Metal-Metal Bonds: Reactivity and Catalysis

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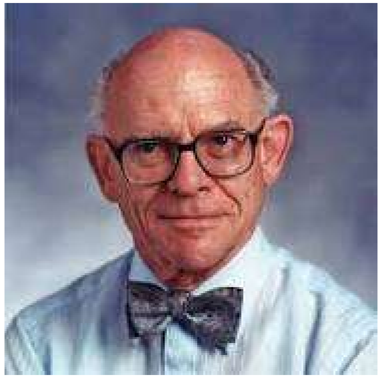
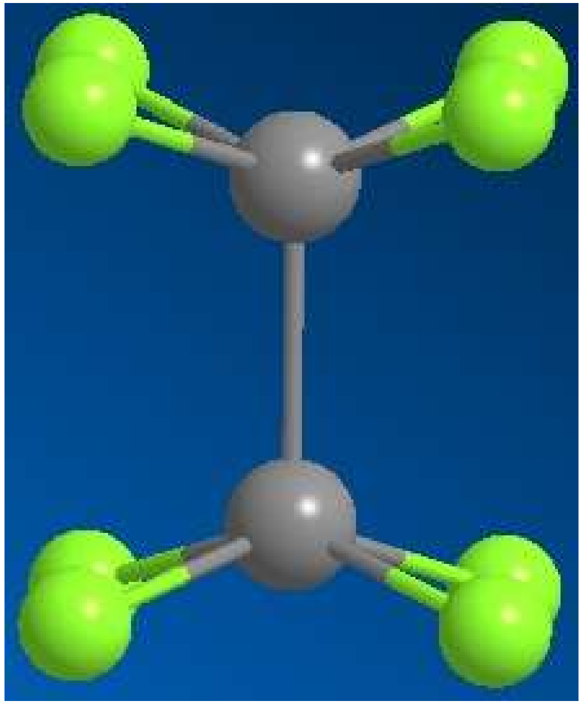
Advisor: Prof. Keary M. Engle
2018. 09. 13

In Memory of Prof. Frank Albert Cotton



F. Albert Cotton
(1930-2007)



$[Re_2Cl_8]^{2-}$, a Re–Re quadruple bond exists
The first complex containing a
metal-metal multiple bond characterized
(1964)

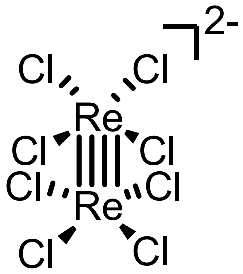
Cotton, F. A. *et al.*, *Science* **1964**, *145*, 1305–1307
Photo courtesy: Wikipedia

Representative metal-metal bond containing complexes

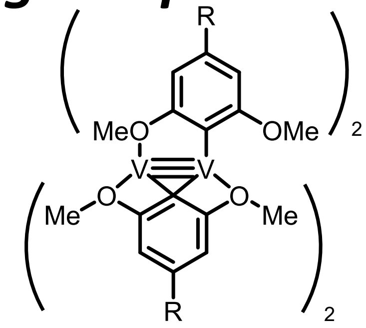
$Cr_2(OAc)_4(OH_2)_2$

Prepared in 1844
Crystallographically solved in 1970

Cr–Cr distance 2.36 Å

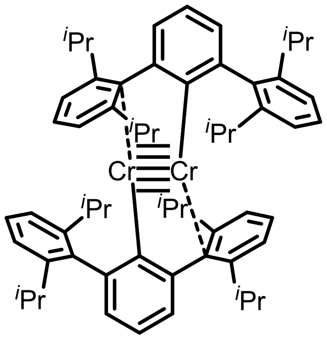


1964
Re–Re distance 2.27 Å

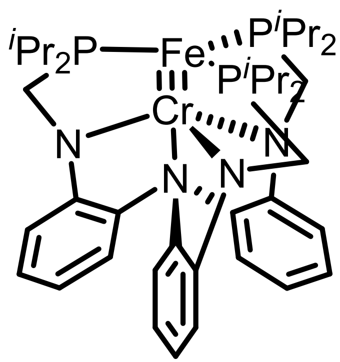


R = H, OMe

1970
V–V distance 1.98 Å



2005
Cr–Cr distance 1.84 Å

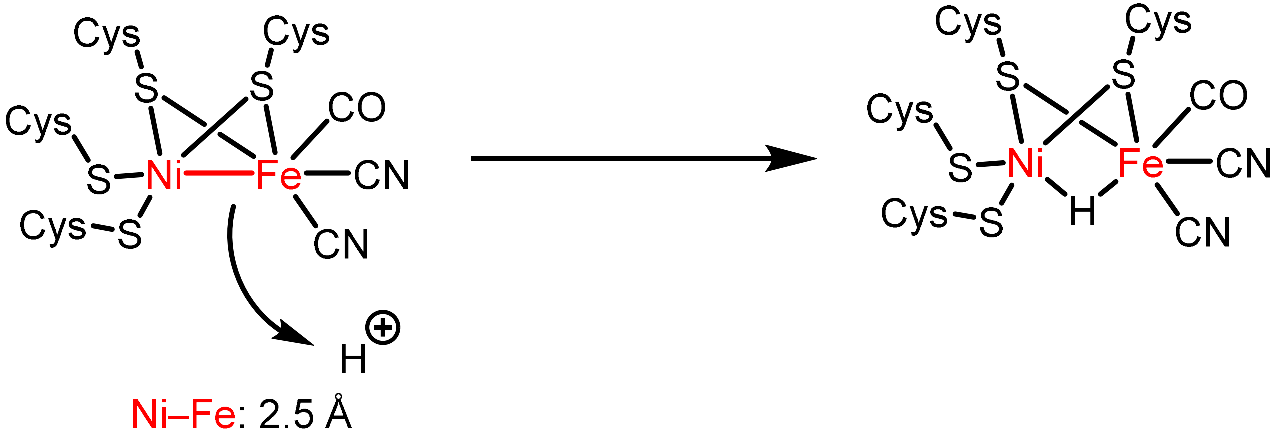


2013
Cr–Fe distance 1.94 Å

Peligot, M. E., *C. R. Acad. Sci.* **1844**, *19*, 609–615
Cotton, F. A. *et al.*, *Science* **1964**, *145*, 1305–1307
Cotton, F. A. *et al.*, *J. Am. Chem. Soc.* **1970**, *92*, 2926–2927
Cotton, F. A. *et al.*, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 737–738
Power. P. P. *et al.*, *Science* **2005**, *310*, 844–847
Lu, C. C. *et al.*, *Angew. Chem. Int. Ed.* **2013**, *52*, 4449–4452

Metal-Metal Bonds in Biology

Metal-metal bonds are rarely known in biology.



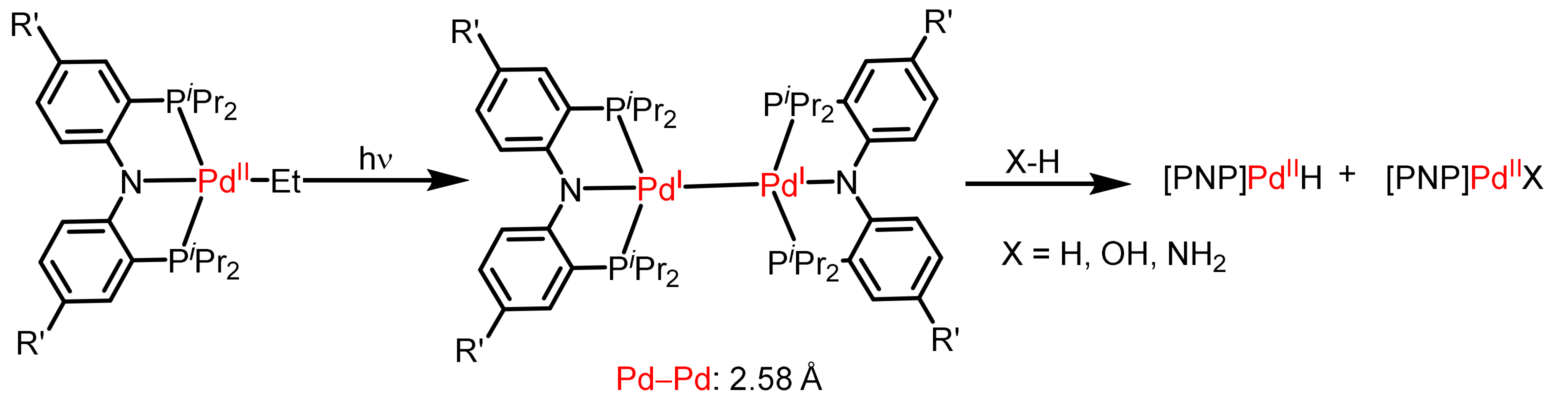
Proposed proton reduction by [NiFe]-hydrogenases

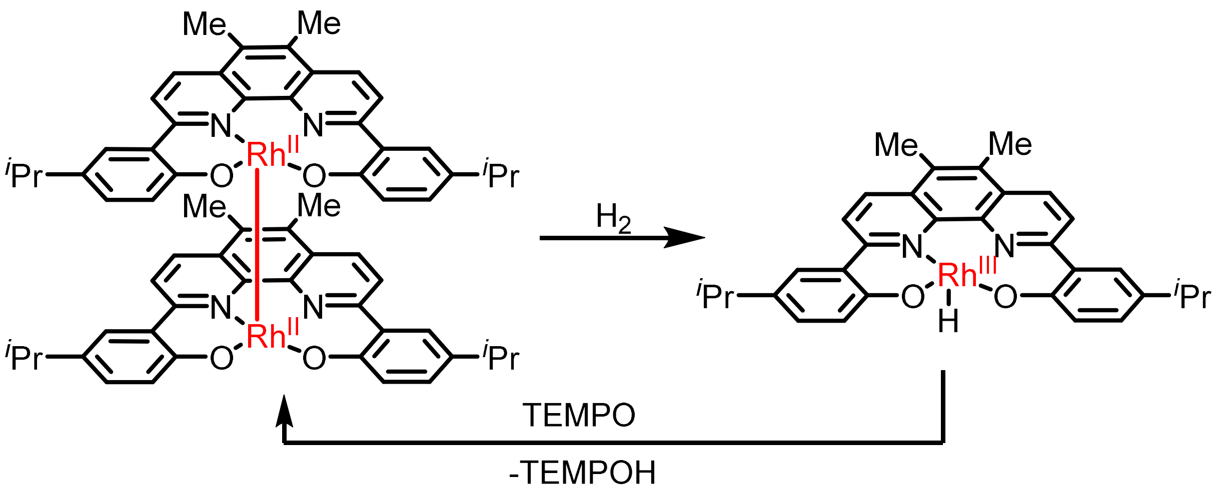
Some weak interaction between metals was also observed in CO dehydrogenase and acety–CoA synthase

Fontecilla-Camps, J. C. *et al. Structure* **1999**, *7*, 557–566
Lindahl, P. A. *J. Inorg. Biochem.* **2012**, *106*, 172–178
Dobbek, H. *et al. J. Am. Chem. Soc.* **2009**, *131*, 9922–9923
Tatsumi, K. *et al. Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 11862–11866

Organometallic Elementary Steps

Oxidative additions.

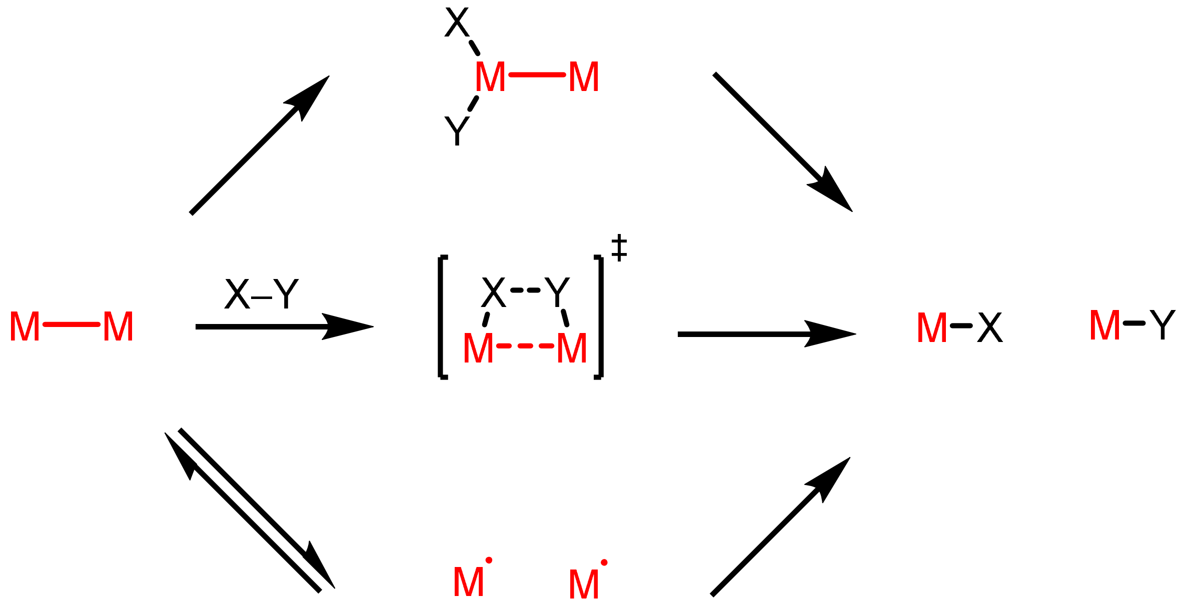




Ozerov, O. V. *et al. J. Am. Chem. Soc.* **2007**, *129*, 10318–10319
Chan, K. S. *Organometallics* **2002**, *21*, 2743–2750

Organometallic Elementary Steps

Oxidative additions.

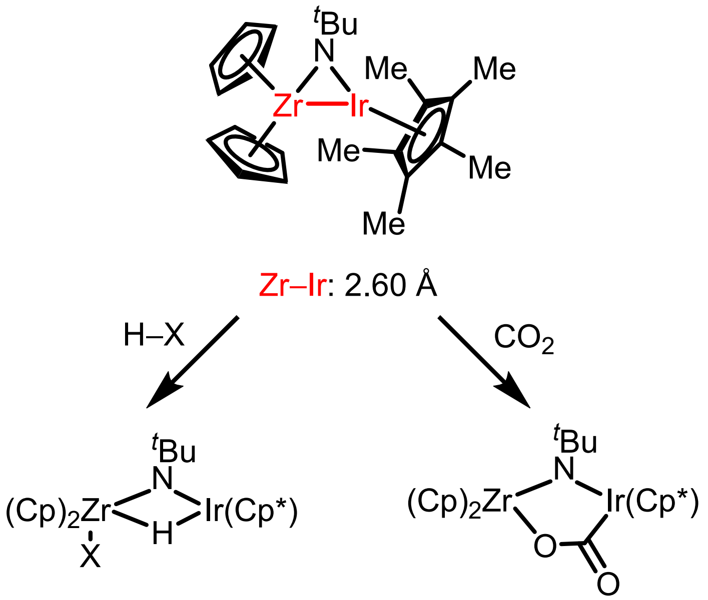


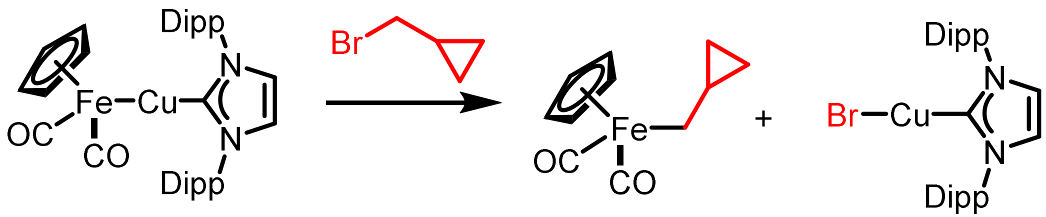
Proposed mechanism of dimetallic oxidative addition

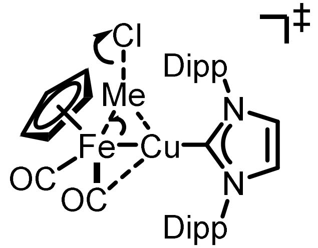
Schoenebeck, F. *et al. J. Org. Chem.* **2014**, *79*, 12041–12046
Hoffmann, R. *Organometallics* **1984**, *3*, 370–380
Sevin, A. *et al. J. Organomet. Chem.* ***1984***, *262*, 391–405
Wayland, B. B. *et al. J. Am. Chem. Soc.* **2004**, *126*, 8266–8274

Organometallic Elementary Steps

Oxidative additions on hetero metal-metal bonds

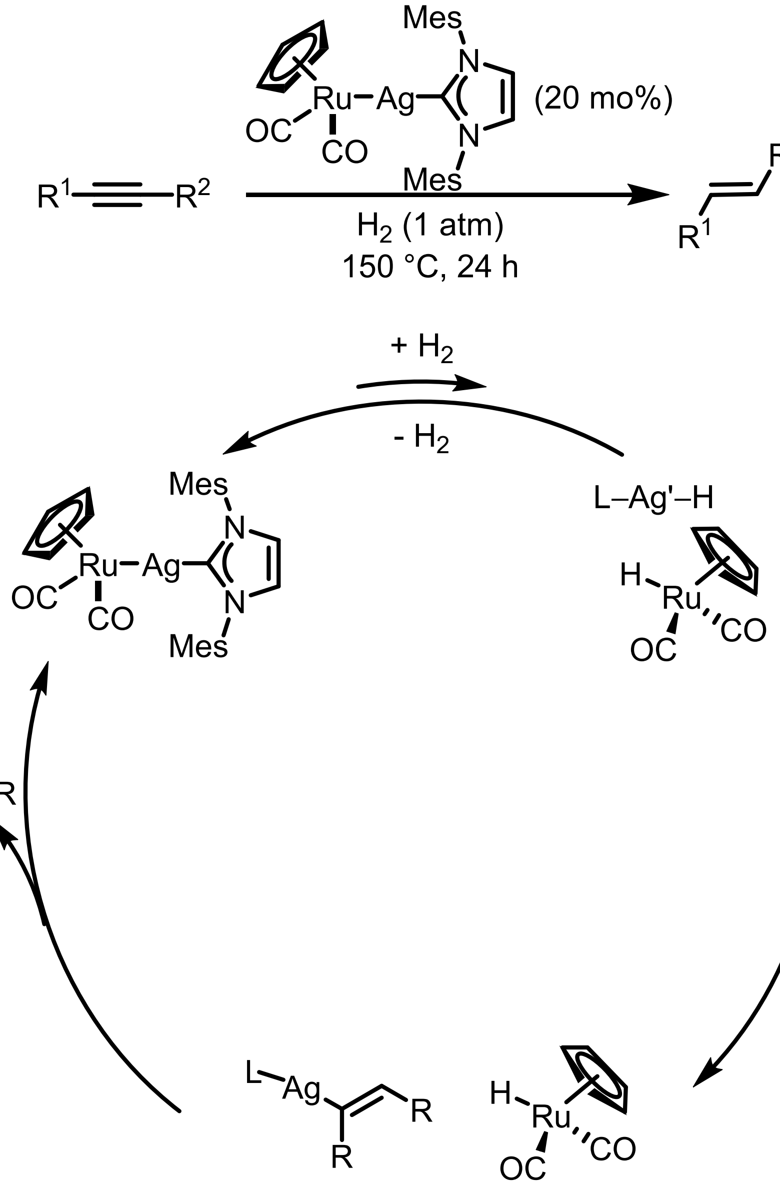






Calculated transition state

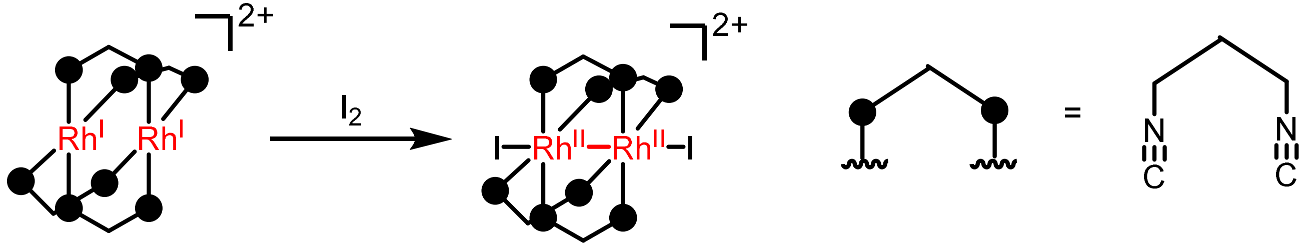
Bergman, R. G. *et al. J. Am. Chem. Soc.* **1994**, *116*, 3822–3835
Bergman, R. G. *et al. J. Am. Chem. Soc.* **1995**, *117*, 11363–11364
Mankad, N. P. *et al. Organometallics.* **2015**, *34*, 3857–3864

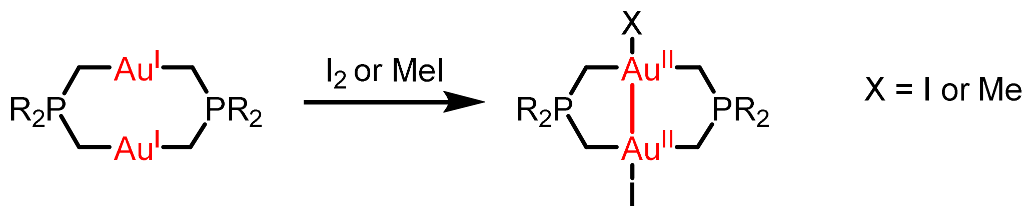


Mankad, N. P. *et al. J. Am. Chem. Soc.* **2015**, *137*, 14598–14601

Organometallic Elementary Steps

Oxidative additions forming a metal-metal bond

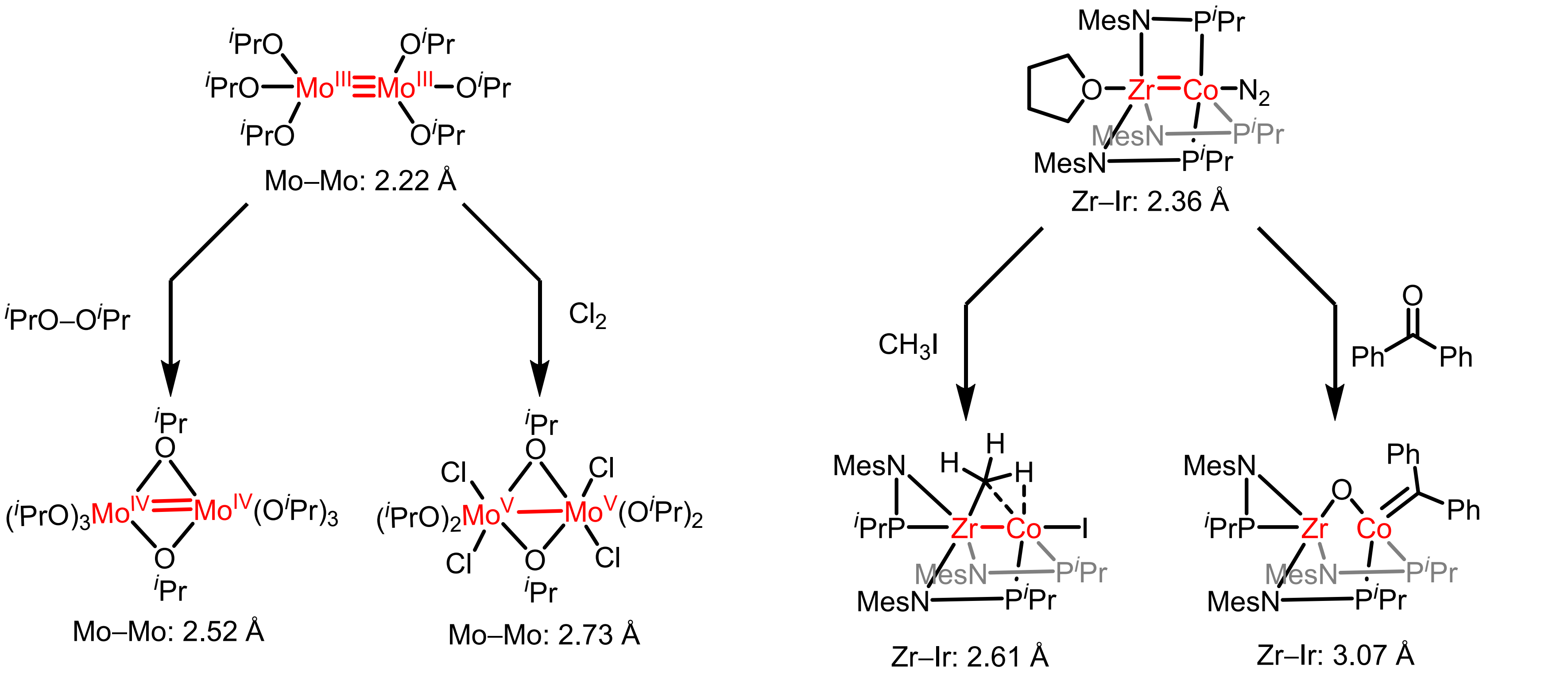




Gray, H. B. *et al. J. Am. Chem. Soc.* **1976**, *98*, 7461–7463
Basil, J. D. *et al. Organometallics* **1982**, *1*, 871–873

Organometallic Elementary Steps

Oxidative additions involving a metal-metal multiple bond



Chrisholm, M. H. *Polyhedron* **1986**, *5*, 25–30

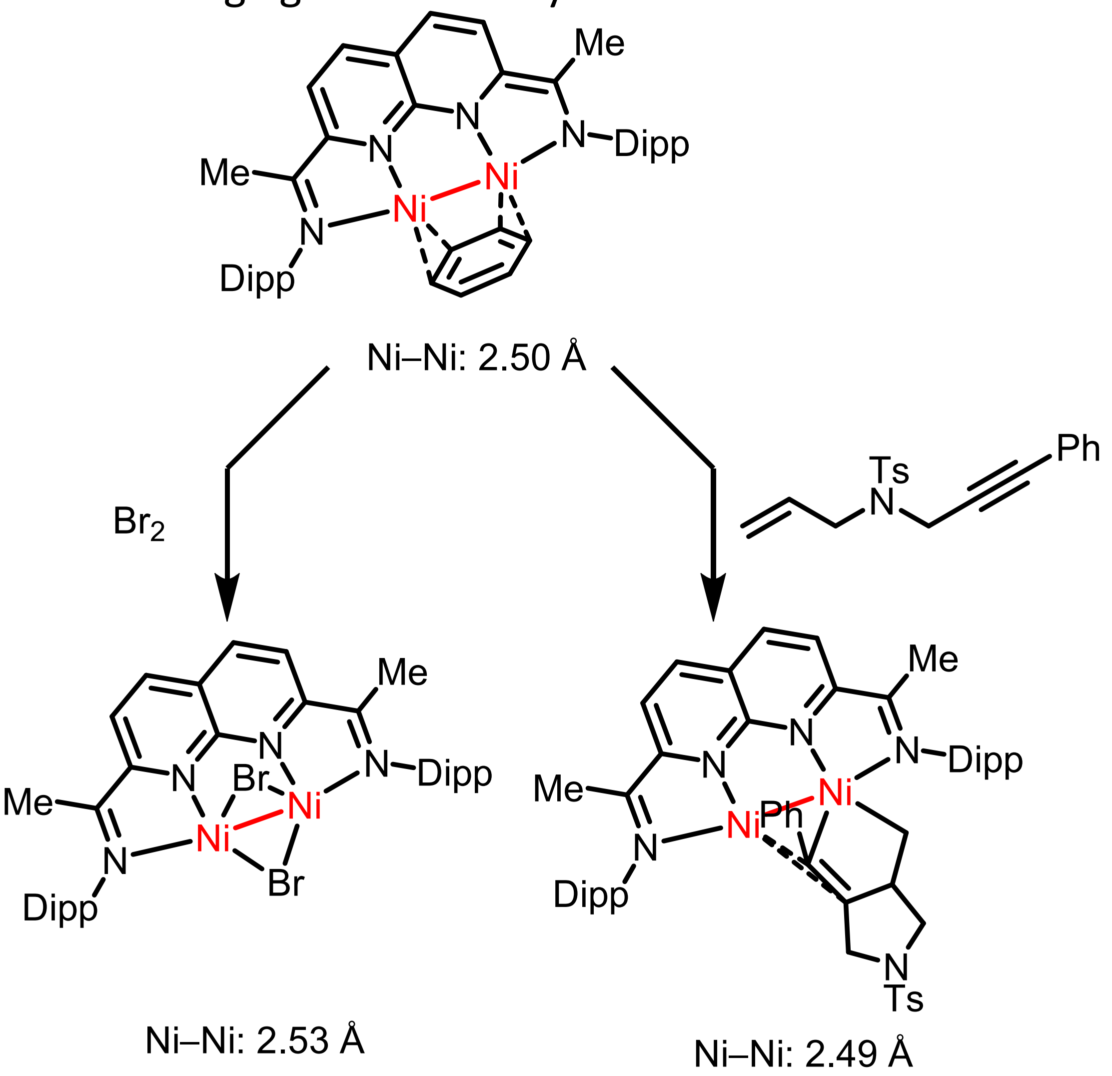
Chrisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 21–30

Thomas, C. M. *et al. Chem. Commun.* **2010**, *46*, 5790–5792

Thomas, C. M. *et al. J. Am. Chem. Soc.* **2013**, *135*, 6018–6021

Organometallic Elementary Steps

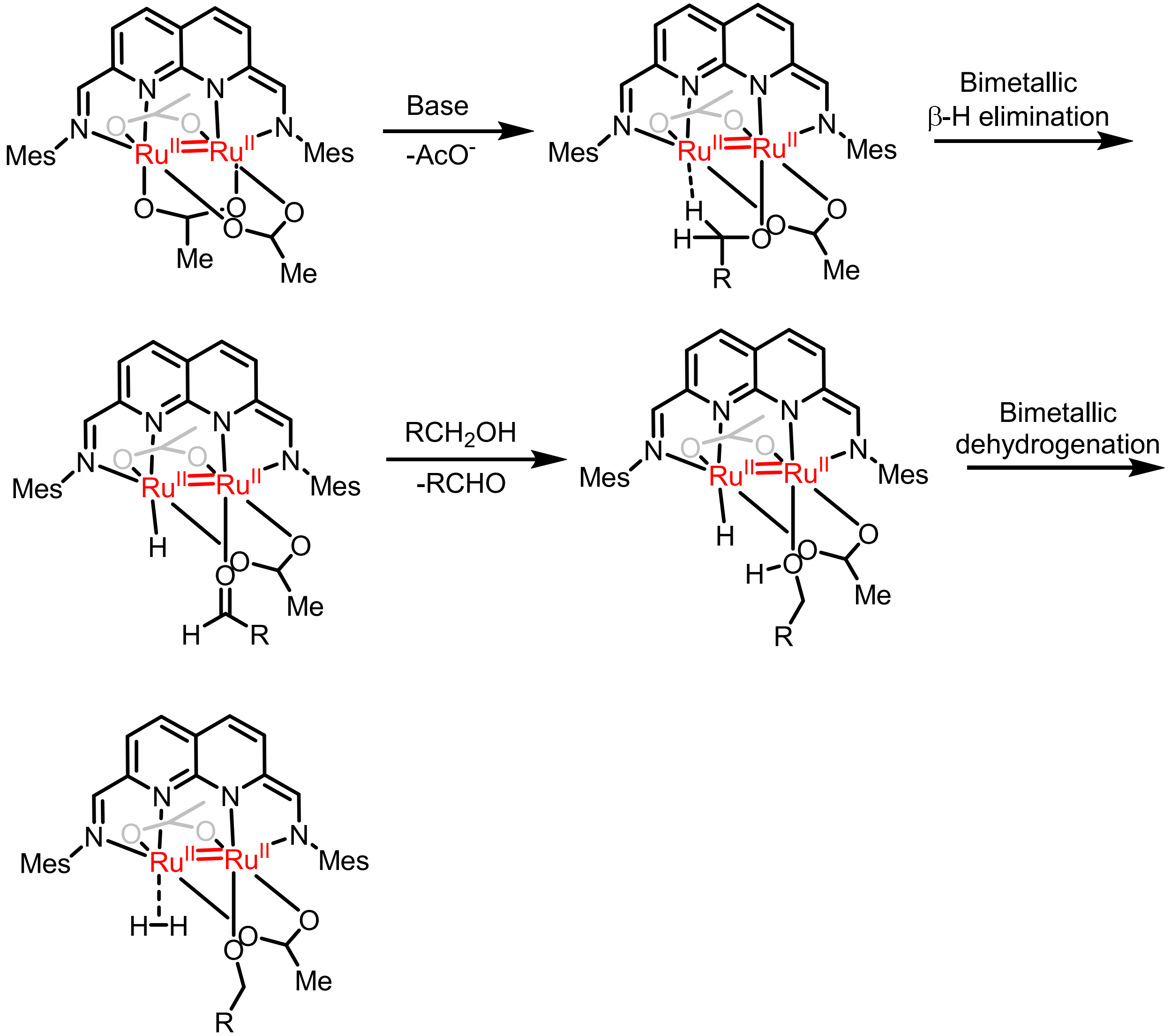
Oxidative additions involving ligand reactivity



Uyeda, C. *Inorg. Chem.* **2014**, *53*, 11770–11777
Uyeda, C. *Angew. Chem. Int. Ed.* **2016**, *55*, 6084–6087

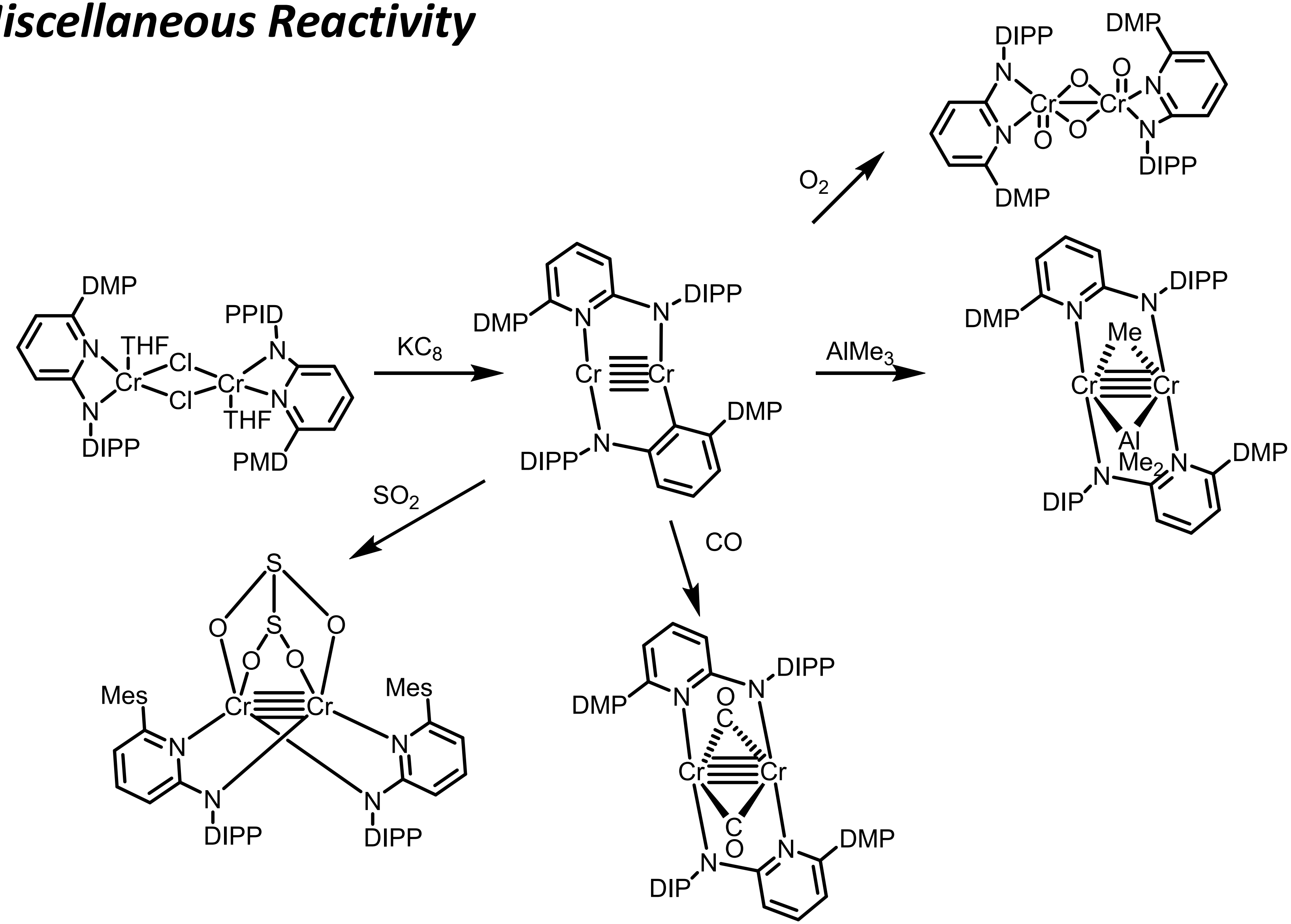
Organometallic Elementary Steps

β-H elimination



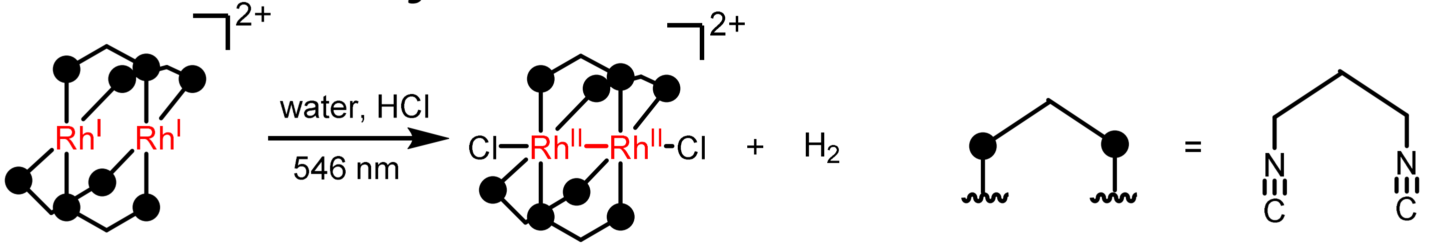
Bera, J. K. *Organometallics* **2016**, *35*, 1505–1513

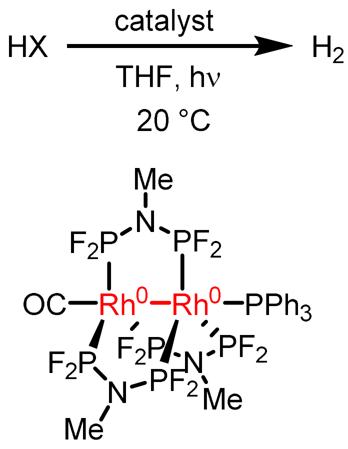
Miscellaneous Reactivity



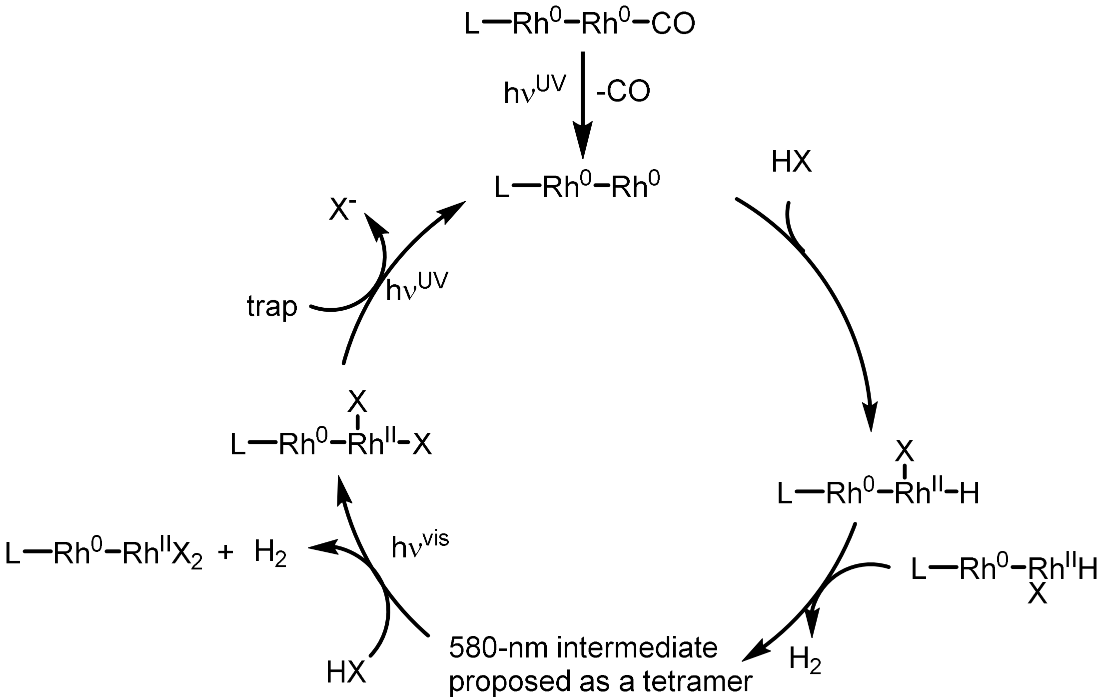
Kempe, R. *et al. Nature Chem.* **2009**, *1*, 322–325
Kempe, R. *et al. Chem. Eur. J.* **2011**, *17*, 6900–6903
Kempe, R. *et al. Chem. Commun.* **2014**, *50*, 13127–13130

Inorganic Reactions of Small Molecules





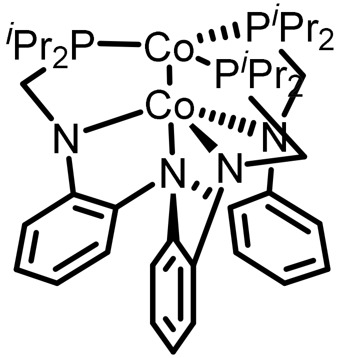
catalyst



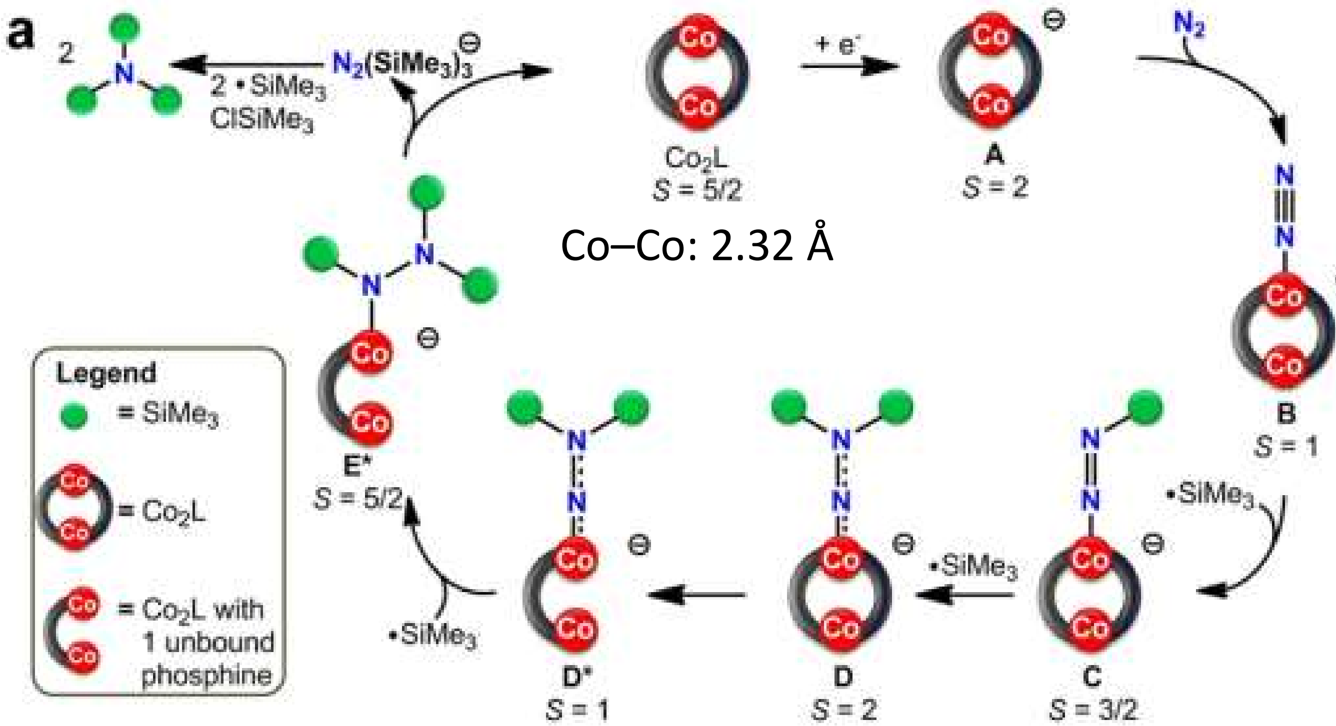
Gary, H. B. *et al. J. Am. Chem. Soc.* **1977**, *99*, 5525–5526
Gary, H. B. *et al. Science* **1981**, *214*, 1201–1205
Nocera, D. G. *et al. Science* **2001**, *293*, 1639–1641
Nocera, D. G. *et al. J. Am. Chem. Soc.* **1999**, *121*, 5023–5032

Inorganic Reactions of Small Molecules

$$N_2 + Me_3SiCl + KC_8 \xrightarrow[\text{THF, 299 K}]{\text{0.05 mol\% precatalyst}} N(SiMe_3)_3$$



precatalyst



Co–Co: 2.32 Å

Co–Co: 2.68 Å

Lu, C. C. *et al. J. Am. Chem. Soc.* **2015**, *137*, 4638–4641
Lu, C. C. *et al. Inorg. Chem.* **2015**, *54*, 9263–9270

Catalytic Reactions

Carbenoid formation with dirhodium tetracarboxylates

$$ROH + N_2CHCO_2Et \xrightarrow[25\ °C]{Rh_2(OAc)_4} ROCH_2CO_2Et + N_2$$

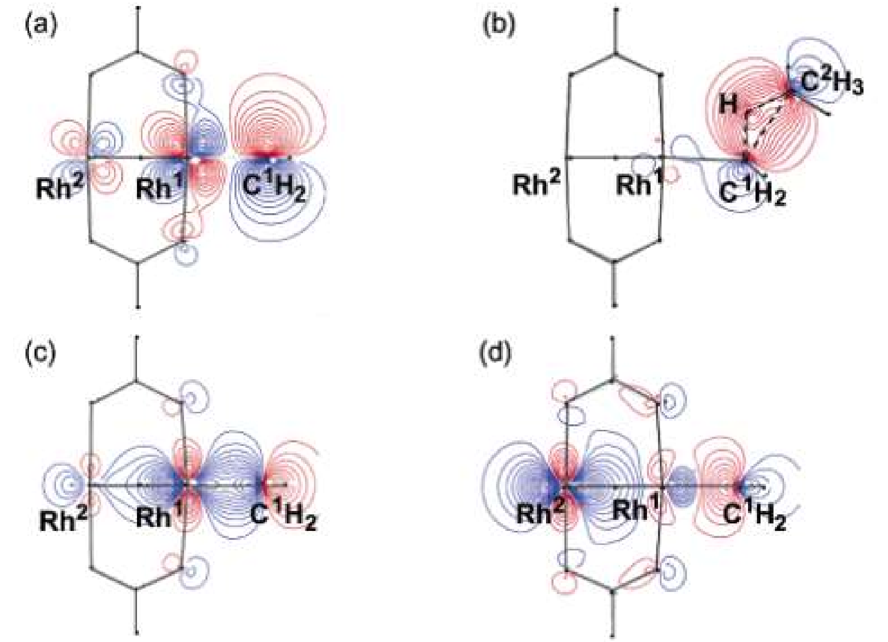
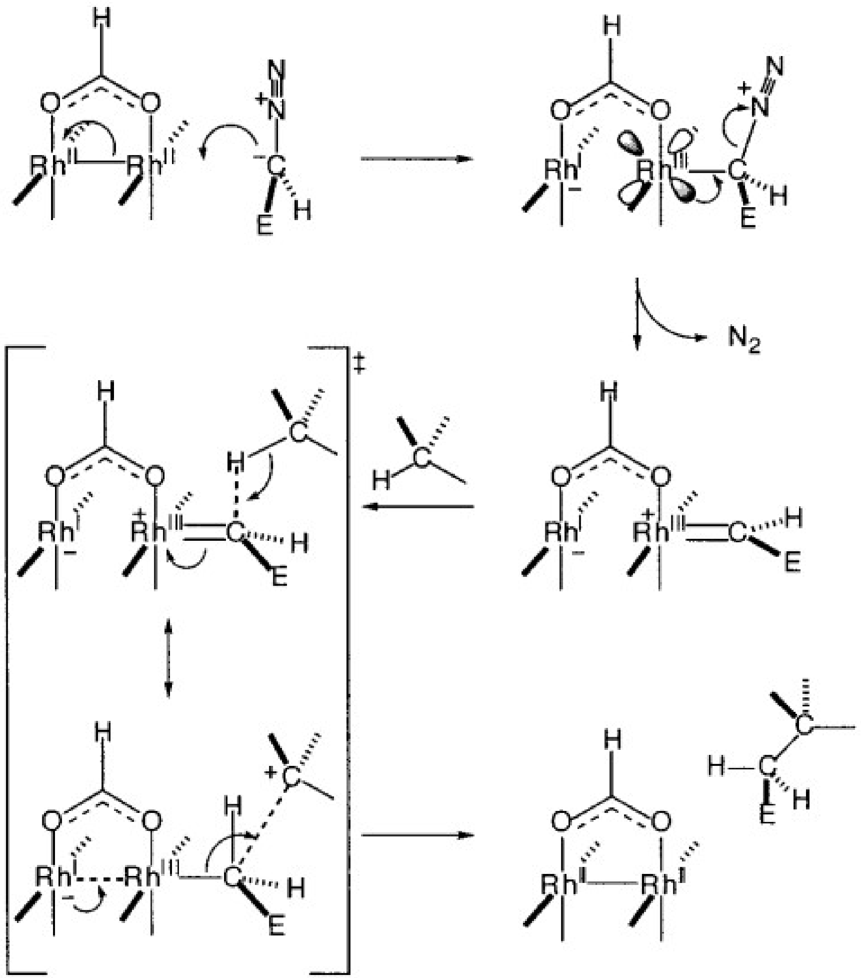
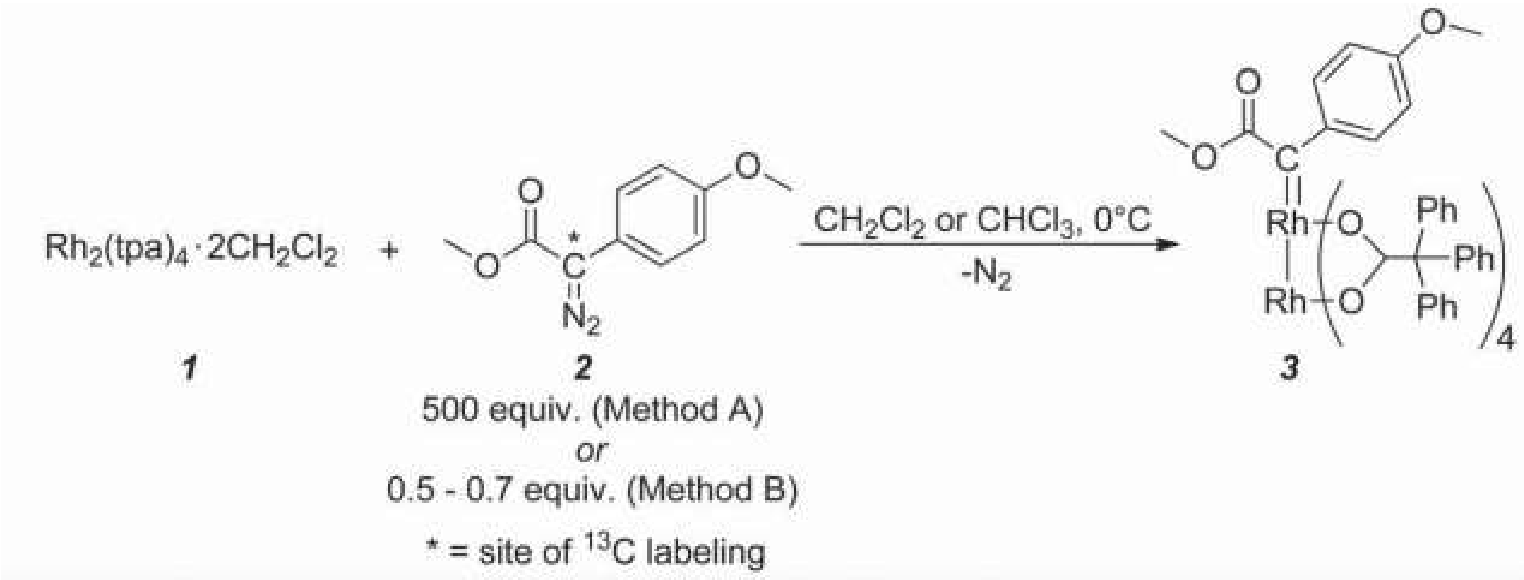
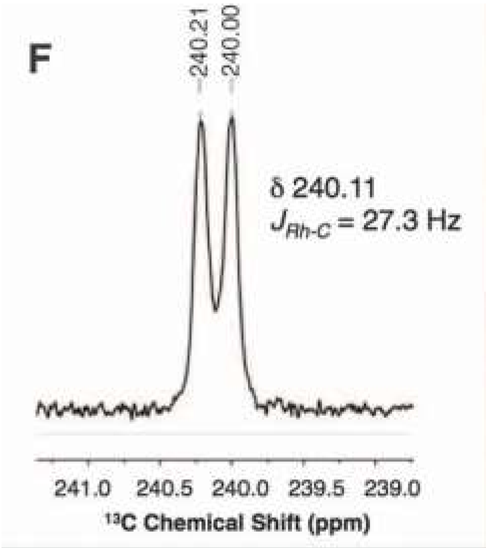


Figure 6. Kohn−Sham orbitals of **V** (a, LUMO; c, HOMO-19; and d, HOMO-3) and LO of **TS-VIIa** responsible for bond alternation (b). The contour intervals are 0.025 e au^{-3}.

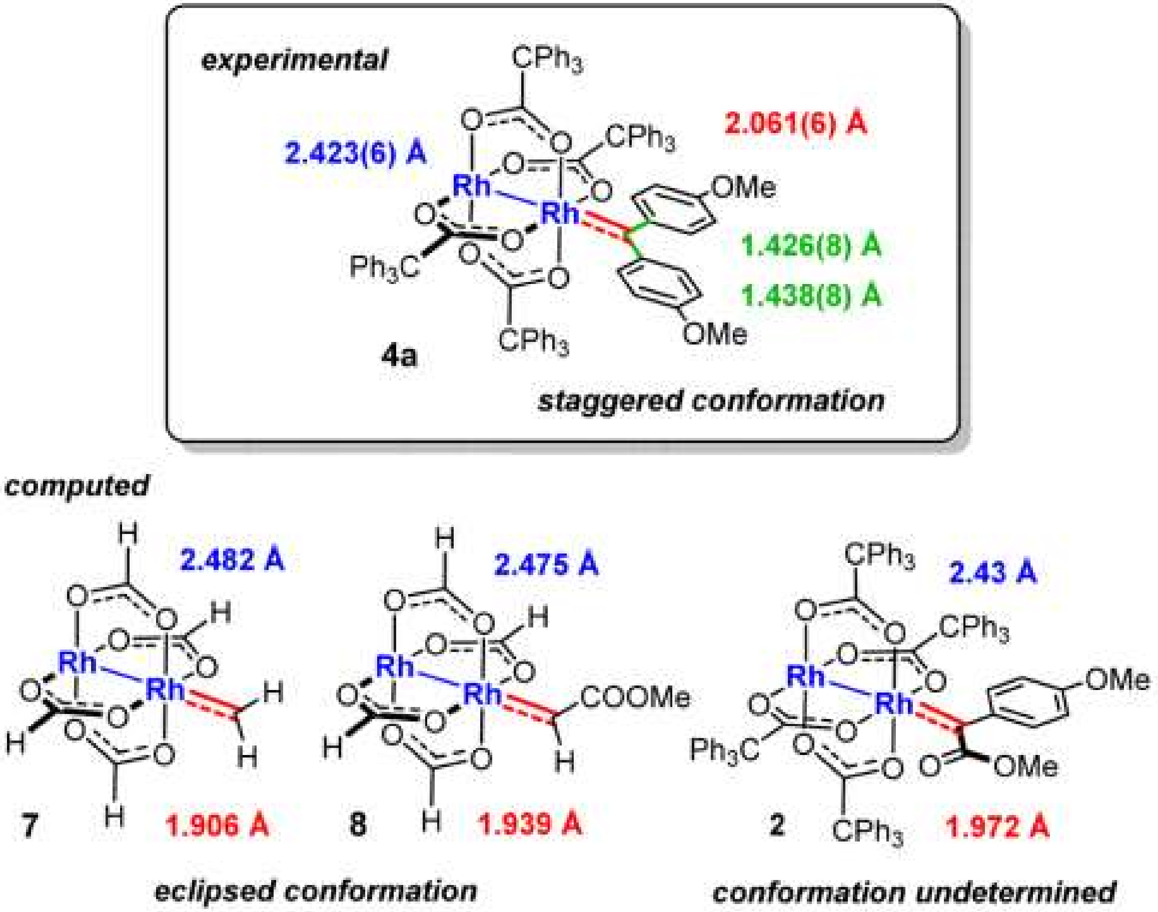


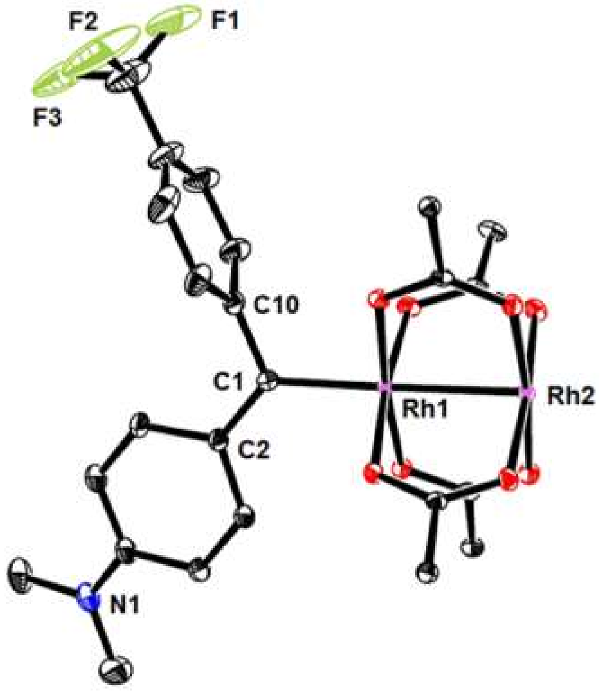
Reimlinger, H. *et al. Tetrahedron Lett.* **1973**, *14*, 2233–2236
Nakamura, E. *et al. J. Am. Chem. Soc.* **2002**, *124*, 7181–7192

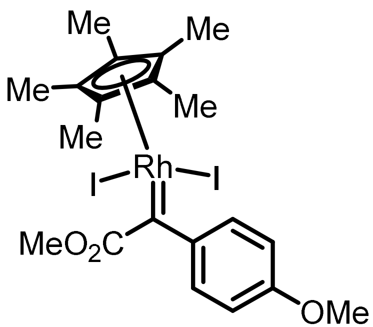


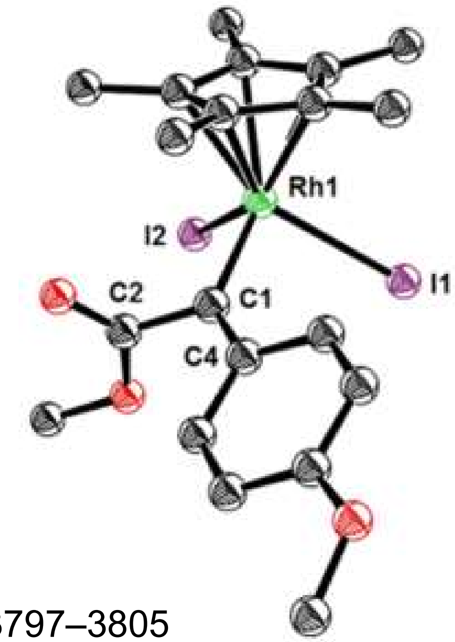


Davis, H. M. L., Berry, J. F. *et al.* *Science* **2013**, *342*, 351–354





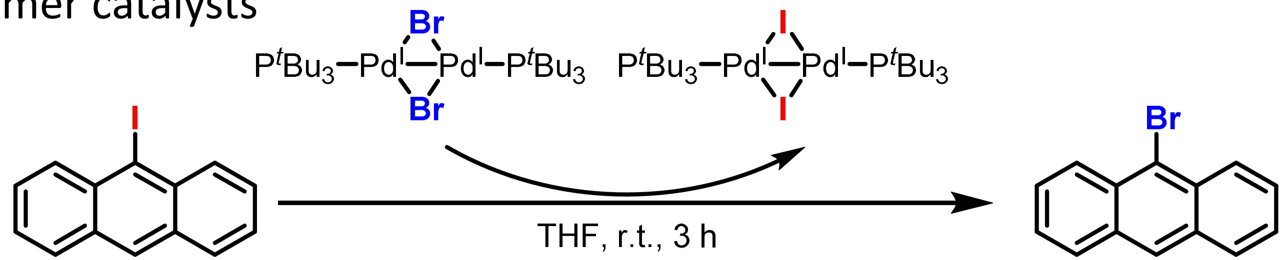


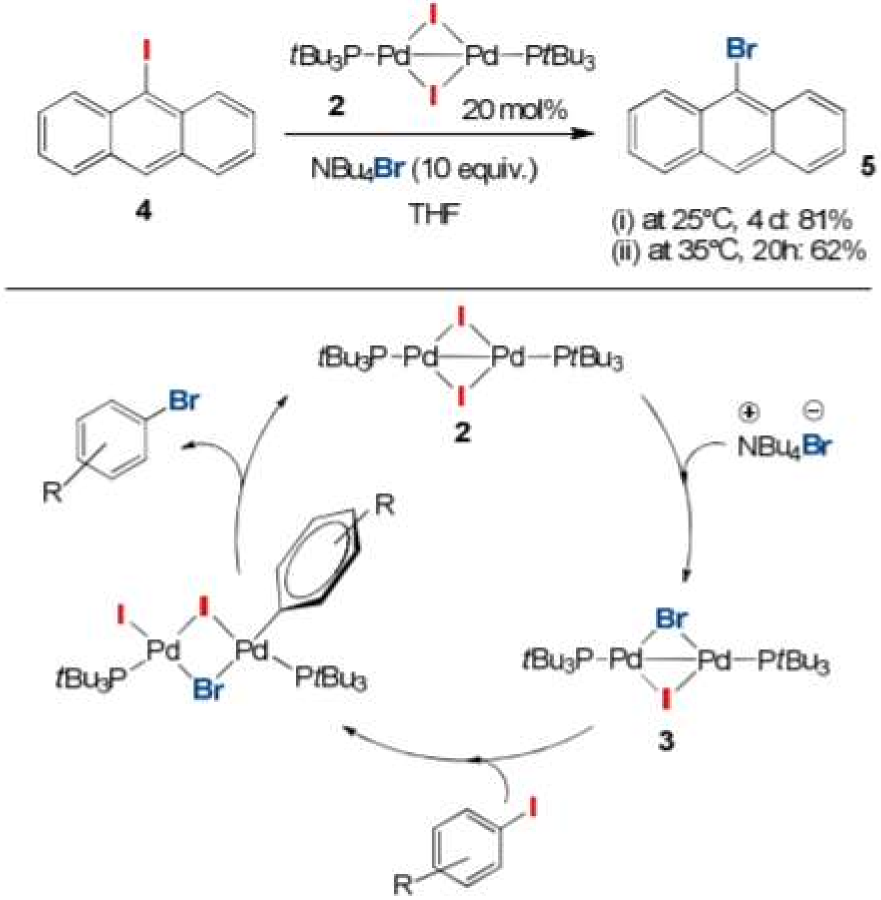


Fürstner, A. *et al. J. Am. Chem. Soc.* **2016**, *138*, 3797–3805

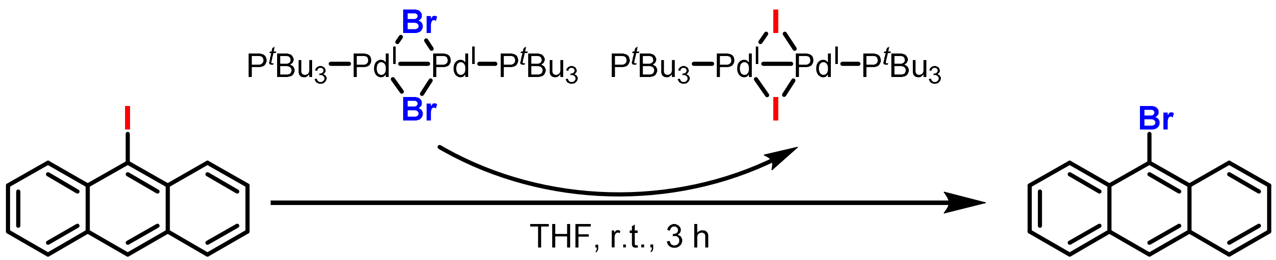
Catalytic Reactions

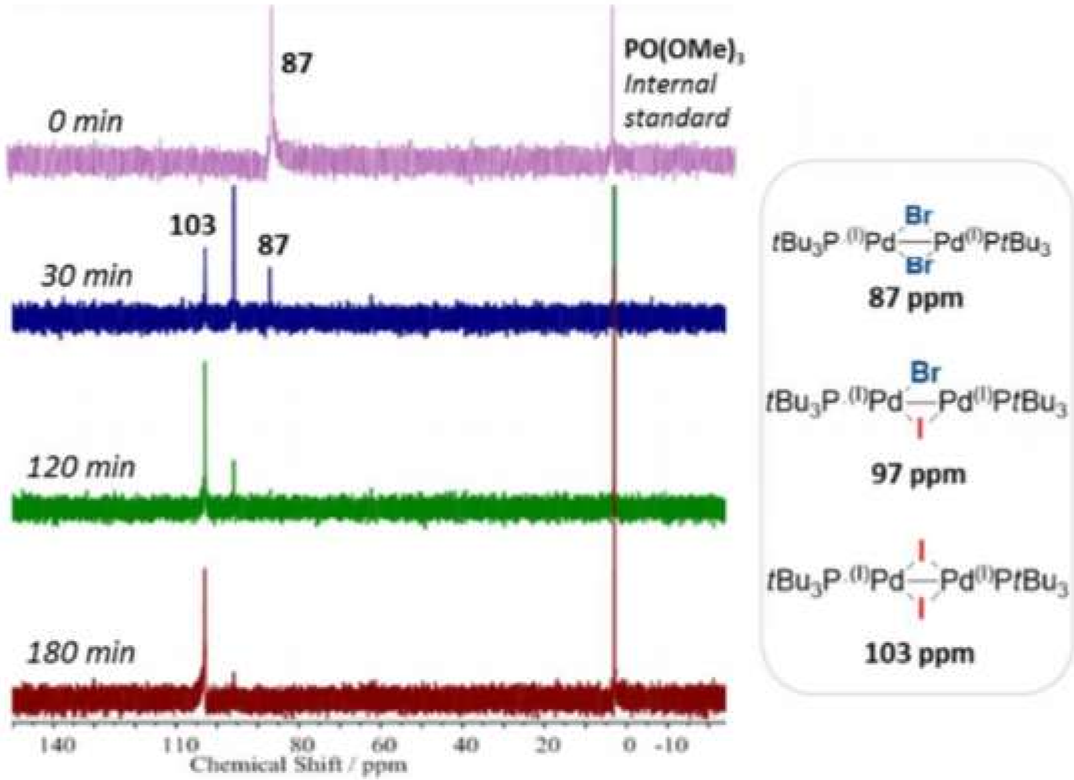
Palladium dimer catalysts



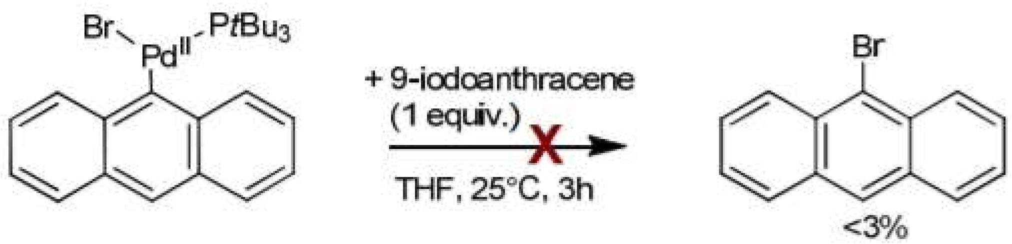


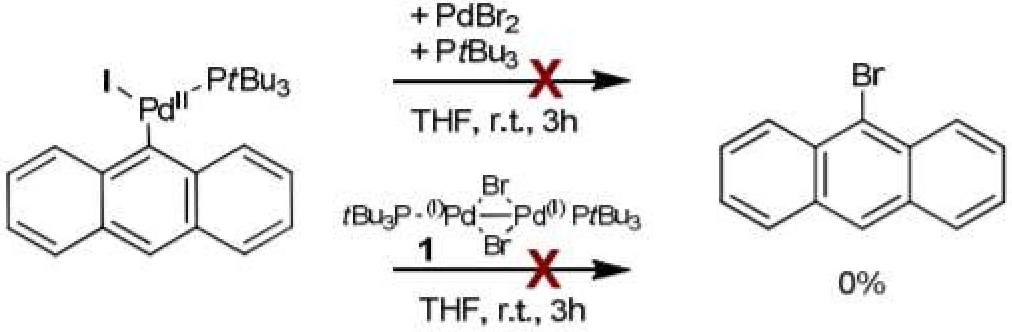
Schoenebeck, F. *et al. Chem. Sci.* **2013**, *4*, 4434–4439

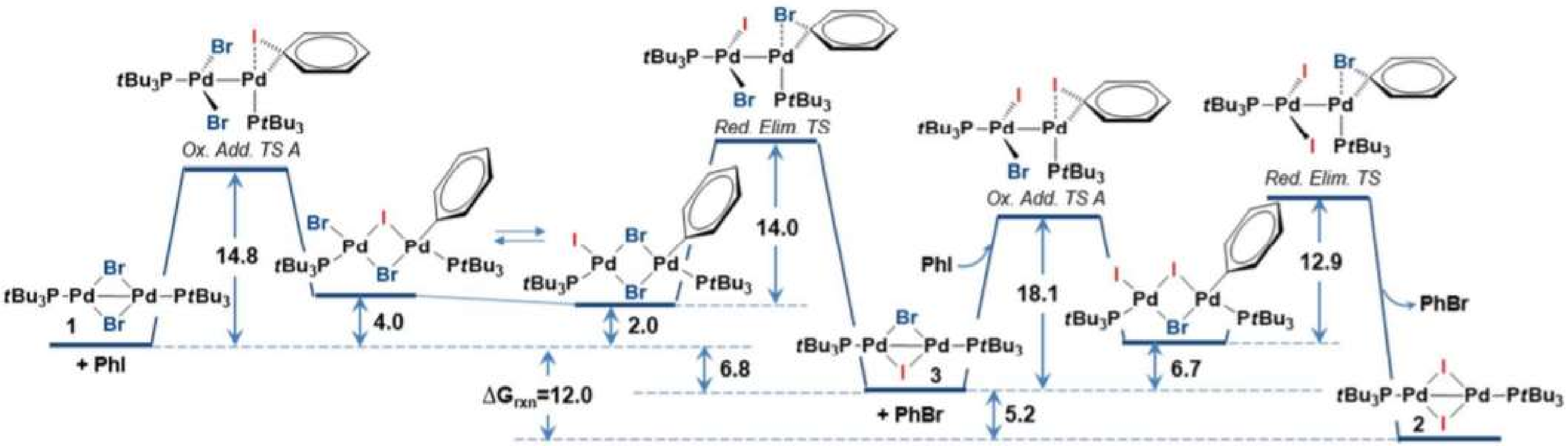




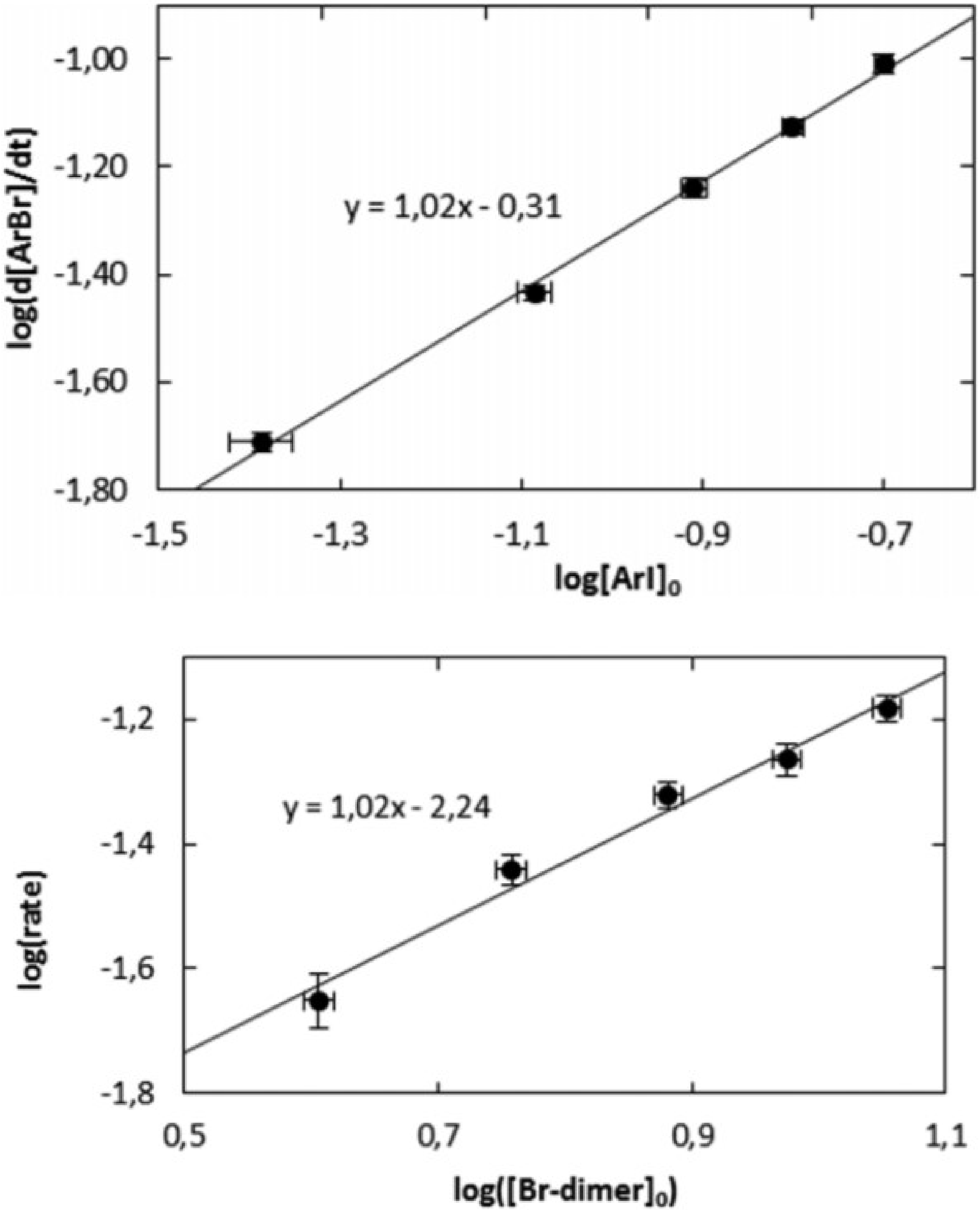
Schoenebeck, F. *et al. Chem. Sci.* **2013**, *4*, 4434–4439







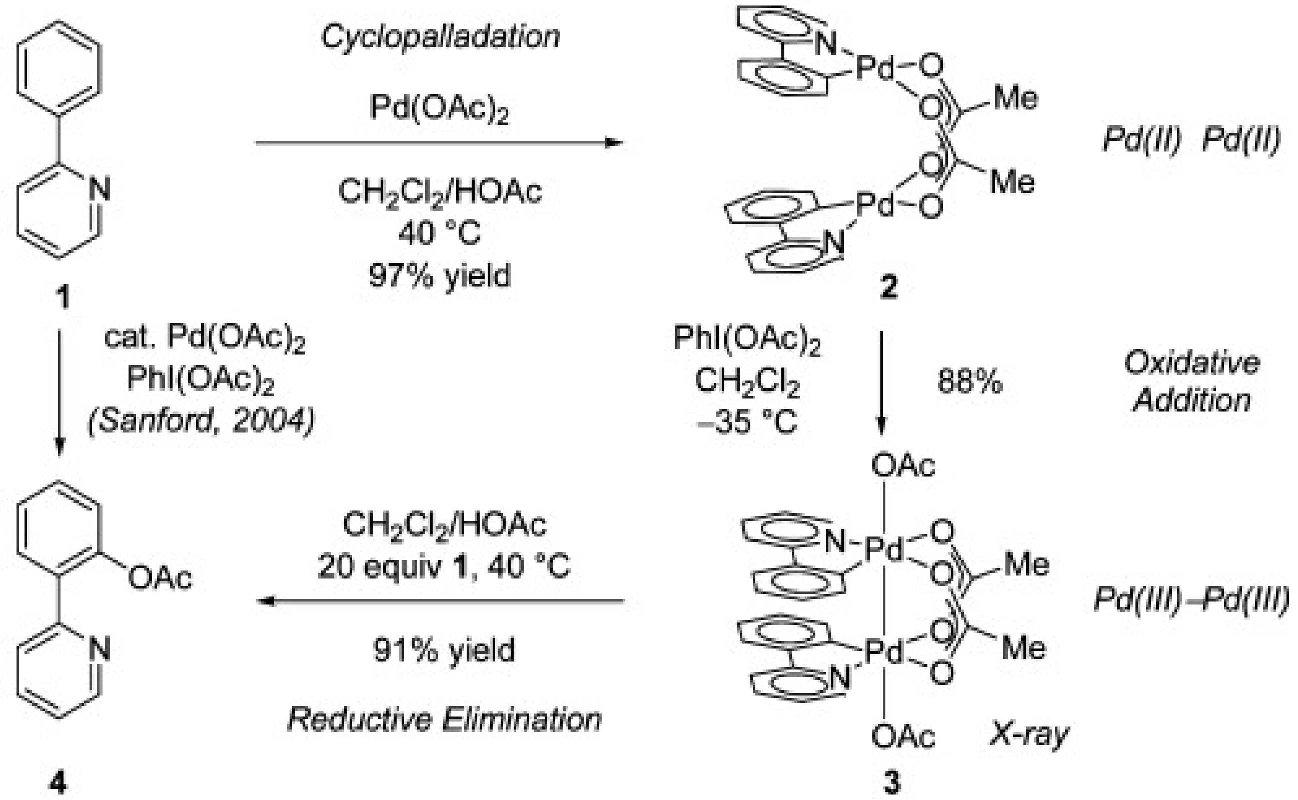
Schoenebeck, F. *et al. Chem. Sci.* **2013**, *4*, 4434–4439



Schoenebeck, F. *et al. J. Org. Chem.* **2014**, *79*, 12041–12046

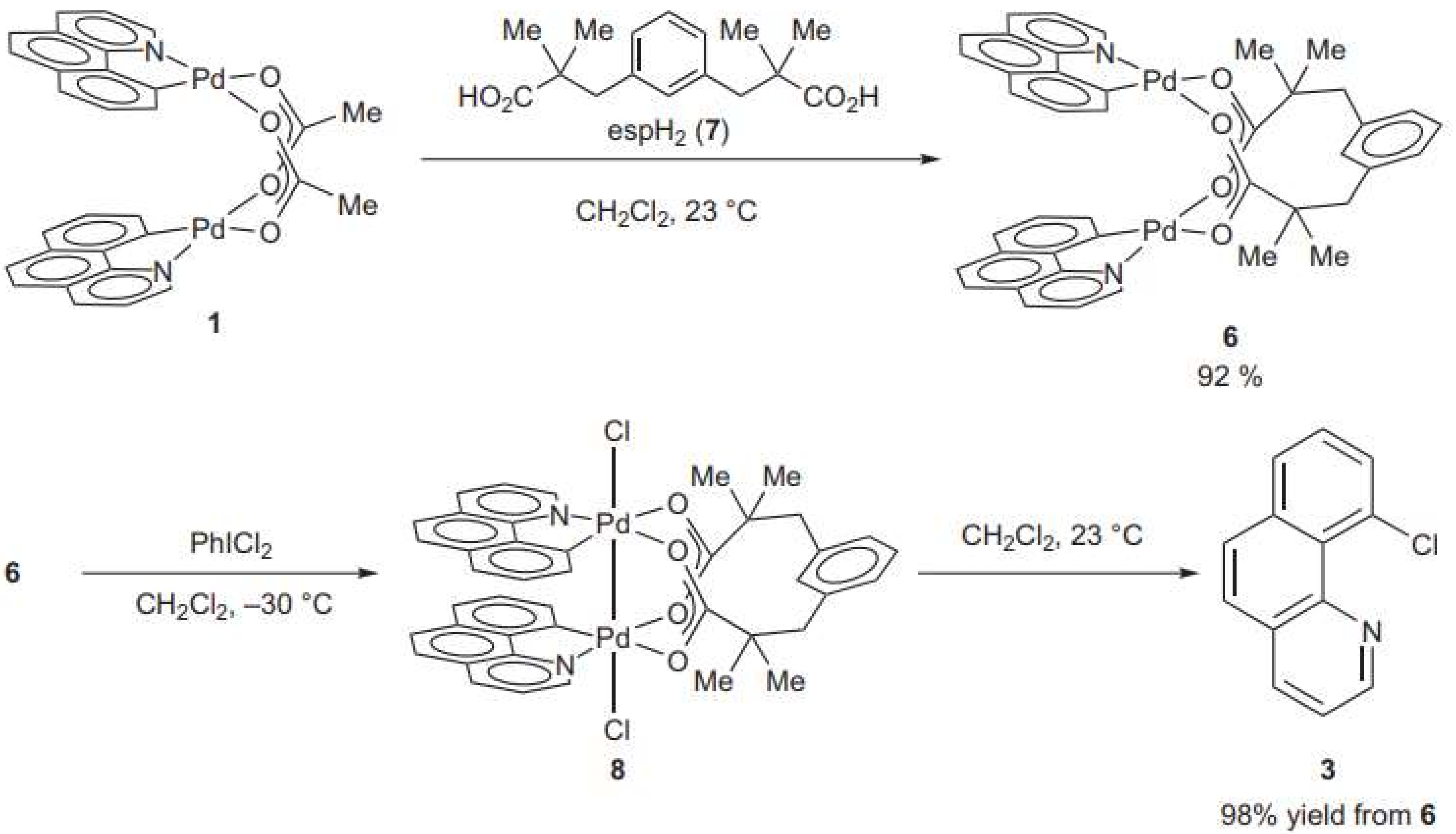
Catalytic Reactions

Palladium(III) dimer

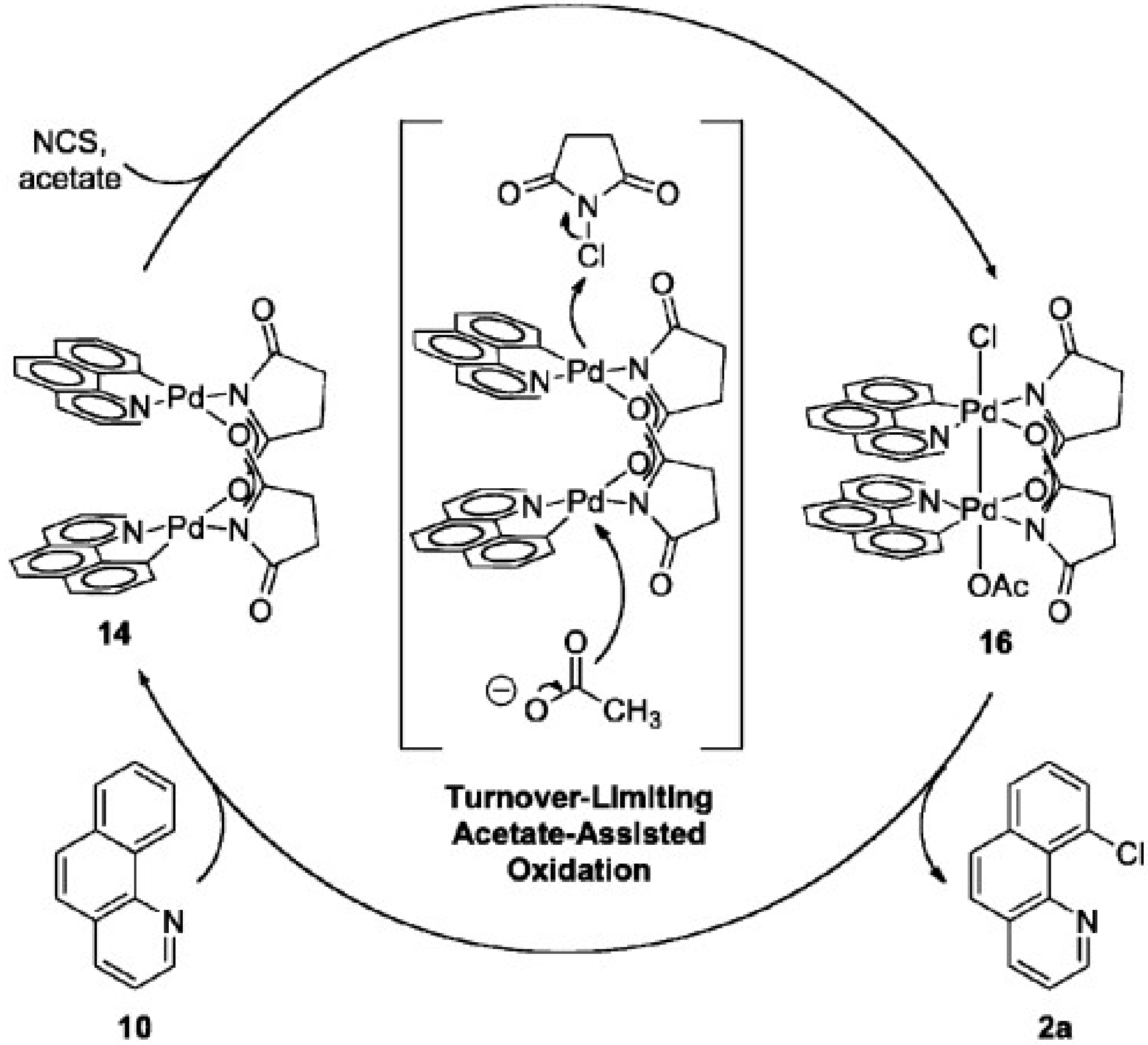


Sanford, M. S. *et al. J. Am. Chem. Soc.* **2004**, *126*, 2300–2301

Ritter, T. *et al. J. Am. Chem. Soc.* **2009**, *131*, 17050–17051

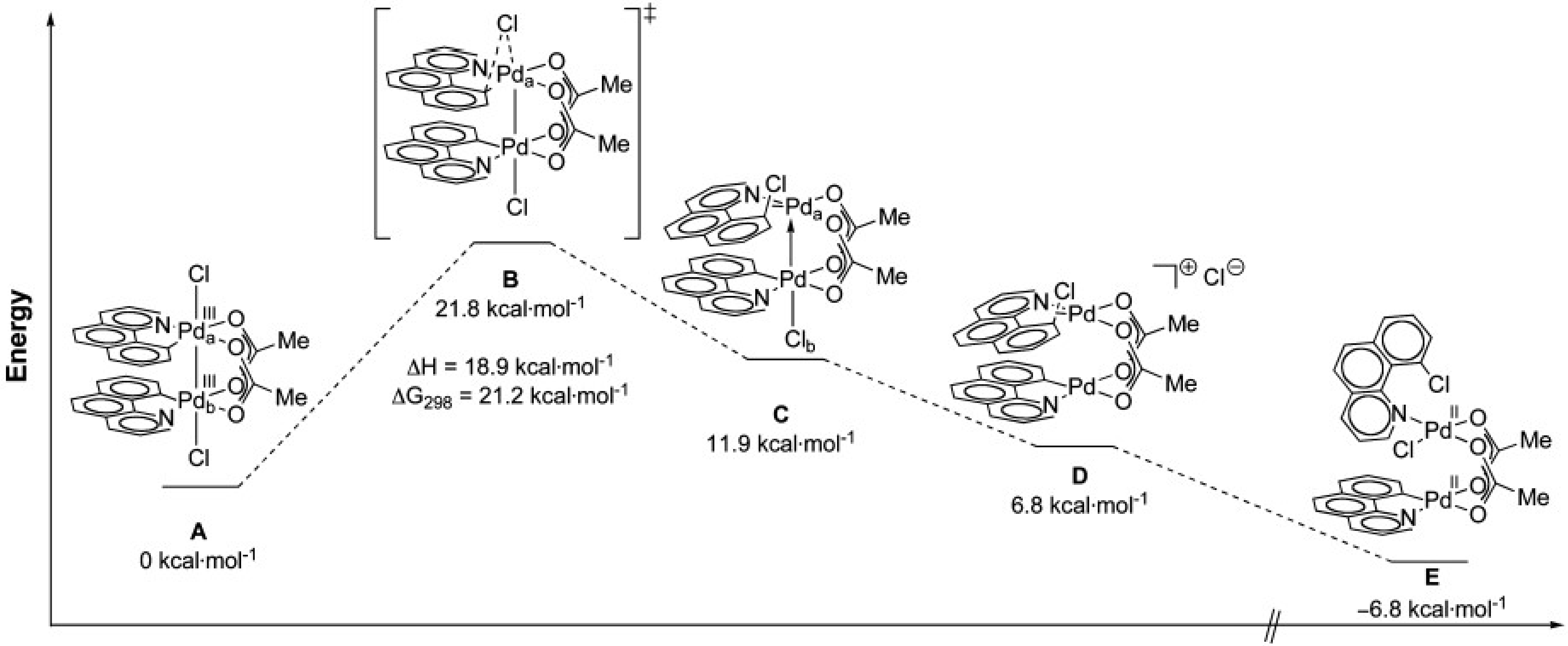


Ritter, T. *et al. Nature Chem.* **2009**, *1*, 302–309



$$\text{rate} = k\,[\mathbf{14}]\,[\text{NCS}]\,[\text{AcO}^-]$$

Ritter, T. *et al. J. Am. Chem. Soc.* **2010**, *132*, 14530–14536

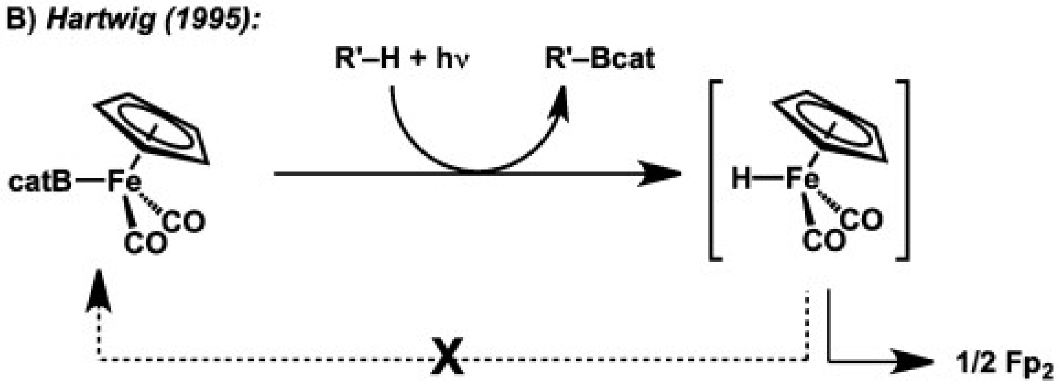


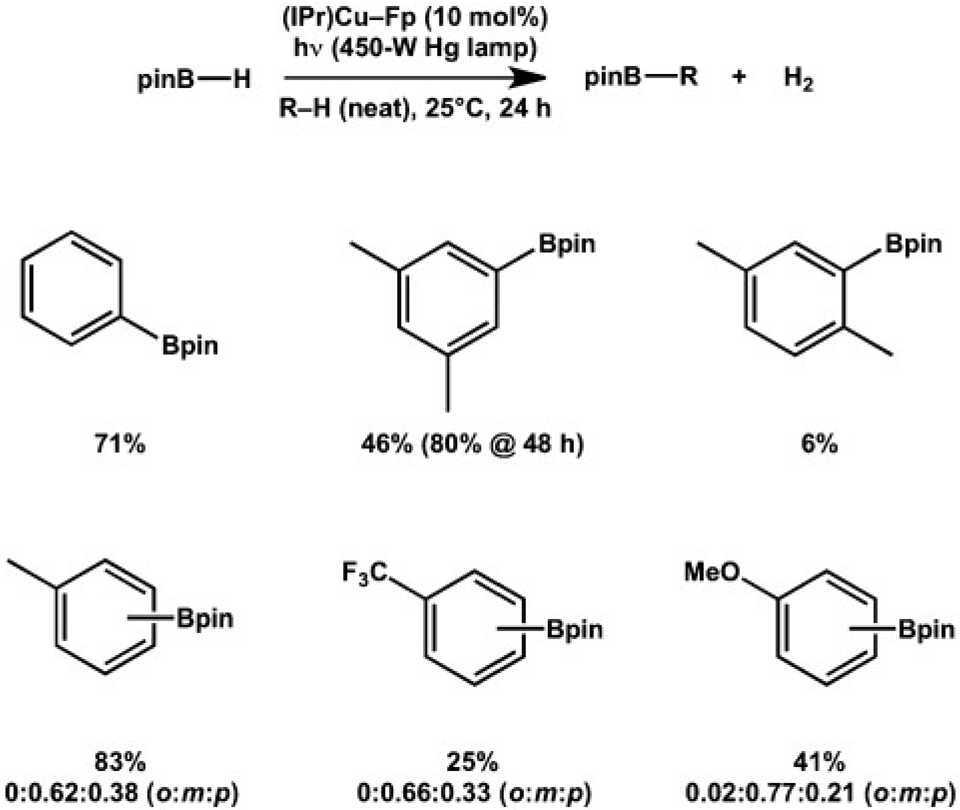
The longer Pd–Pd bond is the higher activation energy

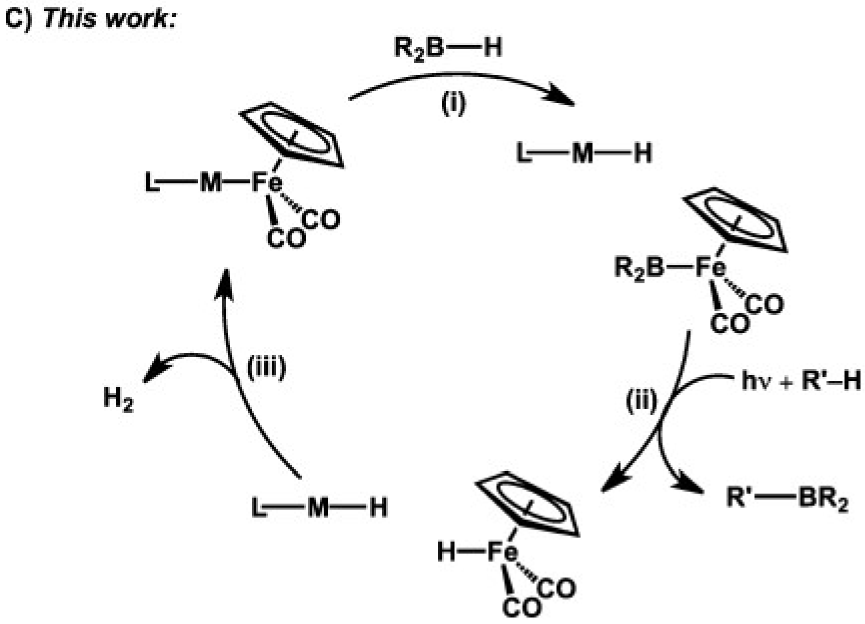
Ritter, T. *et al. J. Am. Chem. Soc.* **2010**, *132*, 14092–14103

Catalytic Reactions

Cu–Fe catalysis



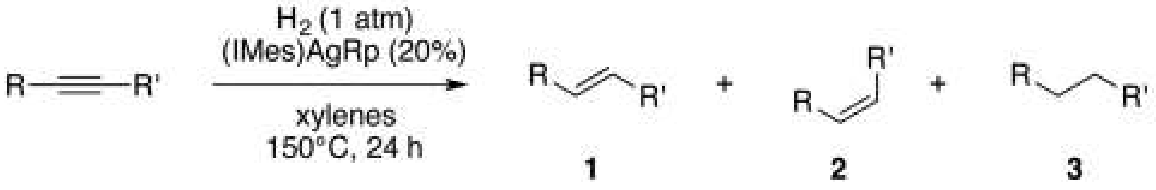




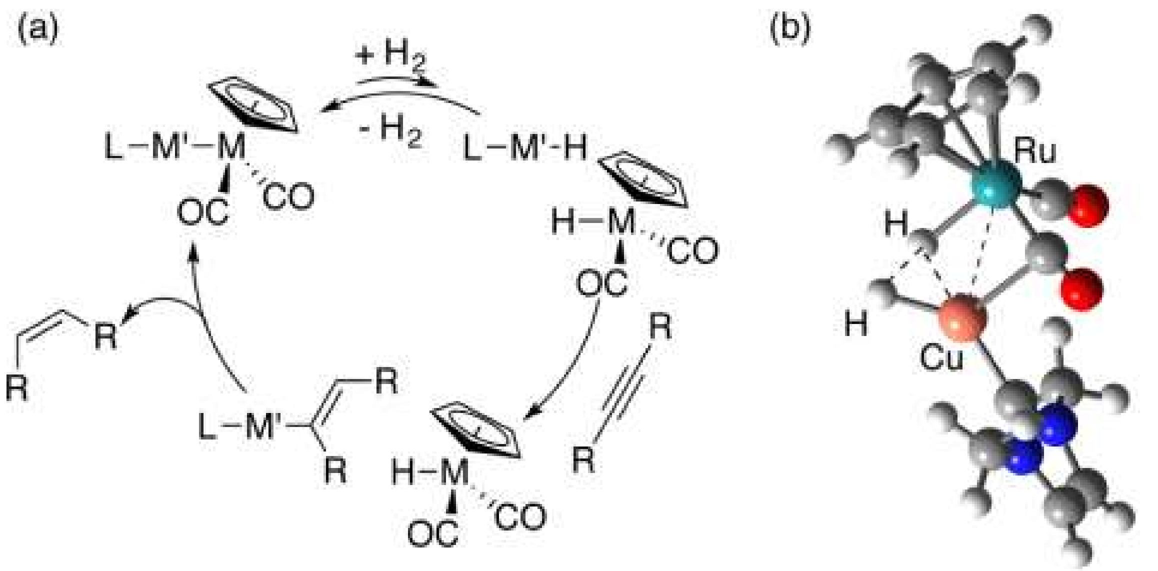
Hartwig, J. F. *et al. J. Am. Chem. Soc.* **1995**, *117*, 11357–11358
Mankad, N. P. *et al. J. Am. Chem. Soc.* **2013**, *135*, 17258–17261

Catalytic Reactions

Ag–Ru catalysis



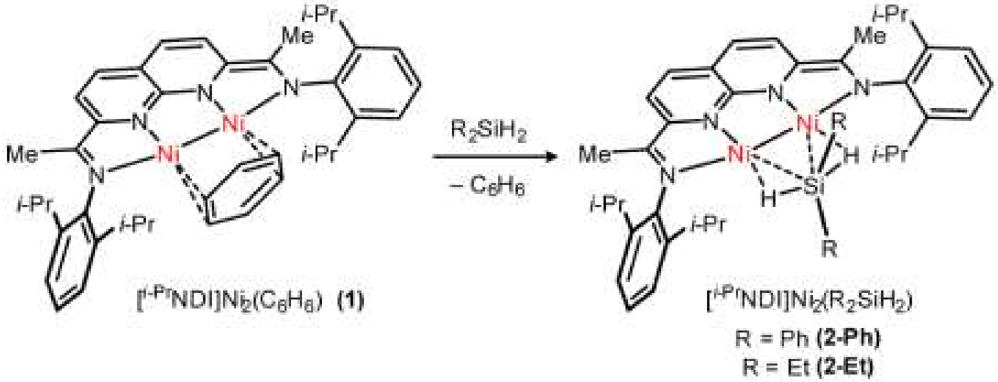
entry	R	R′	conversion (%)[a]	1:2:3[a]
1	Ph	Ph	95.7[b]	90.2:4.2:1.1[b]
2	4-$MeOC_6H_4$	4-$MeOC_6H_4$	>99	71:24:5
3	4-$F_3CC_6H_4$	4-$F_3CC_6H_4$	>99	72:20:8
4	4-(n-$H_{11}C_5$)C_6H_4	H	91	91[c]:n.d.[d]
5	Ph	nBu	>99	n.d.[d]

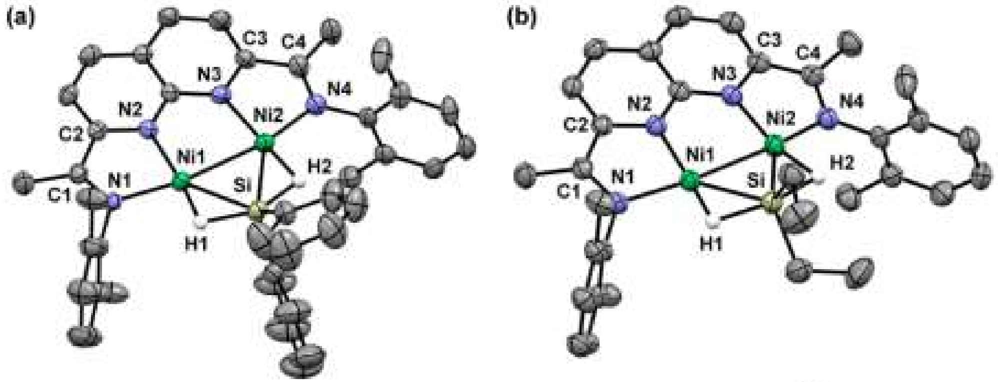


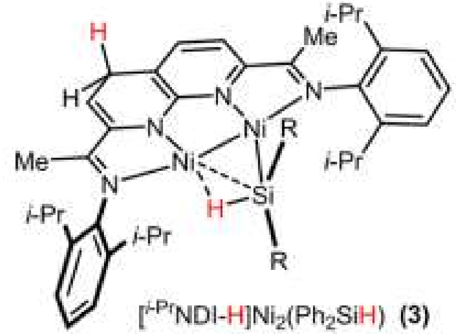
Mankad, N. P. *et al. J. Am. Chem. Soc.* **2015**, *137*, 14598–14601

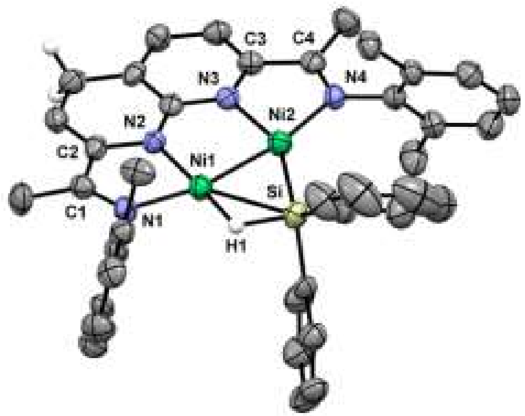
Catalytic Reactions Ni–Ni catalysis

Hydrosilylation

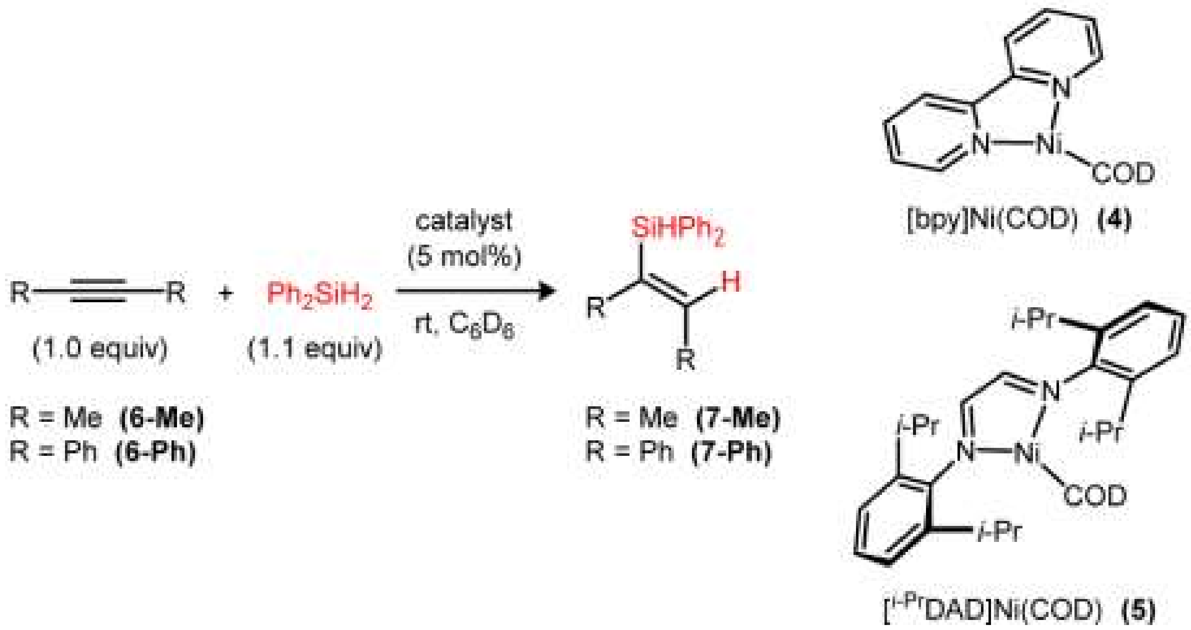








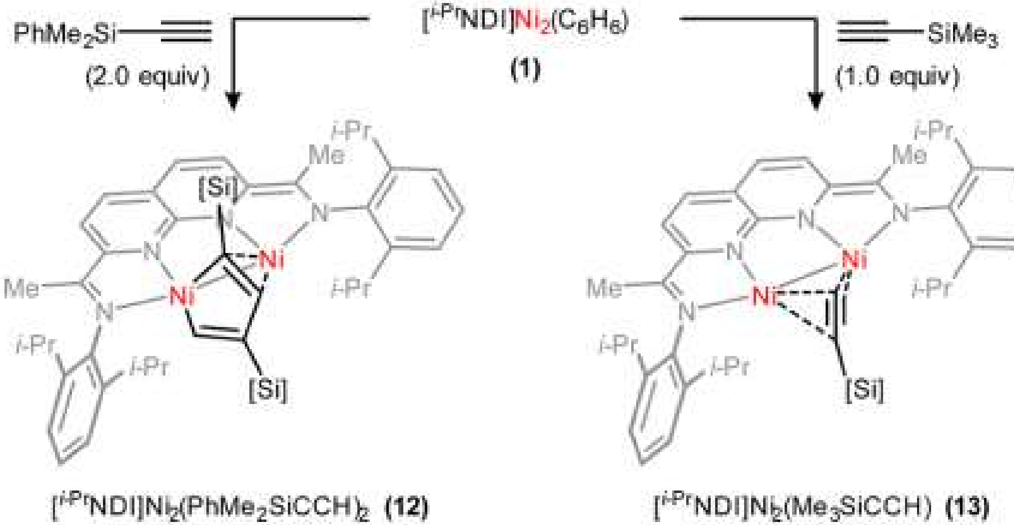
Uyeda, C. *et al. J. Am. Chem. Soc.* **2015**, *137*, 6104–6110

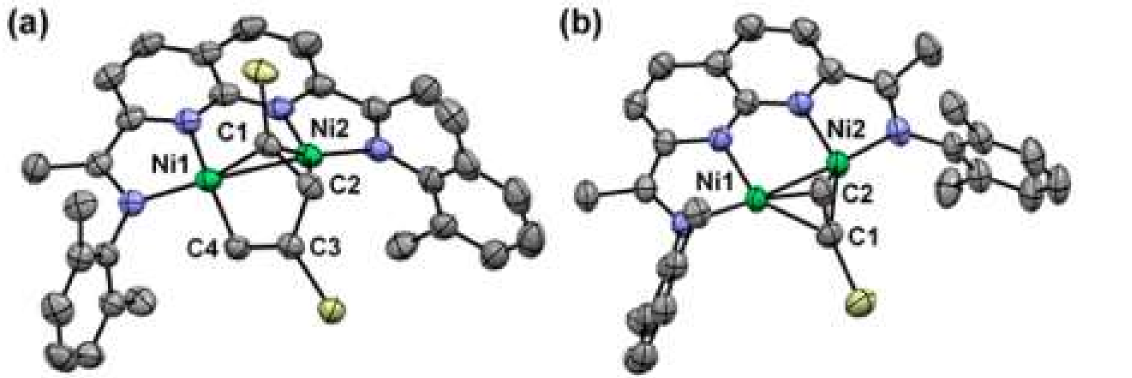


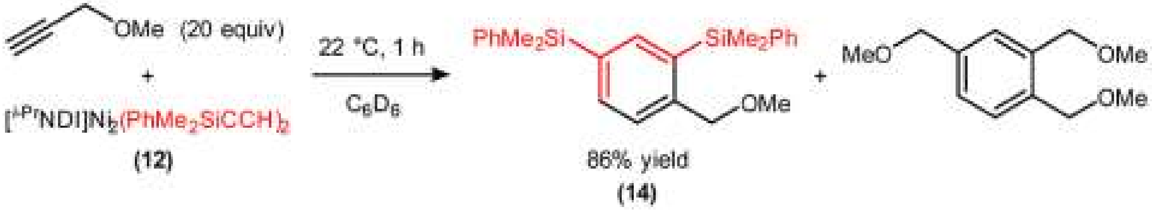
entry	substrate	catalyst	yield of 7
1	**6-Me**	**1**	**93%**
2	6-Me	**4**	77%
3	6-Me	**5**	<1%
4	**6-Ph**	**1**	**93%**
5	6-Ph	**4**	<1%
6	6-Ph	**5**	<1%

Uyeda, C. *et al. J. Am. Chem. Soc.* **2015**, *137*, 6104–6110

Alkyne trimerization



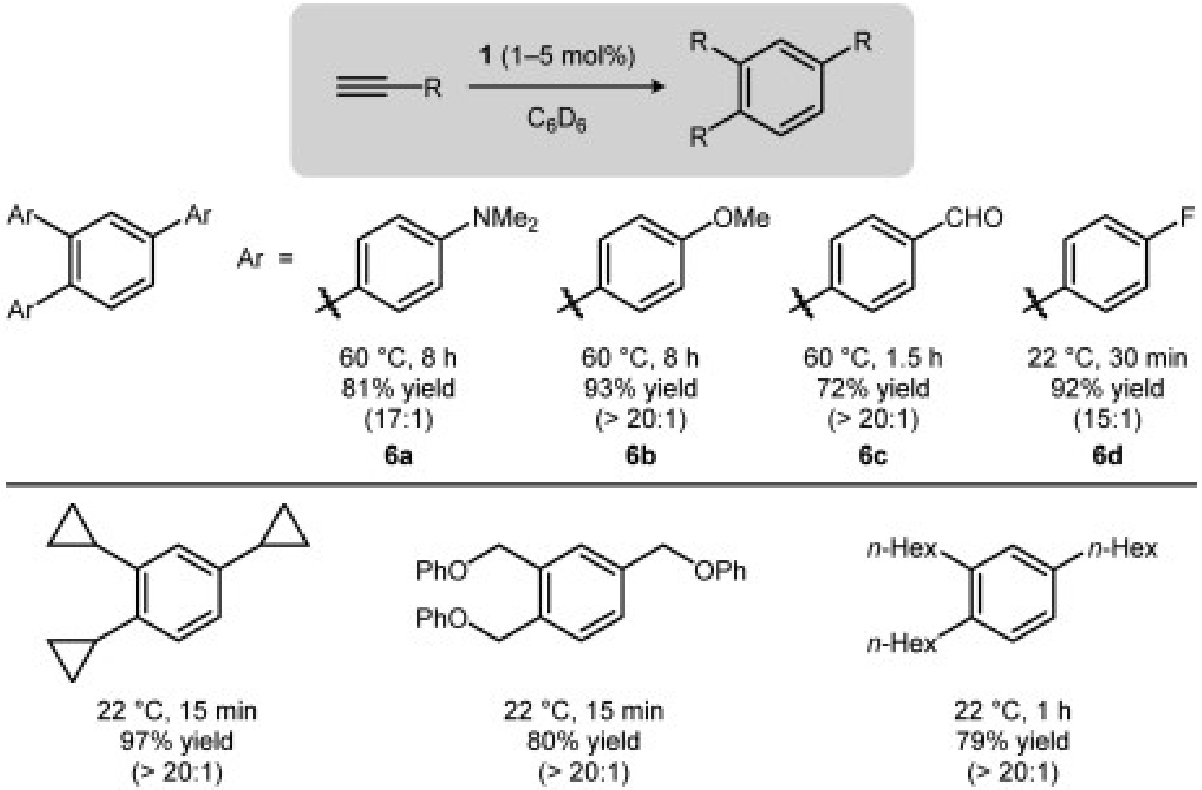




Uyeda, C. *et al. J. Am. Chem. Soc.* **2015**, *137*, 8042–8045

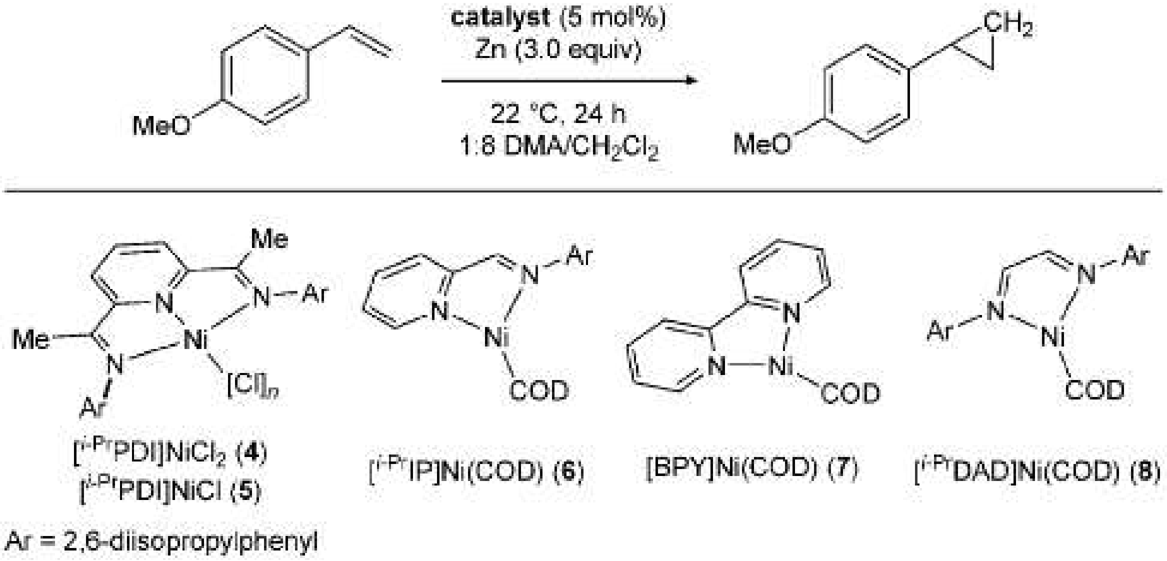
Alkyne trimerization

Superior regioselectivity observed

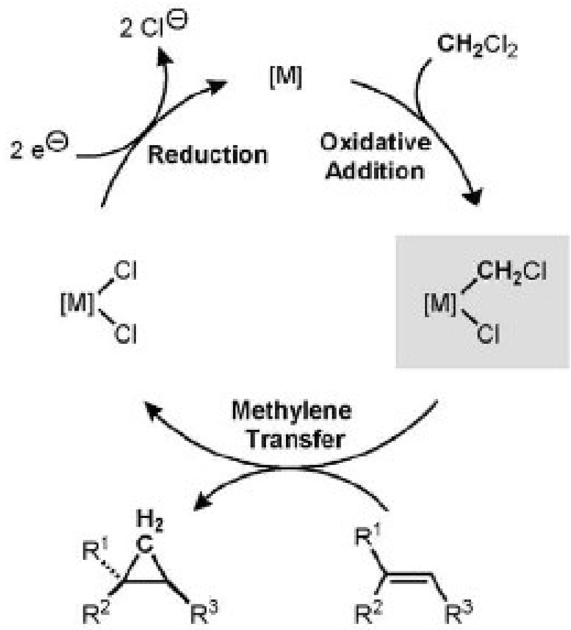


Uyeda, C. *et al. J. Am. Chem. Soc.* **2015**, *137*, 8042–8045

Carbene Transfer

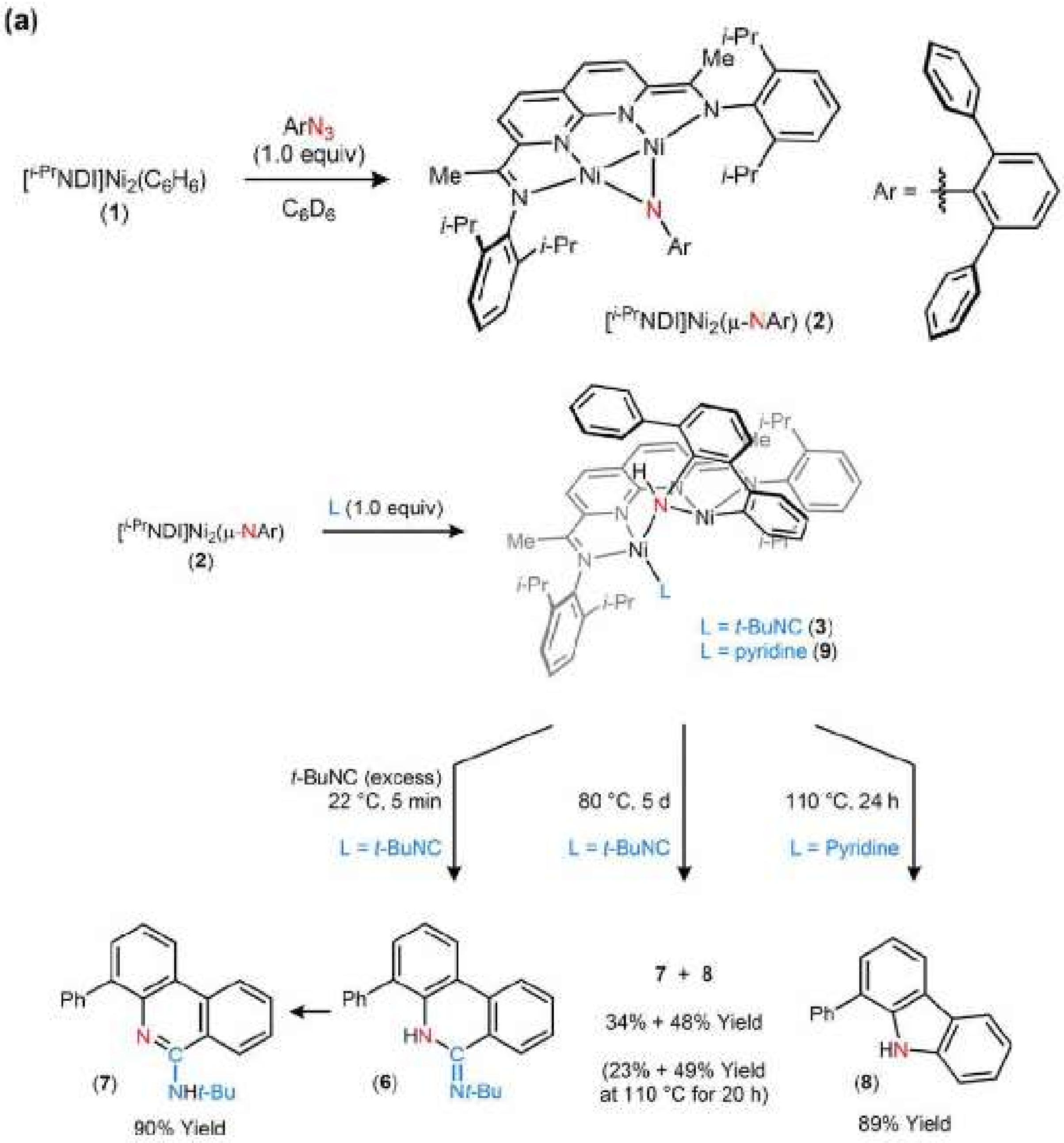


Entry	Catalyst	Conversion [%]	Yield [%]
1	$[^{i\text{-}Pr}NDI]Ni_2(C_6H_6)$ (**1**)	>99	69
2	–	0	0
3	$Ni(COD)_2$	35	2
4	$[^{i\text{-}Pr}PDI]NiCl_2$ (**4**)	>99	19
5	$[^{i\text{-}Pr}PDI]NiCl$ (**5**)	>99	20
6	$[^{i\text{-}Pr}IP]Ni(COD)$ (**6**)	52	19
7	[BPY]Ni(COD) (**7**)	82	8
8	$[^{i\text{-}Pr}DAD]Ni(COD)$ (**8**)	38	2
9	$[^{i\text{-}Pr}NDI]Ni_2Cl$ (**2**)	>99	76
10	$[^{i\text{-}Pr}NDI]Ni_2Cl_2$ (**3**)	>99	64



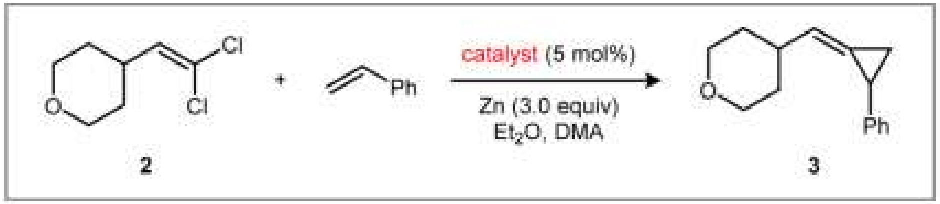
Uyeda, C. *et al. Angew. Chem. Int. Ed.* **2016**, *55*, 3171–3175

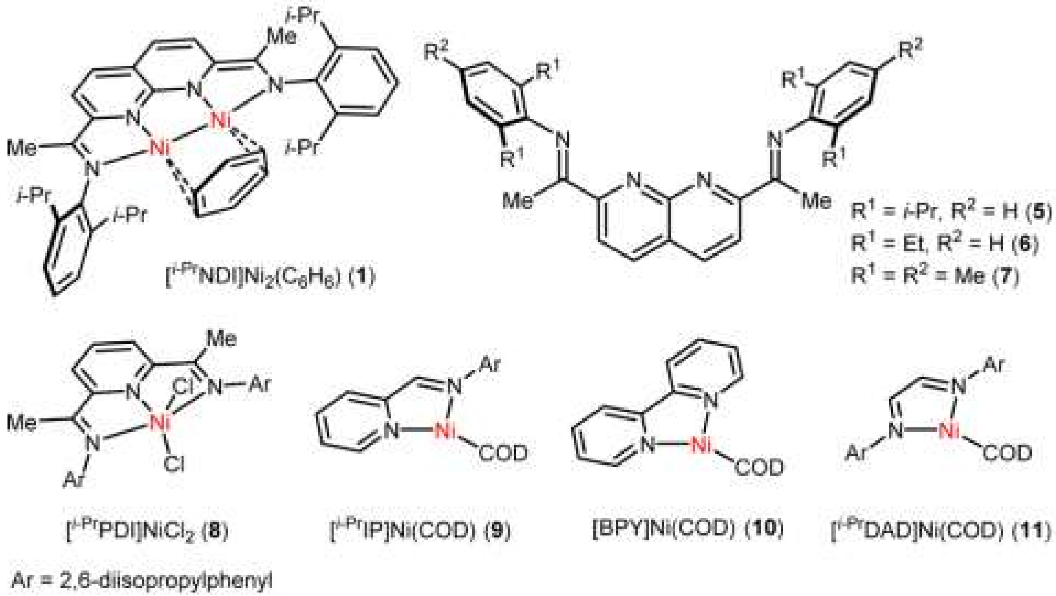
Nitrene Transfer



Uyeda, C. *et al. Chem. Eur. J.* **2017**, *23*, 7694–7697

Vinylidene Transfer





entry	catalyst	yield	E/Z ratio
1	$[^{i\text{-Pr}}$NDI$]Ni_2(C_6H_6)$ (**1**)	94%	1:5
2	$[^{i\text{-Pr}}$NDI$]Ni_2Cl_2$ (**4**)	87%	1:5
3[b]	$^{i\text{-Pr}}$NDI (**5**) + Ni(DME)Cl_2	92%	1:5
4[b]	^{Et}NDI (**6**) + Ni(DME)Cl_2	50%	1:1
5[b]	^{Me}NDI (**7**) + Ni(DME)Cl_2	<2%	–
6	$[^{i\text{-Pr}}$PDI$]NiCl_2$ (**8**)	<2%	–
7	$[^{i\text{-Pr}}$IP$]$Ni(COD) (**9**)	<2%	–
8	[BPY]Ni(COD) (**10**)	<2%	–
9	$[^{i\text{-Pr}}$DAD$]$Ni(COD) (**11**)	<2%	–

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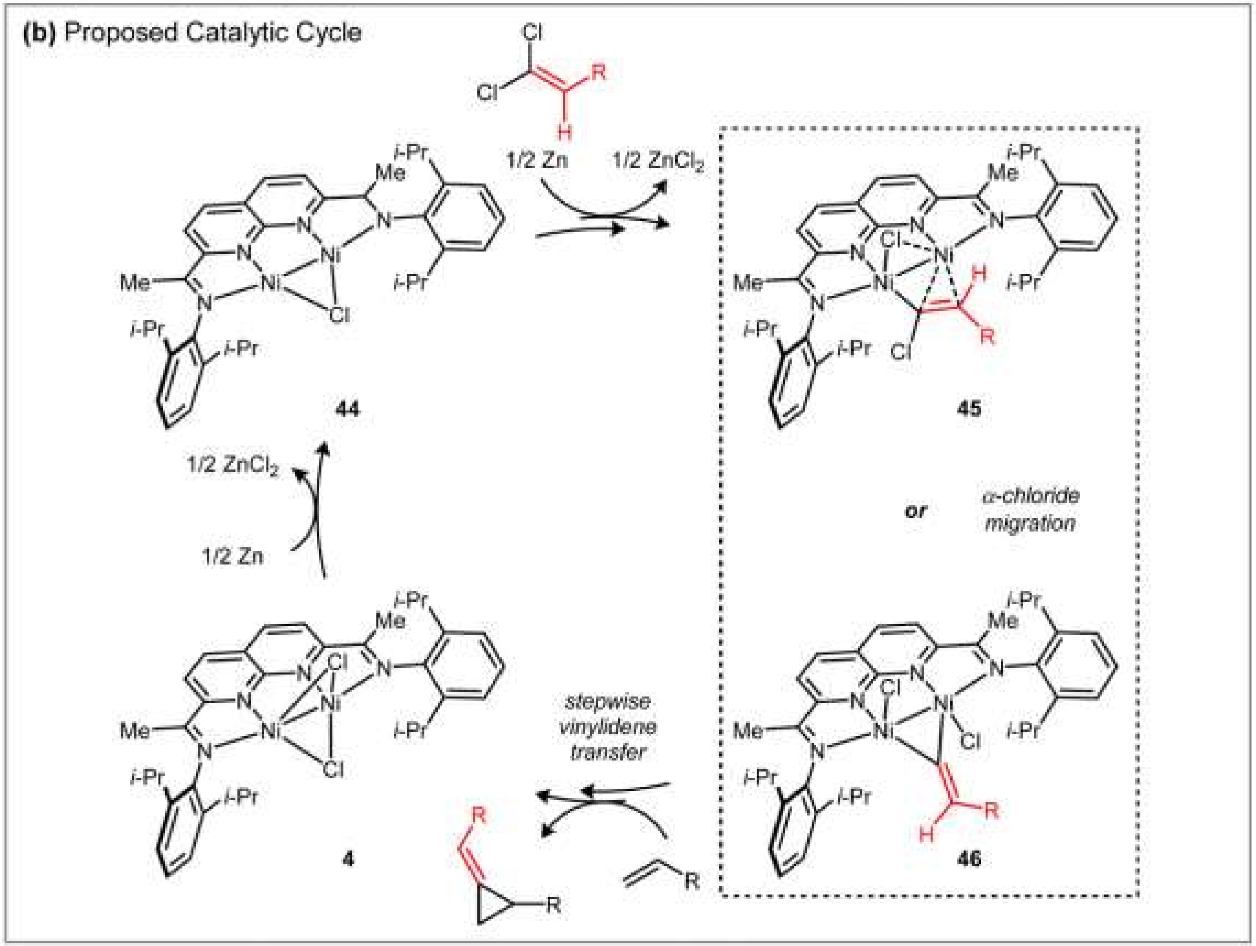
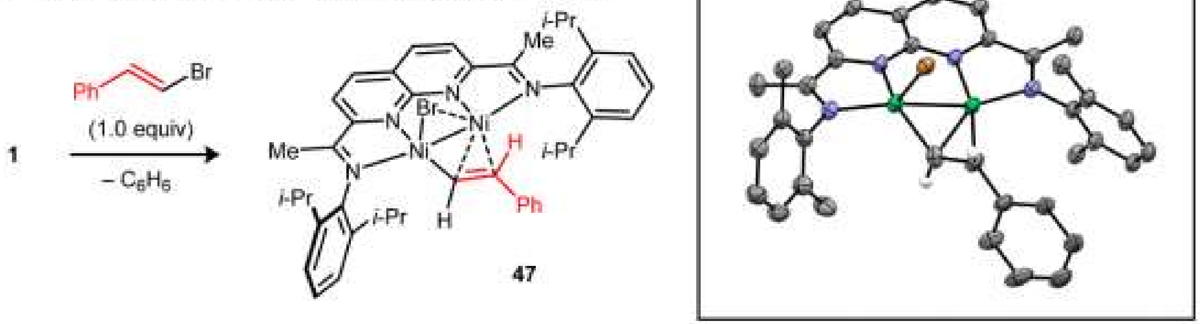
Vinylidene Transfer

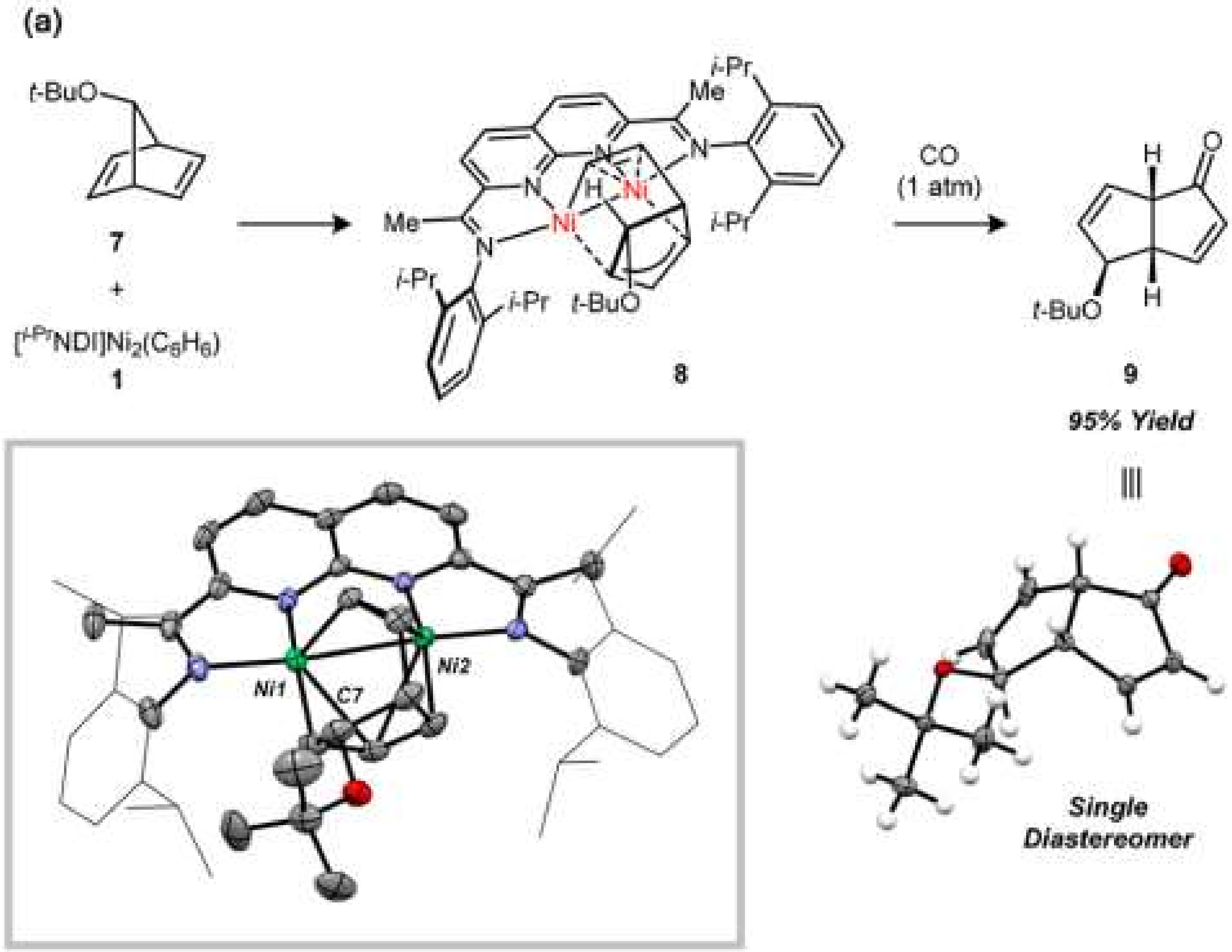


(c) Structural Model for the Oxidative Addition Product



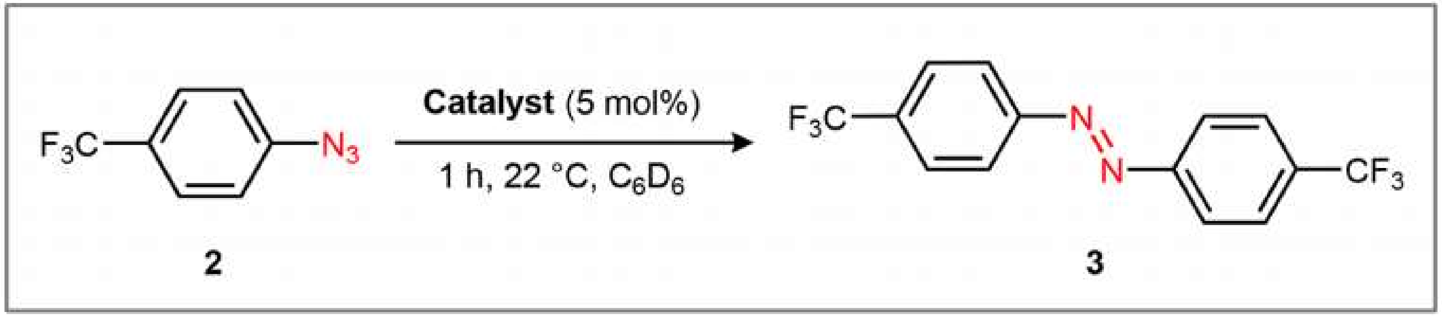
Uyeda, C. *et al.* *J. Am. Chem. Soc.* **2017**, *139*, 11686–11689

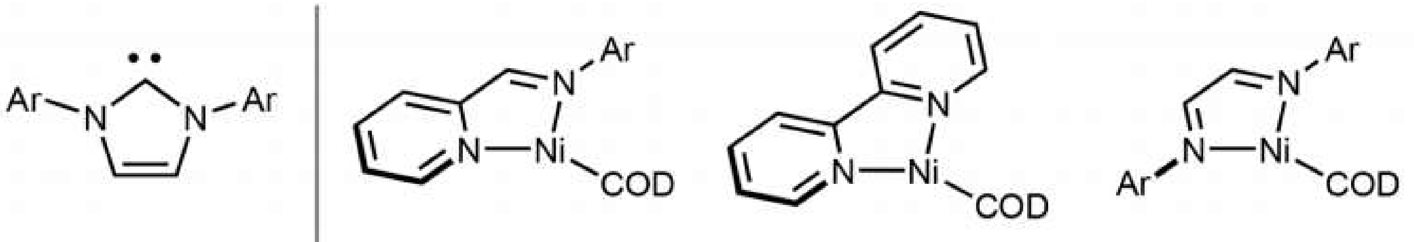
Strain Release C–C activation



Uyeda, C. *et al. J. Am. Chem. Soc.* **2017**, *139*, 13672–13675

Azoarene Formation





IPr | [$^{i\text{-}Pr}$IP]Ni(COD) (**4**) | [BPY]Ni(COD) (**5**) | [$^{i\text{-}Pr}$DAD]Ni(COD) (**6**)

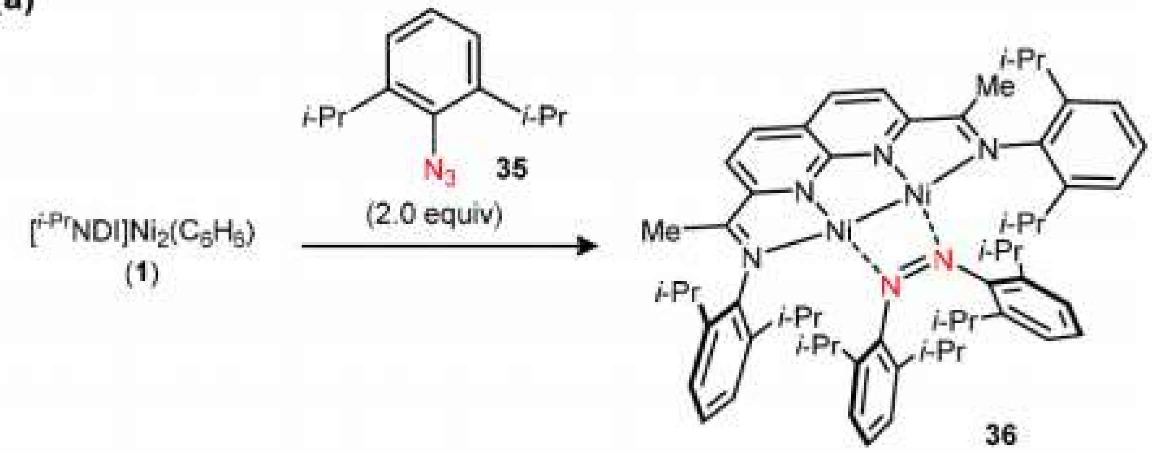
Ar = 2,6-diisopropylphenyl

entry	catalyst	conversion	yield
1	none	<2%	<2%
2	$Ni(COD)_2$	24%	<2%
3[b]	$Ni(COD)_2$ + PPh_3	35%	<2%
4[c]	$Ni(COD)_2$ + IPr	32%	<2%
5	[$^{i\text{-}Pr}$IP]Ni(COD) (**4**)	24%	13%
6	[BPY]Ni(COD) (**5**)	23%	13%
7	[$^{i\text{-}Pr}$DAD]Ni(COD) (**6**)	<2%	<2%
8	[$^{i\text{-}Pr}$NDI]$Ni_2(C_6H_6)$ (**1**)	>98%	90%
9[d]	[$^{i\text{-}Pr}$NDI]$Ni_2(C_6H_6)$ (**1**)	>98%	96%

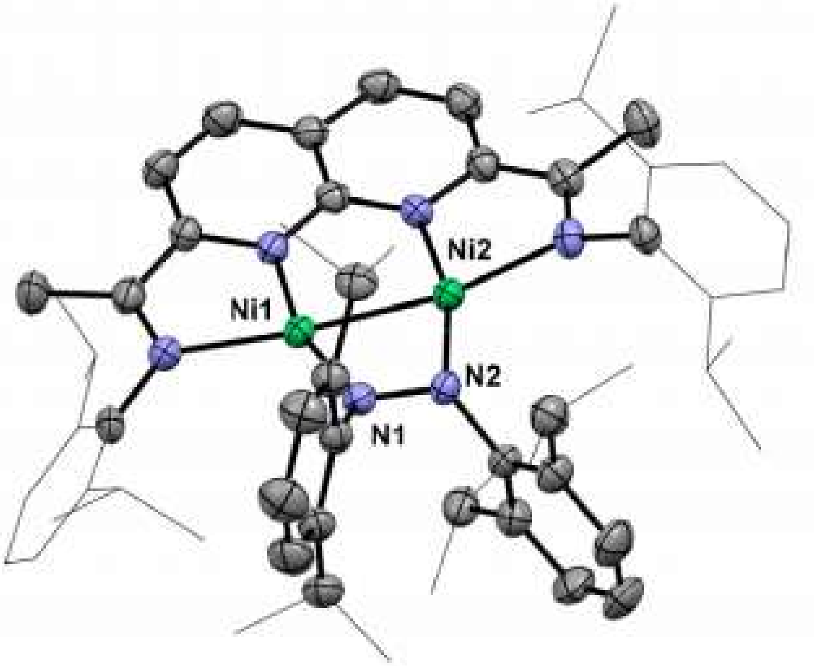
Uyeda, C. *et al. J. Am. Chem. Soc.* **2018**, *140*, 4110–4118

Azoarene Formation

(a)



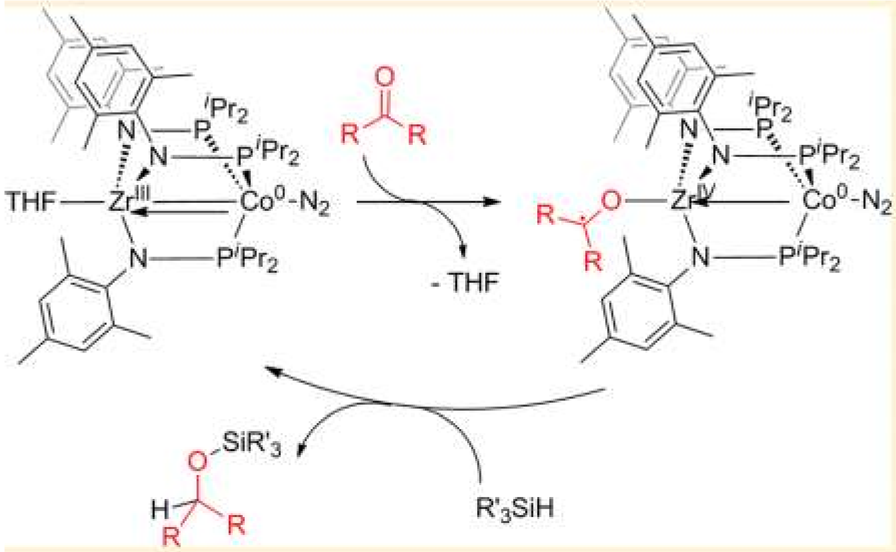
(b)

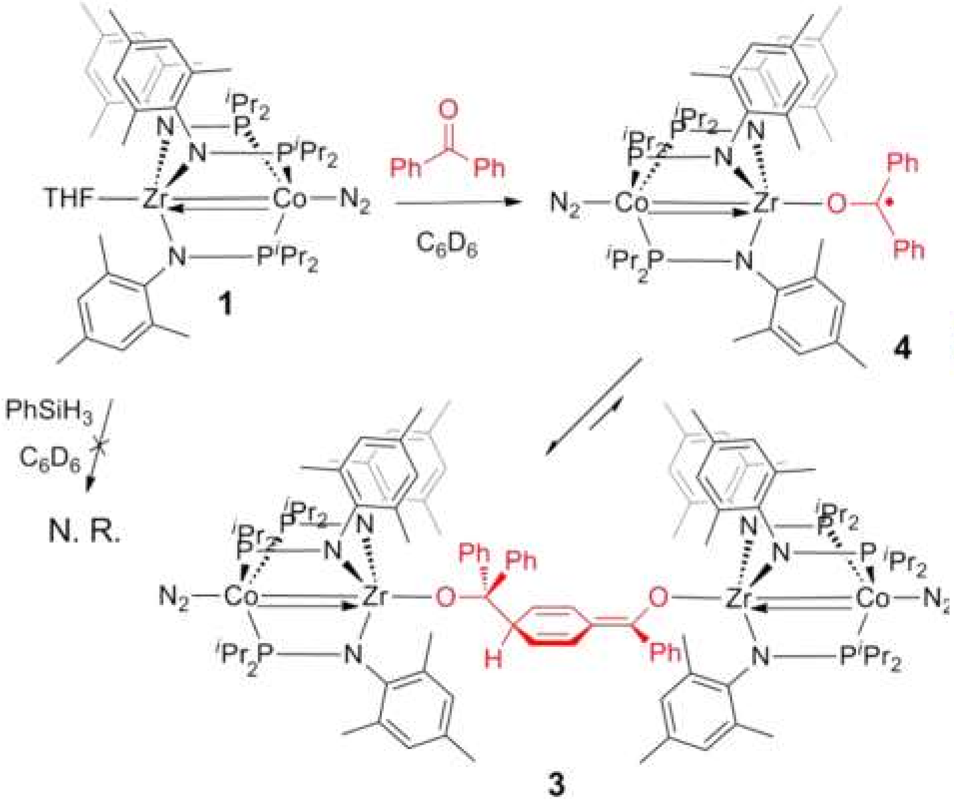


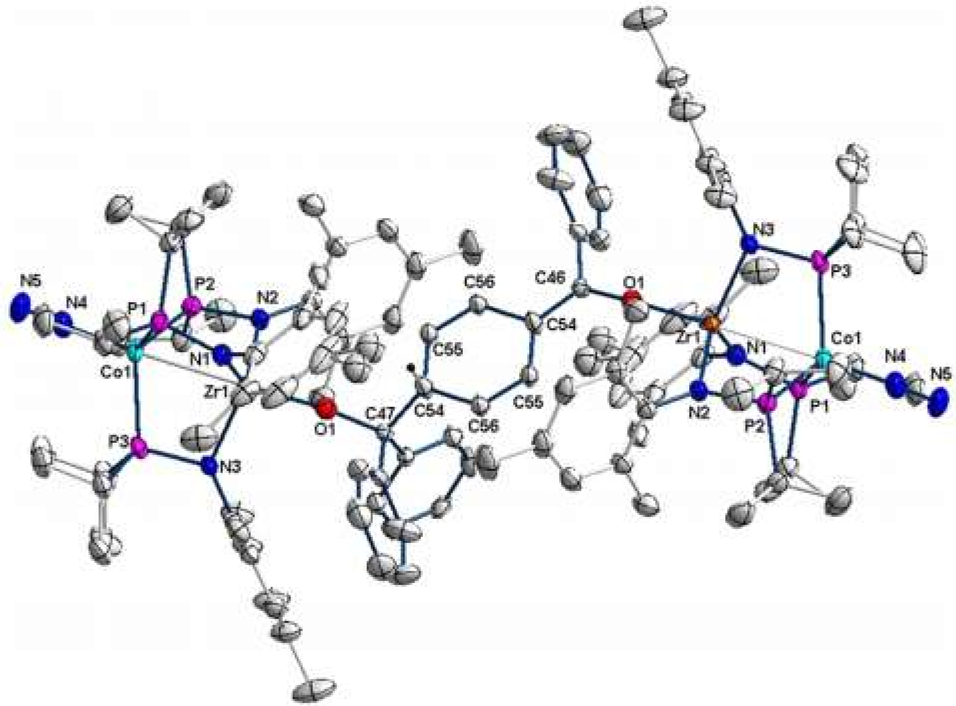
Uyeda, C. *et al. J. Am. Chem. Soc.* **2018**, *140*, 4110–4118

Catalytic Reactions

Zr–Co catalysis



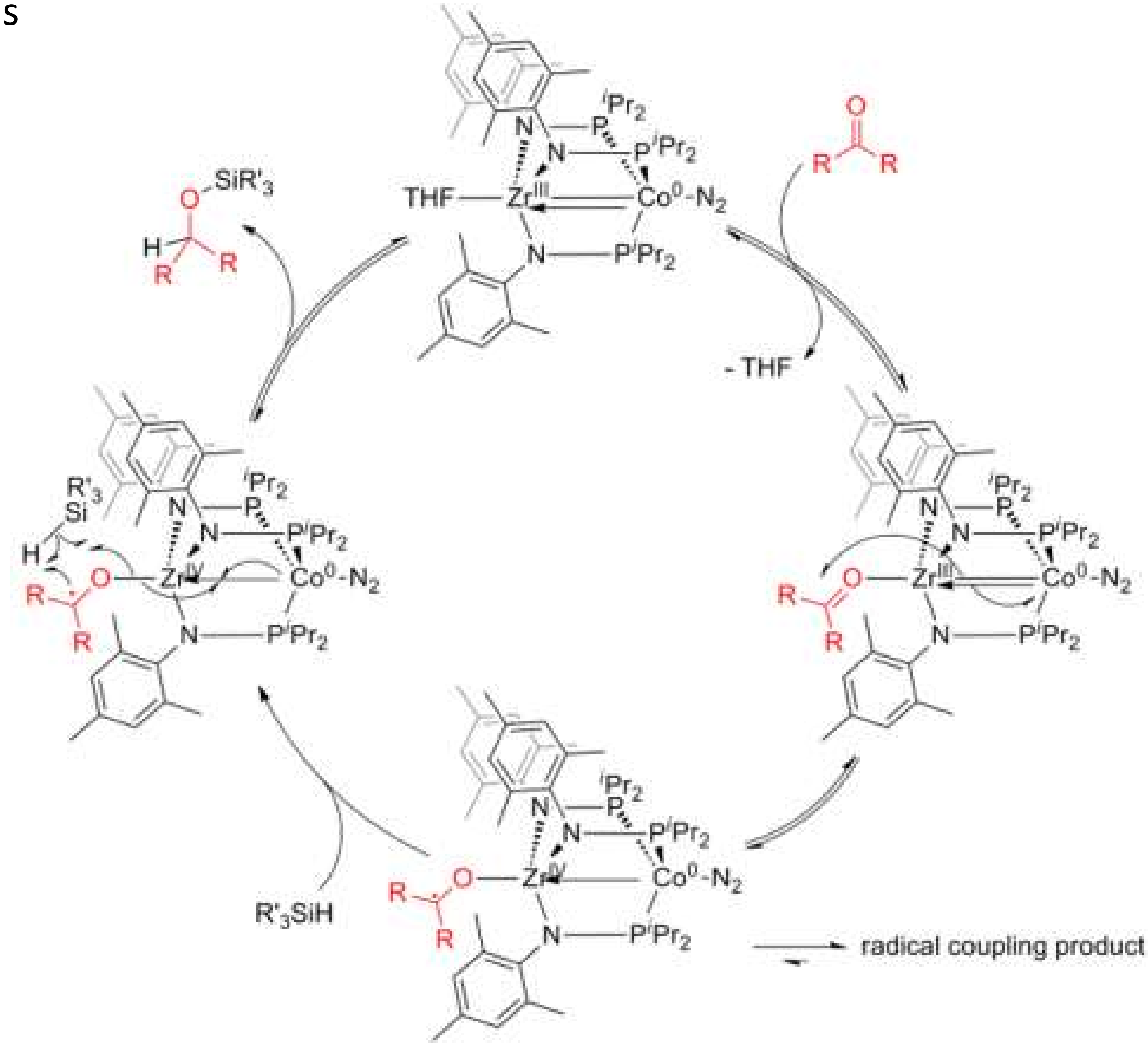




Thomas, C. M. *et al. Organometallics* **2013**, *32*, 1766–1722

Catalytic Reactions

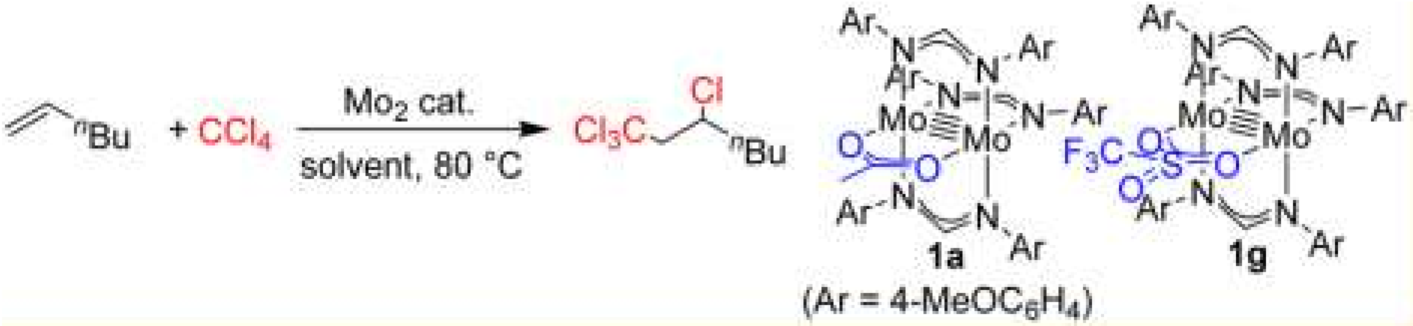
Zr–Co catalysis

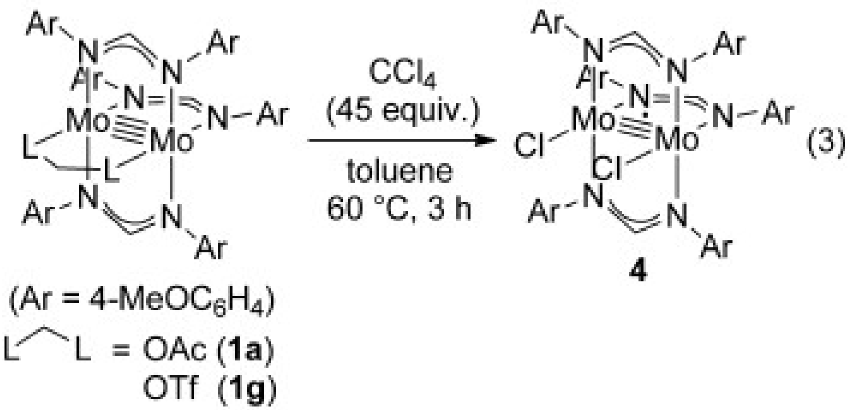


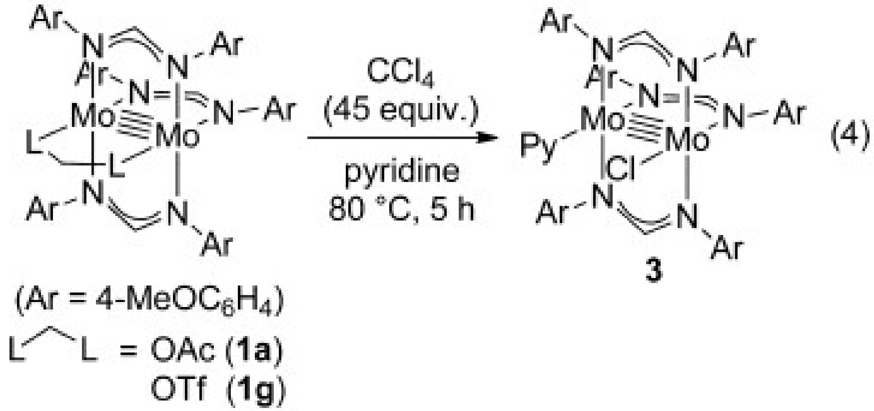
Thomas, C. M. *et al. Organometallics* **2013**, *32*, 1766–1722

Catalytic Reactions

Mo–Mo catalysis



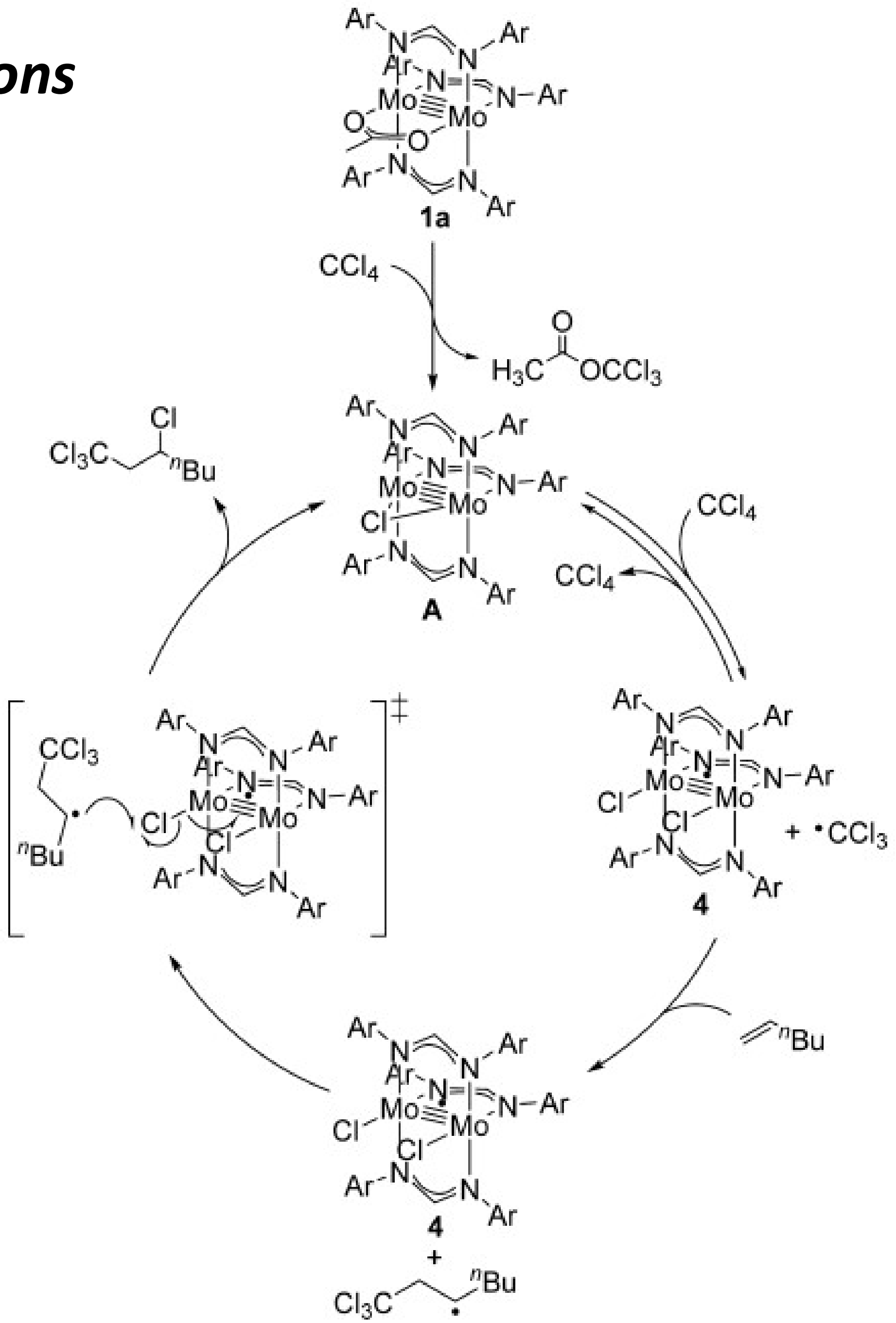




Mashima, K. *et al. Inorg. Chem.* **2017**, *56*, 634–644

Catalytic Reactions

Mo–Mo catalysis



Mashima, K. *et al. Inorg. Chem.* **2017**, *56*, 634–644