Supporting Information

Synthesis and Styrene Polymerisation Catalysis of η^5- and η^1-Pyrrolyl-Ligated Cationic Rare Earth Metal Aminobenzyl Complexes

Masayoshi Nishiura, Tomohiro Mashiko, and Zhaomin Hou

Organometallic Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198 Japan

Experimental Section:

General Methods. All manipulations of air- and moisture-sensitive compounds were performed under an argon atmosphere by use of standard Schlenk techniques or nitrogen atmosphere in an Mbraun glovebox. Argon (Takachiho Chemical Industrial Co., Ltd.) was purified by being passed through a Dryclean column (4 A molecular sieves, Nikka Seiko Co.) and a Gasclean CC-XR column (Nikka Seiko Co.). Anhydrous THF, hexane, benzene, diethyl ether, and toluene were purified by use of a SPS-800 solvent purification system (Mbraun), and further dried over fresh Na chips in the glovebox. Styrene was purchased from Junsei Chem, dried over calcium hydride, vacuum-transferred, and degassed by two freeze-pump-thaw cycles. $[Ph_3C][B(C_6F_5)_4]$ were purchased from Tosoh Finechem Corporation and used without purification. $Sc(CH_2C_6H_4NMe_2\text{-}o)_3$ was prepared according to literature methods.[1a] 2,5-*t*-$Bu_2C_4H_2NH$ were prepared according to literature methods.[2] Tetramethylpyrrole was purchased from Alfa Aesar, and used as received. Deuterated solvents chlorobenzene-d_5 (99 atom% D), benzene-d_6 (99.6 atom% D), 1,1,2,2-tetrachloroethane (99.6 atom% D), and tetrahydrofuran-d_8 (99.5 atom% D) were obtained from Cambridge Isotope.

Samples of rare earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes (Wilmad 528-JY). NMR (^{1}H, ^{11}B, ^{13}C{1H}, ^{19}F) spectra were recorded on a JNM-ECA 600 spectrometer (FT, 193 MHz for ^{11}B, 565 MHz for ^{19}F), on a JEOL-AL400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C{^{1}H}), a JEOL JNM-AL300 spectrometer (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C{^{1}H}), or a JEOL JNM-EX270 (FT, 270 MHz for ^{1}H; 67.5 MHz for ^{13}C{^{1}H}). Elemental analyses were performed on a MICRO CORDER JM10 apparatus (J-SCIENCE LAB Co.). In order to suppress the formation of inert carbide species, an appropriate amount (8–12 mg) of CuO (copper oxide) was added in the combustion analyses. The molecular weight and the molecular weight distribution of the polymer samples were determined at 145 °C by gel permeation chromatography on a TOSOH HLC-8121 GPC equipped with a refractive index detector. 1,2-dichlorobenzene was employed as an eluent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

$Sc(CH_2C_6H_4NMe_2\text{-}o)_3$.[1a] ^{1}H NMR ($C_6D_6$, 22 °C): 1.64 (s, 6H, CH_2), 2.27 (s, 18H, NMe_2), 6.76–6.79 (m, 6H, aryl), 6.93–7.00 (m, 6H, aryl). ^{13}C NMR (C_6D_6, 22 °C): 45.4 (NMe_2), 48.7 (CH_2), 118.3, 120.3, 127.0, 129.7, 143.4, 143.7 (aromatics).

$Y(CH_2C_6H_4NMe_2\text{-}o)_3$. This compound was prepared by a modified literature procedure.[1b] $LiCH_2C_6H_4NMe_2$-*o* instead of $KCH_2C_6H_4NMe_2$-*o* was used here. Anhydrous yttrium chloride (976 mg, 5 mmol) was suspended in 20 mL of THF. A THF solution (20 mL) of $LiCH_2C_6H_4NMe_2$-*o* (2.117 g, 15 mmol) was slowly added at room temperature. After stirring for 30 min, the solvent was removed under reduced pressure. The residue was dissolved in 30 mL of toluene and filtered to remove the lithium salt. The filtrate was concentrated and cooled down to –30 °C to give $Y(CH_2C_6H_4NMe_2\text{-}o)_3$ as yellow cubic crystals (1.843 g, 75%). ^{1}H NMR (C_6D_6, 25 °C): δ 1.63 (s, 6H, CH_2), 2.11 (s, 18H, NMe_2), 6.66 (t, J = 6.6 Hz, 3H, aryl), 6.83 (d, J = 8.1 Hz, 3H, aryl), 7.00 (t, J = 8.1 Hz, 3H, aryl), 7.11 (d, J = 6.6 Hz, 3H, aryl).

$La(CH_2C_6H_4NMe_2\text{-}o)_3$. This compound was prepared by a modified literature procedure.[1b] $LaBr_3$ instead of $LaCl_3$ was used here. 10 mL of THF was added to $LaBr_3$ (900 mg, 2.377 mmol) at room temperature in a Schlenk tube with a Teflon cock. This tube was taken outside and was heated at 70 °C for 2 h. After cooling down to room temperature, a THF solution (10 mL) of $KCH_2C_6H_4NMe_2$-*o* (1.236 g, 7.131 mmol) was added to a THF suspension of lanthanum bromide at room temperature in the glove box. After stirring for 30 min, the solvent was removed under reduced pressure to give an oily residue which was dissolved in 20 mL of toluene and filtered to remove the potassium salt. The filtrate was concentrated and cooled down to –30 °C to give yellow cubic crystals (yield, 1.125 g, 87%). ^{1}H NMR (C_4D_8O, 25 °C): δ 1.58 (s, 6H, CH_2),

2.34 (s, 18H, NMe_2), 6.42 (t, J = 7.5 Hz, 3H, aryl), 6.67 (d, J = 8.1 Hz, 3H, aryl), 6.82 (t, J = 7.5 Hz, 3H, aryl), 7.04 (d, J = 8.1 Hz, 3H, aryl).

2,5-*t*-$Bu_2C_4H_2NH$.[2]
^{1}H NMR (300 MHz, C_4D_8O, 27 °C): δ 1.24 (s, 18H, *t*-Bu), 5.57 (d, J_{H-H} = 2.4 Hz, 2H, pyrrolyl), 8.78 (br s, 1H, NH). ^{13}C NMR (75.45 MHz, C_4D_8O, 27 °C): δ 30.9 (*t*-Bu), 32.0 (*t*-Bu ipso), 102.0 (3,4-pyr), 140.7 (2,5-pyr).

2,3,4,5-Me_4C_4NH.
^{1}H NMR (400 MHz, C_4D_8O, 26 °C): δ 1.83 (s, 6H, Me), 2.03 (s, 6H, Me), 8.70 (br s, 1H, NH). ^{13}C NMR (100 MHz, C_4D_8O, 26 °C): δ 10.0 (Me_4C_4N), 11.1 (Me_4C_4N), 113.0 (3,4-pyr), 120.4 (2,5-pyr).

(2,5-*t*-$Bu_2C_4H_2N$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (1).
^{1}H NMR (270 MHz, C_6D_6, 24 °C): δ 1.37 (s, 18H, *t*-Bu), 1.60 (s, 4H, CH_2), 2.43 (s, 12H, NMe_2), 5.77 (s, 2H, *t*-$Bu_2C_4H_2N$), 6.72 (d, J = 7.8 Hz, 2H, aryl), 6.81 (t, J = 6.2 Hz, 2H, aryl), 6.93-7.01 (m, 4H, aryl). ^{13}C NMR (67.8 MHz, C_6D_6, 24 °C): δ 31.0 (*t*-Bu), 35.5 (*t*-Bu ipso), 47.8 (CH_2), 48.1 (NMe_2), 109.9 (3,4-pyr), 117.1 (aryl), 121.5 (aryl), 126.7 (aryl), 130.4 (aryl), 144.4 (aryl), 147.7 (aryl), 159.2 (2,5-pyr). ^{13}C NMR (75.45 MHz, C_4D_8O, 27 °C): δ 31.2 (*t*-Bu), 36.0 (*t*-Bu ipso), 48.1 (CH_2), 48.7 (NMe_2), 110.7 (3,4-pyrrolyl ring carbons), 117.7 (aryl), 121.9 (aryl), 126.9 (aryl), 130.8 (aryl), 145.0 (aryl), 148.5 (aryl), 159.6 (2,5-pyrrolyl ring carbons). Anal. Calcd. for $C_{30}H_{44}N_3Sc$: C 73.29, H 9.02, N 8.55. Found: C 73.32, H 8.88, N 8.41.

(2,5-*t*-$Bu_2C_4H_2N$)Y($CH_2C_6H_4NMe_2$-*o*)$_2$ (2).
^{1}H NMR (270 MHz, C_6D_6, 22 °C): δ 1.42 (br s, 18H, *t*-Bu), 1.63 (br s, 4H, CH_2), 2.30 (br s, 12H, NMe_2), 5.77 (br s, 2H, *t*-$Bu_2C_4H_2N$), 6.64-6.75 (m, 4H, aryl), 6.86-7.00 (m, 4H, aryl). ^{13}C NMR (67.8 MHz, C_6D_6, 50 °C): δ 31.4 (*t*-Bu), 35.0 (*t*-Bu ipso), 44.2 (d, J_{Y-C} = 33.4 Hz, CH_2), 46.4 (NMe_2), 109.4 (3,4-pyrrolyl ring carbons), 118.3 (aryl), 120.3 (aryl), 127.3 (aryl), 130.4 (aryl), 142.4 (aryl), 143.5 (aryl), 158.4 (2,5-pyrrolyl ring carbons). Anal. Calcd. for $C_{30}H_{44}N_3Y$: C 67.27, H 8.28, N 7.85, Found: C 67.59, H 8.33, N 7.86.

(2,5-*t*-$Bu_2C_4H_2N$)La($CH_2C_6H_4NMe_2$-*o*)$_2$ (3).
^{1}H NMR (270 MHz, C_6D_6, 23 °C): δ 1.45 (s, 18H, *t*-Bu), 1.72 (s, 4H, CH_2), 2.16 (s, 12H, NMe_2), 5.79 (s, 2H, *t*-$Bu_2C_4H_2N$), 6.66 (t, J = 6.8 Hz, 2H, aryl), 6.77 (d, J = 8.4 Hz, 2H, aryl), 6.87 (d, J = 7.8 Hz, 2H, aryl), 6.96 (d, J = 6.8 Hz, 2H, aryl). ^{13}C NMR (67.8 MHz, C_6D_6, 24 °C): δ 31.3 (*t*-Bu), 34.2 (*t*-Bu ipso), 43.5 (CH_2), 57.4 (NMe_2), 111.3 (3,4-pyrrolyl ring carbons), 118.2 (aryl), 121.0 (aryl), 129.4 (aryl), 135.4 (aryl), 141.9 (aryl), 157.7 (2,5-pyrrolyl ring carbons). One of the aromatic carbons was not identified due to overlapping. Anal. Calcd. for $C_{30}H_{44}N_3La$: C 61.53, H 7.57, N 7.18, Found: C 61.47, H 7.70, N 7.10.

(2,3,4,5-Me_4C_4N)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (4).
^{1}H NMR (400 MHz, C_6D_6, 24 °C): δ 1.55 (br s, 2H, CH_2), 1.65 (s, 6H, NC_4Me_4), 2.15 (s, 6H, NC_4Me_4), 2.45 (s, 12H, NMe_2), 6.75 (d, J = 8.0 Hz, 2H, aryl), 6.86 (t, J = 6.4 Hz, 2H, aryl), 6.99-7.05 (m, 4H, aryl). ^{1}H NMR (400 MHz, C_6D_6, 50 °C): δ 1.55 (s, 2H, CH_2), 1.70 (s, 6H, NC_4Me_4), 2.14 (s, 6H, NC_4Me_4), 2.48 (s, 12H, NMe_2), 6.77 (d, J = 8.0 Hz, 2H, aryl), 6.85 (t, J = 6.8 Hz, 2H, aryl), 6.94-7.02 (m, 4H, aryl). ^{13}C NMR (100 MHz, C_4D_8O, 26 °C): δ 10.1 (NC_4Me_4), 14.6 (NC_4Me_4), 46.8 (NMe_2), 49.4 (CH_2), 118.7 (aryl), 119.3 (3,4-pyrrolyl ring carbons), 122.2 (aryl), 127.3 (aryl), 130.8 (aryl), 132.8 (2,5-pyrrolyl ring carbons), 144.3 (aryl), 146.3 (aryl). Anal. Calcd. for $C_{26}H_{36}N_3Sc$: C 71.70, H 8.33, N 9.65, Found: C 71.98, H 8.37, N 9.63.

[(2,5-*t*-$Bu_2C_4H_2N$)Sc($CH_2C_6H_4NMe_2$-*o*)][$B(C_6F_5)_4$] (5).
^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ 1.09 (s, 18H, *t*-Bu), 1.77 (s, 6H, NMe_2), 1.84 (s, 2H, CH_2), 5.95 (s, 2H, pyrrolyl), 6.35-6.75 (m, 4H, aryl).

[(2,5-*t*-$Bu_2C_4H_2N$)Sc($CH_2C_6H_4NMe_2$-*o*)(dme)][$B(C_6F_5)_4$] (6).
^{1}H NMR (300 MHz, C_6D_5Cl, 23 °C): δ 1.03 (br s, 9H, *t*-Bu), 1.35 (br s, 9H, *t*-Bu), 1.44 (s, 1H, CH_2), 1.83 (s, 1H, CH_2), 2.27 (s, 6H, NMe_2), 2.47 (br s, 4H, OC_2H_4O), 3.25 (br s, 6H, OMe), 5.82 (br s, 1H, pyrrolyl), 6.23 (br s, 1H, pyrrolyl), 6.73-6.98 (m, 4H, aryl). ^{13}C NMR (75.45 MHz, C_4D_8O, 26 °C): δ 30.7 (*t*-Bu), 36.3 (*t*-Bu ipso), 47.1 (NMe_2), 55.8 (CH_2), 58.8 (OMe), 72.7 (OC_2H_4O), 114.8 (3,4-pyrrolyl ring carbons), 119.5 (aryl), 125.0 (br s, ipso C_6F_5), 125.4 (aryl), 129.2 (aryl), 132.6 (aryl), 137.0 (d, J_{C-F} = 247.5

Hz, C_6F_5), 139.0 (d, $J_{C\text{-}F}$ = 244.4 Hz, C_6F_5), 139.5 (aryl), 145.5 (aryl), 149.0 (d, $J_{C\text{-}F}$ = 238.8 Hz, C_6F_5), 162.4 (2,5-pyrrolyl ring carbons). ^{11}B NMR (193 MHz, C_4D_8O, 25 °C): δ –16.6 (s, $B(C_6F_5)_4$). ^{19}F NMR (565 MHz, C_4D_8O, 25 °C): δ –168.3, –164.7, –132.6. Anal. Calcd. for $C_{49}H_{42}BF_{20}N_2O_2Sc$: C 52.24, H 3.76, N 2.49, Found: C 51.72, H 4.15, N 3.06.

[(2,3,4,5-Me_4C_4N)Sc($CH_2C_6H_4NMe_2$-*o*)(thf)$_3$][$B(C_6F_5)_4$] (7).
^{1}H NMR (300 MHz, C_4D_8O, 27 °C): δ 1.42 (s, 2H, CH_2), 1.47 (br s, 12H, thf), 1.72 (s, 6H, Me), 1.99 (s, 6H, Me), 2.28 (s, 6H, NMe_2), 3.31 (br s, 12H, thf), 6.78–6.96 (m, 4H, aryl). ^{1}H NMR (300 MHz, C_4D_8O, 50 °C): δ 1.84 (s, 2H, CH_2), 2.05 (s, 6H, Me), 2.29 (s, 6H, Me), 2.81 (s, 6H, NMe_2), 6.98-7.16 (m, 4H, aryl). ^{13}C NMR (67.8 MHz, C_4D_8O, 24 °C): δ 10.9 (Me_4C_4N), 15.4 (Me_4C_4N), 46.5 (NMe_2), 57.3 (CH_2), 119.8 (aryl), 124.8 (aryl), 125.0 (br s, ipso C_6F_5), 128.2 (3,4-pyrrolyl ring carbons), 129.0 (aryl), 131.8 (aryl), 137.1 (d, $J_{C\text{-}F}$ = 253.8 Hz, C_6F_5), 138.7 (2,5-pyrrolyl ring carbons), 139.0 (d, $J_{C\text{-}F}$ = 242.1 Hz, C_6F_5), 139.9 (aryl), 143.8 (aryl), 148.8 (d, $J_{C\text{-}F}$ = 247.7 Hz, C_6F_5). ^{11}B NMR (193 MHz, C_4D_8O, 25 °C): δ –16.6 (s, $B(C_6F_5)_4$). ^{19}F NMR (565 MHz, C_4D_8O, 25 °C): δ –168.3, –164.8, –132.7.

A typical procedure for the polymerization of styrene by use of an in-situ generated cationic pyrrolyl scandium aminobenzyl species (Table 1, entry 1): In the glove box, a toluene solution (3 mL) of [Ph_3C][$B(C_6F_5)_4$] (23 mg, 25 μmol) was added to a toluene solution (4 mL) of **1** (12 mg, 25 μmol) at 25 °C in a 100-mL flask under vigorous stirring. 1.30 g of styrene (0.125 mmol) was then added rapidly. After 1 min, the flask was taken outside of the glove box and methanol was added to terminate the polymerisation. The mixture was poured into methanol (200 mL) to precipitate the polymer product. The white polymer solid was collected by filtration, and dried under vacuum at 60 °C to a constant weight (1.30 g, >3100 kg of copolymer/mol-Sc.h). The syndiotacticity of the polymer was confirmed by ^{1}H and ^{13}C NMR.[3] Atactic polystyrene was not observed. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 145 °C): δ 1.42 (t, 7.2 Hz, 2H, CH_2), 1.93 (quintet, 6.9 Hz, 1H, CH), 6.51–6.66 (m, 2H, Ph), 6.99–7.15 (m, 3H, Ph). ^{13}C NMR (75.5 MHz, $C_2D_2Cl_4$, 145 °C): δ 41.0, 44.3, 125.2, 127.6, 145.2. T_m = 272 °C.

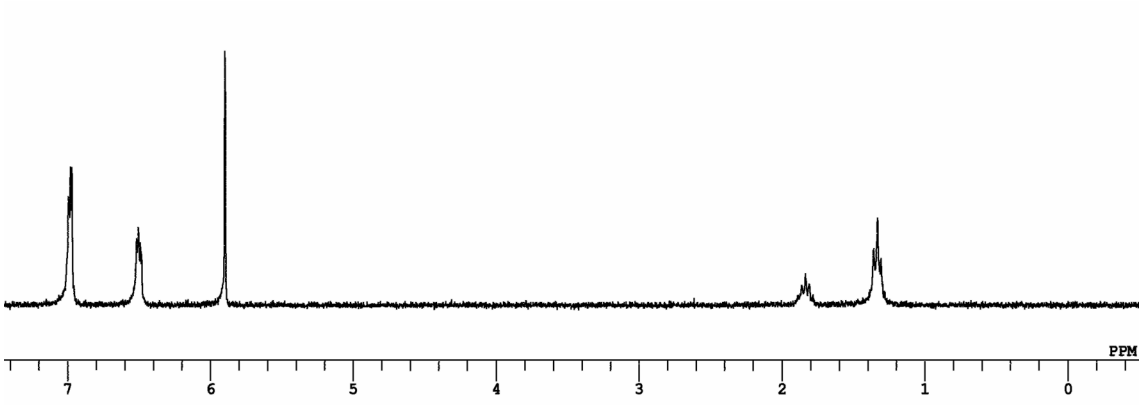

Figure S1. **^{1}H NMR spectrum of the syndiotactic polystyrene obtained in Table 1, entry 1.**

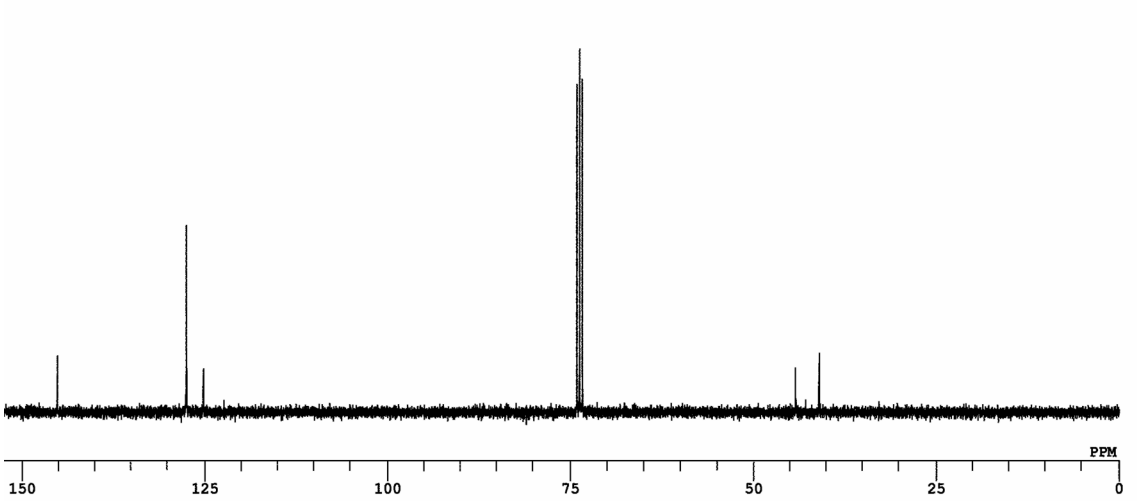

Figure S2. ^{13}C NMR spectrum of the syndiotactic polystyrene obtained in Table 1, entry 1.

X-Ray Crystallographic Studies: A crystal was sealed in a thin-walled glass capillary under a microscope in the glove box. Data collections were performed at –100 °C on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated Mo K_α radiation (λ = 0.71069 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL program. Refinements were performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance.

References

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(3) Y. Luo, J. Baldamus, Z. Hou, *J. Am. Chem. Soc.,* 2004, **126**, 13910–13911.