Four-coordinate erbium organometallic and coordination complexes: Synthesis and structure

Kevin R.D. Johnson a, Adrien P. Côté b, Paul G. Hayes a,*

a Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive, Lethbridge, AB, Canada T1K 3M4
b Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, ON, Canada L5K 2L1

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In memory of Professor Herbert Schumann.

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The synthesis and reactivity of several erbium organometallic and coordination complexes supported by a β-diketiminato ancillary ligand are described. The reaction of ErCl₃(THF)₃ with LiL (L = ArNC(Me)CHC(Me)NAr; Ar = 2,6-Pr₂-C₆H₄) afforded the dimeric complex Er(L)Cl(Cl(ClI))₂(THF). 1. Reaction of complex 1 with four equiv of the bulky silylamide Li(N(SiMe₃)₂)₂ generated the unexpected four-coordinate adduct dimer [Er(L(N(SiMe₃)₂)Cl(μ-(Li(N(SiMe₃)₂))))₂]₂. 2. Conversely, reaction of 1 with two or four equiv of LiCH₂SiMe₃ led to the base-free mixed chloro/alkyl species [Er(L(CH₂SiMe₃)(μ-Cl))₂]. 3. and the four-coordinate dialkyl Er(L(CH₂SiMe₃)₂), 4, respectively. The protonolysis reactivity of 4 was demonstrated by reaction with [Et₂NH]⁺ to generate Er(L)₂. 5. By contrast, reaction of complex 1 with trimethylsilyl iodide resulted in the formation of Er₂I₃(THF), 6, through a ligand redistribution process. Compounds 1–6 were characterized by single crystal X-ray diffraction, multinuclear NMR spectroscopy, FT-IR spectroscopy, solution magnetic susceptibility measurements and CHN combustion analysis.

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1. Introduction

Although the cyclopentadienyl ligand (Cp) has been extremely influential in the development of organolanthanide chemistry [1], it is limited in the extent to which it can be electronically or sterically tuned [2]. Consequently, significant attention has recently been devoted to the exploration of non-Cp ancillaries for supporting rare earth metals [3]. In particular, the monoanionic β-diketiminato or “nacnac” ancillary ligand [R’NC(R’CHC(R’N)R’]⁻ has proven extremely useful in synthetic organometallic and coordination chemistry [4,5].

The nacnac ligand is an attractive scaffold for supporting lanthanide metal complexes of generic form LLnR₂. The modular nature of the ligand at the nitrogen atoms and carbon backbone allows facile incorporation of various substituents for fine-tuning of electronic properties and adjustment of the steric environment [5,6]. In particular, bulky N-aryl groups, such as 2,6-disopropylphenyl (Dipp) can be readily installed in high yield [7]. The steric stabilization imparted by such bulky groups often allows for the preparation of isolable low-coordinate species; many of which may not have been accessible with alternative ligands [5,8].

Of the smallest rare earth metals, well-defined organometallic and coordination complexes of scandium [9], lutetium [9r,10], and ytterbium(III) [11] supported by the nacnac ligand have been prepared over the past decade. Similarly, several groups have reported nacnac complexes of the larger yttrium ion and unique reactivity thereof [9r,s,10,11j,12]. While a large degree of attention has been focused on such yttrium complexes, presumably due to the fact that yttrium is diamagnetic, only limited investigations have involved late lanthanide congeners, such as erbium. This is surprising considering that size-based differences in reactivity are well-established [1a,c,13]. For example, a recent study comparing the ethylene polymerization ability of aminopyridinate-stabilized organolanthanide cations (Sc, Lu, Er and Y) reported that the highest activity, by a substantial margin, was exhibited by the erbium complex [14]. An investigation of erbium species, rather than those of yttrium, might be viewed as a disadvantage because the paramagnetic nature of the heavier f-element limits the usefulness of NMR spectroscopy. However, the technology of alternative characterization techniques, such as X-ray crystallography, easily allows for rapid and unambiguous structural determination of paramagnetic species [15]. In light of this, we believe that rich
organometallic and coordination chemistry can be harvested from the development of erbium complexes supported by nacnac ancillaries. Such complexes may prove valuable as catalysts for olefin polymerization [16], hydroamination [17], or lactone polymerization [18], to mention just a few possibilities. Furthermore, these species are likely to provide fundamental insight into rare bonding and structural motifs.

Previously, an erbium diiodide complex supported by a unique tetradeinate nacnac ligand ErL1 [L−1 = (2,6-Me2-C6H3)NC(Me)CHC(Me)N(2,6-Me2-C6H3)] was prepared [19], but only limited investigations into reactivity have since been published [20]. More recently, a complex of form ErL2Cl2(THF)2[15] [L2− = [(2,6-Me2-C6H3)NC(Me)CHC(Me)N(2,6-Me2-C6H3)]2] was reported as a pre-catalyst for isoprene polymerization [21]. Herein, we present the synthesis and characterization of a novel erbium dichloride dimer of the Dipp-substituted nacnac ligand, [ArNC(Me)CHC(Me)NAr]− [L−2], and the rare four-coordinate and base-free products which result from reaction with lithium bis(trimethylsilyl)amide and trimethylsilylmethyl lithium. Further derivatization at products which result from reaction with lithium bis(trimethylsilyl)amide and trimethylsilylmethyl lithium. Further derivatization at

2. Results and discussion

Complexation of the ancillary ligand L was achieved through the salt metathesis reaction of ErCl3(THF)3.5 with LiL (Scheme 1). Following reflux of the reagents in THF for 6.5 h, and subsequent recrystallization from toluene, the dimeric complex Er(LCl2(μ-Cl))2Er(L)(THF) (1) was isolated on a multigram scale in 79.5% yield as analytically pure, pale pink needles.

Single crystals of 1 suitable for X-ray diffraction were readily obtained from a concentrated toluene solution at −35 °C. The molecular structure of 1 is illustrated in Fig. 1 as a thermal ellipsoid plot. This complex adopts an asymmetric dimeric geometry with three chlorides bridging the two erbium(III) centers. Each erbium metal exhibits distorted octahedral geometry, with three sites occupied by the facially arranged bridging chlorides. Two of the six coordination sites of each erbium center are defined by the nacnac ligand coordinated in a κ2 fashion through its two nitrogen donors. The metal centers sit above the plane of the NCCCN backbone by 0.928 Å for Er(1) and 0.710 Å for Er(2). The sixth site of the octahedron is occupied by a chloride for one erbium center (Er(1)) and a neutral THF donor for the other (Er(2)). It is noteworthy that the distance between the bridging chlorides and Er(2) is shorter than that to Er(1), with average distances of 2.657 Å and 2.744 Å, respectively. As expected, the terminal Er(1)–Cl(1) distance (2.525 Å) is significantly less than that to the bridging chlorides. The solid-state structure for 1 is essentially isomorphous with the analogous samarium [22], ytterbium [11a] and ytrrium [12d] complexes.

Reaction of complex 1 with four equiv of Li[SmMe3]2 led to the formation of a unique mixed chloride/silylamido species, 2 (Scheme 2). Intriguingly, complex 2 contains Li[SmMe3]2 as a bridging adduct. In the solid-state, the Li[SmMe3]2 moiety coordinates to the chloride of the complex via the lithium atom, and bridges through the nitrogen atoms of each silylamido group, giving a dimeric species of formula [Er(L)[SmMe3]2Cl(μ-Li[SmMe3]2)]2. 2. It would appear that the dimeric structure of 2 stems from the propensity of group 1 metals, such as lithium, to dimerize and oligomerize in order to saturate their coordination spheres [23]. While lanthanide metals exhibit the same tendency, the bulky nacnac and silylamido substituents sterically saturate the erbium center, thus resulting in a reduced coordination number. The molecular structure of complex 2, as determined from an X-ray diffraction experiment, is depicted in Fig. 2 as a thermal ellipsoid plot.

Compound 2 represents a rare example of a bimetallic erbium coordination complex where each metal center is only four-coordinate. The complex exhibits distorted tetrahedral geometry at both erbium atoms. Each tetrahedron is defined by coordination of one chloride ligand, one silylamido group and the κ2 nacnac ancillary bound through the two nitrogen atoms. In the case of this complex, the metal sits significantly further above the plane defined by the NCCCN backbone (1.448 Å for Er(1) and 1.459 Å for Er(2) c.f. 0.928 Å for Er(1) and 0.710 Å for Er(2) in 1). Situation of the metal out of plane from the ancillary can be attributed to the extremely sterically congested environment in which it resides. Bonding of this nature is typical of four-coordinate rare earth metal complexes of L [5,9,12a].

As a further consequence of the bulk of L, it is speculated that steric hindrance from the Dipp groups inhibits the bridging silylamido moieties (N(4) and N(5)) from directly coordinating to each
Er(2) depicted in (B). Selected bond distances (shown in (A), while a monomeric moiety (with hydrogen atoms omitted for clarity) is 

\[ \begin{align*}
2.198(3), & \quad \text{Er(2)} \\
2.499(6), & \quad \text{Li(2)} \\
105.71(7), & \quad \text{N(1)} \\
2.256(3), & \quad \text{Er(1)} \\
116.3(1), & \quad \text{N(3)} \\
74.9(3), & \quad \text{N(5)} \\
2.261(3), & \quad \text{Er(2)} \\
114.4(1), & \quad \text{N(8)} \\
125.5(1), & \quad \text{N(3)} \\
84.3(1), & \quad \text{N(4)} \\
107.86(8), & \quad \text{N(6)} \\
114.31(8), & \quad \text{N(7)} \\
113.93(8), & \quad \text{N(6)} \\
75.7(3), & \quad \text{N(8)} \\
114.4(1), & \quad \text{N(7)} \\
106.91(8), & \quad \text{N(2)} \\
113.93(8), & \quad \text{N(5)} \\
104.8(3). & \quad \text{N(4)}
\end{align*} \]

Fig. 2. ORTEP diagram (50% probability) of \([\text{Er}_2(\text{N(SiMe}_3)_2)\text{Cl}_2(\mu-\text{LiN(SiMe}_3)_2)])_2\) (2). The dimeric structure (with hydrogen atoms and Pr groups omitted for clarity) is shown in (A), while a monomeric moiety (with hydrogen atoms omitted for clarity) is depicted in (B). Selected bond distances (Å and angles (°): Er(1)–N(1) = 2.259(3), Er(1)–N(2) = 2.256(3), Er(1)–N(3) = 2.193(3), Er(1)–Cl(1) = 2.5382(9), Er(2)–N(6) = 2.198(3), Er(2)–N(7) = 2.261(3), Er(2)–N(8) = 2.248(3), Er(2)–Cl(2) = 2.533(1), Li(1)–Cl(1) = 2.499(6), Li(2)–Cl(2) = 2.492(6), Li(1)–N(5) = 2.005(7), Li(2)–N(5) = 2.013(7), Li(1)–N(4) = 2.034(7), Li(2)–N(4) = 2.024(7), N(1)–Er(1)–N(2) = 84.3(1), N(1)–Er(1)–Cl(1) = 105.71(7), N(1)–Er(1)–N(3) = 124.8(1), N(2)–Er(1)–Cl(1) = 106.91(8), N(2)–Er(1)–N(3) = 116.3(1), N(3)–Er(1)–Cl(1) = 114.31(8), N(8)–Er(2)–N(7) = 87.1(1), N(7)–Er(2)–Cl(2) = 104.35(8), N(7)–Er(2)–N(6) = 125.5(1), N(8)–Er(2)–Cl(2) = 107.86(8), N(8)–Er(2)–N(6) = 114.4(1), N(6)–Er(2)–Cl(2) = 113.93(8), Li(1)–N(5)–Li(2) = 75.7(3), Li(1)–N(4)–Li(2) = 74.9(3), N(5)–Li(1)–N(4) = 104.7(3), N(5)–Li(2)–N(4) = 104.8(3).

Scheme 2. Reactivity of 1.

Er(1)–Cl bond length of 2.343(7) Å and Er–Cl bond lengths in complex 2 are relatively short. These distances are comparable to the Er–Cl bond of 2.593(9) Å in Er[N(Si(CH3)2CH2CH2Si(CH3)2]2(N2LiCl)2 [24], which is the only other structurally characterized four-coordinate chloride-containing erbium complex.

Multiple attempts to force elimination of LiCl from complex 2, in order to generate Er(L)(N(SiMe3)2)2, were unsuccessful. For example, extending the reaction period from 1.25 h to 18 h resulted in isolation of Er[N(SiMe3)2]3 [25], as the sole product (identified by combustion analysis and single crystal X-ray diffraction unit cell determination). This homoleptic compound likely arose via ligand scrambling to give a final product with reduced steric crowding at the erbium center. Conversely, addition of 18-crown-6 to complex 2 afforded two equiv of (18-crown-6)LiN(TMS)2 (identified by 7Li NMR spectroscopy) and presumably two equiv of Er(L)CIN(TMS)2. Unfortunately the latter species could not be unambiguously identified due to the presence of additional intractable reaction products.

The salt metathesis reaction of complex 1 with two equiv of LiCH2SiMe3 afforded the mixed alkyl/chloro complex [Er(L)(CH3)2SiMe3]2[N(μ-Chloride)], [Scheme 2]. Single crystals of 3 suitable for an X-ray diffraction experiment were readily obtained from a toluene solution at −35 °C. Complex 3 crystallized as a centrosymmetric dimer in the space group P21/n with bridging chloride ligands. The molecular structure of 3 is depicted in Fig. 3 as a thermal ellipsoid plot. Each Er center is five-coordinate with two sites occupied by the κ2 bound nacnac, and the other three sites de

\[ \begin{align*}
\text{Reactivity of } 1 \text{ reacts with } 4 \text{ equiv of } \text{NaN(SiMe}_3)_2 \text{ to generate the expected complex, Sm(L)(N(SiMe}_3)_2)\text{Cl}_2 \text{ [22]. It is likely that the difference in reactivity between erbium and samarium is due to the larger ionic radius of samarium, thus permitting coordination of two bulky silylamine ligands, rather than only one.}
\end{align*} \]
solid-state, this complex adopts a distorted tetrahedral geometry with half of a molecule of toluene in the asymmetric unit. In the structure (with hydrogen atoms and the monomeric dialkyl species Er(\((\text{CH}_2\text{SiMe}_3)\text{Pr}_2\)) [30], and Er(\((\text{CH}_2\text{SiMe}_3)\text{Pr}_2)(\text{ImMe}_2\text{Pz}_2)\)) [30], and Er(\((\text{CH}_2\text{SiMe}_3)\text{Pr}_2)(\text{Pr}_{	ext{trtriso}x})\)) [31], all of which are composed of three alkyl ligands and either one or two neutral donors. In comparison to the bond lengths in 3 and 4, these tris(alkyl) erbium complexes exhibit considerably elongated Er–C distances ranging from 2.392(3) Å to 2.428(3) Å. Significantly, complex 4 represents the first example of a structurally characterized neutral four-coordinate organoerbium complex. In comparison, there have only been five other four-coordinate erbium compounds previously characterized by X-ray crystallography, including a neutral erbium coordination complex [26], three anionic coordination complexes [24,27], and one anionic organometallic species [28]. Remarkably, the Er(1)–C(30) bond in 3 at 2.334(7) Å and the Er(1)–C(30) bond in 4 at 2.342(3) Å are not significantly different, and as such, represent the shortest Er–R (R = CH$_3$SiMe$_3$) bond lengths to date. There are only three other structurally characterized complexes containing an Er–CH$_2$SiMe$_3$ bond: Er(\((\text{CH}_2\text{SiMe}_3)\text{Pr}(\text{THF})_2\)) [29], Er(\((\text{CH}_2\text{SiMe}_3)\text{Pr}(\text{THF})(\text{ImMe}_2\text{Pz}_2)\)) [30], and Er(\((\text{CH}_2\text{SiMe}_3)\text{Pr}(\text{Pr}_{	ext{trtriso}x})\)) [31], all of which are composed of three alkyl ligands and either one or two neutral donors. In comparison to the bond lengths in 3 and 4, these tris(alkyl) erbium complexes exhibit considerably elongated Er–C distances ranging from 2.392(3) Å to 2.428(3) Å. Similar to that of 2, at 1.237 Å the erbium center in 4 sits significantly above the NCCCN backbone. While this out-of-plane bonding is not as dramatic as that observed in 2, it is more evident than that in five-coordinate 3 and six-coordinate 1. As expected, implementation of the sterically demanding –CH$_2$SiMe$_3$ and –N(SiMe$_3$)$_2$ ligands resulted in steric saturation of the erbium coordination sphere, thus giving rise to monomeric four-coordinate erbium complexes. Complex 4 is slightly thermally sensitive. In the solid-state, 4 decomposes at temperatures above 107 °C as evidenced by change from a pale pink solid to an oily brown residue and visible effervescence (presumably SiMe$_4$). The complex is, however, indefinitely stable if stored as a solid at -35 °C. Although lack of crystallinity of the decomposition product prevented unambiguous identification, it is speculated that intramolecular ligand metatation with concomitant loss of tetramethylsilane, as documented for other rare earth complexes, is probable [9a,12a,32]. When the thermal stability of complex 4 was monitored in solution (benzene-\(d_6\)) by $^1$H NMR spectroscopy, slight decomposition was observed.

after 24 h at 295 K. Under these conditions, approximately 15% product loss was observed with the concomitant generation of tetramethylsilane. Unfortunately, due to the paramagnetic nature of complex 4, the relative amount of decomposition versus tetramethylsilane formation could not be accurately established by NMR spectroscopy; therefore, no kinetic details about this process can be presented at this time.

In the context of the potentially reactive Er–C bonds in 3 and 4, it was expected that these species would serve as useful precursors for further derivatization at the metal center. Specifically, it was anticipated that access to an erbium iodide derivative could be achieved through the acid-base reaction of 4 with the iodide delivery reagent [Et3NH][I]. As expected, treatment of 4 with two equiv of [Et3NH][I] cleanly afforded the diiodide complex, Er(I)2 (5), with simultaneous production of tetramethylsilane and triethylamine (Scheme 3).

Recrystallization of complex 5 from a toluene/THF solution at −35 °C generated pale pink plates of 5 THF suitable for an X-ray diffraction experiment. Under these conditions, complex 5 THF crystallized in the monoclinic space group P21/c and is depicted in Fig. 5 as a thermal ellipsoid plot. In the solid-state, 5 THF is defined by coordination of two iodide ligands, one THF donor and the nacnac ancillary. The five-coordinate erbium center exhibits distorted trigonal bipyramidal geometry with the iodide ligands and one nitrogen atom of the nacnac in the equatorial positions. The apical sites of the complex are occupied by a molecule of THF and the second nitrogen of the nacnac ligand. Complex 5 THF exhibits relatively short Er–I contacts of 2.9077(5) Å and 2.9278(4) Å, which are slightly less than values previously reported for Er(I)2I3 (5), Er(I)2–I(2) = 2.9278(4), Er(I)–O(1) = 2.361(3), N(I)–Er(I)–N(2) = 128.4(1), I(1)–Er(1)–I(2) = 132.24(1), I(1)–Er(I)–O(1) = 101.39(7), I(2)–Er(I)–N(1) = 126.34(7), O(1)–Er(1)–N(2) = 168.4(1) Å.

In an effort to prepare complex 5 via an alternative route, complex 1 was reacted with 4 equiv of trimethylsilyliodide in toluene solution over 21 h at ambient temperature. Following removal of solvent and recrystallization, the unexpected complex ErL3[THF]6 (6) was isolated as a sparingly soluble pale pink solid in 89.8% yield (Scheme 2). By this route, formation of complex 6 is accompanied by elimination of trimethylsilylchloride, and generation of one equiv of “ErL2I”.

The formulation of “ErL2I” as a reaction by-product is tentative as we have been unable to isolate or characterize such a species; it is possible that it is unstable and prone to ligand redistribution.

Recrystallization of 6 from methylene chloride gave rise to pale pink prisms that were suitable for X-ray diffraction. Complex 6 crystallized in centrosymmetric orthorhombic space group Pbcn (#60). In the unit cell of the crystal structure, each erbium center sits on a 2-fold rotation axis. This symmetry is exhibited in the molecular structure along the O(1)–Er(1)–I(2) vector. In the solid-state, complex 6 displays a distorted meridional octahedral geometry comprised of three iodide ligands and three THF donors (Fig. 6). Contrary to the previously reported erbium iodide ion pair, ErL3[THF]3.5 [34], which was only characterized by IR spectroscopy and combustion analysis, 6 is a neutral erbium triiodide THF adduct. Inspection of the IR spectrum of complex 6 revealed many similar absorption bands to other previously reported rare earth complexes of the generic form LnCl3[THF]3 [35]. Distinct differences were noted, however, between the IR spectra of 6 and that of the ion pair, ErL3[THF]3.5 [34]. The Er(1)–I(1)–I(2) and Er(1)–I(1)–I(1) bond lengths of 2.9276(6) Å and 2.9504(4) Å, respectively, are quite similar to the values reported for 5-THF and agree well with other previously reported Er–I bonds [19,33].

In the attempted synthesis of 5 via reaction of complex 1 with trimethylsilyliodide, significant reactivity issues were observed. Specifically, a ligand redistribution process led to the formation of 6 rather than 5. Comparably, the ease in which complex 5 was synthesized by reaction of 4 with [Et3NH][I] supports the value of protonolysis reactivity in lanthanide chemistry as a means for accessing certain structural motifs.

While erbium chloride complex 1 has been demonstrated here as a useful precursor for salt metathesis reactions with various amido- and organo-lithium reagents, the iodide complexes, 5 and 6, are of interest to us due to their potential for reactivity with...
organio-potassium reagents. It has previously been shown that an iodide ligand can be more labile than chloride when allowed to react with potassium compounds [12b,34]. Therefore, it is expected that diiodide ErL2I (5) may facilitate access to the dibenyl analog of complex 4 (ErL2(THF)2) upon reaction with benzyl potassium. We are currently in the process of investigating the viability of this synthetic pathway.

3. Conclusions

The compound Er(L)Cl[μ-Cl]2Er(L)(THF) (1) was readily prepared via the reaction of erbium chloride and LiL. Salt metathesis of 1 with four equiv of LiN(SiMe3)2 generated the mixed chloro/silylamido dimer [Er(L)[N(SiMe3)2]2Cl[μ-(LiN(SiMe3)2)]2] (2) as an unusual example of a four-coordinate erbium coordination complex. Reaction of 1 with either two or four equiv of LiCH2SiMe3 generated the mixed chloro/alkyl dimer [Er(L)(CH2SiMe3)[μ-LiCl]2] (3) or the dialkyl monomer Er(L)(CH2SiMe3)2 (4), respectively. As complex 4 represents a rare example of a relatively stable four-coordinate dialkyl lanthanide complex, we are currently investigating its small molecule reactivity in an effort to further obtain unique structures and bonding modes. As a preliminary investigation into the reactivity of 4, the erbium diiodide complex ErL2I (5) was prepared via reaction of 4 with [Et3NH]I. Complex 5, in addition to the iodide complex ErL3(THF)5 (6) (obtained by reaction of 1 with trimethylsilyliodide), will likely serve as useful precursors for salt metathesis reactions with organo-potassium reagents and we are currently exploring the full range of their utility.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere with the rigorous exclusion of oxygen and water using standard glove box (MBraun) or high vacuum line techniques. The solvents THF, pentane, toluene and methylene chloride were dried and purified using a solvent purification system (MBraun) and distilled under vacuum prior to use from sodium benzophenone ketyl (THF), "titanocene" (pentane and toluene) or calcium hydride (methylene chloride). Unless specified otherwise, solvents were introduced directly into reaction flasks by vacuum transfer with condensation at −78 °C. Deuterated solvents were dried over sodium benzoate (Ultrashield) spectrometer (1H 300.13 MHz, 7Li 116.64 MHz) and distilled under vacuum and stored in glass bombs under argon. Samples for NMR spectroscopy were recorded on a 300 MHz Bruker Avance II (Ultrashield) spectrometer (1H 300.13 MHz, 13C 75.47 MHz, 19F 376.26 MHz, 11B 116.64 MHz) and referenced relative to either SiMe4 or external LiCl for 1Li. Peak width at half-height is given for the paramagnetically broadened resonances. Solution magnetic moments were determined by the Evans method [36] with an appropriate diamagnetic correction [37] and are the average value of at least two independent measurements. FT-IR spectra were recorded on a Bruker ALPHA FT infrared spectrometer with Platinum ATR sampling. Elemental analyses were performed using an Elementar Americas Vario MicroCube instrument. The reagents [Et3NH][Cl] [38], and LiL [39], were prepared according to literature procedures. [Et3NH]I was further purified by recrystallization from an acetone-methanol mixture (1:1) at −35 °C and dried thoroughly under vacuum. The synthesis of ErCl3(THF)3.5 was carried out by a modified literature procedure [40]. Anhydrous ErCl3 was purchased from Strem Chemicals and used as received. All other reagents were obtained from Aldrich Chemicals or Alfa Aesar and used as received.

4.2. Synthesis of complexes

4.2.1. Er(L)Cl(μ-Cl)2Er(L)(THF) (1)

To a 100 mL bomb charged with LiL (5.12 g, 12.0 mmol) and ErCl3(THF)3.5 (6.35 g, 12.1 mmol) THF (70 mL) was added to give a brown suspension. The reaction mixture was heated to 85 °C for 6.5 h resulting in a clear red solution. The solvent was removed in vacuo leaving a yellow–beige residue that was taken into a glove box. Toluene (20 mL) was added to reconstitute the solid, and the resulting suspension was filtered through a fine frit to remove LiCl. The frit was washed with toluene (2 × 1 mL) and the dark red filtrate was concentrated under vacuum. Upon cooling the solution to −35 °C for 48 h, pink needles of 1 developed, and were collected by filtration, washed with pentane, and dried in vacuo. Yield: 6.63 g (79.5%). Magnetic moment (chloroform-d, 295 K): μeff 11.8 μB. 1H NMR (benzene-d6, 295 K): δ 121.39 (J1/2 = 864 Hz), 56.64 (J1/2 = 97 Hz), 55.01 (J1/2 = 301 Hz), 39.51 (J1/2 = 89 Hz), 37.35 (J1/2 = 177 Hz), 36.59 (J1/2 = 80 Hz), 34.71 (J1/2 = 115 Hz), 28.99 (J1/2 = 62 Hz), 27.70 (J1/2 = 80 Hz), 20.38 (J1/2 = 89 Hz), 17.49 (J1/2 = 159 Hz), 15.31 (J1/2 = 97 Hz), −1.41 (J1/2 = 132 Hz), −2.59 (J1/2 = 192.4 Hz), −6.80 (J1/2 = 180 Hz), −11.90 (J1/2 = 96 Hz), −17.51 (J1/2 = 175 Hz), −21.01 (J1/2 = 144 Hz), −26.07 (J1/2 = 166 Hz), −29.63 (J1/2 = 68 Hz), −36.62 (J1/2 = 89 Hz), −42.96 (J1/2 = 263 Hz), −61.77 (J1/2 = 201 Hz), −166.27 (J1/2 = 874 Hz). Anal. Calcd. (%) for C32H58Cl2Er2Li2N8Si8: C, 51.94; H, 8.19; N, 5.91. Found: C, 54.32; H, 6.62; N, 5.31. Complex 1 can be alternatively prepared in approximately the same yield through an analogous procedure utilizing anhydrous ErCl3 in place of ErCl3(THF)2.5.

4.2.2. [Er(L)(N(SiMe3)2)2Cl2(μ-(LiN(SiMe3)2))2] (2)

In a glove box, toluene (10 mL) was added at ambient temperature to an intimate mixture of 1 (0.371 g, 0.268 mmol) and LiN(SiMe3)2 (0.196 g, 0.117 mmol) in a 25 mL Erlemeyer flask. As the reaction mixture was stirred for 1.25 h, it rapidly took on a cloudy peach-orange appearance. The solution was filtered through a fine porosity frit and the clear orange filtrate was concentrated in vacuo to 2 mL and left at −35 °C to crystallize. Analytically pure pale pink crystals of 2 were collected by filtration, washed with pentane, and dried under reduced pressure. Yield: 0.302 g (59.4%). Magnetic moment (benzene-d6, 295 K): μeff 13.1 μB. 1H NMR (benzene-d6, 295 K): δ 116.79 (J1/2 = 619 Hz), 99.84 (J1/2 = 214 Hz), 79.05 (J1/2 = 128 Hz), 44.23 (J1/2 = 48 Hz), 29.04 (J1/2 = 80 Hz), 9.35 (J1/2 = 103 Hz), 4.71 (J1/2 = 44 Hz), −40.41 (J1/2 = 90 Hz), −59.66 (J1/2 = 167 Hz), −94.61 (J1/2 = 378 Hz), −238.83 (J1/2 = 322 Hz), 1Li NMR (benzene-d6, 295 K): δ 11.17. Anal. Calcd. (%) for C32H58Cl2Er2Li2N8Si8: C, 51.94; H, 8.19; N, 5.91. Found: C, 52.16; H, 8.12; N, 5.91.

4.2.3. [Er(L)(CH2SiMe3)[μ-Cl]2]2 (3)

In a glove box, a 25 mL Erlemeyer flask was charged with 1 (0.248 g, 0.179 mmol) and LiCH2SiMe3 (0.0340 g, 0.361 mmol) and then cooled to −35 °C. Cold toluene (5 mL) was added at −35 °C and the reaction mixture was left at this temperature for 1 h with mixing. The cloudy orange solution was then allowed to warm to ambient temperature where it was stirred for a further 0.5 h. The reaction mixture was filtered through a fine porosity frit and the frit was washed with 2 × 1 mL of toluene. The clear yellow filtrate was concentrated slightly under vacuum and left at −35 °C to crystallize. Small pale pink crystals of 3 were collected by filtration, washed with cold pentane, and dried under reduced pressure. Yield: 0.057 g (22.3%). Magnetic moment (chloroform-d, 295 K): μeff 4.05 μB. 1H NMR (chloroform-d, 295 K): δ 179.16 (J1/2 = 1475 Hz), 48.86 (J1/2 = 65 Hz), 41.23 (J1/2 = 300 Hz), 39.73 (J1/2 = 76 Hz), 28.44 (J1/2 = 38 Hz), 22.92 (J1/2 = 130 Hz), 1.51 (132 Hz), −1.21 (J1/2 = 59 Hz), −49.53 (J1/2 = 55 Hz), −83.60
(Δν/2 = 171 Hz), –222.75 (Δν/2 = 849 Hz). Anal. Calcld. (%) for C60H98Cl2Er4Na4Si2: C, 56.02; H, 7.41; N, 3.96. Found: C, 55.85; H, 7.18; N, 3.96.

4.2.4. Er(L)(CH2SiMe3)2 (4)
In a glove box, a 25 mL Erlenmeyer flask was charged with 1 (1.11 g, 0.802 mmol) and LiC2H5Me3 (0.302 g, 3.21 mmol) and then cooled to –35 °C. Cold toluene (10 mL) was added at –35 °C and the reaction mixture was left at this temperature for 1 h with mixing. The cloudy orange solution was then allowed to warm to ambient temperature where it was stirred for a further 0.5 h. The reaction mixture was filtered through a fine porosity frit and the filtrate was washed with 2 × 1 mL of toluene. The clear orange filtrate was concentrated to 5 mL under vacuum and then left at –35 °C to crystallize. Small pale pink crystals of 4 were collected by filtration, washed with cold pentane, and dried under reduced pressure. Yield: 0.763 g (62.6%). Magnetic moment (benzene-d6, 295 K): μeff 7.2 μB. 1H NMR (benzene-d6, 295 K): δ 217.74 (Δν/2 = 1973 Hz), 104.09 (Δν/2 = 1252 Hz), 87.04 (Δν/2 = 1252 Hz), 70.21 (Δν/2 = 123 Hz), 32.29 (Δν/2 = 1802 Hz), 15.81 (Δν/2 = 183 Hz), –40.29 (Δν/2 = 189 Hz), –51.03 (Δν/2 = 241 Hz), –134.05 (Δν/2 = 693 Hz), –265.36 (Δν/2 = 2447 Hz), –519.18 (Δν/2 = 6164 Hz). Anal. Calcld. (%) for C80H56Cl2Er4N2Si2: C, 58.52; H, 8.36; N, 3.69. Found: C, 58.41; H, 8.37; N, 3.54.

4.2.5. Er(L)(5)
To a 100 mL round-bottom flask charged with 4 (0.333 g, 0.438 mmol) and [Et3NH]+Cl (0.203 g, 0.886 mmol) methylene chloride was added (20 mL) to give a clear pale orange solution. The reaction mixture was allowed to warm to ambient temperature and then stirred for 1 h. All volatiles were removed from the reaction mixture to afford a pink residue that was taken into a glove box. The residue was reconstituted in toluene (5 mL), filtered to remove excess [Et3NH]+, concentrated under reduced pressure to ~2 mL and left at –35 °C to crystallize. Pink-orange crystals of 5 were collected by filtration, washed with pentane, and dried in vacuo. Yield: 0.0928 g (25.3%). Magnetic moment (THF, chloroform-d, 295 K): μeff 9.0 μB. 1H NMR (THF, benzene-d6, 295 K): δ 32.87 (Δν/2 = 1122 Hz), 30.34 (Δν/2 = 597 Hz), 25.90 (Δν/2 = 670 Hz), 21.50 (Δν/2 = 47 Hz), –13.91 (Δν/2 = 529 Hz), –19.07 (Δν/2 = 103 Hz), –30.22 (Δν/2 = 1104 Hz), –62.62 (Δν/2 = 195 Hz). Anal. Calcld. (%) for C60H98Er4N2 (5-Toluene): C, 46.45; H, 5.31; N, 3.01. Found: C, 46.15; H, 5.73; N, 2.97.

4.2.6. Er3f(THF)3 (6)
Addition of toluene (40 mL) to a 100 mL round bottom flask charged with 1 (0.924 g, 0.686 mmol) generated a clear pink solution. Trimethylsilyl iodide (0.40 mL, 2.8 mmol) was added via syringe at ambient temperature giving a clear pale yellow solution. The reaction mixture was stirred for 21 h, over which time the product precipitated as an off-white solid. The volatiles were removed in vacuo leaving a pale yellow residue. In a glove box, the residue was reconstituted in toluene and hot filtration was performed to remove remaining solids. Upon cooling the toluene solution to ambient temperature the product separated as an oil. Addition of THF (1 mL) liberated a sparingly soluble off-white solid. The supernatant was decanted, and the solid was washed with pentane (5 × 1 mL) and dried under vacuum to give 6 as a very pale pink amorphous solid. Additional product was obtained by removing all volatiles from the toluene/THF supernatant. The

Table 1
Summary of crystallography data collection and structure refinement for compounds 1–6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Z</th>
<th>1°</th>
<th>2°</th>
<th>3°</th>
<th>4°</th>
<th>5°</th>
<th>6°</th>
</tr>
</thead>
<tbody>
<tr>
<td>C60H98Cl2Er4N2O</td>
<td>1475.83</td>
<td>1896.95</td>
<td>Monoclinic</td>
<td>P21/n</td>
<td>P21/n</td>
<td>Monoclinic</td>
<td>P21/n</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>C60H98Cl2Er4Li4N2Si4</td>
<td>1599.40</td>
<td>804.90</td>
<td>Monoclinic</td>
<td>P21/c</td>
<td>C2/c</td>
<td>Monoclinic</td>
<td>P21/c</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>C60H98Er4N2Si2</td>
<td>956.37</td>
<td>Monoclinic</td>
<td>P21/c</td>
<td>P21/c</td>
<td>P21/c</td>
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<td>P21/c</td>
<td></td>
</tr>
<tr>
<td>C60H98Er4N2</td>
<td>764.27</td>
<td>Orthorhombic</td>
<td>Pbca</td>
<td>Pbca</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Crystallographic data for compounds 1–6.
* Z: Crystal system.
* 1°: Space group.
* 2°: Crystal color.
* 3°: Crystal habit.
* 4°: Crystal size.
* 5°: Crystal density.
* 6°: Complement.

* a: Crystal system.
* b: Space group.
* c: Crystal color.
* d: Crystal habit.
* e: Crystal size.
* f: Crystal density.
* g: Complement.

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residual oil was extracted with THF (5 mL) and the THF solution was layered with pentane. The product precipitated and the supernatant was decanted. The solid was washed with pentane (5 × 1 mL) and dried under reduced pressure to yield a second crop of product. Combined yield: 0.459 g (89.8%). Magnetic moment (chloroform-d, 295 K): $\mu_{\text{eff}} = 8.7$ μB. IR: $v$ (cm$^{-1}$) 1368 (w), 1342 (w), 1294 (w), 1247 (w), 1178 (w), 1038 (m), 998 (m), 953 (w), 915 (w), 858 (sh, m), 828 (m), 752 (m), 476 (m), Anal. Calcld. (%) for C12H24ErI3O3: C, 18.86; H, 2.87; N, 2.51; Br, 8.64; O, 6.35.

4.3. X-ray crystallography

Single crystals suitable for X-ray diffraction were obtained by recrystallization of compounds 1–4 from concentrated toluene solutions at –35 °C, complex 5 from a concentrated toluene/THF mixture at –35 °C and complex 6 from a concentrated methylene chloride solution at –35 °C. Crystals were cooled in dry Paratone oil under an argon atmosphere and mounted onto a glass fiber. Data were collected at –100 °C using a Bruker SMART APEX II diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) outfitted with a CCD area-detector and a KRYO-FLEX liquid nitrogen vapor cooling device. A data collection strategy using APEX2 software [41]. Data reduction and correction for Lorentz polarization were performed using SAINT-Plus software [42]. Absorption corrections were applied using SQUEEZE [43]. Positions were calculated and isotropically re

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