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σ-Bonded organometallic derivatives of yttrium(III) and thulium(III): An unusual ligand coupling reaction mediated by thulium(III)

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Abstract

The reaction between $LnI_3(THF)_{3.5}$ and 2 equiv. of $\{(Me_3Si)_2(Me_2MeOSi)C\}K$ (**1**) in THF at room temperature yields only the mono-substituted products $\{(Me_3Si)_2(Me_2MeOSi)C\}LnI_2(THF)_2$ [Ln = Y (**5**), Tm (**6**)]; under more forcing conditions decomposition occurs. In contrast, the metathesis reaction between $TmI_3(THF)_{3.5}$ and 2 equiv. of the lithium iodide-containing salt $\{(Me_3Si)_2(Me_2MeOSi)C\}K(LiI)_x$ yields the highly unusual separated ion pair complex $[[\{(Me_3Si)_2C(SiMe_2)\}_2O]TmI_2\{Li(THF)_3\}_2][[\{(Me_3Si)_2C(SiMe_2)\}_2O]TmI_2]$ (**8**). The dianionic ligand in **8** is derived from the coupling of 2 equiv. of $(Me_3Si)_2(Me_2MeOSi)C^-$, accompanied by the *formal* elimination of Me_2O. The structures of compounds **5**, **6**, and **8** have been determined by X-ray crystallography; compound **8** crystallizes as an unusual ion pair, the cation and anion of which differ only in the inclusion of 2 equiv. of $Li(THF)_3$ in the former, bridged to thulium by iodide ions.

Keywords: Lanthanide; Organometallic; Rearrangement; Crystal structure

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1. Introduction

The organometallic chemistry of the lanthanide(III) ions is dominated by complexes containing (substituted) cyclopentadienyl ligands. In such complexes the cyclopentadienyl ligands typically act as spectator groups which do not take part in reactions. In contrast, organolanthanide complexes containing alkyl ligands such as the triorganosilylmethyls, $(Me_3Si)_nCH^-_{(3-n)}$, exhibit remarkable structures and reactivities and many such species are catalytically active for olefin transformations such as polymerization, hydrosilylation and hydroamination/cyclization [1].

We recently reported that the incorporation of donor functionality into the periphery of a tris(triorganosilyl)methyl ligand can have a pronounced effect on the chemistry of its complexes with lanthanide(III) ions. Reactions between either of the larger, lighter lanthanide triiodides $LaI_3(THF)_4$ or $NdI_3(THF)_{3.5}$ and 2 equiv. of the potassium alkyl $\{(Me_3Si)_2(Me_2MeOSi)C\}K$ (**1**) do not proceed smoothly [2]. With $LaI_3(THF)_4$ this reaction yields an inseparable mixture of the mono- and di-substituted products $\{(Me_3Si)_2(Me_2MeOSi)C\}LaI_2(THF)$ (**2**) and $\{(Me_3Si)_2(Me_2MeOSi)C\}_2LaI(THF)$ (**3**), whereas with $NdI_3(THF)_{3.5}$ this reaction yields the alkoxo-bridged dimer $[\{(Me_3Si)_2(Me_2MeOSi)C\}Nd(I)(THF)(\mu\text{-}OMe)]_2$ (**4**), via Si–O cleavage of one of the ligands (Scheme 1); attempts to force the former reaction to completion led to extensive decomposition.

We were interested to see whether the smaller ionic radii, and the consequent increased Lewis acidity, of the mid-to-late lanthanide(III) ions would influence their chemistry with this methoxy-functionalized ligand and, in particular,

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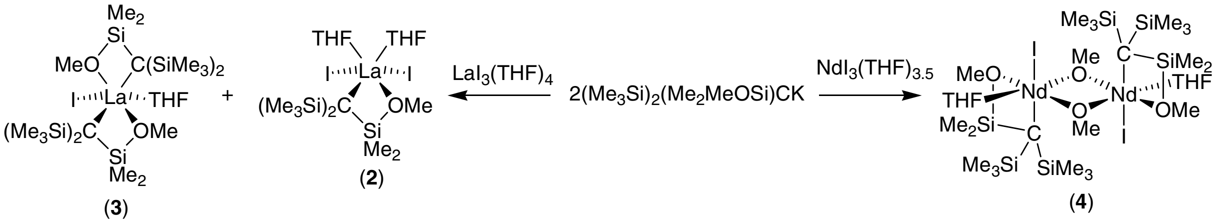

Scheme 1.

whether the Si–O cleavage reaction observed with Nd(III) would find any parallel. We report herein the results of reactions between **1** and both the late lanthanide triiodide $TmI_3(THF)_{3.5}$ and $YI_3(THF)_{3.5}$, which is representative of the mid-lanthanide(III) ions [the ionic radii of Y(III) and Ho(III) are 0.900 and 0.901 Å, respectively, for six-coordination] [3], but which gives diamagnetic complexes amenable to characterization by NMR spectroscopy.

2. Results and discussion

Reactions between either $YI_3(THF)_{3.5}$ or $TmI_3(THF)_{3.5}$ and 2 equiv. of the potassium salt $\{(Me_3Si)_2(Me_2MeOSi)C\}K$ (**1**) in THF at room temperature yield the *mono*-alkyl derivatives $\{(Me_3Si)_2(Me_2MeOSi)C\}LnI_2(THF)_2$ [Ln = Y (**5**), Tm (**6**)] as the sole lanthanide-containing products, irrespective of the reaction time (Eq. (1)); there is no evidence for the formation of the expected dialkyl compounds $\{(Me_3Si)_2(Me_2MeOSi)C\}_2LnI(THF)_n$. Compounds **5** and **6** are initially isolated as colorless or pale yellow oils, respectively, which may be crystallized from cold methylcyclohexane/THF to give colorless or pale yellow blocks, respectively. The ^1H and $^{13}C\{^1H\}$ NMR spectra of diamagnetic **5** are as expected and are consistent with the above formulation.

$$\begin{aligned}&2\{(Me_3Si_2)(Me_2MeOSi)C\}K\ (\mathbf{1}) + LnI_3(THF)_{3.5}\\&\quad\xrightarrow{THF}\{(Me_3Si)_2(Me_2MeOSi)C\}LnI_2(THF)_2\\&\qquad[Ln = Y\ (\mathbf{5}), Tm\ (\mathbf{6})] + KI\end{aligned}\tag{1}$$

Although only one alkyl ligand is bound to the yttrium center in **5**, we find no evidence for residual **1** after removal of both **5** and volatiles from the crude reaction mixture. The ^1H NMR spectrum of this residue exhibits a multitude of signals in the $SiMe_3$ and OMe regions which do not correspond to **1**, but which we are unable to assign unambiguously. Attempts to force these reactions to completion by heating under reflux or by using a substantial excess of **1** led only to extensive decomposition to highly viscous oils from which no organolanthanide products could be isolated. This behavior recalls that of the larger lanthanum(III) ion, which gives an inseparable mixture of the mono- and di-substituted complexes **2** and **3** at room temperature, but only decomposition products at elevated temperatures [2]. The inaccessibility of a dirganoyttrium complex with this ligand contrasts markedly with the successful synthesis of the closely related triorganoyttrium complex $\{(Me_3Si)(Me_2MeOSi)CH\}_3Y$ (**7**) recently reported by Lappert and co-workers [4].

Compounds **5** and **6** are both isomorphous and isostructural. The molecular structure of **5** is shown in Fig. 1 and details of selected bond lengths and angles for both **5** and **6** are given in Table 1. In each case the lanthanide ion is coordinated by both the carbanion center and the methoxy group of the alkyl ligand to give a four-membered chelate ring [C–Ln–O bite angle 67.43(16)° (**5**), 68.16(14)° (**6**)]. The coordination sphere of the lanthanide ions is completed by two iodide ligands and the oxygen atoms of two THF ligands to give a six-coordinate lanthanide center with a distorted octahedral geometry.

The Y–C distance of 2.547(6) Å is rather long for this type of contact; for example, the Y–C distances in the six-coordinate complex **7** are 2.476(3), 2.468(3) and 2.485(3) Å and the Y–C distances in three-coordinate $\{(Me_3Si)_2CH\}_3Y$ are 2.475(7) Å [4]. The long Y–C distance in **5** compares more closely with the Y–C distance of 2.558(19) Å in $Me_2Si(N\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)\}_2Y\{CH(SiMe_3)_2\}$ [5]. The Tm–C distance of 2.502(5) Å is only the second Tm(III)–C(sp^3) distance to be measured crystallographically; the Tm–C distances in $(\eta^2\text{-}C_{10}H_{14})TmI(DME)_2$, prepared from the reaction between TmI_2 and anthracene and the only other reported complex containing a Tm(III)–C(sp^3) bond, are 2.479(5) and 2.471(6) Å [DME = 1,2-dimethoxyethane] [6]. The Tm–C distance in **6** compares with Tm–C(sp^2) distances of 2.421(6), 2.425(6) and

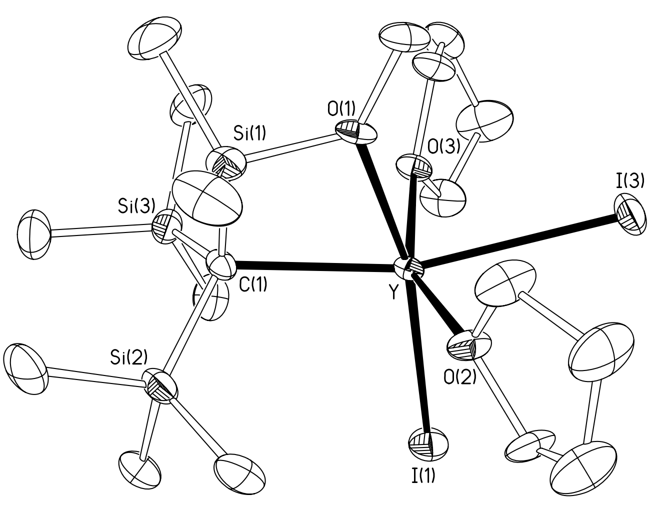

Fig. 1. Molecular structure of **5** with 40% probability ellipsoids and with H atoms omitted for clarity.