Articles

Redox Behavior of an Organometallic Palladium(II)/ Palladium(IV) System. A New Method for the Synthesis of Cationic Palladium(IV) Complexes

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A new method for the synthesis of cationic Pd(IV) complexes, based on the chemical oxidation of an anionic Pd(II) metallacycle in the presence of an additional ligand, is presented. Electrochemical analysis of these compounds reveals that the stability of the +4 oxidation state is sensitive to the electron-donor capability of the added co-ligand and to the steric features of the Tp′ ligand.

Introduction

Palladium is one of the most widely studied elements in organometallic chemistry, partly owing to the significant role of palladium complexes in organic synthesis and catalysis.[1] Pd(IV) complexes are thought to be intermediates in many important processes such as the Heck[2] and cross-coupling reactions[3] among others. Despite this, electrochemical data linking the II and IV oxidation states of Pd in organometallic systems relevant to catalysis are still lacking. We report herein a new method for the synthesis of Pd(IV) complexes based on the chemical oxidation of an anionic Pd(II) precursor with 2 equiv of the one-electron oxidant $[FeCp_2][PF_6]$ and preliminary electrochemical data regarding these complexes. While stable alkyl Pd(IV) complexes have been known since 1986,[4] their methods of synthesis are still very limited. The majority of Pd(IV) complexes are formed by oxidative addition of halogens, alkyl halides, or other electrophilic reagents to a suitable Pd(II) precursor.[5] Far less common are the methods of ligand exchange[6] and RX transfer[5] between Pd(IV) and Pd(II) molecules.

Results and Discussion

Synthesis and Characterization of Anionic Pd(II) Precursors. Although anionic palladacycles containing rigid tripodal ligand (e.g., hydrotris(pyrazolyl)borate, Tp) are good starting materials for the synthesis of Pd(IV)-alkyl (or aryl) derivatives, their characterization is in most cases limited to ^{1}H NMR spectroscopy.[7] We have recently shown that the anionic metallacycles $K[\overline{Pd(CH_2CMe_2\text{-}o\text{-}C_6H_4)}(\kappa^2\text{-Tp}')]$ (Tp′ = Tp (**1a**) or Tp^{Me2} (**1b**)) can be used as precursors for the synthesis of different types of Pd(IV) complexes.[8] Continuing our studies we have isolated and characterized these, and some related, anionic derivatives.

Compounds **1a** and **1b** are easily prepared by reaction of $[\overline{Pd(CH_2CMe_2\text{-}o\text{-}C_6H_4)}(cod)]$ (cod = cycloocta-1,4-diene) with KTp′ (Scheme 1). Extraction of the reaction mixture with diethyl ether allows the isolation of analytically pure samples of **1a**·Et_2O and **1b** as white microcrystalline solids. Once isolated, the complexes are no longer soluble in diethyl ether or other nonpolar solvents. In the IR spectra of **1a** and **1b**, the ν(B−H) absorption appears at 2453 and 2471 cm^{-1}, respectively, suggesting a κ^2 coordination of the Tp′ ligand, as shown in Scheme 1.[9] Their $^{11}B\{^1H\}$ resonances (δ = 40.6 and

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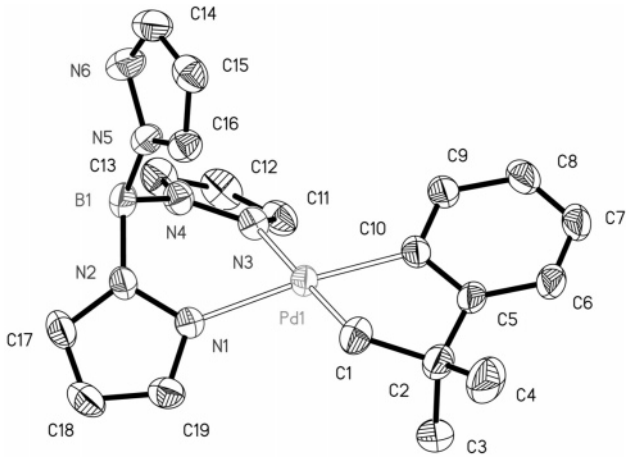
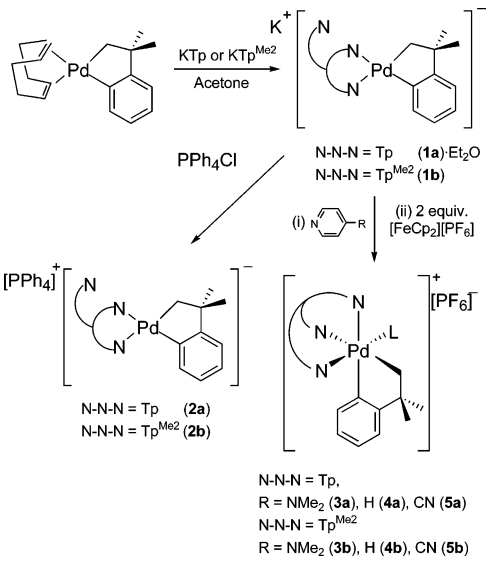


Figure 1. ORTEP diagram of the anionic part of **2a**. Hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Pd1−C1 = 2.001(2) Å, Pd1−C10 = 2.030(3) Å, Pd1−N1 = 2.1354(19) Å, Pd1−N3 = 2.149(2) Å, C1−Pd1−C10 = 79.49(12)°, N1−Pd1−N3 = 86.81(7)°.

Scheme 1



36.1 ppm for **1a** and **1b**) are also consistent with a bidentate Tp′ ligand.[10] At room temperature, the ^{1}H and ^{13}C{^{1}H} spectra show broad signals for both the metallacyclic and pyrazolyl moieties, due to fluxional processes that exchange the positions of the pyrazolyl rings. The slow exchange limit is reached at −35 °C for **1a** and −15 °C for **1b** at 400 MHz.

Although anionic alkyl complexes are common in palladium chemistry, few have been characterized by X-ray diffraction.[11] In an attempt to obtain a crystal suitable for an X-ray diffraction study that could confirm the proposed structures, complexes **1a** and **1b** were transformed into more crystalline derivatives by substitution of the K^+ cation by $[PPh_4]^+$ (**2a**, **2b**)[12] (Scheme 1). The IR and multinuclear NMR spectroscopic features of these new complexes are very similar to those of complexes **1a** and **1b** and suggest similar structures for all of them. Figure 1 shows the ORTEP diagram of complex **2a**.[13] The most salient feature of the solid state structure of complex **2a** is the κ^2 coordination mode of the Tp ligand. The nitrogen of the uncoordinated pyrazolyl ring is pointing away from the palladium atom. Bond distances and angles are similar to those observed in related neutral palladacycles.[12]

Table 1. Values of $(E_p)_{Ox}$ for 2 and $(E_p)_{Red}$ for 3−5 (V) versus SCE[a]

	Tp (**a**)		Tp^{Me2} (**b**)	
compound (R)	$(E_p)_{red}$	$(E_p)_{ox}$	$(E_p)_{red}$	$(E_p)_{ox}$
2		0.38		0.20
3 (R = NMe_2)	−0.81		−0.71	
4 (R = H)	−0.62		−0.50	
5 (R = CN)	−0.53		−0.47	

[a] In CH_3CN, $E^{\circ\prime}$ = 0.86 V for the one-electron oxidation of [Fe(η^5-C_5H_4(COMe))$_2$] added to the test solution as an internal calibrant.

Redox Oxidation of Anionic Pd(II) Complexes. New Method of Synthesis of Pd(IV) Compounds. The methods used for the synthesis of Pd(IV) complexes usually involve the oxidative addition of halogens, alkyl halides, or other electrophilic reagents to a suitable Pd(II) precursor. An alternative to this methodology is the redox oxidation of Pd(II) complexes in the presence of an auxiliary ligand. Thus, treatment of **1a** or **1b** with 2 equiv of $[FeCp_2][PF_6]$ in the presence of pyridine derivatives produces an orange-green solution from which the new cationic Pd(IV) complexes [Pd(CH_2CMe_2-*o*-C_6H_4)(κ^3-Tp′)(L)][PF_6] (L = 4-dimethylaminopyridine (**3a**,**b**), pyridine (**4a**,**b**), and 4-cyanopyridine (**5a**,**b**)) can be isolated after the appropriate workup (Scheme 1). The proposed structures are fully supported by the spectroscopic data. Thus, the frequency of the IR ν(B−H) bands[9] (within the ranges 2466−2499 and 2564−2569 cm^{-1} for the Tp and Tp^{Me2} derivatives, respectively) and the ^{11}B{^{1}H} spectra[10] (δ = 38.4 and 32.8 ppm for Tp and Tp^{Me2} complexes, respectively) are consistent with κ^3 coordination for the Tp′ ligand. As a consequence of the asymmetry of the metal center, the ^{1}H and ^{13}C{^{1}H} NMR spectra show three sets of signals for the inequivalent pyrazolyl rings, and diastereotopic CH_2 protons and methyl CMe_2 groups. The resonances in these spectra are generally sharp. However, for the Tp^{Me2} derivatives those resonances corresponding to the pyridine ligands are broad at room temperature, becoming sharp at temperatures below −30 °C. The most likely explanation for this observation would be the restricted rotation of the pyridine around the Pd−N axis, which could be hindered by the sterically demanding Tp^{Me2} ligand. Dissociation of the pyridine ligand appears less likely, because it would render the molecule conformationally labile and would cause the broadening of the remaining signals in the spectra.

Electrochemical Studies. The availability of pure samples of both the anionic Pd(II) and the cationic Pd(IV) complexes makes this system appropriate for electrochemical studies (Table 1). Figure 2 displays the cyclic voltammograms (CVs) of the Pd(IV) complexes **3a**−**5a**, recorded in acetonitrile using a platinum elec-

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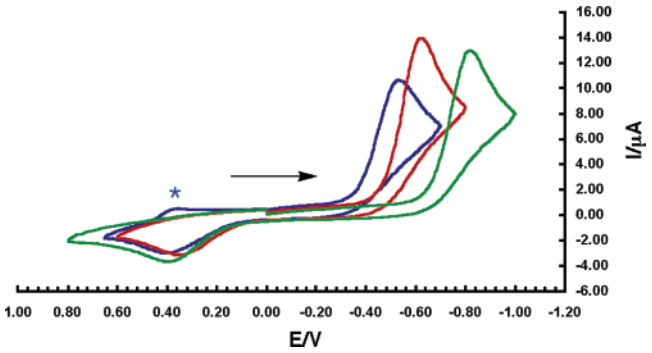

Figure 2. CV corresponding to the reduction of **3a** (green), **4a** (red), and **5a** (blue) in CH_3CN. The arrow indicates the direction of the scan, starting at 0.0 V, and the asterisk corresponds to a small impurity of $Fe(\eta^5\text{-}C_5H_5)_2$. Scan speed: 200 $mV{\cdot}s^{-1}$.

trode. Each CV shows one irreversible reduction wave accompanied by a product wave on the return scan, at an appreciably higher potential. The peak potentials $(E_p)_{red}$ associated with the reduction of the Pd(IV) species show a remarkable dependency on the nature of the substituent attached to the pyridine ligand, shifting to more negative values as the electron-releasing capability increases, i.e., CN < H < NMe_2. In contrast, the position of the oxidation wave is nearly the same in the three CVs, suggesting that it could be associated with the oxidation of an anionic Pd(II) species generated in the forward scan, which has lost the pyridine ligand. In agreement with this proposal, the CV of the anionic complex **2a** displays an oxidation wave in the same region, +0.38 V, with an associated product wave at ca. −0.45 V. Overall, therefore, the conversion of Pd(IV) to Pd(II) involves reduction followed by rapid loss of the pyridine ligand.

The CVs of the Tp^{Me2} derivatives are similar to those of their Tp counterparts. Not unexpectedly, the anionic complex **2b** is more readily oxidized than **2a**, presumably due to the greater electron-donor capability of the Tp^{Me2} ligand.[13] However, although the $(E_p)_{red}$ values corresponding to the reduction waves of complexes **3b**−**5b** follow the same pyridine ligand-dependent trend observed for **3a**−**5a**, they are ca. 0.1 V more positive, indicating that the Pd(IV) complexes containing Tp^{Me2} are more easily reduced. Though small, this effect may be steric rather than electronic in origin.

Summary and Conclusion

In summary, we have shown that chemical oxidation of anionic Tp-containing Pd(II) metallacycles in the presence of an additional ligand produces stable cationic Pd(IV) complexes. Electrochemical analysis of these compounds reveals that the stability of the +4 oxidation state is sensitive to the electron donor capability of the added co-ligand and to the steric features of the Tp′ ligand.

Experimental Section

General Information. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The complex $Pd(CH_2CMe_2\text{-}o\text{-}C_6H_4)(cod)$[12] and the potassium salts of the hydrotris(pyrazolyl)borate ligands (KTp and KTp^{Me2})[14] were prepared according to literature procedures. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were recorded on a Bruker Vector 22 spectrometer, and NMR spectra on Bruker DRX 300, 400, and 500 MHz spectrometers. The ^1H and $^{13}C\{^1H\}$ resonances of the solvent were used as the internal standard, but the chemical shifts are reported with respect to TMS. The assignment of NMR spectra has been done with the help of two-dimensional spectra ($^1H-^1H$ COSY, $^1H-^1H$ NOESY, $^1H-^{13}C$ HMQC, and $^1H-^{13}C$ HMBC).

Electrochemical studies were carried out on an EG&G model 273A potentiostat in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire and the working electrode a platinum disk. The reference was an aqueous saturated calomel electrode separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Solutions were 1.0×10^{-3} $mol{\cdot}dm^{-3}$ in the test compound and 0.1×10^{-3} $mol{\cdot}dm^{-3}$ in $[NBu^n_4][PF_6]$ as the supporting electrolyte in CH_3CN. Under the conditions used for voltammetry, $E^{\circ\prime}$ for the one-electron oxidation of $[Fe(\eta^5\text{-}C_5H_4\text{-}COMe)_2]^{0/+}$ (added to the test solution as an internal calibrant) is 0.86 V.

Synthesis of $K[Pd(CH_2CMe_2\text{-}o\text{-}C_6H_4)(\kappa^2\text{-}Tp')]$ (Tp′ = Tp (1a·Et₂O) and Tp^{Me2} (1b)). A 346 mg sample of $Pd(CH_2CMe_2\text{-}o\text{-}C_6H_4)(cod)$ (1 mmol) and 252 mg of KTp (1 mmol) were dissolved in 40 mL of acetone, and the mixture was stirred at room temperature for one hour. The solvent was removed under reduced pressure and the oily residue extracted with 30 mL of diethyl ether. The solution was evaporated again and the residue extracted with 30 mL of petroleum ether (40−60 °C). Complex **1a** was obtained as a white crystalline solid in quantitative yield upon cooling the solution at −30 °C.

Complex **1b** was similarly prepared; the solvent used for the second extraction was diethyl ether. The complex was isolated as a white crystalline solid after addition of some petroleum ether and cooling at −30 °C.

Spectroscopic and Analytical Data for 1a·Et₂O. Anal. Calcd. for $C_{23}H_{32}BKN_6OPd$: C, 48.90; H, 5.71; N, 14.88. Found: C, 48.81; H, 5.51; N, 15.16. IR (Nujol mull): ν(B−H) 2453 cm^{-1}. ^1H NMR (CD_2Cl_2, −35 °C): δ 1.10 (t, 6H, $O(CH_2CH_3)_2$), 1.16 and 1.37 (s, 3H, CH_3), 1.75 (d, 1H, $^2J_{HH}$ = 8.8 Hz, CH_2), 1.97 (d, 1H, $^2J_{HH}$ = 9.1 Hz, CH_2), 3.38 (q, 4H, $O(CH_2CH_3)_2$), 6.10 (bs, 1H, $CH(4)_{pz}$), 6.30 (t, 1H, $^3J_{HH}$ = 1.8 Hz, $CH(4)_{pz}$), 6.37 (t, 1H, $^3J_{HH}$ = 2.1 Hz, $CH(4)_{pz}$), 6.76 (m, 2H, $C_{ar}H$), 6.87 (t, 1H, $^3J_{HH}$ = 7.4 Hz, $C_{ar}H$), 6.93 (bs, 1H, $CH(3\ or\ 5)_{pz}$), 7.12 (d, 1H, $^3J_{HH}$ = 7.1 Hz, $C_{ar}H$), 7.19, 7.65, and 7.74 (bs, 1H, $CH(3\ or\ 5)_{pz}$), 7.76 (d, 1H, $^3J_{HH}$ = 1.5 Hz, $CH(3\ or\ 5)_{pz}$) and 7.81 (d, 1H, $^3J_{HH}$ = 1.4 Hz, $CH(3\ or\ 5)_{pz}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −35 °C): δ 15.7 (s, $O(CH_2CH_3)_2$), 33.0 and 35.3 (bs, CMe_2), 42.4 (s, CH_2), 48.1 (s, CMe_2), 66.3 (s, $O(CH_2CH_3)_2$), 105.1, 105.8, and 106.1 (s, $CH(4)_{pz}$), 123.0, 123.8, 125.1, and 135.2 (s, $C_{ar}H$), 135.6 (s, $CH(3)_{pz}$), 137.5 (bs, $CH(3)_{pz}$), 140.7, 141.9, and 143.7 (s, $CH(5)_{pz}$), 159.8 and 169.6 (s, C_{ar}).

Spectroscopic and Analytical Data for 1b. Anal. Calcd. for $C_{25}H_{34}BKN_6Pd$: C, 52.23; H, 5.96; N, 14.62. Found: C, 51.93; H, 5.91; N, 14.82. IR (Nujol mull): ν(B−H) = 2457 and 2374 cm^{-1}. ^1H NMR (CD_2Cl_2, −15 °C): δ 1.06 and 1.44 (s, 3H, CH_3), 1.23 (bs, 1H, CH_2), 1.61, 2.05, 2.29, 2.31, 2.36, and 2.46 (s, 3H, Tp^{Me2}), 1.70 (bs, 1H, CH_2), 5.74, 5.89, and 5.90 (s, 1H, $CH(4)_{pz}$), 6.66 (m, 2H, $C_{ar}H$), 6.79 (tm, 1H, J_{HH} = 7.3 Hz, $C_{ar}H$), 6.96 (dm, 1H, J_{HH} = 7.2 Hz, $C_{ar}H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 13.6, 14.3, and 14.9 (bs, Tp^{Me2}), 30.3 and 32.5 (bs, CMe_2),

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38.3 (s, CH_2), 48.7 (s, CMe_2), 106.2, 106.2, and 106.5 (s, $CH(4)_{pz}$), 122.1, 122.6, 123.8, and 136.9 (s, $C_{ar}H$), 146.2 and 148.4 (bs, $C(3\text{ or }5)_{pz}$), 146.9 and 149.7 (s, $C(3\text{ or }5)_{pz}$) 161.4 and 168.5 (s, C_{ar}). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 36.1 ppm.

Synthesis of [PPh_4][Pd(CH_2CMe_2-*o*-C_6H_4)(κ^2-Tp′)] (Tp′ = Tp (2a) and Tp^{Me2} (2b)). A 126 mg (0.5 mmol) sample of KTp was added to a solution of 174 mg (0.5 mmol) of Pd(CH_2-CMe_2-*o*-C_6H_4)(cod) in 20 mL of acetone. The mixture was stirred at room temperature for 1 h, cooled at −60 °C, and treated with 187 mg (0.5 mmol) of PPh_4Cl. The mixture was stirred at this temperature for 30 min and at room temperature for 2 h. Afterward, 20 mL of CH_2Cl_2 was added and the suspension was centrifuged, the solution taken to dryness, and the white residue washed with petroleum ether (2 × 10 mL). The solid can be crystallized from acetonitrile and isolated as white crystals in 94% yield.

Complex **2b** was analogously prepared. It can be crystallized from a mixture of acetonitrile/petroleum ether (1:1) and isolated in 96% yield.

Spectroscopic and Analytical Data for 2a. Anal. Calcd. for $C_{47}H_{52}BN_6OPPd$: C, 65.29; H, 5.35; N, 10.62. Found: C, 65.06; H, 5.24; N, 10.49. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.32 (bs, 6H, CH_3), 2.0 (bs, 2H, CH_2), 6.09 (bs, 3H, $CH(4)_{pz}$), 6.67 (m, 2H, $C_{ar}H$), 6.76 (m, 1H, $C_{ar}H$), 7.30 (m, 1H, $C_{ar}H$), 7.54 (m, 8H, $C_{ar}H$ (PPh_4)), 7.68 (m, 8H, $C_{ar}H$ (PPh_4)), 7.80 (bs, 3H, $CH(3\text{ or }5)_{pz}$), and 7.88 (m, 4H, $C_{ar}H$ (PPh_4)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 34.4 (bs, CMe_2), 41.4 (s, CH_2), 48.0 (s, CMe_2), 103.8 (s, 3C, $CH(4)_{pz}$), 117.8 (d, 4C, J_{CP} = 90 Hz, C_{ar} (PPh_4)), 121.4, 121.7, 123.3, and 136.7 (s, $C_{ar}H$), 131.0 (d, 8C, J_{CP} = 13 Hz, $C_{ar}H$ (PPh_4)), 134.7 (d, 8C, J_{CP} = 11 Hz, $C_{ar}H$ (PPh_4)), 135.7 (s, 3C, $CH(3\text{ or }5)_{pz}$), 136.0 (d, 4C, J_{CP} = 3 Hz, $C_{ar}H$ (PPh_4)), 140.9 (bs, 3C, $CH(3\text{ or }5)_{pz}$), 162.5 and 169.1 (s, C_{ar}).

Spectroscopic and Analytical Data for 2b. Anal. Calcd. for $C_{49}H_{54}BN_6PPd$: C, 67.25; H, 6.22; N, 9.60. Found: C, 66.91; H, 6.26; N, 8.99. ^1H NMR ($(CD_3)_2CO$, 20 °C): δ 1.22 (s, 6H, Tp^{Me2}), 1.66 (s, 2H, CH_2), 1.98 and 2.02 (s, 6H, Tp^{Me2}), 2.28 and 2.38 (s, 3H, CH_3), 5.46 (s, 2H, $CH(4)_{pz}$), 5.60 (s, 1H, $CH(4)_{pz}$), 6.37, 6.43, 6.46, and 6.96 (m, 1H, $C_{ar}H$), 7.80 (m, 16H, $C_{ar}H$ (PPh_4)), 7.96 (m, 4H, $C_{ar}H$ (PPh_4)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 13.1, 13.9, 15.3, and 15.5 (s, Tp^{Me2}), 34.9 (s, CMe_2), 38.4 (s, CH_2), 48.8 (s, CMe_2), 105.0 and 105.3 (s, $CH(4)_{pz}$), 119.0 (d, 4C, J_{CP} = 90 Hz, C_{ar} (PPh_4)), 120.6, 120.7, 122.2, and 138.5 (s, $C_{ar}H$), 131.4 (d, 8C, J_{CP} = 13 Hz, $C_{ar}H$ (PPh_4)), 135.7 (d, 8C, J_{CP} = 11 Hz, $C_{ar}H$ (PPh_4)), 136.4 (d, 4C, J_{CP} = 3 Hz, $C_{ar}H$ (PPh_4)), 143.5, 144.6, 146.5 and 148.0 (s, $C(3\text{ or }5)_{pz}$), 164.1 and 167.9 (s, C_{ar}).

Synthesis of [Pd(CH_2CMe_2-*o*-C_6H_4)(κ^3-Tp′)][(4-R-NC_5H_4)][PF_6] (R = −NMe_2 (3), −H (4), −CN (5); Tp′ = Tp (a) and Tp^{Me2} (b)). These compounds were prepared by the general method: To a solution of 346 mg of Pd(CH_2CMe_2-*o*-C_6H_4)(cod) (1 mmol) in 40 mL of acetone was added 1 mmol of KTp′ (252 mg of KTp or 346 mg of KTp^{Me2}) and the mixture stirred at room temperature for 1 h. The solution was cooled at −80 °C and 1 mmol of the corresponding pyridine added. Then the mixture was allowed to reach room temperature. After a few minutes, the solution was cooled again at −80 °C and 662 mg (2 mmol) of [Cp_2Fe][PF_6] were added. The color turned immediately to orange and then dark green. The reaction mixture was stirred at room temperature for 3 h and the solvent removed under reduced pressure. The residue was extracted with 20 mL of CH_2Cl_2, the resulting suspension centrifuged, and the solution evaporated under vacuum. The solid was washed with diethyl ether (4 × 50 mL) and the product isolated as a pale yellow solid in 80% yield.

Spectroscopic and Analytical Data for 3a (Tp′ = Tp, R = −NMe_2). Anal. Calcd. for $C_{26}H_{32}BF_6N_8PPd$: C, 43.43; H, 4.45; N, 15.59. Found: C, 43.73; H, 4.37; N, 15.61. IR (Nujol mull): ν(B−H) 2466 cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.12 (s, 3H, CH_3, B), 1.56 (s, 3H, CH_3, A), 3.06 (s, 6H, NMe_2), 4.51 (d, 1H, $^2J_{HH}$ = 7.0 Hz, CH_2, B), 4.88 (d, 1H, $^2J_{HH}$ = 7.0 Hz, CH_2, A), 6.20 (t, 1H, $^3J_{HH}$ = 2.4 Hz, $CH(4C)_{pz}$), 6.41 (t, 1H, $^3J_{HH}$ = 2.2 Hz, $CH(4A)_{pz}$), 6.51 (t, 1H, $^3J_{HH}$ = 2.2 Hz, $CH(4B)_{pz}$), 6.54 (d, 2H, $^3J_{HH}$ = 7.5 Hz, $C_{ar}H$(3-Py)), 6.86 (d, 1H, $^3J_{HH}$ = 2.2 Hz, $CH(5C)_{pz}$), 7.05 (tm, 1H, $^3J_{HH}$ = 7.6 Hz, $C_{ar}H(5)$), 7.12 (dm, 1H, $^3J_{HH}$ = 7.7 Hz, $C_{ar}H(6)$), 7.16 (dm, 1H, $^3J_{HH}$ = 7.6 Hz, $C_{ar}H(3)$), 7.31 (tm, 1H, $^3J_{HH}$ = 7.6 Hz, $C_{ar}H(4)$), 7.51 (d, 1H, $^3J_{HH}$ = 1.9 Hz, $CH(5A)_{pz}$), 7.80 (d, 1H, $^3J_{HH}$ = 2.5 Hz, $CH(3C)_{pz}$), 7.86 (d, 2H, $^3J_{HH}$ = 7.5 Hz, $C_{ar}H$(2-Py)), 7.89 (d, 1H, $^3J_{HH}$ = 2.3 Hz, $CH(3A)_{pz}$), 7.90 (d, 1H, $^3J_{HH}$ = 2.3 Hz, $CH(3B)_{pz}$) and 7.99 (d, 1H, $^3J_{HH}$ = 2.0 Hz, $CH(5B)_{pz}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 31.8 and 32.2 (s, CMe_2), 39.6 (s, NMe_2), 46.7 (s, CMe_2), 72.7 (s, CH_2), 107.0, 107.2, and 107.3 (s, $CH(4)_{pz}$), 109.0 (s, $C_{ar}H$(3-Py)), 128.0, 128.4, 129.5, and 130.2 (s, $C_{ar}H$), 136.5, 137.3, and 137.7 (s, $CH(3)_{pz}$), 139.8, 140.8, and 142.5 (s, $CH(5)_{pz}$), 149.5 (s, $C_{ar}H$(2-Py)), 155.5 (s, C_{ar}), 156.4 (s, C_{ar}(4-Py)), and 159.2 (s, C_{ar}).

Spectroscopic and Analytical Data for 3b (Tp′ = Tp^{Me2}, R = −NMe_2). Anal. Calcd. for $C_{32}H_{44}BF_6N_8PPd$: C, 47.87; H, 5.52; N, 13.96. Found: C, 47.55; H, 5.41; N, 13.67. IR (Nujol mull): ν(B−H) 2564 cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.35 and 1.45 (s, 3H, Tp^{Me2}) 1.50 (s, 3H, CH_3, A), 1.55 (s, 3H, CH_3, B), 2.28, 2.42, 2.43, and 2.49 (s, 3H, Tp^{Me2}) 3.02 (s, 6H, NMe_2), 4.80 (d, 1H, $^2J_{HH}$ = 6.9 Hz, CH_2, A), 4.98 (d, 1H, $^2J_{HH}$ = 7.0 Hz, CH_2, B), 5.80, 5.83, and 6.07 (s, 1H, CH_{pz}), 6.28 (d, 2H, $^3J_{HH}$ = 7.6 Hz, $C_{ar}H$(3-Py)), 7.06 (tm, 1H, $^3J_{HH}$ = 7.6 Hz, $C_{ar}H(5)$), 7.16 (dm, 1H, $^3J_{HH}$ = 8.1 Hz, $C_{ar}H(6)$), 7.24 (dm, 1H, $^3J_{HH}$ = 7.6 Hz, $C_{ar}H(3)$), 7.36 (tm, 1H, $^3J_{HH}$ = 7.2 Hz, $C_{ar}H(4)$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 12.6, 12.7, 12.8, 14.1, 14.4, and 15.3 (s, Tp^{Me2}), 30.7 and 32.9 (s, CMe_2), 39.5 (s, NMe_2), 46.6 (s, CMe_2), 67.5 (s, CH_2), 107.8 (bs, $C_{ar}H$(3-Py)), 107.8, 108.9, and 110.6 (s, $CH(4)_{pz}$), 128.4, 128.5, 128.8, and 132.8 (s, $C_{ar}H$), 145.1, 145.9, and 147.1 (s, $C(3)_{pz}$), 149.6 and 150.1 (s, $C(5)_{pz}$), 151.4 (s, $C_{ar}H$(2-Py)), 151.8 (s, $C(5)_{pz}$), 155.3, 156.4, and 156.9 (s, C_{ar} and C_{ar}(4-Py)). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 32.7 ppm.

Spectroscopic and Analytical Data for 4a (Tp′ = Tp, R = −H). Anal. Calcd. for $C_{24}H_{27}BF_6N_7PPd$: C, 42.66; H, 4.03; N, 14.51. Found: C, 42.88; H, 3.39; N, 14.21. IR (Nujol mull): ν(B−H) 2499 cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.02 (s, 3H, CH_3, B), 1.57 (s, 3H, CH_3, A), 4.62 (d, 1H, $^2J_{HH}$ = 7.1 Hz, CH_2, B), 5.00 (d, 1H, $^2J_{HH}$ = 7.0 Hz, CH_2, A), 6.23 (t, 1H, $^3J_{HH}$ = 2.4 Hz, $CH(4C)_{pz}$), 6.40 (t, 1H, $^3J_{HH}$ = 2.2 Hz, $CH(4A)_{pz}$), 6.55 (t, 1H, $^3J_{HH}$ = 2.2 Hz, $CH(4B)_{pz}$), 6.87 (d, 1H, $^3J_{HH}$ = 2.2 Hz, $CH(5C)_{pz}$), 7.10 (tm, 1H, $^3J_{HH}$ = 7.6 Hz, $C_{ar}H(5)$), 7.14 (dm, 1H, $^3J_{HH}$ = 7.7 Hz, $C_{ar}H(6)$), 7.19 (dm, 1H, $^3J_{HH}$ = 7.6 Hz, $C_{ar}H(3)$), 7.36 (tm, 1H, $^3J_{HH}$ = 7.3 Hz, $C_{ar}H(4)$), 7.43 (d, 1H, $^3J_{HH}$ = 1.8 Hz, $CH(5A)_{pz}$), 7.62 (t, 2H, $^3J_{HH}$ = 5.4 Hz, $C_{ar}H$(3-Py)), 7.83 (d, 1H, $^3J_{HH}$ = 2.3 Hz, $CH(3C)_{pz}$), 7.91 (d, 1H, $^3J_{HH}$ = 2.2 Hz, $CH(3A)_{pz}$), 7.94 (d, 1H, $^3J_{HH}$ = 2.2 Hz, $CH(3B)_{pz}$), 8.08 (d, 1H, $^3J_{HH}$ = 1.8 Hz, $CH(5B)_{pz}$), 8.12 (t, 1H, $^3J_{HH}$ = 5.4 Hz, $C_{ar}H$(4-Py)), and 8.54 (d, 2H, $^3J_{HH}$ = 5.4 Hz, $C_{ar}H$(2-Py)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 31.9 and 32.2 (s, CMe_2), 46.8 (s, CMe_2), 74.2 (s, CH_2), 107.3, 107.4, and 107.7 (s, $CH(4)_{pz}$), 128.1 (s, $C_{ar}H$(3-Py)), 128.5, 128.9, 129.9, and 130.2 (s, $C_{ar}H$), 136.8, 137.6, and 138.1 (s, $CH(3)_{pz}$), 139.7 and 141.0 (s, $CH(5)_{pz}$), 142.3 (s, $C_{ar}H$(4-Py)), 142.8 (s, $CH(5)_{pz}$), 151.7 (s, $C_{ar}H$(2-Py)), 155.9 and 159.2 (s, C_{ar}). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 38.4 ppm.

Spectroscopic and Analytical Data for 4b (Tp′ = Tp^{Me2}, R = −H). Anal. Calcd. for $C_{30}H_{39}BF_6N_7PPd$: C, 47.42; H, 5.17; N, 12.90. Found: C, 47.52; H, 5.08; N, 12.98. IR (Nujol mull): ν(B−H) 2569 cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.10 and 1.48 (s, 3H, Tp^{Me2}) 1.48 (s, 3H, CH_3, A), 1.58 (s, 3H, CH_3, B), 2.23, 2.43, 2.44, and 2.52 (s, 3H, Tp^{Me2}), 4.87 (d, 1H, $^2J_{HH}$ = 6.9 Hz, CH_2, A), 5.12 (d, 1H, $^2J_{HH}$ = 6.9 Hz, CH_2, B), 5.80, 5.87, and 6.12 (s, 1H, CH_{pz}), 7.10 (t, 1H, $^3J_{HH}$ = 7.6 Hz, $C_{ar}H(5)$), 7.17 (d, 1H, $^3J_{HH}$ = 8.0 Hz, $C_{ar}H(6)$), 7.31 (d, 1H, $^3J_{HH}$ = 7.1 Hz, $C_{ar}H(3)$), 7.38 (t, 2H, $^3J_{HH}$ = 6.4 Hz, $C_{ar}H$(2-Py)), 7.43 (t, 1H, $^3J_{HH}$ = 7.3 Hz, $C_{ar}H(4)$), 8.04 (t, 1H, $^3J_{HH}$ = 7.5 Hz, $C_{ar}H$(4-Py)), and 8.11 (bs, 2H, $C_{ar}H$(3-Py)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20

°C): δ 12.1, 12.7, 12.8, 14.2, 14.5, and 15.4 (s, Tp^{Me2}), 30.6 and 33.0 (s, C*Me*$_2$), 46.7 (s, *C*Me$_2$), 68.9 (s, *C*H$_2$), 108.1, 109.2, and 110.9 (s, *C*H(4)$_{pz}$), 126.9 (bs, *C*$_{ar}$H(3-Py)), 129.0, 129.4, and 132.9 (s, *C*$_{ar}$H), 142.3 (s, *C*$_{ar}$H(4-Py)), 145.7, 146.3, and 147.5 (s, *C*(3)$_{pz}$), 149.6, 150.0, and 152.0 (s, *C*(5)$_{pz}$), 153.6 (bs, *C*$_{ar}$H(2-Py)), 155.7 and 156.8 (s, *C*$_{ar}$). ^{11}B{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 32.9 ppm.

Spectroscopic and Analytical Data for 5a (Tp′ = Tp, R = −CN). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.07 (s, 3H, C*H*$_3$, A), 1.58 (s, 3H, C*H*$_3$, B), 4.70 (d, 1H, $^2J_{HH}$ = 7.1 Hz, C*H*$_2$, B), 5.02 (d, 1H, $^2J_{HH}$ = 7.1 Hz, C*H*$_2$, A), 6.24 (t, 1H, $^3J_{HH}$ = 2.4 Hz, C*H(4C)*$_{pz}$), 6.41 (t, 1H, $^3J_{HH}$ = 2.2 Hz, C*H(4A)*$_{pz}$), 6.56 (t, 1H, $^3J_{HH}$ = 2.2 Hz, C*H(4B)*$_{pz}$), 6.87 (d, 1H, $^3J_{HH}$ = 2.0 Hz, C*H(5C)*$_{pz}$), 7.10 (tm, 1H, $^3J_{HH}$ = 7.0 Hz, C$_{ar}$*H(5)*), 7.14 (dm, 1H, $^3J_{HH}$ = 7.1 Hz, C$_{ar}$*H(6)*), 7.22 (dm, 1H, $^3J_{HH}$ = 7.6 Hz, C$_{ar}$*H(3)*), 7.38 (m, 1H, C$_{ar}$*H(4)*), 7.38 (m, 1H, C*H(5A)*$_{pz}$), 7.84 (m, 1H, C*H-(3C)*$_{pz}$), 7.84 (m, 2H, C$_{ar}$*H*(3-Py)), 7.91 (d, 1H, $^3J_{HH}$ = 2.1 Hz, C*H(3A)*$_{pz}$), 7.94 (d, 1H, $^3J_{HH}$ = 2.2 Hz, C*H(3B)*$_{pz}$), 8.12 (d, 1H, $^3J_{HH}$ = 2.0 Hz, C*H(5B)*$_{pz}$), 8.72 (d, 2H, $^3J_{HH}$ = 5.5 Hz, C$_{ar}$*H*(2-Py)). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 32.0 and 32.5 (s, C*Me*$_2$), 46.9 (s, *C*Me$_2$), 74.9 (s, *C*H$_2$), 107.5, 107.6, and 107.9 (s, *C*H-(4)$_{pz}$), 114.5 (s, *C*N), 125.9 (s, *C*$_{ar}$(4-Py)), 128.8 and 129.2 (s, *C*$_{ar}$H), 130.0 (s, *C*$_{ar}$H(3-Py)) 130.2 and 130.3 (s, *C*$_{ar}$H), 136.9, 137.7, and 138.3 (s, *C*H(3)$_{pz}$), 139.8, 141.4, and 142.9 (s, *C*H-(5)$_{pz}$), 152.9 (s, *C*$_{ar}$H(2-Py)), 155.5 and 158.7 (s, *C*$_{ar}$). It has not been possible to obtain a satisfactory elemental analysis for this complex. IR (Nujol mull): ν(B−H) 2486 cm^{-1}. ^{11}B{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 38.4 ppm.

Spectroscopic and Analytical Data for 5b (Tp′ = Tp^{Me2}, R = −CN). Anal. Calcd. for $C_{31}H_{38}BF_6N_8PPd$: C, 47.44; H, 4.88; N, 14.28. Found: C, 47.53; H, 5.12; N, 13.74. IR (Nujol mull): ν(B−H) 2569 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.10 (s, 3H, Tp^{Me2}) 1.45 (s, 3H, C*H*$_3$, A), 1.47 (s, 3H, Tp^{Me2}), 1.58 (s, 3H, C*H*$_3$, B), 2.21, 2.43, 2.44, and 2.52 (s, 3H, Tp^{Me2}), 4.87 (d, 1H, $^2J_{HH}$ = 7.0 Hz, C*H*$_2$, A), 5.16 (d, 1H, $^2J_{HH}$ = 7.0 Hz, C*H*$_2$, B), 5.81, 5.88, and 6.14 (s, 1H, C*H*$_{pz}$), 7.14 (m, 2H, C$_{ar}$*H(5)* and C$_{ar}$*H(6)*), 7.34 (dm, 1H, $^3J_{HH}$ = 7.6 Hz, C$_{ar}$*H(3)*), 7.46 (tm, 1H, $^3J_{HH}$ = 6.8 Hz, C$_{ar}$*H(4)*), 7.64 (d, 2H, $^3J_{HH}$ = 5.5 Hz, C$_{ar}$*H*(3-Py)), and 8.33 (bs, 2H, C$_{ar}$*H*(2-Py)). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 12.4, 12.7, 12.7, 14.2, 14.6, and 15.5 (s, Tp^{Me2}), 30.5 and 33.0 (s, C*Me*$_2$), 46.8 (s, *C*Me$_2$), 70.1 (s, *C*H$_2$), 108.3, 109.4, and 111.2 (s, *C*H(4)$_{pz}$), 114.4, 126.0 (s, *C*$_{ar}$, *C*$_{ar}$(4-Py) or *C*N), 128.7 (bs, *C*$_{ar}$H(3-Py)), 129.3, 129.4, 129.8, and 133.0 (s, *C*$_{ar}$H), 145.8, 146.7, and 147.9 (s, *C*(3)$_{pz}$), 149.6, 149.7, and 152.1 (s, *C*(5)$_{pz}$), 154.4 (bs, *C*$_{ar}$H(2-Py)), 155.2 and 156.0 (s, *C*$_{ar}$, *C*$_{ar}$(4-Py) or *C*N). ^{11}B{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 32.7 ppm.

X-ray Structure Analysis of 2a. A typical colorless crystal was chosen (0.35 × 0.15 × 0.10 mm) and mounted in epoxy resin (Araldite) onto a glass fiber at room temperature (296 K). X-ray diffraction data were collected on a Bruker SMART 6000 CCD area-detector diffractometer, equipped with a laboratory rotating-anode source, coupled to Göbel mirror optics to obtain monochromated Cu Kα (λ = 1.54184 Å) radiation. The Cu target X-ray generator was adjusted at a power of 3150 W (45 kV, 70 mA), and the crystal-to-detector distance was fixed at 4.19 cm. Six sets of ω-scans (Δω = 0.3°/frame, time per frame 10 s) at different φ settings were collected covering a hemisphere of the reciprocal space (3 × 600 frames to φ = 0°, 120°, and 240°, respectively, with the CCD detector placed to 2θ = −40°, and others 3 × 600 frames to φ = 60°, 180°, and 300°, respectively, with the CCD detector placed to 2θ = −100°). Cell parameters were determined and refined using the SMART software,[15a] and raw frame data were integrated using the SAINT+ program.[15b] The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL software.[15c] Reflection intensities were corrected for absorption effects by numerical integration based on measurements and indexing of the crystal faces (using SHELXTL software[15c]). Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined isotropically riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. Atomic scattering factors, corrected for anomalous dispersion, were implemented by the program. Crystal data and details of data collection and structure refinements are given in Table 2. Further details are included in the Supporting Information.

Table 2. Crystal Data and Structure Refinement for 2a

empirical formula	$C_{43}H_{42}BN_6PPd$
fw	791.01
temperature	296(2) K
wavelength	1.54178 Å
cryst syst	monoclinic
space group	*P*2(1)/*n*
unit cell dimens	a = 10.68100(10) Å, α = 90° b = 28.0254(3) Å, β = 100.2320(10)° c = 13.03040(10) Å, γ = 90°
volume	3838.48(6) Å^3
Z	4
density (calcd)	1.369 Mg/m^3
absorp coeff	4.591 mm^{-1}
F(000)	1632
cryst size	0.35 × 0.15 × 0.10 mm^3
θ range for data collection	3.15 to 70.44°
index ranges	$-12 \le h \le 12$, $-30 \le k \le 34$, $-13 \le l \le 15$
no. of reflns collected	24 574
no. of indep reflns	6821 [*R*(int) = 0.0374]
completeness to θ = 68.5°	96.5%
absorp corr	semiempirical from equivalents
max. and min. transmn	0.6567 and 0.2964
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	6821/0/469
goodness-of-fit on F^2	1.043
final *R* indices [$I>2\sigma(I)$]	R1 = 0.0305, wR2 = 0.0808
R indices (all data)	R1 = 0.0354, wR2 = 0.0838
largest diff peak and hole	0.400 and −0.272 e Å^{-3}

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Supporting Information Available: Additional cyclic voltammograms, complete tables of bond lengths and angles, and X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) *SMART-WNT/2000*, Data Collection Software, Version 5.625; Bruker AXS, Inc.: Madison, WI, 2001. (b) *SAINT-WNT/2000*, Data Reduction Software, Version 6.04; Bruker AXS, Inc.: Madison, WI, 2001. (c) *SHELXTL-WNT/2000*, Structure Refinement and Solution Software, Version 6.10; Bruker AXS, Inc.: Madison, WI, 2000.