

Examination of the LnCl_3/RLi alkylation system for organic synthesis using yttrium as a probe including the X-ray crystal structure of $\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$

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Abstract

The LnCl_3/RLi reagent system commonly used with $\text{Ln}=\text{Ce}$ for organic alkylation reactions has been studied with $\text{Ln}=\text{Y}$ to make use of the ^{89}Y nucleus ($I = 1/2$) in NMR analyses. The ' YCl_3 ' obtained by the current literature methods of dehydrating $\text{LnCl}_3(\text{H}_2\text{O})_x$ reagents in the LnCl_3/RLi system contains water by elemental analysis, by reactivity with $\text{LiCH}_2\text{SiMe}_3$ and LiMe , and by X-ray analysis of recrystallized material which proved to be $[\text{YCl}_2(\text{H}_2\text{O})_6]\text{Cl}$. The complexity of the intermediates that may be present in these systems when reagents are not rigorously purified is shown by the structure of $\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$, which was isolated from a $\text{YCl}_3/\text{LiCH}_2\text{SiMe}_3$ reaction. The complex contains a tetracapped tetrahedron of yttrium atoms with two outlying lithium atoms all of which are connected by four $\mu_4\text{-O}$, fourteen $\mu_2\text{-Cl}$, and two $\mu_3\text{-Cl}$ atoms. Each lithium and each capping yttrium are ligated by two THF groups. © 1997 Elsevier Science S.A.

Keywords: Alkylation reagents; Yttrium; Alkyl; Polymetallic; Anhydrous lanthanide halides

1. Introduction

One of the popular lanthanide-based reagents currently being used in organic synthesis is the CeCl_3/RLi alkylation system which can effect alkylations not possible with Grignard or alkyllithium reagents alone [1–12]. Although this reagent is sometimes written as RCeCl_2 , recent studies have shown that the general method for preparing anhydrous CeCl_3 for this reaction by heating $\text{CeCl}_3(\text{H}_2\text{O})_7$ under vacuum at $140^\circ\text{--}150^\circ\text{C}$ leads to the monosolvate $[\text{CeCl}_3(\text{H}_2\text{O})]_n$ instead of CeCl_3 [13,14]. This complicates the reaction since at least some of the RLi can react with the water to form LiOH , Li_2O , etc. Use of excess RLi may well lead to the anhydrous combination CeCl_3/RLi , but since lithium salts frequently form bridging structures with lanthanides [15,16], it is possible that the $[\text{CeCl}_3(\text{H}_2\text{O})]_n/\text{RLi}$ reagent may have a formula as

complicated as $\text{Ce}_a\text{Cl}_b\text{R}_c(\text{OH})_d\text{O}_e\text{Li}_f$. If the complex is polymetallic, the ligands could be bridging instead of terminal and this can affect their reactivity [17,18].

The precise nature of the $[\text{CeCl}_3(\text{H}_2\text{O})]_n/\text{RLi}$ reagent is difficult to study *in solution* by spectroscopic means owing to the paramagnetism of $\text{Ce}(\text{III})$ [19]. Hence, in this study of the LnCl_3/RLi reaction, we have used diamagnetic ^{89}Y as a model. Since yttrium has a 100% naturally abundant $I = 1/2$ nucleus more definitive NMR information can be obtained on alkyl complexes in solution.

It is interesting to note that although cerium is the most commonly-used metal in these LnCl_3/RLi systems, any of the lanthanides or yttrium, which is very similar in its chemistry to erbium [20], could be used. Moreover, since there is ample evidence in the organolanthanide literature that reaction yields vary considerably depending on the appropriateness of the size of the lanthanide for the reaction to be accomplished [17,18,21], it is likely that cerium is not the metal of optimal size for all applications. Cerium appears to be used predominantly only by precedent.

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In this study, we present more evidence that the commonly used 150–160° dehydration procedure for drying $\text{YCl}_3(\text{H}_2\text{O})_x$ ($x = 6$ or 7) precursors for organic reactions does not provide a totally anhydrous material. Evidence is presented for a product of average composition $\text{YCl}_3(\text{H}_2\text{O})_{1.5}$ which reacts with RLi to form RH . In addition, we report the isolation and structure of a polymetallic complex from a $\text{YCl}_3/\text{Me}_3\text{SiCH}_2\text{Li}$ reaction which suggests that complicated, highly bridged compounds significantly different from RLnCl_2 can form when lanthanide and yttrium trihalides are treated with alkyllithium reagents in the presence of oxygen-containing impurities.

2. Experimental

$\text{YCl}_3(\text{H}_2\text{O})_6$ was obtained from Rhône-Poulenc. Rigorously anhydrous yttrium trichloride was dried by the literature procedure of heating the hydrate with NH_4Cl under vacuum followed by separation of the NH_4Cl by sublimation [22–27]. Trimethylsilyl-methylolithium (Aldrich, 1.0 M in pentanes) was dried in vacuo to remove solvent and purified by sublimation. Elemental analysis was obtained from Analytische Laboratorien (Gummersbach, Germany). Karl Fischer analysis was conducted on a Fisher Scientific Accumet 150. Infrared spectra were obtained on a Perkin Elmer 1600 Series FTIR spectrometer. NMR data were obtained on General Electric GN 500 spectrometer.

2.1. $\text{YCl}_3(\text{H}_2\text{O})_x$, **1**

$\text{YCl}_3(\text{H}_2\text{O})_6$ (4.8 g, 15.8 mmol) was placed in a 500 ml Schlenk flask containing a magnetic stir bar. The flask was attached to a vacuum manifold connected to a liquid nitrogen trap and a mechanical pump. Following a literature procedure [12], but at a lower pressure, the flask was evacuated to 0.03 Torr, slowly heated to 150°C over 3 h with an oil bath, and agitated at this temperature for an additional 12 h to make **1**, a colorless solid. The vessel was moved from the vacuum line to a nitrogen-containing glovebox in which samples of **1** were taken for analysis. Anal. Calcd. for $\text{YCl}_3(\text{H}_2\text{O})$: Y, 41.69; Cl, 49.87; H, 0.94; O, 7.50. Calcd. for $\text{YCl}_3(\text{H}_2\text{O})_{1.5}$: Y, 39.99; Cl, 47.84; H, 1.36; O, 10.80. Found: Y, 40.30; Cl, 47.64; H, 1.60; O (by difference), 10.46. A 1 ml sample of a saturated solution of **1** in THF was prepared and found by Karl Fischer analysis to contain $116 \mu\text{g H}_2\text{O ml}^{-1}$ which corresponds to 54% of the water expected from the formula $\text{YCl}_3(\text{H}_2\text{O})_{1.5}$ [which is equivalent to an 81% yield from $\text{YCl}_3(\text{H}_2\text{O})$] based on a measured solubility of 9.5 mg ml^{-1} . Compound **1** (102 mg, 0.457 mmol) was placed in a tube fitted with two greaseless high vacuum stopcock adapters, one attached to a 24/40 joint and the

other to a septum-capped sidearm. Excess MeLi (3.5 mmol) obtained by removing Et_2O from a commercial solution (Aldrich) was added to the tube and the apparatus was attached to a high vacuum line connected to a Toepler pump. THF was added by syringe through the sidearm and gas evolution was observed when it contacted the solids. The gas was collected by Toepler pump and identified as methane by mass spectrometry (13.7 ml, 0.315 mmol, 44%). Recrystallization at 25°C from a THF solution which had been saturated by stirring **1** in boiling THF followed by removal of excess solid via centrifugation gave crystals of $[\text{YCl}_2(\text{H}_2\text{O})_6]\text{Cl}$, **2**, which was identified by X-ray crystallography to be identical to the structure in the literature [28].

2.2. Alkylation reactions

Compound **1** (23 mg, 0.11 mmol) and excess $\text{LiCH}_2\text{SiMe}_3$ (10 mg, 0.11 mmol) were placed in an NMR tube. $\text{THF-}d_8$ was condensed onto the solids and the NMR tube was flame sealed. After the mixture was shaken at room temperature, tetramethylsilane was the only product observed by NMR spectroscopy. A second experiment was conducted using **1** (1.3 mg, 0.005 mmol) and excess $\text{LiCH}_2\text{SiMe}_3$ (4.5 mg, 0.05). NMR spectroscopy revealed tetramethylsilane and $\text{LiCH}_2\text{SiMe}_3$ but no yttrium alkylation product. Periodically, NMR spectra were obtained on this sample over several months, but failed to reveal any alkylation of yttrium.

Analogously, $\text{LiCH}_2\text{SiMe}_3$ (185 mg, 1.98 mmol) was dissolved in THF and anhydrous YCl_3 (195 mg, 1.00 mmol) was added. The YCl_3 dissolved in 10 min and the THF was removed with rotary evaporation to afford a gray oil. $^1\text{H NMR}$ ($\text{THF-}d_8$, 25°C): δ 0.85 (d, $J_{\text{YH}} = 2$ Hz, 2H, CH_2SiMe_3), δ 0.095 (s, 9H, CH_3SiMe_3).

2.3. X-ray data collection, structure determination, and refinement for $\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$, **3**

Crystals of **3** were obtained from THF from a reaction of YCl_3 (196 mg, 1.00 mmol) with a tan-colored sample of $\text{LiCH}_2\text{SiMe}_3$ (94 mg, 1.00 mmol) in ca. 10 ml of THF. A colorless crystal of approximate dimensions $0.30 \times 0.35 \times 0.40$ mm was coated with Paratone oil, mounted on the tip of a glass fiber, and transferred to the nitrogen coldstream of a Siemens P4 rotating anode diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out according to standard procedures [29]. Intensity data were collected by use of the $2\theta/\omega$ scan technique. The raw data were processed with a local version of CARESS [30] which employs a modified version of the Lehman–Larsen algorithm to obtain intensities and standard deviations

Table 1
Experimental X-ray data for $\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$, **3**

3	
Formula	$\text{C}_{48}\text{H}_{96}\text{Cl}_{18}\text{Li}_2\text{O}_{16}\text{Y}_8$
Fw	2292.51
Temp. (K)	158(2)
Space group	$C2/c$
a (Å)	20.674(4)
b (Å)	17.534(4)
c (Å)	23.871(5)
β (°)	102.804(12)
V (Å ³)	8438.1(31)
Z	4
ρ_{calc} (g cm ⁻³)	1.805
λ (Mo K α)	0.71073
μ (mm ⁻¹)	6.055
$R1, wR2$ [$I > 2\sigma(I)$]	0.0619, 0.1366
$R1, wR2$ (all data)	0.1450, 0.1697

$$R1 = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}; \quad wR2 = \frac{[\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}}$$

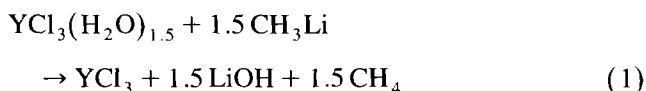
from the measured 96-step peak profiles. All data were corrected for absorption [31] and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/m with the systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The two possible monoclinic space groups are Cc and $C2/c$. The centrosymmetric space group $C2/c$ was determined to be correct and is consistent with $Z = 4$. Crystal data are listed in Table 1; full experimental details have been deposited.

All calculations were carried out using SHELXTL Version 5.03 [31]. The analytical scattering factors for neutral atoms were used throughout the analysis [32]. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. The molecule is located about a site of twofold symmetry. Three of the THF groups are disordered. Each of these groups was included with two orientations. Hydrogen atoms associated with the disordered ligands were not included in the refinement. At convergence, $wR2 = 0.1697$ and $\text{GOF} = 1.026$ for 341 variables refined against 5524 unique data (for comparison for refinement on F , $R1 = 0.0629$ for those 2968 data with $F > 4.0\sigma(F)$).

3. Results

Heating $\text{YCl}_3(\text{H}_2\text{O})_6$ at 150°C and 0.03 Torr for 15 h following the extremes of literature procedures for preparing LnCl_3/RLi produces a colorless powder, **1**, which has an elemental analysis consistent with the composition $\text{YCl}_3(\text{H}_2\text{O})_{1.5}$. The infrared spectrum of **1** contained a strong absorption at 3460 cm⁻¹, which is

consistent with an OH stretch. The presence of water in **1** was detected by dissolving a sample in THF and analyzing the solution by the Karl Fischer technique. On the basis of the measured solubility of **1**, the analysis detected 54% of the amount of water expected for the composition $\text{YCl}_3(\text{H}_2\text{O})_{1.5}$. When THF was added to a mixture of **1** and MeLi in a Toepler pump system, gas was immediately evolved which proved to be methane by mass spectrometry. The amount of methane obtained accounted for a 44% yield according to the stoichiometry of Eq. (1). The incomplete yield may be:



due to incomplete dissolution of **1** under the reaction conditions.

The reaction of **1** with $\text{LiCH}_2\text{SiMe}_3$ in THF- d_8 was monitored by NMR to see if an $\text{Y}-\text{CH}_2\text{SiMe}_3$ linkage would form. Such a unit should generate a doublet in the ¹H NMR spectrum for the methylenic protons with a J_{YH} value of 2–4 Hz due to the $I = 1/2$ ⁸⁹Y nucleus [33–38]. Addition of one equivalent of $\text{LiCH}_2\text{SiMe}_3$ to **1** formed only Me_4Si in the ¹H NMR spectrum. In fact, addition of excess $\text{LiCH}_2\text{SiMe}_3$ generated peaks only for Me_4Si and $\text{LiCH}_2\text{SiMe}_3$. In contrast, reaction of two equivalents of $\text{LiCH}_2\text{SiMe}_3$ with rigorously dried YCl_3 gave a spectrum with a doublet at δ 0.85 ppm ($J_{\text{YH}} = 2$ Hz) consistent with an $\text{Y}-\text{CH}_2\text{SiMe}_3$ unit and no unreacted $\text{LiCH}_2\text{SiMe}_3$.

Recrystallization of **1** from THF was expected to form a product related to the previously characterized $[\text{CeCl}_3(\text{H}_2\text{O})(\text{THF})]_n$ [13,14]. Crystals were obtainable from THF in an analogous fashion, but X-ray crystallographic analysis revealed the presence of $[\text{YCl}_2(\text{H}_2\text{O})_6]\text{Cl}$, **2** [28]. Complex **2** is a common form of hydrated lanthanide trihalide. In addition to the structure of the yttrium complex [28], gadolinium [39], europium [40], samarium [41,42], neodymium [41,42], and erbium [28] analogs have been structurally characterized. The isolation of **2** is curious considering the analytical data, but it is consistent with the presence of water in the system and the results of a water sorption/desorption study of YCl_3 [43]. This study showed using thermogravimetric, powder X-ray, and IR data on the hydration and dehydration of yttrium trichloride that dehydration/rehydration depends on the crystalline or amorphous nature of the starting materials. The study revealed that amorphous anhydrous YCl_3 rehydrates to the hexahydrate only. A similar situation is observed in the recrystallization of **1** from THF.

In the course of these studies, crystals of $\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$, **3**, Fig. 1, were obtained from a reaction between YCl_3 and an old sample of $\text{LiCH}_2\text{SiMe}_3$. The structure of **3** showed that the system had been contaminated with an oxygen-containing im-

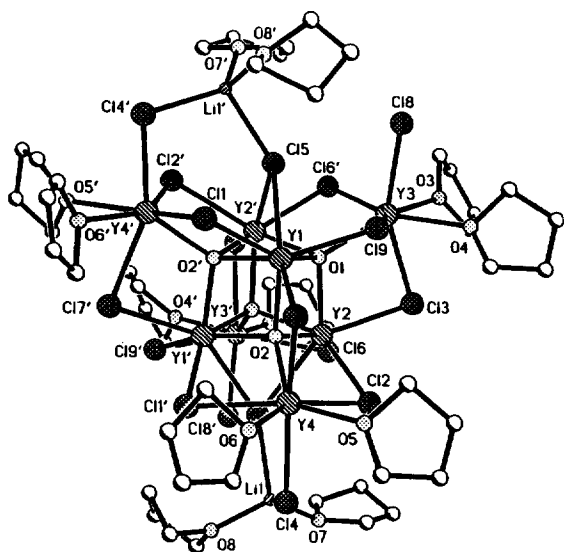


Fig. 1. Ball and stick diagram of $\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$, **3**.

purity and it is presented here to show how complicated lithium/lanthanide/halide/oxide systems can be. However, no claims can be made about the method of formation of **3**.

$\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$, **3**, has a crystallographic C_2 rotation axis which bisects the five $M(\#)-M(\#')$ vectors in the molecule. As shown in Fig. 2, the eight yttrium atoms in this complex are best described as a tetracapped tetrahedron. $\text{Y}(1)$, $\text{Y}(1')$, $\text{Y}(2)$, and $\text{Y}(2')$ comprise the inner tetrahedron and $\text{Y}(3)$, $\text{Y}(3')$, $\text{Y}(4)$, and $\text{Y}(4')$ are in the capping positions. The four outer-capping yttrium positions also describe a tetrahedron. The regularity of the tetrahedra in **3** can be evaluated by examining the dihedral angles between the faces of the various tetrahedra. In **3**, the dihedral angles in the central tetrahedron and the four surrounding tetrahedra each formed by a capping vertex and a face of the central tetrahedron range from 65.2 to 73.8° compared to the ideal angle of 70.53° .

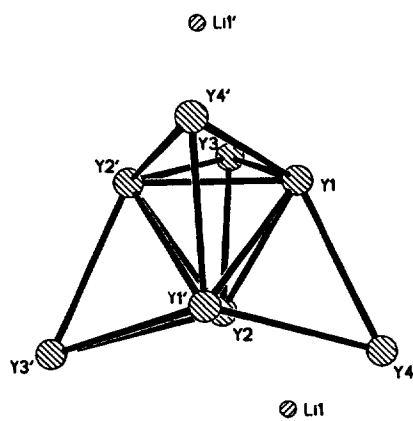


Fig. 2. Orientation of the metals in $\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$, **3**, with lines connecting the yttrium atoms to show their tetracapped tetrahedral structure.

The Li atom positions break the otherwise tetrahedral symmetry of the Y_8 tetracapped tetrahedron. $\text{Li}(1)$ is located in the plane of $\text{Y}(3')$, $\text{Y}(4)$, $\text{Y}(1)$, and $\text{Y}(2')$, but it is not located symmetrically below the middle of the $\text{Y}(3')-\text{Y}(4)$ vector. The asymmetry of the Li position is evident from the way it is bridged to the Y_8 skeleton. It is connected to $\text{Y}(4)$ by a μ_2 -Cl ligand, to $\text{Y}(1)$ and $\text{Y}(2')$ by a μ_3 -Cl ligand (which also connects the $\text{Y}(1)$ and $\text{Y}(2')$ positions), and it does not bridge to $\text{Y}(3)$. Each Li is ligated by two terminal THF groups as is each of the four capping yttrium atoms.

The $\text{Y}(1)-\text{Y}(1')-\text{Y}(2)-\text{Y}(2')$ central tetrahedron is connected by four μ_4 -oxide ions. Each oxide caps a face of the inner tetrahedron and the four oxides thereby also define a tetrahedron. The interpenetrating oxide and inner yttrium tetrahedra comprise a distorted cube which has, for example, one face comprised of $\text{Y}(1)$, $\text{O}(2')$, $\text{Y}(1')$, and $\text{O}(2)$. Each of these oxides is also bridging to one of the four capping yttrium atoms. This arrangement of face capping oxides attached to the four outer yttrium atoms sets up the tetracapped tetrahedral geometry. This arrangement puts each oxide in a tetrahedral hole created by one capping vertex and a face of the inner tetrahedron.

Each capping yttrium atom is also bridged to the inner tetrahedron by three μ_2 -chloride ions. For example, $\text{Y}(3)$ is bridged to $\text{Y}(1)$, $\text{Y}(2)$, and $\text{Y}(2')$ by $\text{C}(19)$, $\text{C}(16')$, and $\text{C}(13)$, respectively, and $\text{Y}(4')$ is connected to $\text{Y}(1)$, $\text{Y}(1')$, and $\text{Y}(2')$ by $\text{Cl}(1)$, $\text{Cl}(17')$, and $\text{Cl}(2')$, respectively. The $\text{Y}(3)$ and $\text{Y}(3')$ positions also have terminal Cl ligands. The analogous chloride atoms on $\text{Y}(4)$ and $\text{Y}(4')$ are bridged to Li. The 18 chloride ligands therefore are of four types: 2 terminals on outer yttrium atoms, 2 doubly-bridging between outer Y atoms and Li, 2 triply-bridging between Li and two inner Y atoms, and 12 doubly-bridging between inner and outer yttrium positions. The overall ligand arrangement results in seven coordinate $\text{Y}(3)$ and $\text{Y}(4)$, six coordinate $\text{Y}(1)$ and $\text{Y}(2)$, and four coordinate Li.

The $\text{Y}-(\mu_4\text{-O})$ distances vary from $2.202(8)$ to $2.281(8)$ Å and average to $2.24(2)$ Å. These distances are in the range observed for $\text{Y}-(\mu_4\text{-O})$ units in $\text{Y}_{14}(\text{OCMe}_3)_{28}\text{O}_2\text{Cl}_{10}(\text{THF})_4$ [$2.13(2)$ – $2.37(2)$ Å] [44] and $[\text{Y}_4\text{O}(\text{OCMe}_3)_{10}\text{Cl}_2]^{2-}$ [$2.40(2)$ – $2.52(2)$ Å] [45] in $\text{Y}-(\mu_5\text{-O})$ units in $\text{Y}_5(\text{O}^i\text{Pr})_{13}\text{O}$ [$2.31(4)$ – $2.39(4)$ Å] [46] and $\text{Y}_5(\text{C}_5\text{H}_5)_5(\text{OMe})_8\text{O}$ [$2.27(2)$ – $2.41(2)$ Å] [47]. The yttrium chloride distances follow the usual pattern in that distances to terminal ligands [$-\text{Cl}(8)$, $2.592(4)$ Å] are shorter than distances to doubly-bridging ligands [$2.681(4)$ – $2.757(4)$ Å] which are shorter than distances to triply-bridging ligands [$-\text{Cl}(5)$, $2.813(4)$ – $2.847(4)$ Å]. These ranges are very close to those previously observed in yttrium *tert*-butoxide halide complexes [44,45]. The six distinct (outer Y)– μ_2 -Cl distances have a $2.718(4)$ – $2.757(4)$ Å range whereas the six distinct (inner Y)– μ_2 -Cl distances range from $2.681(4)$ to

Table 2
Selected bond distances (Å) for $\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$, **3**

Y(1)–O(2)	2.230(8)	Y(1)–O(2)#1	2.265(8)
Y(1)–O(1)	2.267(7)	Y(1)–Cl(9)	2.681(4)
Y(1)–Cl(7)	2.686(4)	Y(1)–Cl(1)	2.690(4)
Y(1)–Cl(5)	2.813(4)	Y(1)–Y(2)#1	3.366(2)
Y(1)–Y(2)	3.525(2)	Y(1)–Y(1)#1	3.531(3)
Y(1)–Y(4)#1	3.799(2)	Y(1)–Y(3)	3.807(2)
Y(2)–O(1)	2.234(8)	Y(2)–O(1)#1	2.253(7)
Y(2)–O(2)	2.281(8)	Y(2)–Cl(6)	2.688(4)
Y(2)–Cl(3)	2.689(4)	Y(2)–Cl(2)	2.693(4)
Y(2)–Cl(5)#1	2.847(4)		
Y(2)–Y(2)#1	3.491(3)	Y(2)–Y(4)	3.813(2)
Y(2)–Y(3)#1	3.821(2)	Y(3)–O(1)	2.228(8)
Y(3)–O(4)	2.406(9)	Y(3)–O(3)	2.421(9)
Y(3)–Cl(8)	2.594(4)	Y(3)–Cl(3)	2.718(4)
Y(3)–Cl(9)	2.733(4)	Y(3)–Cl(6)#1	2.757(4)
Y(4)–O(2)	2.202(8)	Y(4)–O(5)	2.376(9)
Y(4)–O(6)	2.42(2)	Y(4)–O(6B)	2.45(2)
Y(4)–Cl(4)	2.660(4)	Y(4)–Cl(7)	2.726(4)
Y(4)–Cl(1)#1	2.729(4)	Y(4)–Cl(2)	2.748(4)
Cl(4)–Li(1)	2.37(4)	Cl(5)–Li(1)#1	2.39(3)

2.693(4) Å. The Y...Y distances in the inner tetrahedron range from 3.366(2) to 3.531(3) Å. Y...Y distances from yttrium atoms in the inner tetrahedron to yttrium atoms in the capping positions range from 3.799(2) to 3.821(2) Å. The narrowness of these distance ranges reveals a high degree of regularity in this structure. Table 2 lists selected bond distances for $\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$, **3**.

4. Discussion

As in the cerium case [13], attempts to dehydrate $\text{YCl}_3(\text{H}_2\text{O})_6$ by the conventional method used in the LnCl_3/RLi literature of heating the hydrate at 140°C for 12 h and 0.1 Torr proved to be insufficient to obtain anhydrous material. This is fully consistent with previous literature on lanthanide dehydration [22–27,43,48–50] including a detailed thermogravimetric/fluorescence study in the europium case [48], thermogravimetric, IR, and X-ray powder studies on yttrium trichloride [43], and difficulties in obtaining CeCl_3/RLi reagents [49,50].

The yttrium case reported here is more complicated than the cerium system in two respects. First, the isolated product of the conventional dehydration, **1**, contains an average of one and a half molecules of water per YCl_3 unit. This suggests that a mixture of products may be present since pure hydrated material of composition $\text{YCl}_3(\text{H}_2\text{O})_{1.5}$ has not been previously identified to our knowledge. Second, since recrystallization from THF formed the hexahydrate, $[\text{YCl}_2(\text{H}_2\text{O})_6]\text{Cl}$, **2** [28], some ligand redistribution must have happened during the crystallization process. This is consistent with yttrium trichloride rehydration studies [43] which show

that the hexahydrate can form exclusively in some cases depending on the crystalline or noncrystalline form of the starting yttrium trichloride.

In any case, the isolation and crystallographic characterization of an yttrium chloride hydrate from this system unequivocally demonstrates the presence of water in the 'anhydrous' yttrium trichloride. This is fully consistent with the analytical data on the solid including the elemental analysis, the Karl Fischer measurements, and the MeLi reactions which form methane. This is also consistent with the data obtained in solution via ^{89}Y coupling constants. Truly anhydrous YCl_3 can be alkylated to generate alkyl resonances which show Y–H coupling, whereas alkylation of conventionally dried YCl_3 does not yield evidence of the formation of an Y–C bond.

The isolation of $\text{Li}_2\text{Y}_8\text{Cl}_{18}\text{O}_4(\text{THF})_{12}$, **3**, shows how lithium can be incorporated into a heavily bridged yttrium chloride structure in the presence of a source of the oxide ion. We previously suggested that formulas as complicated as $\text{Ln}_a\text{Cl}_b\text{R}_c(\text{OH})_d\text{O}_e\text{Li}_f$ could arise from the $\text{LnCl}_3/\text{H}_2\text{O}/\text{RLi}$ systems. The structure of **3** provides a tangible example of such a system.

5. Conclusion

These results and the earlier cerium [13,14], europium [48], and yttrium [43] studies show that for large (Ce), intermediate size (Eu), and small (Y) metals in the lanthanide series, heating the trichlorides at 140–150°C for 12–15 h at 0.1–0.03 Torr as is commonly done in LnCl_3/RLi alkylation is insufficient to remove all of the water. Solution NMR studies in this yttrium system showed no evidence of alkylation of the metal and a structural study showed that large, bridged polymetallic lithium/lanthanide/oxide/chloride structures can form in these systems. None of these results diminish the utility of the LnCl_3/RLi systems as it is currently and successfully used. However, they do suggest that (a) mechanistic deductions should not be based only on RLnCl_2 intermediates, and (b) to precisely control the reproducibility of these reactions, the amount of water present in the system should be determined.

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