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Cyclooctatetraene complexes of yttrium and the lanthanides with chiral and achiral aminotroponiminates

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

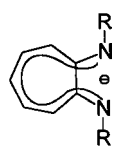
Abstract

The combination of dilithium-1,4-bis(trimethylsilyl)cyclooctatetraene, $Li_2\{1,4\text{-}(Me_3Si)_2C_8H_6\}$, with anhydrous yttrium or lutetium trichloride and potassium *N*-isopropyl-2-(isopropylamino)troponiminate, $K\{(^iPr)_2ATI\}$, leads to the corresponding mono cyclooctatetraene complexes $[\{\eta^8\text{-}1,4\text{-}(Me_3Si)_2C_8H_6\}Ln\{(^iPr)_2ATI\}(THF)]$ (Ln = Y (**1a**), Lu (**1b**)). The solid-state structure of **1a** was established by single-crystal X-ray diffraction. Using the same synthetic strategy, the chiral complex $[\{\eta^8\text{-}1,4\text{-}(Me_3Si)_2C_8H_6\}Y\{((S)\text{-}PhCHCH_3)_2ATI\}(THF)]$ (**2**) can be obtained by using the enantiomerically pure ligand, potassium *N*-(*S*)-1-phenylethyl-2-((*S*)-1-phenylethylamino)troponiminate, $K\{((S)\text{-}PhCHCH_3)_2ATI\}$. Furthermore, $[(\eta^8\text{-}C_8H_8)Sm\{(^iPr)_2ATI\}\text{-}(THF)]$ (**3**) was obtained by the reaction of $[(C_8H_8)SmI(THF)]$ and $K\{(^iPr)_2ATI\}$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aminotroponiminate; Cyclooctatetraene; Lanthanides; N ligands; Yttrium

1. Introduction

In the last 15 years, enormous progress has been observed in the design and application of organometallic compounds as α-olefin polymerization catalysts. The vast majority of the compounds investigated have been metallocenes and amido–cyclopentadienyl (constrained geometry) complexes of Group 4 metals. Since it is known that one class of catalysts cannot control all product parameters, there is considerable interest in finding a new generation of catalysts [1]. One synthetic approach for the design of the new catalysts is the incorporation of non-cyclopentadienyl ligands into the coordination sphere of the metal. Today, a number of research groups are investigating various main and transition metal complexes with bi- and multi-dentate amides and amidinates as ligands in the coordination sphere [1,2]. Amidinates are mono-anionic ligands that may formally be considered as a combination of an amido and an imido donor. The most prominent examples of this class are the benzamidinates, which form four-membered metallacycles [3,4], and aminotroponiminates, which can form five-membered metallacycles upon coordination to a metal atom [5]. Aminotroponiminates ($\{(R)_2ATI\}^-$) (**A**) are bidentate, monoanionic ligands containing a 10π-electron backbone. Owing to the presence of the highly delocalized π-electron system, the nearly planar $\{(R)_2ATI\}^-$ ligand framework shows minimal reactivity towards most nucleophiles and electrophiles. The advantage of using $\{(R)_2ATI\}^-$ compared with other amidinates is the facile introduction of enantiomerically pure substituents into the ligand [6,7].



A

The anion $\{(R)_2ATI\}^-$ has recently been introduced as a cyclopentadienyl alternative for Group 3 [8–10], Group 4 [11,12], and the lanthanide elements [8]. It was

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shown that, in lanthanide chemistry, $\{(R)_2ATI\}^-$ acts in a similar way to other well known systems, such as diazadienes, benzamidinates, and guanidinates [5]. Thus, the steric demand of the $\{(^iPr)_2ATI\}^-$ ligand in complexes such as $[\{(^iPr)_2ATI\}YCp'_2]$ ($Cp' = C_5Me_5$, $C_5H_3(SiMe_3)_2$) is somewhat similar to that of the cyclopentadienyl group [10]. Since cyclooctatetraene half-sandwich complexes of the lanthanides $[(C_8H_6R_2)Ln–R']$ ($R = H$, $SiMe_3$) are known, in which R' is cyclopentadienyl [13–15] or one of the already mentioned replacements such as diazadienes [16] or amidinates [17], it should also be possible to synthesize mono cyclooctatetraene–$\{(R)_2ATI\}^-$ complexes.

In this report mono cyclooctatetraene complexes of yttrium, samarium, and lutetium with chiral and achiral aminotroponiminates will be presented first, followed by a discussion of some structural aspects.

2. Results and discussion

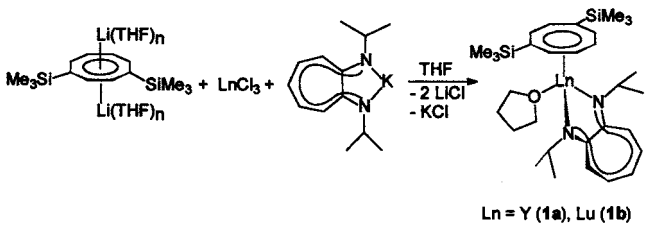
2.1. Ligand synthesis

The synthesis of the chiral ligand *N*-(*S*)-1-phenylethyl-2-((*S*)-1-phenylethylamino)troponimine, $H\{((S)\text{-}PhCHCH_3)_2ATI\}$, was reported for the first time by Brunner and Knott [6]. I report here on a modified synthesis of this ligand, which is shown in Scheme 1. Reaction of 2-(tosyloxy)tropone with (*S*)-1-phenylethylamine forms 2-(*N*-(*S*)-1-phenylethylamino)tropone in high yield. Further treatment of 2-(*N*-(*S*)-1-phenylethylamino)tropone with $Et_3O{\cdot}BF_4$ and (*S*)-1-phenylethylamine leads to the desired product, $H\{((S)\text{-}PhCHCH_3)_2ATI\}$, as an analytically pure yellow solid in 66% yield. $H\{((S)\text{-}PhCHCH_3)_2ATI\}$ was characterized by ^1H- and ^{13}C-NMR spectroscopy. Reaction of $H\{((S)PhCHCH_3)_2ATI\}$ with an excess of potassium hydride suspension in THF affords the potassium salt $K\{((S)\text{-}PhCHCH_3)_2ATI\}$ as a yellow, air-sensitive crystalline solid, which was characterized by ^1H- and ^{13}C-NMR spectroscopy. The NMR spectra indicate that the alkali metal cation of $K\{((S)\text{-}PhCHCH_3)_2ATI\}$ is coordinated by an average 0.25 equivalents of THF. In comparison with the neutral ligand, the ^1H- and ^{13}C-NMR signals of $K\{((S)\text{-}PhCHCH_3)_2ATI\}$ show only slight shifts. Thus the phenylethyl C*H* resonance (δ 4.65) is shifted only 0.12 ppm upfield upon metallation of the ligand.

The synthesis of the achiral potassium salt of *N*-isopropyl-2-(isopropylamino)troponimine, $K\{(^iPr)_2ATI\}$, which is obtained by treatment of the neutral ligand, $H\{(^iPr)_2ATI\}$, with an excess of KH in THF was reported previously [8].

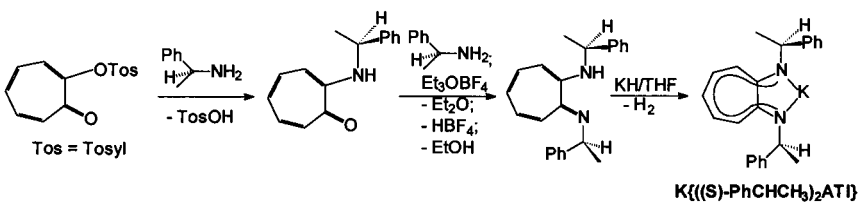
2.2. Metal complexes

Transmetallation of dilithium-1,4-bis(trimethylsilyl)cyclooctatetraene, $Li_2\{1,4\text{-}(Me_3Si)_2C_8H_6\}$, with anhydrous yttrium or lutetium trichloride in a 1:1 molar ratio in THF at room temperature followed by the addition of one equivalent of $K\{(^iPr)_2ATI\}$ to the reaction mixture afforded the corresponding mono cyclooctatetraene complexes $[\{\eta^8\text{-}1,4\text{-}(Me_3Si)_2C_8H_6\}Ln\{(^iPr)_2ATI\}(THF)]$ (Ln = Y (**1a**), Lu (**1b**)) as yellow crystals in good yields (1). The reagent $Li_2\{1,4\text{-}(Me_3Si)_2C_8H_6\}$ was prepared by in situ lithiation of 1,4-bis(trimethylsilyl)cycloocta-2,5,7-triene in THF solution [18,19].



(1)

The new complexes have been characterized by standard analytical/spectroscopic techniques. The ^1H- and ^{13}C-NMR spectra point to a symmetrical coordination of the $\{(^iPr)_2ATI\}^-$ ligand in solution. The signals of the isopropyl C*H* of **1a**,**b** are well resolved into a septet. Their chemical shifts (δ 3.56 (**1a**), 3.69 (**1b**)) are in the range of the free ligand $\{(^iPr)_2ATI\}H$ (δ 3.60) [20]. This is in contrast to other $\{(^iPr)_2ATI\}Y$ complexes, in which the signal of the isopropyl C*H* group shows usually a marked downfield shift (δ 4.15 $[\{(^iPr)_2ATI\}_3Y]$ [8], 4.17 $[\{(^iPr)_2ATI\}_2Y\text{–}O(2,6\text{-}{}^tBu_2C_6H_3)]$ [8], 3.82 $[\{(^iPr)_2ATI\}Y(C_5Me_5)_2]$ [10]). Obviously, the chemical shift of this group depends significantly on the nature of the other substituents attached to the lanthanide atom. Thus, electron-rich substituents such as C_5Me_5, and especially



Scheme 1.

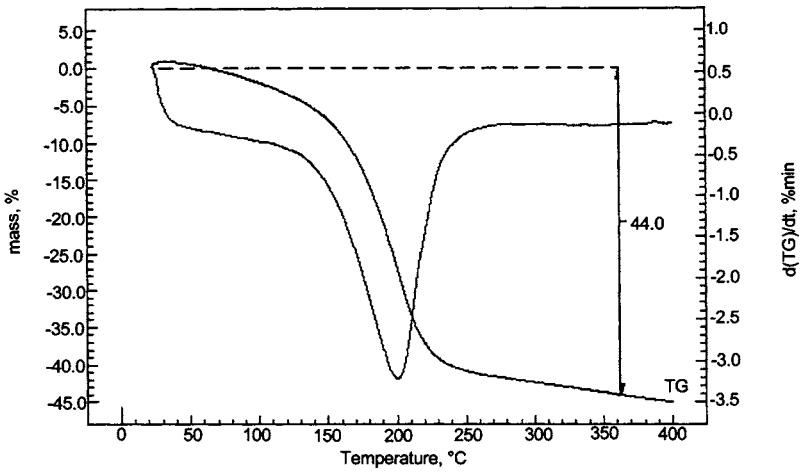
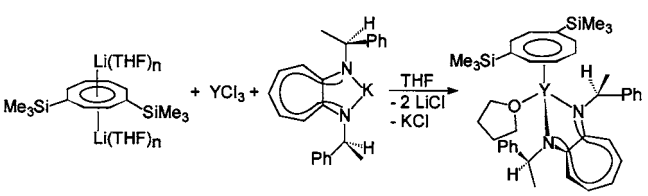


Fig. 1. TGA and differential TGA curve of **1a**.

$(Me_3Si)_2C_8H_6$, lead to an upfield shift of the signal of the isopropyl C*H* group. Since the ^{1}H- and ^{13}C-NMR spectra were recorded in C_6D_6, the coordinated THF molecule in **1a**,**b** is easy to identify. In contrast to non-coordinated THF, a significant upfield shift of the signals in the ^{1}H-NMR spectra is observed (**1a**: δ 0.97, 3.05; **1b**: δ 0.93, 3.12). For **1a**, ^{89}Y-NMR spectra were recorded in THF-d_8 (δ 65.4) and C_6D_6 (δ 59.7). The difference in the chemical shift in dependence of the solvent is not surprising. Whereas in THF-d_8 an exchange between the coordinated THF molecule of **1a** and the solvent can be assumed, it is unlikely that a similar process will take place in benzene. The ^{89}Y-NMR chemical shifts observed for **1a** are in the range of comparable mono cyclooctatetraene benzamidinate complexes (δ(THF-d_8) 62.4 [(η^8-C_8H_8)Y{*p*-$MeOC_6H_4$-$C(NSiMe_3)_2$}(THF)] [17], δ(THF-d_8) 61.8 [(η^8-C_8H_8)Y{*p*-$CF_3C_6H_4C(NSiMe_3)_2$}(THF)] [17]).

Compounds **1a**,**b** were also characterized by electron impact mass spectroscopy (EI-MS). For both compounds, molecular ions without coordinated THF and their characteristic fragmentation patterns were observed. To obtain a better understanding of the fragmentation, thermogravimetric analysis (TGA) of **1a** was performed. Loss of the coordinated solvent first, followed by loss of the $\{(^i Pr)_2ATI\}^-$ ligand is confirmed in TGA. One peak was observed at 200°C for **1a** in the TGA (Fig. 1). The predominant decomposition products are THF and $\{(^i Pr)_2ATI\}^-$. The TGA onset is ill defined. The weight of the residue suggests the fragment of $\{\eta^8$-1,4-$(Me_3Si)_2C_8H_6\}Y$ as the final product.

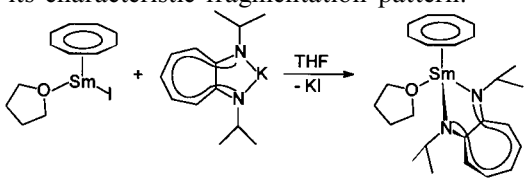
Similar to the preparation of **1a**,**b**, the chiral complex [$\{\eta^8$-1,4-$(Me_3Si)_2C_8H_6\}Y\{((S)$-$PhCHCH_3)_2ATI\}$(THF)] (**2**) can be obtained by using $Li_2\{1,4$-$(Me_3Si)_2C_8H_6\}$, anhydrous yttrium trichloride, and $K\{((S)$-$PhCHCH_3)_2ATI\}$ in a 1:1:1 molar ratio in THF at room temperature (2). Complex **2** was characterized by EI-MS, ^{1}H-, ^{13}C-, ^{29}Si-, and ^{89}Y-NMR spectroscopy and elemental analysis. Owing to the lack of a mirror plane, which is observed in **1a**,**b**, all atoms of the ring cyclooctatetraene ligand of **2** are non-equivalent in the NMR spectrum. Thus, two signals for the trimethylsilyl groups are observed in the ^{1}H- and ^{13}C-NMR spectra (δ (^{1}H): 0.42, 0.44; δ (^{13}C): 1.9, 1.9). Of the expected eight signals for the eight-membered ring in the ^{13}C-NMR spectrum only seven are observed, since two signals coincide. The ^{1}H-NMR signal of the phenylethyl C*H* group of **2** is well resolved into a quartet, but it shows a marked downfield shift (δ 5.14) compared with the free ligand $H\{((S)$-$PhCHCH_3)_2ATI\}$ (δ 4.65). This is in contrast to **1a**,**b**, where almost no change in the isopropyl C*H* chemical shift is observed upon coordination of the ligand to the yttrium atom. Since **2** is the first lanthanide complex having the enantiomerically pure $\{((S)$-$PhCHCH_3)_2ATI\}^-$ ligand in the coordination sphere, no comparable NMR data are available. As seen for **1a**,**b**, one coordinated THF molecule is easily identifiable in the ^{1}H-NMR spectrum of **2** (δ 0.91, 3.34). The ^{89}Y-NMR chemical shift of **2** in THF-d_8 (δ 66.7) is close to that of **1a** (δ(THF-d_8) 65.4). Compound **2** was also characterized by EI-MS. In the mass spectrum, the molecular ion without coordinated THF and its characteristic fragmentation pattern were observed.



(2)

To extend the concept of mixed aminotroponiminate cyclooctatetraene complexes, [(C_8H_8)SmI(THF)] [21] was reacted with $K\{(^i Pr)_2ATI\}$ in THF at room tem-

perature to yield $[(\eta^8\text{-}C_8H_8)Sm\{(^iPr)_2ATI\}(THF)]$ (**3**) as a red powder (3). Complex **3** was characterized by EI-MS, ^{1}H- and ^{13}C-NMR spectroscopy and elemental analysis. Owing to the paramagnetic influence of the samarium atom, the signals in the ^{1}H-NMR spectrum are shifted over a wide range. Thus, the signal of the cyclooctatetraene protons is detected at δ 9.33 as a singlet; the resonance of the isopropyl CH_3 is found at δ −1.69. The range of the signals is not unusual. In $[Li(THF)_3\{\mu\text{-}(\eta^2{:}\eta^8\text{-}C_8H_8)\}Sm(C_8H_8)]$ the signal of the cyclooctatetraene ring is observed in the ^{1}H-NMR spectrum at δ 13.2 [22], and in $[(C_8H_8)Sm(hmpa)_3]$-$[(C_8H_8)_2Sm]$ at δ 13.5 [23]. In $[\{(^iPr)_2ATI\}_3Sm]$ the signal of isopropyl CH_3 is found as a broad peak in the range of δ −3.3 to −1.5 [8]. The EI mass spectrum of **3** shows the molecular ion without coordinated THF and its characteristic fragmentation pattern.



(3)

3

2.3. Molecular structure of $[\{\eta^8\text{-}1,4\text{-}(Me_3Si)_2C_8H_6\}Y\{(^iPr)_2ATI\}(THF)]$ (**1a**)

By recrystallizing **1a** from benzene, single crystals were obtained. The solid-state structure was established by single-crystal X-ray diffraction (Fig. 2). Compound **1a** crystallizes in the monoclinic space group $P2_1/c$, having four molecules in the unit cell. The structure shows the expected η^8-coordination of the cyclooctatetraene ligand. The planar η^8-ring shows no significant distortion within the carbon framework (average C–C bond distances 140.9 pm). The Y–C_{ring} distances are in the range between 256.3(5) and 267.9(6) pm (average 262.3 pm) with a Y–ring centroid distance of 186(3) pm. These data are in good agreement with $[\{\eta^8\text{-}C_8H_8\}Y(\mu\text{-}OPh)(THF)]_2$ (Y–C_{ring} 259.5(11)–262.5(10) pm; Y–ring centroid 184.6(9) pm) [24]. Slightly shorter bond distances are observed in $[\{\eta^8\text{-}C_8H_8\}Y(\eta^5\text{-}C_5H_4CH_3)(THF)]$ (Y–C_{ring} 250.4(10)–263.3(10) pm; Y–ring centroid 181.8(8) pm) [14]. The longer bond distances in **1a** might be caused by the steric influence of the trimethylsilyl groups, which are disordered in the structure. One $MeSi_3$ group is located directly above the seven-membered ring of the $\{(^iPr)_2ATI\}^-$ ligand; thus, in the solid state the trimethylsilyl and the isopropyl groups are in a kind of staggered conformation to each other. The $\{(^iPr)_2ATI\}^-$ group is almost symmetrically attached to the metal center (Y–N1 239.2(5) pm; Y–N2 235.5(5) pm). A similar symmetric coordination mode is observed in $[\{(^iPr)_2ATI\}Y(C_5Me_5)_2]$ (N–Y 239.8(2) and 239.0(3) pm) [10]. On the other hand, in $[\{(^iPr)_2ATI\}YCl_2(THF)_2]_2$ a significant difference in the Y–N bonds is observed (N–Y 233.1(5) and 243.0(5) pm) [8]. The seven-membered ring of the $\{(^iPr)_2ATI\}^-$ group in **1a** is slightly disordered.

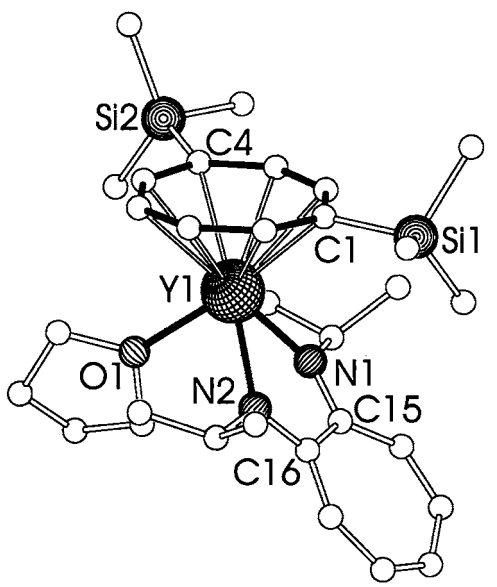


Fig. 2. Perspective SCHAKAL view of the molecular structure of **1a**. Selected bond lengths (pm): C1–Si1, 187.9(6); C4–Si2, 189.0(6); C1–Y1, 261.9(6); C2–Y1, 256.3(5); C3–Y1, 260.2(5); C4–Y1, 267.9(6); C5–Y1, 264.6(6); C6–Y1, 263.5(6); C7–Y1, 262.1(6); Y1–N1, 239.2(5); Y1–N2, 235.5(5); Y1–O1, 240.2(4). Selected bond angles (°): N1–Y1–N2, 67.3(2); N1–Y1–O1, 86.13(15); N2–Y1–O1, 82.6(2); N1–Y1–C1, 103.0(2); N2–Y1–C1, 100.4(2); O1–Y1–C1, 170.90(15); N1–Y1–C2, 91.0(2); N2–Y1–C2, 123.1(2); O1–Y1–C2, 150.6(2).

3. Conclusions

As seen from spectroscopic and X-ray data, the new compounds **1a**,**b**, and **2** fit well into the series of compounds $[\{\eta^8\text{-}C_8H_8\}Y(L)(THF)]$ in which L is a cyclopentadienyl ligand [14,15] or one of its replacements, such as benzamidinates (e.g. $\{p\text{-}MeOC_6H_4C(NSiMe_3)_2\}^-$ [17], $\{p\text{-}CF_3C_6H_4C(NSiMe_3)_2\}^-$ [17], $\{Ph_2P(NSiMe_3)_2\}^-$ [17]). Thus, the steric demands of the $\{(^iPr)_2ATI\}^-$ and the $\{((S)\text{-}PhCHCH_3)_2ATI\}^-$ ligands are comparable to those of cyclopentadienyl groups. By using the $\{((S)\text{-}PhCHCH_3)_2ATI\}^-$ ligand, the first complex of the early transition metals having an enantiomerically pure aminotroponiminate in the coordination sphere has been prepared.

4. Experimental

4.1. 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 interface 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 vacuum over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Aldrich Inc. (all 99 at.% D) and were degassed, dried, and stored in vacuum 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. ^{89}Y-NMR shifts are reported versus 3 M YCl_3 in D_2O. Mass spectra were recorded at 70 eV on Varian MAT 711. TGA was performed under N_2 at a scan rate of 10°C min^{-1} using an STA 409 Netsch system. Elemental analyses were performed at the microanalytical laboratory of the Institute of Inorganic Chemistry at Karlsruhe. YCl_3 [25], $SmCl_3$ [25], $LuCl_3$ [25], 1,4-$(Me_3Si)_2C_8H_8$ [18], 2-(tosyloxy)tropone [26], [(C_8H_8)SmI(THF)] [21], and K{(^{i}Pr)$_2$ATI} [8] were prepared according to literature procedures.

4.2. 2-(N-(S)-1-Phenylethylamino)tropone

Finely powdered 2-(tosyloxy)tropone (5.0 g, 18 mmol) was slowly added at 0°C to 20 ml of (*S*)-1-phenylethylamine. After the addition, the resulting solution was allowed to stir for 4 h at 0°C and then overnight at room temperature (r.t.). During this period, the solid slowly dissolved in the amine solution. The excess (*S*)-1-phenylethylamine was then evaporated in vacuum, and the resulting yellow residue was extracted with toluene (50 ml) and filtered through Celite. Removal of the solvent yielded 2-(*N*-(*S*)-1-phenylethylamino)tropone as a yellow solid. Yield 3.80 g (95%). ^{1}H-NMR ($CDCl_3$, 250 MHz, 25°C): δ 1.65 (d, 3H, CH_3CH, J(H,H) = 6.8 Hz), 4.67 (q, 1H, (CH_3CH, J(H,H) = 6.9 Hz), 6.34 (d, 2H, $H_{3,7}$, J(H,H) = 10.4 Hz) 6.63 (dd, 2H, $H_{4,6}$), 7.04 (t, 1H, H_5, J(H,H) = 9.9 Hz), 7.18–7.38 (m, 5H, phenyl H). ^{13}C{^{1}H}-NMR ($CDCl_3$, 62.9 MHz, 25°C): δ 24.6 (CH_3CH), 53.1 (CH_3CH), 110.7, 122.7, 125.8, 127.6, 128.6, 129.1, 136.3, 137.3 142.7, 154.6, 177.2.

4.3. H{((S)-PhCHCH$_3$)$_2$ATI}

A CH_2Cl_2 solution (20 ml) of $Et_3O{\cdot}BF_4$ (3.40 g; 17.0 mmol) was slowly added to a CH_2Cl_2 solution (20 ml) of 3.80 g (17.0 mmol) of 2-(*N*-(*S*)-1-phenylethylamino)tropone under nitrogen. While stirring for 3 h at r.t. the solution slowly turned brown–yellow. Then, 10 ml of (*S*)-1-phenylethylamine was added to the solution. Immediately, the color of the solution became yellow and then slowly turned red. The resulting mixture was stirred overnight, and then the volatiles were removed under vacuum. The residue was extracted with pentane, filtered through Celite, and concentrated under vacuum to give H{((*S*)-PhCHCH$_3$)$_2$ATI} as a yellow solid. Yield 3.90 g (66%). ^{1}H-NMR ($CDCl_3$, 250 MHz, 25°C): δ 1.60 (d, 6H, CH_3CH, J(H,H) = 6.6 Hz), 4.77 (q, 2H, CH_3CH, J(H,H) = 6.6 Hz), 6.06 (t, 1H, H_5, J(H,H) = 8.7 Hz), 6.23 (d, 2H, $H_{3,7}$, J(H,H) = 11.0 Hz) 6.62 (dd, 2H, $H_{4,6}$), 7.20–7.41 (m, 10H, phenyl H). ^{13}C{^{1}H}-NMR ($CDCl_3$, 62.9 MHz, 25°C): δ 25.1 (CH_3CH), 55.3 (CH_3CH), 112.2 (C_5), 119.0 ($C_{3,7}$), 126.3 (phenyl C), 127.0 (phenyl C), 128.7 (phenyl C), 133.6 ($C_{4,6}$), 145.0 (phenyl C), 152.0 ($C_{1,2}$).

4.4. K{((S)-PhCHCH$_3$)$_2$ATI}·(0.25THF)

To a suspension of 944 mg (23.0 mmol) KH in THF, 3.90 g (11.8 mmol) of H{((*S*)-PhCHCH$_3$)$_2$ATI} dissolved in 40 ml of THF was slowly added at r.t. The mixture was stirred for 16 h. Then, the unreacted KH was filtered off and the filtrate was concentrated in vacuum. The remaining yellow residue was washed with pentane (3 × 30 ml) and dried in vacuum. Yield 3.80 g (66%). ^{1}H-NMR (THF-d_8, 250 MHz, 25°C): δ 1.31 (d, 6H, CH_3CH, J(H,H) = 6.5 Hz), 1.40 (br, THF), 3.50 (m, THF), 4.65 (q, 2H, CH_3CH), 5.66 (t, 1H, H_5, J(H,H) = 8.8 Hz), 5.88 (d, 2H, $H_{3,7}$, J(H,H) = 11.6 Hz) 6.60 (dd, 2H, $H_{4,6}$), 6.99–7.32 (m, 10H, phenyl H). ^{13}C{^{1}H}-NMR (THF-d_8, 62.9 MHz, 25°C): δ 24.3 (CH_3CH), 26.5 (THF), 59.2 (CH_3CH), 68.6 (THF), 107.0 (C_5), 107.3 ($C_{3,7}$), 127.5 (phenyl C), 127.9 (phenyl C), 129.2 (phenyl C), 133.2 ($C_{4,6}$), 149.2 (phenyl C), 163.2 ($C_{1,2}$).

4.5. Preparation of [{η^8-1,4-(Me$_3$Si)$_2$C$_8$H$_6$}Ln{(^{i}Pr)$_2$ATI}(THF)] (1)

To a stirred solution of 250 mg (1 mmol) of 1,4-$(Me_3Si)_2C_8H_8$ in 40 ml of THF at −78°C was slowly added 1.25 ml (2 mmol) of a 1.6 M solution of ^{n}BuLi in hexane. The solution was allowed to warm to r.t. with stirring for another 16 h; during this time the color of the solution changed from yellow to green–brown. The solvent was removed in vacuum and the oily residue was dissolved in 10 ml of pentane. The pentane was also removed in vacuum and 1.0 mmol of solid $LnCl_3$ was added to the remaining residue. Then, 10 ml of THF was condensed at −196°C onto the mixture and the suspension was stirred for 2 h at r.t. The solvent was then evaporated in vacuum and 240 mg (1.0 mmol) of solid K{(^{i}Pr)$_2$ATI} was added to the remaining solid. Again, 10 ml of THF was condensed at −196°C onto the mixture and the suspension was stirred for 18 h at r.t. The solvent was then evaporated in vacuum 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 vacuum.

Ln = Y (**1a**). Yield 420 mg (69%). ^{1}H-NMR (C_6D_6, 250 MHz, 25°C): δ 0.46 (s, 18H, $SiMe_3$), 0.97 (br, 4H, THF), 1.34 (d, 12H, $(CH_3)_2CH$, J(H,H) = 6.6 Hz), 3.05 (br, 4H, THF), 3.56 (sept, 2H, $(CH_3)_2CH$, J(H,H) = 6.6 Hz), 6.20 (t, 1H, H_5, J(H,H) = 9.9 Hz), 6.42 (d, 2H, $H_{3,7}$, J(H,H) = 11.6 Hz), 6.82 (m, 6H, $H_{4,6}$, ring H), 7.03 (s, 2H, ring H). ^{13}C{^{1}H}-NMR (C_6D_6, 62.9 MHz, 25°C): δ 2.3 ($SiMe_3$), 22.8 ($(CH_3)_2CH$), 25.7 (THF), 50.6 ($(CH_3)_2CH$), 70.8 (THF), 97.2 (ring C), 99.1 (ring C), 100.8 (ring C), 102.5 (ring C), 114.1 (C_5), 117.9 ($C_{3,7}$), 134.5 ($C_{4,6}$), 164.7 ($C_{1,2}$). ^{29}Si-NMR (C_6D_6, 49.7 MHz, 25°C): δ 4.3. ^{89}Y-NMR (C_6D_6, 14.7 MHz, 25°C): δ 59.7. ^{89}Y-NMR (THF-d_8, 14.7 MHz, 25°C): δ 65.4. EI-MS (70 eV) m/z (%): 540 ([M − THF]$^+$, rel. int. 4), 496 ([M − ^{i}Pr − THF]$^+$, 9), 467 ([M − $SiMe_3$ − THF]$^+$, 4), 250 ([$C_{14}H_{26}Si_2$]$^+$, 13), 204 ([$C_{13}H_{20}N_2$]$^+$, 87), 73 ([$SiMe_3$]$^+$, 100). Anal. Found: C, 59.49; H, 8.50; N, 5.07. Calc. for $C_{31}H_{51}N_2OSi_2Y$ (612.83): C, 60.67; H, 8.39; N, 4.57%.

Ln = Lu (**1b**). Yield 455 mg (65%). ^{1}H-NMR (C_6D_6, 250 MHz, 25°C): δ 0.47 (s, 18H, $SiMe_3$), 0.93 (br, 4H, THF), 1.34 (d, 12H, $(CH_3)_2CH$, J(H,H) = 6.7 Hz), 3.12 (br, 4H, THF), 3.69 (sept, 2H, $(CH_3)_2CH$, J(H,H) = 6.7 Hz), 6.20 (t, 1H, H_5, J(H,H) = 9.0 Hz), 6.47 (d, 2H, $H_{3,7}$, J(H,H) = 11.7 Hz), 6.79 (m, 6H, $H_{4,6}$, ring H), 6.99 (s, 2H, ring H). ^{13}C{^{1}H}-NMR (C_6D_6, 62.9 MHz, 25°C): δ 2.2 ($SiMe_3$), 22.6 ($(CH_3)_2CH$), 25.8 (THF), 51.1 ($(CH_3)_2CH$), 71.2 (THF), 96.0 (ring C), 97.2 (ring C), 100.1 (ring C), 101.4 (ring C), 115.2 (C_5), 118.3 ($C_{3,7}$), 134.2 ($C_{4,6}$), 165.0 ($C_{1,2}$). ^{29}Si-NMR (C_6D_6, 49.7 MHz, 25°C): δ 4.2. EI-MS (70 eV) m/z (%): 626 ([M − THF]$^+$, rel. int. 76), 553 ([M − $SiMe_3$ − THF]$^+$, 47), 250 ([$C_{14}H_{26}Si_2$]$^+$, 5), 204 ([$C_{13}H_{20}N_2$]$^+$, 62), 73 ([$SiMe_3$]$^+$, 100). Anal. Found: C, 52.89; H, 7.50; N, 3.10. Calc. for $C_{31}H_{51}LuN_2OSi_2$ (698.90): C, 53.28; H, 7.36; N, 4.01%.

4.6. [{η^8-1,4-(Me_3Si)$_2$$C_8H_6$}Y{((S)-PhCHCH$_3$)$_2$-ATI}(THF)] (2)

To a stirred solution of 250 mg (1 mmol) of 1,4-$(Me_3Si)_2C_8H_8$ in 40 ml of THF at −78°C was slowly added 1.25 ml (2 mmol) of a 1.6 M solution of ^{n}BuLi in hexane. The solution was allowed to warm to r.t. with stirring for another 16 h, during which time the color of the solution changed from yellow to green–brown. The solvent was removed in vacuum and the oily residue was dissolved in 10 ml of pentane. The pentane was also removed in vacuum and 195 mg (1.0 mmol) of solid YCl_3 was added to the remaining residue. Then, 10 ml of THF was condensed at −196°C onto the mixture and the suspension was stirred for 2 h at r.t. The solvent was then evaporated in vacuum and 384 mg (1.0 mmol) of solid K{((S)-PhCHCH$_3$)$_2$ATI}·(0.25THF) was added to the remaining solid. Again, 10 ml of THF was condensed at −196°C onto the mixture and the suspension was stirred for 18 h at r.t. The solvent was then evaporated in vacuum 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 vacuum. Yield 420 mg (69%). ^{1}H-NMR (C_6D_6, 250 MHz, 25°C): δ 0.42 (s, 9H, $SiMe_3$), 0.44 (s, 9H, $SiMe_3$), 0.91 (br, 4H, THF), 1.68 (d, 6H, CH_3CH, J(H,H) = 6.9 Hz), 3.34 (br, 4H, THF), 5.14 (q, 2H, CH_3CH), 5.90 (t, 1H, H_5, J(H,H) = 11.6 Hz), 6.35 (m, 4H, $H_{3,7}$, $H_{4,6}$), 6.76 (m, 8H, ring H, phenyl H), 6.88 (s, 2H, ring H), 7.04–7.35 (m, 6H, phenyl H). ^{13}C{^{1}H}-NMR (C_6D_6, 62.9 MHz, 25°C): δ 1.9 ($SiMe_3$), 1.9 ($SiMe_3$), 21.9 (CH_3CH), 26.0 (THF), 57.5 (CH_3CH), 70.9 (THF), 98.5 (ring C), 98.8 (ring C), 100.5 (ring C), 100.8 (ring C), 101.0 (ring C), 101.7 (ring C), 102.4 (ring C), 118.1 (C_5), 119.3 ($C_{3,7}$), 127.4 (phenyl C), 127.5 (phenyl C), 129.6 (phenyl C), 134.0 ($C_{4,6}$), 144.5 (phenyl C), 165.0 ($C_{1,2}$). ^{29}Si-NMR (C_6D_6, 49.7 MHz, 25°C): δ 4.1. ^{89}Y-NMR (THF-d_8, 14.7 MHz, 25°C): δ 66.7. EI-MS (70 eV) m/z (%): 664 ([M − THF]$^+$, rel. int. 5), 416 ([M − $(Me_3Si)_2C_8H_6$ − THF]$^+$, 9), 328 ([$C_{23}H_{24}N_2$]$^+$, 87), 223 ([$C_{15}H_{15}N_2$]$^+$, 100). Anal. Found: C, 66.78; H, 6.57; N, 3.79. Calc. for $C_{41}H_{55}N_2OSi_2Y$ (736.98): C, 66.82; H, 7.52; N, 3.80%.

4.7. [(η^8-C_8H_8)Sm{(^{i}Pr)$_2$ATI}(THF)] (3)

10 ml of THF was condensed at −196°C onto a mixture of 225 mg (0.5 mmol) of [(C_8H_8)SmI(THF)] and 120 mg (0.5 mmol) of K{(^{i}Pr)$_2$ATI} and the mixture was stirred for 18 h at r.t. The solvent was then evaporated in vacuum 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 vacuum. Finally, the product was crystallized from pentane/THF (3:1). Yield 205 mg (40%). ^{1}H-NMR (C_6D_6, 250 MHz, 25°C): δ −1.69 (d, 12H, $(CH_3)_2CH$, J(H,H) = 6.4 Hz), 0.88 (br, 2H, $(CH_3)_2CH$, J(H,H) = 6.7 Hz), 1.77 (br, 4H, THF), 3.61 (br, 4H, THF), 7.11 (m, 2H), 7.96 (m, 3H), 9.33 (s, 8H, ring H). ^{13}C{^{1}H}-NMR (C_6D_6, 62.9 MHz, 25°C): δ 20.5 ($(CH_3)_2CH$), 26.2 (THF), 53.7 ($(CH_3)_2CH$), 66.9 (THF), 83.3 (ring C), 116.4 (C_5), 115.0 ($C_{3,7}$), 136.7 ($C_{4,6}$), 177.5 ($C_{1,2}$). EI-MS (70 eV) m/z (%): 459 ([M − THF]$^+$, rel. int. 12), 355 ([M − C_8H_8 − THF]$^+$, 55), 204 ([$C_{13}H_{20}N_2$]$^+$, 98), 189 ([$C_{12}H_{17}N_2$]$^+$, 100). Anal. Found: C, 54.99; H, 5.80; N, 5.30. Calc. for $C_{25}H_{35}N_2OSm$ (529.92): C, 56.66; H, 6.66; N, 5.29%.

4.8. X-ray crystallographic studies of 1a

Crystals of $C_{31}H_{51}N_2OSi_2Y$ were grown from a benzene 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 a STOE IPDS diffractometer. Subsequent computations were carried out on an Intel Pentium III Personal Computer.

Stoe-IPDS diffractometer (Mo–K_α radiation); $T = 200(3)$ K; data collection and refinement: SHELXS-97 [27], SHELXL-97 [28]; monoclinic, space group $P2_1/c$ (no. 14); lattice constants $a = 1248.3(8)$, $b = 1680.2(5)$, $c = 1619.9(5)$ pm, $\beta = 90.74(6)°$, $V = 3397(3) \times 10^6$ pm^3, $Z = 4$; $\mu(\text{Mo–K}_\alpha) = 1.811$ mm^{-1}; $\theta_{max} = 25.00$; 5789 ($R_{int} = 0.0852$) independent reflections measured, of which 3558 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.485 and −0.718 e$^-$ A^{-3}; 338 parameters (all non-hydrogen atoms, except C9–C14, C17–C21, and C29 were calculated anisotropically; the positions of the H atoms were calculated for idealized positions) $R_1 = 0.0627$; $wR_2 = 0.1670$.

5. Supplementary material

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. CCDC 147578. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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