Synthesis and Structural Characterization of Rare Earth Metal Disulfonamide Complexes[☆]

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The reaction of rare earth silylamides $Ln[N(SiHMe_2)_2]_3(thf)_n$ [n = 1 for Sc (**1a**); n = 2 for Y (**1b**), La (**1c**), Nd (**1d**)] with *trans*-1,2-bis(2,4,6-triisopropylbenzenesulfonamido)cyclohexane (H_2L, *rac*-**2**) in toluene at ambient temperature proceeds via an extended silylamide route, affording highly soluble complexes $Sc(L)[N(SiHMe_2)_2]$ (**3**) and $Ln(L)[N(SiHMe_2)_2](thf)$ (**4a–c**) in excellent yields. An X-ray crystallographic study performed on the solvent-free, dinuclear yttrium derivative **5** revealed an unusual $\mu_2,\eta^4:\eta^1$-coordination of the disulfonamide ligand, involving bridging S=O groups. In solution, equilibria between dimeric and monomeric forms, dependent on the presence of a donor molecule, were observed by NMR techniques.

In the last decade rare earth metals have gained considerable interest as highly efficient catalysts for a variety of organic transformations.[1] Dicyclopentadienyl complexes, e.g., *ansa*-lanthanidocenes as depicted in Figure 1, represent key compounds in precatalyst design. Although the cyclopentadienyl backbone imposes a unique electronic and steric situation including complex chirality, broader application of these systems is hampered by their pronounced sensibility towards moisture. Recently, alternative ligands were successfully introduced to cope with the peculiarities of organolanthanide chemistry, e.g., lanthanide binaphthol derivatives in Lewis acid catalysis.[2] Our current research interests put main emphasis on the replacement of the dicyclopentadienyl backbone by other divalent auxiliary ligands, which are prone to fine-tuning in the sense of solubility, chirality and steric and electronic factors. In the course of these studies we found synthetic access to the first monomeric salen complexes of the lanthanide elements via an extended silylamide route (Figure 1).[3] Encouraged by these results we anticipated application of this synthetic route to other catalytically relevant ligand systems. Disulfonamides constitute a class of ligands well established in the coordination chemistry of strongly Lewis acidic metal centers such as boron(III),[4] aluminum(III),[5] and titanium(IV).[6][7] These complexes are of significant importance in several catalytic transformations such as the Diels-Alder reaction or the alkylation of carbonyl groups.[8] Analogous lanthanide complexes, though postulated once,[9] have never been characterized. Here, we report the synthesis and characterization of the first soluble rare earth complexes derived from chelating disulfonamides.

Results and Discussion

The synthesis of the novel disulfonamide complexes **3** and **4a−c** was achieved by an extended silylamide route,[3][10][11] utilizing $Ln[N(SiHMe_2)_2]_3(thf)_n$ as synthetic precursors as shown in Scheme 1. The ligand *trans*-1,2-bis(2,4,6-triisopropylbenzenesulfonamido)cyclohexane (*rac*-**2**) was chosen according to the following considerations: (i) *trans*-1,2-diaminocyclohexane provides a relatively rigid backbone. Additionally, it offers easy access to enantiomerically pure ligands, which should lead to enantioselective precatalysts.[12] (ii) The sterically demanding triisopropylphenyl groups should favor monomeric complexes, and (iii) induce increased solubility in non-polar solvents. The rare earth elements Sc, Y, and La were selected to cover the entire range of cation radii and in the case of Nd to visually follow the reaction by color effects. Our examinations on rare earth salen derivatives revealed that cation size and ligand bite angle are important factors to direct the formation of monomeric complexes.[3b]

The disulfonamide complexes **3** and **4a−c** are formed by the subsequent aminolysis of two rare earth bis(dimethylsilyl)amide bonds[*] by the more acidic sulfonamide (pK_a ca. 10−11, measured in water).[13] The remaining third bis(dimethylsilyl)amide ligand was characterized by a sharp Si−H vibration at ca. 2065 cm^{-1}. Interestingly, the reaction is accompanied by the loss of one molecule THF (GC-MS analysis). Compounds **3** and **4a−c** are obtained in yields > 90% after evaporation of the volatiles. Their excellent solubility even in non-polar solvents such as toluene or *n*-hexane indicates the formation of non-oligomerized products for the differently sized cations. Although the enhanced solubility hampered further purification by recrystallization, satisfying elemental analyses were obtained in most

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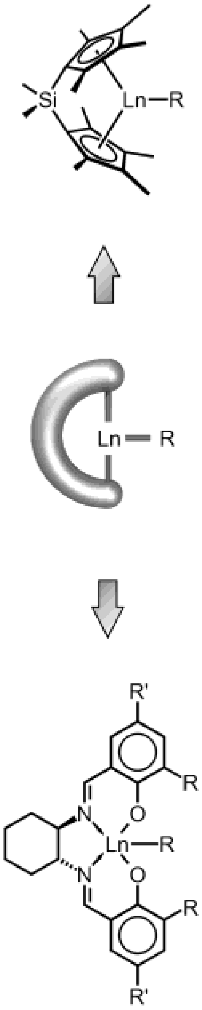
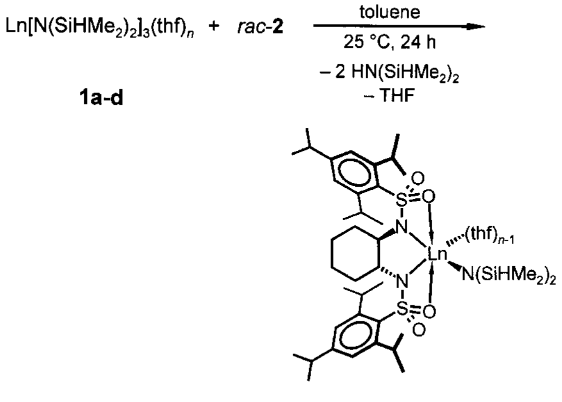
[*] The use of $Ln[N(SiMe_3)_2]_3$ as a synthetic precursor is hampered by partial product oligomerization.

Figure 1. Conceptional design of divalent auxiliary ligands



Scheme 1. Synthesis of the complexes **3** and **4a-c** via an extended silylamide route



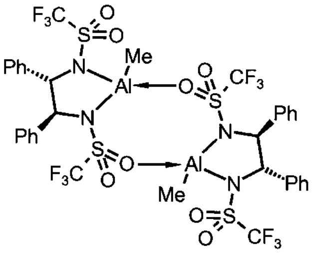
3 (Ln = Sc; *n* = 1)

4a-c (Ln = Y, La, Nd; *n* = 2)

cases, indicating a very clean reaction under mild conditions. Elemental analysis revealed that one THF solvent molecule coordinates to the larger lanthanide cations while scandium can accomodate no THF molecule. This finding could also be confirmed by ^{1}H-NMR spectroscopy. The yttrium derivative **4a** could be further desolvated by prolonged exposure to high vacuum to yield the less soluble compound **5**, crystals of which could be grown from hot *n*-hexane.

First NMR spectroscopic examinations of compounds **3–5** in C_6D_6 revealed spectra rather difficult to understand with broad, poorly resolved, overlapping signals. We assume two major effects to be responsible for this behavior. Firstly, sulfonyl moieties are known to serve as electron donors capable of forming Lewis acid-base adducts with metal cations. Depending on geometric and electronic factors Lewis acid-base adduct formation can occur in both an intra- and intermolecular fashion. As shown previously for aluminum (**6**)[5a] and indium (**7**)[14] sulfonamides, organization to dimers leads to extended heterocyclic ring systems (Figure 2).

Figure 2. Intermolecular bridging of sulfonamide ligands via S=O donor interactions; for **7**, even intramolecular interactions are discussed



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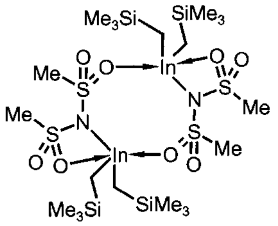

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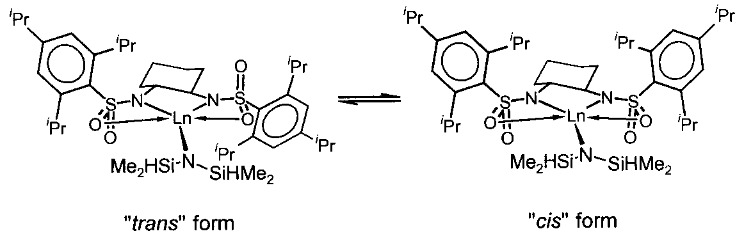
A monomer-dimer equilibrium in solution is supposed to partly contribute to the poor NMR spectra observed in C_6D_6. The second reason can be found in an unusually strong *intramolecular* coordination of the sulfonamido group. Very recently, Walsh and Gagne independently reported a η^2-coordination of the sulfonamido group in titanium complexes, resembling strongly our lanthanide derivatives.[6][7] Although these monomeric complexes do not show similar solution behavior, we postulate *cis/trans* isomers observable on NMR time scale, resulting from a hindered rotation around the S–N bond (Scheme 2). Evidence for both of these assumptions is given by an X-ray diffraction study performed on the yttrium complex **5** (vide infra).

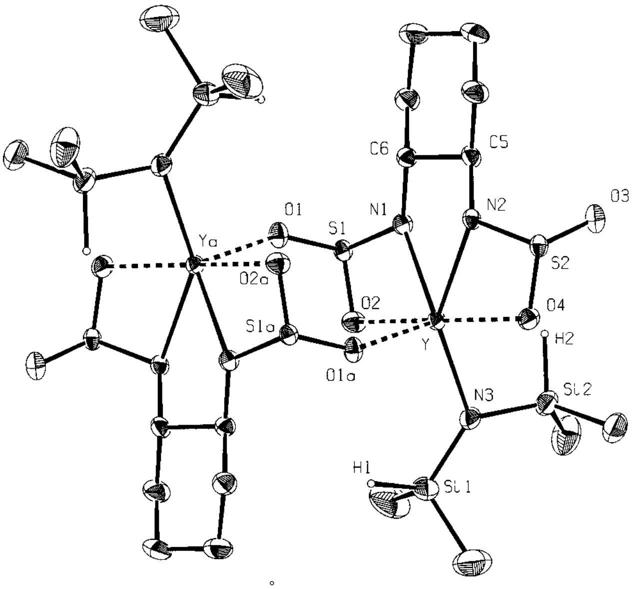
Consequently, the NMR spectra simplified remarkably when recorded in a donor solvent like [D_8]THF. THF coor-

Scheme 2. Dynamic equilibrium between *trans*- and *cis*-rotamers (coordinated THF has been omitted for clarity)



dination reduces the Lewis acidity of the metal center and thus lowers the rotation barrier around the S−N bond. Furthermore, THF coordination counteracts dimerization by replacing *intermolecular* sulfonyl bridging. The observed set of resonances is in agreement with a C_2-symmetric structure on the NMR time scale. As expected, ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra of **3−5** are very similar to each other. Moreover, addition of only one equivalent of a strong donor, e.g., triphenylphosphane oxide, is sufficient to achieve the same result, proven in case of the ^{1}H-NMR spectrum of THF-free **5** in C_6D_6. Trends within the series cannot be determined easily, except the rising high field shift of the ^{29}Si resonance from $\delta = -23.4$ to $\delta = -26.1$ which correlates to the decreasing Lewis acidity from Sc to La. No fluxional behavior could be observed by variable temperature NMR studies in the range of −80 to 110°C in [D$_8$]toluene.

Figure 3. Solid-state structure of dimeric complex **5** (PLATON[16] plot). Thermal ellipsoids are drawn at the 50% probability level. 2,4,6-Triisopropylphenyl groups at the sulfur atoms and all carbon bonded hydrogen atoms are omitted for clarity[a]



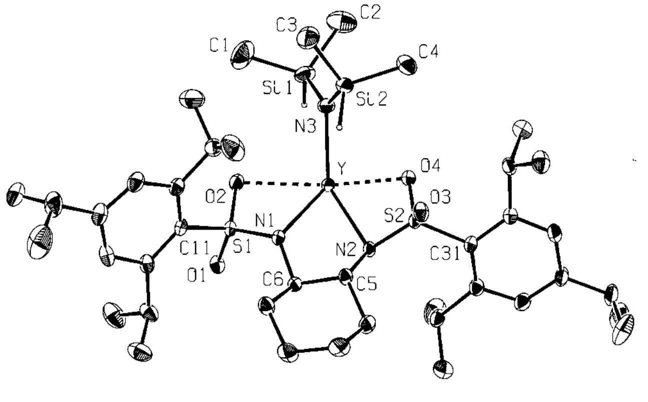
[a] Selected bond lengths [A] and angles [°]: Y−N(1) 2.365(2), Y−N(2) 2.403(2), Y−N(3) 2.239(2), Y−O(1)a 2.234(2), Y−O(2) 2.600(2), Y−O(4) 2.358(2), S(1)−O(1) 1.482(2), S(1)−O(2) 1.463(2), S(2)−O(3) 1.438(2), S(2)−O(4) 1.491(2), S(1)−N(1) 1.546(2), S(2)−N(2) 1.563(2), Y−Si(1) 3.5401(3), Y−Si(2) 3.1058(7), Y−H(1) 3.573(9), Y−H(2) 2.619(1); N(1)−Y−N(2) 66.41(6), Y−N(1)−S(1) 101.64(9), Y−N(2)−S(2) 96.45(8), O(2)−S(1)−N(1) 103.11(9), O(4)−S(2)−N(2) 100.87(9), Y−O(2)−S(1) 94.25(7), Y−O(4)−S(2) 100.45(7), O(2)−Y−N(1) 56.45(5), O(4)−Y−N(2) 59.29(5), Y−N(3)−Si(1) 127.6(1), Y−N(3)−Si(2) 103.57(9), Si(1)−N(3)−Si(2) 128.4(1).

The X-ray structure determination of **5** (triclinic, space group *P*1) both revealed its dimeric nature and an unusual coordination of the formally bidentate disulfonamide ligand. Complex **5** consists of the two enantiomers located on a crystallographic inversion center, forming a structure which could be described as a "racemic dimer" (Figure 3). The sulfonyl oxygen bridging results in the formation of an eight-membered chair-shaped ring system comparable to those in **6** and **7**.[5][14] A similar structural motif is also found in μ,η^2-SO$_3$CF$_3$ bridged lanthanidocene triflate complexes (cf. $[(C_5H_5)_2Yb(\mu\text{-}O_2SOCF_3)]_2$).[15] The resulting coordination polyhedron of the central yttrium is best considered as a bi-capped tetrahedron with the intramolecularly coordinating O(2) and O(4) in the capping positions.

In the solid state complex **5** adopts a *trans* configuration, which is fixed via intramolecular coordination of two sulfonyl oxygen atoms, as depicted in Figure 4. The detection of the *trans* form gives additional evidence of the solution behavior of compound **5** (Scheme 2).

Closer inspection of the yttrium disulfonamide bonding reveals an unprecedented μ$_2$,η^4:η^1-coordination mode of this ligand system. The η^4-coordination results from two Y−N$^{(\text{sulfonamide})}$ and two intramolecular Y−O$^{(\text{sulfonyl})}$ bonds. The Y−N$^{(\text{sulfonamide})}$ bond distances of 2.365(2) A and 2.403(2) A are longer than Y−N$^{(\text{dialkylamide})}$ or Y−N$^{(\text{silylamide})}$ bond lengths and are comparable to Y−N bonds containing delocalized charge density within the organic amide ligand. Representative examples include benzamidinate $[\{p\text{-MeOC}_6\text{H}_4\text{C(NSiMe}_3)_2\}_2\text{YCH(SiMe}_3)_2]$

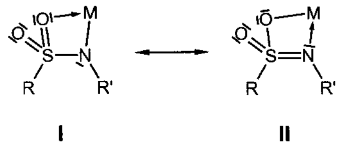
Figure 4. Structure of the mononuclear unit of **5** (PLATON[16] plot). Thermal ellipsoids are drawn at the 50% probability level. All carbon bonded hydrogen atoms are omitted for clarity



[Y−N 2.325(4)−2.345(4) Å],[17] aminotroponiminate (ATI) [(iPr$_2$ATI)YCl$_2$(thf)$_2$]$_2$ [2.331(5), 2.430(5) Å],[18] phthalocyanine (Pc) [Y(Pc^{2-})(Pc$^-$)]·CH$_2$Cl$_2$ [2.395(3)−2.406(4) Å],[19] or alkoxydimethylsilylamide [{Me$_2$Si(NtBu)(OtBu)}$_2$-YCH(SiMe$_3$)$_2$] [2.20(2), 2.32(1) Å].[20] The Y−O distances range between 2.234(2)−2.600(2) Å. The Y−O(4) distance of 2.358(2) Å of the non-bridging sulfonyl moiety together with the adjacent Y−N(2) bond of similar length resemble the bonding in η^2-coordinating carboxylates, e.g., [Cp$_2$Y{η^2-O$_2$C(CH$_2$)$_3$NMe$_2$}] [2.390(3), 2.406(3) Å].[21] The bridging sulfonyl moiety forms a long intramolecular contact of 2.600(2) Å [Y(1)−O(2)] which lies in the long range order of Y−O$^{(donor)}$ bonds and a relatively short Y−O(1a) contact which approaches bridging Y−O$^{(alkoxide)}$ bond lengths.[22] The marked differences in the Y−O bond distances arise from two effects: While the attractive interaction in Y−O(4) is affected by ring tension of the four-membered Y−N−S−O cycle [cf. Y−N(1)−S(1) 101.64(9)°, Y−N(2)−S(2) 96.45(8)°], reduced partial charge of the doubly coordinating SO$_2$ moiety additionally weakens the Y−O(2) interaction. The Y−O(1a) displays the unperturbed case and hence shows the shortest contact.

The charge delocalization in the disulfonamide ligand is also clear from the S=O and S−N bonding. The S=O bonds of the Y-bonded oxygen atoms average 1.479(2) Å, whereas the bond distance of S(2)=O(3) [1.434(2) Å] lies in the typical non-interacting range (1.423−1.444 Å).[23] The S−N distances amount to an average of 1.555(2) Å, clearly indicating a partial double bond character (cf. RNH−SO$_2$R′ 1.600-1.623 Å).[23] The special mode of coordination is best understood by a charge delocalized model, as shown in Scheme 3. While **I** represents the classic case of a deprotonated sulfonamide, **II** displays a sulfonate type coordination, resulting in elongated S=O distances and shortened S−N bonds.

Scheme 3. Charge delocalized description of a η^2-coordinating sulfonamido group



In contrast, the metal sulfonyl interactions in similar titanium complexes are weak and ascribed to crystal packing forces.[6] In fact, all Ti−O contacts are by far longer (0.17−0.38 Å) than the Ti−N bonds.[6][7] In compound **5** the Y−N and Y−O bonds approximately equal each other which is consistent with strong metal oxygen interaction. The different metal oxygen bonding in the titanium and lanthanide complexes is also reflected in the different solution behavior described above.

The Y−N(3) bond length [2.239(2) Å] of the silylamide ligand is comparable to that of the precursor silylamide [2.229(4)−2.276(4) Å].[11] Interestingly, the N(SiHMe$_2$)$_2$ moiety coordinates asymmetrically to the yttrium center, featuring structural details previously ascribed to β-SiH agostic interactions.[24] The Y−N−Si angles differ significantly [103.57(9), 127.6(1)°] and the H(2) of one SiHMe$_2$ group could be localized relatively close to the yttrium center [Y−Si(2) 3.1058(7) Å]. However, the sharp Si−H stretch frequencies in complexes **3**−**5** clearly range in the area of non-interacting Si−H groups,[25] although shoulders often termed as agostic could be detected at ca. 1950 cm^{-1}. If electronically forced, e.g., agostic, the Y···(Si−H) interaction in **5** would indicate electron deficiency at the metal center, which is highly desirable for the anticipated catalytic applications.

In conclusion, we have synthesized highly soluble rare earth complexes with formally bidentate disulfonamide ligands according to an extended silylamide route. The obtained heteroleptic complexes of type "(L)Ln^{III}R" bearing the disulfonamide ligand as a divalent auxiliary ligand L and the silylamide ligand R as a reactive, readily exchangeable moiety are potential candidates for rare earth mediated catalysis. The complexes show unprecedented ligand coordination, as evidenced by a μ$_2$,η^4:η^1-coordination of a desolvated dinuclear complex in the solid state. The presence of a strong metal sulfonyl coordination is further suggested by the solution behavior (NMR experiments). The asymmetric coordination of the bis(dimethylsilyl)amide ligand appears to be sterically forced, albeit the metal···(Si−H) coordination might qualify as a sensitive probe to evaluate the electronic situation at early transition metal centers. Current studies concentrate on ligand variations and examinations of the resulting complexes in Lewis acid catalysis.

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Experimental Section

General: All rare earth complexes were synthesized and manipulated under an argon atmosphere using either standard high-vacuum techniques or a glovebox (MBraun MB150B; O$_2$ < 2 ppm, H$_2$O < 1 ppm). Toluene and *n*-hexane were distilled from Na/K/benzophenone and stored under argon. Deuterated THF was dried by stirring over Na/K alloy. All starting materials were purchased from Aldrich Chemical Co. and used without further purification. The synthesis of the disulfonamide *rac*-**2** is described in detail, because slight modifications of the established synthesis procedures were applied.[26] The bis(dimethylsilyl)amides of Sc, Y, La, and Nd (**1a**−**d**) were prepared according to the literature procedure.[27] − NMR: Jeol JNM-GX-400 (399.80, 100.51, and 79.43 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively). Spectra were referenced internally using the residual solvent resonances (^{1}H, ^{13}C) or referenced externally to TMS (^{29}Si; $\delta = 0$). [D$_8$]THF as solvent $\delta_H = 3.58/1.73$, $\delta_C = 67.7/25.5$. − FTIR: Perkin-Elmer 1650. − Elemental analyses: Mikroanalytisches Laboratorium at the department of inorganic chemistry of the Technische Universität München.

trans-1,2-Bis(2,4,6-triisopropylbenzenesulfonamido)cyclohexane (*rac*-**2**): Racemic **2** was prepared by addition of a pre-cooled solution of 6.36 g (21.0 mmol) of 2,4,6-triisopropylbenzene sulfonyl chloride in 30 ml of CH$_2$Cl$_2$ to an ice-cold, stirred solution of 1.14 g (10.0 mmol) of *trans*-1,2-diaminocyclohexane and 2.13 g (21.0 mmol) of triethyl amine in 50 ml of CH$_2$Cl$_2$. The mixture was stirred overnight while it was allowed to warm up to room temperature. The solution was washed successively with 50 ml of hydrochloric acid (1 N), saturated $NaHCO_3$ solution, and brine. Drying of the organic phase over Na_2SO_4 and evaporation of the solvent gave a crude product which was purified by column chromatography (silica, CH_2Cl_2/EtOAc, 40:1 v/v, $R_f = 0.32$) to yield 5.96 g of *rac*-**2** (92%) as a white solid, m.p. 206−207°C. NMR and IR spectroscopic data and elemental analysis are in agreement with the data reported for (1*R*,2*R*)-1,2-bis(2,4,6-triisopropylbenzenesulfonamido)cyclohexane.[26]

General Procedure for the Preparation of the Rare Earth Metal Disulfonamide Complexes (**3** *and* **4a−c**): To a stirred solution of 0.50 mmol of the rare earth bis(dimethylsilyl)amide $Ln[N(SiHMe_2)_2]_3(thf)_n$ (Y, La, Nd: $n = 2$; Sc: $n = 1$) in 15 ml of toluene an equimolar amount (0.50 mmol) of *rac*-**2** was added slowly. The ligand dissolved within a few minutes (Sc: 1 h). To ensure complete reaction the mixture was stirred for further 24 h. Then the solvent and volatile products were evaporated in vacuo to yield the complexes **3** and **4a−c**.

[trans-1,2-Bis(2,4,6-triisopropylbenzenesulfonamidato)cyclohexane-N,N′][bis(dimethylsilyl)amido]scandium(III) (**3**): 385 mg (94%), colorless, amorphous solid. The compound starts to decompose at 130°C to yield a material that forms a homogeneous melt at 230°C. − ^{1}H NMR ([D$_8$]THF, 25°C): δ = 7.14 (s, 4 H, -C$_6$*H*$_2$*i*Pr$_3$), 4.58 [sept, ^3J = 6.8 Hz, 4 H, *o*-C*H*(CH$_3$)$_2$], 4.47 [sept, ^3J = 3.0 Hz, 2 H, -Si(CH$_3$)$_2$*H*], 3.48 [m, 2 H, -C*H*$_\alpha$(N−Sc)-], 2.86 [sept, ^3J = 6.9 Hz, 2 H, *p*-C*H*(CH$_3$)$_2$], 1.86 (m, 2 H, CH*H*$_\beta$), 1.60 (m, 2 H, C*H*H$_\beta$), 1.24 [d, ^3J = 6.8 Hz, 24 H, *o*-CH(C*H*$_3$)$_2$], 1.23 [d, ^3J = 6.9 Hz, 12 H, *p*-CH(C*H*$_3$)$_2$], 0.86 (m, 4 H, C*H*$_{2,\gamma}$), 0.12 [d, ^3J = 3.0 Hz, 12 H, -Si(C*H*$_3$)$_2$H]. − ^{13}C{^{1}H} NMR ([D$_8$]THF, 25°C): δ = 151.8 (*C*-4), 148.9 (*C*-2,6), 124.1 (*C*-3,5), 66.2 [-*C*H$_\alpha$(N−Sc)-], 35.0 (*C*H$_{2,\beta}$), 34.5 [*p*-*C*H(CH$_3$)$_2$], 30.6 [*o*-*C*H(CH$_3$)$_2$], 26.1 [*o*-CH(*C*H$_3$)$_2$], 24.0 [*p*-CH(*C*H$_3$)$_2$], 1.4 [-Si(*C*H$_3$)$_2$H]; *C*-1 not detected; *C*H$_{2,\gamma}$ might be hidden by the residual solvent signal. − ^{29}Si{^{1}H} NMR ([D$_8$]THF, 25°C): δ = −23.4. − IR (Nujol): ν = 2068 m [ν(Si−H)], 1601 m, 1565 w, 1423 m, 1363 m, 1315 w, 1243 s [ν(S=O)], 1207 w, 1167 s, 1150 m, 1133 m, 1106 s, 1064 m, 1046 m [ν(S=O)], 1019 m, 1007 m, 987 m, 971 m, 938 m, 900 s, 842 m, 802 w, 783 w, 699 w, 676 m, 660 m, 630 w, 586 w, 552 w cm^{-1}. − $C_{40}H_{70}N_3O_4S_2ScSi_2$ (822.3): calcd. C 58.43, H 8.58, N 5.11, S 7.80; found C 58.5, H 8.8, N 4.4, S 7.2.

(Tetrahydrofurane)[trans-1,2-bis(2,4,6-triisopropylbenzenesulfonamidato)cyclohexane-N,N′][bis(dimethylsilyl)amido]yttrium(III) (**4a**): 455 mg (97%), colorless, brittle solid. − ^{1}H NMR ([D$_8$]THF, 25°C): δ = 7.15 (s, 4 H, -C$_6$*H*$_2$*i*Pr$_3$), 4.66 [sept, ^3J = 3.0 Hz, 2 H, -Si(CH$_3$)$_2$*H*], 4.49 [sept, ^3J = 6.7 Hz, 4 H, *o*-C*H*(CH$_3$)$_2$], 3.41 [m, 2 H, -C*H*$_\alpha$(N−Y)-], 2.87 [sept, ^3J = 6.9 Hz, 2 H, *p*-C*H*(CH$_3$)$_2$], 1.84 (m, 2 H, CH*H*$_\beta$), 1.57 (m, 2 H, C*H*H$_\beta$), 1.25 [d, ^3J = 6.9 Hz, 12 H, *p*-CH(C*H*$_3$)$_2$], 1.23 [d, ^3J = 6.7 Hz, 24 H, *o*-CH(C*H*$_3$)$_2$], 0.89 (m, 4 H, C*H*$_{2,\gamma}$), 0.11 [d, ^3J = 3.0 Hz, 12 H, -Si(C*H*$_3$)$_2$H]. − ^{13}C{^{1}H} NMR ([D$_8$]THF, 25°C): δ = 151.3 (*C*-4), 149.2 (*C*-2,6), 142.1 (*C*-1), 124.2 (*C*-3,5), 64.0 [-*C*H$_\alpha$(N−Y)-], 35.7 [*p*-*C*H(CH$_3$)$_2$], 34.9 (*C*H$_{2,\beta}$), 30.0 [*o*-*C*H(CH$_3$)$_2$], 26.0 [*o*-CH(*C*H$_3$)$_2$], 25.7 (*C*H$_{2,\gamma}$), 24.0 [*p*-CH(*C*H$_3$)$_2$], 3.7 [-Si(*C*H$_3$)$_2$H]. − ^{29}Si{^{1}H} NMR ([D$_8$]THF, 25°C): δ = −25.7. − IR (Nujol): ν = 2069 m [ν(Si−H)], 1948 w sh, 1601 m, 1564 w, 1423 m, 1364 m, 1317 w, 1241 s [ν(S=O)], 1164 s, 1106 m, 1076 m, 1048 s [ν(S=O)], 1022 m, 984 s, 939 m, 899 s, 842 m, 813 w, 795 w, 777 w, 759 w, 673 s, 658 m, 587 m, 555 w cm^{-1}. − $C_{44}H_{78}N_3O_5S_2Si_2Y$ (938.3): calcd. C 56.32, H 8.38, N 4.48, S 6.83; found C 55.9, H 7.3, N 4.2, S 7.0.

(Tetrahydrofurane)[trans-1,2-bis(2,4,6-triisopropylbenzenesulfonamidato)cyclohexane-N,N′][bis(dimethylsilyl)amido]lanthanum(III) (**4b**): 450 mg (91%), colorless, brittle solid. − ^{1}H NMR ([D$_8$]THF, 25°C): δ = 7.13 (s, 4 H, -C$_6$*H*$_2$*i*Pr$_3$), 4.75 [sept, ^3J = 3.0 Hz, 2 H, -Si(CH$_3$)$_2$*H*], 4.63 [sept, ^3J = 6.8 Hz, 4 H, *o*-C*H*(CH$_3$)$_2$], 3.39 [m, 2 H, -C*H*$_\alpha$(N−La)-], 2.88 [sept, ^3J = 6.8 Hz, 2 H, *p*-C*H*(CH$_3$)$_2$], 1.73 (m, 2 H, CH*H*$_\beta$), 1.47 (m, 2 H, C*H*H$_\beta$), 1.27 [d, ^3J = 6.8 Hz, 12 H, *p*-CH(C*H*$_3$)$_2$], 1.23 [d, ^3J = 6.8 Hz, 24 H, *o*-CH(C*H*$_3$)$_2$], 1.01 (m, 4 H, C*H*$_{2,\gamma}$), 0.11 [d, ^3J = 3.0 Hz, 12 H, -Si(C*H*$_3$)$_2$H]. − ^{13}C{^{1}H} NMR ([D$_8$]THF, 25°C): δ = 151.1 (*C*-4), 149.4 (*C*-2,6), 142.5 (*C*-1), 123.7 (*C*-3,5), 64.8 [-*C*H$_\alpha$(N−La)-], 35.0 (*C*H$_{2,\beta}$), 34.6 [*p*-*C*H(CH$_3$)$_2$], 29.8 [*o*-*C*H(CH$_3$)$_2$], 26.0 [*o*-CH(*C*H$_3$)$_2$], 25.4 (*C*H$_{2,\gamma}$), 24.1 [*p*-CH(*C*H$_3$)$_2$], 3.2 [-Si(*C*H$_3$)$_2$H]. − ^{29}Si{^{1}H} NMR ([D$_8$]THF, 25°C): δ = −26.1. − IR (Nujol): ν = 2062 m [ν(Si−H)], 1945 w sh, 1601 m, 1563 w, 1241 s [ν(S=O)], 1219 m, 1195 m, 1163 s, 1126 m, 1074 m, 1063 m, 1046 s [ν(S=O)], 1012 m, 980 m, 940 m, 896 s, 879 m, 842 m, 810 m, 789 w, 764 w, 671 s, 629 w, 596 m, 578 w, 492 w cm^{-1}. − $C_{44}H_{78}LaN_3O_5S_2Si_2$ (988.3): calcd. C 53.47, H 7.95, N 4.25, S 6.49; found C 53.9, H 7.7, N 4.3, S 6.7.

(Tetrahydrofurane)[trans-1,2-bis(2,4,6-triisopropylbenzenesulfonamidato)cyclohexane-N,N′][bis(dimethylsilyl)amido]neodymium(III) (**4c**): 421 mg (85%), pale blue, brittle solid. − IR (Nujol): ν = 2071 m [ν(Si−H)], 1951 w sh, 1601 m, 1563 w, 1314 w, 1241 s [ν(S=O)], 1219 s, 1193 m, 1163 s, 1130 m, 1106 m, 1064 m, 1046 s [(S=O)], 1013 s, 980 s, 940 m, 897 vs, 842 m, 810 m, 764 w, 671 s, 630 w, 586 m, 557 w cm^{-1}. − $C_{44}H_{78}N_3NdO_5S_2Si_2$ (993.7): calcd. C 53.19, H 7.91, N 4.23, S 6.45; found C 52.7, H 7.5, N 4.0, S 5.7.

Bis{[trans-1,2-bis(2,4,6-triisopropylbenzenesulfonamidato)cyclohexane-N,N′][bis(dimethylsilyl)amido]yttrium(III)} (**5**): In a Schlenk tube 1.877 g (2.00 mmol) of finely powdered **4a** was exposed to high vacuum ($p < 10^{-5}$ mbar) for 24 h. Afterwards 25 ml of *n*-hexane was added in the cold, leading to an insoluble residue and a clear solution, which was separated. Recrystallization of the white residue from hot *n*-hexane yielded 534 mg of **5** (31%) as colorless crystals suitable for X-ray structure determination. − ^{1}H NMR ([D$_8$]THF, 25°C): δ = 7.15 (s, 4 H, -C$_6$*H*$_2$*i*Pr$_3$), 4.66 [sept, ^3J = 3.0 Hz, 2 H, -Si(CH$_3$)$_2$*H*], 4.49 [sept, ^3J = 6.7 Hz, 4 H, *o*-C*H*(CH$_3$)$_2$], 3.41 [m, 2 H, -C*H*$_\alpha$(N−Y)-], 2.87 [sept, ^3J = 6.9 Hz, 2 H, *p*-C*H*(CH$_3$)$_2$], 1.84 (m, 2 H, CH*H*$_\beta$), 1.57 (m, 2 H, C*H*H$_\beta$), 1.25 [d, ^3J = 6.9 Hz, 12 H, *p*-CH(C*H*$_3$)$_2$], 1.23 [d, ^3J = 6.7 Hz, 24 H, *o*-CH(C*H*$_3$)$_2$], 0.89 (m, 4 H, C*H*$_{2,\gamma}$), 0.11 [d, ^3J = 3.0 Hz, 12 H, -Si(C*H*$_3$)$_2$H]. − ^{13}C{^{1}H} NMR ([D$_8$]THF, 25°C): δ = 151.3 (*C*-4), 149.2 (*C*-2,6), 142.1 (*C*-1), 124.2 (*C*-3,5), 64.0 [-*C*H$_\alpha$(N−Y)-], 35.7 [*p*-*C*H(CH$_3$)$_2$], 34.9 (*C*H$_{2,\beta}$), 30.0 [*o*-*C*H(CH$_3$)$_2$], 26.0 [*o*-CH(*C*H$_3$)$_2$], 25.7 (*C*H$_{2,\gamma}$), 24.0 [*p*-CH(*C*H$_3$)$_2$], 3.7 [-Si(*C*H$_3$)$_2$H]. − ^{29}Si{^{1}H} NMR ([D$_8$]THF, 25°C): δ = −25.7. − IR (Nujol): ν = 2088 m [ν(Si−H)], 1917 w sh, 1602 m, 1566 w, 1423 m, 1365 s, 1314 w, 1296 w, 1239 s [ν(S=O)], 1206 m, 1182 s, 1160 s, 1146 m, 1128 m, 1079 s, 1067 s [ν(S=O)], 1042 m, 1019 m, 988 m, 965 m, 940 m, 903 s, 882 s, 838 m, 820 m, 792 m, 762 m, 674 s, 652 w, 633 w, 621 w, 594 w, 587 m, 564 w, 556 m, 495 w, 485 w, 411 w cm^{-1}. − $C_{80}H_{140}N_6O_8S_4Si_4Y_2$ (1732.4): calcd. C 55.46, H 8.15, N 4.85, S 7.40; found C 55.6, H 8.1, N 4.7, S 8.5.

X-ray Crystal Structure Analysis of **5**: $C_{80}H_{140}N_6O_8S_4Si_4Y_2$; M_r = 1732.44; a = 12.3022(5), b = 13.4696(8), c = 14.8607(9) A, α = 74.823(6), β = 79.688(5), γ = 78.454(5)°; triclinic, $P\bar{1}$ (Int. Table Nr.: 2); V = 2307.6(2) A^3; Z = 1; D_{calc} = 1.247 g cm^{-3}; μ = 1.45 mm^{-1} (Mo-K_α); F(000) = 924; A colorless crystal was mounted on a STOE IPDS[28] diffractometer (graphite-monochromated Mo-K_α radiation). 32070 reflections (Θ range: 1.65°−26.05°; $-13 < h < 13$, $-16 < k < 16$, $-18 < l < 18$) were collected at 193 K and corrected for Lorentz, polarization and X-ray absorption effects (program FACEIT[28]: $T_{\min} = 0.6779$; $T_{\max} = 0.8307$). Preliminary positions of heavy atoms were found by direct methods,[29] while positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotropic least square refinement.[30] All none-H atoms were refined anisotropically. The hydrogen atoms, except for Si−H, were placed in calculated positions. They were included in the structure factor calculation but not refined. The final refinement (on F_o^2) of 477 parameters with 8176 independent reflections ($R_{\text{merge}} = 0.049$) converged at $R_1 = 0.0399$, $wR_2 = 0.0660$ and $GOF = 0.931$. The final weighting scheme was calculated to $w^{-1} = \sigma^2(F_o^2)+(0.0392\cdot P)^2$ with $P = (F_o^2+2\cdot F_c^2)/3$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 101422. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(0)1223/ 336-033, e-mail: teched@chemcrys.cam.ac.uk].

☆ Dedicated to Professor *William J. Evans* on the occasion of his 50th birthday.

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