2-Phenylimidazole−$PdCl_2$ and 2-Phenylimidazoline−$PdCl_2$ Complexes: Single-Crystal and Powder X-ray Diffractometry, ^{1}H NMR Spectra, and Comparison of Catalytic Activities in Coupling Reactions†

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Single-crystal X-ray diffractometry and powder X-ray diffractometry of the complexes dichlorobis(2-phenyl-1*H*-imidazole)palladium(II) (**1**) and dichlorobis(2-phenyl-4,5-dihydro-1*H*-imidazole)palladium(II) (**2**) and ^{1}H NMR structure elucidation in DMF-d_7 solution are discussed. In the case of complex **1**, we found that changing the solvent for recrystallization from a mixture of DMF and toluene (method A) to only DMF (method B) afforded complexes **2** and **2′**, having crystallographically different structures. ^{1}H NMR studies indicated that the spectra of the solid samples **2** and **2′** are the same in DMF-d_7. This indicated that the Pd−N bond rotates easily in solution, whereas complexes **2** and **2′** coexist through strong packing in the solid state. The catalytic activities of Pd complexes **1** and **2** in coupling reactions such as the Mizoroki−Heck reaction and Suzuki−Miyaura coupling will also be disclosed.

Introduction

Palladium complexes play crucial roles as homogeneous catalysts in a variety of coupling reactions in organic synthesis.[1] Recently, well-designed ligands have contributed significantly to improving catalytic activity. Most of them are phosphine-based ligands, because increasing bulkiness and introducing electron-donating functions increase the reactivity of aryl chlorides, enabling their use as substrates.[2] The development of palladacyclic catalysts[3] and N-heterocyclic carbene palladium catalysts[4] should be mentioned as well. With regard to other types of ligands in coupling reactions, Dai and co-workers have focused on the development of amide-based phosphines as the P,O-ligands for coupling reactions.[5] Čermák and co-workers have reported on diphosphinoazine−Pd(II) complexes that feature a novel tridentate ligand for Mizoroki−Heck reactions with high TON and TOF (h^{-1}).[6] There have been various attempts to improve the Mizoroki−Heck reaction by activating aryl chloride using Pd compounds such as $(CH_3CN)_2PdCl_2-PPh_4Cl$,[7] $Pd(OAc)_2$ with excess $P(OEt)_3$,[8] and heterogeneous Pd/C[9] as catalysts.[10]

On the other hand, nitrogen-based ligands, such as pyridine or imidazole derivatives, have attracted much interest among organic chemists because of their low toxicity and high stability compared to phosphine-based ligands. However, there are few reports of highly catalytic reactive complexes bearing nitrogen ligands, although there are many reports of nitrogen ligands.[11,12] We are interested in the possibility of using imidazoles and 4,5-

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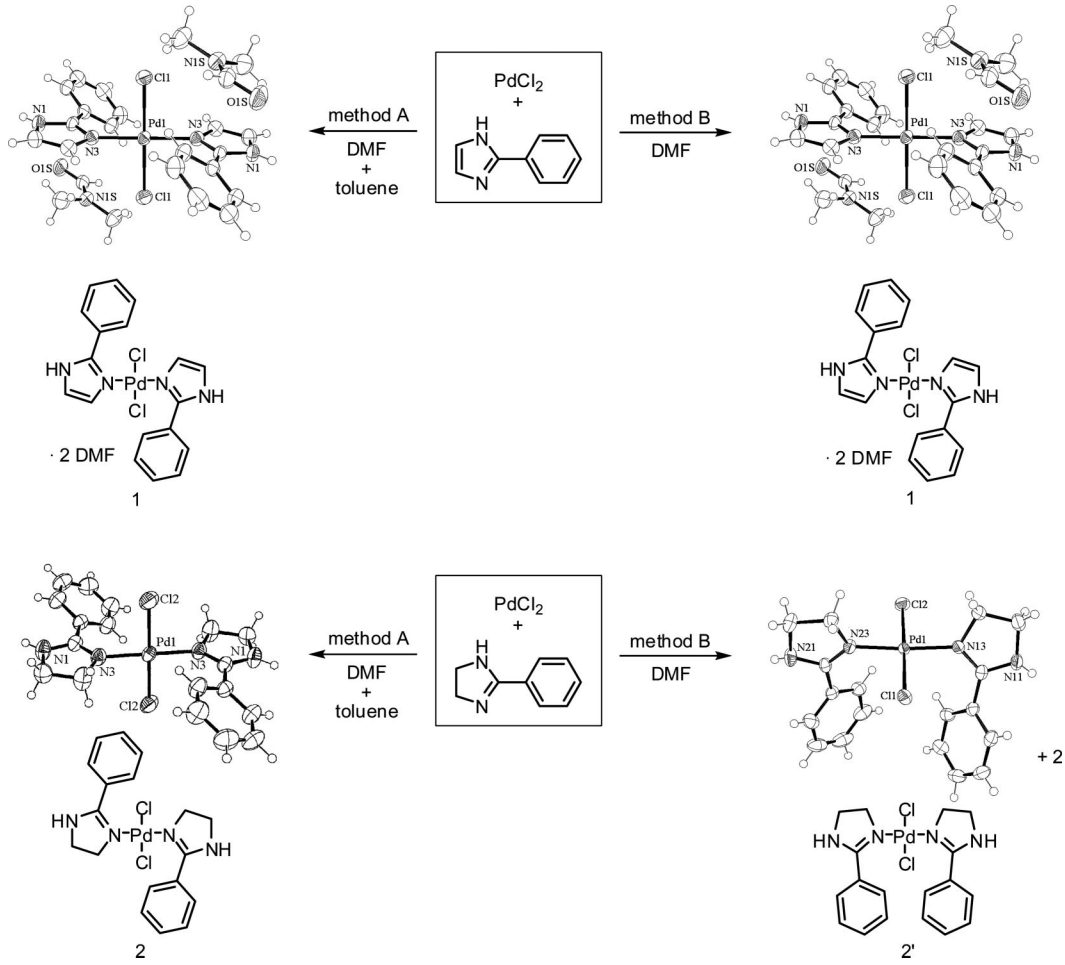
Scheme 1. ORTEP Drawings of Palladium Complexes 1, 2, and 2′ (50% Thermal Ellipsoids)



dihydroimidazoles (imidazolines) as ligands because they are structurally simple, readily available, and inexpensive, and they allow for facile introduction of various substituents into their framework.

Herein, we report on the crystal structure analyses of the complexes dichlorobis(2-phenyl-1*H*-imidazole)palladium(II) (2-phenylimidazole−$PdCl_2$) (**1**) and dichlorobis(2-phenyl-4,5-dihydro-1*H*-imidazole)palladium(II) (2-phenylimidazoline−$PdCl_2$) (**2**) using single-crystal X-ray diffractometry (XRD) and powder XRD and a structure analysis in solution (DMF-d_7) using ^{1}H NMR spectroscopy. We also discuss their catalytic activities in the Mizoroki−Heck reaction[13] and the Suzuki−Miyaura coupling reaction.[14]

Results and Discussion

Synthesis of 2-Phenylimidazole−$PdCl_2$ (1) and 2-Phenylimidazoline−$PdCl_2$ (2) Complexes. Navarro-Ranninger et al. reported that complex **1** was synthesized by reacting Li_2PdCl_4 with phenylimidazole in methanol at 20 °C for 3 days.[15] Our present method for the preparation of **1** and **2** is much simpler. The complexes 2-phenylimidazole−$PdCl_2$ (**1**) and 2-phenylimidazoline−$PdCl_2$ (**2**) were easily prepared by mixing 1 equiv of $PdCl_2$ and 2 equiv of 2-phenylimidazole and 2-phenylimidazoline, respectively, in DMF at 50−70 °C for 1−2 h. Complexes **1** and **2** were both recrystallized from a mixture of DMF and toluene (method A) and from only DMF (method B).

Single-Crystal X-ray Diffractometry (XRD) Study. Navarro-Ranninger et al. reported only the NMR chemical shifts of complex **1**, and an X-ray analysis was not reported. As far as we know, we are the first to report the XRD result of **1** and the synthesis and characterization of **2** by XRD and NMR spectroscopy. Scheme 1 summarizes the single-crystal XRD structures of 2-phenylimidazole−$PdCl_2$ (**1**) and 2-phenylimidazoline−$PdCl_2$ (**2**) obtained by methods A and B. It was found that Pd complex **1** alone was produced by both methods A and B. On the other hand, when method B was used, complex **2**, having two Cl atoms and the phenyl moieties of 2-phenylimidazole coordinating to Pd in a trans fashion, was produced together with complex **2′**, which had the two phenyl groups cis to each other. In contrast, method A yielded only the trans isomer **2** in the solid state. Powder XRD patterns disclosed in Figure 1 also confirmed these observations.

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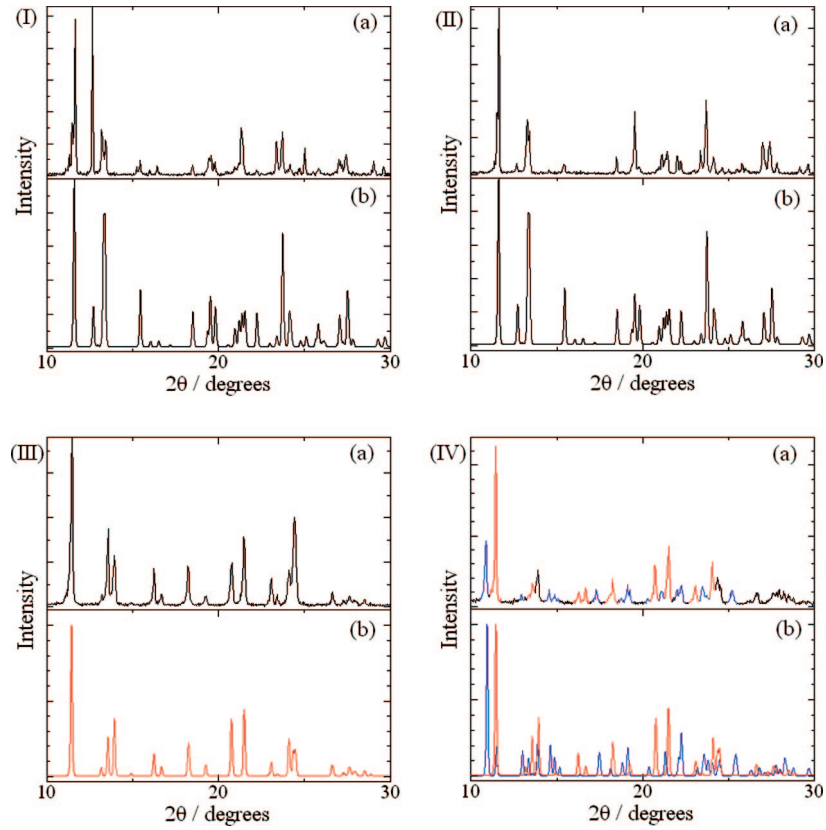

Figure 1. Powder X-ray diffraction patterns of (I) the 1-phenylimidazole−$PdCl_2$ complex prepared by method A, (II) the 1-phenylimidazole−$PdCl_2$ complex prepared by method B, (III) the 1-phenylimidazoline−$PdCl_2$ complex prepared by method A, and (IV) the 1-phenylimidazoline−$PdCl_2$ complex prepared by method B: (a) measured patterns; (b) simulation of powder XRD data using RIETAN-2000.[16]

Powder XRD Study. All of the X-ray diffraction patterns I−IV in Figure 1 include both the actual measurements (a) and simulation patterns calculated by RIETAN-2000[16] using the data collected by single-crystal XRD (b). Parts I and II of Figure 1 show powder XRD patterns of Pd complex **1** prepared by methods A and B, respectively. The same patterns were observed, as the complexes prepared by methods A and B had the same stereochemical and crystallographical structure. Part III of Figure 1 shows powder XRD patterns of complex **2** prepared by method A, while part IV shows the patterns of a mixture of complexes **2** and **2′** obtained by method B. In the case of part IV ($PdCl_2$−2-phenylimidazoline, method B), when we obtained the single crystal by slow evaporation of the solvent, we observed the formation of **2′** by single-crystal XRD; however, this Pd complex **2′** should have conformational polymorphism (complex **2**). Actually, each colored peak in part IVa of Figure 1 is assigned to either complex **2** or **2′**. In simulated patterns (part IVb of Figure 1), the pattern shown in red is for complex **2**, while that in blue is for complex **2′**. These results confirmed that the reaction of 2 equiv of 2-phenylimidazoline with 1 equiv of $PdCl_2$ gives a mixture of trans and cis (with regard to the phenyl group in 2-phenylimidazoline) complexes in the solid state.

^{1}H NMR Analysis of Pd Complexes 1 and 2. Figure 2 shows the ^{1}H NMR spectra of 2-phenylimidazole, 2-phenylimidazoline, and their $PdCl_2$ complexes. Analysis of the spectra of the $PdCl_2$ complexes in DMF-d_7 revealed that the solid sample **2′** gave the same spectrum as that of **2**. This indicates that the Pd−N bond rotates easily in solution, whereas complexes **2** and **2′** are formed in the solid state as a result of crystal packing.

Mizoroki−Heck Reaction Catalyzed by Pd Complexes 1 and 2. To compare the catalytic activities of complexes **1** and **2** in the Mizoroki−Heck reaction, we examined the reaction of 4-bromotoluene and *tert*-butyl acrylate in the presence of 0.1 mol % Pd catalyst in DMF at 120 °C.

de Vries mentioned the role of Pd species in the Mizoroki−Heck reaction under high temperature, and he proposed the mechanism of ligand dissociation to produce quasi-naked Pd species under these conditions.[17] Considering his proposal, it is interesting to investigate whether there is a difference in catalytic activity between Pd complexes **1** and **2**. Actually, as shown in Table 1 and Figure 3, we observed a difference in catalytic activity. That is, Pd complex **2** exhibited higher catalytic activity than Pd complex **1**. In the case of the 2-phenylimidazoline−$PdCl_2$ complex **2**, the precipitation of Pd black occurred partially during the coupling reaction. On the other hand, in the case of the 2-phenylimidazole−$PdCl_2$ complex **1**, Pd black was not formed at all under the same conditions. This observation suggested that the 2-phenylimidazoline ligand dissociated more easily than the 2-phenylimidazole ligand. However, we do not think Pd black worked as a catalyst. Therefore, the above observation, that the partial formation of Pd black in the case of Pd complex **2** and no formation of Pd black in the case of Pd complex **1**, should suggest that the ease of dissociation of the 2-phenylimidazoline ligand promoted the formation of the more reactive unsaturated Pd species. A more detailed elucidation still remains to be solved in the future. The reason for the induction period of catalysts **1** and **2** as shown in Figure 3 is also not clear at present. However, we believe

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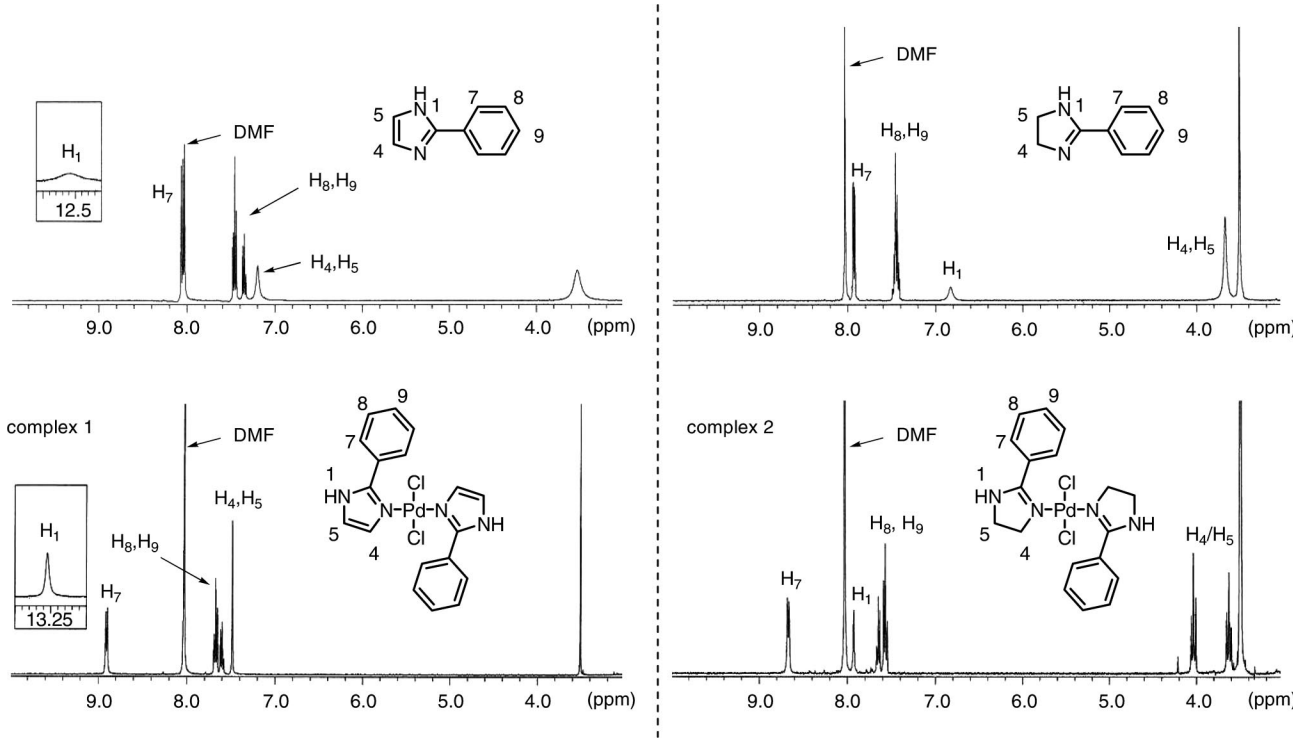


Figure 2. ^{1}H NMR spectra of 2-phenylimidazole, 2-phenylimidazoline, and their $PdCl_2$ complexes **1** and **2**.

Table 1. Mizoroki−Heck Reaction Catalyzed by 1 and 2

		yield of Mizoroki−Heck product/%[a]	
entry	time/h	**1**	**2**
1	3	3	12
2	6	11	73
3	9	11	89
4	12	18	97
5	18	88	96
6	24	96	96

[a] Yields described in this table indicate isolated yields averaged from two or three experiments.

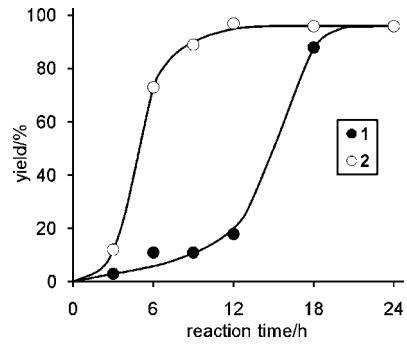
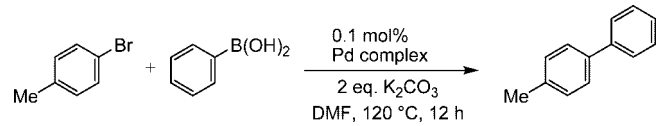


Figure 3. Relationship between reaction time and yield of Mizoroki−Heck reaction product.

the difference in the rate of ligand dissociation to produce the real catalytic species causes the different induction periods between Pd catalysts **1** and **2**.

Suzuki−Miyaura Coupling Catalyzed by Pd Complexes 1 and 2. Pd complexes **1** and **2** also catalyzed the Suzuki−Miyaura coupling reaction. Here as well, complex **2** exhibited higher reactivity than **1** (Scheme 2); that is, the reaction of 4-bromotoluene with phenylboronic acid in the presence of 0.1 mol % of Pd complex **2** in DMF at 120 °C for 12 h gave the coupling product in 78% yield, whereas use of Pd complex **1** under the same conditions afforded the product in 61% yield.

Scheme 2. Suzuki−Miyaura Coupling Catalyzed by Pd Complexes 1 and 2



In conclusion, we determined the structures in the solid state of the complexes 2-phenylimidazole−$PdCl_2$ (**1**) and 2-phenylimidazoline−$PdCl_2$ (**2**) by single-crystal X-ray diffractometry and powder X-ray diffractometry and the structures in DMF-d_7 solution by ^{1}H NMR spectroscopy. Pd complex **2** was found to exhibit higher reactivity than complex **1** in the Mizoroki−Heck reaction and the Suzuki−Miyaura coupling reaction.

Experimental Section

Synthesis of Dichlorobis(2-phenyl-1*H*-imidazole)palladium(II) (1). To a suspension of $PdCl_2$ (177.3 mg, 1.0 mmol) in DMF (5 mL) was added 2-phenylimidazole (288.4 mg, 2.0 mmol) under an argon atmosphere. The mixture was stirred at 50 °C for 2 h, until a clear orange-yellow solution was formed. After dilution of the resultant 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 toluene, and dried in air. Yield: 438.0 mg (93%). Anal. Calcd for $C_{18}H_{16}N_4Cl_2Pd$: C, 46.47; H, 3.46; N, 12.03. Found: C, 46.47; H, 3.53; N, 12.06.

A single crystal of complex **1** ((2-phenylimidazole)$_2$$PdCl_2$·2DMF) suitable for XRD analysis was obtained by slow diffusion of toluene (2 mL) into a solution containing 60.0 mg of (2-phenylimidazole)$_2$$PdCl_2$ powder in DMF (5 mL) (method A). Yield:

Table 2. Crystal Data and Collection Parameters for Complexes 1, 2, and 2′

	1	2	2′
formula	$C_{24}H_{30}N_6O_2Cl_2Pd$	$C_{18}H_{20}N_4Cl_2Pd$	$C_{18}H_{20}N_4Cl_2Pd$
formula wt	611.86	469.68	469.68
T (K)	193(2)	296(2)	193(2)
radiation	Mo−K α (λ = 0.71073 Å)	Mo−K α (λ = 0.71073 Å)	Mo−K α (λ = 0.71073 Å)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
unit cell dimens (Å)			
a (Å)	10.6460(15)	7.745(3)	10.5073(15)
b (Å)	9.0631(13)	12.647(4)	13.1943(18)
c (Å)	14.374(2)	11.215(3)	14.060(2)
β (deg)	105.509(2)	120.353(17)	105.395(2)
V (Å^3)	1336.4(3)	947.9(6)	1879.3(5)
Z	2	2	4
D_{calcd} (Mg/m^3)	1.520	1.646	1.660
F(000)	624	472	944
μ(Mo Kα) (mm^{-1})	0.927	1.269	1.280
cryst size (mm^3)	0.28 × 0.19 × 0.14	0.25 × 0.19 × 0.18	0.30 × 0.25 × 0.08
θ range (deg)	1.99−26.55	2.65−27.13	2.01−26.55
index ranges	$-13 \le h \le 7$, $-10 \le k \le 10$, $-18 \le l \le 7$	$-9 \le h \le 9$, $-14 \le k \le 15$, $-14 \le l \le 8$	$-11 \le h \le 13$, $-16 \le k \le 16$, $-17 \le l \le 11$
no. of rflns measd			
total	6639	5139	9426
unique	2463	1917	3505
R_{int}	0.0466	0.0232	0.0499
structure soln	direct methods		
refinement	full-matrix least squares on F^2		
no. of variables	162	115	306
GOF	1.024	1.052	1.025
R1	0.0287	0.0254	0.0309
wR2	0.0788	0.0723	0.0780

31.7 mg (41%). Mp: >300 °C. IR (KBr): ν_{max} (cm^{-1}) 3184, 3158, 3117, 1661, 1568, 1506, 1390, 1108, 777, 718, 708, 694, 664. ^{1}H NMR (400 Hz, DMF-d_7): δ 13.27 (s, 1H), 8.89 (d, 2H, J = 7.6 Hz), 7.67 (dd, 2H, J = 6.4, 7.6 Hz), 7.60 (t, 1H, J = 6.4 Hz), 7.48 (d, 2H, J = 1.2 Hz). Anal. Calcd for $C_{24}H_{30}N_4O_2Cl_2Pd$: C, 47.11; H, 4.94; N, 13.74. Found: C, 46.99; H, 4.95; N, 13.61.

A single crystal of complex **1** ((2-phenylimidazole)$_2$PdCl$_2$·2DMF) suitable for XRD analysis was obtained directly by slow evaporation of the resultant solution under vacuum (method B).

Synthesis of Dichlorobis(2-phenyl-4,5-dihydro-1*H*-imidazole)-palladium(II) (2). To a suspension of $PdCl_2$ (177.3 mg, 1.0 mmol) in DMF (3 mL) was added 2-phenylimidazoline (292.4 mg, 2.0 mmol) under an argon atmosphere. The mixture was stirred at 70 °C for 1 h, until a clear orange solution was formed.

A single crystal of complex **2** suitable for XRD analysis was obtained by slow diffusion of toluene into the resultant solution (method A). After dilution of the resultant solution with DMF (10 mL), toluene (40 mL) was carefully added to the DMF solution of the complex. After 3 days, orange crystalline **2** was obtained by filtration and dried in air. Yield: 329.0 mg (70%). Mp: 239 °C dec. IR (KBr): ν_{max} (cm^{-1}) 3267, 3242, 2963, 2879, 1616, 1598, 1578, 1511, 1485, 1469, 1274, 1185, 1147, 776, 701. ^{1}H NMR (400 Hz, DMF-d_7): δ 8.67 (d, 2H, J = 7.6 Hz), 7.96 (s, 1H), 7.65 (t, 1H, J = 7.2 Hz), 7.57 (dd, 2H, J = 7.6, 7.2 Hz), 4.03 (t, 2H, J = 10.4 Hz), 3.63 (t, 2H, J = 10.4 Hz). Anal. Calcd for $C_{18}H_{20}N_4Cl_2Pd$: C, 46.03; H, 4.29; N, 11.93. Found: C, 45.45; H, 4.41; N, 11.86.

A single crystal of complex **2′** suitable for X-ray diffraction analysis was directly obtained by slow evaporation of the resultant solution under vacuum (method B), whereas the orange crystal **2** coexisted. This mixture of complexes **2** and **2′** was also used for the sample for powder XRD analysis. The mixture of **2** and **2′** was filtered, and then a yellow-orange crystal of **2′** was isolated and dried in air. Mp: 230 °C dec. IR (KBr): ν_{max} (cm^{-1}) 3271, 2875, 1610, 1601, 1577, 1512, 1472, 1270, 1187, 775, 698. ^{1}H NMR (400 Hz, DMF-d_7): δ 8.67 (d, 2H, J = 7.6 Hz), 7.96 (s, 1H), 7.65 (t, 1H, J = 7.2 Hz), 7.57 (dd, 2H, J = 7.6, 7.2 Hz), 4.03 (t, 2H, J = 10.4 Hz), 3.63 (t, 2H, J = 10.4 Hz). Anal. Calcd for $C_{18}H_{20}N_4Cl_2Pd$: C, 46.03; H, 4.29; N, 11.93. Found: C, 45.99; H, 4.27; N, 11.88.

X-ray Crystallography. X-ray data for **1**, **2**, and **2′** 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.[18] Crystal data and details of the data collection and structure refinement are summarized in Table 2.

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Supporting Information Available: Text and figures giving experimental procedures and compound characterization data and CIF files giving X-ray crystal data for **1**, **2**, and **2′**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 660480 for complex **1**, 675645 for complex **2**, and 660479 for complex **2′** contain supplementary crystallographic data for this paper. 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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