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 $\{(Me_3Si)_2(Me_2MeO-Si)C\}K(LiI)_x$ 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.
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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 triorganosilyl-methyls, $(Me_3Si)_nCH^-_{(3-n)}$, 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(triorganosi-lyl)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 $[\{(Me_3Si)_2(Me_2MeOSi)C\}Nd(I)(THF)(\mu-OMe)]_2$ (**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,
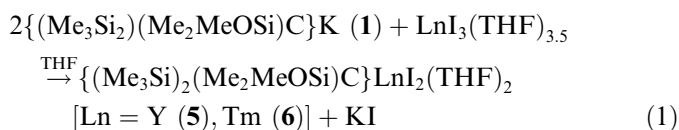
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Scheme 1.
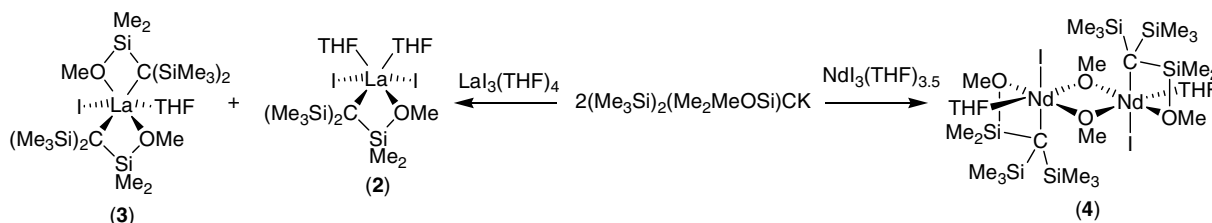
whether the Si–O cleavage reaction observed with Nd(III) would find any parallel. We report herein the results of reactions between **1** and both the late lanthanide triiodide $TmI_3(THF)_{3.5}$ and $YI_3(THF)_{3.5}$, which is representative of the mid-lanthanide(III) ions [the ionic radii of Y(III) 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.

$$2\{(Me_3Si)_2(Me_2MeOSi)C\}K \ (\mathbf{1}) + LnI_3(THF)_{3.5}$$
$$\overset{THF}{\rightarrow} \{(Me_3Si)_2(Me_2MeOSi)C\}LnI_2(THF)_2$$
$$[Ln = Y \ (\mathbf{5}), Tm \ (\mathbf{6})] + KI \quad (1)$$

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 $Me_2Si(N-t-Bu)(O-t-Bu)\}_2Y\{CH(SiMe_3)_2\}$ [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 $(\eta^2-C_{10}H_{14})TmI(DME)_2$, 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
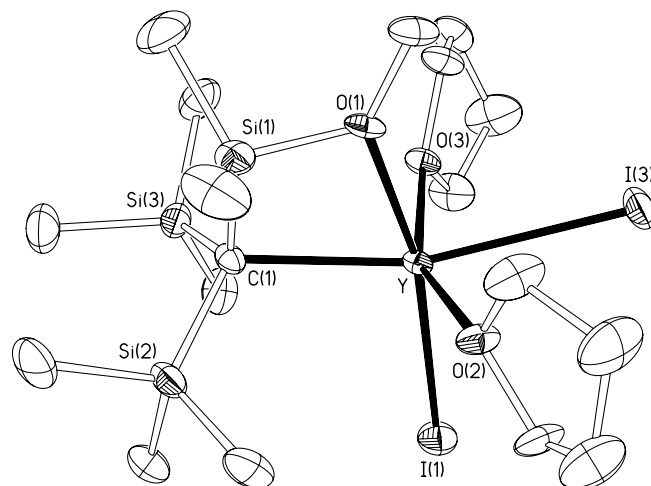

Fig. 1. Molecular structure of **5** with 40% probability ellipsoids and with H atoms omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **5** and **6**

5

Y–I(1)	2.9511(7)	Y–I(2)	3.0837(7)	Y–C(1)	2.547(6)
Y–O(1)	2.303(4)	Y–O(2)	2.362(4)	Y–O(3)	2.320(4)
C(1)–Si(1)	1.822(5)	C(1)–Si(2)	1.877(6)	C(1)–Si(3)	1.878(6)
Si(1)–C(Me)$_{av.}$	1.883(8)	Si(1)–O(1)	1.739(5)		

I(1)–Y–I(2)	96.29(2)		I(1)–Y–O(2)	93.53(10)
I(1)–Y–O(3)	97.77(10)		I(1)–Y–C(1)	100.35(12)
C(1)–Y–O(1)	67.43(16)		C(1)–Y–O(2)	102.26(17)
C(1)–Y–O(3)	97.09(17)		O(1)–Y–O(2)	85.41(14)
O(1)–Y–O(3)	88.21(14)		O(2)–Y–I(2)	77.74(11)
O(3)–Y–I(2)	79.37(10)		O(1)–Y–I(2)	96.05(10)

6

Tm–I(1)	2.9159(4)	Tm–I(2)	3.0467(4)	Tm–C(1)	2.502(5)
Tm–O(1)	2.276(3)	Tm–O(2)	2.335(3)	Tm–O(3)	2.292(3)
C(1)–Si(1)	1.815 (5)	C(1)–Si(2)	1.879(5)	C(1)–Si(3)	1.874(5)
Si(1)–C(Me)$_{av.}$	1.870(6)	Si(1)–O(1)	1.729(4)		

I(1)–Tm–I(2)	95.923(12)		I(1)–Tm–O(2)	93.46(8)
I(1)–Tm–O(3)	97.68(8)		I(1)–Tm–C(1)	100.19(11)
C(1)–Tm–O(1)	68.16(14)		C(1)–Tm–O(2)	102.21(13)
C(1)–Tm–O(3)	97.29(13)		O(1)–Tm–O(2)	85.36(11)
O(1)–Tm–O(3)	88.21(11)		O(2)–Tm–I(2)	77.99(9)
O(3)–Tm–I(2)	79.12(8)		O(1)–Tm–I(2)	95.87(8)

2.416(7) Å in Ph$_3$Tm(THF)$_3$ [7] and 2.413(3) Å in (2,6-Ar$_2$C$_6$H$_3$)TmCl$_2$(THF)$_2$ [Ar = 1-naphthyl] [8]. Surprisingly, the difference in the Y–C and Tm–C distances in **5** and **6** (0.045 Å) is somewhat larger than the difference in ionic radii of Y(III) and Tm(III) [ionic radii for six-coordinate Y(III) 0.900, Tm(III) 0.880 Å [3]]. This is particularly notable since it might be expected that the increase in steric compression about the Tm(III) ion in **6** compared to the larger Y(III) ion in **5** would lead to a concomitantly longer than expected Ln–C bond in the former.

The Y–I distances are 2.9511(7) and 3.0837(7) Å, the longer distance corresponding to the iodide ligand *trans* to the carbanion center; these are similar to the Y–I distances in YI$_3$(THF)$_{3.5}$ [2.9984(7) and 3.0181(6) Å] [9]. Similarly, the Tm–I distance for the iodide *trans* to the carbanion center [3.0467(4) Å] is also slightly longer than the other Tm–I distance [2.9159(4) Å], and both distances are similar to the Tm–I distances of 3.0338(11) and 3.0145(4) Å in (COT)TmI(THF)$_2$ [6] and (η^5-C$_5$H$_4$-CH$_2$CH$_2$NMe$_2$)$_2$TmI [10], respectively. The Y–O and Tm–O distances are typical for this type of contact [6,9–11].

During the course of this investigation we were surprised to observe a highly unusual ligand coupling reaction mediated by Tm(III). The organopotassium reagent **1** is derived from the reaction between MeK and (Me$_3$Si)$_2$(Me$_2$MeO-Si)CH [12]. This latter reaction proceeds smoothly when the MeK is prepared from low halide content MeLi purchased from Aldrich. However, in one case we prepared our MeK from MeLi purchased from an alternative supplier (Acros Organics). In this case an undisclosed lithium

impurity was carried forward in the reaction, ultimately yielding a batch of **1** contaminated by lithium. The ^{1}H and ^{13}C{^{1}H} NMR spectra of this contaminated batch of **1** were indistinguishable from clean samples; however, a strong signal was observed in the ^{7}Li spectrum, clearly indicating an inorganic source of contamination such as a lithium halide.

This lithium contamination has a remarkable effect on the course of the reaction between **1** and TmI$_3$(THF)$_{3.5}$. The reaction of TmI$_3$(THF)$_{3.5}$ with 2 equiv. of lithium-containing **1** gives the novel ate complex [[{(Me$_3$Si)$_2$C(Si-Me$_2$)}$_2$O]TmI$_2${Li(THF)$_3$}$_2$][[{(Me$_3$Si)$_2$C(SiMe$_2$)}$_2$O]TmI$_2$] (**8**) in good yield as pale yellow blocks after crystallization from methylcyclohexane/THF. As long as **1** was prepared from the same batch of MeLi this reaction was entirely reproducible. The reaction appears to proceed via the coupling of two (Me$_3$Si)$_2$(Me$_2$MeOSi)C$^-$ ligands, with the formal elimination of Me$_2$O, to give a new dianionic ligand [{(Me$_3$Si)$_2$C(SiMe$_2$)}$_2$O]$^{2-}$ (Scheme 2) [this dianionic ligand may be deliberately prepared from the reaction of 2 equiv. of {(Me$_3$Si)$_2$CH}Li with ClSiMe$_2$OSiMe$_2$Cl [12]]. Reactions between TmI$_3$(THF)$_{3.5}$ and clean samples of **1** under the same conditions proceed smoothly to give the mono-alkyl complex **6** (see above) and compound **1** is stable both in the solid state and in solution for long periods [12]. Thus, the ligand rearrangement observed in reactions with lithium-contaminated **1** appears to be a consequence of the presence of both Tm(III) and the lithium impurity. However, when TmI$_3$(THF)$_{3.5}$ was reacted with 2 equiv. of **1** in the presence of LiI only an intractable oil was produced, from which no thulium-containing products could
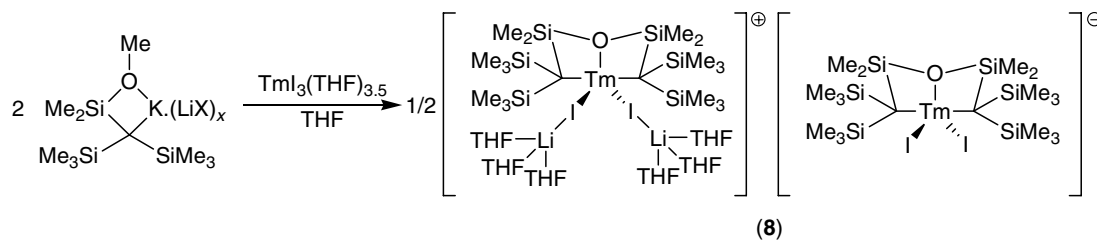
Scheme 2.

be isolated. Similarly, the reaction between KOBu^t and commercially sourced MeLi·LiI in ether yields only an inactive colorless solid which does not metalate $(Me_3Si)_2(Me_2MeOSi)CH$.

The formal elimination of Me_2O during the ligand coupling reaction appears to involve both Si–O and C–O cleavage and Si–O bond formation. To our knowledge, such a metal-mediated rearrangement is without precedent [13]; although we and others have observed the ready cleavage of Si–O bonds in this and related ligands mediated by a variety of metal centers, giving products containing metal alkoxide functionalities [2,14], such a reaction has not previously been accompanied by C–O cleavage or Si–O bond formation. Similarly, although the formation of silaethene intermediates such as $(Me_3Si)_2C=SiMe_2$ is known to occur on thermolysis of $(Me_3Si)_2(Me_2XSi)CM$ [X = e.g. halogen; M = Li, Na] [15], a mechanism involving such an elimination seems somewhat unlikely in the present case.

Compound **8** adopts a highly unusual structure in the solid state, consisting of a separated ion pair; the X-ray crystallographic data for **8** are rather poor, despite repeated attempts at crystallization and data collection; however, the gross features of the structure are clear. The structure of **8** is shown in Fig. 2 and details of selected bond lengths and angles are given in Table 2.

The anion consists of a thulium(III) ion coordinated by the oxygen and the two carbanion centers of a $[\{(Me_3Si)_2-C(SiMe_2)\}_2O]^{2-}$ ligand [C–Tm–O bite angles 67.8(6)° and 68.9(6)°] and by two iodide ligands. Thus, the thulium ion in the anion is five-coordinate with a highly distorted trigonal bipyramidal geometry, in which the two carbanion centers lie in the "axial" positions [C(4)–Tm(1)–C(12) 135.1(7)°]. The cation of **8** is remarkably similar to the anion: the thulium(III) center is coordinated by the oxygen atom and the two carbanion centers of a $[\{(Me_3Si)_2-C(SiMe_2)\}_2O]^{2-}$ ligand and by two iodide ligands in a distorted trigonal bipyramidal geometry [C–Tm–O bite angles 67.9(5)° and 68.7(5)°, C(22)–Tm(2)–C(30) 135.1(6)°]. The cation and anion in **8** differ only in the coordination of a $Li(THF)_3$ group to each of the iodide ions in the former, giving the cation an overall unipositive charge. The coordination of the $Li(THF)_3$ groups to the cation has little effect on the Tm–C, Tm–O and Tm–I distances compared to those of the anion [anion: Tm(1)–C(4) 2.48(2), Tm(1)–C(12) 2.557(17), Tm(1)–O(1) 2.259(12), Tm(1)–I(1) 2.933(5), Tm(1)–I(2) 2.915(8) Å; cation: Tm(2)–C(22) 2.524(15), Tm(2)–C(30) 2.510(15), Tm(2)–O(2) 2.250(10), Tm(2)–I(3) 2.889(1), Tm(2)–I(4) 2.917(2) Å]. These distances are similar to the Tm–C, Tm–O and Tm–I distances in **6** and related molecules (see above).

In summary, the products from metathesis reactions between lanthanide triiodides and potassium alkyls are strongly dependent upon the nature of the metal center and the precise reaction conditions. Reactions between $YI_3(THF)_{3.5}$ or $TmI_3(THF)_{3.5}$ and 2 equiv. of the potassium alkyl **1** yield only mono-substituted products due to
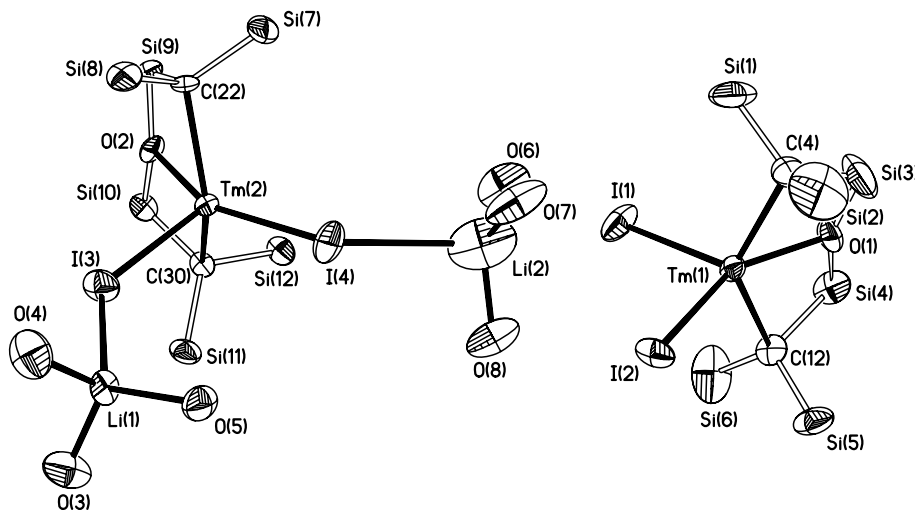

Fig. 2. Structure of **8** with 40% probability ellipsoids. Methyl groups, THF C atoms, H atoms and minor disorder components are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **8**

Anion

Tm(1)–C(4)	2.48(2)	Tm(1)–C(12)	2.563(17)	Tm(1)–I(1)	2.930(5)
Tm(1)–I(2)	2.915(8)	Tm(1)–O(1)	2.255(12)		

C(4)–Tm(1)–O(1)	67.8(6)	C(12)–Tm(1)–O(1)	69.0(6)
C(4)–Tm(1)–C(12)	135.1(7)	I(1)–Tm(1)–I(2)	97.0(2)
I(1)–Tm(1)–O(1)	112.2(4)	I(1)–Tm(1)–C(4)	111.1(6)
I(1)–Tm(1)–C(12)	95.7(5)	I(2)–Tm(1)–C(4)	106.8(6)
I(2)–Tm(1)–C(12)	104.6(5)	I(2)–Tm(1)–O(1)	150.4(4)

Cation

Tm(2)–C(22)	2.525(15)	Tm(2)–C(30)	2.505(15)	Tm(2)–I(3)	2.8990(15)
Tm(2)–I(4)	2.9169(15)	Tm(2)–O(2)	2.250(10)	I(3)–Li(1)	2.78(4)
I(4)–Li(2)	3.08(6)	Li(1)–O(3)	1.895(17)	Li(1)–O(4)	1.891(17)
Li(1)–O(5)	1.885(16)	Li(2)–O(6)	1.902(18)	Li(2)–O(7)	1.897(19)
Li(2)–O(8)	1.896(18)				

C(22)–Tm(2)–O(2)	67.9(5)	C(30)–Tm(2)–O(2)	68.6(5)
C(22)–Tm(2)–C(30)	135.0(6)	I(3)–Tm(2)–I(4)	100.44(5)
I(3)–Tm(2)–O(2)	105.0(3)	I(3)–Tm(2)–C(22)	105.5(4)
I(3)–Tm(2)–C(30)	96.3(4)	I(4)–Tm(2)–C(22)	102.9(4)
I(4)–Tm(2)–C(30)	111.4(4)	I(4)–Tm(2)–O(2)	154.4(3)

the small ionic radii of Y(III) and Tm(III). Somewhat surprisingly, the presence of lithium ions in the reaction leads to a remarkable ligand coupling to give a di-carbanionic ligand $[\{(Me_3Si)_2C(SiMe_2)\}_2O]^{2-}$, the thulium(III) complex of which crystallizes as an unusual separated ion pair.

3. Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. THF, methylcyclohexane and light petroleum (b.p. 40–60°C) were distilled under nitrogen from potassium or sodium/potassium alloy. THF was stored over activated 4A molecular sieves; all other solvents were stored over a potassium film. Deuterated THF was distilled from potassium and was deoxygenated by three freeze–pump–thaw cycles and stored over activated 4A molecular sieves. The compounds $YI_3(THF)_{3.5}$ [9], $TmI_3(THF)_{3.5}$ [9] and $\{(Me_3Si)_2(Me_2MeOSi)C\}K$ [12] were prepared by previously published procedures.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL Lambda500 spectrometer operating at 500.16, and 125.65 MHz, respectively; ^{1}H, and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University. In spite of several attempts we were unable to obtain meaningful mass spectra for **5** or **6**, the spectra obtained exhibit only signals for ligand fragments.

3.1. $\{(Me_3Si)_2(Me_2MeOSi)C\}YI_2(THF)_2$ (**5**)

To a suspension of $YI_3(THF)_{3.5}$ (1.14 g, 1.58 mmol) in THF (10 mL) was added a solution of $\{(Me_3Si)_2(Me_2MeO-$

Si)C}K (0.91 g, 3.16 mmol) in THF (20 mL). This mixture was stirred at room temperature for 16 h. Solvent was removed *in vacuo* and the residue was extracted into light petroleum (30 mL) and filtered. Solvent was removed *in vacuo* from the filtrate and the resulting colorless, viscous oil was crystallized from cold (−30 °C) methylcyclohexane/THF (10:1) to give **5** as colorless blocks. Yield 0.62 g, 71% (based on $YI_3(THF)_{3.5}$). Anal. Calcd. for $C_{18}H_{43}I_2O_3Si_3Y$: C, 29.43; H, 5.90. Found: C, 29.31; H, 5.80%. ^{1}H NMR (d_8-THF, 23 °C): δ 0.07 (s, 18H, SiMe_3), 0.13 (s, 6H, SiMe_2), 1.70 (m, 8H, THF), 3.31 (s, 3H, OMe), 3.53 (m, 8H, THF). ^{13}C{^{1}H} NMR (d_8-THF, 23 °C): δ 4.30 (SiMe_2), 4.58 (SiMe_3), 27.04 (THF), 57.84 (OMe), 69.43 (THF).

3.2. $\{(Me_3Si)_2(Me_2MeOSi)C\}TmI_2(THF)_2$ (**6**)

To a suspension of $TmI_3(THF)_{3.5}$ (0.85 g, 1.06 mmol) in THF (10 mL) was added a solution of $\{(Me_3Si)_2(Me_2MeO-Si)C\}K$ (0.61 g, 2.12 mmol) in THF (20 mL). This mixture was stirred at room temperature for 16 h. Solvent was removed *in vacuo* and the residue was extracted into light petroleum (30 mL) and filtered. Solvent was removed *in vacuo* from the filtrate and the resulting pale yellow, viscous oil was crystallized from cold (−30 °C) methylcyclohexane/THF (10:1) to give **6** as yellow blocks. Yield: 0.58 g, 67% (based on $TmI_3(THF)_{3.5}$). Anal. Calcd. for $C_{18}H_{43}I_2O_3Si_3Tm$: C, 26.54; H, 5.32. Found: C, 26.50; H, 5.65%.

3.3. $[[\{(Me_3Si)_2C(SiMe_2)\}_2O]TmI_2\{Li(THF)_3\}_2]$-$[\{(Me_3Si)_2(Me_2MeOSi)\}TmI_2]$ (**8**)

To a suspension of $TmI_3(THF)_{3.5}$ (0.60 g, 0.75 mmol) in THF (10 mL) was added a solution of $\{(Me_3Si)_2(Me_2MeO-Si)C\}K \cdot (LiX)_x$ (0.43 g, approx. 1.50 mmol) in THF

Table 3
Crystallographic data for **5**, **6** and **8**

Compound	5	6	8
Formula	$C_{18}H_{43}I_2O_3Si_3Y$	$C_{18}H_{43}I_2O_3Si_3Tm$	$C_{60}H_{144}I_4Li_2O_8Si_{12}Tm_2$
M	734.5	814.5	2190.2
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	17.1401(16)	17.0624(10)	17.4444(12)
b (Å)	10.5821(7)	10.4959(6)	13.5453(9)
c (Å)	18.258(4)	18.2001(11)	40.173(3)
β (°)	117.577(12)	117.537(1)	91.478(1)
V (Å^3)	2935.4(7)	2890.1(3)	9489.2(11)
Z	4	4	4
μ (mm^{-1})	4.227	5.345	3.351
Data collected	36,506	13,982	51,708
Unique data	6609	5021	12,412
R_{int}	0.056	0.028	0.047
Data with $F^2 > 2\sigma$	4556	4272	11056
Refined parameters	253	253	893
R (on F, $F^2 > 2\sigma$)	0.045	0.026	0.091
R_w (on F^2, all data)	0.128	0.061	0.204
Goodness of fit on F^2	1.086	1.067	1.309
min, max electron density (e Å^{-3})	1.35, − 1.96	1.05, − 0.97	1.88, − 2.32

(20 mL) and this mixture was stirred for 16 h. Solvent was removed *in vacuo* and the residue was extracted into light petroleum (30 mL) and filtered. Solvent was removed from the filtrate *in vacuo* and the resulting yellow oil was crystallized from cold (−30°C) methylcyclohexane/THF (10:1) to give **8** as yellow blocks. Yield: 1.02 g, 62% (based on TmI$_3$(THF)$_{3.5}$). Anal. Calcd. for $C_{60}H_{144}I_4Li_2O_8Si_{12}Tm_2$: C, 32.90; H, 6.63. Found: C, 32.07; H, 6.98%.

3.4. Crystal structure determinations of 5, 6 and 8

Measurements were made at 150 K on Bruker AXS SMART CCD and Nonius KappaCCD diffractometers using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). For all compounds cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and were refined on F^2 values for all unique data. Table 3 gives further details. All non-hydrogen atoms were refined anisotropically, and H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Disorder was resolved and successfully modeled for four of the THF ligands in the cation and for two of the trimethylsilyl groups and the two iodide ligands in the anion of **8**. Programs were Bruker AXS SMART (control) and SAINT (integration), Nonius COLLECT and associated programs, and SHELXTL for structure solution, refinement, and molecular graphics [16].

Acknowledgements

Appendix A. Supplementary material

CCDC 614221, 614222, and 614223 contain the supplementary crystallographic data for **5**, **6**, and **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.017.

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