Synthesis and reactivity of phosphine-arenesulfonate palladium(II) alkyl complexes that contain methoxy substituents

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Phosphine-arenesulfonate ligands that contain 1-3 methoxy substituents on the benzo linker, P[2-OMePh]$_2$(2-SO$_3$Na-5-OMe-Ph) (Na[1a]), P[2-MeO-Ph]$_2$(2-SO$_3$Na-4,5-(OMe)$_2$-Ph) (Na[1b]) and P[2-MeO-Ph]$_2$(2-SO$_3$Li-3,4,5-(OMe)$_2$-Ph) (Li[1c]) were synthesized and isolated in 52–85% yield. Reaction of Na [1a,b] and Li[1c] with (COD)PdMeCl and pyridine generates the corresponding (PO)PdMe(pyridine) complexes 2a-c. 2a and 2b were isolated in crystalline form in 59% and 86% yield, respectively, while 2c decomposed during attempted isolation. 2a,b polymerize ethylene to linear polyethylene and copolymerize ethylene with vinyl fluoride (VF) to linear copolymer with ca. 0.5 mol % VF incorporation.

1. Introduction

Palladium alkyl complexes that contain phosphine-arenesulfonate ligands ([PO]PdRL, A, Chart 1) polymerize ethylene to linear polyethylene (PE) and copolymerize ethylene with a wide range of polar CH$_2$=CHX vinyl monomers (e.g. X = CO$_2$R, OR, OAr, CN, F) [1,2]. However, (PO)PdRL catalysts usually exhibit lower activity and produce PEs with lower molecular weights (MWs) compared to other single-site catalysts [3]. Moreover, the catalyst performance is further compromised by the polar monomers, which can function as inhibitors, poisons and chain transfer agents.

Electronic modifications of the P$_2$R$_2$ groups on the PO$^-$ ligands have also been explored [5]. Incorporation of an electron-donating Me group para to the sulfonate group in (OPO$_2$-C$_6$H$_4$SO$_3$)PdMe(py) results in lower ethylene polymerization activity but does not affect the MW of the PE product significantly [5a]. Replacement of the benzo linker that connects the phosphine and sulfonate units in A with a 1,2-naphthalene linker increases the ethylene polymerization activity 2 to 10-fold but has only a minor effect on the MW of the PE that is produced [5b].

The present work is focused on (PO)PdMe(py) catalysts of type A that contain methoxy substituents on the benzo ring that links the phosphino and sulfonate groups. The motivation for this work was twofold. First, we were interested to probe how the incorporation of such substituents influences catalyst performance. A methoxy group is electron-donating to the ortho and para positions through the resonance effect ($\sigma_{para} = -0.27$) and electron-withdrawing through the inductive effect ($\sigma_{meta} = 0.12$). Second, we recently reported that (OPO–Li)PdMeL complexes based on the phosphine bis-arenesulfonate ligand PPh$_2$(2-SO$_3$-4,5-(OMe)$_2$-Ph)$_2$ (OPO$^-$), which contains two methoxy groups on each benzo linker, self-assemble into Pd$_4$ species that are held together by a Li$_4$S$_4$O$_12$ cage (C, Chart 1) [6]. These Pd species function as single-site catalysts for the polymerization of ethylene to high-molecular weight PE ($M_n = 640,000$, PDI = 2.3) in hexanes suspension. Studies of mononuclear analogues are of
interest for understanding the origins of this behavior.

We report the synthesis of three new ligands (1a-c, Scheme 1) that contain 1-3 methoxy groups on the benzo linker and the corresponding (PO)PdMe(py) complexes. The ethylene polymerization and ethylene/vinylfluoride (VF) copolymerization behavior of these complexes is also discussed.

2. Results and discussion

2.1. Synthesis of Na[1a-b] and Li[1c]

The synthetic route used to prepare the new ligands studied here is shown in Scheme 1. The appropriate methoxy-substituted aryl lithium reagents were generated by ortho-lithiation or lithium-halogen exchange of the corresponding arene or aryl-bromide 3a-c-iBu with nBuLi, and reacted with P(2-OMe-Ph)2Cl to afford pro-ligands 1a-c-iBu [7]. 1a-c-iBu were purified by chromatography and isolated in 30-49% yield. 1a-iBu and 1b-iBu were converted to the corresponding Na⁺ sulfonate salts Na[1a, b] by reaction with NaI in CH₃CN. Na[1a, b] precipitated from the reaction mixture and were isolated by filtration in 57-85% yield. Na[1c] was generated in an analogous manner but is soluble in CH₃CN and thus is difficult to separate from the excess NaI used in the reaction. Therefore, Li[1c] was generated by reaction of 1c-iBu with LiI in CH₃CN and isolated in 52% yield.

2.2. Synthesis of methoxy-substituted (PO)PdMe(py) complexes

The reaction of Na[1a, b] with (COD)PdMeCl and pyridine in CH₂Cl₂ generated a clear yellow solution of 2a,b (Scheme 2). 2a,b were isolated by layering pentane onto the CH₂Cl₂ solution to give X-ray quality crystals in 59-86% yield. The synthesis of 2c by this route was unsuccessful. The reaction of Li[1c] with (COD)PdMeCl and pyridine in CH₂Cl₂ gave a cloudy solution, and the formation of Pd black was observed upon attempted isolation of the product.

An alternative metalation procedure was explored that involves the direct reaction of 1c-iBu with (COD)PdMeCl and pyridine (Scheme 3). This reaction results in the clean generation of 2c, which was characterized by NMR. However 2c could not be isolated in pure form due to apparent thermal decomposition. It is likely that this metalation process proceeds by initial formation of [k₂-P,O-1c-iBu]PdMeCl, displacement of chloride by pyridine, and nucleophilic attack of the free Cl⁻ on the activated iBu group to form 2c and iBuCl, as shown in Scheme 3. 2b was synthesized by this route on a preparatory scale.

2.3. X-ray crystallography

The solid-state structures of 2a,b were determined by X-ray crystallography and are shown in Figs. 1 and 2. In each case, k²-P,O coordination of the PO⁻ ligand and a cis relationship of the phosphine and methyl group are observed. The six-membered (PO)Pd chelate rings adopt boat conformations. The Pd–C distances in 2a and the reaction mixture were isolated by filtration in 57-85% yield. Na[1c] was generated in an analogous manner but is soluble in CH₃CN and thus is difficult to separate from the excess NaI used in the reaction. Therefore, Li[1c] was generated by reaction of 1c-iBu with LiI in CH₃CN and isolated in 52% yield.

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values/C20 (2.022(2) Å) and N1.

Fig. 2. Molecular structure of 2b. Hydrogen atoms are omitted. Atom color scheme: C: grey; O: red; P: orange; S: yellow; N: blue; Pd: teal. Selected bond lengths (Å) and angles (deg): Pd1–P1 2.2234(4), Pd1–O1 2.1768(11), Pd1–N1 2.3398(13), Pd1–C1 2.022(2), O1–S1 1.4834(14), O1–P1–Pd1 94.09(4), N1–Pd1–P1 174.86(4), N1–Pd1–O1 87.07(5), C1–Pd1–P1 87.37(6), C1–Pd1–O1 176.32(7), C1–Pd1–N1 91.77(7). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3. Conclusions

The phosphine-arenesulfonate ligands Na[1a-b] and Li[1c], which contain 1-3 methoxy substituents on the arenesulfonate rings, have been synthesized. Na[1a,b] and Li[1c] react with (COD)PdMeCl to form (PO)PdMe(pyr dine) complexes 2a-c, however 2c decomposed during attempted isolation. The structures of 2a,b have been analyzed by X-ray crystallography. 2a,b polymerize ethylene to linear PE and copolymerize ethylene with VF to linear copolymer with ca. 0.5 mol% VF incorporation. Catalysts 2a,b exhibit similar polymerization behavior compared to the benchmark catalysts 4 and 5, indicating that the methoxy groups have only a modest influence on the reactivity.

4. Experimental section

4.1. General procedures

All experiments were performed under a nitrogen atmosphere using drybox or Schlenk techniques. Nitrogen was purified by passage through Q-5 oxygen scavenger and activated molecular sieves. Methylene chloride, diethyl ether and THF were dried by
passage over activated alumina. Toluene, pentane and hexane were purified by passage through BASF R3-11 oxygen scavenger and activated alumina. CDCl₂ and CHCl₃ were dried over 4 Å molecular sieves. CD₂Cl₂ was dried over P₂O₅. The following materials were obtained from commercial sources and used without further purification: 4-methoxybenzenesulfonyl chloride (Aldrich, 99%), 4-bromoveratrole (Aldrich, 98%), 5-bromo-1,2,3-trimethoxybenzene (Aldrich, 97%), chlorosulfonic acid (Aldrich, 99%), 2-methyl-1-propanol (Aldrich, 99%), 2-bromoanisole (Aldrich, 97%), pyridine (Aldrich, 99.8%), dichloro(diethylamino)phosphine (Alfa aesar, 97%), nBuLi solution (Aldrich, 2.5 M in hexanes), HCl solution (Aldrich, 2 M in diethyl ether), sodium iodide (Aldrich, >99%), lithium iodide (Aldrich, 99.9%). The following compounds were prepared by literature procedures: 2-bromo-4,5-di-methoxybenzenesulfonyl chloride [12] and (COD)PdMeCl [13].

NMR spectra were acquired on Bruker DRX-500 or Bruker DRX-400 spectrometers at ambient temperature unless otherwise indicated. ¹H and ¹³C chemical shifts are reported relative to SiMe₄ and are internally referenced to residual ¹H and ¹³C solvent resonances. ³¹P chemical shifts are reported relative to externally referenced

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**Table 1**

Homopolymerization of ethylene by 2a and 2b.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>Pd (µmol)</th>
<th>Solvent</th>
<th>Yield (g)</th>
<th>Activity (kg·mol⁻¹·h⁻¹)</th>
<th>Mₙ (10⁴)</th>
<th>PDF</th>
<th>Tm(°C)</th>
</tr>
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<tr>
<td>1⁺</td>
<td>2a</td>
<td>10</td>
<td>toluene</td>
<td>8.92</td>
<td>446</td>
<td>29.6</td>
<td>2.0</td>
<td>136.3</td>
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<td>2a</td>
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<td>toluene</td>
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<td>494</td>
<td>29.9</td>
<td>1.8</td>
<td>134.8</td>
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<td>hexanes</td>
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<td>2.1</td>
<td>132.0</td>
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<td>toluene/PhCl</td>
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<td>869</td>
<td>29.7</td>
<td>1.7</td>
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<td>6ᵇᵇ</td>
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<td>toluene/PhCl</td>
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<td>983</td>
<td>27.5</td>
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<td>515</td>
<td>26.1</td>
<td>1.8</td>
<td>134.5</td>
</tr>
<tr>
<td>8ᵇᵇ</td>
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<td>toluene</td>
<td>10.1</td>
<td>505</td>
<td>25.6</td>
<td>1.7</td>
<td>135.4</td>
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<tr>
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<td>62.0</td>
<td>18.8</td>
<td>2.3</td>
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<td>19.1</td>
<td>2.3</td>
<td>131.8</td>
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<td>toluene/PhCl</td>
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<td>1462</td>
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<td>135.1</td>
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<td>2.5</td>
<td>134</td>
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<tr>
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<td>10</td>
<td>toluene</td>
<td>9.10</td>
<td>210</td>
<td>91.0</td>
<td>2.8</td>
<td>129.0</td>
</tr>
</tbody>
</table>

⁻ Conditions: 410 psi C₂H₄, 80 °C, 2 h, 50 mL solvent.
⁻⁻ Solvent = 49 mL toluene + 1 mL chlorobenzene; catalyst added to the reactor as a stock solution in chlorobenzene to facilitate accurate control of catalyst loading.
⁻⁻⁻ Determined by GPC.
⁻⁻⁻⁻ Determined by DSC.
⁻⁻⁻⁻⁻ ref [9]. Conditions: 580 psi C₂H₄, 80 °C, 1 h, 100 mL toluene.
⁻⁻⁻⁻⁻⁻ ref [10]. Conditions: 300 psi C₂H₄, 85 °C, 1 h, 200 mL toluene.

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**Table 2**

Ethylene/vinyl fluoride copolymerization by 2a and 2b.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>Yield (mg)</th>
<th>Activity (kg·mol⁻¹·h⁻¹)</th>
<th>Mₙ (10⁴)</th>
<th>PDF</th>
<th>VF incorp (mol %)</th>
<th>Tm(°C)</th>
</tr>
</thead>
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<td>2a</td>
<td>115</td>
<td>5.8</td>
<td>13.5</td>
<td>2.3</td>
<td>0.59</td>
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<tr>
<td>2⁻</td>
<td>2a</td>
<td>102</td>
<td>5.1</td>
<td>12.1</td>
<td>2.0</td>
<td>0.51</td>
<td>131.4</td>
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<tr>
<td>3ᵇᵇ</td>
<td>5</td>
<td>90</td>
<td>4.5</td>
<td>15.0</td>
<td>1.9</td>
<td>0.48</td>
<td>131.6</td>
</tr>
<tr>
<td>13ᵉ</td>
<td>4</td>
<td>20</td>
<td>toluene</td>
<td>9.97</td>
<td>498</td>
<td>46.6</td>
<td>134</td>
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<tr>
<td>14ᵉ</td>
<td>4</td>
<td>10</td>
<td>toluene</td>
<td>9.10</td>
<td>210</td>
<td>91.0</td>
<td>129.0</td>
</tr>
</tbody>
</table>

⁻ Conditions: 220 psi ethylene, 80 psi VF, [Pd] = 10 µmol, temperature = 80 °C, time = 2 h, solvent = 40 mL toluene + 10 mL chlorobenzene.
⁻⁻ ref [10].
⁻⁻⁻ Determined by GPC.
⁻⁻⁻⁻ VF incorporation in copolymer determined by ¹H NMR.
⁻⁻⁻⁻⁻ Determined by DSC.

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Fig. 3. ¹⁹F{¹H} NMR spectrum of ethylene/VF copolymer (α-dichlorobenzene-d₄, 100 °C) produced by 2b (Table 2, entry 2). P = polymeryl.
85% H3PO4. 19F spectra were referenced to external BF3·Et2O, and 19F chemical shifts are reported relative to CFCl3. NMR resonances were assigned based on COSY, HMBC, HMBD and 1H[13P] experiments, as well as trends in chemical shifts and coupling constants derived from these experiments. Coupling constants are given in Hz. Mass spectrometry was performed on Agilent 6224 TOF-MS (high resolution) or Agilent 6130 LCMS (low resolution) instruments.

Gel permeation chromatography (GPC) data were obtained on a Polymer Laboratories PL-GPC 220 instrument at 150 °C with 1,2,4-trichlorobenzene (stabilized with 125 ppm BHT) as the mobile phase. Three PLgel 10 μm Mixed-B LS columns were used. Molecular weights were calibrated using narrow polystyrene standards (ten-point calibration with Mn from 570 Da to 5670 kDa) and are corrected for linear polyethylene by universal calibration using the following Mark-Houwink parameters: polystyrene, K = 1.75 × 10−2 cm2 g−1, a = 0.67; polyethylene, K = 5.90 × 10−2 cm2 g−1, a = 0.69 [14]. DSC measurements were performed on a TA Instruments DSC 2920 instrument. DSC samples (10 mg) were annealed by heating to 170 °C at 20 °C/min, cooled to 0 °C at 20 °C/min, and then analyzed while being heated to 170 °C at 20 °C/min.

4.2. Synthesis of compounds

4.2.1. 3a-iBu

[15] A flask was charged with BuOH (5.0 mL, 54 mmol), pyridine (8.4 mL, 0.10 mol) and CHCl3 (50 mL), and cooled to 0 °C. A solution of 4-methoxybenzenesulfonfyl chloride (10.0 g, 50 mmol) in CHCl3 (30 mL) was added, and the mixture was stirred for 18 h at room temperature. HCl solution (0.1 M in H2O, 40 mL) was added, and the mixture was stirred for 5 min and transferred to a separatory funnel. The CHCl3 layer was separated and washed with H2O (3 × 50 mL) and brine (10 mL), and dried over MgSO4. The volatiles were removed under vacuum to yield a yellow oil. The crude product was purified by silica gel chromatography using CH2Cl2 as the eluent. The product was isolated as a colorless oil (11 g, 88%). The ethyl ester of 4-methoxybenzenesulfonfyl chloride (10.0 g, 50 mmol) in CHCl3 (30 mL) was added, and the mixture was stirred for 18 h at room temperature. HCl solution (0.1 M in H2O, 40 mL) was added, and the mixture was stirred for 5 min and transferred to a separatory funnel. The CHCl3 layer was separated and washed with H2O (3 × 50 mL) and brine (10 mL), and dried over MgSO4. The volatiles were removed under vacuum to yield a yellow oil. The crude product was purified by silica gel chromatography using CH2Cl2 as the eluent. The product was isolated as a colorless oil (11 g, 88%). The ethyl ester of 4-methoxybenzenesulfonate, which is formed by the reaction with EtOH instead of BuOH, was present as a minor impurity. Commercial CHCl3 contains EtOH as stabilizer. 1H NMR (CDCl3): δ 7.81 (d, JHH = 7.3 Hz, H2), 7.03 (d, JHH = 9.2 Hz, H1), 4.05 (q, JHH = 7.3 Hz, -SO2CH2CH3), 3.88 (s, 3H, -OCH3), 3.75 (d, JHH = 6.2 Hz, -SO2CH2CH2CH3), 1.91 (sept, JHH = 7.3 Hz, -SO2CH2CH2CH3). 12C{1H} NMR (CDCl3): δ 165.2 (s, C8), 130.4 (s, C5), 127.9 (s, C1), 114.8 (s, C2), 76.6 (s, -SO2CH2CH2CH3), 67.2 (s, -SO2CH2CH3), 56.1 (s, -OCH3), 28.4 (s, -SO2CH2CH2CH3), 18.7 (s, -SO2CH2CH2CH3), 149.5 (s, -SO2CH3). HRMS (APCI/ESI-Mixed mode; m/z): Calcd. for [C13H19O6BrS]+ + H+ 789.0, Found: 789.1.

4.2.2. 3b-iBu

The ethyl ester of 4-methoxybenzenesulfonate, which is formed by the reaction with EtOH instead of BuOH, was present as a minor impurity. Commercial CHCl3 contains EtOH as stabilizer. 1H NMR (CDCl3): δ 7.53 (s, 1H, H6), 7.20 (s, 1H, H4), 3.91 (s, 3H, H2), 3.89 (s, 3H, H2), 3.80 (d, JHH = 6.2 Hz, H1), 1.58 (sept, JHH = 7.3 Hz, H1), 0.93 (d, JHH = 7.3 Hz, H1). 13C{1H} NMR (CDCl3): δ 153.3, 148.1, 127.0, 117.7, 114.4, 112.2, 77.1, 56.5, 56.4, 28.1, 18.5. HRMS (ESI mode; m/z): Calcd. for [C12H17BrO3S + Na]+ 374.08398, Found: 374.0836.

4.2.3. 3c-iBu

A flask was charged with chlorosulfonic acid (12 mL, 0.18 mol) and cooled to 0 °C. A solution of 5-bromo-1,2,3-trimethoxybenzene (8.0 g, 32 mmol) in CH2Cl2 (40 mL) was added and the mixture was stirred for 90 min. The mixture was slowly poured onto ice. After the ice had thawed, the mixture was transferred to a separatory funnel, and the aqueous layer was extracted with CH2Cl2 (3 × 40 mL). The organic fractions were combined and dried with MgSO4, and the volatiles were removed under vacuum to yield yellow oil. The oil was dissolved in CHCl3 (60 mL), and a solution of BuOH (4.5 mL, 49 mmol) and pyridine (8.0 mL, 99 mmol) in CHCl3 (20 mL) was added. The mixture was stirred for 18 h at room temperature. HCl solution (0.1 M in H2O, 80 mL) was added, and the mixture was stirred for 5 min and transferred to a separatory funnel. The CHCl3 layer was separated and washed with H2O (3 × 50 mL) and brine (10 mL), and dried over MgSO4. The volatiles were removed under vacuum to yield a yellow oil. The crude product was purified by silica gel chromatography using a mixture of 4/1 hexanes/ethyl acetate as the eluent. The product was isolated as a yellow oil (3.0 g, 24%). 1H NMR (CD2Cl2): δ 7.08 (s, 1H, H1), 3.94 (s, 3H, H2), 3.92 (s, 3H, H2), 3.87 (d, JHH = 6.2 Hz, H10), 3.84 (s, 3H, H2), 1.98 (sept, JHH = 7.3 Hz, H10), 0.93 (d, JHH = 6.2 Hz, H1), 13C{1H} NMR (CD2Cl2): δ 157.7, 155.4, 143.3, 128.7, 116.6, 115.1, 77.2, 62.6, 61.1, 56.8, 28.5, 18.8. ESI-MS (1/1 CH3OH/H2O; m/z): Calcd. For [C13H19O6BrS]+ + Na+ 789.0, Found: 789.1.

4.2.4. (2-0Me-Ph)3Cl

[4a,16] A Schlenk flask was charged with 2-bromoanisole (5.0 mL, 40 mmol) and THF (210 mL), and cooled to –78 °C. BuLi (2.5 M solution in hexanes, 16 mL, 40 mmol) was added via syringe over 15 min. The mixture was stirred at –78 °C for 1 h and a solution of PCl2NET2 (3.5 g, 20 mmol) in Et2O (30 mL) was added. The mixture was stirred at room temperature for 18 h to yield a clear yellow solution. The volatiles were removed under vacuum. The resulting yellow solid was taken up in Et2O (100 mL) and washed with H2O (100 mL). The aqueous layer was extracted with Et2O (3 × 75 mL). The combined organic fractions were washed with brine (20 mL) and dried over MgSO4. The volatiles were removed under vacuum to afford 2-0Me-Ph)3Cl as a white solid (5.7 g, 87%). A Schlenk flask was charged with (2-O-Me-Ph)2NET2 (3.1 g, 10 mmol) and THF (50 mL), and cooled to –78 °C. HCl solution (2.0 M solution in diethyl ether, 10 mL, 20 mmol) was added via syringe to form a white cloudy solution. The mixture was stirred at –78 °C for 1 h and filtered, and the volatiles were removed from the filtrate under vacuum to yield a white solid (2.5 g, 89%). The typical purity was ca. 93% as determined by 31P{1H} NMR. The product was used without further purification. 31P{1H} NMR (CD2Cl2): δ 69.6. 1H NMR (CD2Cl2): δ 7.43 (t, JHH = 8, 2H), 7.36–7.34 (m, 2H), 7.00 (t, JHH = 8, 2H), 6.93 (dd, JHH = 8, JHP = 5, 2H), 3.82 (s, 6H).

4.2.5. 1a-iBu

A Schlenk flask was charged with 3a-iBu (1.2 g, 5.0 mmol) and THF (38 mL), and cooled to –78 °C. BuLi (2.5 M solution in hexanes,
2.0 mL, 5.0 mmol) was added via syringe over 5 min. The mixture was stirred at 78 °C for 1 h and a solution of P(2-Ome-Ph)_2Cl (1.4 g, 5.0 mmol) in THF (10 mL) was added. The mixture was stirred at room temperature for 18 h to yield a clear yellow solution. The volatiles were removed under vacuum. The resulting yellow oil was taken up in H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic fractions were washed with brine (20 mL) and dried over MgSO_4, and the volatiles were removed under vacuum to yield a yellow solid. The crude product was purified by silica gel chromatography using a 5/1 hexanes/ethyl acetate mixture as the eluent. The product was isolated as a white solid (0.800 g, 49%). 31P{1H} NMR (CD_2Cl_2): δ = 212.9. H NMR (CD_2Cl_2): δ 7.36 (t, J_HH = 8, 2H, H_11), 6.93 (dd, J_HH = 8, J_HH = 5, 2H, H_16), 6.87 (t, J_HH = 8, 2H, H_11), 3.38 (s, 3H, H_13), 3.64 (s, 3H, H_14), 3.36 (s, 3H, H_15), 3.72 (s, 6H, H_14), 1.86 (sept, J_HH = 3, 2H, H_11), 6.70 (br, 2H, H_12), 6.32 (s, 1H, H_6), 3.99 (s, 3H, H_12), 3.86 (s, 3H, H_13), 3.75 (s, 6H, H_14), 3.72 (dd, J_HH = 6, 2H, H_16), 3.18 (s, 3H, H_14). 13C{1H} NMR (CD_2Cl_2): δ 161.7 (d, J_{13C-1H} = 17, C_13), 156.8 (s, C_12), 154.4 (d, J_{13C-1H} = 4, C_4), 143.1 (s, C_3), 136.4 (d, J_{13C-1H} = 37, C_11), 134.5 (s, C_11), 130.8 (s, C_10), 126.5 (d, J_{13C-1H} = 21, C_2), 126.5 (d, J_{13C-1H} = 19, C_19), 121.5 (s, C_1), 113.9 (s, C_9), 110.8 (s, C_6), 76.7 (d, J_{13C-1H} = 2, C_10), 62.1 (s, C_10), 60.9 (s, C_10), 56.1 (s, C_10), 55.7 (s, C_10), 28.5 (s, C_10), 18.8 (s, C_10). HRMS (ESI mode; m/z): Calcd. for [C_25H_29O_6PS Na]^{+} 549.1712, Found: 549.1710.

4.2.8. Na[1a]
A flask was charged with 1b-iBu (0.72 g, 1.5 mmol), NaI (0.64 g, 4.0 mmol) and CH_3CN (20 mL). CH_3Cl (15 mL) was added to afford a clear solution. The mixture was stirred at room temperature for 2 d to afford a white suspension, which was filtered to afford Na[1a] as a white powder. The product was dried under vacuum. The product was dried under vacuum for 18 h (0.29 g, 85%). 31P{1H} NMR (CD_2OD): δ = 284.4. H NMR (CD_2OD): δ 8.02 (dd, J_HH = 8, J_HH = 4, 1H, H_11), 7.30 (t, J_HH = 8, 2H, H_16), 6.93 (dd, J_HH = 8, J_HH = 5, 2H, H_16), 6.91 (dd, J_HH = 9, J_HH = 3, 1H, H_6), 6.50 (d, J_{13C-1H} = 1, C_1), 69.6 (d, J_{13C-1H} = 3, C_1), 56.0 (d, J_{13C-1H} = 1, C_1), 18.9 (s, C_1). HRMS (ESI mode; m/z): Calcd. for [C_25H_29O_6PS Na]^{+} 549.0304, Found: 549.0325.

4.2.9. Na[1b]
Na[1b] was synthesized analogously to Na[1a] from 1b-iBu (0.36 g, 0.70 mmol), Na (0.450 g, 3.0 mmol) and CH_3CN (5 mL). The mixture was stirred at room temperature for 2 d to afford a white suspension, which was filtered to afford Na[1b] as a white powder. The product was dried under vacuum for 18 h (0.29 g, 85%). 31P{1H} NMR (CD_2OD): δ = 276.4. H NMR (CD_2OD): δ 7.59 (d, J_{13C-1H} = 3, 1H, H_11), 7.35 (t, J_HH = 8, 2H, H_16), 6.91 (dd, J_HH = 8, J_HH = 5, 2H, H_16), 6.65 (br, 2H, H_12), 6.50 (d, J_{13C-1H} = 2, 1H, H_11), 3.92 (s, 3H, H_13), 3.84 (d, J_{13C-1H} = 6, 2H, H_16), 3.72 (s, 6H, H_14), 3.41 (s, 3H, H_14), 1.86 (sept, J_HH = 7, 1H, H_7), 0.89 (d, J_{13C-1H} = 6, 6H, H_14), 13C{1H} NMR (CD_2Cl_2): δ 161.4 (d, J_{13C-1H} = 17, C_13), 152.5 (s, C_15), 149.3 (s, C_14), 134.0 (s, C_12), 133.2 (d, J_{13C-1H} = 28, C_2), 131.5 (d, J_{13C-1H} = 31, C_14), 130.7 (s, C_16), 125.7 (d, J_{13C-1H} = 17, C_12), 121.4 (s, C_11), 118.4 (s, C_6), 113.7 (d, J_{13C-1H} = 5, C_5), 110.7 (s, C_5), 76.8 (d, J_{13C-1H} = 4, C_6), 56.5 (s, C_5), 56.0 (s, C_5), 55.8 (s, C_14), 28.4 (s, C_14), 18.9 (s, C_14). HRMS (ESI mode; m/z): Calcd. for [C_26H_31O_7PS Na]^{+} 519.1606, Found: 519.1616.
A vial was charged with 1c-8Bu (0.31 g, 0.60 mmol), Li (0.35 g, 2.6 mmol) and CH3CN (10 mL), and covered with aluminum foil. The mixture was stirred at room temperature for 4 d. The volatiles were removed under vacuum. THF was added to afford a white suspension, which was filtered to afford 1Li[1c] as a white powder. The product was dried under vacuum for 18 h (0.14 g, 52%). 31P{1H} NMR (CD2Cl2): δ 22.7. 1H NMR (CD2Cl2): δ 7.29 (t, 3JHH = 8, 2H, H1), 7.68 (dd, 3JHH = 8, 3JHP = 5, 2H, H2), 6.82 (tt, 3JHH = 8, 1H, H3), 7.56–7.46 (br, overlap with H10 and H13, 2H, H12), 7.03 (t, 3JHH = 8, 2H, H11), 6.68 (br, 2H, H14), 6.27 (dd, 3JHH = 2, 1H, H13), 3.97 (s, 3H, H15), 3.71 (s, 3H, H16), 3.50 (s, 3H, H17), 0.29 (d, 3JPC = 3, 3H, Pd=P–CH3). 13C{1H} NMR (CD2Cl2): δ 48.2 (d, 4JPC = 3, 3C, C5), 150.5 (s, C4), 149.0 (d, 3JPC = 8, 1C, C3), 143.3 (d, 3JPC = 16, 1C, C2), 133.5 (s, C6), 125.5 (s, C7), 120.9 (d, 3JPC = 11, 1C, C8), 118.9 (d, 3JPC = 53, 1C, C9), 117.6 (d, 3JPC = 4, C6), 117.0 (d, 3JPC = 57, 1C, C10), 111.7 (d, 3JPC = 5, C1), 111.6 (d, 3JPC = 12, C5, 56.4 (s, C16), 56.0 (s, C17), 55.8 (s, C18), 0.3 (d, 3JPC = 4, Pd–CH3). The H12 and C12 resonance are broad because the rate of anisyl group exchange is not in the fast exchange limit. HRMS (APCI/ESI-Mixed mode; m/z): Calcd. for [C23H24O8PS]− 491.1, Found: 491.3.

2a

A vial was charged with Na[1a] (0.14 g, 0.30 mmol), (COD)PdMeCl (80 mg, 0.30 mmol) and CH2Cl2 (6 mL), and the mixture was stirred at room temperature for 1 h to afford a cloudy yellow solution. Pyridine (24 µL, 0.30 mmol) was added, and the mixture was stirred for 18 h, filtered through Celite, layered with pentane and cooled to −40 °C. After 1 d, colorless X-ray quality crystals formed. The crystals were collected by filtration and dried under vacuum for 18 h (34 mg, 51%).

2.12. Generation of 2c

A J-Young valved NMR tube was charged with 1c-8Bu (11 mg, 0.020 mmol) and (COD)PdMeCl (10 mg, 0.037 mmol), and CH2Cl2 was added by vacuum transfer. The mixture was thawed and formed a clear yellow solution. 31P{1H} NMR (CD2Cl2): δ 25.0. 1H NMR (CD2Cl2) Pd–Me region: δ 0.81 (d, 3JHP = 3 Hz). After 18 h, pyridine (1.6 µL, 0.020 mmol) was added, and the reaction was monitored by NMR and found to be complete after 3 d. 31P{1H} NMR (CD2Cl2): δ 20.1. 1H NMR (CD2Cl2) Pd–Me region: δ 0.46 (d, 3JHP = 2 Hz). These data indicate that 2c was successfully generated by this route. However, attempted isolation of 2c was unsuccessful due to decomposition.

4.3. Polymerization procedures

4.3.1. Ethylene homopolymerization

Polymerization reactions were performed in a Parr 300 mL stainless steel autoclave, which was equipped with a mechanical stirrer, thermocouple and water cooling loop and controlled by a Parr 4842 controller. In a glovebox, a 200 mL glass autoclave liner was charged with solution of the catalyst in chlorobenzene (1 mL), and toluene (49 mL) was then added. For catalyst loadings larger than 5 µmol, the catalyst was weighed directly into the glass liner and 50 mL of solvent was added. The glass liner was placed in a stainless steel autoclave, which was sealed and removed from the glovebox. The autoclave was heated to the target temperature and pressurized with ethylene while the contents were stirred. After 2 h, the autoclave was cooled to 25 °C and vented. Acetone (50 mL)
was added to precipitate the polymer. The polymer was collected by filtration, rinsed with acetone, and dried under vacuum.

4.3.2. Ethylene/VF copolymerization

In a glove box, an injection cylinder was charged with a solution of the catalyst (10 µmol) in chlorobenzene (10 mL) and connected to the autoclave. Toluene (40 mL) was added to glass autoclave liner. The liner was placed in the autoclave, and the autoclave was sealed and removed from the glove box. The autoclave was pressurized with VF to the desired pressure and ethylene was added until the total pressure reached 300 psi, while the mixture was stirred (100 rpm). The reactor was heated to the 80 °C and the catalyst solution was injected from the injection cylinder by 450 psi/C14.

References

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.06.012.