Supporting Information

Triisobutylaluminium-promoted formation of lanthanide hydrides

Eric C. Moinet,^a Olivier Tardif,^b Cäcilia Maichle-Mössmer,^a and Reiner Anwander^{a,*}

^a Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany. E-mail: <u>reiner.anwander@uni-tuebingen.de</u>

^b Bridgestone Corporation, Ogawahigashi-cho, Kodaira-shi, Tokyo, 187-8531, Japan

Table of Contents

Experimental	S3
NMR Spectra	S7
Crystallography	S17
References	

Experimental

General Considerations

All manipulations were performed under rigorous exclusion of air and moisture, using standard Schlenk, high-vacuum, and glovebox techniques (MBraun MB200B <1 ppm O₂, <1 ppm H₂O, argon atmosphere). Solvents were supplied by Merck KGaA, purified using a SPS solvent purification system (MBraun) and stored inside a glovebox. Benzene- d_6 , toluene- d_8 and o-difluorobenzene were obtained from Merck KGaA and dried over Na/K alloy prior to use. Triisobutylaluminum (TIBA), and fluorene were purchased from Merck KGaA and used as received. 18-Crown-6 was purchased from abcr and used without further purification. Argon (99.999 Vol%) was supplied by Westfalen AG. Complexes $Ln[N(SiMe_3)_2]_3$ (Ln = La, Pr, Nd) were prepared following standard procedures.^[1] Chemicals were stored at -40 °C. Glassware and polymer fittings were dried prior to use for several hours at 120 °C or 80 °C, respectively. IR spectra were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific), and samples were mixed with KBr powder and measured in a DRIFT cell equipped with KBr windows. Elemental analyses were performed on an Elementar vario MICRO cube. NMR spectra of air and moisture sensitive compounds were recorded using J. Young-valved NMR tubes on a Bruker AVII+400 spectrometer (¹H: 400.13 MHz; ¹³C: 100.61 MHz). ¹H and ¹³C NMR chemical shifts are referenced to solvent residual resonances and reported in parts per million, relative to tetramethylsilane.

Caution! Note that organoaluminum compounds may react violently with air or moisture and may explode with water.

Procedures

La[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (1^{La})

A solution of TIBA (20.478 g, 103.257 mmol, 4.1 equiv.) in *n*-pentane (30 mL) was added to $La[N(SiMe_3)_2]_3$ (15.616 g, 25.185 mmol, 1 equiv.) in *n*-pentane (100 mL) in portions under stirring at ambient temperature. After stirring overnight, the yellowish solution was concentrated and

cooled to -40° C. Repeated recrystallization afforded 4.945 g (6.558 mmol, 26%) of combined fractions of La[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (**1**^{La}) in the form of colourless, big crystals. DRIFT (KBr, cm⁻¹): 2947 (vs), 2860 (s), 2735 (w), 1457 (s), 1381 (w), 1360 (m), 1315 (w), 1249 (s), 1161 (m), 1060 (m), 1036 (m), 958 (s), 847 (vs), 824 (s), 736 (s), 677 (vs), 648 (vs), 439 (s). C₃₄H₈₂Al₂LaNSi₂ (754.06 g/mol): calcd. C 54.16, H 10.96, N 1.86; found C 53.97, H 11.13, N 1.81. ¹H NMR (400.1 MHz, C₆D₆, 26 °C): δ 6.46 (s, 1 H, HAl*i*Bu₃); 2.27 (m, 3 H, CH {HAl*i*Bu₃}); 1.97 (m, 4 H, CH {Al*i*Bu₄}); 1.25 (d, 18 H, CH₃ {HAl*i*Bu₃}); 1.14 (d, 24 H, CH₃ {Al*i*Bu₄}); 0.45 (d, 8 H, CH₂ {Al*i*Bu₄}); 0.42 (d, 6 H, CH₂ {HAl*i*Bu₃}); 0.32 (s, 18 H, CH₃ {N(SiMe₃)₂}) ppm. ¹³C{¹H} NMR (100.6 MHz, 26 °C): δ 34.5 (CH₂ {Al*i*Bu₄}); 30.6 (CH₂ {HAl*i*Bu₃}); 29.1 (CH {Al*i*Bu₄}); 29.0 (CH {HAl*i*Bu₃}); 28.7 (CH₃ {HAl*i*Bu₃}); 28.5 (CH₃ {Al*i*Bu₄}); 3.9 (CH₃ {N(SiMe₃)₂}) ppm.

Pr[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (1^{Pr})

To a solution of Pr[N(SiMe₃)₂]₃ (4.911 g, 7.895 mmol) in *n*-pentane (50 mL), TIBA (6.452 g, 32.533 mmol, 4.1 equiv.) in *n*-pentane (20 mL) was added in portions. After stirring 12 h at ambient temperature, the yellow-green solution was concentrated *in vacuo* and cooled to -40 °C. Repeated recrystallization afforded 1.674 g (2.214 mmol, 28%) yellow-green crystals of Pr[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄). DRIFT (KBr, cm⁻¹): 2950 (vs), 2861 (s), 2732 (vw), 1463 (w), 1381 (vw), 1361 (vw), 1318 (vw), 1260 (w), 1250 (m), 1159 (vw), 1064 (w), 1017 (w), 943 (m), 859 (m), 835 (m), 814 (m), 779 (w), 734 (w), 682 (m), 656 (w), 619 (w), 572 (vw). C₃₄H₈₂Al₂PrNSi₂ (756.06 g/mol): calcd. C 54.01, H 10.93 N 1.85; found C 53.86, H 10.65, N 1.67.

Nd[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (1Nd)

To a solution of Nd[N(SiMe₃)₂]₃ (2.624 g, 4.196 mmol) in *n*-hexane (100 mL), TIBA (4.161 g, 20.98 mmol, 5 equiv.) in *n*-hexane (20 mL) was added in portions. After stirring 12 h at ambient temperature, the solution was concentrated *in vacuo* to a volume of 10 mL. The red-green solution yielded dark blue crystals suitable for X-ray diffraction upon storage at -40 °C. The crystals were purified by recrystallization, yielding 1.060 g (1.396 mmol, 33%) big blue column-

shaped crystals (see Fig. S1). DRIFT (KBr, cm⁻¹): 2950 (vs), 2861 (s), 2729 (w), 1463 (vs), 1381 (m), 1359 (m), 1317 (m), 1249 (s), 1159 (m), 1051 (m), 1017 (m), 983 (w), 861 (s), 850 (s), 833 (s), 778 (s), 736 (m), 684 (m), 652 (m), 600 (m), 553 (w), 435 (w). C₃₄H₈₂Al₂NdNSi₂ (759.40 g/mol): calcd. C 53.77, H 10.88, N 1.84; found C 53.86, H 10.54, N 1.94.



Figure S1. Crystals of $\mathbf{1}^{Nd}$. The solution of pure $\mathbf{1}^{Nd}$ is deep blue, whereas minor contamination of $\mathbf{1}^{Nd}$ with TIBA/reaction side products results in a solution showing both blue and purple color (right). The reaction mixture containing $\mathbf{1}^{Nd}$ prior to crystallization exhibits both red and green color at the same time (left), a behavior known for other neodymium compounds.^[2]

[Nd(18-C-6){N(SiMe₃)₂}(HAliBu₃)][AliBu₄] (2)

To a solution of 250 mg (0.329 mmol) Nd[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (**1**Nd) in *n*-pentane (4 mL), a solution of 18-crown-6 (82.9 mg, 0.314 mmol, 0.95 equiv.) in toluene (1 mL) was added dropwise under stirring at ambient temperature. The immediately formed suspension was stirred for five minutes. Removal of the solvent in vacuum, and washing of the residue three times with cooled *n*-pentane yielded a sticky, pale bluish white powder (324 mg, 96%). Single crystals suitable for X-ray crystallography were grown from *o*-difluorobenzene at –40 °C. DRIFT (KBr, cm⁻¹): 2948 (vs), 2855 (vs), 2765 (m), 2581 (vw), 1457 (s), 1403 (w), 1369 (m), 1354 (s), 1289 (m), 1258 (s), 1201 (vw), 1161 (m), 1085 (s), 1009 (w), 962 (s), 914 (s), 859 (s), 776 (m), 696 (m), 666 (s), 617 (m), 430

(w). C₄₆H₁₀₆Al₂NNdO₆Si₂ (1023.52 g/mol): calcd. C 53.97, H 10.44, N 1.37; found C 53.97, H 10.38, N 1.17.

$[(\mu-fluorenyl)_{3}La_{2}(\mu-H)(HAliBu_{3})_{2}]$ (3) and $(fluorenyl)_{2}La[N(SiMe_{3})_{2}]$ (4)

A mixture of 500 mg (0.666 mmol) La[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (**1**^{La}) and fluorene (222 mg, 0.666 mmol, 1 equiv.) was suspended in benzene and left in a sealed vial for ten days without stirring, after which crystalline product suitable for X-ray analysis was formed. The solvent of the obtained orange-red suspension was removed *in vacuo*, and the residue was washed twice with *n*-pentane (1 mL) and dried. The product mixture was obtained as orange-red powder (250.2 mg, 139 mmol, 63%). DRIFT (KBr, cm⁻¹): 3082 (w), 2942 (s), 2854 (m), 2769 (vw), 1594 (w), 1558 (m), 1472 (m), 1458 (m), 1431 (m), 1371 (m), 1355 (m), 1331 (m), 1243 (w), 1197 (w), 1156 (w), 1111 (vw), 1053 (w), 1015 (w), 974 (vw), 948 (w), 860 (w), 820 (m), 786 (vs), 754 (vs), 733 (m), 722 (m), 694 (m), 638 (w), 567 (w), 496 (vw), 434 (m), 425 (w). C₉₅H₁₂₀Al₂La₃NSi₂ (**3** and **4**,1802.83 g/mol): calcd. C 63.29, H 6.71, N 0.78; found C 63.71, H 6.76, N 0.56.

NMR Spectra

In general, solvent residual signals are labeled with an asterisk (*). In some cases, the paramagnetic nature of Pr(III), and Nd(III) ($\mathbf{1}^{Pr}$, $\mathbf{1}^{Nd}$, $\mathbf{2}$), or poor solubility ($\mathbf{3}$) did not allow conclusive NMR analysis.



Figure S2. ¹H-NMR spectrum (400 MHz, C₆D₆, 26 °C) of La[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (1^{La}).



Figure S3. ¹³C-NMR spectrum (101 MHz, C₆D₆, 26 °C) of La[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (1^{La}).



Figure S4. ¹H-¹³C-HSQC NMR spectrum (400/101 MHz, C₆D₆, 26 °C) of La[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (1^{La}).



Figure S5. ¹H-NMR spectrum (400 MHz, C₆D₆, 26 °C) of the reaction of $La[N(SiMe_3)_2](HAl$ *i* $Bu_3)(Al$ *i* $Bu_4)$ (**1**^{La}) with 2 equiv. TIBA in C₆D₆.



Figure S6. ¹H-NMR spectra (400 MHz, C_6D_6 , 26 °C) of the reaction of $La[N(SiMe_3)_2](HAliBu_3)(AliBu_4)$ (**1**^{La}) with 1, and 3 equiv. TIBA in C_6D_6 , and **1**^{La} for comparison.





Figure S7. Variable temperature ¹H-NMR spectra (500 MHz, toluene- d_8) of La[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (1^{La}).



Figure S8. ¹H-NMR spectrum (400 MHz, C_6D_6 , 26 °C) of the reaction of $La[N(SiMe_3)_2]_3$ with 4 equiv. of TIBA, or DIBAH.



Figure S9. ¹H-NMR spectrum (400 MHz, C₆D₆, 26 °C) of La[N(SiMe₃)₂](HAl*i*Bu₃)(Al*i*Bu₄) (1^{La}) after heating for 1 h at 70°C.



Figure S10. ¹H-MAS NMR spectrum (500 MHz, 26 °C) of $(\mu$ -fluorenyl)₃La₂(μ -H)(HAl*i*Bu₃)₂ (**3**) and (fluorenyl)₂La[N(SiMe₃)₂] (**4**) including spinning sidebands (*).



Figure S11. ¹H NMR spectrum (400 MHz, C₆D₆, 26 °C) of the reaction of (μ -fluorenyl)₃La₂(μ -H)(HAl*i*Bu₃)₂ (**3**) and (fluorenyl)₂La[N(SiMe₃)₂] (**4**) with 20 equiv. isopropanol in C₆D₆ showing the formation of hydrogen (4.47 ppm).



Figure S12. ¹H NMR spectrum (400 MHz, C₆D₆, 26 °C) of the reaction of (μ -fluorenyl)₃La₂(μ -H)(HAl*i*Bu₃)₂ (**3**) and (fluorenyl)₂La[N(SiMe₃)₂] (**4**) with 20 equiv. isopropanol- d_8 in C₆D₆, showing the formation of HD-gas (nonbinomial triplett; 4.43 ppm), and dihydrogen (singulett; 4.47 ppm).

Crystallography

Crystal Structure Determination and Crystallographic Data

Single crystals suitable for X-ray diffraction were selected in a glovebox, coated with Parabar 10312 (Hampton Research), and fixed on a nylon/loop glass fiber. X-ray data for all compounds were collected on a Bruker APEX II DUO diffractometer equipped with an I μ S microfocus sealed tube and QUAZAR optics for MoK_a (λ = 0.71073 Å). The data collection strategy was determined using COSMO,^[3] employing ω -scans. Raw data were processed using APEX^[4], and SAINT^[5]. Corrections for absorption effects were applied using SADABS.^[6] The structures were solved by direct methods and refined against all data by full-matrix least-squares methods on F² using SHELXTL^[7], and ShelXle.^[8] All structures except **2** showed disorder. Compound **1-Pr** is not a single crystal, but it was not possible to refine the date as a twin or 'Drilling'. For compound **3/4** disorder was calculated using DSR, a program for refining structures in ShelXl.^[9] For compound **3/4** a global restraint (RIGU/SIMU) was applied to all atoms to achieve a more chemically reasonable model, furthermore twinning was found. All graphics were produced employing Mercury 4.2.011^[10] and POV-Ray12.^[11]

For X-ray crystallography, single-crystalline of $\mathbf{1}^{La}$ and $\mathbf{1}^{Pr}$ were grown from saturated solutions in *n*-pentane at -40 °C, and of $\mathbf{1}^{Nd}$ from *n*-hexane at -40 °C. Single crystals of **2** suitable for X-ray crystallography were grown from *o*-difluorobenzene at -40 °C. (μ -fluorenyl)₃La₂(μ -H)(HAl*i*Bu₃)₂ (**3**) and (fluorenyl)₂La[N(SiMe₃)₂] (**4**) were crystallized from benzene at ambient temperature.



Figure S13. Crystal structure of 1^{La} . Hydrogen atoms except the bridging hydride are omitted for clarity. Atomic displacement ellipsoids were set at 50% probability. Selected interatomic distances [Å] and angles [°]: La(1)–C(1) 2.782(4), La(1)–C(5) 2.755(4), La(1)–C(9) 3.155(1), La(1)–C(17) 2.823(4), La(1)^{...}Si(1) 3.432(1), La(1)^{...}Si(2) 3.428(1), Al(1)–C(1) 2.078(4), Al(1)–C(5) 2.096(4), Al(1)–C(9) 2.024(4), Al(2)–C(17) 2.058(4), Al(2)–H(1) 1.66(3), La(1)–N(1) 2.276(3), La(1)^{...}Al(1) 3.0243(1), La(1)^{...}Al(2) 3.330(1), La(1)–H(1) 2.22(3), La(1)-Al(1)-C(1) 62.9(1), La(1)-Al(1)-C(5) 162.0(1), La(1)-Al(2) 74.4(1), La(1)-Al(1)-C(9) 74.4(1), Al(2)-C(17)-La(1) 84.5(1), C(17)-Al(2)-La(1) 57.5(1), La(1)-Al(2)-H(1) 36.2(10), N(1)-La(1)-C(1) 126.12(11), N(1)-La(1)-C(5) 135.56(10), N(1)-La(1)-C(17) 90.75(10), C(1)-La(1)-Al(1) 41.69(8), C(5)-La(1)-Al(1) 42.20(8), C(17)-La(1)-Al(1) 140.79(8), N(1)-La(1)-Al(1) 112.302(7), N(1)-La(1)-Al(2) 106.69(7), N(1)-La(1)-H(1) 112.4(8), C(1)-La(1)-H(1) 75.4(8), C(5)-La(1)-H(1) 111.1(8), C(17)-La(1)-H(1) 64.1(8), La(1)-N(1)-Si(1) 117.64(14), La(1)-N(1)-Si(2) 117.27(15), Si(1)-N(1)-Si(2) 124.48(17).



Figure S14. Crystal structure of 1^{Pr} . Hydrogen atoms except the bridging hydride are omitted for clarity. Atomic displacement ellipsoids were set at 50% probability. Selected interatomic distances [Å] and angles [°]: Pr(1)–C(1) 2.565(8), Pr(1)–C(5) 2.715(4), Pr(1)–C(9) 3.2499(5), Pr(1)–C(17) 2.808(4), Pr(1)^{...}Si(1) 3.434(3), Pr(1)^{...}Si(2) 3.634(2), Al(1)–C(1) 2.173(8), Al(1)–C(5) 2.102(3), Al(1)–C(9) 2.158(13), Al(2)–C(17) 2.105(5), Al(2)–H(2C) 1.55(5), Pr(1)–N(1) 2.356(9), Pr(1)–N(1A) 2.136(8), Pr(1)^{...}Al(1) 2.9944(12), Pr(1)^{...}Al(2) 3.182(4), Pr(1)–H(1) 2.22(5), C(1)-Al(1)-Pr(1) 56.9(2), C(5)-Al(1)-Pr(1) 61.5(1), C(9)-Al(1)-Pr(1) 71.1(3), Al(2)-C(17)-Pr(1) 79.3(1), C(17)-Al(2)-Pr(1) 60.1(1), Pr(1)-Al(2) -40(2) 39(2), N(1)-Pr(1)-C(1) 111.0(3), N(1)-Pr(1)-C(5) 146.1(2), N(1)-Pr(1)-C(17) 90.6(2), N(1)-Pr(1)-Al(1) 125.4(2), C(1)-Pr(1)-Al(1) 45.2(2), C(5)-Pr(1)-Al(1) 42.85(7), C(17)-Pr(1)-Al(1) 141.61(7), N(1)-Pr(1)-Al(1) 125.4(2), N(1)-Pr(1)-Al(2) 103.9(2), N(1)-Pr(1)-H(2C) 104.8(14), C(1)-Pr(1)-H(2C) 74.9(1), C(5)-Pr(1)-H(2C) 109.1(1), C(17)-Pr(1)-H(2C) 66.5(1). Pr(1)-N(1)-Si(1) 113.30 (4), Pr(1)-N(1)-Si(2) 124.81 (4), Si(1)-N(1)-Si(2) 121.73 (5).



Figure S15. Crystal structure of **1**Nd. Hydrogen atoms except the bridging hydride are omitted for clarity. Atomic displacement ellipsoids were set at 50% probability. Selected interatomic distances [Å] and angles [°]: Nd(1)–C(1) 2.542(11), Nd(1)–C(5) 2.708(5), Nd(1)–C(9) 3.237(6), Nd(1)–C(17) 2.763(7), Nd(1)^{...}Si(1) 3.277(6), Nd(1)^{...}Si(2) 3.354(5), Al(1)–C(1) 2.101(16), Al(1)–C(5) 2.093(6), Al(1)–C(9) 2.019(6), Al(2)–C(17) 2.054(7), Al(2)–H(2) 1.63(5), Nd(1)–N(1) 2.208(5), Nd(1)^{...}Al(1) 2.999(2), Nd(1)^{...}Al(2) 3.243(2), Nd(1)–H(2) 2.17(5), Nd(1)-Al(1)-C(1) 56.5(3), Nd(1)-Al(1)-C(5) 61.3(2), Nd(1)-Al(2) 77.6(2), Nd(1)–C(17)-Al(2) 83.3(2), Nd(1)-Al(2)-C(17) 57.8 (2), Nd(1)-Al(2)-H(2) 37.0(17), N(1)-Nd(1)-C(1) 111.6(5), N(1)-Nd(1)-C(5) 141.6(2), N(1)-Nd(1)-C(17) 94.3(2), N(1)-Nd(1)-Al(1) 120.7(1), C(1)-Nd(1)-Al(2) 103.5(2), N(1)-Nd(1)-H(2) 105.5(14), C(1)-Nd(1)-H(2) 78.6(14), C(5)-Nd(1)-H(2) 112.9(13), C(17)-Nd(1)-H(2) 65.8(13). Nd(1)-N(1)-Si(1) 107.37(3), Nd(1)-N(1)-Si(2) 126.44(4), Si(1)-N(1)-Si(2) 125.99(4).



Figure S16. Crystal structure of **2**. Hydrogen atoms except the bridging hydride are omitted for clarity. Atomic displacement ellipsoids were set at 50% probability. Selected interatomic distances [Å] and angles [°]: Nd(1)–N(1) 2.329(2), Nd(1)^{...}Si(1) 3.6329(9), Nd(1)^{...}Si(2) 3.519(1), Nd(1)–O(1) 2.500(2), Nd(1)–O(2) 2.578(2), Nd(1)–O(3) 2.545(2), Nd(1)–O(4) 2.537(2), Nd(1)–O(5) 2.545(2), Nd(1)–O(6) 2.541(2), Nd(1)–H(1) 2.39(3), Al(1)–H(1) 1.70(3), N(1)-Nd(1)-H(1) 170.1(7), Nd(1)-H(1) 157.5(16), Nd(1)-N(1)-Si(1) 126.08(13), Nd(1)-N(1)-Si(2) 119.12(13), Si(1)-N(1)-Si(2) 114.78(14).



Figure S17. Crystal structure of **3** and **4** (left), core motif of **3** showing disorder of the fluorenyl rings (right). Hydrogen atoms except the bridging hydrides, as well as the disorder in fluorenyl ions are omitted for clarity; isobutyl moieties are displayed as capped sticks. Atomic displacement ellipsoids were set at 50% probability. Selected interatomic distances [Å] and angles [°] for **3**: La(1)–H(1) 2.39(1), La(1)–H(2) 2.29(2), Al(1)–H(1) 1.63(1), La(1)-centroid(1) 2.680, La(1)-centroid(2) 2.634, La(1)-centroid(3) 2.629, range La–C 2.893-3.018, La(1)-H(1)-Al(1) 169.4, H(1)-La(1)-H(2) 166(3). Selected interatomic distances [Å] for **4**: La(1)-N(1) 2.309(2), La(1)-centroid(1) 2.585, La(1)-centroid(2) 2.623.

	1 ^{La}	1 ^{Pr}	1 Nd
formula	$C_{34}H_{82}Al_2LaNSi_2 \\$	$C_{34}H_{82}Al_2NPrSi_2$	C ₃₄ H ₈₂ Al ₂ NNdSi ₂
CCDC	2249268	2249269	2249266
$M \left[g \text{ mol}^{-1}\right]$	754.05	756.05	759.38
color/shape	colourless/column	colourless/block	turquoise/needle
crystal dimensions [mm]	0.235 x 0.100 x 0.081	0.187 x 0.150 x 0.143	0.182 x 0.070 x 0.041
cryst. system	triclinic	triclinic	triclinic
space group	$P\overline{1}$	PĪ	PĪ
a [Å]	9.304(1)	9.309(1)	9.339 (1)
<i>b</i> [Å]	11.606(1)	11.525(2)	11.492(2)
<i>c</i> [Å]	21.098(2)	21.018(3)	20.898(3)
α[°]	93.848(2)	94.562(1)	94.846(2)°.
eta[°]	102.114(2)	101.615(1)	101.606(2)°.
γ[°]	92.747(2)	92.784(1)°.	92.456(2)°.
<i>V</i> [Å ³]	2218.0(4)	2196.9(6)	2184.8(6)
Ζ	2	2	2
<i>T</i> [K]	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073
$ ho_{ m calcd} [m Mg \ m^{-3}]$	1.129	1.143	1.154
$\mu[\mathrm{mm}^{-1}]$	1.077	1.224	1.304
F (000)	808	812	814
θ range [°]	2.089/27.138	1.776/30.640	2.124/24.806
unique reflns	9764	13495	7459
observed reflns	92155	126853	57683
R1 ^[b] /wR2 (I>20) ^[c]	0.0420/0.0841	0.0456/0.1024	0.0558/0.1212
R1 ^[b] /wR2 (all data) ^[c]	0.0645/0.0943	0.0609/0.1167	0.0817/0.1359
GOF ^[a]	1.036	1.131	1.040

Table S1. Crystallographic data for compounds $\mathbf{1}^{La},\,\mathbf{1}^{Pr}$ and $\mathbf{1}^{Nd}$

 ${}^{[a]}G\overline{\mathsf{OF}} = [\Sigma w(F_0^2 - F_c^2)^2 / (n_0 - n_p)]^{1/2} \cdot [^{[b]}\mathsf{R}_1 = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|, F_0 > 4\sigma(F_0) \cdot [^{c]}w\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_1 = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|, F_0 > 4\sigma(F_0) \cdot [^{c]}w\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_1 = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|, F_0 > 4\sigma(F_0) \cdot [^{c]}w\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_1 = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|, F_0 > 4\sigma(F_0) \cdot [^{c]}w\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_1 = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|, F_0 > 4\sigma(F_0) \cdot [^{c]}w\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_1 = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|, F_0 > 4\sigma(F_0) \cdot [^{c]}w\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2 - F_c^2)^2] \cdot [^{b]}\mathsf{R}_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2$

	2	3/4
formula	$C_{46}H_{106}Al_2NNdO_6Si_2$	$C_{95}H_{120}Al_2La_3NSi_2$
CCDC	2249267	2249265
M [g mol ⁻¹]	1023.69	1802.78
color/shape	colourless/needle	orange/plate
crystal dimensions [mm]	0.187 x 0.097 x 0.051 mm3	0.079 x 0.068 x 0.048
cryst. system	monoclinic	monoclinic
space group	$P2_{1}/c$	$P2_1/m$
a [Å]	14.134(2)	9.0290(7)
<i>b</i> [Å]	15.570(2)	28.770(2)
<i>c</i> [Å]	26.282(3)	16.089(1)
<i>α</i> [°]	90	90
β [°]	91.616(2)°.	89.983(2)
γ[°]	90	90
V [Å ³]	5781(1)	4179.2(6)
Z	4	2
<i>T</i> [K]	100(2)	100(2)
wavelength [Å]	0.71073	0.71073
$ ho_{ m calcd}$ [Mg m ⁻³]	1.176	1.433
μ[mm ⁻¹]	1.009	1.601
F (000)	2204	1844
θ range [°]	1.441/28.342	1.266/26.390
unique reflns	14361	8677
observed reflns	90248	36003
R1 ^[b] /wR2 (I>2ơ) ^[c]	0.0395/0.0806	0.0738/0.1838
R1 ^[b] /wR2 (all data) ^[c]	0.0633/0.0916	0.1027/0.2022
GOF ^[a]	1.020	1.035

Table S2. Crystallographic data for compounds 2, and 3/4

 $\overline{[a]GOF = [\Sigma w(F_0^2 - F_c^2)^2 / (n_0 - n_p)]^{1/2} \cdot [b]R_1} = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|, F_0 > 4\sigma(F_0) \cdot [c]wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [b]R_1 = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|, F_0 > 4\sigma(F_0) \cdot [c]wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2)^2]\}^{1/2} \cdot [b]R_1 = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|, F_0 > 4\sigma(F_0) \cdot [c]wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2 / \Sigma [w(F_0^2$

References

- [1] D. C. Bradley, J. S. Ghotra and F. A. Hart, J. Chem. Soc., Dalton Trans. 1973, 1021-1023.
- [2] A. C. Fecker, M. Freytag, P. G. Jones and M. D. Walter, *Dalton Trans.* 2019, **48**, 8297-8302.
- [3] COSMO v. 1.61, Bruker AXS Inc., Madison, WI, 2012.
- [4] APEX3 V. 2019.11-0, Bruker AXS Inc., Madison, WI, 2019.
- [5] SAINT V. 8.40B, Bruker Nano, Inc., 2019.
- [6] L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, J. Appl. Crystallogr. 2015, 48, 3-10.
- [7] G. Sheldrick, *Acta Crystallogr. Sect. C.* 2015, **71**, 3-8.
- [8] C. B. Hübschle, G. M. Sheldrick and B. Dittrich, J. Appl. Crystallogr. 2011, 44, 1281-1284.
- [9] D. Kratzert, J. J. Holstein and I. Krossing, J. Appl. Crystallogr. 2015, 48, 933-938.
- [10] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, J. Appl. Crystallogr. 2006, **39**, 453-457.
- [11] POV-Ray v.3.6, Persistence of Vision Pty. Ltd., POV-Ray Williamstown, Victoria, Australia. http://www.povray.org, 2004.