Metallocene(III) Tetrahydridoborates of the Group 3A Elements and the *X*-Ray Structure of $[Sc\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2(\mu\text{-}H)_2BH_2]$†

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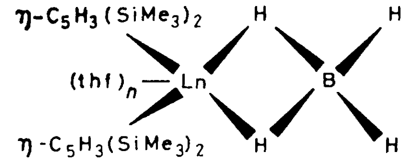
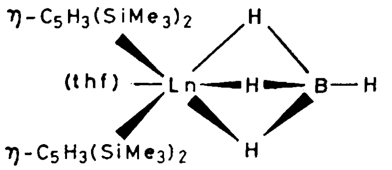
Complexes of a range of group 3A metals (Ln) of formula $[Ln\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2(BH_4)(thf)_n]$ (thf = tetrahydrofuran, n = 1 or, for Ln = Sc, n = 0) have either a $(\mu\text{-}H)_2$ (for the smaller metals: Ln = Sc, Y, or Yb) or a $(\mu\text{-}H)_3$ (Ln = La, Pr, Nd, or Sm) bridge, and only with the smallest of these (Sc) is the BH_4^- ligand non-fluxional (^{11}B n.m.r. spectroscopy) at ambient temperature although rapid bridging hydrogen ⇌ terminal hydrogen exchange occurs at 100 °C; the *X*-ray crystal structure of this title Sc compound shows Sc–H 2.03(4) and Sc. . . . B 2.52(3) Å and confirms the bidentate mode of BH_4^- bonding.

We report the synthesis, characterisation, and structures of a representative and substantial series of Group 3A element tetrahydridoboratometallocene(III) complexes of formula $[Ln\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2(BH_4)(thf)_n]$, in which Ln^{3+} is $Sc^{3+}(3d^0)$, $Y^{3+}(4d^0)$, $La^{3+}(4f^0)$, $Pr^{3+}(4f^2)$, $Nd^{3+}(4f^3)$, $Sm^{3+}(4f^5)$, or $Yb^{3+}(4f^{13})$ and $n = 1$ except for Ln = Sc when $n = 0$ (thf = tetrahydrofuran). We conclude, from the i.r. spectra, that the Sc, Y, and Yb complexes (*i.e.*, those of the smallest Ln^{3+} radius) have bidentate BH_4^-, (**1**) whereas for the remainder the tetrahydridoborate is acting as a tridentate ligand, (**2**); structure (**1**) is confirmed in the solid state for the Sc^{3+} title complex (**1a**) by *X*-ray crystallography.

We further find that the complex (**1a**) formed by the smallest of the metal ions, Sc^{3+}, is unique not only in that it does not bind solvent thf but also that at ambient temperature the fluxional exchange process between bridge (H_b) and terminal (H_t) hydrogens is slow on the n.m.r. time scale. This latter phenomenon is demonstrated most readily by ^{11}B n.m.r. spectroscopy by a procedure which does not appear to have been observed previously for the many known metal tetrahydridoborates. Thus at ambient temperature the ^{11}B n.m.r. spectrum at 25.71 MHz of complex (**1a**) in $[^2H_8]$toluene shows a broad featureless band ($w_{\frac{1}{2}}$ *ca.* 320 Hz and *ca.* 120 Hz when broad-band proton decoupled) which with increase of temperature gradually reveals structure until at *ca.* 100 °C a 1:4:6:4:1 quintet is observed [similar to that found for the other complexes (**1**), (**2a**), and (**2d**) under ambient conditions] which is due to coupling with four equivalent protons, arising from fast $H_b \rightleftharpoons H_t$ exchange, $J(^{11}B^1H)$ 75 Hz.



(**1**) **a**; Ln = Sc (n = 0), m.p. 82—84 °C, white
b; Ln = Y (n = 1), m.p. 130—132 °C, white
c; Ln = Yb (n = 1), m.p. 125—128 °C, maroon



(**2**) **a**; Ln = La, m.p. 93—95 °C, white
b; Ln = Pr, m.p. 105—107 °C, green
c; Ln = Nd, m.p. 113—115 °C, blue-violet
d; Ln = Sm, m.p. 115—117 °C, yellow

Complexes (**1**) and (**2**) were prepared by $Cl^-/[BH_4]^-$ displacement, as is illustrated for (**2b**). A mixture containing $[(Nd\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2\{\mu\text{-}Cl\})_2]$(2.62 g, 4.38 mmol) and excess of $NaBH_4$ (1.46 g, 38.59 mmol) in thf was stirred at 20 °C for about 48 h and then filtered. The volatile components were removed under vacuum. The residue was dissolved in n-pentane, filtered, concentrated, and cooled (−10 to −30 °C) to give mauve coloured crystals of complex (**2b**) (1.25 g, 44%).

The seven complexes (**1**) and (**2**) gave satisfactory microanalyses, i.r. spectra, and [for (**1a**), (**1b**), (**2a**), and (**2d**)] ^1H, ^{13}C, and ^{11}B n.m.r. spectra.‡ Our i.r. structural conclusions [structures (**1**) and (**2**)] with regard to the mode of BH_4^- bonding are based on the rules summarised in ref. 2. The diagnostic features for the bidentate complexes (**1**) are (i) a strong broad band centred at around 2415 cm^{-1} [assigned to $B(H_t)_2$ A_1 and B_1 modes] and (ii) a sharp singlet at *ca.* 2125 cm^{-1} [$B(H_b)_2$ A_1 and B_2 modes]; and for the tridentate complexes (**2**): (iii) a sharp singlet at *ca.* 2420 cm^{-1} [$B(H_t)$, A_1] and (iv) a strong broad band centred at *ca.* 2240 cm^{-1} [$B(H_b)_2$ A_1 and E modes]. The ^{11}B n.m.r. data may be compared with those summarised in ref. 3. The ambient temperature ^{11}B n.m.r. spectra of all complexes (**1**) and (**2**) apart from the Sc compound (**1a**) resemble those previously obtained for other tetrahydridoborates, except for some Ir^{III} complexes $[IrH_2(BH_4)L_2]$ (L = a bulky phosphine, such as $PBu^t{}_2Me$)[4] which are similar to those of (**1a**). Our observation that the $H_b \rightleftharpoons H_t$ exchange is appreciably slower for Sc (**1a**) than Y (**1b**) is consistent with the same trend in $Me_b \rightleftharpoons Me_t$ exchange in $[Ln(\eta\text{-}C_5H_5)_2(\mu\text{-}Me)_2AlMe_2]$.[5] Another BH_4^- complex which is fluxional on the n.m.r. time scale has recently been reported: $[Ru(H)(\eta^2\text{-}BH_4)\{Ph_2P(CH_2CH_2CH_2PPh_2)_2\}]$, for which the mechanism of H_b/H_t exchange was studied by variable temperature ^1H n.m.r. spectroscopy.[6]

The present communication provides a further illustration (*cf.* ref. 1) of the use of the $^-C_5H_3(SiMe_3)_2$ ligand to gain access to hydrocarbon-soluble functionalised complexes of the early (f^0—f^3) metallocene(III)s of the lanthanoids, in this instance of the tetrahydridoborates. Some analogues of the later (and more covalent) lanthanoids of formula $[Ln(\eta\text{-}C_5H_5)_2(BH_4)(thf)]$, the f^5 (Ln = Sm), f^{11} (Ln = Er), and f^{13} (Ln = Yb) have been obtained and i.r. data indicated structures similar to (**1**) (Er or Yb) or (**2**) (Sm);[7] the Lu (f^{14}) analogue has been identified in solution.[8]

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† No reprints available.

‡ ^{11}B N.m.r. chemical shift, centre of multiplet, in p.p.m. from $BF_3{\cdot}OEt_2$, and in parentheses coupling constant (Hz): (**1b**), −22.03 (81); (**2a**), −26.68 (81); (**2d**), −43.11.

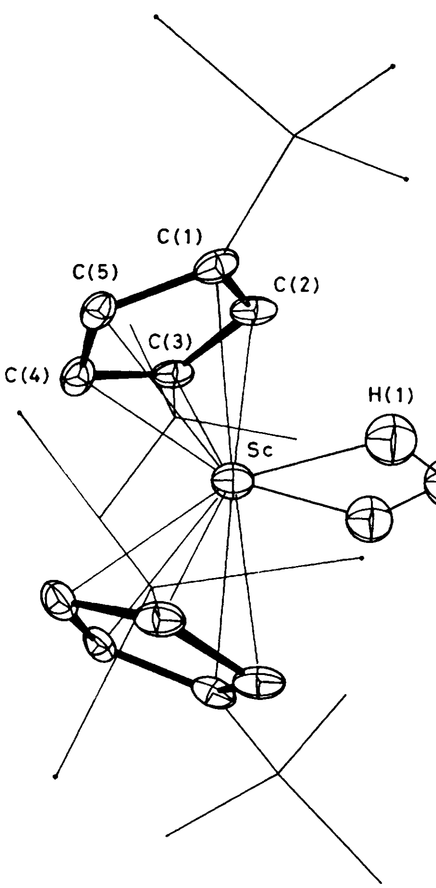

Figure 1. Molecular structure of [Sc{η-$C_5H_3(SiMe_3)_2$}$_2$(μ-H)$_2BH_2$], (**1a**), which contains a crystallographic two-fold axis which passes through Sc and B; the hydrogen atoms of the cyclopentadienyl ligand are omitted. Some important bond lengths and angles: Sc–H(1) 2.03(4), Sc–C(1) 2.496(5), Sc–C(2) 2.475(5), Sc–C(3) 2.473(6), Sc–C(4) 2.463(6), Sc–C(5) 2.457(6), B–H(1) 1.19(4), B–H(2) 1.19(7), Sc . . . . B 2.52(2) Å; H(1)–Sc–H(1′) 55(2), H(1)–B–H(1′) 105(3), H(2)–B–H(2′) 128(5), Cent–Sc–Cent′ 136.0, Cent–Sc–H(1) 110°.

Three group 3A metal tetrahydridoborates have previously been characterised by single crystal *X*-ray crystallography; two are members of the series [Ln$(BH_4)_3$(thf)$_n$] [Ln = Sc with n = 2,[9] (**3a**), and Ln = Y with n = 3,[10] (**3b**)] and a third is [Y$(BH_4)_2$(thf)$_4$][Y$(BH_4)_4$].[11] We now add to this a member of the metallocene(III) series, the title compound (**1a**). In each of the complexes (**3**) there is one bi- and two tri-dentate BH_4^- ligands. It appears that the tridentate form of bonding is found only for the larger metal ions, *i.e.*, those with an ionic radius greater than *ca.* 0.7 Å,[10] of which the first example appears to be that of [Zr$(BH_4)_4$].[12]

[Ln$(BH_4)_3$(thf)$_n$] [{Y(η-$C_5H_4Me)_2$(μ-H)(thf)}$_2$]
(**3**) (**4**)

a; Ln = Sc, n = 2
b; Ln = Y, n = 3

The bidentate co-ordination of BH_4^- in [Sc{η-$C_5H_3(SiMe_3)_2$}$_2(BH_4)$], (**1a**), is indicated both directly and by inference. The hydrogen atoms were clearly located and refined to convergence. The resulting bond lengths and angles are all reasonable. The Sc . . . B separation, 2.52(3) Å, agrees well with the Y . . . B distance of 2.68(2) Å for the bidentate BH_4^- in (**3b**), after allowing 0.20 Å for the difference in metal radii.[13] The $\overline{\mathrm{ScHBH}}$ ring also bears a resemblance to the $\overline{\mathrm{YHYH}}$ unit in [{Y(η-$C_5H_4Me)_2$(μ-H)(thf)}$_2$],[14] (**4**). In (**4**) the Y–H length is 2.18(9) Å, which compares well with the Sc–H value in (**1a**) of 2.03(4) Å, after radius correction (*q.v.*).[13]

The Sc–C(η) average, 2.47 Å, is comparable to that of the 2.48, 2.49, and 2.51 Å standards in [{Sc(η-$C_5H_5)_2$(μ-Cl)}$_2$],[15] [Sc(η-$C_5H_5)_3$],[16] and [(Sc{η-$C_5H_3(SiMe_3)_2$}$_2${μ-Cl})$_2$],[1] respectively. Thus, even with the bulky $^-C_5H_3(SiMe_3)_2$ ligand, a close metal–ring approach is found for complex (**1a**), the molecular structure of which is illustrated in Figure 1.

Crystal data for (**1a**): $C_{22}H_{46}BScSi_4$, monoclinic, $P2/c$, $M = 478.77$, $a = 11.245(3)$, $b = 13.114(3)$, $c = 10.588(3)$ Å, $\beta = 103.31(2)°$, $U = 1519.4$ Å^3, $Z = 2$, $D_c = 1.05$ g cm^{-3}, μ(Mo-K_α) = 4.07 cm^{-1}. The structure was refined to R = 0.032, R_ω = 0.036, based on 811 observed reflections.§

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§ The atomic co-ordinates for this work are available on request from the Director of the Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.