

# New Single-Site Palladium Catalysts for the Nonalternating Copolymerization of Ethylene and Carbon Monoxide

Andrew K. Hearley, Rüdiger J. Nowack, and Bernhard Rieger\*

Department of Materials Science and Catalyst Design, University of Ulm,  
Albert Einstein Allee 11, D-89069 Ulm, Germany

Received November 25, 2004

The synthesis and first examples of structurally characterized, single-site palladium complexes containing a phosphine sulfonate chelate (PSO) for the nonalternating copolymerization of ethylene and carbon monoxide are reported. Extra incorporation of ethylene up to 30% has been achieved relative to the alternating polyketone structure with modest activities. As exemplarily shown, high molecular weight random copolymers have been produced with  $M_w \approx 370\,000$ , polydispersity ( $M_w/M_n$ ) = 2, and melting points of 220–230 °C.

## Introduction

The development of new, well-defined, functional group tolerant, late transition metal catalysts for the synthesis of polymers comprised of a nonpolar backbone and a controlled amount of a polar monomer is of considerable interest to both academia and industry.<sup>1</sup> However, metal-catalyzed copolymerization reactions of monomers containing functional groups and olefins is by no means a trivial task. It is clear from the literature that many attempts have been made within this area, but so far, very few new materials have been realized.<sup>2</sup> The palladium-catalyzed copolymerization of ethylene and carbon monoxide on the other hand is one of the exceptions to this general trend. It is probably one of the most widely studied and best understood polymerization reactions.<sup>3</sup> Both ethylene and carbon monoxide feedstocks are cheap and readily available, and the perfectly alternating polyketone products thus formed possess very interesting properties.<sup>4</sup> In over 20 years of research, in the area of late transition metal catalyzed polymerizations of carbon monoxide and ethylene, no “errors” or extra insertions, i.e., no double CO or double C<sub>2</sub>H<sub>4</sub> insertions, have ever been reported. It is clear for thermodynamic reasons that double CO insertions do not occur, but why double or even multiple insertions of ethylene do not occur is somewhat astonishing, particularly because the same catalysts may convert ethylene to butenes very readily.<sup>5</sup> It is also known that

certain cationic palladium complexes ( $\alpha$ -diimines) may polymerize ethylene to high molecular weights.<sup>6</sup> Elegant mechanistic studies based on cationic palladium(II) complexes have clearly demonstrated that the pure alternation arises from the formation of a highly stable five-membered cationic palladium metallacycle by an electrostatic interaction of the oxygen of the carbonyl moiety and the cationic palladium center “back-biting” effect, which may be opened only by a CO molecule.<sup>7</sup>

Very recently, in contrast to the previous research, Drent and co-workers reported three alkoxy-aryl-phosphine ligands bearing sulfonic acid groups that when combined in situ with palladium acetate in a near stoichiometric (1.1:1) ratio, produced double, triple, and quadruple extra insertions (“misinsertions”) of ethylene in the growing polyketone chain.<sup>8a,b</sup>

Our group has been active in the areas of new catalyst design and polymer studies of CO–olefin (co-) and (ter-) polymerization reactions for a number of years.<sup>9</sup> The idea of a random CO–C<sub>2</sub>H<sub>4</sub> copolymer has been an ultimate goal in polyketone research, with the promise of new materials possessing desirable material properties and the opportunity for further functionalization. We now report the synthesis and structural character-

(5) Drent, E. *Pure Appl. Chem.* **1990**, *62*, 661.

(6) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(7) (a) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137. (b) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (c) Nozaki, K.; Sato, N.; Tomomura, Y.; Yasutomi, M.; Takaya, H.; Hiyama, T.; Matsubara, T.; Koga, N. *J. Am. Chem. Soc.* **1997**, *119*, 12779. (d) Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 7337.

(8) (a) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *J. Chem. Soc., Chem. Commun.* **2002**, 964. (b) Drent, E.; Pello, D. H. L. Eur. Pat. Appl. EP0632084 (to Shell), 1995.

(9) (a) Niewhof, R. P.; Marcelis, A. T. M.; Sudhölter, E. J. R.; Wursche, R.; Rieger, B. *Macromol. Chem. Phys.* **2000**, *201*, 248. (b) Wursche, R.; Rieger, B. *Macromol. Chem. Phys.* **2000**, *201*, 2869. (c) Wursche, R.; Debardemaeker, T.; Klinga, M.; Rieger, B. *Eur. J. Inorg. Chem.* **2000**, 2063. (d) Huhn, W.; Hollmann, F.; Hild, S.; Kriewall, Th.; Rieger, B. *Macromol. Mater. Eng.* **2000**, *283*, 115. (e) Mansour, A.; Hollmann, F.; Rieger, B. *Polymer* **2001**, *42*, 93. (f) Privalko, V. P.; Pissis, P.; Polizos, G.; Korskanov, V. V.; Privalko, E. G.; Dolgoshey, V. I.; Kramarenko, V. Yu.; Huhn, W.; Hollmann, F.; Rieger, B. *J. Macromol. Sci.-Phys.* **2002**, *B41* (1), 99.

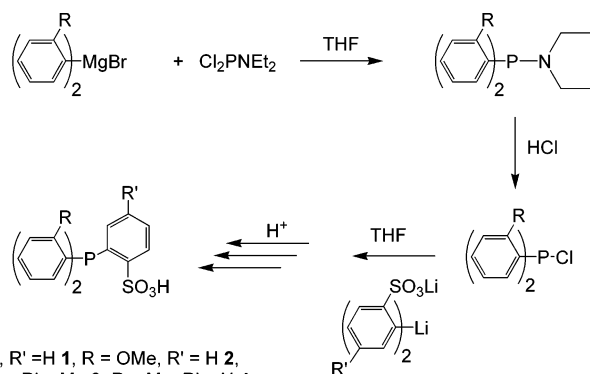
(1) (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429. (b) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479. (c) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(2) (a) Brubaker, M. M.; Coffman, D. D.; Hoehn, H. H. *J. Am. Chem. Soc.* **1952**, *74*, 1509. (b) Deubel, D. V.; Ziegler, T. *Organometallics* **2002**, *21*, 1603. (c) Michalak, A.; Ziegler, T. *Organometallics* **2001**, *20*, 1521. (d) Michalak, A.; Ziegler, T. *J. Am. Chem. Soc.* **2001**, *123*, 12266. (e) Shultz, C. S.; DeSimone, J. M.; Brookhart, M. *Organometallics* **2002**, *20*, 16. (f) Tanaka, K.; Furo, M.; Ihara, E.; Yasuda, H. *J. Polymer Sci., Part A* **2001**, *39*, 1382. (g) Desurmont, G.; Tokimitsu, T.; Yasuda, H. *Macromolecules* **2000**, *33*, 7679.

(3) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663, and references therein.

(4) Ash, C. E. *J. Mater. Educ.* **1994**, *16*, 1.

## Scheme 1. Synthesis of Ligands 1–4



R = H, R' = H **1**, R = OMe, R' = H **2**,  
R = Me, R' = Me **3**, R = Me, R' = H **4**

**Table 1. Results of the in Situ CO–C<sub>2</sub>H<sub>4</sub> Copolymerization Reactions<sup>25e</sup>**

entry	ligand	T/°C	C <sub>2</sub> H <sub>4</sub> (bar)	CO (bar)	activity (g mmol <sup>-1</sup> h <sup>-1</sup> )	extra C <sub>2</sub> insertion (%) <sup>d</sup>
1	<b>1</b>	110	30	10	<1 <sup>a</sup>	1.4
2	<b>2</b>	110	20	10	25 <sup>a</sup>	8.1
3	<b>2</b>	110	30	10	48 <sup>c</sup>	15.0
4	<b>3</b>	110	20	20	38 <sup>a</sup>	2.9
5	<b>3</b>	110	20	10	56 <sup>a</sup>	6.1
6	<b>3</b>	110	30	10	54 <sup>c</sup>	8.1
7	<b>3</b>	110	55	10	26 <sup>b</sup>	15.1
8	<b>3</b>	110	100	10	12 <sup>b</sup>	18.3
9	<b>3</b> (2 equiv)	110	30	10	69 <sup>a</sup>	2.4
10	<b>3</b>	110	30	10	49 <sup>a</sup>	8.4
11	<b>4</b>	110	30	10	47 <sup>c</sup>	8.2
12	<b>4</b>	110	50	10	29 <sup>c</sup>	14.7

<sup>a</sup>In a 100 mL (50 mL solvent) autoclave. <sup>b</sup>25 mL (10 mL solvent) autoclave. <sup>c</sup>250 mL (100 mL solvent) autoclave. <sup>d</sup>Total mol % of C<sub>2</sub>H<sub>4</sub> relative to nonalternating copolymer, calculated from <sup>13</sup>C{<sup>1</sup>H} NMR spectra (measured in 1,1,3,3-hexafluoropropan-2-ol/C<sub>6</sub>D<sub>6</sub>). <sup>e</sup>**1** = *o*-H, **2** = *o*-OMe, **3** = *o*-Me/toluenesulfonic acid, **4** = *o*-Me. Based on Pd over experiment run time of 1 h.

ization of the first examples of *neutral* Pd(II) complexes based on {SO<sub>3</sub>}<sup>-</sup>-containing ligands. The new complexes show higher activities and are able to insert larger amounts of extra ethylene units relative to the perfectly alternating structure as compared to the in situ copolymerization reactions previously reported.<sup>8a,b</sup>

## Results and Discussion

**In Situ Polymerizations.** Ligands **1**, **3**, and **4** were synthesized by addition of the appropriate chlorodiphenylphosphine to a tetrahydrofuran solution of di-lithiated benzenesulfonic acid (**1**, **4**) and toluenesulfonic acid (**3**) at 0 °C, followed by acidic workup (Scheme 1).

Ligand **2** was prepared by the known literature procedure for comparative purposes.<sup>8a</sup> The <sup>31</sup>P NMR in chloroform-*d*<sub>1</sub> of each ligand consists of a single peak at approximately –9 ppm relative to 80% H<sub>3</sub>PO<sub>4</sub>. No <sup>1</sup>J<sub>(P–H)</sub> coupling is observed in the proton NMR spectra, confirming that ligands **1**, **3**, and **4** are not zwitterionic, in contrast to that found for ligand **2**.

Results of the in situ copolymerization reactions of carbon monoxide and ethylene using ligands **1–4** are shown in Table 1.

First, we repeated the copolymerization reaction with the *ortho*-methoxy-substituted ligand **2** and Pd(OAc)<sub>2</sub> under the identical reactions conditions as described in the literature, particularly as it is the only example of

a random copolymerization of CO and C<sub>2</sub>H<sub>4</sub> (extra ethylene insertions) using a palladium catalyst.<sup>8a,b</sup> As expected, the results obtained for **2** were in agreement with those previously reported, in both incorporation of extra ethylene insertions (15%) and the activity (50 g mmol<sup>-1</sup> h<sup>-1</sup>) at 30 bar C<sub>2</sub>H<sub>4</sub> and 10 bar CO.

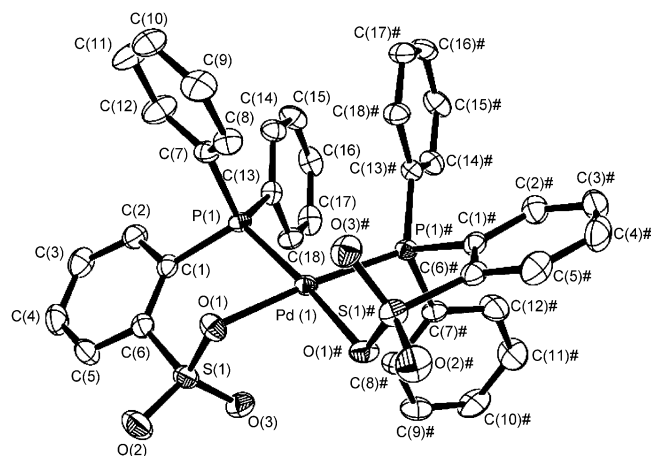
Having established in our laboratories, using our autoclave systems and equipment, that extra ethylene insertions may be produced using ligand **2**, we wanted to address a number of further key points that we felt were still unanswered from the previous study.<sup>8a</sup>

Therefore, 2-(diphenylphosphino)benzenesulfonic acid,<sup>8b</sup> ligand **1**, bearing no substituents was prepared and tested under standard conditions (entry 1). In contrast to ligands **2–4** applying the conditions stated in Table 1, both the percentage of extra ethylene insertions and the amount of polymer produced were very low. We assume, due to the open nature of the system, i.e., no steric bulk in close proximity to the metal center, as would be expected from a catalyst derived from ligand **2**, that the catalyst containing ligand **1** allows β-hydride elimination to become a more significant termination step. This observation, however, does conflict with the patent literature, where it is claimed using the identical ligand **1** and Pd(OAc)<sub>2</sub>, with gas pressures CO/C<sub>2</sub>H<sub>4</sub> (45:40), that up to 15% extra ethylene insertions may be produced.<sup>8b</sup>

We wanted to further establish if an alkoxy group (electron-donating group) is a requirement in the *ortho*-position of the unsulfonated phenyl ring(s) of the ligand or would any relatively bulky group generate the same results in both activity and copolymer composition. Therefore, the *ortho*-methyl-substituted derivative **3** was prepared. The results clearly show (cf. entry 3 vs entry 6) that although the ligand **3**-derived catalyst produces extra insertions, with almost the same activities as compared to ligand **2**, the percentage of extra ethylene insertions relative to the alternating structure is approximately 50% less than that found for ligand **2**. Simple molecular modeling calculations clearly show that the oxygen of the *ortho*-methoxy group orientates itself directly above the palladium center (~3.4 Å). Other ligand derivatives, bearing substituents such as CF<sub>3</sub>, F, and SMe<sub>2</sub>, which may potentially interact with the metal center, are currently under study in our laboratories.

By increasing the pressure to 65 (entry 7) and 110 bar (entry 8), with a gas blend ratio of 10:55 and 10:100 CO/C<sub>2</sub>H<sub>4</sub>, the extra incorporation of ethylene increased to 15.1 and 18.3%, respectively, but the activities decreased to 26 and 12 g mmol<sup>-1</sup> h<sup>-1</sup>. When the ratio of ligand **3** to Pd(OAc)<sub>2</sub> was increased to 2:1, pure white polymers were obtained, with higher activities. However, the number of extra ethylene insertions decreased significantly, for example from 8.4 (entry 12) to 2.4% (entry 9). A detrimental effect from the addition of a second equivalent of ligand to the copolymerization reaction is likely, due to a shift in reaction equilibrium toward a dimeric bis-phosphine species (vide infra), which is capable of producing only purely alternating copolymers (cf. Figure 1).

Comparison between ligand **3** (entry 6) and ligand **4** (entry 10) clearly shows that a methyl group in the *para*-position to the {SO<sub>3</sub>} group has no visible effect on



**Figure 1.** Molecular structure of  $[P^OPdO^P]$  **1a** shown at 50% probability. Hydrogen atoms are omitted for clarity.

either activity or number of extra ethylene insertions. It may be concluded that, both electronically and sterically, there is as expected no appreciable difference observed between benzene or toluenesulfonic acid moieties. Therefore, similar groups in these positions may be used to further aid catalyst solubility.

In summary, sterically bulky substituents and/or R-groups, providing electron density in close proximity to the metal center such as OR (where R = Me, Et,  $i$ Pr) in the *ortho*-position of the unsulfonated phenyl rings of the phosphine ligand, combined with high pressures (high ethylene to carbon monoxide ratios) and temperatures, give suitable conditions for the formation of extra ethylene insertions. Stoichiometric metal-to-ligand ratios are also required, as 2 equiv of ligand to the metal center reduces the number of extra ethylene insertions relative to the alternating copolymer.

**Neutral Palladium Complexes.** Having established the prerequisites of the catalyst system by in situ reactions, we were very interested to ascertain the structural nature of the palladium species formed during the copolymerization reactions, particularly as it is believed that a monoligated  $\{P^OPd\}$  neutral complex is most likely responsible for the incorporation of extra ethylene insertions via a neutral metallacycle, *vide infra*. First, NMR studies were carried out in methanol- $d_4$  at room temperature, to reproduce standard autoclave-loading conditions. However, owing to the poor solubility of  $Pd(OAc)_2$  in pure methanol, further NMR reactions had to be performed using a mixture of  $CD_3OD/CD_2Cl_2$  (1:2). Ligands **1–4** react cleanly to give complexes  $[P^OPdO^P]$  **1a–4a**,  $Pd(OAc)_2$ , and acetic acid in less than 20 min, as shown in Scheme 2.

Complementary IR autoclave reactions were also performed in both dichloromethane and methanol using a 250 mL Büchi (ATR-IR) autoclave). Once again it is clear that the reaction in dichloromethane produces the dimeric palladium complex  $[P^OPdO^P]$ ,  $Pd(OAc)_2$ , and acetic acid as the only detectable species, as shown by comparison of the IR spectra to pure samples. Carbon monoxide ( $\nu_{CO} = 2134\text{ cm}^{-1}$ ) was introduced into the reaction vessel, and almost immediately a new CO band appeared at ca.  $1943\text{ cm}^{-1}$ , which was tentatively assigned to a palladium–carbonyl complex.

As observed in the in situ copolymerization reaction (entry 9), 2 equiv of the ligand lead to a reduced

percentage of extra ethylene insertions, compared to the experiments when only 1 equiv of ligand is used.

To account for the differences observed between the reactions conducted in dichloromethane and those in methanol, we propose that a palladium–acetate intermediate,  $[P^OPd(OAc)]$ , is the most likely candidate as the initiating species, particularly when very low concentrations of ligand and metals are used ( $\sim 10\text{ mg}$ ) and large volumes of solvents (100 mL) as shown in Scheme 3. Many examples of palladium–phosphine complexes containing an acetate moiety are known in the literature.<sup>10</sup> Both the dimeric  $[P^OPdO^P]$  complex and  $Pd(OAc)_2$  are also still likely to be formed in the reactor. The latter provides a simple explanation for the formation of Pd(0) after addition of CO and the discolored polymeric material.

Having established by NMR and in situ reactions that complexes containing two ligands form very readily in dichloromethane solutions, it would seem likely that these bis-phosphine complexes are plausible derivatives in the catalytic cycle, potentially as a resting or deactivated species.

Therefore, pure  $[P^OPdO^P]$  complexes **1a–4a** were synthesized by reacting 2 equiv of the appropriate ligand with 1 equiv of  $Pd(OAc)_2$  in dichloromethane at room temperature. In all cases the yields were quantitative. It must be mentioned that in general the complexes once formed are not particularly soluble in any common organic solvents. However, suitable single crystals for X-ray analysis were grown from dilute solutions of ligands **1–4** and  $Pd(OAc)_2$  in an NMR tube. A representative molecular structure of complex **1a** is illustrated in Figure 1.<sup>11</sup>

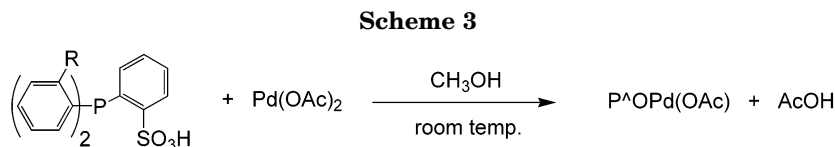
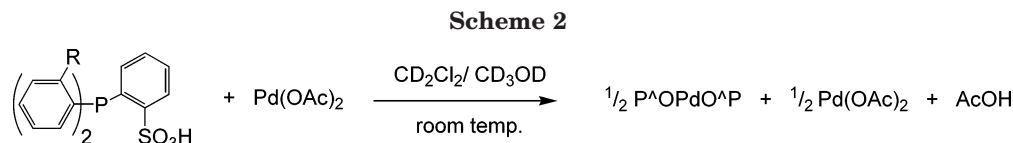
Selected bond lengths and angles of **1a** are depicted in Table 2.

Molecule **1a** is centrosymmetric, with each  $P^O$  ligand located in a *cis*-orientation around the metal center, thus forming two puckered six-membered rings with each P and O atom in a distorted square planar configuration (O(1)–Pd(1)–P(1) angle of  $85.08(7)^\circ$ ). The oxygen O(3) atom of the  $\{SO_3\}$  moiety takes up a position above the Pd(1) atom. The second oxygen O(3#) of the opposite  $\{SO_3\}$  moiety takes up a position below the plane of the Pd(1) atom. A  $\pi$ -interaction between the two unsulfonated phenyl rings, from the two different phosphine ligands, is also observed, with an average  $C_{arom} \cdots C_{arom}$  distance of  $3.66\text{ \AA}$ .

It is apparent from the literature that there are very few examples of complexes containing a direct  $\{M-O-SO_2\}$  bond. To the best of our knowledge the structures reported in this study are the first examples of palladium complexes containing a phosphorus-sulfonate chelate. It is well known that sulfonate  $\{O_2S-O^-\}$  groups are regarded as very weak coordination ligands. The O(1)–Pd(1) bond length is  $2.100(3)\text{ \AA}$ , which is comparable to the other two known palladium structures that contain a  $\{OTs^-\}$  ligand (Pd–O =  $2.151$  and  $2.123\text{ \AA}$ ). In both cases the  $\{OTs^-\}$  group is used as a

(10) (a) Del Piero, G.; Cesari, M. *Acta Crystallogr., Sect. B: Crystallor. Cryst. Chem.* **1979**, *35*, 2411. (b) Louie, J.; Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2359. (c) Bianchini, C.; Lee, H. M.; Meli, A.; Oberhauser, W.; Peruzzini, M.; Vizza, F. *Organometallics* **2002**, *21*, 16.

(11) Analogous crystal structures of **2a** and **3b** will be reported elsewhere.

**Table 2. Selected Bond Distances (Å) and Angles (deg) of Complex 1a**

C(6)–S(1) = 1.778	C(7)–P(1) = 1.825	O(1)–S(1) = 1.500
O(1)–Pd(1) = 2.100	O(2)–S(1) = 1.433	P(1)–Pd(1) = 2.2458
C(6)–C(1)–P(1) = 125.3	C(2)–C(1)–P(1) = 116.4	C(1)–C(6)–S(1) = 122.4
S(1)–O(1)–Pd(1) = 111.01	C(7)–P(1)–C(1) = 105.10	C(1)–P(1)–Pd(1) = 112.86
O(1)–Pd(1)–P(1) = 85.08	O(1)–S(1)–C(6) = 104.00	

**Table 3. Results of the [P<sup>∧</sup>OPdO<sup>∧</sup>P] CO–C<sub>2</sub>H<sub>4</sub> Copolymerization Reactions<sup>g</sup>**

entry	complex	T/°C	C <sub>2</sub> H <sub>4</sub> (bar)	CO (bar)	activity (g mmol <sup>-1</sup> h <sup>-1</sup> )	extra C <sub>2</sub> insertion (%) <sup>d</sup>
1	<b>1a</b>	110	30	10	2.5 <sup>a</sup>	<1
2	<b>2a</b>	110	30	10	106 <sup>a</sup>	1.2
3	<b>2a</b>	150	30	10	89 <sup>a</sup>	4.1
4	<b>2a</b>	110	30	10	5 <sup>a</sup>	<1 <sup>e</sup>
5	<b>2a</b>	110	30	10	105 <sup>a</sup>	1.2 <sup>f</sup>
6	<b>3a</b>	110	30	10	102 <sup>a</sup>	2.1
7	<b>3a</b>	110	60	20	87 <sup>b</sup>	3.3
8	<b>3a</b>	110	110	10	47 <sup>b</sup>	4.9
9	<b>3a</b>	150	30	10	53 <sup>a</sup>	4.3
10	<b>3a</b>	200	60	10	75 <sup>c</sup>	4.9

<sup>a</sup>In a 100 mL (50 mL solvent) autoclave. <sup>b</sup>25 mL (10 mL solvent) autoclave. <sup>c</sup>250 mL (100 mL solvent) autoclave. <sup>d</sup>Total mol % of C<sub>2</sub>H<sub>4</sub> relative to purely alternating copolymer, calculated from <sup>13</sup>C{<sup>1</sup>H} NMR spectra (measured in 1,1,1,3,3,3-hexafluoropropan-2-ol/C<sub>6</sub>D<sub>6</sub>). <sup>e</sup>In dichloromethane. <sup>f</sup>Addition of 1 equiv Pd(OAc)<sub>2</sub>. <sup>g</sup>**1a** = *o*-H, **2a** = *o*-OMe, **3a** = *o*-Me. Based on Pd over experiment run time of 1 h.

weakly coordinating (leaving) group, for example, [dpppPd(H<sub>2</sub>O)(OTs)](OTs).<sup>12</sup> The bond between the oxygen of the {SO<sub>3</sub>} group and the palladium center in the new complexes reported here may be therefore best described as a phosphine-chelate assisted coordination.

Results of the copolymerization reaction of ethylene and carbon monoxide using complexes **1a**, **2a**, and **3a** are shown in Table 3.

As previously observed for ligand **1**, complex **1a** (entry 1) does not produce any significant amounts of polymer under the conditions used. Entries 2 and 6 were more encouraging; both complexes **2a** and **3a** produced pure white polymers with good activities (cf. in situ). However, as expected in both cases, very little extra ethylene was incorporated relative to the purely alternating CO–C<sub>2</sub>H<sub>4</sub> copolymer. In an attempt to increase the number of extra ethylene insertions, 1 equiv of Pd(OAc)<sub>2</sub> was added (entry 5) to complex **2a** under identical reactions conditions. The polymer formed was almost black in color due to reduction of the Pd(OAc)<sub>2</sub> to Pd(0). Analysis revealed no increase in either activity or percentage of extra misinsertions compared to entry 2. Upon increasing the relative pressures (entries 7 and 8), extra

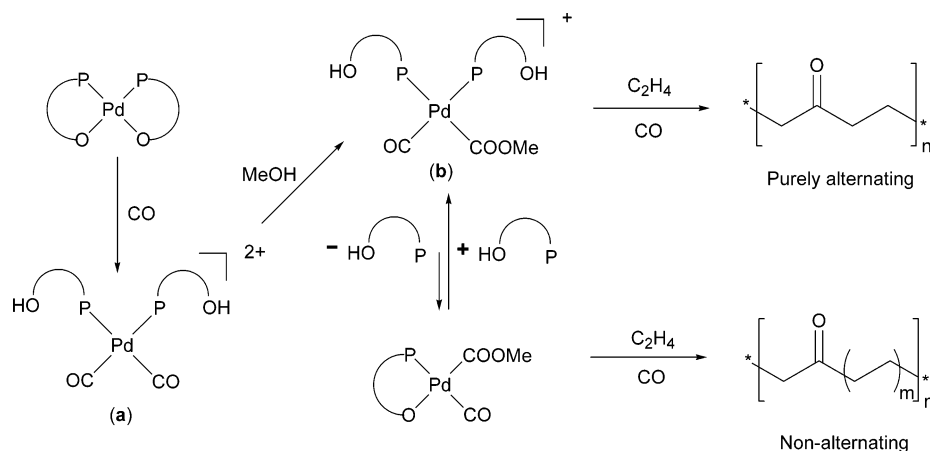
ethylene incorporation was observed. By raising the temperature to 150 °C (entry 9) and 200 °C (entry 10) again, extra incorporation of ethylene was also detected, however, at the expense of activity. It must be noted that even at 200 °C very little decomposition of the catalyst was apparent.

We propose that the [P<sup>∧</sup>OPdO<sup>∧</sup>P] complex in methanol, upon addition of monomer(s), most likely forms two species, as shown in Scheme 4. Cleavage of the Pd–O bonds by protonation and/or carbonylation of the complex would lead to a dicationic *cis*-(bis-phosphine) palladium(II) dicarbonyl complex (**a**). It has been shown that the carbonyl ligand may undergo nucleophilic attack by an alcohol (methanol) to form a monocationic ester complex (**b**).<sup>13</sup> No example of a cationic Pd(II) complex has ever been reported in the literature that is able to introduce extra ethylene insertions in a CO–C<sub>2</sub>H<sub>4</sub> copolymer.

Alternatively, one of the P<sup>∧</sup>O ligands may split off completely, particularly at higher pressures and temperatures, to yield a monoligated {Pd(O<sup>∧</sup>P)} complex, which in turn would be able to insert extra ethylene, as depicted in Scheme 4. It is well known from the literature that tertiary phosphines, such as PPh<sub>3</sub>, are able to dissociate in solution and migrate between metal centers.<sup>14</sup> Having established that a monomeric {Pd(O<sup>∧</sup>P)} complex is responsible for the extra C<sub>2</sub>H<sub>4</sub> insertions, we searched for an alternative preactivated palladium precursor.<sup>15</sup>

**Monosubstituted Palladium Complexes.** Very recently the synthesis and structural characterization of a preactivated cationic palladium 1,3-bis(diphenylphosphino)propane (dppp) complex, bearing a dicyclopentadienylethoxy ligand, was reported by our group.<sup>16</sup> Complexes **2b** and **3b** were synthesized using the similar methodology, by first converting the appropriate ligands **2** and **3** to the corresponding sodium salts using Na<sub>2</sub>CO<sub>3</sub>. The dimeric bis[μ<sup>2</sup>-chloro-1-η<sup>2</sup>,5η<sup>1</sup>-6-ethoxy-exo-5,6-dihydrodicyclopentadienepalladium(II)] complex ([Cp-OEtPdCl]<sub>2</sub>) was added at –20 °C in dichloromethane,

(13) Mücke, A.; Rieger, B. *Macromolecules* **2002**, *35*, 2865.(14) (a) Evans, D.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660. (b) O'Connor, C.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2665.(15) A stoichiometric reaction between [Pd(COD)ClMe] and ligand **3** in dichloromethane yielded [P<sup>∧</sup>OPdO<sup>∧</sup>P] as the only phosphine-containing product.(16) Meinhard, D.; Hollmann, F.; Huhn, W.; Thewalt, U.; Klinga, M.; Rieger, B. *Organometallics* **2004**, *23*, 5637.(12) (a) Benetollo, F.; Bertani, R.; Bombieri, G.; Toniolo, L. *Inorg. Chim. Acta* **1995**, *5*, 233. (b) Tulloch, A. A. D.; Winston, S.; Danapoulos, A. A.; Eastham, G.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2003**, 699.

Scheme 4. Proposed Activation of [P<sup>∧</sup>OPdO<sup>∧</sup>P] in Methanol

## Scheme 5. Synthesis of Complexes 2b and 3b

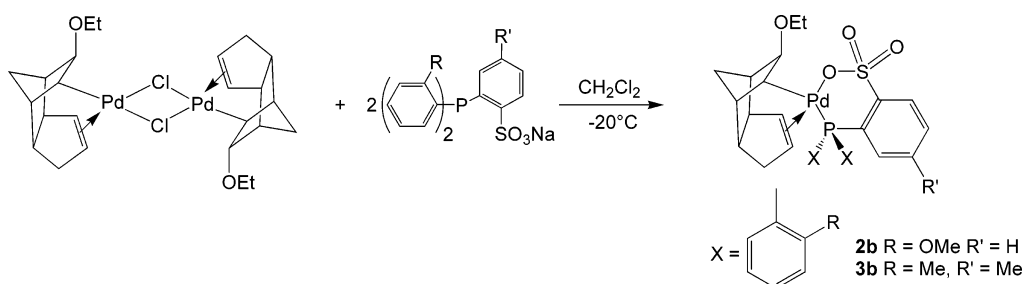


Table 4. Selected Bond Distances (Å) and Angles (deg) of Complex 2b

C(25)–S(1) = 1.765	C(20)–P(1) = 1.847	P(1)–C(26) = 1.829
O(5)–Pd(1) = 2.189	O(5)–S(1) = 1.485	P(1)–Pd(1) = 2.302
Pd(1)–C(4)A = 2.30	Pd(1)–C(10)A = 1.94	P(1)–Pd(1)–O(5) = 93.2
Pd(1)–O(5)–S(1) = 118.4	C(20)–P(1)–C(13) = 105.2	C(20)–P(1)–Pd(1) = 110.2
C25(1)–S(1)–O(5) = 104.6	C(20)–P(1)–C(26) = 108.3	O(6)–S(1)–O(5) = 111.6

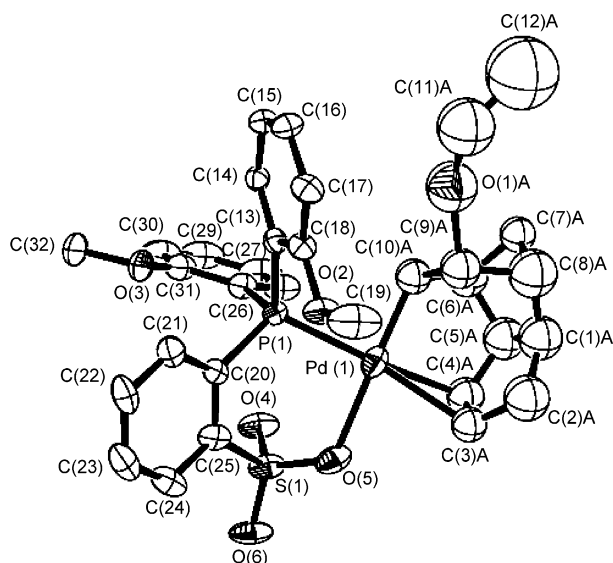
to yield the neutral complexes **2b** and **3b** as pale yellow solids, as depicted in Scheme 5. Each complex was structurally characterized using standard 1D and 2D NMR measurements. Full analyses of complexes **2b** and **3b** are described in the Supporting Information.

Suitable single crystals for X-ray analysis of **2b** were grown from dichloromethane/pentane. A crystal struc-

ture of complex **2b** is shown in Figure 2. Selected bond lengths and angles of **2b** are depicted in Table 4.

The structure of **2b** clearly shows, as Drent and co-workers correctly proposed, that the active catalytic species is based on a {P<sup>∧</sup>O} chelate.<sup>8a</sup> The distance between the O(2) of the *o*-OMe group and the Pd(1) center is 3.35 Å. Such a close proximity of an electron-donating group near the metal center is likely to have a significant influence on the catalysis. The use of a dicyclopentadienylalkoxy ligand provides a simple but highly effective method of generating a preactivated ( $\sigma$  and  $\pi$  bond) catalyst.

The polymerization reactions with complexes **2b** and **3b** are shown in Table 5. In general, all copolymerization reactions were performed in dichloromethane with 2 wt % B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as activator. The use of boranes, such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, as phosphine scavengers with neutral salicylaldiminato Ni(II) complexes<sup>18</sup> and promoters/cocatalysts in combination with cationic palladium bisphosphine complexes has been described in the litera-



**Figure 2.** Molecular structure of **2b** diastereoisomer (A) shown at 30% probability. Hydrogen atoms are omitted for clarity.<sup>17</sup>

(17) It is clear from the structural refinement of complex **2b** that the dicyclopentadienyl ligand exists in two chemically equivalent, diastereomeric forms and each coordinates to the free Pd site in two possible orientations. As a consequence, superimposed electron density is observed in this area of the unit cell, which cannot be resolved or at least it cannot be freely refined. However, it is possible to model an overlay of both diastereoisomers sharing the same sites and to constrain the atomic positions, such that the atoms do not shift to chemically meaningless positions during refinement cycles.

(18) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149.

**Table 5.** Results of the {P<sup>o</sup>OPdCp-OEt} CO–C<sub>2</sub>H<sub>4</sub> Copolymerization Reactions<sup>e</sup>

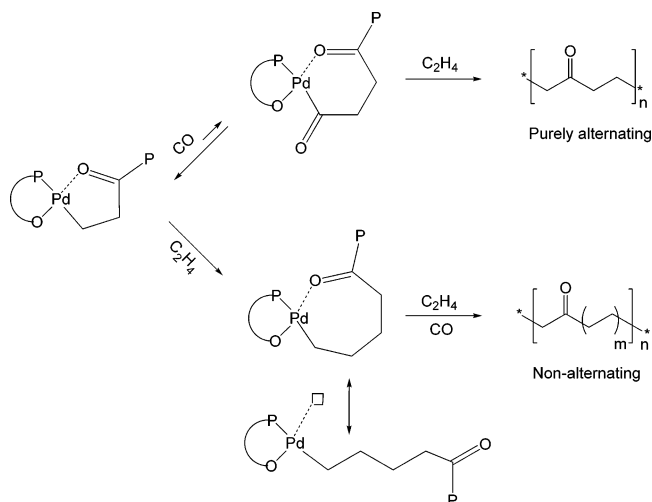
entry	complex	T/°C	slave factor		activity <sup>a</sup> (g mmol <sup>-1</sup> h <sup>-1</sup> )	extra C <sub>2</sub> insertion (%) <sup>d</sup>
			C <sub>2</sub> H <sub>4</sub>	CO		
1	<b>2b</b>	110	100	40	292	3.1
2	<b>2b</b>	110	100	5	89	26.4
3 <sup>b</sup>	<b>2b</b>	110	100	5	126	15.1
4	<b>2b</b>	50	100	5	<5	alternating
5	<b>2b</b>	150	100	5	87	3.3
6 <sup>c</sup>	<b>2b</b>	110	100	5	134	29.6
7	<b>3b</b>	110	100	40	67	2.2
8	<b>3b</b>	110	100	5	40	7.5

<sup>a</sup> Based on Pd over experiment run time of 2 h in a 250 mL autoclave in dichloromethane with 2% B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as activator at 65 bar. <sup>b</sup> No activator. <sup>c</sup> In methanol. <sup>d</sup> Total mol % of C<sub>2</sub>H<sub>4</sub> relative to purely alternating copolymer, calculated from <sup>13</sup>C{<sup>1</sup>H} NMR spectra (measured in 1,1,3,3-hexafluoropropan-2-ol/C<sub>6</sub>D<sub>6</sub>). <sup>e</sup> **2b** = *o*-OMe, **3b** = *o*-Me.

ture.<sup>19</sup> It has been shown that such additives provide increased catalyst stability with respect to reduction and also provide means of regenerating the catalytically active species.

Entry 1 corresponds to the complex **2b** with a C<sub>2</sub>H<sub>4</sub>/CO ratio of 2.5:1 and an overall pressure of 65 bar. The reactivity is very high (approximately 300 g mmol<sup>-1</sup> h<sup>-1</sup>) compared to the in situ reactions. However, the percentage of extra ethylene relative to the purely alternating polyketone as expected is low (3.1%). As previously observed in the in situ polymerizations, the ratio of gas blend plays a significant role for extra ethylene incorporation into the copolymers. The result demonstrates that the catalyst alone is not able to incorporate large quantities of extra ethylene into the growing polymer. Further copolymerization reactions using complex **2b** were performed using a gas blend ratio of C<sub>2</sub>H<sub>4</sub>/CO = 20:1 in the presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (entry 2) or pure dichloromethane (entry 3). The reaction performed in methanol (entry 6) at 110 °C and 65 bar showed high activity (134 g mmol<sup>-1</sup> h<sup>-1</sup>) and the highest number of extra ethylene insertions relative to the purely alternating polymer structure (30%). Other bulkier groups such as biphenyl or phenoxy, which are currently under investigation in our laboratories, may provide a chance to insert even more ethylene relative to the alternating copolymer.<sup>20</sup>

**Polymer Properties.** The <sup>13</sup>C NMR (methylene region) of the copolymer (Table 5, entry 2) is in accordance with that previously found in the literature<sup>8a</sup> (Supporting Information). Analyses of the polymer(s) by differential scanning calorimetry (DSC) showed that the melting points of the materials are reduced from ca. 260–270 °C (perfectly alternating) to 220 °C (entry 2), which indicates a significant decrease in the interactions between the polymer chains. One major reason for the polymer analysis is to establish if a single polymer or reactor blend is produced during the CO–C<sub>2</sub>H<sub>4</sub> copolymerization reaction. Therefore, fractionation of the polymeric material was carried out using benzene/hexafluoro-2-propanol (HFIP). Approximately 2 g of the polymer was dissolved in HFIP and precipitated into four equal portions, by the addition of benzene. <sup>13</sup>C NMR

**Scheme 6.** Proposed Mechanism for the Incorporation of Extra C<sub>2</sub>H<sub>4</sub> Insertions via a Neutral Metal Chelate

analysis of each sample showed that the four samples have an identical chemical structure; that is, each sample retains the same ratio of nonalternating vs alternating regions. Also, further inspection of the peaks in the <sup>13</sup>C NMR spectra, corresponding to double vs triple extra-ethylene insertions, further supports our findings. To further confirm the NMR and fractionation studies, we turned to gel permeation chromatography (GPC) for further insight. The average molecular weight of the crude polymer  $M_w = 370\,000$  with a polydispersity  $M_w/M_n = 2$ . The molecular weight is high and consistent with the <sup>1</sup>H NMR results (HFIP-*d*<sub>2</sub>/benzene-*d*<sub>6</sub>), where no end groups could be detected. The results show that *one type* of polymer is most likely produced in the reaction, consisting of random blocks of both alternating and nonalternating parts.

**Mechanistic Proposal.** To account for the polymers observed, we propose the following mechanism for the extra incorporation of ethylene into the growing CO–C<sub>2</sub>H<sub>4</sub> copolymer, as depicted in Scheme 6. As previously mentioned by Drent and co-workers,<sup>8a</sup> a stereoelectronic destabilization of the neutral chelate enables ethylene to compete with carbon monoxide and to open the five-membered metallacycle. It is known for cationic palladium complexes, under typical polymerization conditions, that a CO insertion is both rapid and reversible.<sup>21</sup> Therefore we assume the neutral chelate provides precedence for the decarbonylation reaction over the formation of a CO inserted six-membered chelate. In turn, increasing the pressure and employing high gas blend ratios CO/C<sub>2</sub>H<sub>4</sub> (1:20) statistically provides higher probability for an ethylene compared to a carbon monoxide insertion. The resulting seven-membered chelate is believed to open more easily, and further ethylene units can be incorporated. A higher energy barrier for the rate-determining ethylene insertion step may account for the low activities found for these systems compared to the cationic palladium catalysts. We propose that the polymerization is able to proceed via two intertwined pathways (Scheme 6), where the same active species may switch between the production of alternating and nonalternating blocks in the same

(19) Barlow, G. K.; Boyle, J. D.; Cooley, N. A.; Ghaffar, T.; Wass, D. F. *Organometallics* **2000**, *19*, 1470.

(20) Schmid, M.; Eberhardt, R.; Klinga, M.; Leskela, M.; Rieger, B. *Organometallics* **2001**, *20*, 2321.

(21) Brumbaugh, J. S.; Sen, A. *J. Am. Chem. Soc.* **1988**, *110*, 803.

polymer chain. The insertion of a C<sub>2</sub>H<sub>4</sub> molecule, directly followed by CO, leads to random blocks of alternating copolymer. Alternatively, an extra insertion of C<sub>2</sub>H<sub>4</sub> yields nonalternating blocks. The pressure, temperature, and gas blend ratio contribute significantly to the polymer composition, thus providing a method to tune material properties.

### Conclusion

In conclusion, we have been able to demonstrate the first structurally characterized, very stable (under the conditions used), neutral, single-site catalysts containing the first example of a phosphorus-sulfonate chelate for the nonalternating copolymerization of ethylene and carbon monoxide. Up to 30% extra ethylene has been incorporated into the CO–C<sub>2</sub>H<sub>4</sub> copolymers. As measured in one case (Table 5, entry 2) the copolymer produced from these new catalysts has high molecular weight with narrow polydispersity, indicating one type of polymer comprised of both alternating and nonalternating parts is formed.

### Experimental Section

**General Considerations.** All reactions were carried out under a dry argon or nitrogen atmosphere using standard Schlenk line techniques or in a glovebox. Solvents were obtained from commercial sources and dried (as appropriate, pentane, hexane, tetrahydrofuran over sodium (ketyl radical), dichloromethane over CaH<sub>2</sub>, and methanol over magnesium turnings) and deoxygenated prior to use. Deuterated solvents were dried over the appropriate drying agent (chloroform-*d*<sub>1</sub>, dichloromethane-*d*<sub>2</sub> over CaH<sub>2</sub>, benzene-*d*<sub>6</sub> over Na, and methanol-*d*<sub>4</sub> over 4 Å molecular sieves). The NMR solvents were deoxygenated using three freeze–thaw–pump cycles and transferred using a high-vacuum line. Commercial reagents were used as supplied, unless otherwise stated. Toluene and benzenesulfonic acid were dried by Dean–Stark distillation from benzene, prior to use. 2-{Bis(2-methylphenyl)chlorophosphine and 2-{bis(2-methoxyphenyl)phosphino}benzenesulfonic acid (ligand **2**) were prepared according to the literature methods.<sup>8a,22</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra (chemical shifts relative to residual solvent) and <sup>31</sup>P{<sup>1</sup>H} (chemical shifts relative to 80% H<sub>3</sub>PO<sub>4</sub>) were recorded on either a Bruker 400 MHz or Bruker 500 MHz spectrometer at ambient temperature unless otherwise stated.

***N,N*-Diethylaminodichlorophosphine [Cl<sub>2</sub>PNEt<sub>2</sub>].** A 1 L Schlenk flask was charged with diethyl ether (400 mL) and PCl<sub>3</sub> (90.6 g, 0.66 mol) and cooled to –20 °C in an ice/NaCl bath. Diethylamine (86.3 g, 1.18 mol) in 100 mL of diethyl ether was added dropwise over a period of 1 h. The reaction mixture was allowed to warm to room temperature and further stirred for 1 h. The diethyl ether was removed by distillation under argon under normal pressure (oil bath 70 °C). The crude product was distilled in vacuo (oil pump), with an oil bath temperature of 190 °C, from the inorganic salts. The pure product was obtained by fractional distillation through a Vigreux column (head temperature 30.5 °C). Yield = 80.4 g, colorless liquid (70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.26–3.35 (sext, 4H, *J* ≈ 7 Hz); 1.15 (t, 6H, *J* = 7.07 Hz), <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ: 13.9 (d, 2C, *J* = 5.12 Hz); 41.4 (d, 2C, *J* = 22.69 Hz), <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ: 163.26 (s). Caution: the solid residue is pyrophoric and should be destroyed carefully, by the slow addition of water.

**Ligand 1. 2-(Diphenylphosphino)benzenesulfonic Acid.** To a solution of dry benzenesulfonic acid (7.34 g, 46.4 mmol)

in THF (60 mL) was added *n*-BuLi (58 mL, 92.8 mmol, 1.6 M in hexane) at 0 °C. After stirring for 6 h at room temperature, a solution of bis(phenyl)chlorophosphine (10.24 g, 46.4 mmol) in THF (30 mL) was added dropwise at 20 °C and the reaction was stirred overnight. After this time, NH<sub>4</sub>Cl (2.48 g, 46.4 mmol) in water (50 mL) was added and the organic solvent removed in vacuo. The aqueous solution was washed with diethyl ether (2 × 50 mL) and the organic phase acidified with HCl (37% in H<sub>2</sub>O). After extraction with dichloromethane (2 × 50 mL) the crude product was dried over MgSO<sub>4</sub>. The solvent was removed in vacuo and recrystallized from dichloromethane/methanol at –20 °C. The resulting white crystals were filtered and dried to give the desired ligand. Yield = 9.7 g (61%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 8.9–7.2 (m, 14H, arom). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ: 4.4 (s); MS: found 341.0, calc 341.4. Anal. Found: C, 65.64, H, 5.53. Calc: C, 65.61, H, 5.51.

**Ligand 3. 2-{Bis(2-methylphenyl)phosphino}toluenesulfonic Acid.** To a solution of dry toluenesulfonic acid (4.34 g, 25.2 mmol) in THF (60 mL) was added *n*-BuLi (31.54 mL, 50.4 mmol, 1.6 M in hexane) at 0 °C. After stirring for 6 h at room temperature, a solution of 2-{bis(2-methylphenyl)chlorophosphine (6.12 g, 25.2 mmol) in THF (30 mL) was added dropwise at 20 °C and the reaction was stirred overnight. After this time, NH<sub>4</sub>Cl (1.34 g, 25.2 mmol) in water (50 mL) was added and the organic solvent removed in vacuo. The aqueous solution was washed with diethyl ether (2 × 50 mL) and the organic phase acidified with HCl (37% in H<sub>2</sub>O). After extraction with dichloromethane (2 × 50 mL) the crude product was dried over MgSO<sub>4</sub>. The solvent was removed in vacuo and the crude product recrystallized from dichloromethane/ethanol at –20 °C. The resulting white crystals were filtered and dried to give the desired ligand. Yield = 5.2 g (54%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.29 (3H, s, CH<sub>3</sub>–C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>H), 2.41 (6H, s, 2CH<sub>3</sub>), 6.8–8.3 (11H, m, arom). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ: –8.75 (br, s). MS: found 384.4, calc 384.4. Anal. Found: C, 65.64, H, 5.53. Calc: C, 65.61, H, 5.51.

**Ligand 4. 2-{Bis(2-methylphenyl)phosphino}benzenesulfonic Acid.** To a solution of dry benzenesulfonic acid (7.17 g, 45.3 mmol) in THF (60 mL) was added *n*-HexLi (36.26 mL, 90.6 mmol, 2.5 M in hexane) at 0 °C. After stirring for 18 h at room temperature, a solution of 2-{bis(2-methylphenyl)chlorophosphine (9.83 g, 40.7 mmol) in THF (40 mL) was added dropwise at 20 °C and the reaction stirred overnight. After this time, NH<sub>4</sub>Cl (2.42 g, 45.3 mmol) in water (50 mL) was added and the organic solvent removed in vacuo. The aqueous solution was washed with dichloromethane (2 × 50 mL) and the organic phase acidified with HCl (37% in H<sub>2</sub>O). After extraction with dichloromethane (2 × 50 mL) the crude product was dried over MgSO<sub>4</sub>. The solvent was further removed in vacuo and the crude product recrystallized from dichloromethane/ether at –20 °C. The resulting white crystals were filtered and dried to give the desired ligand. Yield = 11.1 g (66%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.39 (6H, s, 2CH<sub>3</sub>), 7.0–8.4 (11H, m, arom). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ: –8.43 (s). MS: found 370.4, calc 370.4. Anal. Found: C, 64.43, H, 5.10. Calc: C, 64.85, H, 5.17.

**Complex 1a.** Ligand **1** (0.9 g, 2.88 mmol) was added to a Schlenk flask containing Pd(OAc)<sub>2</sub> (0.35 g, 1.44 mmol). Dichloromethane (30 mL) was added and the solution stirred for 24 h. During this time the desired complex precipitated from the solution as a bright yellow powder. The solvent was removed by cannula, and the complex was washed with dichloromethane (3 × 20 mL). Yield = 1.03 g (98%). Anal. Found: C, 57.70, H, 4.63. Calc: C, 57.76, H, 4.62. Suitable crystals for single-crystal X-ray analysis were grown from a dichloromethane solution, containing 2 equiv of ligand **1** and 1 equiv of Pd(OAc)<sub>2</sub> in dichloromethane under argon in an NMR tube.

**Complex 2a.** Ligand **2** (1 g, 2.48 mmol) was added to a Schlenk flask containing [Pd(OAc)<sub>2</sub>] (0.28 g, 1.2 mmol). Dichloromethane (30 mL) was added and the solution stirred for

24 h. During this time the desired complex precipitates from solution as a bright yellow powder. The solvent was removed by cannula, and the complex was washed with dichloromethane (3 × 20 mL). Yield = 1.1 g (98%).

Note: Complex **2a** is insoluble in all common organic solvents at room temperature. Anal. Found: C, 52.49, H, 4.01. Calc: C, 52.84, H, 3.99.

**Complex 3a.** A Schlenk tube (100 mL) was charged with ligand **3** (0.583 g, 1.52 mmol) and [Pd(OAc)<sub>2</sub>] (0.171 g, 0.76 mmol). Dichloromethane (40 mL) was added and the solution stirred for 24 h at room temperature. The desired complex precipitated during the reaction. The solvent was removed with a cannula and the complex washed with pentane (3 × 20 mL) to afford a bright yellow powder in almost quantitative yield (0.65 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.60 (6H, s, CH<sub>3</sub>), 2.87 (3, s, CH<sub>3</sub>), 2.97 (6H, s, CH<sub>3</sub>), 6.8–8.3 (m, 22H, arom). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ: -3.44 and -4.02. Anal. Found: C, 57.70, H, 4.63. Calc: C, 57.76, H, 4.62.

**Complex 4a.** An NMR tube was charged with ligand **4** (0.02 g, 0.054 mmol) and [Pd(OAc)<sub>2</sub>] (0.012 g, 0.027 mmol). Deuterated dichloromethane (0.5 L) was added. After 30 min at room temperature the solvent and volatiles were removed in high vacuum and the complex washed with pentane (3 × 2 mL) to afford a bright yellow microcrystalline powder. Yield = 0.042 g (92%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 2.58 (3H, s, CH<sub>3</sub>), 2.80 (3H, s, CH<sub>3</sub>), 2.87 (6H, s, CH<sub>3</sub>), 2.99 (3H, s, CH<sub>3</sub>), 6.8–8.3 (m, 24H, arom). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ: -3.1 and -3.8 (*J*<sub>P-P</sub> 109 Hz). Anal. Found: C, 56.80, H, 4.18. Calc: C, 56.84, H, 4.29.

**Complex 2b.** Ligand **2** (2.00 g, 4.97 mmol) was added to a Schlenk flask containing Na<sub>2</sub>CO<sub>3</sub> (0.63 g, 0.59 mmol). Dichloromethane (30 mL) was added and the solution stirred for 4 h. After this time, the desired white sodium salt precipitated. [Cp-OEtPdCl]<sub>2</sub> (1.58 g, 2.48 mmol) was added with stirring at -20 °C, and the solution was allowed to further stir overnight. The complex was filtered and washed with diethyl ether (3 × 20 mL) to yield complex **2b** as a pure pale yellow solid. Yield = 1.49 g (88%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.78 (3H, t, CH<sub>3</sub>), 2.74 and 3.15 (2H, m, CH<sub>2</sub>-O), 3.36 (1H, d, O-CH), 2.69 (1H, m, CH), 2.60 and 2.32 (2H, m, CH<sub>2</sub>), 2.26 (1H, d, CH), 3.74 (1H, s, CH), 2.93 (1H, m, CH), 1.65 (1H, m, CH), 1.04 (1H, d, CH<sub>2</sub>) and 1.33 (1H, d, CH<sub>2</sub>), 6.37 (1H, m, =CH), 6.37 (1H, m, =CH), 7.83 (1H, m, arom), 7.39 (1H, m, arom), 7.48 (1H, m, arom), 8.10 (1H, m, arom), 3.58 (3H, s, CH<sub>3</sub>) and 3.60 (3H, s, CH<sub>3</sub>), 6.89 (2H, m, arom), 7.07 (2H, m, arom), 6.91 (2H, m, arom), 7.24 (2H, m, arom). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ: 15.4 (CH<sub>3</sub>), 63.3 (CH<sub>2</sub>), 80.4 (CH<sub>Cp</sub>), 39.1 (CH<sub>Cp</sub>), 31.6 (CH<sub>2</sub>), 41.4 (CH<sub>Cp</sub>), 51.2 (CH<sub>Pd</sub>), 53.7 (CH<sub>Cp</sub>), 55.0 (CH<sub>Cp</sub>), 35.8 (CH<sub>2</sub>), 129.7 (=CH), 134.6 (=CH), 133.6 (arom<sub>P</sub>), 148.2 (arom<sub>S</sub>), 120.8 (arom), 128.2 (arom), 125.4 (arom), 137.9 (arom), 57.3 (CH<sub>3</sub>), 160.6 (arom<sub>C</sub>), 111.1 (arom), 133.3 (arom), 127.6 (arom), 137.5 (arom), 115.3 (arom<sub>P</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ: 12.1 (s). Anal. Found: C, 56.26, H, 5.21. Calc: C, 56.18, H, 5.01.

**Complex 3b.** Ligand **3** (2.1 g, 5.2 mmol) was added to a Schlenk flask containing Na<sub>2</sub>CO<sub>3</sub> (0.66 g, 0.62 mmol). Dichloromethane (30 mL) was added and the solution stirred for 4 h. After this time, the desired white sodium salt precipitated. [Cp-OEtPdCl]<sub>2</sub> (1.66 g, 2.6 mmol) was added with stirring at -20 °C, and the solution was allowed to stir overnight. The complex was filtered and washed with diethyl ether (3 × 20 mL) to yield complex **3b** as a pure pale yellow solid. Yield = 1.54 g (89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.89 (6H, t, CH<sub>3</sub>), 2.68 and 2.93 (2H, m, CH<sub>2</sub>), 2.83 (1H, s, CH), 1.97 (1H, m, CH), 1.02 and 1.38 (2H, d, CH<sub>2</sub>), 2.11 (1H, m, CH), 3.47 (1H, m, CH), 2.60 (1H, m, CH), 1.84 (1H, m, CH), 1.66 and 1.69 (2H, d, CH<sub>2</sub>), 6.44 (1H, s, CH), 6.44 (1H, s, CH), 7.49 (1H, m, arom), 7.41 (1H, m, arom), 8.11 (1H, m, arom), 2.21 (6H, s, arom), 7.21 (2H, m, arom), 7.31 (2H, d, arom), 6.82 (2H, d, arom), 7.35 (2H, d, arom), 2.3 (3H, m, arom). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ: 15.5 (CH<sub>3</sub>), 63.3 (CH<sub>2</sub>), 81.0 (CH<sub>Cp</sub>), 39.1 (CH<sub>Cp</sub>), 32.4 (CH<sub>2Cp</sub>), 41.1 (CH<sub>Cp</sub>), 54.9 (CH<sub>Pd</sub>), 58.1 (CH<sub>Cp</sub>), 53.6 (CH<sub>Cp</sub>), 35.7 (CH<sub>2Cp</sub>), 126.3 (CH<sub>Cp</sub>), 129.4 (CH<sub>Cp</sub>), 121.9 (CH<sub>P</sub>), 142.3 (CH<sub>S</sub>), 131.4

(arom), 134.5 (arom), 131.7 (arom), 131.6 (arom), 21.3 (CH<sub>3</sub>), 147.1 (arom<sub>q</sub>), 131.9 (arom), 132.1 (arom), 131.7 (arom), 140.1 (arom), 126.4 (arom<sub>q</sub>), 23.3 (arom<sub>q</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ: 12.0 (s). Anal. Found: C, 61.40, H, 5.91. Calc: C, 61.28, H, 5.81.

**In Situ Copolymerizations.** In a typical reaction, 0.04 mmol (~10 mg) of Pd(OAc)<sub>2</sub>, 0.06 mmol of ligand **1–4**, and 10, 50, or 100 mL of MeOH were transferred to a 25 mL (Parr), 100 mL (Roth), or 250 mL (Büchi Limbo) autoclave. The autoclave was quickly closed and purged with argon and then charged with ethylene until a pressure of 30 bar was reached. Subsequently, CO was introduced to reach the pressure of 40 bar (C<sub>2</sub>H<sub>4</sub>/CO = 30:10). After the solution was completely saturated with gas (15 min), the 25 mL or 100 mL autoclave was heated using a preheated silicon oil bath (110 °C) for 1 h. The 250 mL autoclave was heated and temperature maintained using its own electrical heating block and water-cooling system for 2 h. After this time the cooled contents were filtered and washed with methanol (3 × 50 mL) and dried in vacuo.

**Copolymerization Using 1a–4a.** In a typical reaction, 0.012 mmol (~10 mg) of complex **1a–4a** and 50 or 100 mL of MeOH were transferred to a 100 mL (Parr) or 250 mL (Büchi, Limbo) autoclave. The autoclave was quickly closed and purged with argon and then charged with ethylene until a pressure of 30 bar was reached. Subsequently, CO was introduced to reach a pressure of 40 bar (C<sub>2</sub>H<sub>4</sub>/CO = 30:10). After the solution was completely saturated with gas (15 min), the 100 mL autoclave was heated using a preheated silicon oil bath (110 °C) for 1 h. The 250 mL autoclave was heated and temperature maintained using its own electrical heating block and water-cooling system for 2 h. After this time the cooled contents were filtered and washed with methanol (3 × 50 mL) and dried in vacuo.

**Copolymerizations Using 2b–3b, at High Temperature and Pressures.** In a typical reaction, 0.015 mmol (~10 mg) of complex **2b–3b** was dissolved in 10 mL of dichloromethane and added to a gas buret under argon. A 250 mL (Büchi, Limbo) autoclave was charged with the desired solvent (CH<sub>2</sub>Cl<sub>2</sub> or MeOH) and activator (if required). The autoclave was heated to the desired temperature, and the desired pressure (10 bar below actual pressure) of gas was added using an 800 mL reservoir/gas mixing chamber. The carbon monoxide/ethylene gas feed rates were controlled by a remote personal computer (PC). Once the equilibrium of the system had been reached, the contents of the gas buret was added (using the required pressure). Polymerization reactions were run for 2 h. After this time the cooled contents were filtered and washed with methanol (3 × 50 mL) and dried in vacuo.

**NMR Analyses of Copolymers.** <sup>13</sup>C{<sup>1</sup>H} NMR copolymer analyses were measured in hexafluoro-2-propanol/benzene-*d*<sub>6</sub> (5 mm NMR tubes; volume of solvent, 0.5 mL) on a Bruker 500 MHz spectrometer (chemical shifts relative to benzene-*d*<sub>6</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR spectra were simulated (using ACD/ChemSketch, version 4.04) to compare calculated and observed chemical shifts of the nonalternating copolymers, showing good agreement. Further comparisons of spectra were made to the literature.<sup>8a</sup>

**Polymer Fractionation.** Approximately 2 g of the polymer (Table 3, entry 2) was fractionated into five approximately equal parts using hexafluoro-2-propanol/benzene. First, pure polyethylene was removed by filtration from hexafluoro-2-propanol. To the hexafluoro-2-propanol solution, benzene was added and the precipitate filtered, washed with methanol, and dried in a vacuum oven at 80 °C. The same process was repeated three further times. Each sample was analyzed using <sup>13</sup>C NMR in hexafluoro-2-propanol/benzene. Fraction A is pure polyethylene with *M*<sub>w</sub> = 3500 and *M*<sub>w</sub>/*M*<sub>n</sub> = 2. Fractions B, C, D, and E contain identical peaks (structure) with the same extra ethylene incorporation (25–26%) as observed in the crude polymer.

**Gel Permeation Chromatography (GPC).** The polymer (Table 5, entry 2) was dissolved in hexafluoro-2-propanol



**Table 6. Crystallographic Data for 1a and 2b**

	<b>1a</b>	<b>2b</b>
empirical formula	C <sub>36</sub> H <sub>28</sub> O <sub>6</sub> P <sub>2</sub> PdS <sub>2</sub>	C <sub>32</sub> H <sub>35</sub> O <sub>6</sub> PPdS·CH <sub>2</sub> Cl <sub>2</sub>
formula mass	789.05	769.96
habit	yellow plate	pale yellow plate
cryst size [mm]	0.24 × 0.17 × 0.12	0.29 × 0.24 × 0.15
cryst syst	monoclinic	triclinic
space group	C2/c	P1
a [Å]	9.1853 (7)	9.0884(11)
b [Å]	17.5867(10)	10.2010(12)
c [Å]	20.2249(19)	19.395(3)
β [deg]	91.040(11)	86.427(15)
V [Å <sup>3</sup> ]	3266.6(4)	1690.4(4)
Z	4	2
ρ <sub>calcd</sub> [g/cm <sup>-3</sup> ]	1.604	1.513
abs coeff [mm <sup>-1</sup> ]	0.841	0.858
F(000)	1600	788
temp [K]	223(2)	223(2)
abs corr	semiempirical	none
T <sub>min</sub> , T <sub>max</sub>	0.9058, 0.8236	0, 0
λ [Å], Mo Kα	0.707173	0.707173
scan type	image plate/rotation	image plate/rotation
2θ range [deg]	2.01–25.99	2.10–23.99
no. of reflns measd	3188, 3188	10741, 4972
total, unique no. of params	214	382
R1(F <sup>2</sup> > 2σ(F <sup>2</sup> ))	0.0360	0.0826
wR2(F <sup>2</sup> > 2σ(F <sup>2</sup> ))	0.0763	0.2445
Goof, S	0.987	0.973
res electron dens [e <sup>-</sup> /Å <sup>3</sup> ]	0.380, -0.622	2.430, -0.582

(HFIP)/0.05 M potassium trifluoroacetate (KTFAC) to yield a concentration of 3 g/L. The sample was allowed to stand at room temperature for 5 h. Then a 50 μL sample at room temperature was taken, filtered (pore size = 1 μm), and injected into the GPC. Calibration was performed using poly(methyl methacrylate) (PMMA) as standard. Two measure-

ments (samples A and B) were made,  $M_{w(A)} = 367\,800$  and  $M_{w(B)} = 369\,900$ .  $M_w/M_{n(A)} = 2.02$  and  $M_w/M_{n(B)} = 2.04$ . The GPC trace(s) and data are shown in the Supporting Information).

**X-ray Crystallography.** Data of **1a** and **2b** were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation (Table 6). The structures were solved by heavy-atom methods (SHELXS-86)<sup>23</sup> and refined by full-matrix least squares against  $F^2$  (SHELXL-97).<sup>24</sup> Hydrogen atoms were included in the refinement, in calculated positions using a riding model. For complex **1a**, all other non-hydrogen atoms were refined with anisotropic displacement parameters. Complex **2b** is disordered in the dicyclopentadienylethoxy region, due to the presence of two diastereoisomers. Therefore, the cyclopentadienyl moiety of each diastereoisomer was refined isotropically using PART with DANG and DFIX constraints.

**Acknowledgment.** We would like to thank Bayer AG for Funding (A.K.H. and R.J.N.). All would like to express thanks to Mr. Ulrich Ziegler for assistance with polymer NMR measurements and Mr. B. Müller for X-ray data collection.

**Supporting Information Available:** Crystal structure data of **1a** and **2b**, NMR analyses of complex **2b** and **3b**, a selected GPC trace, and <sup>13</sup>C NMR data from the copolymer Table 5, entry 2, are available free of charge via the Internet at <http://pubs.acs.org>.

OM0490785

(23) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(24) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

(25) Polymers were often gray in color, due to catalyst decomposition.