ORGANOMETALLICS

C-CN vs C-H Cleavage of Benzonitrile Using [(dippe)PtH]₂

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Supporting Information

ABSTRACT: The reaction of [(dippe)PtH]₂ with benzonitrile at 140 °C produced two products, the C-H-activated adduct $(dippe)Pt(H)(2-C_6H_4CN)$ (2) and the C-CN-activated adduct (dippe) (dippe)Pt(Ph)(CN) (5), with the kinetically favored C-H activation product forming in a significant majority (\sim 18:1). Further reaction showed a formal β -cyano elimination in 2, forming (dippe)Pt(H)(CN) (3) and benzene. Following the elimination, C-H activation of a second benzonitrile by 3 led to three regioisomers of $(dippe)Pt(CN)(C_6H_4CN)$ (4).



INTRODUCTION

The cleavage of carbon–carbon σ -bonds has become an area of increasing importance and study in the field of organometallic chemistry because of the potential for applications in both organic synthesis and industrial chemistry. This has commonly been achieved through methods such as relief of ring strain or attainment of aromaticity and, more recently, through the insertion of a transition metal center into certain types of carbon-carbon bonds.^{1,2} One area of C-C activation that has become increasingly studied is cleavage using alkyl- and arylnitrile substrates. 3-6 A number of studies have used Ni(0)phosphine and -phosphite catalysts as an efficient method for the activation of C-CN bonds.⁷ One particular Ni(0)-phosphine complex precursor that has been studied by our lab is [(dippe)NiH]₂, which is shown to produce a reactive Ni(0) fragment and has been used to activate complexes including alkyl-, allyl-, and aryl-nitriles, including a recent example provided by Garcia and Jones that demonstrated a reversible activation of benzonitrile (eq 1).^{1c,3a-3c,8}



The reaction of $[(dippe)NiH]_2$ and benzonitrile initially forms an η^2 -Ni(0) complex that is converted to a Ni(II) complex, reaching an equilibrium favoring the latter ($K_{eq} = 1.62$). Unlike the nickel systems described above that preferentially favor C-C activation, platinum systems tend to follow both C–H and C–C activation pathways. 9 Past studies have shown that PtL_2 fragments are reactive toward oxidative additions via C-H bond cleavage.¹⁰ Whitesides et al. demonstrated the activation of a series of alkyl, trimethylsilyl, aryl, benzyl, and alkynyl C-H

bonds via a Pt(0) fragment (eq 2).¹⁰



Although no C-C activation was observed in that system, later work by Jones et al. demonstrated C-C activation of biphenylene with platinum-phosphine systems.^{1c,11} Among the platinum catalysts used for these reactions are the nonchelating $Pt(PEt_3)_3$ phosphine complex and the chelating [(dippe)PtH]₂ phosphine complex.¹² Both species were observed to insert into biphenylene via C-C cleavage (eq 3).

$$Pt(PEt_{3})_{3} + \underbrace{10 \text{ days}}_{C_{6}D_{6}} (PEt_{3})_{2}Pt + \underbrace{(+ PEt_{3})}_{C_{6}D_{6}} (3)$$

As indicated by these previous examples, [Pt(dippe)] has shown the ability to cleave both C-H and C-C bonds, whereas [Ni(dippe)] preferentially cleaves C-C bonds. The work described herein evaluates the reaction of benzonitrile with the analogous [(dippe)PtH]₂ complex for the purpose of comparison with the nickel system.

RESULTS AND DISCUSSION

Reaction of [(dippe)PtH]₂ with Benzonitrile. A solution of [(dippe)PtH]₂ was dissolved in neat benzonitrile, producing a dark brown solution (Scheme 1).13 The reaction could be monitored conveniently by ³¹P{¹H} NMR spectroscopy, and

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Scheme 1. Sequence of Complexes Produced during Reaction of 1 in Benzonitrile



the initial spectrum showed a singlet at δ 105.3 with multiple platinum satellites (90%, J_{Pt-P} = 410, 2210 Hz; J_{P-P} = 45 Hz) assigned to $[(dippe)PtH]_2$ (1a) and a singlet at δ 88.2 with platinum satellites (10%, ${}^{1}J_{Pt-P} = 1862$ Hz) assigned to (dippe)PtH₂ (1b), as reported by Andersen (Figure 1, top).¹² The sample was heated to 140 °C, and after 2 h the color changed from dark brown to yellow-brown. 1a completely disappeared and only traces of 1b (3%) remained (Figure 1, middle). A new complex identified by singlets at δ 84.8 and 71.7 with ${}^{1}J_{Pt-P}$ = 1944 and 1784 Hz, respectively, was observed to grow in (70%) and was assigned to the C-H-activated complex $(dippe)Pt(H)(2-C_6H_4CN)$ (2). One other set of singlets at δ 74.5 and 63.5 with ${}^{1}J_{Pt-P} = 1600$ and 2757 Hz, respectively, was observed in a small quantity (4%) and was assigned to the C-CN-activated product (dippe)Pt(Ph)(CN) (5), as these Pt-P coupling constants are typical for phosphorus trans to phenyl and cyanide ligands, respectively, in this series of compounds.

Further heating showed 1b to disappear and 2 to steadily decrease, while 5 remained unchanged. A new complex with singlets at δ 83.1 and 79.0 with ${}^{1}J_{Pt-P}$ = 2677 and 1720 Hz, respectively, was observed to grow in as 2 decreased and was assigned to the β -cyano elimination product (dippe)Pt(H)(CN) (3). After 22 h, 2 (17%) had decreased, 3 (26%) remained constant, and a new complex (4) was observed with two sets of three singlets closely grouped together at δ 74.8 and 64.5 with ${}^{1}J_{
m Pt-P} pprox$ 1750 and 2680 Hz, respectively. This product was assigned to the three regioisomers of a second C-H-activated complex, $(dippe)Pt(CN)(o/m/p-C_6H_4CN)$. After 7 days at 140 °C, 2 had completely disappeared, a small amount of 3 (3%) remained, and 4 (64%) was the dominant species. The amount of 5 observed did not change. The remaining material is believed to have decomposed into platinum metal and (dippe)Pt(CN)₂. A product distribution plot is shown in Figure 2. No ${}^{2}J_{P-P}$ coupling was observed in any of the platinum complexes possibly due to the geometry of the complexes.

Characterization of 2. After 1 h at 140 °C, the reaction of 1 in benzonitrile was cooled to room temperature. The spectrum showed predominantly 2 (70%) with small amounts of 1 (3%)



Figure 1. NMR spectra for the reaction of $[(dippe)PtH]_2$ in neat benzonitrile at 140 °C at t = 0 (top), t = 2 h (middle), and t = 72 h (bottom) (s denotes platinum satellites).



Figure 2. Distribution of species during the reaction of $[(dippe)PtH]_2$ in neat benzonitrile.

and 3 (12%). The solvent was removed in vacuo, and the remaining brown residue was recrystallized using THF/hexanes vapor diffusion. A colorless crystal of 2 suitable for X-ray

diffraction was obtained. Selected bond distances and angles for **2** are given in Figure 3.



Figure 3. Schematic of **2** and ORTEP drawing showing 30% probability ellipsoids. Selected bond distances (Å): Pt1-C2 (2.065(7)), C7-N1 (1.150(11)). Selected angles (deg): P1-Pt1-P2 (87.92(9)). The hydride ligand could not be located in the difference Fourier map, but was included in the molecular formula.



Figure 4. Schematic of **3** and ORTEP drawing showing 30% probability ellipsoids. Selected bond distances (Å): Pt1-H1 (1.59(8)), Pt1-C1 (1.998(7)), C1-N1 (1.156(9)). Selected angles (deg): C1-Pt1-H1 (86(3)), P1-Pt1-P2 (87.19(7)).

A sample of the remaining crystals was dissolved in C_6D_6 and characterized via ¹H NMR spectroscopy. A doublet of doublets with platinum satellites was observed at $\delta - 0.29$ with ${}^2J_{P-H} = 16$ Hz (*cis*-coupling), ${}^2J_{P-H} = 185$ Hz (*trans*-coupling), and ${}^1J_{Pt-H} = 1159$ Hz consistent with the presence of a terminal hydride in the C-H-activated complex shown above. Additionally, four resonances were observed in the aromatic region at $\delta 6.72$ (d), 6.93 (t), 7.51 (d), and 7.65 (t) indicative of the aromatic protons of the coordinated 2-cyanophenyl group. The ${}^{31}P{}^{1}H{}^{1}$ spectrum showed two singlets with platinum satellites at δ 83.8 and 70.4 with ${}^{1}J_{Pt-P} = 1936$ and 1746 Hz, respectively. IR data of the sample showed $\nu_{CN} = 2280$ cm⁻¹, indicative of a strong CN bond with little to no π -back-bonding.

Characterization of 3. A solution of 1 in benzonitrile was heated to 120 $^{\circ}$ C for 5 days, giving 3 as the dominant product (54%) with 2 (18%), 5 (11%), and 1 (6%) still remaining. The solution was cooled to room temperature, and the solvent was removed in vacuo, leaving an orange-brown residue, which was recrystallized using THF/hexanes vapor diffusion. A colorless crystal of 3 suitable for X-ray diffraction was obtained. Selected bond distances and angles are given in Figure 4.

A portion of the remaining crystals was redissolved in toluened₈ and characterized by ¹H NMR spectroscopy. A doublet of doublets was observed at δ –1.26 with ²J_{P-H} = 16 Hz (*cis*coupling), ²J_{P-H} = 185 Hz (*trans*-coupling), and ¹J_{Pt-H} = 1008 Hz, indicative of the terminal hydride shown in the X-ray crystal structure. The ³¹P{¹H} NMR spectrum (toluene-d₈) showed resonances at δ 81.8 and 77.2 with ¹J_{Pt-P} = 2677 and 1669 Hz, respectively. IR data of the sample showed $\nu_{\rm CN} = 2274$ cm⁻¹, indicating a strong CN bond that is similar in strength to that observed in **2** with little to no π -back-bonding.

Characterization of 4. The solution of 1 in benzonitrile was heated to 140 °C for 7 days, making *ortho-, meta-*, and *para-*4 as almost the exclusive products (73%), with trace (dippe)Pt(CN)₂ (4%) and decomposition products making up the remaining material. The solvent was removed in vacuo, leaving a brown residue, which was recrystallized via slow evaporation from a mixture of hexanes, benzene, ether, and THF, producing colorless crystals of 4 suitable for X-ray diffraction. One selected crystal was found to contain an *ortho*-cyanophenyl group. Another selected crystal was found to contain a 50/50 disorder of the *meta-* and *para-* isomers. Selected bond distances and angles are given in Figure 5.



Figure 5. ORTEP drawings of **4a**, **4b**, and **4c** showing 30% probability ellipsoids. **4a**. Selected bond distances (Å): Pt1-C1 (2.069(5)), Pt1-C8 (2.009 (5)), C8-N2 (1.158(7)), C7-N1 (1.162(8)). Selected angles (deg): C1-Pt1-C8 (86.81(5)), P1-Pt1-P2 (87.3(2)). **4b**. Selected bond distances (Å): Pt1-C1 (2.075(5)), Pt1-C8 (2.026 (4)), C8-N2 (1.128(6)), C7-N1 (1.151(12)). Selected angles (deg): C1-Pt1-C8 (87.6(8)), P1-Pt1-P2 (87.1(4)). **4c**. Selected bond distances (Å): Pt1-C1' (2.078(5)), Pt1-C8 (2.026(4)), C8-N2 (1.128(6)), C7'-N1' (1.167(13)). Selected angles (deg): C1'-Pt1-C8 (88.5(8)), P1-Pt1-P2 (87.1(4)).



Figure 6. (a) ORTEP drawing of 5a showing 30% probability ellipsoids. Selected bond distances (Å): Pt1-C1 (2.077(4)), Pt1-Cl1 (2.3710(12)). Selected angles (deg): C1-Pt1-Cl1 (94.21(13)), P1-Pt1-P2 (88.00(13)). (b) ORTEP drawing of 5 showing 30% probability ellipsoids. Selected bond distances (Å): Pt1-C1 (2.003(4)), Pt1-C2 (2.074(4)), C1-N1 (1.141(5)). Selected angles (deg): C1-Pt1-C2 (88.30(15)), P1-Pt1-P2 (86.71(4)).

The resultant crystal structures show that complex 4 forms with the benzonitrile-CN group in each of the *ortho*, *meta*, and *para* positions. This conclusion is supported by the ³¹P{¹H} NMR spectrum (THF- d_8), where two sets of three singlets are observed centered at $\delta \sim 73.6$ and ~ 63.5 with ${}^{1}J_{\text{Pt-P}} = 1600$ and 2705 Hz, respectively. The ¹H NMR spectrum showed a series of aryl resonances corresponding to these structures (see Experimental Section). IR data of the sample showed $\nu_{\text{CN}} = 2279$ and 2269 cm⁻¹, consistent with the strong CN stretches in the previous complexes, which show little to no π -back-bonding.

Characterization of 5. Although 5 was observed during the reaction of 1 in benzonitrile, it was not present in adequate amounts (as high as 10%) to allow for isolation from the reaction mixture. As a result, 5 was independently synthesized and characterized by first treating (dippe)PtCl₂ with phenylmagnesium chloride to produce (dippe)Pt(Ph)Cl, **5a.** Recrystallization from benzene via slow evaporation yielded a colorless crystal suitable for X-ray diffraction. Selected bond distances and angles are given in Figure 6a.

The resulting complex **5a** was then treated with excess silver cyanide in a solution of THF and stirred for 24 h, yielding **5** as a pink solid. The solid was dissolved in THF and allowed to crystallize via slow evaporation, giving a colorless crystal suitable for X-ray diffraction. Selected bond distances and angles are given in Figure 6b. ³¹P{¹H} NMR spectroscopy (THF-*d*₈) showed two singlets at δ 73.7 and 62.6 with ¹*J*_{Pt-P} = 1582 and 2754 Hz, respectively. The ¹H NMR spectrum (THF-*d*₈) showed three aryl resonances at δ 6.68 (t), 6.86 (t), and 7.18 (d), consistent with the phenyl group as shown in the X-ray structure. IR data of the sample showed $\nu_{\rm CN} = 2278 \text{ cm}^{-1}$, consistent with the CN stretches in the previous complexes and indicative of little to no π -back-bonding.

Mechanism of Reactions. Scheme 1 shows the sequence of complexes produced during the reaction of 1 in benzonitrile. The initial step of the reaction indicates that 1a plus H₂ and 1b are in equilibrium, as demonstrated by Andersen et al.¹² H₂ gas is liberated as 1a/1b react with benzonitrile, leading to an increase in the quantity of 1b. The first step of the reaction with benzonitrile shows two possible pathways, the formation of 2 through the C–H activation of benzonitrile and the formation of

5 through the C–CN activation of benzonitrile. It is noteworthy that while C–CN cleavage was the only type of cleavage observed with [Ni(dippe)], this is only a minor pathway with [Pt(dippe)] (only 4%). **2** was observed in significantly greater quantities (70%) than **5**, which indicates that C–H activation is the kinetically favored reaction. Furthermore, **5** proved to be thermodynamically stable, as heating a sample of **5** in benzonitrile to 140 °C for 2 weeks showed no change. Additional experiments were performed by placing a solution of **5** in benzonitrile, THF, or toluene under varying pressures of H₂ (as high as 250 psi) at temperatures ranging from 25 to 140 °C. However, only decomposition was observed, and no evidence for the

tion of 3 was seen. Therefore, 5 is not an intermediate in the formation of 2.

Upon heating isolated 2 to 140 °C in xylenes for 3 h, 1a and 1b were observed to appear as 2 decomposed; however, no C-CNactivation to form 5 occurred due to the absence of excess benzonitrile (see Supporting Information for NMR spectra). The formation of 1a/1b might occur from the decomposition of 2 releasing H_2 into the system, thereby allowing 1 to form. When the same reaction was run in benzonitrile, 2 was converted completely to 3 and eventually 4, and no evidence for the formation of 1 was observed. These observations suggest that the C-H activation to form 2 may be reversible, but that without excess PhCN decomposition takes place. Several possible pathways were considered for the generation of 3 from 2. One involves the formation of 3 via a Pt(IV)-dihydride intermediate, and a second involves the elimination of benzyne following β cyano elimination to produce 3 directly. A third would be a direct σ -bond metathesis between H₂ and the Pt-Ph bond, although there is little precedent for this at platinum.

Pt(IV)-Hydride Intermediate Pathway. One possible pathway for the conversion of **2** into **3** begins with the reversion of **2** back to **1b** followed by C–CN activation, producing a platinum-(IV)-hydride intermediate (Scheme 2). The reductive elimination of H_2 or benzene would follow, giving **5** or **3**, respectively.

Several attempts were made to independently synthesize such a Pt(IV)-dihydride intermediate via the halogenation of 1 with I_2 and Br_2 , but all attempts led to decomposition or the production

Scheme 2. Possible Pathway for Production of 3 from 2 Involving Pt(IV)-Dihydride Intermediate



of (dippe)PtX₂ (X = I or Br). This procedure was also attempted in the presence of hydride sources including NaH₂AlR₂, LiH-BEt₃, and potassium hydride, all of which led to decomposition. Consequently, this pathway remains viable (vide infra).

β-Cyano/Benzyne Elimination Pathway. The second pathway follows the initial C–H activation of benzonitrile followed by β -cyano elimination with the loss of benzyne, giving 3 directly (eq 4). This type of elimination is unprecedented, as far as we know, and therefore may proceed by a different transition state than the one shown. Benzene is observed by GC-MS after 3 is produced upon heating 2 in benzonitrile. The source of this benzene could be from hydrogenation of benzyne, which might occur via reaction with one of the platinum-hydride species, possibly 1.



As a test of this possibility, $1-d_2$ was prepared and allowed to react with benzonitrile under the same reaction conditions (140 °C, neat benzonitrile). An initial ¹H NMR spectrum of 1 d_2 in THF- d_8 showed no evidence of hydride resonances. The sample was redissolved in benzonitrile, and the ²H NMR spectrum (prior to heating) showed the presence of two broad resonances at δ -0.11 and 0.31, consistent with the deuterated version of 1b- d_2 , as well as two broad resonances at δ 7.5 and 7.7, consistent with the residual natural abundance deuterated benzonitrile solvent. The ³¹P{¹H} NMR spectrum showed a 1:1:1 triplet centered at δ 88.8 with corresponding platinum satellites $(^{2}J_{Pt-P} = 1810 \text{ Hz})$, as is expected from the coupling of deuterium with phosphorus. After 21 h at 140 °C, the ²H NMR spectrum showed the disappearance of the deuteride resonance for $1b-d_2$ (see Supporting Information for NMR spectra). There was no evidence in the ${}^{31}P{}^{1}H$ NMR spectrum that any deuterium was present in compounds 2 and 3 that were formed (i.e., no ²H coupling was observed) after heating for 45 min to 21 h, indicating that the source of the terminal hydride in 3 does not come from $1b-d_2$. The observations *are* consistent with the hydride in 3 arising from the C-H activation of benzonitrile by this formal β -cyano elimination from **2**. Also, this observation

rules out the Pt(IV) pathway shown earlier in Scheme 2, as that pathway would have produced $3-d_1$. As the reaction proceeds to form 4, analysis via GC-MS shows a series of deuterated benzene resonances from benzene- d_1 to benzene- d_5 in small amounts. The small amounts of the deuterated benzene species support the formation and subsequent deuteration of the suspected benzyne species. Additional H/D scrambling resulting from the presence of D₂ is then observed. When the reaction is allowed to proceed to completion (4 as dominant product), no deuterated benzene species are observed via GC-MS, which can be accommodated by metal-catalyzed H/D exchange with the H₂ eliminated in the formation of 4 (eq 5).



A series of experiments was conducted to attempt to trap the proposed benzyne intermediate using anthracene and furan.¹⁴ After **2** was formed, 2 equiv (1 per platinum) of anthracene and 20 equiv (10 per platinum) of furan were added in separate reactions and allowed to proceed to form 3. Subsequent analysis by GC-MS did not show any evidence of the expected compounds that would be formed by interaction of the trap with benzyne. A third experiment followed the same procedure as the first two; however, the solvent used was a 50:50 mixture of benzonitrile/furan. This experiment also showed no evidence via GC-MS analysis for the expected compounds that would have been formed if benzyne was trapped, indicating that if benzyne is indeed an intermediate, its interaction with a platinum-hydride species and subsequent hydrogenation/deuteration would have to be more rapid than the reaction of benzyne with furan or anthracene. Additionally, as the reaction proceeded as expected with no new complexes observed, there does not appear to be any interaction between the platinum complex and furan. Consequently, these experiments do not allow us to conclude that benzyne is formed via β -cyano elimination, although it is still a possibility subject to the above constraint.

Finally, it is worthwhile to compare and contrast the reactivities of the [M(dippe)] fragments where M = Ni or Pt. With nickel, an η^2 -C,N adduct is first formed, which then proceeds to rearrange via an η^2 -C,C-arene complex to the Ni(II) d⁸ squareplanar product Ni(dippe)(Ph)(CN). No C-H activation products are seen at any time during the reaction, which may be attributed to the fact that the nickel-hydride bond is expected to be weak. In contrast, platinum gives a C-H activation product as the first species formed, which can be attributed to the strong Pt-H bond. Thermodynamic preference for the formation of a Pt-cyanide bond then accounts for the successive formation of 3, and the formation of an additional strong Pt-aryl bond accounts for the ultimate thermodynamic preference for 4. Since only traces of C-CN adduct 5 are formed, one can conclude that it must be kinetically preferred to cleave the aryl C-H bond rather than the aryl-CN bond of benzonitrile with platinum.

CONCLUSIONS

The reaction of $[(dippe)PtH]_2$ with benzonitrile at 140 °C produces a series of products beginning with the kinetically favored C-H activation product 2 and only a small amount of the thermodynamically stable C-CN activation product 5.

Further reaction results in a formal β -cyano elimination in 2, leading to 3 and benzene. One additional C—H activation of benzonitrile follows, giving 4 with the aryl-cyano substituent occupying one of all three possible positions (*ortho, meta,* and *para*). The majority of the reaction follows the pathway $2 \rightarrow 3 \rightarrow 4$ as the formation of 2 is kinetically favored and 4 is the thermodynamic product. A series of reactions to evaluate the pathway of $2 \rightarrow 4$ showed the production of benzyne to be a possible pathway, and a pathway via a Pt(IV)-dihydride intermediate was ruled out by deuterium labeling studies. Although the benzyne trapping experiments proved unsuccessful, the formation of benzene and deuterated benzene species (from (dippe)PtD₂) is consistent with the β -cyano elimination and hydrogenation of benzyne as the proposed mechanistic pathway for this system.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation glovebox. Tetrahydrofuran, benzene, and toluene were distilled from dark purple solutions of sodium/benzophenone ketyl. $[(dippe)PtH]_2$ was synthesized according to the previously reported procedure.⁸ Titration of phenylmagnesium chloride was performed following a literature procedure.¹⁵ Benzonitrile and deuterium gas were purchased from Aldrich Chemical Co. All other chemicals, filter aids, and chromatographic materials were used as received. NMR data (¹H and ³¹P{¹H}) were recorded on Bruker Avance 400 and 500 instruments. Chemical shifts are given in δ and referenced to residual solvent resonances (¹H, ²H) or external H₃PO₄ (³¹P). IR data were recorded on a Shimadzu FTIR-8400 S IR spectrophotometer. GC-MS data were analyzed on a Shimadzu GCMS-QP2010 gas chromatograph mass spectrometer.

All reactions were run in J-Young tubes under a nitrogen atmosphere or in a bomb apparatus under a H_2/D_2 atmosphere. Heating of the samples was performed in a temperature-controlled oil bath. **DANGER**: Pressures in sample tubes exceed 1 atm upon heating. Appropriate safety precautions should be observed.

Preparation of (dippe)Pt(H)(2-C₆H₄CN), 2. A solution of 1 (0.010 g, 0.013 mmol) in 1 mL of benzonitrile was heated to 140 °C under a N₂ atmosphere for 1 h. After 1 h, the solvent was removed under vacuum, leaving an orange-brown, oily solid. The solid was dissolved in THF and crystallized via THF/hexanes vapor diffusion, producing 0.007 g (70% yield) of a white, crystalline solid. ¹H NMR (500 MHz, C₆D₆): δ –0.29 (dd, 1 H, *J*_{P-H} = 16.5, 185 Hz, *J*_{Pt-H} = 1159 Hz), 0.63–1.37 (m, 24 H, CH-*M*e₂), 1.80 (t, 4 H, PCH₂CH₂P), 1.93 (q, 4 H, CH-*M*e₂), 6.72 (d, 1 H, *J* = 3.5 Hz, aryl), 7.65 (t, 1 H, *J* = 3.5 Hz, aryl). ³¹Pt¹H} NMR (500 MHz, C₆D₆): δ 83.8 (s, with Pt satellites, ¹*J*_{Pt-P} = 1936 Hz), 70.4 (s, with Pt satellites, ¹*J*_{Pt-P} = 1746 Hz). Anal. Calcd for C₂₁H₃₇NP₂Pt: C 45.00, H 6.65, N 2.50. Found: C 45.32, H 6.73, N 2.30. IR (NaCl): ν_{CN} = 2280 cm⁻¹.

Preparation of (dippe)Pt(H)(CN), 3. A solution of 1 (0.010 g, 0.013 mmol) in 1 mL of benzonitrile was heated to 120 °C for 96 h under a N₂ atmosphere. The solvent was removed under vacuum, leaving a yellow, oily solid. The solid was dissolved in THF and crystallized via THF/hexanes diffusion, producing 0.004 g (40% yield) of a white, crystalline solid. ¹H NMR (500 MHz, toluene- d_8): δ -1.26 (dd, 1 H, $J_{P-H} = 16$, 185 Hz, ¹ $J_{Pt-H} = 1008$ Hz), 0.53–1.45 (m, 32 H, dippe). ³¹P{¹H} (500 MHz, toluene- d_8): δ 81.8 (s, with Pt satellites, ¹ $J_{Pt-P} = 2677$ Hz), 77.2 (s, with Pt satellites, ¹ $J_{Pt-P} = 1669$ Hz). IR (NaCl): $\nu_{CN} = 2274$ cm⁻¹. An elemental analysis was not obtained, as a pure sample of 3 could not be isolated.

Preparation of (dippe)Pt(CN)(C₆H₄CN), 4. A solution of 1 (0.010 g, 0.013 mmol) in 1 mL of benzonitrile was heated to 140 °C for 7 days under a N₂ atmosphere. The solvent was removed under vacuum, leaving a yellow-brown, oily solid. The solid was recrystallized via slow evaporation in a mixture of hexanes, benzene, ether, and THF, producing 0.0064 g (64% yield) of a white, crystalline solid. ¹H NMR (400 MHz, THF- d_8): δ 0.47–1.4 (m, 72 H, CH- Me_2), 1.62–2.12 (m, 24 H, PCH₂CH₂P and CH-Me₂), 6.94 (m, 1 H, aryl PhCN), 7.09-7.16 (m, 3 H, aryl PhCN), 7.23 (d, 1 H, aryl PhCN), 7.30 (s, 1 H, aryl PhCN), 7.37, (m, 1 H, aryl PhCN), 7.45 (m, 1 H, aryl PhCN), 7.60 (t, 1 H, aryl PhCN), 7.68 (d, 2H, aryl PhCN), 7.75 (m, 1 H, aryl PhCN). ³¹P{¹H} NMR (400 MHz, THF- d_8): δ 73.6 (3 singlets, with Pt satellites, ${}^1J_{Pt-P}$ = 1600 Hz), 63.5 (3 singlets, with Pt satellites, ${}^{1}J_{Pt-P} = 2705$ Hz). IR (NaCl): $\nu_{CN} = 2279$ cm⁻¹, $\nu_{CN} = 2269$ cm⁻¹. An elemental analysis was obtained of the mixture of o-, m-, and p-isomers of 4. Anal. Calcd for C₂₂H₃₆N₂P₂Pt: C 45.12, H 6.20, N 4.78. Found: C 45.32, H 6.73, N 2.30.

Preparation of (dippe)Pt(Ph)Cl, 5a. A solution of (dippe)PtCl₂ (0.10 g, 0.189 mmol) in CH₂Cl₂ was treated with 0.10 mL of phenylmagnesium chloride (1.94 M, 0.189 mmol) at 25 °C under a N₂ atmosphere and allowed to stir for 10 min. The solvent was removed under vacuum, giving a white solid, which was then dissolved in benzene and filtered through a Celite plug. The filtrate was dried under vacuum, giving 0.073 g (61% yield) of a white solid. ¹H NMR (400 MHz, C₆D₆): δ 0.94–0.98 (dd, 6 H, CH-*M*e₂), 1.10–1.16 (dd, 6 H, CH-*M*e₂), 1.20–1.25 (dd, 6 H, CH-*M*e₂), 1.36–1.42 (dd, 6 H, CH-*M*e₂), 1.6 (m, 4 H, PCH₂CH₂P), 1.9 (m, 4 H, CH-Me₂), 6.67 (t, 1 H, *J* = 7.6 Hz, aryl PhCN), 6.86 (d, 2 H, *J* = 7.6 Hz, aryl PhCN), 7.17 (d, 2 H, *J* = 7.6 Hz, aryl PhCN). ³¹P{¹H} NMR (400 MHz, C₆D₆): δ 70.2 (s, with Pt satellites, ¹*J*_{Pt-P} = 1701 Hz), 60.7 (s, with Pt satellites, ¹*J*_{Pt-P} = 3941 Hz).

Preparation of (dippe)Pt(Ph)(CN), 5. A solution of (dippe)Pt-(Ph)Cl (0.053 g, 0.093 mmol) in 10 mL of THF was treated with excess AgCN (0.05 g, 0.37 mmol) and stirred at 25 °C for 24 h. The reaction was filtered through a Celite plug, giving a pink solution, which was dried under vacuum, giving 0.05 g (93% yield) of a pink solid. ¹H NMR (400 MHz, THF-*d*₈): δ 0.8–0.9 (dd, 6 H, CH-*Me*₂), 1.14–1.23 (dd, 12 H, CH-*Me*₂), 1.33–1.39 (dd, 6 H, CH-*Me*₂), 1.8–1.9 (m, 4 H, PCH₂CH₂PH), 2.3–2.4 (m, 4 H, CH-Me₂), 6.68 (t, 1H, *J* = 7.6 Hz, aryl), 6.86 (t, 2H, *J* = 7.6 Hz, aryl), 7.18 (d, 2 H, *J* = 7.6 Hz, *J*_{Pt-H} = 70 Hz, aryl). ³¹P{¹H} NMR (500 MHz, THF-*d*₈): δ 73.8 (s, with Pt satellites, ¹*J*_{Pt-P} = 1586 Hz), 62.6 (s, with Pt satellites, ¹*J*_{Pt-P} = 2744 Hz). IR (C₆D₆): $\nu_{CN} = 2278 \text{ cm}^{-1}$.

Preparation of [(dippe)PtD]₂, 1-*d*₂. A solution of 1 (0.010 g, 0.013 mmol) was dissolved in THF and placed in a bomb apparatus. The bomb was pressurized to ~40 psi (~2.7 atm) with D₂ and allowed to sit at 25 °C for 24 h. The sample was dried under vacuum and redissolved in C₆D₆. ¹H NMR (400 MHz, C₆D₆): no resonances observed in the hydride region. ³¹P{¹H} NMR (400 MHz, C₆D₆): δ 88.8 (1:1:1 t, *J*_{P-D} = 27 Hz, with platinum satellites, *J*_{Pt-P} = 1809 Hz). ²H NMR (400 MHz, PhCN): δ -2.17 and -1.72 (br d, 2 D, *J*_{P-D} = 10 Hz). The reactions of this material with benzonitrile are described in the text.

ASSOCIATED CONTENT

Supporting Information. NMR spectra described in the text, a summary of the crystallographic data, intramolecular bond distances and angles, and positional and thermal parameters for **2**, **3**, *ortho*-**4**, *meta/para*-**4**, **5a**, and **5**. CIF files have been deposited with the Cambridge Crystallographic Data Centre, as CCDC 752157–752163. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, via fax: (int. code) +44 1223 336 033, e-mail: deposit@ccdc.

cam.ac.uk, or http://www.ccdc.cam.ac.uk. This material is available free of charge via the Internet at http://pubs.acs.org.

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