Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Near-IR luminescent neodymium complexes: spectroscopic probes of catalytically active species

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Contents

1. Experimental procedures and characterising data

General methods and instrumentation:

All manipulations of air and moisture sensitive species were performed under an atmosphere of argon or dinitrogen using standard Schlenk and glove box techniques. Solvents were dried by passing through an alumina drying column incorporated into a MBraun SPS800 solvent purification system, except in the case of tetrahydrofuran, which was dried over molten potassium for three days and distilled under argon. All solvents were degassed, saturated with argon, and stored under argon in Teflon valve ampoules. Deuterated chloroform was passed through a column of basic alumina before being stored over 4Å molecular sieves prior to use. Deuterated solvents for NMR spectroscopy were dried over molten potassium (benzene-d_6, toluene-d_8) for three days before being vacuum transferred, freeze pump thaw degassed and stored in a glove box. All other reagents were purchased from commercial suppliers and used as received unless otherwise stated. $Nd\{N(SiMe_3)_2\}_3$ was synthesised according to literature procedures.[1]

Air sensitive samples for NMR and luminescence spectroscopy were prepared in a glovebox under a dinitrogen atmosphere using 5 mm Nolan NMR tubes equipped with J. Young Teflon valves. All other samples were prepared in Wilmad 5 mm NMR tubes. NMR spectra were recorded on Bruker Avance DPX 400, 500 or 600 NMR spectrometers. NMR spectra are quoted in ppm relative to tetramethylsilane (δ=0 ppm) and were referenced internally relative to the residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, all coupling constants are quoted in Hertz. Where appropriate, NMR assignments were confirmed by the use of two-dimensional ^{1}H-^{1}H or ^{1}H-^{13}C correlation experiments (HSQC and HMBC). Infrared spectra were prepared as KBr pellets and were recorded on a Jasco 660-Plus FTIR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). All photophysical data were obtained on a Jobin Yvon-Horiba Fluorolog-3 spectrometer fitted with a JY TBX picosecond photodetection module. A Hamamatsu R5509-73 detector (cooled to –80 °C using a C9940 housing) was used for near-IR luminescence measurements. For the near-IR lifetimes the pulsed laser source was a Continuum Minilite Nd:YAG configured for 355 nm output, whilst for fluorescence lifetimes a 459 nm NanoLEDs (operating at 1 MHz) was utilised. All lifetime data were collected using the JY-Horiba FluoroHub single photon counting module in multi-channel scalar mode. Lifetimes were obtained using the provided software, DAS6. Elemental analyses were recorded by Mr. Stephen Boyer at London Metropolitan University.

Modified procedure for the preparation of R-BOPA

A modified literature procedure was used in the preparation of R-BOPA. 2,2'-iminodibenzoic acid was synthesised following the procedure of Xu, which was subsequently converted into the corresponding acid chloride using $SOCl_2$ in THF.[2] A solution of the acid chloride in dichloromethane was reacted with the appropriate amino alcohol, with the addition of catalytic N,N-dimethylaminopyridine (DMAP) to prevent competing side reactions, and purified as reported by Xu. The resulting bis(hydroxyamide) was ring-closed using the procedure of Gade et al:[3] To a dry DCM solution of the bis(hydroxyamide) was added dry Et_3N (8.0 equiv), DMAP (~10 mg) and cooled to 0 °C. To this a dry dichloromethane solution of TsCl (2.0 equiv) was added dropwise and left to stir at room temperature for 3 days. The

dichloromethane solution was washed with aqueous NH_4Cl solution and brine, dried over Na_2SO_4 and the solvent removed under reduced pressure to yield the crude product. The R-BOPA ligands were purified by column chromatography using silica gel and dichloromethane. Data were consistent with that previously reported.[2]

General procedure for [Nd(R-BOPA)(N(SiMe$_3$)$_2$)$_2$] (1a-c):

A dry THF solution (10 mL) of R-BOPA (500 mg) was added dropwise to a dry pentane solution (20 mL) of Nd{N(SiMe$_3$)$_2$}$_3$ (1 eq). The reaction mixture was left to stir overnight and subsequently volatiles were removed under reduced pressure. The resulting yellow solid was washed with cold pentane (-78 ºC) and left to dry *in vacuo* for 2 hours to yield **(1a-c)** as yellow solids.

[Nd(iPr-BOPA)(N(SiMe$_3$)$_2$)$_2$] (1a)

Yield: 84%. ^{1}H NMR (400.1 MHz, C_6D_6, 293 K) δ 16.42 (d, $^3J_{HH}$ = 7.46 Hz, 2 H), 13.04 (d, $^3J_{HH}$ = 7.74 Hz, 2 H), 12.75 (br t, $^3J_{HH}$ = 6.02 Hz, 2 H), 10.72 (t, $^3J_{HH}$ = 6.88 Hz, 2 H), -1.62 (br d, $^3J_{HH}$ = 6.88 Hz, 2 H), -3.90 (d, $^3J_{HH}$ = 7.17 Hz, 2 H), -5.96 (s, 36 H), -9.17 (s, 6 H), 12.83 (s, 6 H), -20.34 (s, 2 H), -39.29 (s, 2 H) ppm; ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 293 K) δ 166.2, 162.4, 147.0, 143.2, 138.2, 135.7, 125.3, 65.4, 28.0, 24.8 5.7, -1.2, -3.4 ppm; IR (υ cm^{-1}) (KBr): 3056 (w), 2959 (s), 2897 (m), 1609 (s), 1584 (m), 1559 (m), 1537 (m), 1481 (m), 1462 (s), 1429 (m), 1371 (m), 1326 (w), 1260 (s), 1220 (m), 1160 (m), 1092 (m), 1065 (s), 1048 (s), 1018 (s), 968 (s), 863 (m), 838 (s), 823 (s), 810 (m), 747 (m), 687 (w), 664 (m), 597 (m) cm^{-1}; Anal. Calcd for $C_{36}H_{64}N_5NdO_2Si_4$: C 50.54, H 7.54, N 8.19. Found: C 50.39, H 7.46, N 8.09.

[Nd(Ph-BOPA)(N(SiMe$_3$)$_2$)$_2$] (1b)

Yield: 80%. ^{1}H NMR (400.1 MHz, C_6D_6, 293 K) δ 20.23 (br d, $^3J_{HH}$ = 4.02 Hz, 2 H), 14.24 (d, $^3J_{HH}$ = 5.74 Hz, 2 H), 13.78 (br s, 2 H), 11.48 (t, $^3J_{HH}$ 5.74 Hz, 2 H), 1.20 (t, $^3J_{HH}$ = 7.74 Hz, 2 H), 0.09 (t, $^3J_{HH}$ = 6.88 Hz, 2 H), - 0.96 (br s, 4 H), -3.60 (br d, $^3J_{HH}$ = 5.45 Hz, 4 H), -5.95 (br s, 36 H), -8.29 (d, $^3J_{HH}$ = 7.17 Hz, 2 H), -22.71 (br s, 2 H) ppm; ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 293 K) δ 179.7, 166.8, 154.4, 146.0, 145.7, 141.1, 140.8, 126.5, 119.0, 118.0, 113.5, 107.2, 73.2, 5.7 ppm; IR (υ cm^{-1}) (KBr): 2963 (s), 2913

(m), 2852 (m), 1635 (m), 1609 (m), 1581 (w), 1534 (w), 1461 (m), 1430 (m), 1261 (s), 1221 (m), 1157 (m), 1092 (s), 1022 (s), 953 (w), 799 (s), 749 (m), 698 (m) cm^{-1}; Anal. Calcd for $C_{42}H_{60}N_5NdO_2Si_4$: C 54.62, H 6.55, N 7.58. Found: C 54.43, H 6.66, N 7.53.

[Nd(Bn-BOPA)(N(SiMe$_3$)$_2$)$_2$] (1c)

Yield: 76%. ^{1}H NMR (400.1 MHz, C_6D_6, 293 K) δ 14.46 (d, $^3J_{HH}$ = 4.45 Hz, 2 H), 12.41 (br s, 2 H), 11.87 (br d, $^3J_{HH}$ = 8.32 Hz, 2 H), 10.31 (t, $^3J_{HH}$ = 8.32 Hz, 2 H), 4.92 (t, $^3J_{HH}$ = 8.03 Hz, 2 H), 4.40 (t, $^3J_{HH}$ = 7.74 Hz, 4 H), 0.75 (br s, 2 H), -1.08 (d, $^3J_{HH}$ = 8.89 Hz, 4 H), -2.96 (d, $^3J_{HH}$ = 6.60 Hz, 2 H), -5.72 (br d, $^3J_{HH}$ = 7.74 Hz, 2 H), -5.93 (br s, 36 H), -17.92 (s, 2 H), -21.95 (s, 2 H), -32.5 (s, 2 H) ppm; ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 293 K) δ 160.4, 157.4, 143.1, 141.7, 136.2, 132.2, 131.3, 128.6, 124.9, 124.7, 123.6, 121.2, 68.8, 8.7, 5.6 ppm; IR (υ cm^{-1}) (KBr): 3064 (w), 3030 (w), 2962 (s), 2902 (m), 1608 (m), 1584 (m), 1558 (w), 1536 (w), 1497 (w), 1462 (m), 1428 (m), 1375 (w), 1323 (w), 1261 (s), 1221 (m), 1182 (w), 1160 (m), 1095 (s), 1021 (s), 975 (m), 933 (m), 863 (m), 801 (s), 747 (m), 700 (m), 665 (m), 598 (w) cm^{-1}; Anal. Calcd for $C_{44}H_{64}N_5NdO_2Si_4$: C 55.54, H 6.78, N 7.36. Found: C 55.38, H 6.75, N 7.28.

General procedure for [Nd(R-BOPA){NHCH$_2$C(Ph)$_2$C$_3$H$_7$}$_2$] (2a-c):

A dry hexane solution (1.eq) of 2,2'-diphenyl-aminopentane was added dropwise to a dry hexane solution (20 mL) of **1**. The reaction mixture was left to stir overnight, filtered and subsequently volatiles were removed under reduced pressure. The resulting yellow solid was washed with cold pentane (-78 ºC) and left to dry *in vacuo* for 2 hours to yield **(2a-c)** as yellow solids.

[Nd(iPr-BOPA){NHCH$_2$C(Ph)$_2$C$_3$H$_7$}$_2$] (2a)

Yield: 65%. ^{1}H NMR (400.1 MHz, C_6D_6, 293 K) δ 16.44 (d, $^3J_{HH}$ = 7.17 Hz, 2 H), 12.99 (d, $^3J_{HH}$ = 8.17 Hz, 2 H), 12.71 (br s, 2 H), 10.66 (t, $^3J_{HH}$ = 7.17 Hz, 2 H), 5.64 (br s, 6 H), 3.04 (br s, 20 H), 0.48 (d, $^3J_{HH}$ = 7.17 Hz, 2 H), -0.05 (s, 4 H), -1.8 (br s, 4 H), -4.14 (d, $^3J_{HH}$ = 6.02 Hz, 4 H), -4.34 (br s, 2 H), -5.41 (br s, 2 H), -9.41 (s, 6 H), -13.12 (s, 6 H), -20.23 (br s, 2 H), -20.76 (br s, 2 H) ppm; ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 293 K) δ 165.2, 154.5, 141.1, 136.2, 133.7, 129.8, 128.3, 123.4, 117.8, 115.5, 112.1, 67.8, 63.3, 30.5, 28.3, 17.0, 15.6, 16.6, 12.7, 3.5, -5.4 ppm; IR (υ cm^{-1}) (KBr): 3087 (w), 3057 (m), 3025 (m),

2960 (s), 2903 (m), 2871 (w), 1652 (m), 1635 (m), 1615 (m), 1574 (m), 1560 (m), 1534 (m), 1507 (m), 1457 (s), 1432 (m), 1364 (m), 1318 (m), 1260 (s), 1221 (m), 1181 (m), 1156 (m), 1092 (m), 1054 (m), 1019 (s), 967 (m), 933 (m), 869 (m), 844 (m), 800 (s) cm^{-1}; Anal. Calcd for $C_{44}H_{60}N_5NdO_2Si_4$: C 68.74, H 6.96, N 6.91. Found: C 68.42, H 6.50, N 6.72.

[Nd(Ph-BOPA){NHCH$_2$C(Ph)$_2$C$_3$H$_7$}$_2$] (2b)

Yield: 68%. ^{1}H NMR (400.1 MHz, C_6D_6, 293 K) δ 20.02 (br s, 2 H), 14.08 (d, $^3J_{HH}$ = 8.03 Hz, 2 H), 13.6 (br s, 2 H), 11.33 (t, $^3J_{HH}$ = 5.59 Hz, 2 H), 8.58 (br s, 4 H), 7.10 (br s, 4 H), 7.01 (br s, 6 H), 1.11 (t, $^3J_{HH}$ = 7.89 Hz, 2 H), 0.05 (br s, 4 H), -0.05 (br s, 4 H), -1.06 (br s, 2 H), -1.58 (br s, 4 H), -1.64 (br s, 2 H), -3.68 (d, $^3J_{HH}$ = 4.73 Hz, 2 H), -3.87 (br s, 20 H), -8.23 (d, $^3J_{HH}$ = 6.45 Hz, 2 H) ppm; ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 293 K) δ 178.5, 165.7, 145.5, 141.6, 140.6, 136.8, 134.8, 121.2, 120.5, 119.3, 118.3, 117.1, 116.3, 114.3, 107.8, 73.4, 48.4, 38.6, 29.8, 17.6, 14.6, -0.9 ppm; IR (υ cm^{-1}) (KBr): 3057 (m), 3027 (m), 2959 (s), 2876 (m), 1637 (m), 1604 (s), 1583 (m), 1534 (w), 1496 (s), 1456 (m), 1442 (m), 1372 (w), 1337 (w), 1316 (m), 1261 (s), 1224 (m), 1156 (m), 1098 (m), 1032 (m), 837 (m), 822 (m), 798 (s) cm^{-1}; Anal. Calcd for $C_{44}H_{60}N_5NdO_2Si_4$: C 71.08, H 6.15, N 6.48. Found: C 70.69, H 6.05, N 6.25.

[Nd(Bn-BOPA){NHCH$_2$C(Ph)$_2$C$_3$H$_7$}$_2$] (2c)

Yield: 74%. ^{1}H NMR (400.1 MHz, C_6D_6, 293 K) δ 14.16 (br s, 2 H), 12.13 (br s, 2 H), 11.60 (d, $^3J_{HH}$ = 6.88 Hz, 2 H), 10.04 (br s, 2 H), 7.10 (s, 4 H), 6.68 (d, $^3J_{HH}$ = 6.02 Hz, 4 H), 6.62 (br s, 4 H), 4.70 (t, $^3J_{HH}$ = 7.60 Hz, 2 H), 4.18 (t, $^3J_{HH}$ = 6.88 Hz, 4 H), 0.60 (br s, 20 H), 0.25 (br s, 6 H), -1.25 (d, $^3J_{HH}$ = 6.74 Hz, 4 H), -2.96 (br s, 2 H), -3.10 (br s, 2 H), -5.89 (br d, $^3J_{HH}$ = 5.31 Hz, 2 H), -17.99 (br s, 2 H), -22.00 (br s, 2 H), -32.49 (br s, 2 H) ppm; ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 293 K) δ 166.3, 155.8, 147.4, 137.5, 131.1, 130.3, 127.6, 127.5, 127.4, 126.1, 124.7, 120.2, 119.2, 113.0, 69.1, 66.1, 50.8, 41.0, 37.5, 16.2, 13.4, 0.0, -0.1, -0.3 ppm; IR (υ cm^{-1}) (KBr): 3087 (m), 3063 (m), 3027 (m), 2962 (s), 2874 (m), 1652 (m), 1635 (m), 1601 (m), 1560 (m), 1534 (m), 1496 (m), 1457 (m), 1445 (w), 1321 (w), 1261 (s), 1219 (m), 1183 (w), 1156 (w), 1096 (s), 1022 (s), 930 (m), 864 (m), 800 (s) cm^{-1}; Anal. Calcd for $C_{44}H_{60}N_5NdO_2Si_4$: C 71.57, H 6.19, N 6.32. Found: C 70.89, H 6.21, N 6.36.

2,2'-diphenyl-aminopentane (*pseudo* hydroamination substrate):

2,2'-diphenyl-aminopentane was prepared differently to those procedure reported.[4] To a solution of LDA in THF (150 ml), diphenylacetonitrile (1 equiv.) was added dropwise at -78 °C under an atmosphere of argon, with rapid stirring over the course of an hour. After stirring at -78 °C for 30 mins, 3-bromo-1-propane was added dropwise. The mixture was then allowed to warm to room temperature and left to stir overnight. Solvent was subsequently removed under reduced pressure and the remaining oil dissolved in DCM and washed with 2 M HCl. The DCM was removed under reduced pressure to yield the nitrile as pale yellow oil (92%). The next step was carried out without further purification. The nitrile was added as a THF solution (50 ml) to $LiAlH_4$ (2 equiv.) suspended in THF (200 ml) at 0 °C under an atmosphere of argon. The reaction mixture flask was then equipped with a reflux condenser and heated to 40 °C over night whilst under an inert atmosphere. Water and sodium hydroxide were subsequently added to the mixture dropwise at 0 °C following the 1:1:3 method to ensure all $LiAlH_4$ is consumed. The resulting white solid was washed well with ether (3 x 150 ml), and the ether extract washed with a brine solution. The ether was removed under reduced pressure to yield a pale yellow oil (78 %) which was purified by column chromatography (ether) to yield the product as an colourless oil (88%). Spectroscopic data are consistent with that reported.

2. Hydroamination catalysis

2,2-diphenyl-1-amino-pent-4-ene was prepared according to literature methods.[5] In a dinitrogen filled glovebox R-BOPA (0.05 mmol) was predissolved in C_6D_6 (0.7 ml) and added to $[Nd\{N(SiMe_3)_2\}_3]$ (0.05 mmol). The resulting mixture was agitated and left for two minutes. To this solution was added the corresponding amino olefin (0.5 mmol). The solution was transferred to a J. Young Teflon valve equipped NMR tube and sealed. All catalyst reactions were monitored *via* ^1H NMR spectroscopy periodically to monitor conversion. Upon completion, the reaction mixture was passed through silica to remove the metal residues, and a solution of (*R*)-(-)-*O*-acetylmandelic acid (0.51 mmol) predissolved in a minimal amount of $CDCl_3$ was added, producing the diastereomeric salts. The resulting enantiomeric

excesses (ee) were then determined by integration of the ^{1}H NMR spectra (methyl resonance) after fitting the signals using the iNMR software program.[6]

3. X-ray crystallography

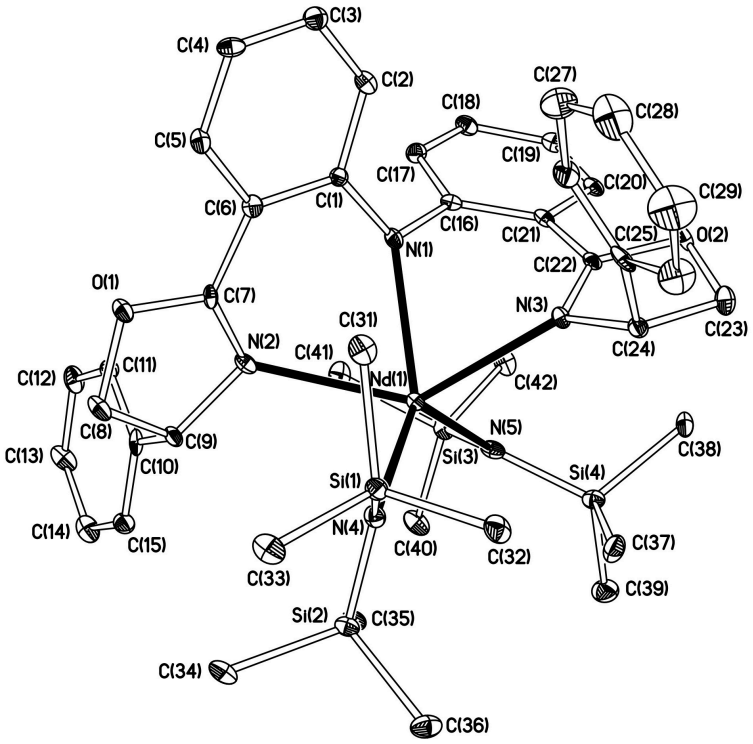


Figure 1. Molecular structure of [Nd(Ph-BOPA){N(SiMe$_3$)$_2$}$_2$] **1b**. Ellipsoids drawn at the 35% probability level. H atoms omitted for clarity

Single crystals of **1b** suitable for X-ray analysis were grown from a saturated solution in hexanes. X-ray data were collected on a Rigaku Saturn 724+ CCD diffractometer at 100 K, by the EPSRC National Crystallographic Service.[7] The structure was solved using direct methods with absorption corrections being applied as part of the data reduction scaling procedure. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations and treated with a riding model, with isotropic temperature factors (U_{iso}(H) = 1.3U_{eq}(C)) but not refined. Full least-square refinement was carried out on F^2. A final difference map revealed no significant maxima of

residual electron density. Structure solution and refinement were performed using the SHELX software suite.[8] Crystal data and experimental details are provided in Table 1.

Table 1. Crystal data and structure refinement for 1b

Empirical formula	$C_{42}H_{60}N_5NdO_2Si_4$	
Formula weight	923.55	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, C2	
Unit cell dimensions	a = 21.7130(15) Å	α = 90 °
	b = 10.0823(7) Å	β = 105.315(7) °
	c = 21.2984(14) Å	γ = 90 °
Volume	4497.0(5) $Å^3$	
Z, Calculated density	4, 1.364 Mg/m^3	
Absorption coefficient	1.301 mm^{-1}	
F(000)	1916	
Crystal size	0.08 × 0.05 × 0.02 mm	
Theta range for data collection	3.09 to 27.48 °	
Limiting indices	-28<=h<=28, -13<=k<=11, -27<=l<=27	
Reflections collected / unique	16161 / 9297 [R(int) = 0.0342]	
Completeness to theta = 27.48	99.5%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9745 and 0.9031	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9297 / 1 / 499	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2σ(I)]	R_1 = 0.0313, wR_2 = 0.0710	
R indices (all data)	R_1 = 0.0344, wR_2 = 0.0766	
Absolute structure parameter	-0.002(9)	
Largest diff. peak and hole	0.797 and -0.716 $e.Å^{-3}$	

Table 2. Selected bond lengths [Å] and angles [°] for 1b.

Nd(1)-N(5)	2.332(3)

Nd(1)-N(4)	2.360(3)
Nd(1)-N(1)	2.415(3)
Nd(1)-N(2)	2.535(4)
Nd(1)-N(3)	2.551(3)
Nd(1)-Si(3)	3.4236(10)
Si(1)-N(4)	1.710(4)
Si(1)-C(32)	1.852(5)
Si(1)-C(31)	1.869(5)
Si(1)-C(33)	1.879(4)
Si(2)-N(4)	1.714(4)
Si(2)-C(36)	1.857(5)
Si(2)-C(35)	1.881(4)
Si(2)-C(34)	1.886(4)
Si(3)-N(5)	1.698(4)
Si(3)-C(42)	1.866(4)
Si(3)-C(40)	1.871(5)
Si(3)-C(41)	1.882(5)
Si(4)-N(5)	1.714(4)
Si(4)-C(38)	1.865(4)
Si(4)-C(39)	1.873(5)
Si(4)-C(37)	1.873(5)
O(1)-C(7)	1.344(4)
O(1)-C(8)	1.443(6)
O(2)-C(22)	1.380(5)
O(2)-C(23)	1.443(5)
N(1)-C(1)	1.376(5)
N(1)-C(16)	1.397(4)
N(2)-C(7)	1.283(5)
N(2)-C(9)	1.504(5)
N(3)-C(22)	1.302(5)
N(3)-C(24)	1.478(5)
C(1)-C(2)	1.411(6)
C(1)-C(6)	1.424(5)
C(2)-C(3)	1.370(6)
C(3)-C(4)	1.388(5)

C(4)-C(5)	1.366(6)
C(5)-C(6)	1.403(6)
C(6)-C(7)	1.444(6)
C(8)-C(9)	1.532(6)
C(9)-C(10)	1.499(6)
C(10)-C(15)	1.375(6)
C(10)-C(11)	1.388(6)
C(11)-C(12)	1.370(6)
C(12)-C(13)	1.388(7)
C(13)-C(14)	1.364(7)
C(14)-C(15)	1.394(6)
C(16)-C(21)	1.415(6)
C(16)-C(17)	1.416(6)
C(17)-C(18)	1.369(5)
C(18)-C(19)	1.405(6)
C(19)-C(20)	1.372(6)
C(20)-C(21)	1.411(5)
C(21)-C(22)	1.442(5)
C(23)-C(24)	1.525(5)
C(24)-C(25)	1.509(6)
C(25)-C(26)	1.375(7)
C(25)-C(30)	1.383(6)
C(26)-C(27)	1.373(7)
C(27)-C(28)	1.379(9)
C(28)-C(29)	1.363(11)
C(29)-C(30)	1.363(8)

N(5)-Nd(1)-N(4)	117.50(12)
N(5)-Nd(1)-N(1)	110.03(11)
N(4)-Nd(1)-N(1)	132.39(11)
N(5)-Nd(1)-N(2)	128.78(12)
N(4)-Nd(1)-N(2)	82.03(11)
N(1)-Nd(1)-N(2)	70.12(11)
N(5)-Nd(1)-N(3)	90.45(11)
N(4)-Nd(1)-N(3)	106.12(11)

N(1)-Nd(1)-N(3)	69.97(11)
N(2)-Nd(1)-N(3)	131.50(11)
N(5)-Nd(1)-Si(3)	26.60(9)
N(4)-Nd(1)-Si(3)	128.73(9)
N(1)-Nd(1)-Si(3)	95.63(8)
N(2)-Nd(1)-Si(3)	103.40(8)
N(3)-Nd(1)-Si(3)	106.83(7)
N(4)-Si(1)-C(32)	112.7(2)
N(4)-Si(1)-C(31)	109.66(19)
C(32)-Si(1)-C(31)	107.8(2)
N(4)-Si(1)-C(33)	114.74(19)
C(32)-Si(1)-C(33)	105.8(2)
C(31)-Si(1)-C(33)	105.7(2)
N(4)-Si(2)-C(36)	114.4(2)
N(4)-Si(2)-C(35)	109.55(18)
C(36)-Si(2)-C(35)	107.8(2)
N(4)-Si(2)-C(34)	115.5(2)
C(36)-Si(2)-C(34)	103.3(2)
C(35)-Si(2)-C(34)	105.6(2)
N(5)-Si(3)-C(42)	113.6(2)
N(5)-Si(3)-C(40)	114.4(2)
C(42)-Si(3)-C(40)	106.7(2)
N(5)-Si(3)-C(41)	107.69(19)
C(42)-Si(3)-C(41)	108.6(3)
C(40)-Si(3)-C(41)	105.3(2)
N(5)-Si(3)-Nd(1)	37.96(12)
C(42)-Si(3)-Nd(1)	126.31(14)
C(40)-Si(3)-Nd(1)	125.90(13)
C(41)-Si(3)-Nd(1)	69.73(14)
N(5)-Si(4)-C(38)	113.14(19)
N(5)-Si(4)-C(39)	114.1(2)
C(38)-Si(4)-C(39)	104.8(2)
N(5)-Si(4)-C(37)	109.48(18)
C(38)-Si(4)-C(37)	109.0(2)
C(39)-Si(4)-C(37)	105.9(2)

C(7)-O(1)-C(8)	107.0(3)
C(22)-O(2)-C(23)	105.1(3)
C(1)-N(1)-C(16)	116.8(3)
C(1)-N(1)-Nd(1)	130.8(2)
C(16)-N(1)-Nd(1)	112.1(3)
C(7)-N(2)-C(9)	107.2(3)
C(7)-N(2)-Nd(1)	123.4(3)
C(9)-N(2)-Nd(1)	121.8(3)
C(22)-N(3)-C(24)	106.4(3)
C(22)-N(3)-Nd(1)	113.7(3)
C(24)-N(3)-Nd(1)	138.3(2)
Si(1)-N(4)-Si(2)	122.46(19)
Si(1)-N(4)-Nd(1)	119.27(18)
Si(2)-N(4)-Nd(1)	118.24(17)
Si(3)-N(5)-Si(4)	123.8(2)
Si(3)-N(5)-Nd(1)	115.43(19)
Si(4)-N(5)-Nd(1)	120.72(18)
N(1)-C(1)-C(2)	121.6(3)
N(1)-C(1)-C(6)	121.0(4)
C(2)-C(1)-C(6)	117.3(4)
C(3)-C(2)-C(1)	121.9(4)
C(2)-C(3)-C(4)	120.4(4)
C(5)-C(4)-C(3)	119.2(4)
C(4)-C(5)-C(6)	122.2(4)
C(5)-C(6)-C(1)	118.8(4)
C(5)-C(6)-C(7)	117.2(3)
C(1)-C(6)-C(7)	124.0(4)
N(2)-C(7)-O(1)	116.7(4)
N(2)-C(7)-C(6)	128.0(3)
O(1)-C(7)-C(6)	115.2(3)
O(1)-C(8)-C(9)	104.1(3)
C(10)-C(9)-N(2)	114.4(3)
C(10)-C(9)-C(8)	113.3(4)
N(2)-C(9)-C(8)	101.9(3)
C(15)-C(10)-C(11)	118.6(4)

C(15)-C(10)-C(9)	118.9(4)
C(11)-C(10)-C(9)	122.4(4)
C(12)-C(11)-C(10)	120.6(4)
C(11)-C(12)-C(13)	120.6(5)
C(14)-C(13)-C(12)	119.2(5)
C(13)-C(14)-C(15)	120.2(5)
C(10)-C(15)-C(14)	120.7(4)
N(1)-C(16)-C(21)	122.5(4)
N(1)-C(16)-C(17)	120.2(4)
C(21)-C(16)-C(17)	117.3(3)
C(18)-C(17)-C(16)	121.7(4)
C(17)-C(18)-C(19)	120.0(4)
C(20)-C(19)-C(18)	120.3(4)
C(19)-C(20)-C(21)	120.1(4)
C(20)-C(21)-C(16)	120.5(4)
C(20)-C(21)-C(22)	118.0(4)
C(16)-C(21)-C(22)	121.2(3)
N(3)-C(22)-O(2)	115.1(3)
N(3)-C(22)-C(21)	129.1(4)
O(2)-C(22)-C(21)	115.7(3)
O(2)-C(23)-C(24)	103.0(3)
N(3)-C(24)-C(25)	111.5(3)
N(3)-C(24)-C(23)	101.8(3)
C(25)-C(24)-C(23)	112.6(3)
C(26)-C(25)-C(30)	117.5(4)
C(26)-C(25)-C(24)	123.6(4)
C(30)-C(25)-C(24)	118.7(5)
C(27)-C(26)-C(25)	121.2(5)
C(26)-C(27)-C(28)	120.1(6)
C(29)-C(28)-C(27)	119.3(5)
C(30)-C(29)-C(28)	120.4(5)
C(29)-C(30)-C(25)	121.6(6)

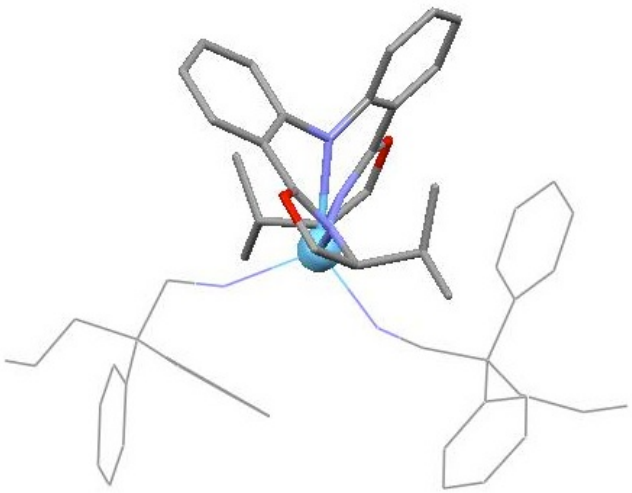
4. Density functional calculations

In consideration of accuracy and computational cost, calculations of the complexes bearing the hydroamination substrate (i.e. the catalyst resting state) were calculated using lanthanum, as a closed shell analogue of the neodymium complexes discussed within this communication. Lanthanum was selected as the closed shell analogue since its ionic radius most closely matches that of neodymium. All calculations were performed on the Gaussian 09 program.[9] Molecular geometries were optimised without restraints, and were followed by frequency calculations to ascertain the nature of the stationary point (minimum *vs.* saddle point). Calculations were performed using the B3LYP hybrid functional, with the Stuttgart/Dresden basis set with *pseudo* core potentials for the La, 6-31G(d,p) for all coordinating atoms, and 6-31G for all remaining centres. The gas phase relative energies in Kcal.mol^{-1} for the *exo* and *endo* isomers, for each of the three stereodirecting groups, are provided in Table 3. Coordinates of all optimised structures are provided in Tables 4 – 9.

Table 3. Relative energies of computed structures

	endo energy (E_h)	*exo* energy (E_h)	delta (Kcal)
iPr	-3107.073869	-3107.078045	2.62
Ph	-3333.251985	-3333.264295	7.72
Bn	-3411.811042	-3411.815289	2.67

Table 4. Calculated coordinates of *exo*-[La(iPr-BOPA)[$NHCH_2CPh_2CH_2CH{=}CH_2)_2$]



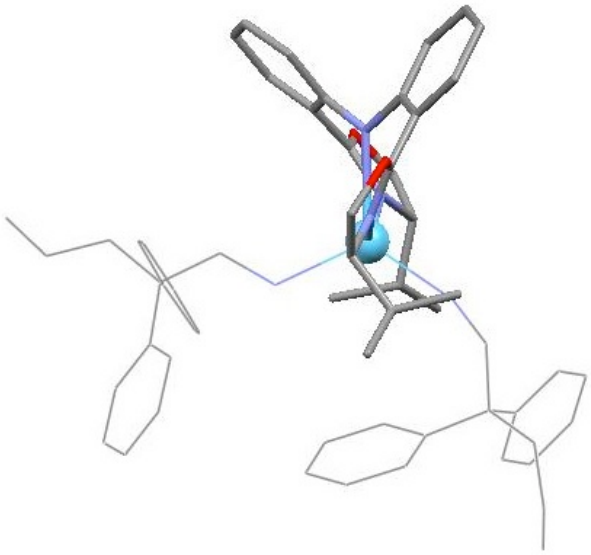
C	0.38	-0.068	0.371
C	0.156	0.113	1.778

C	1.305	0.388	2.577
C	2.584	0.446	2.044
C	2.793	0.242	0.668
C	1.698	-0.005	-0.146
H	1.158	0.525	3.642
H	3.428	0.638	2.7
H	3.792	0.279	0.248
H	1.832	-0.148	-1.21
N	-1.087	-0.031	2.379
C	-1.42	0.844	3.406
C	-1.139	2.237	3.275
C	-2.121	0.438	4.595
C	-1.554	3.17	4.21
H	-0.609	2.56	2.386
C	-2.536	1.418	5.535
C	-2.271	2.765	5.352
H	-1.338	4.222	4.049
H	-3.057	1.081	6.422
H	-2.607	3.494	6.082
C	-0.696	-0.232	-0.594
C	-2.667	-0.448	-1.718
C	-1.522	-0.321	-2.753
H	-1.324	-1.251	-3.291
H	-1.642	0.499	-3.46
N	-1.947	-0.523	-0.413
O	-0.332	-0.02	-1.926
C	-2.34	-0.955	4.97
C	-2.495	-3.22	5.132
C	-2.851	-2.603	6.506
H	-3.914	-2.68	6.742
H	-2.248	-2.968	7.336
N	-2.372	-2.028	4.238
O	-2.531	-1.165	6.334
La	-3.022	-1.555	1.721
C	-5.923	0.191	2.674
H	-6.146	1.199	2.277
H	-5.327	0.361	3.582
C	-2.986	-4.283	-0.682
H	-2.389	-3.653	-1.357
H	-3.877	-4.589	-1.261
N	-5.144	-0.614	1.752
H	-5.724	-0.848	0.941
C	-7.315	-0.411	3.166
C	-7.966	0.734	4.028
H	-7.263	1.037	4.815
H	-8.053	1.597	3.351
C	-9.323	0.468	4.629
H	-10.069	0.053	3.953

C	-8.254	-0.686	1.967
C	-9.258	-1.673	2.034
C	-8.204	0.109	0.804
C	-10.162	-1.866	0.984
H	-9.328	-2.3	2.916
C	-9.105	-0.084	-0.25
H	-7.458	0.891	0.713
C	-10.089	-1.074	-0.166
H	-10.924	-2.635	1.069
H	-9.036	0.542	-1.134
H	-10.788	-1.225	-0.983
C	-7.02	-1.687	3.969
C	-7.016	-1.713	5.375
C	-6.66	-2.877	3.297
C	-6.689	-2.879	6.082
H	-7.296	-0.832	5.936
C	-6.322	-4.04	3.998
H	-6.662	-2.891	2.215
C	-6.34	-4.049	5.399
H	-6.726	-2.872	7.168
H	-6.057	-4.94	3.451
H	-6.103	-4.957	5.946
C	-9.671	0.748	5.891
H	-8.965	1.17	6.604
H	-10.676	0.57	6.262
N	-3.347	-3.502	0.485
H	-4.122	-3.977	0.961
C	-2.108	-5.604	-0.461
C	-2.18	-6.377	-1.828
H	-3.248	-6.586	-1.995
H	-1.874	-5.707	-2.642
C	-2.735	-6.507	0.62
C	-1.95	-7.299	1.48
C	-4.135	-6.638	0.717
C	-2.537	-8.165	2.412
H	-0.87	-7.237	1.423
C	-4.726	-7.501	1.647
H	-4.78	-6.071	0.053
C	-3.928	-8.267	2.506
H	-1.902	-8.764	3.058
H	-5.808	-7.581	1.694
H	-4.384	-8.938	3.227
C	-0.691	-5.127	-0.109
C	0.345	-5.068	-1.059
C	-0.428	-4.591	1.17
C	1.587	-4.5	-0.748
H	0.199	-5.479	-2.049
C	0.809	-4.018	1.482

H	-1.208	-4.629	1.919
C	1.826	-3.966	0.521
H	2.366	-4.475	-1.504
H	0.978	-3.606	2.473
H	2.783	-3.514	0.758
C	-1.424	-7.679	-1.92
H	-1.557	-8.364	-1.084
C	-0.66	-8.05	-2.954
H	-0.165	-9.016	-2.984
H	-0.5	-7.404	-3.815
H	-3.211	-1.389	-1.858
H	-3.323	-3.838	4.768
C	-1.203	-4.082	5.11
H	-1.036	-4.344	4.057
C	-1.42	-5.397	5.887
H	-0.53	-6.032	5.819
H	-1.608	-5.21	6.953
H	-2.268	-5.963	5.485
C	0.041	-3.324	5.608
H	0.204	-2.408	5.03
H	-0.043	-3.05	6.667
H	0.932	-3.953	5.503
C	-3.706	0.708	-1.722
H	-4.362	0.52	-0.858
C	-4.567	0.652	-3
H	-5.354	1.414	-2.967
H	-3.967	0.841	-3.9
H	-5.05	-0.326	-3.116
C	-3.069	2.095	-1.527
H	-2.499	2.141	-0.594
H	-2.396	2.358	-2.354
H	-3.848	2.864	-1.482

Table 5. Calculated coordinates of *endo*-[La(iPr-BOPA)[$NHCH_2CPh_2CH_2CH{=}CH_2)_2$]



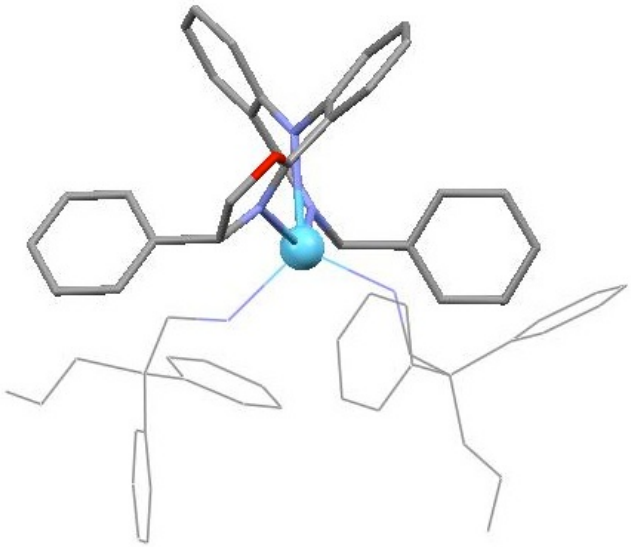
C	2.104	-2.597	-2.949
C	2.436	-3.092	-1.644
C	3.785	-3.507	-1.443
C	4.748	-3.412	-2.435
C	4.414	-2.905	-3.705
C	3.106	-2.518	-3.949
H	4.052	-3.886	-0.463
H	5.767	-3.721	-2.224
H	5.165	-2.823	-4.483
H	2.819	-2.155	-4.928
N	1.534	-3.136	-0.58
C	1.52	-4.306	0.178
C	1.564	-5.571	-0.477
C	1.434	-4.326	1.609
C	1.503	-6.77	0.216
H	1.625	-5.575	-1.559
C	1.39	-5.565	2.294
C	1.411	-6.776	1.62
H	1.519	-7.707	-0.333
H	1.346	-5.547	3.376
H	1.361	-7.711	2.167
C	0.743	-2.265	-3.358
C	-1.454	-1.697	-3.539
C	-0.929	-2.089	-4.947
H	-2.217	-2.413	-3.204
H	-0.968	-1.276	-5.674
H	-1.41	-2.977	-5.361
N	-0.262	-1.858	-2.653
O	0.494	-2.421	-4.722
C	1.483	-3.128	2.439

C	1.303	-1.079	3.416
C	2.137	-1.995	4.341
H	1.872	-0.187	3.135
H	1.759	-2.078	5.36
H	3.197	-1.732	4.357
N	1.099	-1.914	2.19
O	2.017	-3.33	3.713
C	-2.077	-0.279	-3.443
C	-0.056	-0.619	4.017
La	0.112	-1.106	-0.134
C	-3.117	-0.843	1.318
H	-3.732	-1.721	1.584
H	-2.52	-0.624	2.214
C	2.439	1.097	-1.241
H	3.048	0.206	-1.022
H	2.387	1.149	-2.345
N	-2.218	-1.116	0.213
H	-2.747	-1.574	-0.535
C	-4.121	0.396	1.19
C	-5.048	0.287	2.461
H	-4.424	0.19	3.359
H	-5.579	-0.671	2.358
C	-6.066	1.379	2.663
H	-6.689	1.614	1.801
C	-5.03	0.264	-0.049
C	-5.596	1.393	-0.674
C	-5.422	-1.003	-0.526
C	-6.501	1.265	-1.734
H	-5.324	2.384	-0.329
C	-6.327	-1.136	-1.586
H	-5.032	-1.901	-0.061
C	-6.871	-0.002	-2.199
H	-6.921	2.156	-2.19
H	-6.611	-2.128	-1.927
H	-7.575	-0.104	-3.019
C	-3.261	1.667	1.181
C	-2.938	2.353	2.369
C	-2.653	2.117	-0.009
C	-2.061	3.445	2.367
H	-3.384	2.053	3.308
C	-1.781	3.213	-0.016
H	-2.878	1.613	-0.94
C	-1.478	3.884	1.174
H	-1.845	3.958	3.299
H	-1.338	3.543	-0.951
H	-0.805	4.735	1.165
C	-6.275	2.03	3.814
H	-5.685	1.829	4.706

H	-7.045	2.789	3.912
N	1.13	0.926	-0.628
H	0.592	1.79	-0.708
C	3.319	2.341	-0.789
C	4.585	2.295	-1.729
H	4.193	2.378	-2.754
H	5.048	1.302	-1.663
C	2.586	3.674	-1.075
C	2.864	4.84	-0.333
C	1.691	3.795	-2.157
C	2.262	6.064	-0.644
H	3.554	4.787	0.501
C	1.086	5.019	-2.47
H	1.459	2.932	-2.77
C	1.365	6.161	-1.713
H	2.5	6.943	-0.051
H	0.4	5.077	-3.31
H	0.896	7.11	-1.955
C	3.665	2.17	0.698
C	4.879	1.602	1.123
C	2.724	2.514	1.692
C	5.161	1.412	2.482
H	5.631	1.319	0.398
C	3.01	2.344	3.05
H	1.768	2.928	1.399
C	4.233	1.793	3.456
H	6.114	0.982	2.775
H	2.28	2.656	3.792
H	4.46	1.673	4.511
C	5.632	3.362	-1.533
H	5.265	4.386	-1.49
C	6.95	3.138	-1.458
H	7.664	3.949	-1.353
H	7.368	2.134	-1.504
H	-0.569	-0.057	3.222
C	0.171	0.355	5.19
C	-0.961	-1.794	4.431
H	-1.146	-2.473	3.593
H	-1.931	-1.419	4.778
H	-0.522	-2.373	5.252
H	0.796	1.203	4.89
H	0.657	-0.143	6.039
H	-0.786	0.75	5.548
C	-3.367	-0.206	-4.285
C	-1.09	0.844	-3.813
H	-2.358	-0.149	-2.388
H	-0.748	0.766	-4.853
H	-0.215	0.834	-3.155

H	-1.58	1.819	-3.705
H	-3.156	-0.309	-5.358
H	-3.864	0.759	-4.138
H	-4.078	-0.988	-3.996

Table 6. Calculated coordinates of *exo*-[La(Ph-BOPA)[$NHCH_2CPh_2CH_2CH{=}CH_2)_2$]



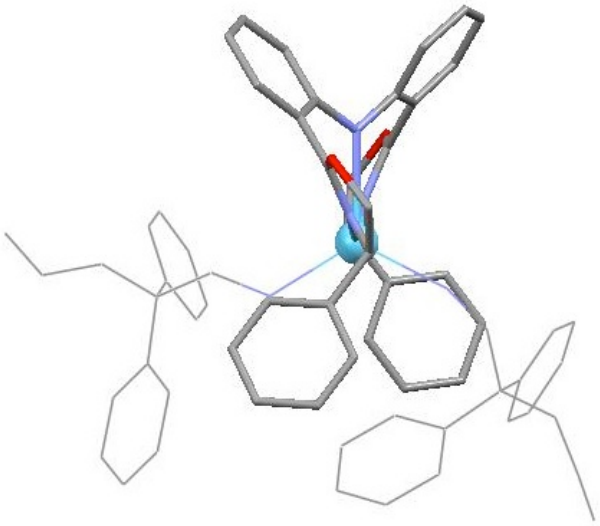
C	0.304	0.003	0.589
C	0.033	0.3	1.967
C	1.163	0.451	2.821
C	2.465	0.358	2.354
C	2.717	0.091	0.996
C	1.644	-0.094	0.138
H	0.975	0.672	3.866
H	3.293	0.505	3.042
H	3.734	0.026	0.624
H	1.815	-0.331	-0.905
N	-1.251	0.501	2.476
C	-1.573	-0.135	3.665
C	-1.103	-1.46	3.92
C	-2.427	0.444	4.668
C	-1.471	-2.176	5.047
H	-0.458	-1.917	3.179
C	-2.786	-0.315	5.811
C	-2.329	-1.608	6.007
H	-1.102	-3.189	5.18
H	-3.427	0.154	6.548
H	-2.626	-2.168	6.887
C	-0.741	-0.325	-0.374
C	-2.674	-0.616	-1.54
C	-1.539	-1.422	-2.248

H	-1.346	-1.088	-3.267
H	-1.7	-2.501	-2.221
N	-1.991	0.011	-0.377
O	-0.334	-1.13	-1.438
C	-2.876	1.826	4.633
C	-3.357	4.001	4.137
C	-3.777	3.722	5.611
H	-4.859	3.751	5.751
H	-3.275	4.362	6.337
N	-2.904	2.667	3.644
O	-3.323	2.334	5.853
La	-2.728	2.073	1.106
C	-6.077	1.169	1.236
H	-6.223	0.207	0.712
H	-5.794	0.905	2.266
C	-2.37	4.948	-0.709
H	-3.361	4.589	-1.032
H	-2.562	5.886	-0.156
N	-5.005	1.961	0.658
H	-5.301	2.311	-0.258
C	-7.517	1.838	1.338
C	-8.457	0.682	1.851
H	-8.045	0.269	2.781
H	-8.371	-0.118	1.1
C	-9.918	1.002	2.036
H	-10.403	1.513	1.206
C	-8.028	2.268	-0.058
C	-8.963	3.312	-0.205
C	-7.651	1.566	-1.22
C	-9.489	3.649	-1.457
H	-9.278	3.872	0.668
C	-8.172	1.905	-2.475
H	-6.945	0.746	-1.156
C	-9.094	2.949	-2.602
H	-10.208	4.459	-1.536
H	-7.856	1.348	-3.352
H	-9.497	3.211	-3.575
C	-7.426	3.024	2.31
C	-7.836	2.934	3.653
C	-6.845	4.24	1.888
C	-7.699	4.017	4.533
H	-8.293	2.026	4.022
C	-6.711	5.324	2.761
H	-6.502	4.333	0.867
C	-7.142	5.221	4.091
H	-8.047	3.92	5.557
H	-6.283	6.255	2.397
H	-7.057	6.069	4.765

C	-10.647	0.663	3.107
H	-10.213	0.144	3.96
H	-11.708	0.885	3.172
N	-1.76	3.929	0.125
H	-0.841	4.249	0.439
C	-1.612	5.366	-2.046
C	-2.454	6.566	-2.622
H	-2.436	7.339	-1.838
H	-3.503	6.258	-2.719
C	-0.193	5.897	-1.736
C	0.832	5.847	-2.702
C	0.098	6.534	-0.513
C	2.093	6.4	-2.456
H	0.642	5.364	-3.654
C	1.361	7.083	-0.262
H	-0.658	6.604	0.261
C	2.367	7.02	-1.231
H	2.861	6.345	-3.222
H	1.554	7.557	0.696
H	3.346	7.445	-1.037
C	-1.587	4.14	-2.97
C	-2.523	3.955	-4.004
C	-0.662	3.1	-2.737
C	-2.522	2.796	-4.79
H	-3.252	4.724	-4.222
C	-0.653	1.943	-3.523
H	0.058	3.203	-1.935
C	-1.582	1.786	-4.56
H	-3.248	2.693	-5.591
H	0.083	1.168	-3.326
H	-1.564	0.899	-5.188
C	-1.985	7.19	-3.911
H	-0.93	7.454	-3.956
C	-2.774	7.475	-4.955
H	-2.39	7.959	-5.849
H	-3.836	7.239	-4.957
H	-4.233	4.304	3.555
H	-3.023	0.188	-2.198
C	-3.865	-1.473	-1.138
C	-4.959	-1.59	-2.011
C	-3.875	-2.191	0.068
C	-6.042	-2.416	-1.69
H	-4.964	-1.03	-2.943
C	-4.96	-3.013	0.392
H	-3.044	-2.091	0.759
C	-6.045	-3.13	-0.486
H	-6.881	-2.497	-2.373
H	-4.96	-3.557	1.332

H	-6.886	-3.767	-0.232
C	-2.28	5.066	3.985
C	-2.63	6.352	3.544
C	-0.94	4.8	4.311
C	-1.663	7.358	3.438
H	-3.663	6.562	3.279
C	0.028	5.803	4.204
H	-0.653	3.804	4.632
C	-0.33	7.086	3.769
H	-1.948	8.348	3.096
H	1.062	5.584	4.455
H	0.421	7.865	3.689

Table 7. Calculated coordinates of *endo*-[La(Ph-BOPA)[$NHCH_2CPh_2CH_2CH{=}CH_2)_2$]



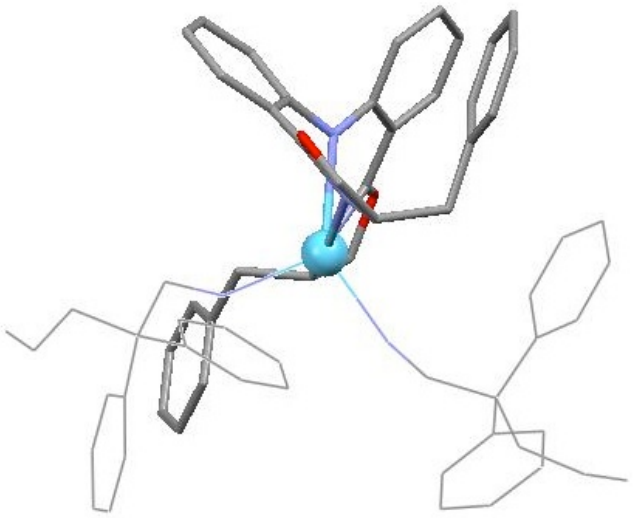
C	-1.962	4.087	-0.405
C	-1.754	3.589	-1.734
C	-2.753	3.921	-2.697
C	-3.876	4.668	-2.38
C	-4.065	5.151	-1.072
C	-3.107	4.868	-0.11
H	-2.617	3.55	-3.707
H	-4.617	4.873	-3.147
H	-4.941	5.737	-0.818
H	-3.219	5.25	0.898
N	-0.663	2.805	-2.11
C	-0.054	3.169	-3.316
C	0.208	4.545	-3.579
C	0.357	2.239	-4.328
C	0.835	4.979	-4.738
H	-0.087	5.265	-2.825

C	0.977	2.708	-5.512
C	1.228	4.055	-5.722
H	1.027	6.038	-4.877
H	1.252	1.979	-6.265
H	1.718	4.387	-6.631
C	-1.005	3.903	0.676
C	0.492	3.153	2.213
C	0.167	4.645	2.515
H	1.568	3.006	2.075
H	-0.159	4.828	3.538
H	0.983	5.32	2.245
N	-0.203	2.912	0.911
O	-0.97	4.935	1.615
C	0.106	0.807	-4.247
C	-0.171	-1.373	-3.642
C	-0.437	-1.24	-5.16
H	-1.036	-1.795	-3.128
H	0.145	-1.919	-5.78
H	-1.499	-1.316	-5.403
N	-0.011	0.055	-3.202
O	-0.004	0.145	-5.473
C	0.003	2.221	3.316
C	0.902	1.793	4.307
C	-1.348	1.851	3.416
C	0.458	1.015	5.383
H	1.953	2.06	4.233
C	-1.792	1.074	4.493
H	-2.051	2.163	2.652
C	-0.891	0.657	5.48
H	1.166	0.687	6.137
H	-2.84	0.798	4.56
H	-1.237	0.057	6.316
C	1.067	-2.184	-3.279
C	1.039	-3.04	-2.166
C	2.253	-2.078	-4.027
C	2.167	-3.793	-1.818
H	0.134	-3.106	-1.57
C	3.378	-2.833	-3.683
H	2.3	-1.403	-4.877
C	3.336	-3.698	-2.581
H	2.132	-4.442	-0.95
H	4.286	-2.746	-4.272
H	4.209	-4.287	-2.318
La	0.135	0.825	-0.709
C	3.554	-0.136	-0.338
H	4.338	0.289	-0.99
H	3.237	-1.069	-0.821
C	-2.785	-0.476	0.344

H	-3.105	0.2	-0.465
H	-3.019	0.061	1.284
N	2.408	0.75	-0.234
H	2.742	1.699	-0.041
C	4.281	-0.588	1.016
C	5.636	-1.236	0.545
H	5.422	-2.017	-0.197
H	6.17	-0.442	0.002
C	6.554	-1.773	1.614
H	6.716	-1.121	2.471
C	4.628	0.63	1.896
C	4.664	0.546	3.302
C	5.016	1.852	1.31
C	5.053	1.639	4.088
H	4.382	-0.382	3.785
C	5.4	2.948	2.092
H	5.032	1.951	0.23
C	5.417	2.849	3.487
H	5.079	1.538	5.169
H	5.693	3.875	1.608
H	5.72	3.696	4.095
C	3.344	-1.585	1.714
C	3.533	-2.978	1.645
C	2.177	-1.12	2.357
C	2.599	-3.868	2.19
H	4.421	-3.383	1.179
C	1.24	-2.007	2.899
H	2.004	-0.055	2.431
C	1.443	-3.389	2.816
H	2.782	-4.937	2.13
H	0.356	-1.613	3.39
H	0.715	-4.077	3.234
C	7.201	-2.943	1.553
H	7.079	-3.627	0.715
H	7.882	-3.264	2.336
N	-1.363	-0.737	0.183
H	-1.057	-1.444	0.855
C	-3.8	-1.698	0.296
C	-5.212	-1.043	0.576
H	-5.138	-0.607	1.584
H	-5.356	-0.198	-0.109
C	-3.527	-2.703	1.44
C	-4.035	-4.018	1.389
C	-2.858	-2.316	2.618
C	-3.874	-4.906	2.457
H	-4.556	-4.352	0.498
C	-2.693	-3.204	3.688
H	-2.449	-1.317	2.711

C	-3.199	-4.505	3.615
H	-4.278	-5.912	2.382
H	-2.168	-2.872	4.579
H	-3.072	-5.193	4.444
C	-3.712	-2.347	-1.094
C	-4.478	-1.874	-2.176
C	-2.794	-3.384	-1.358
C	-4.359	-2.43	-3.456
H	-5.189	-1.071	-2.028
C	-2.678	-3.951	-2.632
H	-2.177	-3.762	-0.552
C	-3.465	-3.48	-3.69
H	-4.977	-2.049	-4.263
H	-1.972	-4.76	-2.796
H	-3.388	-3.929	-4.676
C	-6.419	-1.942	0.529
H	-6.385	-2.821	1.17
C	-7.518	-1.71	-0.199
H	-8.375	-2.376	-0.172
H	-7.607	-0.841	-0.849

Table 8. Calculated coordinates of *exo*-[La(Bn-BOPA)[$NHCH_2CPh_2CH_2CH{=}CH_2)_2$]



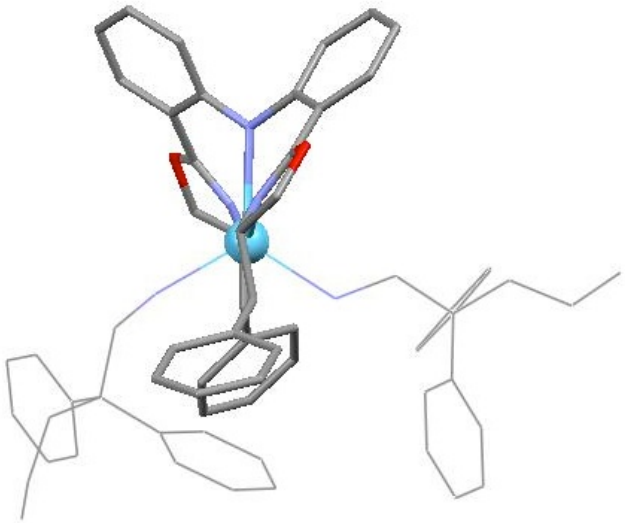
C	0.007	0.22	-0.031
C	0.03	0.256	1.406
C	1.314	0.35	2.021
C	2.49	0.365	1.287
C	2.455	0.299	-0.118
C	1.226	0.235	-0.755
H	1.352	0.381	3.104
H	3.443	0.418	1.805
H	3.373	0.3	-0.695

H	1.173	0.205	-1.835
N	-1.109	0.144	2.193
C	-1.188	0.939	3.333
C	-0.79	2.308	3.273
C	-1.731	0.482	4.585
C	-0.948	3.177	4.34
H	-0.38	2.67	2.337
C	-1.88	1.397	5.66
C	-1.507	2.726	5.55
H	-0.65	4.216	4.232
H	-2.286	1.021	6.591
H	-1.64	3.404	6.385
C	-1.219	0.266	-0.809
C	-3.355	0.369	-1.584
C	-2.394	0.508	-2.785
H	-2.37	-0.38	-3.423
H	-2.56	1.399	-3.39
N	-2.445	0.034	-0.451
O	-1.062	0.64	-2.146
C	-2.05	-0.912	4.874
C	-2.49	-3.145	4.863
C	-2.489	-2.653	6.33
H	-3.483	-2.67	6.784
H	-1.762	-3.156	6.967
N	-2.324	-1.894	4.068
O	-2.068	-1.236	6.227
La	-3.256	-1.148	1.715
C	-5.856	0.741	3.146
H	-6.043	1.793	2.863
H	-5.144	0.786	3.983
C	-3.873	-3.532	-0.942
H	-3.177	-2.952	-1.564
H	-4.858	-3.463	-1.44
N	-5.26	-0.032	2.072
H	-5.952	-0.16	1.329
C	-7.223	0.19	3.751
C	-7.678	1.288	4.785
H	-6.867	1.465	5.503
H	-7.776	2.216	4.202
C	-8.972	1.054	5.522
H	-9.824	0.765	4.907
C	-8.311	0.097	2.654
C	-9.382	-0.812	2.761
C	-8.319	0.982	1.557
C	-10.409	-0.844	1.811
H	-9.41	-1.506	3.594
C	-9.341	0.949	0.601
H	-7.524	1.709	1.439

C	-10.393	0.035	0.722
H	-11.221	-1.556	1.924
H	-9.311	1.639	-0.236
H	-11.187	0.008	-0.017
C	-6.934	-1.174	4.396
C	-6.745	-1.332	5.781
C	-6.763	-2.318	3.584
C	-6.422	-2.578	6.336
H	-6.875	-0.489	6.447
C	-6.436	-3.563	4.132
H	-6.906	-2.231	2.515
C	-6.267	-3.701	5.517
H	-6.313	-2.669	7.413
H	-6.327	-4.425	3.48
H	-6.039	-4.671	5.948
C	-9.145	1.222	6.839
H	-8.329	1.518	7.495
H	-10.111	1.076	7.313
N	-3.899	-2.946	0.385
H	-4.661	-3.39	0.914
C	-3.403	-5.052	-1.088
C	-3.786	-5.456	-2.561
H	-4.878	-5.334	-2.627
H	-3.358	-4.726	-3.261
C	-4.2	-5.972	-0.138
C	-3.641	-7.144	0.408
C	-5.559	-5.715	0.135
C	-4.399	-8.009	1.207
H	-2.602	-7.38	0.209
C	-6.319	-6.576	0.936
H	-6.04	-4.84	-0.289
C	-5.741	-7.727	1.481
H	-3.937	-8.905	1.61
H	-7.364	-6.349	1.125
H	-6.328	-8.397	2.102
C	-1.89	-5.08	-0.829
C	-0.95	-5.07	-1.876
C	-1.393	-4.991	0.489
C	0.425	-4.986	-1.621
H	-1.279	-5.145	-2.904
C	-0.021	-4.909	0.747
H	-2.097	-4.986	1.312
C	0.898	-4.906	-0.309
H	1.123	-4.989	-2.453
H	0.334	-4.845	1.771
H	1.963	-4.843	-0.11
C	-3.438	-6.855	-3
H	-3.711	-7.65	-2.308

C	-2.874	-7.175	-4.171
H	-2.677	-8.205	-4.451
H	-2.587	-6.418	-4.899
H	-4.054	-0.46	-1.731
H	-3.462	-3.582	4.609
C	-1.402	-4.2	4.522
H	-1.455	-4.379	3.442
C	-4.16	1.655	-1.253
H	-4.623	1.507	-0.268
C	-5.215	1.977	-2.292
C	-5.011	2.986	-3.25
C	-6.421	1.252	-2.332
C	-5.977	3.258	-4.226
H	-4.095	3.571	-3.222
C	-7.388	1.521	-3.305
H	-6.608	0.482	-1.588
C	-7.168	2.524	-4.258
H	-5.802	4.044	-4.954
H	-8.312	0.951	-3.318
H	-7.919	2.734	-5.013
C	0.017	-3.849	4.924
C	0.596	-4.425	6.07
C	0.792	-2.957	4.16
C	1.906	-4.112	6.451
H	0.021	-5.135	6.659
C	2.103	-2.646	4.537
H	0.37	-2.503	3.269
C	2.664	-3.221	5.684
H	2.334	-4.57	7.338
H	2.684	-1.961	3.929
H	3.682	-2.98	5.974
H	-3.453	2.489	-1.154
H	-1.697	-5.139	5.009

Table 9. Calculated coordinates of *endo*-[La(Bn-BOPA)[$NHCH_2CPh_2CH_2CH{=}CH_2)_2$]



C	0.202	-0.125	0.383
C	0.008	-0.223	1.8
C	1.172	-0.407	2.598
C	2.445	-0.452	2.051
C	2.626	-0.329	0.662
C	1.514	-0.178	-0.151
H	1.037	-0.484	3.671
H	3.305	-0.571	2.704
H	3.621	-0.357	0.23
H	1.629	-0.11	-1.226
N	-1.237	-0.091	2.417
C	-1.579	-1.028	3.382
C	-1.228	-2.399	3.199
C	-2.342	-0.71	4.56
C	-1.635	-3.394	4.071
H	-0.65	-2.658	2.319
C	-2.747	-1.754	5.433
C	-2.415	-3.077	5.201
H	-1.361	-4.426	3.871
H	-3.319	-1.485	6.312
H	-2.745	-3.854	5.881
C	-0.898	-0.069	-0.574
C	-2.873	0.118	-1.689
C	-1.783	-0.328	-2.697
H	-3.615	-0.677	-1.542
H	-1.567	0.424	-3.46
H	-1.984	-1.287	-3.174
N	-2.129	0.299	-0.408
O	-0.57	-0.489	-1.863
C	-2.635	0.647	4.998

C	-2.85	2.887	5.322
C	-3.333	2.163	6.596
H	-1.872	3.356	5.493
H	-4.421	2.192	6.711
H	-2.853	2.494	7.515
N	-2.644	1.773	4.344
O	-2.931	0.759	6.361
C	-3.617	1.414	-2.092
C	-3.832	3.953	4.796
La	-2.892	1.673	1.719
C	-6.326	1.455	2.26
H	-6.754	0.555	2.739
H	-6.014	2.105	3.093
C	-0.859	3.968	0.245
H	-0.123	3.464	0.89
H	-0.681	3.564	-0.772
N	-5.165	1.153	1.446
H	-5.403	0.401	0.794
C	-7.545	2.231	1.577
C	-8.675	2.243	2.676
H	-8.263	2.632	3.616
H	-8.914	1.185	2.867
C	-9.953	2.968	2.342
H	-10.402	2.723	1.381
C	-8.095	1.454	0.363
C	-8.767	2.11	-0.688
C	-8.044	0.046	0.319
C	-9.354	1.395	-1.738
H	-8.826	3.192	-0.687
C	-8.628	-0.674	-0.731
H	-7.557	-0.505	1.116
C	-9.288	-0.002	-1.767
H	-9.866	1.933	-2.53
H	-8.573	-1.758	-0.733
H	-9.749	-0.559	-2.577
C	-7.035	3.633	1.218
C	-7.18	4.726	2.093
C	-6.277	3.838	0.046
C	-6.6	5.97	1.811
H	-7.765	4.624	2.998
C	-5.7	5.08	-0.242
H	-6.149	3.02	-0.651
C	-5.855	6.154	0.642
H	-6.738	6.793	2.506
H	-5.127	5.211	-1.155
H	-5.407	7.117	0.417
C	-10.574	3.837	3.149
H	-10.171	4.111	4.122

H	-11.513	4.309	2.872
N	-2.194	3.663	0.738
H	-2.883	4.241	0.251
C	-0.409	5.49	0.19
C	1.001	5.466	-0.515
H	0.827	5.019	-1.505
H	1.661	4.77	0.019
C	-1.356	6.319	-0.711
C	-1.533	7.703	-0.517
C	-1.993	5.736	-1.825
C	-2.324	8.467	-1.384
H	-1.053	8.188	0.325
C	-2.786	6.496	-2.694
H	-1.875	4.677	-2.023
C	-2.959	7.867	-2.476
H	-2.439	9.531	-1.204
H	-3.265	6.014	-3.541
H	-3.574	8.457	-3.148
C	-0.355	6.022	1.63
C	0.843	6.07	2.366
C	-1.542	6.402	2.292
C	0.864	6.503	3.697
H	1.778	5.788	1.902
C	-1.523	6.848	3.617
H	-2.485	6.356	1.762
C	-0.318	6.904	4.328
H	1.808	6.54	4.233
H	-2.449	7.154	4.093
H	-0.3	7.263	5.353
C	1.7	6.788	-0.708
H	1.097	7.587	-1.135
C	2.991	7.018	-0.437
H	3.453	7.982	-0.63
H	3.638	6.251	-0.015
H	-3.368	4.46	3.939
H	-4.286	1.687	-1.266
C	-4.24	4.967	5.854
C	-3.28	5.717	6.56
C	-5.598	5.169	6.156
C	-3.67	6.638	7.538
H	-2.226	5.59	6.335
C	-5.99	6.093	7.131
H	-6.352	4.602	5.616
C	-5.026	6.829	7.828
H	-2.915	7.207	8.072
H	-7.045	6.235	7.346
H	-5.327	7.545	8.586
C	-4.413	1.265	-3.375

C	-3.914	1.744	-4.599
C	-5.667	0.627	-3.365
C	-4.639	1.577	-5.785
H	-2.959	2.262	-4.622
C	-6.394	0.462	-4.548
H	-6.086	0.274	-2.427
C	-5.88	0.933	-5.763
H	-4.238	1.956	-6.72
H	-7.365	-0.022	-4.516
H	-6.446	0.807	-6.681
H	-4.73	3.445	4.425
H	-2.879	2.219	-2.187

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