Metal Vapour Synthesis of Bis{1,3-bis(trimethylsilyl)cyclopentadienyl}-calcium, -strontium, and -barium Compounds; *X*-Ray Structures of [M{η-C_5H_3-1,3-$(SiMe_3)_2$}$_2$(thf)] (M=Ca, Sr; thf = tetrahydrofuran)

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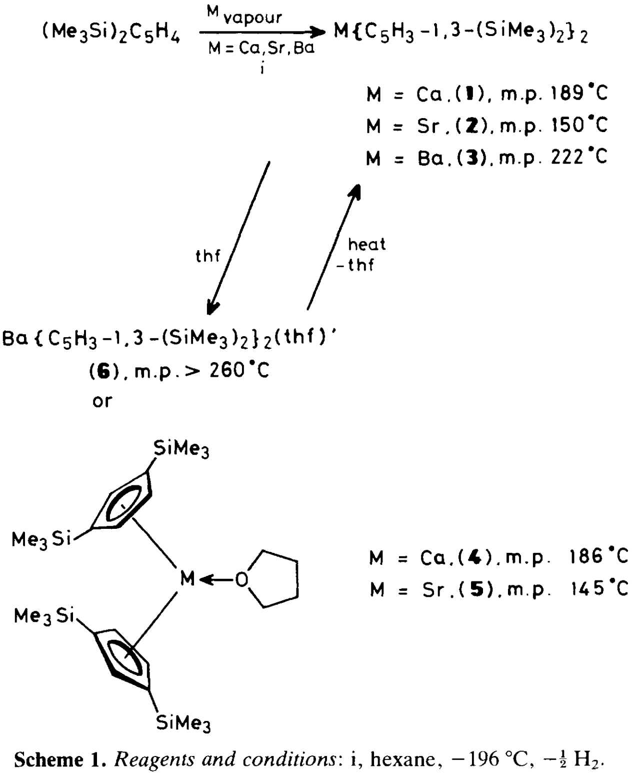
Cocondensation of $C_5H_4(SiMe_3)_2$, hexane, and metal vapour at −196 °C yields M{C_5H_3-1,3-$(SiMe_3)_2$}$_2$ [M = Ca (**1**), Sr (**2**), and Ba (**3**)] which reversibly bind tetrahydrofuran (thf); *X*-ray structure determinations on the adducts [M{η-C_5H_3-1,3-$(SiMe_3)_2$}$_2$(thf)], [M = Ca (**4**) Sr, (**5**)] show they are monomeric bent metallocenes, M–C, M–O 2.662(10)—2.718(9), 2.310(9), (**4**), 2.78(4)—2.84(5), 2.49(3) Å, (**5**); Centroid–M–Centroid, 139.1, (**4**), 134°, (**5**).

The ability of bis(cyclopentadienyl)-calcium, -strontium, and -barium compounds to form isolable Lewis base adducts, *e.g.*, $Ca(C_5H_5)_2(thf)_2$ (thf = tetrahydrofuran),[1] $M(C_5Me_5)_2(OEt_2)$ (M = Ca,[2] Sr[3]) and $Ba(C_5Me_5)_2(thf)_2$,[3] distinguishes them from the corresponding compounds of the lighter group II congeners. However, the degree of association and type of metal–hydrocarbyl interaction in these adducts are unknown. Indeed the only structural information on bis(cyclopentadienyl)s is on some unsolvated species, namely polymeric $Ca(C_5H_5)_2$ (solid) and monomeric [M(η-$C_5Me_5)_2$](M = Ca,[2] Sr and Ba[3])(gas phase).



Scheme 1. *Reagents and conditions*: i, hexane, −196 °C, $-\frac{1}{2}$ H_2.

We report (i) the synthesis of M{C_5H_3-1,3-$(SiMe_3)_2$}$_2$, [M = Ca (**1**), Sr (**2**), Ba (**3**)] *via* cocondensation of $C_5H_4(SiMe_3)_2$, hexane, and metal vapour at −196 °C then warming to room temperature (*cf.* synthesis of $M(C_5H_5)_2$ (M = Ca, Sr, Ba[4]), yields 54, 57, and 83% respectively;‡ (ii) formation of thf adducts of (**1**)—(**3**), M{C_5H_3-1,3-$(SiMe_3)_2$(thf) [M = Ca (**4**), Sr (**5**), Ba (**6**)], yields ~85%; (iii) interconversion of (**1**)—(**3**) and (**4**)—(**6**), Scheme 1; and (iv) the *X*-ray structures of (**4**) and (**5**),§ the latter representing the first solid state structure

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‡ Characterization of new compounds (**1**)—(**6**): (**1**) and (**4**) gave satisfactory elemental analyses; C, H analyses for the strontium and barium compounds were consistently 1—2% low. ^1H N.m.r. data for complexes (**1**)—(**5**) (300 MHz, C_6D_6): (**1**), δ 0.29 (s, 18H, $SiMe_3$), 6.49 (m, 2H, $H_{4,5}$), 6.52 (m, 1H, H_2); (**2**), δ 0.31 (s, 18H, $SiMe_3$), 6.49 (m, 2H, $H_{4,5}$), 6.48 (m, 1H, H_2); (**3**), δ 0.44 (s, 18H, $SiMe_3$), 6.57 (s, 3H, $H_{2,4,5}$); (**4**), δ 0.32 (s, 18H, $SiMe_3$), 1.26 (m, 2H, CH_2CH_2), 3.49 (m, 2H, CH_2O), 6.58 (m, 1H, H_2), 6.77 (m, 2H, $H_{4,5}$); (**5**), δ 0.31 (s, 18H, $SiMe_3$), 1.31 (m, 2H, CH_2CH_2), 3.45 (m, 2H, CH_2O), 6.54 (m, 1H, H_2), 6.63 (m, 2H, $H_{4,5}$). ^{13}C N.m.r. data for complexes (**1**)—(**5**) (75.5 MHz, C_6D_6): (**1**), δ 0.6 ($SiMe_3$), 121.3 ($C_{4,5}$), 125.3 ($C_{1,3}$), 123.0 (C_2); (**2**), δ 1.2 ($SiMe_3$), 120.6 ($C_{4,5}$), 122.1 ($C_{1,3}$), 125.6 (C_2); (**3**), δ 1.5 ($SiMe_3$), 121.5 ($C_{4,5}$), 123.2 ($C_{1,3}$), 126.2 (C_2); (**4**), δ 1.0 ($SiMe_3$), 25.3 (CH_2CH_2), 70.0 (CH_2O), 120.0 ($C_{4,5}$), 121.6 ($C_{1,3}$), 124.3 (C_2); (**5**), δ 1.0 ($SiMe_3$), 25.3 (CH_2CH_2), 70.1 (CH_2O), 119.9 ($C_{4,5}$), 121.9 ($C_{1,3}$), 124.2 (C_2).

§ *Crystal data* for (**4**) {and (**5**)}: M = 531.1 {578.7} orthorhombic, space group *Pnab* (No. 60), a = 21.585(6){21.522(8)}, b = 13.781(9){13.973(6)}, c = 11.471(3){11.801(3)}Å, Z = 4, D_c = 1.03{1.08} g cm^{-3}, $F(000)$ = 1160{1232}, μ(Mo-K_α) = 3.3{17.4}cm^{-1}, 758{356} 'observed' reflections [$I > 2\sigma(I)\{3\sigma(I)\}$], $2\theta_{max.}$ = 45° (both), R = 0.079{0.081}, R_w = 0.043{0.070}; Mo-K_α radiation [T = 295 K]. Syntex $P2_1$ diffractometer. Both data sets were weak and limited in scope (high thermal motion); non-hydrogen atom thermal parameter refinement anisotropic (**4**), isotropic (**5**) (except Sr anisotropic). The structures were solved by the heavy atom method and refined by full-matrix least-squares.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

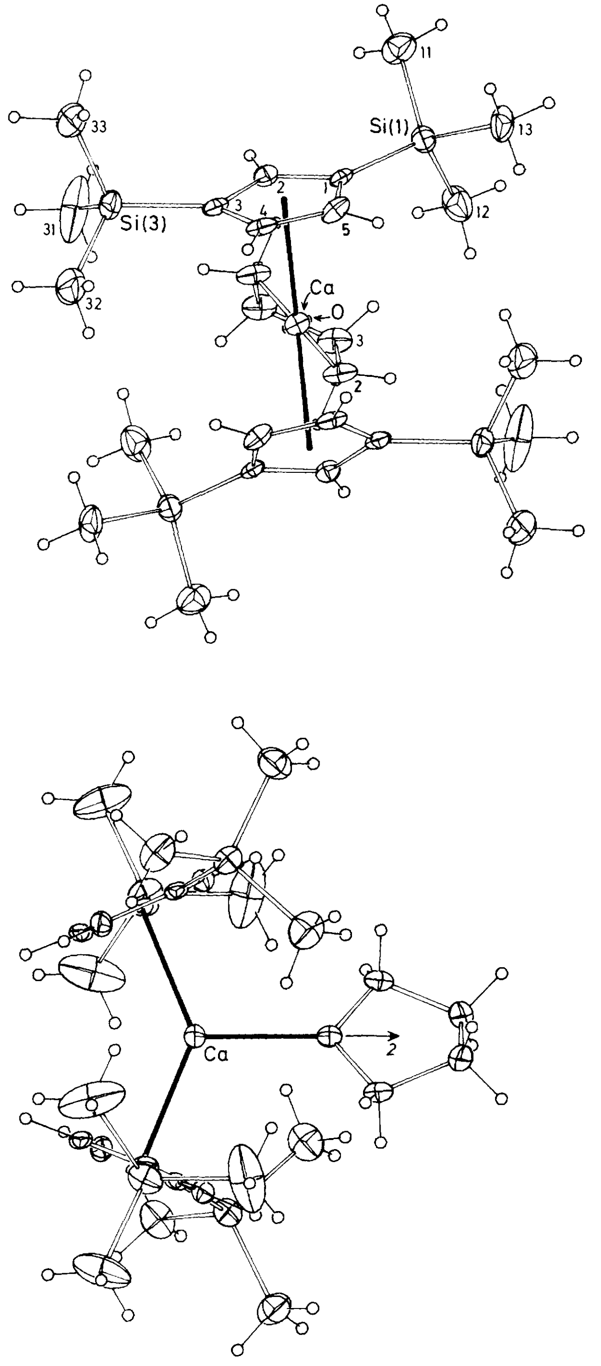

Figure 1. Molecular projections of $[\mathrm{Ca}\{\eta\text{-}\mathrm{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2}\}_2(\mathrm{thf})]$, (**4**), showing atom labelling scheme and 20% thermal ellipsoids for the non-hydrogen atoms, and arbitrary radii for hydrogen atoms. Selected bond distances (Å) and angles (°) and corresponding values [in brackets] for the strontium analogue (**5**) are M–O 2.310(9) [2.49(3)]; M–C 2.662(10)—2.718(9) [2.78(4)—2.84(5)]; M-Centroid 2.397 [2.551]; Centroid-M-Centroid 135.1 [134]; Centroid-M-O 112.4 [112].

determination of an organostrontium compound. Both structures are novel in that the species are monomeric.

Compounds (**1**)—(**3**) can be purified by sublimation, *ca.* 180, 200, and 340 °C, respectively, at *ca.* 10^{-3} mmHg, yielding fine needles, unfortunately unsuitable for *X*-ray structuure determinations. Similar treatment of (**4**)—(**6**) resulted in sublimation with loss of thf, although for (**4**) complete loss of thf required three such operations. All compounds gave the largest ion in the mass spectrum corresponding to $[\mathrm{M\{C_5H_3\text{-}1,3\text{-}(SiMe)_2\}_2}]^+$, further highlighting the ease of loss of thf for (**4**)—(**6**). Crystals of (**4**) and (**5**) for the structural investigations were obtained *via* recrystallization from benzene; compound (**6**) is only sparingly soluble in either benzene or thf which precluded characterization using n.m.r. spectroscopy and suggests a polymeric and/or ionic structure. In contrast, the unsolvated analogue, (**3**), is moderately soluble in benzene, although less soluble than (**1**) and (**2**). This coupled with the volatility inequality (**1**)~(**2**)>(**3**) (above) is consistent with a greater degree of association of (**3**) compared to (**1**) and (**2**). The compound $\mathrm{Ca(C_5H_5)_2}$ is polymeric in the solid and gives $\mathrm{Ca_2(C_5H_5)_3}^+$ in its mass spectrum.[1] The incorporation of four trimethylsilyl groups, (**4**), is expected to reduce molecular aggregation, possibly to monomeric species, and also increase covalency relative to $\mathrm{Ca(C_5H_5)_2}$.[5,6]

Compounds (**4**) and (**5**) are isomorphous and isostructural. They comprise monomeric species of crystallographic C_2 symmetry, the metal centres being trigonal planar, assuming that the cyclopentadienyl ring centroids occupy one co-ordination site. Molecular projections and selected structural parameters are given in Figure 1; Sr–C and Sr–O distances are *ca.* 0.14 and 0.18 Å, respectively, longer than Ca–C and Ca–O distances, paralleling the difference in ionic radii for $\mathrm{Ca^{2+}}$ and $\mathrm{Sr^{2+}}$ which is 0.21 Å.[7] The molecules can be classified as bent metallocenes, the Centroid–M–Centroid angles being 135.1° (**4**) and 134 (**5**), much less than in the unsolvated bent metallocenes $[\mathrm{M(\eta\text{-}C_5Me_5)_2}]$ (M = Ca,[2] Sr[3])(gas phase), 154(3)° and 149(3)°. It is noteworthy that the metal-carbon distances in (**4**) and (**5**) are longer than in these compounds as expected since solvation, by thf, should result in greater ionic character; $\mathrm{M\text{–}C_{mean}}$ 2.68_2 Å in (**4**), *cf.* 2.609(6) Å in $[\mathrm{Ca(\eta\text{-}C_5Me_5)_2}]$,[2] and 2.8_2 Å in (**5**), *cf.* 2.750(8) Å in $[\mathrm{Sr(\eta\text{-}C_5Me_5)_2}]$.[3] Moreover, the $\mathrm{M\text{–}C_{mean}}$ distance in (**4**) is intermediate between that of $[\mathrm{Ca(\eta\text{-}C_5Me_5)_2}]$,[2] and $\mathrm{Ca(C_5H_5)_2}$. The larger distance in the latter (2.83_6 Å) is commensurate with a higher number of metal–ligand contacts compared to (**4**) and the permethylated analogue; the compound is polymeric with 2 × η^5-, η^3-, and σ-metal–ligand interactions.[5]

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