

CHEMISTRY ON THE RHODACARBORANE CLUSTER [9,9-(PPh₃)-*nido*-9,7,8-RhC₂B₈H₁₁]: FORMATION OF BIDENTATE PHOSPHINE AND BIMETALLIC DERIVATIVES

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Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday.

The electronically unsaturated rhodacborane [9,9-(PPh₃)₂-*nido*-9,7,8-RhC₂B₈H₁₁] (**1**), reacts with Ph₂PCH₂PPh₂ (dppm) to afford [9,9-(dppm-κ²P)-9-(dppm-κP)-*nido*-9,7,8-RhC₂B₈H₁₁] (**3**), in which the Rh-bonded PPh₃ ligands have been replaced by two dppm ligands, one in a bidentate mode and the second in a unidentate mode with a free PPh₂ end. The structure of **3** is similar to the related, and isoelectronic, species [8,8-(dppm-κ²P)-8-(dppm-κP)-*nido*-8,7-RhSB₉H₁₀] (**4**), but with a difference in the orientation of the ligands. Reaction of **1** with Ph₂P(CH₂)₂PPh₂ (dppe) affords a species tentatively identified as [9,9-(dppe-κ²P)-9-(dppe-κP)-*nido*-9,7,8-RhC₂B₈H₁₁] (**5**). If allowed to react with [Ru(η⁶-*p*-cym)Cl₂]₂, (**3**) affords [9,9-{Ru(η⁶-*p*-cym)dppm-κ²P-(μ-Cl)₂}-*nido*-9,7,8-RhC₂B₈H₁₁] (**6**) containing the group [(μ-Cl)₂Ru(η⁶-*p*-cym)dppm] that coordinates in a multidentate mode to Rh. Compounds **3** and **6** are characterized by ¹¹B, ¹H and ³¹P NMR spectroscopy, elemental analysis and X-ray structure determinations.

Keywords: Carboranes; Metallacarboranes; Bidentate ligands; Rhodium; Ruthenium; Crystal structures; NMR ¹H, ¹¹B, ³¹P.

The area of heteroborane clusters has been extensively studied, especially the icosahedral carboranes and their derivatives which were discovered in the 1960's¹. Although the initial discoveries were made in North America, substantial contributions elsewhere were made soon afterwards, especially by the Czech group at Řež, co-founded by J. Plešek. The early contributions

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of the Plešek's group in borane chemistry included studies of the hydroborates², larger boranes³, and the icosahedral carboranes and their homologues⁴. It is in the latter area that this paper, dedicated to Prof. Plešek, is written. The related pair of metallaheteroboranes [9,9-(PPh₃)₂-*nido*-9,7,8-RhC₂B₈H₁₁] (**1**)⁵ and [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] (**2**)⁶, compounds which are formally isoelectronic, are two electrons short of the number notionally required to satisfy the polyhedral skeletal electron pair theory (PSEPT)⁷. The latter rhodathiaborane, **2**, is stable, easily prepared, and has been extensively studied by us⁸ and by others⁹⁻¹². Explanations have been proposed to account for the unusual electron count in these systems. One considers the unsaturation of the 16-electron metal center¹³ but alternative explanations have suggested the presence of two unusual *ortho*-CH...Rh agostic interactions^{9,12} which, it is suggested, account for its stability. We favor the former and we, and others¹⁴, have invoked this in descriptions of related systems which contain two electrons short of the number required by the PSEPT⁷. In this paper we extend our studies to the isoelectronic system **1** and undertake parallel studies to those we have under way for **2**.

EXPERIMENTAL

Solvents used were reagent grade and were dried before use. Some reactions were carried out using a Schlenk line and standard techniques for handling air-sensitive compounds¹⁵. [9,9-(PPh₃)₂-*nido*-9,7,8-RhC₂B₈H₁₁] (**1**) was prepared according to the literature method⁵ from the reaction between 5,6-C₂B₈H₁₂ and [RhCl(PPh₃)₃]. 5,6-C₂B₈H₁₂ was prepared according to the method of Plešek *et al.*¹⁶ from C₂B₁₀H₁₂ (Katchem). PPh₃ and dppe were obtained from Aldrich and dppm was obtained from Strem. NMR spectroscopy was carried out on a Bruker ARX 500 spectrometer operating at 500.1 MHz for ¹H, 160.5 MHz for ¹¹B, and at 202.5 MHz for ³¹P. Chemical shifts are reported in ppm (δ -scale) for CD₂Cl₂ solutions to low field (high frequency) of Et₂O·BF₃ for ¹¹B, of SiMe₄ for ¹H and of 85% H₃PO₄ for ³¹P. Coupling constants (*J*) are given in Hz. Elemental analyses were attempted by Atlantic Microlabs Inc., Norcross (GA). NMR spectra were run on all samples sent for mass spectra and crystal growth was generated from NMR samples, after spectral analysis. The samples were evaporated to dryness and then dissolved in the appropriate solvent for subsequent crystallization. Mass spectra were measured in the FAB mode on a JEOL MStation JMS-700 spectrometer using 3-nitrobenzyl alcohol (3-NBA).

Preparation of [9,9-(dppm- κ^2P)-9-(dppm- κP)-*nido*-9,7,8-RhC₂B₈H₁₁] (**3**)

To a solution of [9,9-(PPh₃)₂-*nido*-9,7,8-RhC₂B₈H₁₁] (**1**) (50 mg, 0.067 mmol) in 20 ml of CH₂Cl₂ was added dppm (80 mg, 0.21 mmol) under nitrogen. After 20 min of stirring, the reaction mixture was passed through silica gel (EM Science) and a yellow band was collected and solvent removed *in vacuo*. The residue was recrystallized from CH₂Cl₂/EtOH and characterized as [9,9-(dppm- κ^2P)-9-(dppm- κP)-*nido*-9,7,8-RhC₂B₈H₁₁] (**3**) (49 mg, 0.049 mmol; 73%). For C₅₂H₅₅B₈P₄Rh calculated: 62.88% C, 5.58% H; found: 63.06% C, 5.71% H. LR-MS

(FAB with 3-NBA): calculated 993.3 for $C_{52}H_{55}B_8P_4Rh$, found 992.5. The mass envelopes for the measured masses match quite well with those calculated from the known isotopic abundances of the constituent elements and are as follows [m/q , found intensity (calculated intensity)]: 991, 62.6 (32.5); 992, 87.7 (72.2); 993, 100.00 (100.00); 994, 92.6 (78.8); 995, 76.2 (31.03) for the molecular ion envelope. ^{11}B NMR (160.5 MHz, CD_2Cl_2 , 25 °C): 11.2 (v br, 2 B); -4.1 (v br, 1 B); -12.3 (v br, 1 B); -13.9 (v br, 1 B); -17.5 (v br, 1 B); -22.8 (d, $J(H,B)$ = 125, 1 B); -24.8 (d, $J(H,B)$ = 134, 1 B). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2 , 25 °C): 26.2 (dd, $J(P,Rh)$ = 119, $J(P,P)$ = 14, 1 P); 1.3 (br d, $J(P,Rh)$ = 115, 1 P); -11.9 (m, 1 P); -23.6 (s, 1 P). $^1H\{^{31}P\}$ NMR (500 MHz, CD_2Cl_2 , 25 °C): 8.21-6.54 (m, 42 H, C_6H_5 and $Ph_2PCH_2PPh_2$); 4.86 (d, $J(H,H)$ = 14, 1 H, $Ph_2PCH_2PPh_2$); 2.90 (d, $J(H,H)$ = 14, 1 H, $Ph_2PCH_2PPh_2$); 2.46 (s, 1 H, $C_2H_2B_8H_9$); 1.51 (s, 1 H, $C_2H_2B_8H_9$). Additional $^1H\{^{11}B\}$ NMR (500 MHz, CD_2Cl_2 , 25 °C): 3.94 (1 H, BH); 3.76 (2 H, BH); 3.50 (1 H, BH); 1.95 (1 H, BH); 1.58 (2 H, BH); 1.20 (1 H, BH); -2.03 (1 H, μ -H).

Preparation of [9,9-(dppe- κ^2P)-9-(dppe- κP)-*nido*-9,7,8-RhC₂B₈H₁₁] (5)

A 60 mg (0.08 mmol) portion of [9,9-(PPh₃)₂-*nido*-9,7,8-RhC₂B₈H₁₁] was dissolved in 20 ml of CH_2Cl_2 . The reaction system was evacuated and filled with nitrogen, then 100 mg (0.24 mmol) of dppe was added to the reaction flask. The resulting yellow solution was stirred at room temperature for 10 min. After this time, the solution was reduced in volume, and the reaction mixture was applied to the Chromatotron (a radial chromatograph obtained from Harrison Research, Palo Alto (CA)) using a 25 cm diameter circular plate coated with 0.1 cm of silica gel (EM Science) and CH_2Cl_2 /hexane (3 : 2) mixture as the mobile phase. A yellow component was isolated and after recrystallization from CH_2Cl_2 /hexane was identified as [9,9-(dppe- κ^2P)-9-(dppe- κP)-*nido*-9,7,8-RhC₂B₈H₁₁] (5) (61 mg, 0.06 mmol; 75%). Elemental analysis data were unsatisfactory. LR-MS (FAB with 3-NBA): calculated 1 020.34 for $C_{54}H_{59}P_4B_8Rh$, found 1 020.68. The mass envelopes for the measured masses match quite well with those calculated from the known isotopic abundances of the constituent elements and are as follows [m/q , found intensity (calculated intensity)]: 1 018, 42.3 (9.36); 1 019, 62.7 (32.15); 1 020, 100.00 (100.00); 1 022, 87.8 (79.73); 1 023, 57.2 (32.3); 1 024, 42.12 (8.33) for the molecular ion envelop. ^{11}B NMR (160.5 MHz, CD_2Cl_2 , 25 °C): 12.1 (v br, 2 B); -6.3 (v br, 1 B); -11.3 (v br, 1 B); -13.5 (v br, 1 B); -17.8 (v br, 1 B); -22.8 (d, $J(H,B)$ = 125, 1 B); -23.4 (d, $J(H,B)$ = 111, 1 B). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2 , 25 °C): 51.4 (v br, 1 P); 37.7 (v br, 1 P); 22.3 (br d, $J(P,Rh)$ = 105, 1 P); -10.1 (d, $J(P,P)$ = 34, 1 P). 1H NMR (500 MHz, CD_2Cl_2 , 25 °C): 8.11-6.23 (m, 40 H, C_6H_5); 3.29 (br m, 2 H, $Ph_2PC_2H_4PPh_2$); 2.86 (br m, 2 H, $Ph_2PC_2H_4PPh_2$); 2.52 (s, 1 H, $C_2H_2B_8H_9$); 2.25-2.09 (br m, 4 H, $Ph_2PC_2H_4PPh_2$); 1.87 (s, 1 H, $C_2H_2B_8H_9$). Additional $^1H\{^{11}B\}$ NMR (500 MHz, CD_2Cl_2 , 25 °C): 4.33 (1 H, BH); 3.81 (2 H, BH); 3.40 (1 H, BH); 1.55 (1 H, BH); 1.43 (2 H, BH); 1.26 (1 H, BH); -2.77 (1 H, μ -H).

Preparation of [9,9-{Ru(η^6 -*p*-cym)dpmm- κ^2P -(μ -Cl)₂}-*nido*-9,7,8-RhC₂B₈H₁₁] (6)

A sample of [Ru(η^6 -*p*-cym)Cl₂]₂ (12 mg, 0.02 mmol) was added under nitrogen to a solution of [9,9-(dpmm- κ^2P)-9-(dpmm- κP)-*nido*-9,7,8-RhC₂B₈H₁₁] (3) (20 mg, 0.02 mmol) in CH_2Cl_2 (ca 10 ml) and stirred overnight at room temperature. Then the solution was filtered over SiO₂ to remove chromatographically immobile components. Addition of hexane gave rise to the isolation of 14 mg of a brown product, which was characterized as [9,9-{Ru(η^6 -*p*-cym)dpmm-

$\kappa^2P-(\mu-Cl)_2$ -*nido*-9,7,8-RhC₂B₈H₁₁·C₆H₁₄] (**6**) (0.014 mmol; 70%). For C₃₇H₄₇B₈Cl₂P₂RhRu·C₆H₁₄ calculated: 51.58% C, 6.14% H; found: 52.24% C, 5.56% H. Single crystals of this compound precipitated from CH₂Cl₂/MeOH mixture. ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C): 14.7 (d, *J*(H,B) = 113, 1 B); 11.6 (br, 1 B); 5.2 (d, *J*(H,B) = 122, 1 B); -6.9 (br, 1 B); -17.6 (br, 1 B); -20.9 (d, *J*(H,B) = 125, 1 B); -23.7 (d, *J*(H,B) = 132, 1 B); -25.5 (d, *J*(H,B) = 129, 1 B). ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂, 25 °C): 25.1 (d, *J*(P,P) = 11, 1 P); 23.1 (dd, *J*(P,Rh) = 144, *J*(P,P) = 11, 1 P). ¹H NMR (500 MHz, CD₂Cl₂, 25 °C): 7.76–6.91 (m, 20 H, C₆H₅); 5.71 (d, *J*(H,H) = 6, 1 H, MeC₆H₄CHMe₂); 5.29 (d, *J*(H,H) = 6, 1 H, MeC₆H₄CHMe₂); 4.95 (d, *J*(H,H) = 6, 1 H, MeC₆H₄CHMe₂); 4.62 (d, *J*(H,H) = 6, 1 H, MeC₆H₄CHMe₂); 4.22 and 3.18 (each td, *J*(H,H) = 13, *J*(H,P) = 14, 2 H, Ph₂PCH₂PPh₂); 3.89 (s, 1 H, C₂H₂B₈H₉); 3.06 (s, 1 H, C₂H₂B₈H₉); 2.50 (sept, *J*(H,H) = 7, 1 H, MeC₆H₄CHMe₂); 1.81 (s, 3 H, MeC₆H₄CHMe₂); 1.23 (d, *J*(H,H) = 7, 3 H, MeC₆H₄CHMe₂); 1.01 (d, *J*(H,H) = 7, 3 H, MeC₆H₄CHMe₂). Additional ¹H{¹¹B} NMR (500 MHz, CD₂Cl₂, 25 °C): 3.34 (2 H, BH); 2.83 (1 H, BH); 1.60 (1 H, BH); 1.09 (1 H, BH); 0.45 (3 H, BH); -1.05 (1 H, μ -H).

Crystal Structure Determination¹⁷

Crystals of **3** were grown from CH₂Cl₂/MeOH/EtOH and **6** were grown from CH₂Cl₂/MeOH. Crystals of appropriate dimensions were mounted on glass fibers in random orientations. Preliminary examination and data collection were performed using a Bruker SMART Charge Coupled Device (CCD) Detector system single crystal X-ray diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) equipped with a sealed tube X-ray source at -93 °C. Preliminary unit cell constants were determined with a set of 45 narrow frames (0.4° in ω) scans. The data set collected consists of 3 636 frames with a frame width of 0.3° in ω and counting time of 15 s/frame at a crystal to detector distance of 4.930 cm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages^{17a} were used for data collection and data integration, respectively. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of xyz centroids of 9 108 and 7 107 reflections ($\theta < 27^\circ$), for **3** and **6**, respectively. Collected data were corrected for systematic errors using SADABS^{17b} based on the Laue symmetry using equivalent reflections.

Crystal data and intensity data collection parameters are listed in Table I. Structure solution and refinement were carried out using the SHELXTL software package^{17c}. The structures were solved by direct methods and refined successfully in the space groups *Pbcn* and *P2₁/n* for **3** and **6**, respectively. Full matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. All boron cage hydrogen atoms for **3** and **6** were located and refined freely except H(7c) in the case of **3** and H(3) in case of **6**. These two and rest of the hydrogen atoms were treated using an appropriate riding model (AFIX m3). The final residual values for **3** and **6** were: $R(F) = 10.2\%$ for 8 816 observed reflections and 10.45% for 5 679 observed reflections [$I > 2\sigma(I)$]; $wR(F^2) = 19.8$ and 20.5% for all unique data. Compound **3** has some disordered solvent molecules in the lattice which were modeled as MeOH, EtOH and water (1 molecule each). Structure refinement parameters are listed in Table I. Selected bond distances and bond angles for **3** and **6** are given in Tables II and III, respectively. CCDC 183334 (**3**) and CCDC 183335 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the

TABLE I

Crystal data and structure refinement for [9,9-(dppm- κ^2P)-9-(dppm- κP)-*nido*-9,7,8-RhC₂B₈H₁₁] \cdot EtOH \cdot MeOH \cdot H₂O (**3**) and [9,9-{Ru(η^6 -*p*-cym)dppm- κ^2P -(μ -Cl)₂}-*nido*-9,7,8-RhC₂B₈H₁₁] (**6**)

Parameter	3	6
Empirical formula	C ₅₅ H ₆₇ B ₈ O ₃ P ₄ Rh	C ₃₇ H ₄₇ B ₈ Cl ₂ P ₂ RhRu
Formula weight	1 089.36	915.05
Temperature, K	223(2)	223(2)
Wavelength, Å	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	<i>Pbcn</i>	<i>P2₁/n</i>
<i>a</i> , Å	19.6738(10)	10.359(3)
<i>b</i> , Å	19.5777(9)	22.995(7)
<i>c</i> , Å	29.1315(15)	16.978(5)
α , °	90	90
β , °	90	97.73(2)
γ , °	90	90
<i>V</i> , Å ⁻³	11 220.5(10)	4 008(2)
<i>Z</i>	8	4
<i>D</i> (calc.), mg m ⁻³	1.290	1.517
Absorption coefficient, mm ⁻¹	0.460	1.029
Crystal size, mm	0.36 \times 0.28 \times 0.12	0.38 \times 0.22 \times 0.10
<i>F</i> (000)	4 528	1 848
θ range for data collection, °	1.63 to 25.00	1.50 to 26.00
Index ranges	-23 $\leq h \leq$ 23, -23 $\leq k \leq$ 23, -34 $\leq l \leq$ 34	-12 $\leq h \leq$ 12, -28 $\leq k \leq$ 28, -200 $\leq l \leq$ 200
Reflections collected	170 853	34 724
Independent reflections	9 869 [<i>R</i> (int) = 0.12]	7 811 [<i>R</i> (int) = 0.11]
Max. and min. transmission	0.9468 and 0.8518	0.9041 and 0.6957
Data, restraints, parameters	9 869, 57, 680	7 811, 1, 503
Goodness-of-fit on <i>F</i> ²	1.327	1.127
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.1019	<i>R</i> 1 = 0.1045, <i>wR</i> 2 = 0.1
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1920	<i>R</i> 1 = 0.1472, <i>wR</i> 2 = 0.2
Largest difference peak and hole, e Å ⁻³	1.355 and -0.903	4.706 and -2.801

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RESULTS AND DISCUSSION

Reaction of [9,9-(PPh₃)₂-*nido*-9,7,8-RhC₂B₈H₁₁] (**1**) with dppm in CH₂Cl₂ followed by workup affords the species [9,9-(dppm-κ²P)-9-(dppm-κP)-*nido*-9,7,8-RhC₂B₈H₁₁] (**3**) as a yellow crystalline in 73% yield. Compound **3** is analogous to [8,8-(dppm-κ²P)-8-(dppm-κP)-*nido*-8,7-RhSB₉H₁₀] (**4**), obtained from the reaction of the isoelectronic rhodathiaborane [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] (**2**), but, as we show later, the structure is different (Chart 1). Compound **3** was identified by conventional spectral and analytical methods. The NMR data are completely consistent with the structure seen in Chart 1. They indicate the presence of eight boron atoms and eleven protons associated with the cage. ¹¹B resonances in 2 : 1 : 1 : 1 : 1 : 1 : 1

TABLE II

Selected bond distances (in Å) and angles (in °) in [9,9-(dppm-κ²P)-9-(dppm-κP)-*nido*-9,7,8-RhC₂B₈H₁₁] (**3**)

Rh9-B4	2.214(8)	B5-Rh9-B10	47.6(3)
Rh9-B5	2.214(8)	C8C-Rh9-P1	95.3(2)
Rh9-B10	2.227(8)	B5-Rh9-P1	144.8(2)
Rh9-P1	2.349(2)	B4-Rh9-P1	140.9(2)
Rh9-P2	2.392(2)	B10-Rh9-P1	97.4(2)
Rh9-P3	2.356(2)	C8C-Rh9-P3	165.0(2)
P1-C1	1.837(7)	B5-Rh9-P3	88.1(2)
P2-C1	1.848(7)	B4-Rh9-P3	119.1(2)
B4-B5	1.826(11)	B10-Rh9-P3	93.8(2)
B10-B11	1.890(11)	P1-Rh9-P3	99.71(6)
B11-C7C	1.659(11)	C8C-Rh9-P2	91.19(2)
C7C-C8C	1.530(10)	B5-Rh9-P2	142.9(2)
P1-Rh9-P2	71.22(6)	C1-P1-Rh9	94.6(2)
P3-Rh9-P2	94.21(7)	C1-P2-Rh9	92.9(2)
C2-P1-Rh9	118.2(2)	P1-C1-P2	97.1(2)
C8C-Rh9-B5	79.2(3)	B4-Rh9-P2	99.7(2)
C8C-Rh9-B4	46.0(3)	B10-Rh9-P2	167.1(2)

TABLE III

Selected bond distances (in Å) and angles (in °) in [9,9-{Ru(η^6 -*p*-cym)dppm- κ^2 P-(μ -Cl)₂}-*nido*-9,7,8-RhC₂B₈H₁₁}] (6)

Rh9-B10	2.140(12)	Rh9-B5	2.149(13)
Rh9-C8'	2.151(10)	Rh9-B4	2.154(14)
Rh9-P2	2.304(3)	Rh9-Cl1	2.582(3)
Rh9-Cl2	2.647(3)	Ru1-P1	2.349(3)
Ru1-Cl1	2.426(3)	Ru1-Cl2	2.435(3)
B10-B11	1.89(2)	B11-C7'	1.70(2)
C7'-C8'	1.506(16)	Ru1-centroid	1.74(2)
B10-Rh9-B5	49.1(5)	B10-Rh9-C8'	84.7(5)
B5-Rh9-C8'	80.4(4)	B10-Rh9-B4	86.9(5)
B5-Rh9-B4	49.7(5)	C8'-Rh9-B4	45.9(5)
B10-Rh9-P2	96.8(4)	B5-Rh9-P2	94.1(3)
C8'-Rh9-P2	171.2(3)	B4-Rh9-P2	125.5(4)
B10-Rh9-Cl1	173.2(4)	B5-Rh9-Cl1	130.4(4)
C8'-Rh9-Cl1	88.6(3)	B4-Rh9-Cl1	89.1(4)
P2-Rh9-Cl1	89.90(9)	B10-Rh9-Cl2	104.6(4)
B5-Rh9-Cl2	153.7(4)	C8'-Rh9-Cl2	100.3(3)
B4-Rh9-Cl2	143.9(3)	P2-Rh9-Cl2	87.67(9)
Cl1-Rh9-Cl2	75.75(10)	P1-Ru1-Cl1	87.43(10)
C3-Ru1-Cl2	142.4(4)	C4-Ru1-Cl2	164.3(4)
C5-Ru1-Cl2	126.8(4)	C6-Ru1-Cl2	97.7(4)
C2-Ru1-Cl2	106.7(4)	C1-Ru1-Cl2	87.0(4)
P1-Ru1-Cl2	86.57(9)	Cl1-Ru1-Cl2	82.67(10)
Ru1-Cl1-Rh9	101.30(10)	Ru1-Cl2-Rh9	99.25(11)
C8'-B4-Rh9	67.0(6)	B5-B10-Rh9	65.7(6)
B10-B5-B1	111.1(9)	B10-B5-B6	61.0(8)
B10-B5-Rh9	65.2(6)	B6-B5-Rh9	117.2(8)
B1-B5-Rh9	117.9(8)	B1-B4-Rh9	118.1(8)
C7'-C8'-Rh9	120.9(8)	B11-B10-Rh9	110.7(8)

ratio, in the ascending frequency direction, suggest a cage with no symmetry. This latter is also indicated in the ^1H NMR spectrum in which signals in the relative area ratio 1 : 2 : 1 : 1 : 2 : 1, corresponding to terminal BH groups, are observed. In addition a bridging H atom is seen upfield at -2.03 ppm and the cage H(C-H) resonances are seen at 2.46 and 1.51 ppm. The ^1H and ^{11}B spectra are also quite similar to those for [8,8-(dppm- $\kappa^2\text{P}$)-8-(dppm- κP)-*nido*-8,7-RhSB $_9$ H $_{10}$] (**4**). As expected four signals are observed in the ^{31}P spectrum (26.2, 1.3, -11.9 and -23.6) and they are tentatively assigned as follows. The P atom numbering is given in Chart 1. The resonance at -23.6 is assigned to P(4) since is expected to fall closest to that of the free ligand dppm (-22.26). The two doublets that couple strongly to the Rh are assigned to P(1) and P(2) which leaves the multiplet at -11.9 ppm as P(3). This assignment is supported by our observations for **5** below.

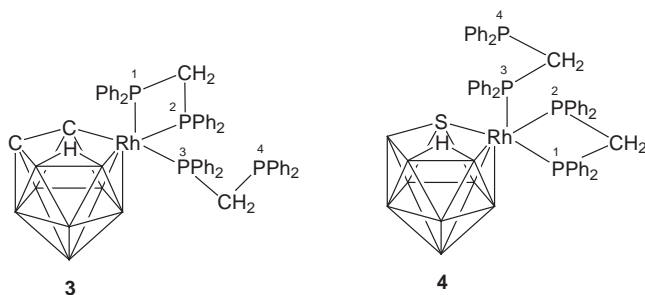


CHART 1

Crystals suitable for a diffraction study were grown from $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{EtOH}$ solutions and the structure is given in Fig. 1. The structure clearly resembles that of **4** but an important difference is that the bidentate ligand in **4** lies in the plane of the open face of the RhSB $_9$ cage whereas in **3** the bidentate dppm ligand bridges axial and equatorial positions and the monodentate one occupies the other equatorial (in the plane of the open face) position. This is illustrated in Chart 1. Actual bond distances and angles are very similar in **3** and **4** and we have no explanation for the difference in structure. In both **3** and **4**, the orientation around the Rh atom is pseudo-octahedral and very similar indeed, in spite of the differing arrangement of ligands. The angles P(3)-Rh-C(8C) and P(2)-Rh-B(10) in **3** are *ca* 165.0 and 167.1°, respectively, whereas the related angles in **4** are 174.4 and 157.3°^{8b}. In both molecules a Rh-P vector is directed perpendicular to the open face of the cage, again in spite of the fact that in **3** the P atom is part of a bidentate ligand whereas for **4** the P atom has the freedom of a monodentate ligand. Thus the angles P(1)-Rh-P(3), P(1)-Rh-P(2),

P(1)–Rh–C(8C) and P(1)–Rh–B(10), are 99.72(6), 71.72(6), 95.3(2) and 97.5(2)° for **3** and the corresponding angles in **4** are 99.12(7), 108.1(3), 97.24(7) and 83.5(2)°, respectively. If there is a constraining aspect of the coordination around the Rh, then perhaps there would be a difference in the P–C–P angles in the dpmm ligands; however, these are quite similar, at 97.1 and 96.0°, respectively, in **3** and **4**.

During our studies of complex **2**, we found that analogues of **4** were not obtained when the bases Ph₂P(CH₂)₂PPh₂ (dppe) or Ph₂P(CH₂)₃PPh₂ (dppp) were allowed to react with it^{8b}. Rather we found that species containing one bidentate ligand on Rh, which replaces the two PPh₃ ligands, or species containing two ligands in which one has transferred to the boron cage, displacing a H atom which “moves” to the Rh atom. We had surmised that the dpmm ligand did not transfer to the cage although some recent results, a discussion of which is beyond the scope of this paper, suggest that this may not be true^{8d}. Thus we expected something different from the results of the reaction of **1** with dppe and dppp. Reaction of dppe with **1** under the same conditions as for the reaction with dpmm gave an unstable product, identified by NMR spectroscopy and mass spectrometry as [9,9-(dppe-κ²P)-9-(dppe-κP)-*nido*-9,7,8-RhC₂B₈H₁₁] (**5**). NMR spectra suggested a rhoda-

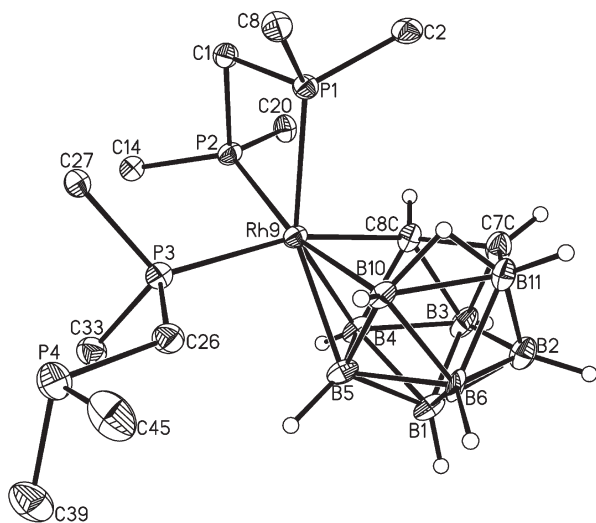


FIG. 1

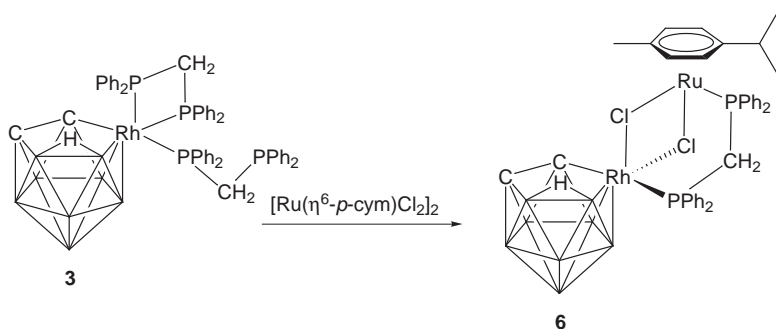
A view of the molecular structure of **3** with 30% thermal ellipsoids. Only the *ipso*-carbon atoms on the phenyl groups and the cage H atoms are included to aid clarity. Also omitted are solvent molecules

dicarbaundecaborane cage with two dppe ligands bonded to the Rh, one in a bidentate manner and the other monodentate. The ^1H and ^{11}B NMR spectra are very similar to those for **3**; the ^{11}B spectrum indicating the presence of eight boron atoms and the ^1H spectrum identifying eight terminal BH groups, two CH groups and a bridging H atom. The ^{31}P NMR spectra were key to identifying the coordination details. Four resonances are observed falling at 51.4, 37.7, 22.3 and -10.1 ppm. The two low-field ones, which couple to both Rh and P, are assigned to a bidentate dppe ligand from comparison with the spectra of $[8,8\text{-}(\text{dppe-}\kappa^2\text{P})\text{-nido-}8,7\text{-RhSB}_9\text{H}_{10}]$ ^{8b} for which the two ^{31}P resonances are observed at *ca* 66 and 49 ppm. The resonance at -10.1 ppm is assigned to the pendent PPh_2 group since its chemical shift is close to that for the free ligand (-11.9) and this is what we have observed for related systems containing such dangling PPh_2 groups. This leaves the remaining PPh_2 group which is assigned to the P(3), the P atom of the monodentate ligand bonded directly to Rh which couples strongly to the Rh. We were unable to grow crystals suitable for X-ray analysis nor to obtain satisfactory elemental analysis. Compound **5** was quite unstable and the related species obtained from dppp was even more difficult to handle. Mass spectral data for **5** are consistent with the formulation and we are confident that we indeed isolated and characterized **5**. On the other hand, it is not clear to us why the chemistry of the dppe and dppp adducts of the RhC_2B_8 cage are so different from those of the RhSB_9 cage.

An important consequence of the preparation of **3** is that the range of chemistry exhibited by **4** is potentially available for **3**. The molecular cage is effectively the same as **4** except that the S-BH moiety in the open face is replaced by a HC-CH group. Thus **3**, similar to **4**, with three electron pair donors on the Rh atom, has 26 skeletal electrons and thereby conforms to the *nido* classification both structurally and electronically. We had originally avoided the carborane system **1** because species containing less crowded phosphine ligands have a tendency to rearrange to afford the *iso-nido* species^{5,18}, but this was not reported for the PPh_3 derivatives and we observed no such rearrangement. We had reported earlier that **4** will react with $[\text{Ru}(\eta^6\text{-}p\text{-cym})\text{Cl}_2]_2$ leading to the formation of a new bimetallic complex, $[8,8\text{-}\eta^2\text{-}\{\text{Ru}(\eta^6\text{-}p\text{-cym})\text{dppm-}\kappa^2\text{P-}(\mu\text{-Cl})_2\}\text{-nido-}8,7\text{-RhSB}_9\text{H}_{10}]$ (**6**), containing the group $[(\mu\text{-Cl})_2\text{Ru}(\eta^6\text{-}p\text{-cym})\text{Ph}_2\text{PCH}_2\text{PPh}_2]$ that coordinates in a multidentate mode to Rh^{8c}. Thus we decided to see if the same chemistry was manifested by the isoelectronic species **3**.

Reaction between $[\text{Ru}(\eta^6\text{-}p\text{-cym})\text{Cl}_2]_2$ and $[9,9\text{-}(\text{dppm-}\kappa^2\text{P})\text{-}9\text{-}(\text{dppm-}\kappa\text{P})\text{-nido-}9,7,8\text{-RhC}_2\text{B}_8\text{H}_{11}]$ (**3**) in CH_2Cl_2 , affords a brown crystalline product,

[9,9-{Ru(η^6 -*p*-cym)dppm- κ^2 P-(μ -Cl) $_2$]-*nido*-9,7,8-RhC $_2$ B $_8$ H $_{11}$] (**6**) in 70% yield. Elemental analysis and NMR spectrometry support the identity of the species. The overall reaction is shown in Scheme 1.



SCHEME 1

During the formation of **6**, presumably the [Ru(η^6 -*p*-cym)Cl $_2$] $_2$ dimer is cleaved by the dangling PPh $_2$ group on **3**. This is then followed by replacement of the bidentate dppm ligand in **3** by a lone pair of electrons on each of the two Cl ligands on Ru. Crystals suitable for X-ray analysis precipitated from a CH $_2$ Cl $_2$ /MeOH mixture. The structure of **6** is given in Fig. 2 and it is

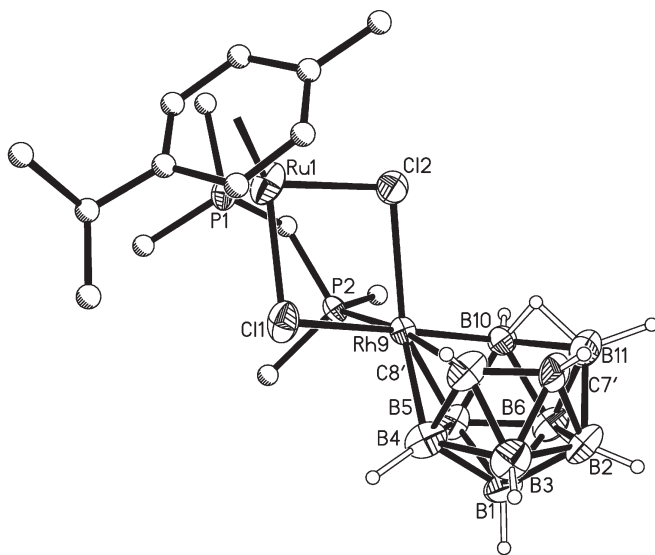


FIG. 2

A view of the molecular structure of **6** with 50% thermal ellipsoids. Only the *ipso*-carbon atoms on the phenyl groups and the cage H atoms are included to aid clarity. The *p*-cym ligand is shown as a ball and stick representation. Solvent molecules are omitted

an 11-vertex *nido*-rhodacarborane with an *exo*-polyhedral ligand chelating the rhodium center through a phosphine and a pair of Cl ligands on the Ru atom. The orientation around the Rh atom in **6** is pseudo-octahedral, as it is in the starting complex **3**. One Cl ligand, Cl(1), is in the plane of the open face of the cluster, *trans* to B(10), and the other, Cl(2), is perpendicular to the face *trans* to the B(4)–B(5) axis, with the Cl–Rh–Cl angle *ca* 76°. The P atom coordinated to Rh, which is P(2), is *trans* to C(8') and the angle P(2)–Rh–C(8') is 171.2(3)°. The Cl(1)–Rh–B(10) axis, perpendicular to the latter, and also essentially in the plane of the open cage face, is 173.2(2)°. The other angles around Rh are very close to octahedral and the four-atom ring Ru–Cl(2)–Rh–Cl(1) is almost a perfect square. The other angles in the “square” are Ru–Cl(1)–Rh, *ca* 101°, Ru–Cl(2)–Rh 99° and Cl(1)–Ru–Cl(2) 83°. The cage bond distances adjacent to the Rh atom in **6** are shorter in **3**, reflecting the influence of the Cl ligands.

Another interesting feature of **6** is the “chelating” ligand $[(\mu\text{-Cl})_2\text{Ru}(\eta^6\text{-}p\text{-cym})\text{dppm}]$. The orientation of the ligand is shown in the view of **6** given as Fig. 3. This view shows the open face of the cage pointing away

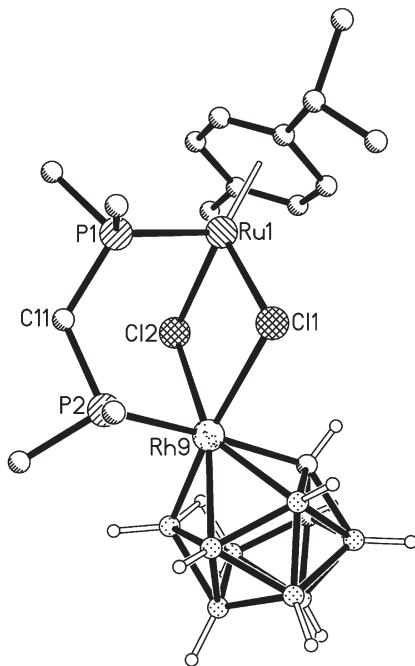


FIG. 3

A ball-and-stick view of **6** along the B(1)–B(2) axis

from the reader such that the axis B(1)–B(2) is perpendicular to the plane of the page. The view shows the nature of the two six-membered rings, Ru–P(1)–C(11)–P(2)–Rh–Cl. The ring involving Cl(1) is a distorted chair conformation and that involving Cl(2) is a distorted boat; the distortions arising from the octahedral arrangement around Rh rendering the three angles in each ring involving the Cl atoms relatively close to 90°. The other angles in the six-membered rings are normal, the interesting one, P(2)–C(11)–P(1) is *ca* 123°, in contrast to the angle P(1)–C(1)–P(2) in **3** which is *ca* 97°. The former angle is slightly larger than typical bond angles at the CH₂ group for dpmm ligands which are bridging two centers, for example in A-frame complexes¹⁹ but that latter conforms well to such angles for dpmm ligands chelating a metal center²⁰.

We have demonstrated that similar chemistry is available for the two systems **1** and **2** and we expect to note more similarities in their derivative chemistry. Species derived from **1** are less stable than those derived from **2**, and thus we have seen less success in developing the chemistry of **1** than we did of **2**. We expect to be reporting further on derivative chemistry of **1** and **2**.

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