Ethylene Polymerization by Palladium Alkyl Complexes Containing Bis(aryl)phosphino-toluenesulfonate Ligands

Javier Vela, Graham R. Lief, Zhongliang Shen, and Richard F. Jordan*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

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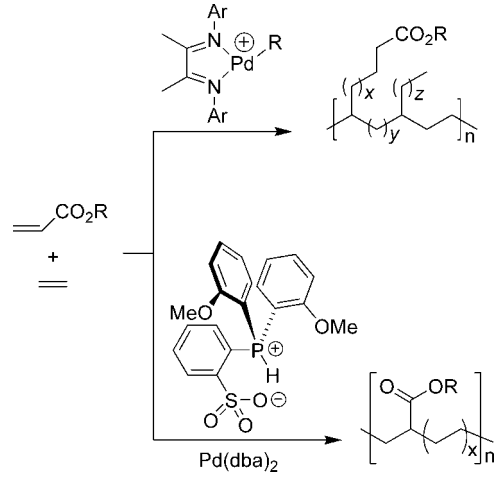
The reaction of L'_2PdR_2 (L' = pyridine (py), pyridazine; L'_2 = cyclooctadiene, TMEDA) with 2-{(2-OMe-Ph)$_2$P}-4-Me-benzenesulfonic acid ([PO-OMe]H, [**1a**]H) or 2-{(2-Et-Ph)$_2$P}-4-Me-benzenesulfonic acid ([PO-Et]H, [**1b**]H) yields [PO-OMe]Pd(R)(L) (L = py, R = CH_2SiMe_3 (**2a**), $CH_2{}^tBu$ (**3a**), CH_2Ph (**4a**); R = Me, L = pyridazine (**5a**), py (**6a**), PPh_3 (**7a**)) or [PO-Et]Pd(Me)(py) (**6b**). **2a** and **6b** have square-planar structures in which the alkyl group is cis to the phosphine and the [PO]Pd chelate rings are puckered. The reaction of **2a** and **3a** with $B(C_6F_5)_3$ yields {[PO-OMe]Pd(R)}$_2$ (R = CH_2SiMe_3 (**8a**), $CH_2{}^tBu$ (**9a**)). **8a** is a sulfonate-bridged dimer in the solid state. **2a**, **6a**, and **6b** polymerize ethylene to linear polyethylene that contains low levels of Me branches, one C=C unit per chain (mostly 1- or 2-olefins), and M_n in the range 6000 to 19 000. **6a** is slightly more active but produces polymers with similar molecular weight and structure compared to **6b**. **6a** copolymerizes ethylene and hexene at low ethylene pressure (5 atm), but no α-olefin incorporation is observed at high pressure (30 atm). An ethylene polymerization mechanism is proposed, which involves insertion and chain transfer of [PO]Pd(R)(ethylene) species (**II**) and ethylene trapping and much slower chain-walking of the [PO]Pd(CH_2CH_2R) species (**III**) formed by insertion of **II**.

Introduction

The development of catalysts that can incorporate polar vinyl monomers in olefin insertion polymerization reactions would enable the direct synthesis of functionalized polyolefins under mild conditions.[1] Brookhart and co-workers showed that (α-diimine)PdR$^+$ catalysts copolymerize ethylene and alkyl acrylates (Scheme 1).[2] However, (α-diimine)PdR$^+$ species undergo fast chain-walking (reversible β-H elimination/reinsertion), which results in the formation of highly branched copolymers in which the acrylate units are located at branch ends.[3] In contrast, Pugh and co-workers reported that catalysts generated *in situ* from 2-{(2-OMe-Ph)$_2$P}-benzenesulfonic acid and Pd(dba)$_2$ (dba = dibenzylidene acetone) or Pd(OAc)$_2$ produce *linear* ethylene/acrylate copolymers with in-

Scheme 1



chain acrylate incorporation (Scheme 1).[4] It was proposed that the active species in these reactions are [PO]PdR complexes ([PO] = generic phosphine sulfonate ligand). The formation of linear copolymers by [PO]PdR catalysts suggests that chain-walking is slow relative to chain growth. DFT calculations by Ziegler indeed show that the barrier to β-H elimination is higher for [PO]PdR species than for (α-diimine)Pd(R)$^+$ species.[5] Pugh and co-workers also showed that *in situ*-generated [PO]PdR species catalyze the nonalternating copolymerization of ethylene and CO.[6]

* Corresponding author. E-mail: rfjordan@uchicago.edu.

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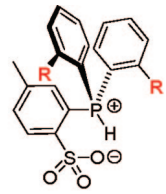
Scheme 2



[1a]H: [PO-OMe]H; R = OMe
[1b]H: [PO-Et]H; R = Et

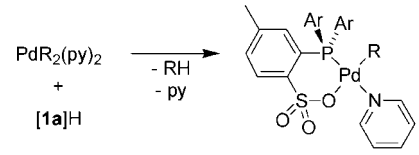
Following the work of Pugh and co-workers, several groups have investigated the chemistry of discrete [PO]Pd(R)(L) complexes and their performance in ethylene/acrylate and ethylene/CO copolymerization.[7–10] In addition, *in situ*-generated and discrete [PO]PdR species have been found to catalyze other interesting copolymerizations, including vinyl acetate/CO,[11] ethylene/norbornene,[12] ethylene/functionalized-norbornene,[13] ethylene/acrylonitrile,[14] and ethylene/vinyl ether copolymerization,[15] to produce linear copolymers.

To help understand the copolymerization behavior of [PO]PdR catalysts, we have investigated their ethylene polymerization properties.[16] Here we describe the synthesis and ethylene polymerization characteristics of [PO]Pd(R)(L) complexes containing 2-{(2-OMe-Ph)$_2$P}-4-Me-benzene-sulfonate) (**1a**, [PO-OMe]$^-$) or 2-{(2-Et-Ph)$_2$P}-4-Me-benzene-sulfonate) (**1b**, [PO-Et]$^-$) ligands (Scheme 2). The phosphine unit in **1a** is slightly smaller and more electron-donating than that in **1b**.[17,18]

Results and Discussion

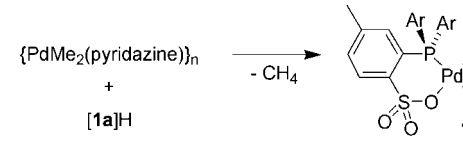
[PO] Ligands. The phosphine-sulfonic acids [PO-OMe]H ([**1a**]H) and [PO-Et]H ([**1b**]H) were synthesized by literature routes.[4b,8e,9] A methyl group was incorporated *para* to the sulfonate to simplify NMR spectra. These compounds are zwitterions in solution, as indicated by low-field ^{1}H NMR chemical shifts (δ = ca. 10) and large $^1J_{PH}$ values ([**1a**]H, 597 Hz; [**1b**]H, 556 Hz) for the P*H* hydrogen.

[PO]Pd(R)(py) Complexes. The reaction of *cis*-Pd(R)$_2$(py)$_2$ (py = pyridine) with [**1a**]H affords [PO-OMe]Pd(R)(py) (R = CH_2SiMe_3 (**2a**), $CH_2{}^tBu$ (**3a**), CH_2Ph (**4a**); eq 1). Similarly, the reaction of {PdMe$_2$(pyridazine)}$_n$ with [**1a**]H affords [PO-OMe]Pd(Me)(pyridazine) (**5a**, eq 2). Complex **2a** is also formed by the reaction of (COD)Pd(CH_2SiMe_3)$_2$ (COD = 1,5-cyclooctadiene) with [**1a**]H and pyridine (eq 3). As described by Allen et al., the reaction of (TMEDA)PdMe$_2$ with [**1a**]H or [**1b**]H and pyridine affords [PO-OMe]Pd(Me)(py) (**6a**) and [PO-Et]Pd(Me)(py) (**6b**, eq 4).[8a] Similarly, the reaction of (TMEDA)PdMe$_2$ with [**1a**]H and PPh_3 affords [PO-OMe]Pd(Me)(PPh_3) (**7a**, eq 5). The [PO]Pd(R)(py) complexes are soluble in $CHCl_3$, CH_2Cl_2, and hot toluene (80 °C) and are stable in the solid state but decompose slowly (days) in CD_2Cl_2 solution at room temperature.



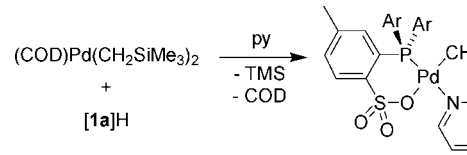
Ar = 2-OMe-Ph
R = CH_2SiMe_3 (**2a**)
$CH_2{}^tBu$ (**3a**)
CH_2Ph (**4a**)

(1)



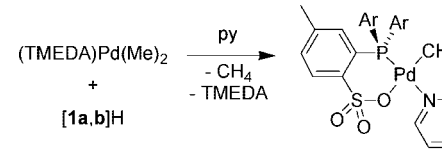
5a, Ar = 2-OMe-Ph

(2)



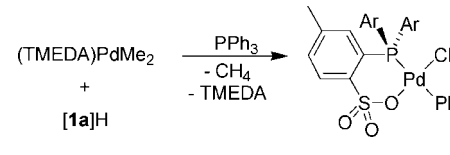
2a, Ar = 2-OMe-Ph

(3)



6a, Ar = 2-OMe-Ph
6b, Ar = 2-Et-Ph

(4)



7a; Ar = 2-OMe-Ph

(5)

Molecular Structures of [PO]Pd(R)(py) Complexes. The molecular structures of [PO-OMe]Pd(CH_2SiMe_3)(py) (**2a**) and [PO-Et]Pd(Me)(py) (**6b**) were determined by X-ray diffraction (Figures 1 and 2). In both cases, the geometry at palladium is square planar, the alkyl ligand is cis to the phosphine, and the [PO]Pd chelate ring adopts a puckered conformation, with one P-*aryl* group occupying a pseudoaxial position and the other a pseudoequatorial position. In **2a**, the methoxy group of the

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(18) The Tolman electronic parameters show that P(2-OMe-Ph)$_3$ (ν_1 = 2058 cm^{-1}) is a better donor than P(2-Et-Ph)$_3$ (ν_1 = 2066 cm^{-1}) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

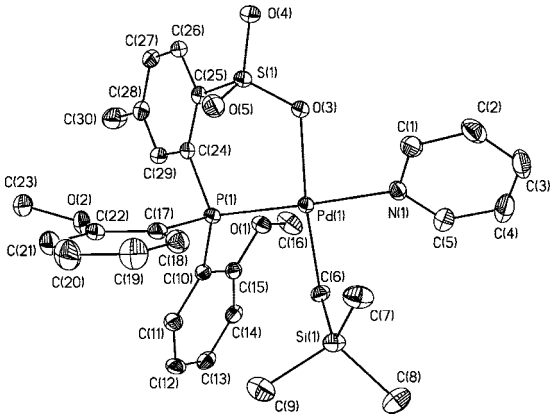


Figure 1. Molecular structure of [PO-OMe]Pd(CH_2SiMe_3)(py) (**2a**). Hydrogen atoms are omitted. Selected bond distances (Å) and angles (deg): Pd(1)−C(6) 2.041(3), Pd(1)−P(1) 2.2430(8), Pd(1)−N(1) 2.130(2), Pd(1)−O(3) 2.149(2), S(1)−O(3) 1.484(2), S(1)−O(4) 1.431(2), S(1)−O(5) 1.437(2), O(3)−Pd(1)−P(1) 94.01(6), C(6)−Pd(1)−N(1) 90.8(1), C(6)−Pd(1)−P(1) 91.23(9), N(1)−Pd(1)−O(3) 83.97(8).

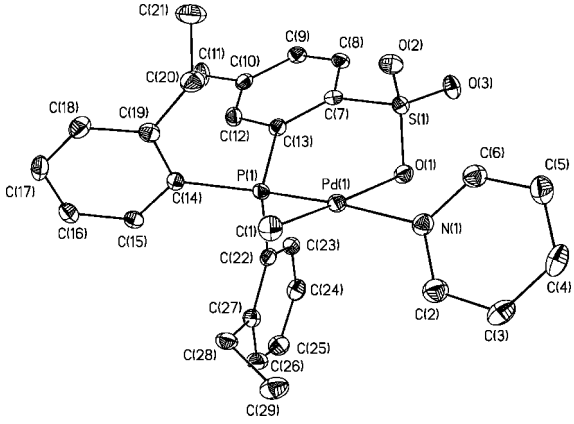


Figure 2. Molecular structure of [PO-Et]PdMe(py) (**6b**). Hydrogen atoms are omitted. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 2.026(3), Pd(1)−P(1) 2.231(1), Pd(1)−N(1) 2.103(2), Pd(1)−O(3) 2.177(2), S(1)−O(1) 1.484(2), S(1)−O(2) 1.448(2), S(1)−O(3) 1.443(2), O(1)−Pd(1)−P(1) 86.48(5), C(1)−Pd(1)−N(1) 89.55(9), C(1)−Pd(1)−P(1) 95.47(8), N(1)−Pd(1)−O(1) 88.83(7).

equatorial 2-OMe-Ph ring (O(1)) sits above an axial coordination site, but the Pd---O distance (Pd(1)−O(1), 3.52 Å)[19] is too long for a significant Pd---O interaction.[20] There are no close Pd---H contacts involving the $[PO]^-$ ligands in **2a** or **6b**.[19b]

Solution Structures and Dynamics of [PO]Pd(R)(L) Complexes. The ambient-temperature ^{1}H NMR spectra of [PO-OMe]Pd(R)(L) complexes **2a**−**6a** contain one doublet for the Pd-CH_2R′ hydrogens ($^3J_{PH}$ = 2–7 Hz) and one 2-*OMe*-Ph resonance. The ^{13}C NMR spectra contain one Pd-CH_2R′ resonance with a small $^2J_{PC}$ value (<4 Hz) and one 2-*OMe*-Ph resonance.[21] These results are consistent with a cis arrangement of alkyl and phosphine ligands and fast inversion of the [PO-OMe]Pd chelate ring. Similarly, for PPh_3 adduct **7a**, a small $^3J_{PH}$ (6 Hz) for the methyl group, a large $^2J_{PP}$ value (403 Hz), and one 2-*OMe*-Ph ^{1}H and ^{13}C resonance are observed, consistent with a cis arrangement of the methyl and phosphine groups and fast chelate ring inversion.

The variable-temperature ^{1}H NMR spectra of **2a** (O*Me* and PdCH_2 regions) are shown in Figure 3. As the temperature is lowered from 20 to −80 °C, the 2-*OMe*-Ph resonance splits into two singlets. Also, as the temperature is lowered, the −CH_2SiMe$_3$ resonance splits into two doublets (J_{HH} = 11), indicating that these methylene hydrogens are diastereotopic in the static structure, as expected in the limit of slow chelate ring inversion. The activation parameters determined by line shape analysis of the 2-*OMe*-Ph and −CH_2SiMe$_3$ signals are identical ($\Delta H^‡$ = 8.5 kcal/mol, $\Delta S^‡$ = −8 eu, $\Delta G^‡$= 10.1 kcal/mol at −60 °C), indicating that the line shape changes result from the same dynamic process. The NOESY spectrum (−80 °C) of **2a** contains cross-peaks between the −CH_2SiMe$_3$ hydrogens and the *ortho* and *meta* hydrogens of one 2-OMe-Ph ring. These results show that the solution structure of **2a** is similar to the solid-state structure and that [PO-OMe]Pd chelate ring inversion is facile. Similar results are observed for **6a**. The activation parameters for ring inversion in **6a** ($\Delta H^‡$ = 7.5 kcal/mol, $\Delta S^‡$ = −14 eu, $\Delta G^‡$ = 10.5 kcal/mol at −50 °C) are similar to those for **2a**, despite the large steric difference between the Pd-alkyl ligands in the two species.

In contrast, the ^{1}H NMR spectrum of **6b** at 22 °C contains two sets of 2-*Et*-Ph resonances (1:1 intensity ratio), which coalesce to a single set of resonances at elevated temperature due to chelate ring inversion (see Supporting Information). The activation parameters determined by line shape analysis are $\Delta H^‡$ = 15.7 kcal/mol, $\Delta S^‡$ = 1.2 eu, and $\Delta G^‡$ = 15.3 kcal/mol at 55 °C). The higher barrier for chelate ring inversion for **6b** versus **2a** and **6a** probably results from the larger size and greater attendant steric crowding of the *o*-Et substituent in **6b** compared to the *o*-OMe group in **2a** and **6a**.

Base-Free {[PO-OMe]Pd(R)}$_2$ Complexes. The reaction of **2a** and **3a** with 1 equiv of $B(C_6F_5)_3$ results in quantitative formation of {[PO-OMe]Pd(R)}$_2$ (R = CH_2SiMe_3 (**8a**), $CH_2{}^tBu$ (**9a**)) and $B(C_6F_5)_3$(py) (Scheme 3). X-ray crystallographic analysis shows that **8a** exists as a sulfonate-bridged dimer in the solid state (Figure 4). The central eight-membered ring adopts a chair conformation, with O(1), S(1), O(3), O(1A), S(1A), and O(3A) forming a plane and Pd(1) and Pd(1A) lying above and below this plane. The geometry at palladium is square planar, and the [PO]Pd chelate ring is puckered. The methoxy group of the pseudoequatorial 2-OMe-Ph ring (C(12)−C(17)) points toward Pd, but as for **2a**, the long Pd(1A)−O(4) distance (3.67 Å) rules out a significant interaction. The *ortho* hydrogen (H(20)) of the pseudoaxial 2-OMe-Ph ring (C(19)−C(24)) makes a short contact with Pd (H(20)−Pd(1A), 2.67 Å). Close M---H contacts involving the *ortho*-hydrogens of diarylphosphine ligands are common in square-planar d^8 metal complexes

(19) (a) Σ(Pd and O covalent radii) = 2.04 Å; Σ(Pd and O van der Waals radii) = 3.15 Å); Σ(Pd and H covalent radii) = 2.68 Å; Σ(Pd and H van der Waals radii) = 2.83 Å; radii taken from Webelements, see: http://www.webelements.com/. (b) The shortest Pd---H contacts are as follows: **2a**: Pd(1)−H(18), 2.9 Å; **6b**: Pd(1)−H(20A), 2.8 Å.

(20) Pd−OR_2 distances in neutral square-planar Pd(II) complexes are in the range 2.11–2.20 Å. (a) Bei, X.; Uno, T.; Norris, J.; Turner, H. W.; Weinberg, W. H.; Guram, A. S. *Organometallics* **1999**, *18*, 1840. (b) Kim, Y.; Verkade, J. G. *J. Organomet. Chem.* **2003**, *669*, 32. Pd−OR_2 distances in neutral five-coordinate Pd(II) complexes are in the range 2.92–3.00 Å. (c) Ma, J.-F.; Kojima, Y.; Yamamoto, Y. *J. Organomet. Chem.* **2000**, *616*, 149.

(21) Similar $^3J_{PH}$ values were reported for phosphinosulfonamide nickel methyl complexes in which the alkyl group is cis to the phosphine. Rachita, M. J.; Huff, R. L.; Bennett, J. L.; Brookhart, M. J. *Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 4627.

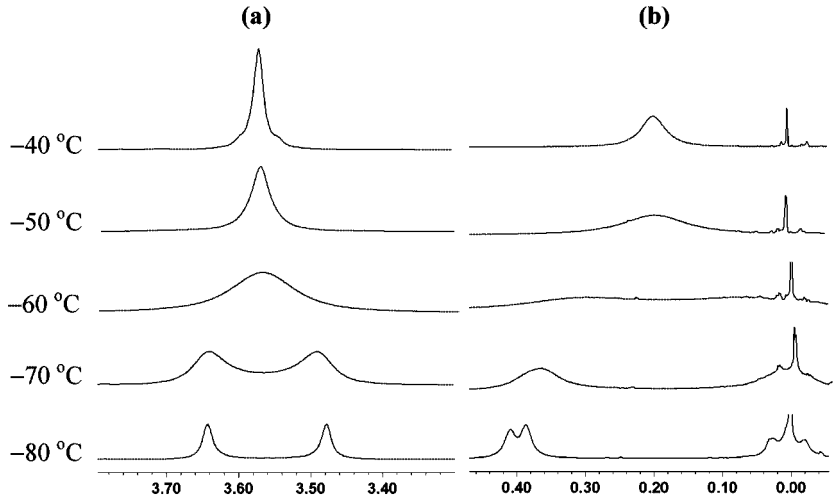
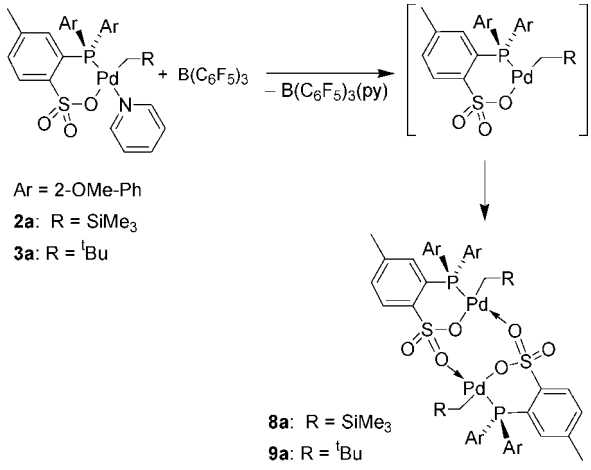


Figure 3. Variable-temperature ^{1}H NMR spectra (500 MHz) of [PO-OMe]Pd(CH_2SiMe_3)(py) (**2a**). The *OMe* (a) and Pd*C*H_2SiMe$_3$ (b) regions are shown. The singlet at $\delta = 0$ is due to $SiMe_4$. The chemical shift scale is in units of δ.

Scheme 3



and have been characterized as weak hydrogen bonds or agostic interactions.[22]

The NMR spectra of **8a** generated *in situ* in CD_2Cl_2 are identical to those of solutions of crystalline **8a**. The ^{1}H spectrum of **8a** contains a sharp OMe resonance (δ 3.57) and broad singlets for the methylene (δ 0.67) and methyl hydrogens (δ −0.31) of the $-CH_2SiMe_3$ group, and the ^{31}P spectrum contains a broad singlet at δ 28.1. These data do not differentiate between monomeric and dimeric structures. Complex **9a** is insufficiently soluble for NMR analysis.

Generation of [PO-OMe]Pd(η^3-CH_2Ph). Abstraction of pyridine from **4a** by $B(C_6F_5)_3$ produces the CD_2Cl_2-soluble complex [PO-OMe]Pd(η^3-CH_2Ph) (**10a**), which is presumed to be monomeric (eq 6). The ^{13}C NMR Pd*C*H_2Ph resonance is shifted downfield by 16.9 ppm from the corresponding signal

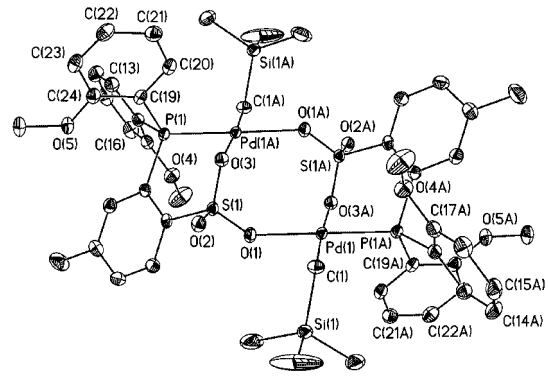
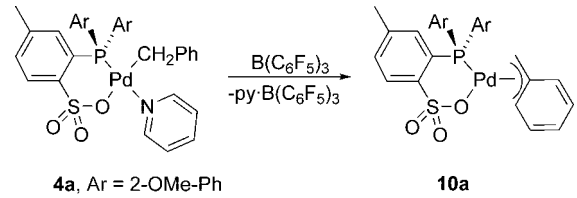


Figure 4. Molecular structure of {[PO-OMe]Pd(CH_2SiMe_3)}$_2$ (**8a**). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): Pd(1)−P(1A) 2.2009(9), Pd(1)−O(3A) 2.201(2), Pd(1)−C(1) 2.027(3), Pd(1)−O(1) 2.142(2), S(1)−O(3) 1.469(2), S(1)−O(2) 1.435(2), S(1)−O(1) 1.471(2), O(3A)−Pd(1)−P(1A) 81.05(6), C(1)−Pd(1)−O(1) 93.2(1), O(3A)−Pd(1)−O(1) 89.60(8), P(1A)−Pd(1)−C(1) 95.97(9).

in **4a** and has a large $^1J_{CH}$ value (154 Hz) consistent with η^3-coordination.[23]



(6)

Ethylene Polymerization by [PO]Pd(R)(py) Catalysts. Ethylene polymerization results are summarized in Table 1. Under conditions similar to those used by Pugh and co-workers for ethylene/MA copolymerization (toluene, 80 °C, 30 atm ethylene, 1 h),[4] [PO-OMe]PdR catalysts generated *in situ* from $Pd(dba)_2$ and 1.2 equiv of [**1a**]H produce polyethylene in low and variable yield (entry 1). Ethylene uptake monitoring experiments show that the activity of the *in situ*-generated catalyst ceases after ca. 1 h at 80 °C. The loss of activity is

(22) (a) Angulo, I. M.; Bouwman, E.; van Gorkum, R.; Lok, S. M.; Lutz, M.; Spek, A. L. *J. Mol. Catal.* **2003**, *202*, 97. (b) Dossett, S. J.; Gillon, A.; Orpen, A. G.; Fleming, J. S.; Pringle, P. G.; Wass, D. F.; Jones, M. D. *Chem. Commun.* **2001**, *699*. (c) Cooley, N. A.; Green, S. M.; Wass, D. F.; Heslop, K.; Orpen, A. G.; Pringle, P. G. *Organometallics* **2001**, *20*, 4769. (d) Yao, W.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, *254*, 105. (e) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(23) Albers, I.; Álvarez, E.; Cámpora, J.; Maya, C. M.; Palma, P.; Sánchez, L. J.; Passaglia, E. *J. Organomet. Chem.* **2004**, *689*, 833.

Table 1. Ethylene Polymerization with [PO]-Palladium Catalysts[a]

run	catalyst	[Pd] (mM)	T (°C)	P (atm)	time (h)	yield (g)	productivity (g/mol·h·atm)	M_n[b] GPC (10^3)	M_w/M_n[b] GPC	M_n NMR (10^3)	Me br[c]	no. chains/Pd	% int. unsat.[d]	T_m (°C)
1	[**1a**]H/Pd(dba)$_2$	0.40	80	30	1	0.40	700	12.1	2.3	14.2	2.2	1.4	39	133.9
2	[**1b**]H/Pd(dba)$_2$	2.0	135	15	3	4.70	3100			4.10	5.8	11		100.0
3[e]	[**1b**]H/Pd(dba)$_2$	2.0	135	15	3	15.9	10 600			0.20	9.0	800		80.1
4	**6b**	0.10	80	30	1	1.47	9800	18.8	2.1	21.8	1.4	14	44	136.1
5	**6b**	0.20	80	30	1	2.30	7700	24.7	2.5	27.2	1.2	8.5	42	134.4
6	**6a**	0.20	80	30	1	4.09	13 600	17.1	2.2	17.9	0.8	23	30	133.4
7	**2a**	0.25	80	30	1	2.87	7700	17.9	2.3	20.8	1.1	11	26	138.4
8	**6a**	0.20	80	15	1	3.43	22 900	15.9	2.4	17.4	1.6	20	38	131.6
9	**6a**	0.20	120	15	1	3.18	21 200	4.00	2.5	4.80	5.1	66	57	124.3
10	**6a**	0.20	80	30	18	22.9	4200	14.8	2.9	17.6	1.0	130	26	133.6
11	**6a**	0.10	80	2	1	0.76	76 100	10.5	2.4	11.5	7.0	13	74	125.9
12	**6a**	0.10	80	5	1	1.06	42 500	18.6	2.0	17.7	3.4	12	38	130.1
13	**6a**	0.10	80	10	1	1.82	36 400	18.9	2.1	19.3	1.8	19	47	131.9
14	**6a**	0.10	80	20	1	2.32	23 200	18.9	2.1	20.1	1.8	23	30	133.0
15	**6a**	0.10	80	30	1	2.50	16 600	19.1	2.1	19.3	1.2	26	18	134.2
16	**6a**	0.20	80	5	1	1.54	30 800	13.5	2.5	16.1	3.2	9.6	47	130.4
17[f]	**6a**	0.22	80	5	1	1.82	33 000	6.20	2.0	7.20	3[g]	23	60[h]	110.7

[a] These data are representative for [PO]Pd catalysts. Under the specified isothermal conditions, polymer yields varied 10–15%, but polymer structure varied very little. The solvent was toluene in all cases. Total solution volume was 50 mL in all cases. [b] Determined by GPC using universal calibration. [c] Number of methyl branches per 1000 C. Does not include Me end groups. Determined by ^{1}H NMR assuming one Me end per chain. [d] (internal unsaturation)/(total unsaturation) × 100. [e] CH_3CN (2.2 M) also added. [f] Hexene (0.80 M) also added. [g] Also contains 16 Bu branches and 2 Me chain ends/1000 C. [h] Also contains 7% vinylidene unsaturation.

accompanied by Pd^0 formation. Complexes **2a**, **6a**, and **6b** polymerize ethylene in toluene at 80 °C over the ethylene pressure range of 2−30 atm. These discrete catalysts exhibit sustained catalyst activity even after 18 h at 80 °C (entry 10).

Polyethylene Structure. Complexes **2a**, **6a**, and **6b** produce linear polyethylene with low levels of methyl branches. Longer branches were not observed by ^{13}C NMR. The polyethylene T_m values vary between 130 and 138 °C.[24] The ^{1}H NMR spectra of the polyethylenes contain resonances for terminal (PCH═CH$_2$, i.e., vinyl end groups) and internal (PCH═CHP) double bonds (P = polymer chain, Figure 5). The ^{1}H NMR data do not establish the position of the internal double bonds relative to the chain ends. However, the ^{13}C NMR spectra of low molecular weight polyethylenes generated at high polymerization temperature (entries 2, 9) and/or in the presence of acetonitrile (entry 3) show that the internal olefins are mainly 2-olefins (90%), with only small amounts of 3-olefins (10%), and that the *E*/*Z* ratio is ca. 3:1 (Figure 6).[25–27] The polyethylenes obtained with **2a**, **6a**, and **6b** have number average molecular weights (M_n's) between 6000 and 19 000 and polydispersities in the range of 2.0 to 2.9, as determined by GPC. The M_n values determined by ^{1}H NMR assuming that there is one C═C unit per chain are similar to those obtained by GPC.

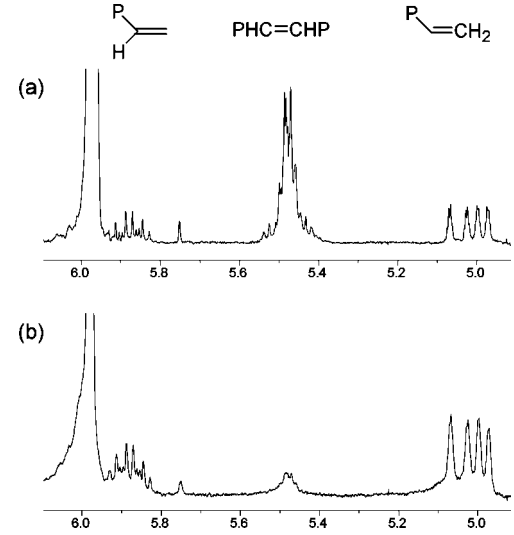


Figure 5. Olefin region of the ^{1}H NMR spectra of polyethylenes obtained with [PO-OMe]PdMe(py) (**6a**). The chemical shift scale is in δ units. The assignments are indicated by the structures (P = polyethylene chain). ^{1}H NMR conditions: 120 °C in $CDCl_2CDCl_2$ (residual ^{1}H peak at δ 5.98 and one ^{13}C satellite at δ 5.76). (a) Polymer from entry 11 in Table 1; ethylene pressure 2 atm; 74% internal olefins. (b) Polymer from entry 15 in Table 1; ethylene pressure 30 atm; 18% internal olefins.

Influence of Reaction Conditions on Polymerization Behavior. Increasing the polymerization temperature from 80 to 120 °C results in a significant drop in M_n but does not strongly influence the polymer yield or the number of methyl branches (entry 8 vs 9, Table 1).

As shown by entries 11−15 in Table 1, and Figure 7, the polymer yield increases as the ethylene pressure is raised but begins to level off above ca. 20 atm, and M_n increases between 2 and 10 atm but is constant between 10 to 30 atm. Increasing the ethylene pressure decreases the number of Me branches (entries 11−15). There is some tendency for the internal-olefin/terminal-olefin ratio to decrease as the ethylene pressure is raised (entries 11–15); however these values are somewhat variable.

[PO]Ligand Effects. [PO-OMe]Pd(Me)(py) (**6a**) is slightly more active in ethylene polymerization than [PO-Et]Pd(Me)(py)

(24) For a discussion of the relationship between branching and thermal behavior of polyethylene see: Sworen, J. C.; Smith, J. A.; Wagener, K. B.; Baugh, L. S.; Rucker, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 2228.

(25) ^{1}H NMR assignments for polymers are based on ref 24 and: (a) Smith, J. A.; Brzezinska, K. R.; Valenti, D. J.; Wagener, K. B. *Macromolecules* **2000**, *33*, 3781. (b) Baughman, T. W.; Sworen, J. C.; Wagener, K. B. *Macromolecules* **2006**, *39*, 5028. (c) Cheng, H. N.; Lee, G. H. *J. Polym. Sci. B: Polym. Phys.* **1987**, *25*, 2355.

(26) ^{13}C NMR assignments for polymers are based on: (a) Barrera-Galland, G.; de Souza, R. F.; Santos-Mauler, R.; Nunes, F. F. *Macromolecules* **1999**, *32*, 1620. (b) Randall, J. C.; Hsieh, E. T. In *NMR and Macromolecules*; ACS Symposium Series 247; Randall, J. C., Ed.; American Chemical Society: Washington, D.C., 1984; Chapter 9. (c) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: New York, 1987; pp 192–193.

(27) Control experiments show that the internal olefins are produced during the polymerization reaction, that only a minor degree of isomerization occurs during polymer isolation and NMR analysis, and that palladium black does not cause isomerization of polymer double bonds under the conditions used for polymerization, polymer isolation, or NMR analysis.

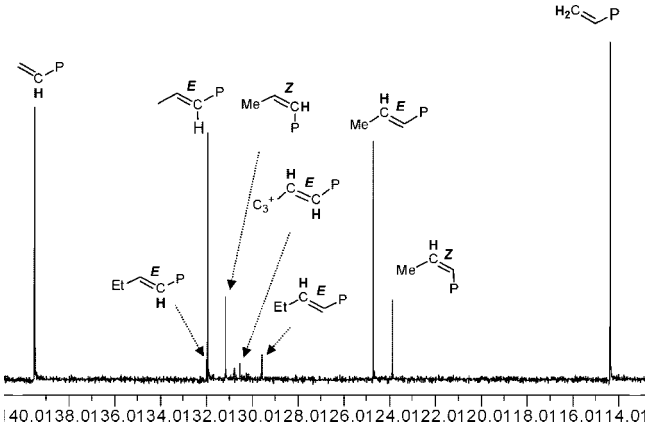


Figure 6. Olefin region of the $^{13}C\{^1H\}$ NMR spectrum of a low molecular weight polyethylene produced by *in situ*-generated [PO-Et]PdR catalyst (entry 3 in Table 1). The chemical shift scale is in units of δ. NMR conditions: 120 °C in $CDCl_2$.

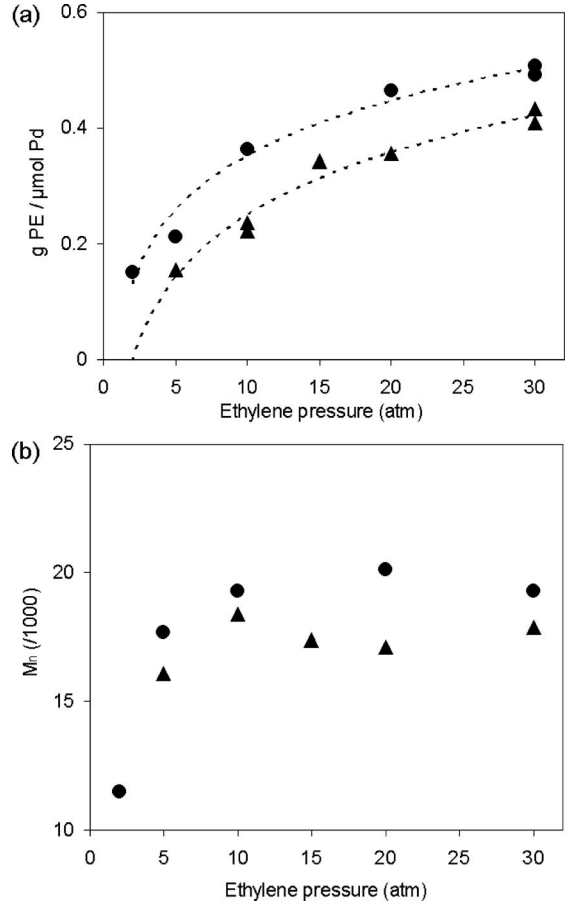
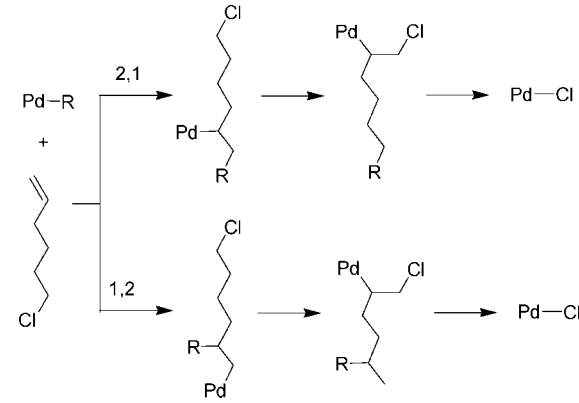


Figure 7. Effect of ethylene pressure on (a) polymer yield and (b) molecular weight in ethylene polymerization by **6a**. Polymerization conditions: toluene (50 mL), 80 °C, 1 h reaction. Circles: 5 μmol of **6a** (entries 11–15 in Table 1). Triangles: 10 μmol of **6a**. The curves merely guide the eye.

(**6b**), but the two catalysts produce polymers with very similar molecular weight and structure (entries 4 vs 15; 5 vs 6).

α-Olefin Copolymerization. The addition of 1-hexene or 1-tridecene at high ethylene pressure (30 atm) does not affect polymer yield, M_n, or structure. Under these high-pressure conditions, the α-olefin is not incorporated in the polymer. In addition, analysis of the liquid phase after the polymerization showed that no significant α-olefin isomerization occurs.

Scheme 4



In contrast, at 5 atm ethylene pressure, the addition of 1-hexene (0.8 M, which corresponds to ca. twice the ethylene concentration under these conditions)[28] results in the formation of an ethylene/1-hexene copolymer (entry 17, Table 1; 3.4 mol % hexene incorporation). The ^{13}C NMR spectra of the ethylene/hexene copolymers show that methyl and butyl branches are present but that ethyl, propyl, and pentyl branches are not. Compared to an ethylene homopolymerization under similar conditions (entry 16 in Table 1), the incorporation of 1-hexene does not affect the polymer yield or the number of Me branches, but causes a ca. 2-fold drop in M_n. The ^1H NMR spectrum of the ethylene/hexene copolymers contain resonances for the 1- and 2-olefin chain ends observed in the ethylene homopolymers and a vinylidene resonance ($H_2C{=}CRR'$; δ 4.76, 120 °C, $CDCl_2CDCl_2$). The vinylidene units are most likely formed by 1,2-hexene insertion followed by β-H elimination.[29]

Chain-Walking and Olefin Isomerization. To probe if [PO]PdR species can chain-walk, the reaction of the base-free dimer **9a** with 6-chloro-1-hexene was investigated. As shown in Scheme 4, insertion of 6-chloro-1-hexene followed by chain-walking would produce a β-chloro-alkyl complex, which is expected to undergo fast β-Cl elimination to produce [PO-OMe]PdCl.[30]

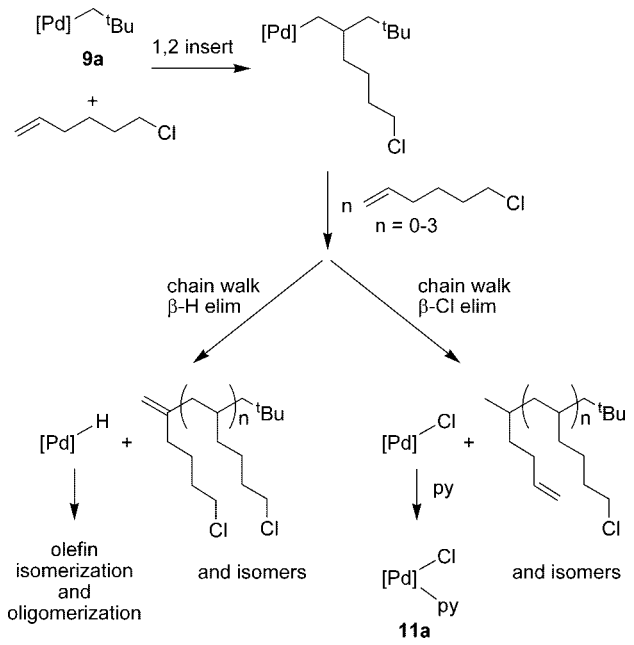
The reaction of **9a** with 6 equiv of 6-chloro-1-hexene in CD_2Cl_2 at room temperature does yield [PO-OMe]PdCl, which was characterized as the pyridine adduct [PO-OMe]Pd(Cl)(py) (**11a**), along with a complex mixture of chlorohexenes (≥4 isomers), undecenes (≥6 isomers), chloroundecenes (≥6 isomers), and oligomers derived from multiple (1−4) insertions of 6-chloro-1-hexene into [PO-OMe]Pd$CH_2{}^t$Bu or [PO-OMe]-PdH followed by β-H or β-Cl elimination. These products are likely formed by insertion, chain-walking, β-H elimination, and β-Cl elimination, as outlined in Scheme 5 (similar chemistry could occur after 2,1 insertion). To rule out the possibility that [PO-OMe]PdCl is formed by direct reaction of the C−Cl bond of 6-chloro-1-hexene (e.g., by oxidative addition), **9a** was treated with a mixture of 6-chloro-1-hexene and 1-chloropentane. The 6-chloro-1-hexene was converted to similar products observed in the absence of 1-chloropentane, while the 1-chloropentane

(28) Lee, L.; Ou, H.; Hsu, H. *Fluid Phase Equilib.* **2005**, *231*, 221.

(29) Competitive 2,1 hexene insertion cannot be ruled out, since this process would produce a Bu branch following further chain growth, or an internal olefin following chain transfer, both of which are observed.

(30) (a) Foley, S. R.; Stockland, R. A., Jr.; Shen, H.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 4350. (b) Shen, H.; Jordan, R. F. *Organometallics* **2003**, *22*, 1878. (c) Gaynor, S. G. *Macromolecules* **2003**, *36*, 4692. (d) Stockland, R. A., Jr.; Foley, S. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 796. (e) Zhu, G.; Lu, X. *Organometallics* **1995**, *14*, 4899. (f) Kang, M.; Sen, A.; Zakharov, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 12080.

Scheme 5



was not consumed. These results provide strong evidence that [PO]Pd(R) species can chain-walk and isomerize olefins.

Polymerization Mechanism. The polymerization mechanism in Scheme 6 is consistent with the observations described above. The active [PO]Pd(1-alkyl) species likely exist as equilibrium mixtures of the pyridine and ethylene adducts **I** and **II**. NMR studies show that this equilibrium lies far to the side of **I** at room temperature and low ethylene pressure. The increase in polymer yield at higher ethylene pressures results from shifting of the equilibrium to the ethylene adduct **II**. **II** can undergo chain transfer to monomer to generate the observed 1-olefin chain ends. Alternatively **II** can undergo insertion to give a base-free [PO]Pd(1-alkyl) species, **III**, which may exist transiently as a β-agostic species (not shown).[5] **III** can be trapped by ethylene to regenerate **II** or isomerize by chain-walking to a [PO]Pd(CMeHP) secondary alkyl species (**IV**). **IV** is trapped by ethylene, generating a [PO]Pd(CMeHP)(ethylene) complex, **V** (which would be in equilibrium with the corresponding pyridine adduct). **V** can undergo chain transfer to release a 2-olefin or insertion to generate a methyl branch. The observed increase in the number of methyl branches and the tendency for increased internal unsaturation with decreasing ethylene pressure are consistent with competitive ethylene trapping and chain-walking of **III**. **IV** can chain-walk further, leading to 3-olefin or (3+)-olefin chain ends or longer branches, but because chain-walking is slow, these products are present only at trace levels or are not observed. Our results are also consistent with chain transfer by associative olefin exchange of the [PO]Pd(H)(olefin) species formed by β-H elimination of **III** or **IV** (i.e., chain-walk intermediates). An alternative source of Me branches is 2,1 insertion of vinyl chain ends into [PO]PdH followed by growth. However, the lack of reactivity of added α-olefin at high ethylene pressure and the lack of an increase in Me branches in ethylene/1-hexene copolymerization compared to ethylene homopolymerization at low ethylene pressure imply that this process is unimportant. An alternative source of internal olefins is Pd-catalyzed isomerization of vinyl chain ends under the reaction conditions, as observed in Scheme 5. This process is probably important at low ethylene pressure, but the lack of reactivity of added α-olefin at 30 atm ethylene pressure suggests that it is insignificant at high ethylene pressure. The polymerization behavior of base-free $\{[PO]PdR\}_2$ species such as **8a** and **9a** will be discussed elsewhere.

Conclusions

[PO-OMe]Pd(R)(L) and [PO-OMe]Pd(R)(L) complexes are easily prepared by the reaction of [PO-OMe]H ([**1a**]H) or [PO-Et]H ([**1b**]H) with L'_2PdR_2 precursors. [PO]Pd(R)(L) complexes have square-planar structures in which the alkyl group is cis to the phosphine, and the [PO]Pd chelate rings are puckered and invert rapidly on the NMR time scale. The reaction of [PO-OMe]Pd(R)(py) (R = CH_2SiMe_3 (**2a**), $CH_2{}^tBu$ (**3a**)) with $B(C_6F_5)_3$ yields $\{[PO\text{-}OMe]Pd(R)\}_2$ (R = CH_2SiMe_3 (**8a**), $CH_2{}^tBu$ (**9a**)). **8a** is a sulfonate-bridged dimer in the solid state. **2a**, [PO-OMe]Pd(Me)(py) (**6a**), and [PO-Et]Pd(Me)(py) (**6b**) polymerize ethylene to linear polyethylene that contains low levels of Me branches, one C=C unit per chain (mostly 1- or 2-olefins), and M_n in the range 6000 to 19 000. **6a** is slightly more active but produces polymers with similar molecular weight and structure compared to **6b**. **6a** copolymerizes ethylene and hexene at low ethylene pressure (5 atm), but no α-olefin incorporation is observed at higher pressure (30 atm). A polymerization mechanism involving insertion and chain transfer of [PO]Pd(R)(ethylene) species (**II**), and ethylene trapping and much slower chain-walking of the $[PO]Pd(CH_2CH_2R)$ species (**III**) formed by insertion of **II**, is consistent with these results. The similarity of the ethylene polymerization behavior of **6a** and **6b** and the absence of Pd---OMe interactions in the solid-state structures of **2a** and **8a** suggest that Pd---OMe coordination is not important in the chemistry discussed here.

Experimental Section

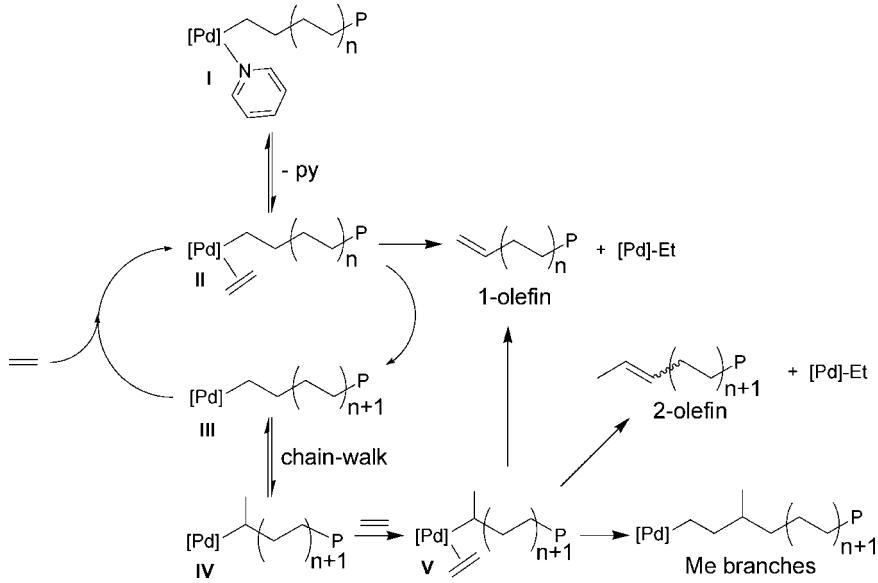
General Procedures. All experiments were performed using drybox or Schlenk techniques under a nitrogen atmosphere. Nitrogen was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. Diethyl ether was distilled from sodium benzophenone ketyl. CH_2Cl_2 and CD_2Cl_2 were distilled from CaH_2. Pentane and toluene were purified by passage through columns of activated alumina and BASF R3-11 oxygen scavenger. $Pd(dba)_2$ and $PdCl_2$ (Strem), and $(COD)PdCl_2$ (Boulder) were used as received. [PO-OMe]H ([**1a**]H) and [PO-Et]H ([**1b**]H) were synthesized by literature routes; details are provided in the Supporting Information.[4b,8e,9] $\{PdMe_2(pyridazine)\}_n$,[31] $(TMEDA)PdMe_2$,[32] and $(COD)Pd(CH_2Si(CH_3)_3)_2$[33] were prepared by literature procedures or modifications thereof. Ethylene (polymer grade) was purchased from Matheson and used as received. 1-Hexene was dried over sodium and vacuum distilled prior to use. Elemental analyses were performed by Midwest Microlab, LLC.

NMR spectra of organometallic complexes were recorded at ambient temperature unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent resonances. ^{11}B chemical shifts are reported relative to $BF_3(Et_2O)$, and ^{19}F chemical shifts are reported relative to $CFCl_3$. Coupling constants are given in Hz. J_{CH} values were determined from gated-$\{^1H\}^{13}C$ spectra.

NMR assignments for **2a** were determined by NOESY, HMQC, and $^1H\{^{31}P\}$ NMR experiments. NMR assignments for all other complexes were made by comparison of chemical shift patterns

(31) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1987**, *336*, C55.
(32) De Graaf, W.; Boersma, J.; Smeets; Wilberth, J. J.; Spek, A. L.; Van Koten, G. *Organometallics* **1989**, *8*, 2907.
(33) Pan, Y.; Young, G. B. *J. Organomet. Chem.* **1999**, *577*, 257.

Scheme 6



and J_{HH} and J_{PC} values to those for **2a**. The numbering scheme for NMR assignments is given in Figure 8.

NMR spectra for polymers were obtained as follows. A mixture of polymer (^{1}H NMR: 30–60 mg; ^{13}C NMR: 85–95 mg) and $CDCl_2CDCl_2$ (0.7 g) in an NMR tube was heated to 120 °C (≤15 min), affording a homogeneous solution. The tube was inserted into a preheated NMR probe at 120 °C, and NMR spectra were obtained after a 5 min temperature equilibration period. ^{1}H NMR: 400 MHz, pulse width 90°, acquisition time 3.7 s, pulse delay 42 s; ^{13}C{^{1}H} NMR: 100 MHz, pulse width 60°, acquisition time 4.0 s; pulse delay 4.0 s.

Pd(R)$_2$(py)$_2$ Complexes. Pd(R)$_2$(py)$_2$ complexes (R′ = CH_2SiMe_3, $CH_2{}^tBu$, CH_2Ph) were prepared by the method of Cámpora.[34] *cis*-Pd(CH_2SiMe_3)$_2$(py)$_2$ was isolated as a yellow crystalline solid (50%). Isolation of *cis*-Pd(CH_2Ph)$_2$(py)$_2$ and *cis*-Pd($CH_2{}^tBu$)$_2$(py) was more difficult due to their thermal sensitivity, and crude samples of these complexes were used in the syntheses of [PO-OMe]Pd($CH_2{}^tBu$)(py) and [PO-OMe]Pd(CH_2Ph)(py), resulting in lower yields in these cases.

Synthesis of [PO-OMe]Pd(CH_2SiMe_3)(py) (2a) from Pd(CH_2SiMe_3)$_2$(py)$_2$. A solution of Pd(CH_2SiMe_3)$_2$(py)$_2$ (0.482 g, 1.10 mmol) in CH_2Cl_2 (20 mL) was cooled to −78 °C. A solution of [PO-OMe]H (0.458 g, 1.10 mmol) in CH_2Cl_2 (15 mL) was added dropwise while the mixture was stirred. The resulting clear brown solution was warmed to room temperature and stirred for 1 h. The mixture was concentrated under vacuum to 5 mL and placed in a freezer at −20 °C. Several fractions of colorless crystals were collected by filtration. The crystals became opaque upon drying under vacuum. Yield: 0.511 g (68%). Mp: 186 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 8.82 (d, J_{HH} = 5, 2H, *o*-py), 7.88 (m, 4H, *p*-py/H^3-$ArSO_3$/H^6-ArOMe), 7.52 (m, 4H, *m*-py/H^4-ArOMe), 7.24 (d, J_{HH} = 8, 1H, H^4-$ArSO_3$), 7.20 (d, J_{PH} = 11, 1H, H^6-$ArSO_3$), 7.08 (t, J_{HH} = 8, 2H, H^5-ArOMe), 6.95 (dd, J_{HH} = 8, J_{PH} = 4.6, 2H, H^3-ArOMe), 3.61 (s, 6H, O*Me*), 2.26 (s, 3H, *Me*-$ArSO_3$), 0.30 (d, J_{PH} = 5, 2H, C*H*$_2$SiMe$_3$), −0.58 (s, 9H, CH_2SiMe_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 161.0 (s, C^2-ArOMe), 151.5 (s, *o*-py), 146.2 (d, J_{PC} = 14, C^2-$ArSO_3$), 139.0 (s, *p*-py), 138.5 (d, J_{PC} = 8, C^3-$ArSO_3$), 135.6 (d, J_{PC} = 2, C^6-$ArSO_3$), 133.8 (d, J_{PC} = 2, *m*-py), 131.1 (s, C^4-$ArSO_3$), 127.8 (d, J_{PC} = 9, C^6-ArOMe), 127.6 (s, C^5-$ArSO_3$), 126.9 (d, J_{PC} = 88, C^1-$ArSO_3$), 125.7 (d, J_{PC} = 2, C^5-ArOMe), 120.9 (d, J_{PC} = 13, C^4-ArOMe), 116.8 (d, J_{PC} = 55, C^1-ArOMe), 111.9 (d, J_{PC} = 4, C^3-ArOMe), 55.4 (s, O*Me*), 21.5 (s, *Me*-$ArSO_3$), 7.0 (s, *C*H$_2$SiMe$_3$), 1.4 (s, CH$_2$Si*Me*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 24.6 (s). Anal. Calcd for $C_{30}H_{36}NO_5PPdSSi$: C, 52.36; H, 5.27; N, 2.04. Found: C, 52.10; H, 5.23; N, 2.18.

Synthesis of [PO-OMe]Pd(CH_2SiMe_3)(py) (2a) from (COD)Pd(CH_2SiMe_3)$_2$. A flask was charged with (COD)Pd(CH_2SiMe_3)$_2$ (0.233 g, 0.60 mmol) and [PO-OMe]H (0.224 g, 0.539 mmol) and cooled to −78 °C, and THF (25 mL) was added by vacuum-transfer. The mixture was stirred for 45 min and then allowed to warm to room temperature. Pyridine (0.220 mL, 2.70 mmol) was added by syringe, and the mixture was stirred for 2.5 h. The volatiles were removed under vacuum. The resulting solid was triturated with pentane (25 mL) and dried under vacuum. The solid was dissolved in CH_2Cl_2 (25 mL) and filtered through Celite. The filtrate was concentrated to ca. 3 mL and stored at −35 °C, yielding several crops of colorless crystals. Yield: 0.280 g (81%).

[PO-OMe]Pd($CH_2{}^tBu$)(py) (3a). A solution of *cis*-Pd($CH_2{}^tBu$)$_2$(py)$_2$ (0.559 g, 1.37 mmol) and pyridine (1.0 mL, 12 mmol) in CH_2Cl_2 (15 mL) was cooled to −78 °C, and a solution of [PO-OMe]H (0.572 g, 1.37 mmol) in CH_2Cl_2 (10 mL) was added dropwise. The mixture was allowed to warm to room temperature and was stirred for 1.5 h. The resulting solution was filtered through a medium-porosity frit, concentrated under vacuum to 5 mL, and placed in a freezer at −20 °C. Several crops of colorless crystals were obtained by filtration. The crystals became opaque when dried under vacuum. Yield: 0.325 g (35%). Mp: 181 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 8.88 (d, J_{HH} = 5, 2H, *o*-py), 7.94 (m, 2H, H^6-ArOMe), 7.90 (t, J_{HH} = 8, 1H, *p*-py), 7.82 (dd, J_{HH} = 8, J_{PH} = 5, 1H, H^3-$ArSO_3$), 7.56 (t, J_{HH} = 8, 2H, *m*-py), 7.50 (t, J_{HH} = 8, 2H, H^4-ArOMe), 7.22 (m, 2H, H^2/H^4-$ArSO_3$), 7.10 (t, J_{HH} = 8, 2H, H^5-ArOMe), 6.96 (dd, J_{HH} = 8, J_{PH} = 4, 2H, H^3-ArOMe), 3.62 (s, 6H, O*Me*), 2.25 (s, 3H, *Me*-$ArSO_3$), 1.44 (d, J_{PH} = 6, 2H, C*H*$_2$CMe$_3$), 0.38 (s, 9H, C*Me*$_3$). ^{13}C{H} NMR (CD_2Cl_2): δ 161.4 (s, C^2-ArOMe), 151.5 (s, *o*-py), 146.4 (d, J_{PC} = 15, C^2-$ArSO_3$), 139.3 (d, J_{PC} = 14, C^5-$ArSO_3$), 138.9 (s, C^3-$ArSO_3$), 138.2 (d, J_{PC} = 8, C^6-$ArSO_3$), 135.5 (s, *p*-py), 133.8 (s, *m*-py), 131.0 (d, J_{PC} = 2, C^4-$ArSO_3$), 128.2 (d, J_{PC} = 9, C^6-ArOMe), 127.1 (d, J_{PC} = 50, C^1-$ArSO_3$), 125.6 (s, C^5-ArOMe), 121.0 (d, J_{PC} = 11, C^4-ArOMe), 116.3 (d, J_{PC} = 52, C^1-ArOMe), 111.8 (d, J_{PC} = 5, C^3-ArOMe), 55.6 (s, O*Me*), 39.6 (s, *C*Me$_3$), 35.1 (s, *C*H$_2$CMe$_3$), 32.4 (s, C*Me*$_3$), 21.5 (s, *Me*-$ArSO_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 25.7 (s). Anal. Calcd for $C_{31}H_{36}NO_5PPdS$: C, 55.40; H, 5.40; N, 2.08. Found: C, 55.15; H, 5.29; N, 1.98.

[PO-OMe]Pd(CH_2Ph)(py) (4a). A solution of *cis*-Pd(CH_2Ph)$_2$(py)$_2$ (0.864 g, 1.93 mmol) in CH_2Cl_2 (20 mL) was cooled to −78 °C. A solution of [PO-OMe]H (0.805 g, 1.93 mmol) in CH_2Cl_2

(34) Cámpora, J.; Conejo, M. D. M.; Mereiter, K.; Palma, P.; Pérez, C.; Reyes, M. L.; Ruiz, C. *J. Organomet. Chem.* **2003**, *683*, 220.

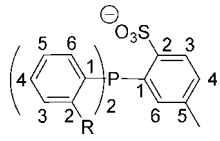


Figure 8. Numbering scheme used for NMR labeling.

(15 mL) was added dropwise. The dark solution was warmed to room temperature and stirred for 1 h. The solvent was removed under vacuum, and ether (20 mL) was added. The resulting suspension was stirred for 10 min at room temperature and filtered to afford a yellow solid. The solid was dried under vacuum, taken up in CH_2Cl_2 (20 mL), filtered, concentrated under vacuum, and cooled to −20 °C. Several crops of a bright yellow powder were obtained by filtration. Yield: 0.31 g (23%). Mp: 219 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 8.47 (d, J_{HH} = 5, 2H, *o*-py), 7.86 (dd, J_{HH} = 8, J_{PH} = 5, 1H, H^3-$ArSO_3$), 7.73 (m, 3H, *p*-py/H^6-ArOMe), 7.58 (t, J_{HH} = 7, 2H, *m*-py), 7.29 (t, J_{HH} = 6, 2H, H^5-ArOMe), 7.27 (d, J_{HH} = 8, 1H, H^4-$ArSO_3$), 7.15 (d, J_{PH} = 12, 1H, H^6-$ArSO_3$), 7.08 (t, J_{HH} = 7, 2H, H^4-ArOMe), 7.01 (dd, J_{HH} = 8, J_{PH} = 4, 2H, H^3-ArOMe), 6.84 (t, J_{HH} = 7, 1H, *p*-CH_2Ph), 6.73 (t, J_{HH} = 8, 2H, *m*-CH_2Ph), 6.40 (d, J_{HH} = 8, 2H, *o*-CH_2Ph) 3.69 (s, 6H, ArO*Me*), 2.45 (d, J_{PH} = 5, 2H, C*H*$_2$Ph), 2.25 (s, 3H, *Me*-$ArSO_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 161.3 (s, C^2-ArOMe), 151.0 (s, *o*-py), 146.4 (d, J_{PC} = 15, C^2-$ArSO_3$), 138.9 (d, J_{PC} = 6, C^3-$ArSO_3$), 138.4 (m, *ipso*-CH_2Ph), 138.1 (s, C^6-$ArSO_3$), 135.6 (s, *p*-py), 133.9 (s, *m*-py), 131.2 (d, J_{PC} = 2, C^5-$ArSO_3$), 128.6 (s, *o*-CH_2Ph), 128.3 (s, *m*-CH_2Ph), 128.0 (d, J_{PC} = 9, C^6-ArOMe), 127.6 (s, C^4-$ArSO_3$), 125.3 (s, *p*-CH_2Ph), 124.2 (s, C^5-ArOMe), 121.2 (d, J_{PC} = 11, C^4-ArOMe), 116.2 (d, J_{PC} = 55, C^1-ArOMe), 112.0 (d, J_{PC} = 4, C^3-ArOMe), 55.8 (s, O*Me*), 22.9 (s, *C*H_2Ph), 21.5 (s, *Me*-$ArSO_3$); the C^1-$ArSO_3$ was not observed, probably due to overlap with signals in the δ 124−128 region. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 20.7 (s). Anal. Calcd for $C_{33}H_{32}NO_5PPdS$: C, 57.27; H, 4.66; N, 2.02. Found: C, 57.41; H, 4.80; N, 2.04.

[PO-OMe]Pd(Me)(pyridazine) (5a). A suspension of [$PdMe_2$(pyridazine)]$_n$ (0.132 g, 0.610 mmol) in CH_2Cl_2 (15 mL) was cooled to −78 °C, and a solution of [PO-OMe]H (0.254 g, 0.610 mmol) in CH_2Cl_2 (15 mL) was added dropwise while the mixture was stirred. The resulting bright yellow suspension was allowed to warm to room temperature to afford a colorless solution. The solution was stirred at room temperature for 1 h, concentrated to 4 mL, and placed in a freezer at −20 °C. Several fractions of a microcrystalline white solid were collected by filtration. Yield: 0.263 g (70%). Mp: 80 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 9.42 (br s, 2H, $C_4H_4N_2$), 7.95 (dd, J_{HH} = 7.9, J_{PH} = 5, 1H, H^3-$ArSO_3$), 7.74 (br s, 2H, $C_4H_4N_2$), 7.60 (br s, 2H, H^6-ArOMe), 7.54 (t, J_{HH} = 8, 2H, H^4-ArOMe), 7.28 (d, J_{HH} = 8, 1H, H^4-$ArSO_3$), 7.10 (d, J_{PH} = 12, 1H, H^6-$ArSO_3$), 7.03 (t, J_{HH} = 8, 2 H, H^5-ArOMe), 6.97 (dd, J_{HH} = 8, J_{PH} = 5, 2H, H^3-ArOMe), 3.66 (s, 6H, ArO*Me*), 2.26 (s, 3H, *Me*-$ArSO_3$), 0.44 (d, J_{PH} = 2, 3H, Pd-*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 161.2 (d, J_{PC} = 2, C^2-ArOMe), 153.5 (br s, $C_4H_4N_2$), 146.4 (d, J_{PC} = 15, C^2-$ArSO_3$), 139.1 (d, J_{PC} = 6, C^6-$ArSO_3$), 138.0 (br s, C^5-$ArSO_3$), 135.6 (d, J_{PC} = 2, C^3-$ArSO_3$), 133.7 (s, C^5-ArOMe), 131.2 (s, C^4-$ArSO_3$), 129.7 (br s, $C_4H_4N_2$), 128.1 (d, J_{PC} = 9, C^6-ArOMe), 127.7 (d, J_{PC} = 49, C^1-$ArSO_3$), 121.0 (d, J_{PC} = 11, C^4-ArOMe), 116.9 (d, J_{PC} = 57, C^1-ArOMe), 112.1 (d, J_{PC} = 5, C^3-ArOMe), 55.9 (s, ArO*Me*), 21.5 (s, *Me*-$ArSO_3$), 3.6 (s, Pd-*Me*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 22.2 (s). Anal. Calcd for $C_{26}H_{27}N_2O_5PPdS$: C, 50.62; H, 4.41; N, 4.54. Found: C, 50.31; H, 4.46; N, 4.53.[35]

[PO-OMe]Pd(Me)(py) (6a). A solution of (TMEDA)$PdMe_2$ (7.37 g, 29.2 mmol) in CH_2Cl_2 (130 mL) was prepared, and [PO-OMe]H (12.2 g, 29.2 mmol) was added. The mixture was stirred for 1 h at room temperature. Pyridine (12.1 mL, 150 mmol) was added, and the resulting pale yellow solution was stirred for 35 min. The mixture was concentrated to ca. 20 mL under vacuum, and Et_2O (100 mL) was added. A pale yellow precipitate formed and was collected by filtration and purified twice by dissolution in CH_2Cl_2 (20 mL) and precipitation with Et_2O (100 mL). The final product was dried under vacuum to give **6a** as a white powder. Yield: 12.5g, 69%. ^{1}H NMR (CD_2Cl_2): δ 8.75 (d, J_{HH} = 5, 2H, *o*-py), 7.94 (dd, J_{HH} = 6, J_{PH} = 5, 1H, H^3-$ArSO_3$), 7.87 (t, J_{HH} = 8, 1H, *p*-py), 7.70–7.52 (br, 4H, H^4-ArOMe/H^6-ArOMe), 7.50 (t, J_{HH} = 7, 2H, *m*-py), 7.27 (d, J_{HH} = 8, 1H, H^4-$ArSO_3$), 7.11–6.97 (m, 5H, H^6-$ArSO_3$/H^3-ArOMe/H^5-ArOMe), 3.67 (s, 6H, O*Me*), 2.25 (s, 1H, *C*H_3ArSO_3), 0.23 (d, 3H, J_{PH} = 3, Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 161.0 (s, C^2-ArOMe), 150.7 (s, *o*-py), 146.3 (d, J_{PC} = 16, C^2-$ArSO_3$), 138.9 (d, J_{PC} = 8, C^3-$ArSO_3$), 138.6 (s, C^6-$ArSO_3$), 137.8 (br s, C^4-ArOMe), 135.4 (s, *p*-py), 133.5 (s, *m*-py), 131.1 (s, C^4-$ArSO_3$), 127.8 (d, J_{PC} = 8, C^5-$ArSO_3$), 127.5 (d, J_{PC} = 50, C^1-$ArSO_3$), 125.4 (s, C^5-ArOMe), 120.8 (d, J_{PC} = 12, C^6-ArOMe), 116.7 (d, J_{PC} = 57, C^1-ArOMe), 111.8 (s, C^3-ArOMe), 55.6 (s, O*Me*), 21.2 (s, *C*H_3ArSO_3), 0.27 (d, J_{PC} = 4, PdMe). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 19.8 (s). ESI-MS (CH_2Cl_2/MeOH, 1:1 by volume, positive ion scan, *m*/*z*): 616.0 (MH^+).

[PO-Et]Pd(Me)(py) (6b). A solution of [PO-Et]H (1.61 g, 3.90 mmol) and (TMEDA)$PdMe_2$ (0.985 g, 3.90 mmol) in CH_2Cl_2 (40 mL) was cooled to −78 °C and stirred for 20 min. Pyridine (1.57 mL, 19.5 mmol) was added dropwise over 2 min. The mixture was stirred at −78 °C for 30 min, warmed to room temperature, and stirred for 45 min. A pale yellow solution formed. The volatiles were removed under vacuum to afford a pale yellow solid. This material was recrystallized from CH_2Cl_2/hexanes (1:1 by volume, −30 °C, 4 days) to afford [PO-Et]Pd(Me)(py) as pale yellow crystals, which were isolated by filtration, washed with hexanes, and dried under vacuum. Yield: 0.980 g, 41%. ^{1}H NMR (CD_2Cl_2): δ 8.80 (m, 2H, H^2-py), 8.05 (dd, J_{HH} = 8, J_{PH} = 5, 1H, H^3-$ArSO_3$), 7.88 (m, 1H, H^4-py), 7.50 (m, 2H, H^3-py), 7.4–7.2 all other aromatic protons (broadened due to exchange), 6.85 (d, J_{PH} = 10, 1H, H^6-$ArSO_3$), 3.22 (s, 2H, ArC*H*$_2$CH$_3$), 3.10 (s, 1H, ArC*H*$_2$CH$_3$), 2.77 (s, 1H, ArC*H*$_2$CH$_3$), 2.22 (s, 3H, C*H*$_3$$ArSO_3$), 1.58 (s, $ArCH_2CH_3$), 0.88 (s, $ArCH_2CH_3$), 0.40 (d, J_{PH} = 2, 3H, Pd-C*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 150.7 (s, *o*-py), 148.5 (d, J_{PC} = 43, C^1-ArEt), 147.2 (d, J_{PC} = 14, C^2-$ArSO_3$), 140.4 (d, J_{PC} = 8, C^3-$ArSO_3$), 138.8 (s, C^5-$ArSO_3$), 136.3 (br, C^6-ArEt), 135.2 (s, *p*-py), 134.1 (br s, C^5-ArEt), 132.3 (s, *m*-Py), 131.7 (d, J_{PC} = 43, C^2-ArEt), 129.9 (br s, C^3-ArEt), 129.3 (d, J_{PC} = 9, C^6-$ArSO_3$), 126.8 (d, J_{PC} = 48, C^1-$ArSO_3$), 126.4 (br s, C^4-ArEt), 125.6 (s, C^4-$ArSO_3$), 29.0 (s, Ar*C*H_2CH$_3$), 28.0 (s, $ArCH_2CH_3$), 21.2 (s, *C*$H_3$$ArSO_3$), 15.6 (s, $ArCH_2CH_3$), 13.9 (s, $ArCH_2CH_3$), 3.2 (s, Pd-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 19.5 (s). ESI-MS (CH_2Cl_2/MeOH, 1:1 by volume, positive ion scan, *m*/*z*): 612.0 (MH^+). Anal. Calcd for $C_{29}H_{32}NO_3PPdS(0.12CH_2Cl_2)$ (CH_2Cl_2 content determined by ^{1}H NMR): C, 56.75; H, 5.57; N, 2.20. Found: C, 56.77; H, 5.13; N, 2.13.

[PO-OMe]Pd(Me)(PPh_3) (7a). A solution of (TMEDA)$PdMe_2$ (0.129 g, 0.511 mmol) and PPh_3 (0.134 g, 0.511 mmol) in CH_2Cl_2 (5 mL) was cooled to −78 °C, and a solution of [PO-OMe]H (0.213 g, 0.511 mmol) in CH_2Cl_2 (10 mL) was added dropwise while the mixture was stirred. The mixture was allowed to warm to room temperature and was stirred for 2 h. The solvent was removed under vacuum to give an off-white solid. The solid was recrystallized from a mixture of CH_2Cl_2 (8 mL) and hexanes (2 mL) at −20 °C. Yield: 0.160 g (39%). Mp: 174.3 (dec). ^{1}H NMR (CD_2Cl_2): δ 7.90 (dd, J_{HH} = 8, J_{PH} = 6, 1H, H^3-$ArSO_3$), 7.68 (m, 6H, PPh_3/H^6-ArOMe), 7.44 (m, 13H, PPh_3/H^4-ArOMe), 7.28 (dd, J_{HH} = 8, J_{PH} = 1, 1H, H^4-$ArSO_3$), 7.06 (dd, J_{PH} = 9, J_{PH} = 2, 1H, H^6-$ArSO_3$), 7.00 (t, J_{HH} = 8, 2H, H^5-ArOMe), 6.96 (dd, J_{HH} = 88, J_{PH} = 5, 2H, H^3-ArOMe), 3.67 (s, 6H, ArO*Me*), 2.24 (s, 3H, *Me*-$ArSO_3$), −0.12 (t, J_{PH} = 6, 3H, Pd-*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 161.3

(35) The reaction of **5a** with $B(C_6F_5)_3$ does not result in pyridazine abstraction, but rather proceeds by methide abstraction to yield $[MeB(C_6F_5)_3]^-$, which was identified by NMR and ESI-MS, and unidentified Pd products.

(d, J_{PC} = 4, C^2-ArOMe), 146.7 (d, J_{PC} = 16, C^2-$ArSO_3$), 139.4 (d, J_{PC} = 6, C^3-$ArSO_3$), 137.8 (br s, PPh_3), 135.9 (d, J_{PC} = 4, C^6-$ArSO_3$), 135.2 (d, J_{PC} = 13, PPh_3), 133.4 (s, C^4-$ArSO_3$), 131.2 (d, J_{PC} = 2, C^5-$ArSO_3$), 131.0 (d, J_{PC} = 2, C^6-ArOMe), 128.9 (d, J_{PC} = 10, PPh_3), 128.4 (d, J_{PC} = 53, C^1-$ArSO_3$), 127.9 (d, J_{PC} = 8, C^4-ArOMe), 121.0 (d, J_{PC} = 11, C^5-ArOMe), 116.8 (d, J_{PC} = 46, C^1-ArOMe), 111.7 (d, J_{PC} = 5, C^3-ArOMe), 55.8 (s, ArO*Me*), 21.5 (s, *Me*-$ArSO_3$), 0.04 (d, J_{PC} = 4, Pd-*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 27.3 (d, J_{PP} = 403), 7.90 (d, J_{PP} = 403, PPh_3).

$B(C_6F_5)_3$(py).[36] Pyridine (0.280 mL, 3.50 mmol) was added by syringe to a solution of $B(C_6F_5)_3$ (0.598 g, 1.17 mmol) in CH_2Cl_2 (10 mL) at room temperature. The solution was stirred for 30 min. The solvent was removed under vacuum to afford an oily white product. This product was recrystallized from CH_2Cl_2/hexanes (3:8 by volume) at room temperature to afford large colorless crystals after 2 days. The crystals were washed with hexanes and dried under vacuum. ^1H NMR (CD_2Cl_2): δ 8.60 (d, J_{HH} = 6, 2 H, *o*-py), 8.21 (t, J_{HH} = 8, 1 H, *p*-py), 7.71 (t, J_{HH} = 8, 2 H, *m*-py). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 148.2 (d, J_{CF} = 250, C^2-C_6F_5), 147.2 (s, *o*-py), 143.2 (s, *p*-py), 140.6 (d, J_{CF} = 249, C^4-C_6F_5), 137.8 (d, J_{CF} = 248, C^3-C_6F_5), 126.2 (s, *m*-py), 118.5 (br, C^1-C_6F_5). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −131.8 (d, J_{FF} = 38), −157.5 (t, J_{FF} = 38), −164.0 (t, J_{FF} = 38). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −3.7 (br s). Anal. Calcd for $C_{23}H_5BF_{15}N$: C, 46.74; H, 0.85; N, 2.37. Found: C, 46.63; H, 1.18; N, 2.26.

{[PO-OMe]Pd(CH_2SiMe_3)}$_2$ (8a). A resealable NMR tube was charged with [PO-OMe]Pd(CH_2SiMe_3)(py) (0.0320 g, 0.0465 mmol) and $B(C_6F_5)_3$ (0.0238 g, 0.0465 mmol), and CD_2Cl_2 (0.5 mL) was added by vacuum transfer at −196 °C. The tube was warmed to room temperature and agitated, producing a dark yellow solution. The tube was maintained at 21 °C for 12 h, during which time a mixture of yellow crystals and a dark brown supernatant formed. ^1H NMR analysis showed that [PO-OMe]Pd(CH_2SiMe_3)(py) was completely consumed and that $B(C_6F_5)_3$(py) and {[PO-OMe]Pd(CH_2SiMe_3)}$_2$ were present. The yellow crystals were isolated by removal of the solvent by syringe under a stream of nitrogen, washed with pentane (2 × 1 mL), dried under vacuum, and identified as {[PO-OMe]Pd(CH_2SiMe_3)}$_2$. Yield: 0.020 g (71%). Mp: 190 °C (dec). ^1H NMR (CD_2Cl_2): δ 7.9 (m, 3H, H^6-ArOMe/H^3-$ArSO_3$), 7.51 (t, J_{HH} = 8, 2H, H^4-ArOMe), 7.27 (d, J_{HH} = 8, 1H, H^4-$ArSO_3$), 7.17 (d, J_{PH} = 11, 1H, H^6-$ArSO_3$), 7.03 (t, J_{HH} = 8, 2H, H^5-ArOMe), 6.92 (dd, J_{PH} = 5, J_{HH} = 8, 2H, H^3-ArOMe), 3.57 (s, 6H, ArO*Me*), 2.25 (s, 3H, *Me*-$ArSO_3$), 0.67 (br s, 2H, C*H*$_2$SiMe$_3$), −0.31 (s, 9H, CH$_2$Si*Me*$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 160.9 (s, C^2-ArOMe), 147.3 (s, C^2-$ArSO_3$), 135.4 (s, C^3-$ArSO_3$), 134.0 (s, C^6-$ArSO_3$), 131.3 (s, C^4-Ar-SO_3), 129.0 (s, C^6-ArOMe), 128.9 (s, C^5-$ArSO_3$), 127.8 (d, J_{PC} = 53, C^1-$ArSO_3$), 126.6 (s, C^5-ArOMe), 121.2 (d, J_{PC} = 12, C^4-ArOMe), 116.4 (d, J_{PC} = 62, C^1-ArOMe), 111.9 (d, J_{PC} = 4, C^3-ArOMe), 55.6 (s, ArO*Me*), 21.5 (s, *Me*-$ArSO_3$), 12.0 (br s, *C*H$_2$SiMe$_3$), 1.69 (s, CH$_2$Si*Me*$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.2 (br s). Anal. Calcd for $C_{26}H_{33}Cl_2O_5PPdSSi$: C, 45.00; H, 4.79. Found: C, 44.85; H, 4.64.

{[PO-OMe]Pd(CH_2^{t}Bu)}$_2$ (9a). A solution of [PO-OMe]Pd(CH_2^{t}Bu)(py) (0.643 g, 0.958 mmol) in CH_2Cl_2 (10 mL) was cooled to −78 °C, and a solution of $B(C_6F_5)_3$ (0.491 g, 0.958 mmol) in CH_2Cl_2 (10 mL) was added slowly. The mixture was allowed to warm to room temperature and was stirred for 1 h. The solvent was removed under vacuum, and the resulting tan solid was rinsed with benzene (2 × 10 mL) and hexanes (2 × 10 mL). The resulting white solid was dried under vacuum. Yield: 0.292 g (51.4%). Mp: 190 °C. Anal. Calcd for $C_{52}H_{62}O_{10}P_2Pd_2S_2$: C, 52.66; H, 5.27. Found: C, 52.49; H, 5.22.

Generation of [PO-OMe]Pd(η^3-CH_2Ph) (10a). An NMR tube was charged with [PO-OMe]Pd(CH_2Ph)(py) (0.030 g, 0.043 mmol) and $B(C_6F_5)_3$ (0.022 g, 0.043 mmol), and CD_2Cl_2 (0.6 mL) was added by vacuum transfer at −196 °C. The tube was warmed to room temperature and shaken to dissolve the solids. NMR spectra were obtained after 1 h and showed that [PO-OMe]Pd(η^3-CH_2Ph) and $B(C_6F_5)_3$(py) had formed. ^1H NMR (CD_2Cl_2): δ 8.40 (br s, 1H, Ar), 7.91 (m, 1 H, Ar), 7.55 (m, 5 H, Ar/Bn), 7.26 (d, J_{HH} = 8, 1H, Ar), 7.02 (m, 7 H, Ar/Bn), 6.78 (br s, 1H, Bn), 3.70 (s, 6H, *Me*OPh), 2.58 (br s, 2H, C*H*$_2$Bn), 2.18 (s, 3H, C*H*$_3$ArSO$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 160.9 (d, J_{PC} = 5, ArOMe), 146.5 (d, J_{PC} = 16, $ArSO_3$), 141.7 (d, J_{PC} = 6, $ArSO_3$), 135.8 (br s, $ArSO_3$), 135.0 (s, $ArSO_3$), 133.7 (d, J_{PC} = 3, Bn), 133.5 (s, $ArSO_3$), 131.6 (d, J_{PC} = 2, Bn), 130.4 (d, J_{PC} = 5, $ArSO_3$), 128.7 (d, J_{PC} = 45, $ArSO_3$), 128.6 (d, J_{PC} = 9, ArOMe), 121.3 (d, J_{PC} = 10, ArOMe), 117.4 (d, J_{PC} = 52, ArOMe), 117.3 (br s, Bn), 111.6 (d, J_{PC} = 5, ArOMe), 55.9 (s, ArO*Me*), 39.7 (br s, J_{CH} = 154, Bn), 21.4 (s, *Me*-$ArSO_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 6.61 (s).

[PO-OMe]PdCl(py) (11a). A mixture of [**1a**]H (0.512 g, 1.23 mmol), CH_2Cl_2 (15 mL), and pyridine (0.25 mL, 3.1 mmol) was stirred at room temperature. A solution of (COD)$PdCl_2$ (0.351 g, 1.23 mmol) in CH_2Cl_2 (15 mL) was added dropwise, and the mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum to afford an orange solid. The solid was dissolved in CH_2Cl_2 (30 mL), and the solution was washed with H_2O (2 × 10 mL), dried over $MgSO_4$, filtered, and dried under vacuum. The resulting solid was recrystallized from CH_2Cl_2/hexanes (3:1 v/v) to afford several crops of orange crystals, which were identified as [PO-OMe]PdCl(py)·(1/3CH_2Cl_2) by ^1H NMR and elemental analysis. Yield: 0.688 g (56%) Mp: 195 °C (dec). ^1H NMR (CD_2Cl_2): δ 8.86 (m, 2H, py), 7.99 (m, 2H, H^6-ArOMe), 7.88 (m, 2H, py, H^3-$ArSO_3$), 7.61 (t, J_{HH} = 7, 2H, py), 7.48 (t, J_{HH} = 6, 2H, H^4-ArOMe), 7.36 (d, J_{HH} = 8, 1H, H^4-$ArSO_3$), 7.14 (d, J_{HP} = 12, 1H, H^6-$ArSO_3$), 7.11 (t, J_{HH} = 6, 2H, H^5-ArOMe), 6.98 (dd, J_{HH} = 8, J_{PH} = 5, 2H, H^3-ArOMe), 3.71 (s, 6H, ArO*Me*), 2.29 (s, 3H, *Me*-$ArSO_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.0 (s, C^2-ArOMe), 150.5 (s, py), 144.1 (d, J_{PC} = 13, C^2-$ArSO_3$), 140.1 (d, J_{PC} = 8, C^3-$ArSO_3$), 139.5 (s, py), 138.6 (d, J_{PC} = 11, C^6-$ArSO_3$), 135.4 (d, J_{PC} = 2, C^4-$ArSO_3$), 134.7 (d, J_{PC} = 2, py), 132.1 (d, J_{PC} = 2, C^5-$ArSO_3$), 127.4 (d, J_{PC} = 9, C^6-ArOMe), 126.4 (d, J_{PC} = 57, C^1-$ArSO_3$), 125.5 (d, J_{PC} = 2, C^5-ArOMe), 121.1 (d, J_{PC} = 13, C^4-ArOMe), 114.8 (d, J_{PC} = 67, C^1-ArOMe), 112.1 (d, J_{PC} = 5, C^3-ArOMe), 56.1 (s, ArO*Me*), 21.6 (s, *Me*-$ArSO_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 5.8 (s). Anal. Calcd for $C_{26.3}H_{25.7}Cl_{1.7}NO_5PPdS$: C, 47.58; H, 3.89; N, 2.11. Found: C, 47.59; H, 3.91; N, 2.07.

Ethylene Polymerization. Ethylene polymerizations were performed in a 300 mL stainless steel Parr autoclave equipped with a water cooling loop, thermocouple, and magnetically coupled stirrer and controlled by a Parr 4842 controller. In the glovebox, the catalyst or catalyst precursors were weighed into a glass autoclave liner. Anhydrous toluene (50 mL) was added. The liner was placed in the autoclave, and the autoclave was assembled, brought out of the box, and hooked to the controller and to an ethylene delivery system. The reactor was heated to the desired temperature (typically 80 °C), and stirring (200 rpm) was started. The desired temperature was usually reached after 12 min. The autoclave was maintained at this temperature for 20 min to ensure complete dissoluton of the catalyst. (Control experiments showed that complete dissolution of the [PO]Pd(R)(py) complexes to make a 0.4 mM solution in toluene occurs within ca. 12 min at 80 °C.) The reactor was pressurized with ethylene, and the ethylene uptake was monitored with a mass flow-meter. After the desired reaction time, the ethylene flow was terminated and the pressure was released. The mixture was cooled to room temperature, and the polymer was collected by filtration, washed with boiling toluene, acetone, and hexanes

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Table 2. X-Ray Diffraction Data for [PO-OMe]Pd(CH_2SiMe_3)(py) (2a), [PO-Et]Pd(Me)(py) (6b), and {[PO-OMe]Pd(CH_2SiMe_3)}$_2$ (8a)

	[PO-OMe]Pd(CH_2SiMe_3)(py) (**2a**)	[PO-Et]Pd(Me)(py) (**6b**)	{[PO-OMe]Pd(CH_2SiMe_3)}$_2$ (**8a**)
formula	$C_{30}H_{36}NO_5PPdSSi + 1.5\ CH_2Cl_2$	$C_{29}H_{32}NO_3PPdS$	$C_{25}H_{30}O_5PPdSSi + CH_2Cl_2$
fw	818.76 (including solvent)	611.99	692.94 (including solvent)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$C2/c$
b (Å)	18.043(3)	22.544(4)	23.794(5)
c (Å)	16.306(3)	14.590(5)	12.759(3)
β (deg)	104.454(3)	127.19(2)	100.44(3)
γ (deg)	90.0	90.0	90.0
V(Å^3)	3496(1)	2685(1)	6276(2)
Z	4	4	8
T (K)	100	100	100
cryst color, habit	clear, brick	clear, plate	clear, prism
GOF on F^2	1.023	1.155	1.082
R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0325, wR2 = 0.0918	R1 = 0.0367, wR2 = 0.0791	R1 = 0.0361, wR2 = 0.0871
R indices (all data)[a]	R1 = 0.0366, wR2 = 0.0936	R1 = 0.0418, wR2 = 0.0815	R1 = 0.0374, wR2 = 0.0881

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

(10 mL each), and dried under high vacuum overnight. Unless otherwise stated, all polymerizations proceeded under isothermal conditions. Exotherms were avoided by using total palladium concentrations below 0.4 mM for the *in situ*-generated catalysts and below 0.2 mM for the discrete catalysts.

When less than 6 mg of catalyst was used (i.e., [Pd] < 0.1 mM), the catalyst was introduced by means of a freshly prepared stock solution. In this case, an aliquot of a solution of the catalyst in CH_2Cl_2 (1 mg/mL) was added to the glass autoclave liner. The liner was placed in a desiccator, and the CH_2Cl_2 was removed under vacuum. Toluene was added to the liner, the reactor was assembled, and the polymerization was carried out as described above.

Ethylene/1-Hexene Copolymerizations. The procedure described above was used, but 1-hexene was added to the reactor via a syringe port after the catalyst solubilization period, immediately prior to pressurizing with ethylene.

Polymer Characterization. Gel permeation chromatography was performed with a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 150 °C. A set of three PLgel 10 μm mixed-B LS columns was used. Samples were prepared at 160 °C. Molecular weights were determined by GPC using narrow polystyrene standards and are corrected for linear polyethylene by universal calibration using the Mark–Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ cm^3/g and $\alpha = 0.67$ for polystyrene and $K = 5.90 \times 10^{-2}$ cm^3/g and $\alpha = 0.69$ for polyethylene.[37,38]

DSC measurements were performed on a TA Instruments DSC 2920 instrument. Samples (10 mg) were annealed by heating to 170 °C at 20 °C/min, cooled to 40 °C at 40 °C/min, and then analyzed while being heated to 170 °C at 20 °C/min.

Analysis of the polymers by inductively coupled plasma (ICP) atomic absorption revealed that ca. 50% of the initial palladium content is present in the isolated polymers. The speciation of the residual palladium is unknown, and the polymers themselves are not active as ethylene polymerization catalysts.

Reaction of 9a with 6-Chloro-1-hexene. An NMR tube was charged with **9a** (0.0150 g, 0.0253 mmol) and hexamethylbenzene (4.1 mg, 0.025 mmol, internal standard), and CD_2Cl_2 (0.5 mL) and 6-chloro-1-hexene (0.1518 mmol, 6 equiv) were added by vacuum transfer at −196 °C. The mixture was warmed to room temperature and shaken to afford a white suspension. The suspension gradually became orange. After 19 h at room temperature, the volatiles were vacuum transferred to a separate tube and analyzed by GC-MS, which showed that a mixture of chlorohexenes ($M^+ = 118$, 4 isomers), undecenes ($M^+ = 154$, 6 isomers), and chloroundecenes ($M^+ = 188$, 6 isomers) was present. The nonvolatiles were suspended in CH_2Cl_2 (0.5 mL), and pyridine (0.1 mmol, 4 equiv) was added. The mixture was warmed to room temperature, shaken for 5 min to afford a red solution, extracted with hexanes (3 × 1 mL), and dried under vacuum to afford an orange solid. The orange solid was dissolved in CD_2Cl_2 (0.5 mL) and analyzed by ^{1}H and ^{31}P{^{1}H} NMR, which established that **11a** was the major Pd species present (>93%). The hexanes extract was concentrated under vacuum to afford an oily white solid (10 mg), which was analyzed by GC-MS, which showed that a mixture of chlorohexene oligomers was present; MS (n = number of 6-chloro-1-hexene units in the oligomer): $M^+ = 202$ ($n = 2 + H - Cl$; 11 isomers), 236 ($n = 2$; 8 isomers), 272 ($n = 2 + CH_2{}^tBu - Cl$; 9 isomers), 306 ($n = 2 + CH_2{}^tBu$ - H; 8 isomers), 320 ($n = 3 + H - Cl$; 9 isomers), 354 ($n = 3$; 9 isomers), 390 ($n = 2 + CH_2{}^tBu - Cl$; 2 isomers, other isomers are likely present but were not observed due to overlap with peaks from trimers, which have much higher intensities), 424 ($n = 3 + CH_2{}^tBu - H$; 9 isomers); analogous $n = 4$, 5 oligomers were also observed.

Reaction of 9a with 6-Chloro-1-hexene in the Presence of 1-Chloropentane. An NMR tube was charged with **9a** (0.0158 g, 0.0266 mmol), CD_2Cl_2 (0.5 mL), 6-chloro-1-hexene (0.0071 g, 0.0596 mmol), 1-chloropentane (0.0125 g, 0.117 mmol), and tetramethylsilane (0.0028 g, 0.0263 mmol, internal standard). The resulting suspension was shaken for 20 h at room temperature. The volatiles were vacuum transferred to a separate tube and analyzed by ^{1}H NMR and GC-MS, which showed that 100% of the starting 1-chloropentane was present (relative to tetramethylsilane) along with a mixture of chlorohexenes (4 isomers), undecenes (8 isomers), and chloroundecenes (8 isomers). The nonvolatile fraction was worked up, analyzed as described above, and found to contain a mixture of **11a** and chlorohexene oligomers similar to that observed in the absence of 1-chloropentane.

X-Ray Crystallography. Crystallographic data are summarized in Table 2, and full details are provided in the Supporting Information. Data were collected on a Bruker Smart Apex diffractometer using Mo Kα radiation (0.71073 Å). Direct methods were used to locate many atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected non-hydrogen atoms. Following anisotropic refinement of all non-H atoms, ideal H atom positions were calculated. Final refinement was anisotropic for all non-H atoms and isotropic-riding for H atoms. ORTEP diagrams are drawn with 50% probability ellipsoids. Specific comments for each structure follow. **2a**: Crystals of **2a** were obtained by crystallization at −20 °C. Two CH_2Cl_2 molecules are present, one of which is disordered between two positions at a center

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of symmetry. **6b**: Crystals of **6b** were obtained from CH_2Cl_2/hexanes (1:1 v/v) at −30 °C. **8a**: Crystals of **8a** were obtained from the reaction of **2a** with $B(C_6F_5)_3$ in CD_2Cl_2 at 21 °C. One CH_2Cl_2 molecule is present, which is disordered between two positions with 0.5 occupancy at each site.

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Supporting Information Available: Ligand synthesis procedures, additional NMR data for complexes and polymers, and crystallographic data for **2a**, **6b**, and **8a** (cif files). This material is available free of charge via the Internet at http://pubs.acs.org.

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