Synthesis of a new stable, neutral organothulium(II) complex by reduction of a thulium(III) precursor

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Received (in Cambridge, UK) 19th October 2005, Accepted 15th November 2005
First published as an Advance Article on the web 7th December 2005
DOI: 10.1039/b514818a

The new stable, neutral Tm^{II} complex $(Cp^{ttt})_2Tm$ [Cp^{ttt} = 1,2,4-tris(*tert*-butyl)cyclopentadienyl] can be obtained either by direct reaction of $NaCp^{ttt}$ with TmI_2 or by reduction of $(Cp^{ttt})_2TmI$ in non-polar solvents; this latter route may prove itself useful for the isolation of other neutral "non-classical" low-valent organolanthanide species.

Molecular complexes of "non-classical" divalent lanthanides, as defined by the compounds in which the divalent element is different from the "classical" samarium, europium or ytterbium, have recently received much attention, and a review[1] has summarised significant advances in this field. Access to "non-classical" organolanthanides has involved two methods: a) a metathetical reaction of anionic ligand precursors with LnI_2: neutral complexes such as $L_2Ln(THF)_x$ (L = substituted cyclopentadienyl or phospholyl, Ln = Tm, x = 0 or 1) have been synthesised this way,[2] and b) reduction of trivalent precursors: a La^{II} anionic complex has been described and characterised by X-ray and ESR;[3] this route appears advantageous because lanthanide(III) organometallics are the most easily available.

However, earlier attempts at the synthesis of neutral cyclopentadienyl complexes of Ln^{II} (Ln = Nd, Tm) by this latter route have proven unsuccessful, although Ln^{II} species seemed to be involved at early stages of the reaction. In these attempts, polar solvents such as THF[4] or DME[5] were used. Since decomposition of "non-classical" divalent organolanthanides proceeds *via* electron transfer to the coordinated solvent, we reasoned that non-polar solvents would constitute a better reaction medium for the access to Ln^{II} complexes by reduction of Ln^{III} precursors. So, we tried the synthesis of $(Cp^{ttt})_2Tm$ [Cp^{ttt} = 1,2,4-tris(*tert*-butyl)cyclopentadienyl], a very sterically crowded, unsolvated Tm^{II} complex, by reduction of the Tm^{III} precursor $(Cp^{ttt})_2TmI$ (it can be noted that bulky Cp ligands have been previously used to stabilise the divalent Yb^{II}).[6] We selected KC_8 as reducing agent because it had been shown to reduce a Sc^{III} homoleptic compound into a low-valent scandium complex,[7] and also NdI_3 into Nd^{II} species.[8] As a comparison, we also describe the synthesis of $(Cp^{ttt})_2Tm$ by the direct metathetical route.

Attempts to prepare $(Cp^{ttt})_2TmI$ by the reaction of $(Cp^{ttt})K$ or $(Cp^{ttt})Na$ with TmI_3 in THF were unsuccessful. The reaction did not go to completion, even at reflux temperature for several days. However, we found that heating 2 equivalents of $(Cp^{ttt})K$ with TmI_3 in toluene at 110 °C for three days resulted in the formation of bright yellow $(Cp^{ttt})_2TmI$ in good yield.† An X-ray crystallographic study‡ (Fig. 1), an elemental analysis and magnetic susceptibility measurements confirmed the structure of this compound. The most noteworthy feature is the monomeric nature of this complex in the solid state. The other known bis(cyclopentadienyl)thulium(III) iodides are either a μ-iodo dimer,[4] or solvated[9] or chelated[5,10] monomers. The recently reported $(Cp^{ttt})_2CeF$, a related halide complex of Ce^{III} with Cp^{ttt}, is also monomeric in the solid state.[11]

We found that, despite its high paramagnetism, $(Cp^{ttt})_2TmI$ displayed a characteristic, reproducible proton NMR spectrum in which two very broad bands ($w_{1/2} \approx$ 2–3 kHz) at *ca.* 92 ppm and −15 ppm (in C_6D_{12}), presumably due to the *tert*-butyl groups, are present. Due to their width and to baseline roll, these bands are difficult to integrate accurately and thus the spectrum is more of the "fingerprint" type.

This useful feature allowed us to undertake the reduction of $(Cp^{ttt})_2TmI$ with KC_8 in C_6D_{12} and to follow the reaction by NMR spectroscopy. The reaction proceeded slowly at room temperature with progressive disappearance of the bands due to $(Cp^{ttt})_2TmI$ and the appearance of three new bands at −63.7, 22.2

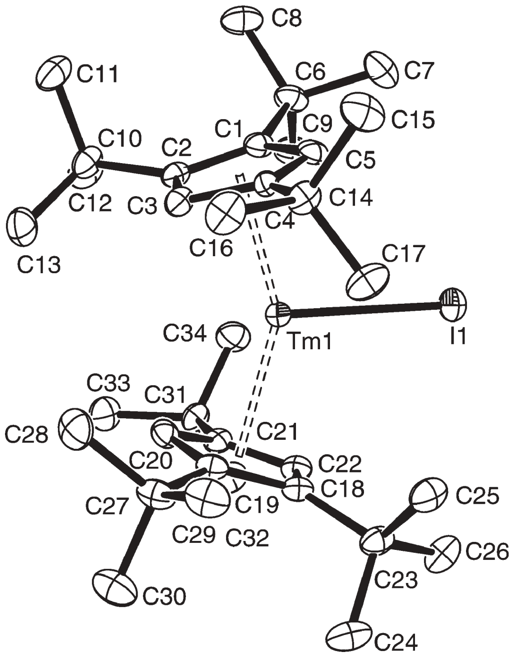

Fig. 1 An ORTEP plot of $(Cp^{ttt})_2TmI$ (50% ellipsoids, H atoms omitted). Selected distances [Å] and angles [°] = Tm1–I1: 2.8999(5), Tm1–C(av.): 2.66, centroid(Cp)–Tm1–centroid(Cp): 148.

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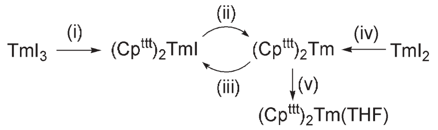

Scheme 1 *Reagents and conditions:* (i) (Cp^{ttt})K, toluene, 110 °C, 3 d; (ii) KC$_8$ (10 eq.), toluene, RT, 48 h; (iii) AgI, THF, 0 °C, 30 min; (iv) (Cp^{ttt})Na·0.5THF, THF, 0 °C, 2 h, then evaporation of THF, extraction and crystallisation from pentane; (v) crystallisation, THF–pentane.

and 32.4 ppm while the solution turned from light yellow to dark purple. After 24 h, the (Cp^{ttt})$_2$TmI bands had completely disappeared. The reaction was repeated in a preparative scale in toluene and the product obtained after filtration and evaporation to dryness was a very deep purple microcrystalline powder, extremely soluble in hydrocarbons. Unfortunately, we were not able to grow crystals of this material suitable for an X-ray study; however, we are able to ascribe to it the composition (Cp^{ttt})$_2$Tm on the following bases: (a) the measured magnetic susceptibility (Evans' method) is $\mu_{\mathrm{eff}} = 5.0\ \mu_{\mathrm{B}}$ per mole of (Cp^{ttt})$_2$Tm, compatible with Tm$^{\mathrm{II}}$; (b) oxidation of this complex with AgI in THF gives (Cp^{ttt})$_2$TmI as indicated by its NMR spectrum which is identical to that of (Cp^{ttt})$_2$TmI obtained by the metathetical route; (c) reaction of NaCp^{ttt} with TmI$_2$(THF)$_3$ in THF gives, after evaporation of the solvent and crystallisation from pentane, a product having an NMR spectrum identical to that of unsolvated (Cp^{ttt})$_2$Tm obtained by reduction; (d) after treatment of this complex with THF and pentane, we were able to isolate extremely air-sensitive crystals with composition (Cp^{ttt})$_2$Tm(THF), as shown by X-ray crystallography (Scheme 1 and Fig. 2).†‡

An examination of the lattice parameters revealed that the X-ray structure of (Cp^{ttt})$_2$Tm(THF) is isomorphous to that of the previously reported (Cp^{ttt})$_2$Sm(THF) and (Cp^{ttt})$_2$Sr(THF).[12] The Tm–C(av.) and Tm–O bond distances are of course shorter than in these two compounds, according to the lanthanide contraction, but the centroid(Cp)–Tm–centroid(Cp) angles are identical.

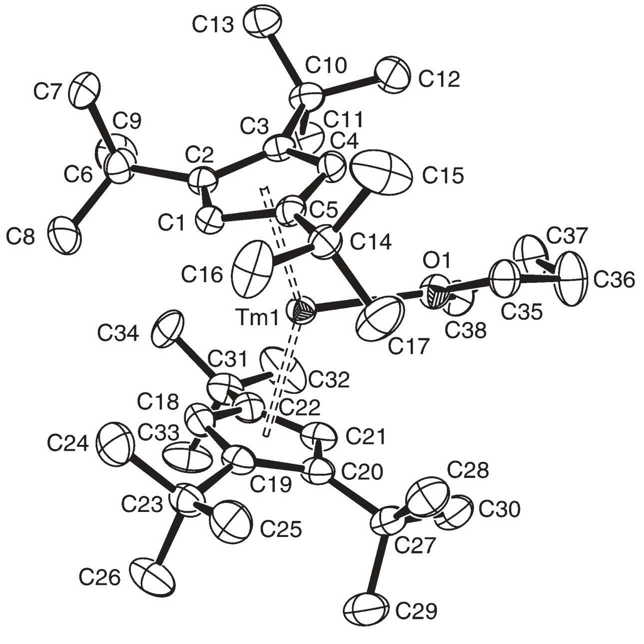

Fig. 2 An ORTEP plot of (Cp^{ttt})$_2$Tm(THF) (50% ellipsoids, H atoms omitted). Selected distances [Å] and angles [°]: Tm1–O1: 2.473(2), Tm1–C(av.): 2.75, centroid(Cp)–Tm1–centroid(Cp): 149.

Solutions of (Cp^{ttt})$_2$Tm in non-polar solvents are stable for more than 48 h at room temperature, as judged by proton NMR spectroscopy. Three bands could be respectively attributed, from low to high field, to the single *tert*-butyl, the two adjacent *tert*-butyls and the two protons on the Cp ring, from their relative integration. Introduction of THF into a solution of this compound in C$_6$D$_{12}$ induced noticeable changes in the proton chemical shifts§. This observation, which parallels the described behaviour of (Cp^{ttt})$_2$Sm and (Cp^{ttt})$_2$Sr,[12] can be attributed to chemical exchange of THF around Tm in solution, and is in contrast to the case of (Cp^{ttt})$_2$Yb for which no change has been reported upon addition of THF. One can also note that unsolvated (Cp^{ttt})$_2$Yb has been reported to crystallise even from THF,[12] whilst we obtained the solvated (Cp^{ttt})$_2$Tm(THF) from THF–pentane. Thus, despite the small difference in ionic radius[13] between Tm$^{\mathrm{II}}$ and Yb$^{\mathrm{II}}$, the divalent ion is much less shielded by the two Cp^{ttt} ligands in (Cp^{ttt})$_2$Tm than in (Cp^{ttt})$_2$Yb, although, of course, desolvation of THF from (Cp^{ttt})$_2$Tm(THF) could be easily achieved, as previously described for the closely related (Cp^{ttt})$_2$Sm(THF) and (Cp^{ttt})$_2$Sr(THF).[12]

In summary, we have found a donor-solvent-free route to a stable, neutral, homoleptic complex of Tm$^{\mathrm{II}}$, by reduction of a Tm$^{\mathrm{III}}$ precursor that could be characterised by proton NMR spectroscopy. We will now try to generalise this route to the synthesis of other unsolvated Tm$^{\mathrm{II}}$ complexes bearing less bulky substituents, and of complexes with other "non-classical" divalent lanthanides: the potential of these complexes in the field of nitrogen activation appears promising.[14]

Notes and references

† **Synthesis of (Cp^{ttt})$_2$TmI: (a)** TmI$_3$ (0.40 g, 0.73 mmol) and (Cp^{ttt})K (0.40 g, 1.46 mmol) were refluxed in toluene (10 mL) for 72 h. After centrifugation, the solvent was evaporated and the residue rinsed with cold hexane. Pure (Cp^{ttt})$_2$TmI was obtained as a yellow powder in 62% yield (0.34 g, 0.45 mmol). **(b)** A solution of (Cp^{ttt})$_2$Tm (0.15 g, 0.24 mmol) in THF (5 mL) and AgI (0.06 g, 0.24 mmol) was stirred for 30 min at 0 °C. After centrifugation, evaporation of the solvent resulted in the formation of yellow crystals which were washed with cold hexane. The pure product was isolated in 38% yield (0.07 g, 0.09 mmol). Anal. Calcd for C$_{34}$H$_{58}$ITm: C, 53.55 H, 7.67. Found: C, 53.94; H, 7.57%. ^{1}H NMR (C$_6$D$_{12}$, 300 MHz): δ (ppm) −15 (br s, $w_{1/2} \approx$ 1700 Hz, *t*-Bu), 92 (br s, $w_{1/2} \approx$ 2700 Hz, *t*-Bu). $\mu_{\mathrm{eff}} = 7.0\ \mu_{\mathrm{B}}$. **Synthesis of (Cp^{ttt})$_2$Tm: (a)** A mixture of (Cp^{ttt})$_2$TmI (90 mg, 0.12 mmol) and KC$_8$ (193 mg, 1.43 mmol) was stirred in toluene (3 mL) at room temperature for 48 h. After evaporation of the solvent, pentane was added to the residue and the dark purple solution was filtered. Concentrating the solution and washing the resulting solid with cold pentane yielded pure, dark purple (Cp^{ttt})$_2$Tm in 47% yield (35 mg, 0.06 mmol). **(b)** A mixture of TmI$_2$(THF)$_3$ (0.50 g, 0.78 mmol) and (Cp^{ttt})Na·0.5THF (0.46 g, 1.57 mmol) was stirred at 0 °C in THF (15 mL) for 2 h, evaporated to dryness and pentane was added to the residue. After filtration and evaporation of the solvent, the crude product was washed with cold pentane to yield the pure crystalline product in 32% yield (0.16 mg, 0.25 mmol). ^{1}H NMR (C$_6$D$_{12}$, 300 MHz): δ (ppm) −63.7 (br s, $w_{1/2}$ 800 Hz, 4H), 22.2 (br s, $w_{1/2}$ 300 Hz, 36H), 32.4 (br s, $w_{1/2}$ 270 Hz, 18H). $\mu_{\mathrm{eff}} = 5.0\ \mu_{\mathrm{B}}$.

‡ *Crystal data for (Cp^{ttt})$_2$TmI*: C$_{34}$H$_{58}$ITm = 762.63, monoclinic, space group $P2_1/c$ (n° 14), a (Å) = 10.3340(10), b (Å) = 15.7470(10), c (Å) = 20.4740(10), β (°) = 99.4000(10), V (Å^3) = 3287.0(4), Z = 4, T (K) = 150.0(1), reflections measured: 17047, reflections used: 7786 [$I > 2\sigma(I)$], R_1 = 0.0492, wR_2 = 0.1626, GoF = 1.058. An unusually large residual electron density peak (8 e$^-$·Å^3) is located 1.3 Å from Tm(1) opposite to I(1), and, due to its position, was attributed to an artefact. *Crystal data for (Cp^{ttt})$_2$Tm(THF)*: C$_{38}$H$_{66}$OTm = 707.84, monoclinic, space group $P2_1/n$

(n° 14), a (Å) = 10.2120(10), b (Å) = 15.6790(10), c (Å) = 23.3570(10), β (°) = 94.3800(10), V (Å^3) = 3728.9(5), Z = 4, T (K) = 150.0(1), reflections measured: 16147, reflections used: 7324 [$I > 2\sigma(I)$], R_1 = 0.0392, wR_2 = 0.0891, GoF = 1.025. One *tert*-butyl group is disordered over two positions. CCDC 286776–286777 for $(Cp^{ttt})_2TmI$ and $(Cp^{ttt})_2Tm(THF)$, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514818a

§ *NMR of* $(Cp^{ttt})_2Tm$ + n *equivalents of THF:* (C_6D_{12}, 300 MHz): δ (ppm) −79.9, 21.5, 40.1 (n = 3); −106.4, 19.6, 55.2 (n = 22).

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