Preparation and Characterization of the Metallaphosphaborane 2-Ph-1,3,6,7,2-[(η^5-C_5H_5)Co]$_4$$PB_2H_2$

Jiang Feilong[a], **Thomas P. Fehlner***[a] **and Arnold L. Rheingold***[b]

[a] *Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.*
[b] *Department of Chemistry, University of Delaware, Newark, Delaware 19716, U.S.A.*

The reaction of BH_3·THF (THF = tetrahydrofuran) with (η^5-C_5H_5)Co(PPh_3)$_2$ has resulted in the isolation and characterization of the first example of a metal-rich metallaphosphaborane.

A few metal-rich metallaboranes (M/B > 1 with unbridged M–B interactions) are known[1] but none contain other main group atoms. Mononuclear metallaphosphaboranes have been reported[2] and some examples of metallaphosphacarbaboranes with large borane fragments have been characterized.[3] Here we report the first example of a metal rich metallaphosphaborane prepared directly from simple starting materials. The new cluster is analogous to a known M–P–C cluster system.

Recently we reported the preparation of [μ-H]$_2$(cpCo)$_4$$B_2H_2$ (cp = η^5-C_5H_5) from the reaction of BH_3·THF (THF = tetrahydrofuran) with cpCo_2(PPh_3)(PhCCPh) in which the borane plays a dual role both producing the appropriate organometallic fragments and providing the source of the borane fragment for the cluster.[4] This fragment condensation bears an apparent relationship to the preparation of Fe–S clusters in which 'spontaneous self assembly' is thought to take place.[5] In the latter case, simple variation of reagent stoicheiometry results in a range of cluster stoicheiometries. Thus, we have varied reaction conditions in our system and, in doing so, have prepared additional metal–boron clusters. For example, by reducing the borane/cobalt ratio to 2.5 : 1 and by adding BH_3·THF slowly over a period of 1 h, the production of a new compound was revealed by the ^{11}B n.m.r. spectrum of the products. After precipitation of the BH_3·PPh_3 formed as a byproduct, chromatography on silica gel (toluene–hexane) yielded a green band (R_f 0.18, toluene : hexane 1 : 1) which produced green crystals in 5% yield (based on cobalt). On the basis of the spectroscopic information† and the electron counting rules for clusters[6] (8 pair, 7 vertex *closo*) we formulate the compound as 2-Ph-1,3,6,7,2-[(η^5-C_5H_5)-Co]$_4$$PB_2H_2$, (**1**). One alternate possibility, 2-Ph-1,4,5,7,2-[(η^5-C_5H_5)Co]$_4$$PB_2H_2$, is ruled out as no P–B coupling is observed. The other, 2-Ph-3,4,5,6,2-[(η^5-C_5H_5)Co]$_4$$PB_2H_2$ is excluded by the low field ^{11}B n.m.r. shift and the high field ^1H shift of one pair of cp resonances.

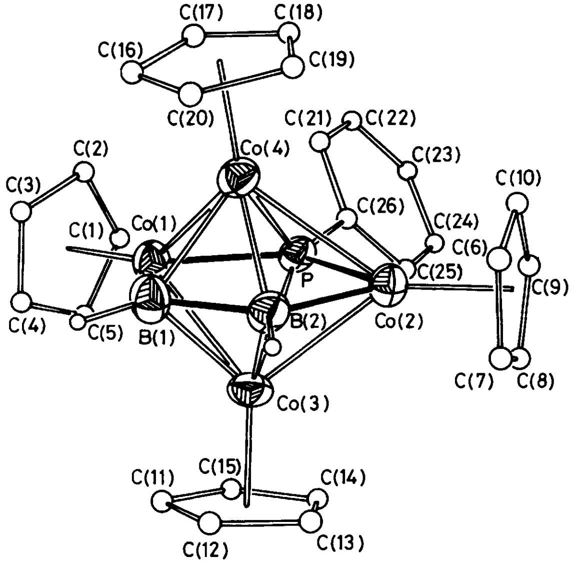

Figure 1. Molecular structure and labelling scheme for (**1**). Co(1)–Co(3) 2.517(1), Co(1)–Co(4) 2.517(1), Co(2)–Co(3) 2.520(1), Co(2)–Co(4) 2.521(1), P–Co(1) 2.105(2), P–Co(2) 2.093(2), P–Co(3) 2.271(2), P–Co(4) 2.247(2), B(1)–Co(1) 1.937(9), B(1)–Co(3) 2.080(9), B(1)–B(4) 2.057(9), B(2)–Co(2) 1.956(9), B(2)–Co(3) 2.069(9), B(2)–Co(4) 2.044(8), B(1)–B(2) 1.79(1) Å, Co(1)–P–Co(2) 125.5(1), P–Co(2)–B(2) 87.2(3), Co(2)–B(2)–B(1) 120.5(5), B(2)–B(1)–Co(1) 119.6(6), B(1)–Co(1)–P 87.8(3)°.

The structure of (**1**) in the solid state was determined by a single crystal *X*-ray diffraction study‡ with the results shown in Figures 1 and 2. In agreement with the electron counting rules, the structure is adequately represented as a pentagonal bipyramid containing four cobalt, one phosphorus, and two boron atoms in the cluster core. Each cobalt has a η^5-C_5H_5 ligand, each boron a terminal hydrogen and the phosphorus a Ph substituent. Two of the cobalts are in apical positions and, considering the cluster atoms only, there is a plane of symmetry containing the phosphorus and apical cobalt atoms.

Although the mechanism for the formation of (**1**) is unknown, one point is clear. Separate experiments under appropriate reaction conditions show that (**1**) is not formed by the direct reaction of PPh_3 with (μ-H)$_2$(cpCo)$_4$$B_2H_2$ with the elimination of two C_6H_6 molecules. Hence, this suggests that under BH_3 deficient conditions a cpCo(PPh_3) fragment is incorporated into the cluster building process. This, in turn, may be followed by reductive elimination of C_6H_6 to yield the PPh fragment found in (**1**).

---

† *Selected spectroscopic data* for (**1**): mass : M^+ 628 (isotope peaks corresponding to two B); $C_{26}H_{27}B_2PCo_4$; i.r. (toluene) 2440 cm^{-1} (B–H); ^{11}B n.m.r. δ 103.8 p.p.m. (d, *J* 130 Hz, B–H); ^{31}P n.m.r. δ 156.6 p.p.m. (s, μ_4-PPh); ^1H n.m.r. δ 8.42, 7.52 (m, 5H, Ph), δ 4.62 (s, 5H, C_5H_5), δ 3.85 (s, 5H, C_5H_5).

‡ *Crystal data* for (**1**): $C_{26}H_{27}B_2PCo_4$, monoclinic, $P2_1/n$, a = 13.495(2), b = 11.493(2), c = 15.615(4) Å, β = 95.74(2)°, T = 23 °C, U = 2410(1) Å^3, Z = 4, D_c = 1.73 g cm^{-3}, μ (Mo-K_α) = 28.9 cm^{-1}. A Nicolet R3m/μ diffractometer was used to collect 4268 data ($4° \leqslant 2\theta \leqslant 50°$) of which 3884 were independent ($R_{int.}$ = 1.90%) and 2547 with $F_o \geqslant 3\sigma(F_o)$ were considered observed. The laminar dimensions (0.08 × 0.28 × 0.36 mm) of the black crystal used for the data collection gave rise to edge effects in the intensity data. An empirical absorption correction, based upon a laminar model, rejected all data for which the glancing angle was $\leqslant$3.5° to the major face (001); by this process 366 data were ignored ($T_{min.}/T_{max.}$ = 0.864/0.573). The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms of the cp and Ph rings were idealized. The B–H hydrogen atoms were found and isotropically refined. At convergence R = 5.14%, R_w = 6.04%, G.O.F. = 1.190, Δ/σ = 0.037, $\Delta(\rho)$ = 0.49 e Å^{-3} [0.83 Å from C(22)], N_o/N_v = 8.63. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

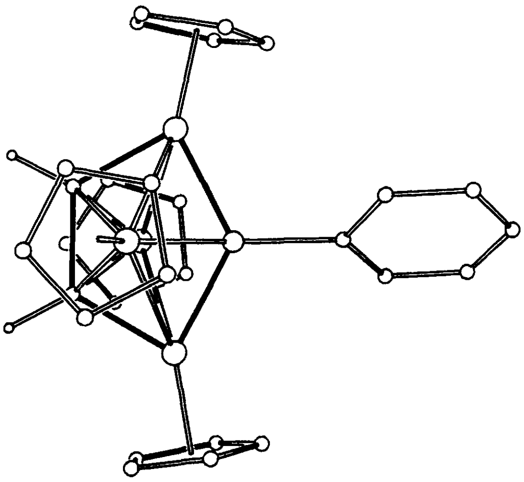

Figure 2. Cluster (**1**) as viewed perpendicular to the Co(1)–P–Co(2)–B(2)–B(1) plane. The maximum deviation from planarity is at P (0.012 Å). This view reveals approximate two-fold rotational symmetry along a vertical axis through P and the midpoint of the Co(3)· · ·Co(4) vector.

The metallaphosphaborane (**1**) is a direct analogue of a carbon–phosphorus–ruthenium cluster, $Ru_4(CO)_9(\mu\text{-}CO)_2\text{-}PPh[C(Ph)C(Ph)]$, that has been recently reported.[7] The cluster core structure of the latter compound can be generated from that in Figure 1 by replacing B with C and Co with Ru. The metallaphosphaborane is similarly analogous to $[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)CHCH)(\mu\text{-}CO)_2(CO)_9]^-$ which has also been recently reported.[8] Both organometallic compounds are, like (**1**), 7-vertex, 8 electron pair *closo* clusters. Thus, (**1**) constitutes another example of a metal–borane mimic of known organometallic clusters.[9]

The support of the National Science Foundation under Grant CHE 8498251 and of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Received, 30th March 1987; Com. 415

References

1 N. N. Greenwood, *Chem. Soc. Rev.*, 1984, **13**, 353; R. N. Grimes, *Acc. Chem. Res.*, 1983, **16**, 22; J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 519; C. E. Housecroft and T. P. Fehlner, *Adv. Organomet. Chem.*, 1982, **21**, 57.
2 R. T. Paine, W. F. McNamara, and E. N. Duesler, 192nd Meeting of the American Chemical Society, 1986, Abstract INORG 97.
3 L. J. Todd, I. C. Paul, J. L. Little, P. S. Welcker, and C. R. Peterson, *J. Am. Chem. Soc.*, 1968, **90**, 4489.
4 J. Feilong, T. P. Fehlner, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1987, **109**, 1860.
5 M. A. Whitener, J. D. Bashkin, K. S. Hagen, J.-J. Girerd, E. Gamp, N. Edelstein, and R. H. Holm, *J. Am. Chem. Soc.*, 1986, **108**, 5607.
6 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1; D. M. P. Mingos, *Acc. Chem. Res.*, 1984, **17**, 311.
7 J. Lunniss, S. A. MacLaughlin, N. J. Taylor, A. J. Carty, and E. Sappa, *Organometallics*, 1985, **4**, 2066.
8 M. Kalam-Alami and R. Mathieu, *J. Organomet. Chem.*, 1986, **299**, 363.
9 J. Vites, C. E. Housecroft, C. Eigenbrot, M. L. Buhl, G. J. Long, and T. P. Fehlner, *J. Am. Chem. Soc.*, 1986, **108**, 3304.