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Convenient syntheses, spectroscopic and structural characterisation of bi-functional boranes

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Dedicated to Professor Sheldon Shore on the occasion of his 70th birthday.

Abstract

The first examples of bi-functional borane derivatives based around a 1,2,4,5-tetrasubstituted benzene framework are reported. Synthesis of $ClBO_2C_6H_2O_2BCl$ (**4**) is accomplished in three steps (69% overall yield) through the intermediacy of the trimethylsilyl derivative 1,2,4,5-$(Me_3SiO)_4C_6H_2$ (**3**). The bis(borane) species $HBO_2C_6X_2O_2BH$ ($X = H$, **7**; $X = Cl$, **8**) on the other hand, can be synthesised in a single step from substituted *para*-quinone precursors. Crystal structures are reported for compounds **3** and **4**.

Keywords: Boron; Borane; Bi-functional; Tetrasubstituted benzene

1. Introduction

Hydroboration of carbon–carbon multiple bonds is a well-established and extremely versatile method for introducing functionality in organic chemistry [1]. In the case of less reactive B–H bonds such as those found in catecholborane ($HBO_2C_6H_4$, HB*cat*), it has been shown that the rate of reaction can be enhanced by the use of a transition metal catalyst such as $RhCl(PPh_3)_3$ [2,3]. In certain cases the catalysed reaction offers complementary chemo-, regio- and stereoselectivity to that obtained from the uncatalysed reaction [4]. Transition metal boryl complexes ($L_nM–BR_2$) have been shown to be intermediates in these reactions [3,4] and recent reviews have also highlighted the involvement of such complexes in transition metal catalysed diboration of multiple bonds [5–8] and in selective photolytic functionalisation of the terminal position of alkanes [9,10].

Boryl complexes of mid and late transition metals have thus become the focus of much recent interest. The vast majority of structurally characterised species feature the catecholboryl ligand ($BO_2C_6H_4$, B*cat*) bound to a metal centre in η^1 fashion, in part because of the ready availability of HB*cat* and XB*cat* ($X = Cl$, Br) starting materials. In recent work we have been interested in synthesising examples of transition metal complexes incorporating boryl ligands adopting bridging or chelating modes of coordination [11]. In the case of bridging boryl ligands, synthesis of complexes via either oxidative addition or metathetical routes requires as precursors bi-functional boron hydrides or halides. We therefore report the syntheses of the bi-functional. boranes $ClBO_2C_6H_2O_2BCl$ (**4**) and $HBO_2C_6X_2O_2BH$ ($X = H$, **7**; $X = Cl$, **8**) from commercially available dihydroxy-*para*-quinone precursors, together with the results of crystal structure determinations for **4** and the trimethylsilyl substituted intermediate 1,2,4,5-$(Me_3SiO)_4C_6H_2$ (**3**).

2. Experimental

All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or dry box techniques. Solvents were pre-dried over 4 Å

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molecular sieves (THF) or KOH (40:60 petrol–toluene) and purged with nitrogen prior to distillation. THF, toluene and petrol were all distilled from sodium before use. Triethylamine was dried over sodium wire prior to use. Starting materials 2,5-dihydroxy-*para*-quinone, chloranilic acid, trimethylsilyl chloride, $BH_3{\cdot}THF$ and BCl_3 were used as received (Aldrich) without further purification. 1,2,4,5-Tetrahydroxybenzene (**2**) was prepared in essentially quantitative yield from 2,5-dihydroxy-*para*-quinone by the method of Hegedus and coworkers [12].

NMR spectra were measured on a Bruker AM-400 or Bruker AMX-360 FT-NMR spectrometer. Residual protons of solvent were used as the reference for ^{1}H- and ^{13}C-NMR, while a sealed tube containing $[(^nBu_4N)(B_3H_8)]$ was used as an external reference for ^{11}B-NMR. IR spectra were measured for each compound pressed into a disk with an excess of dried KBr on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales Swansea. Perfluorotributylamine was used as the standard for high-resolution EIMS. Elemental analyses were carried out both by the departmental analysis service and by Warwick Analytical Service, University of Warwick.

Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; sl, singlet; d, doublet; pcq, partially collapsed quartet; b, broad.

2.1. 1,2,4,5-$(Me_3SiO)_4C_6H_2$ (**3**)

A 2.0 g (14 mmol) sample of 1,2,4,5-$(HO)_4C_6H_2$ (**2**) was suspended in toluene (20 cm^3) and ten equivalents of trimethylsilyl chloride (17.8 cm^3, 140 mmol) and ten equivalents (19.6 cm^3, 140 mmol) of triethylamine were then added by syringe to the rapidly stirred reaction mixture. After 12 h at room temperature (r.t.) the supernatant toluene solution was separated from the $(Et_3NH)Cl$ precipitate by filtration. The precipitate was washed with toluene (2×10 cm^3) and the combined washings reduced to dryness in vacuo. Extraction with petrol (15 cm^3) and cooling to −30°C for 48 h resulted in the formation of **3** as pale pink acicular crystals in 78% yield. Compound **3** was characterised by ^{1}H- and ^{13}C-NMR, IR, EIMS, elemental analysis and single crystal X-ray diffraction. ^{1}H-NMR (chloroform, 20°C): δ 0.05 (sl, 36H, Me_3Si), 6.13 (sl, 2H, aromatic). ^{13}C-NMR (chloroform, 20°C): δ 0.2 (Me_3Si), 113.4 (CH aromatic), 139.9 (quaternary aromatic). IR (cm^{-1}): 2957 m, 2900 w [ν(C–H)], 1401 m, 1186 s [$\delta(CH_3)$], 1505 s, 1249 s, 1217 m, 945 s, 917 s, 83.9 s. EIMS P$^+$: 431 (100%). Anal. Calc. for $C_{18}H_{38}O_4Si_4$: C, 50.18; H, 8.89. Found: C, 50.42; H, 8.64%.

2.2. $ClBO_2C_6H_2O_2BCl$ (**4**)

To a solution of 2.5 g (5.8 mmol) of **3** in petrol at r.t. was added dropwise by syringe four equivalents of BCl_3 (14.5 cm^3 of a 1.0 M solution in heptane, 14.5 mmol). The initially colourless solution became pale yellow but lost its colour on heating to 60°C for 3 h. At this point volatiles were removed in vacuo and the residual solid extracted with 15 cm^3 of petrol. Cooling to −30°C for 48 h resulted in the formation of **4** as colourless acicular crystals in 89% yield. Compound **4** was characterised by ^{1}H-, ^{13}C- and ^{11}B-NMR, IR, EIMS, elemental analysis and single crystal X-ray diffraction. ^{1}H-NMR (benzene, 20°C): δ 6.45 (sl, 2H, aromatic). ^{13}C-NMR (benzene, 20°C): δ 99.1 (CH aromatic), 144.2 (quaternary aromatic). ^{11}B-NMR (petrol, 20°C): δ 29.2. IR (cm^{-1}): 3123 m, 1463, s sh, 1410 s, 1341 s, 1108 s, 980 m, 859 m, 822 m. EIMS P$^+$: 230 (100%) expected isotopic distribution for two boron and two chlorine atoms. Anal. Calc. for $C_6H_2B_2Cl_2O_4$: C, 31.25; H, 0.87. Found: C, 30.83; H, 0.79%.

2.3. $HBO_2C_6H_2O_2BH$ (**7**)

To a rapidly stirred solution/suspension of 1.12 g (9.7 mmol) of 2,5-dihydroxy-*para*-quinone in THF at r.t. were added dropwise by syringe four equivalents of $BH_3{\cdot}THF$ (38.7 cm^3 of a 1.0 M solution in THF, 38.7 mmol). Within 1 h the reaction mixture became a yellow solution, which lost its colour on stirring for a further 12 h. Removal of volatiles in vacuo at −20°C followed by sublimation at 40°C onto a cold finger held at −20°C gave **7** as large colourless crystals in yields of 40–60%. Higher yields of a less pure product could be achieved by extraction of the crude product into petrol and cooling the resultant solution, rather than by sublimation. Compound **7** was characterised by ^{1}H-, ^{13}C- and ^{11}B-NMR, IR, EIMS (including exact mass determination) and elemental analysis. ^{1}H-NMR (benzene, 20°C): δ 6.94 (sl, 2H, aromatic), ca. 4.6 (b pcq, 2H, BH). ^{13}C-NMR (benzene, 20°C): δ 97.2 (CH aromatic), 141.9 (quaternary aromatic). ^{11}B-NMR (petrol, 20°C): δ 29.4 (d, $^1J_{B\text{–}H} = 191$ Hz). IR (cm^{-1}): 2678 m sh, 2660 s [ν(B–H)]. EIMS P$^+$: 162 (100%) expected isotopic distribution for two boron atoms. Exact mass calc. for $C_6H_4B_2O_4$: 162.0296; found: 162.0296. Anal. Calc. for $C_6H_4B_2O_4$: C, 44.56; H, 2.49. Found: C, 44.22; H, 2.43%.

2.4. $HBO_2C_6Cl_2O_2BH$ (**8**)

Compound **8** was prepared from 2,5-dihydroxy-3,6-dichloro-*para*-quinone (chloranilic acid) by a method analogous to that described above for **7**. By contrast to **7**, crude **8** was best purified by recrystallisation from petrol (yield ca. 45%), as sublimation invariably resulted in the evolution of substantial quantities of as yet unidentified decomposition products. Compound **8** was characterised by ^{1}H-, ^{13}C- and ^{11}B-NMR, IR, EIMS (including exact mass determination) and elemental analysis. ^{1}H-NMR (benzene, 20°C): δ 4.4 (b pcq, 2H, BH). ^{13}C-NMR (benzene, 20°C): δ 124.7 (CCl aromatic), 139.0 (quaternary aromatic). ^{11}B-NMR (petrol, 20°C): δ 28.3 (doublet, $^1J_{\text{B–H}} = 157$ Hz). IR (cm^{-1}): 2677 m sh, 2658 m [ν(B–H)]. EIMS P$^+$: 230 (100%) expected isotopic distribution for two boron and two chlorine atoms. Exact mass calc. for $C_6H_2B_2Cl_2O_4$: 229.9516; found: 229.9518. Anal. Calc. for $C_6H_2B_2Cl_2O_4$: C, 31.25; H, 0.87. Found: C, 30.91; H, 1.04%.

2.5. *Crystallographic data for **3** and **4***

2.5.1. *$C_{18}H_{38}O_4Si_4$ (3)*

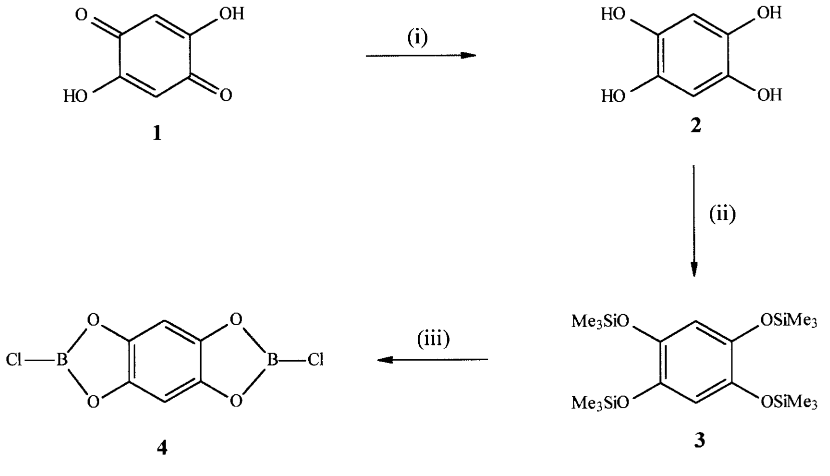
Triclinic, space group $P\bar{1}$, $a = 6.436(6)$, $b = 9.109(5)$, $c = 11.403(4)$ Å, $\alpha = 101.69(5)$, $\beta = 91.17(4)$, $\gamma = 96.08(3)$°, $U = 650.2(7)$ Å^3, $Z = 2$, $D_{\text{calc}} = 1.100$ g cm^{-3}. Crystals were mounted on a thin glass fibre and data collected on a turbo CAD4 four-circle diffractometer at r.t. Of the 2449 reflections collected, 2247 were unique [$R_{\text{int}} = 0.1772$] and 1000 were observed with $I > 2\sigma(I)$. All non-hydrogen atoms were modelled anisotropically, while hydrogen atoms are assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride. $R_1 = 0.0979$, $wR_2 = 0.2183$ for observed unique reflections [$I > 2\sigma(I)$] and $R_1 = 0.$ 1981, $wR_2 = 0.2714$ for all 2247 unique reflections. The maximum and minimum residual electron densities on the final difference Fourier map were 0.496 and -0.549 e Å^{-3}, respectively. The weakly diffracting nature of all crystals of **3** obtained precluded the collection of a better data set and hence a more reliable crystal structure. The results of this structure determination are included as proof of connectivity only and no detailed analysis of bond lengths and/or angles is attempted.

2.5.2. *$C_6H_2B_2Cl_2O_4$ (4)*

Triclinic, space group $P\bar{1}$, $a = 4.4108(9)$, $b = 6.7612(14)$, $c = 7.5147(15)$ Å, $\alpha = 105.64(3)$, $\beta = 93.604(3)$, $\gamma = 91.38(3)$°, $U = 208.56(7)$ Å^3, $Z = 1$, $D_{\text{calc}} = 1.836$ g cm^{-3}. Crystals were mounted on a thin glass fibre using silicon grease and cooled to 100 K on a Nonius Kappa CCD diffractometer with a detector to a crystal distance of 30 mm. Of the 1535 reflections collected, 949 were independent [$R_{\text{int}} = 0.0492$] and were used in all calculations. The images were processed using the DENZO-SMN and SCALEPACK programs [13]. Structures were solved using SHELXS-97 [14] and developed via alternating least-squares cycles and difference Fourier synthesis (SHELXL-97 [14]) with the aid of the program XSEED [15]. All non-hydrogen atoms were modelled anisotropically, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride. $R_1 = 0.0419$, $wR_2 = 0.0779$ for observed unique reflections [$I > 2\sigma(I)$] and $R_1 = 0.0630$, $wR_2 = 0.0854$ for all 949 unique reflections. The maximum and minimum residual electron densities on the final difference Fourier map were 0.341 and -0.382 e Å^{-3}, respectively.

3. Results and discussion

The synthesis of the bi-functional boranes $ClBO_2C_6H_2O_2BCl$ (**4**) and $HBO_2C_6X_2O_2BH$ (X = H, **7**; X = Cl, **8**) can be conveniently accomplished in reasonable yield from commercially available dihydro-*para*-quinones. $ClBO_2C_6H_2O_2BCl$ (**4**) can be synthesised in three steps (overall yield 69%) from 2,5-dihydroxy-*para*-quinone (**1**) through the intermediacy of the



Scheme 1. Synthesis of $ClBO_2C_6H_2O_2BCl$ (**4**). Reagents and conditions: (i) Sn, HCl, 1 h at 95°C, 99%; (ii) Me_3SiCl (ten equivalents), Et_3N, toluene, 12 h at r.t., 78%; (iii) BCl_3 (four equivalents), petrol, 3 h at 50°C, 89%.

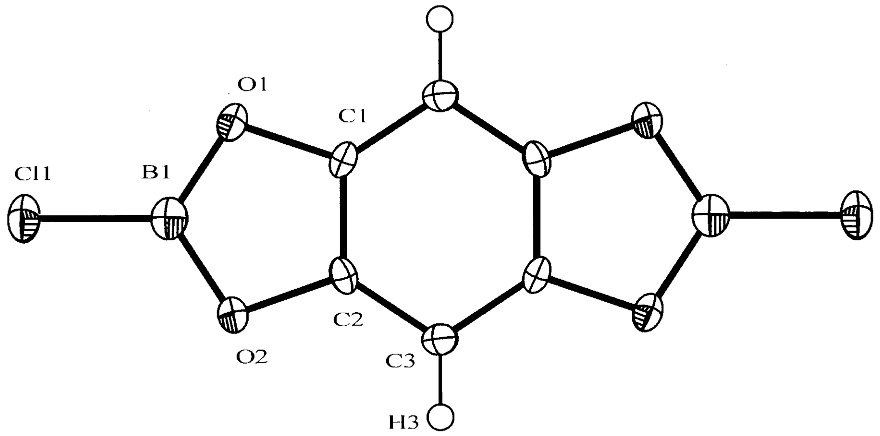


Fig. 1. Molecular structure of $ClBO_2C_6H_2O_2BCl$ (**4**). Relevant bond lengths (Å) and angles (°): B(1)–Cl(1) 1.737(3), B(1)–O(1) 1.377(3), B(1)–O(2) 1.377(3), O(1)–B(1)–O(2) 113.4(2), O(1)–B(1)–Cl(1) 123.0(2), O(2)–B(1)–Cl(1) 123.6(2).

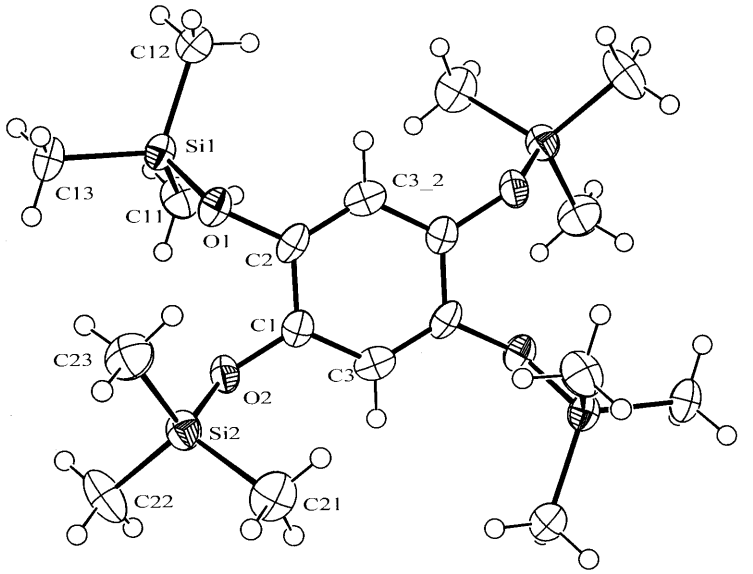


Fig. 2. Molecular structure of 1,2,4,5-$(Me_3SiO)_4C_6H_2$ (**3**).

trimethylsilyl substituted species **3** (Scheme 1). This synthetic route has several advantages over direct synthesis of **4** from the tetrahydroxy derivative, **2**. Firstly the solubility of **3** in non-polar organic media such as 40:60 petrol and toluene confers a significantly higher yield for the reaction with BCl_3 leading to the final product **4**. In addition, since the synthesis of the tetrahydroxy species, **2**, is carried out in aqueous media and rigorous drying is difficult, formation of the trimethylsilyl derivative, **3**, by reaction with a large excess of trimethylsilyl chloride and extraction into petrol, effectively constitutes a simple method of ensuring that there is no moisture present in the final reaction step with BCl_3. Any moisture present is simply converted by the excess of trimethylsilyl chloride into hexamethyldisiloxane which is removed in vacuo. Using this methodology we have been able to synthesise a range of borane halide species derived from polyhydroxy benzene frameworks [16].

Compound **4** is a colourless crystalline material, stable indefinitely in an inert atmosphere, but highly susceptible to hydrolysis. The ^{1}H- and ^{13}C-NMR data for **4** are consistent with a symmetrical molecule in which both pairs of *ortho* oxygen substituents are bridged by a BCl unit. The MS data are also consistent with this formulation, displaying both the expected molecular ion peaks and the correct isotopic distribution for two boron and two chlorine atoms. The ^{11}B-NMR shift (δ 29.2) is also very similar to that reported for the mono-functional analogue ClB*cat* (δ 29.0) [17]. These structural inferences are confirmed by the results of a single crystal X-ray diffraction study (Fig. 1). Compound **4** is the first example of a structurally characterised bi-functional borane based around a

1,2,4,5-tetrasubstituted benzene framework. Surprisingly, a survey of the Cambridge Structural Database also revealed no other examples of crystallographically characterised species containing a three-coordinate boron centre bound to a single chlorine atom and two oxygen centres. B–Cl (1.737(3) Å) and B–O (1.377(3) and 1.397(3) Å) bond lengths are however similar to those found in $[(^iPr_2N)BCl]_2(\mu\text{-}O)$ (which average 1.809 and 1.368 Å, respectively) [18]. As expected, the angles at the boron centre in **4** sum to 360.0(3)°. The structure of the 1,2,4,5-tetrasubstituted benzene framework differs little from that of the trimethylsilyl substituted precursor **3** (Fig. 2). Full details of the data collection and refinement for **4** together with a listing of bond lengths and angles can be found in Tables 1 and 2.

Table 1
Crystallographic data for **4**

Empirical formula	$C_6H_2B_2Cl_2O_4$
Formula weight	230.60
Temperature (K)	100(2)
Wavelength (Å)	0.71070
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	4.4108(9)
b (Å)	6.7612(14)
c (Å)	7.5147(15)
α (°)	105.64(3)
β (°)	103.88(3)
γ (°)	91.38(3)
Volume (Å^3)	208.56(7)
Z	1
D_{calc} (g cm^{-3})	1.836
Absorption coefficient (mm^{-1})	0.753
$F(000)$	114
Crystal size (mm)	$0.40 \times 0.10 \times 0.05$
θ Range for data collection (°)	2.91–27.49
Index ranges	$-5 \le h \le 5$, $-8 \le k \le 8$, $-9 \le l \le 9$
Reflections collected	1535
Independent reflections	949 [$R_{int} = 0.0492$]
Completeness to $\theta = 27.49°$	98.9(%)
Absorption correction	SCALEPACK
Maximum and minimum transmission	0.9633 and 0.7528
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	949/0/69
Goodness-of-fit on F^2	1.099
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0419$, $wR_2 = 0.0779$
R indices (all data)	$R_1 = 0.0630$, $wR_2 = 0.0854$
Extinction coefficient	0.022(7)
Largest difference peak and hole (e Å^{-3})	0.341 and −0.382

Table 2
Bond lengths (Å) and angles (°) for **4** [a]

Cl(1)–B(1)	1.737(3)	C(2)–C(3)	1.375(3)
O(1)–B(1)	1.377(3)	C(2)–C(1)	1.384(3)
O(1)–C(1)	1.397(3)	C(1)–C(3) # 1	1.384(3)
O(2)–B(1)	1.377(3)	C(3)–C(1) # 1	1.384(3)
O(2)–C(2)	1.396(3)		
B(1)–O(1)–C(1)	104.15(19)	C(2)–C(1)–O(1)	109.1(2)
B(1)–O(2)–C(2)	104.1(2)	C(3) # 1–C(1)–O(1)	127.4(2)
C(3)–C(2)–C(1)	123.9(2)	C(2)–C(3)–C(1) # 1	112.6(2)
C(3)–C(2)–O(2)	126.8(2)	O(2)–B(1)–O(1)	113.4(2)
C(1)–C(2)–O(2)	109.3(2)	O(2)–B(1)–Cl(1)	123.6(2)
C(2)–C(1)–C(3)	123.5(2)	O(1)–B(1)–Cl(1)	123.0(2)

1

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x+2$, $-y+1$, $-z+2$.

The arrangement of molecules of **4** in the solid state (Fig. 3) is consistent with the existence of π-stacking and weak C–H···O interactions between adjacent molecules. The closest distances between adjacent aromatic ring systems (3.2–3.3 Å), for example, are consistent with those typically found for similar π-stacking interactions [19]. Shortest C–H···O distances are of the order of 2.6–2.7 Å.

Syntheses of the corresponding boron hydride derivatives **7** and **8** are conveniently carried out in a single step from commercially available starting materials (Scheme 2).

Reduction of the *para*-quinone and complexation of *ortho* oxygen substituents is readily accomplished by the addition of four equivalents of $BH_3 \cdot THF$ at r.t. The reaction is exothermic and complete in 12 h at r.t. In the case of **7**, sublimation from the crude reaction residue gives a reasonable yield (40–60%) of high purity product. Compound **7** is extremely sensitive to moisture, but stable indefinitely in an inert atmosphere. ^1H- and ^{13}C-NMR data are consistent with a symmetrical molecule in which both pairs of *ortho* oxygen substituents are bridged by a BH unit. Indeed, the ^1H- and ^{13}C-NMR signals attributed to the bridging $O_2C_6H_2O_2$ moiety are found at very similar positions to those measured for the same unit in the structurally characterised molecule **4**. The presence of a doublet (δ 29.4, $^1J_{B-H} = 191$ Hz) in the ^{11}B-NMR spectrum, at a position similar to that reported for HB*cat* (δ 28.3) [20], is indicative of a three-coordinate boron centre bound to two oxygen atoms and a single terminal hydrogen atom. MS and microanalytical data confirm the formulation $C_6H_4B_2O_4$ and a structure for **7** analogous to that determined for **4** featuring two terminal B–H (rather than B–Cl) linkages seems very likely.

$HBO_2C_6Cl_2O_2BH$ (**8**) is readily synthesised from chloranilic acid in a manner analogous to that used for **7**. Yields of ca. 45% can be achieved for this single-step reaction, although in this case recrystallisation from 40:60 petrol is preferable to sublimation for purification of the final product. Again ^1H-, ^{13}C- and ^{11}B-NMR, IR, MS and microanalytical data are consistent with a symmetrical molecule analogous to **4** and **7** in which pairs of *ortho* oxygen substituents are bridged by a BH unit.

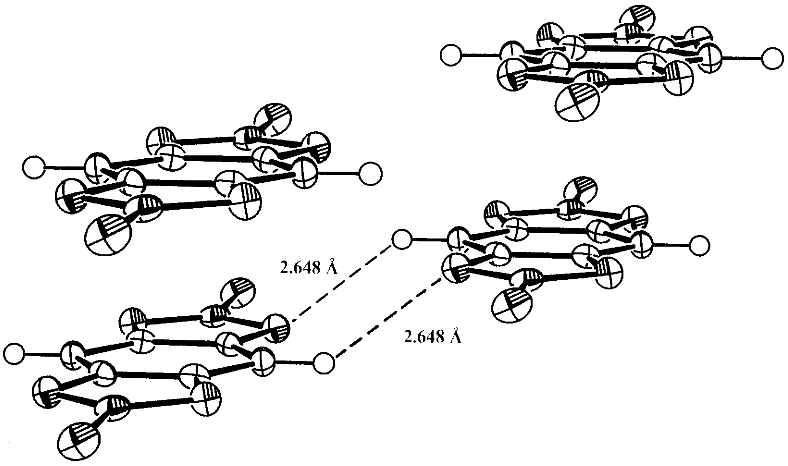
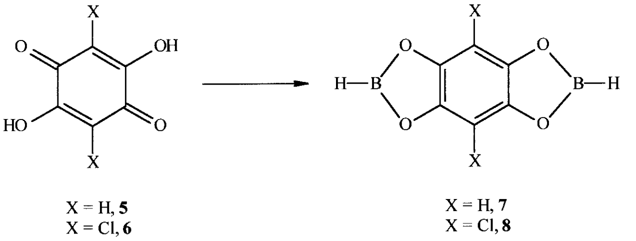


Fig. 3. Packing of molecules of **4** in the solid state. Both π-stacking and weak C–H···O interactions are observed in the solid state. These are characterised by closest intermolecular distances of 3.1–3.2 and 2.6–2.7 Å, respectively.



Scheme 2. Syntheses of $HBO_2C_6X_2O_2BH$ (X = H, **7**; X = Cl, **8**). Reagents and conditions: BH_3·THF (four equivalents), THF, 12 h at r.t., 40–60%.

The synthesis of **4** in good yield and on a multigramme scale has allowed us to investigate the chemistry of bridging boryl ligands formed by metathesis with organometallic anions [11]. In addition, the convenient one-step syntheses of **7** and **8** from commercially available starting materials has allowed us to utilise oxidative addition as an alternative route to transition metal complexes containing bridging boryl linkages. The results of these studies will be reported soon.

4. Conclusions

The first examples of bi-functional borane derivatives based around a 1,2,4,5-tetrasubstituted benzene framework have been synthesised. In the case of $ClBO_2C_6H_2O_2BCl$ (**4**), synthesis from commercially available starting materials is accomplished in three steps (69% overall yield) through the intermediacy of the trimethylsilyl derivative 1,2,4,5-$(Me_3SiO)_4C_6H_2$ (**3**). The bis(borane) species $HBO_2C_6X_2O_2BH$ (X = H, **7**; X = Cl, **8**) on the other hand, can be synthesised in a single step from substituted *para*-quinone precursors. Studies are currently underway to investigate the synthesis of symmetrically bridged boryl complexes from these boranes. In addition, we are investigating the hydroboration of alkenes using compounds **7** and **8**.

5. Supplementary material

Crystallographic data have been deposited (as CIF files) with the Cambridge Crystallographic Data Centre. Data may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on request by quoting the deposition numbers CCDC-142393 and CCDC-142394 for compounds **3** and **4**, respectively.

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