



## Synthesis, Characterization and Reactivity of [exo-nido-Rh(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Me<sub>2</sub>)]

Işil Topaloğlu

To cite this article: Işil Topaloğlu (1996) Synthesis, Characterization and Reactivity of [exo-nido-Rh(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Me<sub>2</sub>)], Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 26:8, 1295-1305, DOI: [10.1080/00945719608005125](https://doi.org/10.1080/00945719608005125)

To link to this article: <http://dx.doi.org/10.1080/00945719608005125>



Published online: 21 Aug 2006.



Submit your article to this journal [↗](#)



Article views: 5



View related articles [↗](#)



Citing articles: 1 View citing articles [↗](#)

SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF  
[*exo-nido*-Rh(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Me<sub>2</sub>)]

Işıl Topaloğlu

Department of Chemistry, Faculty of Science, Izmir Institute of Technology,  
Izmir, Turkey

ABSTRACT

In this work, the reaction of the 16-electron species [Rh(η<sup>3</sup>-C<sub>8</sub>H<sub>13</sub>)-(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] with PPh<sub>3</sub> was investigated and the product, [*exo-nido*-Rh-(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Me<sub>2</sub>)], which is in an equilibrium with the *closo* analogue was characterized by <sup>31</sup>P{<sup>1</sup>H}, <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B NMR spectroscopy. A mechanism for the complex formation is suggested which is related to the previously reported reactions between the 16-electron complex and PR<sub>3</sub> (R = Me and Et) ligands.

INTRODUCTION

The *nido*-icosahedral cage fragments η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R<sub>2</sub> (R = H or Me), known as carborane ligands, assigned formally a dinegative charge, are regarded as a tridentate ligand and are isolobal with the more familiar

uninegative  $\eta\text{-C}_5\text{R}_5$  (R = H or Me) groups of organometallic complex chemistry.<sup>1,2</sup> These similarities have led to the synthesis of carborane analogues of metallocenes, arenes and other known types of metal complexes.<sup>3</sup> The salt  $[\text{NEt}_4][\text{Rh}(\text{CO})(\text{PPh}_3)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})]$  was first reported by Hawthorne *et al.*<sup>4</sup> as part of an extensive study of hydrogenation reactions homogeneously catalysed by rhodocarborane complexes.<sup>5-8</sup> Stone and co-workers<sup>9,10</sup> have synthesised the salts  $[\text{NEt}_4][\text{Rh}(\text{CO})(\text{L})(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  (L=CO or  $\text{PPh}_3$ ). The salt  $[\text{NEt}_4][\text{Rh}(\text{cod})(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  was also prepared by these workers by a different method<sup>11</sup> to that described by Hawthorne *et al.*<sup>12</sup>

The carborane ligands are isolobal with the familiar  $\eta\text{-C}_5\text{R}_5$  (R = H or Me) groups, therefore, the anionic rhodacarborane complexes will be isolobal with the species  $[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]^-$  and  $[\text{M}(\text{CO})_5]^-$  (M = Mn or Re), and the latter complexes have been known as useful synthons for preparing mixed metal complexes.<sup>13-16</sup> Anionic rhodacarborane complexes were expected to behave in a similar manner and Stone *et al.* have reported several heteropolynuclear metal complexes using these anions as precursors.<sup>9,10,17-21</sup>

Hawthorne *et al.*<sup>22</sup> described the synthesis and reactivity of 12-vertex-*closo*-bis(triphenylphosphine)hydridorhodacarborane complexes, many of which show catalytic activity in a variety of reactions including the hydrogenation and isomerization of alkenes.

Related to the above bis(triphenylphosphine)hydridorhodacarborane compounds is  $[\text{RhH}(\text{PEt}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]^{11}$ , prepared as one of the products of the reaction of  $[\text{Rh}(\eta^3\text{-C}_8\text{H}_{13})(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]^{23}$  with  $\text{PEt}_3$ .

## RESULTS AND DISCUSSION

### Reaction with $\text{PPh}_3$

The reaction between the 16-electron compound  $[\text{Rh}(\eta^3\text{-C}_8\text{H}_{13})(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  with  $\text{PPh}_3$  in  $\text{CH}_2\text{Cl}_2$  at 25°C gave the *exo-nido* species

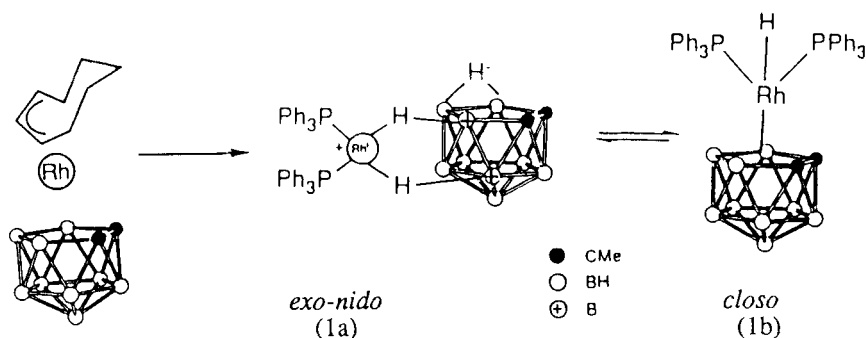


Fig. 1. The Reaction of the 16-Electron Compound [Rh(η<sup>3</sup>-C<sub>8</sub>H<sub>13</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] with PPh<sub>3</sub> and the *closo-exo-nido* Equilibrium in Solution

[*exo-nido*-Rh(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Me<sub>2</sub>)] (1a) which is in an equilibrium with the *closo* species, [RhH(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] (1b), in solution (Fig. 1).

Analytical, physical and <sup>31</sup>P{<sup>1</sup>H}, <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B NMR data for the complex [*exo-nido*-RhH(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Me<sub>2</sub>)] are given in Table I.

### NMR Spectra

The <sup>31</sup>P-{<sup>1</sup>H}-NMR data of the compound [Rh(η<sup>3</sup>-C<sub>8</sub>H<sub>13</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] (Table I) revealed two doublets at δ 44.8 [J(RhP) = 188 Hz] and δ 43.5 [J(RhP) = 143 Hz] in the ratio of *ca.* 2:1 which is attributed to the *exo-nido* and *closo* species, respectively. The <sup>1</sup>H NMR data (Table I) showed a multiplet for the terminal metal hydride of (1b) at δ -9.16 and a broad resonance at *ca.* δ -2.5 which indicated the presence of a B-H-B bridge in the *exo-nido* species (1a). As mentioned above, Hawthorne *et al.* reported the compound [RhH(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] obtained from the reaction of [RhCl(PPh<sub>3</sub>)<sub>3</sub>] and [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> or [*nido*-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> in absolute ethanol at reflux temperature. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum of (1a) displayed a doublet at δ 39.5 [J(RhP) = 125 Hz] and the <sup>1</sup>H NMR

**Table I.** NMR Data for ( $^{31}\text{P}\{^1\text{H}\}$ ,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ ) the Complex  
 $[\text{exo-nido-Rh}(\text{PPh}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_{10}\text{Me}_2)]$

$^{31}\text{P}_{\text{a,b,c}}$	44.8 [d, RhP, <i>nido</i> J(RhP) 188] 43.5 [d, RhP, <i>closo</i> J(RhP) 143]
$^1\text{H}_{\text{b,f}}$	*-9.16 [m, 1H, RhH], *2.17 (s, 6H, Me), 2.30 (s, 6H, Me), 7.12-7.85 (m, Ph)
$^{13}\text{C}_{\text{a,d,f}}$	135.7-134.1 (Ph), 72.0 (s, CMe), *70.6 (s, CMe), *29.4 (s, CMe), 28.5 (s, CMe)
$^{11}\text{B}_{\text{a,b,e}}$	3.5 (1B), -3,5 (2B), -8.8 (1B), -11.6 (3B), -14.1 (2B)

<sup>a</sup>Proton decoupled, <sup>b</sup>Chemical shifts in ppm, Coupling constants in Hz, Measurements in  $\text{CD}_2\text{Cl}_2$  at ambient temperatures. <sup>c</sup>Chemical shifts are relative to 85%  $\text{H}_3\text{PO}_4$  (external), <sup>d</sup>Chemical shifts are referenced versus  $\text{SiMe}_4$  (0.0 ppm), <sup>e</sup>Chemical shifts are referenced versus  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (external), <sup>f</sup>Peaks asterisked are due to minor isomer.

spectrum revealed a peak at  $\delta$  -8.40 [J(PH) = 29 Hz, J(RhH) = 17 Hz]. It should be noted that these data are in good agreement with those obtained for the complex (1b).

#### Reaction with $\text{PMe}_3$

The reaction of the compound  $[\text{Rh}(\eta^3\text{-C}_8\text{H}_{13})(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  with excess  $\text{PMe}_3$  and  $\text{PEt}_3$  has previously been investigated.<sup>11</sup> In the case of  $\text{PMe}_3$ , the reaction was carried out in  $\text{CH}_2\text{Cl}_2$  at 25°C and instead of the

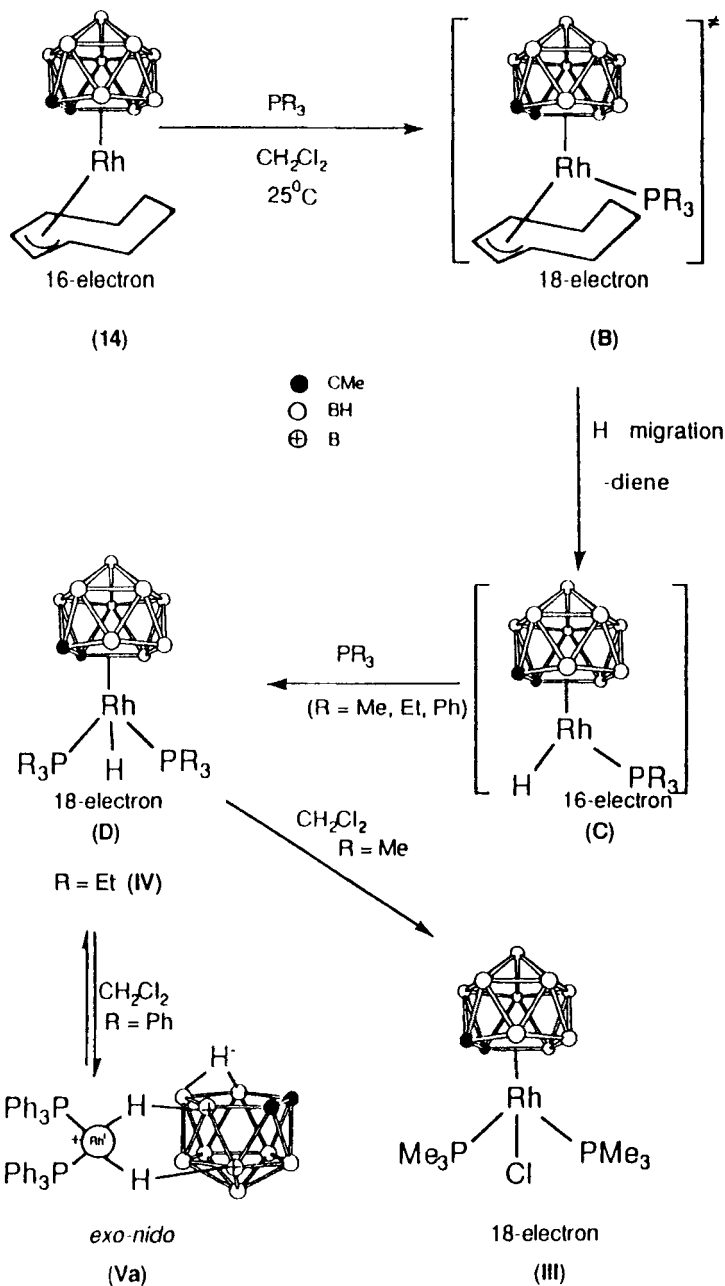
expected product, [Rh(PMe<sub>3</sub>)(η<sup>3</sup>-C<sub>8</sub>H<sub>13</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)], a chlorobis-(trimethylphosphine) species, formulated as [RhCl(PMe<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)], was obtained. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum of this compound revealed a doublet at δ 3.17 [J(RhP) = 125 Hz] which showed a PMe<sub>3</sub> group coordinated to rhodium. The molecular structure of the compound [RhCl(PMe<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] was fully established by a single crystal X-ray diffraction study.<sup>11</sup>

### Reaction with PEt<sub>3</sub>

The reaction between the compound [Rh(η<sup>3</sup>-C<sub>8</sub>H<sub>13</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] with excess PEt<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 25°C afforded the hydrido compound [RhH(PEt<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)]. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum displayed a doublet at δ 32.6 [J(RHP) = 135 Hz] and the <sup>1</sup>H NMR spectrum revealed a high-field resonance at δ -9.87 [t, J(PH) = 31 Hz].<sup>11</sup> Hawthorne *et al.*<sup>22</sup> have also obtained the compound [RhH(PEt<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] from the reaction of [Rh(PEt<sub>3</sub>)<sub>3</sub>[BF<sub>4</sub>]] and [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-</sup> in methanol.

### Proposed Mechanism for the Reaction of [Rh(η<sup>3</sup>-C<sub>8</sub>H<sub>13</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] with Phosphine Ligands

Related to the reactions of the compound [Rh(η<sup>3</sup>-C<sub>8</sub>H<sub>13</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] with phosphine ligands, a mechanism can be suggested for the reaction described herein. (Scheme 1). The first step of the reaction involves the addition of the phosphine ligand to the 16-electron compound [Rh(η<sup>3</sup>-C<sub>8</sub>H<sub>11</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] to form an 18-electron intermediate (B) in which both groups η<sup>3</sup>-C<sub>8</sub>H<sub>11</sub> and PR<sub>3</sub> are coordinated to the rhodium metal centre. Migration of a hydride from the η<sup>3</sup>-C<sub>8</sub>H<sub>13</sub> ligand to rhodium and loss of cyclooctadiene would then produce the 16-electron intermediate (C) which then reacts with an additional phosphine ligand to form the 18-electron hydride complex (D). In case of PPh<sub>3</sub>, a *closo-exo-nido* equilibrium is established. Examples of *closo-exo-nido* tautomers have been demonstrated and *exo-nido* rhodium species have been reported by



Scheme 1. Proposed Mechanism For The Complexes Formed by the Reaction of  $[\text{Rh}(\eta^3\text{-C}_8\text{H}_{13})(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  with  $\text{PR}_3$  (R = Me, Et, Ph) Ligands

Hawthorne *et al.*<sup>24</sup> They prepared the compound [Rh(PPh<sub>3</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>-{μ-(*o*-xylylene)})] by heating [RhCl(PPh<sub>3</sub>)<sub>3</sub>] with [Me<sub>3</sub>NH][*nido*-7,8-μ-(*o*-xylylene)-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] in ethanol. Reaction of this compound with two equivalents of PCy<sub>3</sub> (Cy = cyclohexyl) exchanged one PPh<sub>3</sub> by PCy<sub>3</sub> and produced a red-orange species. The distinguishing feature associated with rhodocarboranes of this class is the presence of an [RhL<sub>2</sub>]<sup>+</sup> (L = phosphine) moiety tightly held to a [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> fragment through the agency of a pair of B-H→Rh three-centre, two electron bonds. Since the carborane anion and the rhodium cation retain their formal charges in the *exo-nido* compounds, these species may be thought of as ion pairs whose Coulombic binding interaction is greatly augmented by the two *cis*-B-H→Rh bridge bonds.

Hawthorne *et al.*<sup>24</sup> suggested a general *closo-exo-nido* equilibrium for all phosphinerhodocarboranes derived from the isomeric *nido*-[C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> anions and their substituted derivatives. The *closo-exo-nido* tautomerism reported was formally viewed as a reversible oxidative addition-reductive elimination equilibrium in which the 12-electron [Rh(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> moiety oxidatively adds the B-H→B bridge system of the *nido*-carborane anion accompanied by η<sup>5</sup>-bonding to the open face of the anion.

#### *closo-exo-nido* Tautomerism

Hawthorne *et al.*<sup>24</sup> have reported that the *exo-nido* tautomers exhibited interesting behaviour in their <sup>1</sup>H NMR spectra in the B-H→B and Rh-H→B bridging region (*ca.* δ -2 to -8) which is consistent with the broad band at δ -2.5 observed for the compound [*exo-nido*-Rh(PPh<sub>3</sub>)<sub>2</sub>-(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)].

In the view of these results, interconversions between the tautomers (1a) and (1b) must be slow on the NMR time scale since peaks due to both the *closo* and *exo-nido* species were observed in the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra.

In the reaction of [Rh(η<sup>3</sup>-C<sub>8</sub>H<sub>11</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] with PEt<sub>3</sub>, the *closo*-hydrido complex [RhH(PEt<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] was obtained as the



final product and no peaks due to *exo-nido* species were observed in any of the spectra.<sup>11</sup>

It was reported that<sup>11</sup> the reaction between the compound  $[\text{Rh}(\eta^3\text{-C}_8\text{H}_{13})(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  and  $\text{PMe}_3$  afforded the *closo* chloro compound  $[\text{Rh}(\text{PMe}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  which was characterised by an X-ray diffraction study. It was suggested<sup>11</sup> that this reaction proceeds in the same way to produce the hydrido compound  $[\text{RhH}(\text{PMe}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  which subsequently exchanges the hydride ligand for chloride in  $\text{CH}_2\text{Cl}_2$  solution.

Hawthorne and co-workers<sup>22</sup> have synthesized *closo*-chlororhodacarborane complexes bearing phosphine ligands. The compound  $[\text{RhCl}(\text{PPh}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})]$  was prepared by heating the hydrido species  $[\text{RhH}(\text{PPh}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})]$  in  $\text{CHCl}_3$ -aqueous HCl, whereas the compound  $[\text{RhCl}(\text{PMe}_2\text{Ph})(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})]$  was simply obtained by recrystallisation of the compound  $[\text{RhH}(\text{PMe}_2\text{Ph})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})]$  in  $\text{CH}_2\text{Cl}_2$ .

It was reported<sup>22</sup> that a bright orange crystalline complex  $[\text{RhClH}(\text{PPh}_3)(\eta^5\text{-C}_2\text{B}_9\text{H}_{10}\text{Ph})]$  was obtained, as well as the expected chloro compound  $[\text{RhCl}(\text{PPh}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_{10}\text{Ph})]$ , when the complex  $[\text{RhClH}(\text{PPh}_3)(\eta^5\text{-C}_2\text{B}_9\text{H}_{10}\text{Ph})]$  was recrystallised slowly by layering heptane over a  $\text{CH}_2\text{Cl}_2$  solution of the complex.

## EXPERIMENTAL

The synthesis was carried out using Schlenk-tube techniques, under a dry, oxygen-free nitrogen atmosphere. All solvents were rigorously dried before use. Light petroleum refers to the fraction of b.p. 40-60°C.

Alumina used in chromatography columns (*ca.* 20 cm in length and 3.0 cm in diameter) was BDH aluminium oxide (Brockman Activity II). The NMR spectra were recorded on JEOL JNM FX90Q, GX270 or GX400 spectrometers. The compound  $[\text{Rh}(\eta^3\text{-C}_8\text{H}_{13})(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  was prepared by treating  $[\text{NEt}_4][\text{Rh}(\text{cod})(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  with excess  $\text{HBF}_4$  in  $\text{CH}_2\text{Cl}_2$  at -78°C, a method which is slightly different from the one described previously by Hawthorne *et al.*<sup>23</sup>

Preparation of the Complex [*exo-nido*-Rh(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)]

The complex [Rh(η<sup>3</sup>-C<sub>8</sub>H<sub>13</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)]<sup>23</sup> (0.20 g, 0.53 mmol) was treated with PPh<sub>3</sub> (0.14 g, 0.53 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) at 25°C and the mixture was stirred for *ca.* 8 h. The solvent was removed *in vacuo* and the residue was chromatographed on alumina. Elution with CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (1:3) afforded one major orange band. Removal of solvent *in vacuo* gave a red solution. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (1:4) gave brick-red microcrystals of [*exo-nido* Rh(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Me<sub>2</sub>)], m.p. 162 °C (decomp.); yield, 0.18 g (43 %).

*Anal.* Found: C, 58.4, H, 5.9, P, 7.6 %

Calcd. for C<sub>40</sub>H<sub>46</sub>P<sub>2</sub>B<sub>9</sub>Rh.1/2CH<sub>2</sub>Cl<sub>2</sub>: C, 58.5, H, 5.7, P, 7.5 %

M.W: 831.35

ACKNOWLEDGEMENT

This work was carried out at the University of Bristol, England. The author is grateful to Prof. F. G. A. Stone and Dr. J. C. Jeffery for their interest, encouragement and advice.

REFERENCES

1. M. F. Hawthorne, *Acc. Chem. Res.*, **1**, 281 (1968).
2. K. P. Callahan and M. F. Hawthorne, *Adv. Organomet. Chem.*, **14**, 145 (1976).
3. L. I. Zakharin and V. N. Kalinin, *Vsp. Khim.*, **43**, 1207 (1974).
4. J. A. Walker, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, **24**, 2688 (1985).
5. T. E. Paxson and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 4674 (1974).

6. R. T. Baker, M. S. DeLaney, R. E. King, C. B. Knobler, J. A. Long, T. B. Marder, T. E. Paxson, R. G. Teller and M. F. Hawthorne, *J. Am. Chem. Soc.*, **106**, 2965 (1984).
7. P. E. Behnken, J. A. Belmont, D. C. Busby, M. S. Delaney, R. E. King, C. W. Kreimendahl, T. B. Marder, J. J. Wilczynski and M. F. Hawthorne, *J. Am. Chem. Soc.*, **106**, 3011 (1984).
8. M. F. Hawthorne, "Advances in Boron and the Boranes", VCH, Weinheim, 1988; Chapter 10 and references therein.
9. M. U. Pilotti, I. Topaloğlu and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1355 (1991).
10. N. Carr, M. C. Gimeno, J. E. Goldberg, M. V. Pilotti, F. G. A. Stone and I. Topaloğlu, *J. Chem. Soc., Dalton Trans.*, 2253 (1990).
11. J. C. Jeffery, F. G. A. Stone and I. Topaloğlu, *Polyhedron*, **12**, 319 (1993).
12. D. M. Speckman, C. B. Knobler and M. F. Hawthorne, *Organometallics*, **4**, 1692 (1985).
13. R. B. King, P. M. Treichel and F. G. A. Stone, *Chem. Ind.*, 747 (1961).
14. D. A. Roberts and G. L. Geoffroy, "Comprehensive Organometallic Chemistry", Pergamon Oxford, Vol. 6, Chapter 40 (1982).
15. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **21**, 711 (1982).
16. F. G. A. Stone, *Adv. in Organomet. Chem.*, **31**, 53 (1990).
17. M. U. Pilotti, F. G. A. Stone and I. Topaloğlu, *J. Chem. Soc., Dalton Trans.*, 1621 (1991).
18. J. R. Fernandez, G. F. Helm, J. A. K. Howard, M. U. Pilotti and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1747 (1990).
19. J. E. Goldberg, J. A. K. Howard, H. Müller, M. U. Pilotti and F. G. A. Stone *J. Chem. Soc., Dalton Trans.*, 3055 (1990).

20. J. E. Goldberg, D. F. Mullica, E. L. Sappanfield, F. G. A. Stone, J. Chem. Soc., Dalton Trans., 2495 (1992).
21. J. E. Goldberg and F. G. A. Stone, Polyhedron, 11, 2841 (1992).
22. R. T. Baker, M. S. Delaney, R. E. King III, C. B. Knobler, J. A. Long, T. B. Marder, T. E. Paxson, R. G. Teller and M. F. Hawthorne, J. Am. Chem. Soc., 106, 2965 (1984).
23. D. M. Speakman, C. B. Knobler and M. F. Hawthorne, Organometallics, 4, 426 (1985).
24. J. A. Long, T. B. Marder, P. E. Behnken and M. F. Hawthorne, J. Am. Chem. Soc., 106, 2979 (1984).

Received: 28 November 1995  
Accepted: 2 May 1996

Referee I: L. Barton  
Referee II: L. J. Todd