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Rhodium Complexes of 2,6-Bis(dialkylphosphinomethyl)pyridines: Improved C−H Activation, Expanded Reaction Scope, and Catalytic Direct Arylation

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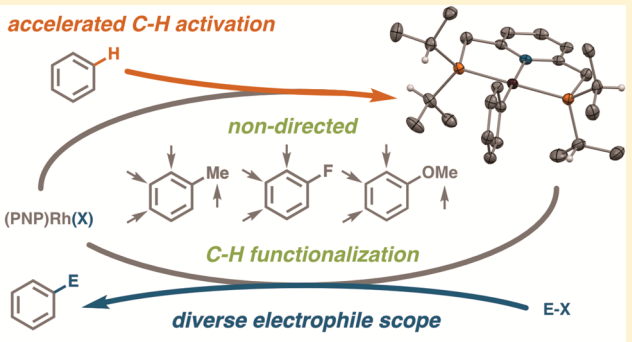
Supporting Information

ABSTRACT: The reactivity of (PNP)Rh(Ph) (PNP = 2,6-bis(dialkylphosphinomethyl)pyridine) toward a variety of electrophiles (Ar−I, $ArCH_2Cl$, O_2, I_2, B_2pin_2, and $ArSO_3H$) was explored, and several new modes of oxidative reactivity were observed. Substituting $^tBu_2P$ for $^iPr_2P$ provided 100-fold rate enhancement toward C−H bond activation and addressed the previously reported challenge of N_2 inhibition. Studying the stoichiometric reactivity of (PNP)Rh complexes toward C−H cleavage and oxidative functionalization led to (PNP)Rh-catalyzed cross-coupling of aryl iodides with sp^2 and sp^3 C−H bonds.



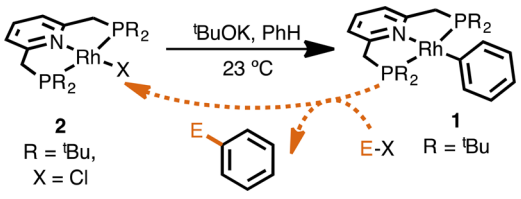
INTRODUCTION

The ability to selectively functionalize C−H bonds is changing the way chemists construct organic molecules by enabling the use of new strategic disconnections and synthetic inputs.[1−6] In particular, direct reaction of C−H bonds in organic substrates can sidestep the need to install functional groups required for conventional reactions. Most methods for selective C−H functionalization, however, rely on directing effects of functional groups, which act by facilitating activation of a particular C−H bond on a given class of substrates (e.g., ortho to a Lewis basic aromatic substituent). While this approach leads to convenient predictability, it inherently limits the possibility of functionalizing other sites in a molecule (e.g., meta to a Lewis basic substituent on an aromatic substrate) without changing the directing group. Directed strategies can also reduce synthetic efficiency if the directing group is not desired in the final product[7] and can be complicated by unwanted directing effects of desired functional groups.[8]

Methods that do not depend on functional group directing effects to promote cleavage of a particular C−H bond (often termed "nondirected" in the literature),[9] on the other hand, are far less developed than the corresponding directed approaches. Beyond the obvious practical reason that in the absence of simplifying symmetry in a substrate nondirected reactions afford product mixtures,[10] metal complexes with sufficient reactivity to activate a C−H bond under conditions that enable catalytic turnover of the resulting organometallic intermediates are remarkably rare. One notable exception in this regard is iridium-catalyzed C−H borylation, which reliably functionalizes aromatic C−H bonds distal to substituents with only minor contributions from substituent directing effects.[11] The ability of such catalysts to functionalize multiple C−H bonds within a given substrate without assistance from substrate directing effects has been harnessed to control site selectivity via molecular recognition elements in the secondary coordination sphere.[12−16] Achieving this level of catalyst control for other transformations first requires the development of catalysts that are capable of functionalizing C−H bonds without assistance from functional group directing effects. These catalysts could then be integrated into scaffolds containing secondary sphere elements to control their selectivity.[12−23]

Of course, fundamental studies on a number of stoichiometric, nondirected C−H activation reactions predate most catalytic systems, and this much needed pursuit continues to this day.[24−29] In one recent example, ^{t}Bu(PNP)RhCl was reported to cleave aromatic C−H bonds at room temperature to generate the corresponding ^{t}Bu(PNP)Rh(Ph) complex (**1**).[30] We envisioned that this reaction could be exploited for catalytic C−H functionalization if **1** could react with an oxidant to give a functionalized arene and a rhodium complex capable of subsequent C−H activation (Scheme 1). Moreover, since

Scheme 1. Proposed Substrate Functionalization and Catalyst Regeneration



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assistance from substrate directing effects was not required for mild C−H cleavage, we hypothesized that a catalytic system might afford the desired nondirected reactivity required for designing catalysts that control site selectivity through molecular recognition in the secondary coordination sphere.

RESULTS AND DISCUSSION

Despite the impressive reactivity of ^{t}Bu(PNP)RhCl toward C−H bonds, we hypothesized that steric crowding about the metal center and the benzylic methylene in ^{t}Bu(PNP)[31] complexes could be limiting reaction rates. Substituting the ^{t}Bu substituents on this ligand for ^{i}Pr substituents could accelerate both ligand deprotonation and C−H activation by reducing steric clashes with bulky bases and arene substrates, respectively. Consistent with this hypothesis, the calculated barrier to C−H oxidative addition was lower for **5** than for **1** ($\Delta\Delta G^{\ddagger}$ = 3.9 kcal/mol) (see section S1.2 in the Supporting Information). In addition, decreased steric bulk could reduce nitrogen inhibition[30] by decreasing the ability of the environment about the metal center to differentiate between small (N_2)- and medium-sized (C_6H_6) ligands.

Indeed, when 5 mM solutions of **2** and **3** were treated with 1.2 equivalents of potassium *tert*-butoxide (^{t}BuOK) in side by side reactions, complex **3** gave product formation at an initial rate 100 times greater than that for **2** (101 and 0.95 μM/min, respectively, Figure 1). The initial rate of starting material

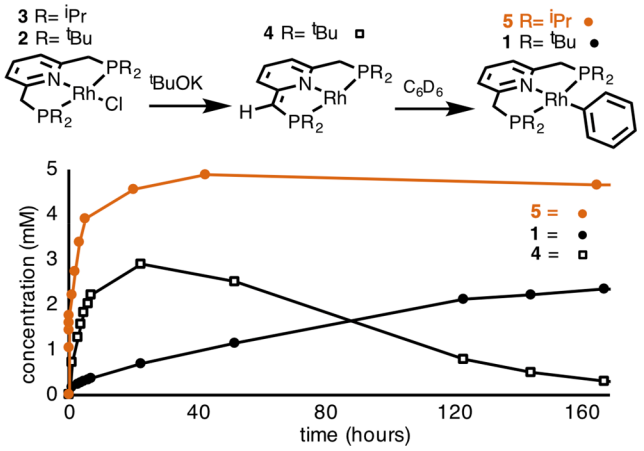


Figure 1. Overlaid C−H activation reaction profiles for ^{i}Pr and ^{t}Bu complexes **2** and **3**.

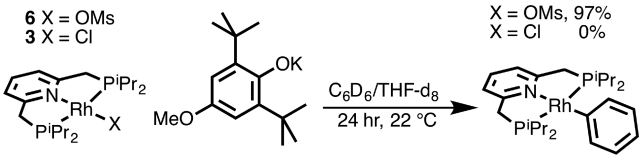
consumption (a lower bound for rate of ligand deprotonation) was only 7-fold faster for complex **3** (113 vs 16 μM/min), and no buildup of dearomatized intermediate (**4**) was observed during the reaction of **3**. These results suggest that substituting ^{t}Bu for ^{i}Pr accelerates the overall reaction by a modest increase in the rate of ligand deprotonation and a larger acceleration in C−H cleavage. Surprisingly, the rate and maximum yield of stoichiometric C−H activation revealed a strong dependence on alkali-metal counterion (K > Na ≫ Li: see section S1.3 in the Supporting Information).

Having improved the rate and yield of C−H activation, we next investigated different methods to functionalize the resulting metal−carbon bond in **5**. Several reactions, including oxidative addition (of Me-I and I_2) and reductive elimination of CH_3-X (X = Cl, Br, I, CN),[32−34] that could enable turnover of **5** have been observed at related (PNP)Rh phenyl and methyl complexes. Notably, however, only a fraction of this reactivity has been studied on (PNP)Rh(Ar) complexes relevant to aromatic C−H functionalization.[32,35,36] As such, progress[37,38] has been limited in developing catalytic methods for nondirected C−H functionalization of simple arenes, i.e. by coupling the nondirected C−H activation illustrated in Scheme 1 with the addition/elimination chemistry discussed above.

One notable exception in this regard is the recent stepwise reaction of (PNP)Rh complexes with ^{t}BuOK, H_2, CO_2, and *p*-toluenesulfonic acid to give net carbonylation of benzene (catalytic reactions yielded 1.3 turnovers after 5 days).[36] This stepwise reactivity demonstrates the necessary steps for catalyst turnover; however, it also illustrates a key challenge in developing (PNP)Rh-catalyzed C−H functionalization: incompatibility between bases required for ligand deprotonation and electrophiles required to cleave Rh−C bonds.

In light of the limitations imposed by the strong bases required for ligand deprotonation, we sought to develop complexes capable of C−H activation under milder conditions. We envisioned that weakly coordinating anions could decrease the pK_a of the benzylic methylene by generating a formally cationic Rh center to withdraw electron density from the dearomatized ligand. Gratifyingly, the methanesulfonate (OMs) complex ^{i}Pr(PNP)Rh(OMs) (**6**) reacted with benzene in the presence of potassium 2,6-bis(*tert*-butyl)-4-methoxyphenolate to give the corresponding phenyl complex in excellent yield (97%), whereas ^{i}Pr(PNP)Rh(Cl) was inert under these conditions (Scheme 2).

Scheme 2. C−H Activation with Milder Base



Although weakly coordinating anions were previously[39,40] used on (PNP)Ir complexes to provide a coordination site for Ph-H oxidative addition, we did not observe C−H activation with ^{i}Pr(PNP)Rh(OMs) in the absence of base. In contrast to the methanesulfonate complex (**6**), 4-toluenesulfonate (OTs) complex ^{i}Pr(PNP)Rh(OTs) (**7**) reacted with the ortho C−H bond of the weakly coordinating anion to give Rh(III) hydrido arylsulfonate **8**—notably, the first direct observation of C−H oxidative addition to afford a stable (PNP)Rh^{III} aryl hydride.[41]

In contrast to the observed C−H activation via **7**, complex **9** (generated in the presence of excess 4-toluenesulfonic acid) did not undergo ortho metalation upon prolonged heating (Figure 2). The differential reactivity of **7** and **9** toward C−H activation underscores a salient point. When (PNP)Rh(Ph) is functionalized in the presence of excess arene and oxidant (Scheme 1), the resulting (PNP)Rh(X) can access productive and unproductive pathways: namely, C−H activation or further reaction with electrophile to generate complexes incapable of C−H activation. As such, a key challenge in developing (PNP)Rh catalyzed C−H functionalization is finding electrophiles that react readily with (PNP)Rh(Ph) to give (PNP)Rh(X) and react negligibly with (PNP)Rh(X) relative to the rate of C−H activation.

With this balance in mind, we sought to explore the reactivity of (PNP)Rh(Ph) toward a variety of electrophiles both to understand the basic reactivity of adducts of C−H activation and to find reagents amenable to (PNP)Rh-catalyzed, non-

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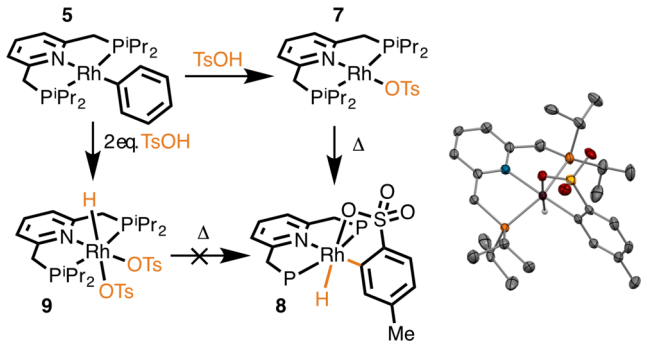

Figure 2. Reactivity of **5** with 4-toluenesulfonic acid and ORTEP drawing of **8** with 50% thermal ellipsoids and all hydrogens except Rh−H omitted for clarity.

directed C−H functionalization. A recent report of oxidative addition of O_2 to (PNP)Ir(Ph) suggested that **1** might react with O_2 to afford dearomatized Rh(III) hydroxo complex **10**.[42] Moreover, reductive elimination of phenol from **10** would afford dearomatized complex **4** and thereby circumvent the need for harsh exogenous bases. Complex **1** did indeed react with O_2 to give a dearomatized species consistent with complex **10** as the major product (Figure 3A). Precipitation of the crude

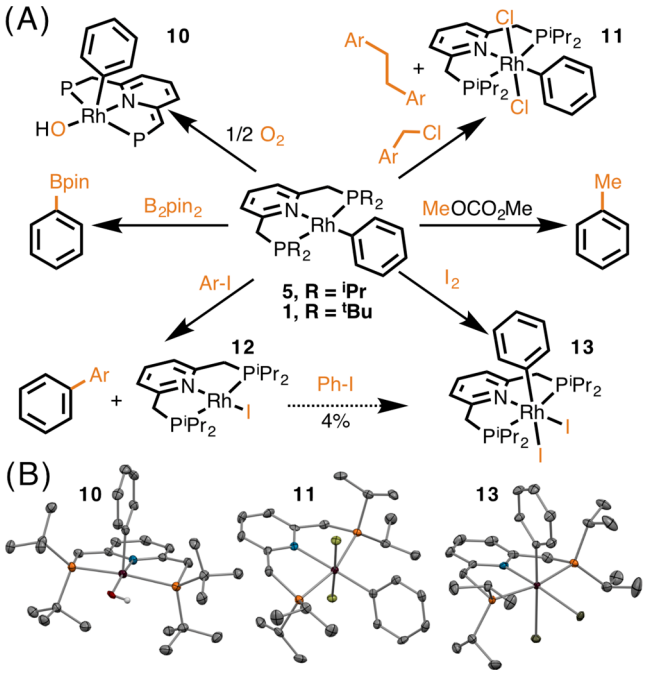

Figure 3. (A) Reactivity of C−H activation products **1** and **5** with various electrophiles. (B) ORTEP drawings of **10**, **11**, and **13** with 50% thermal ellipsoids and hydrogens removed for clarity, except OH.

reaction mixture with pentane afforded single crystals of complex **10** suitable for X-ray diffraction (Figure 3B), but attempts to purify and isolate complex **10** in bulk were not successful. Moreover, reductive elimination of phenol from the crude mixture was not observed with prolonged heating. In an attempt to lower the barrier to reductive elimination, we next explored the reactivity of **5** with C_{sp3}−X electrophiles. When **5** was treated with *p*-tolylbenzyl chloride, an intermediate consistent with the desired oxidative addition product was observed by ^{1}H NMR (see section S1.5 in the Supporting Information) but disproportionated to complex **11** and 4,4′-dimethyldibenzyl (Figure 3) rather than the desired reductive elimination. In contrast, reaction of **5** with dimethylcarbonate afforded alkylated arene (toluene) in good yield (76%), and reaction with B_2pin_2 at 140 °C afforded phenylboronic acid pinacol ester in excellent yield (97%) (Figure 3A and section S1.13 in the Supporting Information).

Previous studies on oxidative addition of aryl halides to pincer complexes and on the stability of aryl halides to base led us to pursue reactions of **5** with aryl iodides (Figure 3).[43−46] To our delight, **5** reacted with aryl iodides at elevated temperature (120 °C) to yield the desired biaryl product and (PNP)Rh(I) (**12**) (Figure 3). Among the electrophiles assessed in Figure 3, aryl iodides stood out as the least likely to undergo further, unproductive addition to the organometallic product (PNP)-Rh(X). To confirm this, we heated **12**—the product of the reaction of **5** with aryl iodides—with excess iodobenzene (Figure 3). After 40 h at 140 °C, only 4% of unproductive oxidative addition product **13** was formed, as confirmed by independent synthesis of **13** via reaction of **5** with I_2 (Figure 3 and section S1.6 in the Supporting Information). Moreover, iodo complex **12** reacted with C_6D_6 to give the desired adduct **5** (Figure 4). In contrast to the C−H activation reactions in

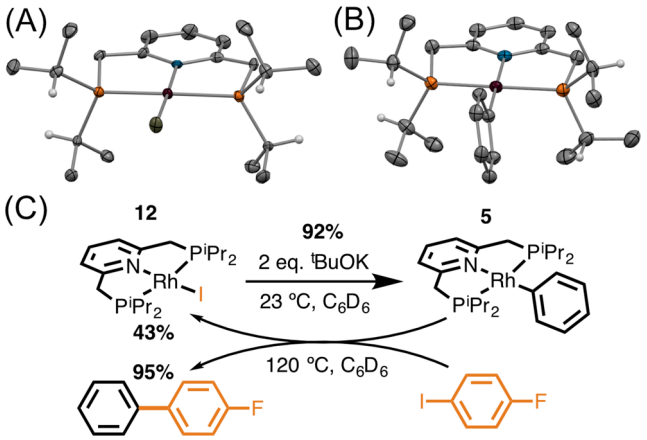

Figure 4. (A) ORTEP drawing of complex **12** with 50% thermal ellipsoids (one of two conformers in the unit cell shown for clarity). (B) ORTEP drawing of complex **5** with 50% thermal ellipsoids. (C) C−H activation with complex **12** and functionalization of C−H activation adduct **5** with 4-fluoroiodobenzene.

Figure 1, which were conducted in sealed tubes with evacuated head space to reduce N_2 inhibition, C−H activation with complex **12** was conducted under an N_2 atmosphere, indicating that isopropyl ligand substitution effectively resolved the problem of N_2 inhibition. C−H activation with complex **12**, coupled with the reaction of **5** with aryl iodides as shown in Figure 4, demonstrates the feasibility of steps in the desired cycle outlined in Scheme 1.

With an improved complex for rhodium-mediated C−H activation (**3**) in hand and a deeper understanding of the reactivity of C−H activation adducts **1** and **5** in mind, we sought to establish whether these complexes were capable of catalytic C−H functionalization of simple arenes. Gratifyingly, complex **3** catalyzed direct C−H arylation of benzene with a variety of aryl iodides (Figure 5A). Control reactions revealed that in the absence of rhodium catalyst there is a minor background reaction (reported parenthetically for each reaction).

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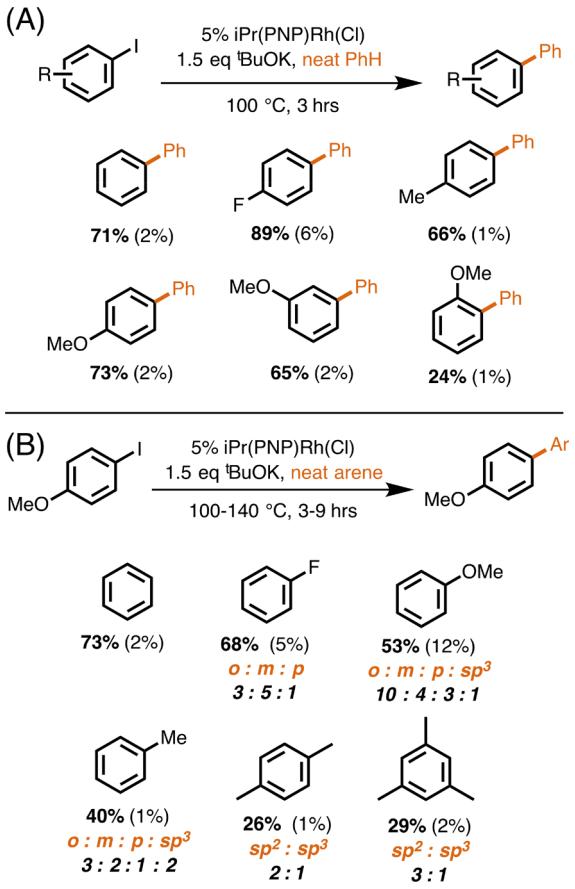
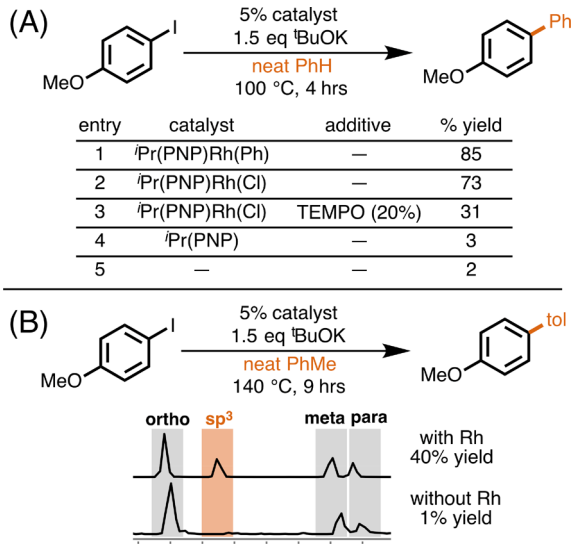


Figure 5. (A) Direct arylation of benzene with various aryl iodides, with yields given in boldface and yields of background reactions given in parentheses. (B) Direct arylation of various arenes with 4-iodoanisole, with yields given in boldface and yields of background reactions given in parentheses.



entry	catalyst	additive	% yield
1	iPr(PNP)Rh(Ph)	—	85
2	iPr(PNP)Rh(Cl)	—	73
3	iPr(PNP)Rh(Cl)	TEMPO (20%)	31
4	iPr(PNP)	—	3
5	—	—	2

Figure 6. (A) Control reactions with alternative precatalysts and TEMPO additive. (B) Extracted ion GCMS chromatograms of toluene reaction mixtures showing no sp^3 functionalization in the absence of rhodium.

Complex **3** also catalyzes arylation of several simple arenes with moderate electronic and steric variation (Figure 5B). Importantly, this system enables functionalization of all C−H bonds (ortho, meta, para, benzylic, and methoxy) in each substrate tested with only minor contributions from substituent directing effects. As noted above, the design of catalysts which can override functional group directing effects and electronic bias to give catalyst-controlled selectivity first requires the development of catalysts—like those described above—that do not require particular functional groups to promote C−H functionalization.

Given reports of direct arylation reactions using aryl iodides in the presence of ^{t}BuOK and an organic catalyst, control reactions were conducted to compare the yield of ^{t}BuOK-mediated benzene arylation in the presence of no additives, 5 mol % of ^{i}Pr(PNP)Rh(Cl), or 5 mol % of the ^{i}Pr(PNP) ligand (Figure 6A, entries 2, 4, and 5). These reactions revealed comparable and dramatically reduced yields under the last two conditions relative to the first, indicating that the reaction is not catalyzed by demetalated ligand alone.[47] Whereas organocatalytic transformations of this type show no activity in the presence of a catalytic radical trap (TEMPO),[48] the (PNP)Rh-catalyzed reaction maintained substantial activity under the same conditions (Figure 6A, entry 3). Notably, the less hindered complexes (**3** and **5**) were much more efficient precatalysts than bulkier complexes **2** and ^{t}Bu(PNP)Ir(coe)-(PF_6)—consistent with metal-centered reactivity see section S1.8 in the Supporting Information).

The sp^2 selectivity in rhodium-catalyzed direct arylation is most consistent with previously reported radical-based arylations (Figure 5B).[47] Notably, reactions in the presence or absence of rhodium catalyst had similar sp^2 selectivity. This finding could indicate that the rhodium complexes studied herein catalyze C−H functionalization by initiating or accelerating the background reaction, which has been proposed to proceed through radical intermediates (Figure 6B).[47,49] On the other hand, the sp^3 C−H functionalization observed for toluene, anisole, *p*-xylene, and mesitylene was not observed in the ^{t}BuOK-mediated background reaction, indicating that the rhodium catalyst enables access to pathways that are not accessible to the active species in the background reaction (Figure 6B).

CONCLUSION

Overall, we harnessed the ability of the (PNP)Rh platform to mediate nondirected C−H activation and translated this reactivity into a catalytic system capable of functionalizing a variety of C−H bonds. This was enabled by the fact that this complex does not require directing groups to enable C−H activation. This was achieved by a ligand modification to dramatically enhance the rate of C−H activation and an expanded understanding of the stoichiometric reactivity of the C−H activation complex (PNP)Rh(Ph) with a variety of electrophiles. Moreover, we found that key drawbacks to the (PNP)Rh platform (nitrogen inhibition and dependence on strong base) were readily mitigated by simple modifications (smaller phosphines and weakly coordinating anions, respectively). The resulting catalytic method, like others based on the PNP platform that emerged from stoichiometric reactions,[50,51] sheds new light on the reactivity of the (PNP)Rh platform in the form of unexpected sp^3 functionalization and potential catalysis of radical-based transformations.

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EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all reactions and manipulations were performed under a circulating nitrogen atmosphere in an Innovative Technologies glovebox or using standard Schlenk techniques with dried and degassed solvents. As noted previously,[52] due to strong $^{31}P-^{31}P$ coupling in the pincer ligand, many ^{1}H and ^{13}C signals appear as virtual triplets (vt) and are reported as such with the apparent coupling constant noted. In $^{31}P\{^{1}H\}$ experiments the sweep width of the decoupling channel is insufficient to simultaneously decouple aliphatic and hydridic ^{1}H resonances: as such, $^{31}P\{^{1}H\}$ spectra of rhodium hydrides include coupling to Rh−H. Literature procedures were used to prepare $[Rh(coe)_2(Cl)]_2$,[53] ^{i}Pr-(PNP),[54] pyrr-^{i}Pr(PNP),[51] ^{t}Bu(PNP),[55] ^{i}Pr(PNP)Rh(Cl) (**3**),[33] ^{t}Bu-(PNP)Rh(Cl) (**2**),[56] ^{t}Bu(PNP)Rh(Ph) (**2**),[37] potassium 2,6-bis(*tert*-butyl)-4-methoxyphenolate,[57] and ^{t}Bu(PNP)Ir(coe)(PF_6).[39]

Synthesis and Characterization. *^{i}Pr(PNP)Rh(Ph) (**5**).* A 500 mL round-bottom flask was charged with **3** (4.778 g, 10 mmol, 1 equiv), a stir bar, and 100 mL of THF. To the deep red, stirred solution was added phenylmagnesium chloride in THF (10.4 mmol, 4.55 mL, 2.2 M, 1.04 equiv). Reaction progress was monitored by ^{31}P NMR of 50 μL aliquots dissolved in 500 μL of C_6D_6. After 43 h, all of the starting material had been consumed and the solvent was removed under reduced pressure. To remove any residual THF, the dark solid mixture was suspended in 10 mL of toluene and concentrated in vacuo. The mixture was extracted with refluxing pentane (40 mL) which was filtered over a medium frit into a warm side-arm flask. The mixture of product and magnesium salts in the original reaction vessel was extracted six times in this manner while the collection flask was gently warmed to prevent precipitation. Over the course of the extractions approximately half of the pentane evaporated to give a concentrated solution of **5** in warm pentane. The filtrate was transferred to a 200 mL jar, sealed, cooled to room temperature, and transferred to a −35 °C freezer. After 48 h at −35 °C the supernatant was decanted to give 3.66 g (70% yield) of large black-red crystals of complex **5**. Single crystals suitable for X-ray diffraction were grown by slow evaporation of pentane from the supernatant solution at −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.94 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, Rh-Ph ortho), 7.21 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, Rh-Ph meta), 7.01 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, pyr-para), 6.93 (t, $^{3}J_{HH}$ = 7.1 Hz, 1H, Rh-Ph para), 6.51 (d, J = 7.6 Hz, 2H, pyr-meta), 2.72 (vt, $^{3}J_{PH}$ = 3.3 Hz, 4H, PCH_2), 1.91 (m, 4H, ^{i}Pr CH), 1.14 (m, (doublet by $^{1}H\{^{31}P\}$ $^{3}J_{HH}$ = 7.1 Hz), 12H, $^{i}PrCH_3$), 1.04 (m, (doublet by $^{1}H\{^{31}P\}$ $^{3}J_{HH}$ = 6.9 Hz), 12H, $^{i}PrCH_3$). $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6): δ 42.64 (d, $^{1}J_{RhP}$ = 168.8 Hz). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ 167.64 (vtd, $^{2}J_{PC}$ = 13.5, $^{1}J_{RhC}$ 32.3 Hz, Rh-Ph C ipso), 161.20 (dvt, $^{2}J_{RhC}$ = 1.4, $^{2}J_{PC}$ = 6.6 Hz, pyr C-ortho), 141.11 (vt, $^{3}J_{PC}$ = 3.1 Hz, Rh-Ph C ortho), 130.35 (s, pyr C-para), 124.79 (m, Rh-Ph C meta), 119.13 (vt, $^{3}J_{PC}$ = 4.6 Hz, pyr C meta), 118.13 (vt, $^{5}J_{PC}$ = 1.3 Hz, Rh-Ph C para), 37.03 (vt, $^{1}J_{PC}$ = 5.9 Hz, PCH_2), 24.15 (dvt, $^{2}J_{RhC}$ = 2.9, $^{1}J_{PC}$ = 8.9 Hz, ^{i}Pr CH), 18.85 (vt, $^{2}J_{PC}$ = 3.6 Hz, $^{i}PrCH_3$), 17.77 (m, $^{i}PrCH_3$). Anal. Calcd for $C_{25}H_{40}NP_2Rh$: C, 57.81; H, 7.76; N, 2.70. Found: C, 58.99; H, 8.02; N, 2.57. Material prepared by this method gave carbon analysis outside the range viewed as establishing analytical purity (Δ1.81%). Elemental analysis and graphical ^{1}H, ^{31}P, and ^{13}C NMR data are provided to illustrate the degree of purity of the bulk material obtained by this method without additional purification.

*^{i}Pr(PNP)Rh(OMs) (**6**).* A J. Young tube was charged with **5** (100 mg, 0.192 mmol, 1 equiv) and 500 μL of C_6D_6. To the blackish solution was added 12.5 μL of methanesulfonic acid. The tube was capped, shaken, and analyzed by ^{1}H and ^{31}P NMR within 5 min of mixing. The reaction was monitored 1 h later, which revealed no further reaction. The contents of the J. Young tube were poured into 10 mL of stirring pentane in a 20 mL scintillation vial at −35 °C to give an orange-red precipitate. The precipitate settled to the bottom of the vial overnight at −35 °C, at which time the supernatant was decanted to give 97.2 mg (95% yield) of complex **6**. ^{1}H NMR (500 MHz, C_6D_6): δ 6.79 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, pyr para), 6.22 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, pyr meta), 2.76 (s, 3H, OMs-CH_3), 2.39 (vt, $^{3}J_{PH}$ = 3.5 Hz, 4H, PCH_2), 2.28 (m (septet by $^{1}H\{^{31}P\}$ $^{3}J_{HH}$ = 7.0 Hz), 4H, ^{i}PrCH), 1.55 (m, (doublet by $^{1}H\{^{31}P\}$ $^{3}J_{HH}$ = 7.0 Hz), 12H, $^{i}PrCH_3$), 1.03 (m, (doublet by $^{1}H\{^{31}P\}$ $^{3}J_{HH}$ = 7.0 Hz), 12H, $^{i}PrCH_3$). $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6): δ 47.88 (d, $^{2}J_{RhP}$ = 148.8 Hz, 2P). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ 165.03 (vtd, $^{2}J_{PC}$ = 6.3, $^{3}J_{RhC}$ = 1.1 Hz, ortho pyr), 129.76 (s, para pyr), 119.38 (vtd, $^{3}J_{PC}$ = 5.3, $^{4}J_{RhC}$ = 1.2 Hz, meta pyr), 38.74 (s, OMs-CH_3), 34.49 (vtd, $^{1}J_{PC}$ = 6.7, $^{2}J_{RhC}$ = 1.5 Hz, PCH_2), 24.25 (vtd, $^{1}J_{PC}$ = 9.6, $^{2}J_{RhC}$ = 1.0 Hz, ^{i}PrCH), 19.23 (vt, $^{2}J_{PC}$ = 3.9 Hz, $^{i}PrCH_3$), 17.70 (s (br), $^{i}PrCH_3$). Anal. Calcd for $C_{20}H_{38}NO_3SP_2Rh$: C, 44.70; H, 7.13; N, 2.61. Found: C, 46.57; H, 7.52; N, 2.78. Material prepared by this method gave carbon analysis outside the range viewed as establishing analytical purity (Δ1.87%). Elemental analysis and graphical ^{1}H, ^{31}P, and ^{13}C NMR data are provided to illustrate the degree of purity of the bulk material obtained by this method without additional purification.

*^{i}Pr(PNP)Rh(OTs) (**7**).* In a J. Young tube was placed a stock solution of **5** in C_6D_6 (14 μmol, 583 μL, 24 mM, 1 equiv) which also contained mesitylene (4.66 μmol, 8 mM) as an internal standard. To this solution was added a stock solution in C_6D_6 of 4-toluenesulfonic acid (14 μmol, 93.3 mM, 150 μL). The mixture was immediately capped, shaken, and analyzed by ^{1}H NMR, which revealed conversion to **7** with concomitant elimination of benzene as the major products. However, during the first 6 min of the reaction, an intermediate was observed with ^{1}H and ^{31}P NMR spectra consistent with metal-centered protonation (see the Supporting Information)— specifically a rhodium hydride resonance (δ −18.94, m by ^{1}H NMR, d by $^{1}H\{^{31}P\}$ NMR, $^{1}J_{RhH}$ = 19.0 Hz) and broken symmetry of the PCH_2 and ^{i}Pr resonances. After 12 h at 21 °C the reaction had gone to 98% of the desired product by ^{1}H NMR with respect to mesitylene internal standard. The reaction mixture was poured into a 1 dram vial, concentrated under reduced pressure, and suspended in 1 mL of pentane. After 12 h at −35 °C the supernatant was removed by pipet to afford 5.8 mg (68% yield) of complex **7**. The precipitated material contains several minor (PNP)Rh impurities and is estimated to be 80% pure as determined by integration of the ^{31}P NMR spectrum. ^{1}H NMR (500 MHz, C_6D_6): δ 8.17 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, OTs CH), 6.91 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, pyr meta), 6.85 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, pyr para), 6.28 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, OTs CH), 2.43 (m, 4H, PCH_2), 2.27 (m, (septet by $^{1}H\{^{31}P\}$ $^{3}J_{HH}$ = 7.0 Hz), 4H, ^{i}PrCH), 1.97 (s, 3H, OTs CH_3), 1.56 (m, (doublet by $^{1}H\{^{31}P\}$ $^{3}J_{HH}$ = 7.0 Hz), 12H, $^{i}PrCH_3$), 1.02 (m, (doublet by $^{1}H\{^{31}P\}$ $^{3}J_{HH}$ = 6.9 Hz) 12H, $^{i}PrCH_3$). $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6): δ 48.41 (d, $^{1}J_{RhP}$ = 147.8 Hz). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ 165.10 (vtd, $^{2}J_{PC}$ = 6.4 Hz, $^{3}J_{RhC}$ = 1.1 Hz, pyr ortho), 143.74 (s, OTs quaternary), 138.48 (s, OTs quaternary), 130.04 (s, pyr para), 128.21 (s,OTs CH), 126.65 (s, OTs CH), 119.49 (vtd, $^{3}J_{PC}$ = 5.4, $^{4}J_{RhC}$ = 0.9 Hz, pyr meta), 34.48 (vtd, $^{1}J_{PC}$ = 6.9, $^{2}J_{PC}$ = 1.4 Hz, PCH_2), 24.26 (vt, $^{1}J_{PC}$ = 9.5 Hz, ^{i}PrCH), 20.74 (s, OTs CH_3), 19.32 (vt, $^{2}J_{PC}$ = 3.9 Hz, $^{i}PrCH_3$), 17.70 (s, $^{i}PrCH_3$).

*^{i}Pr(PNP)Rh(H)(OTs) (**8**).* In a J. Young tube was placed a stock solution of **5** in C_6D_6 (14 μmol, 583 μL, 24 mM, 1 equiv) which also contained mesitylene (4.66 μmol, 8 mM) as an internal standard. To this solution was added a stock solution in C_6D_6 of 4-toluenesulfonic acid (14 μmol, 93.3 mM, 150 μL). The mixture was immediately capped, shaken, and analyzed by ^{1}H NMR, which revealed conversion to **7** with concomitant elimination of benzene as the major products. After 12 h, the reaction had gone to complete conversion to complex **7**. The reaction mixture was heated to 100 °C for 12 h, during which time a white solid precipitated from the reaction mixture. The suspension was transferred to a 1 dram vial and the supernatant removed by pipet. The precipitate was washed with diethyl ether and dried under vacuum to give 8.1 mg (94% yield) of **8** as an off-white precipitate. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.68 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, pyr para), 7.34 (d, $^{2}J_{HH}$ = 7.6 Hz, 1H, pyr ortho), 7.23 (s, 1H, OTs), 7.19 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, OTs), 6.71 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, OTs), 3.73 (d br, $^{2}J_{HH}$ = 16.2 Hz, 2H, PCH_2), 3.49 (d br, $^{2}J_{HH}$ = 16.2 Hz, 2H, PCH_2), 2.93 (m, 2H, ^{i}PrCH), 2.24 (m, 5H, ^{i}PrCH′ overlapped with OTs-CH_3), 1.10 (m, (doublet by $^{1}H\{^{31}P\}$ $^{3}J_{HH}$ = 7.1 Hz), 6H, $^{i}PrCH_3$), 1.05 (m, 12H, $^{i}PrCH_3$), 0.86 (m, 6H, $^{i}PrCH_3$), −18.65 (vtd, $^{2}J_{HP}$ = 12.7, $^{1}J_{HRh}$ = 32.4 Hz, 1H, Rh−H). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2): δ 58.55 (td, $^{2}J_{PH}$ = 12.7, $^{1}J_{PRh}$ = 109.2 Hz). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): δ 161.42 (m, pyr ortho), 145.57 (s, OTs quaternary), 143.46 (m, OTs CH), 137.84 (s, pyr para), 137.08 (s, OTs quaternary), 129.80 (m, Rh−C), 124.82 (s, OTs CH),

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122.14 (s, OTs CH), 120.34 (vt, $^3J_{PC}$ = 4.1 Hz, pyr meta), 38.02 (vt, $^1J_{PC}$ = 9.7 Hz, PCH_2), 23.54 (vt, $^1J_{PC}$ = 10.0 Hz, ^{i}PrCH), 22.82 (vt, $^1J_{PC}$ = 13.8 Hz, ^{i}PrCH), 20.99 (s, OTs-CH_3), 18.75 (m, ^{i}PrCH$_3$), 18.51 (s br, ^{i}PrCH$_3$), 17.73 (s br, ^{i}PrCH$_3$), 17.16 (s br, ^{i}PrCH$_3$). Anal. Calcd for $C_{26}H_{42}NO_3SP_2Rh$: C, 50.90; H, 6.90; N, 2.28. Found: C, 51.09; H, 6.94; N, 2.22.

*^{i}Pr(PNP)Rh(H)(OTs)$_2$ (**9**).* In a J. Young tube was placed a stock solution of **5** in C_6D_6 (14 μmol, 583 μL, 24 mM, 1 equiv) which also contained mesitylene (4.66 μmol, 8 mM) as an internal standard. To this solution was added a stock solution in C_6D_6 of 4-toluenesulfonic acid (28 μmol, 93.3 mM, 300 μL). The mixture was immediately capped, shaken, and analyzed by ^{1}H NMR, which revealed complete conversion to **9** with concomitant elimination of benzene as the major products. The reaction was monitored again 1 h later and revealed no further reaction. The reaction mixture was transferred to a 1 dram vial, concentrated in vacuo, washed with pentane, and dried under vacuum to give 8.6 mg (78% yield) of **9** as an off-white precipitate. ^{1}H NMR (500 MHz, C_6D_6): δ 8.12 (d, $^3J_{HH}$ = 8.0 Hz, 2H, OTs), 8.07 (d, $^3J_{HH}$ = 8.1 Hz, 2H, OTs), 7.03 (t, $^3J_{HH}$ = 7.7 Hz, 1H, pyr para), 6.87 (d, $^3J_{HH}$ = 7.8 Hz, 2H, OTs), 6.83 (d, $^3J_{HH}$ = 8.0 Hz, 2H, OTs), 6.62 (d, $^3J_{HH}$ = 7.7 Hz, 2H, pyr meta), 4.49 (vtd, $^3J_{HP}$ = 4.4, $^2J_{HH}$ = 17.0 Hz, 2H, PCH_2), 3.30 (m, (septet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.2 Hz), 2H, ^{i}PrCH), 2.77 (vtd, $^3J_{HP}$ = 3.5, $^2J_{HH}$ = 17.1 Hz, 2H, PCH_2), 2.20 (m, (septet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.1 Hz), 2H, ^{i}PrCH), 1.94 (s, 3H, OTs-CH_3), 1.92 (s, 3H, OTs-CH_3), 1.55 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.2 Hz), 6H, ^{i}PrCH$_3$), 1.47 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.0 Hz), 6H, ^{i}PrCH$_3$), 1.29 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.2 Hz), 6H, ^{i}PrCH$_3$), 0.88 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 6.8 Hz), 6H, ^{i}PrCH$_3$), −18.97 (vtd, $^2J_{HP}$ = 10.2, $^1J_{HRh}$ = 19.5 Hz, 1H, Rh−H). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 49.85 (dd, $^2J_{PH}$ = 9.1, $^1J_{PRh}$ 100.6 Hz, 2P). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 167.06 (vt br, $^2J_{CP}$ = 4.5 Hz, pyr ortho), 141.32 (s, OTs quaternary), 139.47 (s, OTs quaternary), 137.71 (s, pyr para), 128.52 (s br, OTs CH), 128.47 (s, OTs CH), 126.63 (s, OTs CH), 126.33 (s br, OTs CH), 120.59 (vt, $^3J_{CP}$ = 5.5 Hz, pyr meta), 36.01 (vt, $^1J_{CP}$ = 9.4 Hz, PCH_2), 25.87 (vt, $^1J_{CP}$ = 12.7 Hz, ^{i}PrCH), 25.49 (vt, $^1J_{CP}$ = 11.0 Hz, ^{i}PrCH), 20.72 (br, 2xOTs-CH_3), 19.03 (vt, $^2J_{CP}$ = 2.0 Hz, ^{i}PrCH$_3$), 18.64 (br, ^{i}PrCH$_3$),18.17 (br, ^{i}PrCH$_3$), 17.86 (br, ^{i}PrCH$_3$). Anal. Calcd for $C_{33}H_{50}NO_6S_2P_2Rh$: C, 50.44; H, 6.41; N, 1.78. Found: C, 50.72; H, 6.49; N, 1.78.

*^{i}Pr(PNP)Rh(Ph)(Cl)$_2$ (**11**).* In a J. Young tube was placed a stock solution of **5** in C_6D_6 (6.8 μmol, 200 μL, 35 mM, 1 equiv) which also contained 1,3,5-trimethoxybenzene (1.4 μmol, 7 mM) as an internal standard. The solution was diluted with 250 μL of C_6D_6. To this solution was added a stock solution in C_6D_6 of 4-methylbenzyl chloride (20.4 μmol, 204 mM, 100 μL, 3 equiv). The mixture was immediately capped, shaken, and analyzed by ^{1}H and ^{31}P NMR, which revealed complete consumption of **5**, major conversion to **11** and 4,4′-dimethylbibenzyl, and an additional (PNP)Rh product consistent with oxidative addition of benzyl chloride (see section S1.5 in the Supporting Information for spectra: broken symmetry about ^{i}Pr and PCH_2, Rh-CH_2 (δ 4.20 (m by ^{1}H, d by ^{1}H{^{31}P} $^2J_{RhH}$ = 2.4 Hz), ^{31}P{^{1}H} (δ 34.35, d, $^1J_{RhP}$ = 113.0 Hz)). After 5 h, the concentration of the intermediate had decreased and a yellow precipitate (**11**) began to form. The solution was heated to 80 °C for 12 h, which gave a 74% yield of **11** and 95% of 4,4′-dimethylbibenzyl by ^{1}H NMR with respect to trimethoxybenzene internal standard. The product mixture was transferred to a 1 dram vial, and dichloromethane was added dropwise until the yellow precipitate dissolved. This mixture was layered with diethyl ether, which afforded yellow single crystals of **11** suitable for X-ray diffraction. The supernatant of the crystallization mixture was analyzed by GCMS, which revealed a single organic product with a mass consistent with 4,4′-dimethylbibenzyl. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.06 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Rh-Ph ortho), 7.71 (t, $^3J_{HH}$ = 7.7 Hz, 1H, pyr para), 7.39 (d, $^3J_{HH}$ = 7.4 Hz, 2H, pyr meta), 6.89 (t, $^3J_{HH}$ = 7.3 Hz, 2H, Rh-Ph meta), 6.83 (t, $^3J_{HH}$ = 7.0 Hz, 1H, Rh-Ph para), 3.92 (vt, $^2J_{PC}$ = 4.2 Hz, 4H, PCH_2), 2.89 (m, (septet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.3 Hz), 4H, ^{i}PrCH), 1.32 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.2 Hz), 12H, ^{i}PrCH$_3$), 1.05 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.3 Hz), 12H, ^{i}PrCH$_3$). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 37.02 (d, $^1J_{RhP}$ = 93.7 Hz). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 160.88 (vt, $^2J_{PC}$ = 3.2 Hz, pyr ortho), 144.11 (vtd, $^1J_{RhC}$ = 8.6, $^2J_{PC}$ = 24.8 Hz, Rh-Ph ipso), 139.98 (vtd, $^3J_{PC}$ = 2.4, $^2J_{RhC=}$ 0.7 Hz, Rh-Ph ortho), 137.86 (s, pyr para), 125.05 (s, Rh-Ph meta), 121.47 (s, Rh-Ph para), 120.78 (vt, $^3J_{PC}$ = 4.4 Hz, pyr meta), 40.28 (vt, $^1J_{PC}$ = 11.4 Hz, PCH_2), 24.00 (vtd, $^1J_{PC}$ = 10.5, $^2J_{RhC}$ = 1.1 Hz, ^{i}PrCH), 19.08 (s, ^{i}PrCH$_3$), 18.67 (s, ^{i}PrCH$_3$). Anal. Calcd for $C_{25}H_{40}NP_2RhCl_2$: C, 50.86; H, 6.38; N, 2.37. Found: C, 51.93; H, 6.57; N, 2.28. Material prepared by this method gave carbon analysis outside the range viewed as establishing analytical purity (Δ1.07%). Elemental analysis and graphical ^{1}H, ^{31}P, and ^{13}C NMR data are provided to illustrate the degree of purity of the bulk material obtained by this method without additional purification.

*^{i}Pr(PNP)Rh(I) (**12**).* In a 20 mL glass vial charged with a stir bar was placed 0.5 mL of an acetone solution of iPr(PNP)Rh(Cl) (72 mg, 0.15 mmol, 1 equiv) and 0.6 mL of an acetone solution of NaI (45 mg, 0.30 mmol, 2 equiv). After the mixture was stirred at room temperature for 10 min, ^{31}P NMR analysis indicated complete consumption of ^{i}Pr(PNP)Rh(Cl). The acetone solvent was removed by vacuum. The remaining solids were suspended in a minimal amount of benzene and syringe filtered. The filtrate was then concentrated and transferred to a small vial. Vapor diffusion of pentane was used to crystallize the product, iPr(PNP)Rh(I). ^{1}H NMR (500 MHz, C_6D_6): δ 6.98 (t, $^3J_{HH}$ = 7.8 Hz, 1H, pyr para), 6.4 (d, $^3J_{HH}$ = 7.69 Hz, 2H, pyr meta), 2.47 (vt, $^2J_{PH}$ = 3.5 Hz, 4H, PCH_2), 2.18 (m, (septet by ^{1}H{^{31}P} $^3J_{HH}$ = 6.9 Hz), 4H, ^{i}PrCH), 1.52 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.0 Hz), 12H, ^{i}PrCH$_3$), 0.97 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 6.9 Hz), 12H, ^{i}PrCH$_3$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 50.40 (d, $^1J_{RhP}$ = 139.4 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 163.29 (vt, $^2J_{CP}$ = 7.0 Hz, pyr ortho), 129.45 (s, pyr para), 119.69 (vt, $^3J_{CP}$ = 6.1 Hz, pyr meta), 36.57 (vt, $^1J_{PC}$ = 6.0 Hz, PCH_2), 24.18 (vt, $_1J_{PC}$ = 10.5 Hz, ^{i}Pr CH), 19.35 (t, $^2J_{PC}$ = 3.2 Hz, ^{i}Pr CH_3), 17.58 (s br, ^{i}Pr CH_3). Suitable elemental analysis was not obtained for complex **12**. Graphical ^{1}H, ^{31}P, and ^{13}C NMR data are provided to illustrate the degree of purity of the bulk material obtained by this method; however, the possible presence of residual sodium iodide cannot be excluded.

*^{i}Pr(PNP)Rh(Ph)(I)$_2$ (**13**).* In a J. Young tube was placed a stock solution of **5** in C_6D_6 (14 μmol, 500 μL, 28 mM, 1 equiv) which also contained mesitylene (4.0 μmol, 8 mM) as an internal standard. The solution was diluted with 100 μL of C_6D_6. To this solution was added a stock solution of iodine in C_6D_6 (14 μmol, 140 mM, 100 μL). The mixture was immediately capped, shaken, and analyzed by ^{1}H NMR, which revealed complete consumption of starting material, major conversion to **13**, and an additional species with a ^{1}H NMR spectrum consistent with the trans isomer of **13** (^{31}P{^{1}H} NMR δ 27.94 ppm, d, $^1J_{PRh}$ = 94.2 Hz). After 90 min the mixture had undergone complete conversion to **13** in 98% yield by ^{1}H NMR with respect to 1,3,5-trimethoxybenzene internal standard. The reaction mixture was transferred to a 1 dram vial, concentrated in vacuo, washed with pentane, and dried under vacuum to give 9.4 mg (87% yield) of **13** as an orange solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.86 (d br, $^3J_{HH}$ = 7.0 Hz, 1H, Ph ortho), 7.76 (t, $^3J_{HH}$ = 7.7 Hz, 1H, pyr para), 7.45 (d, $^3J_{HH}$ = 7.7 Hz, 2H, pyr meta), 6.94 (t br, $^3J_{HH}$ = 7.3 Hz, 1H, Ph meta), 6.89 (t, $^3J_{HH}$ = 6.9 Hz, 1H, Ph para), 6.70 (t br, $^3J_{HH}$ = 7.1 Hz, 1H, Ph meta), 5.59 (d br, $^3J_{HH}$ = 7.3 Hz, 1H, Ph ortho), 4.28 (vtd, $^2J_{HP}$ = 4.3, $^2J_{HH}$ = 17.2 Hz, 2H, PCH), 3.79 (m, (septet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.3 Hz), 2H, ^{i}PrCH), 3.63 (vtd, $^2J_{HP}$ = 4.0,$^2J_{HH}$ = 17.2 Hz, 2H, PCH), 2.02 (m, (septet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.2 Hz) 2H, ^{i}PrCH), 1.69 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.4 Hz), 6H, ^{i}PrCH$_3$), 1.49 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.3 Hz), 6H, ^{i}PrCH$_3$), 1.18 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.3 Hz), 6H, ^{i}PrCH$_3$), 1.13 (m, (doublet by ^{1}H{^{31}P} $^3J_{HH}$ = 7.3 Hz), 6H, ^{i}PrCH$_3$). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 33.56 (d, $^1J_{RhP}$ = 96.1 Hz). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 163.19 (vt, $^4J_{PC}$ = 4.1 Hz, pyr ortho), 145.78 (br, Ph ortho), 145.00 (vtd, $^2J_{PC}$ = 8.8, $^1J_{RhC}$ = 30.5 Hz, Ph ipso), 137.59 (s, pyr para), 132.16 (br, Ph ortho), 127.30 (br, Ph meta), 127.07 (br, Ph meta), 123.24 (s, Ph para), 122.21 (vtd, $^3J_{PC}$ = 5.1, $^4J_{RhC}$ = 0.8 Hz, pyr meta), 41.76 (vt, $^1J_{PC}$ = 10.9 Hz, PCH_2), 30.99 (vt, $^1J_{PC}$ = 11.7 Hz, ^{i}PrCH), 26.45 (vtd, $^1J_{PC}$ = 11.1 Hz, $^2J_{RhC}$ = 1.9 Hz, ^{i}PrCH), 21.33 (br, ^{i}PrCH$_3$), 20.28 (br, ^{i}PrCH$_3$), 19.48 (br, ^{i}PrCH$_3$), 18.77 (br, ^{i}PrCH$_3$). Graphical ^{1}H, ^{31}P,

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and ^{13}C NMR data are provided to illustrate the degree of degree of purity of the bulk material obtained by this method; however, the possible presence of residual iodine cannot be excluded.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00532.

General and synthetic procedures (PDF)
Coordinates of calculated structures (XYZ)

Accession Codes

CCDC 1564239−1564244 and 1572210 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451* (7177), 417.
(2) Davies, H. M. L.; Morton, D. *Chem. Soc. Rev.* **2011**, *40* (4), 1857.
(3) Hartwig, J. F. *J. Am. Chem. Soc.* **2016**, *138* (1), 2.
(4) Hartwig, J. F.; Larsen, M. A. *ACS Cent. Sci.* **2016**, *2* (5), 281.
(5) Davies, H. M. L.; Morton, D. *J. Org. Chem.* **2016**, *81* (2), 343.
(6) Cernak, T.; Dykstra, K. D.; Tyagarajan, S.; Vachal, P.; Krska, S. W. *Chem. Soc. Rev.* **2016**, *45* (3), 546.
(7) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.* **2012**, *45* (6), 936.
(8) Hartwig, J. F. *Acc. Chem. Res.* **2017**, *50* (3), 549.
(9) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51* (41), 10236.
(10) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110* (2), 1147.
(11) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110* (2), 890.
(12) Kuninobu, Y.; Ida, H.; Nishi, M.; Kanai, M. *Nat. Chem.* **2015**, *7* (9), 712.
(13) Davis, H. J.; Mihai, M. T.; Phipps, R. J. *J. Am. Chem. Soc.* **2016**, *138* (39), 12759.
(14) Li, H. L.; Kuninobu, Y.; Kanai, M. *Angew. Chem.* **2017**, *129* (6), 1517.
(15) Hoque, M. E.; Bisht, R.; Haldar, C.; Chattopadhyay, B. *J. Am. Chem. Soc.* **2017**, *139* (23), 7745.
(16) Roosen, P. C.; Kallepalli, V. A.; Chattopadhyay, B.; Singleton, D. A.; Maleczka, R. E., Jr.; Smith, M. R., III *J. Am. Chem. Soc.* **2012**, *134* (28), 11350.
(17) Das, S.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2008**, *130* (5), 1628.
(18) Andorfer, M. C.; Park, H. J.; Vergara-Coll, J.; Lewis, J. C. *Chem. Sci.* **2016**, *7* (6), 3720.
(19) Davis, H. J.; Phipps, R. J. *Chem. Sci.* **2017**, *8* (2), 864.
(20) Toste, F. D.; Sigman, M. S.; Miller, S. J. *Acc. Chem. Res.* **2017**, *50* (3), 609.
(21) Knowles, R. R.; Jacobsen, E. N. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107* (48), 20678.
(22) Kaphan, D. M.; Levin, M. D.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. *Science* **2015**, *350* (6265), 1235.
(23) Levin, M. D.; Kaphan, D. M.; Hong, C. M.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. *J. Am. Chem. Soc.* **2016**, *138* (30), 9682.
(24) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97* (8), 2879.
(25) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.
(26) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110* (26), 8729.
(27) Shinomoto, R. S.; Desrosiers, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 704.
(28) Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32* (2), 131.
(29) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122* (44), 10846.
(30) Schwartsburd, L.; Iron, M. A.; Konstantinovski, L.; Ben Ari, E.; Milstein, D. *Organometallics* **2011**, *30* (10), 2721.
(31) Goldberg, J. M.; Wong, G. W.; Brastow, K. E.; Kaminsky, W.; Goldberg, K. I.; Heinekey, D. M. *Organometallics* **2015**, *34* (4), 753.
(32) Hahn, C.; Spiegler, M.; Herdtweck, E.; Taube, R. *Eur. J. Inorg. Chem.* **1999**, *1999* (3), 435.
(33) Feller, M.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2013**, *135* (30), 11040.
(34) Feller, M.; Iron, M. A.; Shimon, L. J. W.; Diskin-Posner, Y.; Leitus, G.; Milstein, D. *J. Am. Chem. Soc.* **2008**, *130* (44), 14374.
(35) Hahn, C.; Spiegler, M.; Herdtweck, E.; Taube, R. *Eur. J. Inorg. Chem.* **1998**, *1998* (10), 1425.
(36) Anaby, A.; Feller, M.; Ben-David, Y.; Leitus, G.; Diskin-Posner, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2016**, *138* (31), 9941.
(37) Hanson, S. K.; Heinekey, D. M.; Goldberg, K. I. *Organometallics* **2008**, *27* (7), 1454.
(38) Kloek, S. M.; Heinekey, D. M.; Goldberg, K. I. *Angew. Chem., Int. Ed.* **2007**, *46* (25), 4736.
(39) Ben Ari, E.; Cohen, R.; Gandelman, M.; Shimon, L. J. W.; Martin, J. M. L.; Milstein, D. *Organometallics* **2006**, *25* (13), 3190.
(40) Ben Ari, E.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2006**, *128* (48), 15390.
(41) Zhang, X.; Kanzelberger, M.; Emge, T. J.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126* (41), 13192.
(42) Feller, M.; Ben Ari, E.; Diskin-Posner, Y.; Carmieli, R.; Weiner, L.; Milstein, D. *J. Am. Chem. Soc.* **2015**, *137*, 4634.
(43) Gatard, S.; Çelenligil-Çetin, R.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2006**, *128* (9), 2808.
(44) Puri, M.; Gatard, S.; Smith, D. A.; Ozerov, O. V. *Organometallics* **2011**, *30* (9), 2472.
(45) Fan, L.; Parkin, S.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127* (48), 16772.
(46) Gatard, S.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2007**, *26* (25), 6066.

DOI: 10.1021/acs.organomet.7b00532
Organometallics XXXX, XXX, XXX−XXX

(47) Sun, C.-L.; Shi, Z.-J. *Chem. Rev.* **2014**, *114* (18), 9219.
(48) Sun, C.-L.; Li, H.; Yu, D.-G.; Yu, M.; Zhou, X.; Lu, X.-Y.; Huang, K.; Zheng, S.-F.; Li, B.-J.; Shi, Z.-J. *Nat. Chem.* **2010**, *2* (12), 1044.
(49) Studer, A.; Curran, D. P. *Nat. Chem.* **2014**, *6* (9), 765.
(50) Neely, J. M.; Bezdek, M. J.; Chirik, P. J. *ACS Cent. Sci.* **2016**, *2* (12), 935.
(51) Obligacion, J. V.; Semproni, S. P.; Pappas, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2016**, *138* (33), 10645.
(52) Bernskoetter, W. H.; Hanson, S. K.; Buzak, S. K.; Davis, Z.; White, P. S.; Swartz, R.; Goldberg, K. I.; Brookhart, M. *J. Am. Chem. Soc.* **2009**, *131* (24), 8603.
(53) Giordano, G.; Crabtree, R. H. *Inorganic Syntheses*; Wiley: Hoboken, NJ, USA, 1990; Vol. *28*, pp 90−91.
(54) Leung, W.-P.; Ip, Q. W.-Y.; Wong, S.-Y.; Mak, T. C. W. *Organometallics* **2003**, *22* (22), 4604.
(55) Kawatsura, M.; Hartwig, J. F. *Organometallics* **2001**, *20* (10), 1960.
(56) Hermann, D.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2002**, *21* (5), 812.
(57) Kubota, Y.; Hanaoka, T.-A.; Takeuchi, K.; Sugi, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1553.

DOI: 10.1021/acs.organomet.7b00532
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