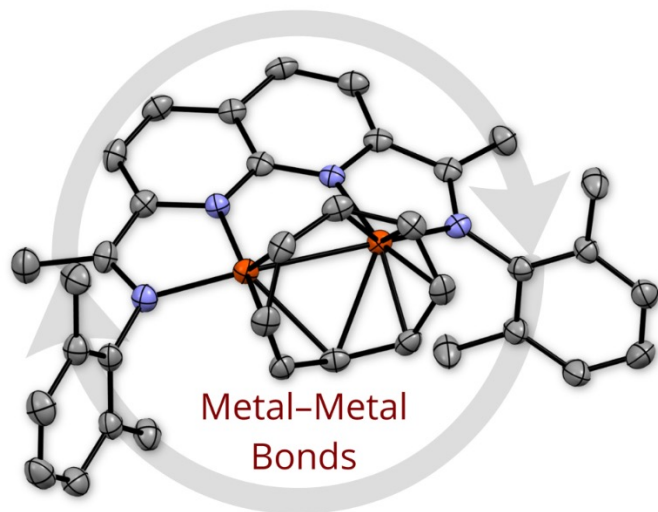


Metal-Metal Bonds Using Redox-Active Ligands



2021. 6. 3

Literature Seminar #2

M1 Yuri Katayama

Contents

1. Introduction

2. Catalysis of [NDI]Ni₂ complexes

I. Hydrosilylation

II. Alkyne cyclotrimerization

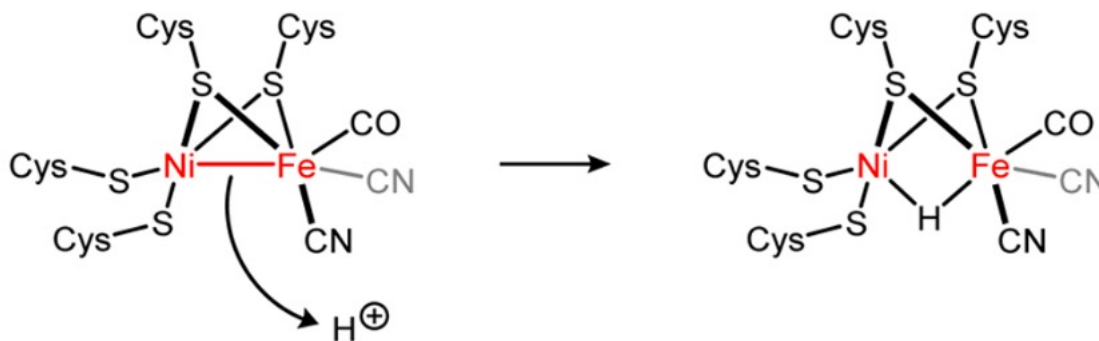
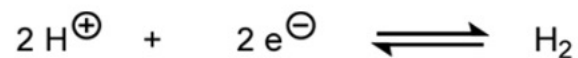
III. Carbene and vinylidene transfer

IV. C(sp²)-H amination

3. Summary

Metal—metal bond in biology

- redox transformations
- Ni-Fe hydrogenase

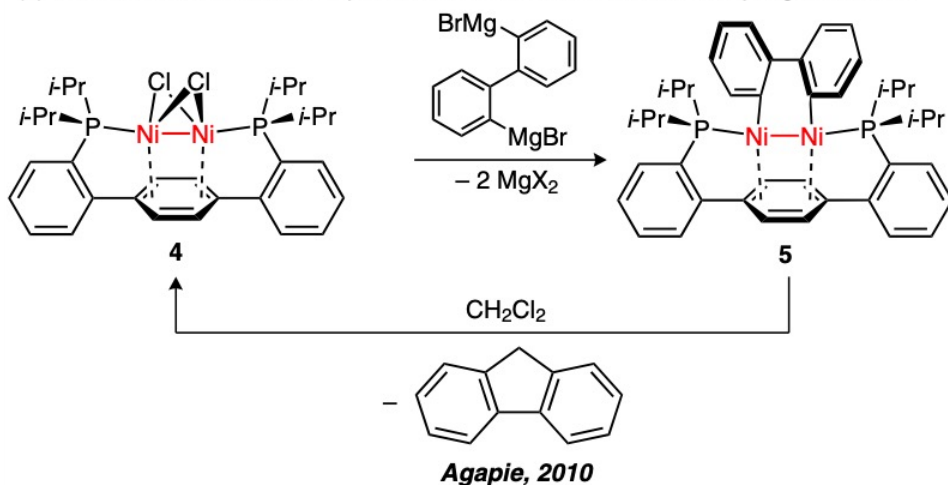


Powers, I. G. and Uyeda, C., *ACS Catal.* **2017**, 7, 936.

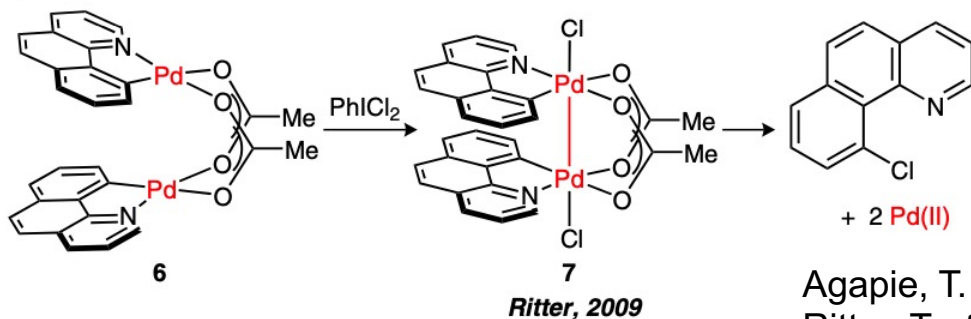
Group 10 dinuclear complexes

Ni, Pd, Pt : M(I)-M(I), M(III)-M(III) dimer

(c) Well-Defined Dinickel Complexes for Stoichiometric Cross-Coupling Reactions

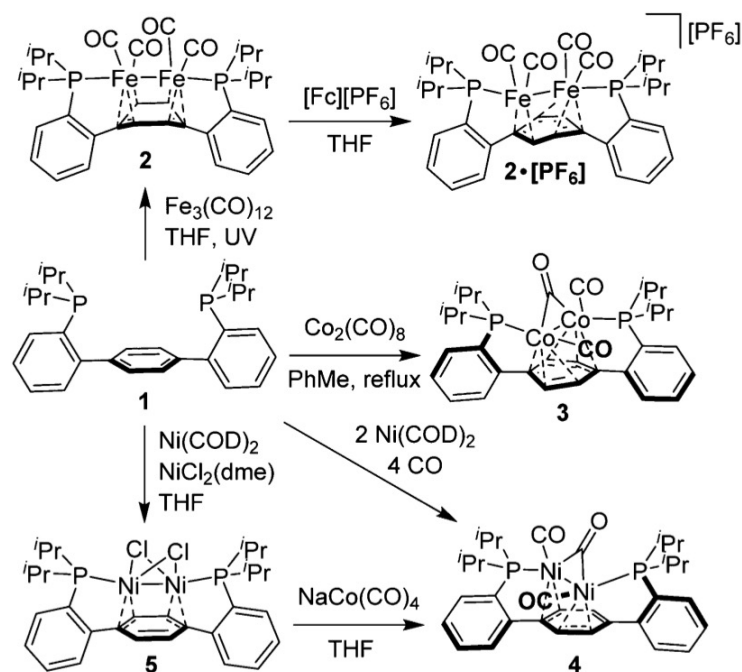


(d) Dipalladium Intermediates in C-H Functionalization Reactions

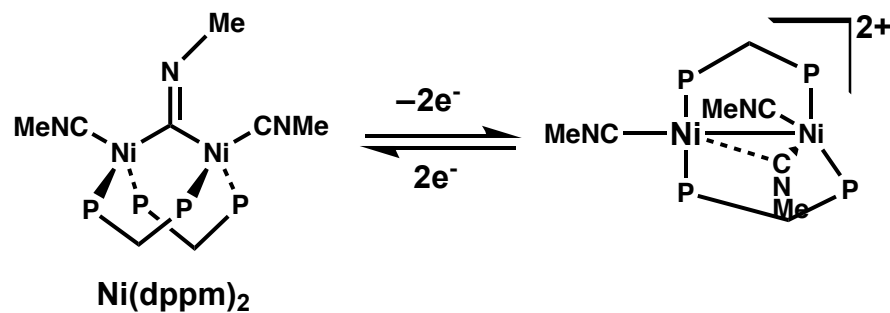


Agapie, T. *et al.*, *J. Am. Chem. Soc.* **2010**, *132*, 6296.
Ritter, T *et al.*, *Nat. Chem.* **2009**, *1*, 132.
Uyeda, C. *et al.*, *Synlett* **2016**, *27*, 814.

Group 10 dinuclear complexes



Scheme 1 Synthesis of dinuclear Fe, Co, and Ni carbonyl complexes.



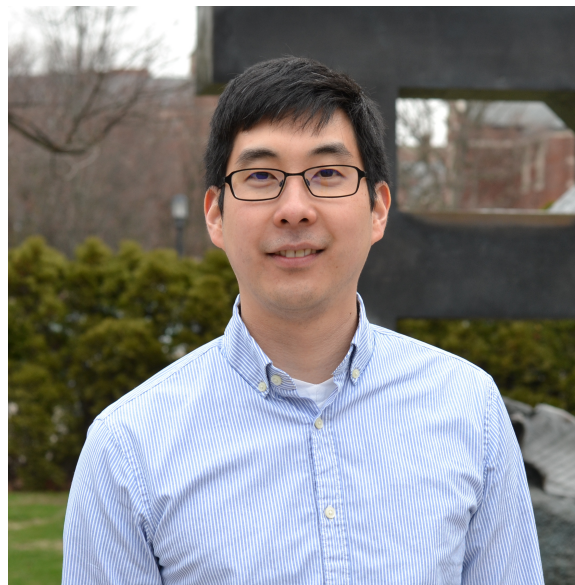
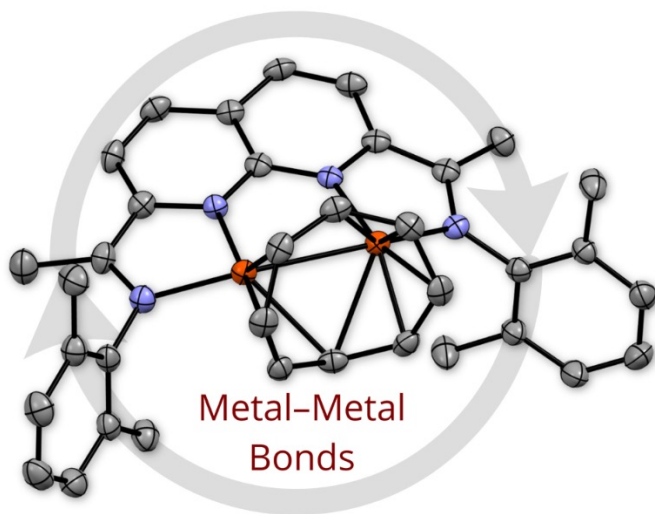
Kubiak, C. P. *et al.*, *J. Am. Chem. Soc.* **1987**, *109*, 754.

Agapie, T. *et al.*, *Chem. Commun.* **2014**, *50*, 4427.

There are few examples of Ni(I)-Ni(I) complexes which are redox active.
Most dinuclear Ni₂ complexes ... **nonredox-active, strong field ligands**

Christopher Uyeda

- Associate Professor at Department of Chemistry, Purdue University, US
- Research theme : Catalysis at metal-metal bonds

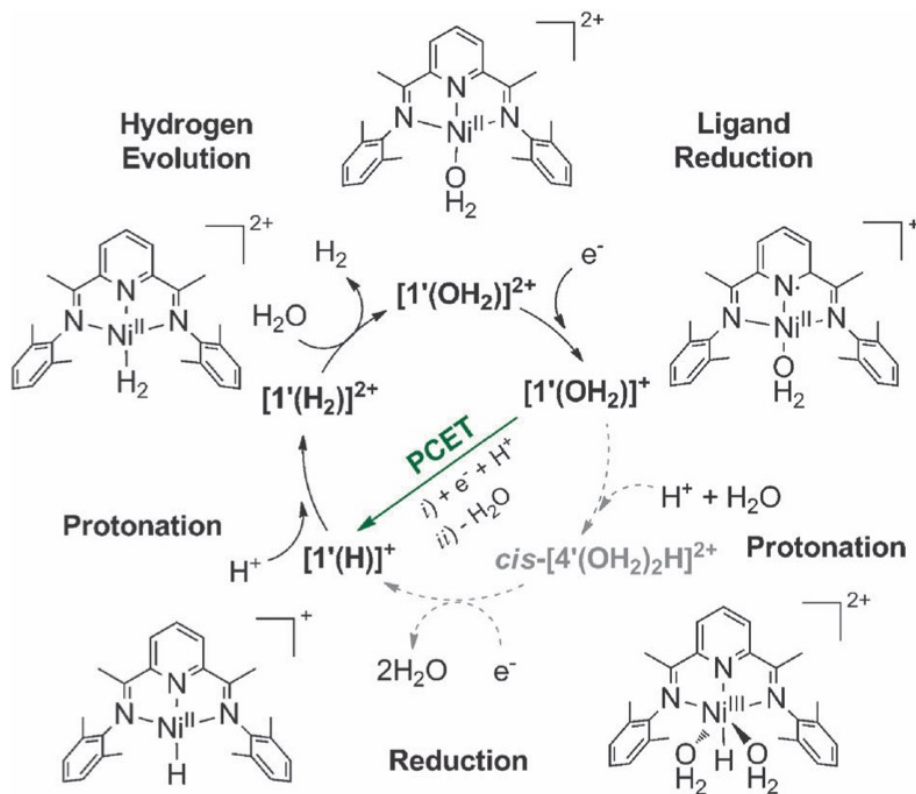


- Dinuclear nickel complexes using redox-active ligands
- The Uyeda group :
<https://www.chem.purdue.edu/uyeda/index.html>

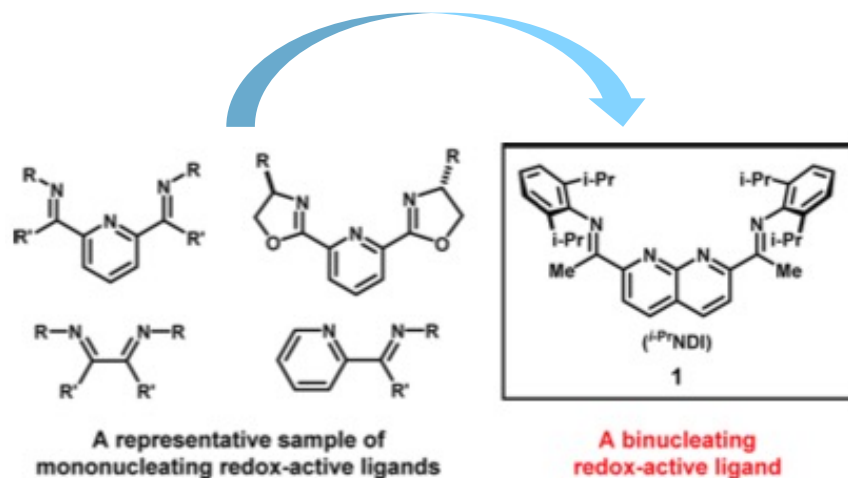
Redox-active ligands

One example of redox-active ligands

act as electron reservoirs in redox processes

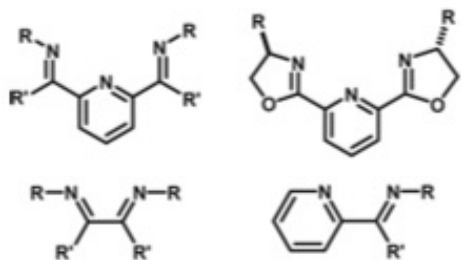


from mononuclear complexes
to dinuclear complexes

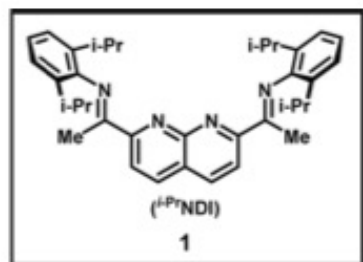


NDI = naphthyridine diimine

Ni₂ complexes using NDI ligand

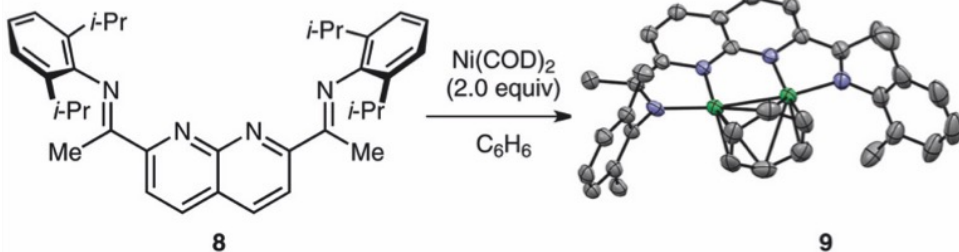


A representative sample of mononucleating redox-active ligands

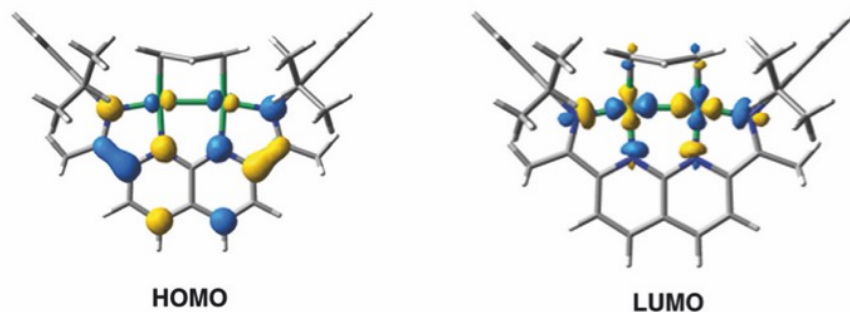


A binucleating redox-active ligand

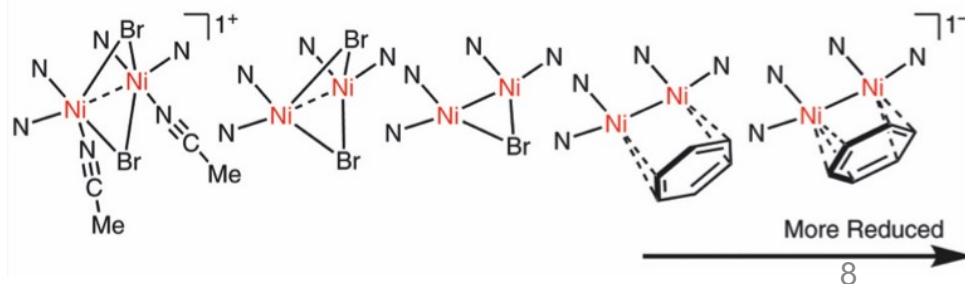
(a) Synthesis of $[{}^i\text{PrNDI}]_2\text{Ni}_2(\text{C}_6\text{H}_6)$ (9)



(b) Calculated Frontier Orbitals for $[{}^i\text{PrNDI}]_2\text{Ni}_2(\text{C}_6\text{H}_6)$ (9)



(c) A Redox Series of $[{}^i\text{PrNDI}]_2\text{Ni}_2$ Complexes



NDI : redox-active ligands
→ redox flexibility

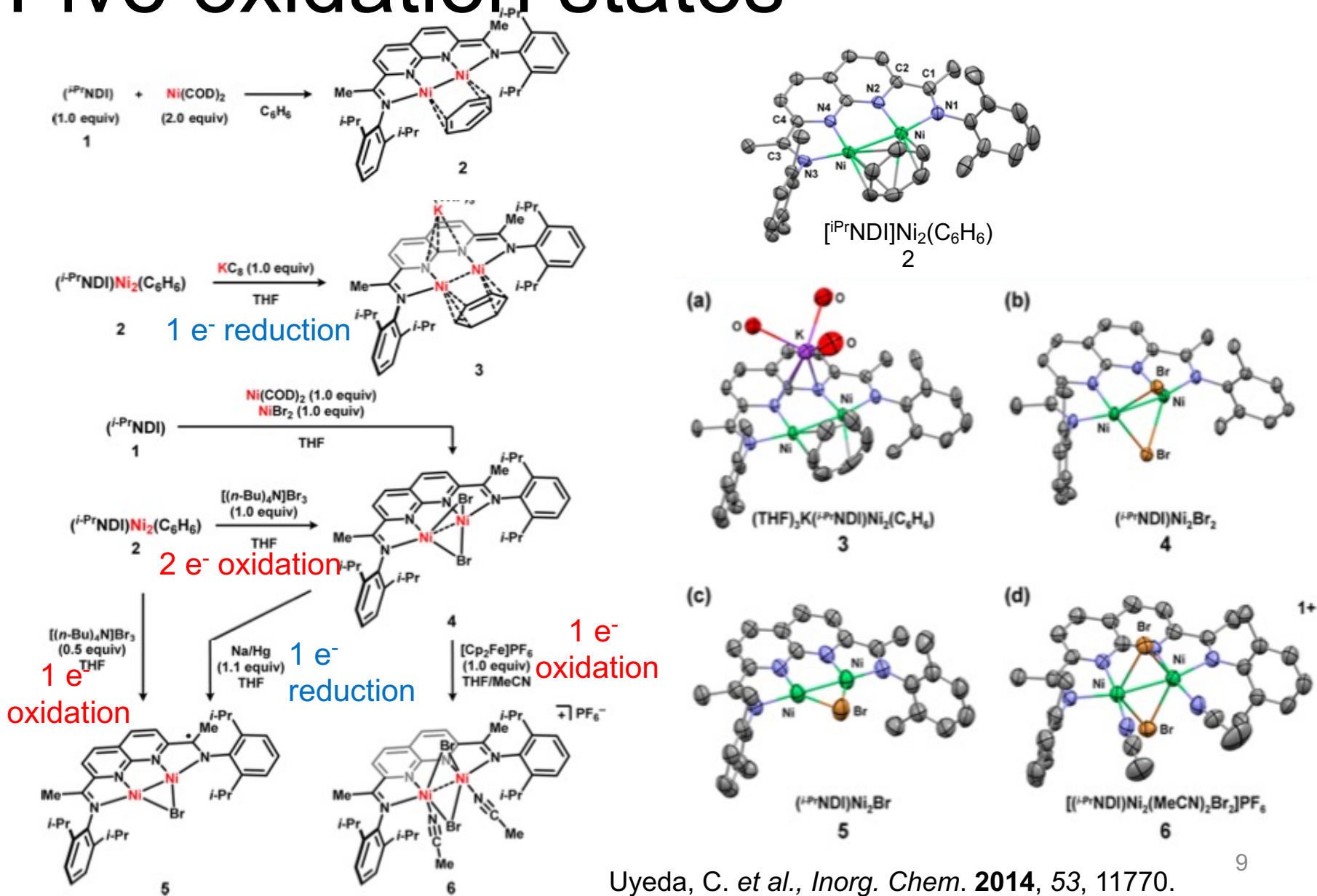
$[{}^i\text{PrNDI}]_2\text{Ni}_2(\text{C}_6\text{H}_6)$

- HOMO : ligand-centered π orbital
- LUMO : Ni-Ni σ^* orbital
- NDI^{2-} & Ni(I)-Ni(I)

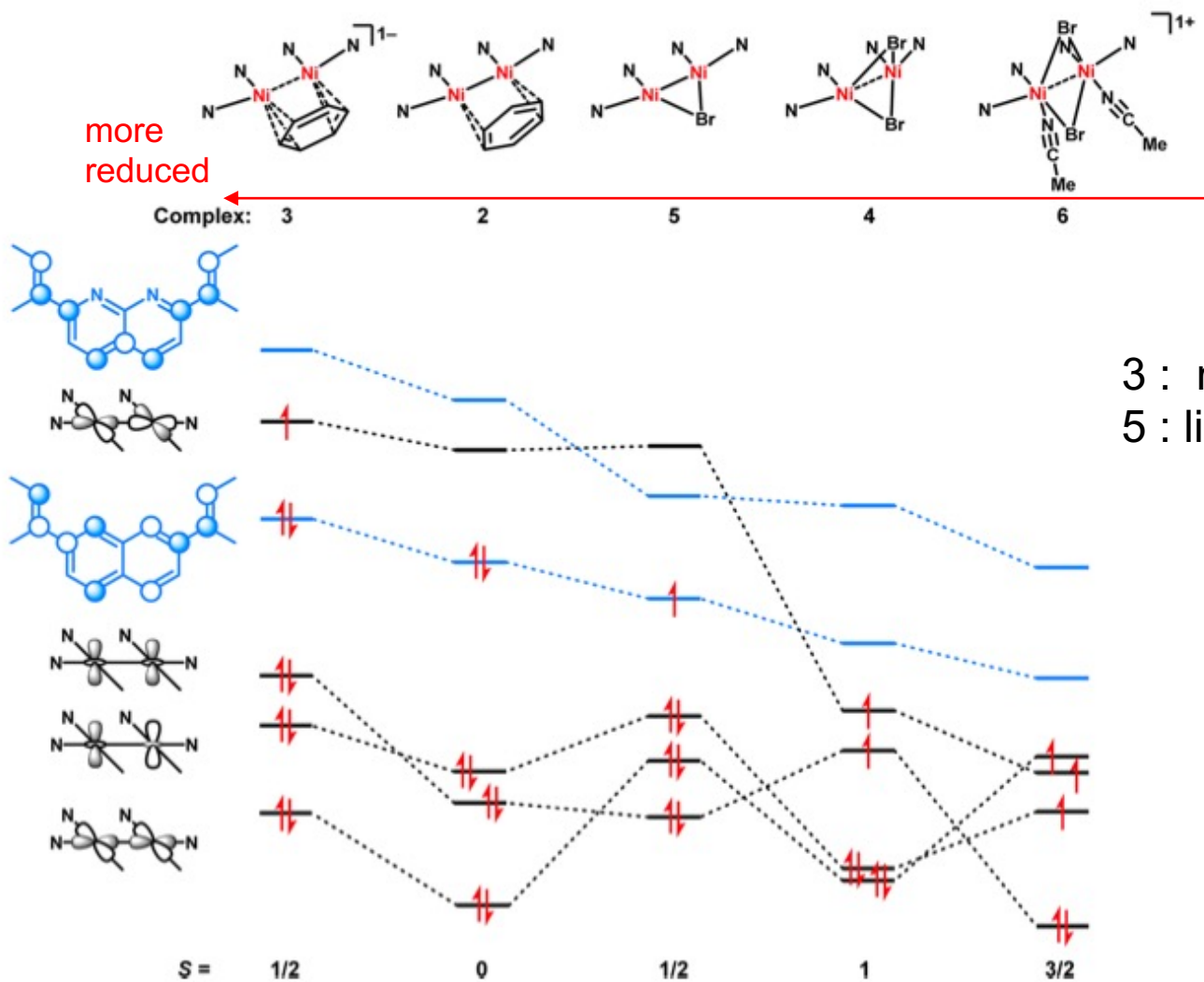
Uyeda, C. *et al.*, *Inorg. Chem.* **2014**, 53, 11770.

Uyeda, C. *et al.*, *Synlett* **2016**, 27, 814.

Five oxidation states



MO diagrams



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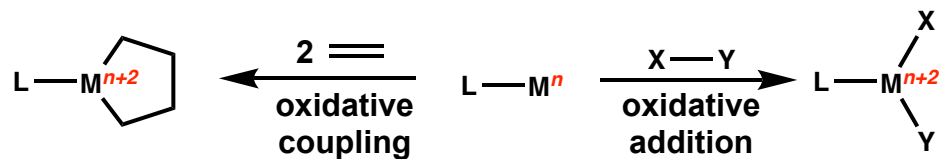
III. Carbene and vinylidene transfer

IV. C(sp²)-H amination

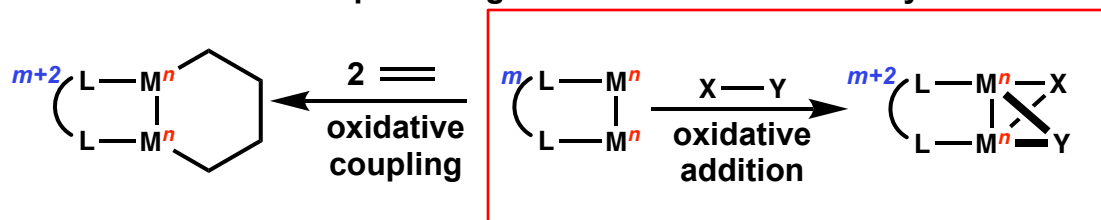
3. Summary

Redox process in transition-metal

Prototypical two-electron redox processes in transition-metal catalysis



Dinuclear reactions coupled to ligand-centered redox activity

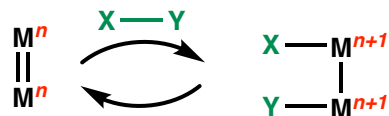


Metal-centered redox - two-electron oxidative addition

cleavage of M-M bond (σ -bond) formation of M-M bond (σ -bond)

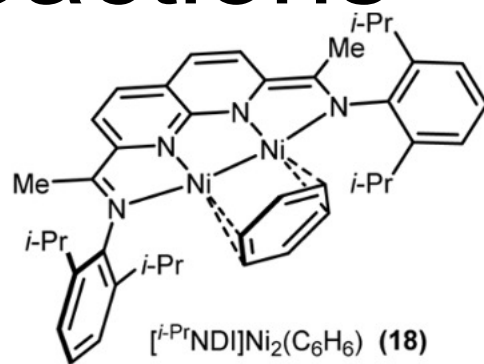


change in bond order (π/δ -bond)



Two-electron oxidative addition at metal-metal bonds

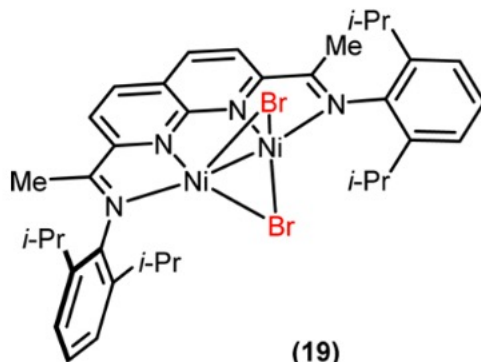
Two type reactions



$[i\text{-PrNDI}]Ni_2(C_6H_6)$ (18)

Ni–Ni: 2.496(1) Å

$[Br_2]$

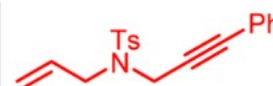


(19)

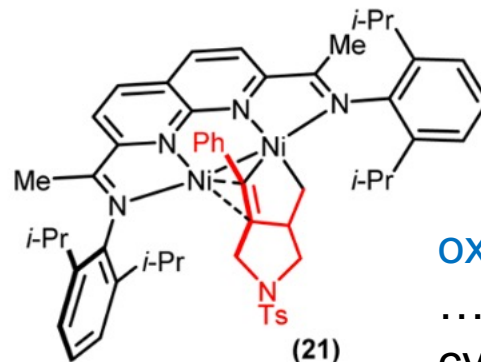
Ni–Ni: 2.5316(7) Å

oxidative addition

... hydrosilylation,
reactions involving carbenes,
vinylidenes, and C–C bond
activation



(20)



(21)

Ni–Ni: 2.4917(6) Å

oxidative crosscoupling
... alkyne
cyclootrimerization,
Pauson-Khand reaction

Catalysis at an intact M-M bond

explored

Stoichiometric redox reactions,
Precatalysts or
transient intermediates



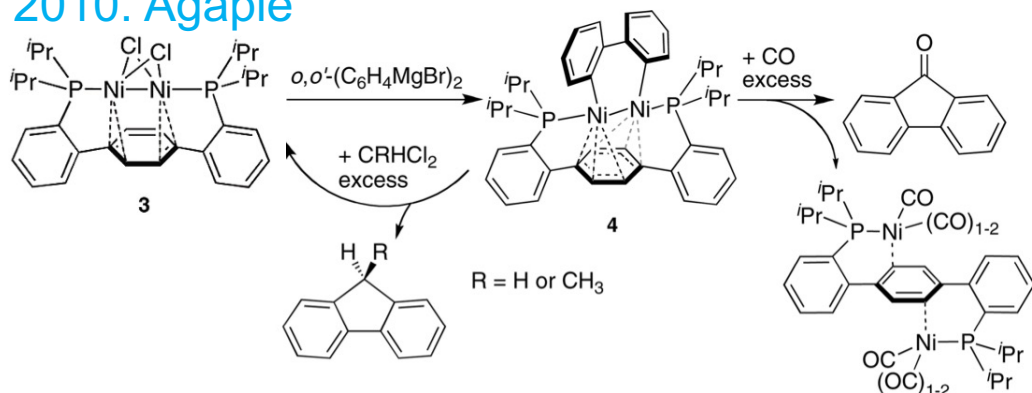
however, ...

unexplored

Challenges for catalysis

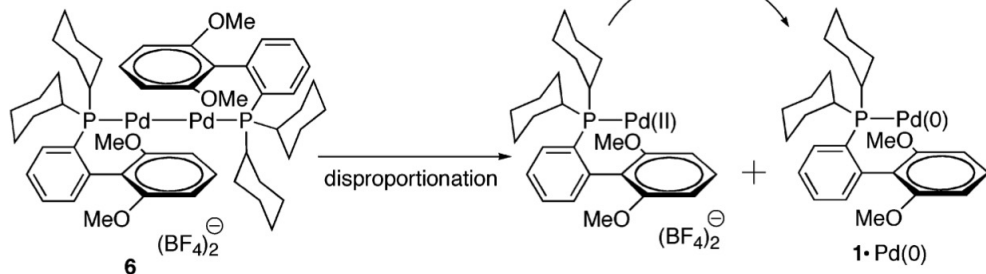
- Instability of metal-metal bond toward redox processes
- Lack of redox flexibility

2010. Agapie



mononuclear complexes
under turnover conditions

2005. Barder Suzuki-Miyaura coupling

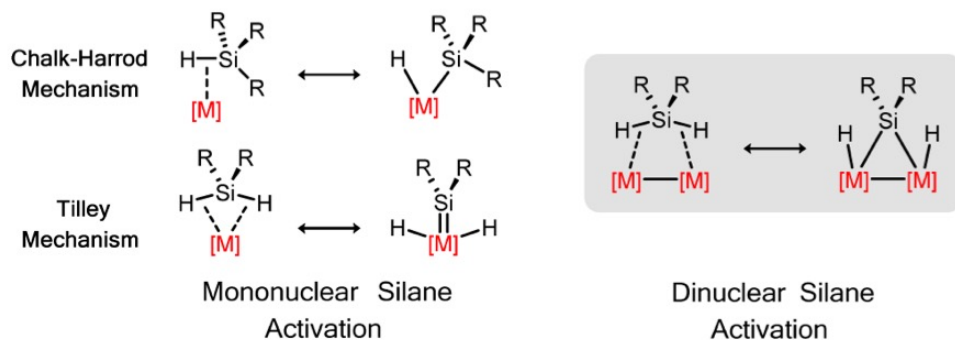


6 : Pd(I)-Pd(I)
as precatalysts

Agapie, T. *et al.*, *J. Am. Chem. Soc.* **2010**, *132*, 6
Barder, T. E. *J. Am. Chem. Soc.* **2005**, *128*, 898.

First M-M catalysis

Catalytic hydrosilylation reaction



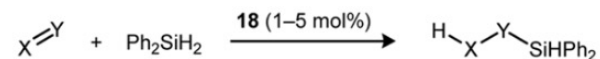
H-Si-H activation

- Back-donation from the Ni-Ni d_{xy} - d_{xy} π orbital into the LUMO of the silane
- Charge transfer from the reduced NDI ligand π system affords a sufficiently electron-rich Ni(I)-Ni(I) bond.

Steiman, T. J. and Uyeda, C. *J. Am. Chem. Soc.* **2015**, *137*, 6104.

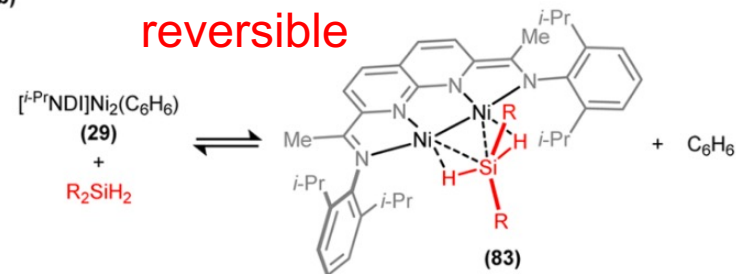
Powers, I. G. and Uyeda, C., *ACS Catal.* **2017**, *7*, 936.

(a)

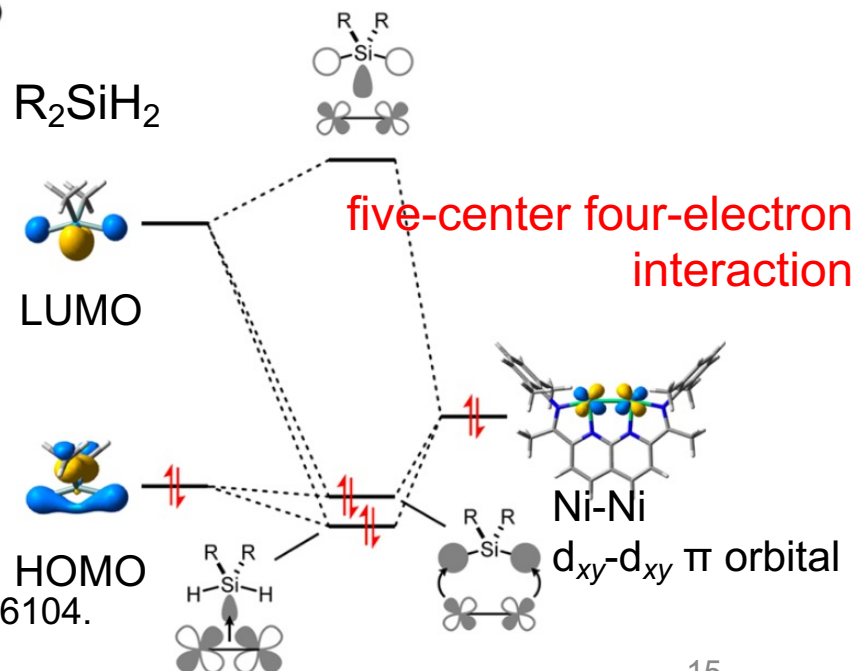


X=Y = alkenes, alkynes, dienes, ketones, aldehydes, or enones

(b)



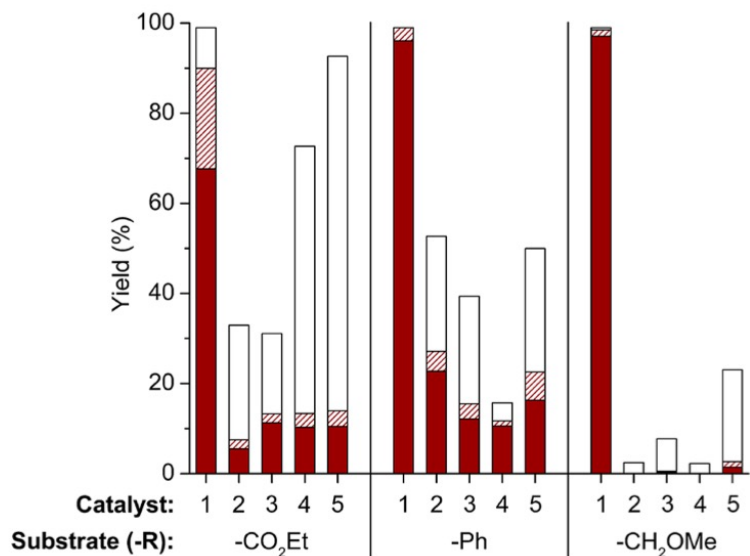
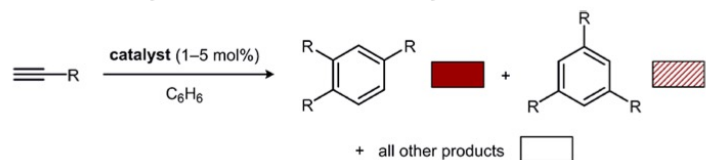
(c)



Contents

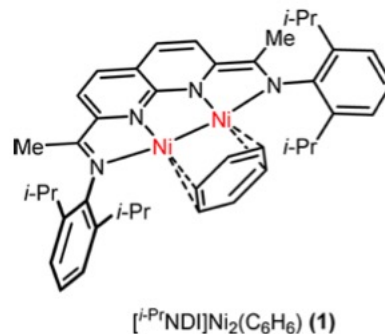
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 - IV. C(sp²)-H amination
3. Summary

Alkyne cyclotrimerization

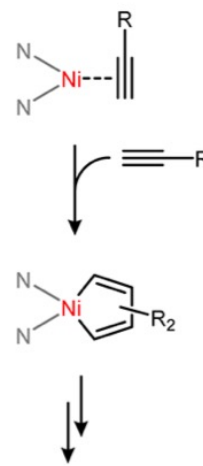


A comparison of catalyst reactivity
*5 = Ni(COD)₂

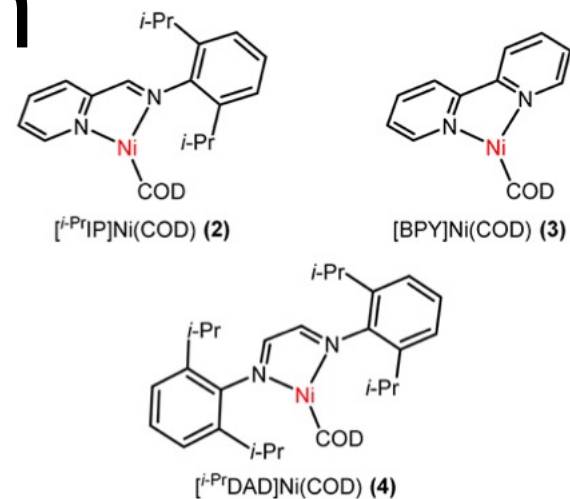
- ✓ Rapid and selective cyclotrimerization
- ✓ Major 1, 2, 4- trisubstituted arenes



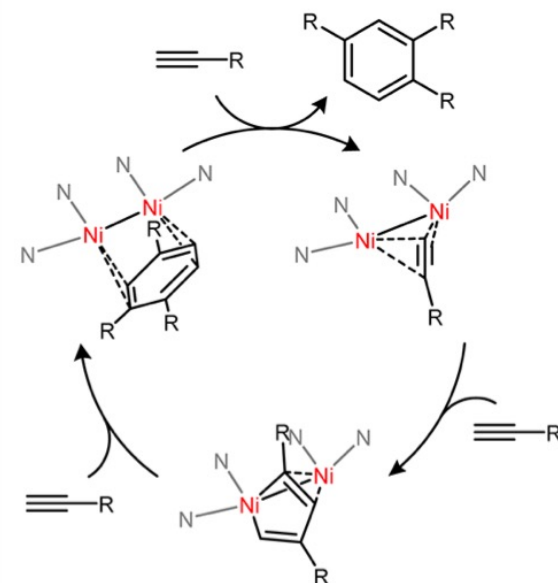
Non-Selective Alkyne Oligomerization Using Mononuclear [N,N]Ni Catalysts



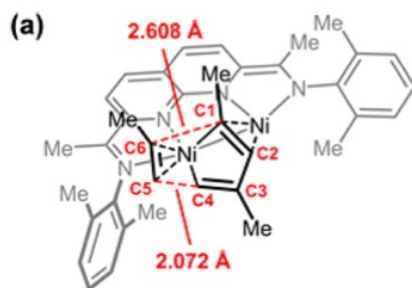
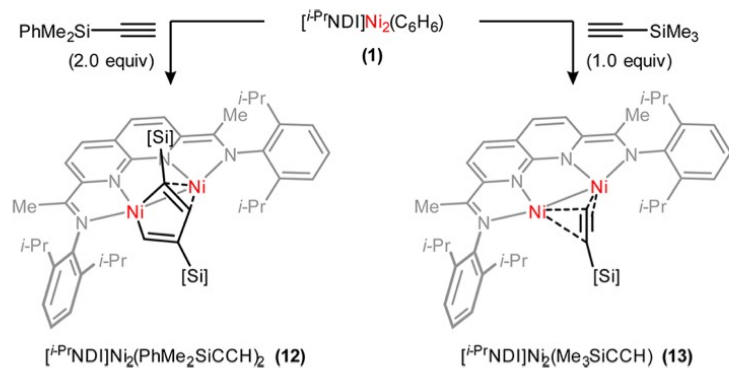
cyclotrimers, cyclotetramers, linear oligomers, and polymers



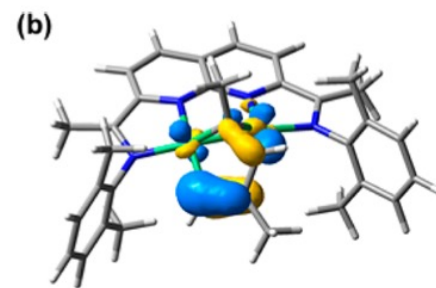
Selective Alkyne Cyclotrimerization at a Ni-Ni Bond



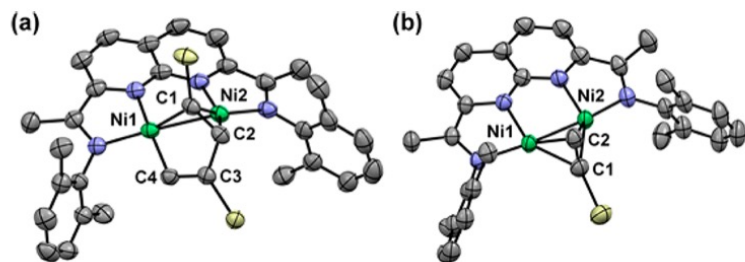
Stoichiometric reactivity studies



[4+2] cycloaddition transition structure



HOMO-1 the metallacycle intermediate

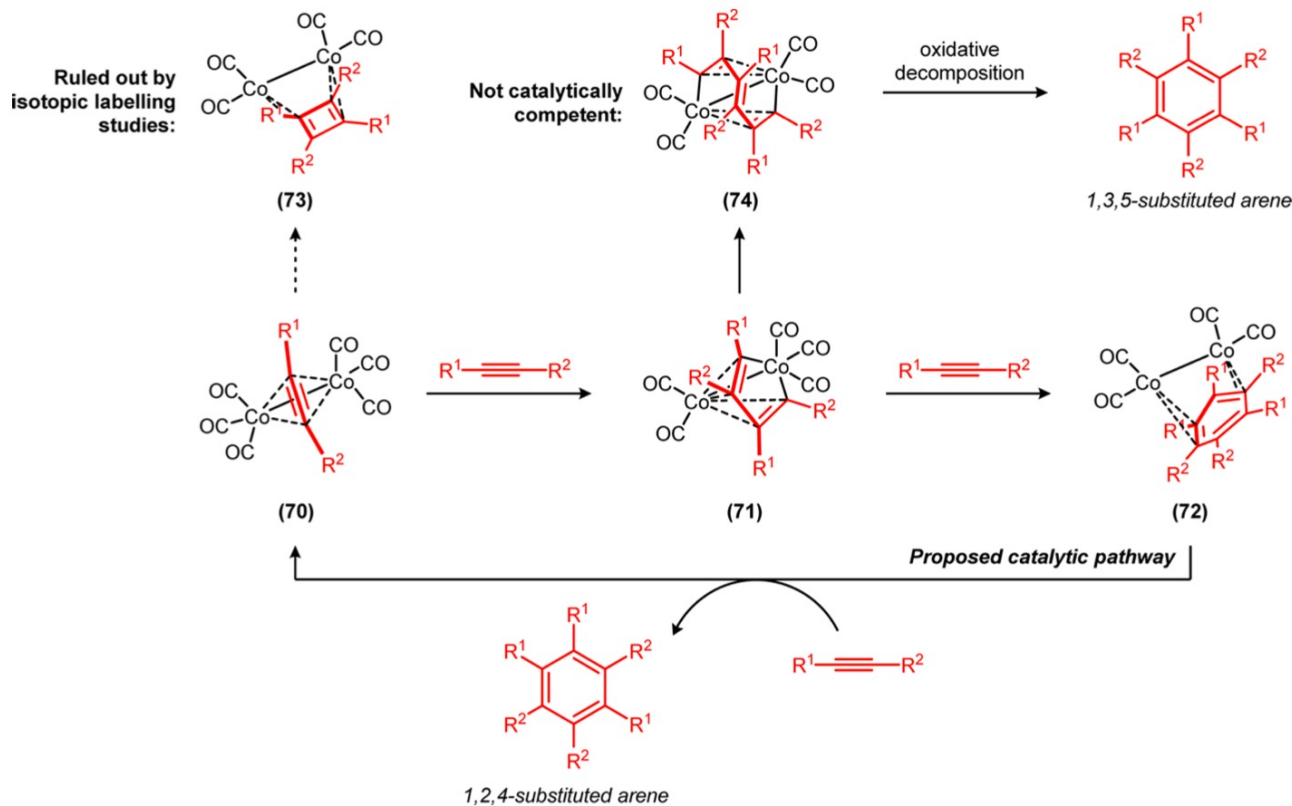


Regioselectivity

- Head-to-tail coupling (12) because of steric hindrance of *i*Pr
- η^2 interaction : the second Ni & one double bond of diene \rightarrow Asymmetry results in a steric preference (C1-C6)

Other cyclotrimerization

Co₂(CO)₈ catalyzed cyclotrimerization



71 : dicobaltacyclopentadiene intermediate

η^4 interaction : the second Co & dienyl π system

$\leftrightarrow \eta^2$ interaction : the second Ni & one double bond of diene (Uyeda's complex)

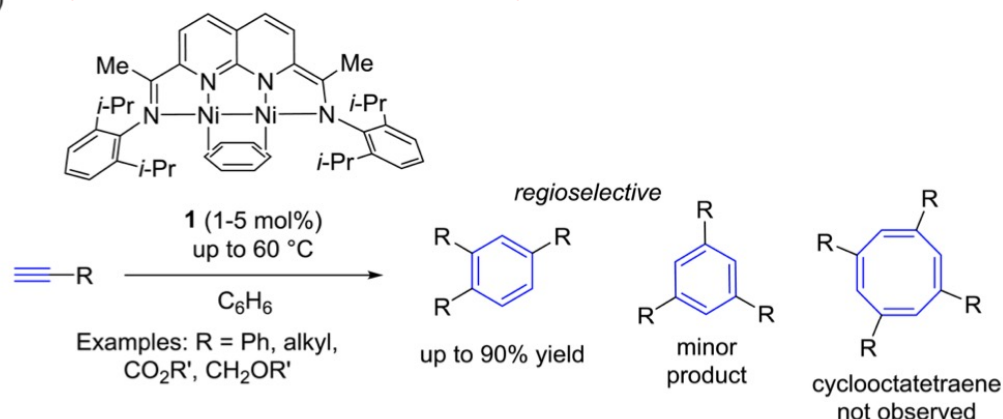
→ Higher regioselectivity

Spin crossover mechanism

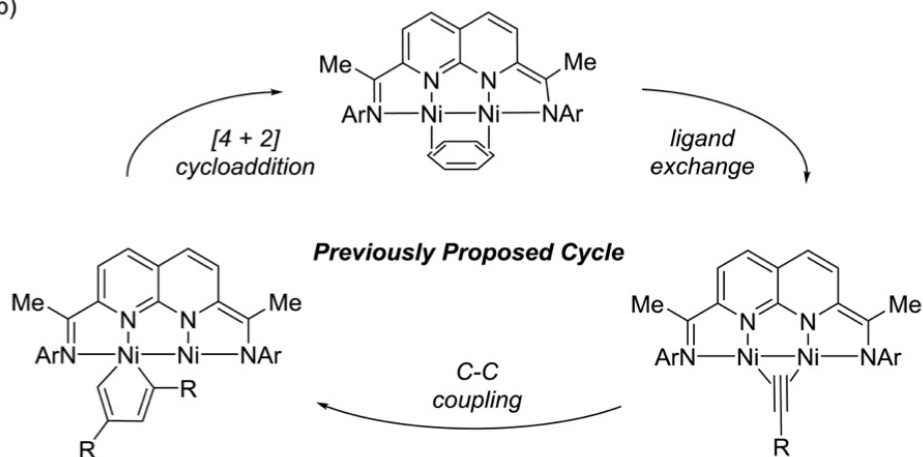
DFT calculations considering multiple spin states revealed another mechanism – a spin crossover mechanism.

- Regioselectivity
- Cyclotrimerization vs cyclotetramerization selectivity

a)



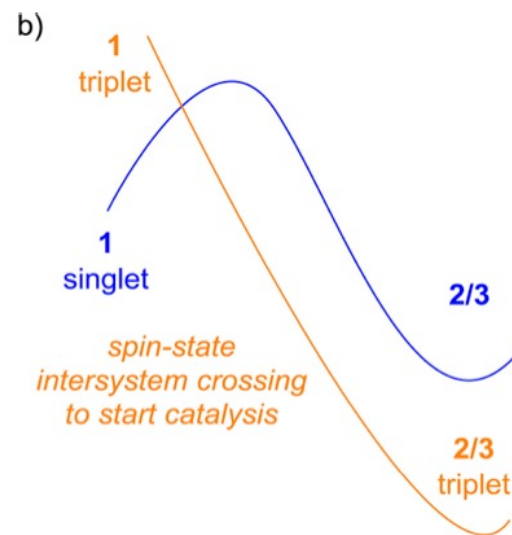
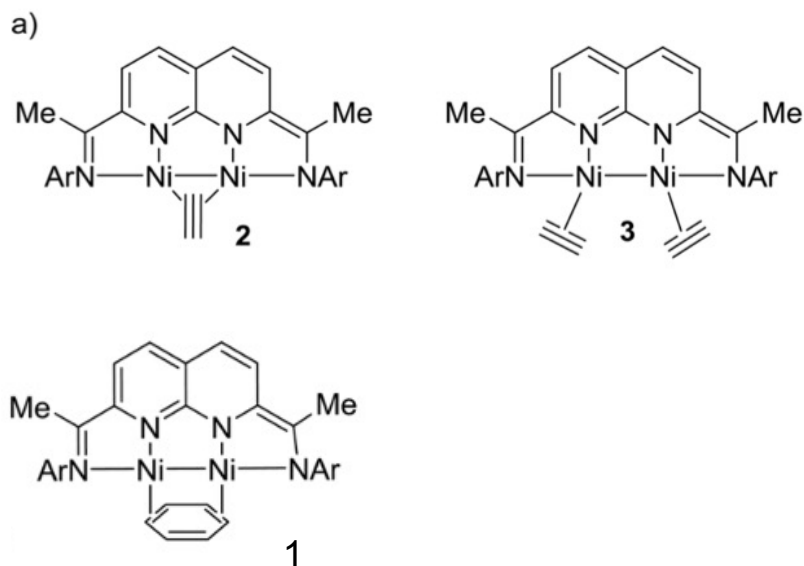
b)



Ligand coordination

① Ligand coordination

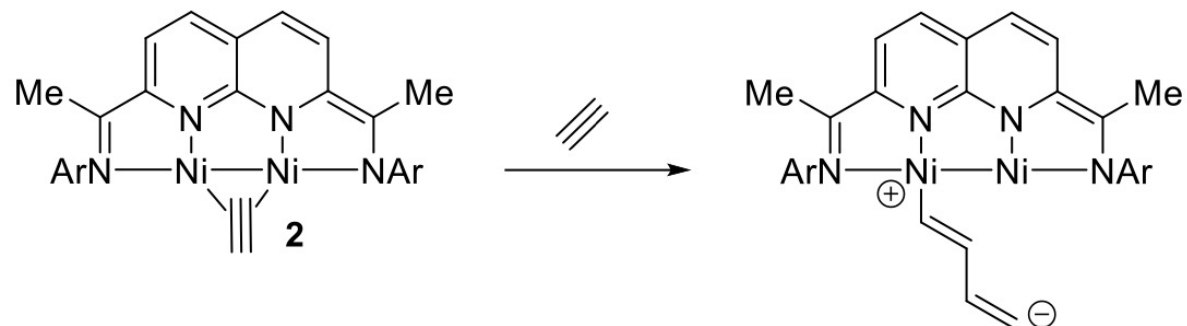
1 → 2/3 spin-state intersystem crossing



Metallacyclopentadiene

② Formation of metallacyclopentadiene

Stepwise zwitterionic and diradical pathway → unfavored

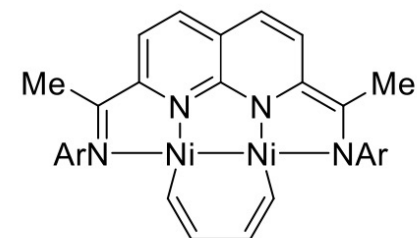


$\Delta G = 36.6$ (singlet)

$\Delta G = 30.7$ (triplet)

$\Delta G = 40.6$ (quintet)

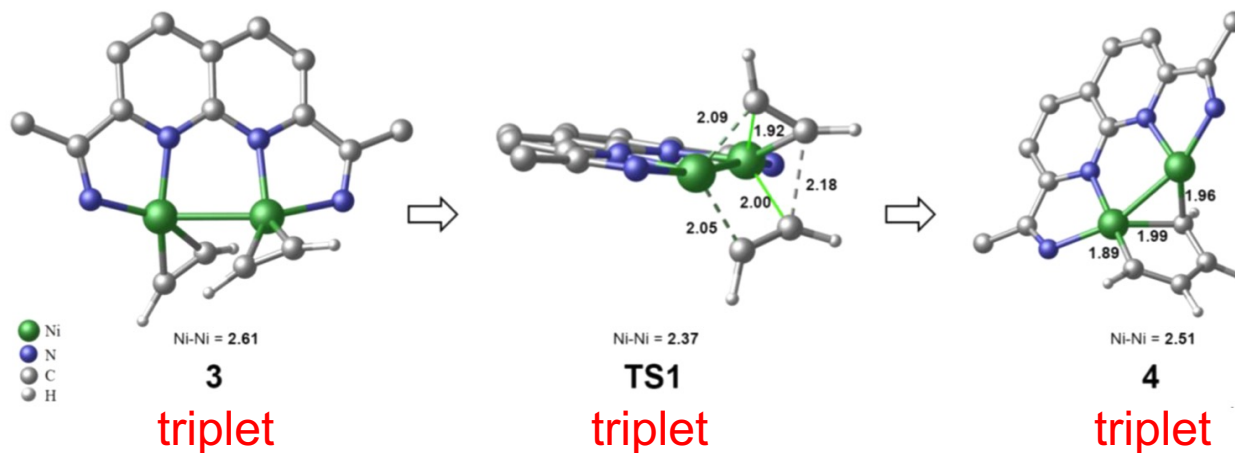
Bimetallacyclohexadiene intermediate → unstable



15.9 kcal/mol (singlet)

unstable on triplet-spin surface
unstable on quintet-spin surface

One-step oxidative coupling

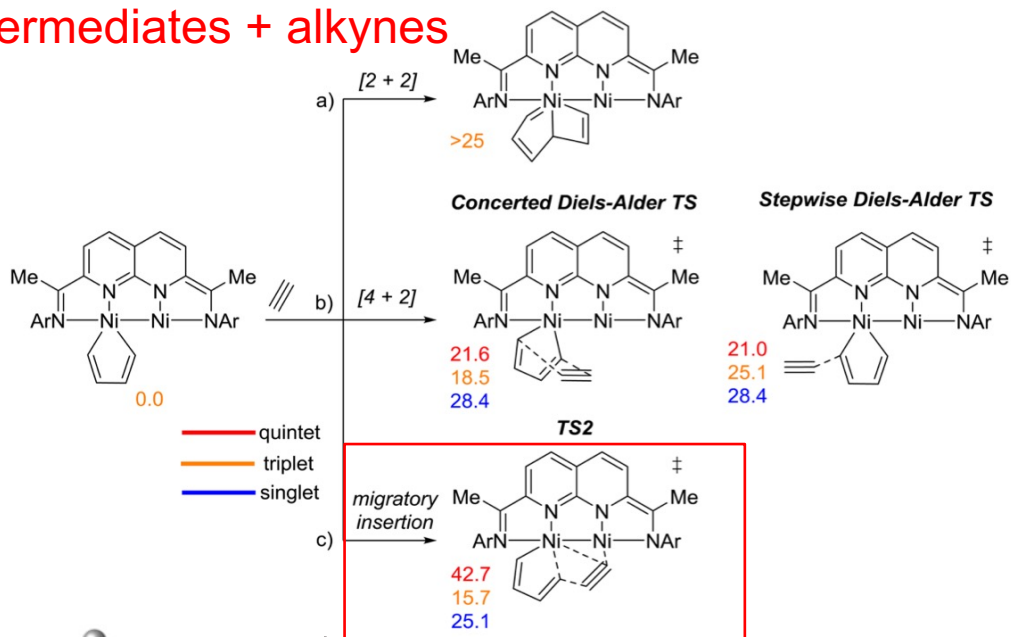
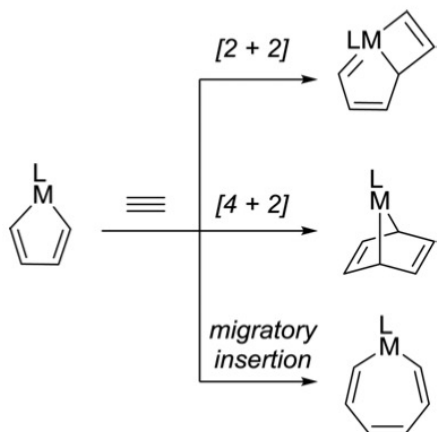


← observed in stoichiometric reaction in the previous study

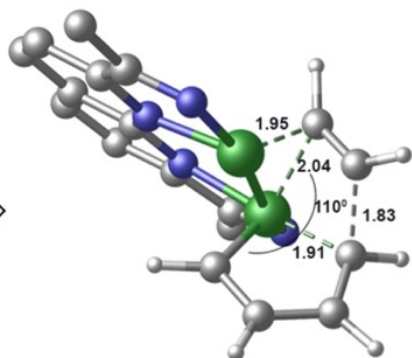
Reaction with the third alkyne

③ Metallacyclopentadiene intermediates + alkynes

3 proposed mechanisms

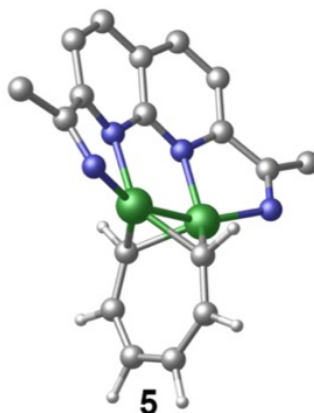


4 →

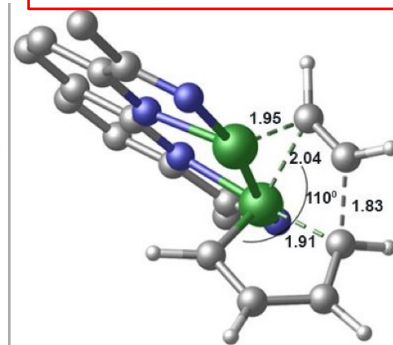


TS2

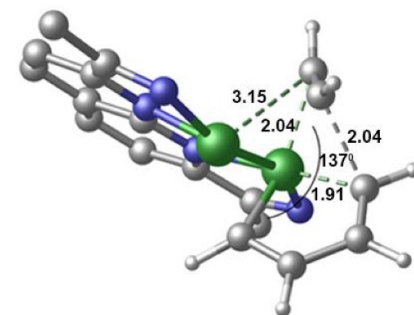
→



5



TS2 cis

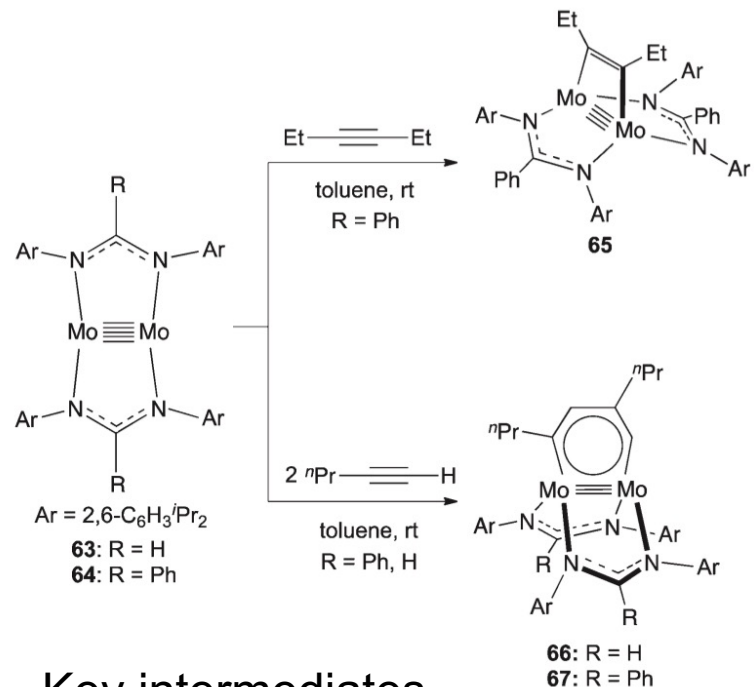
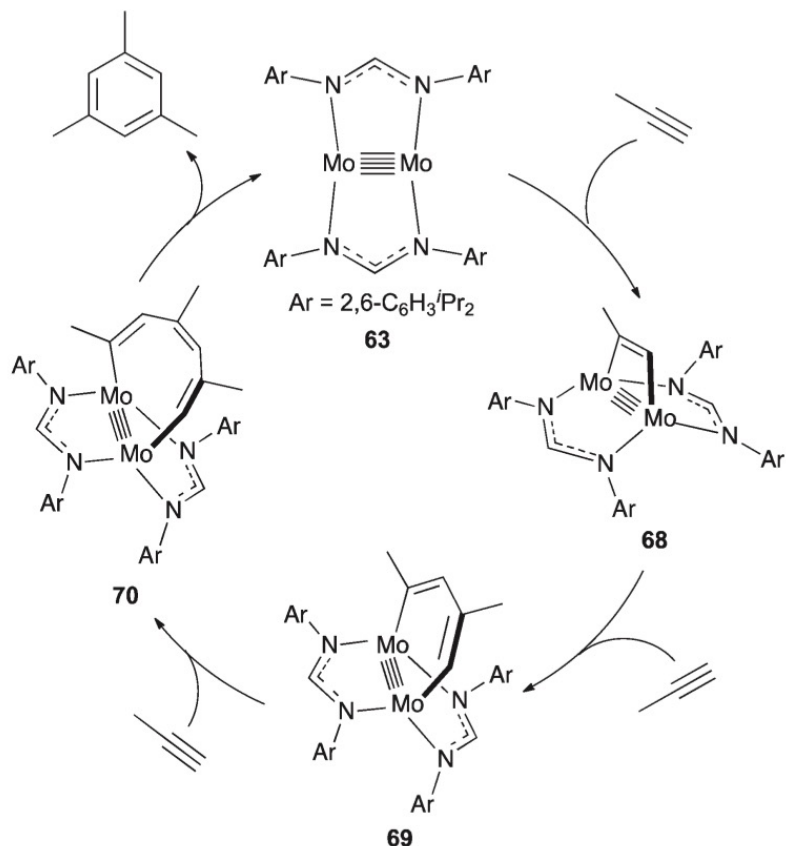


TS2 trans

6.3 kcal/mol higher

Other cyclootrimerization

Tsai reported



Key intermediates

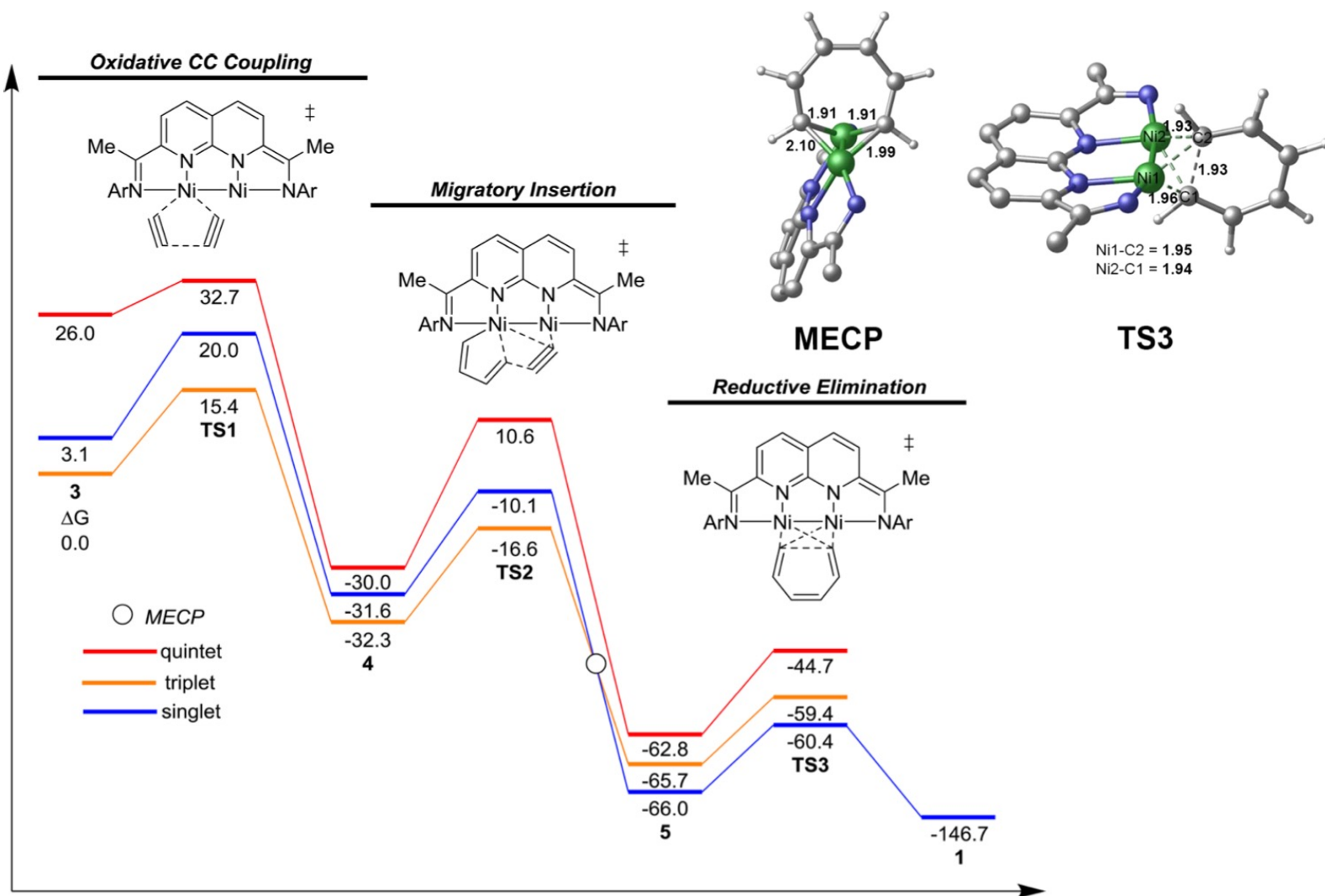
65 : [2+2+] cycloaddition

66 : [2+2+2] cycloaddition
dimetallacyclopentadiene

- Dinuclear molybdenum complexes
- 1, 3, 5-trisubstituted arene
- Different cycloheptatriene intermediates

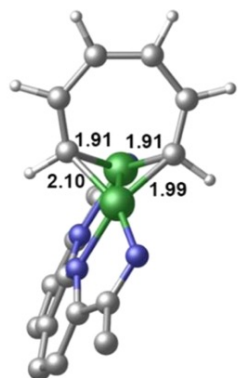
Mashima, K. *et al.*, *Dalton Trans.* **2016**, 45, 17072.
Tsai, Y. C. *et al.*, *Angew. Chem., Int. Ed.* **2012**, 51, 10342.

Outline of the cyclotrimerization

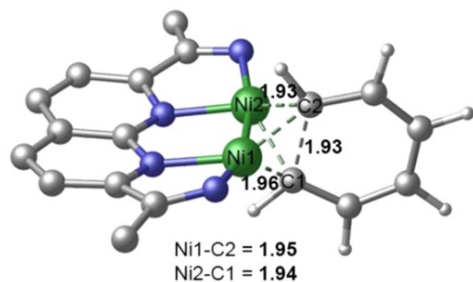


Cyclotrimerization selectivity

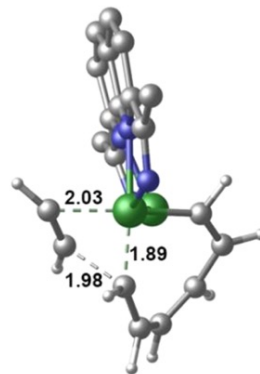
cyclotrimerization vs cyclotetramerization selectivity



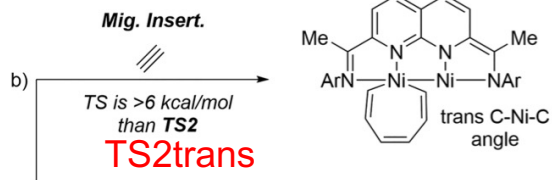
MECP



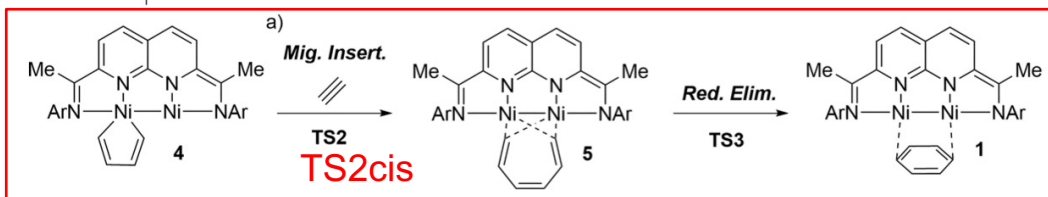
TS3



TS4



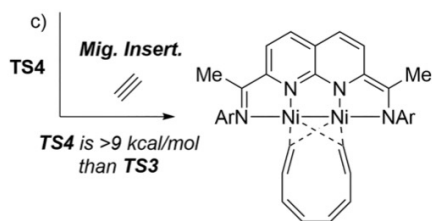
b) Mononuclear Ni complexes favors TS of **trans**.
→ Migratory insertion instead of reductive elimination occurs to form to **metallacyclononatetraene**.



This dinickel complex favors TS of **cis** (4→5).

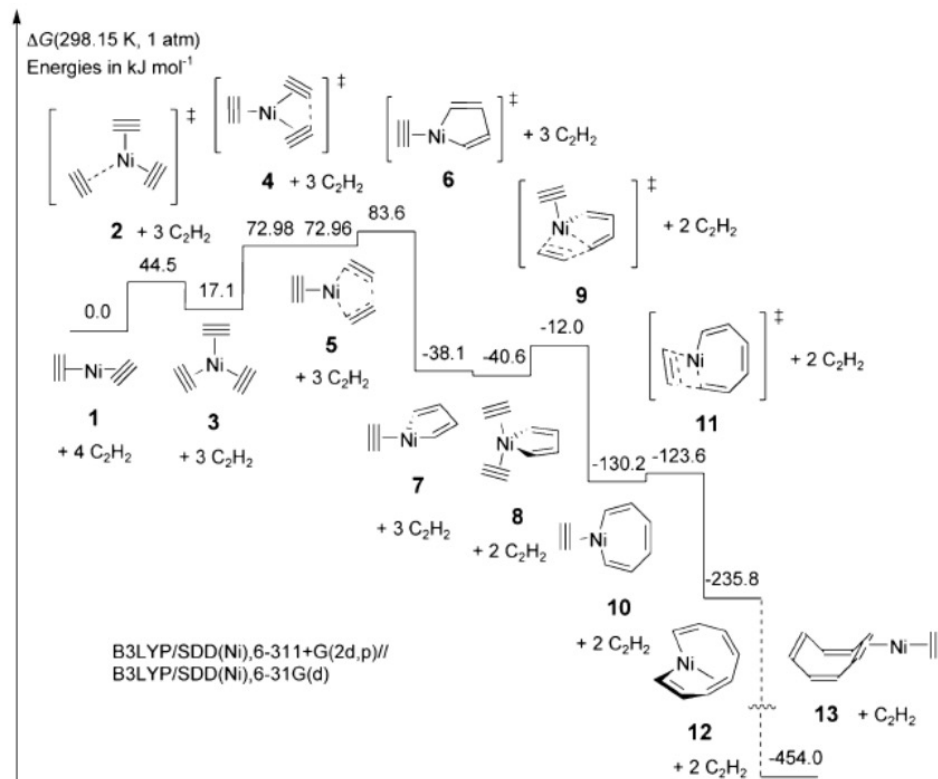
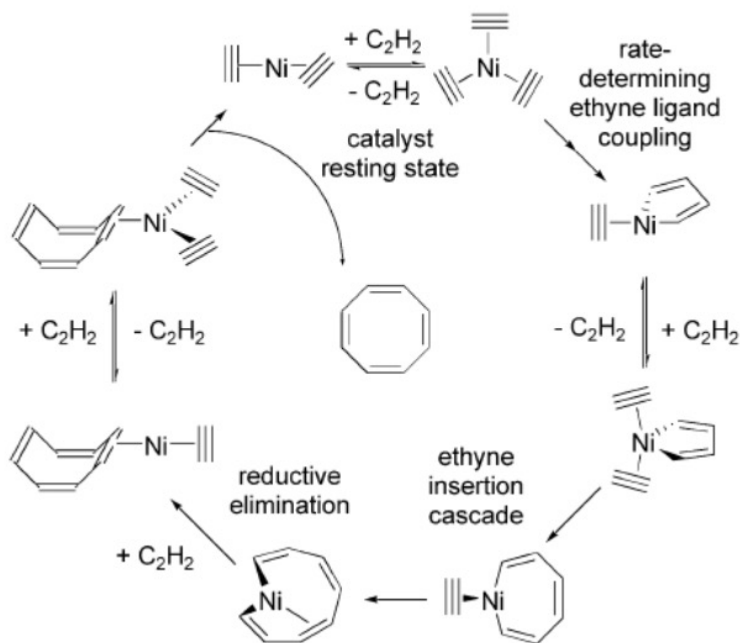
Reductive elimination is more favorable than migratory insertion (5→1).

→ cyclotrimerization selectivity



Mononuclear Ni-cyclotetramerization

Reppe reported

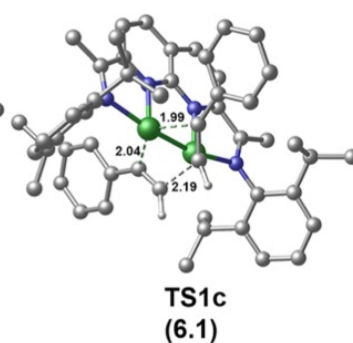
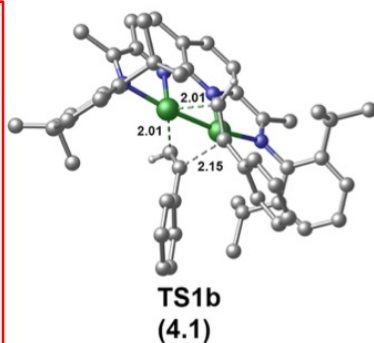
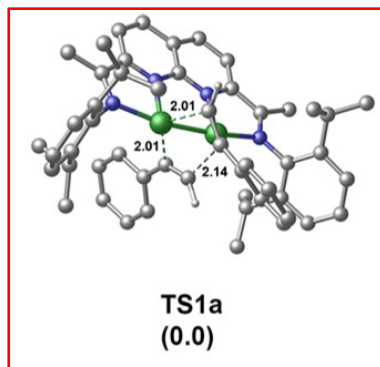


- Mononuclear Ni-catalyzed cyclotetramerization
- Favorable **trans** metallacycloheptatriene intermediates
- Another migratory insertion → **metallacyclononatetraene**

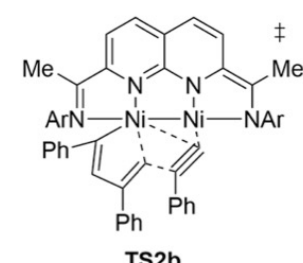
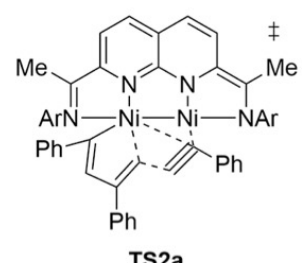
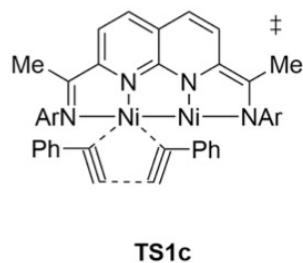
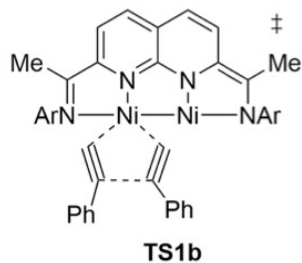
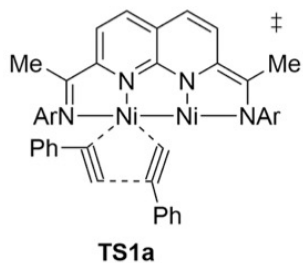
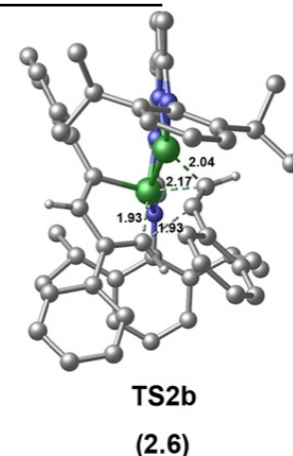
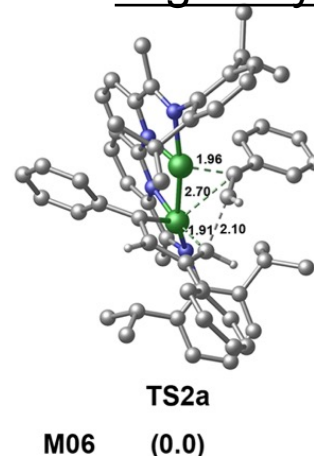
Regioselectivity

regioselectivity controlled by **TS1** and **TS2**

Oxidative CC coupling



Migratory insertion



Lower by 1-3 kcal/mol

↓
1, 2, 4-isomer
major products

↓
1, 3, 5-isomer
minor products

Short summary

- A unique spin crossover mechanism
nonclassical bridging metallacyclopentadiene and
metallacycloheptatriene intermediates
- Cyclotrimerization selectivity
the metallacycloheptatriene of cis configuration
- Regioselectivity
Oxidative C-C coupling TS
& migratory insertion TS to the metallacycloheptatriene
intermediate

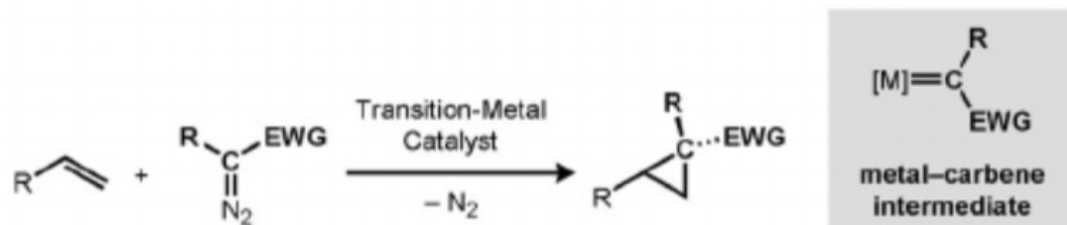
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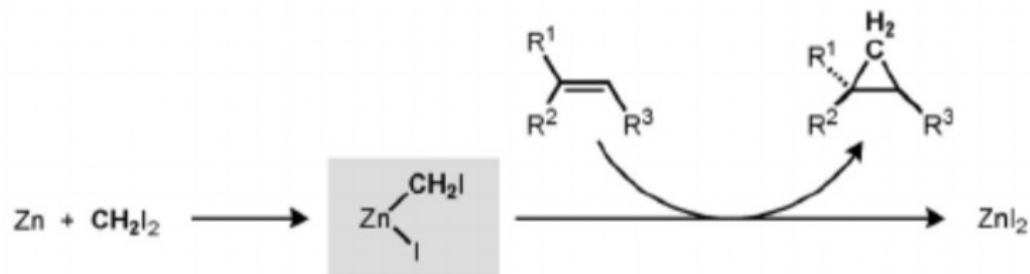
Cyclopropanation

Alkene + Carbene \rightarrow Cyclopropane

(a) Catalytic Redox-Neutral Cyclopropanations



(b) Simmons–Smith Cyclopropanations



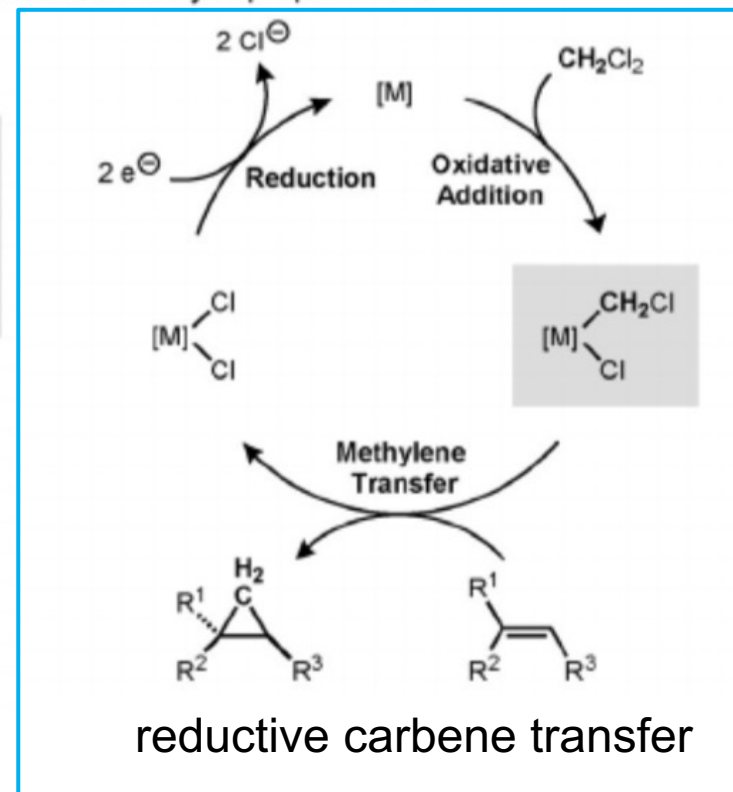
(a) Diazoalkane : requirement of EWG substituents

\rightarrow diazoacetates ...

(b) Low generality

(c) **This work : reductive carbene transformations from CH₂Cl₂, [M] = [i^{Pr}NDI]Ni₂(C₆H₆)**

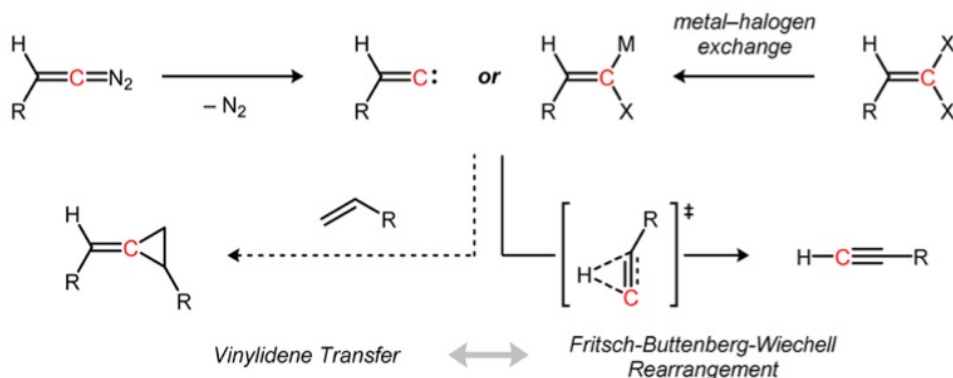
(c) Catalytic Reductive Cyclopropanations



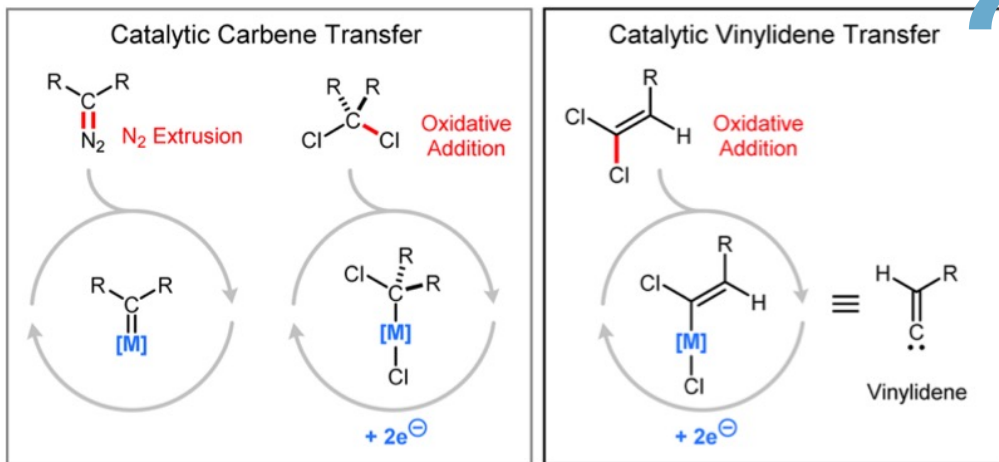
Zhou, Y. and Uyeda, C. *Angew. Chem. Int. Ed.* **2016**, 55,

Vinylidene transfer

Vinylidenes as Reactive Intermediates

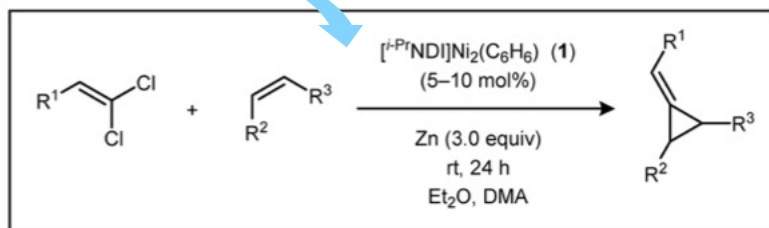


For vinylidenes possessing a β -hydrogen, FBW rearrangement is the dominant reaction pathway



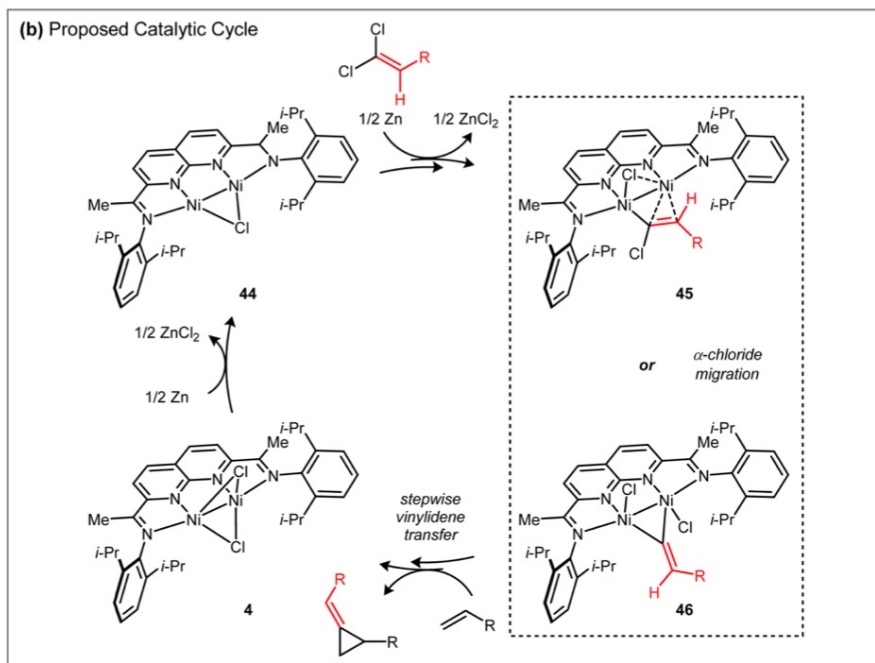
Reductive vinylidene transfer

Vinylidene transfer vs Fritsch-Buttenberg-Wiechell rearrangements



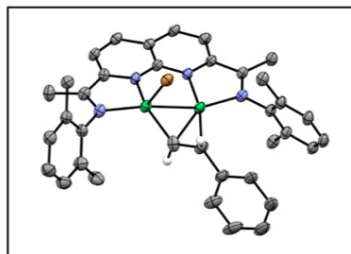
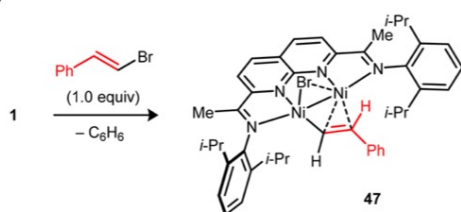
- ✓ No FBW rearrangement
- ✓ No vinylidene transfer was observed using mononickel complexes bearing related N-donor ligands.

Mechanism and dinuclear effects



- Reversible reduction of 4 are exploited to close the catalytic cycle by using Zn as a reductant.

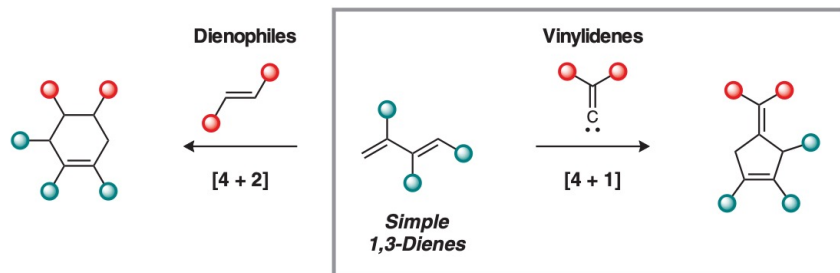
(c) Structural Model for the Oxidative Addition Product



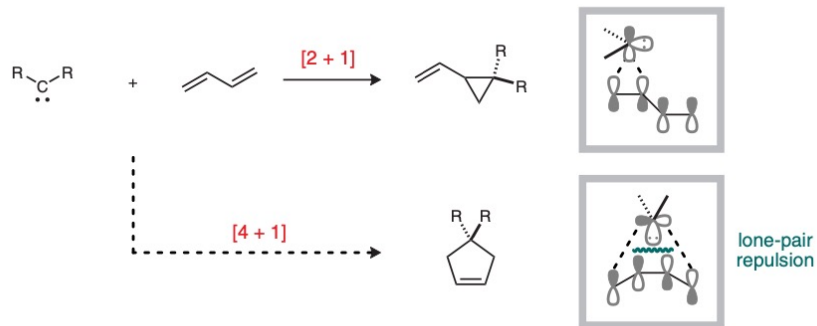
- 47 : η^2 – coordination of the alkenyl system to the second Ni
 \rightarrow β -hydrogen constrained, no FBW rearrangement

Catalytic [4+1]-cycloaddition

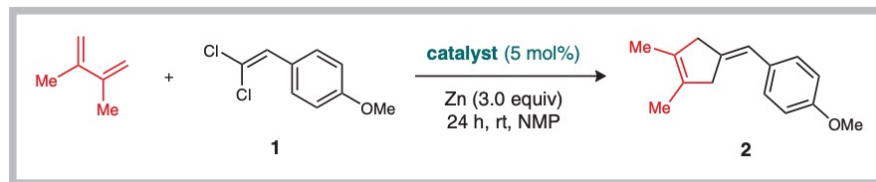
A Cycloaddition Methods Using 1,3-Dienes



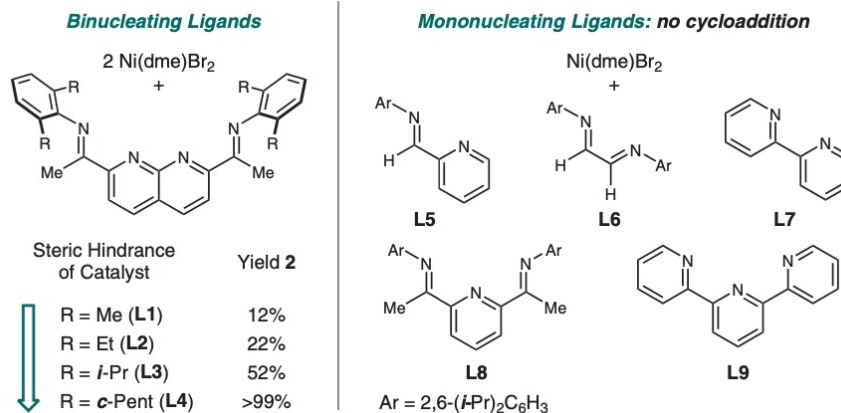
B [4 + 1]-Cycloadditions are Disfavored for Reactions of Carbenes with 1,3-Dienes



C A Dinickel-Catalyzed [4 + 1]-Cycloaddition of Vinylidenes and Dienes

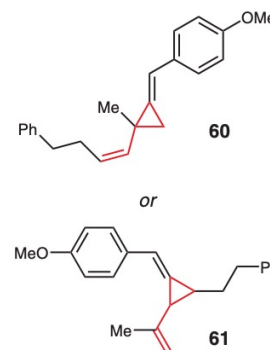
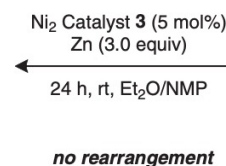
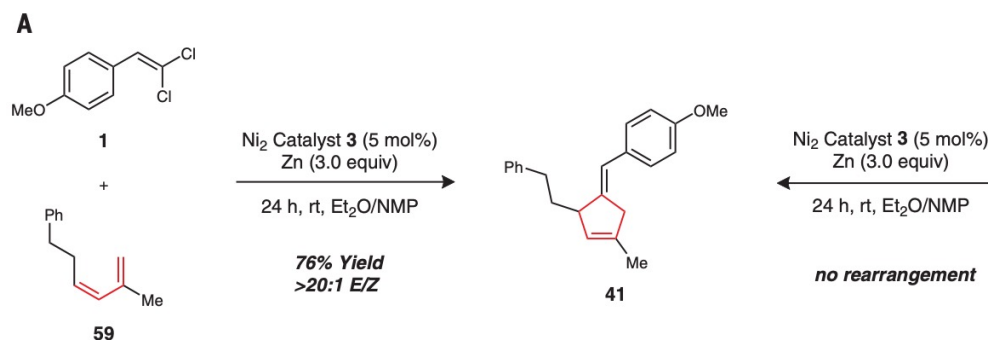
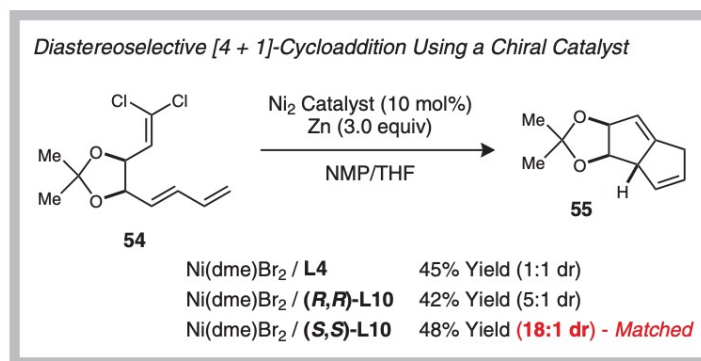
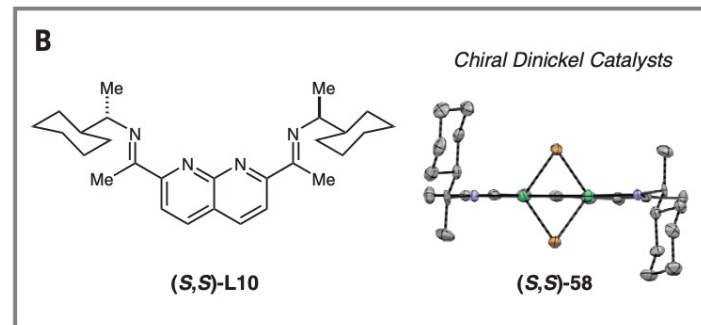


- A : 1, 3-dienes + vinylidene from 1,1-dichloroalkenes [4+1]-cycloaddition **this work**
- B : Challenging synthesis of five-membered rings (background)
- C : dinickel catalysts L4 with bulky NDI ligands afforded the products in the highest yield.

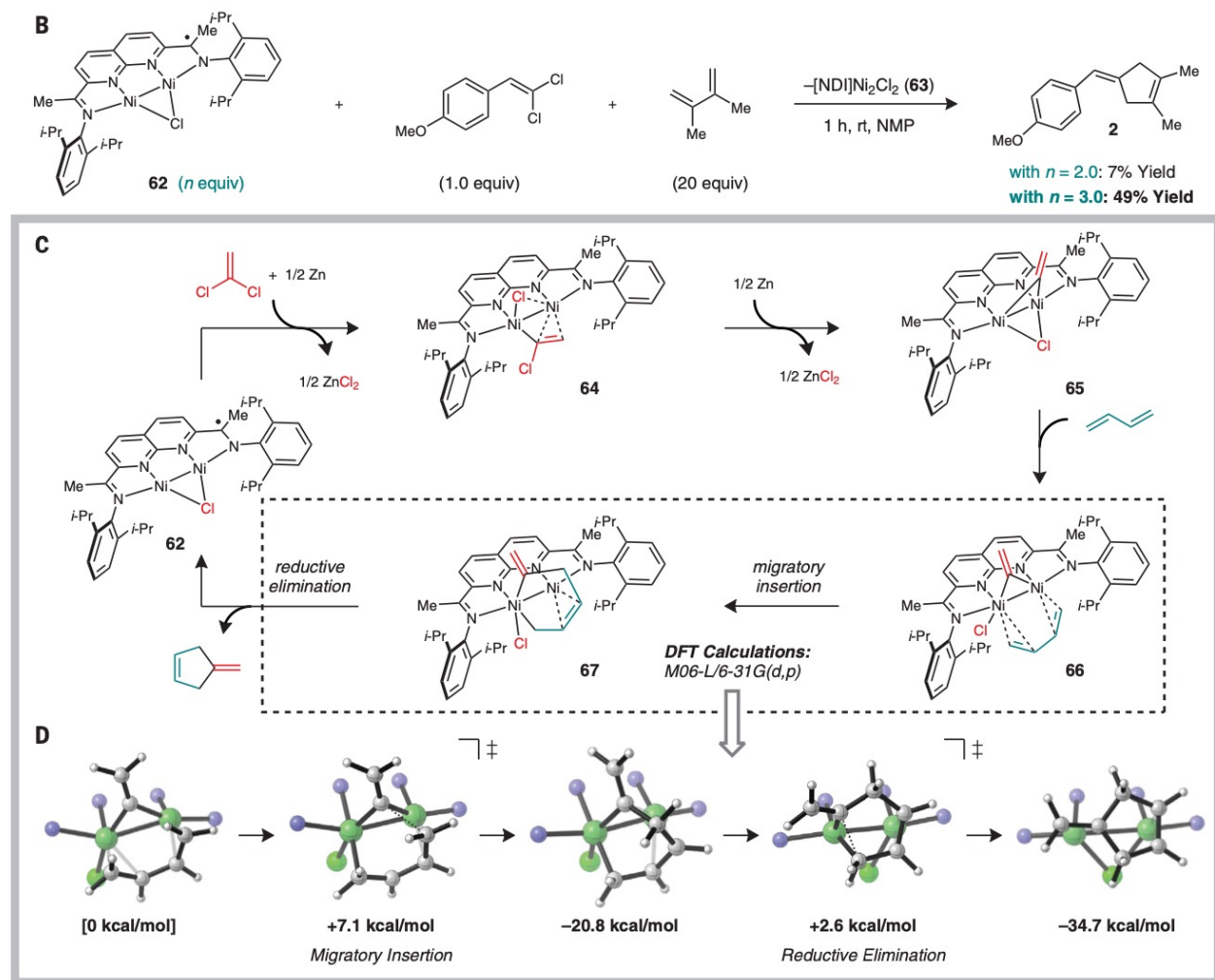


Mechanism analysis

- B : Chiral dinickel catalysts (S, S)-L10 high diastereoselectivity
- A : A direct [4+1] cycloaddition or a tandem [2+1] cycloaddition followed by 1,3-rearrangement



Mechanism and dinuclear effects



- Proposed mechanism
- Ni_2 cooperatively stabilize π systems in the diene and vinylidene

Fig. 4. Mechanistic investigations. (A) Distinguishing between direct [4 + 1]-cycloaddition and tandem [2 + 1]-cycloaddition/1,3-rearrangement mechanisms. (B) Stoichiometric [4 + 1]-cycloaddition using an isolable low-valent [NDI] Ni_2Cl complex. (C) Proposed catalytic mechanism. (D) DFT models for the stepwise migratory insertion–reductive elimination pathway. Energies are relative to that of **66**, and all structures are fully optimized at the M06-L/6-31G(d,p) level of DFT ($S = 1/2$ spin state). ‡Transition state.

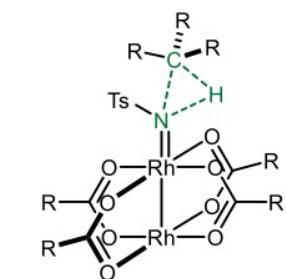
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C (sp²) – H amination

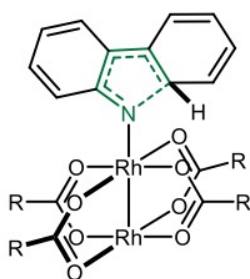
Rh₂ Catalysis

C(sp³)–H Activation



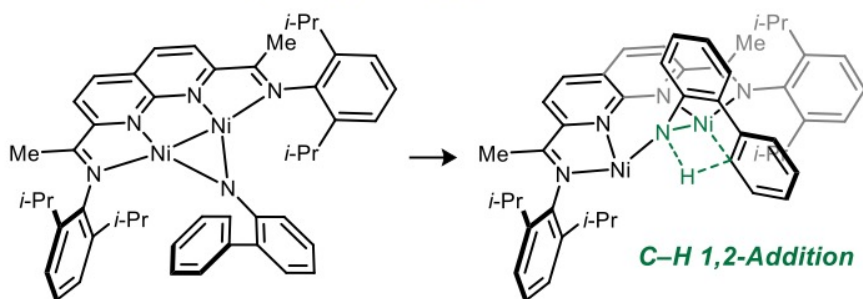
Concerted C–H Insertion

C(sp²)–H Activation

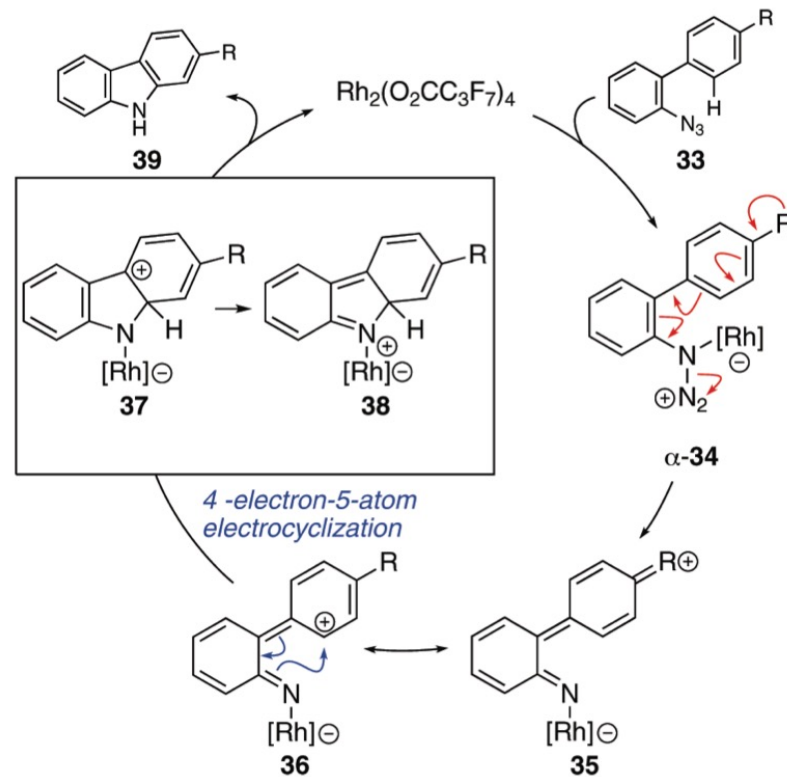


Electrocyclization/1,2-Shift

Ni₂ Catalysis: C(sp²)–H Activation



C–H 1,2-Addition



Electrocyclization / 1, 2-shift

C (sp²) – H amination

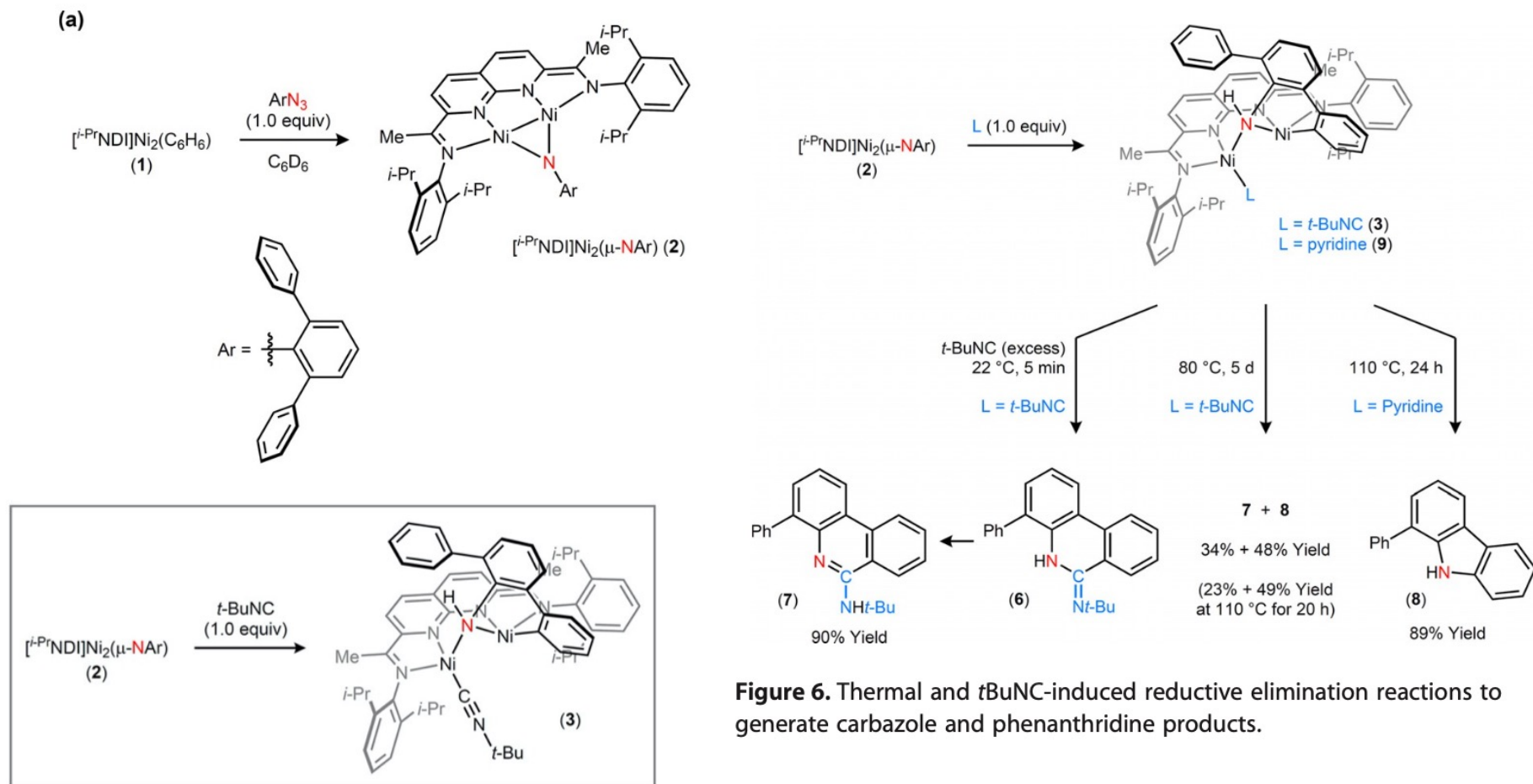
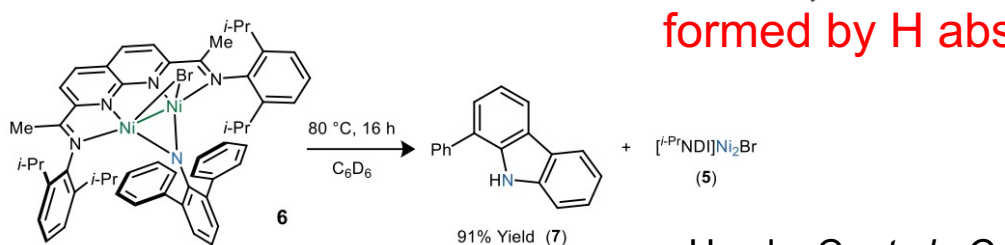
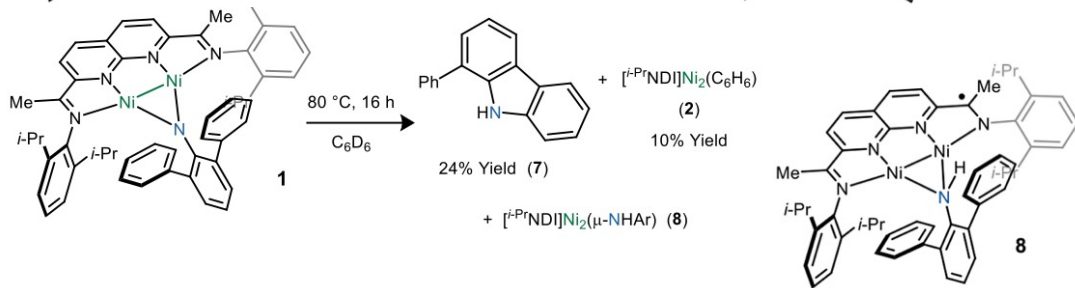
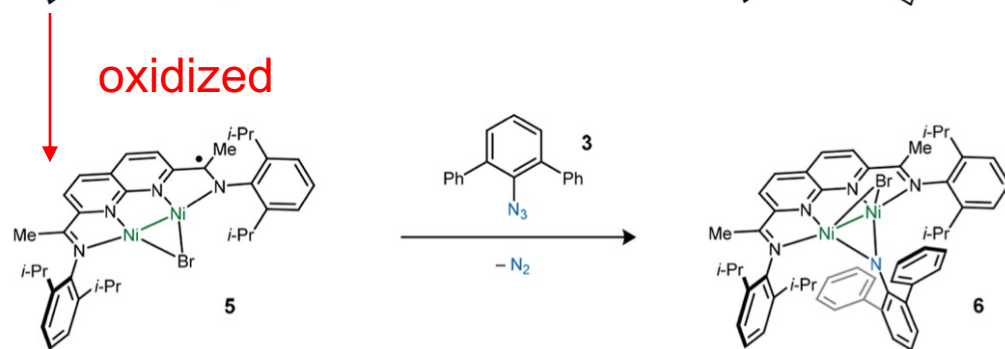
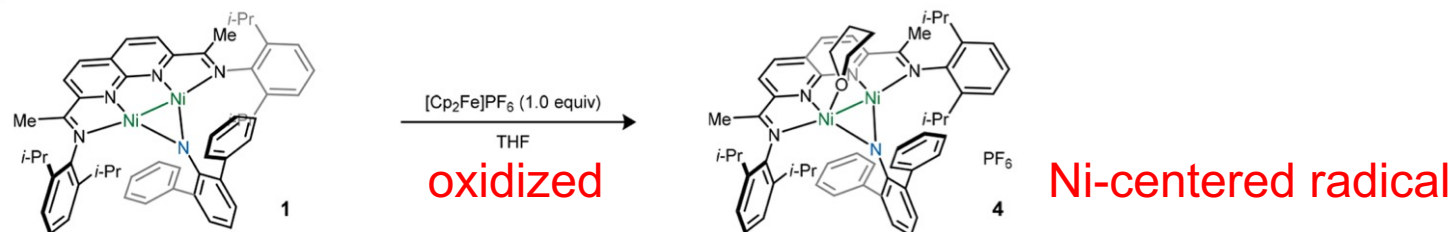


Figure 6. Thermal and *t*BuNC-induced reductive elimination reactions to generate carbazole and phenanthridine products.

C-H bond activated by addition of an exogenous ligand
 → C-N reductive elimination

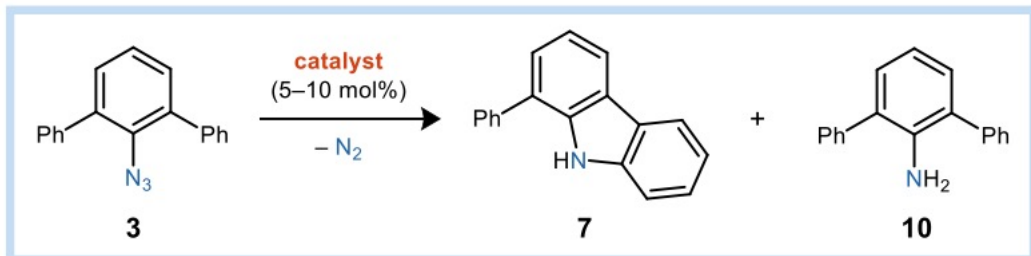
Oxidation states of imido complexes



formed by H abstraction

Oxidized (NDI) Ni_2 complexes may serve as more viable platforms for catalytic C-H amination.

Catalytic C-H amination reactions



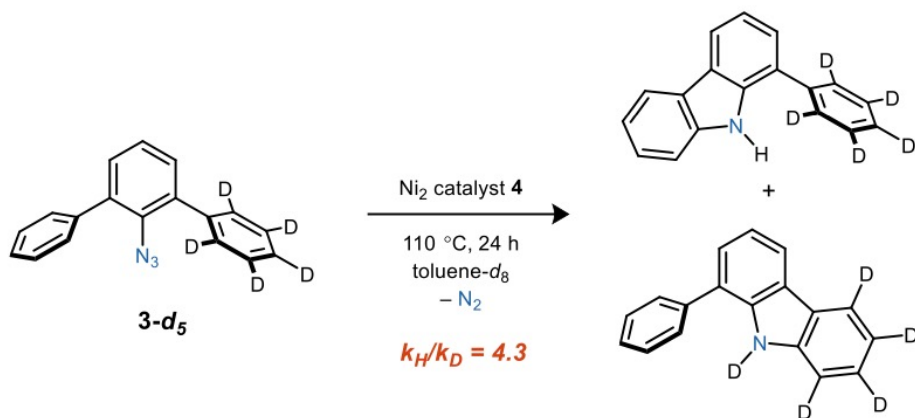
entry	catalyst	yield (%)	
		7	10
1	$Ni_2(\mu-NAr)$ 1	39	33
2	$Ni_2(\mu-NHAr)$ 8	44	39
3	$Ni_2(\mu-Br)$ 5	77	16
4	$[Ni_2(\mu-NAr)(thf)]^+$ 4	89	6
5 ^b	$[Ni_2(\mu-NAr)(thf)]^+$ 4	96	<2

^aReaction conditions unless stated otherwise: 10 mol % catalyst loading at 80 °C for 72 h. Yields of **7** and **10** were determined by 1H NMR integration against an internal standard. ^bReaction conditions: 5 mol % catalyst loading at 110 °C for 24 h.

- **8** → **1** via H atom abstraction by amides to generate free aniline **10**
- **5** : Generation of $(NDI)Ni_2Br_2$ by disproportionation is a limiting factor.
- **4** : halide-free cationic imido complex
→ highest yield

Mechanism analysis

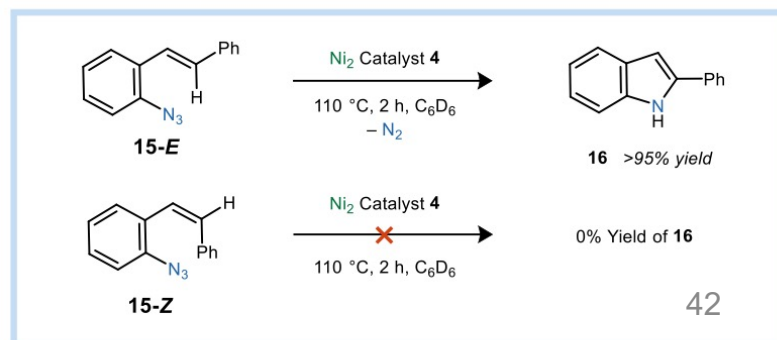
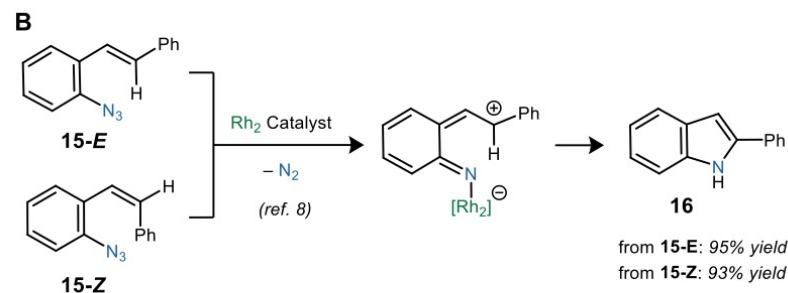
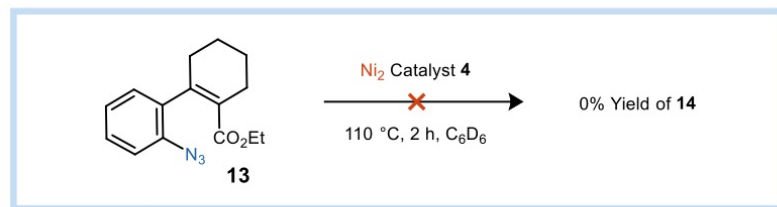
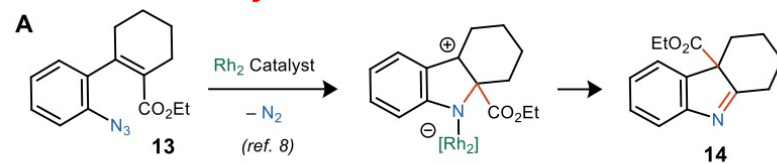
Kinetic isotope effect



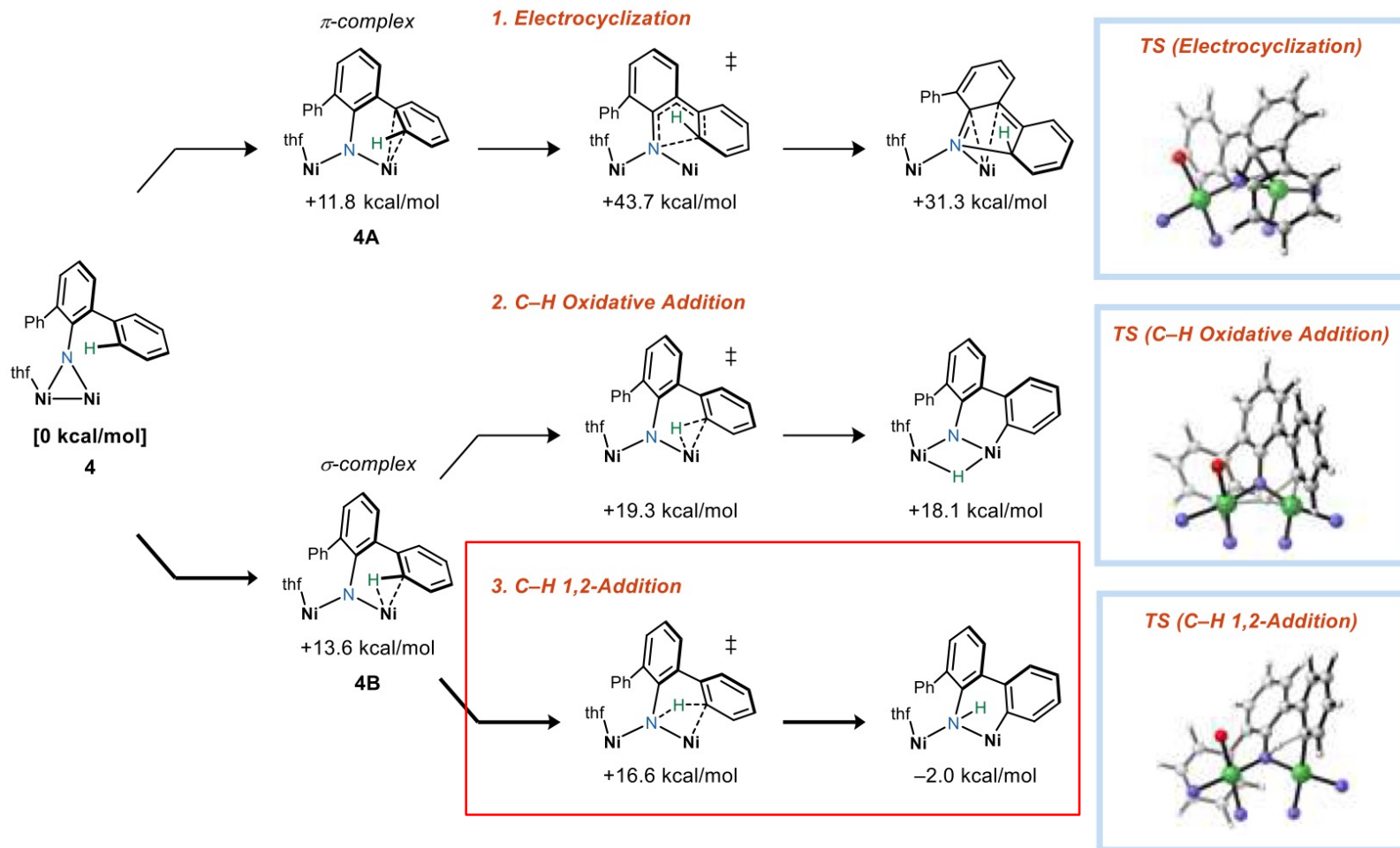
- KIE \rightarrow C-H cleavage is slow.
- Inaccessibility of an electrocyclization mechanism
- A – The ester blocks the position of C(sp²)-H activation
- B – E / Z difference of C-H bond orientations

Uyeda, C. *et al.*, *Organometallics* **2020**, 39, 3794.

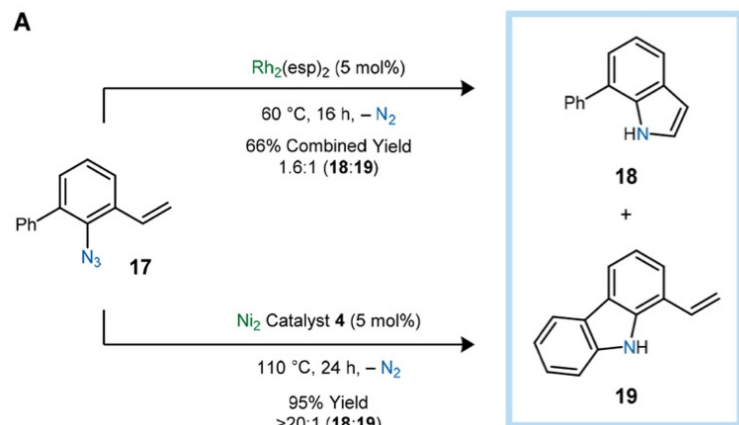
Electrocyclization or 1, 2-addition



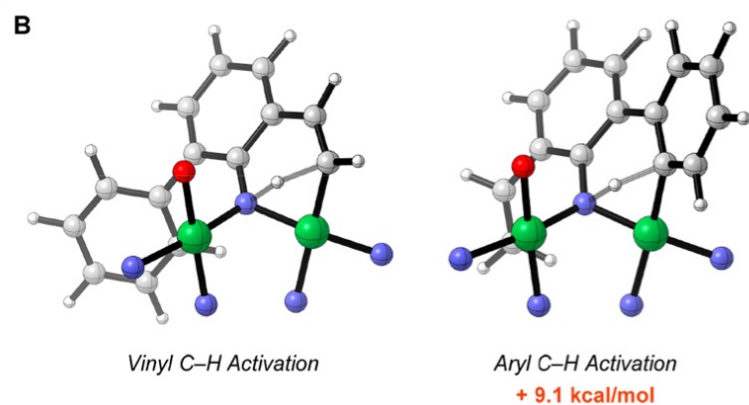
DFT models



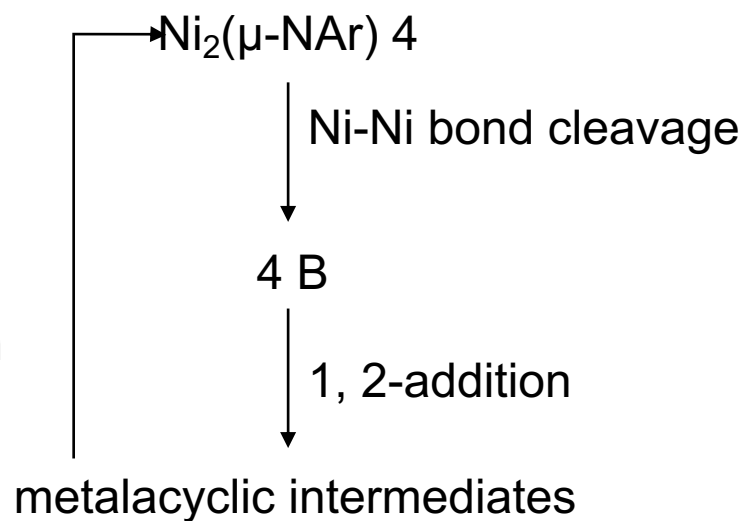
C (sp²) – H bond chemoselectivity



Catalytic cycle



C–N
reductive
amination



High selective nitrene insertions into
olefinic C–H bonds

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3. Summary

Summary

- NDI ligands supports coordinately unsaturated Ni-Ni bonds across a broad range of formal oxidation states.
- Ligand-centered redox activity enables various catalytic transformations.
- The electronic properties of M-M bonds are exploited for controlling regioselectivity.