Inorganic Chemistry

Note

Unique 2:1 Complex with a *trans*-Chelating Bis-Pyridine Ligand

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Introduction

The chelation of metal centers by polypyridine ligands is believed to occur by a stepwise mechanism, beginning with coordination of the most sterically accessible pyridine moiety.[1] While this initial coordination may occur at any of the available binding sites on the metal center, subsequent coordination steps are limited to those metal sites with orientations which complement the binding geometry of the ligand. For example, while the initial coordination of Pd(II) by one of the pyridine moieties of 2,2′-bipyridine (bpy) may occur on any of the four available sites in the square planar coordination sphere of the metal, the second coordination is limited by the geometry of the ligand to either of the two sites which are 90° (*cis*) to the site of initial binding. Coordination to the site which is 180° (*trans*) to the site of initial binding is precluded. In our continuing search for ligands with unusual metal binding properties, we considered analogues of bpy capable of coordinating to *trans* metal binding sites. Thus, a ligand consisting of two 2-pyridyl moieties joined by a well organized tether that orients the nitrogens at an appropriate distance for chelation to *trans* binding sites was envisioned. Ligand **1**, with a 1,2-dialkynylbenzene tether, affords exactly the required geometry.

Stang and co-workers have used this same tether to connect two 4-pyridyl groups orienting them at a 60° angle, thus affording interesting helical and syndiotactic zinc-based coordination polymers.[2] These same authors have also examined a 2,5-dialkynylfuran tether while the analogous thiophene and 1,4-dialkynylbenzene have been utilized by Sun and Lees.[3] When the 1,2-dialkynylbenzene tether is used to link two diphenyl phosphine moieties, *cis*-ligation is still preferred, and a tetrahedal 2:1 complex is reported for Pd(0).[4] After our completion of this work, a report has appeared on the synthesis of ligand **1** and its PdCl$_2$ complex.[5,6]

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(3) Sun, S.-S.; Lees, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 8956.

Syntheses

Ligand **1** was synthesized in a single step by a Sonogashira cross-coupling reaction[7] between 1,2-diiodobenzene and 2-ethynylpyridine catalyzed by tris(dibenzylideneacetone)-dipalladium(0). The ligand was characterized by its ^{1}H and ^{13}C NMR spectra. The H6′ proton adjacent to nitrogen gave a characteristic downfield doublet ($J = 4.8$ Hz) at 8.64 ppm. The remaining three pyridyl protons could be identified by their 2D COSY cross-peaks while H3(6) and H4(5) appeared at 7.65 and 7.37 ppm, respectively. The two alkynyl carbons were observed at 88.0 and 93.3 ppm.
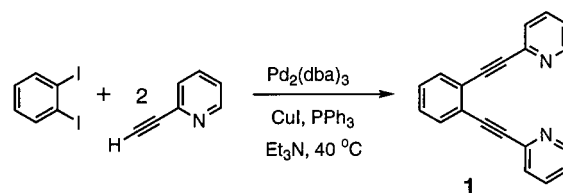
The *trans*-chelated complex [Pd(**1**)Cl$_2$] was prepared in 61% yield by treating **1** with *trans*-bis(acetonitrile)palladium chloride in CH$_2$Cl$_2$ at room temperature. The *trans*-chelated 2:1 complex [Pd(**1**)$_2$][BF$_4$]$_2$ was prepared in 70% yield by treating 2 equiv of **1** with tetrakis(acetonitrile)palladium(II) tetrafluoroborate in CH$_2$Cl$_2$−CH$_3$CN (1:1) at room temperature.
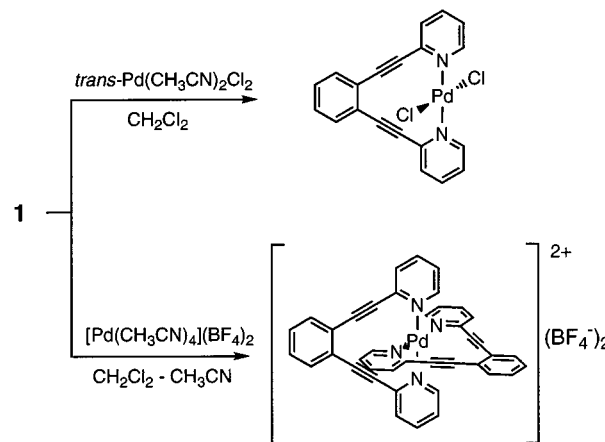
The ligand **1** and both of its Pd(II) complexes show similar ^{1}H NMR spectra exhibiting six aromatic resonances of equal
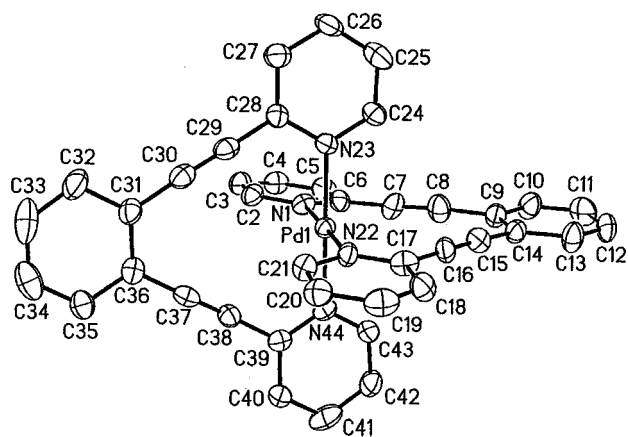
Figure 1. ORTEP drawing of the dication of [Pd(**1**)$_2$](BF$_4$)$_2$ showing the atom numbering scheme.

intensity. The H6′ peak is shifted downfield to 8.88 ppm in [Pd(**1**)Cl$_2$] because of complexation-induced charge depletion of the pyridine ring. This deshielding effect is magnified in the 2:1 complex where H6′ is now oriented toward the deshielding cones of the alkynyl moieties of the orthogonal ligand and appears at 9.33 ppm (CDCl$_3$, δ 9.72 in acetone-d_6).

Properties

Suitable crystals of both complexes were analyzed by X-ray crystallography, and the results for [Pd(**1**)Cl$_2$] were in excellent accord with the values reported by Bosch and Barnes.[5] For this complex, the Cl—Pd—Cl angles are almost exactly linear, the ligand is planar, and the Pd—Cl bonds are orthogonal to this plane. Interestingly, the molecule is almost perfectly triangular with the C—C≡C—C (4.05 Å) and N—Pd—N (4.02 Å) distances being about equal. The molecule closely resembles the shape of tribenzo-1,5,9-cyclododecatriyne.[8]

An ORTEP drawing of the [Pd(**1**)$_2$]$^{2+}$ cation is shown in Figure 1, and some pertinent geometric features are summarized in Table 1. The Pd—N bonds lie in the range 2.02–2.06 Å, slightly longer than the 2.01 Å found for [Pd(**1**)Cl$_2$], and similar to the 2.01–2.04 Å bond lengths observed for the distal pyridines of [Pd(tpy)Cl](Cl) dihydrate (tpy = 2,2′;6′,2″-terpyridine).[9] The relatively unstable material[10] [Pd-(pyridine)$_4$](I$_3$)$_2$ has been isolated in two crystalline forms, triclinic and orthorhombic, and both forms show Pd—N bonds in the range 2.01–2.03 Å.[11]
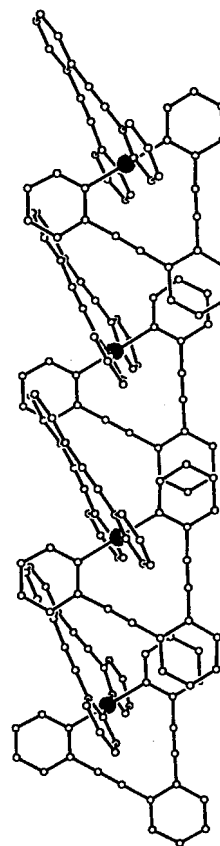
Figure 2. Partial drawing of the unit cell illustrating two pairs of [Pd-(**1**)$_2$](BF$_4$)$_2$ molecules. The anions and water of crystallization have been omitted for clarity.

**Table 1.** Selected Structural Data for [Pd(**1**)$_2$](BF$_4$)$_2$

Bond Lengths (Å)	
N1—Pd	2.050(7)
N22—Pd	2.024(7)
N23—Pd	2.038(6)
N44—Pd	2.057(7)
C7—C8	1.198(11)
C15—C16	1.186(10)

Bond Angles (deg)	
N1—Pd—N22	178.8(3)
N23—Pd—N44	179.1(3)
N1—Pd—N23	90.0(3)
N22—Pd—N23	90.9(2)
Pd—N1—C6—C7	8.1(10)
C8—C9—C14—C15	2.3(14)
C16—C17—N22—Pd	1.6(10)

The ligands in [Pd(**1**)$_2$]$^{2+}$ are quite planar, with N—Pd—N angles essentially linear (179°), and the ligand planes orthogonal to one another as evidenced by interligand N—Pd—N angles of 90° and 91°. A unique feature of the *trans*-chelating situation is that, unlike [Pd(bpy)$_2$]$^{2+}$, the planes of all four bound pyridine rings are orthogonal to the coordination plane. Furthermore, the dialkynylbenzene tethers "cap" the apical sites of the complex and thus hinder intermetallic interactions. The unit cell contains two independent molecules, and Figure 2 depicts the arrangement of a pair of these two molecules. The orthogonal arrangement of the two ligands considerably inhibits the sort of columnar

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(6) During the review of this manuscript, two separate reports have appeared involving 1:1 Cu complexes of ligands closely related to **1**: (a) Fiscus, J. E.; Shotwell, S.; Layland, R. C.; Smith, M. D.; zur Loye, H.-C.; Bunz, U. H. F. *Chem. Commun.* **2001**, 2674. (b) Kawano, T.; Kuwana, J.; Shinomaru, T.; Du, C.-X.; Ueda, I. *Chem. Lett.* **2001**, 1230.
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(11) Tebbe, K.-F.; Gräfe-Kavoosian, A.; Freckmann, B. *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 999.
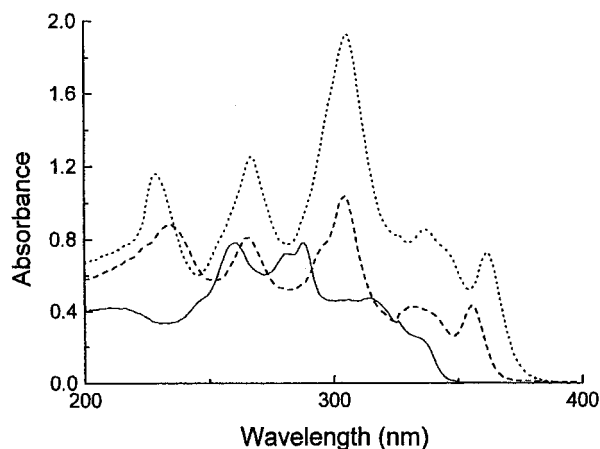
Figure 3. Electronic absorption spectra of **1** (—), [Pd(**1**)Cl$_2$] (- - -), and [Pd(**1**)$_2$](BF$_4$)$_2$ (•••); 2.5 × 10^{-5} M in CH$_2$Cl$_2$ ([Pd(**1**)$_2$](BF$_4$)$_2$ contains 5% MeOH).

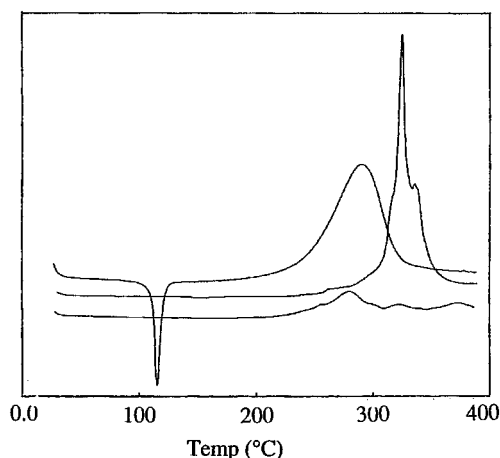**Table 2.** Electronic Absorption and Emission Data for **1** and Its Pd(II) Complexes[a]

compound	absorption, λ_{max} (nm)(ϵ)	emission, λ_{max} (nm)
1	332(sh, 10480), 315(19040), 288(31280), 280(28840), 260(31330), 247(sh 18800), 216(16860)	390 (strong)
[Pd(**1**)Cl$_2$]	355(17230), 331(17080), 304(41600), 295(sh, 30170), 265(32520), 234(35300)	422 (weak)
[Pd(**1**)$_2$](BF$_4$)$_2$[b]	361(29000), 346(29200), 337(34160), 326(33300), 305(77000), 267(50300), 228(46450)	436 (weak)

[a] 2.5 × 10^{-5} M CH$_2$Cl$_2$ at 25 °C. [b] Contains 5% CH$_3$OH.

stacking observed for the [Ag(**1**)](OTf) complex.[5] The closest approach of one molecule to the next is promoted by a π-stacking interaction between a pyridine ring and the central benzo ring, with a mean interplanar distance of 3.36 Å. The palladium cations are far apart from one another, with an average distance of approximately 9.0 Å. Compared to many other similar square planar Pd(II) complexes, the solubilty of [Pd(**1**)$_2$]$^{2+}$ is quite good, being soluble in acetonitrile, acetone, methanol, DMF, and DMSO. It is also slightly soluble in CH$_2$Cl$_2$ and CHCl$_3$.

The complex [Pd(**1**)$_2$]$^{2+}$ exhibits a much better organized square planar geometry than the analogous *cis*-chelated complex [Pd(bpy)$_2$]$^{2+}$. For the latter system, interligand steric interactions involving H6 and H6′ cause a distortion toward tetrahedral geometry resulting in angle of about 24.3° between the mean planes of the two bpys.[12] The inter- and intraligand N−Pd−N angles (102.2° and 80.0°, respectively) also deviate considerably from the square planar ideal of 90°.

The electronic absorption spectra for ligand **1** and both Pd complexes are shown in Figure 3, and the data are collected in Table 2. The ligand shows seven overlapping bands in the π−π* region from 240 to 350 nm. Comparison with the absorption spectrum for 2-phenylpyridine which shows bands at 247 and 275 nm clearly identifies the three most intense bands as π−π* transitions associated with the benzene and pyridine rings. The longer wavelength band at

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Figure 4. DSC traces for **1** (top), [Pd(**1**)Cl$_2$] (middle), and [Pd(**1**)$_2$](BF$_4$)$_2$ (bottom).

315 nm is thus assigned to the alkynyl π−π* absorption. The two complexes show very similar absorption spectra with three well resolved ligand-based bands appearing at 228−234, 265−267, and 304−305 nm. The intensity of the [Pd-(**1**)$_2$]$^{2+}$ complex is nearly twice that of the [Pd(**1**)Cl$_2$] complex. Both complexes exhibit a distinct long wavelength band, appearing at 355 nm for [Pd(**1**)Cl$_2$] and 361 nm for [Pd(**1**)$_2$]$^{2+}$. These bands are tentatively assigned to a metal-to-ligand charge-transfer transition which has also been observed for [Pd(bpy)Cl$_2$].[13] The free ligand shows a strong blue luminescence at 390 nm. The two complexes are only slightly emissive. When solutions having the same absorbance at 355 nm are excited at this wavelength, the [Pd(**1**)-Cl$_2$] complex emits weakly at 422 nm while the [Pd(**1**)$_2$]$^{2+}$ complex shows an emission about 40% as intense at 436 nm.

The tether which links the two pyridine rings in ligand **1** is an enediyne moiety, and such species are well-known to undergo the thermally induced Bergman cyclization to form benzenoid products.[14] There has been considerable recent interest in functionalizing such species, especially through metal complexation, in an attempt to mediate the cyclization process.[15] To probe the possible thermal reactivity of our systems, we examined their behavior by differential scanning calorimetry (DSC), and the results are illustrated in Figure 4. The ligand shows a melting endotherm which peaks at about 114 °C followed by a broad exotherm which peaks at 289 °C. The smooth curve implies a single reaction is occurring, and subsequent cooling and reheating did not evidence any further activity indicating an irreversible and complete reaction. Free ligand **1** was combined with 1,4-

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cyclohexadiene as a hydrogen donor and heated under a variety of conditions in attempts to provide the cyclization product, but no identifiable material was obtained. Heating in the absence of a hydrogen donor led to similar results. Others have made the same observation upon heating a similar enediyne in the absence of metal mediation.[15d]

The [Pd(**1**)Cl$_2$] complex shows a more narrow exotherm which occurs at higher temperature, peaking at 333 °C. The main band shows at least three components which could correspond to the stepwise decomplexation of the two pyridines, followed by thermolysis of the ligand. The [Pd-(**1**)$_2$]$^{2+}$ complex shows far less thermal activity with only small peaks in evidence, corresponding approximately to peaks observed for **1** and its dichloro complex. As expected, metal complexation, which holds the C7 and C16 alkynyl carbons about 4.0 Å apart, hinders direct Bergman cyclization because of the *trans*-chelation geometry where a *cis*-chelated system would be expected to cyclize more readily. Furthermore, the 2:1 complex appears to be thermally stable, while in solution we observed this same complex to be fairly labile toward attack by acetonitrile. Further chemistry of **1** as well as other *trans*-chelating ligands are under examination.

Experimental Section

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Absorption spectra were recorded with a Perkin-Elmer λ-3B spectrophotometer. Luminescence studies employed 10^{-5} M solutions at room temperature using a Perkin-Elmer LS-50B spectrofluorimeter. Absorption and emission maxima were reproducible to within ±2 nm. NMR spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. All commercial reagents were used as received.

1,2-Bis(2′-pyridylethynyl)benzene (1). A mixture of 1,2-di-iodobenzene (236 mg, 0.72 mmol), 2-ethynylpyridine (147 mg, 1.43 mmol), Pd$_2$(dba)$_3$ (28 mg, 0.03 mmol), triphenylphosphine (37 mg, 0.141 mmol), and CuI (6 mg, 0.0315 mmol) in triethylamine (7 mL) was stirred under Ar at 40 °C for 65 h. After evaporation of solvent, the oily residue was dissolved in CH$_2$Cl$_2$ (30 mL) and washed twice with water. The organic layer was dried with MgSO$_4$ and filtered, and the solvent was evaporated. The residue was purified by chromatography on silica gel eluting with CH$_2$Cl$_2$ and CH$_2$Cl$_2$−MeOH (33:1). The bright fluorescent fraction was collected and further purified by a second chromatography on silica gel eluting with EtOAc−petroleum ether (1:1). Compound **1** was obtained as a yellow solid (123 mg, 61%): mp 113−115 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.64 (d, J = 4.8 Hz, 2H, H6′), 7.69 (m, 4H, H3′, H4′), 7.65 (dd, J = 3.3, 6.0 Hz, 2H, H3), 7.37 (dd, J = 3.3, 6.0 Hz, 2H, H4), 7.25 (m, 2H, H5′); ^{13}C NMR (CDCl$_3$) δ 150.3, 143.8, 136.2, 132.5, 128.9, 127.9, 125.7, 123.1, 93.3, 88.0.

Dichloro-(1,2-bis(2′-pyridylethynyl)benzene)palladium. *Trans*-bis(acetonitrile)palladium chloride (39 mg, 0.15 mmol) in CH$_2$Cl$_2$ (25 mL) was added to a stirred solution of **1** (30 mg, 0.11 mmol) in CH$_2$Cl$_2$ (20 mL) under Ar. Stirring at 25 °C was continued for 10 min. After filtration, the solvent was evaporated, and the residue was purified by chromatography on silica gel eluting with CH$_2$-Cl$_2$−MeOH (100:1). Slow evaporation of solvent from the early fractions afforded **2** as single crystals (30 mg, 61%), which were suitable for X-ray analysis: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.88 (dd, J = 1.5, 6.3 Hz, 2H; pyridyl H6′), 7.77 (m, 4H), 7.65 (dd, J = 1.5, 8.7 Hz, 2H), 7.51 (dd, J = 3.3, 6.0 Hz, 2H), 7.35 (m, 2H).

Table 3. Data Collection and Processing Parameters for [Pd(**1**)$_2$](BF$_4$)$_2$

space group	*Ia* (monoclinic)
cell constants	$a = 22.8098(12)$ Å
	$b = 12.1354(6)$ Å
	$c = 28.9445(15)$ Å
	$\alpha = 90.00°$
	$\beta = 112.105(1)°$
	$\gamma = 90.00°$
	$V = 7423.1(7)$ Å^3
molecular formula	C$_{40}$H$_{24}$B$_2$F$_8$N$_4$Pd·1.5H$_2$O
fw	867.68
formula units per cell	$Z = 8$
density	$\rho = 1.553$ g cm^{-3}
abs coeff	$\mu = 5.81$ cm^{-1}
T	$T = -50$ °C
R1 $= \sum||F_o| - |F_c||/\sum|F_o|$	0.0366
wR2 $= [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$	0.0953
weights	$w = [\sigma(F_o^2) + (0.0637P)^2 + (1.805P)]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$

Bis(1,2-bis(2′-pyridylethynyl)benzene)palladium tetrafluoroborate. Tetrakis(acetonitrile)palladium tetrafluoroborate (62 mg, 0.14 mmol) in CH$_3$CN (10 mL) was added to a solution of **1** (80 mg, 0.28 mmol) in CH$_2$Cl$_2$−CH$_3$CN (1:1, 40 mL) under Ar. The solution was stirred at 25 °C for 10 min. After filtration, the solvent was evaporated, and the residue was purified by chromatography on silica gel eluting with CH$_2$Cl$_2$−MeOH (19:1) to afford **3** as a white solid (70 mg, 60%): ^{1}H NMR (acetone-d_6, 300 MHz) δ 9.72 (d, J = 5.4 Hz, 4H; pyridyl H6′), 8.19 (dd, J = 3.3, 5.7 Hz, 4H), 8.13 (m, 8H), 7.92 (dd, J = 3.3, 6.0 Hz, 4H), 7.75 (m, 4H); MALDI-TOF MS (m/z) 840 (M$^+$), 839 (M$^+$ − 1). Slow evaporation of a CH$_2$Cl$_2$−MeOH solution of **3** afforded single crystals suitable for X-ray analysis.

X-ray Analysis of [Pd(1)$_2$](BF$_4$)$_2$. All measurements were made with a Siemens SMART platform diffractometer equipped with a 1K CCD area detector. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 25 s/frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction on I was <1%. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A ψ scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 5371 reflections having $I > 10\sigma(I)$, and these, along with other information pertinent to data collection and refinement, are listed in Table 3. The Laue symmetry was determined to be $2/m$, and from the systematic absences noted, the space group was shown to be either *Ia* or *I*2/*a*. The asymmetric unit consists of two independent cations, four anions, and three waters of solvation. Three of the anions and two of the waters are each disordered over two slightly different positions, and ideal rigid body refinement was used for the affected anions. After applying the proper symmetry operation, the two cations are related by an inversion center; however, the anions and solvent waters do not conform to this center. Because of the extreme disorder of most of the anions and waters, this is a bit difficult to determine; however, it was finally decided that the noncentrosymmetric space group *Ia* is the correct choice, while noting that the two independent cations are related by a pseudoinversion center.

Thermal Analysis. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7. Samples were encapsulated in aluminum pans. During measurement, the DSC cell was flushed with nitrogen. The temperature range was 30−400 °C, and the

heating rate was 10 °C/min. Sample weight varied between 1 and 5 mg. Analysis was performed in duplicate, showing good agreement.

Supporting Information Available: X-ray crystallographic file for $[[Pd(1)_2](BF_4)_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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