Synthesis and Structures of Ln(II) and Ln(III) Dialkyls Derived from LnI_2 (Ln = Nd, Tm, Yb)

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Whereas the reactions between either NdI_2 or TmI_2 and 1 equiv of the dipotassium salt $[\{(Me_3Si)_2C(SiMe_2)\}_2O]K_2(OEt_2)$ (**2**) yield only intractable mixtures of products, reactions between LnI_2 and 1 equiv of $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2K_2$ (**3**) yield the lanthanide(III) compounds $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2Ln(OMe)(THF)$ [Ln = Tm (**9**), Nd (**10**)] via a ligand degradation reaction. In contrast, YbI_2 reacts smoothly with either **2** or **3** to give the ytterbium(II) alkyls $[\{(Me_3Si)_2C(SiMe_2)\}_2O]Yb(THF)_2$ (**4**) and $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2Yb(THF)$ (**5**), respectively, in excellent yields. Compounds **4** and **5** have been characterized by multielement (^{1}H, $^{13}C\{^{1}H\}$, ^{29}Si, and ^{171}Yb) NMR spectroscopy, and compounds **4**, **5**, **9**, and **10** by elemental analyses and X-ray crystallography. Compounds **9** and **10** crystallize as structurally similar monomers with a distorted trigonal prismatic geometry about the Ln(III) ions; in **4** and **5** the Yb centers lie in a distorted trigonal bipyramidal geometry. Compound **5**, although potentially diastereomeric, gives rise to a single set of NMR signals over the temperature range 20 to −80 °C, suggesting either the presence of only one diastereomer or that exchange between diastereomers is rapid on the NMR time scale.

Introduction

Until recently the low oxidation state chemistry of the lanthanides was confined to derivatives of the readily accessible ions Sm^{2+}, Eu^{2+}, and Yb^{2+} [$E°(Ln^{2+}/Ln^{3+}$; V vs NHE) = −0.35 (Eu), −1.15 (Yb), −1.55 (Sm)].[1] Although the majority of the remaining lanthanide elements had been identified spectroscopically as +2 ions in the solid state, there were no examples of stable molecular species containing these ions. However, a significant breakthrough was made in 1997 when Evans, Bochkarev, and co-workers reported the synthesis and structural characterization of the thulium(II) complex $TmI_2(DME)_3$ [DME = 1,2-dimethoxyethane].[2] This was quickly followed by the isolation of the analogous Nd(II) and Dy(II) diiodides [the ions Tm^{2+}, Nd^{2+}, and Dy^{2+} have the next lowest redox potentials of all the lanthanides after Sm^{2+} [$E°(Ln^{2+}/Ln^{3+}$; V vs NHE) = −2.22 (Tm), −2.56 (Dy), −2.62 (Nd)]].[3−6] The chemistry of these “nonclassical” Ln^{2+} ions (i.e., Ln ≠ Sm, Eu, Yb) has recently been comprehensively reviewed.[7]

The first organometallic compound of thulium(II), $\{\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3\}_2Tm(THF)$ (**1**),[8] was reported by Evans and co-workers in 2002, and since then, two further bis(cyclopentadienyl) complexes, $\{\eta^5\text{-}1,3\text{-}(t\text{-}Bu)_2C_5H_3\}_2Tm(THF)$[9] and $\{\eta^5\text{-}1,2,4\text{-}(t\text{-}Bu)_3C_5H_2\}_2Tm(THF)$,[10] and a handful of closely related phospholyl and arsolyl complexes, $\{\eta^5\text{-}Me_2(Me_3Si)_2C_4As\}_2Tm(THF)$,[11] $\{\eta^5\text{-}(t\text{-}Bu)_2C_4H_2P\}_2Tm(THF)$,[9] $\{\eta^5\text{-}(Me_3Si)_2C_4H_2P\}_2Tm(THF)$,[9] $\{\eta^5\text{-}Me_2(t\text{-}Bu)_2C_4P\}_2Tm(THF)$,[11] and $\{\eta^5\text{-}Me_2(t\text{-}Bu)_2C_4P\}_2Tm$,[12] have been reported. There have been no reports of stable Dy(II) or Nd(II) organometallic complexes nor of organometallic complexes of any of the ions Nd(II), Dy(II), or Tm(II) with σ-donor alkyl or aryl ligands.

The correct choice of ligand and reaction conditions is paramount for the successful synthesis of organometallic derivatives of these ions. Evans and co-workers have shown that, whereas the reaction between TmI_2 and 2 equiv of $[1,3\text{-}(Me_3Si)_2C_5H_3]K$ in THF under argon gives the organothulium(II) complex **1**,[8] the corresponding reaction between TmI_2 and 2 equiv of Cp*K in diethyl ether gives the thulium(III) complex $Cp^*_2Tm(\mu\text{-}OEt)_2TmCp^*(\mu\text{-}O)TmCp^*_2$ via cleavage of the solvent.[13]

We recently reported the syntheses of the dicarbanionic, sterically hindered, O-functionalized ligands $[\{(Me_3Si)_2C(SiMe_2)\}_2O]^{2-}$ and $[\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2]^{2-}$, their potassium salts $[\{(Me_3Si)_2C(SiMe_2)\}_2O]K_2(OEt_2)$ (**2**) and $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2K_2$ (**3**) (Chart 1),[14] and their complexes with the trivalent lanthanide ions La(III), Y(III), Nd(III), and Tm(III).[15,16] We were optimistic that the chelating

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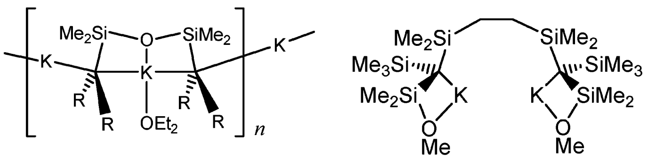
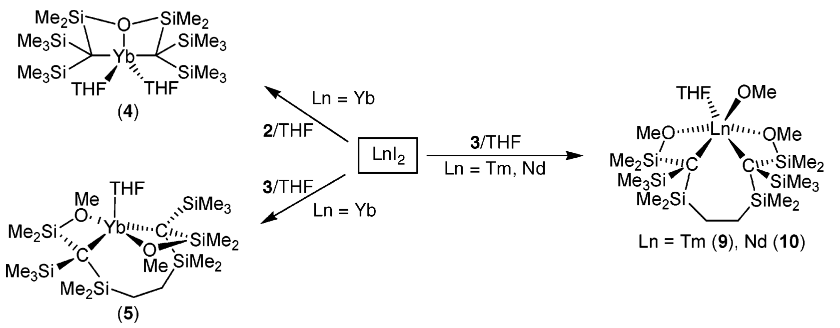
Chart 1. [a]



(**2**) (**3**)

[a] R = $SiMe_3$.

Scheme 1



nature of these ligands and their steric bulk would enable the synthesis of "nonclassical" lanthanide(II) alkyl complexes and report here our initial attempts to synthesize such compounds, including the isolation of two new Tm(III) and Nd(III) complexes formed via an unexpected ligand degradation reaction. For comparison, we also describe the synthesis of stable Yb(II) complexes with these ligands.

Results and Discussion

Reactions between YbI_2 and 1 equiv of either of the dipotassium reagents **2** and **3** in THF proceed cleanly to give the corresponding dialkylytterbium(II) compounds $[\{(Me_3Si)_2C(SiMe_2)\}_2O]Yb(THF)_2$ (**4**) and $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2Yb(THF)$ (**5**), respectively (Scheme 1).

It has been shown previously that the ytterbium(II) dialkyls $\{(Me_3Si)_2(Me_2XSi)C\}_2Yb$ [X = Me (**6**), $CH{=}CH_2$ (**7**)], which are closely related to **4** and **5**, react rapidly with ethyl ethers; **6** also reacts instantaneously with THF to give a red-brown material, which was not fully characterized.[17] Remarkably, both **4** and **5** are isolated as THF adducts; the smaller tridentate ligand in **4** allows the incorporation of two molecules of THF in the coordination sphere of the ytterbium(II) ion, whereas a single molecule of THF is bound to the ytterbium ion in **5**.

The stability of **4** and **5** toward THF may possibly be ascribed to the incorporation of both carbanion centers into a single chelate ligand in each case. It has been noted that the reactivity of the compounds $\{(Me_3Si)_2(Me_2XSi)C\}_2Yb$ [X = Me, Ph, OMe, $CH{=}CH_2$] toward ethers is sharply attenuated when the carbanion forms part of a chelate ring.[17] Similarly, the cyclic dialkylytterbium(II) complex $\{(Me_3Si)_2(Me_2SiCH_2)C\}_2Yb$ reacts much more slowly with diethyl ether than does the acyclic complex **6**.[18]

The ^1H and $^{13}C\{^1H\}$ NMR spectra of freshly prepared solutions of **4** are as expected. However, although compound **5** is chiral at both carbanion centers, a single set of ligand resonances is observed in the ^1H, $^{13}C\{^1H\}$, and ^{29}Si NMR spectra of **5** at room temperature and a single ^{171}Yb signal is observed for this complex, suggesting either that only one diastereomer is present or that interconversion between diastereomers is rapid on the NMR time scale. A variable-temperature ^1H NMR study showed no evidence for dynamic behavior; a single set of sharp ligand resonances is observed for **5** over the temperature range 20 to −80 °C. Similar behavior has previously been observed in the lithium, potassium, and lanthanum derivatives of this ligand.[14−16] The ^{29}Si spectrum of **4** consists of two singlets at −11.25 and 5.56 ppm, each exhibiting satellites due to coupling to ^{171}Yb ($J_{SiYb} = 15.0$ and 16.4 Hz, respectively); the ^{29}Si NMR spectrum of **5** contains singlets at −9.71, −4.92, and 16.15 ppm, each exhibiting ytterbium satellites ($J_{SiYb} = 17.0$, 16.0, and 22.8 Hz, respectively). The ^{171}Yb NMR spectra of **4** and **5** exhibit relatively sharp singlets at 500 and 1049 ppm, respectively.

Somewhat surprisingly, samples of **4** that had been allowed to stand in sealed NMR tubes at room temperature for several days exhibited no signals for THF in their ^1H NMR spectra. A variable-temperature ^1H NMR study of one of these aged samples revealed that signals due to THF gradually appear from the baseline as the temperature is reduced, until, at −80 °C, the spectrum is essentially identical to that obtained from a freshly prepared sample; the Me_3Si and Me_2Si signals remain sharp over the entire temperature range. This behavior is consistent with the formation over several days of a paramagnetic ytterbium(III) species. The THF is subject to dynamic exchange between diamagnetic **4** and the paramagnetic ytterbium(III) species, which is rapid on the NMR time scale, giving a time-averaged, extremely broad signal for the THF ligands that is indistinguishable from the baseline. As the temperature is reduced, the THF exchange is slowed such that, below −60 °C, the THF molecules coordinated to diamagnetic **4** may be observed; signals due to the paramagnetic Yb(III) species are not seen. This sample degradation does not appear to be caused by ingress of air into the tubes since the NMR tubes were flame sealed and since this behavior is entirely reproducible. We attribute the formation of the paramagnetic Yb(III) species to a

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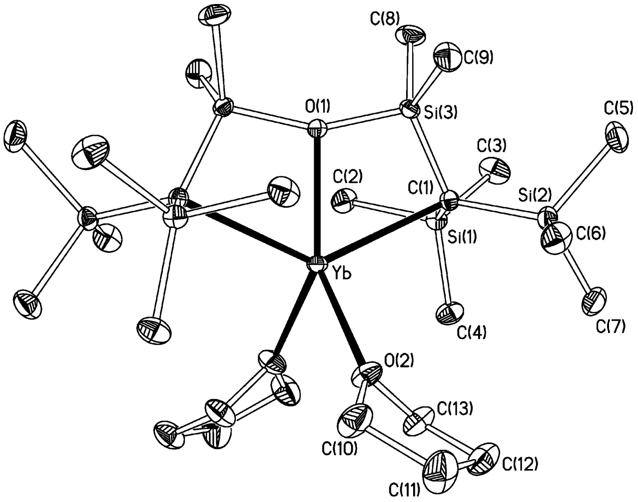

Figure 1. Molecular structure of **4** with 40% probability ellipsoids and with H atoms and minor disorder components omitted for clarity.

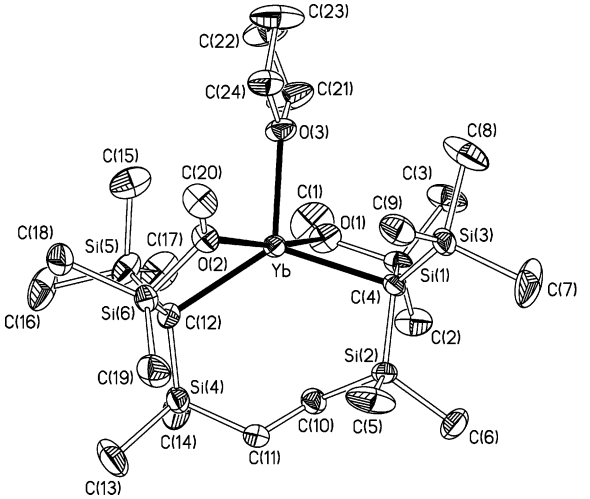

Figure 2. Molecular structure of **5** with 40% probability ellipsoids and with H atoms omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4[a]

Yb−C(1)	2.713(2)	Yb−O(1)	2.373(2)	Yb−O(2)	2.4455(19)
C(1)−Si(1)	1.845(2)	C(1)−Si(2)	1.850(2)	C(1)−Si(3)	1.832(3)
O(1)−Si(3)	1.6775(9)	Si−C(Me)$_{avge}$	1.893(3)		

C(1)−Yb−O(1)	65.35(5)	O(1)−Yb−O(2)	138.20(5)
C(1)−Yb−O(2)	99.74(7)	C(1)−Yb−C(1A)	130.71(10)
Si(1)−C(1)−Si(2)	115.53(13)	Si(2)−C(1)−Si(3)	113.57(12)
Si(1)−C(1)−Si(3)	113.65(12)		

[a] Symmetry operation A: 1−*x*, *y*, 1/2−*z*.

decomposition reaction, perhaps related to the reactions of the dialkylytterbium(II) compound **6** with THF.[17] In contrast to **4**, compound **5** appears to be indefinitely stable in solution.

Compounds **4** and **5** may be obtained as single crystals suitable for X-ray crystallography by crystallization from cold methylcyclohexane/THF or cold *n*-hexane, respectively. The molecular structures of **4** and **5** are shown in Figures 1 and 2, respectively, and selected bond lengths and angles are given in Tables 1 and 2. Both **4** and **5** crystallize as discrete molecular species, with no unusually short contacts between molecules.

Compound **4** possesses a crystallographic C_2 axis coincident with the Yb−O(1) bond; in addition to this Yb−O contact the ligand binds the ytterbium ion via its two carbanion centers, generating two four-membered chelate rings [C−Yb−O bite angle 65.35(5)°]. The coordination sphere of the Yb ion is completed by the oxygen atoms of two molecules of THF, conferring a distorted trigonal bipyramidal geometry on the ytterbium ion with the two carbanion centers in the “axial” positions [C−Yb−C 130.71(10)°]. As a consequence of its incorporation into a chelate ring, the Yb−O(Si_2) distance of 2.373(2) Å is somewhat shorter than the Yb−O(THF) distance of 2.4455(19) Å. The Yb−O(Si_2) distance in **4** is similar to the corresponding distance in $[\{(Me_3Si)_2(Me_2MeOSi)C\}YbI(OEt_2)]_2$ (**8**) [2.380(10) Å];[17] the Yb−O(THF) distance in **4** is longer than typical Yb−O(THF) distances,[19] but is similar to the corresponding distances in $[(C_6F_5)Yb(THF)_5][BPh_4]$,[20] which range from 2.41(1) to 2.46(1) Å (averaged over the three independent cations in the asymmetric unit). The Yb−C distance of 2.713(2) Å is significantly longer than Yb−C distances in related Yb(II) alkyls; for example, the Yb−C distances in the formally two-coordinate complex **6** are 2.490(8) and 2.501(9) Å and the Yb−C distance in the five-coordinate complex **8** is 2.580(12) Å.[17]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5

Yb−C(4)	2.607(3)	Yb−C(12)	2.642(3)	Yb−O(1)	2.405(3)
Yb−O(2)	2.421(2)	Yb−O(3)	2.423(3)	Si(1)−O(1)	1.734(4)
C(4)−Si(1)	1.806(4)	C(4)−Si(2)	1.837(4)	C(4)−Si(3)	1.832(3)
C(12)−Si(4)	1.845(4)	C(12)−Si(5)	1.826(4)	C(12)−Si(6)	1.813(4)
Si−C(Me)$_{av}$	1.878(4)				

C(4)−Yb−C(12)	128.52(11)	C(4)−Yb−O(1)	67.21(12)
C(4)−Yb−O(2)	121.30(10)	C(4)−Yb−O(3)	104.99(10)
C(12)−Yb−O(1)	113.25(12)	C(12)−Yb−O(2)	66.39(10)
C(12)−Yb−O(3)	126.49(11)	O(1)−Yb−O(2)	170.11(10)
O(1)−Yb−O(3)	84.40(11)	O(2)−Yb−O(3)	88.20(10)
Si(1)−C(4)−Si(2)	114.01(17)	Si(2)−C(4)−Si(3)	115.2(2)
Si(1)−C(4)−Si(3)	120.94(19)	Si(4)−C(12)−Si(5)	115.10(19)
Si(5)−C(12)−Si(6)	113.9(2)	Si(4)−C(12)−Si(6)	116.0(2)

In compound **5** the dicarbanion ligand is tetradentate, binding the ytterbium ion via its two carbanion centers, generating a seven-membered chelate ring [C−Yb−C bite angle 128.52(11)°], and via its two oxygen atoms, generating two four-membered chelate rings [C−Yb−O bite angles 67.21(12)° and 66.39(10)°]. Compound **5** is chiral at both carbanion centers, and the crystal of **5** studied by X-ray crystallography was of the *S*,*S*-enantiomer. The coordination sphere of the ytterbium ion is completed by the oxygen atom of one molecule of THF, conferring a distorted trigonal bipyramidal geometry on the ytterbium center in which the two oxygen atoms of the dicarbanion ligand occupy the axial positions [O(1)−Yb−O(2) 170.11(10)°]. The Yb−C distances of 2.607(3) and 2.624(3) Å are shorter than the corresponding distance in **4** but are still at the longer end of the typical range of Yb(II)−C σ-bonds (see above); the Yb−O distances of 2.405(3), 2.421(2), and 2.423(3) Å are similar to the Yb−O(THF) distance in **4**.

In contrast to the ready isolation of **4** and **5**, reactions between LnI_2 [Ln = Tm, Nd] and either **2** or **3** do not proceed smoothly. Although the reaction between TmI_2 and 1 equiv of **2** in THF at −78 °C initially yields a deep green solution, suggesting the formation of a Tm(II) species, this color dissipates as the reaction approaches room temperature and a yellow solution containing pale solids is obtained, clearly indicating oxidation to Tm(III). Unfortunately, we were unable to isolate a thulium-containing species from this reaction. Similarly, the reaction between NdI_2 and 1 equiv of **2** yields a pale blue solution

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(19) For examples see: (a) Rabe, G. W.; Guzei, I. A.; Rheingold, A. L. *Inorg. Chem.* **1997**, *36*, 4914. (b) van den Hende, J. R.; Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Leung, W.-P.; Mak, T. C. W.; Prashar, S. *J. Chem. Soc., Dalton Trans.* **1995**, 1427.

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containing pale solids, from which we were unable to extract a neodymium-containing product.

The reaction between TmI$_2$ and 1 equiv of **3** in THF at −78 °C also initially generates a deep green solution, most likely containing Tm(II). Once again, as the temperature is increased toward −10 °C, this color dissipates and a pale yellow solution containing a pale precipitate is obtained. Removal of solvent, extraction of the residue into light petroleum, and crystallization from *tert*-butyl methyl ether/THF at −30 °C gives crystals of the Tm(III) compound $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2Tm(OMe)(THF)$ (**9**) in good yield (Scheme 1). A similar reaction between **3** and 1 equiv of NdI$_2$ in THF gives the corresponding Nd(III) complex $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2Nd(OMe)(THF)$ (**10**) in low yield after crystallization from cold methylcyclohexane/THF.

Both thulium(II) diiodide and its solvate $TmI_2(THF)_5$ are stable in THF for limited periods, even at room temperature.[7] However, we observe rapid decomposition, as judged by the disappearance of the typical malachite green color associated with Tm(II) species, below −10 °C, suggesting that the target dialkylthulium(II) species is formed, but that this is unstable under the conditions employed, decomposing to give the Tm(III) species **9**.

The methoxy ligands present in **9** and **10** appear to be derived from Si−O cleavage of a second equivalent of dicarbanion ligand. We have, as yet, been unable to identify the organosilicon byproducts from this ligand degradation, and so the source of the methoxy substituent has not been determined unambiguously. In this regard, it has been noted previously that the compounds $\{(Me_3Si)_2(Ph_2XSi)C\}M$ [M = Li, Na; X = F, Br] decompose irreversibly at room temperature to give MX and the corresponding transient silaethene $Ph_2Si{=}C(SiMe_3)_2$.[21] However, the potassium compound **3** is stable indefinitely both in the solid state and in solution, and we have been unable to find any evidence for the formation of silaethene byproducts or their derivatives in the reactions leading to **9** and **10**.[14]

The lanthanide(III)-mediated cleavage of Si−O bonds in complexes of closely related methoxy-functionalized, silicon-stabilized carbanions has recently been observed both by Lappert and co-workers and in our own laboratories. Reactions between $[(Me_3Si)\{(MeO)_2MeSi\}CH]M$ [M = Li, K] and either CeCl$_3$ or Ce(OTf)$_3$ yield the methoxy-substituted Ce(III) compounds $[(Me_3Si)\{(MeO)_2MeSi\}CH]_4(\mu_3\text{-}OMe)Li_2Ce$ and $[[(Me_3Si)\{(MeO)_2MeSi\}CH](\mu_2\text{-}OMe)Ce(\mu_2\text{-}OTf)]_2$, respectively.[22] Similarly, reactions between $NdI_3(THF)_{3.5}$ and 2 equiv of $[(Me_3Si)_2(Me_2MeOSi)C]K$ yield the methoxy-bridged dimer $[\{(Me_3Si)_2(Me_2MeOSi)C\}NdI(\mu\text{-}OMe)(THF)]_2$.[15] In these cases the Si−O cleavage reaction is not accompanied by redox chemistry at the metal center; these reactions appear to be effected by the Lewis acidic Ln(III) ions themselves. In contrast, the reaction between **3** and $NdI_3(THF)_{3.5}$ in the presence of a lithium-containing impurity proceeds without ligand degradation to give the complex $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2Nd(\mu\text{-}I)_2Li(THF)_2$ (**11**), and a similar reaction between **3** and $LaI_3(THF)_{3.5}$ yields the complex $[\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2]LaI(THF)$.[15]

The stability of the dicarbanion in **11** suggests that the ligand degradation reaction observed in the formation of **10** is mediated by Nd(II) rather than Nd(III). The related cleavage of C−O, and even C−C, bonds accompanied by oxidation of Tm(II) to Tm(III) has been reported recently; for example, the reaction between TmI$_2$ and 2 equiv of Cp*K yields the Tm(III) product $Cp^*_2Tm(\mu\text{-}OEt)_2TmCp^*(\mu\text{-}O)TmCp^*_2$ via C−O cleavage of the diethyl ether solvent,[13] whereas the reaction between $TmI_2(DME)_3$ and $(Et_8\text{-}calix[4]tetrapyrrole)[K(DME)]_4$ gives the Tm(III) compound $[\{Et_2C(C_4H_3N)_2\}_3Tm][K(PhMe)]_3$ in low yield via C−C cleavage of the macrocyclic ligand.[23]

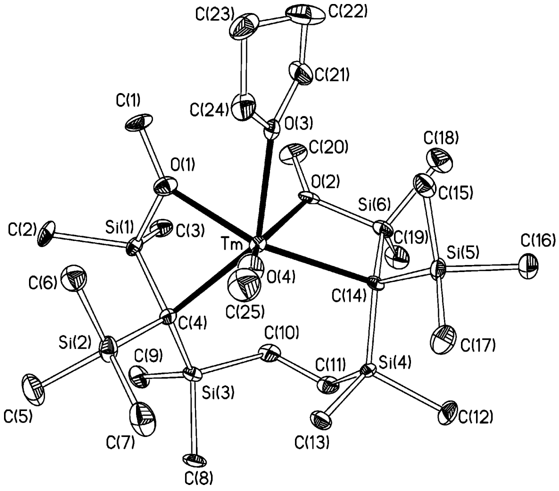

Figure 3. Molecular structure of **9** with 40% probability ellipsoids and with H atoms omitted for clarity.

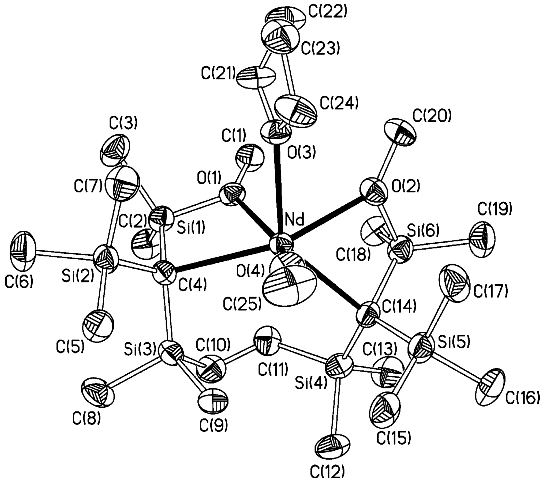

Figure 4. Molecular structure of **10** with 40% probability ellipsoids and with H atoms omitted for clarity.

Compounds **9** and **10** adopt similar structures in the solid state, but are not crystallographically isostructural. The molecular structures of **9** and **10** are shown in Figures 3 and 4, and selected bond lengths and angles are given in Table 3. In both compounds the dicarbanion ligand is tetradentate, coordinating the Ln(III) ions via the two carbanion centers to give seven-membered chelate rings [C−Tm−C 116.6(2)°, C−Nd−C 118.55(16)°] and via the two methoxy oxygen atoms to give two four-membered chelate rings in each case [C−Tm−O 65.7(2)° and 65.6(2)°; C−Nd−O 62.82(15)° and 62.87(16)°]. The coordination sphere of the lanthanide ions is completed by the oxygen atoms of one methoxide ligand and one molecule of THF, conferring a distorted trigonal prismatic geometry on the lanthanide ions in each case. In contrast to **5**, the crystals of **9** and **10** examined were both of the *meso* diastereomer, although both molecules are devoid of crystallographic symmetry.

The Tm−C distances of 2.575(8) and 2.561(8) Å are rather long in comparison to the corresponding distances in the few

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for 9 and 10

	9 (Ln = Tm)	**10** (Ln = Nd)
Ln−C(4)	2.575(8)	2.674(5)
Ln−C(14)	2.561(8)	2.694(5)
Ln−O(1)	2.403(6)	2.531(4)
Ln−O(2)	2.390(6)	2.536(4)
Ln−O(3)	2.408(7)	2.506(4)
Ln−O(4)	1.999(5)	2.110(4)
C(4)−Si(1)	1.840(8)	1.813(6)
C(4)−Si(2)	1.858(8)	1.848(6)
C(4)−Si(3)	1.857(8)	1.844(6)
C(14)−Si(4)	1.862(8)	1.857(6)
C(14)−Si(5)	1.853(9)	1.846(5)
C(14)−Si(6)	1.809(9)	1.828(6)
Si−C(Me)$_{av}$	1.886(9)	1.881(7)
C(4)−Ln−C(14)	116.6(2)	118.55(16)
C(4)−Ln−O(1)	65.7(2)	62.82(15)
C(14)−Ln−O(2)	65.6(2)	62.87(16)

other crystallographically characterized compounds containing a Tm−C σ-bond, although we note that **9** is the first crystallographically characterized thulium(III) alkyl compound and that Tm(III)−C(sp^3) distances will necessarily be longer than corresponding Tm(III)−C(sp^2) distances; for comparison, the Tm−C distances in $Ph_3Tm(THF)_3$ are 2.421(6), 2.425(6), and 2.416(7) Å[24] and the Tm−C distance in (Dnp)Tm(Cl)$_2$(THF)$_2$ is 2.413(3) Å [Dnp = 2,6-di(1-naphthyl)phenyl].[25] The Nd−C distances in **10** [2.674(5) and 2.694(5) Å] are also substantially longer than typical Nd(III)−C σ-bonds; for example, the Nd−C distances in Cp*$_2$Nd{CH(SiMe$_3$)$_2$}[26] and (2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$O)$_2$Nd(THF)$_2$(CH$_2$SiMe$_3$)[27] are 2.517(7) and 2.482(4) Å, respectively. The long Ln−C distances in **4**, **5**, **9**, and **10** may be ascribed to steric crowding at the lanthanide centers and to the strain associated with the formation of four-membered chelate rings in these compounds. The Tm−O(alkoxide) and Nd−O(alkoxide) distances in **9** and **10** [1.999(5) and 2.110(4) Å, respectively] are substantially shorter than the Tm−O(ether) distances [2.403(6) and 2.390(6) Å] and Nd−O(ether) distances [2.531(4) and 2.536(4) Å], as expected. The Tm−O(alkoxide) and Nd−O(alkoxide) distances are similar to the corresponding distances in other terminal alkoxides; for example, the Tm−O distances in {(Bu$^t_3$CO)$_3$Tm}$_2$(H$_2$NSiMe$_2$CH$_2$SiMe$_2$NH$_2$) are 2.021(4), 2.028(4), and 2.044(3) Å[28] and the terminal Nd−O distances in Nd$_5$(μ_5-O)(μ_3-OPr^i)$_4$(μ_2-OPr^i)$_4$(OPr^i)$_5$ range from 2.082(11) to 2.123(11) Å.[29] The Tm−O(ether) distances compare with a Tm−O(ether) distance of 2.276(3) Å in {(Me$_3$Si)$_2$(Me$_2$MeOSi)C}TmI$_2$(THF)$_2$, and the Nd−O(ether) distances compare with Nd−O distances of 2.496(2) and 2.468(2) Å in {(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$Nd(μ-I)$_2$Li(THF)$_2$.[15]

Conclusions

Whereas the Yb(II) complexes **4** and **5** are readily synthesized, complexes of the more reducing Tm(II) and Nd(II) ions with the same ligands are inaccessible. The greater redox potentials of these latter ions lead to a fragmentation reaction of the [{(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$]$^{2-}$ ligand and isolation of the Tm(III) and Nd(III) complexes **9** and **10**, both of which contain methoxide ligands apparently derived from cleavage of a Si−O bond. This clearly suggests that, while these ligands may have suitable steric properties, the reactivity of the Si−O bond prevents their use in stabilizing “nonclassical” lanthanide(II) alkyls; we are currently investigating the use of related ligands that are free of reactive Si−X bonds for the synthesis of these compounds. However, it is notable that the ytterbium(II) complex **4** is also unstable in solution, slowly decomposing to an ytterbium(III) species (possibly via a reaction with coordinated THF), indicating that care must also be taken with the choice of solvent in these systems.

Experimental Section

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. THF, methylcyclohexane, *n*-hexane, diethyl ether, *tert*-butyl methyl ether, and light petroleum (bp 40−60 °C) were distilled under nitrogen from potassium or sodium/potassium alloy. THF was stored over activated 4 Å molecular sieves; all other solvents were stored over a potassium film. Deuterated toluene was distilled from potassium and was deoxygenated by three freeze−pump−thaw cycles and stored over activated 4 Å molecular sieves. The compounds YbI$_2$,[30] TmI$_2$,[6,12] NdI$_2$,[6] [{(Me$_3$Si)$_2$C(SiMe$_2$)}$_2$O]K$_2$(OEt$_2$),[14] and {(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$K$_2$[14] were prepared by previously published procedures.

^{1}H, ^{13}C{^{1}H}, ^{29}Si INEPT, and ^{171}Yb NMR spectra were recorded on a Jeol Lambda500 spectrometer operating at 500.16, 125.65, 99.25, and 46.00 MHz, respectively; ^{1}H, ^{13}C, and ^{29}Si chemical shifts are quoted in ppm relative to tetramethylsilane; ^{171}Yb chemical shifts are quoted in ppm relative to (C$_5$Me$_5$)$_2$Yb(THF). Quaternary carbon signals for **4** and **5** were identified using a ^{13}C refocused INEPT experiment. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

[{(Me$_3$Si)$_2$C(SiMe$_2$)}$_2$O]Yb(THF)$_2$ (4). A solution of [{(Me$_3$Si)$_2$C(SiMe$_2$)}$_2$O]K$_2$ (0.64 g, 1.21 mmol) in THF (20 mL) was added dropwise to a cold (−78 °C), stirred suspension of YbI$_2$ (0.52 g, 1.21 mmol) in THF (10 mL). The reaction mixture was allowed to attain room temperature and was stirred overnight. The solvent was removed *in vacuo*, and the residue was extracted into diethyl ether (30 mL). The solution was filtered, and the solvent was removed *in vacuo* from the filtrate. The resulting orange oil was crystallized from cold (−20 °C) methylcyclohexane/THF (10:1 ratio) to give **4** as orange plates. Isolated yield: 0.63 g, 68%. Anal. Calcd for $C_{26}H_{64}Si_6O_3Yb$: C 40.75; H 8.42. Found: C 40.72; H 8.50. ^{1}H NMR (d_8-toluene, 23 °C): δ 0.26 (s, 36H, SiMe$_3$), 0.44 (s, 12H, SiMe$_2$), 1.37 (m, 8H, THF), 3.55 (m, 8H, THF). ^{13}C{^{1}H} NMR (d_8-toluene, 22 °C): δ 5.55 (SiMe$_2$), 7.97 (SiMe$_3$), 22.56 (Si$_3$CYb [$^1J_{YbC}$ = 163.4 Hz]), 25.25 (THF), 69.73 (THF). ^{29}Si INEPT NMR (d_8-toluene, 22 °C): δ −11.25 ($^2J_{YbSi}$ = 15.0 Hz), 5.56 ($^2J_{YbSi}$ = 16.4 Hz). ^{171}Yb NMR (d_8-toluene, 22 °C): δ 500.

{(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$Yb(THF) (5). A solution of {(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$K$_2$ (1.19 g, 2.08 mmol) in THF (20 mL) was added, dropwise, to a cold (−78 °C), stirred suspension of YbI$_2$ (0.89 g, 2.08 mmol) in THF (10 mL). The reaction mixture was allowed to attain room temperature and was stirred overnight. The solvent was removed *in vacuo*, and the residue was extracted into light petroleum (30 mL). The solution was filtered, and the solvent was removed *in vacuo* from the filtrate. The resulting orange oil was crystallized from cold (−20 °C)

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Table 4. Crystallographic Data for 4, 5, 9, and 10

	4	5	9	10
formula	$C_{26}H_{64}O_3Si_6Yb$	$C_{24}H_{60}O_3Si_6Yb$	$C_{25}H_{63}O_4Si_6Tm$	$C_{25}H_{63}NdO_4Si_6$
fw	766.4	738.3	765.2	740.5
cryst size/mm	0.54 × 0.45 × 0.28	0.05 × 0.04 × 0.02	0.32 × 024 × 0.13	0.08 × 0.08 × 0.02
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$C2/c$	$P2_12_12_1$	$Pna2_1$	$P2_1$
a/Å	13.151(2)	12.7912(6)	23.6067(15)	9.6531(7)
b/Å	17.290(5)	16.5615(8)	9.6827(6)	16.9051(12)
c/Å	16.972(5)	16.8787(8)	16.0840(10)	12.0511(9)
β/deg	96.502(14)			107.460(1)
V/Å^3	3834.3(17)	3575.6(3)	3676.4(4)	1875.6(2)
Z	4	4	4	2
μ/mm^{-1}	2.649	2.838	2.635	1.601
transmn coeff range	0.299−0.477	0.871−0.945	0.486−0.726	0.883−0.969
no. of reflns measd	24 593	38 114	25 600	20 957
no. of unique reflns	4333	10 863	6438	20 957
R_{int}	0.048	0.040	0.041	
no. of reflns with $F^2 > 2\sigma$	3992	10 007	6053	15 758
no. of params	182	324	316	344
R (on F, $F^2 > 2\sigma$)[a]	0.022	0.032	0.049	0.053
R_w (on F^2, all data)[a]	0.061	0.082	0.091	0.130
goodness of fit[a]	1.179	1.048	1.372	0.984
min., max. electron density/e Å^{-3}	0.43, −1.24	3.07, −0.76	1.38, −3.39	1.08, −0.81
absolute struct param		0.026(6)	0.047(12)	0.119(12)

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $S = [\sum w(F_o^2 - F_c^2)^2/(\text{no. data} - \text{no. params})]^{1/2}$ for all data.

n-hexane to give **5** as orange needles. Isolated yield: 0.92 g, 60%. Anal. Calcd for $C_{24}H_{60}Si_6O_3Yb$: C 39.04; H 8.19. Found: C 38.97; H 8.02. ^1H NMR (d_8-toluene, 20 °C): δ 0.18 (s, 18H, $SiMe_3$), 0.29 (s, 12H, $SiMe_2$), 0.32 (s, 12H, $SiMe_2O$), 0.82 (s, 4H, CH_2), 1.29 (m, 4H, THF), 3.15 (s, 6H, OMe), 3.47 (m, 4H, THF). $^{13}C\{^1H\}$ NMR (d_8-toluene, 22 °C): δ 4.56 ($SiMe_2$), 6.29 (CH_2), 6.85 ($SiMe_3$), 12.68 ($SiMe_2O$), 19.60 (Si_3CYb [$^1J_{YbC}$ = 167.9 Hz]), 24.29 (THF), 49.99 (OMe), 68.30 (THF). ^{29}Si INEPT NMR (d_8-toluene, 22 °C): δ −9.71 ($^2J_{YbSi}$ = 17.0 Hz), −4.92 ($^2J_{YbSi}$ = 16.0 Hz), 16.15 ($^2J_{YbSi}$ = 22.8 Hz). ^{171}Yb NMR (d_8-toluene, 22 °C): δ 1049.

$\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2Tm(OMe)(THF)$ (9). A solution of $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2K_2$ (1.28 g, 2.25 mmol) in THF (20 mL) was added, dropwise, to a suspension of freshly prepared TmI_2 (0.95 g, 2.25 mmol) in cold (−78 °C) THF (10 mL), and the deep green reaction mixture was stirred at −78 °C for 2 h. The mixture was allowed to attain room temperature while stirring, the solvent was removed *in vacuo*, and the residue was extracted into light petroleum (30 mL). The solution was filtered, and the solvent was removed *in vacuo* from the filtrate. The resulting brown oil was crystallized from cold (5 °C) *tert*-butyl methyl ether/THF (10:1 ratio) to give **9** as yellow blocks. Isolated yield: 1.04 g, 61%. Anal. Calcd for $C_{25}H_{63}Si_6O_4Tm$: C 39.24; H 8.30. Found: C 38.42; H 7.64.

$\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2Nd(OMe)(THF)$ (10). A solution of $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2K_2$ (1.44 g, 2.51 mmol) in THF (20 mL) was added, dropwise, to a cold (−78 °C) suspension of freshly prepared NdI_2 (1.00 g, 2.51 mmol) in THF (10 mL), and this reaction mixture was stirred at −78 °C for 2 h. The reaction was allowed to attain room temperature while stirring, the solvent was removed *in vacuo*, and the residue was extracted into light petroleum (30 mL). The solution was filtered, and the solvent was removed *in vacuo* from the filtrate. The resulting blue-green oil was crystallized from cold (−20 °C) methylcyclohexane/THF (10:1 ratio) to give **10** as pale blue plates. Isolated yield: 0.50 g, 27%. Anal. Calcd for $C_{25}H_{63}Si_6O_4Nd$: C 39.24; H 8.30. Found: C 38.79; H 8.15.

Crystal Structure Determinations of 4, 5, 9, and 10. For **4** and **9** measurements were made at 150 K on Bruker AXS SMART CCD and Nonius KappaCCD diffractometers using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å); for **5** and **10** measurements were made at 120 K on a Bruker Nonius APEX2 CCD diffractometer using a synchrotron X-ray source (λ = 0.6771 and 0.6751 Å for **5** and **10**, respectively). For all compounds cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semiempirically 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 4 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 successfully resolved and modeled for the two THF molecules in **4**. The crystal of **10** was twinned, and reflections from both components were used; the twinning prevents merging of symmetry-equivalent reflections before refinement because of overlap. The Flack absolute structure parameter was successfully refined for all three non-centrosymmetric structures.[31] Programs were Bruker AXS SMART and APEX2 (control) and SAINT (integration), Nonius COLLECT and associated programs, and SIR97 and SHELXTL for structure solution, refinement, and molecular graphics.[32]

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Supporting Information Available: For **4**, **5**, **9**, and **10** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

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