A Monomeric Solvent-Free Bent Lanthanide Dialkyl and a Lanthanide Analogue of a Grignard Reagent. Crystal Structures of Yb{C(SiMe$_3$)$_3$}$_2$ and [Yb{C(SiMe$_3$)$_3$}I·OEt$_2$]$_2$

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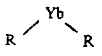
Received May 25, 1994

There is much current interest in the organometallic chemistry of the f-block elements. Considerable progress has been made in developing the chemistry of the +3[1a] and 0[1b] oxidation states: work on the +2 oxidation state has been mainly concerned with polyhapto ligands,[2] especially substituted cyclopentadienyls.

We report the synthesis and crystal structure of bis{tris(trimethylsilyl)methyl}ytterbium, Yb{C(SiMe$_3$)$_3$}$_2$ (**1**), obtained in good yield[4] as a highly air- and moisture-sensitive orange solid from the reaction between YbI$_2$ and K{C(SiMe$_3$)$_3$}[5] in benzene, and the determination of its crystal structure.[6] As far as we are aware this is the first solvent-free dialkyl lanthanide to be characterized. We also describe the preparation and structure of an Yb analogue of a Grignard reagent; these have been used in synthesis but have not previously been isolated.[3]



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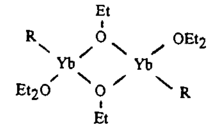

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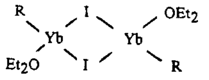

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R = C(SiMe$_3$)$_3$

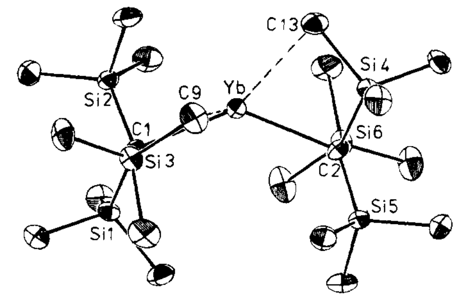

Figure 1. The molecular structure of Yb{C(SiMe$_3$)$_3$}$_2$ (**1**) (50% thermal ellipsoids). Selected distances (Å) and angles (deg): Yb−C(1) 2.490(8), Yb−C(2) 2.501(9), Si(3)−C(9) 1.911(14), Si(4)−C(13) 1.923(12), mean Si−C (1 or 2) 1.838(11), mean Si−Me 1.881(12), Yb···C(9) 2.900(12), Yb···C(13) 2.852(13), C(1)−Yb−C(2) 137.0(4), mean Si−C−Si 114.2(5), mean C−Si−C 104.8(5), Yb−C(1)−Si(1) 125.6(4), Yb−C(1)−Si(2) 89.7(4), Yb−C(1)−Si(3) 96.6(4), Yb−C(2)−Si(4) 94.0(4), Yb−C(2)−Si(5) 125.8(4), Yb−C(2)−Si(6) 89.6(4).

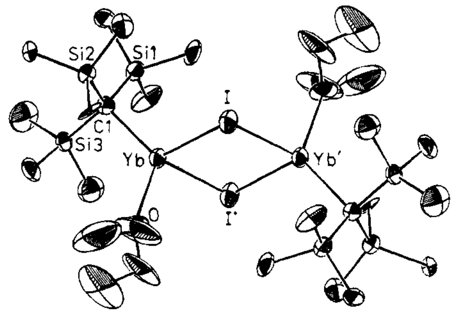

Figure 2. The molecular structure of [Yb{C(SiMe$_3$)$_3$}I·OEt$_2$]$_2$ (**3**) (50% thermal ellipsoids). Selected distances (Å) and angles (deg): Yb−I 3.084(2), Yb−O 2.348(13), Yb−C(1) 2.47(2), mean Si−C(1) 1.84(2), mean Si−Me 1.87(2), I−Yb−I′ 91.92(4), Yb−I−Yb′ 88.08(4), C(1)−Yb−O 123.3(5), C(1)−Yb−I 117.5(4), mean Si−C(1)−Si 113.8(9), mean Me−Si−Me 105(1).

The most interesting and surprising feature of the solid-state structure is that the C−Yb−C angle is 137°. All other known bis{tris(trimethylsilyl)methyl}metal species, whether neutral, *e.g.*, Mg{C(SiMe$_3$)$_3$}$_2$,[7a] or anionic, *e.g.*, [Na{C(SiMe$_3$)$_3$}$_2$]$^-$,[7b] are linear, and we had assumed that interligand Me···Me interactions would force the lanthanide(II) species to be linear also. However, molecules MX$_2$ where M is a heavier group 2 or a divalent group 3 element and X is halogen or cyclopentadienyl appear generally to be bent, and reasons for this have been advanced.[8] For Yb(C$_5$Me$_5$)$_2$, which is bent in both solid and gas phases,[1,9] there appear to be only small differences in energy between linear and nonlinear systems. Our work suggests that dialkyls as well as bis(cyclopentadienyls)[10a] of heavier elements may in general be bent; SrMe$_2$ and BaMe$_2$ have recently been predicted to be nonlinear.[10b] The bending in the case of **1** is possible because the metal−carbon distance (average 2.495(9) Å) is longer than those (*ca.* 2.0 Å) previously observed in linear species[7] (for comparison, the Yb−CH$_3$ distance in (C$_5$H$_5$)$_2$Yb(CH$_3$)THF is 2.36(1) Å),[11] so that interactions between SiMe$_3$ groups are reduced. Further, considerable intraligand distortions are possible. Interactions between the metal and methyl groups of the ligand are shown by short

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[4] A solution of K{C(SiMe$_3$)$_3$} (1.31 g, 4.84 mmol) in benzene (40 cm^3) was added to a suspension of YbI$_2$ (1.03 g, 2.41 mmol) in benzene (20 cm^3), and the mixture was stirred at 20 °C for 48 h. Solvent was removed in vacuum and the orange residue extracted into light petroleum (bp 40−60 °C). Solvent was removed from this extract to give orange plates of **1** (1.30 g, 85%): mp *ca.* 180 °C dec, sublimes 95 °C/10^{-4} Torr; NMR (toluene-d_8, 25 °C chemical shifts relative to SiMe$_4$) ^{1}H (360 MHz) 0.20; ^{13}C (125.76 MHz) 6.17 (Me), 25.77 (Si$_3$*C*) $^1J(^{171}\text{Yb}-^{13}\text{C})$ 126.9 Hz, $^1J(^{29}\text{Si}-^{13}\text{C})$ 20.4 Hz; ^{29}Si (99.36 MHz) −12.08 $^2J(^{171}\text{Yb}-^{29}\text{Si})$ 11.2 Hz (only slightly above noise); ^{171}Yb (43.77 MHz) 812 relative to external (C$_5$Me$_5$)$_2$Yb(THF)$_2$; EI-MS *m/z* 637 (M), 622 (M − Me), 405 (M − C(SiMe$_3$)$_3$), 201, 73.

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[6] A crystal was obtained from cold (−30 °C) methylcyclohexane. Crystal data: space group $P1$, $M = 636.2$, $a = 8.785(3)$ Å, $b = 8.829(4)$ Å, $c = 11.352(3)$ Å, $\alpha = 100.61(3)°$, $\beta = 101.53(2)°$, $\gamma = 109.98°$, $Z = 1$, $D_{\text{calcd}} = 1.36$ g cm^{-3}; monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å), $\mu = 32.2$ cm^{-1}, $T = 173$ K. Significant relections ($|F^2| > 2\sigma(F^2)$) = 2185, $R = 0.0468$, $R' = 0.0548$. Data from a crystal 0.3 × 0.3 × 0.15 mm were collected from an Enraf-Nonius CAD4 diffractometer and corrected for absorption. Non-H atoms were located by direct methods (SHELXS-86), and refinement was by full matrix least squares, with non-H atoms anisotropic and H atoms fixed in calculated positions.

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Yb$\cdots$C(9) and Yb$\cdots$C(13) distances. Similar interactions have been observed in [Li{C(SiMe$_3$)$_3$}]$_2$;[12a] Ln{CH(SiMe$_3$)$_2$}, Ln = La or Sm,[12b] [Yb{N(SiMe$_3$)$_2$}$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$)]$_3$ and [NaYb{N(SiMe$_3$)$_2$}$_3$][13] and discussed in ref 13. The intraligand distortions are at C(1) and C(2) rather than at Si; thus Si(2), Si(3), Si(4), and Si(6) are pulled toward the metal (Yb−C−Si 90−96°), and Si(1) and Si(5) are moved away (Yb−C−Si *ca.* 125°). As in other tris(methylsilyl)methyl−metal derivatives the Si−C−Si angles are larger than, and the C−Si−C angles are smaller than, tetrahedral values. The mean Si−Me distance is similar to that in Mg{C(SiMe$_3$)$_3$}$_2$, but the mean distance from the central C to Si is somewhat shorter (1.834(11) Å compared with 1.877(3) Å), suggesting that negative charge is more effectively delocalized from the metal to carbon in the Yb compound. The bonds from Si to the methyl groups interacting with the Yb (Si(3)−C(9) and Si(4)−C(13)) are longer than the average for all Si−Me bonds.

An attempt to distinguish methyl groups by low-temperature NMR at 500 MHz was unsuccessful: all protons appeared to be equivalent even at −95 °C, as found for the (Me$_3$Si)$_2$N compounds previously mentioned.[13]

The chemistry of **1** is currently being studied. It reacts with diethyl ether in C$_6$D$_6$ at 20 °C according to eq 1 (R = C(SiMe$_3$)$_3$). Both RH and ethene were identified by ^{1}H NMR spectroscopy, and formation of RH was shown to be quantitative.

$$\underset{\mathbf{1}}{\mathrm{YbR_2}} + 2\mathrm{Et_2O} \rightarrow \underset{\mathbf{2}}{0.5[\mathrm{RYb(OEt)(OEt_2)}]_2} + \mathrm{RH} + \mathrm{CH_2{=}CH_2} \quad (1)$$

Compound **2** has been made independently[14] from the reaction between Li{C(SiMe$_3$)$_3$}, KOBu^t, and YbI$_2$ in Et$_2$O, and its crystal structure has been determined. In light of our work, it is probable that it is formed via the intermediates KR and YbR$_2$, **1**. The hydride Lu(η^5-C$_5$Me$_5$)$_2$H also attacks Et$_2$O.[15]

Bis(cyclopentadienyl)ytterbium(II) derivatives react with a variety of alkyl halides to give bis(cyclopentadienyl)ytterbium(III) compounds.[1,2] We considered that **1** was unlikely to do the same because the product would be too crowded. Instead the reaction of **1** with iodomethane led to the highly unusual cleavage of one Yb−C bond and formation of a new Yb(II) compound, [Yb{C(SiMe$_3$)$_3$}I·OEt$_2$]$_2$ (**3**).[16] The same compound was isolated from the reaction between **1** and an excess of ICH$_2$CH$_2$I or more simply from the reaction between Yb metal and (Me$_3$Si)$_3$CI in diethyl ether. The structure of **3** has been confirmed by single-crystal X-ray diffraction.[17] The molecule has a center of symmetry so that the central Yb$_2$I$_2$ ring is planar; as usual in such systems the angle at Yb is slightly larger, and that at I slightly smaller, than 90°. The Yb−C distance is similar to those in **1**. The exocyclic C−Yb−O angles are large, and the (Me$_3$Si)$_3$C ligand displays the usual features; *e.g.*, the Si−C−Si angles are larger and the Me−Si−Me angles smaller than the tetrahedral value. The Si−C(1) and Si−Me bond distances are similar to those in Mg{C(SiMe$_3$)$_3$}$_2$. Analogous structures are adopted by a number of Grignard reagents,[18] but the tris(trimethylsilyl)methylmagnesium halides characterized so far have been complexed by lithium or magnesium halides.[19]

Acknowledgment. We thank the Science and Engineering Research Council for financial support.

Supplementary Material Available: Crystal structure determination details for **1** and **3**, table of torsion angles for **1**, and tables of fractional atomic coordinates and equivalent isotropic parameters, intramolecular distances and angles, hydrogen atom coordinates, and anisotropic temperature factors for **1** and **3** (20 pages); listing of observed and calculated structure factors for **1** and **3** (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[16] (a) An excess of MeI (0.1 cm^3, 1.6 mmol) was added to a solution of **1** (0.33 g, 0.5 mmol) in petroleum ether (bp 40−60 °C, 20 cm^3), and the mixture was stirred for 16 h. The precipitate was filtered off, washed with light petroleum (10 cm^3), and recrystallized from cold (−30 °C) diethyl ether to give exceedingly air- and moisture-sensitive yellow-green plates of **3**: NMR (THF-d_8, 25 °C) ^{1}H (360 MHz) −0.1 (s br, 27 H, Me$_3$Si), 1.10 (t, 6H), and 3.37 (q, 4H, Et). (b) Yb powder (2.07 g, 11.96 mmol) was added to (Me$_3$Si)$_3$CI (4.29 g, 11.96 mmol) in Et$_2$O (60 cm^3) and the mixture stirred for 12 h at 20 °C. The solution was filtered, solvent was removed from the filtrate in vacuum, and the yellow solid residue was washed with light petroleum (2 × 20 cm^3) to give **3**.

[17] Crystal data: space group *Pbca*, $M = 1112.3$, $a = 15.072(4)$ Å, $b = 13.814(6)$ Å, $c = 25.544(5)$ Å, $Z = 4$, $D_{\mathrm{calcd}} = 1.39$ g cm^{-3}; monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å), ($\mu = 30.6$ cm^{-1}, $T = 173$ K. Data from a crystal cut to 0.4 × 0.4 × 0.1 mm. Significant reflections ($|F^2| > 2\sigma(F^2)$) = 2215 corrected for absorption. Non-H atoms were found by heavy atom methods (SHELXS-86), and refinement was by full matrix least squares with most non-H anisotropic and C(1) and Et$_2$O atoms isotropic. H atoms fixed at calculated positions. $R = 0.062$, $R' = 0.063$. The Et$_2$O is disordered over an inversion center.

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