Enantiomerically Pure Constrained Geometry Complexes of the Rare-Earth Metals Featuring a Dianionic N-Donor Functionalised Pentadienyl Ligand: Synthesis and Characterisation

Katharina Münster, Ann Christin Fecker, Jan Raeder, Matthias Freytag, Peter G. Jones, and Marc D. Walter
Table of contents

1. Crystallographic details
2. NMR spectroscopy
3. References
1. Crystallographic details
1.1. Special refinement details

1.1.1. 6-Sc
Hydrogen atoms at C1, C3 and C5 were refined freely. Methyls were refined as idealised rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.2. 4-Y
The hydrogens at C1, C3 and C5 were refined freely. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.3. 4-Y*
The hydrogens at C1, C3, C5, C20, C22 and C24 were found and refined freely. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.4. 5-Ce
One badly resolved region of residual electron density was tentatively identified as a molecule of THF but could not be refined satisfactorily. For this reason, the program SQUEEZE (part of the PLATON suite; A. Spek, University of Utrecht, Netherlands, 2009) was used to remove mathematically the effects of the solvent. Derived parameters such as the formula weight correspond to eight molecules of uncoordinated THF (four ordered, four squeezed) per cell. The hydrogens at C1, C3, C5, C24, C26, C28, C1', C3', C5', C24', C26' and C28' were refined freely. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions. One SiMe$_2$ (Si1') group and one THF (O1' etc.) at Ce1' are disordered and were refined on two positions. Appropriate restraints were employed to stabilise the refinement, but the dimensions of disordered groups should always be interpreted with caution.

1.1.5. 5-Nd
In both molecules the hydrogens at C1, C3, C5, C24, C26 and C28 were refined freely but with C-H distance restraints ("SADI") for chemically equivalent bonds. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.6. 4-Gd
The hydrogens at C1, C3 and C5 were refined freely. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.7. 4-Dy
Hydrogen atoms at H1, H3 and H5 were refined freely. Methyl groups were refined as idealised rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.8. 4-Ho
Hydrogen atoms at H1, H3 and H5 were refined freely. Methyl groups were refined as idealised rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.9. 4-Er
The hydrogens at C1, C3 and C5 were refined freely. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.
1.1.10. 4-Tm

The hydrogens at C1, C3 and C5 were refined freely. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.11. 4-Tm*

The hydrogens at C1, C3, C5, C20, C22 and C24 were refined freely. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions. One of the ether positions at Li1 is occupied partly by a THF and partly by a diethyl ether molecule in the ratio 38:62 (the corresponding oxygen atoms are O92 and O92'; O92" is a dummy atom with occupancy zero). One of the ethyl groups of the diethyl ether is further disordered over two positions. Appropriate restraints were employed to improve the refinement stability. Although this description appears acceptable, the dimensions of the disordered groups should be interpreted with caution.

1.1.12. 7-Y

The H atoms at C1, C3 and C5 were refined freely, but with C-H distance restraints (SADI). Methyls were refined as idealised rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions. The THF is disordered; to a first approximation, the atoms C27 and C28 display two alternative positions. Appropriate restraints were employed to improve refinement stability, but the dimensions of the THF are not entirely satisfactory and should be interpreted with caution.

1.1.13. 7-La

The hydrogens at C1, C3 and C5 were refined freely. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.14. 7-Nd

The hydrogens at C1, C3 and C5 were refined freely. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.15. 7-Dy

The hydrogen atoms at C1, C3 and C5 were refined freely. Methyls were refined as idealised rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions. The THF molecule is disordered. A simple model was refined that involved twofold disorder of atoms C21 and C22 only, although the true disorder may be more complicated. Appropriate restraints were employed to improve refinement stability, but the dimensions of disordered groups should always be interpreted with caution.

1.1.16. 7-Ho

The hydrogen atoms at C1, C3 and C5 were refined freely. Methyls were refined as idealized rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions. The THF molecule is disordered. A simple model was refined that involved twofold disorder of atoms C21 and C22 only, although the true disorder may be more complicated. Appropriate restraints were employed to improve refinement stability, but the dimensions of disordered groups should always be interpreted with caution.

1.1.17. 8-La

In both molecules the hydrogens at C1, C3, C5, C24, C26, C28 and around the boron atoms were refined "freely", but with restraints ("SADI") applied to the C-H or B-H bond lengths. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.
1.1.18. 8-Nd

In both molecules the hydrogens at C1, C3, C5, C24, C26, C28 and around the boron atoms were refined freely but with SADI restraints to B-H bond lengths. Methyls were refined as rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

1.1.19. 9-Lu

Hydrogen atoms at C1, C3, C5, C1', C3' and C5' were refined freely but with a C-H distance restraint (SADI). The fluorine atoms F1, F2, F3 display high and extremely anisotropic displacement parameters. Attempts to refine split sites for these atoms led to no improvement in the refinement. It is possible that they are distributed in a torus of electron density around C24.

1.1.20. 10-Lu

The hydrogen atoms at C1, C3 and C5 were refined freely. Methyls were refined as idealised rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions. Atoms C21 and C22 of the THF molecule are disordered. Appropriate restraints were employed to improve refinement stability, but the dimensions of disordered groups should always be interpreted with caution.

1.1.21. 11-Lu

Hydrogen atoms at C1, C3 and C5 were refined freely. Methyls were refined as idealised rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions. The THF molecule is disordered (at C21 and C22). Appropriate restraints were employed to improve refinement stability, but the dimensions of disordered groups should always be interpreted with caution.
## 1.2. Crystallographic data tables

### S1. Crystallographic details.

| Compound reference | 6-Sc | 4-Y | 4-Y* | 5-Ce | 5-Nd | 4-Gd |
|--------------------|------|-----|------|------|------|------|
| Chemical formula   | $\text{C}_3\text{H}_6\text{ClNO}_5\text{ScSi}$ | $\text{C}_7\text{H}_9\text{ClNO}_9\text{SiY}$ | $\text{C}_5\text{H}_9\text{LiN}_2\text{O}_2\text{Si}_2$ | $\text{C}_9\text{H}_9\text{CeCl}_2\text{N}_2\text{O}_3\text{Si}_2$ | $\text{C}_{46}\text{H}_{46}\text{Cl}_2\text{N}_2\text{Nd}_2\text{O}_3\text{Si}_2$ | $\text{C}_{47}\text{H}_6\text{ClGdNO}_2\text{Si}$ |
| Formula mass       | 456.07 | 572.12 | 925.31 | 1174.55 | 1146.76 | 640.46 |
| Crystal system     | monoclinic | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| $a$/Å              | 10.1248(3) | 10.5107(2) | 11.2977(2) | 10.4109(2) | 10.35383(10) | 10.5089(3) |
| $b$/Å              | 13.7872(5) | 20.1961(4) | 32.6910(7) | 32.6341(3) | 13.8411(4) | 20.0233(5) |
| $c$/Å              | 20.0013(7) | 23.9206(4) | 32.7731(8) | 32.6909(3) | 20.0233(5) | 20.0233(5) |
| $\alpha$/°         | 90.0000(6) | 90.0000(6) | 90.0000(6) | 90.0000(6) | 90.0000(6) | 90.0000(6) |
| $\beta$/°          | 90.0000(6) | 90.0000(6) | 90.0000(6) | 90.0000(6) | 90.0000(6) | 90.0000(6) |
| $\gamma$/°         | 90.0000(6) | 90.0000(6) | 90.0000(6) | 90.0000(6) | 90.0000(6) | 90.0000(6) |
| Unit cell volume/Å³ | 1251.51(6) | 2898.45(16) | 5457.94(17) | 11154.1(4) | 11045.83(18) | 2912.49(14) |
| Temperature/K       | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Space group         | $P2_1$ | $P2_12_1$ | $P2_12_1$ | $P2_12_1$ | $P2_12_1$ | $P2_12_1$ |
| No. of formula units per unit cell, Z | 2 | 4 | 4 | 8 | 8 | 4 |
| Radiation type      | Mo Kα | Mo Kα | Cu Kα | Mo Kα | Cu Kα | Mo Kα |
| Absorption coefficient, $\mu$/mm⁻¹ | 0.462 | 2.169 | 2.203 | 1.789 | 15.745 | 2.433 |
| No. of reflections measured | 121990 | 59999 | 129820 | 255482 | 214967 | 80282 |
| No. of independent reflections | 10137 | 8346 | 11334 | 31597 | 22837 | 8743 |
| $R_{int}$           | 0.0516 | 0.0697 | 0.0399 | 0.0922 | 0.0567 | 0.0603 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0303 | 0.0358 | 0.0210 | 0.0372 | 0.0266 | 0.0246 |
| Final wR($F^2$) values ($I > 2\sigma(I)$) | 0.0670 | 0.0603 | 0.0529 | 0.0637 | 0.0641 | 0.0446 |
| Final $R_1$ values (all data) | 0.0363 | 0.0492 | 0.0212 | 0.0452 | 0.0270 | 0.0297 |
| Final wR($F^2$) values (all data) | 0.0686 | 0.0639 | 0.0531 | 0.0661 | 0.0644 | 0.0462 |
| Goodness of fit on $F^2$ | 1.070 | 1.030 | 1.051 | 1.120 | 1.038 | 1.061 |
| Flack parameter     | 0.009(7) | -0.021(2) | -0.021(19) | -0.019(4) | -0.0083(9) | -0.024(4) |
| $\Delta \rho$ / e Å³ | 0.359 / -0.251 | 0.416 / -0.346 | 0.650 / -0.386 | 0.900 / -0.807 | 0.622 / -0.819 | 0.917 / -0.813 |
## Crystallographic details.

| Compound reference | 4-Dy | 4-Ho | 4-Er | 4-Tm | 4-Tm* | 7-Y |
|--------------------|------|------|------|------|-------|-----|
| Chemical formula   | C$_{27}$H$_{49}$ClDyNO$_2$Si | C$_{27}$H$_{49}$ClHoNO$_2$Si | C$_{27}$H$_{49}$ClErNO$_2$Si | C$_{27}$H$_{49}$ClTmNO$_2$SiTm | C$_{27}$H$_{49}$ClLN$_2$O$_2$SiTm | C$_{27}$H$_{49}$NO$_2$Si$_2$Y |
| Formula mass       | 645.71 | 648.14 | 650.47 | 652.14 | 928.42 | 624.96 |
| Crystal system     | orthorhombic | orthorhombic | orthorhombic | orthorhombic | monoclinic | Monoclinic |
| a/Å                | 10.4999(3) | 10.5066(6) | 10.4998(3) | 10.5055(4) | 12.0786(4) | 18.4260(3) |
| b/Å                | 13.7917(4) | 13.7695(3) | 13.7441(5) | 13.7405(6) | 17.3397(4) | 18.4791(5) |
| c/Å                | 19.9951(6) | 19.9929(3) | 19.9694(6) | 19.9484(7) | 12.8282(3) | 11.5243(4) |
| α/°                | 90 | 90 | 90 | 90 | 90 | 90 |
| β/°                | 90 | 90 | 90 | 112.985(3) | 90 | 90 |
| γ/°                | 90 | 90 | 90 | 90 | 90 | 90 |
| Unit cell volume/Å$^3$ | 1895.50(15) | 2892.40(3) | 2881.78(16) | 2879.582(17) | 2473.40(13) | 1727.74(10) |
| Temperature/K       | 100(2) | 102(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Space group         | P2$_2$1$_2$ | P2$_2$1$_2$ | P2$_2$1$_2$ | P2$_2$1$_2$ | P2$_2$1$_2$ | P2$_2$1$_2$ |
| No. of formula units per unit cell, Z | 4 | 4 | 4 | 4 | 2 | 2 |
| Radiation type      | Mo Kα | Cu Kα | Mo Kα | Cu Kα | Mo Kα | Mo Kα |
| Absorption coefficient, μ/mm$^2$ | 2.737 | 6.521 | 3.069 | 7.189 | 1.877 | 1.814 |
| No. of reflections measured | 53108 | 119895 | 78920 | 107316 | 64462 | 108361 |
| No. of independent reflections | 8578 | 6052 | 8698 | 5978 | 14333 | 9986 |
| R$_{int}$           | 0.0582 | 0.0392 | 0.0614 | 0.0464 | 0.0412 | 0.0601 |
| Final R$_1$ values ($I > 2\sigma(I)$) | 0.0307 | 0.0154 | 0.0278 | 0.0210 | 0.0256 | 0.0300 |
| Final wR(F$^2$) values ($I > 2\sigma(I)$) | 0.0645 | 0.0420 | 0.0539 | 0.0516 | 0.0470 | 0.0561 |
| Final R$_1$ values (all data) | 0.0367 | 0.0154 | 0.0339 | 0.0214 | 0.0312 | 0.0365 |
| Final wR(F$^2$) values (all data) | 0.0675 | 0.0420 | 0.0560 | 0.0520 | 0.0491 | 0.0578 |
| Goodness of fit on $F^2$   | 1.048 | 1.025 | 1.076 | 1.036 | 1.052 | 1.055 |
| Flack parameter       | -0.033(5) | -0.030(14) | -0.027(4) | -0.029(2) | -0.028(3) | -0.0195(12) |
| $\Delta$$\rho$ / e Å$^3$ | 2.116 / -1.055 | 0.336 / -0.294 | 1.331 / -0.787 | 0.436 / -1.105 | 0.802 / -0.431 | 0.348 / -0.357 |
### Crystallographic details.

| Compound reference | 7-La | 7-Nd | 7-Dy | 7-Ho | 8-La | 8-Nd |
|--------------------|------|------|------|------|------|------|
| Chemical formula   | C_{29}H_{59}LaN_2O_3Si_3 | C_{29}H_{59}NdN_2O_3Si_3 | C_{29}H_{59}DyN_2O_3Si_3 | C_{29}H_{59}HoN_2O_3Si_3 | C_{48.5}H_{96}B_{2}La_2N_2O_2Si_2 | C_{48.5}H_{96}B_{2}NdN_2O_2Si_2 |
| Formula mass       | 674.96 | 680.29 | 698.55 | 700.98 | 1094.89 | 1105.55 |
| Crystal system     | triclinic | triclinic | monoclinic | monoclinic | orthorhombic | orthorhombic |
| a/Å               | 8.5260(2) | 8.5032(3) | 8.42382(12) | 8.42265(14) | 10.4330(2) | 10.4296(2) |
| b/Å               | 10.3800(2) | 10.4172(4) | 18.4847(2) | 18.5037(3) | 32.8541(8) | 32.6815(4) |
| c/Å               | 11.2223(2) | 11.1816(4) | 11.52869(18) | 11.5189(2) | 32.8850(7) | 32.7588(2) |
| α/°               | 113.227(2) | 113.899(3) | 90 | 90 | 90 | 90 |
| β/°               | 96.353(2) | 96.604(3) | 105.2248(16) | 105.5675(16) | 90 | 90 |
| γ/°               | 99.786(2) | 100.100(3) | 90 | 90 | 90 | 90 |
| Unit cell volume/Å³ | 881.91(3) | 872.26(6) | 1732.15(4) | 1729.36 | 11271.9(4) | 11166.0(3) |
| Temperature/K      | 100(2) | 100(2) | 101(2) | 100(2) | 100(2) | 100(2) |
| Space group        | P1 | P1 | P2₁ | P2₁ | P2₁, P2₁, P2₁ | P2₁, P2₁ |
| No. of formula units per unit cell, Z | 1 | 1 | 2 | 2 | 8 | 8 |
| Radiation type     | Mo Kα | Mo Kα | Cu Kα | Mo Kα | Mo Kα | Mo Kα |
| Absorption coefficient, μ/mm² | 1.335 | 1.613 | 12.690 | 2.414 | 1.572 | 1.917 |
| No. of reflections measured | 100101 | 64080 | 35898 | 92603 | 334988 | 342738 |
| No. of independent reflections | 10202 | 10067 | 6703 | 10335 | 32213 | 31819 |
| R₁ values (I > 2σ(I)) | 0.0340 | 0.0470 | 0.0358 | 0.0318 | 0.1012 | 0.0516 |
| Final R₁ values (all data) | 0.0180 | 0.0247 | 0.0225 | 0.0165 | 0.0407 | 0.0244 |
| Final wR(F²) values (I > 2σ(I)) | 0.0419 | 0.0513 | 0.0574 | 0.0369 | 0.0655 | 0.0460 |
| Final R₁ values (all data) | 0.0182 | 0.0251 | 0.0228 | 0.0172 | 0.0550 | 0.0278 |
| Final wR(F²) values (all data) | 0.0420 | 0.0515 | 0.0577 | 0.0372 | 0.0690 | 0.0470 |
| Goodness of fit on F² | 1.083 | 1.048 | 1.050 | 1.062 | 1.064 | 1.097 |
| Flack parameter | -0.024(2) | -0.026(3) | -0.0079(18) | -0.017(2) | -0.033(4) | -0.038(2) |
| Δρ / e Å³ | 1.130 / -0.412 | 1.071 / -0.878 | 0.408 / -0.717 | 0.851 / -0.451 | 0.795 / -0.504 | 0.670 / -0.343 |
54. Crystallographic details.

| Compound reference | 9-Lu | 10-Lu | 11-Lu |
|--------------------|------|-------|-------|
| Chemical formula   | C_{4}H_{3}F_{2}Lu_{2}O_{5}S_{2}Si_{2} | C_{5}H_{5}LuNOSi | C_{5}H_{5}LuNOSi |
| Formula mass       | 1399.39 | 621.76 | 683.83 |
| Crystal system     | orthorhombic | monoclinic | orthorhombic |
| a/Å                | 10.47510(12) | 10.11068 | 11.43371(12) |
| b/Å                | 20.1438(2) | 14.87486(16) | 15.96821(18) |
| c/Å                | 27.2208(3) | 10.17980(12) | 18.16046(18) |
| α/°                | 90 | 90 | 90 |
| β/°                | 90 | 95.8882(10) | 90 |
| γ/°                | 90 | 90 | 90 |
| Unit cell volume/Å³| 5743.81(11) | 1522.91(3) | 3315.66(6) |
| Temperature/K      | 102(2) | 100(2) | 100(2) |
| Space group        | P2_{1}2_{1}2_{1} | P2_{1} | P2_{1}2_{1}2_{1} |
| No. of formula units per unit cell, Z | 4 | 2 | 4 |
| Radiation type     | Cu Kα | Cu Kα | Cu Kα |
| Absorption coefficient, μ/mm⁻¹ | 8.079 | 6.697 | 6.207 |
| No. of reflections measured | 119453 | 61905 | 69234 |
| No. of independent reflections | 12010 | 6370 | 6909 |
| R_{int}            | 0.0783 | 0.0543 | 0.0342 |
| Final R₁ values (I > 2σ(I)) | 0.0268 | 0.0263 | 0.0184 |
| Final wR(F²) values (I > 2σ(I)) | 0.0674 | 0.0658 | 0.0475 |
| Final R₁ values (all data) | 0.0273 | 0.0270 | 0.0186 |
| Final wR(F²) values (all data) | 0.0678 | 0.0665 | 0.0477 |
| Goodness of fit on F² | 1.037 | 1.044 | 1.046 |
| Flack parameter    | -0.038(5) | -0.035(8) | -0.027(3) |
| Δρ / e Å⁻³         | 0.904 / -0.959 | 0.529 / -1.803 | 0.352 / -1.099 |
1.3. Molecular structures
1.3.1. Rare-Earth Metal Halide Complexes
1.3.1.1. 6-Sc

55. Molecular structure of 6-Sc. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

1.3.1.2. 4-Y

56. Molecular structure of 4-Y. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
1.3.1.3. **4-Y**

![Structure of 4-Y](image1.png)

**57.** Molecular structure of 4-Y*. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

1.3.1.4. **5-La**

![Structure of 5-La](image2.png)

**58.** Molecular structure of 5-La. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
1.3.1.5. 5-Ce

S9. Molecular structure of 5-Ce. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

1.3.1.6. 4-Dy

S10. Molecular structure of 4-Dy. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
1.3.1.7. 4-Ho

**S11.** Molecular structure of 4-Ho. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

1.3.1.8. 4-Er

**S12.** Molecular structure of 4-Er. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
1.3.1.9. 4-Tm

S13. Molecular structure of 4-Tm. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

1.3.1.10. 4-Tm*

S14. Molecular structure of 4-Tm*. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
1.3.2. Rare-Earth Bis(trimethyl)silyl Amide Complexes

1.3.2.1. 7-Y

S15. Molecular structure of 7-Y. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

1.3.2.2. 7-La

S16. Molecular structure of 7-La. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
1.3.2.3. 7-Nd

S17. Molecular structure of 7-Nd. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

1.3.2.4. 7-Dy

S18. Molecular structure of 7-Dy. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
1.3.3. Rare-Earth Tetraborohydride Complexes

1.3.3.1. 8-Nd

S19. Molecular structure of 8-Nd. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, that are not part of the BH₄ moieties, are omitted for clarity.
1.3.4. Lutetium Complexes

1.3.4.1. 9-Lu

S20. Molecular structure of 9-Lu. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

1.3.4.2. 11-Lu

S21. Molecular structure of 11-Lu. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
1.4. Selected bond lengths and angles
1.4.1. Rare-Earth Metal Halide Complexes

S22. Selected bond lengths and angles for compounds 4-Y* and 4-Tm*.

|         | 4-Y*          | 4-Tm*          |
|---------|---------------|---------------|
| C1-C2   | 1.385(3) / 1.445(3) (Li) | 1.389(5) / 1.427(7) (Li) |
| C2-C3   | 1.411(3) / 1.380(3) (Li) | 1.409(5) / 1.379(7) (Li) |
| C3-C4   | 1.450(3) / 1.453(3) (Li) | 1.448(5) / 1.454(6) (Li) |
| C4-C5   | 1.360(3) / 1.351(3) (Li) | 1.364(6) / 1.349(6) (Li) |
| C1--C5  | 3.157(4) / 3.244(3) (Li) | 3.187(6) / 3.255(5) (Li) |
| M-pdlent | 2.491(1) / 2.048(5) (Li) | 2.449(1) / 1.930(9) (Li) |
| M-pdlplane | 2.425(1) / 1.990(5) (Li) | 2.356(1) / 1.872(9) (Li) |
| M-C1    | 2.781(2) / 2.357(4) (Li) | 2.607(4) / 2.377(9) (Li) |
| M-C2    | 2.605(2) / 2.312(5) (Li) | 2.611(3) / 2.372(11) (Li) |
| M-C3    | 2.648(2) / 2.387(5) (Li) | 2.733(3) / 2.391(10) (Li) |
| M-C4    | 3.037(2) / 2.604(4) (Li) | 3.143(4) / 2.434(9) (Li) |
| M-C5    | 3.419(3) / 3.037(5) (Li) | 3.247(5) / 2.727(8) (Li) |
| M-Nigand | 2.253(2) / 2.271(2) (Li) | 2.213(3) / 2.242(2) (Li) |
| Li-O1   | 1.980(4) | 1.926(7) |
| Li-O2   | 1.964(4) | 1.916(1) |
| C1-C2-C3| 126.0(2) / 128.0(2) (Li) | 125.2(3) / 127.6(4) (Li) |
| C2-C3-C4| 128.5(2) / 129.4(2) (Li) | 128.7(3) / 130.1(3) (Li) |
| C3-C4-C5| 129.2(2) / 128.2(2) (Li) | 130.1(4) / 129.2(3) (Li) |
| C13-Si-N1 | 109.06(9) | 108.7(2) |
| Si-N1-M  | 113.76(8) | 114.9(2) |
| pdlent-M-N1 | 115.8(1) | 113.3(1) |

(Li) values refer to the second pdl unit, which coordinates to the Li atom (see molecular structure in section xxx).
### 1.4.2. Rare-Earth Metal Bis(trimethyl)silyl Amide Complexes

S23. Selected bond lengths and angles for HMDS compounds 7-M.

|                  | 7-Y | 7-La | 7-Nd | 7-Dy | 7-Ho |
|------------------|-----|------|------|------|------|
| C1-C2            | 1.356(4) | 1.358(4) | 1.362(5) | 1.365(6) | 1.367(4) |
| C2-C3            | 1.440(4) | 1.441(3) | 1.439(5) | 1.437(6) | 1.440(4) |
| C3-C4            | 1.435(4) | 1.432(4) | 1.434(6) | 1.435(6) | 1.439(4) |
| C4-C5            | 1.367(4) | 1.372(4) | 1.367(6) | 1.374(6) | 1.372(4) |
| C1···C5          | 3.160(5) | 3.184(4) | 3.187(5) | 3.169(7) | 3.161(5) |
| M-pdlcent       | 2.352(1) | 2.521(1) | 2.460(1) | 2.366(1) | 2.353(1) |
| M-pdlplane       | 2.349(1) | 2.506(1) | 2.441(1) | 2.363(1) | 2.352(1) |
| M-C1             | 3.015(4) | 3.184(4) | 3.146(5) | 3.011(4) | 3.028(4) |
| M-C2             | 2.688(3) | 2.848(2) | 2.790(3) | 2.695(4) | 2.690(3) |
| M-C3             | 2.931(3) | 2.702(2) | 2.631(3) | 2.542(4) | 2.525(3) |
| M-C4             | 2.790(3) | 2.914(4) | 2.861(5) | 2.816(4) | 2.791(3) |
| M-C5             | 2.923(3) | 3.039(2) | 2.993(4) | 2.954(4) | 2.926(3) |
| M-Nligand        | 2.230(3) | 2.358(2) | 2.298(3) | 2.234(3) | 2.225(2) |
| M-O1ter         | 2.413(2) | 2.604(2) | 2.551(2) | 2.432(3) | 2.420(2) |
| M-N2             | 2.261(2) | 2.396(2) | 2.339(3) | 2.263(3) | 2.253(2) |
| Ln-Si2(HMDS) [Å] | 3.537(1) | 3.642(1) | 3.614(2) | 3.552(3) | 3.536(1) |
| Ln-Si3(HMDS) [Å] | 3.380(1) | 3.438(1) | 3.394(1) | 3.363(2) | 3.374(1) |
| Ln-CH3Si3(HMDS) [Å] | 3.317(4) | 3.245(4) | 3.218(5) | 3.264(5) | 3.312(4) |
| C1-C2-C3        | 125.7(3) | 125.9(2) | 126.1(3) | 125.8(4) | 125.8(3) |
| C2-C3-C4        | 127.8(3) | 128.5(2) | 128.2(4) | 128.1(4) | 127.6(3) |
| C3-C4-C5        | 129.3(3) | 129.3(3) | 129.5(5) | 129.0(4) | 128.9(3) |
| C13-Si-N1       | 107.4(2) | 107.6(1) | 107.7(2) | 107.4(2) | 107.5(2) |
| Si-N1-M         | 120.5(2) | 120.6(1) | 120.7(1) | 120.6(2) | 120.2(2) |
| pdlcent-M-N1    | 110.6(6) | 106.3(1) | 107.9(1) | 110.4(1) | 110.8(1) |
| Ln-N2-Si2(HMDS) [°] | 124.9(2) | 124.1(1) | 125.4(2) | 125.6(2) | 125.1(2) |
| Ln-N2-Si3(HMDS) [°] | 115.9(2) | 113.0(1) | 113.3(2) | 115.0(2) | 115.9(2) |
| Si2-N2-Si3(HMDS) [°] | 119.1(2) | 122.8(1) | 121.2(2) | 119.4(2) | 119.0(2) |
## Rare-Earth Metal Tetraborohydride Complexes

S24. Selected bond lengths and angles for compounds 8-La and 8-Nd.

|          | 8-La          | 8-Nd          |
|----------|---------------|---------------|
| C1-C2    | 1.373(9) [1.367(8)] | 1.376(6) [1.371(6)] |
| C2-C3    | 1.420(7) [1.428(8)] | 1.422(5) [1.421(6)] |
| C3-C4    | 1.435(7) [1.434(8)] | 1.436(5) [1.433(5)] |
| C4-C5    | 1.361(8) [1.373(8)] | 1.364(5) [1.373(5)] |
| C1···C5  | 3.172(9) [3.195(8)] | 3.172(6) [3.184(5)] |
| M-pdlcent | 2.448(1) [2.443(1)] | 2.385(1) [2.383(1)] |
| M-pdplanx | 2.425(1) [2.415(1)] | 2.361(1) [2.353(1)] |
| M-C1     | 2.854(6) [2.850(6)] | 2.792(4) [2.785(4)] |
| M-C2     | 2.760(5) [2.784(5)] | 2.709(3) [2.724(4)] |
| M-C3     | 2.728(5) [2.748(5)] | 2.669(3) [2.687(4)] |
| M-C4     | 2.953(5) [2.928(6)] | 2.904(3) [2.887(4)] |
| M-C5     | 3.018(6) [3.062(6)] | 3.038(4) [3.024(4)] |
| M-Nligand | 2.346(4) [2.345(5)] | 2.290(3) [2.288(3)] |
| M-Othf   | 2.631(3) [2.617(4)] | 2.568(2) [2.571(3)] |
| M1-B1    | 2.899(5) [2.907(6)] | 2.890(4) [2.869(4)] |
| M1-B2    | 3.073(6) [3.082(7)] | 3.007(5) [3.013(5)] |
| M2-B1    | 2.907(5) [2.884(6)] | 2.899(5) [2.836(4)] |
| M2-B2    | 3.109(6) [3.121(7)] | 3.056(5) [3.092(5)] |
| H01A-M1  | 2.654(44) [2.603(62)] | 2.565(60) [2.554(43)] |
| H01A-M2  | 2.826(35) [2.665(53)] | 2.889(48) [2.618(38)] |
| H01B-M1  | 2.801(54) [2.855(53)] | 3.003(58) [2.779(38)] |
| H01C-M1  | 2.792(39) [2.759(54)] | 2.712(32) [2.791(38)] |
| H01C-M2  | 2.615(41) [2.732(52)] | 2.611(31) [2.617(40)] |
| H01D-M2  | 2.722(59) [2.633(51)] | 2.596(49) [2.587(41)] |
| H02A-M1  | 2.508(52) [2.526(42)] | 2.450(42) [2.417(42)] |
| H02B-M2  | 2.576(6) [2.608(47)] | 2.468(41) [2.514(42)] |
| H02C-M1  | 2.713(44) [2.759(34)] | 2.616(36) [2.688(33)] |
| H02C-M2  | 2.771(50) [2.783(40)] | 2.755(42) [2.724(35)] |
| C1-C2-C3 | 126.0(5) [126.0(5)] | 125.6(4) [124.8(4)] |
| C2-C3-C4 | 129.5(5) [129.5(5)] | 129.1(4) [130.1(4)] |
| C3-C4-C5 | 129.6(5) [129.8(5)] | 129.6(3) [130.0(4)] |
| Si-Si-N1 | 106.9(2) [107.2(3)] | 106.3(2) [107.2(2)] |
| Si-N-M1  | 120.4(2) [121.5(3)] | 120.5(2) [121.3(2)] |
| pdlcent-M-N1 | 105.3(2) [105.3(1)] | 106.7(1) [107.0(1)] |

Values in parentheses are given for compounds with two independent molecules in the asymmetric unit.
2. NMR spectroscopy

2.1. $\text{H(pdl*SiMe}_2\text{HN'}\text{Bu)} (2)$

$^{1}$H NMR spectrum (400 MHz, $\text{C}_6\text{D}_6$, 298 K) of compound 2.
2.2. \([\text{[K}_2\text{pdl}}*\text{SiMe}_2\text{N}^1\text{Bu}]]\) (3) and rearrangement product 3’

S26. \(^1\text{H NMR spectrum (300 MHz, THF-d}_8 \text{, 298 K)} \) of compound 3.

S27. \(^{13}\text{C}[^1\text{H}] \text{NMR spectrum (151 MHz, THF-d}_8 \text{, 298 K)} \) of compounds 3 and 3’ (mixture). Marked signals correspond to 3.
S28. $^1$H NMR spectrum (600 MHz, THF-d$_8$, 298 K) of compounds 3 and 3' (mixture). Marked signals correspond to 3'.

S29. $^{13}$C($^1$H) NMR spectrum (151 MHz, THF-d$_8$, 298 K) of compounds 3 and 3' (mixture). Marked signals correspond to 3'.
2.3. Rare-Earth Metal Halide Complexes

2.3.1. 6-Sc

[S30. \(^1\)H NMR spectrum (500 MHz, C\(_6\)D\(_6\), 298 K) of compound 6-Sc.]

[S31. \(^{13}\)C\(^{1}\)H NMR) spectrum (126 MHz, C\(_6\)D\(_6\), 298 K) of compound 6-Sc.]
2.3.2. 4-Y

**S32.** $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 298 K) of compound 4-Y.

**S33.** $^{13}$C($^1$H) NMR spectrum (101 MHz, C$_6$D$_6$, 298 K) of compound 4-Y.
2.3.3. 5-La

$S34$. $^1$H NMR spectrum (400 MHz, $C_{6}D_{6}$, 298 K) of compound 5-La.

$S35$. $^{13}$C($^1$H NMR) spectrum (101 MHz, $C_{6}D_{6}$, 298 K) of compound 5-La.
2.3.4. S-Ce

Figure S36. $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 298 K) of compound S-Ce.
2.3.5. S-Pr

**S37.** $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 298 K) of compound S-Pr.

**S38.** $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 298 K) of compound S-Pr.
2.3.6. 5-Nd

S39. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of compound 5-Nd.
2.4. Rare-Earth Metal Bis(trimethyl)silyl Amide Complexes

2.4.1. 7-Y

S40. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of compound 7-Y.

S41. $^{13}$C($^1$H NMR) spectrum (101 MHz, C$_6$D$_6$, 298 K) of compound 7-Y.
2.4.2. 7-La

**S42.** $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of compound 7-La.

**S43.** $^{13}$C($^1$H NMR) spectrum (101 MHz, C$_6$D$_6$, 298 K) of compound 7-La.
2.4.3. 7-Nd

S44. $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 298 K) of compound 7-Nd.
2.5. Rare-Earth Metal Tetraborohydride Complexes

2.5.1. 8-La

S45. $^1$H NMR spectrum (600 MHz, C$_6$D$_6$, 298 K) of compound 8-La.

S46. $^{13}$C($^1$H) NMR spectrum (156 MHz, C$_6$D$_6$, 298 K) of compound 8-La.
\[ \text{S47. } ^{1}H \text{ NMR spectrum (128 MHz, } C_{6}D_{6}, 298 \text{ K) of compound 8-La.} \]
2.5.2. 8-Nd

**S48.** $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of compound 8-Nd.

**S49.** $^{11}$B ($^1$H) NMR spectrum (96 MHz, C$_6$D$_6$, 298 K) of compound 8-Nd.
2.6. Lutetium Triflate and Alkyl Complexes

2.6.1. 9-Lu

550. $^1$H NMR spectrum (500 MHz, $C_6D_6$, 298 K) of compound 9-Lu.

551. $^{13}$C($^1$H) NMR spectrum (101 MHz, $C_6D_6$, 298 K) of compound 9-Lu.
$^{19}$F$\mathrm{[}^1\mathrm{H}]$ NMR spectrum (471 MHz, C$_6$D$_6$, 298 K) of compound 9-Lu.
2.6.2. 10-Lu

S53. $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of compound 10-Lu.

S54. $^{13}$C($^1$H) NMR spectrum (126 MHz, C$_6$D$_6$, 298 K) of compound 10-Lu.
SS5. $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of compound 11-Lu.

SS6. $^{13}$C($^1$H) NMR spectrum (126 MHz, C$_6$D$_6$, 298 K) of compound 11-Lu.