Preparation and Properties of $Cp_2Zr(\mu\text{-}N{=}CAr_2)_2PdCl(Me)$, New Zr/Pd Heterobimetallic Complexes with Bridging Alkylideneamido Ligands

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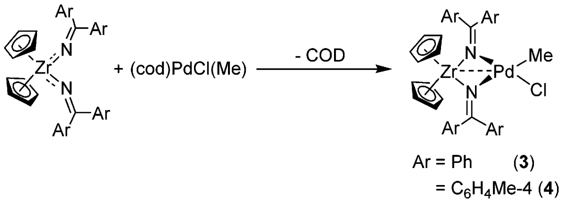
Summary: Zr/Pd heterobimetallic complexes with bridging alkylideneamido ligands, $Cp_2Zr(\mu\text{-}N{=}CAr_2)_2PdCl(Me)$ (Ar = Ph, C_6H_4Me-4), were prepared from the reaction of $Cp_2Zr(N{=}CAr_2)_2$ with PdCl(Me)(cod) (cod = 1,5-cyclooctadiene). $Cp_2Zr(\mu\text{-}N{=}CAr_2)_2PdCl(Me)$ complexes have puckered ZrN_2Pd rings with Zr−Pd distances of 2.8135(5) Å (Ar = Ph) and 2.8416(4) Å (Ar = C_6H_4Me-4), respectively. The complexes reacted with HCl to afford trans-$PdCl(Me)(NH{=}CAr_2)_2$ and Cp_2ZrCl_2. Exposure of a CH_2Cl_2 solution of trans-$PdCl(Me)\{NH{=}C(C_6H_4Me\text{-}4)_2\}_2$ to light results in the formation of a mixture of cis- and trans-$PdCl(CHCl_2)\{NH{=}C(C_6H_4Me\text{-}4)_2\}_2$.

Introduction

Heterobimetallic complexes[1] containing early and late transition metals exhibit unique characters such as donor−acceptor bonding between the two different metal centers[2] and cooperative activation of the organic bridging ligand by the metal centers.[3] Transmetalation of an organic ligand between the early- and late-transition-metal complexes involves these dinuclear complexes as the intermediate.[4] There have been a number of reports of heterobimetallic complexes having metallocenes of group 4 transition metals with two anionic ligands such as amido, thiolate, and phosphido, $Cp_2M(ER_n)_2$ (M = Ti, Zr, Hf; E = N ($n = 2$), S($n = 1$), P ($n = 2$)), as the metalloligands of late transition metals (Co, Rh, Fe, Ni, Pd, Pt).[2−5] Alkylideneamido (imido) groups would be suited as the bridging ligand of the early−late heterobimetallic complexes because they show high basicity and coordinate to both early and late transition metals. There have been only a few reports on such complexes with bridging alkylideneamido ligands.[6] $(Cp_2Ti)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}2{:}3,6{:}7\text{-}PhHC{=}NNCHPhCHPhNN{=}CHPh)$ reacts with $Cp_2Co(C_2H_4)_2$ to produce $Cp_2Ti(\mu\text{-}N{=}CHPh)_2CoCp$ via cleavage of the N−N bond of the ligand.[6a] In this paper we report the formation of new Zr/Pd heterobimetallic complexes and conversion of them into mononuclear alkylpalladium complexes with imine ligands.

Results and Discussion

Erker et al. reported the preparation of the zirconium alkylideneamido complex $Cp_2Zr(N{=}CPh_2)_2$ (**1**).[7] $Cp_2Zr\{N{=}C(C_6H_4Me\text{-}4)_2\}_2$ (**2**) is prepared similarly in this study. Complexes **1** and **2** react with PdCl(Me)(cod) at 3 °C to form the Zr/Pd heterobimetallic complexes $Cp_2Zr(\mu\text{-}N{=}CAr_2)_2PdCl(Me)$ (**3**, Ar = Ph, 32%; **4**, Ar = C_6H_4Me-4, 50%) (eq 1). Figure 1 shows the molecular structures of **3** and **4** determined by X-ray crystallography. The molecules have a crystallographic mirror plane containing Zr and Pd, which causes the disorder of positions of the methyl and chloro groups in equal probability. The Pd center has a slightly distorted square-planar coordination with Pd−N bond distances of 2.130(3) Å (**3**) and 2.127(2) Å (**4**), while Zr is bonded to the nitrogen atoms with bond distances of 2.152(3) Å (**3**) and 2.150(2) Å (**4**). Short Zr−Pd distances (2.8235(5) and 2.8416(4) Å) and the puckered structure of the ZrN_2-Pd four-membered ring (tilt angles of 42.6° (**3**) and



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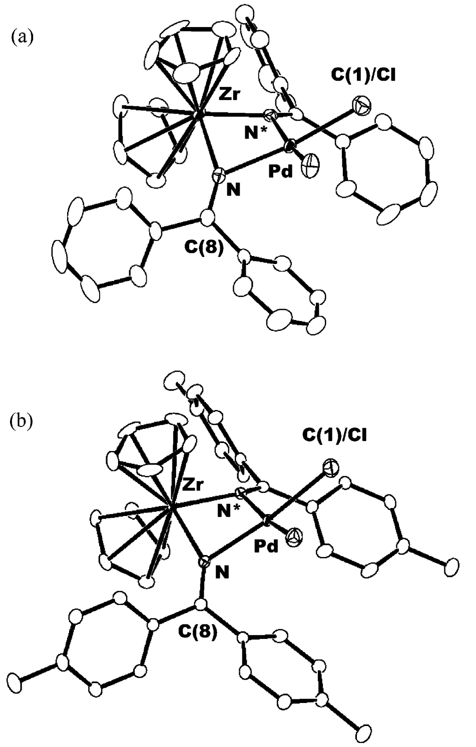


Figure 1. ORTEP drawing of (a) **3** and (b) **4** at the 30% ellipsoidal level. Each molecule has a crystallographic mirror plane. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Selected bond distances (Å) and angles (deg) are as follows. **3**: Zr−Pd, 2.8235(5); Zr−N, 2.152(3); Pd−N, 2.130(3); Pd−C1, 2.253(1); N−C8, 1.278(4); N−Zr1−N*, 89.34(7); N−Pd−N*, 90.45(7); Zr−N−Pd, 82.5(1); Zr−N−C8, 148.0(2); Pd−N−C8, 127.5(2). **4**: Zr−Pd, 2.8416(4); Zr−N, 2.150(2); Pd−N, 2.127(2); Pd−C1, 2.2926(7); N−C8, 1.275(4); N−Zr1−N*, 89.66(9); N−Pd−N*, 90.88(8); Zr−N−Pd, 83.27(8); Zr−N−C8, 145.7(2); Pd−N−C8, 128.4(2).

Table 1. Metal−Metal Distances and Dihedral Angles of the Central ME_2M' Ring (E = N, P, S)

	dihedral angle (deg)	metal−metal dist (Å)	ref
3	42.6	2.8235(5)	this work
4	48.3	2.8416(4)	this work
$Cp_2Ti(\mu\text{-}N{=}CHPh)_2CoCp$	0.0	2.569(3)	6a
$Cp_2Hf(\mu\text{-}PPh_2)_2PdPPh_3$	24.5	2.896(1)	5c
$(C_5H_4SiMe_3)_2Ti(\mu\text{-}SPh)_2Pd(C_6F_5)_2$	19.3	3.140(3)	5d

48.3° (**4**) between the ZrN_2 and N_2Pd planes) are observed in the crystal structures. Table 1 compares the angles of the coordination planes with those of analogous early−late heterobimetallic complexes. $Cp_2Hf(\mu\text{-}PPh_2)_2PdPPh_3$ has a longer metal−metal distance (2.896 (1) Å) and a smaller dihedral angle (24.5°) than those of **3** and **4**.[5c,8]

Complex **1** has large Zr−N−C angles of 173.7 and 164.1° and short Zr−N bonds (2.058(2) and 2.063(2) Å).[7] They were attributed to a heteroallene-type coordination of the alkylideneamido group. The heterobimetallic complexes **3** and **4** contain smaller Zr−N−C(8) angles (**3**, 148.0°; **4**, 145.7°) and longer Zr−N bond lengths (**3**, 2.152(3) Å; **4**, 2.150(2) Å) than **1**. The bond distances are similar to those of $Cp_2Zr(NC_4H_4)_2$ (2.171(2) and 2.169(2) Å).[9] Figure 2 compares the absorption spectra of **2** and **4** in THF. Complex **2** exhibits absorption at 490 nm (ϵ = 480), while the Zr/Pd heterobimetallic complex **4** shows no absorption in that region. These crystallographic and spectroscopic results indicate that the Zr−N bond of the bridging alkylideneamido ligands do not have double-bond character.

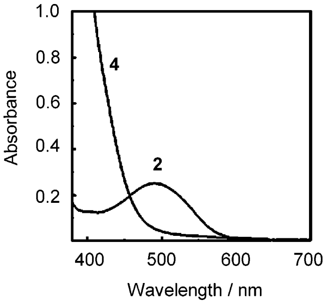
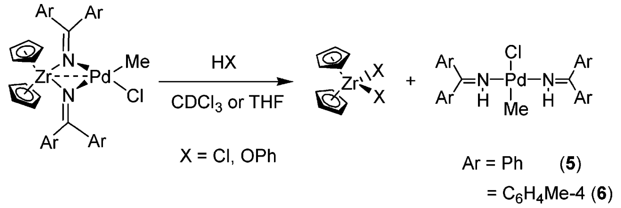


Figure 2. UV/vis spectra of **2** and **4** (solvent THF).

The ^1H NMR spectrum of **4** shows two signals assigned to Cp hydrogens at δ 5.24 and 6.58, indicating that the puckered ZrN_2Pd ring is kept in solution. The resonances of methyl hydrogens of the imido ligands are observed as four magnetically unequivalent peaks at δ 2.42, 2.43, 2.46, and 2.67. This can be contrasted with the ^1H NMR spectra of mononuclear **1** and **2**, which show a set of signals due to the methyl and phenyl hydrogens.[7] Complexes **1** and **2** undergo exchange of the two aryl groups on the NMR time scale, probably via rotation of the Zr−N bond, although the rigid structure of **3** and **4** prevents such bond rotation.

The Zr/Pd heterobimetallic complexes are treated with HCl to afford Cp_2ZrCl_2 and *trans*-$PdCl(Me)(NH{=}CAr_2)_2$ (Ar = Ph (**5**), C_6H_4Me-4 (**6**)) in 83 and 93% yields, respectively (eq 2). Addition of PhOH to a solution of **4** produces **6** and $Cp_2Zr(OPh)_2$[10] quantitatively. Figure 3 depicts the molecular structure of **5** obtained by X-ray crystallography. The molecule has a slightly distorted square-planar coordination around the Pd center. Two alkylideneamine ligands are located at trans positions. This is the first example of an alkylpalladium complex with a monodentate imine ligand. The Pd−N bonds of **5** (2.007(6) and 2.013(5) Å) are shorter than those of **4** and *trans*-PdCl(Me)(NNHC(*t*-Bu)CHC-*t*-Bu)$_2$, having



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[8] The puckered ZrN_2Pd ring, observed in the crystal structures of **3** and **4**, may be related to the existence of a Zr/Pd interaction. An EHMO calculation of the model compound $Cp_2Zr(\mu\text{-}N{=}CMe_2)_2PdCl(Me)$ shows a Zr/Pd reduced overlapped population (ROP) of 5.4%, which is much smaller than the average value of ROP between Pd and N (20.0%). These results are not sufficient to discuss the presence or absence of interaction between the metals. The calculations were conducted on the basis of the method in the following reports: (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179. (c) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489. (d) Ammeter, J. H.; Burgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. (e) Mealli, C.; Prosterpio, D. *J. Chem. Educ.* **1990**, *67*, 399.

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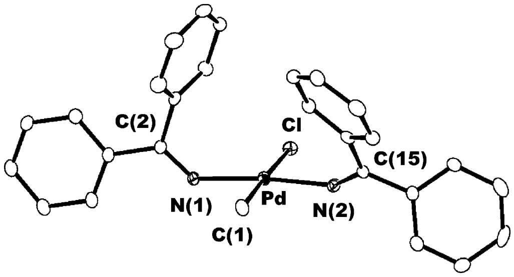

Figure 3. ORTEP drawing of **5** at the 30% ellipsoidal level. The hydrogen atoms are omitted for simplicity. Selected bond distances (Å) and angles (deg): Pd−C1, 2.039(7); Pd−Cl, 2.447(2); Pd−N1, 2.007(6); Pd−N2, 2.013(5); N1−C2, 1.298(8); N2−C15, 1.267(8); C1−Pd−N1, 90.7(3); C1−Pd−N2, 86.4(3); Cl−Pd−N1, 89.6(2); Cl−Pd−N2, 93.0(2); Pd−N1−C2, 139.7(4); Pd−N2−C15, 131.5(4).

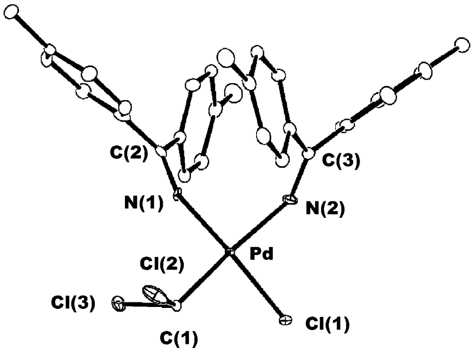

Figure 4. ORTEP drawing of **7** at the 30% ellipsoidal level. The hydrogen atoms are omitted for simplicity. Selected bond distances (Å) and angles (deg): Pd−C1, 1.995(4); Pd−Cl, 2.3100(9); Pd−N1, 2.039(3); Pd−N2, 2.107(4); N1−C2, 1.289(5); N2−C3, 1.312(6); C1−Cl2, 1.805(4); C1−Cl3, 1.795(4); C1−Pd−N1, 88.4(1); C1−Pd−N2, 175.9(1); Cl−Pd−N1, 176.8(1); Cl−Pd−N2, 87.22(8); Pd−N1−C2, 133.7(3); Pd−N2−C3, 136.5(3); Pd−C1−Cl2, 111.3(2); Pd−C1−Cl3, 112.0(2).

two pyrazole ligands at trans positions (2.035(3) and 2.041(2) Å).[11] Complex **5** is prepared also by the reaction of benzophenoneimine with PdCl(Me)(cod).

Dissolution of **6** in CH_2Cl_2 leads to formation of a mixture of *cis*- and *trans*-$PdCl(CHCl_2)\{NH{=}C(C_6H_4Me\text{-}4)_2\}_2$. The reaction does not take place in the dark and is induced by exposure of the solution to light. Figure 4 shows the crystallographic structure of **7** having $CHCl_2$ and Cl ligands at cis positions around the square-planar Pd center. Jordan et al. reported the photoassisted conversion of PdCl(Me){(hexyl)HC(*N*-methylimidazol-2-yl)$_2$} into PdCl(CHCl$_2$){(hexyl)HC(*N*-methylimidazol-2-yl)$_2$} via a radical pathway.[12] The above reactions also involve a radical intermediate, formed via cleavage of the C−Pd bond caused by photoirradiation.

In summary, this study revealed that an alkylideneamido group coordinates to Zr and Pd as a bridging ligand to form a heterobimetallic complex and that the complexes react with HCl or HOPh easily to produce a monometallic Zr complex and alkylideneamine complexes of Pd. Transfer of the imido ligand from Zr to Pd accompanied by its conversion into the imine ligand is observed.

Experimental Section

General Procedure, Materials, and Measurement. All the manipulations of the air-unstable complexes were carried out under nitrogen or argon using standard Schlenk techniques. Benzene and THF were distilled from sodium benzophenone ketyl and stored under nitrogen. $CDCl_3$ was distilled from CaH_2 and stored under nitrogen. C_6D_6 was distilled from Na and stored under nitrogen. Benzophenoneimine and other chemicals were used as received from commercial suppliers. $Cp_2Zr(N{=}CPh_2)_2$ (**1**)[7] and PdCl(Me)(cod)[13] were prepared according to the literature. The NMR spectra (^1H and ^{13}C) were recorded on Varian Mercury 300 and JEOL JNM LA-500 spectrometers. UV/vis spectra were measured with a JASCO V-530 UV/vis spectrometer. Elemental analysis was carried out on a Yanaco MT-5 CHN autocorder.

Preparation of $Cp_2Zr\{N{=}C(C_6H_4Me\text{-}4)_2\}_2$ (2). The reaction of $LiN{=}C(C_6H_4Me\text{-}4)_2$ with Cp_2ZrCl_2 was conducted in a manner similar to the preparation of $Cp_2Zr(N{=}CPh_2)_2$[7] to produce **2** in 30% yield. ^1H NMR (300 MHz, C_6D_6): δ 7.25 (d, $J = 8$ Hz, 8H, C_6H_4), 7.09 (d, $J = 8$ Hz, 8H, C_6H_4), 5.86 (s, 10H, Cp), 2.20 (s, 12H, Ar−*Me*). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 170.1 (N=C), 139.4 (C_6H_4 ipso), 138.0 (C_6H_4 ipso), 128.9 (C_6H_4 ortho and meta), 108.8 (C_5H_5), 21.3 (C_6H_4−Me).

Preparation of $Cp_2Zr(\mu\text{-}N{=}CPh_2)_2PdCl(Me)$ (3). Complex **1** (130 mg, 0.21 mol) and PdCl(Me)(cod) (51.7 mg, 0.20 mmol) were dissolved in benzene (2.6 mL). The reaction mixture was left for 12 h at 3 °C. The yellow powder that formed was collected by filtration, washed with benzene (1 mL × 2) and hexane (1 mL × 2), and dried under reduced pressure to give **3** (51.3 mg, 32%). Anal. Calcd for $C_{37}H_{33}ClN_2PdZr$: C, 60.15; H, 4.50; N, 3.79; Cl, 4.80. Found: C, 60.21; H, 4.71; N, 3.45; Cl, 4.56. ^1H NMR (300 MHz, $CDCl_3$): δ 8,21 (d, $J = 8$ Hz, 2H, C_6H_5), 7.75 (d, $J = 8$ Hz, 2H, C_6H_5), 7.32−7.62 (m, 16H, C_6H_5), 6.60 (br, 5H, C_5H_5), 6.25 (br, 5H, C_5H_5), 0.28 (s, 3H, Pd−Me).

Preparation of $Cp_2Zr\{\mu\text{-}N{=}C(C_6H_4Me\text{-}4)_2\}_2PdCl(Me)$ (4). Complex **2** (38.3 g, 60 μmol) and PdCl(Me)(cod) (15.8 mg, 60 μmol) were dissolved in benzene (3 mL). The reaction mixture was left for 36 h at 3 °C to form yellow crystals, which were collected by filtration, washed with benzene (1 mL × 2) and hexane (1 mL × 2), and dried under reduced pressure to give **4**·C_6H_6 (23.9 mg, 50%). Anal. Calcd for $C_{41}H_{41}ClN_2PdZr\cdot C_6H_6$: C, 64.66; H, 5.43; N, 3.21; Cl, 4.06. Found: C, 65.20; H, 5.39; N, 3.05; Cl, 3.89. ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, $J = 8$ Hz, 2H, C_6H_4), 7.36 (s, 6H, benzene), 7.35 (d, $J = 8$ Hz, 2H, C_6H_4), 7.20−7.36 (m, 12H, C_6H_4), 6.58 (br, 5H, C_5H_5), 6.24 (br, 5H, C_5H_5), 2.47 (s, 3H, C_6H_4−Me), 2.46 (s, 3H, C_6H_4−Me), 2.43 (s, 3H, C_6H_4−Me), 2.42 (s, 3H, C_6H_4−Me), 0.25 (s, 3H, Pd−Me).

Preparation of *trans*-$PdCl(Me)(NH{=}CPh_2)_2$ (5). To a suspension of **3** (7.3 mg, 9.0 μmol) in $CDCl_3$ (0.9 mL) was added a Et_2O solution of HCl (20 μL, 20 μmol) and mesitylene (1.0 μL, 7.2 μmol). After 15 min of stirring, the reaction mixture became a clear yellow solution. The quantitative formation of Cp_2ZrCl_2 and **5** was confirmed by ^1H NMR measurement using mesitylene as an internal standard. Complex **5** was prepared also from the reaction of PdCl(Me)(cod) with $NH{=}CPh_2$.

To a solution of PdCl(Me)(cod) (52.6 mg, 0.20 mmol) in toluene (5 mL) was added $NH{=}CPh_2$ (6.72×10^{-4} mL, 0.40 mmol). After it was stirred at room temperature for 5 h, the solution was evaporated to dryness at reduced pressure. The residue was extracted with toluene/THF (8/92). After the solvent was reduced under vacuum, Et_2O was added to the solution to cause the separation of **5**·$0.5C_7H_8$ as a pale yellow

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Table 2. Crystallographic Data and Details of Refinement of 3−5 and 7

	3	**4**	**5**	**7**
empirical formula	$C_{37}H_{33}ClN_2PdZrC_6H_6$	$C_{41}H_{41}ClN_2PdZrC_6H_6$	$C_{27}H_{25}ClN_2Pd$	$C_{31}H_{31}Cl_3N_2Pd$
formula wt	816.87	872.97	519.36	644.36
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	*Pnma* (No. 62)	*Pnma* (No. 62)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	17.262(6)	18.641(5)	12.602(8)	16.97(1)
b, Å	18.244(6)	18.013(5)	13.727(8)	9.739(6)
c, Å	11.419(4)	11.793(3)	13.601(8)	18.54(1)
β, deg			104.43(1)	109.313(8)
V, Å^3	3596(2)	3960(2)	2279(2)	2893(3)
Z	4	4	4	4
μ, cm^{-1}	8.97	8.20	9.49	9.42
F(000)	1656.00	1784.00	1056.00	1312.00
D_{calcd}, g cm^{-3}	1.509	1.464	1.514	1.479
cryst size, mm	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.3 × 0.3 × 0.2	0.8 × 0.5 × 0.5
exposure rate s/deg	40.0	20.0	60.0	10.0
no. of obsd data ($I > 3\sigma(I)$)	12 303	4202	3627	15 166
no. of variables	254	270	305	365
$R(F_o)$ ($R_w(F_0)$)	0.049 (0.054)	0.038 (0.052)	0.061 (0.070)	0.085 (0.096)
GOF	3.18	1.09	0.95	8.12

solid (82.6 mg, 74%). Anal. Calcd for $C_{27}H_{25}ClN_2Pd\cdot C_{3.5}H_4$: C, 64.79; H, 5.17; N, 4.92; Cl, 6.27. Found: C, 64.72; H, 5.07; N, 4.95; Cl, 6.19. ^{1}H NMR (300 MHz, at 25 °C in $CDCl_3$): δ 9.22 (br, 2H, NH), 8.21 (d, 4H, $J = 8$ Hz, C_6H_5 ortho), 7.58 (t, 2H, $J = 8$ Hz, C_6H_5 para), 7.52 (t, 2H, $J = 8$ Hz, C_6H_5 para), 7.45 (t, 4H, $J = 8$ Hz, C_6H_5 meta), 7.41 (t, 4H, $J = 8$ Hz, C_6H_5 meta), 7.34 (d, 4H, $J = 8$ Hz, C_6H_5 ortho), 7.25 (t, $J = 7$ Hz, toluene, meta), 7.17 (m, toluene, ortho and para), 2.36 (s, toluene), −1.80 (s, 3H, Pd−*Me*). ^{13}C{^{1}H} NMR (75 MHz, at 25 °C in $CDCl_3$): δ 180.2 (N═C), 138.7 (C_6H_5 ipso), 137.2 (C_6H_5 ipso), 131.8 (C_6H_5 para), 131.4 (C_6H_5 para), 130.8, 128.7, 128.4, 127.7 (C_6H_5 ortho and meta), −4.1 (Pd−*Me*).

Preparation of *trans*-PdCl(Me){N═C(C_6H_4Me-4)$_2$}$_2$ (6). To a suspension of **4** (103 mg, 0.12 mmol) in THF (5 mL) was added an Et_2O solution of HCl (0.26 mmol; 1 M, 0.26 mL) at room temperature. After 15 min of stirring, H_2O was added to the pale yellow solution. The organic layer was extracted with Et_2O and washed with H_2O. The extracts were evaporated and extracted with toluene. After filtration, the volatiles were removed at reduced pressure to give **6** (55.8 mg, 83%). Analytically pure complex was obtained by recrystallization from toluene/hexane. Anal. Calcd for $C_{31}H_{33}ClN_2Pd\cdot C_{3.5}H_4$: C, 66.67; H, 6.00; N, 4.51; Cl, 5.70. Found: C, 66.96; H, 6.17; N, 4.62; Cl, 6.10. ^{1}H NMR (300 MHz, at 25 °C in $CDCl_3$): δ 8.96 (br, 2H, NH), 8.10 (d, 4H, $J = 8$ Hz, C_6H_4), 7.24 (d, 4H, $J = 8$ Hz, C_6H_4), 7.23 (d, 4H, $J = 9$ Hz, C_6H_4), 7.18 (d, 4H, $J = 9$ Hz, C_6H_4), 2.46 (s, Ar−Me), 2.38 (s, Ar−Me), −0.19 (s, 3H, Pd−Me). ^{13}C{^{1}H} NMR (75 MHz, at 25 °C in $CDCl_3$): δ 179.8 (N═C), 142.1 (C_6H_4 ipso), 141.6 (C_6H_4 ipso), 136.2 (C_6H_4 ipso), 134.5 (C_6H_4 ipso), 130.9, 129.3, 128.5, 128.3 (C_6H_4 ortho and meta), 21.7 (Ar−Me), 21.4 (Ar−Me), −4.1 (Pd−Me).

Reaction of Cp_2Zr{μ-N═C(C_6H_4Me-4)$_2$}$_2$PdCl(Me) (4) with PhOH. A $CDCl_3$ solution of **4** (8.1 mg, 9.3 μmol) and PhOH (1.9 mg, 21 μmol) was stirred for 15 min. The quantitative formation of **6** and $Cp_2Zr(OPh)_2$[10] was confirmed by ^{1}H NMR measurement.

Preparation of *cis*- and *trans*-PdCl($CHCl_2$){NH═C(C_6H_4Me-4)$_2$}$_2$ (7). Complex **6** (55.1 mg, 0.096 mmol) was dissolved in CH_2Cl_2 (7.7 mL). After it was stirred for 19 h under light, the yellow solution was filtered and evaporated to dryness. The residue was washed with hexane (10 mL × 1, 3 mL × 2) and dried under reduced pressure to give **7** (50.5 mg, 82%). Recrystallization of the product from CH_2Cl_2/hexane afforded a complex with CH_2Cl_2 solvate as crystals. Anal. Calcd for $C_{31}H_{31}Cl_3N_2Pd\cdot C_{0.25}H_{0.5}Cl_{0.5}$: C, 56.39; H, 4.77; N, 4.21; Cl, 18.64. Found: C, 56.97; H, 4.70; N, 4.17; Cl, 18.76. It may be assigned to *cis*-**7**, which was confirmed by X-ray crystallography. A solution of the crystals showed the ^{1}H NMR signals of a mixture of the cis and trans isomers (1:2 ratio) which were equilibrated via isomerization in solution. ^{1}H NMR (300 MHz, at 25 °C in $CDCl_3$, obtained as a mixture of the cis and trans isomers): δ 8.82 (br, NH), 8.38 (br, NH), 8.15 (d, $J = 8$ Hz, C_6H_4), 8.03 (d, $J = 8$ Hz, C_6H_4), 7.95 (d, $J = 8$ Hz, C_6H_4), 7.37 (d, $J = 8$ Hz, C_6H_4), 7.34 (d, $J = 8$ Hz, C_6H_4), 7.32 (d, $J = 8$ Hz, C_6H_4), 7.28 (d, $J = 8$ Hz, C_6H_4), 7.25 (d, $J = 8$ Hz, C_6H_4), 7.05 (d, $J = 8$ Hz, C_6H_4), 6.99 (d, $J = 8$ Hz, C_6H_4), 6.58 (d, $J = 8$ Hz, C_6H_4), 6.46 (d, $J = 8$ Hz, C_6H_4), 6.34 (s, cis, $CHCl_2$), 4.81 (s, trans, $CHCl_2$), 2.57 (s, Ar−Me), 2.56 (s, Ar−Me), 2.47 (s, Ar−Me), 2.41 (s, Ar−Me), 2.35 (s, Ar−Me), 2.32 (s, Ar−Me).

Molecular Orbital Calculations. Extended Hückel molecular orbital calculations were carried out by using parameters of the Coulomb integrals and the orbital exponents taken from ref 8. The calculation was performed by using the program CACAO.[8] The geometrical assumption was derived from simplification of the crystal structure of **4**.

Crystal Structure Determination. Crystals of **3** and **4** suitable for an X-ray diffraction study were obtained by recrystallization from benzene at 3 °C and mounted in glass capillary tubes under Ar. The data for **3** were collected at a temperature of −160 ± 1 °C to a maximum 2θ value of 55.0° on a Rigaku Saturn CCD area detector. Calculations were carried out by using the program package CrystalStructure for Windows. The structure was solved by direct methods and expanded using Fourier techniques. A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotoropic thermal parameters. Atomic scattering factors were obtained from the literature.[14] Crystals of **5** suitable for X-ray diffraction study were obtained by crystallization from THF/Et_2O.

Data for **4**, **5**, and **7** were collected under conditions similar to those for **3**. Crystallographic data and details of refinement of the complexes are summarized in Table 2.

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Supporting Information Available: Crystallographic data for **3**−**5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.