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Investigation of Steric and Electronic Factors of (Arylsulfonyl)phosphane-Palladium Catalysts in Ethene Polymerization

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(Arylsulfonyl)phosphane ligands, *o*-$Ar_2PC_6H_4SO_3H$ in which Ar is phenyl (Ph), naphthyl (Np), phenanthryl (Pa), or anthracenyl (An) were prepared. These bulky phosphanes were used to generate phosphanepalladium complexes [(*o*-$Ar_2PC_6H_4SO_3$)PdMe(pyridine)]. These complexes catalyze ethene polymerization and yield linear polyethene. The catalytic activity of these compounds and the molecular weight of the polymer decreases in the following order: Ph > Np > Pa > An, which corresponds to increasing cone angles and decreasing basicity.

Introduction

The evolution of olefin polymerization catalysis since Ziegler's discovery in 1953 has involved a prolific coupling of polymer science with organometallic chemistry. However, there are still no commercially viable catalysts for the controlled copolymerization of simple olefins with polar functional monomers. Currently, commercial processes for the copolymerization of ethene with polar functional monomers such as acrylates employ free-radical processes that require extreme pressures and afford little or no control over polymer architecture (tacticity or crystallinity, blockiness, molecular-weight distribution), and thus limit the range of material performances. A need exists for new molecular catalysts capable of polymerizing polar monomers with controlled microstructure under mild conditions.[1–3]

A significant advance was reported by Johnson et al.,[4] who discovered that cationic palladium diimines can copolymerize ethene and acrylates to afford branched copolymers where the acrylate is placed in a terminal position. In 2002, Drent et al.[5] disclosed that an ill-defined catalytic system that contained a phosphane sulfonate and a palladium complex, either tris(dibenzylideneacetone)dipalladium(0) or palladium(II) acetate, permits the preparation of ethene acrylate copolymers in which the acrylates are incorporated in main chain positions. Well-defined palladium catalysts that contain a phosphane aryl sulfonate ligand were then disclosed by Hearley et al.,[6] Goodall et al.,[7,8] Kochi et al.,[9,10] Liu et al.,[11] Skupov et al.,[12] Luo et al.,[13] Vela et al.,[14] and most recently Guironnet et al.[15] Among those reports, acrylate copolymerization with ethene was mentioned by Goodall,[7,8] Skupov,[12] and Guironnet.[15] These studies employ the catalyst [(*o*-$Ar_2PC_6H_4SO_3$)PdMe(**L**)] with Ar = *o*-OMePh, which corresponds to the ligand originally presented by Drent.[5] The role of the ancillary ligand **L** (**L** = pyridine,[12,16] lutidine,[17] DMSO,[15] or allyl group[11]) on the catalytic activity has been studied in detail. However, at this time, little is known on the influence of the arylphosphane sulfonate structure. We recently reported that introduction of the bulky and electron-rich aryl groups (Ar = –{*o*-[2′,6′-$(OMe)_2C_6H_3$]-C_6H_4}) resulted in a very active catalyst that affords polyethylene of high molecular weight[12] but with a modest propensity to incorporate any other monomer than ethene. We infer that this behavior stems from the steric hindrance, which precludes the facile coordination of any olefin larger than ethene. Thus, it appears that there might be a trade-off between, on one side, the high activity and high molecular weights favored by bulky and electron-rich P^O sulfonated aryl ligands and, on the other side, the propensity to incorporate polar comonomers, which is observed with less bulky phosphanes. To clarify this issue, we have turned our attention toward catalysts based on polyaromatic sulfonated phosphanes *o*-$Ar_2PC_6H_4SO_3H$ in which Ar is phenyl, naphthyl (Np), phenanthryl (Pa), or anthracenyl (An). Nonsulfonated polyaromatic phosphane analogues were initially developed by Müller et al., who demonstrated that their properties are changed by altering the number of aromatic rings associated with the phosphane.[18] These phosphanes become better donors as the number of aromatic rings increases and their Tolman cone angle increases from 145° for PPh_3 to 177° for PNp_2Ph and 186° for PAn_2Ph. Thus, the larger phosphanes are the better donors, and we

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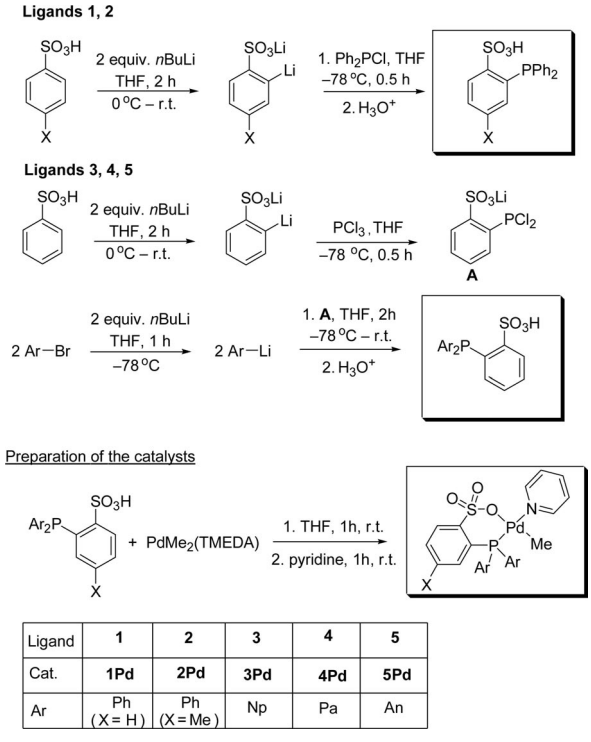
should expect that catalysts based on the larger phosphanes would be more active and generate polyethylene of high molecular weight.

Results and Discussion

The synthesis of the sulfonated arylphosphane is a one-pot procedure (Scheme 1). For phenyl-substituted phosphanes **1** and **2**, the dilithiated salt of benzene or toluenesulfonic acid is treated with commercial diphenylchlorophosphane. For the other phosphanes **3**–**5**, the sulfonated phenyl group is introduced first upon reaction of trichlorophosphane with the lithiated salt. The resulting dichlorophosphane salt is not isolated, but it is reacted directly with two equivalents of the lithium salt of the desired aryl group. This procedure was found to be very rapid and reproducible as long as the benzyl sulfonic acid was sufficiently anhydrous. The *n*BuLi concentration needs also to be carefully adjusted, as an excess amount of *n*BuLi leads to the formation of *n*-butylphosphanes (as shown by MS), and a default of *n*BuLi leads to the isolation of phosphane oxides (R_2POH, also shown by MS).



Ligand	1	2	3	4	5
Cat.	**1Pd**	**2Pd**	**3Pd**	**4Pd**	**5Pd**
Ar	Ph (X = H)	Ph (X = Me)	Np	Pa	An

Scheme 1.

Although MS indicates the presence of one single compound for ligands **3** and **4**, ^{31}P and ^{13}C NMR spectroscopy clearly shows the presence of two distinct species,[19] which correspond to two possible rotational isomers (Figure 1). Calculations by density functional theory (DFT) indicate that the two rotamers correspond to *syn* and *anti* conformations of the aryl groups across the P atom, with energies differing by less than 2 kcal mol^{-1}, which is in good agreement with the 80:20 proportion found by ^{31}P NMR spectroscopy at room temperature. The activation barrier is above 10 kcal mol^{-1}, which is high enough for the structures to appear as distinct species in the NMR spectroscopic timescale, even at higher temperature (no coalescence observed at T = 120 °C). Bis(phenanthryl)phenylphosphane[20] shows only one resonance in the ^{31}P NMR spectra, thereby indicating that the presence of the *ortho* sulfonic acid group contributes to the slow conversion between both rotamers. From the phosphane structures (optimized by DFT), we have calculated Tolman cone angles,[21] that is to say, the apex angle of a cylindrical cone with origin 2.28 Å from the center of the phosphorus atom, the sides of which just touch the van der Waals surfaces of the outermost atoms of the organic substituents. The Tolman angles for the *syn* conformers of **3** and **4** are respectively 192 and 190°, whereas they are 206 and 207° for the *anti* conformers. This is significantly higher than *tert*-butylphosphane (182°), but slightly smaller than the highly hindered tris(2,4,6-trimethylphenyl)phosphane (212°). Therefore, these sulfonated arylphosphanes exhibit considerable bulk. Based on the pioneering work of Mingos,[22] the availability of the P lone pair increases when the size of the aryl group increases, thus the larger phosphanes are better electron donors. Thus, the order of basicity of these phosphanes is expected to be **1** ≈ **2** < **3** ≈ **4** < **5**. It also corresponds to the observed ranking for the ^{31}P chemical shifts, which decreases from 4 ppm (**1** and **2**) to –30 ppm (**5**).

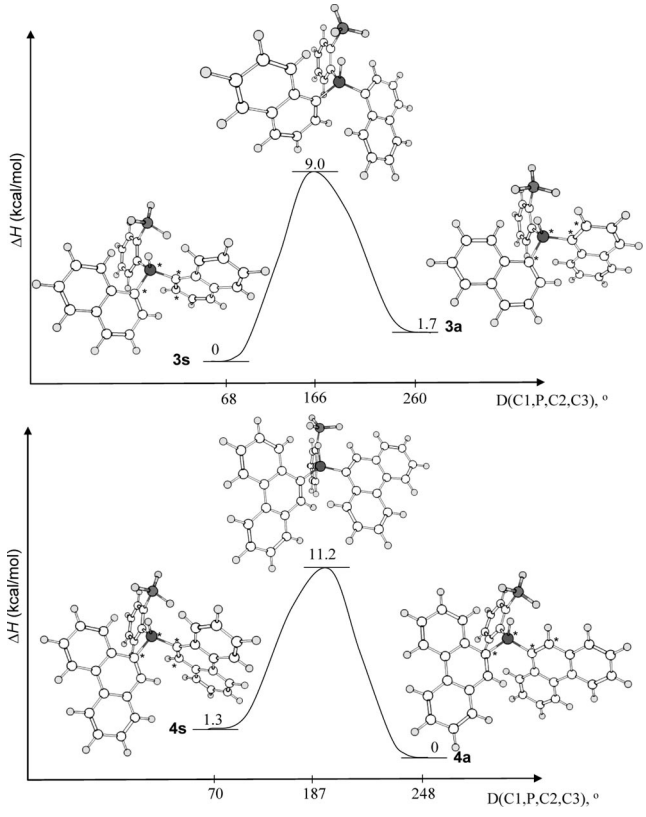


Figure 1. Enthalpic changes between the *syn* and *anti* conformations of phosphanes **3** and **4** as a function of the dihedral angle C1–P–C2–C3 (D, indicated with stars). Only the lowest transition state (TS) is shown: the other TS (located at D ≈ 0°) is at least several kcal mol^{-1} higher in energy.

The catalyst synthesis proceeds smoothly following the procedure highlighted in the literature.[12] The yields are in the following order: **1Pd** ≈ **2Pd** > **3Pd** > **4Pd** > **5Pd**, which does not follow the expected basicity of those ligands, thereby indicating that steric factors are the dominant influence in determining the reactivity of these sulfonated phosphanes towards Pd centers. For the sake of clarity, the term catalyst will be used for compounds **1Pd** to **5Pd**, although they are only catalysts once pyridine is replaced by ethene (initiating efficiency may be vastly different for each of them). Catalysts **3Pd**, **4Pd**, and **5Pd** are sparingly soluble in most common solvents except DMSO. The overall structure observed for **1Pd** resembles those of other [P^OPdMe(**L**)] complexes (Figure 2), with the Pd atom in a square-planar environment and the Me group *trans* to the sulfonate group. The six-membered ring Pd1–P1–C131=C132–S1–O11– adopts a half-boat conformation, with C111 and O13 in pseudoaxial positions and C121 and O12 in pseudoequatorial positions. This half-boat conformation has been reported for the majority of aryl sulfonate catalysts,[11,14,17,23] except for bulky aryl groups or when pyridine is replaced by DMSO.[12,15]

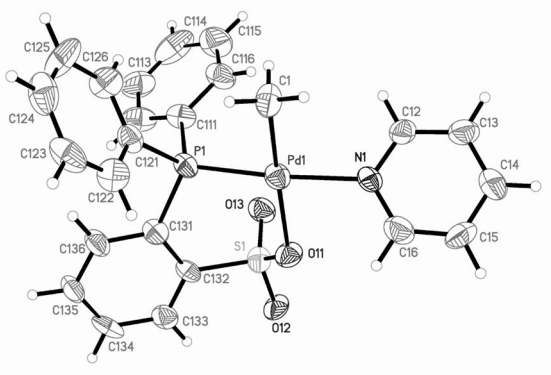


Figure 2. ORTEP view of **1Pd**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Pd1–C1 2.057(10), Pd1–O11 2.164(7), Pd1–P1 2.229(3), Pd1–N1 2.110(8); C1–Pd1–N1 90.6(4), C1–Pd1–P1 89.1(3), C1–Pd1–O11 174.7(4), N1–Pd1–P1 172.4(3).

The complete characterization of catalysts **3Pd** and **4Pd** is complicated by the fact that each rotamer reacts to give a separate catalyst, thus resulting in a doubling of all phosphane resonances (Figure 3). The analysis is further complicated by the presence of two distinct exchange processes.[16] The first one is the exchange between bound pyridine (BP) and free pyridine (FP; excess amount of 3% for **3Pd**, Figure 3). It has been demonstrated that the substitution of pyridine proceeds by means of an associative mechanism,[16] and calculation of exchange kinetic constants by NMR spectroscopic lineshape analysis is a lengthy process that was not undertaken here. Therefore, we can only state that under the conditions of the experiment (T = 25 °C, **3Pd** = 6×10^{-2} mol L^{-1}, FP = 2×10^{-3} mol L^{-1} in [D$_6$]DMSO), the exchange is slow. The second one is the inversion of the six-membered ring Pd–O–S–C=C–P. The nonsulfonated phosphane aryl substituents occupy a pseudoequatorial and pseudoaxial position. For catalysts **1Pd** and **2Pd**, the exchange process is fast on the NMR spectroscopic timescale, even at –90 °C in CD_2Cl_2. For catalysts **3Pd** to **5Pd**, the exchange is slow. This ring-inversion process is very sensitive to steric bulk. For example, for Ar = Ph(*o*-OMe), the coalescence occurs at T = –80 °C with an inversion barrier of 5.7 kcal mol^{-1} in CD_2Cl_2, whereas for Ar = Ph[*o*-C_6H_3(2,6-OMe)$_2$] coalescence occurs at T = –20 °C and the barrier is 8.3 kcal mol^{-1} in CD_2Cl_2 (see the Supporting Information).

All the catalysts are able to polymerize C_2H_4 at 85 °C (P = 300 psi), with the activity decreasing from **1Pd** to **5Pd**. The resulting polymers are highly linear, as shown by ^{13}C NMR spectroscopy and by examination of the Mark–Houwink plot in triple-detection gel permeation chromatog-

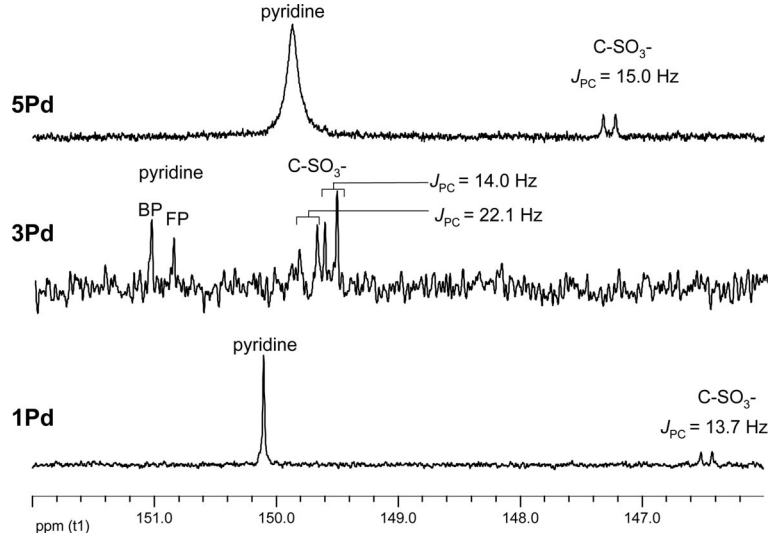


Figure 3. Superposition of ^{13}C NMR spectra (downfield region): **1Pd**: $CDCl_3$; **3Pd** and **5Pd**: [D$_6$]DMSO; T = 25 °C. For **1Pd**, bound pyridine (BP) is in rapid exchange with free pyridine (FP), whereas for **5Pd**, the exchange is intermediate on the NMR spectroscopic timescale. For **3Pd**, the exchange is slow and the two rotamers are observed, as indicated by the C–SO_3 resonances.

raphy (GPC). Unexpectedly, the drastic increase of steric hindrance from **1Pd** to **4Pd** results in a decrease of the average molecular weight. Thus, the least bulky and more acidic phosphane yields a catalyst with the highest activity and produces polymers with the highest molecular weights. Contrary to what was reported by us,[12,24] we found that **1Pd** and **2Pd** are also able to copolymerize acrylates with ethene with similar activities to those obtained with [MePd(pyridine)P(3-Me-6-SO_3-C_6H_3)(*o*-OMe-Ph)$_2$]. For example, at P = 100 psi, T = 100 °C, and for a concentration of *tert*-butyl acrylate of 1.70 mol L^{-1}, an insertion of 6% was obtained with catalyst **1Pd**, whereas under similar conditions (P = 100 psi, T = 100 °C, and monomer concentration: 0.85 mol L^{-1}), an insertion of 15% of *tert*-butyl acrylate was observed with catalyst **2Pd**. The molecular weights of the polymers (ca. 9500 g mol^{-1}) and copolymers (ca. 4000 g mol^{-1}) prepared with catalysts **1Pd** and **2Pd** are approximately twice as low as those previously obtained with [MePd(pyridine)P(3-Me-6-SO_3-C_6H_3)(*o*-OMe-Ph)$_2$].[12] However, catalysts **3Pd**, **4Pd**, and **5Pd** do not yield any copolymer under comparable conditions. Surprisingly, catalyst **5Pd** produces polyethylene that shows a bimodal distribution, a phenomenon we cannot explain at this moment.

High activities are observed for the bulky 2-[2,6-$(MeO)_2C_6H_3$]-C_6H_4- aryl groups[12] but not for the bulky groups studied here. If we use the ^{31}P chemical shift of the phosphane as a measure of basicity, then the basicity of the phosphane with R = 2-[2,6-$(MeO)_2C_6H_3$]-C_6H_4- (δ = –2 ppm) should be close to that of **1** and **2** (δ = 4 ppm). Polyaromatic phosphanes are more basic (δ = –25, –24, and –29 ppm, respectively, for **3**, **4**, and **5**). Thus, one may speculate that a high-activity catalyst is obtained for less basic ligands. This is in good agreement with the observed high activity reported for late-transition-metal polymerization catalysts that bear electron-deficient ligands.[25,26] Furthermore, as a reviewer pointed out, for the catalyst that bears 2-[2,6-$(MeO)_2C_6H_3$]-C_6H_4- aryl groups, the bulk is mostly located in the axial faces.[12] By contrast, it is possible to imagine that catalysts **3Pd** to **5Pd** are encumbered in the complex plane, with the result that monomer coordination is slowed, but with no rate decrease for β-H elimination. In the absence of X-ray structural determination, however, this last point is speculative (see Tables 1 and 2).

Table 1. Ethene polymerization data (T = 85 °C; P = 300 psi; solvent: toluene).

Cat.	[Cat.] [μmol L^{-1}]	TON[a] (mol_E/mol_{Pd})	Polymer wt. [g]	M_n[b] [g mol^{-1}]	PDI[b]
1Pd	47	43×10^3	11.3	9600	1.8
2Pd	54	24×10^3	7.4	9300	1.7
3Pd	76	1.7×10^3	0.71	5000	1.4
4Pd	43	14×10^3	3.4	3100	1.5
5Pd	85	4000	0.38	3000[c]	1.2
				35000	4

[a] TON = turnover number (E = ethene, Pd = Pd catalyst). [b] Determined by GPC analysis at 160 °C in 1,2,4-trichlorobenzene. M_n = number average molecular weight; PDI = polydispersity index. [c] Bimodal distribution.

Table 2. Ethene–*tert*-butyl acrylayte (TBA) copolymerization data (T = 100 °C, P = 100 psi).

Cat.	[Cat.] [μmol L^{-1}]	[TBA] [mol L^{-1}]	TON (mol_E/mol_{Pd})	M_n[a] [g mol^{-1}]	PDI[a]	TBA [mol-%][b]
1Pd	94	1.7	704	5170	1.4	6
2Pd	185	0.85	below 300	3000	1.2	15

[a] Determined by GPC analysis at 160 °C in 1,2,4-trichlorobenzene. [b] Determined by NMR spectroscopic analysis at 110 °C in [D_2]tetrachloroethane.

Conclusion

Phosphane sulfonate–palladium complexes were prepared and used as catalysts for ethene polymerization without the need for activation. Linear polyethylenes were obtained with these catalysts, but acrylate–ethene copolymers could only be obtained with **1Pd** and **2Pd**. Surprisingly, the introduction of steric hindrance in the catalyst scaffold results in lower molecular weights and lower activities. The origin of these phenomena is not totally clear at this moment. We believe that several other ligand structures will need to be prepared and characterized before being able to derive structure–property relationships.

Experimental Section

General: All manipulations were done under an inert atmosphere using standard Schlenk techniques. Solvents were degassed and dried with activated molecular sieves. Benzene and toluenesulfonic acid were dried by azeotropic distillation with benzene. Dimethyl(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)palladium(II), [$PdMe_2$(tmeda)], was prepared according to de Graaf et al.[27] All acrylic monomers were purified under argon by passing them over a bed of inhibitor-remover resin (Aldrich) because acrylic monomers are usually protected with quinones, which interfere with the catalyst. The monomers were then spiked with *tert*-butylcatechol (0.25 wt.-%) to prevent spontaneous radical polymerization of the acrylate during the polymerization process. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Varian Inova 600 MHz spectrometer at ambient temperature except for the polymers, which were analyzed in deuterated tetrachloroethane at 115 °C. The molecular-weight distributions were determined by gel permeation chromatography (GPC) with a Viscotek HT GPC equipped with triple detection operating at 160 °C. For lower molecular weights, the light-scattering detector was not used. The eluent was 1,2,4-trichlorobenzene, and separation was performed with three PolymerLabs Mixed B(-LS) columns. The refractive index increment, dn/dc, of pure linear polyethylene was found to be 0.106 mL g^{-1} at this temperature. Electrospray mass spectra (ESI-MS) of organic compounds were recorded with an Agilent 6210 LC-MSD TOF mass spectrometer. Standard numbering of polyaromatic C and H was used below.

Preparation of the Ligand 1. 2-(Diphenylphosphanyl)-4-methylbenzenesulfonic Acid: *n*BuLi (2.5 M in hexanes; 4.8 mL, 12 mmol) was added at 0 °C to a solution of dry toluenesulfonic acid (1.03 g, 6 mmol) in THF (30 mL). After stirring for 1 h at room temperature, the solution was added dropwise to a solution of chlorodiphenylphosphane (1.32 g, 6 mmol) in THF (20 mL) at 0 °C. After stirring for 4 h at room temperature, the solvent was removed in vacuo to leave a white solid. The solid was dissolved in dichloro-

methane (50 mL) and extracted with acidic water (2 mL of concentrated HCl in 30 mL of water), and then twice with water (30 mL). The organic solvent was removed in vacuo. The product was then recrystallized from dichloromethane/diethyl ether at –32 °C. The resulting white crystals were dried in vacuo; yield 0.9 g (42%). ^{1}H NMR ($CDCl_3$): δ = 8.15 [s, 1 H, C(P)-C(SO_3)=C*H*-], 7.70–7.45 (m, 11 H, H^4-Ph, H^4-ArSO_3, H^2-Ph, H^3-Ph), 6.96 [d, $J_{P,H}$ = 14 Hz, 1 H, C(P)-C*H*=C(Me)], 2.28 (s, 3 H, CH_3-ArSO_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 150.0 (*C*-CH_3), 140.6 ($J_{P,C}$ = 12.4 Hz, *C*SO_3), 135.7 [C(P)-*C*H=C(Me)], 134.8 ($J_{P,C}$ = 11.4 Hz, C_{ipso} in phenyl), 134.7 [$J_{P,C}$ = 11.0 Hz, *C*(P)-C(SO_3)], 134.0 [$J_{P,C}$ = 11.4 Hz, C(P)-*C*H- in phenyl], 130.1 [$J_{P,C}$ = 13.1 Hz, C(P)-CH=*C*H-CH- in phenyl], 130.1 [$J_{P,C}$ = 13.1 Hz, C(P)-CH=CH-*C*H- in phenyl], 129.4 [-*C*H-C(SO_3)=C(P)], 129.3 [-*C*H=CH-C(SO_3)=C(P)], 21.5 (Ar*C*H_3) ppm. ^{31}P NMR ($CDCl_3$): δ = 3.6 (s) ppm. MS: *m*/*z* = calcd. 356.0636; found 356.0626.

Preparation of the Ligand 2. 2-(Diphenylphosphanyl)benzenesulfonic Acid: *n*BuLi (2.5 M in hexanes; 4.0 mL, 10 mmol) was added at 0 °C to a solution of dry benzenesulfonic acid (0.80 g, 5 mmol) in THF (25 mL). After stirring for 1 h at room temperature, the solution was added dropwise to a solution of bis(phenyl)chlorophosphane (1.10 g, 5 mmol) in THF (15 mL) at 0 °C. After stirring for 4 h at room temperature, the solvent was removed in vacuo to leave a white solid. The solid was dissolved in dichloromethane (40 mL) and extracted with acidic water (2 mL of concentrated HCl in 30 mL of water), and then twice with degassed water (30 mL). The organic solvent was removed in vacuo. The product was then recrystallized from dichloromethane/diethyl ether at –32 °C. The resulting white crystals were dried in vacuo; yield 0.9 g (53%). ^{1}H NMR ($CDCl_3$): δ = 8.31 [s, 1 H, C(P)-C(SO_3)=C*H*-], 7.75–7.42 (m, 12 H, H^4-Ph, H^4-ArSO_3, H^5-ArSO_3 H^2-Ph, H^3-Ph), 7.22 [m, 1 H, C(P)-C*H*=CH- in ArSO_3] ppm. ^{13}C NMR ($CDCl_3$): δ = 151.8 ($J_{P,C}$ = 12.0 Hz, *C*SO_3), 134.6 ($J_{P,C}$ = 9.2 Hz, C_{ipso} in phenyl), 133.5 [$J_{P,C}$ = 12.8 Hz, -C(P)-*C*H- in phenyl], 133.3 [C(P)-*C*H=CH- in $C_6H_4SO_3$], 132.8 {[*C*(P)-C(SO_3)], 129.8 [$J_{P,C}$ = 10.1 Hz, -*C*H-C(SO_3)=C(P)], 129.3 [$J_{P,C}$ = 11.9 Hz, C(P)-CH=*C*H-CH- in phenyl], 129.3 [C(P)-CH=CH-*C*H- in phenyl], 128.7 [C(P)-CH=*C*H- in ArSO_3], 128.6 [$J_{P,C}$ = 8.2 Hz, -*C*H=CH-C(SO_3)=C(P)]} ppm. ^{31}P NMR ($CDCl_3$): δ = 4.3 (s) ppm. MS: *m*/*z* = calcd. 342.0480; found 342.0488.

Preparation of Ligand 3. 2-(Dinaphthalen-1-yl-phosphanyl)benzenesulfonic Acid: *n*BuLi (2.5 M in hexanes; 4.2 mL, 10.5 mmol) was added at 0 °C to a solution of benzenesulfonic acid (0.8 g, 5 mmol) in THF (20 mL). The excess amount (0.5 mmol) was used to quench residual water (0.5 mmol) in benzenesulfonic acid. After stirring for 2 h at room temperature, this solution was added dropwise to a mixture of PCl_3 (0.69 g, 5 mmol) in THF (20 mL) maintained at –78 °C. The resulting whitish suspension was stirred for 1 h. In a separate Schlenk flask, *n*BuLi (2.5 M in hexanes; 4 mL, 10 mmol) was added to 9-bromonaphthalene (2.07 g, 10 mmol) in THF (30 mL) at 0 °C. This mixture was left for one hour at room temperature and then introduced dropwise to the off-white suspension. After stirring for 2 h at room temperature, the solvent was removed in vacuo to leave a purple solid. After dissolution in dichloromethane (40 mL), acidic ion-exchange resin [Amberlite IRC-50 (H) 16–50 mesh, 10 g] was added and the mixture was stirred for 3 h. The supernatant was dried in vacuo. The resulting solid, dissolved in acetonitrile, was stirred for 3 h. After filtration, the solvent was removed. The resulting white crystals were dried in vacuo; yield 1.4 g (63%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.14 (dd, ^3J = 7.36, ^3J = 4.21 Hz, 1 H, H^3-ArSO_3), 8.10 (d, J = 7.85 Hz, 1 H, H^4-ArSO_3), 7.88–7.83 (m, 2 H, H^3-Np), 7.82 (d, J = 8.09 Hz, 2 H, H^2-Np), 7.46 (dd, ^3J = 6.28 Hz, ^3J = 3.11 Hz, 2 H, H^4-Np), 7.43–7.40 (m, 2 H, H^5-Np), 7.33 (m, 4 H, H^{7,6}-Np), 7.25 (m, 2 H, H^8-Np), 7.13 (m, 1 H, H^5-ArSO_3), 7.01 (m, 1 H, H^6-ArSO_3) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 154.0 [$J_{P,C}$ = 28.8 Hz, *C*(SO_3)], 136.8 [$J_{P,C}$ = 20.9 Hz, *C*(P)-C(SO_3)], 136.7 [C(P)-*C*H=CH- in ArSO_3], 135.7 & 135.5 (C^5-Np), 133.8 & 133.7 (C^{4a}-Np), 133.7 [C(P)-CH=*C*H- in phenyl], 132.5 [C(P)-CH=CH-*C*H- in phenyl], 129.2 (C^{8a}-Np), 129.2 ($J_{P,C}$ = 15 Hz, C_{ipso} in naphthyl), 128.4 (C^7-Np), 127.8 [$J_{P,C}$ = 5.0 Hz, C(P)-C(SO_3)-*C*H=], 127.2 ($J_{P,C}$ = 26 Hz, C^2-Np), 126.6 (C^4-Np), 126.4 (C^3-Np), 126.19 & 126.21 (C^6-Np), 134.4 (C^8-Np) ppm. ^{31}P NMR ([D$_6$]DMSO): δ = –23.0 (s), –26.8 (s) ppm. MS: *m*/*z* = calcd. 442.0793; found 442.0796.

Preparation of Ligand 4. 2-(Diphenanthren-9-yl-phosphanyl)benzenesulfonic Acid: *n*BuLi (2.5 M in hexanes; 4.2 mL, 10.5 mmol) was added at 0 °C to a solution of benzenesulfonic acid (0.8 g, 5 mmol) in THF (20 mL). After stirring for 2 h at room temperature, this solution was added dropwise to a mixture of PCl_3 (0.69 g, 5 mmol) in THF (20 mL) maintained at –78 °C. The resulting whitish suspension was stirred for 1 h. In a separate Schlenk flask, *n*BuLi (2.5 M in hexanes; 4 mL, 10 mmol) was added to 9-bromophenanthrene (2.57 g, 10 mmol) in THF (30 mL) at 0 °C. This mixture was left for one hour at room temperature and then introduced dropwise to the off-white suspension. After stirring for 2 h at room temperature, the solvent was removed in vacuo to leave a purple solid. After dissolution in dichloromethane (40 mL), acidic ion-exchange resin [Amberlite IRC-50 (H) 16–50 mesh, 10 g] was added and the mixture was stirred for 3 h. The supernatant was dried in vacuo. The resulting solid, dissolved in acetonitrile, was stirred for 3 h. After filtration, the solvent was removed. The resulting pale yellow crystals were dried in vacuo; yield 1.0 g (37%). ^{1}H NMR ([D$_6$]-DMSO): δ = 8.80–8.72 (m, 4 H, H^{6,5}-Pa), 8.65 (m, 2 H, H^7-Pa), 8.12 (m, 1 H, H^3-ArSO_3), 8.02 (d, J = 7.7 Hz, 1 H, H^5-ArSO_3), 7.92 (dd, ^3J = 7.9 Hz, ^3J = 1.2 Hz, 1 H, H^4-ArSO_3), 7.67 (m, 2 H, H^{10}-Pa), 7.62 (m, 2 H, H^4-Pa), 7.45 (dd, ^3J = 16.2 Hz, ^3J = 7.8 Hz, 2 H, H^3-Pa), 7.38 (d, J = 7.5 Hz, 2 H, H^2-Pa), 7.35 (d, J = 7.7 Hz, 1 H, H^6-ArSO_3), 7.23 (d, J = 3.3 Hz, 2 H, H^1-Pa), 7.15 (m, 2 H, H^8-Pa) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 152.5, 134.8, 132.3, 132.2, 132.1, 132.0, 130.4, 129.8, 128.9, 128.5, 127.7, 127.6, 127.3, 127.2, 126.1, 125.7, 125.5, 125.4, 124.4, 122.0, 121.7, 121.6 ppm. ^{31}P NMR ([D$_6$]DMSO): δ = –22.4 (s), –24.8 (s) ppm. MS: *m*/*z* = calcd. 542.1106; found 542.1113.

Preparation of Ligand 5. 2-(Dianthracen-9-yl-phosphanyl)benzenesulfonic Acid: *n*BuLi (2.5 M in hexanes; 5.2 mL, 13 mmol) at 0 °C was added to a solution of dry benzenesulfonic acid (0.92 g, 5.8 mmol) in THF (20 mL). After stirring for 2 h at room temperature, the solution was added dropwise to a solution of PCl_3 (0.787 g, 5.8 mmol) in THF (20 mL) at –78 °C and stirred for 1 h. In a separate Schlenk flask, *n*BuLi (2.5 M in hexanes; 4.64 mL, 11.6 mmol) was added to 9-bromoanthracene (3.00 g, 11.6 mmol) in THF (30 mL) at 0 °C. This mixture was left for one hour at room temperature and then introduced dropwise to the whitish suspension. After stirring for 2 h at room temperature, the solvent was removed in vacuo to leave a purple solid. After dissolution in dichloromethane (40 mL), acidic ion-exchange resin [Amberlite IRC-50 (H) 16–50 mesh, 12 g] was added and the mixture was stirred for 3 h. The supernatant was dried in vacuo. The resulting solid, dissolved in acetonitrile, was stirred 3 h. After filtration, the solvent was removed. The resulting dark yellow crystals were dried in vacuo; yield 1.9 g (49%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.45 (s, 2 H, H^{10}-An), 8.40 (dd, ^3J = 3.5 Hz, ^3J = 9.1 Hz, 4 H, H^{1,8}-An), 7.89 (d, J = 8.4 Hz, 4 H, H^{4,5}-An), 7.44 (m, 4 H, H^{3,6}-An), 7.31 [t, J = 7.0 Hz, 1 H, C(P)-C(SO_3)=CH-C*H*-], 7.22 (m, 4 H, H^{2,7}-An), 6.95 [t, J = 7.0 Hz, 1 H, C(P)-C(SO_3)=C*H*-], 6.90 [m, 2 H, C(P)-C*H*=C*H*-] ppm. ^{13}C NMR ($CDCl_3$): δ = 153.9 (*C*SO_3), 135.3 [C(P)-

C(SO_3)=*C*H-], 134.6 [C(P)-C(SO_3)=CH-*C*H=], 134.2 [$J_{P,C}$ = 19.9 Hz, *C*(P)-CSO_3], 134.2 [$J_{P,C}$ = 14.9 Hz, C(P)-*C*H=CH- in ArSO_3], 131.0 ($C^{4,5}$-An), 129.1 ($C^{1,8}$-An), 128.6 ($C^{8a,9a}$-An), 127.9 [C(P)-CH=*C*H- in ArSO_3], 127.7 ($C^{4a,10a}$-An), 126.7 ($J_{P,C}$ = 22.9 Hz, C_{ipso} in An), 125.4 (C^{10}-An), 125.1 ($C^{2,7}$-An), 124.6 ($C^{3,6}$-An) ppm. ^{31}P NMR ([D_6]DMSO): δ = –29.4 (s) ppm. MS: *m*/*z* = calcd. 556.1262; found 556.1247.

Preparation of 1Pd. [MePd(pyridine)P(-3-Me-6-SO_3-C_6H_3)(Ph)$_2$]: [$PdMe_2$(tmeda)] (0.063 g, 0.25 mmol) and ligand **1** (0.089 g, 0.25 mmol) were dissolved in dry THF (10 mL) under an inert atmosphere and stirred for 30 min. Pyridine (0.0965 g, 1.25 mmol) was then added followed by stirring for another 30 min. During the stirring, a white precipitate was formed. After adding Et_2O (25 mL), the precipitate was collected, washed with Et_2O, and dried under vacuum; yield 0.100 g (72%). ^{1}H NMR ($CDCl_3$): δ = 8.81 (d, *J* = 4.9 Hz, 2 H, H_{ortho} pyridine), 8.17 [dd, ^3J = 4.5 Hz, ^3J = 8.0 Hz, 1 H, C(P)-C(SO_3)=C*H*-], 7.86 (t, *J* = 7.7 Hz, 1 H, H_{para} pyridine), 6.63 (m, 4 H, H_{ortho} phenyl) 7.51 (m, 2 H, H_{meta} pyridine), 7.46 (m, 6 H, H_{meta} + H_{para} phenyl), 7.33 [d, *J* = 7.9 Hz, 1 H, C(P)-C*H*=], 6.80 [d, *J* = 9.5 Hz, 1 H, C(P)-CH=C(Me)-C*H*-], 2.25 (s, 3 H, ArCH_3), 0.49 (d, $J_{P,H}$ = 2.63 Hz, 3 H, Pd-Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 150.5 (N-*C*=C), 146.9 ($J_{P,C}$ = 13.7 Hz, *C*SO_3), 140.2 ($J_{P,C}$ = 6.6 Hz, *C*-CH_3), 138.5 (br., C_{ipso} in phenyl), 135.1 (C_{para} in pyridine), 134.4 [$J_{P,C}$ = 12.1 Hz, C(P)-*C*H=CH- in ArSO_3], 131.8 [C(P)-*C*H=C(Me)-], 131.1 [C(P)-C(SO_3)=*C*H-], 130.4 [C(P)-C(SO_3)=CH-*C*H-], 130.0 [C(P)-CH=CH-*C*H in phenyl], 128.8 [$J_{P,C}$ = 11.1 Hz, C(P)-CH=*C*H-CH- in phenyl], 125.2 (C_{meta} in pyridine), 21.6 (Ar*C*H_3), 0.9 (*C*H_3-Pd) ppm. ^{31}P NMR ($CDCl_3$): δ = 28.9 (s) ppm.

Preparation of 2Pd. [MePd(pyridine)P(-6-SO_3-C_6H_3)(Ph)$_2$]: [$PdMe_2$(tmeda)] (0.113 g, 0.44 mmol) and ligand **2** (0.152 g, 0.44 mmol) were dissolved in dry THF (10 mL) under inert atmosphere and the resulting solution was stirred for 30 min. Pyridine (0.04 g, 0.50 mmol) was then added followed by stirring for another 60 min. During the stirring, a white precipitate formed. After adding Et_2O (25 mL), the white precipitate was collected, washed with Et_2O, and dried under vacuum; yield 0.110 g (81%). ^{1}H NMR ($CDCl_3$): δ = 8.80 (d, *J* = 4.2 Hz, 2 H, H_{ortho} pyridine), 8.28 [m, 1 H, -C(SO_3)-C*H*-], 7.86 (t, *J* = 7.4 Hz, 1 H, H_{para} pyridine), 7.63 (m, 4 H, H_{ortho} phenyl), 7.49 (d, *J* = 7.1 Hz, 2 H, H_{meta} pyridine), 7.45 (m, 6 H, H_{meta}, H_{para} phenyl), 7.36 [t, *J* = 7.4 Hz, 2 H, C(SO_3)-CP-C*H*, C(SO_3)-CH=C*H*], 7.05 [t, *J* = 8.6 Hz, 1 H, C(SO_3)-CP-CH=C*H*], 0.50 (d, $J_{P,H}$ = 2.4 Hz, 3 H, Pd-Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 150.2 (N-*C*=C), 149.2 ($J_{P,C}$ = 13.0 Hz, *C*SO_3), 138.1 (br., C_{ipso} in phenyl), 134.5 (C_{para} in pyridine), 134.2 ($J_{P,C}$ = 12.2 Hz, CP-*C*H=CH- in ArSO_3), 130.9 (CP-CH=CH-*C*H in phenyl), 129.9 (CP-CH=*C*H in ArSO_3), 129.8 ($J_{P,C}$ = 6.9 Hz, PC=*C*H in ArSO_3), 129.6 [-*C*H-C(SO_3)=CP], 128.7 [$J_{P,C}$ = 11.2 Hz, C(P)-CH=*C*H-CH- in phenyl], 128.6 [$J_{P,C}$ = 7.8 Hz, -*C*(P)-C(SO_3)-], 125.0 (C_{meta} in pyridine), 0.6 (CH_3-Pd) ppm. ^{31}P NMR ($CDCl_3$): δ = 29.2 (s) ppm.

Preparation of 3Pd. [MePd(pyridine)P(-6-SO_3-C_6H_3)(naphthalene)$_2$]: [$PdMe_2$(tmeda)] (0.063 g, 0.25 mmol) and ligand **3** (0.111 g, 0.25 mmol) were dissolved in dry THF (10 mL) under an inert atmosphere and the resulting solution was stirred for 30 min. Pyridine (0.02 g, 0.30 mmol) was then added followed by stirring for another 60 min. After adding Et_2O (10 mL), the purple precipitate was collected, washed with Et_2O, and dried under vacuum; yield 0.081 g (50%). ^{1}H NMR ([D_6]DMSO): δ = 8.58 (d, *J* = 7.1 Hz, 2 H, H_{ortho} pyridine), 8.51 [d, *J* = 7.6 Hz, 1 H, C(SO_3)-C*H*-], 8.38–8.21 [m, 3 H, C(SO_3)-CH=C*H*-C*H*=C*H*-], 8.08–7.71 (m, 14 H, Np-H), 7.39 (t, *J* = 8.9 Hz, 1 H, H_{para} pyridine), 7.34 (dd, ^3J = 7.2, ^3J = 6.50 Hz, 2 H, H *meta* pyridine), 0.62 (d, $J_{P,H}$ = 2.8 Hz, 3 H, Pd-Me) ppm. ^{13}C NMR ([D_6]DMSO): δ = 154.0, 153.8, 151.8, 151.6, 150.5, 150.3, 136.6, 135.6, 134.3, 133.7, 133.4, 133.1, 132.4, 130.6, 129.7, 129.3, 128.8, 128.3, 127.9, 127.5, 127.0, 126.5, 126.2, 126.0, 125.7, 0.5 ppm. ^{31}P NMR ([D_6]DMSO): δ = –18.0 (s), –22.2 (s) ppm.

Preparation of 4Pd. [MePd(pyridine)P(-6-SO_3-C_6H_3)(phenanthrene)$_2$]: [$PdMe_2$(tmeda)] (0.063 g, 0.25 mmol) and ligand **4** (0.136 g, 0.25 mmol) were dissolved in dry THF (10 mL) under an inert atmosphere and the resulting solution was stirred for 30 min. Pyridine (0.02 g, 0.30 mmol) was then added followed by stirring for another 60 min. After adding Et_2O (10 mL), the light brown precipitate was collected, washed with Et_2O, and dried under vacuum; yield 0.076 g (41%). ^{1}H NMR ([D_6]DMSO): δ = 8.52 (d, *J* = 8.3 Hz, 2 H, H_{ortho} pyridine), 8.40–8.15 [m, 4 H, C(SO_3)-C*H*=C*H*-C*H*=C*H*], 8.05–7.65 (m, 18 H, HPa), 7.57 (t, *J* = 7.5 Hz, 1 H, H_{para} pyridine), 7.30 (dd, ^3J = 7.7 Hz, ^3J = 6.9 Hz, 2 H, H_{meta} pyridine), 0.63 (d, $J_{P,H}$ = 3.4 Hz, 3 H, Pd-Me) ppm. ^{13}C NMR ([D_6]DMSO): δ = 152.3, 149.5, 135.3, 134.8, 132.3, 132.1, 130.4, 129.8, 128.9, 128.6, 127.8, 127.6, 127.3, 127.2, 126.4, 126.2, 125.7, 125.4, 124.4, 123.2, 122.5, 122.0, 121.7, 0.6 ppm. ^{31}P NMR ([D_6]DMSO): δ = –8.88 (s), –11.45 (s) ppm.

Preparation of 5Pd. [MePd(pyridine)P(-6-SO_3-C_6H_3)(anthracene)$_2$]: [$PdMe_2$(tmeda)] (0.063 g, 0.25 mmol) and ligand **5** (0.136 g, 0.25 mmol) were dissolved in dry THF (10 mL) under an inert atmosphere and the resulting solution was stirred for 30 min. Pyridine (0.02 g, 0.30 mmol) was then added followed by stirring for another 60 min. After adding Et_2O (10 mL), the yellow precipitate was collected, washed with Et_2O, and dried under vacuum; yield 0.069 g (37%). ^{1}H NMR ([D_6]DMSO): δ = 9.26 (d, *J* = 9.3 Hz, 2 H, H_{ortho} pyridine), 8.96–8.65 [m, 4 H, C(SO_3)-C*H*=C*H*-C*H*=C*H*], 8.82 (dd, ^3J = 9.0 Hz, ^3J = 3.5 Hz, 2 H, H_{meta} pyridine), 8.52–7.50 (m, 18 H, HAn), 7.39 (t, *J* = 7.5 Hz, 1 H, H_{para} pyridine), 0.66 (d, $J_{P,H}$ = 3.0 Hz, 3 H, Pd-Me) ppm. ^{13}C NMR ([D_6]DMSO): δ = 152.9, 152.8, 152.2, 149.9, 147.3, 139.7, 136.7, 135.9, 135.7, 135.0, 134.9, 134.6, 131.8, 131.7, 130.4, 129.9, 129.8, 129.7, 129.4, 128.7, 127.6, 127.4, 127.3, 126.8, 126.7, 126.4, 126.2, 125.9, 125.7, 125.4, 0.5 ppm. ^{31}P NMR ([D_6]DMSO): δ = –19.1 (s) ppm.

Polymerizations: Polymerizations were carried out in a stainless steel reactor (100 or 450 mL, Parr). Catalyst, toluene, and comonomer were added to a Schlenk flask in a nitrogen-filled glovebox. The reactor, which was first dried and kept under nitrogen, was loaded with the toluene solution by cannula transfer from the Schlenk flask under nitrogen. The reactor was then sealed, pressurized with ethene, stirred, and heated. The polymerizations were performed at constant pressure in the feed reactor and the activities were calculated from the rate of ethene consumption, which was monitored by the decrease of the ethene pressure in the feed tank. Once the reaction was over, the reactor was cooled down to room temperature and slowly depressurized. The polymers were precipitated in four volumes of methanol, collected by centrifugation or filtered, washed with methanol, and dried under vacuum.

Computational Details: All geometry optimizations were performed with the Gaussian03 suite of programs[28] using the B3LYP functional, which includes the three-parameter gradient-corrected exchange functional of Becke[29] and the correlation functional of Lee, Yang, and Parr, which includes both local and nonlocal terms.[30] The basis set chosen was the standard 6-31+G**, which includes both polarization and diffuse functions. For the calculation of the Tolman angle, only the zwitterionic form of the phosphanes was considered. Solvent effects and neutral structures (sulfonic acid and nonprotonated phosphanes) were not calculated.

CCDC-779758 (for **1Pd**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Experimental results for the ring exchange process.

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