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FULL PAPER

Linking of metal centres through boryl ligands: synthesis, spectroscopic and structural characterisation of symmetrically bridged boryl complexes

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Dinuclear species containing iron centres linked *via* various bridging boryl ligands have been synthesised and a combination of crystallographic, computational and spectroscopic (Mössbauer, IR, Raman) techniques have been used to probe the bonding in these complexes.

1 Introduction

Transition metal boryl complexes ($L_nM–BX_2$) have been the subject of considerable research interest over the past decade,[1] partly as a result of their implication in several highly useful organic transformations, including the metal-catalysed hydro- and diboration of carbon to element multiple bonds.[1,2] More recently the highly selective functionalization of unactivated hydrocarbons to boronate esters through the intermediacy of metal boryl species has also been reported by a number of groups.[3,4] It has been suggested that the unusual regiochemistry and activity of such systems with regard to C–H activation may be due to the Lewis acidic properties of the boryl ligand, which provide favourable kinetics for the formation of boron–carbon bonds.[3d]

While the unusual reactivity of transition metal boryl complexes has provided the impetus for much research effort, there has also been considerable interest in determining the fundamental ligand properties of boryl systems through a combination of spectroscopic, crystallographic and computational approaches.[1,5,6] Ultimately a better understanding of the nature of the metal boron interaction may help provide insight into the underlying reasons for the unusual reactivity of such systems. Almost exclusively, however, such studies have focussed on monodentate boryl ligands (often Bcat, $BO_2C_6H_4$) adopting a terminal mode of coordination with respect to the metal centre, with alternative ligand types (*e.g.* bridging, chelating, base-stabilised) being almost totally ignored.[6d,7] In this and other recent work we have sought to expand the coordination chemistry of these highly topical ligand systems,[5o,6i,6j,8,9] and hereby report the synthesis, spectroscopic and structural investigation of a number of dinuclear iron systems featuring bridging boryl ligands. Such complexes not only offer useful comparison with analogous terminally bound ligand systems, but also provide a platform for further investigation of the metal to boryl linkage through previously under-utilized techniques (DFT, electrochemistry, Mössbauer and FT-Raman spectroscopies).

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 sodium wire (hexanes, toluene) or molecular sieves (dichloromethane) and purged with nitrogen prior to distillation. Hexanes (potassium), toluene (sodium), and dichloromethane (calcium hydride) were then distilled from the appropriate drying agent before use. C_6D_6 (Goss) was degassed and dried over potassium prior to use; trimethylamine was dried over sodium wire prior to use. BCl_3 (1.0 M solution in heptane, Aldrich), pentaerythrol (Avocado) and trimethylsilyl chloride (Aldrich) were used as received, without further purification. $(\eta^5\text{-}C_5R_4R')Fe(CO)_2Na$ ($R = R' = H$; $R = H$, $R' = Me$; and $R = R' = Me$) and hexahydroxybenzene (**5**) were prepared by minor modification of literature methods;[10,11] 1,2,4,5-$(Me_3SiO)_4C_6H_2$ (**2a**), $(ClBO_2)_2C_6H_2$ (**3a**) and $(HBO_2)_2C_6H_2$ (**3c**) were prepared as described previously.[8]

NMR spectra were measured on a Bruker AM-400 or JEOL Eclipse 300 Plus FT-NMR spectrometer. Residual protons of solvent were used for reference for ^1H and ^{13}C NMR, while a sealed tube containing a solution of $[(^nBu_4N)(B_3H_8)]$ in $CDCl_3$ was used as an external reference for ^{11}B NMR. Infrared spectra were measured for each compound pressed into a disk with an excess of dried KBr on a Nicolet 500 FT–IR spectrometer. FT-Raman spectra were measured for powdered samples sealed in glass ampoules using a LabRam spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales Swansea and by the departmental service. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Mössbauer spectra were recorded at 77 K on an ES-Technology MS-105 spectrometer with a 135 MBq ^{57}Co source in a rhodium matrix at ambient temperature. Spectra were referenced to a 25 μm iron foil at 298 K. Measurements were in zero field on solid samples ground with boron nitride. Parameters were obtained by fitting the spectra by Lorenzian curves. 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, s = singlet, m = multiplet, br = broad.

Syntheses

$(Me_3SiOCH_2)_4C$ (2b). 5.4 g (39.7 mmol) of pentaerythrol (**1b**) were suspended in toluene (100 cm^3) and 10 equiv. of trimethyl-

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silyl chloride (50 cm^3, 397 mmol) and 10 equiv. (55.3 cm^3, 397 mmol) of triethylamine were then added by syringe to the rapidly stirred reaction mixture. After 12 h at room temperature the supernatent toluene solution was separated from the $(Et_3NH)Cl$ precipitate by filtration. The precipitate was washed with toluene (2×50 cm^3) and the combined washings reduced to dryness *in vacuo* yielding **2b** as a colourless oil (*ca.* 70% yield). Examination of the product at this point by ^1H and ^{13}C NMR revealed it to be >99% pure and no further purification was therefore attempted. **2b** was characterised by ^1H and ^{13}C NMR and IR spectroscopy, and CI mass spectrometry (including exact mass determination). ^1H NMR (400 MHz, C_6D_6, 21 °C), δ 0.14 (36H, s, $Si(CH_3)_3$), 3.70 (8H, s, $C(CH_2)_4$). ^{13}C NMR (76 MHz, C_6D_6, 21 °C), δ −0.7 ($Si(CH_3)_3$), 47.3 ($\mathit{C}(CH_2)_4$), 59.9 ($C(\mathit{C}H_2)_4$). IR (neat, cm^{-1}): 2959m, 2919m, 2876m, 1475m, 1402w, 1304w, 1249s, 1172m, 1074s, 909s, 883s, 747m, 728m, 694m. Mass spectrum (CI): $[M + H]^+ = 425$ (100%), exact mass (calc.) *m*/*z* 425.2395, (observed) 425.2394.

***Spiro*-$[ClBO_2(CH_2)_2]_2C$ 3b.** To a solution of 11.7 g (27.6 mmol) of **2b** in hexanes at room temperature was added dropwise by syringe 2 equiv. of BCl_3 (55 cm^3 of a 1.0 M solution in heptane, 55 mmol). The reaction mixture was warmed to 55 °C and stirred for 12 h, after which the white precipitate so formed was separated from the supernatent solution by filtration, washed with hexanes (3×30 cm^3) and dried *in vacuo*. The crude material was then recrystallized from toluene to give **3b** as a white microcrystalline solid in yields of up to 86%. **3b** was characterised by ^1H, ^{13}C and ^{11}B NMR and IR spectroscopy, and EI mass spectrometry. ^1H NMR (400 MHz, C_6D_6, 21 °C), δ 2.90 (8H, s, $C(CH_2)_4$). ^{13}C NMR (76 MHz, C_6D_6, 21 °C), δ 35.2 ($\mathit{C}(CH_2)_4$), 65.1 ($C(\mathit{C}H_2)_4$). ^{11}B NMR (96 MHz, C_6D_6, 21 °C), δ 23.1. IR (KBr disk, cm^{-1}): 2963m, 2908w (sh), 1490m, 1436m, 1374m, 1262s, 1097s, 1021s, 864w, 801s. Mass spectrum (EI): $[M]^+ = 225$ (weak).

$(\eta^5\text{-}C_5R_4R')Fe(CO)_2BO_2C_6H_2O_2BFe(CO)_2(\eta^5\text{-}C_5R_4R')$ (R = R′ = H 4a; R = H, R′ = Me 4b; and R = R′ = Me 4c). The three complexes were synthesized in a similar manner. To a suspension of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Na$ (0.2 g, 1.0 mmol) in toluene at −30 °C was added a toluene solution containing 0.5 equiv. of **3a**. The reaction mixture was warmed to room temperature and stirred for one week at which time examination of the solution by ^{11}B NMR spectroscopy revealed that all of **3a** had been consumed. In each case, the product is only sparingly soluble in toluene and can therefore be isolated by removal of the supernatent by filtration, extraction of the residual beige solid with CH_2Cl_2 and subsequent crystallisation either by controlled cooling or by layering with hexanes at −30 °C. This method generated crystals of **4a** and **4b** suitable for X-ray diffraction. Isolated yields of the pale yellow crystalline solids **4a**–**c** are typically of the order of 50–60% and the compounds have been characterized by ^1H, ^{13}C and ^{11}B NMR, IR spectroscopy, mass spectrometry, elemental analysis and (in the cases of **4a** and **4b**) by single crystal X-ray diffraction. **4a**: ^1H NMR (400 MHz, C_6D_6, 21 °C), δ 4.95 (10H, s, $\eta^5\text{-}C_5H_5$), 6.99 (s, 2H, $(\eta^5\text{-}C_5H_5)Fe(CO)_2BO_2C_6\mathit{H}_2O_2BFe(CO)_2(\eta^5\text{-}C_5H_5)$). ^{13}C NMR (76 MHz, C_6D_6, 21 °C), δ 82.9 ($\eta^5\text{-}C_5H_5$), 94.7 (aromatic CH), 143.8 (aromatic quaternary), 212.5 (CO). ^{11}B NMR (96 MHz, toluene, 21 °C), δ 48 (br). IR (KBr disk, cm^{-1}) ν(CO) 2006s, 1954s. Mass spectrum (EI): $[M]^+ = 514$ (100%), expected isotopic distribution for 2 B, 2 Fe atoms, fragment ion peaks at *m*/*z* 486, 458, 430, 402 corresponding to sequential loss of four CO molecules, exact mass (calc.) *m*/*z* 513.9417, (observed) 513.9424. Elemental analysis: calc. for $C_{20}H_{12}B_2Fe_2O_8$, C 46.74, H 2.35; observed, C 46.22, H 2.14%. **4b**: ^1H NMR (400 MHz, C_6D_6, 21 °C), δ 1.43 (s, 6H, $\eta^5\text{-}C_5H_4C\mathit{H}_3$ 4.14 (4H, m, $\eta^5\text{-}C_5\mathit{H}_4\text{-}CH_3$), 4.26 (4H, m, $\eta^5\text{-}C_5\mathit{H}_4CH_3$), 7.24 (s, 2H, $(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2BO_2C_6\mathit{H}_2O_2BFe(CO)_2(\eta^5\text{-}C_5H_4CH_3)$). ^{13}C NMR (76 MHz, C_6D_6, 21 °C), δ 12.7 ($\eta^5\text{-}C_5H_4\mathit{C}H_3$), 82.7, 84.4 ($\eta^5\text{-}\mathit{C}_5H_4\text{-}CH_3$), 96.0 (aromatic CH), 145.3 (aromatic quaternary), 214.3 (CO). ^{11}B NMR (96 MHz, toluene, 21 °C), δ 51 (br). IR (KBr disk, cm^{-1}) ν(CO) 2001s, 1943s. Mass spectrum (CI): $[M + H]^+ = 543$ (100%), expected isotopic distribution for 2 B, 2 Fe atoms, exact mass (calc.) *m*/*z* 542.9808, (observed) 542.9809. Elemental analysis: calc. for $C_{22}H_{16}B_2Fe_2O_8$, C 48.78, H 2.98; observed, C 48.85, H 2.94%. **4c**: ^1H NMR (400 MHz, C_6D_6, 21 °C), δ 1.89 (30H, s, $\eta^5\text{-}C_5Me_5$), 7.08 (s, 2H, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BO_2C_6\text{-}\mathit{H}_2O_2BFe(CO)_2(\eta^5\text{-}C_5Me_5)$). ^{13}C NMR (76 MHz, C_6D_6, 21 °C), δ 10.2 ($\eta^5\text{-}C_5\mathit{Me}_5$), 94.7 (aromatic CH), 95.8 (C_5Me_5), 143.8 (aromatic quaternary), 213.3 (CO). ^{11}B NMR (96 MHz, toluene, 21 °C), δ 53 (br). IR (KBr disk, cm^{-1}) ν(CO) 2001s, 1943s. Mass spectrum (EI): $[M]^+ = 654$ (30%), expected isotopic distribution for 2 B, 2 Fe atoms, fragment ion peaks at *m*/*z* 626, 598 and 542, corresponding to sequential loss of one, two and four CO molecules, exact mass (calc.) *m*/*z* 654.0982, (observed) 654.0980.

***Spiro*-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2BO_2(CH_2)_2]_2C$ 4d.** Complex **4d** was synthesized from **3b** in a manner analogous to that described above for **4c**. Purification of the final product was achieved by recrystallization from toluene at −30 °C and crystals suitable for X-ray diffraction were grown by layering a toluene solution with hexanes. Yields of the pale yellow crystalline material are typically of the order of 40% and **4d** has been characterized by ^1H, ^{13}C and ^{11}B NMR, IR spectroscopy, EI mass spectrometry and single crystal X-ray diffraction. ^1H NMR (400 MHz, C_6D_6, 21 °C), δ 3.56 (8H, s, $C(CH_2)_4$), 4.26 (10H, s, $\eta^5\text{-}C_5H_5$). ^{13}C NMR (76 MHz, C_6D_6, 21 °C), δ 36.6 ($\mathit{C}(CH_2)_4$), 65.7 ($C(\mathit{C}H_2)_4$), 83.3 ($\eta^5\text{-}C_5H_5$), 216.0 (CO). ^{11}B NMR (96 MHz, C_6D_6, 21 °C), δ 45.3. IR (KBr disk, cm^{-1}) ν(CO) 1998s, 1932s. Mass spectrum (EI): $[M - CO]^+ = 480$ (weak), expected isotopic distribution for 2 B, 2 Fe atoms, fragment ion peaks at *m*/*z* 452 (30%), 424 (weak) and 396 (20%) corresponding to sequential loss of the three remaining CO ligands.

$(Me_3SiO)_6C_6$ 6. Compound **6** was prepared from hexahydroxybenzene (**5**)[11] using a method analogous to that described above for **2b**. The final product was isolated as a pale pink crystalline solid in yields of up to 65% and has been characterized by ^1H and ^{13}C NMR, EI mass spectrometry (including exact mass determination) and single crystal X-ray diffraction. ^1H NMR (400 MHz, C_6D_6, 21 °C), δ 0.40 (s, $SiMe_3$). ^{13}C NMR (76 MHz, C_6D_6, 21 °C), δ 0.0 ($SiMe_3$), 134.0 (aromatic quaternary). Mass spectrum (EI): $[M]^+ = 606$ (100%), exact mass (calc.) *m*/*z* 606.2530, (observed) 606.2536.

Attempts to synthesize $(ClBO_2)_3C_6$ 7. Attempts were made to synthesise **7** from **6** using a method analogous to that used to prepare **3a** and **3b**. Addition of 3 equivalents of BCl_3 to a solution of **6** in hexanes however produced a mixture of two boron-containing species giving rise to resonances at δ 33.0 and 30.1, together with unreacted BCl_3. The use of elevated reaction temperatures (50–60 °C) or longer reaction times (120 h) did not lead to significant changes in the product distribution. Removal of volatiles *in vacuo* and examination of the resulting solid by ^1H and ^{13}C NMR revealed the presence of unreacted trimethylsilyl functions within the product mixture.

General crystallographic method

Data were collected on either an Enraf Nonius Kappa CCD diffractometer (**3a**, **3c**, **4a**, **4b**, **4d**) or CAD4 four-circle diffractometer (**6**). For the former structures data collection and cell refinement were carried out using DENZO and COLLECT,[12] and structure solution and refinement using SHELXS-97 and SHELXL-97, respectively.[13] Details of each data collection, structure solution and refinement can be found in Table 1, relevant bond lengths and angles are included in figure captions.

Table 1 Crystallographic data for **3a**, **3c**, **4a**, **4b**, **4d** and **6**

	3a	**3c**	**4a**	**4b**	**4d**	**6**
Empirical formula	$C_6H_2B_2Cl_2O_4$	$C_6H_4B_2O_4$	$C_{20}H_{12}B_2Fe_2O_8$	$C_{22}H_{16}B_2Fe_2O_8$	$C_{19}H_{18}B_2Fe_2O_8$	$C_{24}H_{54}O_6Si_6$
M	230.60	161.71	513.62	541.67	507.66	607.21
T/K	100(2)	150(2)	100(2)	120(2)	120(2)	150(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$Pbca$	$P2_1/n$	$P\bar{1}$	$C2/c$	$C2/m$
a/Å	4.4108(9)	10.416(2)	6.4542(3)	6.4039(13)	26.798(2)	18.520(2)
b/Å	6.7612(14)	5.2697(11)	12.2543(4)	6.8417(14)	6.0907(6)	17.898(2)
c/Å	7.5147(15)	12.231(2)	12.4180(6)	12.547(3)	12.6373(15)	12.451(3)
α/°	105.64(3)	90	90	83.82(3)	90	90
β/°	103.88(3)	90	93.604(3)	86.64(3)	108.968(3)	96.00(2)
γ/°	91.38(3)	90	90	77.38(3)	90	90
V/Å^3	208.56(7)	671.3(2)	980.22(7)	532.97(19)	1950.7(3)	4104.3(12)
Z	1	4	2	1	4	4
D_c/Mg m^{-3}	1.836	1.600	1.740	1.688	1.729	0.983
μ/mm^{-1}	0.753	0.128	1.528	1.410	1.534	0.230
F(000)	114	328	516	274	1032	1320
Crystal size/mm	0.40 × 0.10 × 0.05	0.25 × 0.13 × 0.13	0.30 × 0.15 × 0.15	0.44 × 0.28 × 0.12	0.15 × 0.15 × 0.02	0.60 × 0.50 × 0.50
Reflections collected	1535	6589	6704	8293	4641	3943
Independent reflections	949	768	2243	2401	1649	3817
R_{int}	0.0492	0.0363	0.0340	0.0764	0.0580	0.0257
Goodness-of-fit on F^2	1.099	0.991	1.029	1.051	1.089	1.104
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0419$, $wR2 = 0.0779$	$R1 = 0.0367$, $wR2 = 0.1077$	$R1 = 0.0257$, $wR2 = 0.0582$	$R1 = 0.0328$, $wR2 = 0.0830$	$R1 = 0.0427$, $wR2 = 0.0886$	$R1 = 0.0689$, $wR2 = 0.2193$
R indices/all data)	$R1 = 0.0630$, $wR2 = 0.0854$	$R1 = 0.0419$, $wR2 = 0.1065$	$R1 = 0.0315$, $wR2 = 0.0605$	$R1 = 0.0340$, $wR2 = 0.0840$	$R1 = 0.0732$, $wR2 = 0.1054$	$R1 = 0.1033$, $wR2 = 0.2391$
Largest diff. peak and hole/e Å^{-3})	0.341, −0.382	0.186, −0.222	0.331, −0.225	0.0672, −0.644	0.474, −0.412	0.896, −0.484

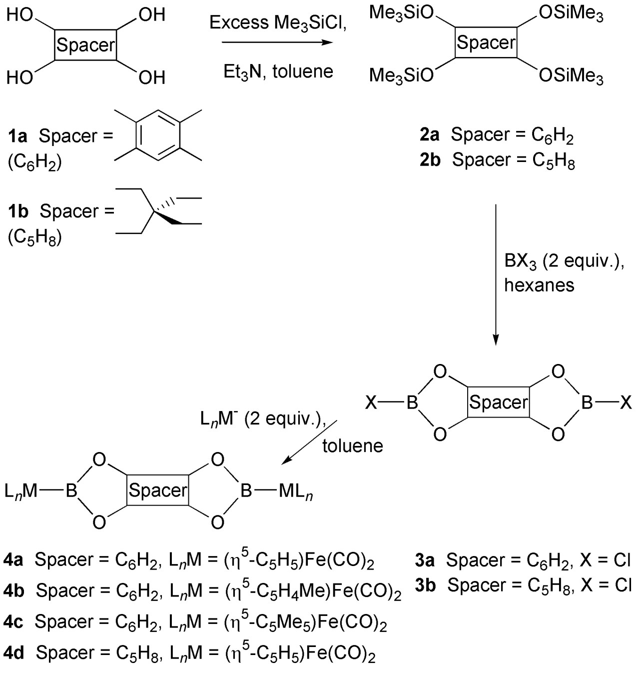
CCDC reference numbers 142393 (see ref. 8), 148084 (see ref. 6*i*) and 177260–177263.

See http://www.rsc.org/suppdata/dt/b2/b200695m/ for crystallographic data in CIF or other electronic format.

3 Results and discussion

Synthetic methodology

Dinuclear complexes featuring metal centres linked *via* bridging boryl ligands can be synthesised in yields of 50–60% according to the synthetic route outlined in Scheme 1. This methodology can be applied both to unsaturated bridging 'spacer' groups such as those based around a 1,2,4,5-tetrasubstituted benzene framework, and also to saturated aliphatic systems such as the *spiro* species derived from pentaerythrol precursors. The bifunctional boron halide reagents (**3a**, **3b**) required in the final metathesis step are most conveniently prepared from trimethylsilyl-substituted precursors (*i.e.* **2a**, **2b**) which are freely soluble in the non-polar organic media employed. By contrast, direct synthesis from polyhydroxy species and boron trichloride, for example, suffers from low yields resulting from the difficulty in adequately drying compounds such as **1a** and **1b**.



Scheme 1

The final metathetical step in the reaction sequence requires the use of samples of the organometallic anion from which traces of tetrahydrofuran have been rigorously removed (thf is a contaminant inherent in the synthetic route used). Yields of the final products **4a**–**d** are otherwise significantly reduced (conceivably, this may be due to the susceptibility of metal boryl complexes to decomposition in the presence of nucleophilic/Lewis basic reagents[1a] or to the direct reaction of the chloroborane precursors with thf). Not unexpectedly, dinuclear species **4a**–**d** are significantly less soluble in organic media than their mononuclear counterparts, with those containing unsaturated spacer groups (**4a**–**c**) being less soluble than those such as **4d** containing saturated bridging units. Attempts to prepare dinuclear boryl complexes containing other organometallic fragments [*e.g.* $Mn(CO)_5$ or $(\eta^5\text{-}C_5H_5)_2M(H)$ (M = Mo or W)] suffered from a lack of solubility of the products in solvents which did not bring about decomposition. Finally, attempts to prepare the corresponding trinuclear derivatives through the intermediacy of the hexa-substituted trimethylsilyl derivative **6** (Fig. 1) appear to suffer from problems arising from the isolation of a mixture of products during the synthesis of the required polyfunctional boron halides (for which the chemistry outlined in Scheme 2 is proposed).

Structural and spectroscopic studies

Single crystals of metal complexes **4a**, **4b** and **4d** suitable for X-ray crystallography proved to be accessible by layering with

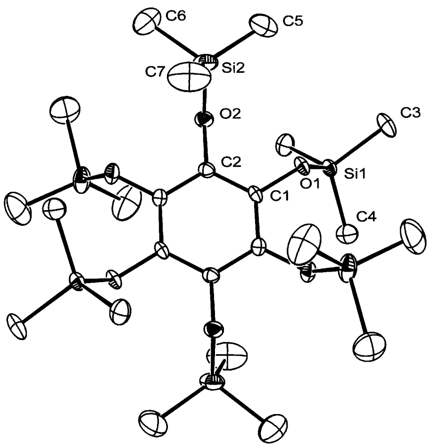
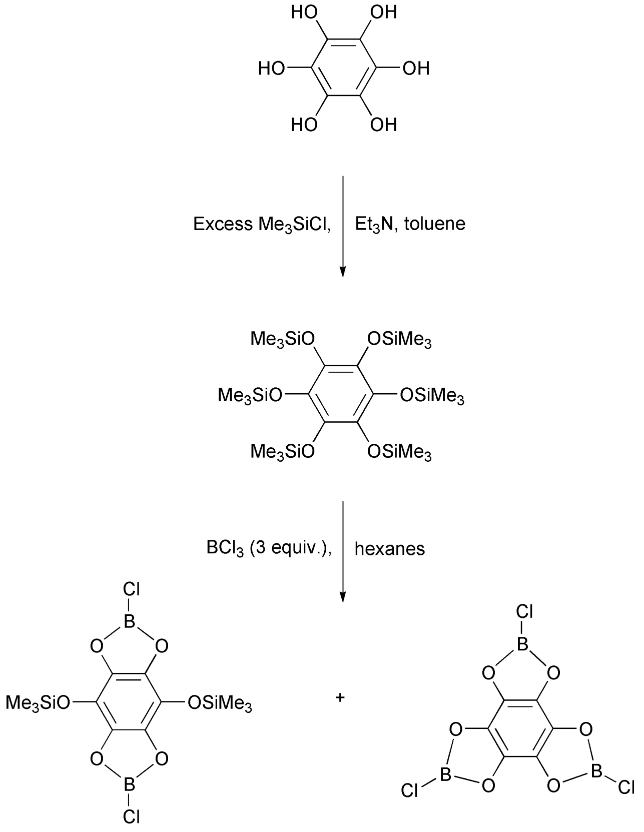


Fig. 1 Molecular structure of one of the two independent molecules of $(Me_3SiO)_6C_6$, **6**. Ranges of relevant bond lengths (Å) and angles (°): Si–O 1.655(3)–1.673(4), Si–C 1.780(8)–1.936(9), C–O 1.370(6)–1.389(6), O–Si–C 102.6(2)–110.5(2). Each independent molecule has crystallographically imposed 2/*m* symmetry.



Scheme 2

hexanes of concentrated solutions in either dichloromethane (**4a**, **4b**) or toluene (**4d**). In each case the molecular structure consists of two piano stool $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ fragments linked in μ_2,η^1,η^1 fashion by a bridging boryl ligand (see Figs. 2–4 and Table 1). In the case of **4a** and **4b** the molecule is centrosymmetric (sitting on a crystallographically imposed inversion centre) with the geometry of the ligand itself differing little from that found in chloride or hydride derivatives **3a** or **3c** (Figs. 5 and 6). The molecular structures of **4a** and **4b** are very similar, with essentially identical Fe–B distances, and a small (*ca.* 6°) difference in the orientation of the boryl ligand. By contrast, the molecular structure of **4d** is bent [Fe(1)–C(10)–Fe(1′) 130.4(4)°] reflecting the conformation of the six-membered chelate rings, and in particular the angle [132.3(5)°] between the planes defined by C(9), C(10), C(11) and O(3), B(1), O(4).

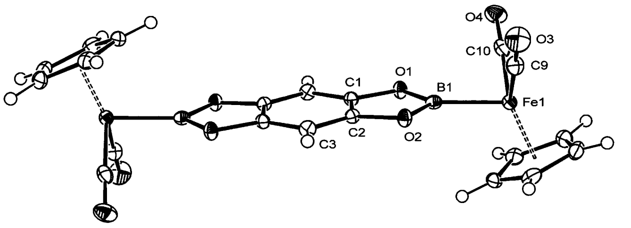


Fig. 2 Molecular structure of $(\eta^5\text{-}C_5H_5)Fe(CO)_2BO_2C_6H_2O_2BFe(CO)_2(\eta^5\text{-}C_5H_5)$, **4a**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 1.971(2), Fe(1)–C(10) 1.751(2), Fe(1)–Cp 1.721(2), B(1)–O(1) 1.406(2); C(9)–Fe(1)–C(10) 93.97(8), O(1)–B(1)–O(2) 109.15(14), O(1)–B(1)–Fe(1) 121.94(12), O(2)–B(1)–Fe(1) 125.79(13), O(1)–B(1)–Fe(1)–Cp 82.2(1). Cp = $(\eta^5\text{-}C_5H_5)$ centroid.

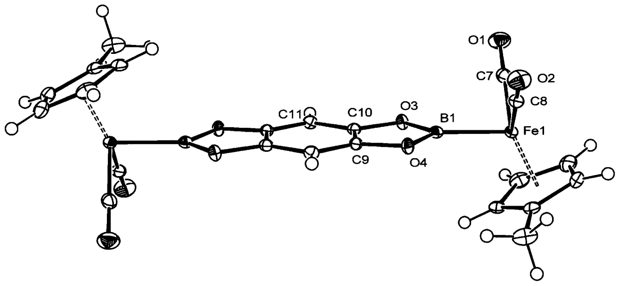


Fig. 3 Molecular structure of $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2BO_2C_6H_2O_2BFe(CO)_2(\eta^5\text{-}C_5H_4Me)$, **4b**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 1.973(2), Fe(1)–C(7) 1.753(2), Fe(1)–Cp 1.718(3), B(1)–O(3) 1.403(2); C(7)–Fe(1)–C(8) 95.56(9), O(3)–B(1)–O(4) 109.07(15), O(3)–B(1)–Fe(1) 124.67(14), O(4)–B(1)–Fe(1) 126.15(13), O(3)–B(1)–Fe(1)–Cp 87.7(2).

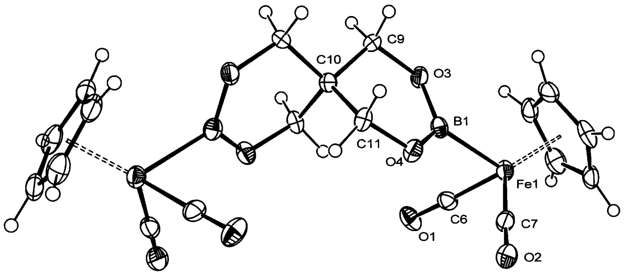


Fig. 4 Molecular structure of $(\eta^5\text{-}C_5H_5)Fe(CO)_2BO_2C_5H_8O_2BFe(CO)_2(\eta^5\text{-}C_5H_5)$, **4d**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 2.030(5), Fe(1)–C(7) 1.743(5), Fe(1)–Cp 1.722(6), B(1)–O(3) 1.369(6); C(6)–Fe(1)–C(7) 95.1(2), O(3)–B(1)–O(4) 121.2(4), O(3)–B(1)–Fe(1) 118.7(3), O(4)–B(1)–Fe(1) 120.2(3), Fe(1)–C(10)–Fe(1′) 130.4(4), O(3)–B(1)–Fe(1)–Cp 43.5(3). Each molecule of **4d** has crystallographically imposed two-fold symmetry.

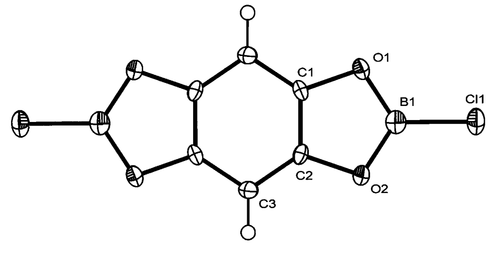


Fig. 5 Molecular structure of $ClBO_2C_6H_2O_2BCl$, **3a**. Relevant bond lengths (Å) and angles (°): B(1)–Cl(1) 1.737(3), B(1)–O(1) 1.377(3), B(1)–O(2) 1.377(3), O(1)–B(1)–O(2) 113.4(2), O(1)–B(1)–Cl(1) 123.0(2), O(2)–B(1)–Cl(1) 123.6(2). Each molecule of **3a** has crystallographically imposed inversion symmetry.

Of particular interest is the significantly longer Fe–B bond length found in **4d** [2.030(5) Å] compared to those found in **4a** [1.971(2) Å], **4b** [1.973(2) Å] and in the terminally bound Bcat analogue $(\eta^5\text{-}C_5H_5)Fe(CO)_2Bcat$ [1.959(6) Å].[6a] The latter three compounds all feature five-membered BO_2C_2 chelate rings in

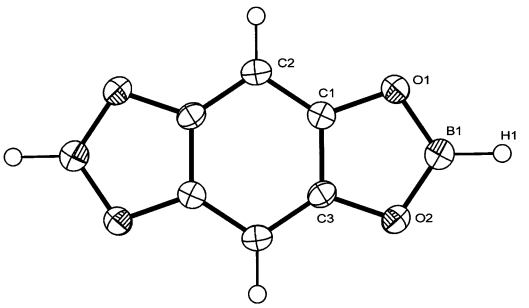


Fig. 6 Molecular structure of $HBO_2C_6H_2O_2BH$, **3c**. Relevant bond lengths (Å) and angles (°): B(1)–H(1) 1.100, B(1)–O(1) 1.386(2), B(1)–O(2) 1.382(2), O(1)–B(1)–O(2) 111.9(1), O(1)–B(1)–H(1) 123.4(4), O(2)–B(1)–H(1) 124.7(4). Each molecule of **3c** has crystallographically imposed inversion symmetry.

which conjugation of the appropriate symmetry lone pairs of the oxygen centres [*e.g.* O(1) and O(2) in **4a**] into the aromatic ring system is possible. In the case of **4d**, however, no such conjugation is possible, and as a consequence O ⟶ B π donation is likely to be more significant. This in turn renders the boryl boron centre less π acidic, and consequently the extent of π back donation from the iron centre is reduced. Hence the Fe–B distance in **4d** is similar to that found in $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2B_3ClN_3H_3$ [mean 2.043(1) Å[6d]] and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2B(NMe_2)Cl$ [2.027(5) Å[6e]] where little if any π back bonding is thought to exist. A further consequence is that the B–O distances in **4d** [mean 1.365(5) Å] are significantly shorter than those found in **4a** [1.406(2) Å] or **4b** [1.408(2) Å].

The Fe–B distances found in compounds **4a**, **4b** and the terminally bound Bcat analogue $(\eta^5\text{-}C_5H_5)Fe(CO)_2Bcat$ are among the shortest known for iron boryl complexes [mean 2.008 Å]. In the case of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Bcat$ the short Fe–B distance [1.959(6) Å] and angle (ϑ) of 7.9° between Cp–Fe–B [Cp = $(\eta^5\text{-}C_5H_5)$ centroid] and BO_2 planes have been ascribed to a π back bonding interaction between the HOMO of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2^+$ fragment (an a″ symmetry orbital lying parallel to the plane of the cyclopentadienyl ligand[14]) and the LUMO of the boryl ligand fragment.[6a] Dinuclear compounds **4a** and **4b** display a different orientation of the boryl ligand with respect to the Cp–Fe–B plane [ϑ = 82.2(1) and 87.7(2)°, respectively]. As a consequence any π back bonding interaction in these complexes must originate not in the metal-based HOMO but in the HOMO − 2 orbital of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2^+$ fragment (a deeper lying a′ symmetry orbital perpendicular to the HOMO). Furthermore the magnitude of this π interaction is clearly smaller in **4a** and **4b** than in $(\eta^5\text{-}C_5H_5)Fe(CO)_2Bcat$, as reflected by the significantly lower carbonyl stretching frequencies for the dinuclear species [ν(CO) = 2006 and 1954; 2001 and 1943; 2024 and 1971 cm^{-1} for **4a**, **4b** and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Bcat$, respectively].

Computational studies carried out using Density Functional Theory (DFT) for these complexes and others,[5a] however, reveal that in general alkoxo-substituted boryl complexes $[L_nM\text{–}B(OR)_2]$ display a relatively minor π contribution to bonding [*e.g.* 10.9% for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Bcat$].[5a] In addition, an energetic profile for rotation about the Fe–B bond calculated for the model compound $(\eta^5\text{-}C_5H_5)Fe(CO)_2BO_2C_2H_2$ (featuring a C=C double bond, rather than an *ortho*-substituted benzene ring within the five-membered chelate) shows that (i) the barrier to rotation about the Fe–B bond is of the order of 3–4 kJ mol^{-1}; and (ii) that near co-planar (ϑ = 8°) and near perpendicular (ϑ = 81°) orientations of the boryl ligand plane with respect to that defined by Cp–Fe–B are of essentially equal energy.[5a] These findings are therefore consistent with a description of boryl ligands as very good σ donors, but relatively poor π acceptors,[15] and imply that the differences in orientation of the boryl ligand between terminally coordinated Bcat and bridging $BO_2C_6H_2O_2B$ ligands may well be due to factors such as crystal packing in the solid state.

For systems of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$, ^{57}Fe Mössbauer spectroscopy offers an extensively used alternative to crystallographic methods to probe the electronic properties of a ligand X.[16] In general, a decrease in the Mössbauer effect isotope shift (i.s.) corresponds to an increase in the s electron density at the iron nucleus. Such an increase usually results from the presence of a ligand (X) which has good σ donor or π acceptor properties.[16]

The ^{57}Fe Mössbauer spectra of the dinuclear complexes **4a** and **4d** at 77 K are reproduced in Fig. 7, and associated spectral parameters listed in Table 2. The spectrum of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$ was also measured and spectral parameters are in good agreement with those reported previously.[16b] The very low values of the isomer shifts for both **4a** (0.02 mm s^{-1}) and **4d** (0.00 mm s^{-1}) are comparable to those reported for complexes containing either good π acceptor ligands (*e.g.* CN$^-$, 0.07 mm s^{-1} [16b]), or for those containing good σ donor ligands (*e.g.* $SiMe_3$, 0.05 mm s^{-1} and CH_3, 0.08 mm s^{-1} [16c]). That the bridging boryl ligands in **4a** and **4d** fit into the latter category as giving low isomer shifts due to strong σ donor rather than strong π acceptor properties is confirmed by analysis of the IR data listed in Table 2. The low carbonyl stretching frequencies found for **4a** and **4d** (2006, 1954 and 1998, 1932 cm^{-1}, respectively) are clearly more consistent with strong σ donor properties [*cf.* 2010, 1958 and 1996, 1994 cm^{-1} for $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3$, respectively[16c]] than with an appreciable π acceptor role [2060, 2015 cm^{-1} for $(\eta^5\text{-}C_5H_5)Fe(CO)_2CN$]. Indeed, it is noticeable how similar are both

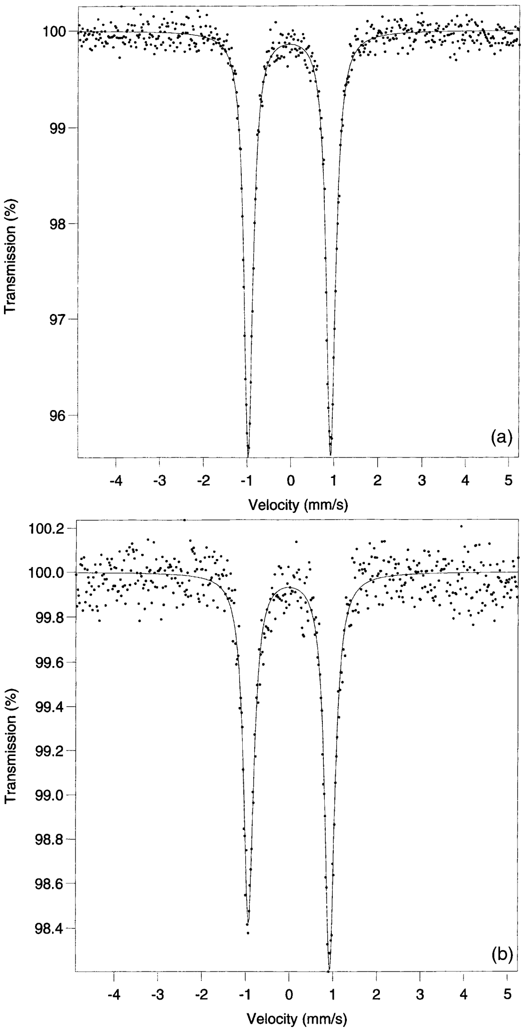


Fig. 7 ^{57}Fe Mössbauer spectra of (a) **4a** and (b) **4d** at 77 K.

Table 2 Comparison of Mössbauer and IR spectral data for complexes of the type (η^5-C_5H_5)Fe(CO)$_2$X (including dinuclear boryl complexes **4a** and **4d**)

Complex	Isomer shift/mm s^{-1}	Quadrupole splitting/mm s^{-1}	ν(CO)/cm^{-1}	Ref.
4a	0.02	1.91	2006, 1954	This work
4d	0.00	1.86	1998, 1932	This work
(η^5-C_5H_5)Fe(CO)$_2$Br	0.22	1.88	2045, 1999	This work
(η^5-C_5H_5)Fe(CO)$_2$Br	0.23	1.87	2045, 1999	16*b*
(η^5-C_5H_5)Fe(CO)$_2$CN	0.07	1.90	2060, 2015	16*b*
(η^5-C_5H_5)Fe(CO)$_2$SCN	0.19	1.81	2050, 2005	16*b*
(η^5-C_5H_5)Fe(CO)$_2$SiMe$_3$	0.05	1.77	1996, 1944	16*c*
(η^5-C_5H_5)Fe(CO)$_2$CH$_3$	0.08	1.76	2010, 1958	16*c*
(η^5-C_5H_5)Fe(CO)$_2$B$_5$H$_8$	0.04	1.84	2005, 1947	16*d*

Mössbauer and IR spectral parameters for **4a** and **4d** to those reported for (η^5-C_5H_5)Fe(CO)$_2$B$_5$H$_8$.[16d] This complex contains a (η^5-C_5H_5)Fe(CO)$_2$ fragment terminally bound to the basal boron of a square pyramidal cluster, which by implication must have little or no π acceptor properties.[16d]

By contrast, FT-Raman and electrochemical probes of boryl complexes **4a**–**d** have proved to be less informative. Raman spectra of the four dinuclear complexes show little variation, strong features in the region 520–530 cm^{-1} in each case being assigned to Fe–B stretching modes. Interestingly however, the analogous stretching vibration for the more Lewis acidic pentafluorophenyl substituted derivative (η^5-C_5H_5)Fe(CO)$_2$B(C$_6$F$_5$)$_2$ is found at 577 cm^{-1}. Electrochemical methods have been used to great effect to assess the possibility for communication between metal centres through bridging ligand systems. Consequently, it was hoped that cyclic voltametry (CV) measurements for complexes **4a**–**c** might indicate whether communication between metal centres through bridging boryl ligands was possible. CV measurements for all four dinuclear complexes (including complex **4d** containing a comparative saturated spacer group) were unfortunately complicated by problems of irreversibility, which were only partially alleviated by the use of bulkier ligand systems (η^5-C$_5$Me$_5$ *vs.* η^5-C_5H_5), glassy carbon electrodes or low temperature. Consequently it proved impossible to definitively assign spectra and therefore to use electrochemical methods as a probe of the electronic structure of these systems.

4 Conclusions

A series of dinuclear complexes containing iron centres linked *via* boryl ligands has been synthesised by metathesis from bifunctional boron halides. This synthetic approach is applicable to different ligand backbones ('spacer groups') and relies heavily on the use of trimethylsilyl substituted precursors to generate complexes such as **4a**–**d** in reasonable yield. Comparative structural studies of **4a** and **4d** reveal the importance of the chelating alkoxo backbone of the boryl ligand in determining its electronic properties. In addition, structural characterization of the bridged boryl systems allows comparison with terminally bound Bcat analogues. The origins of the different ligand orientations found have been probed by DFT methods which suggest (i) that π contributions to bonding and barriers to Fe–B rotation are small for dialkoxoboryl systems, and (ii) that crystal packing forces rather than ligand electronics are almost certainly responsible for the different orientations observed. Finally, ^{57}Fe Mössbauer spectroscopy has been used for the first time to probe the bonding in boryl systems, with the findings being entirely consistent with a description of these ligands as very good σ donors, but poor π acceptors.

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