Synthesis and Characterisation of the Mixed-sandwich Complex *closo*-[3-(η-C_5Me_5)Fe-4-Me_2S-1,2-$C_2B_9H_{10}$] and its Charge-transfer Salts; Crystal Structure of [Fe(η-C_5Me_5)($C_2B_9H_{10}SMe_2$)]$^+$[ddq]$^{•-}$·CH_2Cl_2 (ddq = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone)†

Yaw-Kai Yan,[a] **D. Michael P. Mingos,***[,a] **Thomas E. Müller,**[a] **David J. Williams**[a] **and Mohamedally Kurmoo**[b]

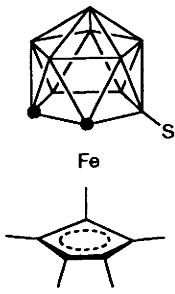
[a] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK*

[b] *The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK*

The mixed-sandwich ferracarborane complex *closo*-[3-(η-C_5Me_5)Fe-4-Me_2S-1,2-$C_2B_9H_{10}$] has been synthesised and characterised by cyclic voltammetry, infrared, ^{1}H and ^{11}B NMR spectroscopy. This complex forms stable 1 : 1 charge-transfer salts with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (ddq) and 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane. Both salts are paramagnetic between 5 and 300 K with Weiss constants of −0.9 and −0.7 K respectively. The organic radical anions do not contribute to the bulk magnetic susceptibilities of these salts. Single-crystal X-ray diffraction analysis of the ddq salt shows that the ddq$^{•-}$ anions form isolated stacked dimers within which there is a short interplanar separation of 2.90 Å. Short S···O contacts (3.15 Å) occur between the [Fe(η-C_5Me_5)($C_2B_9H_{10}SMe_2$)]$^+$ cations and the quinoidal oxygen atoms of the anions. The room-temperature electrical conductivity of single crystals of the ddq salt is less than 10^{-7} S cm^{-1}.

One of the approaches which have been proposed for the synthesis of molecular ferromagnets is to form charge-transfer salts between metallocene derivatives and planar organic electron acceptors.[1,2] For example, the charge-transfer salt between decamethylferrocene, [Fe(η-C_5Me_5)$_2$], and tetracyanoethylene (tcne), [Fe(η-C_5Me_5)$_2$]$^+$[tcne]$^{•-}$, is a bulk ferromagnet below 5 K.[1d] Its crystal structure consists of chains of alternating cations and anions, with the [tcne]$^{•-}$ anions lying essentially parallel to the C_5Me_5 rings.[1d] The ferromagnetic behaviour was initially explained using the extended-McConnell model,[1] which attributes the stabilisation of the triplet ground state of each cation–anion pair to configurational mixing with the lowest-energy electronic state (a triplet) associated with the excited charge-transfer state [Fe(η-C_5Me_5)$_2$]$^{2+}$[tcne]$^{2-}$. It was later pointed out that the distances between the magnetic orbitals of the cations and anions are too large (> 5 Å) for significant orbital overlap and hence configurational mixing between the ground and excited charge-transfer states would be negligible.[3] The extended-McConnell model also neglects the other possible excited electronic states, most of which are singlets.[4]

An alternative mechanism for the ferromagnetic coupling in [Fe(η-C_5Me_5)$_2$]$^+$[tcne]$^{•-}$ has been proposed by Kahn and co-workers.[3,5] In this mechanism the strong antiferromagnetic coupling between the spins on the [tcne]$^{•-}$ anions and the small negative spin densities on the C_5Me_5 rings of the [Fe(η-C_5Me_5)$_2$]$^+$ cations stabilises the overall ferromagnetic coupling between the spins on the cations and anions within a chain. The presence of low negative spin densities on the cyclopentadienyl rings of several alkylated ferrocenium cations has been observed in NMR and ESR experiments.[6] Moreover, the interplanar distance between a [tcne]$^{•-}$ anion and the nearest C_5Me_5 ring within a chain (3.5 Å) is short enough for significant spin interaction to occur.[3]



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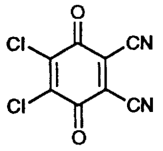
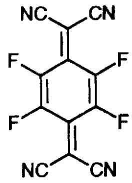
(● = Cage carbon atom)



ddq



tcntfq

In an attempt to study the effect of the C_5Me_5 ligand on interionic magnetic interactions in sandwich compounds related to [Fe(η-C_5Me_5)$_2$]$^+$[tcne]$^{•-}$, the mixed-sandwich complex *closo*-[3-(η^5-C_5Me_5)Fe-4-Me_2S-1,2-$C_2B_9H_{10}$] **1** was synthesised and treated with several organic electron acceptors. In this compound one of the C_5Me_5 ligands has been replaced by a *nido*-icosahedral carborane cage. We report the synthesis and spectroscopic properties of **1** and its charge-transfer salts with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (ddq) and 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane (tcntfq) in this paper. The magnetic properties of the charge-transfer salts and the crystal structure and electrical properties of the ddq salt are also described.

Results and Discussion

(*a*) *closo*-[3-(η^5-C_5Me_5)Fe-4-Me_2S-1,2-$C_2B_9H_{10}$] **1**.—(*i*) *Synthesis*. The synthesis of compound **1** is summarised in

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† *Supplementary data available*: see instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

equations (1) and (2) (thf = tetrahydrofuran). It gave a 40%

$$\mathrm{Li(C_5Me_5)} + [\mathrm{FeCl_2(thf)_2}] \xrightarrow{\mathrm{thf}} [\mathrm{FeCl}(\eta\text{-}\mathrm{C_5Me_5})] + \mathrm{LiCl} + 2\mathrm{thf} \tag{1}$$

$$[\mathrm{FeCl}(\eta\text{-}\mathrm{C_5Me_5})] + \mathrm{Li}[\mathrm{C_2B_9H_{10}SMe_2}] \xrightarrow{\mathrm{thf}} [\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{C_2B_9H_{10}SMe_2})] + \mathrm{LiCl} \tag{2}$$

yield of compound **1**, with very small amounts of $[\mathrm{Fe(C_2B_9H_{10}SMe_2)_2}]$ and decamethylferrocene formed as side products. The crude product was also contaminated by some $\mathrm{C_2B_9H_{11}SMe_2}$ which was derived from the protonation of unreacted $\mathrm{Li[C_2B_9H_{10}SMe_2]}$ during the work-up procedure. Since the $[\mathrm{Fe(C_2B_9H_{10}SMe_2)_2}]$ impurity could not be completely removed by fractional recrystallisation and **1** is rapidly oxidised on silica, the crude product was chromatographed on alumina thin-layer chromatography (TLC) plates. The alumina plates, however, could not effectively separate **1** and $\mathrm{C_2B_9H_{11}SMe_2}$. It was thus necessary to recrystallise the chromatographed product again from a dichloromethane–toluene mixture to obtain analytically pure samples of **1**. Compound **1** forms orange crystals which are air- and moisture-stable, although the compound is air-sensitive in $\mathrm{CDCl_3}$ solution; orange solutions of **1** turn brown overnight in air.

(*ii*) *Spectroscopic characterisation*. The room-temperature 300 MHz ^{1}H NMR spectrum of complex **1** in $\mathrm{CDCl_3}$ exhibits an intense broad singlet at δ 1.69, which is attributed to the 15 methyl protons of the rapidly rotating $\mathrm{C_5Me_5}$ ligand. The signals due to the non-equivalent sulfur-bonded methyl groups occur at δ 2.40 and 2.60 respectively, whilst the cage CH protons resonate at δ 2.74 and 3.33 respectively. The 87 MHz ^{11}B-{^{1}H} NMR spectrum in $\mathrm{CDCl_3}$ at room temperature shows nine broad signals of equal area; one of these signals (at *ca.* δ −6.0) is a shoulder. Only this resonance remains as a singlet in the proton-coupled ^{11}B spectrum, indicating that it is from the $\mathrm{Me_2S}$-substituted boron. The infrared (IR) spectrum (as a KBr pellet) features an intense broad absorption band at 2507 cm^{-1}, which is assigned to the B–H stretching vibrations. The C–H stretching absorptions of the methyl groups occur as a broad, strong multiplet centred at 2905 cm^{-1}. A relatively weak peak occurs at 3017 cm^{-1}; it is assigned to the C–H stretching vibration of the carborane cage.

(*iii*) *Electrochemistry*. Complex **1** undergoes a reversible (ΔE_p = 75 mV) one-electron oxidation at an $E_{\frac{1}{2}}$ value of 0.18 V [*vs.* saturated calomel electrode (SCE), 25 °C, 0.1 mmol dm^{-3} MeCN solution with 0.1 mol dm^{-3} $\mathrm{NBu^n{}_4PF_6}$ supporting electrolyte]. This value is considerably lower than that of *commo*-[3,3′-Fe(4-$\mathrm{Me_2S}$-1,2-$\mathrm{C_2B_9H_{10}}$)$_2$] (0.45 V *vs.* SCE, MeCN),[7] indicating that the $[\mathrm{C_5Me_5}]^-$ ligand is more electron-donating than the $[\mathrm{C_2B_9H_{10}SMe_2}]^-$ ligand. It is also noteworthy that the replacement of each $[\mathrm{C_2B_9H_{10}SMe_2}]^-$ ligand of $[\mathrm{Fe(C_2B_9H_{10}SMe_2)_2}]$ by $[\mathrm{C_5Me_5}]^-$ lowers the $E_{\frac{1}{2}}$ by *ca.* 0.3 V {$E_{\frac{1}{2}}$ of $[\mathrm{Fe(C_5Me_5)_2}]$ = −0.12 V *vs.* SCE}.[8]

(*iv*) *Attempted reaction with tcne*. Since the half-wave potential of compound **1** is higher than that of tcne (0.15 V *vs.* SCE),[9] no charge transfer is expected between **1** and tcne in solution. Accordingly, no colour change was observed when dichloromethane solutions of **1** and tcne were mixed at room temperature. Cooling the solution to −20 °C caused the solution to turn dark green, but no precipitation occurred. Slow evaporation of a solution of **1** and tcne in hexane–dichloromethane (1 : 1) at room temperature under a stream of nitrogen gave an intractable mixture of a brown oily material and a brown powdery solid which slowly turned orange (over 2 weeks) when left at room temperature under nitrogen.

(*b*) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{C_2B_9H_{10}SMe_2})]^+[\mathrm{ddq}]^{\bullet-}\cdot\mathrm{CH_2Cl_2}$ **2** *and* $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{C_2B_9H_{10}SMe_2})]^+[\mathrm{tcntfq}]^{\bullet-}$ **3**.—(*i*) *Synthesis and crystal growth*. The salts $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{C_2B_9H_{10}SMe_2})]^+[\mathrm{ddq}]^{\bullet-}\cdot\mathrm{CH_2Cl_2}$ **2** (black) and $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{C_2B_9H_{10}SMe_2})]^+[\mathrm{tcntfq}]^{\bullet-}$ **3** (deep turquoise blue) were obtained as microcrystalline precipitates in direct charge-transfer reactions of compound **1** with ddq ($E_{\frac{1}{2}}$ = 0.51 V *vs.* SCE)[9] and tcntfq ($E_{\frac{1}{2}}$ = 0.52 V *vs.* SCE),[10] respectively, in dichloromethane. Larger crystals of **2** were grown from a dilute solution of **1** and ddq (*ca.* 1.3 mmol dm^{-3} each) in dichloromethane at *ca.* 8 °C and crystals of **3** were grown by slow interdiffusion of dichloromethane solutions of **1** and tcntfq through a glass frit at −20 °C. Crystals of both charge-transfer salts are solvated, but whilst those of **2** are stable under ambient conditions, crystals of **3** rapidly desolvate on removal from the mother-liquor, even if maintained in an atmosphere saturated with dichloromethane vapour. Crystals of **3** grown from chlorobenzene were of poorer quality; they also desolvated rapidly when they were removed from their mother-liquor. Attempts to grow crystals of **3** from 1,1,2,2-tetrachloroethane and by layering 1,1,2,2-tetrachloroethane solutions of **3** with toluene or *o*-xylene were unsuccessful.

(*ii*) *Infrared spectra*. The IR spectra of compounds **2** and **3** exhibit an intense, broad absorption band at *ca.* 2550 cm^{-1}, which is assigned to the B–H stretching vibrations of the $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{C_2B_9H_{10}SMe_2})]^+$ cation. This represents a high-energy shift of *ca.* 40 cm^{-1} for the B–H stretching absorptions when **1** is oxidised to its cationic form. The sensitivity of B–H stretching frequencies of carboranes and metallacarboranes to changes in the electron densities at the boron atoms is well documented[11] and has been used as a probe for ligand and metal charge densities in polymetallic metallacarborane complexes.[12]

The methyl C–H stretching absorptions of the $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{C_2B_9H_{10}SMe_2})]^+$ cation in compounds **2** and **3** occur at 2929 and 2932 cm^{-1} respectively; their intensities relative to the B–H stretching absorptions are considerably lower than that of the methyl C–H stretching absorptions of **1**. On the other hand, the cage C–H stretching absorptions (at 3010 and 3024 cm^{-1} for compounds **2** and **3** respectively) gain intensity on oxidation of **1**, becoming more intense than the methyl C–H absorptions.

The diagnostic peaks of the $[\mathrm{ddq}]^{\bullet-}$ anion in complex **2** occur at 2209vs [ν(C≡N)], 1575vs [ν(C=O)] and 1532vs cm^{-1} [ν(C=O)]. These positions are consistent with the 1 − charge of the $[\mathrm{ddq}]^{\bullet-}$ anion.[13] The C≡N stretching absorptions of the $[\mathrm{tcntfq}]^{\bullet-}$ anion in compound **3** occur at 2195vs and 2176vs cm^{-1}. The wavenumbers of these absorptions are also consistent with the 1 − charge of the $[\mathrm{tcntfq}]^{\bullet-}$ anion.[13]

(*iii*) *Crystal structure of* $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{C_2B_9H_{10}SMe_2})]^+[\mathrm{ddq}]^{\bullet-}\cdot\mathrm{CH_2Cl_2}$ **2**. Compound **2** crystallises in the centrosymmetric space group $P\bar{1}$. Thus equal numbers of both the D and L isomers of the $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{C_2B_9H_{10}SMe_2})]^+$ cation are present in the crystal. The molecular structures of the cation and anion in **2** are shown in Fig. 1, crystal data, final atomic coordinates and selected bond lengths and angles in Tables 1–3.

The iron atom of the cation is sandwiched asymmetrically between the pentagonal faces of the $[\mathrm{C_5Me_5}]^-$ and $[\mathrm{C_2B_9H_{10}SMe_2}]^-$ ligands at distances of 1.72 and 1.52 Å from the $\mathrm{C_5}$ and $\mathrm{C_2B_3}$ ring planes respectively. These distances are close to the corresponding values observed in $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})_2]^+$ (1.70 Å)[14d] and $[\mathrm{Fe(C_2B_9H_{10}SMe_2)_2}]^+$ (1.54 Å).[7] The ligating pentagonal faces are rotated by *ca.* 38° with respect to each other about the axis between their centroids, and are inclined by *ca.* 6° to each other. Both the $\mathrm{C_5}$ and $\mathrm{C_2B_3}$ faces are planar, with maximum deviations of 0.009 and 0.004 Å [for C(7) and B(7) respectively] from their respective mean planes. Although the Fe–C ($\mathrm{C_2B_3}$) bond lengths of **2** [2.083(5) and 2.069(5) Å] are close to those observed in $[\mathrm{Fe(C_2B_9H_{10}SMe_2)_2}]^+$ [Fe–C 2.072(5)–2.095(5) Å],[7] the Fe–B bond lengths in **2** [2.111(4)–2.137(5) Å] are noticeably much

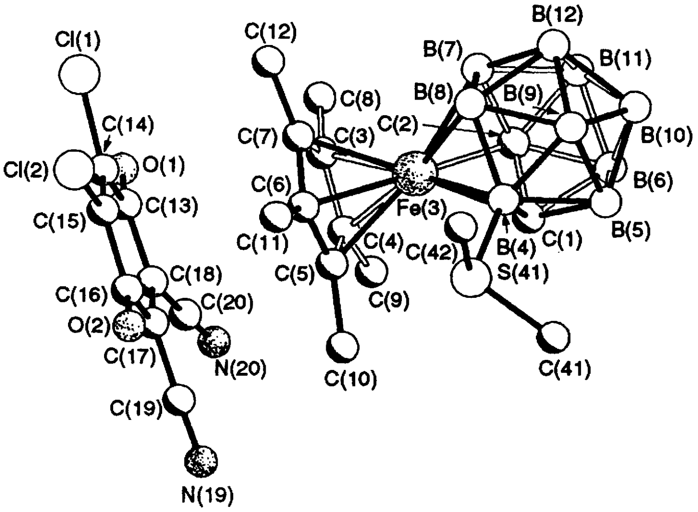

Fig. 1 Molecular structures of the cation and anion in complex **2**. The carbon atoms of the dicarbollide cages are hatched

Table 1 Crystal and refinement data for compound **2**

Chemical formula	$C_{23}H_{33}B_9Cl_4FeN_2O_2S$
M	696.5
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.730(4)
b/Å	12.246(7)
c/Å	14.637(8)
α/°	70.98(2)
β/°	76.02(2)
γ/°	65.93(2)
U/Å^3	1647.0(14)
D_c/g cm^{-3}	1.404
Z	2
F(000)	712
Colour, habit	Black prisms
Crystal dimensions/mm	0.20 × 0.37 × 0.67
μ/cm^{-1}	8.7 (Mo-Kα)
Diffractometer	Siemens P4/PC
X-Radiation (λ/Å)	Mo-Kα (0.710 73)
Scan mode	ω
Scan width/°	0.90
2θ limits/°	3.0–50.0
No. of reflections	
Total	5791
Unique (R_{int})	5791 (0.00)
Observed [$F > 4.0\sigma(F)$]	4055
Absorption correction	None
No. of parameters	392
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0006F^2$
R (observed data)	0.0491
R' (observed data)	0.0481

more uniform than those in $[Fe(C_2B_9H_{10}SMe_2)_2]^+$ [Fe–B 2.109(6)–2.173(6) Å]. On the other hand, the Fe–C bond lengths involving the C_5Me_5 ring cover a wider range of 2.090(4)–2.130(5) Å. The longest Fe–C (C_5Me_5) bonds involve C(5) and C(6), which lie closest to the SMe_2 group. The pattern of bond lengths in **2** involving Fe(3) thus indicates that the FeC_2B_3 fragment is more rigid than the FeC_5 fragment, since the latter is preferentially distorted to meet the steric demands of the SMe_2 group.

The bond lengths within the $[ddq]^{\bullet -}$ anion (see Table 3) are similar to those observed in $[Fe(C_2B_9H_{10}SMe_2)_2]^+[ddq]^{\bullet -}$ (ref. 7) and $[NEt_4]^+[ddq]^{\bullet -}$.[14] The C_6 ring of the anion is nearly planar, with a maximum deviation of 0.020 Å [for C(13)] from the mean plane of the ring. The ring substituents are, however, substantially displaced from the ring plane, with C(20) lying 0.17 Å from the ring plane.

Inspection of the packing of the anions and cations in the crystal structure of complex **2** shows that the $[ddq]^{\bullet -}$ radical anions form isolated stacked dimers. These dimers are arranged in rows which fit into channels which are lined by rows of cations, as shown in Fig. 2. Both the cation and anion rows extend in the (1 −1 0) direction. There are also cavities in the array of cations which contain the disordered dichloromethane solvent molecules.

Within each $[(ddq)_2]^{2-}$ dimer the pair of $[ddq]^{\bullet -}$ anions are centrosymmetrically related, and have their permanent dipoles pointing in opposite directions and their C_6 rings partially eclipsed, as shown in Fig. 3. There is a short interplanar separation of 2.90 Å between the $[ddq]^{\bullet -}$ units in the dimer indicative of strong bonding interactions and spin pairing between the two radical anions.[15] Similar stacking modes and interplanar distances are observed within the $[(ddq)_2]^{2-}$ dimers in the crystal structures of $[NEt_4]^+[ddq]^{\bullet -}$ (interplanar distance 2.91 Å)[14] and $[ttf]^{\bullet +}[ddq]^{\bullet -}$ [ttf = tetrathiafulvalene = 2-(1,3-dithiol-2-ylidene)-1,3-dithiole] (interplanar distance 2.97 Å).[16] However, adjacent $[(ddq)_2]^{2-}$ dimers in **2** are not stacked face-to-face as are those in $[NEt_4]^+[ddq]^{\bullet -}$ and $[ttf]^{\bullet +}[ddq]^{\bullet -}$.

Each $[(ddq)_2]^{2-}$ dimer is sandwiched between the C_5Me_5 faces of two neighbouring $[Fe(\eta\text{-}C_5Me_5)(C_2B_9H_{10}SMe_2)]^+$ cations, as shown in Fig. 2. There is significant overlap between the anion and the C_5Me_5 ring of the cation (Fig. 4). The distances of the $[ddq]^{\bullet -}$ ring atoms from the C_5Me_5 ring plane are in the range 3.52 [C(16)]–3.83 Å [C(13)]. The two rings are inclined by *ca.* 6° and the distance between their centroids is 3.72 Å.

Short intermolecular S(41) ··· O(2) contacts (3.15 Å) also occur between the SMe_2 groups of the cations and the quinoidal oxygen atoms of the anions, as indicated in Fig. 2. This interaction is most probably electrostatic in nature, *i.e.* $S^{\delta +} \cdots O^{\delta -}$. There are also weak O ··· H interactions between the quinoidal oxygens and some of the methyl hydrogens of the C_5Me_5 and SMe_2 groups [O(1) ··· H(41a) 2.50, O(1) ··· H(42a) 2.50, and O(2) ··· H(10c) 2.48 Å].

(*c*) *Magnetic Properties.*—Both compounds **2** and **3** behave as paramagnets between 5 and 300 K, with small Weiss constants, θ, of −0.9 and −0.7 K respectively. The effective moments, $\mu_{eff}(=\sqrt{8\chi T})$, of the compounds are virtually independent of temperature in the above temperature range, and both have an average value $\mu_{av}(=\sqrt{8C})$ of 2.4 μ_B. This value, being close to that expected for a low-spin iron(III) complex (2.3 μ_B), indicates that the organic radical anions in compounds **2** and **3** do not contribute to their bulk magnetic susceptibilities. This is consistent with the presence of $[(ddq)_2]^{2-}$ dimers in the crystal structure of **2** and suggests that the $[tcntfq]^{\bullet -}$ radical anions in **3** are similarly clustered to form spin-paired aggregates. It is thus not surprising that co-operative magnetic phenomena are not observed in compounds **2** and **3**.

(*d*) *Electrical Conductivity.*—Conductivity measurements were performed at room temperature on single crystals of compound **2**, the conductivity of which was found to be less than 10^{-7} S cm^{-1}. The insulating nature of compound **2** is consistent with the presence of a strongly dimerised ddq stack with negligible overlap between the $[(ddq)_2]^{2-}$ dimers.

Conclusion

This investigation has shown that it is possible to synthesise the mixed-sandwich complex *closo*-$[3\text{-}(\eta^5\text{-}C_5Me_5)Fe\text{-}4\text{-}Me_2S\text{-}1,2\text{-}C_2B_9H_{10}]$ **1** from $[FeCl_2(thf)_2]$, $Li(C_5Me_5)$ and $Li[C_2B_9H_{10}SMe_2]$ in moderate yield with minimum contamination by decamethylferrocene and *commo*-$[3,3'\text{-}Fe(4\text{-}Me_2S\text{-}1,2\text{-}C_2B_9H_{10})_2]$. Since the C_5Me_5 ligand is more electron donating than $[C_2B_9H_{10}SMe_2]^-$, the half-wave electrode potential for **1**

Table 2 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Fe(3)	1895(1)	3759(1)	7799(1)
C(1)	1556(4)	2214(3)	7767(3)
C(2)	424(4)	2974(4)	8496(3)
B(4)	3153(4)	1866(4)	8018(3)
B(5)	2380(5)	716(4)	8392(3)
B(6)	609(5)	1451(5)	8671(4)
B(7)	1144(5)	3209(4)	9281(3)
B(8)	2960(5)	2481(4)	9001(3)
B(9)	3239(5)	860(5)	9206(3)
B(10)	1646(5)	639(5)	9610(4)
B(11)	370(5)	2084(5)	9660(4)
B(12)	2000(6)	1710(5)	9996(3)
S(41)	4733(1)	1606(1)	7057(1)
C(41)	5097(5)	206(4)	6753(4)
C(42)	6105(4)	1159(5)	7739(3)
C(3)	769(4)	5659(4)	7513(3)
C(4)	918(4)	5234(4)	6679(3)
C(5)	2349(4)	4755(3)	6353(3)
C(6)	3081(4)	4875(3)	6981(3)
C(7)	2094(4)	5421(4)	7715(3)
C(8)	−573(5)	6317(4)	8043(3)
C(9)	−226(5)	5332(4)	6216(3)
C(10)	2942(5)	4297(4)	5455(3)
C(11)	4598(4)	4587(4)	6866(4)
C(12)	2433(5)	5743(4)	8506(3)
Cl(1)	447(1)	−574(1)	7294(1)
Cl(2)	3485(1)	−1904(1)	6392(1)
O(1)	−1612(3)	−308(3)	6172(2)
O(2)	3549(3)	−2805(3)	4764(2)
C(13)	−430(4)	−907(4)	5867(3)
C(14)	774(4)	−1102(3)	6284(3)
C(15)	2075(4)	−1712(4)	5913(3)
C(16)	2372(4)	−2230(3)	5082(3)
C(17)	1175(4)	−2078(3)	4700(3)
C(18)	−144(4)	−1459(3)	5074(3)
C(19)	1406(4)	−2605(4)	3906(3)
N(19)	1578(4)	−3033(4)	3283(3)
C(20)	−1302(5)	−1437(4)	4729(3)
N(20)	−2201(4)	−1468(4)	4455(3)
Cl(3a)	4579(5)	3168(6)	1139(4)
Cl(4a)	6345(4)	3468(4)	−663(3)
C(21a)	6011(10)	2571(7)	429(5)
Cl(3b)	4092(12)	3342(10)	2040(9)
Cl(4b)	5833(22)	2992(20)	309(15)
C(21b)	4419(30)	2847(36)	1040(17)

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

Cl(1)–C(14)	1.708(5)	Fe(3)–C(3)	2.090(4)
Cl(2)–C(15)	1.717(5)	Fe(3)–C(4)	2.100(4)
O(1)–C(13)	1.236(4)	Fe(3)–C(5)	2.123(4)
O(2)–C(16)	1.230(4)	Fe(3)–C(6)	2.130(5)
C(13)–C(14)	1.460(7)	Fe(3)–C(7)	2.094(5)
C(13)–C(18)	1.438(7)	C(1)–C(2)	1.606(5)
C(14)–C(15)	1.360(5)	C(1)–B(4)	1.690(7)
C(15)–C(16)	1.462(7)	C(2)–B(7)	1.682(8)
C(16)–C(17)	1.443(7)	B(4)–B(8)	1.766(8)
C(17)–C(18)	1.378(5)	B(7)–B(8)	1.787(7)
C(17)–C(19)	1.430(7)	C(3)–C(4)	1.428(7)
C(18)–C(20)	1.437(8)	C(4)–C(5)	1.423(5)
C(19)–N(19)	1.137(8)	C(5)–C(6)	1.419(7)
C(20)–N(20)	1.149(8)	C(6)–C(7)	1.436(6)
Fe(3)–C(1)	2.083(5)	C(3)–C(7)	1.415(7)
Fe(3)–C(2)	2.069(5)	B(4)–S(41)	1.912(4)
Fe(3)–B(4)	2.114(4)	S(41)–C(41)	1.777(6)
Fe(3)–B(7)	2.111(4)	S(41)–C(42)	1.777(5)
Fe(3)–B(8)	2.137(5)		
C(1)–C(2)–B(7)	112.1(3)	B(4)–Fe(3)–C(3)	175.9(2)
C(2)–B(7)–B(8)	105.8(4)	B(7)–Fe(3)–C(5)	165.8(2)
B(4)–B(8)–B(7)	104.9(4)	B(8)–Fe(3)–C(4)	170.5(2)
C(1)–B(4)–B(8)	107.2(3)	B(4)–S(41)–C(41)	109.1(2)
C(2)–C(1)–B(4)	110.0(4)	B(4)–S(41)–C(42)	102.8(2)
C(1)–Fe(3)–B(7)	173.8(2)	C(41)–S(41)–C(42)	100.8(3)
C(2)–Fe(3)–C(6)	168.9(1)		

(0.18 V *vs.* SCE) is 0.30 V higher than that reported for [Fe(C_5Me_5)$_2$]. Compound **1** forms stable 1 : 1 charge-transfer salts with ddq and tcntfq which behave as paramagnets between 5 and 300 K. The lack of co-operative magnetic phenomena in these salts is attributed to the clustering of their radical anions to form spin-paired aggregates. The [ddq]$^{\bullet -}$ salt was found to be electrically insulating, in accordance with the presence of strongly dimerised [ddq]$^{\bullet -}$ stacks in its crystal structure.

Experimental

a) *General.*—1,2,3,4,5-Pentamethylcyclopentadiene (C_5HMe_5), ddq, tcntfq and butyllithium (1.6 mol dm^{-3} solution in hexanes) were obtained from Aldrich and used as received. The compounds [$FeCl_2$(thf)$_2$][17] and *nido*-9-Me_2S-7,8-$C_2B_9H_{11}$[7] were made as described in the literature. Organic solvents were of reagent grade and were dried by published procedures[18] and distilled under nitrogen. Reactions were routinely carried out under nitrogen using standard Schlenk techniques.

(*b*) *Physical Measurements.*—Infrared spectra were recorded on a Perkin-Elmer 1720 Fourier-transform spectrometer and UV/VIS spectra using a Perkin-Elmer Lambda 2 UV/VIS spectrophotometer. The ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer and the ^{11}B spectra on a JEOL JNM-EX270 FT-NMR spectrometer; ^1H and ^{11}B-{^1H} chemical shifts are referenced to tetramethylsilane and $BF_3(OEt_2)$ respectively. Fast atom bombardment (FAB) mass spectra were recorded at the Mass Spectrometry Service of the School of Pharmacy, University of London, on a VG ZAB-SE mass spectrometer, using 3-nitrobenzyl alcohol as the matrix. Cyclic voltammograms were recorded under nitrogen on a Princeton Applied Research cyclic voltammetry instrument with platinum-disc working and counter electrodes. The potentials are quoted relative to the SCE using the ferrocene–ferrocenium couple as an internal reference.

Magnetic susceptibility measurements were performed in the range $5 \leqslant T \leqslant 300$ K using a Quantum Design MPMS-7 SQUID magnetometer under a magnetic field strength of 0.4 T. Microcrystalline samples were loaded in gelatin capsules and then fixed in plastic straws. The magnetic susceptibilities were corrected for the temperature-independent contributions from the sample and capsule by fitting the susceptibility data by the expression $\chi^{-1} = (T - \theta)[C + k(T - \theta)]^{-1}$, where k comprises the total diamagnetism and any temperature-independent paramagnetism of the sample and capsule.

Electrical conductivity measurements were carried out on single crystals of compound **2**, using the two-probe d.c. method. Contacts were made with platinum paint and 25 μm gold wires.

(*c*) *Syntheses.*—(*i*) *closo*-[3-(η^5-C_5Me_5)Fe-4-Me_2S-1,2-$C_2B_9H_{10}$] **1**. A 0.32 cm^3 volume of C_5HMe_5 (0.28 g, 2.1 mmol) was added *via* a syringe to thf (16 cm^3) in a Schlenk tube. While the resultant solution was vigorously stirred magnetically at room temperature, a 1.6 mol dm^{-3} solution of LiBu in hexanes (1.6 cm^3, 2.6 mmol) was added dropwise *via* a syringe. The resultant fine white suspension was stirred for 1 h at room temperature and then transferred dropwise *via* a 16-gauge steel

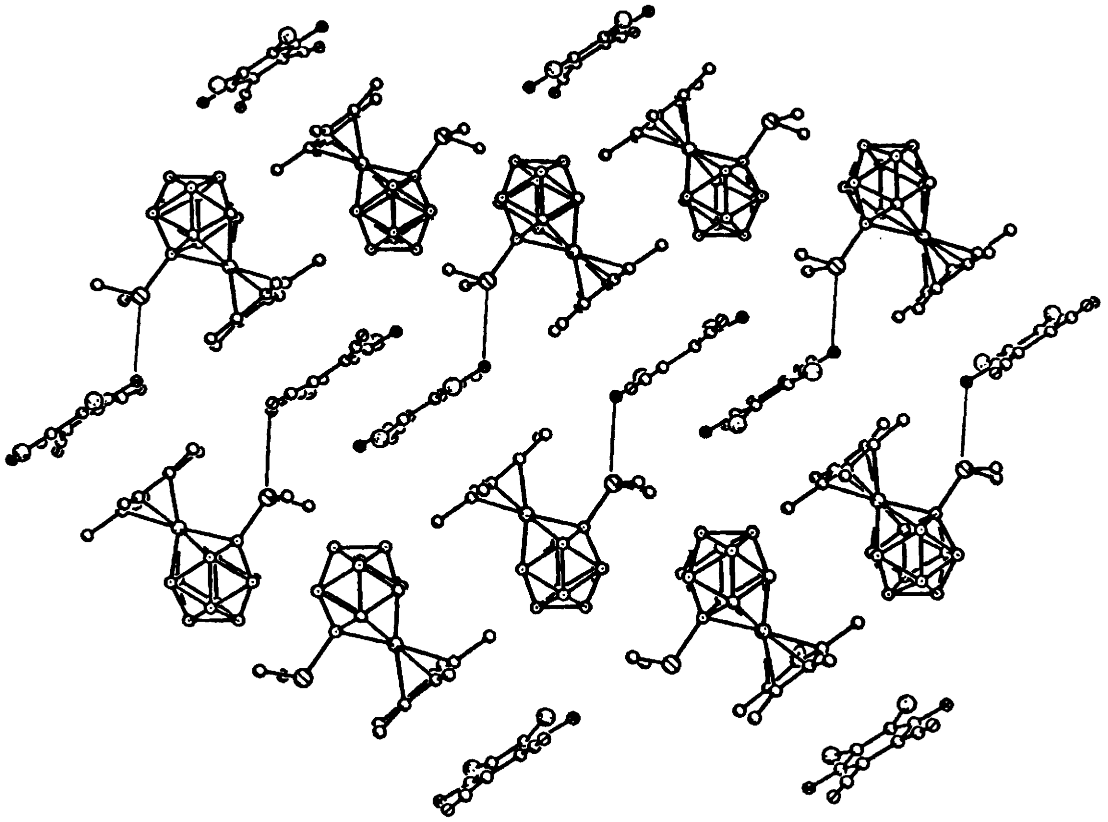

Fig. 2 Molecular packing in complex **2**. The thin lines indicate short S ⋯ O contacts

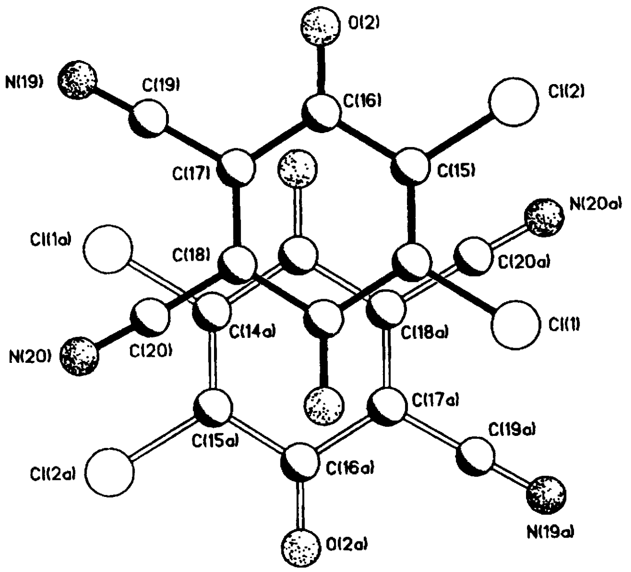

Fig. 3 A dimer of ddq$^{\bullet -}$ units in complex **2**, viewed down the normal to the ring planes

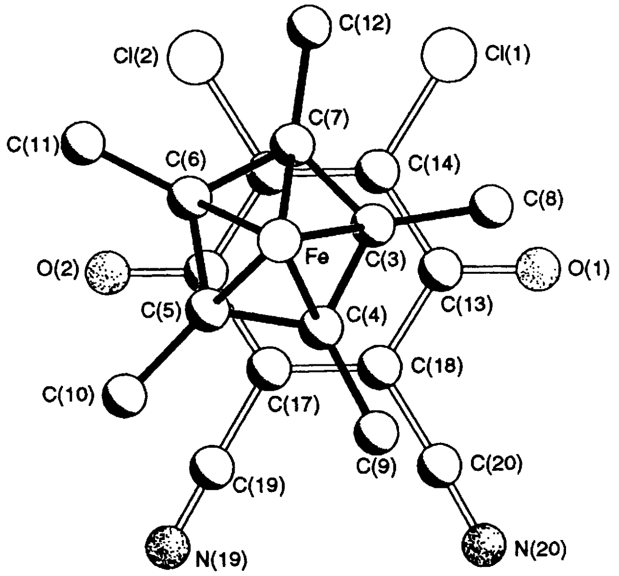

Fig. 4 Degree of overlap between the ddq$^{\bullet -}$ anion and the C_5Me_5 ring of the cation in complex **2**, viewed down the normal to the C_5Me_5 ring plane

cannula to a magnetically stirred suspension of $[FeCl_2(thf)_2]$ (0.48 g, 1.8 mmol) in thf (16 cm^3) at room temperature. A dark green solution was obtained, together with a white precipitate. The mixture (hereafter referred to as mixture A) was stirred for 2.5 h at room temperature. Meanwhile, a 1.6 mol dm^{-3} solution of LiBu in hexane (1.7 cm^3, 2.7 mmol) was added to a solution of *nido*-9-Me_2S-7,8-$C_2B_9H_{11}$ (0.52 g, 2.7 mmol) in thf (10 cm^3) at room temperature and the resultant solution was stirred for 1 h at room temperature. The colourless solution of $Li[C_2B_9H_{10}SMe_2]$ formed was added dropwise to the stirred mixture A at room temperature to give a dark brown solution and a white precipitate. The brown mixture was stirred for 2 h at room temperature and then evaporated to dryness under reduced pressure. The residue was quickly extracted with acetone in air and the extract was filtered by suction through a glass frit. The filtrate was evaporated to dryness under reduced pressure to give a brown residue which was extracted with dichloromethane. The dichloromethane extract was applied to alumina TLC plates. Elution with hexane–dichloromethane (13:7) moved a prominent orange band, which was quickly scraped off and extracted with dichloromethane. The extracted product was recrystallised from dichloromethane–toluene mixture to give orange crystals of compound **1** (0.28 g, 40%)

[Found: C, 43.8; H, 8.2%; m/z (FAB) 385 (M^+). $C_{14}H_{31}B_9FeS$ requires C, 43.7; H, 8.1%; M 385]; λ_{max}/nm (MeCN) 214 (infl) (ε/dm^3 mol^{-1} 25 000), 223 (29 000), 285 (sh) (4800), 369 (260) and 480 (240); $\tilde{\nu}_{max}$/cm^{-1} 3017w (cage CH), 2905s (br m) (methyl CH), 2507vs (br m)(BH), 1482m, 1424s, 1375s, 1326w, 1098m, 1071w, 1027s, 1009s, 980s, 931m, 858m, 824s, 741w, 614m and 436m (KBr); δ_H(300 MHz, $CDCl_3$) 3.33 (1 H, br s, cage CH), 2.74 (1 H, br s, cage CH), 2.60 (3H, s, SMe), 2.40 (3 H, s, SMe) and 1.69 (15 H, br s, C_5Me_5); δ_B(^{11}B-{H}, 87 MHz, $CDCl_3$, −5.2 (1B), −6.0 (sh, 1B), −9.3 (1B), −12.7 (1B), −13.6 (1B), −18.2 (1B), −25.1 (1B), −27.3 (1B) and −29.0 (1B).

(*ii*) $[Fe(\eta\text{-}C_5Me_5)(C_2B_9H_{10}SMe_2)]^+[ddq]^{\bullet-}\cdot CH_2Cl_2$ **2**. A solution of ddq (17.7 mg, 0.078 mmol) in dichloromethane (6 cm^3) was transferred to a magnetically stirred solution of compound **1** (30.0 mg, 0.078 mmol) in dichloromethane (14 cm^3) at room temperature under nitrogen. The resultant deep purple solution was immediately filtered into another Schlenk tube and kept at *ca.* −20 °C for 3 d. The black shiny microcrystals of $[Fe(\eta\text{-}C_5Me_5)(C_2B_9H_{10}SMe_2)]^+[ddq]^{\bullet-}\cdot CH_2Cl_2$ **2** formed were filtered off. Yield: 41.0 mg, 75% (Found: C, 39.8; H, 4.5; N, 4.0. $C_{23}H_{33}B_9Cl_4FeN_2O_2S$ requires C, 39.7; H, 4.8; N, 4.0%); $\tilde{\nu}_{max}$/cm^{-1} 3010s (br) (cage CH), 2929m (methyl CH), 2546vs (br) (BH), 2209vs (CN), 1575vs (CO), 1532vs (CO), 1512vs, 1497vs, 1464s, 1424s, 1381s, 1266w, 1230s, 1190vs, 1094m, 1047vs, 1021s, 973m, 925w, 882s, 832m, 783s, 739s, 709s, 638w, 587w, 518s and 474s (KBr).

(*iii*) $[Fe(\eta\text{-}C_5Me_5)(C_2B_9H_{10}SMe_2)]^+[tcntfq]^{\bullet-}$ **3**. A solution of tcntfq (7.3 mg, 0.026 mmol) in chlorobenzene (17 cm^3) was transferred to an agitated solution of compound **1** (10.5 mg, 0.027 mmol) in chlorobenzene (12 cm^3) at room temperature under nitrogen. The resultant dark green solution was filtered into another Schlenk tube and kept at *ca.* −20 °C for 6 d. The deep turquoise-blue microcrystals of compound **3** formed were filtered off, washed with hexane on a Hirsch funnel and dried by suction. Yield: 15.5 mg, 90% (Found: C, 47.0; H, 4.6; N, 8.3. $C_{26}H_{31}B_9F_4FeN_4S$ requires C, 47.3; H, 4.7; N, 8.5%); $\tilde{\nu}_{max}$/cm^{-1} 3024m (cage CH), 2932w (methyl CH), 2551s (br) (BH), 2195vs (CN), 2176vs (CN), 1634s, 1537vs, 1499vs, 1425s, 1391vs, 1339s, 1265w, 1243w, 1199s, 1143s, 1101w, 1020m, 970s, 925w, 872w, 830w, 789w, 747w, 638w, 549w and 472w (KBr).

(*d*) *X-Ray Crystallography*.—The crystal and refinement data for compound **2** are summarised in Table 1, atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3.

The structure was solved by direct methods. Positional and anisotropic thermal parameters for non-hydrogen atoms were refined by the full-matrix least-squares method. High equivalent isotropic thermal parameters were observed for the atoms C(21a), Cl(3a) and Cl(4a) of the CH_2Cl_2 solvate. In addition, difference peaks corresponding to a second solvate position [C(21b), Cl(3b) and Cl(4b)] were observed in the vicinity of the first. Refinement of the first and second solvate positions with the occupancy ratio 80:20 gave good agreement (atoms of the second position were refined isotropically). Hydrogen atoms of the Me_2S group and CH_2Cl_2 solvate were introduced in calculated positions and refined isotropically. Those on the carborane cage were located by difference syntheses and refined with the bond length constraints C–H 0.960 ± 0.002 and B–H 1.080 ± 0.002 Å and assigned isotropic thermal parameters $U(H) = 1.2\ U_{eq}(C, B)$. One hydrogen atom on each C_5Me_5 methyl group was located from the difference map; the positions of the other two hydrogen atoms were calculated from the position of the first and that of the *ipso*-cyclopentadienyl carbon atom. Calculations were performed on a VAX station 3100 model 76 computer using the SHELXTL PLUS software package.[19]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

Support of this work by the EPSRC is acknowledged. Y.-K. Y. thanks the Nanyang Technological University, Singapore, for a scholarship and D. M. P. M. thanks BP for a generous endowment.

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Received 14*th February* 1995; *Paper* 5/00885I