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Palladium Complexes Containing Large Fused Aromatic N−N Ligands as Efficient Catalysts for the CO/Styrene Copolymerization

Sheba D. Bergman,[†] Israel Goldberg,[†] Carla Carfagna,[‡] Luca Mosca,[‡] Moshe Kol,*,[†] and Barbara Milani*,[§]

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, 69978, Israel, Istituto di Scienze Chimiche, Università di Urbino, P.zza Risorgimento 6, 61029 Urbino, Italy, and Dipartimento di Scienze Chimiche, Università di Trieste, Via Licio Giorgieri 1, 34127 Trieste, Italy

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Bis(homoleptic) palladium(II) complexes of the extended aromatic ligands eilatin ($[Pd(eil)_2][BF_4]_2$ (**1a**)) and dipyridophenazine ($[Pd(dppz)_2][BF_4]_2$ (**2a**), $[Pd(dppz)_2][PF_6]_2$ (**2b**)) were synthesized and employed in the copolymerization of carbon monoxide and styrene. The eilatin ligand in the complex $[Pd(eil)_2]$-$[BF_4]_2$ is bound via its less hindered "head" coordination site. The X-ray structure of **2b** was solved and indicated a highly twisted square planar geometry around the palladium center and the presence of π-stacking interactions of two types. All complexes were found to be active catalysts for the synthesis of the syndiotactic CO/styrene polyketone, their activity exceeding that of the parent complex $[Pd(phen)_2]$-$[BF_4]_2$.

Introduction

The alternating copolymerization of terminal alkenes with carbon monoxide to produce polyketones has been extensively investigated over the past decades.[1] Despite polyketones being withdrawn from the market, the research in this field is still flourishing at both academic[2] and industrial levels.[3]

This copolymerization reaction is homogeneously catalyzed by cationic Pd(II) complexes bearing phophorus- and/or nitrogen-donor chelating ligands (P−P or N−N ligands), in the presence of different cocatalysts (e.g., Brønsted acids) and/or coreagents (usually quinones).[1] In particular, it has been reported that dicationic, bischelated Pd(II) complexes of general formula $[Pd(N{-}N)_2][PF_6]_2$ are efficient precatalysts for the perfectly alternating copolymerization of CO and vinyl arenes, such as styrene and 4-methylstyrene.[4] When the reaction is carried out in 2,2,2-trifluoroethanol (TFE) (instead of methanol) and the N−N ligand belongs to the homologous series of 1,10-phenanthroline (phen), the resulting catalyst is highly active and long-lived, yielding the corresponding syndiotactic polyketone in high yield and with high molecular weight and narrow molecular weight distribution without requiring the addition of any coreagent or cocatalyst.

The proposed mechanism for the catalyst generation from the bischelated precursor includes two possible pathways (Scheme 1):[4b] (i) reaction of the precursor with trifluoroethanol and CO to yield the trifluorocarboalkoxy species (top); (ii) reaction of the precursor with traces of water and CO, leading to the Pd−H intermediate (bottom). These steps require either the prior detachment of at least one Pd−N bond or the complete dissociation of one of the two N−N molecules bound to palladium. Both of them produce a proton, whose concentration can be controlled by the equilibrium reaction with the free ligand. On the basis of these considerations, we decided to study ligands that bear additional basic nitrogen functions that might regulate proton concentration more efficiently than phenanthrolines. In addition, a large fused aromatic N−N ligand might expedite the insertion of the monomers by hydrophobic effect and, possibly, by π-stacking with the vinyl arene. Ligands featuring these requirements are eilatin (eilatin = eil, **1**)[5] and dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz, **2**)[6] (Scheme 2).

Dppz can be viewed electronically as a phen unit attached to an azine unit.[7] Eilatin combines several properties that make it

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* Corresponding authors. E-mail: moshekol@post.tau.ac.il; milani@dsch.units.it.

[†] Tel Aviv University.

[‡] Università di Urbino.

[§] Università di Trieste.

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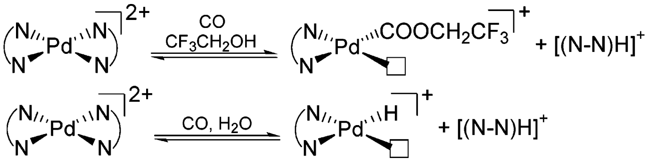
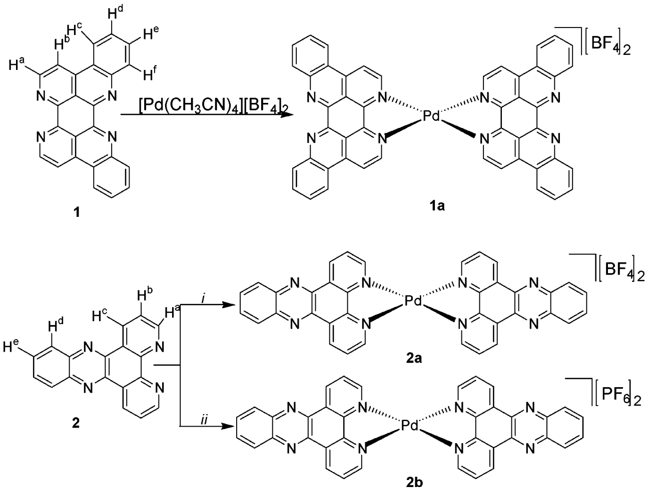
Scheme 1. Top: Carbotrifluoroethoxy Pathway. Bottom: Hydride Pathway



Scheme 2. Synthetic Scheme for Complexes 1a, 2a, and 2b, Together with the Labeling Scheme of Eilatin 1 and dppz 2



i. $[Pd(CH_3CN)_4][BF_4]_2$

ii. $[Pd(OAc)_2]$ + CF_3COOH; KPF_6

a unique ligand for late transition metals: two distinct binding sites, a bpy-type “head” and a biq-type “tail” (biq = 2,2′-biquinoline); a large, planar fused-aromatic surface of C_{2v} symmetry; and a low-lying π* orbital.[5,8] Up to now, the study of its coordination chemistry has been limited to group 8 metals.[9−11] In this paper we describe the synthesis and characterization of the dicationic, bischelated Pd(II) complexes with eilatin or dppz, $[Pd(eil)_2][BF_4]_2$ (**1a**), $[Pd(dppz)_2][BF_4]_2$ (**2a**), and $[Pd(dppz)_2][PF_6]_2$ (**2b**), together with their catalytic behavior in the CO/styrene copolymerization reaction.

Results and Discussion

Synthesis and Characterization of the Palladium Complexes 1a, 2a, and 2b. Complexes $[Pd(eil)_2][BF_4]_2$, **1a**, and $[Pd(dppz)_2][BF_4]_2$, **2a**, were easily synthesized by addition of 2 equiv of the coresponding ligand to an acetonitrile/dichloromethane solution of $[Pd(CH_3CN)_4][BF_4]_2$ (Scheme 2). Complex **1a** precipitated from the reaction mixture as a red solid, while complex **2a** was an off-white solid.

Complex $[Pd(dppz)_2][PF_6]_2$, **2b**, was obtained by a modification of the published procedure.[4a] The dppz ligand was initially reacted with $[Pd(OAc)_2]$ and CF_3COOH in methanol to give $[Pd(CF_3COO)_2(dppz)]$. This compound was subsequently reacted with a second equivalent of dppz and KPF_6 in methanol, yielding **2b** as an off-white solid.

Single crystals of **2b**, suitable for X-ray analysis, were obtained by recrystallization from the solvent mixture DMF/methanol/diethyl ether at room temperature (Figure 1).

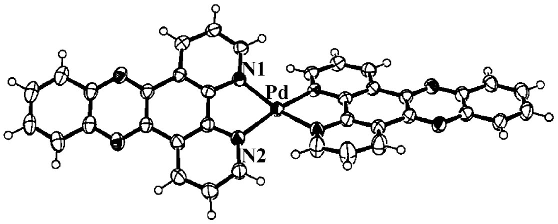


Figure 1. ORTEP view and partial atom numbering of **2b**; counterions and solvent molecules omitted for clarity. Coordination bond lengths (Å) and angles (deg): Pd−N1, 2.028(4); Pd−N2, 2.037(4); N1−Pd−N2, 80.62(16).

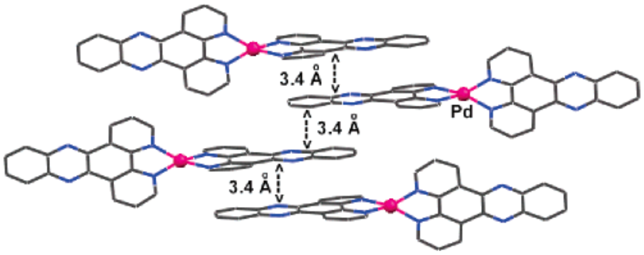


Figure 2. Crystal packing of **2b**, exhibiting a $\pi-\pi$ stacking interaction between the dppz moieties, in almost full and partial overlap.

The complex crystallizes in a monoclinic $C2/m$ space group, the asymmetric unit containing half a molecule of the complex, which is located on an inversion center. The palladium atom has a tetrahedrally distorted square planar coordination geometry, which leads to a twist conformation of the complex,[12] with dihedral angles of 24.4° and 28.6° (the difference in the angles arising from the greater distortion of one side of the dppz ligand due to crystal packing). The Pd−N bond lengths, 2.028(4) and 2.037(4) Å for Pd−N1 and Pd−N2, respectively, are comparable to those reported for similar complexes.[4a,12,13]

In the crystal lattice, the complex units undergo π stacking through the dppz ligands, as shown in Figure 2. Molecules displaced along the *c*-axis reveal almost complete overlap of the dppz moieties at an average distance of 3.4 Å, thus creating continuous supramolecular chains stabilized by $\pi-\pi$ stacking interactions between the aromatic fragments. In addition, side packing of these chains along the *c*-axis is characterized by partial overlap of the dppz fragments in adjacent chains, also with an average separation of 3.4 Å, thus forming layered domains parallel to the *ac*-plane. The counterions and diethyl ether solvent molecules are intercalated between these layers.

The ^1H and ^{13}C NMR characterization was performed in DMF-d_7 solution at room temperature (Table 1). Full assignment was achieved by two-dimensional NMR techniques. As expected, the spectra of **2a** and **2b** are not substantially affected by the different counterions of the two complexes.

The spectra of the three complexes **1a**, **2a**, and **2b** share some common features: no signal due to the free ligand is observed; the number of signals indicates the equivalence of both molecules of the N−N ligand bound to palladium and of the two halves of each of them, thus confirming their coordination in a completely symmetric chemical environment on the NMR time scale.

Comparison of the spectrum of **2** with the spectra of its metal complexes **2a** and **2b** reveals that upon binding to the Pd(II)

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Table 1. ^{1}H NMR Data for Free Ligands 1 and 2 and for the Related Complexes 1a, 2a, and 2b[a]

proton	eilatin (**1**)	$[Pd(eil)_2][BF_4]_2$ (**1a**)[b]	CIS ($\delta_c - \delta_l$)[c]	dppz (**2**)	$[Pd(dppz)_2][BF_4]_2$ (**2a**)	$[Pd(dppz)_2][PF_6]_2$ (**2b**)	CIS ($\delta_c - \delta_l$)[c]
A	d, 9.297, $J = 5.5$	9.508	0.211	dd, 9.266, $J = 4.4$ and 1.8	d, 9.810, $J = 5.3$	d, 9.767, $J = 5.2$	0.544 (**2a**) 0.501 (**2b**)
B	d, 8.979, $J = 5.5$	9.339	0.360	dd, ~8.0[d]	dd, 8.682, $J = 8.0$ and 5.6	dd, 8.633, $J = 7.8$ and 5.6	0.682 (**2a**) 0.633 (**2b**)
C	d, 9.044, $J = 8.2$	9.169	0.125	dd, 9.635, $J = 8.1$ and 1.8	d, 10.191, $J = 8.0$	d, 10.147, $J = 8.0$	0.556 (**2a**) 0.512 (**2b**)
D	t, ~8.0[d]	8.099	0.099	dd, 8.440, $J = 6.5$ and 3.4	dd, 8.612, $J = 6.5$ and 3.4	dd, 8.587, $J = 6.5$ and 3.4	0.172 (**2a**) 0.147 (**2b**)
E	t, 8.093, $J = 8.1$	8.254	0.161	dd, 8.095, $J = 6.5$ and 3.4	dd, 8.324, $J = 6.6$ and 3.4	dd, 8.302, $J = 6.5$ and 3.4	0.229 (**2a**) 0.207 (**2b**)
F	d, 8.477, $J = 8.2$	8.577	0.100				

[a] Recorded in d_7-DMF at 298 K; d in ppm; *J* in Hz. [b] Broad signals; the splitting pattern and coupling constants (*J*) could not be determined. [c] CIS = coordination induced shift for the protons in the complexes (δ_c) and in the free ligand (δ_l). [d] Signal coincides with the solvent peak.

metal center, all the dppz protons undergo a shift to high frequency. The coordination-induced shift (CIS) is larger for protons in the vicinity of the phen-binding site of the dppz ligand (H^a, H^b, and H^c; see Table 1), thus confirming the coordination of dppz to palladium as a chelating ligand even in solution. Comparison of the spectrum of complex **1a** with that of free eilatin reveals a similar trend. The CIS values for H^a and H^b are larger than those for the other protons and are similar to those found for the corresponding $[Pd(bpy)_2][PF_6]_2$ and $[Pd(phen)_2][PF_6]_2$ complexes,[4a] indicating that these protons are affected the most upon binding to the Pd(II) center and thus suggesting that the eilatin molecules are bound to palladium through the less hindered bpy-like coordination site. The same binding preference was observed for all octahedral eilatin complexes of group 8 metals.[8−11,14,15]

In the spectrum of **1a**, at room temperature, the signals are quite broad, indicating the occurrence of a dynamic process, such as the fast exchange between bound and unbound eilatin.[16] Such a dynamic process was previously observed for the analogous bpy and phen complexes.[4a]

CO/styrene Copolymerization Reactions. Complexes **1a**, **2a**, and **2b** were investigated as potential precatalysts for CO/styrene copolymerization. The copolymerization experiments were carried out in 2,2,2-trifluoroethanol as solvent, at various CO pressures ranging from 10 to 40 bar, and with no added benzoquinone coreagent. These are the same conditions that were employed when using the corresponding bischelated complexes $[Pd(N-N)_2][PF_6]_2$, where the N−N = bpy or phen.[4]

The solids recovered at the end of the runs are perfectly alternating polyketones, and according to their ^{13}C NMR spectra, they are syndiotactic with the typical triad distribution of the polyketones synthesized by palladium complexes bearing phen-like ligands (80% of *uu* triad and 20% of the *ul* + *lu* triads).[17] No effect of the nature of the ligand on the tacticity was found.

The three new complexes, **1a**, **2a**, and **2b**, generate very efficient catalysts for the investigated reaction, and in all cases, catalyst decomposition to inactive palladium metal was not observed, in agreement with the well-known stabilizing effect of the fluorinated alcohol.[4] The dppz-containing catalysts **2a** and **2b** show a higher productivity than the eilatin complex **1a**, and between **2a** and **2b**, the most productive is **2b** (Table 2), thus confirming that, for this copolymerization, hexafluorophosphate is a more suitable anion than tetrafluoroborate.[4,18] An effect of the anion on the molecular weight of the synthesized polyketones is also observed: the polyketones synthesized with the BF_4^- derivatives, **1a** and **2a**, have similar M_w values that are higher than that obtained for the polyketones prepared with the PF_6^- catalyst (Table 2). The origin of the influence of the anion on the molecular weight is difficult to envisage, since both hexafluorophosphate and tetrafluoroborate are noncoordinating ions.

Table 2. CO/Styrene Copolymerization: Effect of the N−N Ligand[a]

N−N/X	kg CP/g Pd	g CP/g Pd·h	M_w (M_w/M_n)
phen/BF_4^-	6.5	270	144 000 (2.6)
eilatin/BF_4^- **1a**	8.0	334	108 000 (2.6)
dppz/BF_4^- **2a**	11.8	494	102 000 (2.2)
dppz/ PF_6^- **2b**	12.5	519	88 000 (2.7)

[a] Reaction conditions: $n_{Pd} = 0.54 \times 10^{-5}$ mol; styrene $V = 30$ mL; TFE $V = 20$ mL; $P_{CO} = 20$ bar; $T = 50$ °C; $t = 24$ h.

The comparison of the catalytic behavior of the new complexes with that of $[Pd(phen)_2][BF_4]_2$ demonstrates that both **1a** and **2a** show a higher productivity than that of the phen catalyst (Table 2). Moreover, the comparison of the molecular weight values indicates that the increase in the productivity realized with complexes **1a** and **2a** is mainly related to an increase in the number of polymeric chains rather than to their length.

The effect of CO pressure was investigated in the range 10−40 bar (Figure 3), revealing several trends: (1) *Productivity versus CO pressure:* catalysts generated by **1a** and **2b** showed a bell-type curve behavior typical of a carbonylation reaction, whereas the catalyst derived from **2a** was much less affected by the CO pressure, its maximum value achieved at 40 bar (Figure 3a). Its maximum productivity per hour is 570 g CP/g Pd·h, representing the highest ever reported for this reaction, when carried out in the absence of any coreagent or cocatalyst. In all cases, no formation of inactive palladium metal was observed, indicating that the decrease of productivity observed on increasing the CO pressure is due to the inhibiting effect of this comonomer. (2) *Counterion effect:* at higher CO pressures the tetrafluoroborate derivative (**2a**) is more active than the hexafluorophosphate species (**2b**), thus suggesting that the counterion might play a role in determining the influence of

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[16] Addition of free eilatin to the eilatin complex **1a** in DMF-d_7 resulted in a single set of peaks, supporting the fast exchange hypothesis.

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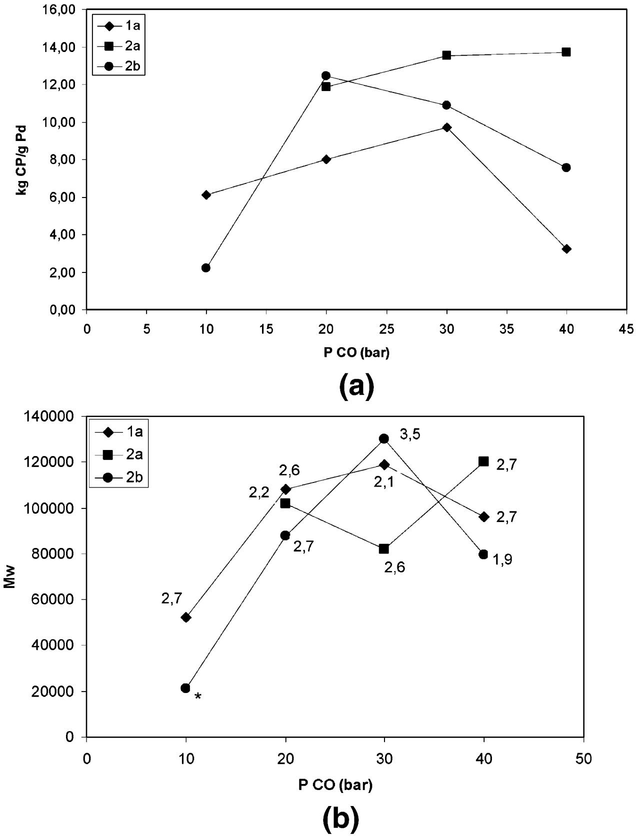

(a)

(b)

Figure 3. CO/styrene copolymerization. Effect of CO pressure on (a) productivity; (b) molecular weight. Precatalyst: [Pd(N−N)$_2$]-[X]$_2$. Reaction conditions: see Table 2. M_w/M_n values are reported close to the corresponding data of M_w. *GPC profile shows a bimodal distribution.

the CO pressure on the activity. (3) *Molecular weight versus CO pressure:* similar to that of the productivity for catalysts **1a** and **2b**, i.e., M_w values increase up to a maximum, which is reached at 30 bar for both catalysts (Figure 3b). The trend reported for **2a** differs from the other two.[19]

The polydispersity values, higher than 2.0 in all cases (Table 1 and Figure 3b), might indicate the presence of active species of different nature, homogeneous and heterogeneous (the copolymer precipitates during the polymerization process), each of them having different kinetic behavior. Similar behavior was reported by us for the catalytic system based on the bischelated complexes with phenanthroline ligands[4d] and was previously pointed out in the CO/ethylene copolymerization reaction.[20]

Conclusions

This work demonstrates that palladium complexes of conjugated heterocyclic phenanthroline-type ligands lead to highly active catalysts for the copolymerization of CO/styrene to form syndiotactic polyketones. Similar values of productivity per hour have been very recently reported for the palladium catalytic system [Pd(CH$_3$)(CH$_3$CN)(F$_4$-phen)][PF$_6$] (F$_4$-phen = 5,5,6,6-tetrafluoro-5,6-dihydro-1,10-phenanthroline).[21] However, in the catalytic system based on F$_4$-phen the addition of benzoquinone was required. The main difference between the catalytic systems presented herein and those based on the phenanthroline ligands concerns the molecular weight values. The phenanthroline-based catalysts lead to the enhancement of productivity, with a concomitant increase in the molecular weight of the polyketones synthesized; this is not the case for the eilatin and the dppz catalysts, which efficiently promote the synthesis of polymers with M_w values around 100 000. This behavior suggests that, upon a proper modification of the reaction conditions, Pd complexes of these ligands could be tested in the synthesis of oligoketones.

Experimental Section

For details about general experimental procedures see the Supporting Information.

Synthesis of Complexes. [Pd(eil)$_2$][BF$_4$]$_2$ (1a). A filtered solution of [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ (100.0 mg, 0.225 mmol) in 3 mL of acetonitrile was added to a solution of **1** (168.5 mg, 0.473 mmol) in 100 mL of CH$_2$Cl$_2$, and the reaction mixture stirred at RT for 1 h. The precipitate that formed was isolated by filtration, purified by repeated washing with CH$_2$Cl$_2$, and dried in vacuo. The red complex **1a** was obtained in a yield of 68% (151.9 mg). Anal. Calcd (Found) for C$_{48}$H$_{24}$B$_2$F$_8$N$_8$Pd·6H$_2$O: C, 52.37 (52.10); H, 3.30 (3.36); N, 10.18 (10.15). ^{1}H NMR (d_7-DMF, 298 K): δ 9.508 (4H, H^a), 9.339 (4H, H^b), 9.169 (4H, H^c), 8.577 (4H, H^f), 8.254 (4H, H^e), 8.099 (4H, H^d). ^{13}C NMR (d_7-DMF, 298 K): δ 149.3 (*C*-H^a), 133.6 (*C*-H^e), 132.0 (*C*-H^f), 131.2 (*C*-H^d), 125.3 (*C*-H^c), 121.9 (*C*-H^b). ^{1}H NMR (CD$_3$CN, 298 K): δ 8.95 (m, 8H, H^b, H^c), 8.736 (d, J = 6.3 Hz, 4H, H^a), 8.579 (d, J = 7.3 Hz, 4H, H^f), 8.245 (t, J = 7.3 Hz, 4H, H^d), 8.097 (t, J = 8.3 Hz, 4H, H^e). FAB-MS: 818.0 [M − 2BF$_4^-$]$^+$.

[Pd(dppz)$_2$][BF$_4$]$_2$ (2a). This complex was prepared and purified as described for **1a**, using [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ (126.0 mg, 0.283 mmol) and dppz (170.5 mg ,0.604 mmol). The off-white complex **2a** was obtained in a yield of 86% (205.6 mg). Anal. Calcd (Found) for C$_{36}$H$_{20}$B$_2$F$_8$N$_8$Pd·2H$_2$O: C, 49.10 (49.27); H, 2.75 (2.60); N, 12.72 (13.00). ^{1}H NMR (d_7-DMF, 298 K): δ 10.191 (d, J = 8.0 Hz, 4H, H^c), 9.810 (d, J = 5.3 Hz, 4H, H^a), 8.682 (dd, J = 5.6 and 8.0 Hz, 4H, H^b), 8.612 (dd, J = 3.4 and 6.5 Hz, 4H, H^d), 8.324 (dd, J = 3.4 and 6.6 Hz, 4H, H^e). ^{13}C NMR (d_7-DMF, 298 K): δ 154.4 (*C*-H^a), 138.6 (*C*-H^c), 133.0 (*C*-H^e), 130.2 (*C*-H^d), 128.7 (*C*-H^b). FAB-MS: 670.0 [M − 2BF$_4^-$]$^+$.

[Pd(dppz)$_2$][PF$_6$]$_2$ (2b). [Pd(OAc)$_2$] (35.7 mg, 0.159 mmol) was added to 5 mL of CH$_3$OH, the orange-yellow suspension obtained was stirred at RT for 5 min, and then dppz (53.4 mg, 0.189 mmol) was added. Stirring was continued until all the solids dissolved (ca. 5 min), the reaction mixture was filtered, and then 0.35 mL of TFA (CF$_3$COOH) was added dropwise, yielding a white precipitate. Filtration, washing with CH$_3$OH, and drying in vacuo gave the intermediate complex [Pd(CF$_3$COO)$_2$(dppz)] as an off-white solid in 89% yield (87.0 mg).

To a suspension of [Pd(CF$_3$COO)$_2$(dppz)] (30.6 mg, 0.042 mmol) in 2 mL of CH$_3$OH was added dppz (17.7 mg, 0.063 mmol). The reaction mixture turned yellow, and an additional 8 mL of CH$_3$OH was added to dissolve all the solids. Then, a solution of 21.8 mg of KPF$_6$ in 5 mL of CH$_3$OH was added dropwise. A white precipitate formed immediately. Filtration, washing with CH$_3$OH, and drying in vacuo gave complex **2b** as an off-white solid in 92% yield (44.1 mg). Anal. Calcd (Found) for C$_{36}$H$_{20}$P$_2$F$_{12}$N$_8$Pd: C, 45.00 (44.74); H, 2.10 (2.40); N, 11.66 (11.83). ^{1}H NMR (d_7-DMF, 298 K): δ 10.147 (d, J = 8.0 Hz, 4H, H^c), 9.767 (d, J = 5.2 Hz, 4H, H^a), 8.633 (dd, J = 5.6 and 7.8 Hz, 4H, H^b), 8.587 (dd, J = 3.4 and 6.5 Hz, 4H, H^d), 8.302 (dd, J = 3.4 and 6.5 Hz, 4H, H^e). ^{13}C NMR (d_7-DMF, 298 K): δ 152.4 (*C*-H^a), 137.0 (*C*-H^c), 131.1 (*C*-H^e), 128.6 (*C*-H^d), 126.8 (*C*-H^b).

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(19) The catalytic experiments were repeated twice and molecular weight measurements four times; reproducible data were obtained.

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Crystal data for 2b: $C_{36}H_{20}F_6N_8PdP$, formula weight 815.97, monoclinic, space group $C2/m$, $a = 24.8560(5)$ Å, $b = 21.4614(5)$ Å, $c = 8.2591(2)$ Å, $\beta = 104.1563(12)°$, $V = 4271.98(17)$ Å^3, $Z = 4$, $D_{calcd} = 1.269$ g·cm^{-3}, $F(000) = 1628$, μ(Mo Kα) = 5.30 mm^{-1}, $2\theta_{max} = 50°$, 3854 unique reflections were measured. The final refinement converged at $R_1 = 0.051$ and $wR_2 = 0.138$ for 3260 unique observations with $[I > 2\sigma(I)]$ and $R_1 = 0.060$ and $wR_2 = 0.143$ for all data. The crystallographic analysis represents a reliable determination of the $[Pd(dppz)_2]^{2+}$ structure. However, the diethyl ether solvent and one of the PF_6^- counterions are severely disordered and could not be modeled by discrete atoms. Correspondingly, their contribution was subtracted from the diffraction pattern by the SQUEEZE procedure (A. Spek, 2003) using the PLATON software. The final refinement calculations refer to thus modified data. In addition, the other PF_6^- ion is also rotationally disordered. Although this disorder was modeled, the positions of the F atoms are not very precise. CCDC number 279096 containing the crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: A pdf file contatining general experimental procedures. CIF files giving crystallographic data for **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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