

Catalytic C–S Cross-Coupling Reactions Employing Ni Complexes of Pyrrole-Based Pincer Ligands

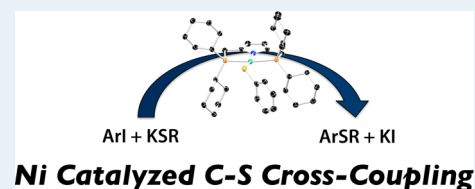
Gopaladasu T. Venkanna, Hadi D. Arman, and Zachary J. Tonzetich*

Department of Chemistry, University of Texas at San Antonio, San Antonio, Texas 78249, United States

S Supporting Information

ABSTRACT: A series of catalytic C–S coupling reactions utilizing well-defined Ni(II) PNP pincer complexes as precatalysts are reported (PNP = anion of 2,5-bis[(dialkyl/aryl-phosphino)methyl]pyrrole, abbreviated as $P_2^R\text{Pyr}$). Coupling reactions employing a variety of aryl iodides and thiols in the presence of base and DMF proceed in good to excellent yield at 80 °C with low catalyst loadings. Aryl bromides were found to result in substantially lower yields, and aryl chlorides were found to be unreactive under the catalytic conditions. In an effort to further understand the reactivity of the nickel PNP precatalysts, complexes of Ni(II) containing amide, alkoxide, hydroxide, thiolate, and hydrosulfide ligands have been prepared and examined in stoichiometric reactions relevant to carbon-heteroatom coupling. Full characterization of each nickel complex is provided, including solid-state structures. The results of stoichiometric reactions implicate a reduced Ni(I) species as the active catalyst, which forms by reduction of the Ni(II) precatalyst in the presence of excess thiolate. The facility in forming Ni(I) species is invoked to rationalize the observed activity among different Ni PNP precatalysts.

KEYWORDS: C–S cross-coupling, nickel catalysis, PNP ligands, nickel(II), mechanistic studies



INTRODUCTION

Carbon–heteroatom (C–X) bond forming reactions have emerged as a very important class of synthetic methods that now rival C–C bond forming reactions in their scope and simplicity. By in large, C–N, C–O, and C–S couplings are of primary focus due to the prevalence of these linkages in natural products and pharmaceutically important small molecules.^{1,2} A variety of catalyst systems have been reported for these transformations, with the majority incorporating late transition metals such as Ni, Cu, or Pd.^{3–8} The success of these metals in mediating C–X bond-forming reactions can be traced to the unique aspects of M–X bonding within their complexes, a topic of considerable theoretical interest.^{9–15}

As part of our continuing investigations into new PNP pincer ligands that feature a central pyrrole group,^{16–19} we sought to examine the catalytic efficacy of Ni PNP complexes in C–heteroatom cross-coupling reactions. We have previously demonstrated that such Ni complexes are efficient precatalysts for a variety of Kumada-type C–C cross-coupling reactions under mild conditions.²⁰ Moreover, examples of catalytic C–X cross-coupling reactions with Ni pincer complexes where X = N, O, or S are quite rare, with the best-studied examples involving formation of C–S bonds.^{21–24} Guan has reported elegant mechanistic work concerning C–S cross-coupling reactions catalyzed by Ni pincer complexes containing the bis(phosphinite) POCOP ligand.^{25,26} These studies delineated the thermodynamic role of pincer ligand substituent and thiol in stoichiometric C–S bond forming steps and demonstrated that lower valent Ni complexes resulting from decomposition of the pincer ligand are likely the true catalytically active species. Zargarian has also studied such ligand decomposition pathways

in detail for related POCOP pincers containing a central C_{sp^3} donor atom.²⁷ Thus, the question remains if intact phosphine-based Ni pincer complexes are capable of effecting catalytic C–X bond formation at all, or if all observed catalytic activity is an artifact of pincer ligand decomposition. Such a scenario is counterintuitive given the thermal stability traditionally associated with pincer ligands²⁸ yet logical given the precedent for C–S cross-coupling with simple binary Ni(0) systems.^{29,30}

Herein we describe the chemistry of Ni(II) complexes of the pyrrole-based pincer ligand, $P_2^R\text{Pyr}$ ($P_2^R\text{Pyr} = (2,5\text{-}\{R_2\text{PCH}_2\}_2\text{C}_4\text{H}_2\text{N})^-$; R = Ph, Cy, *t*-Bu), relevant to C–X cross-coupling catalysis. Of the C–X cross-coupling reactions examined (X = N, O, and S), only C–S couplings were found to proceed. The nature of the active species in these reactions has been probed by investigating the stoichiometric chemistry of well-defined Ni(II) precatalysts. The results support an important role for Ni(I) in the catalytic cycle.

RESULTS AND DISCUSSION

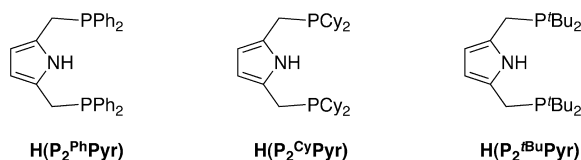
Synthesis of the $P_2^{t\text{Bu}}\text{Pyr}$ Ligand. Previous reports of pyrrole-diphosphine pincer ligands from our group and others feature either phenyl or cyclohexyl substitution at the phosphine arms.^{16–18,20} In order to compare the catalytic reactivity of a nickel(II) complex possessing a more bulky ligand, we pursued the synthesis of the di-*tert*-butylphosphino analog (Chart 1). Bulky *tert*-butyl phosphine substituents in nickel pincers bearing pyridine and aryl central units have

Received: June 20, 2014

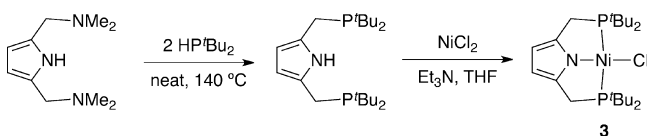
Revised: July 22, 2014

Published: July 23, 2014

Chart 1. PNP Ligands Used in This Study



proven effective in supporting complexes active toward catalysis.^{31,32} Reaction of 2,5-bis-(dimethylaminomethyl)-pyrrole with neat di-*tert*-butylphosphine at 140 °C afforded the desired pyrrole-diphosphine, $\text{H}(\text{P}_2^{\text{tBu}}\text{Pyr})$, in good yield after removal of all volatiles (Scheme 1). Metalation to give

Scheme 1. Preparation of $\text{H}(\text{P}_2^{\text{tBu}}\text{Pyr})$ and $[\text{NiCl}(\text{P}_2^{\text{tBu}}\text{Pyr})]$ 

$[\text{NiCl}(\text{P}_2^{\text{tBu}}\text{Pyr})]$ (**3**) was accomplished by combining $\text{H}(\text{P}_2^{\text{tBu}}\text{Pyr})$ with anhydrous nickel(II) chloride in the presence of triethylamine in identical fashion to that reported for the $\text{P}_2^{\text{Ph}}\text{Pyr}$ and $\text{P}_2^{\text{Cy}}\text{Pyr}$ ligands.

Much like the diphenyl- and dicyclohexylphosphine analogs, the $\text{P}_2^{\text{tBu}}\text{Pyr}$ ligand gives rise to a thermally stable (decomp. > 250 °C), diamagnetic nickel(II) chloride complex. The ³¹P NMR resonance of complex **3** is found at 64.9 ppm, demonstrating a trend to more downfield chemical shifts upon moving to more electron-donating phosphine substituents on the PNP ligand (cf. 30.3 ppm for $[\text{NiCl}(\text{P}_2^{\text{Ph}}\text{Pyr})]$ (**1**) and 51.1 ppm for $[\text{NiCl}(\text{P}_2^{\text{Cy}}\text{Pyr})]$ (**2**)). The solid-state structure of complex **3** is depicted in Figure 1 and displays

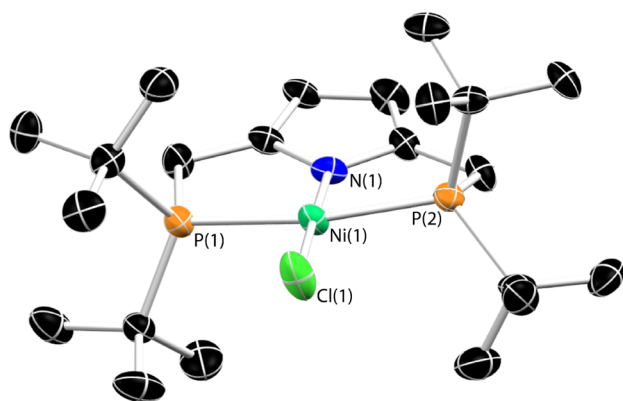


Figure 1. Thermal ellipsoid drawing (50%) of $[\text{NiCl}(\text{P}_2^{\text{tBu}}\text{Pyr})]$ (**3**). Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–Ni(1) = 1.860(5); Ni(1)–P(1) = 2.2352(18); Ni(1)–P(2) = 2.2190(18); Ni(1)–Cl(1) = 2.1830(18); N(1)–Ni(1)–Cl(1) = 178.64(15); P(1)–Ni(1)–P(2) = 168.08(6).

the expected square-planar geometry about nickel. Despite the larger steric bulk of the *tert*-butyl groups, the distances and angles about the nickel atom are comparable to those observed for complexes **1** and **2**.

Catalytic Reactions. Complex **1** was used to test for catalytic activity in C–N, C–O, and C–S coupling reactions in the presence of base employing bromobenzene as the

electrophile and either aniline, phenol, or thiophenol as the nucleophile. Under several conditions utilizing THF, toluene, or DMF as solvent and KO^tBu, Cs₂CO₃, or KOH as base at elevated temperatures (60–110 °C), no products of C–N or C–O cross-coupling were detected. Such an observation is consistent with the absence of any examples of C–N or C–O cross-coupling with Ni pincer catalysts reported in the literature. In contrast, however, the C–S coupling reaction was found to proceed to the coupled diphenylsulfide product.

The catalytic C–S coupling reaction was optimized using 4-iodotoluene and thiophenol with precatalysts **1**, **2**, and **3** as displayed in Table 1. Of the conditions examined, only DMF

Table 1. C–S Coupling of Thiophenol with 4-Iodotoluene under Various Conditions^a

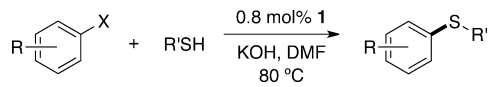
entry	catalyst	solvent	base	% yield ^b
1	none	DMF	KOH	0 ^c
2	1	DMF	None	0
3	1	DMF	KOH	97
4	2	DMF	KOH	64
5	3	DMF	KOH	55
6	1	Toluene	KOH	0
7	1	THF ^d	KOH	0
8	1	DMSO	KOH	trace
9	1	DMF	K ₃ PO ₄	30
10	1	DMF	Cs ₂ CO ₃	trace
11	1	DMF	KO ^t Bu	0
12	1	DMF	NaOH	89
13	1	DMF	NaOMe	40


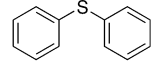

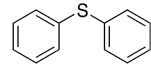
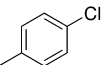
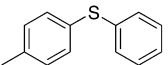
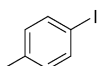
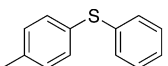
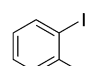
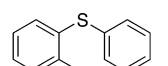
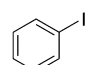
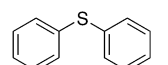
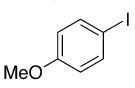
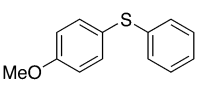
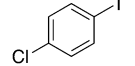
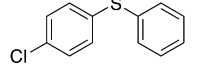
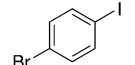
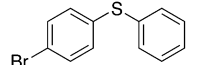
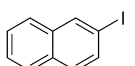
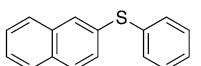
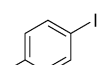
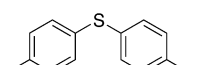

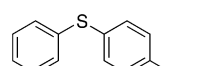
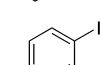
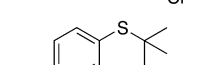
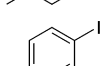
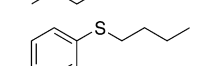
^aReaction conditions: Ni cat., 0.8 mol %; 4-iodotoluene, 1.1 mmol; thiophenol, 1.0 mmol; base, 2.0 mmol; solvent, 3 mL; 80 °C; N₂ atmosphere. ^bIsolated yield. ^cReaction time up to 6 h. ^d60 °C.

was found to result in substantial quantities of the coupled thioether product. Both KOH and NaOH were found to be effective bases, although limited yields were also obtained with NaOMe and K₃PO₄. We note that the role of base has previously been demonstrated to play an important role in C–S cross-coupling reactions mediated by Cu catalysts.³³ Complex **1** was found to be superior to either **2** or **3** as a precatalyst for the C–S cross-coupling reaction (entries 4 and 5). The better performance of **1** may stem from the decreased steric bulk of the $\text{P}_2^{\text{Ph}}\text{Pyr}$ ligand versus $\text{P}_2^{\text{Cy}}\text{Pyr}$ and $\text{P}_2^{\text{tBu}}\text{Pyr}$; however, stoichiometric reactions with the nickel precatalysts also point to an important role for the Ni^{II}/Ni^I redox couple (*vide infra*).

Having identified **1** as an effective precatalyst for the coupling of 4-iodotoluene and thiophenol, we next examined the substrate scope of the reaction. Examining several different haloarenes quickly identified aryl iodides as the best electrophilic coupling partners (Table 2, entries 1–3). Bromobenzene was found to afford diphenylsulfide, albeit in lower isolated yields and only after additional reaction time. In contrast, aryl chlorides were found to be completely unsuitable electrophiles for cross-coupling reactions. Aryl chlorides containing electron-donating substituents were found to be unreactive, and those containing electron-withdrawing substituents such as CN, CF₃, and NO₂ were found to react without added catalyst in control experiments.

Table 2. Nickel Catalyzed C–S Coupling Reactions Employing **1**^a



Entry	Ar-X	Product	Time (h)	%Yield ^b
1			3	94
2			6	44
3			6	0
4			3	97
5			3	94
6			3	96
7			3	92
8			4	90
9			4	89
10			5	85
11			4	97
12			4	96
13			4	87
14			4	76

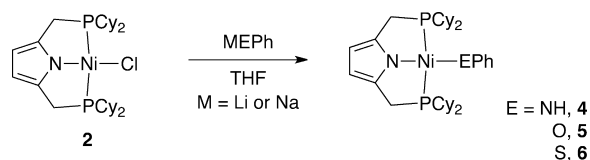
^aReaction conditions: Ni cat., 0.8 mol %; electrophile, 1.1 mmol; thiol, 1.0 mmol; KOH, 2.0 mmol; DMF, 3 mL; 80 °C; N₂ atmosphere. ^bIsolated yield.

The results in Table 2 demonstrate effective cross-coupling for a variety of aryl iodides and thiols. Both electron-withdrawing and electron-donating substituents on the electrophile were tolerated as well as substitution at the 2-position. Aryl iodides containing halide substituents were also successful coupling partners (entries 8 and 9), yielding selective substitution of the iodide to generate halogenated thioethers. In addition to arene thiols, aliphatic thiols were found to yield the desired thioethers in good yields (entries 13 and 14). In sum, C–S cross-coupling reactions of thiols with aryl iodides employing **1** as a precatalyst demonstrate good efficacy for a range of different substrates.

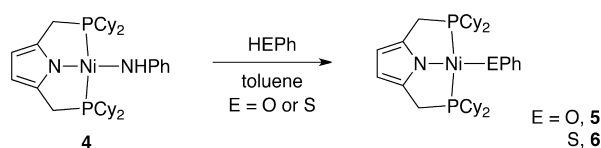
Synthesis of Nickel(II) Complexes Containing N, O, and S-Bound Ligands. Given the precedent for decom-

position of phosphinite-based pincer ligands during C–S coupling,²⁵ we next investigated the synthesis and reactivity of several Ni(II) complexes relevant to the catalytic reaction to examine if similar processes are responsible for the activity observed in our PNP system. Since catalytic activity was observed for nickel(II) complexes of each of the three ligands displayed in Chart 1, we elected to focus on P₂^{Cy}Pyr, as complexes of this ligand have proven to be more stable and easier to work with in terms of solubility and crystallinity.

The synthesis of Ni(II) complexes containing heteroatom ligands proceeded in good yield from **2** via simple salt metathesis (4–6, Scheme 2). Related complexes have been reported previously for both Ni-PCP and Ni-PNP systems.^{26,34–36} Several of the compounds display intense colors

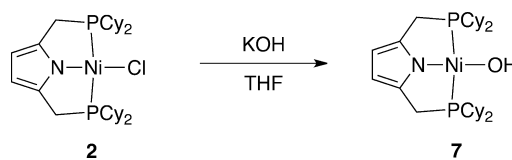
Scheme 2. Preparation of $[\text{NiX}(\text{P}_2^{\text{CyPyr}})]$ Complexes

resulting from transitions in the visible region of the spectrum (see the Supporting Information). Alternatively, the phenolate and thiophenolate complexes, **5** and **6**, could be prepared by protonolysis reactions of the amide complex **4** with the corresponding conjugate acids (Scheme 3). The synthetic procedures in Scheme 2 were also amenable to complexes of the $\text{P}_2^{\text{PhPyr}}$ ligand for $\text{E} = \text{O}$ and S (see the Supporting Information).

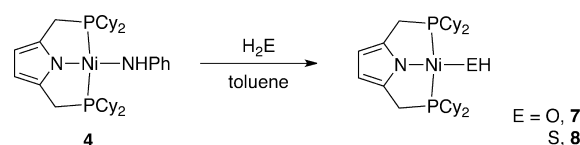
Scheme 3. Protonolysis of $[\text{Ni}(\text{NHPh})(\text{P}_2^{\text{CyPyr}})]$ by HOPh and HSPH

The solid-state structures of complexes **4**–**6** are displayed in Figure 2. Each structure contains a square-planar Ni(II) ion with PNP ligand metrics similar to those observed for previously reported nickel halide and alkyl complexes of $\text{P}_2^{\text{CyPyr}}$.²⁰ Complexes **4** and **5** feature short Ni–X bond distances consistent with reports of other amide and alkoxide complexes of Ni(II) PNP compounds.^{26,34,37} The N-bound hydrogen atom in **4** could not be identified from the electron density map and the location of this atom in Figure 2 represents a calculated position.

The requirement of KOH or NaOH in the C–S cross-coupling reactions prompted us to explore the preparation of a terminal Ni(II) hydroxide complex because of the possible involvement of such a species during catalysis. Treatment of **2** with NaOH or KOH in THF was found to produce the hydroxide complex, $[\text{Ni}(\text{OH})(\text{P}_2^{\text{CyPyr}})]$ (**7**), after 24 h at room temperature (Scheme 4).^{38,39} Alternatively, complex **7** could be prepared from the amide complex **4** by treatment with H_2O in

Scheme 4. Synthesis of $[\text{Ni}(\text{OH})(\text{P}_2^{\text{CyPyr}})]$ 

toluene.⁴⁰ The Brønsted basicity of **4** also permitted the synthesis of the rare terminal hydrosulfide complex, **8**, through an analogous reaction with H_2S (Scheme 5). Despite the

Scheme 5. Protonolysis of $[\text{Ni}(\text{NHPh})(\text{P}_2^{\text{CyPyr}})]$ Complexes by H_2O and H_2S 

successful synthesis of both nickel hydroxide and hydrosulfide complexes with the $\text{P}_2^{\text{CyPyr}}$ ligand, attempts to prepare a nickel hydroxide complex bearing the $\text{P}_2^{\text{PhPyr}}$ ligand were unsuccessful.

Complexes **7** and **8** display sharp upfield ^1H NMR resonances for the EH protons at -4.79 and -2.26 ppm, respectively. The resonances appear as triplets, consistent with coupling to the two phosphorus atoms of the PNP ligand. The solid-state structures of **7** and **8** are displayed in Figure 3. The Ni–X distances are shorter than those in the corresponding alkoxide and thiolate complexes (Figure 2). Inspection of the packing diagrams for both **7** and **8** demonstrates no intermolecular interactions suggestive of hydrogen bonding in the solid state.

Stoichiometric Reactions Relevant to C–S Cross-Coupling. In order to gain more information about the nature of the active nickel species present during C–S cross-coupling catalysis, we next examined several stoichiometric reactions with the well-defined Ni pincer complexes. We first investigated the reaction of **6** with 4-iodotoluene in $\text{DMF-}d_7$ at 80°C to determine if the Ni(II) thiolate species is capable of effecting C–S bond formation under conditions present during catalysis. Prolonged heating (20 h) of **6** and 4-iodotoluene at 80°C led

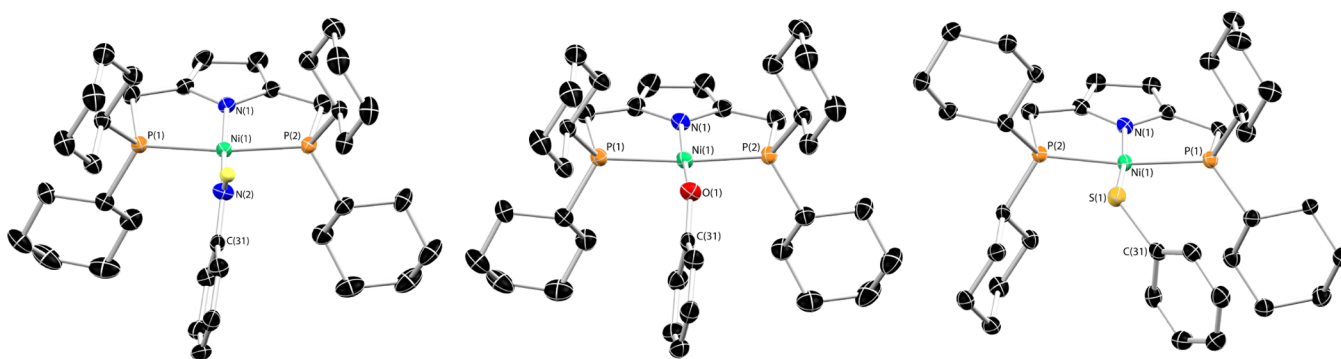


Figure 2. Thermal ellipsoid drawings (50%) of $[\text{Ni}(\text{NHPh})(\text{P}_2^{\text{CyPyr}})]$ (**4**), $[\text{Ni}(\text{OPh})(\text{P}_2^{\text{CyPyr}})]$ (**5**), and $[\text{Ni}(\text{SPh})(\text{P}_2^{\text{CyPyr}})]$ (**6**). Hydrogen atoms and cocrystallized solvent molecules omitted for clarity. Selected bond lengths (Å) and angles (deg) for **4**: Ni(1)–N(1) = 1.8509(16); Ni(1)–N(2) = 1.8891(18); Ni(1)–P_{avg} = 2.193(1); N(1)–Ni(1)–N(2) = 176.50(8); P(1)–Ni(1)–P(2) = 169.28(2); for **5**: Ni(1)–N(1) = 1.850(2); Ni(1)–O(1) = 1.867(2); Ni(1)–P_{avg} = 2.199(1); N(1)–Ni(1)–O(1) = 173.22(10); P(1)–Ni(1)–P(2) = 169.32(3); for **6**: Ni(1)–N(1) = 1.873(3); Ni(1)–S(1) = 2.1956(12); Ni(1)–P_{avg} = 2.202(1); N(1)–Ni(1)–S(1) = 171.51(10); P(1)–Ni(1)–P(2) = 168.38(4).

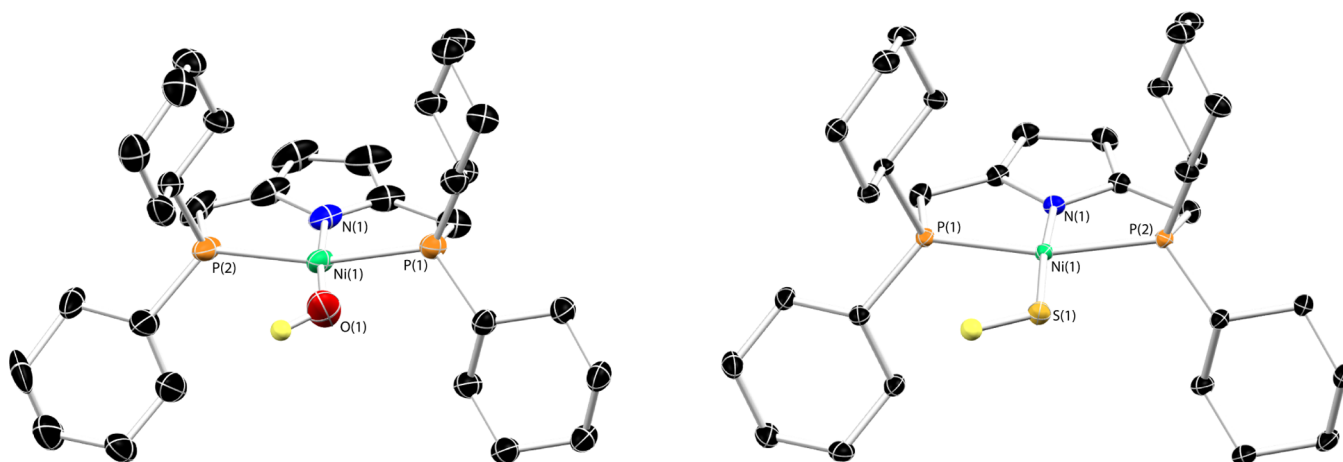
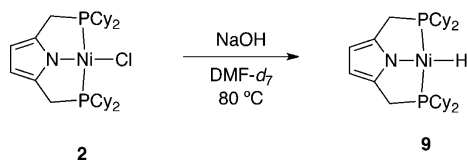


Figure 3. Thermal ellipsoid drawings (50%) of $[\text{Ni}(\text{OH})(\text{P}_2^{\text{CyPyr}})]$ (**7**) and $[\text{Ni}(\text{SH})(\text{P}_2^{\text{CyPyr}})]$ (**8**). Hydrogen atoms and minor disordered component of **7** omitted for clarity. Selected bond distances (Å) and angles (deg) for **7**: $\text{Ni}(1)\text{--}\text{N}(1) = 1.843(3)$; $\text{Ni}(1)\text{--}\text{O}(1) = 1.789(9)$; $\text{Ni}(1)\text{--}\text{P}_{\text{avg}} = 2.188(2)$; $\text{N}(1)\text{--}\text{Ni}(1)\text{--}\text{O}(1) = 173.7(4)$; $\text{P}(1)\text{--}\text{Ni}(1)\text{--}\text{P}(2) = 165.13(4)$; for **8**: $\text{Ni}(1)\text{--}\text{N}(1) = 1.8635(13)$; $\text{Ni}(1)\text{--}\text{S}(1) = 2.1719(4)$; $\text{Ni}(1)\text{--}\text{P}_{\text{avg}} = 2.189(1)$; $\text{N}(1)\text{--}\text{Ni}(1)\text{--}\text{S}(1) = 175.65(4)$; $\text{P}(1)\text{--}\text{Ni}(1)\text{--}\text{P}(2) = 165.294(16)$.

to no formation of 4-tolylphenylsulfide as judged by NMR spectroscopy (see Supporting Information, Figure S12). In addition, no decomposition of **6** was apparent during the reaction. This result demonstrates that direct reaction of a Ni(II) thiolate species with aryl iodide is not responsible for C–S bond formation during catalysis. Such a finding is consistent with the observations of Guan with the nickel POCOP system, where only minor amounts of coupled C–S products were detected from the reaction of a nickel thiolate complex with iodobenzene.²⁵

The lack of reactivity of **6** with iodotoluene suggested that decomposition of precatalyst **2** to give a new nickel species might be responsible for the catalytic activity observed in our system in similar fashion to that reported for Ni POCOP. Therefore, we next examined the stability of **2** in the presence of NaOH and DMF-*d*₇ at 80 °C. Unexpectedly, **2** was not found to decompose appreciably under these conditions but rather to generate the nickel(II) hydride species, $[\text{NiH}(\text{P}_2^{\text{CyPyr}})]$ (**9**), as judged by ¹H and ³¹P NMR spectroscopy (Scheme 6 and Figure 4). A small amount of decomposition

Scheme 6. Reaction of $[\text{NiCl}(\text{P}_2^{\text{CyPyr}})]$ with NaOH in DMF



does appear to occur in tandem with hydride formation as resonances for the free ligand can be observed in both ¹H and ³¹P NMR spectra (Figure 4). However, this decomposition amounts to less than 5%. Similar results were obtained when complex **3** was heated in DMF-*d*₇ in the presence of NaOH. In contrast, however, subjecting complex **1** to the aforementioned reaction conditions was found to lead to no detectable nickel hydride species as judged by ¹H and ³¹P NMR. Unassignable resonances due to decomposition were observed, but, as with complex **2**, these peaks accounted for only a small fraction of the total species in solution, with complex **1** remaining as the major species. Lack of reactivity with **1** under these conditions is consistent with our inability to isolate a nickel hydroxide

complex with this ligand and with the previously reported failure to generate a nickel hydride complex of $\text{P}_2^{\text{PhPyr}}$.^{17,20}

Control experiments with **2** in DMF at 80 °C in the absence of NaOH lead to no detectable change after several hours demonstrating that NaOH is necessary for formation of **9**. Likewise, DMF is also essential, as reaction of **2** with NaOH in benzene-*d*₆ at 80 °C leads only to formation of the hydroxide complex, **7**. One possible mechanism for the transformation in Scheme 6 is decarbonylation of a transient formate species formed from DMF and OH[−] under the reaction conditions. However, the resonance for Ni–H in Figure 4 appears to be predominantly protio and not deutero, arguing against the acyl C–H(D) bond of DMF as the source of the hydride ligand. Furthermore, reactions of excess NaO₂CH with **2** in benzene-*d*₆ or acetonitrile-*d*₃ at 80 °C failed to produce **9** as judged by ¹H NMR spectroscopy. An alternative mechanism for formation of **9** is insertion of CO, formed from DMF in the presence of base at elevated temperature,⁴¹ into **7** to give a hydroxycarbonyl complex that rapidly undergoes β-H elimination (Scheme 7). Cámpora and Palma have demonstrated formation of a bridged hydroxycarbonyl species upon treatment of a related $[(\text{PCP})\text{Ni}(\text{OH})]$ (PCP = anion of C₆H₃-2,6-(CH₂PⁱPr₂)₂) with CO in hexanes.³⁸ Likewise, Lee has recently reported formation of a hydroxycarbonyl species and its subsequent decarbonylation with a PNP Ni(II) system.⁴² In order to discern if similar reactivity is responsible for the observed formation of **9**, we examined the reaction of excess CO(g) with **7** in benzene-*d*₆ in the presence and absence of added NaOH. Very little reaction was evident at room temperature for either case as judged by ¹H NMR, but heating to 80 °C for 2 h did lead to complete consumption of the OH resonance at −4.79 ppm. Of the multitude of compounds formed in the reaction, however, none corresponded to **9**. Therefore, if CO is responsible for formation of **9**, DMF must play an important role in selecting for formation of the hydride.

Although unlikely, given the activity of **1**, we nonetheless examined the reactivity of **9** with 4-iodotoluene to determine if the hydride complex could play a role in catalysis. Upon prolonged heating (20 h) of **9** with 4-iodotoluene in DMF-*d*₇ at 80 °C a new nickel(II) species was observed to form. This new species was identified as the iodide complex, $[\text{NiI}(\text{P}_2^{\text{CyPyr}})]$ (**10**), based on its ¹H and ³¹P NMR spectra, and on the

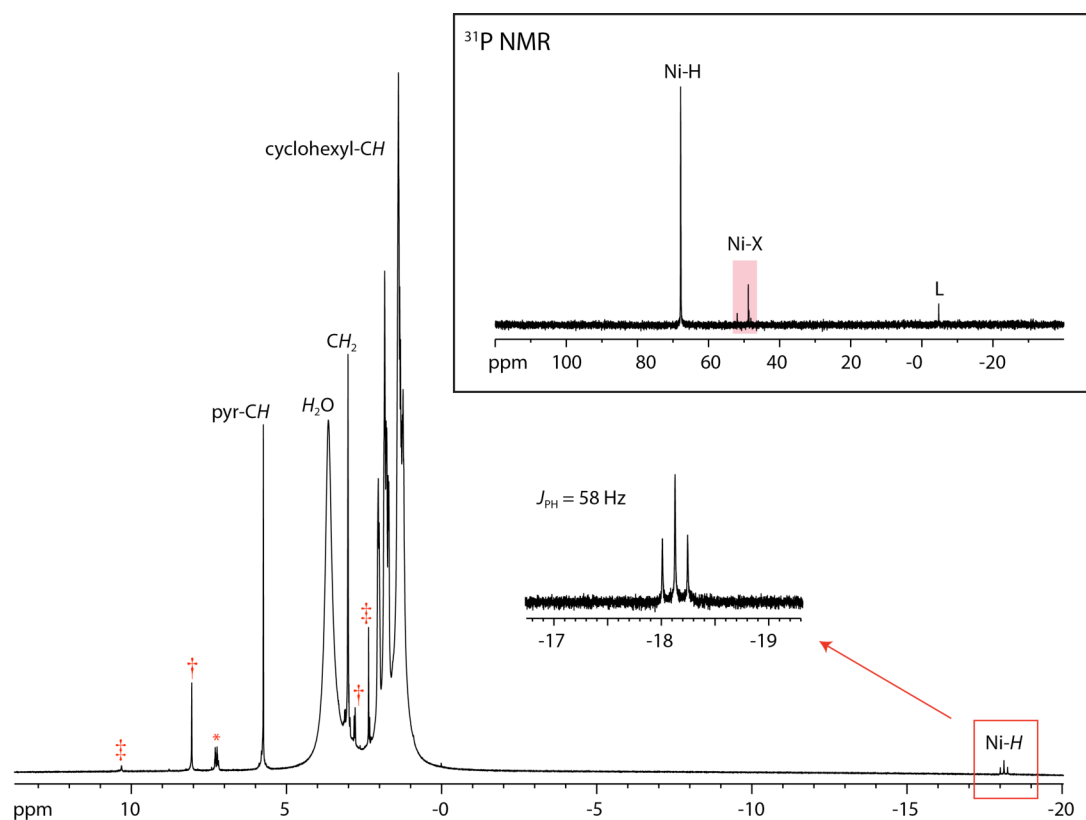
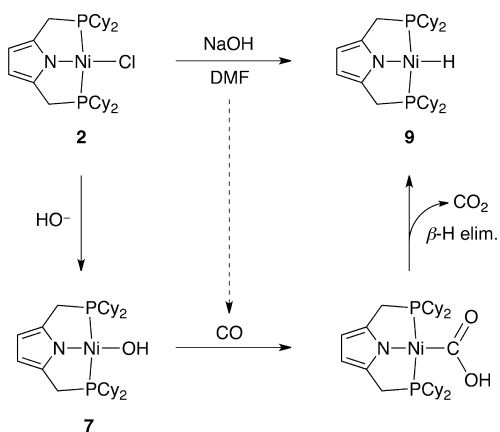


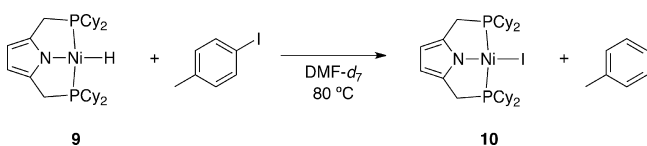
Figure 4. 500 MHz ^1H NMR spectrum of the reaction of $[\text{NiCl}(\text{P}_2^{\text{Cy}}\text{Pyr})]$ with NaOH in $\text{DMF-}d_7$ after heating to 80°C for 2 h. † = $\text{DMF-}d_7$ solvent; ‡ = $\text{H}(\text{P}_2^{\text{Cy}}\text{Pyr})$; * = residual toluene from purification. Inset displays corresponding ^{31}P NMR.

Scheme 7. Possible Pathway for Formation of $[\text{NiH}(\text{P}_2^{\text{Cy}}\text{Pyr})]$ (9) from $[\text{NiCl}(\text{P}_2^{\text{Cy}}\text{Pyr})]$ (2)



observation that addition of KI to a $\text{DMF-}d_7$ solution of **2** produces the identical compound (Figures S13). The iodide complex forms concomitantly with toluene demonstrating that hydride transfer from **9** has taken place (Scheme 8). At this time we do not know the mechanism for the reaction in

Scheme 8. Reaction of $[\text{NiH}(\text{P}_2^{\text{Cy}}\text{Pyr})]$ with 4-Iodotoluene



Scheme 8, but we note that Agapie has observed a related hydride transfer to arene with a nickel(II) phosphine complex at elevated temperature, which proceeds through the intermediacy of a $\eta^3\text{-aryl}$.⁴³ A second nickel(II) species was also identified during the reaction shown in Scheme 8 albeit in very minor quantities and only after heating for 20 h (Figure S13). The ^{31}P resonance for this species is very similar to that observed for $[\text{Ni}(\text{Ph})(\text{P}_2^{\text{Cy}}\text{Pyr})]$, and therefore we assign this complex as the putative nickel tolyl. Nonetheless, the reaction of an intermediate hydride complex with 4-iodotoluene appears to be too slow to account for any observed catalytic activity.

As a final experiment, we investigated the reaction of **2** with excess NaSPh to determine if thiolate is capable of reducing **2** under catalytic conditions and providing access to Ni(I) or Ni(0) species. Morales-Morales has proposed that both Ni(I) and Ni(0) are involved in C–S cross-coupling reactions employing a Ni(II) bis(imino)pyridine precatalyst.²² In the Morales-Morales system, however, external reductant is present during catalysis. Gratifyingly, reaction of **2** with 3 equiv of NaSPh in $\text{DMF-}d_7$ at 80°C for 2 h produced several new species (Figure 5). Complex **2** is completely consumed, and the major Ni species in solution is **6**. In addition to **6** and free NaSPh, peaks in the ^1H NMR spectrum assignable to PhSSPh and a new species (-11.6 ppm) are also present in minor amounts. Based on the ^1H chemical shift and our inability to identify a ^{31}P NMR signal for this new species, we tentatively assign it as a paramagnetic Ni(I) complex. Addition of 4-iodotoluene to this mixture followed by additional heating for 2 h led to complete consumption of both free NaSPh and the species responsible for the peak at -11.6 ppm (Figure 5). Furthermore, peaks due to the expected C–S coupling product, 4-tolylphenylsulfide, were observed to form. Throughout the

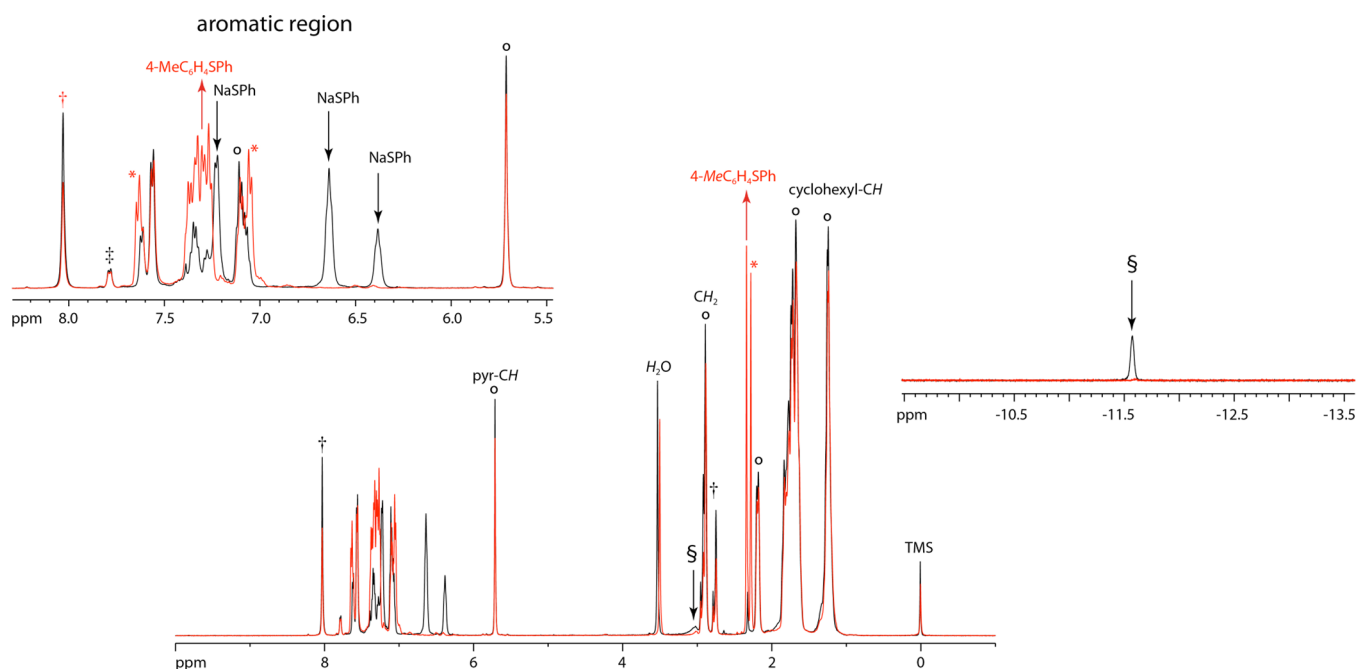
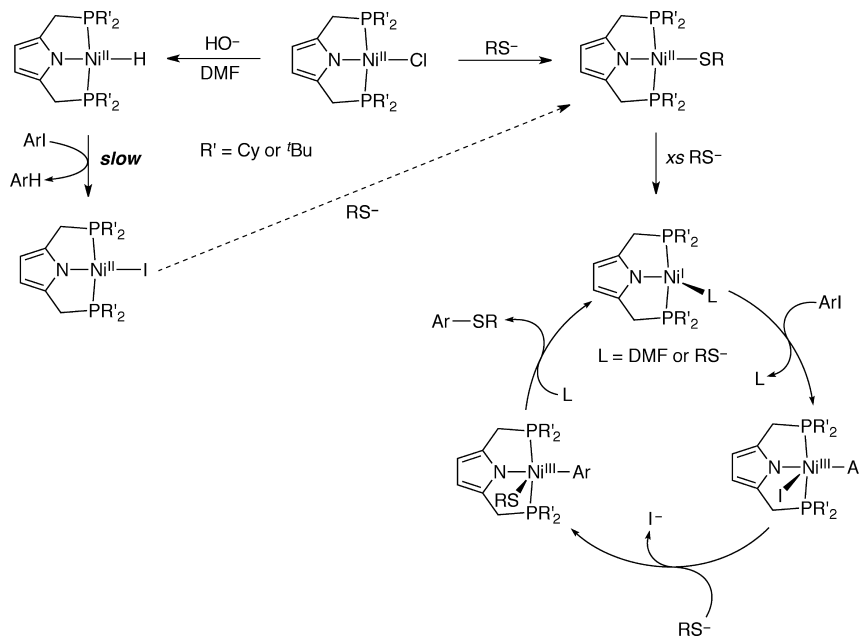


Figure 5. 500 MHz ^1H NMR spectra of the reaction of $[\text{NiCl}(\text{P}_2^{\text{Cy}}\text{Pyr})]$ (**2**) with 3 equiv of NaSPh in $\text{DMF-}d_7$ after heating to $80\text{ }^\circ\text{C}$ for 2 h (black) and after addition of 4-iodotoluene and additional heating (red). † = $\text{DMF-}d_7$ solvent; ° = $[\text{Ni}(\text{SPh})(\text{P}_2^{\text{Cy}}\text{Pyr})]$ (**6**); ‡ = PhSSPh; § = new Ni species; * = 4-iodotoluene.

Scheme 9. Proposed Catalytic Cycle for C–S Cross-Coupling with PNP Ni Complexes



reaction with 4-iodotoluene, resonances attributable to **6** remained unchanged. An analogous reaction of **1** with excess NaSPh in $\text{DMF-}d_7$ at $80\text{ }^\circ\text{C}$ produced a similar resonance at -11.6 ppm consistent with a closely related active species for both catalysts (Figure S14). Cyclic voltammery experiments with **6** identified an irreversible reduction event at potentials below 2 V (i.e., -2.61 V in THF and -2.33 in DMF; see the SI). This low value indicates that simple outer-sphere electron transfer to generate a Ni(I) species is unlikely and that coordination of additional PhS^- to **6** may be required for reduction.

The results of stoichiometric reactions with well-defined nickel complexes suggest that the active species in C–S cross-coupling reactions employing Ni precatalysts **1–3** is a PNP Ni(I) species formed by reduction in the presence of thiolate. A proposed catalytic cycle based on this proposal that incorporates the results of other stoichiometric reactions is shown in Scheme 9. The catalytic cycle in Scheme 9 accounts for several observations. First, the inactivity of thiolate complex **6**: this species most likely represents a dormant state for the catalyst. Second, the superiority of complex **1** as a precatalyst: complex **1** is both the easiest to reduce to Ni(I) based on measured reduction potentials (see the SI) and is incapable of

forming a Ni–H species.^{16,20} Third, the inability to observe cross-coupling with anilines or phenols: these nucleophiles are incapable of effecting reduction to Ni(I) under the catalytic conditions. Finally, the electrophile scope of the catalytic reaction: the reducing potential of the Ni(I) species is modest and only capable of undergoing oxidative addition with activated electrophiles (aryl iodides).

CONCLUSIONS

In this contribution we have described the catalytic activity of a series of Ni PNP complexes in C–S cross-coupling reactions. The most successful electrophilic coupling partners were found to be aryl iodides, which demonstrated good substrate scope for a variety of substitution patterns. Coupling reactions were successful with both aryl and alkyl thiols with isolated yields between 76 and 97%. Synthesis of several PNP nickel complexes containing heteroatom ligands has permitted an examination of the nickel species responsible for catalytic activity. The results of these studies support the proposal that intact PNP Ni pincer complexes are capable of catalyzing C–S cross-coupling reactions and that a cycle involving Ni(I) is likely operative. Such a conclusion is consistent with Ni-catalyzed C–C cross-coupling reactions where well-defined paramagnetic complexes are now believed to play an important role.^{44–46}

EXPERIMENTAL SECTION

General Comments. Unless otherwise noted, all manipulations were performed under an atmosphere of nitrogen gas using standard Schlenk technique or in a Vacuum Atmospheres glovebox. Tetrahydrofuran, diethyl ether, pentane, dichloromethane, and toluene were purified by sparging with argon and passage through two columns packed with 4 Å molecular sieves. Benzene and benzene-*d*₆ were dried over sodium ketyl and vacuum-distilled prior to use. Melting points were obtained in glass capillaries sealed with a plug of silicone grease and are reported as uncorrected values. NMR spectra were recorded in benzene-*d*₆ on a Varian spectrometer operating at 500 MHz (¹H). Chemical shift values were referenced to the residual ¹H (7.16 ppm) or ¹³C (128.39 ppm) resonance of solvent, except in the case of ³¹P NMR, where an external standard of 85% aq H₃PO₄ (0.00 ppm) was used. Coupling constants (*J*) are reported in units of Hz. FT-IR spectra were recorded with a Thermo Nicolet iS 10 spectrophotometer as thin films on a NaCl plate or as solid samples pressed into KBr disks. UV–vis spectra were recorded in toluene on a Cary-60 spectrophotometer in airtight Teflon-capped quartz cells. Elemental analyses were performed by Atlantic Microlab of Norcross, GA.

Materials. 2,5-Bis(dimethylaminomethyl)pyrrole and the nickel complexes [NiCl(P₂^{Ph}Pyr)], [NiCl(P₂^{Cy}Pyr)], [NiH-(P₂^{Cy}Pyr)], and [Ni(Ph)(P₂^{Cy}Pyr)] were prepared by published procedures.^{16,20,47} Aniline, phenol, thiophenol, triethylamine, sodium phenoxide, sodium thiophenolate, and sodium/potassium hydroxide were purchased from commercial suppliers and used as received. Hydrogen sulfide was purchased from Praxair and used as received. LiNHPPh was prepared by deprotonation of aniline with *n*-BuLi in THF.

X-ray Data Collection and Structure Solution Refinement. Crystals suitable for X-ray diffraction were mounted in Paratone oil onto a glass fiber and frozen under a nitrogen cold stream maintained by a X-Stream low-temperature apparatus. The data were collected at 98(2) K using a Rigaku AFC12/

Saturn 724 CCD fitted with Mo K α radiation ($\lambda = 0.71073$ Å). Data collection and unit cell refinement were performed using *Crystal Clear* software.⁴⁸ Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with *Crystal Clear* and ABCOR, respectively.⁴⁹ All structures were solved by direct methods and refined on F² using full-matrix, least-squares techniques with SHELXL-97.^{50,51} All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. Crystallographic data and refinement parameters can be found in the Supporting Information.

H(P₂^{tBu}Pyr). A sealable flask was charged with 1.08 g (6.0 mmol) of 2,5-bis-(dimethylaminomethyl)pyrrole and 2.2 mL (12 mmol) of di-*tert*-butylphosphine. The contents of the sealed flask were heated to 140 °C and allowed to stir for 20 h. The reaction mixture was cooled to room temperature, and all volatiles were removed in vacuo to afford 2.0 g (88%) of the desired compound as a white solid. The material was used immediately for nickel chemistry without further purification. ¹H NMR: δ 8.59 (br s, 1 pyr-NH), 6.08 (d, 2 pyr-CH, *J*_{HH} = 2.7), 2.73 (s, 4 CH₂), 1.04 (d, 36 *t*-Bu, *J*_{HP} = 10.5). ¹³C{¹H} NMR: δ 129.24 (d, *J*_{CP} = 12.6), 107.27 (m), 31.73 (d, *J*_{CP} = 23.0), 30.09 (d, *J*_{CP} = 12.8), 21.08 (d, *J*_{CP} = 23.5). ³¹P{¹H} NMR: δ -7.66. ESI-MS (positive mode): calcd for [M + H]⁺ *m/z* 384.3; found for [M + H]⁺ *m/z* 384.1.

[NiCl(P₂^{tBu}Pyr)]. A flask was charged with 1.14 g (2.97 mmol) of H(P₂^{tBu}Pyr) and 30 mL of THF. To the solution was added 0.388 g (2.99 mmol) of NiCl₂ and 0.83 mL (6.0 mmol) of Et₃N. The mixture was allowed to stir for 12 h at room temperature during which time it became dark red. All volatiles were removed in vacuo leaving a dark red residue, which was extracted into 50 mL of benzene. The benzene extract was filtered through a pad of Celite to remove Et₃NHCl. The resulting solution was evaporated to dryness to afford 1.20 g (85%) of the desired complex as a red solid. Crystals suitable for X-ray diffraction were grown by cooling of a saturated diethyl ether solution at -35 °C. Mp: 260 °C (decomp). ¹H NMR: δ 6.22 (s, 2 pyr-CH), 2.64 (app t, 4 CH₂, *J*_{HP} = 4.2), 1.37 (app t, 36 *t*-Bu, *J*_{HP} = 6.5). ¹³C{¹H} NMR: δ 138.67 (t, *J*_{CP} = 6.8), 105.53 (t, *J*_{CP} = 4.8), 35.42 (t, *J*_{CP} = 6.7), 29.61 (t, *J*_{CP} = 1.9), 23.60 (t, *J*_{CP} = 9.7). ³¹P{¹H} NMR: δ 64.93. Anal. Calcd for C₂₂H₄₂ClN₂NiP₂: C, 55.43; H, 8.88; N, 2.94. Found: C, 55.70; H, 8.88; N, 2.90.

[Ni(NHPPh)(P₂^{Cy}Pyr)]. A flask was charged with 0.116 g (0.200 mmol) of [NiCl(P₂^{Cy}Pyr)] and 10 mL of THF. To the resulting solution was added 0.030 g (0.30 mmol) of solid LiNHPPh. The reaction mixture was allowed to stir for 6 h at room temperature during which time it slowly darkened from red to purple. All volatiles were removed in vacuo, and the remaining residue was extracted into 10 mL of benzene. The purple extract was filtered through a pad of Celite and the benzene evaporated to dryness. The residue was then washed with pentane and dried in vacuo to afford 0.109 g (86%) of the desired compound as a purple microcrystalline solid. Crystals suitable for X-ray diffraction were grown by cooling of a saturated diethyl ether solution of the complex at -30 °C. Mp: 184–186 °C. ¹H NMR: δ 7.19 (m, 2 *m*-NHPPh), 6.97 (d, 2 *o*-NHPPh), 6.50 (t, 1 *p*-NHPPh), 6.36 (s, 2 pyr-CH), 2.67 (app t, 4 CH₂, *J*_{HP} = 4.2), 2.23 (app d, 4 Cy-CH), 1.77 (m, 4 Cy-CH), 1.69–1.45 (overlapping m, 24 Cy-CH), 1.12 (m, 8 Cy-CH), 1.01 (m, 4 Cy-CH), -1.20 (s, 1 NHPPh). ¹³C{¹H} NMR: δ 160.91, 137.67 (t, *J*_{CP} = 7.5), 129.24, 117.80, 110.72, 105.87 (t,

$J_{CP} = 5.0$), 33.85 (t, $J_{CP} = 9.6$), 28.91, 28.60, 27.58 (t, $J_{CP} = 5.9$), 27.39 (t, $J_{CP} = 4.8$), 26.85, 23.23 (t, $J_{CP} = 10.4$). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 42.71. IR (KBr) ν , cm^{-1} : 3352 (ν_{NH}). UV-vis λ , nm, (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 350 (6500), 446 (500), 561 (1400). Anal. Calcd for $\text{C}_{36}\text{H}_{56}\text{N}_2\text{NiP}_2$: C, 67.83; H, 8.85; N, 4.39. Found: C, 67.81; H, 9.09; N, 4.26.

[Ni(OPh)(P₂^{Cy}Pyr)]. A flask was charged with 0.116 g (0.200 mmol) of $[\text{NiCl}(\text{P}_2^{\text{Cy}}\text{Pyr})]$ and 10 mL of THF. To the resulting solution was added 0.034 g (0.29 mmol) of NaOPh. The reaction mixture was allowed to stir for 8 h at room temperature during which time the red color brightened slightly. All volatiles were removed in vacuo, and the remaining residue was extracted into 10 mL of benzene. The red extract was filtered through a pad of Celite and the benzene evaporated to dryness. The residue was then washed with pentane and dried in vacuo to afford 0.122 g (96%) of the desired compound as a bright red microcrystalline solid. Crystals suitable for X-ray diffraction were grown by cooling of a saturated diethyl ether solution of the complex at -30°C . Mp: 191–193 $^\circ\text{C}$. ^1H NMR: δ 7.34 (d, 2 *o*-OPh), 7.25 (t, 2 *m*-OPh), 6.68 (t, 1 *p*-OPh), 6.31 (s, 2 pyr-CH), 2.61 (app t, 4 CH₂, $J_{\text{HP}} = 4.5$), 2.32 (app d, 4 Cy-CH), 1.72 (m, 16 Cy-CH), 1.62 (app d, 4 Cy-CH), 1.56 (m, 8 Cy-CH), 1.16 (m, 8 Cy-CH), 1.01 (m, 4 Cy-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 169.37, 138.08 (t, $J_{CP} = 7.2$), 129.21, 121.62, 114.05, 106.27 (t, $J_{CP} = 4.8$), 33.49 (t, $J_{CP} = 9.3$), 28.53, 28.45, 27.53 (t, $J_{CP} = 6.1$), 27.38 (t, $J_{CP} = 5.0$), 26.81, 22.09 (t, $J_{CP} = 10.9$). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 42.33. UV-vis λ , nm, (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 304 (12000), 335 (sh), 477 (1300). Anal. Calcd for $\text{C}_{36}\text{H}_{55}\text{NNiOP}_2$: C, 67.72; H, 8.68; N, 2.19. Found: C, 68.00; H, 8.67; N, 2.36.

[Ni(SPh)(P₂^{Cy}Pyr)]. A flask was charged with 0.116 g (0.200 mmol) of $[\text{NiCl}(\text{P}_2^{\text{Cy}}\text{Pyr})]$ and 10 mL of THF. To the resulting solution was added 0.039 g (0.30 mmol) of NaSPh. The reaction mixture was allowed to stir for 8 h at room temperature during which time the color changed slowly from red to pinkish-red. All volatiles were removed in vacuo, and the remaining residue was extracted into 10 mL of benzene. The pinkish-red extract was filtered through a pad of Celite and the benzene evaporated to dryness. The residue was then washed with pentane and dried in vacuo to afford 0.119 g (92%) of the desired compound as a pinkish-red microcrystalline solid. Crystals suitable for X-ray diffraction were grown by cooling of a saturated diethyl ether solution of the complex at -30°C . Mp: 187–189 $^\circ\text{C}$. ^1H NMR: δ 7.91 (d, 2 *o*-SPh), 7.01 (t, 2 *m*-SPh), 6.94 (t, 1 *p*-SPh), 6.44 (s, 2 pyr-CH), 2.78 (app t, 4 CH₂, $J_{\text{HP}} = 4.2$), 2.32 (app d, 4 Cy-CH), 1.71 (m, 12 Cy-CH), 1.64–1.52 (overlapping multiplets, 16 Cy-CH), 1.13 (m, 8 Cy-CH), 1.00 (m, 4 Cy-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ one peak obscured by solvent, 147.56 (t, $J_{CP} = 6.4$), 137.34 (t, $J_{CP} = 7.2$), 135.62, 123.55, 105.72 (t, $J_{CP} = 5.1$), 33.95 (t, $J_{CP} = 10.6$), 29.14, 28.67, 27.53 (overlapping triplets), 26.86, 24.46 (t, 10.7). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 50.02. UV-vis λ , nm, (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 294 (19000), 336 (sh), 424 (1000), 540 (730). Anal. Calcd for $\text{C}_{36}\text{H}_{55}\text{NNiP}_2\text{S}$: C, 66.06; H, 8.47; N, 2.14; S, 4.90. Found: C, 65.96; H, 8.57; N, 2.06; S, 5.00.

[Ni(OH)(P₂^{Cy}Pyr)]. **Procedure A.** A flask was charged with 0.127 g (0.199 mmol) of $[\text{Ni}(\text{NHPh})(\text{P}_2^{\text{Cy}}\text{Pyr})]$ and 10 mL of toluene. To the resulting solution was added 0.1 mL of H₂O via syringe. The reaction mixture was allowed to stir for 12 h at room temperature during which time the color darkened from red to brown. All volatiles were removed in vacuo, and the remaining residue was extracted into 10 mL of benzene. The brown extract was filtered through a pad of Celite and the

benzene evaporated to dryness. The residue was washed with pentane and dried in vacuo to afford 0.099 g (89%) of the desired compound as a yellowish-orange solid.

Procedure B. A flask was charged with 0.116 g (0.200 mmol) of $[\text{NiCl}(\text{P}_2^{\text{Cy}}\text{Pyr})]$ and 10 mL of THF. To the resulting solution was added 0.056 g (1.0 mmol) of KOH as a ground solid. The reaction mixture was allowed to stir for 24 h at room temperature during which time the red color slowly lightened to yellowish-orange. All volatiles were removed in vacuo, and the remaining residue was extracted into 10 mL of benzene. The orange extract was filtered through a pad of Celite and the benzene evaporated to dryness. The residue was then washed with pentane and dried in vacuo to afford 0.079 g (71%) of the desired compound as a yellowish-orange solid. Crystals suitable for X-ray diffraction were grown by cooling of a saturated diethyl ether solution of the complex at -30°C . ^1H NMR: δ 6.35 (s, 2 pyr-CH), 2.69 (app t, 4 CH₂, $J_{\text{HP}} = 4.2$), 2.41 (app d, 4 Cy-CH), 1.81 (m, 4 Cy-CH), 1.74 (m, 16 Cy-CH), 1.66 (m, 4 Cy-CH), 1.59 (m, 4 Cy-CH), 1.16 (m, 8 Cy-CH), 1.07 (m, 4 Cy-CH), -4.79 (t, 1 OH, $J_{\text{HP}} = 5.8$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 137.43 (t, $J_{CP} = 7.5$), 105.73 (t, $J_{CP} = 5.0$), 32.80 (t, $J_{CP} = 9.4$), 28.90, 28.56, 27.55 (t, $J_{CP} = 6.2$), 27.39 (t, $J_{CP} = 4.9$), 26.91, 23.03 (t, $J_{CP} = 10.8$). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 43.32. IR (KBr) ν , cm^{-1} : 3355 (ν_{OH}). UV-vis λ , nm, (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 293 (2800), 317 (3000), 421 (1000), 514 (150). Anal. Calcd for $\text{C}_{30}\text{H}_{51}\text{NNiOP}_2\cdot\text{H}_2\text{O}$: C, 62.08; H, 9.20; N, 2.41. Found: C, 61.68; H, 8.78; N, 2.39.

[Ni(SH)(P₂^{Cy}Pyr)]. A flask was charged with 0.127 g (0.199 mmol) of $[\text{Ni}(\text{NHPh})(\text{P}_2^{\text{Cy}}\text{Pyr})]$ and 10 mL of toluene. The flask was sealed with a septum, and H₂S gas (~ 1 atm) was added to the headspace of the reaction vessel. Upon addition of H₂S, the purple solution immediately changed to reddish-brown. The reaction mixture was allowed to stir for a further 2 min at room temperature before all volatiles were removed in vacuo. The remaining solid was washed with pentane to afford 0.112 g (97%) of the desired compound as brown microcrystals. Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a saturated benzene solution at room temperature. Mp: 183–185 $^\circ\text{C}$. ^1H NMR: δ 6.43 (s, 2 pyr-CH), 2.79 (app t, 4 CH₂, $J_{\text{HP}} = 4.5$), 2.31 (app d, 4 Cy-CH), 1.84 (m, 4 Cy-CH), 1.74–1.44 (overlapping m, 24 Cy-CH), 1.13 (m, 8 Cy-CH), 1.04 (m, 4 Cy-CH), -2.26 (t, 1 SH, $J_{\text{HP}} = 19.5$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 137.05 (t, $J_{CP} = 7.1$), 105.38 (t, $J_{CP} = 5.2$), 33.46 (t, $J_{CP} = 10.9$), 28.91, 28.57, 27.55 (t, $J_{CP} = 6.2$), 27.36 (t, $J_{CP} = 5.1$), 26.84, 25.07 ($J_{CP} = 11.1$). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 55.36. IR (KBr) ν , cm^{-1} : 2539 (ν_{SH}). UV-vis λ , nm, (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 322 (8200), 387 (390), 521 (250). Anal. Calcd for $\text{C}_{30}\text{H}_{51}\text{NNiP}_2\text{S}$: C, 62.29; H, 8.89; N, 2.42; S, 5.54. Found: C, 62.77; H, 8.89; N, 2.49; S, 5.49.

General Procedure for C–S Coupling Reactions. A Schlenk tube was charged with 5 mg (0.008 mmol) of $[\text{NiCl}(\text{P}_2^{\text{Ph}}\text{Pyr})]$ and 3 mL of DMF. To the solution was added 1.1 mmol of electrophile, 1.0 mmol of thiol, and 2.0 mmol of KOH. The reaction mixture was allowed to stir at 80 $^\circ\text{C}$ for 3–8 h as indicated. After this time, the reaction mixture was allowed to cool to room temperature, exposed to the ambient atmosphere, and extracted into ethyl acetate. The organic layer was washed with water and dried over sodium sulfate. The solvent was removed by rotary evaporation to afford crude product. The crude product was then purified by column chromatography on Al₂O₃ (2% EtOAc in hexanes). NMR and LC-MS analysis provided confirmation of the coupled thioether products (see the Supporting Information). Control reactions

without catalyst were performed for each substrate to ensure that uncatalyzed nucleophilic aromatic substitution was not responsible for the observed reactivity.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional experimental procedures, figures, crystal structures, tabulated crystallographic data, and crystallographic information (cif) files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zachary.tonzetich@utsa.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a grant from the Welch Foundation (AX-1772). G.T.V. also acknowledges partial support from the UTSA TRAC program. The authors thank Mr. Jacob Przyojski and Mr. Daniel Meininger for assistance with NMR measurements.

■ REFERENCES

- (1) Hartwig, J. F. *Nature* **2008**, *455*, 314–322.
- (2) Magano, J.; Dunetz, J. R. *Chem. Rev.* **2011**, *111*, 2177–2250.
- (3) Beller, M.; Riermeier, T. H. *Transition metal-catalyzed C-N and C-O bond-forming reactions*; Wiley-VCH Verlag GmbH: 1998; Vol. 1.
- (4) Kondo, T.; Mitsudo, T.-a. *Chem. Rev.* **2000**, *100*, 3205–3220.
- (5) Muci, A.; Buchwald, S. Practical Palladium Catalysts for C-N and C-O Bond Formation. In *Cross-Coupling Reactions*; Miyaura, N., Ed.; Springer: Berlin, Heidelberg, 2002; Vol. 219, p 131–209.
- (6) Bichler, P.; Love, J. Organometallic Approaches to Carbon–Sulfur Bond Formation. In *C-X Bond Formation*; Vigalok, A., Ed.; Springer: Berlin, Heidelberg, 2010; Vol. 31, p 39–64.
- (7) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596–1636.
- (8) Beletskaya, I. P.; Cheprakov, A. V. *Organometallics* **2012**, *31*, 7753–7808.
- (9) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109–13110.
- (10) Vogel, G. C.; Drago, R. S. *J. Chem. Educ.* **1996**, *73*, 701–707.
- (11) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *Comments Inorg. Chem.* **1999**, *21*, 115–129.
- (12) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44–56.
- (13) Hartwig, J. F. *Inorg. Chem.* **2007**, *46*, 1936–1947.
- (14) Devarajan, D.; Gunnoe, T. B.; Ess, D. H. *Inorg. Chem.* **2012**, *51*, 6710–6718.
- (15) Freitag, C. R.; Birk, F. J.; Ou, W. C.; Cundari, T. R. *Polyhedron* **2014**, <http://dx.doi.org/10.1016/j.poly.2014.1002.1031>.
- (16) Venkanna, G. T.; Ramos, T. V. M.; Arman, H. D.; Tonzetich, Z. *J. Inorg. Chem.* **2012**, *51*, 12789–12795.
- (17) Grüger, N.; Wadepohl, H.; Gade, L. H. *Dalton Trans.* **2012**, *41*, 14028–14030.
- (18) Kumar, S.; Mani, G.; Mondal, S.; Chattaraj, P. K. *Inorg. Chem.* **2012**, *51*, 12527–12539.
- (19) Kumar, S.; Mani, G.; Dutta, D.; Mishra, S. *Inorg. Chem.* **2014**, *53*, 700–709.
- (20) Venkanna, G. T.; Tammineni, S.; Arman, H. D.; Tonzetich, Z. *J. Organometallics* **2013**, *32*, 4656–4663.
- (21) Gómez-Benítez, V.; Baldovino-Pantaleón, O.; Herrera-Álvarez, C.; Toscano, R. A.; Morales-Morales, D. *Tetrahedron Lett.* **2006**, *47*, 5059–5062.
- (22) Baldovino-Pantaleón, O.; Hernández-Ortega, S.; Morales-Morales, D. *Adv. Synth. Catal.* **2006**, *348*, 236–242.
- (23) *The Chemistry of Pincer Compounds*; Morales-Morales, D., Jensen, C. G. M., Eds.; Elsevier B. V.: Amsterdam, 2007.
- (24) Adhikary, A.; Guan, H. Nickel-Catalyzed Cross-Coupling Reactions. In *Pincer and Pincer-Type Complexes*; Wiley-VCH Verlag GmbH & Co. KGaA: 2014; p 117–148.
- (25) Zhang, J.; Medley, C. M.; Krause, J. A.; Guan, H. *Organometallics* **2010**, *29*, 6393–6401.
- (26) Zhang, J.; Adhikary, A.; King, K. M.; Krause, J. A.; Guan, H. *Dalton Trans.* **2012**, *41*, 7959–7968.
- (27) Hao, J.; Mougang-Soumé, B.; Vabre, B.; Zargarian, D. *Angew. Chem., Int. Ed.* **2014**, *53*, 3218–3222.
- (28) van Koten, G. *Top. Organomet. Chem.* **2013**, *40*, 1–20.
- (29) Zhang, Y.; Ngeow, K. C.; Ying, J. Y. *Org. Lett.* **2007**, *9*, 3495–3498.
- (30) Xu, X.-B.; Liu, J.; Zhang, J.-J.; Wang, Y.-W.; Peng, Y. *Org. Lett.* **2013**, *15*, 550–553.
- (31) Zargarian, D.; Castonguay, A.; Spasyuk, D. *Top. Organomet. Chem.* **2013**, *40*, 131–173.
- (32) Szabó, K. *Top. Organomet. Chem.* **2013**, *40*, 203–241.
- (33) Chen, H.-Y.; Peng, W.-T.; Lee, Y.-H.; Chang, Y.-L.; Chen, Y.-J.; Lai, Y.-C.; Jheng, N.-Y.; Chen, H.-Y. *Organometallics* **2013**, *32*, 5514–5522.
- (34) Liang, L.-C.; Chien, P.-S.; Lee, P.-Y.; Lin, J.-M.; Huang, Y.-L. *Dalton Trans.* **2008**, 3320–3327.
- (35) van der Vlugt, J. I.; Lutz, M.; Pidko, E. A.; Vogt, D.; Spek, A. L. *Dalton Trans.* **2009**, 1016–1023.
- (36) Martínez-Prieto, L. M.; Melero, C.; del Río, D.; Palma, P.; Cámpora, J.; Álvarez, E. *Organometallics* **2012**, *31*, 1425–1438.
- (37) Liang, L.-C.; Li, C.-W.; Lee, P.-Y.; Chang, C.-H.; Man Lee, H. *Dalton Trans.* **2011**, *40*, 9004–9011.
- (38) Cámpora, J.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652–1655.
- (39) Adhikari, D.; Mossin, S.; Basuli, F.; Dible, B. R.; Chipara, M.; Fan, H.; Huffman, J. C.; Meyer, K.; Míndiola, D. J. *Inorg. Chem.* **2008**, *47*, 10479–10490.
- (40) Cámpora, J.; Palma, P.; del Río, D.; Mar, C. M.; Alvarez, E. *Organometallics* **2004**, *23*, 5653–5655.
- (41) Wan, Y.; Alterman, M.; Larhed, M.; Hallberg, A. *J. Org. Chem.* **2002**, *67*, 6232–6235.
- (42) Yoo, C.; Kim, J.; Lee, Y. *Organometallics* **2013**, *32*, 7195–7203.
- (43) Lin, S.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2011**, *133*, 3828–3831.
- (44) Hu, X. *Chem. Sci.* **2011**, *2*, 1867–1886.
- (45) Breitenfeld, J.; Ruiz, J.; Wodrich, M. D.; Hu, X. *J. Am. Chem. Soc.* **2013**, *135*, 12004–12012.
- (46) Zheng, B.; Tang, F.; Luo, J.; Schultz, J. W.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2014**, *136*, 6499–6504.
- (47) Kim, I. T.; Elsenbaumer, R. L. *Tetrahedron Lett.* **1998**, *39*, 1087–1090.
- (48) *Crystal Clear*; Rigaku/MSI Inc.; Rigaku Corporation: The Woodlands, TX, 2005.
- (49) ABCOR; Higashi; Rigaku Corporation; Tokyo, Japan, 1995.
- (50) Sheldrick, G. M. *SHELXL97: Program for Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
- (51) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *A64*, 112–122.