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Synthesis, structure and reactivity of *tert*-butyldimethylsilylcyclopentadienyl lanthanide chlorides, including crystal structures of $[(C_5H_4SiMe_2Bu^t)_2Gd(\mu\text{-}Cl)]_2$ and $(C_5H_4SiMe_2Bu^t)_2Er(SBT)(THF)$

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Abstract

Reactions of anhydrous lanthanide trichloride with one or two equivalent of *tert*-butyldimethylsilylcyclopentadienyl (Cp^t) potassium salt in THF afford mono(*tert*-butyldimethylsilylcyclopentadienyl)lanthanide dichloride complexes $Cp^tLnCl_2(THF)_3$ [Ln = Y(**1**), Er(**2**)] and bis(*tert*-butyldimethylsilylcyclopentadienyl)lanthanide chlorides $[Cp^t_2Ln(\mu\text{-}Cl)]_2$ [Ln = Gd(**3**), Er(**4**), Yb(**5**)], respectively. $DyCl_3$ reacts with KCp^t in THF, followed by the treatment with two equivalents of C_5H_5Na to form the mixed-ring complex $Cp^tCp_2Dy(THF)$ (**6**). Reaction of **4** with $LiNPr^i_2$ and subsequently with one equivalent of PhNCO in THF give the PhNCO insertion product $Cp^t_2Er[OC(NPr^i_2)NPh](THF)$ (**7**). Complex **4** reacts with one equivalent of sodium benzothiazole-2-thiolate (NaSBT) to yield $Cp^t_2Er(SBT)(THF)$ (**8**). Complexes **1**–**8** have been characterized by elemental analyses, infrared, ^{1}H-NMR and mass spectroscopies. The molecular structures of **3** and **8** were determined by single crystal X-ray diffraction. © 2002 Published by Elsevier Science B.V.

Keywords: Organolanthanide; Substituted cyclopentadienyl; Crystal structures; Insertion

1. Introduction

Substituted cyclopentadienyl lanthanide complexes continue to attract considerable attention, since they differ greatly in reactivities, structures and physical properties from the unsubstituted counterparts [1–3]. The effectiveness of such ligands arises from a combination of steric and electronic factors with the former often predominant. The advantages of replacement of one or more cyclopentadienyl ring hydrogens by the bulky substituents are to result in significant changes in both steric and electronic effects at the metal center as well as to enhance the stabilization and solubility in nonpolar solvents of their metal complexes. Recently, Schumann and Lappert synthesized some lanthanide metallocene complexes containing *tert*-butyldimethylsilylcyclopentadienyl ligands, such as $[(C_5H_4SiMe_2Bu^t)_2Ln(\mu\text{-}Cl)]_2$, $[(C_5H_4SiMe_2Bu^t)_2Y(\mu\text{-}Me)]_2$ (Ln = Y, Sm, Lu) [4], $(C_5H_4SiMe_2Bu^t)_3Nd$ [5], K([18]-crown-6)(η^2-PhMe)$_2$(μ-H)$(Ln(C_5H_4SiMe_2Bu^t)_3)_2$ (Ln = La, Ce) [6], $(C_5H_4SiMe_2Bu^t)_2Yb$ [7], etc, showing that the steric bulk exerted by the $SiMe_2Bu^t$ group exhibits an important effect on stability, solubility and crystallinity of these complexes. Continuing our recent investigations of systems on reactivities of organolanthanide complexes [3,8–13], and to learn more about the *tert*-butyldimethylsilylcyclopentadienyl group as a ligand, we report here the synthesis and reactivity of some new Bu^tMe_2Si-substi-

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tuted cyclopentadienyl lanthanide derivatives, including the X-ray structures of $[(C_5H_4SiMe_2Bu^t)_2Gd(\mu\text{-}Cl)]_2$ and $(C_5H_4SiMe_2Bu^t)_2Er(SBT)(THF)$.

2. Results and discussion

2.1. Synthesis of $Cp^tLnCl_2(THF)_3$ (Ln = Y, Er)

Treatment of $LnCl_3$ with one equivalent of KCp^t (Cp^t = *tert*-butyldimethylsilylcyclopentadienyl) in THF results in the formation of monocyclopentadienyl lanthanide complexes $Cp^tLnCl_2(THF)_3$ [Ln = Y(**1**), Er(**2**)], which have not been accessible in the past (Eq. (1)).

$$LnCl_3 + Cp^tK \overset{THF}{\rightarrow} Cp^tLnCl_2(THF)_3 + KCl \qquad (1)$$
$$Ln = Y(\mathbf{1}),\ Er(\mathbf{2})$$

Complexes **1** and **2** were characterized by elemental analysis, IR and mass spectroscopies. The diamagnetic compound **1** was additionally identified by ^1H-NMR spectroscopy. The IR spectra of complexes **1** and **2** show characteristic absorptions of the η^5-Cp^t group at about 3085, 1460, 1007 and 764 cm^{-1} and coordinated THF molecules near 910 and 1070 cm^{-1}. The EIMS spectra of **1** and **2** revealed them to be monomeric, the molecular ions $[M]^+$ being of relatively low intensity. Both of monocyclopentadienyl lanthanide chlorides showed the typical fragments $[M-Cl]^+$, $[M-THF]^+$, $[M-THF-Cl]^+$, $[M-THF-Bu^t]$, $[M-3THF]^+$, $[M-3THF-Cl]^+$, $[Cp^t]^+$ and $[THF]^+$. Complexes **1** and **2** are only soluble in THF, and less soluble in hydrocarbons. Based on the above results of elemental and spectral analyses, the structure of complexes **1** and **2** may be proposed as shown in Fig. 1.

2.2. Synthesis of $[Cp^t_2Ln(\mu\text{-}Cl)]_2$ (Ln = Gd, Er, Yb)

The reaction of anhydrous lanthanide trichloride with two equivalents of *tert*-butyldimethylsilylcyclopentadienylpotassium in THF, followed by removal of the solvent in vacuo and extraction of the residue with *n*-hexane, yielded the dimeric complexes $[Cp^t_2Ln(\mu\text{-}Cl)]_2$ (**3**–**5**) in medium yield.

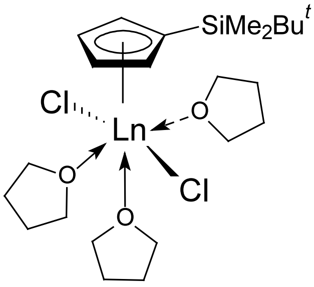

Fig. 1. The proposed structure for complexes **1** and **2**.

$$LnCl_3 + 2KCp^t \rightarrow [Cp^t_2Ln(\mu Cl)]_2 + 2KCl \qquad (2)$$
$$Ln = Gd(\mathbf{3}),\ Er(\mathbf{4}),\ Yb(\mathbf{5})$$

Complexes **3**–**5** can also be obtained by sublimation of the compounds from the dry reaction mixture at 160–190 °C (10^{-3} Torr), indicating that these complexes exhibit higher volatility than the corresponding unsubstituted cyclopentadienyl complexes [14]. The three complexes are sensitive to air and moisture. They are extremely soluble in polar solvents (e.g. THF), aromatic solvents and hydrocarbons, which allowed them to be easily separated from the reaction mixture by extraction with hexane rather than by sublimation. The elemental analyses and IR and mass spectra obtained are in agreement with their molecular formulae. The mass spectra of **3**–**5** show the molecular ions as the peaks of the highest mass.

X-ray quality single crystals of **3** are obtained by sublimation of the compound from the residue. Although the crystallization method of **3** is different to that of $[(C_5H_4SiMe_2Bu^t)_2Lu(\mu\text{-}Cl)]_2$ [4], they are isostructural in solid state. The molecular structure of **3** is shown in Fig. 2. Selected bond distances and bond angles are listed in Table 1. The complex is a centrosymmetric dimer in which each gadolinium is coordinated by two *tert*-butyldimethylsilylcyclopentadienyl ligands and two bridging chlorine atoms. Assuming the centroid of the η^5-bonded $C_5H_4SiMe_2Bu^t$ ring as ligand center, the coordination geometry around the gadolinium atom is a distorted pseudo tetrahedron. The $C_5H_4SiMe_2Bu^t$ ring is in an eclipsed conformation with respect to the gadolinium atom and the carbon (ring) with the $SiMe_2Bu^t$ substituent is far away from the metal due to the steric hindrance. The Gd–C distances range from 2.634(8) to 2.674(7) Å and are in normal ranges observed for the gadolinium metallocenes [15–17]. The average Gd–C(η^5) distance of 2.657(8) Å is compatible with those found in related compounds: $[(C_5H_5)_2Gd(\mu\text{-}\eta^2\text{-}ONCMe_2)]_2$, 2.68(2) Å [15], $[(C_5H_5)_2GdCl]_4$, 2.67(4) Å [16], and $[\{(C_5H_4CH_3)(C_5H_5)Gd(\mu\text{-}Tz)\}_2][\{(C_5H_4CH_3)_2Gd(\mu\text{-}Tz)\}_2]$, 2.64(1) Å [17]. The lengths of the Gd–Cl bonds of 2.706(2)–2.710(2) Å

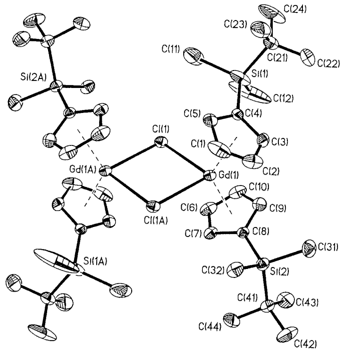

Fig. 2. Molecular Structure of $[(C_5H_4SiMe_2Bu^t)_2Gd(\mu\text{-}Cl)]_2$ (**3**).

Table 1
Selected bond lengths (Å) and angles (°) for complex **3**

Bond lengths			
Gd(1)–C(9)	2.634(8)	Gd(1)–C(3)	2.640(7)
Gd(1)–C(2)	2.643(9)	Gd(1)–C(10)	2.655(8)
Gd(1)–C(1)	2.656(9)	Gd(1)–C(7)	2.658(7)
Gd(1)–C(8)	2.668(6)	Gd(1)–C(5)	2.671(7)
Gd(1)–C(6)	2.671(9)	Gd(1)–C(4)	2.674(7)
Gd(1)–Cl(1)	2.706(2)	Gd(1)–Cl(1A)	2.710(2)
Cl(1)–Gd(1A)	2.710(2)	Gd(1)–Gd(1A)	4.076(1)
Cent1–Gd(1) [a]	2.384(4)	Cent2–Gd(1)	2.372 (4)
Bond angles			
Cl(1)–Gd(1)–Cl(1A)	82.40(6)	Gd(1)–Cl(1)–Gd(1A)	97.60(6)
Cent1–Gd(1)–Cent(2)	131.3(4)		

[a] Cent1 and Cent2 define the centroid of the ring atoms C(1)–C(5) and C(6)–C(10), respectively.

are in good consistency with the Ln–Cl bond lengths in $[(C_5H_4SiMe_2Bu^t)_2Lu(\mu\text{-}Cl)]_2$ (2.618(3) Å)[4], $[(C_5H_3(SiMe_3)_2)_2Yb(\mu\text{-}Cl)]_2$ (2.65 Å) and $[(C_5H_3(SiMe_3)_2)_2Sc(\mu\text{-}Cl)]_2$ (2.58 Å) [18], considering the different ionic radii of the central metals [19]. The substituted cyclopentadienyl rings are planar within the estimated S.D. (Table 2).

It is interesting to note that $(C_5H_4SiMe_2Bu^t)_2GdCl$ adopts a dimeric structure as opposed to tetrameric structure of $(C_5H_5)_2GdCl$ [16]. Obviously, it is possible that the enlarged steric effect of the $SiMe_2Bu^t$ substituent on the cyclopentadienyl ring favors the observed structure over a tetrameric alternative.

Table 2
Selected bond lengths (Å) and angles (°) in **8**·1/2THF

Bond lengths			
Er–S(1)	2.818(2)	Er–C(13)	2.655(5)
Er–N(1)	2.388(4)	Er–C(14)	2.612(5)
Er–O(1)	2.449(3)	Er–C(15)	2.642(5)
Er–C(1)	2.716(5)	Er–C(16)	2.687(5)
Er–C(2)	2.684(5)	S(1)–C(27)	1.700(5)
Er–C(3)	2.623(5)	S(2)–C(28)	1.747(5)
Er–C(4)	2.614(6)	S(2)–C(27)	1.751(4)
Er–C(5)	2.666(5)	N(1)–C(27)	1.315(6)
Er–C(12)	2.710(4)	N(1)–C(29)	1.397(5)
Er–Cent1 [a]	2.383	Er–Cent2	2.379
Bond angles			
N(1)–Er–O(1)	138.9(1)	C(27)–S(1)–Er	77.1(2)
N(1)–Er–S(1)	60.1(1)	C(27)–N(1)–Er	101.5(3)
O(1)–Er–S(1)	78.7(1)	C(29)–N(1)–Er	146.0(3)
C(27)–N(1)–C(29)	112.4(4)	C(29)–C(28)–S(2)	109.5(3)
N(1)–C(27)–S(1)	121.3(3)	C(30)–C(29)–N(1)	125.8(5)
N(1)–C(27)–S(2)	113.9(3)	N(1)–C(29)–C(28)	114.2(4)
S(1)–C(27)–S(2)	124.8(3)	Cent1–Er–Cent2	126.3
C(33)–C(28)–S(2)	129.8(4)		

[a] Cent1 and Cent2 define the centroid of the ring atoms C(1)–C(5) and C(12)–C(16), respectively.

2.3. Synthesis of $(C_5H_4SiMe_2Bu^t)(C_5H_5)_2Dy(THF)$ (6)

The reaction of $DyCl_3$ with $KC_5H_4SiMe_2Bu^t$ and subsequently with C_5H_5Na results in the formation of the mixed-ring coordinated complex $(C_5H_4SiMe_2Bu^t)(C_5H_5)_2Dy(THF)$ (**6**). Complex **6** is soluble in ethers such as THF but less soluble in hydrocarbon solvents such as hexane at room temperature, and sensitive toward air and moisture. Complex **6** has been characterized by elemental analysis, infrared and mass spectroscopies. The mass spectra data such as [M+2], [M–THF], $[THF]^+$ indicate that complex **6** has a solvated mononuclear structure.

2.4. Synthesis of $(C_5H_4SiMe_2Bu^t)_2Er[OC(NPr^i_2)NPh](THF)$ (7)

Recently, insertions of isocyanate into the lanthanide–ligand bond attract considerable attention [20–22,8]. The accumulated information indicates that the steric crowding around the central metal ion and the nature of the lanthanide–ligand bond have an important influence on the insertion. To further study the influence of modification of the cyclopentadienyl ligand on the insertion reaction, we synthesized the amide complex $(C_5H_4SiMe_2Bu^t)_2Er(NPr^i_2)(THF)$ by the treatment of $[(C_5H_4SiMe_2Bu^t)_2Er(\mu\text{-}Cl)]_2$ with two equivalents of $LiNPr^i_2$ in THF, and studied the reaction of $(C_5H_4SiMe_2Bu^t)_2Er(\mu\text{-}NPr^i_2)(THF)$ with PhNCO, as shown in the following equation:

$$[Cp^t_2ErCl]_2 + LiNPr^i_2 \xrightarrow{THF} Cp^t_2ErNPr^i_2(THF)$$

$$\xrightarrow{PhNCO} Cp^t_2Er[OC(NPr^i_2)NPh](THF) \quad (\mathbf{7}) \qquad (3)$$

Like the corresponding methylcyclopentadienyl lanthanide amide species, $(C_5H_4SiMe_2Bu^t)_2Er(NPr^i_2)(THF)$ also exhibit high reactivity. It reacts with one equivalent of phenyl isocyanate in THF at −10 °C to give the mono PhNCO insertion product $(C_5H_4SiMe_2Bu^t)_2Er[OC(NPr^i_2)NPh](THF)$ (**7**). Complex **7** was characterized by elemental analysis and IR and mass spectroscopy.

Complex **7** is moderately sensitive toward moisture and air. It is soluble in THF and toluene. In the mass spectra of **7**, the compound is characterized by the loss of the THF molecule from the molecule ion with the $[M-THF]^+$ ion as a highest mass peak. In the IR spectral data of **7**, the band is observed at ca. 1595 cm^{-1}, which may be assigned to the absorption of the delocalized mode of $-O\underset{..}{-}C\underset{..}{-}N-$ unit of the resulting amido ligand [8]. Unfortunately, their crystal structures have not been solved yet by X-ray analysis due to poor crystalline quality.

2.5. *Synthesis of Bu^tMe_2Si-substituted cyclopentadienylerbium benzothiazole-2-thiolate complex $(C_5H_4SiMe_2Bu^t)_2Er(SBT)(THF)$ (**8**)*

The reaction of $[(C_5H_4SiMe_2Bu^t)_2Er(\mu\text{-}Cl)]_2$ with two equivalents of sodium benzothiazole-2-thiolate (NaSBT) in THF at room temperature produced the corresponding benzothiazole-2-thiolate complex $(C_5H_4SiMe_2Bu^t)_2Er(SBT)(THF)$ (**8**) in excellent yield. In the mass spectra of complex **8** the highest mass peak corresponds to the ion formed by abstraction of one THF molecule from the molecular ion. The IR spectra of **8** show that the characteristic absorption of $\nu_{C=N}$ for the free HSBT at 1496 cm^{-1} is shifted on complexation to lower frequency 1456 cm^{-1}.

Fig. 3 shows the molecular structure of **8**. The Er^{3+} ion is coordinated by two $C_5H_4SiMe_2Bu^t$ groups, one nitrogen and one sulfur atom from the benzothiazole-2-thiolate ligand and one oxygen atom of THF molecule leading to a distorted trigonal-bipyramidal geometry with two η^5-$C_5H_4SiMe_2Bu^t$ ring centroids in axial positions. The coordination number of central metal is 9, if each $C_5H_4SiMe_2Bu^t$ group is regarded as occupying three coordination sites. The average Er–C(ring) bond length of 2.66(1) Å and Er–Cp(centroid) distance (2.381 Å) in **8** are in normal range [23–25]. The Er–O(THF) distance of 2.449(3) Å is longer than the value found in complex $Cp_2Er(PzMe_2)(THF)$, 2.32(1) Å [3].

Examinations of the distances involving the metal atom in **8** show that when the differences in metallic radii are subtracted, the Er–S distance of 2.818(2) Å is longer than the value found in $Cp_2Yb(SC_6H_2(CF_3)_3)$-(THF), 2.639(3) Å [26]. The Er–N distance of 2.388 Å is between those expected for the Ln–N single bond and the Ln ← :N donor bond [27–29]. Presumably, the rather long Er–S bond distance and the rather short Er–N(donating) one may result from the fact that the negative charge of S(1) is partially delocalized to the N atom. Consistent with this, the C(27)–S(1) bond length of 1.700(5) Å is slightly shorter than the usually observed C(sp^2)–S bond distances, showing the bond between the C(27) and S(1) atoms has the partial double bond character [30].

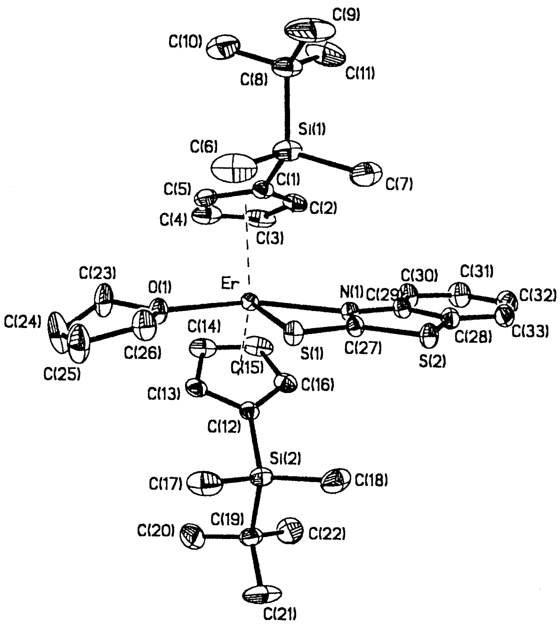

Fig. 3. Molecular structure of $(C_5H_4SiMe_2Bu^t)_2Er(SBT)(THF)$ (**8**).

3. Experimental

3.1. *Materials and methods*

All manipulations were carried out under argon with rigorous exclusion of air and moisture using Schlenk, vacuum-line and glovebox techniques. All solvents were refluxed and distilled over sodium benzophenone ketyl prior to use. Anhydrous $LnCl_3$ [31], *tert*-butyldimethylsilylcyclopentadiene [32] and $(C_5H_4SiMe_2Bu^t)_2Er(N\text{-}Pr^i_2)(THF)$ [20] were prepared by the literature procedures. Others were purchased and purified by standard procedures. $KC_5H_4SiMe_2Bu^t$ was prepared by the reaction of *tert*-butyldimethylsilylcyclopentadiene and potassium in THF at ambient temperature.

Elemental analyses for carbon, hydrogen and nitrogen were performed on a Rapid CHN-O analyzer. Metal analyses for lanthanides were accomplished using the literature method [33]. Melting points (m.p.) were determined in sealed nitrogen-filled capillaries and are uncorrected. Infrared spectra were obtained on a NICOLET FT-IR 360 spectrometer with samples prepared as Nujol mulls. Mass spectra were recorded on a Philips HP5989A instrument operating in the EI mode at 70 eV. Crystal samples of the respective complexes were rapidly introduced by the direct inlet techniques with a source temperature of 200 °C. ^{1}H-NMR data were obtained on a Bruker DMX-500 NMR spectrometer.

3.2. *Synthesis of $(C_5H_4SiMe_2Bu^t)YCl_2(THF)_3$ (**1**)*

A solution of Cp$'$K (0.651 g, 2.98 mmol) in tetrahydrofuran (20 ml) was added to a stirred suspension of YCl_3 (0.582 g, 2.98 mmol) in tetrahydrofuran (40 ml). The mixture was stirred at room temperature (r.t.) for 24 h and then centrifuged. The solution was decanted from undissolved KCl, concentrated to ca. 10 ml and cooled to −18 °C to provide 1.2 g (72.6%) of yellow crystalline **1**. M.p. 92 °C. Anal. Calc. for $C_{23}H_{43}O_3Cl_2YSi$: C, 49.73; H, 7.80; Y, 16.00. Found: C, 49.21; H, 7.66; Y, 16.27%. ^{1}H-NMR (THF-d_8): δ 6.51 (s, 2H, C_5H_4), 6.03 (s, 2H, C_5H_4), 3.54 (m, 12H, THF), 1.73 (m, 12H, THF), 0.91 (s, 9H, $SiC(CH_3)_3$), 0.06 (s, 6H, $Si(CH_3)_2$). EIMS:

m/*z* (fragment, relative intensity%) = 553 [M − 1, 1], 437 [M–HSiMe$_2$Bu^t, 1], 353 [M–THF–Bu^t, 1], 338 [M–3THF, 2], 301 [M–3THF–Cl–2, 2], 268 [M–3THF–2Cl, 1], 281 [M–3THF–Bu^t, 5], 211 [M–3THF–2Cl–Bu^t, 1], 179 [Cp^t, 10], 72 [THF, 53], 57 [Bu^t, 12], 42 [C$_3$H$_6$, 100]. IR (KBr): 3084 w, 2959 s, 2849 s, 2731 m, 1460 s, 1378 m, 1343 m, 1298 m, 1246 w, 1177m, 1068 m, 1013 m, 1007 m, 937 m, 912 m, 862 m, 834 s, 764 m, 724 m, 669 m, 646 m, 576 m, 498 m, 483 s, 476 s, 434 s cm^{-1}.

3.3. Synthesis of $(C_5H_4SiMe_2Bu^t)ErCl_2(THF)_3$ (2)

In analogy to the preparation of **1**, 0.890 g (3.25 mmol) of ErCl$_3$ reacted with KCp^t (0.710 g, 3.25 mmol) to give 1.26 g (65%) pink crystalline **2**. M.p. 116 °C. Anal. Calc. for $C_{23}H_{43}OCl_2ErSi$: C, 43.58; H, 6.84; Er, 26.39. Found: C, 42.98; H, 6.67; Er, 25.92%. EIMS: *m*/*z* (fragment, relative intensity%) = 631 [M, 2], 544 [M–THF–Me, 4], 529 [M–THF–2Me, 3], 524 [M–THF–Cl, 8], 502 [M–THF–Bu^t, 75], 452 [M–2THF–Cl, 1], 444 [M–THF–SiMe$_2$Bu^t, 2], 432 [M–THF–2Cl–Bu^t, 2], 415 [M–3THF, 2], 380 [M–3THF–Cl, 11], 358 [M–3THF–Bu^t, 2], 338 [M–3THF–Cl–C$_3$H$_6$, 6], 323 [M–3THF–Cl–Bu^t, 4], 308 [ErCl$_2$(THF), 2], 179 [Cp^t, 2], 123 [Cp^{t}H–Bu^t, 51], 115 [SiMe$_2$Bu^t, 3], 72 [THF, 12], 57 [Bu^t, 12]. IR (KBr): 3085 m, 2954 s, 2849 s, 1469 s, 1410 m, 1384 m, 1358 m, 1308 w, 1247 m, 1170 m, 1075 m, 1044 m, 1007 m, 937 m, 913 m, 834 s, 764 s, 727 m, 668 m, 646 w, 576 m, 498 m, 483 m, 476 s, 434 s cm^{-1}.

3.4. Synthesis of $[(C_5H_4SiMe_2Bu^t)_2Gd(\mu\text{-}Cl)]_2$ (3)

To a suspension of GdCl$_3$ (1.83 g, 6.94 mmol) in THF (30 ml) was added *tert*-butyldimethylsilylcyclopentadienylpotassium (0.408 M, in THF, 35 ml) at r.t. After stirring for 24 h, the solvent was removed in vacuo. Pale yellow crystals of **3** were obtained by sublimating the residue at 170 °C under 0.1 Pa. Yield, 1.65 g (43%). M.p. 193 °C. Anal. Calc. for $C_{44}H_{76}Cl_2Gd_2Si_4$: C, 47.92; H, 6.95; Gd, 28.52. Found: C, 47.63; H, 7.01; Gd, 28.11%. IR (KBr): 3075 m, 2986 s, 2882 s, 2826 s, 2729 s, 1512 m, 1473 s, 1441 s, 1381 s, 1304 s, 1249 m, 1170 m, 1155 m, 1041 m, 1007 m, 966 m, 937 w, 897 m, 833 m, 768 m, 722 s, 671 m, 579 m cm^{-1}. EIMS: *m*/*z* (fragment, relative intensity%) = 1102 [M, 1], 1067 [M–Cl, 25], 1045 [M–Bu^t, 18], 923 [M–Cp^t, 5], 866 [M–Cp^t–Bu^t, 2], 629 [M–Cl–2Cp^t, 1], 551 [M/2, 2], 516 [M/2–Cl, 100], 494 [M/2–Bu^t, 64], 458 [M/2–Cl–Bu^{t}H, 15], 436 [M/2–SiMe$_2$Bu^t, 3], 402 [M/2–Cl–2Bu^t, 3], 401 [M/2–Cl–SiMe$_2$Bu^t, 1], 386 [M–4Cp^t, 2], 372 [M/2–Cp^t, 1], 315 [M/2–Cp^t–Bu^t, 1.4], 57 [Bu^t, 11].

3.5. Synthesis of $[(C_5H_4SiMe_2Bu^t)_2Er(\mu\text{-}Cl)]_2$ (4)

A solution of KC$_5$H$_4$SiMe$_2$Bu^t (4.63 g, 21.2 mmol) in THF (40 ml) was added to a stirred suspension of ErCl$_3$ (2.90 g, 10.6 mmol) in THF. The reaction mixture was stirred for 24 h at r.t., and then allowed to evaporate to dry in vacuo. The resulting solid residue was extracted with 120 ml *n*-hexane. The clear *n*-hexane solution was concentrated to 20 ml and cooled to −18 °C to provide 3.57 g of orange crystalline **4** (yield 60%). M.p. 220 °C. Anal. Calc. for $C_{44}H_{76}Cl_2Er_2Si_4$: C, 47.06; H, 6.82; Er, 29.79. Found: C, 47.19; H, 6.88; Er, 29.47%. EIMS: *m*/*z* (fragment, relative intensity%) = 1118 [M, 1], 1060 [M–HBu^t, 1], 945 [M–Bu^{t}H–SiMe$_2$Bu^t, 67], 939 [M–Cp^t, 1], 559 [M/2, 1], 546 [M–3Cp^t–Cl, 9], 524 [M/2–Cl, 74], 502 [M/2–Bu^t, 77], 467 [M/2–Cl–Bu^t, 30], 452 [M/2–Cl–Bu^t–Me, 2], 444 [M/2–SiMe$_2$Bu^t, 3], 431 [M–3Cp^t–Cl–SiMe$_2$Bu^t, 2], 410 [M/2–Cl–2Bu^t, 6], 409 [M/2–Cl–SiMe$_2$Bu^t, 4], 394 [M–Cl–SiMe$_2$Bu^t–Me, 10], 380 [M/2–Cp^t, 3], 352 [M/2–Cl–SiMe$_2$Bu^t–Bu^t, 20], 338 [M/2–Cp^t–2Me, 5], 323 [M/2–Cp^t–Bu^t, 3], 57 [Bu^t, 8]. IR (KBr): 3076 m, 2984 s, 2883 s, 2828 s, 2728 m, 2671 m, 1471 s, 1441 s, 1375 s, 1304 s, 1251 m, 1171 m, 1042 m, 965 m, 1008 w, 900 m, 833 m, 769 m, 722 s, 669 m, 578 w, 508 m, 489 s cm^{-1}.

3.6. Synthesis of $[(C_5H_4SiMe_2Bu^t)_2Yb(\mu\text{-}Cl)]_2$ (5)

Using the procedure described for **4**, the reaction of KC$_5$H$_4$SiMe$_2$Bu^t (1.14 mmol) and YbCl$_3$ (1.59 g, 5.69 mmol) afforded 2.05 g of red crystals of compound **5** (yield, 63%). Anal. Calc. for $C_{44}H_{76}Cl_2Yb_2Si_4$: C, 46.58; H, 6.75; Yb, 30.51. Found: C, 46.97; H, 6.98; Yb, 30.07%. EIMS: *m*/*z* (fragment, relative intensity%) = 1134 [M, 1], 1099 [M–Cl, 1], 1077 [M–Bu^t, 2], 1019 [M–SiMe$_2$Bu^t, 1], 940 [M–Cp^t–Me, 3], 920 [M–Cl–Cp^t, 7], 741 [M–Cl–2Cp^t, 2], 567[M/2, 1], 532 [M/2–Cl, 100], 520 [M–Cl–3Cp^t–C$_3$H$_6$, 14], 510 [M/2–Bu^t, 11], 475[M/2–Cl–Bu^t, 4], 447 [M–3Cp^t–Cl–SiMe$_2$Bu^t, 5], 418 [M–4Cp^t, 3], 417 [M/2–Cl–SiMe$_2$Bu^t, 3], 388 [M/2–Cp^t, 1], 353 [[M/2–Cp^t–Cl, 4], 296 [M/2–Cp^t–Bu^t–Cl, 2], 238 [M/2–Cp^t–Cl–SiMe$_2$Bu^t, 2], 115 [SiMe$_2$Bu^t, 3], 57 [Bu^t, 12]. IR (KBr): 3078 m, 2924 s, 2854 s, 2729 m, 2360 m, 1464 s, 1377 s, 1365 m, 1308 w, 1249 m, 1176 m, 1043 m, 1006 m, 903 m, 831 m, 802 m, 769 m, 723 m, 579 m, 484 s, 425 s, 414 m cm^{-1}.

3.7. Synthesis of $(C_5H_4SiMe_2Bu^t)(C_5H_5)_2Dy(THF)$ (6)

A THF solution of Cp^{t}K (2.50 mmol) was added dropwise to a slurry of DyCl$_3$ (0.672 g, 2.50 mmol) in 30 ml THF solution at −30 °C. After stirred for 24 h at r.t., to the reaction mixture 10 ml of a THF solution of C$_5$H$_5$Na (5.00 mmol) was added. The reaction mixture was stirred for 12 h. After centrifugation, the clear solution was concentrated and cooled at −20 °C to give yellow powder. Recrystallization of the powder from THF gave **6** as yellow crystals. Yield: 0.85 g (62.5%). M.p. 178 °C. Anal. Calc. for $C_{25}H_{37}ODySi$: C, 55.18;

H, 6.85; Dy, 29.87. Found: C, 55.03; H, 6.61; Dy, 30.04%. MS: *m/z* [fragment, relative intensity%] = 547 [M+2, 1.00], 473 [M−THF, 4], 408 [M−THF−Cp, 88], 358 [M−THF−$SiMe_2Bu^t$, 4], 351 [M−THF−Cp−Bu^t, 27], 322 [M−THF−Cp−2Me−Bu^t, 2], 294 [M−THF−Cp^t, 26], 229 [M−THF−Cp−Cp^t, 8], 179 [Cp^t, 2], 164 [Dy, 2], 65 [Cp, 54], 57 [Bu^t, 6]. IR (KBr): 3085 m, 2958 s, 2854 s, 1464 s, 1377 s, 1340 m, 1304 m, 1261m, 1155 w, 1076 w, 1009 m, 966 w, 890 w, 837 w, 771 m, 722 s, 667 w, 483 m, 475 m, 468 s, 437 s cm^{-1}.

3.8. Synthesis of $(C_5H_4SiMe_2Bu^t)_2Er[OC(NPr^i_2)NPh](THF)$ (7)

To a solution of $[(C_5H_4SiMe_2Bu^t)_2Er(\mu\text{-}Cl)]_2$ (0.373 g, 0.332 mmol) in THF (30 ml) was added 10 ml of THF solution of $LiNPr^i_2$ (0.664 mmol) at 0 °C. After stirring for 4 h, to the mixture was added phenyl isocyanate (0.073 ml, 0.664 mmol) at −10 °C. The reaction mixture was then warmed up to ambient temperature and stirred overnight. The solvent was removed by reduced pressure. The solid was extracted with toluene (20 ml). The resulting yellow solution was concentrated by reduced pressure to about 5 ml, and a yellow solid (0.29 g, 53.4%) was obtained upon cooling at −20 °C. Anal. Calc. for $C_{39}H_{65}N_2O_2Si_2Er$: C, 57.31; H, 8.02; N, 3.42; Er, 20.46. Found: C, 57.06; H, 7.93; N, 3.40; Er, 20.67%. IR (KBr pellet, cm^{-1}): 3359 m, 3161 m, 3080 w, 2976 s, 2935 s, 2852 s, 2729 m, 1595 m, 1525 m, 1480 s, 1440 s, 1378 s, 1306 s, 1250 m, 1153 m, 1076 m, 1043 w, 1007 m, 966 m, 893 m, 831 m, 819 w, 769 m, 722 s, 669 w, 487 m, 474 m, 450 s, 443 s, 420 s cm^{-1}. MS: *m/z* [fragment, relative intensity%] = 743 [M−THF, 2], 564 [M−THF−Cp^t, 5], 524 [Cp^t_2Er, 1], 385 [Er(OC(N-Pr^i_2)NPh), 3], 345 [Cp^tEr,12], 220 [OC(NPr^i_2)NPh+1, 11],180 [Cp^tH, 5], 128 [$OCNPr^i_2$, 23], 100 [NPr^i_2, 2], 77 [Ph, 4], 72 [THF, 17], 57 [Bu^t, 3], 43 [Pr^i, 27].

3.9. Synthesis of $(C_5H_4SiMe_2Bu^t)_2Er(SBT)(THF)$ (**8**)

To a mixture of $[(C_5H_4SiMe_2Bu^t)_2Er(\mu\text{−}Cl)]_2$ (0.357 g, 0.318 mmol) and benzothiazole-2-thiolate sodium (NaSBT) (0.120 g, 0.636 mmol) was added 20 ml of THF at r.t. After stirring for 24 h, the solution was decanted from undissolved NaCl, concentrated to ca. 4 ml and cooled to −20 °C to provide **8**·1/2THF as pink crystals. Yield: 0.326 g (67%). M.p. 164 °C. Anal. Calc. for $C_{35}H_{54}NO_{1.5}S_2Si_2Er$: C, 52.52; H, 6.80; N, 1.75; Er, 20.90. Found: C, 52.80; H, 6.57; N, 1.80; Er, 21.12%. MS: *m/z* [fragment, relative intensity%] = 690 [Cp^t_2Er(SBT), 2], 648 [Cp^t_2Er(SBT)−C_3H_6, 1], 288 [Cp^tEr−Bu^t, 1], 296 [Er(SCN)(THF), 12], 226 [Er(SCN)O, 6], 224 [Er(SCN), 39], 180 [Cp^tH, 2], 167 [HSBT, 100], 134 [SBT−S, 3], 115[$SiMe_2Bu^t$, 2]. IR (KBr): 3081 m, 2966 s, 2851 s, 2729 m, 2671 m, 1587 w, 1556 w, 1456 s, 1440 m, 1378 s, 1308 m, 1249 s, 1178 m, 1155 m, 1077 m, 1014 m, 974 m, 950 m, 915 m, 831 m, 802 m, 769 m, 723 m, 687 m, 669 w, 474 m cm^{-1}.

3.10. X-ray crystal structure determination of $[(C_5H_4SiMe_2Bu^t)_2Gd(\mu\text{-}Cl)]_2$ (3)

A suitable single crystal was sealed in thin-walled glass capillaries under argon. The preliminary examination and intensity data collection were carried out with an Enraf–Nonius CAD4-automatic diffractometer using graphite-monochromatized Mo–K_α radiation. Accurate cell parameters were obtained by the least-squares refinement of the setting angles of 25 reflections with $14.04 < \theta < 15.79°$. Intensity data were collected using the $\omega - 2\theta$ scan mode and corrected for Lorentz, polarization and absorption. During data collection, the intensities of three standard reflections measured every 300 reflections showed 0.7% decay. The structure was solved by direct methods and refined with full-matrix least-squares on F^2 [34]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included in idealized positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in refinement. All calculations were performed on a Micro VAX 3100 computer using MOLEN program [35].

3.11. X-ray crystal structure determination of **8**·1/2THF

Suitable crystals of **8**·1/2THF were obtained from THF. The general procedure for solving the structure is outlined above. The final orientation matrices and cell parameters were obtained from least-squares fits 25 reflections having $10.01 < \theta < 13.26°$. No significant change was detected in the intensities of three standard reflections. A summary of crystallographic data and data collection parameters is given in Table 3.

A combination of direct methods and difference Fourier techniques provided the locations of all non-hydrogen atoms, which were refined with anisotropic thermal parameters by full-matrix least-squares methods. There are two tetrahydrofuran solvent molecules present per cell unit. The solvent molecule THF was disordered and no 'model' could be proposed to 'fit' THF to the observed electron density maps, so bond distances were constrained.

4. Supplemental material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 178626 for compound **3**, and CCDC no. 178627 for compound **8**. Copies of this information may be obtained free of charge from The

Table 3
Crystal data and structure refinements for complexes **3** and **8**·1/2THF

Compound	**3**	**8**·1/2THF
Empirical formula	$C_{44}H_{76}Cl_2Gd_2Si_4$	$C_{35}H_{54}ErNO_{1.5}S_2Si_2$
Formula weight	1102.81	800.35
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	C_2/c
Lattice parameters		
a (Å)	11.570(2)	9.950(2)
B (Å)	14.164(3)	11.890(2)
c (Å)	16.294(3)	34.936(7)
β (°)	91.58(3)	95.36(3)
V (Å^3)	2669.1(9)	4115.4(14)
Z	2	4
D_{calc} (g cm^{-3})	1.372	1.292
μ (mm^{-1})	2.679	2.225
F(000)	1116	1644
Crystal size (mm)	0.52 × 0.45 × 0.40	0.50 × 0.38 × 0.30
θ range (°)	1.76–25.99	1.81–26.00
Index ranges	$-14 \leq h \leq 0$, $-17 \leq k \leq 0$, $-20 \leq l \leq 20$	$0 \leq h \leq 12$, $0 \leq k \leq 14$, $-43 \leq l \leq 42$
Reflections collected	5499	7246
Unique reflections	5234 [$R_{int} = 0.0275$]	6857 [$R_{int} = 0.0182$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5234/0/235	6857/0/406
Goodness-of-fit on F^2	1.040	0.997
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0519$, $wR_2 = 0.1376$	$R_1 = 0.0349$, $wR_2 = 0.0939$
R indices (all data)	$R_1 = 0.0752$, $wR_2 = 0.1469$	$R_1 = 0.0546$, $wR_2 = 0.0968$
Largest peak and hole (e Å^{-3})	1.118, −1.342	1.125, −0.970

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