

Styrene-containing Phosphine-sulfonate Ligands for Nickel- and Palladium-catalyzed Ethylene Polymerization

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Electronic Supplementary Information

Abstract A series of phosphine-sulfonate ligands bearing 2-, 3- and 4-vinylphenyl on the phosphorus atom were designed, synthesized, characterized and investigated in Ni- and Pd-catalyzed ethylene polymerization. The structure of the phosphine-sulfonate Pd complex bearing 2-vinylphenyl on the phosphorus atom showed 2,1-insertion for the 2-vinyl group. The phosphine-sulfonate Ni complex bearing 2-vinylphenyl resulted in significantly increased thermal stability and polyethylene molecular weights ($M_n=3.69\times10^4$ g·mol⁻¹ at 80 °C) versus the counterparts bearing 3-/4-vinyl groups as well as previously reported phosphine-sulfonate Ni complexes bearing bulky biaryl substituents.

Keywords Phosphine-sulfonate; Ethylene polymerization; Steric effect; Palladium; Nickel

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INTRODUCTION

Late transition metal catalysts have been playing increasingly important roles in the field of olefin polymerization.^[1–15] Nickel compounds were initially known as a "poison" for olefin polymerization, since the famous nickel effect was observed by Ziegler and co-workers.^[16] Now, the situation has changed dramatically,^[17] since many nickel catalysts have been developed for producing high molecular weight polyethylenes, such as α -diimine^[1,18–32] (Chart 1, I), salicylaldimine^[33–36] (Chart 1, II), pyridine-imine^[37–39] (Chart 1, III), 2-iminopyridine-*N*-oxide^[40] (Chart 1, IV) and α -iminoketone^[41] (Chart 1, V) nickel catalysts. Moreover, some phosphine-ligand-based nickel catalysts exhibit the capabilities of producing high molecular weight polyethylenes, including tri-1-adamantylphosphine^[42] (Chart 1, VI) and some SHOP (shell higher olefin process) type^[43–46] (Chart 1, VII) nickel catalysts.

To improve catalytic performances of catalysts, many efforts have been directed towards modifying ligand structures by introducing various substituents. Many systematic researches on either steric or electronic effects of substituents have been reported.^[1–3,9–15] For instance, the dicyclohexyl-

substituted phosphine-sulfonate nickel catalyst can only produce oligomers of ethylene ($M_n<10^3$ g·mol⁻¹) at 30 °C^[47] (Chart 1, VIII). In contrast, sterically bulky biaryl based phosphine-sulfonate nickel catalysts can generate high molecular weight polyethylenes at 25 °C (M_n up to 4.05×10^5 g·mol⁻¹)^[48–54] (Chart 1, IX). It was indicated that the sterically bulky substituent at the axial position with respect to the nickel center is essential, since the steric effect could suppress β -H elimination. However, most of these catalysts generated moderate molecular weight polyethylenes (M_n up to 1.03×10^4 g·mol⁻¹, typically $<10^4$ g·mol⁻¹) at 80 °C, making them not suitable for industrially used gas-phase ethylene polymerization conditions (80–100 °C). Jian and co-workers reported a series of asymmetrically menthyl/biaryl-substituted phosphine-sulfonate nickel catalysts.^[55] These catalysts can generate moderate molecular weight polyethylenes at 90 °C (M_n up to 8.8×10^3 g·mol⁻¹). It is possible that phosphine-sulfonate nickel catalysts bearing sterically even bulkier substitute might generate polyethylenes with higher molecular weight. However, the strategy based on endless exploration on substitute effects poses formidable challenges on ligand syntheses.

In this contribution, we wish to explore an alternative strategy by introducing a polymerizable moiety to the ligand structure. This way, a polymeric substituent could be generated *in situ* during polymerization and significantly alters ligand steric effects. A series of phosphine-sulfonate ligands bearing 2-, 3- and 4-vinylphenyl groups on the phosphorus

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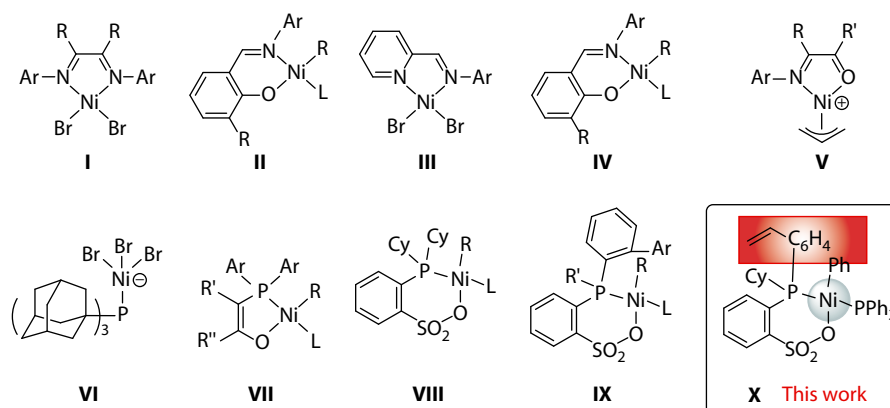


Chart 1 Selected nickel catalysts for ethylene polymerization.

atom (Chart 1, X) (Scheme 1) were designed, synthesized, characterized and investigated in Ni- and Pd-catalyzed ethylene polymerization. These phosphine-sulfonate nickel and palladium catalysts are well-defined single component catalysts. For the nickel catalysts, the dissociated ligand PPh_3 was used. For the palladium catalysts, the dissociated ligand DMSO (dimethylsulfoxide) was used. It is hypothesized that the copolymerization of the 2-vinyl group on ligand with ethylene can generate a bulky polymer substituent on ligand^[45,56–63] associated with enhanced steric effect. Consequently, the catalyst bearing 2-vinylphenyl group might result in increased molecular weight of polyethylene product compared with the catalysts bearing 3- or 4-vinylphenyl groups.

EXPERIMENTAL

General

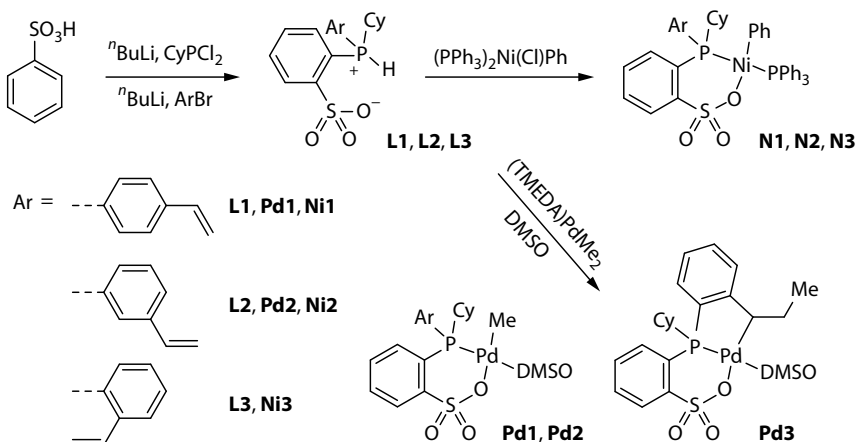
All experiments were carried out under dry nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^1H -, ^{13}C - and ^{31}P -NMR spectra were recorded on a Bruker AscendTm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^1H - and ^{13}C -NMR spectra were referenced to tetramethylsilane; the ^{31}P -NMR spectra were referenced to an external 85% H_3PO_4 solution. Coupling constants are in Hz. Elemental analysis was performed

by the Analytical Center of the University of Science and Technology of China. X-ray diffraction data were collected at 298 (2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071073$ nm). The molecular weights and molecular weight distributions of the polymers were determined using gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 150 °C using trichlorobenzene as a solvent. The calibration curve was constructed from polystyrene standards and was corrected for linear polyethylene by universal calibration using the Mark-Houwink parameters of Rudin: $K=5.90\times 10^{-2}$ $\text{cm}^3\cdot\text{g}^{-1}$ and $R=0.69$ for polyethylene. Dichloromethane, THF, and hexanes were purified by solvent purification systems.

Synthesis of Ligands and Catalysts

Synthesis of L1

At 0 °C, $n\text{BuLi}$ (2.5 $\text{g}\cdot\text{mol}^{-1}$, 16 mL, 40 mmol) was added slowly to a solution of benzenesulfonic acid (3.16 g, 20 mmol) in THF (50 mL). The suspension was stirred for 1 h and added to a solution of dichlorocyclohexyl-phosphine (3.68 mL, 20 mmol) in THF (30 mL) at -78 °C. The mixture was stirred for another 12 h at room temperature to yield lithium [chloro(cyclohexyl)-phosphino]benzenesulfonate. In a separate Schlenk flask, 4-bromostyrene (3.66 g, 20 mmol) was dissolved in dry THF (100 mL) under nitrogen and cooled to -78 °C. $n\text{BuLi}$ (2.5



Scheme 1 Generation of polyethylene substituent on the phosphine-sulfonate ligand.

g·mol⁻¹ in hexane, 8 mL, 20 mmol) was added dropwise. The resulting red solution was stirred for 1.0 h at -78 °C before the lithium [chloro(cyclohexyl)phosphino]benzenesulfonate was added dropwise. The mixture was stirred for another 24 h at room temperature. The volatiles were removed, and the residue was taken up in distilled water (150 mL). The mixture was acidified to pH ~2 with concentrated HCl/H₂O solution, and extracted three times with CH₂Cl₂ (total volume 250 mL). The extracts were combined, dried over MgSO₄, and concentrated under vacuum. The crude product was recrystallized from dichloromethane/ether at room temperature. The resulting white crystals were filtered and dried to give the desired ligand **L1** (4.56 g, 61%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 8.25–7.86 (m, 4H), 7.63 (s, 1H), 7.51 (s, 1H), 7.41 (s, 2H), 6.59 (s, 1H), 5.76 (d, *J*=16.9 Hz, 1H), 5.35 (d, *J*=8.8 Hz, 1H), 3.50 (br, 1H), 1.84 (br, 2H), 1.65 (d, *J*=19.3 Hz, 3H), 1.37 (d, *J*=34.9 Hz, 4H), 1.13 (br, 1H). ³¹P-NMR (162 MHz, CDCl₃, δ, ppm): 19.06 (s). ¹³C-NMR (101 MHz, CDCl₃, δ, ppm): 150.51 (d, *J*=7.2 Hz), 142.67 (s), 134.72 (s), 134.50 (d, *J*=10.3 Hz), 134.03 (s), 133.92 (s), 130.26 (d, *J*=12.5 Hz), 127.87 (d, *J*=8.4 Hz), 126.84 (d, *J*=13.3 Hz), 117.90 (s), 115.83 (s), 114.97 (s), 114.74 (s), 113.87 (s), 31.49 (d, *J*=48.1 Hz), 27.25 (s), 26.80 (s), 25.19 (d, *J*=6.4 Hz), 25.04 (d, *J*=5.9 Hz), 24.67 (s). ESI-MS (*m/z*): [M+H]⁺ Calcd. for C₂₀H₂₄O₃PS, 375.1178; Found: 375.1164.

Synthesis of **L2**

Similar procedure to the above was employed except 3-bromostyrene was used. **L2** was obtained as a light white solid (4.1 g, 55%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 8.29 (s, 1H), 7.92 (d, *J*=14.5 Hz, 1H), 7.88–7.65 (m, 4H), 7.54 (br, 2H), 6.69 (dd, *J*=17.4, 10.9 Hz, 1H), 5.83 (d, *J*=17.6 Hz, 1H), 5.38 (d, *J*=10.9 Hz, 1H), 3.39 (d, *J*=13.7 Hz, 1H), 1.95 (d, *J*=23.3 Hz, 2H), 1.87–1.71 (m, 3H), 1.43 (m, 3H), 1.24 (s, 2H). ³¹P-NMR (162 MHz, CDCl₃, δ, ppm): 20.74 (s). ESI-MS (*m/z*): [M+H]⁺ Calcd. for C₂₀H₂₄O₃PS, 375.1178; Found: 375.1166.

Synthesis of **L3**

Similar procedure to the above was employed except 2-bromostyrene was used. **L3** was obtained as a light white solid (5.8 g, 77%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 8.25 (s, 1H), 7.98 (br, 2H), 7.70 (s, 1H), 7.61 (br, 2H), 7.48 (s, 1H), 7.37 (s, 1H), 7.30 (dd, *J*=15.8, 11.4 Hz, 1H), 5.66 (d, *J*=16.7 Hz, 1H), 5.48 (d, *J*=10.5 Hz, 1H), 3.36 (d, *J*=10.2 Hz, 1H), 1.78 (s, 4H), 1.66 (s, 1H), 1.62–1.56 (m, 1H), 1.52 (d, *J*=10.4 Hz, 1H), 1.37 (s, 2H), 1.26–1.17 (m, 1H). ³¹P-NMR (162 MHz, CDCl₃, δ, ppm): 7.29 (s). ¹³C-NMR (101 MHz, CDCl₃, δ, ppm): 151.23 (d, *J*=7.5 Hz), 143.77 (d, *J*=7.2 Hz), 134.49 (d, *J*=14.0 Hz), 134.23 (s), 133.51 (d, *J*=8.8 Hz), 133.12 (d, *J*=9.5 Hz), 130.23 (d, *J*=12.5 Hz), 128.54 (d, *J*=7.7 Hz), 128.38 (s), 128.08 (d, *J*=9.9 Hz), 121.50 (s), 114.53 (d, *J*=83.1 Hz), 113.07 (d, *J*=87.5 Hz), 32.08 (d, *J*=47.6 Hz), 27.29 (d, *J*=31.1 Hz), 25.62 (d, *J*=30.0 Hz), 25.62 (s), 24.90 (s). ESI-MS (*m/z*): [M+H]⁺ Calcd. for C₂₀H₂₄O₃PS, 375.1178; Found: 375.1166.

Synthesis of **Pd1**

Ligand **L1** (200 mg, 0.53 mmol) was suspended in dioxane (3 mL). (TMEDA)PdMe₂ (134 mg, 0.53 mmol) was added at room temperature. After 5 min the evolution of gas stopped and the suspension turned clear. The solution was stirred for 2 h at room temperature. The resulting white precipitate was filtered, washed with diethyl ether and dried under reduced pressure. Then it was dispersed in 10 mL of DMSO at room temperature. The solvent was removed under reduced pressure at 70 °C. After

removal of DMSO under reduced pressure, the resulting solid was dispersed in diethyl ether, and isolated by filtration to yield a gray solid **Pd1** (203 mg, 67%). ¹H-NMR (400 MHz, d⁶-DMSO, δ, ppm): 7.96 (s, 1H), 7.78–7.70 (m, 2H), 7.58 (d, *J*=7.4 Hz, 2H), 7.52 (d, *J*=7.3 Hz, 1H), 7.45–7.40 (m, 1H), 7.32 (t, *J*=8.3 Hz, 1H), 6.75 (dd, *J*=17.0, 11.2 Hz, 1H), 5.93 (d, *J*=17.7 Hz, 1H), 5.36 (d, *J*=10.6 Hz, 1H), 2.82 (s, 1H), 2.54 (s, 6H, DMSO), 2.07 (s, 1H), 1.76 (s, 1H), 1.67 (s, 2H), 1.45 (br, 4H), 1.30 (s, 1H), 1.21 (s, 1H), 0.20 (s, 3H, Pd-Me). ³¹P-NMR (162 MHz, d⁶-DMSO, δ, ppm): 32.93 (s). ¹³C-NMR (101 MHz, d⁶-DMSO, δ, ppm): 149.43 (d, *J*=12.5 Hz), 139.15 (d, *J*=2.1 Hz), 135.71 (s), 134.33 (s), 132.89 (d, *J*=10.9 Hz), 130.98 (s), 130.35 (s), 130.20 (d, *J*=5.9 Hz), 129.84 (s), 127.28 (s), 127.18 (d, *J*=7.4 Hz), 126.87 (s), 126.48 (d, *J*=10.7 Hz), 116.72 (s), 40.43 (s, DMSO), 36.17 (d, *J*=30.6 Hz), 30.07 (d, *J*=3.5 Hz), 28.26 (s), 26.02 (d, *J*=21.0 Hz), 26.01 (d, *J*=5.9 Hz), 25.64 (s), -0.27 (s, Pd-Me). Anal. Calcd. for C₂₃H₃₁O₄PPdS₂: C, 48.21; H, 5.45. Found: C, 48.39; H, 5.19.

Synthesis of **Pd2**

Similar procedure was employed to catalyst **Pd1** except **L2** (200 mg, 0.53 mmol) was used. **Pd2** was obtained as a gray solid (221 mg, 73%). ¹H-NMR (400 MHz, d⁶-DMSO, δ, ppm): 7.96 (s, 1H), 7.80 (d, *J*=10.3 Hz, 1H), 7.69 (br, 1H), 7.61 (br, 1H), 7.54 (br, 1H), 7.47 (d, *J*=7.7 Hz, 2H), 7.38 (d, *J*=7.3 Hz, 1H), 6.88–6.71 (m, 1H), 5.89 (d, *J*=17.1 Hz, 1H), 5.34 (d, *J*=10.4 Hz, 1H), 2.91 (br, 1H), 2.54 (s, 6H, DMSO), 2.08 (br, 1H), 1.78 (br, 1H), 1.69 (br, 2H), 1.45 (br, 4H), 1.33 (br, 1H), 1.22 (br, 1H), 0.19 (s, 3H, Pd-Me). ³¹P-NMR (162 MHz, d⁶-DMSO, δ, ppm): 33.65 (s). ¹³C-NMR (101 MHz, d⁶-DMSO, δ, ppm): 149.43 (d, *J*=12.5 Hz), 137.55 (d, *J*=10.2 Hz), 135.87 (s), 134.27 (s), 132.12 (d, *J*=11.0 Hz), 131.63 (s), 131.02 (s), 130.27 (d, *J*=3.1 Hz), 130.18 (s), 129.21 (d, *J*=11.1 Hz), 127.87 (s), 127.17 (d, *J*=4.3 Hz), 126.77 (s), 115.92 (s), 40.43 (s, DMSO), 36.04 (d, *J*=30.8 Hz), 30.10 (d, *J*=2.8 Hz), 28.28 (s), 26.03 (d, *J*=6.1 Hz), 25.90 (d, *J*=4.5 Hz), 25.65 (s), -0.27 (s, Pd-Me). Anal. Calcd. for C₂₃H₃₁O₄PPdS₂: C, 48.21; H, 5.45. Found: C, 48.57; H, 5.59.

Synthesis of **Pd3**

Similar procedure was employed to catalyst **Pd1** except **L3** (200 mg, 0.53 mmol) was used. **Pd3** was obtained as a gray solid (201 mg, 66%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 8.33 (s, 1H), 7.75 (s, 2H), 7.55 (s, 1H), 7.41 (d, *J*=18.9 Hz, 4H), 4.33 (s, 1H, CH), 2.98 (s, 1H, PCH), 2.82 (s, 6H, DMSO), 2.16 (s, 1H), 1.96 (s, 2H, CH₂), 1.66 (s, 4H), 1.46–1.21 (m, 4H), 1.07 (s, 1H), 0.93 (s, 1H), 0.70 (s, 3H, CH₃). ³¹P-NMR (162 MHz, CDCl₃, δ, ppm): 58.99 (s). ¹³C-NMR (101 MHz, d⁶-DMSO, δ, ppm): 161.07 (d, *J*=31.6 Hz), 149.22 (d, *J*=13.6 Hz), 132.73 (s), 132.31 (s), 131.00 (s), 130.53 (s), 130.24 (s), 129.98 (d, *J*=6.4 Hz), 129.75 (s), 129.11 (d, *J*=8.2 Hz), 127.45 (s), 127.12 (d, *J*=6.0 Hz), 127.02 (s), 125.57 (d, *J*=41.3 Hz), 47.88 (d, *J*=5.8 Hz), 40.43 (s), 28.51 (d, *J*=3.0 Hz), 27.95 (d, *J*=2.8 Hz), 26.28 (s), 26.14 (d, *J*=3.8 Hz), 25.47 (s), 13.67 (d, *J*=2.8 Hz). Anal. Calcd. for C₂₃H₃₁O₄PPdS₂: C, 48.21; H, 5.45. Found: C, 48.51; H, 5.23.

Synthesis of **Ni1**

A suspension of **L1** (200 mg, 0.53 mmol) and Na₂CO₃ (169 mg, 1.53 mmol) in 15 mL of dichloromethane was stirred for 6 h at room temperature. *trans*-[(PPh₃)₂Ni(Cl)Ph] (368 mg, 0.53 mmol) was added in small portions. Dichloromethane was added until the volume of the solution reached 20 mL, and the reaction mixture was stirred for 24 h at room temperature. The resulting yellow-orange mixture was filtered over Celite and the volatiles

were removed under vacuum. Toluene (3 mL) was added to the orange residue to afford a slurry, then hexane (5 mL) was added and the mixture was stirred for 5 min. The precipitate was recovered by filtration, washed with hexane (3×10 mL) and dried for 20 h under dynamic vacuum to yield a yellow solid **Ni1** (245 mg, 60%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 8.11 (dd, *J*=7.3, 4.1 Hz, 1H), 7.48 (t, *J*=7.5 Hz, 2H), 7.40–7.32 (m, 12H), 7.29 (d, *J*=7.0 Hz, 2H), 7.23 (d, *J*=7.3 Hz, 4H), 7.03 (t, *J*=8.8 Hz, 3H), 6.80–6.71 (m, 1H), 6.59–6.51 (m, 2H), 6.25 (t, *J*=8.1 Hz, 1H), 5.87 (d, *J*=17.6 Hz, 1H), 5.79 (d, *J*=7.7 Hz, 1H), 5.39 (d, *J*=10.9 Hz, 1H), 3.23–3.13 (m, 1H), 1.93–1.78 (m, 2H), 1.61 (d, *J*=19.8 Hz, 2H), 1.47 (s, 1H), 1.29 (d, *J*=13.0 Hz, 1H), 1.16 (d, *J*=13.2 Hz, 1H), 1.05 (d, *J*=7.7 Hz, 3H). ³¹P-NMR (162 MHz, CDCl₃, δ, ppm): 17.16 (d, *J*=276.9 Hz), 4.07 (d, *J*=276.9 Hz). Anal. Calcd. for C₄₄H₄₂NiO₃P₂S: C, 68.50; H, 5.49. Found: C, 68.70; H, 5.64.

Synthesis of **Ni2**

Similar procedure was employed to catalyst **Ni1** except **L2** (200 mg, 0.53 mmol) was used. **Ni2** was obtained as a yellow powder (258 mg, 63%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 8.10 (s, 1H), 7.47 (s, 3H), 7.34 (d, *J*=8.7 Hz, 12H), 7.23 (d, *J*=8.1 Hz, 5H), 7.06 (s, 2H), 6.94 (s, 1H), 6.65 (dd, *J*=17.0, 11.1 Hz, 1H), 6.55 (s, 2H), 6.23 (s, 1H), 5.70 (dd, *J*=20.0, 12.5 Hz, 2H), 5.29 (d, *J*=10.6 Hz, 1H), 3.18 (s, 1H), 1.85 (d, *J*=19.2 Hz, 2H), 1.67–1.44 (m, 4H), 1.29 (d, *J*=11.5 Hz, 1H), 1.17 (d, *J*=9.8 Hz, 1H), 1.04 (s, 2H). ³¹P-NMR (162 MHz, CDCl₃, δ, ppm): 17.35 (d, *J*=276.1 Hz), 4.38 (d, *J*=276.1 Hz). ¹³C-NMR (101 MHz, CDCl₃, δ, ppm): 149.94 (d, *J*=13.0 Hz), 141.07 (s), 140.74 (s), 140.41 (s), 137.64 (s), 137.15 (d, *J*=9.1 Hz), 136.48 (d, *J*=30.8 Hz), 135.85 (s), 134.08 (d, *J*=10.7 Hz), 132.00 (d, *J*=7.9 Hz), 130.71 (s), 129.79 (s), 129.15 (d, *J*=5.4 Hz), 128.77 (s), 128.32 (s), 127.94 (d, *J*=9.5 Hz), 127.10 (d, *J*=6.1 Hz), 126.94 (s), 125.82 (d, *J*=12.1 Hz), 124.81 (d, *J*=26.9 Hz), 121.79 (s), 115.00 (s), 32.48 (d, *J*=25.6 Hz), 29.56 (d, *J*=6.2 Hz), 27.27 (d, *J*=7.7 Hz), 27.08 (d, *J*=17.5 Hz), 26.83 (d, *J*=7.5 Hz), 25.73 (s). Anal. Calcd. for C₄₄H₄₂NiO₃P₂S: C, 68.50; H, 5.49. Found: C, 68.34; H, 5.16.

Synthesis of **Ni3**

Similar procedure was employed to catalyst **Ni1** except **L3** (200 mg, 0.53 mmol) was used. **Ni3** was obtained as a yellow powder (267 mg, 65%). ³¹P-NMR (162 MHz, CDCl₃, δ, ppm): 16.74 (d, *J*=274.8 Hz), 1.03 (d, *J*=274.8 Hz). Anal. Calcd. for C₄₄H₄₂NiO₃P₂S: C, 68.50; H, 5.49. Found: C, 69.10; H, 5.94.

Procedure for Ethylene Polymerization

In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with 20 mL of toluene and a magnetic stir bar under an inert atmosphere. The vessel was pressurized with ethylene gas with stirring. Then catalyst (in 1 mL of CH₂Cl₂) was injected to initiate polymerization and stirred continuously for the desired time. The polymerization was quenched by adding ethanol (30 mL) and the polymer was precipitated and dried overnight in vacuum at 50 °C.

RESULTS AND DISCUSSION

Synthesis and Characterization of Ligands and Pd, Ni Complexes

The phosphine-sulfonate ligands (**L1**, **L2** and **L3**) bearing 2-, 3- and 4-vinylphenyl groups were prepared through the sequential reactions of CyPCl₂ with lithiated benzenesulfonic acid and lithiated bromostyrenes (Scheme 1). The syntheses of these

ligands were easier than those of the previously reported phosphine-sulfonate ligands bearing bulky biaryl or menthyl groups, since the synthetic routes were shorter and all the starting materials, including benzenesulfonic acid, dichlorocyclohexylphosphine, bromostyrenes and butyl lithium, are commercially available.^[48–54] The nickel complexes (**Ni1**, **Ni2** and **Ni3**) were synthesized through the reactions between the ligands and *trans*-[(PPh₃)₂Ni(Cl)Ph].^[52] The reactions of the phosphine-sulfonate ligands with (TMEDA)PdMe₂ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) and DMSO (dimethyl sulfoxide)^[50] resulted in the palladium complexes **Pd1**, **Pd2** and **Pd3**. The ligands were characterized by NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). The nickel and palladium complexes were characterized by NMR spectroscopy and elemental analysis. The structure of the complex **Pd3** bearing 2-vinylphenyl on the phosphorus atom showed the 2,1-insertion for the 2-vinyl group, indicating the 2-vinyl group would be a polymerizable moiety during coordination-insertion polymerization. The nickel complex **Ni1** was characterized by X-ray crystallographic analysis (Fig. 1) (CCDC number: 1528274). The observed bond lengths are typical for phosphine-sulfonate nickel complexes.^[47–54] The Ni center exhibited square planar geometry.

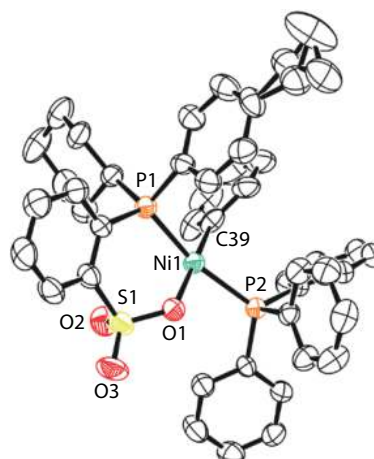


Fig. 1 Molecular structure of **Ni1** with 30% probability level, and H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ni1–P1 = 2.197(1), Ni1–P2 = 2.237(1), Ni1–O1 = 1.963(3), Ni1–C39 = 1.890(5). The nickel center exhibits a square-planar geometry with P1–Ni1–C39 angle of 88.32(13), P1–Ni1–O1 angle of 92.04(8), P2–Ni1–O1 angle of 89.37(8), and P2–Ni1–C39 angle of 90.51(13).

Ethylene Polymerization

The results of the nickel and palladium catalyzed ethylene polymerizations are summarized in Table 1. The phosphine-sulfonate nickel and palladium catalysts are single component catalysts. They can mediate ethylene polymerizations in the absence of any co-catalysts or scavengers.^[47–55] Catalysts **Pd1** and **Pd2** exhibited high catalytic activities in ethylene polymerization (activity >10⁵ g·mol_{Pd}^{−1}·h^{−1}), generating high molecular weight polyethylene (*M_n* up to 3.35×10⁴ g·mol^{−1}) (Table 1, entries 1 and 2). The above asymmetrically cyclohexyl/vinylphenyl phosphine-sulfonate based Pd catalysts resulted in higher molecular weights of polyethylene compared with

Table 1 Ethylene polymerization catalyzed by styrene-containing phosphine-sulfonate nickel and palladium catalysts.^a

Ent.	Cat.	<i>T</i> (°C)	Yield (g)	Act. ^b	<i>T_m</i> ^c (°C)	<i>M_n</i> ^d × 10 ⁻⁴	<i>M_w</i> / <i>M_n</i> ^d
1	Pd1	80	2.11	2.1	135	3.35	3.2
2	Pd2	80	3.08	3.1	135	1.79	4.1
3	Pd3	80	Trace	—	—	—	—
4	Ni1	25	0.55	0.55	129	16.63	3.8
5	Ni2	25	0.10	0.10	76	12.39	1.6
6	Ni3	25	0.07	0.07	136	25.11	3.0
7	Ni1	80	1.02	1.0	118	0.12	1.5
8	Ni2	80	0.25	0.25	70	0.11	1.4
9	Ni3	80	3.43	3.4	132	3.69	3.7

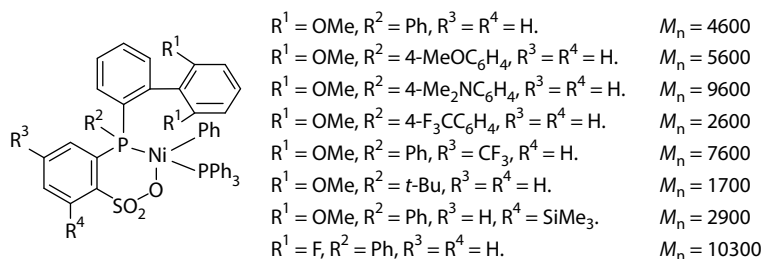
^a Polymerization conditions: toluene=20 mL, CH₂Cl₂=1 mL, ethylene=0.8 MPa, time=1 h, 10 μmol of catalysts. ^b Activity is in unit of 10⁵ g·mol⁻¹·h⁻¹. ^c Melting temperature determined by DSC. ^d *M_n* and *M_w*/*M_n* determined by GPC using polystyrene standards.

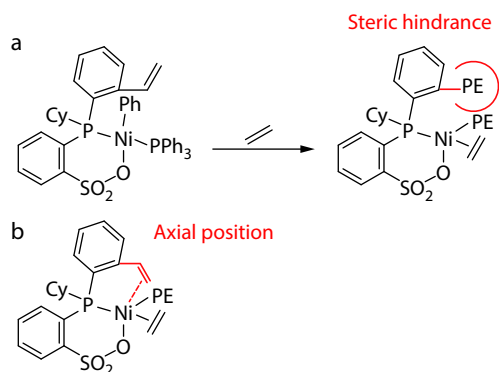
symmetrical dicyclohexyl- or diphenyl-substituted phosphine-sulfonate based Pd catalysts.^[64] Catalyst **Pd1** resulted in higher molecular weight of polyethylene compared with **Pd2**, which could be due to the electronic effects. 3-Vinyl group is more electron-withdrawing than 4-vinyl group (σ_m of vinyl is 0.06 and σ_p of vinyl is -0.04),^[65] resulting in reduced electron density from the palladium center associated with decreased molecular weight of polyethylene.^[50,66–68] Catalyst **Pd3** showed no catalytic activity in ethylene polymerization (Table 1, entry 3), which could be due to the formation of stable five-membered ring in the structure of **Pd3**.

The nickel catalysts **Ni1**, **Ni2** and **Ni3** exhibited low catalytic activities in ethylene polymerization at room temperature (Table 1, entries 4–6), generating high molecular weight polyethylene (*M_n* up to 2.51×10⁵ g·mol⁻¹). Similar to **Pd1** and **Pd2**, catalyst **Ni1** resulted in higher molecular weight of polyethylene compared with **Ni2**, which could be due to the electronic effects (for vinyl, $\sigma_m > \sigma_p$).^[50,65–68] Catalyst **Ni2** resulted in low-melting branched polyethylenes (Table 1, entries 5 and 8). For the formation of the branched polyethylenes, the exact mechanism is currently unknown. Generally, the electronically unsymmetrical nature of phosphine-sulfonate ligands was believed to inhibit β-H (X) elimination, resulting in the formation of highly linear polyethylenes.^[14] 3-Vinyl group is a more electron-withdrawing group compared with 4-vinyl group (σ_m of vinyl is 0.06 and σ_p of vinyl is -0.04).^[65] Consequently, the 3-vinyl group may alleviate the electronic unsymmetry in the ligand, resulting in the formation of branched polyethylene.^[52] The catalytic activities of the nickel catalysts increased significantly with increasing temperat-

ure, while the polyethylene molecular weight decreased (Table 1, entries 7–9). Catalysts **Ni1** and **Ni2** showed moderate catalytic activities and generated low molecular weight polyethylene products (*M_n*<1500 g·mol⁻¹) at 80 °C (Table 1, entries 7 and 8), indicating the β-H elimination was accelerated significantly with increasing temperature. Remarkably, catalyst **Ni3** bearing 2-vinylphenyl exhibited high catalytic activity (activity=3.4×10⁵ g·mol⁻¹·h⁻¹) and resulted in much higher molecular weight of polyethylene (*M_n*=3.69×10⁴ g·mol⁻¹, *M_w*=1.38×10⁵ g·mol⁻¹) (Table 1, entry 9) compared with **Ni1** and **Ni2**, indicating it is potentially suitable for industrially used gas-phase ethylene polymerization conditions (80–100 °C).^[21,69] The polyethylenes' molecular weights declined more than 2 orders of magnitude for **Ni1** and **Ni2** with increasing temperature. In contrast, the polyethylenes molecular weight was decreased less than 7 times for **Ni3** (Table 1, 7 versus 4, 8 versus 5, 9 versus 6), demonstrating the great thermal stability of **Ni3**.

We do not currently fully understand the effect of the 2-vinyl group in this system. Nevertheless, there are several possible explanations on the good catalytic performance of **Ni3**. First, the 2-vinyl group is more sterically hindered compared with 3- and 4-vinyl groups. However, **Ni3** resulted in much higher molecular weight compared with the phosphine-sulfonate nickel catalysts bearing bulkier biaryl groups (*M_n* up to 1.03×10⁴ g·mol⁻¹, typically <10⁴ g·mol⁻¹) at 80 °C (Scheme 2).^[48–54] Therefore, the superior catalytic performance of **Ni3** cannot solely be explained by the steric hindrance of the 2-vinyl group. Second, the 2-vinyl group on ligand could be copolymerized with ethylene via nickel catalyzed polymerization, resulting in the formation of a bulky polymer substituent (Scheme 3a) associated with the enhanced steric effect. This was reported by literature evidences that some nickel complexes can efficiently catalyze copolymerization of ethylene with styrene.^[57–59] As a result, **Ni3** can generate high molecular weight polyethylene at 80 °C, since the sterically bulky polymer substituent at the axial position with respect to the nickel center suppressed β-H elimination during ethylene polymerization. The significantly increased PDI value also supported this hypothesis (Table 1, entry 9). Third, the 2-vinyl substituent at the axial position might form a secondary interaction with the nickel center (Scheme 3b), preventing ethylene coordination and subsequently chain transfer to monomer.^[2,3,10,50,70–72]

**Scheme 2** Selected previously reported phosphine-sulfonate nickel catalysts bearing bulkier biaryl groups and the *M_n* values of the polyethylenes generated by these catalysts at 80 °C.^[48–54]



Scheme 3 (a) Generation of the polyethylene substituent on the phosphine-sulfonate ligand. (b) Formation of the secondary coordination bond between the nickel center and the 2-vinyl substituent at the axial position. (PE = polyethylene chain).

CONCLUSIONS

In summary, a series of phosphine-sulfonate ligands containing styrene moieties (**L1**, **L2** and **L3**) and the corresponding nickel (**Ni1**, **Ni2** and **Ni3**) and palladium (**Pd1**, **Pd2** and **Pd3**) catalysts have been synthesized, characterized and investigated in ethylene polymerization. The syntheses of the ligands were easier than the traditional phosphine-sulfonate ligands bearing bulky biaryl or menthyl groups. Catalysts **Ni1** and **Pd1** bearing 4-vinyl group led to polyethylenes with higher molecular weights than those from **Ni2** and **Pd2** bearing 3-vinyl group, which could be due to the electronic effects (for vinyl, $\sigma_m > \sigma_p$). The more electron-withdrawing 3-vinyl group resulted in reduced electron density from the metal center, resulting in decreased molecular weight of polyethylene. **Pd3** bearing 2-vinylphenyl showed 2,1-insertion for the 2-vinyl group, indicating that the 2-vinyl group was a polymerizable moiety during coordination-insertion polymerization. Catalyst **Pd3** possesses no catalytic activity in ethylene polymerization, which could be due to the formation of the stable five-membered ring in the structure of **Pd3**. Catalyst **Ni3** bearing 2-vinylphenyl resulted in higher activity and much higher polyethylene molecular weight ($M_n = 3.69 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$, $M_w = 1.38 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$) compared with **Ni1**, **Ni2** as well as previously reported nickel catalysts bearing bulky biaryl groups (M_n up to $1.03 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$, typically $< 10^4 \text{ g} \cdot \text{mol}^{-1}$) at 80 °C.^[48–54] Some possible explanations on the superior catalytic performance of **Ni3** have been discussed. It is envisaged that vinyl-containing ligands will be applicable to other catalytic systems for olefin polymerization and other types of organic transformations.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2509-z>.

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