

Alkyl Derivatives of Europium(+2) and Ytterbium(+2). Crystal Structures of $\text{Eu}[\text{C}(\text{SiMe}_3)_3]_2$, $\text{Yb}[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{CH}=\text{CH}_2)]\text{I}\cdot\text{OEt}_2$ and $\text{Yb}[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{OMe})]\text{I}\cdot\text{OEt}_2$

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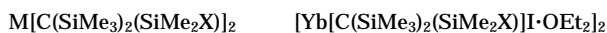
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The alkyls EuR_2 ($\text{R} = \text{C}(\text{SiMe}_3)_3$) and YbR_2 ($\text{R} = [\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{X})]$, $\text{X} = \text{Me}$, $\text{CH}=\text{CH}_2$, or $\text{CH}_2\text{CH}_2\text{OEt}$) have been obtained from reactions between KR and MI_2 , and the ytterbium analogues of Grignard reagents, $\text{Yb}[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{X})]\text{I}\cdot\text{OEt}_2$ ($\text{X} = \text{Me}$, $\text{CH}=\text{CH}_2$, Ph or OMe) from reactions between RI and Yb metal. The compounds YbR_2 and EuR_2 crystallize as solvent-free monomers with $\text{C}-\text{M}-\text{C} = 136-137^\circ$. The alkylytterbium iodides crystallize from diethyl ether as solvated iodide-bridged dimers in which the coordination at Yb is four when $\text{X} = \text{Me}$ but is increased to five by chelation from the group X when $\text{X} = \text{OMe}$. When $\text{X} = \text{CH}=\text{CH}_2$, the $\text{Yb}\cdots\text{X}$ interaction is weak. The reaction $2\text{RYbI} = \text{R}_2\text{Yb} + \text{YbI}_2$ is not observed when $\text{X} = \text{Me}$, but takes place readily when $\text{X} = \text{Ph}$, $\text{CH}=\text{CH}_2$, or OMe and provides a route to the dialkyls MR_2 when the alkylpotassium KR cannot be obtained, e.g., when $\text{X} = \text{OMe}$. The dialkyl $\text{Yb}[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{X})]_2$ with $\text{X} = \text{Me}$ reacts with ethers $\text{R}'\text{OEt}$ ($\text{R}' = \text{Et}$, Bu , Bu^t) to give ethene and alkoxides RYbOR' . The corresponding reaction does not take place when $\text{X} = \text{OMe}$ and is very slow when $\text{X} = \text{CH}=\text{CH}_2$.

Introduction

We recently reported in a preliminary communication^{1a} the synthesis and crystal structure of $\text{Yb}[\text{C}(\text{SiMe}_3)_3]_2$ (**1**), the first well-characterized, solvent-free, homoleptic σ -bonded organometallic compound of an f-block element in oxidation state +2 and also the synthesis and structure of $\text{Yb}[\text{C}(\text{SiMe}_3)_3]\text{I}\cdot\text{OEt}_2$ (**7**), the first f-block analogue of a Grignard reagent to be characterized by X-ray crystallography. This paper gives a more detailed account of these and the related compounds **2–5** and **7–9**. The organometallic chemistry of f-block elements



- | | |
|--|--|
| 1 M = Yb, X = Me | 6 X = Me |
| 2 M = Yb, X = CH=CH ₂ | 7 X = CH=CH ₂ |
| 3 M = Yb, X = CH ₂ CH ₂ OEt | 8 X = OMe |
| 4 M = Yb, X = OMe | 9 X = Ph |
| 5 M = Eu, X = Me | 10 $\text{KC}(\text{SiMe}_3)_2\text{-}$
$(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{OEt})\cdot x\text{C}_6\text{H}_6$ |
| | 11 $[\text{Yb}[\text{C}(\text{SiMe}_3)_3]\text{OEt}\cdot\text{OEt}_2]_2$ |
| | 12 $[\text{Yb}[\text{C}(\text{SiMe}_3)_2\text{-}$
$(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{OEt})]\text{OEt}]_2$ |

in oxidation state +2 has, with few exceptions,^{2a,b} been confined to substituted cyclopentadienyl derivatives.^{2c} As far as we are aware, the only other reported $\text{Yb}(+2)$ compounds containing $\text{Yb}-\text{C}$ σ -bonds are the complexes $\text{Yb}[\text{CH}(\text{SiMe}_3)_2]_2\cdot\text{L}_2$ ($\text{L}_2 = (\text{OEt}_2)_2$ or $\text{Me}_2\text{PCH}_2\text{CH}_2\text{-}$

PMe_2), the alkyl alkoxide $[\text{Yb}[\text{C}(\text{SiMe}_3)_3]\text{OEt}\cdot\text{OEt}_2]_2$ (**11**), the azaallyl derivative $\text{Yb}[\text{N}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)\text{CHSiMe}_3]_2$,^{1b} the hydrotris(3-*tert*-butyl-5-methylpyrazolyl)-borate (Tp) compounds $\text{YbTpCH}(\text{SiMe}_3)_2$ and $\text{YbTpCH}_2\text{-SiMe}_3\cdot\text{OEt}_2$,^{1c} some pentafluorophenyl derivatives, e.g., $\text{Yb}(\text{C}_6\text{F}_5)_2(\text{THF})_4$ ^{1d-f} ($\text{THF} = \text{tetrahydrofuran}$), and the not very well characterized phenylalkynyl derivative $\text{Yb}(\text{C}\equiv\text{CPh})_2$.^{1g} In this paper we describe a series of solvent-free dialkyls of Yb , **1–4**, and Eu , **5**, and several compounds $\text{Yb}[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{X})]\text{I}$, **6–9**, which are analogues of Grignard reagents. We also show that the reactions of these compounds and the interconversions between the dialkyls and alkylytterbium iodides are strongly influenced by the nature of the group X , in particular by the extent to which it is able to chelate to Yb and increase the coordination number at the metal center.

Experimental Section

Air and moisture were excluded as rigorously as possible by use of Schlenk techniques and flame-dried glassware. Solvents were dried by standard methods and freshly distilled before use. In spite of repeated attempts, satisfactory C and H analytical data for most compounds could not be obtained from commercial analysts. However, all were shown to be pure by multinuclear NMR methods involving Bruker AC-P 250, AC 360, or AMX 500 instruments, with signals from quaternary ¹³C nuclei enhanced by polarization transfer (INEPT). Except where indicated C₆D₆ was used as solvent. Chemical shifts/ppm are relative to SiMe₄ or external $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{THF})_2$. ¹H spectra were obtained at 360, ¹³C at 125.75, ²⁹Si at 99.36,

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and ^{171}Yb at 43.77 MHz. MS(EI) assignments were confirmed by comparison of calculated and observed isotope patterns; m/z values refer to ions containing ^{153}Eu and ^{174}Yb , and intensities (%) are relative to those of the strongest peak.

(Dimethylvinylsilyl)bis(trimethylsilyl)methane. A solution of $\text{LiCH}(\text{SiMe}_3)_2$ (4.8 g, 29 mmol)^{3a} in Et_2O (30 cm^3) was added dropwise during 30 min to a stirred solution of $\text{SiMe}_2(\text{CH}=\text{CH}_2)\text{Cl}$ (10.0 g, 83 mmol) in Et_2O (25 cm^3) at 0 °C. The mixture was stirred for 3 h at 0 °C and then filtered, and the filtrate was washed with water to remove LiCl. The organic layer was dried (MgSO_4) and the solvent removed to leave an oil. This was distilled and the fraction distilling between 80 and 100 °C (0.01 Torr) was collected. Yield 5.0 g, 68%. Anal. Calcd for $\text{C}_{11}\text{H}_{28}\text{Si}_3$: C, 54.02; H, 11.54. Found: C, 53.31; H, 11.27. MS(EI) m/z (relative intensity): 229 ($M - \text{Me}$, 50), 217 ($M - \text{CH}=\text{CH}_2$, 15), 141 ($M - \text{SiMe}_4$, 100), 73 (SiMe_3 , 90). ^1H NMR (CDCl_3): δ -0.73 (s, 1H, CH), 0.07 (s, 18H, SiMe_3), 0.16 (s, 6H, SiMe_2), 5.63 dd, 5.90 dd, 6.27 dd (3H, $\text{CH}=\text{CH}_2$). ^{13}C NMR (CDCl_3): δ 1.2 (SiMe_2), 3.2 (CSi_3), 3.3 (SiMe_3), 130.1 ($\text{CH}_2=\text{CH}$), 142.6 ($\text{CH}_2 = \text{CH}$). ^{29}Si NMR: δ -7.5 (SiMe_2), -0.2 (SiMe_3).

Chloro(2-ethoxyethyl)dimethylsilane. A mixture of SiMe_2HCl (10.2 g, 0.109 mol), vinyl ethyl ether (7.54 g, 0.105 mol), THF (100 cm^3), and 2 drops of H_2PtCl_4 (5% in PrOH) was heated under reflux for 2 h and, after the addition of more of the ether (3.7 g) and catalyst (2 drops), for a further 3 h. Solvent was removed by distillation at 1 atm and $\text{SiMe}_2(\text{CH}_2\text{CH}_2\text{OEt})\text{Cl}$ was distilled as a colorless oil, bp 32 °C (10⁻³ Torr). Yield 10.4 g, 57% based on SiMe_2HCl . Anal. Calcd for $\text{C}_6\text{H}_{15}\text{ClOSi}$: C, 43.19; H, 9.07. Found: C, 43.47; H, 9.95. ^1H NMR: δ 0.46 (s, 6H, SiMe_2), 1.19 (t, 3H, CH_3CH_2), 1.25 (t, 2H, $\text{CH}_2\text{CH}_2\text{Si}$), 3.46 (q, 2H, $\text{CH}_3\text{CH}_2\text{O}$), 3.60 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$). There was no evidence for formation of the alternative isomer $\text{SiMe}_2(\text{CHMeOEt})\text{Cl}$.

(2-Ethoxyethyl)dimethylsilyl)bis(trimethylsilyl)methane. A solution of freshly sublimed $\text{LiCH}(\text{SiMe}_3)_2$ (6.14 g, 37 mmol) in THF (70 cm^3) was added to $\text{SiMe}_2(\text{CH}_2\text{CH}_2\text{OEt})\text{Cl}$ (6.15 g, 37 mmol) in THF (30 cm^3), and the mixture was stirred for 2 h at 25 °C. Solvent was removed under vacuum, the residue extracted with light petroleum (bp 40–60 °C), the extract filtered, and the solvent pumped away. The residue was distilled to give $(\text{Me}_3\text{Si})_2[(\text{EtOCH}_2\text{CH}_2)\text{Me}_2\text{Si}]\text{CH}$ as a colorless oil, bp 55–60 °C (10⁻³ Torr), shown by GC–MS to be >95% pure (8.0 g, 74%). Anal. Calcd for $\text{C}_{13}\text{H}_{34}\text{OSi}_3$: C, 53.72; H, 11.79. Found: C, 53.05; H, 11.53. ^1H NMR: δ -0.71 (s, 1H, Si_3CH), 0.14 (s, 18H, SiMe_3), 0.17 (s, 6H, SiMe_2), 1.08 (t, 2H, CH_2Si), 1.13 (t, 3H, CH_3CH_2), 3.29 (q, 2H, CH_3CH_2), 3.46 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR: δ 3.56 (q, SiMe_3), 2.94 (d, $\text{J}(\text{CH})$ 99 Hz, CH), 1.85 (q, SiMe_2), 15.6 (q, CH_3), 20.4 (t, CH_2Si), 65.9 (t, OCH_2), 68.0 (t, OCH_2). ^{29}Si NMR: δ -0.55 (SiMe_3), -0.16 (SiMe_2). MS(EI): m/z 247 ($M - \text{CH}_3 - \text{C}_2\text{H}_4$, 50), 217 ($M - \text{CH}_2\text{CH}_2\text{OEt}$, 90), 73 (SiMe_3 , 50), 28 ($\text{CH}_2=\text{CH}_2$, 100).

(Dimethylvinylsilyl)iodobis(trimethylsilyl)methane. A solution of $\text{KC}(\text{SiMe}_3)_2(\text{SiMe}_2\text{CH}=\text{CH}_2)$ ^{3b} (1.45 g, 5.14 mmol) in Et_2O (50 cm^3) was added slowly to 1,2-diiodoethane (1.45 g, 5.14 mmol) in Et_2O (30 cm^3) at -30 °C. The mixture was stirred for 15 min, then allowed to warm to 25 °C, and filtered. The solvent was removed from the filtrate to leave colorless crystals of $(\text{Me}_3\text{Si})_2[\text{Me}_2(\text{CH}_2=\text{CH})\text{Si}]\text{Cl}$. Anal. Calcd for $\text{C}_{11}\text{H}_{27}\text{I}_2\text{Si}_3$: C, 35.66; H, 7.35. Found: C, 35.20; H, 7.11. NMR (CDCl_3): δ 0.27 (s, 18H, SiMe_3), 0.42 (s, 6H, SiMe_2), 5.71 (dd, 1H, $\text{CH}_2=\text{CH}$), 5.98 (dd, 1H, $\text{CH}_2=\text{CH}$), 6.37 (dd, 1H, $\text{CH}_2=\text{CH}$).

(Dimethylphenylsilyl)iodobis(trimethylsilyl)methane. The compound $(\text{Me}_3\text{Si})_2(\text{Me}_2\text{PhSi})\text{Cl}$ was made from $(\text{Me}_3\text{Si})_2\text{CCl}_2$ and BuLi at -110 °C as previously described,⁴ except that the reaction mixture was not treated with water;

instead the precipitated LiCl was filtered off and solvent removed from the filtrate. The residue was extracted with pentane and solvent removed from the extract. The resulting oil was recrystallized from MeOH to give colorless crystals. Yield 67%; cf. lit.⁴ 33%. ^1H NMR: δ 0.07 (18H, SiMe_3), 0.48 (6H, SiMe_2), 7.15–7.65 (5H, Ph).

A solution of BuLi (35 mmol) in hexane (14 cm^3) was added dropwise to a stirred solution of $(\text{Me}_3\text{Si})_2(\text{Me}_2\text{PhSi})\text{CCl}$ (10 g, 30 mmol) in Et_2O (50 cm^3) at -78 °C. The mixture was stirred for 2 h at -78 °C, then 1,2-diiodoethane (10 g, 30 mmol) was added, and the mixture was allowed to warm to 25 °C and filtered. The filtrate was treated first with aqueous sodium metabisulfite and then with water, and the organic layer was dried (MgSO_4). The solvent was removed in vacuum and the residue recrystallized from MeOH to give colorless crystals (7.7 g), which were shown by ^1H NMR spectroscopy to be a mixture of $(\text{Me}_3\text{Si})_2(\text{Me}_2\text{PhSi})\text{CCl}$ (40%)⁴ and $(\text{Me}_3\text{Si})_2(\text{Me}_2\text{PhSi})\text{Cl}$ (60%). For the latter, ^1H NMR (C_6D_6): δ 0.15 (s, 18H, SiMe_3), 0.58 (s, 6H, SiMe_2), 7.15–7.80 (m, 5H, Ph). This mixture was used (see below) without further purification.

Iodo(methoxydimethylsilyl)bis(trimethylsilyl)methane. The synthesis of $(\text{Me}_3\text{Si})_2[(\text{MeO})\text{Me}_2\text{Si}]\text{Cl}$ is described elsewhere.^{3c}

KC(SiMe₃)₂(SiMe₂CH₂CH₂OEt)·x(C₆H₆) (10). A solution of $(\text{Me}_3\text{Si})_2[(\text{EtOCH}_2\text{CH}_2)\text{Me}_2\text{Si}]\text{CH}$ (2.32 g, 7.98 mmol) in cold (-10 °C) Et_2O (20 cm^3) was added to a suspension of KMe^{sd} (10.2 mmol) in Et_2O (30 cm^3) at -10 °C; the mixture was allowed to warm slowly to 25 °C and then stirred overnight. The solvent was removed in vacuum to give an orange oil, which was extracted with benzene (40 cm^3). The extract was filtered and the filtrate cooled to 6 °C to give colorless plates, which were recrystallized from benzene. Yield 1.5 g, 57%. ^1H NMR (THF- d_6): δ -0.07 (s, 18H, SiMe_3), 0.13 (s, 6H, SiMe_2), 0.81 (m, 2H, $\text{CH}_2\text{CH}_2\text{O}$), 1.10 (t, 3H, CH_3CH_2), 3.36 (q, 2H, CH_2CH_3), 3.48 (m, 2H, $\text{CH}_2\text{CH}_2\text{O}$), 7.30 (s, ca. 3H, C_6H_6). ^{13}C NMR: δ 2.3 (CSi_3), 6.5 (SiMe_2), 8.4 (SiMe_3), 15.8 (CH_3CH_2), 25.8 ($\text{CH}_2\text{CH}_2\text{Si}$), 65.1 ($\text{CH}_3\text{CH}_2\text{O}$), 71.3 ($\text{CH}_2\text{CH}_2\text{O}$), 128.9 (C_6H_6). ^{29}Si NMR: δ -7.8 (SiMe_3), -8.1 (SiMe_2).

Bis(dimethylvinylsilyl)bis(trimethylsilyl)methyl]ytterbium (2). A solution of $\text{KC}(\text{SiMe}_3)_2(\text{SiMe}_2\text{CH}=\text{CH}_2)$ (0.53 g, 1.87 mmol) in benzene (70 cm^3) was added to a suspension of YbI_2^5 (0.40 g, 0.94 mmol) in benzene (10 cm^3), and the mixture was stirred for 48 h. Solvent was removed in vacuum and the residue extracted with light petroleum (bp 40–60 °C, 70 cm^3). The extract was filtered and solvent removed to leave a sticky solid, which was recrystallized from cold (-30 °C) methylcyclohexane to give irregularly shaped orange-red crystals of $\text{Yb}[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{CH}=\text{CH}_2)]_2$, mp 188–189° (dec). Yield 0.5 g, 80%. ^1H NMR: δ 0.26 (s, 6H, SiMe_2), 0.32 (s, 18H, SiMe_3), 5.70 (dd, 1H, $\text{CH}_2=\text{CH}$), 5.78 (dd, 1H, $\text{CH}_2=\text{CH}$), 6.74 (dd, 1H, $\text{CH}_2=\text{CH}$). ^{13}C NMR: δ 2.8 (SiMe_2), 7.4 (SiMe_3), 27.5 (Si_3C , $^1\text{J}(\text{SiC})$ 40 Hz, $^1\text{J}(\text{YbC})$ 233 Hz), 132.6 ($\text{CH}_2=\text{CH}$), 156.4 ($\text{CH}_2=\text{CH}$). ^{29}Si NMR: δ -12.1 (SiMe_2), -9.4 (SiMe_3). ^{171}Yb NMR: δ 987.2; MS(EI): m/z 660 (M, 25), 645 (M - Me, 5), 417 (M - R, R = C(SiMe_3)₂($\text{SiMe}_2\text{CH}=\text{CH}_2$), 65), 228 (R - Me, 50), 217 (RH - C_2H_3 , 100), 73 (SiMe_3 , 75).

Bis[(2-ethoxyethyl)dimethylsilyl]bis(trimethylsilyl)methyl]ytterbium (3). A solution of $\text{KC}(\text{SiMe}_3)_2(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{OEt})$ (2.09 g, 6.37 mmol) in benzene (60 cm^3) was added to a suspension of YbI_2 (1.14 g, 2.67 mmol) in benzene (30 cm^3), and the mixture was stirred at 25 °C for 48 h. The solvent was removed in vacuum, the residue was extracted with light petroleum (bp 40–60 °C, 80 cm^3), and the extract was filtered. The solvent was removed from the extract to leave a solid, which was recrystallized from methylcyclohexane to give orange needles of $\text{Yb}[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{OEt})]_2$. Yield 1.35 g, 70%. ^1H NMR: δ 0.27 (s, 6H, SiMe_2), 0.43 (s, 18H, SiMe_3), 0.78 (t, 2H, SiCH_2), 0.83 (t, 3H, CH_3CH_2), 3.41 (q, 2H, CH_3CH_2), 3.50 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR: δ 6.2 (SiMe_2), 8.2 (SiMe_3), 13.0 (CH_3CH_2), 18.5 (Si_3C , $^1\text{J}(\text{SiC})$ 36.3, $^1\text{J}(\text{YbC})$

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Table 1. Reaction of Dialkyls with Ethers

	compound								
	1	1	1	1	1	2	4	5	
ether	Et ₂ O	Pr ₂ O	Bu ₂ O	BuOEt	Bu ^t OEt	Et ₂ O	Et ₂ O	Et ₂ O	
time before detection of alkene	<i>a</i>	<i>b</i>	<i>b</i>	2 days	40 days	100 days	<i>b</i>	<i>b</i>	

^a Less than 5 min. ^b No alkene observed in 120 days.

265.7 Hz), 20.8 (CH₂Si), 65.7 (CH₃CH₂O), 68.3 (CH₂CH₂O). ²⁹Si NMR: δ -7.6 (SiMe₂), -8.6 (SiMe₃). ¹⁷¹Yb NMR: δ 543.5. The MS(EI) showed weak peaks at 752 (M), 724 (M - C₂H₄), 696 (M - 2C₂H₄) with the isotope patterns expected for **3**.

Bis[tris(trimethylsilyl)methyl]europium (5). A solution of KC(SiMe₃)₃^{3d} (0.81 g, 2.99 mmol) in benzene (50 cm³) was added to a suspension of EuI₂ (0.66 g, 1.63 mmol) in benzene (20 cm³), and the mixture was stirred at 25 °C for 48 h. Solvent was removed in vacuum and the residue extracted with light petroleum (bp 40–60 °C, 70 cm³). The extract was filtered, solvent pumped away, and the residue recrystallized from cold (-30 °C) methylcyclohexane to give yellow rectangular crystals of Eu[C(SiMe₃)₃]₂. Yield 0.6 g, 65%. Anal. Calcd for C₂₀H₅₄EuSi₆: C, 39.0; H, 8.9. Found: C, 38.7; H, 8.7. MS(EI): *m/z* 600 (60%, M - Me), 384 (90%, EuC(SiMe₃)₃), 201 (80%, Me₂Si=C(SiMe₃)SiMe₂), 73 (100%, SiMe₃). An NMR spectrum could not be obtained, presumably because the compound is paramagnetic, but the structure was confirmed by an X-ray study.

Bis(μ-iodo)bis(diethylether)bis[(dimethylvinylsilyl)-bis(trimethylsilyl)methyl]diytterbium (7). A mixture of (Me₃Si)₂[Me₂(CH₂=CH)Si]Cl (0.5 g, 5.4 mmol), Yb powder (1.0 g, 5.8 mmol, 40 mesh), and Et₂O (50 cm³) was stirred at 25 °C for 16 h and then filtered. Solvent was removed from the filtrate under vacuum and the sticky residue recrystallized from cold (-30 °C) Et₂O to give orange rhombic plates, mp 150 °C (dec). Yield 2.0 g, 65%. ¹H NMR (THF-*d*₆): δ -0.1 (m, br, 18H, SiMe₃), 0.08 (m, br, 6H, SiMe₂), 1.10 (t, 6H) and 3.37 (q, 4H, OEt) 5.5 and 6.4 (m, br, 3H, CH=CH₂). ¹³C NMR (THF-*d*₆, 240 K): -1.5 (CSi₃, *J*(CSi) 65.3 Hz, no *J* (CYb) observed), 7.0 (SiMe₂), 8.8 (SiMe₃), 15.8 (CH₃CH₂O), 66.4 (CH₃CH₂O), 123.8 (CH₂CH), 154.8 (CH₂CH). The mass spectrum showed only peaks attributable to the dialkyl compound **2** (see eq 4 in Discussion).

Bis(μ-iodo)bis(diethyl ether)bis[(methoxydimethylsilyl)bis(trimethylsilyl)methyl]diytterbium (8). A mixture of (Me₃Si)₂(MeOSiMe₂)Cl (1.19 g, 3.18 mmol), Yb (0.55 g, 3.18 mmol), and Et₂O (50 cm³) was stirred at 20 °C for 2 h. The solution was filtered, reduced to 10 cm³, and cooled to -30 °C. The bright yellow plates of [Yb[C(SiMe₃)₂(SiMe₂OMe)]₂·OEt₂ that separated were filtered off and washed with light petroleum (bp 40–60 °C). Yield 1.3 g, 66%. ¹H NMR (THF-*d*₆): δ 0.08 (s, 18H, SiMe₃), 0.22 (s, 6H, SiMe₂), 1.11 (t, 6H, CH₃CH₂O), 3.38 (q, CH₃CH₂O, 4H), 3.55 (s, 3H, OMe). ¹³C NMR: 3.5 (br, SiMe₂), 7.3 (br, SiMe₃), 15.5 (CH₃CH₂), 51.5 (MeO), 66.2 (CH₃CH₂O). The mass spectrum obtained from a sample of **8** was that of compound **4** (see eq 4 in Discussion).

No reaction was observed when a mixture of (Me₃Si)₂(MeOSiMe₂)Cl, Yb metal, and a trace of I₂ in toluene was heated at 80 °C for 3 h or at 60 °C for 72 h. Upon addition of Et₂O, however, reaction was immediate.

Bis[(methoxydimethylsilyl)bis(trimethylsilyl)methyl]ytterbium (4). A sample of [Yb[C(SiMe₃)₂(SiMe₂OMe)]₂·OEt₂ (**8**) was heated at 220 °C/10⁻⁶ Torr to give a residue of YbI₂ and an orange sublimate which was identified spectroscopically as Yb[C(SiMe₃)₂(SiMe₂OMe)]₂ (**4**). ¹H NMR (toluene-*d*₆): δ 0.17 (s, 6H, SiMe₂), 0.21 (s, 18H, SiMe₃), 3.03 (s, 3H, OMe). ¹³C NMR: δ 3.0 (SiMe₂), 7.0 (SiMe₃), 21.9 (CSi₃), ¹*J*(CSiMe₃) 45.2, ¹*J*(CSiMe₂OMe) 56.5, ¹*J*(CYb) 158.4 Hz), 50.5 (OMe). ²⁹Si NMR: δ -8.8 (SiMe₃), +18.8 (SiMe₂). ¹⁷¹Yb NMR: δ 814.4. MS(EI): *m/z* 668 (48, M), 653 (5, M - Me), 437 (30, RYbOMe - Me, R = C(SiMe₃)₂(SiMe₂OMe)), 421 (100, YbR), 233 (65, RH - Me), 217 (55, RH - MeO), 73 (55, SiMe₃). When a sample of **8** was dissolved in toluene-*d*₆, the solution rapidly became red and yellow YbI₂ separated out. The NMR

spectra of the toluene solution showed that it contained only the dialkyl **4**.

[(Dimethylphenylsilyl)bis(trimethylsilyl)methyl]iodo-ytterbium (9). A mixture (1.0 g) of (Me₃Si)₂(Me₂PhSi)Cl (60%) and (Me₃Si)₂(Me₂PhSi)CCL (40%) (see above), an excess of Yb metal (0.5 g), and a crystal of I₂ in Et₂O (20 cm³) was immediately decolorized upon ultrasonic activation but become yellow when subsequently stirred for 22 h. The mixture was filtered and the solvent removed from the filtrate to give an orange oil, which solidified when washed with pentane (the pentane washings contained (Me₃Si)₂(Me₂PhSi)CCL, suggesting that, as expected, this component of the halide mixture did not react). The solid dissolved to give a yellow solution in Et₂O and a red one in toluene: the red crystals obtained from toluene were judged to be [Yb[C(SiMe₃)₂(SiMe₂Ph)]I] (yield not recorded). ¹H NMR (THF-*d*₆): δ -0.15 (s, 18H, SiMe₃), 0.07 (s, 6H, SiMe₂), 7.0–7.72 (m, 5H, Ph). ¹³C NMR: δ -1.1 (CSi₃), 7.7 (SiMe₂), 8.8 (SiMe₃), 135.4, 134.1, 126.2, 125.4 (Ph). ²⁹Si NMR: δ -13.4(SiMe₂), -11.5(SiMe₃). ¹⁷¹Yb NMR: δ 353. MS(EI): *m/z* 467 (M - I). When a solution of **9** in toluene was kept for several days at 20 °C or 2 h at 70 °C, a yellow precipitate appeared. The NMR spectrum of the supernatant solution showed that the signals ascribed to the alkyl ligand in **9** had decreased in intensity and that new signals had appeared alongside. These were consistent with the formation of Yb[C(SiMe₃)₂(SiMe₂Ph)]₂, but a pure sample of this compound has not yet been isolated.

Reaction of Yb[C(SiMe₃)₃]₂ (**1**) with Acyclic Ethers.

When a sample of **1** was dissolved in diethyl ether, gas was immediately evolved and reaction was complete in 5 min. Solvent was pumped off, and the residue was washed with light petroleum (bp 40–60 °C) and then recrystallized from Et₂O to give an orange solid [Yb[C(SiMe₃)₃](OEt)(OEt₂)]₂ (**11**), identical with that described in ref 1b. (Me₃Si)₃CH was identified in the petroleum washings by comparison of its NMR spectra with those of an authentic sample. Reactions of a solution of **1** in C₆D₆ with other ethers were studied in sealed NMR tubes. In each case integration showed that the products (Me₃Si)₃CH and Yb[C(SiMe₃)₃](OR) were formed in 1:1 molar ratio. The relative rates of reaction were assumed to be roughly indicated by the time that elapsed before signals could be observed in the alkene region of the spectra (Table 1).

Reaction of 1 with THF. A solution of **1** (0.6 g) in THF (10 cm³) was stirred at 20 °C for 1.5 days. The initially orange solution became dark red and then red-brown. Solvent was removed in vacuum and the residue washed with light petroleum (bp 40–60 °C, 30 cm³) to leave an extremely pyrophoric brown solid. This was shown by ¹H NMR spectroscopy and MS(EI) to contain the C(SiMe₃)₃ group, but no volatile Yb-containing ions were observed. In a separate NMR tube experiment, the ¹³C spectrum after 3 days showed peaks at δ 3.41 and 7.84 (SiMe₃), and four quaternary signals at 3.85 (t, DCSi₃), 4.39 (*J*(SiC) 37.5 Hz), 6.74, and 19.19 (*J*(SiC) 44.5 *J*(YbC) 204.6 Hz). The peaks at δ 4.39 and 19.19 had similar intensities. The ¹⁷¹Yb NMR spectrum showed a peak at δ 889 ppm.

Reaction of 1 and 5 with Alkyl Iodides. (a) The reaction between **1** and methyl iodide has been described previously.^{1a} The ¹H NMR spectrum of the mother liquor from which the yellow-green product **6** was isolated showed peaks at δ 0.09, 0.99 (RMe, 44%), 0.13 (RH, 28%), and 0.26 (RI, 28%), R = C(SiMe₃)₃, assigned by comparison with spectra of authentic samples.

(b) An excess of ICH₂CH₂I was added to a solution of **1** in C₆D₆ in an NMR tube. The spectrum of the solution above

Table 2. Crystal Data for 5, 7, and 8

formula	C ₂₀ H ₅₄ EuSi ₆ (5)	C ₃₀ H ₇₄ I ₂ O ₂ Si ₆ Yb ₂ (7)	C ₂₈ H ₇₄ I ₂ O ₄ Si ₆ Yb ₂ (8)
Fw	615.13	1235.3	1243.29
cryst size (mm)	0.40 × 0.40 × 0.35	0.5 × 0.5 × 0.05	0.4 × 0.4 × 0.05
temp (K)	173(2)	173(2)	173(2)
space group	<i>P1</i> (No. 1)	<i>P2₁/c</i> (No. 14)	<i>P2₁/n</i> (No. 14)
<i>a</i> (Å)	8.735(4)	14.385(4)	9.319(3)
<i>b</i> (Å)	8.817(3)	10.217(2)	27.743(9)
<i>c</i> (Å)	11.435(7)	17.681(3)	10.074(2)
α (deg)	101.29(4)	90	90
β (deg)	100.21(5)	111.40(2)	112.98(2)
γ (deg)	109.62(3)	90	90
<i>V</i> (Å ³)	784.8(7)	2419.4(9)	2397.8(12)
<i>Z</i>	1	2	2
<i>d_c</i> (Mg m ⁻³)	1.30	1.70	1.72
μ (mm ⁻¹)	2.23	5.29	5.34
<i>F</i> (000)	321	1200	1208
θ range	2–28	2–25	2–25
No. of reflns measd	3793	4404	4456
No of unique reflns	3793	4234	4149
No of reflns with <i>I</i> > 2 σ (<i>I</i>)	3782	2783	2956
wR2 (all data)	0.117	0.230	0.203
R1 (<i>I</i> > 2 σ (<i>I</i>))	0.039	0.077	0.055
goodness of fit on <i>F</i> ²	0.550	1.010	1.041
refined params	264	190	190
highest diff peak/hole e (Å) ⁻³	1.48, -2.01	2.72, -1.49	1.50, -2.70
absorptn correction	<i>T</i> _{max} 1.00, <i>T</i> _{min} 0.79 (ψ scans)	<i>T</i> _{max} 1.40, <i>T</i> _{min} 0.35 (DIFABS)	<i>T</i> _{max} 1.00, <i>T</i> _{min} 0.37 (ψ scans)

the precipitate of (RYbI)₂ showed a signal from the major product (>95%) at δ 0.26 (RI) and weak signals at 0.13(RH) and 5.24 (CH₂=CH₂).

(c) A sample of MeI (0.3 cm³, 4.8 mmol) was added to a solution of **5** (0.43 g, 0.7 mmol) in methylcyclohexane (20 cm³), and the mixture was stirred for 2 h. The yellow precipitate that formed was filtered off and recrystallized from THF to give bright yellow plates which were judged to be EuI₃(THF)₂. Anal. Calcd for C₈H₁₆EuI₃O₂: C, 14.3; H, 2.42. Found: C, 15.5; H, 2.45. The highest peak in the mass spectrum was at *m/z* 254 (I₂⁺). The organic products in the filtrate were identified by GC-MS and ¹H NMR spectroscopy as RH, RMe, and RI in approximately equal amounts.

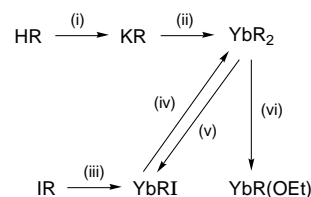
Ethoxy{[(2-ethoxyethyl)dimethylsilyl]bis(trimethylsilyl)methyl}ytterbium (12). A solution of **10** (0.38 g, 0.93 mmol) in Et₂O (20 cm³) was added to a solution of **6** (0.56 g, 0.93 mmol) in Et₂O (30 cm³), and the mixture was stirred at 25 °C for 3 h. The solvent was then removed in vacuum and the red residue extracted with methylcyclohexane (30 cm³). The extract was filtered, reduced to 5 cm³, and cooled to -30 °C to give red crystals, which were shown unambiguously by an X-ray study to be **12**, but the structural data were not sufficiently precise to merit full publication. ¹H NMR: δ 0.35 (6H, s, SiMe₂), 0.42 (18H, s, SiMe₃), 0.90 (2H, t, CH₂Si), 1.08 (t), 1.28 (t, 3H, CH₃) 3.14 (q), 3.35 (t), 4.03 (q, 2H, OCH₂).

Crystal Structure Determinations. Data were collected on an Enraf-Nonius CAD4 diffractometer and corrected for Lorentz and polarization effects and for absorption; details are given in Table 2. The SHELXS-86 and SHELXL-93 programs were used for structure solution and refinement on *F*² using all reflections. All non-hydrogen atoms were anisotropic. For **5** the H atoms were refined in riding mode with *U*_{iso}(H) = 1.5 *U*_{eq}(C) but the hydrogens on C(8), C(14), and C(19) were omitted. The structure is disordered 0.78:0.22 between the major orientation shown and the alternative with common C(1) and C(2) positions and with Eu(1) related by inversion through the midpoint of the C(1)···C(2) vector. For **7** and **8**, the H atoms were included in riding mode with *U*_{iso}(H) = 1.2 *U*_{eq}(C) or 1.5 *U*_{eq}(Me).

Results and Discussion

Synthesis and Reactions of Dialkylytterbiums.

The compounds YbR₂, R = [C(SiMe₃)₂(SiMe₂X)] (X = Me, Ph, CH=CH₂, OMe, CH₂CH₂OEt) were obtained from either HR or IR, or in some cases from both (Scheme 1).

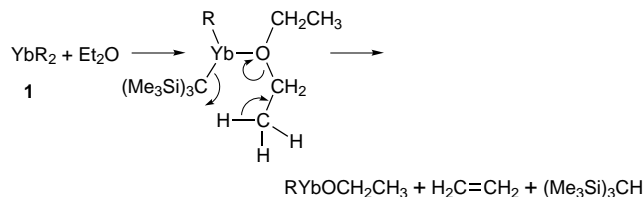
Scheme 1^a

^a Conditions: (i) KMe/Et₂O; (ii) YbI₂/C₆H₆; (iii) Yb metal/Et₂O; (iv) sublime 10⁻³ Torr or warm toluene; (v) MeI or ICH₂CH₂I; (vi) Et₂O in light petroleum or C₆H₆.

Provided that the group R does not contain substituents at silicon that are attacked by methylpotassium, the compounds HR can be converted in cold ether (reaction i) into the potassium alkyls, which are isolated as ether-free solids.^{3b,d} These react with a suspension of YbI₂ in benzene to give the alkyls YbR₂. (It has been assumed that the dialkyls that contain donor groups, e.g., OMe, are monomeric. Dimeric species in solution would show more complicated NMR spectra than have been observed, but further measurements are required before dimerization can be definitely excluded.) Benzene rather than ether is used for reaction ii to avoid decomposition of the alkyl YbR₂ by reaction vi as soon as it is formed. The product YbR(OEt) from the reaction of Yb[C(SiMe₃)₃]₂ with diethyl ether was isolated as a diethyl etherate, the structure of which has been determined independently.^{1b} Reactions in sealed NMR tubes showed that the ease of attack of the dialkyls M[C(SiMe₃)₂(SiMe₂X)]₂ on ether solvents (Table 1) depended on at least three factors: (a) The ether. The ease of attack of Yb[C(SiMe₃)₃]₂ on ethers decreased in the series Et₂O ≫ BuOEt > BuⁱOEt > Prⁱ₂O, Bu₂O. (b) The group X. For M = Yb, the ease of reaction with Et₂O decreased as X was varied in the series Me > CH=CH₂ > MeO. (c) The metal. For R = C(SiMe₃)₃ reaction with Et₂O was rapid for M = Yb, but no reaction was observed for M = Eu. These points are discussed below.

(a) For the range of ethers examined, reaction was observed only with those containing an ethyl group. Further, ethene was the only alkene detected; e.g., there was no evidence that the reaction between YbR₂ and

Scheme 2



BuOEt yielded $\text{YbROEt} + \text{C}_2\text{H}_5\text{CH}=\text{CH}_2$. We therefore tentatively suggest that the mechanism of the ether cleavage may be that shown in Scheme 2.

The absence of a hydrogen atom β to O in the *tert*-butyl group would then account for the fact that reaction with Bu^tOEt was very slow, and the generation of ethene might be inhibited by steric compression in the other product, YbROBu^t . The same effect would operate to some extent in the case of Pr^i_2O ; in this case, there could also be steric hindrance to the approach of the $(\text{Me}_3\text{Si})_3\text{C}$ group to the hydrogen atom to be abstracted. There seems to be no obvious reason, however, why reaction should not occur readily with Bu_2O and, particularly, with BuOEt . Further studies are evidently necessary. Reactions between ethers and f-block organometallic compounds containing metal-hydride bonds give alkanes, rather than alkenes and appear to involve attack by hydride at the carbon α to the ether oxygen.⁶

(b) Coordination of X to the metal in **2–4** could inhibit ligation of Et_2O as required for the reaction shown in Scheme 2. This would account for the lower reactivity of the methoxy derivative **4** and the vinyl derivative **2** compared with the permethyl compound **1**. Evidence for internal coordination in **2** is provided by NMR data. The signal in the ^{13}C spectrum associated with the α -carbon of the vinyl group shifts from δ 142.6 in $(\text{Me}_3\text{Si})_2[\text{Me}_2(\text{H}_2\text{C}=\text{CH})\text{Si}]\text{CH}$ to 156.4 in **2**, and the associated ^1H signals are shifted from δ 6.27 to 6.74. Similar shifts are observed in the spectra of 4-alkenylaluminum compounds, in which internal coordination is well established,⁷ and in **7**, in which weak vinyl-metal interactions are found in the crystal structure.⁸ Even weak $\text{Yb}\cdots\text{vinyl}$ interactions in **2** might inhibit its reaction with Et_2O . Coordination of Et_2O to Yb does not in general result in ether cleavage; there appears to be no incompatibility between $\text{Yb}-\text{C}$ and $\text{Yb}-\text{OEt}_2$ bonds in the monoalkylytterbium derivatives **6–9** or in the less sterically hindered $\text{Yb}[\text{CH}(\text{SiMe}_3)_2]_2$, which crystallizes as an orange bis(diethyl etherate).^{1b} The unusual ease of cleavage of Et_2O by **1** suggests that the rate may be enhanced by relief of steric strain in the $\text{YbR}_2\cdot\text{OEt}_2$ intermediate.

(c) Reduced intramolecular compression may also account, at least in part, for the fact that the bis(alkyl)europium **5** reacts so much more slowly with Et_2O than the ytterbium analogue **1**. The $\text{Eu}-\text{C}$ bond is longer than the $\text{Yb}-\text{C}$ bond, and so the metal is more exposed,

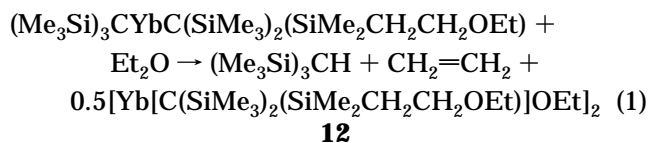
(6) (a) Watson, P. L.; *J. Chem. Soc., Chem. Commun.* **1983**, 276–277. (b) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432. (c) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134–142. (d) Deelman, B.-J.; Booij M.; Meetsma, A.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1995**, *14*, 2306–2317.

(7) (a) Dolzine T. W.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 1737–1740. (b) Benn, R.; Janssen, E.; Lehmkühl, H.; Ruffńska, A. *J. Organomet. Chem.* **1987**, *333*, 155–168.

(8) The $\text{Yb}\cdots\text{C}(\text{vinyl})$ distance in **7** (2.98 Å) is longer than the $\text{Yb}\cdots\text{C}(\text{Me})$ distance (2.852(13) Å) in **1**, but the latter is expected to be exceptionally short because of the low coordination number of Yb. There are no short $\text{Yb}\cdots\text{Me}$ contacts in **6** or **7**.

but perhaps there is room to accommodate coordinated ether without instigating the reaction depicted in Scheme 2.

An attempt was made to synthesize an unsymmetrical dialkylytterbium by treating $(\text{Me}_3\text{Si})_3\text{CYbI}\cdot\text{OEt}_2$ with $\text{KC}(\text{SiMe}_3)_2(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{OEt})$. It was thought that internal coordination from the ethoxyethyl group might inhibit further coordination of electron pair donors and thus make it possible to use diethyl ether as solvent. However, this proved not to be the case; $(\text{Me}_3\text{Si})_3\text{CH}$ was eliminated and an ethoxyytterbium compound **12** was obtained, suggesting that the initially formed unsymmetrical dialkyl was attacked by solvent according to eq 1. The preferential elimination of the alkyl group



$\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{X})$ in which $\text{X} = \text{Me}$ is consistent with the data in Table 1. Further work in this area is in progress.

Preparation of Alkylytterbium Iodides. Reactions between the iodides RI and ytterbium powder in diethyl ether gave the alkylytterbium iodides **6–9** in good yield (Scheme 1, reaction iii). A little YbI_2 was also formed, but the amount was reduced if an excess of Yb metal was used. The compounds RYbI were all stable in Et_2O solution and could be stored as such for several weeks.

Alkylytterbium iodides were also obtained from reactions of compounds **1–4** with iodoalkanes (Scheme 1, reaction v). In the case of the reaction between **1** and methyl iodide, the multiplicity of products, eq 2, and



especially the formation of RH, suggested that the reaction proceeded by a radical pathway. The reaction between **1** and $\text{ICH}_2\text{CH}_2\text{I}$ proceeded more cleanly as in eq 3. The NMR spectra remained sharp, suggesting



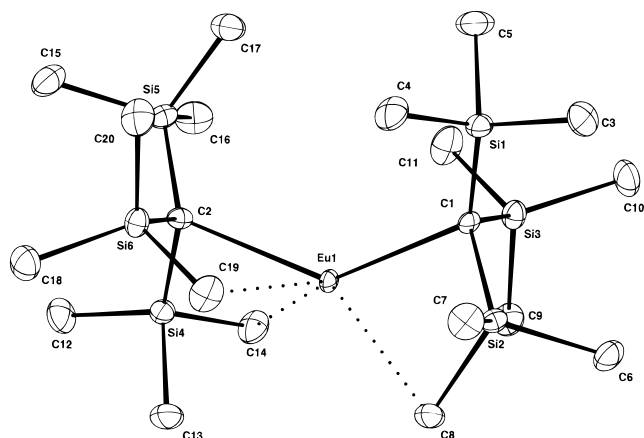
that paramagnetic $\text{Yb}(+3)$ products were not formed.

The reactions shown in eqs 2 and 3 are in contrast to those observed² for the bis(cyclopentadienyl)derivatives MCp_2 , which are oxidized by haloalkanes, usually to the lanthanide (+3) derivatives MCp_2X . As shown above, the ytterbium compounds containing bulky silicon-substituted alkyl groups undergo substitution, with cleavage of one $\text{Yb}-\text{C}$ bond, to give products in which the metal remains in oxidation state +2. The europium compound **5** was oxidized by MeI, but the only product isolated was the iodide $\text{EuI}_3(\text{THF})_2$. Attempts to make alkyleuropium iodide by the reaction between $(\text{Me}_3\text{Si})_3\text{CI}$ and europium metal were unsuccessful.

Crystal Structures. (a) $\text{Eu}[\text{C}(\text{SiMe}_3)_3]_2$ (**5**). Crystals suitable for an X-ray diffraction study were obtained from cold (-30°C) methylcyclohexane. Selected bond lengths and angles are given in Table 3. The species present in the solid are solvent-free monomers with the

Table 3. Selected Bond Lengths (Å) and Angles (deg) in Eu[C(SiMe₃)₃]₂ (5)

		Bonds			
Eu–C(1)	2.605(6)	Eu–C(2)	2.612(7)	Eu···C(8)	2.947(8)
Eu···C(19)	2.952(8)	Eu···C(14)	3.185(9)	Si–C ^a	1.828(6)
Si–Me ^a	1.887(10)				
		Angles			
C(1)–Eu–C(2)	136.0(2)	Eu–C(1)–Si(2)	94.7(2)	Eu–C(1)–Si(3)	89.4(3)
Eu–C(1)–Si(1)	126.0(3)	Eu–C(2)–Si(5)	124.1(3)	Eu–C(2)–Si(6)	96.3(3)
Eu–C(2)–Si(4)	87.8(2)	Si(2)–C(1)–Si(3)	115.5(3)	Si(3)–C(1)–Si(1)	115.1(3)
Si(1)–C(1)–Si(2)	113.3(3)	Si(5)–C(2)–Si(6)	114.9(3)	Si(6)–C(2)–Si(4)	116.6(3)
Si(4)–C(2)–Si(5)	113.9(3)	C(1)–Si(1)–C(4)	112.9(4)	C(1)–Si(1)–C(5)	113.6(4)
C(1)–Si(1)–C(3)	113.8(4)	C(1)–Si(2)–C(7)	116.1(4)	C(1)–Si(2)–C(8)	112.2(3)
C(1)–Si(2)–C(6)	115.4(4)	C(1)–Si(3)–C(10)	118.0(4)	C(1)–Si(3)–C(11)	111.6(3)
C(1)–Si(3)–C(9)	112.7(3)	C(2)–Si(4)–C(13)	113.7(4)	C(2)–Si(4)–C(14)	111.0(3)
C(2)–Si(4)–C(12)	117.3(4)	C(2)–Si(5)–C(16)	114.4(4)	C(2)–Si(5)–C(17)	112.9(3)
C(2)–Si(5)–C(15)	112.6(4)	C(2)–Si(6)–C(19)	110.7(3)	C(2)–Si(6)–C(20)	114.5(3)
C(2)–Si(6)–C(18)	116.2(4)	C(4)–Si(1)–C(5)	103.9(5)	C(5)–Si(1)–C(3)	104.6(3)
C(3)–Si(1)–C(4)	107.2(5)	C(7)–Si(2)–C(8)	101.3(4)	C(8)–Si(2)–C(6)	105.4(3)
C(6)–Si(2)–C(7)	105.0(4)	C(10)–Si(3)–C(11)	107.7(4)	C(11)–Si(3)–C(9)	99.7(3)
C(9)–Si(3)–C(10)	105.4(5)	C(13)–Si(4)–C(14)	100.8(4)	C(14)–Si(4)–C(12)	107.1(3)
C(12)–Si(4)–C(13)	105.3(4)	C(16)–Si(5)–C(17)	103.7(4)	C(17)–Si(5)–C(15)	107.4(3)
C(15)–Si(5)–C(16)	105.1(5)	C(19)–Si(6)–C(20)	102.6(5)	C(20)–Si(6)–C(18)	105.2(3)
C(18)–Si(6)–C(19)	106.4(4)				

^a Mean value.**Figure 1.** Molecular structure of Eu[C(SiMe₃)₃]₂ (5).

C–Eu–C angle 136.0(2)°. This is similar to the centroid–Eu–centroid angle in Eu(C₅Me₅)₂^{9a} and almost the same as the C–Yb–C angle (137.0(4)) in **1**,^{1a} even though the average Eu–C bond length, 2.609(7) Å, is significantly longer than the Yb–C length, 2.490(8) Å.^{1a} There has been much discussion in recent years about whether the angles in molecules MX₂, in which M is a group 2 or divalent group 3 element and X is halogen or cyclopentadienyl, are determined mainly by electronic factors at the metal^{10a,b} or interligand interactions.^{10c} As the latter would be significantly reduced by lengthening the metal–carbon bond, the similarity of the angles observed in the Yb and Eu compounds suggests that in these derivatives the dominant factor determining the C–M–C angle is electronic rather than steric. The bent structures suggest that metal d orbitals are involved in M–C bonds.^{10a} Recent compilations of structural data on compounds containing the C(SiMe₃)₃ and C(SiMe₂Ph)₃ groups show that the inner Si–C bond lengths and Si–C–Si angles are strongly correlated

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with the electronegativity of the atoms adjacent to the central carbon.^{11a,b} The values for **5** lie between those in Yb[C(SiMe₃)₃]₂ (**1**) (1.838(11) Å and 114.2(5)°) and CsC(SiMe₃)₃^{11c} (1.817(11) Å and 117.3(5)°) and suggest that the Eu–C bonds are strongly ionic with delocalization of negative charge into the inner Si–C bonds of the alkyl group. The mean Si–Me bond lengths and Me–Si–Me angles are normal. The ytterbium compound **1** shows two short Yb···Me interactions in the solid state which may help to stabilize the molecule on a rather shallow potential energy surface.^{10b} There are similar interactions in **5**, but now there appears to be room for three Eu···Me interactions, with C(8), C(14) and C(19). This makes the molecule asymmetrical with wide variations in Eu–C–Si angles; Si(1) and Si(5) are pushed away from the metal and the other silicon atoms bent toward it. As in **1**, however, the Si–C(1)–Si angles do not differ significantly from the mean. Although disorder within the crystal leads to some uncertainty in the bond lengths, there is an indication that the methyl groups that show agostic interactions with the europium are drawn away from the attached silicon atoms, since three out of four Si–Me distances that are greater than the mean by more than one standard deviation are to agostic Me groups. Metal–methyl interactions of this kind appear to be widespread in the chemistry of the *f*-block elements^{9c,12a–c} and alkali metals.^{11c} They have been observed in Yb[N(SiMe₃)₂–AlMe₃]₂,^{11d} which is isoelectronic with **1**.^{11e} The crystal structures of the related compounds **1** and **5** may be compared with those of KR^{3c} and RbR,^{11c} R = C(SiMe₃)₃. For each pair there are more metal–methyl interactions in the compound containing the larger metal.

As far as we are aware, the structure of **5** is the first of a homoleptic europium(+2) dialkyl to be determined, and the first to give a value for the Eu–C (sp³) single-bond length. If the normal radius of carbon is subtracted from the measured value a covalent radius for Eu of 1.84 Å is obtained, in agreement with the value

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Table 4. Selected Bond Lengths (Å) and Angles (deg) Yb[C(SiMe₃)₂(SiMe₂X)]I·OEt₂

	X		
	Me, 6 ^a	CH=CH ₂ , 7	OMe, 8
Bonds			
Yb–I	3.084(2)	3.076(2)	3.0990(12)
Yb–I ^b	3.087(2)	3.114(2)	3.1159(13)
Yb–C	2.47(2)	2.50(2)	2.580(12)
Yb–OEt ₂	2.348(13)	2.370(11)	2.354(10)
Yb–X		2.98(2)	2.380(10)
(C(2) 7 ; O(1) 8)			
Si–C(1) mean	1.84(2)	1.84(2)	1.823(13)
Si–Me mean	1.87(2)	1.88(2)	1.871(20)
other		C=C 1.28(3)	Si–O 1.684(10), OMe 1.43(2)
Angles			
Yb–I–Yb	88.08(4)	90.42(4)	85.48(3)
I–Yb–I ^b	91.92(4)	89.58(4)	90.52(3)
I–Yb–C	117.5(4)	123.6(3)	130.4(3)
I [–] –Yb–C	113.6(4)	106.7(4)	111.3(3)
I–Yb–OEt ₂	105.5(3)	111.0(3)	104.5(2)
I [–] –Yb–OEt ₂	99.2(3)	94.7(3)	92.3(3)
I–Yb–X		96.6(4)	84.9(3)
I [–] –Yb–X		172.0(4)	171.2(3)
Et ₂ O–Yb–C	123.3(5)	120.5(5)	117.8(4)
Et ₂ O–Yb–X		87.9(5)	96.1(4)
X–Yb–C		65.6(6)	66.8(4)
Si–C–Si mean	113.8(9)	113.7(9)	116.8(7)
C–Si–C mean	105(1)	104.9(9)	104.6(8)

^a Reference 1a and unpublished results. ^b Symmetry transformation: $-x, -y, -z$.

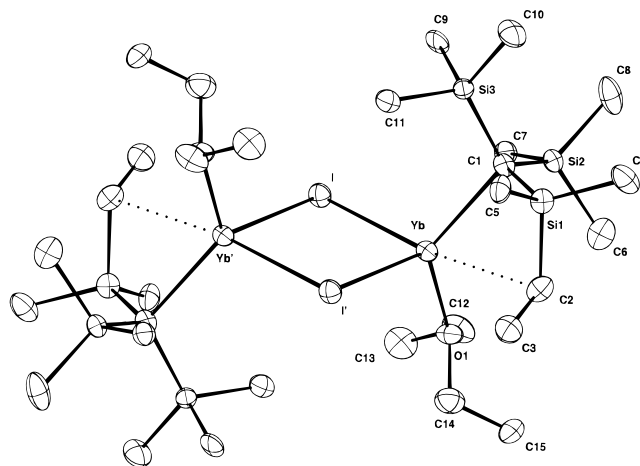
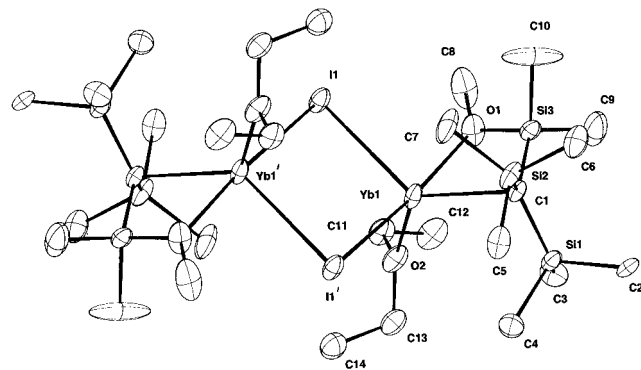
for the single-bond radius estimated by Pauling.^{12d} Other Eu–C bond lengths of 2.79(1) Å,^{9a} 2.795(7) and 2.82(2) Å^{9b} to C₅Me₅, 2.776(6)–2.956(6) Å to C₅H₃(SiMe₃)₂,^{12c} 2.709(7) Å to μ -phenylethynyl,^{9b} and 2.999–(23) Å to η^6 -C₆Me₆^{9c} have been reported.

(b) Iodides [Yb[C(SiMe₃)₂(SiMe₂X)]I·OEt₂ (6**–**8**).** The molecular parameters of these compounds are listed in Table 4. Each molecule is dimeric with a planar, almost square, Yb₂I₂ ring. In **6**, with X = Me, the two Yb–I bond lengths are identical within experimental error. The coordination at Yb is 4-fold, with the sum of the angles 432° (cf. 436° in a tetrahedron) and a wide exocyclic O–Yb–C angle. The C(1)–Si bond lengths and Si–C(1)–Si angles are similar to those in **1**, but the Yb–C–Si angles show that the C(SiMe₃)₃ group as a whole is pushed away from the iodine atoms. In **7** and **8**, the two Yb–I bonds within each dimer are slightly but significantly different. The coordination at Yb is 5-fold and can be described as distorted trigonal bipyramidal with the longer Yb–I and Yb–X bonds axial. The chelating group X in the alkyl ligand is accommodated in such a way that the molecular skeleton in **7** and **8** is very similar to that in **6**.

The Yb(+2)–C(1) bond lengths, 2.47(2)–2.50(2) Å are similar in **1**, **6**, and **7** and perhaps slightly longer in **8** and the ethoxide **11** (2.573(13) Å).^{1b} The reported Yb(+3)–C bond lengths, in the range 2.36(2)–2.39(2) Å,^{13a,b} are shorter by ~0.15 Å, which is the usually

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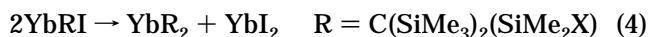
(13) (a) Atwood, L. J.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140–142. (b) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263–270. (c) Shannon, R. D. *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767.

**Figure 2.** Molecular structure of [Yb[C(SiMe₃)₂(SiMe₂-CH=CH₂)]I·OEt₂ (**7**).**Figure 3.** Molecular structure of [Yb[C(SiMe₃)₂(SiMe₂-OMe)]I·OEt₂ (**8**).

quoted^{13c} value for the difference between the Yb²⁺ and Yb³⁺ ionic radii. The interaction between Yb and the vinyl group in **7** is reflected in the Yb–C(1)–Si(1) angle (95.8(7)° (cf. Yb–C(1)–Si(2) 107.4(7), Yb–C(1)–Si(3) 111.0(8)°) but the long Yb···C(2) bond distance and the almost undistorted geometry of the vinyl group suggest that the metal–vinyl bond is weak.

The Yb–OEt₂ bond lengths in **6**–**8** and the Yb–OMe bond length in **8** are similar, slightly shorter than the Yb–OEt₂ bond length in **11** (2.479(13) Å) and slightly longer than the Yb–O bond lengths (2.08(2)–2.276(10) Å) in ytterbium alkoxides.^{2b,14} Similar chelation by the ligand C(SiMe₃)₂(SiMe₂OMe) has been observed in lithium, magnesium,^{3c} and (very weakly) in zinc⁴ compounds and by the ligand C(SiMe₂OMe)₃.¹⁵

Rearrangements of Alkylytterbium Iodides. **7**–**9** decompose when heated under reduced pressure to give dialkylytterbiums and YbI₂, as shown in eq 4. This



reaction was also observed during attempts to obtain the mass spectra of **7**–**9**. The fragment corresponding to YbR₂⁺ was found in all cases, and for **7** and **8**, in which the donor groups X are respectively CH=CH₂ and OMe, no peaks attributable to YbRI were observed. In contrast, the only peaks detected by mass spectrometry from samples of **6** were attributable to RI; there was

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no signal from YbRI or YbR₂ even though the dialkyl **1** is volatile and sublimes without decomposition at 95 °C and 10⁻⁴ Torr.^{1a} When a sample of **6** was heated, crystallinity was lost at ~185 °C but there appeared to be no further change below 250 °C. Reaction of the iodides **7–9** according to eq 4 in toluene-*d*₈ solution was observed by NMR spectroscopy; the spectra showed broad peaks assigned to YbRI and sharp peaks attributed to the dialkyls YbR₂. After 2–3 days at 20 °C, or 2–3 h at 70 °C, the broad peaks had disappeared, the sharp peaks had grown in intensity, and a yellow precipitate of YbI₂ had appeared; under these conditions it is likely that the reactions shown in eq (4) are driven to the right by the insolubility of the diiodide. There appears to be a correlation between the ease with which the alkylttrerbium iodides **6–9** give homoleptic compounds Yb[C(SiMe₃)₂(SiMe₂X)]₂ and YbI₂ and the strength of chelation between the group X and the metal center. Thus the reaction shown in eq (4) is slow when X = Me but is fast when X = OMe. Intra- or intermolecular processes for the ligand transfer shown in eq (4) require the breaking of either or both of the Yb–I bonds in the YbRI dimer, and these processes could be facilitated by the chelation observed in the structures of **7** and **8**. The X-ray data also suggest incipient weakening of Yb–I and Yb–C bonds in **7** and **8** compared with those in **6**, which would facilitate the reorganization reaction. A similar ready conversion of the compound RMgI, R = C(SiMe₃)₂(SiMe₂OMe), into the homoleptic species MgR₂ and MgI₂ has recently been observed.^{3c}

In general, the reactions of the kind depicted in eq (4) are driven to the right by the use of donor solvents, especially if metal halide–donor complexes separate out. This is the basis for the well-established generation of diorganomagnesium compounds from Grignard reagents by removal of magnesium dihalides as, e.g., dioxane complexes.¹⁶ Similarly, when a solution of Sm[N(SiMe₃)₂]I(DME)(THF) in THF (DME = MeOCH₂CH₂OMe) is cooled, crystals of SmI₂(THF)₂ separate out, leaving Sm[N(SiMe₃)₂]₂ in solution.¹⁷ If precipitation of the dihalides can be prevented, it may be possible to find conditions under which the reverse reaction to that in eq (4) can be observed and then to determine whether there is a true Schlenk equilibrium between homo- and heteroleptic species. These considerations led us to record NMR spectra of **6–9** in THF-*d*₈ solution.

Spectra recorded immediately after preparation of the solution were consistent with the structures determined by X-ray crystallography, but the signals in the ¹H spectrum at 20 °C were broad (they sharpened on cooling) and the signals due to the central carbon (enhanced by INEPT experiments) showed coupling to silicon but not to ytterbium. This suggests that the species **6–9** exchange rapidly at room temperature on the NMR time scale with other species, perhaps as indicated in eq (4). When the spectra were rerecorded

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Table 5. NMR Data for the Dialkylttrerbiums

compound	chemical shift (ppm)		coupling constant ¹ J(Hz)	
	¹⁷¹ Yb	¹³ C ^a	²⁹ Si ^b	¹⁷¹ Yb ^b
Yb[C(SiMe ₃) ₃] ₂	812.2	25.8	40.8	253.8
Yb[C(SiMe ₃) ₂ (SiMe ₂ OMe)] ₂	814.3	21.9	45.2, ^c 56.5 ^d	158.4
Yb[C(SiMe ₃) ₂ (SiMe ₂ CH=CH)] ₂	987.2	27.6	40.0	233.0
Yb[C(SiMe ₃) ₂ (SiMe ₂ R)] ₂	543.5	18.5	36.3	265.7

^a Data for central carbon, i.e., YbCSi₃. ^b ¹J(ⁿM–¹³C) for central carbon. ^c ¹J(C–SiMe₃). ^d ¹J(C–SiMe₂OMe). ^e R = CH₂CH₂OCH₂CH₃.

after several days, there were significant changes. Foreexample, the spectrum from **7** showed none of the peaks present originally but only those due to RH, R = C(SiMe₃)₂(SiMe₂CH=CH₂), and a new set of peaks which did not include any attributable to a vinyl group. The spectrum was identical to that obtained by dissolving the dialkyl **2** in THF-*d*₈. It appears that (a) both the reaction shown in eq (4) (X = CH=CH₂) and the reverse reaction take place rapidly in THF and (b) the dialkyl **2** reacts slowly with THF with cleavage of one Yb–C bond to give RH and formation of a new, as yet unidentified, ytterbium-containing species.

The NMR spectra of a solution of **1** in THF-*d*₈ show the presence of an ytterbium-containing compound together with (Me₃Si)₃CH and (Me₃Si)₃CD from reaction with solvent. A pyrophoric brown solid was isolated from this reaction but has not yet been identified. There are precedents for reactions between *f*-block organometallic compounds and THF. For example, [Cp*₂Sm(THF)₂][BPh₄] (Cp* = C₅Me₅) reacts with KCp* in THF to give Cp*₂Sm[O(CH₂)₄Cp*],^{18a} and NdCl₃ reacts with NaCp* in THF to give Cp*₂Nd[O(CH₂)₄Cp*](THF).^{18b} Though ring-opening reactions of this kind have not been observed with the Yb(+2) and Eu(+2) derivatives described here, a few have been found in other work with LiC(SiMe₃)₃.^{18c}

NMR Data for Dialkylttrerbiums. Data for compounds containing Yb(+2)–C σ -bonds, are summarised in Table 5. It is seen that there are considerable variations in the values for the Yb and central C chemical shifts and for the Yb–C coupling constants, but a wider range of data is needed before significant conclusions can be drawn. Further ¹⁷¹Yb NMR studies are in progress.

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Supporting Information Available: Atomic coordinates, bond lengths and angles, temperature factors, and NMR spectra (42 pages). Ordering information is given on any current masthead page.

OM960493+

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