# **ORGANOMETALLICS**

# Cationic Palladium(II) Complexes of Phosphine–Sulfonamide Ligands: Synthesis, Characterization, and Catalytic Ethylene Oligomerization

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# **Supporting Information**



**ABSTRACT:** A series of cationic palladium(II) complexes bearing phosphine—sulfonamide ligands, [(P,O)PdMe(lutidine)]-[SbF<sub>6</sub>], were synthesized and used for catalytic ethylene oligomerization. The molecular structure of the complex {[*N*,*N*-dicyclohexyl-2-(diphenylphosphanyl)benzenesulfonamide]PdMe(lutidine)}[SbF<sub>6</sub>] shows that the phosphorus atom and the oxygen atom coordinate to the palladium center. The ethylene oligomerization behavior is greatly influenced by the phosphino substituents, while the substituents on sulfonamide show only minimal effects. Complexes containing the diphenylphosphanyl group are highly selective for ethylene dimerization, affording 1-butene exclusively with moderate activity. The bulkier bis(2-methoxyphenyl)phosphanyl group leads to higher activity and gives  $\alpha$ -olefins containing mainly 1-butene and 1-hexene, with a 1-hexene content of up to 35%. The palladium complexes bearing alkyl phosphino substituents give 1-butene and 1-hexene as the major products; a small amount of 2-butene (<5%) was observed, suggesting the occurrence of chain walking. The addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> greatly enhances the catalytic activity. Experimental results suggest that the increase in activity is likely due to the abstraction of lutidine, not from the coordination of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to the sulfonamide oxygen atom.

# INTRODUCTION

Late-transition-metal-catalyzed olefin polymerization and oligomerization have attracted tremendous attention since the discovery of  $\alpha$ -diimine Ni(II) and Pd(II) catalysts by Brookhart and of phenoxyminato Ni(II) catalysts by Grubbs.<sup>1-3</sup> Following the establishment of the well-known SHOP process,<sup>4</sup> a large number of (P,O)-type ligands have been developed for olefin polymerization and oligomerization.<sup>5</sup> Recently, neutral Pd(II) catalysts with phosphine-sulfonate ligands have been widely reported for the copolymerization of ethylene with a variety of polar vinyl monomers to form functionalized linear copolymers (A; Chart 1).<sup>6</sup> These anionic (P,O)<sup>-</sup> ligands contain a strong  $\sigma$ -donating phosphine and a very weak  $\sigma$ -donating sulfonate group. The electron-unsymmetric feature of these ligands was believed to inhibit  $\beta$ -H (X) elimination, leading to the formation of linear polymers, as well as the incorporation of polar vinyl monomers in ethylene polymerization.<sup>6i</sup> Some other ligands with a strong/weak  $\sigma$ -donor framework similar to that of phosphine-sulfonate have also been developed. For example, Nozaki and co-workers described the preparation of neutral NHC-sulfonate palladium complexes (B1; Chart 1),

but their catalytic behavior was not reported.<sup>7</sup> Jordan and coworkers synthesized neutral NHC-arenesulfonate palladium complexes (B2; Chart 1), which were not active for ethylene polymerization.<sup>8</sup> Piers and Jordan have independently reported the synthesis of bidentate trifluoroborate-phosphine palladium complexes (C; Chart 1), which dimerize ethylene to butenes with low activity.<sup>9</sup> Brookhart and Nozaki reported the synthesis of neutral Ni(II) and Pd(II) catalysts with phosphinesulfonamide ligands (D1 and D2; Chart 1) in patents. The Ni(II) catalysts catalyzed ethylene oligomerization, and the Pd(II) catalyst can copolymerize methyl acrylate and ethylene at 80 °C.<sup>10</sup> Brookhart and co-workers reported the synthesis of low-molecular-weight polyethylene catalyzed by cationic Pd(II) complexes with bulky phenacyldi-tert-butylphosphine ligands (E1; Chart 1).<sup>11</sup> Recently, Nozaki and co-workers reported the synthesis of cationic Pd(II) catalysts with bis-phosphine monoxide ligands (E2, Chart 1), which exhibit good activity for

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Chart 1. Neutral and Cationic Pd(II) Catalysts with Strong/Weak  $\sigma$  Donors



the copolymerization of ethylene with a variety of polar vinyl monomers.  $^{\rm 12}$ 

Inspired by these studies, we decided to investigate the ethylene polymerization/oligomerization behavior of cationic Pd complexes bearing phosphine–sulfonamide ligands containing unsymmetric strong/weak  $\sigma$  donors similar to the widely studied phosphine–sulfonate ligands. Mahon et al. have reported the synthesis of the two phosphine–sulfonamide ligands **2a**,*c*, and the combination of these ligands with Pd precursors was used in Suzuki and amination cross-coupling reactions.<sup>13</sup> However, the Pd complexes of the phosphine–sulfonamide ligands have never been reported for ethylene polymerization or oligomerization. Herein, we report the preparation of a series of cationic Pd(II) methyl catalysts with phosphine–sulfonamide (P, O) ligands (4; Chart 1). These complexes can catalyze the oligomerization of ethylene to selectively form  $\alpha$ -olefins.

# RESULTS AND DISCUSSION

Synthesis and Characterization of Cationic Palladium-(II) Complexes. The synthetic routes for the phosphine– sulfonamide (P,O) ligands 2a-f and the cationic palladium(II) complexes 4a-f are illustrated in Scheme 1. Ligand 2b was prepared by refluxing a THF mixture of  $(o-OMePh)_2P$ -OMe with the lithiated salt of sulfonamide 1a, using the procedure developed by Drent.<sup>6b</sup> Pure 2b was obtained by chromatography (light petroleum/ethyl acetate 8/1) in 17% yield. The reaction of sulfonamide 1a or 1b with 1 equiv of *n*BuLi in THF followed by the addition of  $R_2PCI$  led to the formation of ligands 2a,c-f in 35-91% yield.<sup>13</sup> Attempts to synthesize the ligand with a  $tBu_2P$  group failed, presumably due to steric effects.

The reactions of ligands 2a-f with (COD)PdMeCl (COD = 1,5-cyclooctadiene) yielded phosphine-sulfonamide complexes (P,O)PdMeCl (3a-f), which reacted with silver hexafluor-oantimonate and 2,6-lutidine to generate the cationic palladium complexes 4a-f in good isolated yields (65–79%). All of the

new ligands and palladium complexes were characterized by elemental analysis and NMR spectroscopy.

The molecular structure of 4a was determined by X-ray diffraction analysis (Figure 1), which shows that the palladium center is coordinated to the phosphorus atom and one of the sulfonamide oxygen atoms. The geometry at palladium is square planar, with the methyl ligand cis to the phosphine group. The (P,O)Pd chelate ring adopts a puckered conformation, with one P-Ph group occupying a pseudoaxial position and the other a pseudoequatorial position. The Pd–O distance (2.2160 Å) is longer than those observed in both E2 (2.119 Å) and phosphine-sulfonate palladium complexes (A in Chart 1: 2.159 Å for R = MeO-Ph, L = lut; 2.156 Å for R = Cy, L = lut; 2.177 Å for R = Et-Ph, L = py).<sup>6d,th</sup> The Pd–P distance (2.2310 Å) is similar to those in phosphine-sulfonate palladium complexes (2.234 Å for R = MeO-Ph, L = lut; 2.234 Å for R = Cy, L = lut; 2.231 Å for R = Et-Ph, L = py).<sup>6d,f,h</sup> The coordination of the sulfonamide group makes the S(1)-O(1) distance (1.464 Å) slightly longer than that of S(1)-O(2) (1.436 Å). The Pd-N distance (2.123 Å) is slightly shorter than the average Pd-N distance (2.133 Å) observed in other Pd-lutidine complexes.<sup>6d,e,7</sup>

Oligomerization of Ethylene by Cationic Palladium(II) **Complexes.** The reactivity of the cationic palladium(II) complexes with ethylene was studied. The results are summerized in Table 1. All of these cationic phosphinesulfonamide palladium(II) complexes can oligomerize ethylene mainly to  $\alpha$ -olefins with moderate activity. The selectivity and activity of the oligomerization are greatly influenced by the substituents on the phosphorus atom, while the substituents in the sulfonamide group show only minimal effects. Ethylene oligomerization with the catalysts bearing aryl phosphino substituents exclusively forms  $\alpha$ -olefins. Specifically, when the aryl group is phenyl (4a,e), 1-butene is the only product (entries 1 and 8). The catalyst with the bulkier o-OMePh group (4b) generates  $\alpha$ -olefins containing mainly 1-butene and 1-hexene, with 35.2% of 1-hexene (entry 2). This suggests that steric hindrance at the ortho position of the phenyl group

#### Scheme 1





Figure 1. ORTEP plot of complex 4a  $(C_{39}H_{50}Cl_2F_6N_2O_2PPdSSb-CH_2Cl_2)$ . Hydrogen atoms and  $SbF_6^-$  and  $CH_2Cl_2$  groups have been omitted for clarity. Thermal ellipsoids are presented at the 30% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)-C(1) 2.034(3), Pd(1)-N(1) 2.123(2), Pd(1)-O(1) 2.216(19), Pd(1)-P(1) 2.231(7), S(1)-O(1) 1.464(2), S(1)-O(2) 1.436(2); O(1)-Pd(1)-P(1) 96.49(5), C(14)-P(1)-Pd(1) 110.10(9), C(15)-C(14)-P(1) 123.6(2), C(14)-C(15)-S1 119.39(19), O(1)-S(1)-C(15) 106.4(12).

has a dramatic effect on retarding the chain transfer process. Both increasing and reducing the reaction temperature reduces the selectivity of 1-hexene (entries 3-5). Finally, the catalysts with alkyl phosphino substituents (4c,d,f) lead to mainly 1-butene, some 1-hexene, and a small percentage of 2-butene (entries 6, 7 and 9). This suggests the occurrence of chain walking during the oligomerization.<sup>2b</sup>

 Table 1. Oligomerization of Ethylene with Cationic

 Palladium Complexes

					selectivity $(\%)^c$		
entry <sup>a</sup>	cat.	$T(^{\circ}C)$	P (psi)	$\mathrm{TOF}^b$	1-C4	1-C6	1-C8
1	4a	50	300	2.6	100		
2	4b	50	300	7.4	61.0	35.2	3.8
3	4b	50	150	5.6	66.6	30.8	2.6
4	4b	25	150	0.4	70.2	29.8	
5	4b	80	150	8.0	84.0	14.9	1.1
$6^d$	4c	50	300	9.7	84.3	12.4	
$7^e$	4d	50	300	4.9	90.8	6.4	
8	4e	50	300	2.1	100		
9 <sup>f</sup>	4f	50	300	7.7	92.9	3.0	
$10^g$	4b	50	300	36.0	67.5	32.5	<1
$11^h$	4b	50	300	51.9	63.4	36.6	<1
12	$3b + AgSbF_6$	50	300	36.1	64.1	35.9	<1

<sup>*a*</sup>Conditions: 5  $\mu$ mol of cat., 100 mL of CH<sub>2</sub>Cl<sub>2</sub>, 30 min reaction time. <sup>*b*</sup>In units of 10<sup>3</sup> (mol of ethylene)/((mol of Pd) h). <sup>*c*</sup>1-Cn (%) = 1-Cn/oligomers × 100, detected by GC. *n*-Heptane was used as internal standard. <sup>*d*</sup>3.3% 2-butene. <sup>*e*</sup>2.8% 2-butene. <sup>*f*</sup>4.1% 2-butene. <sup>*g*</sup>Addition of 1 equiv of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. <sup>*h*</sup>Addition of 2 equiv of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

Catalysts with a phenyl substituent on the phosphorus atom (4a,e) give 1-butene with the highest selectivity, but with the lowest activity (entries 1 and 8), while the catalyst with an *o*-OMe-Ph substituent leads to a 2-fold increase in TOF (entry 2). In contrast, catalysts with alkyl substituents on the phosphorus atom (4c,d,f) show 1–3 times higher TOFs (entries 6, 7, and 9). The reaction conditions such as ethylene pressure and temperature also affect the activity. When the

ethylene pressure is decreased from 300 to 150 psi (entry 2 vs entry 3), the TOF decreases from  $7.4 \times 10^3$  to  $5.6 \times 10^3$  (mol of ethylene)/((mol of Pd) h). Reducing the temperature from 50 to 25 °C (entry 3 vs entry 4) leads to a sharp decrease in TOF from  $5.6 \times 10^3$  to  $0.4 \times 10^3$  (mol of ethylene)/((mol of Pd) h). When the temperature is increased from 50 to 80 °C, the TOF has a moderate increase (entry 3 vs 5).

The addition of 1 equiv of  $B(C_6F_5)_3$  results in a dramatic increase in the TOFs from 7.4  $\times$  10<sup>3</sup> to 36.0  $\times$  10<sup>3</sup> (mol of ethylene)/((mol of Pd) h) (entry 10 vs 2) without changing the oligomer distribution. Interestingly, the addition of 2 equiv of  $B(C_6F_5)_3$  leads to a further increase in TOFs without much perturbation in the oligomer distribution (entry 11).  $B(C_6F_5)_3$ may act as a Lewis acid to abstract the lutidine in the cationic palladium complex or coordinate to the sulfonamide oxygen atom.<sup>14,15</sup> During ethylene oligomerization, ethylene must compete with lutidine to coordinate with the palladium(II) center, which will reduce the activity of the catalyst. When 3b was activated in situ by AgSbF<sub>6</sub> (entry 12), oligomerization results were obtained similar to those on catalysis by 4b with the addition of 1 equiv of  $B(C_6F_5)_3$  (entry 10). Recently, Jordan et al. showed that the binding of  $B(C_6F_5)_3$  to a sulfonate oxygen of (phosphine-sulfonate)PdR catalysts results in a 40-80-fold increase in the rate of chain transfer in ethylene polymerization.<sup>15</sup> In one case, the molecular weight  $(M_n)$  of the resulting polyethylene was reduced from 3000 to 170. In our case, the ratio of 1-hexene to 1-butene was essentially not changed (entries 10 and 11 vs entry 2) with the addition of 0, 1, or 2 equiv of  $B(C_6F_5)_3$ , suggesting the presence of the same catalytically active species. Therefore, the coordination of  $B(C_6F_5)_3$  to the sulfonamide oxygen atom may be minimal under our reaction conditions. The bulky dicyclohexylamino substituent on the sulfonamide group can potentially prevent the coordination of  $B(C_6F_5)_3$  to the oxygen atom.

As discussed above, analogous phosphine-sulfonate palladium complexes (A; Chart 1) and bis-phosphine monoxide palladium complexes (E2; Chart 1) are highly active in ethylene polymerization. This dramatic difference may be attributed to the relatively weak electron donating ability of the sulfonamide group in comparison with the sulfonate and phosphine monoxide groups.<sup>9a</sup> This leads to an electrondeficient palladium center, which makes the palladium-lutidine coordination tighter. This is consistent with the shorter Pd-N bond distance in 4a in comparison to the average Pd-N <sup>5d,e,7</sup> The distance observed in other Pd-lutidine complexes.<sup>6</sup> strong binding affinity of lutidine toward the Pd(II) center in 4 likely leads to the inhibition of the catalytic activity of olefin oligomerization. The electron-deficient feature of the palladium center may promote  $\beta$ -hydride elimination during chain propagation and result in the formation of lower oligomers.<sup>16</sup>

#### CONCLUSIONS

A series of cationic palladium(II) complexes with phosphine– sulfonamide ligands were synthesized. These palladium complexes can oligomerize ethylene mainly to  $\alpha$ -olefins with moderate activity. The longer Pd–O distance and shorter Pd–N distance of **4a** in comparison to the analogous palladium complexes suggest an electron-deficient palladium center. This might be the reason for the high chain transfer rates, resulting in the formation of lower oligomers. Complexes with aryl substituents on phosphine afford  $\alpha$ -olefins exclusively, and complexes with alkyl substituents on phosphine led to the formation of a small portion of 2-butene with the main products as 1-butene and 1-hexene. The addition of  $B(C_6F_5)_3$  was shown to greatly increase the oligomerization activity. This effect is attributed to the abstract of lutidine, which would compete with ethylene for the binding to palladium center during oligomerization.

#### EXPERIMENTAL SECTION

**General Considerations.** Unless otherwise stated, all manipulations were carried out under a dry argon or nitrogen atmosphere using standard Schlenk techniques. Solvents were purified by distillation over sodium benzophenone (diethyl ether, tetrahydrofuran, toluene, *n*-hexane) and CaH<sub>2</sub> (dichloromethane). CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub> were purchased from Cambridge, dried with 4 Å molecular sieves, and stored under nitrogen. Polymerization grade ethylene was used after purification. PhSO<sub>2</sub>NCy<sub>2</sub> (**1a**),<sup>13</sup> PhSO<sub>2</sub>NMe<sub>2</sub> (**1b**),<sup>13</sup> ligands **2a**,*c*,<sup>13</sup> (*o*-OMePh)<sub>2</sub>P-OMe,<sup>6b</sup> and (COD)PdMeCl<sup>14</sup> were prepared according to previously reported procedures. All other reagents and solvents were purchased from commercial sources and used without further purification.

NMR spectra were recorded on Agilent 400 MHz and Varian Mercury 400 MHz instruments. <sup>1</sup>H NMR chemical shifts were referenced to residual protio solvent peaks or the tetramethylsilane signal (0 ppm), and <sup>13</sup>C NMR chemical shifts were referenced to the solvent resonance. <sup>31</sup>P NMR chemical shifts were referenced to an external  $H_3PO_4$  standard. GC-MS measurements were performed on a Agilent 7890A gas chromatograph coupled to an Agilent 5975C inert mass-selective detector. GC analyses were carried out on an Agilent 7890A gas chromatograph equipped with a flame ionization detector. Elemental analyses were carried out by the Analytic laboratory of Shanghai Institute of Organic Chemistry (CAS). IR data were obtained on a Bruker TENSOR 27 instrument.

Preparation of the Ligands and Palladium(II) Complexes. Ligand 2b.



n-BuLi in n-hexane (2.5 mL, 6.0 mmol) was added dropwise to a solution of PhSO2NCy2 (1a; 6.0 mmol, 2.0 g) in 40 mL of THF at -78 °C. After the mixture was stirred for 3 h at room temperature, a solution of 6 mmol of (o-OMePh)<sub>2</sub>P-OMe (1.65 g) in 20 mL of THF was added dropwise at room temperature and the reaction mixture was stirred under reflux for 3 days. Then the reaction mixture was quenched with saturated NH<sub>4</sub>Cl (100 mL) and diluted with 150 mL of CH<sub>2</sub>Cl<sub>2</sub> The organic layer was separated, and the aqueous phase was extracted with  $CH_2Cl_2$  (50 mL). The combined organic layers were dried over anhydrous MgSO4, filtered, and concentrated to give a light yellow solid. The residue was chromatographed on a silica gel column (ethyl acetate/petroleum ether 1/8,  $R_f = 0.55$ ) to give pure **2b** in 17% yield (0.57 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.02–1.15 (2H, m, CH<sub>2</sub>), 1.17–1.35 (4H, m, CH<sub>2</sub>), 1.53–1.65 (2H, m, CH<sub>2</sub>), 1.66-1.90 (10H, m, CH<sub>2</sub>), 3.60-3.80 (2H, m, NCH), 3.70 (6H, s, OCH<sub>3</sub>), 6.52-6.68 (1H, bs, Ar-H), 6.79-6.92 (4H, m, Ar-H), 7.01-7.08 (1H, m, Ar-H), 7.24–7.34 (3H, m, Ar-H), 7.40 (1H, t, J = 7.8 Hz, Ar-H), 8.08–8.14 (1H, m, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  151.04 (d, J = 16.8 Hz), 146.91 (d, J = 25.0 Hz), 137.39 (d, J = 30.8 Hz), 135.21, 134.09, 130.95, 129.99 (d, J = 3.0 Hz), 129.86, 128.23, 125.83 (d, J = 16.6 Hz), 121.00, 110.31, 57.93 (d, J = 5.4 Hz), 55.49, 32.98, 26.63, 25.42. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  –26.39 ppm. Anal. Calcd for C<sub>32</sub>H<sub>40</sub>NO<sub>4</sub>PS: C, 67.94; H, 7.13; N, 2.48. Found: C, 68.16; H, 7.09; N, 2.50. Ligand 2d.



To a solution of PhSO<sub>2</sub>NCy<sub>2</sub> (1a; 6.0 mmol, 2.0 g) in 40 mL of THF was added dropwise 2.5 mL of a hexane solution of *n*-BuLi (6.0 mmol) at -78 °C. After the mixture was stirred for 30 min, *i*Pr<sub>2</sub>PCl (1.0 mL, 6.0 mmol) in 20 mL of THF was added dropwise to the reaction

vessel. The reaction mixture was slowly warmed to room temperature and was stirred overnight. After 20 h, the reaction mixture was quenched with saturated degassed NH<sub>4</sub>Cl (100 mL). The organic layer was separated, and the aqueous phase was extracted with Et<sub>2</sub>O (50 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated to give a white solid of 2d in 89% yield (2.3 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.99 (3H, d, J = 7.0 Hz,  $CH_3$ ), 1.02 (3H, d, J = 7.0 Hz,  $CH_3$ ), 1.05–1.30 (6H, m,  $CH_2$ ), 1.12 (3H, d, J = 7.0 Hz, CH<sub>3</sub>), 1.15 (3H, d, J = 7.0 Hz, CH<sub>3</sub>), 1.52-1.61 (2H, m, CH<sub>2</sub>), 1.66–1.80 (12H, m, CH<sub>2</sub>), 2.06–2.19 (2H, m, PCH), 3.55-3.67 (2H, m, NCH), 7.35-7.47 (2H, m, Ar-H), 7.56 (1H, d, J = 7.4 Hz, Ar-H), 8.03-8.09 (1H, m, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,  $CDCl_{2}$ :  $\delta$  148.64 (d, I = 22.8 Hz), 138.02 (d, I = 35.2 Hz), 133.10 (d, J = 2.0 Hz), 130.45, 129.74 (d, J = 3.6 Hz), 128.14, 57.82 (d, J = 5.4 Hz), 33.00, 26.59, 25.37, 24.69 (d, J = 17.0 Hz), 20.81 (d, J = 16.0 Hz), 19.27 (d, J = 16.6 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  4.71 ppm. Anal. Calcd for C24H40NO2PS: C, 65.87; H, 9.21; N, 3.20. Found: C, 65.66; H, 9.38; N, 3.27.

Ligand 2e.

To a solution of PhSO<sub>2</sub>NMe<sub>2</sub> (1b; 11.0 mmol, 2.1 g) in 40 mL of THF was added dropwise 4.6 mL of a hexane solution of n-BuLi (11.0 mmol) at -78 °C. After the mixture was stirred for 30 min, Ph<sub>2</sub>PCl (2.0 mL, 11.0 mmol) in 20 mL of THF was added dropwise to the reaction vessel. The reaction mixture was slowly warmed to room temperature and was stirred overnight. After 20 h, the reaction was quenched with saturated degassed  $NH_4Cl$  (100 mL). The organic layer was separated, and the aqueous phase was extracted with degassed Et<sub>2</sub>O (50 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated to give a white solid. The crude material was purified by flash chromatography with CH<sub>2</sub>Cl<sub>2</sub> as eluent to yield ligand 2e as a white solid in 67% yield (2.7 g). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  2.63 [6H, s, N( $CH_3$ )<sub>2</sub>], 7.13–7.17 (1H, m, Ar-H), 7.17-7.23 (4H, m, Ar-H), 7.30-7.35 (6H, m, Ar-H), 7.41-7.51 (2H, m, Ar-H), 8.08-8.13 (1H, m, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  142.31 (d, J = 24.2 Hz), 137.92 (d, J = 29.8 Hz), 136.88, 136.74, 133.55 (d, J = 20.6 Hz), 132.32, 130.66 (d, J =3.4 Hz), 128.88, 128.68, 128.46 (d, J = 6.8 Hz), 36.66 (d, J = 4.92 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  –9.09 ppm. Anal. Calcd for C<sub>20</sub>H<sub>20</sub>NO<sub>2</sub>PS: C, 65.03; H, 5.46; N, 3.79. Found: C, 64.76; H, 5.49; N, 3.80.

Ligand 2f.

The same procedure as described for the synthesis of **2d** was employed to prepare **2f**. PhSO<sub>2</sub>NMe<sub>2</sub> (**1b**; 6.0 mmol, 1.1 g), *n*-BuLi in hexane (2.5 mL, 6.0 mmol), and iPr<sub>2</sub>PCl (1.0 mL, 6 mmol) were used to yield ligand **2f** as a white solid (91%, 1.6 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.89 [3H, d, J = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>], 0.92 [3H, d, J = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>], 1.13 [3H, d, J = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>], 1,17 [3H, d, J = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>], 1,17 [3H, d, J = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>], 2.04–2.18 (2H, m, CH), 2.83 [6H, s, N(CH<sub>3</sub>)<sub>2</sub>], 7.44 (1H, td, J = 7.6, 0.8 Hz, Ar-H), 7.52 (1H, td, J = 7.4, 1.2 Hz, Ar-H), 7.69 (1H, d, J = 7.6, Ar-H), 8.03 (1H, dm, J = 8.0, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  144.10 (d, J = 23.8 Hz), 139.09 (d, J = 38.0 Hz), 134.13 (d, J = 2.5 Hz), 131.37, 130.41 (d, J = 4.2 Hz), 128.42, 37.48 (d, J = 7.2 Hz), 25.40 (d, J = 16.4 Hz), 20.32 (d, J = 13.4 Hz), 19.95 (d, J = 19.4 Hz). <sup>31</sup>P{<sup>1</sup>H</sup> NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  3.23 ppm. Anal. Calcd for C<sub>14</sub>H<sub>24</sub>NO<sub>2</sub>PS: C, 55.79; H, 8.03; N, 4.65. Found: C, 55.73; H, 8.03; N, 4.64.

Complex 3a.



Ligand 2a (1.7 mmol, 0.86 g) was dissolved in 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. To the colorless solution was added 1.7 mmol of (COD)PdMeCl (0.47 g), forming a light yellow solution. The mixture was stirred for 3 h at room temperature. Removing the solvent in vacuo yielded a light yellow solid. The solid was washed with hexane  $(2 \times 10 \text{ mL})$  and dried in vacuo for 30 min to give an off-white solid as the product (1.0 g, 93%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.80 (3H, d, J = 2.7 Hz, Pd-CH<sub>3</sub>), 0.92–1.16 (6H, m, CH<sub>2</sub>), 1.42–1.80 (14H, m, CH<sub>2</sub>), 3.10–3.22 (2H, m, CH), 7.11 (1H, t, J = 8.5 Hz, Ar-H), 7.32-7.55 (10H, m, Ar-H), 7.62 (2H, t, J = 8.5 Hz, Ar-H), 7.88–7.96 (1H, m, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  145.86 (d, J = 11.6 Hz), 135.56, 134.21 (d, I = 12.7 Hz), 131.93 (d, I = 5.0 Hz), 131.62 (d, I = 10.0 Hz),131.28, 131.11, 130.90, 128.93 (d, J = 6.8 Hz), 128.67 (d, J =11.0 Hz), 128.46, 127.95 (d, J = 12.8 Hz), 126.78. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 30.19 ppm. Anal. Calcd for C<sub>31</sub>H<sub>39</sub>ClNO<sub>2</sub>PPdS· 0.3CH<sub>2</sub>Cl<sub>2</sub>: C, 54.64; H, 5.80; N, 2.04. Found: C, 54.91; H, 6.05; N. 1.98.

Complex 3b.



The same procedure as described for the synthesis of **3a** was used. Ligand **2b** (0.4 g, 0.7 mmol) and (COD)PdMeCl (0.18 g, 0.7 mmol) were used to give **3b** (0.48 g, 95%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  0.58 (3H, d, J = 2.8 Hz, Pd-CH<sub>3</sub>), 0.98–1.12 (6H, m, CH<sub>2</sub>), 1.48–1.55 (2H, m, CH<sub>2</sub>), 1.60–1.85 (12H, m, CH<sub>2</sub>), 2.99–3.09 (2H, m, NCH), 3.64 (6H, s, OCH<sub>3</sub>), 6.94–7.06 (4H, m, Ar-H), 7.33–7.48 (3H, m, Ar-H), 7.50–7.66 (4H, m, Ar-H), 7.88–7.96 (1H, m, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  161.38 (d, J = 2.9 Hz), 145.21 (d, J = 12.8 Hz), 137.50, 136.17 (d, J = 2.2 Hz), 134.31, 131.49 (d, J = 19.1 Hz), 131.35 (d, J = 35.9 Hz), 130.08 (d, J = 6.5 Hz), 121.80 (d, J = 11.3 Hz), 116.63, 116.11, 112.12 (d, J = 4.4 Hz), 59.12, 56.13, 32.52, 27.00, 25.72, -0.25. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  22.72 ppm. Anal. Calcd for C<sub>33</sub>H<sub>43</sub>ClNO<sub>4</sub>PPdS-CH<sub>2</sub>Cl<sub>2</sub>: C, 50.57; H, 5.62; N, 1.73. Found: C, 50.69; H, 5.37; N, 2.17. *Complex* **3c**.



The same procedure as described for the synthesis of **3a** was used. Ligand **2c** (0.62 g, 1.2 mmol) and (COD)PdMeCl (0.32 g, 1.2 mmol) were used to give **3c** (0.75 g, 93%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.98 (3H, d, J = 2.2 Hz, Pd-CH<sub>3</sub>), 1.02–1.32 (16H, m, CH<sub>2</sub>), 1.51–2.02 (22H, m, 22CH<sub>2</sub>, 2PCH), 2.10–2.30 (4H, m, CH<sub>2</sub>), 3.15–3.30 (2H, m, NCH), 7.58–7.68 (2H, m, Ar-H), 7.76 (1H, t, J = 7.4 Hz, Ar-H), 7.91 (1H, dm, J = 7.6 Hz, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  147.48 (d, J = 9.6 Hz), 133.91, 131.57 (d, J = 4.4 Hz), 130.34, 128.38 (d, J = 29.2 Hz), 127.72 (d, J = 5.0 Hz), 59.19, 35.40 (d, J = 2.4 Hz), 31.92, 31.31, 29.23 (d, J = 4.0 Hz), 28.36, 26.71 (d, J = 2.2 Hz), 26.69 (d, J = 22.0 Hz), 26.21, 25.58, 24.84, 22.38, 13.88, -4.78. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  33.72 ppm. Anal. Calcd for C<sub>31</sub>H<sub>51</sub>ClNO<sub>2</sub>PPdS·CH<sub>2</sub>Cl<sub>2</sub>: C, 50.60; H, 7.03 N, 1.84. Found: C, 50.92; H, 7.43; N, 2.38.

Complex 3d.



The same procedure as described for the synthesis of **3a** was used. Ligand **2d** (0.40 g, 0.91 mmol) and (COD)PdMeCl (0.24 g, 0.91 mmol) were used to give **3d** (0.53 g, 94%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.98 (3H, d, J = 2.2 Hz, Pd-CH<sub>3</sub>), 1.05–1.40 (6H, m, CH<sub>2</sub>), 1.18–1.28 (12H, m, CH<sub>3</sub>), 1.50–1.60 (2H, m, CH<sub>2</sub>), 1.72–1.87 (8H, m, CH<sub>2</sub>), 1.92–2.02 (4H, m, CH<sub>2</sub>), 2.46–2.58 (2H, m, PCH), 3.17–3.30 (2H, m, NCH), 7.58–7.68 (2H, m, Ar-H), 7.69–7.76 (1H, m, Ar-H), 7.88–7.96 (1H, m, Ar-H).  $^{13}C{^{1}H}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  147.15 (d, J = 9.2 Hz), 133.58, 131.70 (d, J = 4.0 Hz), 130.96, 128.39 (d, J = 27.2 Hz), 127.99, 59.11, 31.93, 26.16, 25.74 (d, J = 24.4 Hz), 24.78, 18.76 (d, J = 5.6 Hz), 18.18, –5.42.  $^{31}P{^{1}H}$  NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  40.22 ppm. Anal. Calcd for C<sub>25</sub>H<sub>43</sub>ClNO<sub>2</sub>PPdS: C, 50.51; H, 7.29; N, 2.36. Found: C, 50.30; H, 7.28; N, 2.34.

Complex 3e.



The same procedure as described for the synthesis of **3a** was used. Ligand **2e** (0.53 g, 1.4 mmol) and (COD)PdMeCl (0.37 g, 1.4 mmol) were used to give **3e** (0.53 g, 92%) as a light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.88 (3H, d, J = 3.8 Hz, Pd-CH<sub>3</sub>), 3.04 [6H, s, N(CH<sub>3</sub>)<sub>2</sub>], 7.10 (1H, t, J = 8.8 Hz, Ar-H), 7.42–7.55 (10H, m, Ar-H), 7.64 (1H, t, J = 7.6 Hz, Ar-H), 7.71 (1H, t, J = 7.6 Hz, Ar-H), 8.25–8.31 (m, 1H, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  138.36 (d, J = 12.6 Hz), 137.39 (d, J = 1.6 Hz), 135.29, 135.15 (d, J = 5.8 Hz), 135.01 (d, J = 12.8 Hz), 130.21, 129.66, 129.54 (d, J = 11.4 Hz), 40.91, 3.24 (d, J = 2.0 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  29.93 ppm. Anal. Calcd for C<sub>21</sub>H<sub>23</sub>CINO<sub>2</sub>PPdS: C, 47.92; H, 4.40 N, 2.66. Found: C, 47.37; H, 4.41; N, 2.68.

Complex 3f.

The same procedure as described for the synthesis of **3a** was used. Ligand **2f** (0.49 g, 1.3 mmol) and (COD)PdMeCl (0.34 g, 1.3 mmol) were used to give **3f** (0.60 g, 95%) as a light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.08 (3H, d, J = 2.6, Pd-CH<sub>3</sub>), 1.19–1.30 [12H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 2.58–2.70 (2H, m, CH), 3.00 [6H, s, N(CH<sub>3</sub>)<sub>2</sub>], 7.71 (1H, tt, J = 7.6, 1.2, Ar-H), 7.76 (1H, td, J = 7.6, 1.4, Ar-H), 7.94 (1H, t, J = 7.0, Ar-H), 8.08 (1H, dm, J = 7.8, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  141.96 (d, J = 9.8 Hz), 134.64, 132.94 (d, J = 4.0 Hz), 131.44, 129.99, 128.94 (d, J = 25.6 Hz), 39.23, 25.87 (d, J = 25.4 Hz), 18.84 (d, J = 4.6 Hz), 18.33, -4.80. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz CDCl<sub>3</sub>):  $\delta$  38.67 ppm. Anal. Calcd for C<sub>22</sub>H<sub>36</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>PPdSSb: C, 34.51; H, 4.74; N, 3.66. Found: C, 34.26; H, 4.88; N, 3.74.

Complex 4a.



Complex 3a (0.20 g, 0.30 mmol) was dissolved in 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. To the light yellow solution was added lutidine (35  $\mu$ L, 0.30 mmol), and the solution was stirred for 30 min. Then 0.30 mmol of silver hexafluoroantimonate (AgSbF<sub>6</sub>; 0.1 g) was added to the reaction mixture. The mixture was stirred vigorously at room temperature for 3 h. The gray solid was removed by filtration through Celite, and the filtrate was evaporated and dried under vacuum. The residue was further purified by recrystallization from a dichloromethane/hexane mixture. Crystals suitable for X-ray diffraction were obtained in this mixed solution at room temperature. Pure 4a was obtained as colorless crystals in a yield of 79% (0.23 g). <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ ):  $\delta$ 0.60 (3H, d, J = 2.8 Hz, Pd-CH<sub>3</sub>), 0.82-1.15 (6H, m, CH<sub>2</sub>), 1.45-1.72 (14H, m, CH<sub>2</sub>), 3.05-3.16 (2H, m, NCH), 3.11 (6H, s, py-CH<sub>3</sub>), 7.24-7.29 (1H, m, py-H), 7.29 (2H, d, J = 7.8 Hz, py-H), 7.50-7.70 (11H, m, Ar-H), 7.76 (2H, t, J = 7.8 Hz Ar-H), 7.87–7.93 (1H, m, Ar-*H*). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  159.22, 146.18 (d, *J* = 11.8 Hz), 140.27, 137.45, 134.79 (d, J = 12.6 Hz), 133.99 (d, J = 6.2 Hz),

132.99 (d, *J* = 2.0 Hz), 132.92 (d, *J* = 2.4 Hz), 130.54, 130.18 (d, *J* = 11.4 Hz), 128.81 (d, *J* = 6.6 Hz), 128.44, 127.90, 123.77 (d, *J* = 3.2 Hz), 60.54, 32.98, 26.97, 26.87, 25.67, 0.78. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  28.39 ppm. Anal. Calcd for C<sub>38</sub>H<sub>48</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>PPdSSb-CH<sub>2</sub>Cl<sub>2</sub>: C, 44.16; H, 4.78; N, 2.67. Found: C, 44.40; H, 4.78; N, 2.66. *Complex 4b*.



The same procedure as described for the synthesis of **4a** was used. The complex **3b** (0.35 g, 0.48 mmol), lutidine (55  $\mu$ L, 0.48 mmol), and AgSbF<sub>6</sub> (0.16 g, 0.48 mmol) were used to give **4b** (0.37 g, 75%) as a white solid. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  0.39 (3H, d, J = 3.0 Hz, Pd-CH<sub>3</sub>), 0.85–1.09 (6H, m, CH<sub>2</sub>), 1.42–1.70 (14H, m, CH<sub>2</sub>), 2.96–3.06 (2H, m, NCH), 3.10 (6H, s, py-H), 3.73 (6H, s, OCH<sub>3</sub>), 7.05–7.13 (4H, m, 3Ar-H, py-H), 7.23–7.28 (2H, m, py-H), 7.35–7.76 (8H, m, Ar-H), 7.85–7.92 (1H, m, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  161.36, 159.45, 149.68, 145.02 (d, J = 1.8 Hz), 139.90, 136.85, 135.08, 132.68 (d, J = 6.6 Hz), 132.16 (d, J = 1.8 Hz), 130.58, 130.12, 128.93 (d, J = 7.2 Hz), 123.56 (d, J = 3.4 Hz), 122.02 (d, J = 11.2 Hz), 114.95, 114.30, 112.29 (d, J = 4.8 Hz), 111.78, 59.95, 56.07, 32.59, 26.86, 26.72, 25.69, 0.58. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  18.81 ppm. Anal. Calcd for C<sub>39</sub>H<sub>49</sub>F<sub>6</sub>N<sub>2</sub>O<sub>4</sub>PPdSSb: C, 46.15; H, 4.87, N, 2.76.

Complex **4c**.



The same procedure as described for the synthesis of 4a was used. The complex 3c (0.20 g, 0.30 mmol), lutidine (35  $\mu$ L, 0.30 mmol), and AgSbF<sub>6</sub> (0.10 g, 0.30 mmol) were used to give 4c (0.23 g, 79%) as a white solid. <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ ):  $\delta$  0.68–0.73 (3H, m, Pd-CH<sub>3</sub>), 0.96-1.46 (16H, m, CH<sub>2</sub>), 1.52-1.95 (22H, m, CH<sub>2</sub>), 2.14-2.26 (2H, m, CH<sub>2</sub>), 2.32–2.46 (2H, m, PCH), 3.10 (6H, s, py-CH<sub>3</sub>), 3.07-3.14 (2H, m, NCH), 7.23-7.29 (2H, m, py-H), 7.70-7.93 (5H, m, 4Ar-H, Py-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 159.29, 147.07 (d, J = 8.8 Hz), 140.02, 135.76, 133.59 (d, J = 5.2 Hz), 132.54 (d, J = 2.0 Hz), 128.43 (d, J = 5.2 Hz), 127.73 (d, J = 30.6 Hz), 123.72 (d, J = 3.0 Hz), 60.72, 36.39 (d, J = 25.2 Hz), 32.82, 30.42 (d, J =3.6 Hz), 29.44, 27.64 (d, J = 33.8 Hz), 27.63 (d, J = 8.4 Hz), 27.03, 26.83 (d, J = 1.2 Hz), 26.66, 25.79, -4.61 (d, J = 2.4 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz,  $CD_2Cl_2$ ):  $\delta$  32.73 ppm. Anal. Calcd for C<sub>38</sub>H<sub>60</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>PPdSSb·CH<sub>2</sub>Cl<sub>2</sub>: C, 43.90; H, 5.86; N, 2.63. Found: C, 43.97; H, 6.09; N, 2.75.

Complex 4d.



The same procedure as described for the synthesis of **4a** was used. The complex **3d** (0.20 g, 0.32 mmol), lutidine (37  $\mu$ L, 0.32 mmol), and AgSbF<sub>6</sub> (0.11 g, 0.32 mmol) were used to give **4d** (0.22 g, 76%) as a light yellow solid. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  0.72 (3H, d, *J* = 2.0 Hz, Pd-CH<sub>3</sub>), 1.00–1.22 (6H, m, CH<sub>2</sub>), 1.26–1.38 [12H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 1.52–1.77 (14H, m, CH<sub>2</sub>), 2.63–2.74 (2H, m, PCH), 3.05–3.17 (2H, m, NCH), 3.11 (6H, s, py-CH<sub>3</sub>), 7.27 (2H, d, *J* = 7.8 Hz, py-H), 7.72–7.95 (SH, m, 4Ar-H, py-H).<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  158.85, 146.55 (d, *J* = 8.6 Hz), 139.64, 135.11, 133.25 (d, *J* = 5.2 Hz), 132.29 (d, *J* = 2.0 Hz), 129.12 (d, *J* = 5.6 Hz), 127.25 (d, *J* = 31.2 Hz), 26.17, 25.36, 19.38 (d, *J* = 4.6 Hz), 18.43, -5.57 (d, *J* = 2.8 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  39.99 ppm.

Anal. Calcd for  $C_{32}H_{52}F_6N_2O_2PPdSSb:$  C, 42.61; H, 5.81; N, 3.11. Found: C, 42.27; H, 5.98; N, 2.95.

Complex **4e**.



The same procedure as described for the synthesis of **4a** was used. The complex **3e** (0.20 g, 0.38 mmol), lutidine (44  $\mu$ L, 0.38 mmol), and AgSbF<sub>6</sub> (0.13 g, 0.38 mmol) were used to give **4e** (0.21 g, 67%) as a white solid. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  0.60 (3H, d, J = 3.4 Hz, Pd-CH<sub>3</sub>), 2.73 [6H, s, N(CH<sub>3</sub>)<sub>2</sub>], 3.13 [6H, s, py(CH<sub>3</sub>)<sub>2</sub>], 7.29–7.35 (3H, m, py-2H, Ar-H), 7.52–7.61 (10H, m, Ar-H), 7.71–7.85 (4H, m, py-H, Ar-3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.17, 142.15 (d, J = 12.6 Hz), 140.34, 137.91 (d, J = 1.8 Hz), 134.80 (d, J = 12.6 Hz), 134.69, 133.24 (d, J = 1.8 Hz), 132.91 (d, J = 2.6 Hz), 131.12, 130.71, 130.20 (d, J = 11.4 Hz), 129.82 (d, J = 6.6 Hz), 129.18, 127.63, 124.14 (d, J = 2.2 Hz), 38.49, 27.17, 1.74 (d, J = 2.2 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 M HZ CDCl<sub>3</sub>):  $\delta$  27.63 ppm. Anal. Calcd for C<sub>22</sub>H<sub>36</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>PPdSSb: C, 40.33; H, 3.87; N, 3.36. Found: C, 40.00; H, 3.61; N, 3.61.

Complex 4f.



The same procedure as described for the synthesis of 4a was used. 3f (0.20 g, 0.41 mmol), lutidine (48 µL, 0.41 mmol), and AgSbF<sub>6</sub> (0.14 g, 0.41 mmol) were used to give 4f (0.20 g, 65%) as a light yellow solid. <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ ):  $\delta$  0.71 (3H, d, J = 2.4, Pd-CH<sub>3</sub>), 1.28  $[3H, d, J = 7.0, CH(CH_3)_2], 1.31 [3H, d, J = 2.6, CH(CH_3)_2], 1.33$  $[3H, d, J = 2.6, CH(CH_3)_2], 1.37 [3H, d, J = 7.0, CH(CH_3)_2], 2.52-$ 2.74 (2H, m, CHMe<sub>2</sub>), 3.00 [6H, s, N(CH<sub>3</sub>)<sub>2</sub>], 3.11 (6H, s, py-CH<sub>3</sub>), 7.28 (2H, d, J = 7.8, py-H), 7.54-7.59 (1H, m, Ar-H), 7.75 (1H, t, J = 7.8, py-H), 7.78-7.91 (3H, m, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,  $CDCl_3$ ):  $\delta$  159.39, 145.43 (d, J = 9.2 Hz), 140.03, 135.90, 133.90 (d, J = 5.2 Hz), 133.34 (d, J = 2.0 Hz), 127.36 (d, J = 5.0 Hz), 127.64, 126.63, 124.03 (d, J = 3.0 Hz), 111.43, 39.06, 26.73 (d, J = 26.4 Hz), 26.69, 19.64 (d, J = 4.6 Hz), 18.76, -4.62 (d, J = 3.0 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  39.06 ppm. Anal. Calcd for C22H36F6N2O2PPdSSb: C, 34.51; H, 4.74; N, 3.66. Found: C, 34.26; H, 4.88; N, 3.74.

General Procedure for Ethylene Oligomerization with Complexes 4a–f. Ethylene oligomerization reactions were performed in a 300 mL stainless steel autoclave with a magnetic stirrer. In the glovebox, the catalyst was weighed and dissolved in 5 mL of  $CH_2Cl_2$ . The autoclave was heated under vacuum for 1 h to 100 °C and then cooled to the required reaction temperature under an ethylene atmosphere and charged with 100 mL of  $CH_2Cl_2$ . The solution was stirred for about 30 min. Then the catalyst in  $CH_2Cl_2$  was added. The reactor was then pressurized with ethylene, and the ethylene pressure was kept constant during the oligomerization reaction. After 30 min, the autoclave was cooled quickly with liquid nitrogen/ethanol, and then the ethylene pressure was released slowly. Quantitative GC analysis of the product was performed immediately with *n*-heptane as an internal standard.

#### ASSOCIATED CONTENT

# **Supporting Information**

Text, tables, figures, and CIF files giving crystallographic data for complex 4a, GC methods and GC spectra, and IR spectra of ligand 2f complexes 4a,f in the solid state and in solution. This material is available free of charge via the Internet at http:// pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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