

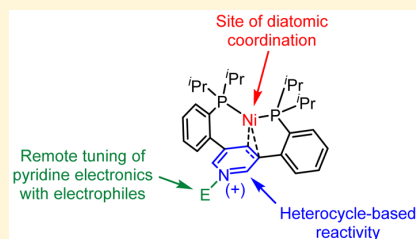
Tuning of Metal Complex Electronics and Reactivity by Remote Lewis Acid Binding to π -Coordinated Pyridine Diphosphine Ligands

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Supporting Information

ABSTRACT: Metal complexes supported by ligands with chemically modifiable pendant groups are of interest for controlling reactivity. We report on the coordination chemistry and reactivity of a multidentate phosphine ligand framework that contains a Lewis acid binding site. 3,5-Bis(2-phosphinophenyl)pyridine coordinates low-oxidation-state metal centers such as Ni⁰ and Pd⁰ via the phosphine donors and the π system of the heterocycle. Electrophilic reagents such as B(C₆F₅)₃, Me⁺, and BCy₂OTf bind the available pyridine nitrogen, generating the Ni complexes 2Ni-B(C₆F₅)₃, 2Ni-Me, and 2Ni-BCy₂OTf, respectively. Analogous compounds were prepared for Pd (2Pd, 2Pd-B(C₆F₅)₃, and 2Pd-H). The effect of Lewis acid binding was evaluated by single-crystal X-ray diffraction studies and spectroscopy. Lewis acid binding to 2Pd leads to a stronger η^1 interaction between the metal and the heterocycle π system. Ni binds in an η^2 fashion, but the Lewis acid free species is not monomeric. Ni coordination results in disruption of pyridine aromaticity, as indicated by localization of double- and single-bond character in the solid state. CO adducts were prepared for Lewis acid free (4Ni) and Lewis acid bound species (H⁺, Me⁺, and B(C₆F₅)₃-bound; 4Ni-H, 4Ni-Me, and 4Ni-B(C₆F₅)₃) that show a significant shift of the CO stretching frequency from 1930 to 1966–1976 cm⁻¹, respectively, indicating communication of ligand electronics to the metal center. An NO adduct (5Ni) with negligible metal–pyridine interactions was obtained upon sequential reaction of 2Ni with [OMe₃][BF₄] and then [NO][BF₄]. Treatment of 2Ni with silanes and boranes results in pyridine dearomatization involving heteroatom–H bond activation, with the heteroatom binding to the pyridine nitrogen and the hydrides delivered to the ortho position of pyridine. This reactivity demonstrates that the pendant pyridine is drastically affected by metal binding, enabling unusual ligand-based substrate activation. The described chemistry highlights a strategy for tuning the properties of metal centers by ligand postsynthetic modifications.



INTRODUCTION

Alterations to ligand electronics can dramatically alter the properties of transition-metal complexes. Chemically switchable ligands that show variable ligand electronics have been explored.¹ One such strategy has involved the binding of the Lewis acids to sites on the ligand framework to remotely tune the electronics.² This approach is amenable to the late-stage, modular tuning of ligand electronics and serves as a way to rapidly assemble a range of complexes from a common precursor, thereby avoiding the potentially time consuming independent synthesis of multiple ligands. For SXS³ and PXP⁴ pincer ligands, where X is either an aryl or pyridine carbon or a pyridine or pyrazine nitrogen, remote hydroxyl, amino, or basic N-heterocycle sites have been incorporated into the ligand scaffold. However, the systematic functionalization of these groups with Lewis acids has not been reported, to the authors' knowledge. Our group has previously studied meta-substituted bis(phosphinoaryl)benzene ligand systems that bind in a P–arene–P pincer geometry (Figure 1).⁵ Related diphosphines with other pendant π systems have been reported.⁶ mP₂Ni was found to coordinate a variety of ligands, and Ni methyldiene and Ni imide complexes were implicated as intermediates that perform further intramolecular chemistry, such as CH

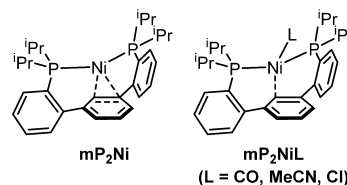


Figure 1. Ni complexes of *m*-terphenyldiphosphine ligands.

amination.⁵ Complexes displaying Ni–ligand multiple bonds have been elegantly synthesized and studied by Hillhouse et al. and others.⁷ As an alternative to the central arene donor in mP₂Ni, pyridine is known to bind a variety of electrophiles under mild conditions that can significantly alter the electronics and reaction chemistry of the heterocycle.⁸ The properties of metal complexes bound to pyridine π systems have been shown to be influenced by N functionalization of the pyridine.⁹ Herein, we report the synthesis and characterization of π -bound

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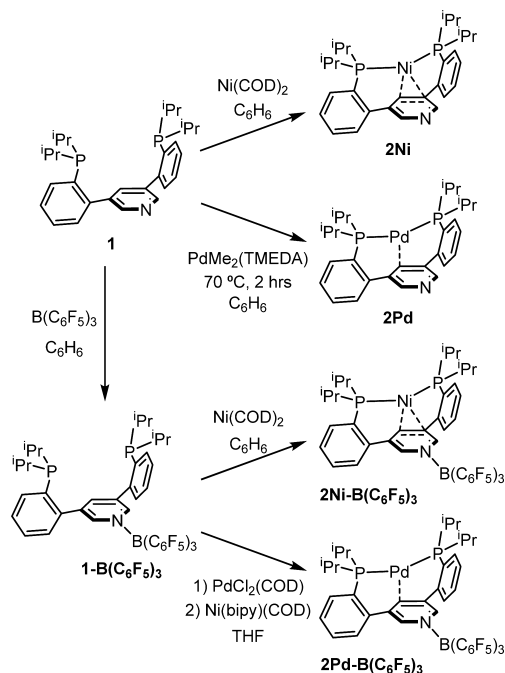
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nickel and palladium complexes supported by a diphosphine ligand containing a π -coordinated pyridine moiety that can be functionalized with electrophiles to alter the properties of the metal complex.

RESULTS AND DISCUSSION

Synthesis and Electrophile Reactivity of Ni and Pd Complexes. The desired ligand **1** was synthesized in two steps from commercially available starting materials. Metalations with nickel and palladium precursors were targeted, as these metals are known to readily bind to related P–arene–P ligands (Scheme 1).^{5a,b,10} Mixing benzene solutions of **1** and bis(1,5-

Scheme 1. Synthesis of Nickel and Palladium Complexes



cyclooctadiene)nickel(0) ($\text{Ni}(\text{COD})_2$) in a stoichiometric ratio yielded **2Ni** as a brown solid after removal of volatile materials. The corresponding palladium complex (**2Pd**) was synthesized cleanly starting from palladium dimethyl (N,N,N',N' -tetramethylethylenediamine) (TMEDA) with mild heating to 70 °C for 16 h. After workup **2Pd** could be isolated as an orange solid.

Solution NMR spectra for **2Ni** and **2Pd** display single ^{31}P resonances at 40.32 and 33.76 ppm and two distinct isopropyl methine ^1H resonances at (2.28, 2.07) and (2.12, 1.86) ppm, respectively. These data indicate either a C_s structure in solution or a fluxional process that exchanges the sides of the molecule related by the plane perpendicular to the pyridine ring and containing the nitrogen and para pyridyl carbon. Such an exchange process involves changes in the metal–pyridine π system coordination modes on the NMR time scale. The ^{31}P NMR spectrum at room temperature for **2Ni** is a broad singlet, which is suggestive of a dynamic process slow on the NMR time scale. This is corroborated by the ^1H NMR, where broadened resonances for the central pyridine protons are observed at 7.82 and 4.35 ppm for the ortho pyridyl (C3 and C4 protons) and para pyridyl (C1 proton) signals, respectively. The proton signals are shifted significantly upfield from that of

the free ligand at 8.96 and 7.89 ppm. This indicates significant disruption of the pyridine electronic environment upon binding of the nickel center, as seen with Ni complexes on related ligand platforms.^{5a,11} The $H\text{-C1}$ shows the largest upfield shift, consistent with that proton being directly bonded to the carbon atom which shows the strongest interactions with the nickel center. The pyridine protons of **2Pd** appear at 8.29 and 7.90 ppm for C3/C4 and C1 protons, respectively. Interestingly, $H\text{-C1}$ does not show any upfield shift and instead $H\text{-C3/C4}$ shows the larger upfield deviation from **1**. This is suggestive of a comparatively weaker metal–pyridine π -system interaction and is consistent with palladium being less effective at back-bonding than nickel.

Attempts to selectively functionalize the pyridine nitrogen of **1** with Lewis acids prior to metalation were challenged by lack of selectivity relative to binding to phosphine. However, tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) was found to coordinate to **1** exclusively through the pyridine nitrogen to yield **1-B(C6F5)3** by NMR spectroscopy. **1-B(C6F5)3** shows a single ^{31}P resonance at -5.58 ppm, which is close to that of **1** (-5.75 ppm). The C3/C4 and C1 protons are also only slightly shifted and appear at 8.82 and 8.04 ppm, respectively. ^{19}F NMR shows three resonances at -131.46 , -155.96 , and -162.87 ppm, shifted from the resonances of free borane (-130.29 , -143.60 , and -161.54 ppm) and consistent with four-coordinate boron.¹² These data are inconsistent with borane binding to a phosphine moiety, as a significant ^{31}P shift is expected¹³ in addition to asymmetry in the pyridine protons if only 1 equiv of borane was bound. The observed binding selectivity is assigned to the large steric profile of the borane, which disfavors binding to more sterically hindered phosphine donors in comparison to the pyridine nitrogen.

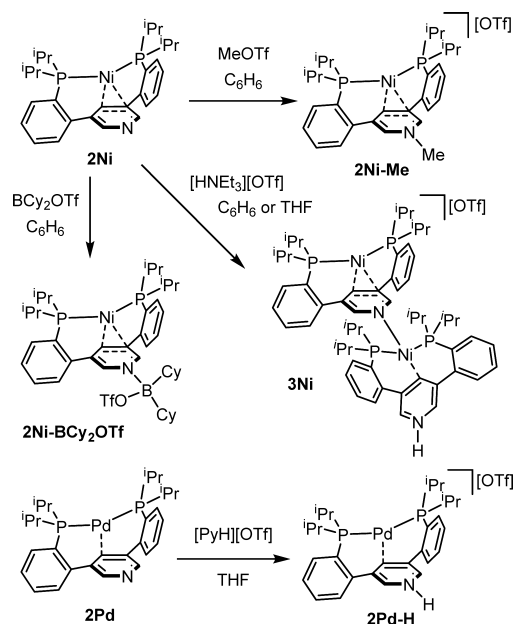
Analogous metalation procedures with $\text{Ni}(\text{COD})_2$ were found to be effective with **1-B(C6F5)3**, yielding **2Ni-B(C6F5)3** as a dark brown solid (Scheme 1). A one-pot procedure starting from Pd^{II} was found to be the most effective way to access **2Pd-B(C6F5)3**. Initial metalation of $\text{PdCl}_2(\text{COD})$ produced a homogeneous orange solution, presumed to be a PdCl_2 complex supported by **1-B(C6F5)3**. This was followed by reduction with (2,2'-bipyridine)(COD)nickel(0) to yield the desired palladium(0) complex. After workup **2Pd-B(C6F5)3** was isolated as a bright pink solid.

^1H NMR data of **2Ni-B(C6F5)3** and **2Pd-B(C6F5)3** show single ^{31}P resonances at 41.94 and 34.06 ppm and two distinct isopropyl methine ^1H resonances at (2.07, 1.78) and (2.02, 1.69) ppm, respectively. As discussed previously, these data are consistent with a C_s -symmetric structure or a fluxional process in solution. Interestingly, only small differences in ^{31}P NMR shifts are seen between **2Ni** and **2Ni-B(C6F5)3**, despite the binding of $\text{B}(\text{C}_6\text{F}_5)_3$ to the pyridine nitrogen, indicating that ^{31}P NMR is not a good indicator of electronic changes caused by Lewis acid binding or that the P atoms are not significantly affected. ^{19}F NMR data show sets of three signals (**2Ni-B(C6F5)3**, -131.35 , -157.46 , -163.85 ppm; **2Pd-B(C6F5)3**, -131.04 , -157.36 , -163.73 ppm) at chemical shifts similar to those for **1-B(C6F5)3**, consistent with pyridine coordination of $\text{B}(\text{C}_6\text{F}_5)_3$. In contrast to ^{31}P NMR, the ^1H NMR spectra of compound **2Ni-B(C6F5)3** show a further upfield shift of the pyridine protons, with the $H\text{-C1}$ signal appearing at 3.18 ppm in comparison to 4.35 ppm for **2Ni**. This shift is likely due to the electronic effect caused by binding of the Lewis acid. The electron-withdrawing $\text{B}(\text{C}_6\text{F}_5)_3$ group at the pyridine nitrogen results in the central pyridine ring becoming a better π -acceptor

ligand for the electron-rich Ni⁰ center. Consequently, strong metal–pyridine π system interactions result in an even greater upfield shift of *H*-C1 in comparison to **2Ni**. Consistent with the NMR data for the analogous nickel complex, **2Pd-B(C₆F₅)₃**, also shows a significant upfield shift in the central pyridine protons with the *H*-C3/C4 signals at 7.69 ppm and the *H*-C1 signal at 6.39 ppm. While **2Pd** showed a *H*-C1 pyridine resonance that was essentially the same as that for free phosphine, **1**, the upfield shift in **2Pd-B(C₆F₅)₃** indicates a significant metal–pyridine π system interaction that results from the more electron deficient borane-bound pyridine.

To expand the series of Lewis acids investigated, functionalization of the pyridine nitrogen was attempted starting with metalated species **2Ni** and **2Pd**, by reaction with various electrophiles. **2Ni** was found to react quantitatively with methyl triflate and dicyclohexylboron triflate to yield **2Ni-Me** and **2Ni-BCy₂OTf**, respectively (Scheme 2), which were both

Scheme 2. Electrophile Functionalization of Pyridine Nitrogen



obtained as dark brown solids. NMR evidence indicates selective derivatization of the pyridine nitrogen by the electrophile rather than a nickel-based reaction such as an oxidative addition. **2Ni-Me** displays a single ³¹P resonance at 31.13 ppm and two distinct isopropyl methine ¹H resonances at 2.57 and 2.45 ppm, indicating a C_s-symmetric structure or a fluxional process in solution. The methyl protons that do not correspond to the isopropyl substituents of **2Ni-Me** appear at 2.77 ppm and do not show ³¹P coupling. This chemical shift and lack of three-bond coupling to phosphorus indicate that methylation has not occurred at the metal center but rather at the pyridine nitrogen. Of particular note is the chemical shift for *H*-C1 of the pyridine, which appears as a triplet (*J* = 5.03 Hz) at 1.95 ppm, further upfield than the aliphatic isopropyl methine protons. ³¹P decoupling of the ¹H spectrum results in a singlet resonance for *H*-C1, indicating that coupling to two equivalent ³¹P nuclei results in the observed triplet. These significantly upfield shifted *H*-C1 and *H*-C3/C4 (6.76 ppm)

resonances again indicate a substantial Ni–pyridine π system interaction which is stronger than that of either **2Ni** or **2Ni-B(C₆F₅)₃**. This likely arises from the cationic nature of the electrophile bound to the pyridine nitrogen (B(C₆F₅)₃ vs Me⁺), which results in a substantially more electron deficient central pyridine. For **2Ni-BCy₂OTf** the cyclohexyl substituents complicate the aliphatic region of the ¹H NMR spectrum. However, *H*-C1 can be assigned to a peak at 3.45 ppm, close to that of **2Ni-B(C₆F₅)₃**. The ³¹P NMR chemical shift at 42.29 ppm again is only slightly shifted from that of **2Ni**.

The reaction of triethylammonium triflate (Scheme 2) with **2Ni** in benzene or THF results in a dinuclear monoprotonated species, **3Ni** (Figure 1, vide infra), which precipitates out of reaction mixtures when the reaction is performed in the less polar solvent. Pyridinium triflate was found to cleanly react with **2Pd** to produce a mononuclear complex, as a pink material (**2Pd-H**). Reactions of **2Pd** with other electrophiles yielded complex mixtures of products and were not pursued further. In line with other complexes, **2Pd-H** is either C_s symmetric or undergoes a fluxional process in solution with a ³¹P NMR resonance at 32.08 ppm and two distinct isopropyl methine ¹H resonances at 2.77 and 2.30 ppm in d₃-acetonitrile. Upfield-shifted *H*-C3/C4 (7.28 ppm) and *H*-C1 (6.16 ppm) resonances are observed and are consistent with metal–pyridine π system interactions that are stronger than in **2Pd** and comparable to those seen in **2Pd-B(C₆F₅)₃**. Importantly, the proton resonance derived from the pyridinium triflate is seen as a broad resonance at 9.88 ppm. This is a region consistent with a pyridinium moiety, not a palladium hydride. Furthermore, no apparent coupling to ³¹P nuclei is observed, which would be expected in the case of a Pd–H moiety. These results are similar to the reactivity of **2Ni** with electrophiles, which demonstrate that selective derivatization of the pyridine nitrogen is also possible for Pd complexes.

Solid-state structures were obtained by single-crystal X-ray diffraction (XRD) studies. **2Ni** was found to crystallize as a dinuclear species with the pyridine nitrogen of 1 equiv of complex (moiety 1) binding to the nickel center of the other (moiety 2) (Figure 2). The observed dimerization in the solid state was investigated in solution by VT NMR spectroscopy. Cooling a sample of **2Ni** in d₈-toluene to –80 °C results in two pairs of coupling ³¹P resonances at (46.07, 40.63 ppm (²*J*_{PP} = 75.0 Hz)) and (23.69, 22.79 ppm (²*J*_{PP} = 85.6 Hz)) with equal integration. These data are consistent with the low-symmetry dimer observed in the solid state. Consistent with structures of Ni(0) complexes on related ligands,^{5a,c,11} the metal center in moiety 1 of **2Ni** binds to the central pyridine in an η^2 fashion with Ni–C1 and Ni–C2 distances of 1.944(1) and 2.067(1) Å, respectively. Disrupted aromaticity is evident from the central pyridine bond metrics by a comparison of bond distances for C2–C3 (1.432(2) Å) to C4–C5 (1.362(2) Å) and C3–N1 (1.320(2) Å) to C4–N1 (1.386(2) Å). The significant differences seen in each of these pairs of bond distances highlights the partial localization of double-bond character around the central pyridine ring. Significant back-bonding from Ni is also evident from the C1–C2 distance (1.439(2) Å), which is longer than all other C–C bonds in the pyridine.

Moiety 2 of **2Ni** shows η^1 coordination of nickel to the central pyridine, a binding mode shift observed upon acetonitrile coordination in a related Ni(0) complex supported by a meta-substituted bis(phosphinoaryl)benzene ligand (Figure 1).^{5a} This binding mode change results in a longer Ni–C30 contact of 1.997(1) Å. Aromaticity still appears to be

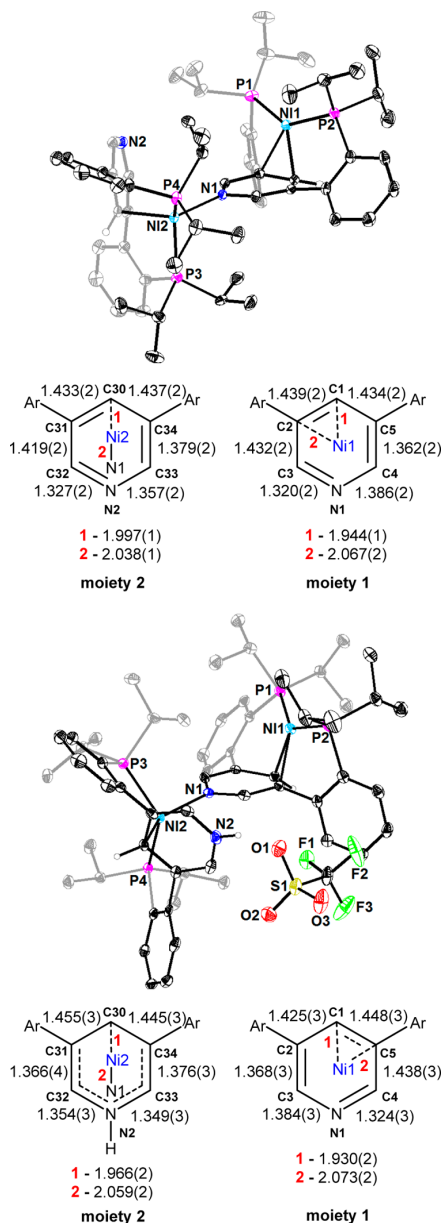


Figure 2. Solid-state structures and selected bond metrics for (top) 2Ni and (bottom) 3Ni. Hydrogen atoms and solvent have been omitted for clarity.

disrupted within the pyridine ring, though to a lesser extent than seen in moiety 1, since the compared distances (C31–C32, 1.419(2) Å; C33–C34, 1.379(2) Å) and (C32–N2, 1.327(2) Å; C33–N2, 1.357(2) Å) show smaller differences. This portion of the structure of 2Ni demonstrates the potential for flexible metal–pyridine π system interactions that vary with ligand coordination.

Structurally characterized complexes of Ni and Pd with a π -bound pyridine are very rare. The only example to the authors' knowledge is a bis-N-heterocyclic carbene complex of Ni bound η^2 to the C3–C4 positions of a pyridine coordinated via the nitrogen to AlMe₃.¹⁴ Though an analogous coordination mode

is observed in moiety 1 of 2Ni, the average Ni–C distances are longer by 0.025 Å in 2Ni. This is consistent with weaker back-bonding into the coordinated C₂ fragment, as evidenced from the 0.17 Å shorter C–C distance in 2Ni. Disrupted aromaticity is also evident in the literature compound, though differences in C–C and C–N distances range between 0.01 and 0.035 Å. This is likely attributable to electronic differences attributable to the N-heterocyclic carbene ligands as well as the coordination of AlMe₃ rather than the Ni center of moiety 2.

The solid-state structure of 3Ni is reminiscent of that of 2Ni, again with a three-coordinate nickel complex (moiety 1) binding through its pyridine nitrogen to a protonated equivalent of the complex (moiety 2). The bond metrics for moiety 1 of 3Ni are similar to the analogous metrics of 2Ni, indicative only of minor perturbation, as the site of protonation is quite remote. More substantial changes are seen in bond metrics of moiety 2 of 3Ni. A different pattern of disruption of aromaticity is observed with similar C31–C32/C33–C34 (1.366(4), 1.376(3) Å) and C32–N2/C33–N2 (1.354(3), 1.349(3) Å) bond distances seen on opposite sides of the pyridine ring relative to the N2–C30 vector. Consistently, C30–C31 and C30–C34 distances are both lengthened, at 1.455(3) and 1.445(3) Å, respectively. Contraction of the Ni–C30 distance to 1.930(2) Å suggests a stronger interaction between the metal and the π system in comparison to 2Ni. These distances are consistent with partial isolation of C30 from the π system of the pyridine, which results in delocalization across the remaining five atoms. The above structural parameters demonstrate the plasticity of the pyridine π system and its potential to rearrange as a function of Lewis acid functionalization of the pyridine nitrogen.

2Ni-B(C₆F₅)₃ and 2Ni-BCy₂OTf both crystallize as discrete complexes (Figure 3). They display four-coordinate boron centers. The nickel center is coordinated in an η^2 fashion to the

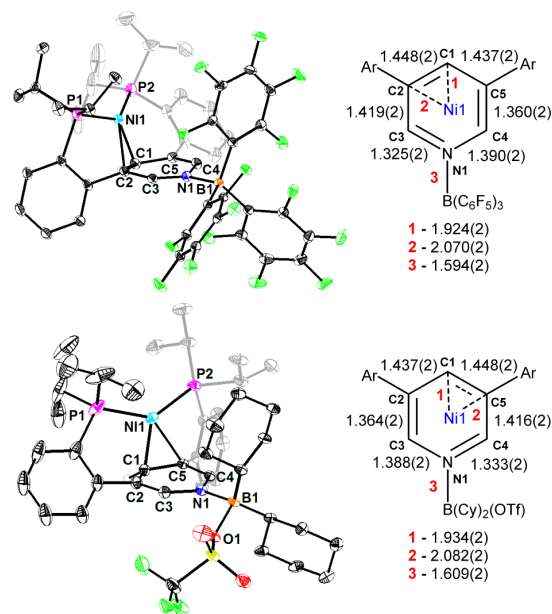


Figure 3. Solid-state structures and selected bond metrics for (top) 2Ni-B(C₆F₅)₃ and (bottom) 2Ni-BCy₂OTf. Hydrogen atoms have been omitted for clarity.

central pyridine in a manner comparable to moiety 1 of **2Ni** and **3Ni**. Furthermore, the distortions observed in the pyridine moiety are very similar among **2Ni-B(C₆F₅)₃**, **2Ni-BCy₂OTf**, and moiety 1 of **2Ni** and **3Ni**. Overall, the structural parameters of these complexes are indicative of stronger interactions between the metal center and the π -bound heterocycle in comparison to moiety 2 of **2Ni**, where the pyridine nitrogen is not coordinated. However, this comparison must be taken cautiously, given that the metal center in moiety 2 of **2Ni** is four-coordinate, while the other compounds display three-coordinate metal centers. In the case of **2Ni**, the comparison is complicated by the dinuclear nature of the crystallized complex. In contrast, Pd complexes and carbon monoxide adducts of Ni complexes (vide infra) provide better points of reference, as they are mononuclear in both Lewis acid bound and free states.

As mentioned above, **2Pd**, **2Pd-B(C₆F₅)₃**, and **2Pd-H** crystallize as discrete monomers, allowing the direct comparison of the effect of the electrophile on the structural parameters (Figure 4). All complexes show η^1 coordination

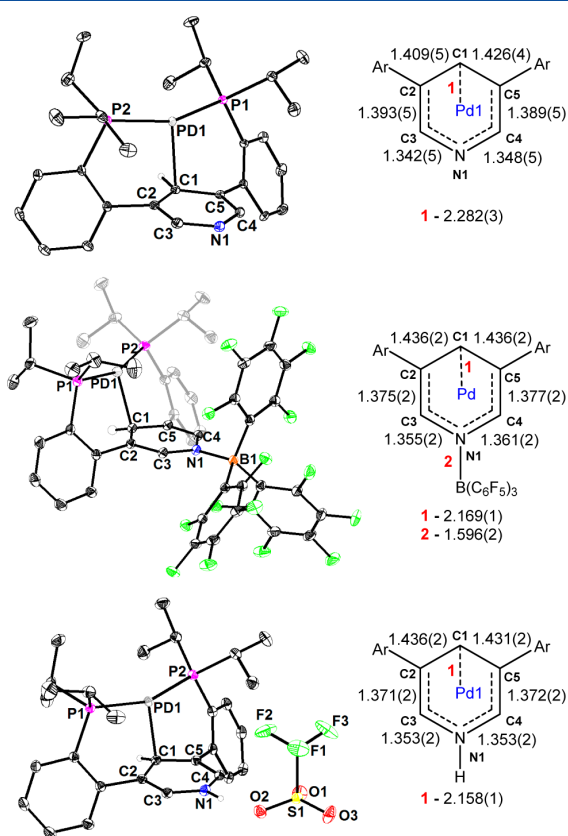


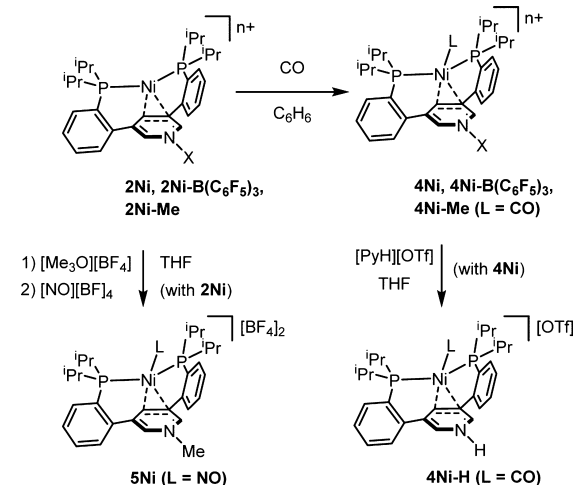
Figure 4. Solid-state structures and selected bond metrics for (top) **2Pd**, (middle) **2Pd-B(C₆F₅)₃**, and (bottom) **2Pd-H**. Hydrogen atoms have been omitted for clarity.

to the central pyridine ring with Pd–C1 distances of 2.282(3), 2.169(1), and 2.158(1) Å, respectively. The significant shortening of the Pd–C1 distance is attributed to a stronger interaction between the electron-rich Pd⁰ and the more electron deficient borane and proton-functionalized pyridine moieties. Symmetric distortions of central pyridine bond metrics relative to the N1–C1 vector are seen, with C2–C3

and C4–C5 (0.002 Å average change) as well as C3–N1 and C4–N1 (0.004 Å average change) showing negligible differences. However, among the complexes differences can be observed. An elongation of C1–C2 and C1–C5 bonds is seen in **2Pd-B(C₆F₅)₃** and **2Pd-H** (ranging between 1.436(2) and 1.431(2) Å) vs **2Pd** (1.409(5) and 1.426(4) Å, respectively), again suggestive of a stronger metal–pyridine interaction. C2–C3 and C4–C5 distances shorten by an average of 0.015 and 0.038 Å, while C3–N1 and C4–N1 elongate by an average of 0.013 and 0.008 Å for **2Pd-B(C₆F₅)₃** and **2Pd-H**, respectively, relative to **2Pd**. The geometry around palladium is T-shaped with P1–Pd1–P2 angles of 155.65(3), 160.89(2), and 156.97(1)° for **2Pd**, **2Pd-B(C₆F₅)₃**, and **2Pd-H**, respectively. For comparison, the P1–Ni–P2 angles are between 133 and 139° in compounds **2Ni-B(C₆F₅)₃** and **2Ni-BCy₂OTf**, moiety 1 of **2Ni**, and **3Ni**. Due to the metal center's increased size, the coordination angle of the diphosphine is larger with palladium. Additionally, the coordination flexibility of the palladium complexes may be limited and a binding akin to that of molecule 1 of **2Ni** may not be sterically accessible.

Binding of Diatomics to Ni Complexes. To further study the effect of pyridine modification of ligand electronics on the properties of the metal centers, a series of carbon monoxide adducts was pursued to take advantage of CO as a spectroscopic reporter on the basis of its infrared stretching frequency (Scheme 3). Treatment of with 1 equiv of CO was

Scheme 3. Synthesis of CO and NO Ni Complexes



found to quantitatively convert **2Ni**, **2Ni-B(C₆F₅)₃**, and **2Ni-Me** to the corresponding mono-CO adducts **4Ni**, **4Ni-B(C₆F₅)₃**, and **4Ni-Me**, respectively. The ν_{CO} band for **4Ni** appears at 1930 cm^{−1}. The related complex supported by the *m*-terphenyl diphosphine ligand shows a more activated CO (ν_{CO} 1916 cm^{−1}) indicative of the more electron rich benzene vs pyridine, resulting in a metal center more prone to undergo π back-bonding with CO.^{5a} The binding of Lewis acids to the pyridine nitrogen results in a shift to higher ν_{CO} values as the pyridine ring becomes more electron deficient and competes as an acceptor ligand with the CO (ν_{CO} (cm^{−1}): 1976 (**4Ni-B(C₆F₅)₃**) and 1966 (**4Ni-Me**)). The addition of 1 equiv of pyridinium triflate to **4Ni** results in the quantitative formation of **4Ni-H**, which shows a ν_{CO} band at 1975 cm^{−1}. Interestingly, **4Ni-B(C₆F₅)₃** and **4Ni-H** show similar ν_{CO} frequencies, despite

the difference in charge. It is notable that changing the supporting π system from benzene to pyridine has a smaller effect ($\sim 14\text{ cm}^{-1}$) on ν_{CO} in comparison to binding Lewis acids to the pyridine nitrogen ($36\text{ to }45\text{ cm}^{-1}$).

NMR data indicate that the introduction of the CO ligand significantly alters the metal–pyridine interaction. Each complex shows NMR data that are consistent with maintaining C_s -symmetric species or fluxional processes in solution, as seen from the sharp ^{31}P singlet (δ (ppm): 33.83 (4Ni), 31.84 (4Ni-B(C_6F_5) $_3$), 34.74 (4Ni-Me), and 35.69 (4Ni-H) (in CD_3CN)) and two distinct ^1H signals observed for the isopropyl methines (δ (ppm): 2.33, 2.06 (4Ni), 2.17, 1.74 (4Ni-B(C_6F_5) $_3$), 2.27, 1.98 (4Ni-Me), and 2.82, 2.49 (4Ni-H) (in CD_3CN)). The signals for H-C1 (δ (ppm): 6.23 (4Ni), 4.61 (4Ni-B(C_6F_5) $_3$), 4.53 (4Ni-Me), and 4.80 (4Ni-H) (in CD_3CN)) and C3/C4 (δ (ppm): 6.23 (4Ni), 4.61 (4Ni-B(C_6F_5) $_3$), 4.53 (4Ni-Me), and 4.80 (4Ni-H) (in CD_3CN)) shift downfield, indicating a weaker metal–pyridine interaction, a consequence of competing π back-bonding between metal and pyridine vs CO. Corroborating the similarities in the IR data, both 4Ni-B(C_6F_5) $_3$ and 4Ni-Me show similar chemical shifts for H-C1 despite the charge difference.

Solid-state structures for 4Ni and 4Ni-H were obtained, allowing for comparison to the CO-free analogues and evaluation of the effect of pyridine derivatization with monometallic Ni species (Figure 5). Both 4Ni and 4Ni-H show η^2 coordination to the central pyridine moiety, differing

from $\text{mP}_2\text{Ni-CO}$, which shows η^1 coordination.^{5a} The shortest Ni–C_{ring} distance is 2.254(1) Å in $\text{mP}_2\text{Ni-CO}$, which is longer than that in both 4Ni (2.119(1) Å) and 4Ni-H (2.029(1) Å), consistent with stronger interactions between the electron-rich Ni^0 center and the electron-deficient heterocycle relative to benzene. These differences in the interactions with the π systems are corroborated by the ν_{CO} values. Disrupted aromaticity is observed in both 4Ni and 4Ni-H, with significant differences in bond metrics observed for C2–C3 vs C4–C5 as well as C3–N1 vs C4–N1 indicating partial localization of double and single bonds. The shortest Ni–pyridine interactions for 4Ni and 4Ni-H, 2.119(1) and 2.029(1) Å, respectively, are elongated relative to moiety 2 of 2Ni (1.997(1) Å) and 3Ni (1.966(2) Å), respectively, consistent with the CO ligand being overall more acidic than the N-bound pyridine and leaving the metal center less prone to back-bonding to the π system of pyridine. It is worth noting that the pattern of aromaticity disruption (localized double-bond character) and coordination mode are different between 4Ni and 4Ni-H vs moiety 2 of 2Ni and 3Ni, despite both complexes being four-coordinate at nickel. This structural difference may be a consequence of CO being smaller than substituted pyridine and accommodating η^2 coordination to the central π system.

A comparison between 4Ni-H and 4Ni provides insight into the effect of protonation on pyridine coordination to metal. 4Ni-H shows shorter Ni–C contacts vs 4Ni consistent with a stronger interaction between the metal and pyridine in 4Ni-H. Additionally, the C1–C5 distance of the Ni-coordinated C_2 moiety is shorter in 4Ni (1.416(2) Å) in comparison to 4Ni-H (1.441(2) Å), suggesting weaker back-bonding into the pyridine in 4Ni. These effects are likely due to the more electron deficient pyridinium moiety being a better π acceptor from the electron-rich Ni^0 center in comparison to pyridine.

To test the ability of ligands derivatized at pyridine to support coordination of other donors to Ni, reaction with nitrosoum ion was pursued as an isoelectronic analogue of carbon monoxide. 2Ni reacts with trimethyloxonium tetrafluoroborate ($[\text{OMe}_3][\text{BF}_4]$) in THF to generate in situ the N-methylated complex. Subsequently, $[\text{NO}][\text{BF}_4]$ was added, causing a color change from a dark brown to a blue-brown solution. Following workup, the desired complex, 5Ni, was isolated as a dark blue crystalline solid. NMR spectra recorded in d_3 -acetonitrile indicated the formation of a species that showed a broad ^{31}P signal at 31.31 ppm. The chemical shifts of the C1 (7.55 ppm) and C3/C4 protons (9.01 ppm) appear in the aromatic region, suggesting weaker metal–pyridine π system interactions in comparison to those in any of the CO complexes. This is corroborated by the solid-state structure. The structure of 5Ni shows substantial differences from all other nickel complexes synthesized. A negligible Ni–pyridine interaction is present, as seen from the long Ni–C1 distance of 2.377(3) Å. The sum of the P–Ni–P and P–Ni–N angles is equal to 350.78° and is approaching the theoretical value for ideal trigonal-planar coordination. Therefore, this complex represents a rare example of a structurally characterized three-coordinate Ni–NO complex where both other donors are phosphines.¹⁵ Central pyridine distances also indicate a negligible Ni–heterocycle interaction, as the C–C (1.386(5)–1.399(5) Å) and C–N distances (1.337(5) and 1.350(5) Å for C3–N1 and C4–N1, respectively) are quite similar. The NO stretching frequency for 5Ni appears at 1846 cm^{-1} (IR). The Ni–N2–O1 angle is $163.1(4)^\circ$, which is consistent with literature linear nitrosyl moieties bound to Ni.¹⁶

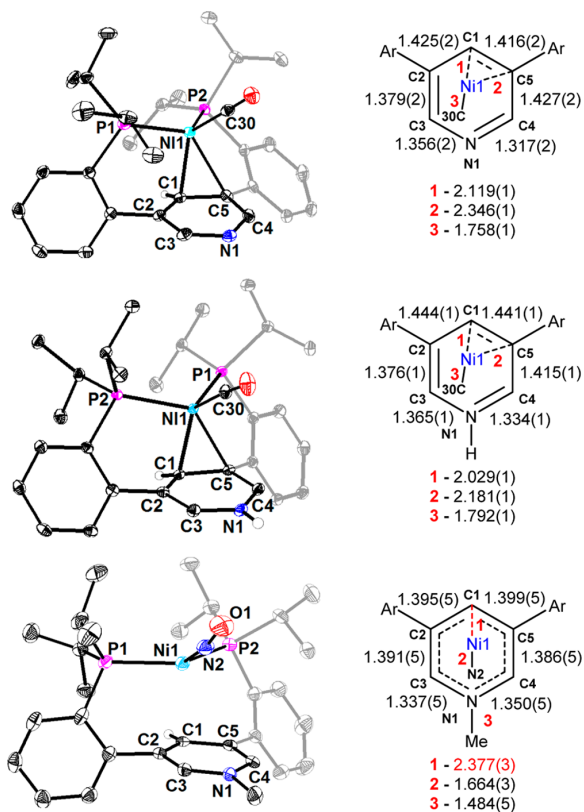


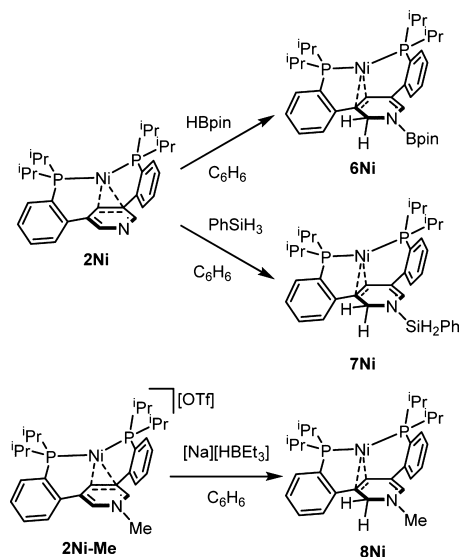
Figure 5. Solid-state structures and selected bond distances of (top) 4Ni, (middle) 4Ni-H, and (bottom) 5Ni. Hydrogen atoms and solvent have been omitted for clarity.

These data indicate that the pyridinium ring cannot compete with the nitrosonium ligand for coordination of nickel.

Overall the crystal structures reported here indicate that the interactions of Ni^0 and Pd^0 with aromatic π systems become stronger upon changing the pendant donor from benzene to pyridine to Lewis acid functionalized pyridine. This trend is maintained upon binding of additional ligands such CO. The electronic effect of these interactions with pendant π -systems is reflected in extent of CO bond weakening.

Pyridine Dearomatization by Small-Molecule Reactivity. With the influence of the aromatic ligand on the metal center demonstrated, the activation of the heterocycle by the metal toward reactivity was also investigated. With the aromaticity of pyridine partially disrupted by metal coordination, reactivity at the $\text{N}=\text{C}$ moiety was targeted. **2Ni** showed no reactivity under an atmosphere of dihydrogen at room temperature in benzene, and increasing the temperature was found to yield free phosphine **1**, presumably with loss of nickel black. However, reactions with pinacolborane and phenylsilane led to the formation of new species, **6Ni** and **7Ni**, respectively, at room temperature by NMR spectroscopy (Scheme 4).

Scheme 4. Reactivity at Pyridine beyond Lewis Acid Binding: Synthesis of Dearomatized Pyridine Complexes



Attempts to obtain X-ray diffraction quality single crystals of **6Ni** and **7Ni** have been unsuccessful to date. A suite of NMR experiments was employed for the structural characterization of these compounds. Both complexes show asymmetric coupling ³¹P doublets at (56.23, 44.70 ppm ($^2J_{\text{PP}} = 55.7$ Hz)) and (56.09, 44.77 ($^2J_{\text{PP}} = 56.2$)) for **6Ni** and **7Ni**, respectively. Furthermore, asymmetric signals for the central pyridine protons are observed that are consistent with the hydroboration or hydrosilylation of a C–N bond of the pyridine rather than a 1,4-selective reaction or a formal oxidative addition at the nickel center. The formation of a methylene moiety with diastereotopic hydrogens is supported by two doublet proton resonances for **6Ni** (4.51, 3.78 ppm ($^2J_{\text{HH}} = 13.7$ Hz)) and **7Ni** (4.13, 3.77 ppm ($^2J_{\text{HH}} = 13.2$ Hz)) that are correlated by gCOSY and couple to the same ¹³C resonance at 52.40 or 55.15 ppm, respectively, by gHSQCAD. The assignments for the

remaining central pyridine protons were completed using a combination of gHSQCAD and gHMBCAD experiments (Figure 6), which confirm the location of the C1 and the remaining ortho pyridine protons at 4.11 and 6.83 ppm and 4.13 and 6.40 ppm for **6Ni** and **7Ni**, respectively. The SiH signal of **7Ni** appears as a multiplet at 5.29 ppm. Complete assignments of the central pyridine carbons have also been made (see the Supporting Information), which support the 1,2-substitution pattern assignment.

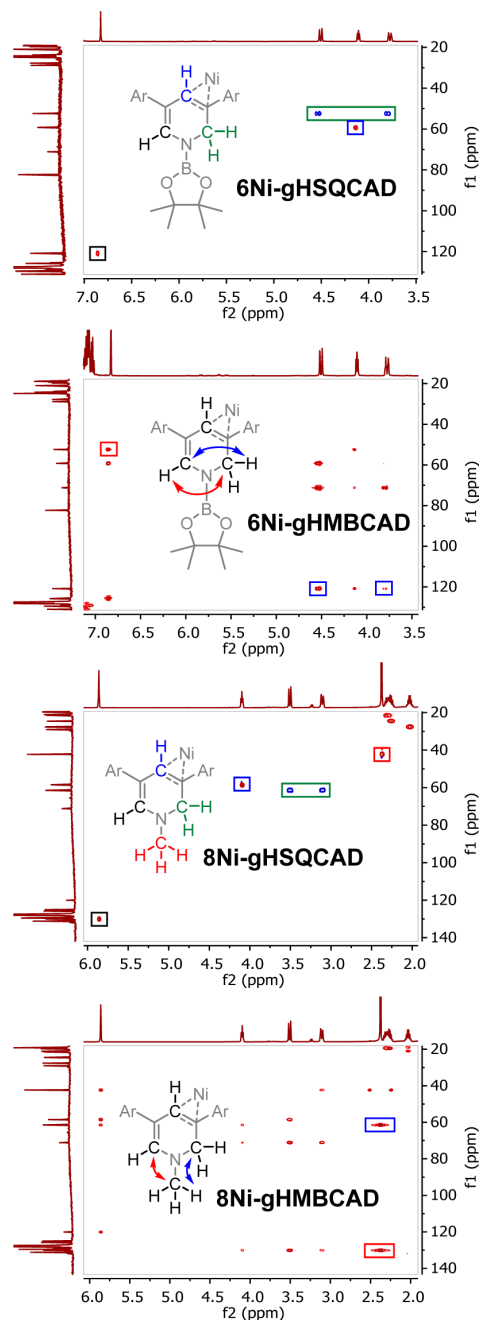


Figure 6. Select portions of the gHSQCAD and gHMBCAD spectra for **6Ni** (top two spectra) and **8Ni** (bottom two spectra).

To further support the NMR-based structural assignments for **6Ni** and **7Ni**, the reactivity of hydrides with **2Ni-Me** was tested to determine if a similar dearomatization occurs. **2Ni-Me** was found to cleanly react with sodium triethylborohydride to yield the asymmetric species **8Ni**. Similar to **6Ni** and **7Ni** coupling, ^{31}P doublets are seen at 56.52 and 44.05 ppm ($^2J_{\text{PP}} = 56.4$ Hz). The pattern of ^1H resonances and the connectivity of the dearomatized central pyridine ring were found to be similar to those of **6Ni**. The methylene protons are observed at 3.49 and 3.09 ppm ($^2J_{\text{HH}} = 12.0$ Hz), while the C1 and remaining ortho pyridine proton are observed at 4.09 and 5.85 ppm, respectively.

Complexes **6Ni**, **7Ni**, and **8Ni** are reminiscent of transition-metal-bound NAD(P)H analogues.¹⁷ The use of pyridine and other heterocycles to store proton and electron equivalents in metal complexes has been previously explored for a variety of transformations.¹⁸ In the context of π -bound ligands, catechol moieties have been shown to act as a source of both electrons and reducing equivalents during dioxygen activation.¹⁹ **6Ni**, **7Ni**, and **8Ni** demonstrate the ability of the pyridine to serve as a reservoir of reducing equivalents in the present system. However, access to these reduced species is sensitive to the steric and electronic properties of the reagents. Diphenylsilane and triethylsilane did not react with **2Ni** even at elevated temperatures. The addition of sodium triethylborohydride to **2Ni-BCy₂OTf** did not result in the formation of a dearomatized product (^{31}P NMR). Although the final products **6Ni**, **7Ni**, and **8Ni** show delivery of hydride to the pyridine, mechanistically the initial site of reactivity, metal vs heterocycle, has not been established. A precise understanding of the factors that govern the pyridine reduction reactivity require further investigation, as do methodologies to transfer the reducing equivalents to an external substrate.

CONCLUSIONS

A new P–pyridine–P ligand that readily binds nickel and palladium via phosphine donors and the heterocycle π system was developed. The interaction between the transition metal and the π system results in partial disruption of aromaticity. Metal coordination to the phosphine donors and pyridine π system leaves the pyridine nitrogen available for Lewis acid functionalization. Binding of groups such as boranes, H^+ , and Me^+ results in stronger interactions of the metal center with the pyridine π system, as reflected in both the NMR spectroscopy and structural characteristics of the complexes. The observed differences in binding are caused by the varied ability of pyridines to act as π back-bonding ligands; the functionalized heterocycles are more electron deficient, resulting in a stronger interaction with the electron-rich M^0 centers. CO and NO adducts of Ni were synthesized. A comparison of the CO stretching frequencies indicates that functionalization of the pyridine nitrogen has a significant effect on the coordinated diatomic ligand, leading to up to 46 cm^{-1} shift to higher energy upon $\text{B}(\text{C}_6\text{F}_5)_3$ binding. Dearomatization of the pyridine ring was observed in stoichiometric reactions between phenylsilane or pinacolborane and **2Ni**, with the heteroatom binding to nitrogen and the hydrogen ortho to N. This ligand-based reactivity is likely a consequence of the activation of the pyridine ring by the metal center, through disruption of aromaticity. Overall, the described results highlight a strategy for tuning the electronic properties and reactivity of metal centers by postsynthetic modifications of the complex instead

of the more typical, and expensive, synthesis of electronically altered ligands.

EXPERIMENTAL SECTION

Unless otherwise specified, all air- and moisture-sensitive compounds were manipulated using glovebox or using standard Schlenk line techniques with an N_2 atmosphere. Anhydrous tetrahydrofuran (THF) was purchased from Aldrich in 18 L Pure-Pac containers. Anhydrous pentanes, hexanes, benzene, toluene, diethyl ether, and THF were purified by sparging with nitrogen for 15 min and then passing under nitrogen pressure through a column of activated A2 alumina (Zapp's).²⁰ Benzene- d_6 , tetrahydrofuran- d_8 , and acetonitrile- d_3 were purchased from Cambridge Isotope Laboratories, Inc., dried over sodium/benzophenone ketyl (benzene and THF) or calcium hydride (MeCN), and vacuum-transferred prior to use. Unless indicated otherwise, all commercial chemicals were used as received. $\text{Ni}(\text{COD})_2$, $\text{PdMe}_2\text{TMEDA}$, PdCl_2COD , and $\text{Pd}(\text{PPh}_3)_4$ were purchased from Strem Chemicals Inc. 3,5-Dibromopyridine, pinacolborane, dicyclohexylboron triflate, methyl triflate, 1 M sodium triethylborohydride in toluene, 1.7 M tBuLi in pentane, chlorodisopropylphosphine, and CO (lecture bottle) were purchased from Sigma-Aldrich. Phenylsilane was purchased from Sigma-Aldrich and was dried over calcium hydride and distilled prior to use. Tris(pentafluorophenyl)borane was purchased from Sigma-Aldrich and sublimed prior to use. 2-Bromophenylboronic acid was purchased from Ark Pharm, Inc., and used as received. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on Varian Mercury 300 and Varian INOVA-500 spectrometers at room temperature unless indicated otherwise. Chemical shifts for ^1H and ^{13}C NMR data are reported relative to residual solvent peaks and are decoupled with respect to each other unless otherwise noted.²¹ ^{31}P NMR chemical shifts are reported with respect to the deuterated solvent used to lock the instrument and are ^1H -decoupled unless otherwise noted. Powder and thin film ATR-IR measurements were obtained by placing a powder or drop of solution of the complex on the surface of a Bruker APLHA ATR-IR spectrometer probe and allowing the solvent to evaporate (Platinum Sampling Module, diamond, OPUS software package) at 2 cm^{-1} resolution. Elemental analyses were performed by Robertson Microlit Laboratories, Ledgewood, NJ.

X-ray Crystallography. In each case, crystals were mounted on a glass fiber or nylon loop using Paratone oil and then placed on the diffractometer under a nitrogen stream. Low-temperature (100 K) X-ray data were obtained on a Bruker APEXII CCD-based diffractometer (Mo sealed X-ray tube, $K\alpha$ 0.71073 Å) or a Bruker PHOTON100 CMOS based diffractometer (Mo microfocus sealed X-ray tube, $K\alpha$ 0.71073 Å). All diffractometer manipulations, including data collection, integration, and scaling, were carried out using the Bruker APEXII software.²² Absorption corrections were applied using SADABS.²³ Space groups were determined on the basis of systematic absences and intensity statistics, and the structures were solved by direct methods using XS,²⁴ by intrinsic phasing using XT (incorporated into SHELXTL), or by charge flipping using Olex2 and refined by full-matrix least squares on F^2 .²⁵ All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. The structure was refined (weighed least-squares refinement on F^2) to convergence. Graphical representation of structures with 50% probability thermal ellipsoids was generated using Diamond visualization software.²⁶ Data collection and refinement details are included in the Supporting Information.

Synthesis of 3,5-(2-Bromophenyl)pyridine (mBr_2N). 3,5-Dibromopyridine (8.50 g, 35.9 mmol, 1 equiv), 2-bromophenylboronic acid (15.13 g, 75.3 mmol, 2.1 equiv), and potassium carbonate (29.8 g, 215.6 mmol, 6 equiv) were placed in a Schlenk tube fitted with a screw-in Teflon stopper. A magnetic stir bar, 810 mL of toluene, 195 mL of water, and 195 mL of ethanol were then added; the resulting biphasic solution was thoroughly degassed by two sequential freeze–pump–thaw cycles on a Schlenk line. Under a strong counterflow of nitrogen, $\text{Pd}(\text{PPh}_3)_4$ (2.07 g, 1.79 mmol, 0.05 equiv) was then added to the reaction mixture. The reaction flask was then sealed and heated

to 65 °C for 16 h. At this point, GC-MS analysis of an aliquot of the organic fraction indicated complete conversion to the desired product. Volatiles were removed by rotary evaporation to yield a light orange residue. Salts were removed by a water/dichloromethane extraction. After drying with magnesium sulfate and filtering, the organic fraction was dried under reduced pressure. The product was recrystallized from dichloromethane/methanol at −35 °C and obtained as a white crystalline solid. Yield: 7.93 g (59%). ¹H NMR (500 MHz, C₆D₆): δ 8.75 (d, ⁴J_{HH} = 2.2 Hz, PyH, 2H), 7.51 (t, ⁴J_{HH} = 2.2 Hz, PyH, 1H), 7.40 (ddd, ³J_{HH} = 8.0, ⁴J_{HH} = 1.2, ⁵J_{HH} = 0.5 Hz, ArH, 2H), 6.92 (ddd, ³J_{HH} = 7.6, ⁴J_{HH} = 1.9, ⁵J_{HH} = 0.5 Hz, ArH, 2H), 6.87 (td, ³J_{HH} = 7.5, ⁴J_{HH} = 1.2 Hz, ArH, 2H), 6.72 (ddd, ³J_{HH} = 8.0, ³J_{HH} = 7.3, ⁴J_{HH} = 1.8 Hz, ArH, 2H). ¹³C NMR (126 MHz, C₆D₆): δ 149.52 (s), 139.37 (s), 137.50 (s), 136.08 (s), 133.51 (s), 131.65 (s), 129.63 (s), 127.71 (s), 123.24 (s). MS (*m/z*): calcd, 389.9316 (M⁺); found, 389.9327 (FAB-MS, M⁺).

Synthesis of 1. mBr₂N (4 g, 10.3 mmol, 1 equiv) was dissolved in 60 mL of THF and transferred to a Schlenk tube fitted with a screw-in Teflon stopper. The reaction mixture was then cooled to −78 °C, and *t*BuLi (1.7 M pentanes, 24.8 mL, 42.2 mmol, 4.1 equiv) was added via syringe, resulting in an immediate color change to deep red. The reaction mixture was then warmed to room temperature and stirred for 2 h. The reaction mixture was again cooled to −78 °C, and then chlorodiisopropylphosphine (3.6 mL, 22.6 mmol, 2.2 equiv) was added via syringe. The reaction mixture was warmed to room temperature and stirred for 16 h, during which time the solution lightened to a homogeneous orange-brown. Volatiles were then removed under reduced pressure to yield a thick residue. This residue was dissolved in toluene and filtered through a Celite pad to remove salts. The volatiles of the filtrate were then removed under reduced pressure. The resulting residue was suspended in acetonitrile (ca. 20 mL), and then the resulting solution was allowed to stand for 1 h. During this time the residue initially became soluble before the product began to precipitate as a yellow solid. This product was collected via filtration and washed with additional acetonitrile until the washes became colorless. After the collected solid was dried under reduced pressure, the product was obtained as a pale yellow solid. Yield: 2.82 g (59%). ¹H NMR (500 MHz, C₆D₆): δ 8.94 (dd, ³J_{HH} = 2.2 Hz, ⁵J_{PH} = 1.3 Hz, PyH, 2H), 7.87 (td, ³J_{HH} = 2.2 Hz, ⁵J_{PH} = 1.1 Hz, PyH, 1H), 7.45–7.36 (m, ArH, 2H), 7.35–7.27 (m, ArH, 2H), 7.15–7.09 (m, ArH, 4H), 1.86 (pd, ³J_{HH} = 6.9, ²J_{PH} = 1.6 Hz, CH, 4H), 0.95 (dd, ³J_{PH} = 14.6, ³J_{HH} = 6.9 Hz, CH₃, 12H), 0.85 (dd, ³J_{PH} = 11.5, ³J_{HH} = 6.9 Hz, CH₃, 12H). ¹³C NMR (126 MHz, C₆D₆): δ 150.33 (d, ⁵J_{PC} = 5.9 Hz), 147.55 (d, ¹J_{PC} = 28.3 Hz), 140.29 (t, ³J_{PC} = 4.9 Hz), 137.11 (d, ³J_{PC} = 6.2 Hz), 135.64 (d, ¹J_{PC} = 24.6 Hz), 133.04 (d, ²J_{PC} = 2.9 Hz), 130.96 (d, ³J_{PC} = 5.4 Hz), 129.01 (s), 127.42 (s), 25.01 (d, ¹J_{PC} = 15.6 Hz), 20.47 (d, ²J_{PC} = 20.2 Hz), 19.75 (d, ²J_{PC} = 11.0 Hz). ³¹P NMR (121 MHz, C₆D₆): δ −5.75. MS (*m/z*): calcd, 464.2638 (M⁺); found, 464.2636 (FAB-MS, M⁺).

Synthesis of 1-B(C₆F₅)₃. Compound 1 (562 mg, 1.21 mmol, 1 equiv) was dissolved in benzene (ca. 10 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. B(C₆F₅)₃ (620.7 mg, 1.21 mmol, 1 equiv) was then added as a benzene solution (ca. 10 mL). The reaction mixture was stirred for 3 h, during which time the solution became a slightly lighter shade of yellow. The reaction mixture was then frozen in a −35 °C freezer and the benzene removed by lyophilization to yield the desired product by NMR and was used without further purification. Yield: 1.06 g (90%). ¹H NMR (500 MHz, C₆D₆): δ 8.82 (s, PyH, 2H), 8.04 (s, PyH, 1H), 7.26–7.18 (m, ArH, 4H), 7.08–6.97 (m, ArH, 4H), 1.70 (pd, ¹J_{HH} = 6.9, ¹J_{PH} = 2.3 Hz, CH, 4H), 0.82 (dd, ²J_{PH} = 14.6, ¹J_{HH} = 6.9 Hz, CH₃, 12H), 0.72 (dd, ²J_{PH} = 12.3, ¹J_{HH} = 6.9 Hz, CH₃, 12H). ¹³C NMR (126 MHz, C₆D₆): δ 149.20 (s), 147.97–146.77 (m), 145.99 (d, ⁵J_{PC} = 7.0 Hz), 142.87 (d, ²J_{PC} = 26.8 Hz), 141.22 (m), 139.65–138.95 (m), 139.18 (d, ³J_{PC} = 5.7 Hz), 136.37 (m), 134.65 (d, ¹J_{PC} = 25.1 Hz), 132.83 (d, ³J_{PC} = 2.4 Hz), 130.22 (d, ⁴J_{PC} = 5.3 Hz), 129.35 (s), 128.76 (s), 128.17 (s), 23.68 (d, ¹J_{PC} = 13.6 Hz), 19.23 (d, ²J_{PC} = 18.1 Hz), 18.93 (d, ²J_{PC} = 11.4 Hz). ³¹P NMR (121 MHz, C₆D₆): δ −5.58. ¹⁹F NMR (282 MHz,

C₆D₆): δ −131.46 (s), −155.96 (s), −162.87 (s). MS (*m/z*): calcd, 976.2484 (M⁺); found, 976.2389 (FAB-MS, M⁺).

Synthesis of 2Ni. Compound 1 (1.00 g, 2.15 mmol, 1 equiv) was transferred as a tetrahydrofuran solution (ca. 20 mL) into a Schlenk flask fitted with a screw-in Teflon stopper and equipped with a magnetic stirbar. Ni(COD)₂ (593.3 mg, 2.15 mmol, 1 equiv) was then added as a tetrahydrofuran suspension (ca. 20 mL). The reaction mixture was then sealed and stirred for 16 h, during which time to solution changed color from a yellow to a dark red-brown. All volatiles were then removed under reduced pressure. The residue was then dissolved in benzene and filtered through a Celite pad. The volatiles of the filtrate were removed under reduced pressure to yield the product as a dark brown clumpy solid. Yield: 833 mg (74%). ¹H NMR (300 MHz, C₆D₆): δ 7.82 (broad s, PyH, 2H), 7.47 (d, *J* = 6.9 Hz, ArH, 2H), 7.22 (d, *J* = 6.0 Hz, ArH, 2H), 7.10 (m, ArH, 4H), 4.35 (s, PyH, 1H), 2.28 (m, CH, 2H), 2.07 (m, CH, 2H), 1.07 (m, CH₃, 7.6 Hz, 18H), 0.91 (m, CH₃, 6H). ¹³C NMR (126 MHz, C₆D₆): δ 150.84 (s), 142.31 (s), 136.58 (s), 132.64 (s), 129.12 (s), 128.42 (s), 128.19 (s), 106.12 (s), 59.21 (s), 27.02 (s), 24.61 (d, ¹J_{PC} = 15.6 Hz), 22.27 (s), 20.07 (d, ¹J_{PC} = 20.1 Hz), 19.25 (s). ³¹P NMR (121 MHz, C₆D₆): δ 40.38 (s). Anal. Calcd for C₂₉H₃₉NP₂Ni (2Ni): C, 66.69; H, 7.53; N, 2.68. Found: C, 65.15; H, 6.89; N, 2.21.

Synthesis of 2Pd. Compound 1 (211.9 mg, 0.457 mmol, 1 equiv) was transferred as a benzene solution (ca. 10 mL) into a Schlenk flask fitted with a screw-in Teflon stopper and equipped with a magnetic stirbar. PdMe₂(TMEDA) (127.05 mg, 0.503 mmol, 1.1 equiv) was then added as a benzene suspension (ca. 20 mL). The reaction mixture was then sealed and heated to 60 °C for 16 h, during which time the reaction changed color from yellow to a bright orange. The solution was then filtered through a Celite pad, and the volatiles of the resulting filtrate were removed under reduced pressure to yield clean product as an orange solid without further purification. Yield: 197.6 mg (76%). ¹H NMR (500 MHz, C₆D₆): δ 8.29 (s, PyH, 2H), 7.90 (s, PyH, 1H), 7.24 (m, ArH, 4H), 7.15–7.10 (m, ArH, 2H), 7.05 (m, ArH, 2H), 2.22–2.01 (m, CH, 2H), 1.86 (p, ³J_{HH} = 7.2 Hz, CH, 2H), 1.28 (dd, ³J_{PH} = 7.8, ³J_{HH} = 7.6 Hz, CH₃, 6H), 1.08 (dd, ³J_{PH} = 8.0, ³J_{HH} = 7.5 Hz, CH₃, 6H), 0.96 (dd, ³J_{PH} = 7.9, ³J_{HH} = 7.7 Hz, CH₃, 6H), 0.73 (dd, ³J_{PH} = 5.9, ³J_{HH} = 5.8 Hz, CH₃, 6H). ¹³C NMR (126 MHz, C₆D₆): δ 147.39 (vt, ¹J_{PC} = 11.1 Hz), 146.18 (s), 134.51 (vt, ¹J_{PC} = 13.6 Hz), 131.64 (s), 131.44 (vt, ³J_{PC} = 5.0 Hz), 130.68 (s), 128.61 (s), 127.24 (s), 105.30 (s), 27.87 (vt, ²J_{PC} = 5.7 Hz), 21.75 (vt, ²J_{PC} = 7.8 Hz), 20.66 (vt, ³J_{PC} = 5.5 Hz), 17.07 (s). ³¹P NMR (121 MHz, C₆D₆): δ 33.76 (s). Anal. Calcd for C₂₉H₃₉NP₂Pd (2Pd): C, 61.11; H, 6.90; N, 2.46. Found: C, 60.87; H, 6.70; N, 2.45.

Synthesis of 2Ni-B(C₆F₅)₃. Compound 1-B(C₆F₅)₃ (126.7 mg, 0.129 mmol, 1 equiv) was transferred as a benzene solution (ca. 10 mL) into a Schlenk flask fitted with a screw-in Teflon stopper and equipped with a magnetic stirbar. Ni(COD)₂ (35.7 mg, 0.129 mmol, 1 equiv) was then added as a benzene suspension (ca. 10 mL). The reaction mixture was stirred for 16 h, during which time the solution changed color from a pale yellow to dark brown. The volatiles were then removed under reduced pressure. The brown residue was then dissolved in benzene and filtered through a Celite pad. The volatiles of the filtrate were removed under reduced pressure to yield the product as a dark brown solid. Yield: 94 mg (70%). ¹H NMR (500 MHz, C₆D₆): δ 7.42 (d, *J*_{HH} = 7.0 Hz, ArH, 2H), 7.37 (s, PyH, 2H), 7.01 (m, ArH, 2H), 7.00–6.94 (m, ArH, 2H), 3.18 (s, PyH, 1H), 2.07 (m, CH, 2H), 1.85–1.70 (m, CH, 2H), 0.88 (dd, ³J_{PH} = 14.7, ³J_{HH} = 7.5 Hz, CH₃, 6H), 0.85–0.77 (m, 18H). ¹³C NMR (126 MHz, C₆D₆): δ 149.07 (s), 147.45 (vt, ²J_{PC} = 10.9 Hz), 147.15 (s), 140.72 (s), 138.74 (s), 138.19 (s), 136.30 (m), 135.93–135.32 (m), 135.07 (s), 131.77 (d, ³J_{PC} = 7.3 Hz), 131.13 (s), 130.48 (s), 130.09–129.14 (m), 128.89 (s), 128.61 (s), 119.66 (s), 104.74 (s), 49.97–47.80 (m), 28.42–26.47 (m), 22.26–20.89 (m), 20.15–18.18 (m). ³¹P NMR (121 MHz, C₆D₆): δ 41.97 (s). ¹⁹F NMR (282 MHz, C₆D₆): δ −131.42 (s), −157.56 (s), −163.95 (s). Anal. Calcd for C₄₇H₃₉BF₁₅NP₂Ni (2Ni-B(C₆F₅)₃): C, 54.48; H, 3.80; N, 1.35. Found: C, 55.71; H, 3.79; N, 1.28.

Synthesis of 2Pd-B(C₆F₅)₃. Compound 1-B(C₆F₅)₃ (110.3 mg, 0.113 mmol, 1 equiv) was dissolved in tetrahydrofuran (ca. 5 mL) and

transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. PdCl₂COD (32.3 mg, 0.113 mmol, 1 equiv) was then added as a suspension in tetrahydrofuran (ca. 5 mL). The reaction mixture was stirred for 3 h, during which time the solution changed color from a yellow suspension to a homogeneous orange color. Ni(bpy)(COD) (36.5 mg, 0.113 mmol, 1 equiv) was then added as a tetrahydrofuran solution (ca. 10 mL), resulting in an immediate color change from orange to a pink-purple heterogeneous solution. The reaction mixture was stirred for 30 min before filtering through a Celite pad. The volatiles of the filtrate were then removed under reduced pressure to yield a pink-purple solid. Yield: 96.7 mg (79%). ¹H NMR (500 MHz, C₆D₆): δ 7.69 (s, PyH, 2H), 7.47 (s, ArH, 2H), 7.09–7.04 (m, ArH, 4H), 7.01 (m, ArH, 2H), 6.39 (s, PyH, 1H), 2.02 (m, CH, 2H), 1.69 (p, ³J_{HH} = 7.0 Hz, CH, 2H), 1.03 (dd, ³J_{PH} = 8.0, ³J_{HH} = 7.7 Hz, CH₃, 6H), 0.88 (dd, ³J_{PH} = 7.9, ³J_{HH} = 7.8 Hz, CH₃, 6H), 0.78 (q, ³J_{PH} = 7.9, ³J_{HH} = 7.8 Hz, CH₃, 6H), 0.66 (dd, ³J_{PH} = 7.9, ³J_{HH} = 6.2 Hz, CH₃, 6H). ¹³C NMR (126 MHz, C₆D₆): δ 148.97 (s), 147.04 (s), 145.25 (t), 140.80 (s), 138.81 (s), 138.22 (s), 138.00 (s), 136.37 (s), 131.56 (t, J = 16.5 Hz), 131.51 (s), 130.35 (s), 130.07 (s), 128.63 (s), 126.81 (t, J = 6.1 Hz), 120.10 (s), 86.87 (s), 27.80 (vt, ²J_{PC} = 6.9 Hz), 21.32 (vt, ²J_{PC} = 9.0 Hz), 19.77 (vt, ²J_{PC} = 6.9 Hz), 19.30 (m), 17.22 (s). ³¹P NMR (121 MHz, C₆D₆): δ 34.06 (s). ¹⁹F NMR (282 MHz, C₆D₆): δ -131.04 (s), -157.36 (s), -163.73 (s). Anal. Calcd for C₄₇H₃₉BF₁₅NP₂Pd (2Pd-B(C₆F₅)₃): C, 52.17; H, 3.63; N, 1.29. Found: C, 51.80; H, 3.69; N, 1.71.

Synthesis of 2Ni-Me. Compound 2Ni (213 mg, 0.408 mmol, 1 equiv) was dissolved in benzene (ca. 12 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. MeOTf (44.7 μL, 0.408 mmol, 1 equiv) was added by Hamilton syringe to a rapidly stirred reaction mixture, which resulted in a color change from red-brown to a darker brown. After the mixture was stirred for 30 min, volatiles were then removed under reduced pressure to yield the desired product as a dark brown solid without the need for further purification. Yield: 260 mg (93%). ¹H NMR (300 MHz, C₆D₆): δ 7.25–7.18 (m, ArH, 2H), 7.16–7.11 (m, ArH, 4H), 7.10–7.01 (m, ArH, 2H), 6.78–6.73 (m, PyH, 2H), 2.77 (t, ⁴J_{HH} = 1.4 Hz, NCH₃, 3H), 2.57 (m, CH, 2H), 2.45 (m, CH, 2H), 1.99–1.90 (t, ²J_{PH} = 5.0 Hz, 1H), 1.22–1.13 (m, CH₃, 6H), 1.13–1.06 (m, CH₃, 6H), 1.06–0.99 (m, CH₃, 6H), 0.99–0.91 (m, CH₃, 6H). ¹³C NMR (126 MHz, C₆D₆): δ 147.30 (s), 133.92 (s), 131.41 (s), 129.38 (s), 129.18 (s), 128.52 (s), 128.42 (s), 128.19 (s), 104.91 (s), 44.95 (s), 41.69 (s), 26.42 (s), 23.30 (s), 19.43 (s), 18.97 (s), 18.65 (s), 18.38 (s). ³¹P NMR (121 MHz, C₆D₆): δ 31.13 (s). ¹⁹F NMR (282 MHz, C₆D₆): δ -77.43 (s). Anal. Calcd for C₃₁H₄₂F₃NNiO₃P₂S (2Ni-Me): C, 54.25; H, 6.17; N, 2.04. Calcd for C₃₇H₄₈F₃NNiO₃P₂S (2Ni-Me-C₆H₆): C, 58.13; H, 6.33; N, 1.83. Found: C, 57.24; H, 6.01; N, 1.70.

Synthesis of 2Ni-BCy₂OTf. Compound 2Ni (113.4 mg, 0.217 mmol, 1 equiv) was dissolved in benzene (ca. 5 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. Dicyclohexylboron triflate (70.8 mg, 0.217 mmol, 1 equiv) was added as a benzene solution (ca. 5 mL), which resulted in an immediate color change from red-brown to a dark green solution before gradually turning a dark brown similar to that of 2Ni-B(C₆F₅)₃. The solution was stirred for 3 h before volatiles were removed under reduced pressure, giving the desired complex as a dark brown solid. Yield: 120 mg (65%). ¹H NMR (300 MHz, C₆D₆): δ 7.43 (s, PyH, 2H), 7.41 (s, ArH, 2H), 7.11–7.00 (m, ArH, 6H), 3.45 (s, PyH, 1H), 2.33 (s, 2H), 2.13 (m, 1H), 2.00–1.80 (m, 8H), 1.71 (s, 1H), 1.43 (m, 10H), 1.30 (m, 2H), 1.10–0.99 (m, 6H), 0.97–0.81 (m, 18H). ¹³C NMR (126 MHz, C₆D₆): δ 147.86 (s), 142.37 (s), 136.04 (s), 133.94 (s), 131.16 (s), 130.29 (s), 104.49 (s), 29.29 (s), 28.83 (s), 28.15 (s), 27.74 (s), 27.41 (s), 27.02 (s), 21.40 (s), 19.71 (s), 18.79 (s). ³¹P NMR (121 MHz, C₆D₆): δ 42.29. ¹⁹F NMR (282 MHz, C₆D₆): δ -77.35.

Synthesis of 2Pd-H. Compound 2Pd (34.7 mg, 0.0609 mmol, 1 equiv) was dissolved in tetrahydrofuran (ca. 4 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. Pyridinium triflate (13.95 mg, 0.0609 mmol, 1 equiv) was then added as a tetrahydrofuran solution (ca. 4 mL). This resulted in an immediate color change from orange to a bright pink solution. The reaction

mixture was stirred for 1 h before all volatiles were removed under reduced pressure to yield clean product as a pink solid without further purification. Yield: 40.3 mg (92%). ¹H NMR (500 MHz, CD₃CN): δ 9.88 (s, PyNH, 1H), 7.75–7.66 (m, ArH, 2H), 7.66–7.54 (m, ArH, 4H), 7.47–7.36 (m, ArH, 2H), 7.28 (s, PyH, 2H), 6.16 (s, PyH, 1H), 2.77 (m, CH, 2H), 2.30 (m, CH, 2H), 1.28 (dd, ³J_{PH} = 9.2, ³J_{HH} = 6.9 Hz, CH₃, 6H), 1.15 (dd, ³J_{PH} = 8.8, ³J_{HH} = 6.8 Hz, CH₃, 6H), 1.11–1.01 (m, CH₃, 12H). ¹³C NMR (126 MHz, CD₃CN): δ 144.81 (s), 132.24 (s), 130.99 (s), 130.38 (s), 129.79 (s), 129.14 (s), 123.78 (s), 77.26 (s), 27.52 (vt, ¹J_{PC} = 7.6 Hz), 21.71 (vt, ¹J_{PC} = 9.6 Hz), 19.69–19.18 (m), 19.05 (s), 16.82 (s). ³¹P NMR (121 MHz, CD₃CN): δ 32.08 (s). ¹⁹F NMR (282 MHz, CD₃CN): δ -79.33 (s). Anal. Calcd for C₃₀H₄₀F₃NO₃P₂PdS (2Pd-H): C, 50.04; H, 5.60; N, 1.95. Found: C, 50.25; H, 5.58; N, 1.81.

Synthesis of 3Ni. Compound 2Ni (53.8 mg, 0.103 mmol, 1 equiv) was dissolved in benzene (ca. 5 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. Triethylammonium triflate (27.9 mg, 0.111 mmol, 1.08 equiv) was added as a benzene solution (ca. 5 mL). The reaction mixture was stirred for 3 h before volatiles were removed under reduced pressure. The material could be recrystallized from tetrahydrofuran/hexanes to yield the desired product as brown crystals of sufficient quality for identification in the solid state by XRD. In acetonitrile the complex decomposes, likely due to acetonitrile coordination. In d₈-tetrahydrofuran the ³¹P NMR shows two very broad signals consistent with the asymmetric solid-state structure. Only very broad peaks were observed by ¹H and ¹³C NMR spectroscopy precluding assignment. Yield: 36.8 mg (60%). ³¹P NMR (121 MHz, d₈-THF): δ 42.12 (broad s), 25.68 (broad s). ¹⁹F NMR (282 MHz, d₈-THF): δ -78.96 (s).

Synthesis of 4Ni. Compound 2Ni (71.7 mg, 0.137 mmol, 1 equiv) was dissolved in benzene (ca. 20 mL) and transferred to a Schlenk flask fitted with a screw-in Teflon stopper and equipped with a magnetic stirbar. This solution was degassed and CO (1.3 equiv) admitted to the reaction flask. The solution was stirred for 3 h, during which time a lightening of the solution was observed. All volatiles were then removed under vacuum. The resulting brown residue was dissolved in benzene and transferred to a 20 mL scintillation vial. Lyophilization of the solvent yielded the desired clean product as a brown powder without further purification. Yield: 71.4 mg (94.5%). ¹H NMR (500 MHz, C₆D₆): δ 8.58 (broad s, PyH, 2H), 7.34–7.26 (m, ArH, 4H), 7.11 (t, ³J_{HH} = 7.4 Hz, ArH, 2H), 7.06 (t, ³J_{HH} = 7.3 Hz, ArH, 2H), 6.23 (s, PyH, 1H), 2.63–2.20 (m, CH, 2H), 2.19–1.94 (m, CH, 2H), 1.13–1.04 (m, CH₃, 6H), 1.00 (dd, ³J_{PH} = 14.6, ³J_{HH} = 6.9 Hz, CH₃, 12H), 0.84 (dd, ³J_{PH} = 6.8, ³J_{HH} = 6.6 Hz, CH₃, 6H). ¹³C NMR (126 MHz, C₆D₆): δ 197.31 (s), 148.37 (s), 145.30 (s), 134.32 (s), 130.54 (s), 129.60 (s), 129.06 (s), 128.20 (s), 83.07 (s), 28.52 (vt, ¹J_{PC} = 10.6 Hz), 25.74 (vt, ¹J_{PC} = 6.5 Hz), 19.72 (t, ²J_{PC} = 4.9 Hz), 18.81 (vt, ²J_{PC} = 4.7 Hz), 18.14 (s), 17.70 (s). ³¹P NMR (121 MHz, C₆D₆): δ 33.81 (s). IR (thin film, ATR) ν_{CO}: 1930 cm⁻¹. Anal. Calcd for C₃₀H₃₉NNiOP₂ (4Ni): C, 65.48; H, 7.14; N, 2.55. Found: C, 65.23; H, 6.87; N, 2.34.

Synthesis of 4Ni-B(C₆F₅)₃. Compound 2Ni-B(C₆F₅)₃ (48.2 mg, 0.046 mmol, 1 equiv) was dissolved in benzene (ca. 10 mL) and transferred to a Schlenk flask fitted with a screw-in Teflon stopper and equipped with a magnetic stirbar. This solution was degassed and CO (1.3 equiv) admitted to the reaction flask. The solution was stirred for 3 h, during which time a lightening of the solution was observed. All volatiles were then removed under vacuum. The resulting brown residue was dissolved in benzene and transferred to a 20 mL scintillation vial. Lyophilization of the solvent yielded the desired clean product as a brown powder without further purification. Yield: 42.6 mg (86%). ¹H NMR (300 MHz, C₆D₆): δ 8.03 (s, PyH, 2H), 7.59 (dd, ³J_{HH} = 7.7, ⁴J_{HH} = 2.9 Hz, ArH, 2H), 7.04 (m, ArH, 2H), 6.96 (d, ³J_{HH} = 4.7 Hz, ArH, 4H), 4.57 (t, ²J_{PH} = 6.8 Hz, PyH, 1H), 2.17 (h, ³J_{HH} = 7.0 Hz, CH, 2H), 1.74 (h, ³J_{HH} = 6.9 Hz, CH, 2H), 0.87–0.73 (m, CH₃, 6H), 0.59 (m, CH₃, 18H). ¹³C NMR (126 MHz, C₆D₆): δ 197.39 (s), 149.10 (s), 147.15 (s), 147.03–146.11 (m), 140.95 (s), 138.64 (s), 138.41 (s), 136.47 (m), 131.61–130.78 (m), 130.41 (d, ²J_{PC} = 32.4 Hz), 129.19 (s), 128.66 (s), 128.18 (s), 119.03 (s), 113.82

(s), 68.61 (s), 27.30 (vt, $^1J_{\text{PC}} = 10.2$ Hz), 24.29 (vt, $^1J_{\text{PC}} = 6.7$ Hz), 19.07–18.32 (m), 17.92–16.97 (m), 16.69 (s). ^{31}P NMR (121 MHz, C_6D_6): δ 31.84 (s). ^{19}F NMR (282 MHz, C_6D_6): δ -130.79 (s), -157.28 (s), -163.66 (s). IR (thin film, ATR) ν_{CO} : 1976 cm^{-1} . Anal. Calcd for $\text{C}_{48}\text{H}_{39}\text{BF}_{15}\text{NNiOP}_2$ (**4Ni-B**(C_6F_5)₃): C, 54.27; H, 3.70; N, 1.32. Calcd for $\text{C}_{60}\text{H}_{51}\text{BF}_{15}\text{NNiOP}_2$ (**4Ni-B**(C_6F_5)₃ $\cdot 2\text{C}_6\text{H}_6$): C, 59.14; H, 4.22; N, 1.15. Found: C, 58.57; H, 4.32; N, 1.12.

Synthesis of 4Ni-H. Compound **2Ni** (72.9 mg, 0.140 mmol, 1 equiv) was dissolved in benzene (ca. 20 mL) and transferred to a Schlenk flask fitted with a screw-in Teflon stopper and equipped with a magnetic stirbar. This solution was degassed and CO (1.3 equiv) admitted to the reaction flask. The solution was stirred for 3 h, during which time a lightening of the solution was observed consistent with the formation of **4Ni**. All volatiles were then removed under vacuum. The residue was then redissolved in tetrahydrofuran (ca. 4 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. Pyridinium triflate (31.98 mg, 0.140 mmol, 1 equiv) was then added as a tetrahydrofuran solution (ca. 2 mL), which resulted in a color change from brown to a red-brown. This reaction was stirred for 1 h before all volatiles were removed under reduced pressure to yield the desired product as a red-brown powder. Yield: 52.0 mg (67.7%). ^1H NMR (500 MHz, CD_3CN): δ 11.78 (broad s, NH , 1H), 7.84 (d, $^4J_{\text{HH}} = 3.7$ Hz, PyH , 2H), 7.75 (m, ArH , 2H), 7.63 (m, ArH , 4H), 7.54 (m, ArH , 2H), 4.79 (t, $^2J_{\text{PH}} = 6.1$ Hz, PyH , 1H), 2.82 (h, $^3J_{\text{HH}} = 6.9$ Hz, CH , 2H), 2.49 (h, $^3J_{\text{HH}} = 7.0$ Hz, CH , 2H), 1.32 (dd, $^3J_{\text{PH}} = 12.2$, $^3J_{\text{HH}} = 7.1$ Hz, CH_3 , 6H), 1.08 (m, CH_3 , 12H), 0.88 (dd, $^3J_{\text{PH}} = 13.6$, $^3J_{\text{HH}} = 7.0$ Hz, CH_3 , 6H). ^{13}C NMR (126 MHz, CD_3CN): δ 198.82 (s), 145.31 (vt, $^2J_{\text{PC}} = 11.5$ Hz), 132.41–131.83 (m), 131.62 (d, $^1J_{\text{PC}} = 12.5$ Hz), 130.50 (s), 129.66 (s), 129.10 (s), 113.51 (vt, $^2J_{\text{PC}} = 5.7$ Hz), 66.74 (s), 27.55 (vt, $^1J_{\text{PC}} = 10.7$ Hz), 24.75 (vt, $^2J_{\text{PC}} = 7.6$ Hz), 19.22 (s), 18.19 (s), 17.54 (s), 17.01 (s). ^{31}P NMR (121 MHz, CD_3CN): δ 35.69 (s). ^{19}F NMR (282 MHz, CD_3CN): δ -79.25 (s). IR (thin film, ATR) ν_{CO} : 1975 cm^{-1} . Anal. Calcd for $\text{C}_{31}\text{H}_{40}\text{F}_3\text{NNiO}_4\text{P}_2\text{S}$ (**4Ni-H**): C, 53.16; H, 5.76; N, 2.00. Found: C, 51.96; H, 5.39; N, 2.54.

Synthesis of 4Ni-Me. Compound **2Ni-Me** (35.9 mg, 0.052 mmol, 1 equiv) was dissolved in benzene (ca. 10 mL) and transferred to a Schlenk flask fitted with a screw-in Teflon stopper and equipped with a magnetic stirbar. This solution was degassed and CO (1.3 equiv) admitted to the reaction flask. The solution was stirred for 3 h, during which time a lightening of the solution was observed. All volatiles were then removed under vacuum. The resulting red-brown residue was dissolved in acetonitrile and transferred to a 20 mL scintillation vial. Removal of the volatiles under reduced pressure yielded the desired clean product as a red-brown powder without further purification. Yield: 34.7 mg (93%). ^1H NMR (500 MHz, C_6D_6): δ 7.95 (dd, $^3J_{\text{HH}} = 7.8$, $^4J_{\text{HH}} = 3.5$ Hz, ArH , 2H), 7.65 (d, $^4J_{\text{HH}} = 4.0$ Hz, PyH , 2H), 7.37 (dd, $^3J_{\text{HH}} = 9.3$, $^4J_{\text{HH}} = 5.7$ Hz, ArH , 2H), 7.22 (dd, $J = 9.0$, 5.8 Hz, ArH , 2H), 7.16 (m, ArH , 2H), 4.51 (t, $^2J_{\text{PH}} = 6.2$ Hz, PyH , 1H), 3.75 (s, NCH_3 , 3H), 2.34–2.22 (m, CH , 2H), 1.98 (p, $^3J_{\text{HH}} = 6.7$ Hz, CH , 2H), 0.89 (m, CH_3 , 12H), 0.70 (dd, $^3J_{\text{PH}} = 13.5$, $^3J_{\text{HH}} = 6.8$ Hz, CH_3 , 12H). ^{13}C NMR (126 MHz, C_6D_6): δ 145.02 (vt, $^2J_{\text{PC}} = 11.4$ Hz), 136.12 (s), 131.82–131.01 (m), 130.79 (s), 130.57 (s), 130.41 (s), 129.33 (s), 128.21 (s), 115.61 (s), 67.44 (s), 45.67 (s), 27.75 (vt, $^1J_{\text{PC}} = 10.4$ Hz), 24.84 (vt, $^1J_{\text{PC}} = 7.1$ Hz), 19.36 (s), 18.39 (s), 17.75 (s), 17.42 (s). ^{31}P NMR (121 MHz, C_6D_6): δ 34.74 (s). ^{19}F NMR (282 MHz, C_6D_6): δ -77.53 (s). IR (thin film, ATR) ν_{CO} : 1966 cm^{-1} . Anal. Calcd for $\text{C}_{32}\text{H}_{42}\text{F}_3\text{NNiO}_4\text{P}_2\text{S}$ (**4Ni-Me**): C, 53.80; H, 5.93; N, 1.96. Found: C, 54.09; H, 5.98; N, 1.71.

Synthesis of 5Ni. Compound **2Ni** (98.8 mg, 0.189 mmol, 1 equiv) was dissolved in tetrahydrofuran (ca. 5 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. With vigorous stirring, $[\text{OMe}_3][\text{BF}_4]$ (28.0 mg, 0.189 mmol, 1 equiv) was added as a suspension in tetrahydrofuran (ca. 5 mL). The reaction mixture was stirred for ca. 2 h, during which time the $[\text{Me}_3\text{O}][\text{BF}_4]$ solubilized and a significant darkening of the solution to a color similar to that of **2Ni-Me** was observed. At this point, $[\text{NO}][\text{BF}_4]$ was added as a suspension in tetrahydrofuran (ca. 5 mL) and the vial was rapidly sealed. The reaction mixture was stirred for 16 h, during which time the solution

became a heterogeneous brown with visible blueish precipitate forming upon standing. The reaction mixture was then filtered over a Celite pad and washed with copious tetrahydrofuran until the washes became colorless, leaving a blue precipitate. The product was eluted from the Celite pad using acetonitrile, and volatiles of the blue filtrate were removed under reduced pressure. The product could be purified by crystallization from acetonitrile/diethyl ether to give the desired complex as blue crystals. Yield: 34 mg (24.3%). The compound is unstable in solution and prone to decomposition. Peaks associated with the dominant decomposition product are indicated in the appropriate NMR spectra. ^1H NMR (500 MHz, CD_3CN): δ 9.01 (s, PyH , 2H), 8.16–8.05 (m, ArH , 2H), 7.89 (m, ArH , 4H), 7.81–7.74 (m, ArH , 2H), 7.55 (s, PyH , 1H), 4.54 (s, NCH_3 , 3H), 2.94 (m, CH , 4H), 1.19–1.04 (m, CH_3 , 24H). ^{31}P NMR (121 MHz, CD_3CN): δ 31.31 (broad s). ^{13}C NMR (126 MHz, CD_3CN): δ 143.96 (s), 143.35 (s), 140.35 (d, $^2J_{\text{PC}} = 14.0$ Hz), 134.41 (s), 133.27 (s), 132.20 (s), 132.09 (s), 131.46 (s), 131.07 (s), 128.50 (s), 128.04 (d, $^1J_{\text{PC}} = 24.4$ Hz), 49.13 (s), 27.19 (s), 24.17 (s), 18.89 (s), 17.25 (s). IR (powder, ATR) ν_{NO} : 1846 cm^{-1} . Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{B}_2\text{F}_8\text{N}_2\text{NiOP}_2$ (**5Ni**): C, 48.63; H, 5.71; N, 3.78. Calcd for $\text{C}_{30}\text{H}_{42}\text{B}_2\text{F}_8\text{N}_2\text{NiOP}_2$ (**5Ni-Me**): C, 49.15; H, 5.80; N, 3.78. Found: C, 48.13; H, 5.42; N, 5.15.

Synthesis of 6Ni. Compound **2Ni** (24.6 mg, 0.047 mmol, 1 equiv) was dissolved in benzene (ca. 2 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. Pinacolborane (6.9 μL , 0.047 mmol, 1 equiv) was then added via Hamilton syringe. The reaction mixture was stirred for 6 h before volatiles were removed under reduced pressure, giving the product without further purification. Yield: 29.1 mg (95%). ^1H NMR (500 MHz, C_6D_6): δ 7.78 (dd, $^3J_{\text{HH}} = 7.4$, $^4J_{\text{HH}} = 2.9$, ArH , 1H), 7.55 (ddd, $^3J_{\text{HH}} = 7.3$, $^4J_{\text{HH}} = 3.8$, $^5J_{\text{HH}} = 2.2$ Hz, ArH , 1H), 7.33 (ddd, $^3J_{\text{HH}} = 8.8$, $^4J_{\text{HH}} = 4.5$, $^5J_{\text{HH}} = 2.2$ Hz, ArH , 1H), 7.13–7.10 (m, ArH , 1H), 7.10–7.06 (m, ArH , 2H), 7.05–7.00 (m, ArH , 1H), 6.83 (d, $^4J_{\text{HH}} = 1.5$ Hz, Py-C(3)H , 1H), 4.51 (dd, $^1J_{\text{HH}} = 13.6$, $^4J_{\text{HH}} = 1.6$ Hz, Py-C(4)H , 1H), 4.14–4.08 (m, Py-C(1)H , 1H), 3.78 (ddd, $^1J_{\text{HH}} = 13.6$, $^4J_{\text{PH}} = 3.3$, $^3J_{\text{HH}} = 1.2$ Hz, Py-C(4)H , 1H), 2.35–2.21 (m, CH , 2H), 2.00 (pd, $^3J_{\text{HH}} = 7.0$, $^3J_{\text{HH}} = 5.0$ Hz, CH , 1H), 1.83–1.73 (m, CH , 1H), 1.25–1.15 (m, overlapping $i\text{Pr}$ and pinacol CH_3 , 9H), 1.12 (s, pinacol CH_3 , 6H), 1.09–0.99 (m, $i\text{Pr}$ CH_3 , 12H), 0.98 (s, pinacol CH_3 , 3H), 0.95–0.84 (m, $i\text{Pr}$ CH_3 , 6H). ^{13}C NMR (126 MHz, C_6D_6): δ 155.90 (d, $^2J_{\text{PC}} = 32.8$ Hz), 150.24 (d, $^2J_{\text{PC}} = 15.2$ Hz), 148.59 (d, $^3J_{\text{PC}} = 11.3$ Hz), 148.33 (d, $^2J_{\text{PC}} = 11.5$ Hz), 131.87 (d, $^1J_{\text{PC}} = 20.1$ Hz), 131.01 (s), 129.66 (d, $^1J_{\text{PC}} = 8.4$ Hz), 129.45 (s), 129.21–128.87 (m), 128.20 (s), 125.75 (m), 125.48 (s, Py(C2)), 120.81 (d, $^4J_{\text{PC}} = 5.3$ Hz, Py(C3)), 82.33 (s), 71.21 (d, $^3J_{\text{PC}} = 14.6$ Hz, Py(C5)), 59.22 (d, $^2J_{\text{PC}} = 10.9$ Hz, Py(C1)), 52.41 (s, Py(C4)), 28.83 (d, $^1J_{\text{PC}} = 10.8$ Hz), 27.73 (d, $^1J_{\text{PC}} = 15.1$ Hz), 24.85 (s), 24.56 (s), 24.23 (d, $^2J_{\text{PC}} = 11.2$ Hz), 23.83 (d, $^2J_{\text{PC}} = 15.7$ Hz), 21.12 (d, $^2J_{\text{PC}} = 12.8$ Hz), 20.91 (d, $^2J_{\text{PC}} = 7.9$ Hz), 19.72 (d, $^2J_{\text{PC}} = 8.6$ Hz), 19.38 (d, $^2J_{\text{PC}} = 11.3$ Hz), 19.27 (d, $^2J_{\text{PC}} = 7.5$ Hz), 18.97 (s), 18.88 (s), 18.78 (s). ^{31}P NMR (121 MHz, C_6D_6): δ 56.23 (d, $^2J_{\text{PP}} = 55.8$ Hz), 44.70 (d, $^2J_{\text{PP}} = 55.6$ Hz).

Synthesis of 7Ni. Compound **2Ni** (213.4 mg, 0.408 mmol, 1 equiv) was dissolved in benzene (ca. 10 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. Phenylsilane (50.4 μL , 0.408 mmol, 1 equiv) was then added via Hamilton syringe. The reaction mixture was stirred for 1 h before volatiles were removed under reduced pressure, giving the product without further purification. Yield: 245 mg (95%). ^1H NMR (500 MHz, C_6D_6): δ 7.70 (m, ArH , 1H), 7.63 (m, ArH , 1H), 7.50 (m, ArH , 1H), 7.37 (t, $^3J_{\text{HH}} = 6.6$ Hz, ArH , 1H), 7.15–7.00 (m, ArH , 6H), 6.40 (d, $^4J_{\text{HH}} = 7.9$ Hz, Py-C(3)H , 1H), 5.29 (m, SiH_2 , 2H), 4.18–4.09 (m, Py-C(1)H , 1H), 4.01 (d, $^1J_{\text{HH}} = 13.2$ Hz, Py-C(4)H , 1H), 3.77 (dd, $^1J_{\text{HH}} = 13.1$, $^4J_{\text{HH}} = 3.7$ Hz, Py-C(4)H , 1H), 2.29 (m, CH , 2H), 2.05 (m, CH , 1H), 1.78 (m, CH , 1H), 1.24 (m, CH_3 , 12H), 1.14–0.98 (m, CH_3 , 6H), 0.94 (m, CH_3 , 6H). ^{13}C NMR (126 MHz, C_6D_6): δ 155.77 (d, $^2J_{\text{PC}} = 33.4$ Hz), 150.32 (d, $^2J_{\text{PC}} = 15.2$ Hz), 148.80 (d, $^1J_{\text{PC}} = 10.9$ Hz), 148.55 (d, $^1J_{\text{PC}} = 11.2$ Hz), 135.69 (s), 134.91 (s), 133.13 (s), 131.72 (d, $^3J_{\text{PC}} = 7.2$ Hz), 131.50 (d, $^3J_{\text{PC}} = 6.9$ Hz), 131.16 (s), 130.11 (s), 129.76 (s), 129.59 (s), 129.43 (s), 128.90 (s), 128.30–127.87 (m), 125.83 (s), 125.58 (s), 124.96 (s, Py(C2)), 123.65 (d, $J = 5.0$ Hz, Py(C3)), 70.71 (d, $^2J_{\text{PC}} = 13.9$ Hz, Py(C5)), 59.00 (d, $^2J_{\text{PC}} = 11.2$ Hz,

Py(C1)), 55.13 (s, Py(C4)), 28.71 (d), 27.68 (d, $^1J_{PC} = 15.3$ Hz), 24.03 (d, $^1J_{PC} = 15.7$ Hz), 21.44 (d, $^1J_{PC} = 12.7$ Hz), 20.95 (m), 19.71 (d, $^2J_{PC} = 8.4$ Hz), 19.45 (d, $^2J_{PC} = 10.9$ Hz), 19.25 (d, $^2J_{PC} = 6.4$ Hz), 19.10 (d, $^2J_{PC} = 4.5$ Hz), 18.97 (d, $^2J_{PC} = 11.7$ Hz), 18.86 (s). ^{31}P NMR (121 MHz, C_6D_6): δ 56.09 (d, $^2J_{PP} = 56.2$ Hz), 44.77 (d, $^2J_{PP} = 56.1$ Hz).

Synthesis of 8Ni. Compound 2Ni-Me (83.7 mg, 0.121 mmol, 1 equiv) was dissolved in benzene (ca. 10 mL) and transferred to a 20 mL scintillation vial equipped with a magnetic stirbar. While the mixture was stirred vigorously, sodium triethylborohydride (1 M toluene solution, 122 μL , 0.122 mmol, 1 equiv) was then added via Hamilton syringe, resulting in an immediately lightening of the solution and precipitation of salts. The reaction mixture was stirred for 1 h before it was filtered through a Celite pad. The volatiles of the filtrate were removed under reduced pressure, giving the desired product without further purification. Yield: 62.4 mg (95%). ^1H NMR (300 MHz, C_6D_6): δ 7.81 (dd, $^3J_{HH} = 7.7$, $^4J_{HH} = 3.0$, ArH, 1H), 7.46 (dd, $^3J_{HH} = 7.7$, $^4J_{HH} = 4.0$, ArH, 1H), 7.34 (dd, $^3J_{HH} = 7.4$, $^3J_{HH} = 5.7$, ArH, 1H), 7.21–7.08 (m, ArH, 1H), 7.10–7.03 (m, ArH, 3H), 7.00 (m, ArH, 1H), 5.85 (m, Py-(C3)H, 1H), 4.09 (t, $^2J_{PH} = 5.9$ Hz, Py-(C1)H, 1H), 3.49 (d, $^1J_{HH} = 12.0$ Hz, Py-(C4)H, 1H), 3.09 (d, $^1J_{HH} = 12.0$ Hz, PyH, 1H), 2.36 (s, NCH_3 , 3H), 2.34–2.17 (m, CH_2 , 2H), 2.00 (m, CH , 1H), 1.81 (m, CH , 1H), 1.31–1.09 (m, CH_3 , 12H), 1.03–0.84 (m, CH_2 , 12H). ^{13}C NMR (126 MHz, C_6D_6): δ 156.12 (d, $^2J_{PC} = 33.1$ Hz), 150.66 (d, $^1J_{PC} = 13.7$ Hz), 148.75 (d, $^1J_{PC} = 11.9$ Hz), 131.99 (d, $^2J_{PC} = 27.6$), 131.17 (s), 130.10 (d, $^1J_{PC} = 5.5$ Hz, Py(C3)), 129.58 (s), 129.33 (s), 129.29–129.16 (m), 125.82 (d, $^2J_{PC} = 4.3$ Hz), 125.06 (d, $^2J_{PC} = 4.1$ Hz), 120.05 (s, Py(C2)), 71.13 (d, $^2J_{PC} = 14.4$ Hz, Py(C5)), 61.43 (d, $^2J_{PC} = 7.4$ Hz, Py(C4)), 58.48 (d, $^2J_{PC} = 10.8$ Hz, Py(C1)), 42.29 (s), 29.84 (s), 29.09 (d, $^1J_{PC} = 10.3$ Hz), 27.63 (d, $^1J_{PC} = 15.2$ Hz), 24.49 (d, $^1J_{PC} = 15.8$ Hz), 21.51 (d, $^1J_{PC} = 12.9$ Hz), 21.19–20.59 (m), 19.67 (m), 19.40–18.80 (m), 10.73 (s). ^{31}P NMR (121 MHz, C_6D_6): δ 56.52 (d, $^2J_{PP} = 56.5$ Hz), 44.05 (d, $^2J_{PP} = 56.4$ Hz). Anal. Calcd for $\text{C}_{30}\text{H}_{43}\text{NNiP}_2$ (8Ni): C, 66.94; H, 8.05; N, 2.60. Found: C, 67.16; H, 7.96; N, 2.43.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00562.

Characterization data and crystallographic details (PDF)

Crystallographic data for 2Ni (CIF)

Crystallographic data for 3Ni (CIF)

Crystallographic data for 2Ni-B(C₆F₅)₃ (CIF)

Crystallographic data for 2Ni-BCy₂OTf (CIF)

Crystallographic data for 2Pd (CIF)

Crystallographic data for 2Ni-B(C₆F₅)₃ (CIF)

Crystallographic data for 2Pd-H (CIF)

Crystallographic data for 4Ni (CIF)

Crystallographic data for 4Ni-H (CIF)

Crystallographic data for 5Ni (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) Allgeier, A. M.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 894–908. (b) Cisnetti, F.; Gibard, C.; Gautier, A. J. *Organomet. Chem.* **2015**, *782*, 22–30.
- (2) (a) Cesar, V.; Castro, L. C. M.; Dombray, T.; Sortais, J. B.; Darcel, C.; Labat, S.; Miqueu, K.; Sotiropoulos, J. M.; Brousses, R.; Lugan, N.; Lavigne, G. *Organometallics* **2013**, *32*, 4643–4655. (b) Benhamou, L.; Cesar, V.; Gornitzka, H.; Lugan, N.; Lavigne, G. *Chem. Commun.* **2009**, 4720–4722. (c) Azoulay, J. D.; Rojas, R. S.; Serrano, A. V.; Ohtaki, H.; Galland, G. B.; Wu, G.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1089–1092. (d) Benhamou, L.; Vujkovic, N.; Cesar, V.; Gornitzka, H.; Lugan, N.; Lavigne, G. *Organometallics* **2010**, *29*, 2616–2630.
- (3) Bergbreiter, D. E.; Frels, J. D.; Rawson, J.; Li, J.; Reibenspies, J. H. *Inorg. Chim. Acta* **2006**, *359*, 1912–1922.
- (4) (a) Walter, M. D.; White, P. S.; Schauer, C. K.; Brookhart, M. *New J. Chem.* **2011**, *35*, 2884–2893. (b) Mehendele, N. C.; Lutz, M.; Spek, A. L.; Klein Gebbink, R. J. M.; van Koten, G. *Organomet. Chem.* **2008**, *693*, 2971–2981. (c) Rivada-Wheelaghan, O.; Dauth, A.; Leitens, G.; Diskin-Posner, Y.; Milstein, D. *Inorg. Chem.* **2015**, *54*, 4526–4538. (d) Weisman, A.; Gozin, M.; Kraatz, H.-B.; Milstein, D. *Inorg. Chem.* **1996**, *35*, 1792–1797. (e) Ashkenazi, N.; Vigalok, A.; Parthiban, S.; Ben-David, Y.; Shimon, L. J. W.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 8797–8798. (f) Gauvin, R. M.; Rozenberg, H.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Chem. - Eur. J.* **2007**, *13*, 1382–1393.
- (5) (a) Herbert, D. E.; Lara, N. C.; Agapie, T. *Chem. - Eur. J.* **2013**, *19*, 16453–16460. (b) Chao, S. T.; Lara, N. C.; Lin, S. B.; Day, M. W.; Agapie, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 7529–7532. (c) Kelley, P.; Lin, S. B.; Edouard, G.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2012**, *134*, 5480–5483.
- (6) (a) Smith, R. C.; Protasiewicz, J. D. *Organometallics* **2004**, *23*, 4215–4222. (b) Morgan, B. P.; Smith, R. C. *J. Organomet. Chem.* **2008**, *693*, 11–16. (c) Baratta, W.; Herdtweck, E.; Martinuzzi, P.; Rigo, P. *Organometallics* **2001**, *20*, 305–308. (d) Chen, C.-S.; Lin, C.-S.; Yeh, W.-Y. *J. Organomet. Chem.* **2011**, *696*, 1474–1478. (e) Robertson, G. B.; Whimp, P. O. *Inorg. Chem.* **1974**, *13*, 2082–2088. (f) Robertson, G. B.; Tucker, P. A.; Whimp, P. O. *Inorg. Chem.* **1980**, *19*, 2307–2315. (g) Bennett, M. A.; Clark, P. W.; Robertson, G. B.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1972**, 1011–1012. (h) Barrett, B. J.; Iluc, V. M. *Organometallics* **2014**, *33*, 2565–2574. (i) Barrett, B. J.; Iluc, V. M. *Inorg. Chem.* **2014**, *53*, 7248–7259. (j) Okamoto, K.; Omoto, Y.; Sano, H.; Ohe, K. *Dalton Trans.* **2012**, *41*, 10926–10929. (k) Dixon, F. M.; Farrell, J. R.; Doan, P. E.; Williamson, A.; Weinberger, D. A.; Mirkin, C. A.; Stern, C.; Incarvito, C. D.; Liable-Sands, L. M.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2002**, *21*, 3091–3093. (l) Dixon, F. M.; Masar, M. S.; Doan, P. E.; Farrell, J. R.; Arnold, F. P.; Mirkin, C. A.; Incarvito, C. D.; Zakharov, L. N.; Rheingold, A. L. *Inorg. Chem.* **2003**, *42*, 3245–3255. (m) Xu, F.-B.; Li, Q.-S.; Wu, L.-Z.; Leng, X.-B.; Li, Z.-C.; Zeng, X.-S.; Chow, Y. L.; Zhang, Z.-Z. *Organometallics* **2003**, *22*, 633–640.
- (7) (a) Harrold, N. D.; Hillhouse, G. L. *Chem. Sci.* **2013**, *4*, 4011–4015. (b) Haas, T.; Kaspar, K.; Forner, K.; Drexler, M.; Fischer, H. J. *Organomet. Chem.* **2011**, *696*, 946–955. (c) Laskowski, C. A.; Miller, A. J. M.; Hillhouse, G. L.; Cundari, T. R. *J. Am. Chem. Soc.* **2011**, *133*, 771–773. (d) Iluc, V. M.; Miller, A. J. M.; Anderson, J. S.; Monreal, M. J.; Mehn, M. P.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2011**, *133*, 13055–13063. (e) Iluc, V. M.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2010**, *132*, 15148–15150. (f) Waterman, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2008**, *130*, 12628–12629. (g) Kogut, E.; Wiencko, H. L.; Zhang, L.; Cordeau, D. E.; Warren, T. H. *J. Am. Chem. Soc.* **2005**, *127*, 11248–11249. (h) Melenkivitz, R.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 3846–3847. (i) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 9976–9977. (j) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623–4624.

- (8) Bull, J. A.; Mousseau, J. J.; Pelletier, G.; Charette, A. B. *Chem. Rev.* **2012**, *112*, 2642–2713.
- (9) (a) Takao, T.; Kawashima, T.; Kanda, H.; Okamura, R.; Suzuki, H. *Organometallics* **2012**, *31*, 4817–4831. (b) Kawashima, T.; Takao, T.; Suzuki, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 7615–7618. (c) Harrison, D. P.; Welch, K. D.; Nichols-Nieler, A. C.; Sabat, M.; Myers, W. H.; Harman, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 16844–16845. (d) Mehnert, C. P.; Haggitt, J.; Green, M. L. H. *J. Organomet. Chem.* **1998**, *550*, 63–70.
- (10) Suseno, S.; Agapie, T. *Organometallics* **2013**, *32*, 3161–3164.
- (11) (a) Velian, A.; Lin, S. B.; Miller, A. J. M.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2010**, *132*, 6296–6297. (b) Lin, S.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2011**, *133*, 3828–3831.
- (12) Jiang, Y.; Blacque, O.; Fox, T.; Berke, H. *J. Am. Chem. Soc.* **2013**, *135*, 7751–7760.
- (13) Welch, G. C.; Prieto, R.; Dureen, M. A.; Lough, A. J.; Labeodan, O. A.; Holtrichter-Rossmann, T.; Stephan, D. W. *Dalton Trans.* **2009**, 1559–1570.
- (14) CSD search run: six-membered ring with one N, any bonds between vicinal atoms, H or C substitution, Pd or Ni bound to any C atoms in the ring.
- (15) Iluc, V. M.; Miller, A. J. M.; Hillhouse, G. L. *Chem. Commun.* **2005**, 5091–5093.
- (16) (a) Haller, K. J.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3552–3558. (b) Landry, V. K.; Parkin, G. *Polyhedron* **2007**, *26*, 4751–4757. (c) MacBeth, C. E.; Thomas, J. C.; Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2004**, *43*, 4645–4662. (d) Muñoz, S. B.; Foster, W. K.; Lin, H.-J.; Margarit, C. G.; Dickie, D. A.; Smith, J. M. *Inorg. Chem.* **2012**, *51*, 12660–12668. (e) Wright, A. M.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2012**, *134*, 9930–9933. (f) Puiu, S. C.; Warren, T. H. *Organometallics* **2003**, *22*, 3974–3976. (g) Varonka, M. S.; Warren, T. H. *Organometallics* **2010**, *29*, 717–720.
- (17) McSkimming, A.; Colbran, S. B. *Chem. Soc. Rev.* **2013**, *42*, 5439–5488.
- (18) (a) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588–602. (b) Kundu, S.; Brennessel, W. W.; Jones, W. D. *Inorg. Chem.* **2011**, *50*, 9443–9453. (c) Gunanathan, C.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2009**, *131*, 3146–3147. (d) Gunanathan, C.; Milstein, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 8661–8664. (e) Gunanathan, C.; Gnanaprakasam, B.; Iron, M. A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 14763–14765. (f) Ohtsu, H.; Tanaka, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 9792–9795. (g) Koizumi, T.-a.; Tanaka, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5891–5894. (h) McSkimming, A.; Bhadbhade, M. M.; Colbran, S. B. *Angew. Chem., Int. Ed.* **2013**, *52*, 3411–3416.
- (19) Henthorn, J. T.; Lin, S.; Agapie, T. *J. Am. Chem. Soc.* **2015**, *137*, 1458–1464.
- (20) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
- (21) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176–2179.
- (22) APEX2, Version 2 User Manual, M86-E01078; Bruker Analytical X-ray Systems: Madison, WI, June 2006.
- (23) Sheldrick, G. M. SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames, University of Göttingen, Göttingen, Germany, 2008.
- (24) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.
- (25) Dolomanov, O. V. OLEX2. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- (26) Brandenburg, K. DIAMOND; Crystal Impact GbR, Bonn, Germany, 1999.