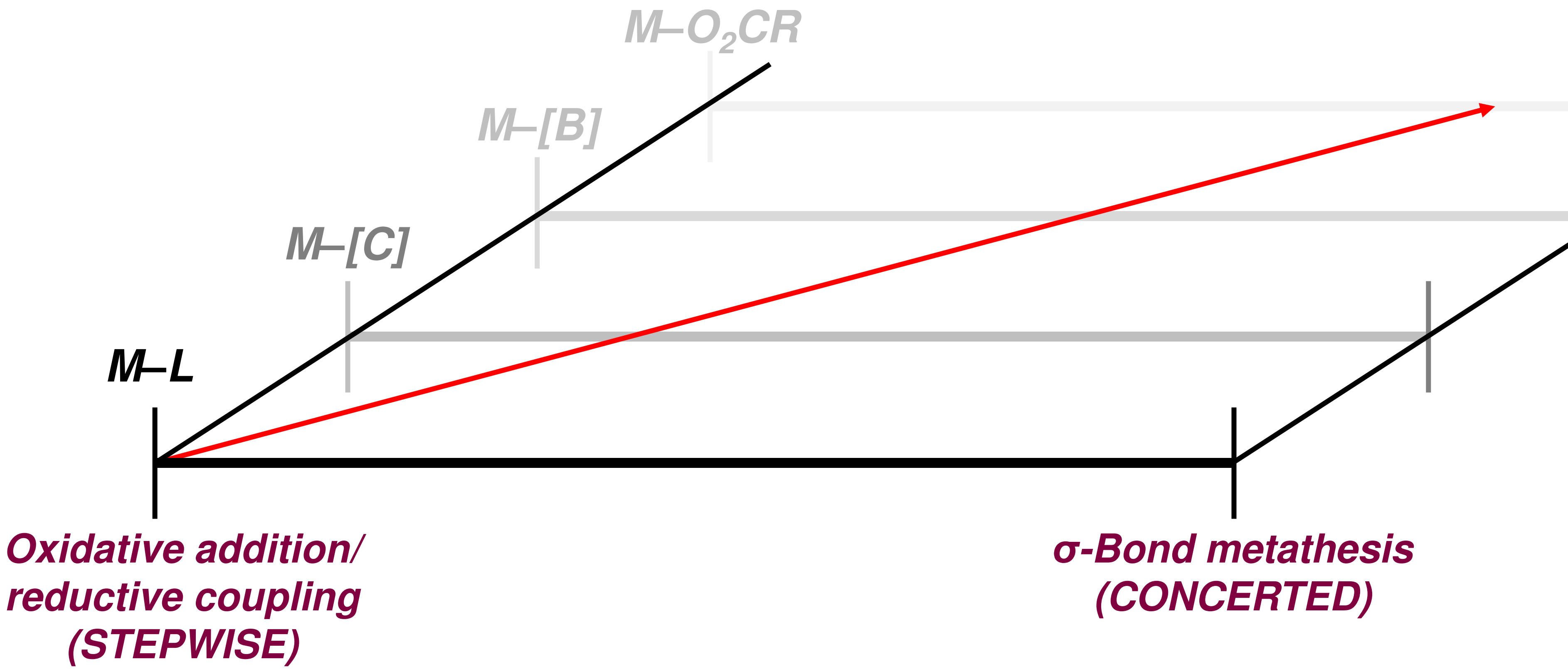
σ-Bond Metathesis by $d^{n>0}$ Transition Metals



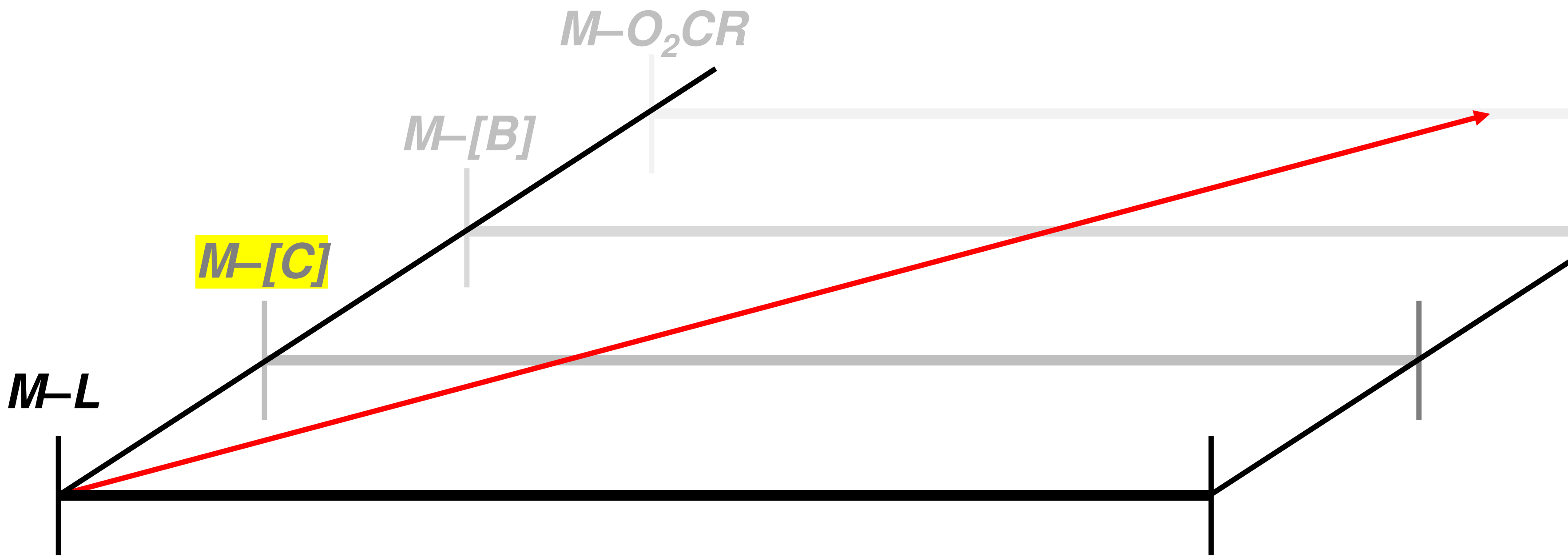
A Topical Seminar

September 27th 2022

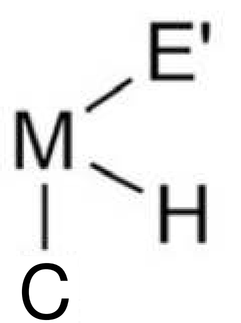
The core of this seminar



The core of this seminar

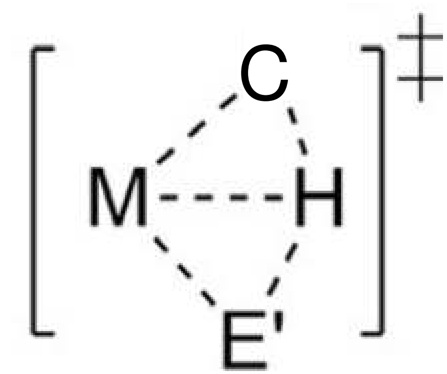


Oxidative addition/ reductive coupling (STEPWISE)



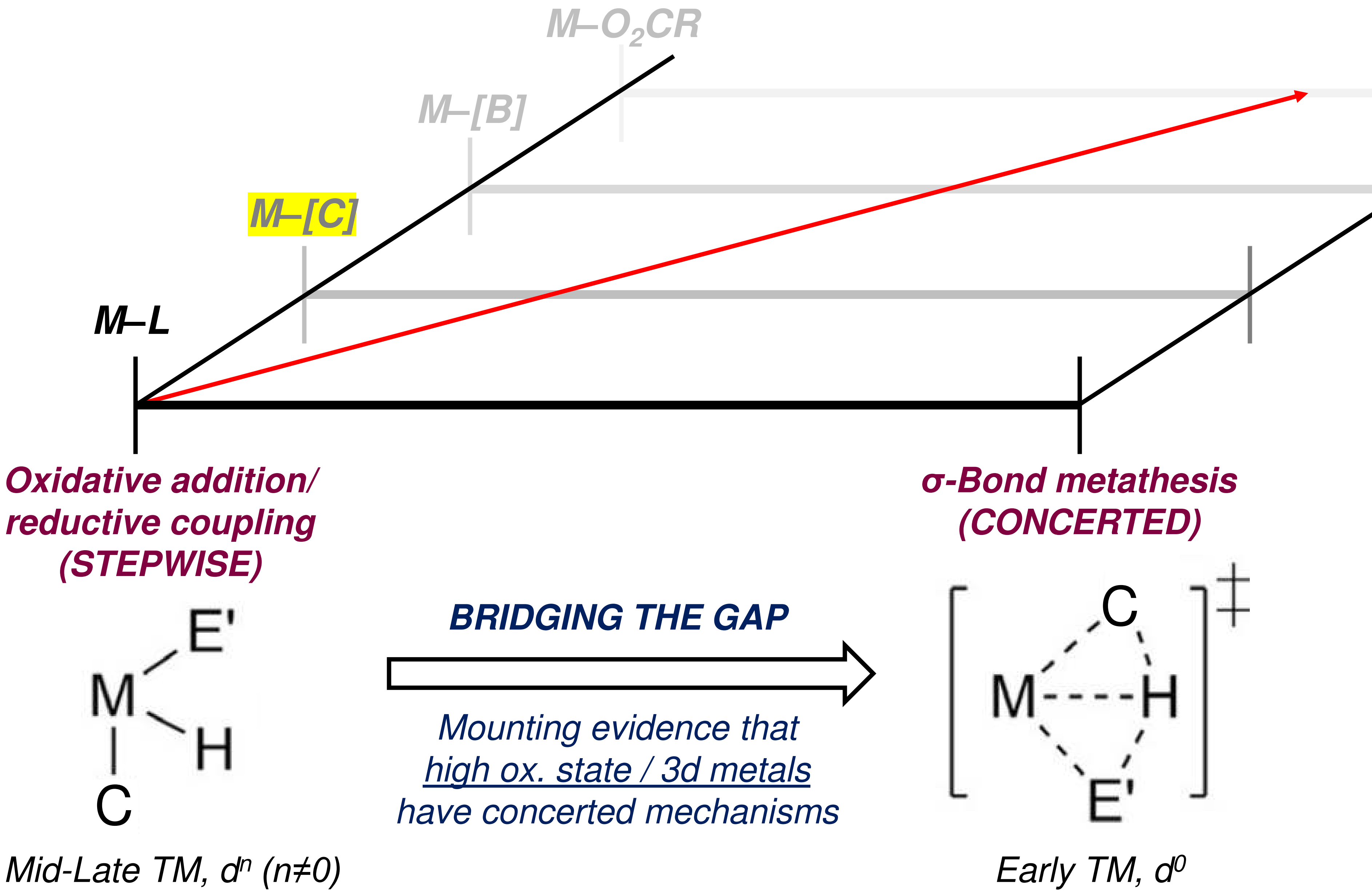
Mid-Late TM, d^n ($n \neq 0$)

σ-Bond metathesis (CONCERTED)



Early TM, d^0

The core of this seminar



The Chirik Group: Why Should We Care?

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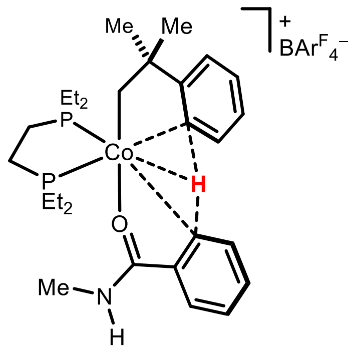
Late 3d metals have <u>less</u> / <u>fewer</u> accessible high oxidation states

Redox-neutral operations become more likely / significant

(P2)Co(III): *proposed σ-CAM*



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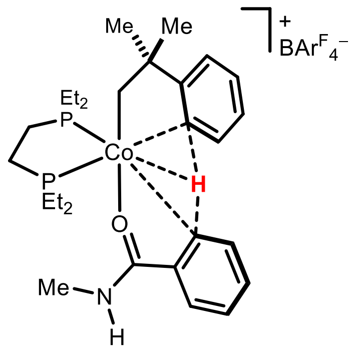
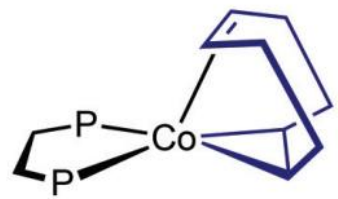
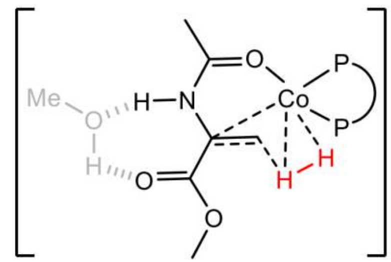


(P2)Co(II): *metallacyclopropane*



Can. J. Chem. **2021**, *99*, 193.

Hydrogenation TS



JACS **2022**, *144*, 15764.

M–H insertion <u>or</u> concerted hydrogenolysis of metallacycle?

The Chirik Group: Why Should We Care?

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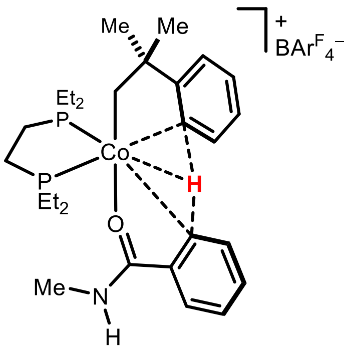
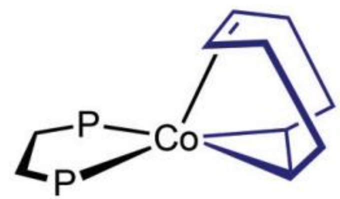
***(P2)Co(III):** proposed σ-CAM*

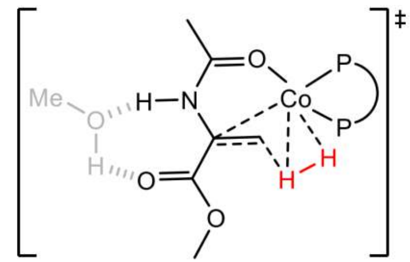


***(P2)Co(II):** metallacyclopropane*



Can. J. Chem. **2021**, *99*, 193.

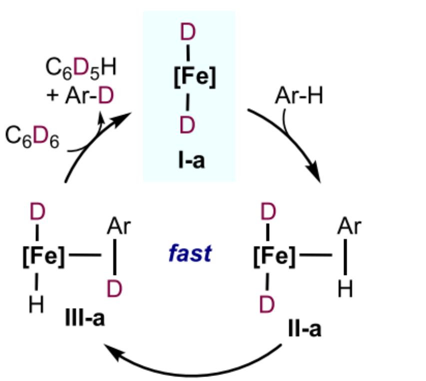
Hydrogenation TS



JACS **2022**, *144*, 15764.

M–H insertion or concerted hydrogenolysis of metallacycle?

***(CNC)Fe:** proposed σ-CAM*



ACS Catal. **2020**, *10*, 8640.

The Chirik Group: Why Should We Care?

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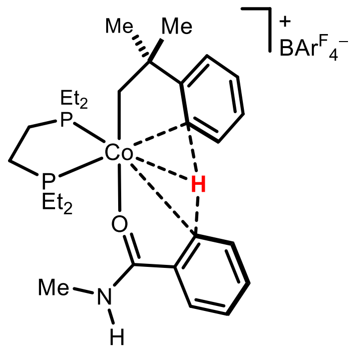

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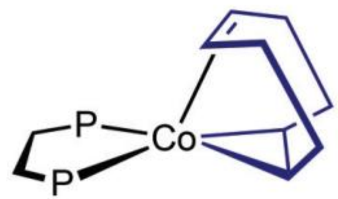
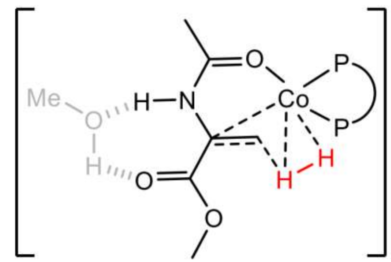


Can. J. Chem. **2021**, *99*, 193.

Hydrogenation TS



JACS **2022**, *144*, 15764.

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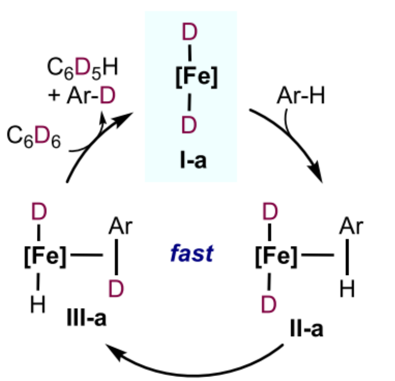
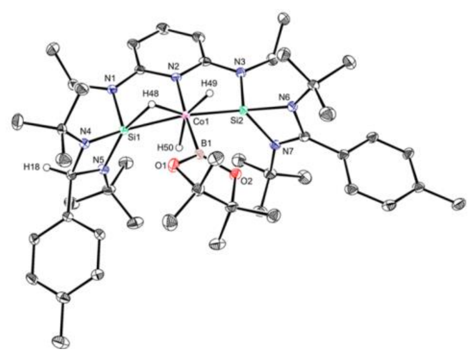


ACS Catal. **2020**, *10*, 8640.

***(SiNSi)Co:** Co(I) not observed*



ACS Catal. **2022**, *12*, 8877.

Analogy between Fe(II) & Co(III) HIE?

The Chirik Group: Why Should We Care?

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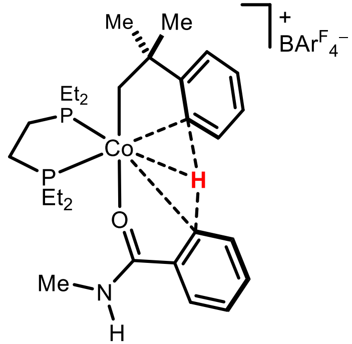
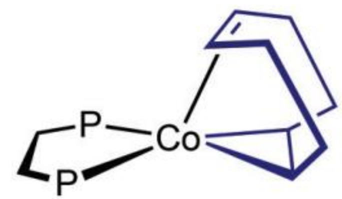
(P2)Co(III): *proposed σ-CAM*

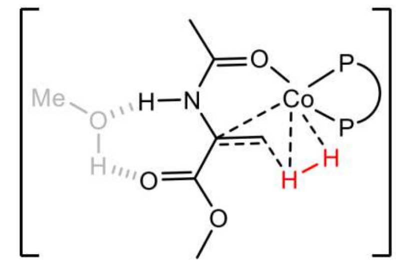


(P2)Co(II): *metallacyclopropane*



Can. J. Chem. **2021**, *99*, 193.

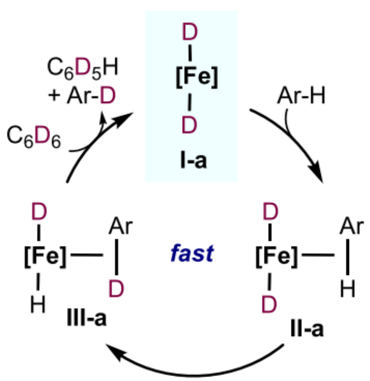
Hydrogenation TS



JACS **2022**, *144*, 15764.

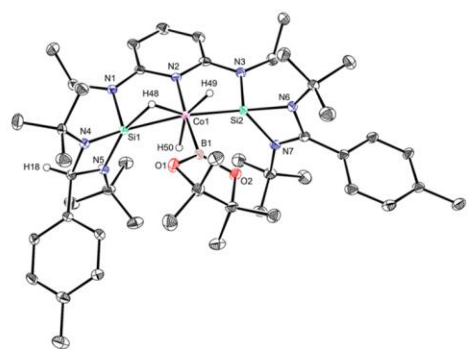
M–H insertion or concerted hydrogenolysis of metallacycle?

(CNC)Fe: *proposed σ-CAM*



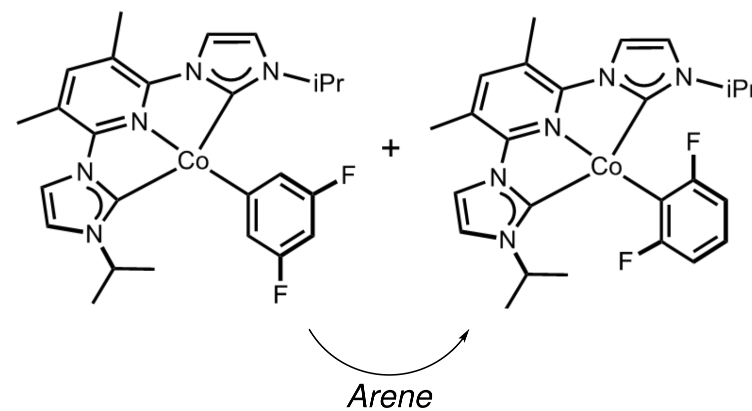
ACS Catal. **2020**, *10*, 8640.

(SiNSi)Co: *Co(I) not observed*



ACS Catal. **2022**, *12*, 8877.

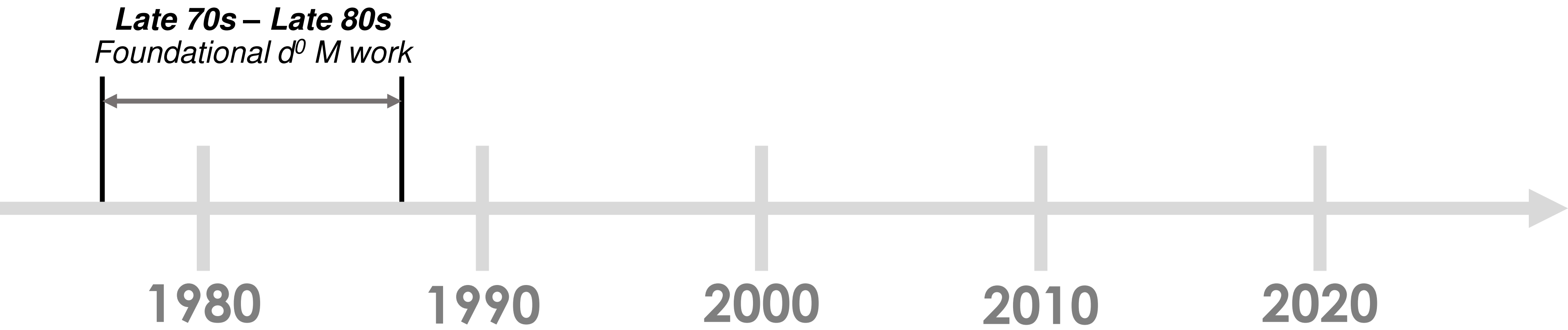
(ACNC)Co: *Co(III) not observed*



Analogy between Fe(II) & Co(III) HIE?

Arene metathesis: Co(III)–H intermediate?

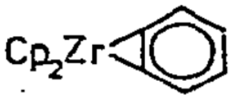
History


Late 70s – Late 80s
Foundational d^0 M work
1980
1990
2000
2010
2020

History

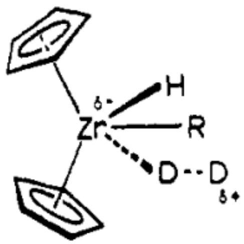
d^0 M C–H activation

1977: Erker[1]

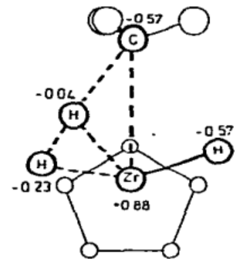


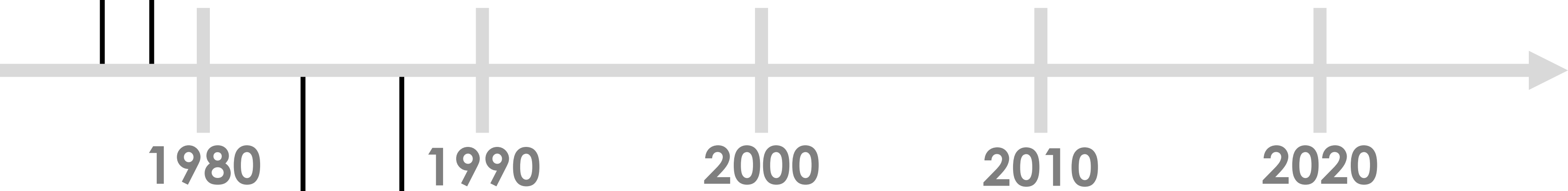
Hydrogenolysis of d^0 M–alkyl

1978: Schwarz[2]



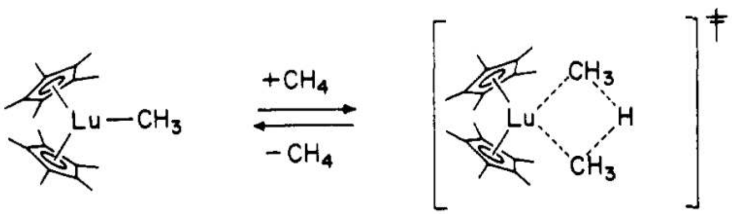
1979: Brintzinger[3]





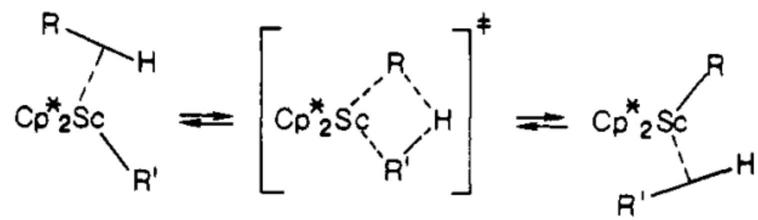
Methane exchange (Lu, Y)

1983: Watson[4]



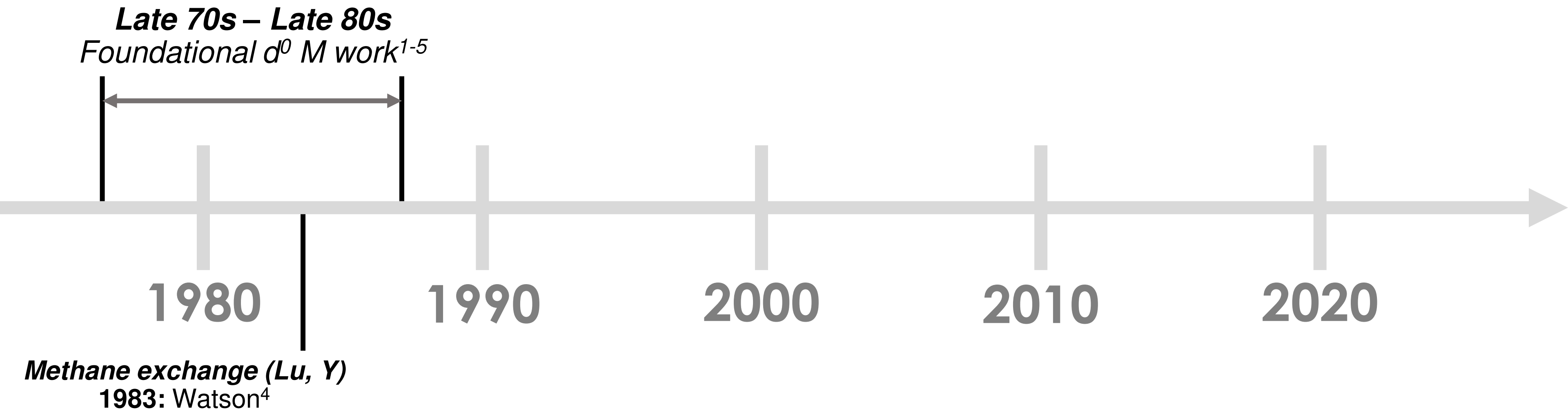
"σ-Bond metathesis"

1987: Bercaw[5]



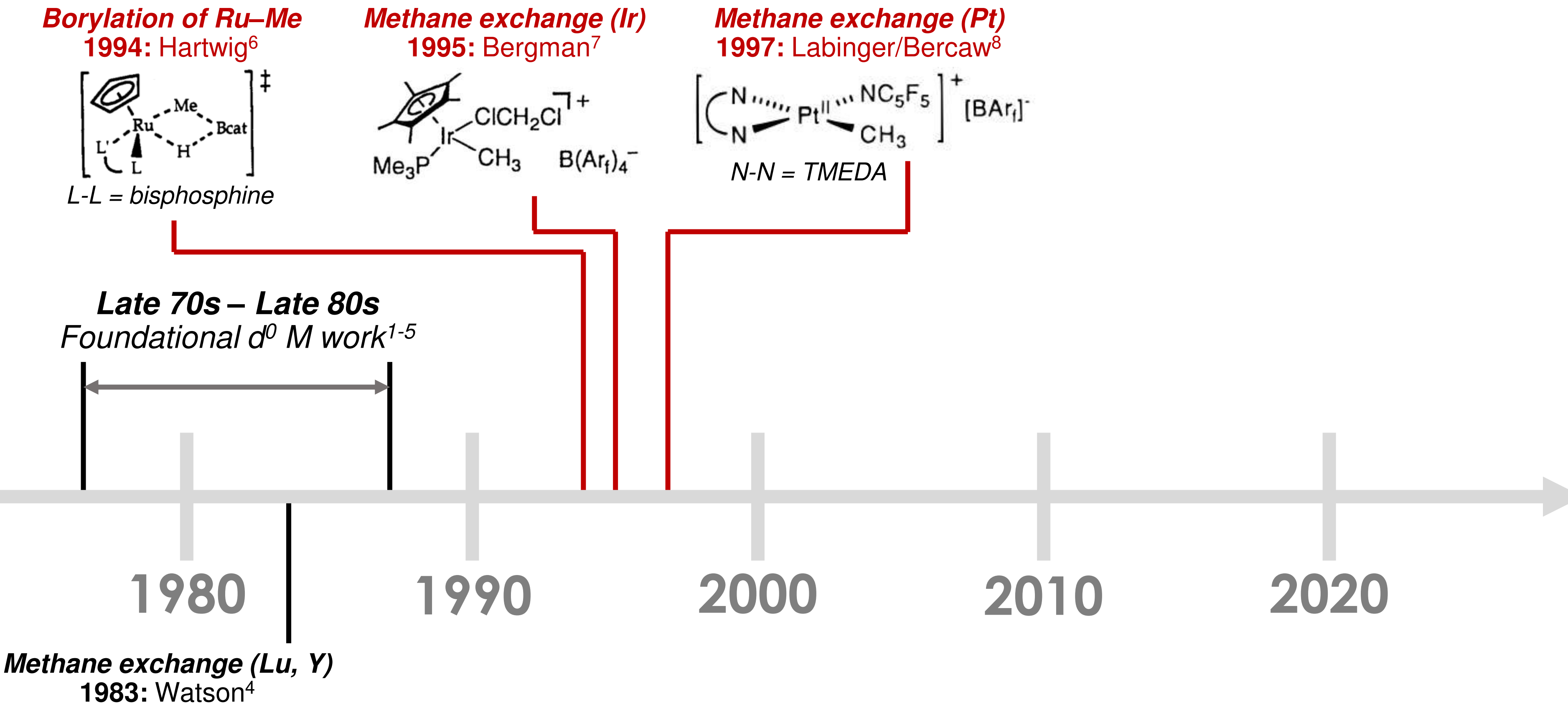
(1) Erker, G. *JOMC* **1997**, *134*, 189. (2) Schwartz, J. *JACS* **1978**, *100*, 3246. (3) Brintzinger, H. H. *JOMC* **1979**, *171*, 337. (4) Watson, P. L. *JACS* **1983***, 105*, 6491. (5) Bercaw, J. E. *JACS* **1987**, *109*, 203.

History



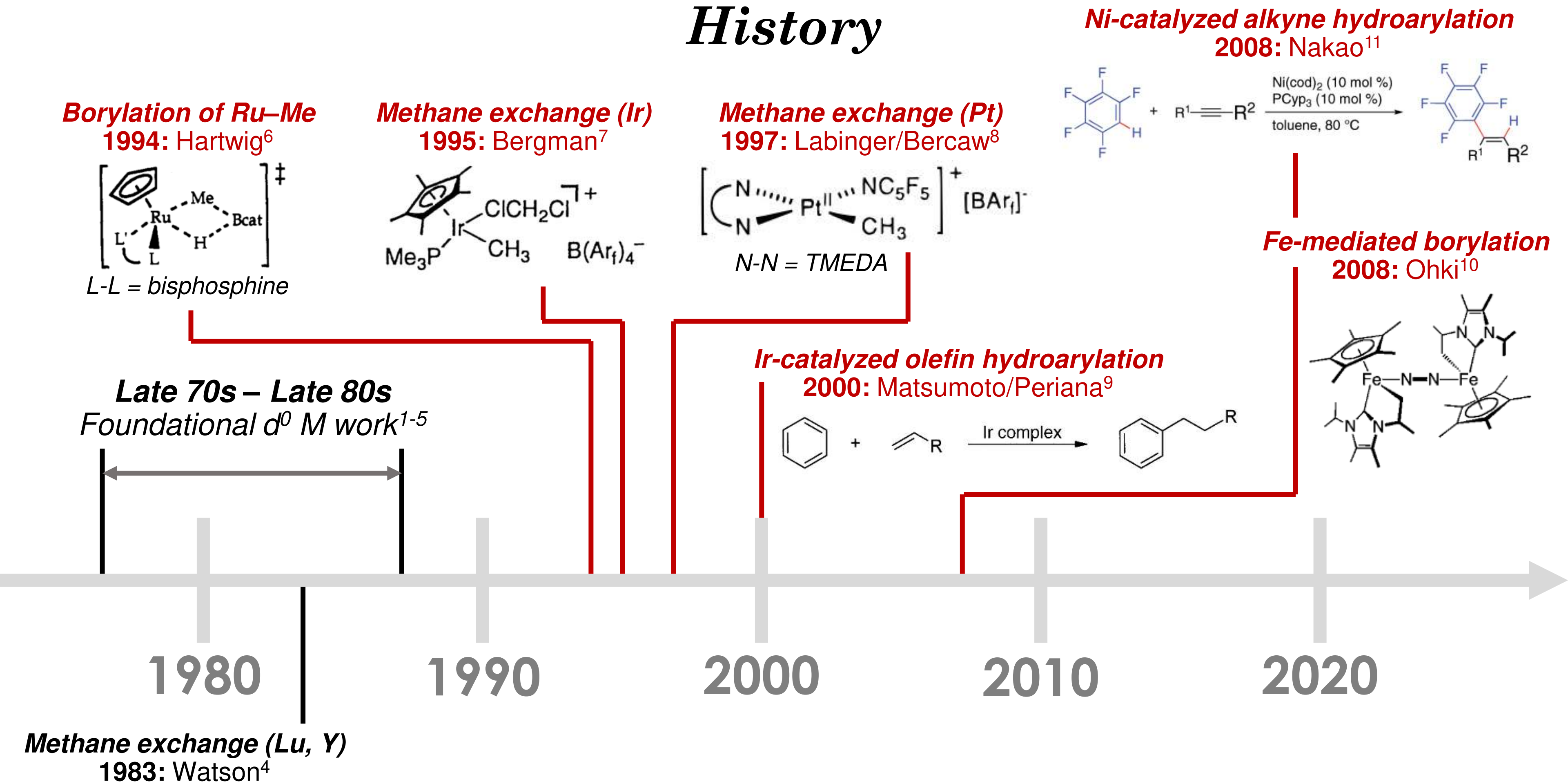
(6) Hartwig, J. F. *JACS* **1994**, *116*, 1839. (7) Bergman, R. G. *Science* **1995**, *270*, 1970. (8) Labinger, J. A.; Bercaw, J. E. *JACS* **1997**, *119*, 848. (9) Matsumoto, T.; Periana, R. A. *JACS* **2000**, *122*, 7414. (10) Ohki, Y. *JACS* **2008**, *130*, 17174. (11) Nakao, Y. *JACS* **2008**, *130*, 16170.

History



(6) Hartwig, J. F. *JACS* **1994**, *116*, 1839. (7) Bergman, R. G. *Science* **1995**, *270*, 1970. (8) Labinger, J. A.; Bercaw, J. E. *JACS* **1997**, *119*, 848. (9) Matsumoto, T.; Periana, R. A. *JACS* **2000**, *122*, 7414. (10) Ohki, Y. *JACS* **2008**, *130*, 17174. (11) Nakao, Y. *JACS* **2008**, *130*, 16170.

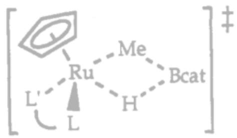
History



(6) Hartwig, J. F. *JACS* **1994**, *116*, 1839. (7) Bergman, R. G. *Science* **1995**, *270*, 1970. (8) Labinger, J. A.; Bercaw, J. E. *JACS* **1997**, *119*, 848. (9) Matsumoto, T.; Periana, R. A. *JACS* **2000**, *122*, 7414. (10) Ohki, Y. *JACS* **2008**, *130*, 17174. (11) Nakao, Y. *JACS* **2008**, *130*, 16170.

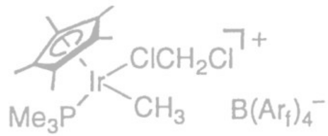
History

Borylation of Ru–Me
1994: Hartwig[6]



L-L = bisphosphine

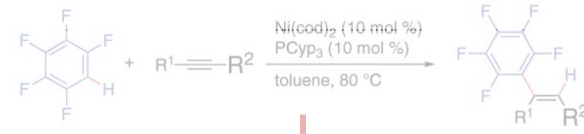
Methane exchange (Ir)
1995: Bergman[7]



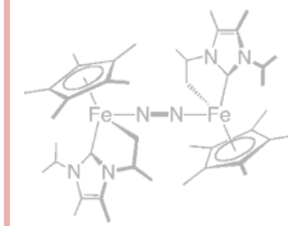
Methane exchange (Pt)
1997: Labinger/Bercaw[8]

N-N = TMEDA

Ni-catalyzed alkyne hydroarylation
2008: Nakao[11]

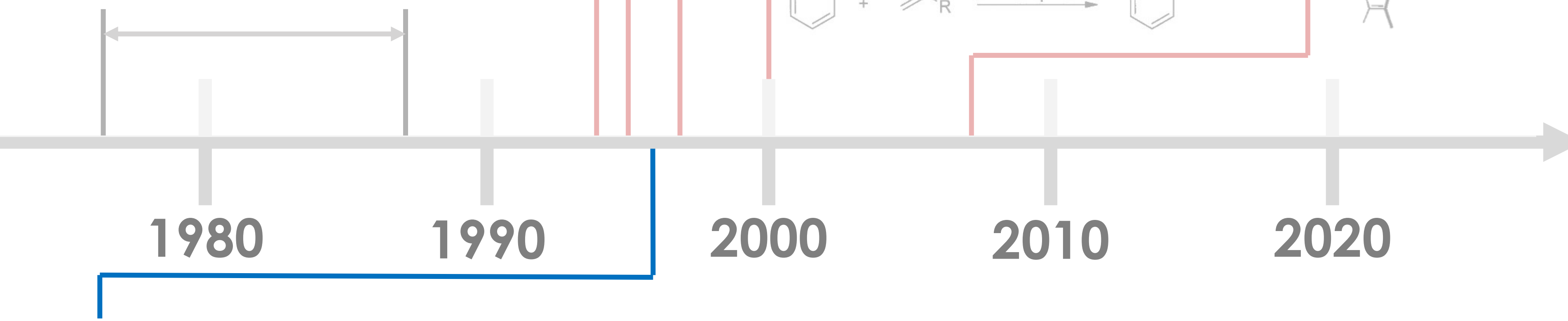


Fe-mediated borylation
2008: Ohki[10]

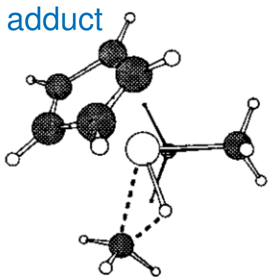


Ir-catalyzed olefin hydroarylation
2000: Matsumoto/Periana[9]

Late 70s – Late 80s
Foundational d[0] M work[1-5]

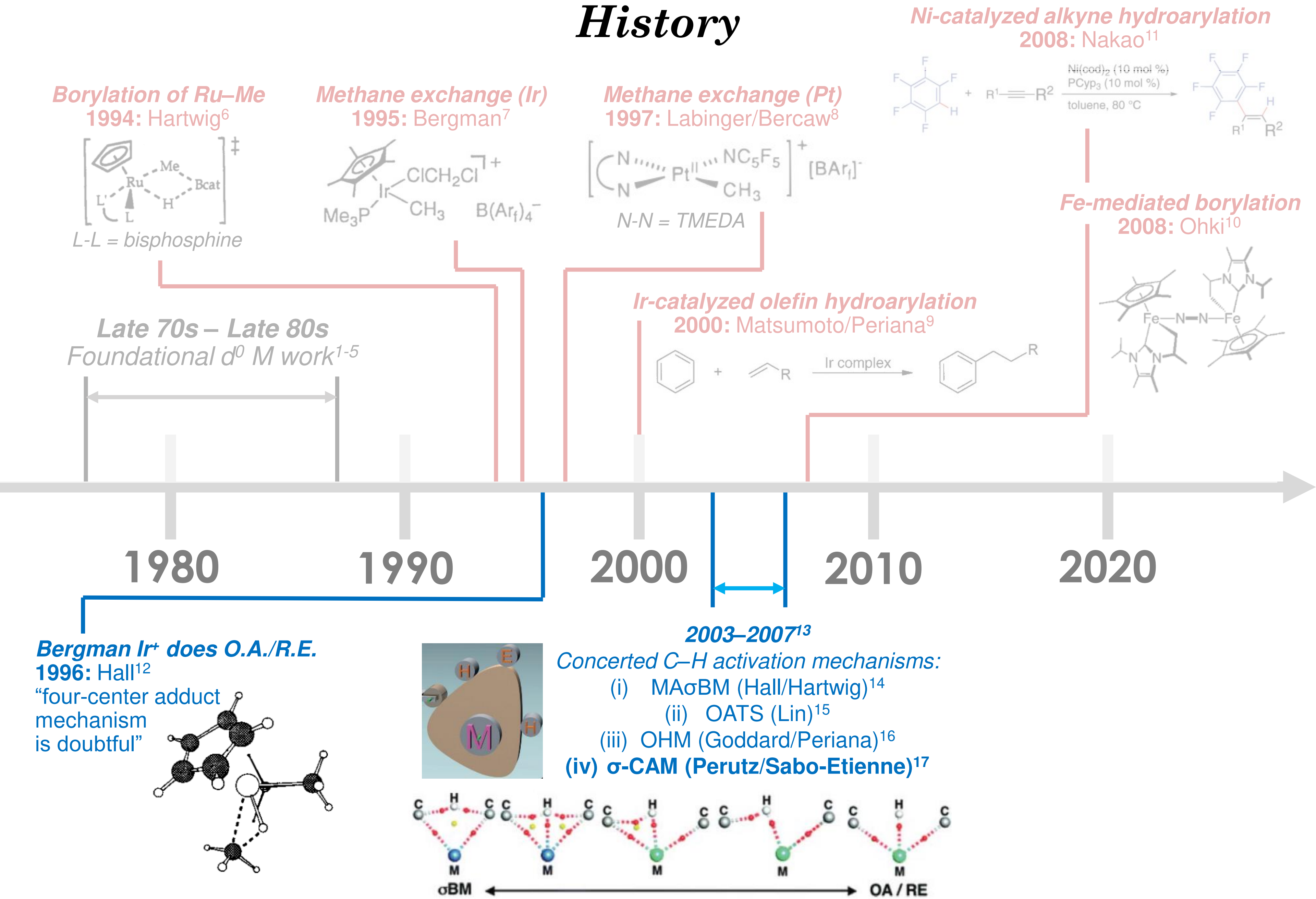


Bergman Ir⁺ does O.A./R.E.
1996: Hall[12]
"four-center adduct
mechanism
is doubtful"



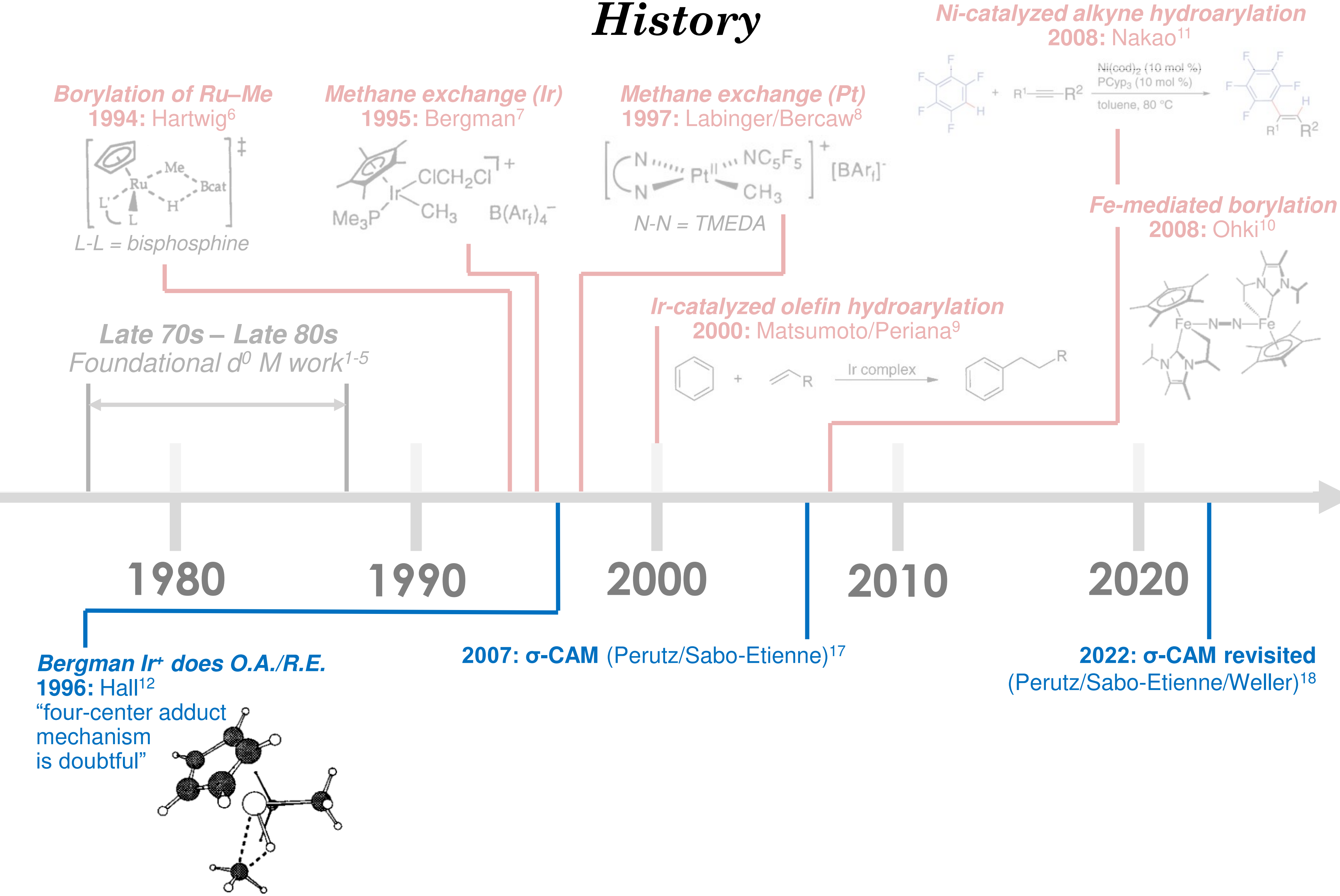
(12) Hall, M. B. *JACS* **1996**, *118*, 6068. (13) Hall, M. B. *JACS* **2007**, *129*, 12068. (14) Hartwig/Hall, *JACS* **2003**, *125*, 858. (15) Lin, Z. *Coord. Chem. Rev.* **2007**, *251*, 2280. (16) Periana/Goddard, *JACS* **2004**, *126*, 11658. (17) Perutz/Sabo-Etienne, *ACIE* **2007**, *46*, 2578

History



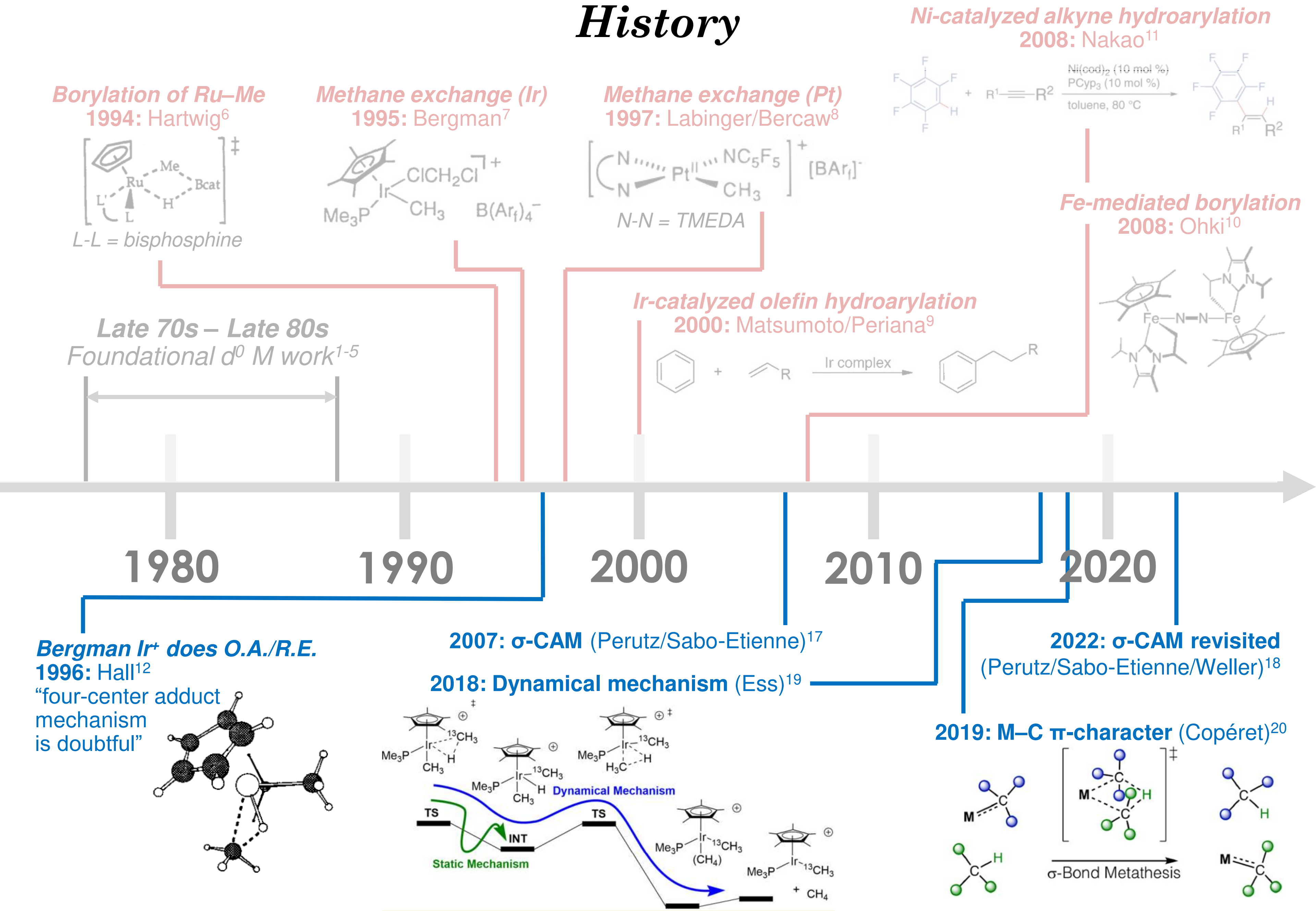
(12) Hall, M. B. *JACS* **1996**, *118*, 6068. (13) Hall, M. B. *JACS* **2007**, *129*, 12068. (14) Hartwig/Hall, *JACS* **2003**, *125*, 858. (15) Lin, Z. *Coord. Chem. Rev.* **2007**, *251*, 2280. (16) Periana/Goddard, *JACS* **2004**, *126*, 11658. (17) Perutz/Sabo-Etienne, *ACIE* **2007**, *46*, 2578

History



(17) Perutz/Sabo-Etienne, *ACIE* **2007**, *46*, 2578. (18) Perutz/Sabo-Etienne/Weller, *ACIE* **2022**, *61*, e202111462. (19) Ess, D. H. *JACS* **2018**, *140*, 11039. (20) Coperet, C. *JACS* **2019**, *141*, 648.

History



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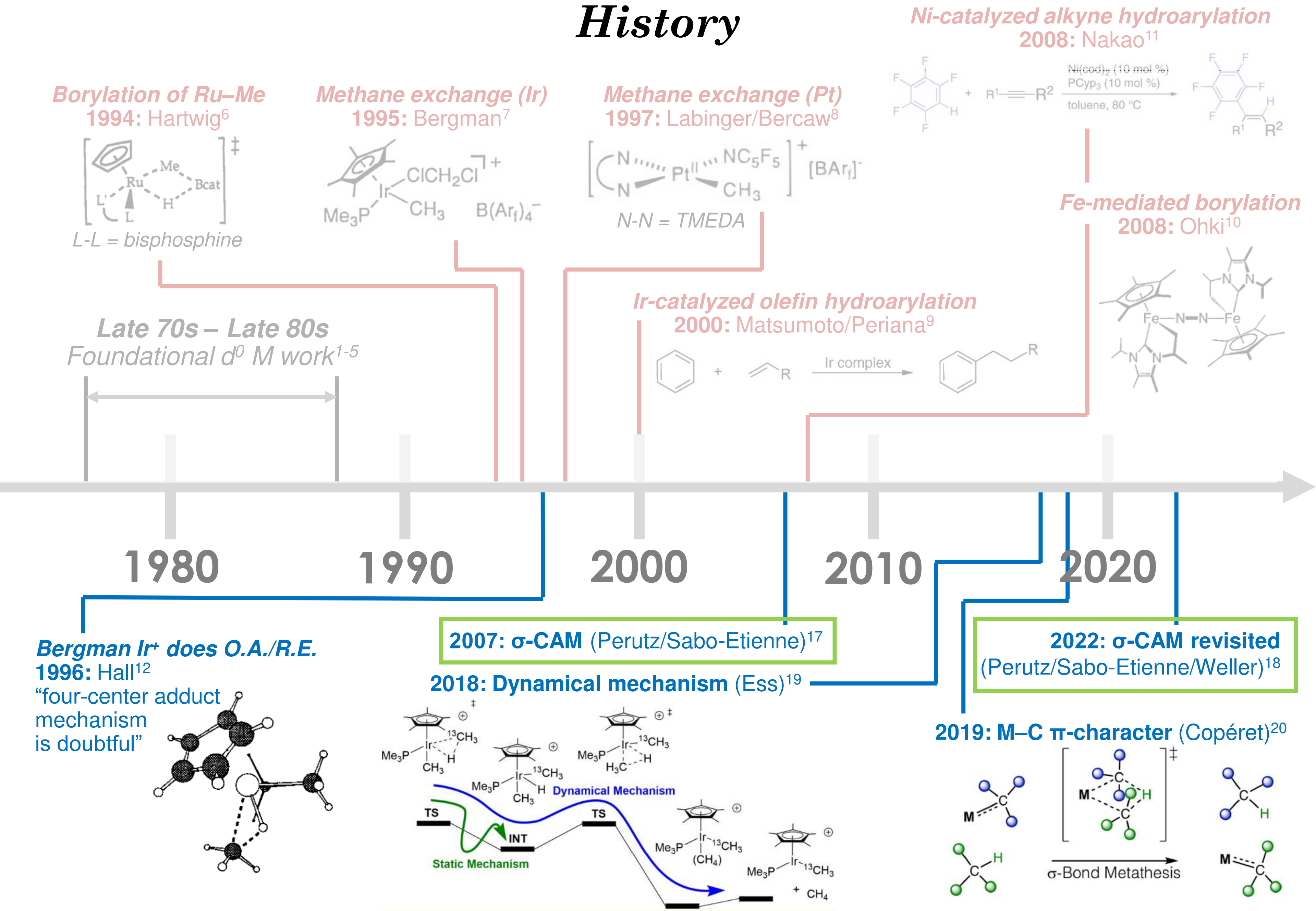
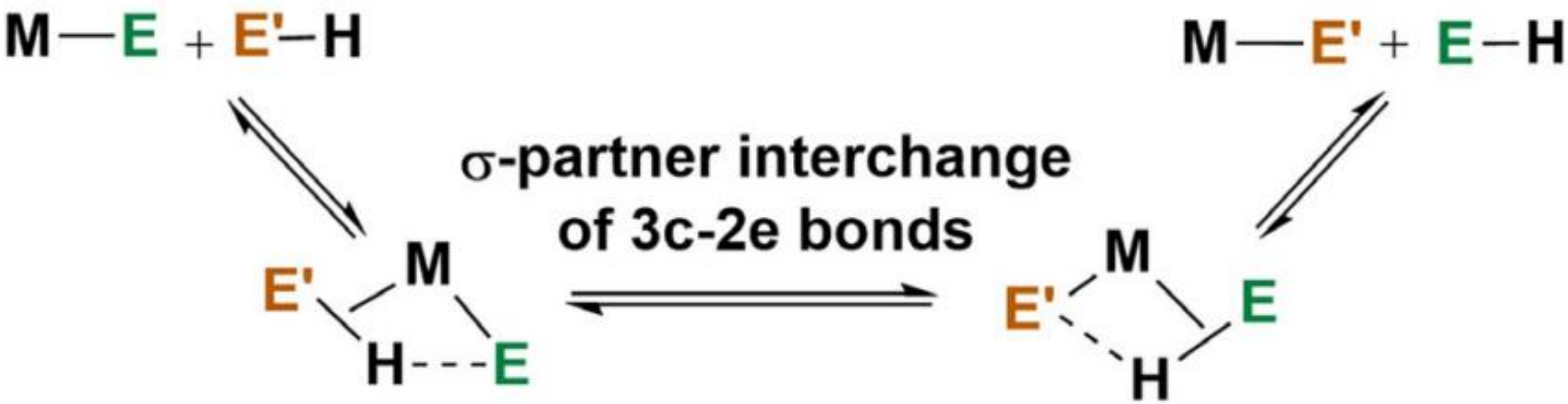


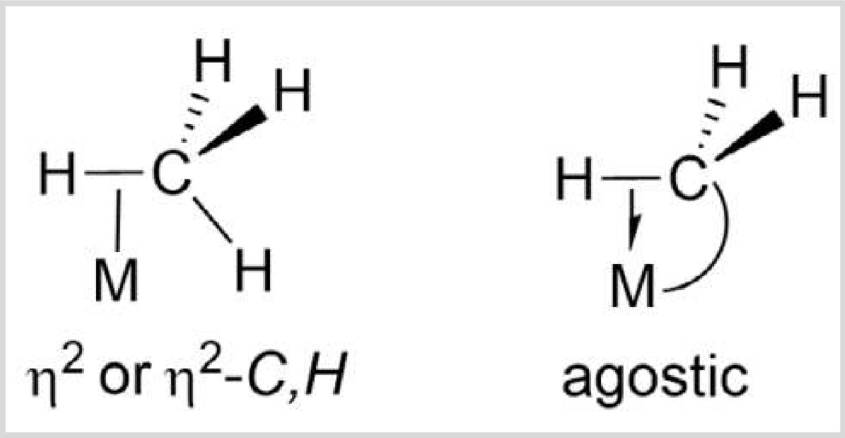
(17) Perutz/Sabo-Etienne, *ACIE* **2007**, *46*, 2578. (18) Perutz/Sabo-Etienne/Weller, *ACIE* **2022**, *61*, e202111462. (19) Ess, D. H. *JACS* **2018**, *140*, 11039. (20) Coperet, C. *JACS* **2019**, *141*, 648.

σ-Complex Assisted Metathesis: "σ-CAM"

Perutz/Sabo-Etienne, *ACIE* **2007**, *46*, 2578.
Perutz/Sabo-Etienne/Weller, *ACIE* **2022**, *61*, e202111462.

***σ-CAM:** σ-Bond metathesis for mid/late-transition metals*





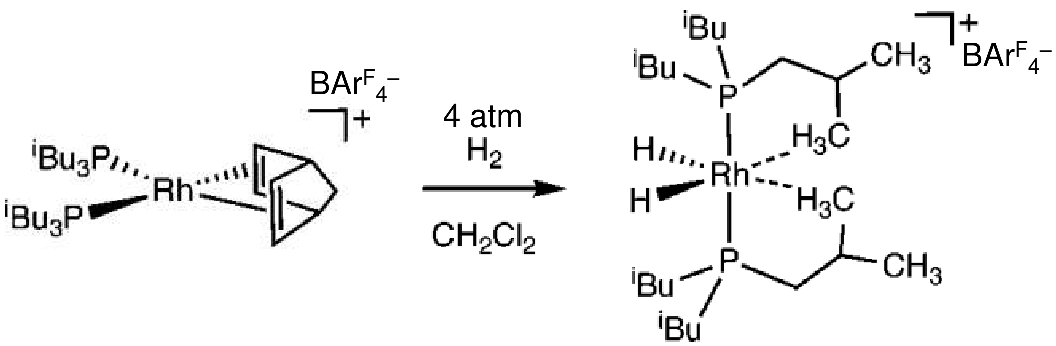
$\sigma_{CH} \rightarrow ML^*$

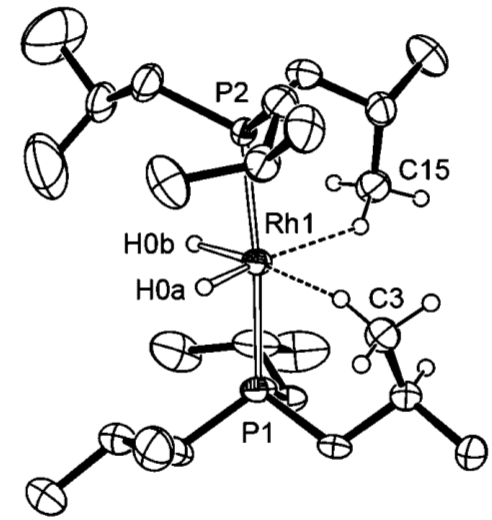
$ML \rightarrow \sigma^*_{CH}$

Requires non-zero d-occupancy

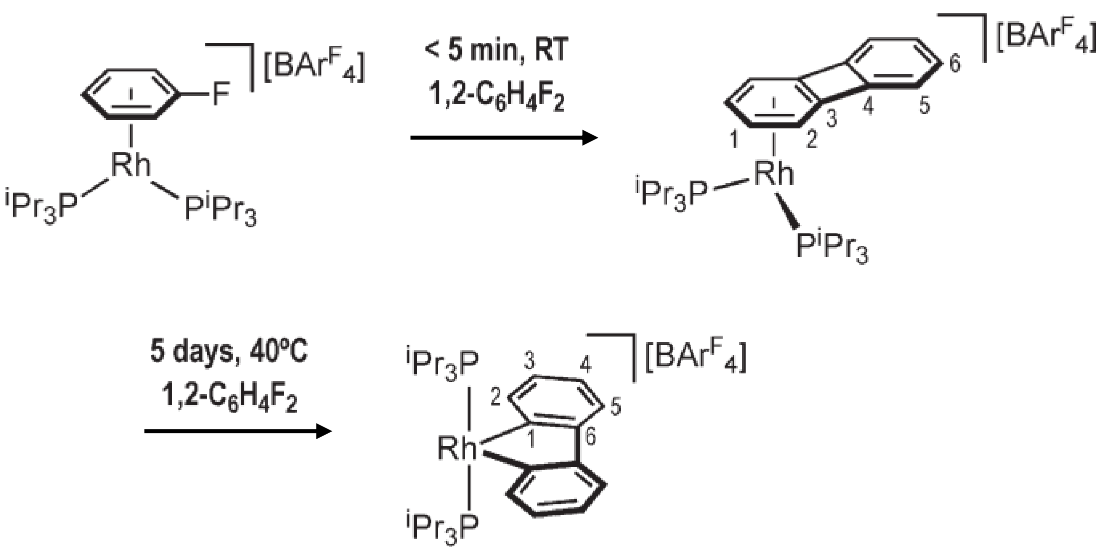
Agostic interactions: "Close to home" examples

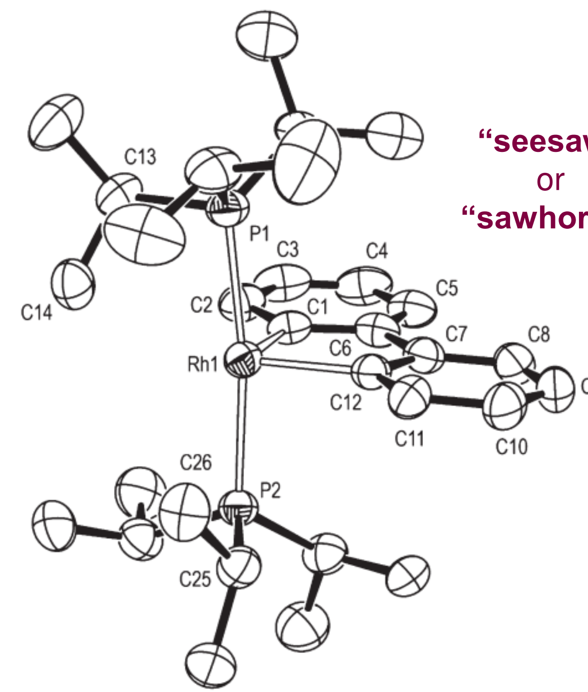
Weller, A. S. *Organometallics* **2008**, *27*, 2918.





Chaplin, A. B.; Weller, A. S. *Organometallics* **2010**, *29*, 2710.



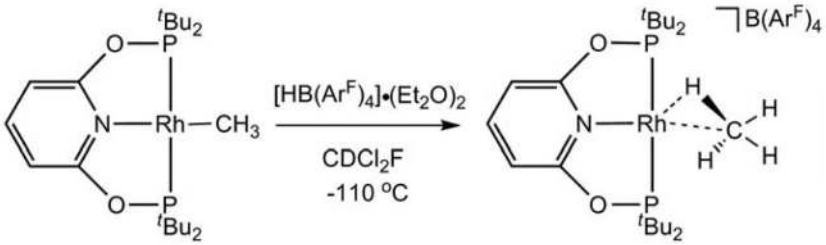


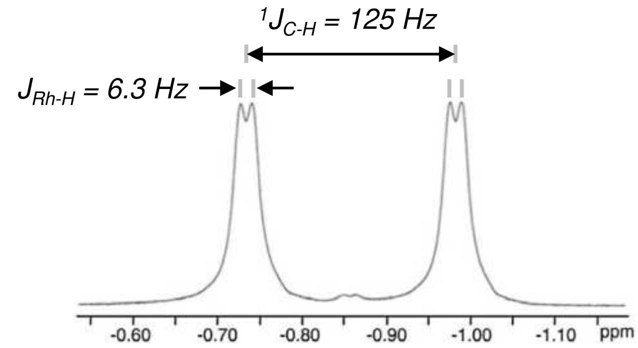
"seesaw"
or
"sawhorse"

Cationic variant of complexes with Rh (Jones, W. D. *Organometallics* **2001**, *20*, 5745) & Ir (Crabtree, R. H. *Organometallics* **1995**, *14*, 1168.

σ-CH_4 complexes by NMR: Recently revitalized

"The original": Bernskoetter, W. H.; Brookhart M. *Science* **2009**, *326*, 553.

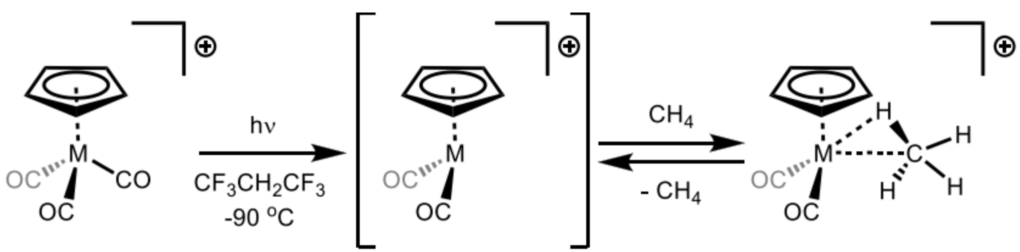




^1H NMR ($CDCl_2F$, –110 °C): ^{13}C-labeled methane

σ-Methane revisited: (i) Ball, G. E. *Nat. Chem.* **2022**, *14*, 801. (ii) Ball, G. E. *JACS* **2022**, *ASAP*.

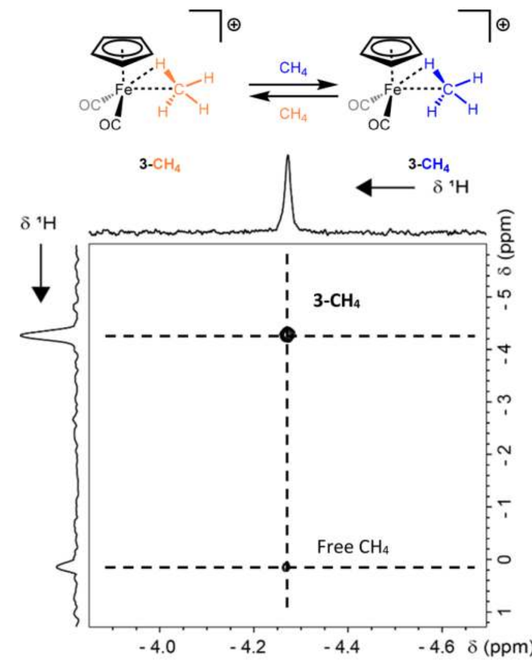
Anion is Krossing's $[Al(OC(CF_3)_3)_4]^-$



1: M = Os
2: M = Ru
3: M = Fe

16 ve
1a: M = Os
2a: M = Ru
3a: M = Fe

1-CH_4: M = Os ($t_{1/2}$ = 13.5 h at –90 °C)
2-CH_4: M = Ru (5% yield, constant *hv*)
3-CH_4: M = Fe (20% yield, constant *hv*)

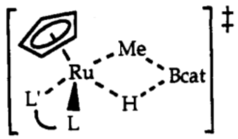


Stability of σ-complexes: *Os >> Fe > Ru*

2D EXSY NMR: rapid CH_4 exchange

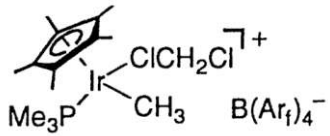
History

Borylation of Ru–Me
1994: Hartwig[6]

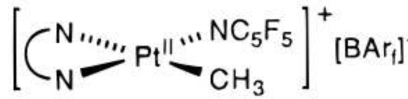


L-L = bisphosphine

Methane exchange (Ir)
1995: Bergman[7]

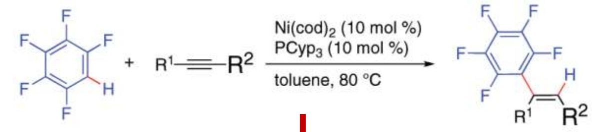


Methane exchange (Pt)
1997: Labinger/Bercaw[8]

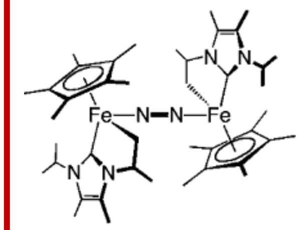


N-N = TMEDA

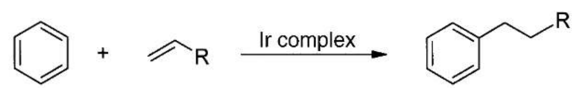
Ni-catalyzed alkyne hydroarylation
2008: Nakao[11]



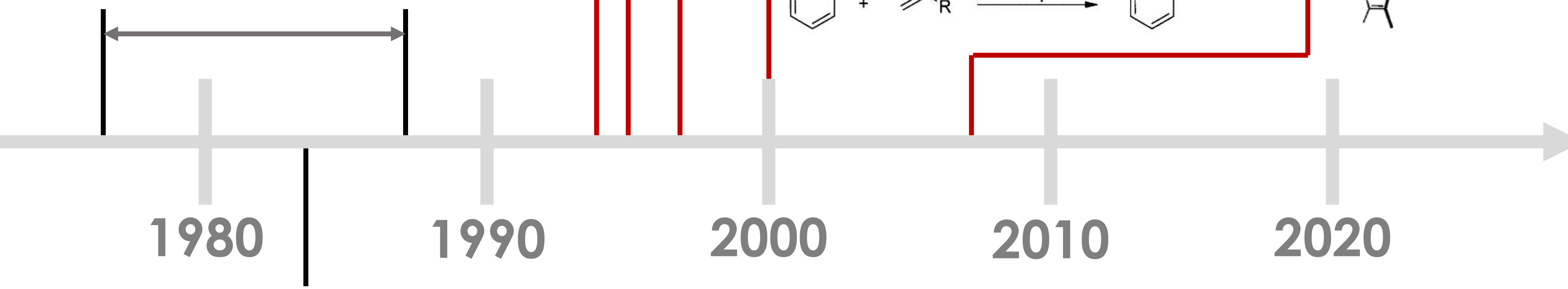
Fe-mediated borylation
2008: Ohki[10]



Ir-catalyzed olefin hydroarylation
2000: Matsumoto/Periana[9]



Late 70s – Late 80s
Foundational d^0 M work[1-5]

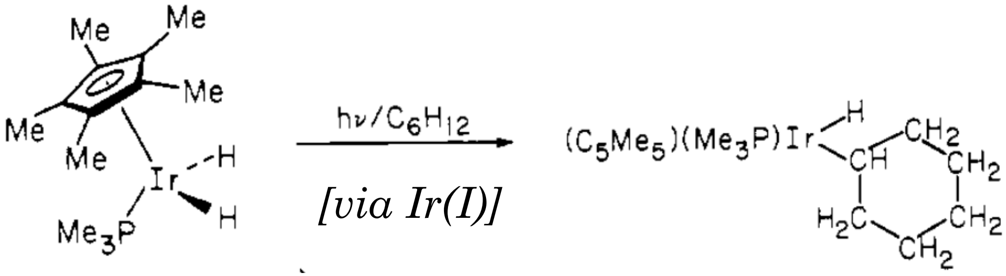


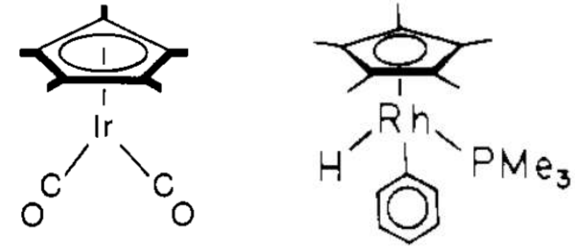
Methane exchange (Lu, Y)
1983: Watson[4]

(6) Hartwig, J. F. *JACS* **1994**, *116*, 1839. (7) Bergman, R. G. *Science* **1995**, *270*, 1970. (8) Labinger, J. A.; Bercaw, J. E. *JACS* **1997**, *119*, 848. (9) Matsumoto, T.; Periana, R. A. *JACS* **2000**, *122*, 7414. (10) Ohki, Y. *JACS* **2008**, *130*, 17174. (11) Nakao, Y. *JACS* **2008**, *130*, 16170.

Bergman, Ir: $\underline{d^8}$ Ir(I) to $\underline{d^6}$ Ir(III) in 10 years

Janowicz, A. H.; Bergman, R. G. *JACS* **1982**, *104*, 352.





Ir: Graham, W. A. G. *JACS* **1982**, *104*, 3723.
Rh: Jones, W. D. *JACS* **1982**, *104*, 4240.

Prevailing view: *Low oxidation state (5d) metal needed for alkane activation*

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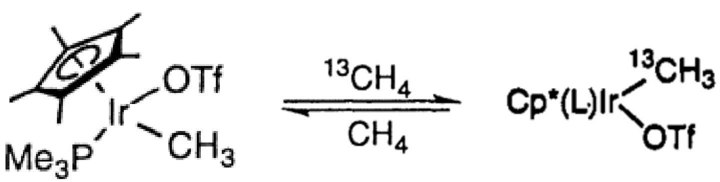
Challenging the dogma: *Cationic Ir(III) activates methane (no hν!)*

Burger, P.; Bergman, R. G. *JACS* **1993**, *115*, 10462.



$\boldsymbol{t_{1/2}}$ **= 6 h** (2 atm $^{13}CH_4$, 45 °C)

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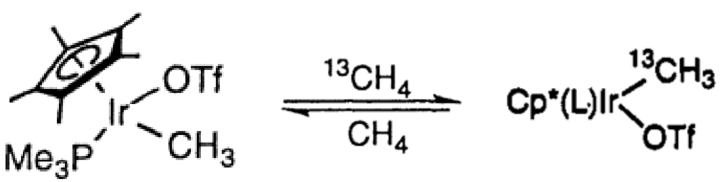

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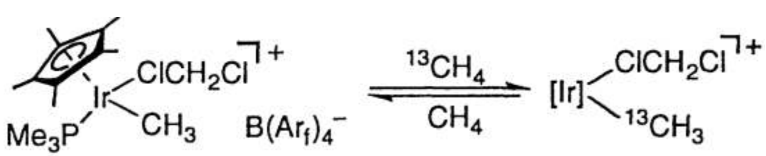
Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.



***$t_{1/2}$* = 50 min** (1 atm $^{13}CH_4$, 10 °C)

Bergman, Ir: d⁸ Ir(I) to d⁶ Ir(III) in 10 years

Janowicz, A. H.; Bergman, R. G. *JACS* **1982**, *104*, 352.

Ir: Graham, W. A. G. *JACS* **1982**, *104*, 3723.
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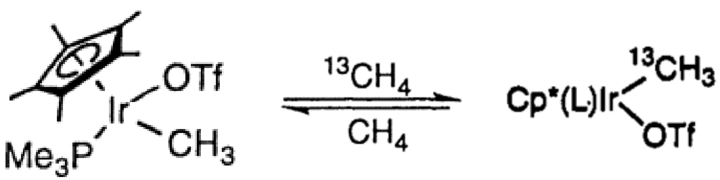

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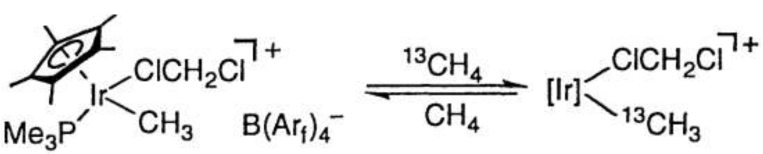
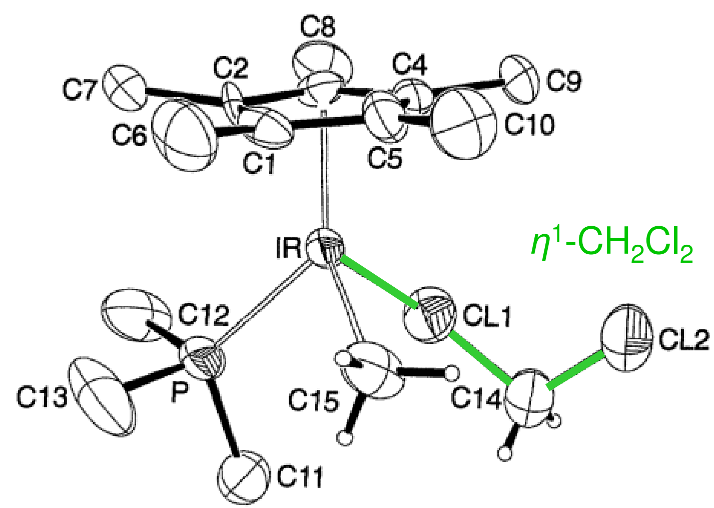


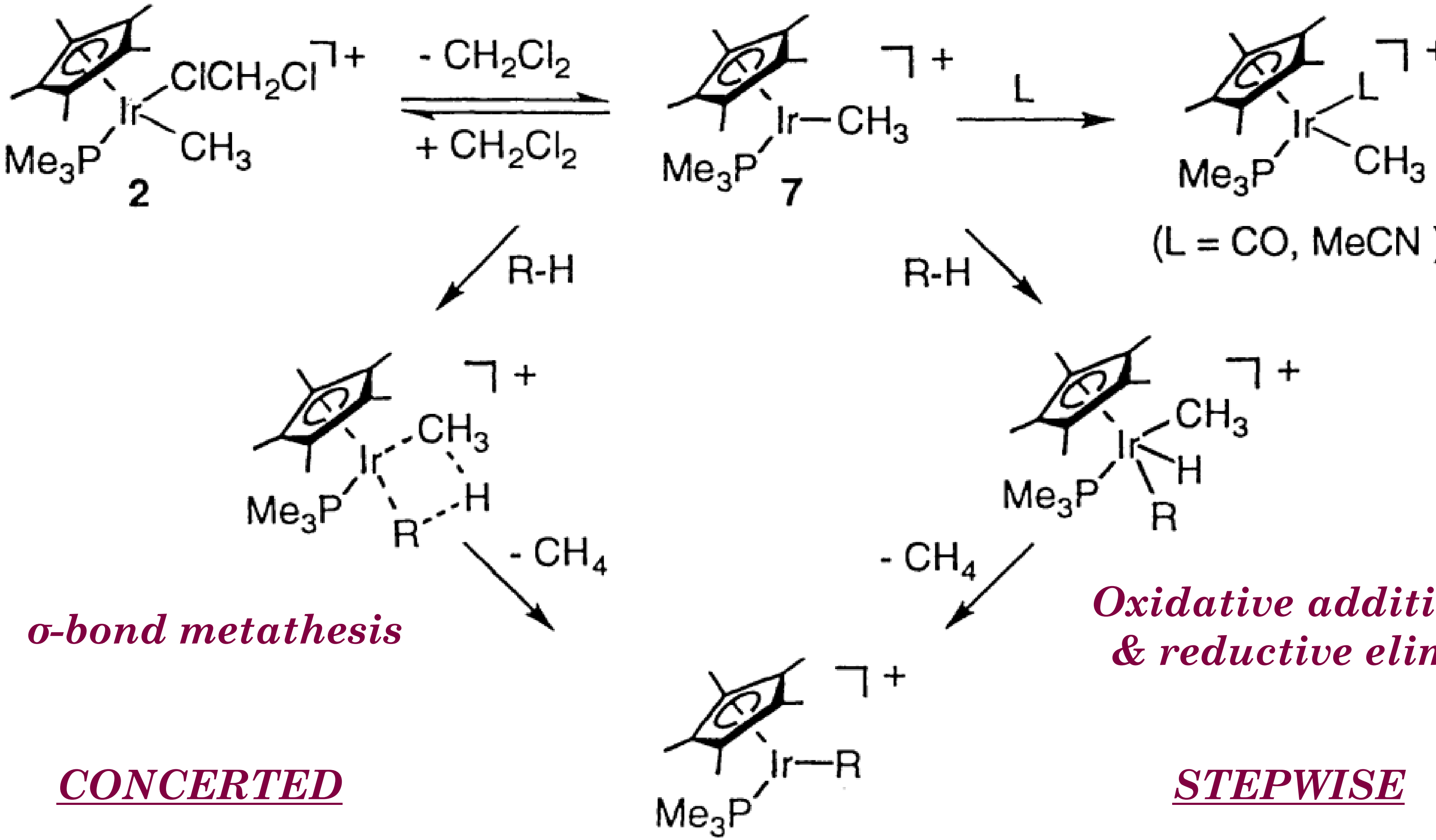
***$t_{1/2}$* = 50 min** (1 atm $^{13}CH_4$, 10 °C)

$[Cp^*(PMe_3)Ir(Me)(CH_2Cl_2)]$**$[BAr^F_4]$**



Difficult synthesis (I'm guessing) – no alkane solvent
VACUUM UNSTABLE

Bergman, Ir: The "mechanistic continuum"



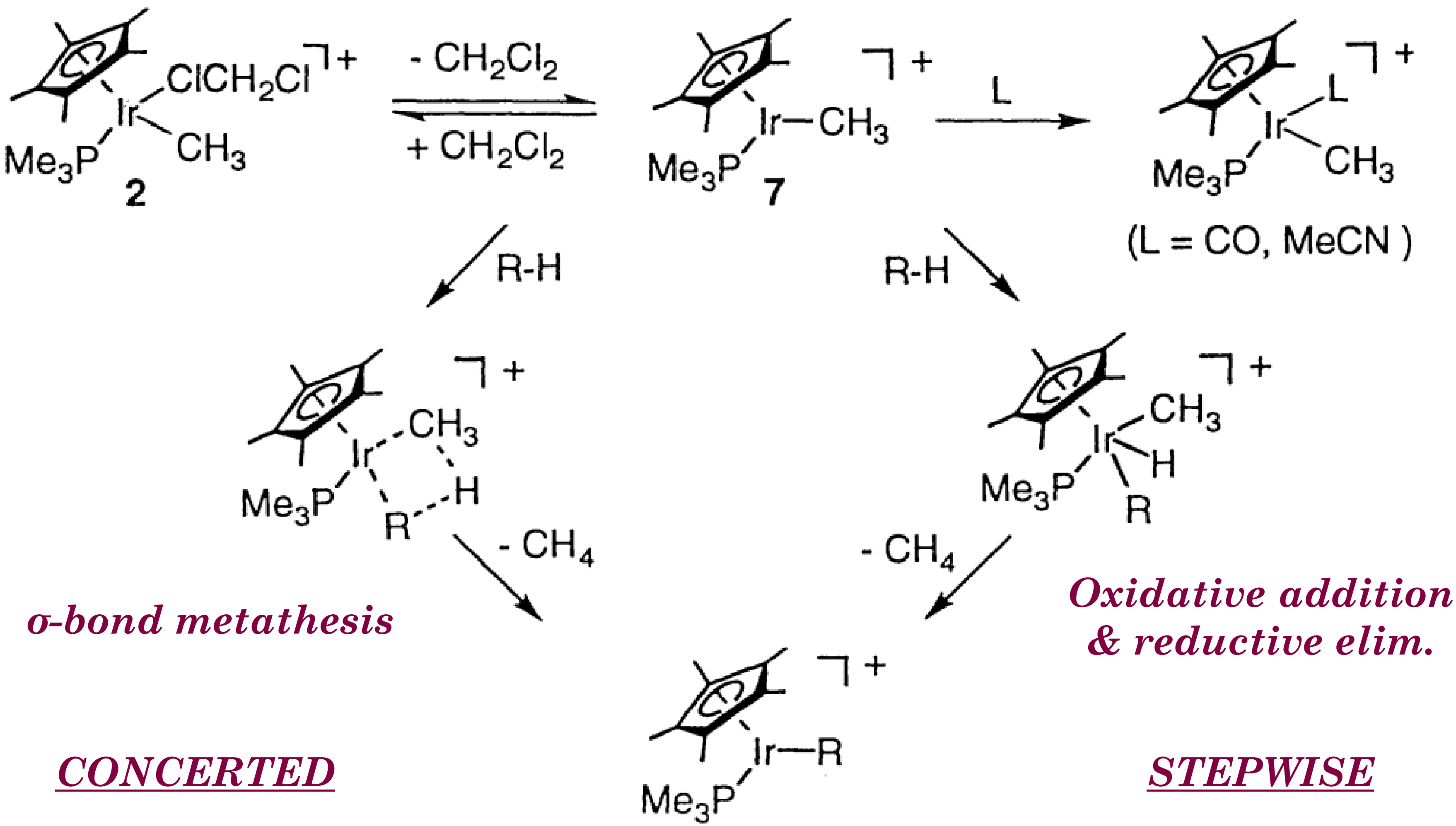
σ-bond metathesis

Oxidative addition & reductive elim.

<u>CONCERTED</u>

<u>STEPWISE</u>

Bergman, Ir: The "mechanistic continuum"



This proposal would spark a 20+ year debate…

…and remains a "borderline case"

Bergman, Ir: The "mechanistic continuum"

Why couldn't they experimentally determine the mechanism? ***What is the limit of experiment?***

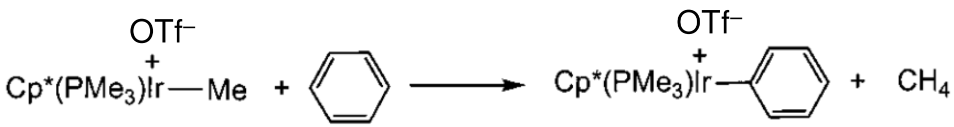
Should we care about this mechanistic nuance?

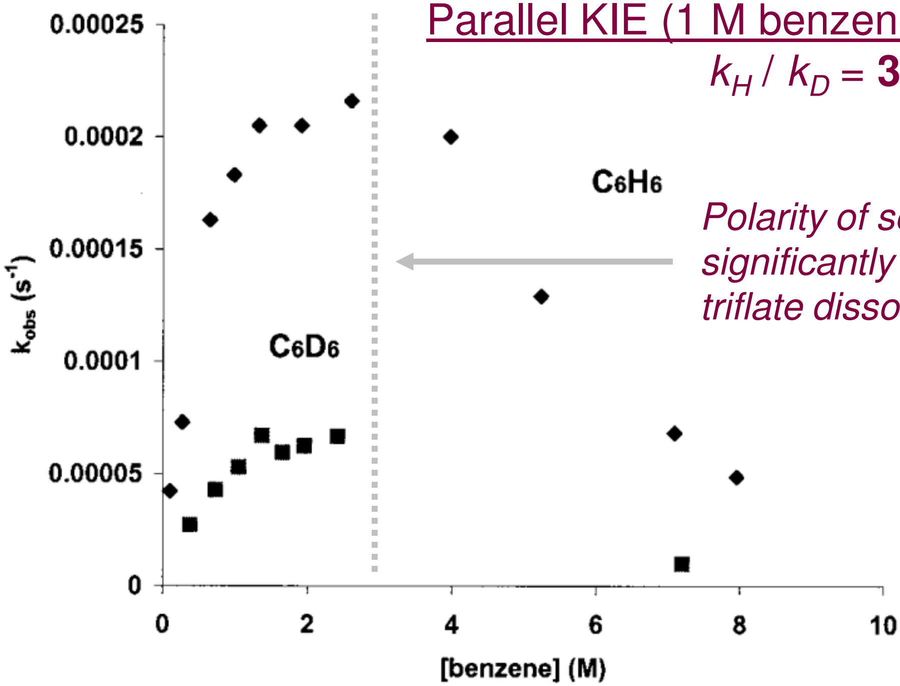
This proposal would spark a 20+ year debate…

…and remains a "borderline case"

Bergman, Ir: Mechanistic studies were not extensive

Tellers, D. M.; Bergman, R. G. *JACS* **2002**, *124*, 1400.





Parallel KIE (1 M benzene)

k_H / k_D = **3.5**

Polarity of solution significantly affects triflate dissociation

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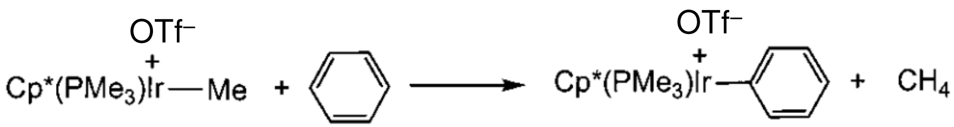
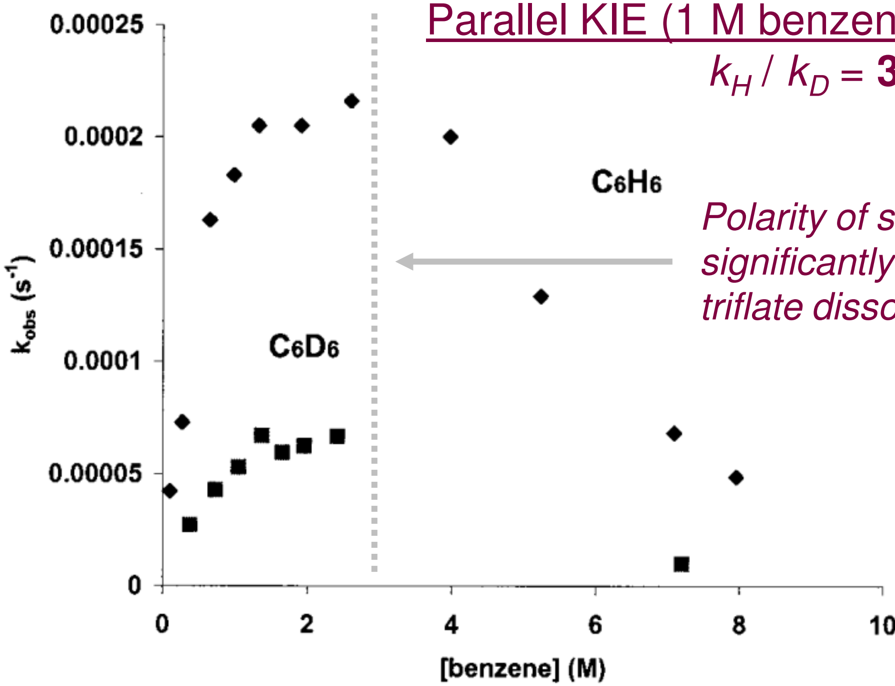
Tellers, D. M.; Bergman, R. G. *JACS* **2002**, *124*, 1400.





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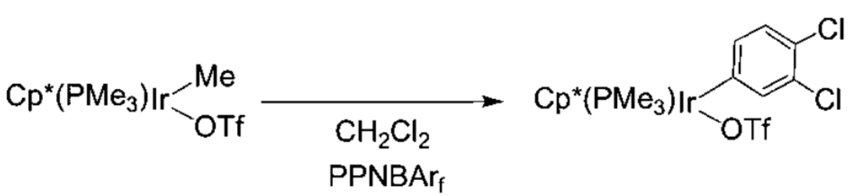
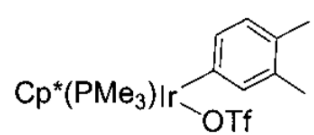
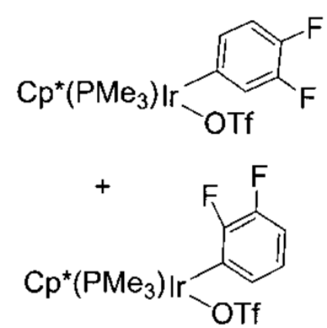
Product distributions







67%

33%

Bergman, Ir: Mechanistic studies were <u>not</u> extensive

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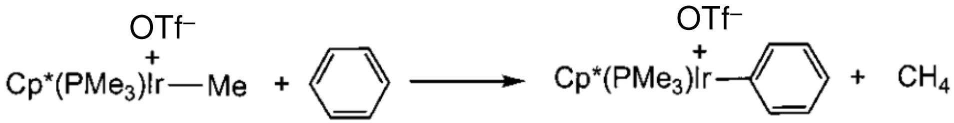

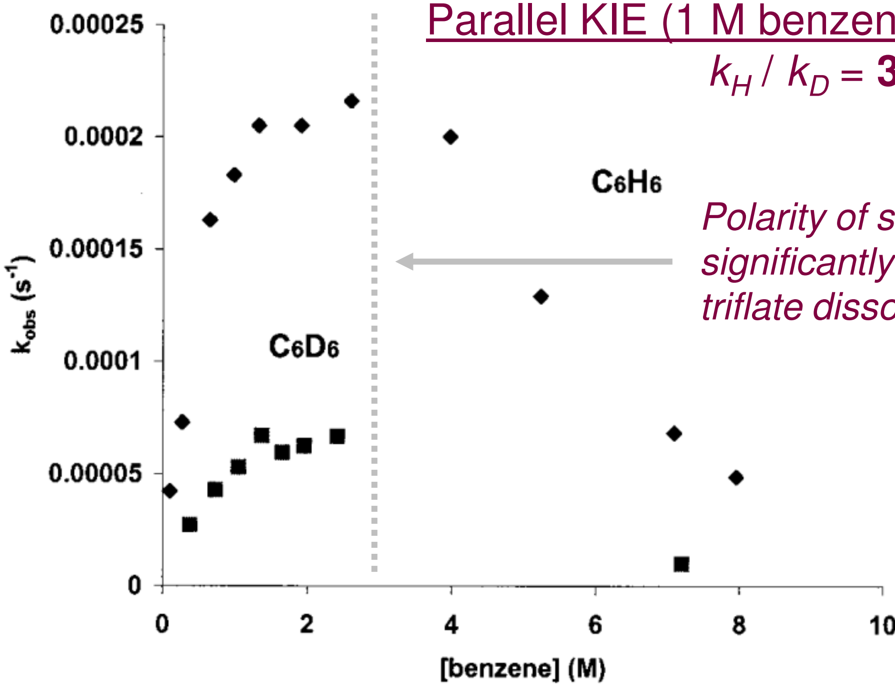

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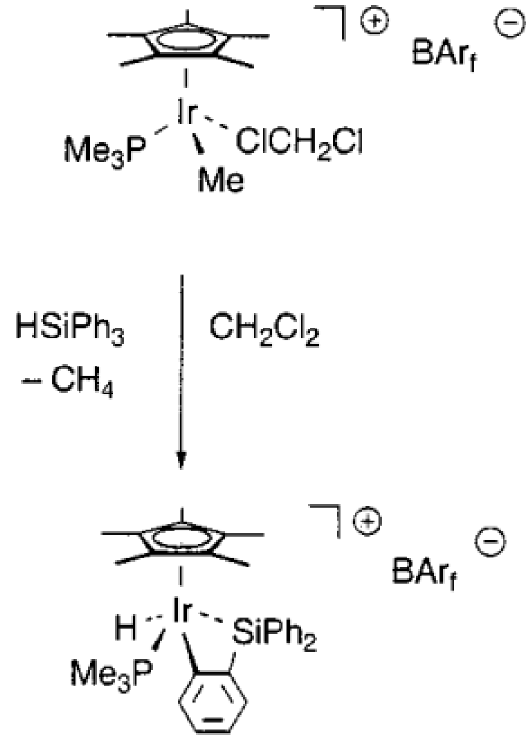
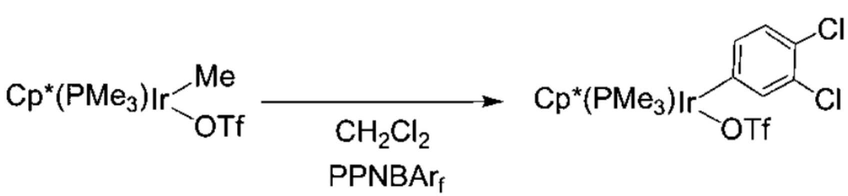
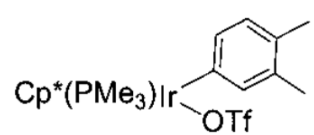
Tilley/Bergman, *JACS* **2000**, *122*, 1816.

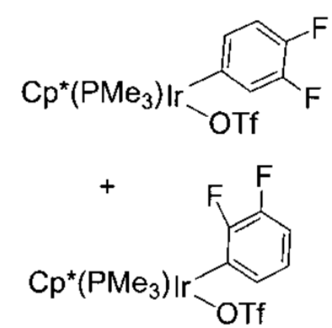


Isolation of cationic Ir(V) complex

Product distributions





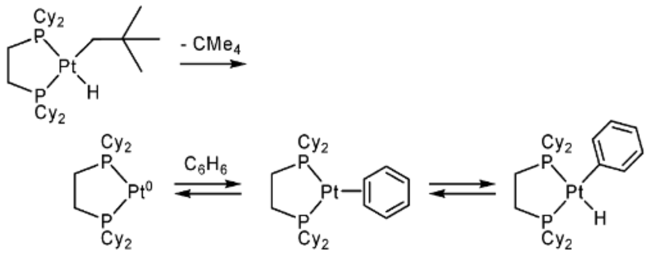


67%

33%

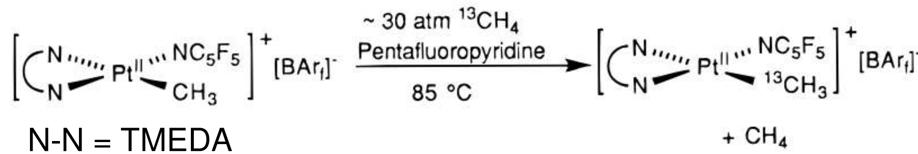
Bercaw, Pt: d^{10} Pt(0) to d^{8} Pt(II), and its evolution

Whitesides, G. M. *JACS* **1988**, *110*, 1436.



Pt(0) does C–H oxidative addition

Labinger/Bercaw, *JACS* **1997**, *119*, 848.



N-N = TMEDA

Cationic Pt(II) does methane exchange

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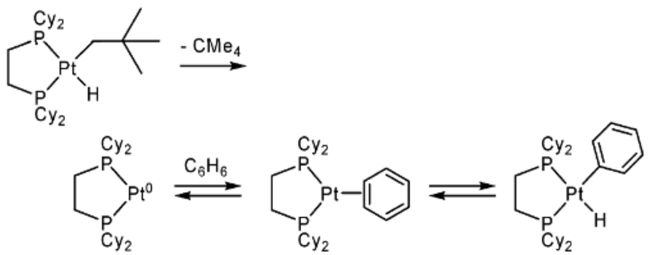

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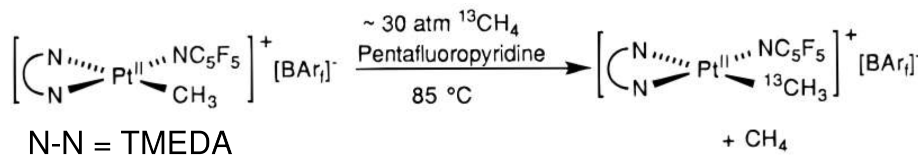
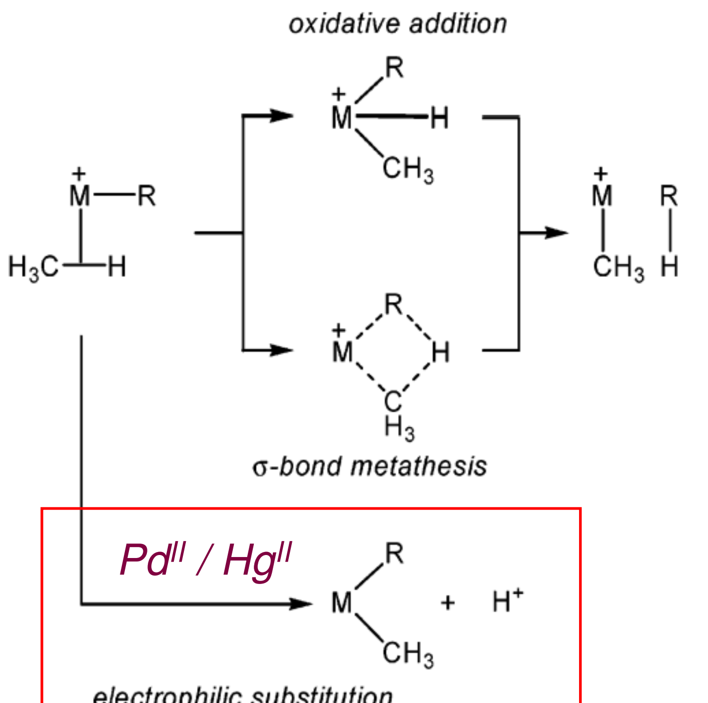
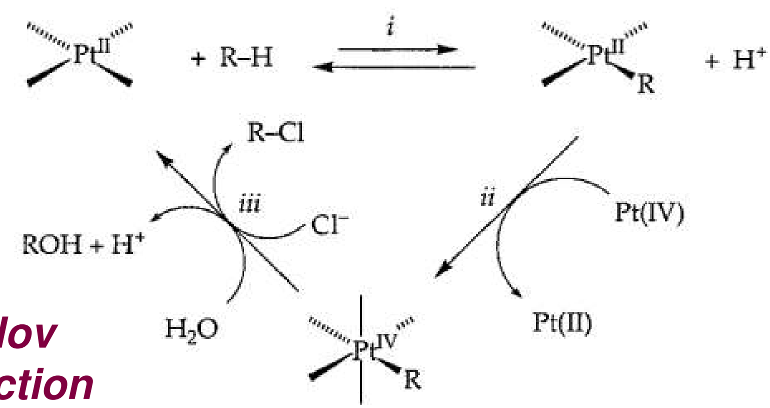


Cationic Pt(II) does methane exchange

Same speculation arose…





Shilov reaction

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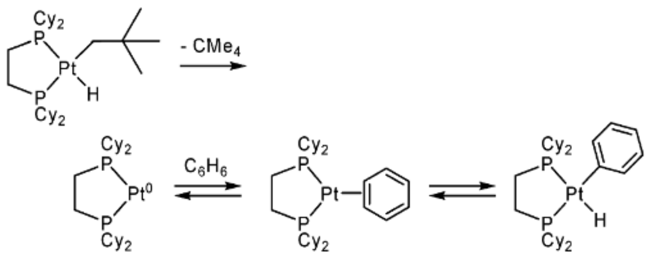

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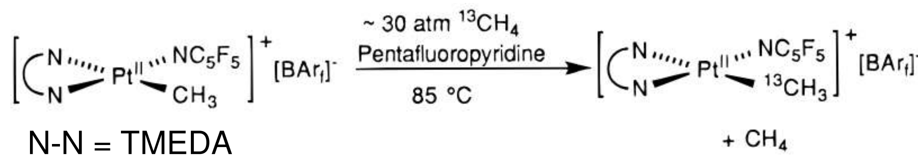

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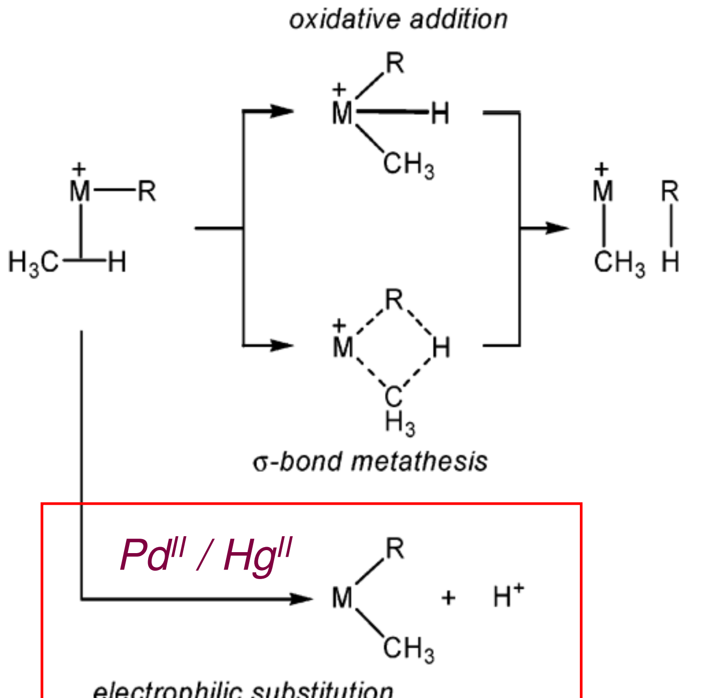
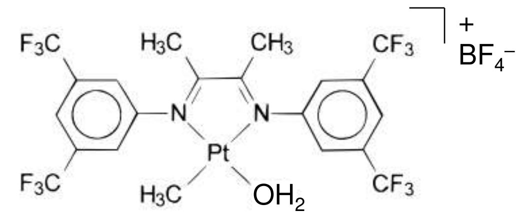
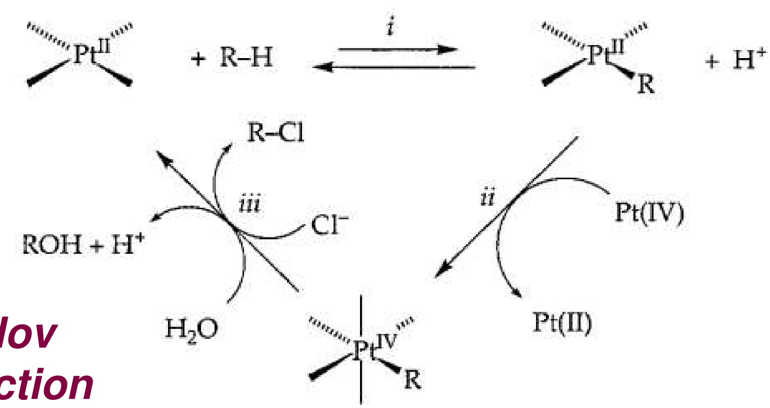


Tilset, M. *JACS* **1999**, *121*, 1974.



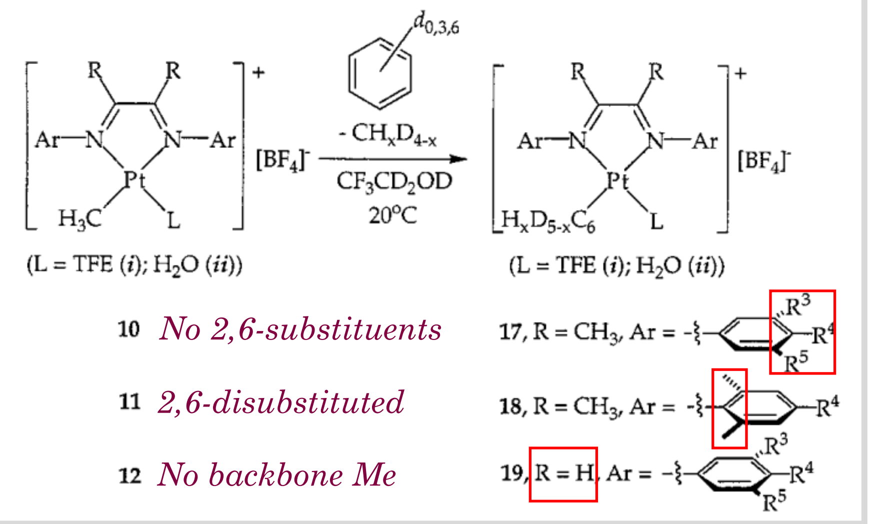


Shilov reaction

Bercaw, Pt: Kinetic studies

Labinger/Bercaw *JACS* **2002**, *124*, 1378.

apparent rate law: rate = k_{obs}[benzene]/[water]



10 *No 2,6-substituents*

11 *2,6-disubstituted*

12 *No backbone Me*

17, R = CH_3, Ar =

18, R = CH_3, Ar =

19, R = H, Ar =

Bercaw, Pt: Kinetic studies

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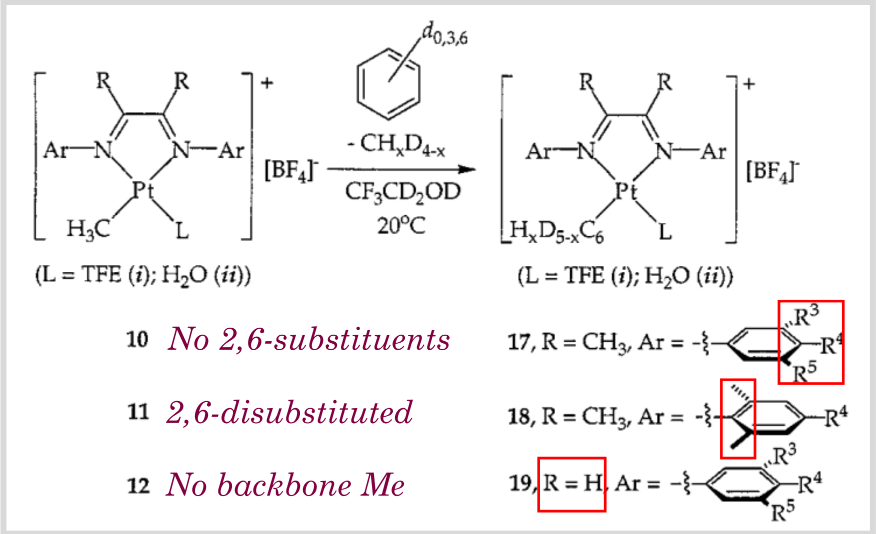
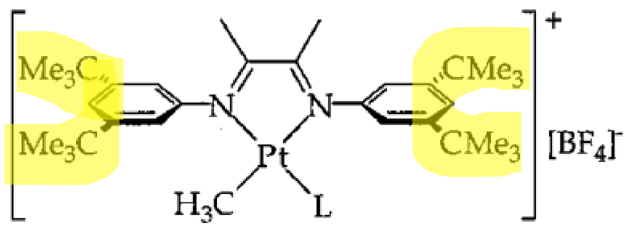




(L = TFE (*i*); H_2O (*ii*))
10b

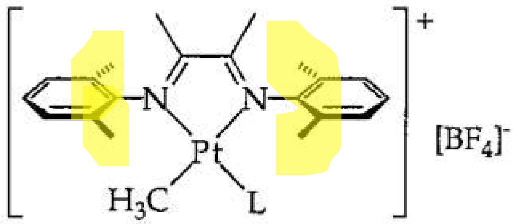
Parallel KIE: k_H / k_D = **2.2** (20 °C)

*$\Delta S^{\ddagger}$ = +**5 e.u.***

Bercaw, Pt: Kinetic studies

Labinger/Bercaw *JACS* **2002**, *124*, 1378.

apparent rate law: rate $= k_{obs}$[benzene]/[water]

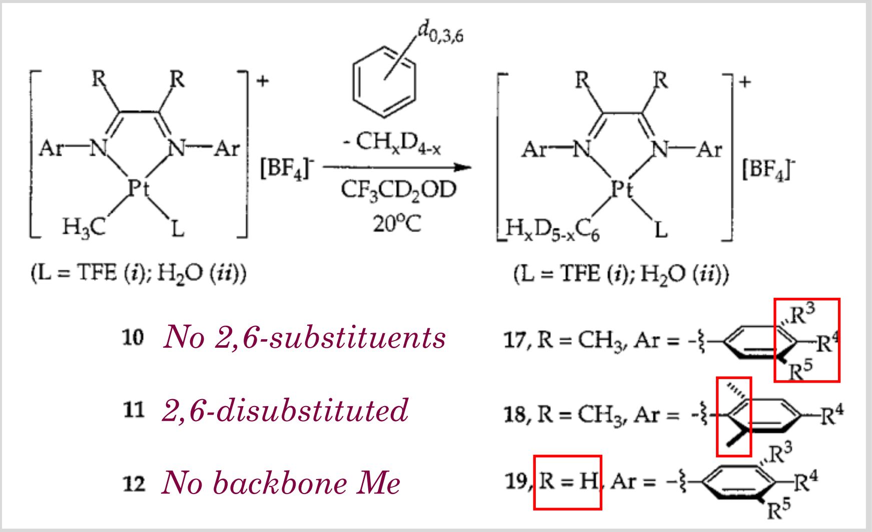


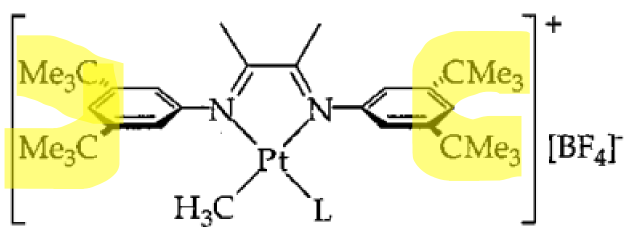
(L = TFE (*i*); H_2O (*ii*))

11b

Parallel KIE: k_H / k_D = **1.1** (35 °C)

ΔS‡ = −16 e.u.





(L = TFE (*i*); H_2O (*ii*))

10b

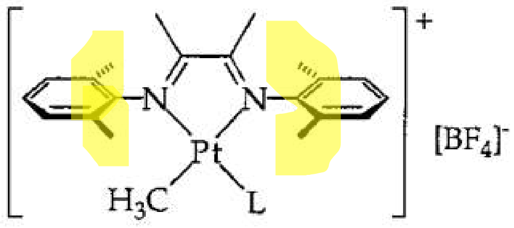
Parallel KIE: k_H / k_D = **2.2** (20 °C)

ΔS‡ = +5 e.u.

Bercaw, Pt: Kinetic studies

Labinger/Bercaw *JACS* **2002**, *124*, 1378.

apparent rate law: rate = k_{obs}[benzene]/[water]



(L = TFE (*i*); H_2O (*ii*))

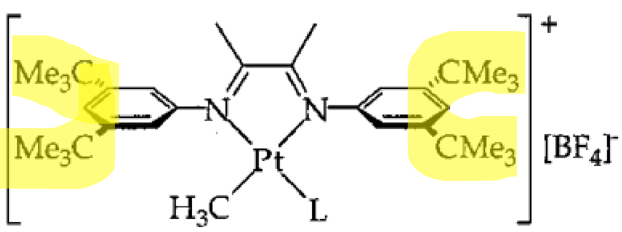
11b

Parallel KIE: k_H / k_D = **1.1** (35 °C)

ΔS‡ = –16 e.u.

RDS: π-benzene adduct

(reversible activation – H/D scrambling)



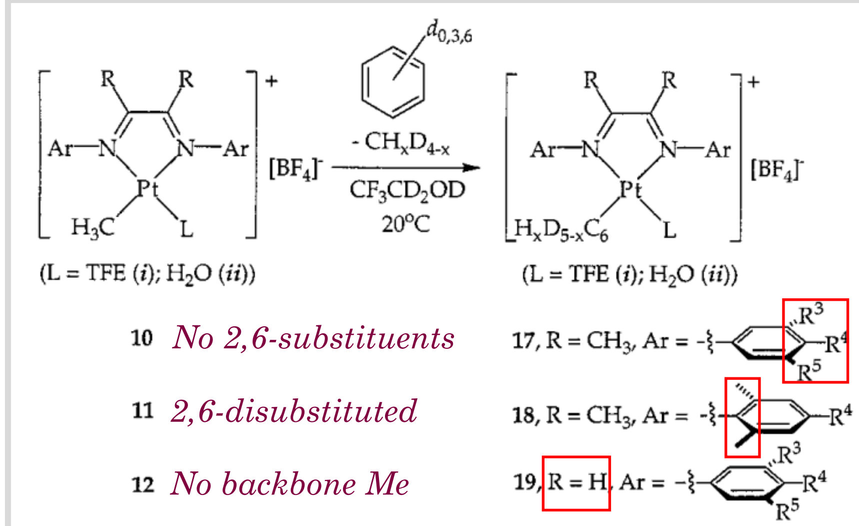
(L = TFE (*i*); H_2O (*ii*))

10b

Parallel KIE: k_H / k_D = **2.2** (20 °C)

ΔS‡ = +5 e.u.

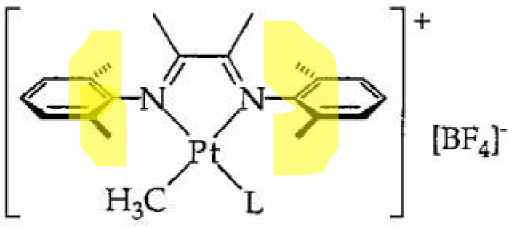
RDS: C–H activation



Bercaw, Pt: Kinetic studies

Labinger/Bercaw *JACS* **2002**, *124*, 1378.

apparent rate law: rate = k_{obs}[benzene]/[water]



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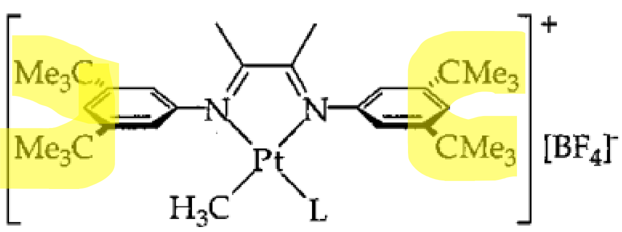

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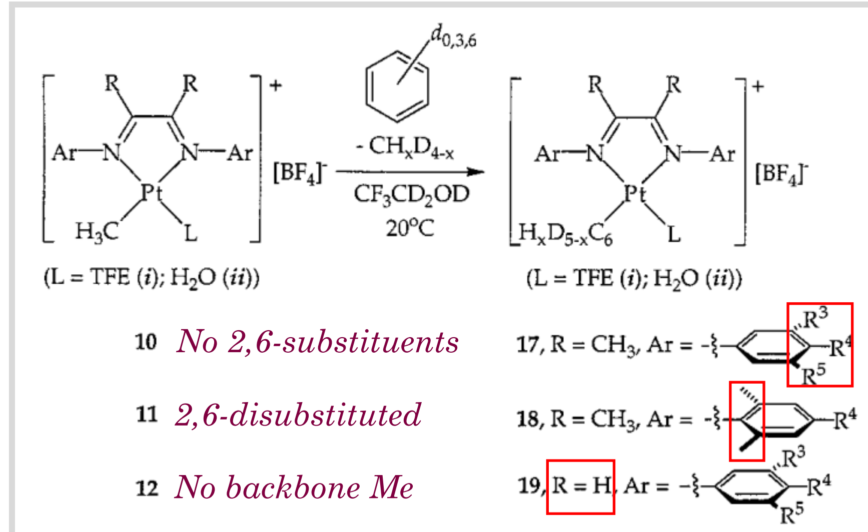
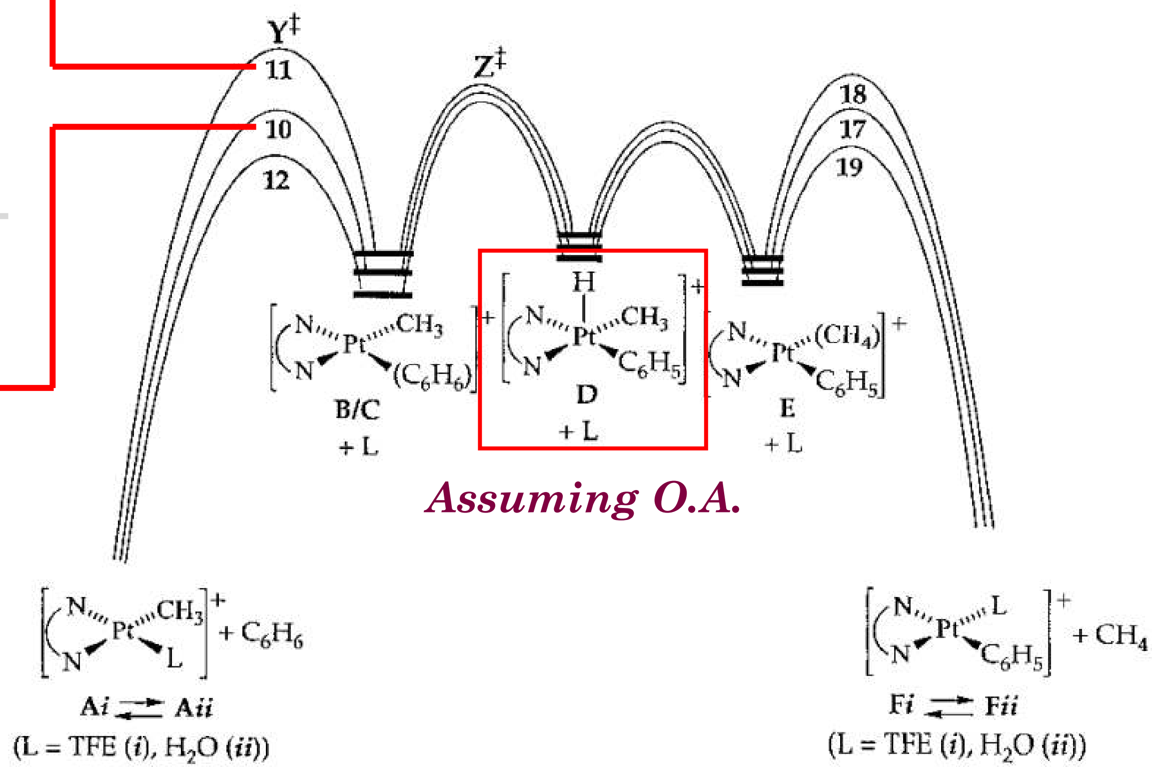
ΔS‡ = +5 e.u.

RDS: C–H activation





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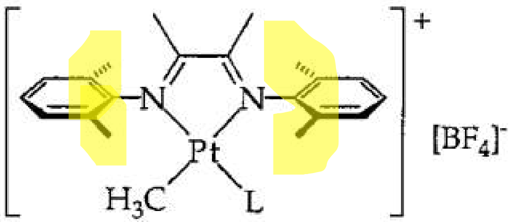

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11b

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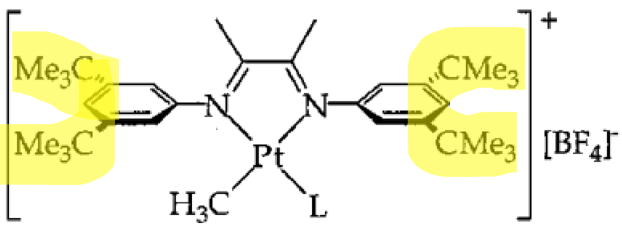

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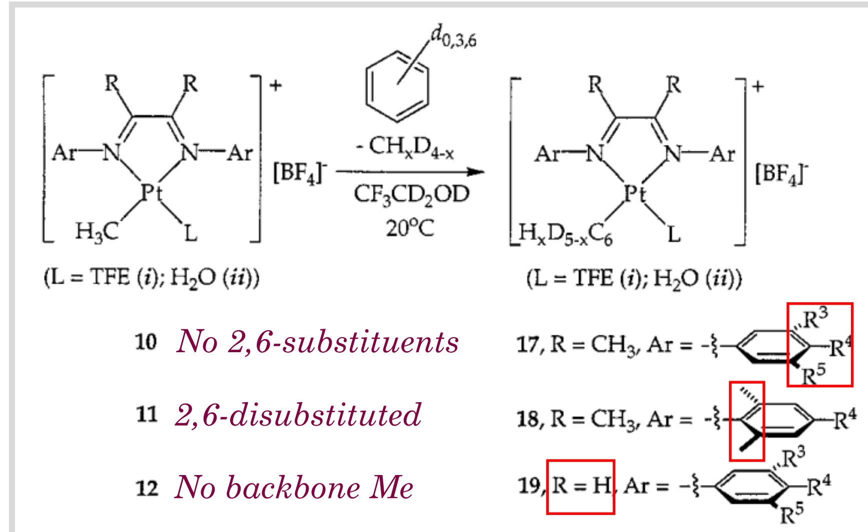
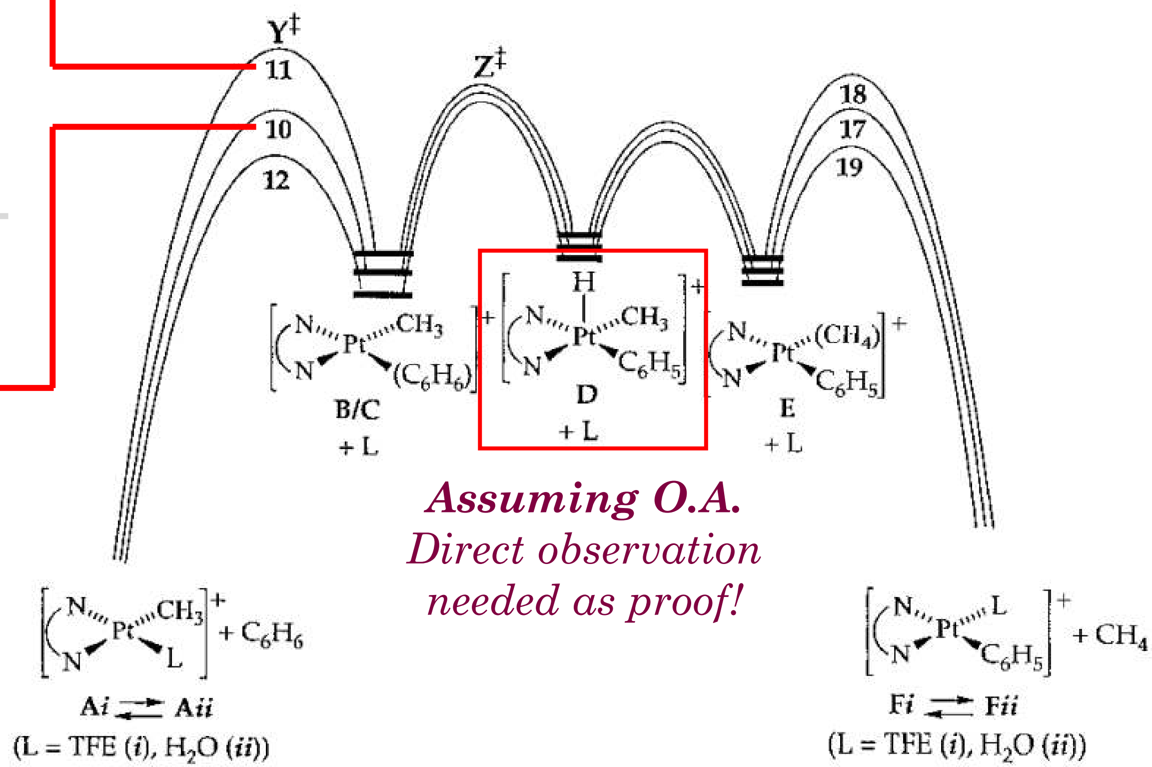


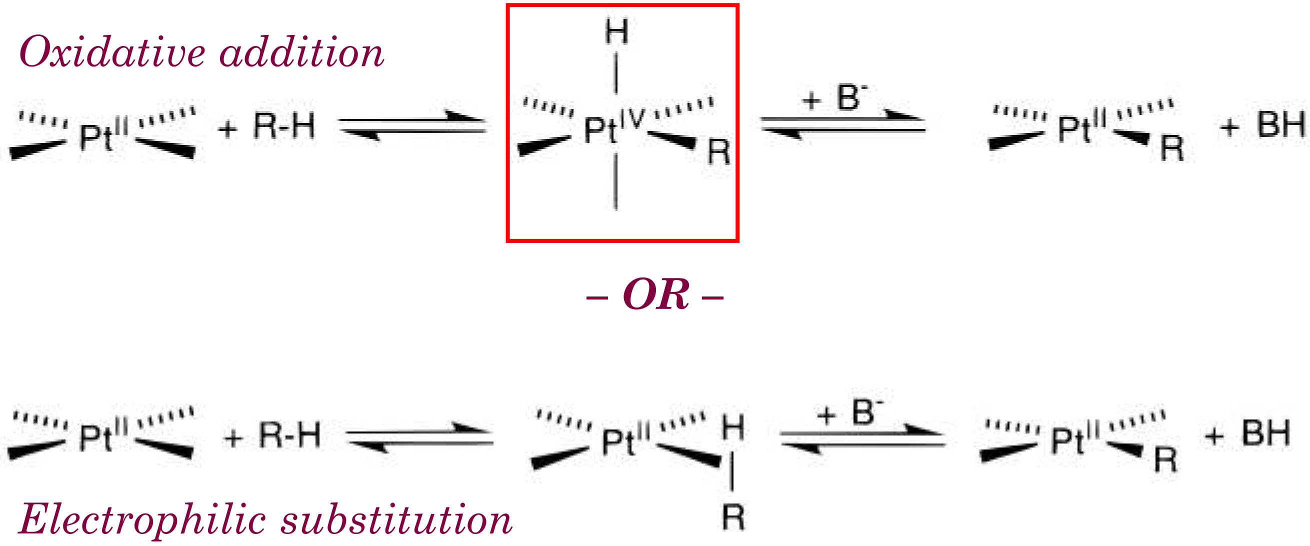


Assuming O.A.

Direct observation needed as proof!

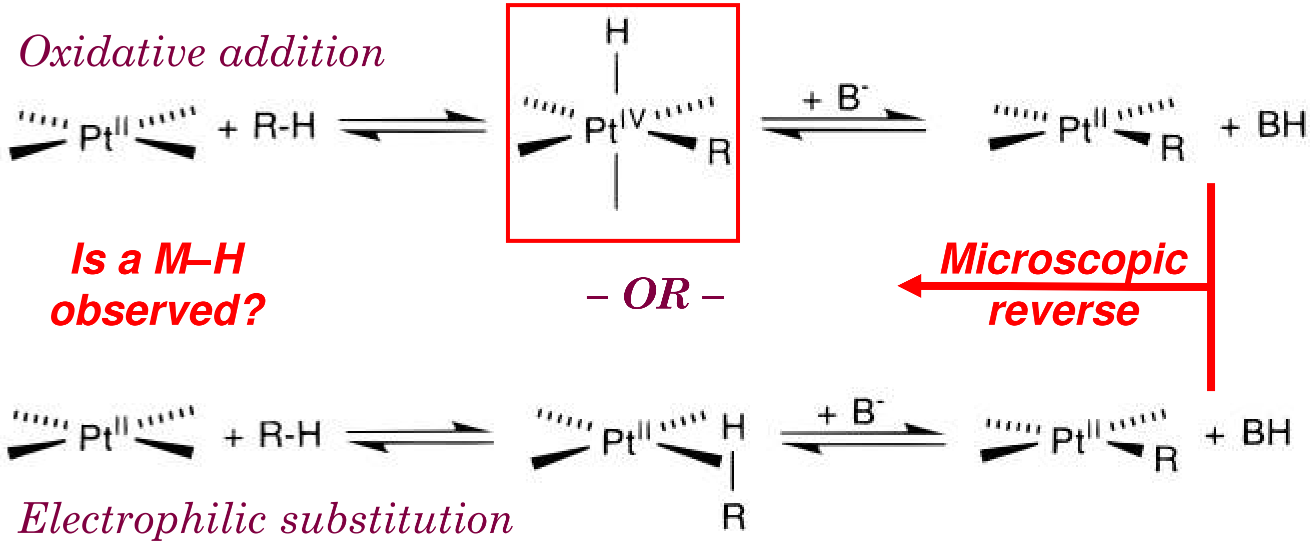
Bercaw, Pt: The protonolysis experiment™

***Shilov reaction:** mechanism of C–H activation*



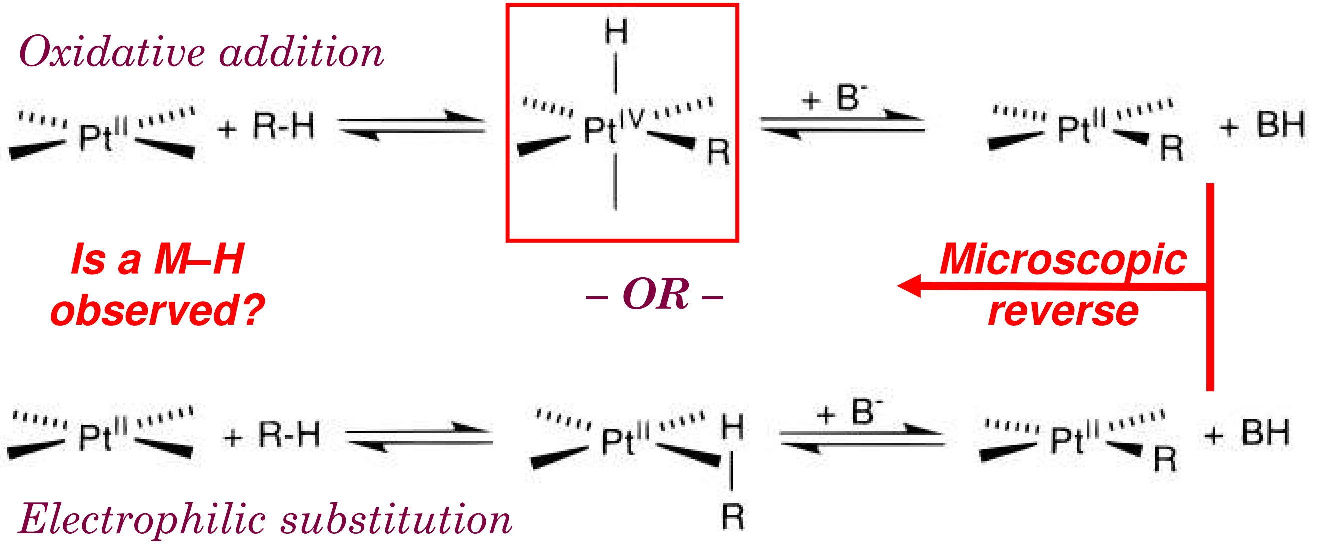
Bercaw, Pt: The protonolysis experiment™

Shilov reaction: *mechanism of C–H activation*



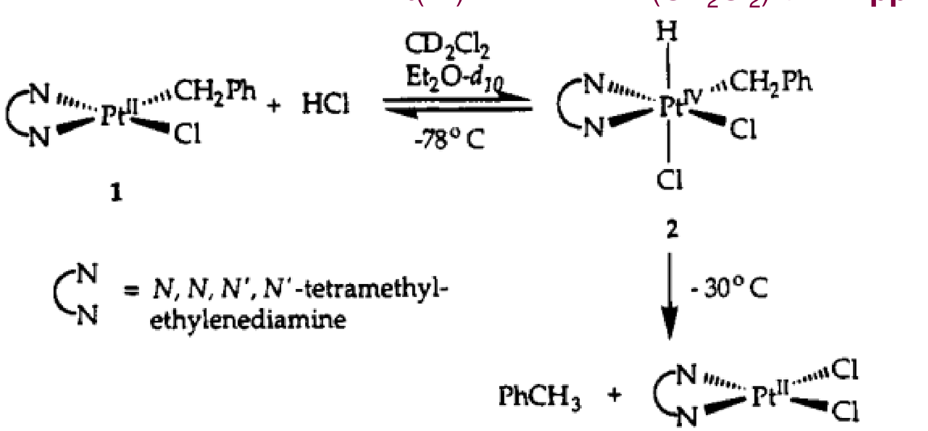
Bercaw, Pt: The protonolysis experiment™

Shilov reaction: *mechanism of C–H activation*

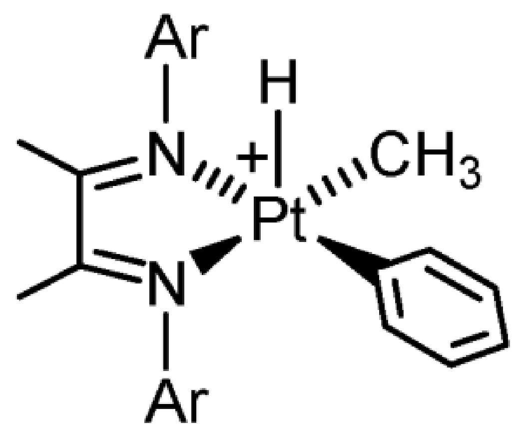


Stahl, S. S.; Labinger/Bercaw *JACS* **1995**, *117*, 9371.

Pt(IV)–H: [1]H NMR (CD_2Cl_2) δ **–24 ppm**



CH_4 or C_6H_6 activation

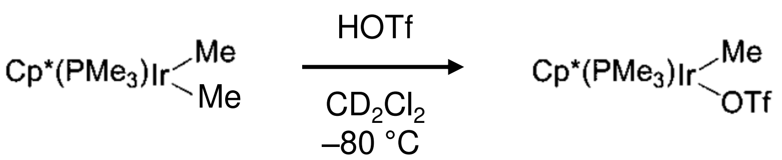


O.A. or σ-BM?

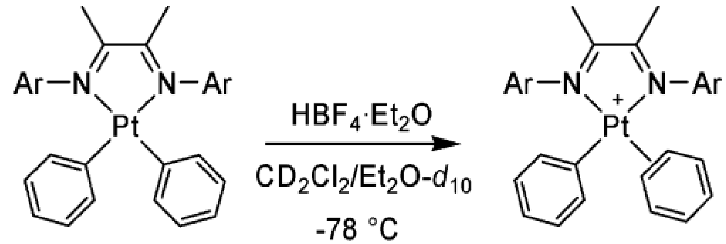
Bergman, Ir & Bercaw, Pt: M–H observed?

Initially inconclusive: *No M(n+2)–H observed for Ir(III) or Pt(II)*

Bergman, R. G. *J. Mol. Catal. A: Chem.* **2002**, *189*, 79.



Tilset, M. *JACS* **2006**, *128*, 2682.



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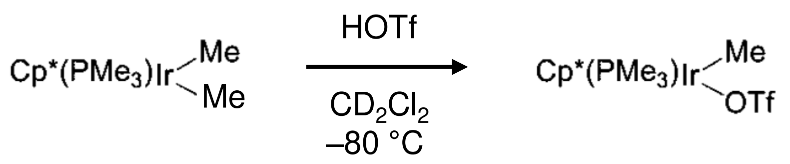

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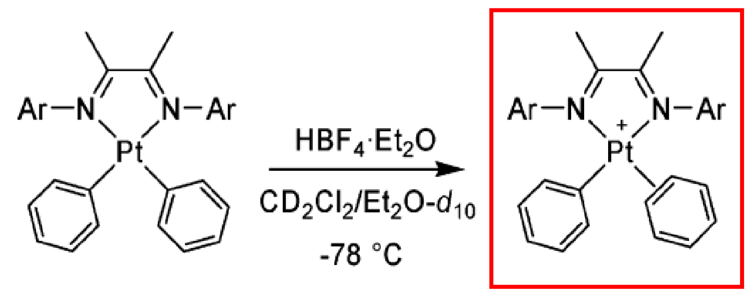
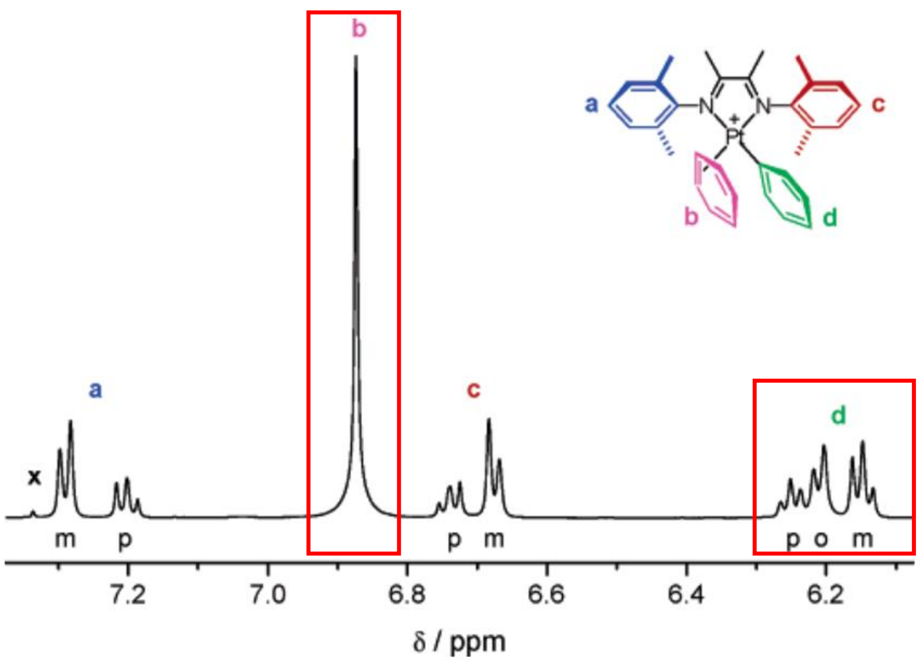
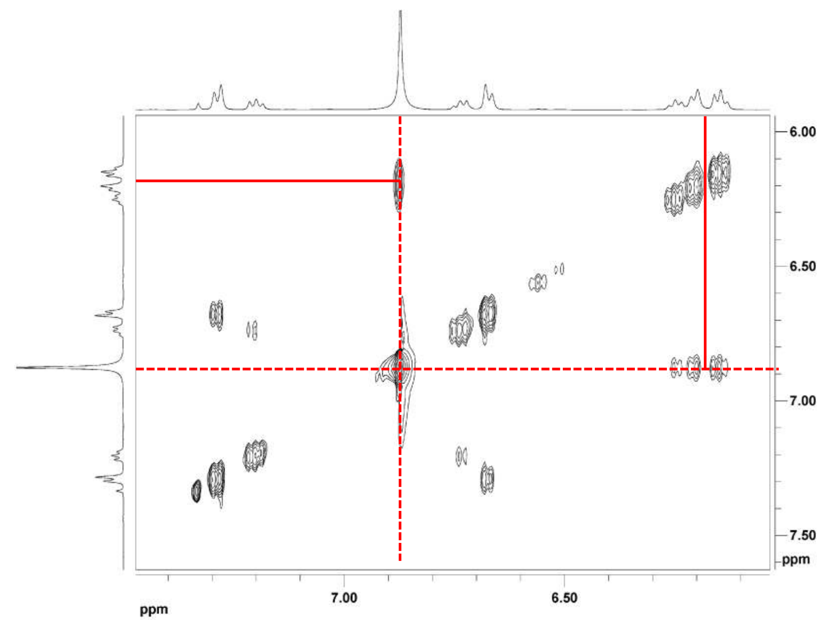


Pt^+(phenyl)(benzene): *Rapid π-benzene to phenyl exchange observed by NMR!*



^1H NMR (–23 °C)

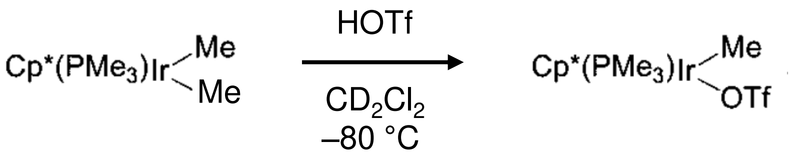


2D EXSY *(+ve phase, NOESY protocol)*

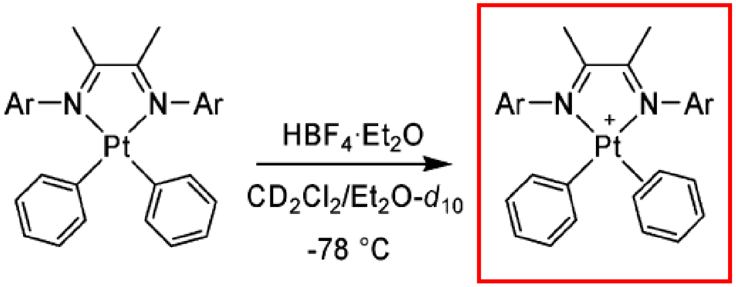
Bergman, <u>Ir</u> & Bercaw, <u>Pt</u>: M–H observed?

Initially inconclusive: *No M(n+2)–H observed for Ir(III) or Pt(II)*

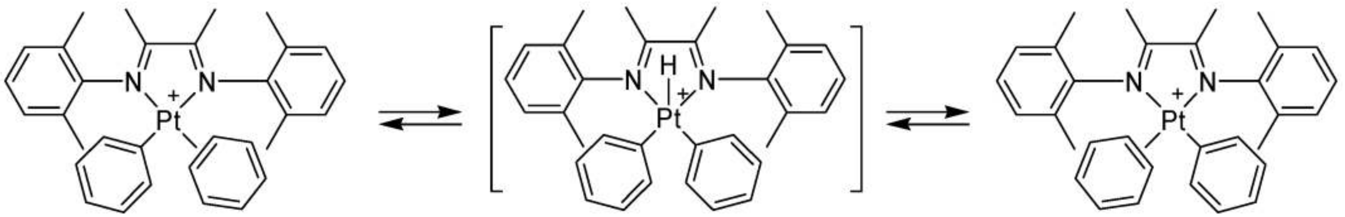
Bergman, R. G. *J. Mol. Catal. A: Chem.* **2002**, *189*, 79.



Tilset, M. *JACS* **2006**, *128*, 2682.



<u>Proposed reaction pathway</u>



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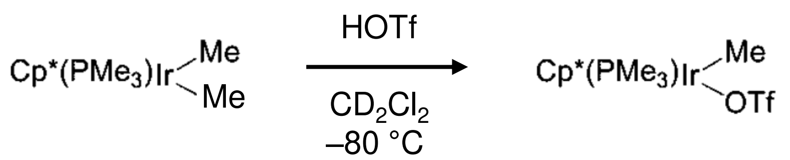
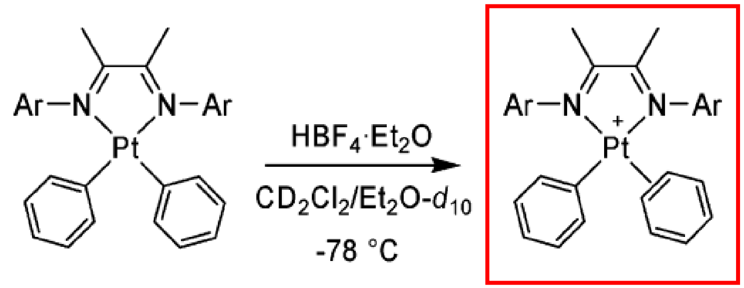
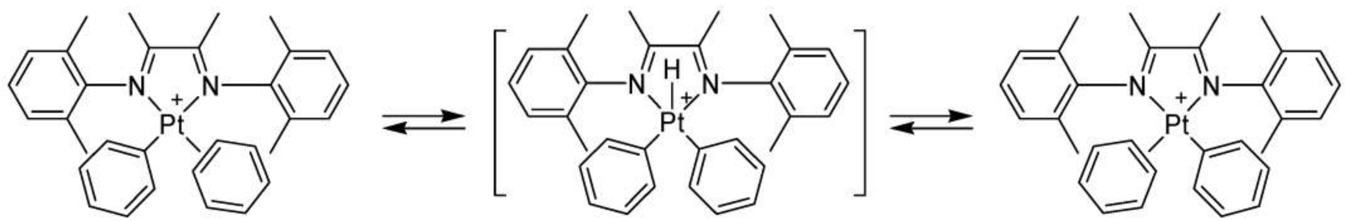


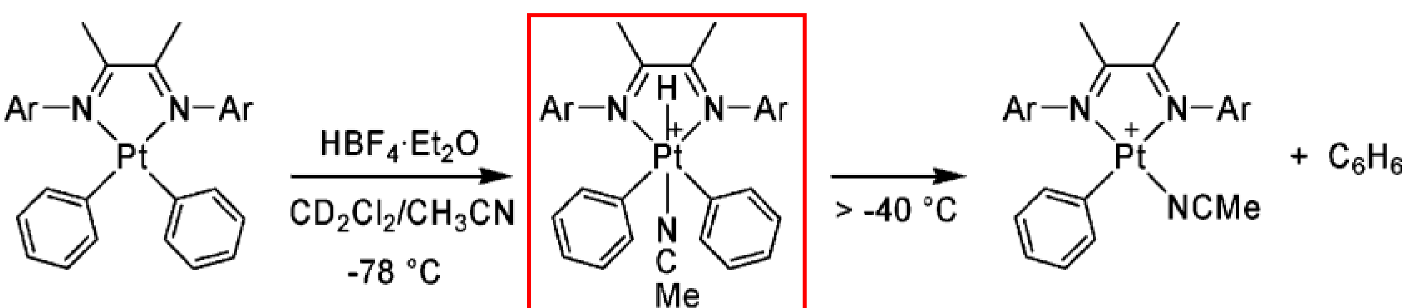
Tilset, M. *JACS* **2006**, *128*, 2682.



Mats Tilset *decided to add CH_3CN to try to "freeze-out" Pt(IV)–H*

Proposed reaction pathway

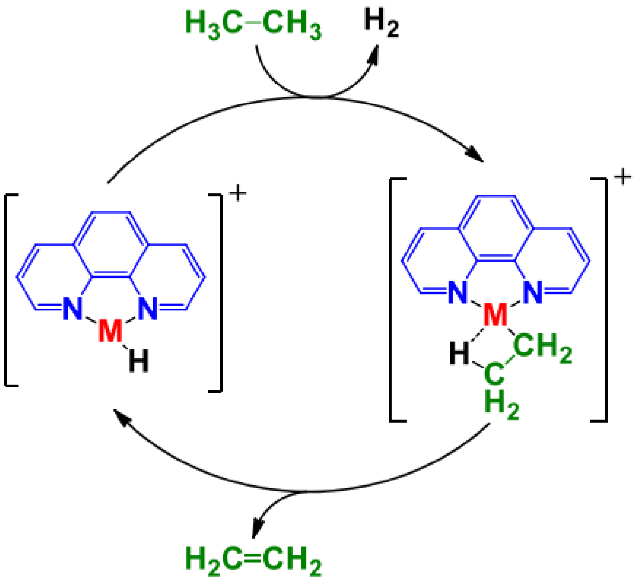




Pt(IV)–H: ^{1}H NMR (CD_2Cl_2) δ **–21.5 ppm**

3d & 4d analogues: Change in mechanism?

O'Hair, R. A. J. *Organometallics* **2020**, *39*, 4027.



Reactivity in gas-phase (MS):

Pt > Ni >> Pd

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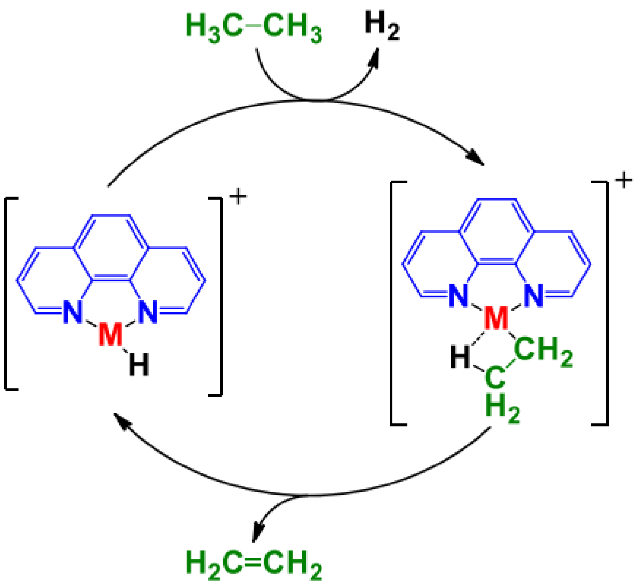
O'Hair, R. A. J. *Organometallics* **2020**, *39*, 4027.



Reactivity in gas-phase (MS):
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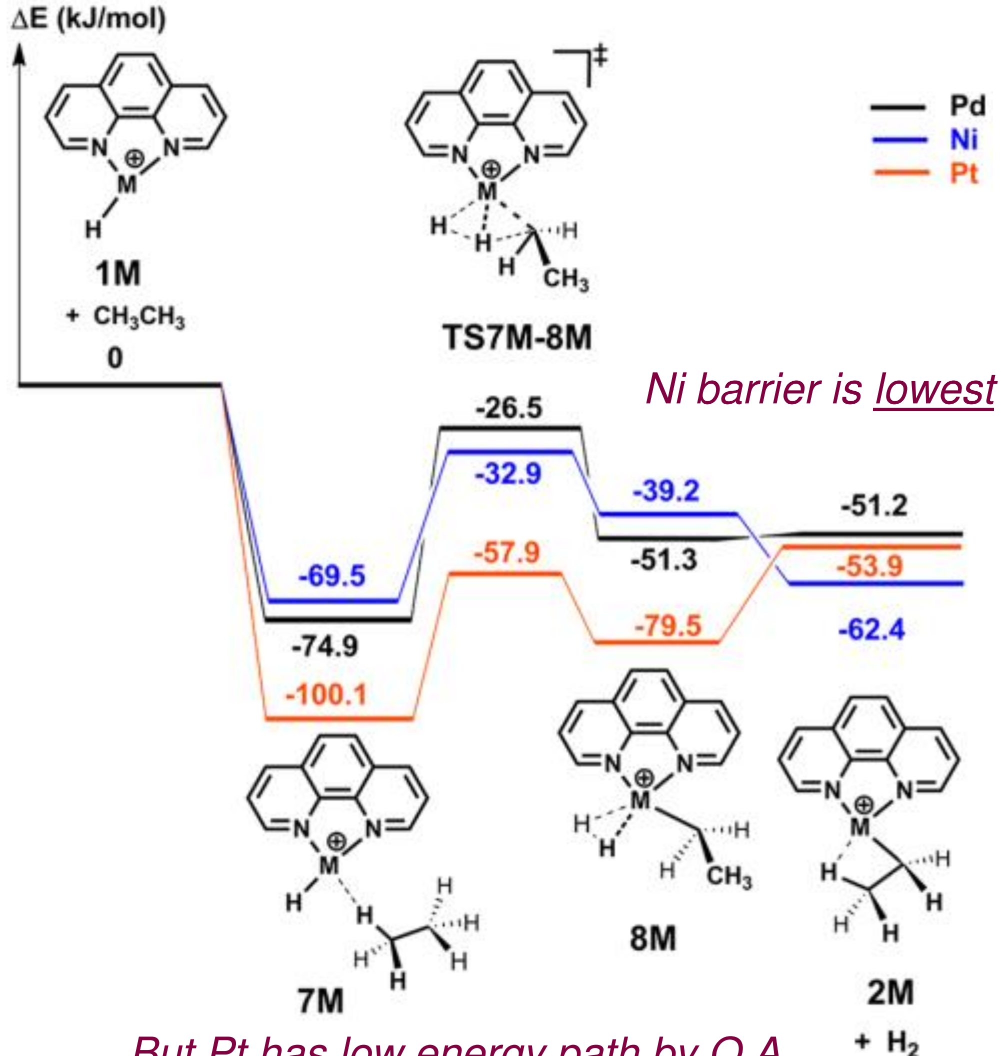
DFT: calculated σ-CAM pathways

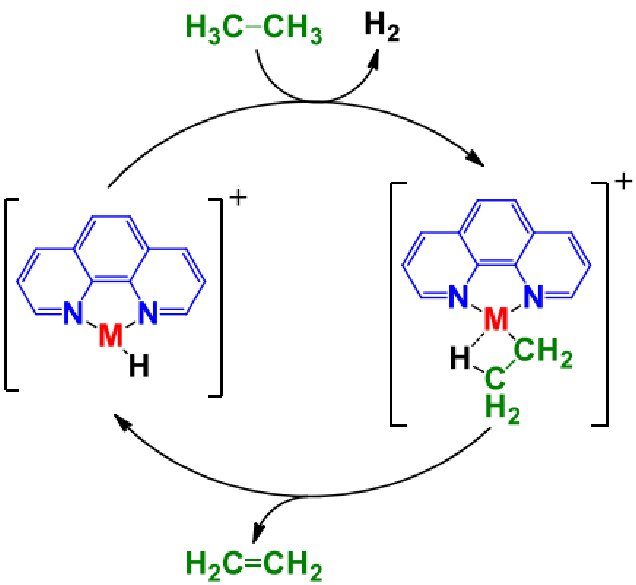


Ni barrier is lowest

But Pt has low energy path by O.A.

3d & 4d analogues: Change in mechanism?

O'Hair, R. A. J. *Organometallics* **2020**, *39*, 4027.



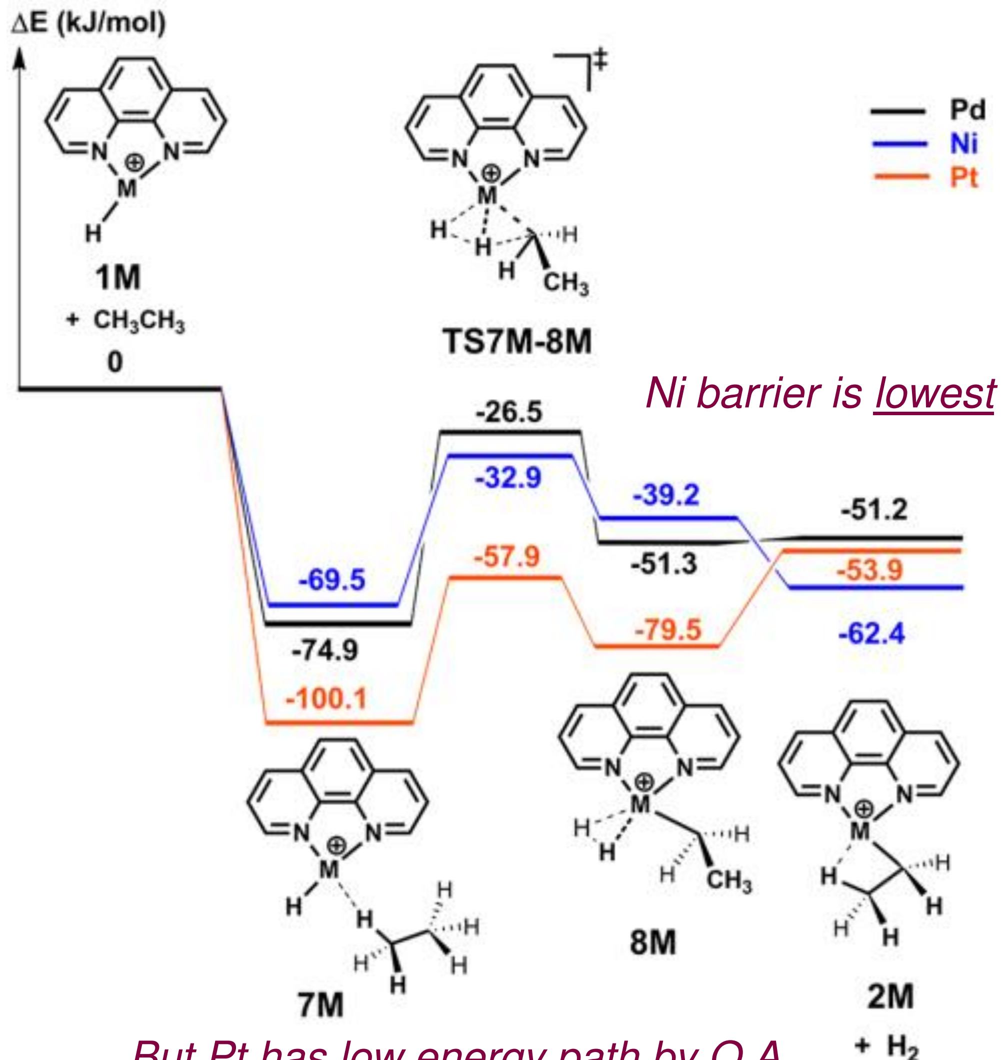
Reactivity in gas-phase (MS):
Pt > Ni >> Pd

Conclusion

Pt: O.A. / R.E. mechanism

Ni (& Pd): σ-CAM mechanism

DFT: calculated σ-CAM pathways



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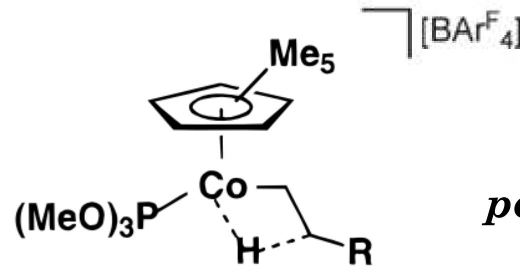
Brookhart, M. *JACS* **1985**, *107*, 1443.



a-olefin polymerization catalyst

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O'Hair, R. A. J. *Organometallics* **2020**, *39*, 4027.

Reactivity in gas-phase (MS):
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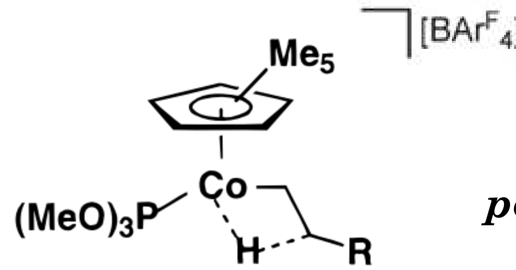
<u>Conclusion</u>

Pt: O.A. / R.E. mechanism

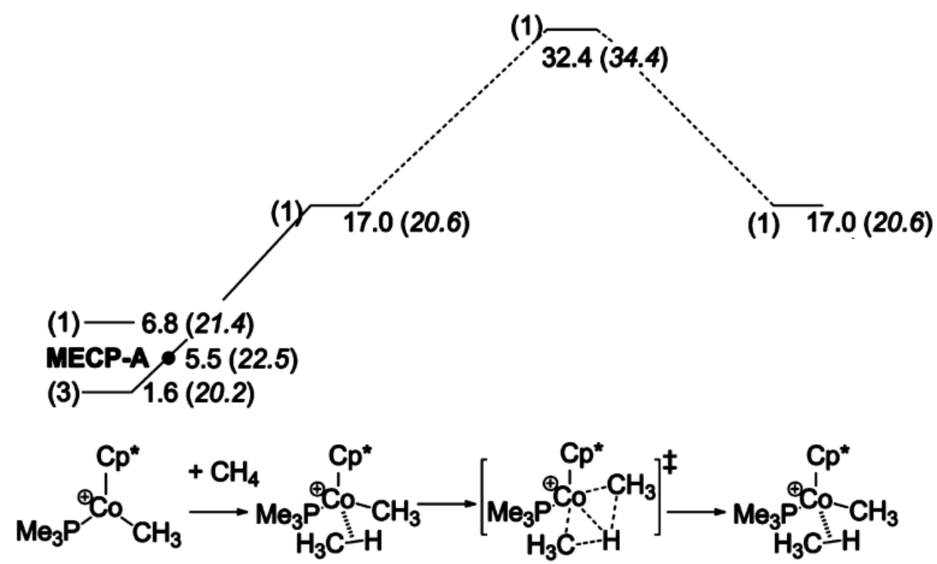
Ni (& Pd): <u>σ-CAM</u> mechanism

Brookhart, M. *JACS* **1985**, *107*, 1443.



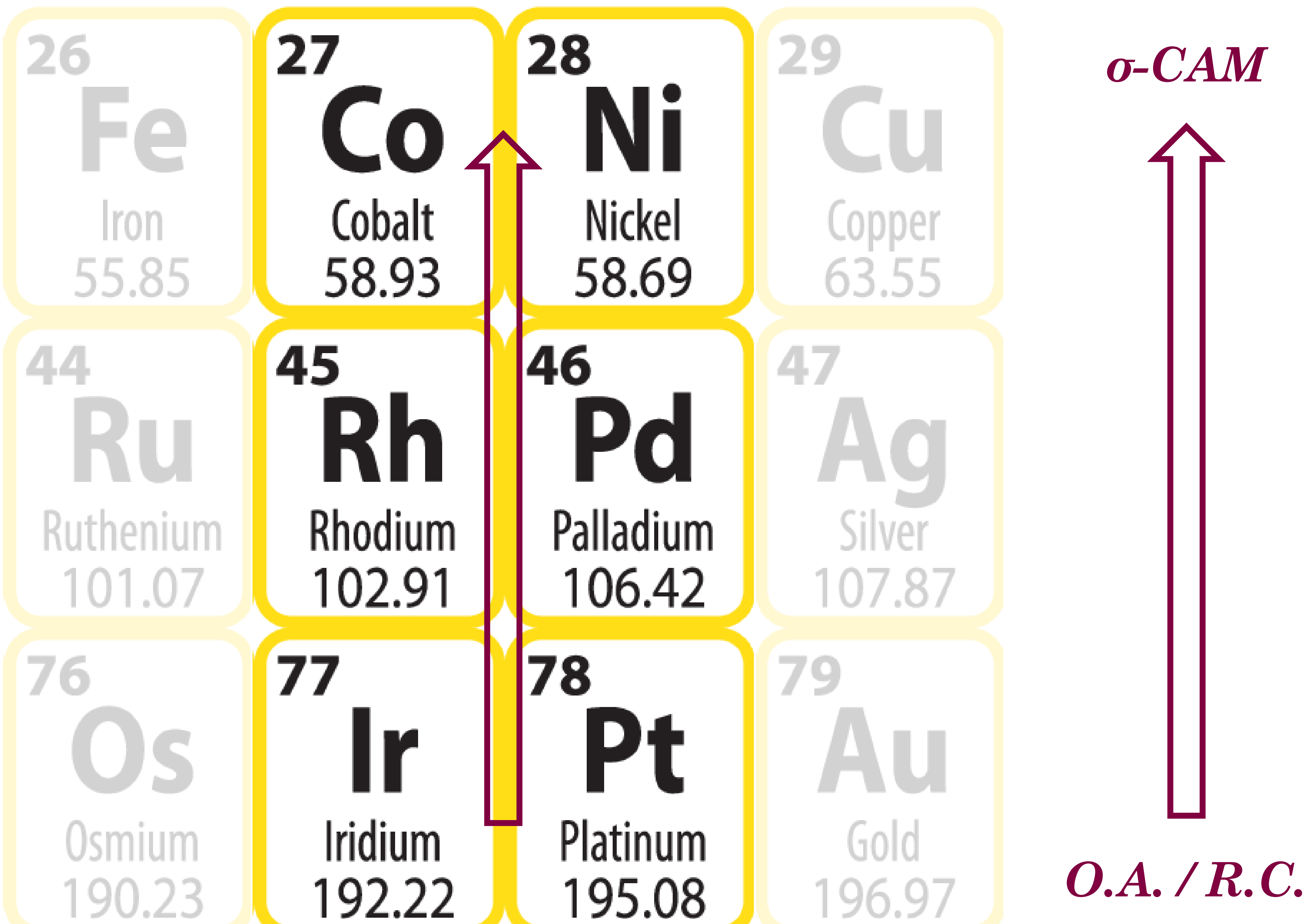
a-olefin polymerization catalyst

DFT: *computed to do methane exchange*
via <u>σ-CAM</u> mechanism

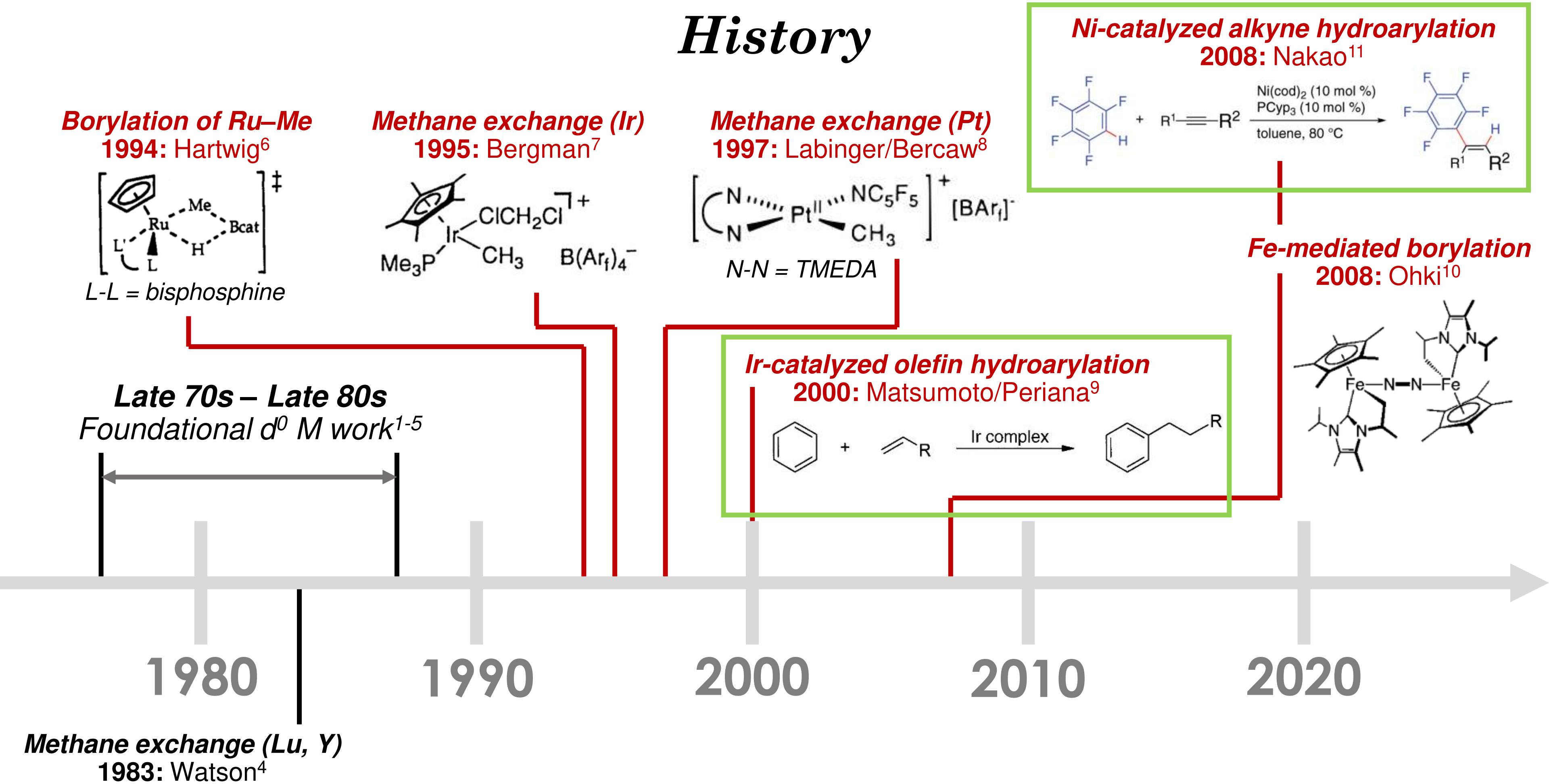


Cundari/Jones, *Organometallics* ***2015***, *34*, 4032.

3d & 4d analogues: Change in mechanism?



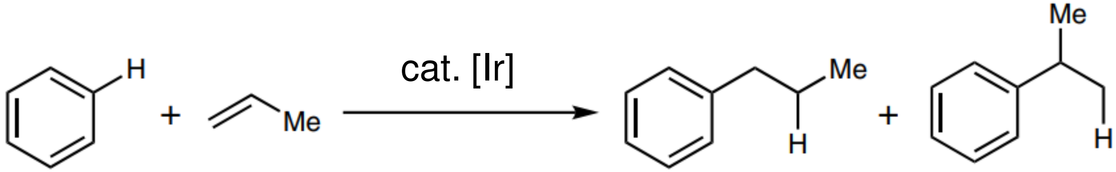
History



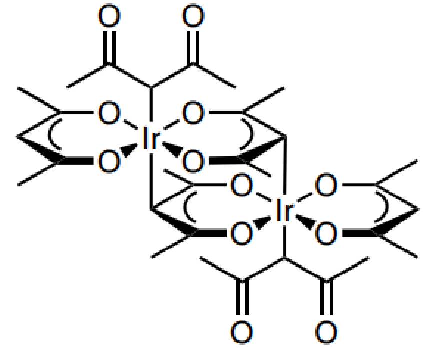
(6) Hartwig, J. F. *JACS* **1994**, *116*, 1839. (7) Bergman, R. G. *Science* **1995**, *270*, 1970. (8) Labinger, J. A.; Bercaw, J. E. *JACS* **1997**, *119*, 848. (9) Matsumoto, T.; Periana, R. A. *JACS* **2000**, *122*, 7414. (10) Ohki, Y. *JACS* **2008**, *130*, 17174. (11) Nakao, Y. *JACS* **2008**, *130*, 16170.

Periana, Ir: Olefin hydroarylation

Matsumoto/Periana, *JACS* **2000**, *122*, 7414.

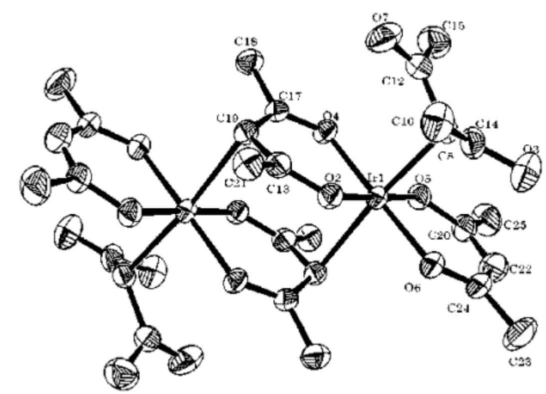


1.6 1.0



TON = 13

l/b = 1.6:1



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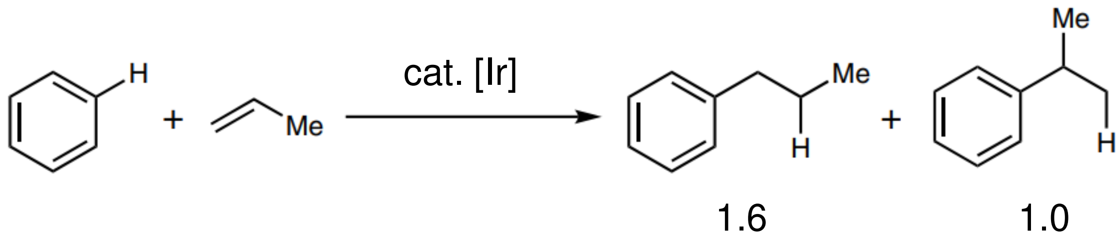
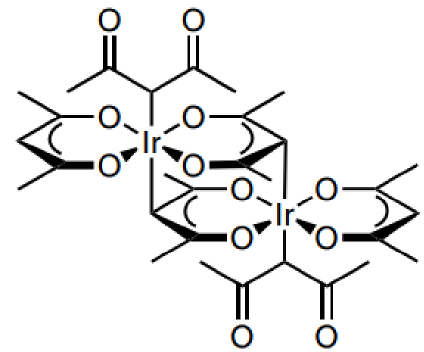


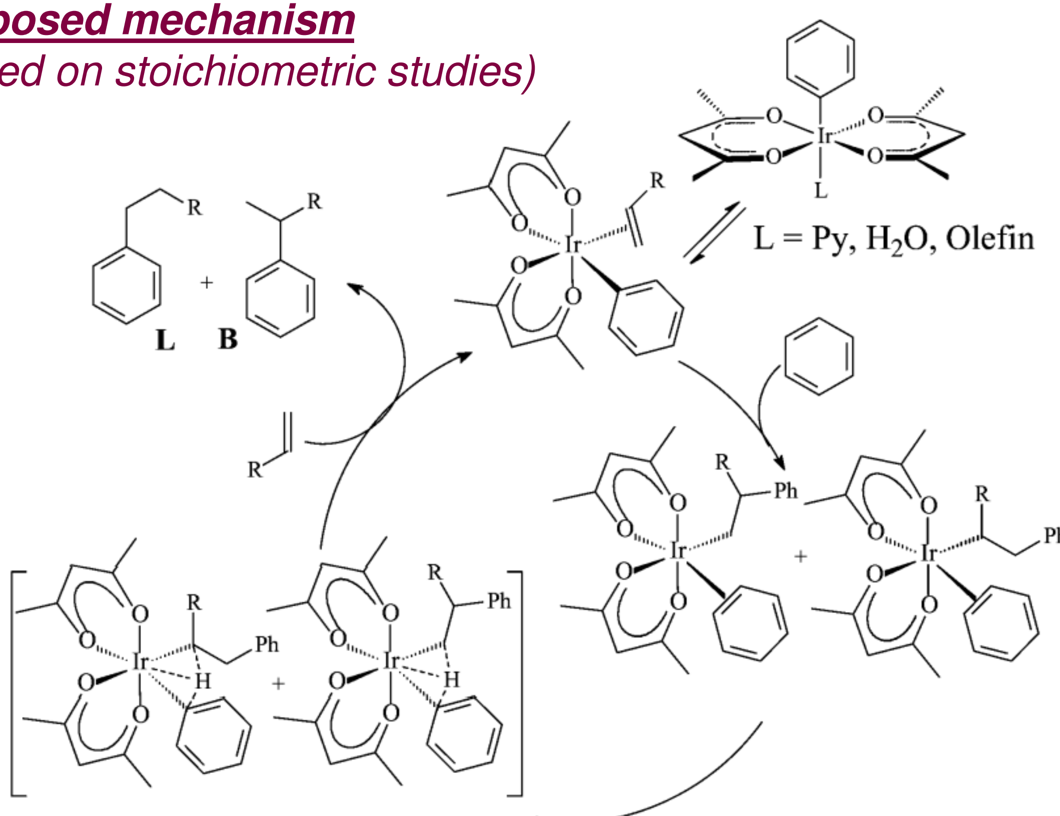


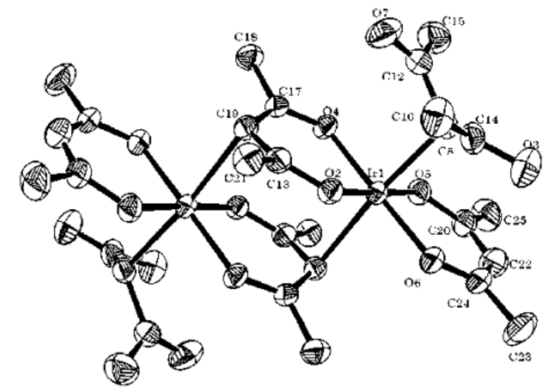
TON = 13

l/b = 1.6:1

Proposed mechanism

(based on stoichiometric studies)

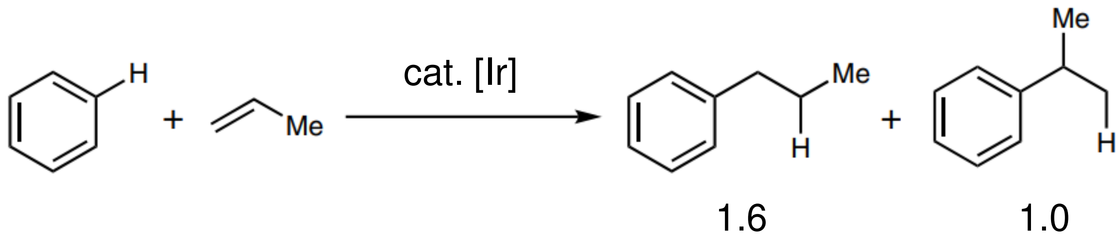


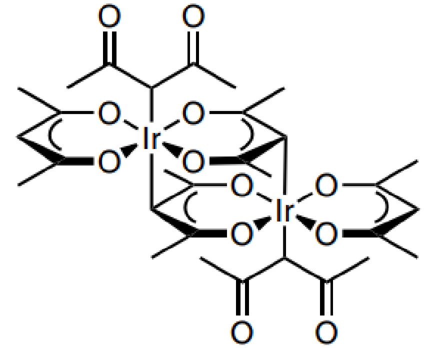


Periana, R. A. *Chem. Commun.* **2002**, 3000.

Periana, Ir: Olefin hydroarylation

Matsumoto/Periana, *JACS* **2000**, *122*, 7414.





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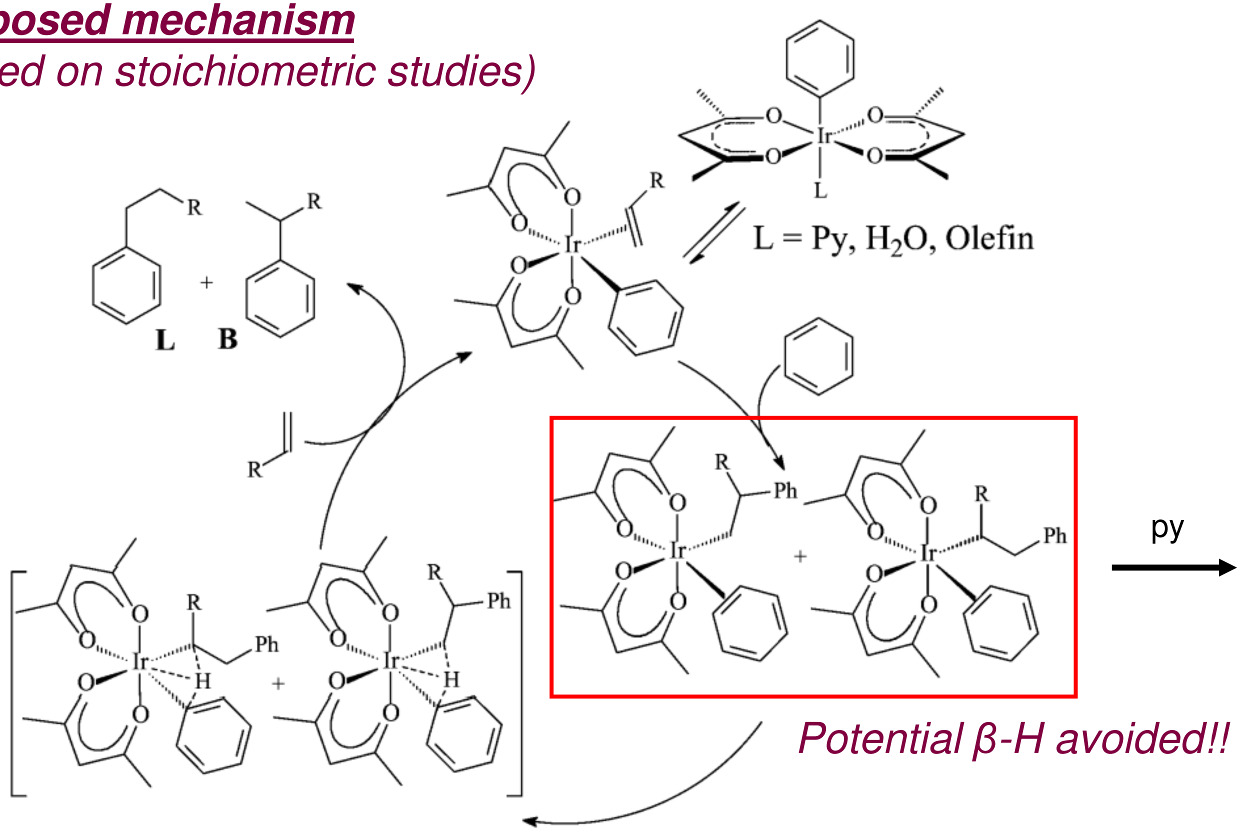

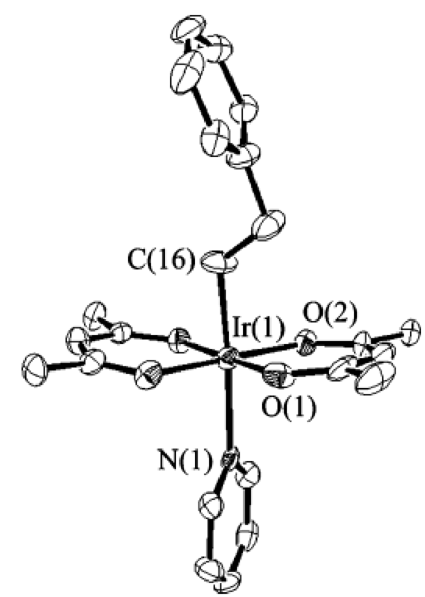

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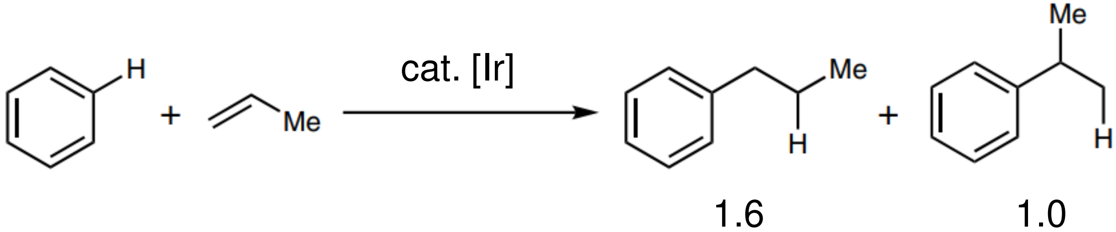

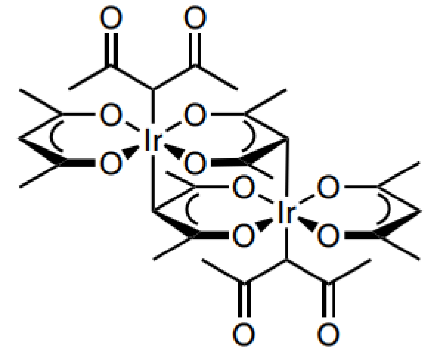

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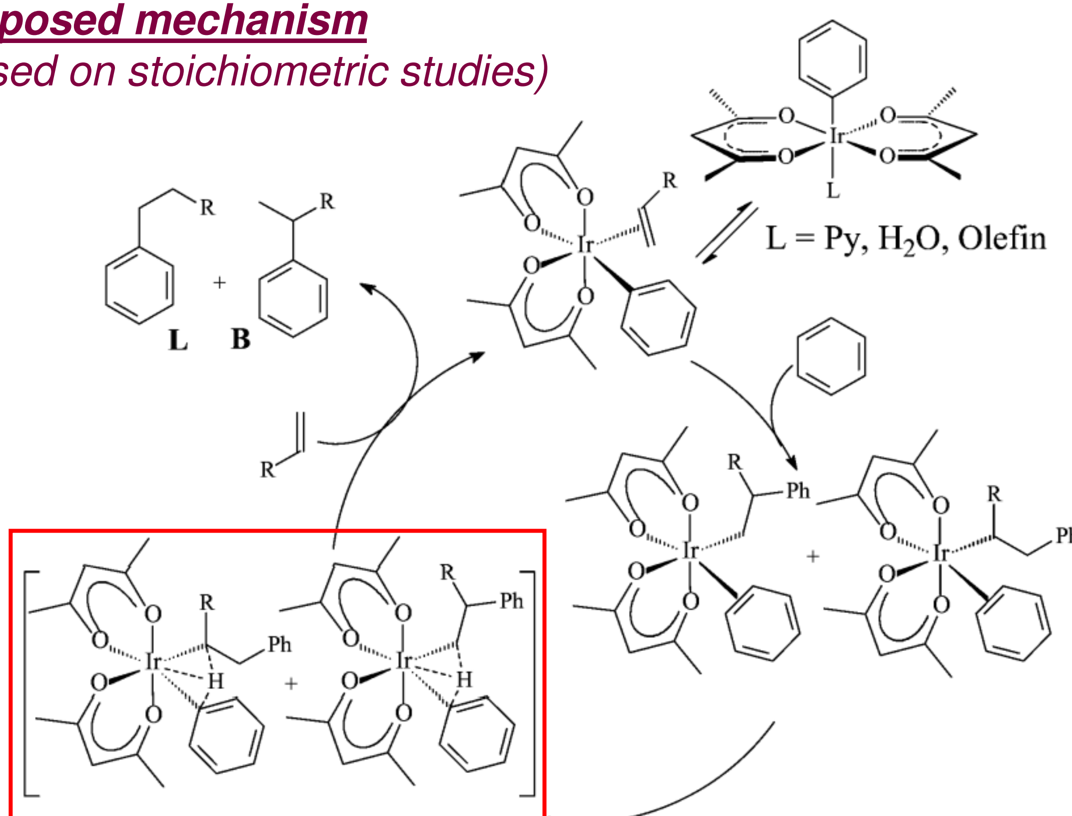
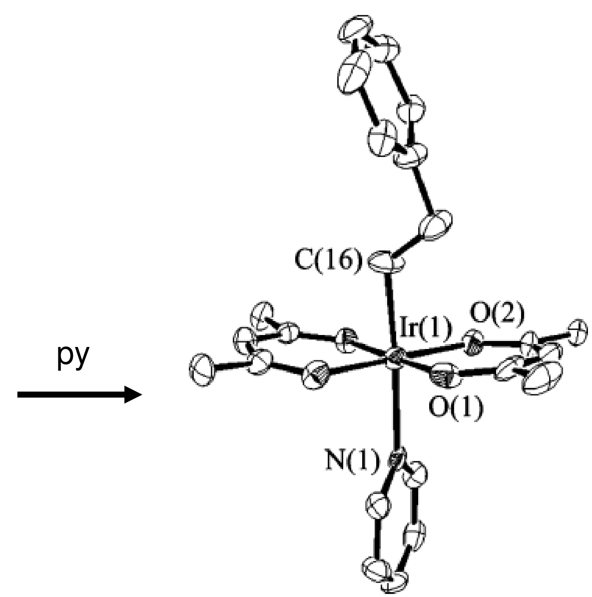


*σ-CAM (**DFT**)*



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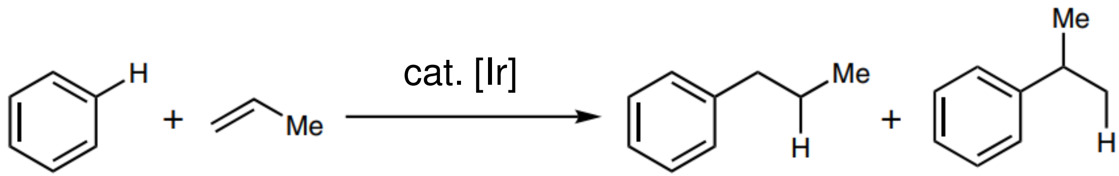
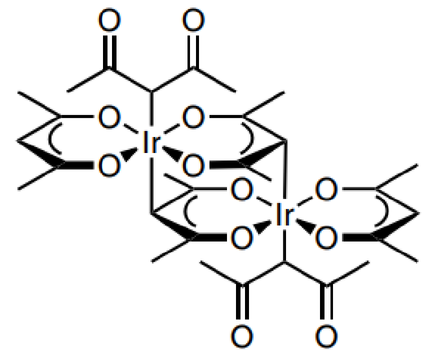


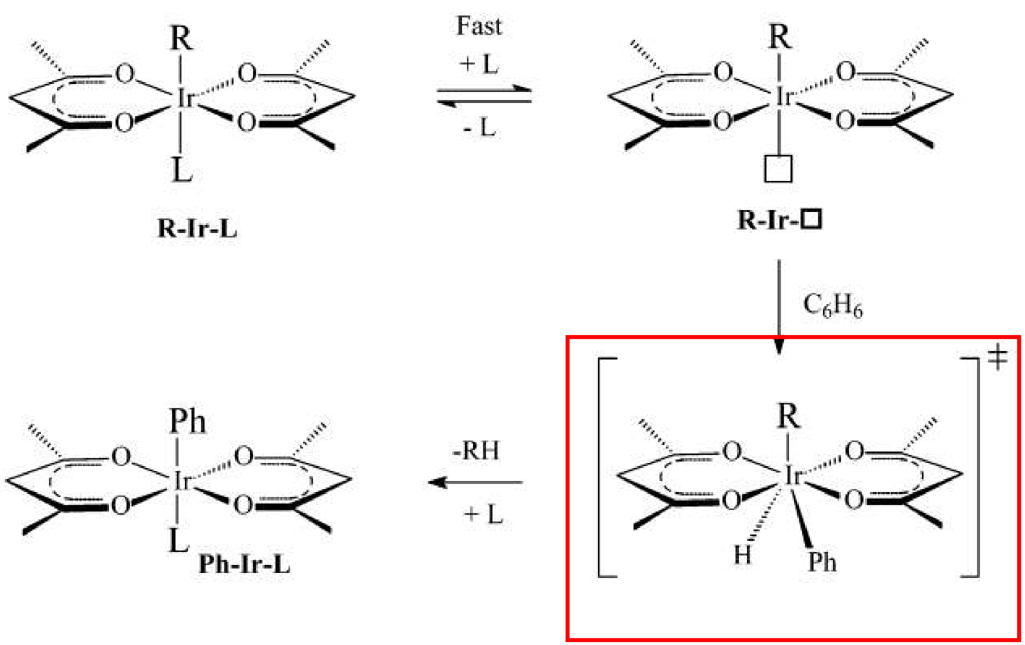
1.6 1.0



TON = 13

l/b = 1.6:1

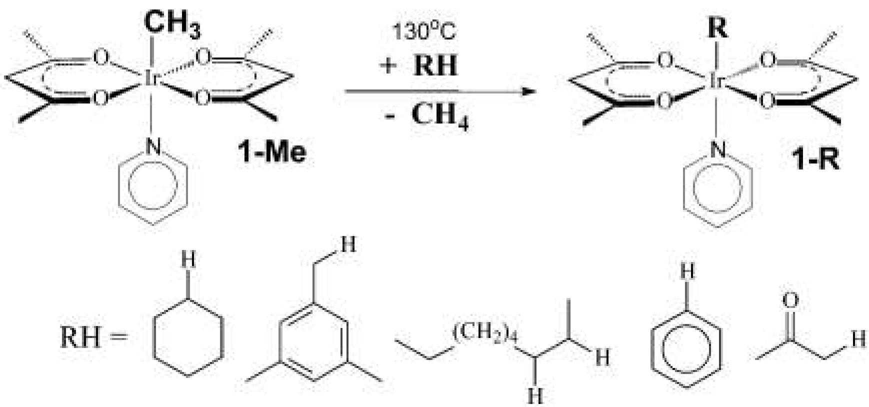
Oxidative addition ruled out by DFT ***(barrier <u>>50 kcal mol[-1]</u>)***

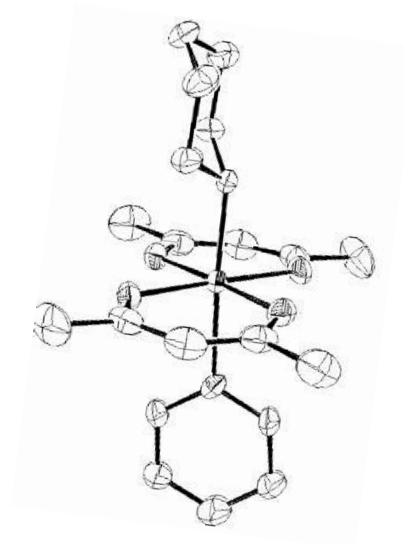


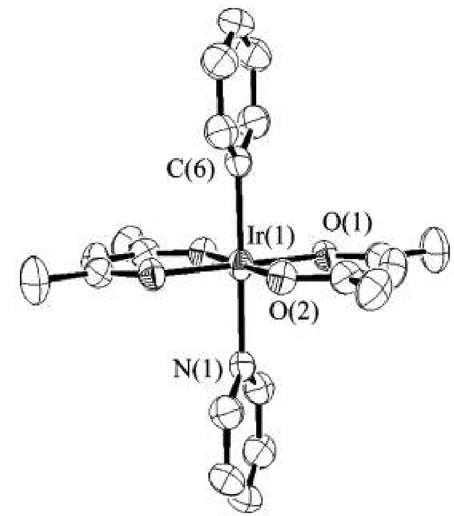
Periana, R. A. *JACS* **2005**, *127*, 11372.

Periana, Ir: Stoichiometric studies

Periana, R. A. *JACS* **2003**, *125*, 14292.







Arene and alkane C–H activation:

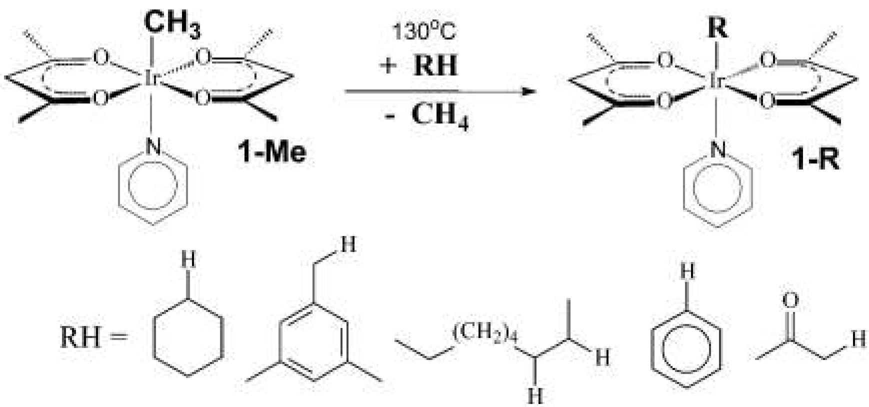
What are the elementary steps?

R = Cy

R = Ph

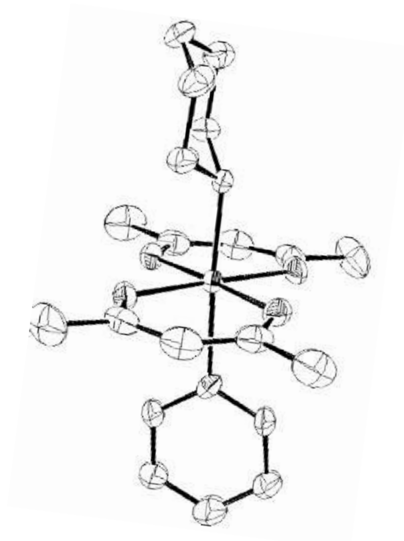
Periana, Ir: Stoichiometric studies

Periana, R. A. *JACS* **2003**, *125*, 14292.

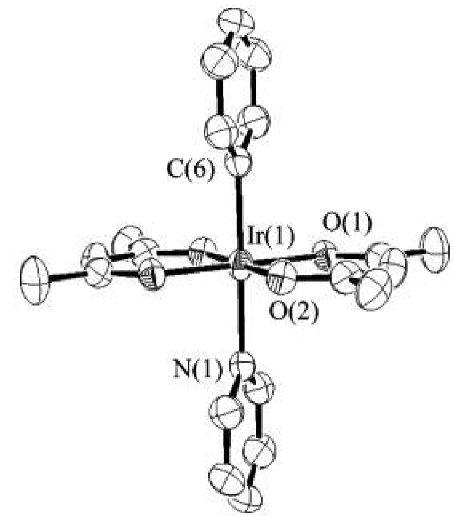


Arene and alkane C–H activation:

What are the elementary steps?

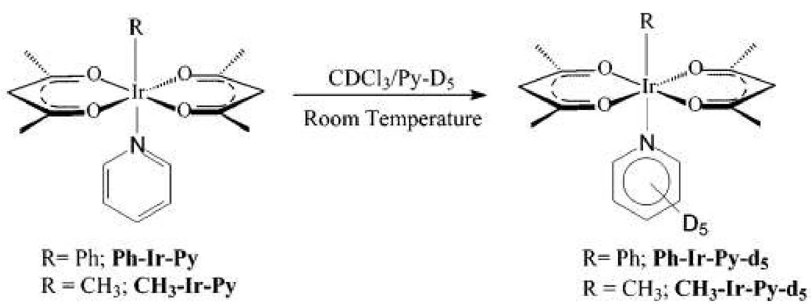


R = Cy



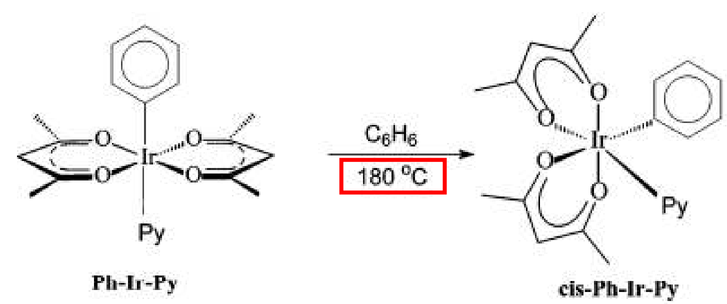
R = Ph

Facile pyridine exchange (dissociative)



Trans effect of the hydrocarbyl group

Trans-to-cis isomerization



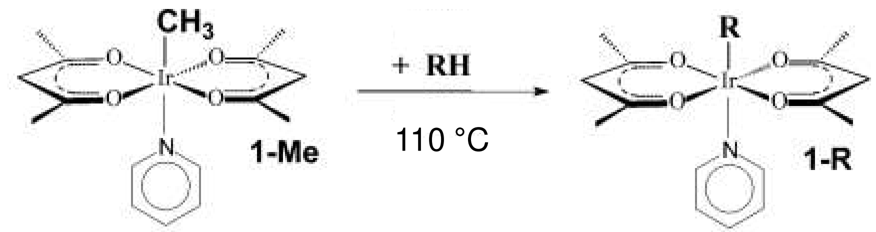
cis-isomer more stable *(& py non-labile!)*

Periana, R. A. *JACS* **2005**, *127*, 11372.

Periana, Ir: Kinetic studies

Periana, R. A. *JACS* **2005**, *127*, 11372.

(py)[Ir]–Me + C_6D_6
Order in pyridine: –1
Order in arene: +1
*$\Delta S^{\ddagger}$ = **+11.5 e.u.***
*$\Delta G^{\ddagger}_{298}$ = **+37.7 kcal mol^{-1}***



isotopomer[a]	C_6D_6
CH_4	0
CH_3D	100

Periana, Ir: Kinetic studies

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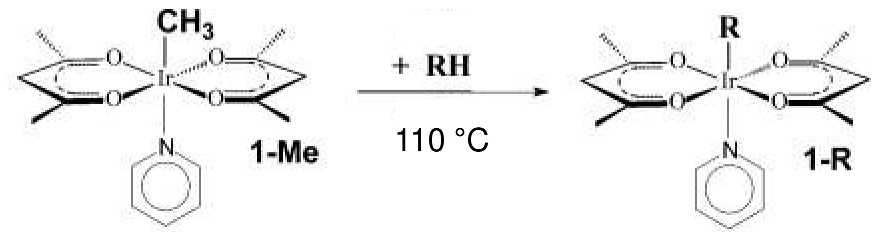
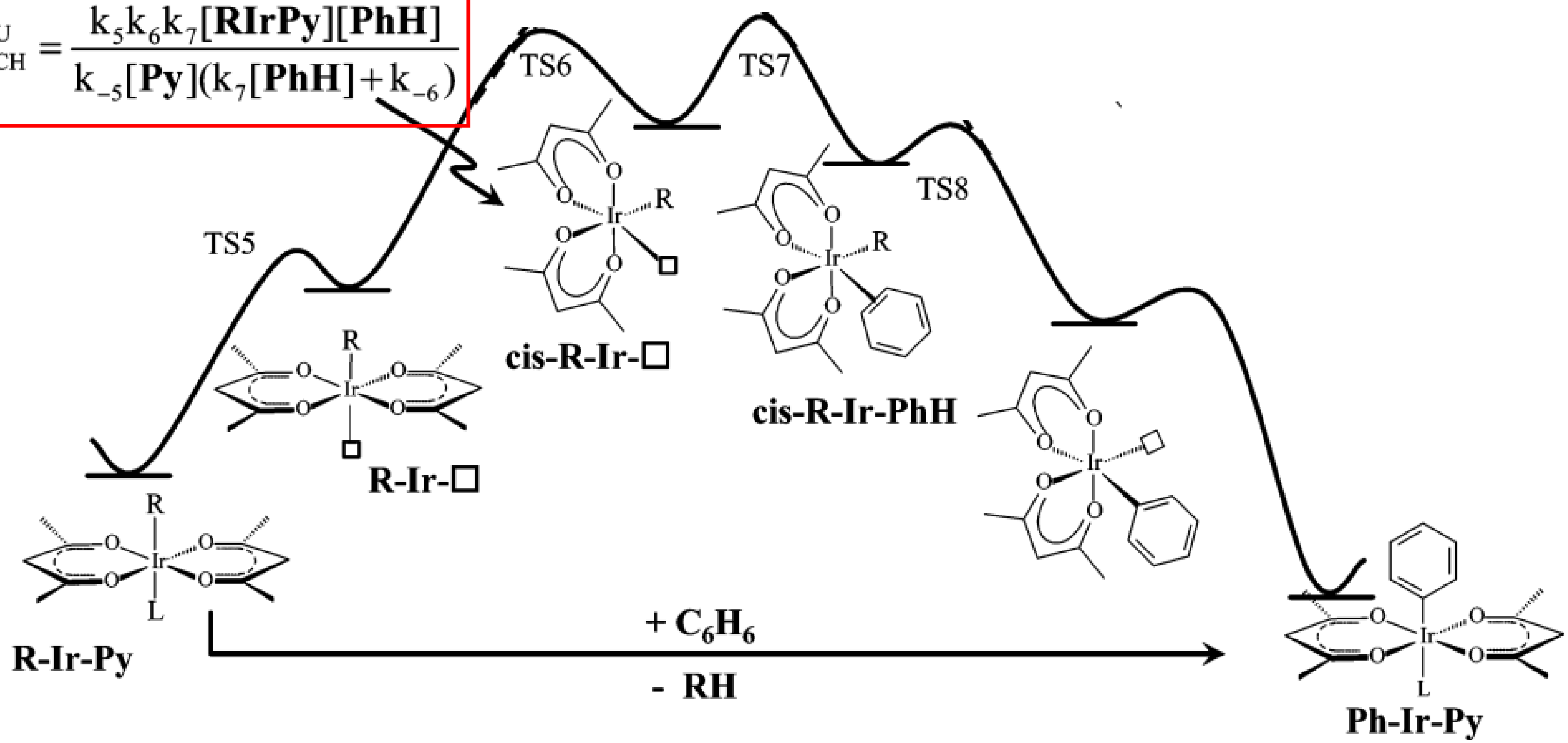


isotopomer[a]	C_6D_6
CH_4	0
CH_3D	100

$$\text{rate}^{U}_{CH} = \frac{k_5 k_6 k_7 [\mathbf{RIrPy}][\mathbf{PhH}]}{k_{-5}[\mathbf{Py}](k_7[\mathbf{PhH}] + k_{-6})}$$



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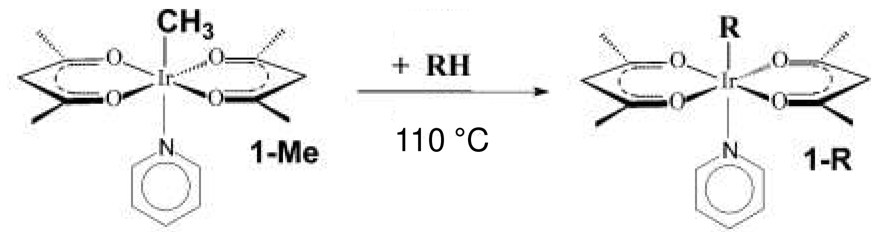
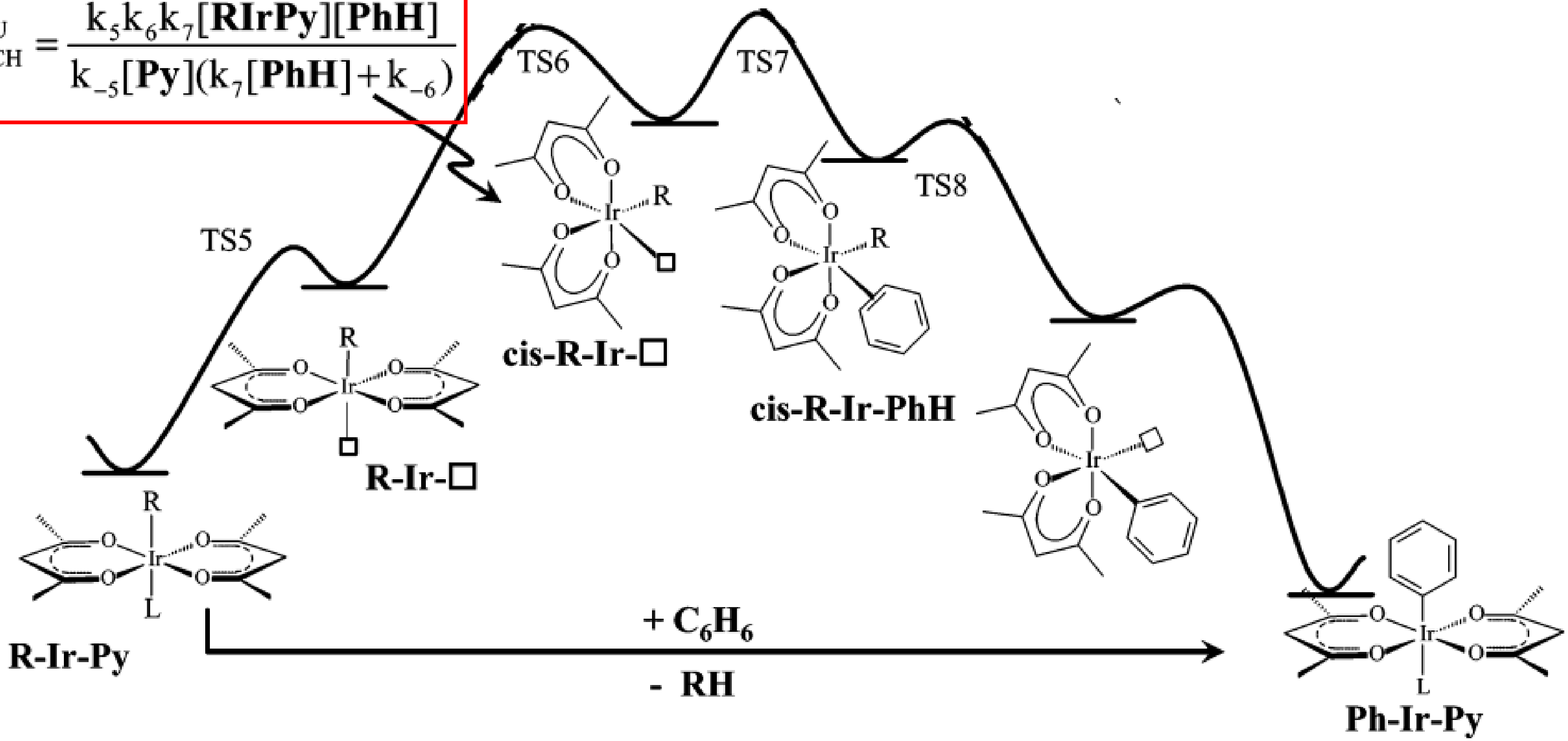


isotopomer[a]	C_6D_6	1,3,5-$C_6H_3D_3$	C_6H_6/C_6D_6 (1:1 molar mixture)
CH_4	0	76	50
CH_3D	100	24	50
KIE		***<u>3.2</u>***	***1***

$$\mathrm{rate}^{U}_{CH} = \frac{k_5 k_6 k_7[\mathbf{RIrPy}][\mathbf{PhH}]}{k_{-5}[\mathbf{Py}](k_7[\mathbf{PhH}]+k_{-6})}$$



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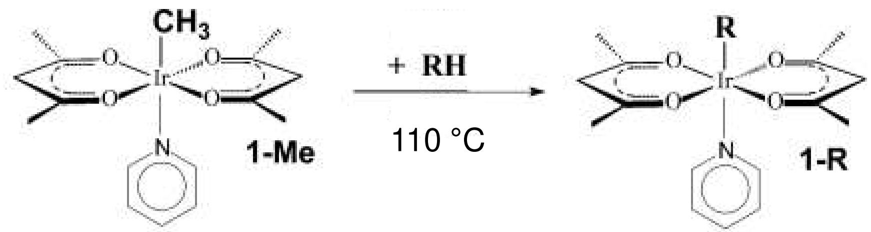

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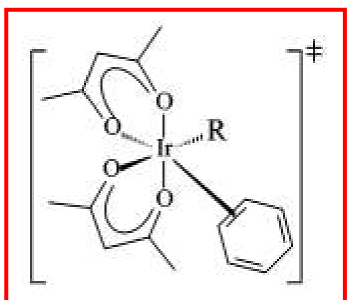
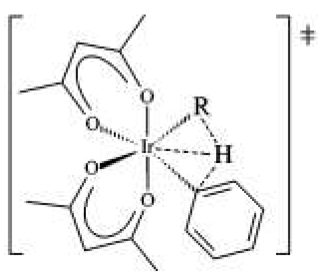
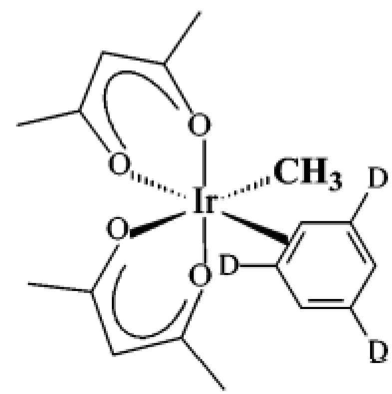
CH_4	0	76	50
CH_3D	100	24	50
KIE		***3.2***	***1***

Rate-determining
formation of π-arene complex





then
facile C–H activation

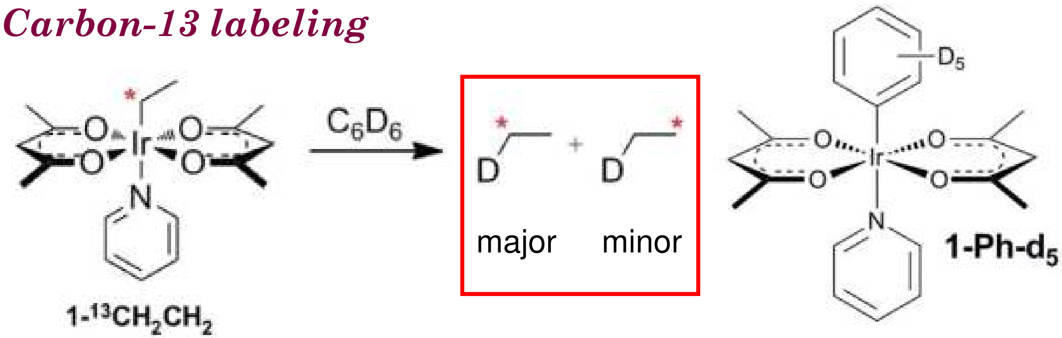


Intramolecular competition

Jones, W. D. *JACS* **1986**, *108*, 4814.

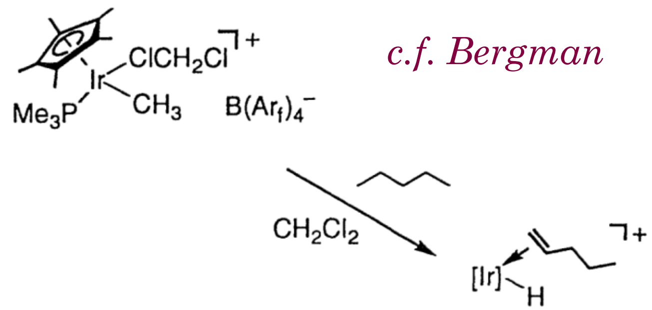
Periana, Ir: The "magic" of this system

Carbon-13 labeling



Periana, R. A. *Green Chem.* **2011**, *13*, 69.

c.f. Bergman



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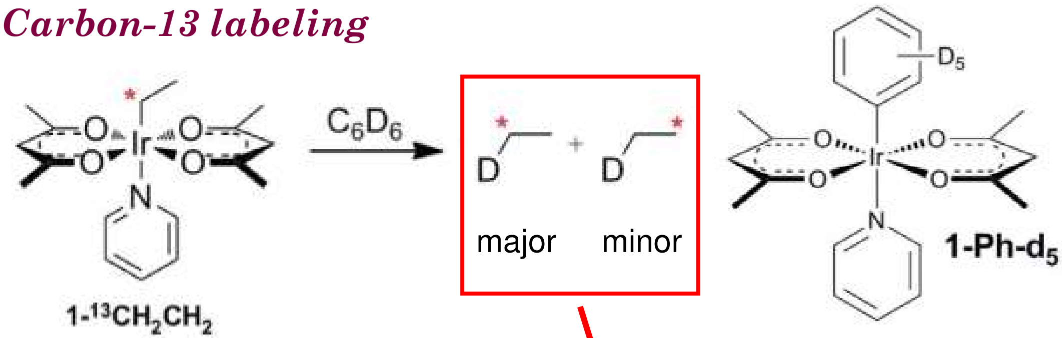

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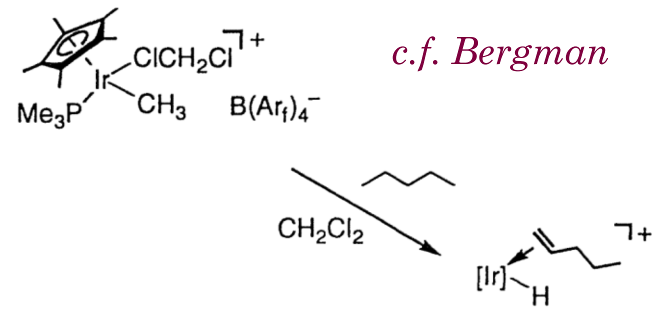
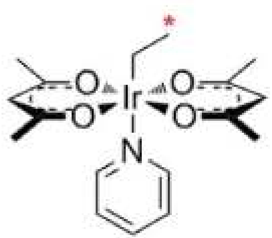
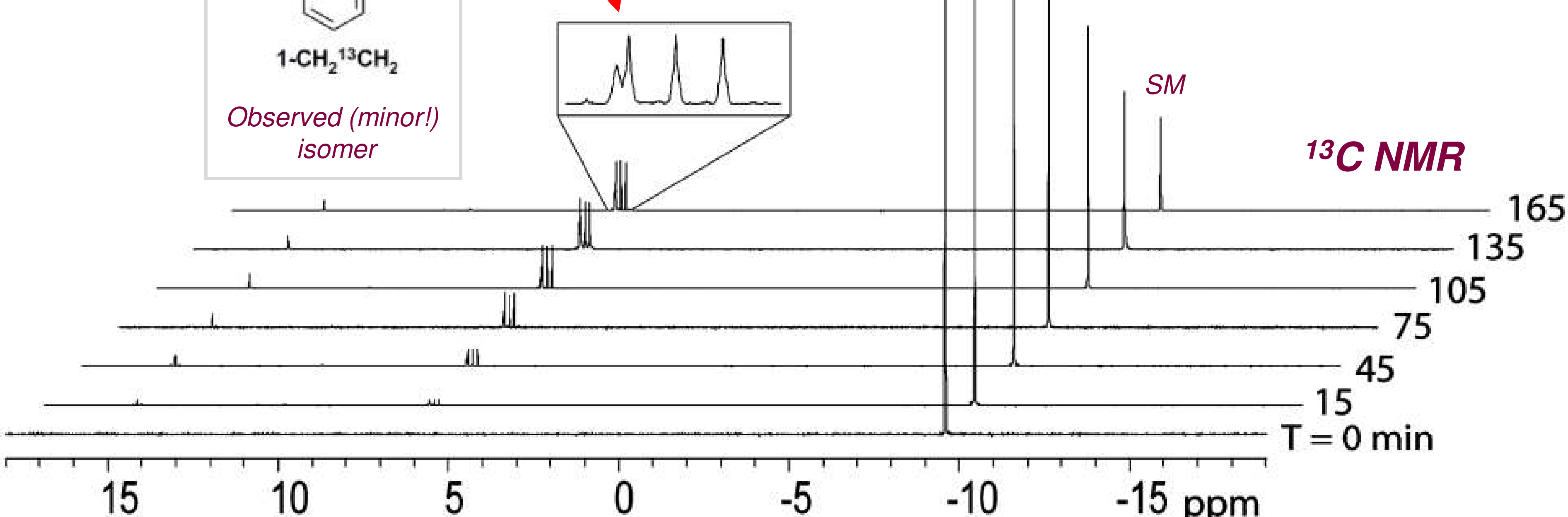




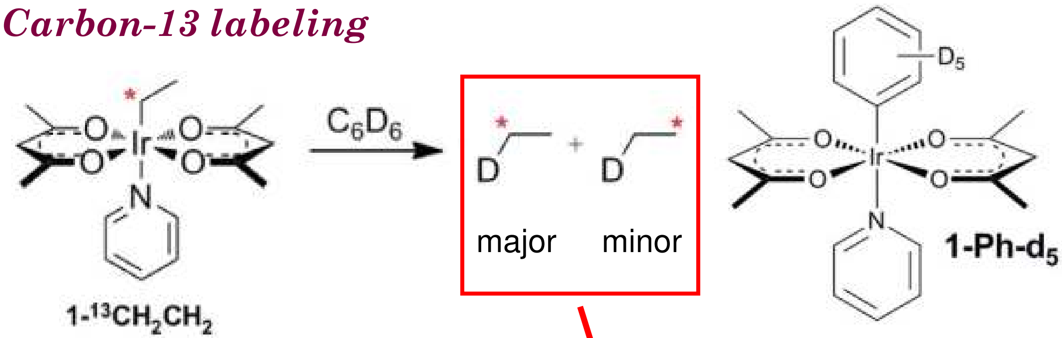
$1\text{-}CH_2{}^{13}CH_2$

Observed (minor!) isomer



Periana, Ir: The "magic" of this system

Carbon-13 labeling



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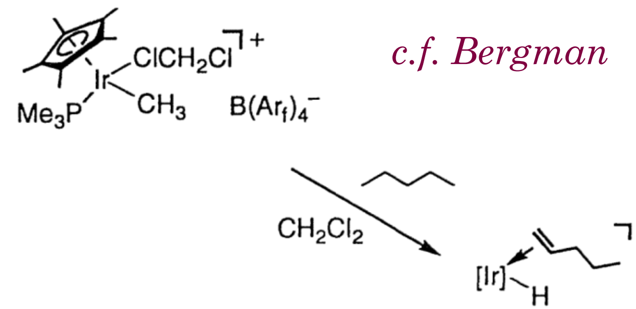


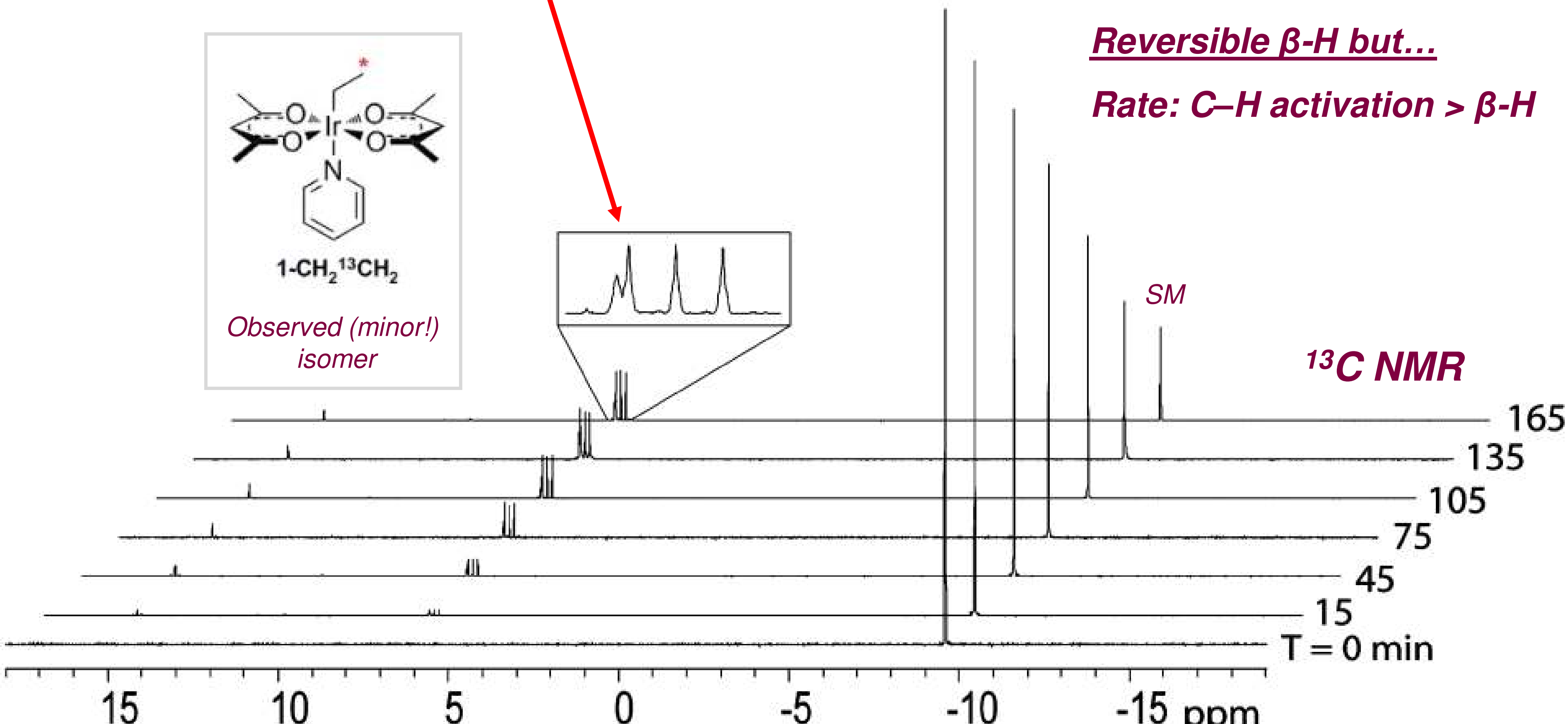
c.f. Bergman

Reversible β-H but…

Rate: C–H activation > β-H

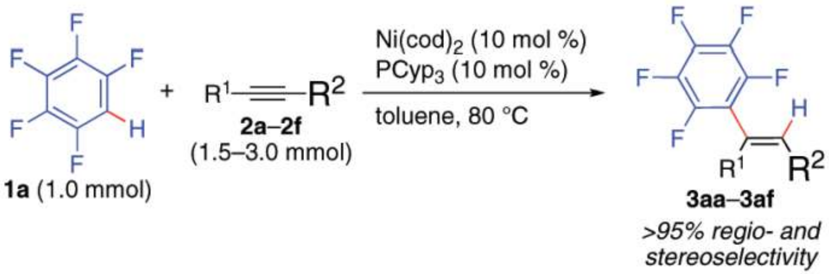
$1\text{-}CH_2{}^{13}CH_2$

Observed (minor!) isomer



Nakao, Ni: The "LLHT" mechanism

Nakao/Hiyama, *JACS* **2008**, *130*, 16170.



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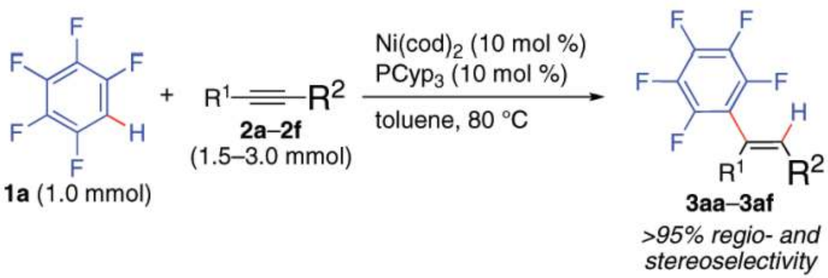
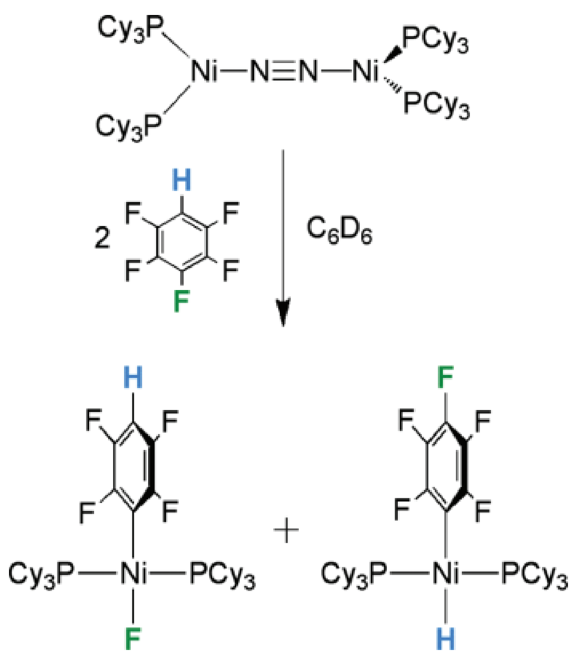


Nakao/Ogoshi, *Dalton Trans.* **2010**, *39*, 10483.

Note: without alkyne



1 : 4

Nakao, Ni: The "LLHT" mechanism

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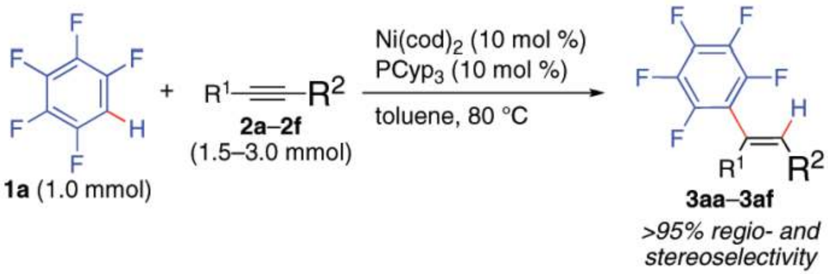

Nakao/Ogoshi, *Dalton Trans.* **2010**, *39*, 10483.

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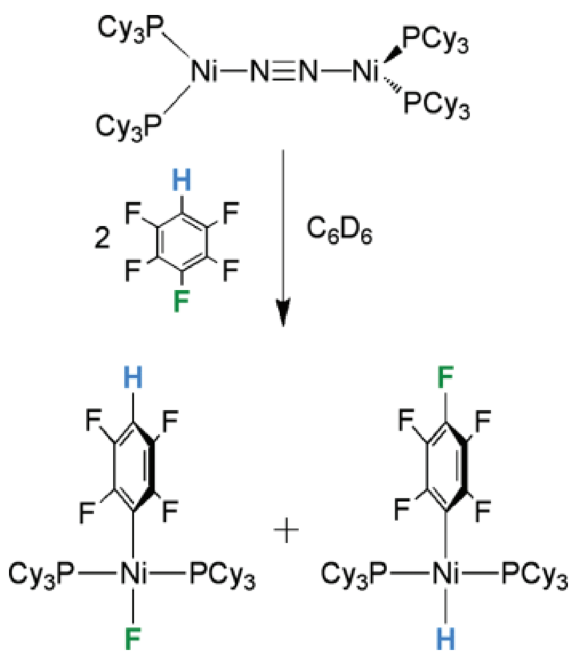
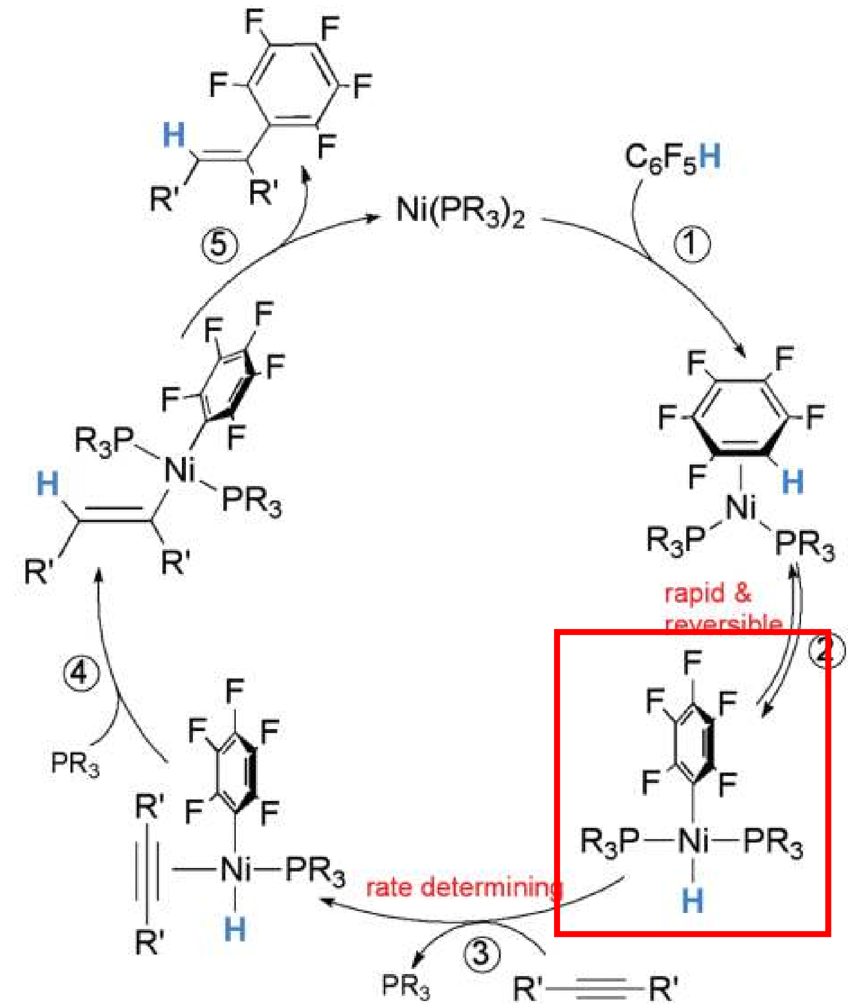


1 : 4

(Initially!) Proposed mechanism

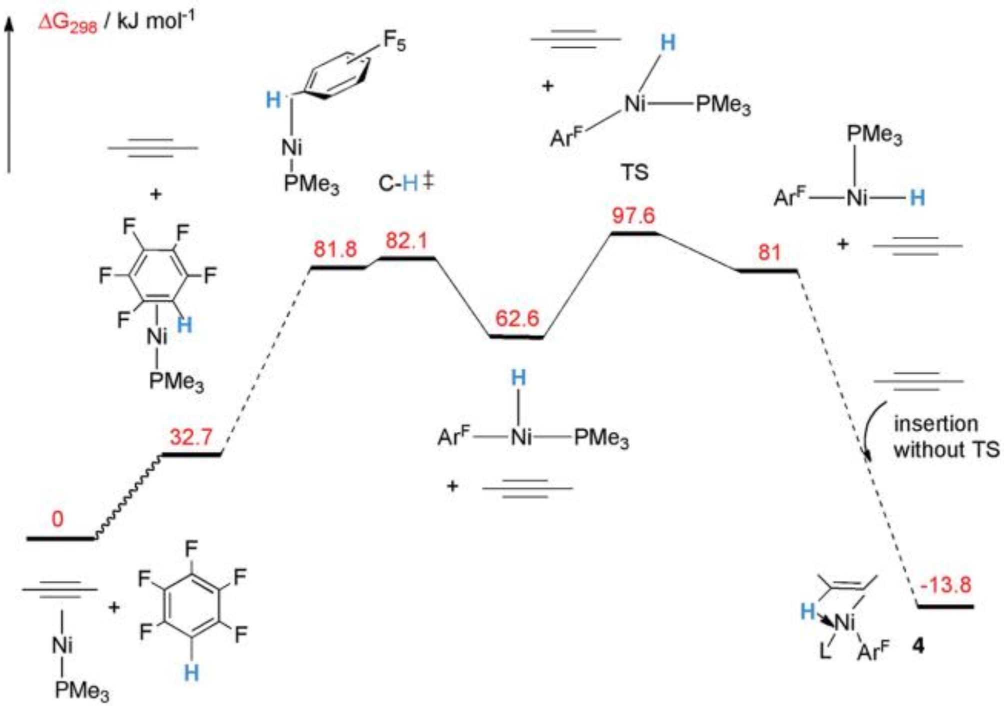


Parallel KIE ~1

Nakao, Ni: The "LLHT" mechanism

Eisenstein/Perutz, *Organometallics* **2012**, *31*, 1300.

DFT: Oxidative addition pathway

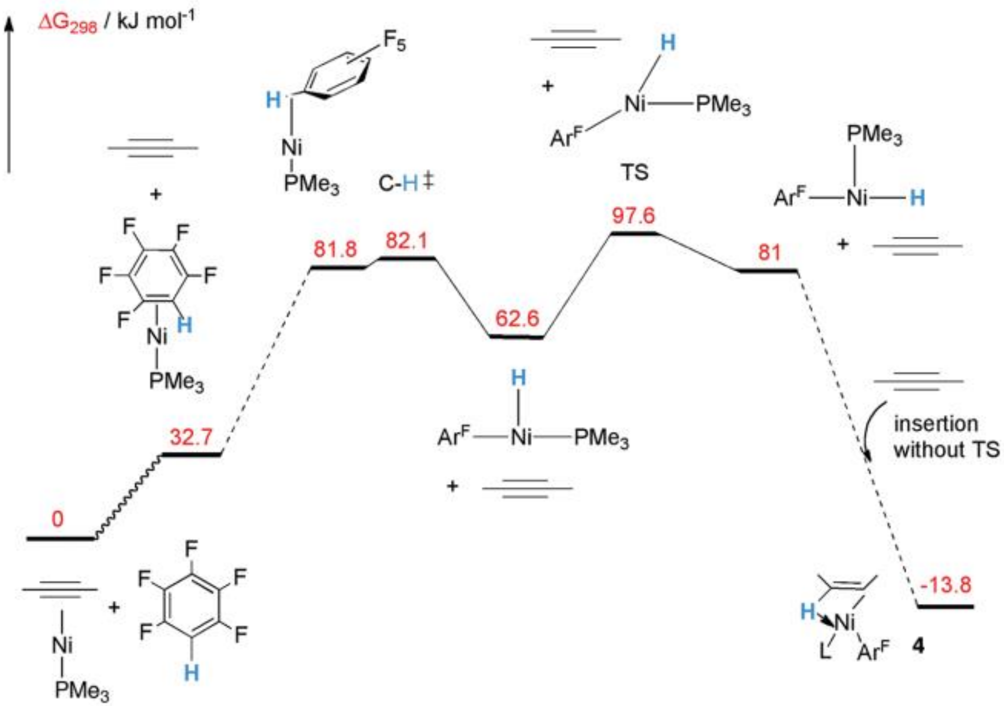


Computed KIE > 1

Nakao, Ni: The "LLHT" mechanism

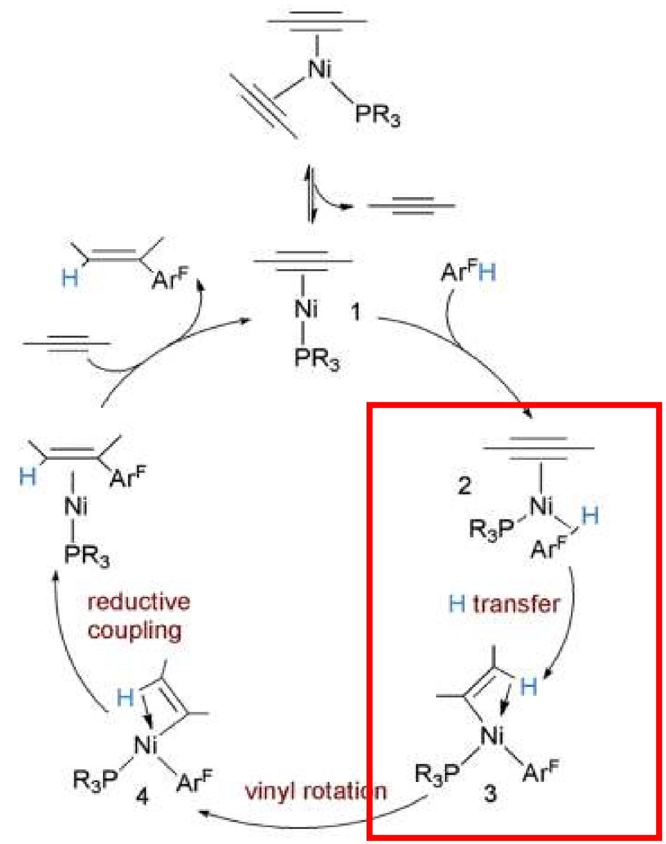
Eisenstein/Perutz, *Organometallics* **2012**, *31*, 1300.

DFT: Oxidative addition pathway



Computed KIE > 1

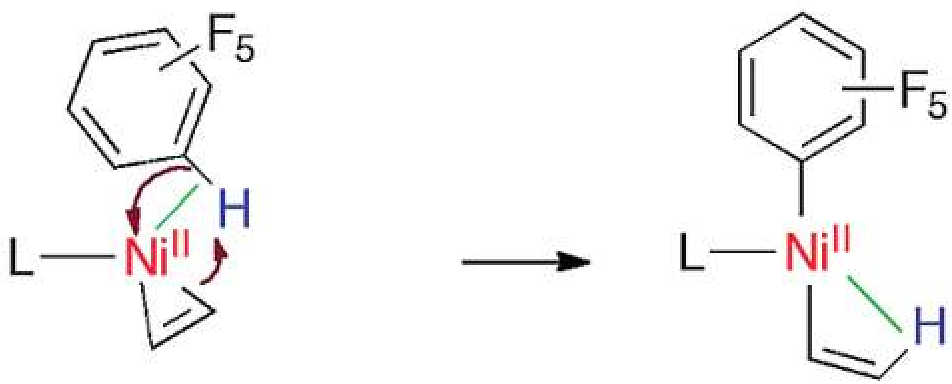
Revised "LLHT" mechanism



Nakao, Ni: The "LLHT" mechanism

Eisenstein/Perutz, *Organometallics* **2012**, *31*, 1300.

Connection to σ-CAM

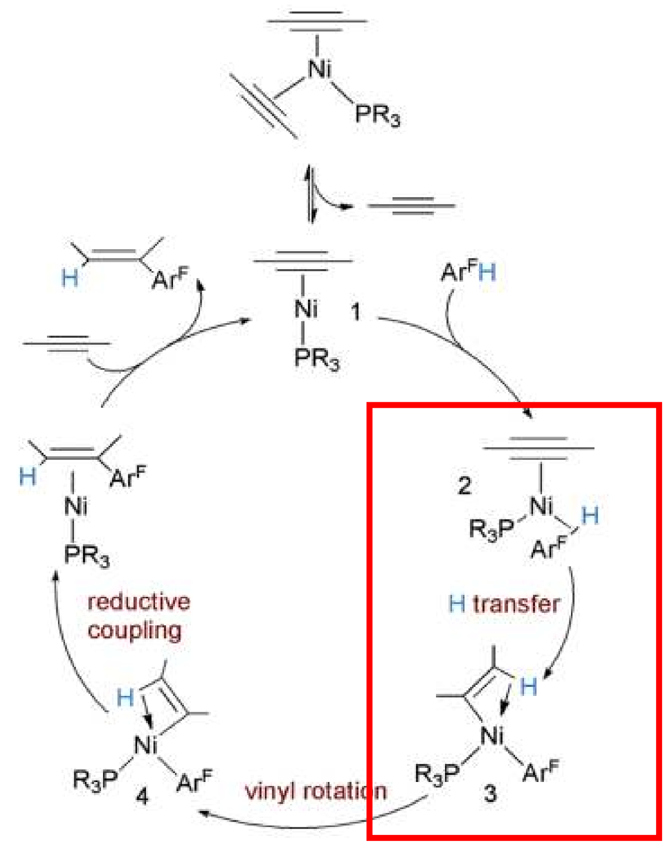


Ni(II) metallacycle

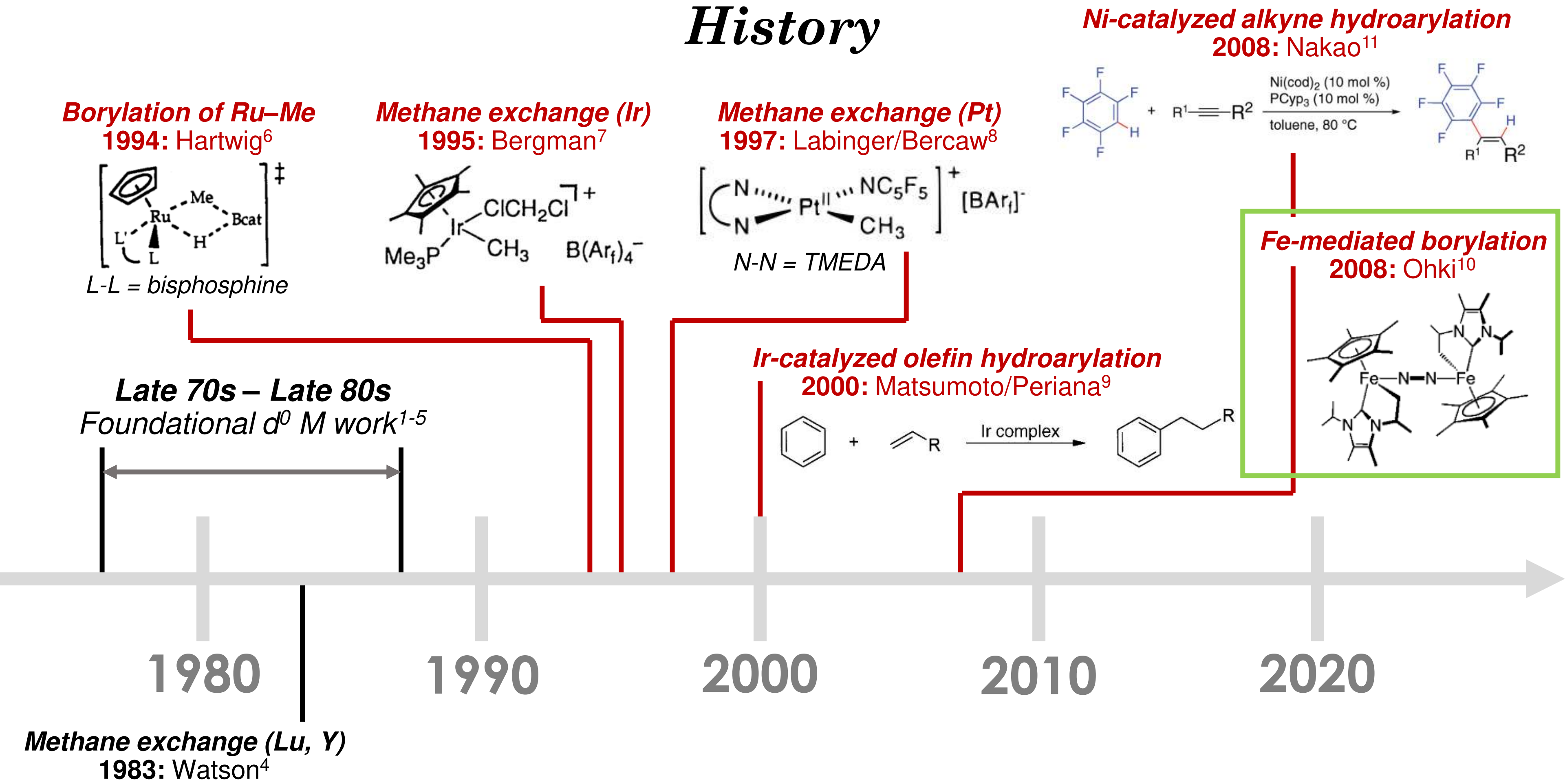
"Reduction first" mechanism

Perutz/Sabo-Etienne/Weller, *ACIE* **2022**, *61*, e202111462.

Revised "LLHT" mechanism



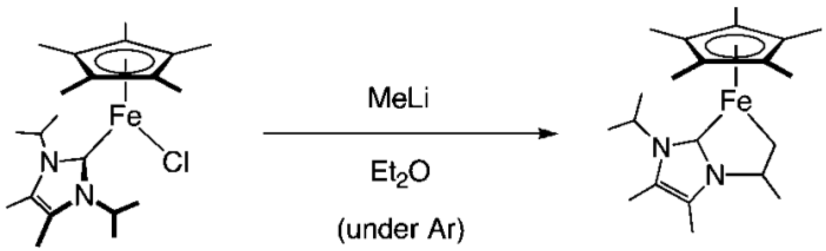
History



(6) Hartwig, J. F. *JACS* **1994**, *116*, 1839. (7) Bergman, R. G. *Science* **1995**, *270*, 1970. (8) Labinger, J. A.; Bercaw, J. E. *JACS* **1997**, *119*, 848. (9) Matsumoto, T.; Periana, R. A. *JACS* **2000**, *122*, 7414. (10) Ohki, Y. *JACS* **2008**, *130*, 17174. (11) Nakao, Y. *JACS* **2008**, *130*, 16170.

Ohki, Fe: Metallacycle-mediated activation

Ohki/Tatsumi, *JACS* **2008**, *130*, 17174.



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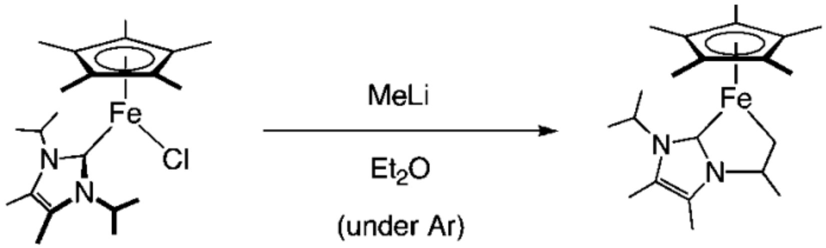
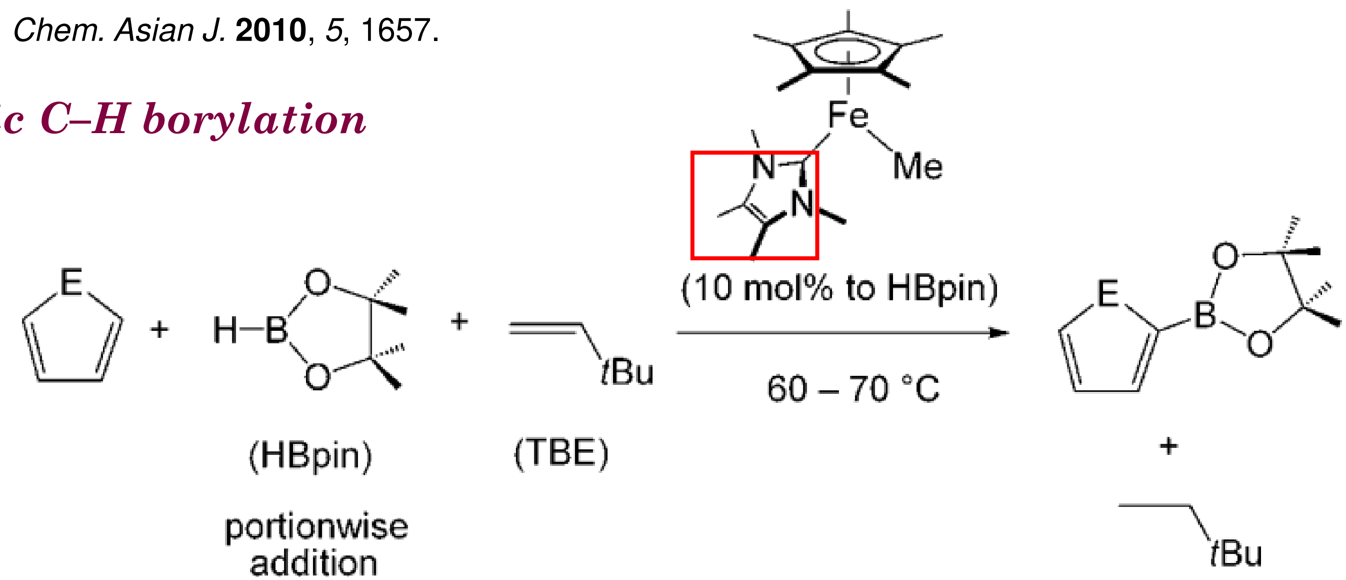


Ohki/Tatsumi, *Chem. Asian J.* **2010**, *5*, 1657.

Catalytic C–H borylation



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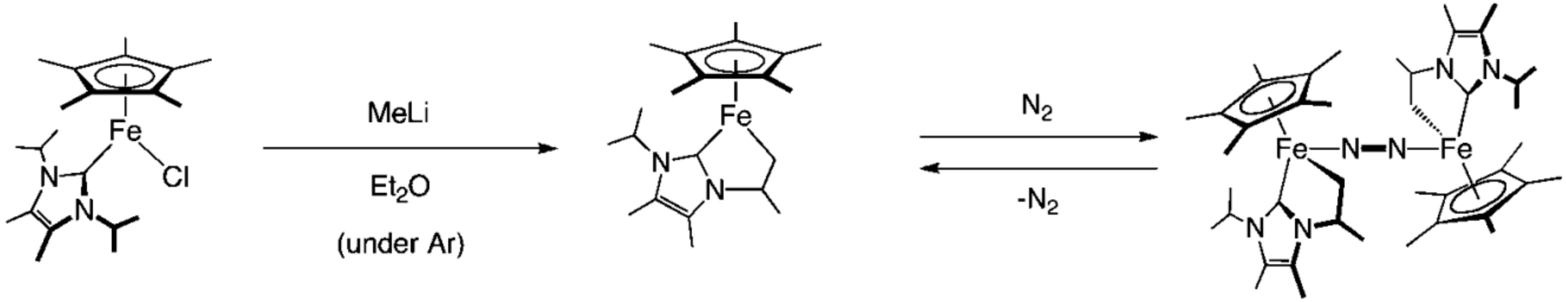
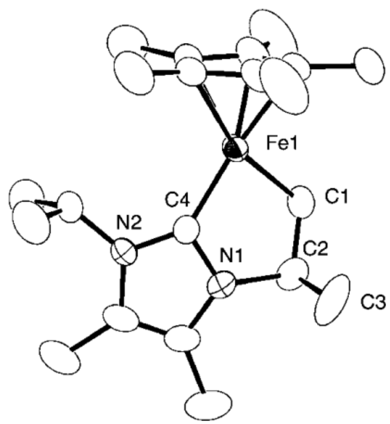
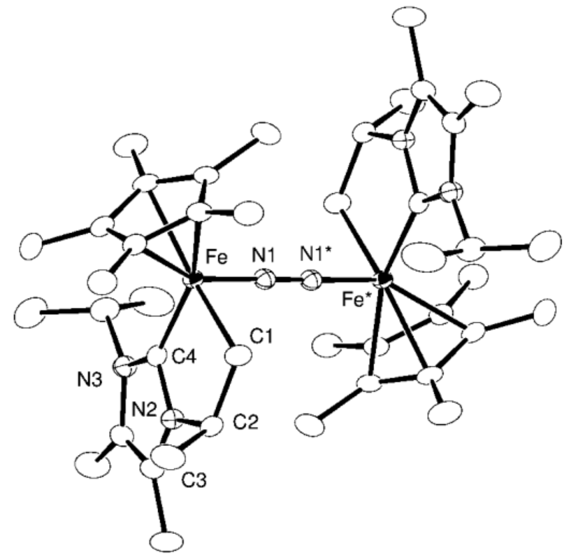
Ohki/Tatsumi, *JACS* **2008**, *130*, 17174.







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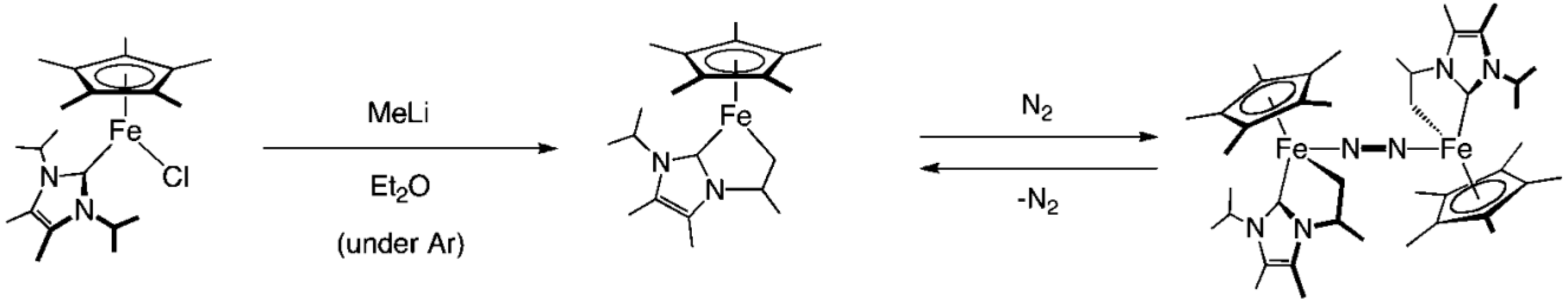
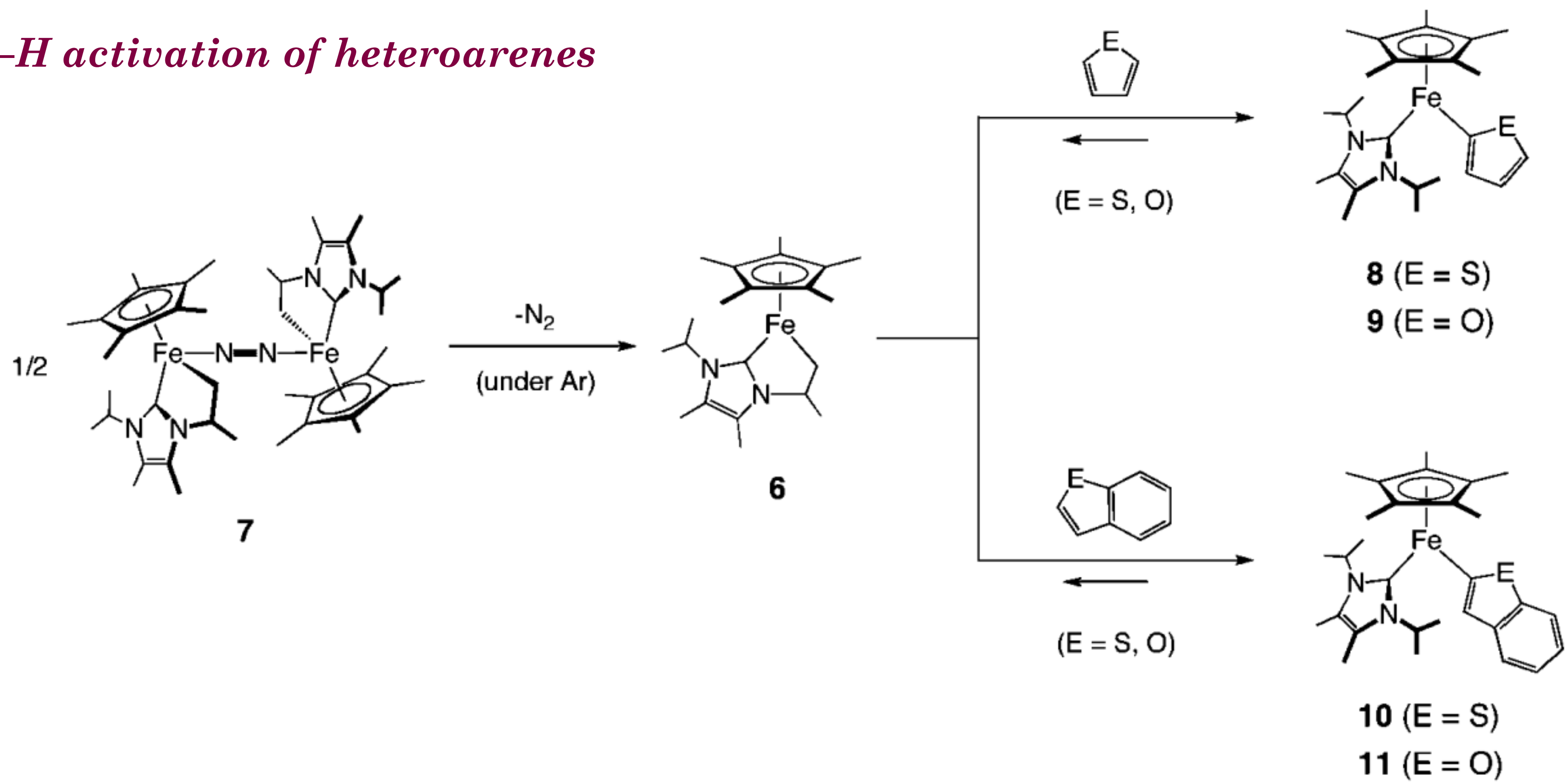
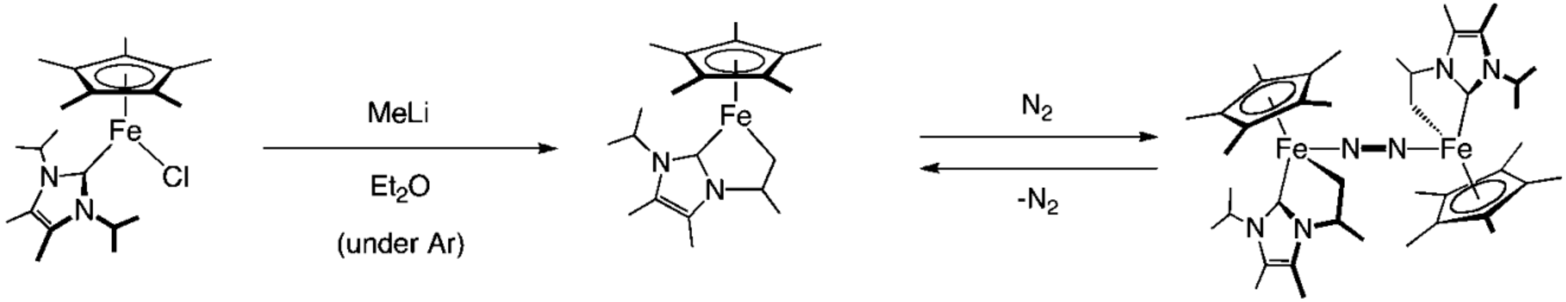


C–H activation of heteroarenes



Ohki, Fe: Metallacycle-mediated activation

Ohki/Tatsumi, *JACS* **2008**, *130*, 17174.



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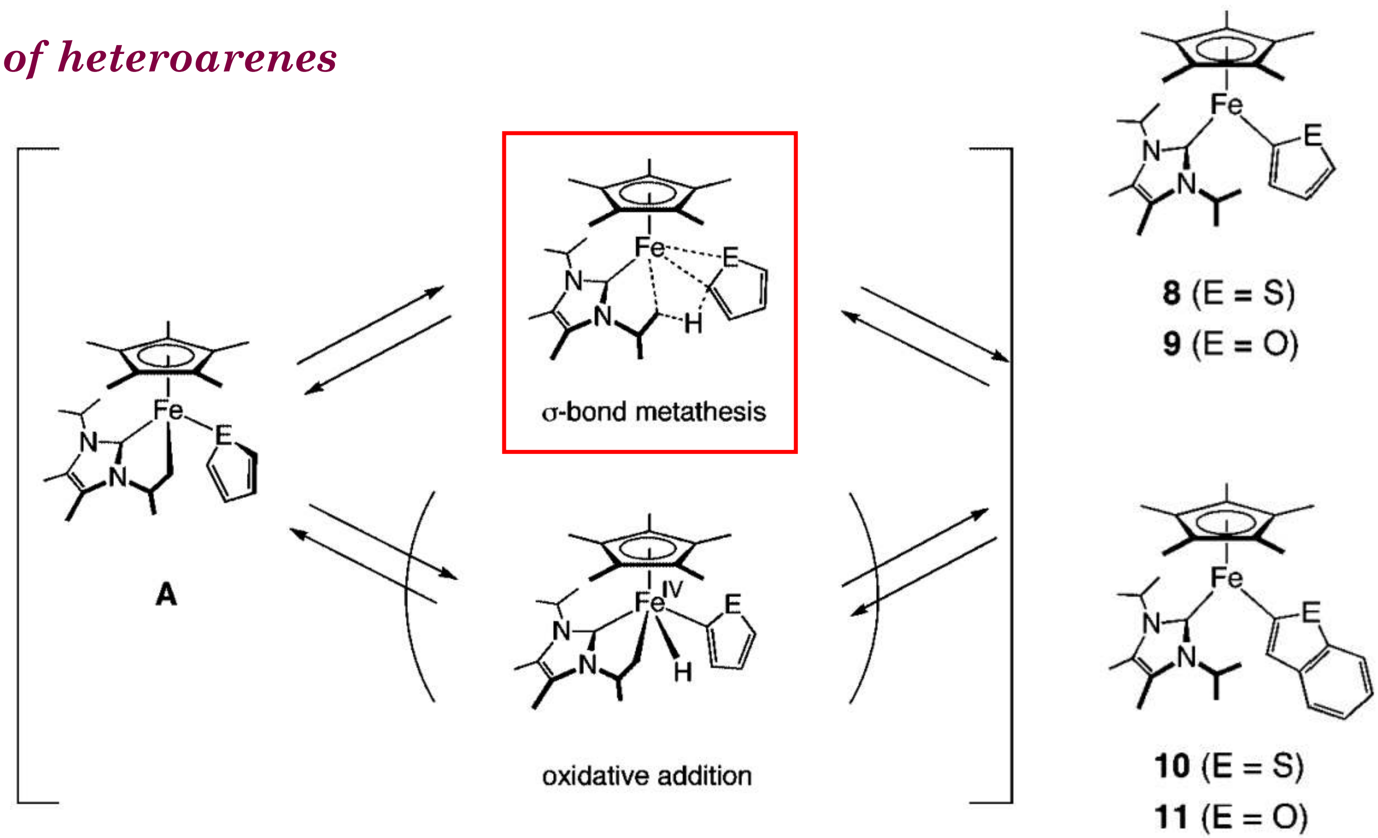
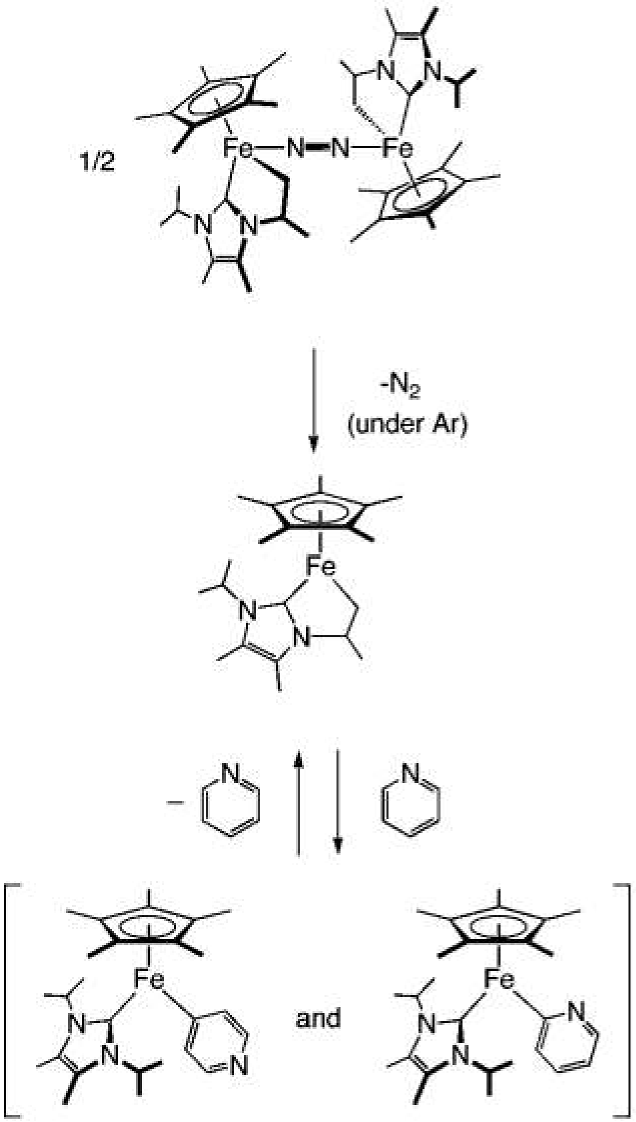


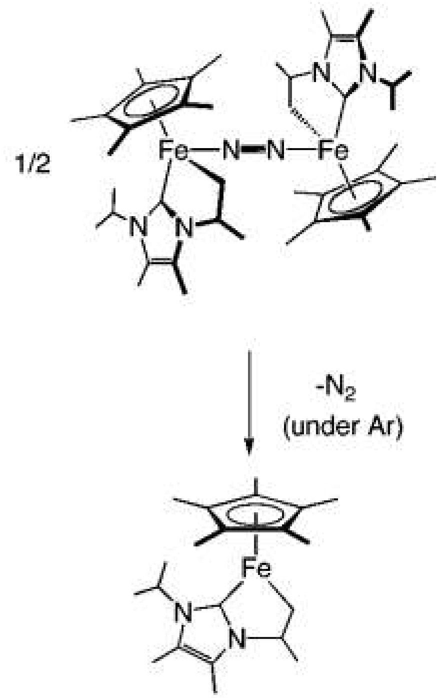
Ohki, Fe: Pyridine activation

Ohki/Tatsumi, *JACS* **2008**, *130*, 17174.

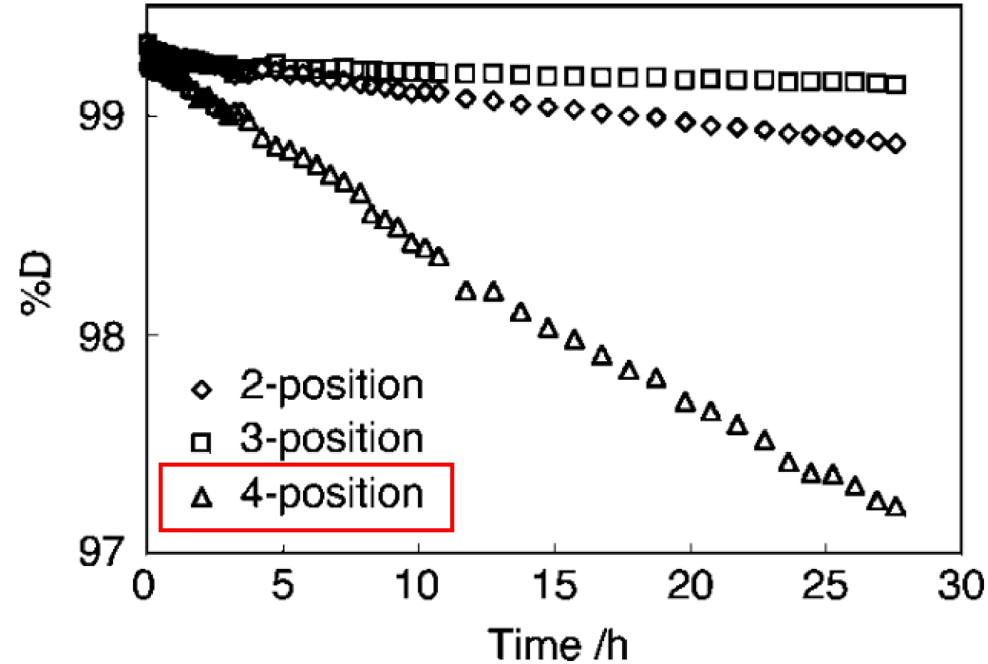


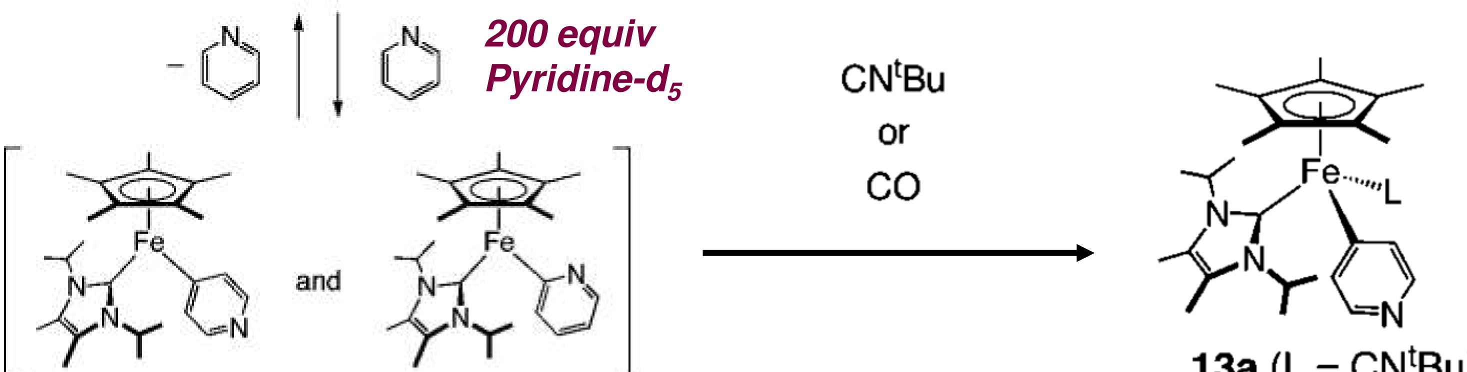
Ohki, Fe: Pyridine activation

Ohki/Tatsumi, *JACS* **2008**, *130*, 17174.



(Surprising?) Selectivity for the 4-position





13a (L = CN^{t}Bu)
13b (L = CO)

Conclusion

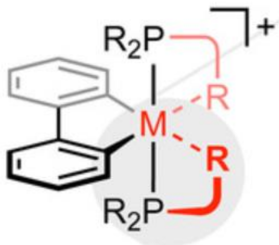
Development of new reactions requires…

…Improved chemical intuition, developed through…

…Consideration of alternative / under-explored mechanisms.

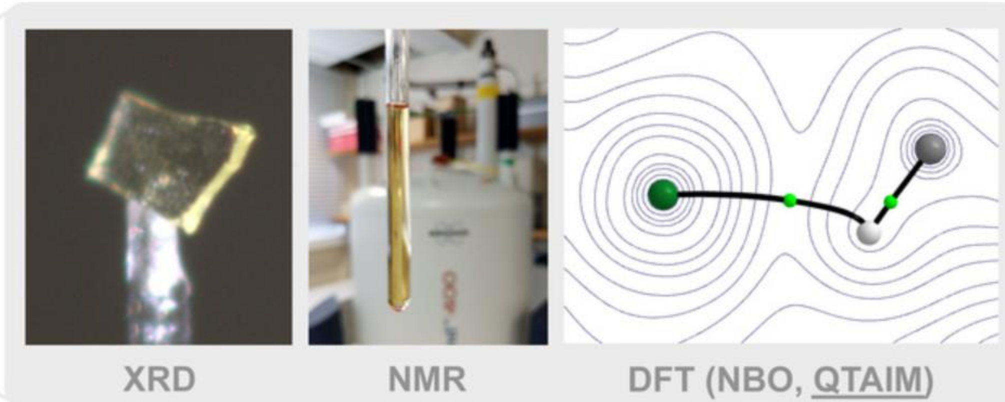
Agostic interactions: (The only) Systematic study

Chaplin, A. B. *Chem. Eur. J.* **2018**, *24*, 4927.



M = Rh, Ir
R = Ph, Cy, *i*Pr, *i*Bu

[Csp² vs. Csp³]
[gamma vs. delta]



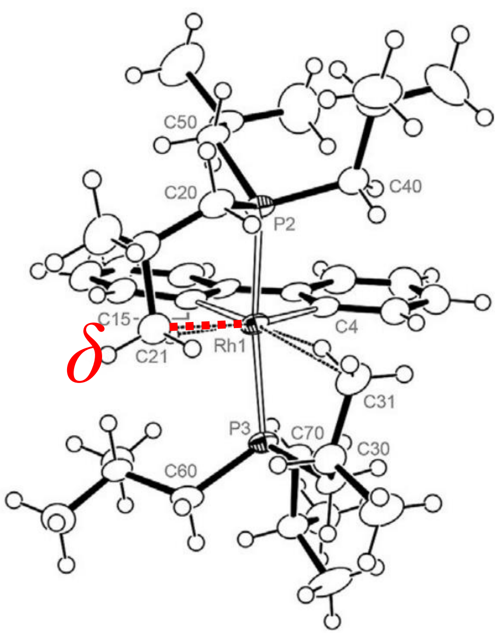
M–C(H) bond distance

(de)coalescence temperature

$\sigma_{CH} \rightarrow ML^*$

$ML \rightarrow \sigma^*_{CH}$

Strong trans influence of 2,2'-biphenyl



The combined data substantiates the adoption of stronger agostic interactions for the Ir^{III} compared to Rh^{III} complexes and, with respect to the phosphine ligands, in the order $P\textit{i}Bu_3 > PCy_3 > P\textit{i}Pr_3 > PPh_3$.

Conclusions

(1) Ir > Rh

(2) alkyl >> aryl

(3) δ > γ