

## A Simple Synthesis of Tetrahydrofuran Complexes of Lanthanoid Trichlorides: Convenient Substitutes for Anhydrous Lanthanoid Chlorides

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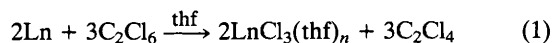
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Reaction of lanthanoid metals with hexachloroethane in tetrahydrofuran under ultrasonication conditions gives  $\text{LnCl}_3(\text{thf})_n$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, n = 2$ ;  $\text{Ln} = \text{Gd}, \text{Yb}, n = 3$ ;  $\text{Ln} = \text{Er}, n = 3.5$ , thf = tetrahydrofuran) in good yield; the X-ray crystal structure of  $[\text{YbCl}_3(\text{thf})_2]_2$ , derived from  $\text{YbCl}_3(\text{thf})_3$  by prolonged treatment with pentane, reveals a chloride-bridged octahedral dimer with *trans* thf ligands.

Anhydrous lanthanoid trichlorides are fundamental reagents for the synthesis of trivalent lanthanoid organometallics,<sup>1</sup> organoamides,<sup>2</sup> alkoxides<sup>3</sup> and aryloxides,<sup>3</sup> and they are also widely used in organic synthesis.<sup>4</sup> Routes to the anhydrous trichlorides including dehydration of the hydrates<sup>5</sup> are complex for small-scale laboratory use. The most satisfactory, the reaction of lanthanoid oxides with ammonium chloride, does not give products of the highest purity.<sup>5</sup> Purification by vacuum distillation or sublimation may be needed. For most purposes,  $\text{LnCl}_3(\text{thf})_n$  (thf = tetrahydrofuran) complexes are an acceptable alternative to the anhydrous chlorides, and there is a satisfactory small-scale preparation from lanthanoid metals and mercury(II) chloride in thf<sup>6,7</sup> [see also an analogous route to Y(or Sc)Cl<sub>3</sub>(thf)<sub>3</sub>].<sup>8</sup> However, the filtration step to remove mercury metal and excess of lanthanoid metal<sup>6,7</sup> is inconvenient as  $\text{LnCl}_3(\text{thf})_n$  complexes have limited solubility in thf. We now report a simpler synthesis of  $\text{LnCl}_3(\text{thf})_n$  complexes and the crystal structure of  $[\text{LnCl}_3(\text{thf})_2]_2$ . Established structures of  $\text{LnCl}_3(\text{thf})_n$  complexes are limited to monomeric  $\text{LnCl}_3(\text{thf})_4$  ( $\text{Ln} = \text{Nd}^9$  or  $\text{Eu}^{10}$ ) [see also  $\text{ScCl}_3(\text{thf})_3^{11}$ ].

Treatment of lanthanoid metal powder with an excess of hexachloroethane in pure dry thf under nitrogen in an ultrasonic bath at room temperature until all metal disappeared from the developing suspension gave  $\text{LnCl}_3(\text{thf})_n$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, n = 2$ ;  $\text{Ln} = \text{Gd}, \text{Yb}, n = 3$ ;  $\text{Ln} = \text{Er}, n = 3.5$ ) in 84–99% yield,<sup>†</sup> and tetrachloroethylene as the major organic product [eqn. (1)]. Reaction also occurred between



$\text{C}_2\text{Cl}_4$  and lanthanoid metals, but at a much slower rate. The simple isolation procedure<sup>†</sup> is based on the low solubility of  $\text{LnCl}_3(\text{thf})_n$  and the high solubility of the organic products in thf or thf–pentane at room temperature. Complete consumption of the lanthanoid metal avoids a difficult filtration step needed in other metal-based syntheses<sup>6–8</sup> and maximises use of the most expensive reagent.

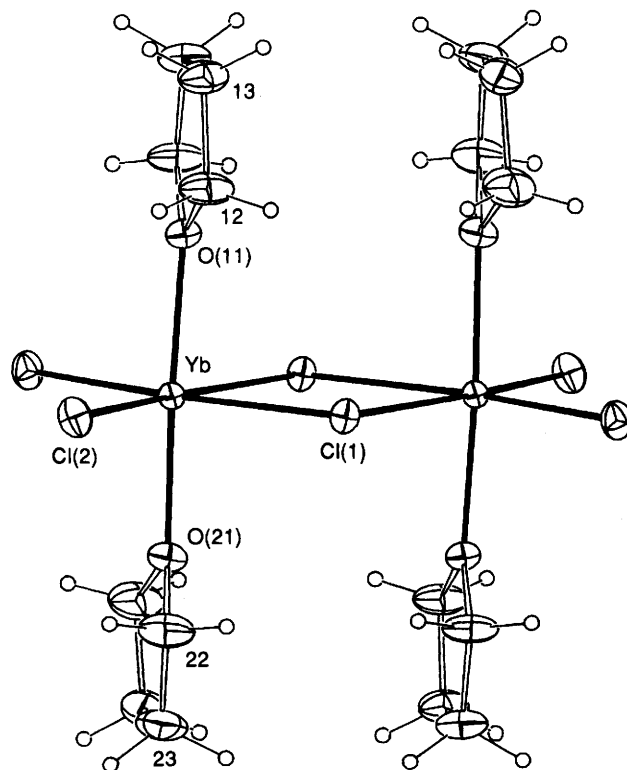
All products gave satisfactory Ln and Cl analyses, and showed intense IR absorptions at 1020–1011 and 870–862  $\text{cm}^{-1}$ , attributable<sup>12</sup> to ring stretching modes of coordinated thf, and at 270–190  $\text{cm}^{-1}$ , attributable to  $\nu(\text{Ln}-\text{Cl})$ .<sup>‡</sup>

<sup>†</sup> In most cases, 1.00 g (5.78–5.93 mmol) of metal powder, 3.00 g (12.67 mmol) of  $\text{C}_2\text{Cl}_6$ , and 40 ml of thf were used (0.50 g, 1.50 g, 40 ml for  $\text{Ln} = \text{La}$ ). Reaction times were 5 h (La), 21 h (Nd), 30 h (Sm, Gd), 7 h (Er), 45 h (Yb). For  $\text{Ln} = \text{La}$ , the product was filtered off in a dry box, and washed with pentane. Otherwise, pentane (20 ml) was added to the reaction mixture, and the liquid was decanted from the precipitated product, which was then washed with pentane by decantation. All compounds were dried at room temperature in the dry box.

<sup>‡</sup> For the X-ray characterized  $\text{YbCl}_3(\text{thf})_n$  complexes,  $\nu(\text{Yb}-\text{Cl})$ : 269s and 238s  $\text{cm}^{-1}$  [ $\text{YbCl}_3(\text{thf})_3$ ]; 274s, 218s and 192s  $\text{cm}^{-1}$  [ $\text{YbCl}_3(\text{thf})_2$ ]. There is variation in the pattern of  $\nu(\text{Ln}-\text{Cl})$  bands for the series of  $\text{LnCl}_3(\text{thf})_2$  complexes, hence a common structure is unlikely

Compositions corresponded to those previously observed from alternative syntheses,<sup>6,7,13,14</sup> except that  $\text{LaCl}_3(\text{thf})_2$  was obtained instead of the reported  $\text{LaCl}_3(\text{thf})_{1.5}$ .<sup>13</sup> However, it is known that the stoichiometries are highly sensitive to washing and drying conditions<sup>6,7,13,14</sup> where the products are to be used *in situ* for further preparations, a yield of ca. 90% can be assumed, and the degree of thf complexation is irrelevant.

An X-ray study showed  $\text{YbCl}_3(\text{thf})_3$  to be isostructural<sup>§</sup> with  $\text{ScCl}_3(\text{thf})_3$ ;<sup>11</sup> hence the complex is monomeric with *mer* octahedral stereochemistry for ytterbium. A similar arrangement has been reported for  $\text{YCl}_3(\text{cpl})_3$  (cpl =  $\epsilon$ -caprolactone) in a recent communication.<sup>16</sup> Prolonged treatment (2 months) of  $\text{YbCl}_3(\text{thf})_3$  powder with pentane gave some  $\text{YbCl}_3(\text{thf})_2$  as single crystals, which were separated by hand-picking. X-Ray crystallography revealed the compound to be a *trans* octahed-



**Fig. 1** A single dimer (crystallographic  $2/m$  symmetry) of  $[\text{YbCl}_3(\text{thf})_2]_2$ . 20% Thermal ellipsoids are shown for the non-hydrogen atoms. Selected bond lengths (Å) and angles (°) are:  $\text{Yb}-\text{Cl}(1)$  2.683(2),  $\text{Yb}-\text{Cl}(2)$  2.490(3),  $\text{Yb}-\text{O}(11)$  2.268(7),  $\text{Yb}-\text{O}(21)$  2.261(8),  $\text{Cl}(1)-\text{Yb}-\text{Cl}(2)$  91.86(9),  $\text{Cl}(1)-\text{Yb}-\text{O}(11)$  87.9(2),  $\text{Cl}(1)-\text{Yb}-\text{O}(21)$  89.9(2),  $\text{Cl}(1)-\text{Yb}-\text{Cl}(1')$  78.15(7),  $\text{Cl}(1)-\text{Yb}-\text{Cl}(2')$  169.97(8),  $\text{Cl}(2)-\text{Yb}-\text{O}(11)$  90.9(2),  $\text{Cl}(2)-\text{Yb}-\text{O}(21)$  90.9(2),  $\text{Cl}(2)-\text{Yb}-\text{Cl}(2')$  98.1(1),  $\text{O}(11)-\text{Yb}-\text{O}(21)$  177.2(4),  $\text{Yb}\cdots\text{Yb}'$  101.8(1). Non-bonding separations  $\text{Yb}\cdots\text{Yb}$  4.165(1),  $\text{Cl}\cdots\text{Cl}$  3.382(4).

ral dimer (Fig. 1).§ The Yb–O distances agree with  $\langle \text{Yb–O} \rangle$  (2.265 Å) and  $\langle \text{Y–O} \rangle$  (2.272 Å) of mutually *trans* thf or cpl ligands of  $\text{YbCl}_3(\text{thf})_3$ <sup>15</sup> and  $\text{YCl}_3(\text{cpl})_3$ <sup>16</sup> respectively. (Ionic radii of six-coordinate  $\text{Yb}^{3+}$  and  $\text{Y}^{3+}$  differ by only 0.03 Å.<sup>17</sup>) As expected, the bridging Yb–Cl bond length is longer than the terminal Yb–Cl distance (Fig. 1). The latter is close to  $\langle \text{Yb–Cl} \rangle$  (2.525 Å) of  $\text{YbCl}_3(\text{thf})_3$ <sup>15</sup> but 0.1 Å shorter than  $\langle \text{Y–Cl} \rangle$  of  $\text{YCl}_3(\text{cpl})_3$ .<sup>16</sup> The structure of  $\text{YbCl}_3(\text{thf})_2$  is of particular interest as it is the first for the composition  $\text{LnCl}_3(\text{thf})_2$ , which is now (including La, Yb above) known for 13 rare earth elements.<sup>6,7,13,14</sup> This arrangement (Fig. 1) contrasts with monomeric six- and seven-coordinate  $\text{ScCl}_3(\text{thf})_3$ <sup>11</sup> and  $\text{LnCl}_3(\text{thf})_4$  (Ln = Nd<sup>9</sup> or Eu<sup>10</sup>), and appears (see ref. 16) to be a new structure for solvates of lanthanoid trichlorides.

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§ *Crystal data* for:  $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{O}_3\text{Yb}$ ,  $M = 495.70$ , monoclinic, space group  $P2_1/c$ ,  $a = 9.057(2)$ ,  $b = 12.857(1)$ ,  $c = 15.713(7)$  Å,  $\beta = 92.26(3)^\circ$ .<sup>15</sup>

*Crystal data* for:  $[\text{YbCl}_2(\mu\text{-Cl})(\text{thf})_2]_2 \cdot \text{C}_{16}\text{H}_{32}\text{Cl}_6\text{O}_4\text{Yb}_2$ ,  $M = 847.21$ , monoclinic, space group  $C2/m$ ,  $a = 11.051(4)$ ,  $b = 11.950(5)$ ,  $c = 10.683(2)$  Å,  $\beta = 108.87(2)^\circ$ ,  $V = 1335$  Å<sup>3</sup>,  $D_c$  ( $Z = 2$  dimers)  $2.11$  g cm<sup>-3</sup>. 1410 'observed' [ $I > 3\sigma(I)$ ] independent absorption corrected diffractometer data were refined by full-matrix least-squares to  $R = 0.043$ ,  $R_w = 0.050$  (statistical weights). Monochromatic Mo-K $\alpha$  radiation ( $\lambda$  0.71073 Å), anisotropic thermal parameter refinement for the non-hydrogen atoms. For this structure, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.