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Synthesis and Structural Analysis of Palladium(II) Complexes Containing Neutral or Anionic C_2-Symmetric Bis(oxazoline) Ligands: Effects of Substituents in the 5-Position

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Ⓢ *Supporting Information*

ABSTRACT: A series of neutral and cationic palladium(II) complexes containing C_2-symmetric bis(oxazoline) (BOX) ligands, (BOX)PdCl$_2$ (**2a−d**), (BOX)Pd(Me)Cl (**3a−d**), and [(BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6^-$ (**4a−d**) [BOX: 2,2′-(2-propylidene)bis{(4R)-4-phenyl-5,5-dimethyl-2-oxazoline}, 2,2′-methylenebis{(4R)-4-phenyl-5,5-dimethyl-2-oxazoline}, 2,2′-methylenebis{(4R)-4,5,5-triphenyl-2-oxazoline}, and 2,2′-methylenebis{(4R,5S)-4,5-diphenyl-2-oxazoline}], were prepared, and their structures were determined by X-ray crystallography. It was found that substituents at the 5-position (Ph, Me) in addition to substituents on the bridgehead carbon directly affect the structure around palladium, especially the BOX bite angle and the dihedral angles between the phenyl rings at the 4-position and the N$_2$Pd plane. Treatment of the bridged methylene proton in the BOX ligand (**1b−d**) with KH afforded the anionic BOX ligand; also, the neutral Pd complexes, (BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N) (**5b−d**), could thus be prepared by reaction with Pd(Me)Cl(cod) (cod = 1,5-cyclooctadiene); **5b−d** showed strong coordination to Pd, as demonstrated by X-ray crystallographic analysis.

$R^1,R^2 = Me,Me$ (**a**); H,Me (**b**); H,Ph (**c**); H,(Ph,H) (**d**)
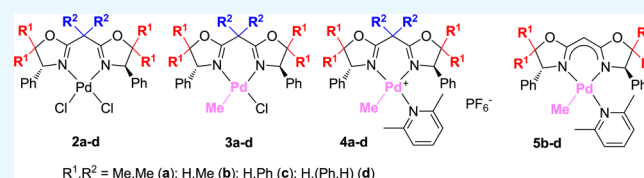
INTRODUCTION

Carbon−carbon bond formation is one of the most important reactions in synthetic chemistry; transition metal−alkyl complexes play roles as reagents or intermediates in stoichiometric/catalytic organic reactions and olefin polymerization.[1−6] The synthesis and reaction chemistry of the metal alkyls are thus important in the design of efficient catalysts as well as to better understand the reaction mechanisms. Palladium complexes are widely used as catalysts in efficient carbon−carbon bond formation reactions, such as coupling reactions and olefin oligomerization/polymerization.[7−16] In particular, palladium complexes containing α-diimine ligands[17−24] and phosphine−sulfonate ligands[25−30] are known to be effective catalysts for ethylene copolymerization, not only with α-olefin, but also with olefins containing polar functional groups.[31−33]

The synthesis and reaction chemistry of transition metal complexes containing optically active C_2-symmetric ligands are an important subject for the design of asymmetric catalytic reactions. Zirconocene complexes containing C_2-symmetric ligands, exemplified as [Me$_2$Si(indenyl)$_2$]ZrCl$_2$,[34,35] and nickel complexes containing C_2-symmetric α-diimine ligands[36−38] have been used as the catalysts for the isospecific polymerization of α-olefins. Chiral bis(oxazoline) (BOX, **1**) has also been employed as a highly attractive neutral C_2-symmetric bidentate ligand in various transition metal catalysts (such as Cu, Pd, Ni, Zn, Fe, Rh, Mg, Li, Mn, and Co);[39−41] various

palladium-catalyzed organic transformations are also known.[42−64] However, in contrast to their wide applications in organic transformations, the synthesis and structural analyses of a series of metal complexes with different ligand substituents have not yet been explored in detail. Such a study would provide important information for the design of efficient catalysts and also increase understanding of catalysis. Some studies have been published concerning the effects of modifications (such as Ph, t-Bu, benzyl, or naphthyl) at the 4-position of BOX ligands, adjacent to the metal center, on the selectivity/activity of catalytic reactions.[39−41] In contrast, we herein focus on modification at the 5-position because we assumed at an early stage that modification at this position should also play a role in asymmetric induction (the structure around the metal center) and thus in the reactivity, probably on the basis of the stabilities of the catalytic intermediates. In fact, the introduction of substituents (methyl and phenyl groups) at the 5-position in BOX affects its reactivity in nickel-catalyzed ethylene polymerization and ethylene/1-hexene copolymerization.[65,66] However, reports concerning the effects of the substituents on the basis of structural analysis (isolated complexes) remain limited.

Chart 1. Neutral or Cationic Pd Complexes Containing C_2-Symmetric BOX Ligands 2−5

R^1 = H, Me, Ph, R^2 = H, Me
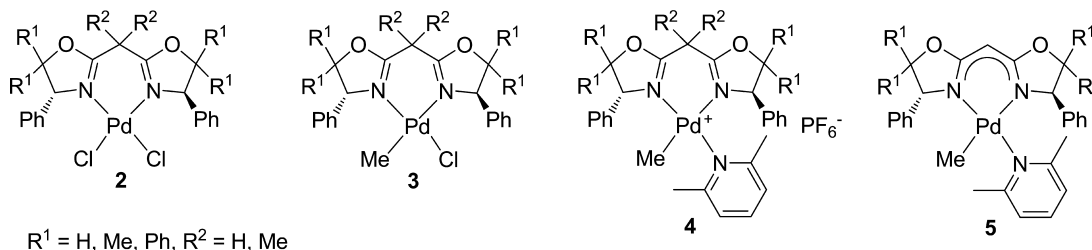
Scheme 1. Synthesis of C_2-Symmetric BOX Ligands (1a−c)

6a: R^1 = Me, 92%
6c: R^1 = Ph, 89%

1a: 74%

6a: R^1 = Me
6c: R^1 = Ph

7b: R^1 = Me
7c: R^1 = Ph

1b: R^1 = Me, 61%
1c: R^1 = Ph, 68%

1b   **1c**   **1d**
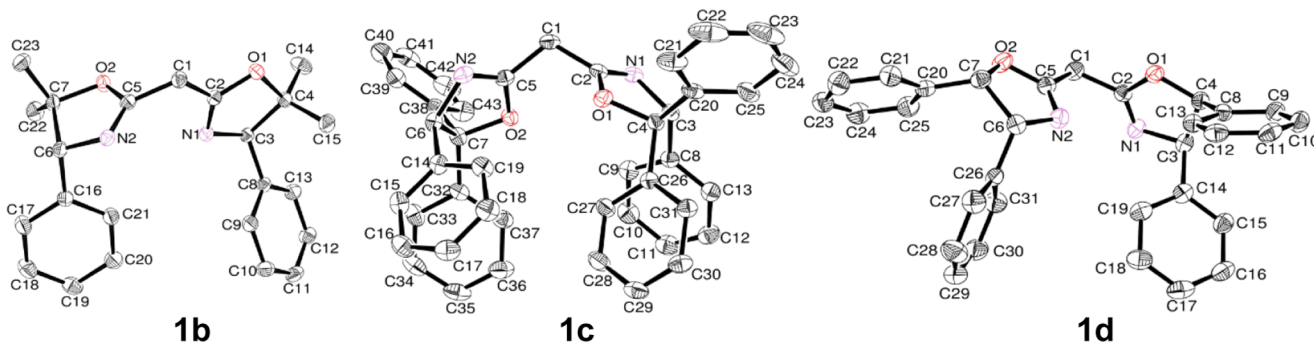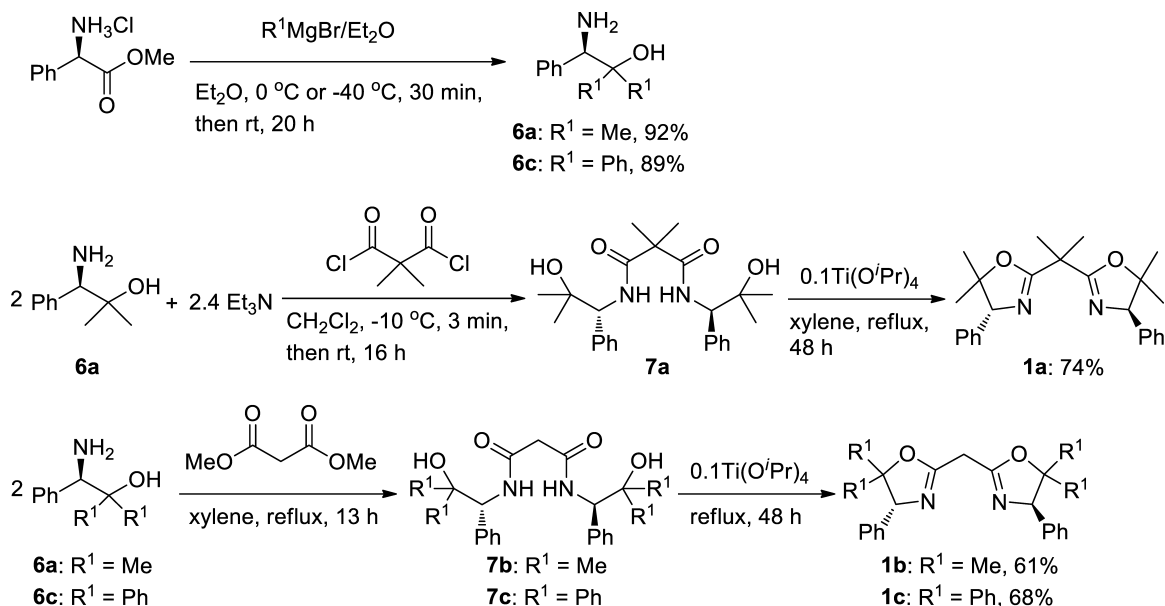
Figure 1. Oak ridge thermal ellipsoid plot (ORTEP) drawings for BOX **1b−d**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Therefore, in this article, we have explored the synthesis and structural analysis of a series of neutral and cationic palladium(II) complexes containing BOX ligands (shown in Chart 1), (BOX)PdCl$_2$ (**2a−d**), (BOX)Pd(Me)Cl (**3a−d**), and [(BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6^-$ (**4a−d**) [BOX: 2,2′-(2-propylidene)bis{(4R)-4-phenyl-5,5-dimethyl-2-oxazoline}, 2,2′-methylenebis{(4R)-4-phenyl-5,5-dimethyl-2-oxazoline}, 2,2′-methylenebis{(4R)-4,5,5-triphenyl-2-oxazoline}, and 2,2′-methylenebis{(4R,5S)-4,5-diphenyl-2-oxazoline}]. Moreover, we have prepared a series of novel neutral (BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N) (**5b−d**) (Chart 1) by deprotonation of the bridgehead methylene protons using KH. Through this research, we sought to obtain basic information concerning the effects of ligands on their structures (coordination modes

and electronic states) for better understanding the performance of catalysts.

■ RESULTS AND DISCUSSION

Synthesis and Molecular Structure of C_2-Symmetric BOX Ligands (1a−d). We focused on C_2-symmmetric BOX ligands containing methyl or phenyl substituents at the 5-position in the oxazoline ring and at the bridgehead carbon between two oxazolines to explore their influences on the structures of a series of BOX−palladium(II) complexes. Because optically active amino alcohol derivatives (**6**) bearing substituents (R^1) can be synthesized by the reaction of amino ester hydrochloride salt with Grignard reagents (Scheme 1),

various substituents (R^1) can be thus introduced in BOX ligands using these amino alcohols as a starting material. First, optically active amino alcohols, (R)-1-amino-2-methyl-1-phenylpropan-2-ol (6a) and (R)-2-amino-1,1,2-triphenyletha-nol (6c), were prepared using modifications of reported procedures (Scheme 1).[67,68] The reaction of chiral amino alcohol 6a with oxalyl chloride in the presence of triethylamine afforded N^1,N^3-bis((R)-2-hydroxy-2-methyl-1-phenylpropyl)-2,2-dimethylmalonamide (7a); then, intramolecular dehydration condensation of 7a using Ti(O^{i}Pr)$_4$ as a catalyst afforded 2,2′-(2-propylidene)bis{(4R)-4-phenyl-5,5-dimethyl-2-oxazo-line} (1a). One-pot syntheses were conducted for 2,2′-methylenebis{(4R)-4-phenyl-5,5-dimethyl-2-oxazoline} (1b) and 2,2′-methylenebis{(4R)-4,5,5-triphenyl-2-oxazoline} (1c). Condensation of amino alcohol 6a or 6c with dimethylmalo-nate afforded the corresponding bisamide alcohol (7b or 7c) in situ; then, the addition of Ti(O^{i}Pr)$_4$ afforded BOX (1b or 1c) in good overall yields. Furthermore, the detailed structures of BOX (1b, 1c) and commercially available BOX (1d) were confirmed by X-ray crystallography (Figure 1). There were no significant differences in the bond lengths or angles, as shown in Table 1.

Table 1. Selected Bond Distances (Å) and Angles (deg) for BOX 1b−d

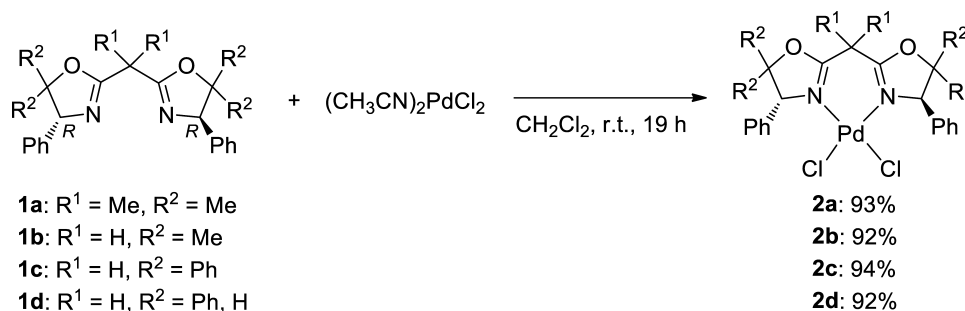|	BOXs		
	1b	1c	1d
Selected Bond Distances (Å)			
C(1)−C(2)	1.501(3)	1.492(3)	1.500(5)
C(1)−C(5)	1.493(3)	1.504(3)	1.506(4)
N(1)−C(2)	1.268(3)	1.262(3)	1.277(4)
N(2)−C(5)	1.272(3)	1.267(3)	1.277(4)
Selected Bond Angles (deg)			
C(2)−C(1)−C(5)	111.24(14)	110.69(16)	109.4(3)
N(1)−C(2)−C(1)	125.21(16)	126.80(18)	126.5(3)
N(2)−C(5)−C(1)	126.03(16)	126.30(18)	126.2(3)

Synthesis and Characterization of Neutral (BOX)PdCl$_2$ (2a−d). Reactions of BOX (1a−d) with equimolar amounts of PdCl$_2$(CH$_3$CN)$_2$ in CH$_2$Cl$_2$ at room temperature (25 °C) afforded the corresponding dichloro complexes, (BOX)PdCl$_2$ (2a−d), in high yields (92−94%, Scheme 2); these were identified by NMR spectra and elemental analyses (shown in the Experimental Section). The structures of 2a−d were also determined by X-ray crystallography (shown below).[69]
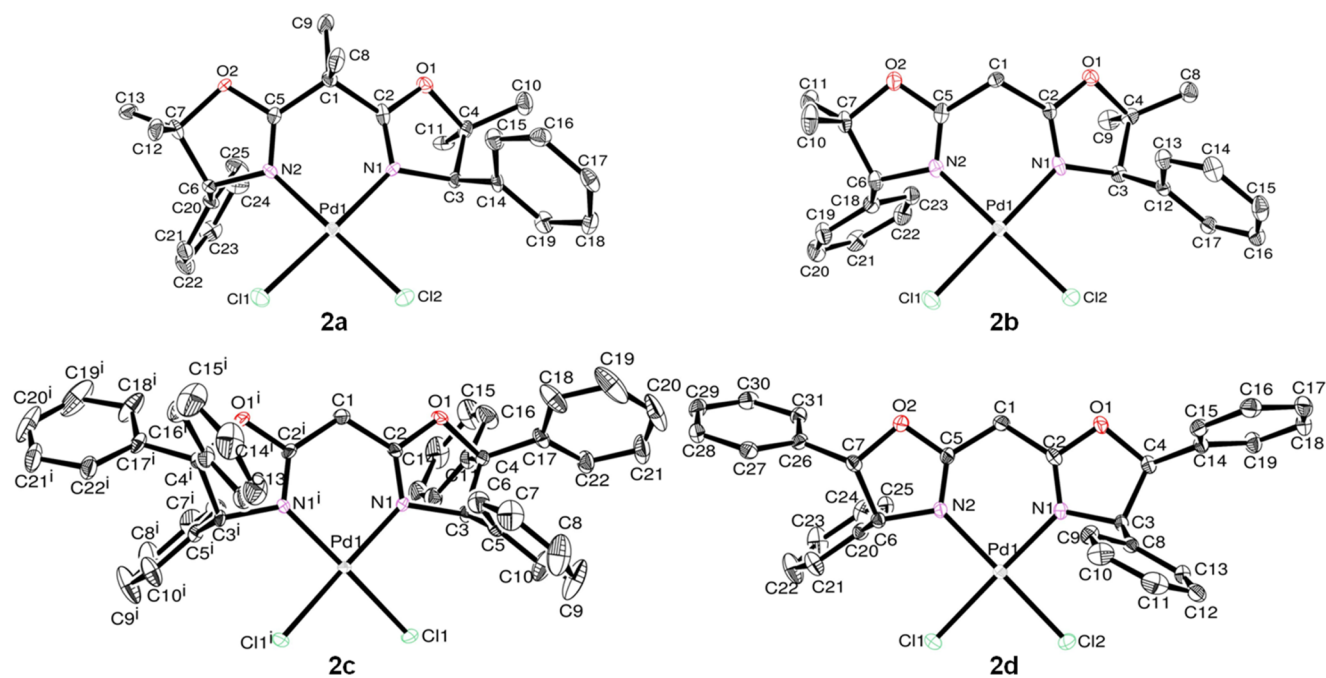
Figure 2 shows ORTEP drawings of complexes 2a−d; their selected bond lengths and angles are summarized in Table 2. These complexes fold around palladium in a square planar

geometry consisting of two chlorine ligands and two nitrogen atoms in the BOX ligand. The total bond angles around palladium are close to 360° [sums of the bond angles of N(1)−Pd(1)−N(2), Cl(1)−Pd(1)−Cl(2), N(1)−Pd(1)−Cl(2), and N(2)−Pd(1)−Cl(1): 2a: 360.03°, 2b: 360.07°, 2c: 360.46°, 2d: 359.95°], suggesting that palladium, two chlorine ligands, and two nitrogen atoms exist almost on the same plane [mean deviations from the plane in 2a: 0.0193 Å, 2b: 0.0292 Å, 2c: 0.0000 Å, 2d: 0.0228 Å]. It was found that the bridge angles of C(2)−C(1)−C(5) in 2b−d [2b: 114.3(3)°, 2c: 115.9(4)°, 2d: 115.3(3)°] are larger than those in 1b−d [1b: 111.24(14)°, 1c: 110.69(16)°, 1d: 109.4(3)°]. These angles are influenced by the coordination of the BOX ligand to palladium, whereas no significant differences in the bond lengths between (BOX)-PdCl$_2$ (2b−d) and BOX (1b−d) were observed (as shown in Tables 1 and 2). It is noteworthy that complex 2a [87.17(16)°] has a smaller coordination angle in the BOX ligand than that of complexes 2b−d [88.88(11)−88.98(13)°], whereas no significant differences in the angles were observed in 2b−d. The bridge angle of C(2)−C(1)−C(5) in 2a [110.1(4)°] is also smaller than that in 2b−d [114.3(3)−115.9(4)°], probably because of the geminal dimethyl groups at the bridgehead carbon C(1) in the BOX ligand. These data suggest that the substituents at the bridgehead carbon (not at the 5-position) control the BOX coordination angle, which should influence both the catalytic reactivity and selectivity.[70−72]

The geometry of the substituent at the 4-position in the oxazoline ring should affect the selectivity and reactivity of BOX-metal catalysts because the substituents influence the size of the coordination site on the metal (Figure 3). In fact, the dihedral angle (the mean value of the Ph^1−N2PdCl2 and Ph^2−N2PdCl2 dihedral angles, Table 2) in 2a−d decreases in the following order: 2a (98.362°) > 2b (93.707°) > 2d (90.667°) > 2c (89.910°). The distance between Pd and the para-carbon (p-C) of the phenyl groups at the 4-position (mean value of Pd−p-C in the Ph^1 and Ph^2 distances, Table 2) also decreases in the following order: 2a (6.057 Å) > 2b (6.017 Å) > 2d (5.886 Å) > 2c (5.773 Å). These results highly suggest that steric bulk in the substituents at the 5-position decreases the dihedral angles as well as the Pd−p-C distances, whereas the geminal dimethyl groups at the bridgehead carbon increase these angles and distances (Figure 3). Consequently, the reactivities and selectivities of catalytic reactions should be attributed to the introduction of substituents, especially at the 5-position, in BOX. In fact, the enhanced reactivities and/or selectivities have been reported for several reactions using (BOX)metal catalysts (palladium: allylic alkylation[48] and hydroarylation;[57] nickel: polymerization[65,66] and conjugate addition;[73] copper: cyclo-

Scheme 2. Synthesis of (BOX)PdCl$_2$ (2a−d)

1a: R^1 = Me, R^2 = Me
1b: R^1 = H, R^2 = Me
1c: R^1 = H, R^2 = Ph
1d: R^1 = H, R^2 = Ph, H

2a: 93%
2b: 92%
2c: 94%
2d: 92%

Figure 2. Oak ridge thermal ellipsoid plot (ORTEP) drawings for (BOX)PdCl₂ ($\mathbf{2a-d}$). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for (BOX)PdCl₂ ($\mathbf{2a-d}$)[a]

	(BOX)PdCl₂			
	2a	**2b**	**2c**	**2d**
	Selected Bond Distances (Å)			
C(1)−C(2)	1.519(7)	1.494(6)	1.488(5)	1.481(5)
C(1)−C(5)	1.522(6)	1.493(5)	1.488(5), C(1)−C(2^{i})	1.492(5)
N(1)−C(2)	1.285(7)	1.285(4)	1.277(4)	1.276(5)
N(2)−C(5)	1.265(7)	1.276(5)	1.277(4), N(1^{i})−C(2^{i})	1.280(4)
Pd(1)−N(1)	2.035(5)	2.031(3)	2.030(3)	2.032(3)
Pd(1)−N(2)	2.030(4)	2.041(3)	2.030(3), Pd(1)−N(1^{i})	2.037(3)
Pd(1)−Cl(1)	2.2975(19)	2.2936(10)	2.2877(12)	2.2951(12)
Pd(1)−Cl(2)	2.2796(16)	2.2827(11)	2.2877(12), Pd(1)−Cl(1^{i})	2.2792(11)
	Selected Bond Angles (deg)			
C(2)−C(1)−C(5)	110.1(4)	114.3(3)	115.9(4) C(2)−C(1)−C(2^{i})	115.3(3)
N(1)−C(2)−C(1)	127.8(5)	127.5(3)	129.3(4)	129.7(3)
N(2)−C(5)−C(1)	127.6(4)	127.5(4)	129.3(4) N(1^{i})−C(2^{i})−C(1)	128.7(3)
N(1)−Pd(1)−N(2)	87.17(16)	88.98(13)	88.94(12) N(1)−Pd(1)−N(1^{i})	88.88(11)
Cl(1)−Pd(1)−Cl(2)	89.10(7)	89.25(4)	88.38(5) Cl(1)−Pd(1)−Cl(1^{i})	87.69(4)
N(1)−Pd(1)−Cl(2)	92.28(12)	91.00(10)	91.57(10) N(1)−Pd(1)−Cl(1)	91.38(9)
N(2)−Pd(1)−Cl(1)	91.48(13)	90.84(10)	91.57(10) N(1^{i})−Pd(1)−Cl(1^{i})	92.00(9)
	Dihedral Angles (deg)			
Ph^{1}−N2PdCl2	95.905	87.827[a]	89.910	81.246
Ph^{2}−N2PdCl2	100.819	99.487[a]	89.910	100.088
	Distances between Pd and *p*-C (Ph) (Å)			
Pd−*p*-C(Ph^{1})	5.994	5.813[a]	5.773	5.705
Pd−*p*-C(Ph^{2})	6.119	6.222[a]	5.773	6.066

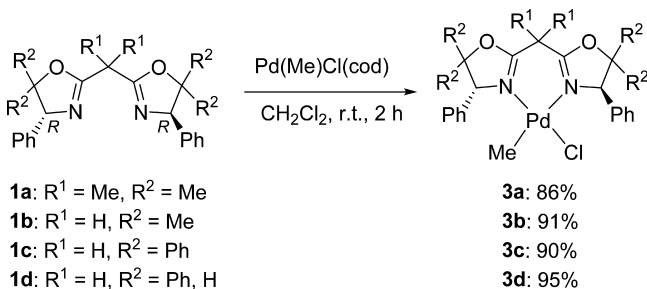[a]Mean values of four structures.
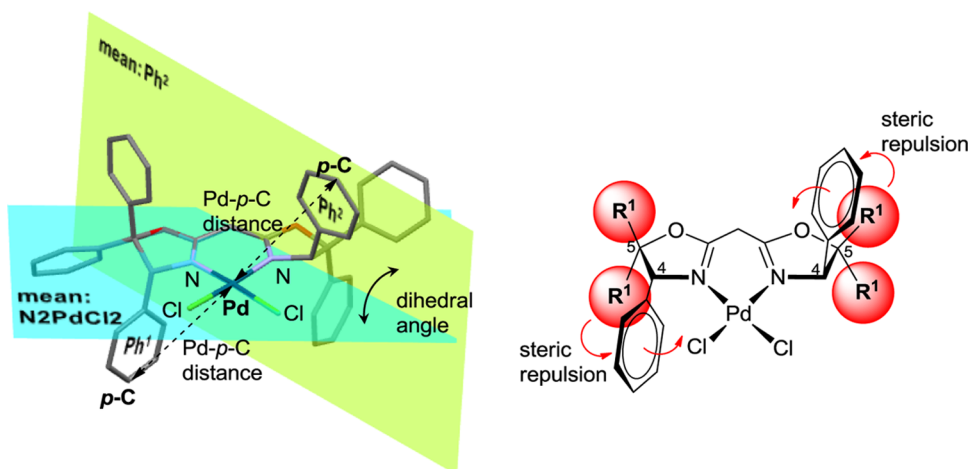
Figure 3. Left: X-ray structure of (BOX)PdCl$_2$ (**2c**). Right: Steric repulsion between the Ph groups at the 4-position and the substituents (R^1) at the 5-position in the oxazoline ring.

propanation[74−76] and dearomatization;[77] and lanthanide: hydroamination/cyclization).[78]

Synthesis and Characterization of Neutral (BOX)Pd-(Me)Cl (3a−d). Reaction of **1a−d** with Pd(Me)Cl(cod) (cod = 1,5-cyclooctadiene) in CH$_2$Cl$_2$ at room temperature afforded (BOX)Pd(Me)Cl (**3a−d**) in high yields (86−95%, Scheme 3);

Scheme 3. Synthesis of (BOX)Pd(Me)Cl (3a−d)

1a: R^1 = Me, R^2 = Me

1b: R^1 = H, R^2 = Me

1c: R^1 = H, R^2 = Ph

1d: R^1 = H, R^2 = Ph, H

3a: 86%

3b: 91%

3c: 90%

3d: 95%

these were identified by NMR spectra and elemental analysis (shown in the Experimental Section). The ^{1}H NMR spectrum of each complex shows resonance of the corresponding protons of the methyl group bound to palladium in a high magnetic field (**3a**: 0.07 ppm, **3b**: 0.10 ppm, **3c**: 0.25 ppm, **3d**: 0.22 ppm in CD$_2$Cl$_2$ at 25 °C).
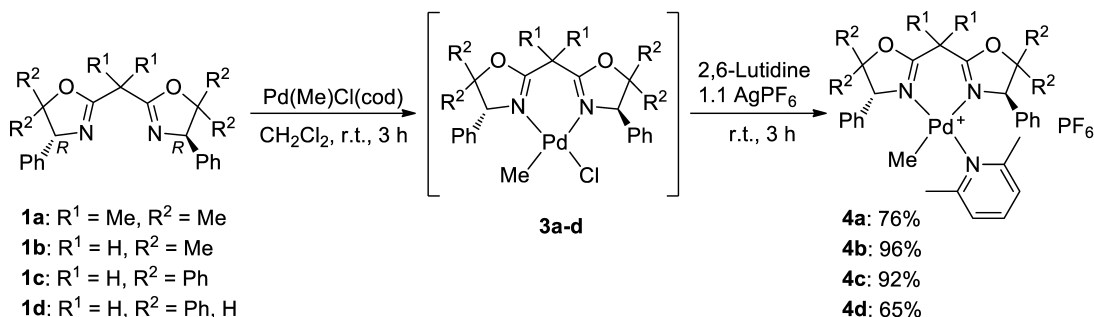
Single crystals of (BOX)Pd(Me)Cl (**3a, 3c**) were grown by slow diffusion of *n*-hexane into dichloromethane solution, and the structures were confirmed by X-ray crystallography (Figure 4, Table 3). In crystallographic analyses of **3a,c**, the R1 and wR2 values are a little higher than those of complexes **2a−d** due to the disordered Me and Cl groups bonding to Pd (**3a**: R1 = 0.0550, wR2 = 0.1442; **3c**: R1 = 0.0493, wR2 = 0.1229; **2a−d**: R1 = 0.0238−0.0279, wR2 = 0.0571−0.0731). Similar to complexes **2a−d**, complexes **3a** and **3c** fold around palladium in a square planar geometry consisting of two nitrogen atoms in the BOX ligand and chlorine and methyl ligands. The total bond angles around palladium are close to 360° (sums of the bond angles of N(1)−Pd(1)−N(2), Cl(1)−Pd(1)−C(1), N(1)−Pd(1)−Cl(1), and N(2)−Pd(1)−C(1): **3a**: 360.1° and **3c**: 360.0°), suggesting that the methyl group attached to palladium exists on the plane consisting of palladium, chlorine, and two nitrogen atoms (mean deviations from the plane in **3a**, 0.0211 Å and in **3c**, 0.0289 Å). The bond lengths of Pd(1)−C(1) [**3a, 3c**: 2.13(2) and 2.018(9) Å, respectively] are shorter than those of Pd(1)−Cl(1) [**3a, 3c**: 2.236(5) and 2.301(2) Å, respectively]. Moreover, the C(3)−C(2)−C(6) and N(1)−Pd(1)−N(2) bond angles in **3a** [108.6(9) and 86.9(4)°, respectively] are smaller than those in **3c** [108.6(9) and 86.9(4)°, respectively], as observed in **2a−d** (Table 2). The dihedral angle in **3c** is smaller than that in **3a**, probably influenced by the steric bulk of the substituents at the 5-
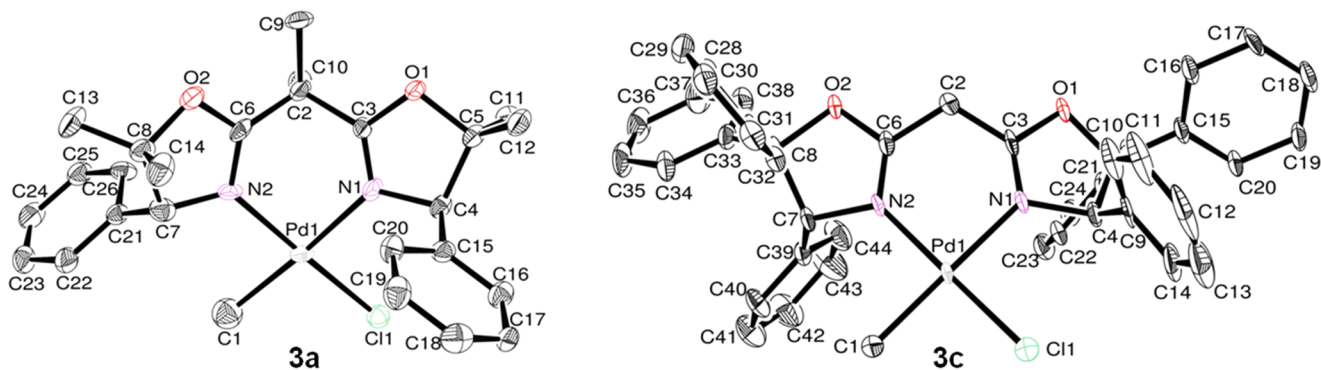
Figure 4. Oak ridge thermal ellipsoid plot (ORTEP) drawings for (BOX)Pd(Me)Cl (**3a, 3c**). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for (BOX)Pd(Me)Cl (3a, 3c), Cationic [(BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6^-$ (4a), and Neutral (BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N) (5b)

	Pd complex			
	3a	3c	4a	5b
		Selected Bond Distances (Å)		
C(2)−C(3)	1.517(15)	1.485(7)	1.500(4), C(1)−C(2)	1.402(5), C(1)−C(2)
C(2)−C(6)	1.508(17)	1.502(6)	1.522(4), C(1)−C(5)	1.392(5), C(1)−C(5)
N(1)−C(3)	1.292(14)	1.270(7)	1.271(4), N(1)−C(2)	1.316(5), N(1)−C(2)
N(2)−C(6)	1.297(14)	1.274(7)	1.283(4), N(2)−C(5)	1.316(5), N(2)−C(5)
Pd(1)−N(1)	2.110(9)	2.114(4)	2.134(3)	2.108(3)
Pd(1)−N(2)	2.090(10)	2.070(4)	2.060(3)	2.036(3)
Pd(1)−X	2.236(5)	2.301(2)	2.043(3)	2.063(3)
X = Cl(1) or N(3)	Pd(1)−Cl(1)	Pd(1)−Cl(1)	Pd(1)−N(3)	Pd(1)−N(3)
Pd(1)−C(1)	2.13(2)	2.018(9)	2.032(3), Pd(1)−C(26)	2.037(4), Pd(1)−C(24)
		Selected Bond Angles (deg)		
C(3)−C(2)−C(6)	108.6(9)	115.7(5)	114.7(3)	122.5(3)
			C(2)−C(1)−C(5)	C(2)−C(1)−C(5)
N(1)−C(3)−C(2)	126.0(10)	128.2(5)	129.6(3)	128.1(3)
			N(1)−C(2)−C(1)	N(1)−C(2)−C(1)
N(2)−C(6)−C(2)	126.2(10)	128.0(4)	132.1(3)	130.3(3)
			N(2)−C(5)−C(1)	N(2)−C(5)−C(1)
N(1)−Pd(1)−N(2)	86.9(4)	87.48(16)	87.81(9)	90.06(12)
X−Pd(1)−C(1)	92.2(6)	86.5(3)	86.28(11)	88.18(14)
X = Cl(1) or N(3)	Cl(1)−Pd(1)−C(1)	Cl(1)−Pd(1)−C(1)	N(3)−Pd(1)−C(26)	N(3)−Pd(1)−C(24)
N(1)−Pd(1)−X	91.9(3)	91.66(13)	91.95(9)	90.89(12)
X = Cl(1) or N(3)	N(1)−Pd(1)−Cl(1)	N(1)−Pd(1)−Cl(1)	N(1)−Pd(1)−N(3)	N(1)−Pd(1)− N(3)
N(2)−Pd(1)−C(1)	89.1(6)	94.4(3)	93.88(12)	90.89(14)
			N(2)−Pd(1)−C(26)	N(2)−Pd(1)−C(24)
		Dihedral Angles (deg)		
Ph^1−N2PdCX	89.308[a]	82.621	77.612	82.004
(X = Cl or N)	Ph^1−N2PdCCl	Ph^1−N2PdCCl	Ph^1−N2PdCN	Ph^1−N2PdCN
Ph^2−N2PdCX	91.958[a]	81.874	90.714	96.131
(X = Cl or N)	Ph^2−N2PdCCl	Ph^2−N2PdCCl	Ph^2−N2PdCN	Ph^2−N2PdCN

[a] Mean values of two structures.

Scheme 4. Synthesis of [(BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6^-$ (4a−d)

1a: R^1 = Me, R^2 = Me
1b: R^1 = H, R^2 = Me
1c: R^1 = H, R^2 = Ph
1d: R^1 = H, R^2 = Ph, H

3a−d

4a: 76%
4b: 96%
4c: 92%
4d: 65%

position (Ph^1−N2PdCCl and Ph^2−N2PdCCl: 3a, 89.308 and 91.958°, respectively; 3c, 82.621 and 81.874°, respectively).

Synthesis and Characterization of Cationic [(BOX)-PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6^-$ (4a−d). The corresponding cationic [(BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6^-$ (4a−d) could be prepared by treating 3a−d, prepared in situ according to the procedure described above, with AgPF$_6$ and 2,6-lutidine (Scheme 4). The resulting complexes (4a−d) were identified by NMR spectroscopy and elemental analysis; the structure of complex 4a was determined by X-ray crystallography (Figure 5, Table 3). In the ^{13}C NMR spectra, resonances ascribed to the methyl groups bound to palladium appear at lower magnetic fields than those of the corresponding neutral (BOX)Pd(Me)
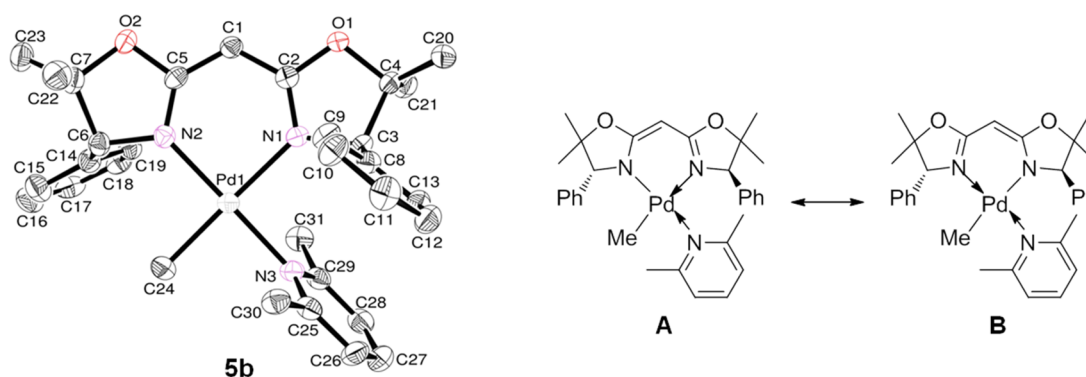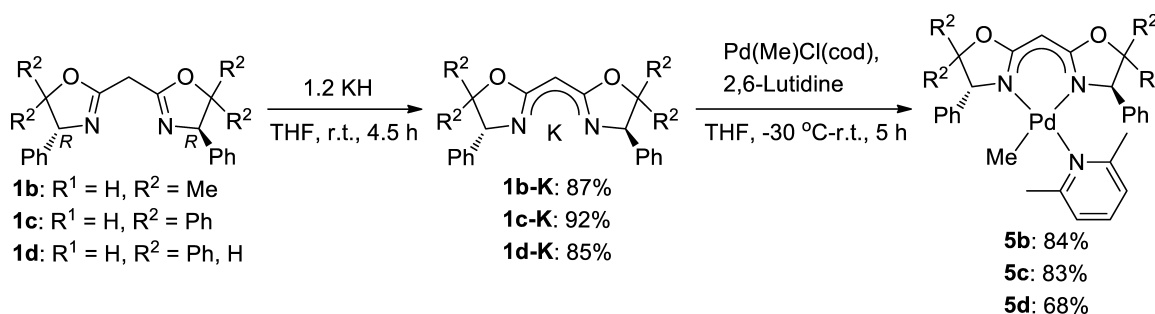
Cl (3) (4a: −4.16 ppm, 4b: −3.65 ppm, 4c: −3.72 ppm, 4d: −3.07 ppm, 3a: −5.85 ppm, 3b: −5.30 ppm, 3c: −5.12 ppm, 3d: −4.26 ppm in CD$_2$Cl$_2$ at 25 °C). These spectral data suggest low electron density at the palladium center in complex 4.

In complex 4a, a square planar geometry is folded around palladium, consisting of three nitrogen atoms in the BOX ligand and 2,6-lutidine and a methyl ligand (sum of the bond angles of N(1)−Pd(1)−N(2), N(3)−Pd(1)−C(26), N(1)−Pd(1)−N(3), and N(2)−Pd(1)−C(26) in 4a: 359.92°; mean deviation from the plane in 4a: 0.0339 Å). Pd(1)−N(3) [2.043(3) Å] is relatively short, which implies that the 2,6-lutidine ligand strongly coordinates to Pd. The dihedral angle of
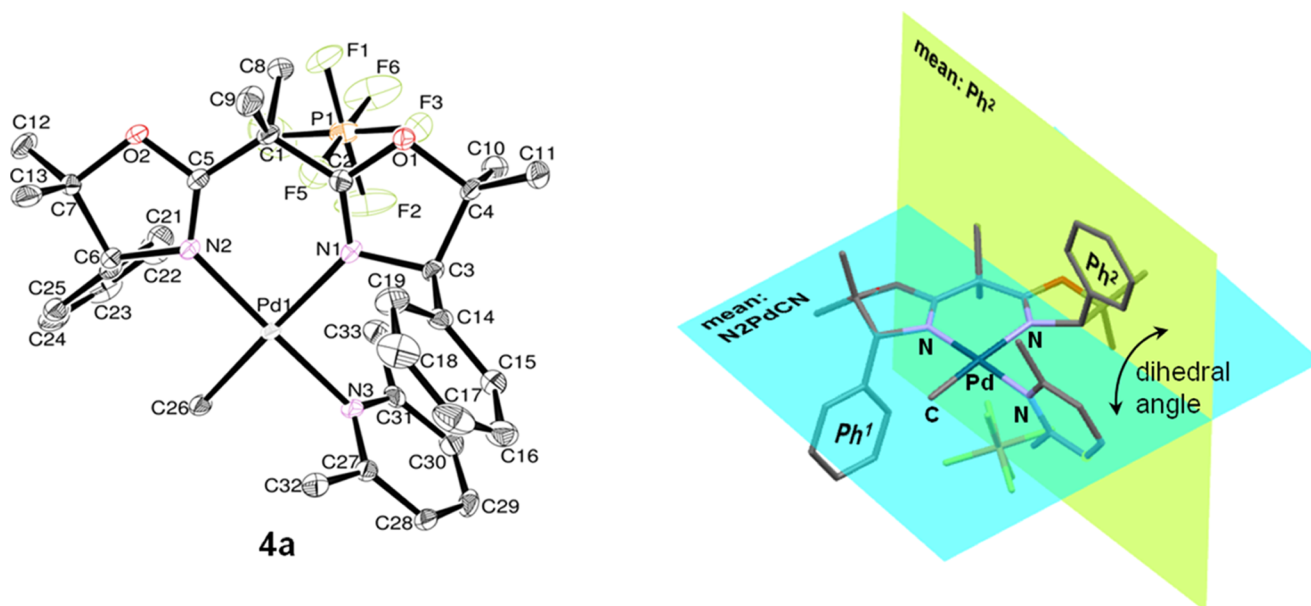
Figure 5. Oak ridge thermal ellipsoid plot (ORTEP) drawings for $[(BOX)PdMe(2,6\text{-}Me_2C_5H_3N)]^+PF_6^-$ (**4a**). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Scheme 5. Synthesis of $(BOX)PdMe(2,6\text{-}Me_2C_5H_3N)$ (5b–d)

1b: R^1 = H, R^2 = Me
1c: R^1 = H, R^2 = Ph
1d: R^1 = H, R^2 = Ph, H

1b-K: 87%
1c-K: 92%
1d-K: 85%

5b: 84%
5c: 83%
5d: 68%

**Figure 6.** Left: Oak ridge thermal ellipsoid plot (ORTEP) drawings for $(BOX)PdMe(2,6\text{-}Me_2C_5H_3N)$ (**5b**). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Right: Local structures of **A** and **B**.

Ph^1−N2PdCN close to the less bulky methyl ligand is much smaller than that of Ph^2−N2PdCN close to the bulky 2,6-lutidine (Ph^1−N2PdCN: 77.612°, Ph^2−N2PdCN: 90.714°).

Synthesis and Characterization of Neutral (BOX)-PdMe(2,6-Me$_2$C$_5$H$_3$N) (5b–d). Interestingly, it was found that a treatment of the BOX ligands (**1b–d**) with KH in tetrahydrofuran (THF) afforded the potassium salts of the anionic BOX ligands (**1b–d-K**) by abstraction of the hydrogen attached to the bridgehead carbon (Scheme 5). Pd(Me)Cl-

(cod) was then treated with the obtained K-salt (**1b–d-K**) in the presence of 2,6-lutidine to afford novel neutral palladium complexes with anionic BOX ligands (**5b–d**); these complexes were identified by NMR spectroscopy and elemental analysis. In the ^{13}C NMR spectra, resonances ascribed to the methyl groups bound to palladium in **5a–d** appear at higher magnetic fields than those in the corresponding cationic $[(BOX)PdMe-(2,6\text{-}Me_2C_5H_3N)]^+PF_6^-$ (**4**) and neutral (BOX)Pd(Me)Cl (**3**) (**5b**: −5.74 ppm, **5c**: −5.93 ppm, **5d**: −5.67 ppm in C_6D_6 at 25

Chart 2. New Palladium(II) Complexes Containing Neutral or Anionic BOX Ligands

R^1,R^2 = Me,Me (**a**); H,Me (**b**); H,Ph (**c**); H,(Ph,H) (**d**)
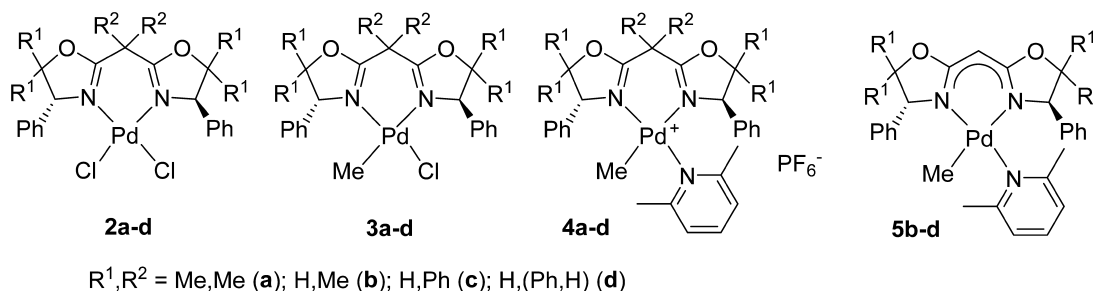
°C, **4b**: −3.65 ppm, **4c**: −3.72 ppm, **4d**: −3.07 ppm in CD$_2$Cl$_2$ at 25 °C, **3b**: −5.30 ppm, **3c**: −5.12 ppm, **3d**: −4.26 ppm in CD$_2$Cl$_2$ at 25 °C). Moreover, the methylene proton signal of **5c** (−0.39 ppm) in the ^{1}H NMR spectrum (in CDCl$_3$ at 25 °C) is observed in a higher magnetic field than that of complexes **4c** and **3c** (0.17 and 0.25 ppm, respectively). These spectral properties of complex **5** compared to those of the other complexes (**3**, **4**) suggest that the palladium in **5** possesses higher electron density because of electron donation from the anionic BOX ligand.

Single crystals of **5b** suitable for X-ray crystallography were grown by slow diffusion of Et$_2$O into dichloromethane solution. The ORTEP drawing is shown in Figure 6, and the selected bond distances and angles are summarized in Table 3 (together with **3a**, **3c**, and **4a** for comparison). Complex **5b** also folds in a distorted square planar geometry around palladium with BOX, 2,6-lutidine, and methyl ligands (sum of the bond angles of N(1)−Pd(1)−N(2), N(3)−Pd(1)−C(24), N(1)−Pd(1)−N(3), and N(2)−Pd(1)−C(24): 360.02°; mean deviation from the plane: 0.0250 Å). The bond lengths of C(1)−C(2), C(1)−C(5), N(1)−C(2), and N(2)−C(5) are between those of single and double bonds [C(1)−C(2): 1.402(5) Å, C(1)−C(5): 1.392(5) Å, N(1)−C(2): 1.316(5) Å, N(2)−C(5): 1.316(5) Å] in contrast to those in BOX (**1**) and complexes **2**−**4** [C(1)−C(2) or C(2)−C(3): 1.481(5)−1.519(7) Å, C(1)−C(5) or C(2)−C(6): 1.488(5)−1.522(6) Å, N(1)−C(2) or N(1)−C(3): 1.270(7)−1.292(14) Å, N(2)−C(5) or N(2)−C(6): 1.265(7)−1.297(14) Å] (Tables 1−3). This structural feature suggests a resonance hybrid of the two local structures, **A** and **B**, in complex **5b** (Figure 6). The high planarity of the plane consisting of Pd(1), C(1), C(2), C(5), N(1), and N(2) (mean deviation from the plane: 0.0208 Å) also indicates a resonance hybrid structure. The Pd−N bond lengths are shorter than those in the corresponding methyl palladium complexes **3** and **4**, indicating strong coordination of the BOX ligand to the metal in **5** [Pd(1)−N(1), Pd(1)−N(2) in **5b**: 2.108(3) and 2.036(3) Å, **3a**: 2.110(9) and 2.090(10) Å, **3c**: 2.114(4) and 2.070(4) Å, **4a**: 2.134(3) and 2.060(3) Å, respectively]. The large C(2)−C(1)−C(5) bond angle in **5b** [122.5(3)°] is derived from the sp^2 hybridization of the bridgehead carbon. In turn, the large bite angle of N(1)−Pd(1)−N(2) [90.06(12)°] is derived from the large bridge angle of C(2)−C(1)−C(5) [122.5(3)°]. The dihedral angle of Ph^1−N2PdCN is much smaller than that of Ph^2−N2PdCN, similar to that in complex **4a** (Ph^1−N2PdCN, Ph^2−N2PdCN in **5b**: 82.004 and 96.131°, **4a**: 77.612 and 90.714°, respectively). However, the dihedral angles in **5b** are larger than those in complex **4a** because of strong coordination of the BOX ligand to Pd in **5b** [Pd(1)−N(1), Pd(1)−N(2) in **5b**: 2.108(3), 2.036(3) Å, **4a**: 2.134(3), 2.060(3) Å, respectively].

Azabis(oxazoline) ligands with electron-donating amino groups in the central bridge are also known to coordinate strongly to metals, resulting in greatly improved stability of the metal complexes;[79,80] this results in higher reactivity, selectivity, and reusability not only for homogeneous catalytic reactions but also for heterogeneous reactions.[41,79−83] Both the spectral and structural features of complex **5** suggest higher stability as well as higher electron density at the palladium center derived from the anionic BOX ligand, similar to that in azabis(oxazoline) metal complexes. Thus, a series of complexes **5** are expected to be applied as new catalytic intermediates, in contrast to complexes **2**−**4**.

■ CONCLUSIONS

As summarized in Chart 2, a series of neutral palladium complexes containing C$_2$-symmetric BOX ligands, (BOX)PdCl$_2$ (**2a**−**d**) and (BOX)Pd(Me)Cl (**3a**−**d**), have been synthesized by reacting PdCl$_2$(CH$_3$CN)$_2$ or Pd(Me)Cl(cod) with BOX ligands (**1a**−**d**) [2,2′-(2-propylidene)bis{(4R)-4-phenyl-5,5-dimethyl-2-oxazoline} (**1a**), 2,2′-methylenebis{(4R)-4-phenyl-5,5-dimethyl-2-oxazoline} (**1b**), 2,2′-methylenebis{(4R)-4,5,5-triphenyl-2-oxazoline} (**1c**), and 2,2′-methylenebis{(4R,5S)-4,5-diphenyl-2-oxazoline} (**1d**)]; the cationic methyl complexes, [(BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6$$^−$ (**4a**−**d**), have been synthesized by in situ preparation of **3a**−**d**, followed by addition of AgPF$_6$. Moreover, novel neutral palladium−methyl complexes containing anionic ligands (**5b**−**d**) have also been prepared by treatment of Pd(Me)Cl(cod) with the ligand potassium salt prepared by hydrogen abstraction of the methylene bridgehead. The X-ray crystal structures reveal that all complexes fold in a distorted square planar geometry around Pd; steric bulk in the substituents at the 5-position in the BOX ligand decreases the dihedral angles between the Ph ring at the 4-position and the N2Pd plane. The bite angle in **2a** (with geminal dimethyl groups at the bridgehead carbon in the BOX ligand) is smaller than that in **2b**−**d** (with no substituents at the bridgehead carbon). Cationic [(BOX)PdMe-(NC$_6$H$_3$Me$_2$)]$^+$PF$_6$$^−$ (**4**) reveals lower electron density at the palladium center compared to that in the corresponding neutral (BOX)Pd(Me)Cl (**3**); this was supported by the ^{13}C NMR spectra. Neutral (BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N) (**5**) also demonstrates higher electron density because of electron donation from the anionic BOX ligand. The high planarity of the plane constructed with Pd(1), C(1), C(2), C(5), N(1), and N(2), the large bridge and bite angles of C(2)−C(1)−C(5) and N(1)−Pd(1)−N(2), and the shorter Pd−N bond lengths indicate a resonance hybrid structure in the BOX ligand. These electronic and steric features are different from those of complexes **2**−**4**; however, they are similar to those of azabis(oxazoline) metal complexes. Because these palladium complexes are highly

promising as precatalysts for efficient organic transformations (C−C bond formation, etc.), the information introduced here may be important for the design of more efficient catalysts and may also increase the general understanding of catalysis.

■ EXPERIMENTAL SECTION

General Procedures. All experimental procedures were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or using a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grades and were purified by standard purification procedures. Diethyl ether (anhydrous grade, Kanto Chemical Co., Inc.), dichloromethane (anhydrous grade, Kanto Chemical Co., Inc.), xylene (anhydrous grade, Kanto Chemical Co., Inc.), and THF (anhydrous grade, Kanto Chemical Co., Inc.) were used as received. (*R*)-Methyl 2-amino-2-phenylacetate hydrochloride (Sigma-Aldrich Co.), 2,2-dimethylmalonyl chloride (Sigma-Aldrich Co.), dimethylmalonate (Wako Pure Chemical Industries Ltd.), Ti(O^{i}Pr)$_4$ (Wako Pure Chemical Industries Ltd.), 2,2′-methylenebis[(4*R*,5*S*)-4,5-diphenyl-2-oxazoline] (**1d**) (Sigma-Aldrich Co.), PdCl$_2$(CH$_3$CN)$_2$ (Sigma-Aldrich Co.), 2,6-lutidine (Tokyo Chemical Industry Co.), and AgPF$_6$ (Sigma-Aldrich Co.) were used as received without further purification. KH (30 wt % dispersion in mineral oil, Sigma-Aldrich Co.) was washed three times with dry hexanes and dried before the preparation of potassium salt of anionic BOX ligands (**1-K**). (Cycloocta-1,5-diene)chloromethylpalladium-(II), Pd(Me)Cl(cod), was prepared according to the literature procedure.[84]

Elemental analyses were performed by using an EAI CE-440 CHN/O/S Elemental Analyzer (Exeter Analytical, Inc.). All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for ^{1}H NMR, 125.77 MHz for ^{13}C NMR) or a JEOL ECS-400 spectrometer (399.8 MHz for ^{1}H NMR, 100.5 MHz for ^{13}C NMR). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Chemical shifts are given in parts per million (ppm) and are referenced to SiMe$_4$ (δ 0.00 ppm, ^{1}H NMR, ^{13}C NMR). Coupling constants are given in hertz (Hz).

Synthesis of (*R*)-1-Amino-2-methyl-1-phenylpropan-2-ol (6a). Methylmagnesium bromide (3.0 M in diethyl ether, 100 mL, 0.300 mol) was added slowly to a suspension of (*R*)-methyl 2-amino-2-phenylacetate hydrochloride (12.2 g, 60.5 mmol) in diethyl ether (200 mL) at −40 °C. After addition, the reaction mixture was stirred at −40 °C for 1 h and then allowed to reach at room temperature with vigorous stirring overnight. Saturated aqueous NH$_4$Cl was added dropwise at 0 °C until the precipitate was dissolved. The aqueous phase was separated from the organic phase and extracted with ethyl acetate (3 × 150 mL). The combined organic extract was washed with water (2 × 100 mL) and dried over Na$_2$SO$_4$. The organic solution was filtered and concentrated under reduced pressure to give yellow oil. Recrystallization of the oil from AcOEt−*n*-hexane gave a pale yellow solid (9.2 g, 92%). ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 7.34−7.28 (m, 5H, Ph), 3.81 (s, 1H, CH), 2.02 (brs, 2H, NH, OH), 1.22 (s, 3H, CH$_3$), 1.00 (s, 3H, CH$_3$). The spectral data were identical to the same compound.[85]

Synthesis of (*R*)-2-Amino-1,1,2-triphenylethanol (6c). (*R*)-Methyl 2-amino-2-phenylacetate hydrochloride (6.0 g, 30.0 mmol) was added in small portions to methylmagnesium bromide solution in diethyl ether (3.0 M, 100 mL, 0.300 mol) at 0 °C for 30 min. After addition, the reaction mixture was stirred at 0 °C for 30 min and then allowed to reach room

temperature with vigorous stirring overnight. The reaction mixture was poured slowly into the iced water (120 mL), and concentrated HCl (45 mL) was added dropwise. After stirring for 1 h, the generated precipitate was collected by filtration and the remaining yellow solid was washed with water three times. The solid was dissolved in aqueous NaOH (2.0 M, 110 mL); then, the solution was stirred for 30 min. The aqueous phase was extracted with diethyl ether (3 × 150 mL), and the combined organic extract was washed with brine (100 mL) and dried over Na$_2$SO$_4$. The organic solution was filtered and concentrated under reduced pressure to give a yellow solid. Recrystallization of the oil from CH$_2$Cl$_2$−*n*-hexane gave a pale yellow solid (7.7 g, 89%). ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 7.75 (d, *J* = 7.55 Hz, 2H, *o*-Ph), 7.41 (dd, *J* = 7.55, 7.25 Hz, 2H, *m*-Ph), 7.28 (t, *J* = 7.25 Hz, 1H, *p*-Ph), 7.15−7.09 (m, 7H, Ph), 7.06−6.98 (m, 3H, Ph), 5.01 (s, 1H, CH), 4.66 (brs, 1H, OH), 1.59 (brs, 2H, NH$_2$). The spectral data were identical to the same compound.[86]

Synthesis of *N*^{1},*N*^{3}-bis((*R*)-2-hydroxy-2-methyl-1-phenylpropyl)-2,2-dimethylmalonamide (7a). A solution of amino alcohol **6a** (1.50 g, 7.53 mmol) and Et$_3$N (1.25 mL, 8.96 mmol) in CH$_2$Cl$_2$ (anhydrous, 13 mL) was cooled to −10 °C. 2,2-Dimethylmalonyl chloride (0.65 g, 3.77 mmol) was then added dropwise over 3 min. The reaction mixture was allowed to warm to 20 °C and stirred for 6 h. Subsequently, aqueous HCl (1 N, 15 mL) was added in one portion. The organic phase was separated, washed with aqueous NaHCO$_3$ (5%, 20 mL), washed with H$_2$O (5 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure to give a white solid **7a**, which was used in the next step without further purification (1.64 g, quant). ^{1}H NMR (270.1 MHz, DMSO-*d$_6$*): δ 7.73 (d, *J* = 8.56 Hz, 2H, NH), 7.21 (brs, 10H, Ph), 4.76 (brs, 2H, OH), 4.64 (d, *J* = 8.75 Hz, 2H, CH), 1.34 (s, 6H, CH$_3$), 1.14 (s, 6H, CH$_3$), 0.89 (s, 6H, CH$_3$). ^{13}C NMR (100.5 MHz, DMSO-*d$_6$*): δ 171.97 (CO), 140.48 (*i*-Ph), 128.38 (Ph), 127.35 (Ph), 126.56 (*p*-Ph), 70.69 (qC), 61.12 (CH), 48.99 (qC), 27.89 (CH$_3$), 27.50 (CH$_3$), 23.72 (CH$_3$).

Synthesis of 2,2′-(2-Propylidene)bis[(4*R*)-4-phenyl-5,5-dimethyl-2-oxazoline] (1a). **7a** (0.859 g, 2.01 mmol) and xylene (anhydrous, 50 mL) were charged into a 2-necked flask equipped with a Dean−Stark apparatus; then, the reaction mixture was heated to reflux to dissolve the bisamide alcohol completely. Ti(O^{i}Pr)$_4$ (57.1 mg, 0.201 mmol) was then added to the solution in one portion. The reaction mixture was refluxed for 48 h with removal of the water byproduct. After the reaction mixture was cooled to room temperature, the solution was concentrated under reduced pressure. The resulting pale yellow oil was purified by column chromatography (neutral almina, hexane/AcOEt = 10:1 to 2:1) to give a white solid **1a** (0.579 g, 74% yield 2 step based on **6a**). ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 7.31−7.20 (m, 10H, Ph), 4.85 (s, 2H, CH), 1.68 (s, 6H, CH$_3$), 1.56 (s, 6H, CH$_3$), 0.86 (s, 6H, CH$_3$). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 168.88 (N=C), 138.63 (*i*-Ph), 127.75 (Ph), 127.07 (Ph), 126.96 (Ph), 87.14 (qC), 77.60 (CH), 38.58 (qC), 28.71 (CH$_3$), 23.65 (CH$_3$), 23.35 (CH$_3$). Anal. Calcd for C$_{25}$H$_{30}$N$_2$O$_2$: C, 76.89; H, 7.74; N, 7.17. Found: C, 76.69; H, 7.86; N, 7.06.

Synthesis of 2,2′-Methylenebis[(4*R*)-4-phenyl-5,5-dimethyl-2-oxazoline] (1b). Dimethylmalonate (0.245 g, 1.86 mmol), amino alcohol **6a** (0.652 g, 3.95 mmol), and xylene (anhydrous, 60 mL) were charged into a 2-necked flask equipped with a Dean−Stark apparatus; then, the reaction mixture was heated to reflux for 13 h. After cooling the reaction

mixture at room temperature, Ti(O^{i}Pr)$_4$ (113 mg, 0.398 mmol) was then added to the solution in one portion. The reaction mixture was refluxed for 43 h with removal of the water byproduct. After the reaction, the mixture was concentrated under reduced pressure. The resulting red-yellow oil was purified by column chromatography (neutral alumina, hexane/AcOEt = 9:1 to 1:1) to give pale yellow oil. Recrystallization from dichloromethane and hexane gave a white solid **1b** (0.414 g, 61% yield 2 step based on dimethylmalonate). Single crystals suitable for X-ray crystallography were grown by slow diffusion of hexane into dichloromethane solution. ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 7.33−7.24 (m, 10H, Ph), 4.90 (s, 2H, CH), 3.53 (s, 2H, CH$_2$), 1.60 (s, 6H, CH$_3$), 0.88 (s, 6H, CH$_3$). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 162.21 (N=C), 138.69 (*i*-Ph), 128.12 (Ph), 127.43 (Ph), 127.20 (Ph), 88.06 (qC), 78.14 (CH), 29.64 (CH$_2$), 29.07 (CH$_3$), 23.79 (CH$_3$). The spectral data were identical to the same compound.[77]

Synthesis of 2,2′-Methylenebis[(4*R*)-4,5,5-triphenyl-2-oxazoline] (1c). The synthetic procedure for **1c** is similar to that for **1b**, except that dimethylmalonate (0.315 g, 2.38 mmol), amino alcohol **6c** (1.38 g, 4.77 mmol) in place of **6a**, xylene (anhydrous, 50 mL), and Ti(O^{i}Pr)$_4$ (68.0 mg, 0.239 mmol) were used. Recrystallization from dichloromethane and hexane gave a white solid **1c** (0.945 g, 68% yield 2 step based on dimethylmalonate). Single crystals suitable for X-ray crystallography were grown by slow diffusion of hexane into dichloromethane solution. ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 7.68 (d, *J* = 7.25 Hz, 4H, *o*-Ph), 7.40 (dd, *J* = 7.25, 6.95 Hz, 4H, *m*-Ph), 7.34 (t, *J* = 6.95 Hz, 2H, *p*-Ph), 7.12−7.10 (m, 4H, Ph), 7.04−6.88 (m, 16H, Ph), 6.05 (s, 2H, CH), 3.91 (s, 2H, CH$_2$). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 161.34 (N=C), 144.33 (*i*-Ph), 139.91 (*i*-Ph), 138.18 (*i*-Ph), 128.44 (Ph), 128.32 (Ph), 128.09 (Ph), 127.59 (Ph), 127.11 (Ph), 127.07 (Ph), 126.81 (Ph), 126.57 (Ph), 126.43 (Ph), 95.23 (qC), 79.38 (CH), 29.54 (CH$_2$). Anal. Calcd for C$_{43}$H$_{34}$N$_2$O$_2$: C, 84.56; H, 5.61; N, 4.59. Found: C, 84.26; H, 5.66; N, 4.56.

Synthesis of (BOX)PdCl$_2$ (2a). PdCl$_2$(CH$_3$CN)$_2$ (40.1 mg, 0.155 mmol) and BOX (**1a**) (64.8 mg, 0.166 mmol) were dissolved with 2 mL of anhydrous CH$_2$Cl$_2$ at room temperature in a glove box; then, the reaction mixture was stirred at room temperature for 19 h. The mixture was filtered through a pad of celite, and the filtrate was concentrated to 0.5 mL. *n*-Hexane (ca. 10 mL) was added dropwise to the concentrated solution with stirring. The resultant orange solid was collected by filtration and washed with *n*-hexane three times. The solid was dried in vacuo to afford an orange powder **2a** (81.8 mg, 93%). Single crystals suitable for X-ray crystallography were grown by slow diffusion of hexane into dichloromethane solution. ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 7.35 (dd, *J* = 7.25, 6.85, 6H, *m*-Ph), 7.31 (d, *J* = 7.25 Hz, 2H, *p*-Ph), 6.99 (d, *J* = 6.85 Hz, 4H, *o*-Ph), 5.47 (s, 2H, CH), 1.90 (s, 6H, CH$_3$), 1.56 (s, 6H, CH$_3$), 1.00 (s, 6H, CH$_3$). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 170.94 (N=C), 136.01 (*i*-Ph), 128.63 (Ph), 128.27 (Ph), 127.08 (Ph), 91.45 (qC), 76.60 (CH), 40.54 (qC), 27.93 (CH$_3$), 25.21 (CH$_3$), 23.03 (CH$_3$). Anal. Calcd for C$_{25}$H$_{30}$Cl$_2$N$_2$O$_2$Pd·(H$_2$O)$_{0.3}$: C, 52.37; H, 5.39; N, 4.89%. Found: C, 52.35; H, 5.30; N, 4.78%.

Synthesis of (BOX)PdCl$_2$ (2b). Synthesis of **2b** was conducted by a similar procedure as that for **2a**, except that BOX **1b** (60.2 mg, 0.166 mmol) was used in place of BOX **1a**. A pale yellow powder **2b** was obtained (76.7 mg, 92%). ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 7.40 (dd, *J* = 7.25, 7.25 Hz, 4H, *m*-Ph), 7.31 (t, *J* = 7.25 Hz, 2H, *p*-Ph), 7.05 (d, *J* = 7.25 Hz,

4H, *o*-Ph), 5.43 (s, 2H, CH), 3.93 (s, 2H, CH$_2$), 1.57 (s, 6H, CH$_3$), 0.98 (s, 6H, CH$_3$). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 164.41 (N=C), 136.12 (*i*-Ph), 128.61 (Ph), 128.22 (Ph), 127.29 (Ph), 92.37 (qC), 76.60 (CH), 28.55 (CH$_2$), 28.41 (CH$_3$), 23.33 (CH$_3$). Anal. Calcd for C$_{23}$H$_{26}$Cl$_2$N$_2$O$_2$Pd: C, 51.18; H, 4.85; N, 5.19%. Found: C, 51.47; H, 5.06; N, 4.99%.

Synthesis of (BOX)PdCl$_2$ (2c). Synthesis of **2c** was conducted by a similar procedure as that for **2a**, except that BOX **1c** (101.2 mg, 0.166 mmol) was used in place of BOX **1a**. A pale yellow powder **2c** was obtained (114.6 mg, 94%). ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ 7.63−7.60 (m, 4H, Ph), 7.52−7.50 (m, 6H, Ph), 7.11 (t, *J* = 7.25 Hz, 2H, *p*-Ph), 7.06 (dd, *J* = 7.25, 7.25 Hz, 4H, *m*-Ph), 7.03−7.00 (m, 6H, Ph), 6.89−6.86 (m, 4H, Ph), 6.76 (d, *J* = 7.25 Hz, 4H, *o*-Ph), 6.56 (s, 2H, CH), 4.16 (s, 2H, CH$_2$). ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$): δ 164.25 (N=C), 141.13 (Ph), 137.64 (Ph), 135.36 (Ph), 130.03 (Ph), 129.39 (Ph), 128.42 (Ph), 128.32 (Ph), 128.27 (Ph), 128.01 (Ph), 127.96 (Ph), 127.59 (Ph), 126.78 (Ph), 99.60 (qC), 75.01 (CH), 28.98 (CH$_2$). Anal. Calcd for C$_{43}$H$_{34}$Cl$_2$N$_2$O$_2$Pd·(H$_2$O): C, 64.07; H, 4.50; N, 3.48. Found: C, 63.91; H, 4.35; N, 3.43.

Synthesis of (BOX)PdCl$_2$ (2d). Synthesis of **2d** was conducted by a similar procedure as that for **2a**, except that BOX **1d** (155.3 mg, 0.339 mmol) was used in place of BOX **1a**. A pale yellow powder **2d** was obtained (199.9 mg, 92%). ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 7.16−7.10 (m, 12H, Ph), 6.90−6.86 (m, 8H, Ph), 6.15 (d, *J* = 8.55 Hz, 2H, CH), 6.08 (d, *J* = 8.55 Hz 2H, CH), 4.31 (s, 2H, CH$_2$). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 165.75 (N=C), 134.35 (Ph), 132.09 (Ph), 128.70 (Ph), 128.24 (Ph), 128.14 (Ph), 128.03 (Ph), 127.75 (Ph), 126.54 (Ph), 88.82 (CH), 72.81 (CH), 28.63 (CH$_2$). Anal. Calcd for C$_{31}$H$_{26}$Cl$_2$N$_2$O$_2$Pd: C, 58.55; H, 4.12; N, 4.41. Found: C, 58.46; H, 4.00; N, 4.53.

Synthesis of (BOX)Pd(Me)Cl (3a). Pd(Me)Cl(cod) (46.0 mg, 0.174 mmol) and BOX (**1a**) (70.6 mg, 0.181 mmol) were dissolved with 2 mL of anhydrous dichloromethane under a nitrogen atmosphere; then, the reaction mixture was stirred for 2 h. The mixture was filtered through a pad of celite, and the filtrate was concentrated to 0.5 mL. The concentrated solution was added dropwise to *n*-hexane (ca. 10 mL) with stirring. The resultant pale yellow solid was collected by filtration and washed with *n*-hexane three times. The solid was dried in vacuo to afford a pale yellow powder **3a** (82.0 mg, 86%). Single crystals suitable for X-ray crystallography were grown by slow diffusion of hexane into dichloromethane solution. ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ 7.42−7.30 (m, 6H, Ph), 7.06−7.02 (m, 4H, *o*-Ph), 5.32 (s, 1H, CH), 4.89 (s, 1H, CH), 1.98 (s, 3H, CH$_3$), 1.75 (s, 3H, CH$_3$), 1.57 (s, 3H, CH$_3$), 1.55 (s, 3H, CH$_3$), 0.96 (s, 3H, CH$_3$), 0.95 (s, 3H, CH$_3$), 0.07 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$): δ 172.87 (N=C), 169.42 (N=C), 138.12 (Ph), 137.16 (Ph), 129.01 (Ph), 128.61 (Ph), 128.55 (Ph), 128.06 (Ph), 127.81 (Ph), 90.29 (qC), 89.69 (qC), 78.41 (CH), 75.79 (CH), 40.52 (qC), 28.59 (CH$_3$), 28.54 (CH$_3$), 26.88 (CH$_3$), 24.04 (CH$_3$), 23.47 (CH$_3$), 23.148 (CH$_3$), −5.85 (CH$_3$). Anal. Calcd for C$_{26}$H$_{33}$ClN$_2$O$_2$Pd·(H$_2$O)$_{0.5}$: C, 56.12; H, 6.16; N, 5.03. Found: C, 56.34; H, 6.10; N, 5.03.

Synthesis of (BOX)Pd(Me)Cl (3b). Synthesis of **3b** was conducted by a similar procedure as that for **3a**, except that BOX **1b** (63.8 mg, 0.176 mmol) was used in place of BOX **1a**. A pale yellow powder **3b** was obtained (75.5 mg, 91%). ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ 7.43−7.31 (m, 6H, Ph), 7.11−7.06 (m, 4H, Ph), 5.27 (s, 1H, CH), 4.89 (s, 1H, CH), 3.85 (d,

J = 20.50, 1H, CH$_2$), 3.73 (d, J = 20.50, 1H, CH$_2$), 1.60 (s, 3H, CH$_3$), 1.58 (s, 3H, CH$_3$), 0.95 (s, 3H, CH$_3$), 0.93 (s, 3H, CH$_3$), 0.10 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$): δ 165.87 (N=C), 162.29 (N=C), 138.12 (Ph), 136.91 (Ph), 129.00 (Ph), 128.71 (Ph), 128.53 (Ph), 128.07 (Ph), 127.81 (Ph), 91.18 (qC), 90.38 (qC), 78.07 (CH), 76.01 (CH), 29.04 (CH$_2$), 28.84 (CH$_3$), 28.37 (CH$_3$), 23.78 (CH$_3$), 23.38 (CH$_3$), −5.30 (CH$_3$). Anal. Calcd for C$_{24}$H$_{29}$ClN$_2$O$_2$Pd: C, 55.50; H, 5.63; N, 5.39. Found: C, 55.41; H, 5.64; N, 5.34.

Synthesis of (BOX)Pd(Me)Cl (3c). Synthesis of **3c** was conducted by a similar procedure as that for **3a**, except that BOX **1c** (107.5 mg, 0.176 mmol) was used in place of BOX **1a**. A pale yellow powder **3c** was obtained (111.0 mg, 90%). ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ 7.65−7.61 (m, 4H, Ph), 7.52−7.43 (m, 6H, Ph), 7.08−6.97 (m, 12H, Ph), 6.94−6.92 (m, 2H, Ph), 6.94−6.88 (m, 2H, Ph), 6.84−6.82 (m, 2H, Ph), 6.74 (d, J = 7.55 Hz, 2H, o-Ph), 6.47 (s, 1H, CH), 5.95 (s, 1H, CH), 4.10 (d, J = 20.50 Hz, 1H, CH$_2$), 4.00 (d, J = 20.50 Hz, 1H, CH$_2$), 0.25 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$): δ 165.44 (N=C), 161.59 (N=C), 142.74 (Ph), 141.99 (Ph), 139.00 (Ph), 137.78 (Ph), 136.86 (Ph), 135.69 (Ph), 129.76 (Ph), 129.38 (Ph), 129.31 (Ph), 129.13 (Ph), 128.79 (Ph), 128.39 (Ph), 128.27 (Ph), 128.17 (Ph), 128.03 (Ph), 127.98 (Ph), 127.88 (Ph), 127.73 (Ph), 127.70 (Ph), 127.41 (Ph), 127.36 (Ph), 127.17 (Ph), 126.94 (Ph), 126.84 (Ph), 98.27 (qC), 97.70 (qC), 77.19 (CH), 74.67 (CH), 28.49 (CH$_2$), −5.12 (CH$_3$). Anal. Calcd for C$_{44}$H$_{37}$ClN$_2$O$_2$Pd·(H$_2$O): C, 67.26; H, 5.00; N, 3.57. Found: C, 67.17; H, 4.74; N, 3.47.

Synthesis of (BOX)Pd(Me)Cl (3d). Synthesis of **3d** was conducted by a similar procedure as that for **3a**, except that BOX **1d** (76.1 mg, 0.166 mmol) was used in place of BOX **1a**. A pale yellow powder **3d** was obtained (93.1 mg, 95%). ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ 7.16−7.10 (m, 12H, Ph), 6.99−6.85 (m, 8H, Ph), 6.09 (brd, J = 9.45 Hz, 2H, CH), 6.01 (brd, J = 9.10 Hz, 1H, CH), 5.53 (brd, J = 9.15 Hz, 1H, CH), 4.21 (d, J = 21.61 Hz, 1H, CH$_2$), 4.13 (d, J = 21.61 Hz, 1H, CH$_2$), 0.22 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$): δ 167.17 (N=C), 163.49 (N=C), 136.46 (Ph), 135.07 (Ph), 134.27 (Ph), 133.04 (Ph), 128.81 (Ph), 128.50 (Ph), 128.40 (Ph), 128.35 (Ph), 128.32 (Ph), 128.30 (Ph), 128.23 (Ph), 128.05 (Ph), 127.77 (Ph), 127.59 (Ph), 126.86 (Ph), 126.71 (Ph), 88.34 (CH), 87.73 (CH), 73.91 (CH), 72.05 (CH), 28.20 (CH$_2$), −4.26 (CH$_3$). Anal. Calcd for C$_{32}$H$_{29}$ClN$_2$O$_2$Pd·(C$_6$H$_{14}$)$_{0.1}$: C, 62.74; H, 4.91; N, 4.49. Found: C, 62.98; H, 4.71; N, 4.58.

Synthesis of [(BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6^-$ (4a). Pd(Me)Cl(cod) (53.7 mg, 0.203 mmol) and BOX (**1a**) (79.1 mg, 0.203 mmol) were dissolved with 2 mL of anhydrous CH$_2$Cl$_2$ at room temperature in a glove box; then, the reaction solution was stirred for 3 h. 2,6-Lutidine (109.0 mg, 1.02 mmol) and AgPF$_6$ (52.0 mg, 0.206 mmol) were added to the solution. The reaction mixture was stirred for additional 3 h at room temperature and filtered through a pad of celite. The volatilities were removed under reduced pressure, and the resultant solid was dissolved with 2.0 mL of chloroform. The yellow suspension was filtered through a pad of celite, and the filtrate was concentrated to 0.5 mL. n-Hexane (10 mL) was added dropwise to the concentrated solution with stirring. The resultant pale yellow solid was collected by filtration with a Hirsch funnel and washed with n-hexane three times. The solid was dried in vacuo to afford a pale yellow powder **4a** (113.7 mg, 76%). Single crystals suitable for X-ray crystallography were grown by slow diffusion of hexane into dichloromethane solution. ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ 7.50−7.42 (m, 3H,

Ph), 7.38−7.29 (m, 1H, Ph), 7.20 (t, J = 7.55 Hz, 1H, Ph), 7.12 (d, J = 7.60 Hz, 2H, o-Ph), 7.06 (d, J = 7.55 Hz, 1H, o-Ph), 6.92 (brs, 1H, lutidine), 6.80 (brs, 1H, lutidine), 6.54 (d, J = 7.60 Hz, 1H, o-Ph), 6.18 (brs, 1H, lutidine), 4.96 (s, 1H, CH), 4.11 (s, 1H, CH), 2.67 (s, 3H, CH$_3$), 2.37 (s, 3H, CH$_3$), 2.19 (s, 3H, CH$_3$), 1.75 (s, 3H, CH$_3$), 1.65 (s, 3H, CH$_3$), 1.58 (s, 3H, CH$_3$), 1.08 (s, 3H, CH$_3$), 0.89 (s, 3H, CH$_3$), 0.02 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$): δ 173.34 (N=C), 172.546 (N=C), 159.81 (Ar), 158.72 (Ar), 138.82 (Ar), 136.49 (Ar), 135.11 (Ar), 129.44 (Ar), 129.25 (Ar), 129.22 (Ar), 129.10 (Ar), 128.73 (Ar), 127.64 (Ar), 125.78 (Ar), 123.25 (Ar), 123.11 (Ar), 91.35 (qC), 90.84 (qC), 78.03 (CH), 77.16 (CH), 40.61 (qC), 29.00 (CH$_3$), 28.87 (CH$_3$), 28.68 (CH$_3$), 27.80 (CH$_3$), 27.02 (CH$_3$), 23.63 (CH$_3$), 22.74 (CH$_3$), 22.24 (CH$_3$), −4.16 (CH$_3$). Anal. Calcd for C$_{33}$H$_{42}$F$_6$N$_3$O$_2$PPd: C, 51.87; H, 5.54; N, 5.50. Found: C, 51.67; H, 5.54; N, 5.43.

Synthesis of [(BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6^-$ (4b). Synthesis of **4b** was conducted by a similar procedure as that for **4a**, except that BOX **1b** (43.0 mg, 0.119 mmol) was used in place of BOX **1a**. A pale yellow powder **4b** was obtained (82.5 mg, 96%). ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ 7.49−7.41 (m, 3H, Ph), 7.38 (t, J = 7.73 Hz, 1H, Ph), 7.22 (t, J = 7.40 Hz, 1H, Ph), 7.17 (d, J = 6.95 Hz, 2H, o-Ph), 7.05 (d, J = 7.85 Hz, 1H, o-Ph), 6.99 (brs, 3H, Ar), 6.56 (d, J = 7.60 Hz, 1H, o-Ph), 6.17 (brs, 1H, Ar), 4.95 (s, 1H, CH), 4.10 (d, J = 19.85 Hz, 1H, CH$_2$), 4.06 (s, 1H, CH), 3.83 (d, J = 19.85 Hz, 1H, CH$_2$), 2.78 (s, 3H, CH$_3$), 2.34 (s, 3H, CH$_3$), 1.68 (s, 3H, CH$_3$), 1.58 (s, 3H, CH$_3$), 1.04 (s, 3H, CH$_3$), 0.87 (s, 3H, CH$_3$), −0.01 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$): δ 166.68 (N=C), 165.26 (N=C), 160.39 (Ar), 158.70 (Ar), 138.78 (Ar), 136.57 (Ar), 135.05 (Ar), 129.19 (Ar), 129.15 (Ar), 129.13 (Ar), 129.07 (Ar), 127.59 (Ar), 123.28 (Ar), 122.98 (Ar), 91.64 (qC), 91.25 (qC), 78.03 (CH), 76.98 (CH), 29.19 (2C, CH$_2$, CH$_3$), 28.61 (CH$_3$), 27.79 (CH$_3$), 27.18 (CH$_3$), 24.00 (CH$_3$), 23.00 (CH$_3$), −3.65 (CH$_3$). Anal. Calcd for C$_{31}$H$_{38}$F$_6$N$_3$O$_2$PPd: C, 50.59; H, 5.20; N, 5.71%. Found: C, 50.35; H, 5.13; N, 5.96%.

Synthesis of [(BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6^-$ (4c). Synthesis of **4c** was conducted by a similar procedure as that for **4a**, except that BOX **1c** (134.6 mg, 0.220 mmol) was used in place of BOX **4a**. A pale yellow powder **4c** was obtained (198.2 mg, 92%). ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ 7.64−7.48 (m, 10H, Ph), 7.43 (t, J = 7.58 Hz, 1H, Ph), 7.16−7.11 (m, 2H, Ph), 7.04−6.87 (m, 16H, Ar), 6.73 (d, J = 7.55 Hz, 2H, Ar), 6.57 (d, J = 7.60 Hz, 1H, Ar), 6.37 (brs, 1H, lutidine), 6.04 (s, 1H, CH), 5.16 (s, 1H, CH), 4.41 (d, J = 19.22 Hz, 1H, CH$_2$), 4.31 (d, J = 19.22 Hz, 1H, CH$_2$), 2.57 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$), 0.17 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$): δ 166.11 (N=C), 165.14 (N=C), 160.31 (Ar), 158.71 (Ar), 143.05 (Ar), 141.97 (Ar), 139.01 (Ar), 137.91 (Ar), 137.42 (Ar), 135.73 (Ar), 134.28 (Ar), 129.88 (Ar), 129.81 (Ar), 129.60 (Ar), 129.49 (Ar), 128.80 (Ar), 128.70 (Ar), 128.67 (Ar), 128.65 (Ar), 128.60 (Ar), 128.09 (Ar), 128.03 (Ar), 127.79 (Ar), 126.61 (Ar), 126.58 (Ar), 126.38 (Ar), 125.72 (Ar), 123.44 (Ar), 123.17 (Ar), 98.44 (qC), 97.88 (qC), 78.30 (CH), 76.73 (CH), 28.75 (CH$_2$), 27.57 (CH$_3$), 26.96 (CH$_3$), −3.72 (CH$_3$). Anal. Calcd for C$_{51}$H$_{46}$F$_6$N$_3$O$_2$PPd·CH$_2$Cl$_2$: C, 58.41; H, 4.52; N, 3.93. Found: C, 58.30; H, 4.46; N, 3.98.

Synthesis of [(BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N)]$^+$PF$_6^-$ (4d). Synthesis of **4d** was conducted by a similar procedure as that for **4a**, except that BOX **1d** (83.5 mg, 0.182 mmol) was used in place of BOX **1a**. A pale yellow powder **4d** was obtained (97.7

mg, 65%). ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ 7.37 (t, J = 7.55 Hz, 1H, Ph), 7.24−7.09 (m, 8H, Ph), 7.05−6.80 (m, 13H, Ar), 6.50 (d, J = 7.90 Hz, 1H, o-Ph), 6.21 (d, J = 9.75 Hz, 2H, CH), 5.64 (d, J = 9.75 Hz, 1H, CH), 4.79 (d, J = 9.75 Hz, 1H, CH), 4.43 (d, J = 21.16 Hz, 1H, CH$_2$), 4.29 (d, J = 21.16 Hz, 1H, CH$_2$), 2.97 (s, 3H, CH$_3$), 2.24 (s, 3H, CH$_3$), 0.06 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$): δ 168.05 (N=C), 166.26 (N=C), 160.57 (Ar), 159.25 (Ar), 138.67 (Ar), 135.18 (Ar), 134.14 (Ar), 133.51 (Ar), 133.20 (Ar), 128.90 (Ar), 128.63 (Ar), 128.59 (Ar), 128.48 (Ar), 128.46 (Ar), 128.42 (Ar), 128.27 (Ar), 128.19 (Ar), 127.98 (Ar), 127.56 (Ar), 127.05 (Ar), 126.42 (Ar), 123.18 (Ar), 123.04 (Ar), 87.76 (CH), 87.72 (CH), 73.57 (CH), 72.73 (CH), 28.29 (CH$_2$), 27.65 (CH$_3$), 27.47 (CH$_3$), −3.07 (CH$_3$). Anal. Calcd for C$_{39}$H$_{38}$F$_6$N$_3$O$_2$PPd·H$_2$O: C, 55.10; H, 4.74; N, 4.94. Found: C, 54.96; H, 4.59; N, 4.82.

Synthesis of Potassium Salt of Anionic BOX (1b-K). BOX (**1b**) (111.0 mg, 0.306 mmol) was dissolved with 2.1 mL of anhydrous THF at room temperature in a glove box, and KH (15.0 mg, 0.374 mmol) was added to the solution. The reaction mixture was heated at reflux temperature using a dryer and then stirred at room temperature for 4.5 h. During the reaction, the mixture was additionally heated at reflux temperature three times. The red solution was filtered through a celite pad, and the filtrate was concentrated to 0.5 mL. n-Hexane (ca. 10 mL) was added dropwise to the concentrated solution with stirring. The resultant yellow solid was collected by filtration with a glass filter and washed with n-hexane three times. The solid was dried in vacuo to afford a yellow powder **1b-K**; this was used in the next step without further purification (107.0 mg, 87%). Other potassium salts of anionic BOX (**1c-K** and **1d-K**) were prepared by a similar procedure as that for **1b-K**.

Synthesis of Neutral (BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N) (5b). A THF solution (4.3 mL) containing 2,6-lutidine (143.1 mg, 1.335 mmol) was added to a mixture of Pd(Me)Cl(cod) (71.0 mg, 0.268 mmol) and **1b-K** (107.0 mg, 0.267 mmol) at −30 °C in a glove box. The reaction mixture was warmed slowly to room temperature; then, the mixture was stirred for 5 h. The orange suspension was filtered through a pad of celite, and the filtrate was concentrated to 0.5 mL. n-Hexane (ca. 10 mL) was added dropwise to the concentrated solution with stirring. The resultant pale yellow solid was collected by filtration and washed with n-hexane three times. The solid was dried in vacuo to afford a pale yellow powder **5b** (133.3 mg, 84%). Single crystals suitable for X-ray crystallography were grown by slow diffusion of Et$_2$O into dichloromethane solution. ^{1}H NMR (500.1 MHz, C$_6$D$_6$): δ 7.85 (brs, 1H, Ar), 7.55 (d, J = 7.60 Hz, 1H, Ar), 7.23 (brs, 4H, Ar), 7.00−6.91 (m, 2H, Ar), 6.71−6.62 (m, 2H, Ar), 6.33 (d, J = 7.55 Hz, 1H, Ar), 6.05 (d, J = 7.55 Hz, 1H, Ar), 5.66 (d, J = 7.25 Hz, 1H, Ar), 4.90 (s, 1H, CH), 4.86 (s, 1H, CH), 3.41 (s, 1H, CH), 3.00 (s, 3H, CH$_3$), 2.08 (s, 3H, CH$_3$), 1.46 (s, 3H, CH$_3$), 1.32 (s, 3H, CH$_3$), 0.90 (s, 3H, CH$_3$), 0.75 (s, 3H, CH$_3$), 0.12 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, C$_6$D$_6$): δ 169.43 (N=C), 169.22 (N=C), 161.81 (Ar), 159.64 (Ar), 144.22 (Ar), 142.69 (Ar), 136.36 (Ar), 128.72 (Ar), 128.58 (Ar), 127.24 (Ar), 126.89 (Ar), 126.76 (Ar), 122.07 (Ar), 121.34 (Ar), 83.88 (qC), 83.52 (qC), 76.64 (CH), 76.15 (CH), 55.68 (CH), 28.90 (CH$_3$), 28.66 (CH$_3$), 27.10 (CH$_3$), 26.87 (CH$_3$), 24.63 (CH$_3$), 23.82 (CH$_3$), −5.75 (CH$_3$). Anal. Calcd for C$_{31}$H$_{37}$N$_3$O$_2$Pd: C, 63.10; H, 6.32; N, 7.12%. Found: C, 62.93; H, 6.27; N, 7.02%.

Synthesis of Neutral (BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N) (5c). Synthesis of **5c** was conducted by a similar procedure as that for **5b**, except that **1c-K** (131.0 mg, 0.202 mmol) was used in place of **1b-K**. A pale yellow powder **5c** was obtained (135.6 mg, 83%). ^{1}H NMR (500.1 MHz, C$_6$D$_6$): δ 7.94 (d, J = 7.85 Hz, 2H), 7.74 (d, J = 7.85 Hz, 2H, Ar), 7.74 (d, J = 7.85 Hz, 2H, Ar), 7.23−7.14 (m, 13H, Ar), 7.11 (d, J = 8.20 Hz, 2H, Ar), 7.04 (t, J = 7.25, 1H, Ar), 6.94−6.81 (m, 5H, Ar), 6.75−6.65 (m, 6H, Ar), 6.40 (d, J = 7.60 Hz, 1H, Ar), 6.05 (d, J = 7.55 Hz, 1H, Ar), 6.02 (s, 1H, CH), 5.25 (s, 1H, CH), 4.47 (s, 1H, CH), 2.73 (s, 3H, CH$_3$), 1.94 (s, 3H, CH$_3$), 0.22 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, C$_6$D$_6$): δ 168.96 (N=C), 168.76 (N=C), 161.91 (Ar), 160.10 (Ar), 145.91 (Ar), 145.12 (Ar), 142.67 (Ar), 141.67 (Ar), 141.44 (Ar), 140.85 (Ar), 136.55 (Ar), 128.91 (Ar), 128.54 (Ar), 128.42 (Ar), 128.35 (Ar), 128.16 (Ar), 127.97 (Ar), 127.66 (Ar), 127.58 (Ar), 127.40 (Ar), 127.33 (Ar), 127.25 (Ar), 126.85 (Ar), 126.64 (Ar), 126.48 (Ar), 126.449 (Ar), 122.11 (Ar), 121.33 (Ar), 92.34 (qC), 92.08 (qC), 77.06 (CH), 74.69 (CH), 56.54 (CH), 27.08 (CH$_3$), 26.80 (CH$_3$), −5.93 (CH$_3$). Anal. Calcd for C$_{51}$H$_{45}$N$_3$O$_2$Pd·(H$_2$O)$_{0.5}$: C, 72.29; H, 5.47; N, 4.96. Found: C, 72.46; H, 5.44; N, 4.92.

Synthesis of Neutral (BOX)PdMe(2,6-Me$_2$C$_5$H$_3$N) (5d). Synthesis of **5d** was conducted by a similar procedure as that for **5b**, except that **1d-K** (93.0 mg, 0.187 mmol) was used in place of **1b-K**. A pale yellow powder **5d** was obtained (86.7 mg, 68%). ^{1}H NMR (500.1 MHz, C$_6$D$_6$): δ 7.27 (brs, 2H, Ar), 7.08 (d, J = 7.58 Hz, 2H, Ar), 6.97 (t, J = 7.25 Hz, 1H, Ar), 6.93 (d, J = 6.60, 2H, Ar), 6.89−6.72 (m, 13H, Ar), 6.62 (t, J = 7.73 Hz, 1H, Ar), 6.35 (d, J = 7.55, 1H, Ar or CH), 6.01 (d, J = 7.90, 1H, CH), 5.64 (d, J = 7.60, 1H, Ar), 5.54 (d, J = 7.55 Hz, 1H, Ar or CH), 5.36 (d, J = 7.55 Hz, 1H, Ar or CH), 5.28 (s, 1H, CH), 4.06 (d, J = 7.90 Hz, 1H, CH), 3.07 (s, 3H, CH$_3$), 2.15 (s, 3H, CH$_3$), 0.23 (s, 3H, CH$_3$). ^{13}C NMR (125.8 MHz, C$_6$D$_6$): δ 170.65 (N=C), 170.45 (N=C), 161.76 (Ar), 159.71 (Ar), 141.64 (Ar), 140.73 (Ar), 137.04 (Ar), 136.98 (Ar), 136.52 (Ar), 128.36 (Ar), 128.33 (Ar), 128.16 (Ar), 127.97 (Ar), 127.76 (Ar), 127.68 (Ar), 127.65 (Ar), 127.40 (Ar), 127.19 (Ar), 127.07 (Ar), 126.77 (Ar), 122.10 (Ar), 121.38 (Ar), 84.95 (CH), 84.79 (CH), 72.88 (CH), 71.86 (CH), 55.66 (CH), 27.54 (CH$_3$), 26.79 (CH$_3$), −5.67 (CH$_3$). Anal. Calcd for C$_{39}$H$_{37}$N$_3$O$_2$Pd: C, 68.27; H, 5.44; N, 6.12. Found: C, 68.27; H, 5.72; N, 5.88.

Crystallographic Analysis. The measurement was made on a Rigaku XtaLAB mini diffractometer using graphite monochromated Mo Kα radiation or a Rigaku XtaLAB P200 diffractometer using multilayer mirror monochromated Mo Kα radiation (XtaLAB mini for BOX **1b−d** and complex **2a**, **2c**, **2d** and XtaLAB P200 for complex **2b**, **3a**, **3c**, **4a**, **5b**). The structures except for **3c** were solved by direct methods[87,88] expanded using Fourier techniques. Heavy-atom Patterson methods[89] expanded using Fourier techniques were conducted for **3c**. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package except for refinement,[90−92] which was performed using SHELXL97, SHELXL2013, or SHELXL version 2014/7.[93] Selected crystal collection parameters are listed in Tables S1−S3.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00457.

Additional data (NMR spectra) for complex **2−5**, BOX **1**, amino alcohol **6a**, **6c**, and bisamide alcohol **7a** and selected crystal collection parameters for BOX **1b−d**, complex **2a−d**, **3a**, **3c**, **4a**, **5b**; these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/data_request/cif (PDF)

CCDC Nos. 1533692, 1533912−1533921 contain the supplementary crystallographic data for this paper (TXT) (XYZ)

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Notes
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