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β-Diiminatolanthanoid(III) halides revisited

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ABSTRACT

The crystalline compounds $[LnCl_2(\mathbf{L})(thf)_2]$ [Ln = Ce (**1**), Tb (**2**), Yb (**3**)], $[NdI_2(\mathbf{L})(thf)_2]$ (**4**), $[LnCl(\mathbf{L}')_2]$ [Ln = Tb (**5**), Yb (**6**) (a known compound)] and $[YbCl(\mathbf{L}'')(\mu\text{-}Cl)_2Li(OEt_2)_2]$ (**7**) have been prepared [$\mathbf{L} = \{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2CPh$, $\mathbf{L}' = \{N(SiMe_3)C(Ph)\}_2CH$, $\mathbf{L}'' = \{N(SiMe_3)C(C_6H_4Ph\text{-}4)\}_2CH$]. The X-ray molecular structures of **2**–**7** have been established; in each, the monoanionic ligand **L**, **L′** or **L″** is *N,N′*-chelating and essentially π-delocalised. Each of **1**–**7** was prepared from the appropriate $LnCl_3$, or for **4** $[NdI_3(thf)_2]$, and *an equivalent* portion of the appropriate alkali metal [Li for **7**, Na for **2**, **3** and **5**, or K for **1**, **4** and **6**] β-diiminate in thf; the isolation of exclusively **5** and **6** (rather than the **L′** analogues of **2** or **3**) is noteworthy, as is the structure of **7** which has no precedent in Group 3 or 4f metal β-diiminato chemistry.

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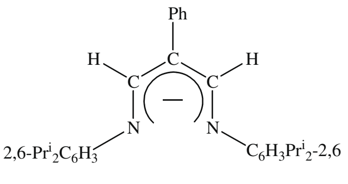
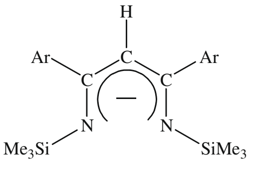
1. Introduction

This paper deals with the synthesis and characterisation of seven crystalline β-diiminatolanthanoid(III) halides $[LnCl_2(\mathbf{L})(thf)_2]$ [Ln = Ce (**1**), Tb (**2**), Yb (**3**)], $NdI_2(\mathbf{L})(thf)_2]$ (**4**), $[LnCl(\mathbf{L}')_2]$ [Ln = Tb (**5**), Yb (**6**)] and $[Yb(\mathbf{L}'')Cl(\mu\text{-}Cl)_2Li(OEt_2)_2]$ (**7**), including the molecular structures of **2**–**7**. The ligand **L**, **L′** and **L″** in each of **1**–**7** is monoanionic, *N,N′*-chelating and essentially π-delocalised, as are $\mathbf{L}^R$ (R = a hydrocarbyl group) in related Ln(III) compounds described in the literature.

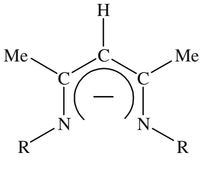
β-Diiminatolanthanoid(III) halides and their scandium and yttrium analogues are useful precursors to a wide range of corresponding metal complexes. The first of these to be reported and X-ray-characterised were $[LnBr(\mathbf{L}^R)_2]$ (Ln = Sm, Gd; R = Pr^i) [1a], $[GdBr_2(\mathbf{L}^R)(thf)_2]$ (R = Ph) [1b] and $[NdCl(\mathbf{L}')_2]$ [2]; the isoleptic Ce, Pr, Sm, Yb chlorides have also been prepared [2]. The complex $[ScCl_2(\mathbf{L}^R)(thf)_2]$ (R = $C_6H_3Pr^i_2$-2,6) and an analogue with Bu^t instead of Me substituents were the forerunners of related compounds, including **1**–**3** [3]. The synthesis and some reactions of $[YbCl_2(\mathbf{L}^R)(thf)_2]$ (R = $C_6H_3Pr^i_2$-2,6) have been presented [4]. The preparation, reactions and structures of $[LnCl_2(\mathbf{L}^R)(thf)_2]$ (R = $C_6H_3Me_2$-2,6) and the $\mathbf{L}^R$ (R = Ph) analogues as well as $[LnCl_2\{N(C_6H_3Pr^i_2\text{-}2,6)\text{-}C(Me)C(H)C(Me)NC_6H_4Cl\text{-}4\}(thf)_2]$ (Ln = Sm, Yb) have been studied [5]. The hetero-binuclear compounds $[LnCl(\mathbf{L}^R)(thf)(\mu\text{-}Cl)_2Li(thf)_2]$ (Ln = Nd, Sm, Tb, Yb; R = $C_6H_3Me_2$-2,6)



L



L′ (Ar = Ph)
L″ (Ar = C_6H_4Ph-4)



$\mathbf{L}^R$

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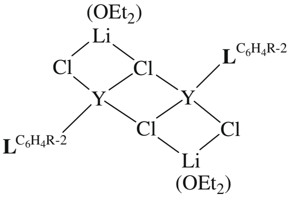
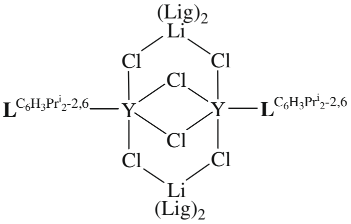
were investigated [6]. We have recently described the crystalline diiminatoyttrium chlorides [YCl$_2$(**L**)(thf)$_2$], [YCl$_2$(**L**^{R})(thf)$_2$] (R = C$_6$H$_4$Bu^t-2), [YCl(**L**′)$_2$] and the complexes **A** and **B** [7]. The homobinuclear compound [SmCl(**L**^{R})(μ-Cl)$_3$Sm(**L**^{R})(thf)] was obtained from SmCl$_3$ and K(**L**^{R}) (R = C$_6$H$_3$Pr$^i_2$-2,6) in thf [8].



A: R = Pr^i, Bu^t



B: Lig = OEt$_2$, thf

Whilst there is now a substantial literature on β-diketiminatometal compounds, with more than 100 publications since 2005, little has been published on β-dialdiminato analogues. The ligand **L** first featured in Cu(I) chemistry [9a]; the X-ray structure and the chemiluminescent behaviour of [Cu(**L**)(PPh$_3$)] has been reported [9b]. Other publications on **L** complexes relate to [Tl(**L**)] [9c] and various indium [9d] and arsenic [9e] complexes.

2. Results and discussion

This is divided into three parts: dealing sequentially with mono-β-dialdiminatolanthanoid(III) halides, bis(β-diketiminato)lanthanoid(III) chlorides, and a hetero-binuclear (Yb/Li) chloride.

2.1. The synthesis and structures of the crystalline complexes **1**–**4**

The crystalline β-dialdiminatolanthanoid(III) halides **1**–**4** were prepared as shown in Scheme 1 from the appropriate LnCl$_3$ (Ce, Tb) or a thf-adduct LnHal$_3$(thf)$_n$ (Yb/Cl, Nd/I). The sodium or potassium, rather than lithium, β-dialdiminate was chosen as the ligand transfer reagent, as the use of Li(**L**) might have favoured the formation of hetero-binuclear Ln(III)/Li complexes (*cf.*, **7**). No attempt was made to optimise yields, and in this respect the outcome for the ytterbium compound **3** was unsatisfactory.

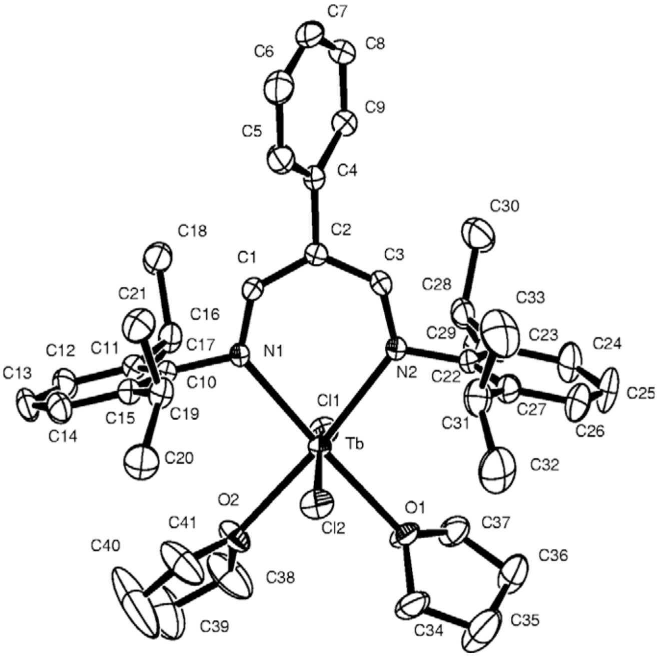
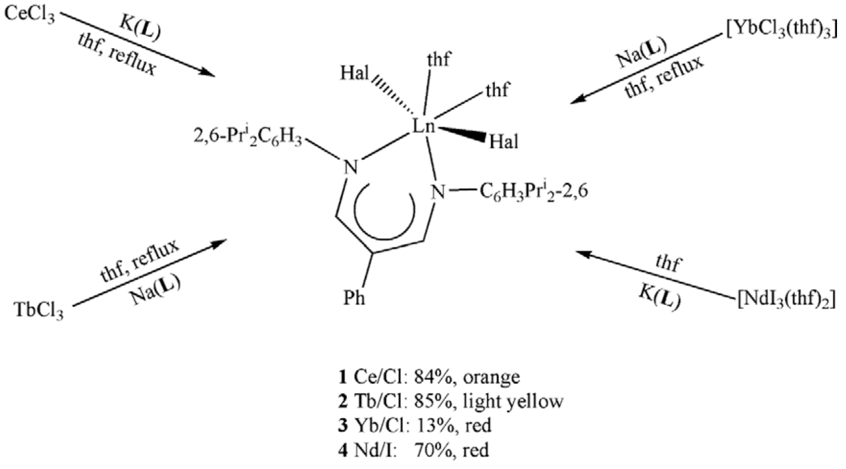


Fig. 1. Molecular structure of crystalline **2** (50% thermal ellipsoids).

The C, H, N microanalytical data, again except for **3**, was gratifying. Detailed analysis of the ^{1}H and ^{13}C NMR spectra of these paramagnetic molecules was undertaken, by Dr. A.G. Avent, only for the terbium compound **2**; the solvent selected was CDCl$_3$ and the assignments showed that the solution structure was consistent with that for the solid, as revealed by X-ray diffraction. Each of **1**–**4** was only sparingly soluble in various hydrocarbon solvents, including benzene.

The molecular structures of distorted octahedral **2**, **3** and **4** were determined by single crystal X-ray diffraction, as illustrated in Figs. 1–3, respectively. Table 1 lists important geometric data, together with selected parameters for [YCl$_2$(**L**)(thf)$_2$] [7]; the latter shows close correspondence with those of the terbium compound **2**. In each of these molecules the NCCCN′ core atoms of the **L** ligand are essentially coplanar; in **2** and **3** the metal atom is only slightly out of this plane (*ca.* 0.1 Å), whilst in **4** the Nd atom is displaced by



Scheme 1. Synthesis of **1**–**4**.

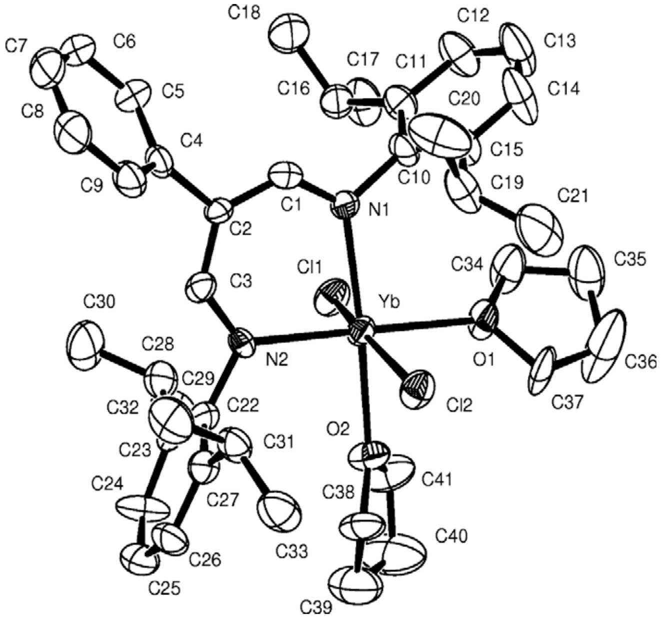


Fig. 2. Molecular structure of crystalline **3** (50% thermal ellipsoids).

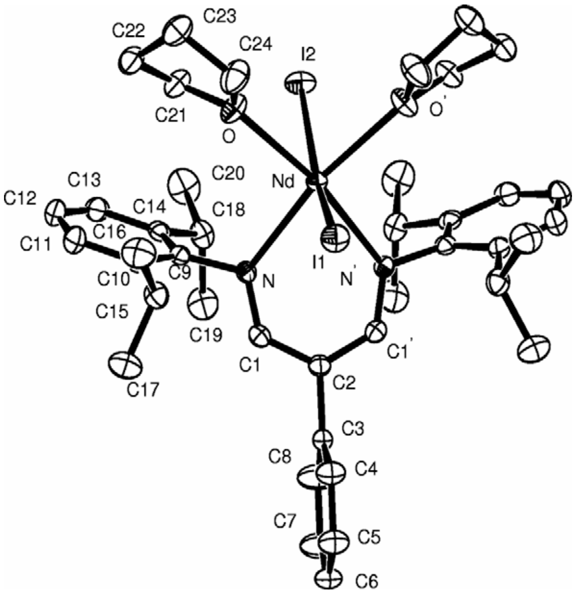


Fig. 3. Molecular structure of crystalline **4** (50% thermal ellipsoids).

0.868(5) Å off the NC1C1′N′ plane. It is evident that there is very substantial π-delocalisation in the NCCCN′ moiety; this is particularly clear for **4**, since that molecule lies on a crystallographic mirror plane; and for **2** and **3** the pairs of M–N, N–C_α and C_α–C_β bond lengths are closely similar (the largest deviation being for the N–C_α values for **3**) and each of the latter two pairs has an intermediate bond distance between a single and double NC and CC bond.

*2.2. The synthesis and structures of the crystalline complexes **5** and **6***

The crystalline *bis*(β-diketiminato)lanthanoid chlorides **5** and **6** were prepared as shown in Scheme 2 from Na(**L**′) or K(**L**′) with *two equivalents* of $TbCl_3$ or $[YbCl_3(thf)_2]$, respectively. This unexpected outcome is attributed to the rapid redistribution of the appropriate kinetically fragile $LnCl_2(\mathbf{L}')(thf)_n$, Eq. (1). An alternative, and possibly a more likely, explanation is that upon concentrating the solution from the 1:1 reaction, the lower solubility of the products of Eq. (1) is the driving force for the forward reaction.

$$2\mathrm{LnCl_2}(\mathbf{L}')(\mathrm{thf})_n \xrightarrow{\mathrm{thf}} [\mathrm{LnCl}(\mathbf{L}')_2] + \mathrm{LnCl_3}(\mathrm{thf})_n \tag{1}$$

Complex **6** had previously been obtained (in 57% yield) by the more rational procedure from $YbCl_3$ and 2K(**L**′) in thf [2]; its characterisation was then based on good C, H and N microanalyses and its EI-mass spectrum. It is noteworthy that the Ce analogue of **6** even with only one equivalent of $Li[CH(SiMe_3)_2]$ had yielded $[Ce\{CH(SiMe_3)_2\}_2(\mathbf{L}')]$ [2], possibly via a transient $Ce\{CH(SiMe_3)_2\}(\mathbf{L}')_2$.

The molecular structures of the isomorphous crystalline compounds **5** and **6** were established by single crystal X-ray diffraction, as illustrated in Fig. 4 for **6** and the selected geometric data listed in Table 2, which includes earlier results for the isoleptic neodymium compound [2]. For the new compound **5**, additional Supporting information relates to its satisfactory C, H and N microanalyses and IR and EI-mass spectral data; attempts to record ^1H NMR spectra in C_4D_8O failed. For **6**, the earlier data [2] has now been supplemented by ^1H and $^{13}C\{^1H\}$ NMR solution data in C_4D_8O; the former spectrum was closely similar to that previously recorded in C_7D_8 [2]. The geometry around the metal in each of these molecules is that of a distorted trigonal bipyramid, with one of the nitrogen atoms of each of the β-diketiminato ligands (N1 and N4) occupying an axial position. As for **2**–**4**, the π-delocalised NCCCN' core atoms of the ligands are almost coplanar.

*2.3. The synthesis and structure of the crystalline complex **7***

The crystalline heterobimetallic Yb/Li complex **7** was obtained as the monoetherate in modest yield from equivalent portions of $YbCl_3$ and Li(**L**")(thf) in thf and subsequent crystallisation from diethyl ether, Scheme 3. Its molecular structure is illustrated in Fig. 5 and selected geometrical parameters are listed in Table 3.

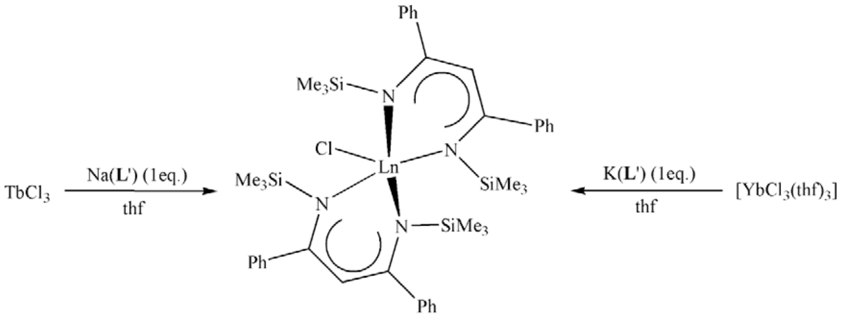
The ytterbium atom is at the centre of a much distorted square pyramid, the basal plane of which comprises the atoms N1N2Cl2Cl1. Thus the widest angles subtended at the ytterbium atom are N2–Yb–Cl1 and N1–Yb–Cl2 and the narrowest are N1–Yb–N2 and C1–Yb–Cl2. The core of the Yb-**L**″ moiety, YbN1C1C2C3N2, has a boat conformation in which the angle between the N1C1C3N2 and N1YbN2 or C1C2C3 planes is 106 and 160°, respectively. The lithium atom is at the centre of the distorted Cl1O1O2Cl2 tetrahedron, in which the angles most deviant from sp^3 values are Cl1–Li–Cl2 and Cl1–Li–O2 at 96.2(3) and 119.5(4)°, respectively. Heterobimetallic Ln/Li complexes related to **7** are well established for cyclopentadienyls, as first demonstrated for $[Nd\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(\mu\text{-}Cl)_2Li(thf)_2]$ [10], but **7** has just one antecedent in Group 3 or 4f metal β-diiminato chemistry, $[NdCl(\mathbf{L}^{C6H3Me2\text{-}2,6})(\mu\text{-}Cl)_2Li(thf)_2]$ [6], although alternative geometries are established as shown in **A** and **B** [7]. The bond lengths for the Yb-**L**″ core and the Yb–$Cl_{terminal}$ bond are available for comparison with those in **3** and **6**; whilst there is broad similarity, the Yb–N and Yb–Cl bonds are somewhat shorter for **7**, whilst the C_α–C_β bonds for **7** are longer.

In conclusion, the synthesis of seven (**6** previously known) crystalline β-diiminatolanthanoid(III) halides and the molecular structures of six of them are reported. In each of these, the ligand is *N*,*N*′-chelating and substantially π-delocalised. Whilst the structures of **2**–**6** are unexceptional, that of $[YbCl(\mathbf{L}'')(\mu\text{-}Cl)_2Li(OEt_2)_2]$ (**7**) has just a single precedent amongst Group 3 or 4f metal β-diiminates. The exclusive formation of $[LnCl(\mathbf{L}')_2]$ [Ln = Tb (**5**), Yb (**6**)] from the appropriate $LnCl_3$ precursor and only one equivalent of M(**L**′) (M = Na, K) is also noteworthy.

Table 1
Selected bond lengths (Å) and angles (°) for **2**, **3, 4** and [YCl_2(**L**)$(thf)_2$] [7].

	2 (M = Tb, Hal = Cl)	**3** (M = Yb, Hal = Cl)	**4** (M = Nd, Hal = I)	[YCl_2(**L**)$(thf)_2$] [7]
M–N	2.392(2), 2.399(2)	2.330(7), 2.334(7)	2.4369(17)	2.3766(17), 2.3746(18)
N–C_α	1.315(3), 1.321(3)	1.308(12), 1.336(11)	1.322(3)	1.324(3), 1.320(3)
C_α–C_β	1.401(3), 1.402(3)	1.399(13), 1.386(13)	1.393(2)	1.400(3), 1.400(3)
M–Hal	2.6046(6), 2.5941(6)	2.544(2), 2.536(2)	3.0963(3), 3.0688(3)	2.5724(6), 2.5823(6)
M–O	2.393(2), 2.428(2)	2.356(6), 2.4950(15)	2.4950(15)	2.3586(16), 2.381(4)
N–M–N’	79.22(6)	81.8(3)	73.68(8)	80.52(6)
M–N–C_α	128.20(5), 128.02(14)	126.8(6), 126.5(6)	126.92(14)	126.88(14), 126.91(14)
N–C_α–C_β	129.2(2), 129.0(2)	129.2(9), 129.7(9)	127.7(2)	129.3(2), 129.3(2)
C_α–C_β–$C_{\alpha'}$	126.1(2)	126.0(8)	124.0(3)	126.5(2)
N–M–O	175.38(16), 173.40(6)	176.2(3), 175.4(3)	170.10(6)	176.80(13), 175.88(6)
	96.07(6), 97.59(6)	95.8(3), 97.6(3)	97.17(6)	96.45(6), 97.70(13)
N–M–Hal	100.62(4), 100.40(5)	100.0(2), 99.49(19)	100.16(14)	99.87(4), 99.69(5)
	93.00(4), 92.98(5)	92.6(2), 92.26(19)	91.93(4)	92.75(4), 92.63(4)
Hal–M–Hal’	162.49(2)	163.89(8)	161.055(8)	163.63(2)
Hal–M–O	82.80(4), 84.27(4)	83.91(18), 83.95(18)	82.34(4)	83.29(4), 83.18(10)
	83.30(4), 84.37(4)	84.13(18), 84.29(18)	84.49(4)	84.83(10), 84.65(4)

Symmetry transformations used to generate equivalents atoms for **4**: x, $-y + 1/2$, z.



5 Tb: 64%, yellow
6 Yb: 43%, yellow

Scheme 2. Synthesis of **5** and **6**.

3. Experimental

3.1. General remarks

Syntheses were carried out under an atmosphere of argon or in a vacuum, using Schlenk apparatus and vacuum line techniques. The solvents used were reagent grade or better and were freshly distilled under dry nitrogen gas and freeze/thaw degassed prior to use. Diethyl ether and thf were dried and distilled from sodium benzophenone. C_6D_6, C_7D_8 and C_4D_8O for NMR spectroscopy were stored over molecular sieves (4 Å) under an argon atmosphere. Elemental analyses were provided by the University of North London. Melting points were taken in sealed capillaries. The ^1H and ^{13}C NMR spectra were recorded in a deuterated solvent and were referenced internally to residual solvent resonances, at ambient temperature using a Bruker DPX 300 machine. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. IR spectra were measured on a Perkin–Elmer 1720 FT spectrometer, as KBr discs. The complexes Li(**L**″) [11], Na(**L**′) and K(**L**′) [12], Na(**L**) [9c] and K(**L**) [9e] were prepared by published procedures. The compounds $LnCl_3$ (Ln = Ce, Tb, Yb), [$YbCl_3(thf)_3$] and [$NdI_3(thf)_2$] were purchased and were rigorously dried before use.

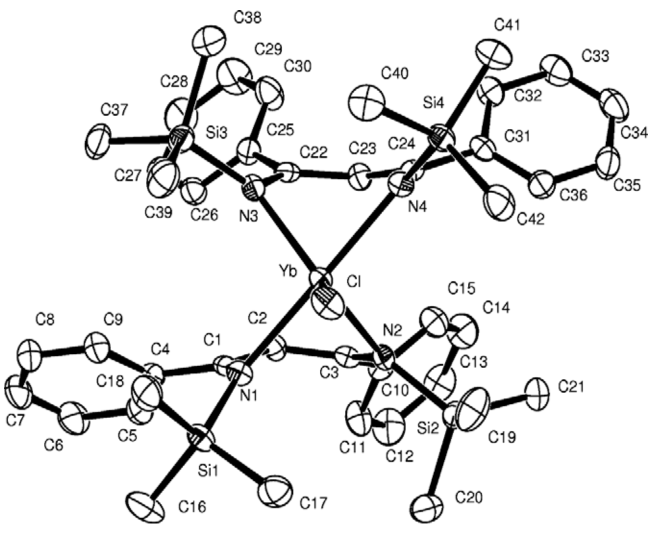


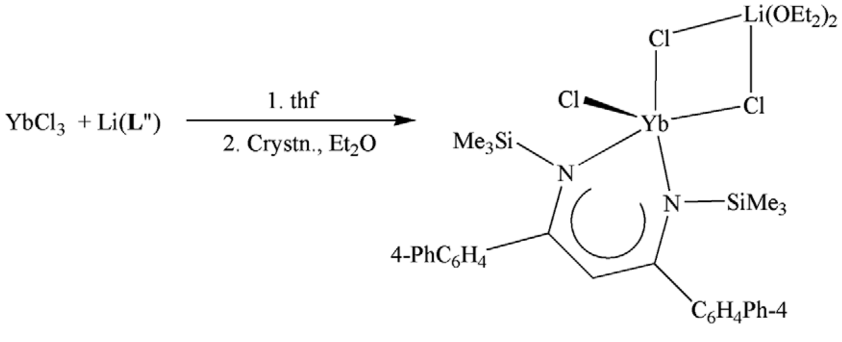
Fig. 4. Molecular structure of crystalline **6** (50% thermal ellipsoids).

3.2. Preparations of [$CeCl_2$(**L**)$(thf)_2$] (**1**)

A solution of K(**L**) (1.19 g, 2.36 mmol) in thf (30 cm^3) was added to a solution of $CeCl_3$ (0.56 g, 2.27 mmol) in thf (20 cm^3) at ambient temperature, whereafter the mixture was heated under reflux for 24 h. Volatiles were then removed *in vacuo* and the residue was extracted with diethyl ether (60 cm^3). The light orange filtered extract was concentrated to *ca*. 20 cm^3; after one day, small orange crystals of **1** (1.56 g, 84%) ($C_{41}H_{57}CeCl_2N_2O_2$ requires C, 60.0; H, 7.00; N, 3.41. Found: C, 60.1; H, 7.12; N, 3.51%), mp 181–182 °C (decomp.) were obtained. EI-MS [*m*/*e* (assignment and rel.

Table 2
Selected bond lengths (Å) and angles (°) for **5**, **6** and [NdCl(**L**′)$_2$] [2].

	5 (M = Tb)	**6** (M = Yb)	[NdCl(**L**′)$_2$] [2]
M–N1 (M–N4)	2.379(2), 2.383(2)	2.314(3), 2.318(3)	2.447(6), 2.464(6)
M–N2 (M–N3)	2.332(2), 2.330(2)	2.282(3), 2.271(3)	2.397(6), 2.410(6)
N1–C1 (N4–C24)	1.328(4), 1.325(4)	1.330(4), 1.329(4)	1.334(9), 1.304(9)
N2–C3 (N3–C22)	1.331(4), 1.336(4)	1.337(4), 1.344(4)	1.334(9), 1.309(9)
C1–C2 (C24–C23)	1.421(4), 1.432(4)	1.418(4), 1.420(4)	1.455(10), 1.431(10)
C2–C3 (C23–C22)	1.412(4), 1.408(4)	1.410(5), 1.410(5)	1.372(11), 1.416(10)
M–Cl	2.5872(8)	2.5154(8)	2.655(2)
N–M–N′	78.99(8), 79.42(8), 99.88(8)	80.69(9), 81.17(9), 97.99(9)	77.6(2), 76.5(2), 104.3(2)
	178.35(8), 125.44(9), 102.63(8)	179.16(10), 124.23(9), 99.75(9)	178.6(2), 124.1(2), 110.9(2)
M–N–C$_\alpha$	124.2(3), 98.19(17)	102.4(2), 99.55(19)	112.3, 111.1
	100.99(18), 99.50(18)	101.5(2), 102.62(19)	
N–C$_\alpha$–C$_\beta$	124.2(3), 123.5(3)	124.0(3), 123.4(3)	122.9(6), 123.4(6)
	123.1(3), 123.4(3)	123.2(3), 123.3(3)	124.4(6), 124.8(7)
N–M–Cl	89.24(6), 89.83(6)	89.84(7), 90.61(7)	90.4(1), 90.4(1)
	114.07(6), 120.47(6)	115.31(7), 120.45(7)	114.2(1), 121.6(1)



7: 31%, yellow

Scheme 3. Synthesis of **7**.

intensity, %)]: 675 ([*M*−2thf]$^+$, 6), 640 ([CeCl(**L**)]$^+$, 2), 615 ([Ce(**L**)]$^+$, 4). Compound **1** (like **2**, **3** and **4**) was sparingly soluble in C_6D_6.

3.3. Preparation of [TbCl$_2$(**L**)(thf)$_2$] (**2**)

A solution of Na(**L**) (0.97 g, 1.98 mmol) in thf (30 cm^3) was added to a suspension of $TbCl_3$ (0.52 g, 1.96 mmol) in thf (20 cm^3) at ambient temperature. The terbium chloride disappeared in about 10 min and the colour of the mixture changed from light brown to orange. The mixture was heated at 60 °C under reflux for *ca.* 12 h. Volatiles were removed *in vacuo* and the residue was extracted with diethyl ether (60 cm^3). The filtered extract was concentrated to *ca.* 20 cm^3 and set aside at 15 °C for 12 h, whereafter light yellow crystals of **2** (1.39 g, 85%) ($C_{41}H_{57}Cl_2N_2O_2Tb$ requires C, 58.6; H, 6.84; N, 3.34. Found: C, 58.7; H, 6.85; N, 3.28%), mp 109–110 °C (decomp.) were obtained. For ^{1}H and ^{13}C NMR data in CDCl$_3$, see Section 3.4. IR [KBr disc; ν_{max} (strong bands only)]: 2960, 1634, 1548, 1284, 757 cm^{-1}. EI-MS [*m*/*e* (assignment and rel. intensity,%)]: 694 ([*M*−2thf]$^+$, 62).

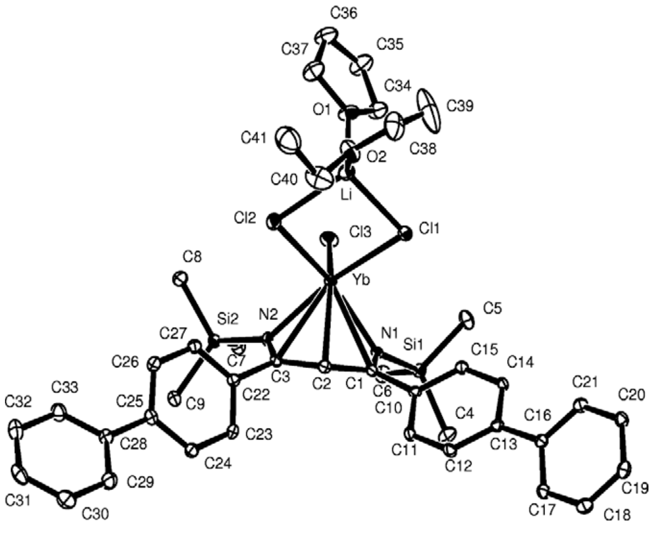
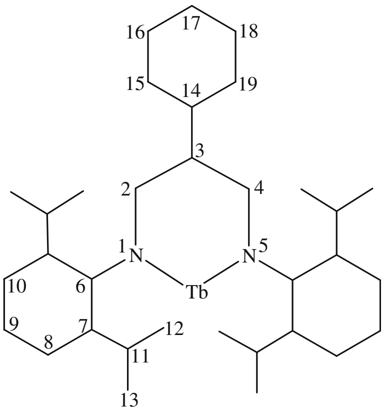


Fig. 5. Molecular structure of crystalline **7** (20% thermal ellipsoids).

Table 3
Selected bond lengths (Å) and angles (°) for **7**.

Yb–N1	2.250(3)	C1–C10	1.491(6)
Yb–N2	2.263(3)	C3–C22	1.505(6)
N1–C1	1.334(5)	Yb–Cl1	2.5890(11)
N2–C3	1.325(5)	Yb–Cl2	2.6054(12)
C1–C2	1.440(6)	Yb–Cl3	2.4860(12)
C2–C3	1.422(6)	Li–Cl1	2.370(8)
N1–Si1	1.760(4)	Li–Cl2	2.362(8)
N2–Si2	1.765(3)	Li–O2	1.940(9)
Li–O1	1.923(9)		
N1–Yb–N2	82.18(12)	N1–Yb–Cl1	90.74(9)
Yb–N1–C1	95.8(3)	N2–Yb–Cl2	88.28(9)
Yb–N2–C3	96.5(2)	N1–Yb–Cl2	150.15(9)
N1–C1–C2	121.9(4)	N2–Yb–Cl1	153.71(9)
N2–C3–C2	124.0(4)	N1–Yb–Cl3	104.99(9)
C1–C2–C3	127.5(4)	N2–Yb–Cl3	104.42(9)
C1–N1–Si1	130.2(3)	Cl2–Yb–Cl3	104.77(4)
C3–N2–Si2	130.4(3)	Cl1–Yb–Cl3	101.87(4)
N1–C1–C10	122.3(4)	Cl1–Li–Cl2	85.41(4)
N2–C3–C22	121.7(4)	Cl1–Yb–Cl2	85.41(4)

3.4. Assignment of the ^1H and ^{13}C NMR spectra in $CDCl_3$ of **2** (by Dr. A.G. Avent)



X

For the purpose of assignment, the ^{13}C (^{1}H) atom labels are shown in **X** (the thf CH_2's are excluded). Consistent with this structure, nine ^{1}H (in intensity ratios: 24:8:8:1) and thirteen ^{1}H-coupled ^{13}C peaks were observed in the NMR spectra in $CDCl_3$. Of the seven CH's only five appeared as doublets, two being singlets (because their protons were relaxing too rapidly): at sites 2/4, 8/10, 9, 11, 15/19, 16/18, and 17. The ^{1}H signal at δ −86.6 ppm and the ^{13}C at −30.5 ppm are assigned to 8/10 because of the ^{1}H intensity (4) and the sp^2 ^1J coupling. The other intense (4) ^{1}H signals must be the methine at C11 at δ −128.6 ppm, but this was relaxing too rapidly to couple to its ^{13}C nucleus. The δ (^{1}H) at δ −63.6 ppm and the ^{13}C at δ −1.9 ppm is assigned to sites 2/4, because of the large $^1J(^{13}C–^1H)$ of 190 Hz. The ^{1}H at δ 69.1 ppm and the ^{13}C at δ 206.3 ppm is assigned to site 17 on the basis of the ^{1}H intensity, although the $^1J(^{13}C–^1H)$ of 110 Hz is smaller than expected. This leaves three CH's at sites 9, 15/19, and 16/18 as the protons at δ 156.2 ppm (coupled to ^{13}C at δ 271.4 ppm), 139.0 ppm (relaxing too fast to couple), and δ 64.7 ppm (coupled to ^{13}C at δ 229.2 ppm).

Finally, the six ^{13}C singlets comprise the four quaternary carbons (6, 7, 3, 14) and two CH's with rapidly relaxing protons (11 and ANO) which are at δ 863.4, 611.7, 419.1, −90.0, −160.7, and −163.1 ppm.

3.5. Preparation of [YbCl$_2$(**L**)(thf)$_2$] (**3**)

A solution of Na(**L**) (0.88 g, 1.80 mmol) in thf (20 cm^3) was added to a solution of [YbCl$_3$(thf)$_3$] (0.85 g, 1.71 mmol) in thf (20 cm^3) at ambient temperature; the colour of the mixture had changed from light brown to red. The mixture was heated under reflux at 60 °C for *ca.* 12 h. Volatiles were then removed *in vacuo* and the residue was extracted with Et$_2$O (60 cm^3). The filtered extract, containing a trace of cyclohexane, was cooled to −25 °C and maintained at that temperature for *ca.* 3 d, then yielding red crystals of **3** (0.21 g, 13%) ($C_{41}H_{57}Cl_2N_2O_2Yb$ requires C, 61.0; H, 7.62; N, 2.90. Found: C, 59.1; H, 8.28; N, 3.26%), mp 78–79 °C (decomp.). IR [KBr disc; ν_{max} (strong bands only)]: 2961, 1635, 1549, 1303, 756 cm^{-1}. EI-MS [*m*/*e* (assignment and rel. intensity, %)]: 709 ([*M*−2thf]$^+$, 6.5), 673 ([YbCl(**L**)]$^+$, 4), 637 ([Yb(**L**)]$^+$, 1).

3.6. Preparation of [NdI$_2$(**L**)(thf)$_2$] (**4**)

A solution of K(**L**) (0.49 g, 0.96 mmol) in thf (20 cm^3) was added to a stirred suspension of [NdI$_3$(thf)$_2$] (0.81 g, 1.04 mmol) in thf (20 cm^3) at ambient temperature. After 48 h, the brown mixture was concentrated to *ca.* 5 cm^3 and extracted with Et$_2$O (50 cm^3). The orange extract was concentrated to *ca.* 20 cm^3 and after one day at 15 °C furnished red crystals of **4** (0.68 g, 70%), mp 175–176 °C ($C_{41}H_{57}I_2N_2NdO_2$ requires C, 48.9; H, 5.70; N, 2.78. Found: C, 48.7; H, 5.84; N, 2.76%). ^{1}H NMR (C_7D_8): δ 53.0 (s, 2 H), 14.85 (s, 2 H), 12.6 (br, 8 H), 10.4 (s, 2 H), 9.15 (s, 1 H), 7.78 (br, 8 H), 5.13 (s, 6 H), 3.35 (s, 12 H), −6.58 (s, 12 H), −9.20 (br, 4 H) ppm; ^{13}C{^{1}H} NMR (C_7D_8): δ 159.6, 146.1, 142.4, 132.4, 130.6, 125.8, 119.1, 74.6 (br), 37.0, 29.4, 23.7, 15.7, 14.5 (br) ppm.

3.7. Preparation of [TbCl(**L**′)$_2$] (**5**)

A solution of Na(**L′**) (1.80 g, 4.63 mmol) in thf (40 cm^3) was added to a stirred suspension of TbCl$_3$ (1.14 g, 4.30 mmol) in thf (30 cm^3) at room temperature. Stirring was continued for *ca.* 48 h, whereafter the mixture was filtered. The yellow filtrate was concentrated to *ca.* 20 cm^3 and set aside at 15 °C for *ca.* 12 h, to give yellow microcrystals of **5** (1.28 g, 64.3%, based on TbCl$_3$). ($C_{42}H_{58}ClN_4Si_4Tb$ requires C, 54.5; H, 6.32; N, 6.05. Found: C, 54.3; H, 6.42; N, 5.90%), mp 226 °C (decomp.). IR [KBr disc; ν_{max} (strong bands only)]: 2956, 1614, 1536, 1252, 842, 756 cm^{-1}. EI-MS [*m*/*e* (assignment and rel. intensity, %)]: 925, ([*M*]$^+$, 28), 890 ([Tb(**L**′)$_2$]$^+$, 4), 559 ([TbCl(**L**′)]$^+$, 57). An attempt to record ^{1}H NMR spectra failed; the paramagnetism of **5** in thf-d$_8$ was too pronounced to lock the field. X-ray quality crystals of **5** were grown from thf/Et$_2$O.

3.8. Preparation of [YbCl(**L**′)$_2$] (**6**)

A mixture of K(**L**′ (0.46 g, 1.14 mmol) and [YbCl$_3$(thf)$_3$] (0.52 g, 1.05 mmol) suspended in thf (40 cm^3) was stirred for *ca.* 24 h at ambient temperature, then filtered. The filtrate was concentrated (to *ca.* 10 cm^3) and Et$_2$O (10 cm^3) was added. The resulting bright yellow solution was cooled to −7 °C and maintained at that temperature for *ca.* 12 h, whereafter yellow crystals of **6** [0.23 g, 43% based on K(**L**′], mp 159 °C (decomp.) were obtained. ^{1}H NMR (C_4D_8O): δ 11.1 (br, 4 H), 10.4 (br, 8 H), 7.3 (s, 2 H), −0.04 (s, 4 H), −18.0 (br, 36 H) ppm; ^{13}C{^{1}H} NMR (C_4D_8O): δ 171.0, 144.2, 138.8, 136.1, 135.4, 129.1, 128.7, 127.8, 102.7, 15.7, 1.9, −21.9 ppm. IR [KBr disc; ν_{max} (strong bands only)]: 2960, 1536, 1488, 1254, 842, 756 cm^{-1}. EI-MS [*m*/*e* (assignment and rel. intensity, %)]: 939, ([*M*]$^+$, 7), 831 ([Yb(**L**′)$_2$–SiMe$_3$]$^+$, 5), 574 ([YbCl(**L**′)]$^+$, 7.5).

3.9. Preparation of [YbCl(**L**″)(μ-Cl)$_2$Li(OEt$_2$)$_2$] (**7**)

YbCl$_3$ (1.22 g, 4.37 mmol) was added to a stirred solution of [Li(**L**″)(thf)] (2.60 g, 4.36 mmol) in thf (150 cm^3). The resulting yellow solution was set aside for 24 h at ambient temperature. The volatiles were removed *in vacuo*; the solid residue was extracted with Et$_2$O. The extract was concentrated and cooled to −27 °C, furnishing yellow crystals of **7**•(OEt$_2$) (1.38 g, 31%). Repeated attempts to obtain C, H, N analyses failed, possibly because of decomposition in transit.

3.10. X-Ray crystallographic studies for **2**–**7**

Diffraction data were collected on a Nonius Kappa CCD diffractometer using monochromated Mo *K*α radiation, λ 0.71073 Å at 173(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. The structures were refined on all F^2 using SHELXL 97 [13]. Absorption corrections (not for **6**) were applied using MULTISCAN. The program package WINGX and drawing by ORTEP-3 for Windows, were used. For **3**, there were two independent molecules of cyclohexane

Table 4
Crystal data and structure refinement for **2**–**7**.

Compound	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{41}H_{57}Cl_2N_2O_2Tb$	$C_{41}H_{57}Cl_2N_2O_2Yb \cdot C_6H_{12} \cdot 0.5(C_4H_{10}O)$	$C_{41}H_{57}I_2N_2NdO_2$	$C_{42}H_{58}ClN_4Si_4Tb$	$C_{42}H_{58}ClN_4Si_4Yb$	$C_{41}H_{55}Cl_3LiN_2O_3Si_2Yb \cdot (C_4H_{10}O)$
M	839.71	975.04	1007.93	925.65	939.77	1024.50
Crystal system	monoclinic	triclinic	orthorhombic	triclinic	triclinic	monoclinic
Space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	*Pnma* (No. 62)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	34.5476(3)	11.3034(3)	17.6472(3)	11.8796(3)	11.8361(2)	15.4756(4)
b (Å)	11.3686(1)	13.6439(4)	18.2785(3)	12.4596(3)	12.4762(3)	18.3363(5)
c (Å)	23.4472(2)	16.2675(5)	13.2142(2)	15.7938(3)	15.7197(5)	18.7743(5)
α (°)	90	82.626(2)	90	84.715(1)	84.423(1)	90
β (°)	116.62	89.300(1)	90	86.132(1)	86.175(2)	108.132(1)
γ (°)	90	69.405(1)	90	89.969(1)	84.832(2)	90
V (Å^3)	8233.10(12)	2327.59(12)	4262.43(12)	2322.44(9)	2305.17(10)	5062.9(2)
Z	8	2	4	2	2	4
Absorption coefficient (mm^{-1})	1.88	2.16	2.70	1.72	2.22	2.09
Unique reflections, R_{int}	7619, 0.040	6717, 0.093	3877, 0.040	8059, 0.045	8014, 0.048	8912, 0.058
Reflections with $I > 2\sigma(I)$	6833	5854	3646	7348	7097	6766
Final *R* indices [$I > 2\sigma(I)$], R_1, wR_2	0.023, 0.052	0.065, 0.141	0.019, 0.046	0.027, 0.062	0.029, 0.058	0.040, 0.084
R indices (all data) R_1, wR_2	0.028, 0.054	0.079, 0.146	0.021, 0.047	0.032, 0.064	0.038, 0.061	0.063, 0.092

solvate, both on inversion centres, and also one molecule of diethyl ether disordered across an inversion centre for which 1,2 and 1,3 distance restraints were applied; for the ether solvent atoms, a common U_{iso} was used. The molecule **4** lies on a crystallographic mirror plane. Further details are in Table 4.

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Appendix A. Supplementary data

CCDC 714961–714966 for complexes **2**–**7** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.06.025.

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