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

Zhibin Gan, Kenjiro Kawamura, Kazuo Eda and Masahiko Hayashi*

Department of Chemistry, Graduate School of Science, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan

Abstract

Palladium complexes composed of [Pd(Ln)2Cl2] (n = 1, 2, 3, 4, 6), [L5a][PdCl4] and [Pd(L5b)2], where L1 = 4,5-dihydro-2-phenyl-1H-imidazole (= 2-phenyl-1H-imidazoline), L2 = 2-(o-fluorophenyl)-1H-imidazoline, L3 = 2-(o-methylphenyl)-1H-imidazoline, L4 = 2-(o-tert-butylphenyl)-1H-imidazoline, L5a = 2-(o-hydroxyphenyl)-1H-imidazolinium, L5b = 2-(1H-imidazolin-2-yl)phenolate, and L6 = 2-(o-methylphenyl)-1H-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(L1)2Cl2] 1a and 1b, [Pd(L2)2Cl2] 2 and [Pd(L6)2Cl2] 6, whereas cis-chlorine geometry was observed for [Pd(L3)2Cl2] 3 and [Pd(L4)2Cl2] 4. PdCl2 reacts with 2-(o-hydroxyphenyl)-1H-imidazoline in DMF to give [L5a]+ and [L5b]− so that [L5a][PdCl4] 5a and [Pd(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 PdCl2 with 2-(o-hydroxyphenyl)-1H-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 PdCl2 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-1H-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)-1H-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 PdCl₂ with 2 equiv of 2-(ortho-substituted phenyl)-1H-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)-1H-imidazolines (Scheme 1). Here, L₁ = 4,5-dihydro-2-phenyl-1H-imidazole (= 2-phenyl-1H-imidazoline), L₂ = 2-(o-fluorophenyl)-1H-imidazoline, L₃ = 2-(o-methylphenyl)-1H-imidazoline, L₄ = 2-(o-tert-butylphenyl)-1H-imidazoline, L₅ = 2-(o-hydroxyphenyl)-1H-imidazoline, and L₆ = 2-(o-methylphenyl)-1H-imidazole. The most common method for transformation of imidazole into imidazol 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)-1H-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)-1H-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)-1H-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)2Cl2] 2, [Pd(L3)2Cl2] 3, [Pd(L4)2Cl2] 4 and [Pd(L6)2Cl2]·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 CH2Cl2 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)2Cl2] 1a and 1b and complex 2, in contrast with the cis-chlorine geometry.
Fig. 1. Preparation of various palladium complexes

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 \([\text{Pd}(\text{L})_2\text{Cl}_2]\) type palladium complexes were isolated from each reaction solution. However, the reaction of \(\text{PdCl}_2\) with 2 equiv of ligand \(\text{L5}\) gave a mixture of palladium compounds. After diffusion of \(\text{CH}_2\text{Cl}_2\) into the resulting solution as an ionic salt having lower solubility in organic solvents, the orange red crystal \([\text{L5a}]_2[\text{PdCl}_4]\) 5a was precipitated first, and it was filtered. After one month, the yellow crystal \([\text{Pd}([\text{L5b}])]_2\) 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-[\(\text{Pd}(\text{L2})_2\text{Cl}_2\)] 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-[\(\text{Pd}(\text{L3})_2\text{Cl}_2\)] 3 and cis-[\(\text{Pd}(\text{L4})_2\text{Cl}_2\)] 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-tBu 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.
**Molecular structure of trans-[Pd(L6)₂Cl₂]-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[PdCl₄] 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-(1H-imidazolin-2-yl)phenolate ligands. This is the 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

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\( ^1 \text{H NMR study of } \text{L5, 5a and 5b.} \)

(Fig. 7)

**Fig. 7.** \(^1 \text{H NMR spectra in DMF}-d_7.\) (A) L5, (B) 5a, (C) 5b, (D) A mixture of PdCl\(_2\) and 2.0 equiv of L5.

The chemical shifts in the \(^1 \text{H-NMR spectra for L5, complex 5a, 5b and the mixture of PdCl}_2\) with 2.0 equiv of L5 in DMF-\(d_7\) are shown in Figure 7. \(^1 \text{H-NMR spectra indicated that there existed more than three palladium compounds, resulting from the coordination of PdCl}_2\) 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, \textit{cis-bis[2-(1H-imidazole-2-yl)phenolato-\(\kappa^2N^3,O\)] 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 \([\text{PdL}_2\text{Cl}_2]\) (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)-1H-imidazole–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-[PdL₂Cl₂] 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 PdCl₂ 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. H and C NMR spectra (400 and 100.4 MHz, respectively) were recorded on a JEOL JNM-LA 400 using Me₄Si 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 F254.

**1-(tert-Butyl)-2-iodobenzene.** 2-tert-Butylaniline (2.2 g, 14.7 mmol) was added to 3.4 M H$_2$SO$_4$ (2 mL) and cooled to -10 °C. 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 °C, 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$_2$O). After stirring at 0 °C 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, 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 °C. 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 CH₂Cl₂ (10 mL) was stirred at 0 °C 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 CH₂Cl₂. The organic layer was dried over Na₂SO₄, and evaporated under vacuum. The residue was purified by silica gel column chromatography to give imidazoline.

2-(o-Fluorophenyl)-1H-imidazoline (L2). Yield: 280 mg (85%). m.p. 85 °C (lit [9b] 85 °C); ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100.4 MHz, DMF-d₇): 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)-1H-imidazoline (L3). Yield: 258 mg (80%). m.p. 87 °C (lit [9b] 88 °C); ¹H NMR (400 MHz, DMF-d₇): 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); ¹³C NMR (100.4 MHz, DMF-d₇): 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)-1H-imidazoline (L4). m.p. 145—147 °C. Yield: 164 mg (25%). IR (KBr): νmax (cm⁻¹) 3138, 2949, 2866, 1614, 1588, 1502, 1483, 1341, 1273, 1260, 1078, 980, 763; ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100.4 MHz, D₂O/DMF-d₇): 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 m 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-(1H-Imidazolin-2-yl)phenol (L5).** m.p. 200—203 °C (lit [9b] DMF-\(d_7\)): \(\delta\) (ppm) 200—203 °C; IR (KBr): \(v_{\text{max}}\) (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-\(d_7\)): \(\delta\) (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-\(d_7\)): \(\delta\) (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)-1H-imidazole (L6).** A mixture of 2-(o-methylphenyl)-1H-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)-1H-imidazole (L6). Yield: 418 mg (53%). m.p. 135—136 °C (lit[13] 138—139 °C); IR (KBr): \(v_{\text{max}}\) (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\(_3\)): \(\delta\) (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-\(d_7\)): \(\delta\) (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 CH₂Cl₂ 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)-1H-imidazoline)] palladium(II) 2.* To a suspension of PdCl₂ (177.3 mg, 1.0 mmol) in DMF (5 mL), 2-(o-fluorophenyl)-1H-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_{2}F_{2}N_{4}Pd: 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): νₘₐₓ (cm⁻¹) 3268, 2962, 2881, 1627, 1604, 1518, 1485, 1451, 1353, 1279, 1236, 1101, 1048, 961, 949, 818, 771, 745, 557, 504, 458; ¹H NMR (400 MHz, DMF-d₇): δ (ppm) 8.82 (t, dd, J = 8.0, 1.2, 0.8, 2.0 Hz, 1H), 7.96 (s, 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); ¹³C NMR (100.4 MHz, DMF-d₇): 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_{2}F_{2}N_{4}Pd: C, 42.75; H, 3.59; N, 11.08. Found: C, 42.71; H, 3.71; N, 11.19.
**cis-Dichlorobis[2-(o-methylphenyl)-1H-imidazole] palladium(II) 3.** To a suspension of PdCl$_2$ (177.3 mg, 1.0 mmol) in DMF (5 mL), 2-(o-methylphenyl)-1H-imidazole (320.4 mg, 2.0 mmol) was added under argon atmosphere. The mixture was stirred at 50 °C 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 °C. IR (KBr): $v_{\text{max}}$ (cm$^{-1}$) 3314, 2957, 2889, 1616, 1602, 1590, 1510, 1474, 1457, 1285, 1048, 772, 730, 210; $^1$H NMR (400 MHz, DMF-$d_7$): $\delta$ (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-$d_7$): $\delta$ (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$_4$Cl$_2$Pd: 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)-1H-imidazole] palladium(II) 4.** To a suspension of PdCl$_2$ (35.5 mg, 0.2 mmol) in DMF (2 mL), 2-(o-tert-butylphenyl)-1H-imidazole (80.8 mg, 0.4 mmol) was added under argon atmosphere. The mixture was stirred at 50 °C 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 °C (dec); $^1$H NMR (400 MHz, DMF-$d_7$): $\delta$ (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-$d_7$): $\delta$ (ppm) 169.6 (170.0), 150.7 (149.1), 132.6, 130.4 (130.3), 128.7 (128.2), ...
trans-Dichlorobis[2-omega-methylphenyl-1H-imidazole] palladium(II) bis(dimethylformamide) solvate 6·2 DMF. To a suspension of PdCl₂ (177.3 mg, 1.0 mmol) in DMF (5 mL), 2-omega-methylphenyl-1H-imidazole (316.4 mg, 2.0 mmol) was added under argon atmosphere. The mixture was stirred at 50 °C 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 °C (dec); IR (KBr): \(v_{\text{max}}\) (cm⁻¹) 3314, 2957, 2889, 1616, 1602, 1590, 1510, 1474, 1457, 1285, 1048, 772, 730, 210; \(^1\)H NMR (400 MHz, DMF-d₇): \(\delta\) (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, \(J = 1.6\) Hz, 1H), 2.29 (s, 3H); \(^{13}\)C NMR (100.4 MHz, DMF-d₇): \(\delta\) (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 C₂₆H₃₆Cl₂N₄Pd: 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-(omega-hydroxyphenyl)-1H-imidazole L5. To a suspension of PdCl₂ (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 °C for 2 h until a clear orange red solution was formed. After dilution of CH₂Cl₂ 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)-1H-imidazolinium] tetrachloro palladate(II) 5a. Yield: 208 mg. IR (KBr): \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3384, 3261, 3218, 1607, 1590, 1560, 1382, 1310, 1289, 1255, 1005, 826, 747, 622; \(^1\)H NMR (400 Hz, DMF-\(d_7\)): \(\delta\) (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-\(d_7\)): \(\delta\) (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\(_4\)Cl\(_2\)O\(_2\)Pd: C, 37.49; H, 4.20; N, 9.72. Found: C, 37.72; H, 4.19; N, 9.77.

bis-[2-(1H-Imidazole-2-yl)phenolato-\(\kappa^2N^3,O\)] palladium(II) 5b. Yield: 112 mg. IR (KBr): \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3238, 2882, 2422, 1608, 1590, 1454, 1500, 1435, 1326, 1282, 1241, 851, 745, 682, 579; \(^1\)H NMR (400 Hz, DMF-\(d_7\)): \(\delta\) (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-\(d_7\)): \(\delta\) (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\(_4\)O\(_2\)Pd: 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.

References


   (d) M. Anasatassiadou, S. Danoun, L. Crane, G. Baziard-Mouysset, M. Payard, D. H. Caignard, M.


(b) A. Weatherwax, C. J. Abraham, T. Lectka, Org. Lett. 7 (2005) 3461.


   

   


   University of Göttingen, Göttingen, Germany, 1997.

Corresponding author. Tel.: +81-78-803-5687; fax: +81-78-803-5688. E-mail address: mhayashi@kobe-u.ac.jp (M. Hayashi).