A Samarium Alkyl–Aryloxide Complex Containing a Trigonal Bipyramidal Carbon Atom: X-ray Structure of [Li(THF)]₂[Sm(O-2,6-i-Pr₂C₆H₃)₃(CH₂SiMe₃)₂]

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Reaction of Sm(O-2,6-i-Pr₂C₆H₃)₃(THF)₂ (**1**) with 3 equiv of LiCH₂SiMe₃ in THF solution produces the salt complex (Me₃SiCH₂)Sm[(μ-OAr)(μ-CH₂SiMe₃)Li(THF)][(μ-OAr)₂Li(THF)] (**2**, Ar = 2,6-i-Pr₂C₆H₃) in 58% yield. ¹H and ¹³C NMR are extremely complex, while ⁷Li NMR is indicative of an equilibrium between **2** and free LiO-2,6-i-Pr₂C₆H₃ in solution. Compound **2** contains a pentacoordinate samarium metal center ligated by one terminal and one bridging CH₂SiMe₃ ligand and three bridging O-2,6-i-Pr₂C₆H₃ ligands. Each lithium atom is coordinated to one molecule of THF and either two aryloxide ligands or one aryloxide and one alkyl bridging ligand. The bridging groups combine to make two fused four-membered metallacyclic rings, one Sm—O—Li—O and one Sm—C—Li—O ring [C—Sm = 2.564-(10) Å, C—Li = 2.219(20) Å]. The molecule crystallizes in the monoclinic space group *C2/c*, with *a* = 32.017(8) Å, *b* = 21.163(5) Å, *c* = 22.354(6) Å, *β* = 128.03(1)°, *V* = 11931.34 Å³, *d*calc = 1.130 g cm⁻³, and *Z* = 8.

Introduction

The preparation of homoleptic lanthanide and actinide alkyl complexes has been an attractive synthetic goal for a considerable period of time, owing in part to their anticipated volatility and reactivity.[2–4] However, frequently utilized preparative routes to alkyl complexes involving the metathesis between a metal halide and an alkyllithium reagent have often produced complexes in which the alkali metal halide is coordinated to the highly electrophilic lanthanide metal center.[2–9] In cases where a stoichiometric excess of alkyl lithium reagent has been employed, "ate" (or salt) complexes such as Li-[Ln(allyl)₄],[10] [Li(OEt₂)₄][Lu(CH₂SiMe₃)₄],[11] [Li(THF)₄]-[Ln(CH₂SiMe₃)₄] (Ln = Er, Tb, Yb),[12] [Li(THF)₄][Ln-(CMe₃)₄] (Ln = Sm, Eu, Lu),[13] [Li(THF)₄][Lu(2,6-Me₂C₆H₃)₄],[14] [Li(TMEDA)]₃[LnMe₆],[15] or [Li(TMEDA)]₃-

[ThMe₇]·TMEDA[16] have been reported. Neutral lanthanide alkyls have been prepared in the presence of excess Lewis base, *e.g.* Ln(CH₂SiMe₃)₃(THF)ₓ (Ln = Er, Tm, x = 3; Ln = Yb, Lu, Tb, x = 2),[13,17] or by using alkyl ligands containing pendant donor groups as in La-(o-C₆H₄CH₂NMe₂)₃,[18] La[CH(PPh₂)₂]₃,[19] or Sc[CH-(SiMe₂C₆H₄-2-OMe)₂]₃,[20] where the formation of chelate rings enhances stability of the alkyl complex. The first examples of neutral, homoleptic f-element alkyls M[CH-(SiMe₃)₂]₃ (M = La,[21] Sm,[21] U[22]) have been reported through use of the bulky bis(trimethylsilyl)methyl ligand. These complexes were prepared by the alkylation of the monomeric aryloxide M(O-2,6-t-Bu₂C₆H₃)₃ (M = La, Sm, U) with 3 equiv of LiCH(SiMe₃)₂ in hexane solution, resulting in metathesis of the aryloxide ligands and precipitation of hydrocarbon-insoluble LiO-2,6-t-Bu₂C₆H₃ as indicated in eq 1.

$$M(OAr)_3 + 3LiR \rightarrow MR_3 + 3LiOAr \qquad (1)$$

M = La, Sm, U; Ar = 2,6-t-Bu₂C₆H₃;

R = CH(SiMe₃)₂

Much lanthanide organometallic chemistry has developed around the use of π-donating cyclopentadienyl

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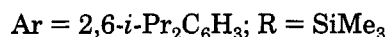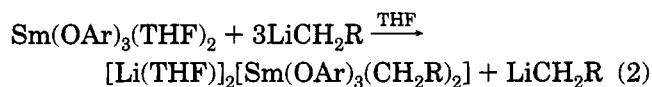
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and substituted cyclopentadienyl ligands as stabilizing groups.[2,3] Recently, the application of alkoxides as π-donor ancillary ligands in f-element chemistry has facilitated the preparation of alkyl alkoxides of the lanthanides,[23-25] and these have shown a rich reaction chemistry. As part of our interest in the application of sterically-demanding alkoxide ligands in f-element chemistry, we have been investigating the structural and reaction chemistry of the moderately bulky 2,6-diisopropylphenoxide ligand. The seemingly trivial decrease in steric bulk from 2,6-di-*tert*-butyl- to 2,6-diisopropylphenoxide has revealed a rich and diverse structural and reaction chemistry producing monomeric Ln-(OAr)$_3$L$_2$,[26] dimeric η-arene bridged Ln$_2$(OAr)$_6$,[26] and polymeric quasi-one-dimensional chain [KLn(OAr)$_4$]$_x$ structures[27] depending on the reaction conditions employed. We report here our results of alkylation of a samarium diisopropylphenoxide complex and compare our findings with those observed by others.[21-25]

Results and Discussion

Synthesis. Treatment of a toluene solution of Sm-(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_3$(THF)$_2$ (1) with 3 equiv of LiCH$_2$SiMe$_3$ at room temperature results in a color change from yellow to orange over a period of several hours, but the anticipated precipitate of lithium aryloxide (eq 1) was not observed. Removal of solvent, followed by crystallization from hexane at −40 °C, leads to the isolation of tan crystals of [Li(THF)]$_2$[Sm(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_3$(CH$_2$SiMe$_3$)$_2$] (2) in moderate yield as outlined in eq 2. The

$$Sm(OAr)_3(THF)_2 + 3LiCH_2R \xrightarrow{THF}$$

$$[Li(THF)]_2[Sm(OAr)_3(CH_2R)_2] + LiCH_2R \quad (2)$$

$$Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3; \ R = SiMe_3$$

empirical formula of compound 2 suggests that *addition* of 2 equiv of alkyllithium to the samarium aryloxide 1 has occurred rather than the substitution reaction originally envisioned (eq 1). Elemental analyses are in good agreement with the formulation of the product as [Li(THF)]$_2$[Sm(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_3$(CH$_2$SiMe$_3$)$_2$].

Solid-State and Molecular Structure. X-ray-quality crystals of **2** were grown by slow cooling of a concentrated hexane solution to −40 °C, and the structure was determined from diffraction data collected at −171 °C. A summary of data collection and crystallographic parameters is given in Table 1. Selected fractional coordinates are given in Table 2, and selected bond lengths and angles are given in Table 3. An ORTEP drawing giving the atom-numbering scheme used in the tables is shown in Figure 1.

The solid-state structure of **2** displays a distorted square-based-pyramidal samarium metal center ligated by one terminal and one bridging CH$_2$SiMe$_3$ ligand and

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Table 1. Summary of Crystal Data for [Li(THF)]$_2$[Sm(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_3$(CH$_2$SiMe$_3$)$_2$]

empirical formula	SmC$_{52}$H$_{89}$Li$_2$O$_5$Si$_2$
color of cryst	transparent
cryst dimens, mm	0.22 × 0.16 × 0.19
space group	C2/c
cell dimens	
a, Å	32.017(8)
b, Å	21.163(5)
c, Å	22.354(6)
β, deg	128.03(1)
temp, °C	−171
Z (molecules/cell)	8
V, Å^3	11 931.34
D_{calc}, g cm^{-3}	1.130
λ (Mo Kα)	0.710 69
Fw	1014.73
abs coeff, cm^{-1}	10.629
2θ range, deg	6–45
no. of measd reflcns	8400
no. of unique intensities	7905
no. of obsd reflcns	6248 [$F > 2.33\sigma(F)$]
R(F)^a	0.0698
R$_w$(F)^b	0.0687
goodness-of-fit	1.479

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F) = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table 2. Selected Fractional Coordinates and Isotropic Thermal Parameters^a (Å^2) for [Li(THF)]$_2$[Sm(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_3$(CH$_2$SiMe$_3$)$_2$]

	10^4x	10^4y	10^4z	$10B_{iso}$
Sm(1)	1554.6(2)	2080.2(2)	1342.3(3)	15
O(2)	1211(2)	2122(3)	1989(3)	24
C(3)	1345(4)	1975(5)	2678(5)	20
C(4)	1169(4)	1413(5)	2785(6)	35
C(5)	1289(7)	1317(7)	3488(7)	61
C(6)	1593(8)	1726(8)	4079(8)	79
C(7)	1775(6)	2262(7)	3975(7)	65
C(8)	1653(4)	2415(6)	3281(6)	34
O(15)	726(2)	2471(3)	519(3)	19
C(16)	328(4)	2724(4)	−165(5)	19
C(17)	−49(4)	2313(5)	−747(5)	22
C(18)	−469(4)	259o(5)	−1433(6)	26
C(19)	−52o(4)	3230(5)	−1547(6)	28
C(20)	−147(4)	3619(5)	−960(7)	38
C(21)	281(4)	3378(5)	−269(6)	27
O(28)	1562(2)	1476(3)	523(3)	17
C(29)	1271(4)	1265(5)	−202(5)	21
C(30)	1149(4)	614(5)	−349(5)	22
C(31)	871(4)	399(5)	−1087(6)	25
C(32)	710(4)	807(5)	−1690(5)	24
C(33)	816(4)	1449(5)	−1525(5)	26
C(34)	1087(4)	1687(5)	−802(5)	21
C(41)	2261(4)	1289(5)	2312(5)	22
Si(42)	2754(1)	693(2)	2998(2)	28
C(46)	2091(4)	3014(5)	1582(6)	29
Si(47)	2810(1)	2980(1)	2074(2)	27
Li(51)	561(7)	2497(10)	1180(10)	30
O(52)	−54(3)	2722(4)	1029(4)	40
C(53)	−565(5)	2875(8)	330(8)	54
C(54)	−901(9)	2976(26)	450(13)	259
C(55)	−602(10)	2907(22)	1304(14)	228
C(56)	−106(6)	2755(8)	1626(8)	54
Li(57)	2219(6)	1081(8)	1303(9)	21
O(58)	2564(3)	656(3)	951(4)	30
C(59)	2505(5)	894(6)	299(8)	40
C(60)	2775(10)	494(8)	146(12)	93
C(61)	2821(8)	−108(7)	481(10)	69
C(62)	2792(7)	49(7)	1110(9)	61

^{a} Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

three bridging O-2,6-*i*-Pr$_2$C$_6$H$_3$ ligands. Each lithium atom is coordinated to one molecule of THF and either two aryloxide ligands or one aryloxide and one alkyl

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for [Li(THF)]₂[Sm(O-2,6-i-Pr₂C₆H₃)₃(CH₂SiMe₃)₂]

|			
Sm(1)—O(2)	2.294(7)	O(2)—Li(51)	1.896(18)
Sm(1)—O(15)	2.257(6)	O(15)—Li(51)	1.853(18)
Sm(1)—O(28)	2.246(6)	O(52)—Li(51)	1.845(17)
Sm(1)—C(41)	2.564(10)	O(58)—Li(57)	1.929(17)
Sm(1)—C(46)	2.451(10)	O(28)—Li(57)	1.909(16)
C(41)—Li(57)	2.219(20)		
O(2)—Sm(1)—O(15)	73.81(22)	Sm(1)—O(2)—Li(51)	95.0(6)
O(2)—Sm(1)—O(28)	141.78(23)	Sm(1)—O(15)—C(16)	151.4(6)
O(2)—Sm(1)—C(41)	90.45(27)	Sm(1)—O(15)—Li(51)	97.4(6)
O(2)—Sm(1)—C(46)	112.0(3)	Sm(1)—O(28)—C(29)	145.0(6)
O(15)—Sm(1)—O(28)	98.11(22)	Sm(1)—O(28)—Li(57)	93.6(5)
O(15)—Sm(1)—C(41)	155.53(28)	Sm(1)—C(41)—Si(42)	177.9(5)
O(15)—Sm(1)—C(46)	101.3(3)	Sm(1)—C(46)—Si(47)	123.2(5)
O(28)—Sm(1)—C(41)	82.60(27)	O(2)—Li(51)—O(15)	93.6(8)
O(28)—Sm(1)—C(46)	106.2(3)	O(2)—Li(51)—O(52)	134.8(11)
C(41)—Sm(1)—C(46)	102.0(3)	O(15)—Li(51)—O(52)	131.2(11)
Sm(1)—O(2)—C(3)	140.2(6)	O(28)—Li(57)—O(58)	114.6(9)
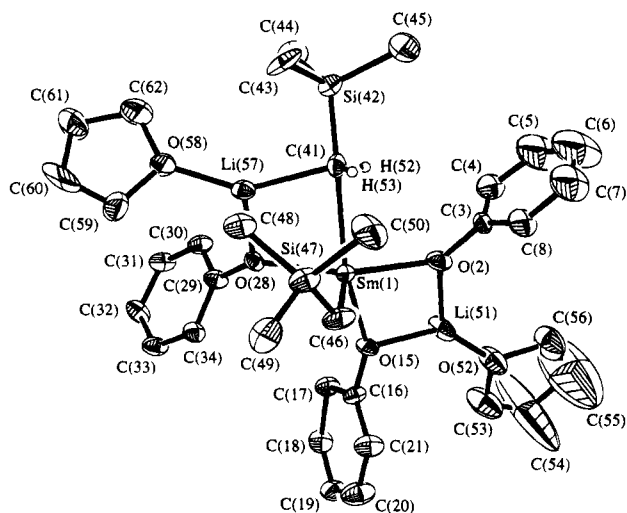
Figure 1. ORTEP drawing of the molecular structure of (Me₃SiCH₂)Sm[(μ-OAr)(μ-CH₂SiMe₃)Li(THF)][(μ-OAr)₂Li(THF)] (**2**, Ar = 2,6-i-Pr₂C₆H₃) emphasizing the five-coordinate square-based pyramidal geometry about the Sm center and the trigonal bipyramidal coordination geometry about the five-coordinate carbon atom C(41). Isopropyl carbon atoms have been omitted for clarity.

bridging ligand. As seen in Figure 1, C(46) occupies the apex of the square-based-pyramid, while O(2), O(15), O(28), and C(41) make up the basal plane with apex—Sm—basal angles (Table 3) ranging from 102 to 112°. The two lithium cations each display a planar, three-coordinate geometry and form bridges between two aryloxide ligands, or one aryloxide and one alkyl ligand, in the basal plane of the square-based-pyramidal metal center. One lithium center is coordinated to oxygen atoms from two aryloxide [Li(51)—O(2) = 1.896(18), Li(51)—O(15) = 1.853(18) Å] and one THF ligand [Li(51)—O(52) = 1.845(17) Å]. The second lithium cation is coordinated to one aryloxide oxygen [Li(57)—O(28) = 1.909(16) Å], one methylene carbon atom of the (trimethylsilyl)methyl ligand [Li(57)—C(41) = 2.219(20) Å], and one THF ligand [Li(57)—O(58) = 1.929(17) Å]. The bridging groups combine to make two fused four-membered metallacyclic rings, one Sm—O—Li—O and one Sm—C—Li—O ring.

The three Sm—O bond lengths for the aryloxide ligands are virtually identical, with an average value of 2.266(7) Å. This value can be compared to the Sm—O

distance of 2.13(1) Å found in the aryloxide ligand of (η-C₅Me₅)₂Sm(O-2,3,5,6-Me₄C₆H)[28] and the average Sm—O distances of 2.08(2), 2.099(9), and 2.101(6) Å found for the aryloxide ligands in [(η-C₅Me₅)₂Sm]₂-(O₂C₁₆H₁₀),[29] [(η-C₅Me₅)₂Sm(THF)]₂(O₂C₁₆H₁₀),[29] and Sm₂(O-2,6-i-Pr₂C₆H₃)₆.[26] Thus the average Sm—O bond lengths in **2** are ca. 0.15 Å longer than the Sm—O distances observed in all other samarium aryloxide complexes, and these longer bonding interactions are presumably due to a loss of electron density at oxygen upon forming a Sm—O—Li bridge. Two different samarium—carbon distances are observed for the two alkyl ligands—2.451(10) Å for the terminal ligand containing C(46) and 2.564(10) Å for the basal (trimethylsilyl)-methyl ligand which is bound additionally to Li(57). These distances are both considerably longer than the Sm—C distance of 2.33(2) Å observed in the homoleptic alkyl Sm[CH(SiMe₃)₂]₃[21] but comparable to the Sm—C alkyl distances found in (η-C₅Me₅)₂SmR(THF) complexes [R = Me, 2.484(14) Å; R = benzyl, 2.498(5) Å; R = Ph, 2.511(8) Å].[30-32]

Both of the methylene hydrogen atoms attached to C(41) were located in a difference Fourier and their positions refined. Thus the five-coordinate geometry about the methylene carbon C(41) is accurately defined in the structure as being trigonal bipyramidal. The axial Sm(1)—C(41)—Si(42) angle is virtually linear at 177.9(5)°, while the angles between the three equatorial atoms [Li(57), H(52), and H(53)] sum to 351°. The Li—C distance of 2.219(20) Å is within the 2.15(2)–2.29(1) range of Li—C distances seen in (LiCH₂SiMe₃)[33] and the expected range for Li—C(sp³) contacts,[34] while the Sm—C distance is well within the range previously reported for lanthanide—carbon single bonds (vide supra). Five-coordinate methylene carbon atoms within (trimethylsilyl)methyl ligands have been observed pre-

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viously but generally with the methylene carbon bridging a dinuclear metal center.[34-38] Girolami has reported an example of a CH_2SiMe_3 ligand bridging between lithium and manganese in the complex [Li(TMEDA)]$_2$-[Mn(CH_2SiMe_3)$_4$], although X-ray structural data are only available for the methyl, ethyl, and neohexyl analogs.[34] Evans has reported a structure of (Me$_3$-SiCH$_2$)Y[(μ-CH$_2$)$_2$SiMe$_2$][(μ-O-t-Bu)Li(THF)$_2$]$_2$ which displays a related pentacoordinate geometry with bridging alkyl and alkoxide ligands.[25]

Spectroscopic Studies. Room-temperature ^1H and ^{13}C NMR spectra of **2** are extremely complex, showing considerable overlap of resonances. Multiplicities and chemical shifts make it possible to identify the aromatic, isopropyl, and THF resonances, but there are too many resonances to constitute a single molecule in solution. A broad high-field ^1H NMR resonance at δ −4.37 ppm is consistent with the methylene protons attached to the five-coordinate carbon C(41) through comparison with the shift of the pseudo-five-coordinate methylene resonance in [(η-C$_5$Me$_5$)$_2$Sm(μ-H)(μ-CH$_2$C$_5$Me$_4$)Sm(η-C$_5$Me$_5$)] which appears at δ −2.15.[31] A single sharp trimethylsilyl resonance is seen at 0.20 ppm. Variable-temperature ^1H and ^{13}C NMR spectra also displayed extremely complex temperature dependent behavior. However, variable-temperature ^7Li NMR did provide some valuable insight into the complex solution behavior of this fascinating compound. Room-temperature ^7Li NMR of a crystalline sample of **2** in toluene-d_8 displayed four lithium environments at δ 11.8, 11.6, 9.5, and 3.5 ppm in the approximate ratio 3:1:1:2. Room-temperature ^7Li NMR of pure LiCH$_2$SiMe$_3$ and LiO-2,6-i-Pr$_2$C$_6$H$_3$ in toluene-d_8 revealed resonances at δ 5.0 and 4.0 ppm, respectively, suggesting that the resonance at δ 3.5 ppm in solutions of **2** may be due to free LiO-2,6-i-Pr$_2$C$_6$H$_3$ and that an equilibrium mixture may be present in solution. Addition of LiO-2,6-i-Pr$_2$C$_6$H$_3$ to the solution of **2** resulted in an increase in the resonance at δ 3.5 ppm and a concomitant shift toward δ 4.0 consistent with this assessment.

Further evidence for a solution equilibrium is obtained from variable-temperature ^7Li NMR studies. The relative ratios of the four ^7Li NMR resonances change in a pairwise manner as a function of temperature. Upon increase of the temperature to +80 °C, the resonances at δ 3.5 and 9.5 ppm increase in intensity while those at 11.6 and 11.8 ppm decrease in intensity. The opposite behavior is observed with decreasing temperature: the resonances at δ 3.5 and 9.5 decrease in intensity relative to the others, and these data are consistent with an equilibrium between **2** and free LiOAr in solution as outlined in eq 3. The approach to

$$[Li(THF)]_2[Sm(OAr)_3R_2] \rightleftharpoons$$
$$[Li(THF)]_{2-x}[Sm(OAr)_{3-x}R_2] + xLiOAr \quad (3)$$
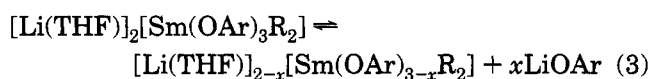
equilibrium is very slow as judged by ^7Li NMR. We note that the ^7Li spectra of a crystalline sample dissolved in toluene-d_8 changes over a period of months of standing at room temperature as equilibrium is approached, but

concomitant decomposition is also observed. Attempts to speed up this equilibrium by heating to 60 °C does show the expected increase in signal intensities for resonances at δ 3.5 and 9.5 ppm, but prolonged heating results in decomposition, and ^1H NMR following prolonged heating shows the appearance of SiMe$_4$. Therefore we are unable to extract a reliable equilibrium constant for this process.

At low temperature, further decoalescence into five distinct ^7Li resonances is observed. We suggest that this behavior is indicative of the freezing out of a number of different lithium isomers, *i.e.*, species in which the lithium atoms have different aryloxide coordination environments such as the isomeric structures depicted in **II** and **III**.

II   III
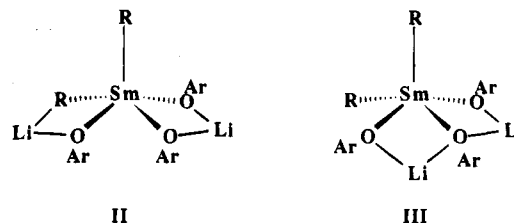
Concluding Remarks

We have shown that the reaction of the lanthanide aryloxide Sm(O-2,6-i-Pr$_2$C$_6$H$_3$)$_3$(THF)$_2$ with a lithium alkyl reagent (LiCH$_2$SiMe$_3$) does not result in the straightforward metathesis reaction we had envisioned but rather leads to the addition of 2 equiv of LiR to the samarium complex. This is perhaps surprising since the expected product, [Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$], has already been documented.[13,17] It can be seen that the 2 equiv of alkyllithium which added to **1** has undergone somewhat differing reactions. One equivalent [containing C(46)] has successfully undergone alkyl transfer to the metal center, with the resulting lithium aryloxide molecule still bound within the coordination sphere of samarium [*i.e.* Li(51) and the O(2)- or O(15)-containing aryloxide]. The second equivalent of alkyl reagent [containing Li(57) and C(41)] may be viewed as being frozen in the transition state from lithium−carbon to lithium−oxygen bonding, as the alkyl ligand is transferred to the samarium metal center.

The observation of an addition reaction of the lithium alkyl reagent, rather than the metathesis reactions observed by Lappert[21] and Sattelberger,[22] may be the result of several contributing factors: (i) The reduced steric requirement of the 2,6-diisopropylphenoxide ligand, compared with 2,6-di-*tert*-butylphenoxide, allows greater freedom for coordination of both alkyl and aryloxide ligands simultaneously to the lithium and samarium centers. (ii) The solubility of lithium 2,6-diisopropylphenoxide in toluene is considerably greater than that of lithium 2,6-di-*tert*-butylphenoxide in hexane; thus, the driving force for precipitation of the lithium aryloxide is significantly lower in the present case. (iii) THF ligands were available in the starting material Sm(O-2,6-i-Pr$_2$C$_6$H$_3$)$_3$(THF)$_2$ which could stabilize three-coordinate lithium cations in the product **2**.

Experimental Details

General Procedures and Techniques. All manipulations were carried out under an inert atmosphere of oxygen-

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free UHP grade argon using standard Schlenk techniques or under oxygen-free helium in a Vacuum Atmospheres glovebox. Anhydrous $SmCl_3$ was purchased from Strem and used as received. Potassium hydride was purchased from Aldrich as a 60% dispersion in mineral oil. The mineral oil dispersion was taken into a Vacuum Atmosphere Co. Drilab, washed with hexane, and vacuum filtered on a coarse porosity frit. The resulting solid was washed with hexane until the filtrate was colorless and then dried *in vacuo* to yield a white, pyrophoric powder. Potassium 2,6-diisopropylphenoxide was prepared by the reaction of potassium hydride with 2,6-diisopropylphenol (Aldrich) in THF. $Sm(O-2,6-i-Pr_2C_6H_4)_3(THF)_2$ was prepared by reaction of $SmCl_3$ with 3 equiv of $KO-2,6-i-Pr_2C_6H_4$ as reported previously.[26] Solvents were degassed and distilled from Na–K alloy under nitrogen. Benzene-d_6 and toluene-d_8 were degassed, dried over Na–K alloy, and then trap-to-trap distilled before use. Solvents were taken into the glovebox, and a small amount was tested with a solution of sodium benzophenone in THF. Solvents that failed to maintain a purple coloration from this test were not used.

NMR spectra were recorded at 22 °C on a Bruker AF 250 spectrometer or at 17 °C on a Varian Unity 300 spectrometer in benzene-d_6 or toluene-d_8. All ^1H NMR chemical shifts are reported in ppm relative to the ^1H impurity in benzene-d_6 or toluene-d_8 set at δ 7.15 or 2.09, respectively. All ^7Li NMR chemical shifts are reported in ppm relative to LiCl set at δ 0 in the same solvents. NMR spectra of paramagnetic samarium species are highly temperature dependent; thus, it is important to note that the temperatures quoted represent average room temperatures and are approximate values. Infrared spectra were recorded as Nujol mulls between KBr plates on a Digilab FTS-40 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

Synthesis. [Li(THF)]₂[Sm(O-2,6-i-Pr₂C₆H₃)₃(CH₂SiMe₃)₂] (2). A solution of $LiCH_2SiMe_3$ (194 mg, 2.06 mmol) in hexane and $Sm(O-2,6-i-Pr_2C_6H_3)_3(THF)_2$ (572 mg, 0.69 mmol) was placed in 50 mL of toluene yielding a yellow solution. The mixture was stirred for several hours at room temperature, during which time the solution became orange. After approximately 8 h, the solvent was removed *in vacuo* to leave an orange oil. A 20 mL volume of hexanes was added with rapid stirring to give an orange glassy solid which was allowed to dry overnight. A 50 mL volume of hexanes was then added to dissolve the solid followed by filtration and slow evaporation of the solution in the drybox to yield large oil-coated crystals. The procedure of redissolving in hexanes and filtering was repeated. Concentration of this orange-red solution to approximately 5 mL and cooling to −40 °C led to the formation of tan crystals, which were collected and dried *in vacuo*. Yield: 408 mg (58%). ^1H NMR (250 MHz, C_6D_6, 23 °C, basic features): δ 6.71–6.87 (m, meta and para OAr); 3.94 (br, THF); 1.9–0 (v br); 1.41; 0.22 (s, Si$\underline{Me}_3$); −4.37 (br, C$\underline{H}_2$SiMe$_3$). IR (Nujol mull, KBr plates, cm^{-1}): 1902 (w), 1846 (w), 1793 (w), 1697 (w), 1649 (w), 1621 (w), 1588 (m), 1550 (w), 1428 (s), 1359 (m), 1326 (s), 1258 (s), 1242 (s), 1204 (s), 1158 (w), 1141 (w), 1110 (w), 1095 (w), 1057 (w), 1034 (s), 947 (w), 933 (w), 915 (w), 885 (s), 858 (s), 844 (s), 815 (m), 750 (s), 729 (m), 711 (w), 682 (m), 593 (w), 560 (m). Anal. Calcd for $C_{52}H_{89}Li_2O_5Si_2Sm$: C, 61.55; H, 8.84. Found: C, 61.33; H, 9.05.

Crystallographic Studies. Crystal data, collection, and processing parameters are given in Table 1. General operating procedures and data reduction programs have been described

elsewhere.[39] The diffractometer utilized for data collection for **2** was designed and constructed locally at the IUMSC. The diffractometer consisted of a Picker four-circle goniostat, equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator interfaced to a Z80 microprocessor and controlled by an RS232 Serial port on an IBM PC microcomputer. Motors are Slo-Syn stepping motors, and a special top/bottom−left/right slit assembly is used to align the crystal. All computations were performed on IBM compatible microcomputer systems.

Crystals of **2** suitable for an X-ray diffraction study were grown from hexane solution at −40 °C. A suitable crystal was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −171 °C for characterization and data collection. Standard inert-atmosphere handling techniques were used.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and extinctions corresponding to one of the space groups *C2* or *C2/c*. Subsequent solution and refinement of the structure revealed the centrosymmetric space group, *C2/c*, to be the correct choice. Data were collected using a moving crystal, moving detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization effects, equivalent data were averaged, and an analytical absorption correction was applied. The programs for data reduction are all locally written and available upon request from the IUMSC. The structure was readily solved by direct methods (MULTAN78) and standard Fourier techniques. A difference map phased on the non-hydrogen atoms clearly located the positions of most hydrogen atoms as well as three peaks lying near a 2-fold axis and of approximate intensity 1.6 e Å^{-3} and well-separated (>4.0 Å) from the remainder of the molecule. The latter are apparently due to an unidentifiable solvent and were assigned occupancies of 25% in the final cycles. Because of the excessive thermal motion of the THF groups, it was not possible to allow all hydrogen atoms to vary in the least squares refinement. For the final cycles, all hydrogens except for those associated with the two THF molecules were allowed to vary isotropically. Although several of the hydrogens (especially those associated with the peripheral groups) were not well behaved, they are qualitatively correct.

A final difference Fourier was essentially featureless with the exception of several peaks of approximate density 0.7 e Å^{-3} in he vicinity of the disordered solvent.

Supplementary Material Available: Text describing X-ray procedures and tables of fractional coordinates and isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters for **2** (11 pages). Ordering information is given on any current masthead page.

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