Heteroleptic Complexes of Lanthanum(III) and Neodymium(III) with Oxygen- or Nitrogen-Functionalized Tris(triorganosilyl)methyl Ligands

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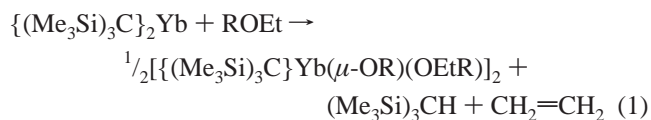
Metathesis reactions between $LaI_3(THF)_4$ and either 2 equiv of $[(Me_3Si)_2\{Me_2(Me_2N)Si\}C]K$ or 1 equiv of $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2K_2$ in THF yield the heteroleptic lanthanum dialkyls $[(Me_3Si)_2\{Me_2(Me_2N)Si\}C]_2LaI$ (**3**) and $[\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2]LaI(THF)$ (**5**), respectively. In contrast, the reaction between $LaI_3(THF)_4$ and 2 equiv of $[(Me_3Si)_2\{Me_2(MeO)Si\}C]K$ in THF, under a variety of reaction conditions, gives a mixture of the mono- and disubstituted compounds $[(Me_3Si)_2\{Me_2(MeO)Si\}C]LaI_2(THF)$ (**7**) and $[(Me_3Si)_2\{Me_2(MeO)Si\}C]_2LaI(THF)$ (**8**), which cannot be separated by crystallization. The reaction between this mixture and 1 equiv of $KN(SiMe_3)_2$ yields the heteroleptic complex $[(Me_3Si)_2\{Me_2(MeO)Si\}C]LaI\{N(SiMe_3)_2\}(THF)$ (**9**). While exact analogues of **3**, **5**, **8**, and **9** could not be isolated for neodymium, a metathesis reaction between $NdI_3(THF)_{3.5}$ and the lithium iodide containing potassium alkyl $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2K_2 \cdot xLiI$ in THF yields the ate complex $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2Nd(\mu-I)_2Li(THF)_2$ (**10**). An unexpected ligand degradation is observed in the reaction between $NdI_3(THF)_{3.5}$ and 2 equiv of $[(Me_3Si)_2\{Me_2(MeO)Si\}C]K$ in THF: this reaction yields the methoxy-bridged dimer $\{[(Me_3Si)_2\{Me_2(MeO)Si\}C]Nd(I)(THF)(\mu-OMe)\}_2$ (**11**), via Si−O cleavage of one of the ligands. Compounds **3**, **5**, and **8**−**11** have been characterized by elemental analyses and X-ray crystallography; the diamagnetic compounds **3**, **5**, **8**, and **9** have additionally been characterized by NMR spectroscopy. The diastereomeric compound **5** gives a single set of resonances in its ^1H and $^{13}C\{^1H\}$ NMR spectra, suggesting either a rapid dynamic equilibrium between the two possible diastereomers on the NMR time scale or the formation of a single diastereomer of this compound.

Introduction

The non-cyclopentadienyl organometallic chemistry of the lanthanides has become a topic of increasing interest over the last two decades and has recently been the subject of several excellent reviews.[1] Among simple alkyl ligands the mono-, bis-, and tris(trimethylsilyl)methyls have provided access to some of the most remarkable non-cyclopentadienyl organolanthanide compounds, including the first homoleptic trialkyllanthanide-(III) and dialkyllanthanide(II) compounds.[2,3] Frequently these compounds exhibit highly unusual structures and undergo unprecedented reactions not observed with less sterically hindered analogues. For example, the trialkyllanthanide compounds $\{(Me_3Si)_2CH\}_3Ln$ (Ln = Y, La, Sm, Ce) adopt

pyramidal geometries,[2] whereas the dialkyllanthanide complexes $\{(Me_3Si)_3C\}_2Ln$ (Ln = Yb, Eu, Sm) adopt bent structures in the solid state (C−Ln−C angles: 137.0(4)° (Yb), 136.0(2)° (Eu), and 143.43° (Sm));[3a−d] the compound $\{(Me_3Si)_3C\}_2Yb$ reacts rapidly with ethyl ethers according to eq 1,[3a,b] whereas the less sterically hindered $\{(Me_3Si)_2CH\}_2Yb(OEt_2)_2$ is isolated as a diethyl ether adduct.[3e]

$$\{(Me_3Si)_3C\}_2Yb + ROEt \rightarrow$$
$$^1/_2[\{(Me_3Si)_3C\}Yb(\mu\text{-}OR)(OEtR)]_2 +$$
$$(Me_3Si)_3CH + CH_2{=}CH_2 \quad (1)$$

The synthesis of heteroleptic lanthanide complexes LnX_2Y and $LnXYZ$ is frequently hampered by Schlenk-type ligand redistribution equilibria. Recently, we and others have become interested in functionalized silicon-stabilized carbanions of the form $(Me_3Si)_n(Me_2XSi)_{3-n}C^-$ ($n = 0-2$), $(Me_3Si)_n(Me_2XSi)_{2-n}$-$CH^-$ ($n = 0, 1$), and $(Me_3Si)(MeX_2Si)CH^-$ (X = OMe, NMe_2, for example) as ligands for the lanthanides;[2c,4,5] complexes of these ligands should have increased stability toward ligand redistribution reactions due to their steric bulk and the formation of chelate rings. We have previously shown that the functionalized tris(silyl)methyl ligand $(Me_3Si)_2(Me_2MeOSi)C^-$ may be used to synthesize the novel samarium(II) complex $\{(Me_3Si)_2$-

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Scheme 1[a]
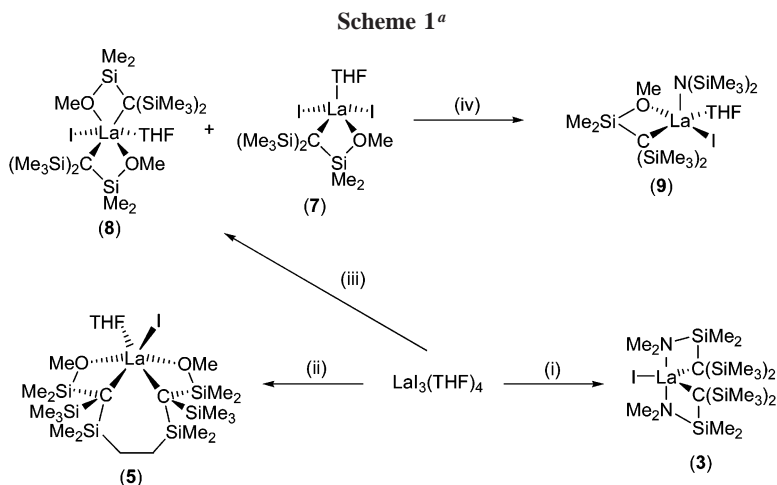
[a] Reagents: (i) $2[(Me_3Si)_2\{Me_2(Me_2N)Si\}C]K$, THF; (ii) $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2K_2$, THF; (iii) $2[(Me_3Si)_2\{Me_2(MeO)Si\}C]K$, THF; (iv) $KN(SiMe_3)_2$, THF.

$(Me_2MeOSi)C\}_2Sm^{II}(THF)$ (**1**).[3c] This compound reacts with benzophenone to give the first structurally characterized complex of the benzophenone ketyl radical anion $\{(Me_3Si)_2(Me_2-MeOSi)C\}_2Sm^{III}(OCPh_2)$ (**2**). Despite the widespread use of such ligands in main-group and transition-metal chemistry, somewhat surprisingly, compound **2** represents the only example to date of an organolanthanide(III) complex supported by tris-(silyl)methyl ligands. We now report the synthesis of a series of lanthanum(III) and neodymium(III) complexes supported by O- and N-functionalized mono- and dicarbanions containing the tris(silyl)methyl framework and an unexpected ligand degradation reaction mediated by neodymium(III).

Results and Discussion

The reaction between $LaI_3(THF)_4$ and 2 equiv of the potassium alkyl $[(Me_3Si)_2\{Me_2(Me_2N)Si\}C]K$ in THF cleanly gives the dialkyllanthanum(III) complex $[(Me_3Si)_2\{Me_2(Me_2N)-Si\}C]_2LaI$ (**3**) as colorless blocks after recrystallization from methylcyclohexane (Scheme 1). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** are as expected, and an X-ray crystallographic study reveals that **3** crystallizes solvent-free as a discrete molecular species; the structure of **3** is shown in Figure 1 along with details of selected bond lengths and angles.

The lanthanum center is bound by the C and N donors of two alkyl ligands (N−La−C bite angles 65.12(9) and 65.17-(10)°) and by an iodide ligand; the five-coordinate lanthanum ion adopts a distorted-trigonal-bipyramidal geometry in which the two amino groups occupy the axial positions, as expected (N(1)−La−N(2) = 171.82(9)°). The La−C distances (2.663-(4) and 2.680(3) Å) are at the longer end of the range of previously reported La−C(sp³) distances, possibly as a consequence of steric compression at the lanthanum center in **3**; for example, the La−C distances in the closely related compounds $\{(Me_3Si)_2CH\}_3La$ and $\{(Me_3Si)_2CH\}_3La(\mu\text{-Cl})Li(pmdeta)$ are 2.515(9) and 2.55(2)−2.68(4) Å, respectively.[2a,6] In contrast, the La−N distances (2.649(3) and 2.635(3) Å) are shorter than typical La−NR₃ contacts; for example, the La−N distances in $La(o\text{-CH}_2C_6H_4NMe_2)_3$ range from 2.695(2) to 2.705(2) Å.[7] The La−I distance in **3** (3.1447(3) Å) is unexceptional; for comparison, the La−I distances in $LaI_3(THF)_4$ range from 3.129(4)

Figure 1. Molecular structure of **3** with 40% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): La−C(1) = 2.663(4), La−C(12) = 2.680(3), La−N(1) = 2.649(3), La−N(2) = 2.635(3), La−I = 3.1447(3); C(1)−La−N(1) = 65.17(10), C(12)−La−N(2) = 65.12(9), C(1)−La−C(12) = 128.17(11), N(1)−La−N(2) = 171.82(9), C(1)−La−I = 115.09(8), C(12)−La−I = 116.73(7), N(1)−La−I = 84.41(7), N(2)−La−I = 87.41(6).

to 3.190(4) Å,[8a] whereas the La−I distances in $LaI_3(9S3)$ range from 3.1141(1) to 3.1856(2) Å (9S3 = 1,4,7-trithiacyclononane).[8b]

The reaction between $LaI_3(THF)_4$ and 1 equiv of the dipotassium salt $\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2K_2$ (**4**) in THF yields the complex $[\{(Me_3Si)(Me_2MeOSi)C(SiMe_2CH_2)\}_2]LaI-(THF)$ (**5**) as colorless blocks after recrystallization from methylcyclohexane/THF. That **5** is isolated as a THF adduct rather than solvent-free is probably a reflection of the reduced steric bulk of the ligand, which possesses OMe rather than the NMe₂ donor substituents of **3**. The dialkyl ligand in **5** is chiral at both carbanion centers; however, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** contain just a single set of ligand resonances. This is consistent either with the presence of a single diastereomer in solution or with rapid interconversion on the NMR time scale of the two possible diastereomers via La−C/La−O cleavage, inversion at the carbanion center, and recoordination. However, it should be noted that the dipotassium salt **4** and the neutral precursor $\{(Me_3Si)(Me_2MeOSi)CH(SiMe_2CH_2)\}_2$ also exhibit a single set of NMR signals, despite the potentially diastereomeric nature of these compounds.[4]

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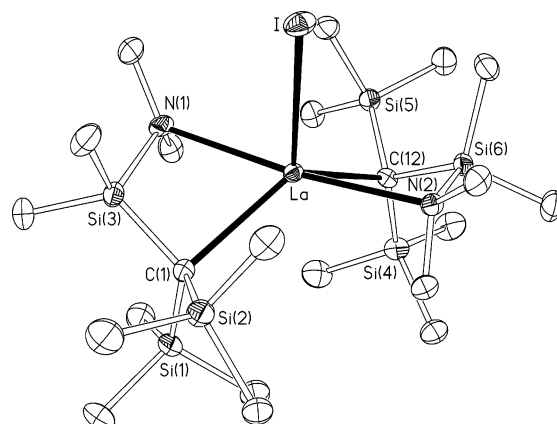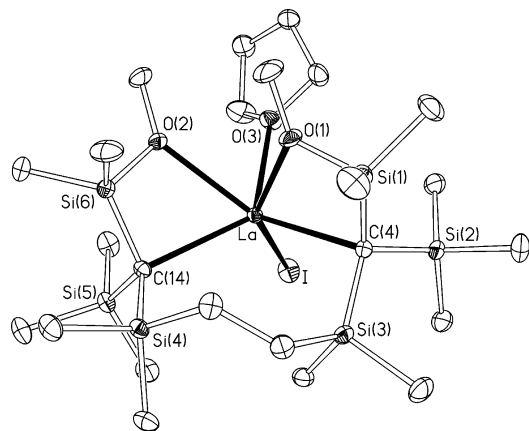
Figure 2. Molecular structure of **5** with 40% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): La−C(4) = 2.711(2), La−C(14) = 2.711(2), La−O(1) = 2.5081(15), La−O(2) = 2.5740(15), La−O(3) = 2.5522-(15), La−I = 3.1744(5); C(4)−La−C(14) = 114.59(6), C(4)−La−O(1) = 62.40(6), C(14)−La−O(2) = 62.24(5), I−La−C(4) = 99.57(5), I−La−C(14) = 109.58(4), I−La−O(1) = 145.82(4), I−La−O(2) = 122.41(4), I−La−O(3) = 79.06(4).

Figure 3. Molecular structure of **8** with 40% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): La−C(1) = 2.813(4), La−C(11) = 2.714(4), La−O(1) = 2.528(3), La−O(2) = 2.516(3), La−O(3) = 2.561(3), La−I = 3.1734(3); C(1)−La−O(1) = 61.16(10), C(11)−La−O(2) = 62.21(10), I−La−O(3) = 81.63(6), C(1)−La−O(2) = 86.72(10), C(1)−La−O(3) = 107.97(10), O(2)−La−O(3) = 77.59(9), C(11)−La−I = 95.81(8), C(11)−La−O(1) = 114.97(11), I−La−O(1) = 77.14(7).

Compound **5** crystallizes as discrete monomers; the molecular structure of **5** is shown in Figure 2 along with details of selected bond lengths and angles.

Compound **5** crystallizes as the meso diastereomer. The lanthanum ion in **5** is bound by the two carbanion centers of the ligand to give a seven-membered chelate ring (C−La−C bite angle 114.59(6)°) and by the two oxygen atoms of the OMe groups to give two four-membered chelate rings (C−La−O bite angles 62.40(6) and 62.24(5)°). The coordination sphere of the lanthanum ion is completed by one iodide ligand and the oxygen atom of a molecule of THF, giving a six-coordinate lanthanum center with a distorted-trigonal-prismatic geometry. The coincidentally identical, but crystallographically independent, La−C distances (2.711(2) Å) are longer than the equivalent distances in **3**, consistent with the higher coordination number of the lanthanum ion in **5**. The La−O(Me) and La−O(THF) distances of 2.5081(15), 2.5740(15), and 2.5522(15) Å, respectively, are typical for this type of contact; for example, the La−O(THF) distance in Cp*{(Me₃Si)₂CH}₂La(THF) is 2.547(6) Å[9] and the corresponding distances in (Ph₃SiO)₃La(THF)₃·THF are 2.635-(8), 2.644(7), and 2.650(8) Å.[10] The La−I distance (3.1744(5) Å) falls in the typical range for this type of contact.[8]

In contrast to the ready preparation of **3** and **5**, the reaction between LaI₃(THF)₄ and 2 equiv of [(Me₃Si)₂{Me₂(MeO)-Si}C]K (**6**) in THF does not proceed cleanly. Despite repeated attempts, we were unable to isolate a pure sample of [(Me₃-Si)₂{Me₂(MeO)Si}C]₂LaI; in all cases we obtained, as judged by ¹H and ¹³C{¹H} NMR spectroscopy, a mixture of the mono- and disubstituted products [(Me₃Si)₂{Me₂(MeO)Si}C]LaI₂(THF) (**7**) and [(Me₃Si)₂{Me₂(MeO)Si}C]₂LaI(THF) (**8**) in an approximately 1:1 ratio, which we were unable to separate cleanly by recrystallization. Attempts to force the metathesis reaction to completion were unsuccessful: the reaction between LaI₃-(THF)₄ and 2 equiv of **6** in refluxing THF led to extensive decomposition, possibly via Si−O cleavage (see below), whereas reactions between LaI₃(THF)₄ and either 2 equiv or an excess of **6** at room temperature over extended periods (up
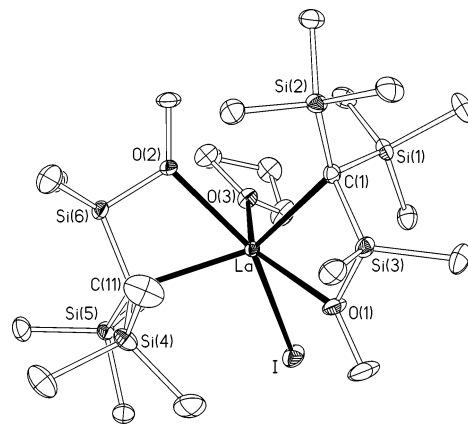
to 1 week) consistently yielded mixtures of **7** and **8** in approximately the same ratio.

The identity of **8** was eventually confirmed by an X-ray crystallographic study on a single crystal, which was selected from the cocrystallized mixture of **7** and **8**. The molecular structure of **8** is shown in Figure 3 along with details of selected bond lengths and angles.

Compound **8** once again crystallizes as discrete molecules. The lanthanum ion is coordinated by the carbanion centers and by the oxygen atoms of the methoxy substituents of the two carbanions to give two four-membered chelate rings (C−La−O bite angles 61.16(10) and 62.21(10)°); the coordination sphere of the lanthanum ion is completed by an iodide ligand and by the oxygen atom of a molecule of THF, giving a six-coordinate, distorted-trigonal-prismatic lanthanum center. The two carbanion ligands are oriented in a head-to-tail fashion and, as in **3** and **5**, the La−C distances (2.813(4) and 2.714(4) Å) are long in comparison to other La−C(sp³) distances.[2a,6] The La−O(Me) (2.528(3) and 2.516(3) Å), La−O(THF) (2.561(3) Å), and La−I distances (3.1734(3) Å) in **8** are similar to the corresponding distances in **3** and **5**.[8]

Further evidence for the identity of the monoalkyl compound **7** was provided by a substitution reaction. Treatment of a 1:1 mixture of **7** and **8** with approximately 1 equiv of KN(SiMe₃)₂ in THF yields a mixture of compounds, from which [(Me₃Si)₂-{Me₂(MeO)Si}C]LaI{N(SiMe₃)₂}(THF) (**9**) may be obtained in reasonable yield by recrystallization from diethyl ether. This strongly suggests that the product which cocrystallizes with **8** is the monosubstituted compound **7**.

Compound **9** is a rare example of a fully heteroleptic lanthanide complex (i.e. LnXYZ as opposed to LnX₂Y).[11] Typically, heteroleptic complexes of the lanthanides are unstable toward ligand redistribution via Schlenk-type equilibria and fully heteroleptic complexes are limited to the later, smaller lanthanide(III) ions.

The identity of **9** was confirmed by X-ray crystallography; the molecular structure of **9** is shown in Figure 4 along with details of selected bond lengths and angles.

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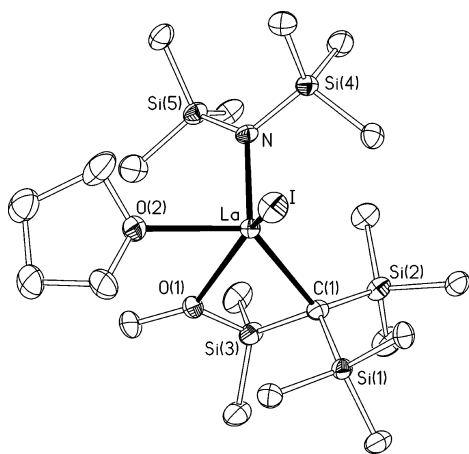
Figure 4. Molecular structure of **9** with 40% probability ellipsoids. H atoms and the disorder component are omitted for clarity. Selected bond lengths (Å) and angles (deg): La−C(1) = 2.682(4), La−O(1) = 2.492(3), La−N = 2.313(3), La−I = 3.2079(4), La−O(2) = 2.530(3); C(1)−La−O(1) = 63.43(11), C(1)−La−I = 120.12(9), I−La−O(2) = 76.30(8), O(2)−La−O(1) = 74.20(11), N−La−C(1) = 111.80(13), N−La−O(1) = 110.59(11), N−La−O(2) = 98.30(11), N−La−I = 110.68(9).

Compound **9** crystallizes as discrete monomers in which the lanthanum ion is coordinated by the C and O atoms of one carbanion ligand, giving a four-membered chelate ring (bite angle 63.43(11)°), by an iodide ligand, by the nitrogen atom of the amide ligand, and by the oxygen atom of a molecule of THF. The lanthanum center is thus five-coordinate with a distorted-square-pyramidal geometry, in which the amide ligand occupies the apical position. Once again, the La−C distance (2.682(4) Å) is long in comparison to other La−C distances;[2,6] the La−O and La−N distances are similar to the corresponding distances in **3**, **5**, and **8**.

The monotonic decrease in ionic radii across the lanthanide series (the lanthanide contraction) may be used to tune the properties of organolanthanide complexes in a controlled manner. We were interested to observe whether the small difference in ionic radii between the early-lanthanide ions La-(III) and Nd(III) would have any significant effect on the stabilities and reactivities of their complexes with functionalized tris(triorganosilyl)methyl ligands (the ionic radii of six-coordinate La(III) and Nd(III) are 1.032 and 0.983 Å, respectively).[12] Somewhat surprisingly, despite this small difference in ionic radii, we find that metathesis reactions between NdI$_3$-(THF)$_{3.5}$ and the potassium alkyls [(Me$_3$Si)$_2${Me$_2$(Me$_2$N)Si}C]K, {(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$K$_2$, and [(Me$_3$Si)$_2${Me$_2$-(MeO)Si}C]K do not give readily isolable analogues of **3**, **5**, and **8**.

Treatment of NdI$_3$(THF)$_{3.5}$ with either 2 equiv of [(Me$_3$Si)$_2$-{Me$_2$(Me$_2$N)Si}C]K or 1 equiv of the dipotassium salt {(Me$_3$-Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$K$_2$ (**4**) in THF yields pale blue solutions from which pale blue, viscous oils may be obtained. Unfortunately, we were unable to obtain solid samples of the supposed organoneodymium products for further analysis from either of these reactions.

In one case, however, we were able to isolate a solid, crystalline organoneodymium complex. The dipotassium salt **4** is synthesized by deprotonation of {(Me$_3$Si)(Me$_2$MeOSi)CH-(SiMe$_2$CH$_2$)}$_2$ with 2 equiv of MeK, which is itself prepared by a metathesis reaction between MeLi and KOBu^t (Scheme

2a).[4,13] This latter metathesis reaction proceeds cleanly to give essentially pure MeK when halide-free MeLi is used; however, in one instance **4** was synthesized from MeK prepared from a batch of MeLi which contained a significant quantity of LiI. The LiI was carried forward in the reaction to give the LiI-containing dipotassium salt {(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$-CH$_2$)}$_2$K$_2$·xLiI (**4a**), and a subsequent reaction between NdI$_3$-(THF)$_{3.5}$ and 1 equiv of **4a** gave the ate complex {(Me$_3$Si)-(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$Nd(μ-I)$_2$Li(THF)$_2$ (**10**) in good yield (Scheme 2b). Compound **10** is isolated as a pale blue oil which may be recrystallized from methylcyclohexane/THF as pale blue plates suitable for X-ray crystallography. The molecular structure of **10** is shown in Figure 5 along with details of selected bond lengths and angles.

Compound **10** crystallizes in two polymorphs, one monoclinic and one triclinic; the molecular structures of both polymorphs are essentially identical, and so only data relating to the triclinic polymorph are discussed below. Compound **10** crystallizes as a discrete molecular species. The neodymium ion is coordinated by the two carbanion centers and the two methoxy oxygen atoms of the dicarbanion ligand, generating one seven-membered chelate ring (C−Nd−C bite angle 120.84(9)°) and two four-membered chelate rings (C−Nd−O bite angles 62.77(9) and 64.31(9)°). The coordination sphere of the neodymium ion is completed by two iodide ligands, giving a six-coordinate neodymium center with a distorted-trigonal-prismatic geometry. The two iodide ligands form a bridge to the lithium ion, which attains a distorted-tetrahedral geometry through the coordination of two molecules of THF. The Nd−C distances (2.714(3) and 2.614(3) Å) are rather long in comparison to other Nd−C(sp^3) distances; for example, the Nd−C(alkyl) distances in Cp*$_2$Nd-{CH(SiMe$_3$)$_2$}[14] and Me$_2$Si(C$_5$Me$_4$)$_2$Nd{CH(SiMe$_3$)$_2$}[15] are 2.517(7) and 2.506(7) Å, respectively. The Nd−O and Nd−I distances (2.496(2) and 2.468(2) Å and 3.1481(5) and 3.1699-(3) Å, respectively) lie within the usual range for these types of contacts.[16,17] Like **5**, compound **10** crystallizes as the meso diastereomer.

In contrast to the formation of **7** and **8**, the reaction between NdI$_3$(THF)$_{3.5}$ and 2 equiv of [(Me$_3$Si)$_2${Me$_2$(MeO)Si}C]K in THF unexpectedly gives the heteroleptic dimer {[(Me$_3$Si)$_2${Me$_2$-(MeO)Si}C]Nd(I)(THF)(μ-OMe)}$_2$ (**11**) in reasonably good yield. The methoxide ligands in **11** appear to be derived from Si−O cleavage of the second equivalent of alkyl ligand; unfortunately, we have been unable to identify the side product-(s) in this reaction and so have been unable to determine the fate of the ligand which loses its methoxy substituent. The apparently facile cleavage of a Si−O bond is somewhat surprising, since this ligand forms stable and robust complexes

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Scheme 2[a]

(a)

KOBu^t $\xrightarrow{\text{(i)}}$ MeK $\xrightarrow{\text{(ii)}}$ {(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$K$_2$ (**4**)

$\xrightarrow{\text{(iii)}}$ MeK·(LiI)$_x$ $\xrightarrow{\text{(ii)}}$ {(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$K$_2$(LiI)$_x$ (**4a**)

(b)

(**10**) $\xleftarrow{\text{(iv)}}$ NdI$_3$(THF)$_{3.5}$ $\xrightarrow{\text{(v)}}$ (**11**)
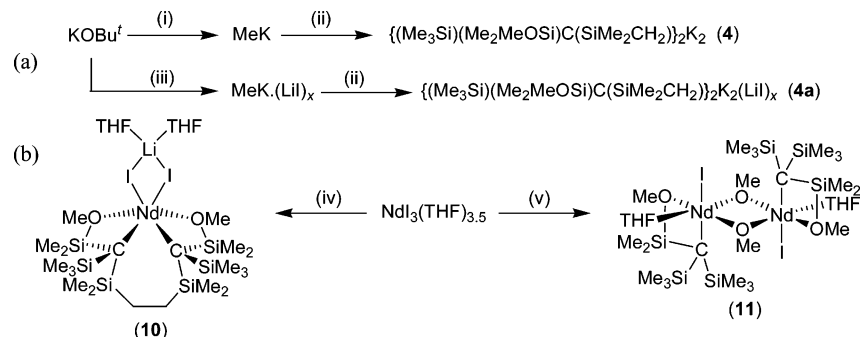
[a] Reagents: (a) (i) MeLi, Et$_2$O; (ii) {(Me$_3$Si)(Me$_2$MeOSi)CH(SiMe$_2$CH$_2$)}$_2$, Et$_2$O; (iii) MeLi·xLiI, Et$_2$O; (b) (iv) {(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$-K$_2$·xLiI, THF; (v) 2[(Me$_3$Si)$_2${Me$_2$(MeO)Si}C]K, THF.
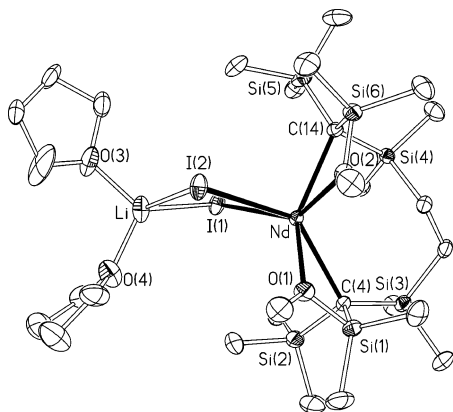
Figure 5. Molecular structure of **10** with 40% probability ellipsoids. H atoms and minor disorder components are omitted for clarity. Selected bond lengths (Å) and angles (deg): Nd–C(4) = 2.714(3), Nd–C(14) = 2.614(3), Nd–O(1) = 2.496(2), Nd–O(2) = 2.468(2), Nd–I(1) = 3.1481(5), Nd–I(2) = 3.1699(3), Li–I(1) = 2.768(6), Li–I(2) = 2.729(7), Li–O(3) = 1.884(7), Li–O(4) = 1.888(8); C(4)–Nd–C(14) = 120.84(9), C(4)–Nd–O(1) = 62.77(9), C(14)–Nd–O(2) = 64.31(9), I(1)–Nd–I(2) = 81.459-(11), C(4)–Nd–I(1) = 102.97(7), C(14)–Nd–I(1) = 91.21(7), O(1)–Nd–I(2) = 80.75(5), O(2)–Nd–I(2) = 78.94(5), O(1)–Nd–O(2) = 77.14(8), I(1)–Li–I(2) = 97.2(2).

with metals from groups 1,[4,18] 2,[18a,19] 5,[20] 12,[21] 13,[22] and 14,[23] all of which exhibit no propensity to undergo decomposition reactions; the potassium alkyl precursor (**6**) is itself stable over long periods both in the solid state and in solution.[4] There are also several examples of complexes of this ligand with low-oxidation-state lanthanide centers: viz. [(Me$_3$Si)$_2${Me$_2$(MeO)-Si}C]$_2$Yb,[3b] [(Me$_3$Si)$_2${Me$_2$(MeO)Si}C]$_2$Sm(THF) (**1**),[3c] and {[(Me$_3$Si)$_2${Me$_2$(MeO)Si}C]YbI(OEt$_2$)}$_2$.[3b] The sole example of a lanthanide(III) derivative of this ligand prior to this report was [(Me$_3$Si)$_2${Me$_2$(MeO)Si}C]$_2$Sm(OCPh$_2$) (**2**),[3c] which is obtained by in situ oxidation of **1** with benzophenone (preclud-
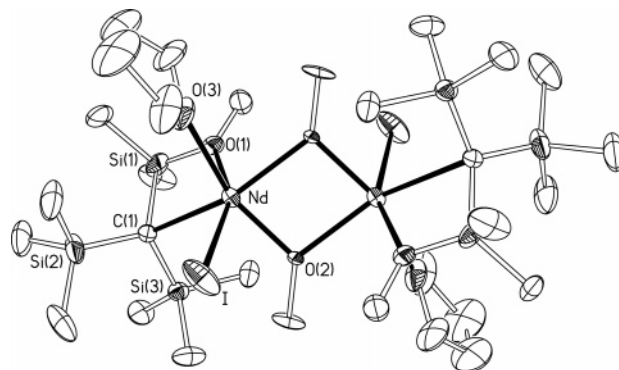
Figure 6. Molecular structure of **11** with 40% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Nd–C(1) = 2.688(11), Nd–O(1) = 2.477-(6), Nd–O(2) = 2.050(8), Nd–O(2′) = 2.333(7), Nd–O(3) = 2.493(7), Nd–I = 3.101(1); C(1)–Nd–O(1) = 63.2(3), C(1)–Nd–O(3) = 102.4(3), C(1)–Nd–O(2) = 110.0(3), C(1)–Nd–I = 97.7-(2), O(2)–Nd–I = 75.0(2), O(2)–Nd–O(1) = 120.3(3), O(2)–Nd–O(2′) = 80.2(3), O(2′)–Nd–O(1) = 81.8(3), O(2′)–Nd–O(3) = 82.6(3), O(2′)–Nd–I = 118.1(2), O(3)–Nd–O(1) = 87.9(3), O(3)–Nd–I = 85.8(3). Symmetry operator for primed atom: 2 − x, 2 − y, 1 − z.

ing comparisons between the syntheses of **11** and **2**). In no previous case has Si–O cleavage been observed with this ligand.

The isolation of the neodymium complex **11** contrasts markedly with the reaction between LaI$_3$(THF)$_4$ and 2 equiv of **6** under similar conditions (see above). While this latter reaction does not proceed cleanly, there is no evidence for Si–O cleavage at room temperature, even after extended reaction periods. However, decomposition occurs when reactions between LaI$_3$-(THF)$_4$ and **6** are heated, although no lanthanum-containing products could be isolated, suggesting that such Si–O cleavage reactions may be relatively common for this type of ligand.

In this regard, Lappert and co-workers have recently shown that the less sterically hindered, methoxy-functionalized lanthanide(III) alkyls [(Me$_3$Si){Me$_2$(MeO)Si}CH]$_3$Ln (Ln = Y, Ce) are readily accessible.[2c] However, these authors have also reported that reactions between the closely related alkali-metal salts [(Me$_3$Si){Me(MeO)$_2$Si}CH]M (M = Li, K) and MgBr$_2$, TlCl, ZnCl$_2$, CeCl$_3$, or Ce(OTf)$_3$ yield products containing methoxy ligands derived from cleavage of a Si–O bond in the ligands.[5,24]

It would therefore appear that certain lanthanide complexes containing methoxy-functionalized, silicon-stabilized carbanions are susceptible to Si–O cleavage reactions, but that their

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predilection for this reaction is highly dependent upon the exact nature of the ligand, the metal center, and the reaction conditions.

Compound **11** was unambiguously identified by X-ray crystallography. The molecular structure of **11** is shown in Figure 6 along with details of selected bond lengths and angles.

Compound **11** crystallizes as centrosymmetric dimers containing a planar Nd_2O_2 core. Each neodymium ion is coordinated by the C and O atoms of a carbanion ligand, generating a four-membered chelate ring (C–Nd–O bite angle 63.2(3)°) and by an iodide ligand and the oxygen atom of a molecule of THF. The halves of the dimer are connected by two μ_2 methoxide ligands, which form unsymmetrical bridges between the Nd ions (Nd–O(2) = 2.050(8) Å, Nd–O(2′) = 2.333(7) Å). Thus, the neodymium ions are six-coordinate, with a highly distorted octahedral geometry. The Nd–C distance (2.688(11) Å) is, once again, rather long in comparison to other Nd–C(sp^3) distances,[14,15] whereas the Nd–I distance is typical for this type of contact.[17] The Nd–O(2) distance is very short for a μ_2 alkoxide; Nd–O distances in μ_2 alkoxides are typically in excess of 2.3 Å. For example, the Nd–OEt distances in (COT)Nd(μ_2-OEt)(THF)}$_2$ are 2.343(2) and 2.344(3) Å (COT = cyclooctatetraenyl),[25] whereas the Nd–O distances to the bridging alkoxide ligands in {(Pr$^i_2$HCO)$_2$(THF)Nd(μ_2-OCHPr$^i_2$)}$_2$ (**12**) are 2.368(4) and 2.394(4) Å.[26] Indeed, the Nd–O(2) distance is substantially shorter than typical Nd–O distances in *terminal* neodymium alkoxides, which are usually in excess of 2.1 Å; for example, the terminal Nd–O distance in **12** is 2.146(4) Å. In contrast, the Nd–O(2′) distance of 2.333(7) Å in **11** is typical for this type of contact.[16]

Conclusions

The synthesis of heteroleptic dialkyllanthanide iodides R_2-LnI(THF)$_n$ of the early-lanthanide ions La(III) and Nd(III) containing oxygen- or nitrogen-functionalized tris(triorganosilyl)methyl ligands is highly dependent upon the nature of the ligands, the metal center, and the precise reaction conditions. Metathesis reactions between 2 equiv of the methoxy-functionalized potassium alkyl [(Me$_3$Si)$_2${Me$_2$(MeO)Si}C]K (**6**) and either LaI$_3$(THF)$_4$ or NdI$_3$(THF)$_{3.5}$ do not proceed as expected. The former reaction yields an inseparable mixture of mono- and dialkyllanthanum complexes, [(Me$_3$Si)$_2${Me$_2$(MeO)Si}C]-LaI$_2$(THF) (**7**) and [(Me$_3$Si)$_2${Me$_2$(MeO)Si}C]$_2$LaI(THF) (**8**), whereas the latter reaction yields the methoxide-bridged dimer {[(Me$_3$Si)$_2${Me$_2$(MeO)Si}C]Nd(I)(THF)(μ-OMe)}$_2$ (**11**) via Si–O cleavage of the second equivalent of alkyl ligand; decomposition via a possible Si–O cleavage reaction is also observed when reactions between **6** and LaI$_3$(THF)$_4$ are heated.

The underlying reasons for the apparently anomalous behavior of this ligand are, as yet, unclear, although facile Si–O cleavage may be associated with the noted oxophilicity of the lanthanides, since this decomposition reaction ultimately results in the formation of a highly favored Ln–O bond. In this regard, it is interesting that compounds **5** and **10**, in which the two carbanion centers are contained within the same ligand, appear to be stable toward Si–O cleavage. This may possibly be associated with the multidentate nature of the alkyl ligand in these two compounds: Si–O cleavage of this ligand may be somewhat disfavored, since it would result in cleavage of both the seven-membered chelate ring and one of the four-membered chelate rings.

We are currently investigating the use of these and related ligands in the synthesis of heteroleptic mid-to-late organolanthanide compounds, with a view to gaining greater insight into how the ionic radius of the metal (i.e. its Lewis acidity) influences the tendency toward Si–O cleavage reactions in these systems.

Experimental Section

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. THF, methylcyclohexane, toluene, diethyl ether, and light petroleum (bp 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 LaI$_3$(THF)$_4$,[27] NdI$_3$(THF)$_{3.5}$,[27] {(Me$_3$Si)$_2$(Me$_2$-MeOSi)C}K,[4] {(Me$_3$Si)$_2$(Me$_2$Me$_2$NSi)C}K,[28] and {(Me$_3$Si)(Me$_2$-MeOSi)C(SiMe$_2$CH$_2$)}$_2$K$_2$[4] 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.

[(Me$_3$Si)$_2${Me$_2$(Me$_2$N)Si}C]$_2$LaI (3). A solution of {(Me$_3$Si)$_2$-(Me$_2$Me$_2$NSi)C}K (0.74 g, 2.47 mmol) in THF (20 mL) was added, dropwise, to a slurry of LaI$_3$(THF)$_4$ (1.0 g, 1.23 mmol) in THF (10 mL), and the reaction mixture 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 from the filtrate in vacuo. The resulting orange oil was recrystallized from cold (−20 °C) methylcyclohexane to give **3** as colorless blocks. Isolated yield: 0.75 g, 78%. Anal. Calcd for C$_{22}$H$_{60}$ILaN$_2$Si$_6$: C, 33.57; H, 7.68; N, 3.56%. Found: C, 33.55; H, 7.70; N, 3.46. ^{1}H NMR (d_8-THF, 27 °C): δ 0.01 (s, 36H, SiMe$_3$), 0.42 (s, 12H, SiMe$_2$), 2.46 (s, 12H, NMe$_2$). ^{13}C{^{1}H} NMR (d_8-THF, 27 °C): δ 3.60 (SiMe$_3$), 5.50 (SiMe$_2$), 38.63 (NMe$_2$).

[{(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$]LaI(THF) (5). A solution of {(Me$_3$Si)(Me$_2$MeOSi)C(SiMe$_2$CH$_2$)}$_2$K$_2$ (0.60 g, 1.05 mmol) in THF (20 mL) was added, dropwise, to a slurry of LaI$_3$(THF)$_4$ (0.85 g, 1.05 mmol) in THF (10 mL), and the reaction mixture 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 from the filtrate in vacuo. The resulting colorless oil was recrystallized from cold (−20 °C) methylcyclohexane/THF (10:1 ratio) to give **5** as colorless needles. Isolated yield: 0.62 g, 71%. Anal. Calcd for C$_{24}$H$_{60}$ILaO$_3$Si$_6$: C, 34.69; H, 7.28. Found: C, 34.75; H, 7.19. ^{1}H NMR (d_8-THF, 25 °C): δ −0.06 (s, 12H, SiMe$_2$), 0.06 (s, 12H, Si*Me$_2$*OMe), 0.11 (s, 18H, SiMe$_3$), 0.24 (s, 4H, CH$_2$), 1.67 (m, 4H, THF), 3.48 (s, 6H, OMe), 3.92 (m, 4H, THF). ^{13}C{^{1}H} NMR (d_8-THF, 30 °C): δ 0.78 (SiMe$_2$), 1.92 (Si*Me$_2$*OMe), 3.65 (SiMe$_3$), 11.88 (CH$_2$), 25.89 (THF), 49.93 (OMe), 69.21 (THF).

[(Me$_3$Si)$_2${Me$_2$(MeO)Si}C]LaI$_2$(THF) (7) and [(Me$_3$Si)$_2${Me$_2$-(MeO)Si}C]$_2$LaI(THF) (8). A solution of {(Me$_3$Si)$_2$(Me$_2$MeOSi)C}K (0.83 g, 3.07 mmol) in THF (20 mL) was added, dropwise, to a slurry of LaI$_3$(THF)$_4$ (1.24 g, 1.54 mmol) in THF (10 mL), and the reaction mixture 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 from the filtrate in vacuo. The resulting colorless oil was recrystallized

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Table 1. Crystallographic Data for 3, 5, and 8−11

	3	5	8	9	10 triclinic	10 monoclinic	11
formula	$C_{22}H_{60}ILaN_2Si_6$	$C_{24}H_{60}ILaO_3Si_6$	$C_{24}H_{62}ILaO_3Si_6$	$C_{20}H_{53}ILaNO_2Si_5$	$C_{28}H_{68}ILiNdO_4Si_6$	$C_{28}H_{68}ILiNdO_4Si_6$	$C_{30}H_{76}I_2Nd_2O_6Si_6$
fw	787.1	831.1	833.1	745.9	1024.3	1024.3	1243.7
cryst size/mm	0.60 × 0.60 × 0.20	0.54 × 0.42 × 0.32	0.60 × 0.60 × 0.20	0.01 × 0.01 × 0.01	0.50 × 0.40 × 0.10	0.40 × 0.40 × 0.20	0.42 × 0.40 × 0.22
cryst syst	tetragonal	triclinic	triclinic	tetragonal	triclinic	monoclinic	triclinic
space group	$P4_32_12$	$P\bar{1}$	$P\bar{1}$	$P4_2/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	17.1751(3)	9.6301(9)	9.9596(3)	27.3564(6)	10.2161(6)	12.9819(11)	9.406(3)
b/Å		12.0261(5)	11.8759(4)		12.1819(19)	10.6242(10)	12.4259(14)
c/Å	25.1600(7)	17.3986(19)	16.6935(6)	9.1519(4)	20.4154(17)	32.628(2)	13.660(2)
α/deg		94.617(8)	95.403(1)		76.075(10)		68.672(14)
β/deg		94.943(13)	92.415(1)		84.620(7)	97.802(9)	72.213(13)
γ/deg		109.325(6)	103.775(1)		67.142(6)		87.620(18)
V/Å^3	7421.8(3)	1881.6(3)	1904.92(11)	6849.0(4)	2272.4(4)	4485.8(6)	1411.7(5)
Z	8	2	2	8	2	4	1
μ/mm^{-1}	2.190	2.168	2.142	2.339	2.686	2.721	3.068
no. of rflns measd	46 946	41 968	17 370	56 296	37 332	35 052	38 418
no. of unique rflns	9268	8605	8895	7014	10218	7820	6450
R_{int}	0.051	0.042	0.023	0.074	0.036	0.041	0.068
no. of rflns with $F^2 > 2\sigma$	7769	7675	8263	5282	7755	6249	4606
no. of params	309	333	334	305	442	405	436
transmissn coeff range	0.353−0.669	0.387−0.544	0.360−0.674	0.960−0.977	0.347−0.775	0.409−0.612	0.330−0.508
R (on F, $F^2 > 2\sigma$)^a	0.029	0.021	0.042	0.034	0.030	0.046	0.052
R_w (on F^2, all data)^a	0.054	0.051	0.089	0.081	0.068	0.140	0.176
goodness of fit^a	1.085	1.066	1.229	1.045	1.054	1.012	1.137
min, max electron density/e Å^{-3}	0.53, −0.56	1.03, −0.66	1.33, −1.64	0.83, −0.84	0.92, −0.60	1.99, −2.49	1.61, −1.68

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

from cold (−20 °C) methylcyclohexane/THF (10:1 ratio) to give **7** and **8** as colorless blocks. A single crystal of **8** was selected for X-ray crystallographic analysis. Isolated yield: 0.73 g, 61%. ^{1}H NMR (d_8-THF, 27 °C): δ 0.22 (s, 36H, SiMe$_3$), 0.25 (s, 18H, SiMe$_3$), 0.38 (s, 12H, SiMe$_2$), 0.42 (s, 6H, SiMe$_2$), 1.76 (m, 8H, THF), 3.64 (m, 8H, THF), 3.78 (s, 3H, OMe), 3.91 (s, 6H, OMe). ^{13}C{^{1}H} NMR (d_8-THF, 27 °C): δ 3.43 (SiMe$_3$), 3.87 (SiMe$_3$), 7.86 (SiMe$_2$), 8.00 (SiMe$_2$), 25.80 (THF), 50.47 (OMe) 50.78 (OMe), 68.43 (THF). NMR data refer to a 50:50 mixture of **7** and **8**.

[(Me₃Si)₂{Me₂(MeO)Si}C]LaI{N(SiMe₃)₂}(THF) (9). A solution of [K{N(SiMe₃)₂}] (0.15 g, 0.76 mmol) in THF (5 mL) was added, dropwise, to a solution of **7** and **8** (0.63 g, approximately 0.8 mmol) in THF (5 mL), and the reaction mixture was stirred overnight. The solvent was removed in vacuo, and the residue was extracted into diethyl ether (10 mL). The diethyl ether solution was filtered, concentrated to 3 mL, and cooled to −20 °C, yielding **9** as colorless blocks. Isolated yield: 0.35 g, 61% (based on **7**). Anal. Calcd for C₂₀H₅₃ILaNO₂Si₅: C, 32.21; H, 7.16. Found: C, 32.45; H, 7.03. ^{1}H NMR (d_8-THF, 26 °C): δ 0.16 (s, 6H, SiMe₂), 0.19 (s, 18H, CSiMe₃), 0.28 (s, 18H, NSiMe₃), 1.80 (m, 4H, THF), 3.45 (s, 3H, OMe), 3.61 (m, 4H, THF). ^{13}C{^{1}H} NMR (d_8-THF, 26 °C): δ 3.10 (SiMe₂), 6.98 (CSiMe₃), 7.63 (NSiMe₃), 26.59 (THF), 51.34 (OMe), 69.21 (THF).

{(Me₃Si)(Me₂MeOSi)C(SiMe₂CH₂)}₂Nd(μ-I)₂Li(THF)₂ (10). A solution of {(Me₃Si)(Me₂MeOSi)C(SiMe₂CH₂)}₂K₂·xLiI (0.85 g, approximately 1.5 mmol) in THF (20 mL) was added, dropwise, to a slurry of NdI₃(THF)₃.₅ (1.16 g, 1.49 mmol) in THF (10 mL), and this mixture was stirred for 16 h. The solvent was removed in vacuo, and the sticky solid was extracted into light petroleum and filtered. The solvent was removed in vacuo from the filtrate, and the pale blue viscous oil was recrystallized from cold (−20 °C) methylcyclohexane to give **10** as pale blue plates. Isolated yield: 0.96 g, 62%. Anal. Calcd for C₂₈H₆₈I₂LiNdO₄Si₆: C, 32.26; H, 6.58. Found: C, 32.36; H, 6.73.

{[(Me₃Si)₂{Me₂(MeO)Si}C]NdI(μ-OMe)(THF)}₂ (11). A solution of {(Me₃Si)₂(Me₂MeOSi)C}K (0.78 g, 2.72 mmol) in THF (20 mL) was added, dropwise, to a slurry of NdI₃(THF)₃.₅ (1.06 g,

1.36 mmol) in THF (10 mL), and this mixture was stirred for 16 h. The solvent was removed in vacuo, and the sticky solid was extracted into light petroleum (30 mL) and filtered. The solvent was removed in vacuo, and the pale blue oil was recrystallized from cold (−20 °C) toluene/THF (10:1) to give **11** as pale blue plates. Isolated yield: 1.01 g, 65%. Anal. Calcd for C₃₀H₇₆I₂Nd₂O₆Si₆: C, 28.97; H, 6.16. Found: C, 28.87; H, 6.14.

Crystal Structure Determinations of 3, 5, and 8−11. For **3**, **5**, **8**, **10**, and **11** measurements were made at 150 K on Bruker AXS SMART CCD and Nonius KappaCCD diffractometers using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å); for **9** measurements were made at 120 K on a Bruker Nonius APEX2 CCD diffractometer using a synchrotron X-ray source (λ = 0.6898 Å). 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, on the basis of symmetry-equivalent and repeated reflections. The structures were solved by direct methods or Patterson synthesis and were refined on F^2 values for all unique data. Table 1 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 one THF ligand in **9** and two THF ligands in **10** (triclinic polymorph); structure **11** is subject to whole-molecule disorder, which was resolved and refined with restraints on geometry and displacement parameters. The absolute configuration of the homochiral compound **3** was determined by refinement of the enantiopole parameter[29] to −0.022(10). Programs were Bruker AXS SMART (control) and SAINT (integration), Nonius COLLECT and associated programs, and SHELXTL for structure solution, refinement, and molecular graphics.[30]

(29) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.
(30) (a) APEX2, SMART, and SAINT software for CCD diffractometers; Bruker AXS, Madison, WI, 1997 and 2004. (b) Sheldrick, G. M. *SHELXTL User Manual, Version 6*; Bruker AXS: Madison, WI, 2001. (c) COLLECT software; Nonius BV, Delft, The Netherlands, 2000.

Supporting Information Available: For **3**, **5**, **8**−**10** (both polymorphs), and **11** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters as CIF files. 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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