Metallaborane Chemistry. Part 14.[1] Icosahedral η^6-Arene Carbametallaboranes of Iron and Ruthenium; Molecular Structures of *closo*-[1-(η^6-C_6H_5Me)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] and *closo*-[3-(η^6-C_6H_6)-3,1,2-$RuC_2B_9H_{11}$]‡

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Icosahedral 2,4-dicarba-1-ferraboranes with η^6-bonded benzene, toluene, *o*-xylene, or naphthalene ligands have been synthesised in moderate yields by reaction of [Fe(cod)(η^5-C_5H_5)] (cod = cyclo-octa-1,5-diene) with 2,3-Me_2-2,3-$C_2B_9H_9$ in the presence of the appropriate arene. In addition, the toluene derivative, *closo*-[1-(η^6-C_6H_5Me)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] (**2**), has also been obtained by treatment of the carbaborane with [Fe_2(μ-η-C_6Me_6)(η^5-C_5H_5)$_2$] in toluene. Reaction of [$RuCl_2$(η^6-C_6H_6)]$_2$ with Tl[$TlC_2B_9H_{11}$] affords *closo*-[3-(η^6-C_6H_6)-3,1,2-$RuC_2B_9H_{11}$] (**7**). Complexes (**2**) and (**7**) have been characterised by single-crystal *X*-ray diffraction. Crystals of (**2**) are orthorhombic, space group $Pna2_1$, with a = 21.793(4), b = 8.6274(15), c = 8.636(3) Å, and Z = 4; R = 0.0499 for 1 676 reflections. Complex (**7**) is also orthorhombic, space group *Pnam*, with a = 18.477(2), b = 9.191(4), and c = 7.704(1) Å, and Z = 4; R = 0.0223 for 1 723 data. Both species have slightly distorted icosahedral cage geometries and overall C_s molecular symmetry, space group imposed for (**7**). The naphthalene derivative [1-(η^6-$C_{10}H_8$)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] undergoes substitution of the arene ligand by CO at 100 bar and 50 °C, to afford the complex [1,1,1-(CO)$_3$-2,4-Me_2-1,2,4-$FeC_2B_9H_9$].

The analogy between the bonding capabilities towards transition-metal centres of the cyclopentadienyl anion and *nido*-carbaborane dianions was first recognised by Hawthorne and co-workers[2] nearly 20 years ago. Since then numerous sandwich complexes, containing both carbaborane and η^5-C_5H_5 ligands, have been synthesised and structurally characterised. There are, by comparison, very few species known in which polyenes other than cyclopentadienyl act as exopolyhedral ligands to carbametallaboranes, rare examples including η^4-C_4Ph_4 in [3-(η^4-C_4Ph_4)-1,2-Me_2-3,1,2-$PdC_2B_9H_9$],[3] η^7-C_7H_7 in [1-(η^7-C_7H_7)-2,3-Et_2-1,2,3-$CrC_2B_4H_4$],[4] and η^8-C_8H_8 in [1-(η^8-C_8H_8)-2,3-Et_2-1,2,3-$MC_2B_4H_4$] (M = Ti or V).[4]

The most commonly found cyclopentadienylmetal fragments in carbametallaboranes are Co(η^5-C_5H_5) and Fe(η^5-C_5H_5), but whilst neutral [Co(dicarbaborane)(η^5-C_5H_5)] complexes are diamagnetic 18-electron species, the iron analogues are paramagnetic and have only 17-electron configurations. The C_5H_5 ligand in such complexes is, moreover, extremely inert with respect to substitution reactions. Clearly, therefore, worthwhile synthetic targets in carbametallaborane chemistry are compounds of the general type [M(dicarbaborane)(η-arene)] (M = Fe, Ru, or Os). As 18-electron diamagnetic neutral complexes these species might be expected to have an interesting derivative chemistry, including substitution reactions involving loss of the neutral arene ligand.

Given the very obvious nature of these considerations, together with well established routes into arene transition-metal chemistry[5] it is somewhat surprising that the first example of an [Fe(carbaborane)(η^6-arene)] was not communicated until 1981.[6] Herein we give full details of the species we have prepared. Since our preliminary communication others have described iron and ruthenium compounds of this class.[7–9]

Results and Discussion

The paramagnetic iron(I) complex [Fe(cod)(η^5-C_5H_5)] (cod = cyclo-octa-1,5-diene) reacts with the carbaborane *closo*-2,3-Me_2-2,3-$C_2B_9H_9$ in pentane to form *closo*-[1-(η^5-C_5H_5)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$], a type of molecule previously well characterised by Hawthorne and co-workers.[2] However, when the same reaction was carried out in an aromatic solvent (benzene, toluene, or *o*-xylene), or in pentane in the presence of an excess of naphthalene, the complexes [1-(η^6-R)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] [R = C_6H_6 (**1**), C_6H_5Me (**2**), $C_6H_4Me_2$-1,3 (**3**), or $C_{10}H_8$ (**4**)] were formed in moderate yields. Compound (**2**) may also be obtained from the reaction between [Fe_2(μ-η-C_6Me_6)(η^5-C_5H_5)$_2$][10] and the carbaborane in toluene. A coproduct in all the above syntheses is ferrocene, formed in about the same yields as those of the derived products (20—40%), but easily separated by column chromatography.

The polyhedral expansion reactions which afford (**1**)—(**4**) provide an easy route to these species. Todd and co-workers[7] have obtained the related compounds [3-(η^6-R)-3,1,2-$FeC_2B_9H_{11}$] [R = $C_6H_3Me_3$-1,3,5 (**5**) or C_6Me_6 (**6**)] from the reactions between [Fe(η^6-R)$_2$][PF_6]$_2$ and Tl[$TlC_2B_9H_{11}$] but in low yield [(**5**) 9%, (**6**) 3%], and, moreover, the benzene and toluene analogues of (**5**) and (**6**) could not be obtained by this method. More successfully, the ruthenium compound [3-(η^6-C_6H_6)-3,1,2-$RuC_2B_9H_{11}$] (**7**) was prepared (32%) by treating [$RuCl_2$(η^6-C_6H_6)]$_2$ with Tl[$TlC_2B_9H_{11}$].[11] Compound (**7**) was independently obtained by the same route[12] using an

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‡ 2,4-Dimethyl-1-(η^6-toluene)-2,4-dicarba-1-ferra-*closo*-dodecaborane and 3-(η^6-benzene)-1,2-dicarba-1-ruthena-*closo*-dodecaborane respectively.

Supplementary data available (No. SUP 56318, 6 pp.): thermal parameters, packing diagrams. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: bar = 10^5 Pa.

improved synthesis (*ca.* 75% yield) of the thallium reagent (see Experimental section).

Two other methods for obtaining (η^6-arene)carbaferraboranes have recently been described. The compound [1-(η^6-C_6H_5Me)-2,3-Et_2-1,2,3-$FeC_2B_4H_4$] has been obtained in *ca.* 1—2% yield *via* the reaction between thermally generated iron atoms, toluene, and *nido*-2,3-Et_2-2,3-$C_2B_4H_6$, a process which affords traces of five other (η^6-toluene)carbaferraboranes involving FeC_2B_3, FeC_2B_6, FeC_2B_7, FeC_4B_8, and FeC_4B_7 cage structures.[8] Grimes and co-workers[9] have prepared the complexes [1-(η^6-R)-2,3-Et_2-1,2,3-$FeC_2B_4H_4$] [R = C_6H_6 (**8**), $C_6H_3Me_3$-1,3,5 (**9**), or C_6Me_6 (**10**)] in yields of *ca.* 15—30% by ligand replacement of the naphthalene group in the compound *closo*-[1-(η^6-C_8H_{10})-2,3-Et_2-1,2,3-$FeC_2B_4H_4$][13] under $AlCl_3$-catalysed reflux in the appropriate arene solvent.

With regard to the mechanism of formation of the compounds (**1**)—(**4**) it is interesting that (**2**) can also be prepared from the reaction between [Fe(η-C_4H_6)(η^6-C_5H_5Me)] and 2,3-Me_2-2,3-$C_2B_9H_9$ implying that (**1**)—(**4**) are produced by an oxidative-insertion of an Fe^0 species into the *closo*-carbaborane, in a manner analogous to our previous syntheses of carbametallaboranes by direct insertion.[14] This might suggest that [Fe(cod)(η^5-C_5H_5)] undergoes a disproportionation reaction in an arene solvent to form [Fe(cod)(η^6-R)] and [Fe(η^5-C_5H_5)$_2$]. However, careful experimentation showed that in the absence of the carbaborane this disproportionation did not occur suggesting a complex reaction sequence for the formation of (**1**)—(**4**), which remains to be defined.

Some reactions of the new compounds were studied. Compounds (**1**)—(**3**) were recovered intact after treatment with excess of CO (100 bar, 50 °C) in tetrahydrofuran (thf). In contrast, the naphthalene ligand of (**4**) was displaced under similar conditions giving [1,1,1-$(CO)_3$-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] (**11**). Reaction of (**4**) with $P(OMe)_3$ in thf at room temperature afforded [1,1,1-$\{(MeO)_3P\}_3$-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] (**12**). The lability of the co-ordinated naphthalene ligand could derive from an ability to undergo 'slippage' from an η^6 to an η^4 bonding mode, like the η^5 to η^3 transformation which enhances the reactivity of certain indenylmetal complexes *versus* their cyclopentadienyl analogues.[15,16] Thus if in (**4**) the naphthalene ligand becomes η^4 bonded, the iron atom becomes co-ordinatively unsaturated and would be readily attacked by CO or $P(OMe)_3$. Moreover, such strongly π-accepting groups might further weaken the remaining naphthalene–iron bonding leading to displacement of the hydrocarbon.

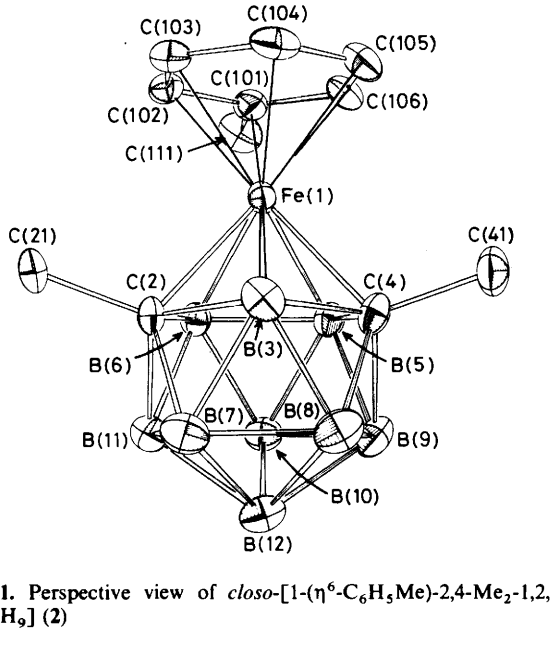

Figure 1. Perspective view of *closo*-[1-(η^6-C_6H_5Me)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] (**2**)

Compound (**7**) in thf solution did not react with CO (10 bar, 40 °C or 1 bar and u.v. irradiation), $P(OMe)_3$, or $Ph_2PCH_2CH_2PPh_2$. It was possible, however, to prepare [3,3,3-$(CO)_3$-3,1,2-$RuC_2B_9H_{11}$] (**13**) by treating [$RuCl_2(CO)_3$(thf)] with Tl[$TlC_2B_9H_{11}$] in thf as solvent.

As a complement to our synthetic studies we have also determined the molecular structures of (**2**) and (**7**) by *X*-ray diffraction. Views of single molecules are given in Figures 1 and 2 respectively, and Tables 1 and 2 list pertinent molecular parameters.

As expected the cluster geometries are essentially icosahedral with the greatest sources of irregularity (such as they are) involving the heteroatoms. In (**2**) the carbon atoms are slightly contracted into the polyhedron, resulting in longer Fe–C than Fe–B connectivities, a phenomenon that is well known[17] and well understood.[18] In (**7**) the metalla-bonded face is also slightly distorted, and in the expected way,[18] but this does not lead to longer bonds from metal to polyhedral carbon than to boron.

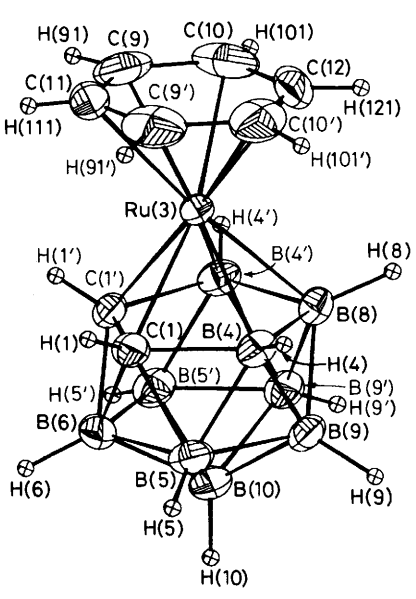

Figure 2. Perspective view of *closo*-[3-(η^6-C_6H_6)-3,1,2-$RuC_2B_9H_{11}$] (**7**)

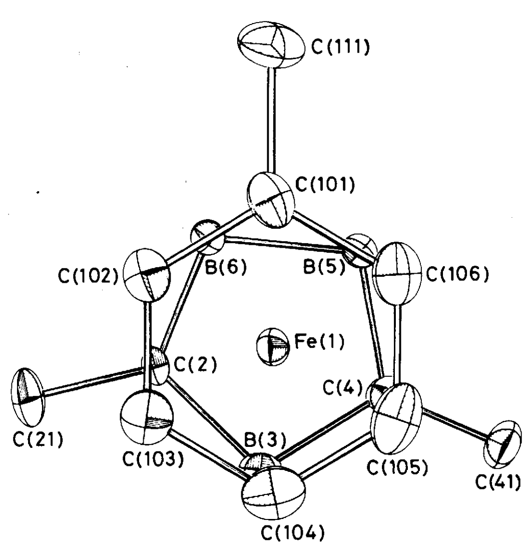

Figure 3. The metalla-bonded carbaborane and arene faces of (**2**)

Table 1. Internuclear distances (Å) and interbond angles (°) in *closo*-[1-(η^6-C_6H_5Me)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] (**2**)*

Fe(1)–C(2)	2.100(5)	Fe(1)–B(5)	2.088(12)	C(2)–B(3)	1.737(9)	B(6)–B(11)	1.758(12)
Fe(1)–B(3)	2.069(7)	Fe(1)–B(6)	2.075(7)	C(2)–B(6)	1.674(10)	B(7)–B(8)	1.779(12)
Fe(1)–C(4)	2.103(7)			C(2)–B(7)	1.700(11)	B(7)–B(11)	1.791(13)
				C(2)–B(11)	1.694(14)	B(7)–B(12)	1.781(13)
Fe(1)–C(101)	2.132(6)	Fe(1)–C(104)	2.122(8)	B(3)–C(4)	1.708(11)		
Fe(1)–C(102)	2.111(7)	Fe(1)–C(105)	2.105(7)	B(3)–B(7)	1.800(10)	B(8)–B(9)	1.751(12)
Fe(1)–C(103)	2.125(10)	Fe(1)–C(106)	2.103(5)	B(3)–B(8)	1.754(13)	B(8)–B(12)	1.808(12)
				C(4)–B(5)	1.725(11)	B(9)–B(10)	1.782(11)
C(101)–C(102)	1.405(9)	C(104)–C(105)	1.391(13)	C(4)–B(8)	1.684(10)	B(9)–B(12)	1.764(12)
C(101)–C(106)	1.419(10)	C(105)–C(106)	1.402(12)	C(4)–B(9)	1.728(11)	B(10)–B(11)	1.787(14)
C(102)–C(103)	1.385(14)	C(101)–C(111)	1.478(10)	B(5)–B(6)	1.790(12)	B(10)–B(12)	1.821(12)
C(103)–C(104)	1.420(12)			B(5)–B(9)	1.807(14)	B(11)–B(12)	1.809(13)
				B(5)–B(10)	1.777(11)	C(2)–C(21)	1.555(12)
				B(6)–B(10)	1.792(11)	C(4)–C(41)	1.532(8)

(*a*) Polyhedral angles

C(2)–Fe(1)–B(3)	49.2(2)	Fe(1)–C(4)–B(3)	64.8(3)	C(2)–B(7)–B(3)	59.4(4)	B(5)–B(10)–B(6)	60.2(5)
C(2)–Fe(1)–B(6)	47.3(3)	Fe(1)–C(4)–B(5)	65.3(5)	C(2)–B(7)–B(11)	58.0(5)	B(5)–B(10)–B(9)	61.0(5)
B(3)–Fe(1)–C(4)	48.3(3)	B(3)–C(4)–B(8)	62.3(5)	B(3)–B(7)–B(8)	58.7(5)	B(6)–B(10)–B(11)	58.8(5)
C(4)–Fe(1)–B(5)	48.6(3)	B(5)–C(4)–B(9)	63.1(5)	B(8)–B(7)–B(12)	61.0(5)	B(9)–B(10)–B(12)	58.6(5)
B(5)–Fe(1)–B(6)	50.9(3)	B(8)–C(4)–B(9)	61.7(5)	B(11)–B(7)–B(12)	60.8(5)	B(11)–B(10)–B(12)	60.2(5)
Fe(1)–C(2)–B(3)	64.5(3)	Fe(1)–B(5)–C(4)	66.1(5)	B(3)–B(8)–C(4)	59.6(4)	C(2)–B(11)–B(6)	58.0(4)
Fe(1)–C(2)–B(6)	65.6(3)	Fe(1)–B(5)–B(6)	64.1(5)	B(3)–B(8)–B(7)	61.3(4)	C(2)–B(11)–B(7)	58.3(5)
B(3)–C(2)–B(7)	63.2(4)	C(4)–B(5)–B(9)	58.5(5)	C(4)–B(8)–B(9)	60.4(5)	B(6)–B(11)–B(10)	60.7(5)
B(6)–C(2)–B(11)	62.9(5)	B(6)–B(5)–B(10)	60.3(4)	B(7)–B(8)–B(12)	59.7(5)	B(7)–B(11)–B(12)	59.4(5)
B(7)–C(2)–B(11)	63.7(5)	B(9)–B(5)–B(10)	59.6(5)	B(9)–B(8)–B(12)	59.4(5)	B(10)–B(11)–B(12)	60.9(5)
Fe(1)–B(3)–C(2)	66.3(3)	Fe(1)–B(6)–C(2)	67.1(3)	C(4)–B(9)–B(5)	58.4(5)	B(7)–B(12)–B(8)	59.4(5)
Fe(1)–B(3)–C(4)	66.9(3)	Fe(1)–B(6)–B(5)	64.9(4)	C(4)–B(9)–B(8)	57.9(5)	B(7)–B(12)–B(11)	59.8(5)
C(2)–B(3)–B(7)	57.4(4)	C(2)–B(6)–B(11)	59.1(5)	B(5)–B(9)–B(10)	59.4(4)	B(8)–B(12)–B(9)	58.7(5)
C(4)–B(3)–B(8)	58.2(5)	B(5)–B(6)–B(11)	59.5(5)	B(8)–B(9)–B(12)	61.9(5)	B(9)–B(12)–B(10)	59.6(4)
B(7)–B(3)–B(8)	60.0(5)	B(10)–B(6)–B(11)	60.4(5)	B(10)–B(9)–B(12)	61.8(5)	B(10)–B(12)–B(11)	59.0(5)

(*b*) Exopolyhedral angles

C(21)–C(2)–Fe(1)	113.9(6)	C(21)–C(2)–B(7)	111.5(6)	C(41)–C(4)–Fe(1)	115.7(5)	C(41)–C(4)–B(8)	113.0(6)
C(21)–C(2)–B(3)	119.4(7)	C(21)–C(2)–B(11)	113.3(4)	C(41)–C(4)–B(3)	122.7(6)	C(41)–C(4)–B(9)	112.3(6)
C(21)–C(2)–B(6)	122.3(6)			C(41)–C(4)–B(5)	120.6(6)		

(*c*) Toluene co-ordination angles

(*d*) Toluene ligand angles

(*c*)				(*d*)			
C(101)–Fe(1)–C(102)	38.7(2)	C(103)–Fe(1)–C(104)	39.1(3)	C(102)–C(101)–C(106)	117.7(4)	C(104)–C(105)–C(106)	121.2(7)
C(101)–Fe(1)–C(106)	39.1(3)	C(104)–Fe(1)–C(105)	38.4(4)	C(101)–C(102)–C(103)	121.5(7)	C(101)–C(106)–C(105)	120.6(8)
C(102)–Fe(1)–C(103)	38.2(4)	C(105)–Fe(1)–C(106)	38.9(3)	C(102)–C(103)–C(104)	120.6(9)	C(102)–C(101)–C(111)	121.4(6)
				C(103)–C(104)–C(105)	118.3(8)	C(106)–C(101)–C(111)	120.8(7)

* Estimated standard deviations are given in parentheses throughout this Table and Tables 2—4.

Table 2. Internuclear distances (Å) and selected interbond angles (°) in *closo*-[3-(η^6-C_6H_6)-3,1,2-$RuC_2B_9H_{11}$] (**7**)*

Ru(3)–C(1)	2.167(2)	Ru(3)–C(11)	2.247(3)	B(4)–B(5)	1.799(3)	B(4)–H(4)	1.10(4)
Ru(3)–B(4)	2.205(2)	Ru(3)–C(9)	2.226(2)	B(4)–B(9)	1.786(3)	B(8)–H(8)	1.160(24)
Ru(3)–B(8)	2.230(3)	Ru(3)–C(10)	2.196(2)	B(8)–B(9)	1.803(4)	B(6)–H(6)	1.111(24)
C(1)–C(1′)	1.626(4)	Ru(3)–C(12)	2.190(3)	B(6)–B(5)	1.755(3)	B(5)–H(5)	1.06(4)
C(1)–B(4)	1.727(3)	C(11)–C(9)	1.378(4)	B(5)–B(9)	1.770(3)	B(9)–H(9)	1.13(4)
B(4)–B(8)	1.808(3)	C(9)–C(10)	1.409(4)	B(9)–B(9′)	1.773(5)	B(10)–H(10)	1.099(24)
C(1)–B(6)	1.723(3)	C(10)–C(12)	1.409(4)	B(6)–B(10)	1.758(4)	C(11)–H(11)	0.86(5)
C(1)–B(5)	1.690(3)	C(1)–H(1)	0.92(3)	B(5)–B(10)	1.769(3)	C(9)–H(91)	1.00(4)
				B(9)–B(10)	1.774(4)	C(10)–H(101)	0.92(4)
						C(12)–H(121)	0.94(5)

(*a*) Polyhedral angles

C(1)–Ru(3)–C(1′)	44.07(11)	B(9)–B(8)–B(9′)	58.91(18)	B(8)–B(4)–B(9)	60.22(14)	B(4)–B(9)–B(5)	60.78(13)
C(1)–Ru(3)–B(4)	46.52(8)	C(1)–B(6)–B(1′)	56.29(16)	C(1)–B(4)–B(5)	57.26(12)	B(8)–B(9)–B(9′)	60.54(9)
B(4)–Ru(3)–B(8)	48.12(7)	C(1)–B(5)–B(4)	59.22(12)	B(4)–C(1)–B(5)	63.52(13)	B(10)–B(6)–B(5)	60.47(12)
B(6)–B(10)–B(5)	59.67(12)	B(4)–B(9)–B(8)	60.50(12)	C(1′)–C(1)–B(6)	61.85(8)	B(10)–B(5)–B(6)	59.86(15)
B(5)–B(10)–B(9)	59.95(13)	C(1)–B(6)–B(5)	58.15(12)	B(6)–C(1)–B(5)	61.86(13)	B(10)–B(5)–B(9)	60.16(15)
B(9)–B(10)–B(9′)	59.98(19)	C(1)–B(5)–B(6)	59.99(15)	B(5)–B(4)–B(9)	59.17(12)	B(10)–B(9)–B(5)	59.89(13)
B(4)–B(8)–B(9)	59.28(12)	B(4)–B(5)–B(9)	60.05(12)			B(10)–B(9)–B(9′)	60.01(10)

(*b*) Benzene co-ordination angles

(*c*) Benzene ligand angles

(*b*)				(*c*)			
C(9)–Ru(3)–C(10)	37.15(11)	C(9)–Ru(3)–C(11)	35.88(9)	C(11)–C(9)–C(10)	120.18(29)	C(10)–C(12)–C(10′)	119.22(33)
		C(10)–Ru(3)–C(12)	37.47(10)	C(9)–C(10)–C(12)	119.73(28)	C(9)–C(11)–C(9′)	120.95(34)

* Primed atoms are generated by reflection in the crystallographic mirror plane at $z = 0.25$.

The Fe–C(arene) distances in **(2)** are slightly, but consistently, longer than those in the smaller cage complexes $[1\text{-}(\eta^6\text{-}C_6H_5Me)\text{-}2,3\text{-}Et_2\text{-}1,2,3\text{-}FeC_2B_4H_4]$,[8] and **(8)**—**(10)**.[9] Moreover, in passing from **(2)** to **(7)**, involving a similar polyhedron, but with iron replaced by ruthenium, there is the expected further expansion of internuclear separations by about the same amount. Individual Ru–C(arene) distances in **(7)** are rather more well spread than is usually observed, but this is systematic: Ru–C(11) > Ru–C(9) > Ru–C(10) ~ Ru–C(12). The possibility that this slight slipping of the benzene ring may be steric in origin, due to intramolecular congestion between H(121) and H(8), atoms that are eclipsed in the observed conformation, is unlikely since the H(121) ··· H(8) contact distance in **(7)** is 2.77 Å. Rather we believe that the unequal Ru–C(arene) distances reflect the differing *trans* influences of cage boron and cage carbon atoms. A similar asymmetry has been previously observed in M–P distances in bis(phosphine)carbametallaboranes.[19]

In **(2)** the relative conformation of metalla-bonded carbaborane and arene faces is clearly seen (Figure 3) to be such that interannular contacts between methyl groups are minimised. There are no significant intermolecular contacts in either crystal structure.

Experimental

N.m.r. spectra were recorded on JEOL PS100, FX 90 Q, and FX 200 spectrometers. Chemical shifts are relative to $SiMe_4$ (^1H), 85% H_3PO_4 (external) (^{31}P), and $BF_3\cdot OEt_2$ (external) (^{11}B), with positive values representing shifts to high frequency. I.r. spectra were measured as Nujol mulls on either a Perkin-Elmer 457 or Pye Unicam SP2000 spectrophotometer. Molecular weights were determined from parent ions in the mass spectra using an AE1902 MS902 mass spectrometer. Melting points were measured in sealed, evacuated tubes. All experiments were carried out under dry, oxygen-free nitrogen using standard Schlenk-tube techniques, and all solvents were dried and distilled under nitrogen and degassed immediately prior to use. Light petroleum refers to that fraction of b.p. 40—60 °C. The precursors $[Fe(cod)(\eta^5\text{-}C_5H_5)]$,[20] $[Fe(\eta\text{-}C_4H_6)(\eta^6\text{-}C_6H_5Me)]$,[21] $[Fe_2(\mu\text{-}\eta\text{-}C_6Me_6)(\eta^5\text{-}C_5H_5)_2]$,[10] $[RuCl_2(CO)_3(thf)]$,[22] $1,2\text{-}C_2B_{10}H_{12}$,[23] and $2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9$[24] were prepared by literature methods.

Reactions between $[Fe(cod)(\eta^5\text{-}C_5H_5)]$ *and* $2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9$.—(a) *In pentane.* To a pentane (10 cm^3) solution of $[Fe(cod)(\eta^5\text{-}C_5H_5)]$ (0.299 g, 1 mmol) was added solid $2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9$ (0.16 g, 1 mmol). After stirring for 2 d at room temperature the solution was concentrated under vacuum and chromatographed on an alumina column, using pentane as stationary phase. An orange band was eluted with methanol. Concentration and cooling afforded an orange solid, identified as *closo*-$[1\text{-}(\eta^5\text{-}C_5H_5)\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}FeC_2B_9H_9]$ from its mass spectrum (parent ion at *m/e* 283) and from a resonance in the ^1H n.m.r. at 4.2 p.p.m. (C_5H_5). The ^{11}B n.m.r. spectrum did not yield useful information because of paramagnetic broadening.

(b) *In toluene.* Solid $2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9$ (0.16 g, 1 mmol) was added to a toluene (15 cm^3) solution of $[Fe(cod)(\eta^5\text{-}C_5H_5)]$ (0.23 g, 1 mmol). After stirring for 24 h the solvent was removed under vacuum and the residue dissolved in the minimum volume of thf and chromatographed on an alumina column. Elution with light petroleum afforded a yellow band, subsequently identified as $[Fe(\eta^5\text{-}C_5H_5)_2]$, in *ca.* 40% yield. Elution with Et_2O yielded a red band, and final elution with thf afforded a trace quantity of a purple product which was not subsequently identified. Concentration and cooling (−20 °C) of the red band afforded red *crystals* of *closo*-$[1\text{-}(\eta^6\text{-}C_6H_5Me)\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}FeC_2B_9H_9]$ **(2)** (0.11 g, 35%) (Found: C, 40.9; H, 7.5%; *M*, 308. $C_{11}H_{23}B_9Fe$ requires C, 42.8; H, 7.5%; *M*, 308); m.p. 198 °C; $\nu_{max.}$(BH) at 2 547s, 2 527s, and 2 504s cm^{-1}. N.m.r. spectra ($C_6D_5CD_3$, room temperature): ^1H, δ 1.27 [s, 6 H, $(CH_3)_2C_2B_9H_9$], 2.20 (s, 3 H, CH_3–C_6H_5), 4.69 (m, 4 H, *ortho*- and *meta*-C_6H_5–CH_3), and 6.01 (t, 1 H, *para*-C_6H_5–CH_3); $^{13}C\text{-}\{^1H\}$, δ 20.7 (CH_3–C_6H_5), 34.6 [$(CH_3)_2C_2B_9H_9$], 92.6, 93.4, 93.6, and 106.4 (C_6H_5–CH_3), and 115.7 p.p.m. [$(CH_3)_2C_2B_9H_9$]; $^{11}B\text{-}\{^1H\}$, δ −1.1 (1 B), −4.1 (2 B), −7.4 (1 B), −12.9 (2 B), −15.2 (1 B), and −16.33 p.p.m. (2 B).

(c) *In benzene.* In an analogous reaction to that described above, 1 mmol of each of the reagents were mixed in benzene. After removal of ferrocene from the chromatography column with pentane, elution of the column with Et_2O and concentration and cooling (−20 °C) yielded red *crystals* of *closo*-$[1\text{-}(\eta^6\text{-}C_6H_6)\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}FeC_2B_9H_9]$ **(1)** (0.06 g, 20%) (Found: C, 41.3; H, 7.9%; *M*, 294. $C_{10}H_{21}B_9Fe$ requires C, 40.8; H, 7.2%; *M*, 294); m.p. 220 °C (with decomp.); $\nu_{max.}$(BH) at 2 578s, 2 530s, 2 520s, and 2 500s cm^{-1}. N.m.r. ($CDCl_3$, room temperature): ^1H, δ 6.2 (s, 6 H, C_6H_6) and 1.5 (s, 6 H, cage CH_3); $^{11}B\text{-}\{^1H\}$, δ −1.09 (1 B), −4.53 (2 B), −7.73 (1 B), −13.22 (2 B), and −16.39 p.p.m. (3 B).

(d) *In* o-*xylene.* Repetition of the above reaction using *o*-xylene as reaction solvent yielded, on work-up, red *crystals* of *closo*-$[1\text{-}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}FeC_2B_9H_9]$ **(3)** (0.12 g, 38%) (Found: C, 46.5; H, 8.9%; *M*, 323. $C_{12}H_{25}B_9Fe$ requires C, 44.7; H, 7.8%; *M*, 323); m.p. 185 °C; $\nu_{max.}$(BH) at 2 540s br and 2 510 (sh) cm^{-1}. N.m.r. spectra ($CDCl_3$, room temperature): ^1H, δ 6.42 (m, 2 H, C_6H_4), 5.02 (m, 2 H, C_6H_4), 2.6 [s, 6 H, $(CH_3)_2C_6H_4$], 1.45 (s, 6 H, cage CH_3); $^{11}B\text{-}\{^1H\}$, δ −2.66 (3 B), −8.49 (1 B), −13.14 (2 B), and −16.27 p.p.m. (3 B).

(e) *In pentane in the presence of naphthalene.* Excess solid naphthalene was added to a stirred solution of $[Fe(cod)(\eta^5\text{-}C_5H_5)]$ (0.29 g, 1.28 mmol) in pentane (10 cm^3). After further stirring for 15 min, 0.21 g (1.29 mmol) of the carbaborane in pentane (10 cm^3) was added. After stirring for a further 8 h the solution had turned dark brown with deposition of a small amount of unidentified black solid. The product was eluted with pentane from an alumina column, producing red and yellow bands that could not be separated. However, removal of solvent under vacuum and vacuum sublimation at 35 °C using a cold finger at −78 °C allowed unreacted naphthalene and (the yellow) ferrocene to be collected. Dissolution of the residual solid in thf and cooling (−20 °C) afforded red *crystals* of *closo*-$[1\text{-}(\eta^6\text{-}C_{10}H_8)\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}FeC_2B_9H_9]$ **(4)** (0.12 g, 27%) (Found: C, 48.6; H, 7.0%; *M*, 345. $C_{14}H_{23}B_9Fe$ requires C, 48.8; H, 6.7%; *M*, 345); m.p. 130 °C (decomp.); $\nu_{max.}$(BH) at 2 563 (sh), 2 530s, and 2 505 (sh) cm^{-1}. N.m.r. spectra ($CDCl_3$, room temperature): ^1H, δ 7.35 (m, 4 H, H^{5-8} of $C_{10}H_8$), 6.89 (m, 2 H, H^1 and H^4), 6.01 (m, 2 H, H^2 and H^3), and 1.61 (s, 6 H, cage CH, cage CH_3); $^{11}B\text{-}\{^1H\}$, δ −2.12 (1 B), −3.61 (2 B), −6.01 (1 B), −13.94 (2 B), and −16.88 p.p.m. (3 B).

Reaction between $[Fe(\eta\text{-}C_4H_6)(\eta^6\text{-}C_6H_5Me)]$ *and* $2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9$.—$[Fe(\eta\text{-}C_4H_6)(\eta^6\text{-}C_6H_5Me)]$ (0.20 g, 1 mmol) was dissolved in pentane (15 cm^3) and the solution cooled to 0 °C. Solid carbaborane (0.16 g, 1 mmol) was added and the solution allowed to warm to room temperature with stirring. Further stirring for 14 h afforded a red solution and a little black deposited solid. The product was filtered and the filtrate purified by column chromatography (alumina with pentane) using Et_2O as eluant. Reduction of solvent a cooling (−20 °C) afforded *crystals* of **(2)** in essentially quantitative yield.

Reaction between $[Fe_2(\mu\text{-}\eta\text{-}C_6Me_6)(\eta^5\text{-}C_5H_5)_2]$ *and* $2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9$ *in Toluene.*—The compound $[Fe_2(\mu\text{-}\eta\text{-}C_6Me_6)(\eta^5\text{-}C_5H_5)_2]$ (0.18 g, 0.44 mmol) was dissolved in toluene (15 cm^3) and the solid carbaborane (0.071 g, 0.44 mmol) added to the stirred solution. The purple mixture gradually gave way to a red colouration. After stirring for a further 48 h the volume of solvent was reduced and the product chromatographed on an alumina column charged with pentane. Elution with the same solvent afforded ferrocene. A second eluate obtained using Et_2O yielded a red solution from which was obtained *crystals* of (**2**) (*ca.* 30%).

Improved Synthesis of $Tl[3,1,2\text{-}TlC_2B_9H_{11}]$.—A mixture of $1,2\text{-}C_2B_{10}H_{12}$ (0.56 g, 3.9 mmol) and a five-fold excess of solid KOH (1.2 g) was stirred in ethanol (25 cm^3) at room temperature for 1 h, then refluxed under nitrogen for 4 h. After cooling and filtering the filtrate was evaporated to dryness. The product was dissolved in water (60 cm^3) and to it was added dropwise an aqueous solution of 0.95 mol equiv. (1.3 g) of thallium(I) acetate. The resulting yellow-green precipitate was filtered off, washed with ethanol and a little Et_2O, and dried under vacuum (1.57 g, 73%). It was identified as $Tl[3,1,2\text{-}TlC_2B_9H_{11}]$ by comparison (i.r.) with an authentic sample. The thallium reagent was used to synthesise *closo*-$[3\text{-}(\eta^6\text{-}C_6H_6)\text{-}3,1,2\text{-}RuC_2B_9H_{11}]$ (**7**), according to the method of ref. 7.

Ligand Displacement Reactions involving Compound (**4**).—(a) *Carbon monoxide.* A 100-cm^3 autoclave was charged with (**4**) (0.06 g, 0.17 mmol) in thf (10 cm^3) and pressurised to 100 bar with CO. After heating to 50 °C for 12 h a yellow solution was obtained. Removal of volatile solvents gave a yellow, non-chromatographable *oil*, *closo*-$[1,1,1\text{-}(CO)_3\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}FeC_2B_9H_9]$ (**11**) (Found: *M*, 300. $C_7H_{15}B_9FeO_3$ requires *M*, 300); $\nu_{max.}$(BH) at 2 573m cm^{-1}; $\nu_{max.}$(CO) at 2 095s and 2 045s cm^{-1}.

(b) *Trimethyl phosphite.* To a stirred solution of (**4**) (0.05 g, 0.15 mmol) in thf (10 cm^3) was added an excess of $P(OMe)_3$ and the solution stirred at room temperature for 48 h. During this time a yellow colouration developed. Volatiles were removed under vacuum and the resultant yellow *oil* washed three times with light petroleum and dried by pumping *in vacuo*. The product was identified as *closo*-$[1,1,1\text{-}\{(MeO)_3P\}_3\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}FeC_2B_9H_9]$ (**12**), by its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum ($C_6D_5CD_3$, room temperature): δ 169.3 (1 P) and 165.1 p.p.m. (2 P).

Synthesis of closo-$[3,3,3\text{-}(CO)_3\text{-}3,1,2\text{-}RuC_2B_9H_{11}]$ (**13**).—To a stirred solution of $[RuCl_2(CO)_3(thf)]$ (0.45 g, 1.4 mmol) in thf (50 cm^3) was added solid $Tl[3,1,2\text{-}TlC_2B_9H_{11}]$ (0.75 g, 1.4 mmol), resulting in an orange colouration. After stirring for 3 h, solid TlCl (0.42 g, 65%) was filtered off and the solute obtained by removal of solvent. The required product was extracted by chloroform (30 cm^3) and recrystallised from chloroform–hexane to yield red *microcrystals* of *closo*-$[3,3,3\text{-}(CO)_3\text{-}3,1,2\text{-}RuC_2B_9H_{11}]$ (**13**) (0.05 g, 12%) (Found: C, 18.0; H, 3.1%; *M*, 318. $C_5H_{11}B_9O_3Ru$ requires C, 18.9; H, 3.5%; *M*, 318); m.p. 139—141 °C; $\nu_{max.}$ at 3 045w, 2 625m, 2 610m, 2 562s br, 2 540m, 2 521m, 2 142m, 2 120vs, 2 059vs, 2 026m, 1 116m, 1 000w, 751m br, 620w, 608w, 580w br, 558s, 510w, and 478s cm^{-1}.

Molecular Structure Determinations.—(a) *closo*-$[1\text{-}(\eta^6\text{-}C_6H_5Me)\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}FeC_2B_9H_9]$. Crystals were obtained from the second synthetic procedure above, and were glued inside a 0.5-mm Lindemann capillary under dry N_2. A full set of Weissenberg and precession photographs were recorded before data collection.

Crystal data. $C_{11}H_{23}B_9Fe$, $M = 308.4$, orthorhombic, $a = 21.793(4)$, $b = 8.6274(15)$, $c = 8.636(3)$ Å, $U = 1\,572.3$ Å^3 (by least-squares refinement on 25 automatically centred diffractometer angles, $12 < \theta < 15°$, $\lambda = 0.710\,69$ Å), space group $Pna2_1$ (C^9_{2v}, no. 33), $D_m = 1.32$—1.37 g cm^{-3}, $Z = 4$, $D_c = 1.311$ g cm^{-3}, $F(000) = 694$, $\mu(Mo\text{-}K_{\alpha}) = 8.9$ cm^{-1}. Burgundy irregular platelets.

Data collection and processing. CAD4 Diffractometer with cooling attachment (268 ± 1 K), $\omega/2\theta$ mode with ω scan width $0.8 + 0.35\tan\theta$, variable scan rate dependent upon initial prescan, with only those reflections with $I \geqslant 1.0\sigma(I)$ rescanned such that final net intensity had $I \geqslant 33\sigma(I)$ subject to maximum measuring time of 60 s. Graphite-monochromated Mo-K_{α} *X*-radiation. 2 109 Unique reflections measured excluding those systematically absent ($1.5 \leqslant \theta \leqslant 30.0°$, $+h + k + l$), yielding 1 676 with $F \geqslant 2.0\sigma(F)$. No crystal decay or movement. No absorption correction applied.

Structure analysis and refinement. Patterson synthesis (Fe atom) followed by iterative full-matrix least-squares refinement and ΔF syntheses, severely complicated in the early stages by pseudo-symmetry. Non-centrosymmetric space group confirmed by ultimately successful refinement although a centrosymmetric one was suggested by *E*-statistics. No hydrogen atoms were located. Anisotropic refinement, with the weighting scheme $w^{-1} = [\sigma^2(F) + 0.001\,15\,F_o^{\,2}]$, with $\sigma(F_o)$ from counting statistics, gave $R = 0.0499$, $R' = 0.0703$ after successful choice between enantiomeric pairs. No peak greater than 0.5 nor trough less than -0.4 e Å^{-3}. Table 3 lists derived atomic co-ordinates. Solution and refinement *via* SHELX 76[25] on the University of London Computer Centre CDC7600 machine using inlaid neutral scattering factors (B, C). For Fe, coefficients for an analytical approximation were taken from ref. 26. Molecular geometry calculations were *via* XANADU[27] and Figures were plotted using ORTEP-II.[28]

(b) *closo*-$[3\text{-}(\eta^6\text{-}C_6H_6)\text{-}3,1,2\text{-}RuC_2B_9H_{11}]$ (**7**). Diffraction quality crystals were obtained by vapour diffusion of OEt_2 into an acetone solution. Crystals were mounted on thin glass fibres and screened for quality and singularity by preliminary photographs.

Crystal data. $C_8H_{17}B_9Ru$, $M = 311.61$, orthorhombic, $a = 18.477(2)$, $b = 9.191(4)$, $c = 7.704(1)$ Å, $U = 1\,308.3$ Å^3 (by least-squares refinement on 25 automatically centred reflections, $22.5 < \theta < 26°$, $\lambda = 0.710\,69$ Å), space group *Pnam* (D^{16}_{2h}, no. 62), $D_m = 1.57(1)$ g cm^{-3}, $Z = 4$, $D_c = 1.58$ g cm^{-3}, $F(000) = 616$, $\mu(Mo\text{-}K_{\alpha}) = 11.6$ cm^{-1}. Yellow well formed plates.

Data collection and processing. As for (**2**) except 293 K, ω scan width $1.0 + 0.35\tan\theta$, 1 736 unique data yielding 1 723 with $F \geqslant 1.5\sigma(F)$.

Table 3. Fractional co-ordinates ($\times 10^5$, Fe; $\times 10^4$, C and B) in *closo*-$[1\text{-}(\eta^6\text{-}C_6H_5Me)\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}FeC_2B_9H_9]$ (**2**)

Atom	*x*	*y*	*z*
Fe(1)	39 612(3)	26 413(7)	75 000
C(2)	3 735(3)	280(5)	644(12)
B(3)	3 120(3)	1 556(7)	7 756(12)
C(4)	3 293(3)	2 764(7)	9 310(9)
B(5)	4 031(4)	2 446(9)	9 982(14)
B(6)	4 307(3)	826(7)	8 885(10)
B(7)	3 096(4)	−362(9)	8 602(12)
B(8)	2 816(4)	1 272(10)	9 675(12)
B(9)	3 372(4)	1 773(10)	11 095(11)
B(10)	4 029(4)	567(8)	10 854(10)
B(11)	3 851(4)	−796(11)	9 313(13)
B(12)	3 254(4)	−211(10)	10 689(11)
C(21)	3 851(5)	−634(10)	6 070(13)
C(41)	2 987(4)	4 384(8)	9 533(11)
C(101)	4 837(3)	3 652(7)	7 054(8)
C(102)	4 681(3)	2 627(7)	5 813(9)
C(103)	4 130(5)	2 753(9)	5 000(13)
C(104)	3 694(4)	3 901(8)	5 436(11)
C(105)	3 843(4)	4 923(8)	6 662(12)
C(106)	4 404(3)	4 808(6)	7 477(15)
C(111)	5 426(3)	3 516(8)	7 918(12)

Table 4. Fractional co-ordinates ($\times 10^5$) in *closo*-[3-(η^6-C_6H_6)-3,1,2-$RuC_2B_9H_{11}$] (7)

Atom	*x*	*y*	*z*
Ru(3)	59 938(1)	70 045(2)	25 000
B(4)	63 571(13)	53 521(23)	43 825(29)
C(1)	70 421(10)	64 258(19)	35 552(27)
B(5)	72 884(13)	47 821(23)	43 430(32)
B(6)	77 208(17)	54 919(35)	25 000
B(10)	74 305(18)	36 702(32)	25 000
B(9)	66 004(12)	35 742(22)	36 508(32)
B(8)	59 151(18)	45 834(32)	25 000
C(9)	56 671(16)	89 365(29)	9 438(41)
C(10)	51 084(15)	78 947(30)	9 226(44)
C(11)	59 331(18)	94 467(33)	25 000
C(12)	48 225(18)	73 729(40)	25 000
H(4)	61 224(196)	55 289(411)	56 867(562)
H(1)	71 664(209)	72 298(396)	41 947(558)
H(5)	75 989(199)	47 714(390)	55 053(527)
H(6)	82 935(146)	58 763(305)	25 000
H(10)	78 398(154)	27 978(296)	25 000
H(9)	64 486(192)	25 650(402)	44 132(637)
H(8)	53 297(146)	41 397(310)	25 000
H(91)	59 102(161)	92 810(365)	−1 385(487)
H(101)	49 643(196)	74 553(339)	− 880(489)
H(111)	62 805(265)	100 705(533)	25 000
H(121)	44 776(271)	66 247(513)	25 000

Structure analysis and refinement. Patterson synthesis (Ru atom) followed by least-squares refinement and ΔF syntheses for B and C atoms. Centrosymmetric space group confirmed by successful refinement. Cage carbon atoms identified by low isotropic thermal parameters after refinement as boron, and confirmed by short C(1)–C(1′) bond. Hydrogen atoms located and allowed independent positional refinement with an overall isotropic thermal parameter refined on a per ligand (carbaborane or benzene) basis. All non-H atoms refined anisotropically, yielding (full-matrix least-squares) $R = 0.0223$, $R' = 0.0270$. Weighting scheme $w^{-1} = \Sigma_{r=1}^{n} ArTr^*(X)$, where n is the number of coefficients, Ar, for a Chebyshev series, Tr^* is the polynomial function, and X is $|F_o|/|F_{o(\max.)}|$.[29] Coefficients used in this scheme were 79.65, 108.02, and 35.98. Derived atomic co-ordinates are in Table 4. Calculations were performed with CRYSTALS[30] on the University of Oxford ICL 2980 computer using scattering factors from ref. 26.

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