Palladium(II) Complexes Containing P∼N∼O Donors. Ligand Effect of Tridentate versus Bidentate Coordination on the Oligomerization of Ethylene

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Received February 20, 2002

Palladium complexes containing the $[(RO)_nC_6H_{5-n}C{=}]N(C_6H_4PPh_2\text{-}o)$ (**P∼N∼O**) ligand were synthesized, and the hemilability of the coordinating oxygen donors toward the metal center was studied. In the case of oxygen being a ether functionality (R = Me), acetonitrile readily replaces the tridentate ether donor in [Pd(**P∼N∼O**)Me]BF_4 (**1**) to yield [Pd(**P∼N∼O**)(MeCN)-Me]BF_4 (**2**). The labile nature of the ether donor assists the complex **1** in catalyzing the oligomerization of ethylene. Presumably, the temporary coordination of the ether donor to the vacant site during migratory insertion suppresses the β-elimination, which allows the elongation of the alkyl chain.

Introduction

Recently, searching of all kinds of catalysts for the polymerization of olefins has received much attention.[1−4] It appears that bulky substituents near the active metal center hinder the chain transfer process or associative displacement, which allows the polymerization to proceed smoothly and afford a high-molecular-weight material.[1−4] On the other hand, a less sterically bulky environment or a combination of hetero-donor bidentate coordination generally activates the oligomerization of olefins.[5−7] We have studied the insertion activity of [(**P∼N**)PdRL]$^+$ toward various unsaturated substrates, and such a mixed-donor system allows us to isolate the metal-capped polymerization intermediates of various monomers.[9] However, it only catalyzes the di- and trimerization of ethylene without any polymerization or oligomerization, presumably due to less steric bulkiness around the metal center and the trans influence of the hetero-donor bidentate ligand.[10] In this work, an intramolecular hemilabile ether donor is introduced into the **P∼N** system (Chart 1), which hopefully would suppress the β-elimination by temporary coordination of the vacant site during migratory insertion of olefins for the chain growth.[7,8,11]

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10.1021/om0201462 CCC: $22.00
Publication on Web 06/22/2002

Table 1. Selected Spectral Data of Complexes and Ligands

compd	^{1}H NMR[a] −C*H*=N−	−OC*H*$_3$	Pd−C*H*$_3$	^{31}P NMR	IR $\nu_{C=N}$[c] (cm^{-1})
L$_1$	8.69	3.81, 3.68		−12.8	1621
L$_2$	8.68			−14.9	1621
[(**P**∼**N**)PdMe(NCMe)]$^+$	9.26		0.58 (J_{P-H} = 1.60)	38.6	1617
1	9.46	4.24, 3.91	0.63 (J_{P-H} = 1.96)	41.7	1615
2	8.85		0.65 (J_{P-H} = 1.84)	43.8	1608
3[b]	9.17			51.1	1609

[a] In $CDCl_3$, in units of ppm, with J in Hz. [b] In acetone-d_6. [c] In KBr.

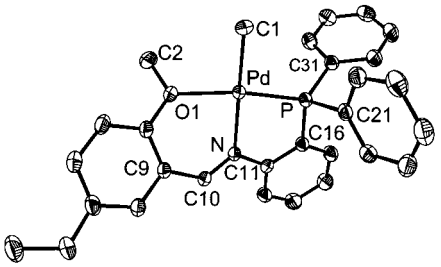
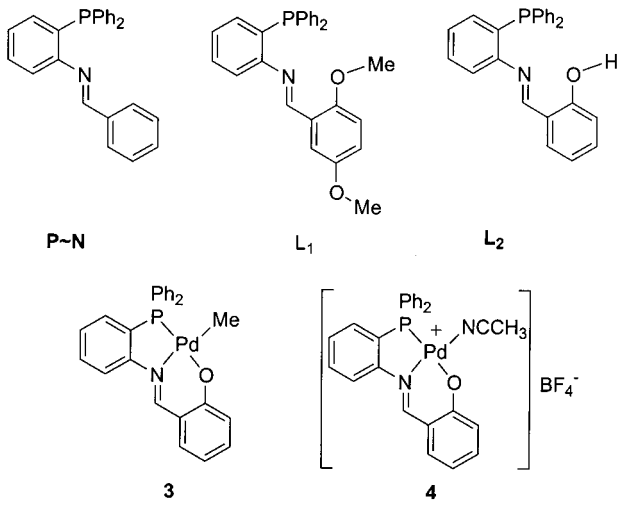


Figure 1. ORTEP plot of the cationic portion of complex **1**.

Chart 1



Results and Discussion

Complexes. Both **P**∼**N**∼**O** ligands (**L$_1$** and **L$_2$**) were prepared by condensation of *o*-(diphenylphosphino)-aniline with 2,4-dimethoxybenzaldehyde and 2-hydroxybenzaldehyde, respectively. Cationic **1** was prepared by the reaction of **L$_1$** with (COD)PdMeCl, followed by the addition of $AgBF_4$ in a dichloromethane solution, and complex **1** was obtained as yellow crystals by recrystallization from a dichloromethane/ether solution, for which a single-crystal X-ray structure has been determined (Figure 1). Spectral data of ligands and complexes are summarized in Table 1 for comparison. The ^{1}H NMR spectrum of **1** shows two different methoxy signals (Figure 2a, 4.24 and 3.91 ppm), where the 2-methoxy group is the one bound to the metal center, as evidenced by both the coordination chemical shift ($\delta_{complex} - \delta_{free\ ligand}$) and X-ray structural analysis. However, the coordinating ether donor readily undergoes a displacement reaction by acetonitrile (Scheme 1). Figure 2 shows the ^{1}H NMR spectra of complex **1** with various amounts of acetonitrile in $CDCl_3$ at room temperature. As the concentration of acetonitrile increases, the signal of the

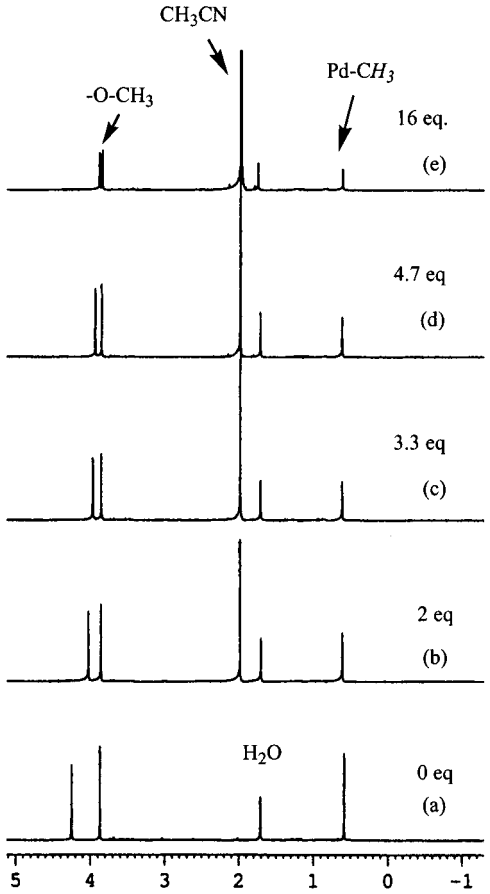
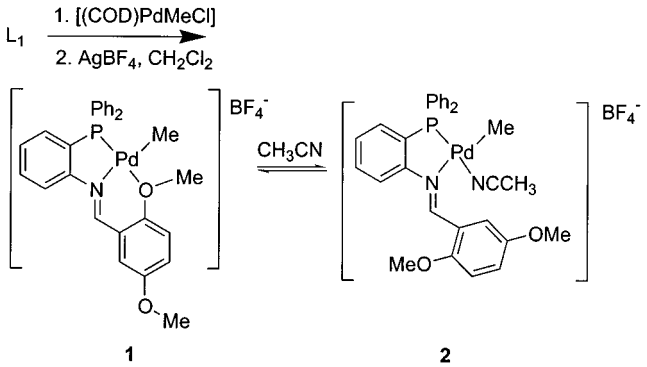


Figure 2. ^{1}H NMR spectra of **1** with various amounts of acetonitrile in $CDCl_3$.

Scheme 1



bound methoxy group shifts to upper field and eventually the ether donor goes to the free state. This observation indicates that the intramolecular coordination of ether to the palladium center is substituted by acetonitrile, which is generally considered as a weak coordinating ligand. The acetonitrile-substituted complex **2**

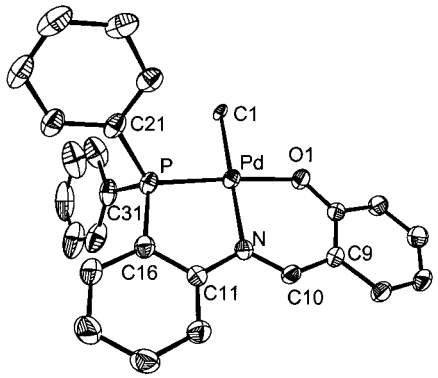


Figure 3. Molecular structure of **3**.

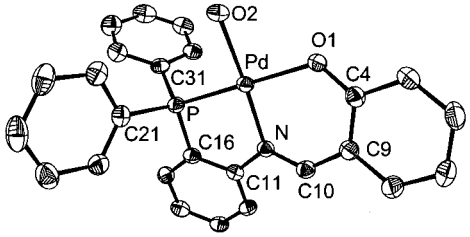


Figure 4. ORTEP plot of $[(\mathbf{P}\sim\mathbf{N}\sim\mathbf{O})Pd(H_2O)]^+$.

is stable as long as it is in the presence of acetonitrile under a nitrogen atmosphere, but the ether donor readily coordinates back to the metal center once the acetonitrile is removed. This observation clearly demonstrates the hemilability of the ether donor in hybrid multidentate species.[12]

The phenol type ligand $\mathbf{L_2}$ could provide two kinds of palladium complexes upon substitution with (COD)PdMeCl. In the presence of triethylamine, the phenoxide readily forms from $\mathbf{L_2}$, which then replaces the chloride ligand to provide the neutral palladium−methyl complex **3**, whereas a cationic complex of the type $[(\mathbf{L_2})Pd(MeCN)]^+$ (**4**) is obtained by mixing $\mathbf{L_2}$, (COD)PdMeCl, and $AgBF_4$ in the presence of acetonitrile. Here the methyl group on the palladium is presumably removed via an elimination of methane. Both complexes **3** and **4** are characterized by spectroscopic and elemental analyses. However, the coordination of the phenolate is confirmed by crystal structure analysis. X-ray-quality crystals of **3** and $[\mathbf{L_2}Pd(H_2O)]BF_4$ were obtained for their structural determination. Figures 3 and 4 display their ORTEP plots, which are clearly in agreement with the structure expected. As for complex **4**, the coordinating acetonitrile, which is different from the coordinating water molecule, appeared in the crystal structure, as confirmed by its ^1H NMR shift at 2.60 ppm in acetone-d_6 and infrared absorptions at 2327 and 2301 cm^{-1} ($\nu_{N\equiv CMe}$).

Complex **3** exhibits an unusual stability in solution, even in air. Unlike complex **1**, the acetonitrile molecule does not undergo a substitution reaction to replace the oxygen donor in both **3** and **4**, indicating that the phenolate donor is strongly bonded to the palladium center. However, the acetonitrile in **4** is readily replaced by other ligands such as water. Thus, the aqua−palladium complex $[\mathbf{L_2}Pd(H_2O)]BF_4$ was obtained upon crystallization in the presence of moisture.

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Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) of Palladium(II) Complexes

	1	**3**	$[\mathbf{L_2}Pd(H_2O)]BF_4$
Pd−P	2.177(1)	2.183(1)	2.2018(8)
Pd−N	2.117(3)	2.071(3)	1.990(2)
Pd−O1	2.178(3)	2.039(2)	2.047(2)
Pd−C1	2.047(4)	2.156(3)	
Pd−O2			2.062(2)
N−C10	1.289(5)	1.304(4)	1.296(4)
N−Pd−P	85.56(9)	86.21(8)	85.65(7)
P−Pd−O1	169.74(9)	175.67(8)	178.16(7)
N−Pd−O1	84.9(1)	93.1(1)	93.70(9)
N−Pd−C1	179.4(2)	177.7(1)	
N−Pd−O2			176.4(1)
C1−Pd−O1	95.6(2)	87.5(1)	
O1−Pd−O2			89.00(9)
C9−C10−N	126.9(4)	129.0(3)	128.9(3)
C10−N−Pd	124.2(3)	121.5(2)	120.9(2)
O1−Pd−N−C10	28.9	2.7	19.4
P−Pd−N−C11	21.4	2.8	11.6
O1−Pd−N−C11	166.6	178.5	154.8
P−Pd−N−C10	155.0	178.4	162.3

Crystallography. For complexes **1**, **3**, and $[(\mathbf{L_2})Pd(H_2O)]BF_4\cdot{}^1/_2CH_2Cl_2$, single crystals were grown by slow solvent evaporation from a mixed solvent of dichloromethane and ether. In case of **4**, it is obtained as the aqua-coordinated form, presumably due to the exchange of water molecules with acetonitrile upon crystallization. Figures 1, 3, and 4 display the ORTEP diagrams of **1**, **3**, and $[(\mathbf{L_2})Pd(H_2O)]BF_4$, respectively. Selected bond distances and bond angles are collected in Table 2. All three complexes show square-planar coordination geometry around palladium, with bond angles slightly deviating from 90° by virtue of the constraints imposed by the fused chelating rings. Thus, the angles of P−Pd−N in these three complexes are slightly larger than those of the type $[(\mathbf{P}\sim\mathbf{N})PdRL]$ reported earier.[5] As for the chelating rings, not all of them are in a planar conformation, as evidenced by the dihedral angles. The P, Pd, N, C10, C11, and O1 atoms lie almost in the same plane, as the dihedral angles of O1−Pd−N−C10, P−Pd−N−C11 and P−Pd−N−C10 are 2.7, 2.8 and 178.4°, respectively, indicating that the two chelating rings in **3** are fused in a planar geometry; those rings in complexes **1** and $[\mathbf{L_2}Pd(H_2O)]BF_4$ do not have such a relationship.

There are no significant differences observed in the Pd−P bond lengths among all complexes. However, the distance of Pd−O1 in **1** appears to be longer by ca. 0.14 Å than those in **3** and $[\mathbf{L_2}Pd(H_2O)]BF_4$, indicating that the coordinating ability of ether is weaker than that of phenolate. This is also consistent with the ligand substitution results described above, showing that the coordinating methoxy group is readily replaced by acetonitrile. However, comparable distances are found in $[\mathbf{L_2}Pd(H_2O)]BF_4$, where the difference between Pd−O1(phenolate) (2.047(2) Å) and Pd−O2(water) (2.062(2) Å) is only about 0.02 Å.

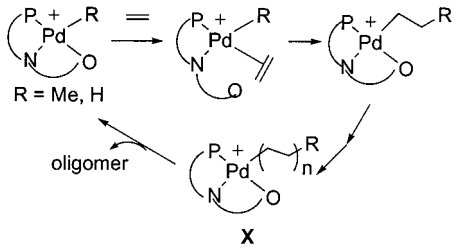
Oligomerization of Ethylene. As mentioned earlier, the complex $[(\mathbf{P}\sim\mathbf{N})PdMeL]^+$ catalyzes the di- and trimerization of ethylene and the introduction of a labile ether donor in the palladium complexes was expected to hinder the β-elimination by temporarily coordinating to the vacant site, which would propagate the chain growth as the olefin inserts. Indeed, we have observed

Table 3. Oligomerization of Ethylene Catalyzed by Palladium Complexes[a]

entry	cat.	*P* (psi)	*T* (°C)	*t* (h)	yield (mg)	activity[d]	major products[e]
1	**1**	150	30	24	33	2.6	C_6-C_8
2	**1**	150	70	24	36	5.3	$C_{10}-C_{14}$
3	**1**	300	30	12	31	0.8	$C_{10}-C_{14}$
4	**1**	300	30	24	40.2	9.0	$C_{12}-C_{16}$
5	**1**[b]	300	30	24	32	0.8	C_8-C_{14}
6	**1**	300	0	24	31	0.8	C_6-C_{10}
7	**1**	500	30	24	46.3	14.3	$C_{10}-C_{14}$
8	**1**[c]	500	70	24	84.7	48.1	$C_{12}-C_{16}$
9	**1**[c]	500	110	24	86.3	49.5	$C_{12}-C_{16}$
10	**3**	500	30	24			
11	**4**	500	30	24			

[a] Catalyst (30 mg) in CH_2Cl_2 (30 mL) was loaded in an 100 mL autoclave. [b] Mixed solvent CH_2Cl_2:CH_3CN = 4:1. [c] Chlorobenzene as solvent, [d] In units of 10^{-3} g mmol^{-1} h^{-1}. [e] Based on ^{1}H NMR and GC analysis.

Scheme 2



the activity of **1** in the oligomerization of ethylene, and the results are summarized in Table 3. Entries 1−9 summarize the activity of compound **1** toward ethylene, whereas entries 10 and 11 show the negative results in the catalytic polymerization of ethylene via compounds **3** and **4**, respectively. The oligomers obtained in this work were characterized by ^{1}H NMR spectroscopy, and the degree of oligomerization is estimated by the integration ratio of the terminal methyl group (δ 0.85) versus the methylene units (δ 1.23). From NMR spectra, we did not observe any branching on these oligomeric products.

Complex **1** does catalyze the conversion of ethylene into oligomers, but the degree of oligomerization is poor as compared to that for the palladium(II) unsymmetrical diimine systems reported by Kress and co-workers.[8] The lower activity of **1** relative to that of the palladium−diimine system is presumably due to the nonsymmetric **P**∼**N** bidentates conferring a reactivity difference at the trans sites. Thus, the insertion may have higher activation energy than the homo-bidentate system does. In addition, the coordination of ether during the chain growth might affect the coordination of ethylene to the metal center, which slows down the reaction. Indeed, increasing the pressure of ethylene or the reaction temperature appears to provide a better activity of the catalyst (entries 1, 4, and 7), but not the degree of oligomerization. Compared to the di- or trimerization of ethylene catalyzed by the cationic complex [(**P**∼**N**)PdRL]$^+$, the extra coordination of ether in **1** does prevent the β-elimination or chain transfer from occurring at the resting state of chain propagation. In fact, the FAB mass spectrum of the reaction product does show an *m*/*z* value corresponding to the metal-capped oligomers **X** (Scheme 2), indicating that such a coordination of ether readily stabilizes the insertion intermediate. Such kinds of intermediates have been isolated from the copolymerization of CO and olefin or the oligomerization of alkynes catalyzed by [(**P**∼**N**)PdR(CH_3CN)]$^+$.[9c] However, attempts to isolate the single ethylene insertion intermediate failed. As for compounds **3** and **4**, no catalytic activity toward ethylene is observed. It is believed that the nonlabile phenolate donor occupies the coordination sphere, which causes insufficient sites for the catalytic cycle.

In summary, the designed **P**∼**N**∼**O** ligand, possessing a labile ether donor, coordinates to the palladium center and forms the stable complex **1**. From crystal structure analyses, this **P**∼**N**∼**O** ligand linked through an *o*-phenylene and aryl imine backbone readily forms a tridentate chelate with palladium metal ion. The hemilabile ether donor is easily replaced by a weakly coordinating ligand such as acetonitrile, and this pendant ether donor plays an important role in the stabilization of the coordinated unsaturated resting species, which hinders the β-elimination and allows further insertion to take place during the ethylene oligomerization process.

Experimental Section

General Information. All reactions, manipulations, and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used as received, unless otherwise stated. Pd(COD)MeCl and *o*-diphenylphosphinoaniline were prepared by procedures reported earlier.[13]

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ or acetone-d_6 on either a Bruker Avance 400 or AM-300 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^{1}H and ^{13}C NMR and relative to 85% H_3PO_4 for ^{31}P NMR. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series II) as KBr pellets, unless otherwise noted.

Ligand L_1. In a 10 mL round-bottom flask was placed a mixture of *o*-(diphenylphosphino)aniline (0.5 g, 1.8 mmol) and 2,5-dimethoxybenzaldehyde (0.5 g, 3 mmol) under nitrogen. The mixture was heated to 55 °C for 20 h. After it was cooled to room temperature, the reaction mixture was dissolved in a mixture of dichloromethane and ethanol. Upon crystallization, the desired compound was obtained as yellow solids (yield 0.49 g, 63%). IR (KBr): 1621 cm^{-1} ($\nu_{N=C}$). ^{1}H NMR (acetone-d_6, 400 MHz): δ 8.69 (s, 1 H, −N=C*H*), 7.39−7.15 (m, 15 H, Ar), 6.97 (d, J = 1.84 Hz, 2 H, Ar *H*), 6.70 (m, 1 H, Ar *H*), 3.81 (s, 3 H, O−CH_3), 3.68 (s, 3 H, O−CH_3). ^{13}C NMR: δ 154.5−153.6 (Ar and −N=*C*H), 137.6−110.3 (m, Ar), 55.8 (s, O−*C*H_3), 55.0 (s, O−*C*H_3). ^{31}P NMR: δ − 12.79. Anal. Calcd for $C_{27}H_{24}NO_2P$: C, 76.22; H, 5.69; N, 3.29. Found: C, 75.89; H, 5.55; N, 3.17.

Ligand L_2. The preparation of L_2 is similar to that for L_1, except 2-hydroxybenzaldehyde was used. L_2 is a yellow solid (yield 78%). IR (KBr): 1621 cm^{-1} ($\nu_{N=C}$). ^{1}H NMR (acetone-d_6, 400 MHz): δ 12.50 (d, J_{P-H} = 0.92 Hz, 1 H, −O*H*), 8.67 (s, 1 H, −N=C-*H*), 7.51−6.86 (m, 18 H, Ar). ^{13}C NMR: δ 163.5 (−N=*C*H), 160.9, 151.9, 136.4−116.7 (Ar). ^{31}P NMR: δ −14.95. Anal. Calcd for $C_{25}H_{20}NOP$: C, 78.73; H, 5.29; N, 3.67. Found: C, 78.70; H, 5.14; N, 3.65.

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Table 4. Selected Crystallographic Data for Complexes 1, 2, and [(L_2)Pd(H_2O)]BF_4

	1	**2**	[($\mathbf{L_2}$)Pd(H_2O)]BF_4
formula	$C_{28}H_{27}BF_4NO_2PPd$	$C_{26}H_{22}NOPPd$	$C_{51}H_{44}B_2Cl_2F_8N_2O_4P_2Pd_2$
fw	633.69	501.82	1268.14
temp, K	295(2)	295(2)	150(2)
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	8.4375(1)	9.8631(2)	11.4929(4)
b, Å	10.7895(1)	13.1038(2)	19.4797(7)
c, Å	15.5608(1)	17.4209(1)	22.8521(8)
α, deg	89.930(1)	90	90
β, deg	87.958(1)	97.482(1)	93.112(1)
γ, deg	74.651(1)	90	90
V, Å^3	1365.15(2)	2232.38(6)	5108.5(3)
Z	2	4	4
D_{calcd}, Mg/m^3	1.542	1.493	1.649
F(000)	640	1016	2536
cryst size, mm	0.20 × 0.20 × 0.15	0.25 × 0.20 × 0.15	0.20 × 0.25 × 0.35
θ range, deg	1.31−25.00	1.95−25.00	2.06−25.00
no. of rflns collected	14 611	23 850	38 433
no. of indep rflns	4792 (R_{int} = 0.0368)	3945 (R_{int} = 0.0335)	8999 (R_{int} = 0.0202)
refined method		full-matrix least squares on F^2	
R ($I > 2\sigma(I)$)	R1 = 0.0426	R1 = 0.0326	R1 = 0.0296
	wR2 = 0.1071	wR2 = 0.0944	wR2 = 0.0789
goodness of fit on F^2	1.037	1.051	1.058

Complex 1. To a solution of [(COD)PdMeCl] (0.6 g, 2.26 mmol) in dichloromethane (5 mL) was added a solution of $\mathbf{L_1}$ in dichloromethane (5 mL) under a nitrogen atmosphere. To this resulting light yellow solution was added $AgBF_4$ (0.42 g, 2.27 mmol) and acetonitrile (5 mL). After it was stirred for 1 h, the reaction mixture was filtered through Celite to remove AgCl. The filtrate was concentrated, and the residue was dissolved in a mixture of dichloromethane and ether for crystallization. Complex **1** crystallized as yellow crystalline solids (yield 1.12 g, 79%). IR (KBr): 1615 cm^{-1} ($\nu_{N=C}$). ^{1}H NMR (acetone-d_6, 400 MHz): δ 9.46 (s, 1 H, −N=C*H*), 8.11(m, 1 H, Ar *H*), 7.90 (m, 1 H, Ar *H*), 7.75−7.25 (m, 15 H, Ar *H*), 4.24 (s, 3 H, −OCH_3), 3.90 (s, 3 H, −OCH_3), 0.62 (s, 3 H, Pd−CH_3). ^{13}C NMR: δ 165.4 (−N=*C*H), 155.6−153.0 (m, Ar), 135.1−128.3 (s, Ar), 123.9−116.8 (s, Ar), 62.0 (O−*C*H_3), 56.4 (O−*C*H_3), 0.5 (d, J_{P-C} = 12.4 Hz, Pd-*C*H_3). ^{31}P NMR: δ 44.7. Anal. Calcd for $C_{28}H_{27}BF_4NO_2PPd$: C, 53.07; H, 4.29; N, 2.21. Found: C, 52.74; H, 4.09; N, 2.13.

Complex 3. In a flask loaded with [(COD)PdMeCl] (0.34 g, 1.3 mmol) was added a solution of $\mathbf{L_2}$ (0.5 g, 1.3 mmol) and triethylamine (0.26 g, 2.6 mmol) in THF (5 mL). The resulting yellow solution was stirred at room temperature for 1 h. The reaction mixture was concentrated, and the residue was extracted with dichloromethane/water. The organic portion was dried with Na_2SO_4 and concentrated to give **3** as a yellow solid (yield 0.5 g, 77%) which is essentially identical with that reported by Parr and Slawin.[7d] IR (KBr): 1608 cm^{-1} ($\nu_{N=C}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.85 (s, 1 H, N=C*H*), 7.66−7.02 (m, 17 H, Ar *H*), 6.55 (m, 1 H, Ar *H*), 0.65 (d, J = 1.84 Hz, 3 H, Pd−CH_3). ^{13}C NMR: δ 169.6 (−N=*C*H), 158.2, 154.7, 136.8−114.5 (Ar), − 1.4 (d, J_{P-C} = 32.4 Hz, Pd−*C*H_3). ^{31}P NMR: δ 43.8. Anal. Calcd for $C_{26}H_{22}NOPPd$: C, 62.23; H, 4.42; N, 2.79. Found: C, 62.16; H, 3.80; N, 2.71.

Complex 4. The preparation of this complex is similar to that for **1**, except ligand $\mathbf{L_2}$ was used (yield 74%). IR (KBr): 1608 cm^{-1} ($\nu_{N=C}$); 2327, 2301 ($\nu_{N\equiv CMe}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.17 (s, 1 H, N=C*H*), 8.38−6.71 (m, 17 H, Ar *H*), 2.60 (s, 3 H, CH_3CN). ^{13}C NMR: δ 166.7 (−N=*C*H), 160.1, 157.6, 138.8−116.4 (Ar), 2.3 (*C*H_3CN). ^{31}P NMR: δ 51.1. Anal. Calcd for $C_{27}H_{22}BF_4N_2OPPd$: C, 52.76; H, 3.61; N, 4.56. Found: C, 52.55; H, 3.42; N, 4.22.

Oligomerization of Ethylene. In an autoclave (100 mL) were placed the complex (30 mg) and predried dichloromethane (30 mL). Upon flushing with ethylene gas several times, a constant pressure of ethylene gas was achieved. During the reaction, ethylene was refilled when the pressure was found to drop. The reaction mixture was stirred for a period of time, and the reaction products were analyzed by GC and spectroscopy. ^{1}H NMR: δ 1.23 (br), 0.85 (br).

Crystallography. Crystals suitable for X-ray determination were obtained for **1, 3**, and [$\mathbf{L_2}$Pd(H_2O)]BF_4 by slow evaporation of dichloromethane/ether solutions at room temperature. Cell parameters were determined by either a Siemens SMART CCD or a CAD-4 diffractometer. Crystal data for complexes **1, 3**, and [$\mathbf{L_2}$Pd(H_2O)]BF_4 are listed in Table 4, and their ORTEP plots are shown in Figures 1−3, respectively (labels of phenyl groups are omitted for clarity). Other crystallographic data are deposited as Supporting Information.

Acknowledgment. We thank the National Science Council for financial support (Grant No. NSC90-2113-M-002-038).

Supporting Information Available: Complete descriptions of the X-ray crystallographic structure determinations of **1**, **3**, and [$\mathbf{L_2}$Pd(H_2O)]BF_4, including tables of atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles, and an FAB mass spectrum of metal-capped oligomers **X**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0201462