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Synthesis and reactivity of transition metal complexes containing halogenated boryl ligands

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Abstract

The synthesis and characterization of iron and manganese complexes containing the tetrachlorocatecholboryl ($BO_2C_6Cl_4$) ligand are reported. Crystallographic study of the methylcyclopentadienyl derivative (η^5-C_5H_4Me)$Fe(CO)_2BO_2C_6Cl_4$ allows comparison of structure and bonding with related complexes of the type (η^5-C_5R_5)$Fe(CO)_2B(OR)_2$ and reveals that the relative orientation of (η^5-C_5H_4Me)$Fe(CO)_2$ and $BO_2C_6Cl_4$ moieties is influenced by intramolecular C–H···O hydrogen bonding. Additionally, an alternative route to catecholboryl complexes from dilithiocatechol is reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Boryl; Boron; Iron; Manganese; Hydrogen bond; Substitution

1. Introduction

Transition metal boryl complexes (L_nM–BX_2) have been the subject of intense recent research activity [1–4], partly because of their involvement in the hydro- and diboration of carbon–carbon multiple bonds [5], but also because of their implication in highly selective stoichiometric and catalytic functionalization of alkanes under either photolytic or thermal conditions [6–14]. The reactivity of boryl complexes towards a variety of substrates has therefore been investigated in some depth [2,4], although the intrinsic reactivity of the metal boron bond is such that substitution reactions at the boron centre that occur with *retention* of the M–B bond are rare [2,4,15]. Such studies of reactivity have been complimented by numerous structural investigations in which the nature of the metal boron bond has been probed by crystallographic, spectroscopic and computational methods [1–4,16,17]. One of the significant questions investigated by such studies is the potential for the extremely strongly σ-donor boryl ligand also to act as a π acid by utilizing the vacant boron-based orbital of π-symmetry; to what extent the nature of the M–B bond can be altered by variation in the electronic properties of X has been the subject of several studies [16,17]. Ultimately a better understanding of the nature of the M–B bond may help to rationalize the unusual reactivity of such complexes.

We have recently begun a research program aimed at a better understanding of the relationship between the structure and reactivity of boryl ligands, which has encompassed the investigation of new types of ligand [18] and new modes of coordination [19,20], together with novel methods for probing the nature of the metal boron bond [17]. One approach has been to investigate the effect on structure and reactivity of variation in electronic properties within the boryl ligand framework (e.g. by introduction of halogen substituents). Complexes containing the BF_2 ligand [21], or containing boryl ligands bearing perhalogenated aryl substituents have only recently been reported [18,22], and although complexes containing the BCl_2 ligand have been synthesised by Roper and Wright [2,15], no structural data are as yet available. We have therefore sought to synthesise iron and manganese complexes containing the $BO_2C_6Cl_4$ ($BcatCl_4$) ligand, which might offer useful comparison with derivatives containing the more widely exploited $BO_2C_6H_4$ (Bcat) fragment. In addition, we have sought to investigate the utility of iron complexes

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Abbreviations: st, strong; md, medium; w, weak; sh, shoulder; s, singlet; m, multiplet; b, broad.

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containing the BCl_2 ligand in the synthesis of other metal boryl complexes.

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 Na wire (hexanes, $C_6H_5CH_3$) or molecular sieves (CH_2Cl_2) and purged with nitrogen prior to distillation. Hexanes (K), $C_6H_5CH_3$ (Na), and CH_2Cl_2 (CaH_2) were then distilled from the appropriate drying agent before use. C_6D_6 (Goss) was degassed and dried over K prior to use. BCl_3 (1 M solution in heptanes, Aldrich) and ^nBuLi (2.5 M solution in hexanes, Aldrich) were used as received, without further purification. Catechol (Aldrich) and tetrachlorocatechol (Lancaster) were dried and sublimed prior to use. Dilithiocatechol, perchlorocatecholborane (**1**), (η^5-C_5H_4R)$Fe(CO)_2Na$ (R = H, Me) and $NaMn(CO)_5$ were prepared by minor modification of literature methods [23–25]. 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. IR spectra were measured for each compound either as a KBr disk or as a solution in hexanes on a Nicolet 500 FT-IR 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. Elemental analyses were carried out both by the departmental analysis service and by Warwick Analytical Service, University of Warwick.

*2.1. (η^5-C_5H_4R)$Fe(CO)_2BO_2C_6Cl_4$ [R = H (**2**) and R = Me (**2′**)]*

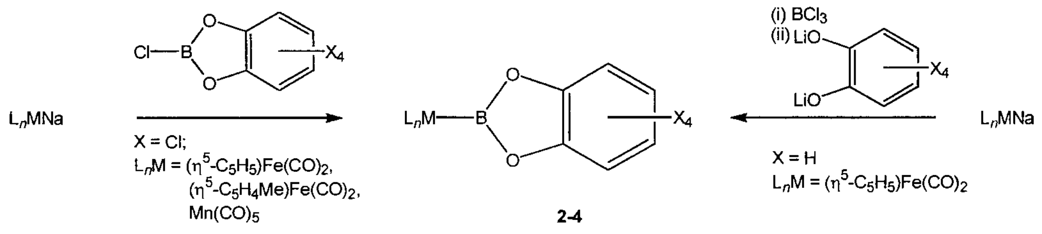
To a suspension of (η^5-C_5H_5)$Fe(CO)_2Na$ (274 mg, 1.37 mmol) in ca. 20 cm^3 $C_6H_5CH_3$ at room temperature (r.t.) was added to one equivalent of perchlorocatecholborane (**1**) (0.400 g, 1.37 mmol) in 10 cm^3 $C_6H_5CH_3$. The reaction mixture was stirred at r.t. for a period of 12 h, volatiles removed in vacuo, and the resulting solid recrystallized from either $C_6H_5CH_3$ or hexanes to yield **2** as pale yellow acicular crystals in yields of up to 62%. Complex **2** has been characterized by ^1H-, ^{13}C- and ^{11}B-NMR, IR, MS and elemental analysis. ^1H-NMR (400 MHz, C_6D_6): δ 4.07 (5H, s, η^5-C_5H_5). ^{13}C-NMR (76 MHz, C_6D_6): δ 84.4 (η^5-C_5H_5), 115.7, 126.5, 146.9 (aromatic), 213.1 (CO). ^{11}B-NMR (96 MHz, C_6D_6): δ 55.2. IR (KBr) (cm^{-1}): 2008 st, 1949 st [ν(CO)]. MS (EI): $[M]^+ = 435$ (100%), isotopic pattern in agreement with that expected for 1B, 4Cl, 1Fe atom. Anal. Calc. for $C_{13}H_5BCl_4FeO_4$: C, 36.00; H, 1.16. Found: C, 35.58; H, 1.23%. Complex **2′** was prepared in an analogous fashion and crystals suitable for X-ray diffraction grown by controlled cooling of concentrated $C_6H_5CH_3$ solutions. Spectroscopic data for **2′**: ^1H-NMR (400 MHz, C_6D_6): δ 1.39 (3H, s, η^5-$C_5H_4CH_3$), 4.06 (2H, m, η^5-$C_5H_4CH_3$), 4.17 (2H, m, η^5-$C_5H_4CH_3$). ^{13}C-NMR (76 MHz, C_6D_6): δ 12.6 (η^5-$C_5H_4CH_3$) 82.3, 84.6 (Cp *C*H), 102.3 (Cp quaternary), 115.1, 125.7, 146.4 ($BO_2C_6Cl_4$), 213.3 (CO). ^{11}B-NMR (96 MHz, C_6D_6): δ 53.4. IR (KBr) (cm^{-1}): 2004 st, 1945 st [ν(CO)].

*2.2. [$(OC)_5MnBO_2C_6Cl_4$] (**3**)*

Complex **3** was prepared in a manner analogous to that described in Section 2.1 for **2**, using $NaMn(CO)_5$ as the organometallic reagent. Complex **3** was isolated as pale yellow plate-like crystals in yields of up to 53%, based on the amount of manganese reagent used and has been characterized by ^{13}C- and ^{11}B-NMR, IR, MS (including exact mass determination) and elemental analysis. ^{13}C-NMR (76 MHz, C_6D_6): δ 106.9, 126.6, 146.0 (aromatic), 209.7 (b, CO). ^{11}B-NMR (96 MHz, C_6D_6): δ 50.6. IR (KBr) (cm^{-1}): 2120 md, 2036 st sh, 2014 st, 1990 st, 1972 md sh [ν(CO)]. MS (EI): $[M]^+ =$ 452 (100%), isotopic pattern in agreement with that expected for 1B, 4Cl, 1Mn atom. Exact mass: Calc. for $C_{11}BCl_4MnO_7$ ($m/z = 449.8$ isotopomer): 449.7872. Found: 449.7867. Anal. Calc. for $C_{11}BCl_4MnO_7$: C, 29.37; H, 0.00. Found: C, 29.02; H, 0.17%.

*2.3. Alternative synthesis of (η^5-C_5H_5)$Fe(CO)_2BO_2C_6H_4$ (**4**)*

To a suspension of 0.295 g (1.48 mmol) of (η^5-C_5H_5)$Fe(CO)_2Na$ in $C_6H_5CH_3$ at −40 °C was added one equivalent of BCl_3 (1.48 mmol, 1.48 cm^3 of a 1 M solution in heptanes). The solution was warmed to r.t. and stirred for 4 h, and the ^{11}B-NMR spectrum of the reaction mixture at this point revealed complete conversion of BCl_3 (δ_B 46.5) to a species with a single ^{11}B resonance at δ_B 90.7. The reaction mixture was then filtered and added to a suspension of one equivalent of dilithiocatechol in 10 cm^3 $C_6H_5CH_3$. After stirring for a further 20 min at r.t., the ^{11}B-NMR spectrum of the reaction mixture revealed a single resonance at δ_B 51.0, characteristic of (η^5-C_5H_5)$Fe(CO)_2BO_2C_6H_4$ (**4**) [6]. Removal of volatiles in vacuo at this point, extraction of the resulting solid into hexanes and cooling to −30 °C led to the crystallization of **4** in 48% isolated yield. ^1H-, ^{13}C-, ^{11}B-NMR, IR and mass spectrometric data for **4** were consistent with those reported by Hartwig and Huber [6]. Alternatively, if the reaction mixture is worked up prior to the addition of dilithiocatechol,



Scheme 1. Synthetic routes to boryl complexes **2**–**4** [L_nM=(η^5-C_5H_5)Fe(CO)$_2$, X = Cl (**2**); L_nM=(η^5-C_5H_4Me)Fe(CO)$_2$, X = Cl (**2′**); L_nM=(OC)$_5$Mn, X = Cl (**3**); L_nM=(η^5-C_5H_5)Fe(CO)$_2$, X = H (**4**)].

characterization of the intermediate species can be carried out. Removal of volatiles in vacuo and recrystallization from hexanes leads to the isolation of a pale yellow microcrystalline material which has been characterized by ^{1}H-, ^{13}C- and ^{11}B-NMR, IR and MS. ^{1}H-NMR (400 MHz, C_6D_6): δ 4.07 (5H, s, η^5-C_5H_5). ^{13}C-NMR (76 MHz, C_6D_6): δ 81.4 (η^5-C_5H_5), 215.8 (CO). ^{11}B-NMR (96 MHz, C_6D_6): δ 90.7. IR (hexanes) (cm^{-1}): 2022 st, 1963 st [ν(CO)]. MS (EI): $[M]^+ = 259$ (28%), isotopic pattern in agreement with that expected for 1B, 2Cl, 1Fe atom. Although spectroscopic data are in agreement with the formulation of the intermediate as (η^5-C_5H_5)Fe(CO)$_2$BCl$_2$, further characterization (e.g. by elemental analysis and X-ray diffraction) were hampered by the fragility of the compound and its ready decomposition to the dark red dimeric species [(η^5-C_5H_5)Fe(CO)$_2$]$_2$.

It should be noted that careful repeated washing of the (η^5-C_5H_5)Fe(CO)$_2$Na starting material with warm $C_6H_5CH_3$ is required to remove traces of THF (which is a contaminant inherent in the synthetic route used). Yields of **4** are otherwise significantly reduced and the side product BCl_3·THF is a major contaminant.

2.4. Crystallographic data for 2′

$C_{14}H_7BCl_4O_4Fe\cdot\frac{1}{2}(C_7H_8)$, $M_r = 493.72$, $T = 120(2)$ K, triclinic, space group $P\bar{1}$, $a = 6.8564(6)$, $b = 10.6520(3)$, $c = 13.7941(10)$ Å, $\alpha = 74.504(5)$, $\beta = 86.866(6)$, $\gamma = 76.658(4)°$, $V = 944.59(11)$ Å^3, $Z = 2$, $\rho_{calc} = 1.736$ g cm^{-3}, $\mu = 1.386$ mm^{-1}, reflections collected: 6734, independent reflections: 2544 ($R_{int} = 0.0639$), final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0462$, $wR_2 = 0.1041$, R indices (all data): $R_1 = 0.0798$, $wR_2 = 0.1203$.

Crystals of **2′** suitable for single crystal X-ray diffraction were mounted on a Bruker Nonius KappaCCD area detector equipped with a molybdenum rotating anode. The initial cell determination was found to be unreasonable and, using the program DirAx [26], it was possible to index all reflections on two smaller cells related by a 180° rotation about *a*. The data collection was carried out using COLLECT [27] and integration performed by EvalCCD [28]. The reflection file consisted of the non-overlapping reflections from the major twin component. The structure was solved via direct methods and refined by full-matrix least-squares on F^2 [29]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealised positions and refined using a riding model; in the case of the methyl group the torsion angle was allowed to vary to locate the maximum electron density. The $C_6H_5CH_3$ solvent molecule was found to be disordered about a centre of inversion and it was necessary to constrain its geometry during refinement.

3. Results and discussion

The metathesis reaction between $ClBO_2C_6Cl_4$ (**1**) and the sodium salt of either [(η^5-C_5H_4R)Fe(CO)$_2$]$^-$ (R = H, Me) or [Mn(CO)$_5$]$^-$ results in the synthesis of the (tetrachlorocatechol)boryl complexes (η^5-C_5H_4R)Fe(CO)$_2$BO$_2$C$_6$Cl$_4$ [R = H (**2**), Me (**2′**)] and [(OC)$_5$MnBO$_2$C$_6$Cl$_4$] (**3**) in yields of 50–60% (Scheme 1). The pale yellow solids are moderately air sensitive, but can be stored indefinitely under argon at −30 °C. Complexes **2** and **3** are characterized by ^{11}B-NMR resonances in the region typical of metal boryl complexes containing two boron-bound oxygen substituents (e.g. δ_B 55.2 and 50.6 ppm, respectively for **2** and **3**, compared to 51.8 and 49 ppm for (η^5-C_5H_5)Fe(CO)$_2$BO$_2$C$_6$H$_4$ and (OC)$_5$MnBO$_2$C$_6$H$_4$ [6,7]). Other spectroscopic and analytical data for **2** and **3** are consistent with the proposed formulation, and although single crystals suitable for diffraction study could not be obtained for either complex, the methylcyclopentadienyl analogue of **2**, (η^5-C_5H_4Me)Fe(CO)$_2$BO$_2$C$_6$Cl$_4$ (**2′**) could be obtained in suitable crystalline form by slow cooling of a concentrated toluene solution.

The X-ray structure analysis reveals the expected half sandwich geometry at the iron centre with the coordination sphere being completed by two carbonyls and one (tetrachlorocatechol)boryl ligand (Fig. 1). To our knowledge **2′** represents only the second crystallographically characterized complex containing this ligand, and the first for iron [22]. The Fe–B distance [1.967(6) Å] is consistent with that found in similar complexes containing catechol-based boryl ligands {e.g. (η^5-C_5H_5)Fe(CO)$_2$BO$_2$C$_6$H$_4$ [1.959(6) Å], (η^5-C_5Me_5)Fe(CO)$_2$BO$_2$C$_6$H$_4$ [1.980(2) Å], and (η^5-

$C_5H_5)Fe(CO)_2BO_2C_6H_2O_2BFe(CO)_2(\eta^5$-$C_5H_5)$ [1.971(2) Å]} [6,20], and significantly shorter than the average value found for Fp boryl complexes in general.[1] By analogy with these related complexes, the bond length is therefore indicative of an (albeit weak) Fe–B back-bonding interaction [6,20]. Comparison of the carbonyl stretching frequencies for **2** and **2′** (2008, 1949 and 2004, 1945 cm^{-1}, respectively) with those obtained for $(\eta^5$-$C_5H_5)Fe(CO)_2BO_2C_6H_4$ (2024 and 1971 cm^{-1}), however, implies that the degree of back bonding is somewhat reduced upon perchlorination of the catecholboryl ligand.

The torsion angle (ϑ) between $(\eta^5$-$C_5H_5)$ centroid–Fe–B and BO_2 planes is found to be 26.6(5)° compared with values of 7.9, 26.7 and 82.2° found in $(\eta^5$-$C_5H_5)Fe(CO)_2BO_2C_6H_4$, $(\eta^5$-$C_5Me_5)Fe(CO)_2BO_2$-C_6H_4 and $(\eta^5$-$C_5H_5)Fe(CO)_2BO_2C_6H_2O_2BFe(CO)_2(\eta^5$-$C_5H_5)$, respectively [6,20]. The wide range of values obtained for ϑ for superficially similar compounds indicates that the orientational preference of $(\eta^5$-$C_5H_4R)Fe(CO)_2$ and BX_2 units is not a strong one and is consistent with a description of catecholboryl ligands as strong σ donors, but as relatively poor π acceptors. In addition, it appears that the conformation adopted in **2′** is influenced by a weak C–H···O hydrogen bond between H(6a) of the methyl group and O(4) of the boryl ligand (Fig. 2). Although structural inferences based on the position of the hydrogen atom must be viewed cautiously, the C···O and O···H distances [3.279(7) and 2.52 Å, respectively] and C–H···O angle (134.4°) are within the ranges expected for hydrogen bonds of this sort [30–32], being similar, for example, to those reported for methyl C–H···O=C bonds in various geometries of the DMF dimer [32]. The ability of a weak hydrogen bonding interaction to influence the conformational geometry is further indicative of the relatively shallow potential surface for rotation about the Fe–B bond. Estimates of typical C–H···O hydrogen bond strengths are of the order of 4–10 kJ mol^{-1} [30–32], whereas a barrier to rotation of ca. 3 kJ mol^{-1} has been calculated for the model catecholboryl complex $(\eta^5$-$C_5H_5)Fe$-$(CO)_2BO_2C_2H_2$ by DFT methods [17]. The assessment of C–H···O hydrogen bond strengths as being comparable to the energetics of conformational processes in small molecules has previously been advanced by Desiraju [30]. It should be noted however that there is no evidence on the basis of spectroscopic data for the existence of intramolecular hydrogen bonding in solution.

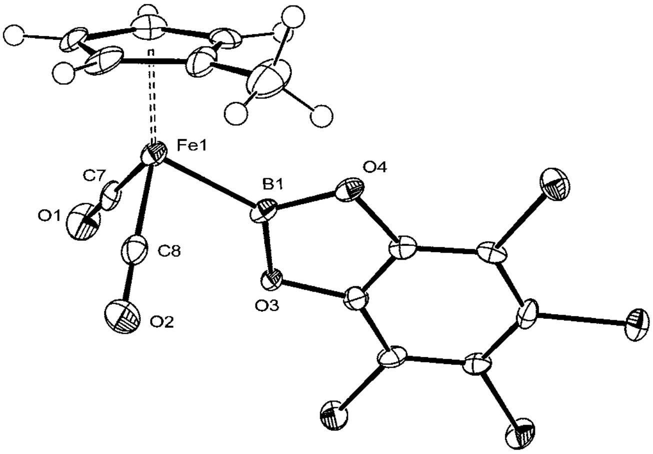


Fig. 1. Molecular structure of the tetrachlorocatecholboryl complex **2′**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 1.967(6), Fe(1)–centroid 1.721(5), Fe(1)–C(7) 1.761(6), Fe(1)–C(8) 1.731(6), B(1)–O(3) 1.423(7), B(1)–O(4) 1.433(7), C(7)–Fe(1)–C(8) 94.4(2), Fe(1)–B(1)–O(3) 126.6(4), Fe(1)–B(1)–O(4) 125.6(4), O(3)–B(1)–O(4) 107.8(4), centroid–Fe(1)–B(1)–O(4) 26.6(5).

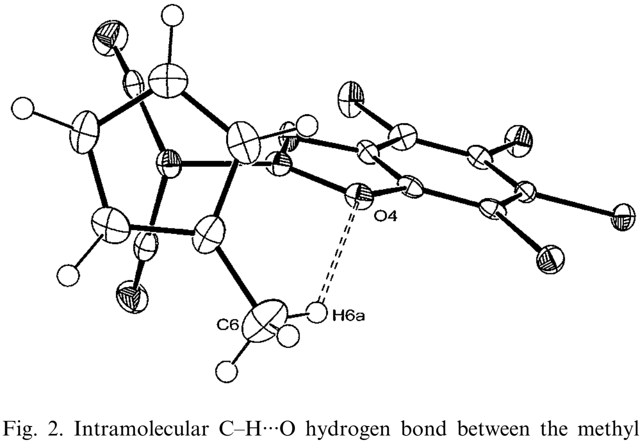


Fig. 2. Intramolecular C–H···O hydrogen bond between the methyl C–H and catecholboryl oxygen O(4) in **2′**. Relevant bond lengths (Å) and angles (°): C(6)···O(4) 3.279(7), H(6a)···O(4) 2.52, C(6)–H(6a) 0.98, C–H···O 134.4.

The reaction of $(\eta^5$-$C_5H_5)Fe(CO)_2Na$ with boron trichloride followed by dilithiocatechol provides an alternative route to catecholboryl derivatives of iron (see Scheme 1). In this case the reaction is thought to proceed via the dichloroboryl intermediate $(\eta^5$-$C_5H_5)Fe$-$(CO)_2BCl_2$ on the basis of multinuclear NMR, IR and mass spectrometric data. Monitoring of the reaction by ^{11}B-NMR reveals that the signal at δ_B 46.5 due to the BCl_3 starting material is quantitatively replaced by a low-field signal at δ_B 90.7 over a period of 4 h. The ^{11}B-NMR resonance for the intermediate species shows the downfield shift (compared to the BCl_3 starting material) expected for replacement of Cl with the $(\eta^5$-$C_5H_5)Fe(CO)_2$ fragment.[2] In addition the mass

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[1] The average Fe–B bond length measured for crystallographically characterised complexes of the type $(\eta^5$-$C_5R_5)Fe(CO)_2BX_2$ containing a three-coordinate boron centre is 2.008(6) Å [6,18,20,34–36].

[2] Typically, downfield shifts of between 20 and 65 ppm are observed for the ^{11}B resonance on replacement of a chlorine (in X_2BCl) with a $(\eta^5$-$C_5R_5)Fe(CO)_2$ fragment [to give $(\eta^5$-$C_5R_5)Fe(CO)_2BX_2$]. Larger shifts are generally observed for weaker π donor X substituents. For example: δ_B 29.0–51.0 for $BX_2 = BO_2C_6H_4$ [37,6]; 35.0–59.1 for $B(NMe_2)Cl$ [37,36]; 37.5–69.5 for $B(NMe_2)B(NMe_2)Cl$ [37,35]; 61.0–121.0 for BPh_2 [37,6]; 59.1–121.5 for $B(C_6F_5)_2$ [37,18].

spectrum displays a peak at $m/z = 259$ [(η^5-C_5H_5)Fe$(CO)_2BCl_2^+$], and the measured carbonyl stretching frequencies [2022 and 1963 cm^{-1}] are consistent with the attachment at the iron centre of a moderately π acidic boryl ligand such as BCl_2. On addition of one equivalent of dilithiocatechol, the signal at δ_B 90.7 is converted over a period of 20 min into a single resonance at δ_B 51.0 characteristic of (η^5-C_5H_5)Fe$(CO)_2BO_2C_6H_4$ (**4**) [6]. The identity of the final isolated product was confirmed by comparison of the measured spectroscopic data with that originally reported by Hartwig and Huber [6].

This reaction represents a rare example of substitution at X within a boryl (BX_2) ligand, with retention of the metal boron bond. This type of reactivity occurs almost exclusively for BCl_2 complexes (in which the stabilization of the boron centre by π electron release is relatively poor), and has also been reported by Roper and Wright for osmium BCl_2 derivatives [2,15]. Similar chemistry has also been reported by Braunschweig for bridging borylene complexes containing the BCl ligand [33]. Attempts to develop the scope of this substitution chemistry in the synthesis of novel iron boryl complexes are ongoing.

4. Conclusions

Complexes of iron and manganese containing the tetrachlorocatecholboryl ($BO_2C_6Cl_4$) ligand can be synthesised in reasonable yield by the reaction of the appropriate organometallic anion with perchlorocatecholborane; in addition catecholboryl complexes of iron can be synthesised by substitution at the boryl centre of an initially-formed BCl_2 complex. Crystallographic data for (η^5-C_5H_4Me)Fe$(CO)_2BO_2C_6Cl_4$ further emphasise the description of such ligands as good σ donors, but poor π acceptors, with the relative orientation of (η^5-C_5H_4Me)Fe$(CO)_2$ and $BO_2C_6Cl_4$ moieties being influenced by weak intramolecular C–H···O hydrogen bonding.

5. Supplementary material

Crystallographic data for the structural analysis of compound **2′** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 171824. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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