Topic report

Yang Group Meeting

2022.4.15. Dai cong

Tianning Diao

Associate Professor

EDUCATION

B.S. in Chemistry, Fudan University, Shanghai, China

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AREAS OF RESEARCH/INTEREST

Organic, Organometallic, Inorganic, Catalysis

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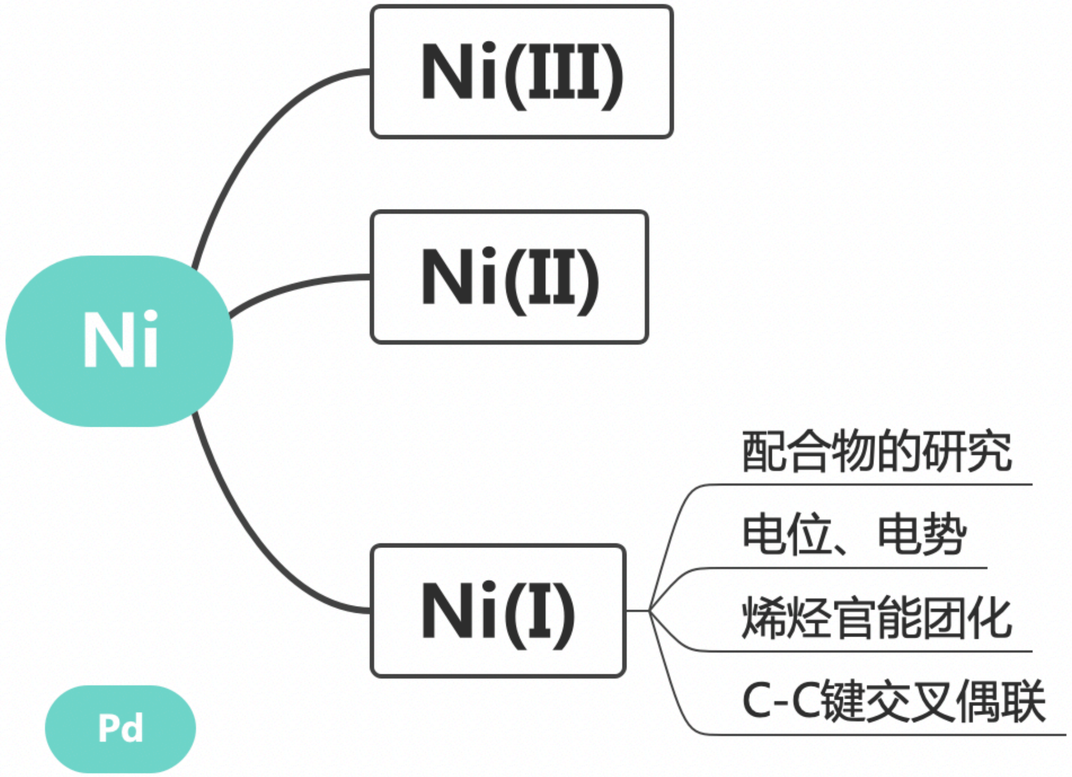
Diao Research Group Page
Link to Google Scholar Citations


Ni
Ni(III)
Ni(II)
Ni(I)
配合物的研究
电位、电势
烯烃官能团化
C-C键交叉偶联
Pd

Research of Ni（III）

JACS
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Article

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Bimetallic C–C Bond-Forming Reductive Elimination from Nickel

Hongwei Xu, Justin B. Diccianni, Joseph Katigbak, Chunhua Hu, Yingkai Zhang, and Tianning Diao*

Department of Chemistry, New York University, 100 Washington Square East, New York, New York 10003, United States

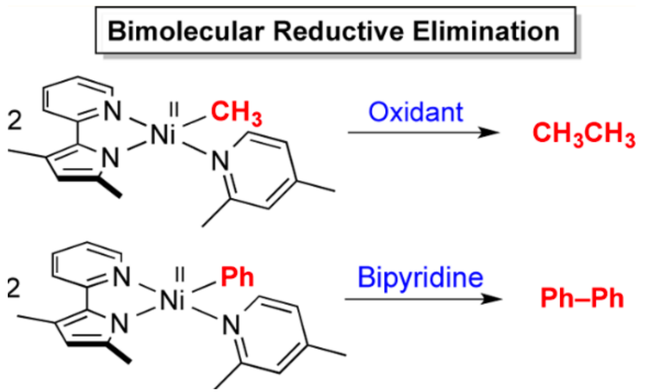
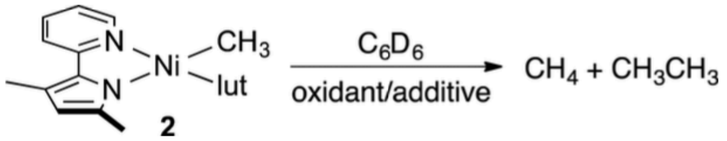
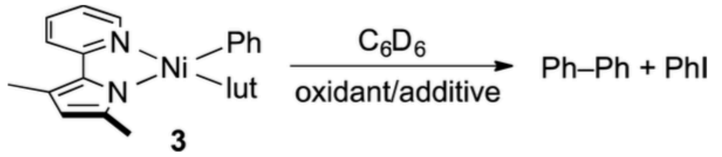


Table 1. Formation of Ethane from 2

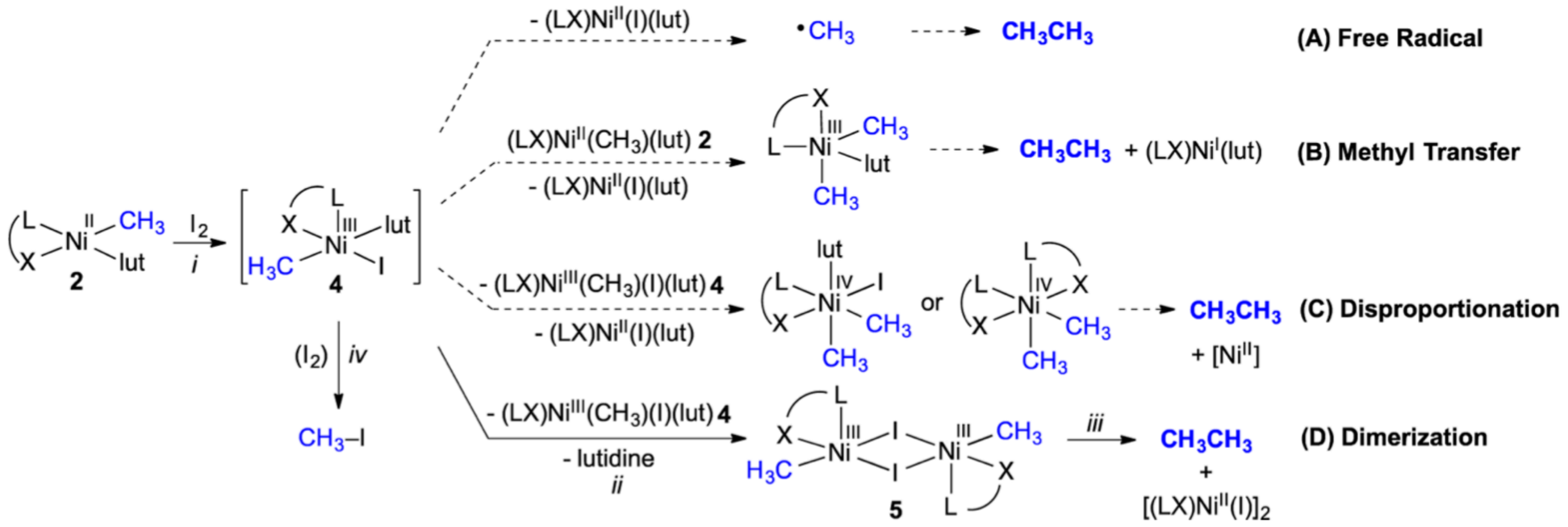


entry	oxidant or additive	temp (°C)	time (h)	yield (%)[a] CH_4	yield (%)[a] CH_3CH_3
1[b]	none	22	12	0	0
2	none	50	4	0	0
3	bpy (5 equiv)	50	4	60	trace
4	CH_3I (1 equiv)	50	4	4	4
5	O_2 (5 equiv)	22	0.1	0	19 ± 2
6	**I_2 (0.5 equiv)**	**22**	**0.1**	**0**	**43**[c]
7	**NBS (1 equiv)**	**22**	**0.1**	**< 1**	**45**[d]

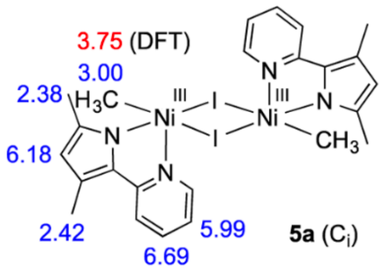
Table 2. Formation of Biphenyl from 3

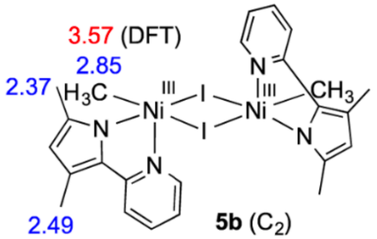


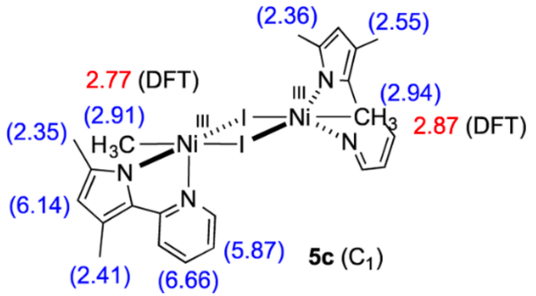
entry	oxidant or additive	temp (°C)	time (h)	yield (%)[a] Ph–Ph	yield (%)[a] PhI	yield (%)[a] $PhCH_3$
1[b]	none	22	12	0		
2	none	50	4	trace		
3	**bpy (5 equiv)**	**50**	**4**	**49**		
4	CH_3I (1 equiv)	50	4	0		0
5	O_2 (5 equiv)	22	0.1	0		
6	I_2 (0.5 equiv)	22	0.1	0	97	

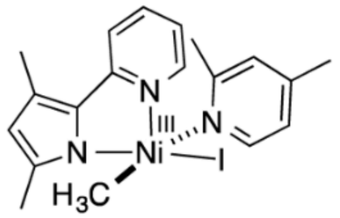

- (LX)Ni^II(I)(lut)
•CH3
CH3CH3
(A) Free Radical
(LX)Ni^II(CH3)(lut) 2
- (LX)Ni^II(I)(lut)
CH3CH3 + (LX)Ni^I(lut)
(B) Methyl Transfer
2
I2
i
4
- (LX)Ni^III(CH3)(I)(lut) 4
- (LX)Ni^II(I)(lut)
or
CH3CH3
+ [Ni^II]
(C) Disproportionation
(I2)
iv
CH3–I
- (LX)Ni^III(CH3)(I)(lut) 4
- lutidine
ii
5
iii
CH3CH3
+
[(LX)Ni^II(I)]2
(D) Dimerization

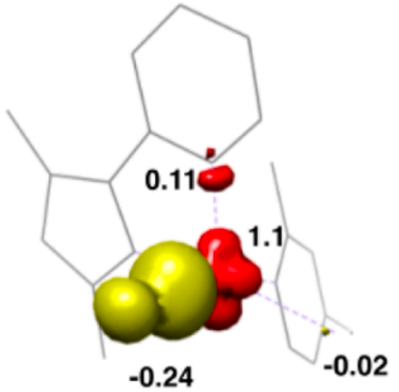
Proposed Structures for Intermediate 5 and Assignments of ^{1}H NMR Resonances









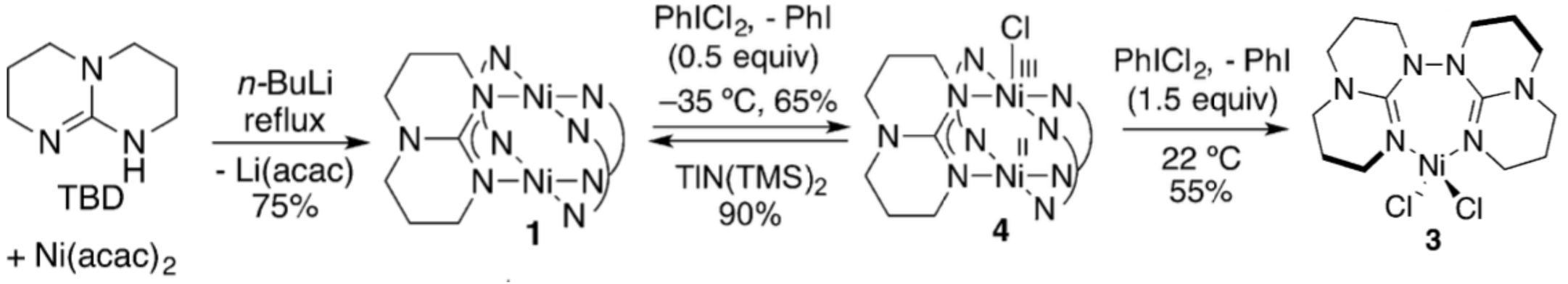


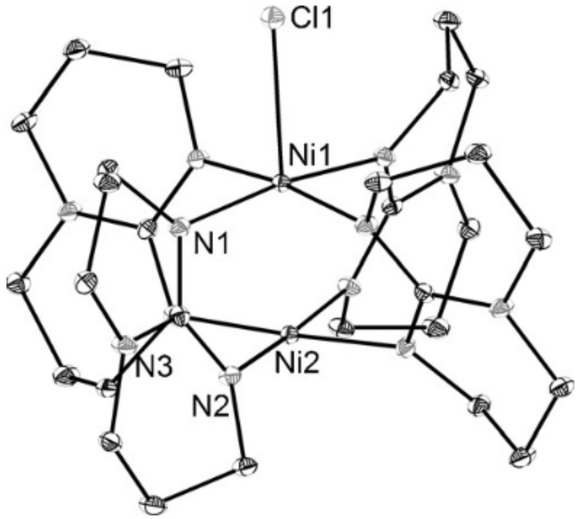
N–N Bond Formation

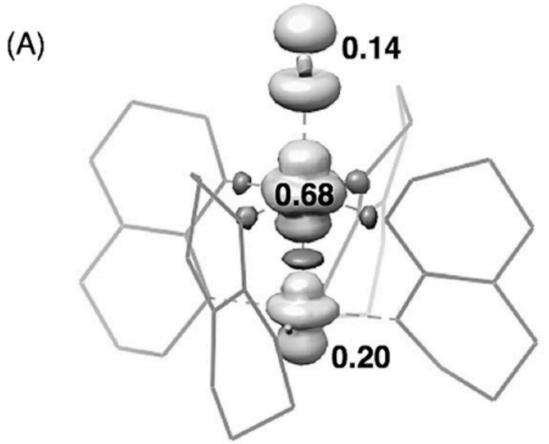
International Edition: DOI: 10.1002/anie.201602566
German Edition: DOI: 10.1002/ange.201602566

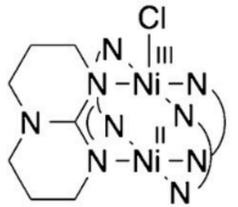
N–N Bond Forming Reductive Elimination via a Mixed-Valent Nickel(II)–Nickel(III) Intermediate

*Justin B. Diccianni, Chunhua Hu, and Tianning Diao**

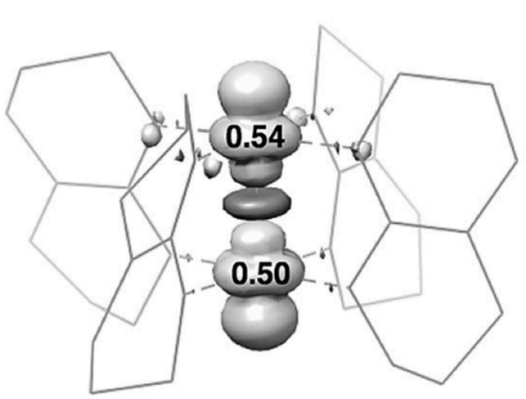

TBD
+ Ni(acac)2
n-BuLi
reflux
- Li(acac)
75%
1
PhICl2, - PhI
(0.5 equiv)
–35 °C, 65%
TlN(TMS)2
90%
4
PhICl2, - PhI
(1.5 equiv)
22 °C
55%
3

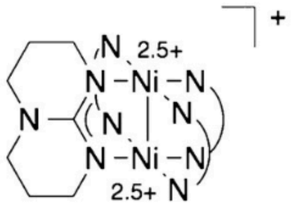






Ni–Ni distance: 2.394 Å
Ni–Ni bond order: 0





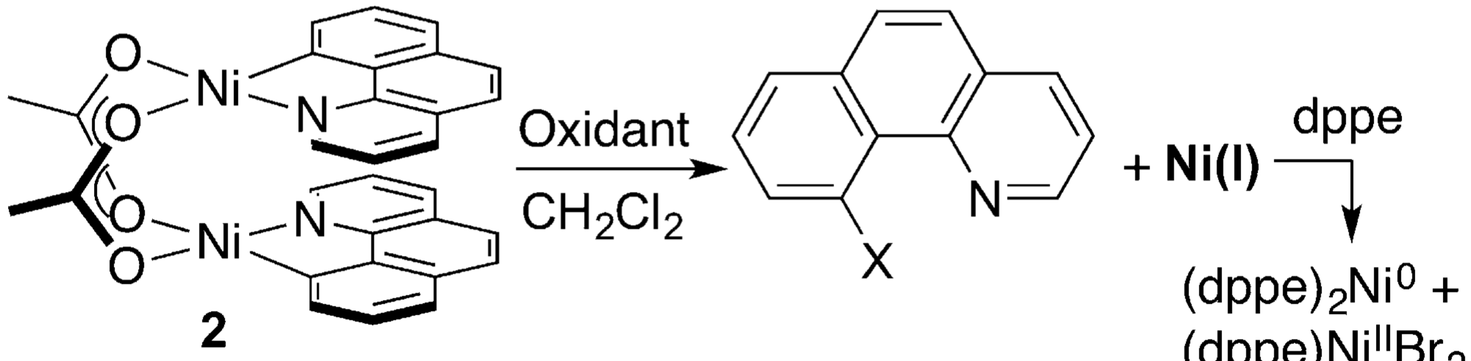
Ni–Ni distance: 2.304 Å
Ni–Ni bond order: 1/2

C–X Bond Formation

International Edition: DOI: 10.1002/anie.201611572
German Edition: DOI: 10.1002/ange.201611572

Binuclear, High-Valent Nickel Complexes: Ni–Ni Bonds in Aryl–Halogen Bond Formation

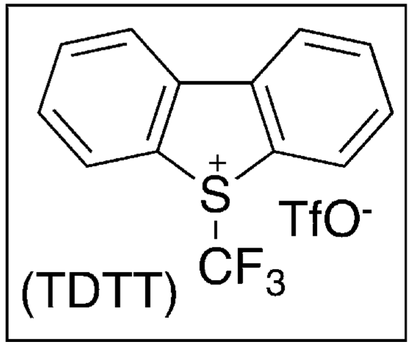
*Justin B. Diccianni, Chunhua Hu, and Tianning Diao**

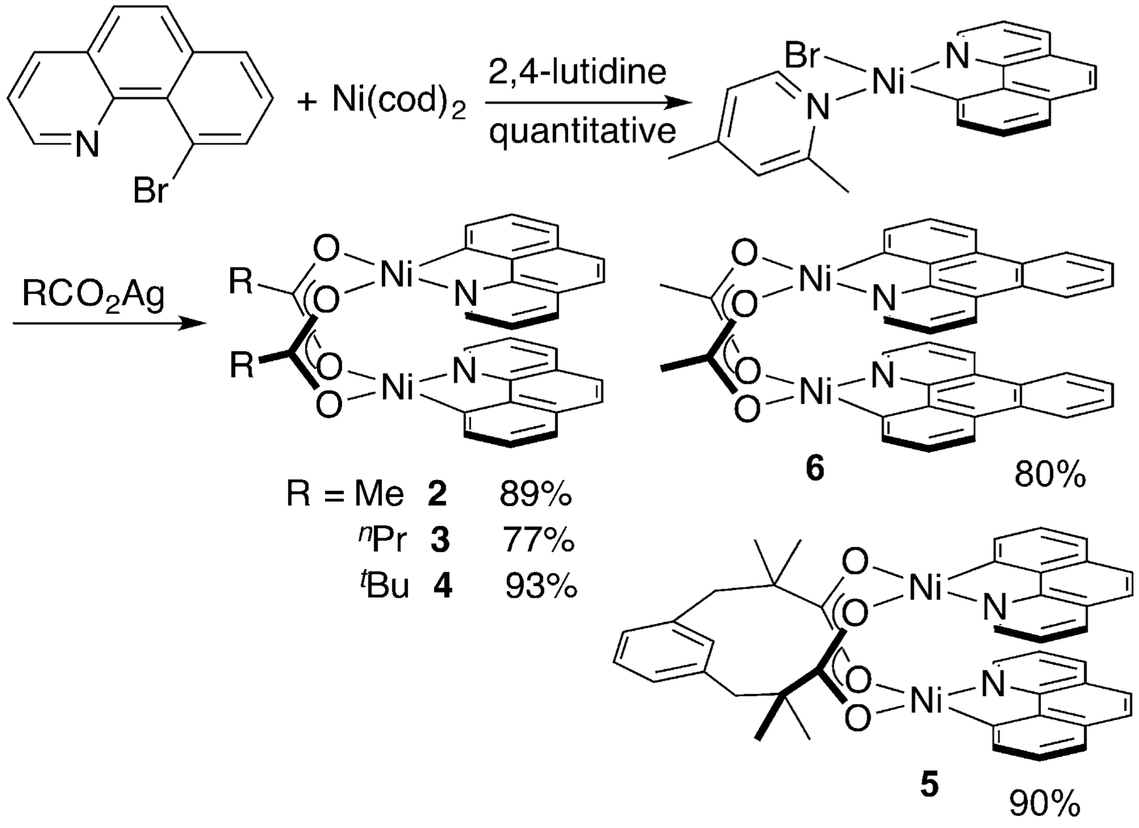


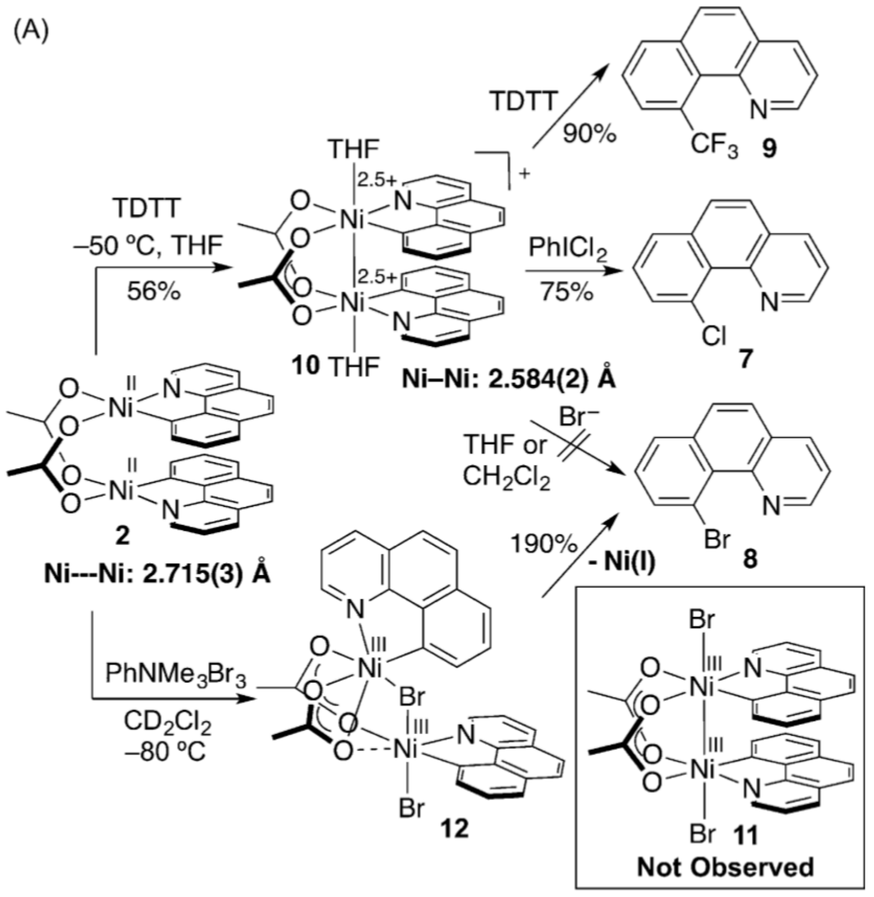
2

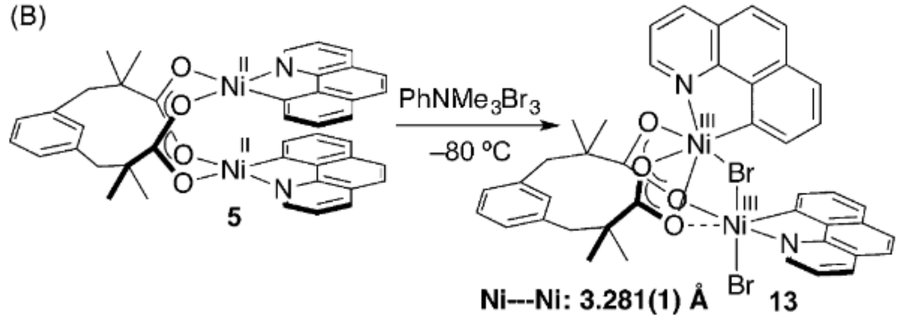
Oxidant = $PhICl_2$, X = Cl (**7**) 160%
Oxidant = $PhNMe_3Br_3$, X = Br (**8**) 190%
Oxidant = TDTT, X = CF_3 (**9**) 140%

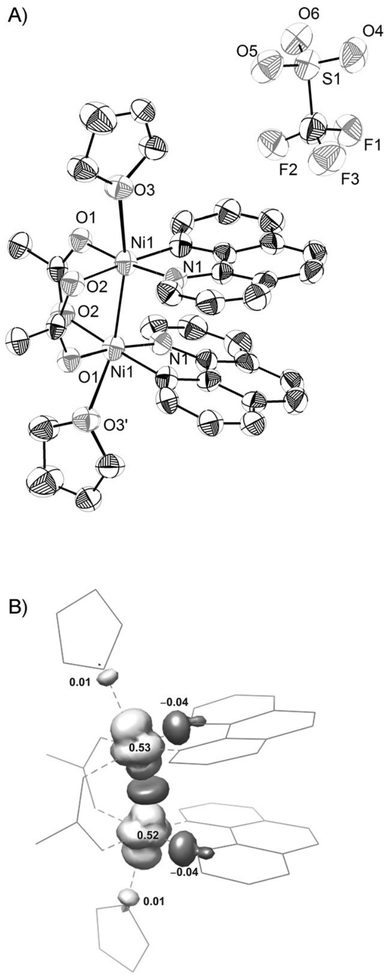
(theoretical yield: 200%)

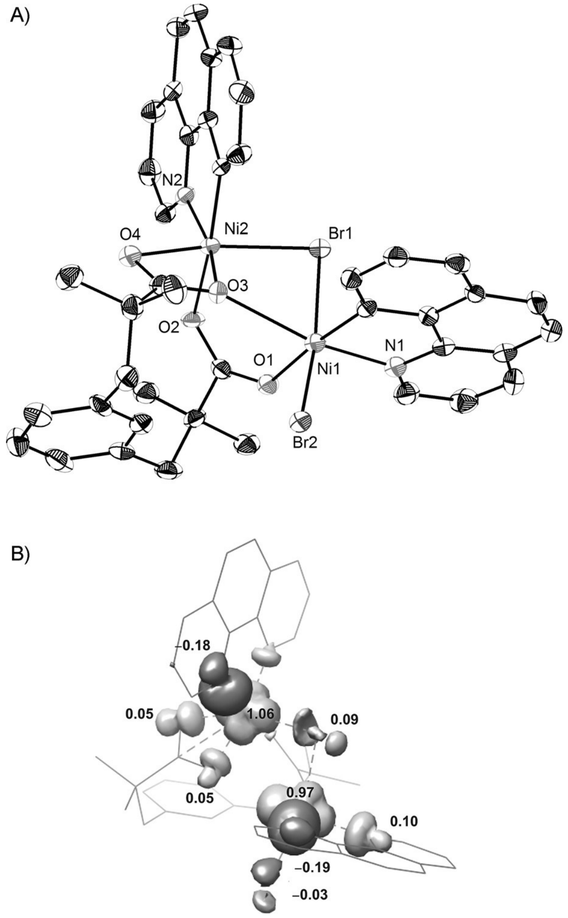



+ Ni(cod)2
2,4-lutidine
quantitative
Br
Ni
N
RCO2Ag
R
O
R = Me 2 89%
nPr 3 77%
tBu 4 93%
6
80%
5
90%


(A)
TDTT
–50 °C, THF
56%
2
Ni---Ni: 2.715(3) Å
THF
2.5+
2.5+
10 THF
Ni–Ni: 2.584(2) Å
TDTT
90%
9
PhICl2
75%
7
Br–
THF or
CH2Cl2
8
190%
- Ni(I)
PhNMe3Br3
CD2Cl2
–80 °C
12
11
Not Observed


(B)
5
PhNMe3Br3
–80 °C
Ni---Ni: 3.281(1) Å
13


A)
O6
O4
O5
S1
F1
F2
F3
O3
O1
Ni1
N1
O2
O2
N1
O1
Ni1
O3'
B)
0.01
−0.04
0.53
0.52
−0.04
0.01


A)
N2
O4
Ni2
Br1
O3
O2
O1
Ni1
N1
Br2
B)
−0.18
0.05
1.06
0.09
0.05
0.97
0.10
−0.19
−0.03

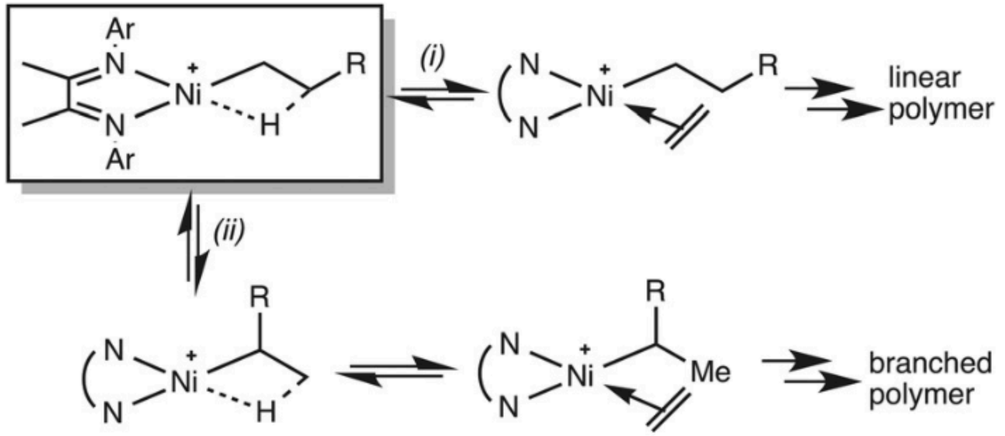
Research of Ni（II）

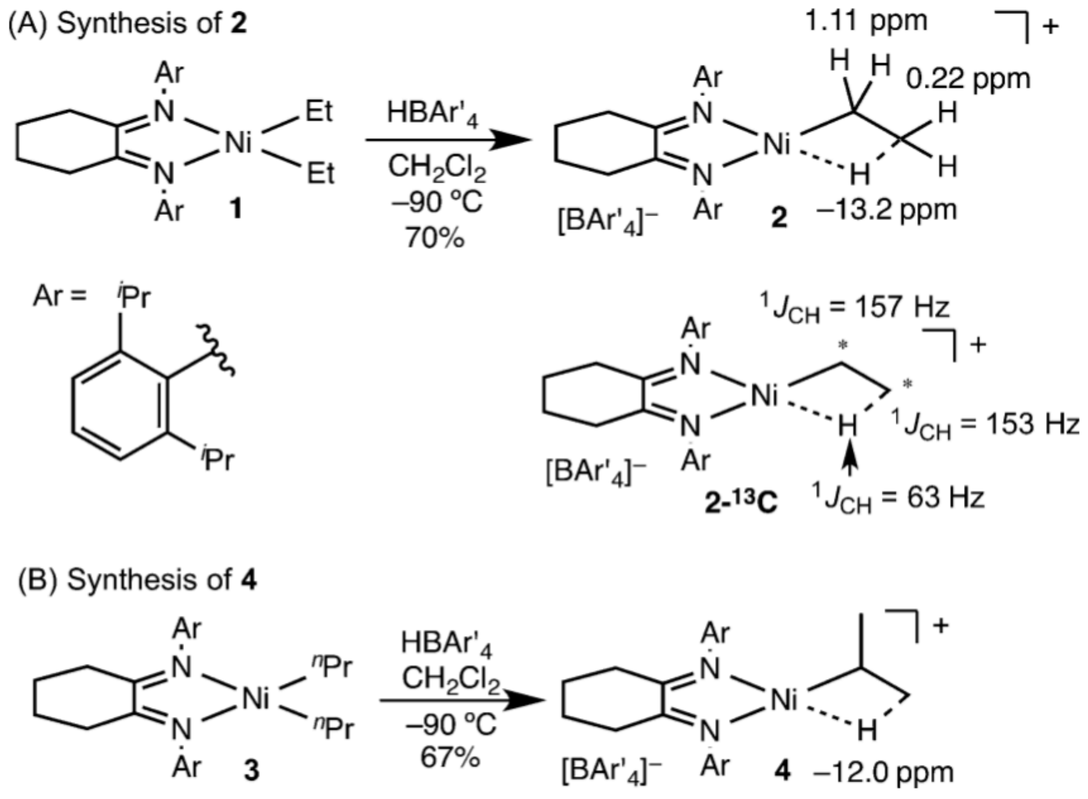
Polymerization Intermediates

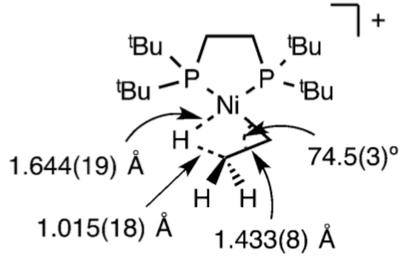
International Edition: DOI: 10.1002/anie.201611282
German Edition: DOI: 10.1002/ange.201611282

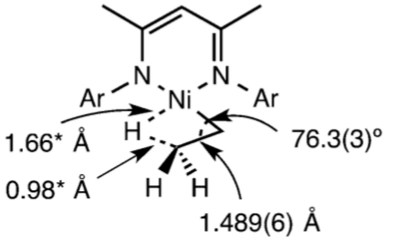
Structure and Isotope Effects of the β-H Agostic (α-Diimine)Nickel Cation as a Polymerization Intermediate

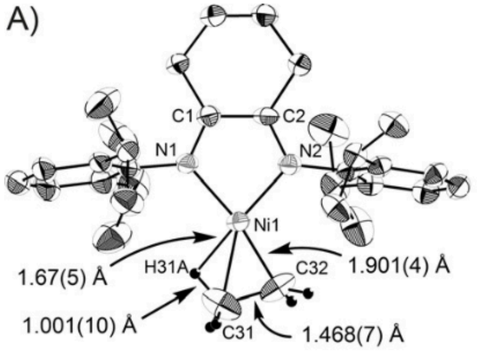
*Hongwei Xu, Paul B. White, Chunhua Hu, and Tianning Diao**

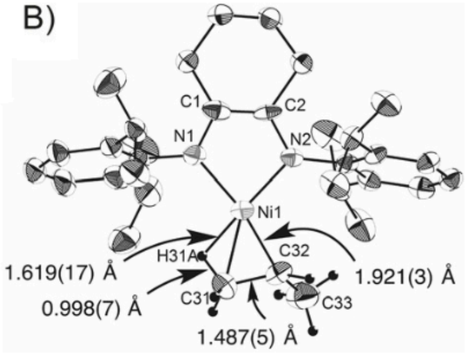


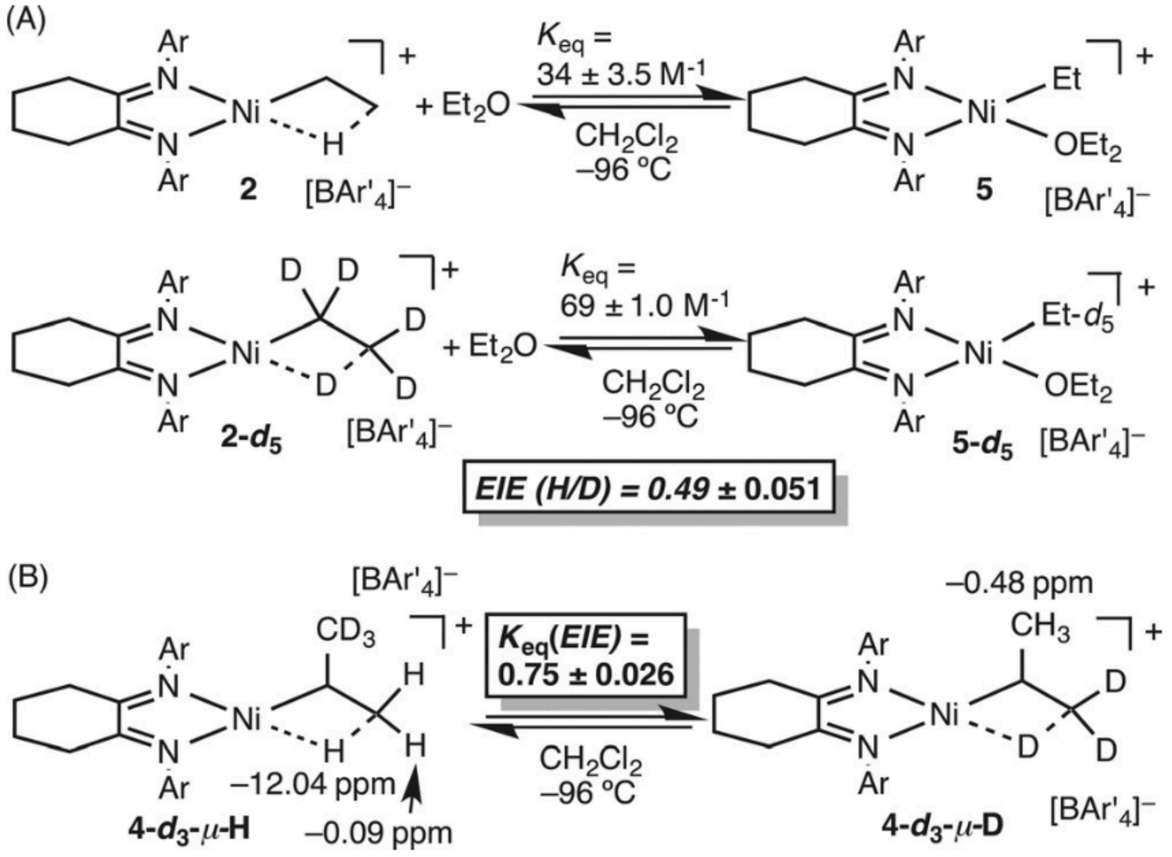

(A) Synthesis of 2
Ar
N
Ni
Et
Et
N
Ar
1
HBAr'4
CH2Cl2
–90 °C
70%
1.11 ppm
H H
0.22 ppm
H
H
H
–13.2 ppm
[BAr'4]–
2
+
Ar = iPr
iPr
iPr
1JCH = 157 Hz
*
*
1JCH = 153 Hz
1JCH = 63 Hz
2-13C
(B) Synthesis of 4
nPr
nPr
3
HBAr'4
CH2Cl2
–90 °C
67%
4
–12.0 ppm


tBu
tBu
P
P
tBu
tBu
Ni
H
1.644(19) Å
74.5(3)°
1.015(18) Å
1.433(8) Å
+


N
N
Ar
Ni
Ar
H
1.66* Å
76.3(3)°
0.98* Å
H
H
1.489(6) Å


A)
C1
C2
N1
N2
Ni1
1.67(5) Å
H31A
C32
1.901(4) Å
1.001(10) Å
C31
1.468(7) Å


B)
C1
C2
N1
N2
Ni1
1.619(17) Å
H31A
C32
1.921(3) Å
0.998(7) Å
C31
C33
1.487(5) Å


(A)
Ar
N
Ni
H
N
Ar
2
[BAr'4]−
+ Et2O
Keq =
34 ± 3.5 M-1
CH2Cl2
–96 °C
Et
OEt2
5
D
2-d5
Keq =
69 ± 1.0 M-1
Et-d5
5-d5
EIE (H/D) = 0.49 ± 0.051
(B)
CD3
–12.04 ppm
–0.09 ppm
4-d3-μ-H
Keq(EIE) =
0.75 ± 0.026
–0.48 ppm
CH3
4-d3-μ-D

ORGANOMETALLICS

Communication

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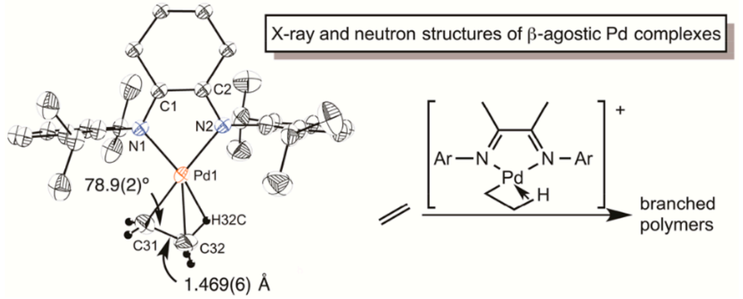
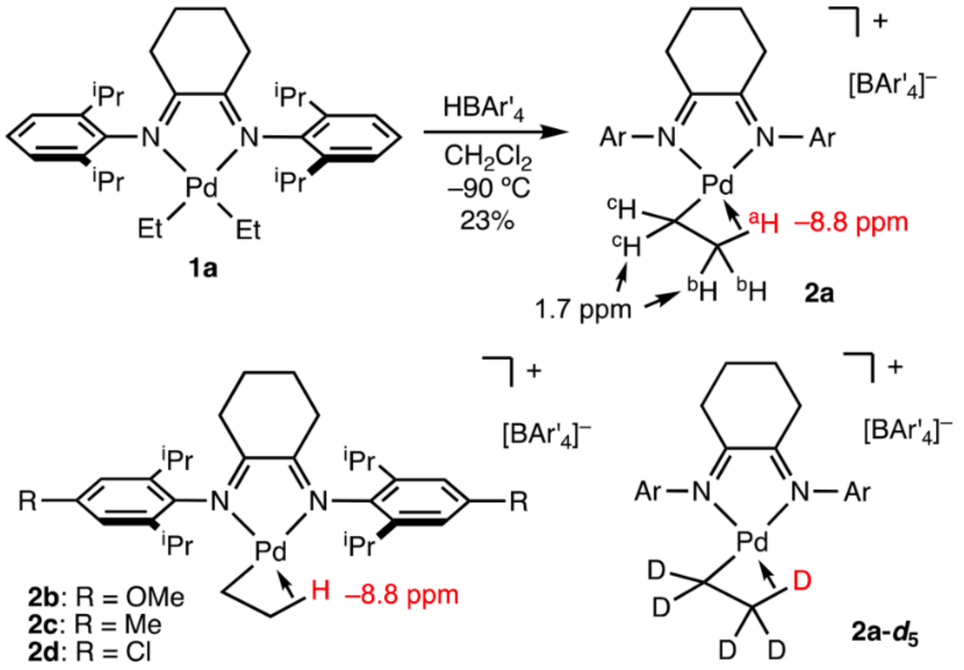
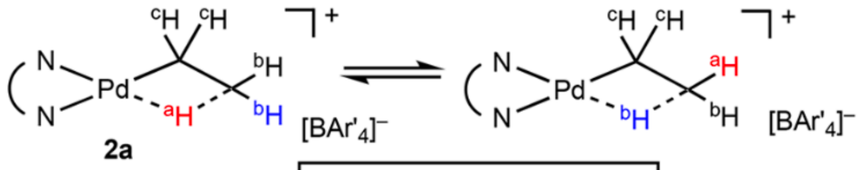
Structural Characterization of β-Agostic Bonds in Pd-Catalyzed Polymerization

Hongwei Xu,[†] Chunhua Tony Hu,[†] Xiaoping Wang,[‡] and Tianning Diao*,[†]



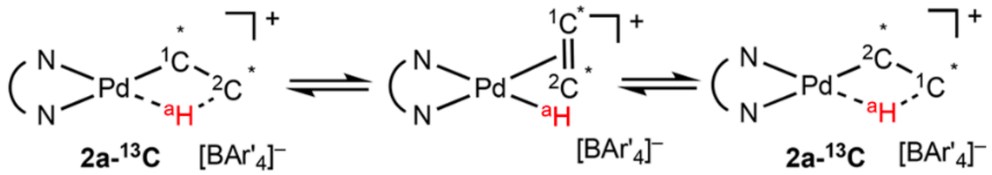

iPr
iPr
iPr
iPr
N
N
Pd
Et
Et
1a
HBAr'4
CH2Cl2
–90 °C
23%
Ar
N
N
Ar
Pd
cH
cH
aH –8.8 ppm
1.7 ppm
bH
bH
2a
+
[BAr'4]–
R
2b: R = OMe
2c: R = Me
2d: R = Cl
H –8.8 ppm
D
D
D
D
D
2a-d5

(A) Exchange of ^{a}H and ^{b}H via C_α–C_β bond rotation

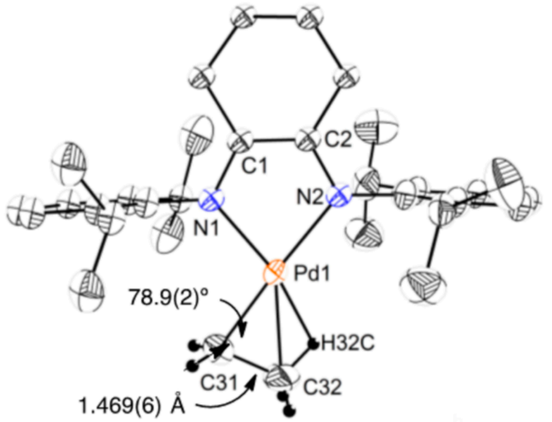


$\Delta G^{\ddagger}$ = 8.5 kcal/mol at -60 °C

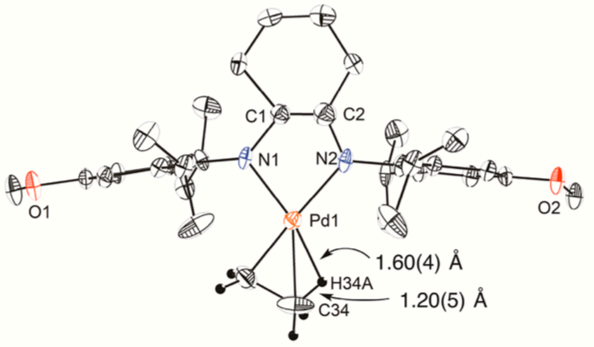
(B) Exchange of C_α and C_β via β–H elimination and reinsertion



(A)



(B)



JOC The Journal of Organic Chemistry

Article

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Nickel-Catalyzed Reductive Cycloisomerization of Enynes with CO_2

Justin B. Diccianni, Tyler Heitmann, and Tianning Diao*

Department of Chemistry, New York University, 100 Washington Square East New York, New York 10003, United States

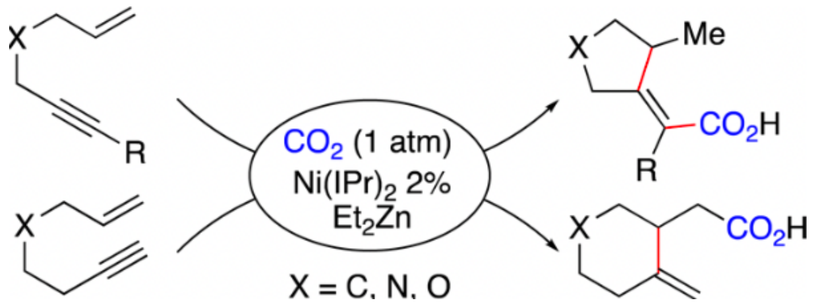
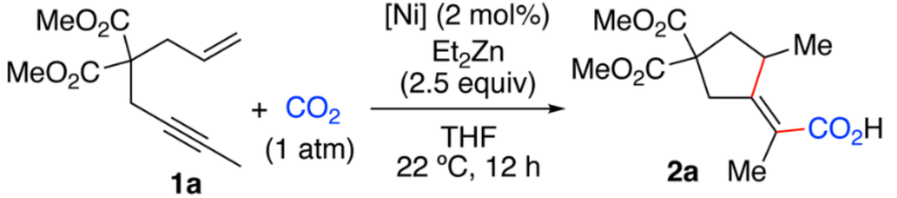
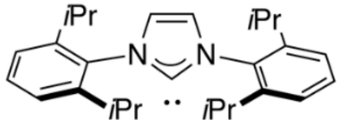


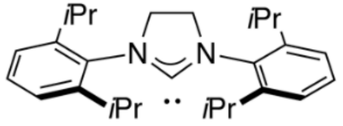
Table 1. Development of the Conditions for the Cycloisomerization of Enyne 1a with CO_2[a]



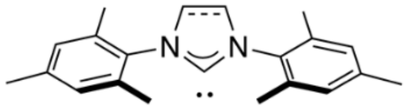
IPr:



SIPr:

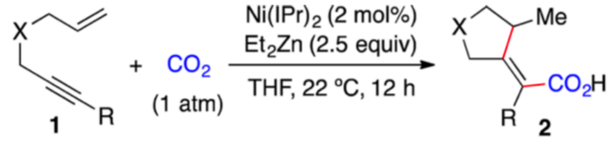


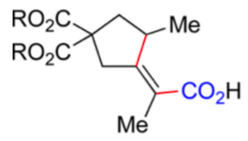
IMes/SIMes:



Entry	Catalyst	Yield (%)[b]
1	$Ni(cod)_2/PPh_3$[c]	0
2	$Ni(cod)_2$/IPr[c]	81
3	$NiCl_2(DME)$/IPr[c]	40
4	**$Ni(IPr)_2$**	**99**
5	$Ni(SIPr)_2$	42
6	$Ni(IMes)_2$	11
7	$Ni(SIMes)_2$	10

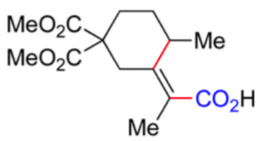
Table 2. Scope of the Reductive Cycloisomerization with CO_2 Incorporated to Alkynes[a]



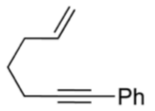


2a: R = Me, 96%
2b: R = Bn, 90%

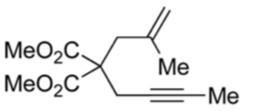
2c: R = H, 64%
2d: R = Ph, 60%



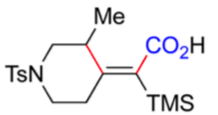
2e: 58% [c]



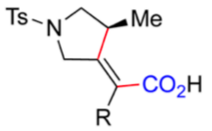
1f: 0%



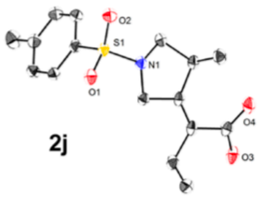
1g: 0%



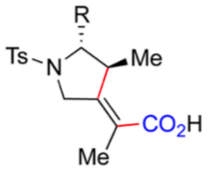
2h: 62%



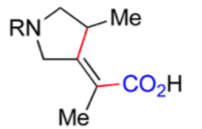
2i: R = Me, 87%
2j: R = Et, 91% [b]
2k: R = TMS, 76% [b]



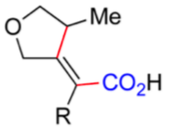
2j



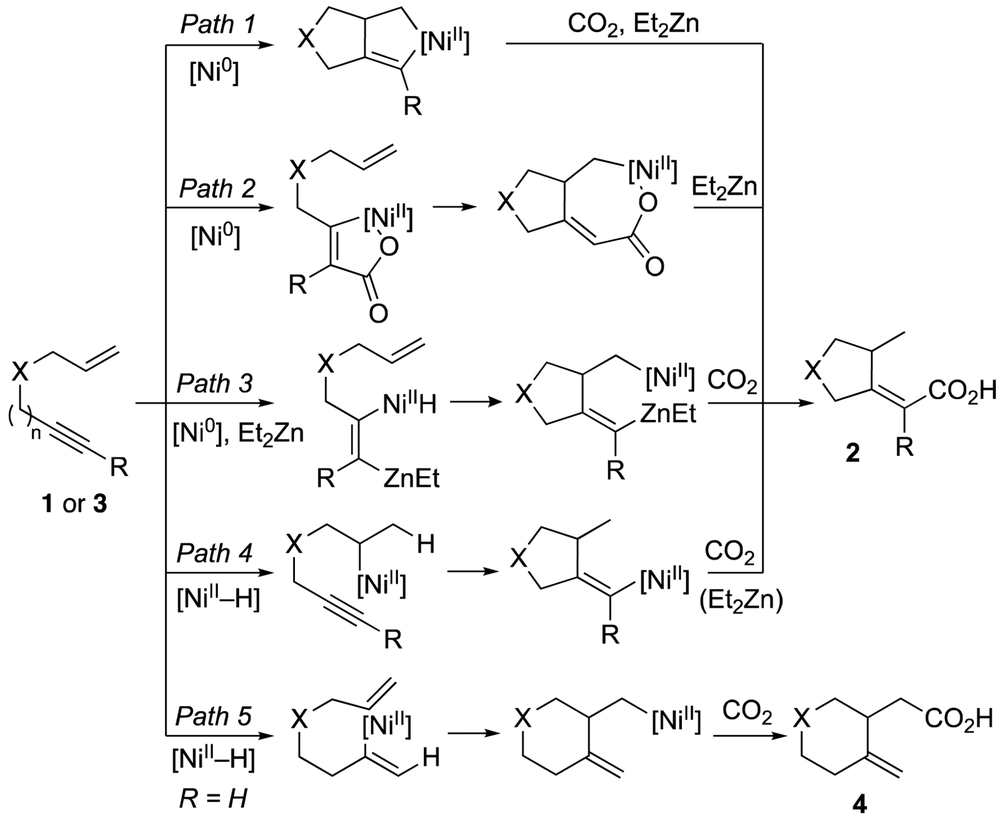
2l: R = Ph, 82%
(*cis: trans* = 1:3)
2m: R = Me, 90%
(*cis: trans* = 1:1)

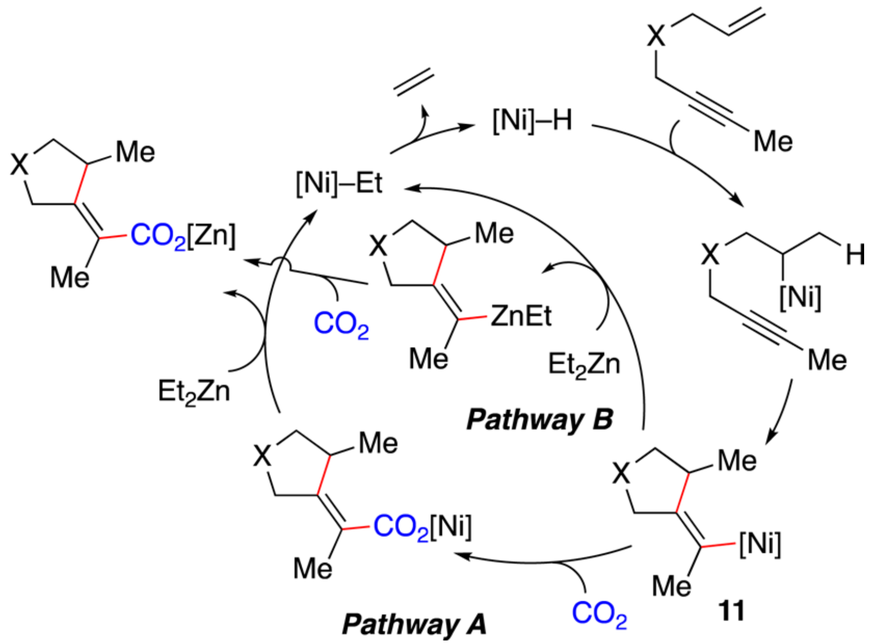


2n: R = Bz, 74% [c]
2o: R = Boc, 57% [b]



2p: R = Me, 72%
2q: R = Ph, 60% [b,c]


Path 1
[Ni0]
[NiII]
CO2, Et2Zn
Path 2
[Ni0]
Et2Zn
Path 3
[Ni0], Et2Zn
NiIIH
ZnEt
CO2
2
1 or 3
Path 4
[NiII–H]
CO2
(Et2Zn)
Path 5
[NiII–H]
R = H
4

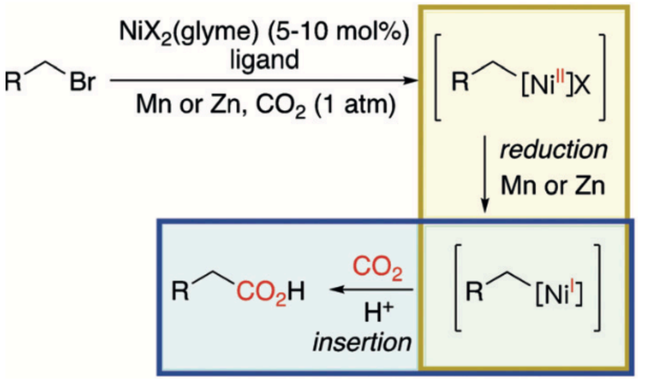

[Ni]–H
[Ni]–Et
CO2[Zn]
CO2
Et2Zn
ZnEt
Pathway B
[Ni]
11
CO2[Ni]
Pathway A
CO2

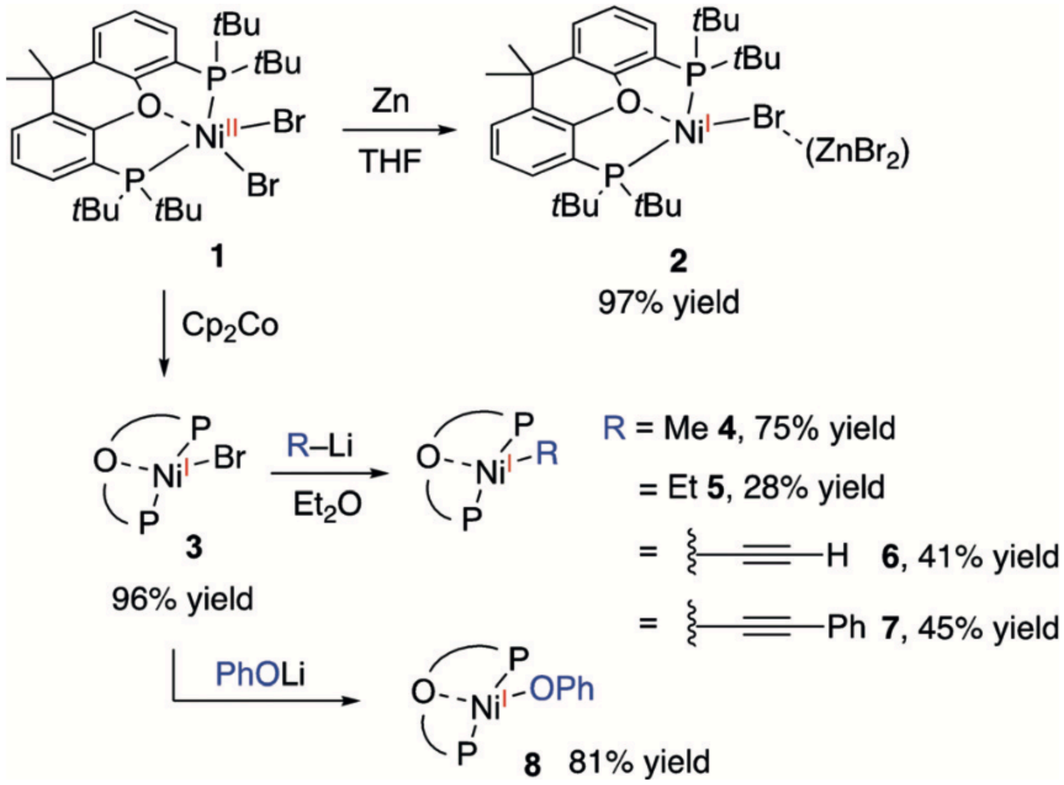
Carboxylation

International Edition: DOI: 10.1002/anie.201906005
German Edition: DOI: 10.1002/ange.201906005

Insertion of CO_2 Mediated by a (Xantphos)Ni^{I}–Alkyl Species

*Justin B. Diccianni, Chunhua T. Hu, and Tianning Diao**





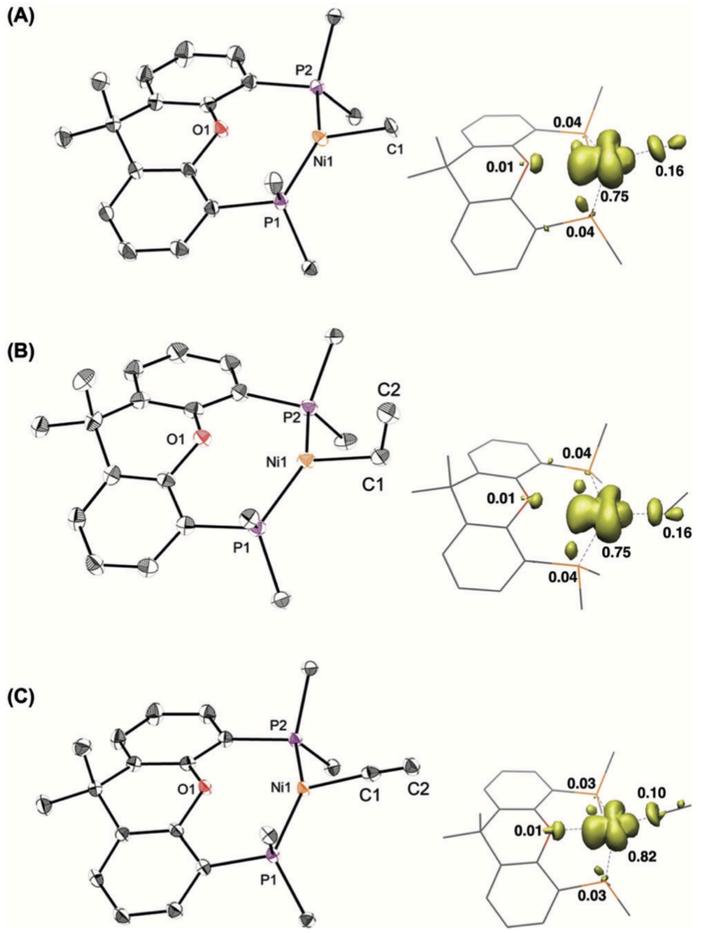
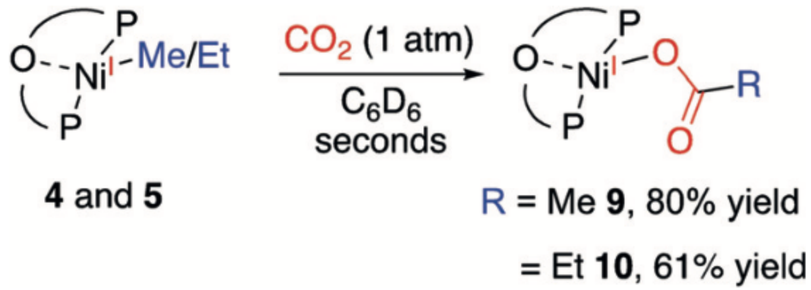


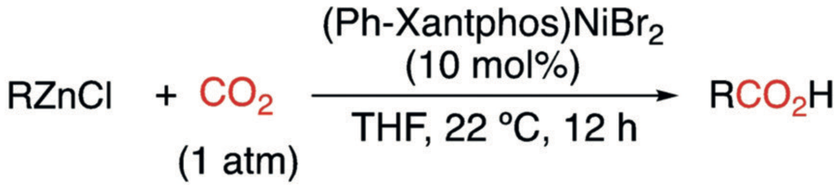
Figure 1. X-ray structures[19] and spin-density plots of **4** (A), **5** (B), and **6** (C) at 50% probability thermal ellipsoids. Hydrogen atoms are omitted and *t*Bu groups are truncated for clarity.



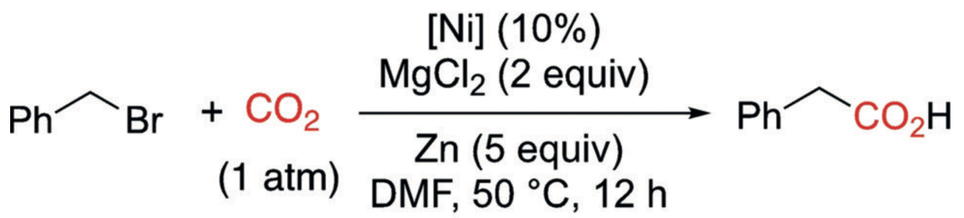
4 and **5**

R = Me **9**, 80% yield

= Et **10**, 61% yield



R	Yield (%)
Bn	66 (0 with no ligand)
Ph	68
n-Bu	30 (51 with (Ph-Xantphos)Ni^{I}Br)



[Ni]	Yield (%)
(*t*-Bu-Xantphos)Ni^{I}Br	7
(Ph-Xantphos)Ni^{II}Br	32

Research of Ni（I）

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Article

Cite This: J. Am. Chem. Soc. 2019, 141, 1788−1796

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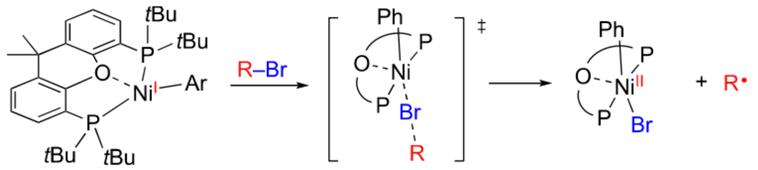
Mechanistic Characterization of (Xantphos)Ni(I)-Mediated Alkyl Bromide Activation: Oxidative Addition, Electron Transfer, or Halogen-Atom Abstraction

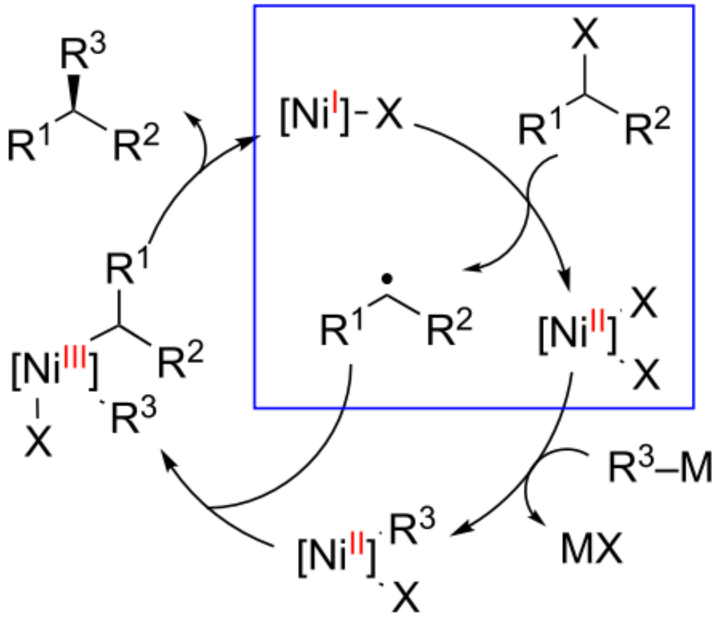
Justin B. Diccianni, Joseph Katigbak, Chunhua Hu, and Tianning Diao*

Department of Chemistry, New York University, 100 Washington Square East, New York, New York 10003, United States

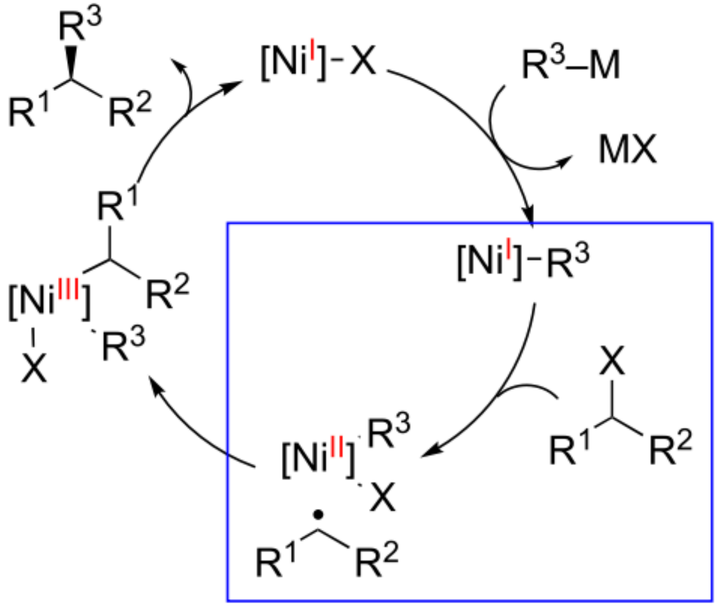


Ni(I)-Mediated Alkyl Bromide Activation:
Halogen-Atom-Abstraction Characterized by Kinetic Studies

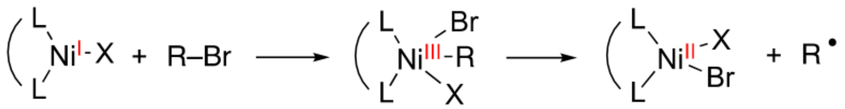
"Transmetalation after oxidative addition"



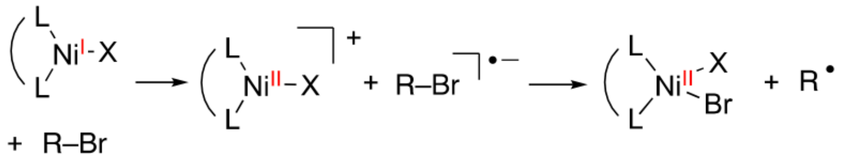
"Transmetalation before oxidative addition"



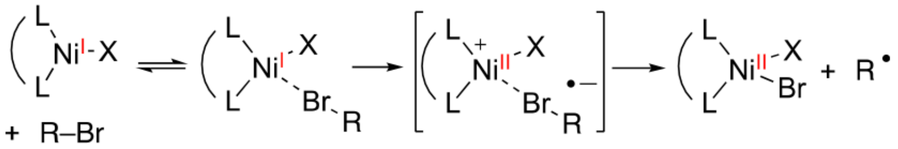
1. Oxidative Addition



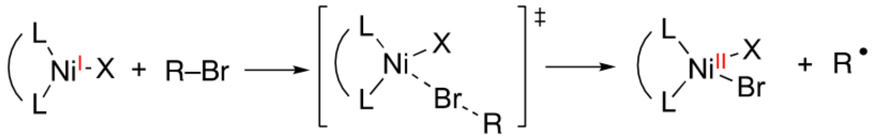
2. Outer-Sphere Electron-Transfer

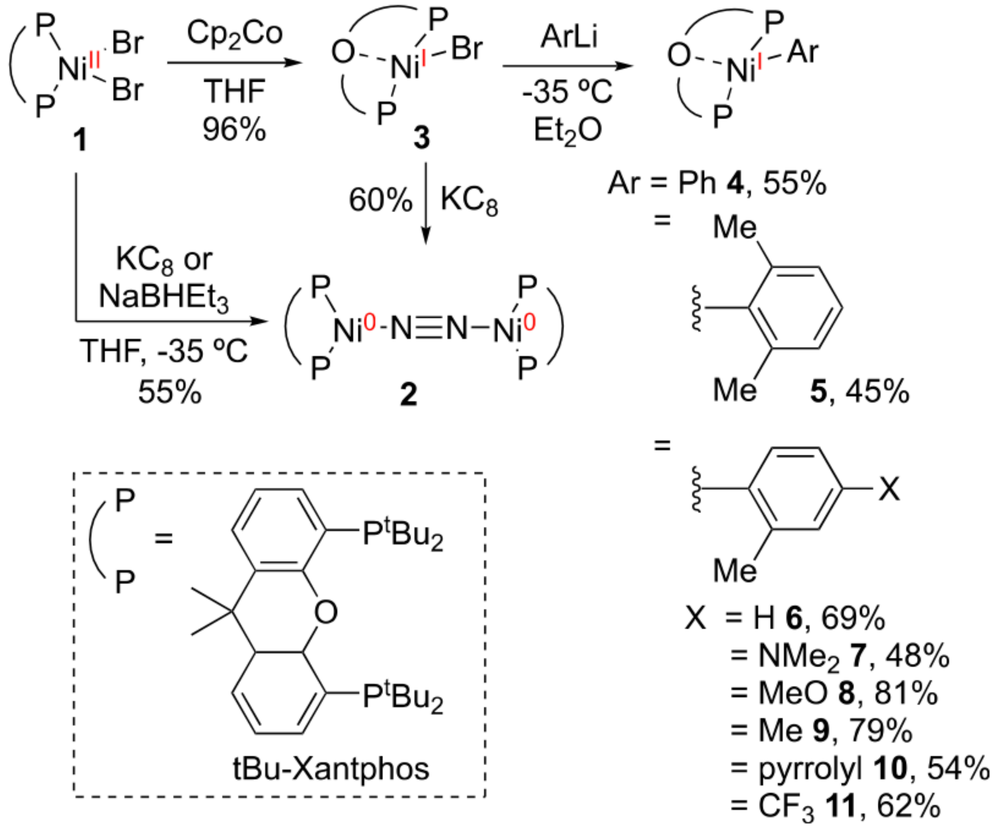


3. Inner-Sphere Electron-Transfer



4. Concerted Halogen Atom Abstraction





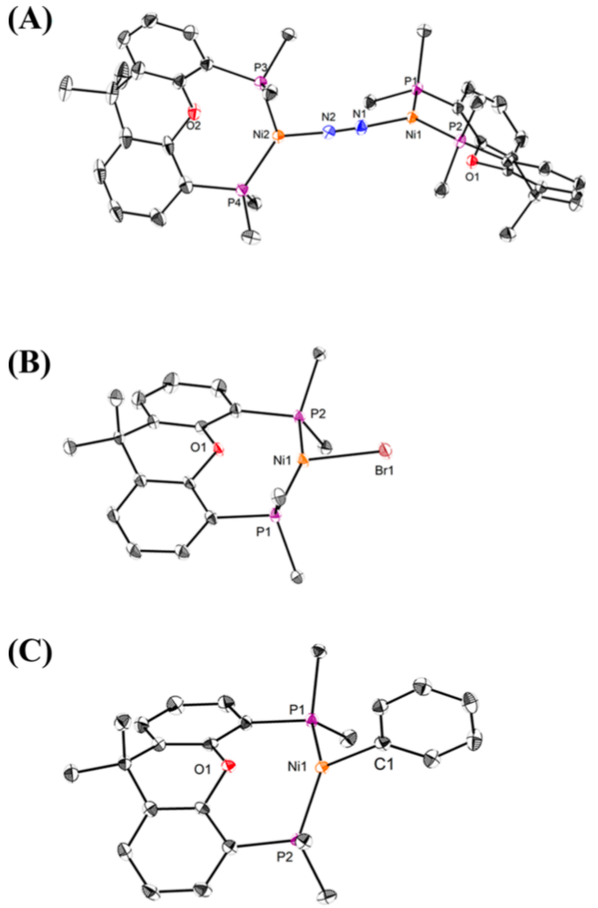


Figure 1. X-ray structures of **2** (A), **3** (B), and **4** (C) at 50% probability thermal ellipsoids. Hydrogen atoms are omitted and *t*-Bu groups are truncated for clarity. Selected bond lengths (Å) for **2**: N(1)≡N(2) = 1.144(3), Ni(1)···O(1) = 2.518. Selected bond length (Å) for **3**: Ni(1)···O(1) = 2.434. Selected bond lengths (Å) for **4**: Ni(1)−C(1) = 1.9795(14), Ni(1)···O(1) = 2.518.

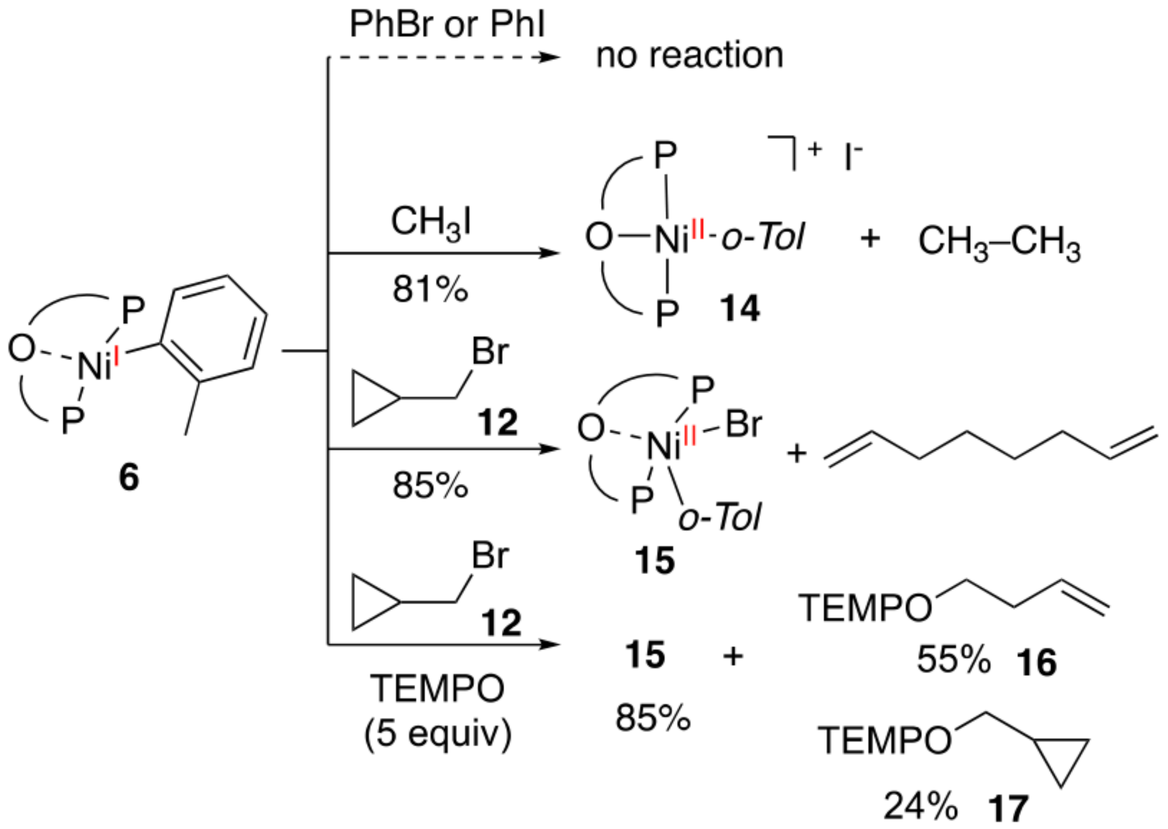
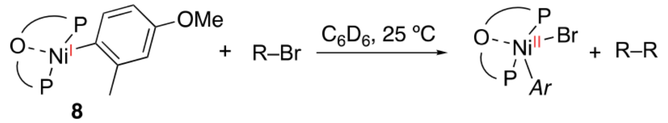

PhBr or PhI
no reaction
CH3I
81%
14
CH3–CH3
6
12
85%
15
12
TEMPO
(5 equiv)
15
85%
TEMPO
55% 16
TEMPO
24% 17

Table 1. Steric Effect of the Ar Group on Ni(I)Ar-Mediated Activation of 12[a]

Ar	$k \times 10^2$ ($M^{-1}s^{-1}$)	yield (%)
4	3.3	85
6	1.1	85
5	no reaction	0

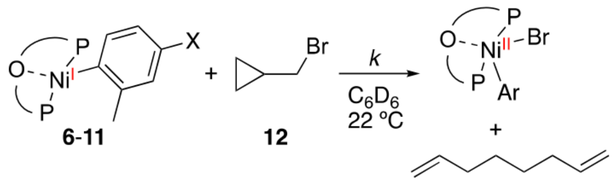
Table 2. Steric Effect of Alkyl Bromides on Ni(I)-Mediated Activation[a]



R–	$k \times 10^3$ ($M^{-1}s^{-1}$)	yield (%)
	1.4	73
	6.0	95
	3.8	90

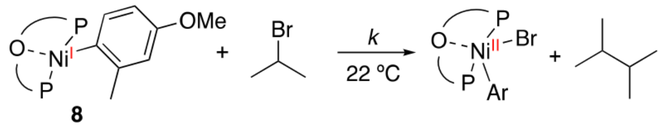
[a]Reaction conditions: $[\mathbf{8}]_0$ = 10 mM, $[R{-}Br]_0$ = 20 mM, C_6D_6 = 0.65 mL. Internal standard = mesitylene.

Table 3. Electronic Effect on Ni(I)-Mediated Alkyl Bromide Activation



X	σ_p	$E_{1/2}(Ni^{I/II})$ (V vs Fc^+/Fc)	$k \times 10^3$ (M^{-1} s^{-1})
NMe_2 **7**	−0.83	−1.60	27
OMe **8**	−0.27	−1.54	14
Me **9**	−0.17	−1.59	11
H **6**	0	−1.51	11
pyrrolyl **10**	0.37	−1.45	4.2
CF_3 **11**	0.54	−1.37	2.8

Table 4. Solvent Effect of 8-Mediated Isopropyl Bromide Activation



solvent	dielectric constant	$k \times 10^3$ (M^{-1} s^{-1})	yield
pentane-d_{12}	1.8	5.3	80
benzene-d_6	2.3	6.0	95
1,2-DME-d_{10}	7.2	1.8	88
THF-d_6	7.5	0.17	85
acetone-d_6	21	4.3	84

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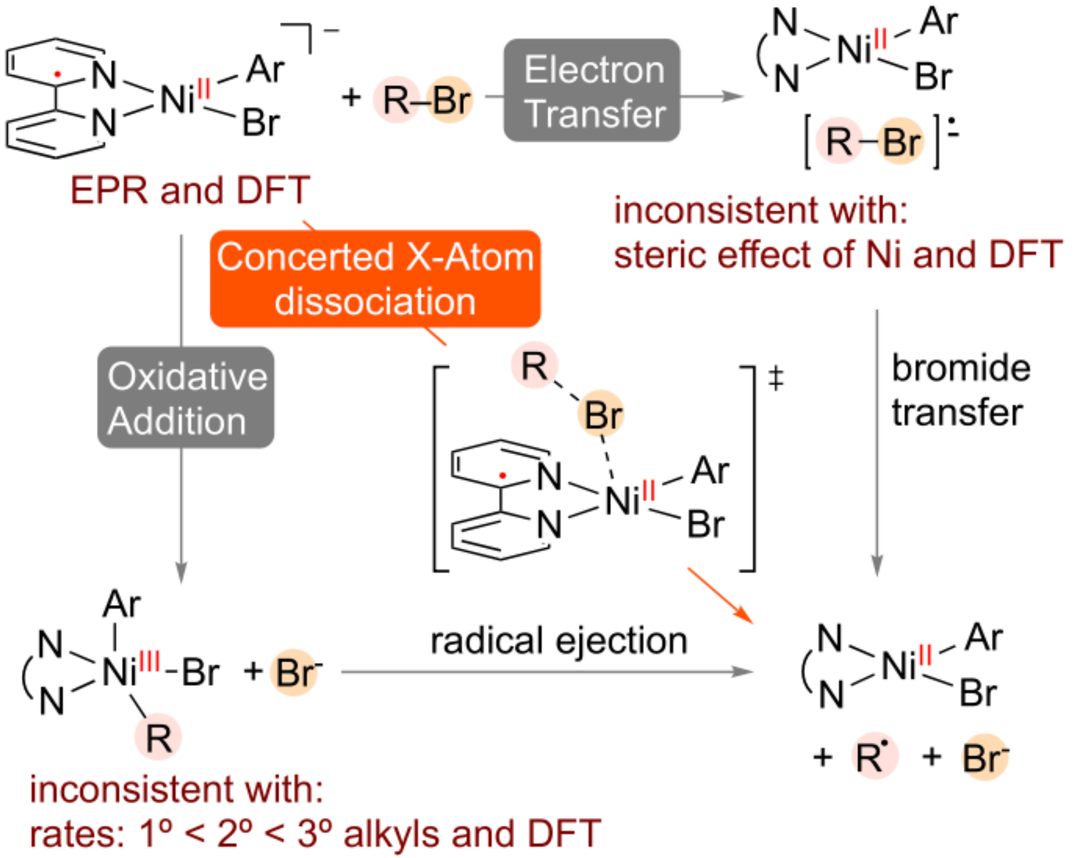
Monovalent Nickel-Mediated Radical Formation: A Concerted Halogen-Atom Dissociation Pathway Determined by Electroanalytical Studies

Qiao Lin, Yue Fu, Peng Liu,* and Tianning Diao*


Electron Transfer
EPR and DFT
inconsistent with:
steric effect of Ni and DFT
Concerted X-Atom dissociation
Oxidative Addition
bromide transfer
radical ejection
inconsistent with:
rates: 1° < 2° < 3° alkyls and DFT

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Communication

Reactivity of (bi-Oxazoline)organonickel Complexes and Revision of a Catalytic Mechanism

Luchuan Ju, Qiao Lin, Nicole J. LiBretto, Clifton L. Wagner, Chunhua Tony Hu, Jeffrey T. Miller,* and Tianning Diao*

Cite This: *J. Am. Chem. Soc.* 2021, 143, 14458–14463

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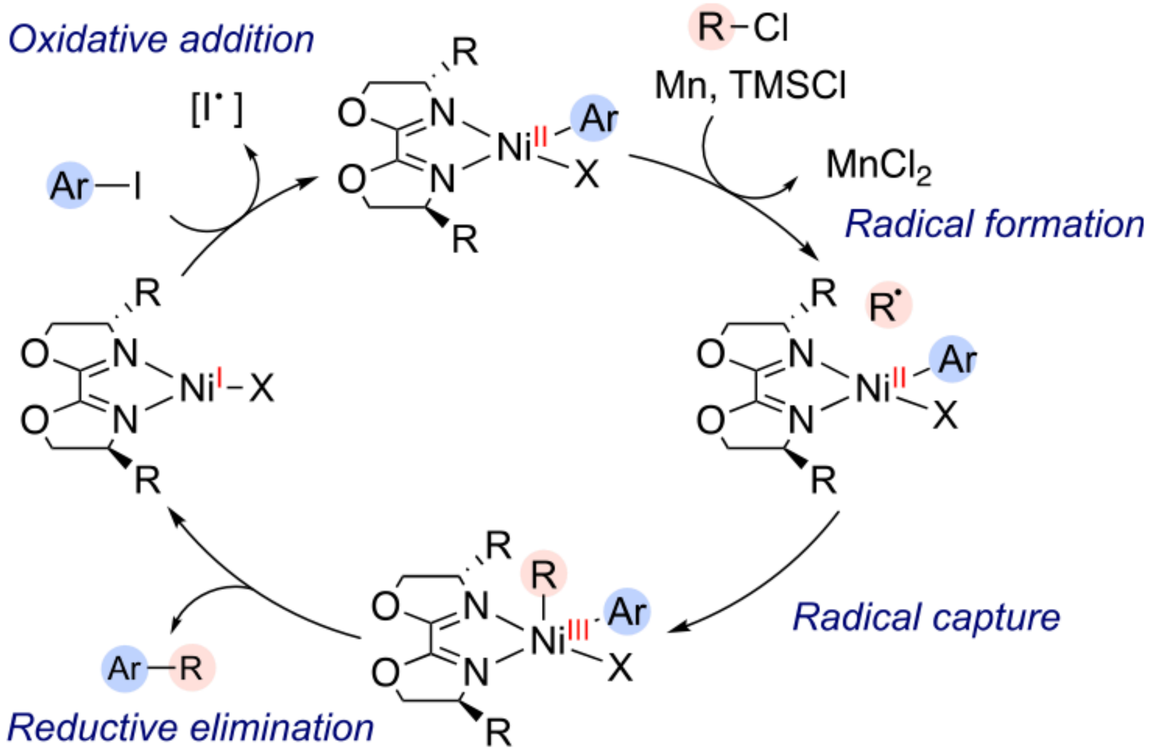
Oxidative addition
[I•]
Ar—I
R–Cl
Mn, TMSCl
MnCl2
Radical formation
R•
Radical capture
Ar—R
Reductive elimination

Experimental Electrochemical Potentials of Nickel Complexes

Qiao Lin
Gregory Dawson
Tianning Diao*

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100 Washington Square East, New York, NY 10003, USA
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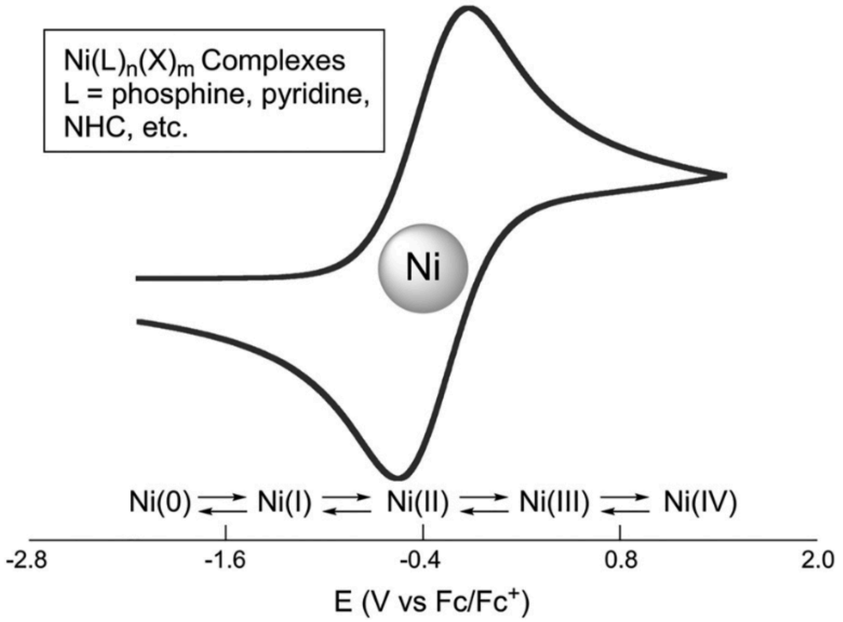
Published as part of the Cluster
Modern Nickel-Catalyzed Reactions



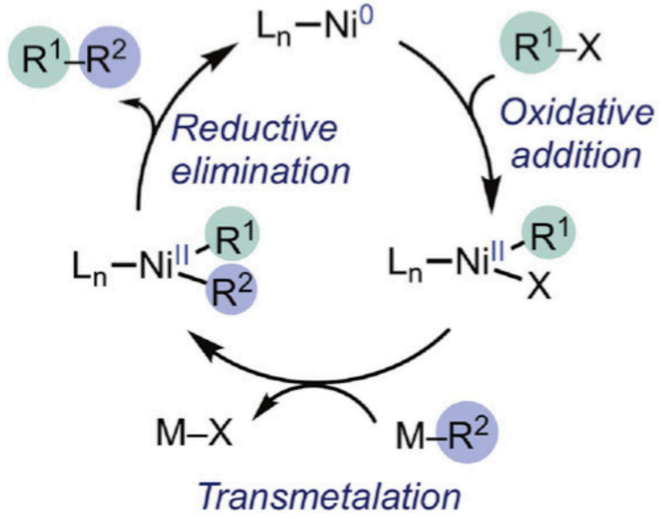
Complex		Process	Solvent	Electrolyte (M)	Potential reference	$E_{1/2}$ (V vs. Fc/Fc^+)
(^{tBu}Xantphos)Ni(2,4-xylene)[21]	**1**	Ni(I) → Ni(0)	THF	$TBAPF_6$ (0.4)	Fc/Fc^+	−2.78
(^{tBu}Xantphos)Ni(o-Tol)[21]	**2**	Ni(I) → Ni(0)	THF	$TBAPF_6$ (0.4)	Fc/Fc^+	−2.70
(dppb)Ni[$(CN)_2C_2S_2$][40]	**3**	Ni(I) → Ni(0)	DMF	$TBABF_4$ (0.1)	Fc/Fc^+	−2.22
[$PhB^-(CH_2P^iPr_2)_3$]Ni(PMe_3)[22]	**4**	Ni(I) → Ni(0)	THF	$TBAPF_6$ (0.35)	Fc/Fc^+	−1.95
(^{acri}PNP)Ni(CO)[23]	**5**	Ni(I) → Ni(0)	THF	$TBAPF_6$ (0.3)	Fc/Fc^+	−1.87
[$PhB^-(CH_2P^iPr_2)_3$]Ni(CN^tBu)[22]	**6**	Ni(I) → Ni(0)	THF	$TBAPF_6$ (0.35)	Fc/Fc^+	−1.85
[$HN(P^iPr_2)_2]_2Ni(NO_3)_2$[24]	**7**	Ni(I) → Ni(0)	THF	$TBAPF_6$ (0.1)	Fc/Fc^+	−1.53
$Ni(P^{Cy}{}_2N^{tBu}{}_2)_2$[25]	**8**	Ni(0) → Ni(I)	PhCN	$TBAPF_6$ (0.2)	Fc/Fc^+	−1.49
[$HN(P^iPr_2)_2]_2Ni(ClO_4)_2$[24]	**9**	Ni(I) → Ni(0)	THF	$TBAPF_6$ (0.1)	Fc/Fc^+	−1.49
[$HN(P^iPr_2)_2]_2Ni(BF_4)_2$[24]	**10**	Ni(I) → Ni(0)	THF	$TBAPF_6$ (0.1)	Fc/Fc^+	−1.45
$Ni(dmpp)_2$[26]	**11**	Ni(0) → Ni(I)	MeCN	Et_4NBF_4 (0.3)	Fc/Fc^+	−1.33
$Ni(PMe_3)_4$[27]	**12**	Ni(0) → Ni(I)	1,2-$C_6H_4F_2$	$TBAPF_6$ (0.1)	Fc/Fc^+	−1.31
$(P^{Me}{}_2N^{Ph}{}_2)_2Ni(BF_4)_2$[28]	**13**	Ni(I) → Ni(0)	PhCN	$TBAPF_6$ (0.2)	Fc/Fc^+	−1.30
$Ni(depe)_2$[26]	**14**	Ni(0) → Ni(I)	MeCN	Et_4NBF_4 (0.3)	Fc/Fc^+	−1.29
$(P^{Ph}{}_2N^{Me(CH)Ph}{}_2)_2Ni(BF_4)_2$[29]	**15**	Ni(I) → Ni(0)	MeCN	$TBABF_4$ (0.1)	Fc/Fc^+	−1.27
$Ni(NHC^{Mes}CH_2P^{Cy2})(cod)$[30]	**16**	Ni(0) → Ni(I)	THF	$TBAPF_6$ (0.1)	Fc/Fc^+	−1.26
$Ni(dppf)_2$[31]	**17**	Ni(0) → Ni(I)	THF	$TBAPF_6$ (0.2)	Fc/Fc^+	−1.18
$(P^{Ph}{}_2N^{Ph(CH)Ph}{}_2)_2Ni(BF_4)_2$[29]	**18**	Ni(I) → Ni(0)	MeCN	$TBABF_4$ (0.1)	Fc/Fc^+	−1.14
$(P^{Ph}{}_2N^{Bn}{}_2)_2Ni(BF_4)_2$[29]	**19**	Ni(I) → Ni(0)	MeCN	$TBABF_4$ (0.1)	Fc/Fc^+	−1.13
$(P^{Ph}{}_2N^{p\text{-}Tol}{}_2)_2Ni(BF_4)_2$[29]	**20**	Ni(I) → Ni(0)	MeCN	$TBABF_4$ (0.1)	Fc/Fc^+	−1.08
(triphos)(PEt_3)Ni$(BF_4)_2$[32]	**21**	Ni(I) → Ni(0)	MeCN	Et_4NBF_4 (0.2)	SCE	−1.05[a]
Ni(dcype)(cod)[30]	**22**	Ni(0) → Ni(I)	THF	$TBAPF_6$ (0.1)	Fc/Fc^+	−0.95
$Ni(dppp)_2$[26]	**23**	Ni(0) → Ni(I)	MeCN	Et_4NBF_4 (0.3)	Fc/Fc^+	−0.91
(triphos)Ni(PPh_3)[33]	**24**	Ni(0) → Ni(I)	THF	$TBAPF_6$ (0.1)	NHE	−0.90[b]
$Ni(dppe)_2$[26]	**25**	Ni(0) → Ni(I)	MeCN	Et_4NBF_4 (0.3)	Fc/Fc^+	−0.88

Review

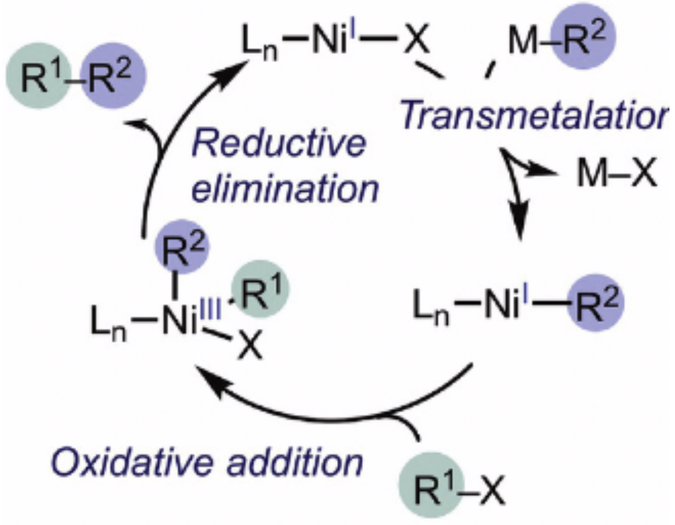
Mechanisms of Nickel-Catalyzed Cross-Coupling Reactions

Justin B. Diccianni[1] and Tianning Diao[1,*]

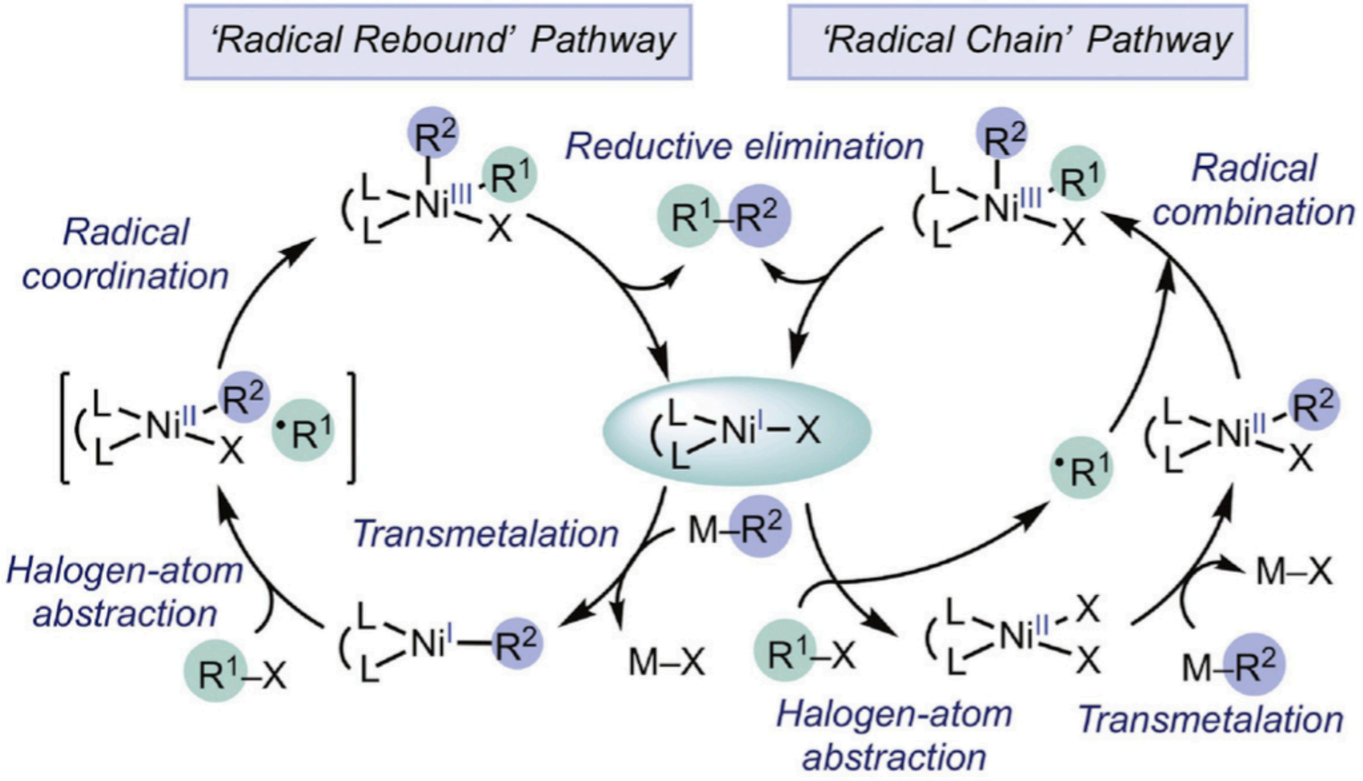
(i) Two-electron pathway via Ni(0)/Ni(II)



(ii) Two-electron pathway via Ni(I)/Ni(II



(iii) Single-electron pathways involving Ni(I), Ni(III), and organic radicals



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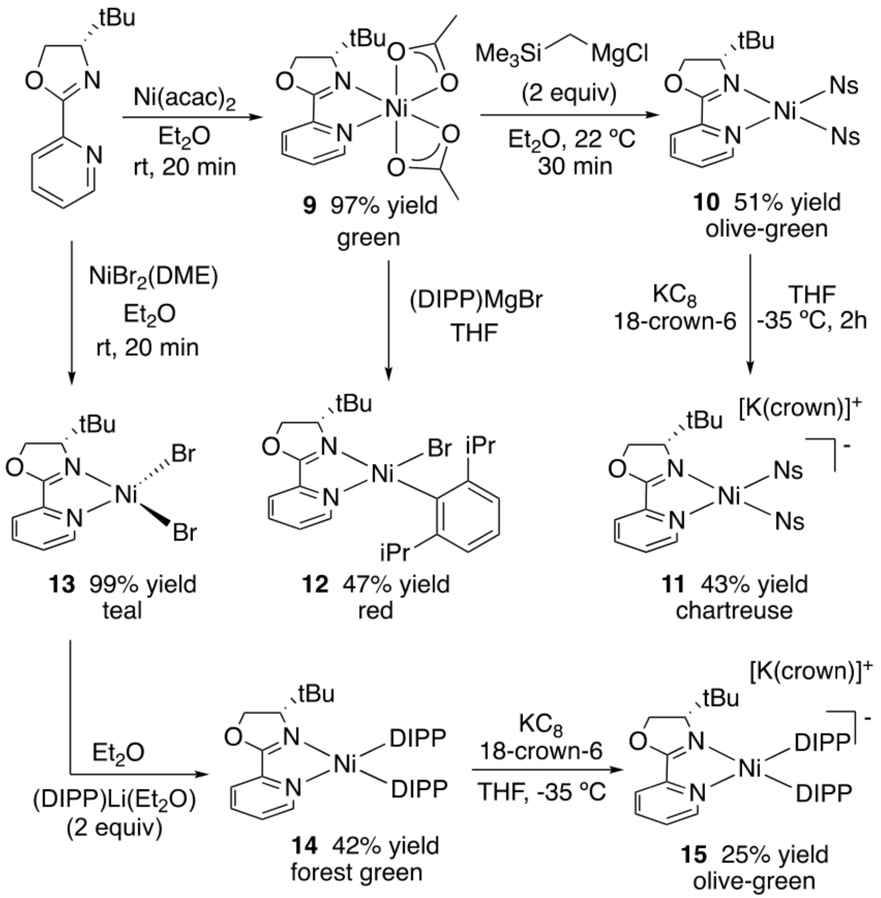
Communication

Redox Activity of Pyridine-Oxazoline Ligands in the Stabilization of Low-Valent Organonickel Radical Complexes

Clifton L. Wagner,[†] Gabriel Herrera,[†] Qiao Lin, Chunhua T. Hu, and Tianning Diao*

Scheme 1. Syntheses of ((*S*)-^{tBu}Pyrox)Ni(II) and Ni(I) Complexes



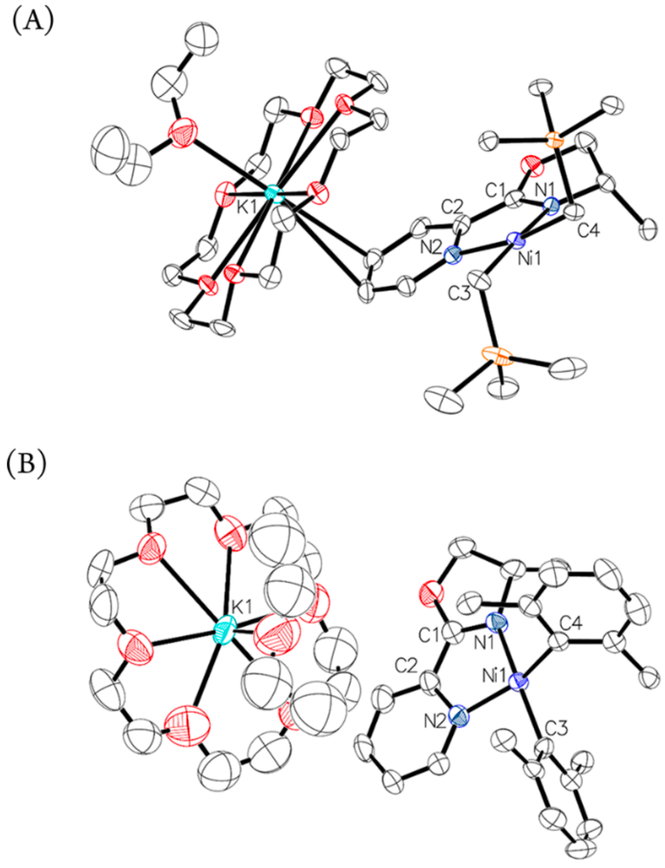


Figure 2. X-ray structures of Ni complexes **11** (A) and **15** (B) at 50% probability thermal ellipsoids. Hydrogen atoms are omitted, and *t*-Bu and isopropyl groups are truncated for clarity.

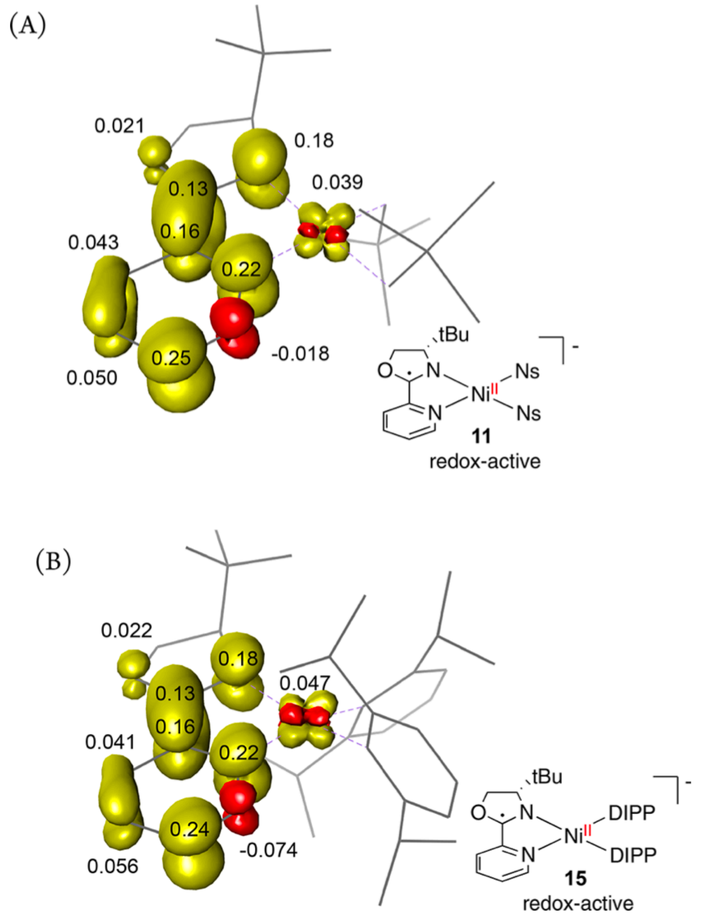
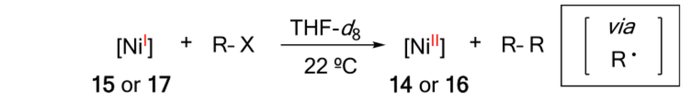
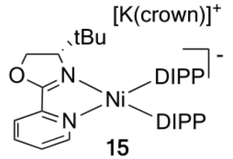
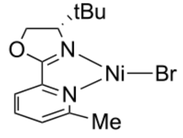
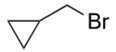
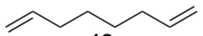
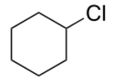
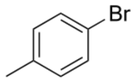


Figure 4. Spin density plots for **11** (A) and **15** (B) obtained from Mulliken population analysis.

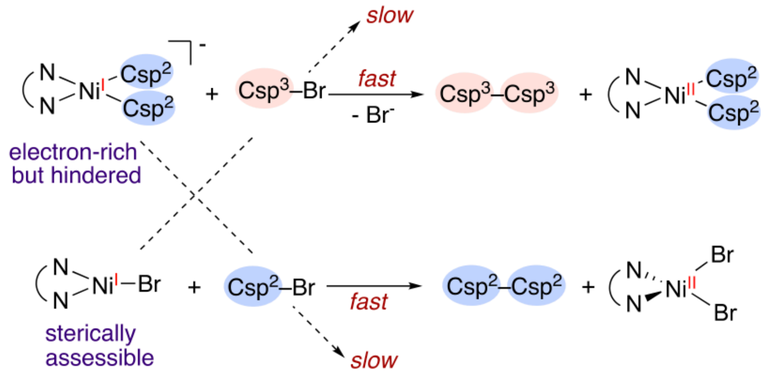
Table 2. Reactivity of 15 and 17 with Electrophiles to Afford Radicals



Ni(I) complex / Electrophile	[K(crown)]+  15		 17
CH_3-I	CH_3-CH_3 (95% yield)	14 (41% yield)	CH_3-CH_3 not observed
	 18 (22% yield)	14 (22% yield)	18 not observed
	no reaction		no reaction
	no reaction		*p*-Tol—*p*-Tol (33% yield) 16 (59% yield)

The preference of C(sp^3) over C(sp^2) electrophiles by **15** could stem from the high electron-density that facilitates electron transfer, whereas the large steric hindrance prevents the approach of Csp^2 electrophiles to the Ni center (Scheme 2). Ni(I)–Br complex **17** favors C(sp^2) to C(sp^3) electro-

Scheme 2. Selectivity of Ni(I) Complexes in Activating Csp^2 and Csp^3 Electrophiles



Synthetic Methods

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International Edition: doi.org/10.1002/anie.202014991
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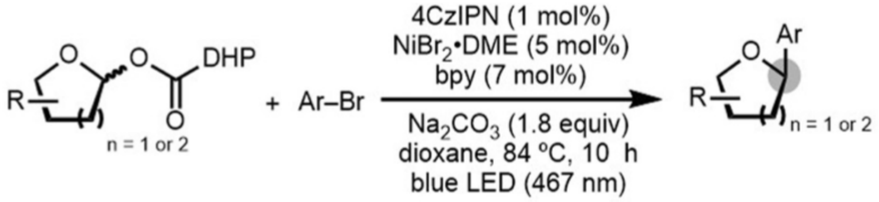
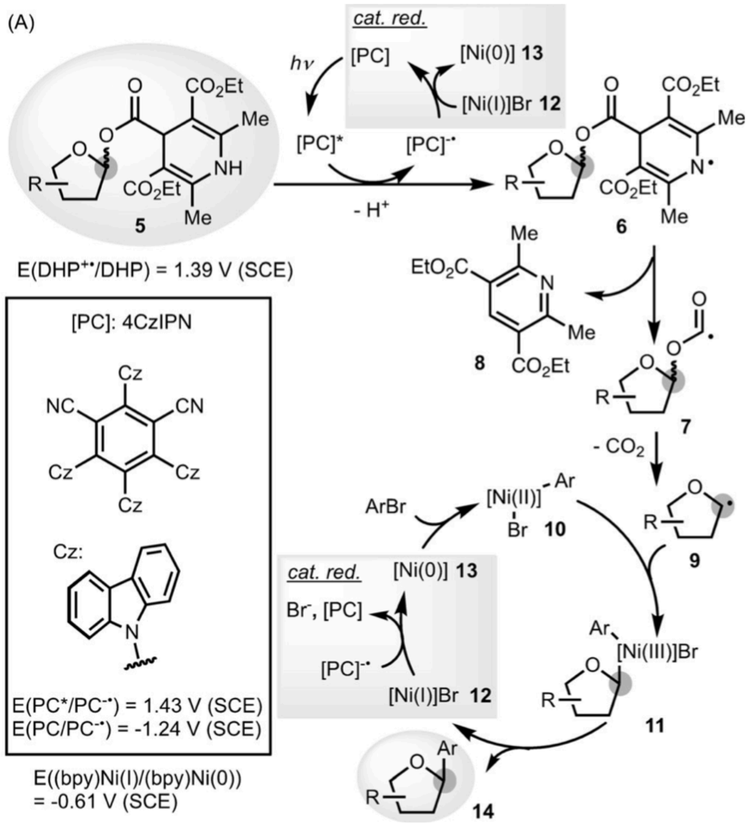
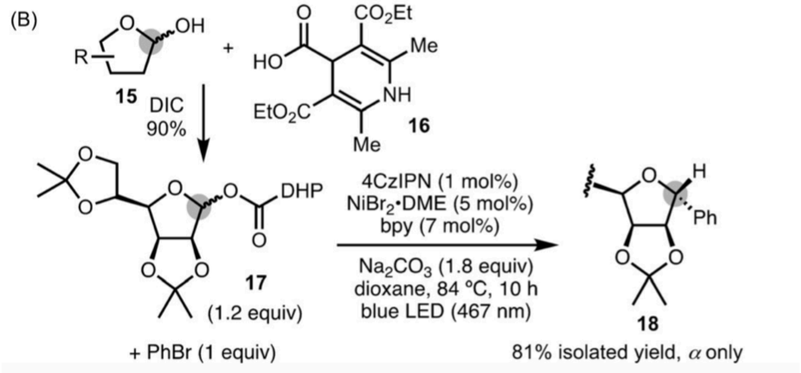
Diastereoselective Synthesis of Aryl *C*-Glycosides from Glycosyl Esters via C–O Bond Homolysis

*Yongliang Wei, Benjamin Ben-zvi, and Tianning Diao**

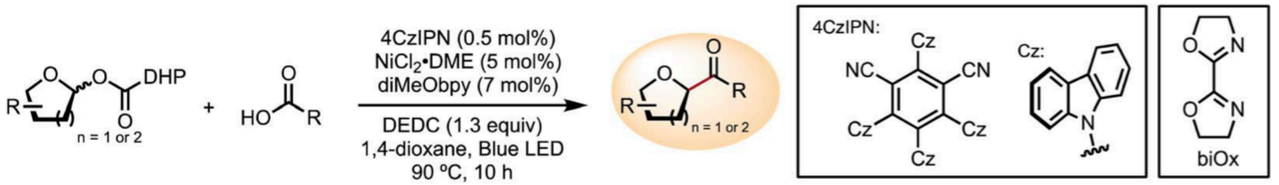


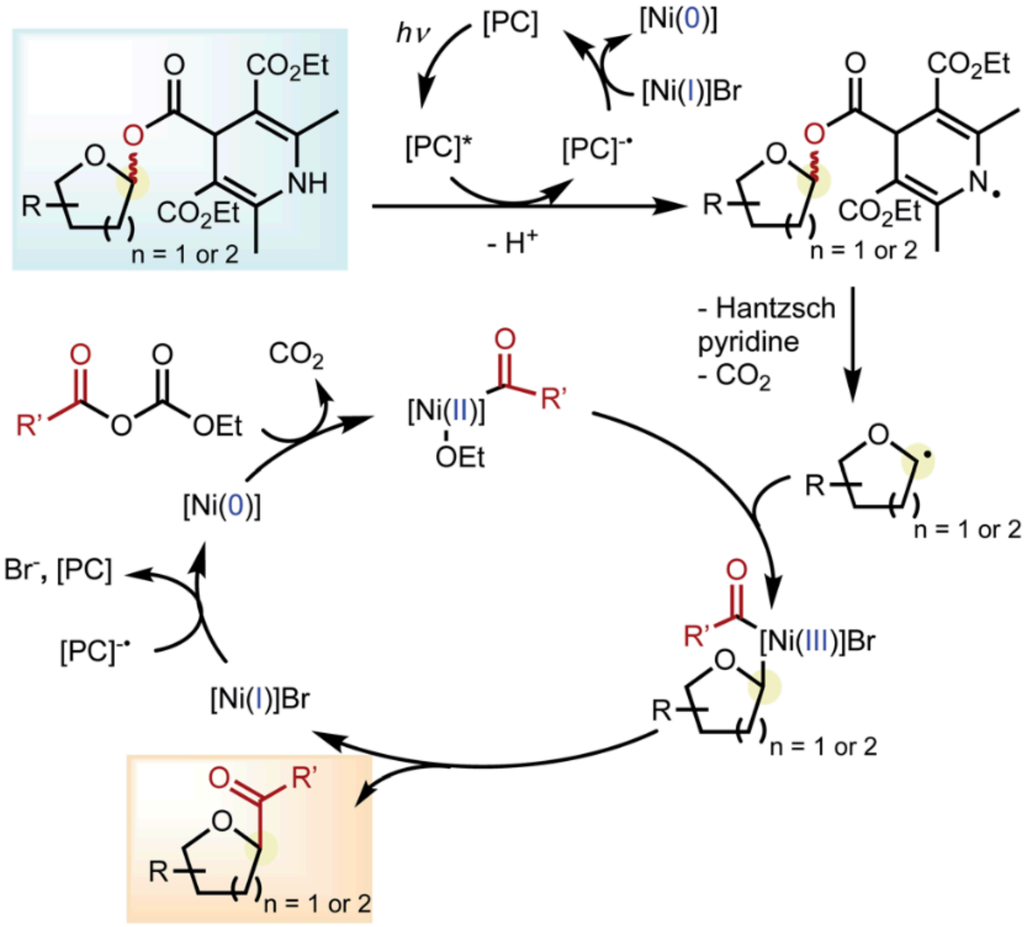

(A)
cat. red.
[PC]
[Ni(0)] 13
[Ni(I)]Br 12
hν
[PC]*
[PC]-•
- H+
5
6
E(DHP+•/DHP) = 1.39 V (SCE)
[PC]: 4CzIPN
Cz:
E(PC*/PC-•) = 1.43 V (SCE)
E(PC/PC-•) = -1.24 V (SCE)
E((bpy)Ni(I)/(bpy)Ni(0))
= -0.61 V (SCE)
8
7
- CO2
ArBr
[Ni(II)]
10
9
Br-, [PC]
[Ni(III)]Br
11
14


(B)
15
DIC
90%
16
17
(1.2 equiv)
+ PhBr (1 equiv)
4CzIPN (1 mol%)
NiBr2•DME (5 mol%)
bpy (7 mol%)
Na2CO3 (1.8 equiv)
dioxane, 84 °C, 10 h
blue LED (467 nm)
18
81% isolated yield, α only

Synthesis of *C*-acyl furanosides *via* the cross-coupling of glycosyl esters with carboxylic acids†

Yongliang Wei, Jenny Lam and Tianning Diao *

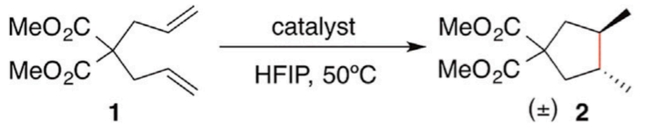



hν
[PC]
[Ni(0)]
[Ni(I)]Br
[PC]*
[PC]-•
- H+
CO2Et
NH
n = 1 or 2
- Hantzsch
pyridine
- CO2
CO2
OEt
[Ni(II)]
[Ni(0)]
Br-, [PC]
[PC]-•
[Ni(I)]Br
[Ni(III)]Br

Article

Ni(I)-Catalyzed Reductive Cyclization of 1,6-Dienes: Mechanism-Controlled *trans* Selectivity

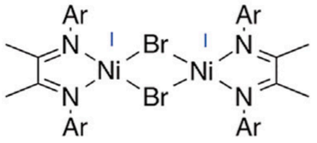
Yulong Kuang,[1] David Anthony,[1] Joseph Katigbak,[1] Flaminia Marrucci,[1] Sunita Humagain,[2] and Tianning Diao[1,3,*]



1 (±) **2**

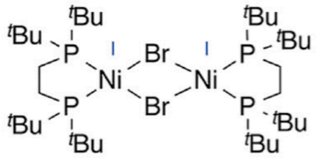
Entry	Catalyst	mol%	Silane (2 equiv)	Yield of **2** (%)[a]
1	$Fe(acac)_3$/EtOH	100	$PhSiH_3$	8 (*cis:trans* = 5.3:1)
2	$Co(sal^{tBu,tBu})Cl$	10	$PhSiH_3$	0
3	($^{Ar}\alpha$-diimine)$Ni^{II}Br_2$ (**3**)	5	Et_2SiH_2	50
4	($^{Ar}\alpha$-diimine)$Ni^{II}Me_2$ (**4**)	5	Et_2SiH_2	0
5	**[($^{Ar}\alpha$-diimine)$Ni^{I}(\mu$-Br)]$_2$ (5)**	**2.5**	**Et_2SiH_2**	**79**
6	[($^{Ar}\alpha$-diimine)$Ni^{I}(\mu$-H)]$_2$ (**6**)	2.5	Et_2SiH_2	41
7	[($^{Bn}\alpha$-diimine)$Ni^{II}Br_2$ (**7**)	10	Et_2SiH_2	76
8	[(dtbpe)$Ni^{I}(\mu$-Br)]$_2$ (**8**)	2.5	Et_2SiH_2	19
9	[($^{Ar}\alpha$-diimine)$Ni^{I}(\mu$-Br)]$_2$ (**5**)	2.5	Et_3SiH	0
10	[($^{Ar}\alpha$-diimine)$Ni^{I}(\mu$-Br)]$_2$ (**5**)	2.5	$PhSiH_3$	14
11	[($^{Ar}\alpha$-diimine)$Ni^{I}(\mu$-Br)]$_2$ (**5**)	2.5	H_2	0

Conditions: [1] = 0.1 M (21 mg, 0.1 mmol), hexafluoroisopropanol (HFIP) (1 mL), N_2, 12 h.
[a] Determined by GC, internal standard = mesitylene.

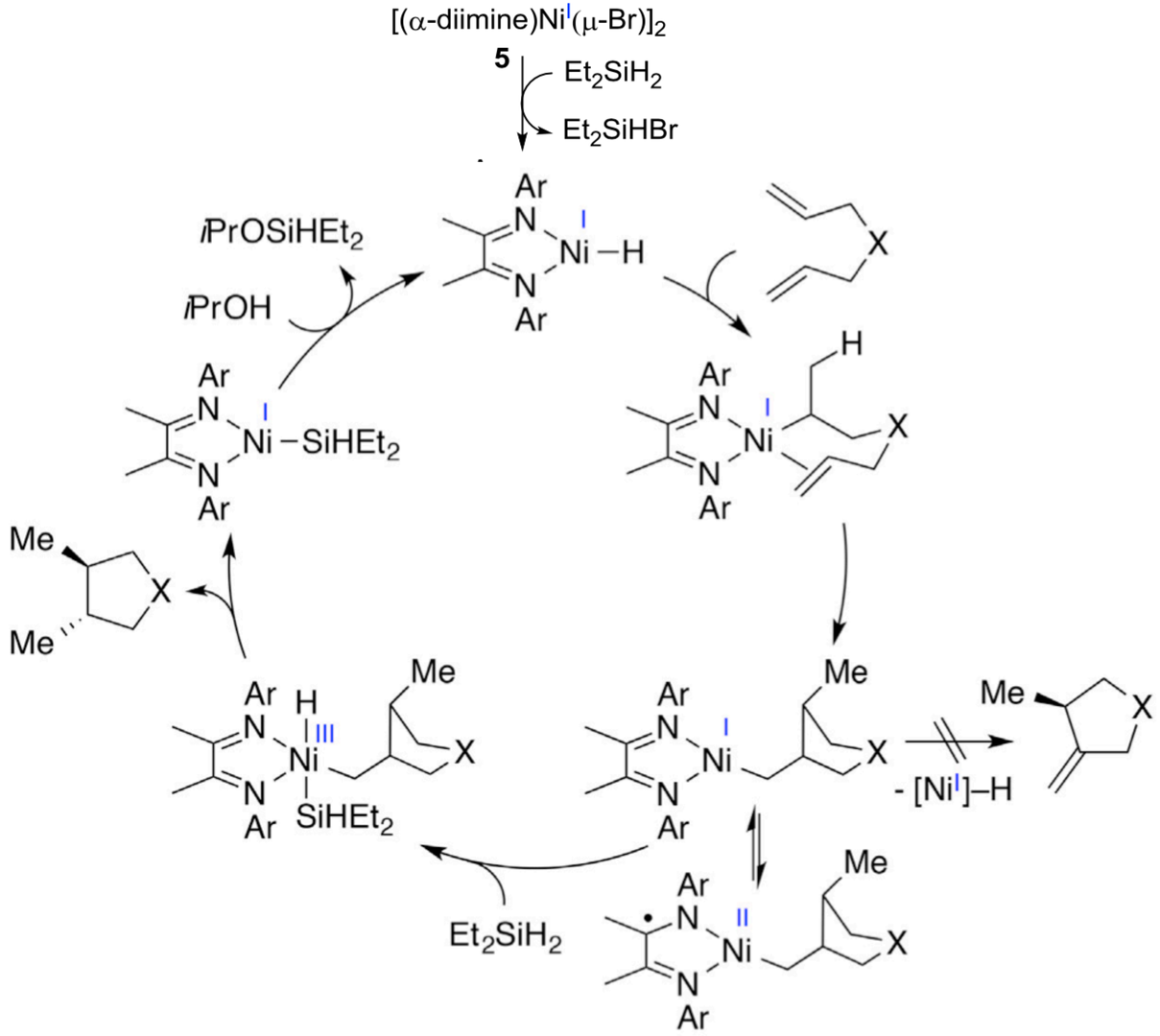


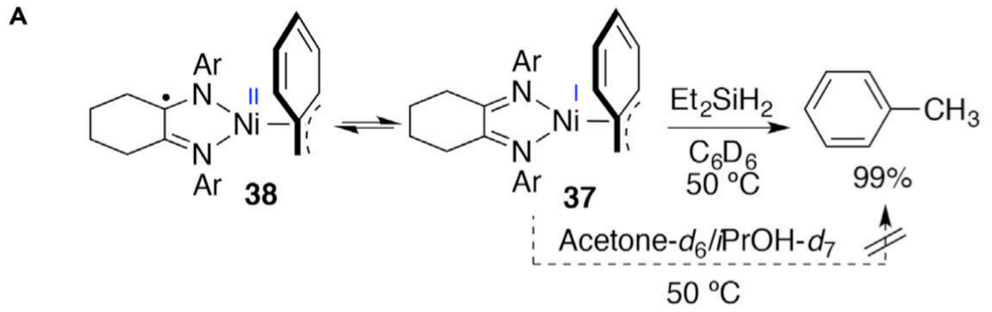
Ar = 2,6-diisopropylphenyl

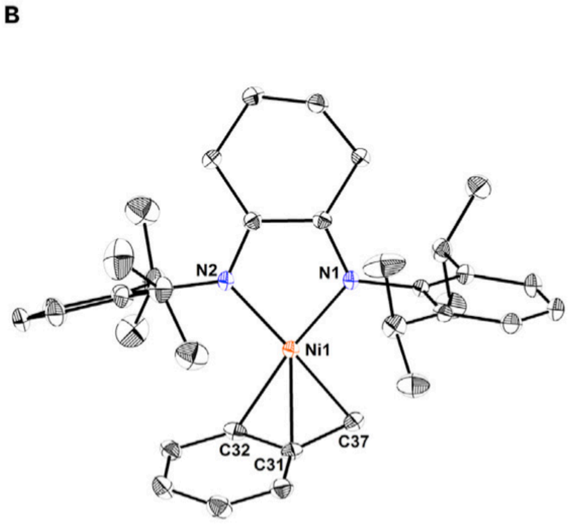
[($^{Ar}\alpha$-diimine)$Ni^{I}(\mu$-Br)]$_2$ (**5**)

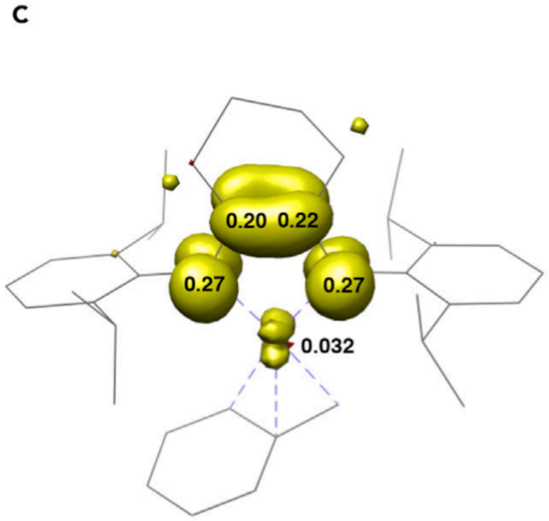


[(dtbpe)$Ni^{I}(\mu$-Cl)]$_2$ (**8**)


[(α-diimine)Ni^{I}(μ-Br)]$_2$
5
Et_2SiH_2
Et_2SiHBr
$iPrOSiHEt_2$
$iPrOH$
Ni–H
Ni–SiHEt$_2$
SiHEt$_2$
Et_2SiH_2
- [Ni^{I}]–H
Me
X
Ar
N
H
I
II
III

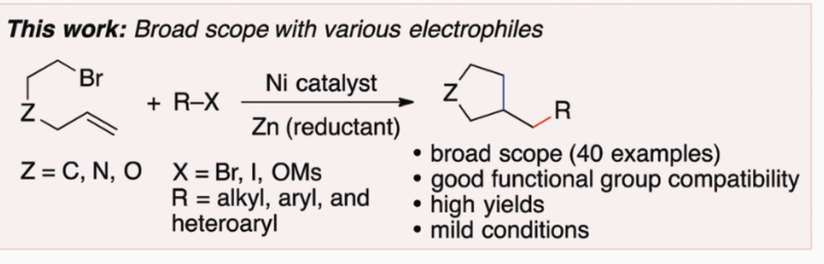

A
Ar
N
Ni
II
N
Ar
38
Ar
N
Ni
I
N
Ar
37
Et2SiH2
C6D6
50 °C
CH3
99%
Acetone-d6/iPrOH-d7
50 °C

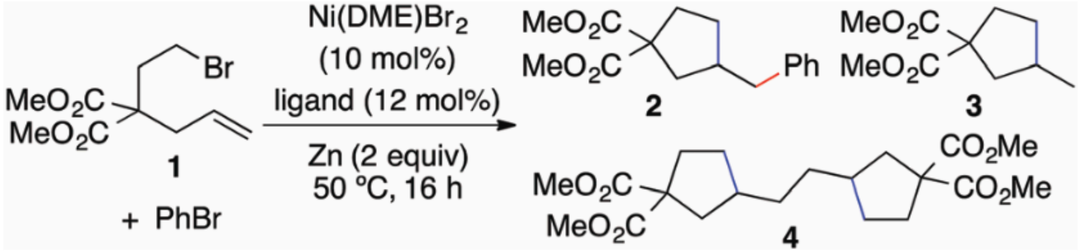

B
N2
N1
Ni1
C32
C31
C37


C
0.20
0.22
0.27
0.27
0.032

Ni-catalyzed two-component reductive dicarbofunctionalization of alkenes *via* radical cyclization†

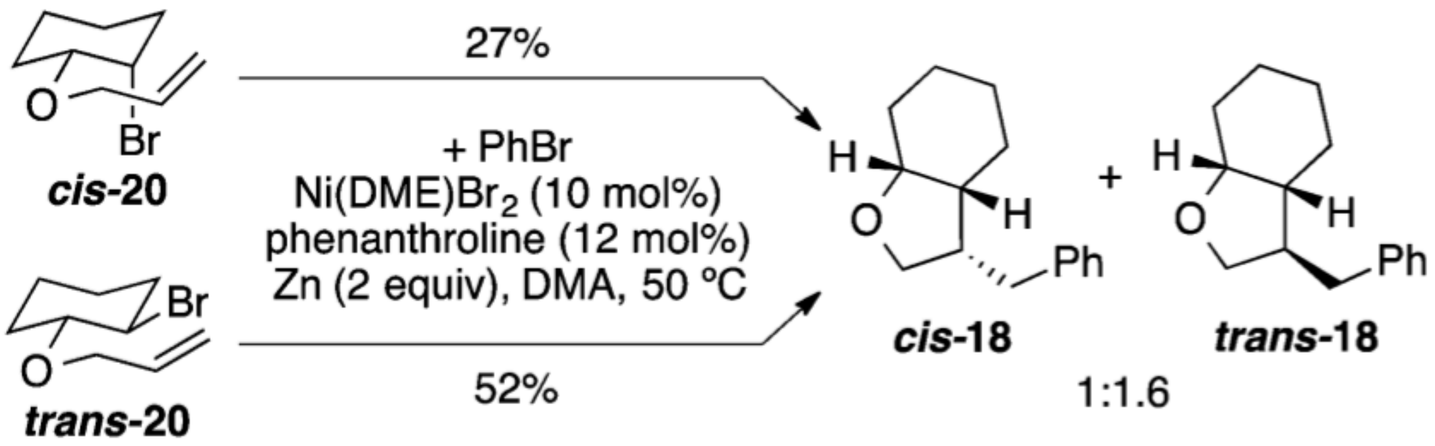
Yulong Kuang, Xuefeng Wang, David Anthony and Tianning Diao *

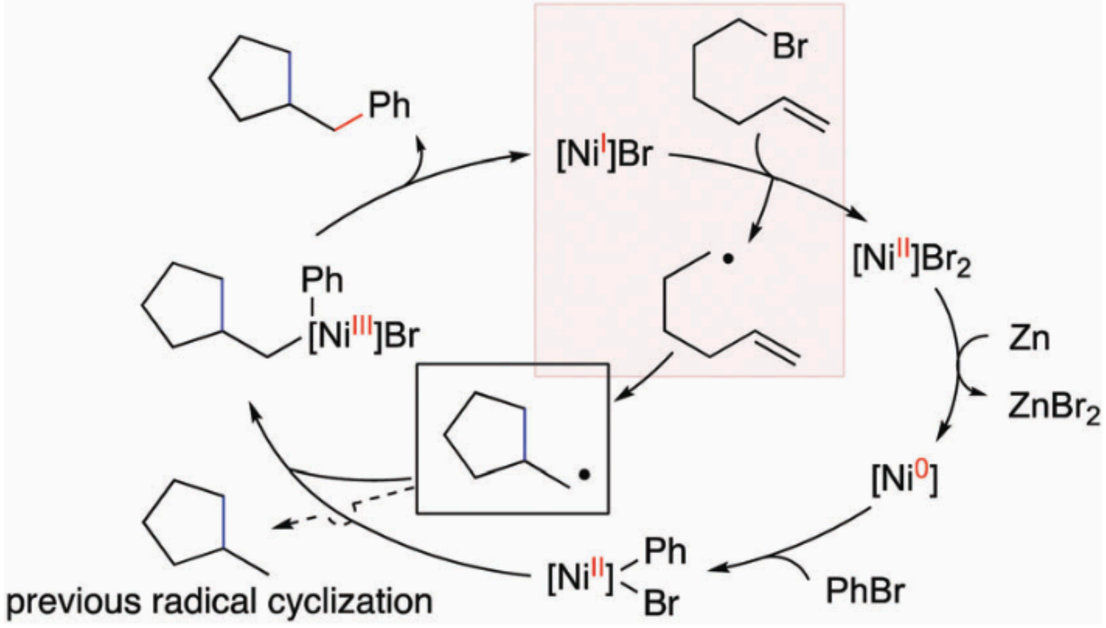




Entry	Ligand	Solvent	2[b] (yield%)	3[b] (yield%)	4[b] (yield%)
1	di-^{t}Bu-bpy	DMA	76	0	7
2	**1,10-Phenanthroline**	**DMA**	**91 (94)**	**0**	**8**
3	Neocuproine	DMA	19	6	30
4	1,10-Phenanthroline	DMF	33	6	45
5	1,10-Phenanthroline	HMPA	53	0	6
6	1,10-Phenanthroline	THF	0	8	0
7[c]	1,10-Phenanthroline	DMA	0	0	0
8[c]	di-^{t}Bu-bpy	DMA	0	0	99 (99)

[a] 0.1 mmol scale, 2 equiv. of PhBr, 2 equiv. of Zn. DMA = *N,N*-dimethylacetamide, DMF = *N,N*-dimethylformamide, HMPA = hexamethylphosphoramide. [b] Calibrated NMR yields using CH_3NO_2 as an internal standard. Isolated yields in parentheses. [c] No PhBr.


27%
+ PhBr
Ni(DME)Br2 (10 mol%)
phenanthroline (12 mol%)
Zn (2 equiv), DMA, 50 °C
52%
cis-20
trans-20
cis-18
trans-18
1:1.6


Ph
Br
[Ni^I]Br
[Ni^II]Br2
Ph
[Ni^III]Br
Zn
ZnBr2
[Ni^0]
[Ni^II]
Ph
Br
PhBr
previous radical cyclization

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Article

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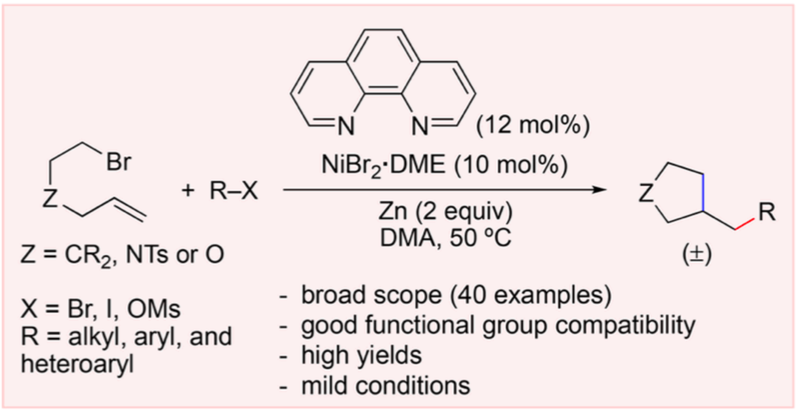
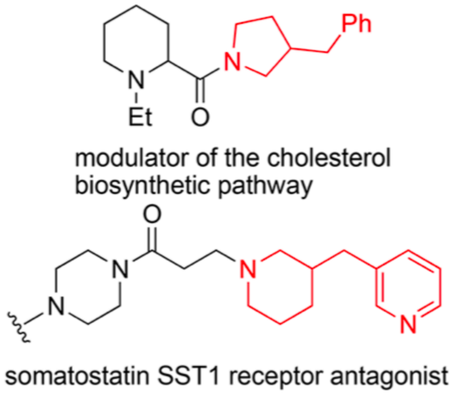
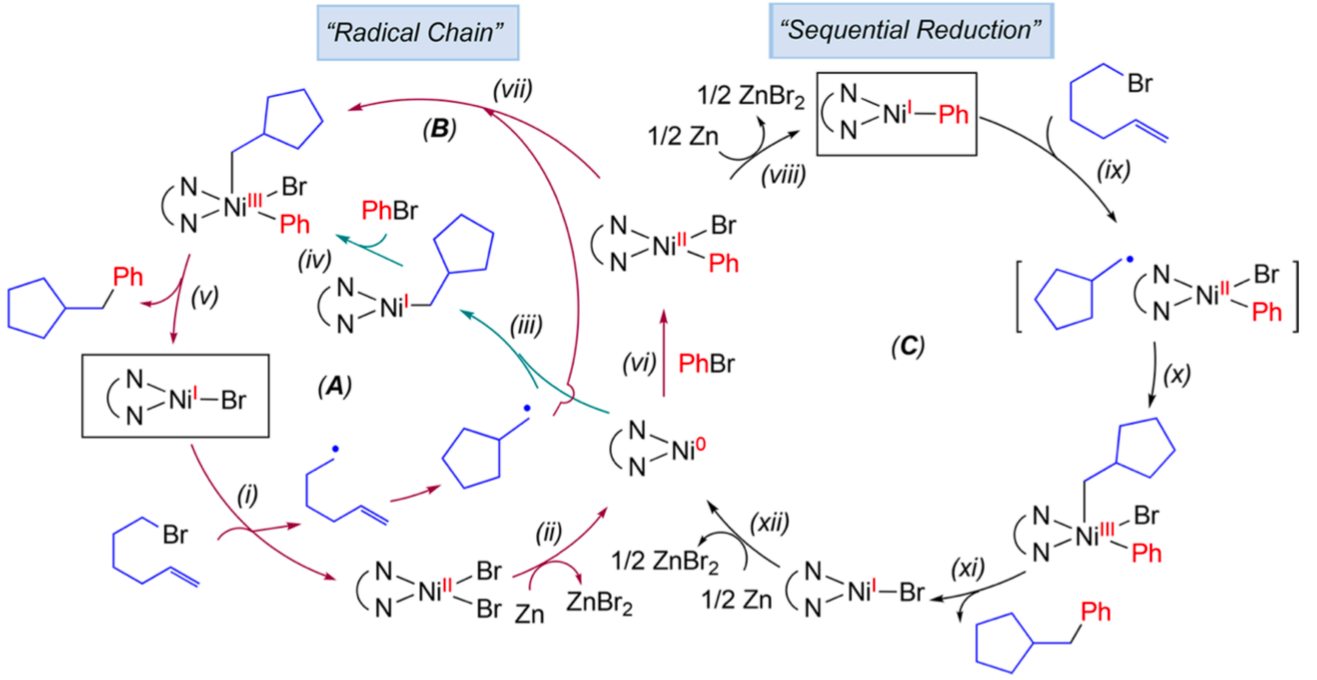
Mechanism of Ni-Catalyzed Reductive 1,2-Dicarbofunctionalization of Alkenes

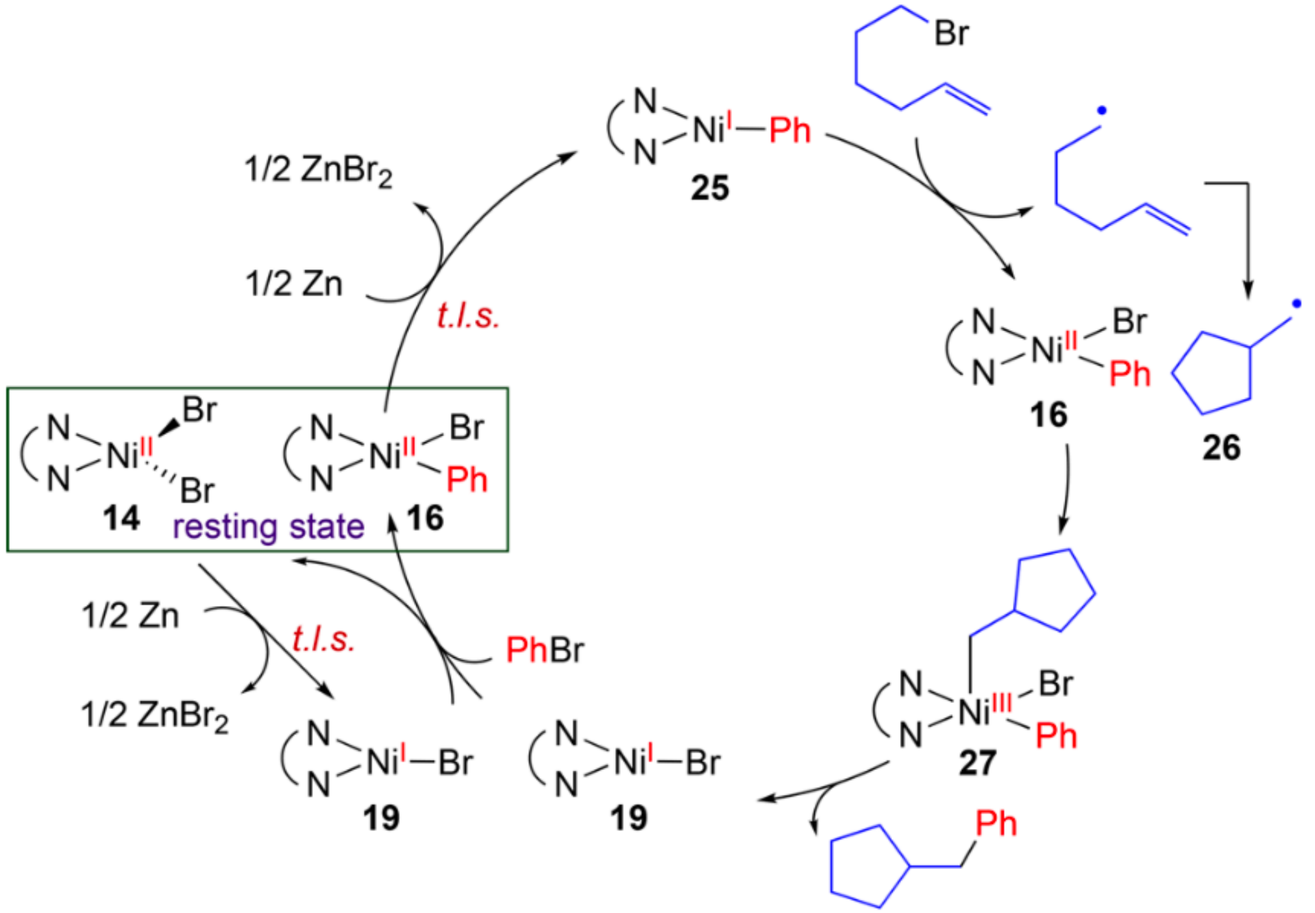
Qiao Lin and Tianning Diao*

Department of Chemistry, New York University, 100 Washington Square East, New York, New York 10003, United States


(12 mol%)
NiBr2·DME (10 mol%)
Zn (2 equiv)
DMA, 50 ºC
+ R–X
Z = CR2, NTs or O
X = Br, I, OMs
R = alkyl, aryl, and heteroaryl
- broad scope (40 examples)
- good functional group compatibility
- high yields
- mild conditions
(±)


modulator of the cholesterol biosynthetic pathway
somatostatin SST1 receptor antagonist


"Radical Chain"
"Sequential Reduction"
(A)
(B)
(C)
(i)
(ii)
(iii)
(iv)
(v)
(vi)
(vii)
(viii)
(ix)
(x)
(xi)
(xii)
PhBr
1/2 ZnBr2
1/2 Zn
Zn
ZnBr2


Br
N
N
Ni^I—Ph
25
1/2 ZnBr2
1/2 Zn
t.l.s.
N
N
Ni^II
Br
Br
14
N
N
Ni^II
Br
Ph
16
resting state
N
N
Ni^II
Br
Ph
16
26
1/2 Zn
t.l.s.
1/2 ZnBr2
PhBr
N
N
Ni^I—Br
19
N
N
Ni^I—Br
19
N
N
Ni^III
Br
Ph
27
Ph

Asymmetric Catalysis

International Edition: DOI: 10.1002/anie.201900228
German Edition: DOI: 10.1002/ange.201900228

Nickel-Catalyzed Asymmetric Reductive Diarylation of Vinylarenes

*David Anthony, Qiao Lin, Judith Baudet, and Tianning Diao**

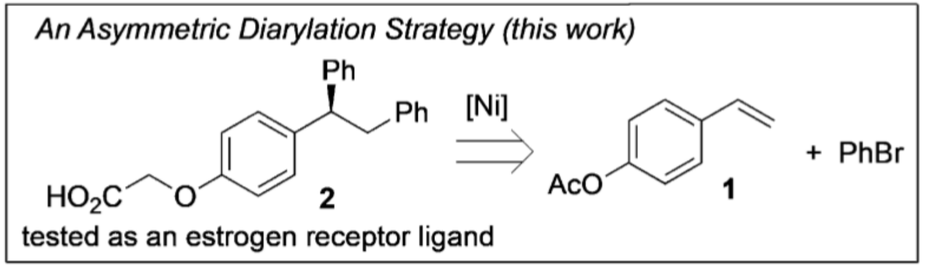
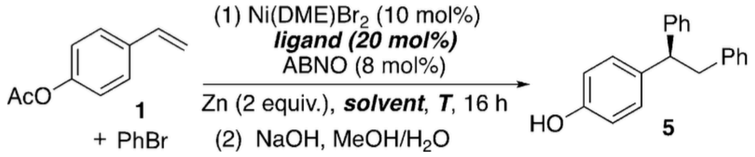
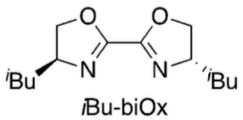


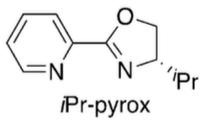
Table 1: Catalyst optimization: Effects of ligands and solvents.[a]



Entry	Ligand	Solvent	*T* [°C]	Yield [%]	*ee* [%]
1	*i*Pr-biOx	DMPU	25	52	83
2	*i*Bu-biOx	DMPU	25	69	89
3	Cy-biOx	DMPU	25	41	87
4	*t*Bu-biOx	DMPU	25	28	0
5	Ph-biOx	DMPU	25	25	0
6	4-hept-biOx	DMPU	25	64	73
7	indane-biOx	DMPU	25	52	64
8	Ph-box	DMPU	25	0	–
9	*i*Pr-pyrox	DMPU	25	30	28
10	*i*Pr-pybox	DMPU	25	5	–
11	*i*Bu-biOx	DMPU	10	38	90
12	*i*Bu-biOx	DMPU/THF (3:1)	10	74	90
13	***i*Bu-biOx**	**DMPU/THF (1:1)**	**10**	**90**	**91**
14	*i*Bu-biOx	DMPU/THF (1:3)	10	28	91

[a] Reaction conditions: **1** (0.2 mmol, 1 M), PhBr (4 M). Yields determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard; *ee* values determined by HPLC analysis on a chiral stationary phase.





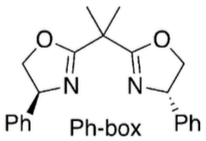
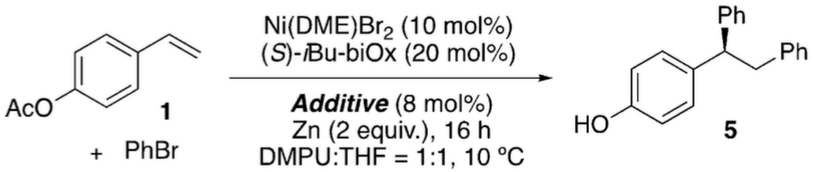
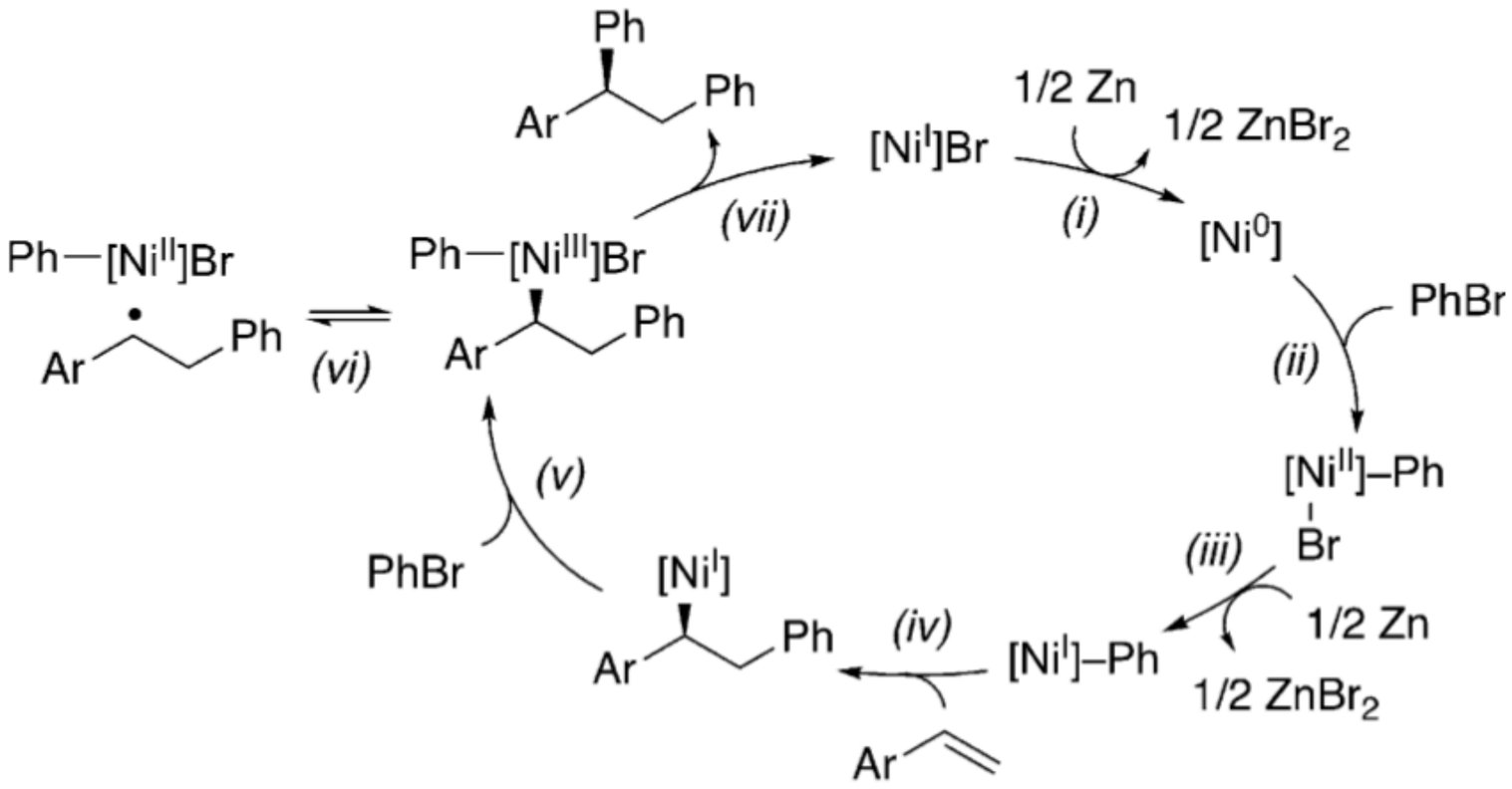


Table 2: Catalyst optimization: Effect of an *N*-oxyl additive.[a]



Additive	Yield [%]	*ee* [%]	Additive	Yield [%]	*ee* [%]
–	78	26	*t*Bu$_2$NO	63	60
TEMPO	60	21	2-Me-AZADO	71	57
4-oxo-TEMPO	50	29	AZADO	76	89
4-OAc-TEMPO	64	33	**ABNO**	**90**	**91**
4-OH-TEMPO	82	46	NO	39	54

[a] Reaction conditions: **1** (0.2 mmol, 1 M), PhBr (4 M). Crude reaction mixtures were treated with aqueous NaOH to saponify the acetate. Yields determined by ^{1}H NMR analysis using mesitylene as an internal standard; *ee* values determined by HPLC analysis on a chiral stationary phase.


Ph
Ar
Ph
[Ni^I]Br
1/2 Zn
1/2 ZnBr2
(vii)
(i)
Ph—[Ni^II]Br
Ar
Ph
(vi)
Ph—[Ni^III]Br
Ar
Ph
[Ni^0]
PhBr
(ii)
[Ni^II]–Ph
Br
(iii)
1/2 Zn
1/2 ZnBr2
[Ni^I]–Ph
(iv)
Ar
[Ni^I]
Ar
Ph
PhBr
(v)

Asymmetric Reductive Dicarbofunctionalization of Alkenes via Nickel Catalysis

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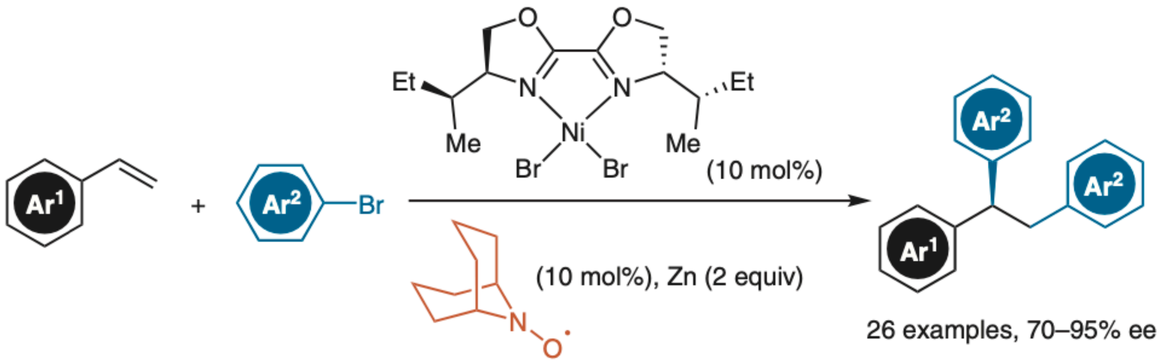
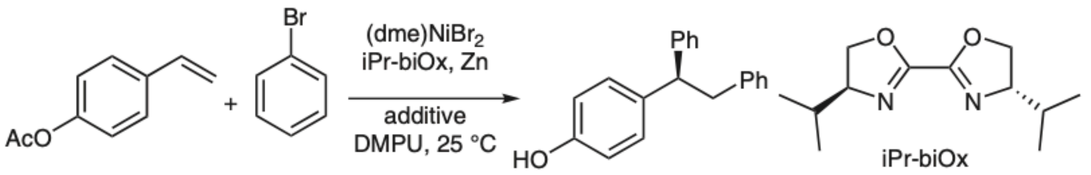
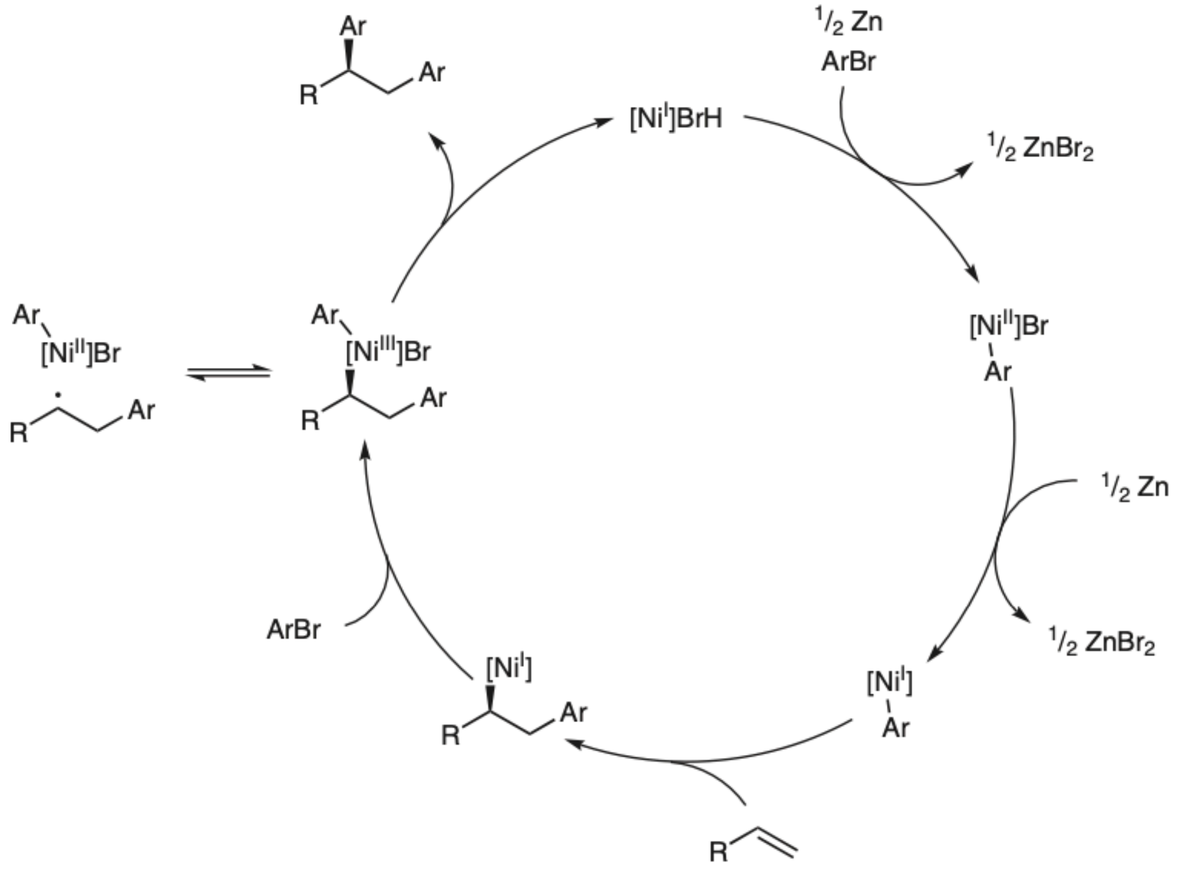


Table 1 Optimization of Reaction Conditions[a]



Entry	Additive (mol%)	Yield (%)[b]	ee (%)[c]
1[d]	none	73	38
2	none	61	2
3	BHT (10%)	62	14
4	TEMPO (10%)	44	49
5	TEMPO (5%)	72	26
6	TEMPO (20%)	1	–
7	ABNO (10 mol%)	57	76
8[e]	**ABNO (8 mol%)**	**90**	**91**


Ar
R
Ar
[Ni^I]BrH
1/2 Zn
ArBr
1/2 ZnBr2
[Ni^II]Br
Ar
1/2 Zn
1/2 ZnBr2
[Ni^I]
Ar
R
[Ni^I]
Ar
R
ArBr
Ar
[Ni^II]Br
R
Ar
Ar
[Ni^III]Br
R
Ar

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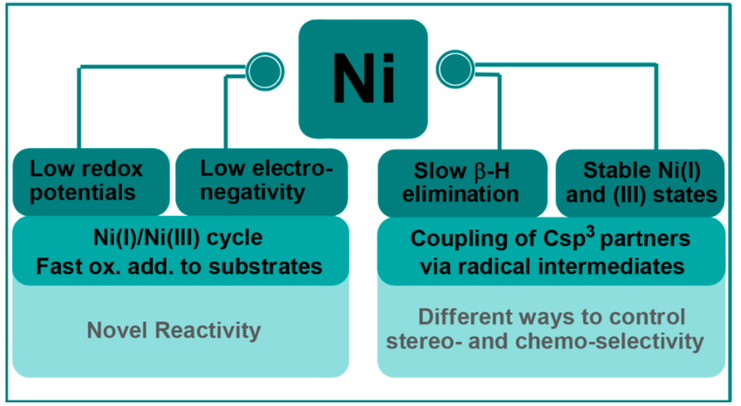
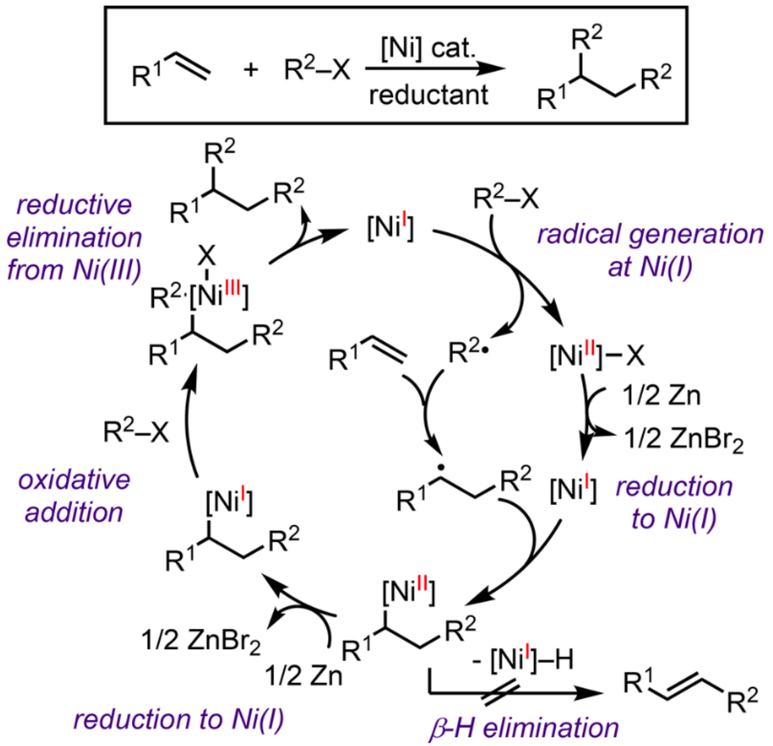
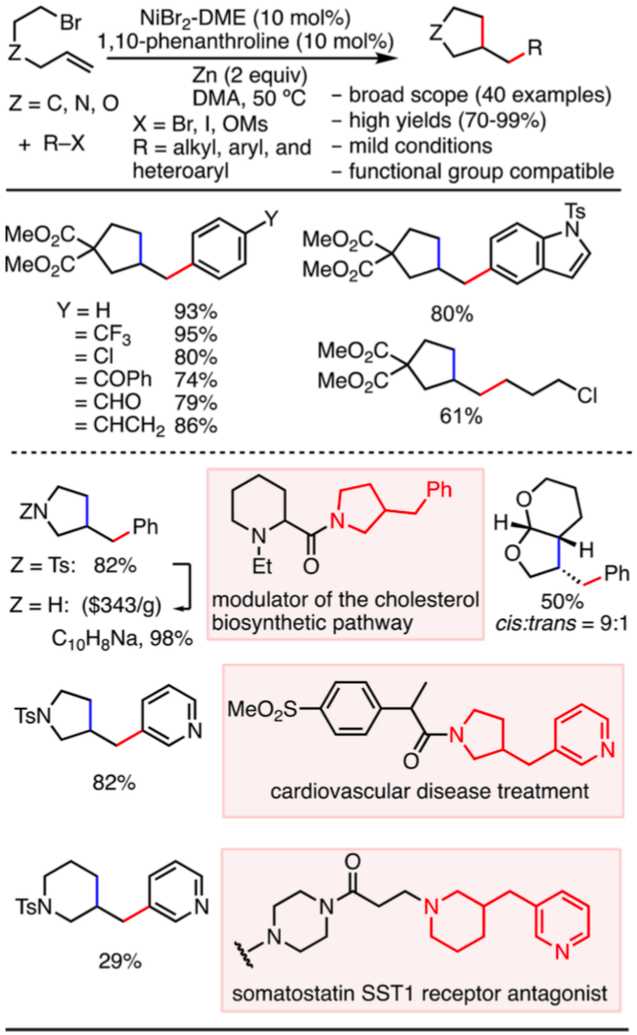
Article

Mechanisms of Nickel-Catalyzed Coupling Reactions and Applications in Alkene Functionalization

Justin Diccianni, Qiao Lin, and Tianning Diao*




[Ni] cat.
reductant
reductive elimination from Ni(III)
radical generation at Ni(I)
oxidative addition
reduction to Ni(I)
reduction to Ni(I)
β-H elimination
1/2 Zn
1/2 ZnBr2
- [Ni]–H


NiBr2-DME (10 mol%)
1,10-phenanthroline (10 mol%)
Zn (2 equiv)
DMA, 50 °C
Z = C, N, O
+ R–X
X = Br, I, OMs
R = alkyl, aryl, and heteroaryl
– broad scope (40 examples)
– high yields (70-99%)
– mild conditions
– functional group compatible
Y = H 93%
= CF3 95%
= Cl 80%
= COPh 74%
= CHO 79%
= CHCH2 86%
80%
61%
Z = Ts: 82%
Z = H: ($343/g)
C10H8Na, 98%
modulator of the cholesterol biosynthetic pathway
50%
cis:trans = 9:1
82%
cardiovascular disease treatment
29%
somatostatin SST1 receptor antagonist

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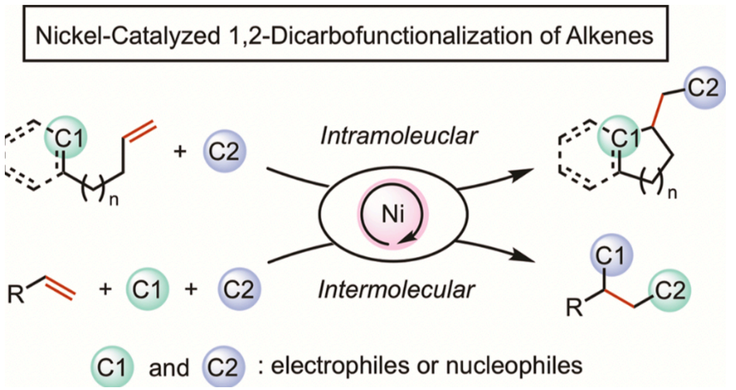
Perspective

Nickel-Catalyzed Dicarbofunctionalization of Alkenes

Xiaoxu Qi and Tianning Diao*



Contents lists available at ScienceDirect

Tetrahedron

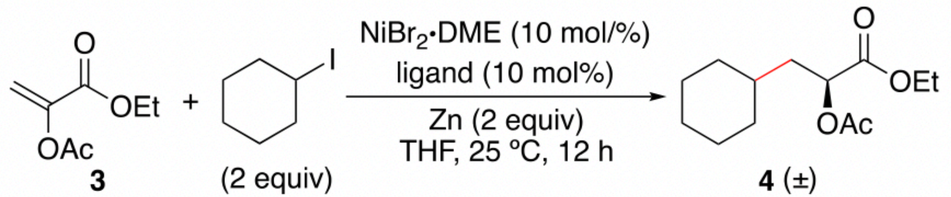
journal homepage: www.elsevier.com/locate/tet

Synthesis of lactate derivatives via reductive radical addition to α-oxyacrylates

Justin B. Diccianni, Mason Chin, Tianning Diao*

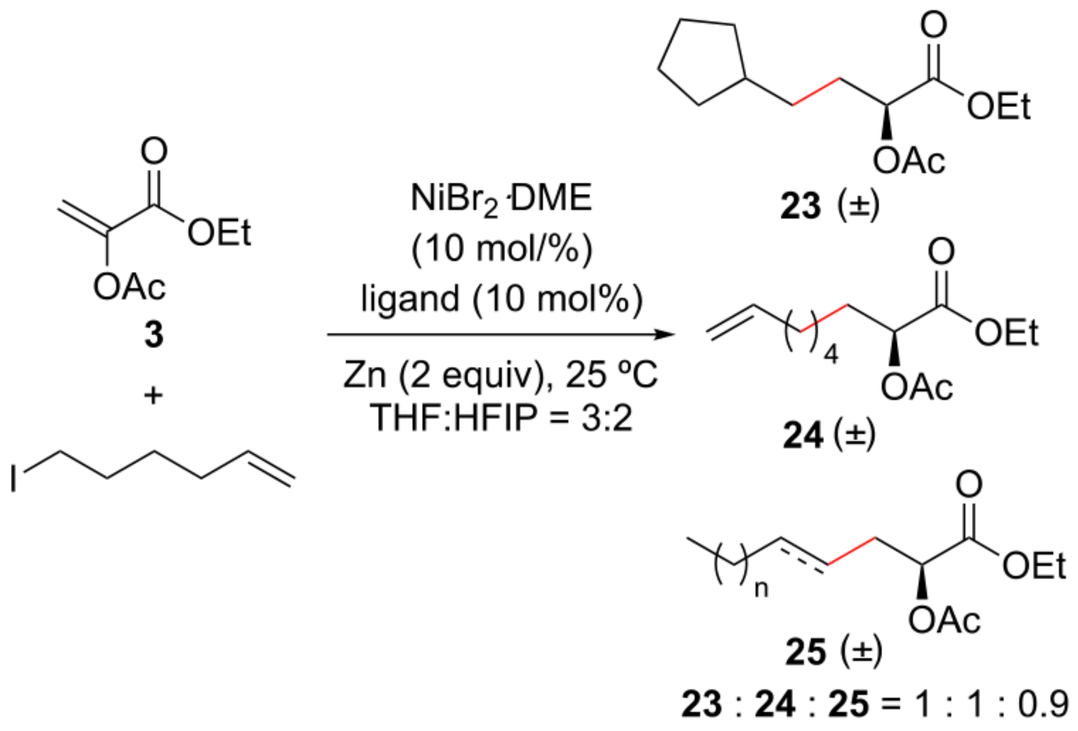
Department of Chemistry, New York University, 100 Washington Square East, New York, NY 10003 United States

Catalyst Optimization.



Entry	Ligand	Proton Source	Yield (%)[a]
1	PPh_3	HFIP	1
2	dppe	HFIP	62
3	dppp	HFIP	65
4	dppb	HFIP	78 (73)[b]
5	dpppe	HFIP	62
6	**dppf**	**HFIP**	**79 (76)**[b]
7	bpy	HFIP	40
8	dppf	*t*BuOH	42
9	dppf	*i*PrOH	31
10	dppf	H_2O	24
11	dppf[c]	HFIP	38

[a] GC yield with mesitylene as the internal standard.
[b] Isolated yields in parenthesis.
[c] Mn was used as the reductant in place of Zn.


O
OEt
OAc
3
+
I
NiBr2·DME
(10 mol/%)
ligand (10 mol%)
Zn (2 equiv), 25 ºC
THF:HFIP = 3:2
O
OEt
OAc
23 (±)
O
OEt
4
OAc
24 (±)
O
OEt
n
OAc
25 (±)
23 : 24 : 25 = 1 : 1 : 0.9

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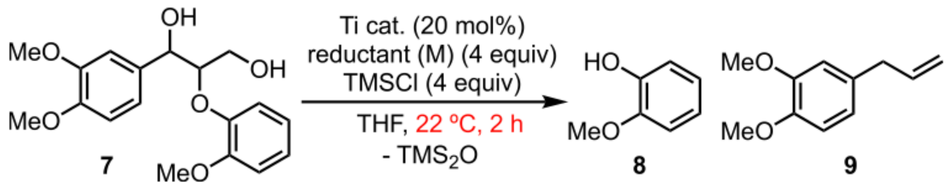
Research Article

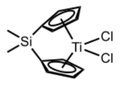
Depolymerization of Lignin via a Microscopic Reverse Biosynthesis Pathway

Mason Chin, Sang Mi Suh, Zhen Fang, Eric L. Hegg, and Tianning Diao*

Table 1. Catalyst Optimization for C–O Bond Cleavage in Lignin Model Compounds[a]

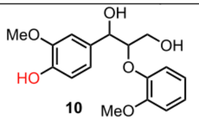


entry	titanium catalyst	M	$E^{o}(M^{2+}/M)$ (V vs. SHE) of M	%yield (**8**)	%yield (**9**)
1	Cp_2TiCl_2	Zn	–0.76	90	62
2[b]	Cp_2TiCl_2	Zn		91	82
3	$TiCl_3 \cdot 3THF$	Zn		73	28
4	$Cp^*_2TiCl_2$	Zn		83	17
5	*ansa*-Me_2Si-Cp_2TiCl_2	Zn		90	24
6	*ansa*-Cy-Cp_2TiCl_2	Zn		87	10
7	Cp^*TiCl_3	Zn		50	46
8	Cp_2TiCl_2	Mn	–1.18	43	0
9	Cp_2TiCl_2	Fe	–0.45	91	2
10	**Cp_2TiCl_2**	**In**	**–0.34**[e]	**95**	**97**
11	None	Zn		0	0
12	Cp_2TiCl_2	None		0	0
13[c]	None	None		58	0
14[d]	Cp_2TiCl_2	In		60	36[d]



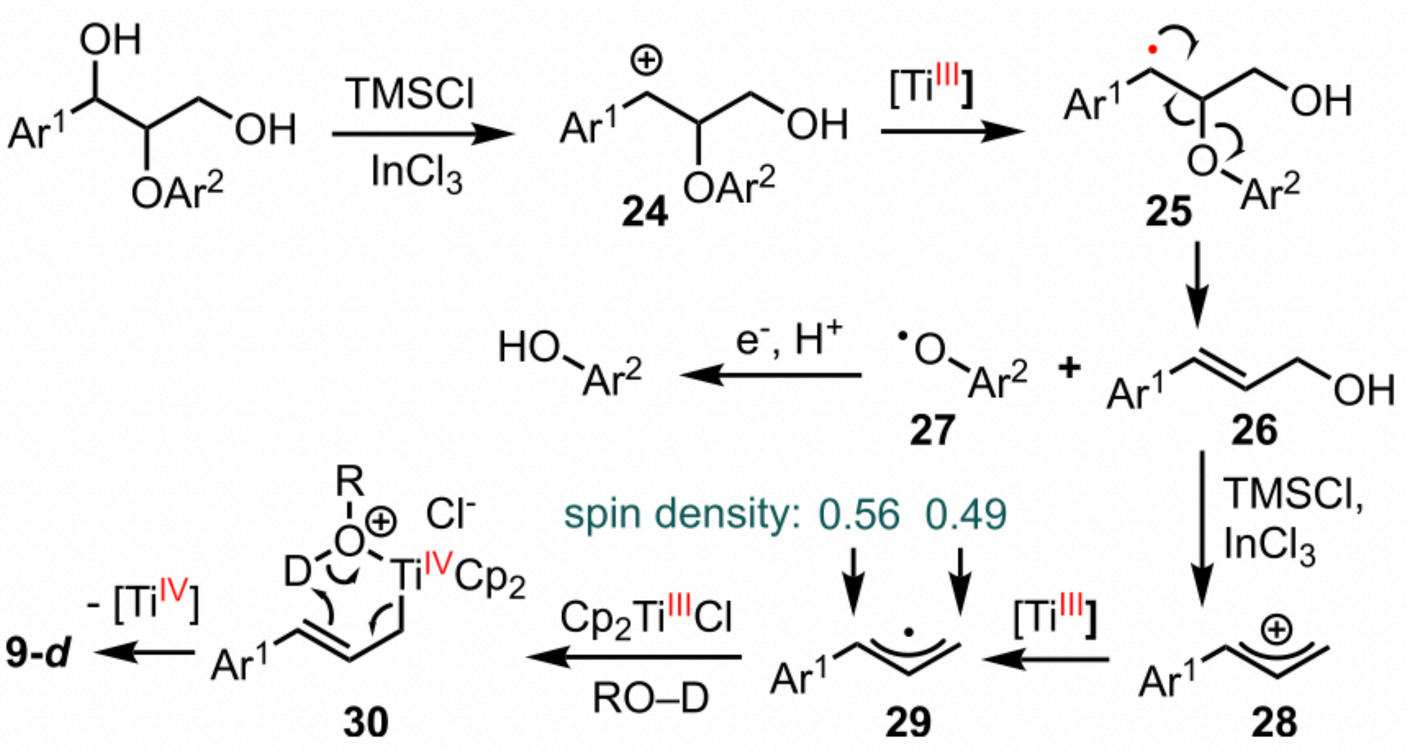
ansa-$Me_2SiCp_2TiCl_2$

ansa-$CyCp_2TiCl_2$



10

[a]Reaction conditions: [**7**] = 0.2 M. Yields were determined by GC against mesitylene as the internal standard. [b][**7**] = 0.1 M, 30 min. [c]$ZnCl_2$ (1 equiv), TMSCl (4 equiv), 30 min. [d]Model substrate **10**, which forms **8** and the corresponding Ar–OH derivative of **9**. [e]In^{3+}/In.


OH
Ar1
OH
OAr2
TMSCl
InCl3
24
[TiIII]
25
HO
Ar2
e-, H+
•O
Ar2
27
+
26
TMSCl,
InCl3
R
Cl-
O
D
TiIVCp2
spin density: 0.56 0.49
- [TiIV]
9-d
Cp2TiIIICl
RO–D
[TiIII]
30
29
28

THANKS