Aminotroponimines as Ligands for Yttrium and Lanthanide Complexes

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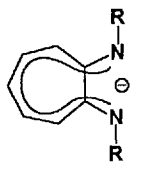
The reaction of *N*-isopropyl-2-(isopropylamino)troponimine, [(*i*-Pr)$_2$ATI]H, with KH in THF affords [(*i*-Pr)$_2$ATI]K. This is a useful starting material for the preparation of the mono-, bis- and tris-substituted compounds {[(*i*-Pr)$_2$ATI]YCl$_2$-(THF)$_2$}$_2$, [(*i*-Pr)$_2$ATI]$_2$Y[O(2,6-*t*-Bu$_2$C$_6$H$_3$)] and [(*i*-Pr)$_2$-ATI]$_3$Ln (Ln = Y, La, Sm), which can be obtained from [(*i*-Pr)$_2$ATI]K and LnX$_3$ (X = Cl, I), or Y[O(2,6-*t*-BuC$_6$H$_3$)]$_3$. All compounds have been characterized by spectroscopic methods. The monosubstituted yttrium complex {[(*i*-Pr)$_2$ATI]YCl$_2$(THF)$_2$}$_2$ has also been investigated by single crystal X-ray diffraction.

Metallocenes of organolanthanides[1] have proven to be highly efficient catalysts[2] for a variety of olefin transformations including hydrogenation[3], polymerization[4], hydroamination[5], hydrosilylation[6], hydroboration[7] and reductive or silylative cyclization of α,ω-dienes[8]. Recently, there has been significant research effort to substitute the cyclopentadienyl ligand[9] by anionic nitrogen-based bidentate ligand systems such as diazabutadienes[10] or benzamidinates[11]. The benzamidinates in particular, which have recently found use in catalytic applications[12], have similar steric properties to the cyclopentadienyl systems.

Herein, the initial results of an investigation of aminotroponiminates, [ATI]$^-$, are reported. [ATI]$^-$, which was very recently introduced into group 4 chemistry as a cyclopentadienyl analogue[13], is a bidentate mono anionic ligand containing a 10 π electron backbone. Upon coordination to a metal atom [ATI]$^-$ forms a five-membered metallacycle. As well as group 4 compounds, [ATI]$^-$ complexes with group 13 metals[14], tin[14] and the first row of transition metals[15] have also been reported.



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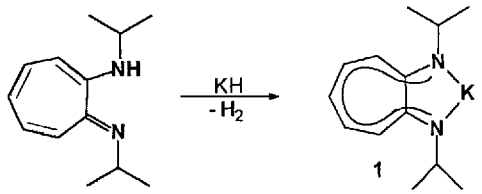
In this paper, the synthesis of potassium *N*-isopropyl-2-(isopropylamino)troponiminate is reported, along with details of further reactions of this reagent with yttrium and lanthanide halides/alkoxides in various stoichiometric ratios. These reactions lead to the first [ATI]$^-$ derivatives of yttrium and the lanthanides.

Results and Discussion

The potassium salt of *N*-isopropyl-2-(isopropylamino)-troponimine, [(*i*-Pr)$_2$ATI]K (**1**), was synthesized by treatment of the neutral ligand with an excess of KH in THF. It was obtained as a very air-sensitive yellow powder and was characterized by ^{1}H- and ^{13}C-NMR (spectroscopy). The spectra indicate that the alkali metal cation of **1** is not coordinated by THF. This is in contrast to the analogous lithium compound, in which 2 equivalents of THF are coordinated[13]. In comparison to the neutral ligand, the NMR signals of **1** show only a slight downfield shift. The isopropyl C*H* resonance (δ = 3.67) is shifted only 0.07 ppm downfield upon metallation of the ligand. As has been observed previously for the corresponding lithium[13] and aluminium[14a] salts of **1**, the room temperature NMR spectrum is indicative of a very symmetrical structure.



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In order to investigate the coordination behavior of [(*i*-Pr)$_2$ATI]$^-$ on yttrium and the lanthanide metals, compounds with one, two, or three ligands attached to the metal center were desired. Transmetallation of **1** with an excess of anhydrous yttrium trichloride in THF, followed by work-up in diethyl ether, afforded the corresponding yttrium chloro complex {[(*i*-Pr)$_2$ATI]YCl$_2$(THF)$_2$}$_2$ (**2**) as a pure crystalline solid in fairly good yield. Although the complex crystallized with two equivalents of THF, it tended to lose some of the loosely-coordinated solvent molecules upon washing with pentane.The decreasing THF ratio could be followed by recording a ^{1}H NMR spectrum after each washing. The process is reversible such that recrystallization of **2** from

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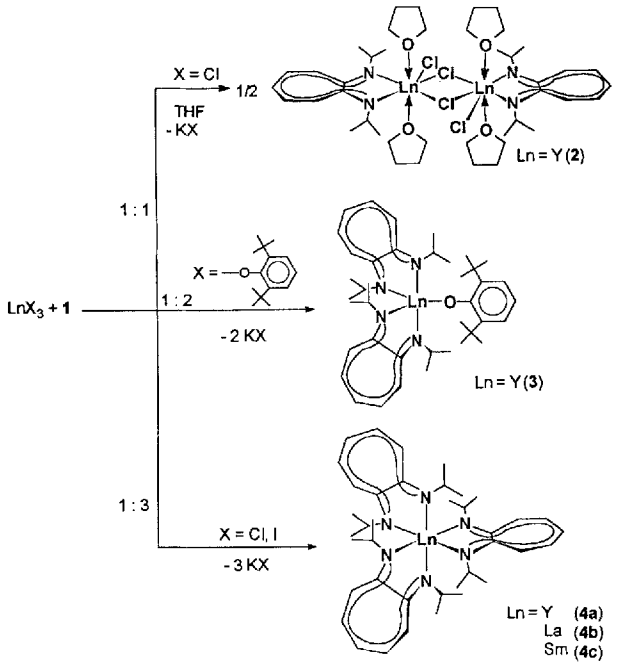
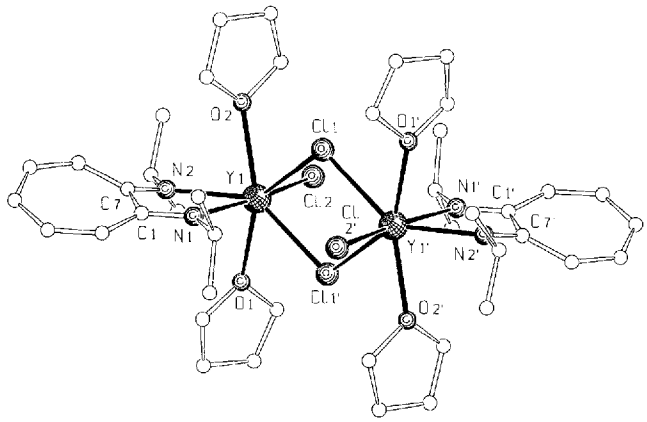
THF/pentane increases the solvent-to-metal ratio once more.



The room temperature ^{1}H- and ^{13}C-NMR spectra point to a symmetrical coordination of the [(*i*-Pr)$_2$ATI]$^-$ ligand in solution, which is in contrast to the asymmetric coordination observed in the solid state (see below). Thus, the ligand may show fluctional behavior in solution. The signal of the isopropyl C*H* of **2** is well-resolved into a septet but shows a marked downfield shift (δ = 4.04) compared to the free ligand [(*i*-Pr)$_2$ATI]H (δ = 3.60). Surprisingly, in the comparable group 4 complexes [(*i*-Pr)$_2$ATI]$_2$MCl$_2$ (M = Zr, Hf) the corresponding resonance is shifted by about 0.7 ppm further downfield[13] than it is in **2**.

The solid-state structure of **2** was investigated by single crystal X-ray diffraction (Figure 1). Clearly, the steric influence of [(*i*-Pr)$_2$ATI]$^-$ is not sufficient to block all coordination sites on the yttrium atom. Therefore, a dimerization via two chloro bridges takes place. The chlorine atoms are coordinated symmetrically between the yttrium atoms with a Y1–Cl–Y1′ angle of 109.09(7)°. Coordination of two equivalents of THF completes the seven-membered coordination sphere around the yttrium atom. Interestingly, the [(*i*-Pr)$_2$ATI]$^-$ ligand is attached asymmetrically to the metal center. The nitrogen atom, which is *trans*-coordinated to the non-bridging chlorine atom, is located about 10 pm closer to the yttrium atom than the other nitrogen atom [N1–Y1 = 233.1(5); N2–Y1 = 243.0(5) pm]. This observation is in sharp contrast to the comparable [(*i*-Pr)$_2$ATI]$_2$MCl$_2$ (M = Zr, Hf)[13] complexes, which show a symmetrical coordination of the ligand. Due to the asymmetric attachment of the [(*i*-Pr)$_2$ATI]$^-$ ligand, the seven-membered ring is slightly distorted. The N1–Y1–N2 angle is 67.4(2)°. A comparable asymmetrical coordination of the ligand was observed for [(Ph$_2$pz)$_3$Nd(THF)$_3$] (Ph$_2$pz = 3,5-Diphenylpyrazolate)[16]. The N1–Y1 bond length is similar to the corresponding Y–N bond in Y[DAC][N(SiMe$_3$)$_2$] (DAC = 4,13-diaza-18-crown-6) [Y–N = 228.3(12) pm][17]. All C–C bond distances of the seven-membered ring are approximately the same (except C1–C7, which is not part of the delocalized π-system).

Figure 1. Solid-state structure of **2** showing the atom labeling scheme, omitting hydrogen atoms (SCHAKAL drawing). Selected distances [pm] and angles [°]: C1–C2 141.1(9), C1–C7 149.6(9), C1–N1 133.2(8), C7–N2 133.2(8), N1–Y1 233.1(5), N2–Y1 243.0(5), Y1–O1 239.7(4), Y1–O2 240.9(4), Y1–Cl1 278.3(2), Y1–Cl2 261.0(2); N1–Y1–O1 92.9(2), N1–Y1–O2 95.0(2), O1–Y1–O2 147.00(15), N1–Y1–N2 67.4(2), O1–Y1–N2 77.2(2), O2–Y1–N2 76.4(2), Cl2–Y1–Cl1 95.25(8), Cl1–Y1–Cl1′ 70.91(7), Y1–Cl1–Y1′ 109.09(7), N1–Y1–Cl1 90.34(14), N1–Y1–Cl2 169.88(13), N2–Y1–Cl1 137.76(14), N2–Y1–Cl2 102.48(14)



Transmetallation of **1** with anhydrous yttrium trichloride in THF in a 2:1 molar ratio does not lead selectively to a product of composition [(*i*-Pr)$_2$ATI]$_2$YCl. An alternative approach to a bissubstituted product is the reaction of **1** with tris(2,6-di-*t*-butylphenoxo)yttrium(III) in a 2:1 molar ratio, which affords [(*i*-Pr)$_2$ATI]$_2$Y[O(2,6-*t*-Bu$_2$C$_6$H$_3$)] (**3**). Even with an excess of **1** a trissubstituted product, [(*i*-Pr)$_2$ATI]$_3$Y, is not obtained. Complex **3** was characterized by MS, IR, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. It was found to be a five-coordinate species which is *not* common for lanthanides[18]. Both the room temperature and low temperature (–60°C) ^{1}H NMR spectra of **3** show a symmetrical pattern for the [(*i*-Pr)$_2$ATI]$^-$ ligand. This may result from a square-pyramidal coordination sphere around the yttrium atom or a high fluctional behavior of the [(*i*-Pr)$_2$ATI]$^-$ ligand, as has been observed for the corresponding group 13 complexes [Me$_2$ATI]$_2$MX (M = Ga, In; X = Cl, I)[14c]. These complexes adopt a trigonal-bipyramidal geometry, with the halide atom occupying an equatorial site in the solid state, but show fluctional behavior in solution at room temperature. The ^{1}H NMR signal of the isopropyl C*H* of **3** appears as a well-resolved septet at δ = 4.17. This signal is shifted 0.13 ppm downfield compared to the corresponding signal in **2**.

The homoleptic compounds [(*i*-Pr)$_2$ATI]$_3$Ln (**4**) [Ln = Y (**4a**), La (**4b**), Sm (**4c**)] were obtained by transmetallation of anhydrous lanthanide trichlorides/triiodides in THF in a 3:1 molar ratio. The products **4** were characterized by MS, IR, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The ^{1}H and ^{13}C NMR spectra of **4a** and **4b** show a diastere-

otopic splitting of the isopropyl CH_3 signals, confirming octahedral coordination around the metal center. For the samarium compound **4c**, only broad signals are observed for the isopropyl groups in the ^1H NMR spectrum whereas the signals of the seven-membered ring are well-resolved. In contrast, in the ^{13}C NMR spectrum the diastereotopic splitting is observed. A similar octahedral coordination has been observed in [*t*-BuDAB]Sm (*t*-BuDAB = bis(*t*-butyl)-glyoxaldiiminene)[10b], whereas the structurally characterized tris(tropolonato)scandium(III) crystallizes with a coordination environment intermediate between trigonal antiprismatic and trigonal prismatic[19].

Attempts to separate the ^1H NMR signals of the Λ and Δ enantiomers of **4d** by the addition of stoichiometric amounts of the chiral shift reagent Eu(hfc)$_3$ (hfc = 3-(heptafluoropropylhydroxymethylene)-(+)-camphorato) failed at room temperature and at −20°C. This suggests that **4a**−**c** have a non-rigid stereochemical structure in solution.

In summary, it has been demonstrated that the [(*i*-Pr)$_2$ATI]$^-$ ligand can be attached in various stoichiometric ratios to yttrium and the lanthanides. The steric demand of the ligand is somewhat similar to that of the well-known cyclopentadienyls and benzamidinates. Therefore, the new compounds **2** and **3** offer a rich synthetic potential, which is currently under investigation.

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Experimental Section

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, or interfaced to a high vacuum (10−4 Torr) line, or in an argon-filled Braun Atmosphere glove box. Ether solvents (tetrahydrofuran and diethyl ether) were predried over Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl. Hydrocarbon solvents (toluene and pentane) were distilled under nitrogen from Na wire. All solvents for vacuum line manipulations were stored *in vacuo* over Na/K alloy in resealable flasks. Deuterated solvents were obtained from Aldrich Inc. (all 99 atom% D) and were degassed, dried, and stored *in vacuo* over Na/K alloy in resealable flasks. Anhydrous lanthanide halides were prepared by literature procedures[20]. NMR spectra were recorded on a Bruker AC 250. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Ir spectra were recorded on a Bruker IFS 28; mass spectra were recorded at 70 eV on a Varian MAT 711. Elemental analyses were performed in the microanalytical laboratory of the author's institute (S. Ariman).

Preparation of Potassium N-Isopropyl-2-(isopropylamino)troponiminate (**1**): To a suspension of 1.20 g (30 mmol) KH in THF, 3.0 g (15 mmol) of *N*-isopropyl-2-(isopropylamino)troponimine dissolved in 30 ml of THF was slowly added at −78°C. The mixture was warmed to room temperature and stirred for 4 h. Then, the remaining KH was filtered off and the filtrate was concentrated *in vacuo*. The remaining yellow residue was washed with pentane (3 × 50 ml) and dried *in vacuo*. Yield 2.8 g (77%). − ^1H NMR ([D$_8$]THF, 250 MHz, 25°C): δ = 1.09 (d, 12H, CH_3, *J*(H,H) = 6.2 Hz), 3.67 (sept, 2H, $(CH_3)_2CH$, *J*(H,H) = 6.2 Hz), 5.08 (t, 1H, H^5, *J*(H,H) = 8.5 Hz), 5.50 (d, 2H, H^{3,7}, *J*(H,H) = 11.5 Hz), 6.21 (dd, 2H, H^{4,6}). − $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 62.9 MHz, 25°C): δ = 24.4 (CH_3), 49.8 ($(CH_3)_2CH$), 103.5 (C^5), 103.7 (C^{3,7}), 131.7 (C^{4,6}), 162.7 (C^{1,2}).

Preparation of {[(i-Pr)$_2$ATI]YCl$_2$(THF)$_2$}$_2$ (**2**): THF was condensed at −196°C onto a mixture of 430 mg YCl_3 (2.2 mmol) and 780 mg (2.0 mmol) of **1**. The mixture was stirred for 14 h at room temperature. The solvent was then evaporated *in vacuo* and diethyl ether was condensed onto the mixture. The solution was filtered and the solvent was removed. This procedure was repeated several times. The remaining solid was washed with pentane (10 ml) and dried *in vacuo*. Finally, the product was crystallized from THF/pentane (1:4). Yield 420 mg (58%). − IR (KBr [cm^{-1}]): 1590 (s), 1490 (vs), 1419 (vs), 1264 (vs9; 727 (s). − ^1H NMR ([D$_8$]THF, 250 MHz, 25°C): δ = 1.46 (d, 24H, CH_3), *J*(H,H) = 6.7 Hz), 1.72 (m, THF), 3.56 (m, THF), 4.04 (sept, 4H, $(CH_3)_2CH$, *J*(H,H) = 6.7 Hz), 6.09 (t, 2H, H^5, *J*(H,H) = 8.1 Hz), 6.37 (d, 4H, H^{3,7}, *J*(H,H) = 11.4 Hz), 6.84 (m, 5H, H^{4,6}, H$_{para}$). − $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 62.9 MHz, 25°C): δ = 22.4 (CH_3), 26.3 (THF), 51.8 ($(CH_3)_2CH$), 67.3 (THF), 111.6 (C^5), 117.7 (C^{3,7}), 134.6 (C^{4,6}), 164.7 (C^{1,2}).

Preparation of [(i-Pr)$_2$ATI]$_2$Y[O(2,6-t-Bu$_2$C$_6$H$_3$)] (**3**): THF was condensed at −196°C onto a mixture of 352 mg (0.5 mmol) [Y(2,6-*t*Bu$_2$C$_6$H$_3$O)$_3$] and 265 mg (1.1 mmol) of **1** and the mixture was refluxed overnight. The solvent was then evaporated *in vacuo* and toluene was condensed onto the mixture. The solution was filtered and the solvent was removed. The remaining solid was washed with pentane (10 ml) and dried *in vacuo*. Yield 280 mg (75%). − IR (KBr [cm^{-1}]): 1590 (s), 1499 (vs), 1410 (vs), 1261 (vs). − ^1H NMR (C$_6$D$_6$, 250 MHz, 25°C): δ = 1.31 (d, 24H, $(CH_3)_2CH$, *J*(H,H) = 6.7 Hz), 1.47 (s, 18H, *t*Bu), 4.17 (sept, 4H, $(CH_3)_2CH$, *J*(H,H) = 6.7 Hz), 6.24 (t, 2H, H^5, *J*(H,H) = 8.9 Hz), 6.54 (d, 4H, H^{3,7}, *J*(H,H) = 9.2 Hz), 6.85 (m, 5H, H^{4,6}, H$_{para}$), 7.35 (d, 2H, H$_{meta}$, *J*(H,H) = 7.8 Hz). − $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 62.9 MHz, 25°C): δ = 22.4 ($(CH_3)_2CH$), 33.1 ($(CH_3)_3CH$), 36.0 ($(CH_3)_3CH$), 49.6 ($(CH_3)_2CH$), 115.4 (C^5), 117.7 (C^{3,7}), 118.4 (phenol), 126.9 (phenol), 135.0 (C^{4,6}), 139.1 (phenol), 161.2 (phenol), 165.4 (C^{1,2}). − EI/MS (70 eV) *m/z* (%): 700 ([*M*]$^+$, rel. int. 0.4), 495 ([*M* − C$_{14}$H$_{21}$O]$^+$, 100%), 206 ([C$_{14}$H$_{22}$O)]$^+$, 19), 204 [(C$_{13}$H$_{20}$N$_2$]$^+$, 88). − C$_{40}$H$_{59}$N$_4$OY (700.84): calcd. C 68.55, H 8.49, N 7.99; found C 68.58, H 8.47, N 7.92.

Preparation of [(i-Pr)$_2$ATI]$_3$Ln (Ln = Y, La, Sm) (**4**) (General Procedure): THF was condensed at −196°C onto a mixture of 0.5 mmol $LnCl_3$ or LnI_3 and 362 mg (1.5 mmol) of **1** and the mixture was stirred for 18 h at room temperature. The solvent was then evaporated *in vacuo* and toluene was condensed onto the mixture. Then, the solution was filtered and the solvent was removed. This procedure was repeated twice. The remaining solid was washed with pentane (10 ml) and dried *in vacuo*.

4a (Ln = Y): Yield 243 mg (70%). IR (KBr [cm^{-1}]): 1589 (s), 1496 (vs), 1415 (vs), 1340 (s), 1260 (s). − ^1H NMR (C$_6$D$_6$, 250 MHz, 25°C): δ = 1.20 (d, 18H, CH_3, *J*(H,H) = 6.7 Hz), 1.28 (d, 18H, CH_3, *J*(H,H) = 6.7 Hz), 4.15 (sept, 6H, $(CH_3)_2CH$, *J*(H,H) = 6.7 Hz), 6.22 (t, 3H, H^5, *J*(H,H) = 8.9 Hz), 6.55 (d, 6H, H^{3,7}, *J*(H,H) = 11.4 Hz), 6.90 (dd, 6H, H^{4,6}). − $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 62.9 MHz, 25°C): δ = 22.0 (CH_3), 22.5 (CH_3), 50.5 ($(CH_3)_2CH$), 114.7 (C^5), 116.9 (C^{3,7}), 134.3 (C^{4,6}), 165.1 (C^{1,2}). − EI/MS (70 eV) *m/z* (%): 698 ([*M*]$^+$, rel. int. 6), 495 ([*M* − C$_{13}$H$_{19}$N$_2$]$^+$, 100), 204 ([C$_{13}$H$_{20}$N$_2$]$^+$, 58). − C$_{39}$H$_{57}$N$_6$Y (698.83): calcd. C 67.03, H 8.22, N 12.03; found C 66.53, H 8.34, N 11.76.

4b (Ln = La): Yield 220 mg (59%). IR (KBr [cm^{-1}]). 1587 (s), 1497 (vs), 1415 (vs), 1344 (s), 1255 (s). ^1H NMR (C$_6$D$_6$, 250 MHz, 25°C): δ = 1.22 (d, 18H, CH_3, *J*(H,H) = 6.6 Hz), 1.27 (d, 18H,

CH_3, J(H,H) = 6.6 Hz), 4.02 (sept, 6H, $(CH_3)_2CH$, J(H,H) = 6.6 Hz), 6.19 (t, 3H, H^5, J(H,H) = 8.9 Hz), 6.36 (d, 6H, $H^{3,7}$, J(H,H) = 11.5 Hz), 6.90 (dd, 6H, $H^{4,6}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz, 25°C): δ = 24.4 (CH_3), 24.8 (CH_3), 49.8 ($(CH_3)_2CH$), 113.2 (C^5), 116.2 ($C^{3,7}$), 134.4 ($C^{4,6}$), 165.3 ($C^{1,2}$). – EI/MS (70 eV) *m/z* (%): 748 ($[M]^+$, rel. int. 0.7), 545 ($[M - C_{13}H_{19}N_2]^+$, 14), 204 ($[C_{13}H_{20}N_2]^+$, 100). – $C_{39}H_{57}LaN_6$ (748.83): calcd. C 62.56, H 7.67, N 11.22; found C 61.73, H 7.94, N 10.84.

4c (Ln = Sm): Yield 235 mg (62%). IR (KBr [cm^{-1}]): 1589 (s), 1497 (vs), 1466 (s), 1415 (vs), 1342 (s), 1258 (s). – ^1H NMR (C_6D_6, 250 MHz, 25°C): δ = −3.3 – −1.5 (br, 36H, CH_3), 3.57 (m, 6H, $(CH_3)_2CH$, J(H,H) = 6.6 Hz), 8.09 (m, 9H, H^5, $H^{4,6}$), 10.38 (d, 6H, $H^{3,7}$, J(H,H) = 10.8 Hz). – $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz, 25°C): δ = 18.7 (CH_3), 19.5 (CH_3), 54.8 ($(CH_3)_2CH$), 108.9 (C^5), 116.2 ($C^{3,7}$), 138.1 ($C^{4,6}$), 183.2 ($C^{1,2}$). – EI/MS (70 eV) *m/z* (%): 761 ($[M]^+$, rel. int. 3), 558 ($[M - C_{13}H_{19}N_2]^+$, 57), 355 ($[M - 2(C_{13}H_{19}N_2)]^+$, 11), 204 ($[C_{13}H_{20}N_2]^+$ 100). – $C_{39}H_{57}N_6Sm$ (760.28): calcd. C 61.61, H 7.56, N 11.05; found C 61.07, H 7.52, N 11.27.

Crystal Structure Analysis of **2**: Stoe-STADI IV diffractometer (Mo-K_α radiation); T = 203(3) K; data collection and refinement: SHELXS-86[21], SHELXL-93[22]; monoclinic, space group P $2_1/c$; lattice constants a = 9.781(6), b = 24.907(13), c = 10.394(5) Å, β = 108.26(4)°, V = 2404.5(22) $Å^3$, Z = 4; μ(Mo-K_α) = 2.666 mm^{-1}; $2\Theta_{max.}$ = 22.50; 2917 independent reflections measured, of which 2163 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.372 and −0.404 e/$Å^{-3}$; 251 parameters (C, Cl, N, O, Y anisotropic; the positions of the H atoms were calculated for idealized positions) R_1 = 0.0524. – Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-406338, the name of the author, and the journal citation.

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