Synthesis of Novel Pd−NCN Pincer Complexes Having Additional Nitrogen Coordination Sites and Their Application as Catalysts for the Heck Reaction

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A novel Pd−NCN pincer complex, **7**, bearing two additional nitrogen atoms has been synthesized and characterized. The dynamic NMR study of **7** shows the two-site exchange reaction in the NCN pincer ligand with a relatively low $\Delta G^{\ddagger}$ value, suggesting easy interconversion in the pincer complex. The use of **7** as a catalyst in the Heck reaction was studied. Catalyst **7** is quite effective for all aryl iodides. A turnover number (TON) value of 4.3×10^6 was observed with 4-tolyl iodide. However, **7** is not an effective catalyst for nonactivated bromobenzene and chlorobenzene substrates. According to the study of the Heck reaction, the facile interconversion of the pincer ligand positively affects the catalytic activity.

Introduction

The pincer complexes having a metal−carbon σ bond assisted by chelation arms ($[2,6\text{-}(ECH_2)_2C_6H_3]^-$ (ECE), where E is a neutral two-electron donor such as NR_2, PR_2, AsR_2, OR, or SR) have been extensively studied.[1] Due to their special properties, the complexes themselves have been the subject of extensive research and accumulated data do not only help to understand their organometallic reactions but also serve to assess their application in materials science and organic synthesis. The synthesis, reactivity, and application of pincer complexes of platinum groups has recently been reviewed.[2]

In contrast to the PCP pincers, NCN pincers have some advantages, such as an easy synthetic access to derive complexes, low cost, and endurance against oxygen under aerobic conditions. Thus, various NCN pincer complexes having diverse functional groups have been synthesized and reported on.[3] Recently, the use of NCN pincer complexes has been extended to other areas of application, such as a reagent for a transcyclometalation reaction,[4] as a gas sensor,[5] as a building block in application to materials science,[6] and as a catalyst for C−C bonding formation reactions.[7] Much effort has been paid to modify the properties of complexes for special purposes. For example, the introduction of chirality in the chelating arms enables the NCN pincer complexes to operate as a chiral catalyst[8] and there was much success in modifying the para position of the central benzene ring.[9]

One of the representative properties of pincer complexes, including the NCN pincers, is the rigidity of the complexes due to the metal−carbon σ bond assisted by the chelating arms. This rigidity may enhance the

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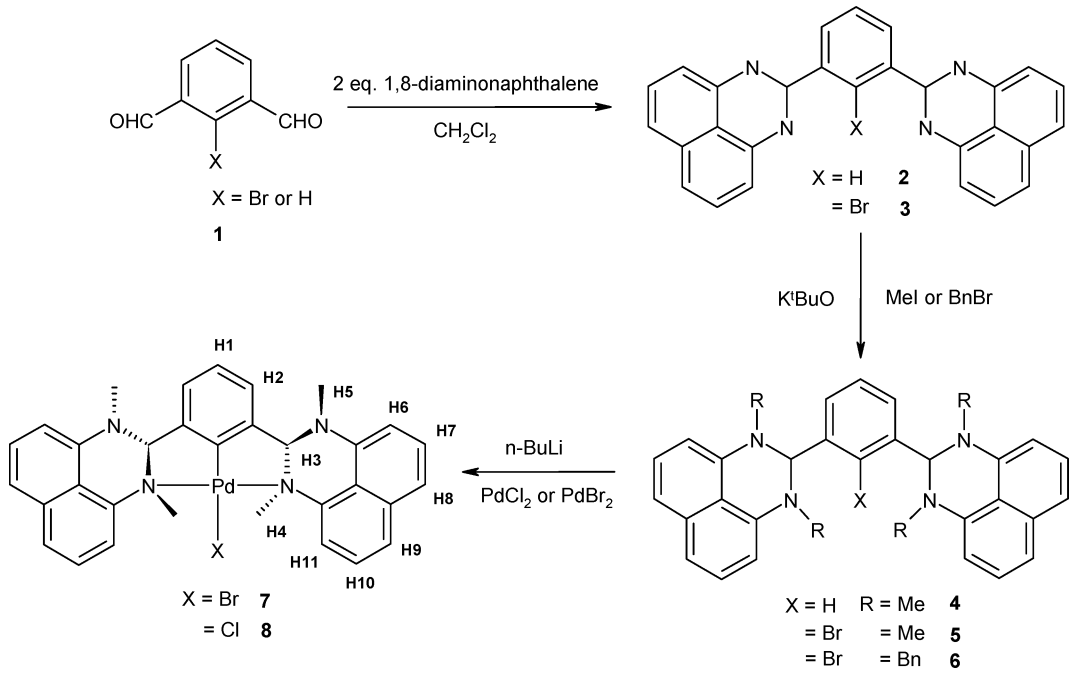
Scheme 1



stability but can be a reason for the decreasing activity of complexes.[10] Recently, a novel NCN pincer complex having additional N-coordination sites attracted our attention because additional N-coordination sites would influence their stability and activity. Herein we report the synthesis of a novel NCN pincer complex having additional N-coordination sites and its temperature-dependent, fluxional behavior. In addition, we investigated the catalytic activity of this complex in the Heck reaction.

Results and Discussion

Synthesis. Several years ago, we reported the formation of a diaminoacetal by condensation of 1,8-diaminonaphthalene with the chromium tricarbonyl complex of benzaldehyde.[11] The N atom of the aminoacetal complex was successfully used as an N-coordination site of a novel planar chiral P,N-ligand in an asymmetric hydroboration reaction. Following the same methodology, we synthesized the novel ligand **2** via a condensation of isopthalic dicarboxaldehyde (**1**) and 2 equiv of 1,8-diaminonaphthalene (Scheme 1). Successive methylation of **2** yielded **4**. The structure of **4** was determined by a single-crystal X-ray analysis (Figure 1a and Table 1).

According to the X-ray structure, the two diaminoacetal groups in **4** face each other. Moreover, the structure of **4** suggested to us that it could be used as a ligand in the synthesis of NCN pincer complexes. Thus, we decided to make an NCN−palladium pincer complex.

At first, we attempted to palladate **4** by a direct reaction with $PdCl_2$, which might involve a C−H activation of the central aromatic ring. However, many attempts at direct palladation of **4** failed. It is well-known[12] that direct palladation is not a good method to synthesize NCN pincer complexes. Next, we introduced a bromide group in the central ring to use a transmeta-

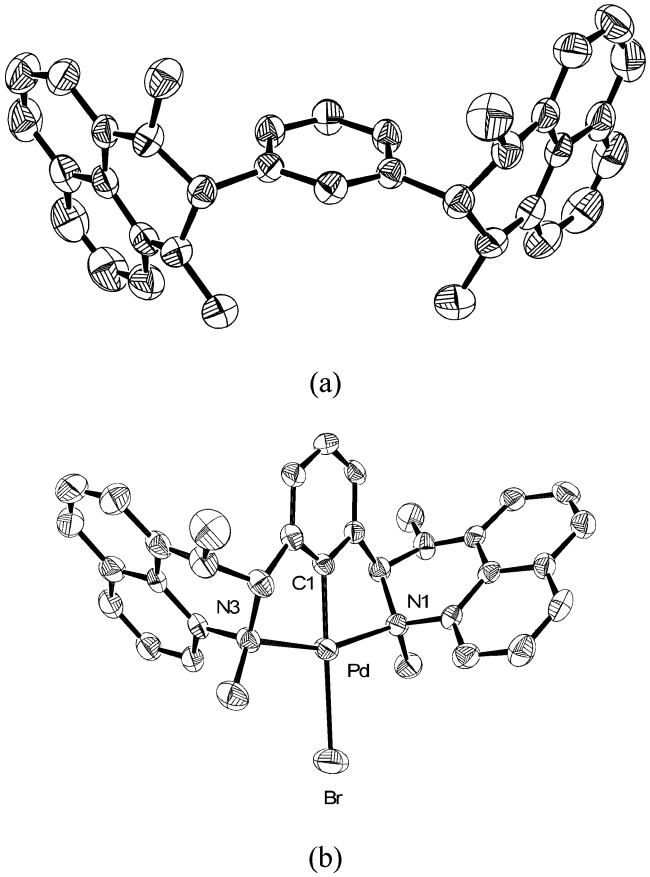


Figure 1. ORTEP drawings of **4** and **7** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Pd−C1 = 1.938(6), Pd−N1 = 2.152(5), Pd−N3 = 2.164(5), Pd−Br = 2.572(1); C(1)−Pd−N(1) = 79.9(2), C(1)−Pd−N(3) = 79.2(2), N(1)−Pd−Br = 100.24(14), N(3)−Pd−Br = 100.66(14).

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Scheme 2

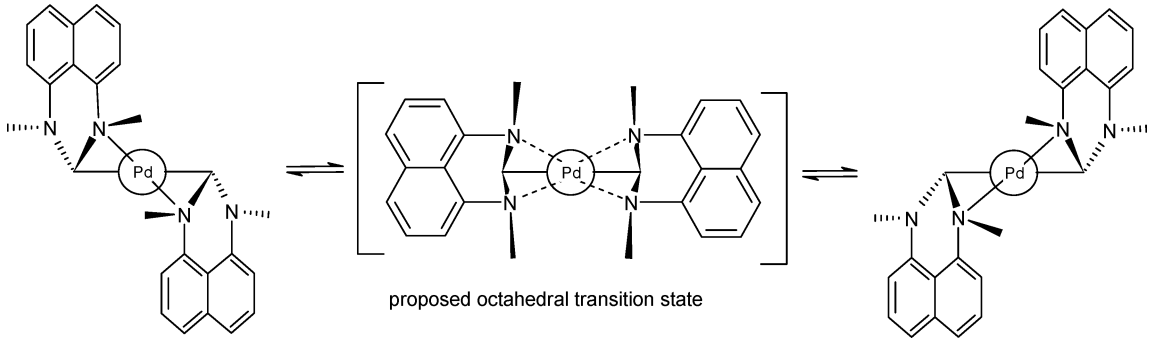

Table 1. Crystal Data for 4 and 7

	4	7
empirical formula	$C_{32}H_{30}N_4$	$C_{33}H_{31}BrCl_2N_4Pd$
fw	470.60	740.83
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	13.186(1)	11.775(1)
b, Å	14.349(1)	13.068(1)
c, Å	13.456(1)	19.776(1)
β, deg	98.560(1)	98.809(1)
V, Å^3	954.2(2)	3007.2(4)
Z	4	4
d(calcd), Mg/m^3	1.242	1.636
θ range, deg	2.02−27.48	1.75−27.52
total no. of data collected	10 854	12 082
no. of unique data	5738	6814
no. of params refined	329	374
R1($I > \sigma(I)$)	0.0454	0.0422
wR2($I > \sigma(I)$)	0.1202	0.1025
GOF	0.906	0.917

lation reaction in the synthesis of NCN pincer complexes and synthesized **3** and **5**.

After the bromide was lithiated, a transmetalation reaction was carried out between lithium and palladium. After workup, a mixture of two pincer complexes was obtained: i.e., of bromide **7** and chloride **8**. When $PdBr_2$ was used as the palladium source, **7** was obtained as the sole product (Scheme 1). In comparison to the pincer ligand **5** having a methyl group at nitrogen, ligand **6**, bearing a more bulky benzyl group, was inert to palladation.

The structure of **7** was determined by a single-crystal X-ray analysis (Figure 1b). As expected, the pincer complex has a C_2-symmetric geometry, with one of the two nitrogen-donating sites of each chelation arm participating in the coordination to palladium. The central palladium shows a distorted-square-planar structure.

Dynamic NMR Study. As previously described, complexes **7** and **8** have two additional N-coordination sites in each chelating arm. We expected that the additional N-coordination site could participate in coordination to the central palladium at an elevated temperature. Thus, we examined the fluxional behavior of **7** by conducting a dynamic ^{1}H NMR study at various temperatures. We screened the temperature range from 40 to 90 °C in DMF-d_7 solution. The variable-temperature ^{1}H NMR spectrum showed a line broadening depending on the temperature. As the temperature increased, the proton peaks of H^6−H^{11} attached to the naphthalene moiety (the mobile part) broadened, but the proton peaks of H^1−H^3 attached to the stationary part sharpened (see the Supporting Information). Especially, the proton peaks assigned to the two methyl groups attached to the nitrogen arms in the pincer ligand show a typical two-site exchange dynamic behavior. We suggest that this interesting two-site exchange reaction may proceed as shown in Scheme 2.

Table 2. Rates and Activation Energies for the Exchange Reaction of 7

temp (K)	k (s^{-1})	$\Delta G^{\ddagger}$ (kJ/mol)	temp (K)	k (s^{-1})	$\Delta G^{\ddagger}$ (kJ/mol)
313	8.8	71.3	343	31.0	74.3
323	12.0	72.3	353	57.3	75.3
333	20.0	73.3	363	73.8	76.3

The line shape analysis of ^{1}H NMR spectra at various temperatures yields the dynamic and activation parameters (Table 2) such as E_a, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ for the two-site exchange reaction.[13] The modified Bloch equations for the exchanging system of two equally populated sites were applied to the line-shape fittings of NMR spectra. The representative fitted spectra, as shown in Figure 2, are in excellent agreement with those observed, and the Arrhenius plots (Figure 3; ln k vs 1000/T) show a good linearity ($R^2 > 0.99$). The activation energy calculated from the Arrhenius plot was 42.4 kJ/mol.

The enthalpy of the transition state of the exchange reaction was 39.6 kJ mol^{-1}, and the entropy of the transition state was −101.2 J mol^{-1} K^{-1}, suggesting a more ordered transition state than the starting material. Thus, we suggest that the more ordered transition state be an octahedral geometry, as shown in Scheme 2. The relatively low $\Delta G^{\ddagger}$ value at various temperatures indicates an easy interconversion to the pincer complex.

Catalytic Heck Reaction. From the above study, we expected that the facile interconversion would influence the reactivity of the palladium NCN-pincer complex. For example, in comparison to the conventional rigid NCN pincer complexes, **7** would exhibit a different behavior to an external substrate. Thus, we decided to study the use of **7** as a catalyst in the Heck reaction because the Heck reaction and related chemistry occupy a special position in organic synthesis.[14] Recently, Cavell

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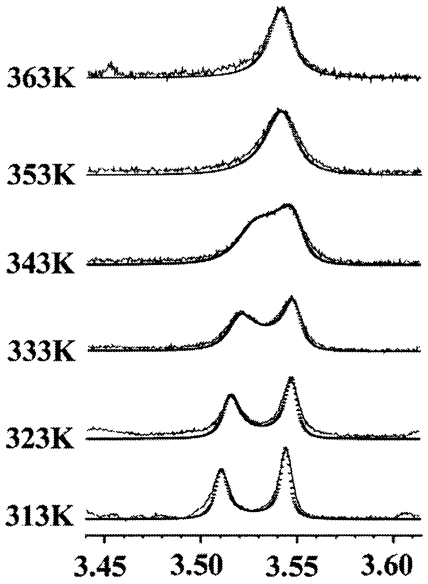


Figure 2. Variable-temperature ^{1}H NMR spectra (observed denoted by solid lines and calculated by dotted lines) of **7** in DMF-d_7 between 40 and 90 °C.

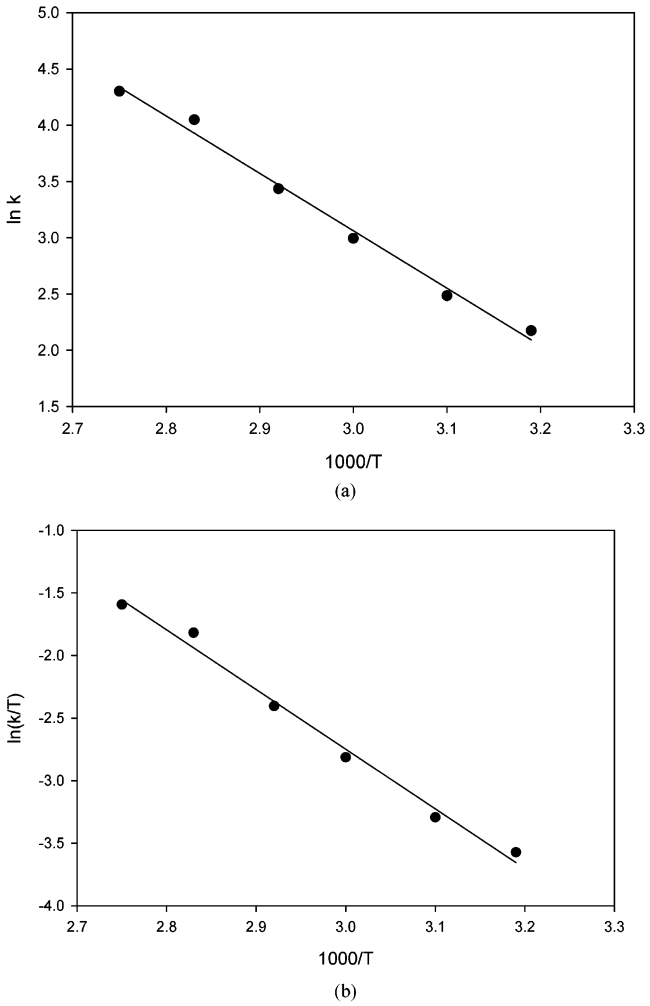


Figure 3. (a) Arrhenius plot and (b) Eyring plot for the interconversion reaction of **7** in DMF-d_7 solution.

et al. reported[7] the use of palladium NCN-pincer complexes in the Heck reaction.

First, to test the catalytic activity of a complex having a rigid pincer ligand in the Heck reaction, compound **9**, known as a catalyst in C−C bond formation and as a starting material in materials science,[15] was prepared.

Scheme 3

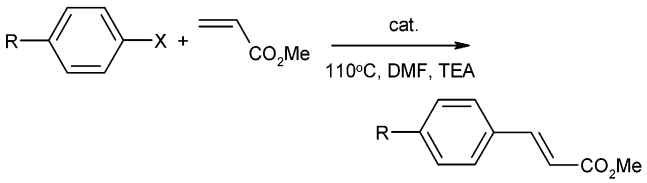
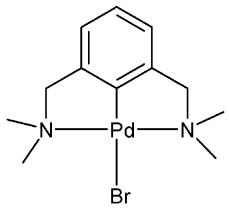


Table 3. Catalytic Activities of NCN Pincer Complexes in the Heck Reaction of Scheme 3[a]

entry	cat.	amt of cat. (mol %)	R	X	yield (%)[b]
1	**7**	0.001	OMe	I	>99
2	**7**	0.001	CO_2H	I	>99[c]
3	**7**	0.001	Me	I	>99
4	**7**	0.0001	Me	I	96
5	**7**	0.00001	Me	I	43
6	**7**	0.000001	Me	I	trace
7	**9**	0.0001	Me	I	25
8	**7**	0.00001	CO_2H	I	48[c]
9	**7**	0.1	NO_2	Br	>99
10	**7**	0.01	NO_2	Br	>99
11	**7**	0.001	NO_2	Br	67
12	**8**	0.001	NO_2	Br	52
13	**9**	0.01	NO_2	Br	trace
14	**7**	0.1	CHO	Br	35
15	**7**	0.1	H	Br	nr
16	**7**	0.1	OMe	Br	nr
17	**7**	1	CO_2H	Cl	trace
18	**7**	0.1	NO_2	Cl	nr

[a] Reaction conditions: 110 °C, DMF, 12 h, Et_3N. [b] Isolated yield. [c] ^{1}H NMR yield.



9

However, the catalytic activity of this compound in the Heck reaction had not been reported, presumably due to poor thermal stability at the reaction temperature. In comparison to the PCP pincer complex, the Pd−N bonding is known to be weak and is easily decomposed to yield palladium black.[16]

We investigated the catalytic activities of **7** and **9** in the Heck reaction (Scheme 3) and summarized the results in Table 3.

Catalyst **7** is quite effective for all aryl iodides. A turnover number (TON) value of 4.3×10^6 was observed with 4-tolyl iodide. Catalyst **9** gave a TON value of 2.5×10^5 with 4-tolyl iodide. Thus, for activated aryl iodides, the difference between catalysts **7** and **9** is

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modest. However, for aryl bromides, the difference between catalysts **7** and **9** is quite clear. When 4-bromonitrobenzene was used, the catalyst **7** gave a TON value of 6.7×10^4 and **9** gave a TON value of less than 100. However, **7** is not an effective catalyst for nonactivated bromobenzene and chlorobenzene substrates. The activity follows in the order $NO_2 \gg CHO \gg H$, OMe. The dependence of the rate on the nature of the aryl halide suggests that the oxidative addition of aryl halide affect the overall rate.[17]

The above observation suggests that **7** is more active and stable than **9**, as we expected.[18] In the case of **9**, as the catalytic reaction started, the color of the solution changed to black, suggesting the formation of palladium black. However, the color of **7** was not changed at all. The higher stability of **7** may be ascribed to the facile interconversion of the pincer ligand.

A mechanistic study was not carried out. Thus, the mechanism and nature of the active species in the Heck reaction is far from clear. However, we envision that the facile interconversion of the pincer ligand gives a positive effect on the catalytic activity in any mechanism.

Conclusion

We have demonstrated that the judicious design of palladium NCN complex allows the synthesis of a new palladium NCN pincer complex (**7**), displaying a dynamic structure. The dynamic NMR study gave activation parameters for the two-site exchange reaction in the NCN pincer ligand. In comparison to the rigid NCN pincer complex (**9**), **7** has a higher activity and stability in the catalytic Heck reaction, presumably due to the additional N-coordination sites in **7**. Study of the use of **7** in other catalytic reactions is currently under way.

Experimental Section

General Considerations. All reactions for preparation of novel compounds were conducted under nitrogen using standard Schlenk-type flasks. Test reactions for the catalytic activity of catalysts in the Heck reaction were conducted in air. Workup procedures were done in air. Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. and were used as received. *m*-Bromoisophthalic dicarboxaldehyde was synthesized by the literature method.[19] ^{1}H NMR spectra were obtained with a Bruker 300 spectrometer, and the DNMR study was done with a Bruker 500 spectrometer. Flash chromatography was performed using Merck silica gel 60 (230−400 mesh). Elemental analyses were performed at the National Center for Inter-University Research Facilities, Seoul National University. High-resolution mass spectra were obtained at Korea Basic Science Institute (Daegu).

Synthesis of 2. 1,8-Diaminonaphthalene (1.18 g, 7.45 mmol), isophthalic dicarboxaldehyde (**1**; 0.50 g, 3.72 mmol), and 4 Å molecular sieves were added to 30 mL of dichloromethane, and the reaction mixture was stirred for 36 h. The solvent was removed by using a rotary evaporator, and **1** was separated by recrystallization from dichloromethane, ether, and hexane (1:1:2). Yield: 1.45 g (94%). ^{1}H NMR ($CDCl_3$): δ 7.92 (s, 1 H), 7.67 (d, 7.6 Hz, 2 H), 7.49 (t, 7.5 Hz, 1 H), 7.23 (m, 8 H), 6.50 (d, 6.2 Hz, 4 H), 5.49 (s, 2 H), 4.52 (br s, 4 H). ^{13}C NMR ($CDCl_3$): δ 142.2, 141.2, 135.2, 129.8, 129.4, 127.6, 127.3, 118.5, 113.8, 106.4, 68.5. HRMS: *m*/*z* calcd, 414.1844; *m*/*z* obsd, 414.1843. Mp: 228∼232 °C. Anal. Calcd for $C_{28}H_{22}N_4$: C, 81.13; H, 5.35; N, 13.52. Found: C, 80.88; H, 5.32; N, 13.65.

Synthesis of 3. Compound **3** was synthesized by the same method as the synthesis of **2**, except using *m*-bromoisophthalic dicarboxaldehyde (which was synthesized by the oxidation of *m*-bromoxylene) instead of isophthalic dicarboxaldehyde. Yield: 90%. ^{1}H NMR ($CDCl_3$): 7.88 (d, 7.7 Hz, 2 H), 7.46 (t, 7.7 Hz, 1 H), 7.26 (m, 8 H), 6.60 (d, 6.6 Hz, 4 H), 6.05 (s, 2 H), 4.64 (brs, 4 H). ^{13}C NMR ($CDCl_3$): δ 141.7, 140.3, 135.1, 134.1, 130.6, 127.3, 124.4, 118.6, 113.6, 106.6, 67.0. HRMS *m*/*z* calcd, 470.2470; *m*/*z* obsd, 470.2468. Mp: 197∼200 °C. Anal. Calcd for $C_{28}H_{21}BrN_4$: C, 68.16; H, 4.29; N, 11.36. Found: C, 68.27; H, 4.71; N, 10.90.

Synthesis of 4. A mixture of **2** (0.10 g, 0.241 mmol) and potassium *tert*-butoxide (0.13 g, 1.156 mmol) in 30 mL of THF was stirred for 4 h at room temperature. To the reaction mixture was added MeI (0.30 g), and the resulting solution was stirred for another 1 h at room temperature. A product was separated by chromatography on a silica gel column (8/2 hexane/ether). Yield: 0.081 g (0.17 mmol, 72%). ^{1}H NMR ($CDCl_3$): δ 7.29 (t, 8.1 Hz, 4 H), 7.13 (d, 8.3 Hz, 4 H), 6.88 (t, 7.4 Hz, 1 H), 6.77 (d, 7.4 Hz, 2 H), 6.70 (s, 1 H), 6.32 (d, 7.6 Hz, 4 H), 4.95 (s, 2 H), 2.70 (s, 12 H). ^{13}C NMR ($CDCl_3$): δ 141.8, 138.2, 134.5, 129.2, 127.7, 126.5, 125.9, 117.2, 113.8, 103.4, 79.9, 38.7. HRMS *m*/*z* calcd, 492.0949; *m*/*z* obsd, 492.0956; Mp: 187∼190 °C. Anal. Calcd for $C_{32}H_{30}N_4$: C, 81.67; H, 6.43; N, 11.90. Found: C, 82.09; H, 6.47; N, 12.07

Synthesis of 5. Compound **5** was synthesized by the same method as for the synthesis of **4**, except for using **3** instead of **2**. Yield: 62%. ^{1}H NMR ($CDCl_3$): δ 7.30 (t, 8.0 Hz, 4 H), 7.15 (d, 8.0 Hz, 4 H), 6.79 (d, 7.6 Hz, 2 H), 6.57 (t, 7.6 Hz, 1 H), 6.39 (d, 7.5 Hz, 4 H), 6.23 (s, 2 H), 2.90 (s, 12 H). ^{13}C NMR ($CDCl_3$): δ 141.0, 139.2, 134.3, 129.2, 127.7, 127.1, 125.3, 117.2, 112.8, 103.6, 35.7. HRMS: *m*/*z* calcd, 548.1575; *m*/*z* obsd, 548.1575. Mp: 239∼243 °C. Anal. Calcd for $C_{32}H_{29}BrN_4$: C, 69.94; H, 5.32; N, 10.20. Found: C, 70.32; H, 5.35; N, 10.21

Synthesis of 6. Compound **6** was synthesized by the same method as for the synthesis of **5**, except for using benzyl bromide instead of iodomethane. Yield: 60%;. ^{1}H NMR ($CDCl_3$): δ 7.22 (m, 20 H), 7.19 (t, 7.5 Hz, 4 H), 7.13 (d, 7.4 Hz, 4 H), 7.07 (d, 7.8 Hz, 2 H), 6.68 (t, 7.7 Hz, 1 H), 6.36 (d, 7.1 Hz, 4 H), 6.16 (s, 2 H), 4.52 (d, 16.5 Hz, 4H), 4.26 (d, 16.5 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 144.6, 143.9, 139.1, 134.5, 127.3, 126.9, 126.8, 124.7, 124.4, 122.3, 118.2, 116.1, 105.6, 88.2, 77.6, 39.2. HRMS *m*/*z* calcd, 852.2827; *m*/*z* obsd, 852.2903. Mp: 217∼220 °C. Anal. Calcd for $C_{56}H_{45}BrN_4$: C, 78.77; H, 5.32; N, 6.56. Found: C, 78.93; H, 5.53; N, 6.15.

Synthesis of 7 and 8. Compound **4** (0.30 g, 0.54 mmol) was stirred in 10 mL of THF at −78 °C for 30 min. To the solution was added *n*-BuLi (0.22 mL of 2.5 M solution, 0.54 mmol). After 1 h, the reaction mixture was placed in a 0 °C bath and $PdCl_2$ 0.089 g (0.5 mmol) was added. After the solution was stirred for another 1 h at room temperature, the solvent was removed by using a rotary evaporator. Compounds **7** and **8** were separated by chromatography on a silica gel column (hexane/ether). Yield: 15% for **7** and 10% for **8**. When $PdBr_2$ was used as the palladium source, the yield was enhanced to 30% of **7**. Data for compound **7** are as follows. ^{1}H NMR ($CDCl_3$): δ 9.06 (d, 7.5 Hz, 2 H), 7.55 (m, 4 H), 7.35 (t, 8.1 Hz, 2 H), 7.24 (d, 8.2 Hz, 2 H), 6.67 (d, 7.3 Hz, 2 H), 6.53 (t, 8.0 Hz, 1 H), 6.41 (d, 7.5 Hz, 2 H), 5.54 (s, 2 H), 3.52 (s, 6 H), 3.44 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 144.6, 143.9, 139.1, 134.5, 127.3, 126.9, 126.8, 124.7, 124.4, 122.3, 118.2, 116.1, 105.6, 88.2, 77.6, 39.2. HRMS: *m*/*z* calcd, 654.0610; *m*/*z* obsd, 654.0611. Mp: 217∼220 °C. Anal. Calcd for $C_{33}H_{31}PdBrCl_2N_4$: C, 53.50; H, 4.22; N, 7.56. Found: C, 53.91; H, 4.18; N, 7.37. Data for compound **8** are as follows. ^{1}H NMR ($CDCl_3$): δ 9.00 (d, 7.5 Hz, 2 H), 7.53 (m, 4 H), 7.35 (t, 8.0 Hz, 2 H), 7.20 (d, 8.4 Hz,

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2 H), 6.66 (d, 7.5 Hz, 2 H), 6.55(t, 8.2 Hz, 1 H), 6.43 (d, 7.1 Hz, 2 H), 5.53 (s, 2 H), 3.46 (s, 6 H), 3.44 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 144.5, 144.1, 139.2, 134.5, 127.3, 126.9, 126.7, 124.5, 122.2, 118.2, 116.1, 116.1, 105.6, 88.5, 77.6, 39.2. HRMS: *m*/*z* calcd, 610.1115; *m*/*z* obsd, 610.1113. Mp: 212∼217 °C. Anal. Calcd for $C_{32}H_{29}PdClN_4$: C, 62.86; H, 4.78; N, 9.16. Found: C, 63.06; H, 5.10; N, 8.55.

Dynamic ^{1}H NMR Study. Temperatures within the NMR probe were controlled by a Bruker variable-temperature unit. Samples for variable-temperature NMR were prepared in DMF-d_7 in 5 mm NMR tubes in air.

Catalytic Reactions. To a 50 mL Schlenk flask were added catalyst (a predetermined amount), triethylamine (0.42 mL, 3 mmol), aryl halide (2.0 mmol), methyl acrylate (0.27 mL, 3 mmol), and DMF (10 mL). The reaction vessel was attached to a reflux condenser and placed into an oil bath and refluxed at 110 °C. After 12 h, the reaction mixture was extracted with CH_2Cl_2 (5 mL) and H_2O (10 mL). The organic layer was washed four times with 10 mL portions of water and dried with $MgSO_4$. The mixture was then filtered and the CH_2Cl_2 removed in vacuo. A pure product was obtained by flash column chromatography on silica gel with a mixture of hexane and diethyl ether as eluent (v/v, 1:9−4:6, depending upon the reaction) or recrystallization. The purified product was confirmed by comparison with ^{1}H NMR of the authentic sample.

Crystal Structure Determinations of 4 and 7. Single crystals of **4** and **7** suitable for an X-ray diffraction study were grown by slow diffusion of diethyl ether into the dichloromethane solution of **4** and **7**, respectively, at room temperature. X-ray data for single crystals were collected on an Enraf-Nonius CCD single-crystal X-ray diffractometer at room temperature using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods (SHELXS-97) and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were treated as idealized contributions.

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Supporting Information Available: Tables of crystal data, atomic coordinates and temperature factors, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates of **4** and **7** and figures giving variable-temperature ^{1}H NMR spectra of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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