

**Attachment of the Bulky Bidentate Ligand  
C(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>Si)<sub>2</sub>C to K, Zn, Sn, and  
Yb. Crystal Structures of  
L<sub>n</sub>MC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>Si)<sub>2</sub>CML<sub>n</sub> (ML<sub>n</sub> =  
K(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>, K(THF)<sub>2</sub>, SnCl<sub>3</sub>, or SnMe<sub>2</sub>Cl) and  
CH<sub>2</sub>SiMe<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>ZnC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub> (THF =  
Tetrahydrofuran)**

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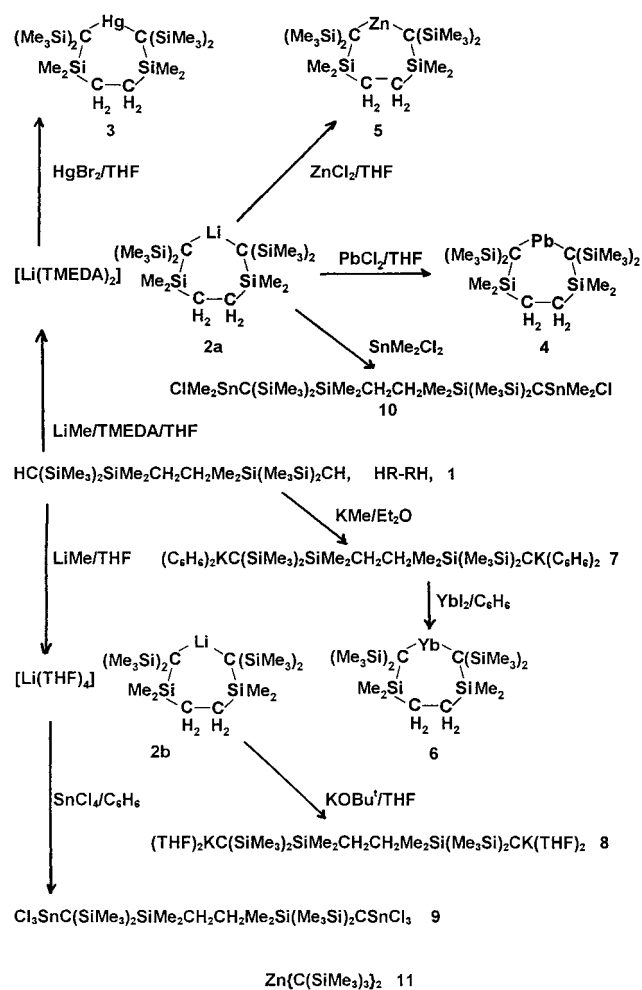
Reaction of the lithate [Li(THF)<sub>4</sub>][CH<sub>2</sub>SiMe<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>LiC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>] with KO<sup>t</sup>Bu in THF has given the organopotassium reagent (THF)<sub>2</sub>KC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>-Si)<sub>2</sub>CK(THF)<sub>2</sub>, **8**, and reaction of HC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>Si)<sub>2</sub>CH with KMe in benzene has given the related ether-free species (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>KC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si-(Me<sub>3</sub>Si)<sub>2</sub>CK(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>, **7**. The structures of **7** and **8** have been confirmed by X-ray studies which indicate that both compounds show K⋯Me contacts in the range 3.3–3.5 Å. The ether-free reagent **7** reacted with YbI<sub>2</sub> in benzene to give the cyclic Yb(II) derivative CH<sub>2</sub>SiMe<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>-YbC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>, which was found to be somewhat more stable toward Et<sub>2</sub>O than the previously studied Yb{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>2</sub>. Reaction of the lithate [Li(TMEDA)<sub>2</sub>][CH<sub>2</sub>SiMe<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>-LiC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>] (**2a**) with ZnCl<sub>2</sub> in THF gave a cyclic compound CH<sub>2</sub>SiMe<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>-ZnC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>, which is stable toward boiling aqueous THF. An X-ray study shows that the angle at Zn is 170°. In contrast, the reactions of **2a** with SnCl<sub>4</sub> or Me<sub>2</sub>SnCl<sub>2</sub> gave linear species ClX<sub>2</sub>SnC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>Si)<sub>2</sub>CSnX<sub>2</sub>Cl, X = Cl or Me, the structures of which were confirmed by single-crystal X-ray diffraction studies.

We have over the years shown that the attachment of the very bulky tris(trimethylsilyl)methyl, “trisyl”, ligand C(SiMe<sub>3</sub>)<sub>3</sub> to a range of metals can give many novel species.<sup>1</sup> Several other research groups have now taken up the use of this ligand in a diverse series of applications.<sup>2</sup> We showed, in particular, that the attachment of two of these ligands or of the closely related ligand C(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>Ph) to a metal center made possible the isolation of, for example, the first diorganolithates or -sodates (i.e., compounds containing ions [M{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>2</sub>]<sup>-</sup>, M = Li<sup>3a</sup> or Na<sup>3b</sup>), the -potassate<sup>3c</sup> [K(C<sub>6</sub>H<sub>6</sub>)][K{C(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>Ph)}<sub>2</sub>], the first σ-bonded diorganoytterbium<sup>4</sup> and diorganocalcium<sup>5a</sup> derivatives,

and the remarkably thermally and chemically stable diorganomercury and -zinc compounds (the latter can even be distilled in steam and is inert to boiling acetyl chloride).<sup>5b</sup> More recently we introduced the closely related, but potentially bidentate, ligand C(SiMe<sub>3</sub>)<sub>2</sub>-SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>Si)<sub>2</sub>C, R–R, derived from the precursor HR–RH, **1**. This ligand can be regarded as two trisyl groups joined together like Siamese twins and thus referred to as the “trisiamyl” ligand. (We avoid the previously suggested<sup>6</sup> “siamyl”, since this trivial name has been used to denote the secondary isoamyl group, CH<sub>3</sub>CH(CH<sub>3</sub>)C(CH<sub>3</sub>)H.) It can be used to make cyclic derivatives of lithium, e.g., [Li(TMEDA)<sub>2</sub>][RLiR], **2a** (TMEDA = *N,N,N,N*-tetramethylethylenediamine), mercury RHgR, **3**, and lead RPbR, **4**,<sup>7</sup> this last being in effect the first dialkyllead species to be structurally character-

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Scheme 1



ized.<sup>7</sup> We now report the attachment of this ligand to potassium, zinc, ytterbium, and tin (Scheme 1).

## Results and Discussion

The synthesis of the cyclic lithate **2a** by metalation of the precursor **1** with methyllithium in tetrahydrofu-

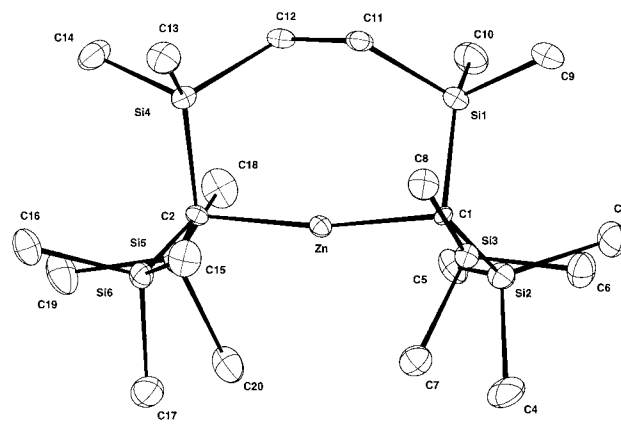


Figure 1. Molecular structure of  $\text{RZnR}$ , **5**.

ran (THF), followed by the addition of TMEDA, was described previously.<sup>6</sup> We now find that if no TMEDA is added, a solid compound, assumed to be **2b**, may be isolated in 80% yield from diethyl ether/hexane and used for further syntheses. Samples of well-defined crystals can be obtained, but so far these have not proved to be suitable for an X-ray study; it seems from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra that the  $\text{Et}_2\text{O}/\text{THF}$  ratio depends on the precise crystallization conditions.

The reaction between **2a** and anhydrous zinc chloride gave a good yield of the cyclic alkylzinc compound **5**. The molecular ion was detected in the gas phase by mass spectrometry, and the structure in the solid state was confirmed by an X-ray diffraction study. The molecule is shown in Figure 1, and the bond lengths and angles are given in Tables 1 and 2. The molecule has no crystallographic symmetry, so data on either side of the molecule are independently determined, but as there is no significant variation between parameters for chemically equivalent bonds, only the mean values are given. The Zn–C bond length, 1.962(7) Å, is greater than those (1.93(3) Å) in unhindered two-coordinate zinc compounds<sup>8</sup> but similar to that in  $\text{Zn}\{\text{C}(\text{SiMe}_3)_3\}_2$ , **11** (1.982(2) Å<sup>9</sup>), and a number of related compounds.<sup>2e,10</sup> The Si–C1 and Si–Me distances and the Si–C1–Si angles are within the expected range. We previously reported<sup>6</sup> that the configurations of the  $\text{CSi}_3$  fragments in compounds **2a** and **3** are almost the same as those in the acyclic species  $[\text{Li}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$  or  $\text{Hg}\{\text{C}(\text{SiMe}_3)_3\}_2$ ,

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**Table 1. Bond Lengths (Å) and Angles (deg) Involving the Metal in Compounds 5, 7, 8, and 9**

5, RZnR	7, (C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> KR–RK(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	8, (THF) <sub>2</sub> KR–RK(THF) <sub>2</sub>	9, Cl <sub>3</sub> SnR–RSnCl <sub>3</sub>
Zn–C1 1.963(7)	K–C1 2.953(4)	K–C1 2.937(3)	Sn–C1 2.132(3)
Zn–C2 1.962(7)	K···M1 3.099(4) <sup>a</sup>	K–O1 2.659(3)	Sn–Cl1 2.320(1)
	K···M2 3.577(5) <sup>b</sup>	K–O2 2.642(3)	Sn–Cl2 2.315(2)
	K···C10' 3.213(4) <sup>c</sup>	K···C7'' 3.30 <sup>d</sup>	Sn–Cl3 2.319(1)
C1–Zn–C2 169.7(3)	C1–K–M1 121.8(1) <sup>e</sup>	C1–K–O1 132.37(9)	C1–Sn–Cl1 115.75(8) <sup>f</sup>
	C1–K–M2 133.5(1) <sup>e</sup>	C1–K–O2 129.44(11)	C1–Sn–Cl2 117.76(9)
	M1–K–M2 100.0(1)	O1–K–O2 94.89(10)	C1–Sn–Cl3 116.34(8)

<sup>a</sup> M1 centroid of benzene ring. K···C11 3.419, K···C12 3.494, K···C13 3.466, K···C14 3.353, K···C15 3.279, K···C16 3.320 Å. <sup>b</sup> M2 centroid of benzene ring. K···C17 4.170, K···C18 3.818, K···C19 3.434, K···C20 3.445, K···C21 3.846, K···C22 4.187 Å. <sup>c</sup> K···C2 3.44, K···C5 3.64. <sup>d</sup> K···C2' 3.33, K···C5 3.47, K···C10 3.49 Å. <sup>e</sup> C1···K···C10' 112.2(1), M1···K···C10' 94.9(1), M2···K···C10' 80.5(1)°. <sup>f</sup> Cl1–Sn–Cl2 100.93(4), Cl2–Sn–Cl3 101.42(4), Cl1–Sn–Cl3 102.06(4).

**Table 2. Intraligand Bond Distances (Å) and Angles (deg)<sup>a</sup>**

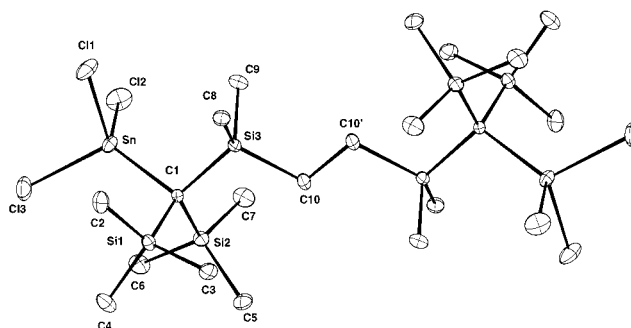
5, RZnR	7, (C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> KR–RK(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	8, (THF) <sub>2</sub> KR–RK(THF) <sub>2</sub>	9, Cl <sub>3</sub> SnR–RSnCl <sub>3</sub>
C1–Si 1.880(7)	1.819(3)	1.810(3)	1.926(3)
Si–Me 1.876(8)	1.889(4)	1.892(4)	1.869(4)
Si–CH <sub>2</sub> 1.886(7)	1.897(3)	1.899(3)	1.876(3)
C–C 1.566(9)	1.551(6)	1.534(6)	1.540(6)
M–C–Si1 101.0(3)	98.8(1)	107.34(13)	106.92(13)
M–C–Si2 115.5(3)	99.1(1)	94.21(13)	106.46(13)
M–C–Si3 100.5(3)	108.7(1)	100.54(13)	106.15(13)
Si–C–Si 113.1(4)	115.6(2)	116.6(2)	112.2(2)
Me–Si–Me 105.7(4)	103.3(2)	103.8(2)	107.1(2)
Me–Si–CH <sub>2</sub> 107.1(4)	103.0(2)	103.6(2)	107.8(2)
	104.4(3)	101.2(2)	108.9(2)
C1–Si–Me 113.2(3)	114.9(2)	114.7(2)	111.7(2)
C1–Si–CH <sub>2</sub> 111.6(3)	112.8(2)	116.84(14)	109.73(14)
Si–C–C' 117.4(5)	117.0(3)	117.8(3)	112.6(3)

<sup>a</sup> Except for M–C–Si and Me–Si–CH<sub>2</sub> angles, average values are given for chemically equivalent bonds and angles; esd's in parentheses indicate the precision of individual measurements, none of which differ significantly from the mean.

and the configuration in the zinc compound **5** is likewise closely similar to that in Zn{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>2</sub>. The CZnC system is almost linear (C–Zn–C = 170°; cf. 166° in the mercury compound **3**<sup>6</sup>). The other angles within the ring are close to the tetrahedral value, suggesting that there is little strain; the small deviation from C<sub>2</sub> symmetry probably results from cross-ring methyl–methyl repulsions or crystal packing effects.

We were intrigued to see whether the compound **5** would show the same remarkable properties noted for the related compound **11**, which is stable in air and can be distilled in steam.<sup>5b,9</sup> Compound **5** was recovered unchanged after it was heated in aqueous THF (1:10) for 5 h at 80 °C. When a sample was treated with an excess of CH<sub>3</sub>COCl in benzene at 80 °C for 7 h, about 75% was recovered, together with some precursor **1** (25%); the formation of the latter suggests that the disappearance of some **5** is to be attributed to traces of HCl rather than to direct reaction with CH<sub>3</sub>COCl. Compound **5**, like compound **11**, is thus remarkably resistant toward water or electrophiles. Also like the acyclic analogue **11**, it appears to be thermally stable at least up to 300 °C.

After the successful synthesis of the chelated compounds **3–5**, we considered it of interest to try to obtain similarly chelated derivatives of tin by reaction of the lithates **2** with SnCl<sub>4</sub> or SnMe<sub>2</sub>Cl<sub>2</sub>. We were not hopeful that chelation would occur since we have never been able to attach two trisyl groups to a four-coordinate metal center, presumably because steric hindrance to attack by a second molecule of the trisyllithium reagent is too great. Accordingly we were not surprised to find that the only product isolated from the reaction of **2b** with SnCl<sub>4</sub> in 1:1 mole ratio was the linear species **9**,

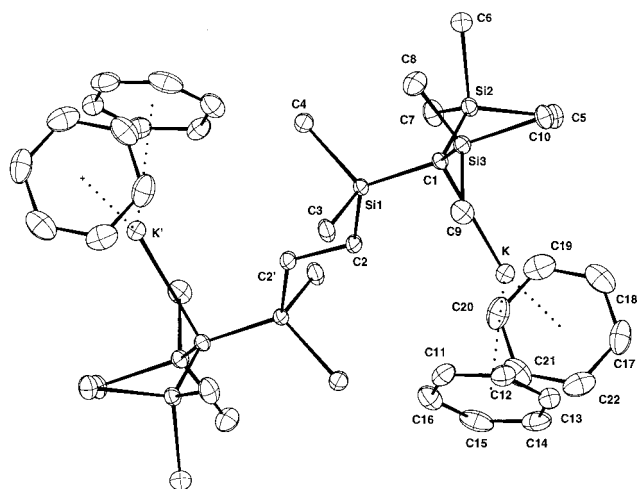
**Figure 2.** Molecular structure of Cl<sub>3</sub>SnC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>Si)<sub>2</sub>CSnCl<sub>3</sub>, **9**.

in which the bidentate ligand bridges two tin centers. (We have since obtained the tin(II) analogue of **4** and converted it by oxidative addition into chelated Sn(IV) derivatives, but these reactions will be described elsewhere.<sup>11</sup>) The centrosymmetric structure of **9** (Figure 2) was confirmed by an X-ray study. The bond lengths and angles are given in Tables 1 and 2. There are no features calling for comment.

The reaction between the lithate **2a** and Me<sub>2</sub>SnCl<sub>2</sub> in THF was studied under a variety of conditions. The products could be separated into crystalline material **10** with composition ClMe<sub>2</sub>SnC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>-Si(Me<sub>3</sub>Si)<sub>2</sub>CSnMe<sub>2</sub>Cl and an oily residue which was shown by <sup>119</sup>Sn NMR spectroscopy to be a complex mixture. The best yields of crystalline material **10** were obtained with a mole ratio of Me<sub>2</sub>SnCl<sub>2</sub> to **2a** of 2:1, concentrated solutions, and short reaction times. An X-ray

(11) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Zhang, S. Unpublished results.



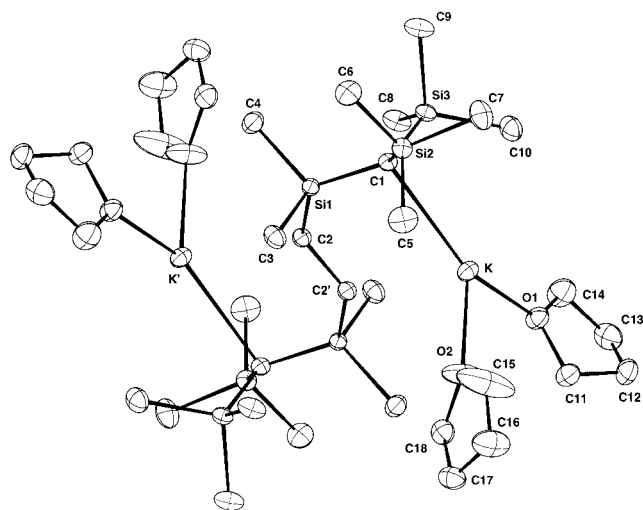


**Figure 3.** Molecular structure of  $(\text{C}_6\text{H}_6)_2\text{K}(\text{SiMe}_3)_2\text{SiMe}_2\text{-CH}_2\text{CH}_2\text{Me}_2\text{Si}(\text{Me}_3\text{Si})_2\text{CK}(\text{C}_6\text{H}_6)_2$ , **7**.

study (see Supporting Information) showed that the colorless needles obtained under these conditions were isostructural with **9** and had a composition  $\text{Cl}_{0.72}\text{Me}_{2.28}\text{-SnC}(\text{SiMe}_3)_2\text{SiMe}_2\text{CH}_2\text{CH}_2\text{Me}_2\text{Si}(\text{Me}_3\text{Si})_2\text{CSnMe}_{2.28}\text{-Cl}_{0.72}$  with about 30% of the residual chlorine atoms attached to tin replaced by methyl groups, and chlorine atoms and methyl groups disordered over tin coordination sites in the crystalline lattice. We later found that the reaction between **2a** and  $\text{Me}_2\text{SnCl}_2$  was cleaner in benzene; NMR data showed that **10** was the only tin-containing product in solution.

We next decided to try to generate the trisiamyl derivative of potassium by metalation of the ligand precursor **1** with methylpotassium. We did this for two reasons: (i) we thought that a cyclic potassate, analogous to the lithate **2a**, might be formed and only one well-characterized diorganopotassate,  $[\text{K}(\text{C}_6\text{H}_6)][\text{K}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{Ph})\}_2]$ , has so far been described,<sup>3c</sup> and (ii) the reagent obtained, whatever its structure, would be likely to be of value in syntheses of derivatives of other metals. For example, we have shown that the isolation of  $\text{K}(\text{C}(\text{SiMe}_3)_3)$  made it possible to synthesize compounds such as  $\text{M}\{\text{C}(\text{SiMe}_3)_3\}_2$ ,  $\text{M} = \text{Ca}^{5a}$  or  $\text{Yb}$ ,<sup>4,12</sup> which react with ethers and so cannot be made from  $\text{LiC}(\text{SiMe}_3)_3$  prepared in THF. The product **7** isolated from the reaction between **1** and  $\text{KMe}$  in benzene was found to contain two potassium atoms per ligand and two molecules of benzene. The product from the reaction between **1** and methyl lithium was stirred with potassium *tert*-butoxide in THF to give the complex **8**, again with two potassium atoms per ligand. Neither **7** nor **8** was a chelated potassate analogous to **2a**.

The structures of compounds **7** and **8** are shown in Figures 3 and 4. Bond lengths and angles are given in Tables 1 and 2. Except for  $\text{M}-\text{C}-\text{Si}$  and  $\text{Me}-\text{Si}-\text{CH}_2$  angles, chemically equivalent bonds and angles, both within each compound and from compound to compound, are identical within experimental error. In the compounds **5**, **7**, **8**, and **9** the  $\text{C}1-\text{Si}$  bond lengths and  $\text{Si}-\text{C}1-\text{Si}$  angles (Table 2) vary systematically in the same way as those in  $(\text{Me}_3\text{Si})_3\text{C}$  derivatives;<sup>13</sup> that is, the  $\text{C}1-\text{Si}$  distances increase in the series  $\text{K} < \text{Zn} <$



**Figure 4.** Molecular structure of  $(\text{THF})_2\text{K}(\text{SiMe}_3)_2\text{SiMe}_2\text{-CH}_2\text{CH}_2\text{Me}_2\text{Si}(\text{Me}_3\text{Si})_2\text{CK}(\text{THF})_2$ , **8**.

$\text{Sn}$ , and the  $\text{Si}-\text{C}1-\text{Si}$  angles decrease. The  $\text{Si}-\text{Me}$  and  $\text{Si}-\text{CH}_2$  bond lengths are almost constant and similar to those in  $\text{SiMe}_4$ , 1.875 Å,<sup>14</sup> showing that although the anionic charge is significantly delocalized over the  $\text{CSi}_3$  system, the delocalization does not extend on to the methyl groups of the ligand. The  $\text{Me}-\text{Si}-\text{Me}$  angles are less than the tetrahedral value. Bond lengths within the central methylene chain remain almost the same over the range of compounds studied here, but the  $\text{Me}-\text{Si}-\text{CH}_2$  angles show that various ring conformations are adopted.

The most interesting feature of the structural data is the coordination at potassium, shown in Figure 5. In **7** the  $\text{K}-\text{C}1$  distance is at the lower end of the range (2.91–3.10 Å) observed for  $\text{K}-\text{C}$   $\sigma$ -bonds,<sup>15</sup> but not as short as those in  $\text{KCPh}_3 \cdot \text{PMDTA}$  (2.931(3) Å) (PMDTA = *N,N,N,N',N'*-pentamethyldiethylenetriamine),<sup>16a</sup>  $[\text{K}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{Ph})\}_2]^-$  (2.914(5) Å),<sup>3c</sup> or  $\text{KC}\equiv\text{CMe}$  (2.55(5) Å).<sup>16b</sup> One benzene solvent molecule is coordinated reasonably symmetrically ( $\text{K}-\text{C}$  3.28–3.49 Å) and the other somewhat less so ( $\text{K}-\text{C}$  3.43–4.19 Å), and if the benzene molecules are viewed as occupying single coordination sites, the configuration at potassium is almost planar (sum of angles 355°). There are also short contacts to methyl groups in adjacent anions; for example, the  $\text{K}-\text{C}(10'')$  distance is only 3.21 Å. These interactions link the cations and anions into chains with two short  $\text{K}\cdots\text{C}$  contacts.

In **8** the  $\text{K}-\text{C}1$  distance is the same as that in **7**, but the lone pairs of the THF molecules replace the  $\pi$ -electrons of the benzene rings in the other two coordination sites. The sum of the bond angles is 357°, so the configuration at potassium is again almost planar. The conformation of the central methylene chain of the anion

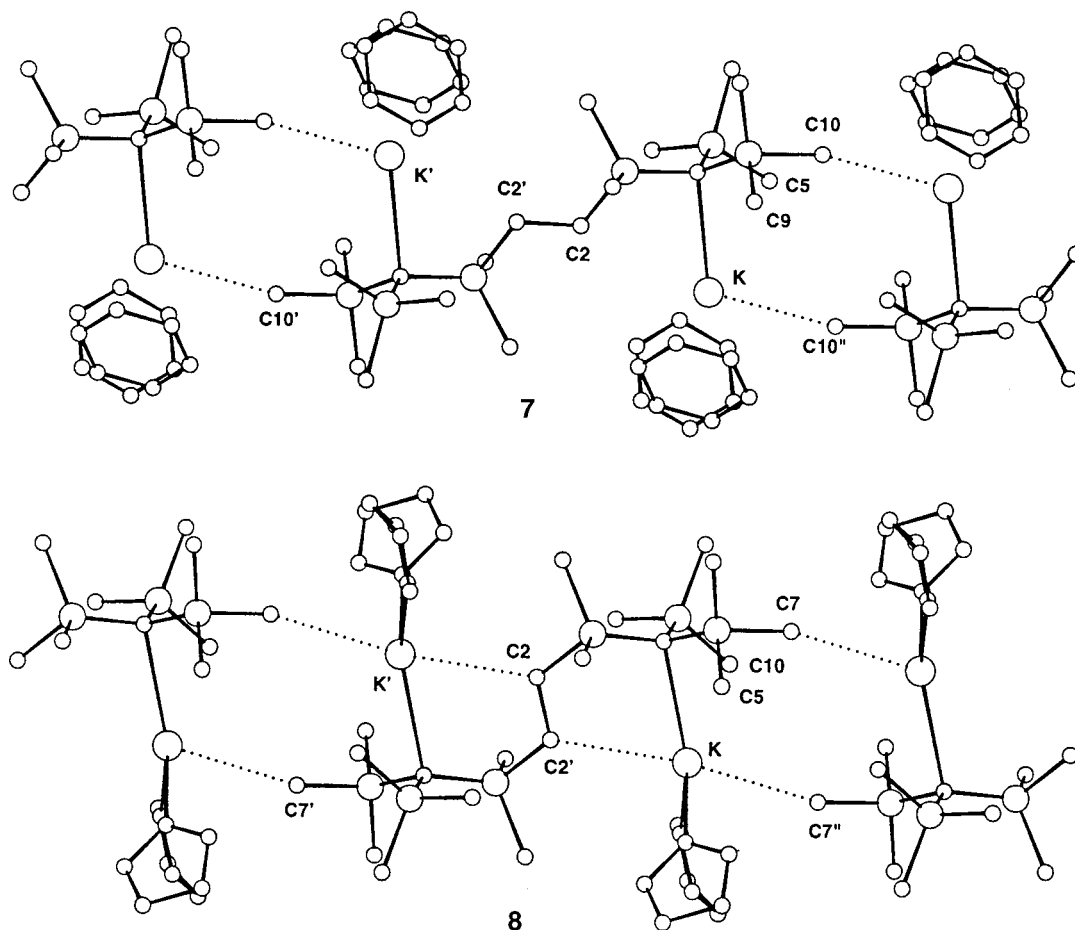
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**Figure 5.** Potassium–anion interactions in the chain structures of **7** and **8**.

changes so that the potassium makes short contacts with the  $\delta$ -CH<sub>2</sub> group (C2'), two methyl groups (C5, C10) from SiMe<sub>3</sub> substituents in the nearest anion, and one (C7') from an SiMe<sub>3</sub> group of an adjacent anion. The ions are linked into chains which pack in the crystal lattice as a whole in a remarkably similar way to those in **7**, with two K $\cdots$ C contacts between each pair of triple ions. The configuration of the central chain in **9** is similar to that in **7**, but there are no short contacts between the tin atom and methyl groups of adjacent anions.

The structures provide further examples of the high coordination numbers shown by potassium in highly ionic organometallic compounds. The structures appear to be determined by electrostatic attraction between the cations and (i) carbanionic charge delocalized over the CSi<sub>3</sub> center in the nearest or next nearest anion, and (ii) lone pairs or  $\pi$ -electrons in solvent molecules. The X-ray data are insufficiently precise to determine whether the high coordination numbers at potassium imply that the K $\cdots$ Me interactions are attractive. The short contacts in the structures described in this paper could result simply from fitting together potassium cations and the bulky doubly charged anions held in a lattice by long-range electrostatic interaction.

As we had envisaged, the availability of the ether-free potassium compound **7** made it possible to synthesize the chelated ytterbium compound **6** from the reaction of YbI<sub>2</sub> with the potassium compound **7**. Orange needles of **6** were found by X-ray diffraction to be highly disordered so that detailed structural data could not be

obtained. The similarity between the NMR spectra of **5** and **6**, the analytical data, and the appearance in the mass spectrum of a prominent molecular ion suggest that the structure of **6** is similar to those of the crystallographically characterized analogues **3**–**5**. The reaction of Et<sub>2</sub>O with the Yb compound **6** was found to be slower than that with Yb{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>2</sub>; a small sample in C<sub>6</sub>D<sub>6</sub> with an excess of ether in a sealed NMR tube gave a detectable signal from C<sub>2</sub>H<sub>4</sub> only after 5 days (cf. <5 min for Yb{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>2</sub>).<sup>4</sup>

### Experimental Section

Air and moisture were excluded as much as possible by the use of Schlenk techniques and Ar as blanket gas. Solvents were dried by standard procedures and distilled immediately before use. NMR spectra were recorded at 300.13 (<sup>1</sup>H), 125.8 (<sup>13</sup>C), 99.4 (<sup>29</sup>Si), 186.6 (<sup>119</sup>Sn), and 43.8 MHz (<sup>171</sup>Yb) and chemical shifts are relative to SiMe<sub>4</sub> for H, C, and Si, SnMe<sub>4</sub> for Sn, and Yb(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub> for Yb. The intensities of the <sup>13</sup>C quaternary and <sup>29</sup>Si signals were enhanced by polarization transfer. Mass spectra were recorded at 70 eV. The synthesis of **2a** has been described.<sup>6</sup>

**[Li(THF)<sub>4</sub>][RLiR] (2b).** A stirred mixture of **1** (3.2 g, 6.9 mmol) and LiMe (14 mmol) in THF (25 mL) was heated under reflux for 6 h. The solvent was removed under vacuum, and the residue was washed with hexane (10 mL) to leave a white solid. This was dissolved in Et<sub>2</sub>O and the solution layered with hexane to give colorless needles of **2b** (yield 4.2 g (80%), mp 221–222 °C). <sup>1</sup>H NMR (THF-*d*<sub>6</sub>):  $\delta$  0.01 (s, 12H, SiMe<sub>2</sub>), 0.03 (s, 36H, SiMe<sub>3</sub>), 0.54 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR:  $\delta$  1.2 (CSi<sub>3</sub>), 5.8 (SiMe<sub>2</sub>), 8.1 (SiMe<sub>3</sub>), 14.7 (CH<sub>2</sub>). <sup>29</sup>Si NMR:  $\delta$  -10.8 (SiMe<sub>3</sub>), -7.2 (SiMe<sub>2</sub>), <sup>7</sup>Li NMR:  $\delta$  -2.5, -1.5.

Table 3. Summary of Crystallographic Data for 5, 7, 8, and 9

	5, RZnR	7, (C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> KR–RK(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	8, (THF) <sub>2</sub> KR–RK(THF) <sub>2</sub>	9, Cl <sub>3</sub> SnR–RSnCl <sub>3</sub>
empirical formula	C <sub>20</sub> H <sub>52</sub> Si <sub>6</sub> Zn	C <sub>44</sub> H <sub>76</sub> K <sub>2</sub> Si <sub>6</sub>	C <sub>36</sub> H <sub>84</sub> K <sub>2</sub> O <sub>4</sub> Si <sub>6</sub>	C <sub>20</sub> H <sub>52</sub> Cl <sub>6</sub> Si <sub>6</sub> Sn <sub>2</sub>
fw	526.5	851.8	827.8	911.2
cryst size (mm)	0.4 × 0.2 × 0.1	0.4 × 0.3 × 0.2	0.3 × 0.3 × 0.3	0.3 × 0.2 × 0.2
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)
<i>a</i> (Å)	9.211(2)	9.343(2)	12.483(1)	9.003(1)
<i>b</i> (Å)	22.562(3)	11.305(3)	12.774(1)	13.877(2)
<i>c</i> (Å)	14.762(4)	13.417(4)	16.597(1)	15.662(2)
α (deg)	90	102.54(2)	90	90
β (deg)	91.31(2)	98.39(2)	109.29(1)	93.12(1)
γ (deg)	90	107.02(2)	90	90
<i>Z</i>	4	1	2	2
<i>V</i> (Å <sup>3</sup> )	3067(1)	1289.0(6)	2497.9(4)	1953.9(4)
<i>d</i> <sub>c</sub> (Mg m <sup>-3</sup> )	1.14	1.10	1.10	1.55
<i>F</i> (000)	1144	462	908	916
μ (mm <sup>-1</sup> )	1.04	0.35	0.37	1.44
θ range (deg)	2–22	2–28	2–28	2–30
index range	0 ≤ <i>h</i> ≤ 9 0 ≤ <i>k</i> ≤ 23 –15 ≤ <i>l</i> ≤ 15	0 ≤ <i>h</i> ≤ 12 –14 ≤ <i>k</i> ≤ 14 –17 ≤ <i>l</i> ≤ 17	0 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 16 –21 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 12 0 ≤ <i>k</i> ≤ 19 –22 ≤ <i>l</i> ≤ 21
no. of reflns collected	4023	6209	6265	5992
no. of unique reflns	3752	6209	6010	5667
no. of reflns with <i>I</i> > 2σ( <i>I</i> )	2418	3570	3659	4231
<i>R</i> 1 ( <i>I</i> > 2σ( <i>I</i> ))	0.057	0.065	0.060	0.038
<i>wR</i> 2 (all data)	0.135	0.138	0.145	0.088
no. of data/restrts/params	3752/0/244	6208/0/247	6010/0/217	5677/0/154
GOF on <i>F</i> <sup>2</sup>	0.988	1.016	0.988	1.038
abs corr (ψ scan)	<i>T</i> <sub>max</sub> 1.00, <i>T</i> <sub>min</sub> 0.90	not applied	not applied	<i>T</i> <sub>max</sub> 1.00, <i>T</i> <sub>min</sub> 0.92

**CH<sub>2</sub>SiMe<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>ZnC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub> (5).** A mixture of **2a** (1.00 g, 1.42 mmol) and ZnCl<sub>2</sub> (0.24 g, 1.76 mmol) in THF (15 mL) was stirred at room temperature for 48 h. The solvent was removed under vacuum, and the white residue was extracted with pentane (50 mL). The extract was filtered, the solvent pumped off, and the residue crystallized from methylenecyclohexane to give the compound **5**. Yield: 0.45 g (60%); mp 212–214 °C. Anal. Calcd for C<sub>28</sub>H<sub>52</sub>Si<sub>6</sub>Zn: C, 45.7; H, 9.9. Found: C, 45.6; H, 9.9. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.28 (s, 36H, SiMe<sub>3</sub>), 0.31 (s, 12H, SiMe<sub>2</sub>), 0.84 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR: δ 3.6 (SiMe<sub>2</sub>), 7.0 (SiMe<sub>3</sub>), 14.3 (CH<sub>2</sub>). <sup>29</sup>Si NMR δ –5.6 (SiMe<sub>3</sub>), –3.0 (SiMe<sub>2</sub>). MS: *m/z* 525 (3, M), 510 (15, M – Me), 217 (100, (Me<sub>3</sub>Si)<sub>2</sub>-CHSiMe<sub>2</sub> or isomer).

**Cl<sub>3</sub>SnC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>Si)<sub>2</sub>CSnCl<sub>3</sub> (9).** Neat SnCl<sub>4</sub> (0.26 g, 1.0 mmol) was added dropwise to a vigorously stirred solution of **2b** (0.77 g, 1.0 mmol) in benzene (25 mL) to give a turbid solution. This was heated under reflux for 2 h, then allowed to cool and filtered. The solvent was removed under vacuum to leave a white solid, which was shown by <sup>1</sup>H, <sup>7</sup>Li, and <sup>119</sup>Sn NMR spectroscopy to contain unchanged **2b** together with at least one other compound. The solid was extracted with hexanes (30 mL) and the extract concentrated until incipient crystallization. The solution was warmed until it became clear, then allowed to cool, whereupon large colorless blocks of **9** separated. Yield: 0.21 g, 47% (based on SnCl<sub>4</sub>), mp 282–285 °C. Anal. Calcd for C<sub>20</sub>H<sub>52</sub>Cl<sub>6</sub>Si<sub>6</sub>Sn<sub>2</sub>: C, 26.4; H, 5.8. Found: C, 27.1; H, 6.0. <sup>1</sup>H NMR: δ 0.29 (s, 36H, SiMe<sub>3</sub>), 0.37 (s, 12H, SiMe<sub>2</sub>), 1.00 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR: δ 0.8 (SiMe<sub>2</sub>), 4.5 (<sup>1</sup>*J*(SiC) = 37.5 Hz, SiMe<sub>3</sub>), 13.3 (CH<sub>2</sub>), 32.3 (<sup>1</sup>*J*(SiC) = 24.8 Hz, <sup>1</sup>*J*(SnC) = 114.3 Hz, CSi<sub>3</sub>Sn), <sup>29</sup>Si NMR: δ 1.0 (<sup>2</sup>*J*(Si<sup>119</sup>Sn) = 84.5, <sup>2</sup>*J*(Si<sup>117</sup>Sn) = 80.9 Hz, SiMe<sub>3</sub>), 4.1 (<sup>2</sup>*J*(Si<sup>117,119</sup>Sn) = 79.5 Hz, SiMe<sub>2</sub>). <sup>119</sup>Sn NMR: δ –36.6 (cf. (Me<sub>3</sub>Si)<sub>3</sub>CSnCl<sub>3</sub> –36.4, <sup>1</sup>*J*(SnC) = 113 Hz<sup>17a</sup>). MS: *m/z* 631 (10), 527(10, Cl<sub>3</sub>Sn(Me<sub>3</sub>Si)<sub>2</sub>CSiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>), 441 (85, Cl<sub>3</sub>Sn(Me<sub>3</sub>Si)<sub>2</sub>CSiMe<sub>2</sub>), 217 (100), 129 (69).

**ClMe<sub>2</sub>SnC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>Si)<sub>2</sub>-CSnMe<sub>2</sub>Cl (10).** A mixture of **2a** (0.25 g, 0.35 mmol) and Me<sub>2</sub>SnCl<sub>2</sub> (0.15 g, 0.7 mmol) in THF (20 mL) was stirred at

room temperature for 1.5 h. The solvent was removed under vacuum and the residue extracted with pentane (10 mL). The extract was filtered and the solvent removed from the extract to leave a white residue, which was crystallized from heptane. Yield: 0.23 g (79%), mp 291–292 °C. Anal. Calcd for C<sub>24</sub>H<sub>64</sub>-Cl<sub>2</sub>Si<sub>6</sub>Sn<sub>2</sub>: C, 34.7; H, 7.8. Found: C, 34.9; H, 7.5. <sup>1</sup>H NMR: δ 0.27 (s, 36H, SiMe<sub>3</sub>), 0.28 (s, 12H, SiMe<sub>2</sub>), 0.66 (s, 12H, SnMe<sub>2</sub>), 0.87 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR: δ 0.0 (SiMe<sub>2</sub>), 3.7 (SiMe<sub>3</sub>), 4.0 (SnMe<sub>2</sub>), 11.8 (CH<sub>2</sub>). <sup>29</sup>Si NMR: δ –0.8 (SiMe<sub>3</sub>), 2.9 (SiMe<sub>2</sub>). <sup>119</sup>Sn NMR: δ 127.8 (cf. (Me<sub>3</sub>Si)<sub>3</sub>CSnMe<sub>2</sub>Cl 133.8<sup>17b</sup>). MS: *m/z* 813 (1, M – Me), 399 (5, M/2 – Me), 217 (100).

**(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>KC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>Si)<sub>2</sub>CK-(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> (7).** A solution of HR–RH, **1** (3.23 g, 0.7 mmol), in Et<sub>2</sub>O (20 mL) was added to a slurry of KMe (1.5 mmol) in Et<sub>2</sub>O (20 mL) at –20 °C, and the stirred mixture was allowed to warm to room temperature during 14 h. The solvent was removed under vacuum, and the residue was washed with hexanes, then recrystallized from hot (60 °C) benzene to give colorless air- and moisture-sensitive crystals of **7**. Yield: 3.5 g, 60%. Accurate C, H analyses could not be obtained because solvent benzene was easily lost. The compound **7** was insufficiently soluble in cold benzene for the recording of NMR spectra; data from solutions in THF were identical with those given below for **8**.

**(THF)<sub>2</sub>KC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si(Me<sub>3</sub>Si)<sub>2</sub>CK-(THF)<sub>2</sub> (8).** A solution of LiMe (16.8 mmol) in Et<sub>2</sub>O (12 mL) was added to **1** (3.9 g, 8.4 mmol), and the solvent was removed under vacuum and replaced by THF (30 mL). The solution was stirred for 15 h, then added to a slurry of KO<sup>t</sup>Bu (1.88 g, 16.8 mmol) in THF (20 mL) at room temperature, and the mixture then stirred for 1 h. The solvent was removed under vacuum and the residue washed three times with hexanes, then dissolved in THF (10 mL). When a layer of heptane was placed over the THF solution, colorless blocks of **8** formed at the interface. Yield: 3.0 g, 43%, mp 150–151 °C (dec). Accurate C, H analyses could not be obtained. <sup>1</sup>H NMR (THF-*d*<sub>6</sub>): δ –0.07 (12H, s, SiMe<sub>2</sub>), –0.04 (36H, s, SiMe<sub>3</sub>), 0.34 (4H, s, CH<sub>2</sub>). <sup>13</sup>C NMR: δ 2.9 (<sup>1</sup>*J*(SiC) 55 Hz, CSi<sub>3</sub>), 5.2 (SiMe<sub>2</sub>), 8.5 (SiMe<sub>3</sub>), 18.4 (CH<sub>2</sub>). <sup>29</sup>Si NMR: δ –13.6 (SiMe<sub>3</sub>), –8.7 (SiMe<sub>2</sub>).

**CH<sub>2</sub>SiMe<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>YbC(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub> (6).** A solution of **7** (1.8 g, 2.1 mmol) in hot (60 °C) benzene was added to a

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suspension of  $\text{YbI}_2$  (0.9 g 2.1 mmol) in benzene (15 mL), and the mixture was stirred at 60 °C for 24 h. The solvent was removed, the residue extracted with hexanes (30 mL), and the extract reduced to 15 mL, then cooled to -20 °C to give orange needles. Yield: 1.1 g, 45%, mp 83–86 °C. Anal. Calcd for  $\text{C}_{28}\text{H}_{52}\text{Si}_6\text{Yb}$ : C, 45.0; H, 9.9. Found: C, 43.8; H, 9.1.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.30 (36H, s,  $\text{SiMe}_3$ ), 0.44 (12H, s,  $\text{SiMe}_2$ ), 0.96 (4H, s,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR:  $\delta$  6.5 ( $^1J(\text{SiC}) = 47.8$  Hz,  $\text{SiMe}_2$ ), 7.5 ( $^1J(\text{SiC}) = 47.3$  Hz,  $\text{SiMe}_3$ ), 15.9 ( $\text{CH}_2$ ), 23.8 ( $^1J(\text{CYb}) = 283$ ,  $^1J(\text{SiC}) = 38.1$  Hz,  $\text{CSi}_3$ ).  $^{29}\text{Si}$  NMR:  $\delta$  -12.4 ( $^1J(\text{SiC}) = 47.3$ ,  $^2J(\text{SiYb}) = 27.0$  Hz,  $\text{SiMe}_3$ ), -6.3 ( $^1J(\text{SiC}) = 48.3$ ,  $^2J(\text{SiYb}) = 21.6$  Hz,  $\text{SiMe}_2$ ).  $^{171}\text{Yb}$  NMR:  $\delta$  740. MS:  $m/z$  634 (15, M), 619 (3, M - Me), 462 (30, HR-RH), 404, (8,  $(\text{Me}_3\text{Si})(\text{Me}_2\text{SiCH}_2)\text{CYb}$ ), 217 (100).

**Crystal Structure Determinations.** Data were collected at 173(2) K on an Enraf-Nonius CAD4 diffractometer using  $\text{Mo K}\alpha$  radiation (0.710 73 Å) and corrected for Lorentz and polarization effects; details are given in Table 3. The structures were determined by direct methods, with SHELXS 86 and

SHELXL 93 programs used for structure solution and refinement. Non-hydrogen atoms were anisotropic. H atoms were refined in riding mode with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or, for Me groups,  $1.5U_{\text{eq}}(\text{C})$ , except for those attached to C(10) in **7**. These were isotropic and freely refined, but showed no distortion from the expected positions.

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**Supporting Information Available:** Tables of atom coordinates, equivalent isotropic displacement factors, bond lengths and angles, and hydrogen coordinates for **5**, **7**, **8**, **9**, and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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