First d^0 Metal-Catalyzed Alkyl–Alkyl Cross Coupling Enabled by a Redox-Active Ligand

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ABSTRACT: Alkyl–alkyl cross coupling through well-defined mechanisms that allow for controlled oxidative addition, prevent β-hydride elimination, and tolerate hindered electrophiles are still challenging. We describe the first report of a redox-active ligand-enabled alkyl–alkyl cross coupling using a d^0 metal. This (tris)amido Sc^{III} complex as well as the oxidized variant are thoroughly characterized (NMR, X-ray, EPR, CV, UV-Vis, DFT). Insight into the likely radical nature of the mechanism is disclosed. Additionally, a substrate scope that includes functional groups incompatible with late transition metal catalysis, and both coupling partners bearing β-hydrogens is reported.

Alkyl-alkyl cross coupling is an incredibly important transformation for constructing C(sp^3)–C(sp^3) bonds. It has wide reaching applications in materials, agro-, and medicinal chemistry. Despite its importance, alkyl–alkyl cross coupling is less developed compared to its aryl–aryl counterpart. There are numerous reasons for this, including 1) uncontrolled oxidative addition that proceeds through unpredictable 1 or 2-electron oxidations, 2) off-cycle pathways such as β-hydride elimination that generate unwanted byproducts, and 3) sterically demanding substrates that are unreactive. Much progress has been made in this field with late transition metals but despite their ready availability and reactivity, d^0 early transition metals are not used for catalytic cross coupling.[1–3] This is in part due to the lack of electrons in the d-orbitals to facilitate oxidative addition as well as their reluctance to undergo reductive elimination to generate a low valent species.[4]

We hypothesize that a number of the outstanding challenges of alkyl–alkyl cross coupling outlined above can be addressed using well-defined systems comprised of d^0 metals bearing redox-active ligands (Figure 1a).[5–8] In particular, first row transition metal Sc^{III} is known to undergo slow β-hydride elimination due to the unstable olefin complex that would result.[9,10] Moreover, a tridentate ligand will also prevent β-hydride elimination by occupying three coordination sites of Sc^{III},[11] as well as by limiting alkyl bond rotation. Using a redox-active ligand will allow for control of the mechanism of oxidative addition since the redox potentials can be finely tuned.[12,13] The steric and electronic control provided by the redox-active ligand will generate an organic radical coupling partner that can participate in outer sphere C–C bond formation.

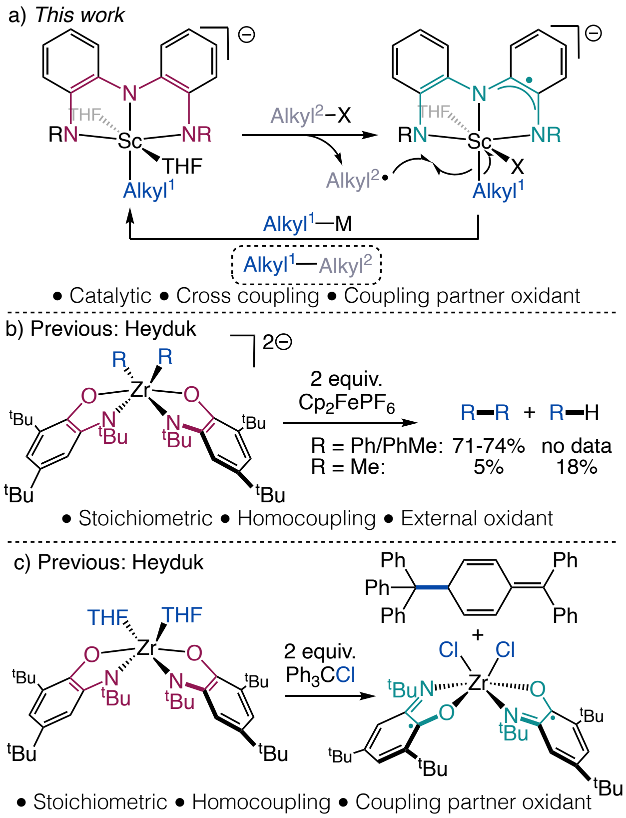
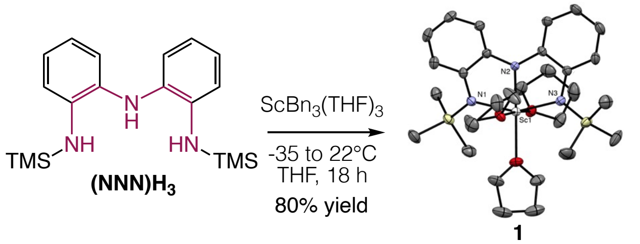


Figure 1. a) Catalytic cross coupling using a well-defined redox-active ligated Sc complex, b) C–C coupling from a redox-active ligand paired with Zr, c) Oxidation of a redox-active ligand Zr complex with an organic oxidant

To our knowledge, no catalytic C–C bond forming cross coupling has been reported by using d^0 metals except as Lewis acids.[14] A single example exists of a reaction to generate aryl–alkyl bonds with an early transition metal catalyst using one Grignard substrate. But the mechanism was not delineated and involves a rearrangement and a non-traditional coupling partner (aryl fluoride) so the reported reaction is not a conventional cross coupling.[15] On the other hand, C–C bond homocoupling is known with d^0 metals. Early studies by Jordan and coworkers describe oxidatively induced C–C bond homocoupling with Zr^{IV} but those studies focused on the utility of the cationic complex byproducts.[16,17] Heyduk and coworkers have examined the role of redox-active ligands to facilitate redox reactions at d^0 early transition metals to form C–C bonds.[18,19] In these studies, an external oxidant induces reductive elimination from a Zr^{IV} complex ligated by two redox-active amidophenolate ligands and two organic groups to generate either biaryl or methyl radical which abstracts a hydrogen to form methane or couples to form ethane (Figure 1b).[18] These studies provide proof of concept that using an oxidant, C–C coupling can be achieved. Interestingly, when the phenyl and tolyl analogs in the same pot are subjected to the oxidant, less than 1% cross product is observed. Heyduk and coworkers also disclosed trityl chloride as an oxidant to form a C–C bond from a d^0 metal with a redox-active ligand through generation of the homocoupled product, Gomberg's dimer (Figure 1c).[19] Using these studies as precedent, herein we report the design of the first catalytic alkyl–alkyl cross coupling achieved with a well defined Sc^{III} catalyst supported by a tridentate redox-active ligand.

Scheme 1. Synthesis and crystal structure of **1**



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In order to initiate these studies, we chose a tridentate tris(amido) ligand popularized by Heyduk and coworkers for redox chemistry of Ta complexes.[12,13] These ligands have been employed to elegantly demonstrate that inorganic oxidants such as $PhICl_2$ and Cl_2 can be used to generate the complexes with a ligand that has been oxidized by either 1 or 2 electrons. Based on the redox potentials of tris(amido) Ta complexes, we hypothesized that a Sc^{III} complex supported by a redox-active ligand would be compatible with mild C-based oxidants such as alkyl halides.

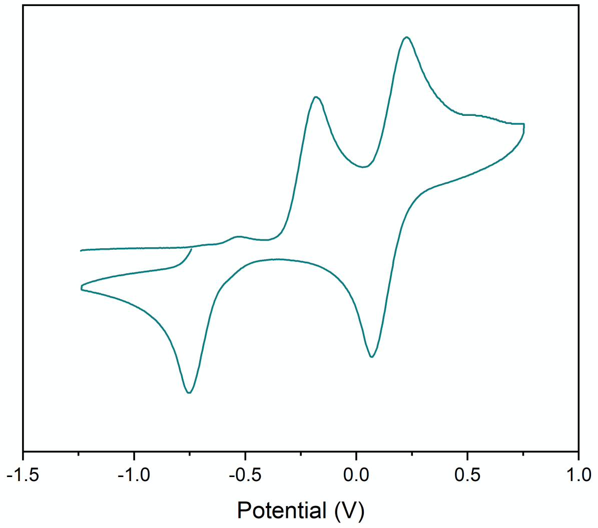


Figure 3. Cyclic voltammogram of 2 mM solution of $(NNN)Sc(THF)_3$ **1** in THF. (0.25 M $[NBu_4]PF_6$, 200 mV/s, referenced to $Cp_2Fe^{0/+}$)

Addition of $(NNN)H_3$ to $ScBn_3(THF)_3$ in THF at −35°C afforded the complex $(NNN)Sc(THF)_3$ (**1**) as a light yellow solid in 80% yield (Scheme 1). This is the fourth known well-defined Sc pincer complex.[20–22] The ^1H NMR spectrum of this complex shows a single product in THF-*d₈;* however in benzene-*d₆* two complexes are observed, which we found are related by the number of THF molecule coordinated to the Sc center (see SI for details). Single crystals of **1** suitable for X-Ray diffraction analysis were grown from concentrated THF solutions stored at −35°C for 3 days. The structure shows that **1** (Scheme 1) has a pseudo-octahedral geometry with three THF molecules bound to the metal center. The geometry at Sc deviates significantly from the idealized octahedron with respect to the terminal nitrogen atoms of the ligand with an N1−Sc−N3 bond angle of 154.01°. The Sc−N bond distances range from 2.064-2.157 Å. The C–N (1.389-1.408 Å) and C–C (1.368-1.434 Å) bond distances along the ligand scaffold are in the appropriate range for C–N single bonds and C–C aromatic bonds. These are also in agreement with other d^0 metal complexes containing similar tris(amido) ligands that have C–N and C–C bond distances in the range of 1.383-1.423 and 1.377-1.416 Å, respectively.[12,13]

Electrochemical analysis of **1** by cyclic voltammetry showed that this complex can undergo two single electron oxidations, consistent with the ability of the ligand to undergo two single electron oxidations (Figure 2). The first oxidation has an $E°_{ox}$ of −0.18 V and is irreversible, whereas the second oxidation at 0.23 V is reversible. We attribute the irreversibility of the first oxidation to possible changes to the structure (e.g. loss of THF) upon oxidation. This represents one of only three known Sc complexes with redox-active ligands and the first example of a redox-active Sc pincer complex.[23,24]

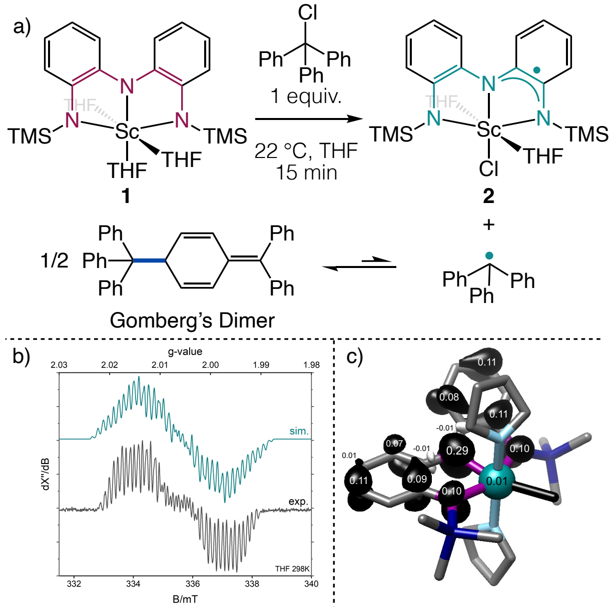
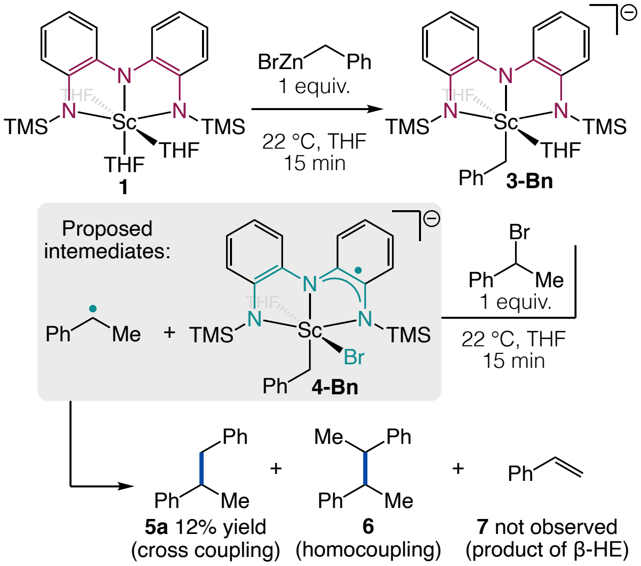


Figure 2. a) Oxidation of **1** using trityl chloride, b) EPR spectrum of **2** in THF at 298 K (exp) and corresponding simulated spectrum (sim), c) Spin density plot of **2**

In order to determine if **1** could be oxidized by 1-electron with an organic oxidant with concomitant formation of a C-based radical, **1** was exposed to one equivalent of trityl chloride (Figure 3a). This results in an immediate color change of the solution from yellow to dark green. The ^1H NMR spectrum of this reaction mixture in THF-*d₈* shows that Gomberg's dimer, the product of trityl radical homocoupling, has formed, which suggests that trityl chloride oxidized **1** via transfer of Cl• to generate (NNN•)ScCl(THF)$_2$ (**2**) and trityl radical. This is proof of concept that alkyl radicals can be generated from oxidation of **1**. The ^{1}H NMR spectrum also shows a single broad peak at ~ -0.6 ppm, which is assigned as the TMS substituents of the ligand and in this paramagnetic complex. Due to challenges in purification of **2** from trityl radical and Gomberg's dimer, addition of half an equivalent of iodobenzene dichloride to **1** also generates a green solution of **2**. The X-band EPR spectrum of the resulting paramagnetic complex **2** collected in fluid THF at 298 K displays a single isotropic signal with $g_{iso} = 2.0028$ (Figure 3), which does not deviate significantly from that of a free electron, suggesting a ligand-centered SOMO. Resolved hyperfine coupling to each nitrogen of the tris(amido) chelate ($A_{iso}(^{14}\text{N}, n = 2) = 4.6$ MHz ; $A_{iso}(^{14}\text{N}, n = 1) = 8.7$ MHz) as well as 4 aryl protons of the chelate ($A_{iso}(^{1}\text{H}, n = 4) = 1.7$ MHz) was observed. Superhyperfine coupling to the ^{45}Sc nucleus ($I = 7/2$, 100% natural abundance) was also observed, with $A_{iso} = 1.2$ MHz.

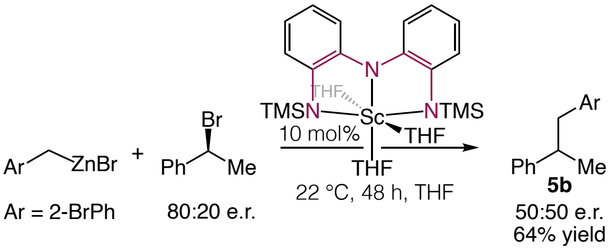
Density functional theory studies (DFT) were performed to simulate the experimentally obtained EPR parameters and to better understand the electronic structure of **2**. The DFT-calculated g_{iso} value of 2.0021 and corresponding A_{iso} values matched well with the experimental values (see Supporting Information for details). The Mulliken spin density plot for complex **2** was also generated and supports the assertion that the SOMO is ligand-centered, as the spin density is located predominately on the trisamido ligand (approximately 99%). Significant spin density at the N-atoms is manifested in hyperfine coupling observed for N in the spectrum. Additionally, significant spin density is observed at certain C-atoms on the aryl rings, which is revealed in superhyperfine coupling observed for H-atoms bound to C. While there is minimal spin density (0.01) at Sc (Sc, I = 7/2), superhyperfine coupling is observed likely due to proximity of the nucleus to the SOMO and/or its high natural abundance and gyromagnetic ratio. These results indicate that the radical is primarily ligand centered. Taken together, the magnetic, EPR, and DFT data suggest that **2** is best described as a Sc^{III} center coordinated to a singly-oxidized (tris)amido ligand.

Scheme 2. Cross coupling and homocoupling from **3-Bn**; β-HE = β-hydride elimination



Given that alkyl–alkyl cross coupling with d^0 metals has not been observed, we wanted to probe if cross selectivity was possible if a transmetallation reagent was used. We also wanted to study if substrates that contain β-hydrogens were compatible with this system so we began our studies where the electrophile has the potential to undergo β-hydride elimination. Upon addition of 1 equivalent of benzylzinc bromide, the product of transmetallation [(NNN)ScBn(THF)$_2$]$^-$ **3-Bn** was observed by ^{1}H NMR spectroscopy within 15 minutes in THF-d_8 at room temperature (Scheme 2). Subsequent addition of (1-bromoethyl)benzene to **3-Bn** gave two organic products. We were gratified to see the cross coupled product **5a** generated in 12% yield. This represents the first example of a C–C bond formed from a Sc complex with a redox-active ligand and the first cross selective reductive elimination from a metal in either group 3 or 4. The other organic product that was observed is the homocoupled electrophile in equimolar amounts compared to the cross coupled product. This result suggests that an alkyl radical was generated in the reaction that likely formed through (NNN•)ScBn(THF)$_2$]$^-$ **4-Bn**. Styrene **7**, the product of β-hydride elimination, was not observed.

Scheme 3. Catalytic cross coupling that racemizes stereocenter



In order to further verify that an alkyl radical is a likely intermediate, and to probe if this system can be translated to catalysis, we synthesized the enantioenriched (1-bromoethyl)benzene substrate with an 80:20 e.r. We hypothesized that because homocoupling likely involves two radical coupling partners generated from two equivalents of **1**, if we use a catalytic amount of **1**, cross selectivity could be favored over homocoupling. Using one equivalent each of the enantioenriched benzylic bromide and benzylzinc bromide and 10 mol% of **1**, the

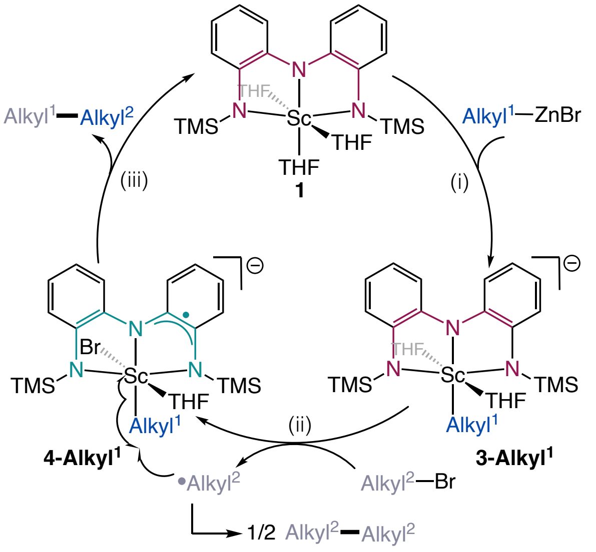
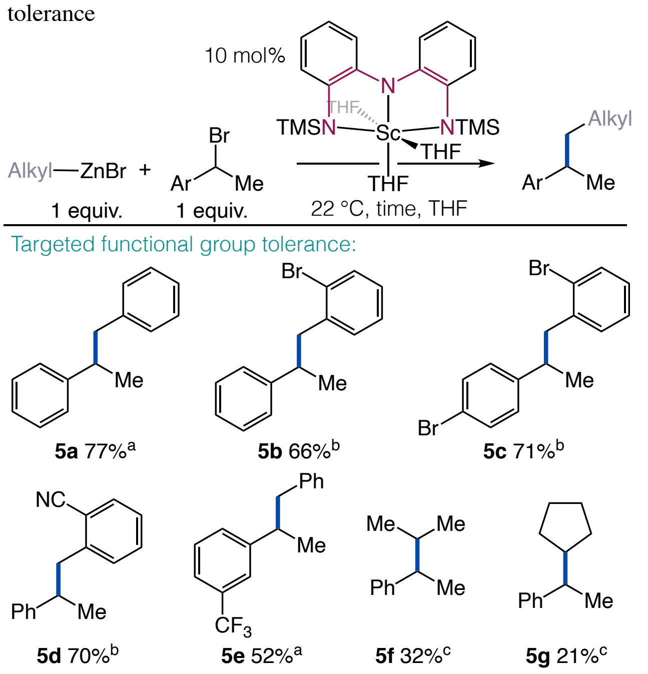


Figure 4. Plausible catalytic cycle for cross coupling

cross coupled product **5b** was generated in 64% yield as a racemic mixture as determine by HPLC analysis. This result further supports the hypothesis that an alkyl radical is the coupling partner in this reaction because the enantioenriched stereocenter in the starting material is racemic in the product. The racemic product]also supports that the cross coupled product is not a product of S_N2 addition to the bromide electrophile which would have inverted the stereocenter. In the absence of **1**, no background reaction is observed. Verifying our hypothesis that catalytic amounts of **1** would favor cross coupling over homocoupling, the remaining electrophile (36%) was converted to homocoupled electrophile. Overall, this represents the first example of a catalytic C–C bond forming cross coupling reaction with a d^0 metal.

Based on these findings, we propose that a possible mechanism of this reaction proceeds through transmetallation from Alkyl^1–Zn bromide to **1** to generate a well-defined anionic alkyl complex $[(NNN)ScAlkyl^1(THF)_2]^-$ (**3-Alkyl^1**) (Figure 4 step (i)). 1-Electron oxidation of **3-Alkyl^1** by Alkyl^2–bromide occurs to generate the $[(NNN\bullet)ScAlkyl^1Br(THF)]^-$ (**4-Alkyl^1**) and the Alkyl^2 radical (step (ii)). Cross coupling occurs when Alkyl^2 radical attacks the Sc–Alkyl^1 bond of **4-Alkyl^1** to form the C–C bond and reduce the Sc complex (step (iii)). If the radical is able to escape the solvent cage, this off-cycle pathway leads to homocoupling.

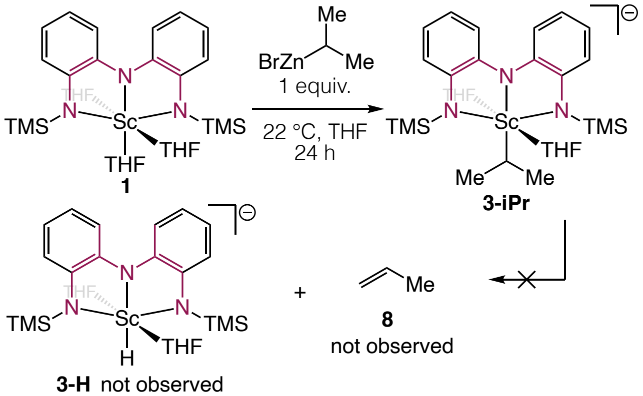
Scheme 4. Targeted substrate scope to explore functional group tolerance



Conditions: 0.5 M, 0.9 mmol, ^{a} 48 h, ^{b}96 h, ^{c}24 h

Next we wanted to explore the scope of the reaction. We chose to target functional groups with possible incompatibilities in order to assess the practicality of this method (Scheme 4). We were gratified to demonstrate that aryl bromides in either the nucleophile (**5b**) or electrophile (**5c**) do not react and are compatible with this reaction despite their prevalence as traditional cross coupling partners. Additionally, the Lewis basic as well as common ligand, nitrile (**5d**) is tolerated in this reaction. Early transition metals famously undergo α- and β-fluoride elimination with fluorine containing functional groups but an aryl CF_3 group (**5e**) is tolerated.[25] Finally, we wanted to see if nucleophilic alkyl coupling partners bearing β-hydrogens is tolerated in catalysis. Turnover is achieved with those partners but low yields are observed (**5f** and **5g**).

Scheme 5. Exploration of possible β-hydride elimination pathway



In order to probe if the cause of low yields of **5f** and **5g** substrates were due to slow transmetallation due to sterics, β-hydride elimination, or slow C–C reductive elimination due to sterics we studied the stoichiometric reaction of isopropylzinc bromide with **1** (Scheme 5). Transmetallation occurred quickly to generate $[(NNN)Sc(iPr)(THF)_2]^-$ (**3-iPr**) and the ^1H NMR spectrum showed full consumption of both starting materials was reached within 15 minutes. After 24 hours, propene **8** or $[(NNN)ScH(THF)_2]^-$ (**3-H**), the products of β-hydride elimination, were not observed. Therefore, we conclude low yields are likely due to the hindered nature of the secondary C that undergoes attack by the radical coupling partner. This leaves room for catalyst development which is ongoing.

In conclusion, we have demonstrated for the first time that d^0 metals bearing redox-active ligands can be utilized for cross coupling. By designing a system where one coupling partner is bound to a metal that is unlikely to undergo β-hydride elimination and the other coupling partner that cannot undergo β-hydride elimination because it is never bound to the metal, we were able to work towards overcoming a long-standing challenge in the field of cross coupling. Preliminary mechanistic studies reveal insight into the radical character of the mechanism. A targeted compatibility scope is also disclosed that demonstrates that orthogonal reactivity to classic aryl cross coupling and tolerance to Lewis basic functional groups can be achieved. Ongoing work involves improvements to the catalysts to achieve a wider reaching scope.

ASSOCIATED CONTENT

Supporting Information

Experimental and Characterization (PDF)
DFT (xyz)
Crystal structure of **1** (CIF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

Funding Sources

We thank the University of Minnesota for startup funding.

ACKNOWLEDGMENT

We thank Prof. Ian Tonks for helpful discussions. We are grateful to the Ian Tonks and Connie Lu labs for equipment use to obtain CV and UV-vis data. X-Ray diffraction experiments were performed using a crystal diffractometer acquired through an NSF-MRI award (CHE-1229400) in the X-ray laboratory supervised by Dr. Victor G. Young, Jr.

ABBREVIATIONS

NNN, tris(amido) ligand; β-HE, β-hydride elimination

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