

***closo*-Carbametalaboranes with Metal–Hydrogen Bonds from Direct Insertion into *arachno*-Carbaboranes: The Molecular Structures of [2-H-2,2-(Et₃P)₂-1,6,2-C₂CoB₇H₉] and [2-H-2,2-(Et₃P)₂-1,6,2-C₂RhB₇H₉], and a Most Unusual Crystallographic Coincidence**

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Summary The *arachno*-carbaborane 1,3-C₂B₇H₁₃ reacts with [Co(PEt₃)₄] and with [Rh(η-C₃H₅)(PEt₃)₂] to afford, respectively, [2-H-2,2-(Et₃P)₂-1,6,2-C₂CoB₇H₉] and [2-H-2,2-(Et₃P)₂-1,6,2-C₂RhB₇H₉]; both structures have been

established by X-ray diffraction studies, but, whilst they crystallise in nearly identical unit cells and the same space group, these species are not isostructural.

DIRECT insertion of $[\text{Co}(\text{PET}_3)_4]$ into *nido*-carbaboranes results in formation of *closo*-carbacobaltaboranes in high yield.¹ Similar reactions with *arachno*-carbaboranes might be expected to give carbametallaboranes with open-cage architectures. Herein are reported results which show that highly nucleophilic transition metal complexes can produce *closo*-carbametallaboranes directly from *arachno*-carbaboranes.

Addition of *arachno*-1,3- $\text{C}_2\text{B}_7\text{H}_{13}$ to $[\text{Co}(\text{PET}_3)_4]$ in pentane at room temperature results in rapid hydrogen evolution. Chromatography (alumina), followed by crystallisations from diethyl ether affords, as major product, deep red crystals of $[\text{2-H-2,2-(Et}_3\text{P)}_2\text{-1,6,2-C}_2\text{CoB}_7\text{H}_9]$ (**(1)**), 73%, m.p. 118 °C, ν_{BH} (Nujol) 2 595m, 2 570m, 2 550m, 2 525sh, and 2 515s cm^{-1} , ν_{CoH} 1 927m cm^{-1} † and a red-brown compound {8%, m.p. 130 °C, ν_{BH} 2 575s, 2 550sh, 2 535s, 2 510s, and 2 470s cm^{-1} }.†

An immediate reaction with gas evolution also occurs when 1,3- $\text{C}_2\text{B}_7\text{H}_{13}$ is added to $[\text{Rh}(\eta\text{-C}_3\text{H}_5)(\text{PET}_3)_2]$ dissolved in tetrahydrofuran. Recrystallisation from toluene-diethyl ether affords bright-yellow crystals of $[\text{2-H-2,2-(Et}_3\text{P)}_2\text{-1,6,2-C}_2\text{RhB}_7\text{H}_9]$ (**(2)**), 70%, m.p. 138 °C, ν_{BH} 2 580m, 2 530s, 2 520sh, and 2 485m cm^{-1} , ν_{RH} 2 070m cm^{-1} ‡ as the only isolable product.

Thus the spectra of **(1)** and **(2)** show strong similarities, whilst the red-brown compound is clearly quite different, there being no spectral evidence for a metal-hydride function. Furthermore, the last is clearly not the compound $[\text{6,6-(Et}_3\text{P)}_2\text{-1,2,6-C}_2\text{CoB}_7\text{H}_9]$.¹ Interestingly, X-ray diffraction photographs of single crystals of **(1)** and **(2)** indicated very similar unit cell dimensions and identical systematic absences, but different intensity patterns. Accordingly, full X-ray diffraction data were collected for both compounds.§

Crystal data: **(1)**, $\text{C}_{14}\text{H}_{40}\text{B}_7\text{CoP}_2$, $M = 404.92$, monoclinic space group Cc , $a = 9.535(2)$, $b = 17.216(4)$, $c = 14.345(3)$ Å, $\beta = 107.398(17)^\circ$, $U = 2.247.0$ Å³, $Z = 4$, $D_c = 1.197$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 8.5$ cm^{-1} . **(2)**, $\text{C}_{14}\text{H}_{40}\text{B}_7\text{P}_2\text{Rh}$, $M = 448.89$, monoclinic, space group Cc , $a = 9.5883(17)$, $b = 17.710(3)$, $c = 13.895(3)$ Å, $\beta = 104.022(16)^\circ$, $U = 2.289.1$ Å³, $Z = 4$, $D_c = 1.302$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 7.9$ cm^{-1} .

Intensity data for both compounds were collected at 23 °C on Nicolet P3 diffractometers (Mo- K_α radiation, $\lambda = 0.71069$ Å). For **(1)** 2 365 reflections out of 2 533 measured to $\theta_{\text{max}} = 27.5^\circ$ were considered significant [$F \geq 2.0 \sigma(F)$], whilst for **(2)** 2 079 data out of 2 126 ($\theta_{\text{max}} = 25.0^\circ$) obeyed the same criterion. Both structures were solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares to $R = 0.040$ and $R = 0.022$, respectively. The positions of the cage-carbon atoms were deduced independently,¹ and in both cases the results refer

† N.m.r. spectroscopy (in $\text{CD}_3\text{C}_6\text{D}_5$). For compound **(1)**, $^{31}\text{P}\{^1\text{H}\}$ (-60 °C), δ (p.p.m., to high frequency of H_3PO_4) 48.5 (d) and 41.1 [d, $J(\text{PP})$ 39 Hz]; $^{11}\text{B}\{^1\text{H}\}$ (25 °C), δ (p.p.m., to high frequency of $\text{BF}_3\cdot\text{OEt}_2$) -19.1 and -30.2; ^1H (-60 °C), δ -11.12 [t, HCo , $J(\text{PH})$ 67 Hz]. For the red-brown compound $^{31}\text{P}\{^1\text{H}\}$ (-60 °C), δ (p.p.m.) 42.6 (d) and 31.5 [d, $J(\text{PP})$ 66 Hz]; $^{11}\text{B}\{^1\text{H}\}$ (25 °C), δ (p.p.m.) 27.0 (1 B), -9.9 (2 B), -15.6 (1 B), -32.1 (1 B), -35.3 (1 B), and -44.3 (1 B).

‡ N.m.r. spectroscopy. $^{31}\text{P}\{^1\text{H}\}$ (C_6D_6 , 25 °C), δ (p.p.m.) 30.5 [d, $J(\text{RhP})$ 122 Hz]; $^{31}\text{P}\{^1\text{H}\}$ [$(\text{CD}_3)_2\text{CO}$, -70 °C], δ (p.p.m.) 32.0 and 30.8 [AB pattern, $J(\text{RhP}_A)$ 124, $J(\text{RhP}_B)$ 114, and $J(\text{P}_A\text{P}_B)$ 24 Hz]; $^{11}\text{B}\{^1\text{H}\}$ (C_6D_6 , 25 °C), δ (p.p.m.) -9.43, -13.59, and -20.39; ^1H [$(\text{CD}_3)_2\text{CO}$, 25 °C], δ 1.94 (m, PCH_2CH_3), 1.08 [d of t, CH_3 , $J(\text{HH})$ 7, $J(\text{PH})$ 16 Hz], and -13.33 [d of t, HRh , $J(\text{RhH})$ 17, $J(\text{PH})$ 27 Hz].

§ 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.

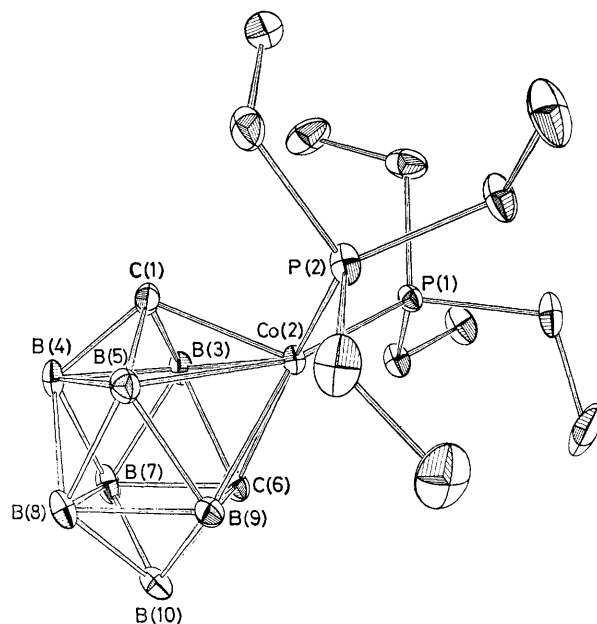


FIGURE 1. The molecular structure of $[\text{2-H-2,2-(Et}_3\text{P)}_2\text{-1,6,2-C}_2\text{CoB}_7\text{H}_9]$ (**(1)**), with H atoms omitted for clarity. Molecular parameters include Co(2)-C(1) 1.984(5), Co(2)-B(3) 2.179, Co(2)-C(6) 2.120(5), Co(2)-B(9) 2.123(6), Co(2)-B(5) 2.194(6), Co(2)-P(1) 2.215 4(16), and Co(2)-P(2) 2.182 6(16) Å, P(1)-Co(2)-P(2) 100.24(6)°.

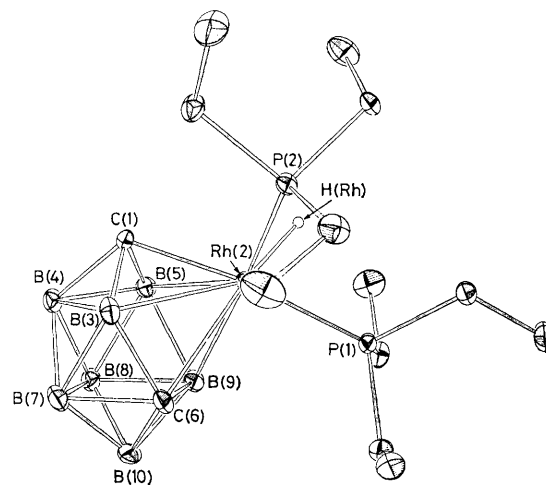


FIGURE 2. Perspective view of the compound $[\text{2-H-2,2-(Et}_3\text{P)}_2\text{-1,6,2-C}_2\text{RhB}_7\text{H}_9]$ (**(2)**), with all hydrogen atoms except H(Rh) omitted. Rh(2)-C(1) 2.101(4), Rh(2)-B(3) 2.384(5), Rh(2)-C(6) 2.358(5), Rh(2)-B(9) 2.209(5), Rh(2)-B(5) 2.320(5), Rh(2)-P(1) 2.306 3(11), Rh(2)-P(2) 2.325 3(11), and Rh(2)-H(Rh) 1.47(6) Å, P(1)-Rh(2)-P(2) 98.95(4), P(1)-Rh(2)-H(Rh) 82.1(19), and P(2)-Rh(2)-H(Rh) 76.2(18)°.

to the significantly better refinements obtained from one enantiomer.

In both species (Figures 1 and 2) the cages adopt *closo* bicapped square antiprismatic geometries in which the heteroatoms occupy identical positions. Although it is clear, from comparison of the two polyhedral fragments, that non-corresponding optical isomers have been chosen for these Figures, it is nevertheless apparent that the two molecules are not isostructural, but rather are related as rotational conformers about the metal-cage axis. In (2) the hydric function H(Rh) is approximately *cis* to the Rh(2)B(5)B(9) deltahedral face and although we have not yet located the hydride of (1), the disposition of the phosphine ligands[¶] shows that H(Co) lies approximately *cis* to the Co(2)C(6)B(9) face. As rotational conformers, the molecular volumes of (1) and (2) should be approximately equal, but there is no apparent reason why their space

groups should be identical and their unit cell dimensions so close.**

Molecular dimensions within the cages of (1) and (2) are closely similar apart from those involving the metal atoms. In (2) the Rh-H distance [1.47(6) Å] is comparable with that found in other systems.^{2,3}

The results show that [Co(PEt₃)₄] and [Rh(η-C₃H₅)(PEt₃)₂] will generate *closo*-carbametallaboranes directly from *arachno*-1,3-C₂B₇H₁₃. This is in distinct contrast with the behaviour of nucleophilic complexes of nickel or platinum which afford⁴ stable *nido*-structures with 1,3-C₂B₇H₁₃.

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[¶] The numbering of the phosphorus atoms in Figures 1 and 2 has no implied significance.

** This coincidence may be taken further in that the compound [1,1-(Et₃P)₂-1,2,4-CoC₂B₈H₁₀] also crystallises in the space group *Cc* and has similar unit cell parameters (ref. 1).

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