Supporting information

Isoprene Polymerization with Aminopyridinato Ligands Supported Rare-Earth Metal Complexes: Switching the Regio- and Stereoselectivity

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Experimental Section

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a glovebox. $ClPPh_2$, 2-aminopyridine, triethylamine, $AlMe_3$, $AlEt_3$, Al*i*Bu_3, $LnCl_3$ and $LiCH_2SiMe_3$ were purchased from Aldrich. Azide,[1] $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, $B(C_6F_5)_3$,[2] $Ln(CH_2SiMe_3)_3(THF)_2$(Ln = Sc, Y, Lu),[3] and **HL**[14] were prepared according to published procedures. Isoprene (99%, Acros) was dried over CaH_2 under stirring for 48 hours and distilled before use. All solvents were purified from MBraun SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film. ^1H, ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by the ^1H-^1H COSY and ^1H-^{13}C HMQC experiments when necessary. The number-average molar mass (M_n) and polydispersity index (PDI) of the polymer were measured by means of Size Exclusion Chromatography on TOSOH HLC-8220 SEC (Column: Super HZM-H×3) at 40 °C using THF as eluent (the flowing rate is 0.35 mL/min) against polystyrene standards. Elemental analyses were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC).

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at –86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 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[5] to yield the reflection data file. The structures were solved by using SHELXTL program.[6] Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method.

Synthesis of Ligands and Complexes

2-pyridyl-NHPPh$_2$ (HL^1)[4]: To a stirred solution of 2-aminopyridine (3.535 g, 37.6 mmol) and Et_3N (5.4 mL, 38.7 mmol) in dry THF (50 ml), cooled to –5 °C and protected by an atmosphere of N_2, was added a THF solution (20 ml) of diphenylchlorophosphine (6.75 mL, 37.6 mmol), over a period of 30 min. After warming the mixture to room temperature for 12 h, triethylamine hydrochloride salt was filtered off, and the solvent was removed from the filtrate to yield crude 2-(diphenylphosphinoamino)pyridine, which was washed with methanol and ether. The colorless crystals were obtained, which were recrystallized from a THF/hexane mixture (7.8 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ5.92 (br, 1H, N*H*), 6.74 (br, 1H, *p*-NC_5H_4N), 7.05 (m, 1H, *o*-NC_5H_4N), 7.43 (m, 1H, *m*-NC_5H_4N, 6H, *m,p*-PC_6H_5), 7.56 (s, 4H, *o*-PC_6H_5), 8.11 ppm (s, 1H, *m*-NC_5H_4N). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ108.96 (s, 1C, *o*-NC_5H_4N), 113.64 (s, 1C, *p*-NC_5H_4N), 128.84 (m,

6C, *m,p*-PC_6H_5), 132.17 (m, 4C, *o*-PC_6H_5), 138.12 (s, 1C, *m*-NC_5H_4N), 141.59 (s, 2C, *ipso*-PC_6H_5), 148.56 (s, 1C, *m*-NC_5H_4N), 162.46 ppm (s, 1C, *ipso*-C_5H_4N). Anal. Calcd. for $C_{17}H_{15}N_2P$ (%): C, 73.37; H, 5.43; N, 10.07. Found: C, 73.51; H, 5.35; N, 9.92.

2-pyridyl-NHPPh$_2$=NC$_6$H$_3$-2,6-Me$_2$ (HL^2): In a 100 mL Schlenk flask, a THF solution (15 mL) of 2,6-Me_2-$C_6H_3N_3$ (0.90 g, 6.1 mmol) was added dropwise to a THF solution (30 mL) of 2-(diphenylphosphinoamino)pyridine (**HL^1**) (1.67 g, 6.0 mmol) at 0°C under nitrogen atmosphere. The reaction mixture was stirred for 12 h at room temperature. Removal of volatiles gave white solids that were further purified by washing with diethyl ether/hexane to afford pure white solids (**HL^2**) (1.80 g, 76%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.11 (s, 6H, $C_6H_3Me_2$), 4.51 (br, 1H, N*H*), 6.53 (br, 1H, *p*-NC_5H_4N), 6.82 (m, 3H, NC_6H_3), 6.95 (m, 1H, *o*-NC_5H_4N), 7.28–7.37 (m, 1H, *m*-NC_5H_4N, 6H, *m,p*-PC_6H_5), 7.74-7.83 (m, 4H, *o*-PC_6H_5), 7.96 ppm (s, 1H, *m*-NC_5H_4N). Anal. Calcd. for $C_{25}H_{24}N_3P$ (%): C, 75.55; H, 6.09; N, 10.57. Found: C, 75.62; H, 6.19; N, 10.38.

L$^1_2$Lu(CH$_2$SiMe$_3$)(THF) (1a): To a toluene solution (5.0 mL) of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.296 g, 0.510 mmol), equivalent **HL^1** (0.142 g, 0.510 mmol in 2 mL toluene) was added dropwise at room temperature. The mixture was then stirred for 5 h. Removal of the volatiles gave a yellow oily residue. The residue was dissolved with 3 mL hexane and then cooled to –30 °C for 12 h to give white solids which were washed carefully by small amount of hexane (0.5 mL) and then dried in vacuum to afford complex **1a** in 35% yield (0.155 g). Colorless single crystals for

X-ray analysis grew from toluene/hexane at –30 °C within a day. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ0.06–0.08 (m, 11H, CH_2SiMe_3), 1.34, 3.71 (s, 8H, THF), 5.99 (m, 2H, *p*-NC_5H_4N), 6.72 (m, 2H, *o*-NC_5H_4N), 6.83 (m, 2H, *m*-NC_5H_4N), 7.09–7.11 (m, 6H, *m,p*-PC_6H_5), 7.23 (m, 4H, *o*-PC_6H_5), 7.60 ppm (m, 2H, *m*-NC_5H_4N). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ5.05 (s, 3C, SiMe_3), 25.56 (s, 2C, THF), 35.18 (s, 1C, *C*H_2SiMe_3), 71.13 (s, 2C, THF), 100.57, 110.84 (s, 2C, *o*-NC_5H_4N), 113.10, 113.30 (s, 2C, *p*-NC_5H_4N), 128.92 (m, 12C, *m,p*-PC_6H_5), 132.43 (m, 8C, *o*-PC_6H_5), 139.62, 140.19 (s, 2C, *m*-NC_5H_4N), 142.96, 143.16 (s, 4C, *ipso*-PC_6H_5), 144.86, 145.15 (s, 2C, *m*-NC_5H_4N), 170.01, 170.11 ppm (s, 2C, *ipso*-C_5H_4N). Anal. Calcd. for $C_{42}H_{47}N_4OP_2SiLu$ (%): C, 56.75; H, 5.33; N, 6.30. Found: C, 56.61; H, 5.29; N, 6.42.

$L^1_2Y(CH_2SiMe_3)(THF)$ (1b): Following the similar procedure described for the preparation of **1a**, treatment of a toluene solution (5.0 mL) of $Y(CH_2SiMe_3)_3(THF)_2$ (0.283 g, 0.572 mmol) with 1 equiv of **HL^1** (0.159 g, 0.572 mmol in 2 mL toluene) afforded complex **1b** (0.138 g, 30%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ–0.35 (s, 2H, CH_2SiMe_3), 0.07 (s, 9H, CH_2SiMe_3), 1.22, 3.70 (s, 8H, THF), 6.00 (m, 2H, *p*-NC_5H_4N), 6.72 (m, 2H, *o*-NC_5H_4N), 6.85 (m, 2H, *m*-NC_5H_4N), 7.10–7.12 (m, 6H, *m,p*-PC_6H_5), 7.23 (m, 4H, *o*-PC_6H_5), 7.60 ppm (m, 2H, *m*-NC_5H_4N). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ4.99 (s, 3C, SiMe_3), 25.65 (s, 2C, THF), 32.58 (s, 1C, *C*H_2SiMe_3), 71.27 (s, 2C, THF), 100.49, 110.76 (s, 2C, *o*-NC_5H_4N), 113.18, 113.29 (s, 2C, *p*-NC_5H_4N), 128.94 (m, 12C, *m,p*-PC_6H_5), 132.46 (m, 8C, *o*-PC_6H_5), 139.82, 140.23 (s, 2C, *m*-NC_5H_4N), 143.11, 143.27 (s, 4C, *ipso*-PC_6H_5), 144.99, 145.22 (s, 2C, *m*-NC_5H_4N), 170.08, 170.15 ppm (s, 2C, *ipso*-C_5H_4N). Anal. Calcd. for

$C_{42}H_{47}N_4OP_2SiY$ (%): C, 62.84; H, 5.90; N, 6.98. Found: C, 62.73; H, 5.81; N, 7.09.

$L^1_2Sc(CH_2SiMe_3)(THF)$ (1c): Following the similar procedure described for the preparation of **1a**, treatment of a toluene solution (5.0 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.274 g, 0.608 mmol) with 1 equiv of **HL^1** (0.169 g, 0.608 mmol in 2 mL toluene) afforded complex **1c** (0.124 g, 27%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ0.07 (s, 9H, $CH_2Si\mathit{Me}_3$), 0.24 (s, 2H, $C\mathit{H}_2SiMe_3$), 1.24, 3.86 (s, 8H, THF), 5.86 (m, 2H, *p*-NC_5H_4N), 6.73 (m, 2H, *o*-NC_5H_4N), 6.92 (m, 2H, *m*-NC_5H_4N), 7.06–7.10 (m, 6H, *m,p*-PC_6H_5), 7.23 (m, 4H, *o*-PC_6H_5), 7.62 ppm (m, 2H, *m*-NC_5H_4N). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ4.86 (s, 3C, $Si\mathit{Me}_3$), 25.37 (s, 2C, THF), 38.92 (s, 1C, $\mathit{C}H_2SiMe_3$), 71.60 (s, 2C, THF), 100.71, 110.98 (s, 2C, *o*-NC_5H_4N), 113.64, 113.89 (s, 2C, *p*-NC_5H_4N), 128.96 (m, 12C, *m,p*-PC_6H_5), 132.37 (m, 8C, *o*-PC_6H_5), 139.93, 140.38 (s, 2C, *m*-NC_5H_4N), 143.11, 143.32 (s, 4C, *ipso*-PC_6H_5), 145.75, 145.99 (s, 2C, *m*-NC_5H_4N), 170.16, 170.28 ppm (s, 2C, *ipso*-C_5H_4N). Anal. Calcd. for $C_{42}H_{47}N_4OP_2SiSc$ (%): C, 66.48; H, 6.24; N, 7.38. Found: C, 56.61; H, 5.29; N, 6.42.

$L^2Lu(CH_2SiMe_3)_2(THF)$ (2): To a toluene solution (5.0 mL) of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.232 g, 0.399 mmol), equivalent **HL^2** (0.160 g, 0.400 mmol in 2 mL toluene) was added dropwise at room temperature. The mixture was then stirred for 1 h. Removal of the volatiles gave a brown oily residue. The residue was dissolved with 3 mL hexane and then cooled to –30 °C for 12 h to give pale solids which were washed carefully by small amount of hexane (0.5 mL) and then dried in vacuum to afford complex **2a** in 55% yield (0.180 g). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ–0.16 (s, 4H, $C\mathit{H}_2SiMe_3$), 0.56 (s, 18H, $Si\mathit{Me}_3$), 1.19 (s, 4H, THF), 1.95 (s, 6H,

$C_6H_3Me_2$), 3.76 (s, 4H, THF), 6.32 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, *o*-NC_5H_4N), 6.43 (t, $^3J_{H-H}$ = 6.4 Hz, 1H, *p*-NC_5H_4N), 6.84 (m, 1H, *p*-NC_6H_3), 6.94 (m, 2H, *m*-NC_6H_3), 7.02 (t, $^3J_{H-H}$ = 6.4 Hz, 1H, *m*-NC_5H_4N), 7.04–7.12 (m, 6H, *m,p*-PC_6H_5), 7.66–7.71 (m, 4H, *o*-PC_6H_5), 8.41 ppm (d, $^3J_{H-H}$ = 6.0 Hz, 1H, *m*-NC_5H_4N). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ5.31 (s, 6C, SiMe_3), 21.17 (s, 2C, $C_6H_3Me_2$), 25.75 (s, 2C, THF), 42.39 (s, 2C, CH_2SiMe_3), 69.70 (s, 2C, THF), 114.92 (s, 1C, *o*-NC_5H_4N), 115.95 (s, 1C, *p*-NC_5H_4N), 128.80 (s, 4C, *m*-PC_6H_5), 129.69 (s, 2C, *m*-NC_6H_3), 131.56 (s, 1C, *p*-NC_6H_3), 131.82 (s, 2C, *p*-PC_6H_5), 132.56 (m, 4C, *o*-PC_6H_5), 135.41 (s, 2C, *ipso*-PC_6H_5), 138.83 (s, 1C, *m*-NC_5H_4N), 142.71 (m, 3C, *ipso*-NC_6H_3), 148.37 (s, 1C, *m*-NC_5H_4N), 161.59 ppm (s, 2C, *ipso*-C_5H_4N). Anal. Calcd. for $C_{37}H_{52}N_3OPSi_2Lu$ (%): C, 54.40; H, 6.42; N, 5.14. Found: C, 54.51; H, 6.39; N, 5.26.

Neodymium Borohydride Complex (3): To a THF solution (5.0 mL) of $Nd(BH_4)_3(THF)_3$ (0.258 g, 0.637 mmol), equivalent **HL^2** (0.254 g, 0.636 mmol in 2 mL toluene) was added dropwise at room temperature. The mixture was then stirred for 12 h. Removal of the volatiles and then cooled to –30 °C for 12 h to give light blue solids which were washed carefully by small amount of THF (0.5 mL) and then dried in vacuum to afford complex **3** in 59% yield (0.380 g). Light blue single crystals for X-ray analysis grew from THF/hexane at –30 °C within a day. Anal. Calcd. for $C_{37}H_{58}B_3N_3O_3PNd$ (%): C, 55.52; H, 7.30; N, 5.25. Found: C, 55.43; H, 7.21; N, 5.33.

Procedure for Isoprene Polymerization. A typical polymerization procedure is as follow (Table 1, run 1): In a glove box, isoprene (1.0 mL, 10 mmol) was added into a 25 mL flask. Then, a toluene solution (5.0 mL) of **1a** (8.7 mg, 0.01 mmol) and 1 equiv $[Ph_3C][B(C_6F_5)_4]$ (9.6 mg, 0.01 mmol) and 10 equiv Al*i*Bu_3 (0.10 mL, 1.0 mol/L), were added to the flask. After stirring for 4 h, methanol was injected to terminate the

polymerization. The viscous mixture was poured into a large quantity of methanol. The obtained white polymer was filtered and then dried under vacuum at ambient temperature to a constant weight.

References

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Legends

Stable 1. Isoprene polymerization with complex **1a**/borate/Al*i*Bu$_3$

Stable 2. Summary of crystallographic data for complexes **1a** and **3**

Sfigures 1–2. X-ray structure and ^{1}H NMR spectrum of complex **1a**

Sfigure 3. ^{1}H NMR spectrum of complex **2**

Sfigures 4–5. ^{1}H NMR and ^{13}C NMR of polyisoprene samples (Table 1, Run 1).

Sfigures 6–7. ^{1}H NMR and ^{13}C NMR of polyisoprene samples (Table 1, Run 4).

Sfigure 8. ^{1}H NMR of polyisoprene sample (Table 1, Run 6).

Sfigures 9–10. ^{1}H NMR and ^{13}C NMR of polyisoprene samples (Table 1, Run 7).

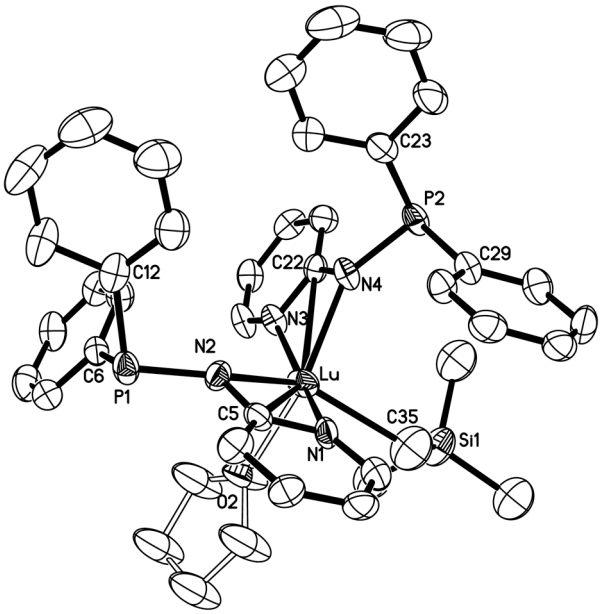
Stable 1. Isoprene polymerization with complex **1a**/borate/Al*i*Bu$_3$

Run	Cat.	[Ip]/[Ln]	[Al]/[Ln]	Time	Yield	1,4 (%)[b]		3,4 (%)[b]	M_n[c]	M_w/M_n[c]
				h	%	*cis*	*trans*		10^{-4}	
1	**1a**+A	1000	10	4	100	95.2	1.1	3.7	2.0	2.11
2	**1a**+C	1000	10	10	trace	-	-	-	-	-
3	**1a**+B	1000	2	4	100	97.3	0.8	1.9	25.6	1.81
4	**1a**+B	1000	5	4	100	97.2	0.9	1.9	13.3	2.08
5	**1a**+B	1000	20	4	100	97.0	1.0	2.0	4.42	2.45
6	**1a**+B	1000	30	4	100	96.9	1.0	2.1	3.22	2.52
7	**1a**+B	2000	10	6	100	97.2	1.0	1.8	15.9	2.29
8	**1a**+B	3000	10	8	94	97.4	0.9	1.7	24.0	2.39
9	**1a**+B	4000	10	10	82	97.3	1.0	1.7	34.2	2.16

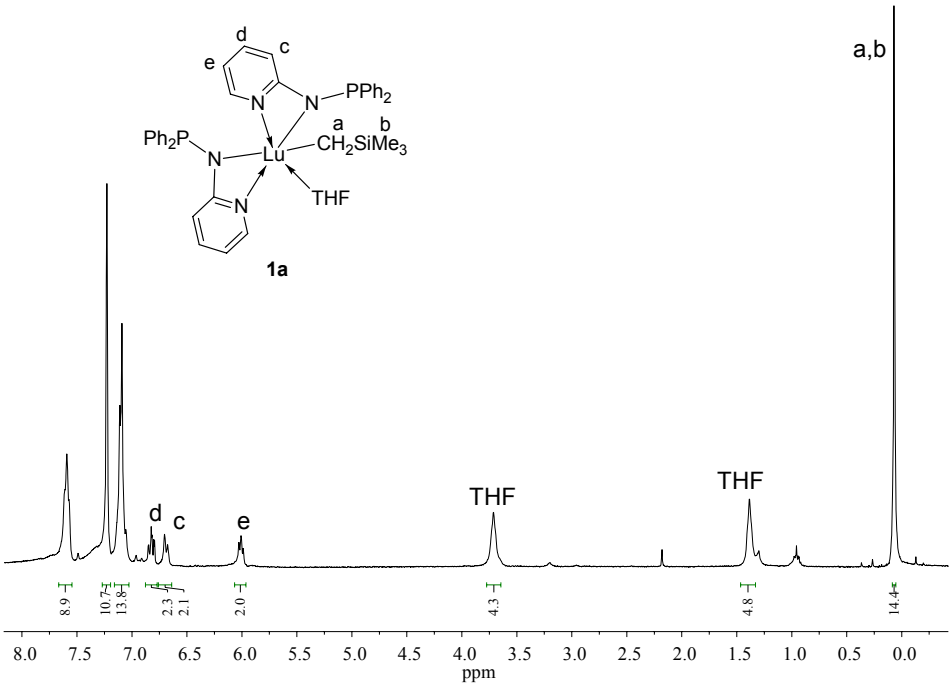
[a] General condition: 20 °C, 5 mL toluene, A = $[PhMe_2NH][B(C_6F_5)_4]$, B = $[Ph_3C][B(C_6F_5)_4]$, C = $B(C_6F_5)_3$, [Borate]/[Ln] = 1.0; [b] determined by ^{1}H NMR and ^{13}C NMR; [c] Measured by GPC calibrated with standard polystyrene samples.

Stable 2. Summary of Crystallographic Data and Refinements for complexes **1a** and **3**

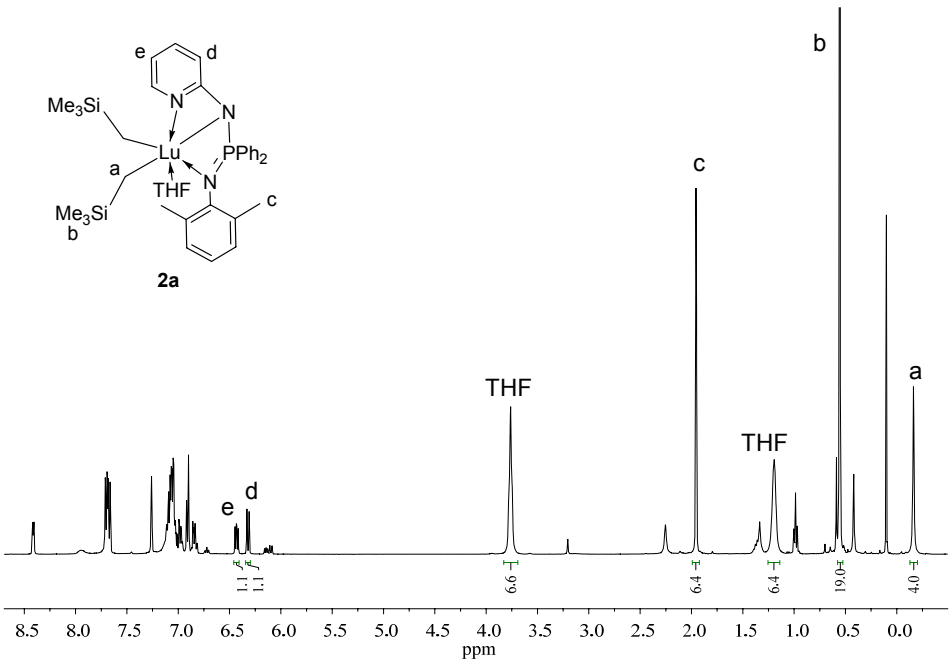
Compound reference	**1a**	**3**·THF
Chemical formula	$C_{42}H_{47}LuN_4OP_2Si$	$C_{37}H_{58}B_3N_3NdO_3P$
Formula Mass	888.84	800.50
Crystal system	Trigonal	Triclinic
a/Å	18.0407(6)	9.5888(5)
b/Å	18.0407(6)	13.5918(8)
c/Å	11.0329(7)	17.0238(9)
α/°	90.00	75.0720(10)
β/°	90.00	87.9480(10)
γ/°	120.00	69.6440(10)
Unit cell volume/Å^3	3109.8(2)	2006.39(19)
Temperature/K	187(2)	187(2)
Space group	*P*3*(2)*	$P\bar{1}$
No. of formula units per unit cell, *Z*	3	2
Radiation type	MoKα	MoKα
Absorption coefficient, μ/mm^{-1}	2.523	1.370
No. of reflections measured	16705	10865
No. of independent reflections	6693	7610
R_{int}	0.0341	0.0115
Final R_1 values ($I > 2\sigma(I)$)	0.0398	0.0273
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0886	0.0714
Final R_1 values (all data)	0.0435	0.0289
Final $wR(F^2)$ values (all data)	0.0903	0.0726
Goodness of fit on F^2	1.047	1.048



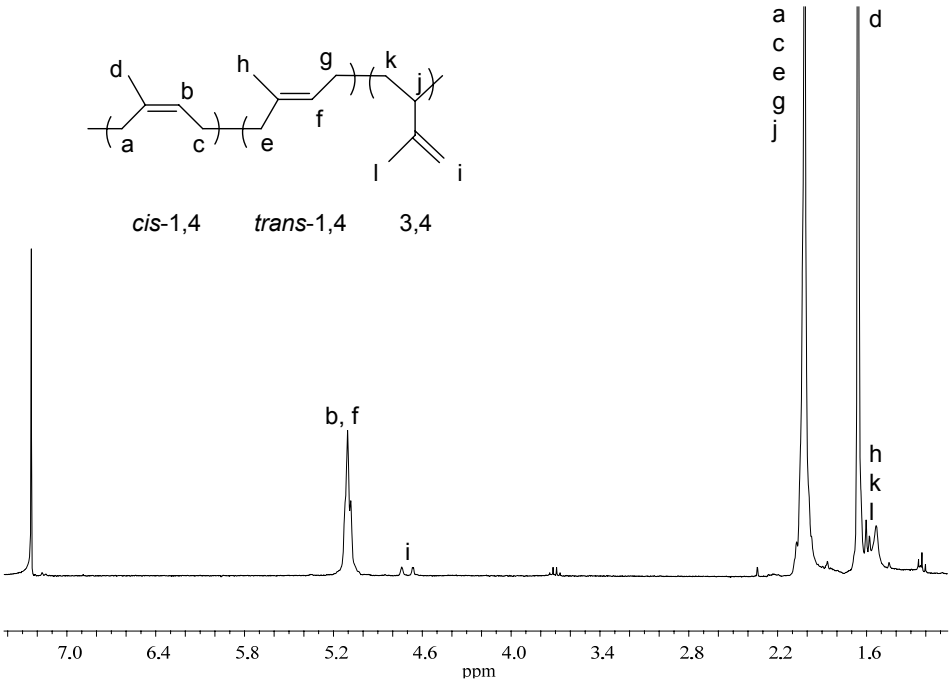
Sfigure 1. X-ray structure of complex **1a** with 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Lu–N(1) 2.350(5), Lu–N(2) 2.360(6), Lu–C(5) 2.814(6), Lu–N(3) 2.367(5), Lu–N(4) 2.316(6), Lu–C(22) 2.803(6), Lu–C(35) 2.507(14), Lu–O(2) 2.229(7), N(1)–C(5) 1.355(8), N(2)–C(5) 1.365(7), N(3)–C(22) 1.356(8), N(4)–C(22) 1.363(7), N(1)–Lu–N(2) 57.48(17), N(3)–Lu–N(4) 57.73(17), C(6) –P(1)–C(12) 98.2(3), C(23)–P(2)–C(29) 98.4(3).



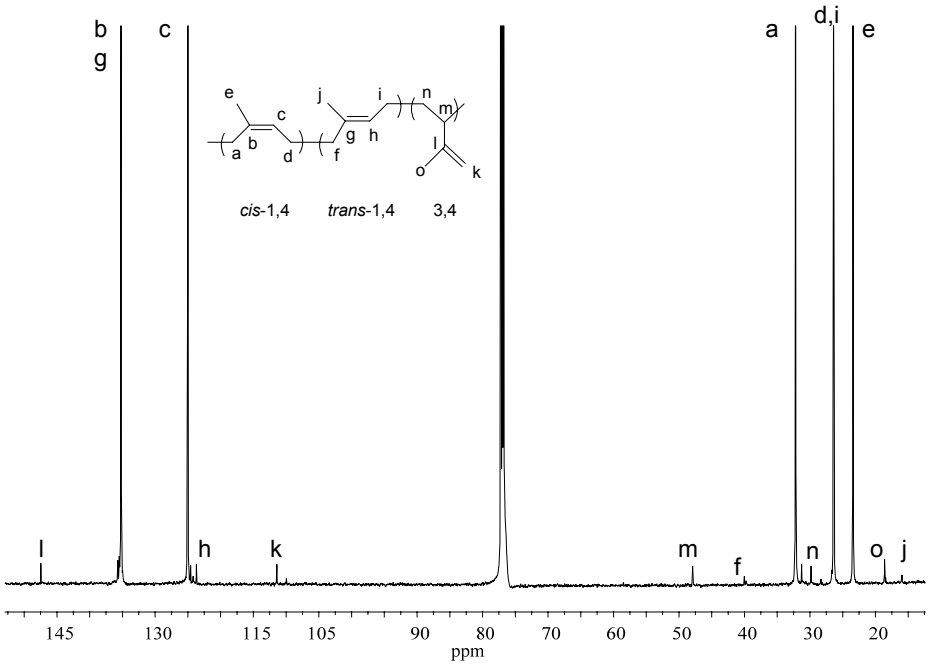
Sfigure 2. ^{1}H NMR spectrum of complex **1a**.



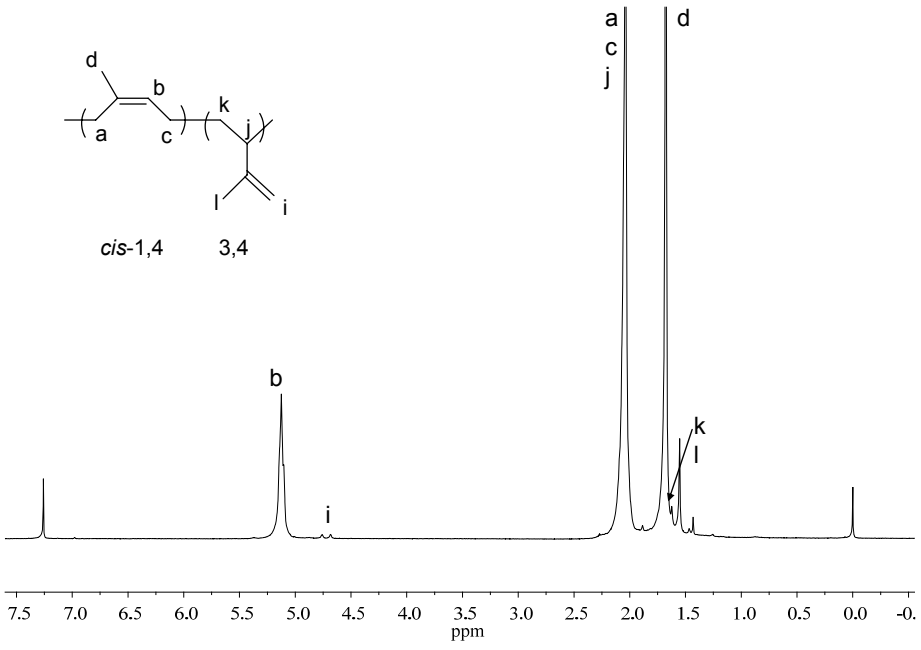
Sfigure 3. ^{1}H NMR spectrum of complex **2a**.



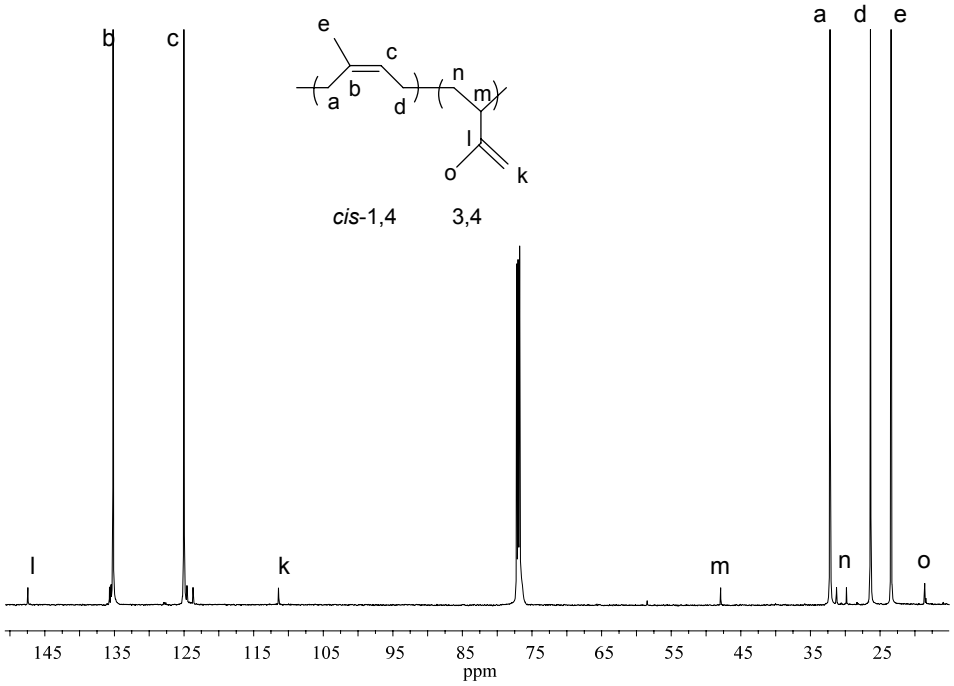
Sfigure 4. ^{1}H NMR spectrum of polyisoprene sample (*cis*-1,4 = 97.2%, Table 1, Run 1)



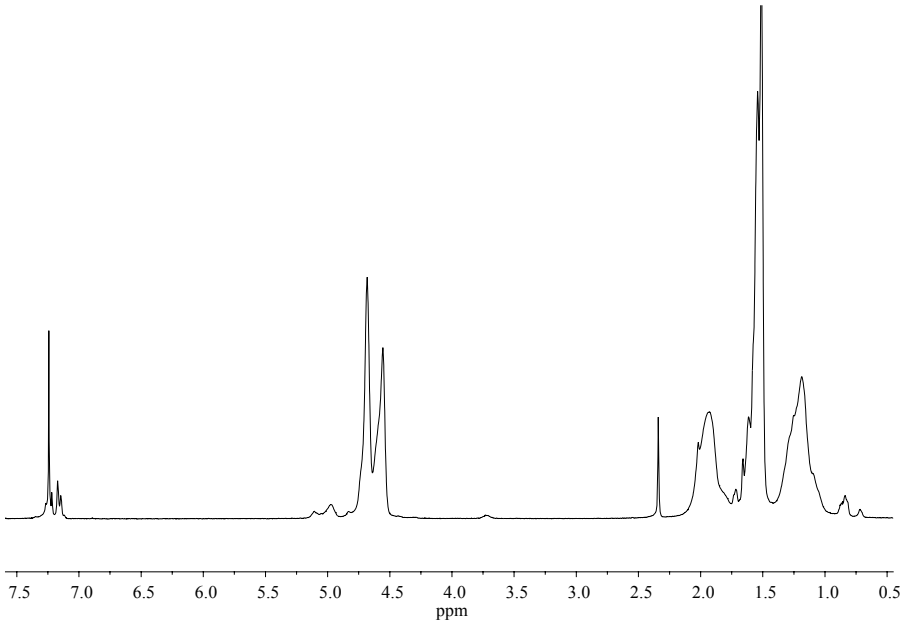
Sfigure 5. ^{13}C NMR spectrum of polyisoprene sample (*cis*-1,4 = 97.2%, Table 1, Run 1)



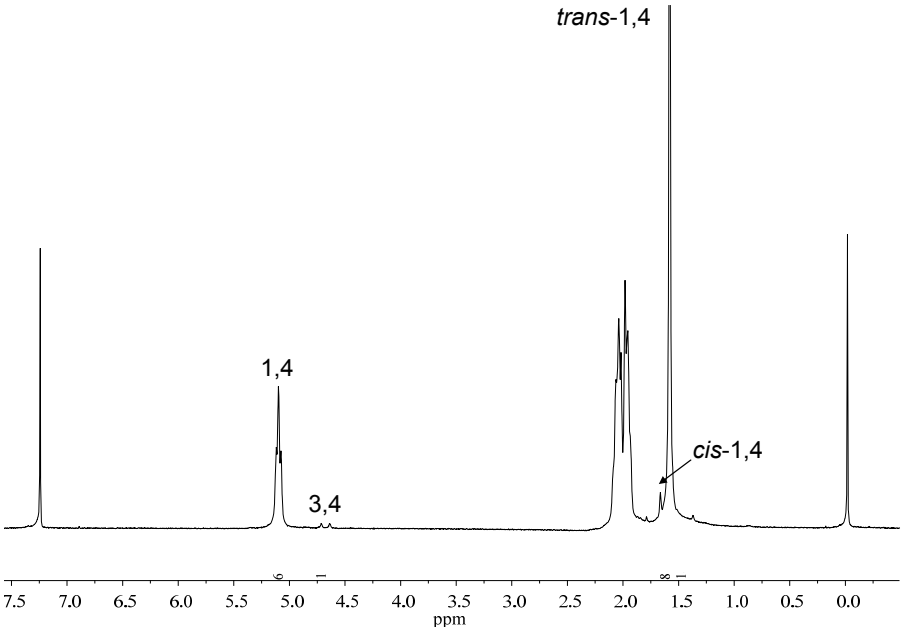
Sfigure 6. ^{1}H NMR spectrum of polyisoprene sample (*cis*-1,4 = 97.7%, Table 1, Run 4)



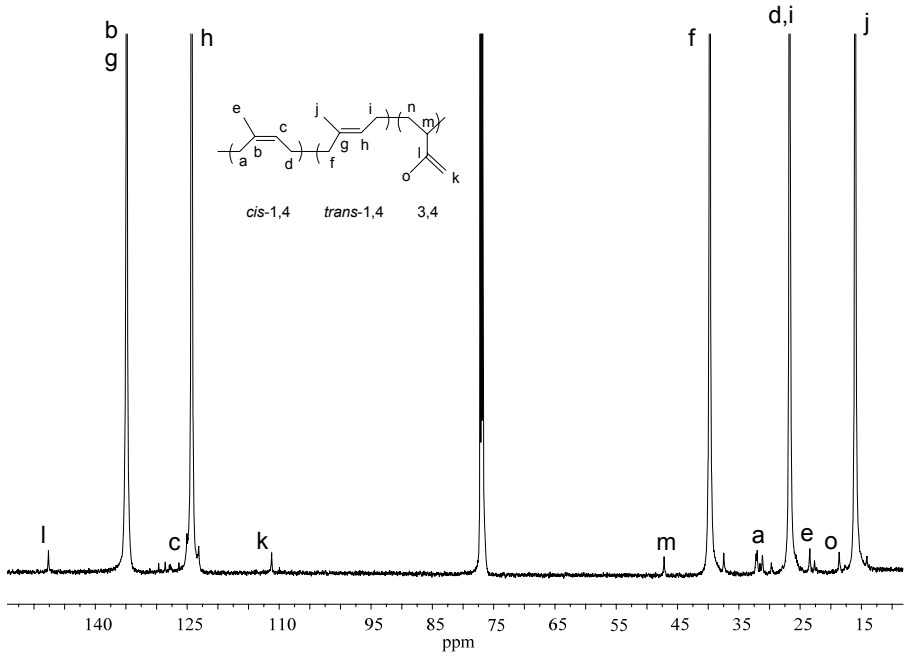
Sfigure 7. ^{13}C NMR spectrum of polyisoprene sample (*cis*-1,4 = 97.7%, Table 1, Run 4)



Sfigure 8. ^{1}H NMR of polyisoprene sample (3,4 = 88.0%, Table 1, Run 6).



Sfigure 9. ^{1}H NMR of polyisoprene sample (*trans*-1,4 = 97.2%, Table 1, Run 7).



Sfigure 10. ^{13}C NMR of polyisoprene sample (*trans*-1,4 = 97.2%, Table 1, Run 7).