Interconvertible Cationic and Neutral Pyridinylimidazole η^3-Allylpalladium Complexes. Structural Assignment by ^{1}H, ^{13}C, and ^{15}N NMR and X-ray Diffraction

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Interconvertible cationic pyridinylimidazole η^3-allylpalladium complex **2** and neutral pyridinylimidazolyl η^3-allylpalladium complex **3** were synthesized and their structures analyzed by ^{1}H, ^{13}C, and ^{15}N NMR and X-ray diffraction. Cationic **2** and neutral **3** can be changed into each other by deprotonation and protonation.

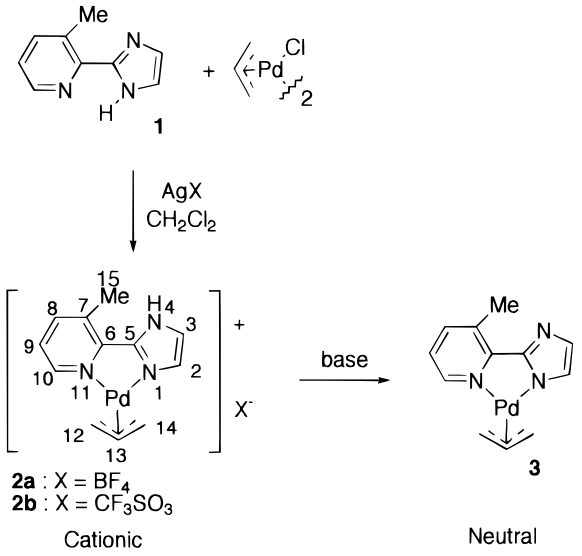
Introduction

Charge is one of the most fundamental elements of a transition metal complex, and a difference in charge affects reactivity in metal-catalyzed reactions.[1] If the charge of complexes is under complete control, the course and rate of a reaction may be changed voluntarily. The charge of a complex is unequivocally determined by the number and kind of ligand when the valence of the metal is not changed. To change the charge, therefore, the ligand must be changed. Recently, we developed a new type of cationic and neutral palladium complex for cyclopropanation of ketene silyl acetal with allylic acetate.[2] In this case, the cationic complex was converted into the neutral complex in situ. If the neutral complex can be converted into the cationic form again, an interconvertible system of palladium complex will have been generated without changing the ligand. In this paper we report that the cationic and neutral η^3-allylpalladium pyridinylimidazole complexes are interconverted only by deprotonation and protonation. Both the cationic and neutral complexes were isolated and characterized by ^{1}H, ^{13}C, and ^{15}N NMR and X-ray diffraction.

Results and Discussion

On the basis of our knowledge of palladium complexes, we planned the synthesis of pyridinylimidazole ligand **1** having a methyl group at the 7-position and its η^3-allylpalladium complexes (Scheme 1). The methyl group was expected to prevent intermolecular coordination[3] by the free N4 nitrogen when the complex was transferred into neutral form **3**. Pyridinylimidazole

Scheme 1



ligands were synthesized by Hughey's method.[4] Reaction of the ligand **1** with a η^3-allylpalladium chloride dimer in the presence of $AgBF_4$ in dichloromethane gave cationic palladium complex **2a** as a white powder. Cationic complex **2a** was converted into neutral **3** by treatment with aqueous $NaHCO_3$ solution in CH_2Cl_2. The neutral complex **3** was recrystallized in benzene to give pale yellow needles. The thermal stability of the neutral **3** was very high; that is, it had a melting point of 138 °C without decomposing.[5] Further, the neutral complex **3** can be transformed into cationic form **2a** again. Actually, treatment of tetrafluoroboric acid (1 equiv) with **3** in ether at 0 °C gave **2a** in 95% yield (eq 1). However, an excess of tetrafluoroboric acid decomposed complex **2a** into a brown precipitate.

Cationic **2a** $\underset{HBF_4,\ \text{ether, 95 \%}}{\overset{NaHCO_3\ \text{aq., 94 \%}}{\rightleftharpoons}}$ Neutral **3** (1)

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(3) We observed the dimer and more complicated complexes in the case of the non-methyl complex (unpublished results).

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Table 1. NMR Data of 2a and 3; Chemical Shifts (ppm) and Coupling Constants (Hz)[a]

	2a	3	3 − 2a
N1	189.9	184.3	−5.6
N4	143.9	234.0	90.1
N11	222.7	217.7	−5.0
H2	7.37 (d, 1.5)	7.13 (s)	−0.24
H3	7.50 (d, 1.5)	7.23 (s)	−0.27
7-Me	2.75 (s, 3H)	2.77 (s, 3H)	0.02
H8	8.01 (dd, 7.8, 1.0)	7.69 (dd, 7.8, 1.0)	−0.32
H9	7.52 (dd, 7.8, 4.9)	7.06 (dd, 7.8, 5.4)	−0.46
H10	8.69 (dd, 4.9, 1.0)	8.39 (dd, 5.4, 1.0)	−0.3
H12syn	4.27 (br.d, 6.8)	3.91 (dd, 6.8, 2.0)	−0.36
H12anti	3.49 (br.d, 12.2)	3.25 (d, 12.7)	−0.24
H13	5.86 (tt, 12.2, 6.8)	5.65 (dddd, 12.7, 12.2, 6.8, 6.8)	−0.21
H14syn	4.38 (br d, 6.8)	4.06 (br d, 6.8)	−0.32
H14anti	3.28 (br d, 12.2)	3.00 (d, 12.2)	−0.28
C2	131.20	130.46	−0.74
C3	122.47	131.14	8.67
C5	147.72	155.48	7.76
C6	146.34	151.63	5.29
C7	133.10	132.19	−0.91
C8	143.98	142.22	−1.76
C9	126.75	121.98	−4.77
C10	153.32	151.50	−1.82
C7Me	19.88	20.71	0.83
C12	63.88	61.72	−2.16
C13	118.74	116.51	−2.23
C14	57.91	53.64	−4.27

[a] $CD_3OD-CD_2Cl_2$ = 1:1, at 25 °C.

Structural assignment of cationic and neutral complexes **2a** and **3** was performed by ^1H, ^{13}C, and ^{15}N NMR analysis, and the data are listed in Table 1.

Because $^2J_{NH}$ values are larger than $^3J_{NH}$ values in the imidazole ring system in general,[6] two nitrogens and protons on the imidazole part were easily assigned by the coupling constant values read from 2D PFG-HMBC spectra. In the case of the cationic complex **2a**, $^2J_{N1,H2}$ and $^2J_{N4,H3}$ were 7.5 and 4.1 Hz, respectively, and $^2J_{N1,H2}$ and $^2J_{N4,H3}$ of the neutral complex **3** were 7.3 and 10.1 Hz, respectively. On the other hand, $^3J_{NH}$ values were smaller than 3 Hz. By conversion of **2a** into **3**, a large downfield shift (from 143.9 into 234.0 ppm) occurred at N4, and the $^2J_{N4,H3}$ value was also changed from 4.1 to 10.1 Hz. Such changes by deprotonation of an organic base are known in the case of simple pyridine,[7] and our results are consistent with them. Further, for definite assignment of **2a**, the deuterium isotope shifts of ^{15}N and ^{13}C NMR were also measured in the case of the 7-demethyl complex of **2a**.[8] All proton NMR signals were moved to the upper field by conversion into the neutral complex **3**. In the neutral **3**, the electron pair on the sp^2-hybridized nitrogen N1 atom is incorporated into the conjugated π-electron system. The charge delocalization leads to increased charge densities on the whole ligand and η^3-allyl portion, and the change of charge densities may cause the upper field shift of ^1H NMR signals. In the ^{13}C NMR, most signals also moved to the upper field except for C3, C5, C6, and C7-Me (see Table 1).

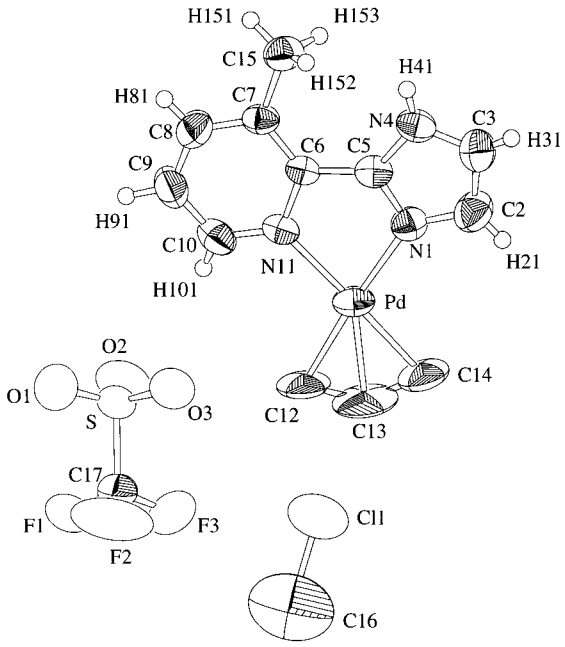

Figure 1. Molecular structure of $[(C_{12}H_{14}N_3Pd)^+(CF_3SO_4)^-\cdot 1/2(CH_2Cl)_2]$ (**2b**).

^1H and ^{13}C NMR signals on the η^3-allyl moiety were assigned by NOE, HMQC, and HMBC data. Thus, in the neutral complex **3** NOEs between H10 and H12syn, and H2 and H14syn, were observed at room temperature. In the case of cationic complex **2a**, the NOE could not be observed at room temperature because chemical exchange[9] of the η^3-allyl moiety occurred. At 233 K chemical exchange almost stopped, and NOEs between H10 and H12syn and between H2 and H14syn were observed. Assignments of C12 and C14 were established by direct correlation from H12 and H14 in PFG-HMQC spectra.

A phenomenon of interconversion between **2a** and **3** was also observed in the ^1H NMR study. A 1:1 mixture of **2a** and **3** showed one set of sharp signals in the ^1H NMR at −50 °C, and all the chemical shifts indicated their average values. This means that the acidic proton of **2** can be exchanged quickly with **3** even at −50 °C.

Although a single crystal of **2a** for X-ray structure determination could not be obtained, a colorless single crystal of **2b** that had trifluoromethanesulfonate ($CF_3SO_3^-$) instead of tetrafluoroborate (BF_4^-) was recrystallized from 1,2-dichloroethane.[10] A single-crystal X-ray structure determination of **2b** and **3** was achieved (Figure 1). Selected interatomic parameters are collected in Tables 2, 3, and 4.

A structural difference between cationic and neutral complexes was observed in the solid state. In particular, bond distances that included the palladium atom were clearly changed. The differences of bond length between neutral complex **3** and cationic complex **2** for Pd−N1, Pd−N11, and Pd−C14 were −0.031, −0.031, and −0.005 Å, respectively; so they were shortened. On the contrary, Pd−C12, Pd−C13, C12−C13, and C13−C14 bonds were extended, and the differences were +0.024, +0.032,

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(5) We treated several η^3-allylpalladium compounds, and only **3** reached the melting point without decomposing.
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(8) ^{13}C and ^{15}N NMR data were measured both in a mixture of CD_2Cl_2 and CD_3OD and in a mixture of CD_2Cl_2 and CD_3OH. Data are not shown here.
(9) Syn−syn and anti−anti exchange of H12 and H14 occurred quickly at room temperature.
(10) ^1H and ^{13}C NMR spectra of **2b** were almost the same as those of **2a**. The crystal included 1,2-dichloroethane.

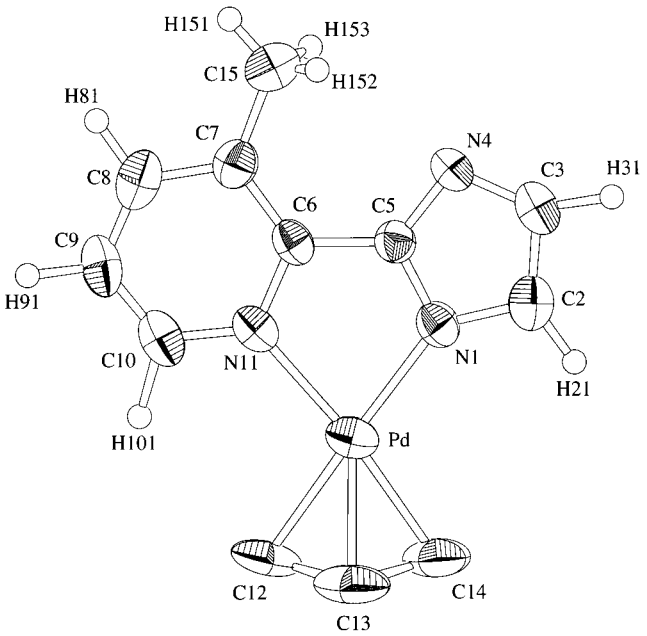

Figure 2. Molecular structure of $C_{12}H_{13}N_3Pd$ (**3**).

Table 2. Summary of Crystal Data and Intensity Collection Parameters for 2b and 3

	2b	3
chem formula	$C_{14}H_{16}ClF_3N_3O_3PdS$ $[(C_{12}H_{14}N_3Pd)^+(CF_3SO_4)^-\cdot 1/2(CH_2Cl)_2]$	$C_{12}H_{13}N_3Pd$
fw	505.21	305.65
cryst color and habit	colorless rod	colorless needle
crystal size (mm)	0.29 × 0.08 × 0.07	1.00 × 0.10 × 0.03
temp, K	296	296
cryst system	orthorhombic	monoclinic
space group	*Pbcn*	$P2_1/a$
unit cell params		
a, Å	15.030(1)	7.361(3)
b, Å	17.726(2)	15.343(2)
c, Å	14.086(2)	10.778(1)
α, deg	90	90
β, deg	90	106.40(2)
γ, deg	90	90
V, Å^3	3752.7(6)	1167.7(4)
Z	8	4
D(calc) (g cm^{-3})	1.788	1.738
μ, mm^{-1}	1.290	1.565
F(000)	2008	608
no. of reflns measd	4313	2871
$2\theta_{max}$ (deg)	55.0°	55.0°
no. of unique data	4313	2668
no. of reflns with I 3.0σ(*I*)	1689	1655
GOF[a]	1.79	2.19
R^b	0.042	0.045
R_w[c]	0.041	0.052
residual ρ_{max} (e Å^{-3})	0.45	0.89

[a] GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o = number of observations and N_v = number of variables. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

+0.07, and +0.10 Å, respectively. This suggested that the trans influence of N1 in neutral **3** was stronger than that of N1 in cationic **2b**. These structural changes slightly raised the allyl plane (C12−C13−C14) from the N1−Pd−N11 plane, and the difference was about 16°. Other bond distances and angles among heteroatoms on the ligand were also changed.

Table 3. Selected Bond Lengths (Å) of 2b and 3

	2b	3	3 − 2b
Pd−N(1)	2.070(7)	2.039(6)	−0.031
Pd−N(11)	2.117(6)	2.086(6)	−0.031
Pd−C(12)	2.12(1)	2.144(8)	+0.024
Pd−C(13)	2.07(1)	2.102(8)	+0.032
Pd−C(14)	2.13(1)	2.125(9)	−0.005
N(1)−C(2)	1.36(1)	1.372(9)	+0.012
N(1)−C(5)	1.322(9)	1.345(9)	+0.023
N(4)−C(3)	1.35(1)	1.35(1)	0.0
N(4)−C(5)	1.366(9)	1.327(8)	−0.039
N(11)−C(6)	1.362(8)	1.365(9)	+0.003
N(11)−C(10)	1.32(1)	1.349(9)	+0.029
C(2)−C(3)	1.34(1)	1.38(1)	+0.04
C(5)−C(6)	1.45(1)	1.458(9)	+0.008
C(6)−C(7)	1.372(10)	1.40(1)	+0.028
C(7)−C(8)	1.38(1)	1.40(1)	+0.02
C(7)−C(15)	1.51(1)	1.49(1)	−0.02
C(8)−C(9)	1.36(1)	1.36(1)	0.0
C(9)−C(10)	1.38(1)	1.35(1)	−0.03
C(12)−C(13)	1.34(2)	1.41(1)	+0.07
C(13)−C(14)	1.30(2)	1.40(1)	+0.10

Table 4. Selected Bond and Least-Squares Plane Angles (deg) of 2b and 3

	2b	3	3 − 2b
N(1)−Pd−N(11)	77.6(3)	78.6(3)	+1.0
C(12)−Pd−C(14)	70.6(4)	69.5(4)	−1.1
C(12)−C(13)−C(14)	136(1)	120.5(10)	−16
plane (N1−Pd−N11)−plane(C12−C13−C14)	126.51	110.56	−15.95
Pd −N(11)−C(6)	116.5(6)	115.3(5)	−1.2
Pd−N(11)−C(10)	125.3(6)	125.7(6)	+0.4
N(1)−C(2)−C(3)	108.1(9)	106.9(7)	−1.2
N(1)−C(5)−N(4)	107.4(8)	114.9(6)	+7.5
N(1)−C(5)−C(6)	121.3(7)	116.9(6)	−4.4
N(4)−C(3)−C(2)	107.4(9)	110.7(7)	+3.3
N(4)−C(5)−C(6)	131.2(8)	128.2(7)	−3.0
N(11)−C(6)−C(5)	110.8(7)	113.5(7)	+2.7
N(11)−C(6)−C(7)	122.3(8)	120.7(7)	−1.6
N(11)−C(10)−C(9)	123.2(8)	123.5(8)	+0.3
C(2)−N(1)−C(5)	108.6(8)	104.0(6)	−4.6
C(3)−N(4)−C(5)	108.4(8)	103.5(6)	−4.9
C(5)−C(6)−C(7)	126.9(7)	125.8(7)	−1.1
C(6)−C(7)−C(8)	117.2(7)	116.6(8)	−0.6
C(6)−C(7)−C(15)	123.6(8)	123.3(7)	−0.3
C(6)−N(11)−C(10)	118.2(7)	119.1(7)	+0.9
C(7)−C(8)−C(9)	121.8(9)	122.5(8)	+0.7
C(8)−C(7)−C(15)	119.2(8)	120.1(8)	+0.9
C(8)−C(9)−C(10)	117.2(9)	117.6(8)	+0.4

Conclusion

Both stable cationic and neutral η^3-allylpalladium pyridinylimidazole complexes **2** and **3** were synthesized and characterized by ^{1}H, ^{13}C, and ^{15}N NMR. The cationic complex **2a** and neutral complex **3** were interconvertible by deprotonation and protonation. The structural difference between cationic and neutral complexes was observed in the solid state. Such structural differences must give different properties to the palladium complex in solution. Now we are investigating a new catalytic system using the interconvertible cationic and neutral complexes.

Experimental Section

General Procedure. Methylene chloride and methanol were dried over activated 4A or 3A molecular sieves prior to use. Commercially available 1,2-dichloroethane (special grade) was used without purification or dryness. HBF_4 (54 wt % ether solution) was purchased from Aldrich Chemical Co. Inc. NMR solvents (CD_2Cl_2 and methanol-d_4) were used without purification or dryness. NMR spectra were recorded using JEOL α-600

and JEOL AL-300 instruments. ^{1}H NMR chemical shifts are reported in ppm from residual CD_2HOD (3.330) in a mixture of CD_2Cl_2 and CD_3OD. ^{13}C NMR chemical shift are reported in ppm from residual CD_3OD (49.00) in a mixture of CD_2Cl_2 and CD_3OD. ^{15}N NMR spectra were obtained by the ^{1}H−^{15}N PFG-HMBC method at natural abundance,[11] and chemical shifts are reported in ppm from NH_4NO_3 (0 ppm) in DMSO-d_6 as an external reference. Melting points were determined on a Yanaco MP-500 melting point apparatus and were not corrected. X-ray analysis was performed on an Enraf-Nonius CAD4.

2-(3-Methylpyridin-2-yl)-imidazole (MePIH, 1). A mixture of 2-cyano-3-methylpyridine (1.04 g, 8.80 mmol) and 2-aminoethylammonium *p*-toluenesulfonate (2.04 g, 8.80 mmol) was heated at 170 °C for 1 h. The resulting mixture was cooled at room temperature, and a 6 N NaOH solution (10 mL) and $CHCl_3$ (20 mL) were added. The mixture was extracted with $CHCl_3$ (10 mL × 4), dried over $MgSO_4$, and concentrated in vacuo to give a white solid (1.23 g). A suspension of the white solid (1.23 g, 7.63 mmol) and $BaMnO_4$ (17 g, 69 mmol) in 1,2-dichloroethane (150 mL) was heated at 80 °C for 3 h. The insoluble solid was separated with Celite, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (Fuji silysia NH, $CHCl_3$) and recrystallizatiom ($CHCl_3$/ether) to give **1** (780 mg, 56%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.1 (br, 1H), 8.37 (br.d, 1H, J = 4.8 Hz), 7.59 (br d, 1H, J = 7.6 Hz), 7.30 (S, 1H), 7.15 (m, 1H), 7.11 (s, 1H), 2.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ 147.2, 145.9, 139.9, 131.8, 130.3, 122.6, 116.5, 20.9; mp 121 °C (dec). Anal. Calcd for $C_9H_9N_3$: C, 67.91; H, 5.70; N, 26.40. Found: C, 67.72; H, 5.69; N, 26.19.

[(η^3-C_3H_5)Pd(MePIH)]$^+BF_4^-$ (2a). Dichloromethane (40 mL) was added at 0 °C in a brown two-necked round-bottom flask containing $AgBF_4$ (285 mg, 1.46 mmol) and (η^3-C_3H_5)-PdCl dimer (268 mg, 0.73 mmol). Ligand **1b** (233 mg, 1.46 mmol) was added to the mixture. After stirring the mixture at room temperature for 1.5 h, methanol (40 mL) was added to the mixture. A white precipitate was filtered off with Celite and a membrane filter (Millipore, LCR25-LH), and the filtrate was concentrated to give a white solid. The white solid was washed with CH_2Cl_2 on a filter paper and dried under reduced pressure to give **2a** (565 mg, 98%). The solids retain a fractional amount of inseparable impurity. Mp: 215 °C (dec). Anal. Calcd for $C_{12}H_{14}N_3BF_4Pd$: C, 36.63; H, 3.59; N, 10.68. Found: C, 36.09; H, 3.50; N, 10.75. ^{1}H NMR, ^{13}C NMR, and ^{15}N NMR in CD_2Cl_2−CD_3OD (1:1): see Table 1.

[(η^3-C_3H_5)Pd(MePIH)]$^+CF_3SO_3^-$ (2b) was prepared from **1** (39 mg, 0.245 mmol), $Ag(CF_3SO_3)$ (63 mg, 0.245 mmol), and (η^3-C_3H_5)PdCl dimer (44.9 mg, 0.123 mmol) using a procedure similar to that of **2a**. After recrystallization in $(CH_2Cl)_2$ **2b** (49 mg) was obtained. The crystals tenaciously retain fractional amounts of solvent. Mp: 210 °C (dec). Anal. Calcd for $C_{13}H_{14}N_3O_3SF_3Pd\cdot 1/2(CH_2Cl)_2$: C, 37.52; H, 3.60; N, 9.38. Found: C, 33.48; H, 3.15; N, 8.31. ^{1}H NMR (300 MHz, CD_2Cl_2−CD_3OD = 1:1, 23 °C): δ 8.68 (dd, J = 5.0, 0.9 Hz), 8.01 (ddd, J = 7.9, 4.7, 0.1 Hz), 7.51 (dd, J = 7.9, 5.2 Hz), 7.49 (d, J = 1.5 Hz), 7.37 (d, J = 1.5 Hz), 5.87 (tt, J = 12.4, 6.9 Hz), 4.38 (br d, J = 6.9 Hz), 4.26 (br d, J = 6.9 Hz), 3.50 (br d, J = 12.4 Hz), 3.28 (br d, J = 12.4 Hz), 2.76 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2−CD_3OD = 1:1, 23 °C): δ 153.25, 147.69, 146.40, 143.97, 133.11, 131.19, 126.69, 122.46, 118.73, 63.85, 57.94, 19.96.

(η^3-C_3H_5)Pd(MePIH) (3). A suspension of **2a** (202 mg) in $CHCl_3$ (15 mL) was washed with saturated aqueous $NaHCO_3$ in a separatory funnel. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to give **3** (147 mg, 94%) as a pale yellow powder. A pure sample for elemental analysis was prepared by recrystallization from benzene. Mp: 138−139 °C. Anal. Calcd for $C_{12}H_{13}N_3Pd$: C, 47.16; H, 4.29; N, 13.75; Pd, 34.81. Found: C, 47.17; H, 4.22; N, 13.71; Pd, 34.79. ^{1}H NMR, ^{13}C NMR, and ^{15}N NMR in CD_2Cl_2−CD_3OD (1:1): see Table 1.

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