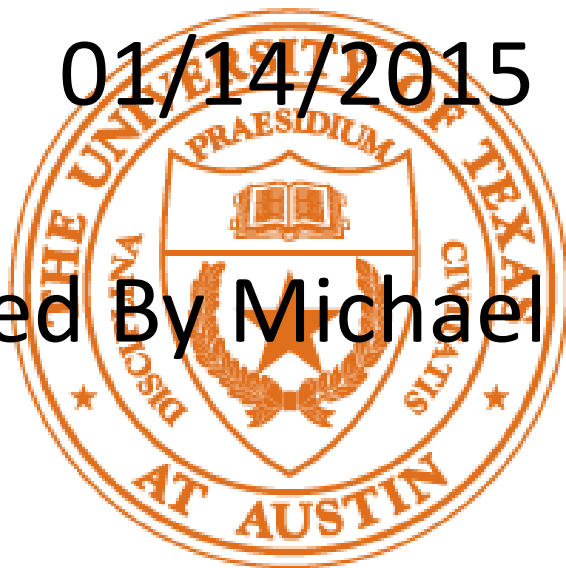


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# Low Valent, Low Coordinate Complexes Using Bulky Ligands

01/14/2015

Presented By Michael C. Young



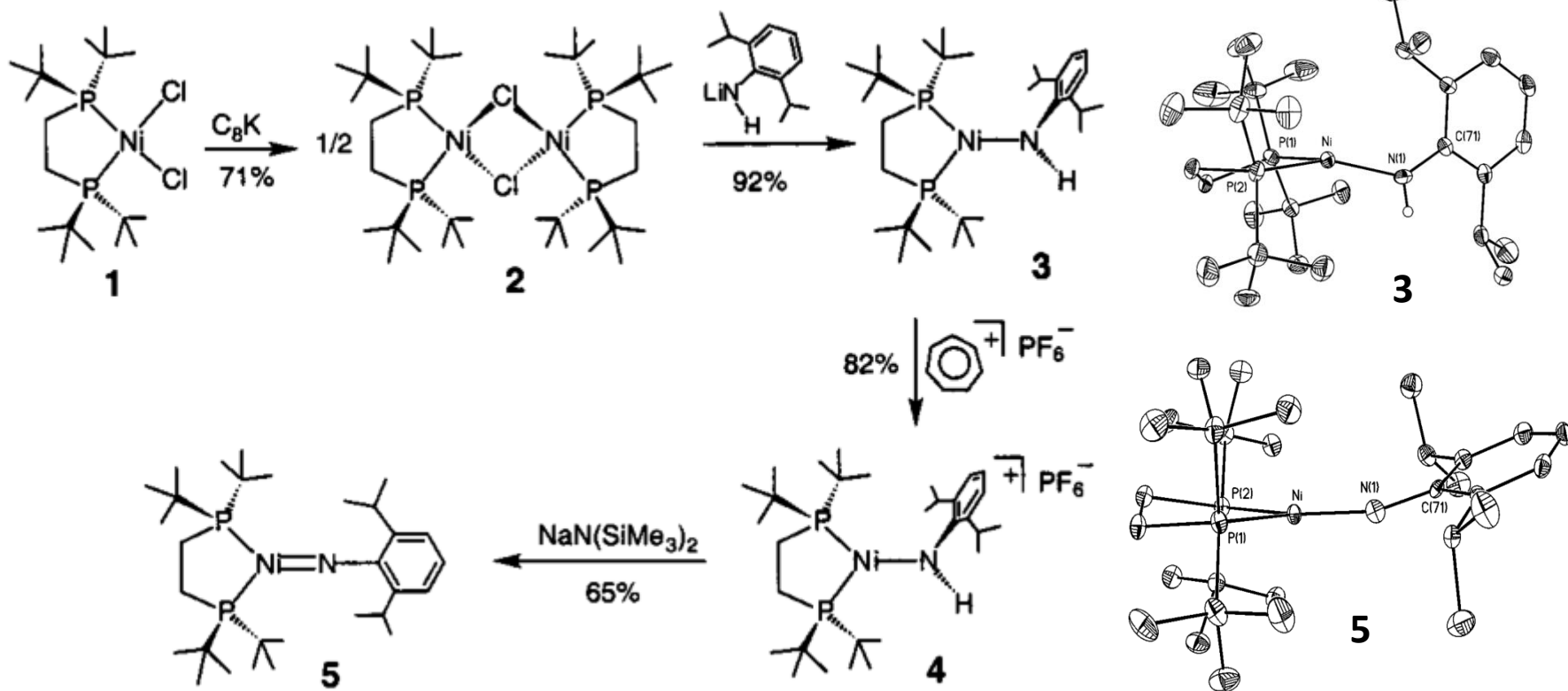
# Topics



- Two and three coordinate low valent complexes of Ni
  - Work by the Hillhouse Group
  
- Bulky m-terphenyl isonitrile ligands for low coordinate transition metal complexes
  - Work by the Figueroa Group
  
- Low coordinate complexes of Fe and Co
  - Work by the Betley Group

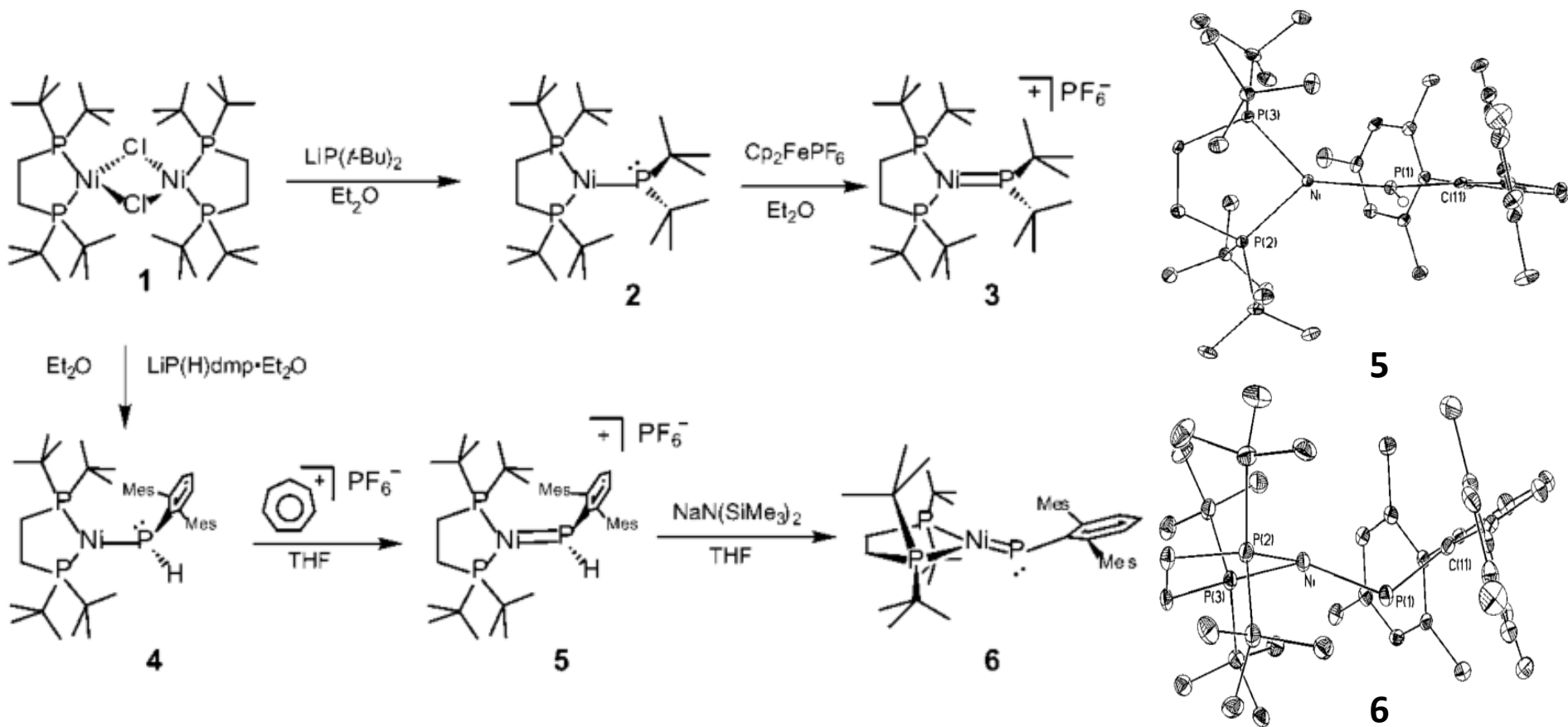
# Monomeric Terminal Ni(II)-Imido

- Impetus: At the time there was a dearth of examples of nickel complexes with hard imido ligands.
- To prevent dimerization, it was desirable to use both a bulky phosphine ligand as well as a bulky nitrogen.



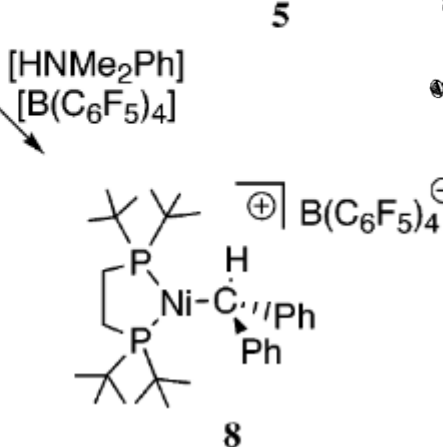
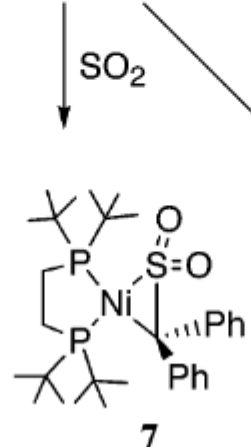
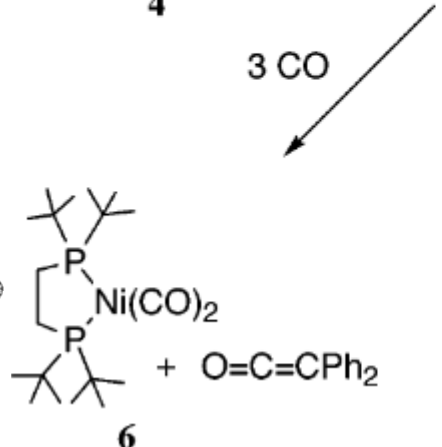
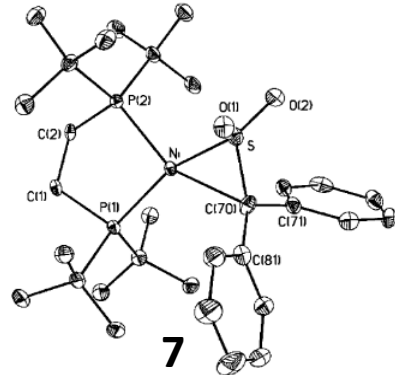
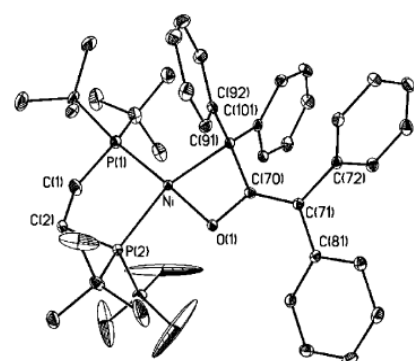
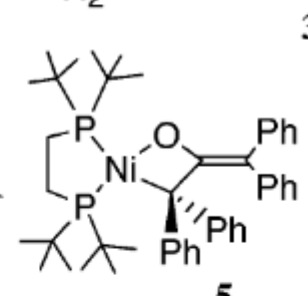
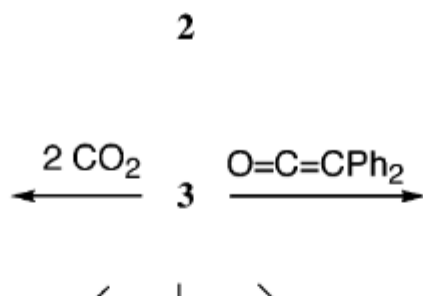
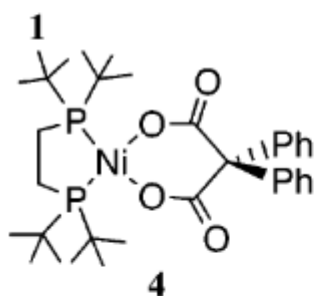
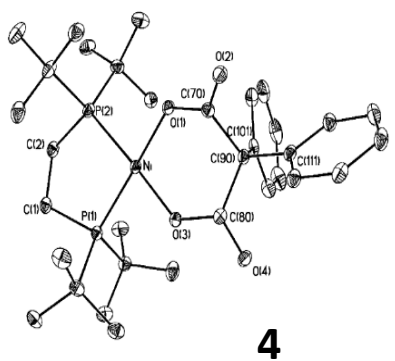
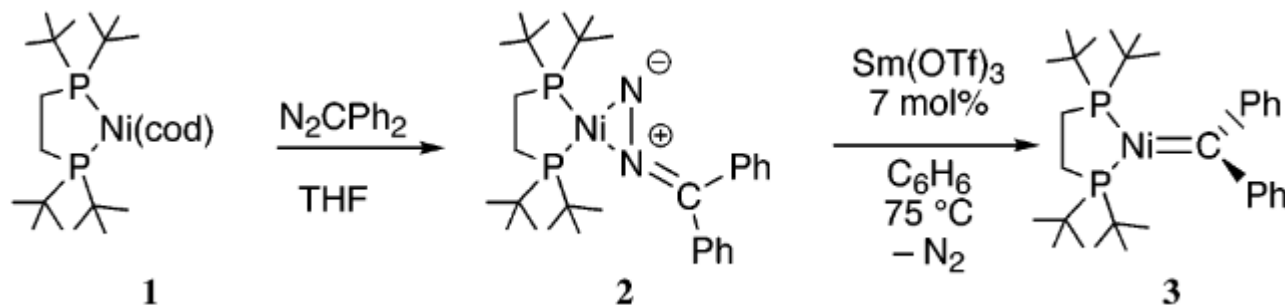
# Monomeric Ni(II)-Phosphinidene

Similarly, there was no good example of a phosphinidene complex, and the imido synthesis suggested the analogous phosphinidene should be easily obtained.



# Ni(II)-Carbene and Reactions

Although Ni(II)-diazo complexes were known, it should be possible to extrude nitrogen to give a carbene.

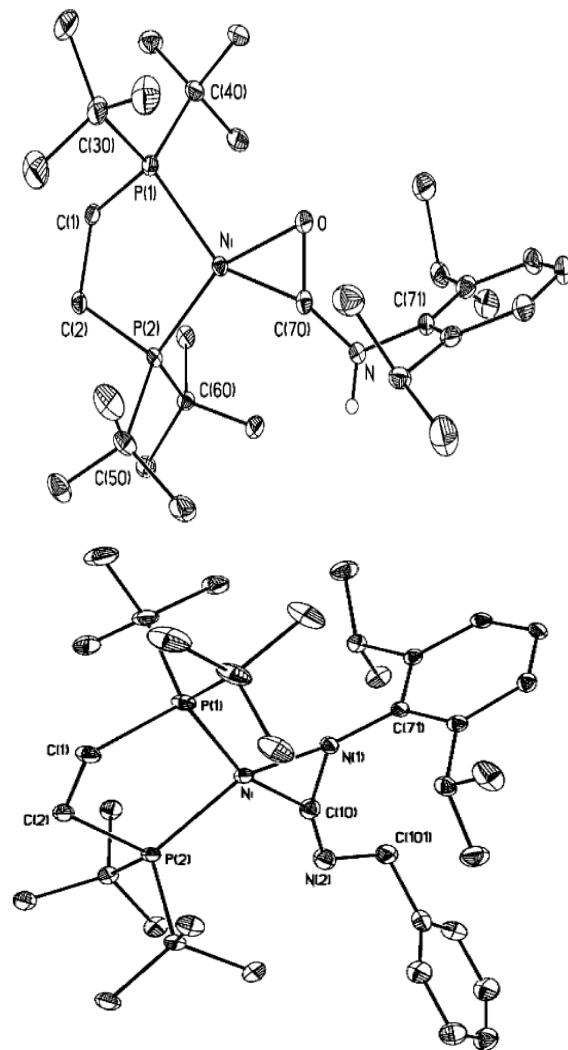
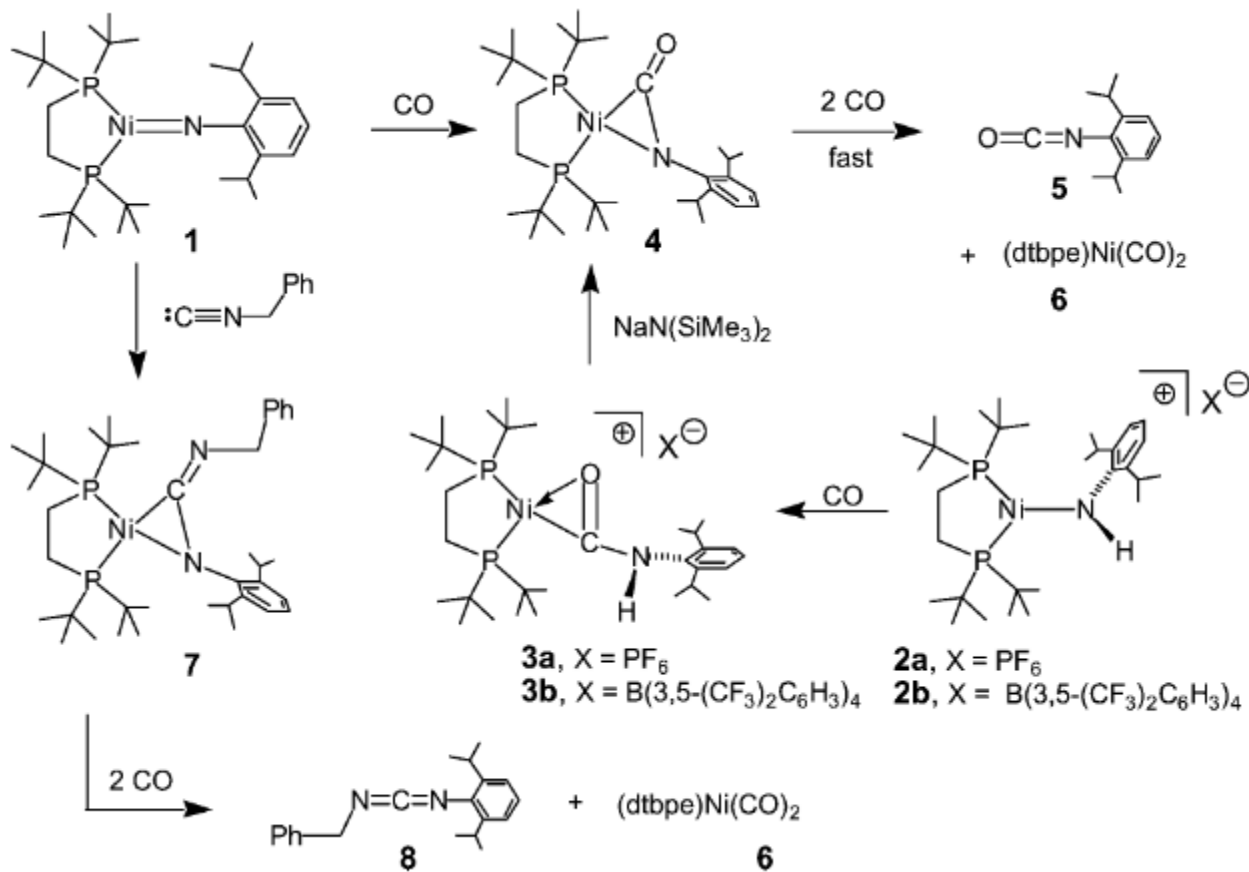


**5**

# Ni(II)-Imido Transfer Reactions

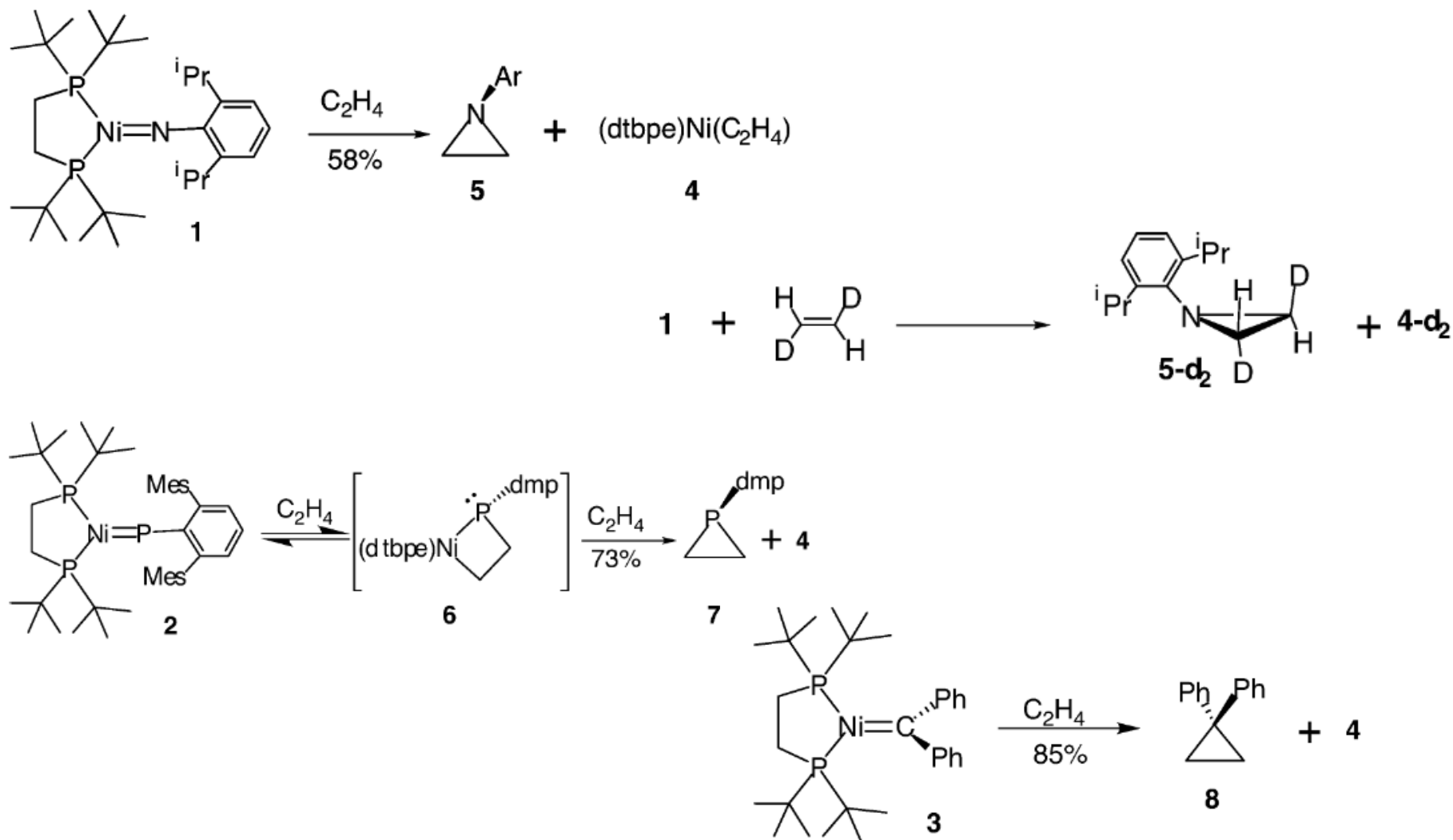


The formed imidos can be used for nitrene transfer reactions.

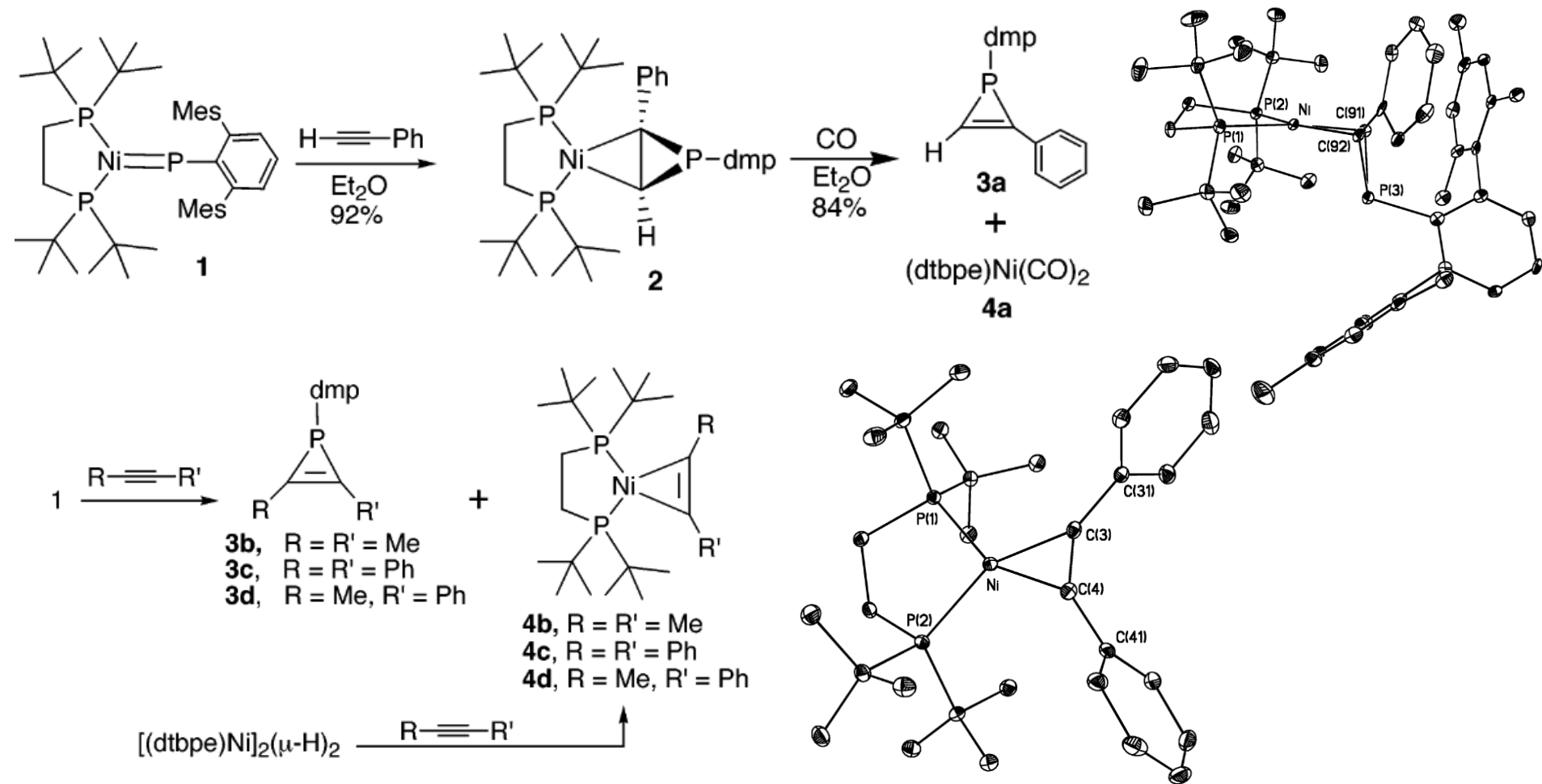


# Ni(II)=X Group Transfer with C<sub>2</sub>H<sub>4</sub>

All of the Ni(II)=X species thus far discussed can react with olefins



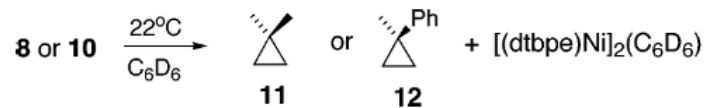
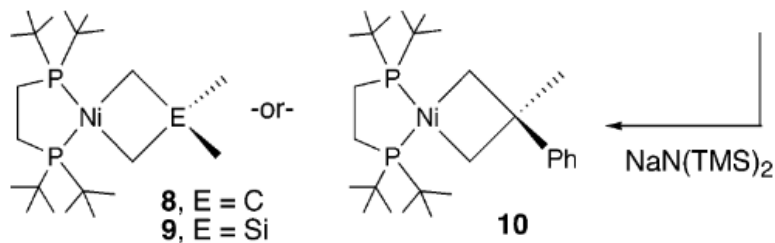
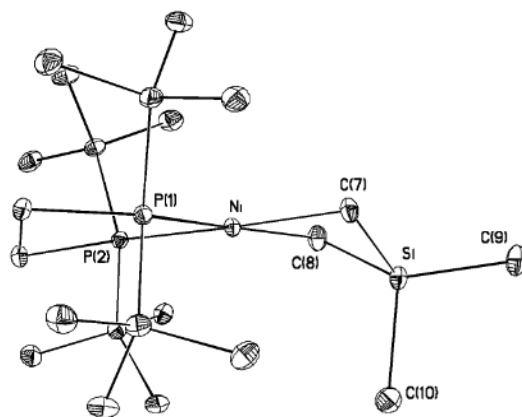
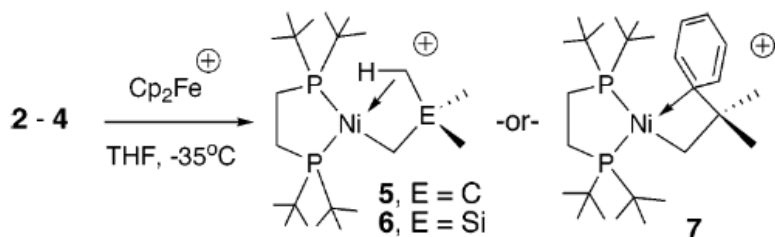
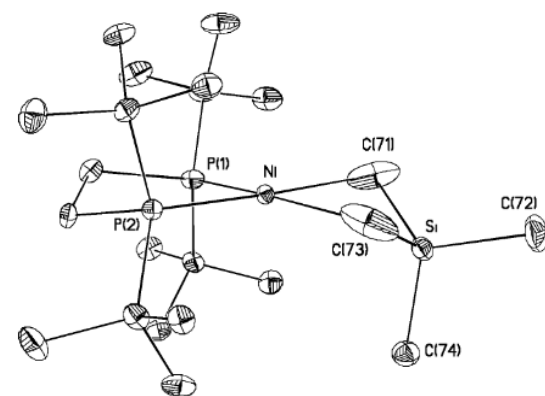
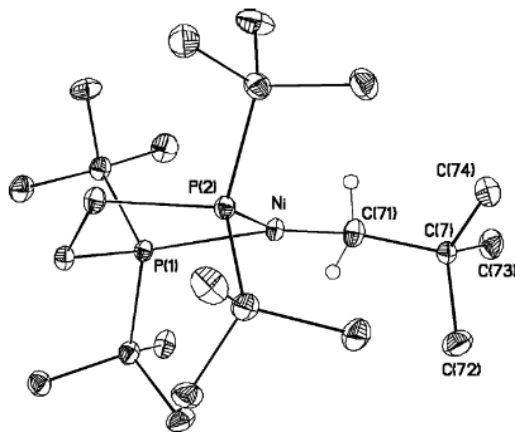
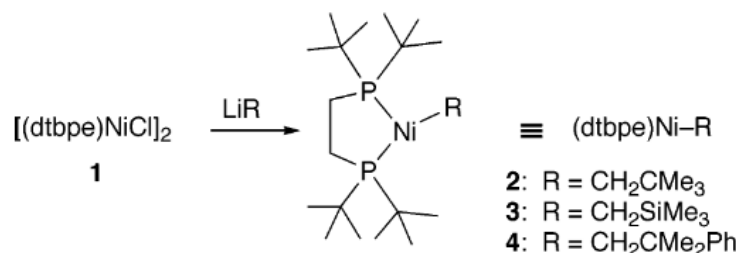
# Ni(II)=P Transfer with Alkynes





# Unsaturated Ni(I) vs Ni(II)-C Species

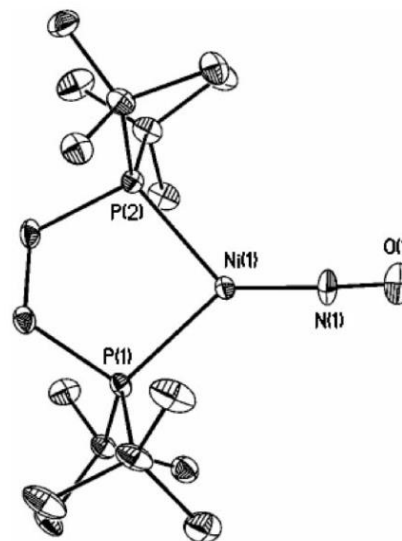
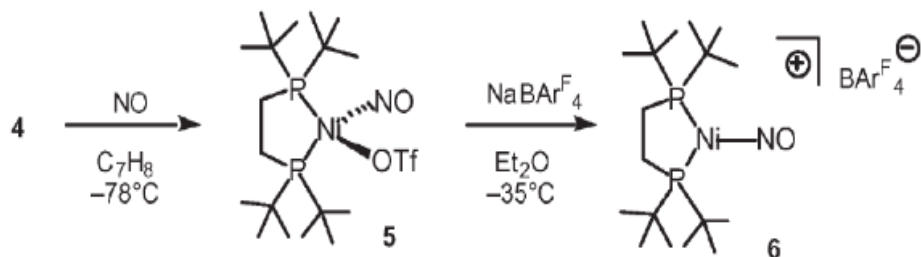
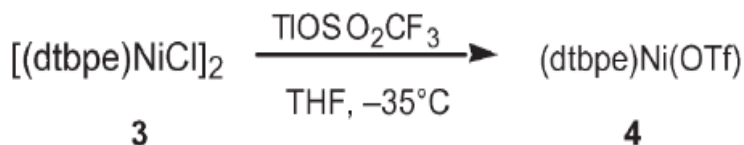
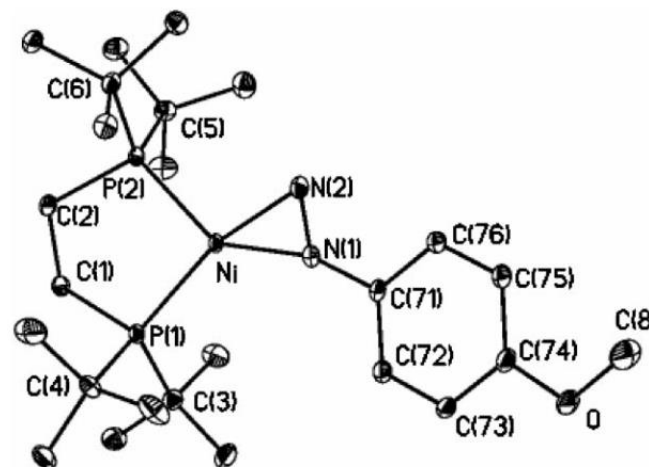
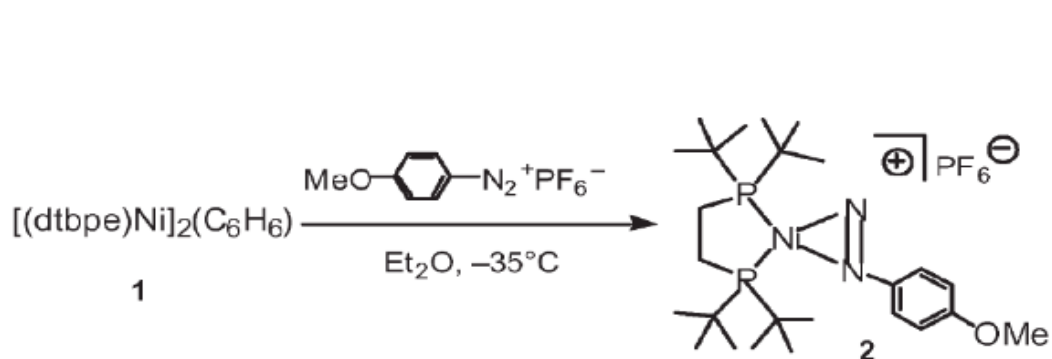
Organolithiums can also be added to Ni(I) to give monoalkyls



# Ni(0) Coordination of N<sub>2</sub> and NO

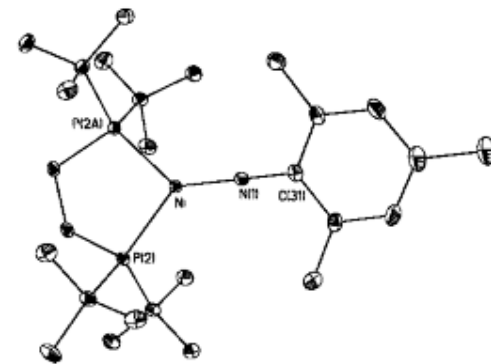
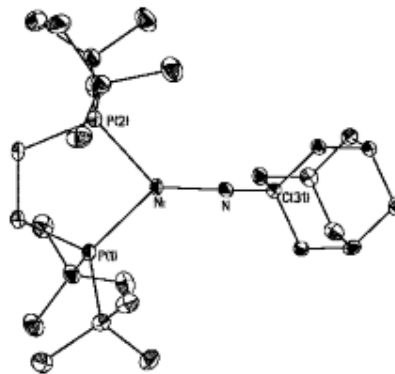
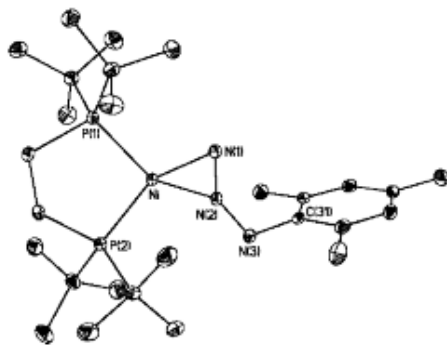
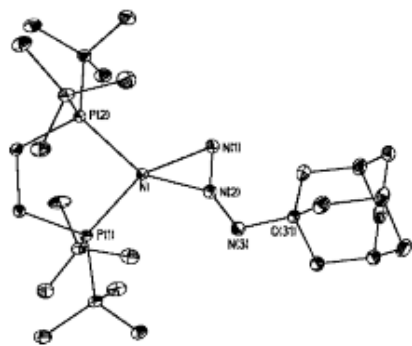
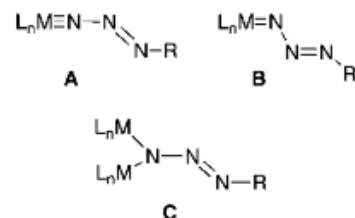
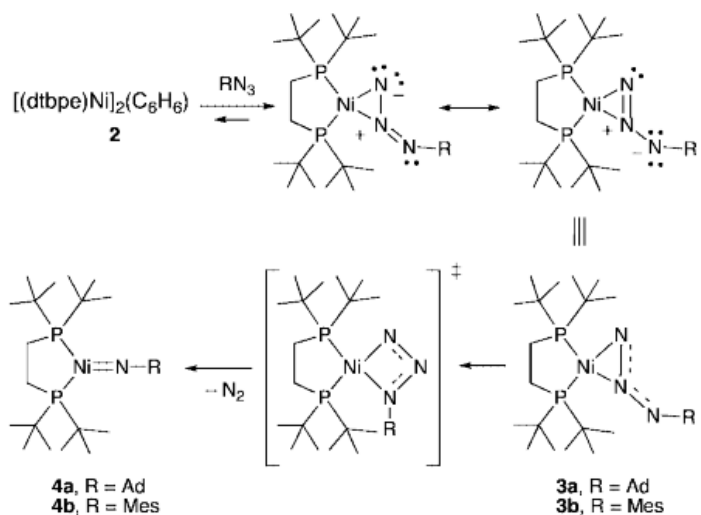


• N<sub>2</sub> binds in a side-on fashion at low temperature

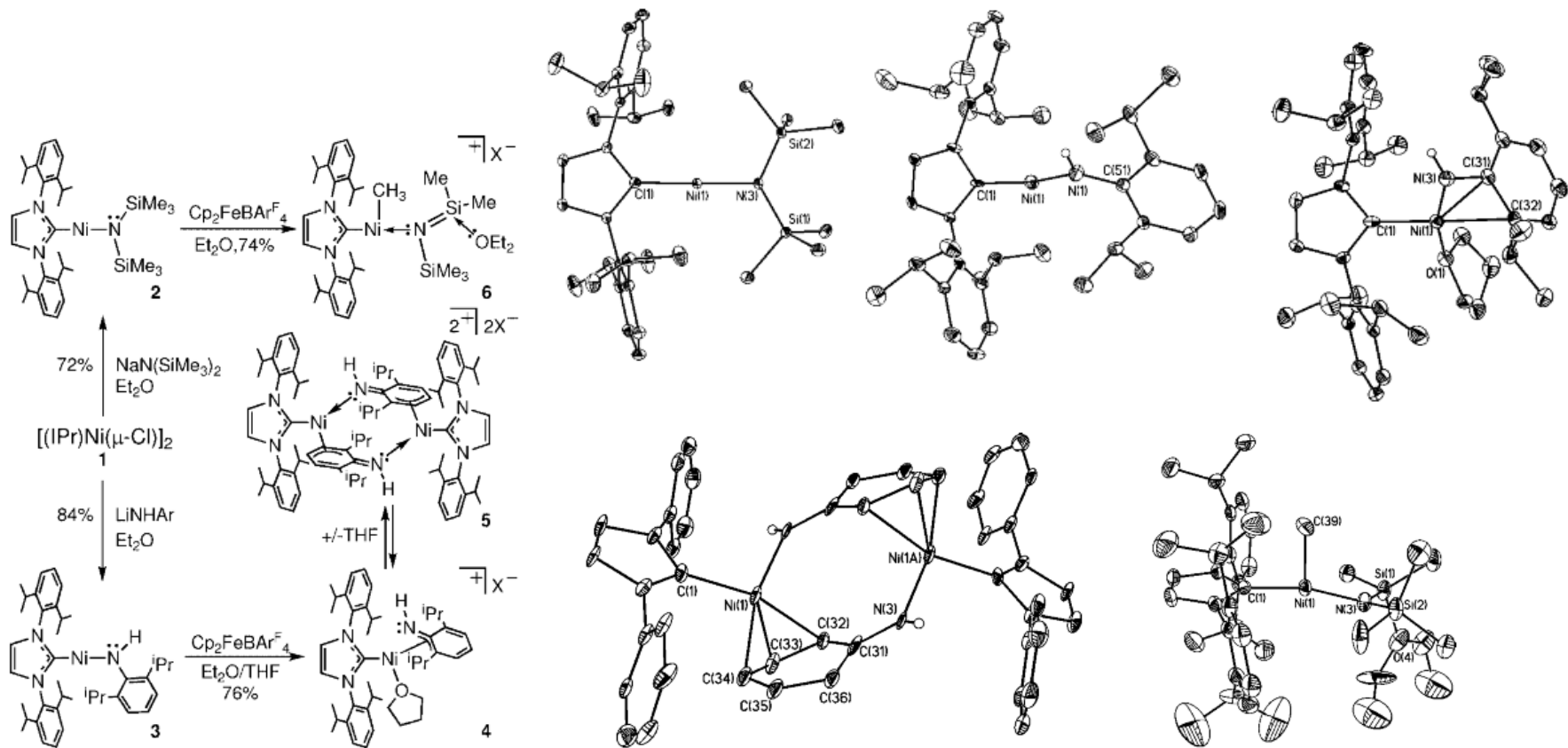


# Ni(0) Coordination of N3

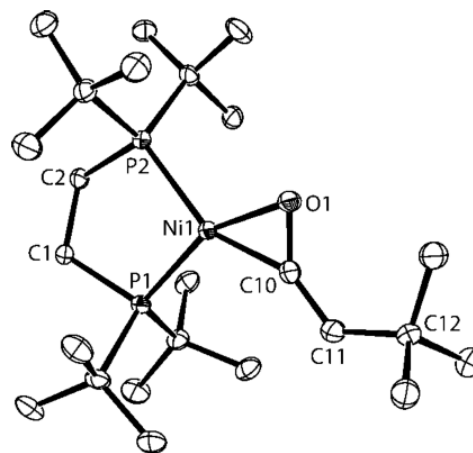
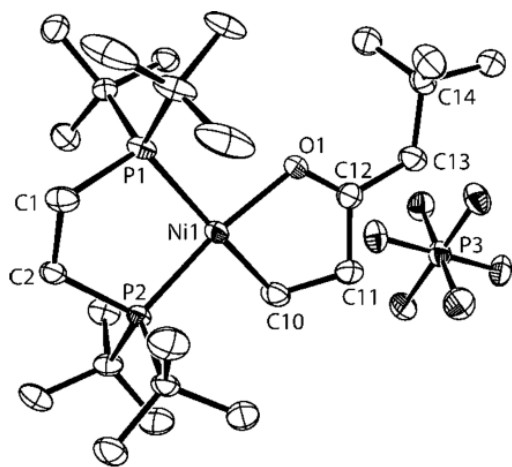
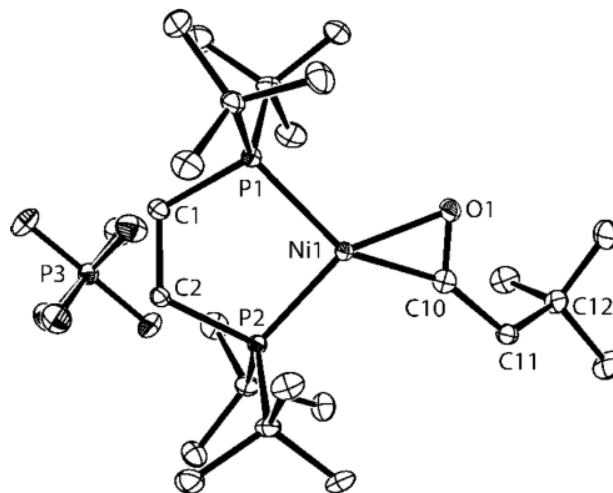
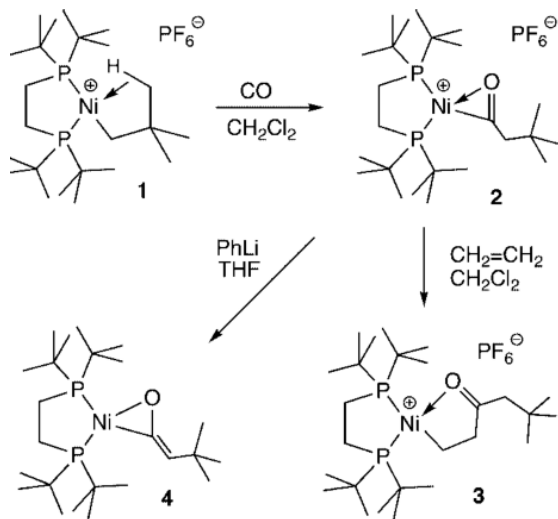
Unsurprisingly, azides can also form stable adducts with this complex.



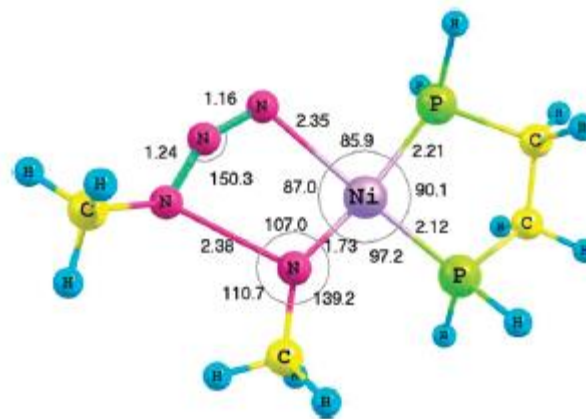
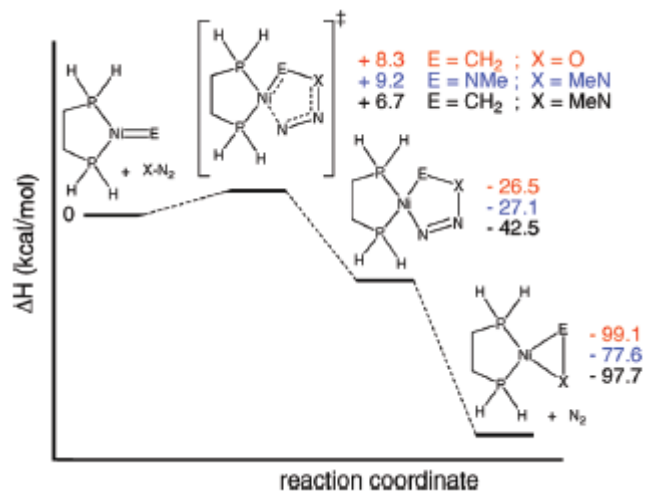
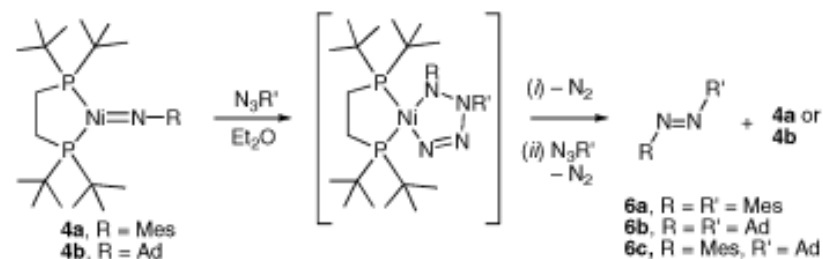
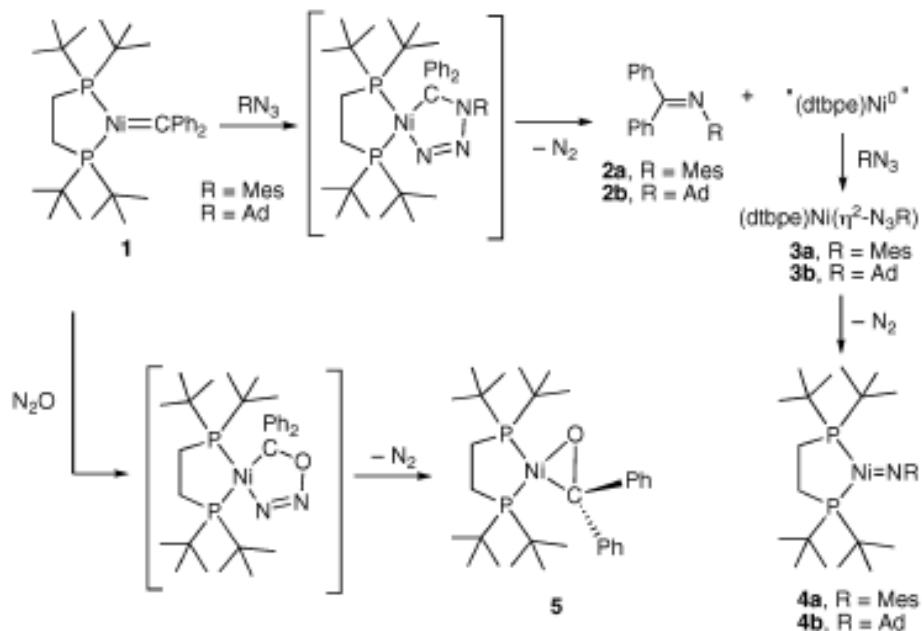
# Dicoordinate Ni(I) and Reactions



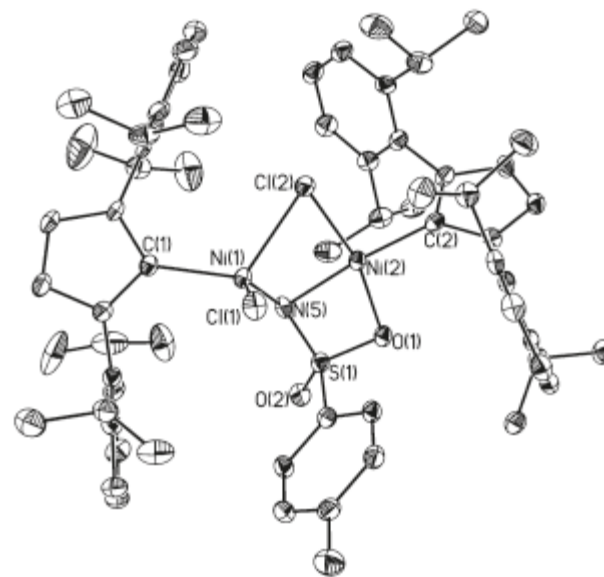
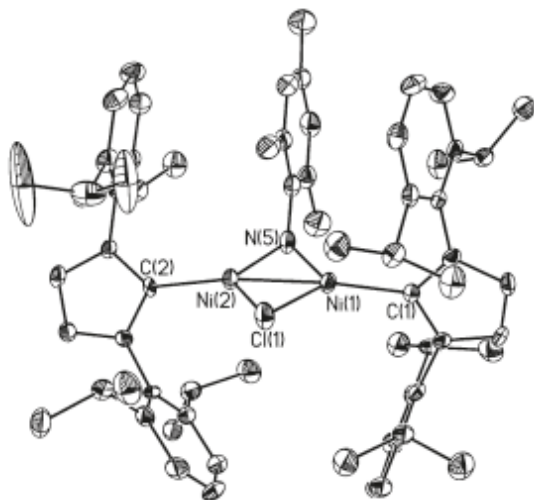
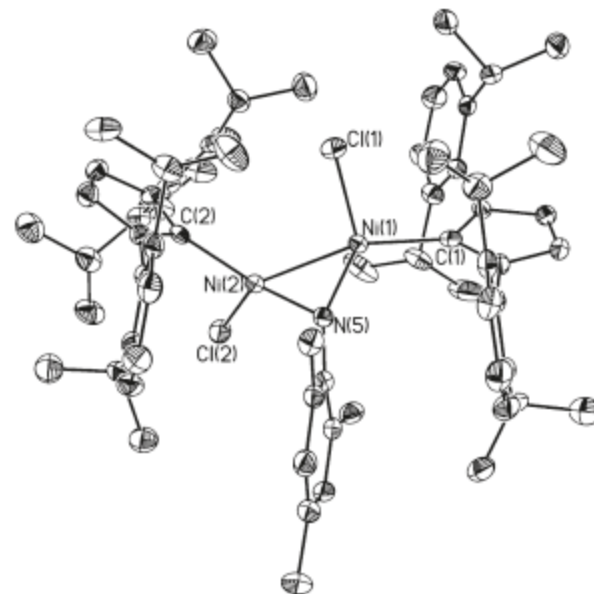
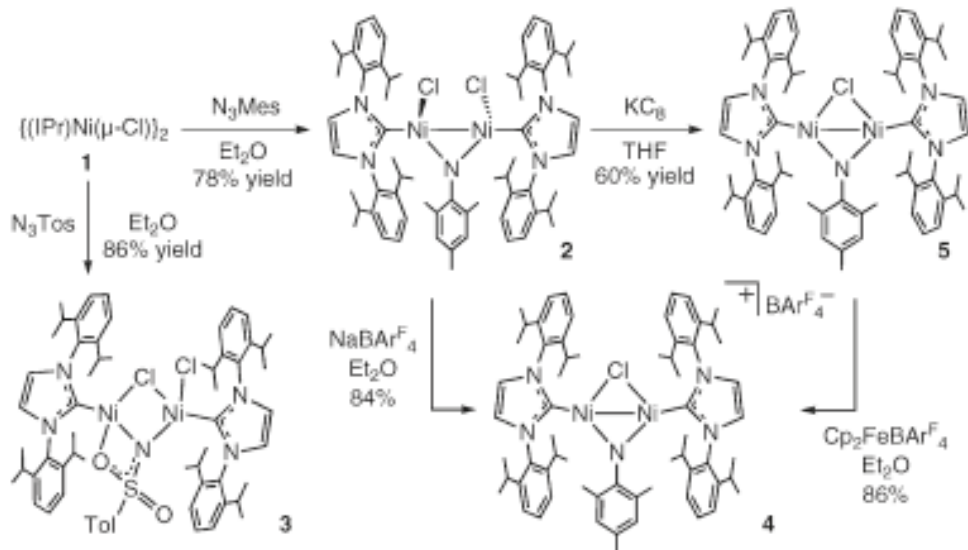
# Insertion into Ni(II)-Alkyl Bonds



# Ni-Carbene Transfer

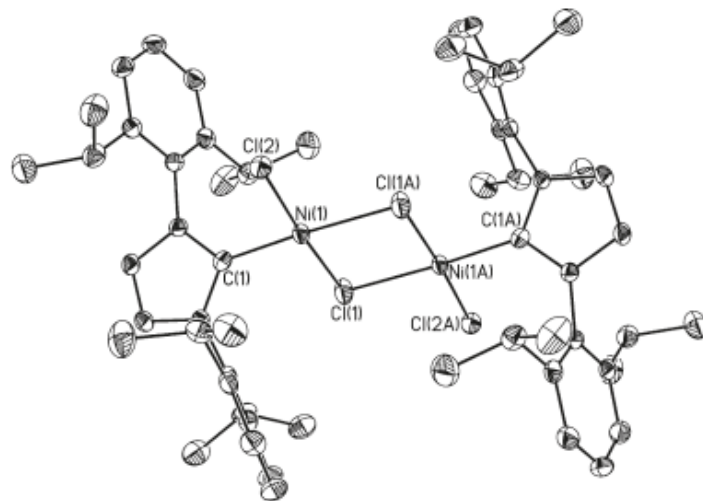
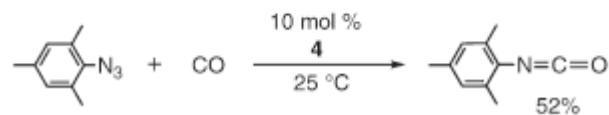
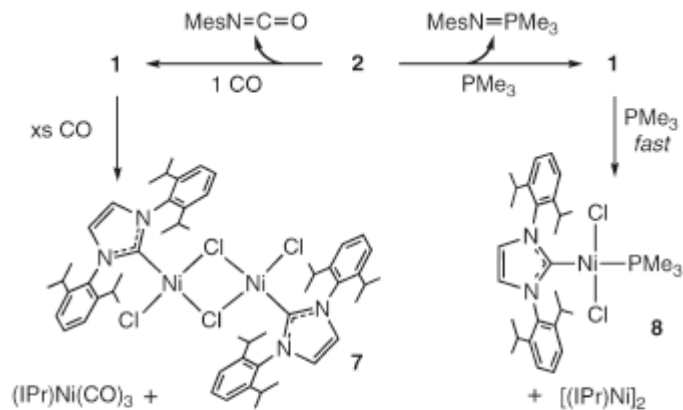
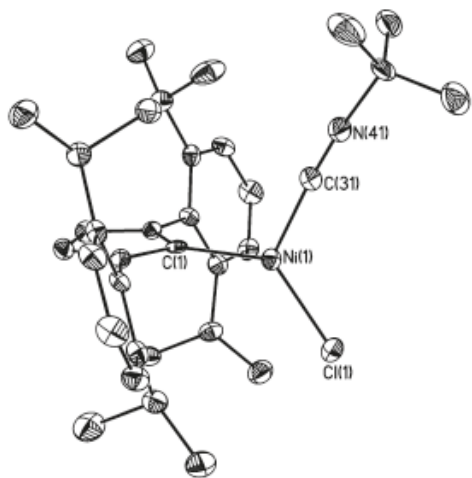
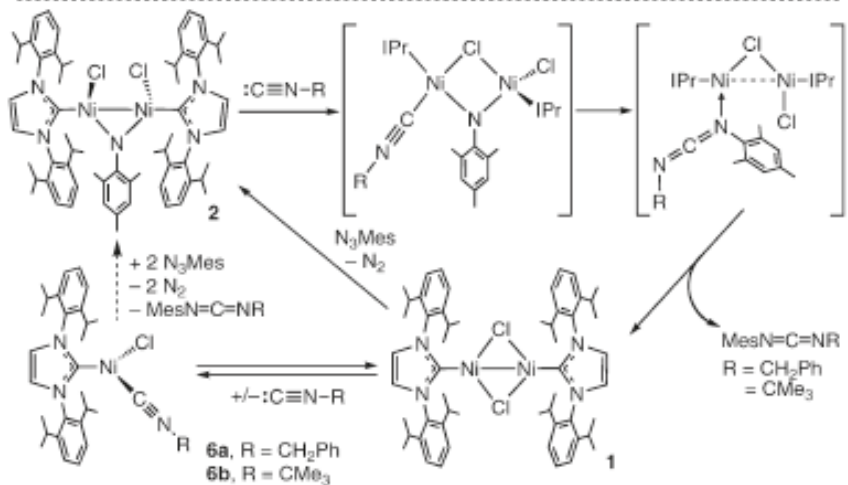
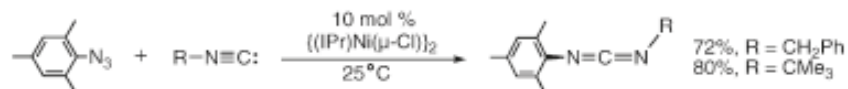


# Catalytic Route to Diimides



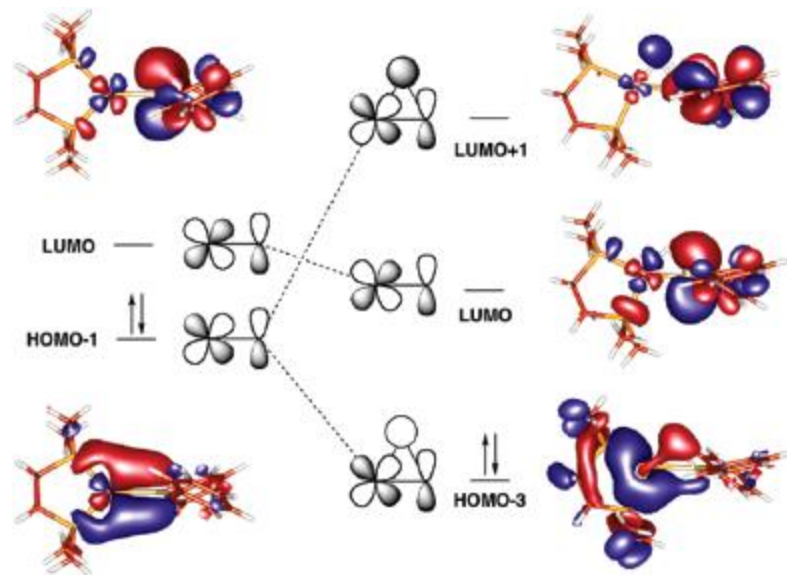
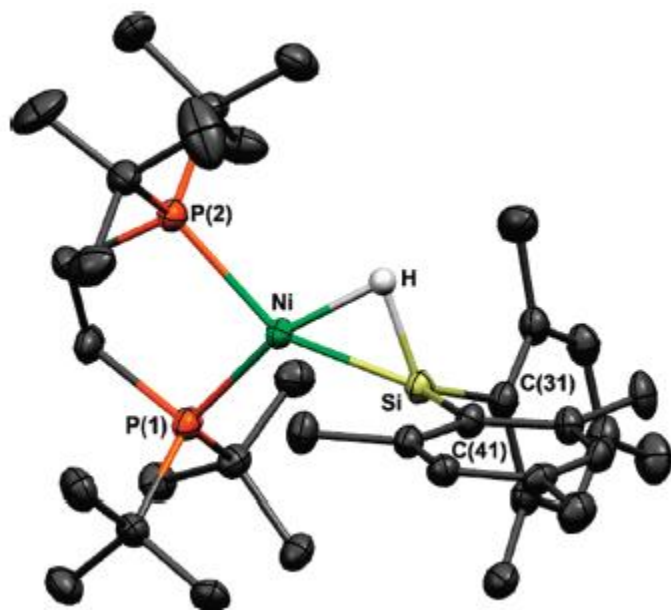
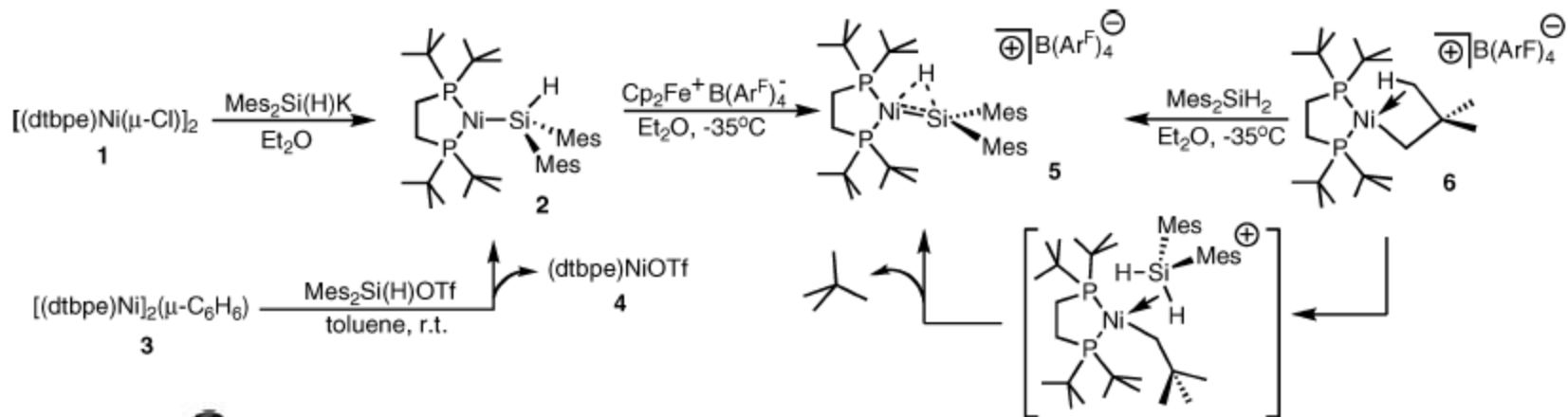


# Catalytic Route to Diimides

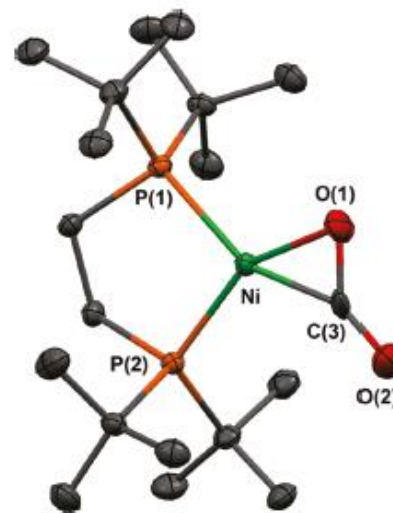
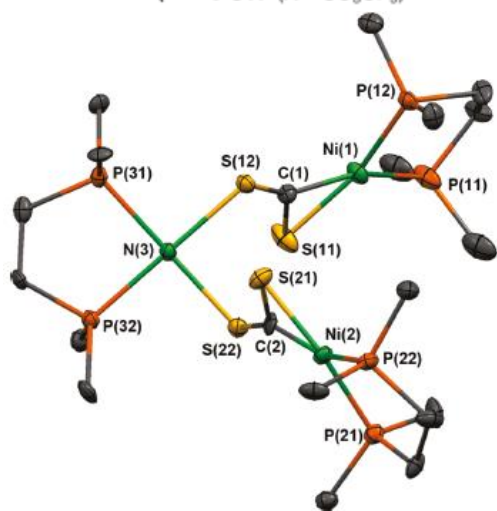
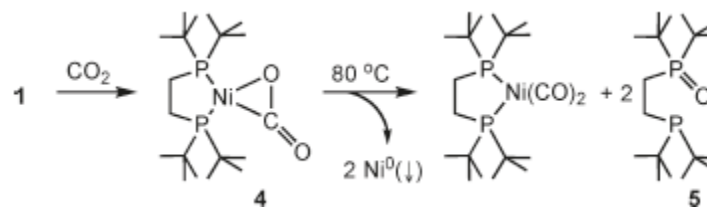
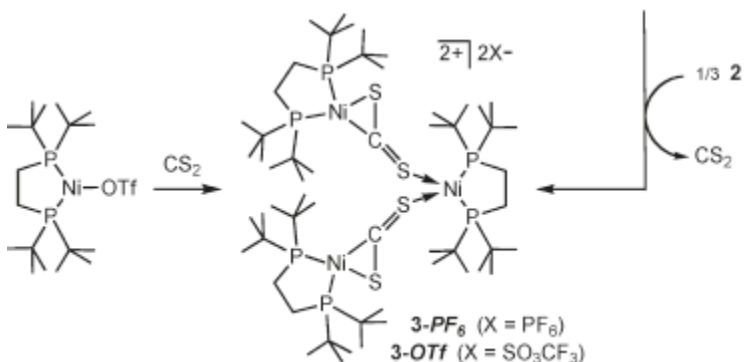
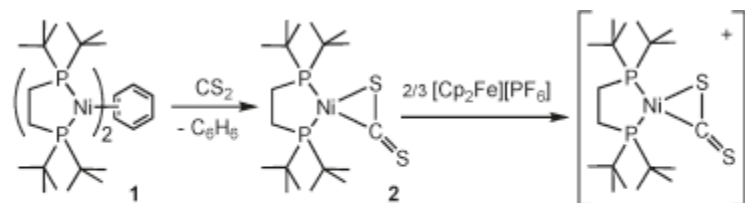




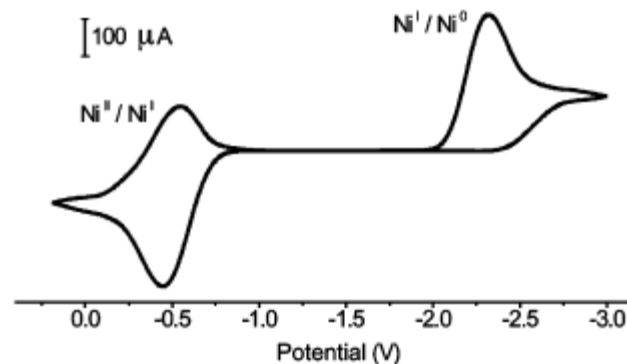
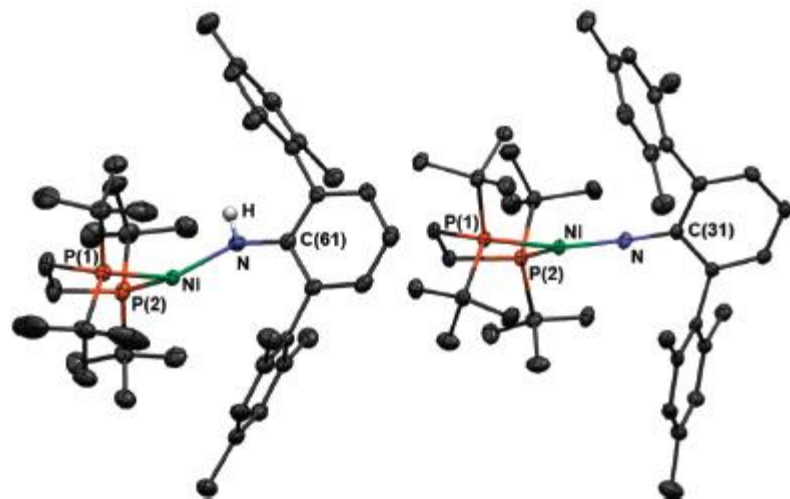
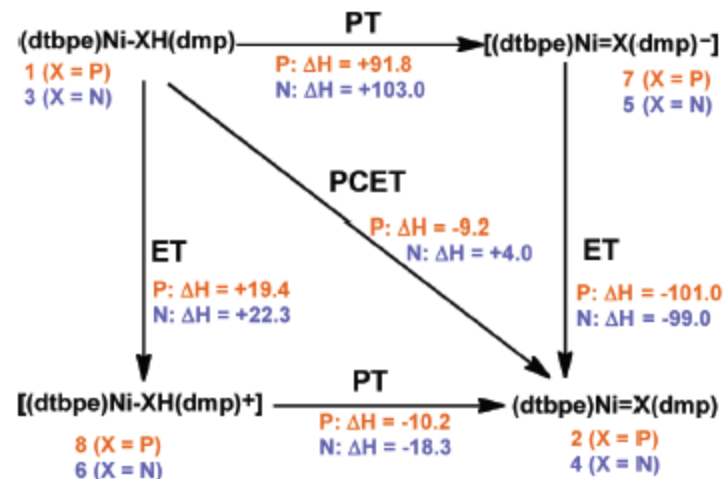
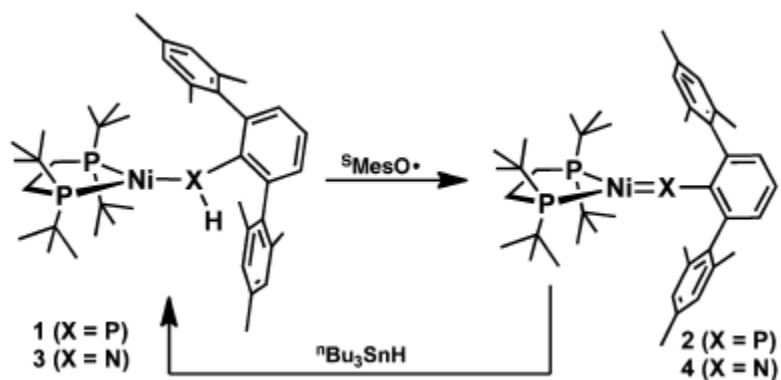
# Towards a Ni(II)-Silylene Complex



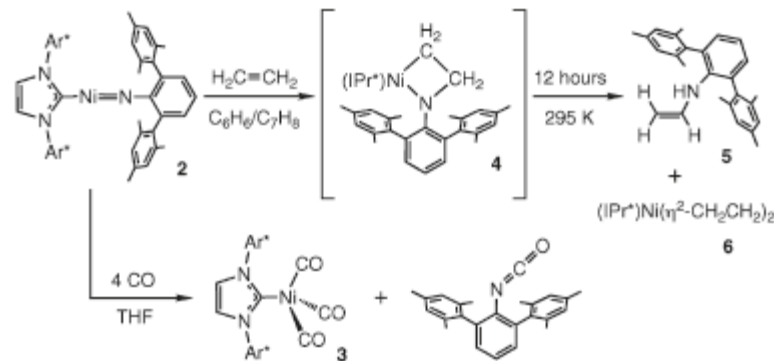
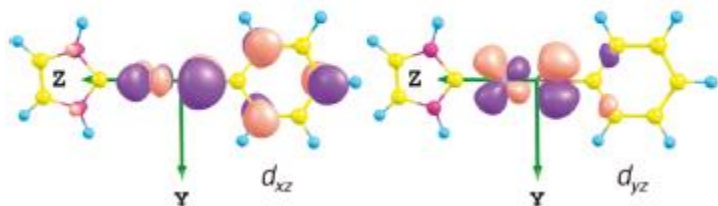
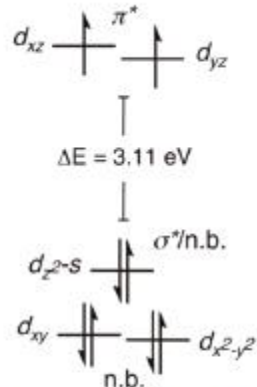
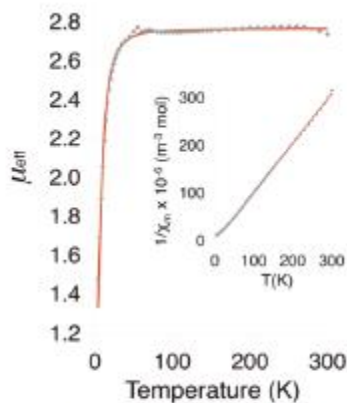
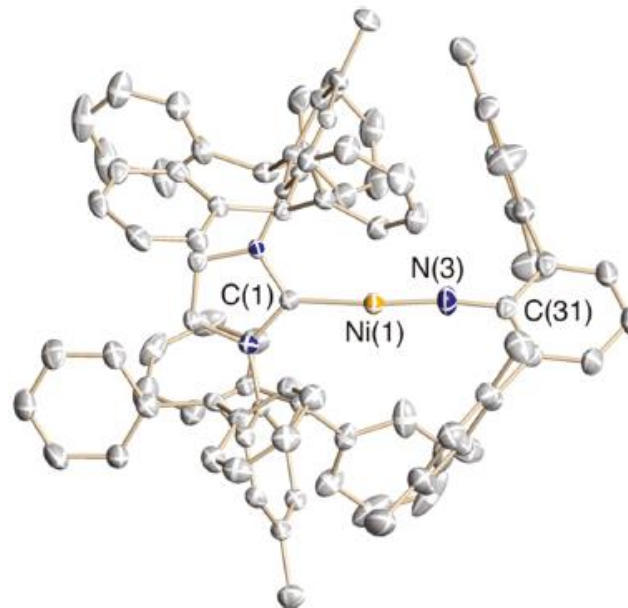
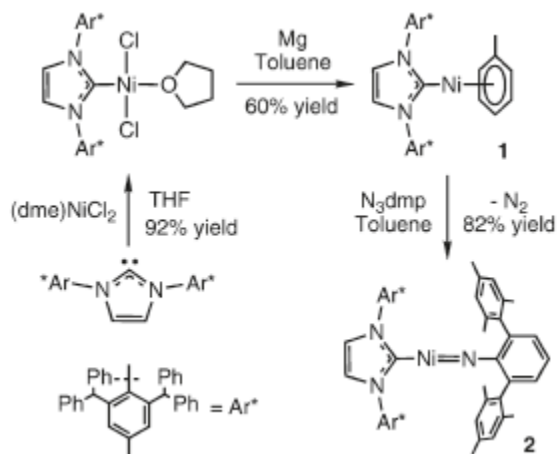
# Reactions of Ni(0) and Ni(I) with CX<sub>2</sub>



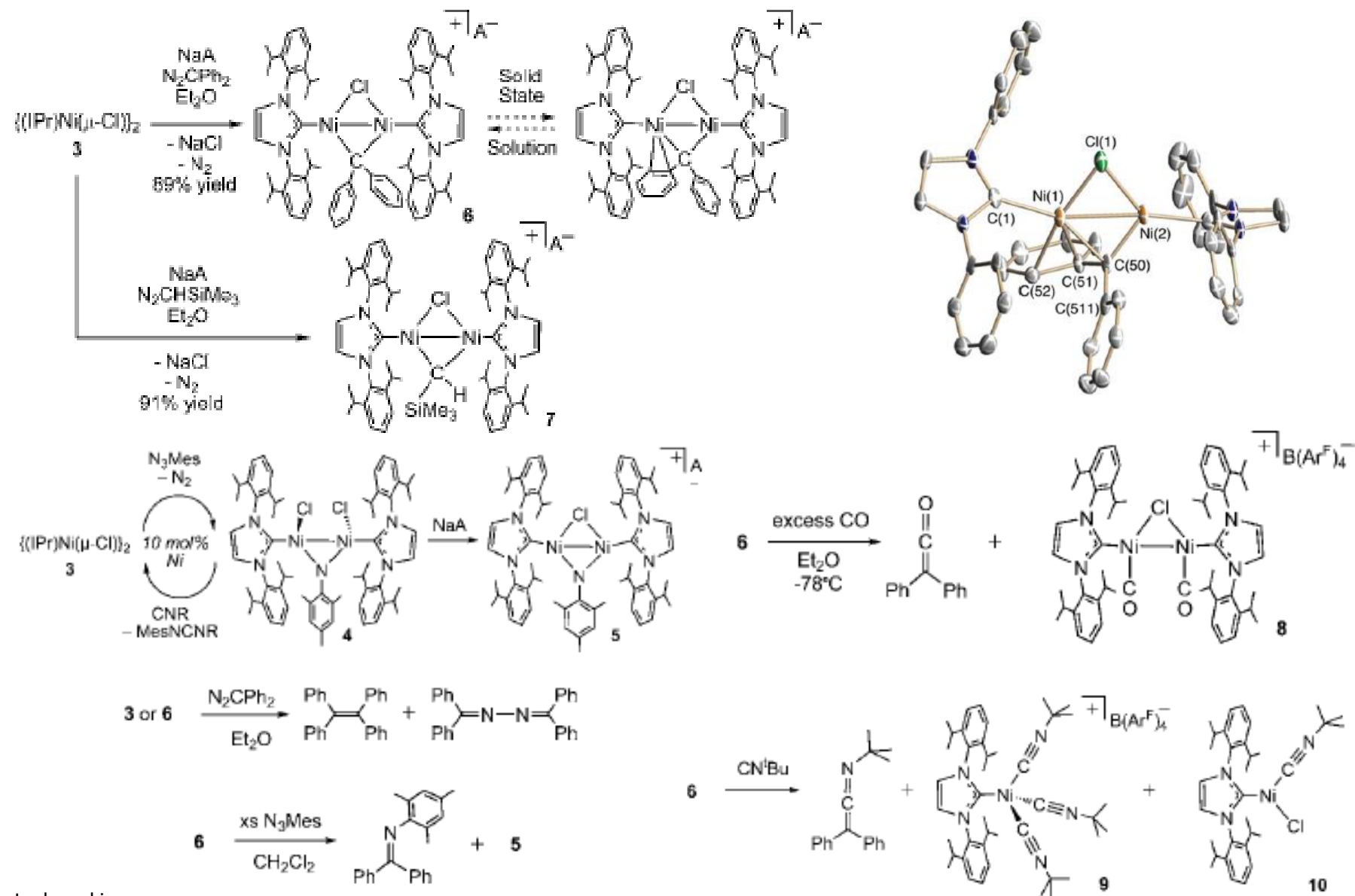
# Ni(I)-XHR to Ni(II)=X Radical Pathway



# Dicoordinate Ni(II) Complexes

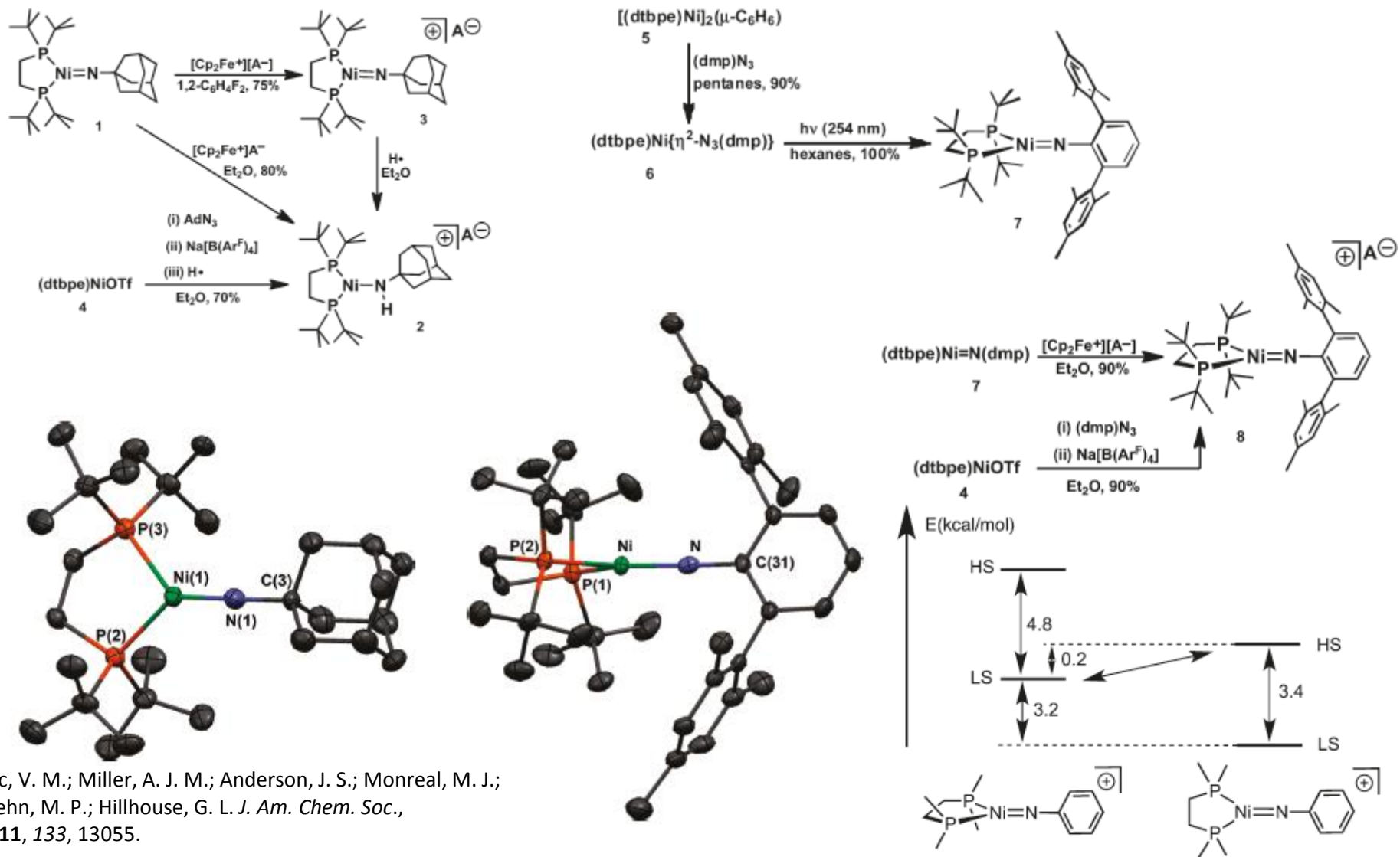


# Ni(II)-Carbene-Bridged Dimers



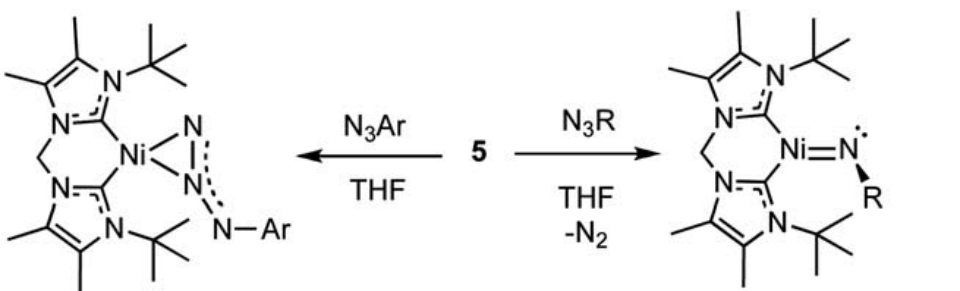
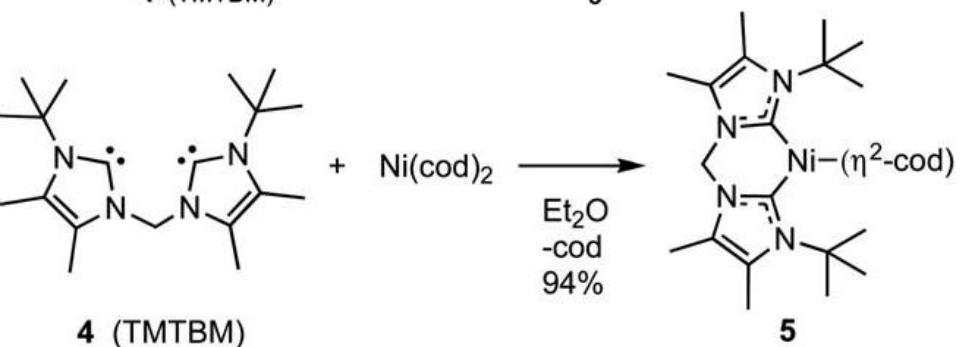
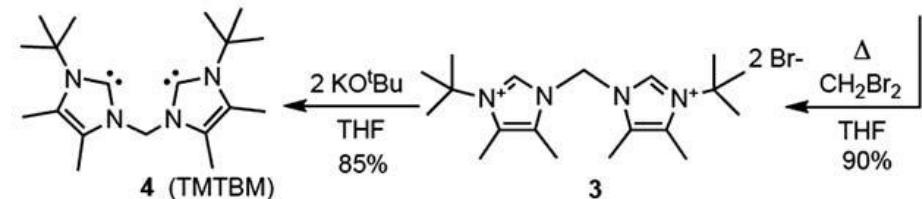
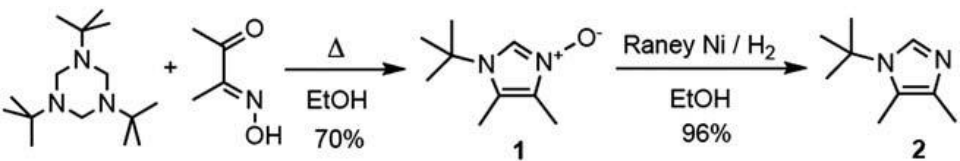
# Ni(III)-Imido Complex

- A terminal Ni(III)-imido should be exceptionally reactive and therefore unstable.





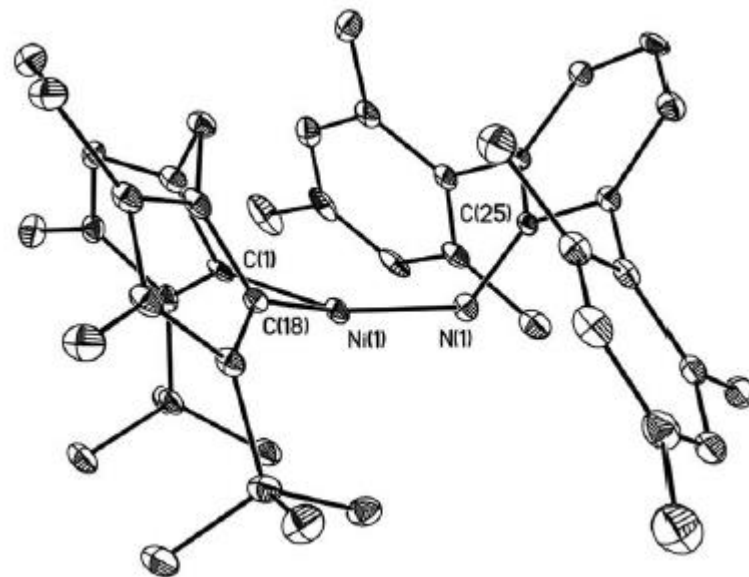
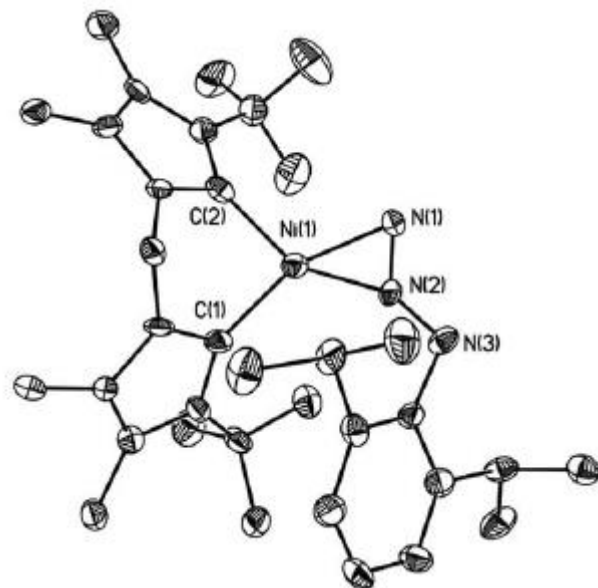
# Bis-NHC-Ni Complexes



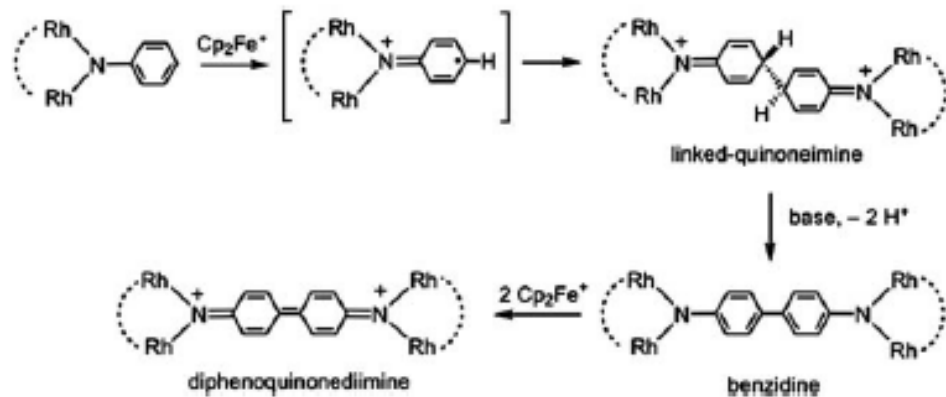
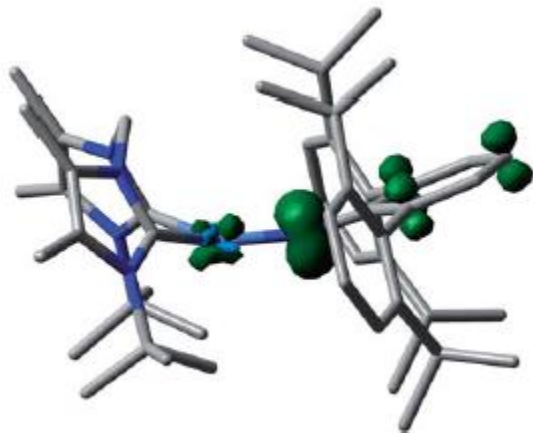
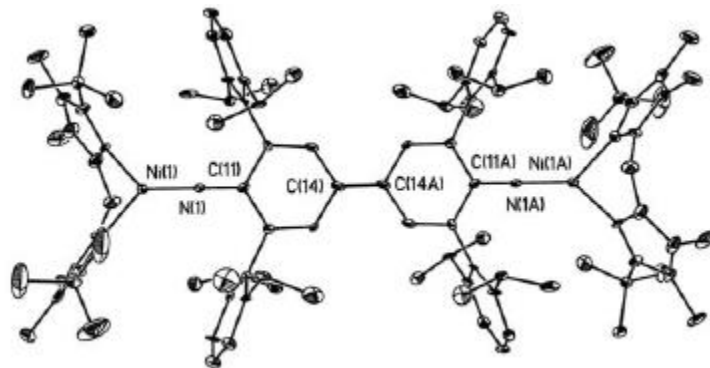
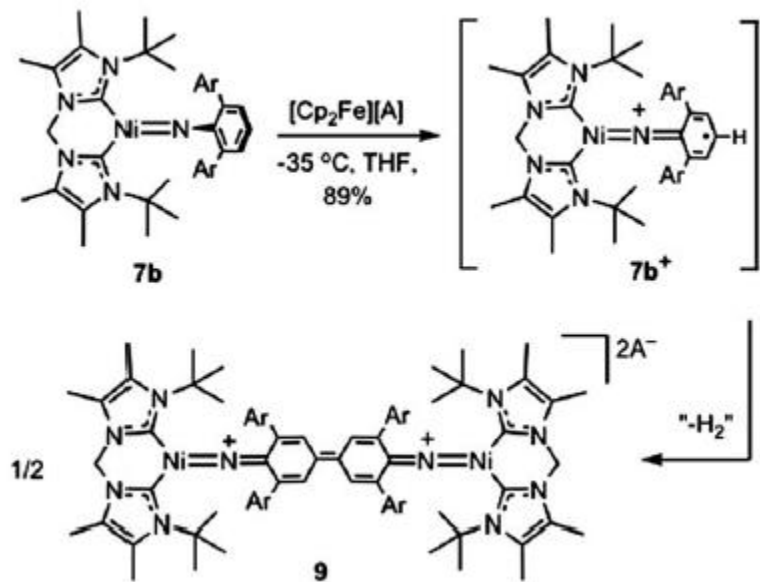
**6**, Ar = 2,6-diisopropylphenyl, 94%

**7a**, R = 2,6-dimesitylphenyl, 86%

**7b**, R = 2,6-Ar<sub>2</sub>phenyl, 89%

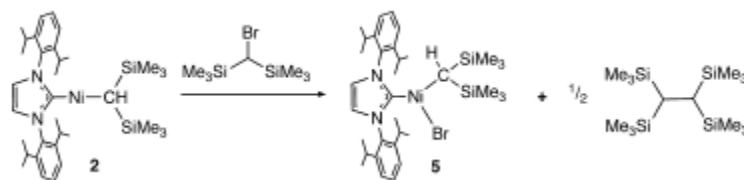
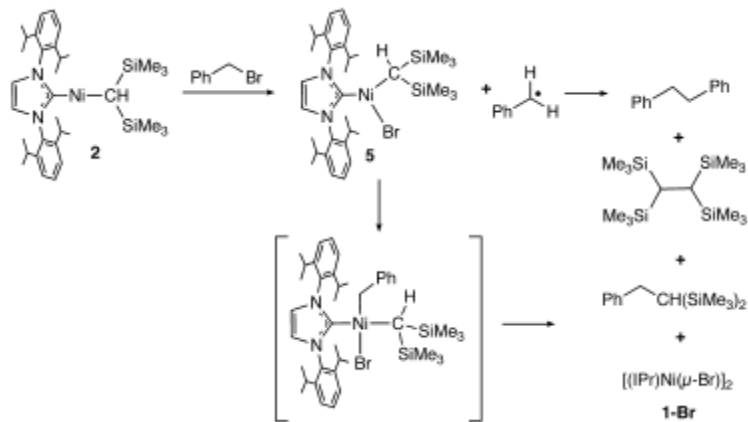
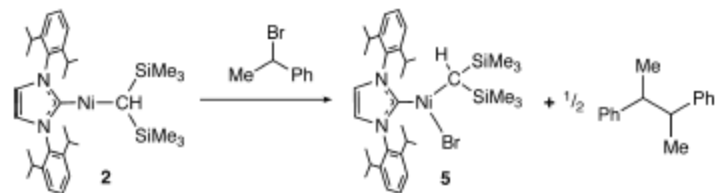
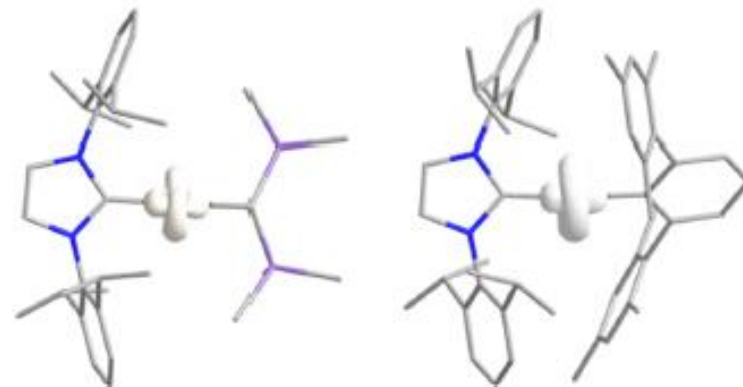
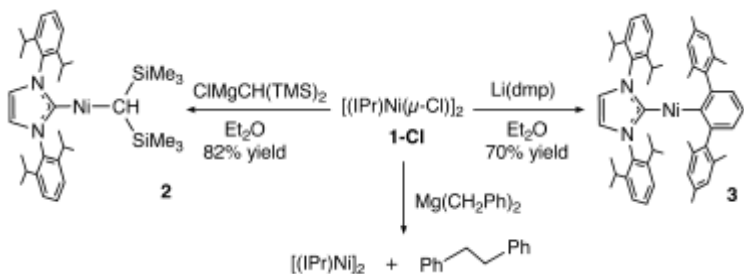


# Bis-NHC-Ni Complexes

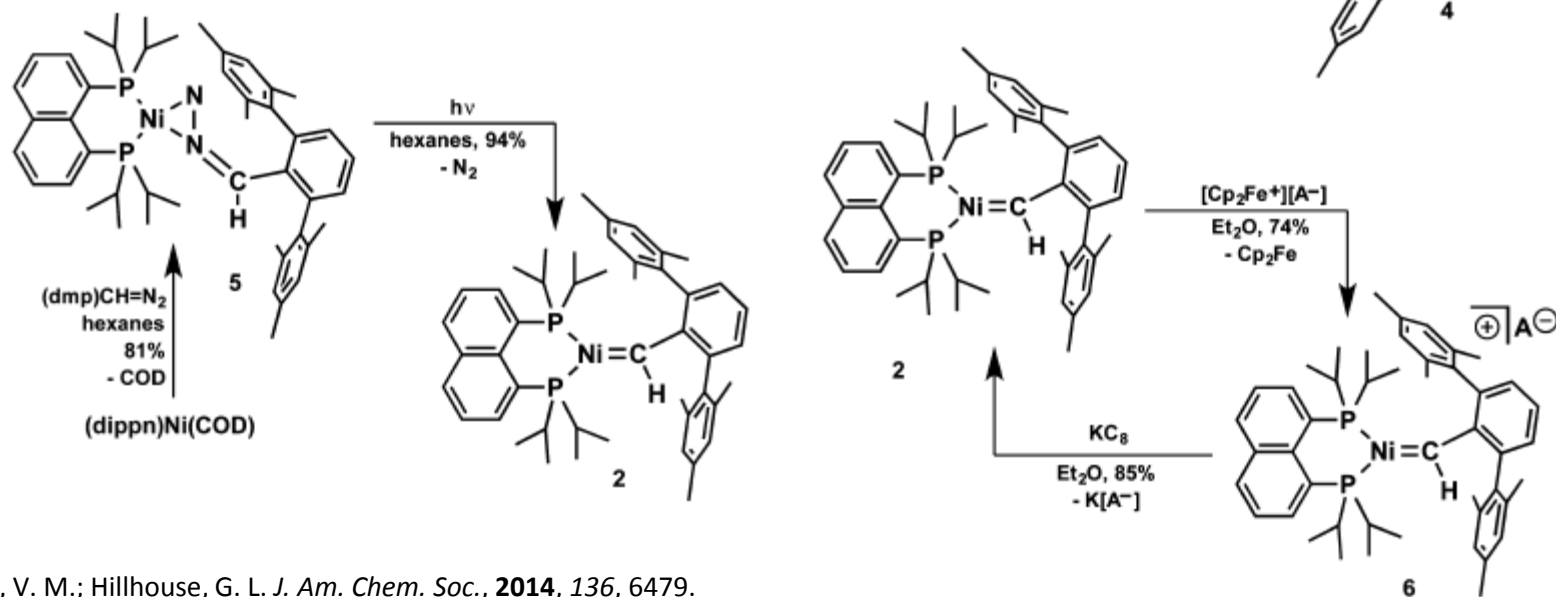
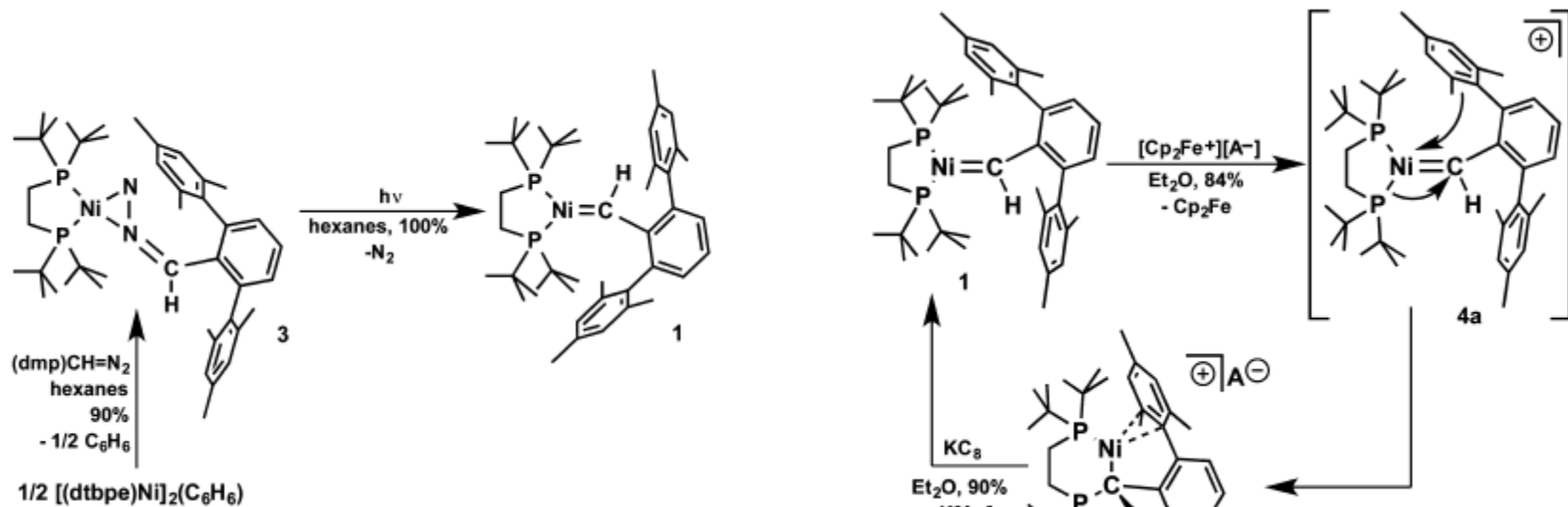




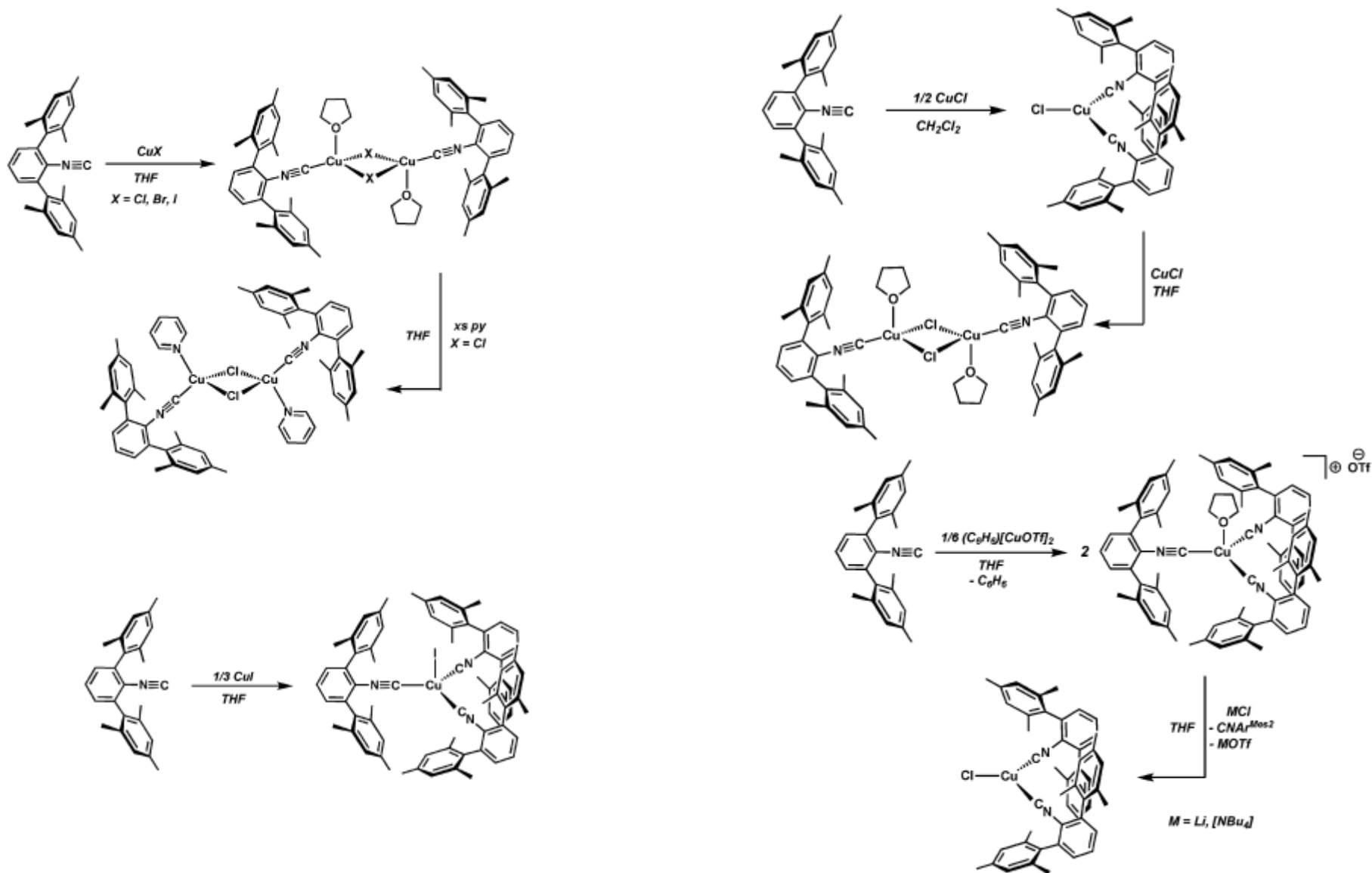
# Towards NHC-Ni(I) Alkyl Complexes



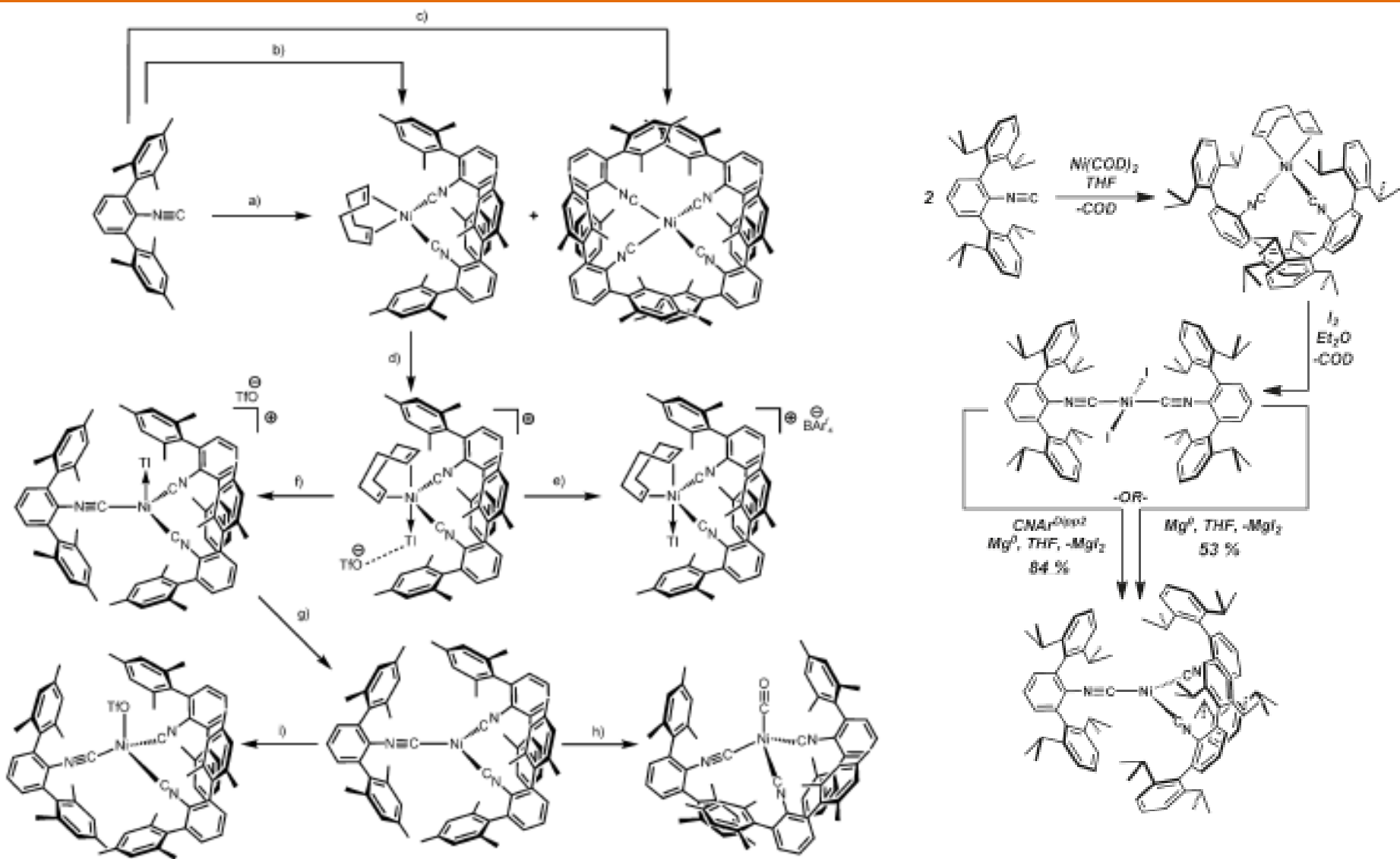
# 3-Coordinate Ni(II) Carbenes



# Isocyano Ligands and Cu(I)



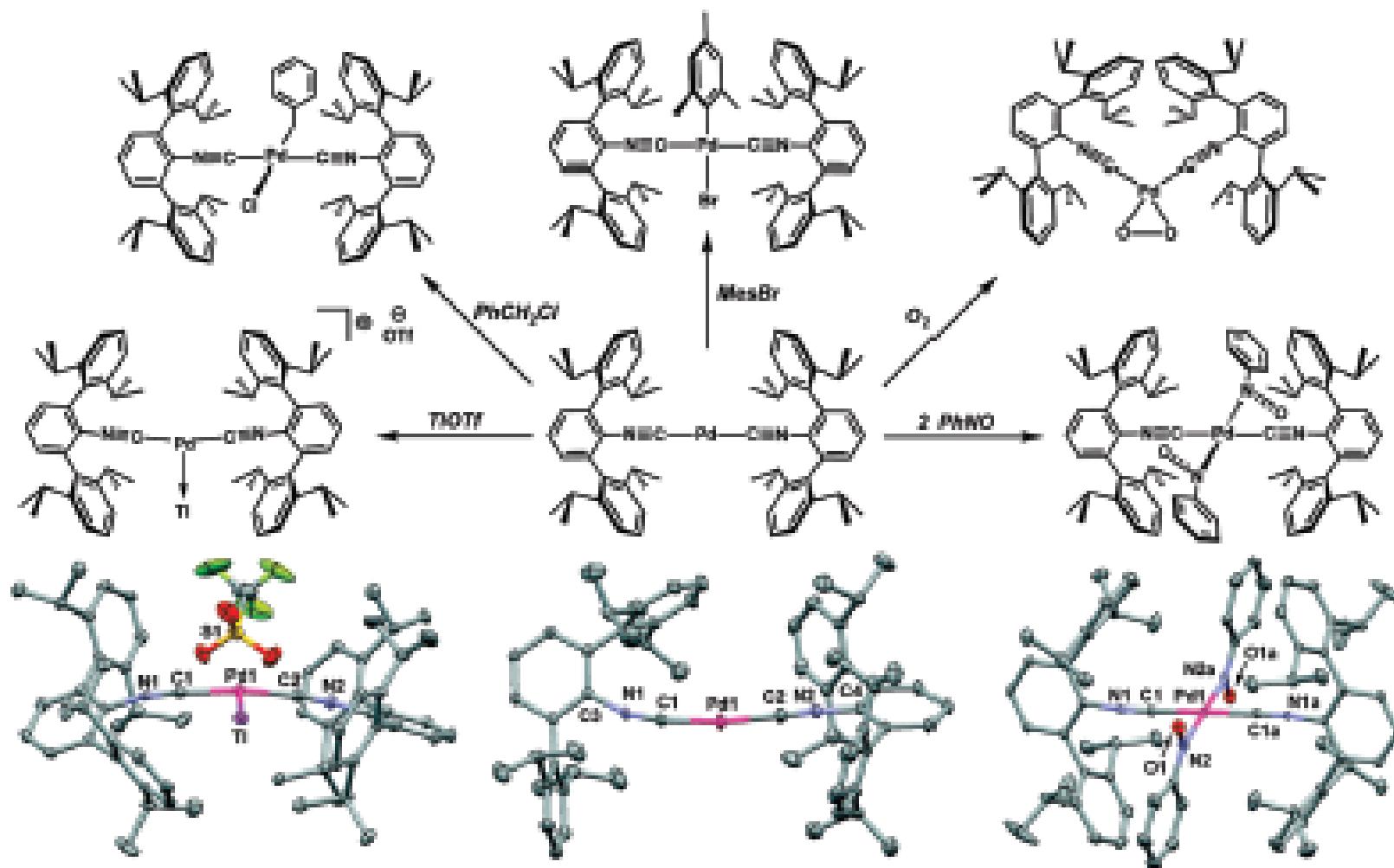
# Isocyano Ligands with Ni(0)



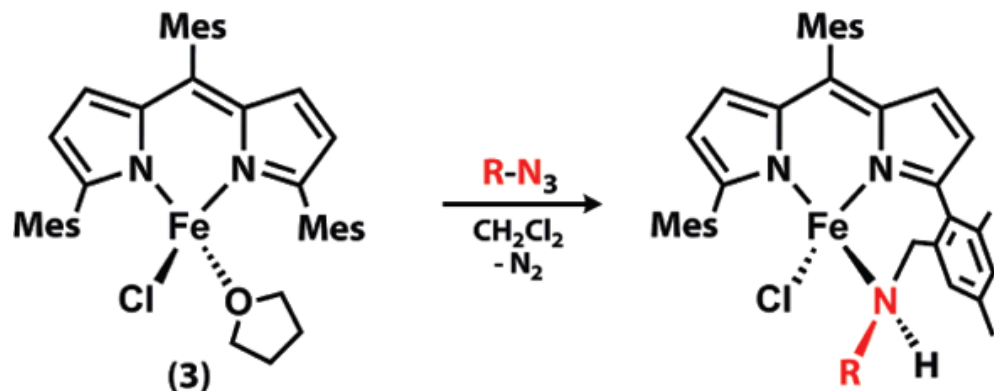
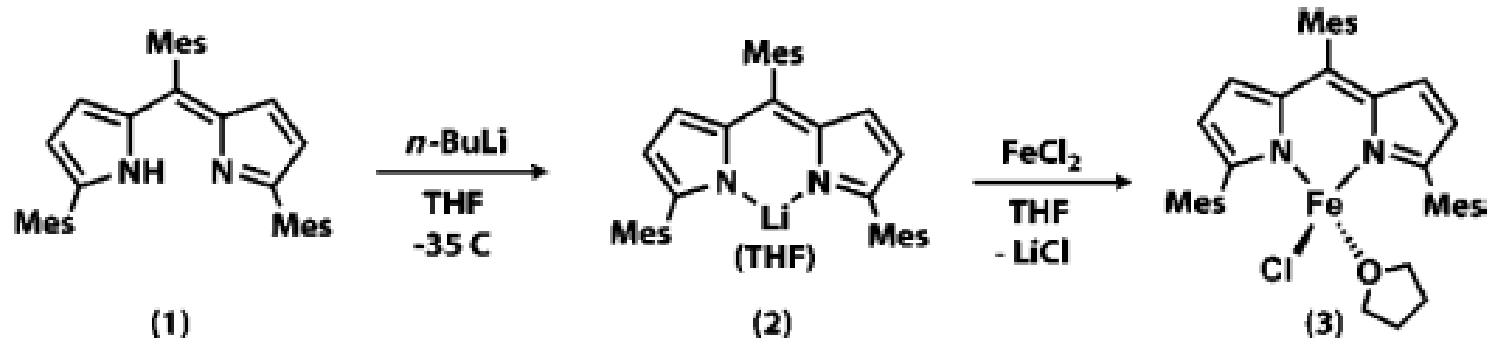
Fox, B. J.; Millard, M. D.; DiPasquale, A. G.; Rheingold, A. L.; Figueroa, J. S. *Angew. Chem., Int. Ed.*, **2009**, *48*, 3473.

Emerich, B. M.; Moore, C. E.; Fox, B. J.; Rheingold, A. L.; Figueroa, J. S. *Organometallics*, **2011**, *30*, 2598.

# 2-Coordinate Pd(0) with Isocyano Ligands



# Ligand C–H Amination with Fe(II)

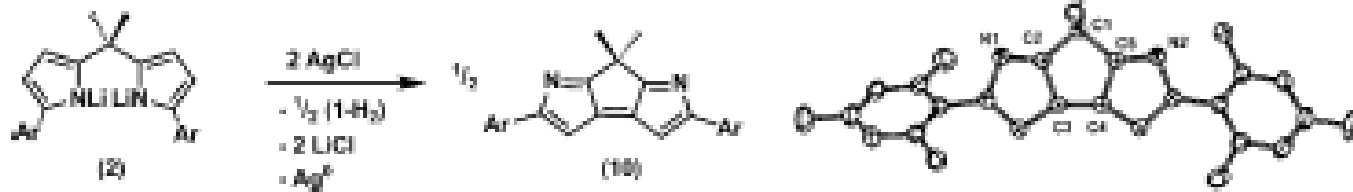
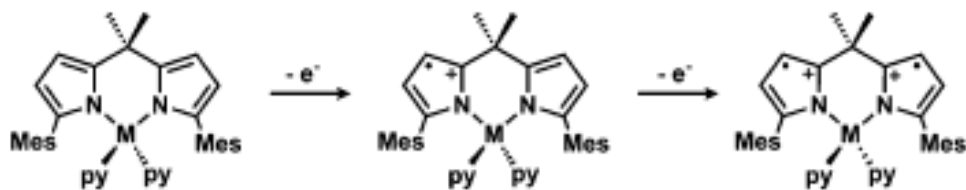
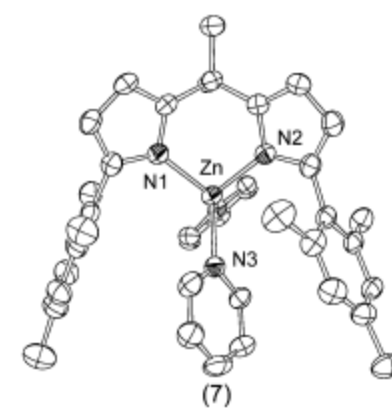
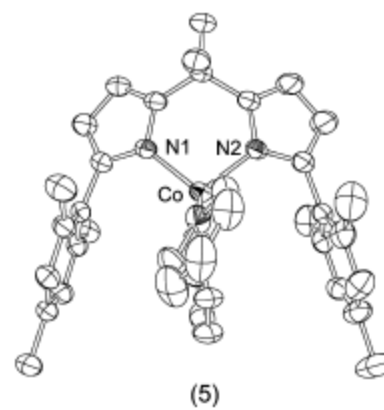
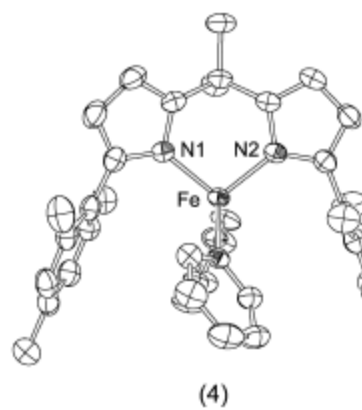
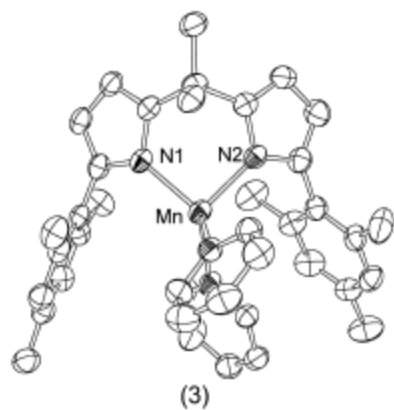
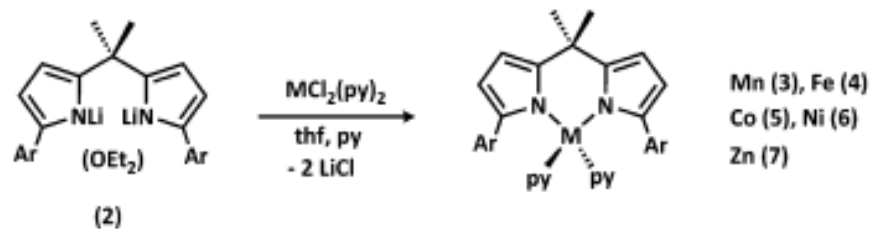


$R$ ( $\text{N}_3\text{-}R$ )	TOF/ESI $m/z^a$ [H(pyac) + NR + H] <sup>+</sup>
Ad	648.4318 (648.4284)
CMe <sub>3</sub>	570.3848 (570.3851)
Ph	590.3535 (590.3509)
Mes	632.4004 (632.3965)
Ts	668.3310 (668.3306)

<sup>a</sup> calculated (observed)

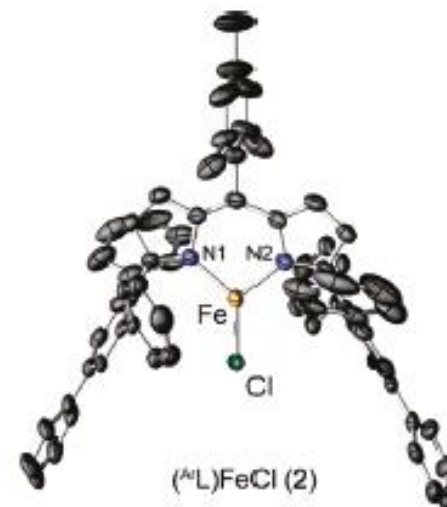
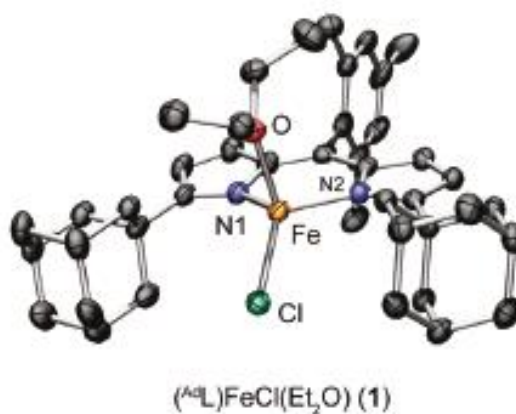
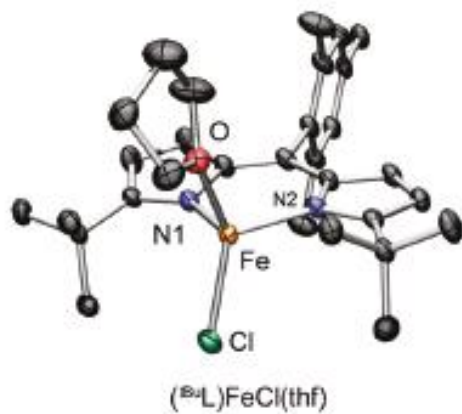
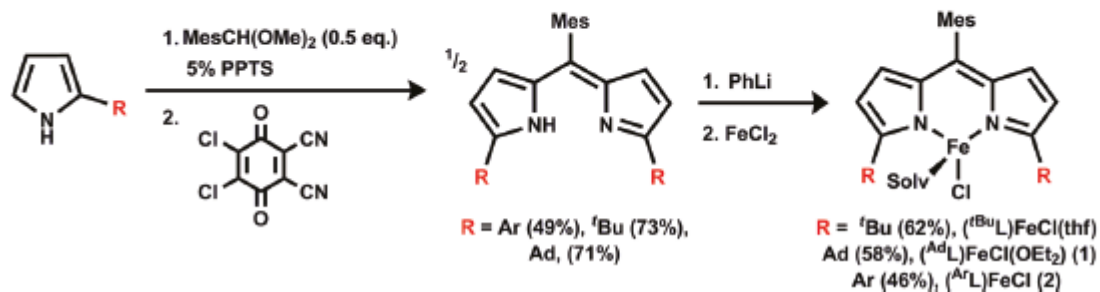
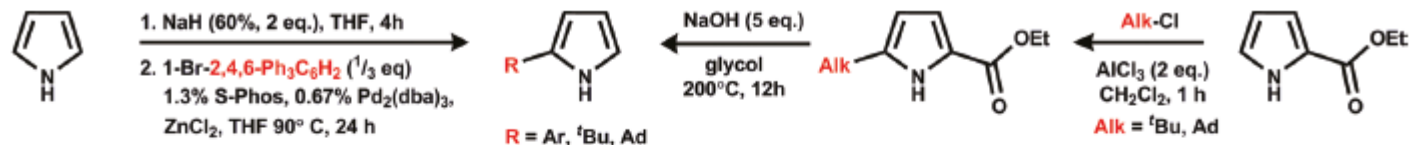
- Replacing Fe(II) with Zn(II) shuts down the reaction.

# Complexes of Dipyrromethane





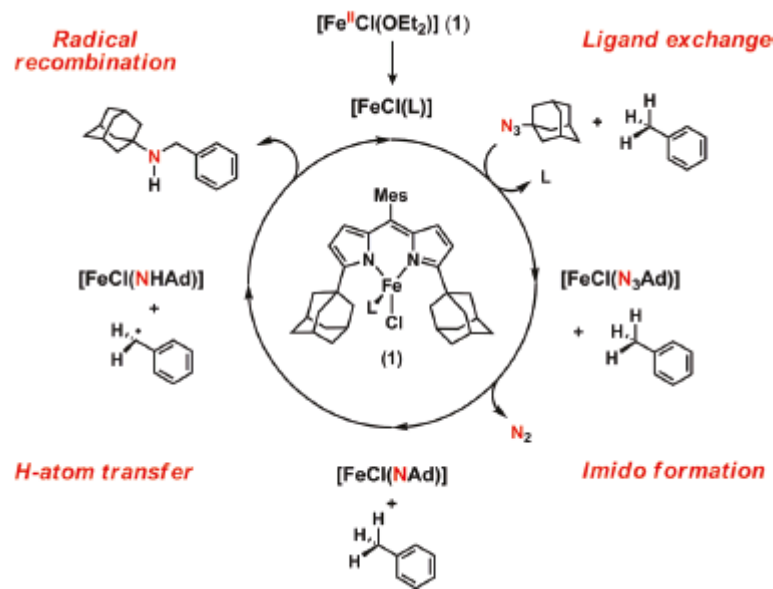
# Complexes of Dipyrromethane





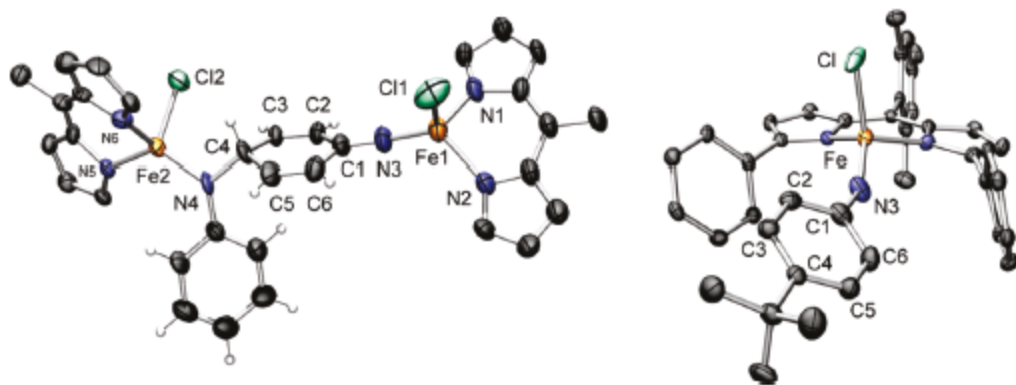
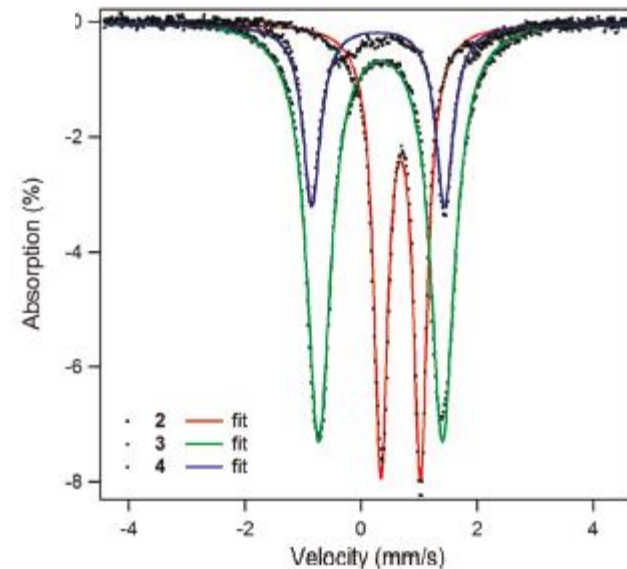
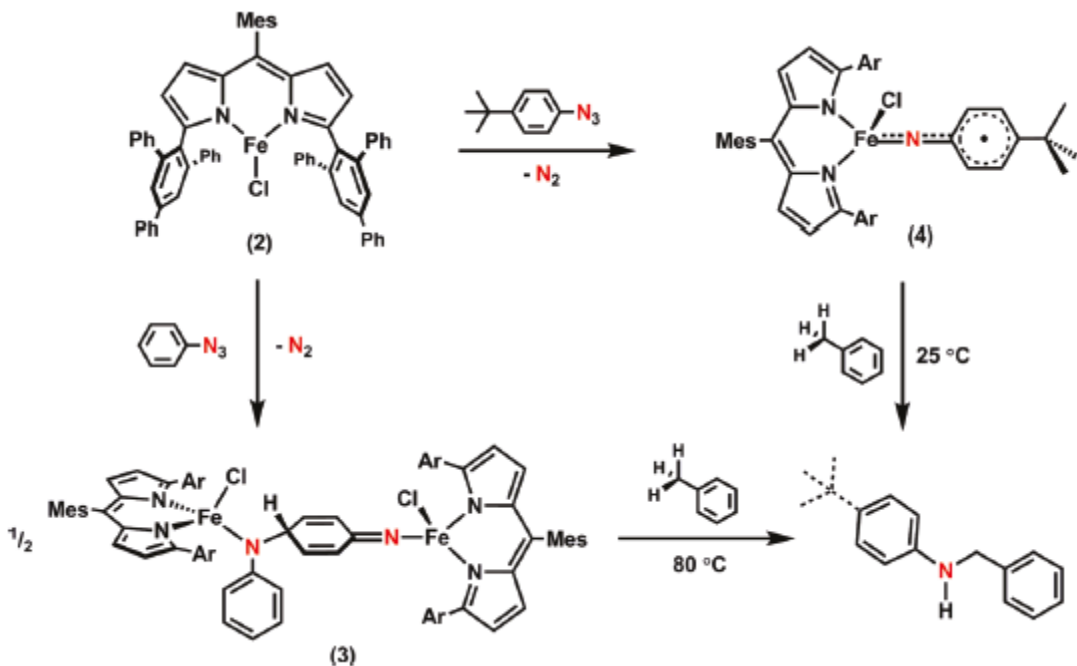
# Complexes of Dipyrromethane

- The reaction of **1** with adamantyl amine in toluene gives 6.7 turnover (amine 95%, imine 2.8%, adamantylamine 1.8%).



- Product inhibited by anything that outcompetes azide for chelation.
- KIE is consistent with H abstraction being the RDS.

# Complexes of Dipyrromethane

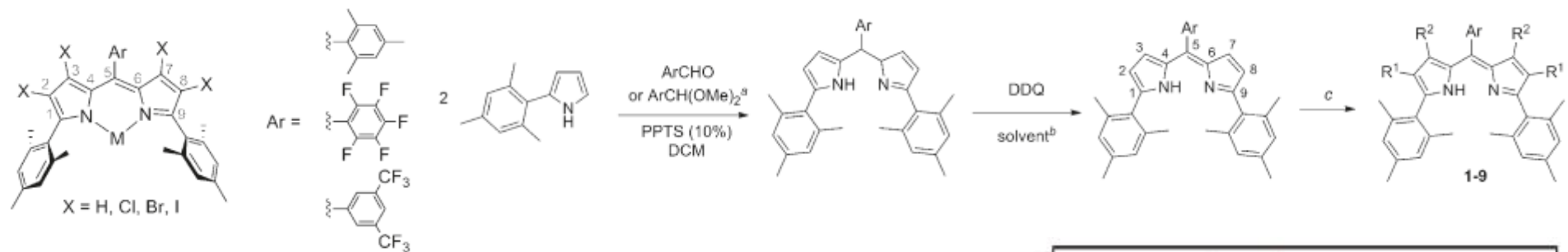


$(\alpha\text{-}\beta) S = 2$

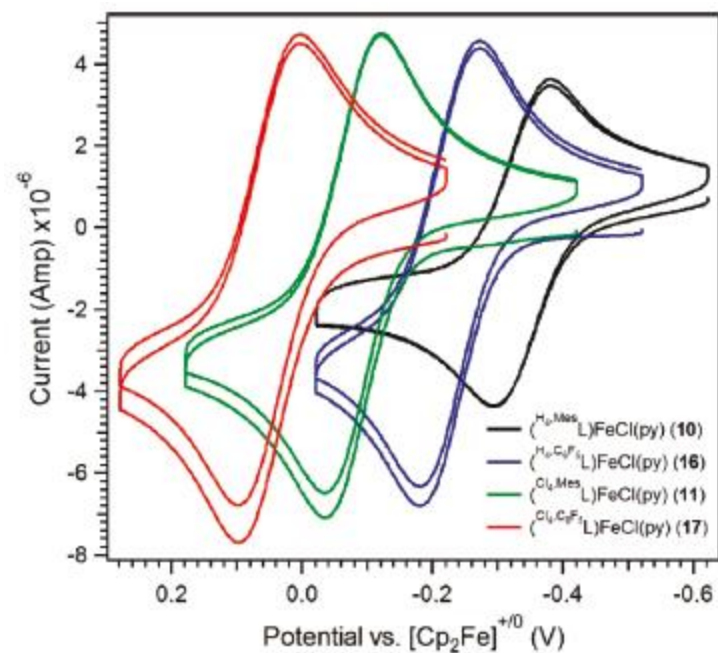
$\text{Fe}^{\text{III}} S = 5/2, (\text{NAr}) S = 1/2$

$\delta_{\text{calc}} 0.34 \text{ mm/s}, \Delta E_{\text{Q calc}} -2.00 \text{ mm/s}$

# Electronic Perturbation of Ligands

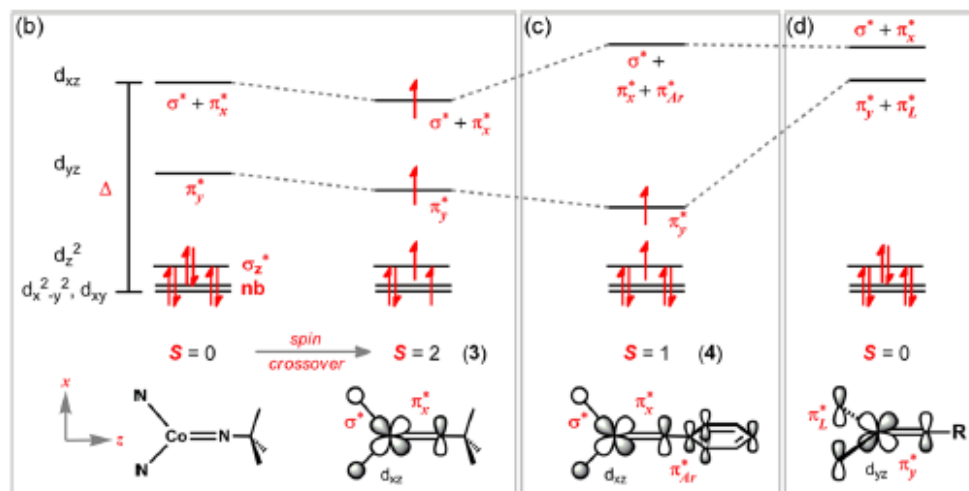
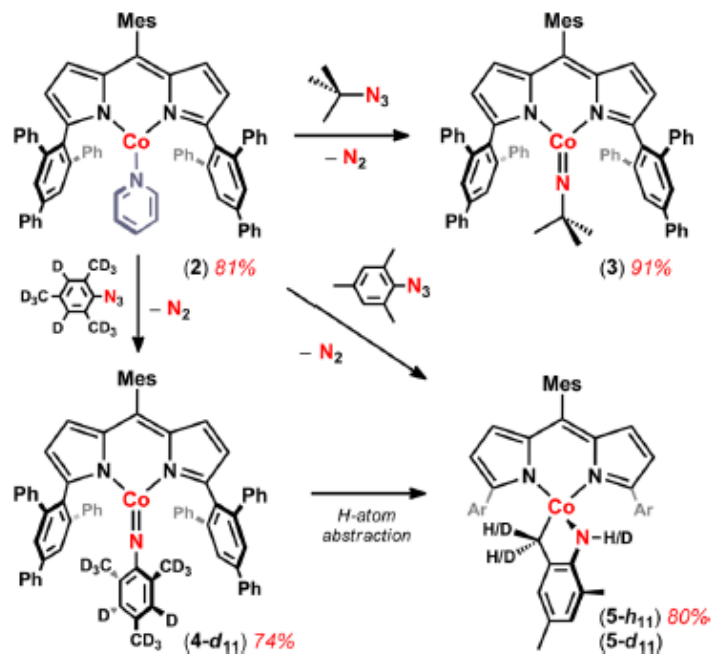


abbrev	Ar	R <sup>1</sup> /R <sup>2</sup>	E <sub>1/2</sub> Fe <sup>III/II</sup> <sup>a</sup> (mV)	λ <sub>max</sub> <sup>b</sup> (nm)
(H <sub>4</sub> MesL)FeCl(py)	Mes	H/H	-336	506.0
(Cl <sub>4</sub> MesL)FeCl(py)	Mes	Cl/Cl	-79	524.5
(Br <sub>2</sub> MesL)FeCl(py)	Mes	Br/H	-154	528.0
(Br <sub>4</sub> MesL)FeCl(py)	Mes	Br/Br	-95	530.5
(I <sub>4</sub> MesL)FeCl(py)	Mes	I/I	-170	545.6
(H <sub>4</sub> CF <sub>5</sub> L)FeCl(py)	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H/H	-238	508.5
(H <sub>4</sub> C <sub>6</sub> F <sub>5</sub> L)FeCl(py)	C <sub>6</sub> F <sub>5</sub>	H/H	-227	516.7
(Cl <sub>4</sub> C <sub>6</sub> F <sub>5</sub> L)FeCl(py)	C <sub>6</sub> F <sub>5</sub>	Cl/Cl	+50	541.5
(Br <sub>4</sub> C <sub>6</sub> F <sub>5</sub> L)FeCl(py)	C <sub>6</sub> F <sub>5</sub>	Br/Br	+20	547.5



<sup>a</sup> For Ar = mesityl, acetal used; Ar = fluoroaryl, aldehyde used. <sup>b</sup> Solvent = hexanes, acetone, or CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Chlorination: 6.0 equiv of *N*-chlorosuccinimide, tetrahydrofuran, 70 °C, 48 h. Bromination: *N*-bromosuccinimide, tetrahydrofuran, room temperature, 1–16 h. Iodination: excess I<sub>2</sub> and excess KOH, dimethylformamide, 70 °C, 48 h.

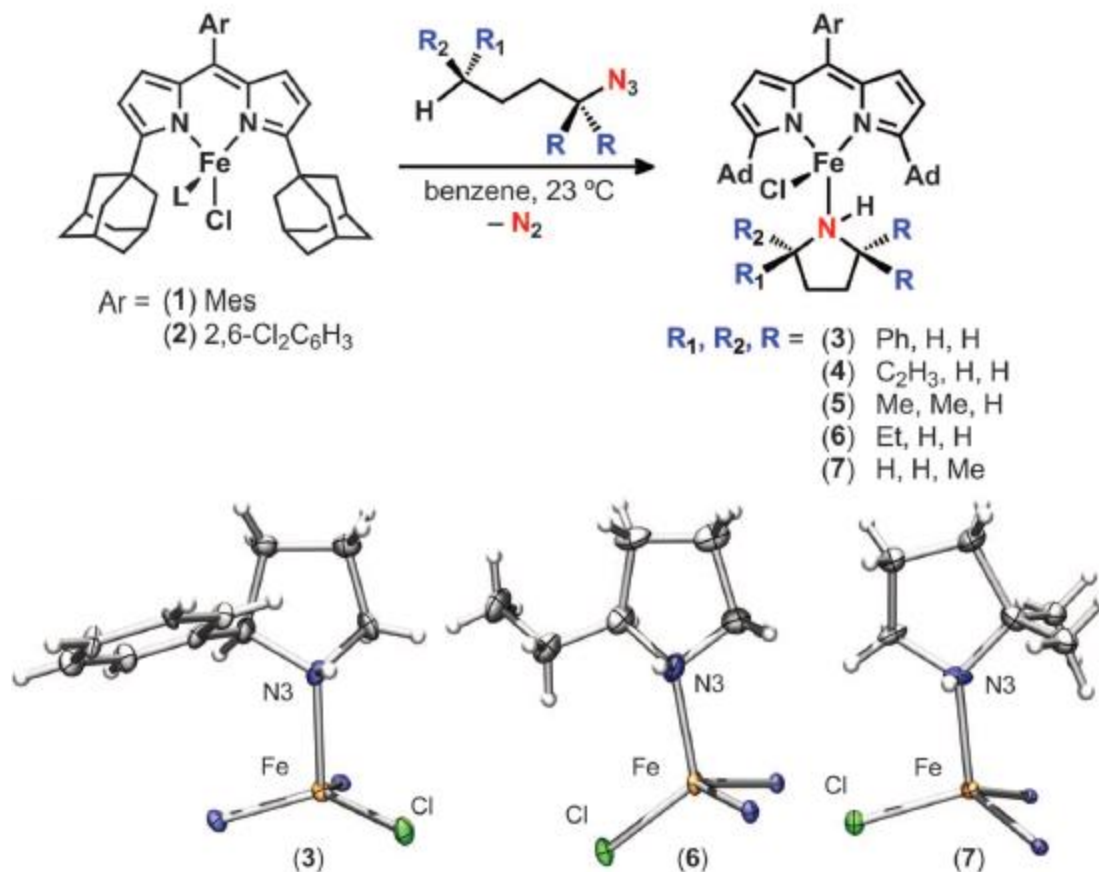
# Co(III) Complexes of Dipyrromethane



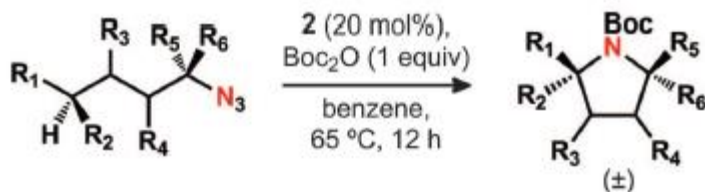
# Intramolecular Cyclization of Alkyl Azides



- Based on the previous results, the group next wanted to explore the substrate scope of their nitrene insertion into aliphatic C-H bonds.



# Intramolecular Cyclization of Alkyl Azides

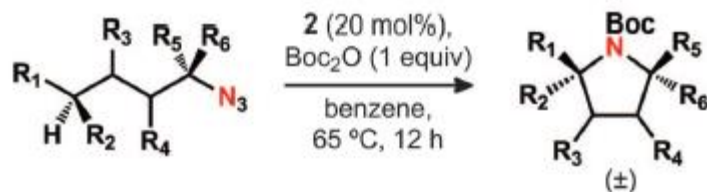


Entry	Azide	Pyrrolidine	Yield (%) <sup>a</sup>
1			98 <sup>†§</sup> (PG = Fmoc) 93 <sup>†§</sup> 57 <sup>†§</sup> (PG = Boc)
2			72 <sup>†§</sup>
3			60 <sup>§</sup> 49 <sup>†§</sup>
4			19 <sup>†§</sup>
5			17 <sup>†§</sup>

Entry	Azide	Pyrrolidine	Yield (%) <sup>a</sup>
6			11
7			47
8			68 <sup>†</sup>
9			60 3.9:1.0 dr



# Intramolecular Cyclization of Alkyl Azides



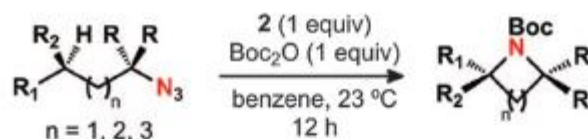
Entry	Azide	Pyrrolidine	Yield (%) <sup>*</sup>
10			66 1.5:1.0 dr
11			70
12			98
13			75 <sup>†</sup> 93% ee
14			84 1.1:1.0 dr

Entry	Azide	Pyrrolidine	Yield (%) <sup>*</sup>
15			67
16			73 2.1:1.0 dr
17			58 5.5:1.5: 1.0:0.08 dr
18			14 (PG = Boc) 78 <sup>†</sup> (PG = Fmoc)

# Intramolecular Cyclization of Alkyl Azides



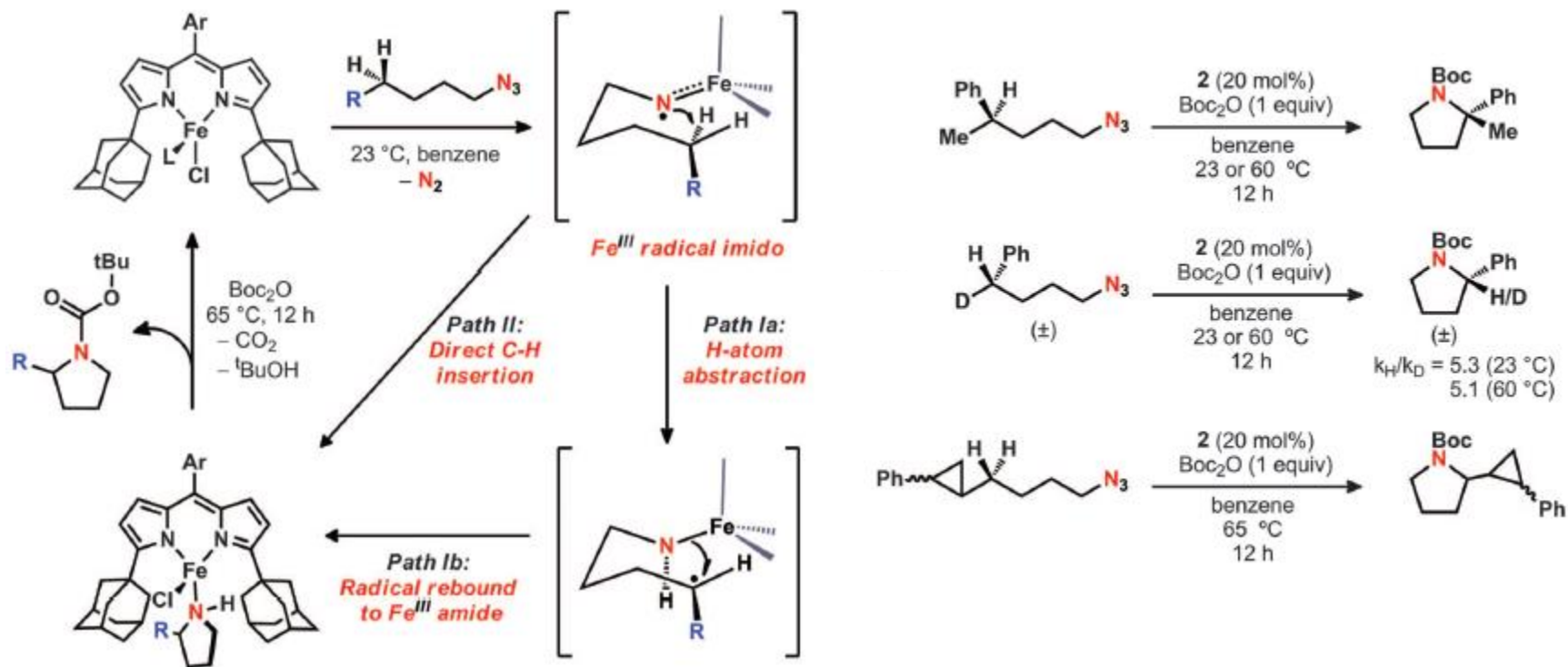
- As the substrates become more complex, so too are the product(s).



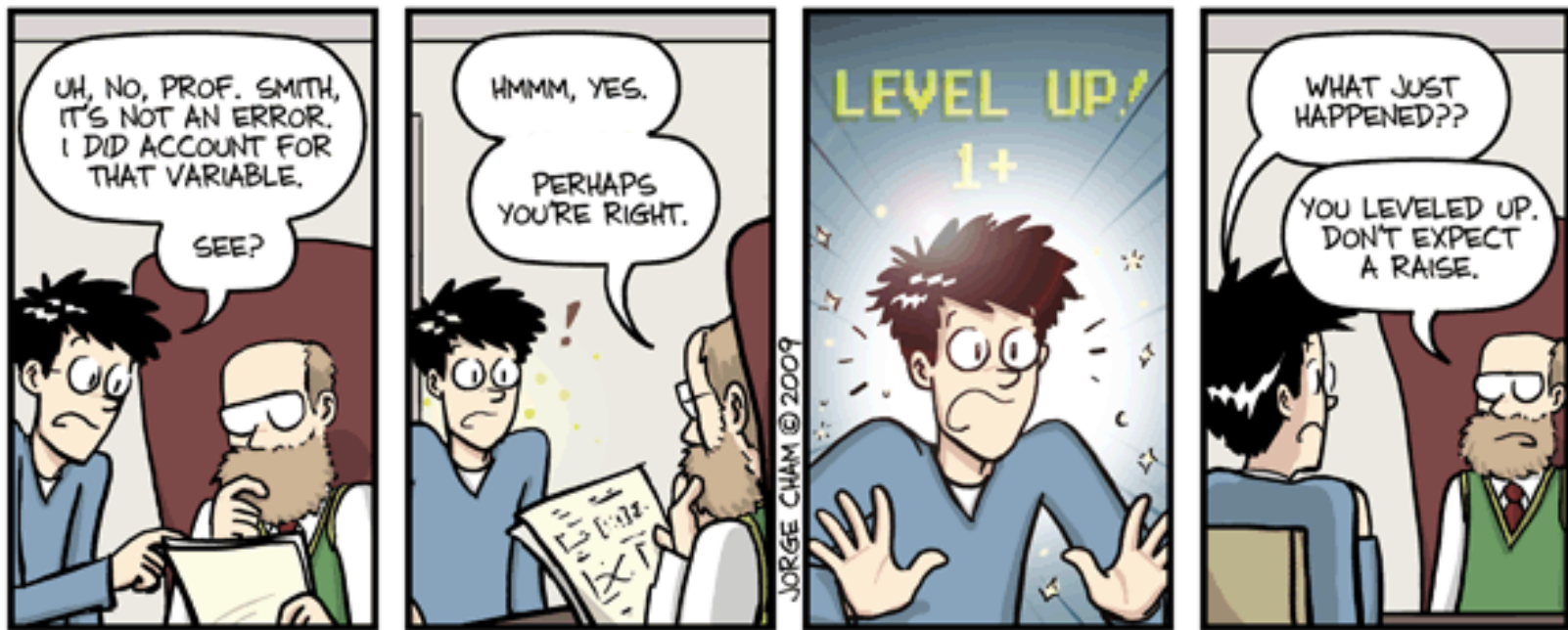
Entry	Azide	Product(s)	Conv. (%) <sup>†</sup>
1			45
2			82
3			52 (1.0:0.9)
4			47 (1.0:1.5)



# Intramolecular Cyclization of Alkyl Azides



# Thank you for your attention!



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