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Bridged Aminotroponiminate Complexes of Lanthanum

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The reaction of the new ligand 1,3-di(2-(*N*-isopropylamino)troponimine)propane, $H_2[(iPr)TP]$, with KH affords $K_2[(iPr)TP]$. The salt of this new ligand is a useful starting material for the preparation of the lanthanum compounds $[[(iPr)TP]_3La_2(THF)]_2$ and $[[(iPr)TP]LaCl(THF)]_2$, respectively. These metal complexes were characterized by NMR and X-ray crystallography. In contrast to macrocyclic ligands the $[(iPr)TP]^{2-}$ anion shows a higher flexibility upon coordination and features two different coordination modes. Further reaction of $[[(iPr)TP]LaCl(THF)]_2$ with 2 equiv of $LiCH(SiMe_3)_2$ or $KN(SiMe_3)_2$ in toluene affords the alkyl or amide derivatives $[[(iPr)TP]_2LaE(SiMe_3)_2]$ (E = CH, N) in high yield. Crystal data: $[[(iPr)TP]_3La_2(THF)]_2$, space group $P2_1/c$, $a = 19.860(2)$ Å, $b = 17.691(3)$ Å, $c = 21.333(3)$ Å, $\beta = 102.211(8)°$, $Z = 4$, $V = 7325.8$ Å^3; $[[(iPr)TP]LaCl(THF)]_2$, space group $P2_1/n$, $a = 12.848(3)$ Å, $b = 32.902(7)$ Å, $c = 16.215(3)$ Å, $\beta = 110.38(3)°$, $Z = 4$, $V = 6425(2)$ Å^3.

Introduction

Numerous advances have been made in the past decade in the design and synthesis of well-defined catalysts of groups 3 and 4, and the lanthanide metals for a variety of olefin transformations such as polymerization of terminal olefins.[1,2] The vast majority of these catalysts are metallocene derivatives, although some contain one cyclopentadienyl ring. Recently, complexes that contain chelating alkoxides or chelating nitrogen-based bidentate ligands have been recognized as potential catalysts.[3] Lately, we reported on the preparation and characterization of aminotroponiminates as cyclopentadienyl alternatives for group 3 and lanthanide elements.[4] It was shown that bis(aminotroponiminate)yttrium amides are active as catalysts for hydroamination/cyclization catalysis.[4c] Since the aminotroponiminate ligand has proven to be a formal substitute for cyclopentadienyl[4,5] we now propose that bridged aminotroponiminates should be alternatives for *ansa*-metallocenes. In this paper the synthesis of a bridged aminotroponiminate, as well as preliminary results for the use of this new ligand system in lanthanum chemistry, is reported.

Experimental Section

General. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture using flamed 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 Atmospheres glovebox. Ether solvents (tetrahydrofuran and ethyl 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. 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 measured on a Bruker IFS 28. Mass spectra were recorded at 70 eV on Varian MAT 711. Elemental analyses were performed in the microanalytical laboratory of the author's institute (S. Ariman). 2-(*N*-Isopropylamino)tropone was prepared according to literature procedures.[6]

$H_2[(iPr)TP]$. A 3.74 g (19.5 mmol) amount of $Et_3O{\cdot}BF_4$ in 20 mL of methylene chloride was slowly added to a methylene chloride solution (10 mL) of 2.9 g (18 mmol) of 2-(*N*-isopropylamino)tropone under nitrogen atmosphere. After the solution was stirred for 3 h at room temperature, 2.4 mL (18 mmol) of NEt_3 was slowly added to the reddish solution. The mixture was stirred for another 5 min, and then 0.75 mL (9 mmol) of 1,3-diaminopropane in 10 mL of NEt_3 was added to the mixture. The mixture was stirred overnight, and the volatiles were removed in vacuo. The residue was extracted into pentane, filtered through Celite, and concentrated under vacuo. Yield: 2.1 g (65%). IR (KBr [cm^{-1}]): 3211 (br), 2962 (m), 1589 (s), 1510 (vs), 1448 (s), 1385 (s), 1271 (s), 702 (m). ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 1.05 (d, 12H, $(CH_3)_2CH$, J(H,H) = 6.3 Hz), 2.05 (quint, 2H, NCH_2CH_2, J(H,H) = 6.9 Hz), 3.30 (t, 4H, NCH_2, J(H,H) = 6.9 Hz), 3.55 (sept, 2H, $(CH_3)_2CH$, J(H,H) = 6.3 Hz), 6.11−6.17 (m, 4H, H_{ring}), 6.30 (d, 2H, H_{ring}), 6.65 (dd, 4H, H_{ring}). $^{13}C\{^1H\}$ NMR-DEPT 135 (C_6D_6, 62.9 MHz, 25 °C): δ 23.6 ($(CH_3)_2CH$), 32.2 (NCH_2), 46.1 (NCH_2CH_2), 46.2

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$((CH_3)_2\mathit{C}H)$, 109.7 (C_{ring}), 112.7 (C_{ring}), 118.5 (C_{ring}), 133.8 (C_{ring}), 134.2 (C_{ring}), 152.6 (C_{ring}), 154.6 (C_{ring}). EI/MS (70 eV) *m/z* (%): 364 ($[M]^+$, relative intensity 20), 202 ($[M - C_{13}H_{18}N_2]^+$, 100%), 133 ($[C_8H_9N_2)]^+$, 83).

K_2[(*i*Pr)TP]. To a suspension of 0.7 g (17.4 mmol) of KH in 20 mL of THF was slowly added 2.1 g (5.8 mmol) of K_2[(*i*Pr)TP] dissolved in 30 mL of THF was slowly added at room temperature, and the resulting solution was stirred for 16 h. The remaining KH was then filtered off, and the filtrate was concentrated in vacuo. The remaining yellow residue was washed with pentane (2 × 20 mL) and dried in vacuo. Yield: 2.2 g (86%). IR (KBr $[cm^{-1}]$): 2962 (m), 1589 (s), 1510 (vs), 1462 (s), 1383 (s), 1272 (s), 703 (m). ^1H NMR (THF-d_8, 250 MHz, 25 °C): δ 1.23 (d, 12H, $(C\mathit{H}_3)_2CH$, $J(H,H) = 6.3$ Hz), 2.04 (m, 2H, $NCH_2C\mathit{H}_2$), 3.35 (dd, 4H, $NC\mathit{H}_2$, $J(H,H) = 6.9$ Hz), 3.76 (sept, 2H, $(CH_3)_2C\mathit{H}$, $J(H,H) = 6.3$ Hz), 5.31 (t, 2H, H_{ring}, $J(H,H) = 8.7$ Hz), 5.55 (d, 2H, H_{ring}, $J(H,H) = 10.6$ Hz), 5.74 (d, 2H, H_{ring}, $J(H,H) = 11.5$ Hz), 6.33−6.44 (m, 4H, H_{ring}). $^{13}C\{^1H\}$ NMR (THF-d_8, 62.9 MHz, 25 °C): δ 24.6 ($(\mathit{C}H_3)_2CH$), 34.7 ($N\mathit{C}H_2$), 50.3 ($NCH_2\mathit{C}H_2$), 55.2 ($(CH_3)_2\mathit{C}H$), 105.2 (C_{ring}), 106.0 (C_{ring}), 106.1 (C_{ring}), 132.4 (C_{ring}), 132.5 (C_{ring}), 163.8 (C_{ring}), 164.2 (C_{ring}).

[[(*i*Pr)TP]$_3$La$_2$(THF)$_2$] (1). A 20 mL amount of THF was condensed at −196 °C onto a mixture of 123 mg (0.5 mmol) of $LaCl_3$ and 328 mg (0.75 mmol) of K_2[(*i*Pr)TP], 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. The solution was then filtered, and the solvent was removed. The remaining solid was washed with pentane (10 mL) and dried in vacuo. Finally, the product was crystallized from THF/pentane (1:3). Yield: 235 mg (62%). IR (KBr $[cm^{-1}]$): 2962 (m), 1589 (s), 1507 (vs), 1416 (s), 1382 (s), 1260 (s), 722 (m). ^1H NMR (toluene-d_8, 250 MHz, 70 °C): δ 1.11−1.26 (m, 36H, $(C\mathit{H}_3)_2CH$), 1.46 (THF), 2.29 (br, 6H, $NCH_2C\mathit{H}_2$), 3.29 (br, 12H, $NC\mathit{H}_2$), 3.57 (THF), 3.87 (m, 12H, $(CH_3)_2C\mathit{H}$), 6.03−6.36 (m, 12H, H_{ring}), 6.48−6.68 (m, 6H, H_{ring}), 6.77−6.87 (m, 12H, H_{ring}). Anal. Calcd for $C_{77}H_{100}La_2N_{12}O_2$ (1503.5): C, 61.51; H, 6.70; N, 11.18. Found: C, 61.11; H, 6.93; N, 10.85.

[[(*i*Pr)TP]$_2$LaCl(THF)]$_2$ (2). A 10 mL amount of THF was condensed at −196 °C onto a mixture of 160 mg (0.65 mmol) of $LaCl_3$ and 220 mg (0.5 mmol) of K_2[(*i*Pr)TP] and the mixture was refluxed for 8 h. The hot solution was then filtered, and solvent was then evaporated in vacuo. Yield 245 mg (81%). IR (KBr $[cm^{-1}]$): 2963 (m), 1589 (s), 1504 (vs), 1414 (s), 1355 (s), 1264 (s), 721 (s). ^1H NMR (THF-d_8, 250 MHz, 25 °C): δ 1.21 (d, 24H, $(C\mathit{H}_3)_2CH$, $J(H,H) = 6.3$ Hz), 1.50 (THF), 2.16 (m, 4H, $NCH_2C\mathit{H}_2$), 3.44 (m, 8H, $NC\mathit{H}_2$), 3.60 (THF), 4.29 (sept, 4H, $(CH_3)_2C\mathit{H}$), 5.99 (t, 4H, H_{ring}, $J(H,H) = 9.0$ Hz), 6.13 (d, 4H, H_{ring}, $J(H,H) = 11.2$ Hz), 6.45 (d, 4H, H_{ring}, $J(H,H) = 11.6$ Hz), 6.77 (dd, 8H, H_{ring}). $^{13}C\{^1H\}$ NMR (THF-d_8, 62.9 MHz, 25 °C): δ 24.9 ($(\mathit{C}H_3)_2CH$), 25.2 (THF), 26.3 ($N\mathit{C}H_2$), 48.9 ($NCH_2\mathit{C}H_2$), 51.8 ($(CH_3)_2\mathit{C}H$), 113.3 (C_{ring}), 115.6 (C_{ring}), 116.3 (C_{ring}), 133.6 (C_{ring}), 134.2 (C_{ring}), 164.5 (C_{ring}), 165.0 (C_{ring}). Anal. Calcd for $C_{62}H_{92}Cl_2La_2N_8O_4$ (1362.2): C, 54.67; H, 6.81; N, 8.23. Found: C, 53.55; H, 6.80; N, 8.29.

[[(*i*Pr)TP]$_2$LaCH(SiMe$_3$)$_2$] (3a). A 10 mL amount of toluene was condensed at −196 °C onto a mixture of 100 mg (0.073 mmol) of **2** and 24 mg (0.146 mmol) of $LiCH(SiMe_3)_2$, and the mixture was stirred for 18 h at room temperature. The solution was then filtered and concentrated. Yield 80 mg (86%). IR (KBr $[cm^{-1}]$): 2941 (m), 1590 (s), 1500 (vs), 1417 (s), 1380 (s), 1262 (s), 842 (s), 721 (s). ^1H NMR (C_6D_6, 250 MHz, 25 °C): δ −1.13 (s, 1H, $LaC\mathit{H}$), 0.30 (s, 18H, $C\mathit{H}_3Si$), 1.17 (d, 6H, $(C\mathit{H}_3)_2CH$, $J(H,H) = 6.4$ Hz), 1.37 (d, 6H, $(C\mathit{H}_3)_2CH$, $J(H,H) = 6.4$ Hz), 3.07 (m, 2H, $NCH_2C\mathit{H}_2$), 3.46 (m, 4H, $NC\mathit{H}_2$), 3.73 (sept, 2H, $(CH_3)_2C\mathit{H}$, $J(H,H) = 6.4$ Hz), 6.25 (m, 6H, H_{ring}), 6.90 (m, 4H, H_{ring}). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz, 25 °C): δ 5.8 ($\mathit{C}H_3Si$), 22.2 ($La\mathit{C}H$), 23.4 ($(\mathit{C}H_3)_2CH$), 23.9 ($(\mathit{C}H_3)_2CH$), 28.9 ($N\mathit{C}H_2$), 49.6 ($NCH_2\mathit{C}H_2$), 52.5 ($(CH_3)_2\mathit{C}H$), 113.3 (C_{ring}), 113.4 (C_{ring}), 118.3 (C_{ring}), 135.6 (C_{ring}), 136.0 (C_{ring}), 165.3 (C_{ring}), 166.0 (C_{ring}). Anal. Calcd for $C_{30}H_{49}LaN_4Si_2$ (660.42): C, 54.53; H, 7.47; N, 8.48. Found: C, 53.67; H, 7.21; N, 8.45.

[[(*i*Pr)TP]$_2$LaN(SiMe$_3$)$_2$] (3b). A 10 mL amount of toluene was condensed at −196 °C onto a mixture of 40 mg (0.03 mmol) of **2** and 12 mg (0.06 mmol) of $KN(SiMe_3)_2$, and the mixture was stirred for 18 h at room temperature. The solution was then filtered and concentrated. Yield 30 mg (75%). IR (KBr $[cm^{-1}]$): 2957 (m), 1590 (s), 1502 (vs), 1416 (s), 1381 (s), 1261 (s), 825 (m), 725 (m). ^1H NMR (C_6D_6, 250 MHz, 25 °C): δ 0.30 (s, 18H, $C\mathit{H}_3Si$), 1.20 (d, 6H, $(C\mathit{H}_3)_2CH$, $J(H,H) = 6.4$ Hz), 1.30 (d, 6H, $(C\mathit{H}_3)_2CH$, $J(H,H) = 6.4$ Hz), 3.05 (m, 2H, $NCH_2C\mathit{H}_2$), 3.48 (m, 4H, $NC\mathit{H}_2$), 3.67 (sept, 2H, $(CH_3)_2C\mathit{H}$, $J(H,H) = 6.4$ Hz), 6.23 (m, 6H, H_{ring}), 6.92 (m, 4H, H_{ring}). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz, 25 °C): δ 5.6 ($\mathit{C}H_3Si$), 23.3 ($(\mathit{C}H_3)_2CH$), 23.3 ($(\mathit{C}H_3)_2CH$), 28.7 ($N\mathit{C}H_2$), 49.6 ($NCH_2\mathit{C}H_2$), 52.0 ($(CH_3)_2\mathit{C}H$), 113.2 (C_{ring}), 113.2 (C_{ring}), 117.8 (C_{ring}), 135.5 (C_{ring}), 135.9 (C_{ring}), 164.4 (C_{ring}), 165.9 (C_{ring}). Anal. Calcd for $C_{29}H_{48}LaN_5Si_2$ (661.81): C, 52.63; H, 7.31; N, 10.58. Found: C, 51.95; H, 7.28; N, 10.31.

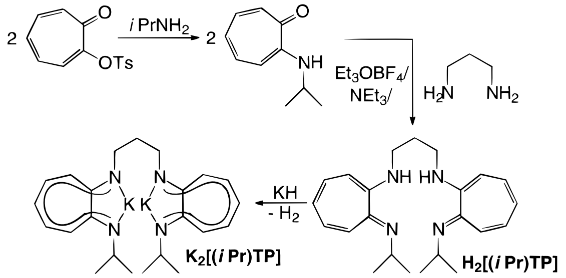
X-ray Crystallographic Studies of 1. Crystals of $C_{77}H_{100}La_2N_{12}O_2$ (**1**) were grown from a pentane/THF (1:1) solution. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the −70 °C cold stream of an STOE STADI/IV diffractometer. Subsequent computations were carried out on an SGI Power Challenge.

Lattice parameters were determined for 30 angle reflections set in the range $15.0 < 2\theta < 24.0°$. Systematic absences and successful refinement of the proposed structure showed **1** to crystallize in the space group $P2_1/c$ (No. 14). Intensities of two standard reflections were measured every 2 h of X-ray exposure and showed no significant variations. An empirical absorption correction on the basis of ψ scan data was applied to **1**. The structure was solved by the Patterson method (SHELXS-86[7]) and refined by full-matrix least-squares methods using the program SHELXL-93.[8] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms positions were calculated in ideal geometry and were not refined. The final cycle of full-matrix least-squares refinement was based on 7077 observed reflections ($I > 2.0\sigma(I)$) and 850 variable parameters and converged with $R1 = 0.0697$, $wR2 = 0.1102$. The maximum and minimum peaks on the final difference Fourier map were 0.766 and −0.775 e/Å^3, respectively. Further details of the crystal structure investigation are available from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-408965, the name of the author, and the journal citation.

X-ray Crystallographic Studies of 2. Crystals of $C_{62}H_{92}Cl_2La_2N_8O_4$ (**2**) were grown from a THF solution. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the −73 °C cold stream of an STOE IPDS diffractometer. Subsequent computations were carried out on an SGI Power Challenge computer.

Systematic absences and successful refinement of the proposed structure showed **2** to crystallize in the space group $P2_1/n$ (No. 14). The structure was solved by the direct methods (SHELXS-86[7]) and refined by full-matrix least-squares methods using the program SHELXL-93.[8] All non-hydrogen atoms were refined anisotropically except C(55)−C(62), O(3), and O(4). The hydrogen atom positions were calculated in ideal geometry and were not refined. The final cycle of full-matrix least-squares refinement was based on 4869 observed reflections ($I > 2.0\sigma(I)$) and 641 variable parameters and converged with $R1 = 0.0904$, $wR2 = 0.2249$. The maximum and minimum peaks on the final difference Fourier map were 1.805 and −1.743 e/Å^3,

Scheme 1



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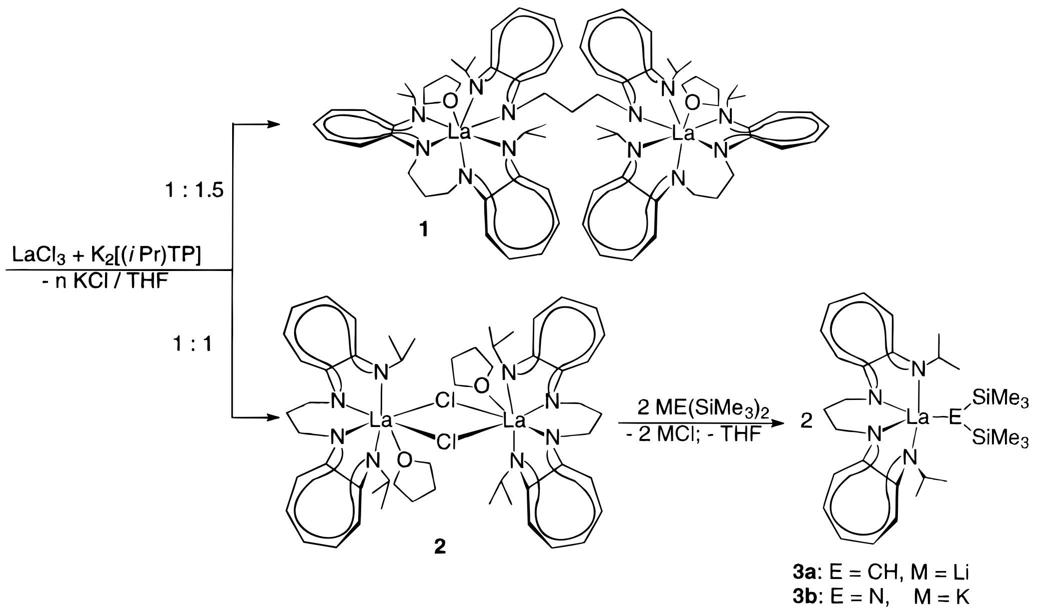
(8) Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Germany, 1993.

Scheme 2



respectively. Further details of the crystal structure investigation are available from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-408966, the name of the author, and the journal citation.

Results and Discussion

The straightforward synthesis of the bridged chelating ligand 1,3-di(2-(*N*-isopropylamino)troponimine)propane (H_2[(*i*Pr)TP]) is shown in Scheme 1. 2-(Tosyloxo)tropone reacts with isopropylamine to form 2-(*N*-isopropylamino)tropone[6] in almost quantitative yield. Further treatment of 2-(*N*-isopropylamino)-tropone with $Et_3O \cdot BF_4$, triethylamine, and 1,3-diaminopropane leads to the desired product H_2[(*i*Pr)TP] as an analytically pure yellow solid in a 60% yield. H_2[(*i*Pr)TP] was characterized by MS, IR, ^1H, and ^{13}C NMR spectroscopy. The ^1H NMR spectrum shows two well-defined sets of multiplets for the propane bridge, indicating the presence of a symmetric species in solution. Reaction of H_2[(*i*Pr)TP] with a potassium hydride suspension in THF affords the dipotassium salt K_2[(*i*Pr)TP] as an orange, air-sensitive crystalline solid, which was characterized by IR, ^1H, and ^{13}C NMR spectroscopy. In comparison to the neutral ligand, the NMR signals of K_2[(*i*Pr)TP] show significant downfield shifts in the ^1H and ^{13}C NMR spectra of all the nuclei which are close to the nitrogen atom.

Table 1. Crystallographic Details for [[(*i*Pr)TP]$_3$La$_2$(THF)$_2$] (**1**) and [[(*i*Pr)TP]$_2$LaCl(THF)]$_2$ (**2**)

	1	**2**
empirical formula	$C_{77}H_{100}La_2N_{12}O_2$	$C_{62}H_{92}Cl_2La_2N_8O_4$
fw	1503.51	1362.16
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	19.860(2)	12.848(3)
b, Å	17.691(3)	32.902(7)
c, Å	21.333(3)	16.215(3)
β, deg	102.211(8)	110.38(3)
V, Å^3	7325(1)	6425(2)
Z	4	4
T, °C	−70	−73
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å)	Mo Kα ($\lambda = 0.710\ 69$ Å)
ρ(calc), g/cm^3	1.363	1.408
μ, cm^{-1}	12.04	14.55
$R1^a$	0.0697	0.0904
$wR2^b$	0.1102	0.2249

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

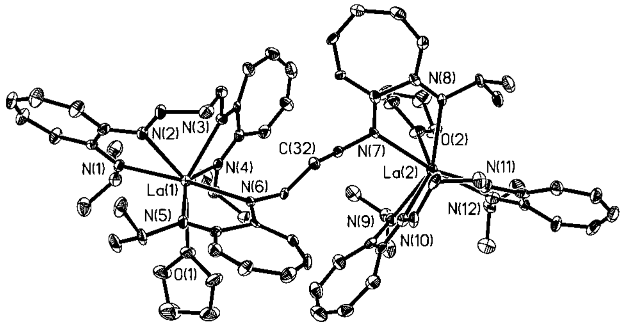


Figure 1. Perspective ORTEP view of the molecular structure of **1**. Thermal ellipsoids are drawn to 30% probability.

The coordination behavior of K_2[(*i*Pr)TP] on lanthanum compounds either with one or two ligand anions attached to the metal center was investigated. Transmetalation of K_2[(*i*Pr)-TP] with anhydrous lanthanum trichloride in a 3:2 molar ratio in THF (Scheme 2) affords the corresponding dinuclear lanthanum complex [[(*i*Pr)TP]$_3$La$_2$(THF)$_2$] (**1**) in fairly good yield. Even with an excess of lanthanum trichloride, **1** is formed preferably at room temperature. The new complex has been characterized by standard analytical/spectroscopic techniques, and the solid-state structure was established by single-crystal X-ray diffraction (Figure 1). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. **1** is a dimeric complex in which the [(*i*Pr)TP]$^{2-}$ anion exhibits two different coordination modes. Two [(*i*Pr)TP]$^{2-}$ units are coordinated as tetradentate chelating ligand anions, whereas the third unit bridges the two lanthanum centers. Both kinds of coordination were observed earlier for *ansa*-metallocenes of the lanthanides.[9] The structure reveals a seven-membered coordination sphere of the ligands around the

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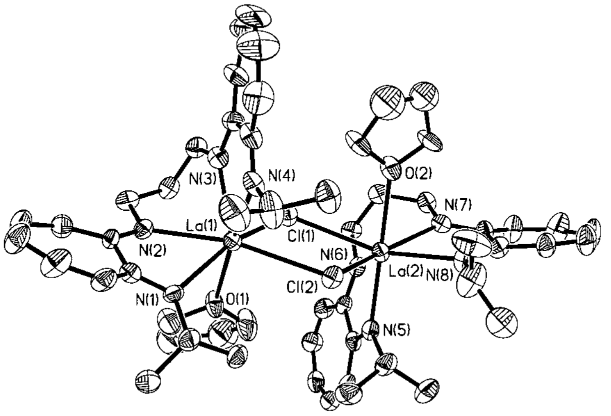

Figure 2. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to 30% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of $[[(i\text{Pr})\text{TP}]_3\text{La}_2(\text{THF})_2]$ (**1**)

La(1)−N(1)	2.590(8)	La(2)−N(7)	2.559(7)
La(1)−N(2)	2.502(8)	La(2)−N(8)	2.618(7)
La(1)−N(3)	2.535(7)	La(2)−N(9)	2.602(8)
La(1)−N(4)	2.585(8)	La(2)−N(10)	2.511(7)
La(1)−N(5)	2.619(7)	La(2)−N(11)	2.508(8)
La(1)−N(6)	2.576(7)	La(2)−N(12)	2.587(7)
La(1)−O(1)	2.718(6)	La(2)−O(2)	2.702(6)
N(1)−La(1)−N(2)	61.6(2)	N(7)−La(2)−N(8)	60.6(2)
N(2)−La(1)−N(3)	75.6(2)	N(11)−La(2)−N(10)	75.5(2)
N(4)−La(1)−N(5)	150.5(2)	N(8)−La(2)−N(9)	151.0(2)
N(5)−La(1)−N(6)	60.7(2)	N(11)−La(2)−N(12)	61.1(2)
N(1)−La(1)−O(1)	94.1(2)	N(8)−La(2)−O(2)	77.7(2)
N(4)−La(1)−O(1)	85.4(2)	N(9)−La(2)−O(2)	85.4(2)
N(5)−La(1)−O(1)	78.0(2)	N(12)−La(2)−O(2)	95.9(2)

lanthanum atom. Thus, one lanthanum atom is coordinated by 1.5 $[(i\text{Pr})\text{TP}]^{2-}$ units and one THF molecule. **1** features a C_2 symmetry axis perpendicular to C(32). The La−N distances (2.502(8)−2.619(7) Å) are in the expected range.[10] Interestingly, the troponimine moieties are asymmetrically coordinated to the metal center. In comparison with the La−N distances of the *i*PrN unit, the La−N distances of the nitrogen atoms which are attached to the propyl bridge are up to 0.09 Å shorter (La(1)−N(1), 2.590(8) Å; La(1)−N(2), 2.502(8) Å). In solution a dynamic behavior for **1** is observed. In the ^{1}H NMR spectrum only a broad peak for the *i*Pr groups is observed at room temperature. At lower temperatures, the signal appears as a set of separate doublets. However, complete separation cannot be observed in toluene.

To obtain a monosubstituted complex with $[(i\text{Pr})\text{TP}]^{2-}$, $\text{K}_2[(i\text{Pr})\text{TP}]$ and anhydrous lanthanum trichloride in THF were refluxed in a 1:1.3 molar ratio to obtain selectively a product of composition $[[(i\text{Pr})\text{TP}]_2\text{LaCl}(\text{THF})]_2$ (**2**) in high yield (Scheme 2). The new dimeric complex has been characterized by standard analytical/spectroscopic techniques. The ^{1}H and ^{13}C NMR spectra point to a symmetrical coordination of the $[(i\text{Pr})\text{TP}]^{2-}$ anion in solution. The signal of the isopropyl C*H* of **2** is well-resolved into a septet but shows a marked downfield shift ($\delta = 4.29$) compared to that of the free ligand $\text{H}_2[(i\text{Pr})\text{TP}]$ ($\delta = 3.55$). As observed for **1**, the single-crystal X-ray structure of **2** (Figure 2) reveals a seven-membered coordination sphere of the ligands around both lanthanum atoms. Data collection parameters and selected bond lengths and angles are given in Tables 1 and 3, respectively. The lanthanum atoms are symmetrical bridged by two chlorine atoms. **2** features a C_2 symmetry along the Cl(1)−Cl(2) axis. The bond distances and angles are in the expected range.[10] A further derivatization of **2** by substituting the chlorine atom offers now the opportunity to prepare a large number of complexes for catalytic applications.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of $[[(i\text{Pr})\text{TP}]_2\text{LaCl}(\text{THF})]_2$ (**2**)

La(1)−N(1)	2.550(11)	La(2)−N(5)	2.464(12)
La(1)−N(2)	2.507(12)	La(2)−N(6)	2.496(11)
La(1)−N(3)	2.450(12)	La(2)−N(7)	2.484(12)
La(1)−N(4)	2.464(13)	La(2)−N(8)	2.543(13)
La(1)−O(1)	2.586(10)	La(2)−O(2)	2.652(11)
La(1)−Cl(1)	2.976(4)	La(2)−Cl(1)	2.941(4)
La(1)−Cl(2)	2.979(4)	La(2)−Cl(2)	2.937(4)
N(1)−La(1)−N(2)	60.7(3)	N(5)−La(2)−N(6)	61.9(4)
N(1)−La(1)−O(1)	81.2(4)	N(5)−La(2)−O(2)	174.2(3)
N(2)−La(1)−O(1)	81.6(4)	N(6)−La(2)−O(2)	123.5(4)
N(1)−La(1)−Cl(1)	157.5(3)	N(5)−La(2)−Cl(1)	103.2(3)
N(2)−La(1)−Cl(1)	116.6(3)	N(6)−La(2)−Cl(1)	75.4(3)
N(1)−La(1)−Cl(2)	107.3(2)	N(5)−La(2)−Cl(2)	87.5(3)
N(2)−La(1)−Cl(2)	167.3(3)	N(6)−La(2)−Cl(2)	129.1(3)
O(1)−La(1)−Cl(1)	76.4(3)	O(2)−La(2)−Cl(1)	77.1(3)
O(1)−La(1)−Cl(2)	92.7(3)	O(2)−La(2)−Cl(2)	87.1(2)
Cl(1)−La(1)−Cl(2)	72.45(9)	Cl(1)−La(2)−Cl(2)	73.57(10)

Thus, reaction of **2** with 2 equiv of $\text{LiCH}(\text{SiMe}_3)_2$ or $\text{KN}(\text{SiMe}_3)_2$ in toluene affords the alkyl or amide derivatives $[[(i\text{Pr})\text{TP}]_2\text{LaE}(\text{SiMe}_3)_2]$ (**3a**, E = CH; **3b**, E = N) in high yield (Scheme 2). The new complexes have been characterized by standard analytical/spectroscopic techniques. Interestingly, the ^{1}H and ^{13}C NMR spectra of **3a** and **3b** show a diastereotopic splitting of the isopropyl CH_3 signals, indicating that the pentacoordinated lanthanum atom is a chiral center. Since metallocene lanthanide alkyls and amides are commonly used as precatalysts for homogeneous catalysis[11] **3a** and **3b** may also have potential catalytic applications.

Conclusion

In conclusion, a new ligand system in which two aminotroponimine moieties are linked together has been introduced. It may be interpreted in terms of a bridged bis-diamino ligand or as semi-tropocoronate[12] (semi-porphyrin analogous). Starting from tropolone, $\text{H}_2[(i\text{Pr})\text{TP}]$, is obtained in much higher yield than the well-established tropocoronates.[12] Furthermore, additional chiral centers can be attached to the ligand by a formal substitution of the isopropyl group or the *n*-propyl bridge. In contrast to porphyrin[13] or other macrocyclic ligands such as

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texaphyrins[14] the $[(i\mathrm{Pr})\mathrm{TP}]^{2-}$ anion has a higher flexibility upon coordination and features two different coordination modes. Thus, $[(i\mathrm{Pr})\mathrm{TP}]^{2-}$ acts more like bridged cyclopentadienyls; this behavior is illustrated for a series of lanthanide complexes and has the potential to be extended for reactions with a wide range of d and f elements.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1** and **2** are available on the Internet only. Access information is given on any current masthead page.

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