

Synthesis, Characterization, and X-Ray Crystal Structure of 1,1-(PPh₃)₂-1-H-1,2,4-RhC₂B₁₀H₁₂, a Supra-icosahedral Metallocarbaborane Catalyst Precursor

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Summary The 13-vertex supra-icosahedral metallocarbaborane 1,1-(PPh₃)₂-1-H-1,2,4-RhC₂B₁₀H₁₂, a hydrogenation catalyst precursor, has been synthesized through routes analogous to 10-, 11-, and 12-vertex phosphinorhodacarbaborane formation, and characterized by n.m.r. studies and an X-ray diffraction crystal structure analysis.

ICOSAHERAL hydridophosphinorhodacarbaboranes of general formula C₂B₉H₁₁RhH(PPh₃)₂ have been shown catalytically to hydrogenate blocked olefins¹ and an intensive study has focused on the elucidation of catalytic pathways² and the associated structural chemistry³ unique to catalytically active metallocarbaboranes. A successful effort to synthesize 10-⁴ and 11-⁵ vertex catalyst-predecessors through routes analogous to the 12-vertex synthesis, *i.e.*, by reaction of the monoanions C₂B₇H₁₂⁻ and C₂B₈H₁₁⁻ with [(PPh₃)₃RhCl], prompted an examination of routes for the synthesis of 13-vertex supra-icosahedral phosphinorhodacarbaboranes utilizing the previously reported⁶⁻⁸ monoanions [9,12-C₂B₁₀H₁₃]⁻ (stable isomer) and [C₂B₁₀H₁₃]⁻ (unstable isomer)[†] whose potential towards metallocarbaborane formation had not yet been exploited.

The thermally unstable [Me₄N]⁺[C₂B₁₀H₁₃]⁻ rearranges at 100 °C to the stable [Me₄N]⁺[9,12-C₂B₁₀H₁₃]⁻. The structural differences between the two isomers probably exist in the position of the carbon atoms, and in the tentative assignment of a B-H-B bridge in the unstable isomer.[‡] In addition, the reactivities of the isomers towards metal complex formation were found to differ significantly.

Refluxing methanolic solutions of the stable [Me₄N]⁺[9,12-C₂B₁₀H₁₃]⁻ with [(PPh₃)₃RhCl] produced no metallocarbaboranes as deduced from the lack of a *ca.* 2500 cm⁻¹ B-H stretching band in the i.r. spectra of the observed products.

Reaction of the unstable [Me₄N]⁺[C₂B₁₀H₁₃]⁻ with [(PPh₃)₃RhCl][§] produced *closo*-1,1-(PPh₃)₂-1-H-1,2,4-RhC₂B₁₀H₁₂ (**1**), which was found catalytically to hydrogenate blocked olefins under mild conditions, and which also exhibited structural chemistry different from that of previously reported^{9,10} 13-vertex metallocarbaboranes derived from the [C₂B₁₀H₁₂]²⁻ ion. Complex (**1**) was characterized by its ³¹P{¹H}, ¹H, and ¹¹B n.m.r. spectra, as well as an X-ray crystal structure analysis.

For the X-ray crystal structure analysis, (**1**) was prepared as described and purified by recrystallizations from

[†] Previously reported (ref. 6) formulae were [Me₄N]⁺[7,10-C₂B₁₀H₁₃]⁻ for the thermally stable isomer, and [Me₄N]⁺[9,11-C₂B₁₀H₁₃]⁻ for the thermally unstable isomer. The numbering of the stable isomer was subsequently corrected to [Me₄N]⁺[9,12-C₂B₁₀H₁₃]⁻ upon X-ray diffraction structure analysis (refs. 7, 8). We prefer to call [Me₄N]⁺[9,11-C₂B₁₀H₁₃]⁻ merely the 'unstable isomer' until definitive structural analyses are completed.

[‡] The variable-temperature 200 MHz ¹H n.m.r. spectrum indicated a B-H-B bridge at δ -4.66 (br) undergoing a process which is not yet understood. Variable-temperature 126 MHz ¹¹B n.m.r. studies have shown cage fluxionality.

[§] Freshly prepared, unstable [Me₄N]⁺[C₂B₁₀H₁₃]⁻ was treated with an equimolar amount of [(PPh₃)₃RhCl] under N₂ in refluxing methanol for 30 min. After cooling, the yellow precipitate was filtered off using Schlenk techniques, and washed with methanol. Recrystallization from tetrahydrofuran (THF)-ethanol and THF-n-heptane gave microcrystalline (**1**) (*ca.* 40% yield).

THF-n-heptane and THF-ethanol. Suitable crystals were grown from 1,2-dichloroethane-n-pentane by vapour diffusion.[¶]

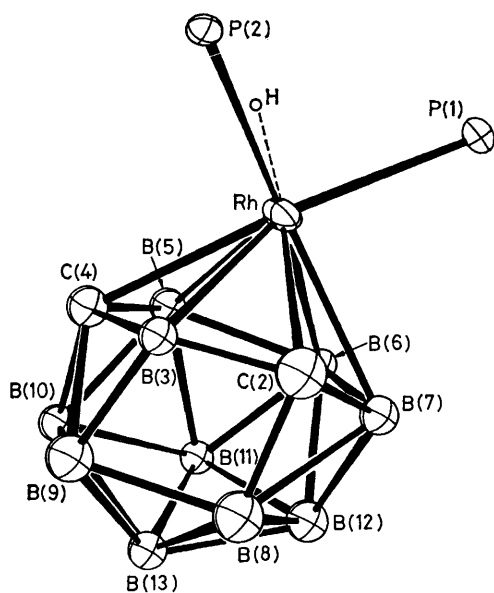


FIGURE. The molecular structure of $[1,1-(\text{PPh}_3)_2-1\text{-H-}1,2,4\text{-RhC}_2\text{B}_{10}\text{H}_{12}] \cdot 5 \text{C}_2\text{H}_4\text{Cl}_2$. The molecules of solvation, the phenyl rings, and the terminal boron hydrides have been omitted for clarity. The metal hydride was located on difference maps.

As shown in the Figure, the cage geometry of (1) differs from the structure of 1-(η -cyclopentadienyl)-1,2,4- $\text{CoC}_2\text{B}_{10}\text{H}_{12}$ reported by Churchill.¹⁰ The most obvious feature is the lack of a bonding interaction between B(3) and B(8) with an internuclear distance of 2.166 Å; this compares with a value of 2.082 Å, which Churchill emphasized was abnormally long, and represents a significant departure

from the normally triangulated polyhedral carborane systems. The B(9) \cdots C(2) diagonal in the C(2)-B(3)-B(9)-B(8) system is 2.720 Å, in the C(2)-B(7)-B(12)-B(8) system the diagonal C(2) \cdots B(12) is 2.841 Å, and in the B(10)-B(9)-B(3)-C(4) system the B(10) \cdots B(3) diagonal is 2.938 Å.

The four boron atoms in the top 'belt' of 1-(η -cyclopentadienyl)-1,2,4- $\text{CoC}_2\text{B}_{10}\text{H}_{12}$ were observed to be exactly coplanar, with C(2) above and C(4) below that plane. The structure of (1) varies in this respect, with small deviations from planarity observed in the top 'belt,' but with the locations of C(2) and C(4) exhibiting greater least squares deviations from planarity than B(3), B(5), B(6), and B(7). The entire top 'belt' is distorted to accommodate the perturbed 13-vertex system.

The structural chemistry of (1) is unique when compared to the systems previously reported.^{9,10} The variable-temperature ^{11}B n.m.r. spectrum indicated no cage fluxionality, and no structural changes were observed for samples which had been refluxed in THF for 3 h. In fact, thermal isomerization was not observed when (1) was heated *in vacuo* to its decomposition temperature (490 K) in 25 K increment steps, the reaction being monitored by i.r. spectroscopy.

Variable-temperature ^1H and $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectra of (1) indicated hindered rotation of the metal vertex about the planar hexagonal bonding face of the carborane cage; this is consistent with previous conclusions based on studies of icosahedral *closo*-bisphosphinometallacarboranes.¹¹

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[¶] *Crystal data*: $\text{C}_{38}\text{H}_{48}\text{B}_{10}\text{P}_2\text{Rh} \cdot 5\text{C}_2\text{H}_4\text{Cl}_2$, M 917.24, monoclinic, space group $P2_1/n$, $a = 12.38(2)$, $b = 21.26(2)$, $c = 16.69(2)$ Å, $\beta = 102.1(1)^\circ$, $U = 4295 \text{ \AA}^3$, $Z = 4$, $D_m = 1.32$, $D_c = 1.42 \text{ g cm}^{-3}$, $F(000) = 1884$, $\mu(\text{Mo-K}\alpha) = 6.16 \text{ cm}^{-1}$. Current R 0.0567, R_w 0.0554. X-Ray intensity data were collected (at $118 \pm 5 \text{ K}$, temp. stability $\pm 1 \text{ K}$) by the θ - 2θ scan technique with Mo- $K\alpha$ radiation (filtered) on a Picker automated diffractometer equipped with a scintillation counter and a pulse-height analyser. 4871 of a total of 8433 observed reflections, with $I > 3\sigma(I)$, were used in the structure determination. Data were corrected for Lorentz and polarization effects. The structure was solved by heavy atom methods and refined anisotropically (Rh, P, Cl) and isotropically (C, B, H). The atomic co-ordinates for this work 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.

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