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Notes

Bridged Aminotroponiminate Complexes of the Lanthanides

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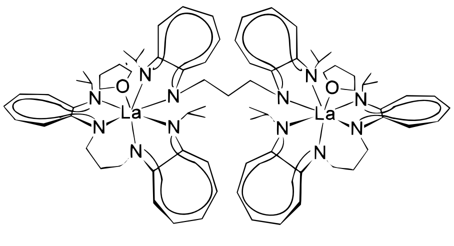
Introduction

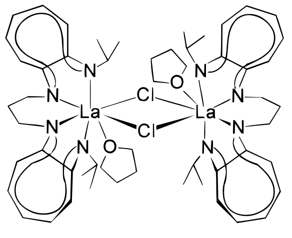
Numerous advances have been made in the past decade in the design and synthesis of well-defined catalysts of groups 3 and 4 and the lanthanide metals for a variety of olefin transformations such as polymerization of terminal olefins.[1−10] The vast majority of these catalysts are metallocene derivatives, although some contain one cyclopentadienyl ring. Recently, there has been significant research activity by academic and industrial chemists to develop a new generation of catalysts in which one or both cyclopentadienyl rings of the metallocene catalyst are formally substituted by other ligands such as alkoxides, amides, or amidinates.[11] Thus complexes that contain chelating alkoxides or chelating nitrogen-based bidentate ligands have been recognized as potential catalysts.[12−16]

Lately, we reported on the preparation and characterization of aminotroponiminates as cyclopentadienyl alternatives for group 3 and lanthanide elements.[17−19] It was shown that bis(aminotroponiminate)yttrium amides are active as catalysts for hydroamination/cyclization catalysis.[19] Since the aminotroponiminate ligand has proven to be a formal substitute for cyclopentadienyl[17−21] we started to prepare bridged aminotroponiminates as alternatives for ansa metallocenes. It was shown that the tris methylene bridged ligand 1,3-bis(2-(isopropylamino)troponiminate)propane ($[(i\mathrm{Pr})\mathrm{TP}]^{2-}$) is able to coordinate in a chelating or in a metal bridging mode to lanthanum (Scheme 1).[22] Both kinds of coordination were also observed earlier for ansa metallocenes of the lanthanides.[23−26] Thus, $[(i\mathrm{Pr})\mathrm{TP}]^{2-}$ acts in a certain way like bridged cyclopentadienyls. 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 porphyrins[27−32] or other macrocyclic ligands such as texaphyrins,[33−35] the $[(i\mathrm{Pr})\mathrm{TP}]^{2-}$ anion has a higher flexibility upon coordination by featuring two different coordination modes.

Scheme 1



1 chelating and metal bridging mode



2 chelating mode only

In our preliminary studies we reported on the synthesis of the new ligand 1,3-bis(2-(isopropylamino)troponimine)propane

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Table 1. Crystallographic Details for [[(*i*Pr)TP]NdCl(THF)]$_2$ (**3**), [[(*i*Pr)TP]ErCl]$_2$ (**4**), and [[(*i*Pr)TP]YbCl]$_2$ (**5**)

	3·2THF	**4**·pentane	**5**·pentane
formula	$C_{62}H_{92}Cl_2N_8Nd_2O_4$	$C_{51}H_{72}Cl_2Er_2N_8$	$C_{51}H_{72}Cl_2Yb_2N_8$
fw	1372.82	1202.58	1214.15
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	12.71.4(3)	9.4158(3)	9.431(2)
b, Å	32.835(7)	11.4180(4)	11.360(3)
c, Å	16.193(3)	13.0820(3)	13.083(2)
α, deg		66.54(2)	66.38(3)
β, deg	110.62(3)	73.770(3)	73.44(2)
γ, deg		84.825(4)	84.68(3)
V, Å^3	6327(2)	1238(1)	1231(1)
Z	4	1	1
T, °C	−73	−70	−70
radiation	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)
μ, mm^{-1}	1.758	3.516	3.929
$R1^a$	0.0887	0.0175	0.0223
w$R2^b$	0.1987	0.0469	0.0562

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

(H$_2$[(*i*Pr)TP]) and its subsequent reaction to give various new lanthanum complexes.[22] In this paper we now report on further mainly structural investigations on the coordination behavior of the [(*i*Pr)TP]$^{2-}$ ligand onto some members of the lanthanide series. We basically focus on how the ion radius of different lanthanide metals influences the coordination mode of the [(*i*Pr)TP]$^{2-}$ ligand.

Experimental Section

General. These have been reported previously.[22] H$_2$[(*i*Pr)TP] was prepared according to literature procedures.[22]

[[(*i*Pr)TP]NdCl(THF)]$_2$ (3). 10 mL of THF was condensed at −196 °C onto a mixture of 325 mg (1.3 mmol) of NdCl$_3$ and 440 mg (1.0 mmol) of K$_2$[(*i*Pr)TP], and the mixture was refluxed for 8 h. Then, the hot solution was filtered and the solvent evaporated in vacuo. Yield: 510 mg (83%). IR (KBr [cm^{-1}]): 2963 (m), 2865 (m), 1589 (s), 1507 (vs), 1466 (s), 1411 (s), 1353 (s), 723 (s). Anal. Calcd for $C_{62}H_{92}Cl_2N_8Nd_2O_4$ (**3**·2THF) (1372.82): C, 54.24; H, 6.75; N, 8.16; Found: C, 52.31; H, 6.85; N, 8.25.

[[(*i*Pr)TP]LnCl]$_2$. 10 mL of THF was condensed at −196 °C onto a mixture of 1.3 mmol of LnCl$_3$ and 440 mg (1.0 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 condensed onto the mixture. Then, the solution was 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 pentane/THF (3:1).

Ln = Er (**4**). Yield: 410 mg (69%). IR (KBr [cm^{-1}]): 2961 (m), 2872 (m), 1590 (s), 1507 (vs), 1420 (s), 1356 (s), 1260 (s), 725 (m). Anal. Calcd for $C_{51}H_{72}Cl_2Er_2N_8$ (**4**·pentane) (1202.58): C, 50.93; H, 5.99; N, 9.31; Found: C, 50.80; H, 5.45; N, 9.62.

Ln = Yb (**5**). Yield: 465 mg (77%). IR (KBr [cm^{-1}]): 2963 (m), 1591 (s), 1505 (vs), 1420 (s), 1357 (s), 1269 (s), 725 (m). Anal. Calcd for $C_{51}H_{72}Cl_2N_8Yb_2$ (**5**·pentane) (1214.15): C, 50.45; H, 5.93; N, 9.22; Found: C, 50.10; H, 5.88; N, 9.00.

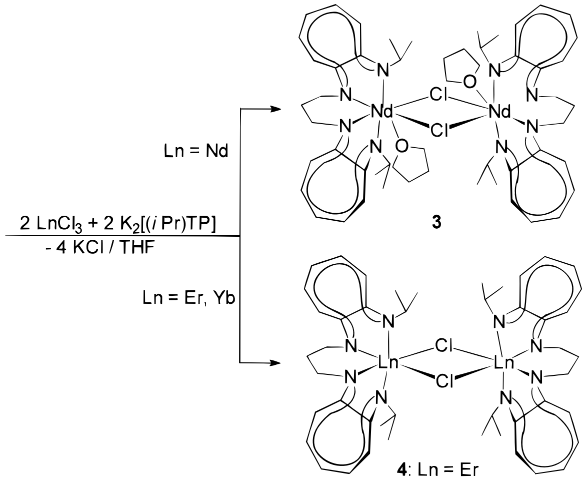
X-ray Crystallographic Studies of 3−5. Crystals of $C_{62}H_{92}Cl_2N_8Nd_2O_4$ (**3**·2 THF) were grown from a THF solution. Crystals of $C_{51}H_{72}Cl_2Er_2N_8$ (**4**·pentane)/$C_{51}H_{72}Cl_2N_8Yb_2$ (**5**·pentane) were grown from a pentane/THF (3:1) solution. Data collection, reduction, solution, and refinement were performed as previously described,[22] and a summary of the data is given in Table 1.

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. CCDC135981−CCDC135983. 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

Recently we reported that transmetalation of K$_2$[(*i*Pr)TP] with anhydrous lanthanum trichloride in a 3:2 molar ratio in THF affords the corresponding dinuclear lanthanum complex [[(*i*Pr)TP]$_3$La$_2$(THF)$_2$] (**1**), whereas the reaction of K$_2$[(*i*Pr)TP] and anhydrous lanthanum trichloride in a 1:1.3 molar ratio in refluxing THF affords [[(*i*Pr)TP]LaCl(THF)]$_2$ (**2**) in high yield (Scheme 1). Now, we are interested in studying the coordination behavior of the [(*i*Pr)TP]$^{2-}$ dianion on three different lanthanides (Nd, Er, and Yb) independent of the ion radius.[36] Transmetalation of K$_2$[(*i*Pr)TP] with anhydrous neodymium trichloride in a 1:1.3 molar ratio in refluxing THF (Scheme 2) affords the corresponding dinuclear complex [[(*i*Pr)TP]NdCl(THF)]$_2$ (**3**) as yellow crystals in high yield.

Scheme 2



4: Ln = Er
5: Ln = Yb

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). **3** crystallizes from hot THF in the monoclinic centrosymmetric space group $P2_1/n$ with four molecules in the unit cell. Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. **3** is a dimeric complex in which two neodymium atoms are symmetrically bridged by two μ_2-chlorine atoms. The [(*i*Pr)TP]$^{2-}$ units are coordinated as tetradentate chelating ligand anions. Additionally, on each neodymium atom 1 equiv of THF is coordinated. Thus, the structure reveals a 7-fold coordination sphere of the ligands around the neodymium atoms. **3**, which is isostructural to **2**,

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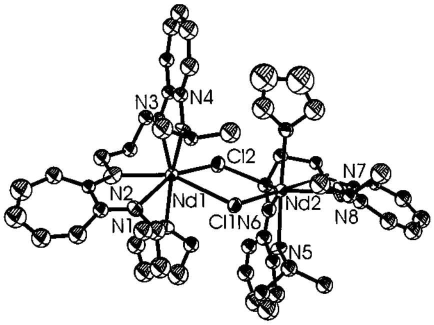

Figure 1. Perspective ORTEP view of the molecular structure of **3**. Thermal ellipsoids are drawn to encompass 50% probability.

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

Nd1−N1	2.51(2)	Nd2−N5	2.43(2)
Nd1−N2	2.41(2)	Nd2−N6	2.40(2)
Nd1−N3	2.40(2)	Nd2−N7	2.445(2)
Nd1−N4	2.38(2)	Nd2−N8	2.52(2)
Nd1−O1	2.59(2)	Nd2−O2	2.56(2)
Nd1−Cl1	2.868(6)	Nd2−Cl1	2.938(5)
Nd1−Cl2	2.886(5)	Nd2−Cl2	2.934(6)
N1−Nd1−N2	64.1(6)	N5−Nd2−N6	63.9(7)
N1−Nd1−O1	81.6(6)	N5−Nd2−O2	170.8(6)
N2−Nd1−O1	78.3(6)	N6−Nd2−O2	126.2(7)
N1−Nd1−Cl1	93.3(4)	N5−Nd2−Cl1	82.2(4)
N2−Nd1−Cl1	153.1(5)	N6−Nd2−Cl1	119.5(4)
N1−Nd1−Cl2	157.5(5)	N5−Nd2−Cl2	108.1(4)
N2−Nd1−Cl2	122.1(4)	N6−Nd2−Cl2	74.4(5)
O1−Nd1−Cl1	84.5(4)	O2−Nd2−Cl1	92.4(4)
O1−Nd1−Cl2	92.7(4)	O2−Nd2−Cl2	77.0(4)
Cl1−Nd1−Cl2	73.51(13)	Cl1−Nd2−Cl2	71.81(13)
Nd1−Cl1−Nd2	107.0(2)	Nd1−Cl2−Nd2	107.6(2)

features almost a C_2 symmetry along the Cl(1)−Cl(2) axis. The Nd−N bond distances are in the range of 2.38(2)−2.52(2) Å. Comparable bond lengths are observed in $[\{(\mathrm{CF_3})_3\mathrm{C_6H_2C}(\mathrm{NSiMe_3})_2\}_2\mathrm{Nd}(\mu\text{-Cl})_2\mathrm{Li(THF)_2}]$ (2.462(5)−2.545(5)[37] Å) or $[\mathrm{Nd}(t\mathrm{Bu_2pz})_3(\mu\text{-DME})]_\infty$ ($t\mathrm{Bu_2pz}$ = 3,5-di-*t*butylpyrazolate) (2.390(5)−2.499(7) Å).[38] The largest Nd−N bond length are observed for those nitrogen atoms which are located trans to a chlorine atom. The Nd−Cl are in the expected range of 2.868(6)−2.938(5) Å.

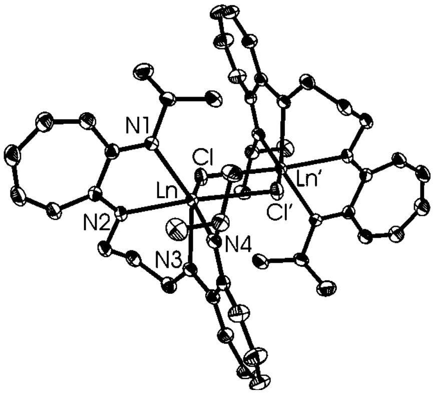

Figure 2. Perspective ORTEP view of the molecular structure of **4** (Ln = Er) and **5** (Ln = Yb). Thermal ellipsoids are drawn to encompass 50% probability.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of $[[(i\mathrm{Pr})\mathrm{TP}]\mathrm{ErCl}]_2$ (**4**) and $[[(i\mathrm{Pr})\mathrm{TP}]\mathrm{YbCl}]_2$ (**5**)

Compound **4**			
Er−N1	2.359(2)	Er−N4	2.328(2)
Er−N2	2.289(2)	Er−Cl	2.684(1)
Er−N3	2.324(2)	Er−Cl′	2.781(1)
N1−Er−Cl	151.36(6)	N2−Er−Cl′	96.63(6)
N2−Er−Cl	96.67(6)	N3−Er−Cl′	171.96(6)
N3−Er−Cl	98.51(6)	N4−Er−Cl′	119.50(6)
N4−Er−Cl	99.15(6)	Cl−Er−Cl′	76.43(2)
N1−Er−Cl′	81.15(6)	Er−Cl−Er′	103.57(2)
Compound **5**			
Yb−N1	2.334(3)	Yb−N4	2.308(3)
Yb−N2	2.262(3)	Yb−Cl	2.665(1)
Yb−N3	2.298(3)	Yb−Cl′	2.763(1)
N1−Yb−Cl	151.42(7)	N2−Yb−Cl′	96.34(8)
N2−Yb−Cl	96.82(7)	N3−Yb−Cl′	172.29(7)
N3−Yb−Cl	99.13(8)	N4−Yb−Cl′	118.60(8)
N4−Yb−Cl	99.10(8)	Cl−Yb−Cl′	76.01(3)
N1−Yb−Cl′	80.94(7)	Yb−Cl−Yb′	103.99(3)

Table 4. Comparison of the Ln−Cl−Ln′ and Cl−Ln−Cl′ Angles of the Four-Membered Ln−Cl−Ln′−Cl′ Ring of **2**−**5**

	angle	
compound	Ln−Cl−Ln′	Cl−Ln−Cl′
2[a]	La1−Cl1−La2 106.94(10)°	Cl1−La1−Cl2 72.45(9)°
	La1−Cl2−La2 106.95(10)°	Cl1−La2−Cl2 73.57(10)°
3	Nd1−Cl1−Nd2 107.0(2)°	Cl1−Nd1−Cl2 73.51(13)°
	Nd1−Cl2−Nd2 107.6(2)°	Cl1−Nd2−Cl2 71.81(13)°
4	Er−Cl−Er′ 103.57(2)°	Cl−Er−Cl′ 76.43(2)°
5	Yb−Cl−Yb′ 103.99(3)°	Cl−Yb−Cl′ 76.01(3)°

[a] Reference 22.

To study the coordination behavior of the $[(i\mathrm{Pr})\mathrm{TP}]^{2-}$ dianion with the heavier lanthanides which feature a smaller ion radius in oxidation state +3 compared to lanthanum and neodymium, the reaction of $\mathrm{K_2}[(i\mathrm{Pr})\mathrm{TP}]$ with anhydrous erbium and ytterbium trichloride in a 1:1.3 molar ratio in THF was investigated. Since the heavier lanthanide trichlorides are more soluble in THF than the lighter ones already at room temperature, compounds of composition $[[(i\mathrm{Pr})\mathrm{TP}]\mathrm{LnCl}]_2$ (Ln = Er (**4**), Yb (**5**)) were obtained as yellow powders (Scheme 2). The new dimeric complexes have been characterized by standard analytical/spectroscopic techniques. By recrystallizing both **4** and **5** from pentane/THF (3:1) single crystals of centimeter size can be obtained. The solid-state structures were established by single-crystal X-ray diffraction (Figure 2). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 3, respectively. Due to the similar ion radius of the center atoms of **4** and **5**, the single-crystal X-ray structures of both compounds are isostructural. They crystallize in the trigonal space group $P\bar{1}$ having one molecule in the unit cell. **4** and **5** are dimeric complexes in which the metal centers are bridged by two μ_2-chlorine atoms. Four coordination sites are occupied by the chelating $[(i\mathrm{Pr})\mathrm{TP}]^{2-}$ ligand, resulting in a 6-fold coordination sphere of the ligands around the lanthanide atoms. Due to the smaller ion radii of erbium and ytterbium compared to neodymium and lanthanum, no additional coordination of THF to the center atom is observed. In the center of the Ln−Cl−Ln′−Cl′ plane a crystallographic inversion point is observed. The bridging chlorine atoms are unsymmetrically located between the lanthanide atoms. The bond lengths differ by about 0.1 Å (**4**, 2.684(1) and 2.781(1) Å; **5**, 2.665(1) and 2.763(1) Å). The

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Ln−N bond lengths are in the expected range of 2.289(2)−2.359(2) Å (**4**) and 2.262(3)−2.334(3) Å (**5**).[39−41]

Conclusion

In conclusion, $[(i\text{Pr})\text{TP}]^{2-}$, a ligand system in which two aminotroponimine moieties are linked together, has been coordinated onto various lanthanides. Depending on the ion radius, the center atom reveals either a 7- (La, Nd) or a 6-fold (Er, Yb) coordination sphere of the ligands around the lanthanide atoms. A comparison of the Ln−Cl−Ln′ and Cl−Ln−Cl′ angles of the central Ln−Cl−Ln′−Cl′ four-membered ring of **2**−**5** is given in Table 4. Compared to **4** and **5** the lighter lanthanides form a larger Ln−Cl−Ln′ angle and a smaller Cl−Ln−Cl′ angle. Obviously the additional equivalent of THF moves the other ligands of **2** and **3** closer together. This effect cannot be compensated by the larger ion radii of lighter lanthanides. Further investigation of the coordination behavior of the $[(i\text{Pr})\text{TP}]^{2-}$ ligand on the main group and transition metals is in progress.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (Habilitation fellowship) and the Fonds der Chemischen Industrie. Additionally, generous support from Prof. Dr. D. Fenske is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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