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Bridged aminotroponiminate complexes of lutetium

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Abstract

The reaction of the salt di-potassium-1,3-di(2-(isopropylamino)troponiminate)-propane, $K_2[(^iPr)TP]$, with lutetium trichloride leads to $[[(^iPr)TP]LuCl]_2$ (**1**). **1** was characterized by single crystal X-ray crystallography. To study the reactivity of **1** some selected derivatives such as alkyl, amide, η^5-cyclopentadienyl, and η^3-borohydride complexes were synthesized by substitution of the chlorine atom of **1**. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Aminotroponiminate; Coordination chemistry; Lanthanides; Lutetium; *N*-Ligands

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1. Introduction

Metallocenes of the lanthanides [1] have been shown 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]. Organolanthanides combine facile ligand exchange and high electrophilicity, while the lanthanide series offers tunable reactivity not only via modification of the ligand sphere but also via variation of metal ionic radius [9]. In an attempt to extend the possibility for modifying and controlling the reactivity, recent research efforts have been directed towards substitution of the cyclopentadienyl ligands in the metallocene setup by other groups such as amidinates [10], diamido ligands [11], or other combinations of nitrogen and oxygen atoms [12] to increase the electrophilicity of the metal center and to create a different steric environment at the reactive site [13].

Recent reports have described the preparation and characterization of aminotroponiminates as cyclopentadienyl alternatives for Groups 3 and 4 and the lanthanide elements [14–17]. Aminotroponiminate complexes with Group 13 metals [18], tin [19] and the first row of transition metals [20] have also been reported. Furthermore complexes with double bridged aminotroponiminates (troponcoronands) were intensively studied [21]. It was shown that bis(aminotroponiminate)yttrium amides are active as catalysts for hydroamination/cyclization catalysis [16]. Since the aminotroponiminate ligand has proven to be a formal substitute for cyclopentadienyl we started to prepare mono bridged aminotroponiminates as alternatives for *ansa* metallocenes [22]. It was shown that the tris methylene bridged ligand 1,3-di(2-(isopropylamino)troponiminate)-propane ($[(^iPr)TP]^{2-}$) is able to coordinate in a chelating or in a metal bridging mode to lanthanum [22]. In further studies the reaction of $K_2[(^iPr)TP]$ with selected lanthanide trichlorides was investigated. Depending on the size of the ion radius of the lanthanide atom [23] products of composition $[[(^iPr)TP]LnCl(THF)]_2$ (Ln = La, Nd) or $[[(^iPr)TP]LnCl]_2$ (Ln = Er, Yb) in which the center atom reveals either a seven- or a six-fold coordination sphere of the ligands were obtained [22,24].

In this report the reaction of $K_2[(^iPr)TP]$ with lutetium trichloride which leads to a lutetium chloro complex, $[[(^iPr)TP]LuCl]_2$ (**1**), will be presented first, followed by a discussion of some structural aspects. The synthesis and characterization of various lutetium complexes which were obtained from further reactions of **1** are then shown.

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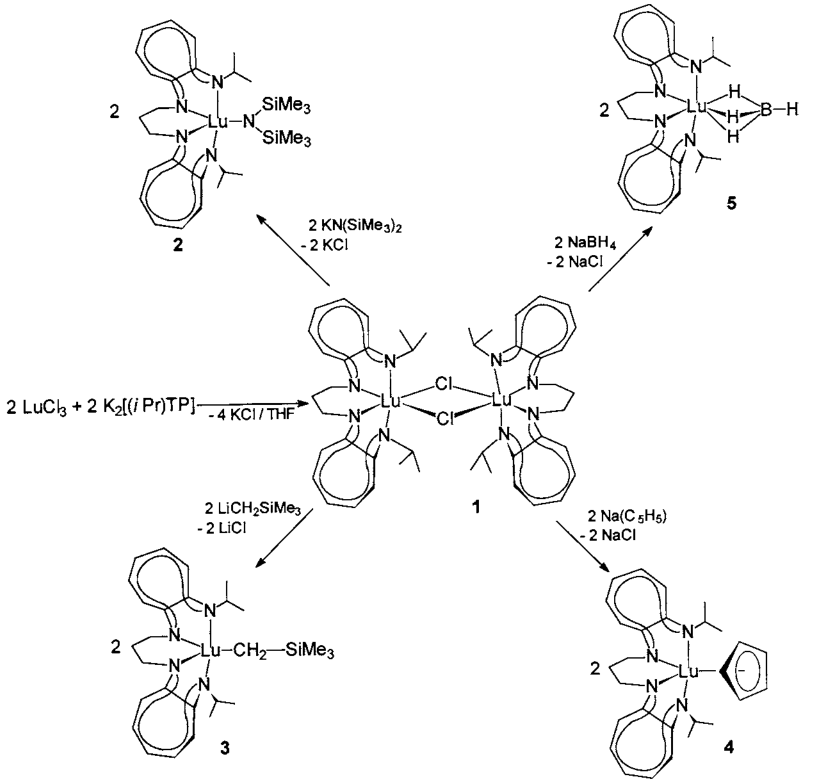
2. Results and discussion

2.1. Lutetium chloro complex

Transmetallation of $K_2[(^iPr)TP]$ with anhydrous lutetium trichloride in a 1:1.3 molar ratio in THF at room temperature affords the corresponding dinuclear complex $[[(^iPr)TP]LuCl]_2$ (**1**) as yellow crystals in high yield (Scheme 1). The new dimeric complex has been characterized by standard analytical/spectroscopic techniques. By recrystallizing from 3:1 pentane–THF single crystals of centimeter size can be obtained. The solid



Scheme 1.

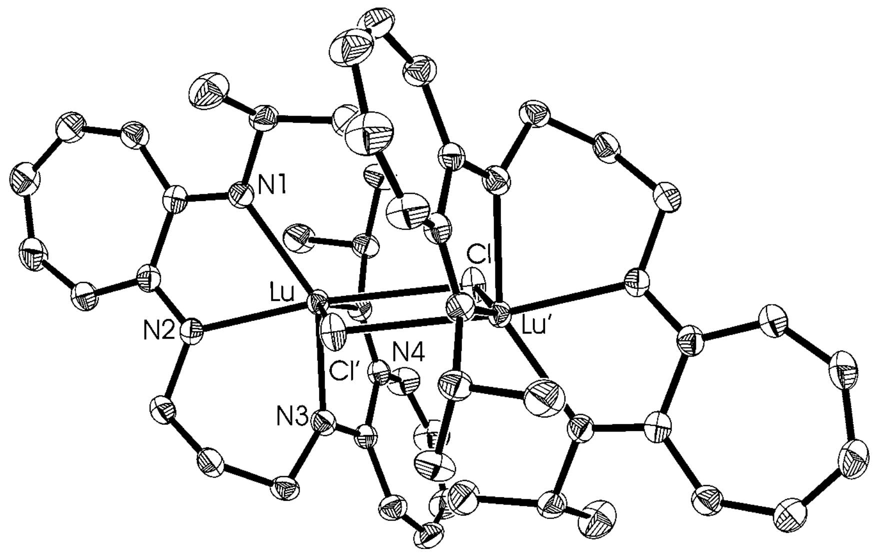


Fig. 1. Perspective ORTEP view of the molecular structure of **1**. Thermal ellipsoids are drawn to encompass at 50% probability. Selected bond lengths (Å) and angles (°): Lu–N1 2.327(3), Lu–N4 2.303(3), Lu–N2 2.253(3), Lu–Cl 2.650(1), Lu–N3 2.292(3), Lu–Cl′ 2.761(1); N1–Lu–Cl 151.57(7), N2–Lu–Cl′ 96.34(7), N2–Lu–Cl 96.69(7), N3–Lu–Cl′ 172.27(7), N3–Lu–Cl 99.04(7), N4–Lu–Cl′ 118.26(7), N4–Lu–Cl 99.20(7), Cl–Lu–Cl′ 76.01(3), N1–Lu–Cl′ 80.89(7), Lu–Cl–Lu′ 103.99(3).

state structure was established by single crystal X-ray diffraction (Fig. 1). Due to the similar ionic radius of the metal atoms **1** is isostructural to $[[(^i\text{Pr})\text{TP}]\text{LnCl}]_2$ (Ln = Er, Yb) [24]. **1** crystallizes in the trigonal space group $P\bar{1}$ having one molecule in the unit cell. **1** is a dimeric complex in which the metal centers are bridged by two μ-chlorine atoms. Four coordination sites are occupied by the chelating $[(^i\text{Pr})\text{TP}]^{2-}$-ligands resulting in a six-fold coordination sphere of the ligands around the lanthanide atoms which are unsymmetrically located between the lanthanide atoms. In contrast to the Er and Yb complexes compound **1** is diamagnetic. Thus an easy characterization of **1** and its derivatives by NMR techniques is possible.

Complex **1** was also characterized by IR, ^{1}H- and ^{13}C-NMR spectroscopy and elemental analysis. The ^{1}H- and ^{13}C-NMR spectra point to a symmetrical coordination of the $[(^i\text{Pr})\text{TP}]^{2-}$ anion in solution. Thus only two sets of signals are observed for the *n*-propyl bridge in **1** (δ 2.44 and 3.44). The signal of the isopropyl C*H* of **1** is well-resolved into a septet but shows a marked downfield shift (δ 4.20) compared to that of the free ligand $\text{H}_2[(^i\text{Pr})\text{TP}]$ (δ 3.55) [22].

2.2. Derivatives of 1

To study the reactivity of **1** some selected derivatives were synthesized by a substitution of the chlorine atom of **1**. A general overview of the reaction is given in Scheme 1. Transmetallation of **1** with two equivalents of $\text{KN(SiMe}_3)_2$ in toluene leads to $[[(i\text{Pr})\text{TP}]\text{LuN(SiMe}_3)_2]$ (**2**). By using $\text{LiCH}_2(\text{SiMe}_3)$ as alkylating reagent the alkyl complex $[[(^i\text{Pr})\text{TP}]\text{LuCH}_2(\text{SiMe}_3)]$ (**3**) was obtained in fairly good yields. In the ^{1}H-NMR spectrum of **3** a characteristic signal of the Lu–CH_2 group is observed at δ −0.32. Due to the lack of a mirror plane through the isopropyl groups the ^{1}H- and ^{13}C-NMR spectra of **2** and **3** show a splitting of the isopropyl CH_3 signals. The signals are observed at δ 1.24 and 1.47 for **2** and δ 1.34 and 1.35 for **3**. As expected the substitution of the chlorine atom in **1** by an alykl or amide group also has an influence on the ^{1}H- and ^{13}C-NMR signals of **2** and **3**. Thus, the signals of the isopropyl C*H* group of **2** (δ 3.89) and **3** (δ 3.93) show a marked upfield shift compared to **1** (δ 4.20). In contrast to $[[(^i\text{Pr})\text{TP}]\text{LaCH(SiMe}_3)_2]$ no dynamic behavior of the penta-coordinated complexes **2** and **3** is observed [22].

For a further investigation of the reactivity of **1** a borohydride and a cyclopentadienyl complex were synthesized. The cyclopentadienyl complex $[[(^i\text{Pr})\text{TP}]\text{Lu}(\eta^5\text{-C}_5\text{H}_5)]$ (**4**) is obtained by transmetallation of **1** and $\text{Na(C}_5\text{H}_5)$ in THF at room temperature (Scheme 1). The ^{1}H- and ^{13}C-NMR spectra of **4** show only one sharp resonance for the cyclopentadienyl ring (δ 6.38 (^{1}H-NMR), δ 111.4 (^{13}C-NMR)) which indicates a η^5-coordination of the five-membered ring on to the lutetium atom. Once again a splitting of the isopropyl CH_3 signals of **4** is observed (δ 1.33 and 1.52 (^{1}H-NMR), δ 21.2 and 22.3 (^{13}C-NMR), respectively). Another interesting ligand in lanthanide chemistry is the BH_4^- anion, which coordinates either as a tridentate, as bidentate, or as metal bridging ligand. As shown by a recent review article the coordination mode can best be determined by IR spectroscopy [25]. Transmetallation of **1** with two equivalents of NaBH_4 in THF leads to a borohydride complex of composition $[[(^i\text{Pr})\text{TP}]\text{Lu}(\eta^3\text{-BH}_4)]$ (**5**). The new complex has been characterized by standard analytical/spectroscopic techniques. An IR mode at 2225 cm^{-1} is indicating a η^3-coordination of the ligand [25]. Furthermore, characteristic ^{1}H- and ^{11}B-NMR resonances are obtained for the BH_4^- group. Thus two broad signals (δ 0.87 and 1.49) are observed in the ^{1}H-NMR spectrum of **5**, whereas a quintett (δ −25.8) having a coupling constant of $^1J(\text{H,B}) = 81.9$ Hz is seen in the ^{11}B-NMR spectrum. Both signals are in the expected range [25]. In contrast to **1**–**4** no splitting is found for the isopropyl CH_3-NMR signals which might indicate a different coordination mode of the $[(^i\text{Pr})\text{TP}]^{2-}$ ligand or a dynamic behavior of the complex. Besides the NMR investigations all derivatives of **1** were characterized by EI mass spectroscopy. For **2**–**5** molecular ions as well as their characteristic fragmentation patterns were observed.

3. Experimental

3.1. General

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in 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 glove box. Ether solvents (tetrahydrofuran and ethyl ether) were predried over Na wire and distilled under nitrogen from Na–K alloy benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and 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 (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. IR spectra were performed on a Bruker IFS 28 and mass spectra were recorded at 70 eV on Varian MAT 711. Elemental analyses were performed at the microanalytical laboratory of the Institute of Inorganic Chemistry at Karlsruhe. $\mathrm{LuCl_3}$ [26] and $\mathrm{K_2[(^iPr)TP]}$ [22] were prepared according to literature procedures.

3.1.1. *$[[(^i\mathrm{Pr})\mathrm{TP}]\mathrm{LuCl}]_2$ (**1**)*

A total of 10 ml of THF was condensed at −196°C onto a mixture of 365 mg (1.3 mmol) of $\mathrm{LuCl_3}$ and 440 mg (1.0 mmol) of $\mathrm{K_2[(^iPr)TP]}$ and the suspension was stirred for 18 h at room temperature (r.t.). The solvent was then evaporated in vacuo and toluene (10 ml) 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 3:1 pentane–THF. Yield 470 mg (77%). -IR (KBr $[\mathrm{cm^{-1}}]$): 2961 (m), 2876 (m), 1591 (s), 1420 (s), 1342 (s), 1270 (s), 1229 (s), 725 (s). ^{1}H-NMR (d_8-THF, 250 MHz, 25°C): δ 1.47 (d, 24 H, $(\mathrm{C}H_3)_2\mathrm{CH}$, J(H,H) = 6.7 Hz), 2.44 (m, 4 H, $\mathrm{NCH_2C}H_2$), 3.44 (m, 8 H, $\mathrm{NC}H_2$), 4.20 (sept, 4 H, $(\mathrm{CH_3})_2\mathrm{C}H$), 6.15 (t, 4 H, $\mathrm{H_{ring}}$, J(H,H) = 9.1 Hz), 6.35 (d, 4 H, $\mathrm{H_{ring}}$, J(H,H) = 11.3 Hz), 6.58 (d, 4 H, $\mathrm{H_{ring}}$, J(H,H) = 11.6 Hz), 6.90 (dd, 8 H, $\mathrm{H_{ring}}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($d_8$-THF, 62.9 MHz, 25°C): δ 21.8 ($(C\mathrm{H_3})_2\mathrm{CH}$), 30.3 ($\mathrm{N}C\mathrm{H_2}$), 49.6 ($\mathrm{NCH_2}C\mathrm{H_2}$,), 51.7 ($(\mathrm{CH_3})_2C\mathrm{H}$), 112.7 ($\mathrm{C_{ring}}$), 114.7 ($\mathrm{C_{ring}}$), 117.3 ($\mathrm{C_{ring}}$), 134.4 ($\mathrm{C_{ring}}$), 135.0 ($\mathrm{C_{ring}}$), 164.9 ($\mathrm{C_{ring}}$), 166.0 ($\mathrm{C_{ring}}$). Anal. Calc. for $\mathrm{C_{51}H_{72}Cl_2Lu_2N_8}$ (1215.92): C, 50.37; H, 5.92; N, 9.21. Found C, 49.93; H, 5.93; N, 9.17%.

3.1.2. *$[[(^i\mathrm{Pr})\mathrm{TP}]\mathrm{LuN(SiMe_3)_2}]$ (**2**)*

A total of 10 ml of toluene was condensed at −196°C onto a mixture of 200 mg (0.175 mmol) of **1** and 70 mg (0.35 mmol) of $\mathrm{KN(SiMe_3)_2}$ and the suspension was stirred for 18 h at r.t. Then, the solution was filtered and concentrated. The remaining residue was washed with pentane (10 ml) and dried in vacuo. Yield 136 mg (56%). IR (KBr $[\mathrm{cm^{-1}}]$): 2962 (m), 1590 (s), 1507 (vs), 1468 (s), 1421 (m), 1386 (m), 1270 (m), 950 (m), 726 (s). ^{1}H-NMR ($\mathrm{C_6D_6}$, 250 MHz, 25°C): δ 0.28 (s, 18 H, $\mathrm{C}H_3\mathrm{Si}$), 1.24 (d, 6 H, $(\mathrm{C}H_3)_2\mathrm{CH}$, J(H,H) = 6.5 Hz), 1.47 (d, 6 H, $(\mathrm{C}H_3)_2\mathrm{CH}$, J(H,H) = 6.6 Hz), 2.99 (m, 2 H, $\mathrm{NCH_2C}H_2$), 3.45 (m, 4 H, $\mathrm{NC}H_2$), 3.89 (sept, 2 H, $(\mathrm{CH_3})_2\mathrm{C}H$, J(H,H) = 6.6 Hz), 6.27 (m, 4 H, $\mathrm{H_{ring}}$), 6.52 (m, 2 H, $\mathrm{H_{ring}}$), 6.94 (d, 4 H, $\mathrm{H_{ring}}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{C_6D_6}$, 62.9 MHz, 25°C): δ 6.1 ($C\mathrm{H_3Si}$), 21.9 ($(C\mathrm{H_3})_2\mathrm{CH}$), 22.9 ($(C\mathrm{H_3})_2\mathrm{CH}$), 29.5 ($\mathrm{N}C\mathrm{H_2}$), 49.7 ($\mathrm{NCH_2}C\mathrm{H_2}$,), 51.8 ($(\mathrm{CH_3})_2C\mathrm{H}$), 114.5 ($\mathrm{C_{ring}}$), 116.2 ($\mathrm{C_{ring}}$), 119.2 ($\mathrm{C_{ring}}$), 135.1 ($\mathrm{C_{ring}}$), 135.9 ($\mathrm{C_{ring}}$), 165.2 ($\mathrm{C_{ring}}$), 165.5 ($\mathrm{C_{ring}}$).-EI/MS (70 eV) m/z (%): 697 ($[\mathrm{M}]^+$, rel. int. 6), 537 ($[\mathrm{M-C_6H_{18}NSi_2}]^+$, 37), 146 ($[\mathrm{C_5H_{16}NSi_2}]^+$, 100). Anal. Calc. for $\mathrm{C_{29}H_{48}LuN_5Si_2}$ (697.87): C, 49.91; H, 6.93; N, 10.04. Found C, 48.99; H, 6.81; N, 10.01%.

3.1.3. *$[[(^i\mathrm{Pr})\mathrm{TP}]\mathrm{LuCH_2(SiMe_3)}]$ (**3**)*

A total 10 ml of toluene was condensed at −196°C onto a mixture of 200 mg (0.175 mmol) of **1** and 33 mg (0.35 mmol) $\mathrm{LiCH_2(SiMe_3)_2}$ and the suspension was stirred for 18 h at r.t. Then, the solution was filtered and concentrated. The remaining residue was washed with pentane (10 ml) and dried in vacuo. Yield 130 mg (60%). ^{1}H-NMR ($\mathrm{C_6D_6}$, 250 MHz, 25°C): δ −0.32 (s, 2 H, $\mathrm{LuC}H_2$), 0.22 (s, 9 H, $\mathrm{C}H_3\mathrm{Si}$), 1.34 (d, 6 H, $(\mathrm{C}H_3)_2\mathrm{CH}$, J(H,H) = 6.5 Hz), 1.35 (d, 6 H, $(\mathrm{C}H_3)_2\mathrm{CH}$, J(H,H) = 6.6 Hz), 3.02 (m, 2 H, $\mathrm{NCH_2C}H_2$), 3.36 (m, 4 H, $\mathrm{NC}H_2$), 3.93 (sept, 2 H, $(\mathrm{CH_3})_2\mathrm{C}H$, J(H,H) = 6.6 Hz), 6.31 (m, 4 H, $\mathrm{H_{ring}}$), 6.47 (m, 2 H, $\mathrm{H_{ring}}$), 6.93 (d, 4 H, $\mathrm{H_{ring}}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{C_6D_6}$, 62.9 MHz, 25°C): δ 5.2 ($C\mathrm{H_3Si}$), 23.4 ($(C\mathrm{H_3})_2\mathrm{CH}$), 23.5 ($(C\mathrm{H_3})_2\mathrm{CH}$), 30.8 ($\mathrm{N}C\mathrm{H_2}$), 41.8 ($\mathrm{Lu}C\mathrm{H_2}$), 50.0 ($\mathrm{NCH_2}C\mathrm{H_2}$,), 52.4 ($(\mathrm{CH_3})_2C\mathrm{H}$), 114.5 ($\mathrm{C_{ring}}$), 115.3 ($\mathrm{C_{ring}}$), 119.3 ($\mathrm{C_{ring}}$), 135.4 ($\mathrm{C_{ring}}$), 135.9 ($\mathrm{C_{ring}}$), 165.5 ($\mathrm{C_{ring}}$), 165.5 ($\mathrm{C_{ring}}$). Anal. Calc. for $\mathrm{C_{27}H_{34}LuN_4Si}$ (617.64): C, 52.51; H, 5.55; N, 9.07. Found C, 52.12; H, 4.99; N, 9.37%.

3.1.4. *$[[(^i\mathrm{Pr})\mathrm{TP}]\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5H_5})]$ (**4**)*

A total of 10 ml of THF was condensed at −196°C onto a mixture of 283 mg (0.25 mmol) of **1** and 44 mg (0.5 mmol) $\mathrm{Na(C_5H_5)}$ and the suspension was stirred for 18 h at r.t. Then, the solution was filtered and concentrated. The remaining residue was washed with pentane (10 ml) and dried in vacuo. Yield 250 mg (85%). IR (KBr $[\mathrm{cm^{-1}}]$): 2963 (m), 2924 (m), 1590 (s), 1507 (vs), 1426 (s), 1381 (s), 1270 (s), 1228 (m), 775 (m), 725 (m). ^{1}H-NMR ($\mathrm{C_6D_6}$, 250 MHz, 25°C): δ 1.33 (d, 6 H, $(\mathrm{C}H_3)_2\mathrm{CH}$, J(H,H) = 6.9 Hz), 1.52 (d, 6 H, $(\mathrm{C}H_3)_2\mathrm{CH}$, J(H,H) = 6.8 Hz), 2.94 (m, 2 H, $\mathrm{NCH_2C}H_2$), 3.20 (m, 4 H, $\mathrm{NC}H_2$), 4.07 (sept, 2 H, $(\mathrm{CH_3})_2\mathrm{C}H$, J(H,H) = 6.9 Hz), 6.32 (m, 2 H, $\mathrm{H_{ring}}$), 6.38 (s, 5 H, Cp), 6.80 (m, 4 H, $\mathrm{H_{ring}}$), 6.94 (m, 4 H, $\mathrm{H_{ring}}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{C_6D_6}$, 62.9 MHz, 25°C): δ 21.2 ($(C\mathrm{H_3})_2\mathrm{CH}$), 22.3 ($(C\mathrm{H_3})_2\mathrm{CH}$), 29.7 ($\mathrm{N}C\mathrm{H_2}$), 49.8 ($\mathrm{NCH_2}C\mathrm{H_2}$,), 52.6 ($(\mathrm{CH_3})_2C\mathrm{H}$), 111.4 (Cp), 113.7 ($\mathrm{C_{ring}}$), 116.5 ($\mathrm{C_{ring}}$), 118.2 ($\mathrm{C_{ring}}$), 134.1 ($\mathrm{C_{ring}}$), 135.3 ($\mathrm{C_{ring}}$), 165.7 ($\mathrm{C_{ring}}$), 166.2 ($\mathrm{C_{ring}}$).-EI/MS (70 eV) m/z (%): 602 ($[\mathrm{M}]^+$, rel. int. 11), 536 ($[\mathrm{M-C_5H_6}]^+$ 28), 364 ($[[(^i\mathrm{Pr})\mathrm{TP}]\mathrm{H_2}]^+$, 10), 202 ($[\mathrm{C_{13}H_{18}N_2}]^+$, 100). Anal. Calc. for $\mathrm{C_{28}H_{35}LuN_4}$ (602.58): C, 55.81; H, 5.85; N, 9.30. Found C, 55.61; H, 5.44; N, 8.89%.

3.1.5. *$[[(^i\mathrm{Pr})\mathrm{TP}]\mathrm{Lu}(\eta^3\text{-}\mathrm{BH_4})]$ (**5**)*

A total of 20 ml of THF was condensed at −196°C onto a mixture of 170 mg (0.15 mmol) of **1** and 11 mg (0.75 mmol) $\mathrm{NaBH_4}$ and the suspension was refluxed for 10 h. Then, the hot solution was filtered and concentrated. Finally, the product was crystallized from 1:3 THF–pentane. Yield 130 mg (79%). IR (KBr $[\mathrm{cm^{-1}}]$): 2963 (m), 2925 (m), 2293 (w) [ν B–H], 2225 (w) [ν B–H], 1590 (vs), 1510 (vs), 1466 (s), 1381 (m), 1270 (m), 721 (m). ^{1}H-NMR (d_8-THF, 250 MHz, 25°C): δ 0.87 (br, 1H, B–H), 1.49 (br, 3 H, B–H), 1.47 (d, 12 H, $(\mathrm{C}H_3)_2\mathrm{CH}$, J(H,H) = 6.7 Hz), 2.29 (br, 2 H, $\mathrm{NCH_2C}H_2$,

J(H,H) = 6.9 Hz), 3.58 (m, 4 H, NCH_2), 4.19 (sept, 2 H, $(CH_3)_2CH$, J(H,H) = 6.8 Hz), 6.13 (t, 2 H, H_{ring}, J(H,H) = 9.0 Hz), 6.59 (d, 4 H, H_{ring}), 6.92 (m, 4 H, H_{ring}). ^{11}B-NMR (d_8-THF, 96.3 MHz, 25°C): δ − 25.8 (qt, J(H,B) = 81.9 Hz). EI/MS (70 eV) m/z (%): 552 ($[M]^+$, rel. int. 1), 364 ($[[(^iPr)TP]H_2]^+$, 12), 319 ($[C_{20}H_{23}N_4]^+$, 27), 202 ($[C_{13}H_{18}N_2]^+$, 100). $C_{23}H_{34}BLuN_4$ (552.33): Anal. Calc. for C, 50.02; H, 6.20; N, 10.14. Found C, 49.72; H, 5.88; N, 9.92%.

3.1.6. X-ray crystallographic studies of **1**

Crystals of $C_{51}H_{72}Cl_2Lu_2N_8$ (**1**·pentane) were grown from a 3:1 pentane–THF 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 a STOE STADI IV diffractometer. Subsequent computations were carried out on a SGI Power Challenge.

Stoe-STADI 4 diffractometer (Mo–K_α radiation); $T = 203(3)$ K; data collection and refinement: SHELXS-86 [27], SHELXL-93 [28]; triclinic, space group $P\bar{1}$ (No. 2); lattice constants $a = 9.4458(4)$, $b = 11.3577(4)$, $c = 13.0877(6)$ Å, $\alpha = 66.329(4)$, $\beta = 73.257(4)$, $\gamma = 84.562(4)°$, $V = 1231.1(1)$ Å^3, $Z = 1$; $\mu(Mo{-}K_\alpha) = 4.138$ mm^{-1}; $\theta_{max} = 26.00$; 4822 independent reflections measured, of which 4553 were considered observed with $I > 2\sigma(I)$; max residual electron density 0.892 and − 0.700 e A^{-3}; 279 parameters (all non hydrogen atoms, except C24–C26 were calculated anisotropically; the positions of the H atoms were calculated for idealized positions) $R_1 = 0.0202$; $wR_2 = 0.0510$.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-139536. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://wwww.ccdc.cam.ac.uk).

5. Summary

In summary, by the reaction of $K_2[(^iPr)TP]$ and lutetium trichloride a chloro complex of composition $[[(^iPr)TP]LuCl]_2$ is obtained. By substitution of the chlorine atom alkyl, amide, η^5-cyclopentadienyl, and η^3-borohydride complexes respectively were obtained.

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