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


Laurence Piche,^[a] Jean-Christophe Daigle,^[a] Rinaldo Poli^[b] and Jerome P. Claverie*^[a]

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Sulfonated arylphosphine ligands o -Ar₂PC₆H₄SO₃H where Ar is phenyl (Ph), naphthyl (Np), phenantryl (Pa) or anthracenyl (An) were prepared. These bulky phosphines were used to generate phosphine sulfonate palladium complexes [(o -Ar₂-PC₆H₄SO₃)PdMe(pyridine)]. These complexes catalyze ethene polymerization, yielding linear polyethene. The activity of the catalyst 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.

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Introduction

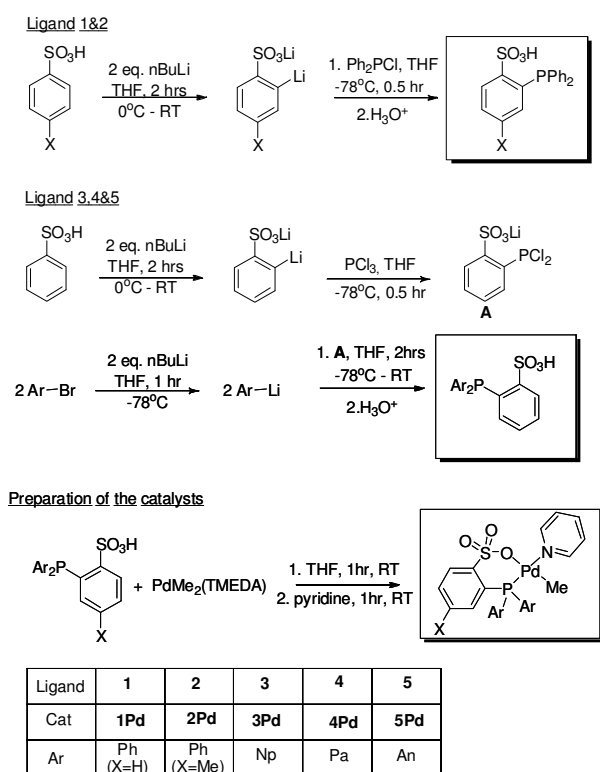
The evolution of olefin polymerization catalysis since Ziegler's discovery in 1953 has involved a prolific coupling of polymer science with organometallic chemistry. However, there are still no commercially viable catalysts for the controlled copolymerization of simple olefins with polar functional monomers. Currently, commercial processes for the copolymerization of ethene with polar functional monomers such as acrylates employ free radical processes which 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]

A significant advance was reported by Johnson *et al.*^[2] who discovered that cationic palladium diimine complexes can copolymerize ethene and acrylates to afford branched copolymers where the acrylate is placed in a terminal position. In 2002, Drent *et al.*^[3] disclosed that an ill-defined catalytic system containing a phosphine sulfonate and a palladium complex, either tris(dibenzylideneacetone)dipalladium(0) or palladium(II) acetate, permits the preparation of ethene-acrylate copolymers where the

acrylates are incorporated in main chain positions. Well-defined palladium catalysts containing a phosphine aryl sulfonate ligand were then disclosed by Hearley *et al.*,^[4] Goodall *et al.*,^[5,6] Kochi *et al.*,^[7,8] Liu *et al.*,^[9] Skupov *et al.*,^[10] Luo *et al.*,^[11] Vela *et al.*^[12] and most recently Guironnet *et al.*^[13] Among those reports, acrylate copolymerization with ethene was mentioned by Goodall,^[5,6] Skupov,^[10] and Guironnet.^[13] These studies employ the catalyst (o -Ar₂PC₆H₄SO₃)PdMe(L) with Ar = o -OMePh, which corresponds to the ligand originally presented by Drent.^[3] The role of the ancillary ligand L (L = pyridine,^[14] lutidine,^[15] DMSO,^[13] allyl group^[9]) on the catalytic activity has been studied in detail. However, at this time, little is known on the influence of the aryl phosphine sulfonate structure. We recently reported that the introduction of the bulky and electron-rich aryl groups (Ar = -[o -(2',6'- $(\text{OMe})_2\text{C}_6\text{H}_3$)-C₆H₄]) resulted in a very active catalyst which affords polyethylene of high molecular weight^[10] 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 phosphines. To clarify this issue, we have turned our attention toward catalysts based on polyaromatic sulfonated phosphines o -Ar₂PC₆H₄SO₃H where Ar is phenyl, naphthyl (Np), phenantryl (Pa) or anthracenyl (An). Non-sulfonated polyaromatic phosphine analogs were initially developed by Müller *et al.*, who demonstrated that their properties are changed by altering the number of aromatic rings associated with the phosphine.^[16] These phosphines become better donors as the number of aromatic rings increases and their Tolman cone angle increases from 145° for PPh₃ to 177° for PNP₂Ph and 186° for PAN₂Ph. Thus, the larger phosphines are the better donors, and we should expect that catalysts based on the larger phosphines would be more active and generate polyethylene of high molecular weight.

Results and Discussion

The synthesis of the sulfonated arylphosphine is a one-pot procedure (Scheme 1). For the phenyl substituted phosphines **1** and **2**, the dilithiated salt of benzene or toluene sulfonic acid is reacted with commercial diphenylchlorophosphine. For the other phosphines (**3-5**), the sulfonated benzyl group is introduced first upon reaction of trichlorophosphine with the lithiated salt. The resulting dichlorophosphine 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 of *n*-BuLi leads to the formation of *n*-butyl phosphines (as shown by MS), and a defect of *n*-BuLi leads to the isolation of phosphine oxides (R_2POH , also shown by MS).



Scheme 1

Although the MS indicates the presence of a single compound for ligands **3** and **4**, the ^{31}P and ^{13}C NMR spectra clearly show the presence of two distinct species^[17] characterized by very similar spectroscopic properties. Calculations by DFT indicate that these species correspond to two rotational isomers (Figure 1) with *syn* and *anti* conformations of the aryl groups across the P atom (Figure 1), with energies differing by less than 2 kcal/mol, which is in good agreement with the 80:20 proportion found by ^{31}P NMR at room temperature. The activation barrier is above 10 kcal/mol, which is high enough for the structures to appear as distinct species in the NMR timescale, even at higher temperature (no coalescence was observed at $T = 120^\circ C$). Bis(phenantril)phenyl phosphine^[18] shows only one resonance in the ^{31}P NMR spectrum indicating that the presence of the ortho sulfonic acid group contributes to the slow conversion between both rotamers. From the phosphine structures (optimized by DFT), we have calculated Tolman cone angles,^[19] that is to say the apex angle of a cylindrical cone with origin 2.28 Å from the center of the phosphorous atom whose sides

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*-butyl phosphine (182°), but slightly smaller than the highly hindered tris(2,4,6-trimethylphenyl)phosphine (212°). Therefore, these sulfonated aryl phosphines exhibit considerable bulk. Based on the pioneering work of Mingos,^[20] the availability of the P lone pair increases when the size of the aryl group increases, thus the larger phosphines are better electron donors. Thus, the order of basicity of these phosphines 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**).

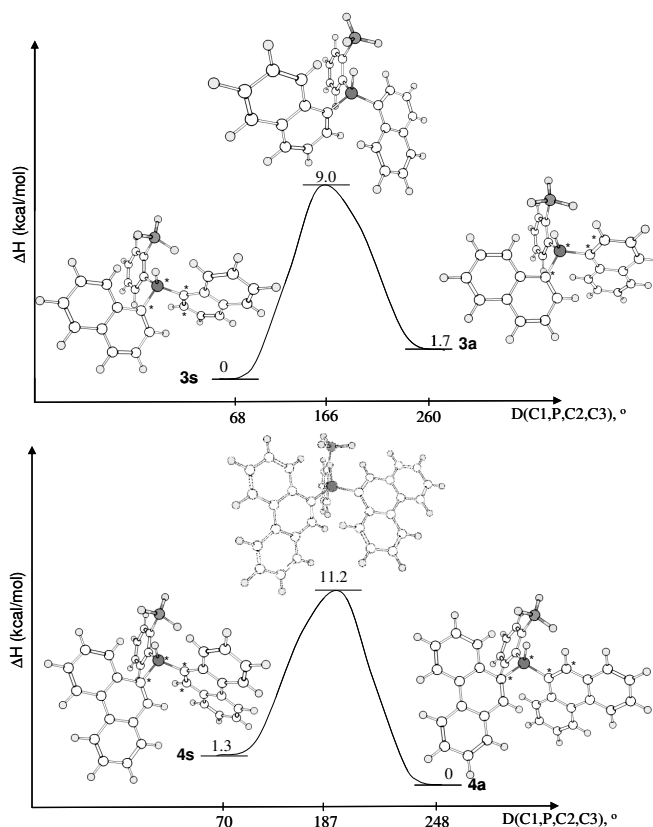


Figure 1. Enthalpic changes between the *syn* and *anti* conformations of phosphines **3** and **4** vs the dihedral angle C1 P C2 C3 (D , indicated with stars). Only the lowest transition state TS is shown : the other TS (located at $D \sim 0^\circ$) is at least several kcal/mol higher in energy.

The catalyst synthesis proceeds smoothly following the procedure highlighted in reference.^[10] The yields are in the following order: **1Pd** ~ **2Pd** > **3Pd** > **4Pd** > **5Pd**, which does not follow the expected basicity of those ligands, indicating that steric factors are the dominant influence in determining the reactivity of these sulfonated phosphines towards Pd centers. Catalysts **3Pd**, **4Pd** and **5Pd** are sparingly soluble in most common solvents except DMSO. The overall structure observed for **1Pd** resembles those of other $(P^{\wedge}O)PdMe(L)$ complexes (Figure 2), with the Pd atom in a square planar environment and the Me group trans to the sulfonate group. The six-member cycle Pd(1)-P(1)-C(131)=C(132)-S(1)-O(11)- adopts a half-boat conformation, with C(111) and O(13) in pseudo axial positions and C(121) and O(12) in pseudo equatorial positions. This half-boat conformation has been reported for the majority of aryl sulfonate catalysts^{[9],[12],[15],[21]} except for bulky aryl groups or when pyridine

is replaced by DMSO.^{[10],[13]} The complete characterization of catalysts **3Pd** and **4Pd** is complex because each rotamer reacts to give a separate catalyst, resulting in a doubling of all phosphine resonances (Figure 3). The analysis is further complicated by the presence of two distinct exchange processes.^[14] The first one is the exchange between bound pyridine and free pyridine (if added in excess, Figure 3). The second one is the inversion of the six member ring -Pd-O-S-C=P-. The *non-sulfonated* phosphine aryl substituents are respectively occupying a pseudo equatorial and pseudo axial position. For catalyst **1Pd** and **2Pd**, the exchange between axial and equatorial positions is fast in the NMR time scale, even at -90°C in CD₂Cl₂. 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 inversion barrier (measured by NMR) of PdMe(py)(PAr₂PhSO₃) is 5.7 kcal/mol in CD₂Cl₂, whereas for Ar = Ph(*o*-C₆H₃(2,6-OMe)₂) the barrier is 8.3 kcal/mol in CD₂Cl₂.

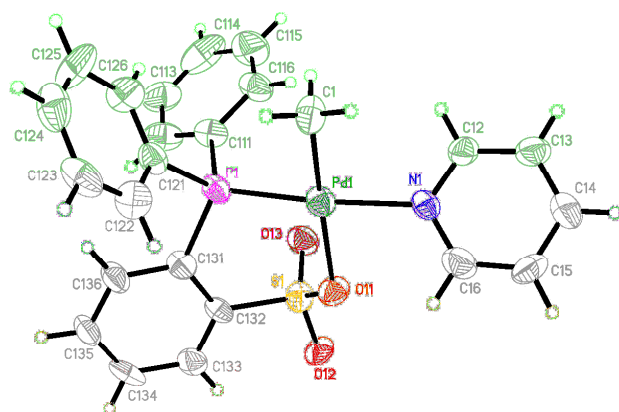


Figure 2. ORTEP view of **1Pd**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Pd(1)-C(1) 2.057(10) ; Pd(1)-O(11) 2.164(7); Pd(1)-P(1) 2.229(3) ; Pd(1)-N(1) 2.110(8); C(1)-Pd(1)- N(1) 90.6(4); C(1)-Pd(1)-P(1) 89.1(3); C(1)-Pd(1)-O(11) 174.7(4); N(1)-Pd(1)-P(1) 172.4(3).

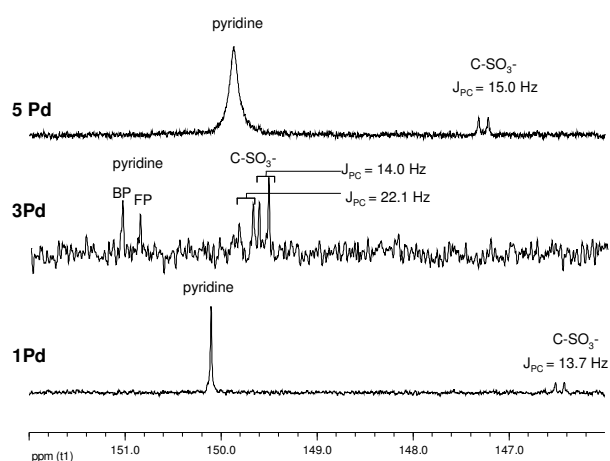


Figure 3. Superposition of ¹³C NMR spectra (downfield region). For **1Pd**, bound pyridine (BP) is in rapid exchange with free pyridine (FP) whereas for **5Pd**, the exchange is intermediate in the NMR time scale. For **3Pd**, the exchange is slow, and the two rotamers are observed, as indicated by the C-SO₃ resonances.

All catalysts are able to polymerize C₂H₄ at 85°C (P = 300 psi), with the activity decreasing from **1Pd** to **5Pd**. The resulting polymers are highly linear, as shown by ¹³C NMR and by examination of the Mark-Houwink plot in triple-detection GPC.

Unexpectedly, the drastic increase in steric hindrance from **1Pd** to **4Pd** results in a decrease of the average molecular weight. Thus, the least bulky and more acidic phosphine yields a catalyst with the highest activity and producing polymers with the highest molecular weights. Contrarily to what was reported by us,^{[10],[22]} we found that **1Pd** and **2Pd** are also able to copolymerize acrylates with ethylene with activities and molecular weights which are nearly identical to those obtained with MePd(pyridine)P(3-Me-6-SO₃-C₆H₃)(*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, an insertion of 6% was obtained with catalyst **1Pd**, while for similar conditions (P = 100 psi, T = 100°C and monomer concentration = 0.85 mol/L), an insertion of 15% of tert-butyl acrylate was observed with catalyst **2Pd**. However, catalysts **3Pd**, **4Pd** and **5Pd** do not yield any copolymer under comparable conditions.

Table 1. Ethene polymerization data (T = 85°C, P = 300 psi)

Cat	[Cat] (μmol/L)	TON (mol _E / mol _{Pd})	Pol. wt (g)	M _n ^[a] (g/mol)	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 ^{b)}	1.2
				35000	4

[a] Determined by GPC analysis at 160°C in 1,2,4 trichlorobenzene. [b] bimodal distribution.

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

Cat	[Cat] (μmol/L)	[TBA] (mol/L)	TON (mol _E / mol _{Pd})	M _n ^[a] (g/mol)	PDI ^[a]	TBA mol% ^[b]
1Pd	94	1.7	704	5170	1.4	6
2Pd	185	0.85	0	3000	1.2	15

[a] Determined by GPC analysis at 160 °C in 1,2,4 trichlorobenzene. [b] Determined by NMR analysis at 110 °C in tetrachlorethane *d*₂

Conclusions

Phosphine sulfonate palladium complexes were prepared and used as catalysts for ethene polymerization without the need of 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 Considerations. All manipulations were done under inert atmosphere using standard Schlenk techniques. Solvents were degassed and dried over activated molecular sieves. Benzene and toluene sulfonic acid were dried by azeotropic distillation with benzene. Dimethyl(*N,N,N',N'*-tetramethylethylenediamine)-palladium(II), PdMe₂(TMEDA), was prepared according to de Graaf.^[23] All acrylic monomers were purified by sparging them with argon and passing them over a bed of inhibitor-remover resin

(Aldrich) as acrylic monomers are usually inhibited with quinones which interfere with the catalyst. The monomers were then spiked with *tert*-butyl catechol (0.25% wt:wt) in order to prevent spontaneous radical polymerization of the acrylate during the polymerization process. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on a Varian Inova 600 MHz spectrometer at ambient temperature except for the polymers which were analyzed in deuterated tetrachlorethane at 115°C . The molecular weight distributions were determined by gel permeation chromatography (GPC) using a Viscotek HT GPC equipped with triple detection operating at 160°C . The eluent was 1,2,4-trichlorobenzene, and separation was performed on three PolymerLabs Mixed B(-LS) columns. The dn/dc of pure linear polyethylene was found to be 0.106 mL/g at this temperature. Electrospray mass spectra (ESI-MS) of organic compounds were recorded on a Agilent 6210 LC-MSD TOF mass spectrometer. Standard numbering of polyaromatic C and H was used below.

Preparation of ligand 1, 2-Diphenylphosphanyl-4-methylbenzenesulfonic acid. To a solution of dry toluenesulfonic acid (1.03 g, 6 mmol) in THF (30 mL) was added *n*BuLi 2.5 M in hexanes (4.8 mL, 12 mmol) at 0°C . After stirring for 1 h at room temperature, the solution was added dropwise to a solution of bis(phenyl)chlorophosphine (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* leaving a white solid. The solid was dissolved in dichloromethane (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/diethylether at -32°C . The resulting white crystals were dried *in vacuo*. Yield = 0.9 g (42 %). ^1H NMR (CDCl_3): δ : 8.15 (s, 1H, C(P)-C(SO₃)=CH-), 7.70-7.45 (m, 11H, H⁴-Ph, H⁴-ArSO₃, H²-Ph, H³-Ph), 6.96 (d, $J_{\text{PH}} = 14 \text{ Hz}$, 1H, C(P)-CH=C(Me)), 2.28 (s, 3H, CH₃-ArSO₃). ^{13}C NMR (CDCl_3): δ : 150.0 (C-CH₃), 140.6 (CSO₃, $J_{\text{PC}} = 12.4 \text{ Hz}$), 135.7 (C(P)-CH=C(Me)), 134.8 (Cipso in phenyl, $J_{\text{PC}} = 11.4 \text{ Hz}$), 134.7 (C(P)-C(SO₃), $J_{\text{PC}} = 11.0 \text{ Hz}$), 134.0 (C(P)-CH- in phenyl, $J_{\text{PC}} = 11.4 \text{ Hz}$), 130.1 (C(P)-CH=CH- in phenyl, $J_{\text{PC}} = 13.1 \text{ Hz}$), 130.1 (C(P)-CH=CH- in phenyl, $J_{\text{PC}} = 13.1 \text{ Hz}$), 129.4 (-CH-C(SO₃)=C(P)), 129.3 (-CH=CH-C(SO₃)=C(P)), 21.5 (ArCH₃). ^{31}P NMR (CDCl_3): δ : 3.6 (s). MS: found 356.0626, calc 356.0636.

Preparation of ligand 2, 2-Diphenylphosphanylbenzenesulfonic acid. To a solution of dry benzenesulfonic acid (0.80 g, 5 mmol) in THF (25 mL) was added *n*BuLi 2.5 M in hexanes (4.0 mL, 10 mmol) at 0°C . After stirring for 1 h at room temperature, the solution was added dropwise to a solution of bis(phenyl)chlorophosphine (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* leaving 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 degased water (30 mL). The organic solvent was removed *in vacuo*. The product was then recrystallized from dichloromethane/diethylether at -32°C . The resulting white crystals were dried *in vacuo*. Yield = 0.9 g (53 %). ^1H NMR (CDCl_3): δ : 8.31 (s, 1H, C(P)-C(SO₃)=CH-), 7.75-7.42 (m, 12H, H⁴-Ph, H⁴-ArSO₃, H⁵-ArSO₃, H²-Ph, H³-Ph), 7.22 (m, 1H, C(P)-CH=CH- in ArSO₃). ^{13}C NMR (CDCl_3): 151.8 (CSO₃, $J_{\text{PC}} = 12.0 \text{ Hz}$), 134.6 (Cipso in phenyl, $J_{\text{PC}} = 9.2 \text{ Hz}$), 133.5 (-C(P)-CH- in phenyl, $J_{\text{CP}} = 12.8 \text{ Hz}$), 133.3 (C(P)-CH=CH- in C₆H₄SO₃), 132.8 (C(P)-C(SO₃), 129.8 (-CH-C(SO₃)=C(P)), $J_{\text{PC}} = 10.1 \text{ Hz}$), 129.3 (C(P)-CH=CH- in phenyl, $J_{\text{PC}} = 11.9 \text{ Hz}$), 129.3 (C(P)-CH=CH- in phenyl), 128.7 (C(P)-CH=CH- in ArSO₃), 128.6 (-CH=CH-C(SO₃)=C(P)), $J_{\text{PC}} = 8.2 \text{ Hz}$). ^{31}P NMR (CDCl_3): δ : 4.3 (s). MS: found 342.0488, calc 342.0480.

Preparation of ligand 3, 2-(Di-naphthalen-1-yl-phosphanyl)benzenesulfonic acid. To a solution of benzenesulfonic acid (0.8 g, 5 mmol) in THF (20 mL) was added *n*BuLi 2.5 M in hexanes (4.2 mL, 10.5 mmol) at 0°C . The 0.5 mmol in excess were used to quench 0.5 mmol of residual water 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-bromo-naphthalene (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 whitish suspension. After stirring for 2 h at room temperature, the solvent was removed *in vacuo*, leaving 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 stirred for 3 hours. The supernatant was dried *in vacuo*. The resulting solid, dissolved in acetonitrile, was stirred for 3 hours. After filtration, the solvent was removed. The resulting white crystals were dried *in vacuo*. Yield = 1.4 g (63 %). ^1H NMR ($\text{DMSO}-d_6$): δ : 8.14 (dd, $^3J = 7.36 \text{ Hz}$, $^3J = 4.21 \text{ Hz}$, 1H, H³-Ar-SO₃), 8.10 (d, $J = 7.85 \text{ Hz}$, 1H, H⁴-Ar-SO₃), 7.88-7.83 (m, 2H, H³-Np), 7.82 (d, $J = 8.09 \text{ Hz}$, 2H, H²-Np), 7.46 (dd, $^3J = 6.28 \text{ Hz}$, $^3J = 3.11 \text{ Hz}$, 2H, H⁴-Np), 7.43-7.40 (m, 2H, H²-Np), 7.33 (m, 4H, H^{7,6}-Np), 7.25 (m, 2H, H⁸-Np), 7.13 (m, 1H, H⁵-Ar-SO₃), 7.01 (m, 1H, H⁶-Ar-SO₃). ^{13}C NMR ($\text{DMSO}-d_6$): δ : 154.0 (C(SO₃), $J_{\text{PC}} = 28.8 \text{ Hz}$), 136.8 (C(P)-C(SO₃), $J_{\text{PC}} = 20.9 \text{ Hz}$), 136.7 (C(P)-CH=CH- in ArSO₃), 135.7 & 135.5 (C⁵-Np), 133.8 & 133.7 (C^{4a}-Np), 133.7 (C(P)-CH=CH- in phenyl), 132.5 ((C(P)-CH=CH-CH- in phenyl), 129.2 (C^{8a}-Np), 129.2 (Cipso in naphthyl, $J_{\text{PC}} = 15 \text{ Hz}$), 128.4 (C⁷-Np), 127.8 (C(P)-C(SO₃)-CH=, $J_{\text{CP}} = 5.0 \text{ Hz}$), 127.2 (C²-Np, $J_{\text{PC}} = 26 \text{ Hz}$), 126.6 (C⁴-Np), 126.4 (C³-Np), 126.19 & 126.21 (C⁶-Np), 134.4 (C⁸-Np). ^{31}P NMR ($\text{DMSO}-d_6$): δ : -23.0 (s), -26.8 (s). MS: found 442.0796, calc 442.0793.

Preparation of ligand 4, 2-(Di-phenanthren-9-yl-phosphanyl)benzenesulfonic acid. To a solution of benzenesulfonic acid (0.8 g, 5 mmol) in THF (20 mL) was added *n*BuLi 2.5 M in hexanes (4.2 mL, 10.5 mmol) at 0°C . 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 1 h 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*, leaving 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 %). ^1H NMR ($\text{DMSO}-d_6$): δ : 8.80-8.72 (m, 4H, H^{6,5}-Pa), 8.65 (m, 2H, H⁷-Pa), 8.12 (m, 1H, H³-ArSO₃), 8.02 (d, $J = 7.7 \text{ Hz}$, 1H, H⁵-ArSO₃), 7.92 (dd, $^3J = 7.9 \text{ Hz}$, $^3J = 1.2 \text{ Hz}$, 1H, H⁴-ArSO₃), 7.67 (m, 2H, H¹⁰-Pa), 7.62 (m, 2H, H⁴-Pa), 7.45 (dd, $^3J = 16.2 \text{ Hz}$, $^3J = 7.8 \text{ Hz}$, 2H, H³-Pa), 7.38 (d, $J = 7.5 \text{ Hz}$, 2H, H²-Pa), 7.35 (d, $J = 7.7 \text{ Hz}$, 1H, H⁶-ArSO₃), 7.23 (d, $J = 3.3 \text{ Hz}$, 2H, H¹-Pa), 7.15 (m, 2H, H⁸-Pa). ^{13}C NMR ($\text{DMSO}-d_6$): 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. ^{31}P NMR ($\text{DMSO}-d_6$): δ : -22.4 (s), -24.8 (s). MS: found 542.1113, calc 542.1106.

Preparation of ligand 5, 2-(Di-anthracen-9-yl-phosphanyl)benzenesulfonic acid. To a solution of dry benzenesulfonic acid (0.92 g, 5.8 mmol) in THF (20 mL) was added *n*BuLi 2.5 M in hexanes (5.2 mL, 13 mmol) at 0°C . 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 1 h 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*, leaving 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 %). ^1H NMR (DMSO- d_6): δ : 8.45 (s, 2H, H¹⁰-An), 8.40 (dd, $^3J = 3.5$ Hz, $^3J = 9.1$ Hz, 4H, H^{1,8}-An), 7.89 (d, $J = 8.4$ Hz, 4H, H^{4,5}-An), 7.44 (m, 4H, H^{3,6}-An), 7.31 (t, $J = 7.0$ Hz, 1H, C(P)-C(SO₃)=CH-CH-), 7.22 (m, 4H, H^{2,7}-An), 6.95 (t, $J = 7.0$ Hz, 1H, C(P)-C(SO₃)=CH-), 6.90 (m, 2H, C(P)-CH=CH-). ^{13}C NMR (CDCl₃): δ : 153.9 (CSO₃), 135.3 (C(P)-C(SO₃)=CH-), 134.6 (C(P)-C(SO₃)=CH-CH=), 134.2 (C(P)-CSO₃, $J_{PC} = 19.9$ Hz), 134.2 (C(P)-CH=CH- in ArSO₃, $J_{PC} = 14.9$ Hz), 131.0 (C^{4,5}-An), 129.1 (C^{1,8}-An), 128.6 (C^{8a,9a}-An), 127.9 (C(P)-CH=CH- in ArSO₃), 127.7 (C^{4a,10a}-An), 126.7 (Cipso in An, $J_{PC} = 22.9$ Hz), 125.4 (C¹⁰-An), 125.1 (C^{2,7}-An), 124.6 (C^{3,6}-An). ^{31}P NMR (DMSO- d_6): δ : -29.35 (s). MS: found 556.1247, calc 556.1262.

Preparation of 1Pd, [MePd(pyridine)P(-3-Me-6-SO₃-C₆H₃)(Ph)₂]. PdMe₂(TMEDA) (0.063 g, 0.25 mmol) and ligand **1** (0.089 g, 0.25 mmol) were dissolved in 10 mL of dry THF 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 25 mL of Et₂O, the precipitate was collected, washed with Et₂O and dried under vacuum. Yield = 0.100 g (72 %). ^1H NMR (CDCl₃): δ : 8.81 (d, $J = 4.9$ Hz, 2H, Hortho pyridine), 8.17 (dd, $^3J = 4.5$ Hz, $^3J = 8.0$ Hz, 1H, C(P)-C(SO₃)=CH-), 7.86 (t, $J = 7.7$ Hz, 1H, Hpara pyridine), 6.63 (m, 4H, Hortho phenyl), 7.51 (m, 2H, Hmeta pyridine), 7.46 (m, 6H, Hmeta + Hpara phenyl), 7.33 (d, $J = 7.9$ Hz, 1H, C(P)-CH=), 6.80 (d, $J = 9.5$ Hz, 1H, C(P)-CH=C(Me)-CH-), 2.25 (s, 3H, ArCH₃), 0.49 (d, $J_{PH} = 2.63$ Hz, 3H, Pd-Me). ^{13}C NMR (CDCl₃): δ : 150.5 (N-C=C), 146.9 (CSO₃, $J_{PC} = 13.7$ Hz), 140.2 (C-CH₃, $J_{PC} = 6.6$ Hz), 138.5 (Cipso in phenyl, br.), 135.1 (Cpara in pyridine), 134.4 (C(P)-CH=CH- in ArSO₃, $J_{PC} = 12.1$ Hz), 131.8 (C(P)-CH=C(Me)-), 131.1 (C(P)-C(SO₃)=CH-), 130.4 (C(P)-C(SO₃)=CH-CH-), 130.0 (C(P)-CH=CH-CH in phenyl), 128.8 (C(P)-CH=CH-CH- in phenyl, $J_{PC} = 11.1$ Hz), 125.2 (Cmeta in pyridine), 21.6 (ArCH₃), 0.9 (CH₃-Pd). ^{31}P NMR (CDCl₃): δ : 28.9 (s).

Preparation of 2Pd, [MePd(pyridine)P(-6-SO₃-C₆H₃)(Ph)₂]. PdMe₂(TMEDA) (0.113 g, 0.44 mmol) and ligand **2** (0.152 g, 0.44 mmol) were dissolved in 10 mL of dry THF 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 25 mL of Et₂O, the white precipitate was collected, washed with Et₂O and dried under vacuum. Yield = 0.110 g (81 %). ^1H NMR (CDCl₃): δ : 8.80 (d, $J = 4.2$ Hz, 2H, Hortho pyridine), 8.28 (m, 1H, -C(SO₃)-CH-), 7.86 (t, $J = 7.4$ Hz, 1H, Hpara pyridine), 7.63 (m, 4H, Hortho phenyl), 7.49 (d, $J = 7.1$ Hz, 2H, Hmeta pyridine), 7.45 (m, 6H, Hmeta + Hpara phenyl), 7.36 (t, $J = 7.4$ Hz, 2H, C(SO₃)-CP-CH, C(SO₃)-CH=CH), 7.05 (t, $J = 8.6$ Hz, 1H, C(SO₃)-CP-CH=CH), 0.50 (d, $J_{PH} = 2.4$ Hz, 3H, Pd-Me). ^{13}C NMR (CDCl₃): δ : 150.2 (N-C=C), 149.2 (CSO₃, $J_{PC} = 13.0$ Hz), 138.1 (Cipso in phenyl, br.), 134.5 (Cpara in pyridine), 134.2 (CP-CH=CH- in ArSO₃, $J_{PC} = 12.2$ Hz), 130.9 (CP-CH=CH-CH in phenyl), 129.9 (CP-CH=CH in ArSO₃), 129.8 (PC=CH in ArSO₃, $J_{PC} = 6.9$ Hz), 129.6 (-CH-C(SO₃)=CP), 128.7 (C(P)-CH=CH-CH- in phenyl, $J_{PC} = 11.2$ Hz), 128.6 (-C(P)-C(SO₃)-), $J_{PC} = 7.8$ Hz), 125.0 (Cmeta in pyridine), 0.6 (CH₃-Pd). ^{31}P NMR (CDCl₃): δ : 29.2 (s).

Preparation of 3Pd, [MePd(pyridine)P(-6-SO₃-C₆H₃)(naphthalene)₂]. PdMe₂(TMEDA) (0.063 g, 0.25 mmol) and ligand **3** (0.111 g, 0.25 mmol) were dissolved in 10 mL of dry THF 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 10 mL of Et₂O, the purple precipitate was collected, washed with Et₂O and dried under vacuum. Yield = 0.081 g (50 %). ^1H NMR (DMSO- d_6): δ : 8.58 (d, $J = 7.1$ Hz, 2H, Hortho pyridine), 8.51 (d, $J = 7.6$ Hz, 1H, C(SO₃)-CH-), 8.38-8.21 (m, 3H, C(SO₃)-CH=CH-CH=CH-), 8.08-7.71 (m, 14H, H-Np), 7.39 (t, $J = 8.9$ Hz, 1H, Hpara pyridine), 7.34 (dd, 3J

= 7.2 Hz, $^3J = 6.50$ Hz, 2H, H meta pyridine), 0.62 (d, $J_{PH} = 2.8$ Hz, 3H, Pd-Me). ^{13}C NMR (DMSO- d_6): 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. ^{31}P NMR (DMSO- d_6): δ : -18.0 (s), -22.2 (s).

Preparation of 4Pd [MePd(pyridine)P(-6-SO₃-C₆H₃)(phenanthrene)₂]. PdMe₂(TMEDA) (0.063 g, 0.25 mmol) and ligand **4** (0.136 g, 0.25 mmol) were dissolved in 10 mL of dry THF 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 10 mL of Et₂O, the light brown precipitate was collected, washed with Et₂O and dried under vacuum. Yield = 0.076 g (41 %). ^1H NMR (DMSO- d_6): δ : 8.52 (d, $J = 8.3$ Hz, 2H, H ortho pyridine), 8.40-8.15 (m, 4H, C(SO₃)-CH=CH-CH=CH), 8.05-7.65 (m, 18H, HPa), 7.57 (t, $J = 7.5$ Hz, 1H, H para pyridine), 7.30 (dd, $^3J = 7.7$ Hz, $^3J = 6.9$ Hz, 2H, H meta pyridine), 0.63 (d, $J_{PH} = 3.4$ Hz, 3H, Pd-Me). ^{13}C NMR (DMSO- d_6): 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. ^{31}P NMR (DMSO- d_6): δ : -8.88 (s), -11.45 (s).

Preparation of 5Pd [MePd(pyridine)P(-6-SO₃-C₆H₃)(anthracene)₂]. PdMe₂(TMEDA) (0.063 g, 0.25 mmol) and ligand **5** (0.136 g, 0.25 mmol) were dissolved in 10 mL of dry THF 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 10 mL of Et₂O, the yellow precipitate was collected, washed with Et₂O and dried under vacuum. Yield = 0.069 g (37 %). ^1H NMR (DMSO- d_6): δ : 9.26 (d, $J = 9.3$ Hz, 2H, Hortho pyridine), 8.96 - 8.65 (m, 4H, C(SO₃)-CH=CH-CH=CH), 8.82 (dd, $^3J = 9.0$ Hz, $^3J = 3.5$ Hz, 2H, H meta pyridine), 8.52-7.50 (m, 18H, HAn), 7.39 (t, $J = 7.5$ Hz, 1H, H para pyridine), 0.66 (d, $J_{PH} = 3.0$ Hz, 3H, Pd-Me). ^{13}C NMR (DMSO- d_6): 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. ^{31}P NMR (DMSO- d_6): δ : -19.1 (s).

Polymerizations. Polymerizations were carried out in a stainless steel reactor (100 or 450 mL, Parr). Catalyst, toluene and eventually comonomer were added to a Schlenk flask in a nitrogen-filled glove box. 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^[24] using the B3LYP functional, which includes the three-parameter gradient-corrected exchange functional of Becke^[25] and the correlation functional of Lee, Yang, and Parr, which includes both local and nonlocal terms.^[26] The basis set chosen was the standard 6-31+G**^{*}, which includes both polarization and diffuse functions.

Supporting Information: CIF file for catalyst **1Pd**

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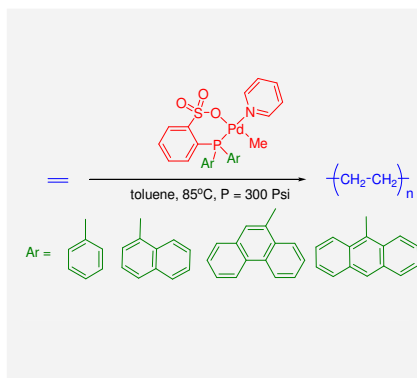
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Laurence Piche, Jean-Christophe Daigle, Rinaldo Poli and Jerome P. Claverie*..... Page No. – Page No.

Investigation of steric and electronic factors in palladium aryl sulfonate phosphine ethene polymerization catalysts

Keywords: Phosphine ligands / Palladium / Polymerization