Reaction of Zero-valent Cobalt and Iron Species with Seven-atom Carbaboranes; Molecular Structures of [4-(Et₃P)-1,7-Me₂-μ₄,₈-{Co(H)-(PEt₃)₂-μ(H)-μ(PEt₂)}-1,4,7-CCoCB₅H₄] and [4,4,4-(BuᵗNC)₃-1,7-Me₂-1,4,7-CFeCB₅H₅]

Geoffrey K. Barker,ᵃ Maria P. Garcia,ᵃ Michael Green,ᵃ F. Gordon A. Stone,ᵃ
Hans E. Parge,ᵇ and Alan J. Welch ᵇ

ᵃ Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.
ᵇ Department of Chemistry, The University, Edinburgh EH9 3JJ, U.K.

Reaction of closo-2,4-Me₂-2,4-C₂B₅H₅ with [Co(PEt₃)₄] affords a novel dicobalthydrido-complex containing a phosphido-bridge, whereas [Fe(CNBuᵗ)₅] reacts to form a mononuclear 8-atom cage, in which the iron atom has a cluster connectivity of five.

In exploiting the direct insertion reaction[1] as a synthetic pathway to metallacarbaboranes, we have examined the reaction of the zero-valent cobalt species [Co(PEt₃)₄]² with closo-2,4-Me₂-2,4-C₂B₅H₅, and have observed an unusual reaction which affords a complex containing a bridged-phosphido-ligand and an exopolyhedral cobalt–cobalt bond. In contrast, the zero-valent iron complex [Fe(CNBuᵗ)₅]³ yields a closo-mononuclear cage.

4-(Et₃P)-1,7-Me₂-μ₄,₈-{Co(H)(PEt₃)₂-μ(H)-μ(PEt₂)}-1,4,7-
CCoCB₅H₄

(1)
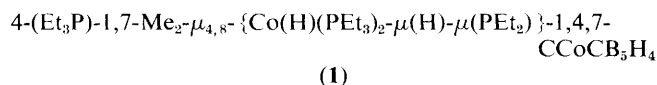
Reaction (2 h, room temperature) of [Co(PEt₃)₄] with an excess of closo-2,4-Me₂-2,4-C₂B₅H₅ in hexane affords dark brown crystals of (1) {70%, νmax(BH) 2 525s, 2 505s, and 2 495s cm⁻¹, νmax(CoH) 1 955m cm⁻¹ (Nujol). N.m.r.: ¹H ([²H₈]toluene), δ 2.36 (s, 3H, cage Me), 2.17 (s, 3H, cage Me), 1.76 [m, 4H, P(CH₂Me)₂], 1.53 [m, 18H, P(CH₂Me)₃], 1.25 [m, 6H, P(CH₂Me)₂], 0.98 [m, 27H, P(CH₂Me)₃], −9.0 (br. s, 1H, CoHB), and −17.5 [d of t, 1H, CoH, J(PH) 55 and 23 Hz]; ³¹P{¹H} ([²H₈]toluene, − 80 °C), δ 104.2 [d of t, Pᴮ, J(PᴮPᴰ) 110, J(PᴮPᶜ) 37, J(PᴮPᴬ) 39 Hz], 36.1 [d of d, Pᴰ, J(PᴰPᴮ) 110, J(PᴰPᶜ) 17 Hz], 29.2 (br. s, Pᶜ), and 25.2 p.p.m. [d, Pᴬ, J(PᴬPᴮ) 39 Hz]; ¹¹B{¹H} ([²H₈]toluene), δ 47.2 (1B), 12.9 (1B), −1.05 (2B), and −11.4 p.p.m. (1B) }. The presence in the n.m.r. spectra of signals assignable to two types of

metal hydride and four ³¹P environments suggested an unusual structure, and therefore a single crystal X-ray diffraction study was carried out.

Crystal data for (1):† C₂₆H₆₇Co₂B₅P₄, M 675.6, triclinic, a = 9.976(2), b = 10.306 8(18), c = 19.355(3) Å, α = 82.923(13), β = 101.363(14), γ = 109.040(15)°, U = 1840.6 Å³, Dc = 1.219 g cm⁻³, Z = 2, F(000) = 724 electrons, μ(Mo-Kα) = 11.23 cm⁻¹, space group P1̄ from E-statistics and successful refinement. Intensity data were collected (291 K) on an Enraf–Nonius CAD4 diffractometer, and the molecular structure solved (Patterson) and refined (full-matrix least squares) using 4 742 [F₀ ⩾ 2.0σ(F₀)] out of 7 136 data to θmax = 26° (Mo-Kα X-radiation, λ̄ = 0.710 69 Å). R is currently 0.046 8.

The structure (Figure 1) is based on a 1,4,7-CCoCB₅ closo-dodecahedron. However, the Co(4)–B(8) connectivity is bridged by a {Co(H)(PEt₃)₂} moiety, with the bridging links themselves bridged, Co(4)–Co(48) by a phosphido-function (PᴮEt₂) and B(8)–Co(48) by a hydride Hᴮ. The atom B(8) carries no terminal hydrogen, but co-ordination at Co(4) is completed by a single phosphine (PᴬEt₃).
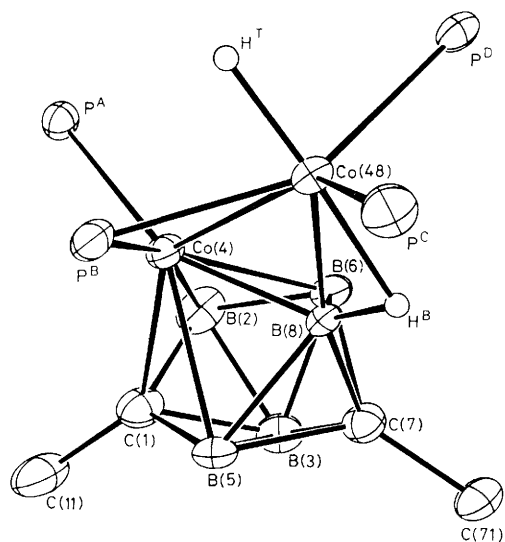
Figure 1. Molecular structure of 4-(Et₃P)-1,7-Me₂-μ₄,₈- {Co(H)-(PEt₃)₂-μ(H)-μ(PEt₂) }-1,4,7-CCoCB₅H₄, (1), with ethyl groups, and methyl and cage terminal H atoms, omitted for clarity. Important internuclear distances: Co(4)–C(1) 2.113(5), Co(4)–B(2) 2.087(6), Co(4)–B(6) 2.297(7), Co(4)–B(8) 1.935(5), Co(4)–B(5) 2.228(6), Co(4)–Pᴬ 2.229(2), Co(4)–Pᴮ 2.161(2), Co(4)–Co(48) 2.683(1), B(8)–Co(48) 2.084(5), B(8)–Hᴮ 1.22(3), Co(48)–Hᴮ 1.60(3), Co(48)–Hᵀ 1.40(3), Co(48)–Pᶜ 2.195(2), and Co(48)–Pᴰ 2.218 Å.
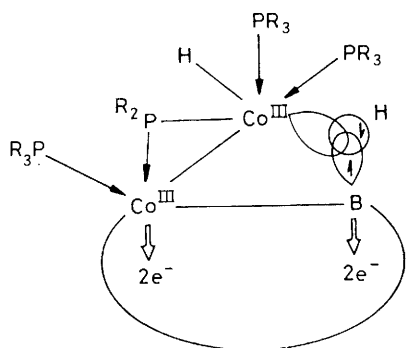

Figure 2. Schematic representation of the bonding in compound (1).

Such a system is without precedent in heteroborane chemistry. A feasible representation of the bonding in (1), which meets the electronic requirements of both a closo-polyhedron and eighteen electron shells for the metal atoms, is given schematically in Figure 2. We have previously synthesised 17-electron bis(triethylphosphine)carbacobaltaboranes and 18-electron hydridobis(triethylphosphine)carbacobaltaboranes from insertion of Co(PEt₃)₂ fragments into closo-carbaboranes,[1] but no analogous compounds were isolated in the reaction affording complex (1).

In contrast, reaction (24 h, 60 °C) of closo-2,4-Me₂-2,4-C₂B₅H₅ with the zero-valent iron complex [Fe(CNBuᵗ)₅] afforded the mononuclear species (2) as orange crystals [65%, νmax(BH) 2 509s, 2 505s cm⁻¹, νmax(NC) 2 035s, 2 022s, 2 015s cm⁻¹ (Nujol)].

4,4,4-(BuᵗNC)₃-1,7-Me₂-1,4,7-CFeCB₅H₅
(2)
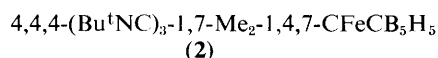
Crystal data for (2):† C₁₉H₃₈FeB₅N₃, M 418.2, monoclinic, space group P2₁/c, a = 16.585(2), b = 9.472(2), c = 19.270(2)
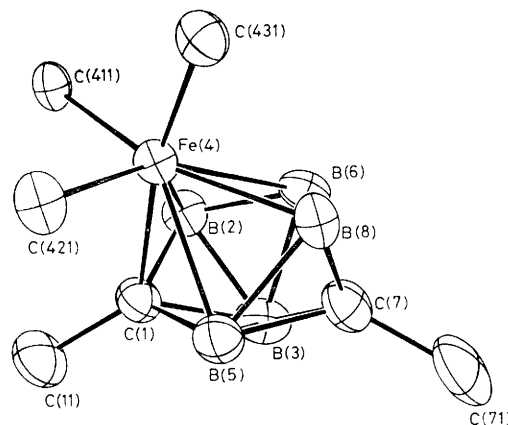

Figure 3. Molecular geometry of 4,4,4-(BuᵗNC)₃-1,7-Me₂-1,4,7-CFeCB₅H₅, (2), with H atoms and BuᵗN functions omitted for clarity. Important molecular parameters include Fe(4)–C(1) 2.065(8), Fe(4)–B(2) 2.117(9), Fe(4)–B(6) 2.282(10), Fe(4)–B(8) 2.017(11), Fe(4)–B(5) 2.197(11), Fe(4)–C(411) 1.855(9), Fe(4)–C(421) 1.829(9), Fe(4)–C(431) 1.781(9), C(411)–N(41) 1.131(10), C(421)–N(42) 1.136(11), and C(431)–N(43) 1.193(11) Å.

Å, β = 114.36(2)°, U = 2 757.5 Å³, D_c = 1.008 g cm⁻³, Z = 4, $F(000)$ = 896 electrons, $\mu(\text{Mo-}K_\alpha)$ = 5.16 cm⁻¹. Out of 6 527 symmetry-independent reflections measured to θ_{max} = 28.5°, 2 927 data [$F_0 > 2.0\sigma(F_0)$] were used to solve and refine, as for (1), to a current R of 0.099 3.

The cage geometry of (2) (Figure 3) is that of a dodecahedron, with the metal occupying a 5-connectivity vertex, adjacent to only one cage carbon atom. Molecular parameters within the polyhedron are unexceptional. Co-ordination of the isocyanide ligands, however, strongly reflects the nature of the cage atoms to which they are trans,[5] that opposite carbon being the most strongly bound. Thus Fe(4)–C(431) is significantly the shortest, and C(431)–N(43) the longest bond of its type. In addition, bending[3] occurs only at N(43) [156.3(11)°].

Similarities and differences are thus shown between reaction products of closo-2,4-Me₂-2,4-C₂B₅H₅ with the molecules [Fe(CNBuᵗ)₅], [Pt₂(μ-cyclo-octa-1,5-diene) (PEt₃)₄], and [Co(PEt₃)₄]. With [Fe(CNBuᵗ)₅], the carbaborane affords a relatively undistorted cage in which the metal is electronically saturated. With platinum[1] the cluster is severely distorted, and susceptible to facile insertion of a second Pt(PEt₃)₂ fragment to generate a 9-vertex carbadimetallaborane. Cobalt, too, yields a dimetallic species, but one in which only one metal atom lies within the polyhedral surface.

We thank the S.E.R.C. for support.

References

1 G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1982, 46; and references therein.

2 Prepared by a simple extension of the procedure described for the trimethylphosphine analogue: H. F. Klein, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 375.

3 J-M. Bassett, D. E. Berry, G. K. Barker, M. Green, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1979, 1003.

4 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.

5 G. K. Barker, M. P. Garcia, M. Green, G. N. Pain, F. G. A. Stone, S. K. R. Jones, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1981, 652; and references therein.