$B(C_6F_5)_3$ as a C_6F_5 transfer reagent in zirconium chemistry: facile formation of the borole-bridged triple-decker complex $[Zr_2Cp''_2(C_6F_5)_2\{\mu\text{-}\eta^5:\eta^5\text{-}C_4H_4BCH_2\text{-}\eta^3,\kappa F\text{-}CHCHCHB(C_6F_5)_3\}]$

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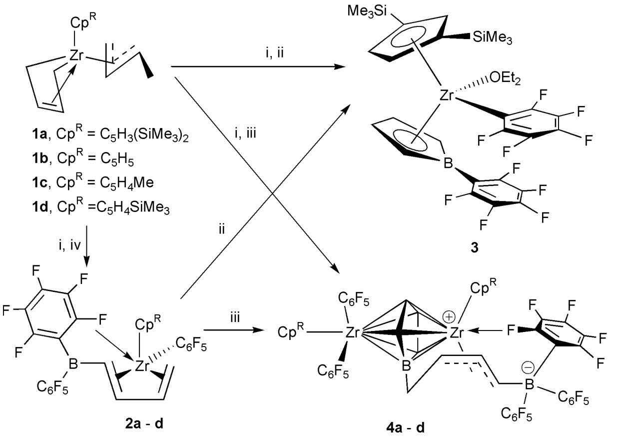
Warming mixtures of $(Cp^R)Zr(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)$ and $B(C_6F_5)_3$ leads to complete transfer of all three C_6F_5 substituents of a $B(C_6F_5)_3$ molecule to give borole-bridged triple-decker complexes with a Zr_2C_4B core, a zwitterionic structure and an unusually strong Zr–F donor interaction.

Early transition complexes of the borole dianion $[C_4H_4BR]^{2-}$ have attracted attention as potential alkene polymerisation catalysts.[1] Two general synthetic strategies have been employed: the dehydrogenation of 2,5-dihydo-1*H*-boroles with various transition metal compounds,[2] or the reaction of metal halides with a pre-formed borole dianion.[3] We found recently that zirconium 1,3-diene complexes $(Cp^R)Zr(\eta^3\text{-allyl})(\eta^4\text{-diene})$ **1** react with $B(C_6F_5)_3$ *via* C–H activation and C_6F_5 transfer steps to give boryldiene compounds **2**;[4,5] for Cp^R = 1,3-$C_5H_3(SiMe_3)_2$ **2a**, this decomposes further under carefully controlled conditions (prolonged storage at 5 °C) *via* another C–H activation step to give the pentafluorophenylborole complex **3** (Scheme 1).[6] We now report a similar reaction sequence leading to the unexpected formation of zirconium triple-decker complexes **4** containing a novel *ansa*borole-allyl ligand.

Warming an equimolar mixture of $B(C_6F_5)_3$ and $Zr(\eta^3\text{-}C_4H_7)(\eta^4\text{-1,3-butadiene})Cp''$ [Cp'' = 1,3-$C_5H_3(SiMe_3)_2$] to 50 °C for 2 h gave a red solution which did not contain the expected **3** but a new product **4a** in high yield. Removal of the volatiles and recrystallisation from diethyl ether provided a red crystalline solid, identified as the triple-decker zirconium complex $Zr_2Cp''_2(C_6F_5)_2\{\mu\text{-}\eta^5:\eta^5\text{-}C_4H_4BCH_2\text{-}\eta^3,\kappa F\text{-}CHCHCHB(C_6F_5)_3\}\cdot 2Et_2O$ (**4a**·$2Et_2O$).† Formation of this product involves complete transfer of all three C_6F_5 substituents of one $B(C_6F_5)_3$ molecule, with C–H activation and loss of one C_6F_5 group as pentafluorobenzene. The role of the boryldiene complex **2a** as a reaction intermediate is supported by the formation of the same product from isolated **2a**.



Scheme 1 *Reagents and conditions*: i, $B(C_6F_5)_3$; ii, $-C_6F_5H$, toluene, 5 °C, 4 weeks, followed by addition of Et_2O; iii, $-C_6F_5H$, toluene, 50 °C, 2 h; iv, toluene, room temperature, reduced pressure, 2 h, $-C_4H_8$.

The ambient temperature ^{19}F NMR spectrum features a signal at δ −217.2 indicative of coordination of one of the *o*-F atoms of the formally anionic butenyl–$B(C_6F_5)_3$ moiety to the metal centre. Signal broadening due to *o*-F exchange is observed on heating to 70 °C. Similar evidence of *o*-F coordination is seen in the zwitterionic complex $Cp_2Zr(\eta^3\text{-}CH_2CHCHCH_2B(C_6F_5)_3]$[7] ($\delta$ −213.2), although in this case cooling to −86 °C was required to reach the slow exchange limit. Evidently the Zr···F interaction in **4a** is significantly stronger. The ^{11}B NMR spectrum shows two signals, one extremely broad peak at δ *ca.* 3 (borole-B) and a sharp peak at δ −12.8 for the butenyl–$B(C_6F_5)_3$ moiety. The borole is low-field shifted by *ca.* 20–30 ppm compared with other alkyl–borole systems,[8] probably due to the bridging nature of the ligand.

The structure of **4a** was confirmed by single crystal X-ray diffraction (Fig. 1).‡ The most striking feature of the structure is the bridging borole ligand, the boron atom of which is derived from $B(C_6F_5)_3$ that has lost all three C_6F_5 substituents. The boron is instead bonded to the butenylborate unit which in turn is η^3-bonded to Zr(1). This Zr atom is further coordinated to an *o*-F atom of the butenylborate ligand. The coordination sphere of the second metal centre Zr(2) is completed by a Cp'' and two C_6F_5 ligands.

There is little difference in the bonding distances of the two zirconium atoms with regard to the borole ring, with an average Zr–C length of 2.522(5) Å for Zr(1) and 2.521(5) Å for Zr(2). The Zr–B distances do differ however, with Zr(1)–B(1) of 2.534(6) Å and Zr(2)–B(1) of 2.609(6) Å; this is most probably due to the distortion imposed by the coordination of the allylic fragment to Zr(1). For the related borole complex $Cp''Zr(C_6F_5)(\eta^5\text{-}C_4H_4BC_6F_5)\cdot OEt_2$[6] the Zr–C distances are shorter (average Zr–C of 2.455 Å). The Zr–F distance of 2.355(3) Å is significantly shorter than Zr···F interactions in comparable complexes, for example $[NEt_4]_2[\{C_5H_4B(C_6F_5)_3\}Zr(\mu\text{-Cl})Cl_2]_2$ [2.430(2) Å],[9] $Cp''Zr(C_6F_5)\{\eta^4\text{-}C_4H_5B(C_6F_5)_2\}$ [2.441(7) Å],[4d] and $Cp_2Zr\{\eta^3\text{-}C_4H_6B(C_6F_5)_3\}$ [2.423(3) Å].[7] This is a reflection of the strength of this interaction, in agreement with the ^{19}F NMR evidence.

The reaction leading to **4a** is remarkable in several respects. Although triple-decker complexes involving a central borole ligand have been reported,[10–13] **4a** is the first example containing a group 4 metal. $B(C_6F_5)_3$, widely used as an activator for metallocene polymerisation catalysts because of its chemical stability,[14] acts here as a boron source after loss of all three of its C_6F_5 groups. The decomposition pathways of the boryldiene system **2a** are evidently strongly temperature dependent and are diverted from the formation of **3** at 5 °C to the binuclear complex **4a** by the simple expedient of raising the temperature. However, while **3** is formed only in the case of Cp'', the selective formation of complexes of type **4** is quite general and has led to isolation in high yields of **4b** (Cp^R = C_5H_5, 73%), **4c** (C_5H_4Me, 72.7%) and **4d**, ($C_5H_4SiMe_3$, 66%).

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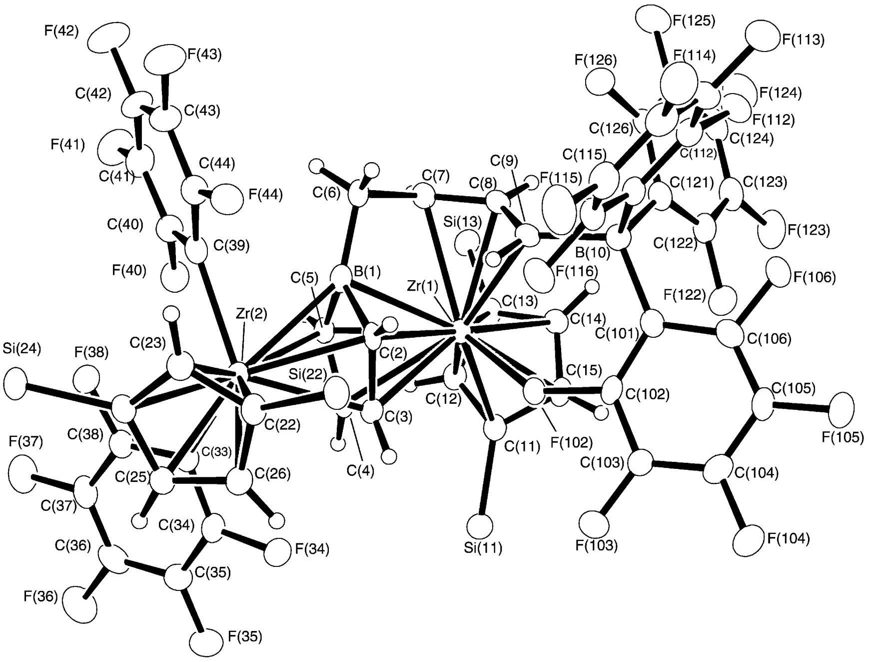

Fig. 1 Molecular structure of **4a**·2Et$_2$O. Selected bond lengths (Å) and angles (°): Zr(1)–F(102) 2.355(3), Zr(1)–B(1) 2.534(6), Zr(2)–B(1) 2.609(6); Zr(1)–B(1)–Zr(2) 117.1(2), B(1)–C(6)–C(7) 100.7(4), C(6)–C(7)–C(8) 126.1(5), C(7)–C(8)–C(9) 125.8(5), C(102)–F(102)–Zr(1) 136.2(3), B(10)–C(9)–C(8) 124.8(5), C(6)–B(1)–Zr(1) 100.4(3), C(6)–B(1)–Zr(2) 142.3(4), C(39)–Zr(2)–C(33) 116.37(19).

Notes and references

† *Synthesis* of **4a**: a solution of Zr(C_4H_7)(C_4H_6)Cp″ (1.63 g, 3.98 mmol) in toluene (30 cm^3) at −78 °C was treated with a solution of $B(C_6F_5)_3$ (1.98 g, 3.87 mmol). The reaction was maintained at this temperature for 30 min and then allowed to reach room temperature. The volatiles were removed *in vacuo*, toluene (40 cm^3) was introduced and the reaction was stirred at 50 °C for 2 h. Removal of the solvent *in vacuo* provided a brown foam which was extracted with diethyl ether (50 cm^3). Concentration of this red solution to *ca*. 10 cm^3 and cooling to −20 °C gave **4a** as red crystals, yield 2.56 g, (82.3%). Anal. Found: C, 45.4; H, 3.3. $B_2C_{60}H_{51}F_{25}Si_4Zr_2$ requires C, 46.1; H, 3.3%. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −0.38, −0.01, 0.08, 0.20 (s, 9H each, SiMe$_3$), 1.51 (d, 2H, J 8.04 Hz, CH_2CHCHCHB(C_6F_5)$_3$), 3.36 (q, 1H, J 8.27 Hz, CH$_2$C*H*CHCHB(C_6F_5)$_3$), 4.81 (d, 1H, J 19.44 Hz, CH$_2$CHCHC*H*B(C_6F_5)$_3$), 5.81 (d, 1H, J 6.46 Hz, CH$_2$CHC*H*CHB(C_6F_5)$_3$), 3.91, 7.87 (m, 2H, *m*-C_4H_4B), 4.98, 6.81 (m, 2H, *o*-C_4H_4B), 5.51, 6.03, 6.66, 7.08 (m, 4H, 4,5-C_5H_3), 5.89, 6.74 (m, 2H, 2-C_5H_3) ^{11}B{^{1}H} NMR (96.2 MHz, C_6D_6, 20 °C): δ 3.0 (vbr, C_4H_4B), −12.8 [B(C_6F_5)$_3$]. ^{13}C NMR (75.6 MHz, C_6D_6, 20 °C): δ −1.20, −0.84, −0.69, −0.21 (SiMe$_3$), 14.95 [*C*H$_2$CHCHCHB(C_6F_5)$_3$], 81.40 [CH$_2$*C*HCHCHB(C_6F_5)$_3$], 98.71, 126.64 (*m*-C_4H_4B), 105.72, 111.34 (*o*-C_4H_4B), 119.73, 124.01, 124.78, 129.95 (4,5-C_5H_3), 121.54 [*C*HB(C_6F_5)$_3$], 123.87 [*C*HCHB(C_6F_5)$_3$], 127.69, 129.50 (2-*C*$_5$H$_3$). ^{19}F NMR (75.6 MHz, C_6D_6, 20 °C): δ −108.2 (s, br, 1F), −112.8 (s, vbr, 1F), −119.9 (s, vbr, 1F), −120.2 (s, br, 1F), −126.2 (s, 1F), −130.0 (s, vbr, 2F), −132.9 (s, br, 2F), −217.2 (m, 1F) (all *o*-C_6F_5), −152.1 (t, $^3J_{FF}$ 19.8 Hz, 1F), −152.5 (t, $^3J_{FF}$ 19.8 Hz, 1F), −157.1 (t, $^3J_{FF}$ 19.8 Hz, 1F), −157.6 (t, $^3J_{FF}$ 19.8 Hz, 1F), −159.0 (t, $^3J_{FF}$ 19.8 Hz, 1F) (all *p*-C_6F_5), −160.2 (t, $^3J_{FF}$ 19.8 Hz, 1F), −160.5 (m, 3F), −161.5 (s, br, 1F), −162.6 (m, 1F), −164.2 (m, 2F), −164.4 (m, 2F) (all *m*-C_6F_5).

‡ *Crystal data* for **4a**·2Et$_2$O: crystals were grown from diethyl ether at −20 °C; $C_{60}H_{51}B_2F_{25}Si_4Zr_2{\cdot}2C_4H_{10}O$, M = 1711.67, triclinic, space group $P\bar{1}$, a = 13.2618(3), b = 13.6828(3), c = 22.1150(6) Å, α = 96.858(2), β = 106.311(2), γ = 102.906(2)°, U = 3682.30(15) Å^3, F(000) = 1732, D_c = 1.544 g cm^{-3}, Z = 2, μ(Mo-Kα, λ = 0.71073 Å) = 0.455 mm^{-1}. Final R indices [$I > 2\sigma(I)$] R_1 = 0.0599, wR_2 = 0.1232 for 8712 absorption-corrected reflections. CCDC 152834. See http://www.rsc.org/suppdata/cc/b0/b009016f/ for crystallographic data in .cif or other electronic format.

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