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

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In memory of Professor Herbert Schumann.

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ABSTRACT

The synthesis and reactivity of several erbium organometallic and coordination complexes supported by a β-diketiminato ancillary ligand are described. The reaction of $ErCl_3(THF)_{3.5}$ with Li**L** (**L** = ArNC(Me)CHC(Me)NAr; Ar = 2,6-$^{i}Pr_2$-C_6H_3) afforded the dimeric complex Er(**L**)Cl(μ-Cl)$_3$Er(**L**)(THF), **1**. Reaction of complex **1** with four equiv of the bulky silylamide $LiN(SiMe_3)_2$ generated the unexpected four-coordinate adduct dimer $[Er(\mathbf{L})N(SiMe_3)_2Cl(\mu\text{-}(LiN(SiMe_3)_2))]_2$, **2**. Conversely, reaction of **1** with two or four equiv of $LiCH_2SiMe_3$ led to the base-free mixed chloro/alkyl species $[Er(\mathbf{L})(CH_2SiMe_3)(\mu\text{-}Cl)]_2$, **3**, and the four-coordinate dialkyl $Er(\mathbf{L})(CH_2SiMe_3)_2$, **4**, respectively. The protonolysis reactivity of **4** was demonstrated by reaction with $[Et_3NH]I$ to generate Er(**L**)I_2, **5**. By contrast, reaction of complex **1** with trimethylsilyliodide resulted in the formation of $ErI_3(THF)_3$, **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.

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 $[R'NC(R)CHC(R)NR']^-$ 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 $LLnR_2$. 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-di*iso*propylphenyl (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,s,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

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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 tetradentate nacnac ligand Er**L**′I_2 ([**L**′]$^-$ = [$Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$]$^-$) was prepared [19], but only limited investigations into reactivity have since been published [20]. More recently, a complex of form Er**L**″$Cl_2(THF)_2$([**L**″]$^-$ = [(2,6-Me_2-C_6H_3)NC(Me)CHC(Me)N(2,6-Me_2-C_6H_3)]$^-$) 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**]$^-$, Ar = 2,6-^{i}Pr$_2$-C_6H_3), and the rare four-coordinate and base-free products which result from reaction with lithium bis(trimethylsilyl) amide and trimethylsilylmethyllithium. Further derivatization at the metal center was accomplished by reaction of the organoerbium complexes with [Et_3NH]I. Additionally, the synthesis of the potentially useful starting material, $ErI_3(THF)_3$, is described. In summary, this work highlights many of the similarities and differences in reactivity patterns that exist between erbium and other rare earth metals.

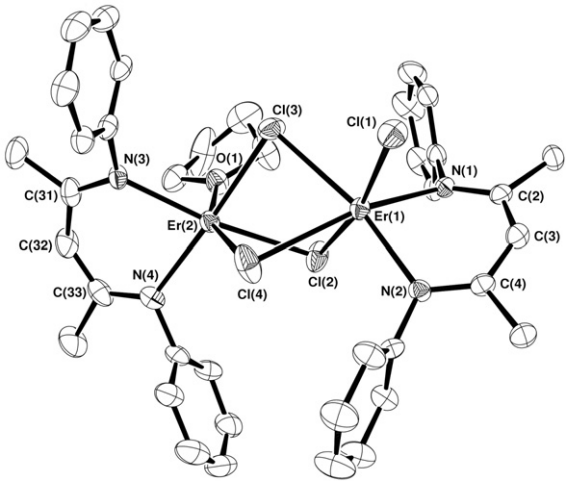
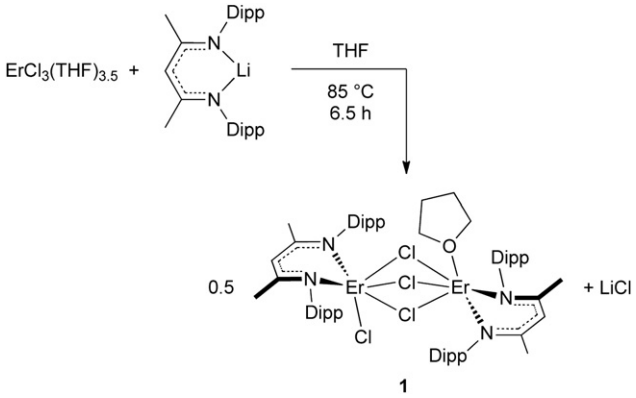


Fig. 1. ORTEP diagram (50% probability) of Er(**L**)Cl(μ-Cl)$_3$Er(**L**)(THF) (**1**) with hydrogen atoms, ^{i}Pr groups and the solvent molecule of crystallization omitted for clarity. Selected bond distances (Å) and angles (°): Er(1)–N(1) = 2.294(4), Er(1)–N(2) = 2.296(4), Er(1)–Cl(1) = 2.525(1), Er(1)–Cl(2) = 2.720(1), Er(1)–Cl(3) = 2.747(1), Er(1)–Cl(4) = 2.767(1), Er(2)–N(3) = 2.312(4), Er(2)–N(4) = 2.302(4), Er(2)–Cl(2) = 2.665(1), Er(2)–Cl(3) = 2.660(1), Er(2)–Cl(4) = 2.646(1), Er(2)–O(1) = 2.295(3), N(1)–Er(1)–N(2) = 83.2(1), Cl(1)–Er(1)–Cl(2) = 165.82(4), Cl(3)–Er(1)–N(2) = 167.8(1), Cl(4)–Er(1)–N(1) = 160.5(1), N(3)–Er(2)–N(4) = 81.2(1), Cl(3)–Er(2)–N(4) = 174.5(1), Cl(2)–Er(2)–N(3) = 170.7(1), Cl(4)–Er(2)–O(1) = 157.20(9).

2. Results and discussion

Complexation of the ancillary ligand **L** was achieved through the salt metathesis reaction of $ErCl_3(THF)_{3.5}$ with Li**L** (Scheme 1). Following reflux of the reagents in THF for 6.5 h, and subsequent recrystallization from toluene, the dimeric complex Er(**L**)Cl(μ-Cl)$_3$Er(**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 κ^2 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 (1) Å) is significantly less than that to the bridging chlorides. The solid-state structure for **1** is essentially isostructural with the analogous samarium [22], ytterbium [11a] and yttrium [12d] complexes.

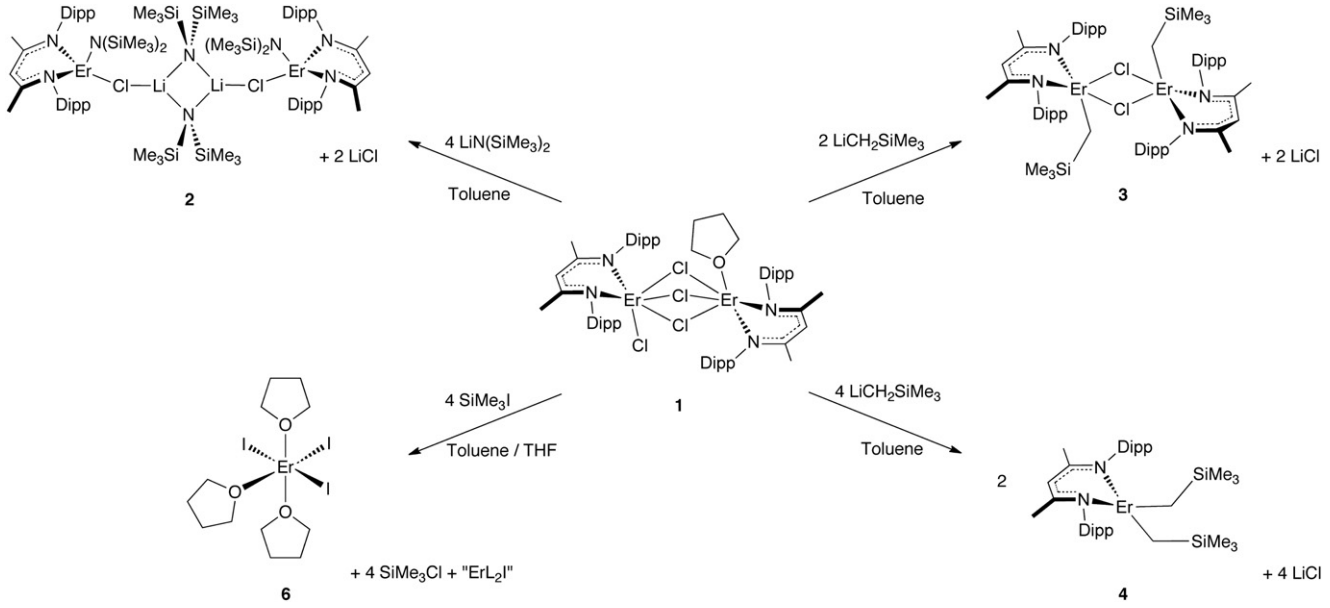


Scheme 1. Synthesis of **1** from $ErCl_3(THF)_{3.5}$ and Li**L**.

Reaction of complex **1** with four equiv of LiN($SiMe_3$)$_2$ led to the formation of a unique mixed chloride/silylamido species, **2** (Scheme 2). Intriguingly, complex **2** contains LiN($SiMe_3$)$_2$ as a bridging adduct. In the solid-state, the LiN($SiMe_3$)$_2$ 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**)N($SiMe_3$)$_2$Cl(μ-(LiN($SiMe_3$)$_2$))]$_2$, **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 silylamide 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 κ^2 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** [5,9i,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



Scheme 2. Reactivity of **1**.

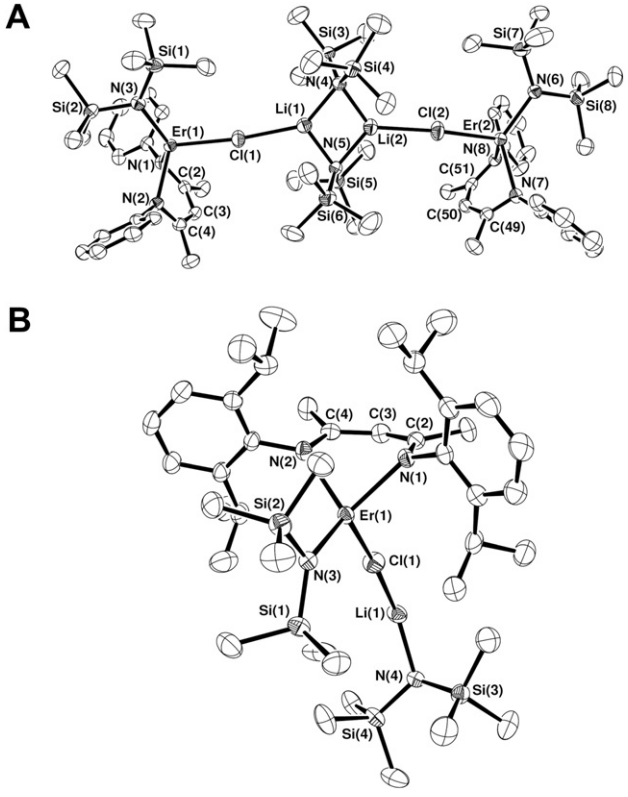


Fig. 2. ORTEP diagram (50% probability) of [Er(**L**)N(SiMe$_3$)$_2$Cl(μ-(LiN(SiMe$_3$)$_2$))]$_2$ (**2**). The dimeric structure (with hydrogen atoms and ^{i}Pr groups omitted for clarity) is shown in (A), while a monomeric moiety (with hydrogen atoms omitted for clarity) is depicted in (B). Selected 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).

erbium center. It is interesting to note that the samarium analog of **1** reacts with 4 equiv of NaN(SiMe$_3$)$_2$ to generate the expected complex, Sm(**L**)(N(SiMe$_3$)$_2$)$_2$ [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 silylamide ligands, rather than only one.

At 2.5382(9) Å (Er(1)–Cl(1)) and 2.533(1) Å (Er(2)–Cl(2)) the 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(CH$_3$)$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$]}$_3$(μ-Cl)Li(Et$_2$O)$_3$ [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(SiMe$_3$)$_2$)$_2$, were unsuccessful. For example, extending the reaction period from 1.25 h to 18 h resulted in isolation of Er[N(SiMe$_3$)$_2$]$_3$ [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 ^{7}Li NMR spectroscopy) and presumably two equiv of Er(**L**)ClN(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 LiCH$_2$SiMe$_3$ afforded the mixed alkyl/chloro complex [Er(**L**)(CH$_2$SiMe$_3$)(μ-Cl)]$_2$, **3** (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 $P2_1/n$ 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 κ^2 bound nacnac, and the other three sites defined by one trimethylsilylmethyl group and two bridging chlorides. To the best of our knowledge, complex **3** is the first structurally characterized erbium complex containing only one trimethylsilylmethyl ligand. Metrical parameters of interest in complex **3** include the Er(1)–C(30) bond length of 2.343(7) Å and Er–Cl distances of 2.653(2) Å (Cl(1)) and 2.638(2) Å (Cl(1)_1). The similarity of the Er–Cl bond

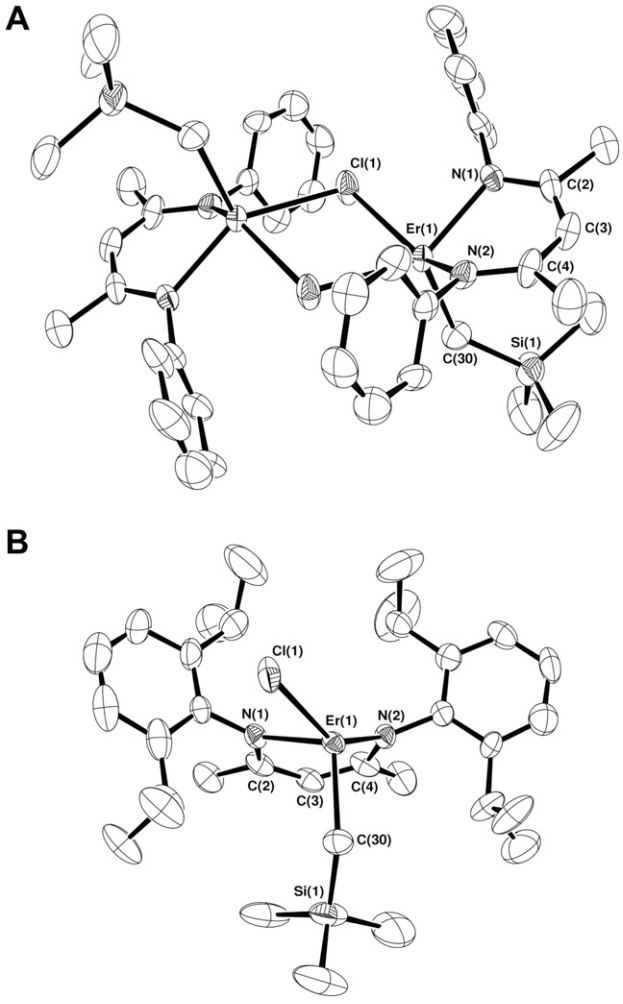


Fig. 3. ORTEP diagram (50% probability) of [Er(**L**)(CH_2SiMe_3)(μ-Cl)]$_2$ (**3**). The dimeric structure (with hydrogen atoms and ^{i}Pr groups omitted for clarity) is shown in (A), while the asymmetric unit (with hydrogen atoms omitted for clarity) is depicted in (B). Selected bond distances (Å) and angles (°): Er(1)–N(1) = 2.284(5), Er(1)–N(2) = 2.270 (5), Er(1)–Cl(1) = 2.653(2), Er(1)–Cl(1)_1 = 2.638(2), Er(1)–C(30) = 2.343(7), N(1)–Er (1)–N(2) = 85.4(2), Cl(1)–Er(1)–Cl(1)_1 = 77.4(1), Cl(1)–Er(1)–N(2) = 142.2(2), Cl(1)–Er(1)–N(1) = 86.3(2), Cl(1)_1–Er(1)–N(2) = 87.9(1), Cl(1)_1–Er(1)–N(1) = 143.5(1), C (30)–Er(1)–N(1) = 107.9(2), C(30)–Er(1)–N(2) = 109.5(2), C(30)–Er(1)–Cl(1) = 108.2 (2), C(30)–Er(1)–Cl(1)_1 = 108.2(2). Note: Cl(1)_1 was generated by the symmetry operator $-x+2$, $-y+1$, $-z+2$.

lengths, which are close to the average Er(2)–Cl distance in **1** (2.657 Å), indicates a nearly symmetric bridging interaction. The metal center in complex **3** sits above the NCCCN plane by 1.043 Å, which is also comparable to that of **1**.

Reaction of complex **1** with four equiv of $LiCH_2SiMe_3$ generated the monomeric dialkyl species Er(**L**)(CH_2SiMe_3)$_2$, **4** in 62.6% yield (Scheme 2). High quality single crystals of **4** were grown from a saturated toluene solution at −35 °C. Under these conditions, complex **4** crystallized in the centrosymmetric space group *C*2/*c* with half of a molecule of toluene in the asymmetric unit. In the solid-state, this complex adopts a distorted tetrahedral geometry defined by the coordination of two alkyl groups and the κ^2 bound nacnac ligand (Fig. 4). The closest contacts between the erbium center and the nacnac backbone are 2.973(2) Å, 3.169(2) Å and 3.030(2) Å for C(2), C(3) and C(4), respectively. These elongated distances suggest little to no bonding interaction with the ligand backbone, and thus, complex **4** is best described as four-coordinate. Similarly, the erbium center does not appear to be supported by any

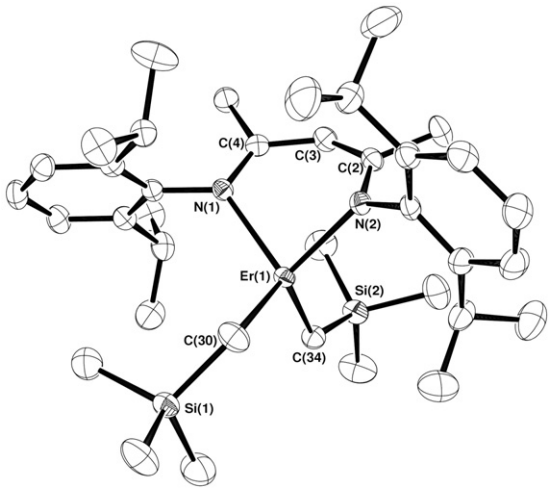


Fig. 4. ORTEP diagram (50% probability) of Er(**L**)(CH_2SiMe_3)$_2$ (**4**) with hydrogen atoms and the solvent molecule of crystallization omitted for clarity. Selected bond distances (Å) and angles (°): Er(1)–N(2) = 2.234(2), Er(1)–N(1) = 2.258(2), Er(1)–C(30) = 2.342 (3), Er(1)–C(34) = 2.380(2), Si(1)–C(30)–Er(1) = 127.0(1), Si(2)–C(34)–Er(1) = 129.8 (1), N(1)–Er(1)–N(2) = 86.8(1), C(30)–Er(1)–C(34) = 117.7(1), C(30)–Er(1)–N(1) = 110.0(1), C(30)–Er(1)–N(2) = 108.7(1), C(34)–Er(1)–N(1) = 111.9(1), C(34)–Er(1)–N (2) = 117.5(1).

agostic interactions. The observed Er–C bond lengths in **4** are 2.342 (3) Å (Er(1)–C(30)) and 2.380(2) Å (Er(1)–C(34)).

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 2.343(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_2SiMe_3) bond lengths to date. There are only three other structurally characterized complexes containing an Er–CH_2SiMe_3 bond: Er(CH_2SiMe_3)$_3$(THF)$_2$ [29], Er(CH_2SiMe_3)$_3$(THF)(Im$Me_2{}^iPr_2$) [30], and Er(CH_2SiMe_3)$_3$(^{i}Pr-trisox) [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 – 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_2SiMe_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 metalation 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

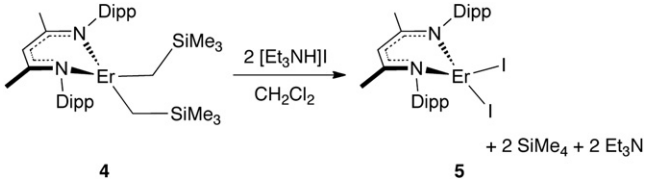
after 24 h at 295 K. Under these conditions, approximately 15% product loss was observed with the concomitant generation of tetramethylsilane. Unfortunately, due to the paramagnetic nature of complex **4**, the relative amount of decomposition versus tetramethylsilane formation could not be accurately 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 [Et_3NH]I. As expected, treatment of **4** with two equiv of [Et_3NH]I cleanly afforded the diiodide complex, Er(**L**)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 $P2_1/c$ 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 containing compounds (2.931(1) Å − 3.0874(9) Å) [19,33]. Thus, the low-end of the range for a typical Er–I bond should be extended to 2.9077(5) 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 $ErI_3(THF)_3$ (**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 "Er**L**$_2$I". The formulation of "Er**L**$_2$I" 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 space in the 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, $ErI_3(THF)_{3.5}$ [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



Scheme 3. Synthesis of **5**.

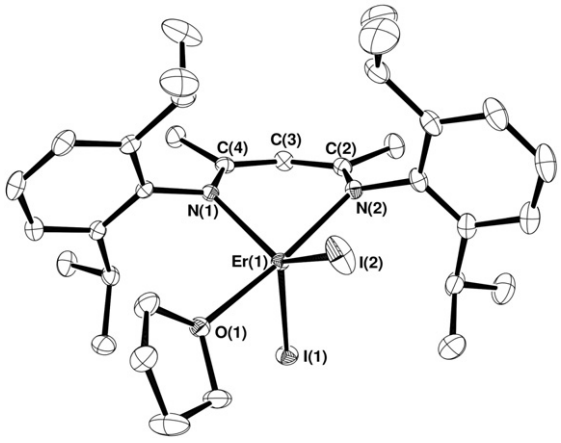


Fig. 5. ORTEP diagram (30% probability) of Er(**L**)I_2(THF) (**5**•THF) with hydrogen atoms and the solvent molecule of crystallization omitted for clarity. Selected bond distances (Å) and angles (°): Er(1)–N(1) = 2.244(3), Er(1)–N(2) = 2.290(3), Er(1)–I(1) = 2.9077 (5), Er(1)–I(2) = 2.9278(4), Er(1)–O(1) = 2.361(3), N(1)–Er(1)–N(2) = 83.4(1), I(1)–Er (1)–I(2) = 132.24(1), I(1)–Er(1)–N(1) = 101.30(7), I(2)–Er(1)–N(1) = 126.14(7), O(1)–Er(1)–N(2) = 168.4(1).

reported rare earth complexes of the generic form $LnCl_3(THF)_3$ [35]. Distinct differences were noted, however, between the IR spectra of **6** and that of the ion pair, $ErI_3(THF)_{3.5}$ [34]. The Er(1)–I(2) and Er (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 [Et_3NH]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 herein 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

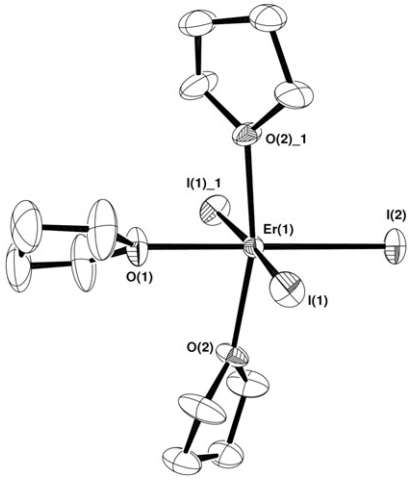


Fig. 6. ORTEP diagram (50% probability) of $ErI_3(THF)_3$ (**6**). Selected bond distances (Å) and angles (°): Er(1)–I(2): 2.9276(6), Er(1)–I(1): 2.9504(4), Er(1)–O(1): 2.327(5), Er (1)–O(2): 2.273(3), I(2)–Er(1)–I(1) = 91.99(1), I(1)–Er(1)–O(1) = 88.01(1), I(2)–Er (1)–O(2) = 97.03(9), I(1)–Er(1)–O(2) = 90.18(9), O(2)–Er(1)–O(1) = 82.97(9). Note: I (1)_1 and O(2)_1 were generated by the symmetry operator $-x+1, y, -z+0.5$.

organo-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 Er**L**I_2 (**5**) may facilitate access to the dibenzyl analog of complex **4** (Er(**L**)$(CH_2Ph)_2$) 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)$_3$Er(**L**)(THF) (**1**) was readily prepared *via* the reaction of erbium chloride and Li**L**. Salt metathesis of **1** with four equiv of LiN$(SiMe_3)_2$ generated the mixed chloro/silylamido dimer adduct [Er(**L**)N$(SiMe_3)_2$Cl(μ-(LiN$(SiMe_3)_2$))]$_2$ (**2**) as an unusual example of a four-coordinate erbium coordination complex. Reaction of **1** with either two or four equiv of $LiCH_2SiMe_3$ generated the mixed chloro/alkyl dimer [Er(**L**)(CH_2SiMe_3)(μ-Cl)]$_2$ (**3**) or the dialkyl monomer Er(**L**)$(CH_2SiMe_3)_2$ (**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 Er(**L**)I_2 (**5**) was prepared *via* reaction of **4** with [Et_3NH]I. Complex **5**, in addition to the iodide complex $ErI_3(THF)_3$ (**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 benzophenone ketyl (benzene-d_6) or calcium hydride (chloroform-*d*), degassed via three freeze–pump–thaw cycles, 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 (^{1}H 300.13 MHz, ^{7}Li 116.64 MHz) and referenced relative to either $SiMe_4$ through the residual solvent resonance(s) for ^{1}H or external LiCl for ^{7}Li. 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 [Et_3NH]I [38], and Li**L** [39], were prepared according to literature procedures. [Et_3NH]I was further purified by recrystallization from an acetone-methanol mixture (1:1) at −35 °C and dried thoroughly under vacuum. The synthesis of $ErCl_3(THF)_{3.5}$ was carried out by a modified literature procedure [40]. Anhydrous $ErCl_3$ 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)$_3$Er(**L**)(THF) (**1**)

To a 100 mL bomb charged with Li**L** (5.12 g, 12.0 mmol) and $ErCl_3(THF)_{3.5}$ (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): μ_{eff} 11.8 μ_B. ^{1}H NMR (benzene-d_6, 295 K): δ 121.39 ($\Delta\nu_{1/2}$ = 864 Hz), 56.64 ($\Delta\nu_{1/2}$ = 97 Hz), 55.01 ($\Delta\nu_{1/2}$ = 301 Hz), 39.51 ($\Delta\nu_{1/2}$ = 89 Hz), 37.35 ($\Delta\nu_{1/2}$ = 177 Hz), 36.59 ($\Delta\nu_{1/2}$ = 80 Hz), 34.71 ($\Delta\nu_{1/2}$ = 115 Hz), 28.99 ($\Delta\nu_{1/2}$ = 62 Hz), 27.70 ($\Delta\nu_{1/2}$ = 80 Hz), 20.38 ($\Delta\nu_{1/2}$ = 89 Hz), 17.49 ($\Delta\nu_{1/2}$ = 159 Hz), 15.31 ($\Delta\nu_{1/2}$ = 97 Hz), −1.41 ($\Delta\nu_{1/2}$ = 132 Hz), −2.59 ($\Delta\nu_{1/2}$ = 192.4 Hz), −6.80 ($\Delta\nu_{1/2}$ = 180 Hz), −11.90 ($\Delta\nu_{1/2}$ = 96 Hz), −17.51 ($\Delta\nu_{1/2}$ = 175 Hz), −21.01 ($\Delta\nu_{1/2}$ = 144 Hz), −26.07 ($\Delta\nu_{1/2}$ = 437 Hz), −29.63 ($\Delta\nu_{1/2}$ = 618 Hz), −36.62 ($\Delta\nu_{1/2}$ = 89 Hz), −42.96 ($\Delta\nu_{1/2}$ = 263 Hz), −61.77 ($\Delta\nu_{1/2}$ = 201 Hz), −166.27 ($\Delta\nu_{1/2}$ = 874 Hz). Anal. Calcd. (%) for $C_{62}H_{90}Cl_4Er_2N_4O$: C, 53.82; H, 6.56; N, 4.05. Found: C, 54.32; H, 6.92; N, 3.81. Complex **1** can be alternatively prepared in approximately the same yield through an analogous procedure utilizing anhydrous $ErCl_3$ in place of $ErCl_3(THF)_{3.5}$.

4.2.2. [Er(**L**)N$(SiMe_3)_2$Cl(μ-(LiN$(SiMe_3)_2$))]$_2$ (**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$(SiMe_3)_2$ (0.196 g, 1.17 mmol) in a 25 mL Erlenmeyer 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-d_6, 295 K): μ_{eff} 13.1 μ_B. ^{1}H NMR (benzene-d_6, 295 K): δ 116.79 ($\Delta\nu_{1/2}$ = 619 Hz), 99.84 ($\Delta\nu_{1/2}$ = 214 Hz), 79.05 ($\Delta\nu_{1/2}$ = 128 Hz), 44.23 ($\Delta\nu_{1/2}$ = 48 Hz), 29.04 ($\Delta\nu_{1/2}$ = 80 Hz), 9.35 ($\Delta\nu_{1/2}$ = 103 Hz), 4.71 ($\Delta\nu_{1/2}$ = 44 Hz), −40.41 ($\Delta\nu_{1/2}$ = 90 Hz), −59.66 ($\Delta\nu_{1/2}$ = 167 Hz), −94.61 ($\Delta\nu_{1/2}$ = 378 Hz), −238.83 ($\Delta\nu_{1/2}$ = 322 Hz). ^{7}Li NMR (benzene-d_6, 295 K): δ 11.17. Anal. Calcd. (%) for $C_{82}H_{154}Cl_2Er_2Li_2N_8Si_8$: C, 51.94; H, 8.19; N, 5.91. Found: C, 52.16; H, 8.12; N, 5.91.

4.2.3. [Er(**L**)(CH_2SiMe_3)(μ-Cl)]$_2$ (**3**)

In a glove box, a 25 mL Erlenmeyer flask was charged with **1** (0.248 g, 0.179 mmol) and $LiCH_2SiMe_3$ (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): μ_{eff} 10.5 μ_B. ^{1}H NMR (chloroform-*d*, 295 K): δ 179.16 ($\Delta\nu_{1/2}$ = 1475 Hz), 48.86 ($\Delta\nu_{1/2}$ = 65 Hz), 41.23 ($\Delta\nu_{1/2}$ = 300 Hz), 39.73 ($\Delta\nu_{1/2}$ = 76 Hz), 28.44 ($\Delta\nu_{1/2}$ = 38 Hz), 22.92 ($\Delta\nu_{1/2}$ = 130 Hz), 1.51 (132 Hz), −1.21 ($\Delta\nu_{1/2}$ = 59 Hz), −49.53 ($\Delta\nu_{1/2}$ = 55 Hz), −83.60

($\Delta\nu_{1/2} = 171$ Hz), −222.75 ($\Delta\nu_{1/2} = 849$ Hz). Anal. Calcd. (%) for $C_{66}H_{104}Cl_2Er_2N_4Si_2$: C, 56.02; H, 7.41; N, 3.96. Found: C, 55.85; H, 7.18; N, 3.96.

4.2.4. Er(**L**)(CH_2SiMe_3)$_2$ (**4**)

In a glove box, a 25 mL Erlenmeyer flask was charged with **1** (1.11 g, 0.802 mmol) and $LiCH_2SiMe_3$ (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 frit 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-d_6, 295 K): μ_{eff} 7.2 μ_B. ^{1}H NMR (benzene-d_6, 295 K): δ 217.74 ($\Delta\nu_{1/2} = 1973$ Hz), 104.09 ($\Delta\nu_{1/2} = 1252$ Hz), 87.04 ($\Delta\nu_{1/2} = 1252$ Hz), 70.21 ($\Delta\nu_{1/2} = 123$ Hz), 32.29 ($\Delta\nu_{1/2} = 1802$ Hz), 15.81 ($\Delta\nu_{1/2} = 183$ Hz), −40.29 ($\Delta\nu_{1/2} = 189$ Hz), −51.03 ($\Delta\nu_{1/2} = 241$ Hz), −134.05 ($\Delta\nu_{1/2} = 639$ Hz), −265.36 ($\Delta\nu_{1/2} = 2447$ Hz), −519.18 ($\Delta\nu_{1/2} = 6164$ Hz). Anal. Calcd. (%) for $C_{37}H_{63}ErN_2Si_2$: C, 58.52; H, 8.36; N, 3.69. Found: C, 58.41; H, 8.37; N, 3.54.

4.2.5. Er(**L**)I_2 (**5**)

To a 100 mL round-bottomed flask charged with **4** (0.333 g, 0.438 mmol) and [Et_3NH]I (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 [Et_3NH]I, 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 (**5**·THF, chloroform-*d*, 295 K): μ_{eff} 9.0 μ_B. ^{1}H NMR (**5**·THF, benzene-d_6, 295 K): δ 32.87 ($\Delta\nu_{1/2} = 1122$ Hz), 30.34 ($\Delta\nu_{1/2} = 597$ Hz), 25.90 ($\Delta\nu_{1/2} = 670$ Hz), 21.50 ($\Delta\nu_{1/2} = 47$ Hz), −13.91 ($\Delta\nu_{1/2} = 529$ Hz), −19.07 ($\Delta\nu_{1/2} = 103$ Hz), −30.22 ($\Delta\nu_{1/2} = 1104$ Hz), −62.62 ($\Delta\nu_{1/2} = 195$ Hz). Anal. Calcd. (%) for $C_{36}H_{49}ErI_2N_2$ (**5**·Toluene): C, 46.45; H, 5.31; N, 3.01. Found: C, 46.15; H, 5.73; N, 2.97.

4.2.6. $ErI_3(THF)_3$ (**6**)

Addition of toluene (40 mL) to a 100 mL round bottom flask charged with **1** (0.924 g, 0.668 mmol) generated a clear pink solution. Trimethylsilyliodide (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 a 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**.

	1[a]	**2**	**3**[b]	**4**[c]	**5**[c]	**6**
Formula[d]	$C_{69}H_{98}Cl_4Er_2N_4O$	$C_{82}H_{154}Cl_2Er_2Li_2N_8Si_8$	$C_{80}H_{120}Cl_2Er_2N_4Si_2$	$C_{40.5}H_{66.5}ErN_2Si_2$	$C_{36.5}H_{52.5}ErI_2N_2O$	$C_{12}H_{24}ErI_3O_3$
FW[d]/g mol^{-1}	1475.83	1896.15	1599.40	804.90	956.37	764.27
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_1/c$	$Pbcn$
a/Å	19.083(2)	23.753(2)	14.329(2)	21.262(3)	14.989(2)	9.328(1)
b/Å	17.800(2)	20.775(1)	16.093(3)	10.489(1)	12.321(2)	14.669(2)
c/Å	20.451(2)	22.594(1)	16.910(3)	38.192(5)	21.174(3)	14.417(2)
α/°	90	90	90	90	90	90
β/°	92.183(1)	115.107(1)	102.420(2)	94.946(1)	102.311(2)	90
γ/°	90	90	90	90	90	90
Volume/Å^3	6942(1)	10095(1)	3808(1)	8486(2)	3820.5(11)	1972.7(4)
Z	4	4	2	8	4	4
D_{calc}[d]/mg m^{-3}	1.412	1.248	1.395	1.260	1.663	2.573
μ[d]/mm^{-1}	2.598	1.840	2.334	2.061	3.841	8.950
Crystal size/mm	0.43 × 0.07 × 0.06	0.30 × 0.14 × 0.11	0.19 × 0.11 × 0.04	0.37 × 0.19 × 0.06	0.34 × 0.27 × 0.03	0.24 × 0.09 × 0.07
Crystal color	Pale pink	Pale pink	Pale pink	Pale pink	Pale pink	Pale pink
Crystal habit	Needle	Prism	Plate	Plate	Plate	Prism
θ Range/°	1.56–24.71	1.81–27.10	1.69–27.10	1.92–27.10	1.92–27.10	2.59–26.72
N	63,004	112,217	52,373	46,724	42,219	20,122
N_{ind}	11,842	22,180	8412	9373	8428	2090
Completeness to $\theta = 27.10°$	99.9%	99.5%	100%	100%	100%	100%
Data/restraints/parameters	11,842/4/713	22,180/0/981	8412/0/356	9373/0/433	8428/7/388	2090/0/88
GoF on F^2	1.009	1.002	1.076 [0.910]	1.151	1.017	1.049
R_1 ($I > 2\sigma(I)$)[e]	0.0351	0.0351	0.0631 [0.0540]	0.0261	0.0292	0.0237
wR_2 ($I > 2\sigma(I)$)[f]	0.0648	0.0663	0.1658 [0.0975]	0.0522	0.0675	0.0667
R_1 (all data)[e]	0.0609	0.0667	0.1515 [0.1168]	0.0306	0.0376	0.0291
wR_2 (all data)[f]	0.0736	0.0775	0.2047 [0.1126]	0.0537	0.0721	0.0700
$\Delta\rho_{max}$ and $\Delta\rho_{min}$/e·Å^{-3}	0.743 and −0.537	1.415 and −0.893	[0.698 and −0.900]	0.765 and −0.811	2.627 and −2.162	1.245 and −1.407

[a] Crystallized with one disordered molecule of toluene in the asymmetric unit.
[b] A highly disordered solvent molecule was removed from the reflection file using the SQUEEZE subroutine of PLATON; statistics following treatment of data with SQUEEZE are listed in square brackets.
[c] Crystallized with half of one molecule of toluene in the asymmetric unit.
[d] For non-SQUEEZED data.
[e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[f] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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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): μ_{eff} 8.7 μ_B. IR: ν (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), 572 (m), 476 (m). Anal. Calcd. (%) for $C_{12}H_{24}ErI_3O_3$: C, 18.86; H, 3.17. Found: C, 19.47; H, 3.29.

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 coated 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 $\omega - 2\theta$ scans at 0.5° steps yielded full hemispherical data with excellent intensity statistics. Unit cell parameters were determined and refined on all observed reflections using APEX2 software [41]. Data reduction and correction for Lorentz polarization were performed using SAINT-Plus software [42]. Absorption corrections were applied using SADABS [43]. The structures were solved by direct methods and refined by the least squares method on F^2 using the SHELXTL software suite [44]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and isotropically refined as riding models to their parent atoms. No decomposition was observed during data collection. Table 1 provides a summary of selected data collection and refinement parameters. Note: In the refinement of **3**, a disordered solvent molecule was removed from the reflection file using the SQUEEZE subroutine of the PLATON program [45]. Information regarding the crystal structure of **3** is given before and after treatment with the SQUEEZE function (Table 1). Reduced residuals were observed in the final SQUEEZED structure confirming that the uncertainty in the model was a result of the disordered solvent [46].

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Appendix A. Supplementary material

CCDC 784848 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.

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