The first structurally characterised solvent-free σ-bonded diorganocalcium, $Ca[C(SiMe_3)_3]_2$

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The monomeric solvent-free compound CaR_2 1 [R = $C(SiMe_3)_3$] is obtained as colourless air- and moisture-sensitive crystals from the reaction between KR and CaI_2; in the solid the C–Ca–C axis is bent with Ca–C 2.459(9) Å and C–Ca–C 149.7(6)°; reactions of 1 with ethers ROEt give RH, ethene and $Ca(OEt)_2$.

The structures of several bis(cyclopentadienyl) derivatives of the heavier group 2 elements have been determined[1] but to our knowledge the only structural determination of a σ-bonded diorgano derivative is that of bis[bis(trimethylsilyl)methyl] calcium which was characterised as a 1,4-dioxane adduct $Ca[CH(SiMe_3)_2]_2 \cdot 2C_4H_8O_2$.[2] Other σ-bonded dialkyls and diaryls have been characterised by the products of their reactions with electrophiles such as CO_2, carbonyl compounds, nitriles, or terminal alkynes.[3,4] We recently showed that the readily available reagent KR [R = $C(SiMe_3)_3$] reacts with LnI_2 (Ln = Yb, Eu) in benzene[5] or Sm in thf–heptane[6] (thf = tetrahydrofuran), to give solvent-free dialkyls LnR_2. Here we report a similar reaction with CaI_2 to give solvent-free bis[tris(trimethylsilyl)methyl]calcium, $Ca\{C(SiMe_3)_3\}_2$ **1** which was isolated as a colourless air- and moisture-sensitive solid.†

The structure of **1** (Fig. 1) was determined by an X-ray diffraction study‡ on a very thin plate that separated from heptane–benzene. Although the molecules lie across a crystallographic inversion centre there are three independent sites for the calcium atom, which is disordered over positions related by an approximate $\bar{3}$ axis. This indicates that the equilibrium structure in the solid is bent. (Refinement with a linear C–Ca–C skeleton led to unacceptably large anisotropic displacement parameters with electron density away from the molecular axis.) Although the atoms of the alkyl group R appear to be well defined, their positions must be an average of closely related sites corresponding to the various Ca positions. However, the values for the Ca–C distance, the C–Ca–C angle and probably the mean C–Si distances are reliable. The Ca–C distance, 2.459(9) Å, is similar to those in the adduct $Ca[CH(SiMe_3)_2]_2 \cdot 2C_4H_8O_2$ [2.483(5) Å], in which the Ca is four-coordinate.[2] It is significantly shorter than the Ca–C distances in cyclopentadienyl derivatives (*ca.* 2.65 Å), in the 2,3-dimethyl-1,4-diphenylbutadiene adduct $Ca(PhCH{=}C\text{-}MeCMe{=}CHPh)(thf)_4$ [2.588(7)–2.777(7) Å], in which the Ca is six-coordinate,[8] and in the electron-deficient methyl-bridged compound $[(C_5Me_5)_2CaAlMe_3(thf)]_2$ [2.948(7), 2.999(7) Å].[9] In **1** there are three Ca···Me contacts of *ca.* 3.08 Å for each position of the Ca atom [from Ca to C(4), C(7′), and C(9), *cf.* Ca···Me 2.98 Å in $Ca(C_5Me_5)_2$ **2**]. The most important feature of the structure is the C–Ca–C angle [149.7(6)°], which is almost the same as those (147 and 154°, respectively) in crystalline[10] and gaseous[11] **2**, a little smaller than that (162°) in the exceedingly crowded $Ca(C_5HPr^i_4)_2$[12] and similar to that (148°) reported for gaseous CaI_2[13] (though the value for CaI_2 may be affected by the presence of dimers and shrinkage effects associated with the ν_2 bending vibration[14]). Simple electron repulsion rules predict that the monomeric calcium compounds CaX_2 (X = halogen, alkyl, *etc.*) should be linear but bent structures have been suggested by recent modifications to the original theory.[15,17] High level *ab initio* calculations also indicate that many calcium compounds, including $CaMe_2$, are quasilinear, *i.e.* the plot of potential energy *vs.* bending angle is almost flat, at least out to 160°;[18,19] angles of 131 and 116°, respectively, are predicted for $SrMe_2$ and $BaMe_2$. For compound **1** in the crystalline state the bending could possibly be attributed to crystal packing forces influenced by the intramolecular Ca···Me interactions but, in contrast to the situation in **2**, there are no significant intermolecular interactions. It is noteworthy and perhaps important that the C–Ca–C angles in compounds **1**, **2** and gaseous CaI_2 are all in the range 148–154°. In the compound $Yb[C(SiMe_3)_3]_2$ **3** and the Eu analogue **4** the C–M–C angles are 136–137° but the Mg compound **5** is linear.[20]

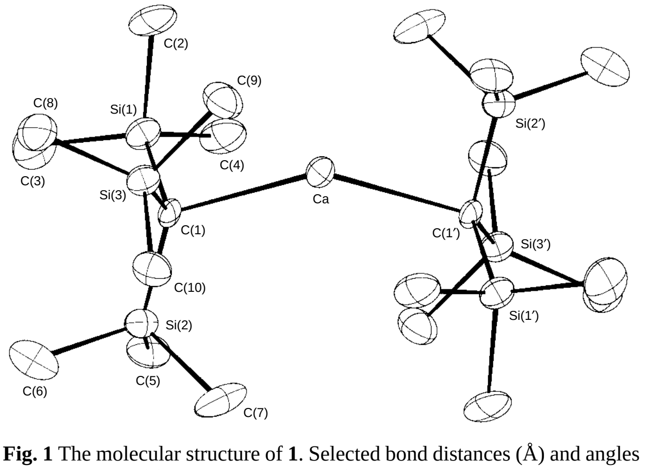

Fig. 1 The molecular structure of **1**. Selected bond distances (Å) and angles (°): Ca–C 2.459(9), mean C(1)–Si 1.83(1), mean Si–Me 1.87(2); C–Ca–C 149.7(6), mean Si–C(1)–Si 114.8(6), mean Me–Si–Me 104.8(6).

The inner Si–C bond length in **1** is similar to those in **3** and **4** but shorter than that in **5**, suggesting that the metal–carbon bonds in the Ca, Yb and Eu derivatives are more ionic than those in the Mg compound.

We showed previously[5] that **3** reacted with diethyl ether to give the alkyl alkoxy compound $Yb[C(SiMe_3)_3](OEt)$, characterised by others as the diethyl etherate.[21] NMR-tube experiments showed that the analogous reaction of **1** with an excess of Et_2O yielded RH [R = $C(SiMe_3)_3$], quantitatively, ethene, identified by its signal at δ_H 5.26, and insoluble $Ca(OEt)_2$ [eqn. (1)].

$$CaR_2 + 2Et_2O \rightarrow 2RH + 2C_2H_4 + Ca(OEt)_2 \qquad (1)$$

With 1 equiv. of Et_2O only half of the CaR_2 was consumed, showing that the intermediate $Ca[C(SiMe_3)_3](OEt)$ reacts faster with Et_2O than the dialkyl. Reactions with other ethers ROEt (R = Bu^t, Ph) proceeded in the same way but more slowly. No reaction was detected with PhOMe or Pr^i_2O. Compound **1** reacted rapidly with thf to give what appeared to be polymeric material (this was surprising since there are reports that organocalcium compounds are formed in much higher yield in thf than in Et_2O[4]). The reaction of **1** (1.99 mmol) with an excess of MeI gave RH (0.47 mmol), RI (0.96 mmol) and RMe (0.56 mmol), behaviour analogous to that of the ytterbium compound

3 but different from that of Mg[C(SiMe$_3$)$_3$]$_2$ **5** which does not react with MeI under similar conditions.[20] The higher reactivity of **1** than of **4** is probably due in part to the structural differences. In **4** the Mg–C bond is short [2.116(2) Å], and the methyl groups interlock tightly round the linear C–Mg–C axis to protect the central atom.[20] In contrast the metal–carbon bond in **1** is longer, the skeleton is bent, and both the metal and the carbanionic centres are more exposed to attack.

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Footnotes and References

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† A solution of KC(SiMe$_3$)$_3$ (2.5 g, 9.23 mmol) in benzene (20 cm^3) was added to a suspension of CaI$_2$[7] (1.45 g, 4.93 mmol) in benzene (20 cm^3) and the mixture was stirred for 48 h. The solvent was removed under vacuum and the residue was extracted with light petroleum (bp 40–60 °C, 60 cm^3). The extract was filtered through Celite and the solvent pumped away. The residue was recrystallised from heptane–benzene (3:1) to give **1** (2.03 g, 87%), mp 244–246 °C. Anal. Calc. for C$_{20}$H$_{54}$CaSi$_6$: C, 47.7, H, 10.7. Found: C, 41.7; H, 9.5%. δ_H (300 MHz, C$_6$D$_6$) 0.24 (s, SiMe$_3$); δ_C 7.2 (SiMe$_3$), 20.3 [*J*(SiC) 39.6 Hz, CSi$_3$]; δ_{Si} 12.1. EIMS *m/z* 502 (1% M), 487.220 (8%, M − Me, C$_{19}$H$_{51}$CaSi$_6$ requires *m/z* 487.223), 271, 100%.

‡ *Crystal data* for **1**: $M = 503.3$; triclinic, space group $P\bar{1}$; $a = 8.948(2)$, $b = 9.104(2)$, $c = 12.067(2)$ Å, $\alpha = 95.53(2)$, $\beta = 104.79(2)$, $\gamma = 119.05(2)°$, $U = 802.1(3)$ Å^3; $D_c = 1.04$ Mg m^{-3}, $Z = 1$, $F(000) = 278$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, crystal size 0.40 × 0.40 × 0.05 mm, μ(Mo-Kα) = 0.43 mm^{-1}, $T = 225(2)$ K. CAD4 diffractometer, θ–2θ scan mode, $2 < \theta < 22°$, 1961 independent reflections. Structure solution by direct methods (SHELXS-86) and full-matrix least-squares refinement (SHELXL-93) with all non-H atoms anisotropic and H atoms in riding mode with $U_{iso} = 1.5\,U_{eq}$(C). The Ca–C(1) distances for the three alternative sites were loosely restrained to a single value. Final R_1 0.102 for 1013 reflections with $I > 2\sigma(I)$, wR_2 0.326 (all data). CCDC 182/585.

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