Synthesis of Palladium Complexes with an Anionic P∼O Chelate and Their Use in Copolymerization of Ethene with Functionalized Norbornene Derivatives: Unusual Functionality Tolerance

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A series of anionic P∼O ligands and corresponding palladium−allyl complexes have been synthesized. The latter, along with palladium species formed in situ, were employed for the copolymerization of ethene with functionalized norbornene derivatives. The formed copolymers had high norbornene content (>40 mol %). The systems are highly tolerant of reactive functionalities, and the copolymerizations can even be carried out in the presence of water.

Introduction

Metal-catalyzed addition polymerization that leads to materials incorporating relatively high amounts of functionalized vinyl monomers is an area of great current interest in synthetic polymer chemistry.[1] The copolymers of ethene with norbornene show such superior properties as excellent transparency, high glass transition temperature, good solvent resistance, and high thermal stability. The range of desirable properties is expected to be further enhanced by the use of appropriately functionalized norbornene derivatives. The inherent difficulty of polymerizing functionalized vinyl monomers stems from the poisoning of the catalyst center by coordination of the functionality. Late transition metals are more tolerant of polar functionalities in the monomer and the formed polymer. A number of nickel and palladium compounds have been shown to catalyze the addition polymerization of functionalized norbornenes.[2] However, most of them are ineffective for the copolymerization of ethene with norbornene because the former act as a chain transfer agent through β-hydrogen abstraction. Therefore, in order to achieve the copolymerization of ethene with functionalized norbornenes, it is necessary for the catalyst to be both tolerant of functional groups and resistant to β-hydrogen abstraction. We,[3] Grubbs,[4] Bazan,[5] Mecking,[6] and others[2m] have recently described nickel-based systems for the copolymerization of ethene with functionalized norbornenes. However, the extent of incorporation of the norbornene monomer is low (<25 mol %). Herein, we report on catalyst systems based on palladium complexes incorporating anionic P∼O ligands. Two π-allyl complexes were synthesized and crystallographically characterized. Copolymerizations carried out using these, along with complexes formed in situ show unusual functionality tolerance from several standpoints. First, they catalyze the copolymerization of ethene with functionalized norbornene derivatives to form copolymers with very high norbornene content (>40 mol %). Second, the system is so highly tolerant of reactive functionalities that the copolymerization can even be carried out in the presence of water.

The catalytic systems are based on that reported by Drent,[7] who also reported the copolymerization of ethene with norbornene derivatives.[7b] Two related P∼O ligands, 2-[bis(2-methoxyphenyl)phosphino]benzenesulfonicacid (**1**) and 2-[bis(2,6-dimethoxyphenyl)phosphino]benzenesulfonicacid (**2**), were employed (Figure 1). The X-ray crystal structure of **2** was determined and is shown in Figure 2. In one series of experiments, the catalytic systems were formed in situ by combining Pd(dibenzylideneacetone)$_2$ [Pd(DBA)$_2$] and one of the ligands in a 1:1.2 molar ratio.

Results and Discussion

Table 1 summarizes the results of copolymerization of ethene with functionalized norbornenes. The polyethene obtained in

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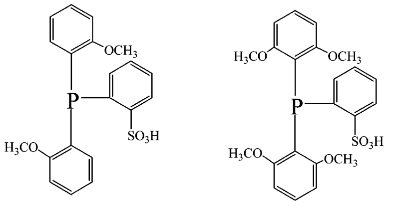
10.1021/om0607402 CCC: $37.00



1 2

Figure 1. Chemical structures of ligands **1** and **2**.

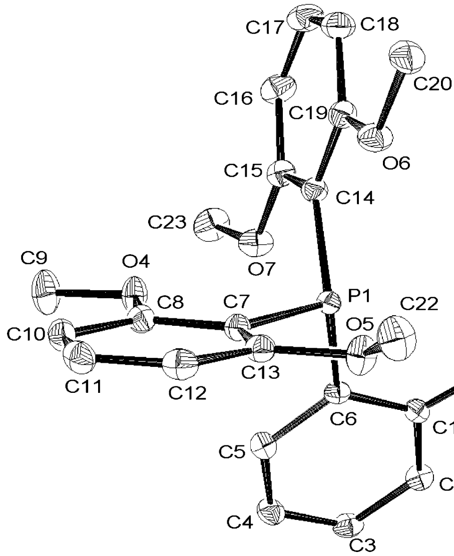


Figure 2. ORTEP diagram of ligand **2**. The hydrogens and methylene chloride are omitted for clarity.

run 1 is predominantly linear, as evidenced by a single dominant ^{13}C NMR resonance at 28 ppm and a melting point (DSC) of 127.8 °C. As shown in Table 1, the activity for ethene copolymerization with norbornene or bicyclo[2.2.1]hept-5-enyl-2-methyl acetate is comparable or even higher than that of ethene homopolymerization (run 1 vs 2, 3). In particular, the high copolymerization rate with bicyclo[2.2.1]hept-5-enyl-2-methyl acetate is remarkable. Lowering the ethene pressure from 500 to 150 psi lowers the copolymerization activity but leads to very high incorporation of functional norbornenes (e.g., runs 4, 5). Both the copolymerization activity and the level of functionalized norbornene incorporation into the resultant copolymer appear to be a sensitive function of the ligand. For example, under the same conditions, the $Pd(DBA)_2$/ligand **1** catalyst produced copolymers with 37.7 mol % of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (run 4) and 22.6 mol % of bicyclo-[2.2.1]hept-5-en-2-ol acetate (run 6), while the $Pd(DBA)_2$/ligand **2** catalyst generated only copolymers with 31.2 mol % of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (run 8) and 13.3 mol % of bicyclo[2.2.1]hept-5-en-2-ol acetate (run 10). On the other hand, there is little effect on copolymer molecular weight (e.g., run 6: M_n, 47 000; M_w/M_n, 2.1; run 10: M_n, 49 700; M_w/M_n, 1.8).

The structures of the obtained copolymers were analyzed by ^1H and ^{13}C NMR spectroscopy (see Figure 3). The relative simplicity of the latter suggests structures with isolated norbornene units. Presumably the size of the norbornene monomer precludes its consecutive insertion. Thus only EEE, NEE, and ENE triads are present (E = ethene, N = norbornene monomer). The ^{13}C NMR assignments are based on our previous report;[3] the resonance at 33.2 ppm can be assigned to the apical carbon of the norbornene. The resonances between 41.6−42.4 and 47.4−48.2 ppm are due to the bridgehead CH and the CH carbons of the norbornene units in the polymer backbone. The CH_2 carbons from ethene and NB units appear at 29.8 and 30−31.8 ppm, respectively.

The effect of solvent on copolymerization of ethene with bicyclo[2.2.1]hept-5-enyl-2-methyl acetate is presented in Table 2. Good activity was observed in aromatic solvent and even in relatively coordinating 1,2-dimethoxyethane (DME), although the incorporation of the functionalized monomer was much lower in the latter. On the other hand, no polymer was obtained when the reaction was carried out in acetonitrile, suggesting stronger coordination of acetonitrile to the metal center. This is supported by the qualitative observation that a purple toluene solution of $Pd(DBA)_2$ and ligand **1** immediately turned bright yellow when a small amount of acetonitrile was added. It is noteworthy that the molecular weights of the copolymers of ethene with bicyclo[2.2.1]hept-5-enyl-2-methyl acetate are much higher than that of copolymers of ethene with acrylates,[7] presumably because the inaccessibility of β-hydrogens in norbornenes prevents chain termination/transfer. The single-site characteristic of the catalyst is supported by the relatively narrow molecular weight distribution of the obtained copolymers ($M_w/M_n < 2$).

Gas chromatography was employed to investigate the relative uptake of the *exo* versus *endo* isomer of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate in the copolymerization reaction. As is clear from Figure 4, there is a high preference for the incorporation of the *exo* isomer in the growing polymer chain. This is in agreement with earlier reports.[2b,e,g,j,n]

A very unusual feature of the present catalytic system is that while it tolerates coordinating functionalities present in norbornene derivatives and in acrylates,[7] allowing the copolymerization of these classes of monomers with ethene, simple 1-alkenes such as propene, 1-hexene, and styrene cannot be polymerized. Analysis of products from attempted copolymerization with ethene reveals no detectable comonomer incorporation into polyethene chains. Furthermore, the rate of polyethene formation in the presence of these monomers is almost an order of magnitude slower. To our knowledge this is the only known alkene polymerization system that shows such a selectivity. We had earlier reported that the rate of insertion of vinyl monomers ($CH_2{=}CHR$) into palladium−alkyl bonds in cationic complexes decreases with increasing donor ability of the substituent ($R = CO_2R > H > \text{alkyl}$).[8] An alkene with an electron-withdrawing substituent coordinates less strongly to the electrophilic metal (i.e., σ-donation is more important than π-back-donation).[9] Thus, a weaker metal−alkene bond has to be broken for the insertion to proceed (i.e., the destabilization of the alkene complex leads to a lower insertion barrier).[9] Therefore, both the failure of 1-alkenes to be incorporated in the present system and the attenuation of polymerization activity in their presence can be ascribed to stronger binding but slower insertion rate for 1-alkenes.

As discussed above, the catalyst system is remarkably tolerant of coordinating functionalities present either in the monomer or in the reaction solvent. To further underscore this, we carried out the emulsion copolymerization of ethene with bicyclo[2.2.1]-hept-5-enyl-2-methyl acetate in a 9:1 (v/v) mixture of water and toluene (the latter was required to dissolve the catalyst and the monomer) (Conditions: $Pd(DBA)_2$, 13.5 μmol; ligand **1**, 16.2 μmol; sodium dodecylsulfate, 0.9 g; ethene, 500 psi;

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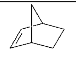
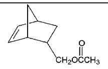
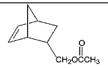
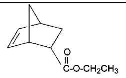
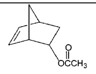
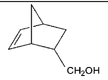
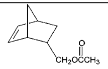
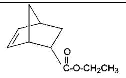
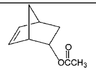
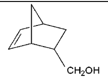
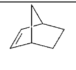
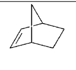
(9) von Schenck, H.; Strömberg, S.; Zetterberg, K.; Ludwig, M.; Åkermark, B.; Svensson, M. *Organometallics* **2001**, *20*, 2813.

Table 1. Ethene/Functional Norbornene Copolymerization

Run	Ligand[a] or Complex[b]	NB derivative g (mmol)	Pd (μmol)	Ethene (psi)	Time (h)	Yield (g)	NB incorp. (mol%)	Activity (kg/mol[Pd]•h)
1	**1**	None	4.5	500	1	2.34	0	520
2	**1**	 1.1 (11.7)	4.5	500	1	2.78	22.6	618
3	**1**	 2 (12.0)	4.5	500	1	3.67	14.9	816
4	**1**	 3 (18.1)	4.5	150	3	2.98	37.7	221
5	**1**	 3 (18.1)	4.5	150	3	3.25	43.9	241
6	**1**	 1.83 (12.0)	4.5	250	3	3.62	22.6	268
7	**1**	 1.50 (12.0)	4.5	250	3	0.64	34.2	48
8	**2**	 3 (18.1)	4.5	150	3	2.62	31.2	194
9	**2**	 2 (12.0)	4.5	250	3	0.98	16.7	73
10	**2**	 1.83 (12.0)	4.5	250	3	3.14	13.3	233
11	**2**	 1.50 (12.0)	7.8	250	2	1.05	24.2	67
12	**3a**	 1.1 (11.7)	4.5	500	1	0.75	31	167
13	**3b**	 1.1 (11.7)	4.5	500	1	2.38	18.5	528

[a] Conditions: [Ligand]/[Pd] = 1.2 (molar ratio); toluene, 10 mL; 95 °C. [b]Conditions: [B(C_6F_5)$_3$]/Pd = 2; toluene, 10 mL; 95 °C.

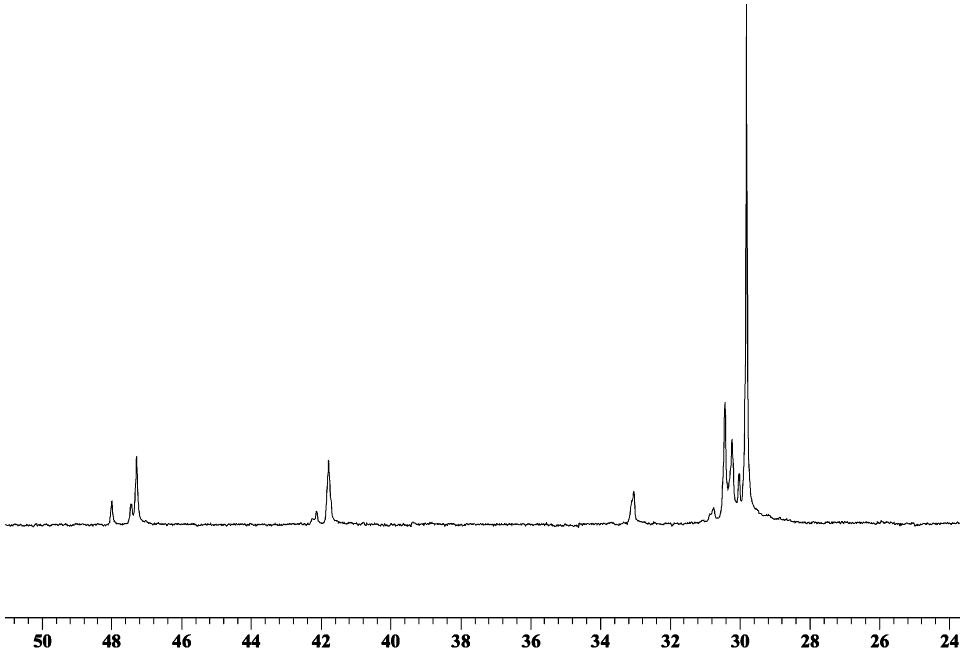


Figure 3. ^{13}C NMR ($C_2D_2Cl_4$) spectrum of copolymer of ethene with norbornene (15.2 mol %).

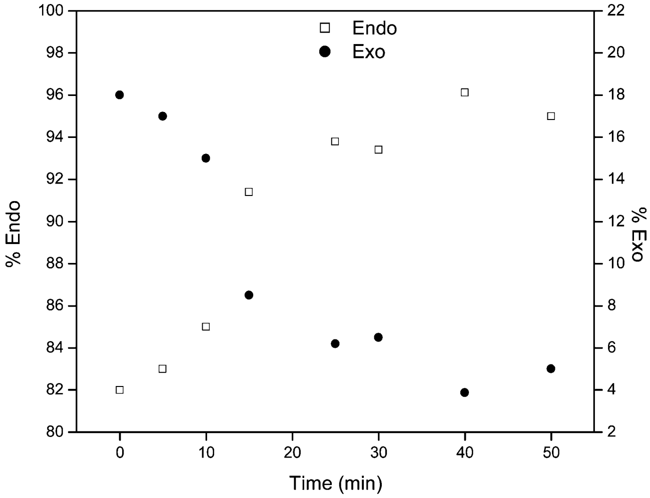


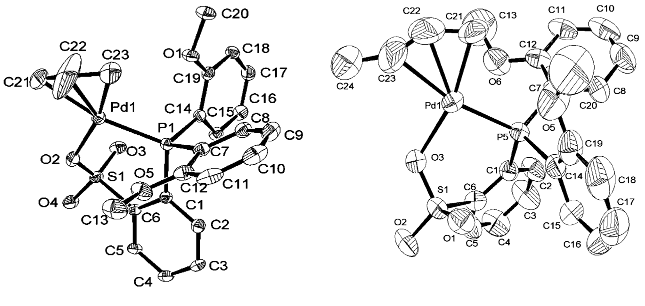
Figure 4. Plot of *endo/exo* isomers present in unreacted bicyclo-[2.2.1]hept-5-enyl-2-methyl acetate as a function of time in its copolymerization with ethene. (Reaction conditions: ethene, 250 psi; bicyclo[2.2.1]hept-5-enyl-2-methyl acetate, 2 g; Pd(DBA)$_2$, 4.5 μmol; ligand 1, 5.4 μmol; toluene, 10 mL; 1,1,2,2-tetrachloroethane, 50 μL; 95 °C.)

Table 2. Solvent Effect[a]

run	solvent	yield (g)	activity (kg/ mol[Pd]·h)	NB incorp (mol %)	M_n[b]	M_w/M_n[b]
1	acetonitrile	n.r.	0	0		
2	DME	1.59	118	5.62	66 900	1.82
3	ethanol	0.43	32	38.2		
4	anisole	1.80	133	34.6	61 100	1.79
5	toluene	2.25	167	31.4	73 000	1.91
6	chlorobenzene	1.40	104	29.0	60 100	1.73

[a] Conditions: solvent, 10 mL; bicyclo[2.2.1]hept-5-enyl-2-methyl acetate, 2 g; ethene, 150 psi; Pd(DBA)$_2$, 4.5 μmol; ligand **1**, 5.4 μmol; 95 °C; 3 h. [b]Determined by SEC relative to polystyrene standards.

bicyclo[2.2.1]hept-5-enyl-2-methyl acetate, 3 g; toluene, 10 mL; water, 90 mL; 95 °C, 3 h. Yield, 7.1 g; activity, 175 kg/mol-[Pd]·h; norbornene, 13.4 mol % M_n, 42 000; M_w/M_n, 1.9). The lower activity is expected due to significantly reduced solubility of ethene in water.



3a **3b**

Figure 5. ORTEP of complexes **3a** and **3b**. Hydrogen atoms in **3a** and hydrogen atoms and chloroform molecule in **3b** are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) of Complexes 3a and 3b

3a	3b
Pd(1)−O(2) = 2.117(2)	Pd(1)−O(3) = 2.154 (4)
Pd(1)−P(1) = 2.3028(8)	Pd(1)−P(5) = 2.3048 (14)
Pd(1)−C(21) = 2.223(3)	Pd(1)−C(21) = 2.100(6)
Pd(1)−C(22) = 2.109(3)	Pd(1)−C(22) = 2.136(7)
Pd(1)−C(23) = 2.087(3)	Pd(1)−C(23) = 2.251(8)
P(1)−C(1) = 1.837(3)	P(5)−C(1) = 1.835(5)
S(1)−C(6) = 1.788(3)	S(1)−C(6) = 1.786(5)
O(2)−Pd(1)−P(1) = 94.00(7)	O(3)−Pd(1)−P(5) = 94.78(10)
C(7)−P(1)−Pd(1) = 114.69(11)	C(7)−P(5)−Pd(1) = 115.30(18)
S(1)−O(2)−Pd(1) = 124.66(13)	S(1)−O(3)−Pd(1) = 118.1(2)
C(14)−P(1)−Pd(1) = 117.29(10)	C(14)−P(5)−Pd(1) = 119.82(19)

In an attempt to better define the catalysts, π-allyl (**3a**) and π-1-methallyl (**3b**) complexes incorporating the P∼O ligand **1** were synthesized by the reaction of the chloro-bridged allyl/π-1-methallyl dimer with the sodium salt of **1** in dichloromethane at −20 °C.[10] The crystal structures of complexes **3a** and **3b** are depicted in Figure 5, and bond length and bond angles are given in Table 3. In view of the expected significantly stronger *trans* effect of the phosphine ligand, it is not surprising that the Pd−C

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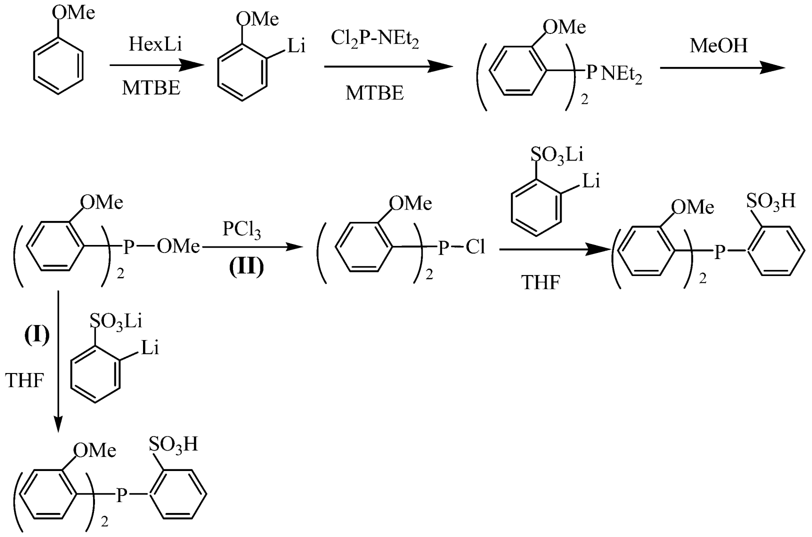
[10] Hearley, A. K.; Nowack, R. J.; Rieger, B. *Organometallics* **2005**, *24*, 2755−2763.

Scheme 1. Outline of Ligand Synthesis



bond of the allyl group *trans* to it is significantly longer than the one *trans* to the sulfonate group (**3a**, 2.22 versus 2.09 Å; **3b**, 2.25 versus 2.10 Å).

Neither complex **3a** nor **3b** showed significant activity toward the copolymerization of ethene and norbornene, presumably because the η^3-allyl group occupies two coordination positions, thereby preventing the coordination of the incoming monomer. However, the polymerization activity was restored when 1−2 molar equiv of $B(C_6F_5)_3$ was added (Table 1). Under these conditions, the polymerization activity of **3b** was similar to that observed when the catalytic system was formed in situ. The activity of **3a** was somewhat lower possibly because the smaller allyl group binds more tightly to the metal than the 1-methallyl group. The specific role played by $B(C_6F_5)_3$ in activating **3a** and **3b** is currently under investigation.

In conclusion, we have described catalyst systems based on palladium complexes incorporating anionic P∼O ligands. Two new π-allyl complexes were synthesized and crystallographically characterized. Copolymerizations carried out using these, along with complexes formed in situ, show functionality tolerance that was unusual from several standpoints. First, they catalyze the copolymerization of ethene with functionalized norbornene derivatives to form copolymers with very high norbornene content (>40 mol %). Second, the system is so highly tolerant of reactive functionalities that the copolymerization can even be carried out in the presence of water.

Experimental Section

Materials. All chemicals were purchased from Aldrich except as stated otherwise. The functionalized norbornene monomers used in this work are a mixture of *endo* and *exo* isomers. Bicyclo[2.2.1]-hept-5-ene-2-carboxylic acid ethyl ester (97%), bicyclo[2.2.1]hept-5-en-2-ol acetate (97%), and bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (97%) were generously donated by the BF Goodrich Company. Palladium(II)acetate and bis(dibenzylideneacetone)-palladium(0) [Pd(DBA)$_2$] were obtained from Johnson Matthey Company. Allylpalladium chloride dimer, 1-methallylpalladium chloride dimer, and tris(pentafluorophenyl)borane were purchased from Strem Chemicals and used without further purification. CP grade ethene was supplied by the Matheson Company and used without further purification.

Characterization. NMR spectra were recorded at 125 °C on a Bruker DPX-300 spectrometer at 300.15 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR spectra. 1,1,2,2-Tetrachloroethane-d_2 was used as solvent. The chemical shifts are referenced relative to the solvent. Molecular weights and molecular weight distributions were measured on a Shimadzu size exclusion chromatograph (SEC) using a flow rate of 1 mL/min and a three-column bed (Styragel HR 7.8 × 300 mm columns with 5 mm bead size: 100−10 000, 500−30 000, and 5000−6 000 000 D), a Shimadzu RID 10A differential refractometer, and SPD-10A UV−vis detector. SEC samples were run in $CHCl_3$ at ambient temperature and calibrated to polystyrene standards obtained from Aldrich. GC data were obtained on a Hewlett-Packard 5890 Series II instrument fitted with an Alltech EC-5 column and a FID detector using 1,1,2,2-tetrachloroethane as an internal standard.

Synthesis of Ligand. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Solvents were degassed in 20 L reservoirs and passed through two sequential purification columns. Oxygen was removed by a copper catalyst, and water was removed by activated alumina.

2-[Bis(2-methoxyphenyl)phosphino]benzenesulfonic Acid (ligand 1). This ligand was synthesized by two different procedures (Scheme 1). Procedure I is the same as the literature procedure[7] except that *n*-butyllithium was used in the last step. In procedure II, bis(2-methoxyphenyl)methoxyphosphine was converted to bis-(2-methoxyphenyl)chlorophosphine as follows before reacting with the lithium salt of benzenesulfonic acid. To a solution of bis(2-methoxyphenyl)methoxyphosphine (1.89 g, 6.85 mmol) in THF (10 mL) was added dropwise a solution of PCl_3 (4.71 g, 34.3 mmol) in THF (10 mL) at 0 °C. The reaction was then allowed to stand for 5 h at room temperature. The unreacted PCl_3 was removed under vacuum. The bis(2-methoxyphenyl)chlorophosphine solution in THF was added slowly to the lithium salt of benzenesulfonic acid at −40 °C. The reaction was allowed to stand at room temperature for 16 h. Water (40 mL) was then added, followed by the removal of THF in vacuum. The aqueous solution was acidified to pH = 1 by adding concentrated HCl (37%). The precipitate was filtered off, and the filtrate was washed with *tert*-butyl methyl ether (15 mL). After extracting with CH_2Cl_2 (20 mL × 3), the crude product was dried over anhydrous $MgSO_4$. Solvent was removed under vacuum to afford a white powder (1.05 g, 38.2%). ^{1}H NMR (CD_2Cl_2, ppm): 9.1 (1H, P-*H*), 6.8−8.4 (m, 12H, phenyl), 3.8 (s, 6H, OC*H*$_3$). ^{31}P NMR ($CDCl_3$): −9.6 ppm.

2-[Bis(2,6-dimethoxyphenyl)phosphino]benzenesulfonic Acid (ligand 2). To a solution of benzenesulfonic acid (1.08 g, 6.84 mmol) in THF (15 mL) was added dropwise *n*-butyllithium (15 mmol, 2.5 M in hexane) at 0 °C. After stirring at room temperature for 18 h a solution of bis(2,6-dimethoxyphenyl)methoxyphosphine (2.30 g, 6.86 mmol) in THF (50 mL) was added at −40 °C, and

Table 4. Crystal Data for Ligand 2 and Complexes 3a and 3b

	2·CH_2Cl_2	**3a**	**3b**·2$CHCl_3$
empirical formula	$C_{23}H_{25}Cl_2O_7PS$	$C_{23}H_{23}O_5PPdS$	$C_{26}H_{25}Cl_6O_5PPdS$
fw	547.36	547.84	799.59
temperature	98(2) K	108(2) K	298(2) K
wavelength (Mo Kα)	0.71073 Å	0.71073 Å	0.71073 Å
cryst size	0.43 × 0.39 × 0.36 mm	0.20 × 0.14 × 0.11 mm	0.38 × 0.36 × 0.24 mm
cryst habit	clear brick	yellow cuboidal	yellow cubical
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2(1)/c$	$P2(1)/n$	$Pna2(1)$
unit cell dimens	$a = 13.979(2)$ Å	$a = 10.8667(11)$ Å	$a = 14.9431(19)$ Å
	$b = 11.9196(17)$ Å	$b = 17.0383(18)$ Å	$b = 10.2521(13)$ Å
	$c = 15.071(2)$ Å	$c = 11.8080(13)$ Å	$c = 21.630(3)$ Å
volume	2475.2(6) Å^3	2176.7(4) Å^3	3313.7(7) Å^3
Z	4	4	4
density(calcd)	1.469 g/cm^3	1.672 g/cm^3	1.603 g/cm^3
absorp coeff	0.453 mm^{-1}	1.055 mm^{-1}	1.189 mm^{-1}
F(000)	1136	1108	1600
R1	3.72%	4.03%	5.35%
wR2	10.36%	11.34%	12.86%
diffractometer	CCD area detector	CCD area detector	CCD area detector
data collection method	phi and omega scans	phi and omega scans	phi and omega scans
θ range for data collection	2.19−28.31°	2.10−28.30°	1.88−28.35°
index ranges	$-18 \leq h \leq 18$,	$-14 \leq h \leq 13$,	$-19 \leq h \leq 13$,
	$-15 \leq k \leq 10$,	$-22 \leq k \leq 21$,	$-12 \leq k \leq 13$,
	$-20 \leq l \leq 19$	$-11 \leq l \leq 15$	$-28 \leq l \leq 28$

the reaction was allowed to stand for a further 12 h. Water (40 mL) was then added, followed by the removal of THF in vacuum. The aqueous solution was acidified to pH = 1 by adding concentrated HCl (37%). The precipitate was filtered off, and the filtrate was washed with *tert*-butyl methyl ether (15 mL). After extracting with CH_2Cl_2 (20 mL × 3), the crude product was dried over anhydrous $MgSO_4$. Solvent was removed under vacuum to afford a white powder (1.25 g, 39.6%). The crystal for X-ray analysis was obtained at −10 °C from a mixture of CH_2Cl_2 and hexane. ^{1}H NMR (CD_2Cl_2, ppm): 10.3 (1H, P-*H*), 6.6−8.4 (m, 10H, phenyl), 3.6 (s, 12H, OC*H*$_3$). ^{31}P NMR ($CDCl_3$): −29.3 ppm.

Synthesis of Complex 3a. Sodium carbonate (Na_2CO_3) (0.315 g, 2.97 mmol) was added to a flask containing ligand **1** (1 g, 2.48 mmol) and 15 mL of dichloromethane. The solution was stirred until it formed a white precipitate (ca. 4 h). To this was added a dichloromethane solution of allylpalladium chloride dimer (0.45 g, 1.24 mmol) at −20 °C, and stirring continued overnight. The reaction mixture was filtered, and the filtrate was recrystallized using pentane as a nonsolvent. Yield: 1.09 g (80%). ^{1}H NMR (CD_2Cl_2, ppm): 8.19 (1H, m, arom), 7.53 (2H, m, arom), 7.39 (1H, m, arom), 6.9−7.2 (8H, m, arom), 5.66 (1H, m, C*H*), 4.74 (1H, m, HC*H*), 3.80 (1H, m, HC*H*), 3.14 (1H, m, HC*H*), 2.65 (1H, d, HC*H*), 3.80 (6H, m, OC*H*$_3$). ^{31}P NMR (CD_2Cl_2, ppm): −2.9 (s). Because of the general instability of this class of palladium compounds, elemental analysis was not attempted. However, **3a** was judged pure by NMR spectroscopy (see Supporting Information). Its structure was further established by X-ray crystallography.

Synthesis of Complex 3b. Complex **3b** was synthesized by using methallylpalladium chloride dimer by following the above procedure. Yield: 1.1 g (78%). ^{1}H NMR (CD_2Cl_2, ppm): 6.9−8.4 (12H, m, arom), 5.45 (1H, m, C*H*═CHCH$_3$), 4.62 (1H, m, CH═C*H*CH$_3$), 3.74 (6H, s, OC*H*$_3$), 3.10 (1H, br, *H*CH−CH═CH), 2.51 (1H, br, HC*H*-CH═CH), 1.76 (3H, m, CH═CHC*H*$_3$). ^{31}P NMR (CD_2Cl_2, ppm): −4.87 (s). **3b** was judged pure by NMR spectroscopy (see Supporting Information). Its structure was further established by X-ray crystallography.

Copolymerization of Ethene and Functionalized Norbornene. In a typical experiment (Table 1, run 4), in a N_2-filled glovebox a 300 mL glass-lined stainless steel autoclave equipped with a magnetic stir bar was charged with toluene (10 mL), Pd(DBA)$_2$ (4.5 μmol), ligand **1** in toluene (5.4 μmol in 1 mL of toluene), and bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (3.0 g, 18.1 mmol). The autoclave was charged with 150 psi of ethene (single charge) and then placed in an oil-bath at 95 °C for 3 h. Following the reaction, the reactor was cooled to room temperature. The contents of the reactor were then poured into 500 mL of HCl-acidified methanol. The precipitated polymer was washed and dried under vacuum. Composition of the copolymer was determined from the integration of the resonances at 3.60−4.20 ppm for the CH_2OCO unit of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate and 1.2 ppm for the CH_2 unit of ethene. Yield: 2.98 g, bicyclo[2.2.1]hept-5-enyl-2-methyl acetate, 37.7 mol %.

Determination of the Relative Uptake of *endo* versus *exo* Isomer of Bicyclo[2.2.1]hept-5-enyl-2-methyl Acetate. In a N_2-filled glovebox, a 300 mL glass-lined stainless steel autoclave equipped with a magnetic stir bar was charged toluene (10 mL), Pd(DBA)$_2$ (4.5 μmol), ligand **1** in toluene (5.4 μmol in 1 mL of toluene), and bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (2.0 g, 12 mmol), and 50 μL of 1,1,2,2-tetrachloroethane as internal reference. The autoclave was charged with 250 psi of ethene and then placed in an oil-bath at 95 °C. The amount of unreacted *exo* and *endo* isomer present during the course of the reaction was determined by GC analysis of samples taken at set intervals.

Emulsion Copolymerization of Ethene with Functionalized Norbornene. In a N_2-filled glovebox, a 600 mL glass-lined stainless steel autoclave equipped with a mechanical stir bar was charged with toluene (7 mL), Pd(DBA)$_2$ (13.5 μmol), ligand **1** in toluene (16.2 μmol in 3 mL toluene), and bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (3.0 g, 18.1 mmol). The autoclave was then taken out of the glovebox, and sodium dodecylsulfate in water (0.9 g in 90 mL of degassed water) was added using a syringe. After pressurizing with 500 psi of ethene, the reactor was placed in an oil-bath at 95 °C for 3 h. Following the reaction, the reactor was cooled to room temperature. The contents of the reactor were then poured into 500 mL of HCl-acidified methanol, and the polymer was recovered by filtration. Yield: 7.1 g; bicyclo[2.2.1]hept-5-enyl-2-methyl acetate, 13.4 mol %, M_n, 42 000; M_w/M_n, 1.9.

Copolymerization with Norbornene Derivatives Using 3a or 3b. In a typical copolymerization experiment, a 300 mL glass-lined stainless steel autoclave equipped with a magnetic stir bar was charged with toluene (10 mL), **3a** or **3b** (4.5 μmol), tris(pentafluorophenyl)borane (9 μmol), and norbornene (1.1 g, 11.7 mmol) inside the nitrogen-filled glovebox. The autoclave was charged with 500 psi of ethene and immersed in an oil-bath preheated at 95 °C. After the desired time period the autoclave was allowed to cool to room temperature and the polymer was precipitated in acidified methanol and dried under vacuum.

X-ray Structure Determination. Crystal data for ligand **2** and complexes **3a** and **3b** are given in Table 4. See Supporting Information for more details. The X-ray intensity data were measured at 98(2) K for **2**, 108(2) K for **3a**, cooled by Rigaku-MSC X-Stream 2000, and 298(2) K for **3b**, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 1600 W power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

Data Collection. *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3.2* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.[11]

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Supporting Information Available: Crystal structure data for **2**, **3a**, and **3b** and ^{1}H NMR spectra of **3a** and **3b** are available free of charge via the Internet at http://pubs.acs.org.

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[11] (a) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565. (b) Sheldrick, G. M. *SHELXTL*; Bruker AXS Inc.: Madison, WI, 1997.