ORGANOMETALLICS

C–CN Bond Activation of Benzonitrile with [Rh^{-I}(dippe)]⁻

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Supporting Information

ABSTRACT: The complex $[Rh(dippe)(\mu-Cl)]_2$ (1) was reduced with potassium metal to produce the highly reactive Rh^{-1} species $[Rh(dippe)(\mu-K\cdotTHF)]_2$ (2). 2 was characterized by NMR spectroscopy (³¹P, ¹H) and IR spectroscopy after forming the derivative K[Rh(dippe)(CO)_2] (2a). The C–CN bond of benzonitrile was cleaved by oxidative addition when it was reacted stoichiometrically with 2 to form the anionic Rh(I) complex K[Rh(dippe)(CN)(Ph)] (3). 3 has been characterized by NMR spectroscopy (³¹P, ¹H, ¹³C), and by the use of



¹³C-labeled benzonitrile. C–CN bond cleavage was also attempted by reacting benzonitrile with the zwitterionic complex [Rh(dippe)(η^6 -Ph-BPh₃)] (4). A product **5** was formed from reaction with 2 equiv of benzonitrile. Reaction with ¹³C-labeled benzonitrile has ruled out the possibility of C–CN cleavage in this species, and a C–H bond activation pathway is operative instead.

INTRODUCTION

The activation of C–CN bonds is a formidable challenge given their high bond strengths. For example, the C–CN bond strength of benzonitrile is 132.3(2.0) kcal/mol.¹ Despite their strength, activation of C–CN bonds has been accomplished previously with [Ni-(dippe)H]₂.² When 2 equiv of benzonitrile was added to [Ni(dippe)-H]₂ in THF, loss of H₂ occurred to give the η^2 -nitrile complex Ni(dippe)(η^2 -NCPh) (eq 1). The η^2 -nitrile complex was longlived and was isolated and characterized by X-ray diffraction and NMR and IR spectroscopies. At room temperature, slow conversion to the C–CN activated product Ni(dippe)(CN)(Ph) occurred and the Ni(II) square-planar product was fully characterized. The reaction is versatile and has been used to activate C–CN bonds in cyanoquinolines,² aromatic nitriles,³ and 2-methyl-3-butenenitrile.⁴ Similar reactivity has been seen with a bis-*N*-heterocyclic carbene analogue.⁵



Reaction of benzonitrile with the group 10 analogue $[Pt(dippe)H]_2$ has also been examined.⁶ The reactivity was more complicated than the nickel case, and a series of C-H and C-CN bond activated complexes were isolated and characterized. The reaction required more strenuous conditions with a reaction temperature of 140 °C in neat benzonitrile being required (eq 2).



Reaction of benzonitrile with $[(dippe)Rh(\mu-H)]_2$ at room temperature has been examined by Fryzuk.⁷ The reactivity of this group 9 analogue was found to be dramatically different than the group 10 dippe-hydrides. Addition of the metal hydride to the nitrile carbon occurred to form the corresponding imide that bridges both Rh centers to give the complex $[Rh(dippe)]_2(\mu-H)$ - $(\mu-N=CHPh)$ (A) (eq 3). The reaction is general for nitriles and gives analogous products $[Rh(dippe)]_2(\mu-H)(\mu-N=CHR)$ (R = CH_3 , *o*-tolyl).⁷ This reactivity is not unexpected since the loss of H₂ would give a pair of odd electron $[Rh^0(dippe)]$ fragments, unlike the group 10 analogues that give saturated d^{10} fragments. Alternative methods were, therefore, sought to generate a reactive d^{10} monomeric $[Rh(dippe)]^-$ fragment that could lead to C– CN bond cleavage, as seen with [Ni(dippe)]. The two different methods that were examined are described herein.



RESULTS AND DISCUSSION

Generation of Reactive [Rh(dippe)(μ -K·THF)]₂. The first method attempted involved reducing the dinuclear Rh^I complex [Rh(dippe)(μ -Cl)]₂ (1) with potassium metal with the intended goal of generating a monomeric reactive [Rh⁻¹(dippe)]⁻ d^{10} fragment. 1 was initially reacted with 2 equiv of potassium in THF, and the reaction was monitored periodically by ³¹P NMR spectroscopy. After several hours of stirring, a new doublet was observed at δ 102.21 (¹ J_{Rh-P} = 190 Hz) in addition to the doublet resonance for 1 at δ 102.53 (¹ J_{Rh-P} = 201 Hz). After 2 days of stirring, all of 1 was converted to the new product, which

Received:April 21, 2011Published:October 13, 2011



Figure 1. IR spectrum of 2a taken in THF.

is believed to be a formally Rh⁰ complex. The observance of an NMR signal for this species suggests it is dimeric $[Rh(dippe)]_2$. Addition of 2 more equiv of potassium resulted in the exclusive formation of a new broadened doublet centered at δ 104.70 $({}^{1}J_{Rh-P} = 171 \text{ Hz})$, and this resonance was assigned to the Rh⁻¹ complex $[Rh(dippe)(\mu-K\cdot THF)]_2$ (2) (eq 4). The proposed structure with bridging potassium ions coordinated by THF is similar to that seen in other anionic metal dimers $(Li_4Cr_2Me_8 (THF)_{4,}^{8}$ Na₂Ni₂Ph₄ $(C_{2}H_{4})(THF)_{5,}^{9}$ Li₄Pt₂Me₈ $(ROR)_{4,}^{10}$ Li₃Fe₂Ph₆H₃ $(THF)_{5,}^{11}$ In addition, DFT calculations show 2 to be a stable, bound structure (see the Supporting Information). The reaction solution changed from yellow-orange (1) to a dark red (2) upon reduction. Eisenberg has shown that the reduction of $[Rh(diphos)_2]^+$ (diphos = $Ph_2PCH_2CH_2PPh_2$) occurred in two discrete single-electron steps, with initial formation of $[Rh(diphos)_2]$, followed by reduction to $[Rh(diphos)_2]^-$ with sodium naphthalenide.¹²



Bogdanovic was able to reduce Rh(diphos)₂Cl with activated magnesium to obtain [Rh(diphos)₂]MgCl.¹³ He called this product a "Grignard analogous" rhodium phosphine complex since the Rh⁻¹ center was nucleophilic and reacted with electrophiles, such as methyl iodide, to give Rh(diphos)₂(CH₃). The [Rh(diphos)₂]MgCl complex shares many similar characteristics to **2**. Rh(diphos)₂Cl was yellow in solution, but the solution changed to dark red upon reduction, the same as observed for conversion of **1** to **2**. The ³¹P NMR spectrum of Rh(diphos)₂Cl displays a doublet at δ 58.2 (¹J_{Rh-P} = 133 Hz), which became a broadened doublet centered at δ 62.0 (¹J_{Rh-P} = 197 Hz) when reduced to [Rh(diphos)₂]MgCl. **2**, like [Rh(diphos)₂]MgCl, is highly air-sensitive in the solid state and decomposed to a white powder after a few seconds of exposure to air.

The ¹H NMR spectrum of **2** is unexceptional with broad resonances ranging from δ 2.35 to 1.10 (THF- d_8), as would be expected for a dippe-metal complex. Reduction of **1** to give **2** could also be accomplished with activated magnesium using Bogdanovic's procedure, or with KC₈. The use of potassium naphthalenide brought about rapid reduction in a matter of minutes; however, this sample of **2** contained additional imurities from this method. All of the reduction methods led to the formation of [Rh(dippe)(μ -H)]₂ as a side product, as detected in the ¹H



Figure 2. ν_{co} stretching frequencies of literature examples related to K[Rh(dippe)(CO)₂]: (a)¹⁶ 1927 (m), 1874 (s) cm⁻¹, (b)¹⁷ 1860 (m), 1805 (s) cm⁻¹, (c)¹⁸ 1929 (s), 1858 (vs) cm⁻¹.



Figure 3. ³¹P NMR of **2a** after evaporation and redissolving in THF- d_8 .

NMR spectrum by the multiplet hydride resonance at δ -5.08 and the ³¹P{¹H} NMR spectrum by a doublet of multiplets at δ 104.6 (eq 5). Formation of [Rh(dippe)(μ -H)]₂ is proposed to form from the protonation of **2**, most likely from residual water in the THF solvent or from the glassware. Typically, 20 mg of **1** (0.025 mmol) was used for a reaction, and given the small amount of **1** used and the highly reactive nature of **2**, it is not surprising that some [Rh(dippe)(μ -H)]₂ formed.



An established method for characterizing low valent metal complexes is to derivatize them with CO to form a low valent metal carbonyl complex.¹⁴ This derivative can then be characterized by IR spectroscopy as a means of determining the degree of backbonding to the carbonyl ligands, as low valent species cause a substantial red shift of the CO vibrations. When one atm of CO was introduced to a THF solution of 2, a rapid reaction ensued as the solution color changed from dark red to clear orange. An IR spectrum of the reaction solution was taken, and carbonyl stretches were observed at $v_{co} = 1833$ (m), 1777 (m), and 1708 (w) cm^{-1} (Figure 1). These stretches are consistent with the formation of $K[Rh(dippe)(CO)_2]$, **2a**, as having been formed. A comparison can be made to similar complexes that are known in the literature (Figure 2). **2a** appears to be in the Rh^{-1} range based on these examples; however, the weak ν_{co} at 1708 cm⁻ might be explained by potassium ion binding to a carbon monoxide ligand (ion paring), which is known to give rise to



Figure 4. ³¹P NMR spectrum of $K[(dippe)Rh(^{13}CN)(Ph)]$ (3) in THF- d_8 .

bands at higher and lower energy.¹⁵ A ³¹P NMR spectrum was taken of **2a**, showing a doublet at δ 95.20 (¹*J*_{Rh-P} = 150 Hz) (Figure 3). Over the period of a day, however, the compound decomposed and only a broad resonance ($\nu_{1/2}$ = 1800 Hz) was also observed centered at δ 74.

Activation of the C–CN Bond in Benzonitrile. A THF solution of 2 was added to a stoichiometric amount of ¹³CN-labeled benzonitrile (2 equiv) and stirred for 2 days at room temperature. During this time, the reaction solution changed from dark red to cherry red, as conversion to the C–CN bond cleavage product K[(dippe)Rh(CN)(Ph)] (3) occurred (eq 6).



The ³¹P NMR spectrum of **3** showed two nonequivalent phosphorus resonances that both have a doublet of doublets of doublets splitting pattern when ¹³CN-labeled benzonitrile was used (Figure 4). A significant trans effect was observed for the Rh–P coupling constants, with P_A trans to the cyano group showing ¹J_{Rh–P} = 154 Hz (δ 82.84), and P_B trans to the phenyl group showing ¹J_{Rh–P} = 115 Hz (δ 91.08). Splitting by the ¹³CN gave a ²J_{P–C} = 95 Hz for P_A, which is trans to the labeled cyano group. P_B is cis to the cyano group and shows a smaller coupling of ²J_{P–C} = 15 Hz.

of ${}^{2}J_{P-C} = 15$ Hz. The 1 H NMR spectrum of 3 (Figure 5) also supports the assignment of the structure, with dippe methyl and ethylene resonances located between δ 0.88–1.39 (28H). The methine resonances show their characteristic multiplet splitting patterns at δ 2.05 and 1.94 (2H each), and the phenyl resonances were located at δ 7.64 (1H), 6.78 (2H), and 6.57 (2H).

A ¹³C NMR spectrum of 3 showed a very large doublet of doublets of doublets resonance for the ¹³CN group centered at δ 160.58 with the aforementioned cis and trans ²*J*_{P-C} couplings, and a rhodium coupling of ¹*J*_{Rh-C} = 47 Hz (Figure 6). The value found for ¹*J*_{Rh-C} is very similar to that found for Milstein's (PNP)Rh(CN) (PNP = 2,6-bis-(di-*tert*-butylphosphinomethyl)-pyridine) complex with a ¹*J*_{Rh-C} = 52 Hz.¹⁴ The aryl resonances



Figure 5. ¹H NMR spectrum of $K[(dippe)Rh(^{13}CN)(Ph)]$ (3) in THF- d_8 .



Figure 6. ¹³C NMR spectrum of $K[(dippe)Rh(^{13}CN)(Ph)](3)$ in THF- d_8 . ¹³CN resonance detail (inset).

were found at δ 142.43, 125.68, and 119.79 and were correlated to their respective proton peaks at δ 7.64, 6.78, and 6.57 by a ¹H–¹³C HSQC experiment. The ipso carbon of the phenyl group was difficult to observe since this weak resonance is predicted to be split into a doublet of doublets of doublets.

The formation of **3** was typically accompanied by the formation of a side product that has been identified as Fryzuk's $[(dippe)Rh]_2(\mu-H)(\mu-N=CHPh)$ (**A**),⁷ which formed when benzonitrile reacted with $[(dippe)Rh(\mu-H)]_2$ that formed during the reduction of **1**. Elimination of **A** can be achieved by eliminating water from the solvent and reaction glassware, although this is not easy with the reactivity of **1**. A ratio of **3**/**A** of 4:1 was observed under typical conditions (see the Experimental Section). Separation of **3** and **A** can be achieved by washing the crude residue with hexanes to remove **A**.

This method is effective in isolating 3 but is also problematic. Coordination of THF to 3 appears to be necessary for the stability of 3. Washing 3 with hexanes and then drying by vacuum caused the red residue to turn into a cinnamon-colored powder. Elemental analysis showed that significant decomposition had



Figure 7. ORTEP drawing of $[(dippe)Rh(\eta^6-Ph-BPh_3)]$ (4). Ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

occurred, as the %C was low by 26%! In a separate trial, the crude mixture was purified by washing with hexanes and then redissolving in THF. The solution was evaporated to dryness and gave a red residue; elemental analysis of this sample revealed that decomposition occurred, but not as significantly as before (8% low on %C).

Attempted C–CN Activation with [(dippe)Rh(η^6 -Ph-BPh₃)]. A second approach to C-CN bond activation of benzonitrile attempted to generate a reactive [(dippe)Rh]⁺ fragment that would employ a Rh(I)/(III) oxidative addition pathway. Initially, AgBF₄ was reacted with 1 in an attempt to abstract chlorides from 1 to generate [(dippe)Rh]⁺. However, this method was problematic and resulted in multiple decomposition products. Instead, the sodium salt NaBPh4 was reacted with 1 in THF solution heated at 60 °C for 8 h (eq 7). This resulted in the precipitation of NaCl and the appearance of a new doublet at δ 104.22 (${}^{1}J_{Rh-P} = 204$ Hz) in the ${}^{31}P$ NMR spectrum. X-ray diffraction of the orange solid (Figure 7) revealed the zwitterionic η^{6} -arene product [(dippe)Rh(η^{6} -Ph-BPh₃)](4). 4 is known in the literature, having been previously used as a hydroboration catalyst.¹⁹ When 4 was reacted with 2 equiv of benzonitrile in THF at 120 °C, a new product (5) was formed.



The ³¹P NMR spectrum (Figure 8) of **5** is similar to that of **3**, with two nonequivalent phosphorus nuclei at δ 91.79 and 87.49 that were each split into a doublet of doublets. The ¹*J*_{Rh-P} coupling constants are 186 and 119 Hz, which are suggestive of C–CN bond cleavage; however, this possibility was eliminated from consideration when the reaction was repeated with ¹³CN-labeled benzonitrile. Only a small coupling of ²*J*_{P-C} = 5.5 Hz was observed for the resonance at δ 87.49. Five different ¹³CN-labeled resonances were observed in the ¹³C NMR spectrum



(integration normalized to the largest resonance): δ 190 (0.66), 177 (0.10), 165 (0.16), 163 (1.00), and 155 (0.15). The only coupling observed was a doublet for the resonance at δ 190 (J =7.5 Hz); all of the other ¹³CN resonances were singlets. A resonance with the doublet of doublets of doublets pattern indicative of a (P_AP_B)Rh–CN group was not observed (see the Supporting Information for these spectra).

The major resonance at δ 163 is proposed to be an imine carbon on the basis of DEPT-135 and ¹H–¹³C HSQC NMR experiments. A positive signal was observed for this resonance when a DEPT-135 NMR experiment was performed, indicative of a carbon bonded to an odd number of hydrogens, and a ¹H correlation for δ 163 was found at δ 7.4 in a ¹H–¹³C HSQC experiment. An IR stretch at 1967 cm⁻¹ was observed for a bound benzonitrile, along with a broad imine absorption at 1455 cm⁻¹ for the Lewis acid coordinated imine. A similar boron adduct of a Lewis acid coordinated metalloimine, (bipy)(Et)Ni-N(BEt₃)= CHPh, has been reported in the literature with "no IR bands above 1500 cm⁻¹".²⁰

The other four ¹³CN resonances were related to one another since addition of their integrations adds up to 1.0 and accounts for the second equivalent of benzonitrile added. The resonance at δ 190 is proposed to be a Rh-coordinated η^1 -benzonitrile due to its small coupling constant (vide supra). The other three resonances appear to be side products that form from the coordinated benzonitrile. The resonance at δ 177 was identified as benzophenone imine (by comparison with an authentic sample), while the resonance at δ 155 was confirmed by independent synthesis to be the allene analogue Ph₂C=N=BPh₂.²¹ The minor resonance at δ 165 was not identified.

An integration of approximately 25H for aryl proton resonances was observed in the ¹H NMR spectrum, corresponding to the large number of resonances observed between δ 130 and 140 in the ¹³C NMR spectrum. Approximately 32H were found in the alkyl region, and it is instructive that the pattern observed is indicative of an approximate mirror plane symmetry. Each of the groups in this region appear in two nonequivalent, but equal, resonances: 12H each for two nonequivalent sets of methyl groups, 2H each for two nonequivalent sets of methylene protons, and 2H each for two nonequivalent sets of methine protons



Figure 9. ¹H NMR and proposed structure for 5.

(Figure 9). On the basis of the experimental data acquired, the proposed structure for **5** is shown in eq 8.



The cyclometalated product is proposed to form by activation of the ortho C–H bond of benzonitrile with concomitant nitrile insertion. This is proposed to be the rate-determining step since only 4 and 5 were observed by ³¹P NMR spectroscopy. Addition of a phenyl group from the BPh₄ anion is also proposed to occur. A report in the literature showed that the analogous complex [(diphos)Rh(η^6 -Ph-BPh₃)] transfers a phenyl to Rh to form [(diphos)Rh(η^6 -Ph-BPh₃)] transfers a phenyl to Rh to form [(diphos)RhPh] upon heating in acetone at 70 °C.²² A phenyl group was not transferred when 4 was heated at 120 °C by itself in THF. 4 has a resonance at δ –7.21 in the ¹¹B NMR spectrum, whereas no signal was observed for 5. This absence of a resonance suggests that the boron atom is coupled to a quadrupolar atom, such as nitrogen, which would account for no resonance being observed.

The formation of **5** was found to be highly dependent on the amount of benzonitrile employed. When 1 equiv of benzonitrile was used in the reaction, decomposition of **5** occurred as **4** was consumed. Benzene, as detected by ¹H NMR, was generated from the decomposition. Use of excess benzonitrile (10 equiv) resulted in the formation of two additional products by ³¹P NMR spectroscopy, which could not be identified. Under these conditions, benzophenone imine became the major ¹³CN-labeled product. It should be noted that **5** is an extremely air-sensitive dark green product that decomposes rapidly in air, but is stable under nitrogen in the solid and solution states for extended periods of time.

CONCLUSION

The formation of the reactive Rh^{-1} complex [(dippe)Rh-(μ -K·THF)]₂ (2) has been achieved by reduction of [(dippe)-Rh(μ -Cl)]₂ (1) by potassium metal. Reaction with CO produced **2a**, which was characterized by IR spectroscopy as K[Rh(dippe)- $(CO)_2$ and has IR data similar to analogous complexes in the literature. Reaction of 2 with stoichiometric benzonitrile produces the C-CN cleavage product Rh(dippe)(Ph)(CN) (3). This formulation for 3 has been confirmed by use of ¹³CNlabeled benzonitrile. Synthesis of 3 was hindered by formation of the side product A. The isolation of pure 3 has been difficult to achieve, as it appears that the stability of 3 is dependent upon the presence of THF. Product 5 was synthesized from reaction of the zwitterionic complex [(dippe)Rh(η^6 -Ph-BPh₃)] (4) with 2 equiv of benzonitrile. The use of ¹³CN benzonitrile in the reaction helped to rule out the possibility of C-CN bond cleavage in 5. The formation of an imine carbon seemed to suggest that the product may arise from C-H bond activation of benzonitrile, followed by nitrile insertion. The reaction is highly dependent upon stoichiometry, with 1 equiv of benzonitrile resulting in decomposition and an excess resulting in the formation of multiple products.

EXPERIMENTAL SECTION

All operations were performed under a nitrogen atmosphere unless otherwise stated. THF was distilled from dark purple solutions of sodium benzophenone ketyl or from NaK. Carbon monoxide was purchased from Air Products Co. 1,2-Bis(diisopropylphosphino)ethane was synthesized according to a literature method.²³ [Rh(dippe)- $(\mu$ -Cl)]₂²⁴ (1) and Ph₂C=N=BPh₂²¹ were synthesized as previously reported. Sodium tetraphenylborate was purchased from Sigma-Aldrich, dried under vacuum, and stored under nitrogen. ¹³C-carbonyl-labeled acetic acid was purchased from Cambridge Isotopes Laboratories and was reacted with benzenesulfonamide (purchased from Sigma-Aldrich) to produce Ph¹³CN using the method of Short.²⁵ Celite was heated to 200 °C under vacuum overnight and stored under nitrogen. A Siemens-SMART 3-Circle CCD diffractometer was used for X-ray crystal structure determinations. Elemental analyses were obtained at the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456. All ¹H, ³¹P, and ¹³C NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer. The ¹H chemical shifts are reported relative to the residual proton resonance in the deuterated solvent. ³¹P chemical shifts are reported relative to the signal of external 85% H₃PO₄. Mass spectra were recorded using a Shimadzu LCMS-2010. DFT calculations were made using Gaussian 09.26

Synthesis of $[(dippe)Rh(\mu-K\cdotTHF)]_2$ (2). In a nitrogen-filled glovebox, $[Rh(dippe)(\mu-Cl)]_2$ (1) (17.8 mg, 0.0222 mmol) was dissolved in 2 mL of THF and added to excess potassium metal (21 mg, 0.537 mmol). The reaction solution was stirred for 5 h, during which time the solution changed from a clear yellow-orange to a cloudy dark red. Filtration through a fine fritted funnel was used to remove precipitated KCl. 2 was isolated by evaporating THF to obtain a dark red residue. ¹H NMR (400 MHz, THF- d_8 , 25 °C): δ 3.62 (s, 8H), 2.05 (m, 2H), 1.85 (m, 2H), 1.78 (m, 8H), 1.30–0.85 (br m, 28 H). ³¹P{¹H} NMR (162 MHz, THF- d_8 , 25 °C): δ 104.70 (d, J_{Rh-P} = 171 Hz).

Synthesis of K[(dippe)Rh(CO)₂] (2a). In a nitrogen-filled glovebox, [Rh(dippe)(μ -Cl)]₂ (1) (9.7 mg, 0.0121 mmol) was dissolved in 2 mL of THF and added to excess potassium metal (5.7 mg, 0.145 mmol). The reaction solution was stirred for 3 h, during which time the solution changed from a clear yellow-orange to a cloudy dark red. The unfiltered solution was placed in a flame-dried ampule. Nitrogen was removed by the freeze—pump—thaw degassing (3×) method. One atmosphere of CO was introduced to the reaction vessel. The solution color changed from dark red to a clear orange. An aliquot of this solution was used to obtain an IR spectrum: 1833 (m), 1777 (m), 1708 (w) cm⁻¹. The reaction solution was later evaporated to dryness and dried for 2 h. It was redissolved in THF- d_8 , and ³¹P and ¹H NMR spectra were taken. ³¹P{¹H} NMR (162 MHz, THF- d_8 , 25 °C): δ 95.20 (d, ¹ J_{Rh-P} = 150 Hz). ¹H NMR (400 MHz, THF- d_8 , 25 °C): δ 2.35 (br s, 4H), 1.67 (br m, 4H), 1.10 (br m, 24H). Anal. Calcd (found) for C₁₆H₃₂KO₂P₂Rh: %C, 41.74 (38.06); %H, 7.01 (6.53); %N, 0.00 (-0.02).

Synthesis of K[(dippe)Rh(¹³CN)(Ph)] (3). In a nitrogen-filled glovebox, unfiltered 2 from the procedure above was added portion-wise by pipet to a Schlenk flask containing 13 CN-labeled benzonitrile (4.62 μ L, 0.0444 mmol). The reaction solution was stirred for 44 h, during which time the solution changed from dark red to cherry red. The reaction was complete after 1 day of stirring. An aliquot of the reaction solution was taken and analyzed by ³¹P NMR spectroscopy, which showed that 80% of 3 and 20% of A had formed (by integration). The reaction solution was filtered through Celite to remove KCl. A was removed by concentrating the reaction solution to dryness and washing the residue with hexanes (3 mL) to remove A. The solid was redissolved in THF, evaporated to dryness, and dried for 1 day by vacuum. Yield: 9.8 mg (43%). Past trials had shown that failure to redissolve in THF leads to significant decomposition typified by the formation of a cinnamon brown powder and poor analytical data (Anal. Calcd (found): %C, 49.70 (23.42); %H, 7.35 (2.94); %N, 2.76 (1.52)). ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ 7.64 (br s, 2H), 6.78 (t, J = 6.8 Hz, 2H), 6.57 (t, J = 6.8 Hz, 1H), 2.05 (m, 2H), 1.94 (m, 2H), 1.39–1.20 (m, 10H), 1.10–1.00 (m, 12H), 0.90 (dd, J = 7, Hz, 6H). ¹³C NMR (100 MHz, THF- d_8 , 25 °C): δ 160.59 (ddd, J_{Rh-P} = 47.3, $J_{P-C} = 94.5$, $J_{P-C} = 15.5$ Hz), 142.43 (s), 125.68 (s), 119.79 (s), 27.42 (s), 27.26 (s), 21.00 (d, J = 6.8 Hz), 20.31 (d, J = 6.8 Hz), 19.55 (s), 19.07, ipso carbon not observed, alkyl resonances may be obscured by overlap with THF. ³¹P{¹H} NMR (162 MHz, THF- d_8 , 25 °C): δ 91.08 $(ddd, {}^{1}J_{Rh-P} = 115, {}^{2}J_{P-C} = 15.5, {}^{2}J_{P-P} = 22 \text{ Hz}), 82.84 (ddd, {}^{1}J_{Rh-P} = 154, {}^{2}J_{P-C} = 94.5, {}^{1}J_{P-P} = 22 \text{ Hz}).$ Anal. Calcd (found) for C₂₁H₃₇-RhP₂NK: %C, 49.70 (41.06); %H, 7.35 (5.58); %N, 2.76 (2.44).

Synthesis of [(dippe)Rh(η⁶-Ph-BPh₃)] (4). 1 (19.2 mg, 0.0240 mmol) and NaBPh₄ (16.0 mg, 0.0467 mmol) were dissolved in 1 mL of THF and placed in a J-Young NMR tube. The tube was placed in an oil bath and heated for 6.5 h, during which time NaCl precipitated from solution. The solution was filtered through Celite and evaporated to dryness to obtain an orange crystalline solid (32.5 mg, 99%). ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ 7.18 (d, *J* = 6.8 Hz, 6H), 6.94 (t, *J* = 8.0 Hz, 6H), 6.84 (t, *J* = 6.0 Hz, 2H), 6.68 (d, *J* = 6.0 Hz, 2H), 6.56 (t, *J* = 6.0 Hz, 1H), 6.13 (t, *J* = 6.0 Hz, 2H), 1.68 (m, 4H), 1.18 (m, 4H), 1.02 (m, 24H). ¹³C NMR (100 MHz, THF-*d*₈, 25 °C): δ 91.79 (dd, ¹*J*_{Rh-P} = 186, ²*J*_{P-P} = 23 Hz), 87.49 (dd, ¹*J*_{Rh-P} = 119 Hz, ²*J*_{P-P} = 23 Hz). ¹¹B{¹H} NMR (160 MHz, THF-*d*₈, 25 °C): δ -7.21 (s). This compound was reported previously in ref 19.

Synthesis of Metalloimine 5. In a nitrogen-filled glovebox, 4 (9.6 mg, 0.014 mmol) was dissolved in 1 mL of THF and placed in a J-Young NMR tube. Benzonitrile (2.9 μ L, 0.028 mmol) was added by syringe to the sample. Nitrogen was removed by the freeze–pump–thaw degassing (2×) method. The tube was then heated at 120 °C for 18 h, during which time the solution colored changed from a clear orange to a opaque dark green. When the solution or solid of 5 turns red, it has decomposed. ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ 7.8–7.0 (br m, 25H), 6.86 (t, *J* = 7.6 Hz, 2H), 6.58 (t, *J* = Hz, 1H), 2.25 (m, 2H), 2.14 (m, 2H), 1.51 (m, 2H), 1.33 (m, 2H), 1.21 (m, 12H), 1.10 (m, 12H). ¹³C NMR (100 MHz, THF-*d*₈, 25 °C): δ 189.8 (d, *J* = 7.5 Hz), 162.8 (s), 149.59 (s), 143–121 (aryl), 27.52–19.48 (dippe).

ASSOCIATED CONTENT

Supporting Information. ³¹P and ¹³C NMR spectra for 5^{-13} C, tables of crystallographic data for 4, and DFT calculations of structure 2. This material is available free of charge via the Internet at http://pubs.acs.org. Crystal structure data for 4 has

been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 818643.

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ACKNOWLEDGMENT

Acknowledgement is made to the U.S. Department of Energy, Office of Basic Sciences, for their support of this work (Grant DOE86-ER-13569), and to the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

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