Synthesis and Dehydrative Condensation of Square-Planar Mono- and Dinuclear Hydroxopalladium Complexes with the Hydrotris(3,5-diisopropylpyrazolyl)borato Ligand (Tp^{iPr_2}), Tp^{iPr_2}(Py)Pd−OH, and $(\mu\text{-OH})_2\{PdTp^{iPr_2}(H_2O)\}_2$

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Received August 27, 1999

Mono- and dinuclear hydroxopalladium complexes (κ^2-$Tp^{iPr_2,X}$)(py)Pd−OH (**1**; X = H, Br) and $(\mu\text{-OH})_2\{Pd(\kappa^2\text{-}Tp^{iPr_2})(H_2O)\}_2$ (**2**) are prepared by base hydrolysis of the corresponding chloride complexes (κ^2-$Tp^{iPr_2,X}$)(py)Pd−Cl (**3**) and $(\mu\text{-Cl})_2\{Pd(\kappa^3\text{-}Tp^{iPr_2})\}_2$ (**4**), respectively. Functionalization of the OH part in **1** is effected via dehydrative condensation with protic substrates (H−A) to give a series of substituted products, (κ^2-Tp^{iPr})(py)Pd−A (**5**), and treatment of the dinuclear complex **2** with excess acetic acid affords the mononuclear diacetato complex **6**, (κ^2-Tp^{iPr_2}−H)Pd(OAc)$_2$(HOAc). Complexes **1**−**4** and **6** have been characterized crystallographically, and it is revealed that complexes **2** and **6** involve cyclic hydrogen-bonding interaction among the nitrogen atom of the pendent noncoordinated pyrazolyl group, the hydrogen atom in the protic part of the ligand (OH, AcOH), and, in the case of **2**, an external water molecule.

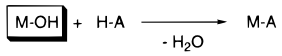
Introduction

Dehydrative condensation of transition metal hydroxo complexes is a versatile synthetic method, when the conjugated acid of the incoming ligand (H−A) is a protic substrate (Scheme 1).[1] In our laboratory, a series of transition metal peroxo complexes bearing hydrotris(pyrazolyl)borato ligands (A = OOR or O_2) have been successfully prepared via this synthetic method.[2−5] Herein we disclose the synthesis of two types of square-planar hydroxopalladium complexes, mononuclear [$Tp^{iPr_2,X}$-(L)Pd−OH] (**1**; X = H, Br) and dinuclear complexes [Tp^{iPr_2}-$Pd(H_2O)(\mu\text{-OH})_2(H_2O)PdTp^{iPr_2}$] (**2**), and some dehydrative condensations of them.[4−6]

Results and Discussion

Synthesis of Mononuclear Hydroxopalladium Complex $Tp^{iPr_2,X}$(py)Pd−OH (1). Synthetic procedures for mononuclear hydroxopalladium complexes are summarized in Scheme 2.

Scheme 1



Chloride complex **3**, a precursor for mononuclear complexes, was prepared by successive addition of pyridine and the potassium salt of the ligand ($KTp^{iPr_2,X}$) to a CH_2Cl_2 solution of $PdCl_2(PhCN)_2$. Upon addition of pyridine to $PdCl_2(PhCN)_2$, the mixture became cloudy, suggesting formation of $PdCl_2(py)_2$, but subsequent treatment with $KTp^{iPr_2,X}$ resulted in replacement of one of the two pyridine ligands to give the chloride complex **3** as a yellow solid. Complex **3a** was also obtained by treatment

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(5) Abbreviations used in this paper. Tp^{iPr_2}, hydrotris(3,5-diisopropylpyrazolyl)borate; $Tp^{iPr_2,Br}$, hydrotris(3,5-diisopropyl-4-bromopyrazolyl)-borate; $Tp^{iPr_2,X}$, Tp^{iPr_2} and $Tp^{iPr_2,Br}$; Tp^{Me_2}, hydrotris(3,5-dimethylpyrazolyl)borate; Tp^{R_x}, a general term for substituted hydrotris(pyrazolyl)-borate; pz^{iPr_2}, 3,5-diisopropylpyrazolyl; 4-pz^{R_2}−H, hydrogen atom at the 4-position of the pz^{R_2} ring.

(6) A part of the present result was already reported as a communication. See ref 3a.

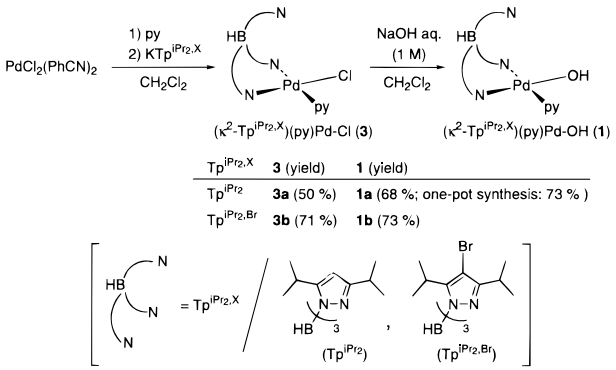
10.1021/ic991034e CCC: $19.00
Published on Web 04/22/2000

Table 1. Spectroscopic Data for the $Tp^{iPr_2,X}Pd$ Complexes **1**−**6**[a]

	^1H NMR/δ_H/ppm				
complex (X)	4-pz^{iPr_2}−H[b]	C*H*$(CH_3)_2$[c,d]	L	X	IR/cm^{-1}
1a	6.21,	4.62, 3.71 (2H),	8.85 (2H, dt, 5, 2)[e]	−1.79[h]	2476,[i] 1607,[k] 1536[j]
(H)	5.95,	2.98, 2.93,	6.67 (1H, tt, 8, 2)[f]		
	5.91	2.35	6.38 (2H, ddd, 8, 5, 2)[g]		
1b		4.63, 3.91,	8.49 (2H, dt, 6. 2)[e]	−1.93[h]	2506,[i] 1607,[k] 1513[j]
(Br)		3.83, 3.21,	6.59 (1H, tt, 8, 2)[f]		
		3.17, 3.09	6.30 (2H, ddd, 8, 6, 2)[g]		
2[m]	6.46 (2H),	4.01 (2H), 3.62 (4H),		−1.71	3556,[n] 2481,[i] 1537[j]
(H)	5.73 (4H)	3.49 (4H), 2.78 (2H)		(2H)	
3a[l]	5.96,[o]	3.98, 3.54	8.75 (2H, dt, 5, 2)[e]		2481,[i] 1607,[k] 1535[j]
(H)	5.82,	3.51, 2.79	7.68 (1H, tt, 8, 2)[f]		
	5.71[o]	2.59, 2.06	7.20 (2H, ddd, 8, 5, 2)[g]		
3b		4.78, 3.86,	8.52 (2H, m)[e]	2512,[i] 1608,[k] 1512[j]	
(Br)		3.77, 3.01	6.48 (1H, m)[f]		
		3.28 (2H)	6.18 (2H, m)[g]		
4[l,p]	6.33 (2H),	3.70 (2H),	2480,[i] 1536[j]		
(H)	5.72 (4H)	3.41 (8H),			
		2.84 (2H)			
5a	6.22,	4.71, 3.79,	9.11 (2H, m)[e]	3.02	2770,[r] 2485,[i] 1606,[k]
(H)	6.01,	3.65, 3.26,	6.72 (1H, m)[f]	(3H, s)[q]	1535,[j] 1217[s]
	5.91	2.98, 2.26	6.38 (2H, m)[g]		
5b	6.38,	4.55, 3.77,	9.11 (2H, d, 2)[e]	7.03 (2H, m)[u]	2475,[i] 1609,[k] 1587,[v]
(H)	5.90,	3.57, 3.25,	6.58 (4H, m),[f,t]	*t*	1535[j]
	5.89	3.08, 2.23	6.30 (2H, t, 7)[g]		
5c	6.33,[w]	4.24, 3.76,	9.21 (2H, dt, 5, 1)[e]	2.04	2478,[i] 1628,[x] 1607,[k]
(H)	5.89,	3.57, 3.15,	6.53 (1H, tt, 7, 1)[f]		1538,[j] 1322[x]
	5.76[o]	2.91, 2.48	*w*		
6	6.32,	3.82 (2H), 3.66,		2.03 (6H),	2552,[i] 1713,[x] 1609,[k]
(H)	5.82 (2H)	3.27 (2H), 3.10,		1.79 (3H)[y]	1575,[x] 1541,[j] 1499,[x]
					1459,[x] 1334[x]

[a] ^1H NMR spectra were observed in C_6D_6 at 400 MHz unless otherwise stated, and multiplicity and coupling constants (in Hz) are shown in parentheses. Signals without indication of multiplicity are singlet signals. IR spectra were recorded as KBr pellets. [b] The 4-pyrazolyl proton signals. [c] Septets with $J \approx 7$ Hz or multiplets. [d] Methyl signals appeared as doublets in the range 2−0 ppm. [e] Ortho proton signals. [f] Para proton signals. [g] Meta proton signals. [h] OH signals. [i] ν(BH). [j] ν(C═C) of pz rings. [k] ν(C═C) of py rings. [l] Observed in $CDCl_3$. [m] Observed in tol-d_8 at −45 °C. [n] ν(OH). [o] Slightly broad signals. [p] Observed at −20 °C. [q] Methyl signals. [r] ν(CH) for the OMe group. [s] ν(C−O). [t] Overlapped with the Ph signals. [u] Ph signals. [v] ν(C═C) of the Ph ring. [w] Overlapped with the 4-pz signal. [x] ν(C═O). [y] NH and OH proton signals could not be located.

Scheme 2



of the Cl-bridged dinuclear complex **4** (see below) with pyridine. A ^1H NMR spectrum of Tp^{iPr_2}(py)Pd−Cl (**3a**) contained three inequivalent 4-pyrazolyl proton signals (4-pz^{iPr_2}−H),[5] and the B−H vibration (IR) was observed in the range for κ^2-Tp^{iPr_2} ligands (<2500 cm^{-1})[3c] (Table 1). These data were consistent with a square-planar geometry, which was confirmed by X-ray crystallography of **3a**. An ORTEP view of **3a** is included in the Supporting Information, and its structural features will be discussed later together with the hydroxo complex.

The hydroxo complex **1** was prepared by treatment of a CH_2Cl_2 solution of the chloride complex **3** with aqueous NaOH solution. A variety of Tp^{R_x}M−OH and Tp^{R_x}(L)M−OH type compounds were prepared by this method.[4] Spectroscopic features of **1** were very similar to those of the precursor **3** (Table 1). Although OH vibration could not be detected by IR, ^1H NMR spectra of **1a** and **1b** contained singlet signals around δ_H −1.8 assignable to OH, which disappeared upon addition of D_2O. These data were consistent with the formulation of **1** as a square-planar hydroxopalladium complex with a κ^2-$Tp^{iPr_2,X}$ ligand, which was verified by X-ray crystallographic analysis of the 4-Br derivative **1b** (Figure 1). According to the CSD database, complex **1b** is a rare example of a structurally characterized mononuclear palladium complex with a terminal hydroxo ligand, whereas dinuclear μ-hydroxo complexes such as **2** have many precedents (see below). In addition, previous examples of mononuclear hydroxopalladium complexes, [(terpy)Pd−OH]-ClO_4·H_2O[7a] and Tp(1,4-butandiyl)Pd(IV)−OH·(μ-cresol)$_2$,[7b] contain hydrogen-bonding interactions with Lewis bases such as oxygen atoms of water and phenol molecules and counteranions, but no such interaction is present in **1**. Single crystals of **1b** contain a CH_2Cl_2 solvate, but the separation between the OH oxygen atom and the chlorine atom in the CH_2Cl_2 solvate (3.623(6) Å) exceeds the acceptable range of hydrogen-bonding interaction. Thus, the structure of the mononuclear complex **1b** reveals that such hydrogen-bonding interactions are not always a requisite for hydroxometal complexes.[4]

Structural parameters for **1a** and **3b** are summarized in Table 2. The square-planar coordination geometry of Pd is revealed by the following two structural features. (i) The Pd···N31 distances of ca. 3.1 Å are much longer than the other Pd−N11 and Pd−N21 distances of ca. 2.0 Å and reveal no bonding interaction between the Pd center and the free pyrazolyl ring

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Table 2. Selected Structural Parameters for the Core Parts of the $Tp^{iPr_2,X}Pd$ Complexes **1**−**6**[a]

	mononuclear complexes			dinuclear complexes	
complexes	**1b**	**3a**[b]	**6**[c]	**2**	**4**
Pd1−N11	2.016(6)	2.002(3)	2.007(4)	1.987(6)	1.989(4)
Pd1−N21	2.047(5)	2.015(3)	2.010(3)	2.019(7)	1.981(4)
Pd1−N31	3.808(6)	3.498(4)	3.199(4)	3.524(8)	2.785(4)
Pd1−N32	3.181(5)	3.105(3)	3.299(4)	3.158(8)	3.372(3)
Pd1-X	2.034(7) (N41)	2.032(3) (N41)	2.026(4) (O1)	2.018(6) (O1)	2.335(1) (Cl1)
Pd1−Y	2.011(4) (O1)	2.285(1) (Cl1)	2.025(3) (O3)	2.016(5) (O1*)	2.318(1) (Cl1*)
others			2.643(7) (N31−O2)	2.932(9) (O1−O2)	3.4694(6)
			2.576(6) (O4−O5)	2.78(1) (N31−O2)	(Pd1−Pd1*)
				3.0514(9) (Pd1−Pd1*)	
N11−Pd1−N12	87.3(2)	86.2(1)	87.6(1)	87.1(3)	86.6(1)
N11−Pd1-X	174.9(2) (N41)	176.7(1) (N41)	178.6(1) (O1)	172.7(2) (O1)	179.0(1) (Cl1)
N11−Pd1−Y	93.1(2) (O1)	92.59(9) (Cl1)	94.2(1) (O3)	93.1(3) (O1*)	95.5(1) (Cl1*)
N21−Pd1−X	95.2(2) (N41)	92.1(1) (N41)	93.1(1) (O1)	98.0(2) (O1)	94.3(1) (Cl1)
N21−Pd1−Y	179.5(2) (O1)	177.72(9) (Cl1)	177.2(2) (O3)	178.7(3) (O1*)	177.70(8) (Cl1*)
X−Pd1−Y	84.3(2)	89.01(9)	85.1(1)	81.7(3)	83.5(3)

[a] Interatomic distances in Å and bond angles in deg. [b] The numbering scheme for the core part of **3a** is the same as that of **1b** except for Cl1 (O1). [c] **6**: C1−O1, 1.286(6) Å; C1−O2, 1.228(7) Å; C3−O3, 1.278(7) Å; C3−O4, 1.217(8) Å; C5−O5, 1.305(8) Å; C5−O6, 1.182(7) Å.

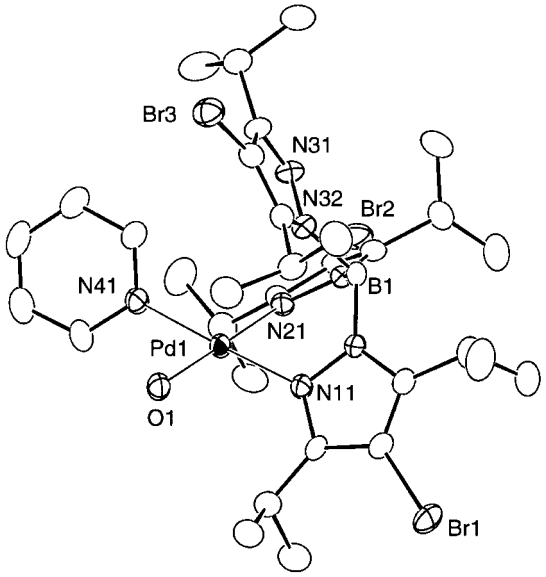
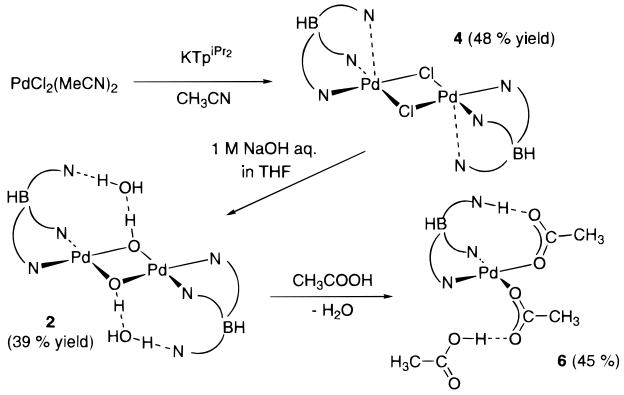


Figure 1. Molecular structure of **1b** drawn at the 30% probability level.

(i.e., κ^2-coordination of the Tp^{R_x} ligand). In κ^2-$Tp^{R_x}M$ complexes, it has been observed that the pendent pz^{R_x} rings are projected away from the metal center to minimize steric repulsions among the pz^{R_x} substituents and the ligands. The situation can be best described by the M···N31 distance being longer than the M···N32 distance (M−N31 > M−N32). (ii) The interligand angles fall in the range 84−95°, close to a right angle. The Pd−N(pyridine) lengths are essentially the same as the Pd−N(pz^{iPr_2}) lengths, which are similar to those in the previously reported $Tp^{iPr_2}Pd$ complexes.[3a,b] The Pd−O distance (2.011(4) Å) is comparable to the reported values of hydroxopalladium complexes (1.966(3) Å in [(terpy)Pd−OH]ClO_4·H_2O;[7a] 2.011(8) Å in Tp(1,4-butandiyl)Pd(IV)−OH·(μ-cresol)$_2$)[7b] and Pd−OPh complexes (2.106(3) Å in $(Me_3P)_2$(Cl)Pd−OPh;[8a] 2.098(6) Å in *cis*-(dmpe)(Me)Pd−OPh;[8b] 1.996(7), 1.983(6) Å in (bipy)Pd$(OPh)_2$).[8c] The Pd−Cl distance (2.285(1) Å) is similar to that in a related compound (2.288(1) Å in [(2,6-bis(2-imidazolin-2-yl)pyridine)Pd−Cl]$^+$).[9]

(8) (a) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1990**, *112*, 1096. (b) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* **1991**, *30*, 3371. (c) Kapteijn, G. M.; Grove, D. M.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg.Chem.* **1996**, *35*, 526.

Scheme 3



Synthesis of Dinuclear Hydroxopalladium Complex 2. Treatment of $PdCl_2(MeCN)_2$ with KTp^{iPr_2} in the absence of pyridine furnished the chloride-bridged dinuclear complex **4** (Scheme 3). It is essential to use the acetonitrile precursor and to carry out the reaction in acetonitrile, otherwise a complex mixture of products is obtained.

The very broad ^{1}H NMR spectrum of **4** observed at room temperature suggested dynamic behavior, and indeed sharp signals were obtained by lowering the temperature. At −45 °C, the 4-pz^{iPr_2}−H signal separated into two sets of absorptions in a 1:2 ratio, indicating a mirror symmetrical structure that was confirmed by X-ray crystallography (Figure 2a and Table 2). The square-planar PdN_2Cl_2 coordination geometry is similar to those of the mononuclear complexes discussed above, but a weak coordination of the third pz^{iPr_2} part is evidenced by the following observation. As for the Pd−N31,32 distances, the situation of complex **4** is opposite those of complexes **1b** and **3a** discussed above. The N31 lone pair electrons are projected toward the Pd center, and the N31 atom is located closer to the Pd center than the N32 atom is (Pd−N31 < Pd−N32), although the Pd−N31 separation (2.785(4) Å) is substantially longer than the coordinated Pd−N distances (∼1.98 Å). The weak coordination of the third pz^{iPr_2} group should be a result of increased Lewis acidity of the palladium center coordinated by the more electronegative Cl atoms. The Pd−Cl lengths are comparable to those in related square-planar dinuclear Cl-bridged (μ-Cl)$_2$-{Pd{κ^2-L)}$_2$ complexes: 2.408(2) and 2.428(2) Å in (μ-Cl)$_2$-

(9) Baker, A. T.; Craig, D. C.; Singh, P. *Aust. J. Chem.* **1991**, *44*, 1659.

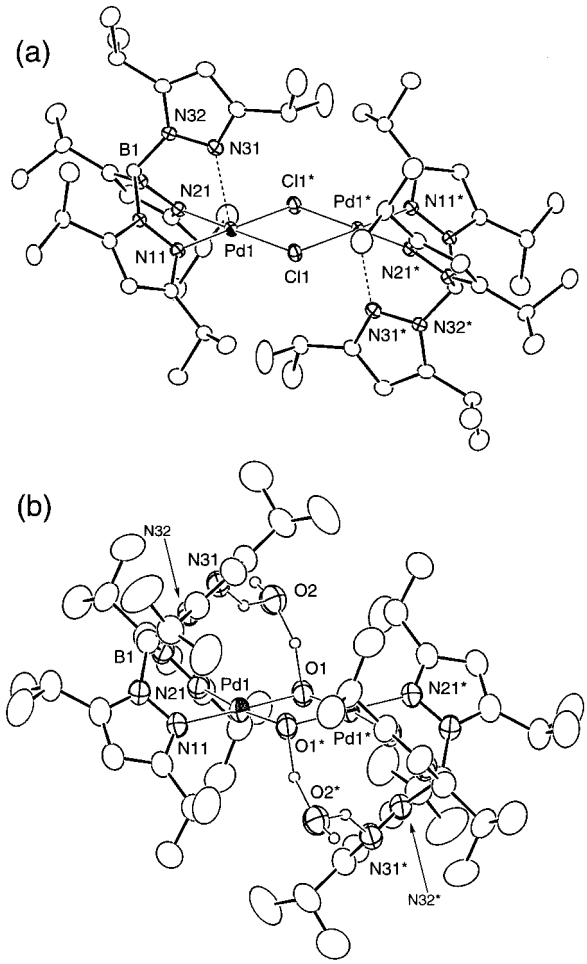
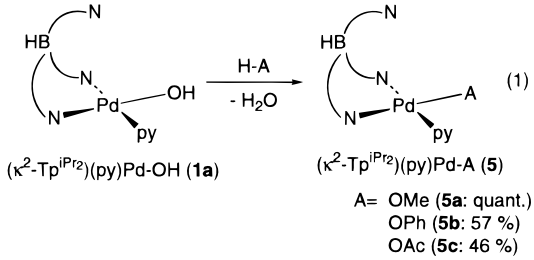


Figure 2. Molecular structures of **4** (a) and **2** (b) drawn at the 30% probability level.

{Pd(η^3-cycloheptenyl)}$_2$;[10a] 2.4630(6) and 2.4719(6) Å in (μ-Cl)$_2${Pd(η^3-cyclooctenyl)}$_2$;[10a] 2.337(1) Å (trans to N) in (μ-Cl)$_2${Pd($CH_2CH_2CH_2NMe_2$)}$_2$.[10b] Thus, the coordination geometry of Pd in **4** is best described as a distorted square pyramid. The weak coordination causes a shift of the ν_{BH} vibration to the κ^2-Tp^{iPr_2} region (<2500 cm^{-1}).[3c] The dynamic behavior of **4** can be explained in terms of a mechanism involving pseudorotation of the Tp^{iPr_2} ligand associated with the κ^2−κ^3 hapticity change, and analogous mechanisms have been well documented for square-planar (κ_2-Tp^{R_x})ML$_2$ complexes (M = Ru, Rh).[11]

Hydrolysis of the Cl-bridged dimer **4** with aqueous NaOH solution successfully afforded the μ-hydroxo complex **2** (Scheme 3). The presence of an OH group is revealed by the ν_{OH} vibration at 3556 cm^{-1}, and the other ^{1}H NMR and IR features are very similar to those of the chloride precursor **2**. A broad ^{1}H NMR spectrum sharpened at a low temperature, and a mirror symmetrical structure was suggested by the 1:2 pattern of the 4-pz^{iPr_2}−H signals. Although these features are apparently consistent with a structure analogous to **4**, Tp^{iPr_2}Pd(μ-Cl)$_2$PdTp^{iPr_2}, X-ray crystallography (Figure 2b) revealed a dinuclear structure containing a unique ternary hydrogen-bonding interaction among a water molecule, the μ-OH oxygen atom, and the noncoordinated pz^{iPr_2} nitrogen atom. The O1···O2 (2.932(9) Å) and O2···N31 distances (2.78(1) Å) are in the range of hydrogen-bonding interactions, and the Pd−O distances (2.018(6) (O1) and 2.016(5) Å (O1*)) are comparable to those in previously reported complexes containing a diamond (μ-OH)$_2$Pd$_2$ core (2.068(6) and 2.077(6) Å in [(μ-OH)$_2${Pd(C_6F_5)$_2$}$_2$]$^{2-}$;[12a] 2.140(4) and 2.142(5) Å in (μ-OH)(μ-NHBu^t){Pd(Ph)(PPh$_3$)}$_2$;[12b] 2.125(6) Å in (μ-OH){Pd(Ph)(PPh$_3$)}$_2$CrCp(CO)$_3$;[12c] 2.052−2.126(10) Å in (μ-OH)$_2${Pd(Ph)(PPh$_3$)}$_2$;[12d] 2.082(4) Å in [(μ-OH)$_2${Pd(dppp)}$_2$]$^{2+}$;[12e] 2.209(5) and 2.034(5) Å in (μ-OH)(μ-Br){Pd(C_6H_4-2-CH_2NMe_2)}$_2$;[12f] 2.093(4) and 2.195(5) Å in (μ-OH)(μ-NHC$_6$H$_4$-4-OMe){Pd(Ph)(PPh$_3$)}$_2$;[12g] 2.075(3) and 2.81(3) Å in [(μ-OH)$_2${Pd(PMe$_3$)$_2$}$_2$]$^{2+}$).[12h] When the ligand (L$_1$, L$_2$) in (κ^2-Tp^{iPr_2})PdL$_1$L$_2$ possesses a protic hydrogen atom located at a distance appropriate for hydrogen-bonding with the nitrogen atom of the noncoordinated pz^{iPr_2} ring, formation of a hydrogen bond leads to a stable chelating structure. Such an interaction has been noted for the hydroperoxopalladium complex (κ^2-Tp^{iPr_2})(Ph$_3$P)Pd−OOH[3b] and the acetato complex **6** (see below), where the protic OOH and AcOH hydrogen atoms are hydrogen-bonded with the pendent pz^{iPr_2} nitrogen atoms, respectively. The situation of **2** is different from these in that the water molecule intervenes between the two components to form a ternary hydrogen bond because the OH···N31 separation is too long for formation of a binary hydrogen bond. The mirror symmetrical ^{1}H NMR features even at low temperatures (1:2 patterns for the 4-pz^{iPr_2}−H signals) may be a result of dissociation of the water molecule in solution because the intensity of the singlet OH signal at δ_H −1.71 is for two protons (water signal could not be located), and ^{1}H NMR spectra with mirror-symmetrical features consistent with the dissociated form similar to **4** were obtained even at low temperatures. The dynamic behavior of the dehydrated form, (μ-OH)$_2$(PdTp^{iPr_2})$_2$, can be explained in terms of a mechanism as discussed for **4**.[11]

Dehydrative Condensation of Hydroxo Complexes 1a and 2 with Protic Substrates. The obtained mononuclear hydroxo complex **1a** was subjected to dehydrative condensation with a couple of protic substrates with varying acidity (eq 1). The acidic



substrates, PhOH and AcOH, readily reacted to give the corresponding condensates **5b** and **5c**, respectively. Even less acidic MeOH was condensed with **1a**, and crystallization of **1a** from MeOH gave **5a**. In addition, condensation with hydroperoxides (ROOH) successfully afforded a series of peroxopalladium complexes as we reported previously in a communication.[3a,b]

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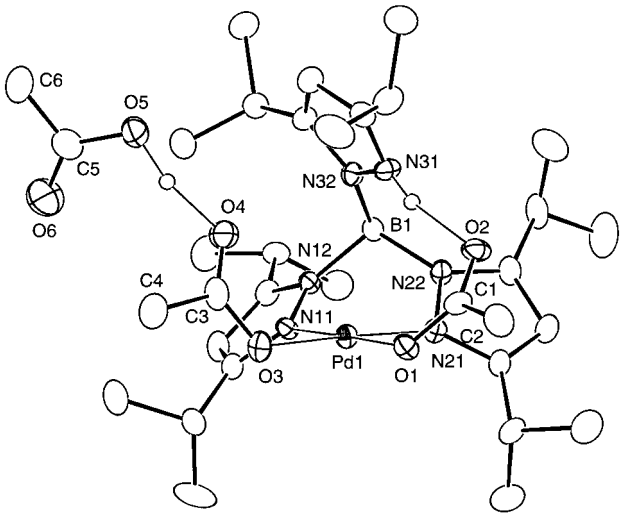


Figure 3. Molecular structures of **6** drawn at the 30% probability level.

The square-planar products (κ^2-Tp^{iPr_2})(py)Pd−A (**5**) were readily characterized on the basis of their spectroscopic features similar to **3**, i.e., (1) ν_{BH} vibration below 2500 cm^{-1} indicating κ^2-coordination of the Tp^{iPr_2} ligand[3c] and (2) three inequivalent 4-pz^{iPr_2}−H signals indicating an unsymmetrical structure.

To examine the condensation ability of the dinuclear complex **2**, the reaction with acetic acid was examined. Treatment of **2** with an excess amount of acetic acid followed by crystallization from pentane afforded a mononuclear diacetate complex hydrogen-bonded to another molecule of acetic acid **6** (Scheme 3). A ^{1}H NMR spectrum of **6** contains two sets of acetate−methyl and 4-pz^{iPr_2}−H signals in a 1:2 ratio, and an IR spectrum containing several $\nu_{C=O}$ vibrations reveals the presence of multiple acetate functional groups. Although the 1:2 ^{1}H NMR pattern suggests a mirror symmetrical structure, X-ray crystallography reveals an unsymmetrical structure containing three acetate groups formulated as (κ^2-Tp^{iPr_2}−H)Pd(OAc)$_2$(HOAc) (Figure 3). One of the two coordinated acetato ligands is hydrogen-bonded to the noncoordinated pz^{iPr_2} nitrogen atom (N31···O2, 2.643(7) Å) in a manner similar to **2** discussed above, and the other acetato ligand is hydrogen-bonded to the third acetic acid molecule (O4···O5, 2.576(6) Å). Because of the hydrogen-bonding interaction, which causes delocalization of π electrons of the two acetato ligands over the O−C−O linkage, bond alternation is not clear for the acetato ligands; i.e., the C−O lengths are in the narrow range (C1−O1, 1.286(6) Å; C1−O2, 1.228(7) Å; C3−O3, 1.278(7) Å; C3−O4, 1.217(8) Å), whereas the C−O and C═O bonds in the third acetate group are in the typical ranges (C5−O5, 1.305(8) Å; C6−O5 Å, 1.182(7) Å). The Pd coordination geometry is a typical square-planar one.

The reaction proceeds in a stepwise manner because dinuclear intermediates such as the mono-μ-hydroxo−mono-μ-acetato complex (μ-OH)(μ-OAc)(PdTp^{iPr_2})$_2$ and the bis-μ-acetato complex (μ-OAc)$_2$(PdTp^{iPr_2})$_2$ were adeventitiously obtained from reactions of **2** with lesser amounts of acetic acid and identified spectroscopically (see Experimental Section). The symmetrical ^{1}H NMR feature of **6** suggests dissociation of the third AcOH molecule in solution and switching of the N··H··O hydrogen bond between the two acetato ligands.

Attempted Diastereoselective Synthesis of Chiral Complexes Using Optically Active N Donors. *cis*-(L′)$_2$Pd(L)−X-type square-planar complexes have no element of asymmetry. But when a pendant that leads to differentiation of the two square-planar faces is attached to the ligand, square-planar

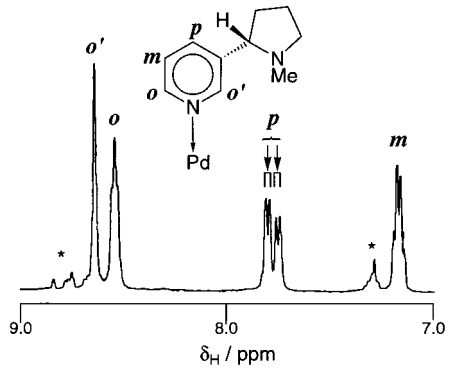
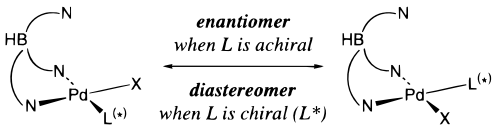


Figure 4. Pyridyl ^{1}H NMR signals of **7** observed at −40 °C (in $CDCl_3$ at 400 MHz). Peaks with asterisks are due to impurities.

Scheme 4



complexes can be chiral. (κ^2-Tp^{iPr_2})(L)Pd−X-type complexes fall in this category (Scheme 4). If a chiral hydroxo complex (X = OH) is obtained, it is expected to work as a unique chiral base.[13] Then we attempted diastereoselective synthesis of chiral complexes using optically active N donors (nicotine and quinidine) and phosphine (PPh$_2$(neomenthyl)).

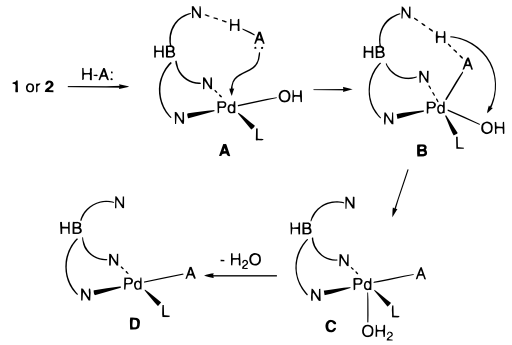
The chloride complex with nicotine ligand, (κ^2-Tp^{iPr_2})-(nicotine)Pd−Cl (**7**), was obtained as a pale-yellow solid by a procedure similar to the preparation of **3**. The spectroscopic features of **7** (ν_{BH} = 2479 cm^{-1}; three 4-pz^{iPr_2}−H ^{1}H NMR signals) were very similar to those of **3**, indicating formation of an analogous square-planar complex. Although a ^{1}H NMR spectrum observed at room temperature contained only a single set of signals suggesting selective formation of one diastereomer, upon cooling the sample to −40 °C the *p*-pyridyl signal separated into two doublets as shown in Figure 4 and diastereoselectivity was estimated to be ca. 15% de. Because it was difficult to recover **7** from the reaction mixture because of its great solubility in organic solvents, the less soluble dimethyl derivative (Tp^{Me_2}) **8** was also prepared but the diastereoselectivity was found to be worse than **7** (5% de). Base hydrolysis of the chloride complex **7** afforded a new complex tentatively assigned as the corresponding hydroxo complex (κ^2-Tp^{iPr_2})-(nicotine)Pd−OH. Attempted syntheses of chloride complexes with quinidine, 2-methyloxazoline, and PPh$_2$(neomenthyl) ligands resulted in a mixture of products from which no characterizable compounds could be isolated.

Conclusions

Mono- (**1**) and dinuclear hydroxopalladium complexes (**2**) are prepared successfully by base hydrolysis of the corresponding chloride precursors **3** and **4**, respectively, and fully characterized by spectroscopic and crystallographic analyses. The mononuclear complex **1** readily reacts with a series of protic substrates (H−A) to give condensates (κ^2-Tp^{iPr_2})(py)Pd−A (**5**), and the dinuclear complex **2** is found to be condensed with acetic acid. In contrast to the static mononuclear complexes **1**, **3**, **5**, and **6**, dinuclear complexes **2** and **4** exhibit dynamic behavior

(13) Fujii, A.; Hagiwara, E.; Sodeoka, M. *J. Am. Chem. Soc.* **1999**, *121*, 5450.

Scheme 5



and the averaging of the pz^{R_x} signals has been interpreted in terms of a combination of fast $\kappa^2-\kappa^3$ interconversion and pseudorotation of the Tp^{R_x} ligand.

In addition to these aspects, a common structural motif involving hydrogen-bonding interactions has been noted for (κ^2-Tp^{iPr_2})(L)Pd−A-type complexes, where A contains a protic hydrogen atom, i.e., **2**, **6**, and (κ^2-Tp^{iPr_2})(PPh_3)Pd−OOH. The pendant, noncoordinated pz^{iPr_2} nitrogen atom is hydrogen-bonded to the protic hydrogen atom in A to form a stable chelating structure. The structural motif suggests a plausible reaction mechanism of dehydrative condensation of the square-planar hydroxopalladium complexes **1** and **2**. The pendent pz^{R_x} group may assist incorporation of a nucleophile via formation of hydrogen-bonding interaction (**A**) as shown in Scheme 5 because the pz^{R_x} nitrogen atom is the most basic site in the molecule. Subsequent nucleophilic attack of the lone pair electrons of A at the Pd center to give a trigonal-bipyramidal intermediate (**B**) followed by proton migration (**C**) and water elimination would furnish the condensate (**D**).

Experimental Section

General Methods. All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques. THF, pentane, hexane (Na−K alloy), MeOH ($Mg(OMe)_2$), CH_2Cl_2, and MeCN (CaH_2) were treated with appropriate drying agents, distilled, and stored under argon. ^1H and ^{13}C NMR spectra were recorded on JEOL EX400 (^1H, 400 MHz; ^{13}C, 100 MHz) and Bruker AC200 spectrometers (^1H: 200 MHz). Solvents for NMR measurements containing 0.5% TMS were dried over molecular sieves, degassed, distilled under reduced pressure, and stored under Ar. IR spectra were obtained on a JASCO FT/IR 5300 spectrometer. KTp^{iPr_2},[14] $NaTp^{iPr_2,Br}$,[3e] $PdCl_2(PhCN)_2$,[15] and $PdCl_2(MeCN)_2$[16] were prepared according to the reported methods. Other chemicals were purchased and used without further purification. Details of X-ray crystallography are included in Supporting Information.

Preparation of (κ^2-Tp^{iPr_2})(py)Pd−Cl (3a). Addition of pyridine (0.80 mL, 9.9 mmol) to a CH_2Cl_2 solution (25 mL) of $PdCl_2(PhCN)_2$ (804 mg, 2.10 mmol) caused an immediate color change from red-brown to pale-yellow, and a yellow precipitate ($PdCl_2(py)_2$) appeared. Then KTp^{iPr_2} (1.07 g, 2.12 mmol) was added to the mixture, and the resultant mixture was stirred for 1 h at room temperature. After removal of insoluble materials by filtration through a Celite plug, the volatiles of the filtrate were removed under reduced pressure. The residue was washed with hexane and crystallized from CH_3CN to give **3a** as yellow crystals (722 mg, 1.05 mmol, 50% yield). Anal. Calcd for $C_{32}H_{51}BN_7ClPd$: C, 55.98; H, 7.50; N, 14.28. Found: C, 56.49; H, 7.61; N, 14.35.

Preparation of (κ^2-$Tp^{iPr_2,Br}$)(py)Pd−Cl (3b). Following the procedure described for **3a** using $PdCl_2(PhCN)_2$ (523 mg, 1.36 mmol), pyridine (0.60 mL, 6.2 mmol), and $KTp^{iPr_2,Br}$ (995 mg, 1.79 mmol), the 4-Br derivative **3b** was obtained as a pale-yellow solid (886 mg, 0.959 mmol, 71% yield) after crystallization from CH_2Cl_2−hexane. Anal. Calcd for $C_{32}H_{48}BN_7ClBr_3Pd$: C, 41.63; H, 5.25; N, 10.62; Cl, 3.84; Br, 25.96. Found: C, 41.64; H, 5.41; N, 10.81; Cl, 4.03; Br, 25.43.

Preparation of (κ^2-Tp^{iPr_2})(py)Pd−OH (1a). (i) Hydrolysis of 3a. To a CH_2Cl_2 solution (5 mL) of **3a** (308 mg, 0.595 mmol) was added aqueous 2 M NaOH solution (2.0 mL), and the mixture was stirred for 15 h at room temperature. The aqueous layer was removed via a syringe, and the organic layer was dried over Na_2SO_4. Concentration followed by addition of hexane gave **1a** as a pale-yellow solid (201 mg, 0.402 mmol, 68% yield).

(ii) One-Pot Synthesis from $PdCl_2(PhCN)_2$. Upon addition of pyridine (3 mL) to a CH_2Cl_2 solution (25 mL) of $PdCl_2(PhCN)_2$ (3.018 g, 7.88 mmol) the solution changed from dark-red to yellow and yellow precipitates ($PdCl_2(py)_2$) appeared. Then KTp^{iPr_2} (3.992 g, 7.91 mmol) was added. After the resulting mixture was stirred for 90 min at room temperature, inorganic salts were removed by filtration through a Celite pad. To the filtrate was added aqueous 1 M NaOH solution (20 mL), and the mixture was stirred for 25 h at room temperature. Then the aqueous layer was removed via a syringe and the organic layer was dried over Na_2SO_4. Filtration through a Celite pad and concentration followed by addition of pentane gave **1a** (3.848 g, 5.76 mmol, 73% yield) as a pale-yellow solid, which was collected on a glass frit and dried under reduced pressure. Anal. Calcd for $C_{32}H_{52}BN_7OPd$: C, 57.52; H, 7.80; N, 14.68. Found: C, 57.10; H, 7.76; N, 14.75.

Preparation of (κ^2-$Tp^{iPr_2,Br}$)(py)Pd−OH (1b). Complex **1b** was obtained from $PdCl_2(PhCN)_2$ (380 mg, 0.99 mol), pyridine (0.4 mL, 4.95 mmol), and $NaTp^{iPr_2,Br}$ (720 mg, 0.99 mol) following method ii described for complex **1a**. Anal. Calcd for $C_{32}H_{51}BN_7O_2Br_3Pd$ (**1b**·H_2O): C, 41.65; H, 5.58; N, 10.63. Found: C, 41.25; H, 5.26; N, 10.30.

Preparation of ($Tp^{iPr_2}Pd)_2(\mu$-Cl)$_2$ (4). A mixture of $PdCl_2(MeCN)_2$ (456 mg, 1.76 mmol) and KTp^{iPr_2} (883 mg, 1.76 mmol) dissolved in MeCN (30 mL) was stirred for 40 min at ambient temperature. After filtration through a Celite pad, the volatiles were removed under reduced pressure. Extraction of the residue with CH_2Cl_2 followed by crystallization from CH_2Cl_2−hexane gave **4** as dark-red crystals (524 mg, 0.423 mmol, 48% yield). Anal. Calcd for $C_{54}H_{92}B_2N_{12}Cl_2Pd_2$: C, 53.38; H, 7.65; N, 13.84. Found: C, 52.90; H, 7.57; N, 13.75.

Preparation of ($Tp^{iPr_2}Pd\cdot OH_2)_2(\mu$-OH)$_2$ (2). To a THF solution (12 mL) of **4** (238 mg, 0.196 mmol) was added aqueous 1 M NaOH solution (2 mL), and the mixture was stirred for 1 h at room temperature. The aqueous layer was removed via a syringe, and the organic layer was dried over Na_2SO_4. Filtration through a Celite pad followed by crystallization from THF gave **2** as yellow crystals (93 mg, 0.076 mmol, 39% yield). Anal. Calcd for $C_{54}H_{98}B_2N_{12}O_4Pd_2$ (**4**·$(H_2O)_2$): C, 53.41; H, 8.15; N, 13.85. Found: C, 53.57; H, 7.97; N, 13.99.

Preparation of (κ^2-Tp^{iPr_2})(py)Pd−OMe (5a). Recrystallization of **1a** from MeOH gave **5a** as a pale-yellow solid. Anal. Calcd for $C_{33.5}H_{56}BN_7O_{1.5}Pd$ (**5a**·$(MeOH)_{0.5}$): C, 57.63; H, 8.10; N, 14.05. Found: C, 57.42; H, 7.86; N, 14.35.

Preparation of (κ^2-Tp^{iPr_2})(py)Pd−OPh (5b): Reaction of 1a with PhOH. A mixture of **1a** (114 mg, 0.171 mmol) and PhOH (20 mg, 0.21 mmol) dissolved in CH_2Cl_2 (2 mL) was stirred for 35 min at ambient temperature. Removal of the volatiles under reduced pressure and washing the residue with hexane gave **5b** (73 mg, 0.098 mmol, 57% yield) as yellow solids. Anal. Calcd for $C_{38}H_{56}BN_7OPd$: C, 61.32; H, 7.60; N, 13.18. Found: C, 60.77; H, 7.53; N, 13.16.

Preparation of (κ^2-Tp^{iPr_2})(py)Pd−OAc (5c): Reaction of 1a with AcOH. A mixture of **1a** (70 mg, 0.105 mmol) and AcOH (7 mL, 0.12 mmol) dissolved in CH_2Cl_2 (2 mL) was stirred for 2 h at ambient temperature. Removal of the volatiles under reduced pressure, extraction with CH_2Cl_2−hexane, filtration through a Celite pad, and crystallization gave **5c** (34 mg, 0.0477 mmol, 46% yield) as a pale-yellow solid. Anal. Calcd for $C_{34}H_{54}BN_7O_2Pd$: C, 57.50; H, 7.68; N, 13.81. Found: C, 58.58; H, 7.83; N, 13.49.

Preparation of ($Tp^{iPr_2,Br}$)PdOAc(AcOH)$_2$ (6): Reaction of 4 with AcOH. A toluene solution (2 mL) of **2** (93 mg, 0.076 mmol) and AcOH (18 mL, 0.31 mmol) was stirred for 20 min at room temperature. After removal of the volatiles under reduced pressure the residue was

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(16) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 218.

crystallized from pentane to give **6** as pale-yellow crystals (52 mg, 0.70 mmol, 45% yield). Anal. Calcd for $C_{33}H_{57}BN_6O_6Pd$: C, 52.76; H, 7.66; N, 11.19. Found: C, 52.38; H, 7.76; N, 11.10.

Dinuclear intermediates (μ-OH)(μ-OAc)($PdTp^{iPr_2}$)$_2$ and (μ-OAc)$_2$-($PdTp^{iPr_2}$)$_2$ were adventitiously obtained from reaction of **2** with 1−2 equiv of acetic acid and characterized spectroscopically. Analytically pure samples could not be obtained. For (μ-OH)(μ-OAc)($PdTp^{iPr_2}$)$_2$, ^{1}H NMR (in $CDCl_3$ at −20 °C): δ_H 6.00, 5.72, 5.61 (s × 3, 2H × 3, 4-pz^{iPr_2}−H), 3.75, 3.37, 3.20, 3.14 (2H × 4, sept, J = 7 Hz, C*H*Me_2), 3.44 (4H, sept, J = 7 Hz, C*H*Me_2), 1.85 (3H, s, CH_3COO), −2.56 (1H, s, OH). IR: 2489 (ν_{BH}), 1537 (ν_{pz}), 1566, 1418 cm^{-1} ($\nu_{C=O}$). For (μ-OAc)$_2$($PdTp^{iPr_2}$)$_2$, ^{1}H NMR (in $CDCl_3$ at −20 °C): δ_H 6.34 (s, 2H, 4-pz^{iPr_2}−H), 5.82 (s, 4H, 4-pz^{iPr_2}), 1.84 (6H, s, CH_3COO × 2). IR: 1564, 1393 cm^{-1} ($\nu_{C=O}$).

Preparation of (Tp^{iPr_2})(nicotine)Pd−Cl (7). Nicotine (91 mL, 0.566 mmol) was added to a CH_2Cl_2 solution (10 mL) of $PdCl_2(MeCN)_2$ (147 mg, 0.566 mmol). After the solution was stirred for 5 min, KTp^{iPr_2} (285 mg, 0.566 mmol) was added and the resulting mixture was stirred for 1 h at room temperature. Resultant TlCl was removed by filtration through a Celite pad. After filtration through a Celite pad, the volatiles under reduced pressure and the yellow oily residue were dissolved in hexane. Stirring the mixture for 1 h caused precipitation of Tp^{iPr_2}Pd-(pz^{iPr_2}−H)Cl. Filtration, concentration to ca. 2 mL and cooling at −70 °C for 3 weeks gave **7** as a trace amount of yellow crystals. ^{1}H NMR ($CDCl_3$ at room temperature): δ_H 5.97, 5.82, 5.68 (1H × 3, s × 3, 4-pz^{iPr_2}−H) (Tp ^{iPr_2}), 8.66 (1H, s, o′-py), 8.57 (1H, d, J = 5.7 Hz, o-py), 7.75 (1H, d, J = 6.3 Hz, p-py), 7.13 (1H, t, J = 6.6 Hz, μ-py) (nicotine). Other signals overlapped with each other and could not be analyzed. (With $CDCl_3$ at −40 °C, see Figure 4.) IR (KBr): 2479 cm^{-1} (ν_{BH}). Anal. Calcd for $C_{37}H_{60}BN_8ClPd$: C, 57.74; H, 7.86; N, 14.56. Found: C, 57.62; H, 7.98; N, 14.14.

Preparation of (Tp^{Me_2})(nicotine)Pd−Cl (8). Nicotine (235 mL, 1.46 mmol) was added to a CH_2Cl_2 solution (15 mL) of $PdCl_2(MeCN)_2$ (379 mg, 1.46 mmol). After the solution was stirred for 5 min, $TlTp^{Me_2}$ (500 mg, 1.46 mmol) was added and the resulting mixture was stirred for 3 h at room temperature. The resultant TlCl was removed by filtration through a Celite pad. Concentration to ca. 2 mL followed by addition of hexane gave pale-yellow precipitates. The supernatant solution was removed via a syringe, and the residue was washed with hexane twice. Crystallization from MeCN gave **8** as pale-yellow solids (593 mg, 68% yield). ^{1}H NMR ($CDCl_3$ at room temperature): δ_H 5.93, 5.84, 5.75 (1H × 3, br s × 3, 4-pz^{Me_2}−H), 1.5−2.6 (3H × 6, d, Me) (Tp^{Me_2}), 8.70 (1H, s, o′-py), 8.61 (1H, d, J = 4.9 Hz, o-py), 7.81 (1H, d, J = 7.3 Hz, p-py), 2.60 (3H, s, NMe) (nicotine). Other signals overlapped with each other and could not be analyzed. IR (KBr): 2460 cm^{-1} (ν_{BH}). Anal. Calcd for $C_{22}H_{36}BN_8ClPd$: C, 49.93; H, 6.03; N, 18.64. Found: C, 49.60; H, 6.15; N, 18.60.

Acknowledgment. We are grateful to the Ministry of Education, Science, Sports, and Culture of the Japanese Government for financial support of this research (Grants-in-Aid for Scientific Research, Nos. 08102006 and 11228201). C.M.-K. thanks the DAAD (German Academic Exchange Service) for a scholarship.

Supporting Information Available: Experimental details of X-ray crystallography. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991034E