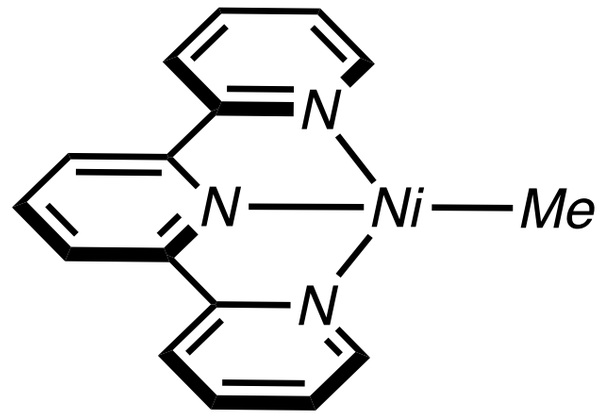
Mechanistic Aspects of Nitrogen-Ligated Nickel(I) Intermediates

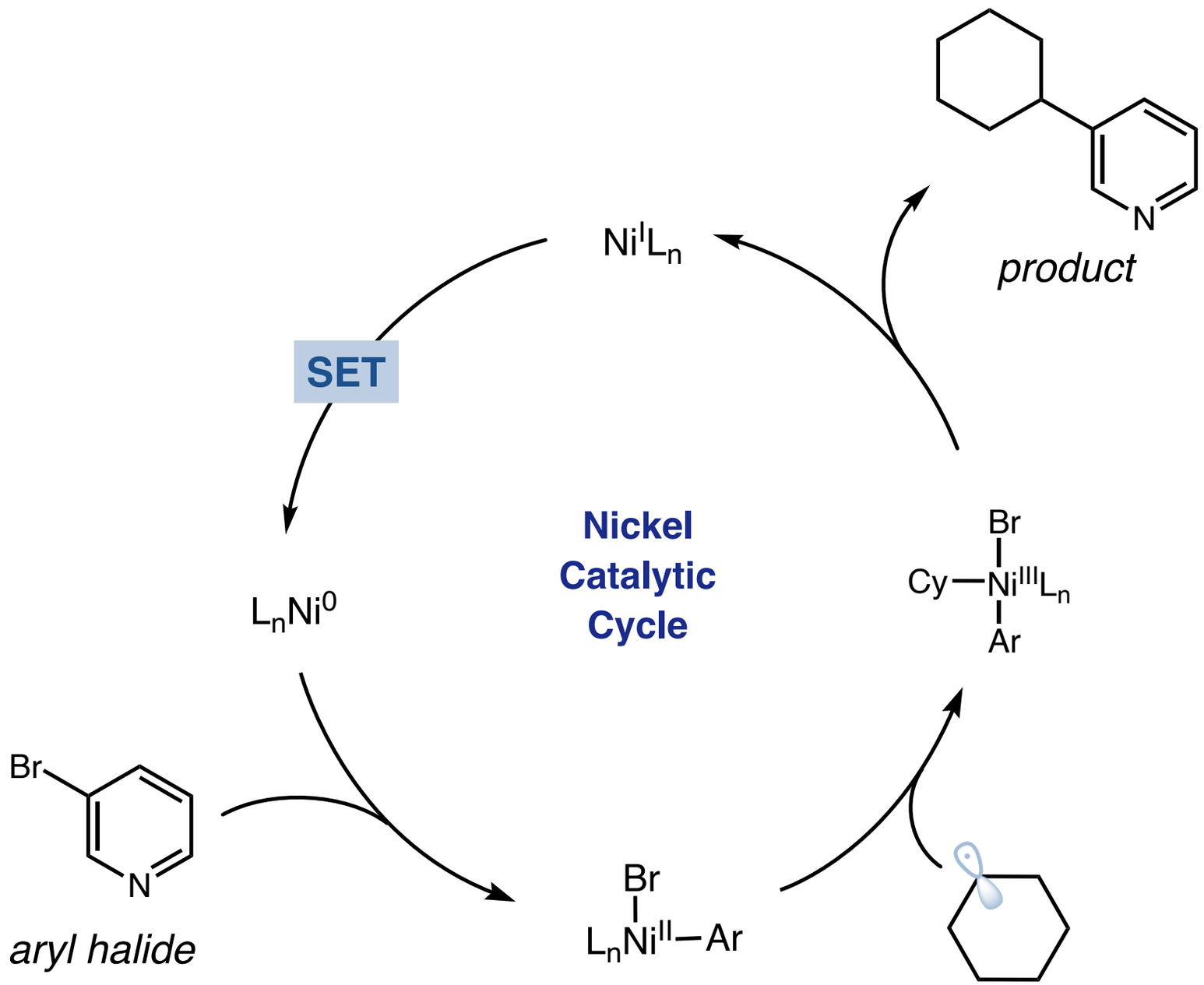


Cesar Nicolas Prieto Kullmer

Literature Talk

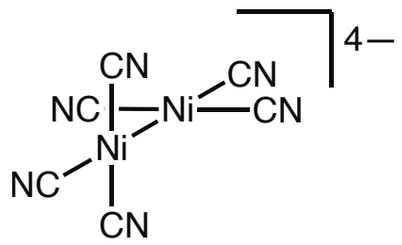
February 8th, 2022

Ubiquitously Invoked, Little Understood

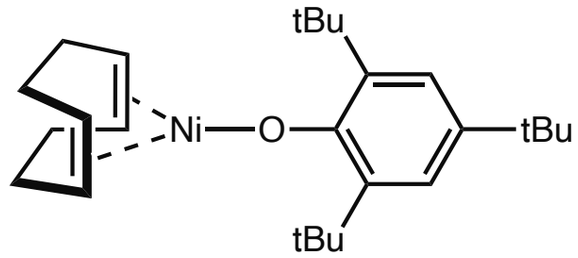


Outline of Talk

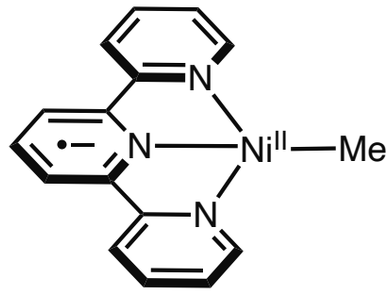
Historical Aspects of Ni(I) Complexes



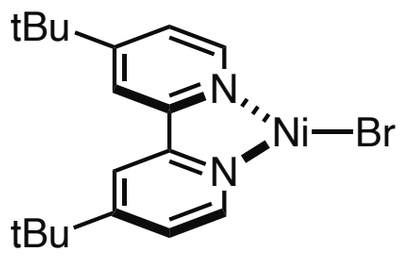
Preparation and Properties of Ni(I) Complexes



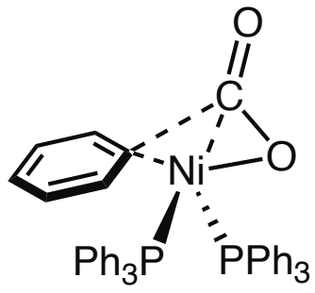
Oxidative Addition to C(sp_3)—X



Oxidative Addition to C(sp_2)—X



Carboxylations with CO_2



Outline of Talk

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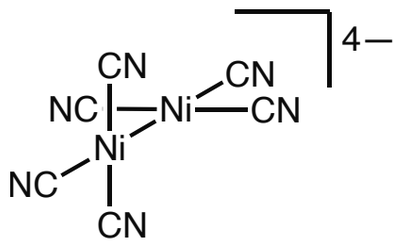
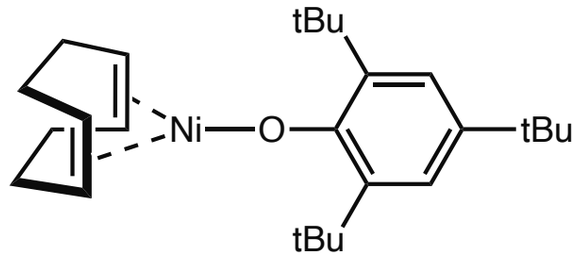
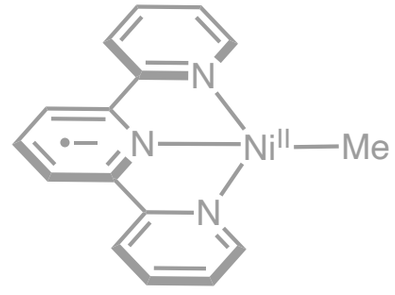


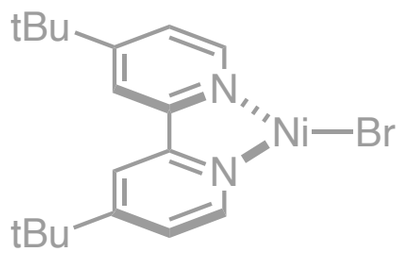
Preparation and Properties of Ni(I) Complexes



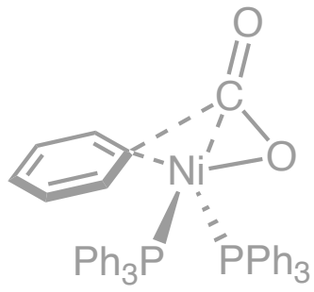
Oxidative Addition to $C(sp_3)—X$



Oxidative Addition to $C(sp_2)—X$

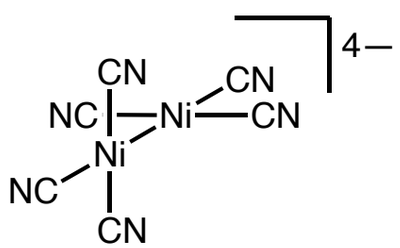


Carboxylations with CO_2

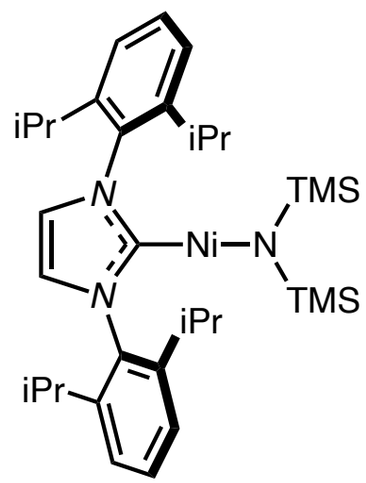


Milestones in Discovery

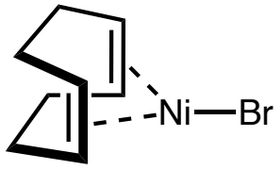
first reported Ni(I) complex: $K_4[Ni_2(CN)_6]$



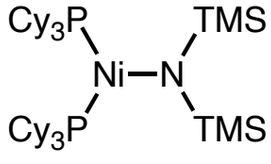
first detection of biologically relevant Ni(I): Cofactor F430



1914

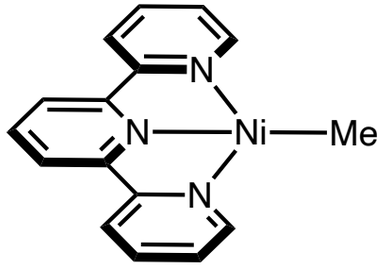


1967



1970

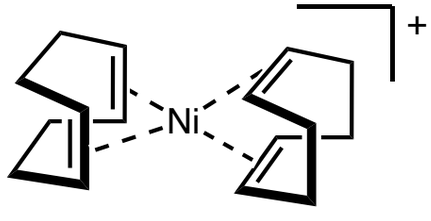
1972



1986

2004

2008



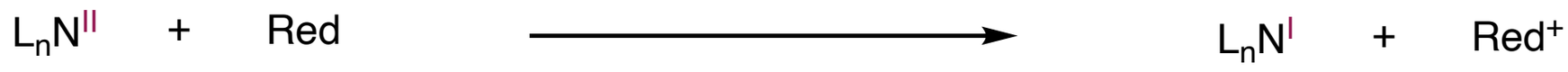
2015

Lin, C.; Power, P. P. *Chem. Soc. Rev.* **2017**, *46*, 5347.

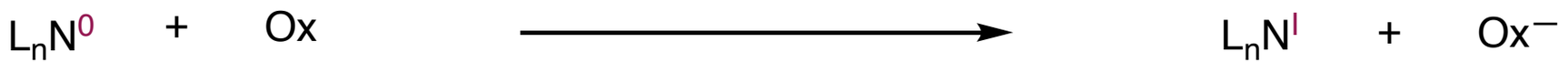
Bismuto, A.; Finkelstein, P.; Müller, P.; Morandi, B. *Helv. Chim. Acta* **2021**, *104*, e202100177.

Synthetic Access to Ni(I) Species

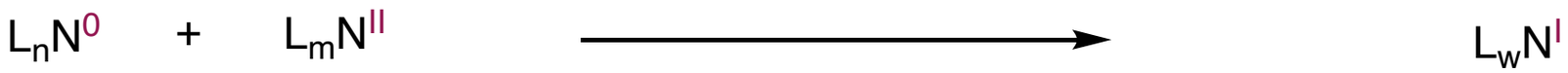
Reduction



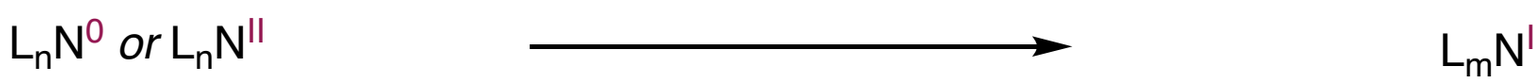
Oxidation



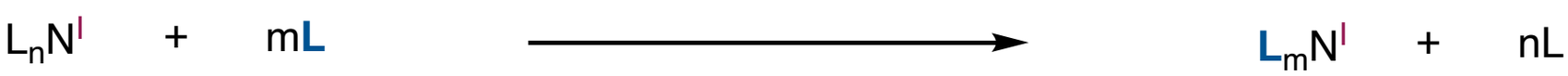
Comproportionation



Decomposition



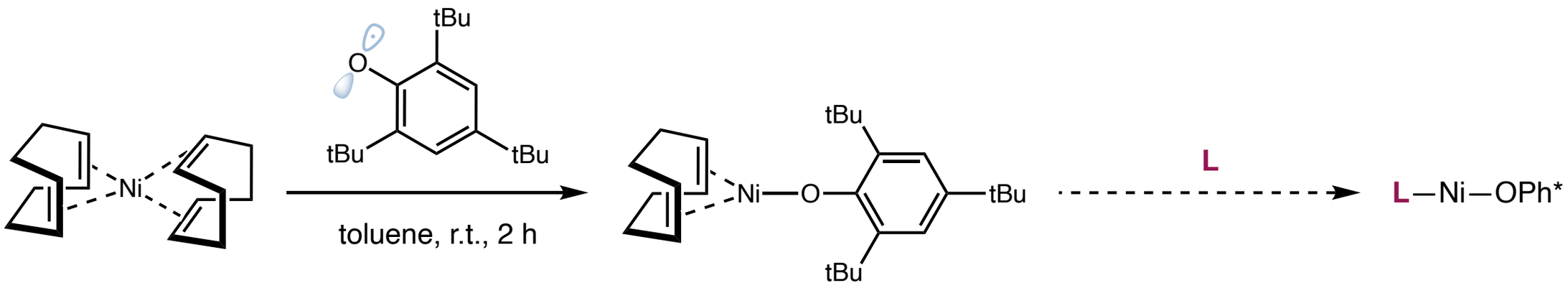
Ligand Exchange



Lin, C.; Power, P. P. *Chem. Soc. Rev.* **2017**, *46*, 5347.
Bismuto, A.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 10642.

Morandi's General Route to Ni(I) Species

■ Promising Synthetic Approach



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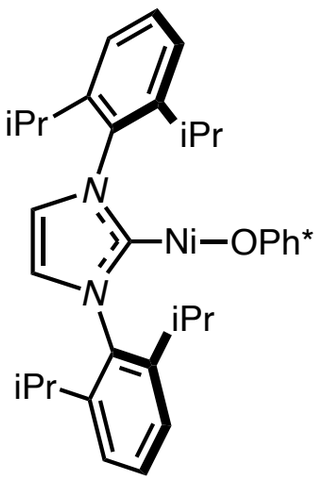
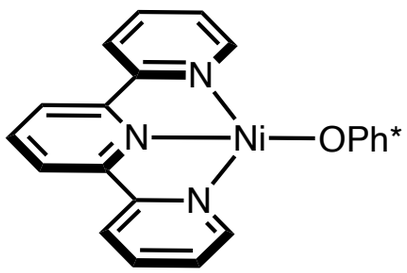
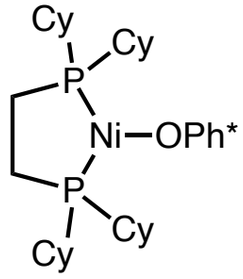


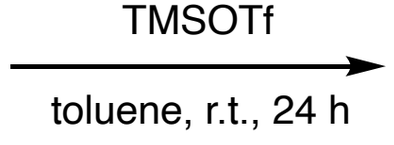
80%

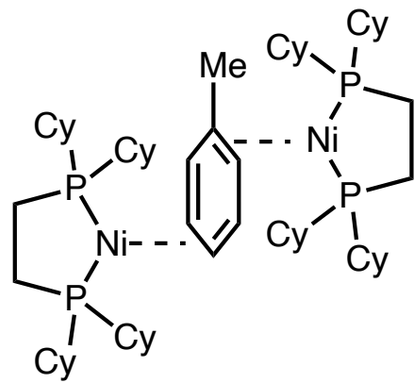


51%



81%



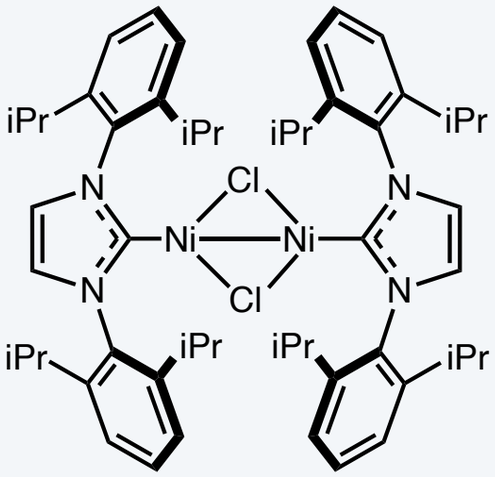


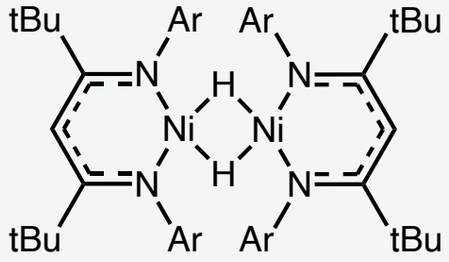
97%

Bismuto, A.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 10642.

Some general features of nickel(I) species

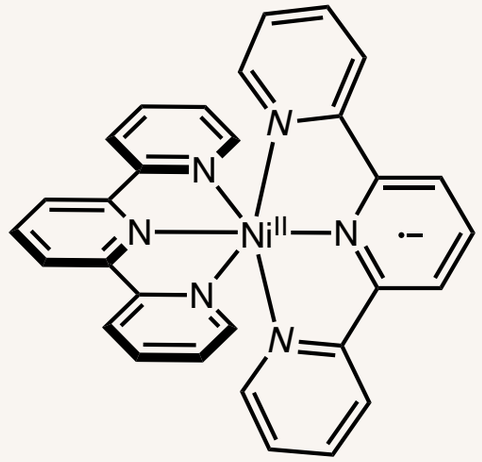
Facile Oligomerization

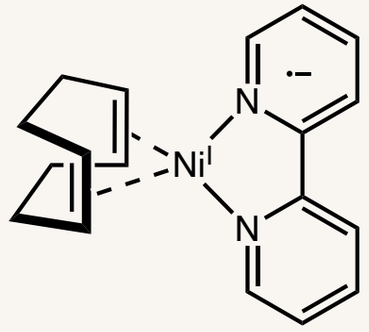




- Speciation sensitive to sterics and ligand properties

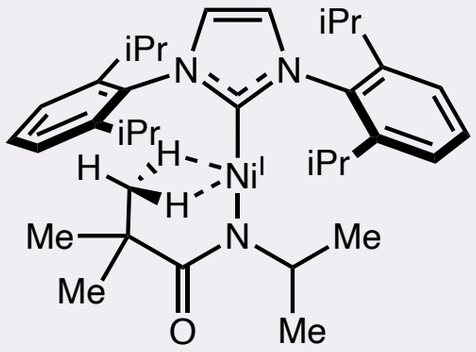
Non-Obvious Electron Density





- Non-innocent ligands complicate electronic description

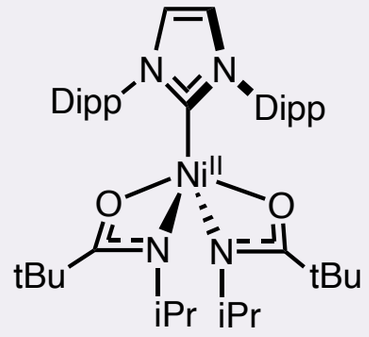
Facile Disproportionation

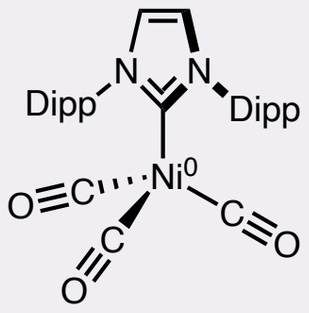


xs CO

PhH, r.t., 5 min

quantitative





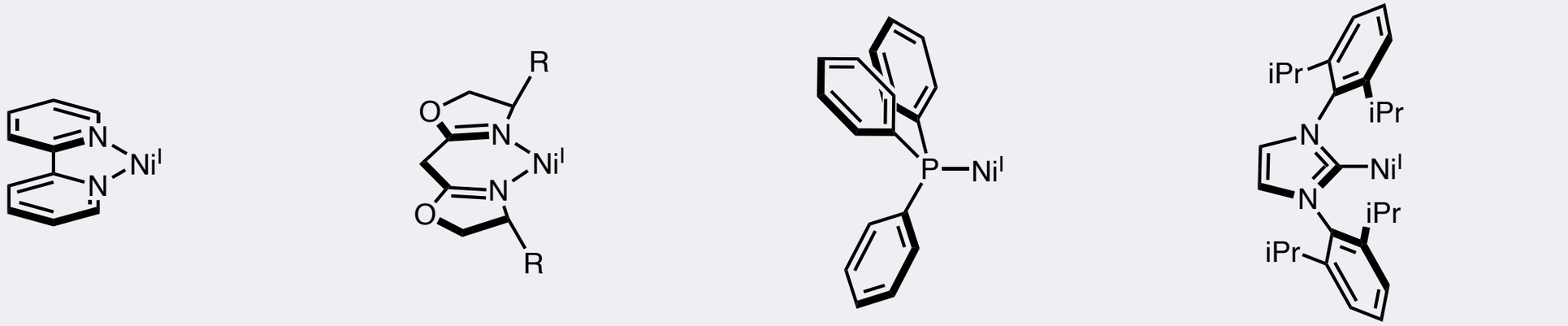
- dependent on stabilization of individual oxidation states

bottom line: complexity and sensitivity of nickel(I) species difficults isolation and evaluation

Lin, C.; Power, P. P. *Chem. Soc. Rev.* **2017**, *46*, 5347.

Dawson Beattie, D.; et al. *Organometallics* **2018**, *37*, 1382.

Difficulties exacerbated for ligands relevant to metallaphotoredox …



Sun, R.; et al. *J. Am. Chem. Soc.* **2019**, *141*, 89.

Beromi, M. M.; et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 6094.

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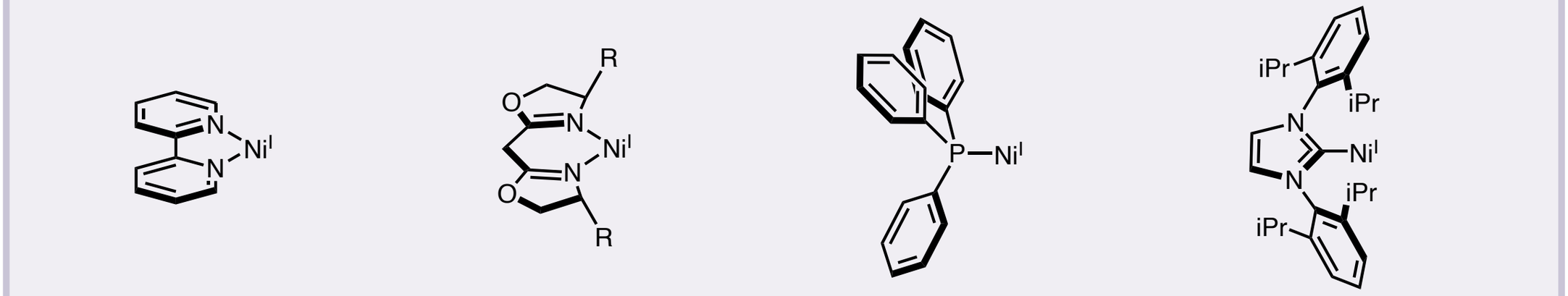
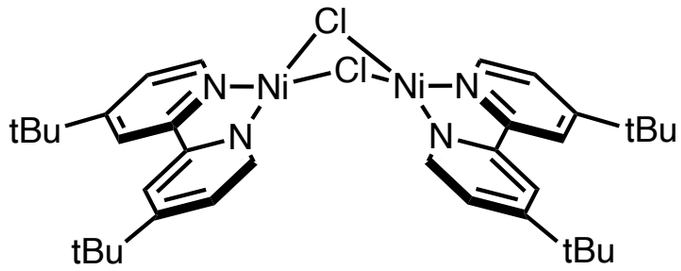
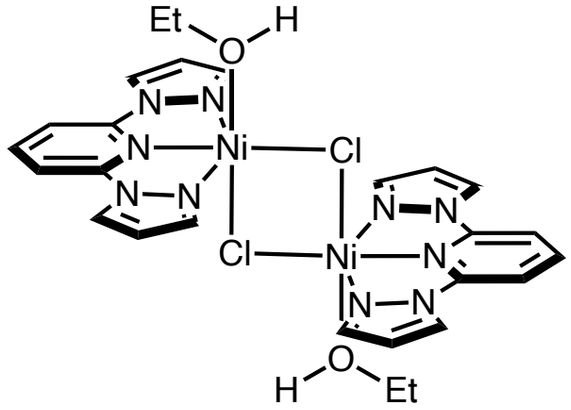


increased steric bulk

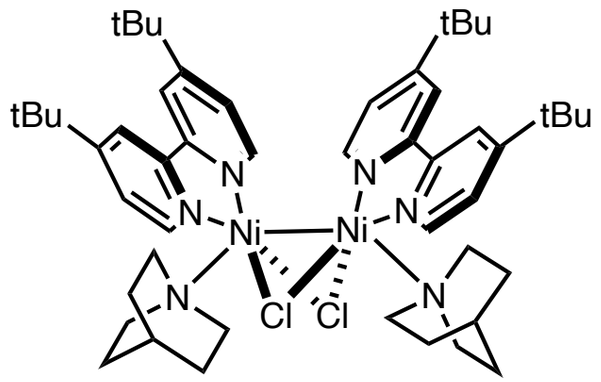
decreased oligomerization



Hazari (2019)



Doyle (2015)



Nocera (2019)

Nickel(I) species relevant to metallaphotoredox are especially finnicky candidates for isolation in active state

Sun, R.; et al. *J. Am. Chem. Soc.* **2019**, *141*, 89.

Beromi, M. M.; et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 6094.

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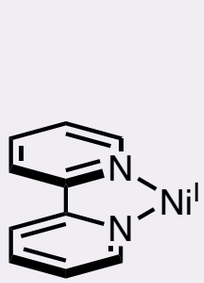
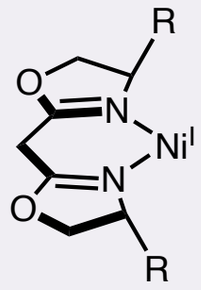
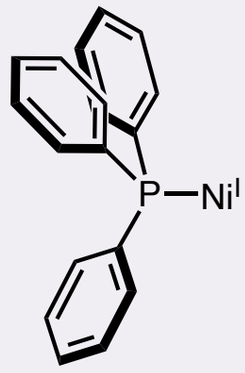
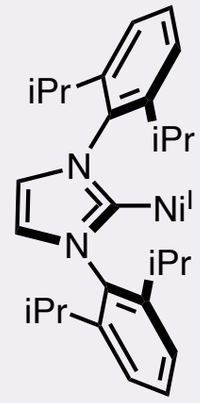








increased σ donicity

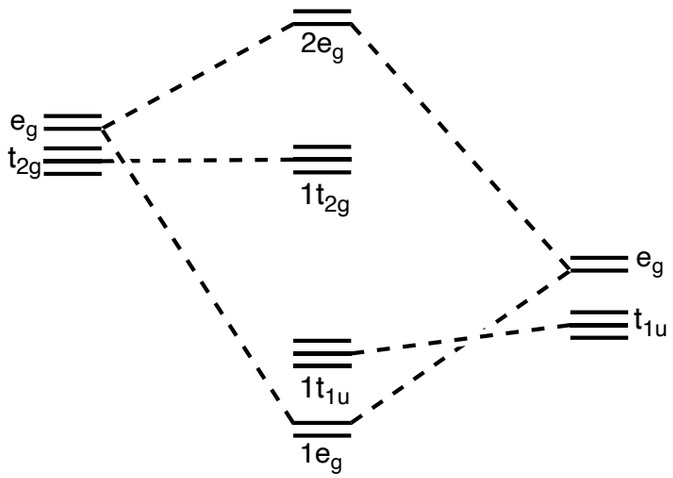
decreased one electron OS changes

Nickel possess contracted orbitals

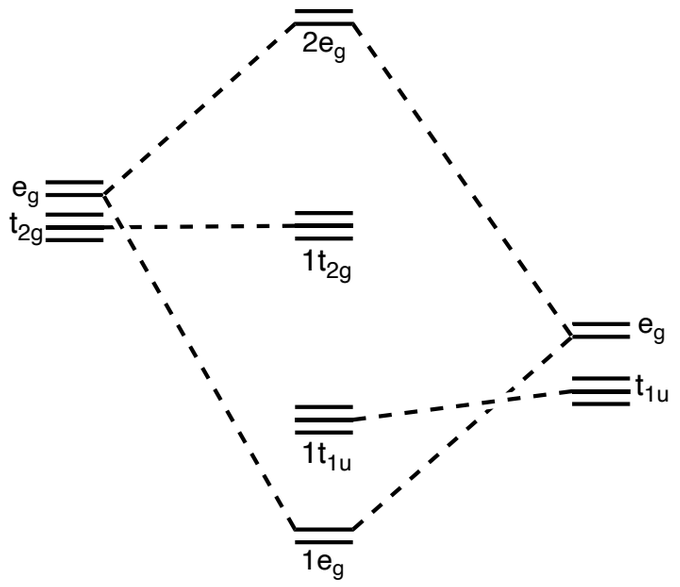
promotes one-electron OS changes

makes nickel sensitive to ligand field splitting

weak σ donor



strong σ donor

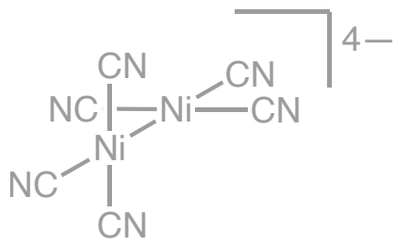


electron pairing energy more important for weak donors — facilitates odd-electron states

Dicianni, J.; Diao, T. *Trends in Chemistry.* **2019**, *1*, 830.

Outline of Talk

Historical Aspects of Ni(I) Complexes



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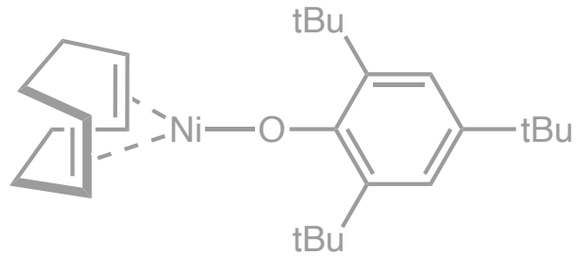
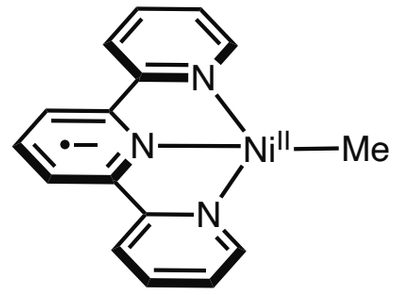
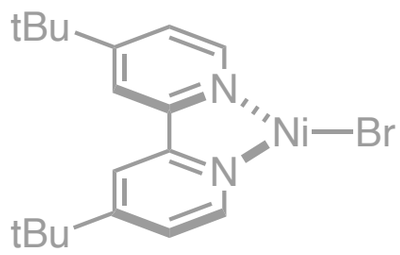


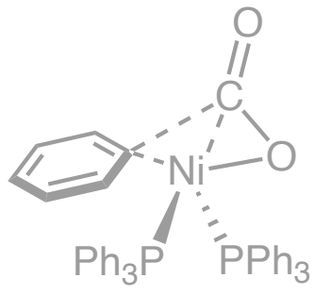
Oxidative Addition to $C(sp_3)—X$



Oxidative Addition to $C(sp_2)—X$

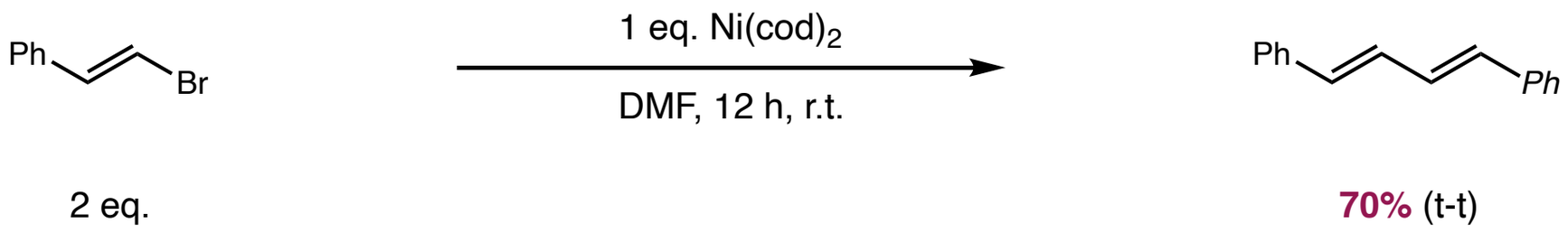


Carboxylations with CO_2

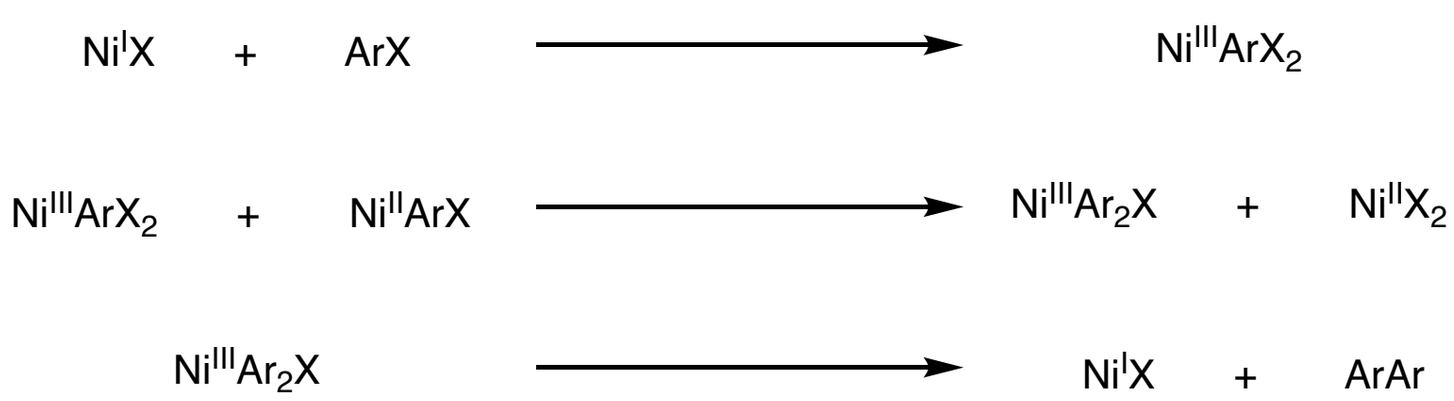


Early invocations of odd-electron nickel

■ Semmelhack Homocoupling (1971)



■ Kochi Study on ArBr Homocoupling (1979)

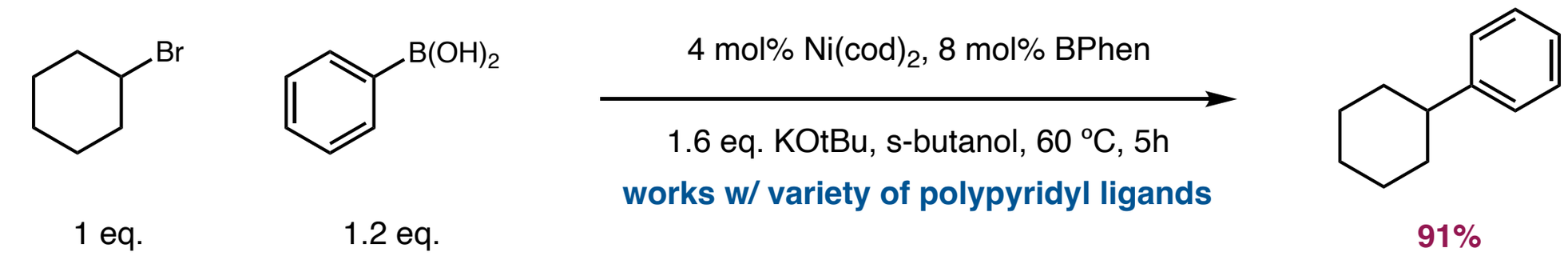


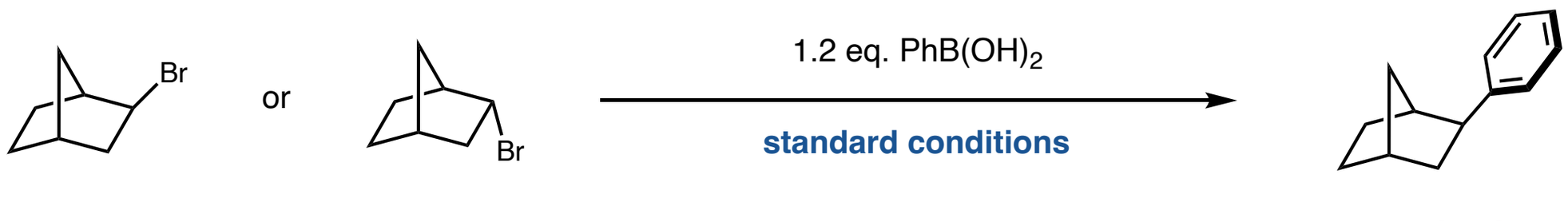
Ni(I) is proposed to be a catalitically relevant species

Semmelhack, M. F.; et al. *J. Am. Chem. Soc.* ***1972***, *94*, 9234.
Tsou, J. J.; Kochi, J. K. *J. Am. Chem. Soc.* ***1979***, *101*, 7547.

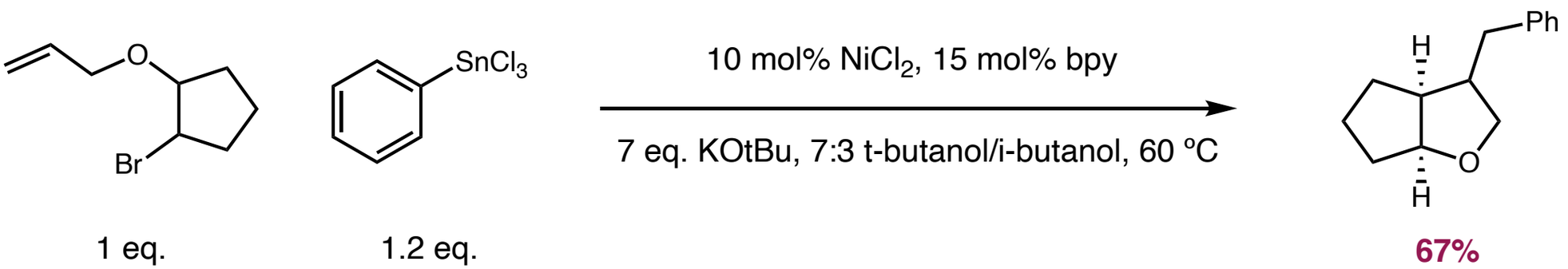
Evidence for radicals in catalytic cycle

Fu $C(sp_2)$-$C(sp_3)$ Suzuki Coupling (2003)





Fu $C(sp_2)$-$C(sp_3)$ Stille Coupling (2005)

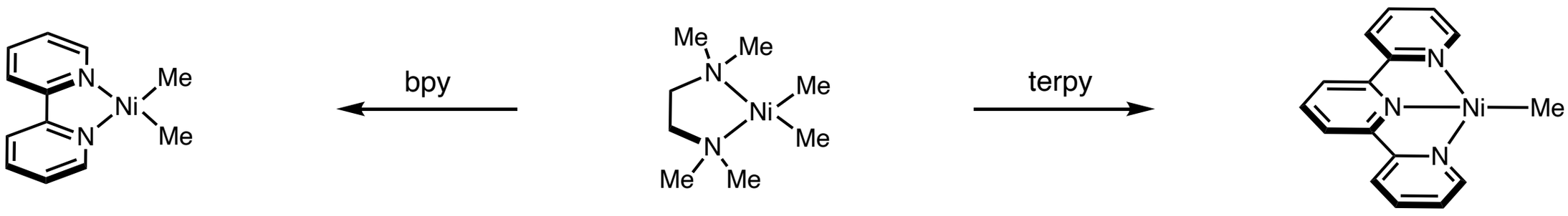


suggests that radical formation is part of cycle **implicates odd-electronic states of nickel**

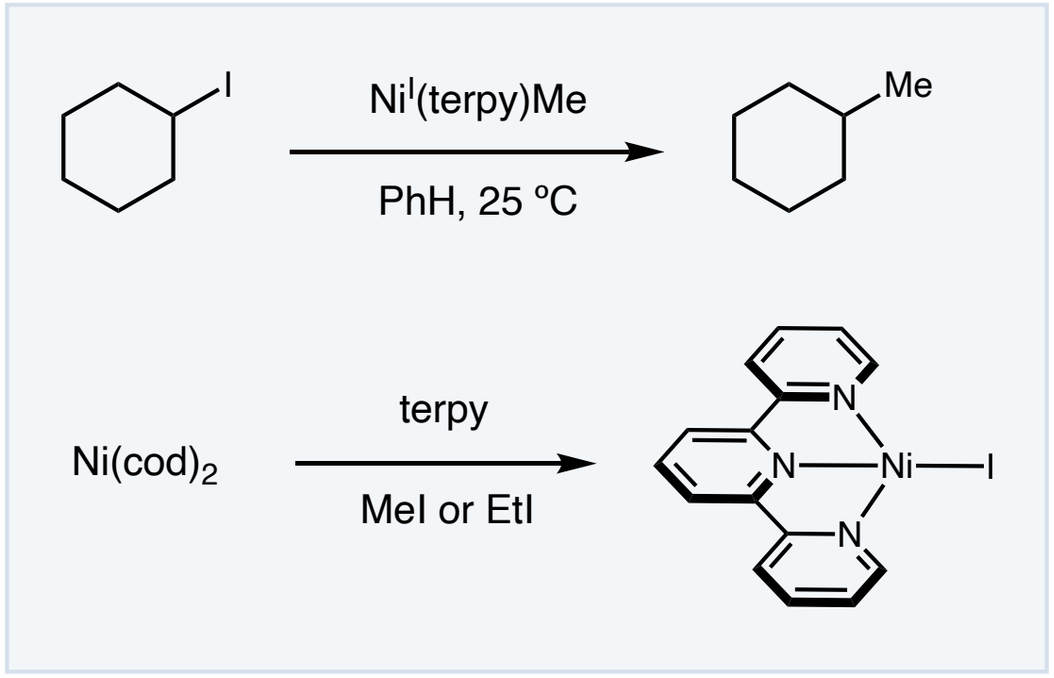
Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* ***2003***, *126*, 1340.
Powell, D. A.; Maki, T.; Fu, G. C. *J. Am. Chem. Soc.* ***2005***, *127*, 510.

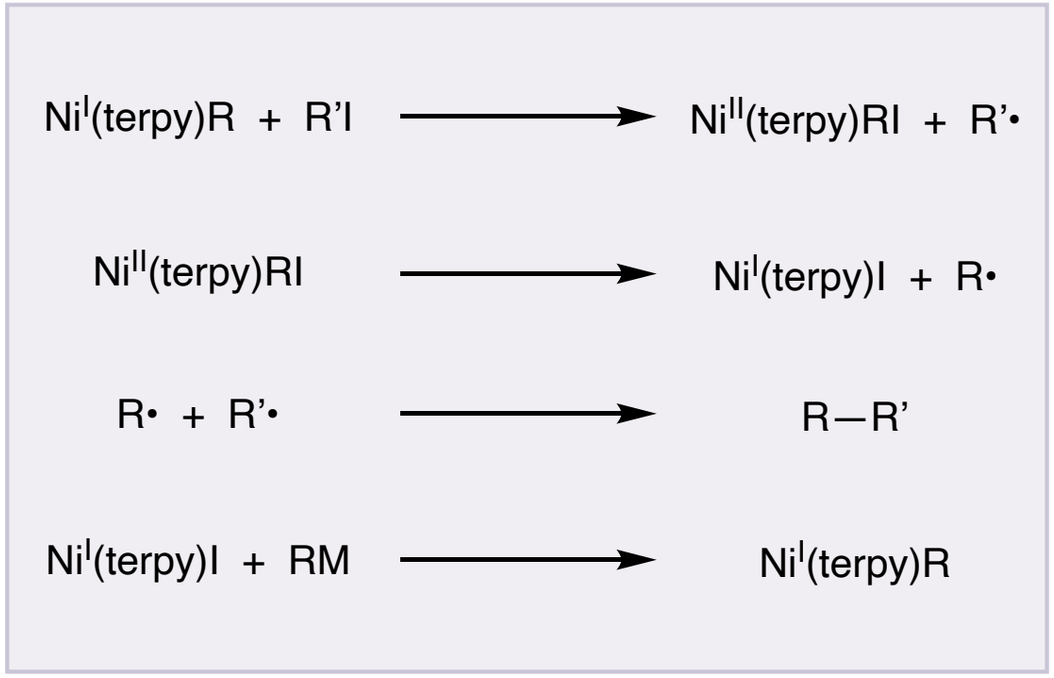
Vicic's investigation of the terpy system

■ Serendipitous Ni(I) Discovery (2004)



suggests that Ni^{II} dialkyl intermediates may not be viable in cross-coupling of saturated alkyl electrophiles

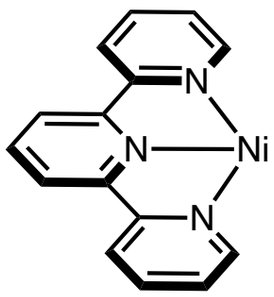


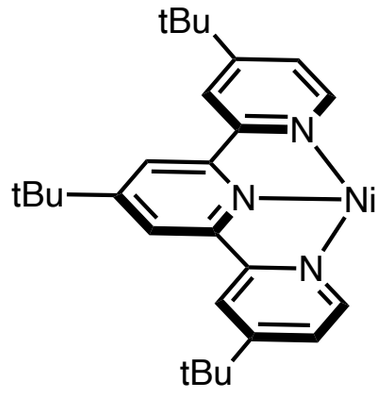


Anderson, T. J.; Jones, G. D.; Vicic, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 8100.

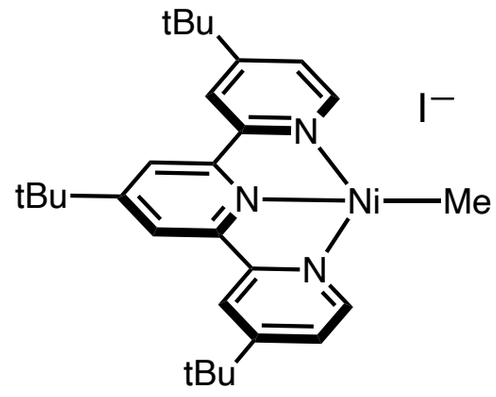
Vicic's investigation of the terpy system

- Uncovering ligand non-innocence (2006)

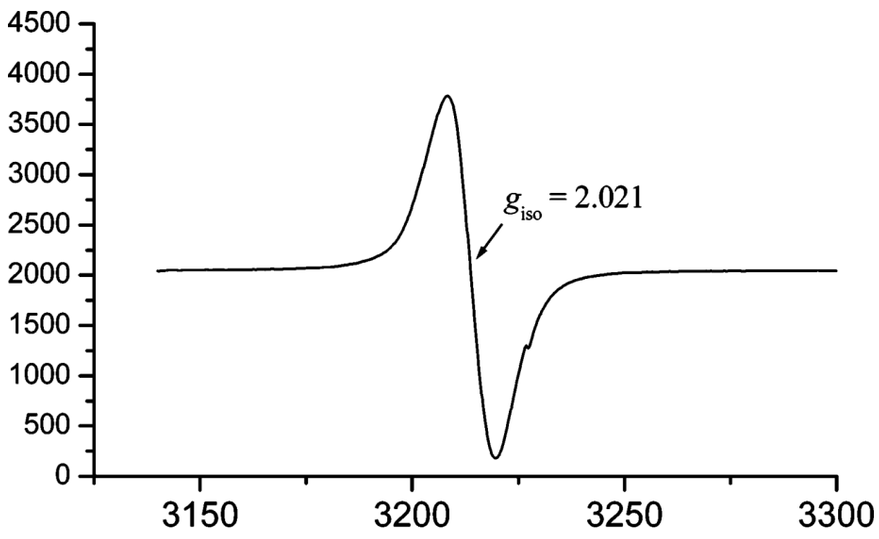


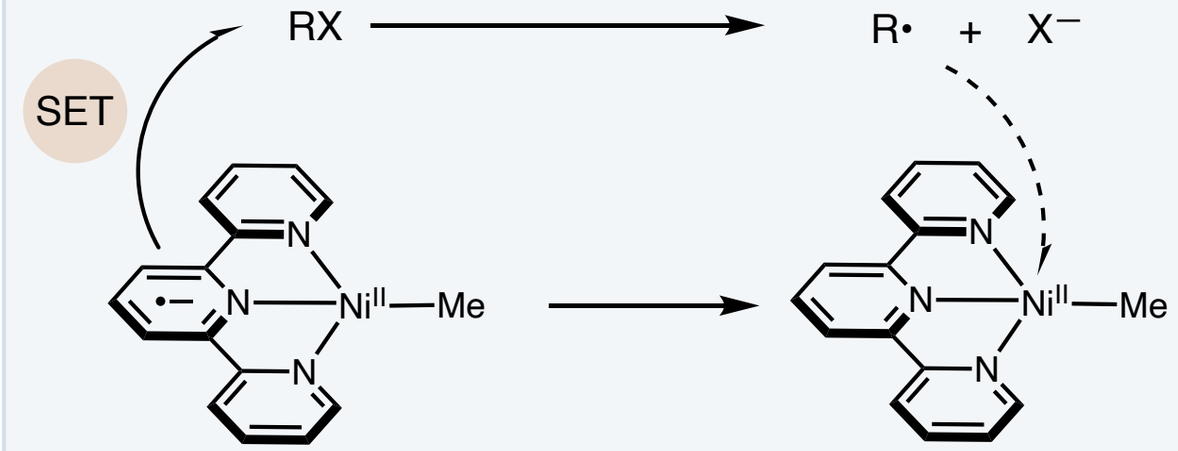


increased performance (AlkBr now viable)



now isolable





best described as Ni(II) with reduced ligand

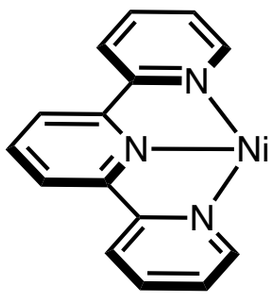
represents entirely new mode of oxidative addition

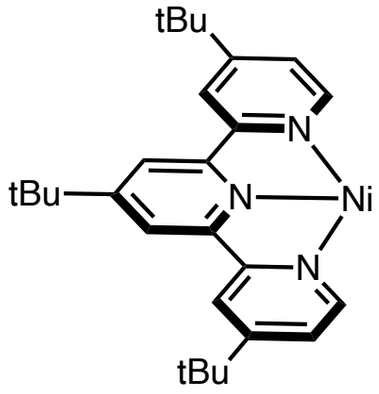
Jones, G. D.; McFarland, C.; Anderson, T. J.; Vicic, D. A. *Chem. Comm.* **2005**, 4211.

Jones, G. D.; et al. *J. Am. Chem. Soc.* **2006**, *128*, 13175.

Vicic's investigation of the terpy system

- Uncovering ligand non-innocence (2006)





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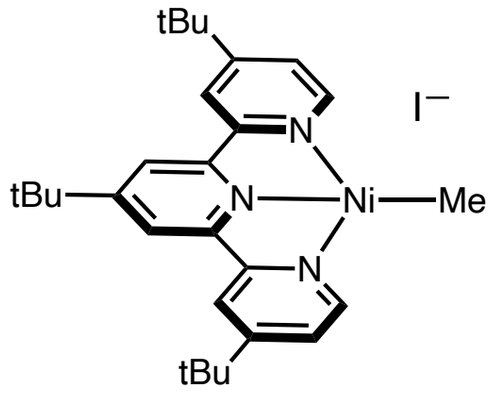
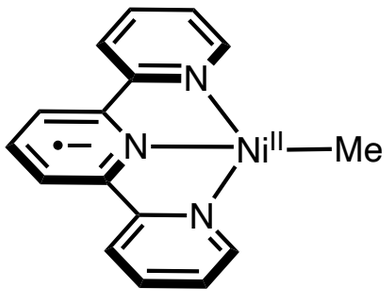
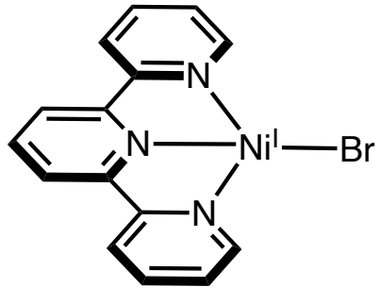
(AlkBr now viable)



now isolable



***can** acticvate AlkBr*



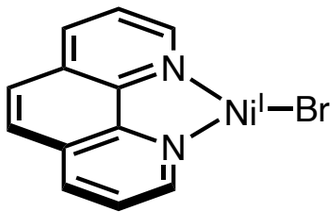
***can't** acticvate AlkBr*

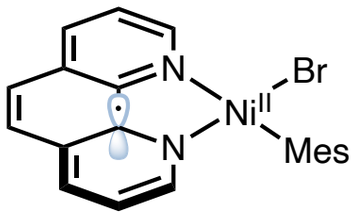
SOMO distribution affects reactivity

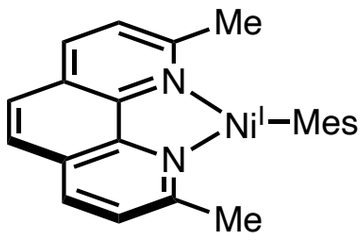
Ciszewski, J. T.; et al. *Inorg. Chem.* **2011**, *50*, 8630.
Jones, G. D.; et al. *J. Am. Chem. Soc.* **2006**, *128*, 13175.

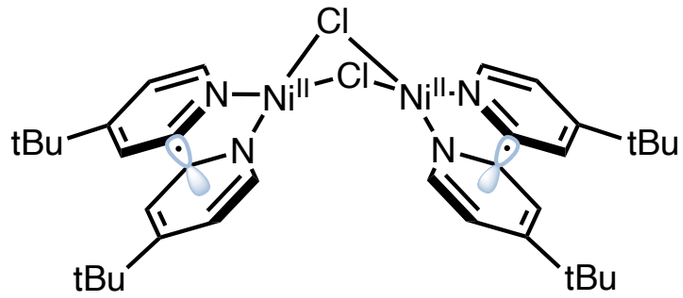
Ligand Non-innocence in Ni(I) Complexes

- Metal— or ligand—centered radicals? A complicated story …

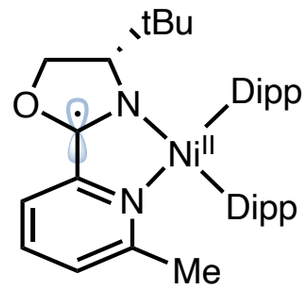




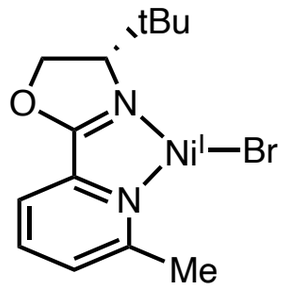




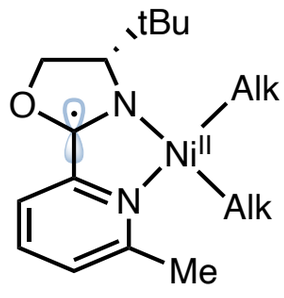
non-obvious from simply looking at a given structure



can *acticvate AlkBr*
can't *acticvate ArBr*



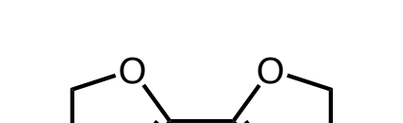
can't *acticvate AlkBr*
can *acticvate ArBr*

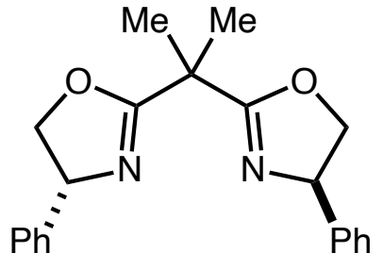


not evaluated

SOMO distribution affects reactivity

sterics also seem to play role



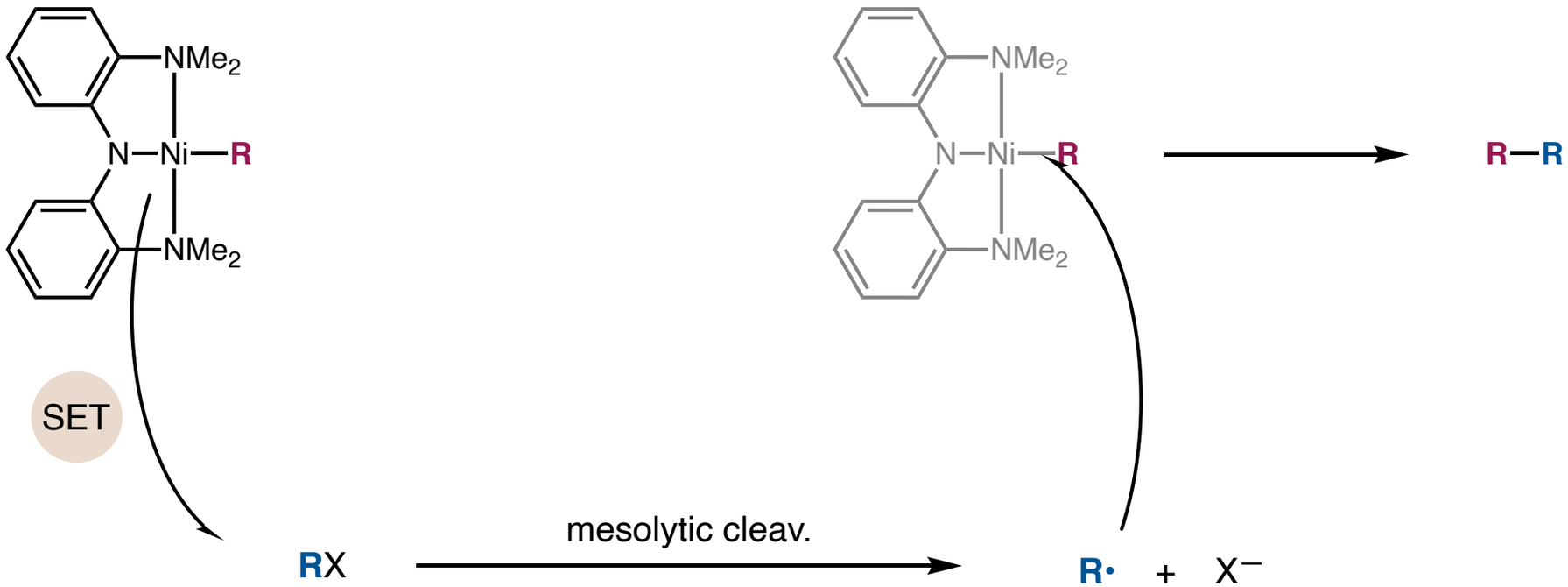


innocent ligands don't participate in this

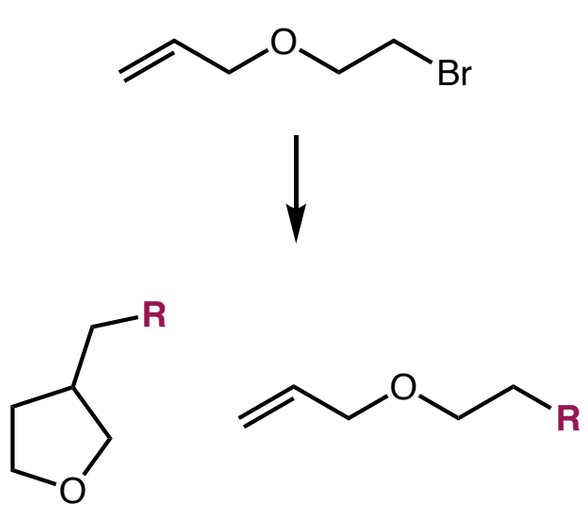
Wagner, C. L.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 5295.
Ju, L.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 14458.

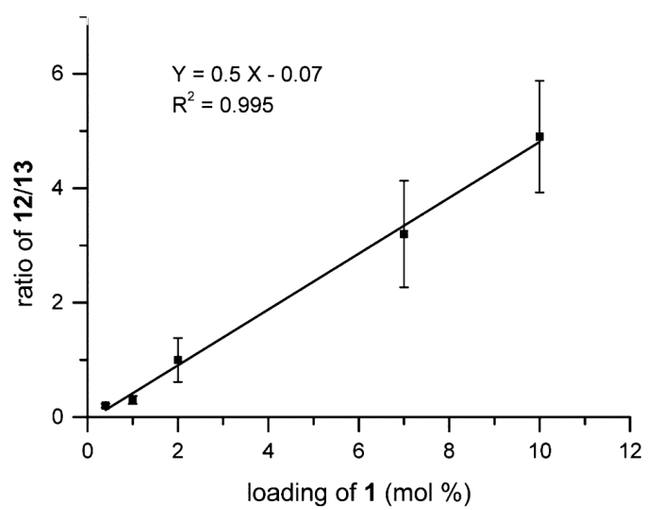
Mono- or bimetallic oxidative addition?

- Evidence of radical bimetallic oxidative addition (2013)



supported by radical clock



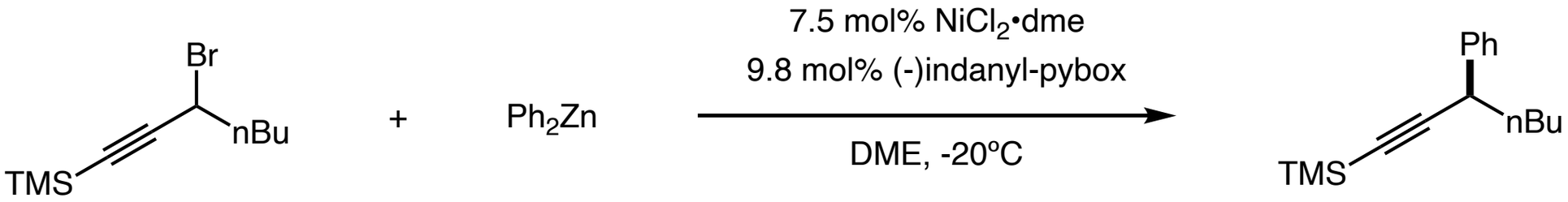


ratios consistent with radical clock experiments in systems that invoke Ni(I)

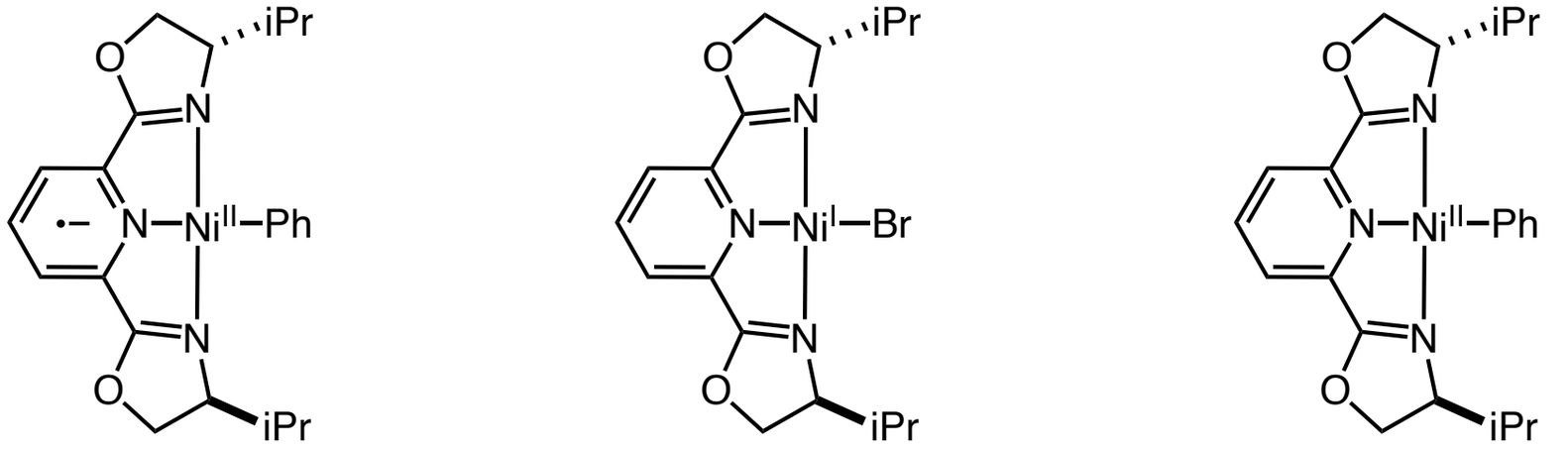
Breitenfeld, J.; Ruiz, J.; Wodrich, M. D.; Hu, X. *J. Am. Chem. Soc.* **2013**, *135*, 12004.

Can only Ni(I)-alkyl species activate AlkBr?

- Fu throws wrench into generalization (2014)



(pybox)NiPh (pybox)NiBr [(pybox)NiPh]Br



reacts **ineffciently** with electrophile

reacts **efficiently** with electrophile

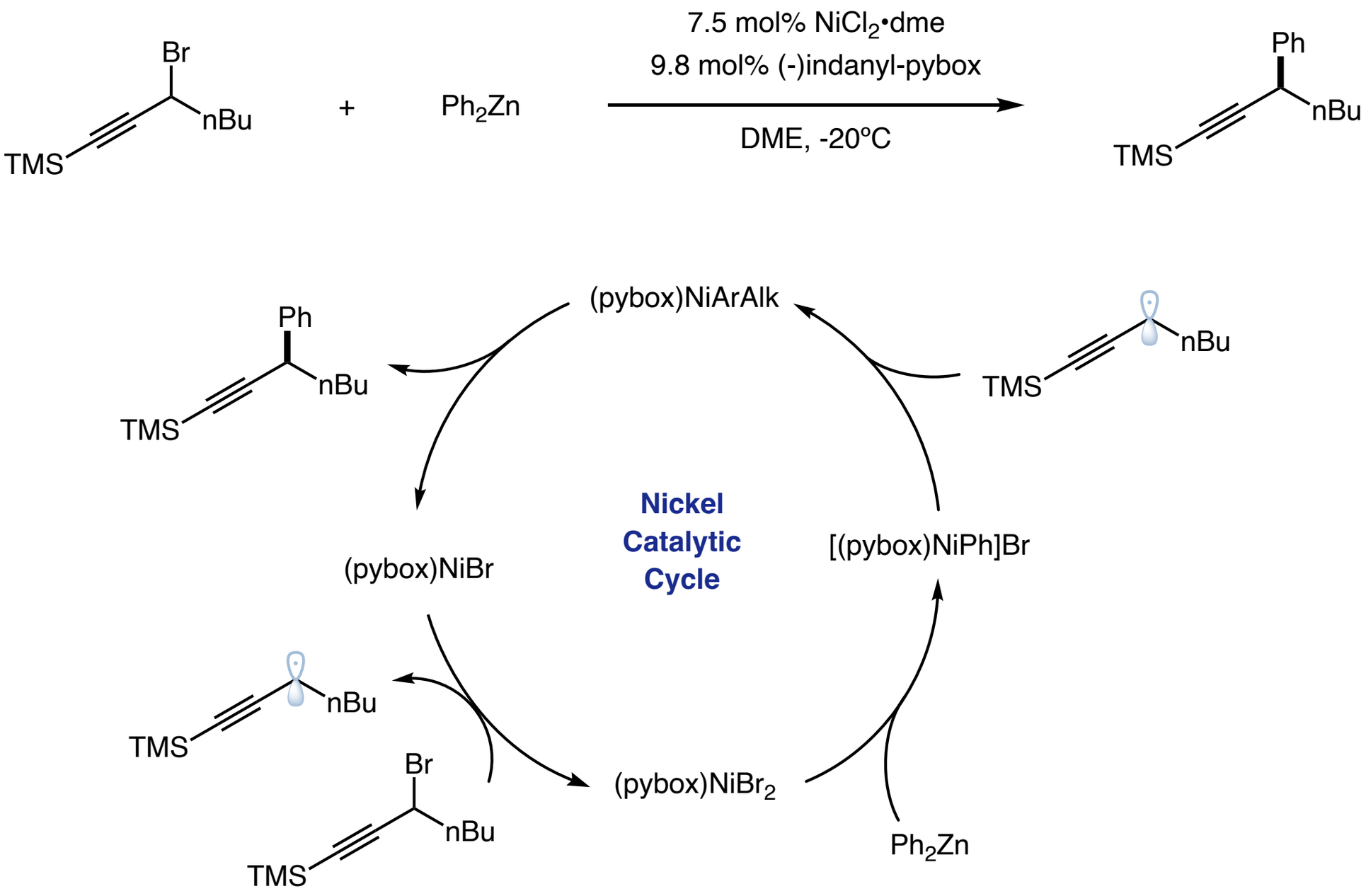
predominant resting state of nickel

opposite reactivity observed as with terpy

Schley, N.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, *47*, 16588.

Can only Ni(I)-alkyl species activate AlkBr?

- Fu throws wrench into generalization (2014)

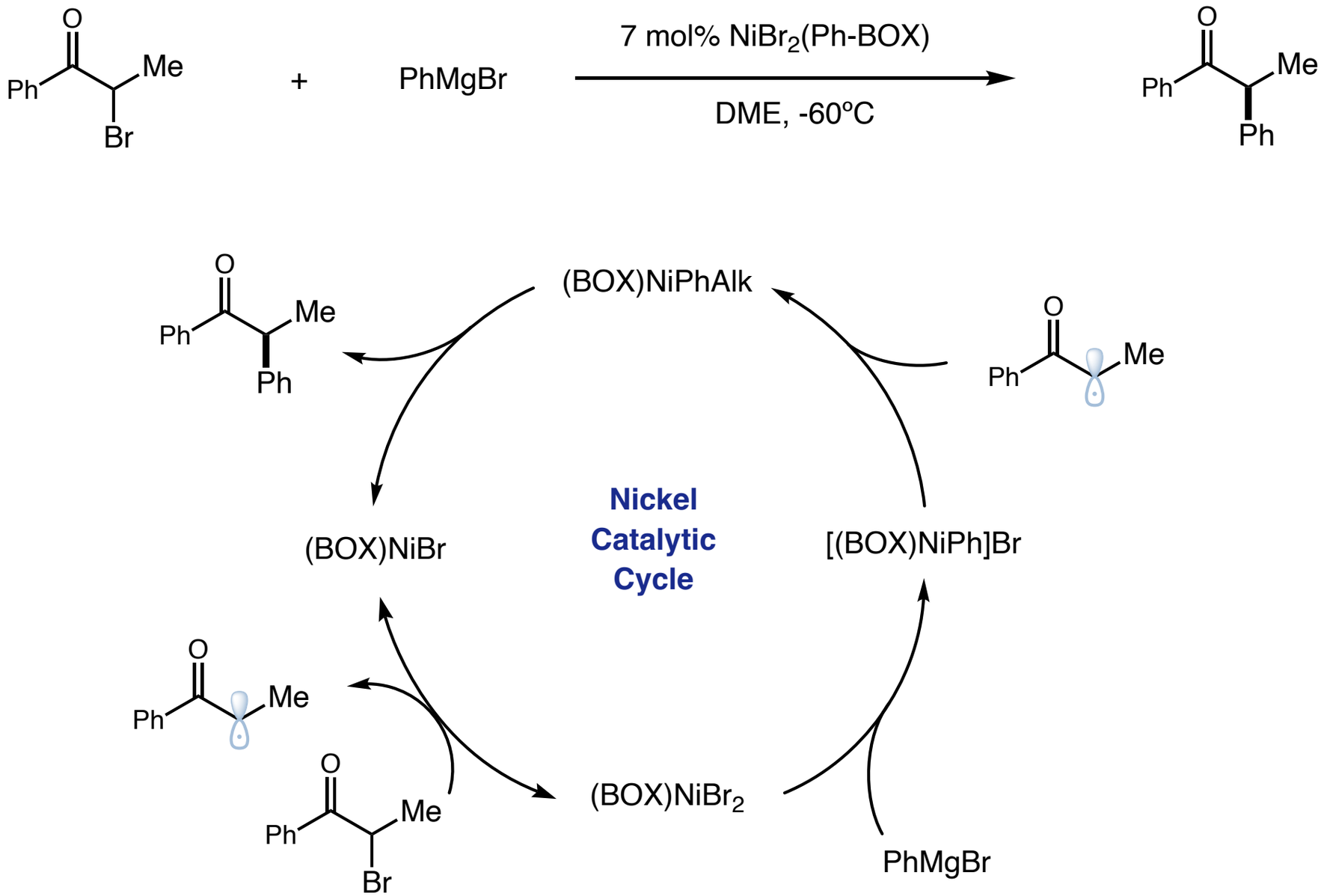


opposite reactivity observed as with terpy

Schley, N.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, *47*, 16588.

Can only Ni(I)-alkyl species activate AlkBr?

- Fu throws wrench into generalization (2019)



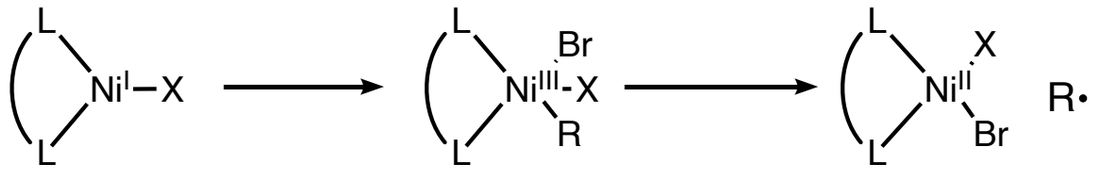
note the activated nature of the electrophiles

Yin, H.; Fu, G. C. *J. Am. Chem. Soc.* **2019**, *141*, 15433.

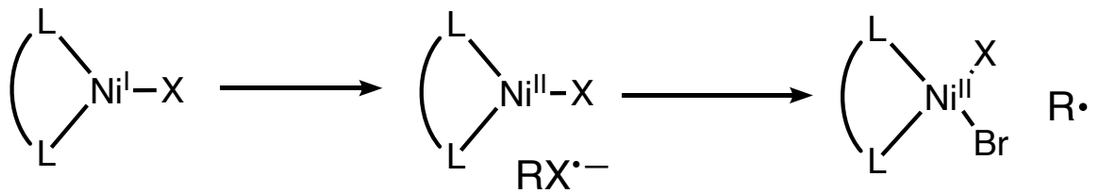
Elucidating the oxidative addition itself

■ (Xantphos)Ni(I)-mediated Alkyl Bromide Activation

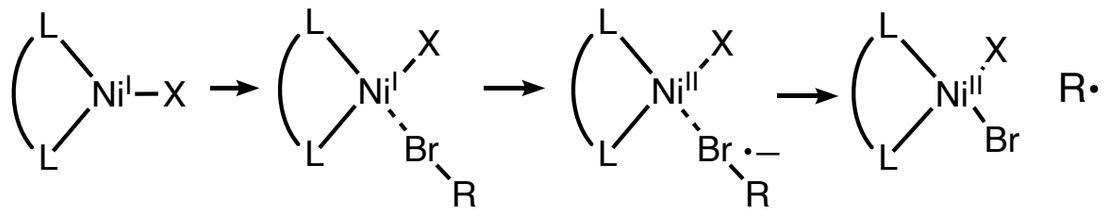
Concerted Addition



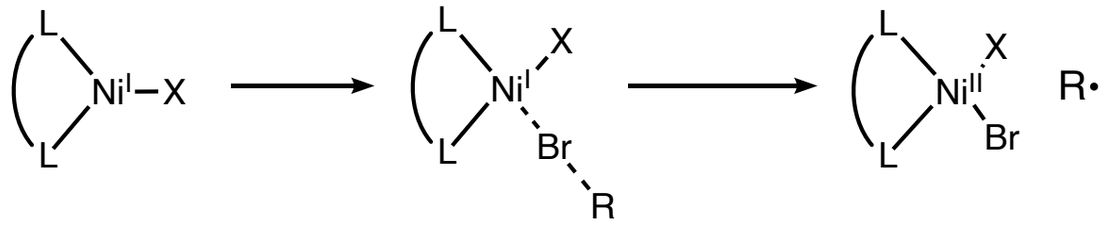
Outer-sphere electron transfer

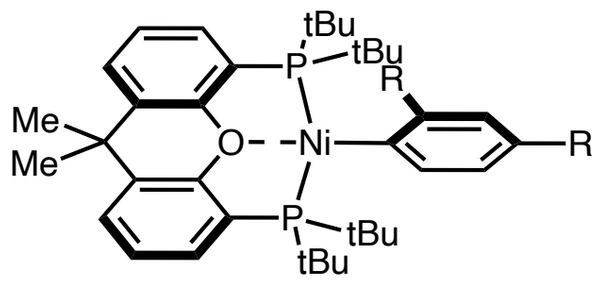


Inner-sphere electron transfer



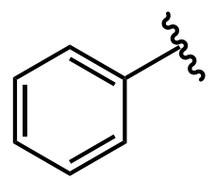
Concerted XAT



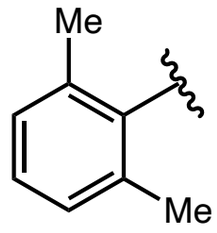


was reacted with various alkyl bromides

1. Rate depends on sterics of aryl

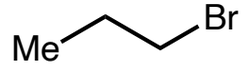


$3.3 \times 10^2\ M^{-1}s^{-1}$

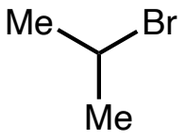


unreactive

2. Rate faster for secondary over primary bromides



$1.4 \times 10^3\ M^{-1}s^{-1}$



$6 \times 10^3\ M^{-1}s^{-1}$

3. Rate independent of solvent polarity

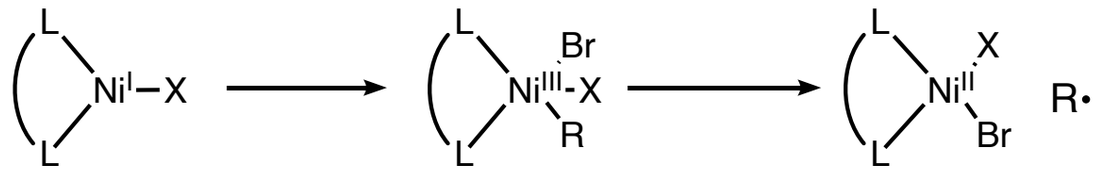
corroborated by DFT calculations

Diccianni, J. B.; et al. *J. Am. Chem. Soc.* **2019**, *141*, 1788.

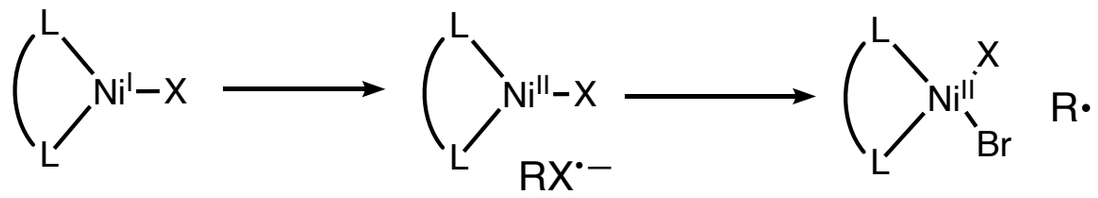
Elucidating the oxidative addition itself

■ Bpy-ligated Ni(I) Alkyl Bromide Activation

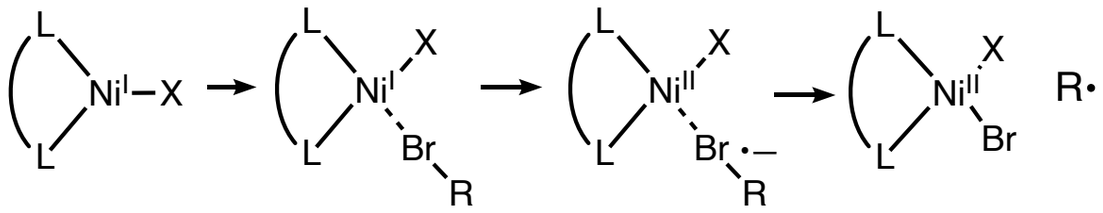
Concerted Addition



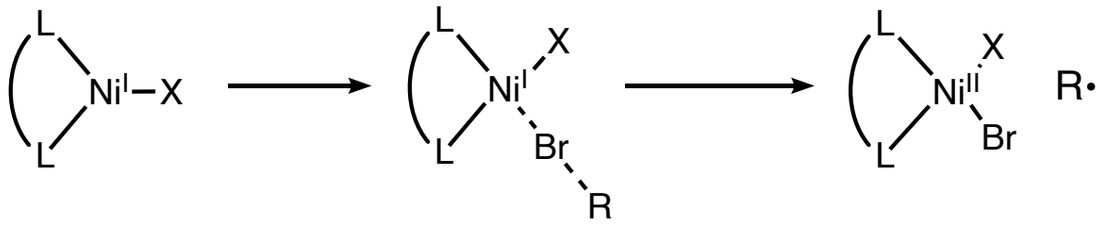
Outer-sphere electron transfer

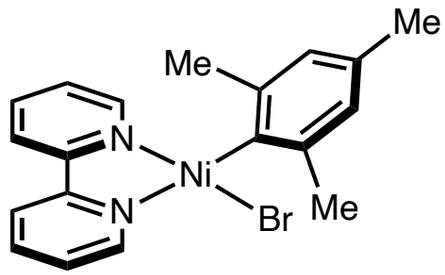


Inner-sphere electron transfer



Concerted XAT



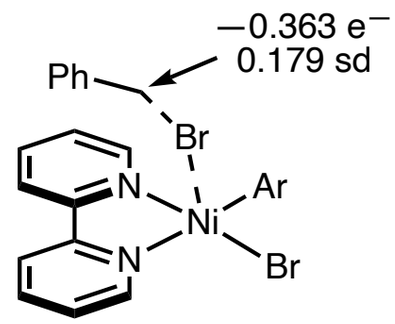


reaction rate with alkyl bromide determined by foot-of-the-wave analysis

1. Rate depends on sterics of aryl

2. Rate faster for secondary over primary bromides

DFT calculation for reaction with BnBr shows:



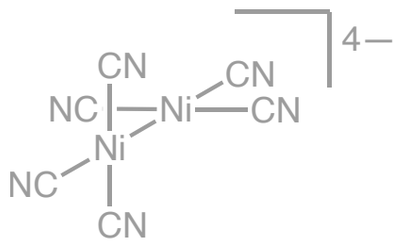
halide never transferred to Ni, dissociates during reaction

best described as inner-sphere electron transfer with concommitant bromide dissociation

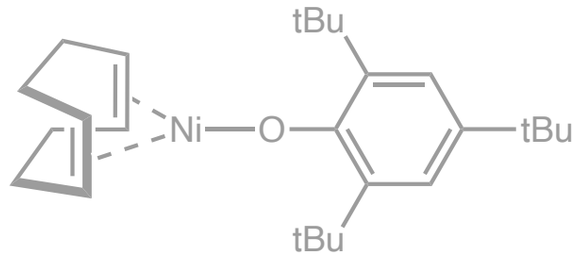
Lin, Q.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 14196.

Outline of Talk

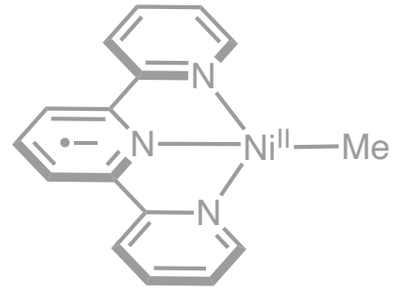
Historical Aspects of Ni(I) Complexes



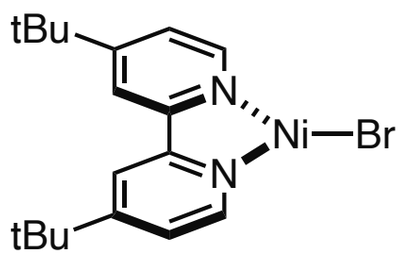
Preparation and Properties of Ni(I) Complexes



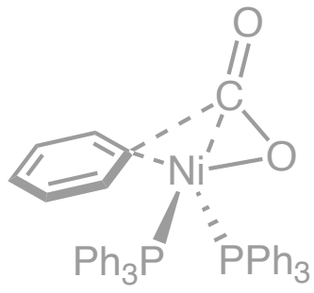
Oxidative Addition to C(sp_3)—X



Oxidative Addition to C(sp_2)—X



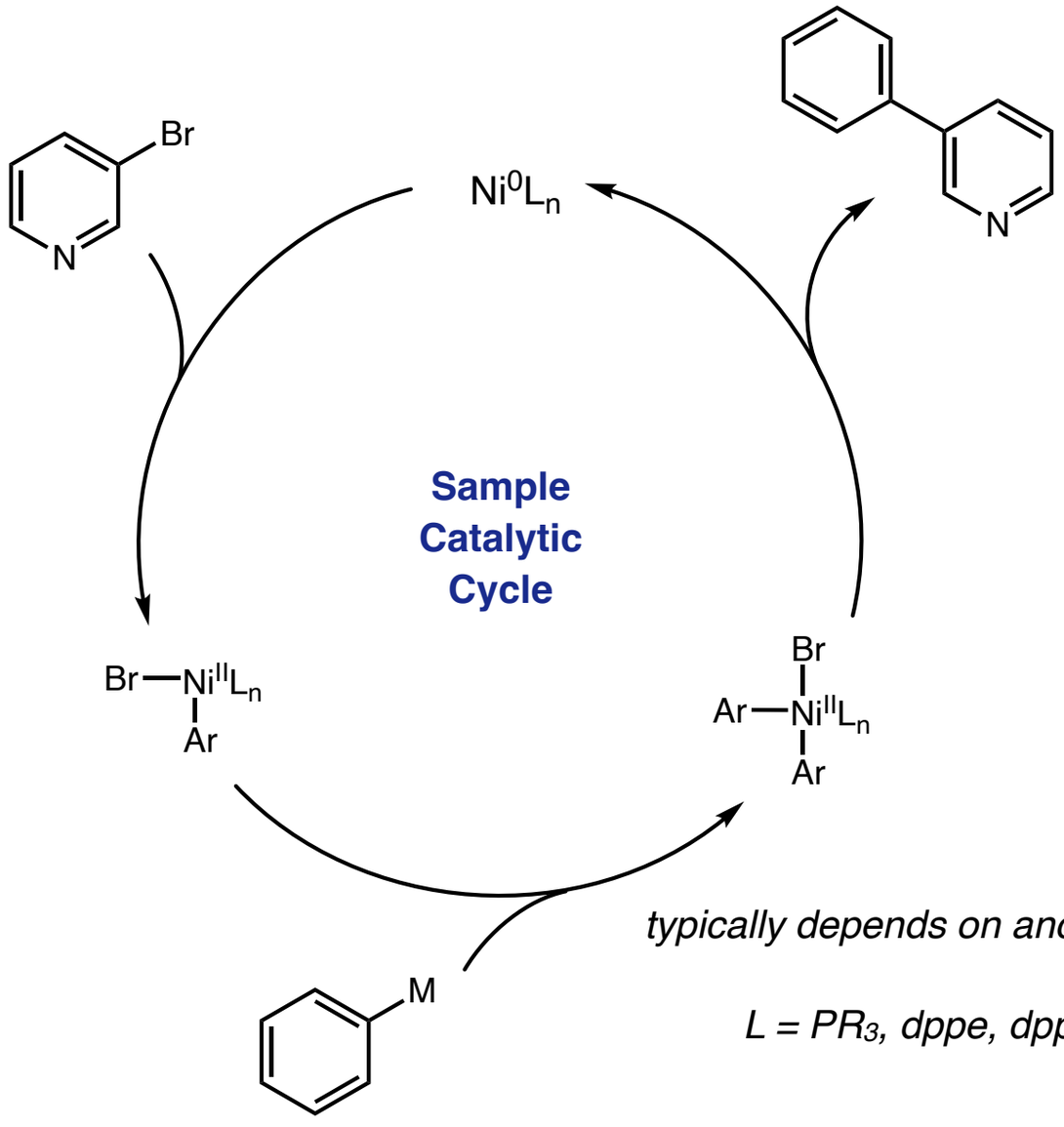
Carboxylations with CO_2



Well-defined Ni(I) species behave like heavier analogues

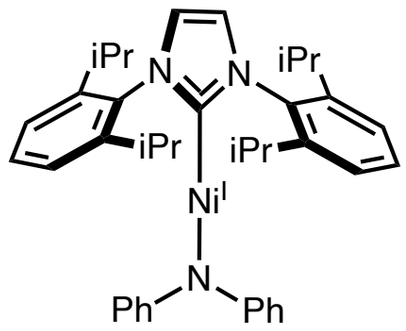
- Strong σ donor ligated Ni(I) acts analogous to Pd(0)

Ni more reducing than Pd	**large ligand field splitting penalizes one electron OS changes**

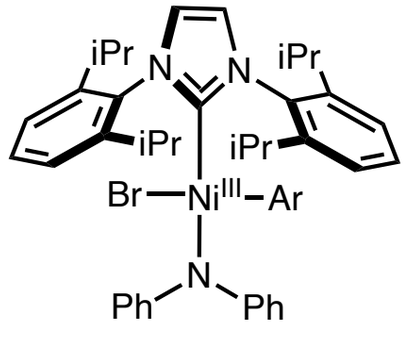


typically depends on ancillary ligands

L = PR_3, dppe, dppf, NHC



4-bromoanisole | Et_2O, 40 °C



less remarkable chemistry compared to other metals

Dicianni, J.; Diao, T. *Trends in Chemistry.* **2019**, *1*, 830.

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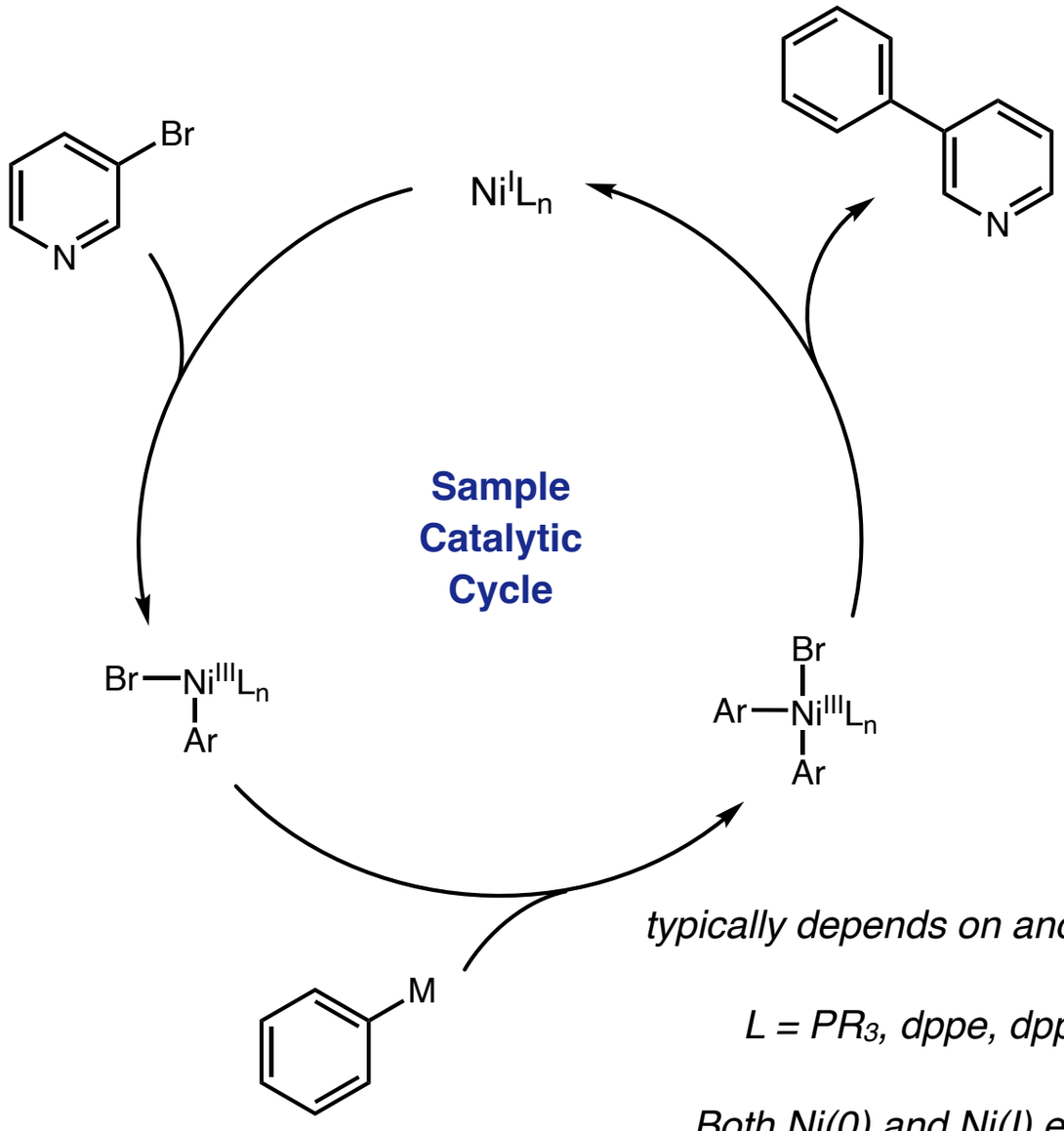

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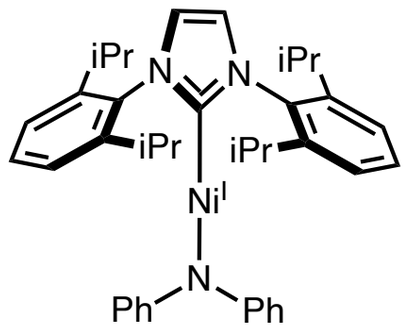
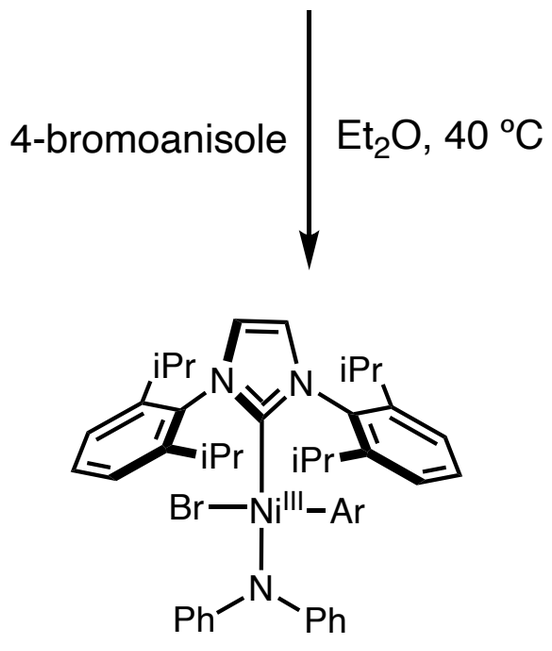
Both Ni(0) and Ni(I) established





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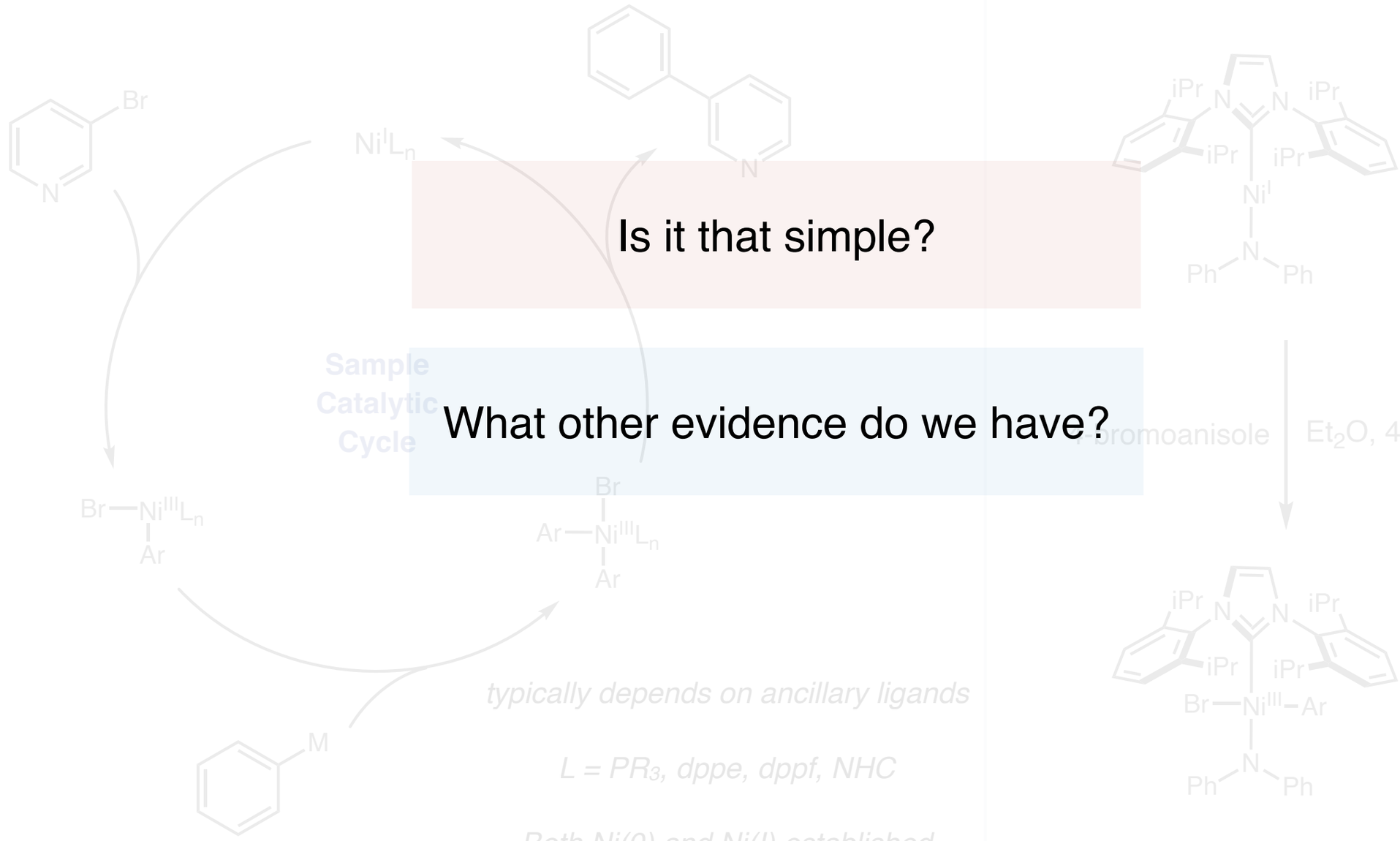


Is it that simple?

What other evidence do we have?

typically depends on ancillary ligands

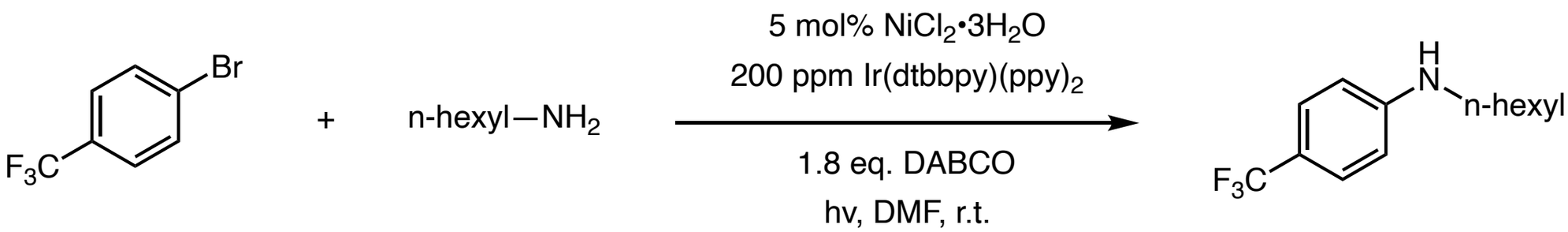
L = PR_3, dppe, dppf, NHC

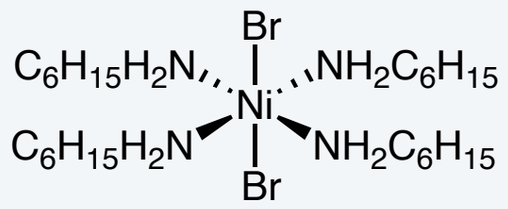
Both Ni(0) and Ni(I) established

less remarkable chemistry compared to other metals

Can Ni(I) species activate aryl bromides?

- Evidence for C(sp_2) OA in amination (2020)



resting states:	$Ir(dtbbpy)(ppy)_2$		**despite** strong SV quenching of DABCO

suggests highly active nickel species responsible for coupling

reductive elimination only from Ni(III)

$\Phi(t) = \Phi(q) \times \Phi(Ir) \times \Phi(Ni)$

$\Phi(q) = 1 \qquad \Phi(Ir) \leq 1$

$\Phi(Ni) \geq 1$

Ni cycle is self-sustained and must go through Ni(III)

Till, N. A.; Tian, L.; Dong, Z.; Scholes, G. D.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2020**, *142*, 15830.

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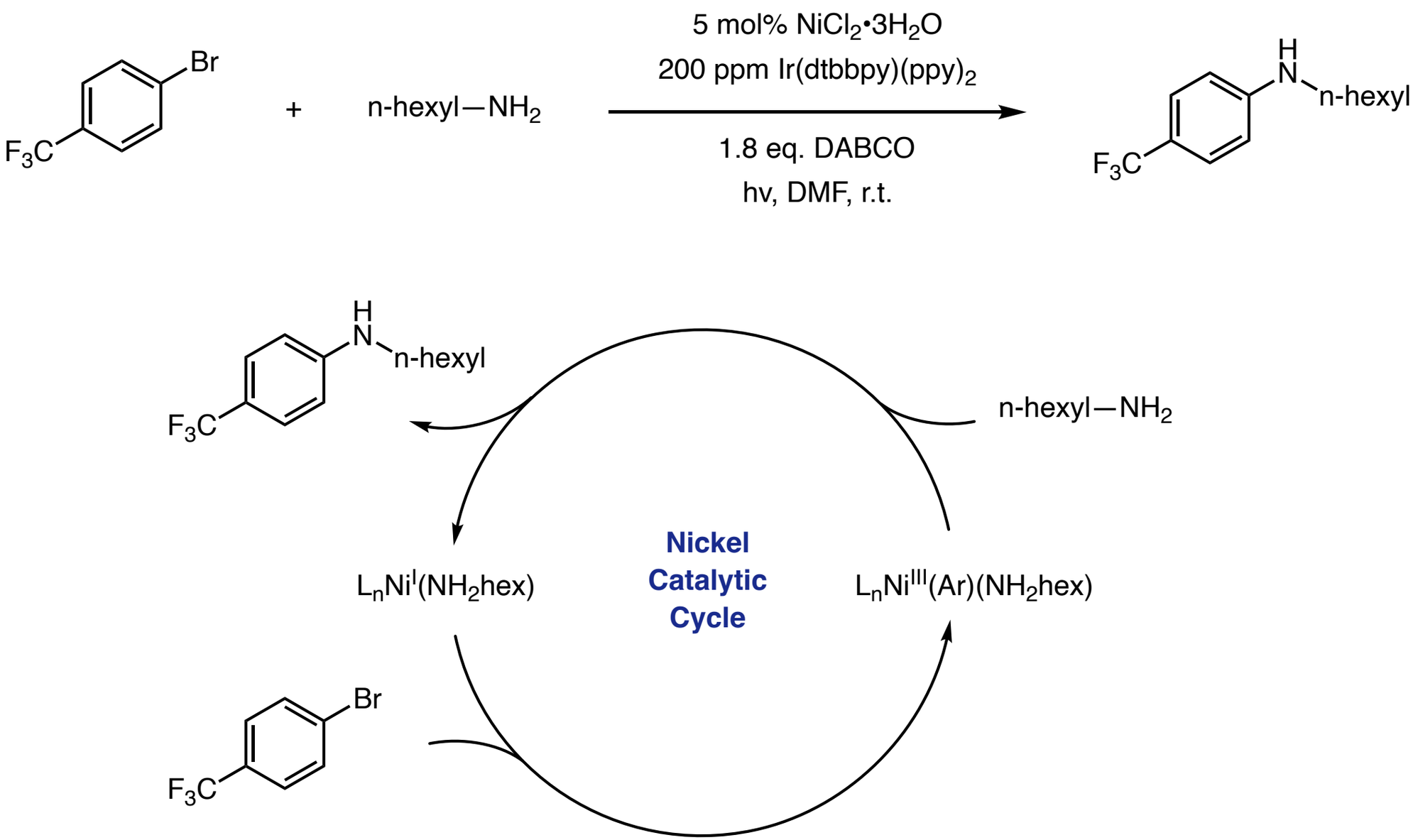

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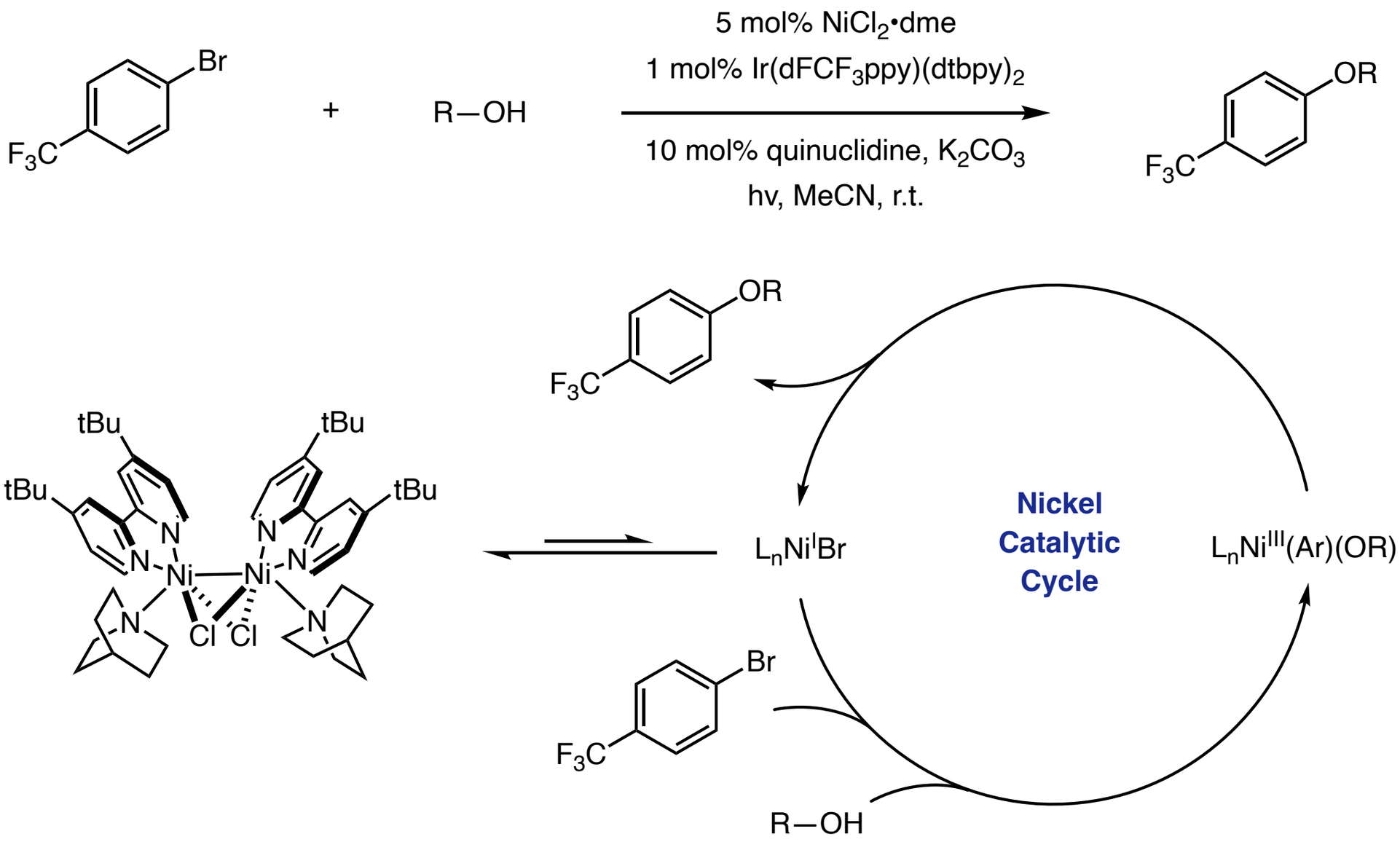
- Evidence for C(sp_2) OA in etherification (2019)



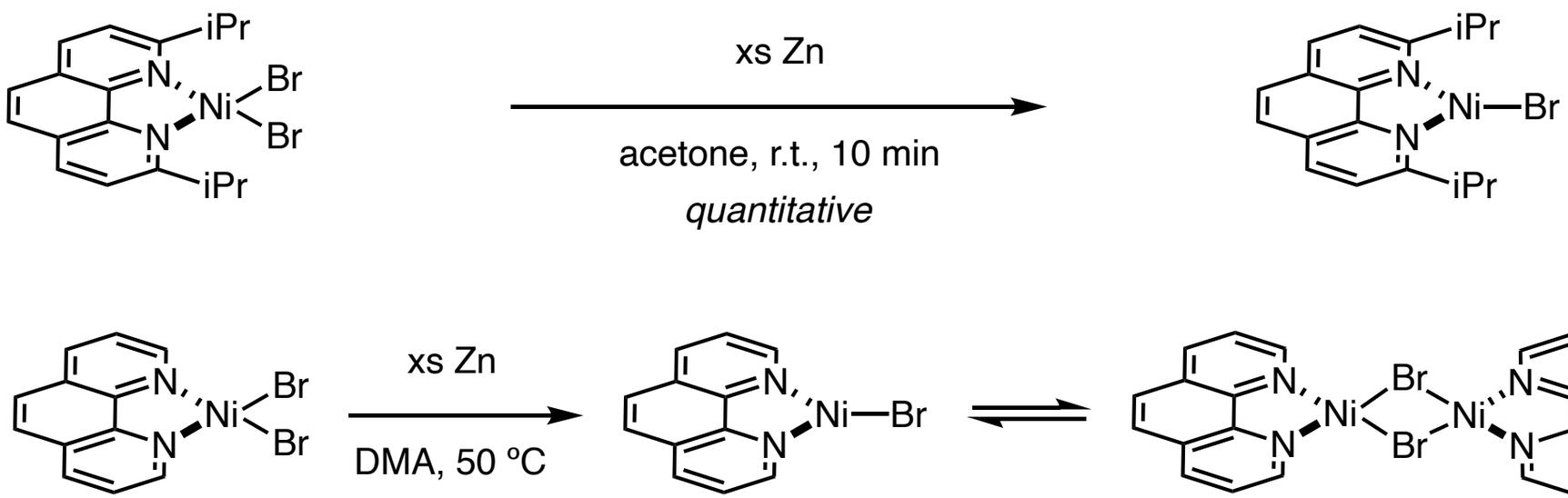
decreased Ni loading increases TON

indirect evidence of a Ni(I) halide complex doing a I/III oxidative addition

Sun, R.; et al. *J. Am. Chem. Soc.* **2019**, *141*, 89.

Can Ni(I) species activate aryl bromides?

- Evidence for C(sp_2) OA in alkene dicarbofunctionalization (2019)



possible bi-metallic oxidative addition?

Sun, R.; et al. *J. Am. Chem. Soc.* **2019**, *141*, 89.

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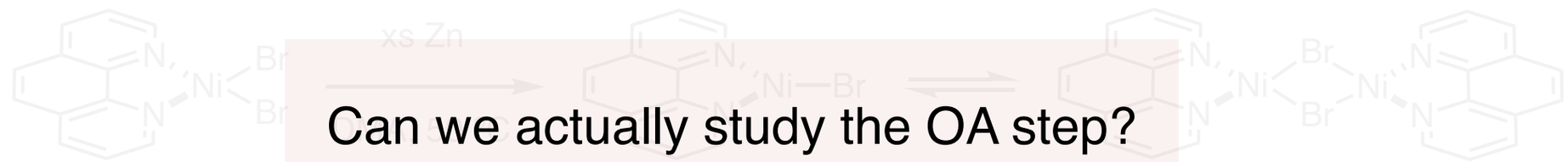
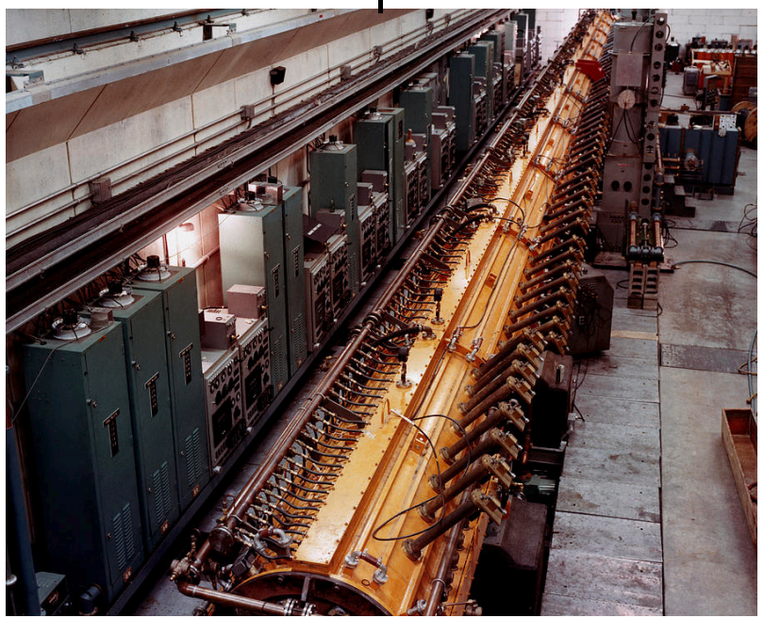


Can we actually study the OA step?

Sun, R.; et al. *J. Am. Chem. Soc.* **2019**, *141*, 89.

What direct evidence on the OA step exists?

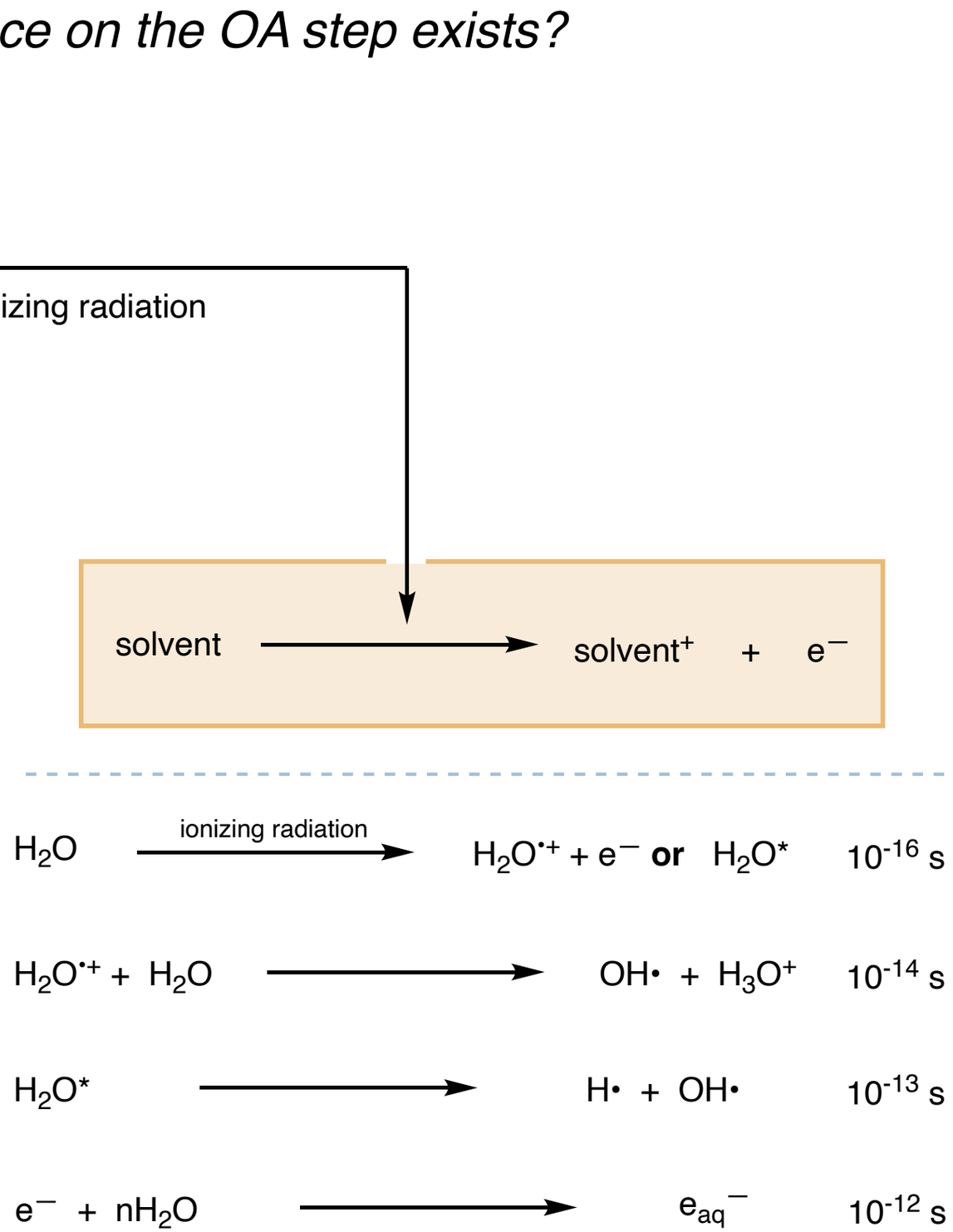
- What is pulse radiolysis?



Linear accelerator at BNL

can monitor downstream reactions of formed reactive species by spectroscopy

generatres ionizing radiation

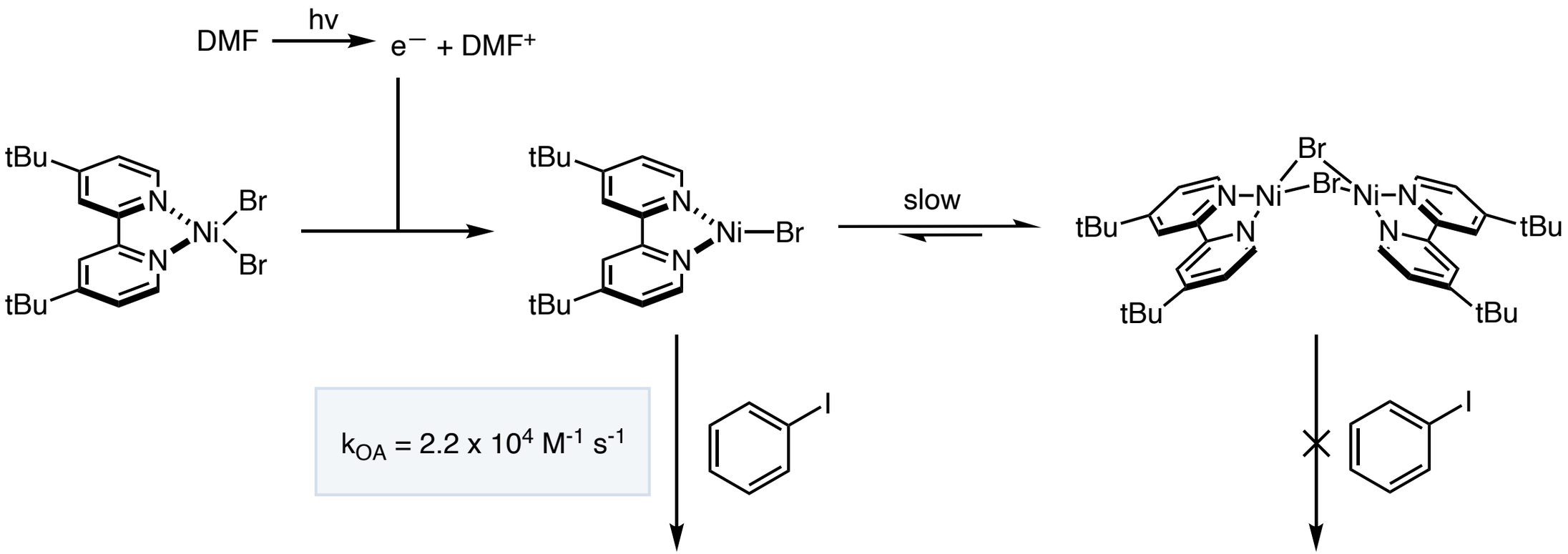


effective tool to study ultrafast processes in radical chemistry

Till, N. A.; Oh, S.; MacMillan, D. W. C.; Bird, M. J. *J. Am. Chem. Soc.* **2021**, *143*, 9332.

What direct evidence on the OA step exists?

- Applying pulse radiolysis to dtbbpy system (2021)



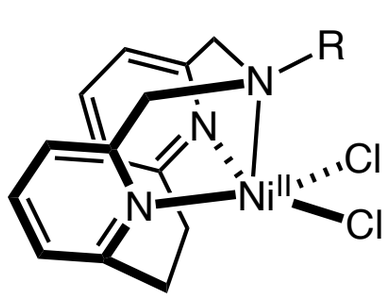
full characterization of OA: $\rho = 3.1$ $\Delta G^{\ddagger} = 10.4$ kcal/mol $\Delta H^{\ddagger} = 5.8$ kcal/mol $\Delta S^{\ddagger} = -15.5$ cal/(mol K)

direct evidence for feasibility of oxidative addtion with dtbbpy ligand

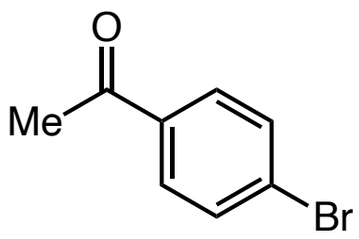
Beromi, M. M.; et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 6094.
Till, N. A.; Oh, S.; MacMillan, D. W. C.; Bird, M. J. *J. Am. Chem. Soc.* **2021**, *143*, 9332.

What direct evidence on the OA step exists?

- Isolation of the OA complex (2022?)

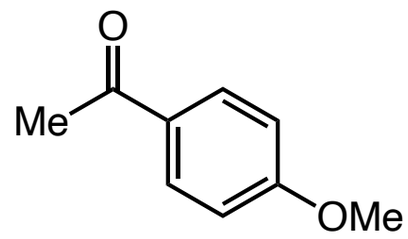


pyridinophane ligand

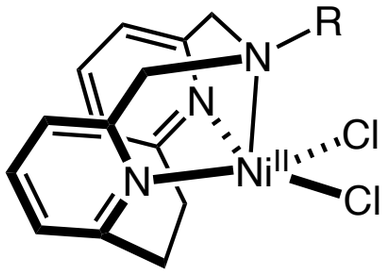


\+ MeOH

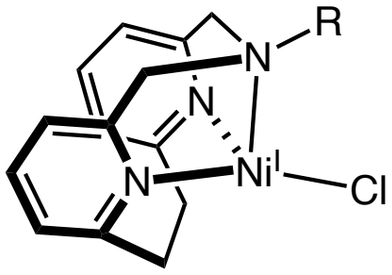
2 mol% **[Ni]**
0.5 mol% $[Ir(dtbbpy)ppy_2]PF_6$
1.1 eq. quinuclidine
hv, THF, r.t.



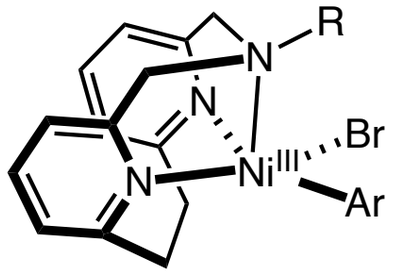
98%



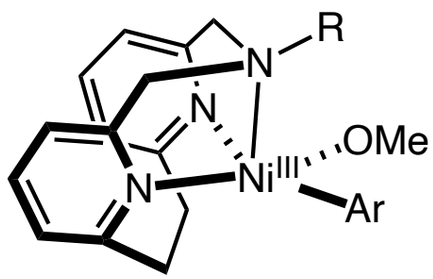
Cp_2^*Co
−95°C



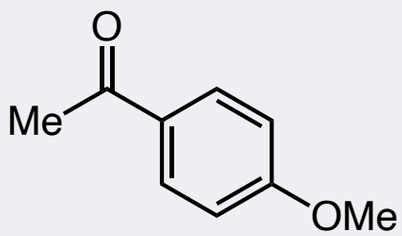
20 eq. ArBr
−80°C



10eq. quinuclidine
MeOH
−80°C



5 min, r.t.



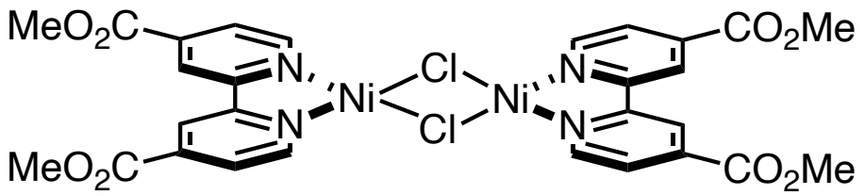
33%

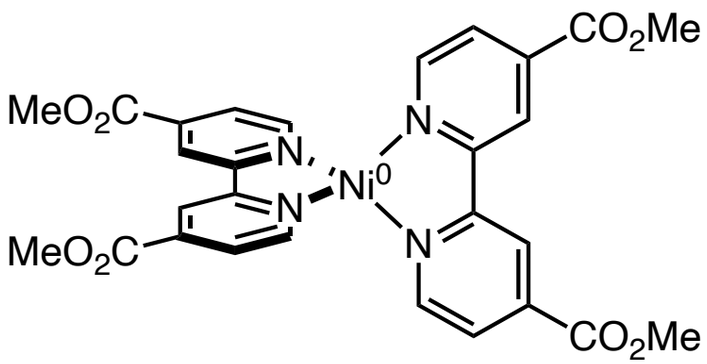
clear observation of Ni(I/III) OA and all other steps in etherification

Na, H.; Mirica, L. *ChemRxiv* **2021**, *DOI: 10.33774/chemrxiv-2021-cwk2r*.

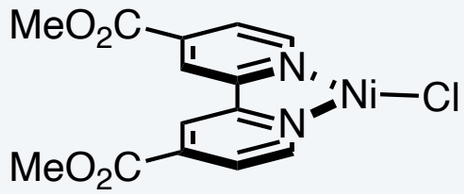
What direct evidence on the OA step exists?

- Discovery of a monomeric bpy-ligated Ni^{I} (2022)



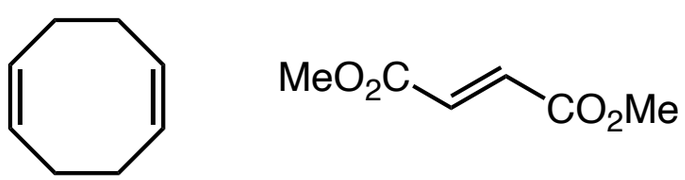


+ $Ni^{II}Cl_2$

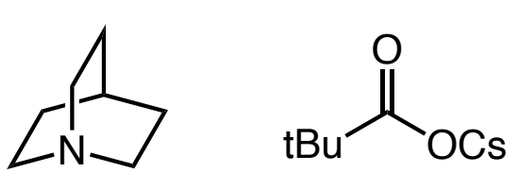


predominant form in solution (THF)

disproportionation induced by:



stabilize Ni^{0}



stabilize Ni^{II}

showcases complexity and sensitivity of bpy-ligated Ni(i) species

Ting, S. I.; Williams, W.; Doyle, A. G. *ChemRxiv* **2022**, *DOI: 10.26434/chemrxiv-2022-m8xj2*.

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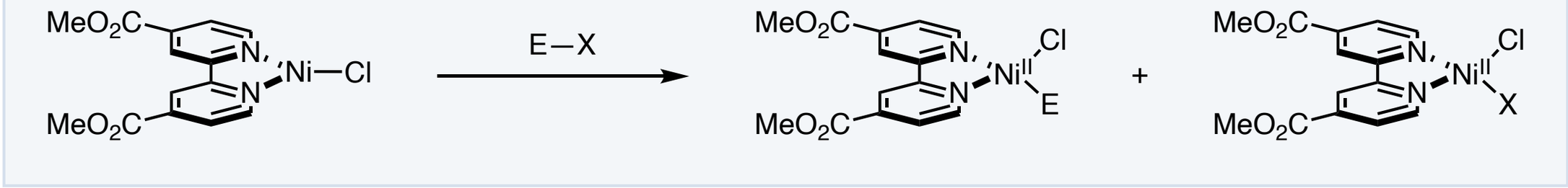
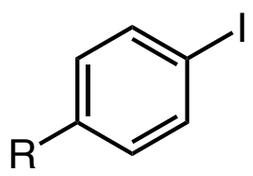
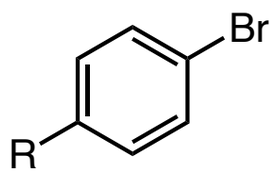
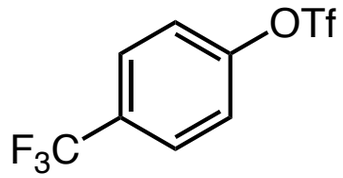


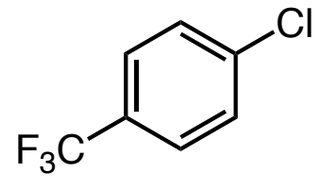
reacts with:







doesn't react with:

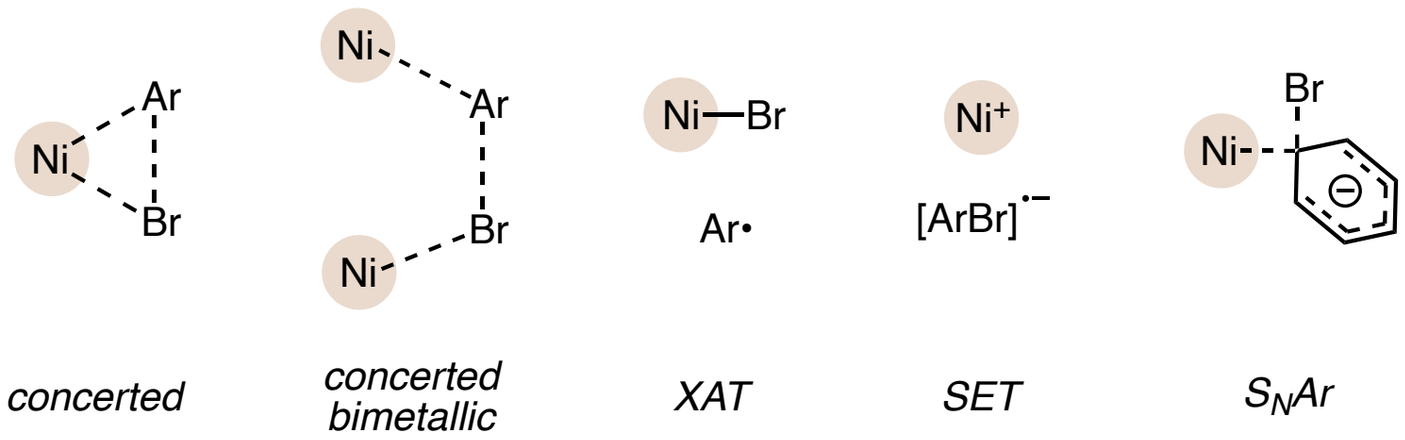


Ting, S. I.; Williams, W.; Doyle, A. G. *ChemRxiv* **2022**, *DOI: 10.26434/chemrxiv-2022-m8xj2*.

What direct evidence on the OA step exists?

- Can we uncover the nature of the OA?

Nature of C—X activation



Nuclearity of Nickel

monomer *dimer* *tetramer*

Sequence of Oxid. States

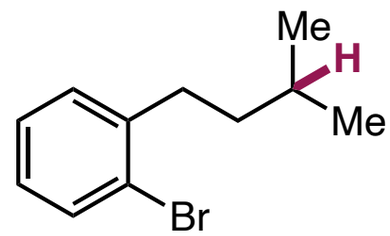
Ni(I/III), then comproportionation	*disproportionation, then Ni(0/II)*	*XAT, then capture at other Ni(I)*	*bimetallic OA*
I ⟶ III ⟶ II	I ⟶ 0 ⟶ II	I ⟶ II	I ⟶ II

first order in Ni and PhBr

$(bpy)_2Ni^0$ reacts **slower** than $(bpy)Ni^I(Cl)$

modest ρ of +1.1 observed

no 1,5-HAT observed by aryl radical



no 1,5-HAT observed during OA

no freely diffusing aryl radical

Ting, S. I.; Williams, W.; Doyle, A. G. *ChemRxiv* **2022**, *DOI: 10.26434/chemrxiv-2022-m8xj2*.

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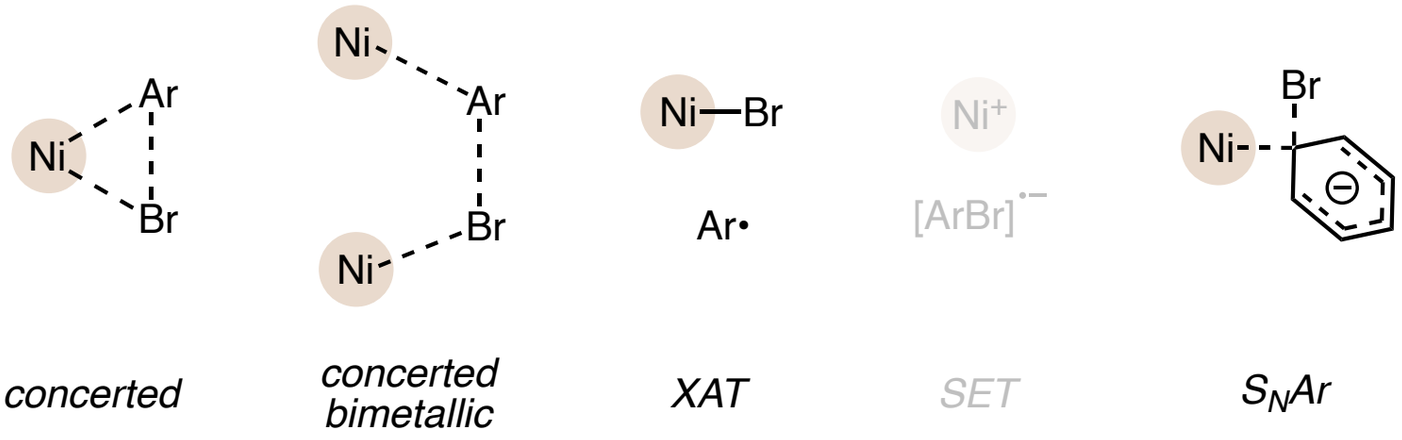

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I ⟶ III ⟶ II	**I ⟶ 0 ⟶ II**	**I ⟶ II**	**I ⟶ II**

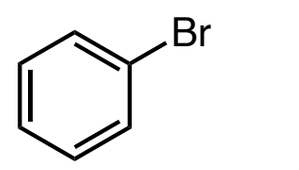
first order in Ni and PhBr

$(bpy)_2Ni^0$ reacts **slower** than $(bpy)Ni^I(Cl)$

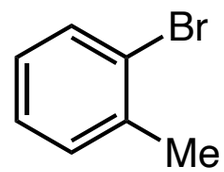
modest ρ of +1.1 observed

no 1,5-HAT observed by aryl radical

Steric dependence of rate



k_{OA} = 7.1 $M^{-1}s^{-1}$



k_{OA} = 1.5 $M^{-1}s^{-1}$

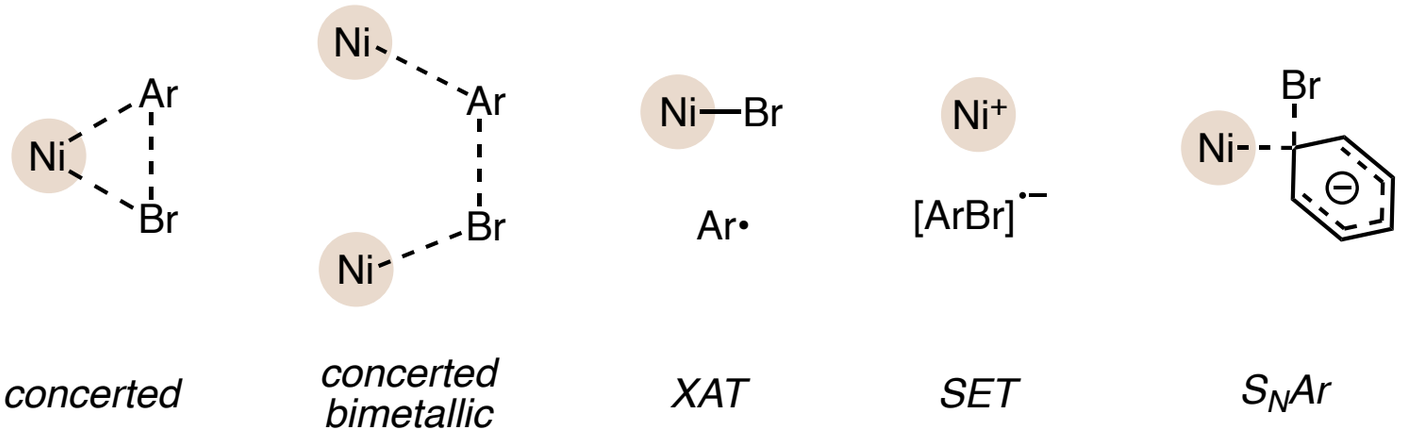
inner-sphere process

Ting, S. I.; Williams, W.; Doyle, A. G. *ChemRxiv* **2022**, *DOI: 10.26434/chemrxiv-2022-m8xj2*.

What direct evidence on the OA step exists?

- Can we uncover the nature of the OA?

Nature of C—X activation



Nuclearity of Nickel

monomer *dimer* *tetramer*

Sequence of Oxid. States

Ni(I/III), then comproportionation	*disproportionation, then Ni(0/II)*	*XAT, then capture at other Ni(I)*	*bimetallic OA*
I ⟶ III ⟶ II	**I ⟶ 0 ⟶ II**	**I ⟶ II**	**I ⟶ II**

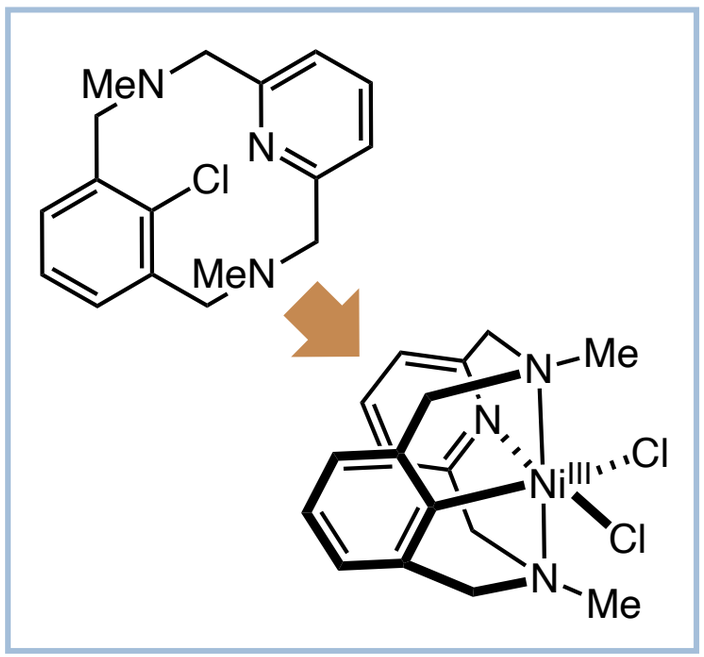
first order in Ni and PhBr

$(bpy)_2Ni^0$ reacts **slower** than $(bpy)Ni^I(Cl)$

modest ρ of +1.1 observed

no 1,5-HAT observed by aryl radical

Steric dependence of rate



Ting, S. I.; Williams, W.; Doyle, A. G. *ChemRxiv* **2022**, *DOI: 10.26434/chemrxiv-2022-m8xj2*.

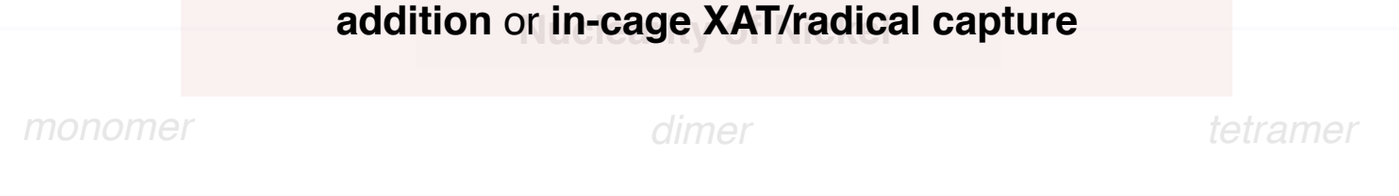
What direct evidence on the OA step exists?

- Can we uncover the nature of the OA?

Nature of C—X activation

bpy-ligated Ni(I) undergoes either **concerted addition** or **in-cage XAT/radical capture**

Nuclearity of Nickel



Sequence of Oxid. States

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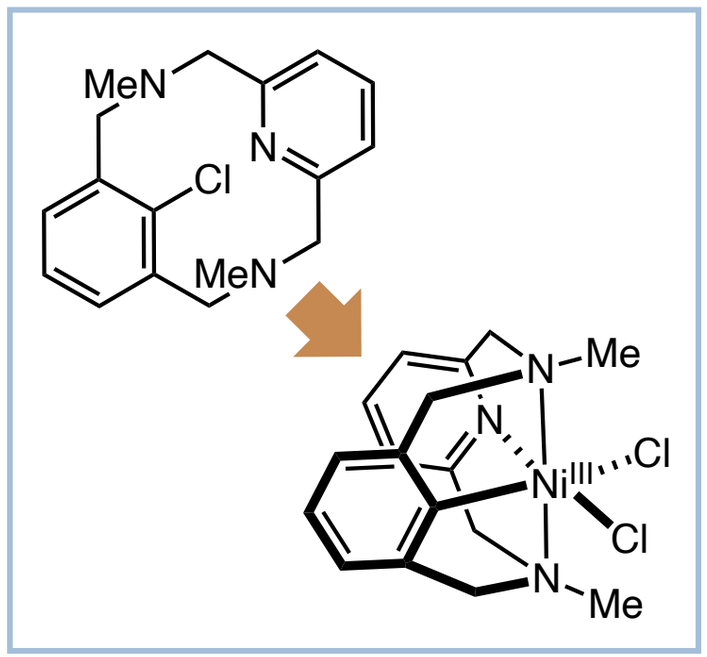
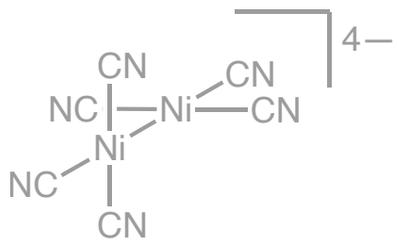


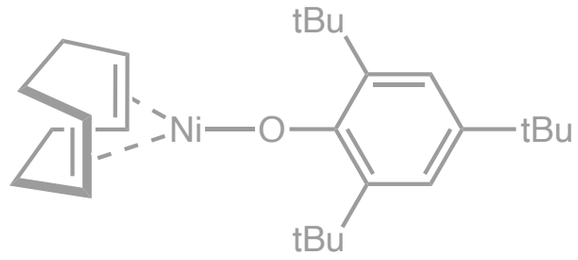
Ting, S. I.; Williams, W.; Doyle, A. G. *ChemRxiv* **2022**, *DOI: 10.26434/chemrxiv-2022-m8xj2*.

Outline of Talk

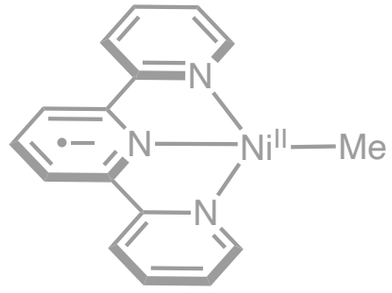
Historical Aspects of Ni(I) Complexes



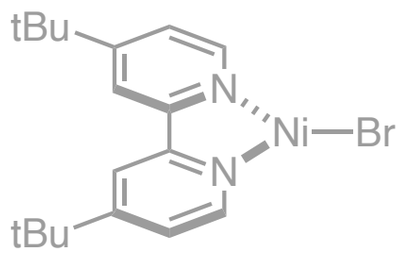
Preparation and Properties of Ni(I) Complexes



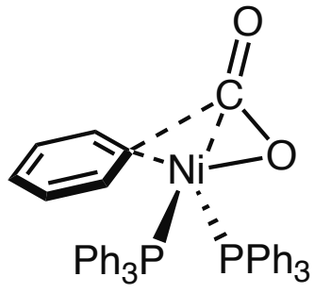
Oxidative Addition to C(sp_3)—X



Oxidative Addition to C(sp_2)—X

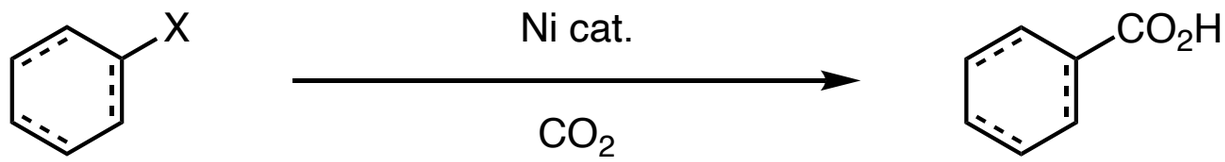


Carboxylations with CO_2

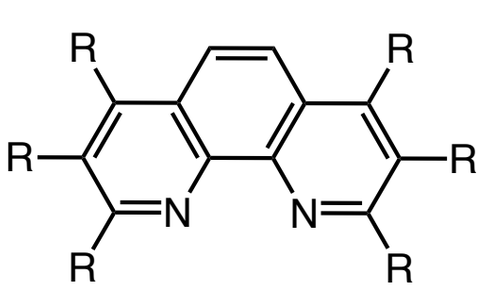


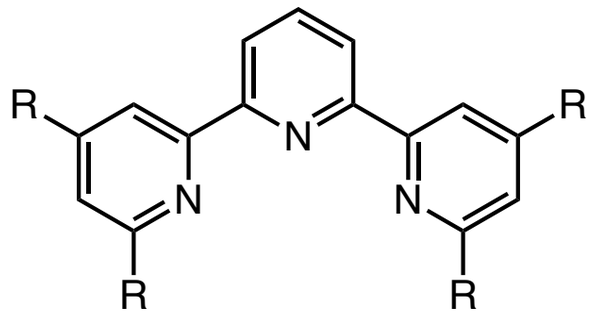
Carboxylation at Ni(I)

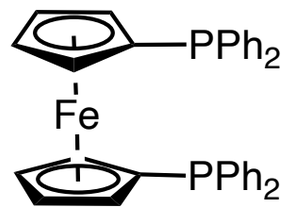
- Nickel-catalyzed carboxylation reactions

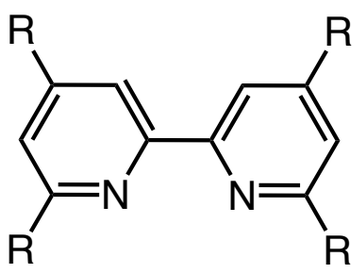


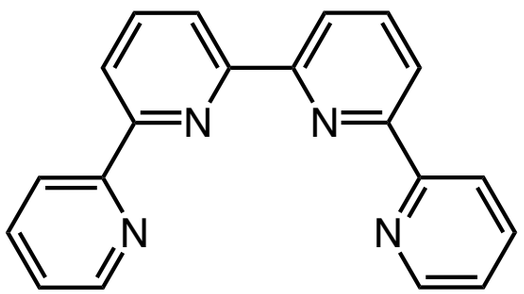
carboxylation often proposed at Ni(I)

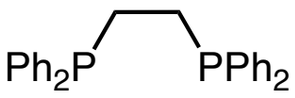










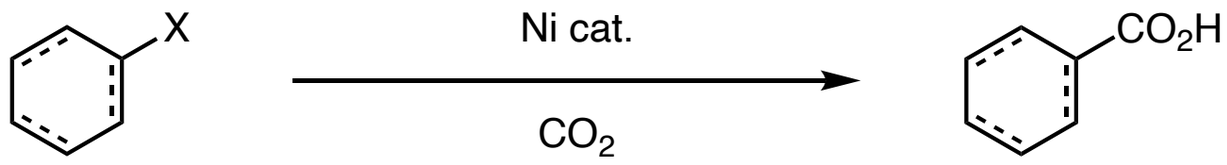


PR_3

similar mechanism proposed across variety of scaffolds

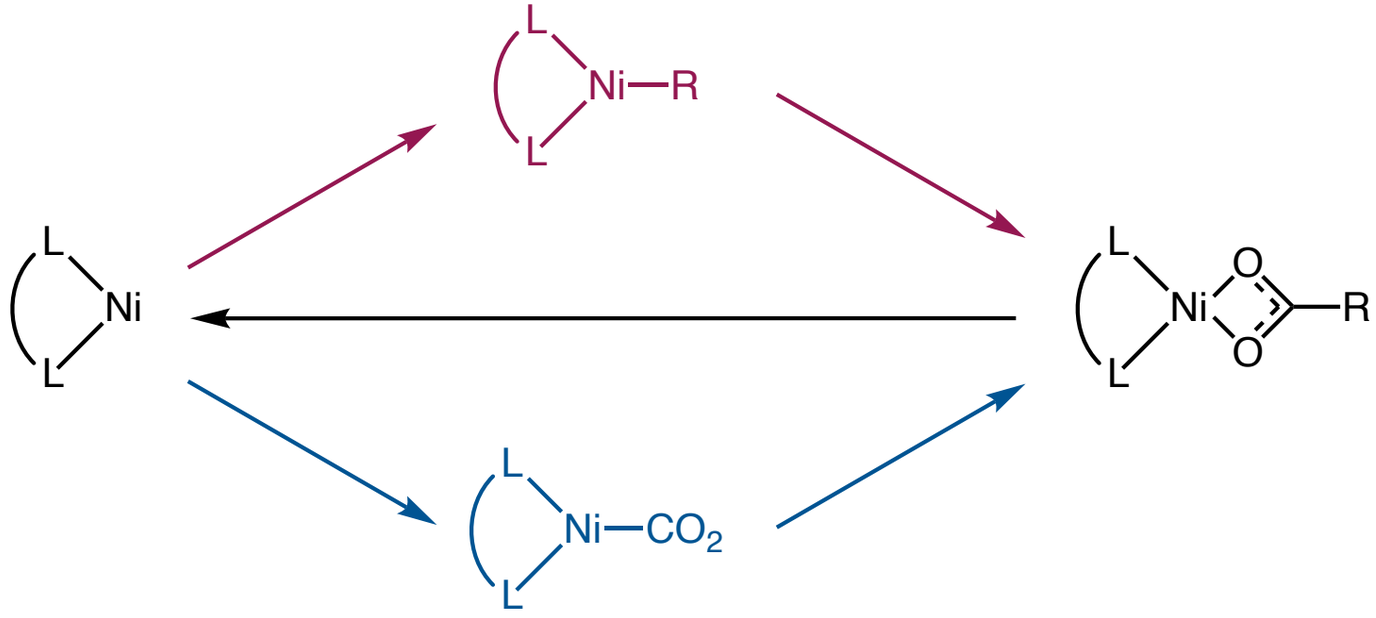
Carboxylation at Ni(I)

- Nickel-catalyzed carboxylation reactions



carboxylation often proposed at Ni(I)

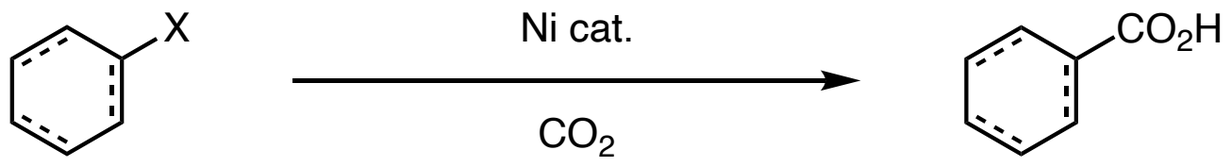
alkyl first pathway



CO_2 first pathway

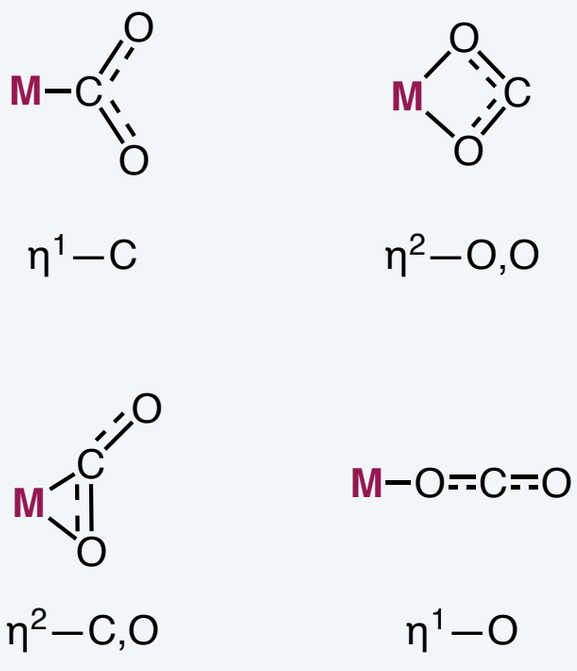
Carboxylation at Ni(I)

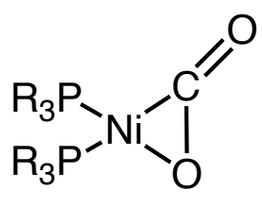
Nickel-catalyzed carboxylation reactions



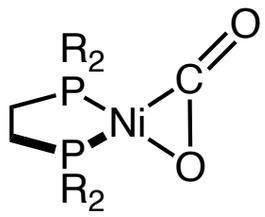
carboxylation often proposed at Ni(I)

Possible Coordination Modes

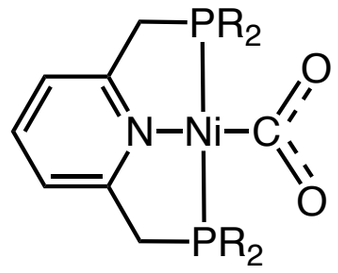




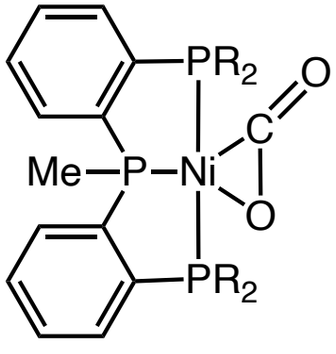
Aresta, Johnson



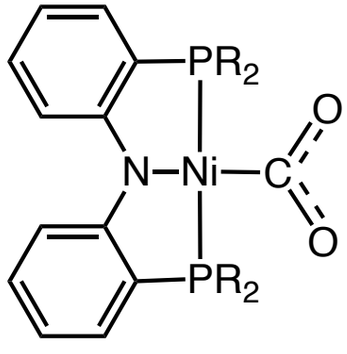
Hillhouse



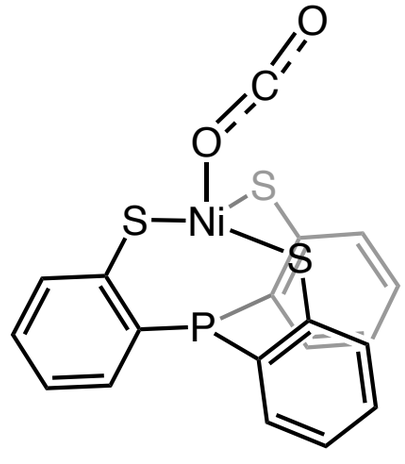
Milstein



Lee



Lee

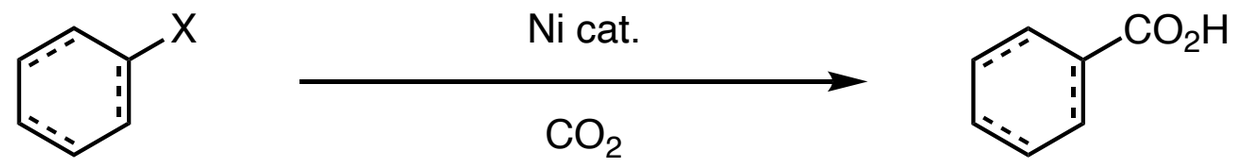


Liaw

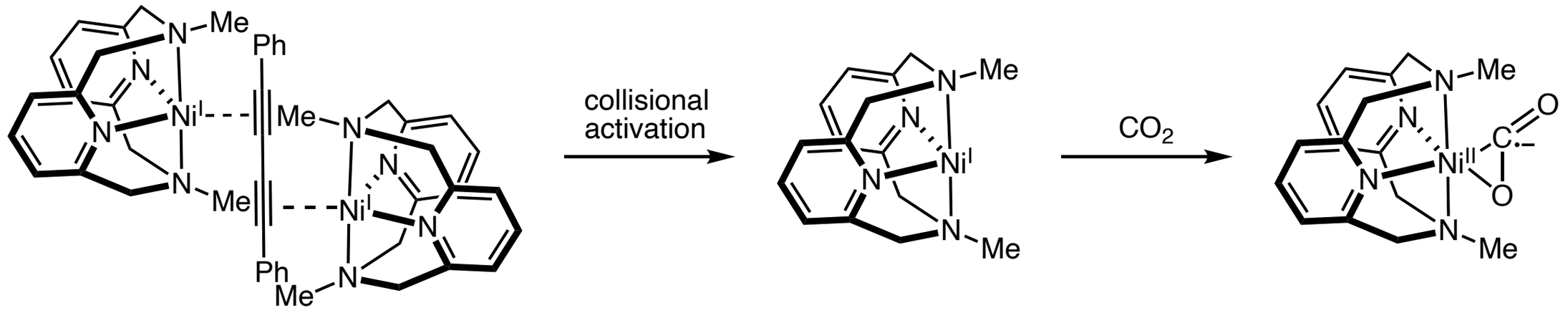
many different complexes known, unclear how they could carboxylate alkyl/aryl

Carboxylation at Ni(I)

- Experimental observation of CO_2 capture



carboxylation often proposed at Ni(I)



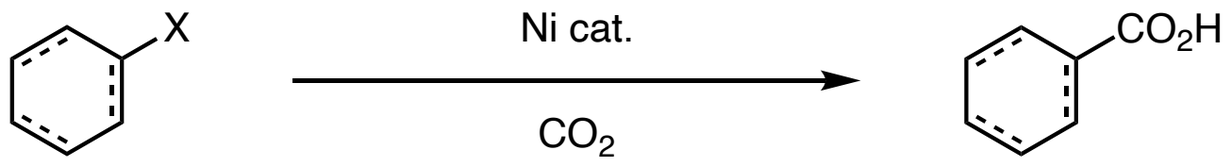
dimer extracted from solution by ESI → **increasing capillary-to-skimmer leads to dissocation of dimer** → **reaction of monomeric Ni with CO_2 conducted in ion trap** → **analysis of carboxylated Ni by photofragmentation MS** → **vibrational predissociation spectrum supports $CO_2^{\bullet-}$ assignment**

natural population analysis suggests reduction driven by ligand electron density

Menges, F. S.; et al. *Angew. Chem. Int. Ed.* **2016**, 55, 1281.

Carboxylation at Ni(I)

- Nickel-catalyzed carboxylation reactions



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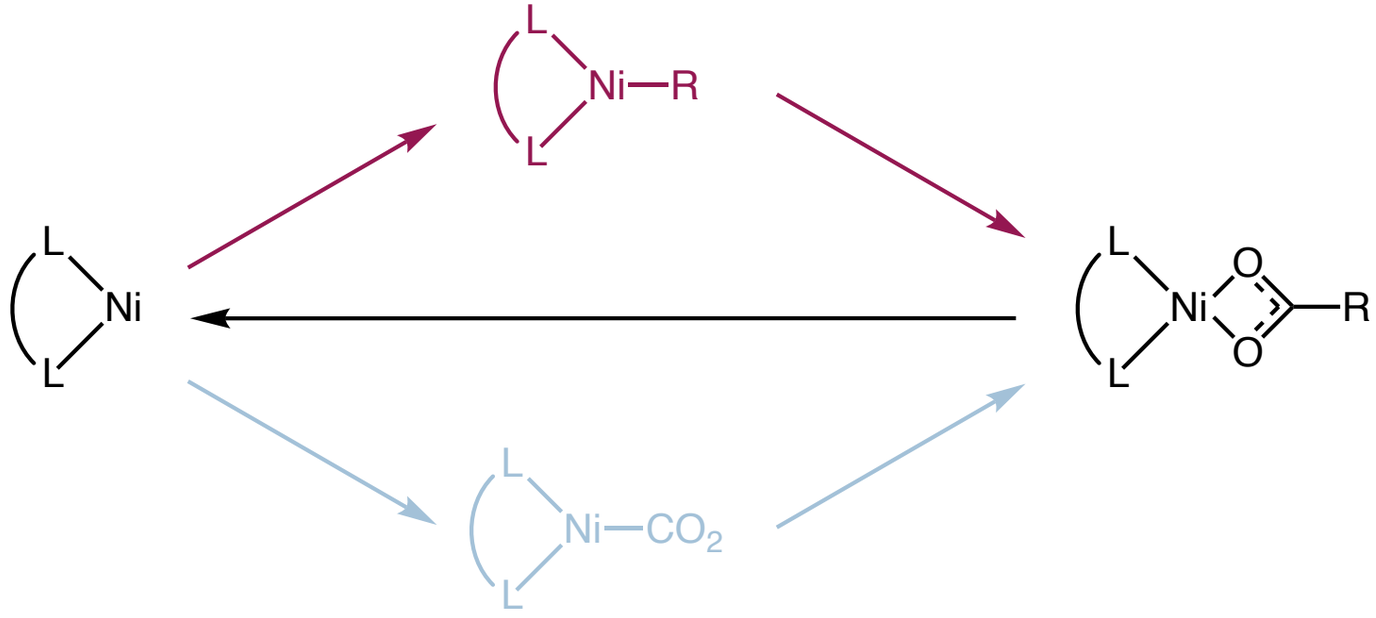
alkyl first pathway



CO_2 first pathway

Carboxylation at Ni(I)

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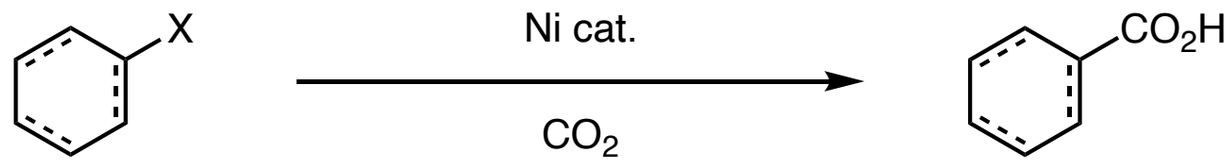

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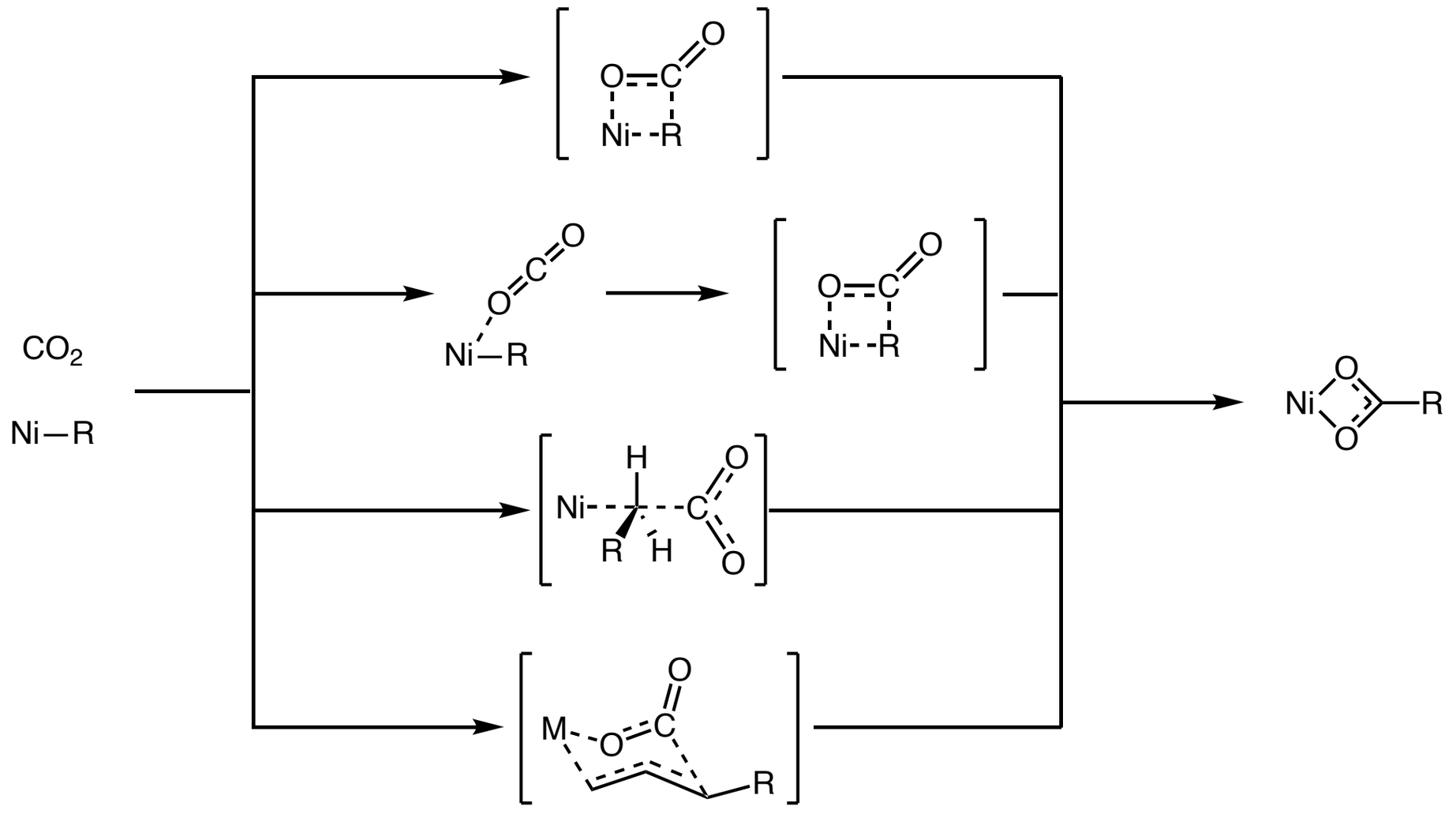
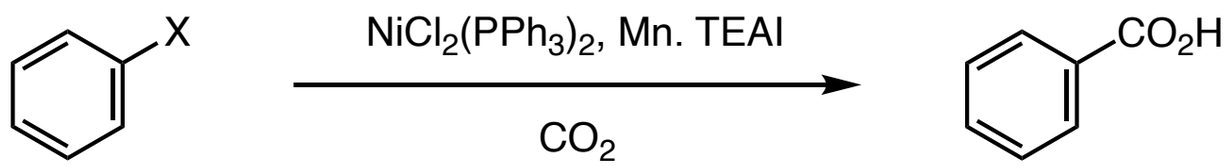
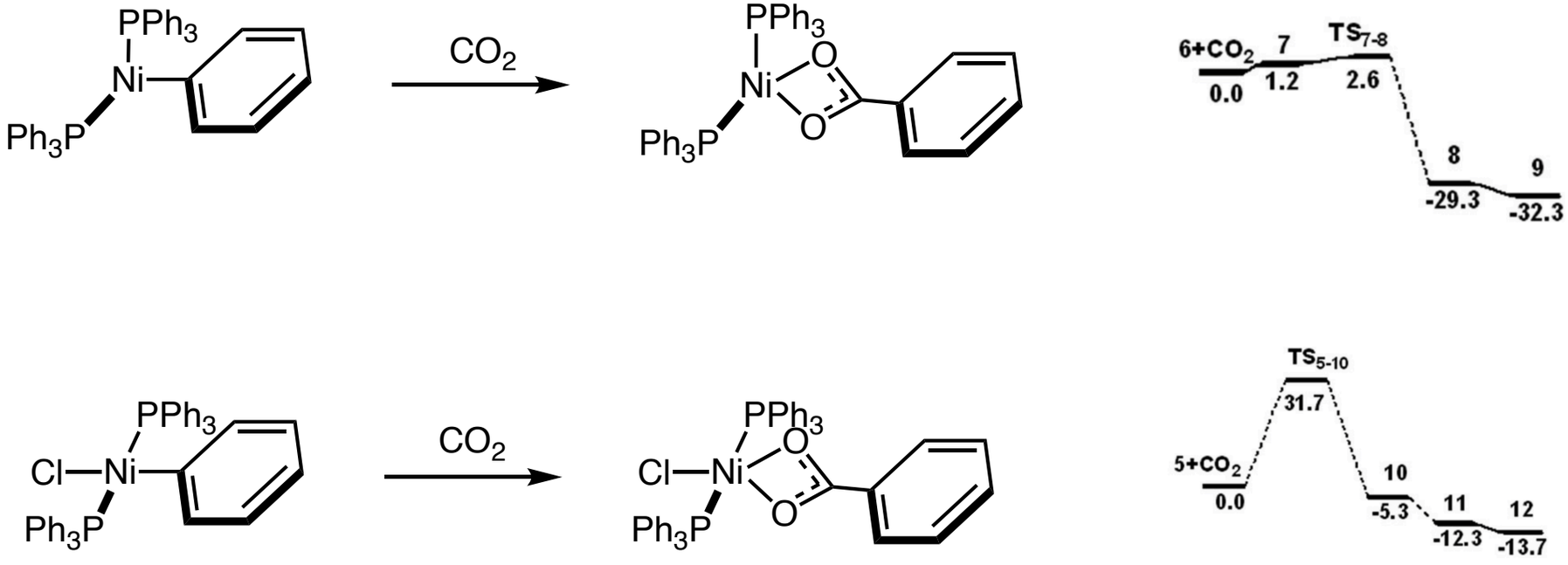


Carboxylation at Ni(I)

- Nickel-catalyzed carboxylation of aryl groups



carboxylation at Ni(I) or Ni(II)?

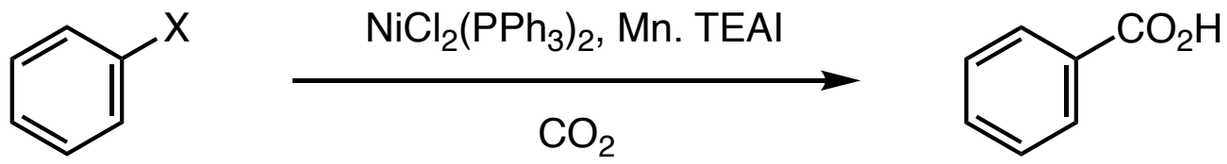


carboxylation at Ni(I) is strongly favored over alternative pathways

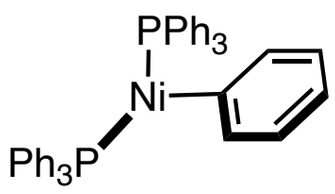
Sayyed, B. S.;Tsuji, Y.; Sakaki, S. *Chem. Comm.* **2013**, 49, 10715.

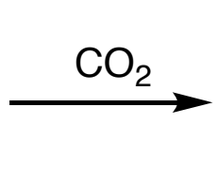
Carboxylation at Ni(I)

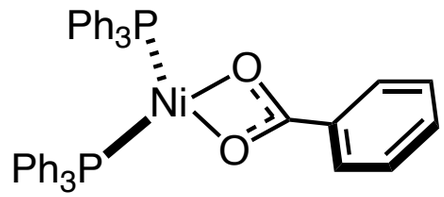
- Nickel-catalyzed carboxylation of aryl groups

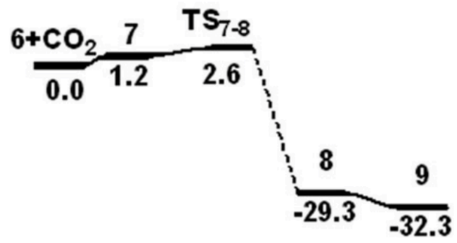


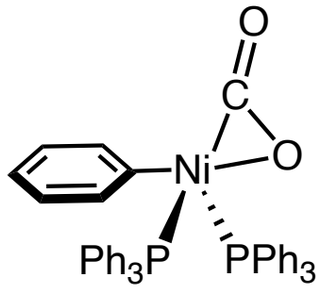
carboxylation at Ni(I) or Ni(II)?



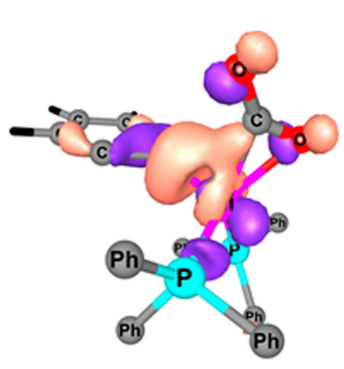


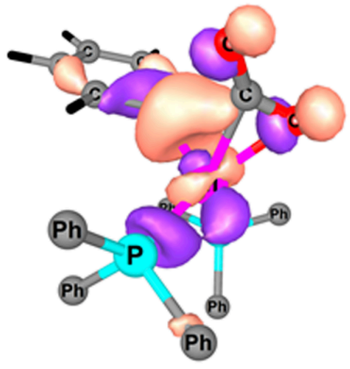


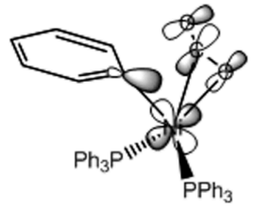


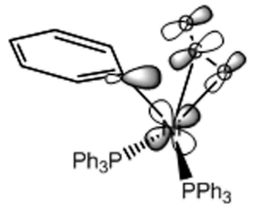


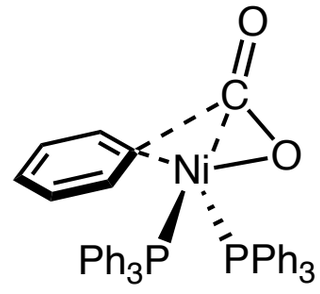
Coordination by η^2—C,O









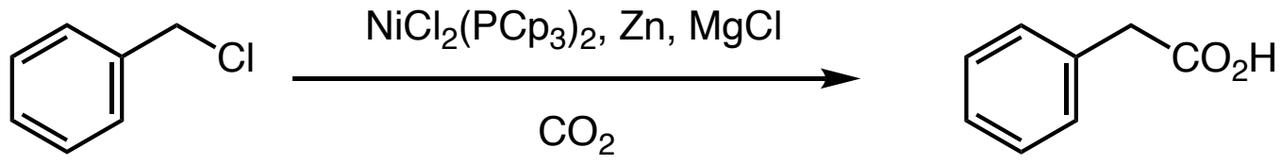


Phenyl to CO_2 charge transfer in TS

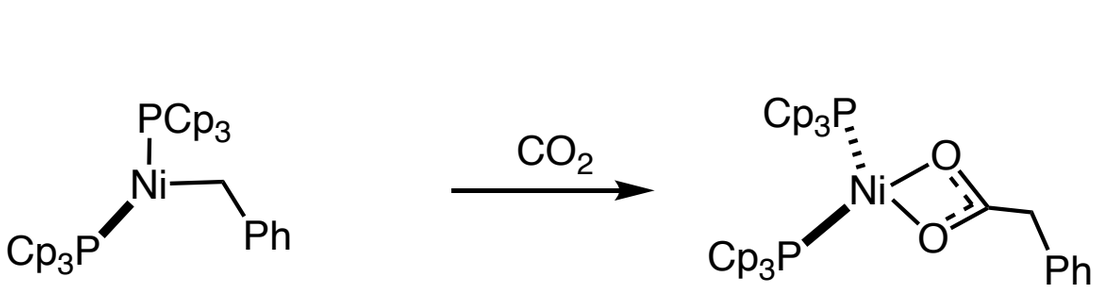
Sayyed, B. S.;Tsuji, Y.; Sakaki, S. *Chem. Comm.* **2013**, 49, 10715.

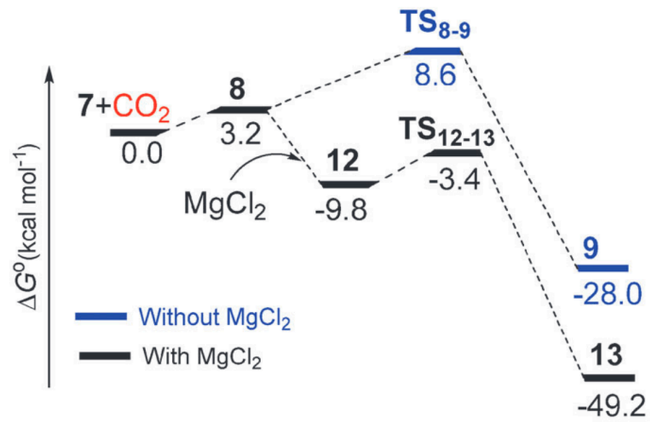
Carboxylation at Ni(I)

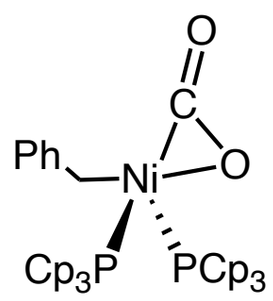
- Nickel-catalyzed carboxylation of benzyl groups



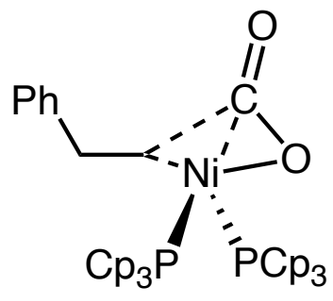
role of $MgCl_2$?



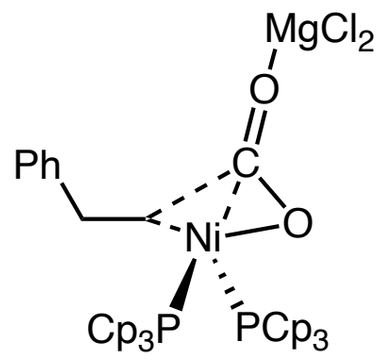




Coordination by η^2—C,O



Same charge transfer in TS observed

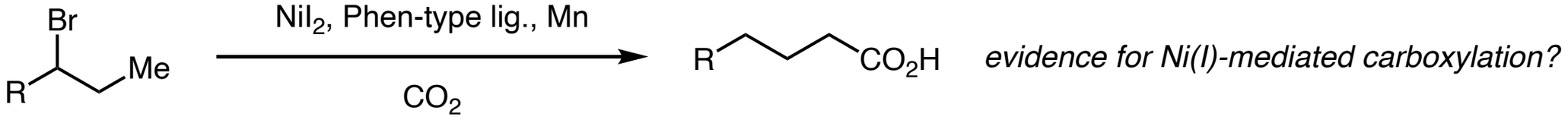


Insertion facilitated by $MgCl_2$

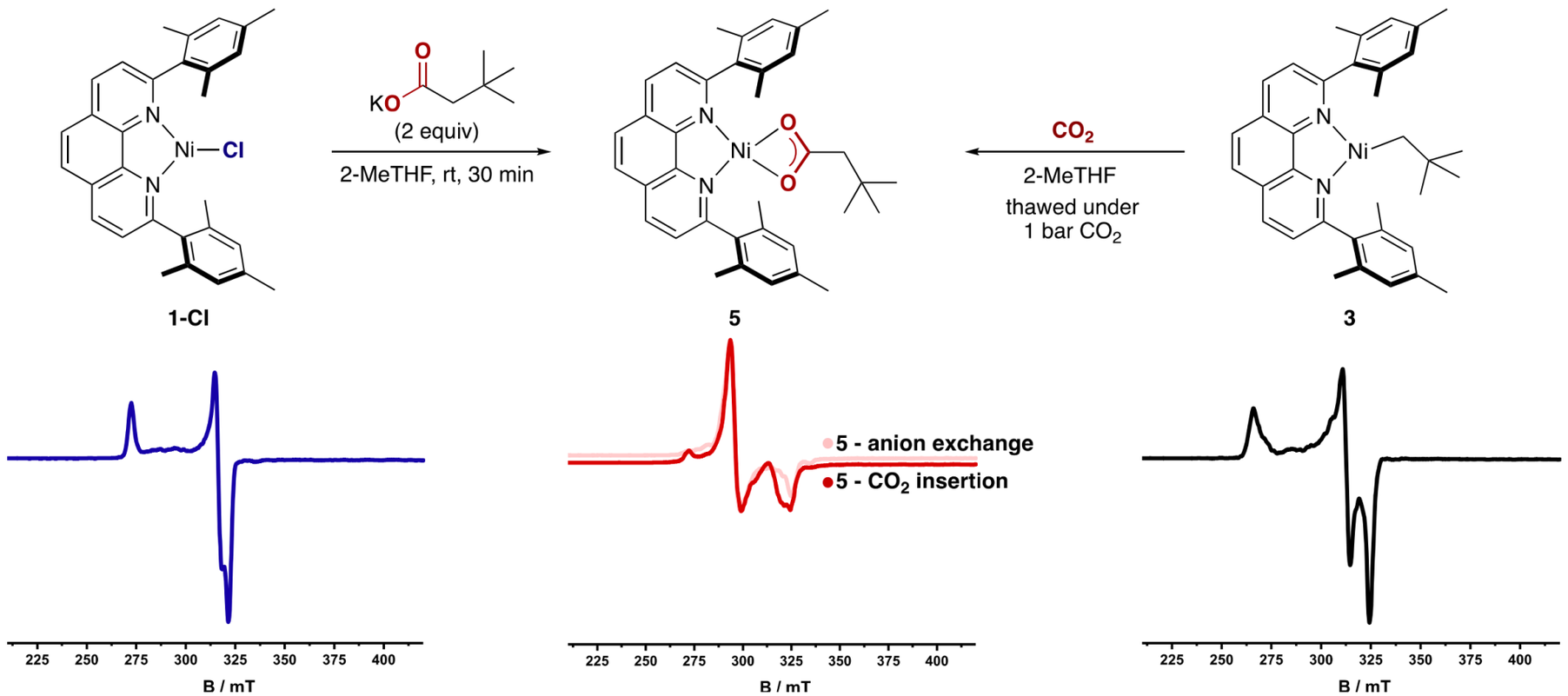
Sayyed, B. S.; Sakaki, S. *Chem. Comm.* **2014**, 50, 13026.

Carboxylation at Ni(I)

- Phen-ligated, Nickel-catalyzed carboxylation of unactivated alkyl groups



evidence for Ni(I)-mediated carboxylation?

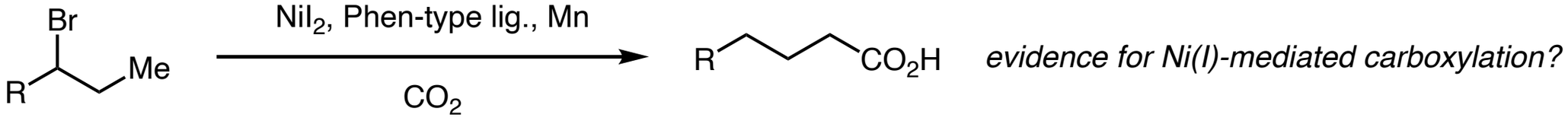


first reported insertion at a catalytically relevant Phen ligand

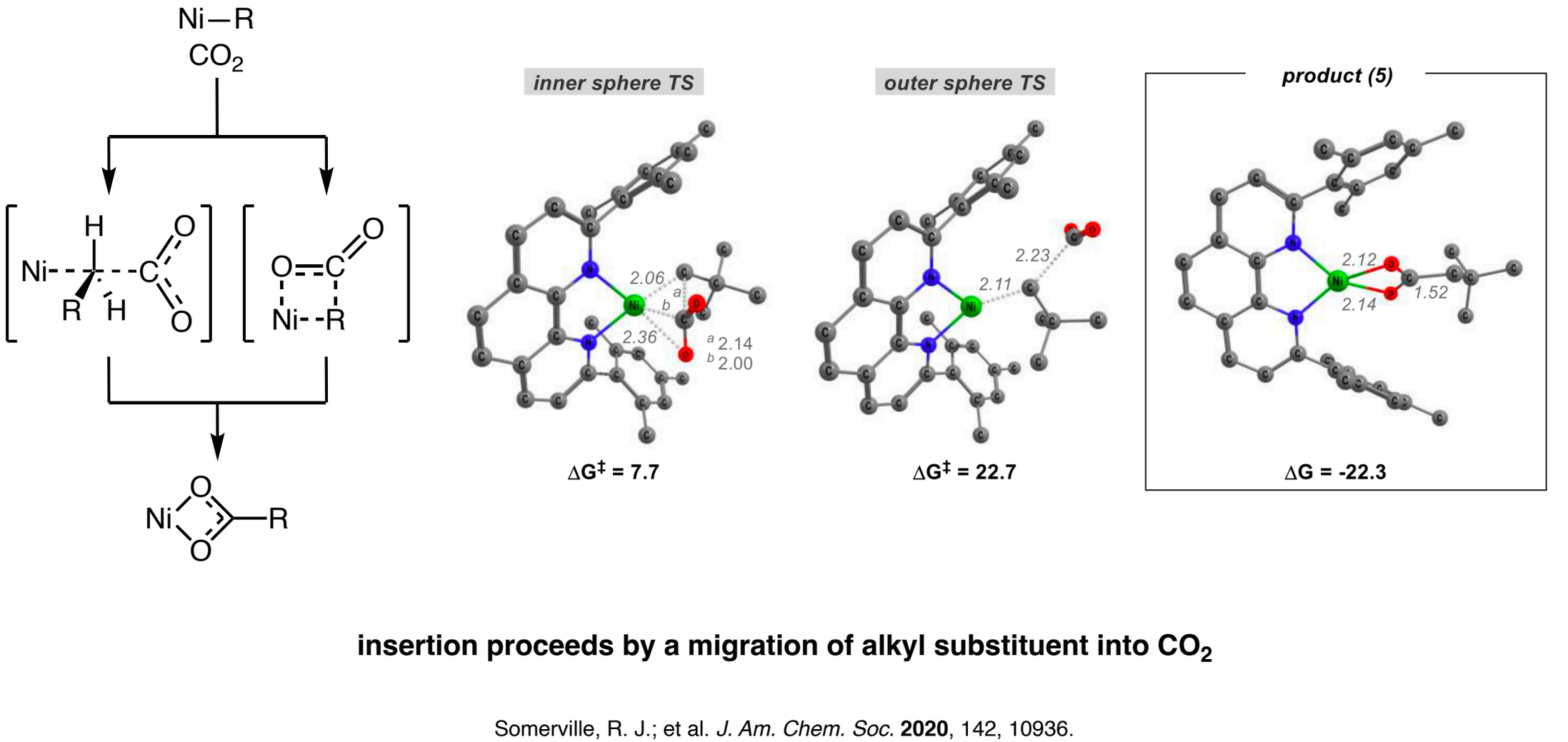
Somerville, R. J.; et al. *J. Am. Chem. Soc.* **2020**, 142, 10936.

Carboxylation at Ni(I)

- Phen-ligated, Nickel-catalyzed carboxylation of unactivated alkyl groups



evidence for Ni(I)-mediated carboxylation?

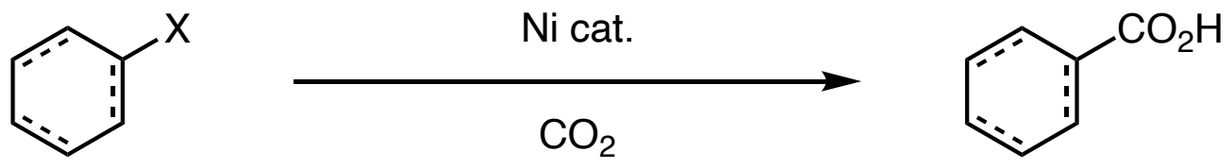


insertion proceeds by a migration of alkyl substituent into CO_2

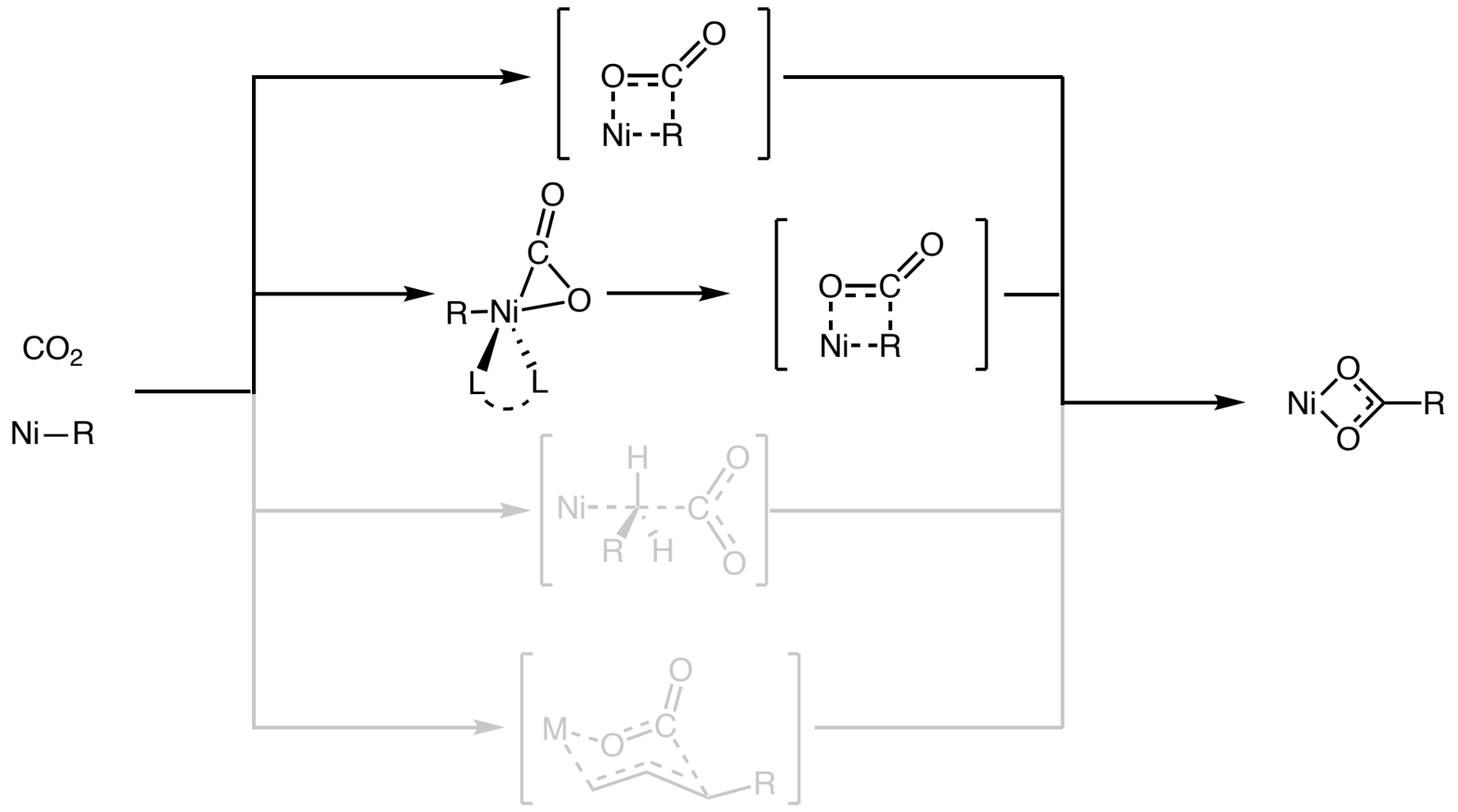
Somerville, R. J.; et al. *J. Am. Chem. Soc.* **2020**, 142, 10936.

Carboxylation at Ni(I)

- Nickel-catalyzed carboxylation reactions



carboxylation often proposed at Ni(I)

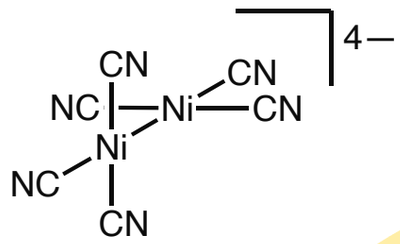


migratory insertion into η^2—C,O ligated Ni is probably your best bet

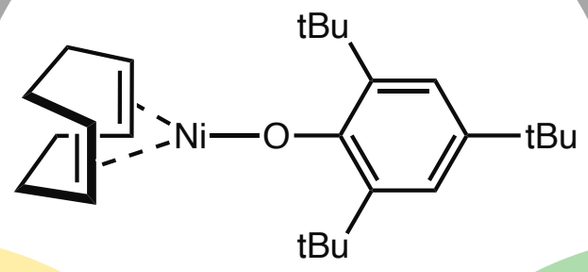
Mechanistic Rules of Thumb

C(sp_3)—X Oxidative Addition	Ligand-centered radical: Inner sphere electron transfer Metal-centered radical: Halogen Atom Abstraction
C(sp_2)—X Oxidative Addition	Inner sphere electron transfer with in-cage collapse Concerted Oxidative Addition
Carboxylation	Migratory Insertion of Alkyl/Aryl into nickel-bound CO_2

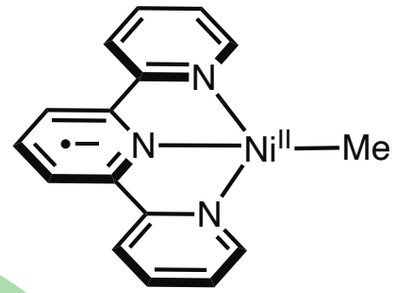
Historical Aspects of Ni(I) Complexes



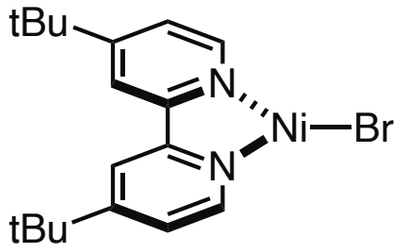
Preparation and Properties of Ni(I) Complexes



Oxidative Addition to C(sp₃)—X



Oxidative Addition to C(sp₂)—X



Carboxylations with CO_2