

Dinickel Active Sites Supported by Redox-Active Ligands

Christopher Uyeda and Conner M. Farley*

Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

CONSPECTUS: Redox reactions that take place in enzymes and on the surfaces of heterogeneous catalysts often require active sites that contain multiple metals. By contrast, there are very few homogeneous catalysts with multinuclear active sites, and the field of organometallic chemistry continues to be dominated by the study of single metal systems. Multinuclear catalysts have the potential to display unique properties owing to their ability to cooperatively engage substrates. Furthermore, direct metal-to-metal covalent bonding can give rise to new electronic configurations that dramatically impact substrate binding and reactivity. In order to effectively capitalize on these features, it is necessary to consider strategies to avoid the dissociation of fragile metal–metal bonds in the course of a catalytic cycle. This Account describes one approach to accomplishing this goal using binucleating redox-active ligands.

In 2006, Chirik showed that pyridine–diimines (PDI) have sufficiently low-lying π^* levels that they can be redox non-innocent in low valent iron complexes. Extending this concept, we investigated a series of dinickel complexes supported by naphthyridine–diimine (NDI) ligands.

These complexes can promote a broad range of two-electron redox processes in which the NDI ligand manages electron equivalents, while the metals remain in a Ni(I)–Ni(I) state.

Using (NDI)Ni₂ catalysts, we have uncovered cases where having two metals in the active site addresses a problem in catalysis that had not been adequately solved using single-metal systems. For example, mononickel complexes are capable of stoichiometrically dimerizing aryl azides to form azoarenes but do not turn over due to strong product inhibition. By contrast, dinickel complexes are effective catalysts for this reaction and avoid this thermodynamic sink by binding to azoarenes in their higher energy *cis* form.

Dinickel complexes can also activate strong bonds through the cooperative action of both metals. Norbornadiene has a ring-strain energy that is similar to that of cyclopropane but is not prone to undergoing C–C oxidative addition with monometallic complexes. Using a (NDI)Ni₂ complex, norbornadiene undergoes rapid ring opening by oxidative addition of the vinyl and bridgehead carbons. An inspection of the resulting metallacycle reveals that it is stabilized through a network of secondary Ni– π interactions. This reactivity enabled the development of a catalytic carbonylative rearrangement to form fused bicyclic dienones.

These vignettes, and others described in this Account, highlight some of the implications of metal–metal bonding in promoting a challenging step in a catalytic cycle or adjusting the thermodynamic landscape of key intermediates. Given that our studies have focused nearly exclusively on the (NDI)Ni₂ system, we anticipate that many more such cases are left to be discovered as other transition metal combinations and ligand classes are explored.

KEY REFERENCES

- Pal, S.; Uyeda, C.* “Evaluating the Effect of Catalyst Nuclearity in Ni-Catalyzed Alkyne Cyclotrimerizations.” *J. Am. Chem. Soc.* **2015**, *137*, 8042–8045.¹ *The activity and selectivity of dinickel and mononickel catalysts are directly compared in alkyne cyclooligomerization reactions. Mechanistic studies provided insight into the structure and reactivity of dinickel metallacycles.*
- Hartline, D. R.; Zeller, M.; Uyeda, C.* “Catalytic Carbonylative Rearrangement of Norbornadiene via Dinuclear Carbon–Carbon Oxidative Addition” *J. Am. Chem. Soc.* **2017**, *139*, 13672–13675.² *Norbornadiene possesses a similar ring-strain energy to that of cyclopropane but is not known to undergo strain-induced C–C oxidative addition. A dinickel complex rapidly activates a C–C σ -bond of norbornadiene, and a catalytic carbonylative rearrangement is described.*
- Powers, I. G.; Andjaba, J. M.; Luo, X.; Mei, J.; Uyeda, C.* “Catalytic Azoarene Synthesis by a Dinuclear Ni Complex” *J. Am. Chem. Soc.* **2018**, *140*, 4110–4118.³ *A dinickel catalyst promotes the dimerization of aryl azides to form azoarenes. Mononickel catalysts are not competent as catalysts for this reaction, and the weak binding of azoarenes to the dinickel active site is critical to achieving turnover.*
- Zhou, Y.-Y.; Uyeda, C.* “Catalytic Reductive [4 + 1]-Cycloadditions of Vinylidenes and Dienes.” *Science* **2019**, *363*, 857–862.⁴ *Thermal pericyclic [4 + 1]-cycloadditions suffer from high electronic barriers due to unfavorable filled–filled orbital interactions that develop in the transition state. Dinickel catalysts can promote [4 + 1]-cycloadditions of 1,3-dienes and vinylidenes through a stepwise organometallic pathway.*

1. Introduction

Cotton's seminal work on the electronic structure of $\text{Re}_2\text{Cl}_8^{2-}$ inspired decades of research aimed at understanding the nature of metal-to-metal covalent bonding.⁵ Unsupported metal–metal bonds can form spontaneously when it is electronically favorable to do so. However, a more reliable synthetic approach is to use binucleating ligands that contain adjacent binding sites with donors suited to the metals and oxidation states of interest. Numerous examples of homobimetallic and heterobimetallic complexes have now been prepared, and key electronic features of metal–metal bonding have been illuminated through a productive interplay of synthetic, spectroscopic, and computational approaches.⁶

Considering the large number of metal–metal bonded complexes that are now available, it is striking that so few of them have made it into the repertoire of catalysts used by synthetic organic chemists. Many dinuclear complexes have been shown to display catalytic activity. However, the benefits that they offer over existing catalysts, in terms of improved activity or selectivity, often do not justify their added complexity. Cases are fewer still where the involvement of a metal–metal bond in a catalytic cycle enables an entirely new transformation that cannot be carried out with any known mononuclear catalyst.⁷

Another consideration is that when a dinuclear complex is tested as a catalyst, there is always uncertainty about whether the metal–metal bond is preserved under turnover conditions. For example, a dinuclear $[\text{Pd}(\text{I})/(\text{II})]_2$ cycle could be an interesting alternative to canonical mononuclear $\text{Pd}(0)/(\text{II})$ cycles for reactions such as cross-coupling. However, in most cases where $\text{Pd}(\text{I})$ dimers have been found to promote these reactions, it is thought that they act as pre-catalysts for on-cycle monopalladium species.⁸ There are only a few studies that provide clear experimental support for a $[\text{Pd}(\text{I})]_2$ ⁹ or a $[\text{Pd}(\text{III})]_2$ ¹⁰ species being a true catalytic intermediate (Figure 1A). In

general, Pd–Pd and other group 10 M–M σ -bonds are only stable in odd-electron oxidation states. Thus, any proposed catalytic process that involves redox changes would inevitably require considering the speciation between dinuclear and mononuclear forms.

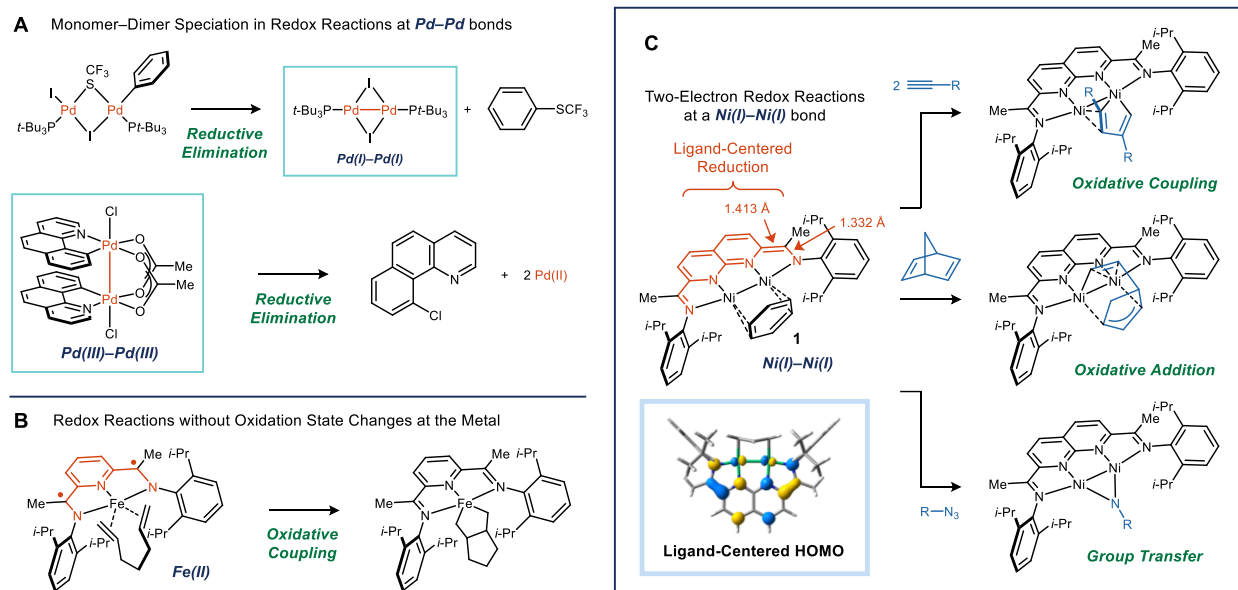


Figure 1. (A) Dinuclear redox reactions often entail the formation or cleavage of a metal–metal bond. (B) Redox active ligands can be used to carry out a two-electron oxidative coupling reactions without perturbing the metal oxidation state. (C) Dinuclear oxidative coupling, oxidative addition, and group transfer reactions at intact Ni(I)–Ni(I) bonds using redox active ligands.

In 2006, Chirik demonstrated that pyridine–diimine (PDI) ligands possess sufficiently low-lying π^* levels that they can be redox non-innocent in reduced Fe complexes (Figure 1B).¹¹ This finding led to the development of Fe-catalyzed cycloaddition reactions where Fe remains in a +2 oxidation state, while the ligand traverses 0 and –2 charge states during the key oxidative coupling and reductive elimination steps.¹²

We wondered whether this concept could prove useful in the design of multinuclear redox processes where a M–M bond would remain intact during the entirety of a catalytic cycle (Figure 1C). In principle, if the responsibility for storing and releasing electrons could be managed by the

ligand,¹³ there should be minimal electronic disruption of the M–M σ -bond during a two-electron reaction. This Account summarizes our exploration of this hypothesis using Ni(I)–Ni(I) bonds supported by redox-active naphthyridine–diimine (NDI) ligands.

2. Synthesis and Electronic Structure of (NDI)Ni₂ Complexes

Our initial efforts to design binucleating redox-active ligands focused on the use of 1,8-naphthyridine heterocycles, which have been used in other ligands to generate well-defined dinuclear complexes.¹⁴ Upon combining *i*-PrNDI (1 equiv) and Ni(COD)₂ (2 equiv) in C₆H₆, the dark brown, diamagnetic (*i*-PrNDI)Ni₂(C₆H₆) complex (**1**) is formed in quantitative yield.¹⁵ The use of an arene solvent is critical for assembling the Ni–Ni bond, and its exclusion during synthesis causes only mononickel complexes to be generated. The weakly bound C₆H₆ ligand rotates rapidly on the ¹H NMR timescale, and it can be readily exchanged with various substrates of interest.

From the bond metrics of the NDI ligand in **1**, it is evident that the π -system is reduced by two electrons (Figure 1C). Additionally, the bond length perturbations are symmetrically distributed over the two halves of the ligand, consistent with the redox-active orbital being fully delocalized. A spectroscopic signature of ligand-centered reduction is a prominent band in the NIR region (λ_{max} = 1040 nm, ϵ = 40,000 cm^{−1} M^{−1}), which is assigned to a ligand-based π – π^* transition. According to DFT models, the HOMO is predominantly ligand-centered but exhibits some mixing with a Ni–Ni π^* orbital. Our collective experimental and computational data are consistent with a $\sigma^2\pi^4\pi^{*4}\delta^4\delta^{*4}$ description for the Ni–Ni interaction, resulting in a net bond order of one.

The (*i*-PrNDI)Ni₂(C₆H₆) complex (**1**) engages in a broad scope of two-electron redox reactions by coupling reactivity at the Ni–Ni bond with electron transfer from the reduced NDI ligand. In the following section, we describe our investigations of stoichiometric oxidative coupling, oxidative addition, and group transfer reactions. Additionally, we highlight cases where the presence of two

metals is beneficial for catalysis, either by offering a rate or selectivity advantage over comparable mononuclear catalysts or by enabling new reactivity.

3. Stoichiometric Reactivity and Catalysis

3.1 Dinuclear Oxidative Coupling

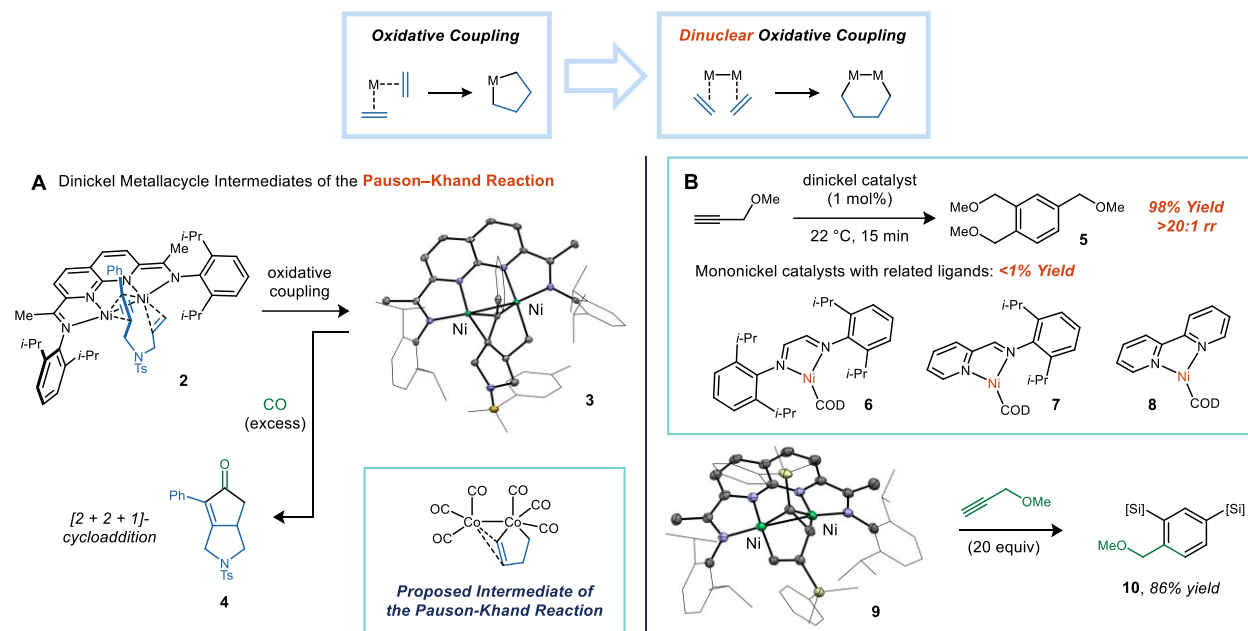


Figure 2. Dinuclear Oxidative Coupling Reactions. (A) A functional model for the dinuclear intermediates of the Pauson–Khand reaction using a Ni–Ni site as a surrogate for $\text{Co}_2(\text{CO})_8$. (B) Comparing the activity and selectivity of alkyne cyclooligomerization reactions using dinickel and mononickel catalysts.

Thermal cycloaddition reactions, such as Diels–Alder reactions, hold high synthetic value in organic chemistry but often require electronically polarized substrates to lower their activation barriers. Low-valent transition metals are capable of coordinating to non-polar π -systems and mediating oxidative coupling reactions to generate metallacycles.¹⁶ This process provides the mechanistic basis for metal-catalyzed cycloaddition reactions, which are not constrained by the electronic considerations of their thermal pericyclic counterparts.¹⁷ A prototypical example is the

Pauson–Khand reaction: a formal $[2 + 2 + 1]$ -cycloaddition of an alkyne, an alkene, and CO mediated by $\text{Co}_2(\text{CO})_8$.¹⁸ The accepted mechanism of the Pauson–Khand reaction is attributed to Magnus, who was seeking to rationalize the diastereoselectivity of an intramolecular variant of the reaction.¹⁹ The key step in his proposal was a dinuclear oxidative coupling step to generate a dicobaltacycle. Despite extensive mechanistic investigations of the Pauson–Khand reaction,²⁰ this putative metallacycle has eluded structural characterization. Kinetics studies suggest that it is a fleeting intermediate that undergoes fast and irreversible CO insertion (Figure 2A inset).

The Pauson–Khand reaction, being a rare example of an organometallic process that occurs at a metal–metal bond, captured our interest as we were initially exploring the chemistry of dinuclear Ni(I) (Figure 2A).²¹ Combining the (*i*-Pr^{NDI})Ni₂(C₆H₆) complex (**1**) with a model enyne yielded a transient alkyne adduct (**2**) that could be observed by ¹H NMR spectroscopy. This intermediate decays with clean first-order kinetics ($\Delta G^\ddagger = 22.7$ kcal/mol at 30 °C) to the product of alkyne–alkene oxidative coupling. The solid-state structure of this product (**3**) maps directly onto Magnus’s proposed Pauson–Khand intermediate and features a five-membered metallacycle with the alkenyl π -system engaged in an η^2 -interaction with the second Ni. When placed under an atmosphere of CO, complex **3** releases the $[2 + 2 + 1]$ -cycloaddition product (**4**) in high yield.

The finding that the (NDI)Ni₂ platform could mediate kinetically facile oxidative coupling reactions motivated us to consider whether a dinuclear active site could be exploited to achieve an improvement in the rate or selectivity of a catalytic cycloaddition.¹ To answer this question, we selected the cyclooligomerization of alkynes as a model reaction, because it was known to be promoted by Ni catalysts but with efficiencies and selectivities that were moderate and highly sensitive to catalyst structure (Figure 2B). Selecting a suitable set of mononickel complexes to serve as a comparison was a non-trivial consideration. Complexes containing bidentate N-donor

ligands were an appealing choice because they could be prepared in a low-valent form, featured donors that mirror those of NDI, and were known to perform oxidative coupling reactions.

Previously, tom Dieck showed that Ni complexes of N-donor ligands function as catalysts for the cyclooligomerization of ethyl propiolate, predominantly forming cyclooctatetraene products.²² We confirmed these results in our own studies. Catalysts **6–8** achieve high conversions of ethyl propiolate and form cyclooctatetraene regioisomers, along with a minor fraction of arenes. Interestingly, Ni₂ catalyst **1** exhibits a very different product profile. In addition to being more active than any of the mononickel catalysts, **1** yields arenes nearly exclusively with very little cyclooctatetraene formation. We observed the most striking differences when examining more electron-rich alkyl-substituted alkynes. Mononickel catalysts **6–8** exhibit little to no activity for the cyclotrimerization of methyl propargyl ether. By contrast, at 1 mol% loading, Ni₂ catalyst **1** affords the 1,2,4-substituted arene (**5**) in 98% yield within minutes at room temperature.

Using sufficiently hindered terminal alkynes, it is possible to arrest the catalytic process and gain insight into the intermediates of the cyclotrimerization reaction. PhMe₂SiCCH (2 equiv) undergoes a head-to-tail oxidative coupling with **1** to yield metallacycle **9**. DFT models suggest that the alternative regioisomers are disfavored due to steric interactions with the aryl substituents of the catalyst. The remaining mechanistic question is regarding the addition of the third alkyne equivalent. This step was examined computationally by optimizing stationary points for a concerted [4 + 2]-cycloaddition, a stepwise [2 + 2]-cycloaddition/ring-expansion, and a stepwise migratory insertion/C–C reductive elimination pathway.²³ The third mechanism was calculated to be the most energetically favorable, and it accurately reproduced the observed regioselectivity of the reaction.

3.2 Dinuclear Oxidative Addition

Oxidative addition is an elementary organometallic process that can be used to activate a strong, non-polar bond in the course of a catalytic transformation.²⁴ In 1955, Tipper described an oxidative addition of cyclopropane by PtCl₂ to generate a high-valent species²⁵ that was later assigned by Chatt as a platinacyclobutane.²⁶ Since this report, activation reactions of cyclopropanes have emerged as useful strategies to generate reactive three-carbon fragments that engage in myriad cycloaddition, isomerization, and rearrangement processes.²⁷ Cyclopropane ring-opening reactions commonly rely on polar activating substituents to enable heterolytic bond cleavage.²⁸ In this context, Louie reported a noteworthy rearrangement of electronically neutral vinylcyclopropanes to cyclopentenenes using Ni(0) catalysts bearing strongly σ -donating NHC ligands.²⁹

Activation Reactions of Three-Membered Rings. When vinylcyclopropane was added to solutions of (*i*-PrNDI)Ni₂(C₆H₆) (**1**) in C₆D₆, the oxidative addition product was not observed.³⁰ However, vinylcyclopropane was catalytically consumed to form cyclopentene (83% yield with 1 mol% **1**, 24 h, rt) (Figure 3A). The putative product of cyclopropane C–C oxidative addition does not build up in significant concentrations under turnover conditions, presumably due to the fast rate of C–C reductive elimination. Thus, in order to characterize the metallacyclic intermediate, it was necessary to modify the substrate to slow down reductive elimination. *N*-Tosyl vinylaziridine undergoes stoichiometric oxidative addition to generate azametallacycle **11**, which features an η^3 -coordinated allyl and an NTs group both occupying bridging positions between the two metals.

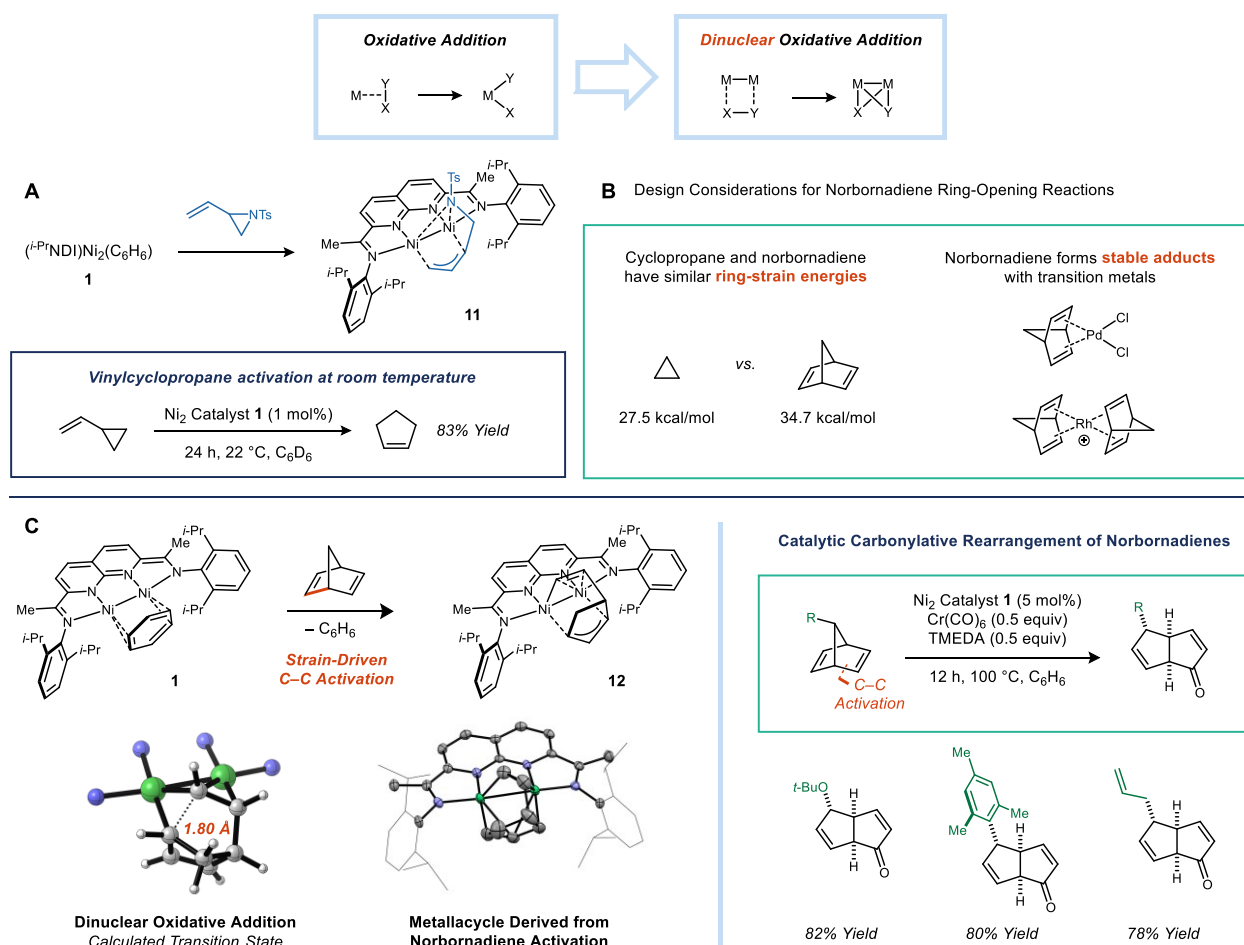


Figure 3. Dinuclear Oxidative Addition Reactions. (A) Catalytic and stoichiometric ring-opening reactions of vinylaziridines and vinylcyclopropanes. (B) Norbornadiene has a similar ring-strain energy to that of cyclopropane but does not readily undergo C–C oxidative addition. (C) Dinuclear oxidative addition of norbornadiene and catalytic carbonylative rearrangements.

Activation Reactions of Bicyclic Compounds. Norbornadiene (nbd) possesses a similar ring-strain energy to that of vinylcyclopropane³² but is not known to undergo similar C–C oxidative addition reactions (Figure 3B).³³ There are likely two factors that contribute to this divergence in reactivity. First, norbornadiene forms stable π -complexes with low-valent transition metals (e.g. $\text{PtCl}_2(\text{nbd})$).³⁴ Indeed, norbornadiene and related [2.2.2]-bicyclodienes have been employed as non-reactive supporting ligands in catalytic reactions.³⁵ Second, the alkenes of norbornadiene are

sufficiently activated by ring strain such that addition or coupling reactions of the π -bonds occur in preference to cleavage of the σ -bonds. One illustrative example is the reaction between $[\text{Ir}(\text{cod})\text{Cl}]_2$ and 2 equiv of norbornadiene to yield an Ir(III) metallacyclopentane.³⁶

The (*i*-PrNDI) $\text{Ni}_2(\text{C}_6\text{H}_6)$ complex (**1**) undergoes a stoichiometric reaction with norbornadiene to generate the oxidative addition product **12** (Figure 3C).² The intermediate diene adduct is not detectable even at partial conversions, indicating that the ligand substitution step is slower than C–C activation. DFT models are consistent with this observation. The calculated oxidative addition barrier is only 10.6 kcal/mol and is exothermic by 14.8 kcal/mol. An apparent driving force for this unusual reaction is the ability of the Ni_2 active site to form a network of stabilizing Ni– π interactions with the allyl and vinyl fragments. From an electron counting perspective, the ring-opened norbornadienyl fragment in **12** is functioning as an 8 e^- donor to the Ni–Ni bond. It is unlikely that a single metal center could geometrically or electronically support such a density of interactions.

Metallacycle **12** reacts with CO to generate a carbonylated product. The carbonylation proceeds with transposition of the allylic system, and the fused bicyclodienone is formed selectively over the alternative bridged isomer. This series of stoichiometric reactions could not be rendered catalytic using CO (g) due to strong inhibition of the catalyst by excess CO. However, turnover could be achieved using $\text{Cr}(\text{CO})_6$,³⁷ which slowly releases free CO at high temperatures. Under optimized conditions, several catalytic carbonylative rearrangements were carried out using 7-substituted norbornadienes as substrates.

3.3 Dinuclear Group Transfer

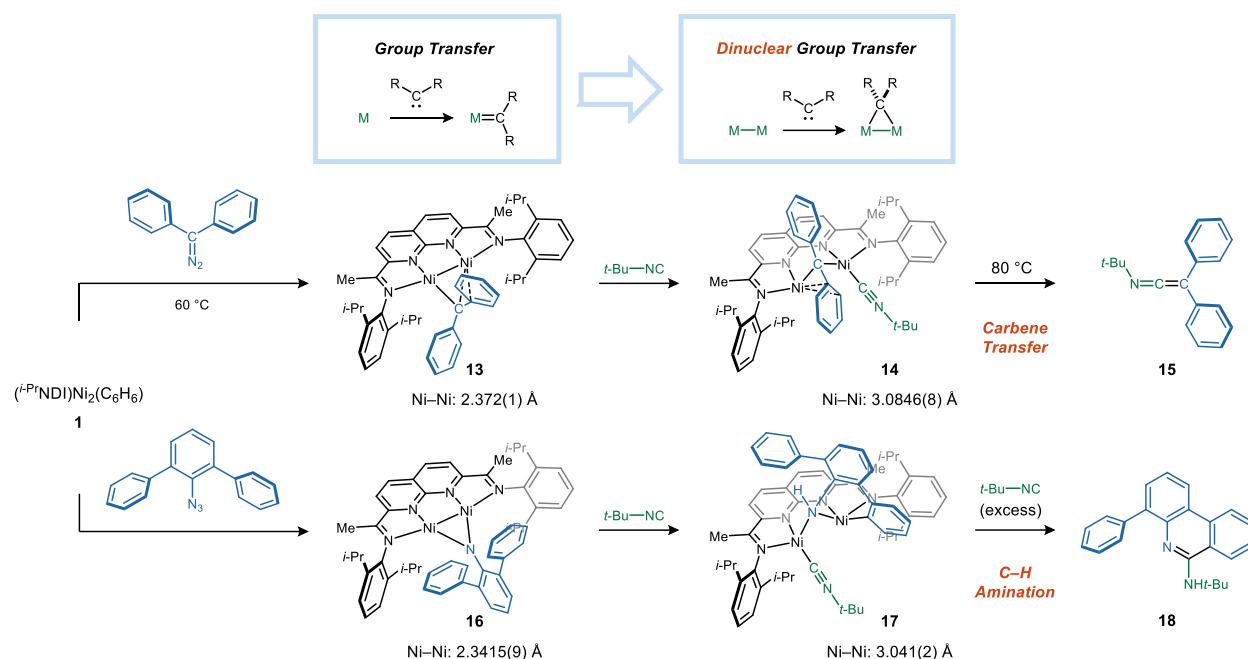


Figure 4. Dinuclear Group Transfer Reactions. Carbene and nitrene transfer reactions at a flexible dinickel active site.

Owing to their valence deficiency, carbenes and nitrenes are highly unstable species. In their free form, they often react indiscriminately with substrates of any structural or functional complexity. Transition metal catalysis has become the primary strategy to control the reactivity of carbenes and nitrenes to achieve high levels of chemo-, regio-, and stereoselectivity. Efforts to characterize the key intermediates of these catalytic processes have largely focused on gaining synthetic access to isolable terminal $M=CR_2$ and $M=NR$ complexes.³⁸ Complexes in which a carbene or nitrene ligand bridge two metals are also known but generally exhibit lower reactivity. For example, Warren found that the reaction between a Cu(I) β -diketiminate complex and an aryl azide generates an equilibrating mixture of dinuclear $Cu_2(NAr)$ and mononuclear $Cu(NAr)$ species.³⁹ Kinetics studies indicate that the $Cu_2(NAr)$ complex is an off-cycle resting state that must dissociate into a monomer before engaging an alkene.

Carbene and Nitrene Transfer. The (NDI)Ni₂ system provided a suitable platform to study the reactivity of bridging carbenes in the absence of dissociation pathways to form mononuclear M=CR₂ species (Figure 4).⁴⁰ Accordingly, Ph₂C=N₂ undergoes a ligand exchange reaction with (*i*-PrNDI)Ni₂(C₆H₆) complex **1** to yield a diazoalkane adduct. The Ni–Ni bond is cleaved in this process (Ni–Ni = 3.135 Å), and the =N₂ unit is bound in an end-on fashion to one Ni and is η²-coordinated to the other. Upon gentle heating at 60 °C, N₂ is eliminated, and the Ni–Ni bond is reestablished to support a bridging carbene. The carbene is capable of transferring to an isonitrile. *t*-BuNC first binds terminally to one Ni (complex **14**), resulting in cleavage of the Ni–Ni bond. This adduct is metastable and decays unimolecularly in C₆H₆ at 80 °C to expel a keteneimine product (**15**) and regenerate **1**. This series of stoichiometric reactions can be rendered catalytic by adding the diazoalkane and isonitrile dropwise to solutions of the catalyst.

Aryl azides also react with **1**, and N₂ elimination is significantly faster than was observed for diazoalkanes (Figure 4).⁴¹ Hindered *m*-terphenylazide reacts with **1** to generate Ni₂(μ-NAr) complex **16**. The putative azide adduct is not detectable as an intermediate. Interestingly, the addition of *t*-BuNC to **16** does not result in the expected group transfer to form a carbodiimide. Rather, it triggers a C(aryl)–H activation reaction. The product is a Ni₂(aryl)(amide) species (**17**) that arises from a 1,2-addition of the aryl C–H bond to the Ni₂(μ-NAr). This C–H activated intermediate is sufficiently stable that it could be isolated, but additional equivalents of *t*-BuNC induce a migratory insertion and C–C reductive elimination sequence to form heterocycle **18** in 90% yield. The same product is also generated, along with 1-phenyl-9*H*-carbazole, if **17** is simply heated at 80 °C. Like the carbene transfer process, the flexibility of the Ni–Ni interaction is critical to the C–H amination. The Ni–Ni distance is short and within bonding range in the Ni₂(μ-NR) complex (**16**) but is capable of expanding to 3.0412(2) Å upon coordination of the isonitrile (**17**).

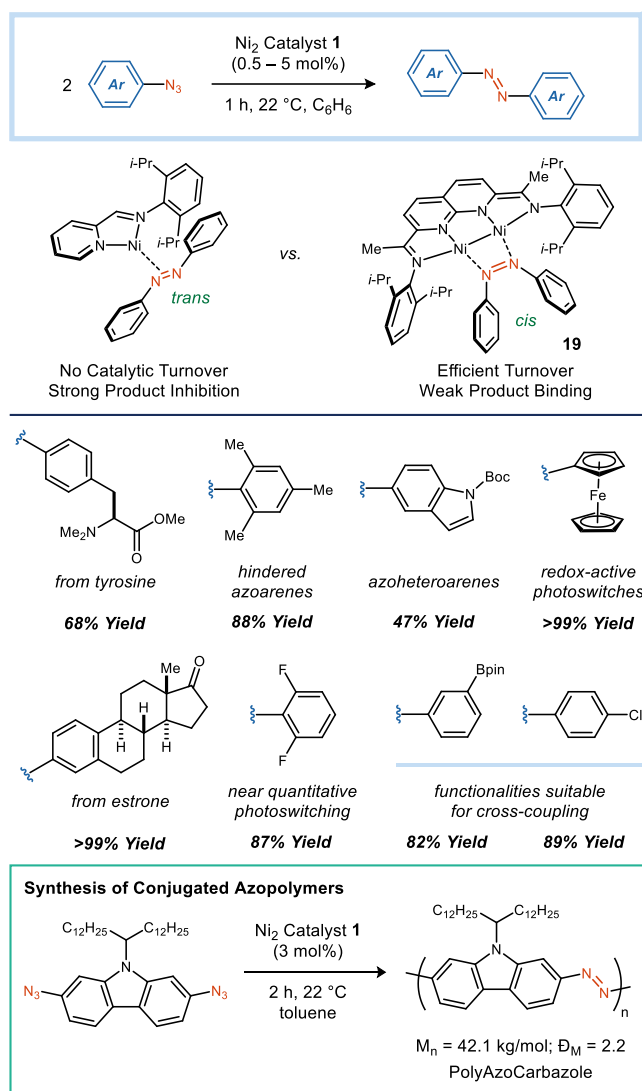


Figure 5. Dinickel complexes are efficient catalysts for the dimerization of aryl azides by avoiding inhibition by the azoarene product. Catalytic syntheses of azoarenes and azopolymers.

When the steric profile of the aryl azide reagent is reduced, the $\text{Ni}_2(\mu\text{-NAr})$ species becomes unstable and is prone to undergoing $\text{N}=\text{N}$ coupling with a second aryl azide equivalent.³ For example, complex **1** reacts with 2 equiv of 2,6- $(i\text{-Pr})_2\text{C}_6\text{H}_3\text{N}_3$ to generate a *cis*-azoarene adduct (**19**). We were motivated by this observation to consider the development of a catalytic $\text{N}=\text{N}$ coupling reaction (Figure 5). Azoarenes are an important class of dye molecules that have seen a resurgence of interest due to their photoswitching properties.⁴² Azoarenes have been incorporated

into biologically active molecules and molecular machines that use light to trigger conformational changes.⁴³

Catalytic dimerizations of >20 aryl azides were carried out using 1–10 mol% of Ni₂ catalyst **1**. By using aromatic diazides as substrates, we were also able to develop catalytic polymerization reactions that generate conjugated materials linked through N=N bonds.⁴⁴ Ongoing studies are aimed at studying the photochemical and electrochemical properties of these polymers.

The rapid and quantitative N=N coupling reaction observed using the (NDI)Ni₂ platform was reminiscent of previous findings from Hillhouse that a (P,P)Ni=NAr species reacts with aryl azides to generate azoarene adducts.⁴⁵ Despite the efficiency of the stoichiometric process, Hillhouse noted in his work that catalytic turnover could not be achieved due to the high binding affinity of the azoarene product relative to the azide starting material. Our mechanistic studies suggest that the ability of the Ni₂ catalyst **1** to achieve turnover may be due to the azoarene only binding to the catalyst in its higher energy *cis* form. Thus, isomerization to the more stable *trans*-azoarene prevents excessive product inhibition.

Vinylidene Transfer. There are several classes of carbenes that are difficult to utilize in transition metal catalysis, because their corresponding diazo precursors are either inaccessible or unstable. For example, H₂C=C=N₂, the precursor to vinylidene, undergoes N₂ elimination at –90 °C with a half-life of 0.3 ms.⁴⁶ In light of this challenge, most catalytic vinylidene transfer reactions use alkynes as vinylidene precursors. The primary drawback of this approach is that only transition metals capable of forming very stable M=C multiple bonds can effect the rearrangement of a metal(alkyne) to a metal(vinylidene), and the reactivity of these metal(vinylidene) species is greatly tempered relative to free vinylidenes.⁴⁷ Consequently, very few catalytic vinylidene

cycloaddition and bond insertion reactions have been developed, particularly those that are enantioselective.

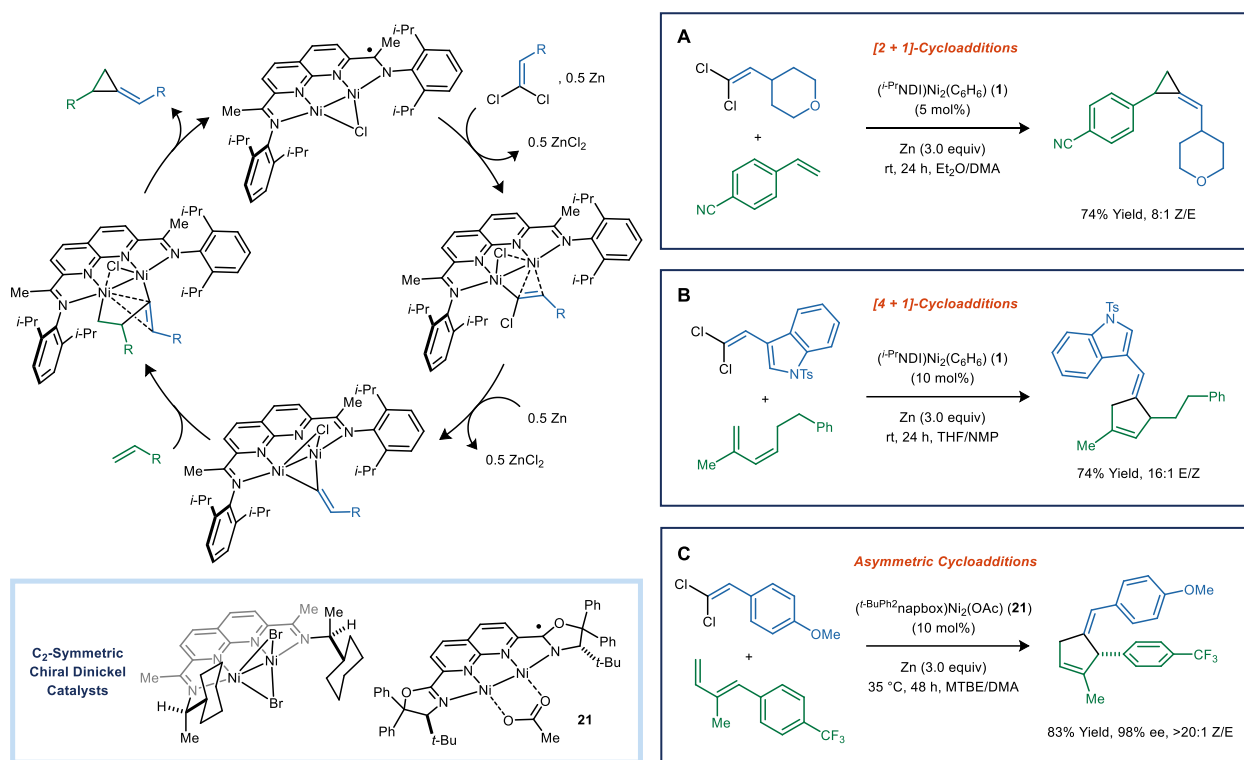


Figure 6. Dinickel catalyzed vinylidene transfer reactions using 1,1-dichloroalkenes. (A) [2 + 1]-cycloaddition and (B) [4 + 1]-cycloaddition reactions. (C) Asymmetric catalysis using chiral naphthyridine–bis(oxazoline) (napbox) ligands.

Dinickel catalysts promote methylenecyclopropanation reactions using 1,1-dichloroalkenes as vinylidene precursors and Zn as a stoichiometric reductant (Figure 6A). Various alkyl, aryl, and heteroaryl-substituted vinylidenes are viable substrates. Monosubstituted alkenes are the most reactive class of partners. However, unhindered or moderately activated internal alkenes, such as cyclopentene or norbornene, can also be used. Recently, Cramer developed an asymmetric variant of this transformation using C₂-symmetric chiral NDI ligands derived from 2,6-di-(1-arylethyl)anilines.⁴⁸

When a (*Z*)-alkene is subjected to the standard methylenecyclopropanation conditions, the product is obtained as a *cis/trans* mixture. This lack of stereospecificity indicates that the two C–C bonds of the cyclopropane are formed in distinct mechanistic steps. This experiment and others led us to propose the general mechanism shown in Figure 6. The 1,1-dichloroalkene is activated by the (*i*-PrNDI)Ni₂Cl complex and, upon reduction with Zn (0.5 equiv), forms a Ni₂(C(Cl)=CHR)Cl species. A second reduction triggers isomerization to a bridging vinylidene complex. Addition of the alkene generates a metallacyclic intermediate, and C–C reductive elimination forms the methylenecyclopropane.

Following our development of the methylenecyclopropanation reaction, we wondered whether vinylidene transfers to 1,3-dienes could produce [4 + 1]-cycloadducts.⁴ Pericyclic [4 + 1]-cycloadditions between 1,3-dienes and free carbenes are disfavored due to closed-shell repulsion of the carbene lone pair and the filled π -orbitals of the diene.⁴⁹ Instead, these reactions generally produce vinylcyclopropanes. Given that our metal catalyzed vinylidene transfer reactions were likely proceeding by stepwise organometallic mechanisms, they would presumably not be subject to these same orbital constraints.

Under similar conditions to those of the methylenecyclopropanation reaction, a broad scope of 1-substituted, 2-substituted, 1,2-disubstituted, 1,3-disubstituted, and 2,3-disubstituted dienes underwent successful [4 + 1]-cycloaddition (Figure 6B). Notably, competing [2 + 1]-cycloaddition was not observed for any of the dienes that we examined, suggesting that the final C–C reductive elimination strongly favors the formation of five- over three-membered rings. Use of a 2-siloxy-1,3-diene yielded cyclopentenones in a process reminiscent of the Danishefsky diene Diels–Alder reaction.⁵⁰ Finally, intramolecular [4 + 1]-cycloadditions could be carried out in high yield using substrates in which the 1,1-dichloroalkene and diene were connected by a two or three-atom tether.

Substituted oxazolines are commonly used in chiral ligands for asymmetric catalysis⁵¹ but have not been widely incorporated into binucleating ligand frameworks (Figure 6C).⁵² We found that chiral naphthyridine–bis(oxazoline) ligands (napbox) could be prepared and subsequently metallated to form (napbox)Ni₂(OAc) complexes.⁵³ Complex **21** is an effective catalyst for enantioselective, intermolecular [4 + 1]-cycloaddition reactions, providing ee values up to 98%.

4. Conclusions and Outlook

The utility of transition metal complexes in catalysis derives from their ability to form and cleave bonds through two-electron redox processes. By combining these elementary steps in different sequences and with different substrate combinations, a broad scope of useful transformations can be developed. Using a redox active ligand, it is also possible to carry out such two-electron oxidations and reductions at metal–metal bonds. In our own work, we have focused on naphthyridine–diimine ligands. However, many other redox-active motifs are currently known. Recently, Tomson described a series of macrocyclic complexes that feature two (PDI)M units connected by alkyl tethers.⁵⁴ Given our observation that (NDI)Ni₂-catalyzed processes can require the reversible formation and cleavage of Ni–Ni bonds, it is interesting to consider the implications of such ligands with added conformational flexibility.

In some of our studies with (NDI)Ni₂ complexes, we have observed activity or selectivity properties that diverge significantly from analogous mononickel catalysts. These results suggest that catalyst nuclearity may represent a useful parameter for catalyst optimization that is complementary to ligand effects. Nuclearity can also be used to adjust the thermodynamic landscape of a catalytic cycle to avoid low-energy sinks that slow down or prevent turnover. For example, while mononickel complexes can promote the rapid stoichiometric dimerization of aryl azides to form azoarenes, catalytic turnover is not observed due to product inhibition. (NDI)Ni₂

complexes form much less stable azoarene adducts, making the product dissociation step favorable.

Finally, in rare cases, dinuclear complexes can promote transformations that are not known with mononuclear complexes. Such is the case with the catalytic carbonylation of norbornadiene, which relies on an unusual C–C oxidative addition. While it cannot be concluded definitively that mononuclear complexes could not be designed to promote this reaction, none have yet been identified, and it is reasonable to speculate that unique ability of a metal–metal bond to form several stabilizing metal– π interactions would not be readily reproduced with just one metal. Uncovering other such examples is the subject of our ongoing research.

AUTHOR INFORMATION

Corresponding Author

*cuyeda@purdue.edu

Christopher Uyeda received a B.S. in biomedical engineering from Columbia University and a Ph.D. in chemistry from Harvard University, where he studied under the guidance of Prof. Eric Jacobsen. After carrying postdoctoral research with Prof. Jonas Peters at the California Institute of Technology, he started his independent career at Purdue University in 2013 and is currently the Richard B. Wetherill Associate Professor of Chemistry. His lab is interested in transition metal catalysis and synthetic methods, with a focus on designing multinuclear catalysts, developing catalytic reductive carbene transfer reactions, and generating azo-materials through catalytic N=N coupling.

Conner M. Farley received B.S. degrees in chemistry and biochemistry from the University of Idaho in 2015 and a Ph.D. degree in chemistry in 2020 under the guidance of Prof. Christopher

Uyeda at Purdue University. He is currently a postdoctoral fellow at the California Institute of Technology with Prof. Sarah E. Reisman. His research interests include transition metal catalysis and the total synthesis of natural products.

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