Formation of η^6-Arene-*closo*-carbaferraboranes by the Reaction of a *closo*-Carbaborane with Cyclo-octadiene(η-cyclopentadienyl)iron in the Presence of Arenes: Molecular Structure of [*closo*-1-(η^6-PhMe)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$]

By Maria P. Garcia, Michael Green, and F. Gordon A. Stone,
(*Department of Inorganic Chemistry, The University of Bristol, Bristol* BS8 1TS)
and Richard G. Somerville and Alan J. Welch
(*Department of Chemistry, The City University, London* EC1V 0HB)

Summary Reaction of 2,3-Me_2-2,3-$C_2B_9H_9$ with [Fe(1,5-C_8H_{12})(η-C_5H_5)] in benzene, toluene, *o*-xylene, or with an excess of naphthalene in light petroleum, affords the complexes [*closo*-1-(η^6-arene)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$], the identity of the toluene complex being established by *X*-ray crystallography; reaction of the η^6-naphthalene complex with the ligands L = CO or P(OMe)$_3$ affords [*closo*-1,1,1-L_3-2,4-Me_2-1,2,4-$FeC_2B_9H_9$].

We have previously reported the facile insertion of nucleophilic Ni, Pd, Pt, and Co species into *closo*-carbaborane cages,[1,2] and in extending these studies to the interesting paramagnetic complex [Fe(1,5-C_8H_{12})(η-C_5H_5)] [3] we have observed an unusual arene-ligand exchange reaction with potential value in synthesis.

Whereas treatment of 2,3-Me_2-2,3-$C_2B_9H_9$ with [Fe(1,5-C_8H_{12})(η-C_5H_5)] in light petroleum gave the complex [*closo*-1-(η-C_5H_5)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$], a structural analogue of the previously reported[4] $C_2B_9H_{11}^{2-}$ derivative, with toluene as solvent an unexpected reaction occurred to give ferrocene (45% yield), and a red crystalline complex (**1**) {35% yield, m.p. 198 °C, ν_{BH} (Nujol) 2 547s, 2 527s and 2 504s cm^{-1}; n.m.r.: ^{11}B,† δ −1·1, −4·1, −7·4, −12·9, −15·2, and −16·3 p.p.m.; ^{13}C, δ 20·7, 34·6, 92·6, 93·4, 93·5, 106·4, and 115·7 p.p.m.}. The n.m.r. data confirmed the presence of a *closo*-carbaborane fragment, and also indicated the possible presence of a co-ordinated toluene ligand. In order to establish the structure of (**1**) a single-crystal *X*-ray diffraction study was carried out.‡

Crystal data: (**1**), $C_{11}H_{23}B_9Fe$, $M = 310{\cdot}24$, orthorhombic, $a = 21{\cdot}793(4)$, $b = 8{\cdot}627\,4(15)$, $c = 8{\cdot}363(3)$ Å, $U = 1\,572{\cdot}3$ Å^3, $Z = 4$, $D_c = 1{\cdot}311$ g cm^{-3}, $F(000) = 640$, $\mu(\text{Mo-}K_{\bar{\alpha}}) = 8{\cdot}9$ cm^{-1}, space group $Pna2_1$ from systematic absences and successful refinement.

Of 2 109 absorption-corrected independent reflections measured to $\theta_{max} = 30{\cdot}0°$ (Mo-K_α *X*-radiation, $\bar{\lambda} = 0{\cdot}710\,69$ Å) on an Enraf–Nonius CAD4 diffractometer at *ca.* 268 K, 1 676 have $F \geqslant 2{\cdot}0\sigma(F)$ and were used to solve (Patterson and Fourier) and refine (full-matrix least-squares) the structure to a current *R* index of 0·050.

The molecular structure and important internuclear distances are given in the Figure. The aryl ring and metalla-bonded polyhedral face are very nearly parallel (dihedral angle 2·5°), and the iron atom bonds symmetrically to each. The relative orientation of the C_6 and C_2B_3 faces is such that inter-annular interactions between their methyl substituents are minimised, the vertical plane of the toluene ligand lying

---

† ^{11}B Shifts are to high frequency of $F_3B.OEt_2$, ^{1}H-decoupled. All n.m.r. spectra were recorded in $CD_3C_6D_5$ at room temperature.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

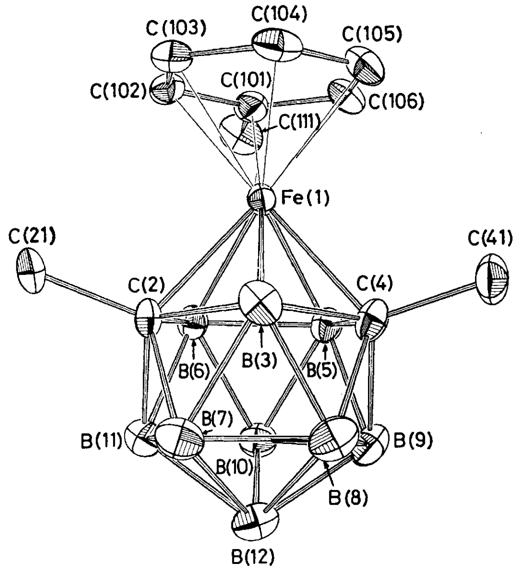

FIGURE. The molecular structure of [*closo*-1-(η^6-PhMe)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] (**1**); interatomic separations include Fe(1)–C(2) 2·100(5), Fe(1)–B(3) 2·069(7), Fe(1)–C(4) 2·103(7), Fe(1)–B(5) 2·088(12), Fe(1)–B(6) 2·075(7), Fe(1)–C(101) 2·132(6), Fe(1)–C(102) 2·111(7), Fe(1)–C(103) 2·125(10), Fe(1)–C(104) 2·122(8), Fe(1)–C(105) 2·105(7), Fe(1)–C(106) 2·103(5) Å.

only 6·4° off the effective mirror plane through the heteroborane cage.

Thus, an apparent disproportionation reaction has occurred resulting in the insertion of an Fe(η-PhMe) fragment into the *closo*-carbaborane 2,3-Me_2-2,3-$C_2B_9H_9$. It is interesting that (**1**) is also formed on reaction of η^4-buta-1,3-diene(toluene)iron[5] with 2,3-Me_2-2,3-$C_2B_9H_9$. However, we suspect that the formation of (**1**) from the carbaborane and [Fe(1,5-C_8H_{12})(η-C_5H_5)] in toluene does not involve an initial disproportionation to form ferrocene and η^4-cycloocta-1,5-diene(toluene)iron, but follows a more complex reaction sequence, which remains to be defined.

Similar reactions of [Fe(1,5-C_8H_{12})(η-C_5H_5)] with the carbaborane using benzene or *o*-xylene as solvent afforded the respective η^6-arene-*closo*-carbaferraboranes, and in light petroleum as solvent in the presence of an excess of naphthalene the η^6-bonded naphthalene complex [*closo*-1-(η^6-$C_{10}H_8$)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] (**2**) was formed in moderate yield. The use of naphthalene in stoicheiometric proportion gave only [*closo*-1-(η-C_5H_5)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$].

[*closo*-1-(η^6-PhMe)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$]
(**1**)

[*closo*-1-(η^6-$C_{10}H_8$)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$]
(**2**)

[*closo*-1,1,1-$(OC)_3$-2,4-Me_2-1,2,4-$FeC_2B_9H_9$]
(**3**)

[*closo*-1,1,1-{$(MeO)_3P$}$_3$-2,4-Me_2-1,2,4-$FeC_2B_9H_9$]
(**4**)

The η^6-bonded benzene, toluene, and *o*-xylene ligands are not labile; however, it is interesting that reaction (100 bar, 50 °C, 12 h) of (**2**) with carbon monoxide afforded [*closo*-1,1,1-$(OC)_3$-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] (**3**) [ν_{BH} (Nujol) 2 573m cm^{-1}, ν_{CO} (Nujol) 2 095s and 2 045s cm^{-1}]. Although complexes with tricarbonyliron fragments bonded to B_4H_8,[6] $C_2B_3H_7$,[7] $C_2B_4H_6$,[7] and $C_2B_5H_7$[8] cages have been previously reported, the formation of (**3**) is particularly interesting in view of its isoelectronic relationship with [$Mn(CO)_3$-(η-C_5H_5)]. Reaction (room temperature) of (**2**) with an excess of trimethylphosphite in tetrahydrofuran gave [*closo*-1,1,1-{$(MeO)_3P$}$_3$-2,4-Me_2-1,2,4-$FeC_2B_9H_9$] (**4**) [$^{31}P\{^1H\}$ n.m.r.: δ (rel. ext. H_3PO_4, positive values to high frequency) 169·29 (1 P) and 165·05 (2 P) p.p.m.].

It is suggested that the reactivity of (**2**) derives from the ability of the η^6-bonded naphthalene ligand to adopt a η^4-bonding mode thus allowing co-ordination of an incoming ligand at the metal centre. This is the first observation of such an effect[9] in carbametallaborane chemistry.

We thank Dr. M. B. Hursthouse for diffractometer facilities and the S.R.C. for support.

(*Received, 5th June* 1981; *Com.* 659.)

[1] M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1979, 1679; and references cited therein.

[2] G. K. Barker, M. Green, M. P. Garcia, F. G. A. Stone, J.-M. Bassett, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1980, 1266.

[3] K. Jonas, *Adv. Organomet. Chem.*, 1981, **19**, 97; K. Jonas and L. Schieferstein, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 549; L. Schieferstein, Dissertation, Ruhr-Universitat Bochum, 1978.

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

[5] D. L. Williams-Smith, L. R. Wolf, and P. S. Skell, *J. Am. Chem. Soc.*, 1972, **94**, 4042.

[6] N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison, and S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, 1974, 718.

[7] R. N. Grimes, *J. Am. Chem. Soc.*, 1971, **93**, 261.

[8] L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, 1973, **95**, 6623.

[9] P. Kündig and P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 1980, 991. The proposed $\eta^6 \rightarrow \eta^4$ slippage of naphthalene is related to the previously noted (P. Caddy, M. Green, E. O'Brien, L. E. Smart, and P. Woodward, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 647) $\eta^5 \rightarrow \eta^3$ slippage of indenyl metal complexes.

Printed by Heffers Printers Ltd Cambridge England