Chiral Bridged Aminotroponiminate Complexes of the Heavy Lanthanides

Markus R. Bürgstein and Peter W. Roesky*

Institut für Chemie, Freie Universität Berlin, Fabeckstrasse 34-36, 14195 Berlin, Germany

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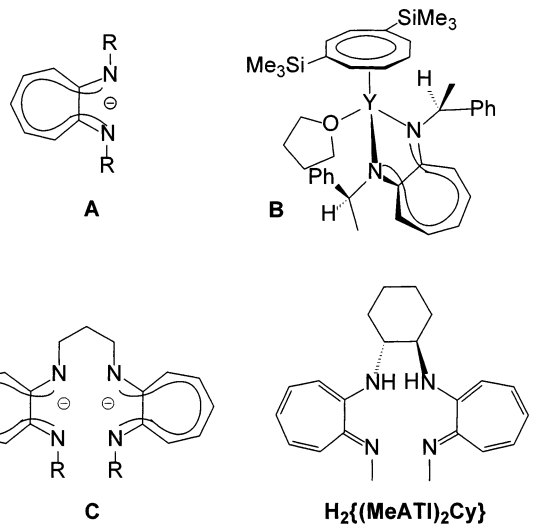
The enantiomerically pure monobridged aminotroponiminate, $H_2\{(i\text{PrATI})_2\text{Cy}\}$, in which two amino-isopropoyl-troponimine moieties are linked by (R,R)-1,2-diammoniumcyclohexane has been prepared. The corresponding dipotassium salt $K_2\{(i\text{PrATI})_2\text{Cy}\}$ can be obtained from a reaction of $H_2\{(i\text{PrATI})_2\text{Cy}\}$ with potassium hydride. Further reactions of $K_2\{(i\text{PrATI})_2$-Cy} with anhydrous ytterbium and lutetium trichloride, respectively, in THF leads to the chiral complexes $[\{(i\text{PrATI})_2\text{Cy}\}\text{LnCl(THF)}]$ (Ln = Yb (**1a**), Lu (**1b**)). The structures of **1a**,**b** were confirmed by single-crystal X-ray diffraction in the solid state. Treatment of the lutetium complex **1b** with an excess of $KN(SiMe_3)_2$ afforded the chiral heteroleptic amido complex $[\{(i\text{PrATI})_2\text{Cy}\}\text{LuN}\{(SiMe_3)\}_2]$ (**2**).

Introduction

Recently many enantiomerically pure lanthanide complexes have been prepared and characterized. These compounds are far from being curiosities of coordination chemistry. Many of these compounds have applications such as chiral shift reagents for resolving NMR spectra of chiral Lewis bases[1,2] and more recently as highly enantioselective catalysts and reagents.[3] In a recent review published this year, it turned out that the vast majority of these complexes have either enantiomerically pure *O*-donor ligands or cyclopentadienyl ligands in the coordination sphere.[4] In contrast to these widely used systems anionic *N*-donors have been only little used in lanthanide chemistry.[4]

Recent reports from our laboratory have described the use of aminotroponiminates (**A**) as cyclopentadienyl alternatives for group 3 and lanthanide elements,[5] whereas a similar approach on group 4 elements was reported by other groups.[6] Aminotroponiminates are monoanionic *N*-donor ligands, which may formally be considered as a combination of an amido and an imido donor.[7] We have shown that bis(aminotroponiminate)-yttrium amides are active as catalysts for hydroamination/cyclization catalysis.[8] A chiral lanthanide complex (**B**) was obtained by incorporation of chiral substituents onto the donor atoms of the ligand.[9]

Since the aminotroponiminate ligand was proved to be a formal substitute for cyclopentadienyl, we started to prepare monobridged aminotroponiminates as alternatives for *ansa* metallocenes. It was shown that the trismethylene-bridged ligand, $\{(i\text{Pr})\text{TP}\}^{2-}$ (**C**), is able to coordinate in a chelating or a metal-bridging mode to various lanthanides.[10] An enantiomerically pure version of a monobridged aminotroponiminate, $H_2\{(\text{MeATI})_2\text{Cy}\}$, in which two aminomethyltroponimine moieties are linked by *trans*-1,2-diaminocyclohexane, was recently reported by Lippard et al. as a ligand in titanium chemistry.[11]



In this article the synthesis of the somewhat larger enantiomerically pure isopropyl ligand $H_2\{(i\text{PrATI})_2\text{Cy}\}$

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is reported, along with its transformation into the corresponding potassium salt, $K_2\{(i\text{PrATI})_2\text{Cy}\}$. Further reactions of the potassium compound with ytterbium and lutetium trichlorides are explored. These reactions lead to new chiral lanthanide aminotroponiminate complexes.

Experimental Section

General Procedures. 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, interfaced to a high-vacuum (10^{-4} Torr) line, or in an argon-filled M. Braun glovebox. Ether solvents (tetrahydrofuran and diethyl ether) were predried over Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum line manipulations were stored in vacuo over $LiAlH_4$ 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. NMR spectra were recorded on Bruker AC 250. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. (R,R)-1,2-Diaminocyclohexane was purchased from Aldrich. $YbCl_3$,[12] $LuCl_3$,[12] and 2-(*N*-isopropylamino)tropone[13] were prepared according to literature procedures.

H_2[(iPrATI)$_2$Cy]. $Et_3O{\cdot}BF_4$ (3.58 g, 22.0 mmol) in 20 mL of methylene chloride was slowly added to a methylene chloride solution (10 mL) of 4.58 g (24 mmol) of 2-(*N*-isopropylamino)tropone under nitrogen atmosphere. After stirring for 3 h at room temperature 3.0 mL (22 mmol) of NEt_3 was slowly added to the reddish solution. The mixture was stirred for another 15 min, and then 1.25 g (11 mmol) of (R,R)-1,2-diaminocyclohexane in 15 mL of NEt_3 was added to the mixture. The mixture was stirred for 16 h, and the volatiles were removed in vacuo. The residue was extracted into *n*-pentane, filtered through Celite, and concentrated under vacuum. The product was obtained as a yellow powder. Yield: 1.8 g (41%). IR (KBr [cm^{-1}]): 3263 (br), 2969 (s), 2924 (s), 1587 (vs), 1502 (vs), 1453 (vs), 1371 (s), 1261 (s), 1204 (m), 1116 (m), 1025 (m), 713 (m). ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 0.92 (d, 6 H, $(CH_3)_2$CH, J(H,H) = 6.3 Hz), 1.00 (d, 6 H, $(CH_3)_2$CH, J(H,H) = 6.3 Hz), 1.30−1.69 (m, 6 H, Cy), 1.98 (m, 2 H, Cy), 3.40 (sept, 2 H, $CH(CH_3)_2$, J(H,H) = 6.2 Hz), 3.88 (m, 2 H, Cy), 5.94 (d, 2 H, H_{ring}, J(H,H) = 10.5 Hz), 6.08 (t, 2 H, H_{ring}), 6.57−6.72 (m, 6 H, H_{ring}), 7.97 (m, 2 H, NH). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz, 25 °C): δ 23.4 ($(CH_3)_2$CH), 25.7 (Cy), 32.3 (Cy), 45.7 ($(CH_3)_2$CH), 61.9 (Cy), 107.7 (C_{ring}), 114.6 (C_{ring}), 118.2 (C_{ring}), 133.4 (C_{ring}), 134.1 (C_{ring}), 152.2 (C_{ring}), 154.4 (C_{ring}). EI/MS (70 eV) *m*/*z* (%): 364 ([M]$^+$, rel int 20), 202 ([M − $C_{13}H_{18}N_2$]$^+$, 100), 133 ([$C_8H_9N_2$]$^+$, 83).

K_2\{(iPrATI)$_2$Cy\}. To a suspension of 0.7 g (17.4 mmol) of KH in 25 mL of THF was slowly added at room temperature 2.1 g (5.2 mmol) of $H_2[(i\text{PrATI})_2\text{Cy}]$ dissolved in 25 mL of THF. The mixture was stirred for 16 h. Then, the remaining KH was filtered off and the filtrate was concentrated in vacuo. The remaining yellow residue was washed with *n*-pentane (25 mL) and dried in vacuo. Yield: 2.2 g (88%). IR (KBr [cm^{-1}]): 2962 (m), 2857 (m), 1589 (s), 1505 (vs), 1446 (s), 1383 (s), 1257 (s), 1166 (s), 1119 (m), 1004 (m), 801 (m), 703 (m). ^{1}H NMR (d_8-THF, 250 MHz, 25 °C): δ 1.06 (d, 6 H, $(CH_3)_2$CH, J(H,H) = 6.3 Hz), 1.08 (d, 6 H, $(CH_3)_2$CH, J(H,H) = 6.3 Hz), 1.16−1.50 (m, 6 H, Cy), 2.40 (d, 2 H, Cy), 3.57 (m, 2 H, Cy), 3.63 (sept, 2 H, $(CH_3)_2$CH), 5.18 (t, 2 H, H_{ring}, J(H,H) = 8.7 Hz), 5.55 (d, 2 H, H_{ring}, J(H,H) = 11.4 Hz), 5.68 (d, 2 H, J(H,H) = 11.1 Hz), 6.09−6.58 (m, 4 H, H_{ring}). ^{13}C{^{1}H} NMR (d_8-THF, 62.9 MHz, 25 °C): δ 23.9 ($(CH_3)_2$CH), 27.2 (Cy), 30.4 (Cy), 50.2 ($(CH_3)_2$CH), 65.6 (Cy), 103.9 (C_{ring}), 104.8 (C_{ring}), 105.2 (C_{ring}), 132.3 (C_{ring}), 133.1 (C_{ring}), 162.9 (C_{ring}), 164.6 (C_{ring}).

[\{(iPrATI)$_2$Cy\}LnCl(THF)] (Ln = Yb (1a), Lu (1b)). General Procedure. A 15 mL portion of THF was condensed at −196 °C onto a mixture of 1.3 mmol of $LnCl_3$ and 480 mg (1.0 mmol) of $K_2[(i\text{PrATI})_2\text{Cy}]$, and the mixture was stirred for 16 h at room temperature. Then, the solution was filtered and solvent was then evaporated in vacuo. Finally, the product was crystallized from hot THF. The product was obtained as yellow crystals.

Ln = Yb (1a). Yield: 570 mg (53%). IR (KBr [cm^{-1}]): 2964 (m), 2925 (m), 1589 (st), 1513 (m), 1465 (st), 1384 (st), 1261 (st), 1097 (st), 1021 (m), 863 (m), 801 (m), 703 (m). Anal. Calcd for $C_{30}H_{42}ClN_4OYb$ (683.18): C, 52.74; H, 6.20; N, 8.20. Found: C, 52.49; H, 6.21; N, 8.45.

Ln = Lu (1b). Yield: 615 mg (57%). IR (KBr [cm^{-1}]): 2964 (m), 2927 (m), 1601 (m), 1589 (st), 1518 (st), 1464 (st), 1431 (m), 1388 (st), 1260 (st), 1097 (st), 1020 (m), 880 (m), 801 (m), 721 (m). ^{1}H NMR (d_8-THF, 250 MHz, 25 °C): δ 1.08−1.62 (m, 6 H, Cy), 1.37 (d, 6 H, $(CH_3)_2$CH, J(H,H) = 6.3 Hz), 1.52 (d, 6 H, $(CH_3)_2$CH, J(H,H) = 6.3 Hz), 2.78 (d, 2 H, Cy), 3.71 (m, 2 H, Cy), 4.09 (sept, 2 H, $(CH_3)_2$CH), 6.03 (t, 2 H, H_{ring}, J(H,H) = 8.9 Hz), 6.13 (d, 2 H, H_{ring}, J(H,H) = 11.0 Hz), 6.31 (d, 2 H, J(H,H) = 11.1 Hz), 6.48−6.75 (m, 4 H, H_{ring}). ^{13}C{^{1}H} NMR (d_8-THF, 62.9 MHz, 25 °C): δ 22.4, 25.2, 26.4, 26.5, 49.7, 69.1, 113.1 (C_{ring}), 113.2 (C_{ring}), 116.5 (C_{ring}), 134.4 (C_{ring}), 135.5 (C_{ring}), 162.1 (C_{ring}), 166.0 (C_{ring}). Anal. Calcd for $C_{30}H_{42}ClLuN_4O$ (685.11): C, 52.59; H, 6.18; N, 8.18. Found: C, 52.77; H, 6.43; N, 8.40.

[\{(iPrATI)$_2$Cy\}LuN\{(SiMe$_3$)$_2$\}] (2). Toluene (20 mL) was condensed at −196 °C onto a mixture of 250 mg (0.30 mmol) of **1b**·(2THF) and 60 mg (0.3 mmol) of $KN(SiMe_3)_2$. The mixture was stirred for 18 h at room temperature. The solvent was removed in a vacuum, and 30 mL of pentane was condensed onto the mixture. Then, the solution was filtered and the solvent removed. The remaining solid was recrystallized from pentane. Yield: 125 mg (57%). IR (KBr [cm^{-1}]): 2964 (m), 2927 (m), 1601 (m), 1589 (s), 1518 (vs), 1464 (s), 1431 (m), 1388 (s), 1260 (s), 1097 (s), 1020 (m), 880 (m), 801 (m), 721 (m). ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 0.32 (s, 18 H, $Si(CH_3)_3$), 1.08−1.66 (m, 6 H, Cy), 1.31 (d, 6 H, $(CH_3)_2$CH, J(H,H) = 6.5 Hz), 1.50 (d, 6 H, $(CH_3)_2$CH, J(H,H) = 6.4 Hz), 2.84 (d, 2 H, Cy), 3.53 (m, 2 H, Cy), 3.93 (sept, 2 H, $(CH_3)_2$CH), 6.16−6.32 (m, 4 H, H_{ring}), 6.51 (d, 2 H, J(H,H) = 12.0 Hz), 6.62−6.94 (m, 4 H, H_{ring}). ^{13}C{^{1}H} NMR (d_8-THF, 62.9 MHz, 25 °C): δ 5.2, 22.4, 25.2, 26.4, 26.5, 49.6, 69.1, 113.2 (C_{ring}), 113.3 (C_{ring}), 116.6 (C_{ring}), 134.4 (C_{ring}), 135.6 (C_{ring}), 162.1 (C_{ring}), 166.0 (C_{ring}). EI/MS (70 eV) *m*/*z* (%): 738 ([M]$^+$, rel int 4), 694 ([M − C_3H_7]$^+$, 2), 576 ([M − $NSiC_3H_9$]$^+$, 8), 161 ([$C_6H_{19}NSi_2$]$^+$, 12), 146 ([$C_5H_{16}NSi_2$]$^+$, 100).

X-ray Crystallographic Studies of 1a,b. Crystals of **1a** and **1b** were grown from hot THF. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C cold N_2 stream of a Stoe STADI IV or a Stoe IPDS diffractometer. Subsequent computations were carried out on an Intel Pentium III PC.

All structures were solved by the Patterson method (SHELXS-86[14]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are

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Table 1. Crystallographic Details of [{(*i*PrATI)$_2$Cy}LnCl(THF)] (Ln = Yb (1a), Lu (1b))[a]

	1a·(2 THF)	**1b**·(2 THF)
formula	$C_{38}H_{58}ClN_4O_3Yb$	$C_{38}H_{58}ClLuN_4O_3$
fw	827.37	829.30
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a, Å	10.141(3)	10.090(2)
b, Å	16.929(9)	16.900(3)
c, Å	22.632(10)	22.530(5)
V, Å3	3885(3)	3841.8(13)
Z	4	4
density (g/cm^3)	1.414	1.434
radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
μ, mm^{-1}	2.515	2.679
abs corr	ψ-scan	none
no. of reflns collected	5267	33475
no. of unique reflns	4675 [R_{int} = 0.0433]	7838 [R_{int} = 0.035]
no. of obsd reflns	3637	7527
absolute struct param	−0.03(3)	−0.018(11)
no. of data; params	4658; 368	7838; 374
GOF on F^2	1.205	1.131
R1[b]; wR2[c]	0.0563; 0.1312	0.0349; 0.0983

[a] All data collected at 203 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

the observed and calculated structure factor amplitudes using the program SHELXL-93.[15] In the final cycles of each refinement, all non-hydrogen atoms except the noncoordinating THF molecules were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-197090 (**1a**) and 197091 (**1b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The Ligand. The straightforward synthesis of the bridged chelating chiral ligand H$_2${(*i*PrATI)$_2$Cy} is shown in Scheme 1. 2-(Tosyloxo)tropone reacts with isopropylamine to form 2-(*N*-isopropylamino)tropone[13] in almost quantitative yield (Scheme 1). Further treatment of 2-(*N*-isopropylamino)tropone with $Et_3O{\cdot}BF_4$, triethylamine, and (R,R)-1,2-diaminocyclohexane leads to the desired product H$_2${(*i*PrATI)$_2$Cy} as an analytically pure yellow solid in a 40% yield. The final step of the synthesis is slightly different from the published one for the corresponding methyl compound H$_2${(MeATI)$_2$-Cy}. Whereas previously (R,R)-1,2-diammoniumcyclohexane mono-(+)-tatrate was used to incorporate the spacer between the aminotroponiminate moieties, we used the free amine for the synthesis. H$_2${(*i*PrATI)$_2$Cy}

(15) Sheldrick, G. M. *SHELXL-93, Program of Crystal Structure Refinement*; University of Göttingen: Germany, 1993.

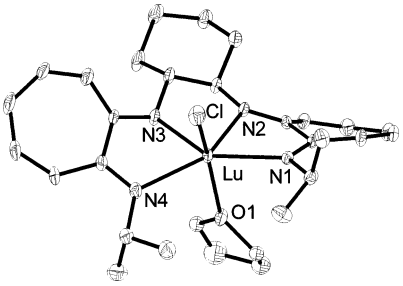
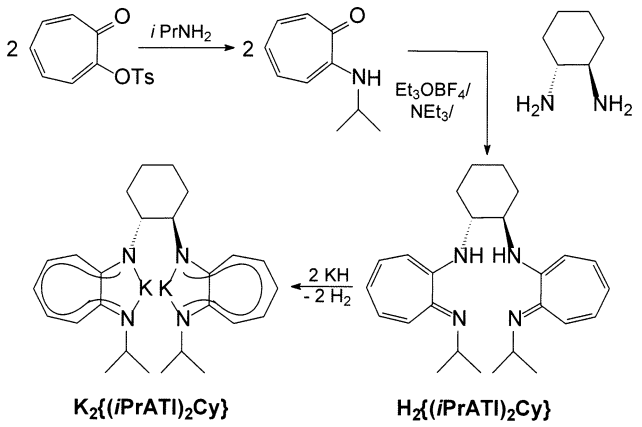


Figure 1. Perspective ORTEP view of the molecular structure of **1b**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

Scheme 1



was characterized by MS, IR, and ^{1}H and ^{13}C NMR spectroscopy. Reaction of H$_2${(*i*PrATI)$_2$Cy} with potassium hydride suspension in THF affords the dipotassium salt K$_2${(*i*PrATI)$_2$Cy} as a yellow-brown, air-sensitive solid, which was characterized by IR and ^{1}H and ^{13}C NMR spectroscopy (Scheme 1). In comparison to the neutral ligand, the NMR signals of the isopropyl C*H* of K$_2${(*i*PrATI)$_2$Cy} show a slight downfield shift in the ^{1}H and ^{13}C NMR spectra.

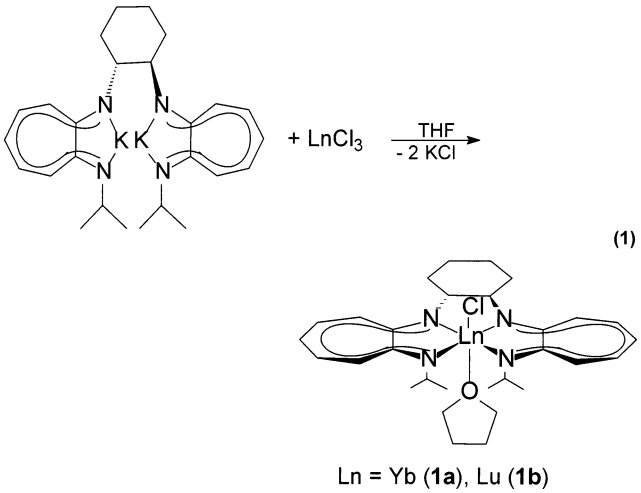
Lanthanide Complexes. Transmetalation of K$_2${(*i*PrATI)$_2$Cy} with anhydrous ytterbium and lutetium trichloride, respectively, in THF at room temperature and crystallization from hot THF leads to the reaction products [{(*i*PrATI)$_2$Cy}LnCl(THF)] (Ln = Yb (**1a**), Lu (**1b**)) (eq 1). The new complexes have been characterized by standard spectroscopic techniques. The ^{1}H spectrum of **1b** shows the expected chemical shifts of the isopropyl CH_3 signals (δ 1.37, 1.52). The structures of **1a**,**b** were confirmed by single-crystal X-ray diffraction in the solid state (Figure 1). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. Due to the similar ion radius of the center atoms of **1a** and **1b**, the single-crystal X-ray structures of both compounds are isostructural. They crystallize in the orthorhombic space group $P2_12_12_1$, having four molecules in the unit cell. Additionally, eight molecules of THF are located in the unit cell. Due to the chiral ligand, **1a**,**b** are enantiomerically pure complexes. Four coordination sites are occupied by the chelating {(*i*PrATI)$_2$Cy}$^{2-}$ ligand; furthermore a chlorine atom and a molecule of THF are coordinated to the central metal, resulting in a 6-fold coordination sphere of the ligands around the lanthanide atoms. The same coordination number was

Table 2. Selected Bond Lengths (Å) and Angles (deg) of [{(*i*PrATI)$_2$Cy}LnCl(THF)] (Ln = Yb (1a), Lu (1b))

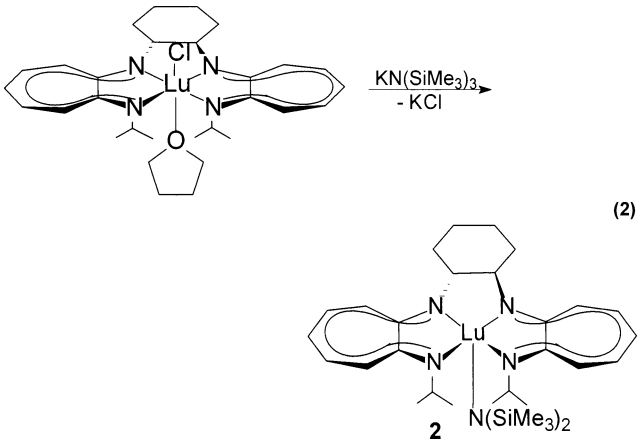
	1a	1b
	Bond Lengths	
Ln−N1	2.383(11)	2.365(3)
Ln−N2	2.285(12)	2.289(4)
Ln−N3	2.282(13)	2.262(4)
Ln−N4	2.354(14)	2.374(4)
Ln−Cl	2.534(6)	2.521(2)
Ln−O1	2.364(11)	2.320(4)
	Bond Angles	
N1−Ln−Cl	91.5(3)	91.43(10)
N2−Ln−Cl	111.2(4)	111.06(11)
N3−Ln−Cl	98.0(3)	97.48(13)
N4−Ln−Cl	89.5(4)	89.60(13)
N1−Ln−N2	69.1(5)	68.63(13)
N1−Ln−N3	140.7(5)	140.07(14)
N1−Ln−N4	150.4(5)	149.97(14)
N2−Ln−N3	71.9(4)	71.85(13)
N2−Ln−N4	137.0(5)	137.90(14)
N3−Ln−N4	68.1(4)	69.28(15)
O1−Ln−Cl	156.2(3)	156.37(11)

observed by using the achiral *n*-propyl aminotroponiminate ({(*i*Pr)TP}$^{2-}$) as ligand.[10a,16] These complexes, [{(*i*Pr)TP}LnCl]$_2$ (Ln = Er, Yb, Lu), are dimeric in contrast to **1a**,**b**. Thus, no THF is incorporated in the coordination sphere, but two μ_2-chlorine atoms are formed between the lanthanide atoms. The dimerization of **1a**,**b** might be prevented by the more rigid and more sterically demanding {(*i*PrATI)$_2$Cy}$^{2-}$ ligand. The Ln−N bond lengths are in the expected range 2.282(13)−2.383(11) Å in **1a** and 2.262(4)−2.365(3) Å in **1b**.[17] Similar bond lengths have been observed in other aminotroponiminate complexes such as [{(*i*Pr)TP}YbCl]$_2$ (2.262(3)−2.334(3) Å) and [{(*i*Pr)TP}LuCl]$_2$ (2.253(3)−2.327(3) Å) and in [{C$_6$H$_5$C(NSiMe$_3$)$_2$}$_2$Yb(SeMes)(THF)] (2.281(7)−2.361(7) Å).[18] Interestingly, the aminotroponiminate moieties are attached asymmetrically to the metal center. The *i*PrN unit is about 0.10−0.11 Å remote from the lanthanide atom compared to the other nitrogen atoms (e.g., Yb−N1 2.383(11) Å, Yb−N2 2.285(12) Å and Lu−N3 2.262(4) Å, Lu−N4 2.374(4) Å). In contrast, the diaminocyclohexane spacer is symmetrically attached to the metal center (Yb−N2 2.285(12) Å, Yb−N3 2.282(13) Å and Lu−N2 2.289(4) Å, Lu−N3 2.262(4) Å). The N−Ln−N angles are fixed by the chelating ligand. Thus, the N−Ln−N angles inside the aminotroponiminate moieties are N1−Ln−N2 69.1(5)° (**1a**), 68.63(13)° (**1b**) and N3−Ln−N4 68.1(4)° (**1a**), 69.28(15)° (**1b**), and inside the cyclohexane part the N2−Ln−N3 angles are 71.9(4)° (**1a**) and 71.85(13)° (**1b**). The Ln−Cl (2.534(6) Å (**1a**), 2.521(2) Å (**1b**)) and Ln−O bond distances (2.364(11) Å (**1a**), 2.320(4) Å (**1b**)) are in the expected range.

Treatment of the lutetium complex **1b** with an excess of KN(SiMe$_3$)$_2$ in toluene, followed by workup in pentane, afforded the corresponding chiral amido complex [{(*i*PrATI)$_2$Cy}LuN{(SiMe$_3$)}$_2$] (**2**) as a yellow crystalline solid (eq 2). Compound **2** was characterized by MS, IR and ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra of **2** show one set of signals for the



isopropyl CH$_3$ signals as well as a sharp singlet for the N(SiMe$_3$)$_2$ group.



Summary

In summary, we have prepared new enantiomerically pure *N*-donor complexes of the heavier lanthanides, by using the chiral bridged aminotroponiminate ligand {(*i*PrATI)$_2$Cy}$^{2-}$. A reaction of the dipotassium salt K$_2${(*i*PrATI)$_2$Cy} with anhydrous ytterbium and lutetium trichloride leads to the chloro complexes **1a**,**b**, respectively. These can be further reacted to give the heteroleptic amido complex **2**. Since it was shown by us that not only a number of lanthanide complexes[7] but also group 12[19] and 13[20] compounds can be obtained with achiral bridged aminotroponiminates, we hope that the {(*i*PrATI)$_2$Cy}$^{2-}$ ligand will find a broad use for preparation of enantiomerically pure coordination compounds.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1a**,**b** are available free of charge via the Internet at http://pubs.acs.org.

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