An Unusual 13-Vertex *closo*-Carbacobaltaborane; Synthesis and Molecular Structure of [1-Me-4-(Et_3P)-$\mu_{4,6\text{-or-}7}$-{$Co(PEt_3)_2$-μ-$(H)_2$}-1,2,4-$C_2CoB_{10}H_{10}$]

Geoffrey K. Barker,[a] **Maria P. Garcia,**[a] **Michael Green,**[a] **F. Gordon A. Stone,**[a] **and Alan J. Welch**[b]

[a] *Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.*
[b] *Dewar Crystallographic Laboratory, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, U.K.*

Reaction (room temperature, toluene) of *closo*-1-Me-1,2-$C_2B_{10}H_{11}$ with two equivalents of [$Co(PEt_3)_4$] affords the title compound, structurally identified by *X*-ray crystallography.

In extending the scope of the direct insertion[1] route to carbametallaboranes we have found a marked difference in reactivity, towards a variety of carbaboranes, between nucleophiles of the nickel and cobalt sub-groups. Thus, whilst fragments ML_2 (M = Ni, Pd, Pt; L = phosphine or isocyanide) insert into *closo*-carbaboranes to yield generally unreactive products,[1] analogous insertion of [$Co(PEt_3)_2$], derived from [$Co(PEt_3)_4$],[2] may proceed with a different regioselectivity, and is sometimes followed by hydrogen abstraction from solvent.[3] Furthermore, with *nido*-carbaboranes nickel-group nucleophiles give *nido*-products that require pyrolysis to achieve cage-closure,[4-6] whereas this occurs spontaneously at room temperature if [Co(PEt$_3$)$_4$] is used.[7] In addition, whilst partial closure (affording *nido*-products) has been observed[8] during the reaction of zerovalent Ni and Pt species with the *arachno*-carbaborane 1,3-$C_2B_7H_{13}$, [Co(PEt$_3$)$_2$] and [Rh(PEt$_3$)$_2$] fragments insert into $C_2B_7H_{13}$ to yield *closo*-hydridocarbametallaboranes as the only isolable products.[9]

In terms of synthetic challenge, structural possibility,[10—12] and theoretical interest,[13,14] one of the most important subgroups of boranes and heteroboranes to have received recent attention is the supraicosahedral group. To date, the direct insertion reaction has not afforded a route to such species because of the inertness of *closo*-$R_2C_2B_{10}H_{10}$ (R = H or Me) towards nucleophiles of the nickel triad. Herein we report the first synthesis by direct insertion of a 13-vertex carbametallaborane, in which we exploit the enhanced reactivity of [Co(PEt$_3$)$_4$].

1-Me-1,2-$C_2B_{10}H_{11}$ was stirred at room temperature for three hours with two equivalents of [Co(PEt$_3$)$_4$] in toluene. The solution thus obtained was evaporated and the residue dissolved in diethyl ether. After purification on an alumina column (twice) a reddish-brown paramagnetic product (**1**) (55% yield) was crystallised from toluene–diethyl ether at −20 °C. I.r. and n.m.r. spectra failed to identify the product, which was accordingly studied by single crystal *X*-ray diffraction.

Crystal data: $C_{21}H_{60}B_{10}Co_2P_3$, M = 631.6, orthorhombic, space group *Pbca*, a = 16.772 3(16), b = 21.662(2), c = 19.149(3) Å, U = 6 957 Å^3, Z = 8, D_c = 1.206 g cm^{-3}, $F(000)$ = 2680 electrons, $\mu(\text{Mo-}K_{\bar{\alpha}})$ = 10.4 cm^{-1}. 6099 Symmetry-independent reflections were measured (291 K) to θ_{max} = 25° (Mo-K_α *X*-radiation, $\bar{\lambda}$ = 0.710 69 Å) on an Enraf Nonius CAD4 diffractometer. Of these, 3385 with $F \geqslant 2.0\sigma(F)$ were used to solve (Patterson and Fourier methods) and refine (full-matrix least-squares) the structure to R = 0.088.†

Figure 1 presents a perspective view of the molecule (**1**), and demonstrates the atomic numbering scheme. It has not proven possible to distinguish between cluster sites 2 and 3 for the non-methylated cage carbon atom, although on the basis of short 1–2 and 1–3 connectivities we are confident that the polyhedral carbon atom adjacency of the precursor is maintained in the product, and thus the correct[15] formulation of the carbacobaltaborane is either [1-Me-4-(Et$_3$P)-$\mu_{4,6}$-{Co(PEt$_3$)$_2$-μ-(H)$_2$}-1,2,4-$C_2CoB_{10}H_{10}$] or [1-Me-4-(Et$_3$P)-$\mu_{4,7}$-{Co(PEt$_3$)$_2$-μ-(H)$_2$}-1,2,4-$C_2CoB_{10}H_{10}$], (**1**). Figure 1 arbitrarily adopts the latter choice.

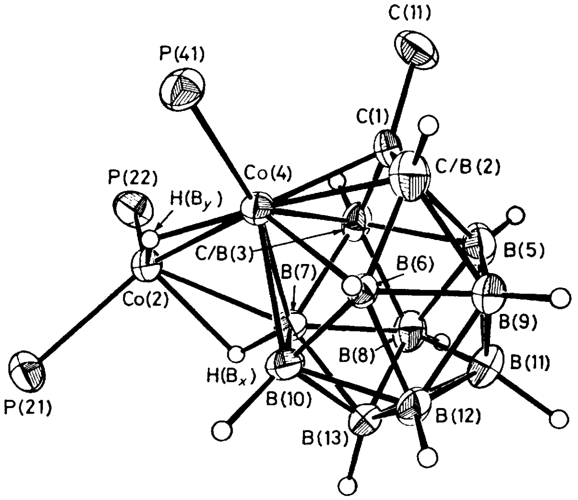

Figure 1. Perspective view of (**1**), with cage methyl H atoms and phosphine ethyl groups omitted for clarity.

The polyhedral framework is that of a distorted docosahedron with carbon atoms in 4- and 5-, and Co(4) in a 6-connectivity vertex,‡ adjacent to both cage carbons. In [Co($C_2B_{10}H_{12}$)(η-C_5H_5)], (**2**)[16] and [Ti(Me$_2C_2B_{10}H_{10}$)$_2$]$^{2-}$, (**3**)[17] *closo*-docosahedra are observed in which the metal atoms also occupy vertices of the highest possible connectivity number. In (**2**) and (**3**) abnormally long B(2)–B(5) and B(3)–B(5)§ bonds occur (1.947—2.081 Å), a feature that is also apparent in the present compound. Furthermore, in (**1**) the marked asymmetry[16] in B(5)–C/B(2) and B(5)–C/B(3) lengths (Δ = 0.126 Å) is compensated by a reversed difference in Co(4)–C/B(2) and Co(4)–C/B(3) distances (Δ = 0.106 Å).

A Co(PEt$_3$)$_2$ moiety lies *exo* to the polyhedron, in a bridging position across the Co(4)–B(7) connectivity, the Co(2)–Co(4) and Co(2)–B(7) bonds themselves being bridged by hydrogen atoms. The arrangement may be compared with that observed in the recently reported[18] species [4-(Et$_3$P)-1,7-Me$_2$-$\mu_{4,8}$-{Co(H)(PEt$_3$)$_2$-μ-(H)-μ-(PEt$_2$)}-1,4,7-CCoCB$_5$H$_4$], (**4**), in which an {(Et$_3$P)$_2$Co(H)} fragment is linked across a Co–B connectivity by μ-PEt$_2$ (to Co) and μ-H (to B) functions. In Figure 2 the bridging systems and important molecular parameters of (**1**) and (**4**) are compared. The substantial structural differences [(**1**) *cf.* (**4**)] may be summarised as follows: (i) a

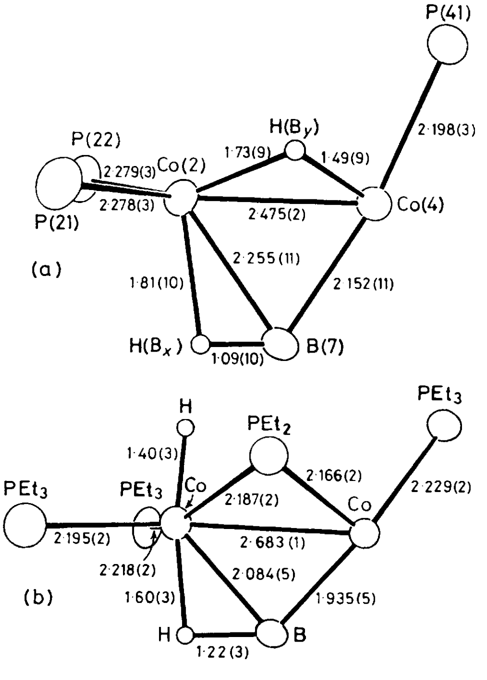

Figure 2. The bridging systems of (a) compound (**1**) and (b) compound (**4**).

---

† Atomic co-ordinates 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.

‡ Connectivity numbers are expressed only with respect to the polyhedron.

§ Renumbered according to (**1**).

$[\text{1-Me-4-(Et}_3\text{P)-}\mu_{4,6\text{-or-}7}\text{-}\{\text{Co(PEt}_3)_2\text{-}\mu\text{-(H)}_2\}\text{-1,2,4-C}_2\text{CoB}_{10}\text{H}_{10}]$

(1)

$[\text{Co(C}_2\text{B}_{10}\text{H}_{12})(\eta\text{-C}_5\text{H}_5)]$ **(2)**

$[\text{Ti(Me}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^{2-}$ **(3)**

$[\text{4-(Et}_3\text{P)-1,7-Me}_2\text{-}\mu_{4,8}\text{-}\{\text{Co(H)(PEt}_3)_2\text{-}\mu\text{-(H)-}\mu\text{-(PEt}_2)\}\text{-1,4,7-CCoCB}_5\text{H}_4]$

(4)

longer Co(cluster)–B(cluster) interaction, presumably a consequence of the greater connectivity numbers of the atoms involved, (ii) a shorter Co–Co separation, as might be expected for bridging by hydrogen as opposed to the phosphido-ligand, and (iii) longer *exo*-polyhedral Co–P bonds, and greater asymmetry in the bridging links with distances to the non-cluster (cobalt) atom increasing.

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

Received, 25th October 1982; Com. 1229

References

1 M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1979, 1679.

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

3 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.

4 G. K. Barker, M. Green, F. G. A. Stone, A. J. Welch, T. P. Onak, and G. Siwapanyoyos, *J. Chem. Soc., Dalton Trans.*, 1979, 1687.

5 G. K. Barker, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1980, 1186.

6 G. K. Barker, M. Green, F. G. A. Stone, A. J. Welch, and W. C. Wolsey, *J. Chem. Soc., Chem. Commun.*, 1980, 627.

7 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.

8 M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1975, 2274.

9 G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone, J.-M. Basset, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1981, 653.

10 W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, 1977, **99**, 4016.

11 J. R. Pipal and R. N. Grimes, *J. Am. Chem. Soc.*, 1978, **100**, 3083.

12 J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, 1978, **17**, 6.

13 L. D. Brown and W. N. Lipscomb, *Inorg. Chem.*, 1977, **16**, 2989.

14 J. Bicerano, D. S. Marynick, and W. N. Lipscomb, *Inorg. Chem.*, 1978, **17**, 2041.

15 J. B. Casey, W. J. Evans, and W. H. Powell, *Inorg. Chem.*, 1981, **20**, 1333.

16 M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1974, **13**, 1411.

17 F. Y. Lo, C. E. Strouse, K. P. Callahan, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1975, **97**, 428.

18 G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone, H. E. Parge, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1982, 688.