Synthesis and Structure of a Charge-compensated Ferracarborane, *commo*-[3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$], and Its Charge-transfer Salt with 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 sandwich complex *commo*-[3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$] **1** was synthesised. Its *meso* and DD/LL isomers are easily separated by fractional recrystallization from acetone and were spectroscopically characterized. The charge-transfer salt [3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$]$^+$[ddq]$^{\bullet-}$ **2** was formed between the DD/LL-**1** racemate and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (ddq). X-Ray crystallography revealed an increase in the iron–dicarbollide distance on oxidation of DD/LL-**1** (Fe–C_2B_3 1.50 Å) to the cation in **2** (Fe–C_2B_3 1.54 Å). The latter is the first example of a cationic bis(dicarbollyl)metal complex to be crystallographically characterized. The cations and anions pack to form alternating layers in the crystal of **2**. Within the [ddq]$^{\bullet-}$ layer the anions form zigzag chains linked *via* intermolecular N···Cl electrostatic interactions (N···Cl 3.21 Å). The cation and anion layers are crossed-linked by weak CH···O hydrogen bonds between the oxygen atoms of the [ddq]$^{\bullet-}$ anions and some of the cage CH hydrogen atoms of the cations. Between 5 and 270 K the corrected molar susceptibility of **2** follows the Curie–Weiss law, with a θ value of −2.5 K. The single-crystal electrical conductivity of **2** at room temperature is less than 10^{-8} S cm^{-1}.

The search for novel molecular materials with desirable physical properties, *e.g.* ferromagnetism,[1] non-linear optical activity[2] and superconductivity,[3] has intensified tremendously in recent years. A large number of organic, inorganic and organometallic molecules have now been studied as possible components in such materials.

As an extension of our previous work using anionic metallacarboranes as building blocks for novel molecular materials,[4] we decided to synthesise the ferracarborane *commo*-[3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$] **1** and study its charge-transfer salt with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (ddq), [3,3'-Fe{4-Me_2S)-1,2-$C_2B_9H_{10}$}$_2$]$^+$ [ddq]$^{\bullet-}$ **2**. Unusual metamagnetic and conducting charge-transfer salts of ddq have previously been reported.[5] The charge-compensated *nido*-[9-(Me_2S)-7,8-$C_2B_9H_{10}$]$^-$ was chosen both for its ease of synthesis[6] and because sulfur atoms have a propensity to engage in intermolecular bonding interactions,[3a] which may enhance the electronic interactions between the cations and anions in the solid state.

In addition, the synthesis of the analogous complexes [3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$]$^{n+}$(n = 0 or 1) provided an ideal opportunity to study the structural consequences of the removal of an electron from the neutral metallacarborane to form the cation. The absence of ancillary ligands, which may act as electron sinks or reservoirs, simplifies the correlation between the structural parameters and the charge on the metallacarboranes. Few examples of cationic metallacarboranes[7] have previously been studied.

Here we report the synthesis, crystal structures and spectroscopic properties of compounds **1** and **2**, and the magnetic and conductivity properties of **2**.

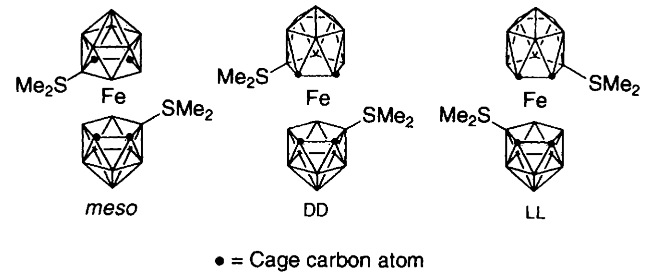

Fig. 1 Diagram of the stereoisomers of complex **1**

Results and Discussion

(*a*) [3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$] **1**.—(*i*) *Synthesis*. The key intermediate in the synthesis of compound **1** is *nido*-9-(Me_2S)-7,8-$C_2B_9H_{11}$ **3**. The reported preparation of the latter involves the slow addition of concentrated H_2SO_4 to a stirred solution of K[$C_2B_9H_{12}$] in aqueous dimethyl sulfoxide (dmso), stirring the resultant mixture for 5 h at room temperature and then leaving it to stand overnight.[6] This method gave a yield of *ca.* 56% of **3**. We achieved a higher yield (64%) in a much shorter reaction time (90 min) by stirring the reaction mixture at 80 °C under N_2.

Reaction of an excess of [$FeCl_2$(thf)$_2$] with a tetrahydrofuran (thf) solution of Na[9-(Me_2S)-7,8-$C_2B_9H_{10}$] (freshly prepared by deprotonation of **3** by NaH) at room temperature yielded a deep purple suspension from which **1** was isolated in 36% yield. Since the asymmetric [9-(Me_2S)-7,8-$C_2B_9H_{10}$]$^-$ is expected to be formed as a racemate, complex **1** should be produced as a mixture of *meso* (DL), DD and LL isomers (see Fig. 1). Interestingly, the isomers have very different solubility properties; while the DD/LL isomers are moderately soluble in acetone and CH_2Cl_2, the *meso* isomer is sparingly soluble in acetone

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 The UV/VIS spectral data for the isomers of compound **1**[a]

Isomer	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
DD/LL	220(26 000), 241(21 000),[b] 273(22 000), 393(64), 512(140)
meso	222(11 000), 243(12 000), 289(1500),[b] 391(73), 524(130)

[a] Measured in MeCN solutions. [b] Shoulder.

and almost insoluble in CH_2Cl_2. Hence, when an acetone solution of the isomeric mixture is slowly concentrated under reduced pressure the *meso* isomer crystallizes out first and can be filtered off and further purified by washing with CH_2Cl_2. (The configurations of the isomers were determined by an X-ray crystallographic characterization of the DD/LL isomers, see below.) All three isomers of **1** are very soluble in dmso. However, the compounds slowly react (overnight) with dmso at room temperature to give unidentified dark brown solutions.

(*ii*) *Spectroscopic characterization*. The room-temperature 270 MHz ^{1}H NMR spectra of the *meso* and DD/LL isomers of compound **1** in $(CD_3)_2SO$ are similar in that both exhibit two signals for the cage CH protons and two signals for the sulfur-bound methyl groups. However, the signals due to the inequivalent SMe groups are further separated in DD/LL-**1** ($\Delta\delta = 0.22$) than in *meso*-**1** ($\Delta\delta = 0.07$). Similarly, the separation between the signals due to the cage CH protons is larger for DD/LL-**1** ($\Delta\delta = 0.73$) than for *meso*-**1** ($\Delta\delta = 0.14$).

The ^{11}B-{^{1}H} and ^{11}B NMR signals of both *meso*- and DD/LL-**1** are broad and poorly resolved in $(CD_3)_2SO$. The resolution is greatly improved for the DD/LL isomers when $(CD_3)_2CO$ is used as the solvent. [The poor solubility of the *meso* isomer in acetone precluded the measurement of its ^{11}B NMR spectrum in $(CD_3)_2CO$]. The 96 MHz ^{11}B-{^{1}H} NMR spectrum of complex **1** in $(CD_3)_2CO$ at room temperature exhibits eight resonances with area ratio 1:1:2:1:1:1:1:1 (high to low frequency). This is consistent with the presence of two equivalent 4-substituted dicarbollide ligands in **1**. Only the ^{11}B resonance at δ −4.14 remained as a singlet in the proton-coupled ^{11}B spectrum, indicating that this resonance is from the Me_2S-substituted boron.

The infrared spectrum of the compound DD/LL-**1** (as a KBr pellet) was found to be identical with that of the *meso*–DD/LL isomeric mixture. The most diagnostic and prominent feature of the spectrum is the intense broad band centred at 2521 cm^{-1}, assigned to the B–H stretching vibrations. The C–H stretching absorption of the SMe groups occurs at 2928 cm^{-1}.

The UV/VIS spectral data for the isomers of complex **1** are given in Table 1. The spectra are similar to those of *commo*-[3,3'-Fe{8-(Et_2S)-1,2-$C_2B_9H_{10}$}$_2$][7a] and the *commo*-[3,3'-Fe(1,2-$C_2B_9H_{11})_2]^{2-}$ anion.[8] It is also noteworthy that the spectra of *meso*- and DD/LL-**1** are distinguishable despite the similarity of the compounds.

The molecular ion of complex **1** is detected in its FAB mass spectrum as a characteristic envelope of peaks, the most intense of which is at m/z = 443. The observed m/z values and relative intensities of the peaks in the envelope are in satisfactory agreement with the calculated values from a computer simulation based on natural isotopic abundances.

(*iii*) *Electrochemistry*. Complex **1** (isomeric mixture) undergoes a reversible (ΔE_p = 72 mV) one-electron oxidation at an $E_{\frac{1}{2}}$ value of +0.45 V [*vs*. saturated calomel electrode (SCE), 25 °C, 0.1 mmol dm^{-3} MeCN solution with 0.1 mol dm^{-3} $NBu^n{}_4PF_6$ supporting electrolyte]. This value is close to that reported for *commo*-[3,3'-Fe{8-(Et_2S)-1,2-$C_2B_9H_{10}$}$_2$] (+0.48 V *vs*. SCE, MeCN).[7a] It is evident that the formal substitution of an anionic hydride with a neutral Me_2S group on each dicarbollide cage greatly increases the oxidation potential of the sandwich complex {*cf*. $E_{\frac{1}{2}}$ for *commo*-[3,3'-Fe(1,2-$C_2B_9H_{11})_2]^{2-}$ = −0.42 V *vs*. SCE, MeCN}.[8]

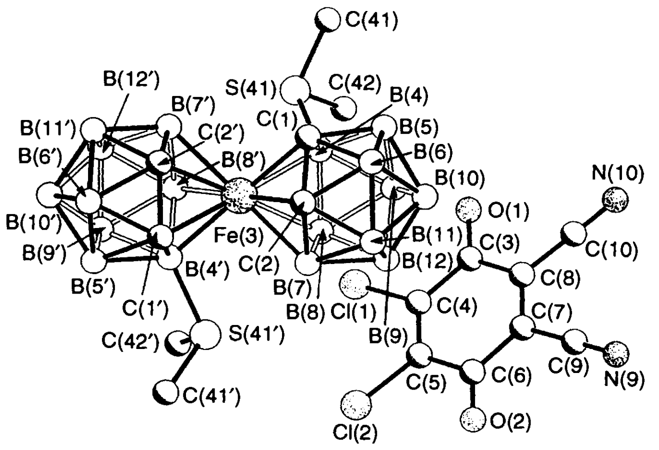

Fig. 2 Molecular structure of the cation and anion in compound **2**. The carbon atoms in the dicarbollide cages are hatched

(*b*) [3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$]$^+$[ddq]$^{\bullet-}$ **2**.—(*i*) *Synthesis*. The high half-wave potential of compound **1** indicated that no stable charge-transfer salt could be formed between it and tetracyanoethylene ($E_{\frac{1}{2}}$ = +0.15 V *vs*. SCE, MeCN)[9] or tetracyanoquinodimethane ($E_{\frac{1}{2}}$ = +0.13 V *vs*. SCE, MeCN).[10] The stronger electron acceptor ddq ($E_{\frac{1}{2}}$ = +0.51 V *vs*. SCE, MeCN)[9] was thus chosen as the possible acceptor to form a charge-transfer salt with **1**. Although no characterizable product could be isolated when the reaction was carried out in acetonitrile, combination of DD/LL-**1** and ddq in anhydrous dichloromethane solution yielded a black shiny crystalline precipitate which analysed correctly for [3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}]$^+$[ddq]$^{\bullet-}$ **2**. Compound **2** is an air- and moisture-stable solid at room temperature.

(*ii*) *Infrared spectrum*. The infrared spectrum of compound **2** (as a KBr pellet) exhibits an intense broad absorption peak at 2551 cm^{-1} due to the B–H stretching [ν(B–H)] vibrations, confirming the presence of the metallacarborane component. It is noteworthy that this wavenumber is 30 cm^{-1} higher than that of **1** (see above).

The diagnostic absorptions of the [ddq]$^{\bullet-}$ anion occur at 2208s [ν(CN)], 1560s [ν(C=O)] and 1532vs cm^{-1} [ν(C=O)]. These positions are consistent with the −1 charge of the [ddq]$^{\bullet-}$ anion.[11]

(*c*) *Crystal Structures*.—To simplify the discussion, the crystal structure of compound **2** will be described first.

(*i*) [3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$]$^+$[ddq]$^{\bullet-}$**2**. The molecular structures of the cation and anion in compound **2** are shown in Fig. 2. This is the first example of a cationic metallacarborane incorporating two dicarbollide ligands to be crystallographically characterized.

The [3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$]$^+$ cation has non-crystallographic C_2 symmetry and adopts a staggered sandwich structure with the carbon atoms of the two dicarbollide cages in a cisoid arrangement. The Me_2S substituents are oriented in a *gauche* configuration, corresponding to a rotation of *ca*. 109° of the C_2B_3 ligating rings about their centroid–centroid axis from the position in which the Me_2S groups are eclipsed. Both C_2B_3 faces are nearly planar, with maximum deviations of 0.014 and 0.010 Å [for B(7) and B(7') respectively] from their respective planes. They are inclined by 1.5° to each other. The distance of the Fe atom from each C_2B_3 face (1.54 Å) is essentially the same as the corresponding distance (1.53 Å) in [ttf]$^{\bullet+}$[Fe$(C_2B_9H_{11})_2$]$^-$ **4** [ttf = 2-(1',3'-dithiol-2'-ylidene)-1,3-dithiole (tetrathiafulvalene)].[4] However, whereas the range of Fe–C bond lengths in **2** (2.072–2.095 Å) is essentially the same as that observed in **4** (2.080–2.096 Å) the Fe–B bonds exhibit a wider spread of values (2.109–2.173 Å in **2** *cf*. 2.114–2.154 Å in **4**.) This may be due to the presence of the Me_2S

Table 2 Crystal and refinement data for compounds **1** and **2**[a]

	$[Fe\{(Me_2S)C_2B_9H_{10}\}_2]$ **1**	$[Fe\{(Me_2S)C_2B_9H_{10}\}_2]^+[ddq]^{\bullet-}$ **2**
(*a*) Crystal data		
Chemical formula	$C_8H_{32}B_{18}FeS_2$	$C_{16}H_{32}B_{18}Cl_2FeN_2O_2S_2$
M	442.9	669.9
Space group	$P2_1/c$	Cc[b]
a/Å	12.693(4)	10.616(8)
b/Å	13.042(5)	17.271(9)
c/Å	14.210(4)	16.738(5)
β/°	109.03(2)	93.57(2)
U/Å^3	2223.8(13)	3063(3)
D_c/g cm^{-3}	1.323	1.453
F(000)	912	1360
Colour, habit	Red plates	Black prisms
Crystal dimensions/mm	0.03 × 0.57 × 0.57	0.10 × 0.13 × 0.27
μ(Mo-Kα)/mm^{-1}	0.861	0.828
(*b*) Data collection and processing		
ω-Scan width/°	0.90	1.00
2θ limits/°	3.0–50.0	3.0–55.0
Minimum, maximum *h*, *k*, *l*	0,15; 0,15; −16,15	0,13; 0,22; −21,21
No. of reflections:		
Total	4096	3700
Unique (R_{int})	3916 (0.0322)	3525 (0.0140)
Observed [$F > 4.0\sigma(F)$]	2737	3144
Absorption correction	Face-indexed numerical	
Minimum, maximum transmissions	0.6992, 0.9779	
(*c*) Structure analysis and refinement		
No. of parameters	262	387
R (observed data)	0.0449	0.0365
R' (observed data)	0.0431	0.0367
Largest difference peak, hole/e Å^{-3}	0.88, −0.37	0.59, −0.30

[a] Details in common: monoclinic; $Z = 4$; Siemens P4/PC diffractometer; Mo-Kα radiation (λ = 0.710 73 Å); ω scan mode; weighting scheme $w^{-1} = \sigma^2(F) + 0.0005F^2$. [b] The polarity of the structure was determined by an *R*-factor test.

Table 3 Atomic coordinates (× 10^4) of compound **2**

Atom	*x*	*y*	*z*
Fe(3)	0	10 021(1)	2 500
C(1)	1 798(4)	9 517(3)	2 584(3)
C(2)	937(5)	9 254(3)	3 294(3)
B(4)	1 865(5)	10 504(3)	2 539(3)
B(5)	3 156(6)	9 952(3)	2 975(4)
B(6)	2 534(6)	9 129(4)	3 455(4)
B(7)	321(7)	10 000(3)	3 765(4)
B(8)	926(6)	10 860(4)	3 307(3)
B(9)	2 626(6)	10 794(4)	3 459(4)
B(10)	3 006(7)	9 950(4)	4 032(4)
B(11)	1 618(6)	9 455(4)	4 212(4)
B(12)	1 663(6)	10 485(4)	4 228(4)
C(1')	−1 771(5)	9 512(3)	2 432(3)
C(2')	−927(5)	9 225(3)	1 727(3)
B(4')	−1 839(6)	10 487(4)	2 458(3)
B(5')	−3 130(6)	9 928(4)	2 035(4)
B(6')	−2 529(6)	9 113(4)	1 588(4)
B(7')	−326(6)	9 983(3)	1 224(3)
B(8')	−932(5)	10 837(3)	1 682(3)
B(9')	−2 624(6)	10 764(4)	1 533(4)
B(10')	−3 061(6)	9 904(4)	999(4)
B(11')	−1 603(6)	9 428(4)	805(3)
B(12')	−1 658(6)	10 449(4)	766(3)
S(41)	2 186(2)	11 039(1)	1 579(1)
C(41)	3 544(6)	10 634(5)	1 204(4)
C(42)	2 777(14)	11 934(4)	1 925(5)
S(41')	−2 174(2)	11 058(1)	3 412(1)
C(41')	−3 508(6)	10 643(4)	3 808(4)
C(42')	−2 698(11)	11 960(3)	3 043(4)
Cl(1)	918(2)	13 287(1)	3 492(1)
Cl(2)	−516(2)	12 641(1)	4 941(1)
O(1)	3 646(4)	13 069(2)	3 692(2)
O(2)	1 208(4)	12 004(2)	6 217(2)
C(3)	3 086(5)	12 835(3)	4 277(3)
C(4)	1 720(5)	12 880(3)	4 306(3)
C(5)	1 102(4)	12 607(3)	4 941(3)
C(6)	1 766(5)	12 253(3)	5 639(3)
C(7)	3 115(5)	12 199(3)	5 605(3)
C(8)	3 749(5)	12 489(3)	4 967(3)
C(9)	3 788(5)	11 847(3)	6 266(3)
N(9)	4 312(5)	11 555(3)	6 808(3)
C(10)	5 074(6)	12 436(3)	4 967(3)
N(10)	6 157(5)	12 386(3)	4 963(3)

substituents, the steric requirements of which significantly influence the conformation of the cation in the crystal.

The bond lengths within the $[ddq]^{\bullet-}$ radical anion (see Table 4) agree well with those observed in $[NEt_4]^+[ddq]^{\bullet-}$.[12] The six-membered ring of the anion is nearly planar, with a maximum deviation of 0.012 Å [for C(7)] from the mean plane. The peripheral atoms and groups attached to the ring are also more or less coplanar with the ring, with a maximum deviation of 0.05 Å [for Cl(2)].

The cations and anions pack to form alternating layers in the crystal [Fig. 3(*a*)]. Within the $[ddq]^{\bullet-}$ layer the anions form zigzag chains linked *via* short intermolecular N ··· Cl interactions [N(9) ··· Cl(1a) 3.21 Å]. These extend in the (101) direction in the crystal. The interanion contact between N(10) and Cl(2a) is significantly longer at 3.56 Å. Although the C(9)–N(9) ··· Cl(1a)–C(4a) unit is bent [N(9)–Cl(1a)–C(4a) 161, Cl(1a)–N(9)–C(9) 149°], no perturbation of the C(9)–N(9) bond length [1.150(7), *cf.* C(10)–N(10) 1.153(8) Å] and the C(7)–C(9)–N(9) bond angle [178.7(6), *cf.* C(8)–C(10)–N(10) 179.3(5)°] is evident. This implies that the N ··· Cl interactions are electrostatic in nature, with a δ− charge on the cyano nitrogen and an induced δ+ charge on the polarizable Cl atom.

Table 4 Selected bond lengths (Å) and angles (°) for compound **2**

Cl(1)–C(4)	1.711(5)	Fe(3)–C(2′)	2.091(5)
Cl(2)–C(5)	1.719(5)	Fe(3)–B(4′)	2.109(6)
O(1)–C(3)	1.244(6)	Fe(3)–B(7′)	2.143(6)
O(2)–C(6)	1.241(6)	Fe(3)–B(8′)	2.161(6)
C(3)–C(4)	1.456(8)	C(1)–C(2)	1.610(7)
C(3)–C(8)	1.444(7)	C(1)–B(4)	1.707(8)
C(4)–C(5)	1.367(7)	C(2)–B(7)	1.666(8)
C(5)–C(6)	1.461(7)	B(4)–B(8)	1.784(8)
C(6)–C(7)	1.440(7)	B(7)–B(8)	1.807(9)
C(7)–C(8)	1.391(7)	C(1′)–C(2′)	1.603(7)
C(7)–C(9)	1.417(7)	C(1′)–B(4′)	1.685(8)
C(8)–C(10)	1.410(8)	C(2′)–B(7′)	1.701(8)
C(9)–N(9)	1.150(7)	B(4′)–B(8′)	1.771(8)
C(10)–N(10)	1.153(8)	B(7′)–B(8′)	1.799(8)
Fe(3)–C(1)	2.095(5)	B(4)–S(41)	1.903(6)
Fe(3)–C(2)	2.085(5)	B(4′)–S(41′)	1.930(6)
Fe(3)–B(4)	2.146(6)	S(41)–C(41)	1.754(8)
Fe(3)–B(7)	2.124(6)	S(41)–C(42)	1.754(8)
Fe(3)–B(8)	2.173(6)	S(41′)–C(41′)	1.753(7)
Fe(3)–C(1′)	2.072(5)	S(41′)–C(42′)	1.754(6)
C(1)–C(2)–B(7)	112.9(4)	B(7)–Fe(3)–B(4′)	97.5(2)
C(2)–B(7)–B(8)	105.9(4)	B(8)–Fe(3)–B(8′)	97.5(2)
B(4)–B(8)–B(7)	104.6(4)	B(4)–Fe(3)–B(4′)	134.7(2)
C(1)–B(4)–B(8)	106.6(4)	B(7)–Fe(3)–B(7′)	177.3(2)
C(2)–C(1)–B(4)	110.0(4)	B(4)–S(41)–C(41)	107.6(3)
C(1)–Fe(3)–C(2′)	99.2(2)	B(4)–S(41)–C(42)	103.2(3)
C(2)–Fe(3)–C(1′)	99.2(2)	C(41)–S(41)–C(42)	100.7(5)
B(4)–Fe(3)–B(7′)	97.7(2)		

Similar electrostatic C≡N···Cl interactions have been observed in the crystal structures of several other chlorocyano-compounds, *e.g.* substituted 1,2-dichloro-4,5-dicyanobenzenes and 4-chlorobenzonitriles,[13] but not previously in ddq and its compounds. The layer motif of the $[\mathrm{ddq}]^{\bullet -}$ anions observed here, which facilitates the formation of such 'molecular tapes', is also unprecedented. In the solid state, $[\mathrm{ddq}]^{\bullet -}$ anions usually form either segregated stacks {frequently with pairwise interactions to form $[(\mathrm{ddq})_2]^{2-}$ dimers}[5b,12,14] or are interleaved with the cations to form mixed stacks.[5a,15]

The $[3,3'\text{-Fe}\{4\text{-}(\mathrm{Me_2S})\text{-}1,2\text{-}\mathrm{C_2B_9H_{10}}\}_2]^+$ cations are arranged in sheets that extend in the *a* and *c* directions. The $\mathrm{Me_2S}$ groups of adjacent cations along the rows point alternately in the ±*b* directions into the troughs of the zigzag chains of anions. There are no intercationic distances shorter than van der Waals contacts.

In addition to their mutual electrostatic attraction, the cation and anion layers are crossed-linked by weak C–H···O hydrogen bonds between the oxygen atoms of the $[\mathrm{ddq}]^{\bullet -}$ anions and the hydrogen atoms attached to C(2), C(1′) and C(2′) on the dicarbollide cages [O(1)···H(1′) 2.37, O(1)···H(2) 2.45 and O(2a)···H(2′) 2.41 Å; O(1)···H(1′)–C(1′) 157, O(1)···H(2)–C(2) 144 and O(2a)···H(2′)–C(2′) 147°]. There is apparently only one precedent in the literature of hydrogen bonding involving hydrogen atoms attached to metallacarborane cages.[7d] Studies by Adler and Hawthorne[16] and Lipscomb and co-workers[17] have indicated that a region of localized electron deficiency exists around the carbon atoms in the neutral carborane *closo*-$1,2\text{-}\mathrm{C_2B_{10}H_{12}}$. In the $[3,3'\text{-Fe}\{4\text{-}(\mathrm{Me_2S})\text{-}1,2\text{-}\mathrm{C_2B_9H_{10}}\}_2]^+$ cation this electron deficiency is expected to be greatly increased by the presence of the charge-compensating $\mathrm{Me_2S}$ groups and the adjacent highly electron-attracting $\mathrm{Fe^{III}}$, thus accounting for the protonic character of the cage CH hydrogens. The co-operative effect of this hydrogen bonding between the cations and anions must play an important role in stabilizing the layered structure of compound **2**.

(*ii*) *commo*-$[3,3'\text{-Fe}\{4\text{-}(\mathrm{Me_2S})\text{-}1,2\text{-}\mathrm{C_2B_9H_{10}}\}_2]$ **1**. The gross structural features of compound **1** (see Fig. 4) are very similar to those of the cation in **2**. The $\mathrm{C_2B_3}$ bonding faces are staggered and in a cisoid configuration. They are rotated by *ca.* 104° (*cf.* 109° in **2**) about their centroid–centroid axis from the position in which the $\mathrm{Me_2S}$ groups are eclipsed. Both $\mathrm{C_2B_3}$ rings are

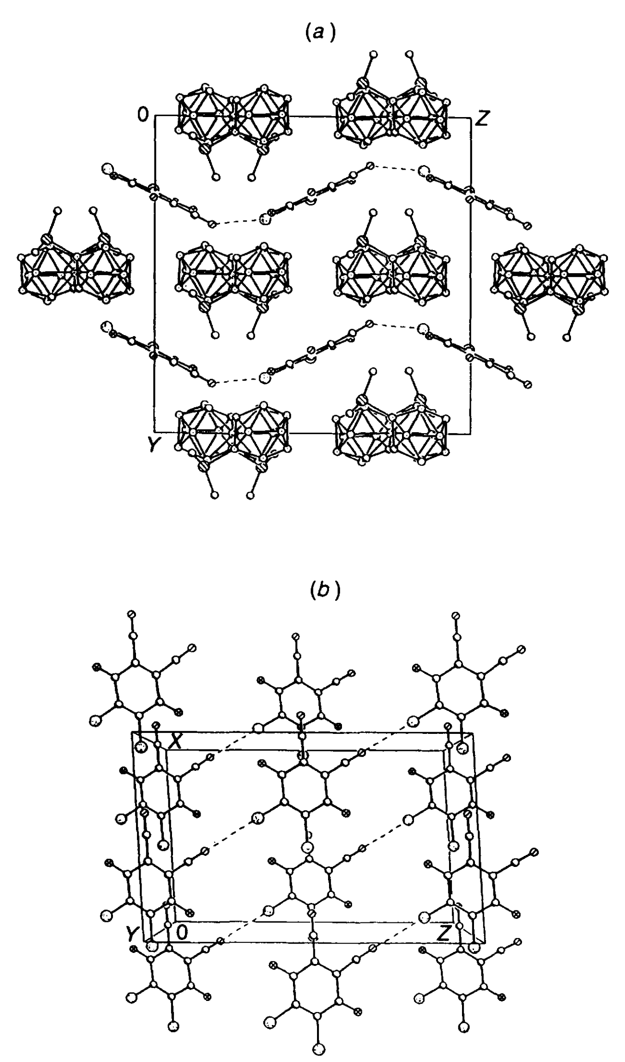

Fig. 3 (*a*) Packing diagram of compound **2**, showing the alternating layers of cations and anions. (*b*) Diagram showing the packing of anions in **2**

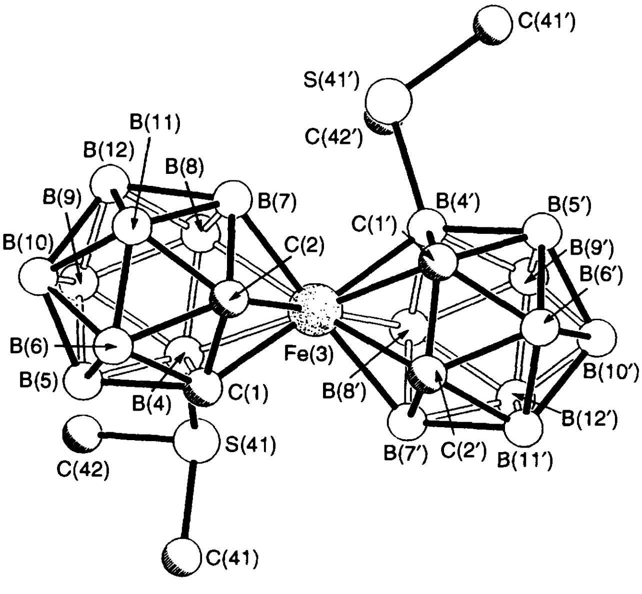

Fig. 4 Molecular structure of complex **1**

Table 5 Atomic coordinates (× 10^4) of compound **1**

Atom	*x*	*y*	*z*
Fe(3)	7 330(1)	604(1)	2 094(1)
C(1)	7 652(3)	560(3)	766(3)
C(2)	6 554(3)	−56(3)	749(3)
B(4)	8 743(4)	169(3)	1 730(3)
B(5)	8 579(4)	−253(4)	489(3)
B(6)	7 150(4)	−374(4)	−158(4)
B(7)	6 791(4)	−899(4)	1 692(4)
B(8)	8 252(4)	−799(3)	2 352(4)
B(9)	8 948(4)	−1 148(4)	1 471(4)
B(10)	7 935(4)	−1 463(4)	310(4)
B(11)	6 619(4)	−1 314(4)	446(4)
B(12)	7 727(4)	−1 808(4)	1 454(4)
S(41)	10 038(1)	1 010(1)	2 280(1)
C(41)	10 020(4)	1 907(4)	1 314(4)
C(42)	11 200(4)	228(4)	2 254(4)
C(1′)	5 926(3)	960(3)	2 411(3)
C(2′)	6 334(3)	1 881(3)	1 832(3)
B(4′)	6 992(4)	601(4)	3 434(3)
B(5′)	5 853(4)	1 371(4)	3 523(4)
B(6′)	5 436(4)	2 195(4)	2 472(4)
B(7′)	7 688(4)	2 183(3)	2 417(3)
B(8′)	8 137(4)	1 371(3)	3 488(3)
B(9′)	7 247(4)	1 687(4)	4 225(4)
B(10′)	6 298(4)	2 661(4)	3 623(4)
B(11′)	6 569(4)	2 976(4)	2 514(4)
B(12′)	7 693(4)	2 676(4)	3 582(4)
S(41′)	7 100(1)	−731(1)	4 062(1)
C(41′)	6 217(5)	−715(4)	4 825(4)
C(42′)	8 432(4)	−632(4)	5 021(3)

Table 6 Selected bond lengths (Å) and angles (°) for compound **1**

Fe(3)–C(1)	2.057(4)	B(4)–B(8)	1.768(7)
Fe(3)–C(2)	2.034(4)	B(7)–B(8)	1.789(7)
Fe(3)–B(4)	2.100(5)	C(1′)–C(2′)	1.633(6)
Fe(3)–B(7)	2.094(5)	C(1′)–B(4′)	1.697(6)
Fe(3)–B(8)	2.139(5)	C(2′)–B(7′)	1.694(6)
Fe(3)–C(1′)	2.029(5)	B(4′)–B(8′)	1.747(7)
Fe(3)–C(2′)	2.051(4)	B(7′)–B(8′)	1.789(6)
Fe(3)–B(4′)	2.084(5)	B(4)–S(41)	1.918(4)
Fe(3)–B(7′)	2.126(5)	B(4′)–S(41′)	1.938(5)
Fe(3)–B(8′)	2.157(4)	S(41)–C(41)	1.798(5)
C(1)–C(2)	1.602(6)	S(41)–C(42)	1.804(5)
C(1)–B(4)	1.679(5)	S(41′)–C(41′)	1.795(7)
C(2)–B(7)	1.683(6)	S(41′)–C(42′)	1.796(4)
C(1)–C(2)–B(7)	112.7(3)	B(7)–Fe(3)–B(4′)	95.8(2)
C(2)–B(7)–B(8)	104.8(4)	B(8)–Fe(3)–B(8′)	99.7(2)
B(4)–B(8)–B(7)	105.3(3)	B(4)–Fe(3)–B(4′)	132.1(2)
C(1)–B(4)–B(8)	107.1(3)	B(7)–Fe(3)–B(7′)	173.5(2)
C(2)–C(1)–B(4)	110.0(3)	B(4)–S(41)–C(41)	105.4(2)
C(1)–Fe(3)–C(2′)	98.7(2)	B(4)–S(41)–C(42)	105.4(2)
C(2)–Fe(3)–C(1′)	96.6(2)	C(41)–S(41)–C(42)	99.2(3)
B(4)–Fe(3)–B(7′)	100.1(2)		

nearly planar, with maximum deviations of 0.014 [for B(7) and B(8)] and 0.012 Å [for B(7′)] from their respective mean planes. The ring planes are inclined by 5.3° to each other (*cf.* 1.5° in **2**) and are both 1.50 Å from the Fe atom (*cf.* 1.54 Å in **2**). The corresponding Fe–C (2.029–2.057 Å) and Fe–B (2.084–2.157 Å) distances are both overall shorter than those in **2**. The increase in Fe–C_2B_3 distance that occurs when **1** is oxidized to the cation in **2** suggests that the highest occupied molecular orbital (HOMO) of **1** is weakly bonding in nature. It is also noteworthy that this increase is inconsistent with the electrostatic model of iron–dicarbollide bonding proposed in ref. 7(*c*), which would predict a stronger interaction when the charge on the Fe atom is increased from +2 to +3.

There are no intermolecular distances shorter than van der Waals contacts.

(*d*) *Magnetic Properties of* $[3,3'\text{-Fe}\{4\text{-}(Me_2S)\text{-}1,2\text{-}C_2B_9H_{10}\}_2]^+[ddq]^{\bullet-}$ **2**.—Between 5 and 270 K the corrected molar susceptibility of compound **2** follows the Curie–Weiss Law, $\chi = C/(T - \theta)$, with a θ value of −2.5 K which indicates that there is very weak interaction between the unpaired spins of the ions. Correspondingly, the effective moment, $\mu\ (= \sqrt{8\chi T})$, of the salt is practically independent of temperature in the above temperature range. The average μ value ($\mu_{av} = \sqrt{8C}$) from 5 to 270 K is 3.01 μ_B. Assuming a spin-only value of 1.73 μ_B for the organic radical anion, the μ value of the $[3,3'\text{-Fe}\{4\text{-}(Me_2S)\text{-}1,2\text{-}C_2B_9H_{10}\}_2]^+$ cation can be calculated from the formula for non-interacting spins, $\mu_{total}^2 = \mu_{cation}^2 + \mu_{anion}^2$, to be 2.45 μ_B. This value is in good agreement with the μ values generally observed for low-spin iron(III) complexes ($\approx$2.3 μ_B).[18]

No spin coupling between the metallacarborane cations in compound **2** is expected because there are no short intercationic contacts. Spin–spin interaction between the $[ddq]^{\bullet-}$ anions *via* the short C≡N···Cl contacts is also unlikely in the light of molecular orbital calculations by Miller *et al.*,[15b] which predict zero spin density on the Cl atoms of $[ddq]^{\bullet-}$. Miller's calculations also indicate that within the $[ddq]^{\bullet-}$ radical anion the highest spin densities reside on the quinoidal oxygen atoms. Thus, the overall lack of significant spin interaction in **2**, despite the fact that two $[ddq]^{\bullet-}$ anions are hydrogen-bonded to each ferracarborane cation *via* the quinoidal oxygen atoms, suggests that there is negligible delocalization of spin density from the iron(III) centre to the cage CH hydrogens in the $[3,3'\text{-Fe}\{4\text{-}(Me_2S)\text{-}1,2\text{-}C_2B_9H_{10}\}_2]^+$ cation.

(*e*) *Electrical Conductivity*.—The electrical conductivity of compound **2** was measured on a single crystal at room temperature. Compound **2** was found to be an insulator under these conditions ($\sigma < 10^{-8}$ S cm^{-1}). Thus, although the difference between the half-wave potentials of **1** and ddq ($|\Delta E_{\frac{1}{2}}| = 0.06$ V) is small enough for the formation of a mixed-valence compound,[5b] the failure to form ddq stacks in the solid state results in the formation of an insulating solid.

Experimental

General.—2,3-Dichloro-5,6-dicyano-*p*-benzoquinone was obtained from Aldrich and used as received. The compounds $K[C_2B_9H_{12}]$[19] and $[FeCl_2(thf)_2]$[20] were prepared following reported procedures. Organic solvents were of reagent grade and were dried by published procedures[21] and distilled under N_2. The solvents were vacuum-degassed before use. All reactions were routinely carried out under N_2 using standard Schlenk techniques.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 1720 Fourier-transform spectrometer and a Perkin-Elmer Lambda 2 UV/VIS spectrophotometer was used to record the electronic spectra. The NMR spectra were recorded either on a Bruker AM-300 spectrometer [for spectra recorded in $(CD_3)_2CO$] or a JEOL JNM-EX270 FT-NMR spectrometer [for spectra recorded in $(CD_3)_2SO$]; ^1H and ^{11}B chemical shifts are referenced to tetramethylsilane and $BF_3(OEt_2)$ respectively. The FAB mass spectrum of compound **1** was recorded at the SERC Mass Spectrometry Service Centre at the University of Swansea on a VG ZAB-E high-resolution double-focusing mass spectrometer, using 3-nitrobenzyl alcohol as the matrix. Cyclic voltammograms were recorded under N_2 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 $5 \leqslant T \leqslant 270$ 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 susceptibility was corrected for the diamagnetism of the gelatin sample capsule and that of the constituent atomic cores 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 at room temperature. Contacts were made with platinum paint and 25 μm gold wires.

Syntheses.—*nido*-9-(Me_2S)-7,8-$C_2B_9H_{11}$ **3**. Concentrated H_2SO_4 (5 cm^3) was added dropwise under N_2 to a magnetically stirred solution of K[$C_2B_9H_{12}$] (0.60 g, 3.5 mmol) and dimethyl sulfoxide (1.20 g, 15.4 mmol) in deionized water (4 cm^3). The resultant suspension was stirred in an oil-bath at 80 °C for 90 min, during which an off-white, sticky solid was formed. The mixture was cooled to room temperature, diluted with deionized water (40 cm^3) and filtered through a glass frit. The solid collected was redissolved in CH_2Cl_2 and chromatographed on silica (100% CH_2Cl_2). The eluent was concentrated under reduced pressure and hexane added. The resultant mixture was slowly evaporated to dryness under reduced pressure to obtain 0.43 g (64%) of compound **3** as a white microcrystalline solid (Found: C, 25.0; H, 9.1. Calc. for $C_4H_{17}B_9S$: C, 24.7; H, 8.8%).

commo-[3,3'-Fe{4-(Me_2S)-1,2-($C_2B_9H_{10}$}$_2$] **1**. A 0.041 g amount of a 60% NaH–mineral oil dispersion (0.025 g NaH, 1.0 mmol) was washed with distilled thf (2 × 1.5 cm^3) in a Schlenk tube. Tetrahydrofuran (2 cm^3) was added, followed by a solution of compound **3** (0.130 g, 0.67 mmol) in thf (10 cm^3) at room temperature. The mixture was stirred at room temperature for 20 min and then refluxed for 45 min. After cooling to room temperature and allowing the excess of NaH to settle, the colourless supernatant was transferred *via* a steel cannula to a stirred suspension of [$FeCl_2(thf)_2$] (0.390 g, 1.4 mmol) in thf (3 cm^3). The purple suspension so formed was stirred in a 60 °C oil-bath for 3 h and then evaporated to dryness under reduced pressure. The residue was washed with deionized water until the washings were colourless, leaving a reddish brown residue which was then extracted with acetone. The pink acetone extract was concentrated under reduced pressure and ethanol was added to effect crystallization of compound **1** (isomeric mixture) as bright pink microcrystals. Yield: 0.057 g, 36% (Found: C, 22.1; H, 7.6; Fe, 12.7. $C_8H_{32}B_{18}FeS_2$ requires C, 21.7; H, 7.3; Fe, 12.6%). NMR: for DD/LL-**1**[in $(CD_3)_2CO$], ^1H, δ 4.09 (br s, 2 H, cage CH), 3.16 (br s, 2 H, cage CH), 2.63 (s, 6 H, CH_3) and 2.59 (s, 6 H, CH_3); ^{11}B-{^1H}, δ −4.14 [2B, B(4) and B(4')], −5.54 (2B), −9.34 (4B), −11.35 (2B), −14.90 (2B), −24.15 (2B), −24.60 (2B) and −27.09 (2B); [in $(CD_3)_2SO$], ^1H, δ 4.06 (br s, 2 H, cage CH), 3.33 (br s, 2 H, cage CH), 2.70 (s, 6 H, CH_3) and 2.48 (s, 6 H, CH_3); for *meso*-**1** [in $(CD_3)_2SO$], ^1H, δ 4.10 (br s, 2 H, cage CH), 3.96 (br s, 2 H, cage CH), 2.60 (s, 6 H, CH_3) and 2.53 (s, 6 H, CH_3).

[3,3'-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$]$^+$ [ddq]$^{\cdot -}$ **2**. A solution of ddq (0.014 g, 0.062 mmol) in CH_2Cl_2 (*ca.* 5 cm^3) was added under N_2 to a solution of the compound DD/LL-**1** (0.027 g, 0.061 mmol) in CH_2Cl_2 (*ca.* 20 cm^3) at room temperature. The resultant deep red solution was filtered under N_2 into another Schlenk tube and kept at *ca.* −10 °C for 4 d. The black shiny microcrystalline solid formed was filtered off and dried under reduced pressure. Yield: 0.031 g, 76% (Found: C, 28.2; H, 4.6; N, 4.0. $C_{16}H_{32}B_{18}Cl_2FeN_2O_2S_2$ requires C, 28.7; H, 4.8; N, 4.2%).

X-Ray Crystallography.—The crystal and refinement data for compounds **1** and **2** are summarized in Table 2, atomic coordinates in Tables 3 and 5 and selected bond lengths and angles in Tables 4 and 6. Single crystals of DD/LL-**1** were grown by slow evaporation of an acetone–ethanol solution at room temperature, while crystals of **2** were grown by slow interdiffusion of CH_2Cl_2 solutions of DD/LL-**1** and ddq through a glass frit at −10 °C.

The structures were solved by direct methods. Positional and anisotropic thermal parameters for non-hydrogen atoms were refined by the full-matrix least-squares method. Hydrogen atoms of the Me_2S groups were introduced in calculated positions and refined isotropically. Those on the carborane cages 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 $U(H) = 1.2\ U_{eq}(C, B)$. Calculations for compound **1** were performed on a VAX station 3100 model 76 computer using the SHELXTL PLUS[22] software package while those for **2** were performed on 386 and 486 personal computers using the PC version of the same program package.

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 SERC is acknowledged. Y.-K. Y. thanks the Nanyang Technological University, Singapore, for a scholarship. We also thank Professor M. F. Hawthorne for his gift of 1,2-dicarba-*closo*-dodecaborane, Dr. E. Fung and Mr. D. White for the electrochemical measurements and Dr. S. Carling for help with the magnetic susceptibility measurements.

References

1 J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff and A. J. Epstein, *J. Am. Chem. Soc.*, 1987, **109**, 769; W. E. Broderick, J. A. Thompson, E. P. Day and B. M. Hoffman, *Science*, 1990, **249**, 401; J. M. Manriquez, G. T. Yee, R. S. McLean, A. J. Epstein and J. S. Miller, *Science*, 1991, **252**, 1415; Y. Pei, O. Kahn, K. Nakatani, E. Codjovi, C. Mathonière and J. Sletten, *J. Am. Chem. Soc.*, 1991, **113**, 6558; V. Gadet, T. Mallah, I. Castro, M. Verdaguer and P. Veillet, *J. Am. Chem. Soc.*, 1992, **114**, 9213; J. S. Miller, R. S. McLean, C. Vazquez, J. C. Calabrese, F. Zuo and A. J. Epstein, *J. Mater. Chem.*, 1993, **3**, 215; E. Hernàndez, M. Mas, E. Molins, C. Rovira and J. Veciana, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 882.

2 D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 690; D. M. Murphy, D. M. P. Mingos, J. L. Haggitt, H. R. Powell, S. A. Westcott, T. B. Marder, N. J. Taylor and D. R. Kanis, *J. Mater. Chem.*, 1993, **3**, 139; M. M. Bader, T. Hamada and A. Kakuta, *J. Am. Chem. Soc.*, 1992, **114**, 6475; H. Nakazumi, S. Watanabe, K. Maeda and T. Kitao, *Chem. Lett.*, 1990, 679; N. Ono, K. Sugi, T. Ogawa and S. Aramaki, *J. Chem. Soc., Chem. Commun.*, 1993, 1781.

3 (*a*) J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz and M.-H. Whangbo, *Prog. Inorg. Chem.*, 1987, **35**, 51; (*b*) J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M.-H. Whangbo, *Organic Superconductors (including Fullerenes): Synthesis, Structure, Properties, and Theory*, Prentice Hall, Englewood Cliffs, NJ, 1992.

4 J. M. Forward, D. M. P. Mingos, T. E. Müller, D. J. Williams and Y.-K. Yan, *J. Organomet. Chem.*, 1994, **467**, 207.

5 (*a*) J. S. Miller, R. S. McLean, C. Vazquez, G. T. Yee, K. S. Narayan and A. J. Epstein, *J. Mater. Chem.*, 1991, **1**, 479; (*b*) J. J. Mayerle and J. B. Torrance, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3170.

6 J. Plešek, Z. Janoušek and S. Heřmánek, *Inorg. Synth.*, 1983, **22**, 239.

7 (*a*) M. F. Hawthorne, L. F. Warren, jun., K. P. Callahan and N. F. Travers, *J. Am. Chem. Soc.*, 1971, **93**, 2407; (*b*) C. J. Jones, J. N. Francis and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1973, **95**, 7633; (*c*) H. C. Kang, S. S. Lee, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1991, **30**, 2024; (*d*) N. L. Douek and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1993, 1917.

8 M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, jun. and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879.

9 R. L. Brandon, J. H. Osiecki and A. Ottenberg, *J. Org. Chem.*, 1966, **31**, 1214.

10 D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, 1962, **84**, 3370.

11 J. S. Miller and D. A. Dixon, *Science*, 1987, **235**, 871.

12 G. Zanotti, A. del Pra and R. Bozio, *Acta Crystallogr., Sect. B*, 1982, **38**, 1225.

13 G. R. Desiraju and R. L. Harlow, *J. Am. Chem. Soc.*, 1989, **111**, 6757; D. S. Reddy, K. Panneerselvam, T. Pilati and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1993, 661.

14 A. Marzotto, D. A. Clemente and L. Pasimeni, *J. Crystallogr. Spectrosc. Res.*, 1988, **18**, 545.

15 (*a*) E. Gebert, A. H. Reis, jun., J. S. Miller, H. Rommelmann and A. J. Epstein, *J. Am. Chem. Soc.*, 1982, **104**, 4403; (*b*) J. S. Miller, P. J. Krusic, D. A. Dixon, W. M. Reiff, J. H. Zhang, E. C. Anderson and A. J. Epstein, *J. Am. Chem. Soc.*, 1986, **108**, 4459.

16 R. G. Adler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1970, **92**, 6174.

17 J. A. Potenza, W. N. Lipscomb, G. D. Vickers and H. Schroeder, *J. Am. Chem. Soc.*, 1966, **88**, 628.

18 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text*, 5th edn., Wiley-Interscience, New York, 1988, p. 720.

19 J. Plešek, S. Heřmánek and B. Štíbr, *Inorg. Synth.*, 1983, **22**, 231.

20 P. Kovacic and N. O. Brace, *Inorg. Synth.*, 1960, **6**, 172; G. W. A. Fowles, D. A. Rice and R. A. Walton, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3119.

21 A. J. Gordon and R. A. Ford, *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*, Wiley-Interscience, New York, 1972.

22 G. M. Sheldrick, SHELXTL PLUS PC, Version 4.2, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990.

Received 28*th January* 1994; *Paper* 4/00532E