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Synthesis and Characterization of Pd Complexes of a Carbazolyl/Bis(Imine) NNN Pincer Ligand

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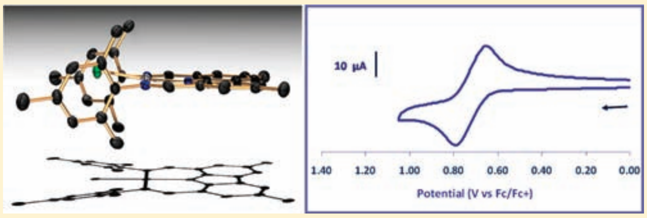
Supporting Information



ABSTRACT: A serendipitously discovered construction of a carbazole nucleus by lithiation of N-methylated bis(4-methyl-2,6-dibromophenyl)amine is described. It was used to synthesize an NNN pincer-type ligand that combines a central carbazole site (N-methylated in the precursor ligand) with two flanking aldimine donors bearing mesityl substituents. The installation of this ligand on Pd was accomplished via an N−Me cleaving reaction with (COD)$PdCl_2$ producing MeCl and (NNN)PdCl (where NNN is an anionic carbazolyl/bis(imine) pincer ligand). Several (NNN)PdX complexes were characterized spectroscopically. (NNN)PdOTf ($^{-}$OTf = triflate or $^{-}O_3SCF_3$) readily reacted with stoichiometric amounts of water in benzene or dichloromethane to give a cationic water adduct [(NNN)Pd(OH_2)]OTf. An X-ray diffraction study on a single crystal of (NNN)PdCl revealed an almost perfectly square planar environment about Pd and an almost perfectly planar carbazole/bis(imine) conjugated system. Cyclic voltammetry of (NNN)PdCl showed quasi-reversible oxidation at $E_{1/2}$ = 0.72 V vs Fc/Fc^{+} which is most likely ligand-based.

INTRODUCTION

Pincer ligands can be generally defined as tridentate, meridionally chelating ligands.[1] They have become popular as tools in transition metal chemistry for their ability to form structurally predictable and highly robust complexes. Our group has been particularly interested in the PNP pincer ligands[2] combining the central diarylamido donor and flanking phosphine arms (Chart 1).[3−5] These PNP ligands have supported, as spectator ligands, a number of unusual and reactive structural fragments at a broad variety of metal centers and maintained integrity while rather remarkable reactions took place at the metal centers with external substrates.[6] There are, nonetheless, limits to their stability which have so far been breached by either oxidation at the phosphorus by atom transfer[7] or one-electron oxidation of the ligand π-system.[8,9] In this context, we desired to adapt the PNP ligand design to be more resistant to both types of oxidation, while maintaining the pincer structure and the advantageous semirigidity of the diarylamido framework.

To this end, we turned our attention to an NNN ligand (Chart 1) incorporating a central carbazole module instead of a diphenylamine and aldimines (−CH=NR) instead of phosphines (-PR_2). The sp^2-N donor should be largely immune to oxidation at the donor N atom. The carbazole system serves two purposes. First, it should be more difficult to oxidize. The ionization potential of carbazole has been reported to be about 0.4 V higher than that of diphenylamine.[10] Second, the extra C−C bond in carbazole should serve to "pull back" the imine donors and partly compensate for the extra atoms in the metallacycles. We were concerned that the formation of two fused six-membered metallacycles upon metalation of the pincer (in contrast to five-membered metallacycles with PNP) would jeopardize the preference of the pincer to bind to the metal in a meridional fashion. Although related diarylamido/bis(oxazoline) complexes of Fe, Co, and Ni possess a meridional NNN^{A} ligand,[11] our concern was reinforced by the recent report of Gardinier et al. on the complexes of the diarylamido/bis(imidazole) NNN^{B} ligands (Chart 1).[12] (NNN^{B})Re$(CO)_3$ displayed facial geometry, in contrast to the meridionality of (PNP)Re$(CO)_3$.[8] Other anionic pincer ligands with a central diarylamido donor and flanking neutral N-donor arms include (NNN^{C})MCl complexes from the Peters group and (NNN^{D})NiX complexes by Hu et al (Chart 1).[13−15]

The carbazolyl/bis(aldimine) NNN ligands we had in mind were first reported by Gibson et al. who examined their Mn, Fe, Co, as well as Rh complexes.[16] A Pd complex of a closely related carbazolyl/bis(pyridine) ligand NNN^{E} (Chart 1) was reported by Thummel et al.[17] Carbazolyl/bis(oxazoline) ligands were also reported by Nakada et al.[18] Very recently, Barbe, Kadish, and co-workers reported Cu complexes of a variation of the NNN ligand (denoted in Chart 1 as NNN^{F})[19] which was synthesized via Gibson's methods.[16] In the present work we report a serendipitously found and superior synthetic route to the formation of the carbazole module in the carbazolyl/bis(imino) ligand, its new (NNN)PdX complexes, and their characterization, including by cyclic voltammetry.

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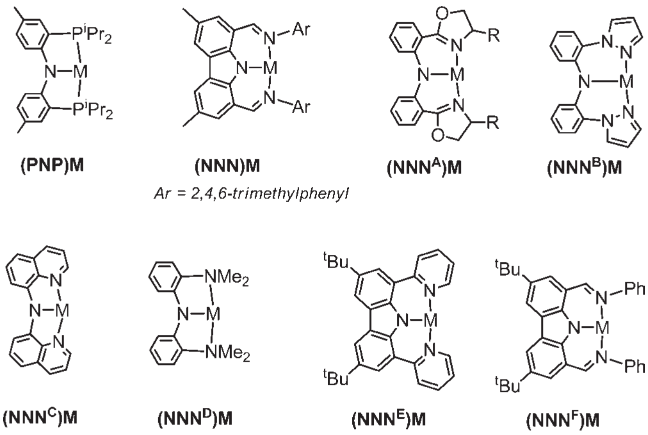
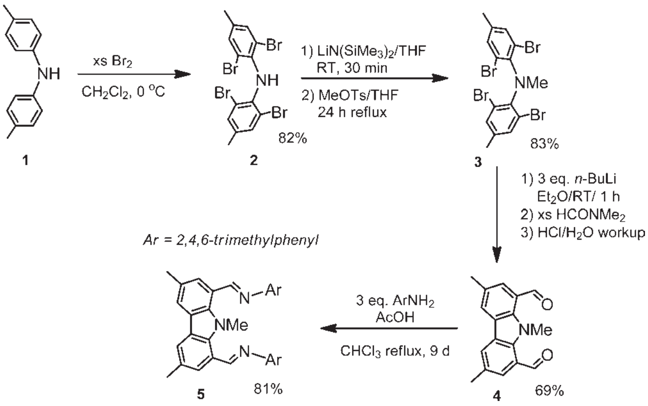
Chart 1. Representations of the Various NNN and PNP Pincer Complexes



Scheme 1

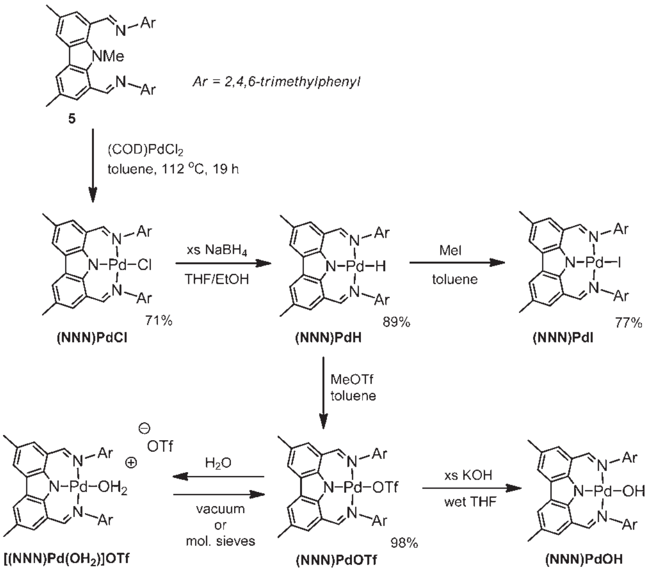


RESULTS AND DISCUSSION

Synthesis of the NNN Ligand. Bromination of **1** with excess Br$_2$ resulted in tetrabromination selectively in *ortho*-positions and produced **2** in high yield (Scheme 1). **2** is a habitual side product in the dibromination of **1** with Br$_2$. N-methylation of **2** to give **3** was accomplished by deprotonation of **2** with LiN(SiMe$_3$)$_2$ and treatment with methyl tosylate in refluxing tetrahydrofuran (THF). The rather harsh conditions are presumably a reflection of the diminished nucleophilicity of the amido site in deprotonated **2** because of the four *ortho*-bromine substituents, both on steric and electronic grounds. Treatment of **3** with 3 equiv of ^{n}BuLi in ether for 1 h, followed by addition of excess dimethylformamide (DMF), resulted in the formation of **4**, isolated in 69% yield in 90−95% purity. This purity was sufficient for the use in the subsequent step. Condensation of **4** with 2,4,6-trimethylaniline to give **5** in 81% isolated yield was accomplished by refluxing the mixture for 9 d in chloroform in the presence of acetic acid.

The key step in our synthesis is the formation of the carbazole system upon lithiation of **3**. N-methylation is necessary for the carbazole-making step. Attempts at producing the carbazole system by lithiation of **2** with varying amounts of ^{n}BuLi led to complex mixtures only. The key C−C bond is ostensibly formed by the intramolecular, interannular elimination of LiBr from the partially lithiated **3**. It is not clear to us at which exact lithiation step does the elimination of LiBr and concomitant C−C bond formation take place. Direct nucleophilic substitution on simple aryl bromides by an aryllithium typically does not proceed. Moreover, dilithiation of (4-Me-2-Br-C$_6$H$_3$)$_2$NMe proceeds cleanly and without carbazole formation,[20,21] so it is not an intrinsic reaction for any *ortho*-brominated diarylamine. We hypothesize that the particular substitution pattern favors a conformation for the critical partially lithiated intermediate that results in a low barrier for the C−C bond formation. At this point, we lack sufficient data to ascertain the particular intimate mechanism by which the C−C bond is formed.[22]

Scheme 2



The groups of Thummel and Gibson have reported several methods for the synthesis of a carbazole-based ligand with imino functionalities that rely on selective substitution of carbazole that requires multiple steps.[16,17] Our procedure is more direct, high-yielding, and requiring fewer synthetic steps. Thummel reported the formation of the carbazole ring directly from bis(*p*-tolyl)amine,[17] but by using stoichiometric Pd(OAc)$_2$ and only in a modest yield. The drawback of our synthesis is in that it requires an N−Me group. Although we have not tested it here, it is likely that another, more easily removed N-protecting group can suffice. Furthermore, our synthesis may very well be compatible with a variety of substituents in the position *para* to the carbazole N, something not easily achieved by syntheses starting with the parent carbazole itself.

Synthesis of the Pd Complexes. We have previously reported that PdCl$_2$ reacts with N-methylated PNP ligands by cleavage of the N−Me bond and the formation of (PNP)PdCl and MeCl.[23] We hoped that this strategy would also work with **5**, and it turned out to be the case, although the N−Me cleavage with **5** is much slower. Heating a mixture of **5** and (COD)PdCl$_2$ in toluene at 112 °C for 19 h resulted in the formation of (NNN)PdCl, isolated as red crystals in 71% yield (Scheme 2). (NNN)PdH, (NNN)PdI, (NNN)PdOTf, and (NNN)PdOH were prepared by methods closely analogous to those used by us in the past for the synthesis of the corresponding (PNP)Pd complexes[5,21,24] and isolated in good to excellent yields (Scheme 2).

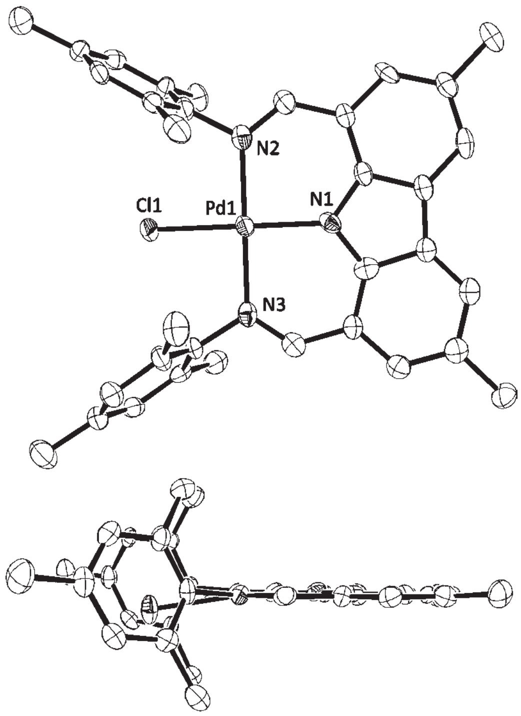


Figure 1. ORTEP drawings[30] (50% probability ellipsoids) of (NNN)PdCl showing selected atom labeling. The top view is approximately perpendicular to the plane of the carbazole backbone; the bottom view is approximately in that plane. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) follow: Pd1−N1, 1.989(5); Pd1−N2, 2.060(5); Pd1−N3, 2.055(5); Pd1−Cl1, 2.3081(15); N1−Pd1−N2, 89.36(19); N1−Pd1−N3, 90.52(19); N2−Pd1−N3, 176.77(17); N1−Pd1−Cl1, 174.05(13); N2−Pd1−Cl1, 90.99(13); N3−Pd1−Cl1, 89.46(13).

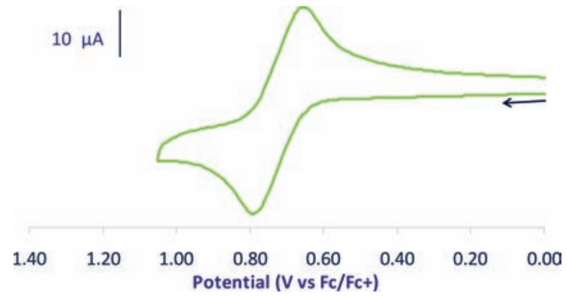


Figure 2. Cyclic voltammogram of (NNN)PdCl in CH_2Cl_2 using 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte and scan rate of 200 mV/s.

The NMR spectra of the (NNN)PdX complexes displayed the same C_{2v} symmetry on the NMR time scale. The NNN pincer ligands are devoid of ^{19}F or ^{31}P reporter NMR nuclei, but the pattern of singlets in the ^1H NMR serves as an appropriate NMR diagnostic tool. The C_{2v} symmetry in (NNN)PdX resulted in three CH_3 resonances (in a 6H:6H:12H ratio), three singlets from aromatic hydrogens (in a 2H:2H:4H ratio), and a 2H singlet arising from the imine CH. C_{2v} symmetry was also observed in the $^{13}C\{^1H\}$ NMR spectra.

(NNN)PdOTf displayed rather unusual reactivity with water (Scheme 2). We found that exposure of solutions of the deep-red (NNN)PdOTf in benzene or dichloromethane to even near-stoichiometric amounts of water resulted in the displacement of the triflate ligand by a water molecule and formation of the orange $[(NNN)Pd(OH_2)]OTf$. The latter is poorly soluble in benzene and can be conveniently isolated by filtration. (NNN)PdOTf could be regenerated by treatment of solutions of $[(NNN)Pd(OH_2)]OTf$ with molecular sieves or by application of vacuum.[25] $[(NNN)Pd(OH_2)]OTf$ displayed C_{2v} symmetry in its NMR spectra at room temperature (RT), including a distinct resonance for the coordinated water (two equivalent hydrogens), which appeared at δ 3.27 ppm in CD_2Cl_2 for the apparently pure material but whose chemical shift and breadth of the peak depended on the amount of extra water present in the system. There exist other reports of displacement of triflate coordinated to a late transition metal by water in solvents of low polarity.[26] Still, this event in the present system was rather surprising to us, given that (PNP)PdOTf shows no evidence of triflate displacement by water whatsoever. It is possible that the steric bulk of the NNN ligand is more imposing and favors expulsion of the bulkier triflate. It is also possible that the facile dissociation of triflate is responsible for the observed conversion of (NNN)PdOTf into (NNN)PdCl in dichloromethane solutions.

X-ray Structure of (NNN)PdCl. An X-ray diffraction study on a single crystal of (NNN)PdCl allowed us to establish its structure in the solid state (Figure 1). The environment about Pd is approximately square-planar. The angular deviations from the idealized square planar geometry in (NNN)PdCl are minor and are smaller than in the analogous (PNP)PdCl complex.[5] The N−Pd−N "pincer bite" angle involving the trans-imine nitrogens in (NNN)PdCl is 176.77(17)°, whereas the P−Pd−P angle in (PNP)PdCl is 163.54(2)°. The Pd−Cl distance in (NNN)PdCl of 2.3081(15) Å is similar to that in (PNP)PdCl (2.3157(7) Å)[5] and is shorter (by ca. 0.06−0.12 Å) than the Pd−Cl distances in various (PCP)PdCl complexes where Cl is trans to a more strongly trans-influencing aryl donor.[27−29] The $Pd−N_{amido}$ distance in (NNN)PdCl of 1.989(5) Å falls in between the analogous Pd−N distance in (PNP)PdCl (2.026(2) Å)[5] and the Pd−N distance in $(NNN^C)PdCl$ of 1.962(2) Å by Peters et al.[13] The $Pd−N_{imine}$ distances in (NNN)PdCl are about 0.07 Å longer than the $Pd−N_{amido}$ distances.

The diiminocarbazole framework in (NNN)PdCl is remarkably planar (Figure 1), reminiscent of the $(NNN^C)MCl$ structures (M = Ni, Pd, Pt).[13] Not surprisingly, the carbazole units are π-stacked in the crystal. The stacking is pairwise, with the two participating molecules being related by a crystallographic center of symmetry. The closest C−C contacts (ca. 3.5 Å) are between the carbons of the carbazole system that link the two six-carbon rings.

Electrochemical Studies of (NNN)PdCl. Cyclic voltammetry was performed to probe the redox activity of (NNN)PdCl. We observed quasi-reversible oxidation of (NNN)PdCl at $E_{1/2}$ = 0.72 V (vs Fc/Fc^+) when carried out in CH_2Cl_2 solvent with $[Bu_4N][PF_6]$ as the supporting electrolyte (Figure 2). Very recently, Barbe et al. reported[19] reversible oxidation at $E_{1/2}$ = 0.71 V (vs Fc/Fc^+)[31] of a Cu^{II} complex $(NNN^F)CuCl$ of a very similar carbazolyl/bis(imino) ligand. The similarity of this redox potential to that observed by us here for (NNN)PdCl strongly suggests that these redox events are ligand-based. Carbazole itself is electrochemically active[32] and was reported[19] to undergo irreversible oxidation at 0.81 V vs Fc/Fc^+ under similar conditions.

As expected, the NNN ligand is much harder to oxidize than the PNP ligand. For example, (PNP)NiCl was reported[7] to undergo reversible oxidation at $E_{1/2}$ = −0.06 V and the more electron-rich (PNP)Mn(CO)$_3$ and (PNP)Re(CO)$_3$ were reported to undergo reversible oxidation at $E_{1/2} = -0.34$ V and -0.25 V, respectively (all vs Fc/Fc$^+$).[8] Peters' [(PNP')Cu]$_2$ underwent two reversible oxidations at -0.49 and 0.30 V vs Fc/Fc$^+$; these redox events in the dimeric amido-bridged system were judged to have "strong ligand contribution".[33] Gardinier's (NNN^B)Re(CO)$_3$ underwent a quasi-reversible oxidation with $E_{1/2} = 0.00$ V vs Fc/Fc$^+$.[12] All in all, it is clear that the NNN ligand allows access to ligand-based redox chemistry in a completely different potential range.

CONCLUSION

In summary, we are reporting on an unexpected synthesis of a carbazole nucleus from a brominated diarylamine that lends itself well to the preparation of carbazolyl/bis(aldimine) NNN pincer ligands. Although these ligands were only obtained with the N-methylated central N function of the carbazole, the NNN pincer complexes of divalent Pd are easily accessible through thermal N−Me cleavage in a reaction of **5** with a PdCl$_2$ source. Subsequent transformations allowed characterization of a series of (NNN)PdX compounds. The triflate ligand in (NNN)PdOTf is remarkably easily displaced by water, even in solvents of low polarity (benzene, dichloromethane). (NNN)PdCl was characterized by X-ray crystallography which revealed an almost perfectly square-planar coordination environment about Pd and the almost perfectly planar (NNN)Pd fragment. Cyclic voltammetry study of (NNN)PdCl revealed a quasi-reversible oxidation at $E_{1/2} = 0.72$ V vs Fc/Fc$^+$ that most likely takes place at the ligand π-system.

EXPERIMENTAL SECTION

General Considerations. All air or water sensitive manipulations were performed under argon with standard Schlenk line techniques or in a glovebox. Solvents were dried with and distilled from an appropriate drying agent (NaK/Ph$_2$CO or CaH$_2$). NMR spectra were recorded on a Mercury 300 MHz, Inova 300 MHz or an Inova 500 MHz spectrometer. FT-IR spectra were collected using a Bruker ALPHA-P FT-IR Spectrometer with a diamond ATR. Elemental analyses were performed by CALI Laboratories, Parsippany, NJ. Hexanes, dichloromethane, chloroform, pentane, and DMF were purchased from BDH, THF and NaBH$_4$ from Mallinckrodt Chemicals, diethyl ether from J. T. Baker, hexamethyldisilazane (HMDS) from Gelest, methyl tosylate, methyl iodide, 2,4,6-trimethylaniline, ^{n}BuLi and MeLi from Sigma-Aldrich, C$_6$D$_6$ from Cambridge Isotope, and Br$_2$ from Alfa Aesar. Bis(p-tolyl)amine (**1**) was prepared by Buchwald−Hartwig amination from *p*-bromotoluene and *p*-toluidine[34] and (COD)PdCl$_2$ also as described in the literature.[35]

Electrochemical studies were carried out using a CH Instruments Model 700D Series Electrochemical Analyzer/Workstation in conjunction with a three-electrode cell. The working electrode was a CHI 104 glassy carbon disk (3.0 mm diameter), and the auxiliary electrode a platinum wire. The reference electrode was a Ag/AgCl electrode separated from the test solution by a fine porosity frit and 1 M KCl solution. CVs were conducted in solutions of CH$_2$Cl$_2$ with 0.1 M NBu$_4$PF$_6$ as supporting electrolyte at scan rates of 200 mV/s. The concentration of analyte was 2.5×10^{-3} M. CVs were referenced to the Fe(η^5-C$_5$H$_5$)$_2$/Fe(η^5-C$_5$H$_5$)$_2^+$ redox couple.

X-ray Crystallography: Data Collection and Reduction, Structure Solution, and Refinement. A Leica MZ 75 microscope was used to identify a suitable red multifaceted crystal with very well-defined faces with dimensions (max, intermediate, and min; in mm) 0.08 × 0.05 × 0.03 from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A BRUKER GADDS X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the FRAMBO software, v.4.1.05.[36] The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 5.0 cm from the crystal sample. The X-ray radiation employed was generated from a Cu sealed X-ray tube ($K_\alpha = 1.5418$ Å with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes). A total of 180 data frames were taken at widths of 0.5° with an exposure time of 15 s. These reflections were used to determine the unit cell using Cell_Now.[37] A suitable cell was found and refined by nonlinear least-squares and Bravais lattice procedures. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No supercell or erroneous reflections were observed. After careful examination of the unit cell, a standard data collection procedure was initiated using ω and φ scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with SAINTplus.[38] The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. SADABS[39] was employed to correct the data for absorption effects. Systematic reflection conditions and statistical tests using XPREP did not indicate any suitable space group. The structure could be, however, solved in the triclinic $P\bar{1}$ space group using XS[40] (incorporated in SHELXTL); and the additional symmetry (space group $P2_1/c$) was determined using PLATON.[41] All non-hydrogen atoms were refined with anisotropic thermal parameters. The Hydrogen atoms were placed in idealized positions [C−H = 0.96 Å, $U_{iso}(H) = 1.2U_{iso}(C)$] and refined using riding model. The structure was refined (weighted least-squares refinement on F^2) to convergence.[36]

Bis-(2,6-dibromo-4-methyphenyl)amine (2). Di-*p*-tolylamine (**1**) (16.8 g, 0.085 mol) was dissolved in CH$_2$Cl$_2$ (100 mL) and stirred in an ice bath. Bromine (20 mL, 0.39 mol) was added dropwise over 40 min. The ice bath was removed, and tubing was attached to the flask, exhausting into a solution of NaOH. A precipitate formed within 1 h in the reaction flask, and the reaction was stirred overnight. Following removal of volatiles under vacuum, the crude residue was redissolved in 850 mL of CH$_2$Cl$_2$, placed in an ice bath, and bromine (2.5 mL, 0.05 mol) was added. The ice bath was removed after addition, and the volatiles were removed from the reaction mixture in vacuo after 4 h. Pentane (500 mL) was added to the solid, then cyclohexene (10 mL) to quench the remaining bromine. The volatiles were then removed under vacuum, the residue dissolved in a CH$_2$Cl$_2$/ether solution. Sodium acetate (4.9 g, 0.06 mol) was added, and the mixture was stirred for 30 min. The solids were filtered off, and the filtrate was concentrated and crystallized at −32 °C to yield white crystals. Yield: 35.8 g (82%) from three crops. ^{1}H NMR (C$_6$D$_6$): δ 7.03 (s, 4H, Ar−H), 5.83 (s, 1H, N−H), 1.70 (s, 6H, Ar−CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 136.7 (C$_{Ar}$), 134.6 (C$_{Ar}$), 133.0 (C$_{Ar}$), 117.9(C$_{Ar}$), 19.5 (Ar−CH$_3$). Mp = 166 °C.

Bis-(2,6-dibromo-4-methylphenyl)methylamine (3). Bis-(2,6-dibromo-4-methylphenyl)amine (**2**) (10 g, 19.5 mmol) was dissolved in THF (75 mL). In a separate flask, hexamethyldisilazane (5.8 mL, 27.7 mmol) and ^{n}BuLi (16.2 mL, 23.5 mmol) were combined in THF (35 mL) and stirred for 15 min. This solution was then transferred to the reaction mixture, and it was stirred for 30 min. All volatiles were removed in vacuo, and the solid was redissolved in THF (75 mL). Methyl tosylate (5.3 mL, 35.1 mmol) was added, and the reaction was refluxed for 24 h. Then a solution resulting from mixing ^{n}BuLi (0.8 mL, 1.2 mmol) and hexamethyldisilazane (0.29 mL, 1.4 mmol) in THF was added to the reaction, stirred for 5 min, and then the volatiles were removed in vacuo.

The residual solid was redissolved in 90 mL of THF and refluxed overnight. The reaction mixture was dried in vacuo, and the residual solid was washed with 9:1 water/ethanol mixture and filtered. After drying, the solid was dissolved in CH_2Cl_2, filtered, concentrated, and crystallized at −32 °C to yield off-white crystals. Yield: 8.52 g (83%). ^1H NMR (C_6D_6): δ 7.14 (s, 4H, Ar−H), 3.55 (s, 3H, N−CH_3), 1.68 (s, 6H, Ar−CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 142.0 (C_{Ar}), 135.6 (C_{Ar}), 135.0 (C_{Ar}), 122.1 (C_{Ar}), 43.2 (N−CH_3), 19.2 (Ar−CH_3). Mp = 167 °C.

1,8-Diformyl-3,6,9-trimethyl-carbazole (4). Compound 3 (21.9 g, 41.7 mmol) was dissolved in ether (1300 mL). 2.5 M ^{n}BuLi (50 mL, 125 mmol) was added to the solution and stirred for 1.75 h, at which point the reaction volume was reduced to 1000 mL in vacuo. DMF (25.0 mL, 255 mmol) was added, and the reaction stirred overnight. The reaction volume was reduced to 300, and 100 mL of a 2% HCl solution was added. The remaining ether was removed in vacuo, and the yellow solid was filtered off. The solids were washed with water, and the aqueous wash was extracted with 100 mL of CH_2Cl_2 and combined with the solids in a CH_2Cl_2 solution. This solution was dried over $MgSO_4$ and filtered through Celite and silica. Yellow solids were obtained from precipitation from CH_2Cl_2/pentane at −32 °C. Yield: 7.6 g (69%). Product so obtained was of about 94% purity by NMR. ^1H NMR (C_6D_6): δ 10.09 (s, 2H, −CHO), 7.63 (s, 2H, Ar−H), 7.56 (s, 2H, Ar−H), 3.60 (s, 3H, N−CH_3), 2.24 (s, 6H, Ar−CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 189.9 (C=O), 140.8 (C_{Ar}), 132.8 (C_{Ar}), 129.6 (C_{Ar}), 126.4 (C_{Ar}), 125.4 (C_{Ar}), 122.0 (C_{Ar}), 41.8 (N−CH_3), 20.9 (Ar−CH_3).

1,8-Bis[(2,4,6-trimethylphenylimino)methyl]-3,6,9-trimethyl-carbazole (5). Compound 4 (7.6 g, 28.7 mmol) was dissolved in $CHCl_3$ (240 mL). 2,4,6-Trimethylaniline (12 mL, 85.4 mmol) and acetic acid (1 mL) were added to the solution. Molecular sieves were added, and the reaction was refluxed for 9 d. The solution was filtered hot through Celite and silica, and the volatiles were removed in vacuo. The crude product was dissolved in hot THF and gradually cooled to −32 °C. Yellow powder precipitated; it was washed with pentane and dried. Yield: 11.6 g (81%). ^1H NMR (C_6D_6): δ 8.61 (s, 2H, N=CH), 8.39 (s, 2H, Ar−H), 7.78 (s, 2H, Ar−H), 6.90 (s, 4H, Ar−H), 3.14 (s, 3H, N−CH_3), 2.41 (s, 6H, Ar−CH_3), 2.22 (s, 12H, Ar−CH_3), 2.22 (s, 6H, Ar−CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.4 (C=N), 149.3 (C_{Ar}), 141.4 (C_{Ar}), 133.1 (C_{Ar}), 129.9 (C_{Ar}), 128.9 (C_{Ar}), 128.4 (C_{Ar}), 127.2 (C_{Ar}), 125.7 (C_{Ar}), 123.4 (C_{Ar}), 120.7 (C_{Ar}), 41.4 (N−CH_3), 21.2 (Ar−CH_3), 20.9 (Ar−CH_3), 18.6 (Ar−CH_3). Mp = 197 °C.

(NNN)PdCl. Compound 5 (290 mg, 0.58 mmol) and (COD)$PdCl_2$ (170 mg, 0.58 mmol) were combined in a PTFE-valved flask with toluene (20 mL). The mixture was degassed and then heated at 112 °C for 19 h. The solution was filtered, and the product was obtained by crystallization from toluene/pentane at −32 °C to yield red crystals. Yield: 260 mg (71%). Crystals suitable for X-ray diffraction were grown from a solution in toluene/pentane at −32 °C. ^1H NMR (C_6D_6): δ 8.02 (s, 2H, Ar−H), 7.70 (s, 2H, N=CH), 6.97 (s, 2H, Ar- H), 6.79 (s, 4H, Ar−H), 2.40 (s, 6H, Ar−CH_3), 2.35 (s, 12H, Ar−CH_3), 2.14 (s, 6H, Ar−CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.1 (C=N), 151.8 (C_{Ar}), 138.0 (C_{Ar}), 135.3 (C_{Ar}), 131.9 (C_{Ar}), 130.3 (C_{Ar}), 128.3 (C_{Ar}), 128.1 (C_{Ar}), 127.8 (C_{Ar}), 125.3 (C_{Ar}), 116.7 (C_{Ar}), 21.4 (Ar−CH_3), 20.9 (Ar−CH_3), 19.1 (Ar−CH_3). M/Z ($M+Li^+$: 631.1818), (M^+, $-Cl^-$: 590.167). Elem. An. Found (Calculated) for $C_{34}H_{34}N_3ClPd$: 65.20 (65.18), 5.53 (5.47), 6.75 (6.71).

(NNN)PdH. (NNN)PdCl (126 mg, 0.200 mmol) was dissolved in THF (15 mL) and ethanol (2 mL). $NaBH_4$ (20 mg, 0.53 mmol) was added, and the solution quickly turned brown/yellow. After 30 min volatiles were removed in vacuo, and the crude residue was redissolved in toluene and filtered through Celite and silica. Toluene was removed in vacuo, and the yellow solid was washed with cold pentane. Yield: 106 mg (89%). ^1H NMR (C_6D_6): δ 8.20 (s, 2H, Ar−H), 7.86 (s, 2H, N=CH), 7.19 (s, 2H, Ar−H), 6.69 (s, 4H, Ar−H), 2.50 (s, 6H, Ar−CH_3), 2.33 (s, 12H, Ar−CH_3), 2.11(s, 6H, Ar−CH_3), −15.73 (s, 1H, Pd−H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 162.2 (C=N), 157.2 (C_{Ar}), 140.9 (C_{Ar}), 134.1 (C_{Ar}), 131.7 (C_{Ar}), 128.7 (C_{Ar}), 128.0 (C_{Ar}), 127.6 (C_{Ar}), 126.1 (C_{Ar}), 125.7 (C_{Ar}), 117.3 (C_{Ar}), 21.3 (Ar−CH_3), 20.5 (Ar−CH_3), 18.8 (Ar−CH_3).

(NNN)PdI. (NNN)PdH (225 mg, 0.38 mmol) was dissolved in toluene. CH_3I (22.5 μL, 0.36 mmol) was added and after 20 min the volatiles were removed in vacuo. The crude product was crystallized at −32 °C from a pentane layered solution of toluene to yield a deep-purple microcrystalline solid. Yield: 210 mg (77%). ^1H NMR (C_6D_6): δ 8.00 (s, 2H, Ar−H), 7.44 (s, 2H, N=CH), 6.91 (s, 2H, Ar−H), 6.79 (s, 4H, Ar−H), 2.41 (s, 12H, Ar−CH_3), 2.39 (s, 6H, Ar−CH_3), 2.14 (s, 6H, Ar−CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 163.8 (C=N), 157.6 (C_{Ar}), 137.4 (C_{Ar}), 135.7 (C_{Ar}), 132.0 (C_{Ar}), 130.2 (C_{Ar}), 128.4 (C_{Ar}), 128.2 (C_{Ar}), 127.7 (C_{Ar}), 124.7 (C_{Ar}), 116.6 (C_{Ar}), 21.3 (Ar−CH_3), 20.9 (Ar−CH_3), 20.0 (Ar−CH_3). Elem. An. Found (Calculated) for $C_{34}H_{34}N_3IPd$: 56.84 (56.88), 4.73 (4.77), 5.90 (5.85).

(NNN)PdOTf. (NNN)PdH (1.13 g, 1.91 mmol) was dissolved in toluene (25 mL). Methyl triflate (216 μL, 1.91 mmol) was added dropwise, and the solution soon bubbled and turned deep red. The volatiles were removed in vacuo after 15 min, and the red solid was recrystallized multiple times at −32 °C from toluene/pentane. Yield: 1.39 g (98%). ^1H NMR (C_6D_6): δ 7.91 (s, 2H, Ar−H), 7.36 (s, 2H, N=CH), 6.89 (s, 2H, Ar−H), 6.88 (s, 4H, Ar−H), 2.53 (s, 12H, Ar−CH_3), 2.37 (s, 6H, Ar−CH_3), 2.19 (s, 6H, Ar−CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.6 MHz): δ 164.3 (C=N), 148.4 (C_{Ar}), 137.1 (C_{Ar}), 136.7 (C_{Ar}), 132.5 (C_{Ar}), 130.0 (C_{Ar}), 129.3 (C_{Ar}), 129.2 (C_{Ar}), 128.9 (C_{Ar}), 125.7 (C_{Ar}), 117.0 (C_{Ar}), 21.3 (Ar−CH_3), 21.0 (Ar−CH_3), 19.7 (Ar−CH_3). *NB: (NNN)PdOTf is slowly converted to (NNN)PdCl in dichloromethane.* ^{19}F NMR (C_6D_6): δ −77.7. Elem. An. Found (Calculated) for $C_{35}H_{34}N_3O_3F_3SPd$: 56.71 (56.80), 4.58 (4.63), 5.73 (5.68).

(NNN)PdOH. (NNN)PdOTf (402 mg, 0.543 mmol) was dissolved in wet THF (20 mL). Finely ground KOH (280 mg, 4.99 mmol) was added, and the deep red solution turned orange within minutes. The volatiles were removed after 1 h. The crude product was redissolved in toluene and filtered through Celite. Pure product was obtained as an orange powder by layering the solution with pentane and cooling to −32 °C. Yield: 208 mg (63%). ^1H NMR (C_6D_6): δ 8.08 (s, 2H, Ar−H), 7.82 (s, 2H, N=CH), 7.09 (s, 2H, Ar−H), 6.74 (s, 4H, Ar−H), 2.44 (s, 6H, Ar−CH_3), 2.32 (s, 12H, Ar−CH_3), 2.11 (s, 6H, Ar−CH_3), −2.61 (br, 1H, −OH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.5 (C=N), 147.8 (C_{Ar}), 139.7 (C_{Ar}), 134.75 (C_{Ar}), 131.7 (C_{Ar}), 130.6 (C_{Ar}), 128.5 (C_{Ar}), 127.4 (C_{Ar}), 126.2 (C_{Ar}), 125.8 (C_{Ar}), 117.2 (C_{Ar}), 21.0 (Ar−CH_3), 20.6 (Ar−CH_3), 18.7 (Ar−CH_3). Elem. An. Found (Calculated) for $C_{34}H_{35}N_3OPd$: 67.07 (67.16), 5.67 (5.80), 6.83 (6.91).

[(NNN)Pd(OH_2)]OTf. To a solution of (NNN)PdOTf (31 mg, 42 μmol) in C_6D_6 was added H_2O (1.5 μL, 83.3 μmol). The deep red solution soon turned orange, and copious amounts of orange red precipitate formed. The precipitates was washed with 2 mL of pentane 3 times, and then dried under vacuum for 15 min. Yield: 24 mg (76%). ^1H NMR (CD_2Cl_2, 499.4 MHz): δ 8.41 (s, 2H, Ar−H), 8.18 (s, 2H, N=CH), 7.72 (s, 2H, Ar−H), 6.99 (s, 4H, Ar−H), 3.27 (s, 2H, H_2O), 2.68 (s, 6H, Ar−CH_3), 2.30 (s, 12H, Ar−CH_3), 2.26 (s, 6H, Ar−CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.6 MHz): δ 162.7 (C=N), 145.2 (C_{Ar}), 138.3 (C_{Ar}), 137.2 (C_{Ar}), 132.8 (C_{Ar}), 131.3 (C_{Ar}), 130.4 (C_{Ar}), 129.8 (C_{Ar}), 129.6 (C_{Ar}), 125.9 (C_{Ar}), 117.9 (C_{Ar}), 21.3 (Ar−CH_3), 21.0 (Ar−CH_3), 19.7 (Ar−CH_3). ^{19}F NMR (CD_2Cl_2, 282.2 MHz): δ −79.8. IR (cm^{-1}): $\nu = 3494$ (OH). It was found that after heating at 80 °C overnight under vacuum about 40% of $[(NNN)PdOH_2]^+$ OTf^- was converted to (NNN)PdOTf.

Regeneraton of (NNN)PdOTf. To a suspension of [(NNN) Pd(OH_2)]OTf (20 mg, 26 μmol) in C_6D_6 was added dry 4A molecular sieves (0.5 g, 8−12 mesh). The mixture was allowed to stay at room temperature for 20 h. ^{19}F and ^1H NMR spectra showed that >95% of the starting [(NNN)Pd(OH_2)]OTf was converted to (NNN)PdOTf.

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic details in the form of a CIF file and a pictorial ^1H NMR spectrum of $[(NNN)Pd(OH_2)]OTf$. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759–92. (b) *The Chemistry of Pincer Compounds*; Morales-Morales, D.; Jensen, C. M., Eds.; Elsevier: Amsterdam, The Netherlands, 2007.

(2) Our diarylamido-based PNP pincer ligands were inspired by the disilylamido-based PNP ligands of Fryzuk that have been more recently employed by Caulton: (a) Fryzuk, M. D. *Can. J. Chem.* **1992**, *70*, 2839. (b) Fryzuk, M. D.; Berg, D. J.; Haddad, T. S. *Coord. Chem. Rev.* **1990**, *99*, 137. (c) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1. (d) Fan, H.; Fullmer, B. C.; Pink, M.; Caulton, K. G. *Angew. Chem., Int. Ed.* **2008**, *47*, 9112. (e) Ozerov, O. V.; Watson, L. A.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2007**, *129*, 6003.

(3) (a) Liang, L.-C. *Coord. Chem. Rev.* **2006**, *250*, 1152. (b) Ozerov, O. V. In *The Chemistry of Pincer Compounds*; Morales-Morales, D. Jensen, C., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; pp 287−309. (c) Mindiola, D. J. *Acc. Chem. Res.* **2006**, *39*, 813.

(4) (a) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007. (b) Winter, A. M.; Eichele, K.; Mack, H.-G.; Potuznik, S.; Mayer, H. A.; Kaska, W. C. *J. Organomet. Chem.* **2003**, *682*, 149.

(5) Fan, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 326.

(6) (a) Calimano, E.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 11161. (b) Whited, M. T.; Grubbs, R. H. *Acc. Chem. Res.* **2009**, *42*, 1607. (c) Cantat, T.; Graves, C. R.; Scott, B. L.; Kiplinger, J. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 3681. (d) Bailey, B. C.; Fan, H.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 8781. (e) Fafard, C. M.; Adhikari, D.; Foxman, B. M.; Mindiola, D. J.; Ozerov, O. V. *J. Am. Chem. Soc.* **2007**, *129*, 10318. (f) Weng, W.; Guo, C.; elenligil-Çetin, R.; Foxman, B. M.; Ozerov, O. V. *Chem. Commun.* **2006**, 197.

(7) Adhikari, D.; Basuli, F.; Fan, H.; Huffman, J. C.; Pink, M.; Mindiola, D. J. *Inorg. Chem.* **2008**, *47*, 4439.

(8) Radosevich, A. T.; Melnick, J. G.; Stoian, S. A.; Bacciu, D.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V.; Nocera, D. G. *Inorg. Chem.* **2009**, *48*, 9214.

(9) Adhikari, D.; Mossin, S.; Basuli, F.; Huffman, J. C.; Szilagyi, R. K.; Meyer, K.; Mindiola, D. J. *J. Am. Chem. Soc.* **2008**, *130*, 3676.

(10) Based on ionization potential data tabulated by the NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/) for carbazole (several values around 7.6 eV reported) and diphenylamine (several values around 7.2 eV).

(11) (a) Kieltsch, I.; Dubinina, G. G.; Hamacher, C.; Kaiser, A.; Torres-Nieto, J.; Hutchison, J. M.; Klein, A.; Budnikova, Y.; Vicic, D. A. *Organometallics* **2010**, *29*, 1451–1456. (b) Inagaki, T.; Phong, L. T.; Furuta, A.; Ito, J.; Nishiyama, H. *Chem.—Eur. J.* **2010**, *16*, 3090–3096. (c) Lu, S.-F.; Du, D.-M.; Zhang, S.-W.; Xu, J. *Tetrahedron: Asymmetry* **2004**, *15*, 3433–3441.

(12) Wanniarachchi, S.; Liddle, B. J.; Toussaint, J.; Lindeman, S. V.; Bennett, B.; Gardinier, J. R. *Dalton Trans.* **2010**, *39*, 3167–3169.

(13) Peters, J. C.; Harkins, S. B.; Brown, S. D.; Day, M. W. *Inorg. Chem.* **2001**, *40*, 5083.

(14) (a) Breitenfeld, J.; Vechorkin, O.; Corminboeuf, C.; Scopelliti, R.; Hu, X. *Organometallics* **2010**, *29*, 3686. (b) Vechorkin, O.; Csok, Z.; Scopelliti, R.; Hu, X. *Chem.—Eur. J.* **2009**, *15*, 3889–3899.

(15) Diarylamido/bis(imino) ligands have also been reported: (a) Black, D. St. C.; Rothnie, N. E. *Tetrahedron Lett.* **1978**, 2835–6. (b) Black, D. St. C.; Rothnie, N. E. *Aust. J. Chem.* **1983**, *36*, 2395–406.

(16) (a) Gaunt, J. A.; Gibson, V. C.; Haynes, A.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, *23*, 1015. (b) Gibson, V. C.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2003**, 2718. (c) Britovsek, G. J. P.; Gibson, V. C.; Hoarau, O. D.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2003**, *42*, 3454.

(17) Mudadu, M. S.; Singh, A. N.; Thummel, R. P. *J. Org. Chem.* **2008**, *73*, 6513–6520.

(18) Inoue, M.; Nakada, M. *Heterocycles* **2007**, *72*, 133.

(19) Barbe, J. M.; Habermeyer, B.; Khoury, T.; Gros, C. P.; Richard, P.; Chen, P.; Kadish, K. M. *Inorg. Chem.* **2010**, *49*, 8929–8940.

(20) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4792.

(21) Gilman, H.; Zuech, E. A. *J. Org. Chem.* **1959**, *24*, 1394.

(22) For an overview of aromatic nucleophilic substitution, see: *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; Smith, M. B., March, J., Eds.; John Wiley and Sons: New York, 2001; Chapter 13, pp 850−893.

(23) Fan, L.; Yang, L.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4778.

(24) Fafard, C. M.; Ozerov, O. V. *Inorg. Chim. Acta* **2007**, *360*, 286.

(25) Because of the sensitivity of $[(NNN)Pd(OH_2)]OTf$ to vacuum, it was only characterized in solution by NMR spectroscopic techniques.

(26) (a) Hughes, R. P.; Sweetser, J. T.; Tawa, M. D.; Williamson, A.; Incarvito, C. D.; Rhatigan, B.; Rheingold, A. L.; Rossi, G. *Organometallics* **2001**, *20*, 3800–3810. (b) Baar, C. R.; Carbray, L. P.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 2482–2497. (c) Svetlanova-Larsen, A.; Hubbard, J. L. *Inorg. Chem.* **1996**, *35*, 3073–6.

(27) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redon, R.; Cramer, R. E.; Jensen, C. M. *Inorg. Chim. Acta* **2000**, *300*−*302*, 958.

(28) Cross, R. J.; Kennedy, A. R.; Muir, K. W. *J. Organomet. Chem.* **1995**, *487*, 227.

(29) Ozerov, O. V.; Guo, C.; Foxman, B. M. *J. Organomet. Chem.* **2006**, *691*, 4802.

(30) ORTEP plots were created using Ortep-3 for Windows: Farugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(31) We use the potential of 0.48 V for the Fc/Fc^+ couple vs SCE (reported in Connelly, N.G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877, in 0.1 M $[Bu_4N][ClO_4]$) to convert the potential values reported vs SCE to the scale referenced to Fc/Fc^+ for consistency of comparison.

(32) (a) Ambrose, J. F.; Carpenter, L. L.; Nelson, R. F. *J. Electrochem. Soc.* **1975**, *27*, 876. (b) Ambrose, J. F.; Nelson, R. F. *J. Electrochem. Soc.* **1968**, *115*, 1159.

(33) Harkins, S. B.; Mankad, N. P.; Miller, A. J. M.; Szilagyi, R. K.; Peters, J. C. *J. Am. Chem. Soc.* **2008**, *130*, 3478; PNP′ = $(4\text{-}^tBu\text{-}2\text{-}^iBu_2P\text{-}C_6H_3)_2N$.

(34) (a) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125. (b) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046.

(35) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1990**, *28*, 346.

(36) *FRAMBO, Program for Data Collection on Area Detectors*, v. 4.1.05; BRUKER-Nonius Inc.: Madison, WI.

(37) Sheldrick, G. M. *Cell_Now, Program for Obtaining Unit Cell Constants from Single Crystal Data*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.

(38) *SAINT, Program for Data Integration from Area Detector Frames*, Version 7; Bruker-Nonius Inc.: Madison, WI.

(39) Sheldrick, G. M. *SADABS, Program for Absorption Correction for Data from Area Detector Frames*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.

(40) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(41) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2006. Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.