

***closo*-Carbametallaboranes from Direct Insertion into *nido*-Carbaboranes:
The Molecular Structures of [6,6-(Et₃P)₂-1,2,6-C₂CoB₇H₉] and
[1,1-(Et₃P)₂-1,2,4-CoC₂B₈H₁₀]**

By GEOFFREY K. BARKER, MARIA P. GARCIA, MICHAEL GREEN, GEOFFREY N. PAIN, and F. GORDON A. STONE
(Department of Inorganic Chemistry, The University, Bristol BS8 1TS)

and STUART K. R. JONES and ALAN J. WELCH
(Department of Chemistry, The City University, London EC1V 0HB)

Summary Reaction of [Co(PEt₃)₄] with *nido*-4,5-C₂B₇H₁₁ and *nido*-5,6-C₂B₈H₁₂ affords the wine-red compound *closo*-[6,6-(Et₃P)₂-1,2,6-C₂CoB₇H₉] and the purple compound *closo*-[1,1-(Et₃P)₂-1,2,4-CoC₂B₈H₁₀], respectively, both products being structurally characterised by single-crystal X-ray diffraction studies.

DIRECT insertion of nucleophilic Ni, Pd, Pt, or Co species into *closo*-carbaborane cages has become an important method for preparing *closo*-carbametallaboranes.^{1,2} However, in reactions between nucleophilic complexes of Ni or Pt and *nido*- or *arachno*-carbaboranes the initial products have open-cage structures.³⁻⁵ Thermolysis has been necessary to remove hydrogen so as to generate a *closo*-carbametallaborane.^{5,6} We now report that [Co(PEt₃)₄] promotes facile loss of hydrogen from *nido*-4,5-C₂B₇H₁₁ and *nido*-5,6-C₂B₈H₁₂ to give *closo*-carbacobaltaboranes directly.

Hydrogen is rapidly evolved on adding *nido*-4,5-C₂B₇H₁₁ to [Co(PEt₃)₄] in pentane at room temperature. Chromatography gives wine-red crystals (from Et₂O) of [6,6-(Et₃P)₂-1,2,6-C₂CoB₇H₉] (**(1)**, 72% yield, ν_{BH} (Nujol) 2580m, 2565m, 2495s, and 2450m cm⁻¹; n.m.r.†: ³¹P, δ (p.p.m.) 34.8(d) and 31.5 [d, $J(\text{PP})$ 53.7 Hz]; ¹¹B, δ (p.p.m.) 49.49, -15.04, and -37.46}. Hydrogen was also rapidly released on mixing pentane solutions of *nido*-5,6-C₂B₈H₁₂ with [Co(PEt₃)₄], this process being accompanied by deposition of purple crystals of [1,1-(Et₃P)₂-1,2,4-CoC₂B₈H₁₀] (**(2)**, 91% yield, m.p. 188 °C, ν_{BH} (Nujol) 2560m, 2510s, 2495sh, and 2425s cm⁻¹; n.m.r.†: ³¹P, δ (p.p.m.) 30.2(d) and 26.1 [d, $J(\text{PP})$ 45 Hz]; ¹¹B, δ (p.p.m.) -14.53 and -29.82}. X-Ray diffraction studies were carried out on **(1)** and **(2)** at -5 °C to elucidate their structures.

Crystal data: **(1)**, C₁₄H₃₉B₇CoP₂, $M = 404.02$, monoclinic, space group $P2_1/c$, $a = 10.708(3)$, $b = 13.615(2)$, $c = 15.627(4)$ Å, $\beta = 97.620(19)^\circ$, $U = 2.258(1)$ Å³, $Z = 4$,

$D_c = 1.188$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 8.4$ cm⁻¹. **(2)**, C₁₄H₄₀B₈CoP₂, $M = 415.84$, monoclinic, space group Cc from E -statistics and successful refinement, $a = 10.429(5)$, $b = 16.624(4)$, $c = 13.961(3)$ Å, $\beta = 109.202(16)^\circ$, $U = 2.285(8)$ Å³, $Z = 4$, $D_c = 1.208$ g cm⁻¹, $\mu(\text{Mo-K}\alpha) = 8.3$ cm⁻¹.

Intensity data were recorded on an Enraf-Nonius CAD4 autodiffractometer (Mo-K α X-radiation, $\lambda = 0.71069$ Å). For **(1)**, 3105 reflections [$F \geq 2.0 \sigma(F)$] out of 4909 measured to $\theta_{\text{max}} = 27^\circ$ were retained, whilst for **(2)** 2750 data were measured ($\theta_{\text{max}} = 27.5^\circ$), of which 2417 had

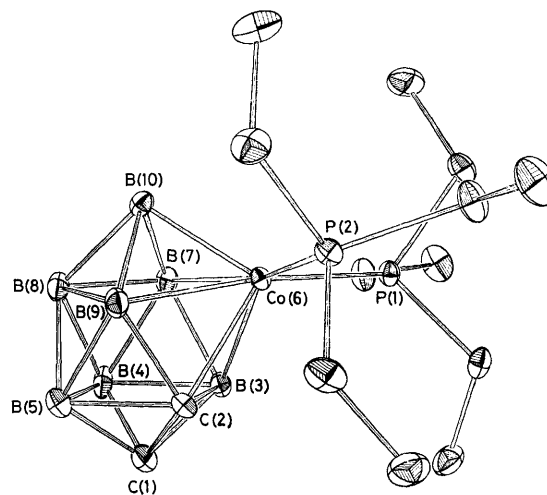


FIGURE 1. The molecular structure of [6,6-(Et₃P)₂-1,2,6-C₂CoB₇H₉] (**(1)**), with hydrogen atoms omitted. Important parameters include Co(6)-C(2) 2.040(5), Co(6)-B(3) 2.113(6), Co(6)-B(7) 2.204(6), Co(6)-B(10) 1.981(6), Co(6)-B(9) 2.128(6), C(1)-C(2) 1.523(8), Co(6)-P(1) 2.225(2), and Co(6)-P(2) 2.236(5) Å P(1)-Co(6)-P(2) 98.56(6)°.

† Phosphorus-31 n.m.r. shifts are to high frequency of H₃PO₄, and ¹¹B shifts are to high frequency of F₃B·OEt₂, both ¹H decoupled. All n.m.r. spectra were recorded at -50 °C in CD₃C₆D₅.

$F \geq 2.0 \sigma(F)$. Both structures were solved by conventional Patterson and Fourier methods and refined by least-squares to current R values of 0.064 and 0.033, respectively.† The carbon atoms of the cages were identified *via* internuclear separations and thermal parameters, having been refined as boron. Compound (2) crystallises in a non-centrosymmetric space group, and all quoted data are taken from, and refer to the results of, the significantly better refinement obtained from one enantiomorphic possibility.

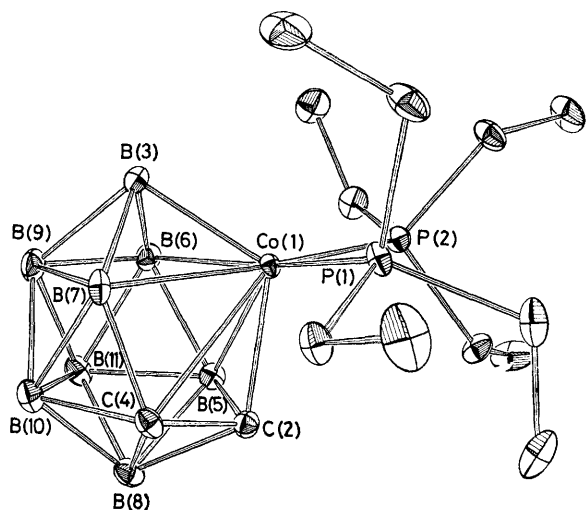


FIGURE 2. The molecular structure of [1,1-(Et₃P)₂-1,2,4-Co₂B₈H₁₀] (2), with hydrogen atoms omitted. Important parameters include Co(1)-C(2) 1.999(4), Co(1)-C(4) 2.525(4), Co(1)-B(7) 2.281(5), Co(1)-B(3) 1.968(5), Co(1)-B(6) 2.227(5), Co(1)-B(5) 2.206(5), C(2)-C(4) 1.483(6), Co(1)-P(1) 2.244 3(12), and Co(1)-P(2) 2.224 8(12) Å, P(1)-Co(1)-P(2) 95.65(4)°.

† Atomic co-ordinates for both compounds 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.

- 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 G. K. Barker, M. Green, F. G. A. Stone, A. J. Welch, T. P. Onak, and G. Siwapanoyos, *J. Chem. Soc., Dalton Trans.*, 1979, 1687.
- ⁴ M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1975, 2274.
- ⁵ G. K. Barker, M. Green, F. G. A. Stone, A. J. Welch, and W. C. Wolsey, *J. Chem. Soc., Chem. Commun.*, 1980, 627.
- ⁶ G. K. Barker, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1980, 1186.
- ⁷ A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1975, 1473.
- ⁸ D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1977, 602.
- ⁹ See, for example, the B-Fe distances in V. Subrtova, A. Linek, and J. Hasek, *Acta Crystallogr., Sect. B*, 1978, **34**, 2720.

closo-Geometries are adopted by both cages (Figures 1 and 2), in which the carbon atoms retain adjacency. The respective cage geometries may be described as bicapped square antiprismatic and octadecahedral and, in both systems, the cobalt atom occupies a vertex of the highest possible connectivity.

In (1) the cobalt-to-cage-atom links are 1.981(6) Å to the 4-connected vertex B(10), and 2.040(5)—2.204(6) Å to the 5-connected vertices. Additional support for the positioning of C(2) is given by the fact that C(1)-C(2) is the shortest cage distance [1.523(8) Å], and that the Co-P bond *trans* to C(2) is significantly the shorter. The latter phenomenon is commonly observed^{6,7} in bis(phosphine)carbometallaboranes in which the metal is bound to an asymmetric polyhedral face, and is related to the relatively small carbon-metal overlap populations in such molecules.⁸

In (2) the separations between metal and low-connectivity vertices C(2) and B(3) are naturally shorter than those to the higher connected vertices,⁹ with the additional factor that within each type the B-Co bonds are shorter than the C-Co, a feature consistent with the short C(2)-C(4) distance [1.483(6) Å]. For both (1) and (2), which are formally paramagnetic, the geometries at the cobalt atoms show that Co-H bonds are not present, in agreement with i.r. and n.m.r. data.

Facile formation of (1) and (2), together with the earlier work⁹ with [Pt₂(μ-cod)(PEt₃)₄] (cod = cyclo-octa-1,5-diene) shows that the cobalt species [Co(PEt₃)₄] affords *closo*-cages directly, and other reaction pathways, such as cage-carbon separations and metal-to-cage phosphine ligand migration as found with the platinum system,^{5,6} are avoided.

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

(Received, 16th March 1981; Com. 294.)