Synthesis of Anionic Methylpalladium Complexes with Phosphine-Sulfonate Ligands and Their Activities for Olefin Polymerization

Takuya Kochi, Kenji Yoshimura and Kyoko Nozaki*

Experimental Section

All manipulations were carried out using the standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11. ^{1}H (500 MHz) and ^{31}P-{1H} NMR (202 MHz) spectra were recorded on a JEOL JNM-ECP-500 spectrometer. Elemental analysis was performed by the Microanalytical Laboratory, Department of Chemistry, Faculty of Science, the University of Tokyo. Gel permeation chromatography (GPC) analyses were carried out with a GL Sciences instrument (model PU610 high-performance-liquid-chromatography pump, 556 liquid chromatography column oven, and RI 704 refractive-index detector) equipped with an SIC GPC board and two columns (Shodex KF-804L). The GPC columns were eluted with tetrahydrofuran (THF) at 40 °C at 1 mL/min. Dichloromethane, toluene and hexanes were purified by the method of Pangborn *et al.*[1] PdMeCl(cod),[2] 2-(diphenylphosphino)benzenesulfonic acid[3] and 2-{di(2-methoxyphenyl)phosphino}benzenesulfonic acid[4] were prepared according to literature procedures. Diisopropylethylamine and triethylamine were distilled from CaH_2.

[^{i}Pr$_2$EtNH][(o-Ph$_2$PC$_6$H$_4$SO$_3$)PdMeCl] (2a)

To a solution of 685 mg of 2-(diphenylphosphino)benzenesulfonic acid (2.00 mmol) in 10 mL of CH_2Cl_2 was added 1.29 g of diisopropylethylamine (9.97 mmol) and the resulting solution was stirred for 10 min at rt. 530 mg of [PdMeCl(cod)] (2.00 mmol) was then added to the solution and the mixture was stirred for 1 h at rt. The resulting mixture was filtered and added dropwise to 60 mL of hexane. The white powder was collected by filtration and washed with hexane to afford palladium complex **2a** (1.18 g, 1.88 mmol, 94% yield) (Found: C, 51.46; H, 5.94; N, 2.06. $C_{27}H_{37}NClO_3PPdS$ requires C, 51.60; H, 5.93; N, 2.23%). δ_H(CDCl$_3$) 0.64 (3 H, d, J_{HH} = 3.0 Hz), 1.44 (6 H, d, J_{HH} = 6.6 Hz), 1.53 (3 H, t, J_{HH} = 7.3 Hz), 1.54 (6 H, d, J_{HH} = 6.6 Hz), 3.29 (2 H, dq, J_{HH} = 5.0, 7.3 Hz), 3.94 (2 H, dqq, J_{HH} = 3.9, 6.6, 6.6 Hz), 6.97 (1 H, ddd, J_{HH} = 9.8, 7.6, 1.1 Hz), 7.32 (1 H, dddd, J_{HH} = 7.6, 7.6, 1.1, 1.1 Hz), 7.37-7.40 (4 H, m), 7.42-7.45 (2 H, m), 7.48 (1 H, dddd, J_{HH} = 7.6, 7.6, 1.6, 1.1 Hz), 7.53-7.57 (4 H, m), 8.15 (1 H, ddd, J_{HH} = 7.6, 4.3, 1.1 Hz), 8.54 (1 H, br s). δ_P(CDCl$_3$) 27.6.

[Et$_3$NH][(o-Ph$_2$PC$_6$H$_4$SO$_3$)PdMeCl] (2a')

To a solution of 68 mg of 2-(diphenylphosphino)benzenesulfonic acid (0.199 mmol) in 1 mL of CH_2Cl_2 was added 101 mg of triethylamine (0.998 mmol) and the resulting solution was stirred for 10 min at rt. 53 mg of [PdMeCl(cod)] (0.200 mmol) was then added to the solution and

the mixture was stirred for 1 h at rt. The resulting mixture was filtered and added dropwise to 20 mL of hexane. The white powder was collected by filtration and washed with hexane to afford palladium complex **2a'** (106 mg, 0.177 mmol, 89% yield) (Found: C, 49.84; H, 5.62; N, 2.15. $C_{25}H_{33}NClO_3PPdS$ requires C, 50.01; H, 5.54; N, 2.33%). δ_H(CDCl$_3$) 0.65 (3 H, d, J_{HH} = 3.2 Hz), 1.38 (9 H, t, J_{HH} = 7.3 Hz), 3.34 (6 H, dq, J_{HH} = 4.6, 7.3 Hz), 6.98 (1 H, m), 7.31-7.57 (12 H, m), 8.12-8.15 (1 H, m), 8.77 (1 H, br s). δ_P(CDCl$_3$) 27.6.

[^{i}Pr$_2$EtNH][{(o-(o-MeOC$_6$H$_4$)$_2$P)C$_6$H$_4$SO$_3$}PdMeCl] (2b)

To a solution of 804 mg of 2-{di(2-methoxyphenyl)phosphino}benzenesulfonic acid (2.00 mmol) in 10 mL of CH$_2$Cl$_2$ was added 1.29 g of diisopropylethylamine (9.97 mmol) and the resulting solution was stirred for 10 min at rt. 530 mg of [PdMeCl(cod)] (2.00 mmol) was then added to the solution and the mixture was stirred for 1 h at rt. The resulting mixture was filtered and added dropwise to 60 mL of hexane. The white powder was collected by filtration and washed with hexane to afford palladium complex **2b** (1.26 g, 1.83 mmol, 92% yield). δ_H(CDCl$_3$) 0.33 (3 H, d, J_{HH} = 3.0 Hz), 1.43 (6 H, d, J_{HH} = 6.6 Hz), 1.53 (3 H, t, J_{HH} = 7.3 Hz), 1.54 (6 H, d, J_{HH} = 6.6 Hz), 3.29 (2 H, dq, J_{HH} = 2.5, 7.3 Hz), 3.96 (2 H, dqq, J_{HH} = 3.4, 6.6, 6.6 Hz), 6.86 (2 H, dd, J_{HH} = 7.6, 5.0 Hz), 6.98 (2 H, dd, J_{HH} = 7.6, 7.6 Hz), 7.23 (1 H, dddd, J_{HH} = 7.6, 7.6, 1.1, 1.1 Hz), 7.32 (1 H, ddd, J_{HH} = 11.2, 7.6, 1.1 Hz), 7.39 (1 H, dddd, J_{HH} = 7.6, 7.6, 1.6, 1.1 Hz), 7.45 (2 H, dd, J_{HH} = 7.6, 7.6 Hz), 7.72 (2 H, br s), 8.06 (1 H, ddd, J_{HH} = 7.6, 4.7, 1.1 Hz), 8.72 (1 H, br s). δ_P(CDCl$_3$) 22.1. The solid form of compound **2b** absorbs one water molecule per one palladium complex under air, and elemental analysis of **2b** was performed with this water adduct. The amount of water absorbed was also confirmed by ^{1}H NMR spectroscopy. (Found: C, 49.27; H, 5.98; N, 2.01. $C_{29}H_{41}NClO_5PPdS$ requires C, 49.30; H, 6.13; N, 1.98%).

Copolymerization of Ethylene with Methyl Acrylate

To a 50 mL-autoclave containing complex 2 (0.01 mmol), additive and a stir bar was transferred a mixture of 2.5 mL of methyl acrylate and 2.5 mL of toluene under argon atomosphere. The mixture was stirred at rt for 10 min and charged with ethylene. The autoclave was heated and the mixture was stirred. After the reaction, the cooled contents of the autoclave were transferred to a 100 mL round-bottom flask with a minimum amount of CH$_2$Cl$_2$ and volatile materials were removed on a rotary evaporator. The remaining solid was dried under vacuum to afford the copolymer, which was analyzed without further purification. The degree of methyl acrylate incorporation into the copolymer was estimated by ^{1}H NMR spectroscopy.

References
1. A. B. Panghorn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
2. R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen and K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769.

3. *Eur. Pat.*, 0 280 380, 1988.
4. E. Drent, R. van Dijk, R. van Ginkel, B. van Oort, and R. I. Pugh, *Chem. Commun.*, 2002, 964.

X-ray Crystallography

Data Collection

A red-orange block crystal of $C_{25}H_{33}ClNO_3PPdS$ having approximate dimensions of 0.50 x 0.30 x 0.05 mm was mounted in mineral oil and transferred to the cold gas stream of the diffractometer. All measurements were made on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation.

Structure Solution and Refinement

The structure was solved by direct methods (SIR97)[1] and expanded using Fourier techniques (SHELXL-97)[2]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. The final cycle of full-matrix least-squares refinement[3] on F was based on 14896 observed reflections (I > 2.00σ(I)) and 302 variable parameters and converged with unweighted and weighted agreement factors of:

$$R = \Sigma \ ||Fo| - |Fc|| \ / \ \Sigma \ |Fo| = 0.0436$$

$$R_W = \{\Sigma[w \ (F_o{}^2 - F_c{}^2)^2] \ / \ \Sigma[w(F_o{}^2)^2]\}^{1/2} = 0.1192$$

The maximum and minimum peaks on the final difference Fourier map corresponded to 2.660 and -0.600 e$^-$/Å^3, respectively.

References

1. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G.Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115.
2. G. M. Sheldrick, *Acta Cryst. A*, 1990, **46**, 467.
3. Least Squares function minimized:
     $\Sigma w(F_o{}^2 - F_c{}^2)^2$