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A New Type of Palladium-Pincer Complexes Generated via Hydrolytic Ring-Opening of Imidazole-2-ylidenes

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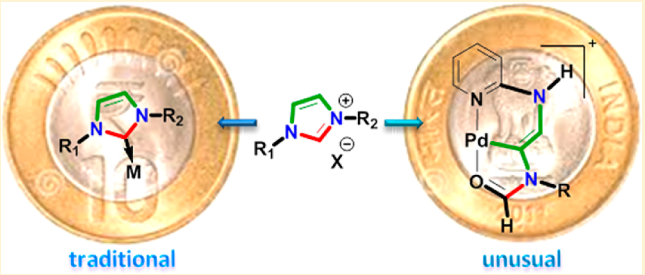
Supporting Information

ABSTRACT: The reaction of a series of pyridine-appended imidazolium salts with $Pd(COD)Cl_2$ in the presence of KO^{t}Bu as base led to hydrolytic ring-opening followed by a new type of pincer tridentate (N,C,O) bonding of the *in situ* generated formamide-based new ligands toward the metal center. This unprecedented type of bonding resulted from a vinylic C−H activation by palladium stabilized with coordination from the pyridine nitrogen and aldehyde oxygen donors in a pincer fashion. The new stable, square-planar palladium(II) complexes (**1**−**3**) were characterized by 1D and 2D NMR spectroscopic and high-resolution mass spectrometric (HRMS) methods. The single-crystal X-ray structure of a representative complex (**2**) confirmed the above interesting bonding features.



INTRODUCTION

Recently, N-heterocyclic carbenes (NHCs) undoubtedly placed themselves on the front rows of the ligand matrix as developed and utilized successfully in the fields of fundamental organometallic chemistry, catalysis, and materials.[1] Their unique stereoelectronic features, such as strong metal−C_{NHC} bonding, electronic/steric tunability via the wingtips, and excellent stability of the metal−NHC complexes toward heat, air, and moisture, are considered as the key to the observed success of this versatile class of ligands. To date, a number of successful methods have been developed to synthesize NHC complexes with different metal centers. One such common and easy strategy involves the use of a base (mild/strong, inorganic/organic) with the parent imidazolium salt, generating the free carbene *in situ* for efficient coordination with the metal (Scheme 1).[2] Although this method has been employed quite successfully with many imidazolium salts, the risk of slow hydrolysis and subsequent decomposition of the *in situ* generated free carbenes with traces of moisture should not be ignored (Scheme 1).[3] Interestingly, beyond this general caution, some unconventional and unique chemistry was observed very recently that can enhance the fundamental knowledge-base in this research area: specifically the diversity of metal−ligand bonding. For example, Braunstein et al. found hydrolytic cleavage of an uncoordinated imidazolium ring within an iridium-based complex without any further coordination of the resulting iminoformamide derivative (Scheme 1).[4] On the other hand, Peris et al. observed an unusual postcleavage bonding of a similar hydrolyzed, ring-opened fragment with two iridium centers where an additional transformation (decarbonylation of the formyl group) took place (Scheme 1).[5] In another surprising chemistry, a triazolyl ring was hydrolytically opened via a C−N bond-breaking process to result in a new type of tridentate ligand that was coordinated to iron and cobalt, as reported by Xue et al. (Scheme 1).[6] Herein, we present another unique and unprecedented bonding chemistry of an imidazolium ring after its hydrolytic ring-opening reaction induced by traces of moisture under basic conditions. This chemistry reveals that the pyridine-appended imidazolium salts generated a new type of (N,C,O) tridentate pincer complexes with palladium(II) that featured a vinylic C−H activation along with coordination from pyridine nitrogen and aldehyde oxygen donors (Scheme 1).

RESULTS AND DISCUSSION

The reaction of the imidazolium salts $[L_1H]PF_6$, $[L_2H]PF_6$, and $[L_3H]PF_6$, with 1.9 equiv of KO^{t}Bu in tetrahydrofuran at ambient temperature for a short time (∼20 min), followed by stirring with $Pd(COD)Cl_2$ for ∼1 h under the same conditions, and a suitable workup with a solvent mixture of acetonitrile−diethyl ether resulted in the air- and moisture-stable complexes **1**, **2**, and **3**, respectively, in good yields (Scheme 2).

The ^{1}H NMR spectra of all the complexes showed the presence of a single palladium complex with an indication of an unusual coordination environment as compared to an expected bidentate $N_{pyridine}$^$C_{carbene}$ mode of bonding of the ligand to the metal center.[7] Three characteristic peaks were observed at 9.23−10.23 ppm (doublet, J = 4.8−5.6 Hz) corresponding to the N*H* proton, at 7.87−8.03 ppm (singlet) corresponding to the C*H*O proton, and at 5.74−6.25 ppm (doublet, J = 5.5−5.8 Hz) corresponding to the vinylic Pd−C═C*H* proton, in

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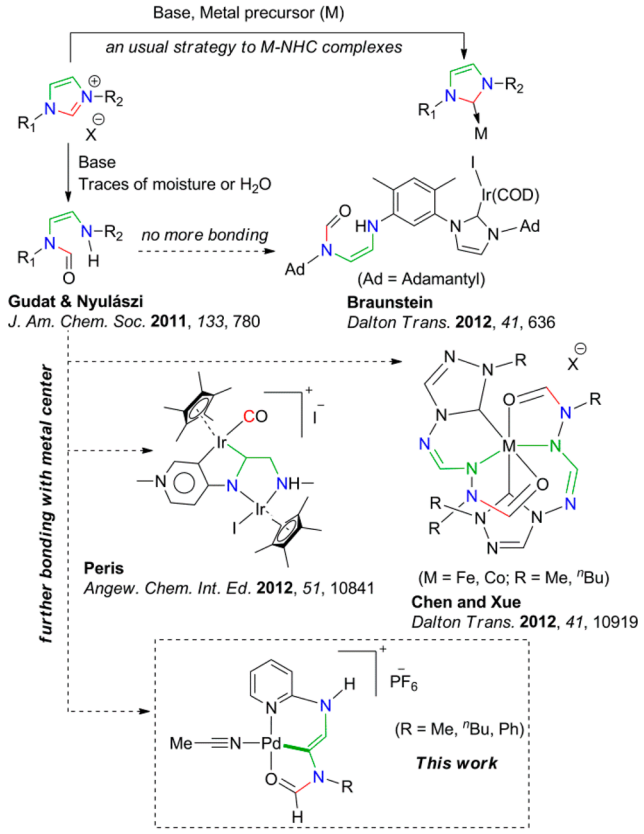
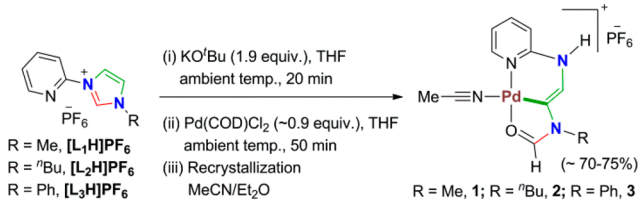
Scheme 1. Conventional and Unconventional Reactions of Imidazolium Salts



Scheme 2. Synthesis of the Complexes 1−3



addition to the expected peaks for the coordinated pyridine ring. 2D NMR spectroscopy of the complexes was performed to confirm the connections.

Thus, for complex **2**, the $^{1}H-^{1}H$ COSY spectrum (Figure 1A) suggested the correlation between the two doublet peaks at 10.17 and 6.25 ppm, whereas the singlet peak at 8.03 ppm did not show any correlation. The $^{13}C\{^{1}H\}$ NMR spectra of the complexes showed the CHO signal at ~167 ppm and a signal at

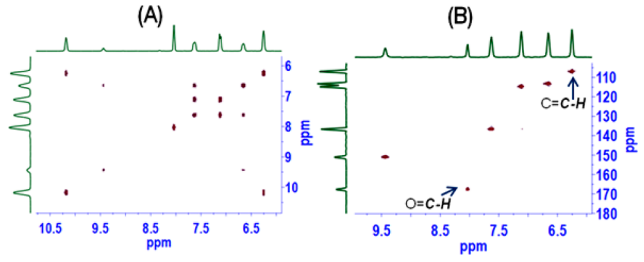


Figure 1. Expanded regions of $^{1}H-^{1}H$ COSY (A) and $^{1}H-^{13}C$ HSQC (B) NMR spectra of complex **2** (DMSO-d_6, 300 K).

~124.9−129.8 ppm assigned to the Pd-*C*= carbon atom. The vinylic C=*C*H carbon appeared at 106.4−108.9 ppm. The $^{1}H-^{13}C$ HSQC spectrum (Figure 1B) of **2** displayed the expected correlation, confirming the above assignment for the vinylic C=*CH* and the *CH*O carbons. In the infrared spectra of the complexes, we observed peaks at ~1620 and ~3430 cm^{-1} characteristic for −N-C(H)=*O* and −*N*−*H* groups, respectively. The positive ion high-resolution electrospray ionization mass spectra (HR-ESIMS) of all the complexes exhibited a major intense peak (at m/z = 281.9874 for **1**, 324.0342 for **2**, and 344.0038 for **3**) with the expected isotopic pattern assigned to the solvent-dissociated molecular ion $[M - CH_3CN]^+$.

To unambiguously confirm the above-suggested structural arrangement in these new complexes, a single-crystal X-ray diffraction study of complex **2** was accomplished. Figure 2

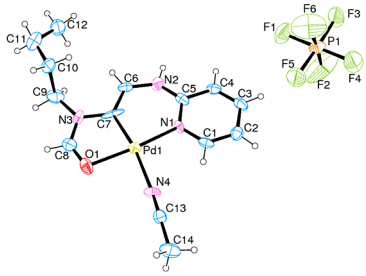


Figure 2. ORTEP diagram of complex **2** (30% ellipsoid probability level). Selected bond lengths (Å) and bond angles (deg): C7−Pd1 = 1.867(10), O1−Pd1 = 2.094(8), N1−Pd1 = 2.052(8), N4−Pd1 = 2.116(9), C5−N2 = 1.304(16), C6−N2 = 1.349(16), C6−C7 = 1.368(18), C7−N3 = 1.42(2), C8−N3 = 1.279(16), C8−O1 = 1.253(15), C7−Pd1−N1 = 92.1(6), C7−Pd1−O1 = 81.8(7), N1−Pd1−N4 = 97.5(4), O1−Pd1−N4 = 88.6(4). Only one molecule is shown here.

represents the ORTEP diagram illustrating the molecular structure of **2** along with important bond lengths and bond angles. The structure shows the formation of two uneven, dissimilar, fused palladacycles where one is six-membered and another is five-membered, leading to a distorted square planar geometry around the Pd(II) metal center with a tridentate (N,C,O) pincer type of bonding. The (N,C,O) donors resulting from a vinylic carbon, the pyridine nitrogen, and an aldehyde oxygen center established the *in situ* generation of a formamide-based new ligand motif possibly via base-promoted hydrolytic ring-opening of the imidazolium salts during the reaction. The Pd−C bond length, 1.867(10) Å, is unusually shorter than normal and abnormal Pd−$C_{carbene}$ bonds[8] or a Pd−$C_{vinylic}$ bond with electron-withdrawing C-substituents.[9] Due to the strong *trans* influence of the vinylic ligand, the Pd−NCMe bond (2.116(9) Å) is relatively longer in comparison to a similar type of bond in reported palladium complexes.[10]

The reactivity of NHC ligands displaying a ring-opening-type rearrangement around the metal-coordination sphere has been reported in the literature, but with preformed metal−NHC complexes, via organometallic migratory insertion of an adjacent anionic (typically methyl, phenyl) ligand to the coordinated C_{NHC}.[11] Although the exact mechanism in our case is not fully clear, at this juncture it is noteworthy to mention that we observed the formation of the above formamide-based free ligand when the imidazolium salts were reacted with KO^{t}Bu in THF. This indicates the plausibility of a prior ring-cleaving hydrolysis of the *in situ* generated free NHC by

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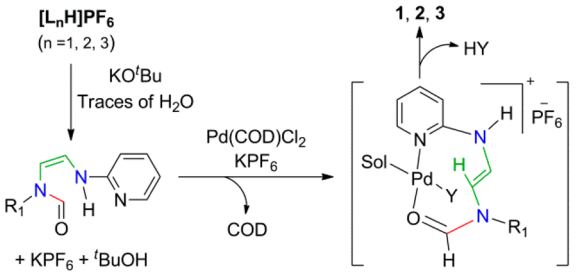
adventitious water before the reaction with the palladium precursor, leading to the desired complexes after coordination and subsequent C−H activation steps (Scheme 3).

Scheme 3. Plausible Mechanistic Steps



[R_1 = Me, ^{n}Bu, Ph; Y = O^{t}Bu or Cl; COD = 1,5-cyclooctadiene; Sol = Solvent]

CONCLUSIONS

In conclusion, the above result highlights an unusual but fascinating coordination chemistry emerging from the other side of the conventional transition metal−NHC research. The possibility of often-ignored hydrolytic ring-opening of NHC ligands has been realized with our new findings, resulting in an unprecedented type of palladium-pincer complexes.

EXPERIMENTAL SECTION

General Methods and Materials. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AVANCE III 400 and 500 MHz NMR spectrometers. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard (DMSO: δ = 2.50 ppm for ^{1}H spectra, 39.5 ppm for ^{13}C{^{1}H} spectra; CH_3COCH_3: δ = 2.05 ppm for ^{1}H spectra, 29.8 ppm for ^{13}C{^{1}H} spectra). All coupling constants (J) are expressed in hertz (Hz) and only given for ^{1}H−^{1}H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublet of doublets), m (multiplet). ESI mass spectrometry was performed on a Bruker microTOF QII spectrometer. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at 202 K. Structure was solved with direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 using SHELXL-97.[12] FTIR spectra were recorded on a PerkinElmer N3896 instrument. Solvents (Spectrochem; water content 0.1−0.5%), reagents (Aldrich), deuterated solvents (Aldrich), and $PdCl_2$ (Johnson Matthey) were obtained from commercial suppliers and used without further purification. [$Pd(COD)Cl_2$] was synthesized according to a reported procedure.[13]

Synthetic Procedures. *Typical Procedure for the Synthesis of [L_1H]PF_6, [L_2H]PF_6, and [L_3H]PF_6.* *N*-Methyl imidazole (0.82 g, 10 mmol), *N*-butyl imidazole (1.24 g, 10 mmol), or *N*-phenyl imidazole (0.57 g, 4.0 mmol) and 2-bromopyridine (equivalent amount) were mixed in a pressure tube and stirred for 60 h at 150−160 °C in neat conditions. After that the reaction mixture was cooled to room temperature, and diethyl ether was added to the oily material, which was washed with diethyl ether (3 × 20 mL) to remove unreacted starting materials. The oily compound was dissolved in a minimum volume of water; an aqueous NH_4PF_6 solution was added and stirred for 30 min, which resulted into a solid precipitate. The precipitate was filtered, washed with water and diethyl ether, and dried in high vacuum to afford the light brown desired product.

[L_1H]PF_6. Yield: 0.95 g (31%). The NMR chemical shift values for this compound were compared with reported values[14] and were found to match satisfactorily. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.02 (s, 1H, NC*H*N of Im), 8.65 (dd, J_{H-H} = 4.8, 0.9 Hz, 1H, pyr*H*), 8.49 (t, J_{H-H} = 1.8 Hz, 1H, Im*H*), 8.22 (dt, J_{H-H} = 8.1, 1.8 Hz, 1H, pyr*H*), 8.00 (d, J_{H-H} = 8.2 Hz, 1H, pyr*H*), 7.95 (t, J_{H-H} = 1.6 Hz, 1H, Im*H*), 7.64 (dd, J_{H-H} = 7.1, 4.9 Hz, 1H, pyr*H*), 3.97 (s, 3H, NCH_3) ppm. HRMS (ESI, positive ion): m/z 160.0880 (calcd for $[C_9H_{12}N_3]^+$ 160.0869).

[L_2H]PF_6. Yield: 1.5 g (44%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.08 (t, J_{H-H} = 1.6 Hz, 1H, NC*H*N of Im), 8.65 (ddd, J_{H-H} = 4.8, 1.8, 0.8 Hz, 1H, pyr*H*), 8.53 (t, J_{H-H} = 1.9 Hz, 1H, Im*H*), 8.22 (ddd, J_{H-H} = 8.2, 7.5, 1.8 Hz, 1H, pyr*H*), 8.05 (m, 1H, Im*H*), 8.01 (dt, J_{H-H} = 8.3, 0.8 Hz, 1H, pyr*H*), 7.64 (ddd, J_{H-H} = 7.5, 4.8, 0.8 Hz, 1H, pyr*H*), 4.29 (t, J_{H-H} = 7.2 Hz, 2H,CH_2 of ^{n}Bu), 1.88 (m, 2H, CH_2 of ^{n}Bu), 1.32 (m, 2H, CH_2 of ^{n}Bu), 0.93 (t, J_{H-H} = 7.4 Hz, 3H, CH_3 of ^{n}Bu) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 149.2 (d), 146.4, 140.5, 135.1 (d), 125.2, 123.5, 119.3, 114.2, 49.3, 31.1, 18 8, 13.3 ppm. HRMS (ESI, positive ion): m/z 202.1355 (calcd for $[C_{12}H_{16}N_3]^+$ 202.1339).

[L_3H]PF_6. Yield: 0.64 g (43%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.59 (s, 1H, NC*H*N of Im), 8.75 (m, 1H, Im*H*), 8.71 (dd, J_{H-H} = 4.7, 0.9 Hz, 1H), 8.57 (m, 1H, Im*H*), 8.28 (dt, J = 8.1, 1.7 Hz, 1H), 8.16 (d, J_{H-H} = 8.2 Hz, 1H), 7.94 (d, J_{H-H} = 7.9 Hz, 2H), 7.69 (m, 3H), 7.65 (m, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 149.3 (d), 146.3, 140.6, 134.7, 134.3 (d), 130.2, 130.2, 125.5, 122.3, 120.1, 119.9, 114.7 ppm. The ^{13}C{^{1}H} NMR chemical shift values for this compound matched satisfactorily with the reported values for the bromide salt of the compound.[15] HRMS (ESI, positive ion): m/z 222.1027 (calcd for $[C_{14}H_{12}N_3]^+$ 222.1026).

Typical Procedure for the Synthesis of Complexes 1, 2, and 3. [L_1H]PF_6 (38.1 mg, 0.125 mmol), [L_2H]PF_6 (43.4 mg, 0.125 mmol), or [L_3H]PF_6 (45.9 mg, 0.125 mmol) and KO^{t}Bu (26.6 mg, 0.24 mmol) were mixed in a Schlenk tube under a stream of nitrogen gas in a Schlenk line; 5 mL of THF was added and the mixture was stirred under a nitrogen atmosphere at ambient temperature for 20 min. $Pd(COD)Cl_2$ (31.4 mg, 0.11 mmol) was added into the solution; an additional 2 mL of THF was added and the reaction mixture was again stirred at the same conditions for 50 min. After that 3 mL of CH_3CN was added to the mixture, and the resulting yellow-red solution was filtered. The volume of the solvent was reduced to 0.5−1 mL. Diethyl ether was added to precipitate out a yellow solid, which was filtered, washed thoroughly with diethyl ether, and dried under high vacuum to afford the desired product. The product was purified by recrystallization via ether diffusion into a CH_3CN solution of the compound.

Complex 1. Yield: 32 mg (~70%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.23 (d, J_{H-H} = 4.8 Hz, 1H, N-H), 9.36 (s, br [note: an H/D exchange was observed for this proton with the deuterated solvent, which sometimes leads to decreased peak integration], 1H, pyrH), 7.98 (s, 1H, CHO), 7.64 (m, 1H, pyrH), 7.12 (d, J_{H-H} = 8.5 Hz, 1H, pyrH), 6.67 (t, J_{H-H} = 6.3 Hz, 1H, pyr), 6.19 (d, J_{H-H} = 5.8 Hz, 1H, Pd-C=CH), 3.40 (s, 3H, NCH_3), 2.07 (s, CH_3CN) ppm. ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 167.4 (CHO), 150.8 (pyrC), 144.8 (pyrC), 136.3 (pyrC), 126.4 (Pd−C), 114.5 (pyrC), 113.0 (pyrC), 106.4 (Pd−C=CH), 30.6 (NCH_3), ppm. HRMS (ESI, positive ion): m/z 281.9874 (calcd for $[C_9H_{10}N_3OPd]^+$ 281.9857). Anal. Found: C, 28.83; H, 3.17; N, 12.30. Calcd for $C_{11}H_{13}N_4OPF_6Pd{\cdot}0.5CH_3CN{\cdot}H_2O$: C, 28.43; H, 3.28; N, 12.44.

Complex 2. Yield: 39 mg (~75%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.17 (d{sometime s}, J_{H-H} = 5.6 Hz, 1H, N-H), 9.43 (d, {ill-defined} [note: an H/D exchange was observed for this proton with the deuterated solvent, which sometimes leads to decreased peak integration], 1H, pyrH), 8.03 (s, 1H, CHO), 7.62 (m, 1H, pyrH), 7.11 (d, J_{H-H} = 8.5 Hz, 1H, pyrH), 6.65 (m, 1H, pyrH), 6.25 (d, J_{H-H} = 5.8 Hz, 1H, Pd-C=CH), 3.90 (t, J_{H-H} = 7.0 Hz, 2H, CH_2 of ^{n}Bu), 2.07 (s, CH_3CN), 1.64 (m, 2H, CH_2 of ^{n}Bu), 1.26 (m, 2H, CH_2 of ^{n}Bu), 0.90 (t, J_{H-H} = 7.3 Hz, 3H, CH_3 of ^{n}Bu) ppm. ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 167.3 (CHO), 150.7 (pyrC), 144.7 (pyrC), 136.3 (pyrC), 124.9 (Pd-C), 118.1 (CH_3CN), 114.5 (pyrC), 113.0 (pyrC), 106.6 (Pd-C=CH), 43.3 (^{n}BuC), 29.7 (^{n}BuC), 19.2 (^{n}BuC), 13.5 (^{n}BuC), 1.1 (CH_3CN) ppm. HRMS (ESI, positive ion): m/z 324.0342 (calcd for $[C_{12}H_{16}N_3OPd]^+$ 324.0328). Anal. Found: C, 33.06; H,

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3.82; N, 11.29. Calcd for $C_{14}H_{19}N_4OPF_6Pd$: C, 32.94; H, 3.75; N, 10.98.

Complex **3**. Yield: 40 mg (~71%). ^{1}H NMR (500 MHz, acetone-d_6): δ 9.79 (d, J_{H-H} = 5.5 Hz, 1H, Pyr*H*), 9.23 (d {ill-defined}, 1H, N-*H*), 7.87 (s, 1H, C*H*O), 7.58 (m, 6H, pyr*H* and Ph*H*), 7.13 (d, J_{H-H} = 8.5 Hz, 1H, pyr*H*), 6.64 (t, J_{H-H} = 6.4 Hz, 1H, pyr*H*), 5.74 (d, J_{H-H} = 5.5 Hz, 1H, Pd-C=C*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ 167.6 (*C*HO), 152.9 (pyr*C*), 146.3 (pyr*C*), 137.3 (pyr*C*), 134.8 (Ph*C*), 13o.7 (Ph*C*), 130.7 (Ph*C*), 129.8 (Pd-*C*), 128.6 (Ph*C*), 115.3 (pyr*C*), 114.0 (pyr*C*), 108.9 (Pd-C=*C*H) ppm. HRMS (ESI, positive ion): *m*/*z* 344.0038 (calcd for $[C_{14}H_{12}N_3OPd]^+$ 344.0015). Anal. Found: C, 37.19; H, 3.14; N, 11.69. Calcd for $C_{16}H_{15}N_4OPF_6Pd\cdot 0.5CH_3CN$: C, 37.06; H, 3.02; N, 11.45.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C{^{1}H}, ^{1}H−^{1}H COSY, and ^{1}H−^{13}C HSQC NMR spectra; ESI-HR mass spectra; FT-IR spectra; CIF file of complex **2** (CCDC 995442). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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