Supplementary Information

IR data of the new compounds, HSQC spectra of **5** and **6** (Figure S1 and S2), and full crystallographic data for compounds **1**, **2**, **8** and **9** (Tables S1–S8). ORTEP representation of compounds **1**, **2**, **8** and **9** (Figures S3–S6).

IR data of the new compounds

Li[Ph–C≡C–C(NCy)$_2$]·THF (**2**). IR (KBr): ν (cm^{-1}) 3678 (w), 3438 (w), 3222 (m), 3081 (m), 3033 (m), 2926 (vs), 2852 (s), 2691 (w), 2663 (w), 2587 (w), 2363 (w), 2217 (m, C≡C), 1941 (w), 1891 (w), 1799 (w), 1635 (m), 1610 (vs, NCN), 1492 (vs), 1446 (m), 1388 (m), 1360 (m), 1343 (m), 1311 (m), 1282 (m), 1213 (m), 1181 (m), 1156 (m), 1125 (m), 1101 (m), 1069 (m), 1027 (m), 912 (w), 889 (m), 843 (w), 797 (w), 755 (m), 709 (w), 690 (m), 639 (w), 616 (w), 555 (w), 527 (w), 448 (w), 428 (w).

Li[Ph–C≡C–C(NCy)$_2$]·Et$_2$O (**3**). IR (KBr): ν (cm^{-1}) 3676 (w), 3369 (w), 3213 (w), 3059 (m), 2961 (vs), 2865 (s), 2705 (w), 2610 (m), 2360 (w), 2211 (w, C≡C), 2126 (w), 1948 (w), 1879 (w), 1752 (w), 1592 (s, NCN), 1504 (vs), 1442 (s), 1372 (s), 1352 (s), 1323 (vs), 1226 (m), 1175 (s), 1133 (s), 1069 (m), 1051 (s), 1031 (s), 998 (m), 946 (m), 913 (s), 849 (m), 821 (m), 755 (vs), 714 (m), 690 (vs), 630 (w), 543 (m), 528 (s), 515 (m), 476 (w), 453 (w), 435 (w).

[Ph–C≡C–C(NCy)$_2$]$_3$Ce (**4**). IR (KBr): ν (cm^{-1}) 3439 (s), 3222 (s), 2973 (s), 2930 (vs), 2855 (w), 2217 (w, C≡C), 1637 (vs, NCN), 1448 (s), 1370 (m), 1309 (w), 1242 (s), 1180 (s), 1153 (s), 1079 (m), 1038 (m), 987 (m), 962 (w), 916 (w), 890 (m), 834 (w), 755 (s), 690 (s), 646 (w), 627 (w), 529 (w), 501 (w), 472 (w).

[Ph–C≡C–C(NCy)$_2$]$_3$Ho (**7**). IR (KBr): ν (cm^{-1}) 3671 (w), 3362 (w), 3222 (w), 3063 (m), 2963 (vs), 2868 (s), 2710 (w), 2622 (m), 2363 (w), 2221 (w, C≡C), 2128 (w), 1952 (w), 1882 (w), 1754 (w), 1599 (s, NCN), 1518 (vs), 1452 (s), 1363 (s), 1318 (s), 1229 (m), 1072 (m), 1065 (s), 1036 (s), 999 (m), 949 (m), 854 (m), 822 (m), 758 (vs), 692 (vs), 652 (w), 534 (m), 531 (s), 512 (m), 479 (w), 451 (w).

[Ph$_2$P(NSiMe$_3$)$_2$]$_2$Ce(μ-Cl)$_2$Li(THF)$_2$ (**9**). IR (KBr): ν (cm^{-1}) 3380 (m), 3222 (m), 3075 (s), 2952 (vs), 2897 (s), 2541 (w), 2029 (w), 1959 (w), 1821 (w), 1776 (w), 1638 (s), 1591 (m), 1437 (s), 1306 (s), 1246 (vs), 1154 (m), 1116 (m), 1044 (w), 1028 (w), 998 (m), 933 (m), 841 (s), 776 (m), 748 (s), 695 (s), 661 (w), 576 (w), 555 (w), 530 (s), 505 (m), 451 (w), 435 (w).

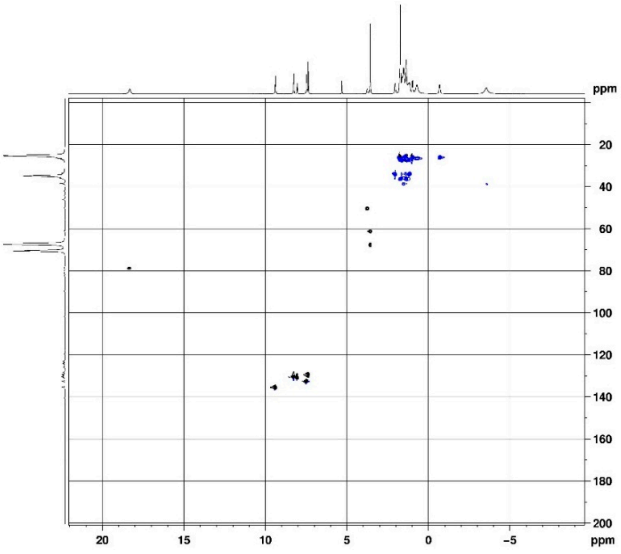

Figure S1. HSQC spectrum (400 MHz, THF-d_8, 25 °C) of [Ph–C≡C–C(NCy)$_2$]$_3$Nd (**5**).

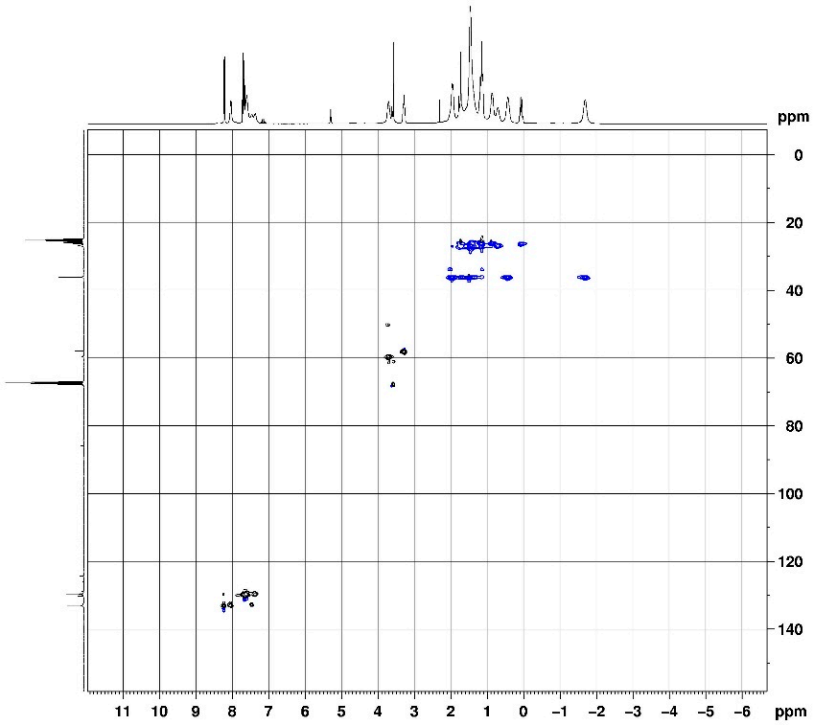

Figure S2. HSQC spectrum (400 MHz, THF-d_8, 25 °C) of $[Ph–C{\equiv}C–C(NCy)_2]_3Sm$ (**6**).

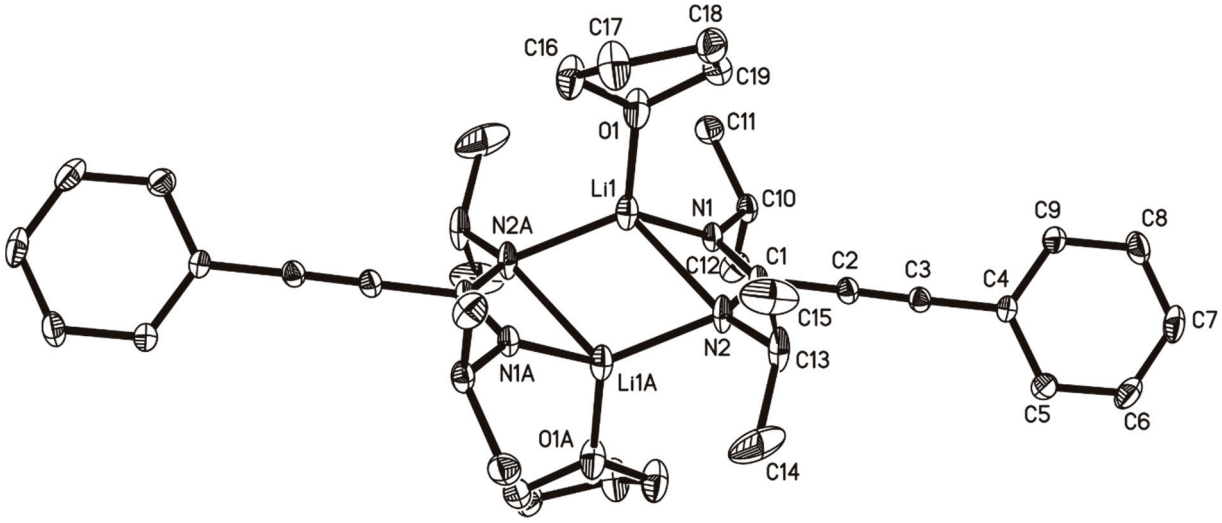

Figure S3. ORTEP representation of **1**. Displacement ellipsoids are drawn at the 50% probability level.

Table S1. Crystal data and structure refinement for **1**.

Identification code	ip276
Empirical formula	$C_{38}\ H_{54}\ Li_2\ N_4\ O_2$
Formula weight	612.73
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.6687(19) Å; α= 93.77(3)°; b = 9.948(2) Å; β= 91.33(3)°; c = 19.611(4) Å; γ = 90.96(3)°
Volume	1881.3(6) $Å^3$
Z	2
Density (calculated)	1.082 Mg/m^3
Absorption coefficient	0.066 mm^{-1}
F(000)	664
Crystal size	0.60 × 0.60 × 0.40 mm^3
θ range for data collection	2.05° to 26.37°
Index ranges	$-11 \le h \le 12$, $-11 \le k \le 12$, $-24 \le l \le 24$
Reflections collected	15,323
Independent reflections	7395 [R(int) = 0.0399]
Completeness to θ = 26.37°	96.2%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7395/0/469
Goodness-of-fit on F^2	1.013
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0520, w$R2$ = 0.1256
R indices (all data)	$R1$ = 0.0782, w$R2$ = 0.1347
Largest difference peak and hole	0.406 and −0.313 e.$Å^{-3}$

Table S2. Bond lengths [Å] and angles [°] for **1**.

O(1)–C(16)	1.423(2)	Li(2)–N(3)#2	2.044(3)
O(1)–C(19)	1.430(2)	Li(2)–N(3)	2.211(3)
O(1)–Li(1)	1.908(3)	Li(2)–C(21)	2.405(3)
Li(1)–N(1)	1.990(3)	Li(2)–Li(2)#2	2.478(6)
Li(1)–N(2)#1	2.043(3)	N(3)–C(21)	1.3314(19)
Li(1)–N(2)	2.261(3)	N(3)–C(30)	1.469(2)
Li(1)–C(1)	2.413(3)	N(3)–Li(2)#2	2.044(3)
Li(1)–Li(1)#1	2.471(6)	N(4)–C(21)	1.319(2)
N(1)–C(1)	1.321(2)	N(4)–C(33)	1.4565(19)
N(1)–C(10)	1.452(2)	C(21)–C(22)	1.464(2)
N(2)–C(1)	1.330(2)	C(22)–C(23)	1.196(2)
N(2)–C(13)	1.468(2)	C(23)–C(24)	1.434(2)
N(2)–Li(1)#1	2.043(3)	C(24)–C(25)	1.385(2)
C(1)–C(2)	1.470(2)	C(24)–C(29)	1.397(2)
C(2)–C(3)	1.189(2)	C(25)–C(26)	1.385(2)
C(3)–C(4)	1.439(2)	C(26)–C(27)	1.377(3)
C(4)–C(9)	1.387(2)	C(27)–C(28)	1.371(3)
C(4)–C(5)	1.391(2)	C(28)–C(29)	1.382(2)
C(5)–C(6)	1.383(2)	C(30)–C(32)	1.514(3)
C(6)–C(7)	1.371(3)	C(30)–C(31)	1.517(3)
C(7)–C(8)	1.371(3)	C(33)–C(35)	1.515(3)
C(8)–C(9)	1.385(2)	C(33)–C(34)	1.516(3)
C(10)–C(11)	1.516(2)	O(2)–C(39)	1.442(19)
C(10)–C(12)	1.517(2)	O(2)–C(36)	1.445(18)
C(13)–C(15)	1.495(3)	C(36)–C(37)	1.574(18)
C(13)–C(14)	1.512(4)	C(37)–C(38)	1.398(18)
C(16)–C(17)	1.466(3)	C(38)–C(39)	1.390(16)
C(17)–C(18)	1.508(3)	O(2′)–C(39′)	1.43(3)
C(18)–C(19)	1.518(3)	O(2′)–C(36′)	1.44(3)
Li(2)–O(2)	1.904(15)	C(36′)–C(37′)	1.38(2)
Li(2)–O(2′)	1.93(2)	C(37′)–C(38′)	1.65(2)
Li(2)–N(4)	1.992(3)	C(38′)–C(39′)	1.75(3)
C(16)–O(1)–C(19)	106.94(14)	O(1)–Li(1)–N(2)#1	112.16(14)
C(16)–O(1)–Li(1)	123.29(15)	N(1)–Li(1)–N(2)#1	125.99(16)
C(19)–O(1)–Li(1)	124.94(13)	O(1)–Li(1)–N(2)	113.49(14)
O(1)–Li(1)–N(1)	118.80(16)	N(1)–Li(1)–N(2)	64.67(10)
N(2)#1–Li(1)–N(2)	110.15(15)	N(2)–C(13)–C(14)	110.91(17)
O(1)–Li(1)–C(1)	114.37(14)	C(15)–C(13)–C(14)	109.07(19)
N(1)–Li(1)–C(1)	33.18(7)	O(1)–C(16)–C(17)	105.93(16)
N(2)#1–Li(1)–C(1)	130.17(16)	C(16)–C(17)–C(18)	105.37(18)
N(2)–Li(1)–C(1)	32.85(7)	C(17)–C(18)–C(19)	104.23(15)
O(1)–Li(1)–Li(1)#1	132.6(2)	O(1)–C(19)–C(18)	106.62(15)
N(1)–Li(1)–Li(1)#1	95.41(17)	O(2)–Li(2)–O(2′)	3.3(13)
N(2)#1–Li(1)–Li(1)#1	59.23(12)	O(2)–Li(2)–N(4)	118.8(5)
N(2)–Li(1)–Li(1)#1	50.92(11)	O(2′)–Li(2)–N(4)	120.1(8)
C(1)–Li(1)–Li(1)#1	76.38(14)	O(2)–Li(2)–N(3)#2	113.8(5)

C(1)–N(1)–C(10)	120.18(12)	O(2′)–Li(2)–N(3)#2	113.7(7)
C(1)–N(1)–Li(1)	91.30(13)	N(4)–Li(2)–N(3)#2	123.00(15)
C(10)–N(1)–Li(1)	144.16(14)	O(2)–Li(2)–N(3)	116.2(4)
C(1)–N(2)–C(13)	118.48(13)	O(2′)–Li(2)–N(3)	113.5(7)
C(1)–N(2)–Li(1)#1	125.81(14)	N(4)–Li(2)–N(3)	65.63(10)
C(13)–N(2)–Li(1)#1	112.23(14)	N(3)#2–Li(2)–N(3)	108.89(13)
C(1)–N(2)–Li(1)	79.87(12)	O(2)–Li(2)–C(21)	117.8(5)
C(13)–N(2)–Li(1)	143.92(15)	O(2′)–Li(2)–C(21)	116.8(7)
Li(1)#1–N(2)–Li(1)	69.85(15)	N(4)–Li(2)–C(21)	33.27(7)
N(1)–C(1)–N(2)	119.13(13)	N(3)#2–Li(2)–C(21)	126.48(14)
N(1)–C(1)–C(2)	120.72(14)	N(3)–Li(2)–C(21)	33.19(6)
N(2)–C(1)–C(2)	120.15(14)	O(2)–Li(2)–Li(2)#2	136.6(6)
N(1)–C(1)–Li(1)	55.52(10)	O(2′)–Li(2)–Li(2)#2	133.5(8)
N(2)–C(1)–Li(1)	67.28(11)	N(4)–Li(2)–Li(2)#2	94.66(16)
C(2)–C(1)–Li(1)	159.71(14)	N(3)#2–Li(2)–Li(2)#2	57.58(11)
C(3)–C(2)–C(1)	179.05(18)	N(3)–Li(2)–Li(2)#2	51.31(11)
C(2)–C(3)–C(4)	178.56(17)	C(21)–Li(2)–Li(2)#2	75.16(13)
C(9)–C(4)–C(5)	119.14(14)	C(21)–N(3)–C(30)	118.85(12)
C(9)–C(4)–C(3)	119.86(14)	C(21)–N(3)–Li(2)#2	122.45(13)
C(5)–C(4)–C(3)	121.00(15)	C(30)–N(3)–Li(2)#2	112.58(12)
C(6)–C(5)–C(4)	119.74(17)	C(21)–N(3)–Li(2)	81.43(11)
C(7)–C(6)–C(5)	120.53(17)	C(30)–N(3)–Li(2)	144.14(13)
C(6)–C(7)–C(8)	120.34(16)	Li(2)#2–N(3)–Li(2)	71.11(13)
C(7)–C(8)–C(9)	119.81(18)	C(21)–N(4)–C(33)	120.23(12)
C(8)–C(9)–C(4)	120.44(16)	C(21)–N(4)–Li(2)	90.81(12)
N(1)–C(10)–C(11)	108.68(13)	C(33)–N(4)–Li(2)	146.92(13)
N(1)–C(10)–C(12)	110.93(14)	N(4)–C(21)–N(3)	119.09(13)
C(11)–C(10)–C(12)	110.71(15)	N(4)–C(21)–C(22)	120.44(13)
N(2)–C(13)–C(15)	110.12(17)	N(3)–C(21)–C(22)	120.45(14)
N(4)–C(21)–Li(2)	55.92(10)	N(4)–C(33)–C(34)	108.73(14)
N(3)–C(21)–Li(2)	65.38(10)	C(35)–C(33)–C(34)	110.27(16)
C(22)–C(21)–Li(2)	165.74(13)	C(39)–O(2)–C(36)	106.5(11)
C(23)–C(22)–C(21)	176.32(17)	C(39)–O(2)–Li(2)	127.1(9)
C(22)–C(23)–C(24)	177.84(18)	C(36)–O(2)–Li(2)	123.2(10)
C(25)–C(24)–C(29)	119.23(14)	O(2)–C(36)–C(37)	99.0(9)
C(25)–C(24)–C(23)	120.02(14)	C(38)–C(37)–C(36)	103.4(10)
C(29)–C(24)–C(23)	120.75(15)	C(39)–C(38)–C(37)	106.7(11)
C(26)–C(25)–C(24)	120.20(15)	C(38)–C(39)–O(2)	109.5(10)
C(27)–C(26)–C(25)	120.13(17)	C(39′)–O(2′)–C(36′)	113.1(19)
C(28)–C(27)–C(26)	120.08(16)	C(39′)–O(2′)–Li(2)	123.1(18)
C(27)–C(28)–C(29)	120.60(16)	C(36′)–O(2′)–Li(2)	119.8(15)
C(28)–C(29)–C(24)	119.73(16)	C(37′)–C(36′)–O(2′)	114.3(14)
N(3)–C(30)–C(32)	109.01(15)	C(36′)–C(37′)–C(38′)	99.6(14)
N(3)–C(30)–C(31)	110.91(16)	C(37′)–C(38′)–C(39′)	97.7(11)
C(32)–C(30)–C(31)	110.84(17)	O(2′)–C(39′)–C(38′)	97.0(18)
N(4)–C(33)–C(35)	110.91(14)		

Symmetry transformations used to generate equivalent atoms: # 1 − x − 1, −y − 1, −z + 1 # 2 − x + 1, −y, −z.

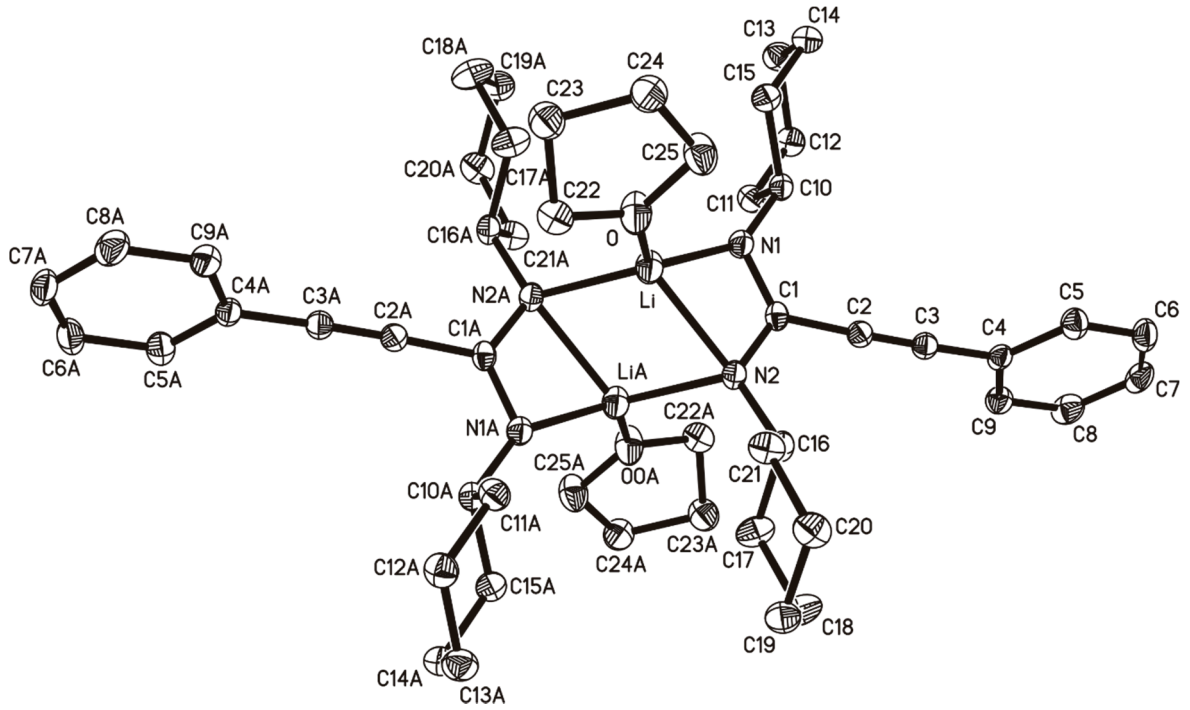

Figure S4. ORTEP representation of **2**. Displacement ellipsoids are drawn at the 50% probability level.

Table S3. Crystal data and structure refinement for **2**.

Identification code	magd78
Empirical formula	$C_{50}H_{70}Li_2N_4O_2$
Formula weight	772.98
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.8768(3) Å; α = 104.144(3)°; b = 10.2082(3) Å; β = 90.248(3)°; c = 11.6883(4) Å; γ = 104.209(2)°
Volume	1105.18(6) Å^3
Z	1
Density (calculated)	1.161 Mg/m^3
Absorption coefficient	0.530 mm^{-1}
F(000)	420
Crystal size	0.12 × 0.10 × 0.10 mm^3
θ range for data collection	3.91° to 76.97°
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-14 \le l \le 12$
Reflections collected	40,575
Independent reflections	4628 [*R*(int) = 0.0274]
Completeness to θ = 76.97°	99.20%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9490 and 0.9392
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4628/0/262

Goodness-of-fit on F^2	1.027
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0392, w$R2$ = 0.0964
R indices (all data)	$R1$ = 0.0403, w$R2$ = 0.0974
Largest difference peak and hole	0.199 and −0.243 e.Å^{-3}

Table S4. Bond lengths [Å] and angles [°] for **2**.

O–C(25)	1.4294(13)	C(8)–C(9)	1.3879(14)
O–C(22)	1.4341(13)	C(10)–C(15)	1.5267(14)
O–Li	1.9518(19)	C(10)–C(11)	1.5305(14)
N(1)–C(1)	1.3201(13)	C(11)–C(12)	1.5294(14)
N(1)–C(10)	1.4560(12)	C(12)–C(13)	1.5307(15)
N(1)–Li	2.031(2)	C(13)–C(14)	1.5276(15)
N(2)–C(1)	1.3407(12)	C(14)–C(15)	1.5262(14)
N(2)–C(16)	1.4646(12)	C(16)–C(17)	1.5289(14)
N(2)–Li#1	2.0580(19)	C(16)–C(21)	1.5294(13)
N(2)–Li	2.188(2)	C(17)–C(18)	1.5337(15)
C(1)–C(2)	1.4681(13)	C(18)–C(19)	1.5232(15)
C(1)–Li	2.425(2)	C(19)–C(20)	1.5219(15)
C(2)–C(3)	1.2018(14)	C(20)–C(21)	1.5310(15)
C(3)–C(4)	1.4366(13)	C(22)–C(23)	1.5132(15)
C(4)–C(9)	1.3979(14)	C(23)–C(24)	1.5317(16)
C(4)–C(5)	1.3989(14)	C(24)–C(25)	1.5269(16)
C(5)–C(6)	1.3903(15)	Li–N(2)#1	2.0580(19)
C(6)–C(7)	1.3833(17)	Li–Li#1	2.476(4)
C(7)–C(8)	1.3869(17)		
C(25)–O–C(22)	108.48(8)	C(2)–C(1)–Li	168.85(8)
C(25)–O–Li	125.85(9)	C(3)–C(2)–C(1)	175.39(10)
C(22)–O–Li	125.50(8)	C(2)–C(3)–C(4)	178.27(11)
C(1)–N(1)–C(10)	119.80(8)	C(9)–C(4)–C(5)	119.23(9)
C(1)–N(1)–Li	90.13(8)	C(9)–C(4)–C(3)	119.93(9)
C(10)–N(1)–Li	149.12(8)	C(5)–C(4)–C(3)	120.84(9)
C(1)–N(2)–C(16)	118.73(8)	C(6)–C(5)–C(4)	119.97(10)
C(1)–N(2)–Li#1	117.48(8)	C(7)–C(6)–C(5)	120.38(10)
C(16)–N(2)–Li#1	115.92(8)	C(6)–C(7)–C(8)	120.02(10)
C(1)–N(2)–Li	83.13(7)	C(7)–C(8)–C(9)	120.15(10)
C(16)–N(2)–Li	142.29(8)	C(8)–C(9)–C(4)	120.25(10)
Li#1–N(2)–Li	71.27(8)	N(1)–C(10)–C(15)	109.76(8)
N(1)–C(1)–N(2)	118.89(8)	N(1)–C(10)–C(11)	111.76(8)
N(1)–C(1)–C(2)	120.49(9)	C(15)–C(10)–C(11)	109.74(8)
N(2)–C(1)–C(2)	120.58(9)	C(12)–C(11)–C(10)	111.56(8)
N(1)–C(1)–Li	56.89(7)	C(11)–C(12)–C(13)	110.87(9)
N(2)–C(1)–Li	63.58(7)	C(14)–C(13)–C(12)	111.43(9)
C(15)–C(14)–C(13)	111.06(9)	O–Li–N(2)#1	108.03(9)
C(14)–C(15)–C(10)	111.38(8)	N(1)–Li–N(2)#1	118.44(9)
N(2)–C(16)–C(17)	111.89(8)	O–Li–N(2)	122.23(9)
N(2)–C(16)–C(21)	108.99(8)	N(1)–Li–N(2)	65.67(6)
C(17)–C(16)–C(21)	109.82(8)	N(2)#1–Li–N(2)	108.73(8)

C(16)–C(17)–C(18)	112.20(9)	O–Li–C(1)	127.75(9)
C(19)–C(18)–C(17)	111.06(9)	N(1)–Li–C(1)	32.98(4)
C(20)–C(19)–C(18)	110.73(9)	N(2)#1–Li–C(1)	123.01(9)
C(19)–C(20)–C(21)	111.50(9)	N(2)–Li–C(1)	33.29(4)
C(16)–C(21)–C(20)	113.11(9)	O–Li–Li#1	136.76(13)
O–C(22)–C(23)	104.21(9)	N(1)–Li–Li#1	91.83(10)
C(22)–C(23)–C(24)	102.73(9)	N(2)#1–Li–Li#1	56.80(7)
C(25)–C(24)–C(23)	103.79(9)	N(2)–Li–Li#1	51.93(7)
O–C(25)–C(24)	107.33(9)	C(1)–Li–Li#1	73.40(8)
O–Li–N(1)	126.92(10)		

Symmetry transformations used to generate equivalent atoms: # 1 −x, −y + 1, −z + 2.

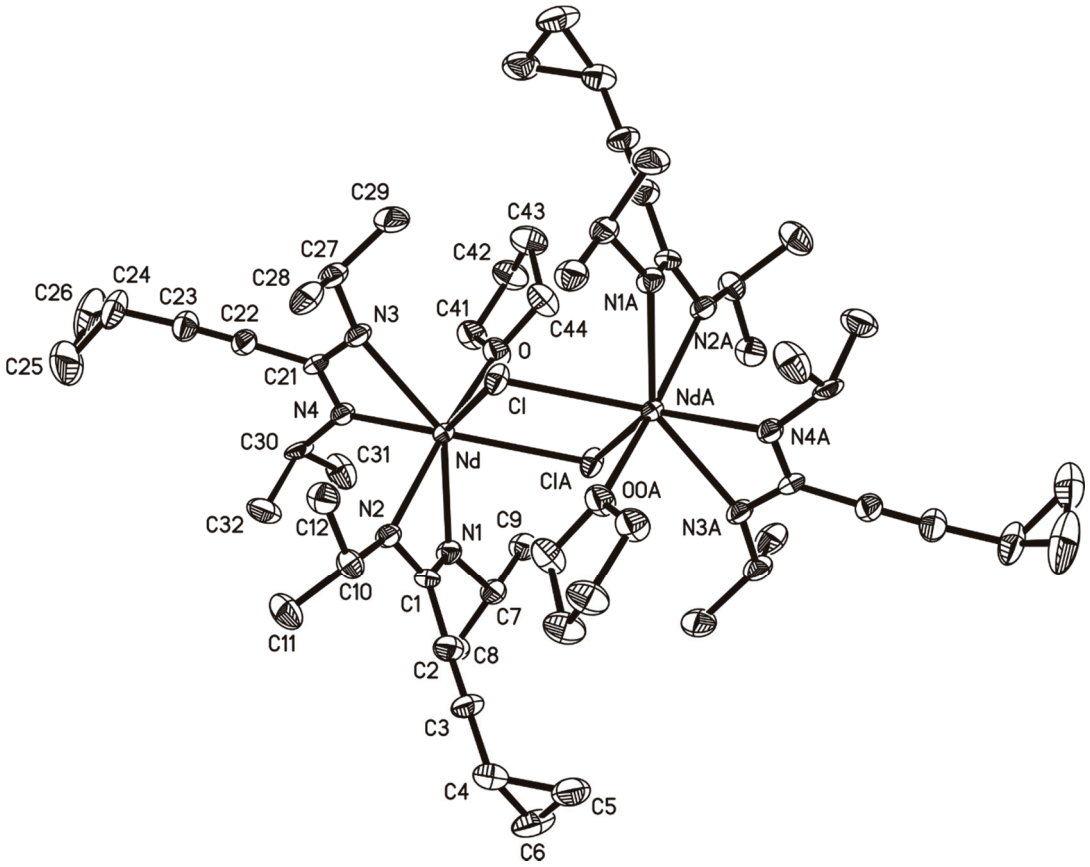

Figure S5. ORTEP representation of **8**. Displacement ellipsoids are drawn at the 50% probability level.

Table S5. Crystal data and structure refinement for **8**.

Identification code	ip407
Empirical formula	$C_{56}H_{92}Cl_2N_8Nd_2O_2$
Formula weight	1268.76
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1

Unit cell dimensions	a = 10.049(2) Å; α= 82.53(3)°; b = 11.337(2) Å; β= 83.02(3)°; c = 14.471(3) Å; γ = 73.74(3)°
Volume	1562.9(5) $Å^3$
Z	1
Density (calculated)	1.348 Mg/m^3
Absorption coefficient	1.771 mm^{-1}
F(000)	654
Crystal size	0.46 × 0.34 × 0.22 mm^3
θ range for data collection	2.45° to 29.17°
Index ranges	$-13 \le h \le 13, -15 \le k \le 13, -19 \le l \le 18$
Reflections collected	17,971
Independent reflections	8340 [*R*(int) = 0.0916]
Completeness to θ = 29.17°	98.80%
Absorption correction	Sphere
Max. and min. transmission	0.3338 and 0.3176
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8340/0/324
Goodness-of-fit on F^2	1.219
Final R indices [$I > 2\sigma(I)$]	*R*1 = 0.0547, w*R*2 = 0.1647
R indices (all data)	*R*1 = 0.0589, w*R*2 = 0.1663
Largest diff. peak and hole	3.507 and −2.740 e.$Å^{-3}$

Table S6. Bond lengths [Å] and angles [°] for **8**.

Cl–Nd	2.7961(16)	C(3)–C(4)	1.425(10)
Cl–Nd#1	2.8908(17)	C(4)–C(6)	1.510(12)
Nd–N(2)	2.423(5)	C(4)–C(5)	1.511(12)
Nd–N(4)	2.464(5)	C(5)–C(6)	1.469(12)
Nd–N(1)	2.478(5)	C(7)–C(9)	1.520(9)
Nd–N(3)	2.484(5)	C(7)–C(8)	1.534(9)
Nd–O	2.504(5)	C(10)–C(12)	1.521(9)
Nd–C(1)	2.810(5)	C(10)–C(11)	1.526(10)
Nd–C(21)	2.865(5)	C(21)–C(22)	1.458(8)
Nd–Cl#1	2.8908(17)	C(22)–C(23)	1.188(9)
O–C(44)	1.443(9)	C(23)–C(24)	1.439(9)
O–C(41)	1.449(8)	C(24)–C(25)	1.450(15)
N(1)–C(1)	1.338(8)	C(24)–C(26)	1.470(12)
N(1)–C(7)	1.463(7)	C(25)–C(26)	1.425(19)
N(2)–C(1)	1.332(7)	C(27)–C(29)	1.513(10)
N(2)–C(10)	1.470(8)	C(27)–C(28)	1.519(11)
N(3)–C(21)	1.321(8)	C(30)–C(32)	1.503(10)
N(3)–C(27)	1.456(7)	C(30)–C(31)	1.519(10)
N(4)–C(21)	1.345(7)	C(41)–C(42)	1.516(10)
N(4)–C(30)	1.456(8)	C(42)–C(43)	1.524(11)
C(1)–C(2)	1.444(8)	C(43)–C(44)	1.513(10)
C(2)–C(3)	1.186(9)		
Nd–Cl–Nd#1	106.85(5)	N(3)–Nd–Cl	82.57(13)

N(2)–Nd–N(4)	91.56(17)	O–Nd–Cl	101.13(12)
N(2)–Nd–N(1)	54.95(17)	N(2)–Nd–C(1)	28.26(17)
N(4)–Nd–N(1)	88.55(16)	N(4)–Nd–C(1)	97.32(17)
N(2)–Nd–N(3)	105.47(19)	N(1)–Nd–C(1)	28.43(17)
N(4)–Nd–N(3)	54.74(16)	N(3)–Nd–C(1)	130.77(19)
N(1)–Nd–N(3)	139.93(17)	O–Nd–C(1)	138.76(18)
N(2)–Nd–O	164.94(17)	Cl–Nd–C(1)	106.44(13)
N(4)–Nd–O	82.40(17)	N(2)–Nd–C(21)	95.32(17)
N(1)–Nd–O	110.87(17)	N(4)–Nd–C(21)	27.97(15)
N(3)–Nd–O	82.31(19)	N(1)–Nd–C(21)	113.37(17)
N(2)–Nd–Cl	92.75(13)	N(3)–Nd–C(21)	27.43(16)
N(4)–Nd–Cl	136.57(11)	O–Nd–C(21)	85.82(16)
N(1)–Nd–Cl	128.07(13)	Cl–Nd–C(21)	108.62(12)
C(1)–Nd–C(21)	112.79(17)	C(3)–C(4)–C(5)	120.5(7)
N(2)–Nd–Cl#1	104.70(12)	C(6)–C(4)–C(5)	58.2(6)
N(4)–Nd–Cl#1	146.09(12)	C(6)–C(5)–C(4)	60.8(6)
N(1)–Nd–Cl#1	77.50(13)	C(5)–C(6)–C(4)	61.0(6)
N(3)–Nd–Cl#1	141.83(13)	N(1)–C(7)–C(9)	108.8(5)
O–Nd–Cl#1	74.27(12)	N(1)–C(7)–C(8)	111.1(5)
Cl–Nd–Cl#1	73.15(5)	C(9)–C(7)–C(8)	109.8(6)
C(1)–Nd–Cl#1	85.00(13)	N(2)–C(10)–C(12)	107.5(5)
C(21)–Nd–Cl#1	159.85(12)	N(2)–C(10)–C(11)	110.8(5)
C(44)–O–C(41)	110.0(5)	C(12)–C(10)–C(11)	110.8(6)
C(44)–O–Nd	118.3(4)	N(3)–C(21)–N(4)	117.1(5)
C(41)–O–Nd	128.2(4)	N(3)–C(21)–C(22)	122.3(5)
C(1)–N(1)–C(7)	119.3(5)	N(4)–C(21)–C(22)	120.6(5)
C(1)–N(1)–Nd	89.7(3)	N(3)–C(21)–Nd	60.0(3)
C(7)–N(1)–Nd	139.0(4)	N(4)–C(21)–Nd	59.2(3)
C(1)–N(2)–C(10)	119.6(5)	C(22)–C(21)–Nd	166.1(4)
C(1)–N(2)–Nd	92.2(4)	C(23)–C(22)–C(21)	177.8(7)
C(10)–N(2)–Nd	144.1(4)	C(22)–C(23)–C(24)	177.6(8)
C(21)–N(3)–C(27)	120.1(5)	C(23)–C(24)–C(25)	120.4(8)
C(21)–N(3)–Nd	92.5(3)	C(23)–C(24)–C(26)	120.3(8)
C(27)–N(3)–Nd	145.0(4)	C(25)–C(24)–C(26)	58.4(9)
C(21)–N(4)–C(30)	119.7(5)	C(26)–C(25)–C(24)	61.5(8)
C(21)–N(4)–Nd	92.8(3)	C(25)–C(26)–C(24)	60.1(8)
C(30)–N(4)–Nd	140.6(3)	N(3)–C(27)–C(29)	110.1(6)
N(2)–C(1)–N(1)	115.9(5)	N(3)–C(27)–C(28)	112.2(6)
N(2)–C(1)–C(2)	121.5(6)	C(29)–C(27)–C(28)	110.3(6)
N(1)–C(1)–C(2)	122.4(6)	N(4)–C(30)–C(32)	113.1(6)
N(2)–C(1)–Nd	59.5(3)	N(4)–C(30)–C(31)	107.9(6)
N(1)–C(1)–Nd	61.9(3)	C(32)–C(30)–C(31)	110.7(6)
C(2)–C(1)–Nd	153.0(4)	O–C(41)–C(42)	106.0(6)
C(3)–C(2)–C(1)	177.5(8)	C(41)–C(42)–C(43)	102.3(6)
C(2)–C(3)–C(4)	179.2(9)	C(44)–C(43)–C(42)	102.5(6)
C(3)–C(4)–C(6)	120.2(8)	O–C(44)–C(43)	105.1(6)

Symmetry transformations used to generate equivalent atoms: #1 −x + 1, −y + 2, −z + 1.

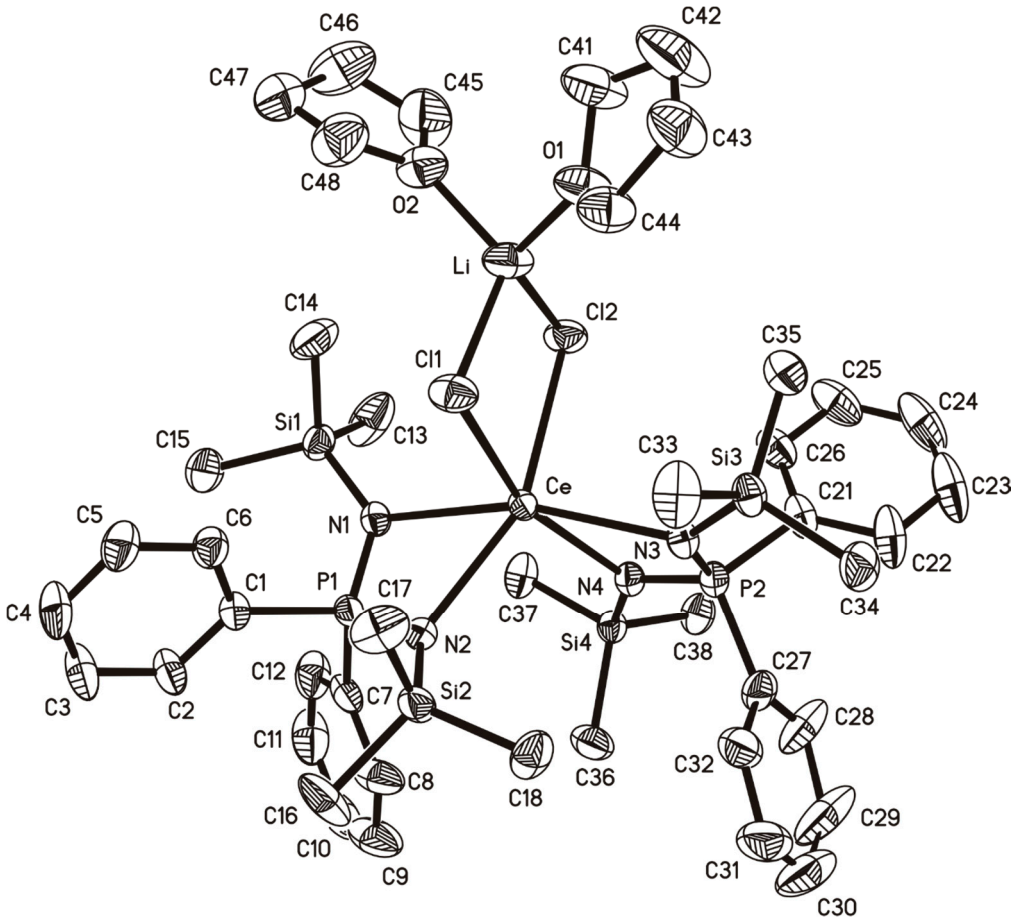

Figure S6. ORTEP representation of **9**. Displacement ellipsoids are drawn at the 50% probability level.

Table S7. Crystal data and structure refinement for **9**.

Identification code	ip223
Empirical formula	$C_{44}H_{72}CeCl_2LiN_4O_2P_2Si_4$
Formula weight	1081.32
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.117(2) Å; α= 90°; b = 36.425(7) Å; β= 96.70(3)°; c = 13.538(3) Å; γ = 90°
Volume	5444.3(19) $Å^3$
Z	4
Density (calculated)	1.319 Mg/m^3
Absorption coefficient	1.118 mm^{-1}
F(000)	2244
Crystal size	0.40 × 0.40 × 0.30 mm^3
θ range for data collection	1.88° to 28.28°
Index ranges	$-14 \le h \le 14$, $-45 \le k \le 48$, $-18 \le l \le 18$
Reflections collected	43,147

Independent reflections	12841 [R(int) = 0.0721]
Completeness to θ = 28.28°	95.10%
Absorption correction	Sphere
Max. and min. transmission	0.5625 and 0.5558
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12841/0/569
Goodness-of-fit on F^2	0.977
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0363$, w$R2 = 0.0806$
R indices (all data)	$R1 = 0.0531$, w$R2 = 0.0859$
Largest difference peak and hole	0.614 and −0.950 e.Å^{-3}

Table S8. Bond lengths [Å] and angles [°] for **9**.

Li–O(1)	1.938(6)	Si(4)–C(37)	1.850(3)
Li–O(2)	1.948(6)	Si(4)–C(36)	1.869(3)
Li–Cl(1)	2.359(6)	Si(4)–C(38)	1.875(3)
Li–Cl(2)	2.385(6)	C(1)–C(6)	1.384(4)
Li–Ce	3.726(5)	C(1)–C(2)	1.396(4)
Ce–N(4)	2.483(2)	C(2)–C(3)	1.382(4)
Ce–N(2)	2.499(2)	C(3)–C(4)	1.371(5)
Ce–N(1)	2.555(2)	C(4)–C(5)	1.379(5)
Ce–N(3)	2.557(2)	C(5)–C(6)	1.383(4)
Ce–Cl(2)	2.8069(8)	C(7)–C(12)	1.387(5)
Ce–Cl(1)	2.8095(8)	C(7)–C(8)	1.390(5)
Ce–P(1)	3.1189(9)	C(8)–C(9)	1.391(5)
Ce–P(2)	3.1290(8)	C(9)–C(10)	1.378(6)
P(1)–N(1)	1.593(2)	C(10)–C(11)	1.360(7)
P(1)–N(2)	1.594(2)	C(11)–C(12)	1.390(5)
P(1)–C(1)	1.815(3)	C(21)–C(26)	1.384(5)
P(1)–C(7)	1.819(3)	C(21)–C(22)	1.388(4)
P(2)–N(4)	1.593(2)	C(22)–C(23)	1.394(5)
P(2)–N(3)	1.598(2)	C(23)–C(24)	1.366(7)
P(2)–C(27)	1.815(3)	C(24)–C(25)	1.382(6)
P(2)–C(21)	1.830(3)	C(25)–C(26)	1.391(4)
Si(1)–N(1)	1.720(2)	C(27)–C(28)	1.390(5)
Si(1)–C(14)	1.856(4)	C(27)–C(32)	1.391(4)
Si(1)–C(13)	1.857(4)	C(28)–C(29)	1.391(6)
Si(1)–C(15)	1.874(3)	C(29)–C(30)	1.360(8)
Si(2)–N(2)	1.721(2)	C(30)–C(31)	1.363(8)
Si(2)–C(16′)	1.751(8)	C(31)–C(32)	1.395(5)
Si(2)–C(17′)	1.772(8)	C(41)–O(1)	1.417(4)
Si(2)–C(18)	1.816(5)	C(41)–C(42)	1.467(6)
Si(2)–C(16)	1.868(6)	C(42)–C(43)	1.468(6)
Si(2)–C(17)	1.984(6)	C(43)–C(44)	1.515(5)
Si(2)–C(18′)	1.987(7)	C(44)–O(1)	1.436(4)
Si(3)–N(3)	1.721(2)	C(45)–O(2)	1.435(4)
Si(3)–C(34)	1.862(3)	C(45)–C(46)	1.469(7)

Si(3)–C(35)	1.865(3)	C(46)–C(47)	1.484(7)
Si(3)–C(33)	1.869(3)	C(47)–C(48)	1.477(6)
Si(4)–N(4)	1.724(2)	C(48)–O(2)	1.443(5)
O(1)–Li–O(2)	99.1(3)	N(4)–Ce–Li	130.39(11)
O(1)–Li–Cl(1)	106.6(3)	N(2)–Ce–Li	128.90(11)
O(2)–Li–Cl(1)	119.4(3)	N(1)–Ce–Li	99.31(11)
O(1)–Li–Cl(2)	124.6(3)	N(3)–Ce–Li	97.89(11)
O(2)–Li–Cl(2)	111.0(3)	Cl(2)–Ce–Li	39.78(9)
Cl(1)–Li–Cl(2)	97.7(2)	Cl(1)–Ce–Li	39.26(10)
O(1)–Li–Ce	128.6(3)	P(1)–Ce–Li	119.20(10)
O(2)–Li–Ce	132.0(2)	P(2)–Ce–Li	115.94(10)
Cl(1)–Li–Ce	48.91(10)	N(1)–P(1)–N(2)	107.10(11)
Cl(2)–Li–Ce	48.87(10)	N(1)–P(1)–C(1)	112.42(13)
N(4)–Ce–N(2)	100.71(7)	N(2)–P(1)–C(1)	111.12(12)
N(4)–Ce–N(1)	106.18(7)	N(1)–P(1)–C(7)	111.59(13)
N(2)–Ce–N(1)	60.96(7)	N(2)–P(1)–C(7)	110.89(14)
N(4)–Ce–N(3)	60.80(7)	C(1)–P(1)–C(7)	103.79(12)
N(2)–Ce–N(3)	108.26(7)	N(1)–P(1)–Ce	54.74(8)
N(1)–Ce–N(3)	162.75(7)	N(2)–P(1)–Ce	52.70(8)
N(4)–Ce–Cl(2)	94.34(5)	C(1)–P(1)–Ce	133.71(9)
N(2)–Ce–Cl(2)	156.49(5)	C(7)–P(1)–Ce	122.44(9)
N(1)–Ce–Cl(2)	97.61(6)	N(4)–P(2)–N(3)	106.18(12)
N(3)–Ce–Cl(2)	94.81(6)	N(4)–P(2)–C(27)	109.90(13)
N(4)–Ce–Cl(1)	158.85(5)	N(3)–P(2)–C(27)	113.00(13)
N(2)–Ce–Cl(1)	92.48(6)	N(4)–P(2)–C(21)	109.97(12)
N(1)–Ce–Cl(1)	94.65(5)	N(3)–P(2)–C(21)	113.65(13)
N(3)–Ce–Cl(1)	99.45(6)	C(27)–P(2)–C(21)	104.17(15)
Cl(2)–Ce–Cl(1)	79.00(3)	N(4)–P(2)–Ce	51.81(8)
N(4)–Ce–P(1)	103.41(5)	N(3)–P(2)–Ce	54.52(8)
N(2)–Ce–P(1)	30.50(5)	C(27)–P(2)–Ce	130.79(10)
N(1)–Ce–P(1)	30.60(5)	C(21)–P(2)–Ce	124.75(11)
N(3)–Ce–P(1)	136.50(5)	N(1)–Si(1)–C(14)	108.97(14)
Cl(2)–Ce–P(1)	128.02(3)	N(1)–Si(1)–C(13)	111.24(14)
Cl(1)–Ce–P(1)	96.36(3)	C(14)–Si(1)–C(13)	107.6(2)
N(4)–Ce–P(2)	30.29(5)	N(1)–Si(1)–C(15)	114.77(14)
N(2)–Ce–P(2)	108.28(5)	C(14)–Si(1)–C(15)	105.12(18)
N(1)–Ce–P(2)	135.93(5)	C(13)–Si(1)–C(15)	108.71(19)
N(3)–Ce–P(2)	30.58(5)	N(2)–Si(2)–C(16′)	116.2(3)
Cl(2)–Ce–P(2)	93.82(3)	N(2)–Si(2)–C(17′)	104.3(3)
Cl(1)–Ce–P(2)	129.34(3)	C(16′)–Si(2)–C(17′)	119.3(5)
P(1)–Ce–P(2)	124.82(2)	N(2)–Si(2)–C(18)	113.16(19)
C(16′)–Si(2)–C(18)	129.1(3)	Si(3)–N(3)–Ce	131.61(12)
C(17′)–Si(2)–C(18)	56.6(4)	P(2)–N(4)–Si(4)	131.34(14)
N(2)–Si(2)–C(16)	116.3(2)	P(2)–N(4)–Ce	97.90(10)
C(16′)–Si(2)–C(16)	34.2(4)	Si(4)–N(4)–Ce	129.88(11)
C(17′)–Si(2)–C(16)	138.6(3)	C(6)–C(1)–C(2)	118.8(3)
C(18)–Si(2)–C(16)	110.1(3)	C(6)–C(1)–P(1)	118.0(2)

N(2)–Si(2)–C(17)	110.78(19)	C(2)–C(1)–P(1)	123.2(2)
C(16′)–Si(2)–C(17)	70.0(4)	C(3)–C(2)–C(1)	119.9(3)
C(17′)–Si(2)–C(17)	53.8(4)	C(4)–C(3)–C(2)	120.6(3)
C(18)–Si(2)–C(17)	103.4(3)	C(3)–C(4)–C(5)	120.1(3)
C(16)–Si(2)–C(17)	101.7(3)	C(4)–C(5)–C(6)	119.6(3)
N(2)–Si(2)–C(18′)	104.8(2)	C(5)–C(6)–C(1)	120.9(3)
C(16′)–Si(2)–C(18′)	106.6(4)	C(12)–C(7)–C(8)	118.8(3)
C(17′)–Si(2)–C(18′)	104.2(4)	C(12)–C(7)–P(1)	120.5(3)
C(18)–Si(2)–C(18′)	47.6(3)	C(8)–C(7)–P(1)	120.7(3)
C(16)–Si(2)–C(18′)	73.9(4)	C(7)–C(8)–C(9)	120.9(4)
C(17)–Si(2)–C(18′)	141.6(3)	C(10)–C(9)–C(8)	119.4(4)
N(3)–Si(3)–C(34)	113.48(14)	C(11)–C(10)–C(9)	119.9(3)
N(3)–Si(3)–C(35)	110.09(13)	C(10)–C(11)–C(12)	121.4(4)
C(34)–Si(3)–C(35)	108.34(16)	C(7)–C(12)–C(11)	119.5(4)
N(3)–Si(3)–C(33)	109.43(14)	C(26)–C(21)–C(22)	119.2(3)
C(34)–Si(3)–C(33)	105.82(16)	C(26)–C(21)–P(2)	118.3(2)
C(35)–Si(3)–C(33)	109.55(19)	C(22)–C(21)–P(2)	122.6(3)
N(4)–Si(4)–C(37)	106.28(13)	C(21)–C(22)–C(23)	119.9(4)
N(4)–Si(4)–C(36)	111.03(13)	C(24)–C(23)–C(22)	120.5(4)
C(37)–Si(4)–C(36)	110.77(16)	C(23)–C(24)–C(25)	120.1(3)
N(4)–Si(4)–C(38)	113.99(12)	C(24)–C(25)–C(26)	119.8(4)
C(37)–Si(4)–C(38)	106.78(13)	C(21)–C(26)–C(25)	120.5(3)
C(36)–Si(4)–C(38)	107.93(15)	C(28)–C(27)–C(32)	117.8(4)
Li–Cl(1)–Ce	91.83(15)	C(28)–C(27)–P(2)	122.1(3)
Li–Cl(2)–Ce	91.35(14)	C(32)–C(27)–P(2)	119.6(3)
P(1)–N(1)–Si(1)	132.97(14)	C(27)–C(28)–C(29)	121.0(5)
P(1)–N(1)–Ce	94.66(10)	C(30)–C(29)–C(28)	120.5(5)
Si(1)–N(1)–Ce	129.68(11)	C(29)–C(30)–C(31)	119.6(4)
P(1)–N(2)–Si(2)	132.10(14)	C(30)–C(31)–C(32)	121.1(5)
P(1)–N(2)–Ce	96.81(10)	C(27)–C(32)–C(31)	120.0(4)
Si(2)–N(2)–Ce	127.99(12)	O(1)–C(41)–C(42)	105.7(4)
P(2)–N(3)–Si(3)	129.65(14)	C(41)–C(42)–C(43)	106.7(4)
P(2)–N(3)–Ce	94.90(10)	C(42)–C(43)–C(44)	105.0(3)
O(1)–C(44)–C(43)	105.8(3)	C(41)–O(1)–Li	123.0(3)
O(2)–C(45)–C(46)	106.8(4)	C(44)–O(1)–Li	125.6(3)
C(45)–C(46)–C(47)	107.7(4)	C(45)–O(2)–C(48)	109.1(3)
C(48)–C(47)–C(46)	104.3(4)	C(45)–O(2)–Li	127.7(3)
O(2)–C(48)–C(47)	106.9(3)	C(48)–O(2)–Li	123.2(3)
C(41)–O(1)–C(44)	107.2(3)		