Dinickel Catalyst with Redox Active Ligand

Literature Seminar

2020/01/25 Koichi Hagiwara

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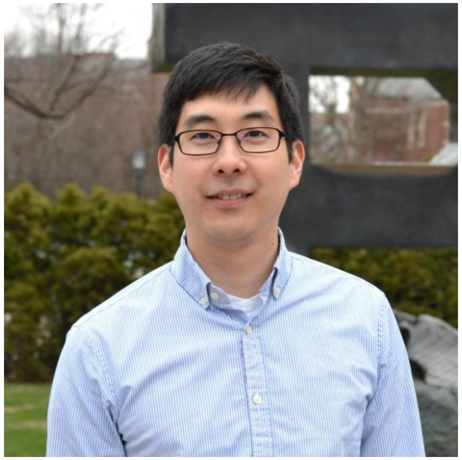
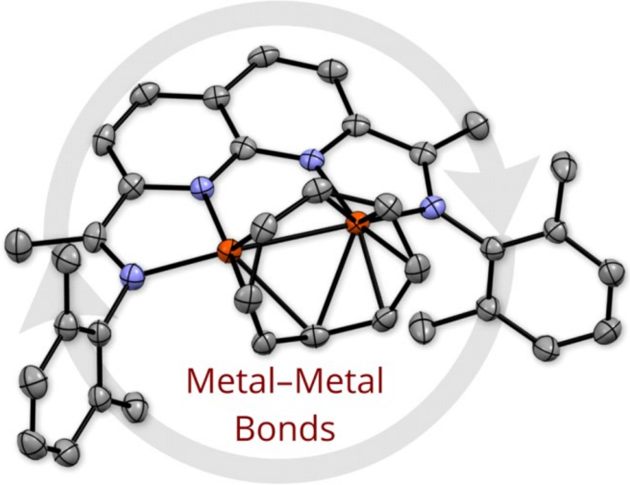
2005 BS; Columbia University (Prof. Ronald Breslow)
2011 Ph. D; Harvard University (Prof. Eric N. Jacobsen)
2011-2013 Postdoctoral fellow; California Institute of Technology (Prof. Jonas Peters)
2013-2018 Assistant Professor; Purdue University
2019- Associate Professor; Purdue University



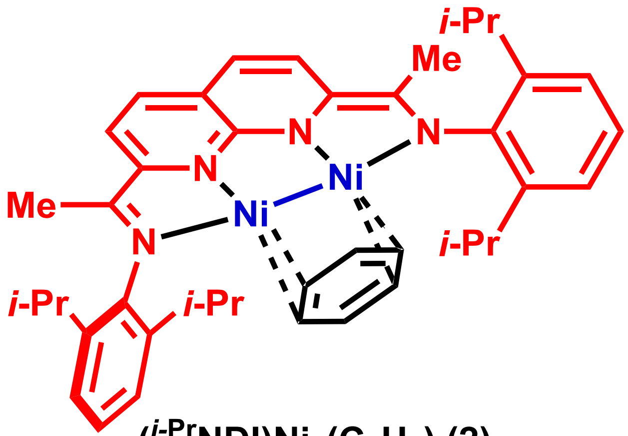
Research topic: Catalysis at Metal-Metal Bonds



"studying new organometallic mechanisms in which two metals function cooperatively to accomplish bond activation reactions"

https://www.chem.purdue.edu/uyeda/index.html

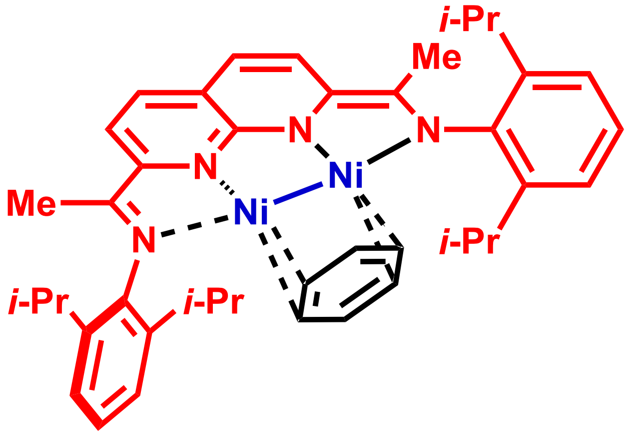
Dinuclear Ni Complex with Redox Active Ligand



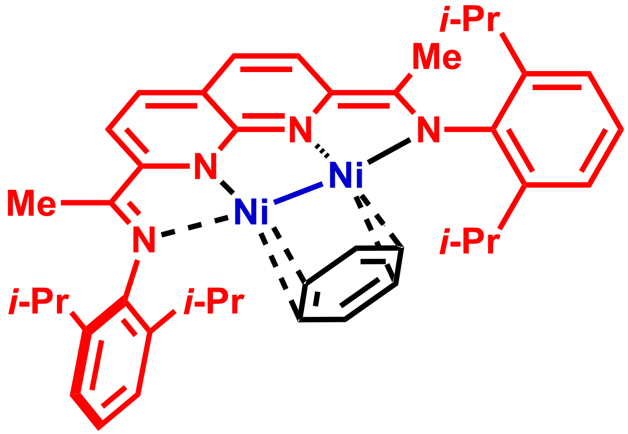
$(^{i\text{-Pr}}\mathrm{NDI})\mathrm{Ni_2(C_6H_6)}$ (2)
author's description

redox active ligand: charge -2

metal-metal bond: $\mathrm{Ni^{i}}$-$\mathrm{Ni^{i}}$



$\mathrm{Ni^{0}}$-$\mathrm{Ni^{ii}}$ structure?



looks $\mathrm{Ni^{i}}$-$\mathrm{Ni^{i}}$ structure

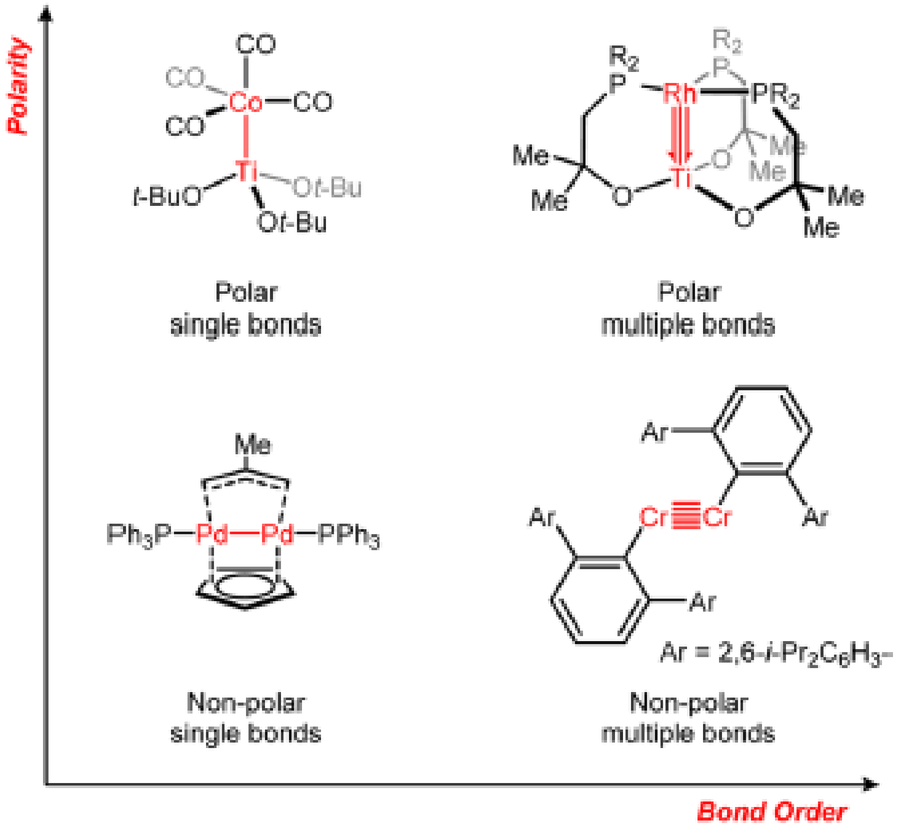
Zhou, Y.-Y.; Hartline, D. R.; Steiman, T. J.; Fanwick, P. E.; Uyeda, C. *Inorg. Chem.* **2014**, *53*, 11770.

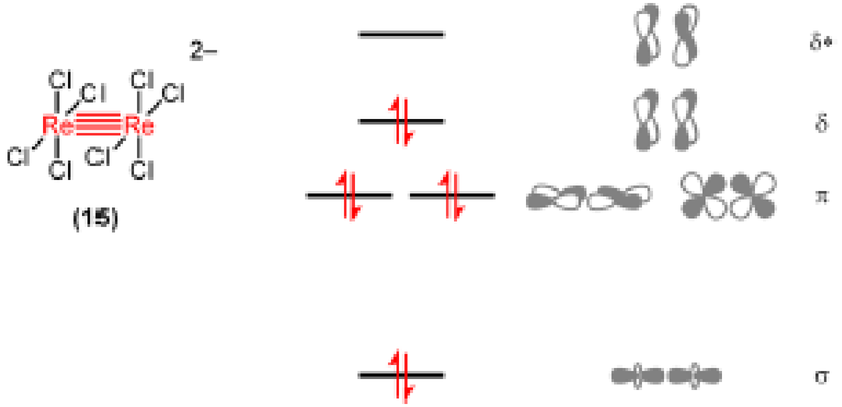
Chemical Species Including Metal-Metal Bond

M—M

covalent (or dative) interaction (d orbital interaction)
→electronic state should be changed
→different reactivity compared to mononuclear metal?

·examples of complexes with covalent M-M bond[1)2)]





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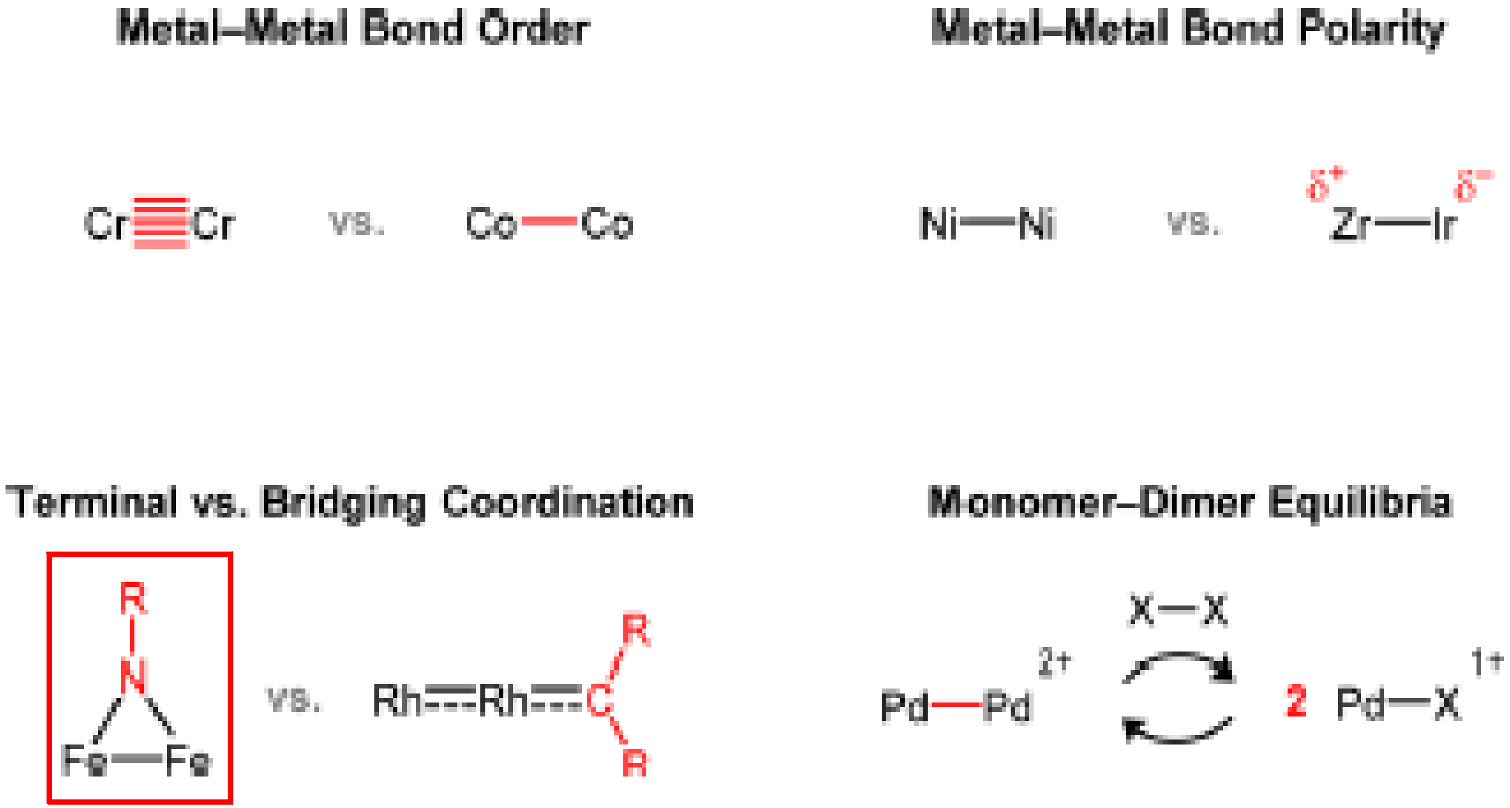
1) Powers, I. G.; Uyeda, C. *ACS Catal.* **2017**, *7*, 936. 2) Cotton, F. A. *Inorg. Chem.* **1965**, *4*, 334.

Additional Parameter Space in Catalyst Design

If a compound with matal-metal bond can be utilized as a catalyst, we might optimize following parameter:

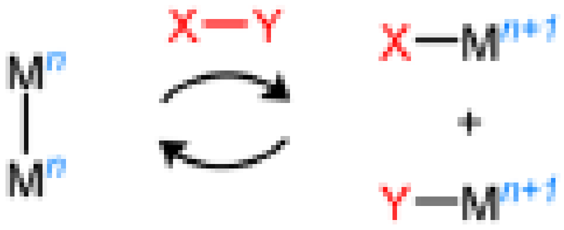


Powers, I. G.; Uyeda, C. *ACS Catal.* **2017**, *7*, 936.

Two-Electron Oxidative Addition at Metal-Metal Bond

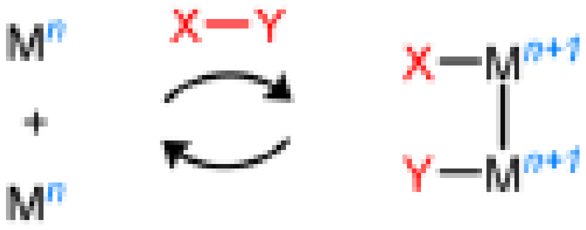
Metal-Centered Redox (σ-Bond)

cleavage of metal–metal bond



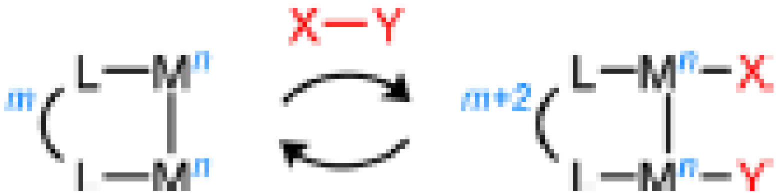
Metal-Centered Redox (σ-Bond)

formation of metal–metal bond



Metal-Centered Redox (π/δ-Bond)

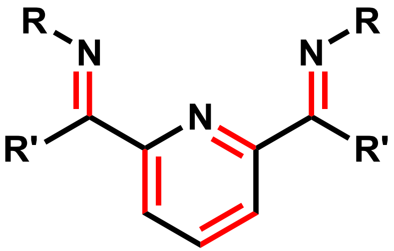
Ligand-Centered Redox



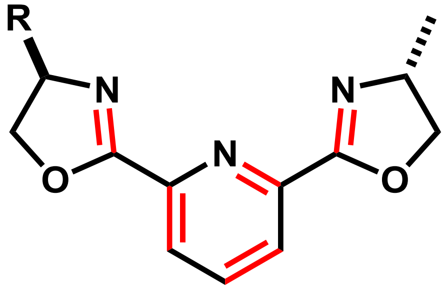
Powers, I. G.; Uyeda, C. *ACS Catal.* **2017**, *7*, 936.

Redox Active Ligand

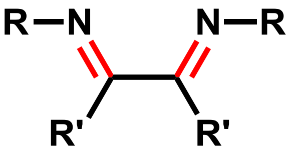
redox active ligand (non-innocent ligand)
→compounds with extended π system

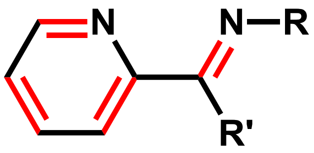


bis(imino)pyridine



pyridine bis(oxazoline)





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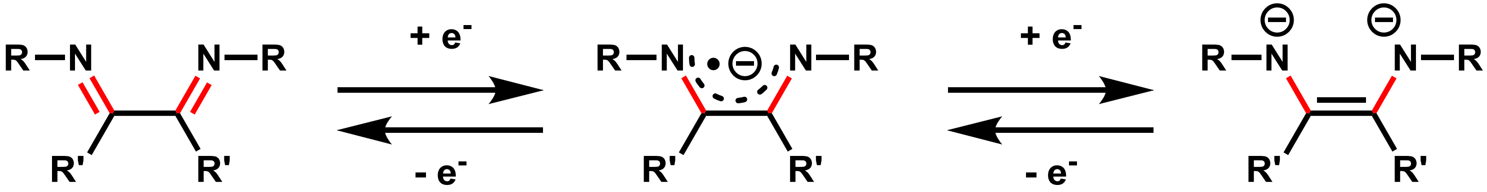
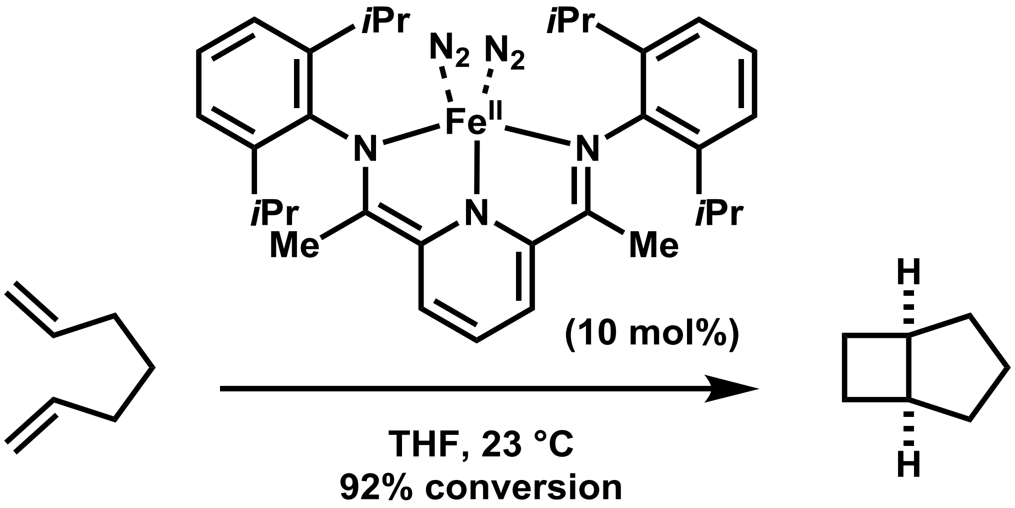
act as electron reservoirs



charge **0** **-1** **-2**

Muresan, N.; Chlopek, K.; Weyheemüller, T.; Neese, F.; Wieghaert, K. *Inorg. Chem.* **2007**, *46*, 5327.

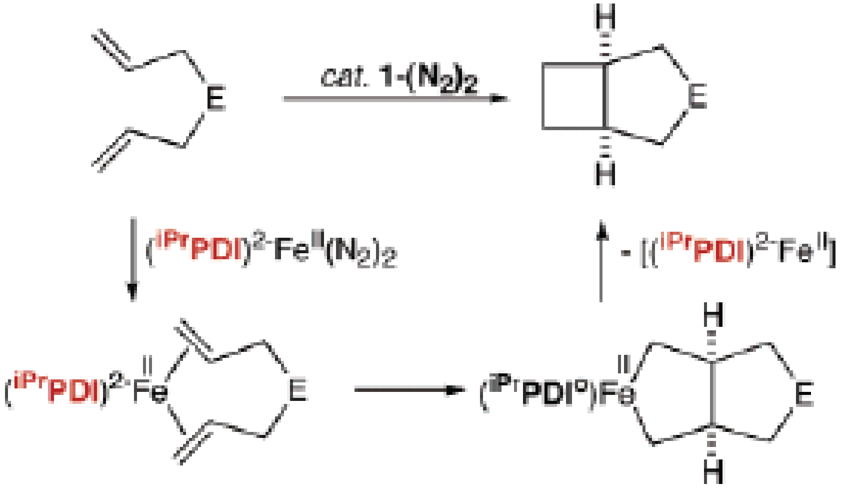
Mononuclear Catalyst with Redox Ative Ligand



(10 mol%)

THF, 23 °C
92% conversion

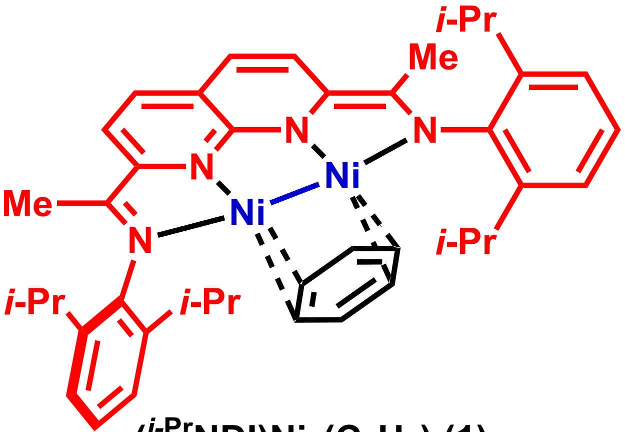
- proposed mechanism



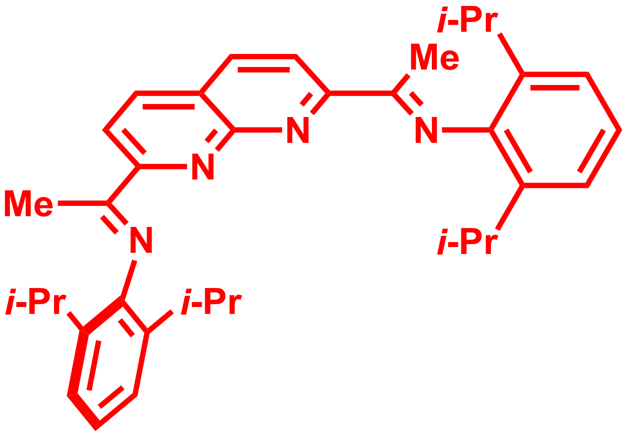
inhibit Fe(0) precipitate?

Bouwkamp, M. W.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13340.

Dimetal Species with Redox Active Ligand



$(^{i\text{-Pr}}NDI)Ni_2(C_6H_6)$ (1)
author's description

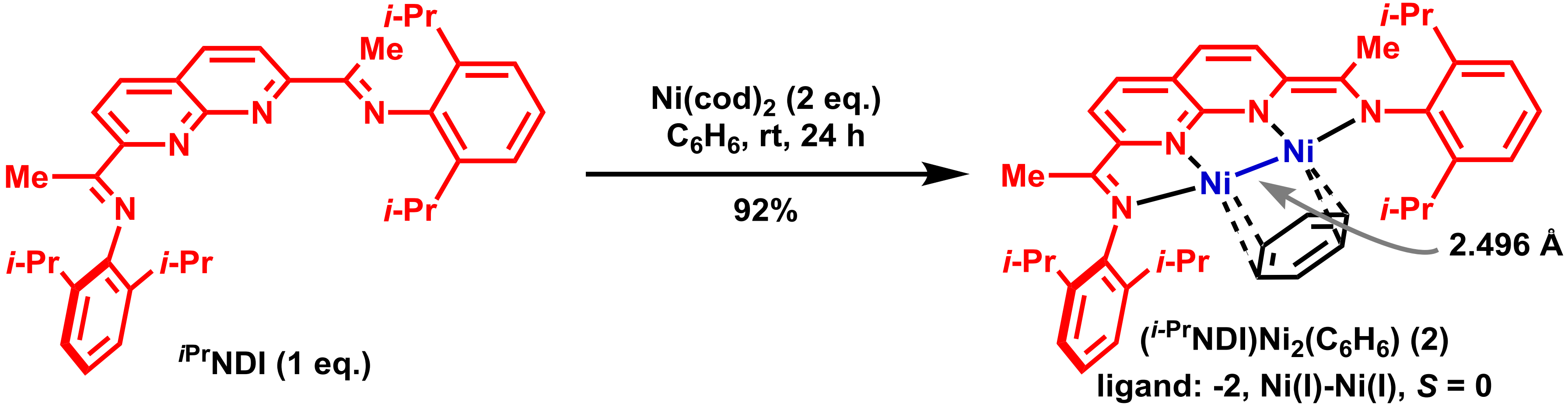


redox active ligand
→ligand-centered redox might stabilize metals in several oxidation states
→new reactivity?

incorporation of 2 metals in close distance
→forming metal-metal bond
→new reactivity?

Zhou, Y.-Y.; Hartline, D. R.; Steiman, T. J.; Fanwick, P. E.; Uyeda, C. *Inorg. Chem.* **2014**, *53*, 11770.

Synthesis of ($^{i\text{-Pr}}$NDI)$Ni_2(C_6H_6)$

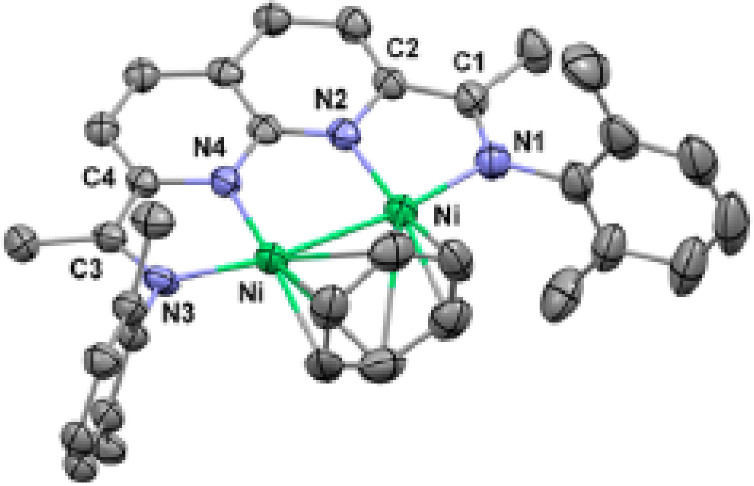


$^{i\text{Pr}}$NDI (1 eq.)

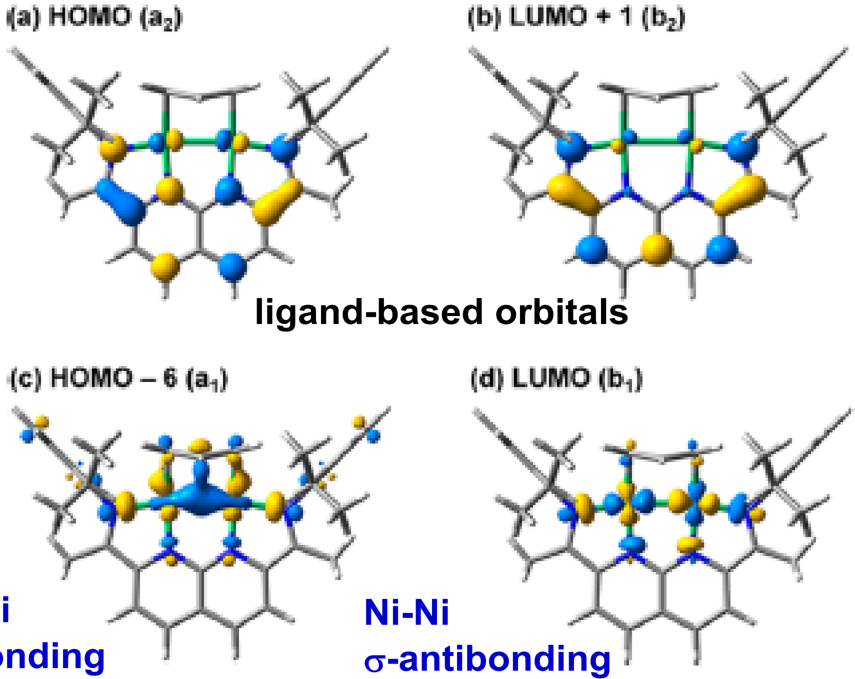
($^{i\text{-Pr}}$NDI)$Ni_2(C_6H_6)$ (2)

ligand: -2, Ni(I)-Ni(I), $S = 0$

X-ray structure



DFT calculation (BP86/6-311G(d,p))



ligand-based orbitals

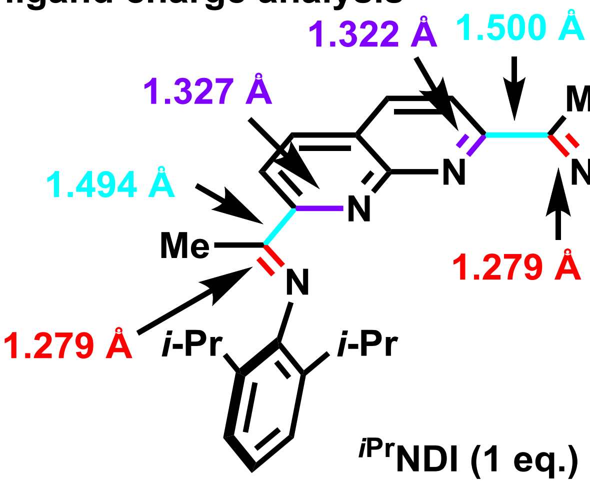
Ni-Ni
σ-bonding

Ni-Ni
σ-antibonding

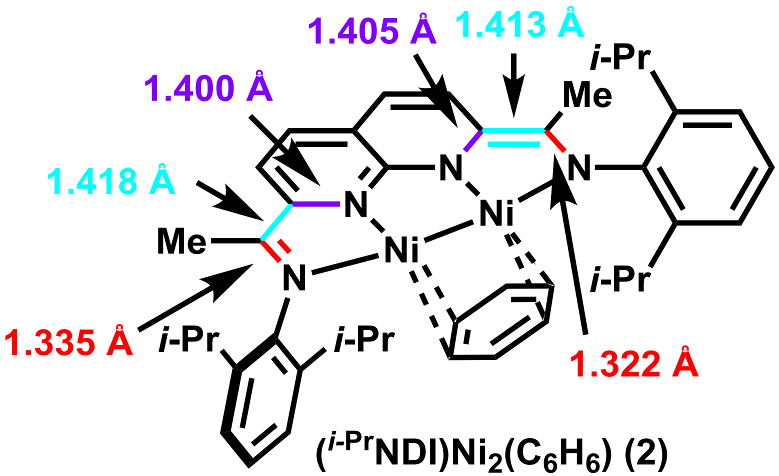
Zhou, Y.-Y.; Hartline, D. R.; Steiman, T. J.; Fanwick, P. E.; Uyeda, C. *Inorg. Chem.* **2014**, *53*, 11770.

Analysis of ($^{i\text{-Pr}}$NDI)Ni$_2$(C$_6$H$_6$)

ligand charge analysis



^{iPr}NDI (1 eq.)



($^{i\text{-Pr}}$NDI)Ni$_2$(C$_6$H$_6$) (2)

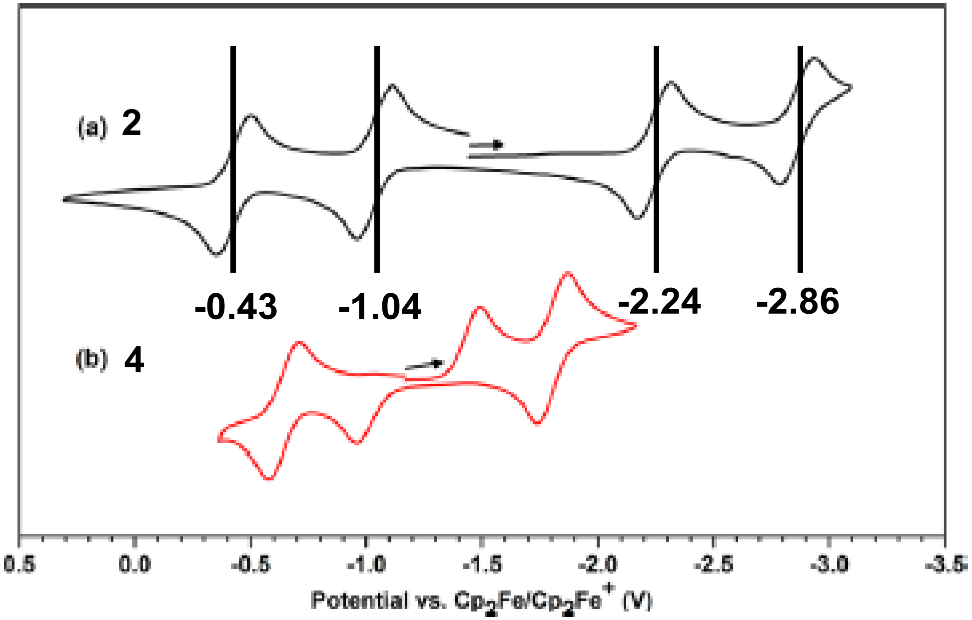
ligand: -2, Ni(I)-Ni(I), *S* = 0

ligand charge

	0	-1	-2
🟥	1.28 Å	1.30 Å	1.32 Å
🟦	1.50 Å	1.45 Å	1.42 Å
🟪	1.32 Å	1.36 Å	1.40 Å

S is determined by magnetic moment.

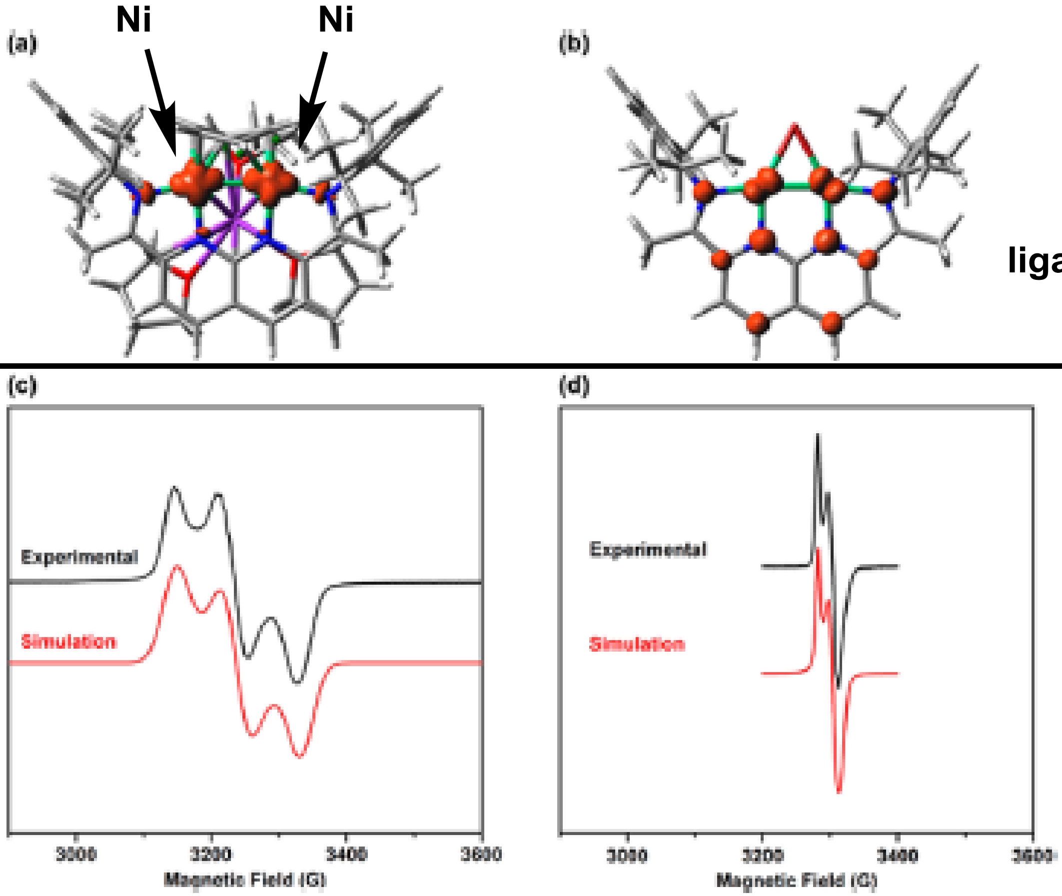
cyclicvoltammogram



Zhou, Y.-Y.; Hartline, D. R.; Steiman, T. J.; Fanwick, P. E.; Uyeda, C. *Inorg. Chem.* **2014**, *53*, 11770.

Analysis of Radical Character

DFT caluculation



metalloradical character

ligand radical character

EPR spectra

$h\nu = g\beta H$

h: Planck constant
ν: frequency
β: Bohr magneton
H: magnetic field

$g_{max} - g_{max} = 0.12$

metalloradical character

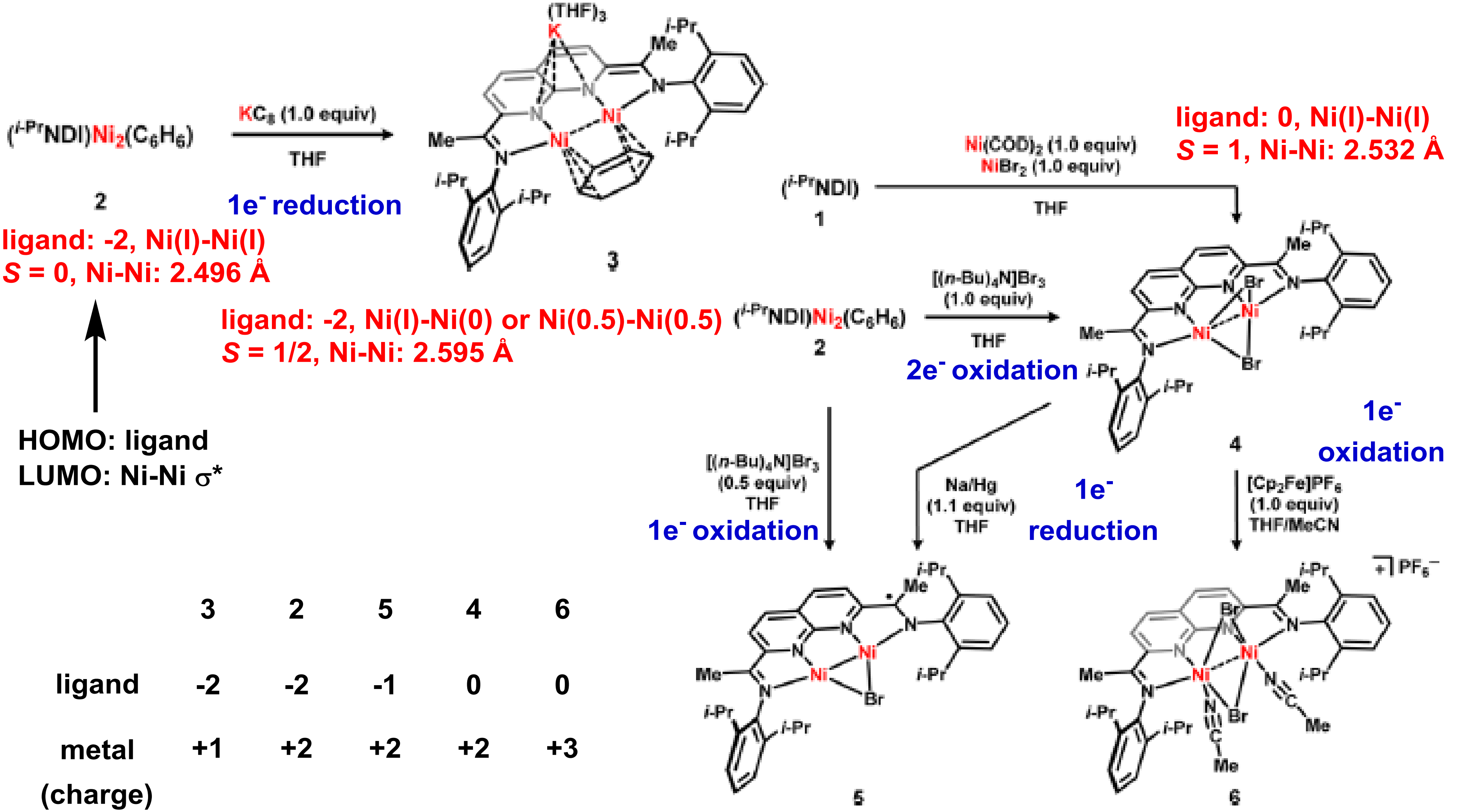
$g_{max} - g_{max} = 0.021$

ligand radical character

Figure 6. Calculated spin-density plots for (a) **3** and (b) **5**. Mulliken spin population for **3** $Ni_2 = 0.90$; Σ over ligand atoms = 0.07. Mulliken spin population for **5**: $Ni_2 = 0.43$; Σ over ligand atoms = 0.57. Frozen solution EPR spectra (125 K) for (c) **3** and (d) **5**. Simulated parameters for **3**: $g_1 = 2.037$, $g_2 = 2.097$, $g_3 = 2.157$. Simulated parameters for **5**: $g_1 = 2.050$, $g_2 = 2.037$, $g_3 = 2.029$.

Zhou, Y.-Y.; Hartline, D. R.; Steiman, T. J.; Fanwick, P. E.; Uyeda, C. *Inorg. Chem.* **2014**, *53*, 11770.

Synthesis of Ni-Ni Complexes with Different Oxidation States



1e$^-$ reduction

ligand: -2, Ni(I)-Ni(I)
S = 0, Ni-Ni: 2.496 Å

ligand: -2, Ni(I)-Ni(0) or Ni(0.5)-Ni(0.5)
S = 1/2, Ni-Ni: 2.595 Å

ligand: 0, Ni(I)-Ni(I)
S = 1, Ni-Ni: 2.532 Å

2e$^-$ oxidation

1e$^-$ oxidation

1e$^-$ reduction

1e$^-$ oxidation

HOMO: ligand
LUMO: Ni-Ni σ*

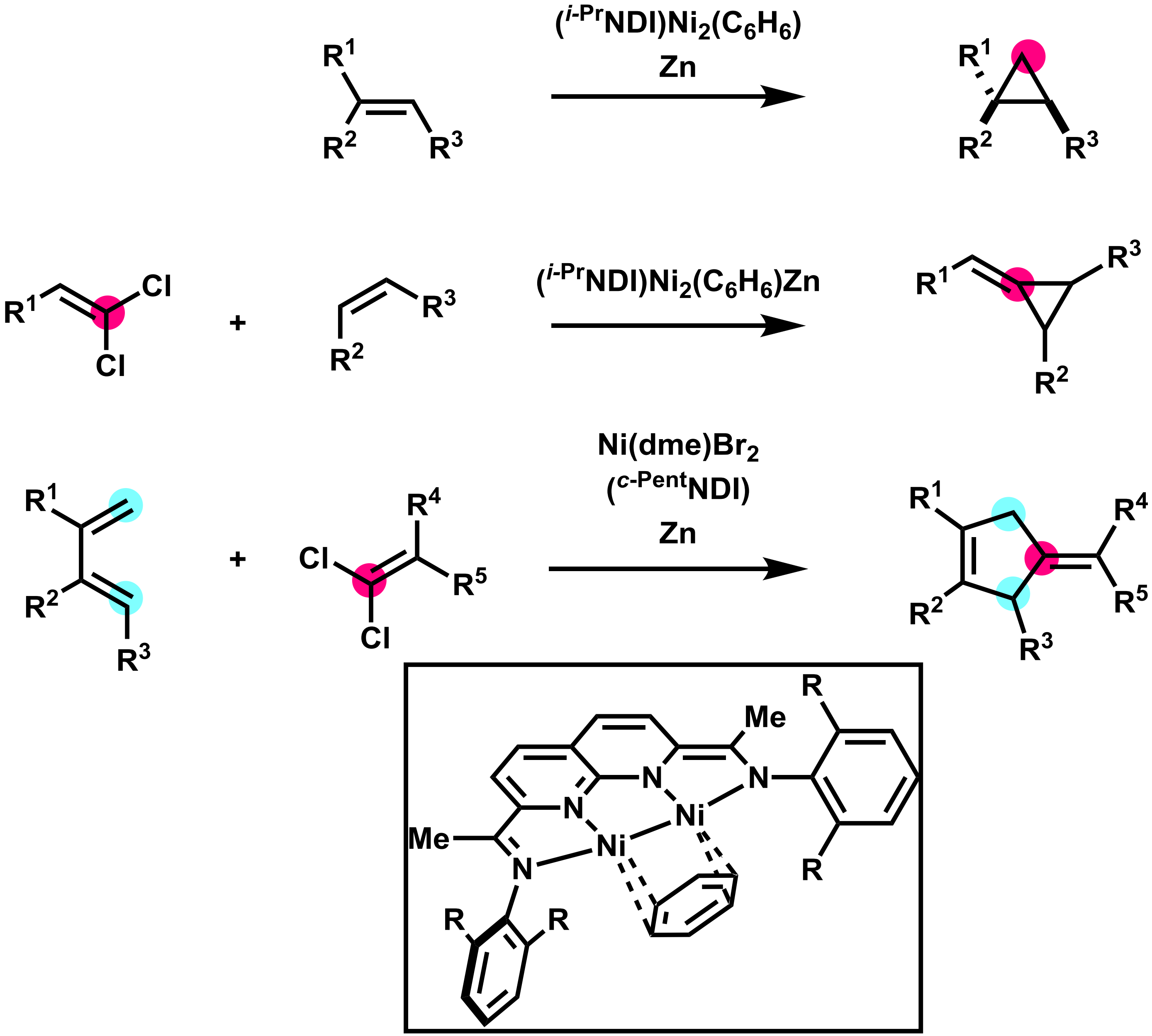
	3	2	5	4	6
ligand	-2	-2	-1	0	0
metal (charge)	+1	+2	+2	+2	+3

ligand: -1, Ni(I)-Ni(I)
S = 1/2, Ni-Ni: 2.371 Å

ligand: 0, Ni(II)-Ni(I) or Ni(1.5)-Ni(1.5)
S = 3/2, Ni-Ni: 2.525 Å

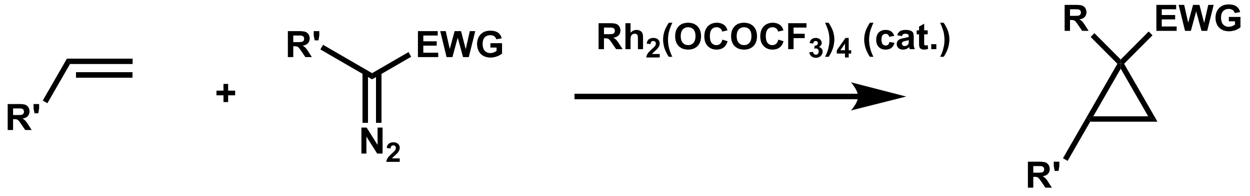
Zhou, Y.-Y.; Hartline, D. R.; Steiman, T. J.; Fanwick, P. E.; Uyeda, C. *Inorg. Chem.* **2014**, *53*, 11770.

Application to Carbene Transfer Type Reaction

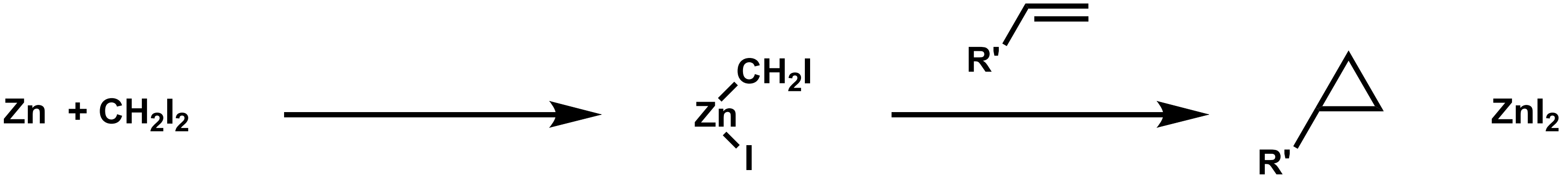


Catalytic Reductive Cyclopropanation

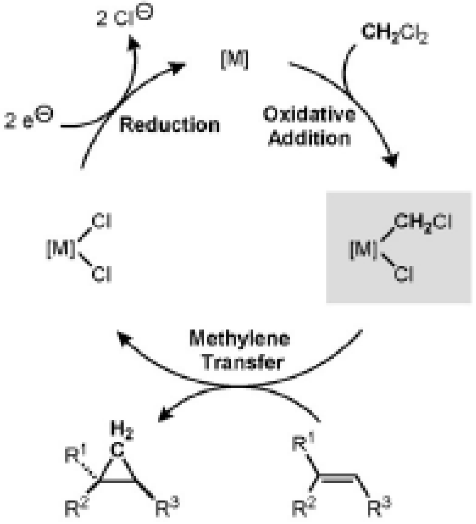
- **redox neutral cyclopropanation**

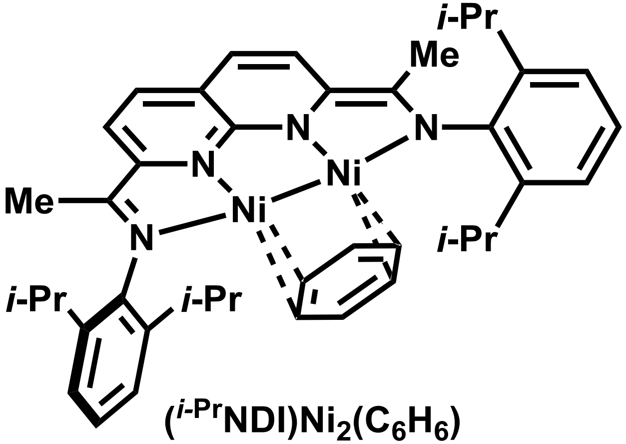


- **reductive cyclopropanation - Simmos-Smith reaction -**

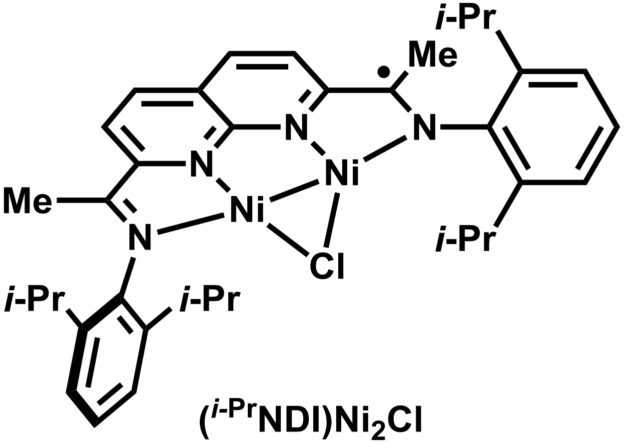


- **catalytic reductive cyclopropanation**





($^{i\text{-Pr}}$NDI)Ni$_2$(C$_6$H$_6$)
ligand: -2, Ni(I)-Ni(I)



($^{i\text{-Pr}}$NDI)Ni$_2$Cl
ligand: -1, Ni(I)-Ni(I)

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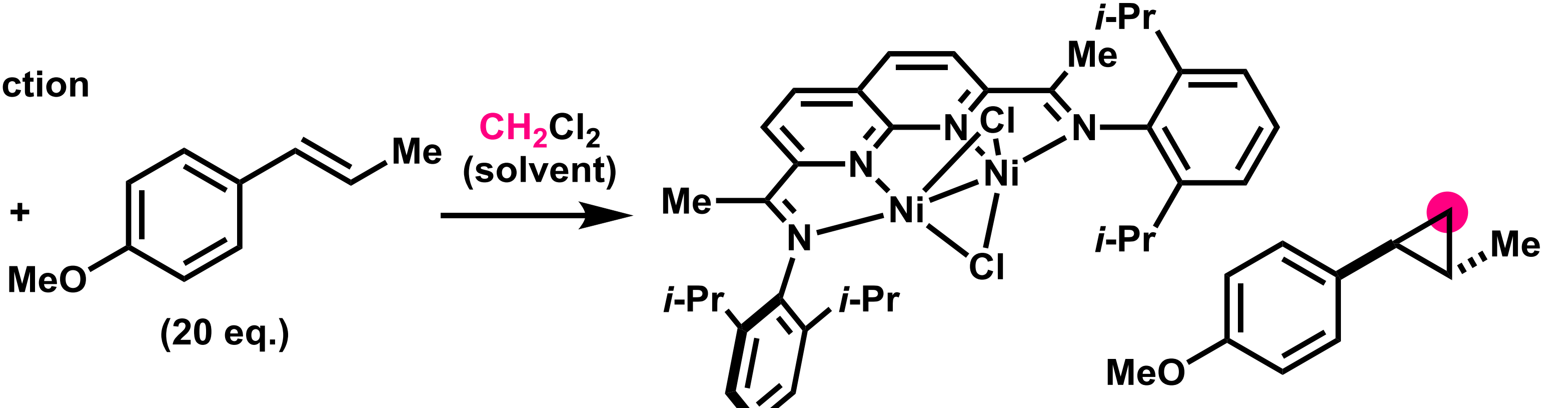
Stoichiometric Cyclopropanation

- stereospecific reaction

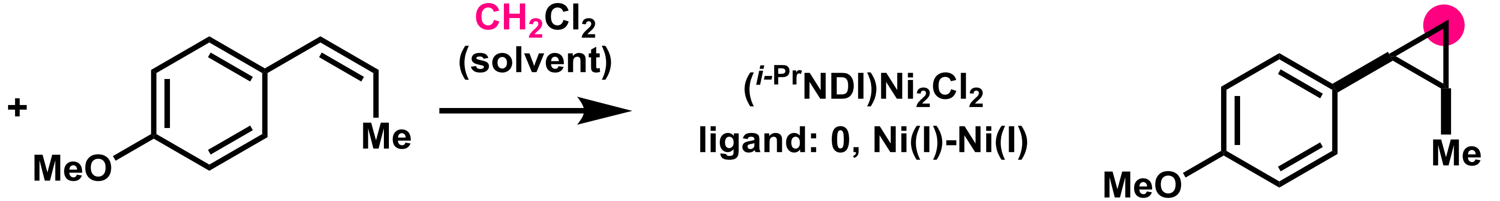
$(^{i\text{-Pr}}NDI)Ni_2(C_6H_6)$
ligand: -2, Ni(I)-Ni(I)
(1.0 eq.)



$(^{i\text{-Pr}}NDI)Ni_2Cl_2$
ligand: 0, Ni(I)-Ni(I)

55%

$(^{i\text{-Pr}}NDI)Ni_2(C_6H_6)$
ligand: -2, Ni(I)-Ni(I)
(1.0 eq.)

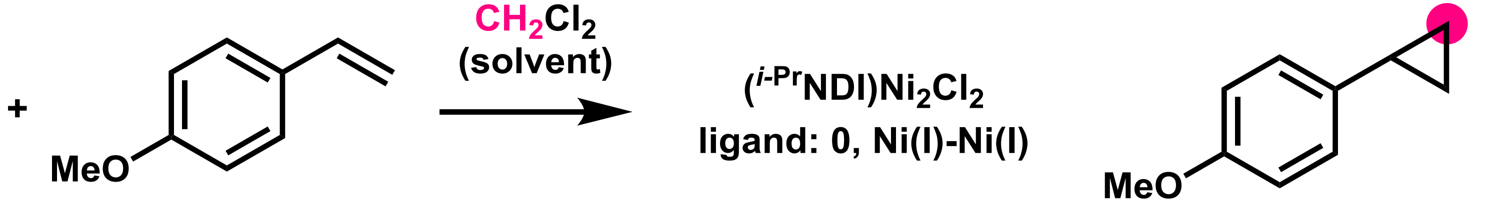


$(^{i\text{-Pr}}NDI)Ni_2Cl_2$
ligand: 0, Ni(I)-Ni(I)

34%

- $(^{i\text{-Pr}}NDI)Ni_2Cl$ acted

$(^{i\text{-Pr}}NDI)Ni_2Cl$
ligand: -1, Ni(I)-Ni(I)
(1.0 eq.)



$(^{i\text{-Pr}}NDI)Ni_2Cl_2$
ligand: 0, Ni(I)-Ni(I)

34%

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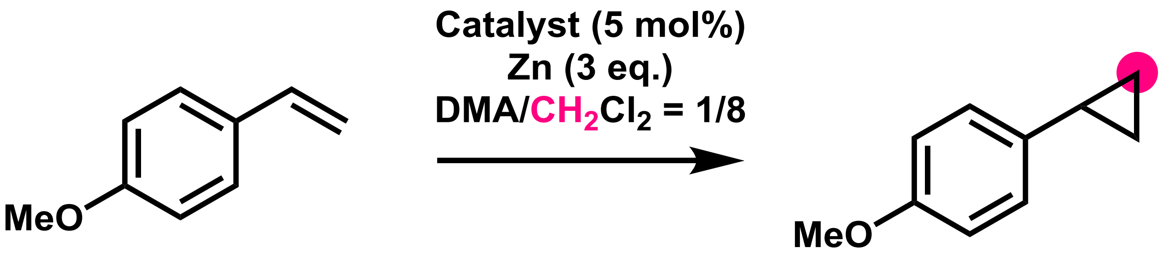
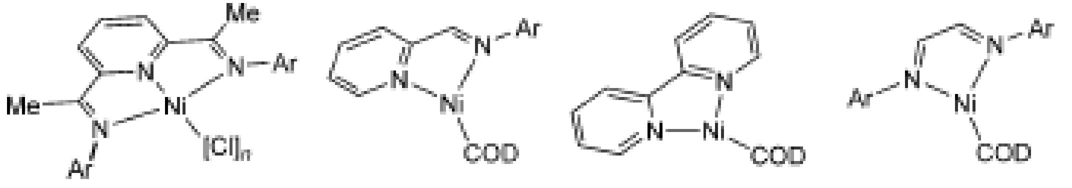
Catalyst Optimization





$[^{i\text{-Pr}}PDI]NiCl_2$ (4)
$[^{i\text{-Pr}}PDI]NiCl$ (5)
Ar = 2,6-diisopropylphenyl

$[^{i\text{-Pr}}IP]Ni(COD)$ (6)

[BPY]Ni(COD) (7)

$[^{i\text{-Pr}}DAD]Ni(COD)$ (8)

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

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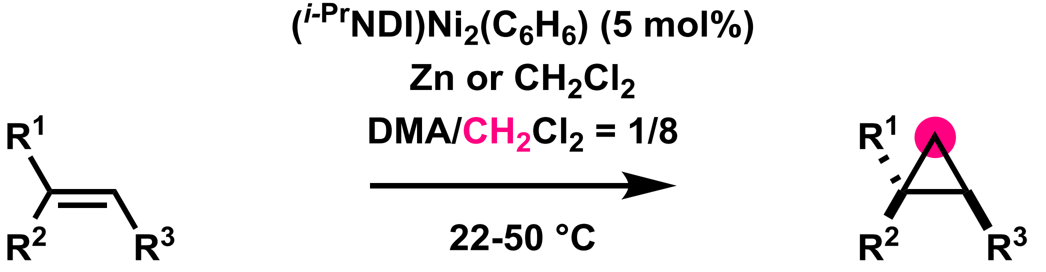
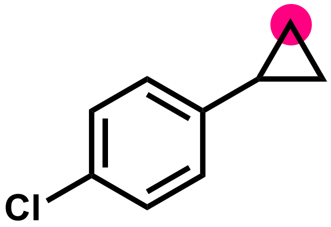
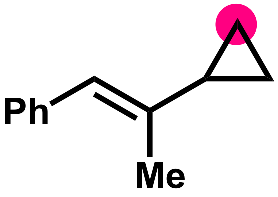
Substrate Scope


$({}^{i\text{-Pr}}\mathrm{NDI})\mathrm{Ni}_2(\mathrm{C}_6\mathrm{H}_6)$ (5 mol%)
Zn or $\mathrm{CH_2Cl_2}$
DMA/$\mathrm{CH_2Cl_2}$ = 1/8
22-50 °C

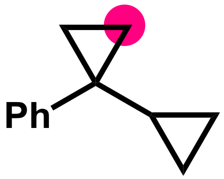
33 examples
55-99%



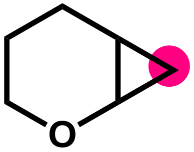
84% (Zn)



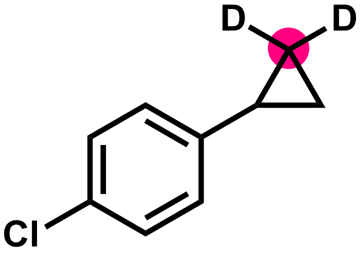
64% (Zn)



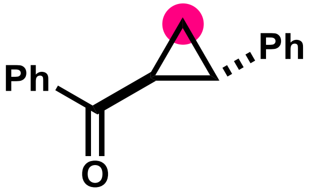
83% ($\mathrm{Et_2Zn}$)



93% (Zn)



66% (Zn)
($\mathrm{CD_2Cl_2}$ instead of $\mathrm{CH_2Cl_2}$)



72% (Zn)
16% (not Ni, but $\mathrm{CH_2I_2}$, Zn conditions)
<5% (not Ni, but $\mathrm{CH_2I_2}$, $\mathrm{Et_2Zn}$ conditions)

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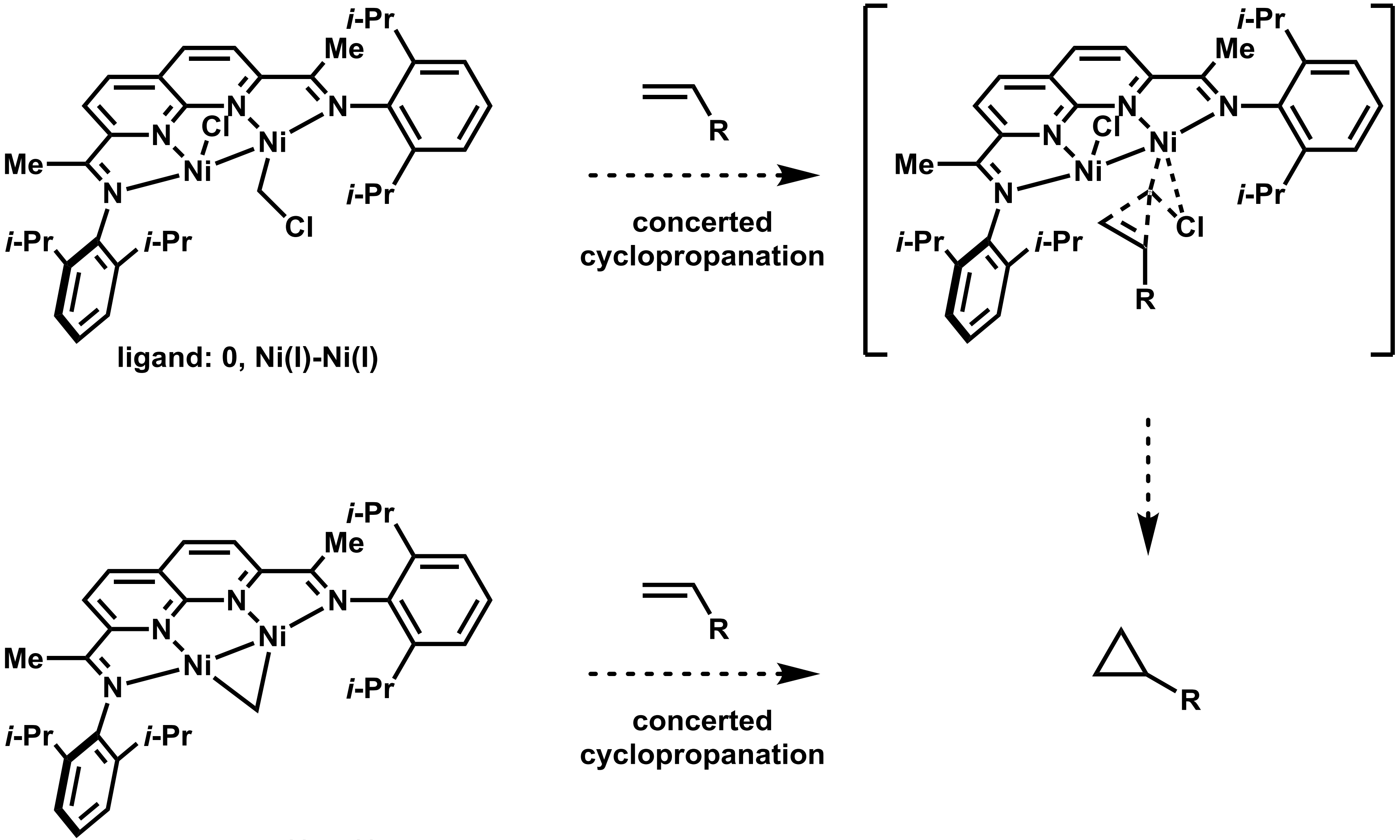
Uncertain Reaction Mechanism

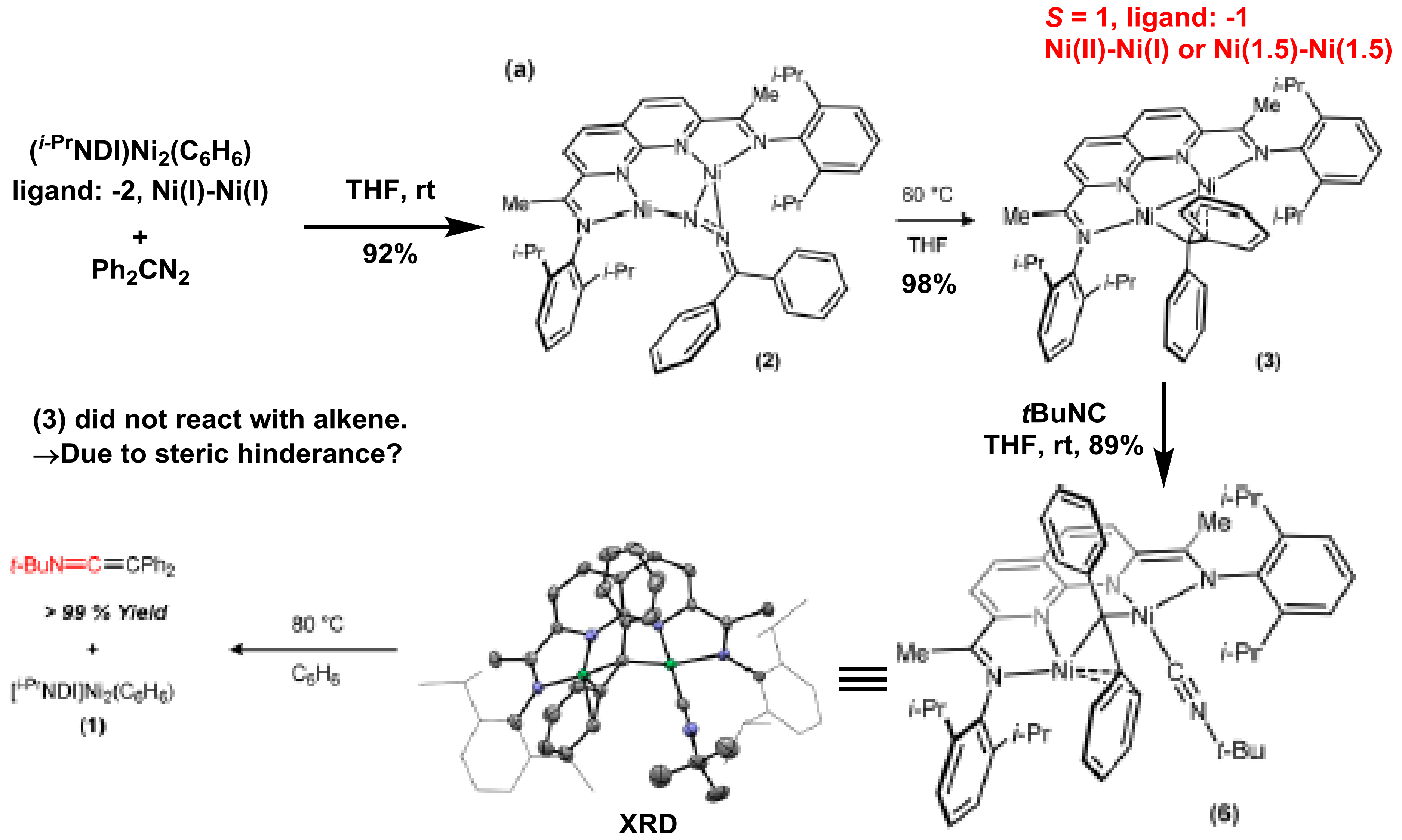
- active species: unclear



ligand: 0, Ni(I)-Ni(I)

ligand: 0, Ni(I)-Ni(I)

Ni-Ni Carbene Complex



$({}^{i\text{-Pr}}NDI)Ni_2(C_6H_6)$
ligand: -2, Ni(I)-Ni(I)

+

Ph_2CN_2

THF, rt

92%

98%

S = 1, ligand: -1
Ni(II)-Ni(I) or Ni(1.5)-Ni(1.5)

*t*BuNC
THF, rt, 89%

(3) did not react with alkene.
→Due to steric hinderance?

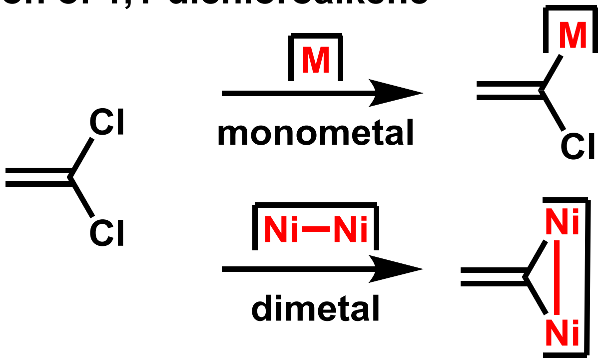
≡

XRD

Maity, A. K.; Zeller, M.; Uyeda, C. *Organometallics* **2018**, *37*, 2437.

Strategy for Carbene Transfer Type Reactions

- activation of 1,1-dichloroalkene

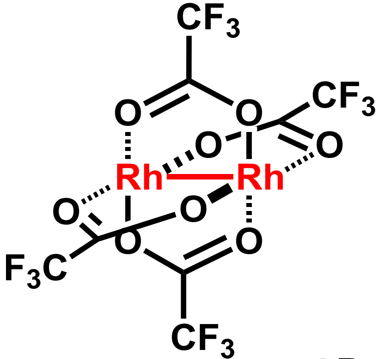


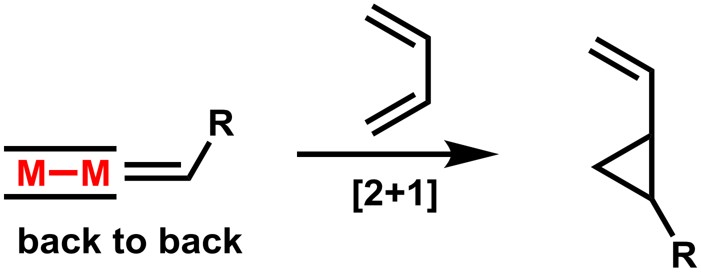
mono activation

di activation
→surrogate of carbene

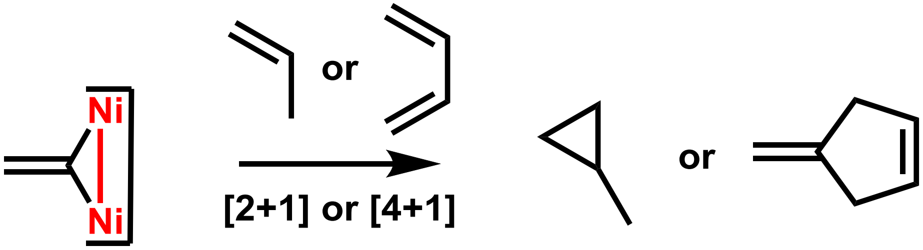
- reactivity with alkenes of dimetal species

example

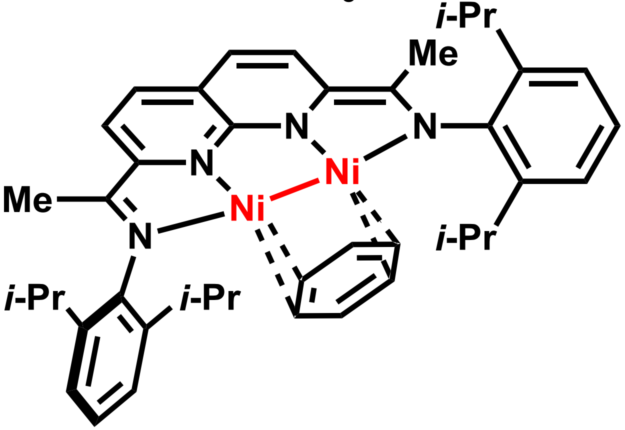




back to back

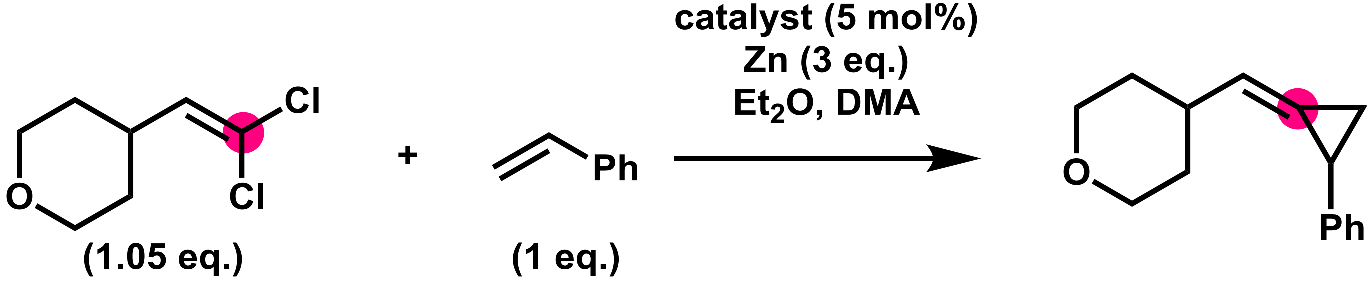


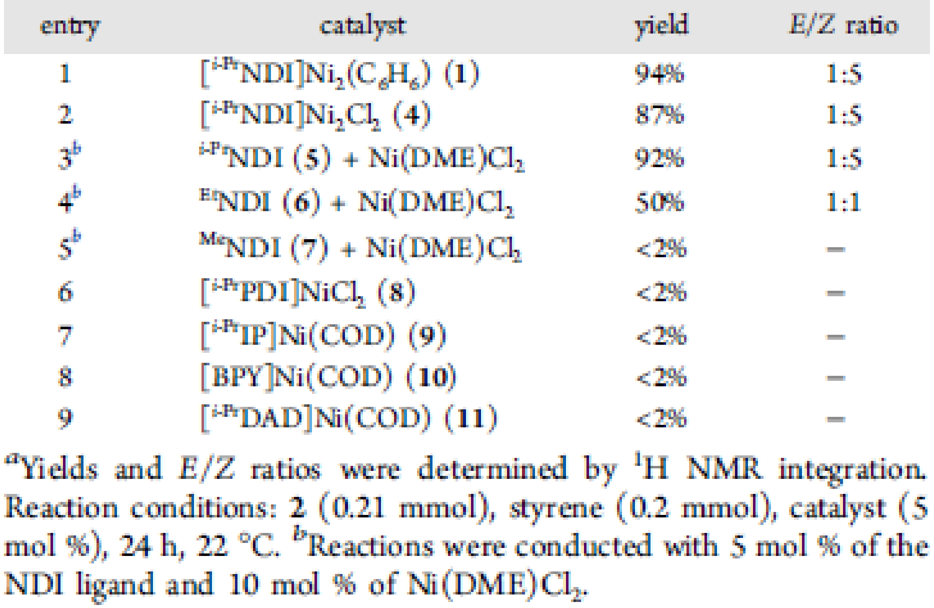
side to side



Johnson, K.; Weix, D. *Science* **2019**, *363*, 6429.

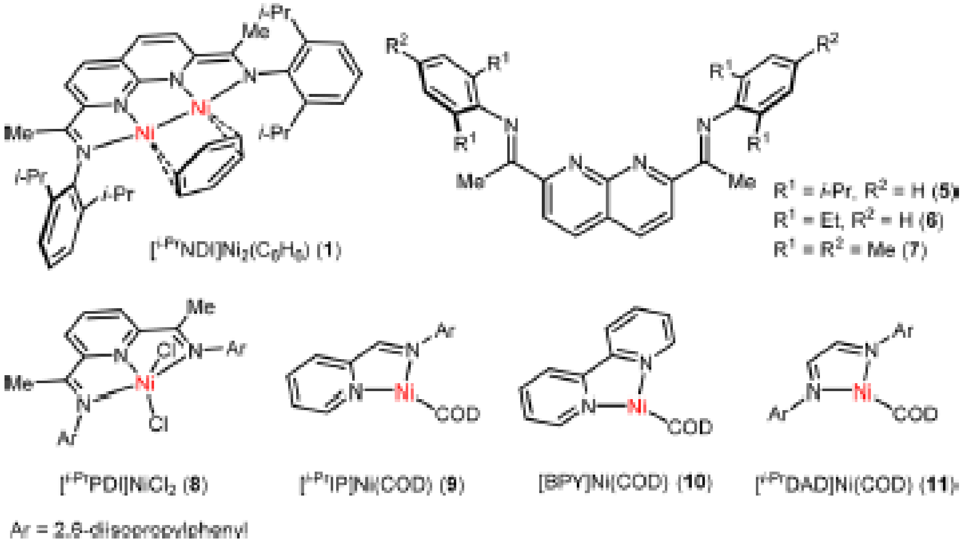
Optimization of Catalyst for Methylenecyclopropanation





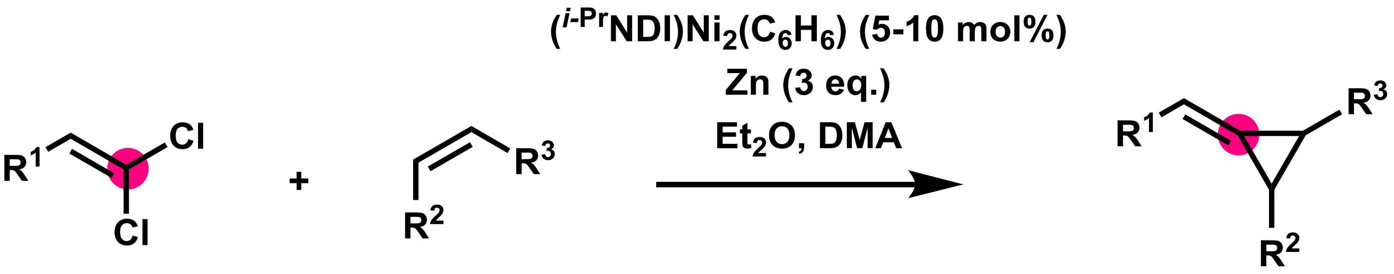
entry	catalyst	yield	E/Z ratio
1	[$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ (**1**)	94%	1:5
2	[$^{i\text{-Pr}}$NDI]Ni_2Cl_2 (**4**)	87%	1:5
3[b]	$^{i\text{-Pr}}$NDI (**5**) + Ni(DME)Cl_2	92%	1:5
4[b]	^{Et}NDI (**6**) + Ni(DME)Cl_2	50%	1:1
5[b]	^{Me}NDI (**7**) + Ni(DME)Cl_2	<2%	–
6	[$^{i\text{-Pr}}$PDI]NiCl_2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

[a] Yields and *E*/*Z* ratios were determined by ^{1}H NMR integration. Reaction conditions: **2** (0.21 mmol), styrene (0.2 mmol), catalyst (5 mol %), 24 h, 22 °C. [b] Reactions were conducted with 5 mol % of the NDI ligand and 10 mol % of Ni(DME)Cl_2.



Pal, S.; Zhou, Y.-Y.; Uyeda, C. *J. Am. Chem. Soc.* **2017**, *139*, 11686.

Substrate Scope

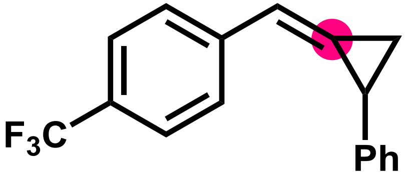


($^{i\text{-Pr}}$NDI)Ni$_2$(C$_6$H$_6$) (5-10 mol%)
Zn (3 eq.)
Et$_2$O, DMA

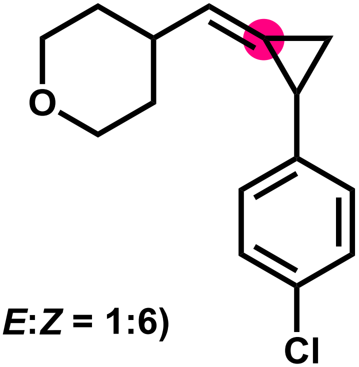
(1.1 eq.)

(1 eq.)

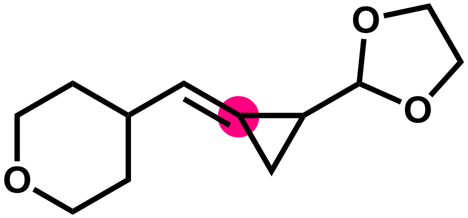
29 examples
50-99% yield



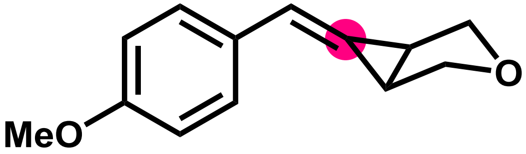
71% (*E*:*Z* = 1:4)



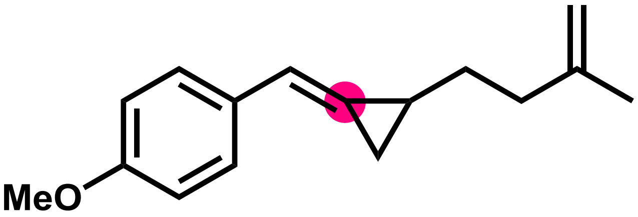
83% (*E*:*Z* = 1:6)



50% (*E*:*Z* = 8:1)



79%



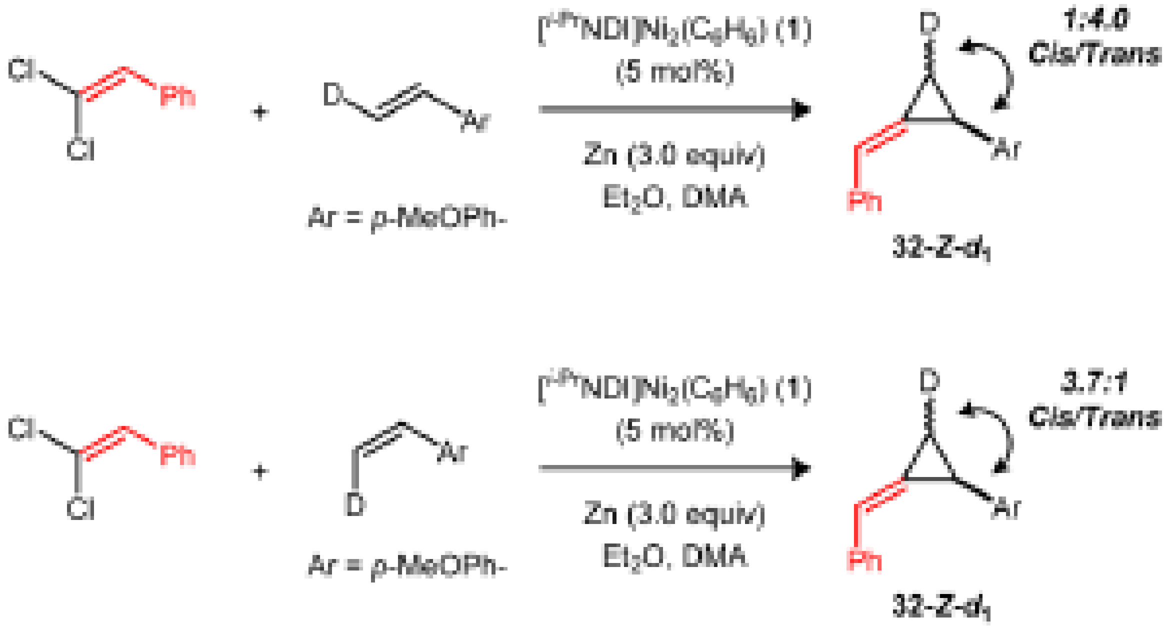
95% (*E*:*Z* = 1:6)

EZ selectivity is unclear.

Hindered alkenes did not work well.

Pal, S.; Zhou, Y.-Y.; Uyeda, C. *J. Am. Chem. Soc.* **2017**, *139*, 11686.

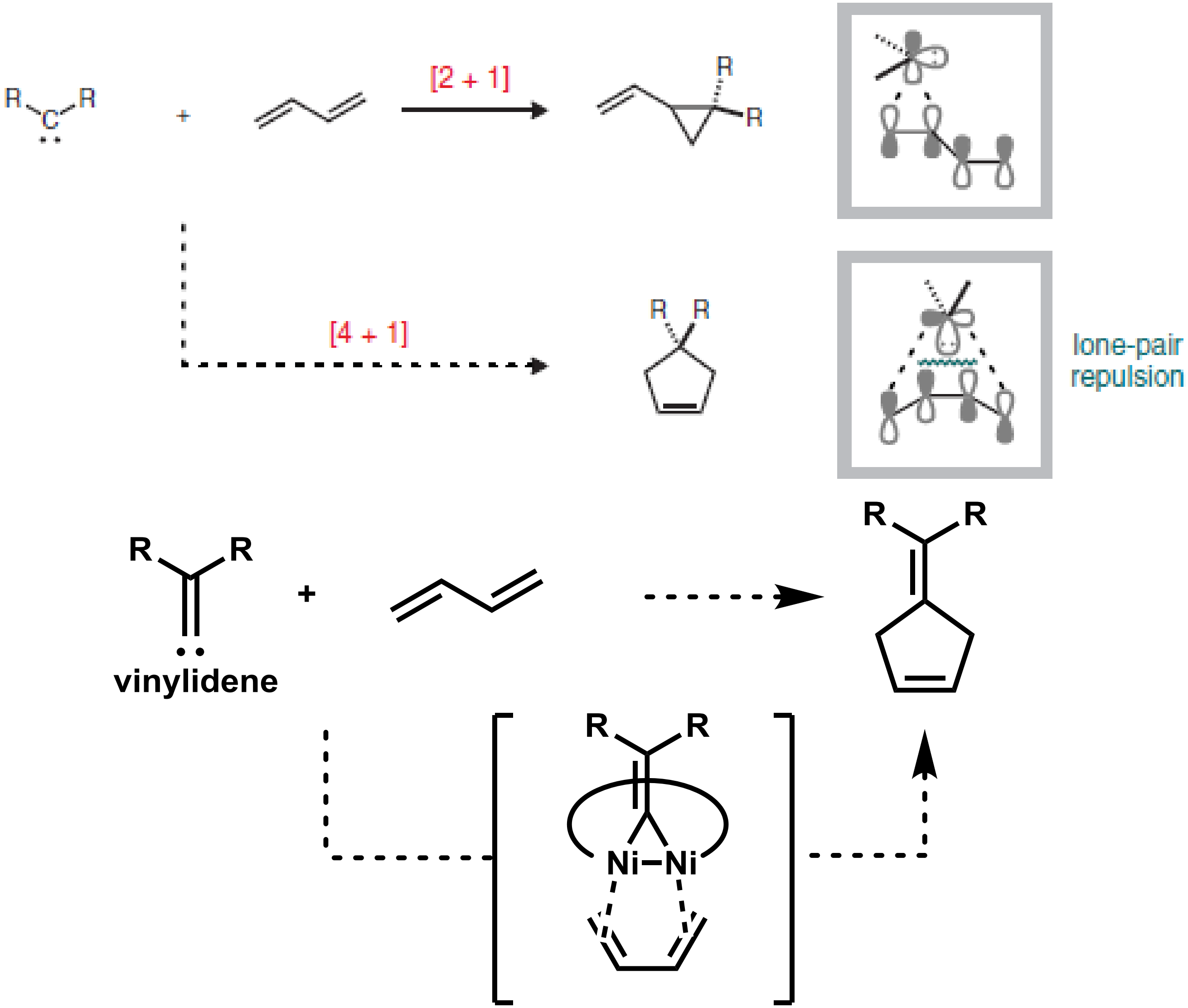
Mechanistic Study



incomplete retention of stereochemistry (alkenes were not isomerized under reaction conditions)
→stepwise mechanism
→metallacycle intermediate?

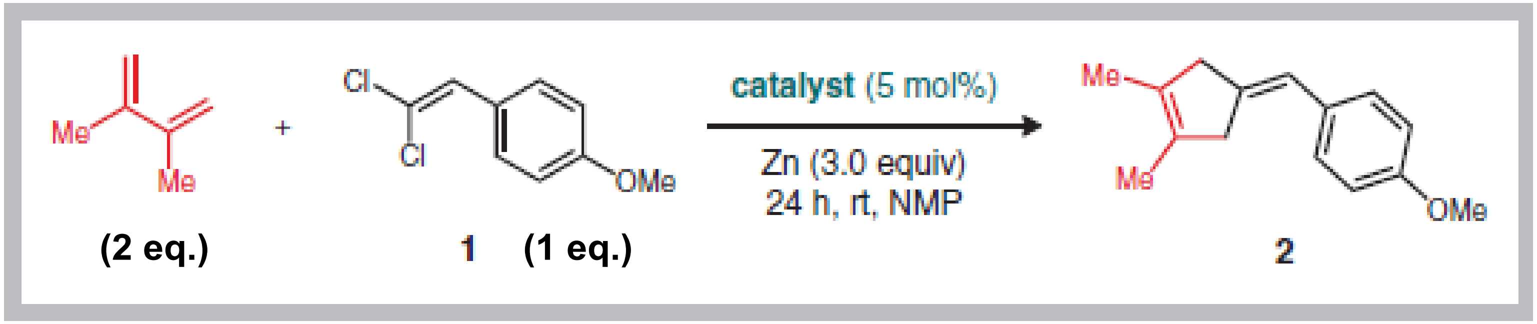
Pal, S.; Zhou, Y.-Y.; Uyeda, C. *J. Am. Chem. Soc.* **2017**, *139*, 11686.

Dinickel Catalyzed [4+1] Cycloaddition

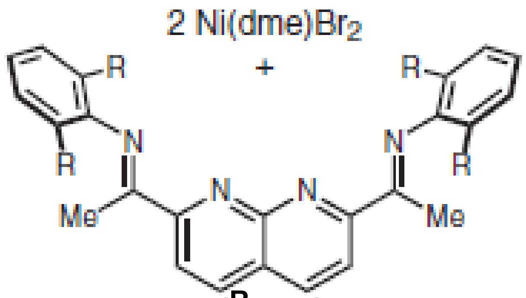


Zhou, Y.-Y.; Uyeda, C. *Science* **2019**, *363*, 857.

Optimization of Catalyst for [4+1] Cycloaddition



Binucleating Ligands

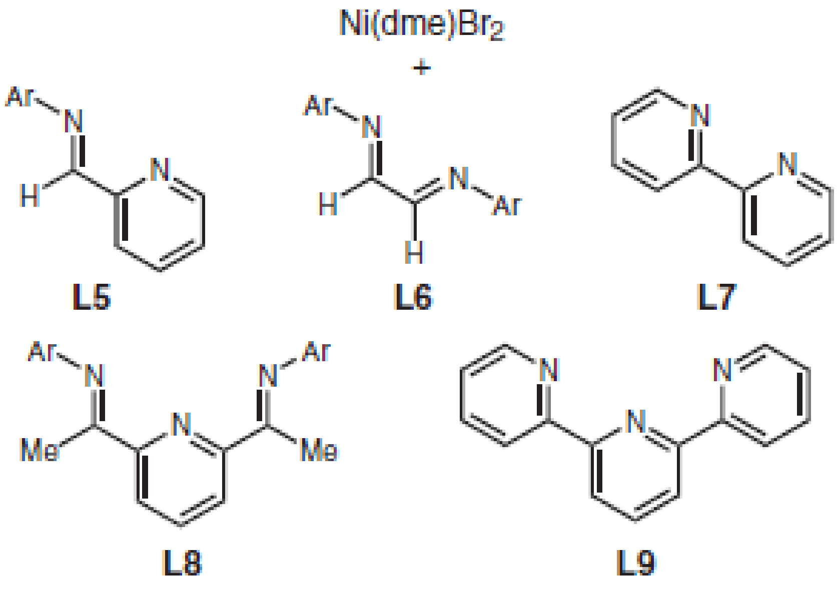


(^{R}NDI)

Steric Hindrance of Catalyst	Yield **2**
R = Me (**L1**)	12%
R = Et (**L2**)	22%
R = *i*-Pr (**L3**)	52%
R = *c*-Pent (**L4**)	>99%

important for reductive elimination?

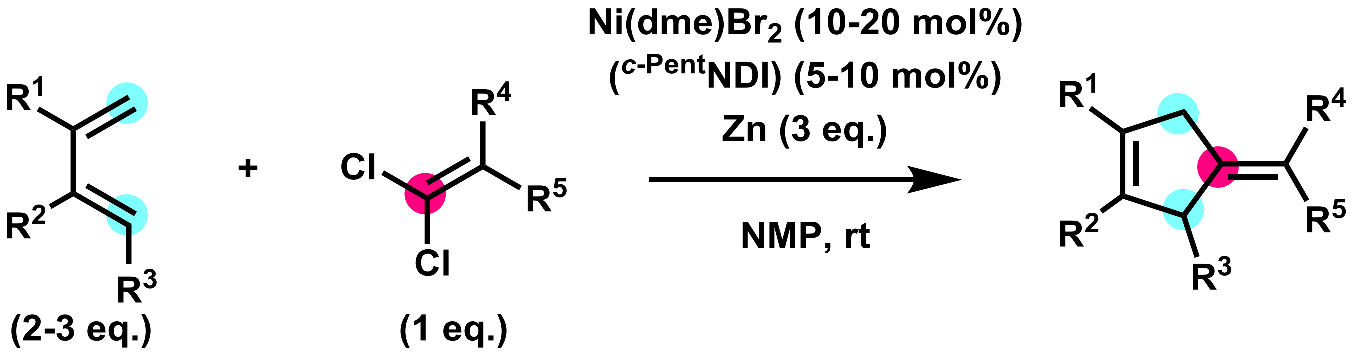
Mononucleating Ligands: no cycloaddition

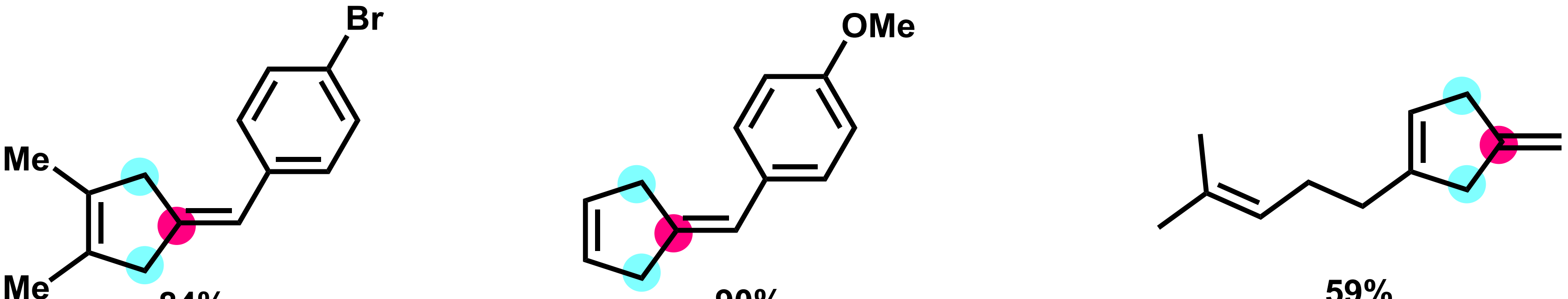


Ar = 2,6-(i-Pr)$_2$C$_6$H$_3$

Zhou, Y.-Y.; Uyeda, C. *Science* **2019**, *363*, 857.

Application



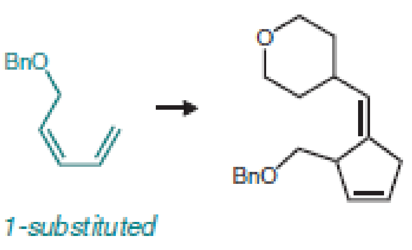


84%

90%

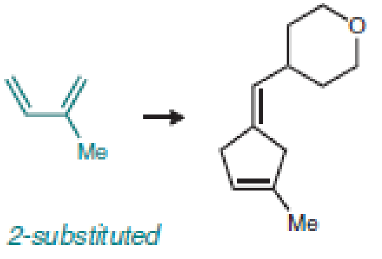
(cat: ($^{i\text{-Pr}}$NDI)Ni$_2$(C$_6$H$_6$))

59%



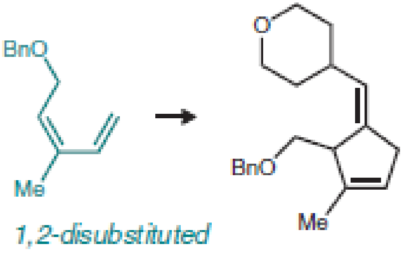
32 62% Yield*
1:3 *E/Z*

(cat: ($^{i\text{-Pr}}$NDI)Ni$_2$(C$_6$H$_6$))



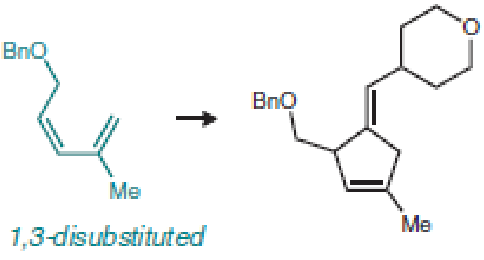
33 98% Yield*
1:6 *E/Z*

(cat: ($^{i\text{-Pr}}$NDI)Ni$_2$(C$_6$H$_6$))



34 62% Yield*
1:5 *E/Z*

(cat: ($^{i\text{-Pr}}$NDI)Ni$_2$(C$_6$H$_6$))

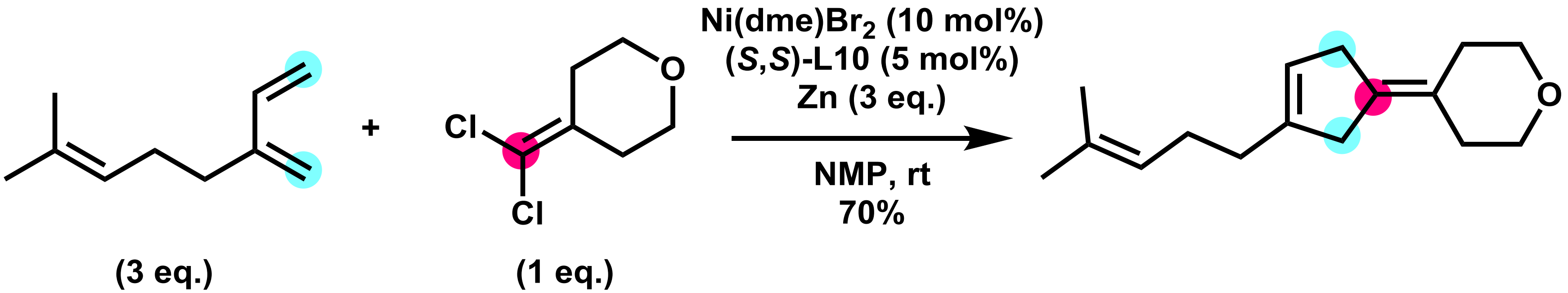


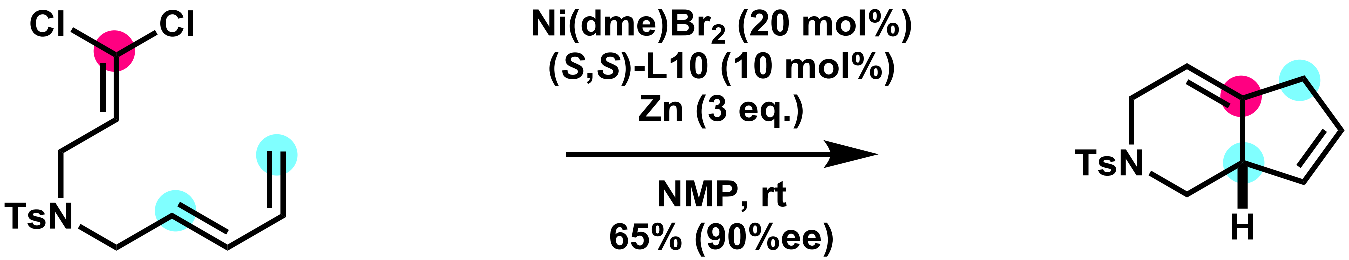
35 74% Yield*
9:1 *E/Z*

(cat: ($^{i\text{-Pr}}$NDI)Ni$_2$(C$_6$H$_6$))

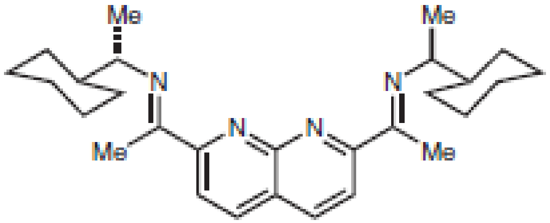
Zhou, Y.-Y.; Uyeda, C. *Science* **2019**, *363*, 857.

Application

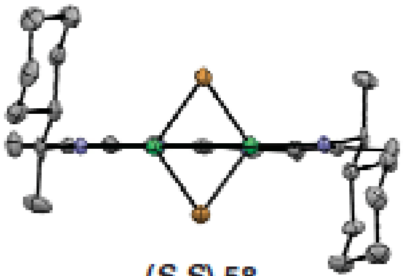




Chiral Dinickel Catalysts



(*S*,*S*)-L10



(*S*,*S*)-58

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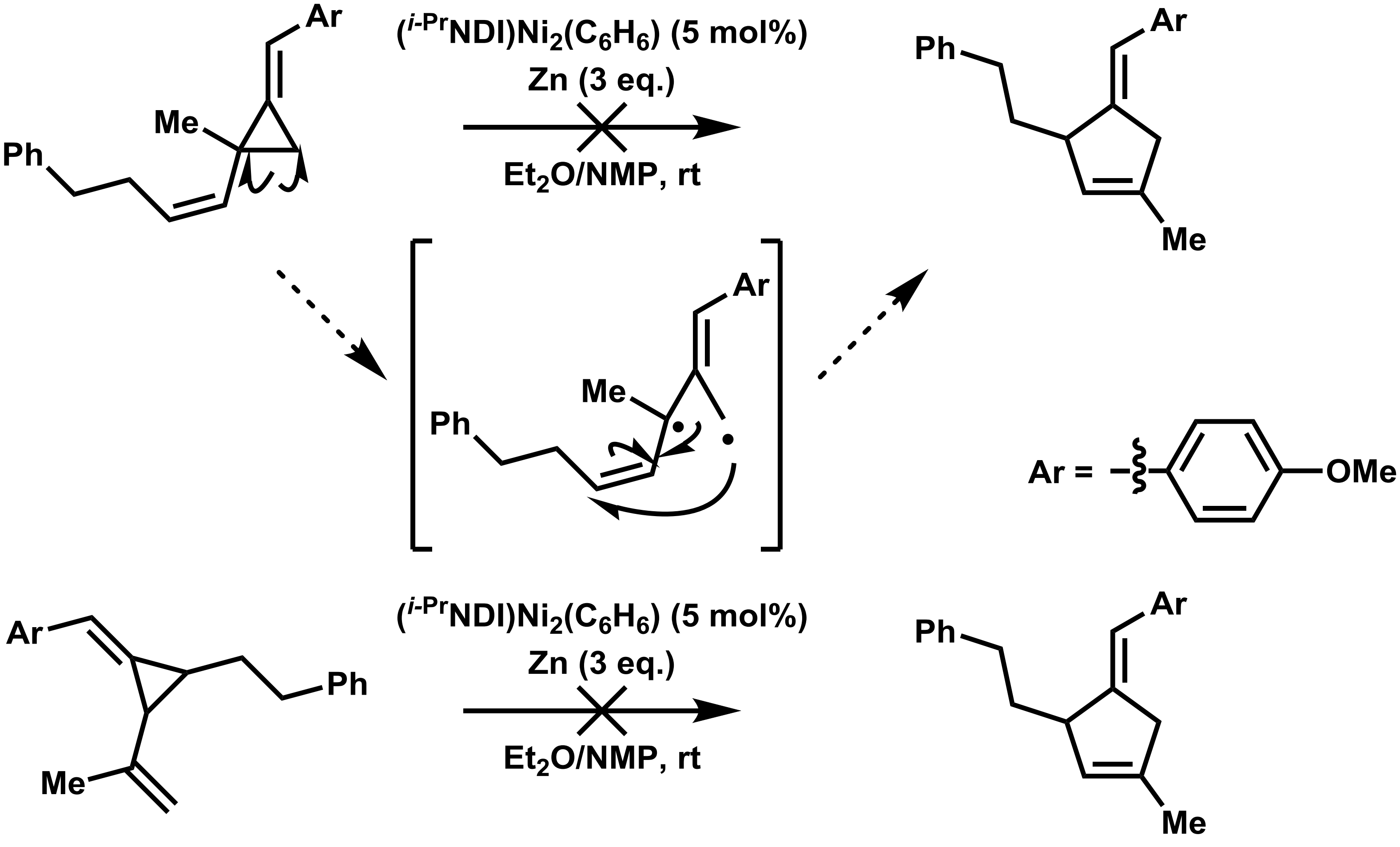
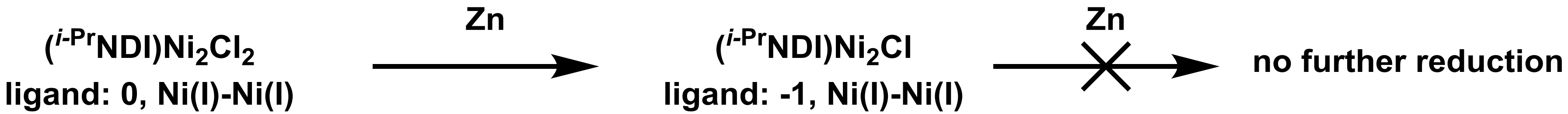
No Vinylcyclopropane [1,3]-Rearrangement



Zhou, Y.-Y.; Uyeda, C. *Science* **2019**, *363*, 857.

Mechanistic Study

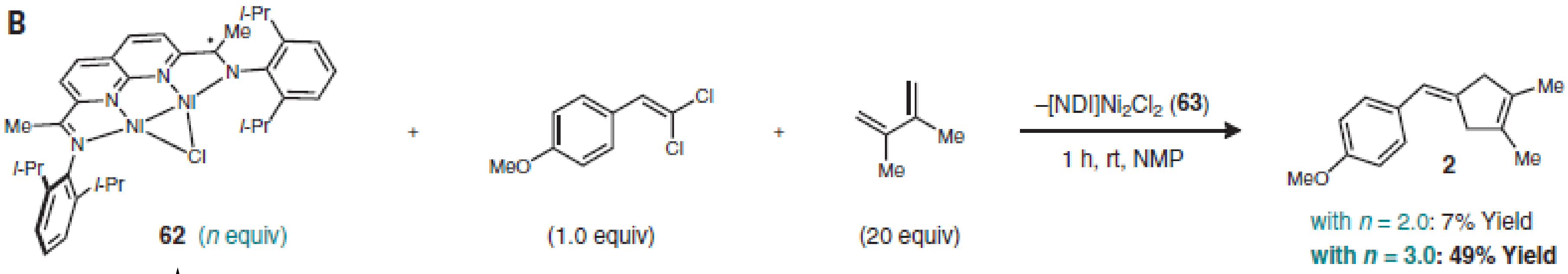

$(^{i\text{-}Pr}NDI)Ni_2Cl_2$
ligand: 0, Ni(I)-Ni(I)

Zn

$(^{i\text{-}Pr}NDI)Ni_2Cl$
ligand: -1, Ni(I)-Ni(I)

Zn

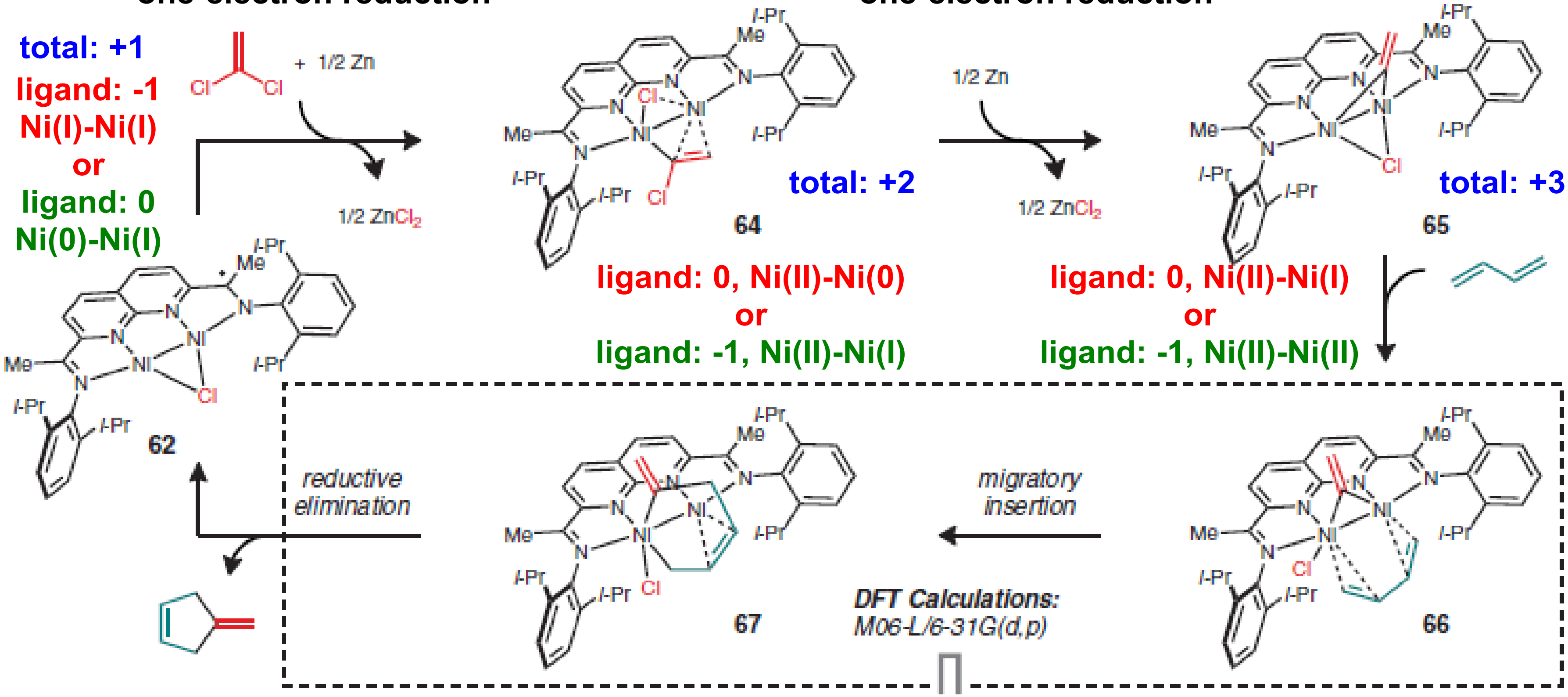
no further reduction



act as 1e$^-$ reductant
→twice 1e$^-$ reduction to obtain product

Zhou, Y.-Y.; Uyeda, C. *Science* **2019**, *363*, 857.

Proposed Mechanism



oxidative addition
&
one-electron reduction

oxidative addition
&
one-electron reduction

total: +1
ligand: -1
Ni(I)-Ni(I)
or
ligand: 0
Ni(0)-Ni(I)

62

64

total: +2

ligand: 0, Ni(II)-Ni(0)
or
ligand: -1, Ni(II)-Ni(I)

65

total: +3

ligand: 0, Ni(II)-Ni(I)
or
ligand: -1, Ni(II)-Ni(II)

67

66

DFT Calculations:
M06-L/6-31G(d,p)

ligand: 0, Ni(III)-Ni(0)
or
ligand: -1, Ni(III)-Ni(I)

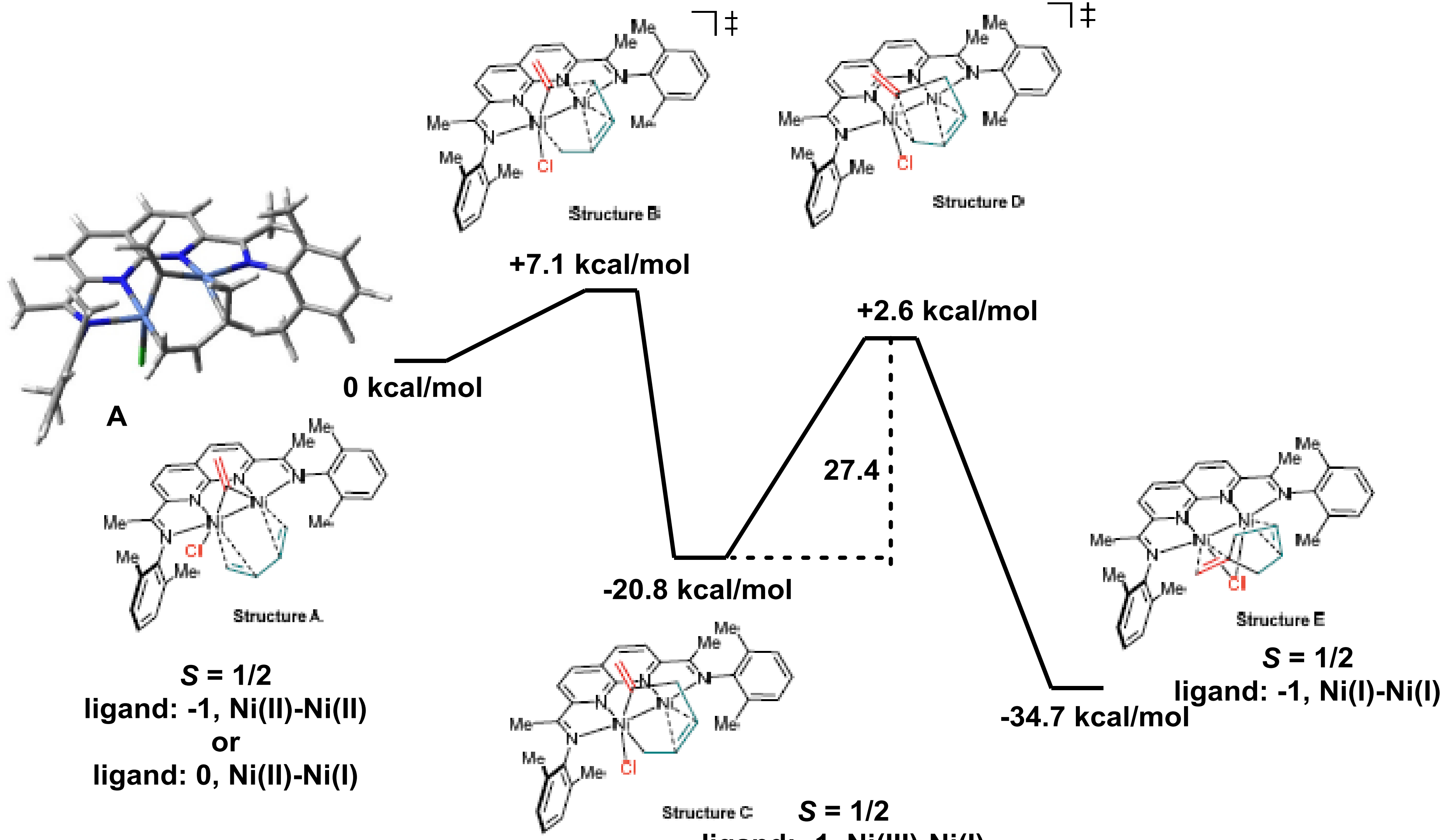
total: +3

ligand: 0, Ni(II)-Ni(I)
or
ligand: -1, Ni(II)-Ni(II)

total: +3

Zhou, Y.-Y.; Uyeda, C. *Science* **2019**, *363*, 857.

DFT Caluculation



S = 1/2
ligand: -1, Ni(II)-Ni(II)
or
ligand: 0, Ni(II)-Ni(I)

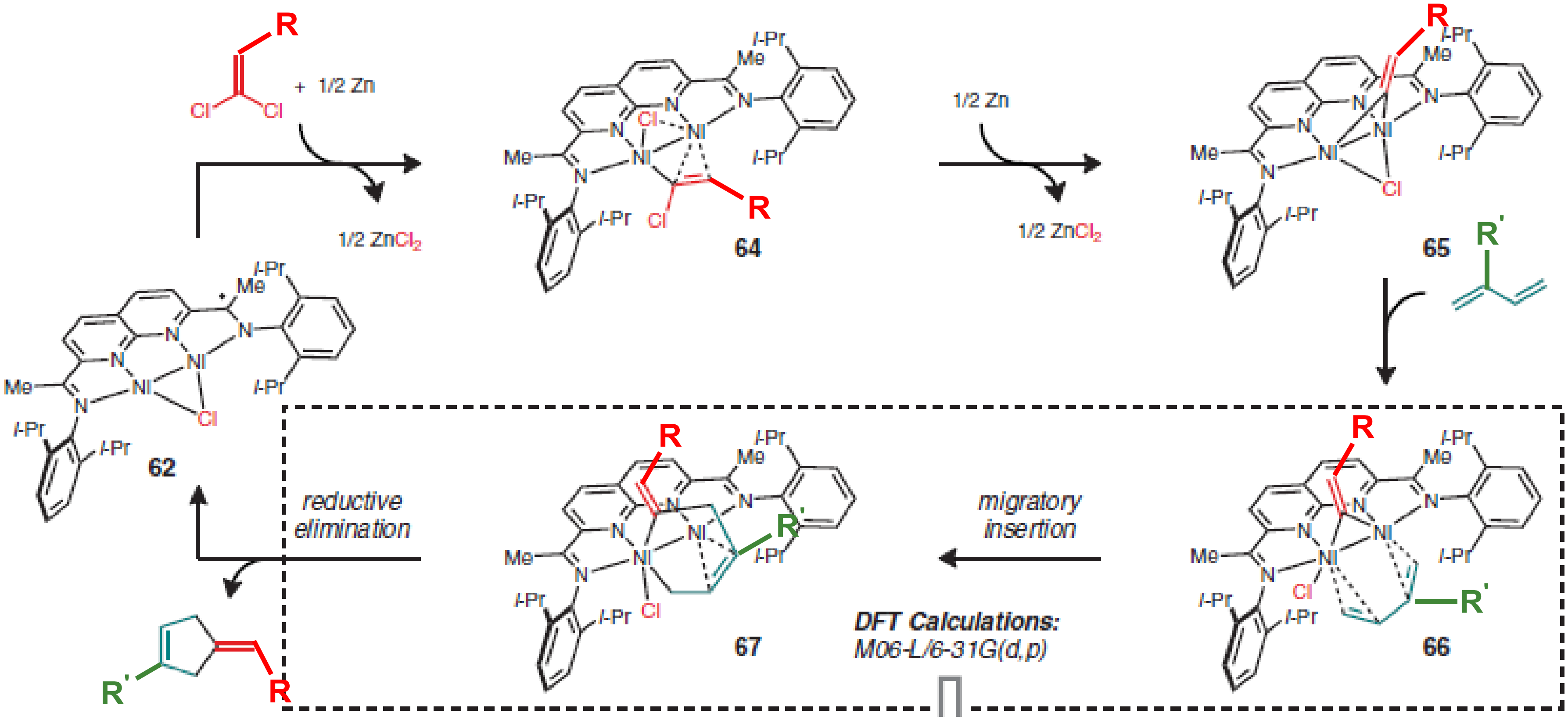
S = 1/2
ligand: -1, Ni(III)-Ni(I)
or
ligand: 0, Ni(III)-Ni(0)

S = 1/2
ligand: -1, Ni(I)-Ni(I)

M06-L/6-31G(d,p)

Zhou, Y.-Y.; Uyeda, C. *Science* **2019**, *363*, 857.

Plausible Explaination of *EZ* Selectivity



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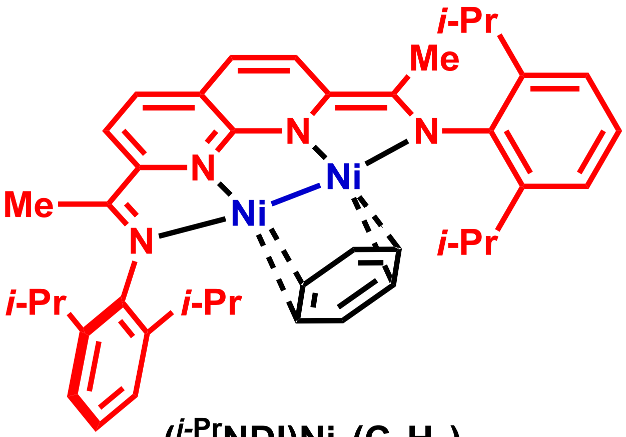
Summary



($^{i\text{-}Pr}$NDI)$Ni_2(C_6H_6)$

redox active ligand: charge -2

metal-metal bond: Ni^{i}-Ni^{i}

redox flexible catalyst
cooperative effect of two Ni atoms

↓

novel reactivity