



The first examples of  $\eta^5$ -bonding of a carbaborylphosphine ligand to transition metals. Synthesis and characterisation of  
7- $\{\text{PPh}_2\text{AuPPh}_3\}$ -8-Ph-7,8-nido- $\text{C}_2\text{B}_9\text{H}_{10}$ ,  
1- $\{\text{PPh}_2\text{AuCl}\}$ -2-Ph-3-(*p*-cymene)-3,1,2-pseudocloso- $\text{RuC}_2\text{B}_9\text{H}_9$  and  
1- $\{\text{PPh}_2\text{AuCl}\}$ -2-Ph-3-( $\eta$ - $\text{C}_5\text{Me}_5$ )-3,1,2-pseudocloso- $\text{RhC}_2\text{B}_9\text{H}_9$ <sup>1,2</sup>

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Received 26 May 1998

## Abstract

The closo carbaborylmonophosphine 1- $\text{PPh}_2$ -2-Ph-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$  is deboronated by reaction with  $\text{ClAuPPh}_3$  in refluxing ethanol to afford the zwitterionic compound 7- $\{\text{PPh}_2\text{AuPPh}_3\}$ -8-Ph-7,8-nido- $\text{C}_2\text{B}_9\text{H}_{10}$ , characterised by NMR spectroscopy and X-ray crystallography. Deprotonation of this species using NaH in THF followed by reaction with either  $[(p\text{-cymene})\text{RuCl}_2]_2$  or  $[(\eta\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$  yields the compounds 1- $\{\text{PPh}_2\text{AuCl}\}$ -2-Ph-3-(*p*-cymene)-3,1,2- $\text{RuC}_2\text{B}_9\text{H}_9$  and 1- $\{\text{PPh}_2\text{AuCl}\}$ -2-Ph-3-( $\eta\text{-C}_5\text{Me}_5$ )-3,1,2- $\text{RhC}_2\text{B}_9\text{H}_9$ , respectively. These latter products, which on the basis of <sup>11</sup>B-NMR spectroscopy and (in the first case) a single crystal diffraction analysis, have pseudocloso structures, are the first reported examples of compounds in which a carbaborylphosphine ligand is  $\eta^5$ -bonded to a transition metal. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Carbaborylphosphine ligand; NMR spectroscopy; Diffraction

## 1. Introduction

There is much current interest in the chemistry of heteroboranes with bulky substituents attached for a number of reasons; (i) such compounds can adopt exo-nido instead of more crowded closo structures (and as such display homogeneous catalytic activity) [1]; (ii) they can distort into unusual pseudocloso geometries [2]

not normally represented on the traditional Wade–Williams structural matrix; (iii) they can undergo low-temperature polytopal isomerisation [3] rendering possible experimental study [4] of the isomerisation process that has been the subject of intense theoretical interest over a number of years, including important contributions from Brian Johnson and co-workers. [5]

An important family of carbaboranes carrying sterically demanding exo-bonded substituents are the carbaborylphosphines, with carbaborylmonophosphines [6] and carbaboraldiphosphines [7] both being well known. Unfortunately, deboronation of these closo species (to prepare nido ligands suitable for complex formation with transition metals) by the conventional method ( $\text{OH}^-/\text{OR}^-$ ) typically leads to cleavage of the  $\text{C}_{\text{cage}}\text{-P}$  bond(s).

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<sup>1</sup> Steric effects in Heteroboranes. Part 20. For part 19 see reference [4]b.

<sup>2</sup> Dedicated to Professor Brian Johnson on the occasion of his 60th birthday.

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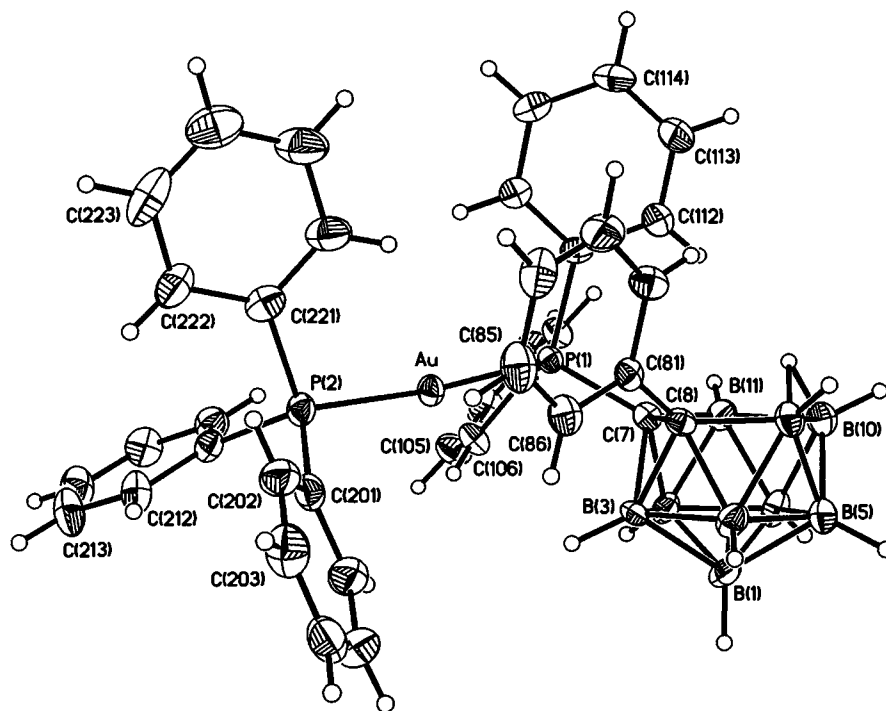


Fig. 1. Perspective view of **1**. Displacement ellipsoids are drawn at the 30% probability level, except for H atoms which have an artificial radius for clarity.

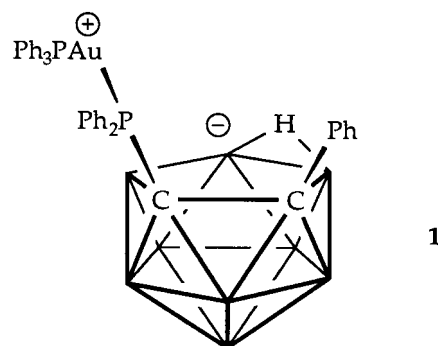
Recently, however, successful deboronation of 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> with Cu<sup>I</sup> [8] and Au<sup>I</sup> [9] species under base-free conditions has been reported. The products of these reactions, 7,8-((PPh<sub>2</sub>)<sub>2</sub>MPR<sub>3</sub>)-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub> are in principle able to function as η<sup>5</sup> ligands to metals following cage deprotonation, but steric pressure from the two PPh<sub>2</sub> units located on the open ligand face has so far prevented this from being realised.

Herein we report similar decapitation of the carbaborylmonophosphine 1-PPh<sub>2</sub>-2-Ph-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> to afford 7-((PPh<sub>2</sub>)<sub>2</sub>AuPPh<sub>3</sub>)-8-Ph-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub> (**1**). Deprotonation of **1** followed by reaction with [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> or [(η-C<sub>5</sub>Me<sub>5</sub>)RhCl<sub>2</sub>]<sub>2</sub> affords the first examples of a carbaborylphosphine ligand bonding in η<sup>5</sup> fashion to transition metals.

## 2. Results and discussion

Heating to reflux an ethanolic solution of 1-PPh<sub>2</sub>-2-Ph-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> [10] and ClAuPPh<sub>3</sub> affords the zwitterionic species 7-((PPh<sub>2</sub>)<sub>2</sub>AuPPh<sub>3</sub>)-8-Ph-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub> (**1**) in high yield. Compound **1** was characterised by multinuclear NMR spectroscopy, mass spectrometry, elemental analysis and a single-crystal X-ray diffraction study. In the <sup>11</sup>B{<sup>1</sup>H}-NMR spec-

trum are seen, in addition to resonances between –6 and –22 ppm, two resonances at low frequency (–31 and –35 ppm) characteristic of a nido species. The <sup>31</sup>P{<sup>1</sup>H} spectrum reveals two doublets (<sup>2</sup>J<sub>PP</sub> = 320 Hz) the higher frequency of which is the broader and tentatively assigned to C<sub>cage</sub>–P.



The molecular structure of **1** is shown in Fig. 1, and selected interatomic distances and interbond angles appear in Table 1. Successful deboronation of the closo carbaborylphosphine is confirmed, and the C(7)–C(8) distance in the carbaborane open face is 1.591(9) Å. The H atom bridging the B(9)–B(10) edge appears to do so asymmetrically, H(B)–B(9) 1.56(9) Å, H(B)–B(10) 1.14(9) Å. The phenyl substituent at

C(8) adopts a conformation defined by  $\theta = 6.5(9)^\circ$  [11] and the stereochemistry at Au in the  $\{\text{PPh}_2\text{AuPPh}_3\}$  substituent at C(7) is approximately linear,  $174.68(8)^\circ$ . Au–P(1) is 2.320 (2) Å and Au–P(2) 2.312(2) Å. Preliminary details of the related compound 7- $\{\text{PPh}_2\text{AuPPh}_3\}$ -8-SCH<sub>2</sub>Ph-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub> have recently been reported. [12]

Deprotonation [H(B)] of **1** with NaH in THF yields Na[7- $\{\text{PPh}_2\text{AuPPh}_3\}$ -8-Ph-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>]. Treatment of this salt with [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> in the same solvent affords the deep red compound 1- $\{\text{PPh}_2\text{AuCl}\}$ -2-Ph-3-(*p*-cymene)-3,1,2-pseudocloso-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> (**2**) in moderate yield following work-up involving preparative TLC. In the <sup>11</sup>B{<sup>1</sup>H}-NMR spectrum, **2** reveals seven resonances (two coincidences) between +36 and –19 ppm., the weighted average <sup>11</sup>B chemical shift,  $\langle \delta(^{11}\text{B}) \rangle$ , being +9.88 ppm. The equivalent value in 1,2-Ph<sub>2</sub>-3-(*p*-cymene)-3,1,2-pseudocloso-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> [2] is +5.58 ppm. However,  $\langle \delta(^{11}\text{B}) \rangle$  for **2** is fully consistent with a pseudocloso geometry once the differing  $\langle \delta(^{11}\text{B}) \rangle$  values of 1,2-Ph<sub>2</sub>-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (–10.66 ppm)

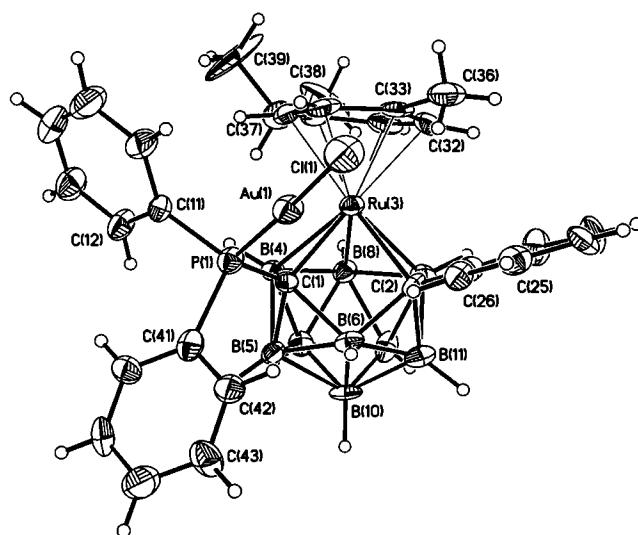
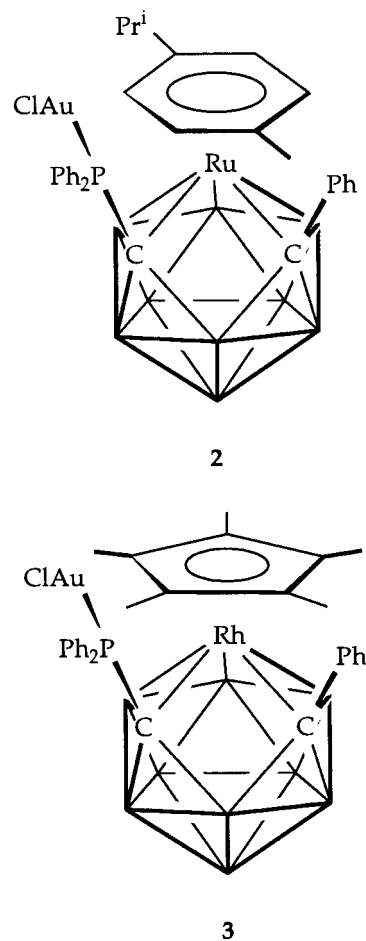


Fig. 2. Perspective view of **2**, showing only one component of the disordered isopropyl group for the sake of clarity. Displacement ellipsoids as in Fig. 1.

and 1-PPh<sub>2</sub>AuCl-2-Ph-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> [13] (–7.75 ppm) are taken into account.

Table 1  
Selected interatomic distances (Å) and interbond angles (°) for **1**

Au–P(2)	2.312(2)	Au–P(1)	2.320(2)
P(1)–C(111)	1.814(8)	P(1)–C(101)	1.816(8)
P(1)–C(7)	1.818(8)	P(2)–C(221)	1.813(9)
P(2)–C(201)	1.817(9)	P(2)–C(211)	1.822(9)
B(1)–B(2)	1.759(13)	B(1)–B(4)	1.774(14)
B(1)–B(6)	1.78(2)	B(1)–B(3)	1.778(13)
B(1)–B(5)	1.811(14)	B(2)–C(7)	1.742(11)
B(2)–B(6)	1.759(13)	B(2)–B(3)	1.771(13)
B(2)–B(11)	1.776(14)	B(3)–C(8)	1.722(10)
B(3)–C(7)	1.739(10)	B(3)–B(4)	1.770(13)
B(4)–C(8)	1.706(11)	B(4)–B(5)	1.775(14)
B(4)–B(9)	1.789(14)	B(5)–B(9)	1.77(2)
B(5)–B(10)	1.78(2)	B(5)–B(6)	1.83(2)
B(6)–B(11)	1.746(13)	B(6)–B(10)	1.77(2)
C(7)–C(8)	1.591(9)	C(7)–B(11)	1.630(11)
C(8)–C(81)	1.513(10)	C(8)–B(9)	1.651(12)
B(9)–B(10)	1.828(14)	B(10)–B(11)	1.81(2)
P(2)–Au–P(1)	174.68(8)	C(111)–P(1)–C(101)	106.9(3)
C(111)–P(1)–C(7)	105.8(4)	C(101)–P(1)–C(7)	107.6(3)
C(111)–P(1)–Au	109.8(3)	C(101)–P(1)–Au	109.5(3)
C(7)–P(1)–Au	116.8(2)	C(221)–P(2)–C(201)	107.9(4)
C(221)–P(2)–C(211)	105.2(4)	C(201)–P(2)–C(211)	105.4(4)
C(221)–P(2)–Au	109.5(3)	C(201)–P(2)–Au	112.6(3)
C(211)–P(2)–Au	115.7(3)	C(8)–C(7)–P(1)	116.4(5)
B(11)–C(7)–P(1)	120.0(5)	B(3)–C(7)–P(1)	114.8(5)
B(2)–C(7)–P(1)	119.4(5)	C(81)–C(8)–C(7)	119.8(6)
C(81)–C(8)–B(9)	119.0(6)	C(7)–C(8)–B(9)	109.1(6)
C(81)–C(8)–B(4)	120.6(6)	C(7)–C(8)–B(4)	111.4(6)
B(9)–C(8)–B(4)	64.4(6)	C(81)–C(8)–B(3)	117.7(6)
C(7)–C(8)–B(3)	63.2(4)	B(9)–C(8)–B(3)	115.6(6)
B(4)–C(8)–B(3)	62.2(5)		



The pseudocloso nature of **2** is confirmed by a crystallographic study. Fig. 2 presents a perspective view of one molecule and demonstrates the atomic numbering scheme used. Table 2 provides a summary of key molecular parameters. The C(1)⋯C(2) separation, 2.481(19) Å, and Ru(3)⋯B(6) separation, 2.940(14) Å, are typical for a pseudocloso carbametallaborane. The distortion results from intramolecular steric crowding, brought about in this case by the requirement of the Ph substituent on C(2) to adopt a high  $\theta$  conformation, 63.9(20)°, due to the presence of the capping {Ru(*p*-cymene)} unit. The presence of the {AuCl} fragment bonded to the P lone pair of electrons in **2** is unexpected, with the source of the Cl clearly the metal substrate. P–Au and Au–Cl distances, 2.244(4) and 2.285(4) Å, respectively, and the P–Au–Cl angle, 176.1(2)°, are typical. [13] Interestingly, one *p*-cymene ring H atom resonates at unusually high frequency (7.2 ppm) in the <sup>1</sup>H-NMR spectrum, ascribed to the adjacency of the {AuCl} unit.

Similarly, reaction of Na[7-{PPh<sub>2</sub>AuPPh<sub>3</sub>}-8-Ph-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>] with [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)RhCl<sub>2</sub>]<sub>2</sub> in THF yields orange 1-{PPh<sub>2</sub>AuCl}-2-Ph-3-( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)-3,1,2-closo-RhC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> (**3**). Although diffraction-quality crystals of **3** proved to be elusive, its pseudocloso nature is clearly demonstrated by a  $\langle \delta(^{11}\text{B}) \rangle$  value of +11.17 ppm.

Compounds **2** and **3** represent the first reported examples of  $\eta^5$ -bonded transition metal complexes of

Table 2  
Selected interatomic distances (Å) and angles (°) for **2**

Au(1)–P(1)	2.244(4)	Au(1)–Cl(1)	2.285(4)
P(1)–C(11)	1.801(13)	P(1)–C(41)	1.83(2)
P(1)–C(1)	1.858(13)	C(1)–C(2)	2.42(2)
C(1)–B(5)	1.62(2)	C(1)–B(4)	1.64(2)
C(1)–C(6)	1.72(2)	C(1)–Ru(3)	2.170(14)
C(2)–C(21)	1.49(2)	C(2)–B(11)	1.60(2)
C(2)–B(7)	1.64(2)	C(2)–B(6)	1.72(2)
C(2)–Ru(3)	2.136(11)	Ru(3)–B(4)	2.189(14)
Ru(3)–C(31)	2.207(14)	Ru(3)–B(7)	2.21(2)
Ru(3)–B(8)	2.209(14)	Ru(3)–C(32)	2.219(14)
Ru(3)–C(35)	2.251(12)	Ru(3)–C(34)	2.331(13)
Ru(3)–C(30)	2.341(14)	Ru(3)–C(33)	2.389(12)
B(4)–B(8)	1.77(2)	B(4)–B(9)	1.85(2)
B(4)–B(5)	1.87(2)	B(5)–B(10)	1.76(2)
B(5)–B(9)	1.80(2)	B(5)–B(6)	1.85(2)
B(6)–B(11)	1.80(2)	B(6)–B(10)	1.91(2)
B(7)–B(12)	1.81(2)	B(7)–B(8)	1.82(2)
B(7)–B(11)	1.84(2)	B(8)–B(9)	1.75(2)
B(8)–B(12)	1.78(2)	B(9)–B(12)	1.76(2)
B(9)–B(10)	1.78(2)	B(10)–B(11)	1.71(3)
B(10)–B(12)	1.73(2)	B(11)–B(12)	1.80(2)
P(1)–Au(1)–Cl(1)	176.1(2)	C(11)–P(1)–C(41)	106.3(7)
C(11)–P(1)–C(1)	108.0(6)	C(41)–P(1)–C(1)	106.1(6)
C(11)–P(1)–Au(1)	112.7(5)	C(41)–P(1)–Au(1)	108.1(5)
C(1)–P(1)–Au(1)	115.1(4)	B(5)–C(1)–P(1)	116.9(10)
B(4)–C(1)–P(1)	129.6(9)	B(6)–C(1)–P(1)	114.2(9)
B(6)–C(1)–Ru(3)	97.4(8)	P(1)–C(1)–Ru(3)	118.8(6)
B(6)–C(2)–Ru(3)	98.9(8)	C(2)–Ru(3)–C(1)	70.4(5)

carbaborylphosphine ligands. Previously, all transition metal complexes of carbaborylphosphines have either involved exo-metal fragments [14] or simple endo bridging ones [9]. In the case of compounds **2** and **3** we believe that having a single phosphine unit as substituent to the cage allows formation of  $\eta^5$ -metal complexation since the carbaborane is not able to function as a chelating ligand and has (at least relative to [7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>]<sup>2-</sup>) reduced steric blocking of the open ligand face. Nevertheless, there is clearly sufficient intramolecular crowding in **2** and **3** to distort the cluster geometries into pseudocloso forms.

Current studies are directed towards the synthesis of analogous species in which the P lone pair of electrons is not co-ordinated to an exo-metal fragment, and to a study of the polytopal isomerisations of this family of molecules. Since such rearrangements are expected to occur at relatively low temperatures they may provide experimental data by which to assess the various isomerisation mechanisms previously suggested by Johnson and others.

### 3. Experimental

#### 3.1. Synthesis and spectroscopy

All syntheses were performed under N<sub>2</sub> atmospheres using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. Solvents were freshly distilled from appropriate drying agents. NMR spectra were recorded from CDCl<sub>3</sub> solutions at r.t. on a Bruker AC200 (<sup>1</sup>H, 200.1 MHz; <sup>11</sup>B, 128.4 MHz; <sup>31</sup>P, 162.0 MHz) spectrometer, and chemical shifts are quoted relative to external TMS, BF<sub>3</sub>·OEt<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>, respectively. Elemental analyses were determined on an Exeter Analytical 440 microanalyser by the Departmental service at H-WU.

The starting materials 1-PPh<sub>2</sub>-2-Ph-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> [10], ClAuPPh<sub>3</sub> [15], [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> [16] and [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)RhCl<sub>2</sub>]<sub>2</sub> [17] were prepared by literature methods or slight variants thereof.

#### 3.2. Synthesis of 7-{PPh<sub>2</sub>AuPPh<sub>3</sub>}-8-Ph-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub> (**1**)

A solution of 1-PPh<sub>2</sub>-2-Ph-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (0.05 g, 1.24 mmol) in degassed EtOH (10 ml) was added to a stirring suspension of ClAuPPh<sub>3</sub> (0.61 g, 1.24 mmol) in the same solvent (30 ml) and the mixture heated to reflux for 2 h. Volatiles were removed in vacuo and CH<sub>2</sub>Cl<sub>2</sub> (20 ml) added to the resultant solid. After filtration through Celite (2 cm) further removal of solvent afforded a white solid. This was washed with EtOH (2 × 10 ml) and dried in vacuo to yield 0.083 g (78%) of the product, 7-{PPh<sub>2</sub>AuPPh<sub>3</sub>}-8-Ph-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub> (**1**).

Calcd. for  $C_{38}H_{40}AuB_9P_2$ ; C 53.5, H 4.72%. Found; C 53.2, H 4.75%.

NMR;  $^1H$   $\delta$  8.08–6.45 (Ph) ppm.  $^{31}P\{^1H\}$   $\delta$  55.9 (d, 1P) and 44.2 (d, 1P,  $^2J_{PP}$  320 Hz) ppm.  $^{11}B\{^1H\}$   $\delta$  – 6.1 (2B), – 8.35 (2B), – 13.16 (1B), – 17.41 (1B), – 21.86 (1B), – 30.94 (1B) and – 34.52 (1B) ppm.

### 3.3. Synthesis of 1-{PPh<sub>2</sub>AuCl}-2-Ph-3-(*p*-cymene)-3,1,2-pseudocloso-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> (2)

A solution of compound **1** (0.15 g, 0.176 mmol) in THF (15 ml) was added to a stirring suspension of NaH (ca. 0.02 g, 0.88 mmol) in the same solvent (10 ml). After 1 h undissolved material was allowed to settle and the supernatant solution was transferred by cannula to a stirring solution of [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (0.053 g, 0.088 mmol) in THF (10 ml). After further stirring for 1 h volatiles were removed in vacuo to reveal a red/brown solid. CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was added and the mixture filtered through Celite (2 cm) and concentrated to ca. 2 ml. Preparative TLC on silica using CH<sub>2</sub>Cl<sub>2</sub>/EtOAc (4:1) as eluant afforded two mobile bands. The slower moving of these was collected (by IR spectroscopy the faster moving band does not contain a heteroborane) and subsequently shown by  $^{31}P\{^1H\}$ -NMR spectroscopy to be a 1:2 mixture of 7-{PPh<sub>2</sub>AuPPh<sub>3</sub>}-8-Ph-9,10-( $\mu$ -AuPPh<sub>3</sub>)-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub> [18] and the target material 1-{PPh<sub>2</sub>AuCl}-2-Ph-3-(*p*-cymene)-3,1,2-pseudocloso-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> (**2**). Recrystallisation by slow diffusion of 60/80 petroleum ether and a CHCl<sub>3</sub> solution of **2** afforded 0.016 g (21%) of product as red plates.

Calcd. for C<sub>30</sub>H<sub>38</sub>AuB<sub>9</sub>ClPRu (crushed, dry powder); C 41.9, H 4.45%. Found; C 42.1, H 4.48%.

NMR;  $^1H$   $\delta$  8.35–8.24 (2H, Ph), 7.97–7.24 (13H, Ph), 7.18 6.02 5.25 and 4.61 (all d, 7Hz, C<sub>6</sub>H<sub>4</sub>), 2.34 (d of q, 7Hz 7Hz, CHMe<sub>2</sub>), 1.45 (s, 3H, Me), 0.97 (d, 7 Hz, CHMe) and 0.62 (d, 7 Hz, CHMe) ppm.  $^{31}P\{^1H\}$   $\delta$  62.4 (s) ppm.  $^{11}B\{^1H\}$   $\delta$  35.84 (1B), 22.68 (1B), 17.98 (1B), 15.95 (1B), 7.91 (2B), – 0.55 (2B) and – 18.22 (1B) ppm.

### 3.4. Synthesis of 1-{PPh<sub>2</sub>AuCl}-2-Ph-3-( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)-3,1,2-pseudocloso-RhC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> (3)

Similarly, compound **1** (0.15 g, 0.176 mmol) was deprotonated (NaH) and reacted with [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)RhCl<sub>2</sub>]<sub>2</sub> (0.054 g, 0.089 mmol) in THF. Work-up by column chromatography (15 cm) on silica, eluting with CH<sub>2</sub>Cl<sub>2</sub>/EtOAc (9:1), afforded a single orange mobile band of 1-{PPh<sub>2</sub>AuCl}-2-Ph-3-( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)-3,1,2-pseudocloso-RhC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> (**3**). Yield 0.018 g (12%).

Calcd. for C<sub>30</sub>H<sub>39</sub>AuB<sub>9</sub>ClPRu; C 41.7, H 4.55%. Found; C 42.1, H 4.83%.

NMR;  $^1H$   $\delta$  8.14–8.07 (2H, Ph), 7.89–7.86 (2H, Ph),

Table 3  
Crystal data and details of data collection and refinement

	Compound 1	Compound 2
Crystal colour, habit	Colourless plate	Red plate
Crystal size (mm)	0.50 × 0.32 × 0.12	0.61 × 0.42 × 0.08
Formula	C <sub>38</sub> H <sub>40</sub> AuB <sub>9</sub> P <sub>2</sub>	C <sub>30</sub> H <sub>38</sub> AuB <sub>9</sub> ClPRu.CHCl <sub>3</sub>
<i>M</i>	852.90	979.72
System	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell dimensions		
<i>a</i> (Å)	11.060(2)	13.626(2)
<i>b</i> (Å)	13.429(3)	20.5341(10)
<i>c</i> (Å)	15.078(3)	13.8129(11)
$\alpha$ (°)	113.568(11)	90.00
$\beta$ (°)	95.98(2)	98.084(12)
$\gamma$ (°)	107.549(8)	90.00
<i>U</i> (Å <sup>3</sup> )	1891.4(7)	3826.4(7)
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub>	1.498	1.701
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	4.00	4.57
$\theta$ <sub>orientation</sub> (°)	5.22–12.44	4.91–12.40
$\theta$ <sub>data collection</sub> (°)	1.5–25.00	1.7–25.00
<i>hkl</i> range	–1 ≤ <i>h</i> ≤ 13; –14 ≤ <i>k</i> ≤ 13; –17 ≤ <i>l</i> ≤ 17	–1 ≤ <i>h</i> ≤ 16; –1 ≤ <i>k</i> ≤ 24; –16 ≤ <i>l</i> ≤ 16
Data measured	14766	8025
Unique data <sup>a</sup>	6371	6668
Observed data [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	5326	3687
<i>R</i> , <i>wR</i> <sup>2</sup> (observed data)	0.0463, 0.1013	0.0631, 0.1126
Variables	454	469
<i>E</i> <sub>max</sub> , <i>E</i> <sub>min</sub> (e Å <sup>-3</sup> )	1.190, –1.098	1.097, –0.879

$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ ,  $wR^2 = \frac{[\sum (w(F_o^2 - F_c^2))^2]}{[\sum w(F_c^2)^2]^{1/2}}$ , where  $w^{-1} = [\sigma_c^2(F_o)^2 + (aP)^2 + bP]$  where  $P = [0.333 \max\{F_o, 0\} + 0.667(F_o)^2]$ ,  $S = \frac{[\sum (w(F_o^2 - F_c^2))^2 / (n - p)]^{1/2}}$  where *n* is the number of data and *p*, the number of parameters.

7.64–7.19 (11H, Ph), and 1.47 (s, 15H, Me) ppm.  $^{31}P\{^1H\}$   $\delta$  55.7 (s) ppm.  $^{11}B\{^1H\}$   $\delta$  41.26 (1B), 19.01 (2B), 12.84 (1B), 10.80 (1B), 7.81 (2B), – 0.02 (1B) and – 17.98 (1B) ppm.

### 3.5. Crystallographic studies

Crystals of **1** and **2** were grown by slow diffusion of chloroform solutions and 60/80 petroleum ether and were mounted in epoxy resin glue in a sealed thin-walled glass capillary. Data were collected at 293 K on a Siemens P4 diffractometer with the program XSCANS [19] by  $\omega$  scans. Standard reflections were re-measured every 100 data, and slight crystal decay (14.5% for **1** and 10% for **2**) was found and subsequently corrected. Data were further corrected for absorption by psi scans.

Both structures were solved by direct and difference Fourier methods and refined by full-matrix least-squares against  $F^2$ . All non-hydrogen atoms were refined with anisotropic thermal parameters. All exo-cage, phenyl and methyl H atom positions were calculated and treated as riding models with isotropic thermal parameters 1.2, 1.2 and 1.5 times the bound carbon atom  $U_{eq}$  respectively. The bridging cage H atom in **1** was found in a difference Fourier map and positionally refined, with  $U_{iso}$  fixed at  $0.05 \text{ \AA}^2$ .

There were two orientations of the isopropyl group on the *p*-cymene ligand in **2**, and all four partial methyl groups were assigned fixed occupancies of 0.5. Two positions for each Cl atom were found for the disordered molecule of  $\text{CHCl}_3$  solvate. One group was assigned occupancy factors of 0.75, the other 0.25.

Crystallographic computing was performed on a Pentium 90 MHz PC using the SHELXTL [20] system. Table 3 lists crystallographic data and further details of solution and refinement.

### Acknowledgements

This work was supported by CIRIT (research grant QFN95-4721) and by NATO (collaborative research grant CRG 971636). AJW thanks the Callery Chemical Company for continued support through a generous gift of decaborane.

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