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Effect of *ortho*-substituents on the stereochemistry of 2-(*o*-substituted phenyl)-1*H*-imidazoline–palladium complexes

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Abstract

Palladium complexes composed of $[Pd(Ln)_2Cl_2]$ (n = 1, 2, 3, 4, 6), $[\mathbf{L5a}]_2[PdCl_4]$ and $[Pd(\mathbf{L5b})_2]$, where **L1** = 4,5-dihydro-2-phenyl-1*H*-imidazole (= 2-phenyl-1*H*-imidazoline), **L2** = 2-(*o*-fluorophenyl)-1*H*-imidazoline, **L3** = 2-(*o*-methylphenyl)-1*H*-imidazoline, **L4** = 2-(*o*-*tert*-butylphenyl)-1*H*-imidazoline, **L5a** = 2-(*o*-hydroxyphenyl)-1*H*-imidazolinium, **L5b** = 2-(1*H*-imidazolin-2-yl)phenolate, and **L6** = 2-(*o*-methylphenyl)-1*H*-imidazole, were synthesized. Molecular structures of the isolated palladium complexes were characterized by single crystal X-ray diffraction analysis. The effect of *ortho*-substituents on the phenyl ring on *trans*-chlorine geometry was noted for complexes $[Pd(\mathbf{L1})_2Cl_2]$ **1a** and **1b**, $[Pd(\mathbf{L2})_2Cl_2]$ **2** and $[Pd(\mathbf{L6})_2Cl_2]$ **6**, whereas *cis*-chlorine geometry was observed for $[Pd(\mathbf{L3})_2Cl_2]$ **3** and $[Pd(\mathbf{L4})_2Cl_2]$ **4**. $PdCl_2$ reacts with 2-(*o*-hydroxyphenyl)-1*H*-imidazoline in DMF to give $[\mathbf{L5a}]^+$ and $[\mathbf{L5b}]^-$ so that $[\mathbf{L5a}]_2[PdCl_4]$ **5a** and $[Pd(\mathbf{L5b})_2]$ **5b** were obtained. In complex **5b**, as an *N*,*O*-bidentate ligand, two ligands **L5b** coordinated with the central Pd(II) ion in the *trans*-form. The coordination of $PdCl_2$ with 2-(*o*-hydroxyphenyl)-1*H*-imidazolines in solution was investigated by NMR spectroscopy.

1. Introduction

Recently, imidazole, imidazoline and their related compounds have received a great deal of attention not only in the field of organic synthesis [1], but also in the area of pharmaceutical chemistry [2], supramolecular chemistry [3], and catalysis [4]. There have been many reports concerning structure and catalytic reactivity on aspects of metal complexes with imidazoles and imidazolines [5]. We also reported a series of studies on some $PdCl_2$ complexes with imidazole

derivatives as catalysts for the Mizoroki—Heck reaction and Suzuki—Miyaura coupling reaction [6]. During the course of this study, we became interested in the stereochemistry of the Pd(II) complexes upon discovering that two distortional isomers of dichlorobis[(2-phenyl-1*H*-imidazoline)]palladium(II) were isolated in the solid state [6e]. Many challenges and problems still remain in the determination of stereochemistry of coordination compounds [7], and in the process of crystallization itself, which can be regarded as a very complicated process. We selected 2-(*ortho*-substituted phenyl)-1*H*-imidazolines in this study because conformational changes in the coordination sphere of the Pd(II) complexes could be expected by tuning properties such as the steric and electronic effects of the substituents at the *ortho*-position of the phenyl ring. Here, we report a series of palladium(II) complexes which were synthesized by mixing one equiv of $PdCl_2$ with 2 equiv of 2-(*ortho*-substituted phenyl)-1*H*-imidazolines or imidazoles in DMF, and the crystal structures obtained by X-ray diffractometry.

2. Results and discussion

Synthesis and properties of ligands

Reaction of 2-substituted benzaldehydes with ethylenediamine gave 2-(*o*-substituted phenyl)-1*H*-imidazolines (Scheme 1). Here, **L1** = 4,5-dihydro-2-phenyl-1*H*-imidazole (= 2-phenyl-1*H*-imidazoline), **L2** = 2-(*o*-fluorophenyl)-1*H*-imidazoline, **L3** = 2-(*o*-methylphenyl)-1*H*-imidazoline, **L4** = 2-(*o*-*tert*-butylphenyl)-1*H*-imidazoline, **L5** = 2-(*o*-hydroxyphenyl)-1*H*-imidazoline, and **L6** = 2-(*o*-methylphenyl)-1*H*-imidazole. The most common method for transformation of imidazoline into imidazole is oxidation. Recently we reported a method of oxidative aromatization with molecular oxygen in the presence of activated carbon [8], which was also adopted for transformation of 2-(*o*-methylphenyl)-1*H*-imidazoline to the corresponding imidazole (Scheme 1) [9].

(Scheme 1)

Scheme 1. Preparation of ligands **L1—L6**

This simple process is not only environmentally friendly but also economical and operationally simple. Only oxygen and commercially available and inexpensive activated carbon were used.

Neither metal oxides nor organic peroxides were required. The same method was not adopted for preparation of 2-(*o*-hydroxyphenyl)-1*H*-imidazoline (**L5**), which was prepared by reaction of methyl salicylate and ethylenediamine following the Rogers and Bruice thermal condensation procedure (Scheme 1) [10]. Excess ethylenediamine was removed along with methanol and water by distillation to give the crude product as a yellow crystal. Higher purity **L5** was obtained by crystallization from water/ethanol (2:1). This method has an advantage due to its large scale applicability and easy isolation by distillation. Ligand **L5** is amphoteric, such that **L5a** and bidentate chelate ligand **L5b** are produced by protonation and deprotonation of **L5**, respectively (Scheme 2).

(Scheme 2)

Scheme 2. Protonation and deprotonation of **L5**

In each 2-(*o*-substituted phenyl)-1*H*-imidazoline, the C—C bond between the aryl and imidazoline rings is freely rotatable. The N_{imine} of the imidazoline ligand usually makes a σ bond with Pd(II) and this N_{imine}—Pd bond is also freely rotatable. Introducing an *o*-substituent on the phenyl ring creates an obstacle to a freely rotatable bond in both ligands and complexes. We propose that the multiaxial rotations are affected by the steric hindrance of a bulky *tert*-butyl group in the *ortho*-position of the phenyl ring after the ligand coordinates with palladium chloride.

Preparation of palladium compounds

Palladium(II) dichloride complexes of [Pd(**L2**)$_2$Cl$_2$] **2**, [Pd(**L3**)$_2$Cl$_2$] **3**, [Pd(**L4**)$_2$Cl$_2$] **4** and [Pd(**L6**)$_2$Cl$_2$]·2DMF **6**·2DMF were prepared by the reaction of the corresponding ligands with palladium chloride in a 2:1 molar ratio (Figure 1). All complexes tended to precipitate from the DMF solution by adding an excessive amount of a poor solvent such as toluene, hexane or CH_2Cl_2 to the reaction solution. By slow diffusion of the solvent into the solution, the solubilities of the complexes were decreased, continually generating a low supersaturated solution for crystal growth. X-ray diffraction and NMR spectroscopic characterization of the palladium complexes were performed, and the structures and complex numbers are shown in Figures 2—6. All of the Pd(II) complexes were crystallized as mononuclear complexes. The effect of the *ortho*-substituent in the phenyl ring on the *trans*-chlorine geometry was noticed for complexes [Pd(**L1**)$_2$Cl$_2$] **1a** and **1b** and complex **2**, in contrast with the *cis*-chlorine

(Fig. 1)

Fig. 1. Preparation of various palladium complexes

geometry for complexes **3** and **4**. Due to the different coordination properties of imidazoline and imidazole, the *cis*-chlorine geometry was noted for complex **3** whereas the *trans*-chlorine geometry was observed for complex **6**. Generally, only $[Pd(L)_2Cl_2]$ type palladium complexes were isolated from each reaction solution. However, the reaction of $PdCl_2$ with 2 equiv of ligand **L5** gave a mixture of palladium coumpounds. After diffusion of CH_2Cl_2 into the resulting solution as an ionic salt having lower solubility in organic solvents, the orange red crystal $[\mathbf{L5a}]_2[PdCl_4]$ **5a** was precipitated first, and it was filtered. After one month, the yellow crystal $[Pd(\mathbf{L5b})_2]$ **5b** was obtained.

Single-crystal X-ray diffractometry (XRD) study.

Crystallographic data for the structures of complexes **2**, **3**, **4**, **5a**, **5b** and **6** are summarized in Table 1.

Molecular structure of *trans*-$[Pd(L2)_2Cl_2]$ 2. Structural views of palladium complex **2** are shown in Figure 2. In the complex, the central Pd(II) cation is four-coordinated in a slightly distorted square planar environment containing two chlorine atoms in the *trans*-position and two 2-arylimidazoline molecules. Ligands bound to Pd(II) *via* their N_{imine} atoms and their aryl rings are situated *cis* to each other. The Molecular structure is similar to that found in *trans*-dichlorobis(2-phenyl-1*H*-imidazoline) palladium(II) **1a**.[6e]

(Fig. 2)

Fig. 2. Structural view of **2** showing 50% probability ellipsoids

Molecular structures of *cis*-$[Pd(L3)_2Cl_2]$ 3 and *cis*-$[Pd(L4)_2Cl_2]$ 4. The structural views of palladium complexes **3** and **4**, are shown in Figure 3. In each palladium complex, the central Pd(II) is coordinated to two 2-arylimidazoline molecules via their unsaturated N_{imine} atoms. *cis*-chlorine geometry, *trans*-Me and *cis*-^{t}Bu geometries were observed in **3** and **4**, respectively. In complex **3**, spontaneous resolution took place. The combination of the *cis*-chlorine and *trans*-Me geometries, which enables the formation of a simple network structure due to the hydrogen bonds (N—H···Cl), might allow the formation of the conglomerate [11]. In complex **4**, the *tert*-butyl group of one ligand molecule **L4** shows rotational disorder in about a 4:1 ratio.

(Fig. 3)

Fig. 3. Structural view of complex **3** and **4** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Molecular structure of *trans*-[Pd(L6)$_2$Cl$_2$]·2DMF 6. The structural views of **6** from different orientations are shown in Figure 4. Contrary to the expected *cis*-chloride as in complex **3**, its molecular structure is similar to that found in **1b**.

(Fig. 4)

Fig. 4. Structural view of **6**·2DMF showing 50% probability ellipsoids. DMF molecules are omitted for clarity.

Structure of the salt of [L5a]$_2$[PdCl$_4$] 5a. The structural view of the ionic salt **5a** is shown in Figure 5. The asymmetric unit of the ionic crystal structure is comprised of the bridge-type counter cation and a square planar tetrachloropalladate(II) anion where four chlorine atoms as ligands in the solid state through formation of intermolecular N—H···Cl and O—H···Cl hydrogen bonds.

(Fig. 5)

Fig. 5. Structural view of **5a** showing 50% probability ellipsoids.

Molecular structure of [Pd(L5b)$_2$] 5b. The complex **5b** was obtained as a yellow crystal. As shown in Figure 6, the Pd(II) ion, on an inversion center, is *trans*-coordinated by two bidentate 2-(1*H*-imidazolin-2-yl)phenolate ligands. This is tha first example of palladium complex of **L5b** [12].

(Fig. 6)

Fig. 6. Structural view of **5b** showing 50% probability ellipsoids with numbering scheme.

Table 1. Crystallographic Data for Complexes 2, 3, 4, 5a, 5b and 6·2DMF

	2	**3**	**4**	**5a**	**5b**	**6**·2DMF
formula	$C_{18}H_{18}Cl_2F_2N_4Pd$	$C_{20}H_{24}N_4Cl_2Pd$	$C_{26}H_{36}Cl_2N_4Pd$	$C_{18}H_{22}N_4$ Cl_4O_2Pd	$C_{18}H_{18}N_4O_2Pd$	$C_{26}H_{34}N_6Cl_2O_2Pd$
formula wt	505.66	496.73	581.89	574.60	428.76	639.89
T (K)	193(2)	297(2)	193(2)	296(2)	198(2)	295(2)
radiation	Mo-Kα (λ = 0.71073 Å)					
cryst syst	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	$C2/c$	$P2_1/c$	$P2_1/c$
unit cell dimens						
a (Å)	10.719(3)	9.3055(11)	10.5531(8)	13.570(5)	7.8697817)	8.264(2)
b (Å)	13.102(4)	15.1358(17)	17.6061(13)	19.628(7)	5.5209(12)	10.245(3)
c (Å)	14.059(4)	15.3710(18)	14.4758(11)	8.317(3)	18.238(4)	10.317(3)
V (Å^3)	1903.7(9)	2164.9(5)	2668.2(3)	2196.9(13)	788.2(3)	724.4(4)
α (deg)	90	90	90	90	90	118.675(4)
β (deg)	105.386(5)	90	97.2360(10)	97.374(6)	95.918(3)	93.297(4)
γ (deg)	90	90	90	90	90	104.707(4)
Z	4	4	4	4	2	1
D_{calcd} (Mg/m^3)	1.764	1.527	1.449	1.731	1.807	1.467
F(000)	1008	1008	1200	1144	432	328
μ(Mo Ka) (mm^{-1})	1.285	1.116	0.917	1.354	1.200	0.858
cryst size (mm^3)	0.30×0.16×0.10	0.28×0.19×0.14	0.32×0.15×0.15	0.30×0.15×0.033	0.33×0.11×0.06	0.25×0.16×0.15
θ range (deg)	1.97–27.42	1.89–26.65	2.26–27.26	1.83–27.47	2.25–27.24	2.30–27.05
index ranges	-13≤h≤13	-10≤h≤11	-11≤h≤13	-9≤h≤17	-10≤h≤9,	-10 ≤h≤10,
	-15≤k≤16	-19≤k≤10	-20≤k≤22	-23≤k≤22	-7≤k≤6,	-11≤k≤12,
	-17≤l≤11	-18≤l≤18	-18≤l≤13	-10≤l≤9	-17≤l≤23	-12≤l≤5
no. of reflns measd						
total	10661	11462	15113	6147	4074	3914
unique	3932	4087	5540	2242	1587	2756
R_{int}	0.0329	0.0275	0.0187	0.0262	0.0436	0.0174
structure soln	direct method					
refinement	full-matrix least squares on F^2					
no. of variables	316	245	357	316	245	172
GOF	1.074	1.015	1.050	1.113	0.973	1.074
R_1	0.0334	0.0238	0.0253	0.0346	0.0263	0.0313
wR_2	0.0883	0.0582	0.0637	0.0852	0.0695	0.0828

^{1}H NMR study of L5, 5a and 5b.

(Fig. 7)

Fig. 7. ^{1}H NMR spectra in DMF-d_7. (A) **L5**, (B) **5a**, (C) **5b**, (D) A mixture of $PdCl_2$ and 2.0 equiv of **L5**.

The chemical shifts in the ^{1}H-NMR spectra for **L5**, complex **5a**, **5b** and the mixture of $PdCl_2$ with 2.0 equiv of **L5** in DMF-d_7 are shown in Figure 7. ^{1}H-NMR spectra indicated that there existed more than three palladium compounds, resulting from the coordination of $PdCl_2$ with 2.0 equiv of **L5** in DMF-d_7, i.e., **5a**, **5b** and **5c** at a molar ratio of 1:0.5:0.5. From the viewpoint of material balance, we suggest that **5c** is an isomer of **5b**, *cis*-bis[2-(1*H*-imidazoline-2-yl)phenolato-κ^2N^3,*O*] Palladium (II) (Scheme 3).

(Scheme 3)

Scheme 3. Proposed structure of $PdCl_2$ with **L5**

Intermolecular proton transfer between **L5** was promoted by reaction with $PdCl_2$. We propose that **5d** was formed first, passing through an intramolecular dehydrochloride to give **5b** and **5c** since the N—Pd bond is freely rotatable. In the meantime, an equivalent amount of **L5a** and tetrachloropalladate (II) anion were also formed to give an ionic salt **5a** that precipitated first due to its low solubility, promoting completion of the reaction.

3. Conclusion

We prepared four novel *N*-monodentate Pd(II) complexes [PdL_2Cl_2] (**2**, **3**, **4** and **6**) and two new Pd

complexes (**5a** and **5b**), and determined their molecular structures by single crystal X-ray analysis. We revealed the following characteristic features of the effect of *ortho*-substituents on the stereochemistry of 2-(*o*-substituted phenyl)-1*H*-imidazoline–palladium complexes. i) To examine the properties of substituents in the *ortho*-position of the phenyl ring, such as steric and electronic effects, two novel *cis*-[PdL_2Cl_2] complexes were prepared. ii) A palladium salt **5a** and a palladium chelate **5b** were successfully isolated and characterized by single crystal X-ray analysis. iii) The results obtained from the NMR coordination studies of $PdCl_2$ with **L5** in solution support the feasibility of an amphoteric ligand. The catalytic behavior of these complexes toward coupling reactions will be studied in due course.

4. Experimental

4.1.General remarks

All melting points were measured on a Yanaco MP-500D and were uncorrected. ^{1}H and ^{13}C NMR spectra (400 and 100.4 MHz, respectively) were recorded on a JEOL JNM-LA 400 using Me_4Si as the internal standard (0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. IR spectra were measured with a PERKIN ELMER FT-IR Spectrometer SPECTRUM 1000 in the range of 4000-400 cm^{-1}. Elemental analyses were performed with a Yanaco CHN Corder MT-5. Mass spectra were measured on a Thermo Quest LCQ DECA plus. Preparative column chromatography was carried out on Fuji Silysia BW-820MH or YMC*GEL Silica (6 nm

I-40—63 μm). Thin layer chromatography (TLC) was carried out on Merck 25 TLC aluminum sheets silica gel 60 F_{254}.

1-(*tert*-Butyl)-2-iodobenzene. 2-*tert*-Butylaniline (2.2 g, 14.7 mmol) was added to 3.4 M H_2SO_4 (2 mL) and cooled to -10 ºC. A saturated aqueous solution of $NaNO_2$ (1.05 g, 15.2 mmol) was added with vigorous stirring over 5 minutes to give a light brown slurry. After stirring for another hour at -10 to 0 ºC, the slurry of the diazonium salt was added rapidly to a concentrated ice-cold solution of KI (7.5 g, 45 mmol/10 g H_2O). After stirring at 0 ºC for 2 h, the suspension was extracted with diethyl ether (15 mL). After removal of solvent, purification by column chromatography (silica, hexane) gave the product as a colorless liquid. Yield: 1.05 g (27.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.00 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 9.6 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 9.6 Hz, 1H), 1.53 (s, *t*-Bu); ^{13}C NMR (100.4 MHz, DMF-d_7): δ (ppm) 150.2, 143.6, 127.9, 127.5, 127.5, 95.1, 36.7, 29.9.

2-(*tert*-Butyl) benzaldehyde. *tert*-Butyllithium (7.7 mL, 12 mmol, 1.6 M in pentane) was added to a solution of 1-(*tert*-butyl)-2-iodobenzene (1.38 g, 5.6 mmol) in THF (10 mL) at -78 ºC. After 30 min at this temperature, DMF (2 mL) was added, and the reaction mixture was allowed to warm to room temperature. HCl (15 mL, 3 M) was added, and the mixture was extracted with diethyl ether (40 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to yield 2-(*tert*-butyl)-benzaldehyde. Yield: 0.81 g (89%). ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) 10.85 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1 H), 7.50—7.48 (m, 2H), 7.4—7.3 (m, 1H), 1.53 (s, 9H); ^{13}C NMR (100.4 MHz, $CDCl_3$): δ (ppm) 192.8, 152.2, 135.5, 133.3, 130.3, 126.3, 115.5, 35.8, 33.0.

4.2. General procedures for synthesis of 2-(o-substituted phenyl)-1H-imidazolines.

Method A. A mixture of aldehyde (2 mmol) and ethylenediamine (2.1 mmol) in dry CH_2Cl_2 (10 mL) was stirred at 0 ºC for 2 h under argon atmosphere. NBS (2.1 mmol) was added to the mixture and the resulting solution was stirred overnight at rt. The reaction was quenched by the addition of 10% aq. NaOH and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, and evaporated under vacuum. The residue was purified by silica gel column chromatography to give imidazoline.

2-(*o*-Fluorophenyl)-1*H*-imidazoline (L2). Yield: 280 mg. (85%). m.p. 85 ºC (lit [9b] 85 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.6—7.5 (m, 1H), 7.3—7.2 (m, 2H), 3.66 (s, 4H); ^{13}C NMR (100.4 MHz, DMF-d_7): δ (ppm) 161.28 (d, *J* = 3.3 Hz), 159.84, 132.75 (d, *J* = 8.2 Hz), 131.40 (d, *J* = 2.5 Hz), 124.96 (d, *J* = 3.3 Hz), 119.92 (d, *J* = 12.4 Hz), 116.96 (d, *J* = 22.3 Hz), 50.47; ESI-MS *m/z*: $[M+H]^+$ 165.1.

2-(*o*-Methylphenyl)-1*H*-imidazoline (L3). Yield: 258 mg (80%). m.p. 87 ºC (lit [9b] 88 ºC); ^{1}H NMR (400 MHz, DMF-d_7): δ (ppm) 7.54 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.3—7.2 (m, 3H), 3.50 (s, 4H), 2.49 (s, 3H); ^{13}C NMR (100.4 MHz, DMF-d_7): δ 166.0, 137.8, 132.6, 131.4, 129.7, 129.1, 126.0, 21.0; ESI-MS *m/z*: $[M+H]^+$ 161.10.

2-(*o*-*tert*-Butylphenyl)-1*H*-imidazoline (L4). m.p. 145—147 ºC. Yield: 164 mg (25%). IR (KBr): ν_{max} (cm^{-1}) 3138, 2949, 2866, 1614, 1588, 1502, 1483, 1341, 1273, 1260, 1078, 980, 763; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 (d, *J* = 8.0 Hz, 1H), 7.4—7.3 (m, 1H), 7.3—7.2 (m, 2H), 3.64 (s, 4H), 1.42 (s, 9H); ^{13}C NMR (100.4 MHz, D_2O/ DMF-d_7): δ 168.4, 148.7, 132.2, 130.6, 129.4, 127.3, 125.8, 51.9, 38.9, 32.0; ESI-MS *m/z*: $[M+H]^+$ 203.26.

Method B. A mixture of methyl salicylate (12 g, 80 m mol) and ethylenediamine (14.4 g, 120 mol) was intensively mixed for 3 h under reflux. The excess ethylenediamine was removed by distillation giving a yellow crystal product in 12.05 g. 93% yield. The higher purity product was recrystallized from water/ethanol (2:1).

2-(1*H*-Imidazolin-2-yl)phenol (L5). m.p. 200—203 ºC (lit [9b] DMF-d_7): δ (ppm) 200—203 ºC); IR (KBr): ν_{max} (cm^{-1}) 3362, 3049, 2959, 2891, 2789, 1609, 1591, 1575, 1530, 1472, 1448, 1350, 1268, 1153, 1029, 991, 836, 774, 688, 558, 536; ^{1}H NMR (400 MHz, DMF-d_7): δ (ppm) 13.0 (br s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.77 (t, J = 8.0 Hz, 1H), 3.8 (br s, 4H), 12.5 to 13.5 (br s, NH and OH); ^{13}C NMR (100.4 MHz, DMF-d_7): δ (ppm) 112.4, 117.6, 118.0, 127.9, 133.0, 162.8, 167.3; MS (ESI) *m/z* : $[M+H]^+$ 163.3.

2-(*o*-Methylphenyl)-1*H*-imidazole (L6). A mixture of 2-(*o*-methylphenyl)-1*H*-imidazoline (2.90 g, 5 mmol) and Shirasagi KL (1.45 g) in xylene (20 mL) was placed in a 250-mL three-necked flask under an oxygen atmosphere and stirred at 120 °C. After confirmation of the completion of the reaction by TLC monitoring, the mixture was filtered using Celite. The filtrate was then concentrated, and the product was isolated by silica gel column chromatography to afford the corresponding 2-(*o*-methylphenyl)-1*H*-imidazole **(L6).** Yield: 418 mg (53%). m.p. 135—136 ºC (lit[13] 138—139 ºC); IR (KBr): ν_{max} (cm^{-1}) 3032, 2907, 2802, 1577, 1499, 1468, 1444, 1412, 1382, 1369, 1170, 1109, 958, 904, 771, 750, 730; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54 (d, J = 8.0 Hz, 1H), 7.3—7.2 (m, 3H), 7.15 (d, J = 2.0 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (100.4 MHz, DMF-d_7): δ (ppm) 146.9, 136.4, 130.9, 130.4, 129.1, 128.6, 125.7, 122.4, 20.6.

4.3. General procedures for preparation of 2-(o-substituted phenyl)-1H-imidazoline–palladium complexes [14] Palladium complexes were prepared by simply mixing the corresponding ligands with palladium chloride in a 2:1 molar ratio. All complexes were precipitated from the DMF solution by adding an excessive amount of a poor solvent such as toluene, hexane or CH_2Cl_2 into the reaction solution. By slow diffusion of a solvent into the solution, the solubility of the complexes decreased, continually generating a low supersaturated solution for crystal growth**.**

***trans*-Dichlorobis[(2-*o*-fluorophenyl)-1*H*-imidazoline)] palladium(II) 2.** To a suspension of $PdCl_2$ (177.3 mg, 1.0 mmol) in DMF (5 mL), 2-(*o*-fluorophenyl)-1*H*-imidazoline (328.4 mg, 2.0 mmol) was added under argon atmosphere. The mixture was stirred at 50 ºC for 2 h until a clear orange yellow solution was formed. After dilution of the resulting solution with DMF (10 mL), toluene (40 mL) was added to precipitate the Pd complex. The Pd complex was isolated as a light yellow powder by filtration, washed with hexane and dried in air. Yield: 470 mg (93%). Anal. Calcd. for $C_{18}H_{18}Cl_2F_2N_4Pd$: C, 42.75; H, 3.59; N, 11.08. Found: C, 42.71; H, 3.71; N, 11.19. A single crystal of complex **2**, suitable for X-ray diffraction analysis, was obtained by slow diffusion of hexane into a solution of complex **2** in DMF. m.p. > 300 ºC. IR (KBr): ν_{max} (cm^{-1}) 3268, 2962, 2881, 1627, 1604, 1518, 1485, 1451, 1353, 1279, 1236, 1101, 1048, 961, 949, 818, 771, 745, 557, 504, 458; ^{1}H NMR (400 MHz, DMF-d_7): δ (ppm) 8.82 (t, dd, *J* = 8.0, 1.2, 0.8, 2.0 Hz, 1H), 7.96 (s, 1H), 7.6—7.5 (m, 1H), 7.39 (t, *J* = 8.0, 0.8 Hz, 1H), 7.30 (dd, *J* = 8, 1.2, 0.8 Hz, 1H), 3.90 (t, *J* = 10.8 Hz, 2H), 3.65 (t, *J* = 10.8 Hz, 2H); ^{13}C NMR (100.4 MHz, DMF-d_7): δ (ppm) 163.55, 159.63, 133.7 (d, *J* = 9.0 Hz), 132.5, 124.9 (d, *J* = 3.3 Hz), 118.7, 116.5 (d, *J* = 21 Hz), 55.18, 44.44; Anal. Calcd. for $C_{18}H_{18}Cl_2F_2N_4Pd$: C, 42.75; H, 3.59; N, 11.08. Found: C, 42.71; H, 3.71; N, 11.19.

***cis*-Dichlorobis[2-(*o*-methylphenyl)-1*H*-imidazoline] palladium(II) 3.** To a suspension of $PdCl_2$ (177.3 mg, 1.0 mmol) in DMF (5 mL), 2-(*o*-methylphenyl)-1*H*-imidazoline (320.4 mg, 2.0 mmol) was added under argon atmosphere. The mixture was stirred at 50 ºC for 2 h until a clear orange yellow solution was formed. After dilution of the resulting solution with DMF (10 mL), toluene (40 mL) was added manually to slowly diffuse into the Pd complex solution of DMF. The palladium complex was isolated as an orange red crystal by filtration, washed with toluene and dried in air. The resulting crystal was suitable for X-ray diffraction analysis. Yield: 323.5 mg (65%). m.p. 228—230 ºC. IR (KBr): ν_{max} (cm^{-1}) 3314, 2957, 2889, 1616, 1602, 1590, 1510, 1474, 1457, 1285, 1048, 772, 730, 210; ^{1}H NMR (400 MHz, DMF-d_7): δ (ppm) 7.95 (d, J = 6.4 Hz, 1H), 7.9 (br s, 1H), 7.6—7.5 (m, 3H), 3.48 (s, 2H), 3.4 (br s, 2H), 2.68 (s, 3H); ^{13}C NMR (100.4 MHz, DMF-d_7): δ (ppm) 167.3 (168.3), 137.8 (137.2), 131.4 (131.4), 131.3 (131.3), 131.0 (131.2), 129.9 (130.4), 126.5 (125.8), 54.4 (55.1), 44.0 (44.2), 20.5 (20.2); Anal. Calcd. for $C_{20}H_{24}N_4Cl_2Pd$: C, 48.26; H, 4.86; N, 11.26. Found: C, 48.33; H, 4.86; N, 11.22.

***cis*-Dichlorobis[2-(*o*-*tert*-butylphenyl)-1*H*-imidazoline)] palladium(II) 4.** To a suspension of $PdCl_2$ (35.5 mg, 0.2 mmol) in DMF (2 mL), 2-(*o*-*tert*-butylphenyl)-1*H*-imidazoline (80.8 mg, 0.4 mmol) was added under argon atmosphere. The mixture was stirred at 50 ºC for 2 h until a clear orange yellow solution was formed. After dilution of the resulting solution with DMF, toluene (5 mL) was slowly added. The Pd complex was isolated as an orange red crystal by filtration, washed with toluene and dried in air. Yield: 52.4 mg (45%). m.p. 255—258 ºC (dec); ^{1}H NMR (400 MHz, DMF-d_7): δ (ppm) 7.97 (s, 1H), 7.85 (d, J = 7.6 Hz), 7.8 (br d), 7.66 (s), 7.58 (t, J = 7.6 Hz), 7.5 (br s), 7.44 (t, J = 7.6 Hz), 7.27, 7.06, 3.77 (m), 3.36 (t, J = 10.4 Hz), 1.67 (s), 1.57 (s), 1.3 (br s); ^{13}C NMR (100.4 MHz, DMF-d_7): δ (ppm) 169.6 (170.0), 150.7 (149.1), 132.6, 130.4 (130.3), 128.7 (128.2),

125.8 (125.3), 101.4, 54.5 (55.2), 43.6 (44.1), 37.9 (37.3), 32.5 (32.2); Anal. Calcd. for $C_{26}H_{36}Cl_2N_4Pd$: C, 53.66; H, 6.24; N, 9.63. Found: C, 53.70; H, 6.25; N, 9.77.

***trans*-Dichlorobis[(2-*o*-methylphenyl-1*H*-imidazole)] palladium(II) bis(dimethylformamide) solvate 6·2 DMF.** To a suspension of $PdCl_2$ (177.3 mg, 1.0 mmol) in DMF (5 mL), 2-*o*-methylphenyl-1*H*-imidazole (316.4 mg, 2.0 mmol) was added under argon atmosphere. The mixture was stirred at 50 ºC for 2 h until a clear orange yellow solution was formed. After dilution of the resulting solution with DMF (10 mL), toluene (40 mL) was slowly added. The Pd complex was isolated as an orange red crystal by filtration, washed with toluene and dried in air. Yield: 416 mg (65%). m.p. 268 ºC (dec); IR (KBr): ν_{max} (cm^{-1}) 3314, 2957, 2889, 1616, 1602, 1590, 1510, 1474, 1457, 1285, 1048, 772, 730, 210; ^{1}H NMR (400 MHz, DMF-d_7): δ (ppm) 12.78 (s, 1H), 7.99 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.4—7.3 (m, 3H), 7.14 (t, *J* = 1.6, 1H), 2.29 (s, 3H); ^{13}C NMR (100.4 MHz, DMF-d_7): δ (ppm) 162.9, 148.0, 138.3, 132.2, 130.8, 130.2, 129.7, 126.1, 118.3, 36.1, 30.9, 20.5; Anal. Calcd. for $C_{26}H_{34}N_6O_2Cl_2Pd$: C, 48.80; H, 5.36; N, 13.13. Found: C, 48.71; H, 5.42; N, 12.96.

4.4. Coordination of palladium chloride with 2-(o-hydroxyphenyl)-1H-imidazoline L5. To a suspension of $PdCl_2$ (177.3 mg, 1.0 mmol) in DMF (4 mL), **L5** (320.4 mg, 2.0 mmol) was added under argon atmosphere. The mixture was stirred at 50 ºC for 2 h until a clear orange red solution was formed. After dilution of CH_2Cl_2 into the resulting solution as an ionic salt having lower solubility in organic solvents, the orange red crystal **5a** was precipitated first, then it was filtered. After one month, the mixture of orange red crystal **5a** and yellow crystal **5b** was precipitated. The crystal **5b** was separated manually from the mixture of **5a** and **5b**.

bis-[2-(*o*-Hydroxyphenyl)-1*H*-imidazolinium] tetrachloro palladate(II) 5a. Yield: 208 mg. IR (KBr): ν_{max} (cm^{-1}) 3384, 3261, 3218, 1621, 1607, 1590, 1560, 1503, 1382, 1349, 1310, 1289, 1255, 1005, 826, 768, 747, 622; ^{1}H NMR (400 Hz, DMF-d_7): δ (ppm) 12.52 (s, 1H), 10.15 (s, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 4.14 (s, 4H); ^{13}C NMR (100.4 MHz, DMF-d_7): δ (ppm) 45.1, 108.9, 118.2, 120.4, 130.8, 136.7, 159.6, 164.1; Anal. Calcd. for $C_{18}H_{22}N_4Cl_2O_2Pd$: C, 37.49; H, 4.20; N, 9.72. Found: C, 37.72; H, 4.19; N, 9.77.

bis-[2-(1*H*-Imidazoline-2-yl)phenolato-κ^2*N*^{3},*O*] palladium(II) 5b. Yield: 112 mg. IR (KBr): ν_{max} (cm^{-1}) 3238, 2882, 2422, 1608, 1590, 1544, 1500, 1435, 1326, 1282, 1241, 851, 745, 682, 579; ^{1}H NMR (400 Hz, DMF-d_7): δ (ppm) 7.75 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.48 (t, *J* = 8.0 Hz, 1H), 4.02 (t, *J* = 12.0 Hz, 2H), 3.65 (t, *J* = 12.0 Hz, 2H); ^{13}C NMR (100.4 MHz, DMF-d_7): δ (ppm) 44.0, 51.4, 112.9, 114.1, 122.2, 129.1, 132.7, 160.8, 166.9; Anal. Calcd. for $C_{18}H_{18}N_4O_2Pd$: C, 50.42; H, 4.23; N, 13.07. Found: C, 49.89; H, 4.68; N, 12.96.

4.5. X-ray Crystallography. Single crystal X-ray diffraction data of the complexes were collected on a Bruker Smart 1000 CCD diffractometer. An empirical absorption correction was applied using the SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 using the SHELXL-97 program package [15]. Crystal data and details of the data collection and structure refinement are summarized in Table 1.

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Supporting information available.

CCDC 751531, 751529, 751530, 741320, 741339 and 751528 contain the supplementary crystallographic data for **2**, **3**, **4**, **5a**, **5b** and **6**·2DMF respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.

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