Palladium Complexes Containing a Hemilabile Pyridylcarbene Ligand

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A series of palladium complexes with a hemilabile terdentate carbene ligand, 1,3-bis(2-pyridyl)imidazol-2-ylidene (pyimypy), has been synthesized. Molecular structures of [pyimypyH]-Cl·H_2O (**1**), [Pd(pyimypy)$_2$][PF_6]$_2$ (**4**), [Pd(pyimypy)$_2$Br]Br·$2H_2O$ (**5**), [Pd(pyimypy)$_2$I][I]$_{1/2}$[PF_6]$_{1/2}$ (**6**), and [Pd(pyimypy)(PPh_3)$_2$Br]Br·CH_3CN·H_2O (**8**) have been determined by single-crystal X-ray diffraction. In compound **4**, the two bidentate pyimypy ligands are in a cis configuration and the palladium center has a highly distorted square-planar geometry. Compounds **5** and **6** have a bidentate and a monodentate pyimypy ligand. Compound **8** has two trans phosphine ligands, and the pyimypy behaves as a monodentate ligand. Compounds **4**, **5**, and **6** are fluxional in solution at room temperature. Halide- and solvent-assisted exchange processes involving coordinated and free pyridines are thought to be responsible for the fluxional behavior. Complex **4** is active toward the catalytic polymerization of CO/norbornylene.

Introduction

Since the isolation of stable imidazol-2-ylidene by Arduengo et al.[1] in 1991, there has been an avalanche of studies[2] of metal complexes of N-heterocyclic carbenes, stimulated by their potential usefulness in many applications, especially metal-catalyzed reactions.[3] It has been proposed[4] that this type of carbene has Lewis basicity comparable to that of phosphines toward metal ions. Studies indicate that metal−carbene bonds are stronger than metal−phosphine bonds.[5] Furthermore, the use of metal−carbene complexes as catalysts in many chemical transformations is superior to the use of metal−phosphine complexes.[2c,3c,e,m] This is the result of phosphine dissociation or the deactivation of metal−phosphine catalysts due to the degradation of phosphine by P−C bond cleavage[5] and orthometalation.[6]

Bidentate or polydentate ligands containing a phosphorus and nitrogen donor atoms normally form strong metal−phosphorus bonds and weak metal−nitrogen bonds when coordinate to a soft metal. These types of ligands, the so-called hemilabile ligands, show interesting coordination ability and are important in many catalytic reactions.[7] For example, metal complexes with pyridylphosphine[8−10] have been widely used as catalysts in reactions such as carbonylation, epoxidation, cycload-

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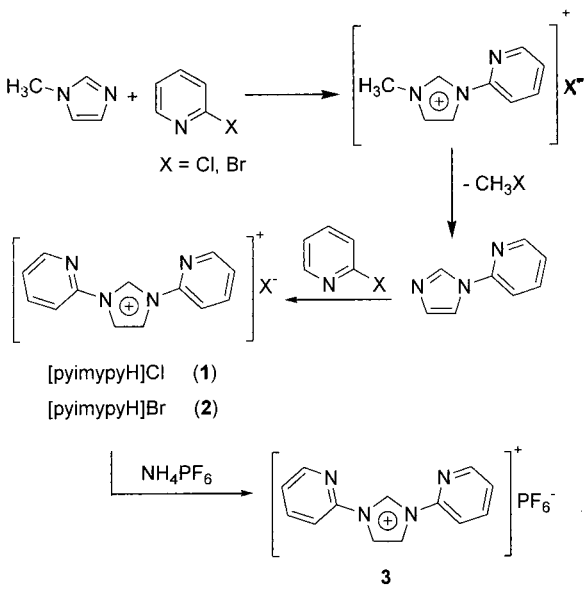
dition, and hydrogenation, to name a few.[9,10] It is interesting to consider the analogous hemilabile carbene ligands. Among the known hemilabile carbene ligands there are only two examples of pyridylcarbenes.[11,12] One example reported by us is 2,6-bis(1-methylimidazol)-2-ylidylpyridine, which contains a pyridine and two carbene donors and reacts with mercury to form a double helical carbene complex.[11] Another ligand is 3-methyl-1-picolyimidazol-2-ylidene (abbreviated C∧N), which forms a six-membered chelate ring with palladium and is active toward catalytic reactions, such as Heck, Suzuki, and Sonogashira coupling reactions.[12]

Our group has been interested in metal−carbene complexes for the past few years. We reported the synthesis of Au^{I}, Ag^{I}, Hg^{II}, and Pd^{II} carbene complexes and their structural, photoluminescent, and liquid crystalline behaviors.[11,13] In this work, we report a new carbene ligand precursor, 1,3-bis(2-pyridyl)imidazolium cation ($[pyimypyH]^{+}$), which upon deprotonation, produces a potential terdentate ligand, 1,3-bis(2-pyridyl)-imidazol-2-ylidene (pyimypy), consisting of a carbene and two pyridines. We have used this ancillary ligand to prepare palladium complexes. The potential terdentate ligand pyimypy can coordinate to palladium in a monodentate or a bidentate of five-membered chelate fashion. Preliminary studies show that the fluxional compound $[Pd(pyimypy)_2][PF_6]_2$ (**4**) is active toward the polymerization of CO/norbornylene.

Scheme 1. Synthesis of the Pyridylcarbene Precusor



Results and Discussion

Although a plausible way to synthesize the terdentate carbene precursor [pyimypyH]X (X = Cl, Br) is to react 2-halopyridine with 1-(2-pyridyl)imidazole, this method is tedious because the latter compound has to be prepared from the reaction of 2-halopyridine with imidazole in the presence of a base.[14] In a parallel work, in an attempt to prepare 1-methyl-3-(2-pyridyl)imidazolium halides [MeimypyH]X (Me = methyl), we carried out the reaction of 1-methylimidazole with 2-halopyridine in a 1:1 molar ratio at 190 °C without solvent for 1 day. Unexpectedly, the major product isolated was [pyimypyH]X. We therefore set out to prepare [pyimypyH]X by using a 1:2 molar ratio of 1-methylimidazole and 2-halopyridine (Scheme 1). This method is preferred because of its simplicity and the ready accessibility of 1-methylimidazole. To understand the reaction pathways, the reaction was quenched after 10 h and was examined by ^{1}H NMR spectroscopy. Compounds 1-methylimidazole, 1-(2-pyridyl)imidazole, 1-methyl-3-(2-pyridyl)imidazolium halide, and the product [pyimypyH]X were identified. This result would suggest that when 1-methylimidazole reacts with 2-halopyridine at the early stage, 1-methyl-3-(2-pyridyl)imidazolium halide forms. Elimination of methyl halide from imidazolium salt produces 1-(2-pyrididyl)imidazole, which upon further reaction with halopyridine generates the final

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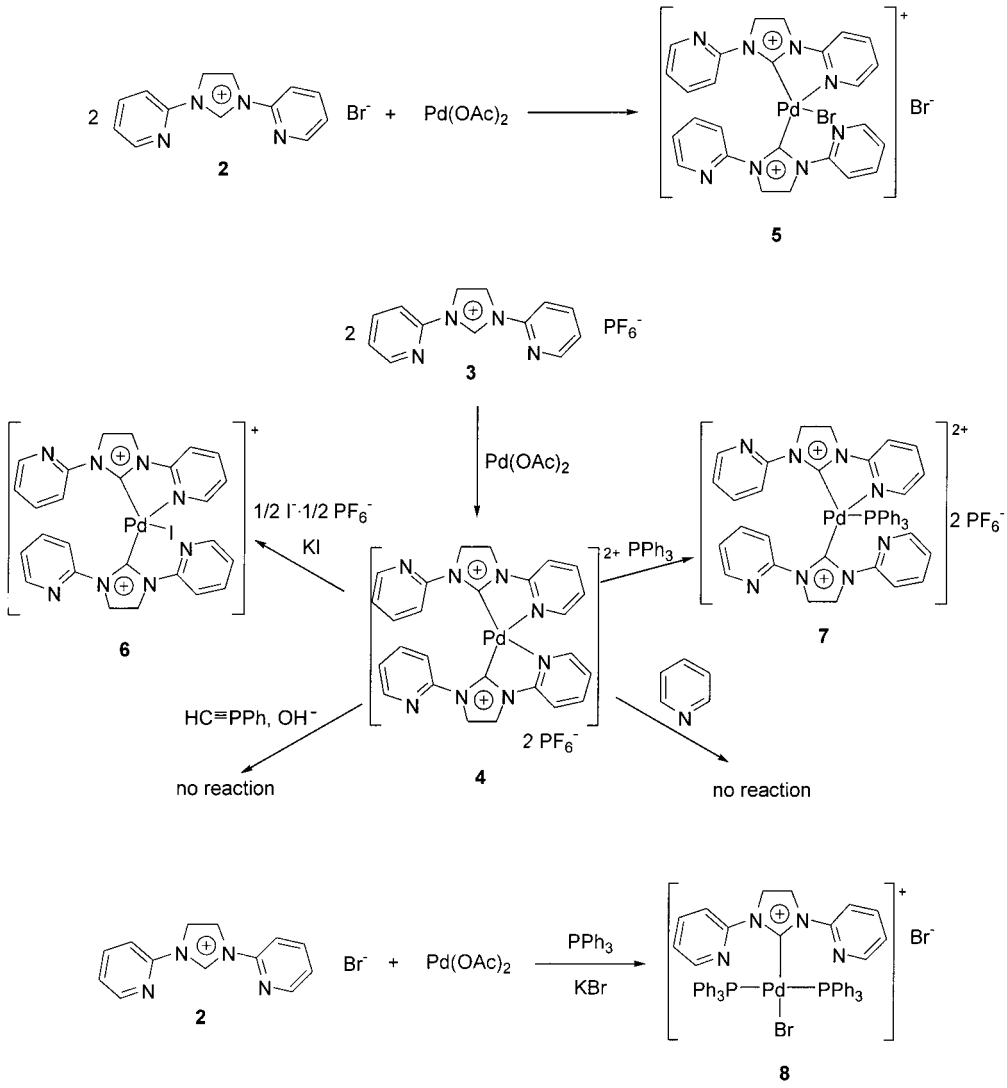
Scheme 2. Synthesis of the Pyridylcarbene Complexes



product. The PF_6^- salt was obtained by a simple metathesis reaction with NH_4PF_6. Slight deviations of the carbon analyses of **1** and **3** are possibly due to the poor solubility of **1** and a slight contamination of NH_4PF_6 salt in **3**.

Metal−carbene complexes have been prepared by several methods.[2,13,15] A popular method is the reaction of imidazolium ions with metal complexes containing basic ligands.[2] Earlier, we described the use of Ag^I−carbene complexes as carbene-transfer agents, which could be obtained readily from the reaction of imidazolium salts either with Ag_2O or with AgCl under basic phase-transfer catalyzed conditions.[13] The use of Ag_2O has been successfully employed by other groups[2n,12] to prepare carbene complexes of late transition metals, including the palladium complexes of hemilabile carbene ligands reported by McGuinness and Cavell.[12] We have also reported the synthesis of liquid crystalline Au^I−carbene complexes under basic phase-transfer catalyzed conditions.[13a] Attempts to prepare pyimypy complexes by our previously published procedures were unsuccessful. Base hydrolysis leads to ring opening of the imidazolium ring[16] in the presence of OH^- or Ag_2O. The ease of the base hydrolysis reaction is likely caused by the highly conjugated electron-withdrawing pyridine. The hydrolysis product *N*-pyridin-2-yl-*N*-[2-(pyridin-2-ylamino)vinyl] formamide was characterized by ^1H NMR spectra analysis. Our palladium−carbene complexes were therefore prepared by the reaction of [pyimypyH]X (X = Cl, Br) and the PF_6 salt with $Pd(OAc)_2$ (Scheme 2). When X was chloride, the reaction was poor, due to the poor solubility of the chloride salt in common organic solvents, except MeOH, in which $Pd(OAc)_2$ tends to decompose. Nonetheless, [pyimypyH]Br·H_2O (**2**) and [pyimypyH][PF_6] (**3**) reacted nicely with $Pd(OAc)_2$ in a 2:1 molar ratio in refluxing acetonitrile to give complexes [Pd(pyimypy)$_2$Br][Br]·$2H_2O$ (**5**) and [Pd(pyimypy)$_2$][PF_6]$_2$ (**4**), respectively. Compounds [Pd(pyimypy)$_2$I][I]$_{1/2}$[PF_6]$_{1/2}$ (**6**) and [Pd(pyimypy)$_2$(PPh_3)][PF_6]$_2$ (**7**) were readily obtained by the reaction of [Pd(pyimypy)$_2$][PF_6]$_2$ (**4**) with I^- and PPh_3, respectively. Attempted reactions of [Pd(pyimypy)$_2$][PF_6]$_2$ (**4**) with pyridine and phenylacetylene were unsuccessful.

When [pyimypyH][PF_6] (**3**) was allowed to react with $Pd(OAc)_2$ in a 1:1 molar ratio, an unstable complex

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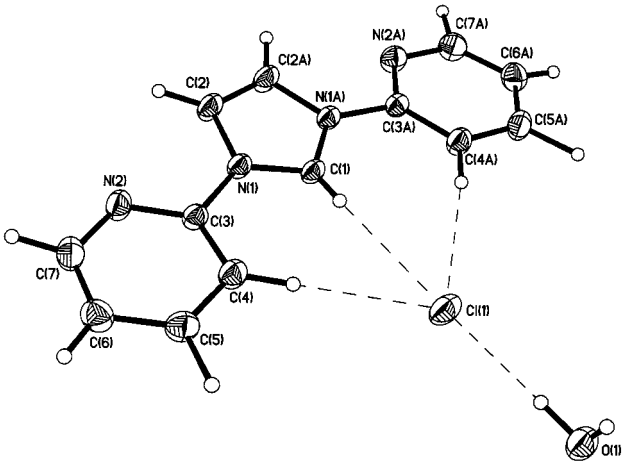

Figure 1. ORTEP diagram (50% probability ellipsoids) of [pyimypyH]Cl·H_2O (**1**). Selected bong lengths (Å) and angles (deg): C(1)−N(1), 1.336(2); C(2)−N(1), 1.386(2); C(3)−N(1), 1.434(2); N(1)−C(1)−N(1A), 107.9(2); C(1)−N(1)−C(2), 108.87(15); C(1)−N(1)−C(3), 125.95(15).

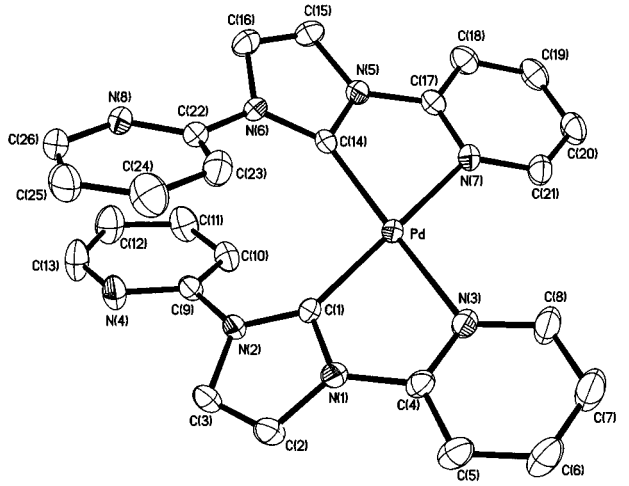

Figure 2. ORTEP diagram (30% probability ellipsoids) of the cation of [Pd(pyimypy)$_2$][PF_6]$_2$ (**4**). Selected bong lengths (Å) and angles (deg): Pd−C(1), 1.969(4); Pd−C(14), 1.959(4); Pd−N(3), 2.124(4); Pd−N(7), 2.120(3); N(1)−C(4), 1.406(6); N(5)−C(17), 1.408(5); N(2)−C(9), 1.438(5); C(1)−Pd−N(3), 78.66(15); C(14)−Pd−N(7), 78.18(15); Pd−C(1)−N(1), 113.3(3); C(4)−N(3)−Pd, 112.9(3); Pd−C(1)−N(2), 140.3(3); Pd−C(14)−N(5), 115.3(3); C(17)−N(7)−Pd, 113.1(3); Pd−C(14)−N(6), 139.8(3).

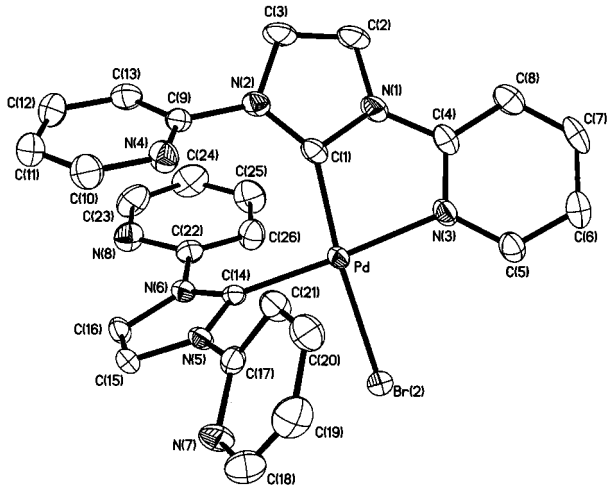

Figure 3. ORTEP diagram (30% probability ellipsoids) of the cation of [Pd(pyimypy)$_2$Br]Br·$2H_2O$ (**5**). Selected bong lengths (Å) and angles (deg): Pd−C(1), 1.973(6); Pd−C(14), 1.980(6); Pd−N(3), 2.083(5); Pd−Br(2), 2.4565(8); C(1)−Pd−N(3), 79.6(2); N(3)−Pd−Br(2), 94.43(15); C(1)−Pd−C(14), 97.3(2); C(14)−Pd−Br(2), 88.70(15).

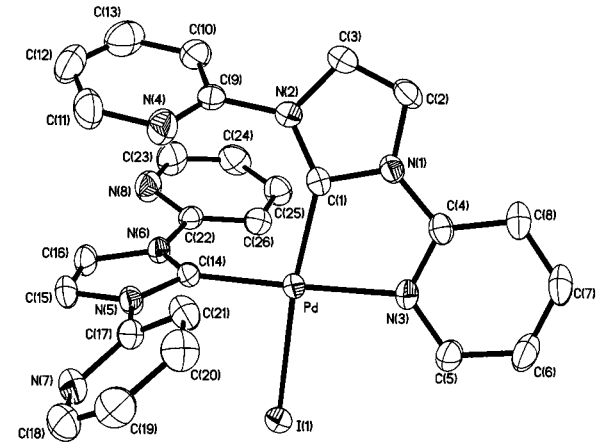

Figure 4. ORTEP diagram (30% probability ellipsoids) of the cation of [Pd(pyimypy)$_2$I][I]$_{1/2}$[PF_6]$_{1/2}$ (**6**). Selected bong lengths (Å) and angles (deg): Pd−C(1), 1.998(4); Pd−C(14), 1.993(4); Pd−N(3), 2.100(3); Pd−I(1), 2.6282(7); C(1)−Pd−N(3), 78.96(14); N(3)−Pd−I(1), 95.47(9); Pd−C(1)−N(1), 113.5(3); C(1)−Pd−C(14), 98.78(15); C(14)−Pd−I(1), 86.92(10).

having a pyimypy and a OAc ligand was observed by ^{1}H NMR spectroscopy. If [pyimypyH]Br·H_2O (**2**) was reacted with Pd(OAc)$_2$ in a 1:1 molar ratio in the presence of PPh_3 and KBr, the compound [Pd(pyimypy)(PPh_3)$_2$Br]Br·CH_3CN·H_2O (**8**) was obtained. Note that this compound cannot be prepared by the reaction of [Pd(pyimypy)$_2$Br]Br with excess PPh_3, a result indicating that metal−carbene bonds are indeed stronger than metal−phosphine bonds.

Molecular structures of [pyimypyH]Cl·H_2O (**1**) (Figure 1), [Pd(pyimypy)$_2$][PF_6]$_2$ (**4**) (Figure 2), [Pd(pyimypy)$_2$Br]Br·$2H_2O$ (**5**) (Figure 3), [Pd(pyimypy)$_2$I][I]$_{1/2}$[PF_6]$_{1/2}$ (**6**) (Figure 4), and [Pd(pyimypy)(PPh_3)$_2$Br]Br·CH_3CN·H_2O (**8**) (Figure 5) were characterized by single-crystal X-ray diffraction. The crystal data are given in Tables 1 and 2. Selected bond distances and bond angles are given in the respective figure captions. As shown in Figure 1, the three rings, one imidazole and two pyridines, in the ligand precursor [pyimypyH]Cl·H_2O (**1**) are essentially coplanar. Extensive hydrogen bondings are observed. The chloride ion sits in the pocket formed by the three rings, in which the three C−H protons (C(4)−H, C(1)−H, and C(4A)−H) from each ring behave as proton donors (Cl···H distances: 2.761(3) and 2.715(4) Å, respectively). The hydrate forms a fourth O···H bond (2.310(2) and 2.436(3) Å) and bridges to another chloride. Weak hydrogen bonds between the pyridine nitrogens and neighboring C−H protons are also observed (N···H 2.290(3) Å). All the other bond distances and angles are normal and are comparable with those reported for imidazoliums and pyridines.[17]

The molecular structure of the cationic [Pd(pyimypy)$_2$]$^{2+}$ (Figure 2) reveals that the pyimypy ligand behaves as a C,N-chelate, with one dangling pyridine. The two chelates adopt a cis arrangement around the palladium atom, such that there is a local helical C_2

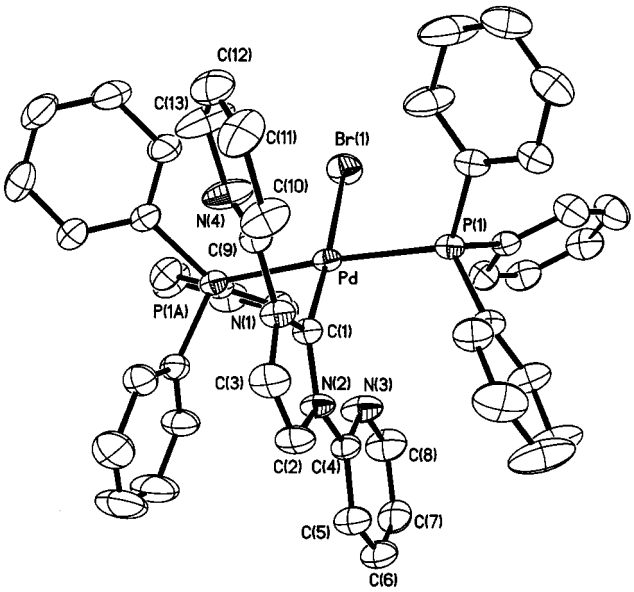

Figure 5. ORTEP diagram (30% probability ellipsoids) of the cation of $[Pd(pyimypy)(PPh_3)_2Br]Br\cdot CH_3CN\cdot H_2O$ (**8**). Selected bong lengths (Å) and angles (deg): Pd−C(1), 2.002(5); Pd−P(1), 2.3452(11); Pd−Br(2), 2.4645(7); C(1)−Pd−P(1), 90.47(3); P(1)−Pd−Br(1), 89.91(2).

symmetry at the palladium center. The helicity is a result of the highly distorted square plane around the metal center. A twist angle of 22.7° between the two five-membered chelate rings is observed. The coordinated imy and pyridine rings are almost coplanar (twist angle ~10°), while the noncoordinated pyridine ring twists ~35° from the central imy ring, such that there is a $\pi-\pi$ interaction (~3.2 Å) between the two noncoordinated pyridine rings. A similar helical chirality, having a strong $\pi-\pi$ interaction has been observed for bis-homoleptic cyclometalated platinum complexes.[18] Recently, using chiral pyridine ligands to prepare highly distorted square-planar palladium[19] and platinum[20] compounds has also been reported. The bond distances and angles for the imy and pyridine rings in $[Pd(pyimypy)_2][PF_6]_2$ (**4**) are normal and are comparable with reported values.[2g,3c,f,21] The two cis carbenes have relatively short Pd−C bonds (1.959(4), 1.969(4) Å) as compared with the averaged Pd−C bonds (2.023−2.137 Å) of trans dicarbene compounds.[22] The two cis pyridines have relatively long Pd−N bonds (2.120(3), 2.124(4) Å) as compared with the Pd−N bonds (2.010−2.040 Å) of trans dipyridine compounds.[23] The Pd−C and Pd−N bond distances observed in this structure suggest the strong trans influence of carbene. The unique geometry adopted by this complex is controlled by the extra ring $\pi-\pi$ interaction and the favorable trans influence of the carbene.

An interesting structural feature between the ligand precursor [pyimypyH]Cl (**1**) and $[Pd(pyimypy)_2][PF_6]_2$ (**4**) is that the C−N bond distance between the imy ring and pyridine ring is substantially shortened (~0.03 Å) from the precursor to the chelated ligand. The C−N distance between the dangling pyridine and the coordinated imy, however, is comparable with the distance found in the precursor. The shortened C−N bond distance in the chelate ring may reflect a delocalization around the imy ring and the pyridine ring.

The molecular structure of $[Pd(pyimypy)_2Br]Br\cdot 2H_2O$ (**5**), given in Figure 3, shows that one pyimypy ligand behaves as a bidentate chelate and the other as a monodentate ligand. Again, the two carbenes are in cis position. The two palladium−carbene bonds trans to the Br and pyridine are 1.973(6) and 1.980(6) Å, respectively. The corresponding Pd−Br and Pd−N bonds are 2.4565(8) and 2.083(5) Å, respectively, and are longer than those Pd−Br (2.412−2.446 Å) and Pd−N (2.010−2.040 Å) bonds found in trans dibromo[24] and dipyridine[23] compounds. These observed values are also consistent with the large trans influence of the carbene.[2c] Unlike the highly strained structure of $[Pd(pyimypy)_2][PF_6]_2$ (**4**), the bromide-substituted compound has a molecular geometry around the Pd^{II} center close to a square plane. Apparently, the steric repulsions between the two pyimypy ligands are substantially lessened due to the formation of the monodentate pyimypy ligand. In the monodentate ligand, the coordinated carbene ring tilts 59.1° from the planes around the palladium center, and the two uncoordinated pyridine rings tilt 40.9° and 23.3°, respectively, from the carbene ring. The bidentate pyimypy has a structure similar to that of the homoleptic $[Pd(pyimypy)_2][PF_6]_2$ (**4**). Other bond distances and angles are comparable with those reported in this work.

The molecular geometry of $[Pd(pyimypy)_2I]\cdot[I]_{1/2}\cdot[PF_6]_{1/2}$ (**6**) (Figure 4) around the palladium center is similar to the bromo analogue except that the tilting angles between the uncoordinated pyridine ring and imy ring are different. The palladium−carbene bonds trans to the iodide and pyridine are 1.998(4) and 1.993(4) Å, respectively. The Pd−I and Pd−N bonds trans to the carbenes are 2.6282(7) and 2.100(3) Å, respectively.

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Table 1. Crystal Data for Ligand Precursor 1 and Complexes 4 and 5

	1	4	5
formula	$C_{13}H_{13}ClN_4O$	$C_{26}H_{20}F_{12}N_8P_2Pd$	$C_{26}H_{20}Br_2N_8O_2Pd$
fw	276.72	840.84	742.72
cryst syst	monoclinic	triclinic	monoclinic
space group	*Cm*	$P\bar{1}$	*P*2(1)/*c*
a, Å	7.5068(8)	8.3793(8)	15.2198(14)
b, Å	16.6911(15)	12.2671(11)	16.363(2)
c, Å	5.2479(4)	15.9844(15)	12.1187(17)
α, deg	90	76.713(7)	90
β, deg	98.013(11)	81.829(8)	109.313(10)
γ, deg	90	70.531(7)	90
V, Å^3	651.12(10)	1503.8(2)	2848.2(6)
Z	2	2	4
D_{calcd}, Mg/m^3	1.411	1.857	1.732
abs coeff, mm^{-1}	0.291	0.833	3.496
F(000)	288	832	1456
cryst size, mm	0.80 × 0.60 × 0.60	0.88 × 0.60 × 0.15	0.50 × 0.48 × 0.20
θ_{min}, θ_{max}, deg	2.44, 29.00	1.80, 25.00	1.89, 25.00
no. of data collected	1161	5671	5223
no. of unique data	1090	5275	4967
no. of refined params	120	442	352
goodness-of-fit on F^2 [a]	1.079	0.976	1.048
final *R* indices[b] [$I>2\sigma(I)$]			
R1	0.0335	0.0410	0.0453
wR2	0.0818	0.1102	0.0858
R indices (all data)			
R1	0.0347	0.1102	0.0845
wR2	0.0831	0.1134	0.0976

[a] Goof = $[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined. [b] R1 = $\sum(||F_o| - |F_c||)/\sum|F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Table 2. Crystal Data for Complexes 6 and 8

	6	8
formula	$C_{26}H_{20}F_3I_{1.50}N_8P_{0.50}Pd$	$C_{51}H_{45}Br_2N_5OP_2Pd$
fw	813.73	1072.13
cryst syst	monoclinic	orthorhombic
space group	*C*2/*c*	*Pnma*
a, Å	28.111(6)	19.7794(19)
b, Å	28.111(6)	15.2628(15)
c, Å	16.329(3)	15.5190(15)
α, deg	90	90
β, deg	99.26(3)	90
γ, deg	90	90
V, Å^3	5671(2)	4685.0(8)
Z	8	4
D_{calcd}, Mg/m^3	1.906	1.507
abs coeff, mm^{-1}	2.368	2.213
F(000)	3136	2124
cryst size, mm	0.40 × 0.20 × 0.20	0.50 × 0.40 × 0.20
θ_{min}, θ_{max}, deg	1.45, 24.96	1.67, 28.25
no. of data collected	4980	27 476
no. of unique data	4980	5647
no. of refined params	362	328
goodness-of-fit on F^2 [a]	1.104	1.024
final *R* indices[b] [$I>2\sigma(I)$]		
R1	0.0269	0.0427
wR2	0.0710	0.1216
R indices (all data)		
R1	0.0326	0.0742
wR2	0.0735	0.1327

[a] Goof = $[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined. [b] R1 = $\sum(||F_o| - |F_c||)/\sum|F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

The molecular structure of $[Pd(pyimypy)(PPh_3)_2Br]Br\cdot CH_3CN\cdot H_2O$ (**8**) (Figure 5) reveals that around the palladium center there is a monodentate pyimypy carbene trans to a bromide, and there are two trans phosphines. The carbene ring is perpendicular to the square plane. One of the pyridine rings is coplanar with the carbene ring, and another disordered pyridine ring tilts 34.7° from the carbene ring. The trans influence of the carbene ligand is also evidenced by the slightly shorter Pd−C(1) (2.002(5) Å) bond and the longer Pd−Br(1) (2.4645(7) Å) bond. The distance between the dangling pyridine N(3) atom and palladium atom is 2.964(5) Å, which is shorter than the van der Waals distance of 3.15 Å between Pd and N.[25]

Note that when $[Pd(pyimypy)_2]^{2+}$ was reacted with excess ligand L (L = PPh_3, Cl^-, Br^-, or I^-), only $[Pd(pyimypy)_2L]^{n+}$ (n = 1 or 2) but no $[Pd(pyimypy)_2L_2]^{n+}$ (n = 0 or 2) was isolated. This result seems different from those reported by McGuinness and Cavell.[12] One possible reason is that pyimypy forms a more stable rigid five-membered chelate ring with palladium metal, while the reported C∧N ligand forms a less stable six-membered chelate ring.

The ^{1}H NMR spectrum of $[Pd(pyimypy)_2][PF_6]_2$ (**4**) in CD_3CN at room temperature exhibits sharp signals (Figure 6a) of equivalent pyridines, indicating the occurrence of a fast exchange between the dangling pyridine and coordinated pyridine. The tentative peak assignments are given with numbering on the spectrum and a drawing of the corresponding molecular fragment on the upper left of the figure. To study low-temperature NMR spectra, low freezing temperature solvents are required. The solubility of $[Pd(pyimypy)_2][PF_6]_2$ (**4**) in CD_2Cl_2 is poor; however, reasonably good solubility can be achieved by using a mixed CD_2Cl_2/CH_3CN solvent. Thus for a mixed CD_2Cl_2/CH_3CN solvent (15:1 by volume), broad signals (Figure 6b) corresponding to a fluxional molecule are observed. The exchange process

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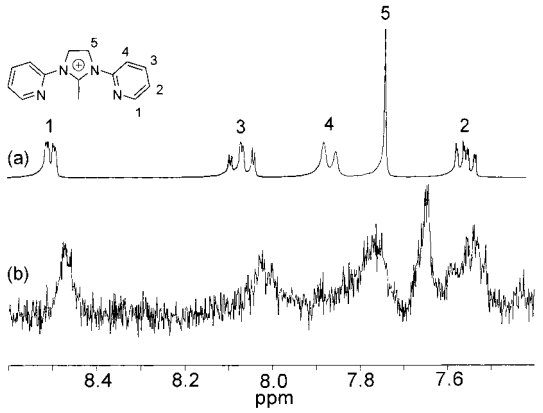


Figure 6. ^{1}H NMR spectra of complex $[Pd(pyimypy)_2][PF_6]_2$ (**4**) (a) in CD_3CN at room temperature; (b) in CD_2Cl_2/CH_3CN (15:1 by volume) at room temperature. Peak assignments are given with numbering on the spectrum and on the corresponding molecular fragment.

that occurs in the mixed solvent is slower than the one in CD_3CN. Upon cooling the latter sample to −80 °C, the fluxional processes are still fast on the NMR time scale. These observations suggest that in the presence of a coordinating solvent $[Pd(pyimypy)_2][PF_6]_2$ (**4**) is fluxional and that the rate of the fluxionality appears to depend on the amount of the coordinating solvent. While the homoleptic Pd-pyimypy compounds is fluxional, the triphenylphosphine-substituted $[Pd(pyimypy)_2PPh_3][PF_6]_2$ (**7**) is nonfluxional in CD_2Cl_2. Sharp signals corresponding to a monodentate and a bidentate pyimypy ligand are observed. Unlike the phosphine-substituted compound, the halide-substituted $[Pd(pyimypy)_2Br]Br$ (**5**) and $[Pd(pyimypy)_2I][I]_{1/2}[PF_6]_{1/2}$ (**6**) are fluxional in CD_2Cl_2, in which broad signals (Figure 7a) are observed. Upon cooling the sample of the halide-substituted Pd-pyimypy compounds, the exchange process slows down, and at the slow exchange limit, three different pyridine signals are observed for the bromide salt (253 K) (Figure 7b) and the iodide salt (228 K). The tentative peak assignments are given with numbering on both the respective spectrum and a drawing of the corresponding molecular fragment on the upper left of the figure. For a rigid structure, four nonequivalent pyridine rings are expected. Assuming that the monodentate pyimypy can freely rotate around the Pd−C bond in solution, the two pyridines of the monodentate pyimypy are equivalent. These give three different pyridine signals. Thus the rigid molecules in solution have a molecular arrangement consistent with their solid-state structures.

Among the three fluxional molecules, the rate of the exchange process follows the order $[Pd(pyimypy)_2Br]Br < [Pd(pyimypy)_2I][I]_{1/2}[PF_6]_{1/2} < [Pd(pyimypy)_2][PF_6]_2$. At first glance, the correlation between the exchange rate and the number of halides in the molecule would suggest that the exchange process involves a dissociation of the halide (Scheme 3), such that the lesser the number of halides presents, the faster the observed exchange rate. However, upon addition of excess (∼10 equiv) ammonium salt Bu_4NX (X = Br and I), the exchange rate of the halide-substituted Pd-pyimypy compounds increases. Take $[Pd(pyimypy)_2Br]Br$ as an example: while a slow exchange process occurs at 253 K, the presence of a 10-fold excess of Br^- lowers the

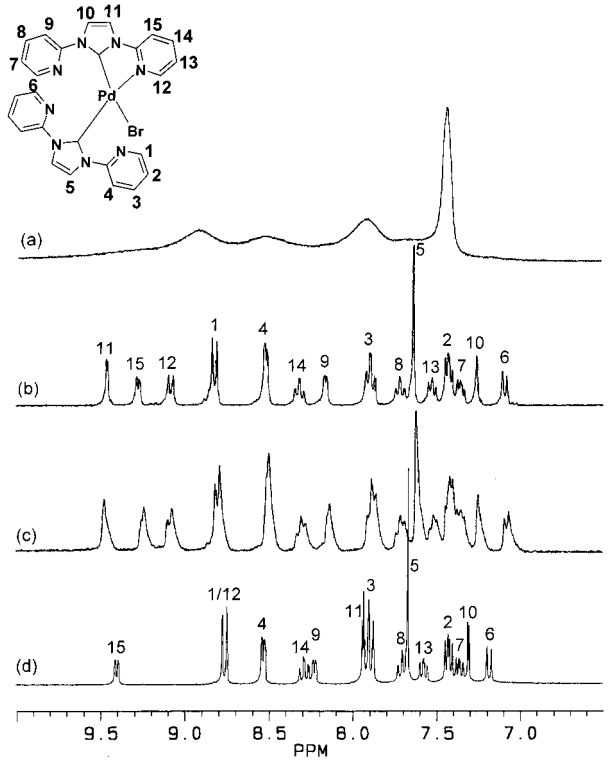
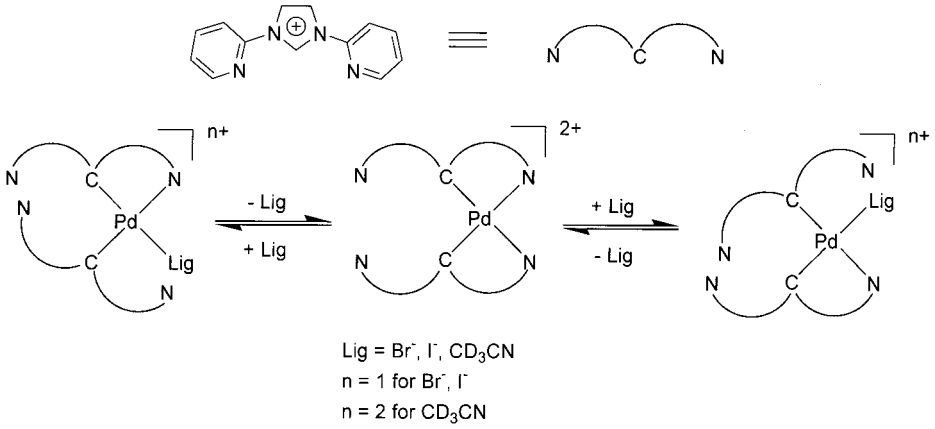


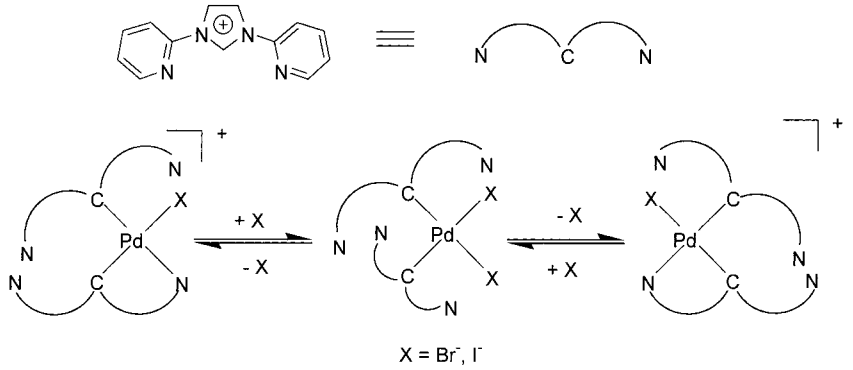
Figure 7. ^{1}H NMR spectra (in CD_2Cl_2) of $[Pd(pyimypy)_2Br]Br\cdot 2H_2O$ (**5**) (a) at room temperature; (b) at 253 K; (c) with 10 equiv of Bu_4NBr at 238 K; and (d) ^{1}H NMR spectrum $[Pd(pyimypy)_2Br][PF_6]$ at room temperature. Peak assignments are given with numbering on the spectrum and on the corresponding molecular fragment.

temperature for the exchange process to <238 K. This experiment suggests that the exchange process involves an association of the halide to produce an unstable intermediate which has two coordinated halides and two monodentate pyimypy ligands (Scheme 4). Further evidence for the halide-promoted exchange process comes from the room-temperature ^{1}H NMR spectrum of $[Pd(pyimypy)_2Br][PF_6]$, which has been prepared by the metathesis reaction of $[Pd(pyimypy)_2Br]Br$ with NH_4PF_6 in acetone. The lack of free bromide anion gives sharp signals corresponding to a rigid molecule in CD_2Cl_2. Note that the chemical shift of H-11 in the Br^- salt (Figure 7b) is substantially different from that of the PF_6^- salt (Figure 7d). This is likely caused by the difference in the H-bonding interaction between the H-11 and Br^- versus PF_6^-. The nonfluxional behavior of $[Pd(pyimypy)_2PPh_3][PF_6]_2$ parallels the result observed for $[Pd(pyimypy)_2Br][PF_6]$. However, unlike the halide-substituted complexes, the presence of free PPh_3 does not enhance the exchange process of the phosphine-substituted complex. This difference may be attributed to the steric bulkiness of PPh_3, such that the addition of PPh_3 to $[Pd(pyimypy)_2PPh_3][PF_6]_2$ (**7**) is sterically unfavorable. Although in this work we have been unable to isolate and observe the presence of a dihalo compound, McGuinness and Cavall did isolate dichloro palladium complexes of hemilabile carbenes.[12] The faster exchange rate observed for the iodo complex, which has a lesser number of iodides and has a faster exchange rate than that of the bromo complex, appears contradictory to the proposed associative process. This can be rationalized by noting that the iodide has a better

Scheme 3. Halide Dissociation or Acetonitrile Solvent-Assisted Exchange Process



Scheme 4. Halide Associative Exchange Process



affinity toward the Pd^{II} ion than bromide, such that the activation energy of the formation of diiodo transition state is lower, and a faster exchange rate may therefore be expected for the iodo complex. The fast exchange rate observed for $[Pd(pyimypy)_2][PF_6]_2$ (**4**) is likely due to the presence of bulk acetonitrile solvent. A fast equilibrium between $[Pd(pyimypy)_2]^{2+}$ and $[Pd(pyimypy)_2(acetonitrile)]^{2+}$ can generate a set of equivalent pyridines (Scheme 2).

We have attempted an initial catalytic copolymerization reaction of CO and norbornylene using $[Pd(pyimypy)_2][PF_6]_2$ (**4**) as a catalyst precursor. When the catalyst (0.014 mmol in 6 mL of CH_3CN), norbornylene (2.7 mmol in 10 mL of $CHCl_3$), and 750 psi of CO gas were charged to a 45 mL autoclave and the mixture was allowed to react for 3 days at 60 °C, white powder was obtained with a yield of ~87%. The IR spectrum revealed a CO stretching frequency of 1694 cm^{-1}. GPC analysis gave a $M_w = 4660$ and $M_n = 3790$, corresponding to a repeating unit of ~37. We expect this series of compounds to have a different catalytic behavior from that reported[12] by McGuinness and Cavell. This is because the chelate ring size, the rigidity of the chelate ring, and the number of potential coordinating pyridines between the two systems are different. Further studies are required to evaluate the catalytic properties of metal complexes using this type of 2-pyridylcarbenes.

In conclusion, a new terdentate ligand and its palladium complexes have been synthesized. This pyimypy ligand coordinates to palladium in a monodentate or bidentate fashion. Monodentate pyimypy bonds to palladium through the imy carbene site with two dangling pyridines. A bidentate pyimypy forms a five-membered chelate ring through an imy carbene and a pyridine. This chelate ring is relatively stable and is highly delocalized. Despite the stable chelate ring, homoleptic $[Pd(pyimypy)_2][PF_6]_2$ (**4**) is susceptible to substitution by halide or phosphine ligands due to the highly strained geometry around the palladium center. However, homoleptic $[Pd(pyimypy)_2][PF_6]_2$ (**4**) with excess halide or phosphine does not produce disubstituted complexes, a result that differs from the known palladium complexes of pyridylcarbene. The fluxional behavior of these complexes reflects the hemilabile properties of the chelate ring, the strong Pd−carbene bond relative to the Pd−pyridine bond, and the steric interactions between the pyimypy ligand and those other ligands around the palladium center. Although only the catalytic polymerization of CO/norbornylene has been examined, other catalytic reactions are promising. This is especially true because the ligand can be modified easily, and a variety of palladium complexes can be synthesized. A change in molecular geometry from square plane to octahedron is also expected for metal ions other than palladium(II).

Experimental Section

General Procedures. All the solvents and chemicals were purchased and used without further purification. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts, δ, in ppm are reported relative to the internal standard TMS for ^1H NMR. Microanalyses were performed by the Instrumentation Center of Taiwan. Melting points were determined in glass capillaries under air. IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer. GPC was recorded on a Viscotek LR40 laser refractometer.

[pyimypyH]Cl·H_2O (1). A mixture of 2-chloropyridine (4 g, 35.2 mmol) and 1-methylimidazole (1.45 g, 17.6 mmol) was heated neat with stirring at 190 °C. After 20 h, the reaction was stopped and the crude product was recrystallized from a mixture of MeOH/acetone (1:1 by volume) several times to give a white product in ~60% yield. Light yellow crystals of [pyimypyH]Cl·H_2O suitable for X-ray diffraction were obtained by recrystallization from MeOH (2.1 g, 43%). Mp: 269−270 °C (dec). ^{1}H NMR ($CDCl_3$, 25 °C): δ 13.01 (s, 1H, CH), 9.33 (d, ^3J = 9 Hz, 2H, CH), 8.56 (dd, ^3J = 4 Hz, ^4J = 2 Hz, 2H, CH), 8.49 (d, ^4J = 2 Hz, 2H, CH), 8.15 (dt, ^3J = 8 Hz, ^4J = 2 Hz, 2H, CH), 7.49 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 2H, CH). Anal. Calcd for $C_{13}H_{11}N_4Cl·H_2O$: C, 56.51; H, 4.75; N, 20.29. Found: C, 55.78; H, 4.83; N, 20.13.

[pyimypyH]Br·H_2O (2). This compound was prepared by the method described for that of [pyimypyH]Cl·H_2O (yield 56%). Mp: 280−282 °C (dec). ^{1}H NMR ($CDCl_3$, 25 °C): δ 12.50 (s, 1H, CH), 9.28 (d, ^3J = 8 Hz, 2H, CH), 8.56 (dd, ^3J = 4 Hz, ^4J = 2 Hz, 2H, CH), 8.50 (d, ^4J = 2 Hz, 2H, CH), 8.17 (dt, ^3J = 8 Hz, ^4J = 2 Hz, 2H, CH), 7.52 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 2H, CH). Anal. Calcd for $C_{13}H_{11}N_4Br·H_2O$: C, 48.62; H, 4.08; N, 17.44. Found: C, 48.60; H, 3.99; N, 17.94.

[pyimypyH][PF_6] (3). NH_4PF_6 (2.45 g, 15 mmol) in 20 mL of H_2O was added to an aqueous solution (10 mL) of [pyimypyH]Br·H_2O (4 g, 12.5 mmol). The resultant solution was stirred for 30 min. The white precipitate formed was filtered out and collected. The residue was recrystallized from CH_3CN to give colorless [pyimypyH][PF_6] (4.14 g, 90%). Mp: 208−211 °C. ^{1}H NMR (CD_3CN, 25 °C): δ 10.06 (s, 1H, CH), 8.67 (d, ^3J = 5 Hz, 2H, CH), 8.33 (s, 2H, CH), 8.17 (dt, ^3J = 8 Hz, ^4J = 2 Hz, 2H, CH), 7.93 (d, ^3J = 8 Hz, 2H, CH). 7.65 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 2H, CH) Anal. Calcd for $C_{13}H_{11}N_4PF_6$: C, 42.40; H, 3.01; N, 15.22. Found: C, 41.67; H, 2.90; N, 15.09.

[Pd(pyimypy)$_2$][PF_6]$_2$ (4). [pyimypyH][PF_6] (0.4 g, 1.1 mmol) and $Pd(OAc)_2$ (0.122 g, 0.55 mmol) were added to CH_3CN (60 mL). The solution was stirred at reflux temperature under N_2. After 16 h, the resultant solution was filtered, and the filtrate was dried under vacuum. The yellow residue was washed with water (15 mL), followed by EtOH (5 mL) and ether (15 mL). The residue was then recrystallized from CH_3CN to yield a pale yellow crystalline product (0.37 g, 80%). Mp: 285−287 °C. ^{1}H NMR (CD_3CN, 25 °C): δ 8.61 (d, ^3J = 5 Hz, 4H, CH), 8.17 (t, ^3J = 8 Hz, 4H, CH), 7.96 (d, ^3J = 8 Hz, 4H, CH), 7.85 (s, 2H, CH), 7.66 (dd, ^3J = 8 Hz, ^3J = 5 Hz, 4H, CH). Anal. Calcd for $C_{26}H_{20}N_8P_2F_{12}Pd$: C, 37.14; H, 2.40; N, 13.33. Found: C, 36.77; H, 2.39; N, 13.25.

[Pd(pyimypy)$_2$Br]Br·2H_2O (5). [pyimypyH]Br·H_2O (0.3 g, 0.94 mmol) and $Pd(OAc)_2$ (0.105 g, 0.47 mmol) were added to CH_3CN (60 mL). The solution was stirred at 70 °C under N_2. After 16 h, the solvent was removed under vacuum, and the yellow residue was washed with ether (15 mL). Recrystallization of the filtrate from CH_3CN yielded a yellow crystalline product (0.25 g, 72%). Mp: 249−251 °C. ^{1}H NMR (CD_3CN, 25 °C): broad bands are observed at δ 8.93, 8.55, 7.93, 7.45. Anal. Calcd for $C_{26}H_{20}N_8Br_2Pd·2H_2O$: C, 41.82; H, 3.24; N, 15.01. Found: C, 41.58; H, 3.15; N, 14.83.

[Pd(pyimypy)$_2$I][I]$_{1/2}$·[PF_6]$_{1/2}$ (6). [pyimypyH][PF_6] (0.4 g, 1.1 mmol) and $Pd(OAc)_2$ (0.122 g, 0.55 mmol) was added to CH_3CN (60 mL). The solution was stirred at reflux temperature under N_2. After 16 h, KI (0.365 g, 2.2 mmol) was added and the solution was maintained at refluxing condition for another 4 h. The resultant solution was filtered to remove the unreacted KI. The filtrate was evaporated to dryness under vacuum. The residue was washed as described for the previous compounds. Recrystallization from CH_3CN produced yellow crystals (0.33 g, 73%). Mp: 297−298 °C. ^{1}H NMR (CD_3CN, 25 °C): broad bands at δ 8.33, 8.01, 7.45. Anal. Calcd for $C_{26}H_{20}N_8I_{3/2}P_{1/2}F_3Pd$: C, 38.38; H, 2.48; N, 13.77. Found: C, 38.28; H, 2.33; N, 13.74.

[Pd(pyimypy)$_2$(PPh_3)][PF_6]$_2$ (7). PPh_3 (0.25 g, 0.96 mmol) in 15 mL of CH_2Cl_2 was added to a CH_3CN solution (30 mL) of [Pd(pyimypy)$_2$][PF_6]$_2$ (0.2 g, 0.24 mmol) and was stirred at room temperature for 16 h. After the reaction, the volume of the yellow solution was reduced to 3 mL. Slow addition of ether (15 mL) to the final solution gave yellow precipitates. Recrystallization from the CH_3CN/*n*-hexane produced pale yellow crystals (0.2 g, 75%). Mp: 255−257 °C. ^{1}H NMR (CD_3CN, 25 °C): δ 8.52 (d, ^3J = 4 Hz, 2H, CH), 8.26 (t, ^3J = 8 Hz, 1H, CH), 8.17 (s, 1H, CH), 8.10 (d, ^3J = 5 Hz, 1H, CH), 8.07 (d, ^3J = 8 Hz, 1H, CH), 7.98 (t, ^3J = 8 Hz, 2H, CH), 7.65 (d, ^3J = 8 Hz, 2H, CH), 7.63 ~ 7.15 (m, 21H, CH), 7.21 (s, 2H, CH), 7.03 (d, ^3J = 7 Hz, 1H, CH), 7.00 (d, ^3J = 7 Hz, 1H, CH). ^{31}P NMR (DMSO-d_6): δ 22.93 (s, PPh_3). Anal. Calcd for $C_{44}H_{35}N_8P_3F_{12}Pd$: C, 47.91; H, 3.20; N, 10.16. Found: C, 48.47; H, 3.10; N, 10.16.

[Pd(pyimypy)(PPh_3)$_2$Br]Br·$CH_3CN·H_2O$ (8). [pyimypyH]Br·H_2O (0.2 g, 0.62 mmol) and $Pd(OAc)_2$ (0.14 g, 0.62 mmol) were added to CH_3CN (60 mL). The solution was stirred at refluxing condition under N_2 atmosphere. After 16 h, PPh_3 (0.65 g, 2.48 mmol) and KBr (0.295 g, 2.48 mmol) were added, and the reaction was continued for 6 h. After the same workup procedures, the residue was recrystallized from CH_3CN/MeOH to afford [Pd(pyimypy)(PPh_3)$_2$Br]Br·$CH_3CN·H_2O$. (0.35 g, 55%). Mp: 268−269 °C. ^{1}H NMR (DMSO-d_6, 25 °C): δ 8.60 (d, ^3J = 6 Hz, 2H, CH), 7.96 (t, ^3J = 8 Hz, 2H, CH), 7.71 (s, 2H, CH), 7.62−7.25 (b, 30H, CH), 7.63 (dd, ^3J = 8 Hz, ^3J = 5 Hz, 2H, CH), 7.10 (d, ^3J = 8 Hz, 2H, CH). Anal. Calcd for $C_{49}H_{40}N_4P_2Br_2Pd·CH_3CN·H_2O$: C, 57.14; H, 4.23; N, 6.53. Found: C, 57.24; H, 3.74; N, 6.43.

Reaction of CO/Norbornylene Copolymerization. A $CHCl_3$ (10 mL) solution of norbornylene (500 mg, 5.3 mmol) and a CH_3CN solution (6 mL) of [Pd(pyimypy)$_2$][PF_6]$_2$ (23 mg, 0.027 mmol) were added to a 45 mL autoclave. This was then charged with 750 psi of CO gas. The reaction was carried out at 60 °C with stirring for 3 days. The resultant solution was then filtered, and the filtrate was evaporated to dryness to afford a white powder. The residual powder was washed with 5 mL of *n*-hexane and dry in a vacuum (575 mg). ^{1}H NMR ($CDCl_3$): δ 3.40−2.10 (b, 4H), 1.80−0.90 (b, 6H). ^{13}C NMR ($CDCl_3$): 227.4 (s), 53.1−49.7 (b), 43.2−37.5 (b), 32.1−23.0 (b). IR (KBr): ν_{CO} 1694 cm^{-1}.

X-ray Stracture Determinations. The diffraction experiments for **1**, **4**, and **5** were carried out on a Siemens P4 diffractometer; **8** was collected on a Siemens SMART diffractometer equipped with a CCD area detector. Complex **6** was carried out on Enraf-Nonius CAD4 diffractometer. Crystal data and details on data collection and refinements are given in Tables 1 and 2. The structure of **1** was solved by the standard direct method, and other palladium complexes **4**, **5**, **6**, and **8** were solved by the heavy metal method. Compound **1** was refined against F^2 by least-squares techniques (SHELXL-97) with all atoms. Other structures were refined against F^2 by least-squares techniques with nonhydrogen atoms, and the hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. For complex **8**, the molecule has mirror plane symmetry, and one of the pyridine rings of pyimypy is disordered.

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Supporting Information Available: Tables of crystal data, positional parameters for non-hydrogen and hydrogen atoms, bond distances and angles, and anisotropic thermal parameters for compounds **1**, **4**, **5**, **6**, and **8.** This material is available free of charge via the Internet at http://pubs.acs.org.

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