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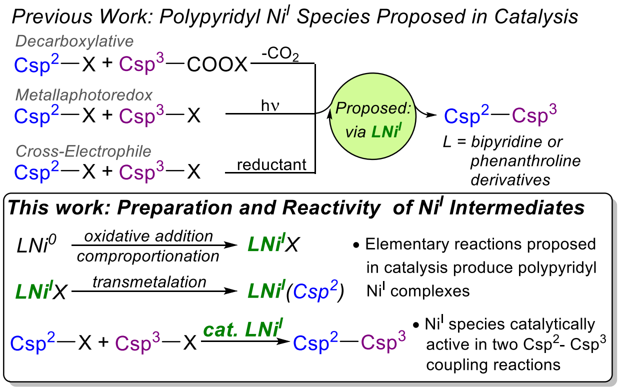
# Synthesis and Reactivity of Paramagnetic Ni Polypyridyl Complexes Relevant to $Csp^2$-$Csp^3$ Coupling Reactions**

Megan Mohadjer Beromi, Gary W. Brudvig, Nilay Hazari,* Hannah M. C. Lant, and Brandon Q. Mercado

**Abstract:** A number of new transition metal catalyzed methods for the formation of $Csp^2$-$Csp^3$ bonds have recently been described. These reactions often utilize bidentate polypyridyl-ligated Ni catalysts, and paramagnetic $Ni^I$ halide or aryl species are proposed in the catalytic cycles. However, there is little knowledge about complexes of this type. Here, we report the synthesis of paramagnetic bidentate polypyridyl-ligated Ni halide and aryl complexes through elementary reactions proposed in catalytic cycles for $Csp^2$-$Csp^3$ bond formation. We investigate the ability of these complexes to undergo organometallic reactions that are relevant to $Csp^2$-$Csp^3$ coupling through stoichiometric studies and also explore their catalytic activity.

Transition metal catalyzed cross-coupling reactions represent one of the most important synthetic methods for the formation of $Csp^2$-$Csp^2$ bonds.[1] Reactions involving $Csp^3$-centers, however, are less advanced.[1] Although there have been major improvements in the development of traditional Suzuki-Miyaura and Negishi reactions involving $Csp^3$-hybridized substrates, these reactions still have some limitations.[2] This has inspired the development of new methods such as cross-electrophile[3],[4],[5] and decarboxylative[6] coupling reactions, as well as metallaphotoredox[7],[8] catalysis for the formation of $Csp^2$-$Csp^3$ bonds. These reactions, which often involve the *in situ* generation of radical intermediates, offer advantages over traditional cross-coupling reactions. For example, in cross-electrophile coupling a reactive organometallic nucleophile is not required, while in decarboxylative coupling readily available esters are used as substrates.

A feature of both cross-electrophile and decarboxylative reactions for $Csp^2$-$Csp^3$ bond formation is the use of Ni catalysts supported by bidentate polypyridyl ligands.[9] Additionally, in most mechanistic proposals for these reactions, the Ni catalysts are suggested to form intermediates in the +1 oxidation state.[3],[6b],[7],[10],[11] For example, in cross-electrophile coupling, a $Ni^I$ halide that reacts with the $Csp^3$-hybridized substrate is proposed to be a key intermediate. Similarly, in decarboxylative $Csp^2$-$Csp^3$ reactions, a $Ni^I$ aryl species is proposed to react with a redox active ester, which ultimately results in the formation of the new C–C bond.[6b] However, there are no examples of well-defined bidentate polypyridyl-ligated $Ni^I$ species containing either halide or aryl ligands. Therefore, the proposed elementary steps cannot be verified and our lack of knowledge about these $Ni^I$ intermediates hinders the development of improved catalysts.



**Scheme 1.** Summary of previous methods to form $Csp^2$-$Csp^3$ bonds and this work.

Here, we report the synthesis and reactivity of polypyridyl supported $Ni^I$ halide and aryl species relevant to $Csp^2$-$Csp^3$ couplings (Scheme 1). Our results indicate that both types of species can be generated through elementary steps which are relevant to contemporary coupling reactions. Further, we explore the role of these complexes in stoichiometric and catalytic reactions related to two $Csp^2$-$Csp^3$ coupling reactions: cross-electrophile[4d] and decarboxylative aryl-alkyl coupling.[6b] Overall, we provide fundamental information about polypyridyl supported $Ni^I$ species, which may assist in the design of new catalysts for $Csp^2$-$Csp^3$ coupling.

Ni precatalysts ligated by 4,4'-di-tert-butylbipyridine (dtbbpy) often give the highest yields in modern $Csp^2$-$Csp^3$ coupling reactions.[3],[6b],[7],[10] Therefore, we attempted to prepare a $Ni^I$ halide complex with this ligand. Attempts to generate a $Ni^I$ halide species through the comproportionation of a well-defined $Ni^0$ species with a $Ni^{II}$ dihalide species were unsuccessful, likely because we were unable to prepare a $Ni^0$ complex, such as $(dtbbpy)Ni^0(COD)$. An alternative synthesis of a $Ni^I$ halide complex could involve initial oxidative addition of an aryl halide to a $Ni^0$ species to generate a $Ni^{II}$ aryl halide complex. Two equivalents of this complex could rearrange to form a bis-aryl $Ni^{II}$ and a $Ni^{II}$ dihalide species. Reductive elimination of biaryl from the $Ni^{II}$ bis-aryl would give a $Ni^0$ species which could comproportionate with the $Ni^{II}$ dihalide to give the desired $Ni^I$ halide (see SI).[12] In this case, reaction of a mixture of $Ni^0(COD)_2$

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Supporting information for this article including experimental procedures and X-ray data is available on the WWW.

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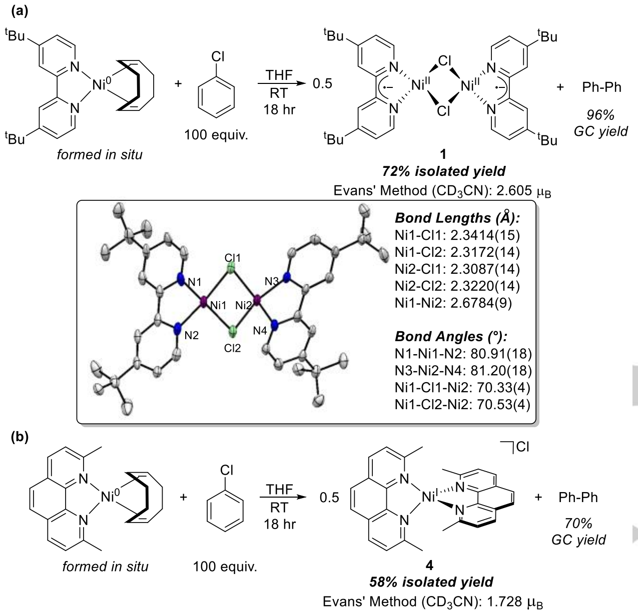
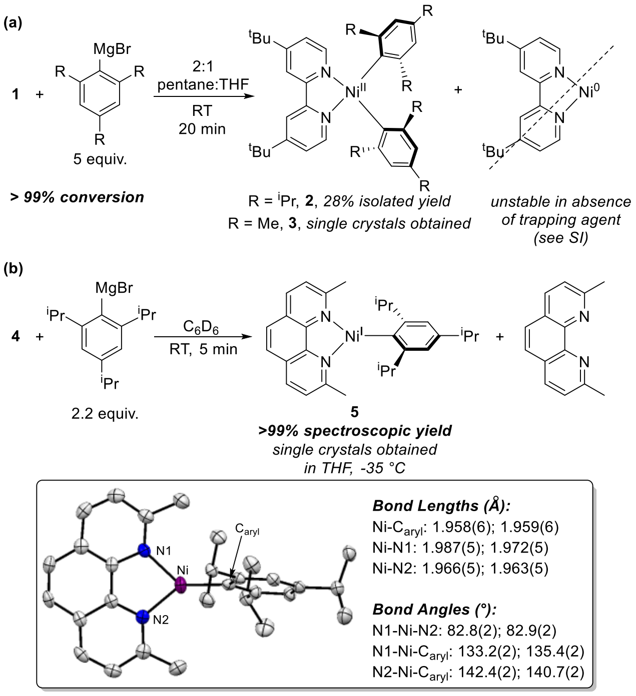
and free dtbbpy with excess chlorobenzene generated a black paragmagnetic complex. X-ray crystallography indicated that the formally Ni$^{I}$ chloride dimer **1** was formed (Scheme 2, **(a)**). Biphenyl was also detected by GC in 96% yield, consistent with a pathway involving initial oxidative addition (see SI). In $CD_3CN$, **1** is ferromagnetically coupled, as indicated by its magnetic moment of 2.605 $\mu_B$ and the absence of a signal in perpendicular mode EPR spectroscopy (see SI). This suggests that **1** maintains its dimeric structure in solution. The Ni–Ni distance of 2.6784(9) is consistent with no significant bonding interaction between the Ni atoms. Surprisingly, the coordination geometry of the two Ni centers is distorted square planar, with the planes formed by each bipyridyl ligand orthogonal to each other. Complex **1** is a rare case of a ferromagnetically coupled Ni dimer with square planar geometries about both Ni centers.[13],[14]



**Scheme 2.** Synthesis of **(a)** **1**. Inset: ORTEP of **1**. Ellipsoids shown at 50% probability. Hydrogen atoms and solvent of crystallization omitted; and **(b)** **4**. Yields of biphenyl reported relative to total Ni in the reaction.

The observed S = 1 spin state for **1** can be rationalized by two possible electronic configurations: one in which two formally Ni$^{I}$ centers are ferromagnetically coupled, and one in which two formally Ni$^{II}$ centers are bound by two reduced dtbbpy ligands (see SI). Analysis of the oxidation state of **1** by X-ray Photoelectron Spectroscopy suggests that the dimer contains two Ni$^{II}$ centers (see SI), indicating that the latter electronic description is likely appropriate. Similar electronic configurations were observed in terpyridine-ligated Ni$^{I}$ complexes.[15] This configuration, however, is different to the only other known bidentate polypyridyl-containing Ni$^{I}$ species, which are cationic homoleptic complexes of phenanthroline derivatives that contain a metal-centered radical.[16] It is also intriguing that **1** is formed through a reaction with a common sp$^2$-electrophile, as it raises the possibility that previously unobserved dinuclear species could be present in catalysis.

In decarboxylative Csp$^2$-Csp$^3$ couplings the reaction of a polypyridyl supported Ni$^{I}$ halide with an organozinc reagent is a proposed elementary step, and thus the reaction of **1** with organometallic reagents is relevant to catalysis. Transmetalation of **1** with an of excess of 2,4,6-triisopropylphenylmagnesium bromide in THF led to the formation of a blue product. X-ray crystallography indicated that the product was not a Ni$^{I}$ aryl species, but the diamagnetic, bis-aryl Ni$^{II}$ species **2** (Scheme 3, **(a)**). Bis-aryl Ni$^{II}$ species have been previously reported in the literature with bipyridine derivatives.[17] Surprisingly, **2** is thermally stable and heating does not result in reductive elimination (see SI). The formation of a bis-aryl Ni$^{II}$ species is not limited to bulky aryl groups, as reaction of **1** with mesitylmagnesium bromide produces the Ni$^{II}$ bis-aryl complex **3**.



**Scheme 3.** Transmetalation of **(a)** **1** to produce **2** or **3** and zerovalent Ni; and **(b)** **4** to produce **5**. Inset: ORTEP of **5**. Ellipsoids shown at 50% probability. Hydrogen atoms and solvent of crystallization omitted. Two independent molecules are present in the asymmetric unit.

The stoichiometry of the transmetalation reaction dictates that another product should be formed – a Ni$^{0}$ center ligated by only one dtbbpy. Under our reaction conditions, we propose that this species is unstable and decomposes. However, when the reaction is performed with 2-iodotoluene as a Ni$^{0}$ trap, (dtbbpy)Ni(o-tolyl)(I) is formed, consistent with the initial formation of a Ni$^{0}$ species (see SI). One pathway for the formation of **2** and Ni$^{0}$ from **1** and a Grignard reagent involves the disproportionation of a Ni$^{I}$ aryl intermediate. Analysis of the transmetalation reaction at 9 K using X-band EPR spectroscopy indicates that a metal-based paramagnetic intermediate is initially formed along with an organic radical. Although this intermediate cannot be **1** or any Ni$^{II}$ species, as these complexes are EPR silent (see SI), the product is too unstable to be unambiguously identified as a Ni$^{I}$ aryl species.

A recurring theme in contemporary coupling reactions catalyzed by polypyridyl Ni complexes is that small changes to the ligand have large effects on catalysis.[6b],[18] We hypothesized that more steric protection around the Ni center could enable the isolation of monomeric Ni$^{I}$ species. The reaction of one equivalent of neocuproine with Ni$^{0}$(COD)$_2$ and excess chlorobenzene resulted in the isolation of [(neocuproine)$_2$Ni$^{I}$](Cl) (**4**), which is a S = ½ species (Scheme 2, **(b)**). Biphenyl was also observed as a product. Although attempts to crystallize **4** were unsuccessful, the $^1$H NMR spectrum is similar to the previously reported homoleptic complex [(neocuproine)$_2$Ni$^{I}$](PF$_6$),[16] and the EPR spectrum is

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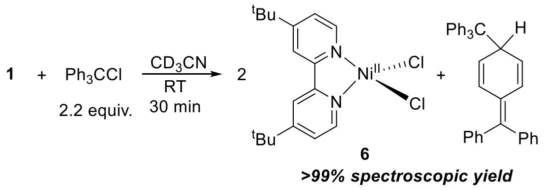
consistent with a metal-centered radical with axial geometry. Mass spectrometry indicates the presence of a cationic, [(neocuproine)$_2$Ni$^I$] unit. Compound **4** was also synthesized by comproportionation between Ni$^0$ and Ni$^{II}$ units or silver salt oxidation of a Ni$^0$ species (see SI). Nevertheless, the formation of **4** through oxidative addition is notable as it suggests that this type of complex could form in catalysis.

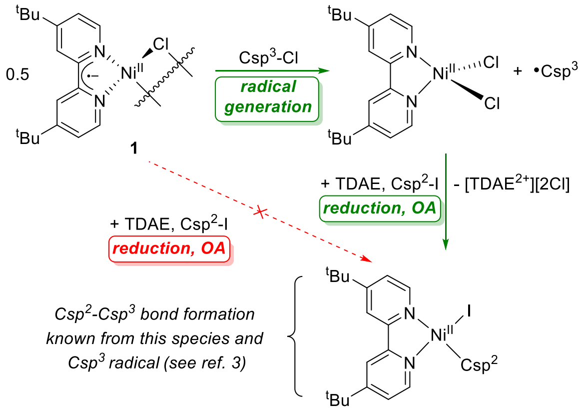
Attempts to remove a neocuproine ligand from **4** to form a complex with a bound chloride ligand or to directly synthesize a neutral Ni$^I$ halide complex supported by one neocuproine ligand were unsuccessful (see SI). However, **4** can be used as a precursor to a Ni$^I$ aryl complex. The reaction of **4** with 2,4,6-triisopropylmagnesium bromide resulted in a new paramagnetic species **5**, as identified by $^1$H NMR spectroscopy (see SI). Complex **5** is unstable in solution and fully decomposes after two hours at room temperature. Although **5** could not be isolated on scale, X-ray crystallography indicated the formation of a Ni$^I$ aryl species (Scheme 3, **(b)**). The Ni-C$_{aryl}$ bond length of 1.959(6) Å is in the range reported for phosphine-[19] and N-heterocyclic carbene-ligated Ni$^I$ aryl species.[20] The 77 K EPR spectrum of **5** shows an axial signal with a metal centered radical (see SI). Two analogues of **5** were generated through the reaction of **4** with mesitylmagnesium bromide or 2,6-xylylmagnesium bromide. These complexes exhibit similar signals in their $^1$H NMR and EPR spectra to **5** (see SI). The instability of these species again prevented isolation; however, our results confirm that polypyridyl Ni$^I$ aryl species are feasible intermediates in catalysis and validate transmetalation as a synthetic route.

We were interested in testing whether **1**, **4**, and **5** could undergo the elementary reactions proposed in cross-electrophile and decarboxylative coupling. In cross-electrophile coupling Ni$^I$ halide complexes are suggested to propagate a Csp$^3$ radical through abstraction of a halogen atom from the Csp$^3$-X substrate.[3] Trityl chloride was used as a model for the Csp$^3$-X substrate. When **1** was treated with a slight excess of trityl chloride per Ni center, oxidation of the Ni occurs to form (dtbbpy)NiCl$_2$, **6** (Scheme 4). The other product is the trityl dimer, which provides evidence for the generation of a Csp$^3$ radical. Radical chain propagation also occurs with **4**, which only has an outersphere chloride anion, resulting in the generation of the Ni$^{II}$ dihalide species and the trityl dimer (see SI).



**Scheme 4.** Reaction of **1** with trityl chloride.

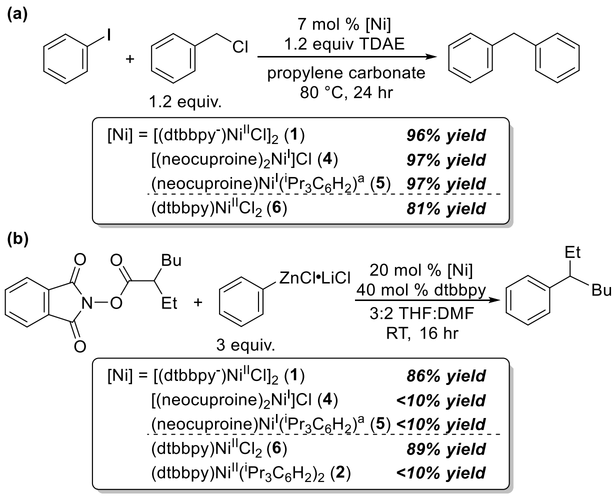
To gain further insight into the role of **1** in cross-electrophile coupling it was exposed to other reagents present in catalysis. **1** does not react with iodobenzene, a Csp$^2$ electrophile (see SI).[4d] This suggests that oxidative addition does not occur from **1**. Another possibility is that **1** is directly reduced in catalysis. However, there is no reaction between **1** and tetrakis(dimethylamino)-ethylene (TDAE), a two-electron reductant used in cross-electrophile coupling.[4d] This is in contrast to the Ni$^{II}$ dihalide **6**, which is reduced by TDAE in the presence of 2-iodotoluene as a Ni$^0$ trap to form (dtbbpy)Ni$^{II}$(o-tolyl)(I) (see SI). Taken together, these data provide support for the proposed mechanism of cross-electrophile coupling (Scheme 5),[3] although it is possible that some dimeric species are involved instead of monomeric species. Specifically, Ni$^I$ halide complexes ligated by polypyridyl ligands are competent in propagating the radical chain, and the resulting Ni$^{II}$ dihalide species can be reduced to zerovalent Ni, which does not occur directly from Ni$^I$.



**Scheme 5.** Summary of mechanistic information relevant to cross-electrophile coupling gained from stoichiometric reactions with **1**.

In the proposed mechanism for decarboxylative Csp$^2$-Csp$^3$ coupling using redox active esters a Ni$^I$ halide complex undergoes transmetalation with an organozinc reagent to generate a Ni$^I$ aryl species, which then reacts directly with the redox active ester.[6b] We have shown that transmetalation of **1** with organomagnesium reagents results in the formation of a Ni$^{II}$ bis-aryl species (i.e., **2** or **3**), with the possibility that a metastable Ni$^I$ aryl complex is an intermediate. Conducting the same reaction with **4** results in a well-defined Ni$^I$ aryl species (i.e. **5**). To validate the proposed next step of the catalytic cycle, we treated **5** with the redox active ester, 1,3-dioxoisoindolin-2-yl 2-ethylhexanoate (see SI). An immediate reaction occurred but no identifiable Ni containing products were formed and we did not observe the organic cross-coupled product. This may be related to the steric bulk of the aryl group in **5**. In contrast, no reaction occurred between the same redox active ester and either **1** or **4** (see SI). Although our results are inconclusive, the fact that **1** and **4** are unreactive with the ester, suggests that a Ni$^I$ aryl species may be necessary for turnover.

To probe the relevance of our new polypyridyl-ligated complexes to catalysis we evaluated their catalytic activity in cross-electrophile and decarboxylative Csp$^2$-Csp$^3$ coupling. Complexes **1**, **4**, and **5** are all active for a prototypical cross-electrophile coupling between iodobenzene and benzyl chloride with TDAE as the reductant (Scheme 6, **(a)**).[4d] In fact, the performance of **1**, **4**, and **5** is slightly superior to that of the analogous Ni$^{II}$ dihalide **6**. In decarboxylative Csp$^2$-Csp$^3$ coupling, neocuproine-ligated Ni$^I$ complexes are markedly less active than their dtbbpy counterparts (Scheme 6, **(b)**). No neocuproine complexes were able to give catalytic turnover for the coupling of dioxoisoindolin-2-yl 2-ethylhexanoate and phenylzinc chloride Knochel reagent. Further, in this coupling reaction, there is an opportunity for bis-aryl complexes to be generated through a competing side reaction either through the double transmetalation of a Ni$^{II}$ dihalide complex or through the transmetalation of **1**. In our screen, the bis-aryl complex **2** is the only dtbbpy-ligated species that is inactive in catalysis, implying that, if these complexes are formed, they may be off-cycle species. However, **1** performs as efficiently as the standard dtbbpy-ligated Ni$^{II}$ dihalide **6**. Our results are the first report showing that some of



**Scheme 6.** Comparison of precatalysts in a prototypical **(a)** cross-electrophile coupling; and **(b)** decarboxylative Csp$^2$-Csp$^3$ coupling. Conditions for each reaction are given in the SI. $^a$Formed in situ, see SI.

the Ni$^I$ intermediates proposed in cross-electrophile and decarboxylative coupling are active in catalysis.

In summary, we have shown that paramagnetic bidentate polypyridyl-ligated Ni species can be formed through sequences involving catalytically-relevant elementary steps. The nuclearity of the paramagnetic complexes is a function of the ligand, and it is possible that dimeric species are present in catalysis. Further, in the case of dtbbpy ligated complexes, we suggest that the ligand can act as an electron reservoir, which may be related to the high catalytic activity of these species. Some of our new paramagnetic species undergo elementary reactions proposed in cross-electrophile or decarboxylative coupling and depending on the ancillary ligand they are catalytically active for these reactions. Overall, this work provides information about highly reactive paramagnetic intermediates which may help the design of more efficient systems for Csp$^2$-Csp$^3$ coupling.

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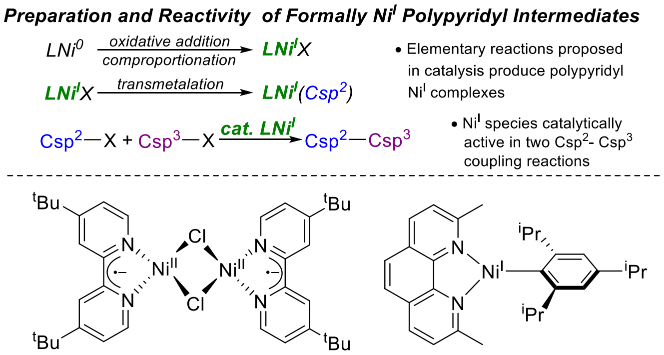
# COMMUNICATION

The synthesis and both the stoichiometric and catalytic reactivity of polypyridyl supported Ni$^{I}$ halide and aryl species relevant to modern Csp$^2$-Csp$^3$ couplings is reported. The complexes can be generated through elementary reactions which are relevant to contemporary coupling reactions, and the nuclearity of the resulting complexes is dependent on the ancillary ligand.



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