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## *Articles*

# A Trinuclear Silver(I) Functionalized N-Heterocyclic Carbene Complex and Its Use in Transmetalation: Structure and Catalytic Activity for Olefin Polymerization[†]

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Deprotonation of an imidazolium salt with silver oxide forms the silver carbene complex $\{[Ag(C\wedge N)_2]_3I\}I_2$ (**2**; C∧N = 3-methyl-1-picolylimidazolin-2-ylidene). The Ag−carbene complex undergoes a facile reaction with $Pd(PhCN)_2Cl_2$ to yield the carbene complex $Pd(C\wedge N)Cl_2$ (**3**). Complexes **2** and **3** have been characterized by IR, $^1H$ and $^{13}C$ NMR spectra, and elemental analyses. The molecular structures of complexes **2** and **3** have been confirmed by X-ray single-crystal analyses. Complex **2** shows moderate catalytic activities of up to $10^5$ g of PE (mol of Ag)$^{-1}$ h$^{-1}$ for ethylene polymerization, and complex **3** shows very high catalytic activities of up to $10^8$ g of PNB (mol of Pd)$^{-1}$ h$^{-1}$ for the addition polymerization of norbornene in the presence of methylaluminoxane (MAO) as cocatalyst.

## Introduction

Since the first isolation of a free carbene by Arduengo,[1] N-heterocyclic carbenes (NHCs) have attracted increasing attention as ancillary ligands in homogeneous catalysis, such as hydrogenation,[2] hydroformaylation,[3] C−C coupling,[4] olefin metathesis,[5] hydrosilylation,[6] and many others.[7] However, few of these compounds have been used as catalysts for olefin polymerization, which is due to the fact that transition-metal-based heterocyclic carbene complexes containing an alkyl group decomposed via the reductive elimination of the hydrocarbyl and carbene moiety, as free NHC tends to undergo 1,2-alkyl migration.[8] The problem might be solved by the use of functionalized bidentate or polydentate NHC ligands developed recently, since these ligands could provide an opportunity to control the stability and reactivity of active centers more efficiently in olefin polymerization. In recent years, pyridine-functionalized bidentate or polydentate NHC ligands have been frequently used as versatile ancillary ligands in organometallic chemistry and catalysis,[4n,9,10] but only a few have been used as catalyst precursors for the copolymerization of CO and norbornene[11a] and the homopolymerization of norbornene,[11b] ethylene,[11b,c] and styrene.[11d]

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[†] Dedicated to Prof. Dr. Max Herberhold on the occasion of his 70th birthday.

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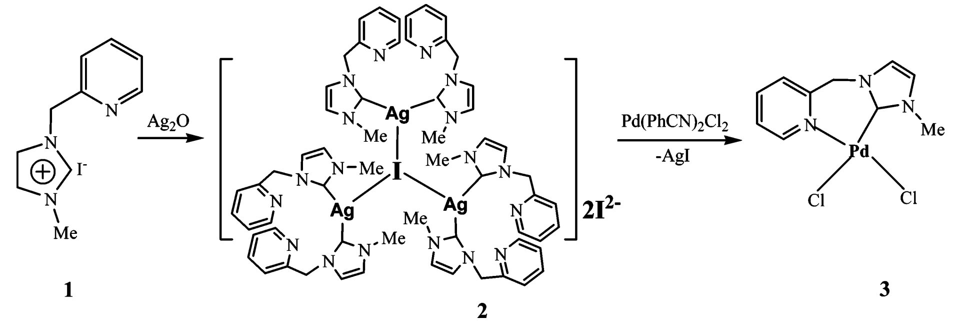
**Scheme 1. Synthesis of Complexes 2 and 3**



The structural diversity of silver(I) N-heterocyclic carbenes has been widely studied, and their application as transmetalation reagents has widened their use as an easy access to various catalytic transition-metal NHC complexes.[12] However, despite the number of silver NHC complexes reported to date, we still do not have much knowledge about their applications in catalytic processes.[13] As part of an effort to design new catalysts for olefin polymerization, we have investigated a pyridine-functionalized NHC silver complex and its corresponding palladium complex by transmetalation. Preliminary studies show that $\{[Ag(C{\wedge}N)_2]_3I\}I_2$ (**2**; C∧N = 3-methyl-1-picolylimidazolin-2-ylidene) exhibits moderate catalytic activity ($10^5$ g of PE (mol of Ag)$^{-1}$ h$^{-1}$) for ethylene polymerization, and complex $[Pd(C{\wedge}N)]Cl_2$ (**3**) is highly active toward the addition polymerization of norbornene.

## Results and Discussion

We report the synthesis of a palladium complex by transmetalation from the corresponding silver carbene derivative by a two-step process, analogously to the method of McGuinness and Cavell,[4i] who first prepared the iodide salts of these materials. The first step involves deprotonation of the imidazolium salt with silver oxide to form the silver carbene species. These can be isolated as the white trinuclear silver complex **2**. The addition of 1 or 0.5 equiv of $Pd(PhCN)_2Cl_2$ (according to the moles of carbene) gave the desired product in each case, along with a white suspension of silver iodide. The reaction was allowed to continue for 16 h to achieve completion, which then gave the chelating palladium mono(carbene) complex **3** in good yields (Scheme 1). It is very surprising that a similar reaction performed by the Cavell group led to $(NHC)_2Ag{\cdot}AgI_2$ and $Pd(NHC)_2Cl_2$, which is obviously different from our results.

The $^1$H NMR spectra of complexes **2** and **3** do not exhibit a signal at 10−11 ppm, where the imidazolium $C_2$−H signals of the precursors are found (10.32 ppm), and the chemical shifts of other hydrogens are similar to those of the corresponding precursors. In the $^{13}$C NMR spectra the signals for the carbene carbon of complexes **2** and **3** appear at 182.1 and 161.9 ppm, respectively, which is characteristic for a metal−carbene signal.[14]

All of the carbene complexes described are very soluble in $CH_3OH$, slightly soluble in $CH_2Cl_2$ and THF, and insoluble in diethyl ether and hydrocarbon solvents. The complexes are moderately stable in dry air.

Crystals suitable for X-ray crystallography of **2** were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the corresponding compound. The structure of the silver−carbene complex of **2** is shown in Figure 1. Complex **2** crystallizes as a symmetrical trinuclear compound of the formula $\{[Ag(carbene)_2]_3I\}I_2$. The geometry at the silver center is planar, with every Ag coordinated by two carbene carbon atoms and one triply bridging iodide. The three Ag(I) cations are linked by the bridging I(1) anion symmetrically with an Ag(1)−I(1) distance of 3.0398(11) Å, which is much longer than those of the Ag−I(bridging) bonds (2.8313(15) and 2.7839(15) Å),[15] and the net 2+ charge is balanced by two noninteracting iodide ions. There is no important interaction between the silver ions and the alkyl groups. The bulky *N*-methyl group favors the formation of a dihedral angle of 72.2° between the two imidazole rings. And the imidazole ring forms an angle of 54.5° with the coordination plane (C(1), C(1D), Ag(1), I(1)). The Ag(1)−C(1) distance of 2.096 Å is within expected values.[14]

Crystals suitable for X-ray crystallography of **3** were obtained by slow diffusion of diethyl ether into $CH_3OH$ solutions of the corresponding compound. The structure of the palladium carbene complex **3** is shown in Figure 2. The molecular structure reveals that the geometry at the palladium atom is essentially square planar (maximum deviation 0.0595 Å), with angles of ∼90° between the four substituents (C1−Pd1−N3, 86.9(3)°; C1−Pd1−Cl1, 91.6(3)°; N3−Pd1−Cl2, 89.53(16)°; Cl2−Pd1−C12, 92.18(7)°). The narrow angle for C1−Pd1−N3 is due to the chelation of the pyridine-functionalized carbene ligand, which is constrained by the methylene bridge. The carbene plane (C(1), N(1), C(2), N(2), C(3)) forms an angle of 49.7° with the square plane (C(1), N(3), Cl(1), Cl(2)) of the palladium. The resulting six-membered ring is puckered to release conformational strain. The bite angle of the chelating ligand is 86.9°. The Pd−

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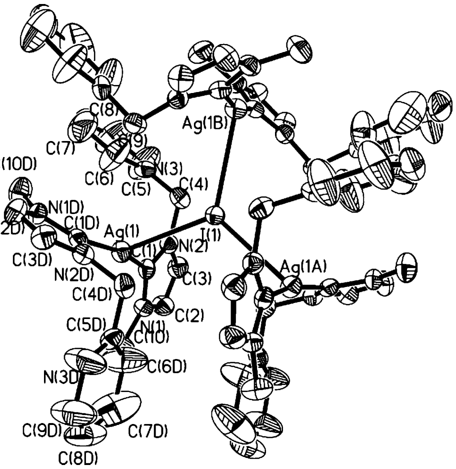

**Figure 1.** Crystal structure of complex **2** showing 30% probability ellipsoids (cation only). The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag(1)−C(1) = 2.096(9), Ag(1)−I(1) = 3.0983(11); C(1D)−Ag(1)−C(1) = 166.0(4), C(1)−Ag(1)−I(1) = 97.0(2), Ag(1)−I(1)−Ag(1A) = 120.0, Ag(1)−I(1)−Ag(1B) = 120.0, Ag(1A)−I(1)−Ag(1B) = 120.0, N(1)−C(1)−Ag(1) = 127.2(7).

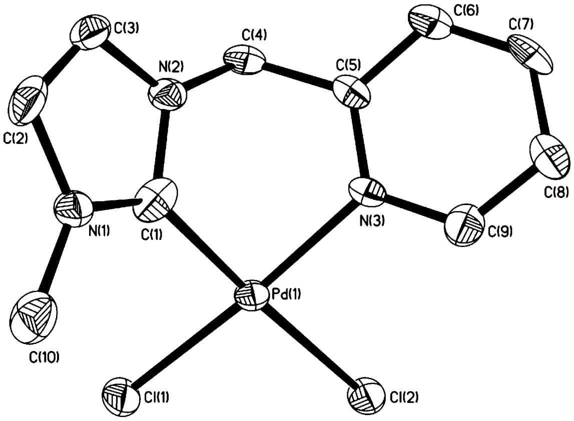

**Figure 2.** Crystal structure of complex **3** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 1.968(7), Pd(1)−N(3) = 2.051(7), Pd(1)−Cl(1) = 2.317(2), Pd(1)−Cl(2) = 2.3626(17); C(1)−Pd(1)−N(3) = 86.9(3), C(1)−Pd(1)−Cl(1) = 91.6(3), N(3)−Pd(1)−Cl(2) = 89.53(16), Cl(1)−Pd(1)−Cl(2) = 92.18(7), N(3)−Pd(1)−Cl(1) = 174.68(17), C(1)−Pd(1)−Cl(2) = 175.6(2).

C(carbene) bond length (1.968(7) Å) is slightly shorter than the predicted value (2.08 Å), where pure Pd−C $\sigma$-bonding is considered.

A preliminary ethylene polymerization study showed that the Ag carbene complex **2** is a moderately active precatalyst for the polymerization of ethylene. For example, ethylene was polymerized under MAO activation of complex **2** at different temperatures (polymerization conditions: solvent, 50 mL of toluene; silver complex **2**, 2 $\mu$mol; Al/Ag (molar) = 3100; ethylene; pressure, 1 atm; reaction time, 30 min) with activities of $5.2 \times 10^5$ (10 °C), $6.0 \times 10^5$ (20 °C), $4.7 \times 10^5$ (30 °C), and $3.0 \times 10^5$ g of PE (mol of Ag)$^{-1}$ h$^{-1}$ (40 °C), respectively. The polymers obtained are insoluble in most organic solvents, such as hydrocarbon solvents, chloroform, tetrachloroethane, benzene, chlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene, which makes it difficult to characterize them.

**Table 1. Addition Polymerization of Norbornene with Palladium Complex 3 Activated by Methylaluminoxane (MAO)[a]**

| run | complex | T (°C) | Al/Pd | time (min) | conversn (%) | activity ($10^6$ g of PNB (mol of Pd)$^{-1}$ h$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | **3** | 0 | 1000 | 7 | 100 | 11.2 |
| 2 | **3** | 10 | 1000 | 2 | 100 | 40 |
| 3 | **3** | 20 | 1000 | 1 | 100 | 77 |
| 4 | **3** | 40 | 1000 | <1 | 100 | *b* |
| 5 | **3** | 20 | 500 | 10 | 64 | 5.2 |
| 6 | **3** | 40 | 500 | 5 | 100 | 16 |
| 7[c] | **3** | 20 | | | | 0 |
| 8[d] | | 20 | | | | 0 |

[a] Polymerization conditions: solvent, chlorobenzene; total volume, 10 mL; palladium complex (**3**), 1.4 $\mu$mol; norbornene, 1.88 g. [b] The systems became highly viscous at once and turned into gellike product mixtures, and the forming polymers were insoluble in 1,2,4-trichlorobenzene. [c] Without cocatalyst MAO. [d] Without palladium complex.

Preliminary experiments indicated that the palladium-based catalyst precursor **3** can be activated for norbornene polymerization by treatment with MAO to afford addition-type polynorbornene (PNB) with very high activities ($10^8$ g of PNB (mol of Pd)$^{-1}$ h$^{-1}$), while under the same conditions, the complex itself and MAO did not produce polymers (run 7 and 8). The norbornene polymerization results are collected in Table 1. We found that the systems catalyzed by the palladium-based catalysts all become highly viscous and turn into gellike product mixtures immediately and the yields are all 100% at high temperature or high Al/Pd molar ratio. The polymers obtained are insoluble in most organic solvents, such as cyclohexane, chloroform, benzene, chlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and tetrachloroethane, even if the polymers are prepared without the appearance of gellike product mixtures; therefore, we had to characterize the polymers by solid-state $^{13}$C CP/MAS NMR. With a decrease in the amount of MAO, from run 3 to run 5, the system does not immediately become highly viscous, but they are all suspensions and the polymers precipitate immediately during the polymerization. The molecular weights of the polymers obtained by the palladium-based catalyst could not be measured because of their insolubility. The catalytic systems always maintain a high activity even if the polymerization conditions are changed. The molar ratio of Al to Pd has a great effect on the activity of the polymerization; the activity increases rapidly as the molar ratio of Al to Pd increases. Also, the polymerization temperature influences the activity as well; the activity increases as the temperature increases. The optimal polymerization temperature for the catalytic system is 40 °C (comparing runs 1−4).

The polynorbornenes obtained with the palladium carbene complex possess an addition structure, as determined from IR and the solid-state $^{13}$C CP/MAS NMR spectra. The absence of bands at 1680−1620 cm$^{-1}$ in the IR spectra indicated no double bonds, which was different from the results found for the polymers of norbornene ring-opening metathesis polymerization.[16] The solid-state $^{13}$C CP/MAS NMR spectrum of PNB shows the main four groups of resonances at $\delta$ 29.0−57.3 ppm (m, maxima at $\delta$ 29.0, 35.3, 48.8, and 52.6), attributed to the vinyl addition polymer structure of polynorbornene, the bridge carbon, the bridgehead carbon, and the backbone carbon, respectively.[17] Therefore, the polymerization took place exclusively in a vinyl addition manner. The microstructures of the

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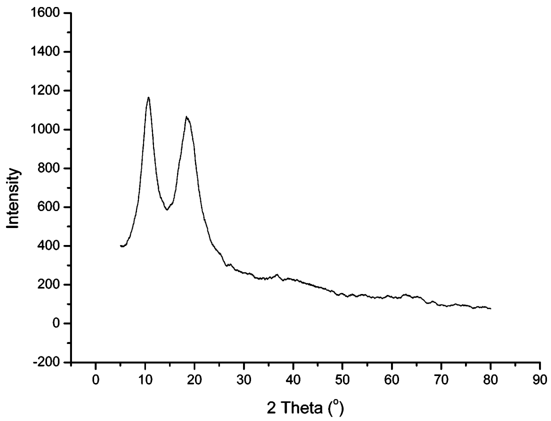

**Figure 3.** WAXD diagrams of polynorbornenes obtained with the Pd-based catalyst.

polymers obtained by the palladium complexes could not be analyzed because of their insolubility. Partial information on the conformation of the polynorbornenes obtained by the palladium-based complex was obtained by means of wide-angle X-ray diffraction (WAXD), as shown in Figure 3. Two broad halos at $2\theta$ values of 10.68° (peak 1) and 18.42° (peak 2) appear in the diagram of the polymers, which is similar to the results reported by Haselwender et al.,[18a] Zhao et al.,[18b] and Hu et al.[18c] According to their results, peak 1 can be regarded as a reflection of the interchain or intersegment distance of the polymer, while peak 2 can be regarded as a reflection of the intrachain distance. No traces of Bragg reflections, characteristic of crystalline regions, are revealed. The polynorbornenes, therefore, are noncrystalline.

## Conclusion

We have successfully synthesized the silver carbene complex **2** and its palladium transmetalation product **3**. A preliminary study shows that the trinuclear silver complex with a pyridine-functionalized NHC ligand shows moderate activity toward ethylene polymerization, while its corresponding palladium carbene complex (**3**) is highly active as a catalyst precursor in norbornene polymerization. To the best of our knowledge, this is the first report of these kinds of pyridine-functionalized NHC silver and palladium complexes exhibiting activity toward the polymerization of ethylene and the addition polymerization of norbornene. Further investigations into olefin polymerization by these kinds of complexes and the polymerization mechanism are ongoing.

## Experimental Section

**General Procedures.** All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Methanol was dried over Mg, $CH_2Cl_2$ and chlorobenzene were dried over $CaH_2$, and norbornene was dried over Na, and then all were distilled under nitrogen immediately prior to use. Methylaluminoxane (MAO) and 1-methylimidazole and 2-picolyl chloride hydrochloride were purchased from Witco and Acros, respectively. Other solvents were used as received as technical-grade solvents. 3-Methyl-1-picolylimidazolium iodide[4i] and $Pd(PhCN)_2Cl_2$[19] were prepared according to literature procedures. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker DMX 500 spectrometer in $CDCl_3$ in DMSO-$d_6$. Cross-polarization magic angle spinning (CP MAS) NMR spectra of solid-state PNB were measured at room temperature on a Bruker DSX 300 NMR spectrometer. $^{13}C$ chemical shifts were calibrated through the external adamantane peak. Elemental analysis was performed on an Elementar Vario EL III analyzer. IR (KBr) spectra were recorded on a Nicolet FT-IR spectrophotometer. WAXD (wide-angle X-ray diffraction) curves of the polymer powders were recorded on a Bruker D4 ENDEAVOR diffractometer using Cu K$\alpha$ radiation at 40 kV and 40 mA with a scan speed of 1°/min. Scanning was performed with $2\theta$ values ranging from 5 to 80°.

**Table 2. Summary of Crystallographic Data for 2 and 3**

| | 2 | 3 |
|---|---|---|
| chem formula | $C_{60}H_{66}Ag_3I_3N_{18}$ | $C_{10}H_{11}Cl_2N_3Pd$ |
| formula wt | 1743.62 | 350.52 |
| temp (K) | 293(2) | 293(2) |
| wavelength (Å) | 0.710 73 | 0.710 73 |
| cryst syst | rhombohedral | triclinic |
| space group | $R\bar{3}c$ | $P\bar{1}$ |
| unit cell dimens | | |
| $a$ (Å) | 13.151(2) | 8.4682(18) |
| $b$ (Å) | 13.151(2) | 8.5914(18) |
| $c$ (Å) | 68.335(16) | 9.122(2) |
| $\alpha$ (deg) | 90 | 104.258(4) |
| $\beta$ (deg) | 90 | 98.156(5) |
| $\gamma$ (deg) | 120 | 98.661(4) |
| $V$ (Å$^3$) | 10 235(4) | 624.7(2) |
| $Z$ | 6 | 2 |
| $D_{calcd}$ (Mg/m$^3$) | 1.697 | 1.864 |
| abs coeff (mm$^{-1}$) | 2.260 | 1.888 |
| $F$(000) | 5112 | 344 |
| cryst size (mm) | 0.20 × 0.15 × 0.10 | 0.25 × 0.10 × 0.05 |
| $\theta$ range for data collecn (deg) | 1.79−25.00 | 2.48−25.00 |
| limiting indices | $-15 \le h \le +11$ | $-10 \le h \le +8$ |
| | $-13 \le k \le +15$ | $-9 \le k \le +4$ |
| | $-81 \le l \le +80$ | $-2 \le l \le +10$ |
| no. of rflns collected | 13 420 | 1409 |
| no. of indep rflns | 2023 ($R$(int) = 0.0475) | 1376 ($R$(int) = 0.0064) |
| completeness to $\theta$ = 25.00° (%) | 100.0 | 62.6 |
| max, min transmissn | 0.8055, 0.6606 | 0.9115, 0.6497 |
| refinement method | full-matrix least squares on $F^2$ | |
| no. of data/restraints/params | 2023/0/130 | 1376/0/146 |
| goodness of fit on $F^2$ | 1.038 | 0.981 |
| final $R$ indices ($I > 2\sigma(I)$)[a] | | |
| R1 | 0.0635 | 0.0371 |
| wR2 | 0.1865 | 0.0849 |
| largest diff peak, hole (e/Å$^3$) | 2.214, −2.002 | 0.598, −0.486 |

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. $wR2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum(F_o^2)]^{1/2}$.

**{[Ag(3-methyl-1-picolylimidazolin-2-ylidene)$_2$]$_3$I}I$_2$ (2).** A mixture of 3-methyl-1-picolylimidazolium iodide (300 mg, 1 mmol) and silver(I) oxide (580 mg, 2.5 mmol) was taken up in 30 mL of $CH_2Cl_2$ and was stirred for 2 h. The solution was filtered through Celite, and the solvent was removed completely under vacuum. Upon addition of diethyl ether, the gray-white solid that formed was filtered, washed with more diethyl ether, and dried under vacuum. The product was recrystallized from $CH_2Cl_2$/ether to give white crystals. Yield: 175 mg (60%). $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 8.53 (d, 1H, pyridyl), 7.65 (m, 1H, pyridyl), 7.47 (m, 1H, HCCH), 7.27 (m, 1H, HCCH), 7.14 (m, 1H, pyridyl), 6.97 (m, 1H, pyridyl), 5.51 (s, 2H, $CH_2$), 3.83 (s, 3H, $NCH_3$) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 182.1 (Ag−C), 155.9 (pyridyl, $C_2$), 149.6 (pyridyl, $C_6$), 137.4 (pyridyl, $C_4$), 123.3 (pyridyl, $C_5$), 123.1 (pyridyl, $C_3$), 122.2 (NCCN), 56.9 ($CH_2$), 39.0 ($NCH_3$) ppm. Anal. Calcd for $C_{60}H_{66}Ag_3N_{18}I_3$: C, 41.29; H, 3.78; N, 14.45. Found: C, 41.23; H, 3.72; N, 14.74.

**[Pd(3-methyl-1-picolylimidazolin-2-ylidene)]Cl$_2$ (3).** To a suspension of **2** (290 mg, 0.17 mmol) in 10 mL of $CH_2Cl_2$ was added

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a $CH_2Cl_2$ solution of $Pd(PhCN)_2Cl_2$ (140 mg, 0.5 mmol). The mixture was stirred at room temperature overnight and filtered; the resulting solid was washed with $CH_2Cl_2$ and then dried under vacuum. The product was recrystallized from MeOH/ether to give yellow crystals. Yield: 134 mg (76%). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 9.03 (s, 1H, pyridyl), 8.09 (m, 1H, pyridyl), 7.60 (s, 1H, HCCH), 7.57(m, 2H, pyridyl), 7.34 (s, 1H, HCCH), 5.70 (d, 1H, $NCH_2$), 5.60 (d, 1H, $CH_2$), 3.92 (s, 3H, $NCH_3$). $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$ 161.9 (Pd−C), 155.2 (pyridyl, C2), 153.7 (pyridyl, C6), 140.9 (pyridyl, C4), 125.5 (pyridyl, C3), 124.3 (pyridyl, C5), 122.4 (NCCN), 121.2 (NCCN), 54.9 ($CH_2$), 39.8 ($NCH_3$). Anal. Calcd for $C_{10}H_{11}Cl_2N_3Pd$: C, 34.23; H, 3.13; N, 11.98. Found: C, 34.19; H, 3.24; N, 11.43.

**X-ray Crystallography.** Crystals suitable for X-ray analysis of **2** and **3** were obtained by slow diffusion of diethyl ether into dichloromethane and methanol solutions of the corresponding compounds, respectively. Neither showed signals of decomposition during X-ray data collection, which was carried out at room temperature. Details of the data collection and refinement are summarized in Table 2. The structures were solved by direct methods using SHELX-97 and refined by full-matrix least-squares calculations, using the program system SHELXTL-97.

**Ethylene Polymerization.** Ethylene polymerization was performed in a 200 mL Schlenk-type glass reactor fitted with a mechanical stirrer. After it was flame-dried three times, the flask was back-filled with ethylene. Then the reactor was charged with 45 mL of toluene and MAO (10%) via syringe under an atmosphere of nitrogen. After the catalyst in 5 mL of solvent was introduced into the polymerization bottle via syringe, stirring was begun and the polymerization was kept at the desired temperature. After 30 min, the polymerization was quenched with ethanol/HCl and the polymer was isolated by filtration and dried under vacuum at 40 °C for 10 h.

**Norbornene Polymerization.** In a typical procedure, 1.4 $\mu$mol of the palladium complex **3** in 2.0 mL of chlorobenzene, 1.88 g of norbornene in 5.0 mL of chlorobenzene, and another 3.0 mL of fresh chlorobenzene were added into a flask (20 mL) with strong stirring under an Ar atmosphere. After the mixture was kept at the desired temperature for 10 min, MAO (10%) was charged into the polymerization system via syringe, and the reaction was started. A certain time later, acidic ethanol ($V_{\mathrm{methanol}}$:$V_{\mathrm{concd\ HCl}} = 20{:}1$) was added to terminate the reaction. The PNB was isolated, washed with methanol, and dried at 80 °C for 48 h under vacuum. For all of the polymerization procedures, the total reaction volume was 10.0 mL, which can be achieved by variation of chlorobenzene when necessary. IR (KBr): 2946 (vs), 2869 (vs), 1473 (m), 1451 (s), 1375 (m), 1295 (m), 1258 (m), 1222 (m), 1148 (m), 1108 (m), 1040 (w), 943 (w), 893 (m) cm$^{-1}$. Solid-state $^{13}$C CP/MAS NMR (300 MHz): $\delta$ 29.0−57.3 ppm (m, maxima at 29.0, 35.3, 48.8, 52.6).

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**Supporting Information Available:** CIF files giving crystallographic data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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