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ARTICLE *in* ORGANOMETALLICS · JULY 2014

Impact Factor: 4.13 · DOI: 10.1021/om5004094

ORGANOMETALLICS

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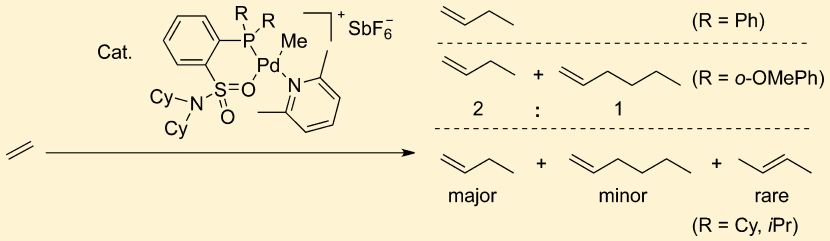
Cationic Palladium(II) Complexes of Phosphine–Sulfonamide Ligands: Synthesis, Characterization, and Catalytic Ethylene Oligomerization

Yanlu Zhang,[†] Yanchun Cao,[†] Xuebing Leng,[†] Changle Chen,*[,‡] and Zheng Huang*[,†]

[†]The State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, 345 Lingling Road, Shanghai 200032, People's Republic of China

[‡]CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science & Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China

Supporting Information



ABSTRACT: A series of cationic palladium(II) complexes bearing phosphine–sulfonamide ligands, [(P,O)PdMe(lutidine)][SbF_6], were synthesized and used for catalytic ethylene oligomerization. The molecular structure of the complex {[*N*,*N*-dicyclohexyl-2-(diphenylphosphanyl)benzenesulfonamide]PdMe(lutidine)}[SbF_6] 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 α-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 $B(C_6F_5)_3$ 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 $B(C_6F_5)_3$ to the sulfonamide oxygen atom.

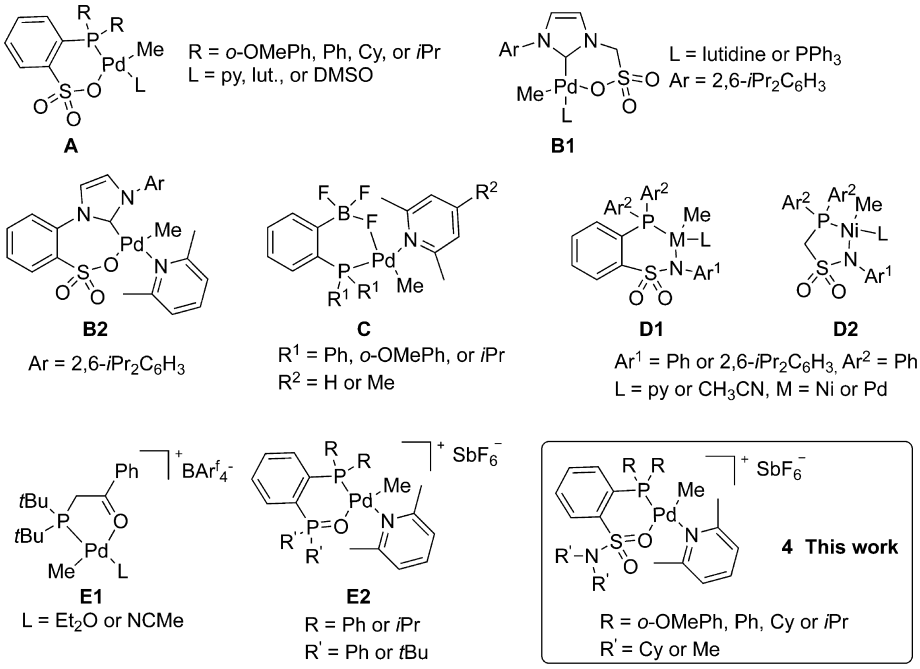
INTRODUCTION

Late-transition-metal-catalyzed olefin polymerization and oligomerization have attracted tremendous attention since the discovery of α-diimine Ni(II) and Pd(II) catalysts by Brookhart and of phenoxyminato Ni(II) catalysts by Grubbs.[1−3] Following the establishment of the well-known SHOP process,[4] a large number of (P,O)-type ligands have been developed for olefin polymerization and oligomerization.[5] 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).[6] These anionic $(P,O)^-$ ligands contain a strong σ-donating phosphine and a very weak σ-donating sulfonate group. The electron-unsymmetric feature of these ligands was believed to inhibit β-H (X) elimination, leading to the formation of linear polymers, as well as the incorporation of polar vinyl monomers in ethylene polymerization.[6i] Some other ligands with a strong/weak σ-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.[7] Jordan and co-workers synthesized neutral NHC–arenesulfonate palladium complexes (**B2**; Chart 1), which were not active for ethylene polymerization.[8] 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.[9] Brookhart and Nozaki reported the synthesis of neutral Ni(II) and Pd(II) catalysts with phosphine–sulfonamide 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.[10] 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).[11] 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

Received: April 17, 2014
Published: July 16, 2014

   dx.doi.org/10.1021/om5004094 | *Organometallics* 2014, 33, 3738–3745

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



the copolymerization of ethylene with a variety of polar vinyl monomers.[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 σ 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.[13] 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 α-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 $(o\text{-OMePh})_2$P-OMe with the lithiated salt of sulfonamide **1a**, using the procedure developed by Drent.[6b] 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_2PCl led to the formation of ligands **2a,c−f** in 35−91% yield.[13] Attempts to synthesize the ligand with a $t\text{Bu}_2$P group failed, presumably due to steric effects.

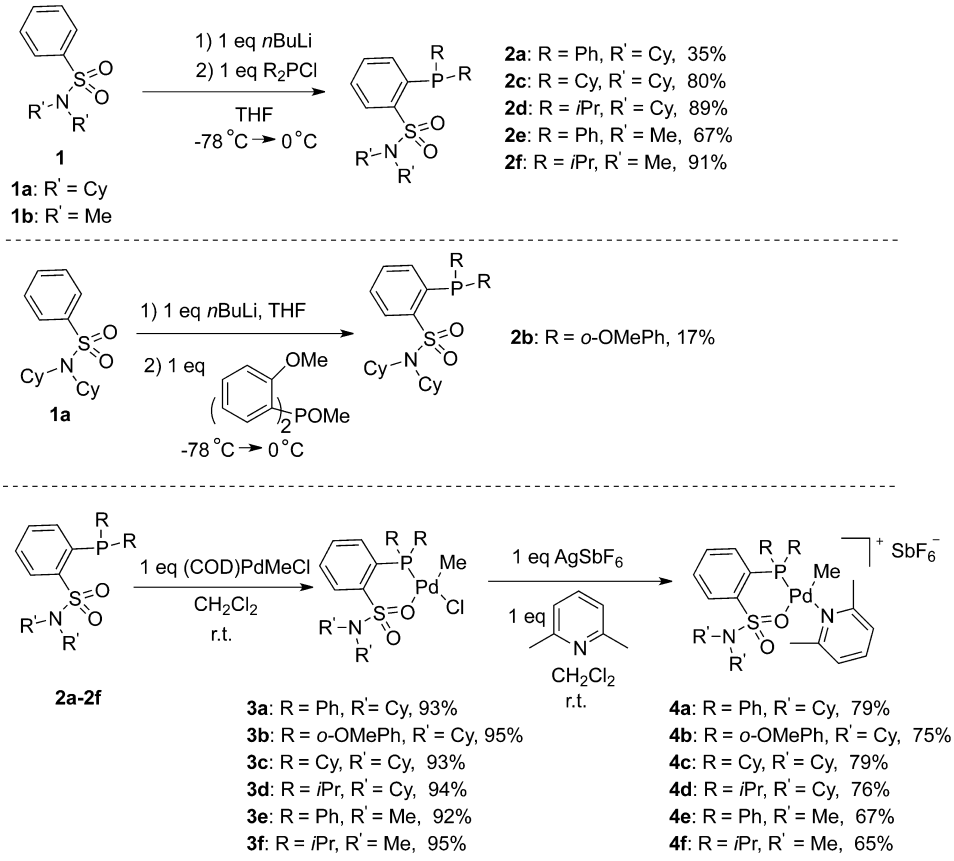
The reactions of ligands **2a−f** with (COD)PdMeCl (COD = 1,5-cyclooctadiene) yielded phosphine−sulfonamide complexes (P,O)PdMeCl (**3a−f**), which reacted with silver hexafluoroantimonate and 2,6-lutidine to generate the cationic palladium complexes **4a−f** in good isolated yields (65−79%). All of 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).[6d,f,h] 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).[6d,f,h] 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.[6d,e,7]

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 phosphine−sulfonamide palladium(II) complexes can oligomerize ethylene mainly to α-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 α-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 α-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

dx.doi.org/10.1021/om5004094 | Organometallics 2014, 33, 3738−3745

Scheme 1



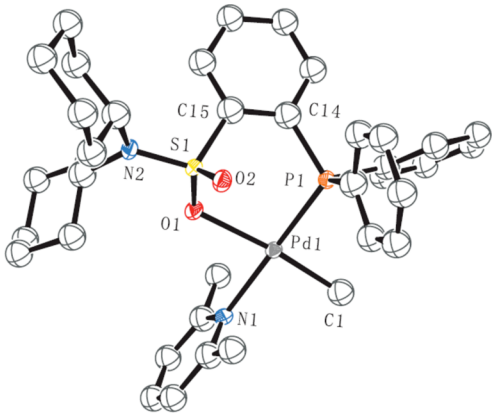


Figure 1. ORTEP plot of complex **4a** ($C_{39}H_{50}Cl_2F_6N_2O_2PPdSSb\cdot CH_2Cl_2$). Hydrogen atoms and SbF_6^- and CH_2Cl_2 groups have been omitted for clarity. Thermal ellipsoids are presented at the 30% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)–C(1) 2.034(3), Pd(1)–N(1) 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).

Table 1. Oligomerization of Ethylene with Cationic Palladium Complexes

					selectivity (%)[c]		
entry[a]	cat.	T (°C)	P (psi)	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[f]	**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

[a]Conditions: 5 μmol of cat., 100 mL of CH_2Cl_2, 30 min reaction time. [b]In units of 10^3 (mol of ethylene)/((mol of Pd) h). [c]1-Cn (%) = 1-Cn/oligomers × 100, detected by GC. n-Heptane was used as internal standard. [d]3.3% 2-butene. [e]2.8% 2-butene. [f]4.1% 2-butene. [g]Addition of 1 equiv of $B(C_6F_5)_3$. [h]Addition of 2 equiv of $B(C_6F_5)_3$.

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.[2b]

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

dx.doi.org/10.1021/om5004094 | Organometallics 2014, 33, 3738–3745

ethylene pressure is decreased from 300 to 150 psi (entry 2 vs entry 3), the TOF decreases from 7.4×10^3 to 5.6×10^3 (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 5.6×10^3 to 0.4×10^3 (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 7.4×10^3 to 36.0×10^3 (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.[14,15] 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 $AgSbF_6$ (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.[15] 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.[9a] This leads to an electron-deficient 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 distance observed in other Pd−lutidine complexes.[6d,e,7] The 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 β-hydride elimination during chain propagation and result in the formation of lower oligomers.[16]

CONCLUSIONS

A series of cationic palladium(II) complexes with phosphine−sulfonamide ligands were synthesized. These palladium complexes can oligomerize ethylene mainly to α-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 α-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.

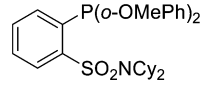
EXPERIMENTAL SECTION

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_2 (dichloromethane). $CDCl_3$ and CD_2Cl_2 were purchased from Cambridge, dried with 4 Å molecular sieves, and stored under nitrogen. Polymerization grade ethylene was used after purification. $PhSO_2NCy_2$ (**1a**),[13] $PhSO_2NMe_2$ (**1b**),[13] ligands **2a**,**c**,[13] $(o\text{-OMePh})_2$P-OMe,[6b] and (COD)PdMeCl[14] 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. ^{1}H NMR chemical shifts were referenced to residual protio solvent peaks or the tetramethylsilane signal (0 ppm), and ^{13}C NMR chemical shifts were referenced to the solvent resonance. ^{31}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***.

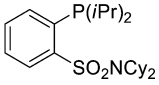
2b



n-BuLi in *n*-hexane (2.5 mL, 6.0 mmol) was added dropwise to a solution of $PhSO_2NCy_2$ (**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 $(o\text{-OMePh})_2$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_4Cl (100 mL) and diluted with 150 mL of CH_2Cl_2. 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 $MgSO_4$, 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). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02−1.15 (2H, m, CH_2), 1.17−1.35 (4H, m, CH_2), 1.53−1.65 (2H, m, CH_2), 1.66−1.90 (10H, m, CH_2), 3.60−3.80 (2H, m, NC*H*), 3.70 (6H, s, OCH_3), 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*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 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. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −26.39 ppm. Anal. Calcd for $C_{32}H_{40}NO_4PS$: C, 67.94; H, 7.13; N, 2.48. Found: C, 68.16; H, 7.09; N, 2.50.

Ligand ***2d***.

2d



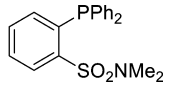
To a solution of $PhSO_2NCy_2$ (**1a**; 6.0 mmol, 2.0 g) in 40 mL of THF was added dropwise 2.5 mL of a hexane solution of *n*-BuLi (6.0 mmol) at −78 °C. After the mixture was stirred for 30 min, iPr$_2$PCl (1.0 mL, 6.0 mmol) in 20 mL of THF was added dropwise to the reaction

dx.doi.org/10.1021/om5004094 | *Organometallics* 2014, 33, 3738−3745

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_4Cl (100 mL). The organic layer was separated, and the aqueous phase was extracted with Et_2O (50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated to give a white solid of **2d** in 89% yield (2.3 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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_3), 1.15 (3H, d, J = 7.0 Hz, CH_3), 1.52−1.61 (2H, m, CH_2), 1.66−1.80 (12H, m, CH_2), 2.06−2.19 (2H, m, PC*H*), 3.55−3.67 (2H, m, NC*H*), 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*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.64 (d, J = 22.8 Hz), 138.02 (d, J = 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). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 4.71 ppm. Anal. Calcd for $C_{24}H_{40}NO_2PS$: C, 65.87; H, 9.21; N, 3.20. Found: C, 65.66; H, 9.38; N, 3.27.

*Ligand **2e**.*

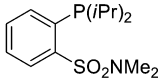
2e



To a solution of $PhSO_2NMe_2$ (**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_2PCl (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_2O (50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated to give a white solid. The crude material was purified by flash chromatography with CH_2Cl_2 as eluent to yield ligand **2e** as a white solid in 67% yield (2.7 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 [6H, s, N(CH_3)$_2$], 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*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 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). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −9.09 ppm. Anal. Calcd for $C_{20}H_{20}NO_2PS$: C, 65.03; H, 5.46; N, 3.79. Found: C, 64.76; H, 5.49; N, 3.80.

*Ligand **2f**.*

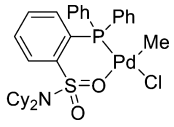
2f



The same procedure as described for the synthesis of **2d** was employed to prepare **2f**. $PhSO_2NMe_2$ (**1b**; 6.0 mmol, 1.1 g), *n*-BuLi in hexane (2.5 mL, 6.0 mmol), and iPr_2PCl (1.0 mL, 6 mmol) were used to yield ligand **2f** as a white solid (91%, 1.6 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 [3H, d, J = 7.0 Hz, CH(CH_3)$_2$], 0.92 [3H, d, J = 7.0 Hz, CH(CH_3)$_2$], 1.13 [3H, d, J = 7.0 Hz, CH(CH_3)$_2$], 1,17 [3H, d, J = 7.0 Hz, CH(CH_3)$_2$], 2.04−2.18 (2H, m, C*H*), 2.83 [6H, s, N(CH_3)$_2$], 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*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 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). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 3.23 ppm. Anal. Calcd for $C_{14}H_{24}NO_2PS$: C, 55.79; H, 8.03; N, 4.65. Found: C, 55.73; H, 8.03; N, 4.64.

*Complex **3a**.*

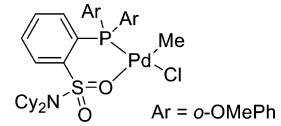
3a



Ligand **2a** (1.7 mmol, 0.86 g) was dissolved in 30 mL of CH_2Cl_2. 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 × 10 mL) and dried in vacuo for 30 min to give an off-white solid as the product (1.0 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (3H, d, J = 2.7 Hz, Pd-CH_3), 0.92−1.16 (6H, m, CH_2), 1.42−1.80 (14H, m, CH_2), 3.10−3.22 (2H, m, C*H*), 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*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.86 (d, J = 11.6 Hz), 135.56, 134.21 (d, J = 12.7 Hz), 131.93 (d, J = 5.0 Hz), 131.62 (d, J = 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. ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 30.19 ppm. Anal. Calcd for $C_{31}H_{39}ClNO_2PPdS\cdot 0.3CH_2Cl_2$: C, 54.64; H, 5.80; N, 2.04. Found: C, 54.91; H, 6.05; N, 1.98.

*Complex **3b**.*

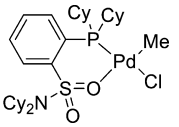
3b



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. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.58 (3H, d, J = 2.8 Hz, Pd-CH_3), 0.98−1.12 (6H, m, CH_2), 1.48−1.55 (2H, m, CH_2), 1.60−1.85 (12H, m, CH_2), 2.99−3.09 (2H, m, NC*H*), 3.64 (6H, s, OCH_3), 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*). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 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. ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 22.72 ppm. Anal. Calcd for $C_{33}H_{43}ClNO_4PPdS\cdot CH_2Cl_2$: C, 50.57; H, 5.62; N, 1.73. Found: C, 50.69; H, 5.37; N, 2.17.

*Complex **3c**.*

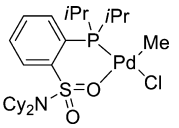
3c



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. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (3H, d, J = 2.2 Hz, Pd-CH_3), 1.02−1.32 (16H, m, CH_2), 1.51−2.02 (22H, m, 22CH_2, 2PC*H*), 2.10−2.30 (4H, m, CH_2), 3.15−3.30 (2H, m, NC*H*), 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*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 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 = 24.4 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. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 33.72 ppm. Anal. Calcd for $C_{31}H_{51}ClNO_2PPdS\cdot CH_2Cl_2$: C, 50.60; H, 7.03 N, 1.84. Found: C, 50.92; H, 7.43; N, 2.38.

*Complex **3d**.*

3d



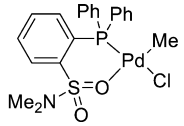
The same procedure as described for the synthesis of **3a** was used. Ligand **2d** (0.40 g, 0.91 mmol) and (COD)PdMeCl (0.24 g, 0.91 mmol) were used to give **3d** (0.53 g, 94%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (3H, d, J = 2.2 Hz, Pd-CH_3), 1.05−1.40 (6H, m, CH_2), 1.18−1.28 (12H, m, CH_3), 1.50−1.60 (2H, m, CH_2), 1.72−1.87 (8H, m, CH_2), 1.92−2.02 (4H, m, CH_2), 2.46−2.58

dx.doi.org/10.1021/om5004094 | *Organometallics* 2014, 33, 3738−3745

(2H, m, PC*H*), 3.17−3.30 (2H, m, NC*H*), 7.58−7.68 (2H, m, Ar-*H*), 7.69−7.76 (1H, m, Ar-*H*), 7.88−7.96 (1H, m, Ar-*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 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. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 40.22 ppm. Anal. Calcd for $C_{25}H_{43}ClNO_2PPdS$: C, 50.51; H, 7.29; N, 2.36. Found: C, 50.30; H, 7.28; N, 2.34.

Complex ***3e***.

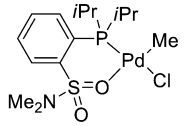
3e



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. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, d, J = 3.8 Hz, Pd-CH_3), 3.04 [6H, s, N(CH_3)$_2$], 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*). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 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), 133.98 (d, J = 6.4 Hz), 132.27 (d, J = 2.0 Hz), 132.01 (d, J = 2.6 Hz), 130.21, 129.66, 129.54 (d, J = 11.4 Hz), 40.91, 3.24 (d, J = 2.0 Hz). $^{31}P\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 29.93 ppm. Anal. Calcd for $C_{21}H_{23}ClNO_2PPdS$: C, 47.92; H, 4.40 N, 2.66. Found: C, 47.37; H, 4.41; N, 2.68.

Complex ***3f***.

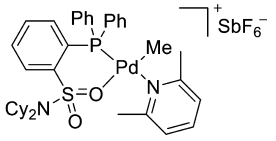
3f



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. ^1H NMR (400 MHz, $CDCl_3$): δ 1.08 (3H, d, J = 2.6, Pd-CH_3), 1.19−1.30 [12H, m, CH(CH_3)$_2$], 2.58−2.70 (2H, m, C*H*), 3.00 [6H, s, N(CH_3)$_2$], 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*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 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. $^{31}P\{^1H\}$ NMR (162 MHz $CDCl_3$): δ 38.67 ppm. Anal. Calcd for $C_{22}H_{36}F_6N_2O_2PPdSSb$: C, 34.51; H, 4.74; N, 3.66. Found: C, 34.26; H, 4.88; N, 3.74.

Complex ***4a***.

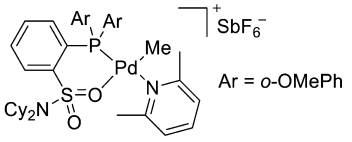
4a



Complex **3a** (0.20 g, 0.30 mmol) was dissolved in 30 mL of CH_2Cl_2. To the light yellow solution was added lutidine (35 μL, 0.30 mmol), and the solution was stirred for 30 min. Then 0.30 mmol of silver hexafluoroantimonate ($AgSbF_6$; 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). ^1H NMR (400 MHz, CD_2Cl_2): δ 0.60 (3H, d, J = 2.8 Hz, Pd-CH_3), 0.82−1.15 (6H, m, CH_2), 1.45−1.72 (14H, m, CH_2), 3.05−3.16 (2H, m, NC*H*), 3.11 (6H, s, py-CH_3), 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*). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 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. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 28.39 ppm. Anal. Calcd for $C_{38}H_{48}F_6N_2O_2PPdSSb\cdot CH_2Cl_2$: C, 44.16; H, 4.78; N, 2.67. Found: C, 44.40; H, 4.78; N, 2.66.

Complex ***4b***.

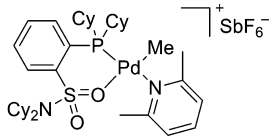
4b



The same procedure as described for the synthesis of **4a** was used. The complex **3b** (0.35 g, 0.48 mmol), lutidine (55 μL, 0.48 mmol), and $AgSbF_6$ (0.16 g, 0.48 mmol) were used to give **4b** (0.37 g, 75%) as a white solid. ^1H NMR (400 MHz, CD_2Cl_2): δ 0.39 (3H, d, J = 3.0 Hz, Pd-CH_3), 0.85−1.09 (6H, m, CH_2), 1.42−1.70 (14H, m, CH_2), 2.96−3.06 (2H, m, NC*H*), 3.10 (6H, s, py-*H*), 3.73 (6H, s, OCH_3), 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*). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 161.36, 159.45, 149.68, 145.02 (d, J = 13.0 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. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.81 ppm. Anal. Calcd for $C_{39}H_{49}F_6N_2O_4PPdSSb$: C, 46.15; H, 4.87, N, 2.76. Found: C, 46.22; H, 5.16; N, 2.70.

Complex ***4c***.

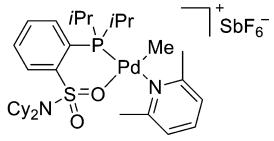
4c



The same procedure as described for the synthesis of **4a** was used. The complex **3c** (0.20 g, 0.30 mmol), lutidine (35 μL, 0.30 mmol), and $AgSbF_6$ (0.10 g, 0.30 mmol) were used to give **4c** (0.23 g, 79%) as a white solid. ^1H NMR (400 MHz, CD_2Cl_2): δ 0.68−0.73 (3H, m, Pd-CH_3), 0.96−1.46 (16H, m, CH_2), 1.52−1.95 (22H, m, CH_2), 2.14−2.26 (2H, m, CH_2), 2.32−2.46 (2H, m, PC*H*), 3.10 (6H, s, py-CH_3), 3.07−3.14 (2H, m, NC*H*), 7.23−7.29 (2H, m, py-*H*), 7.70−7.93 (5H, m, 4Ar-*H*, Py-*H*). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): 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). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 32.73 ppm. Anal. Calcd for $C_{38}H_{60}F_6N_2O_2PPdSSb\cdot CH_2Cl_2$: C, 43.90; H, 5.86; N, 2.63. Found: C, 43.97; H, 6.09; N, 2.75.

Complex ***4d***.

4d



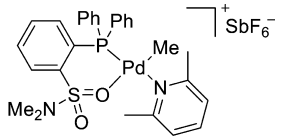
The same procedure as described for the synthesis of **4a** was used. The complex **3d** (0.20 g, 0.32 mmol), lutidine (37 μL, 0.32 mmol), and $AgSbF_6$ (0.11 g, 0.32 mmol) were used to give **4d** (0.22 g, 76%) as a light yellow solid. ^1H NMR (400 MHz, CD_2Cl_2): δ 0.72 (3H, d, J = 2.0 Hz, Pd-CH_3), 1.00−1.22 (6H, m, CH_2), 1.26−1.38 [12H, m, CH(CH_3)$_2$], 1.52−1.77 (14H, m, CH_2), 2.63−2.74 (2H, m, PC*H*), 3.05−3.17 (2H, m, NC*H*), 3.11 (6H, s, py-CH_3), 7.27 (2H, d, J = 7.8 Hz, py-*H*), 7.72−7.95 (5H, m, 4Ar-*H*, py-*H*).$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 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), 123.32 (d, J = 3.0 Hz), 60.30, 32.37, 26.57, 26.55 (d, J = 25.8 Hz), 26.17, 25.36, 19.38 (d, J = 4.6 Hz), 18.43, −5.57 (d, J = 2.8 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 39.99 ppm.

dx.doi.org/10.1021/om5004094 | *Organometallics* 2014, 33, 3738−3745

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***.

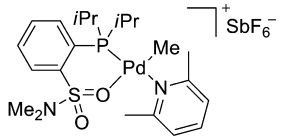
4e



The same procedure as described for the synthesis of **4a** was used. The complex **3e** (0.20 g, 0.38 mmol), lutidine (44 μL, 0.38 mmol), and $AgSbF_6$ (0.13 g, 0.38 mmol) were used to give **4e** (0.21 g, 67%) as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.60 (3H, d, *J* = 3.4 Hz, Pd-C*H*$_3$), 2.73 [6H, s, N(C*H*$_3$)$_2$], 3.13 [6H, s, py(C*H*$_3$)$_2$], 7.29−7.35 (3H, m, py-2*H*, Ar-*H*), 7.52−7.61 (10H, m, Ar-*H*), 7.71−7.85 (4H, m, py-*H*, Ar-3*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 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). ^{31}P{^{1}H} NMR (162 M HZ $CDCl_3$): δ 27.63 ppm. Anal. Calcd for $C_{22}H_{36}F_6N_2O_2PPdSSb$: C, 40.33; H, 3.87; N, 3.36. Found: C, 40.00; H, 3.61; N, 3.61.

Complex ***4f***.

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 $AgSbF_6$ (0.14 g, 0.41 mmol) were used to give **4f** (0.20 g, 65%) as a light yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.71 (3H, d, *J* = 2.4, Pd-C*H*$_3$), 1.28 [3H, d, *J* = 7.0, CH(C*H*$_3$)$_2$], 1.31 [3H, d, *J* = 2.6, CH(C*H*$_3$)$_2$], 1.33 [3H, d, *J* = 2.6, CH(C*H*$_3$)$_2$], 1.37 [3H, d, *J* = 7.0, CH(C*H*$_3$)$_2$], 2.52−2.74 (2H, m, C*H*Me$_2$), 3.00 [6H, s, N(C*H*$_3$)$_2$], 3.11 (6H, s, py-C*H*$_3$), 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*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 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). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 39.06 ppm. Anal. Calcd for $C_{22}H_{36}F_6N_2O_2PPdSSb$: 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.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for C.C.: changle@ustc.edu.cn.

*E-mail for Z.H.: huangzh@sioc.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Sciences Foundation of China (Nos. 21272255, 21121062, 21374108), the Science and Technology Commission of Shanghai Municipality (Nos. 13QA1404200, 13JC1406900), and Anhui Provincial Natural Science Foundation (No. 1408085QB28).

■ REFERENCES

(1) For recent reviews, see: (a) Carrow, B. P.; Nozaki, K. *Macromolecules* **2014**, *47*, 2541. (b) Nakamura, A.; Anselment, T. M. J.; Claverie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N. M.; Nozaki, K. *Acc. Chem. Res.* **2013**, *46*, 1438. (c) Makio, H.; Terao, H.; Iwashita, A.; Fujita, T. *Chem. Rev.* **2011**, *111*, 2363. (d) Delferro, M.; Marks, T. J. *Chem. Rev.* **2011**, *111*, 2450. (e) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215. (f) Chen, E. Y. X. *Chem. Rev.* **2009**, *109*, 5157. (g) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2002**, *103*, 283. (h) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325. (i) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (j) Camacho, D. H.; Guan, Z. *Chem. Commun.* **2010**, *46*, 7879.

(2) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059. (c) Popeney, C. S.; Levins, C. M.; Guan, Z. *Organometallics* **2011**, *30*, 2432. (d) Popeney, C. S.; Rheingold, A. L.; Guan, Z. *Organometallics* **2009**, *28*, 4452. (e) Leung, D. H.; Ziller, J. W.; Guan, Z. *J. Am. Chem. Soc.* **2008**, *130*, 7538. (f) Liu, H.; Zhao, W. Z.; Hao, X.; Redshaw, C.; Huang, W.; Sun, W. H. *Organometallics* **2011**, *30*, 2418. (g) Liu, H.; Zhao, W. Z.; Yu, J. G.; Yang, W. H.; Hao, X.; Redshaw, C.; Chen, L. Q.; Sun, W. H. *Catal. Sci. Technol.* **2012**, *2*, 415. (h) Wang, K.; Shen, M.; Sun, W. H. *Dalton Trans.* **2009**, 4085. (i) Wegner, M. M.; Ott, A. K.; Rieger, B. *Macromolecules* **2010**, *43*, 3624. (j) Liu, F. S.; Hu, H. B.; Xu, Y.; Guo, L. H.; Zai, S. B.; Song, K. M.; Gao, H. Y.; Zhang, L.; Zhu, F. M.; Wu, Q. *Macromolecules* **2009**, *42*, 7789. (k) Song, C. L.; Tang, L. M.; Li, Y. G.; Li, X. F.; Li, Y. S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1964. (l) Bahuleyan, B. K.; Son, G. W.; Park, D. W.; Ha, C. S.; Kim, I. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1066. (m) Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2010**, *132*, 5273. (n) Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2008**, *130*, 12892. (o) Rose, G. M.; Coates, G. W. *J. Am. Chem. Soc.* **2006**, *128*, 4186. (p) Rose, G. M.; Coates, G. W. *Macromolecules* **2008**, *41*, 9548.

(3) (a) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460. (b) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149. (c) Song, D. P.; Wang, Y. X.; Mu, H. L.; Li, B. X.; Li, Y. S. *Organometallics* **2011**, *30*, 925. (d) Delferro, M.; McInnis, J. P.; Marks, T. J. *Organometallics* **2010**, *29*, 5040. (e) Weberski, M. P.; Chen, C.; Delferro, M.; Zuccaccia, C.; Macchioni, A.; Marks, T. J. *Organometallics* **2012**, *31*, 3773. (f) Marks, T. J. *Chem. Eur. J.* **2012**, *18*, 10715. (g) Hu, T.; Li, Y. G.; Liu, J. Y.; Li, Y. S. *Organometallics* **2007**, *26*, 2609. (h) Mu, H. L.; Ye, W. P.; Song, D. P.; Li, Y. S. *Organometallics* **2010**, *29*, 6282. (i) Song, D. P.; Ye, W. P.; Wang, Y. X.; Liu, J. Y.; Li, Y. S. *Organometallics* **2009**, *28*, 5697. (j) Song, D. P.; Wu, J. Q.; Ye, W. P.; Mu, H. L.; Li, Y. S. *Organometallics* **2010**, *29*, 2306. (k) Song, D. P.; Wang, Y. X.; Mu, H. L.; Li, B. X.; Li, Y. S. *Organometallics* **2011**, *30*, 925. (l) Göttker-Schnetmann, I.; Wehrmann, P.; Röhr, C.; Mecking, S. *Organometallics* **2007**, *26*, 2348. (m) Bastero, A.; Göttker-Schnetmann, I.; Röhr, C.; Mecking, S. *Adv. Synth. Catal.* **2007**, *349*, 2307. (n) Berkefeld, A.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 1565.

(o) Osichow, A.; Göttker-Schnetmann, I.; Mecking, S. *Organometallics* **2013**, *32*, 5239.
(4) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466.
(5) (a) Atkinson, R. C. J.; Gibson, V. C.; Long, N. J.; White, A. J. P. *Dalton Trans.* **2010**, *39*, 7540. (b) Kermaqoret, A.; Braunstein, P. *Dalton Trans.* **2008**, 822. (c) Mateus, N.; Routaboul, L.; Daran, J. C.; Manoury, E. *J. Organomet. Chem.* **2006**, *691*, 2297. (d) Malinoski, J. M.; Brookhart, M. *Organometallics* **2003**, *22*, 5324.
(6) (a) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744. (b) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 964. (c) Kochi, T.; Yoshimura, K.; Nozaki, K. *Dalton Trans.* **2006**, 25. (d) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948. (e) Weng, W.; Shen, Z. L.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 15450. (f) Vela, J.; Lief, G. R.; Shen, Z. L.; Jordan, R. F. *Organometallics* **2009**, *28*, 6131. (g) Skupov, K. M.; Piche, L.; Claverie, J. P. *Macromolecules* **2008**, *41*, 2309. (h) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14606. (i) Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14088. (j) Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker, S. I.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 422. (k) Neuwald, B.; Caporaso, L.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2013**, *135*, 1026.
(7) Nagai, Y.; Kochi, T.; Nozaki, K. *Organometallics* **2009**, *28*, 6131.
(8) Zhou, X. Y.; Jordan, R. F. *Organometallics* **2011**, *30*, 4632.
(9) (a) Gott, A. L.; Piers, W. E.; Dutton, J. L.; Mcdonald, R.; Parvez, M. *Organometallics* **2011**, *30*, 4236. (b) Kim, Y.; Jordan, R. F. *Organometallics* **2011**, *30*, 4250.
(10) (a) Bennett, J. L.; Brookhart, M.; Johnson, L. K. PCT Int. Appl. *WO 9830610*, 1998;. (b) Nozaki, K.; kawauchi, T.; Ida, H. Jpn. Kokai Tokkyo Koho, JP 2007332086, 2007.
(11) Liu, W. J.; Malinoski, J. M.; Brookhart, M. *Organometallics* **2002**, *21*, 2836.
(12) Carrow, B. P.; Nozaki, K. *J. Am. Chem. Soc.* **2012**, *134*, 8802.
(13) Chapman, C. J.; Frost, C. G.; Mahon, M. F. *Dalton Trans.* **2006**, 2251.
(14) Burns, C. T.; Jordan, R. F. *Organometallics* **2007**, *26*, 6726.
(15) Cai, Z. G.; Shen, Z. L.; Zhou, X. Y.; Jordan, R. F. *ACS Catal.* **2012**, *2*, 1187.
(16) (a) Gutsulyak, D. G.; Gott, A. L.; Piers, W. E.; Parvez, M. *Organometallics* **2013**, *32*, 3363. (b) Hasanayn, F.; Achord, P.; Braunstein, P.; Magnier, H. J.; Krogh-Jespersen, K.; Goldman, A. S. *Organometallics* **2012**, *31*, 4680.