

# Synthesis and structure of indenyl rhodium(I) complexes containing unsaturated phosphines: catalyst precursors for alkene hydroboration<sup>†</sup>

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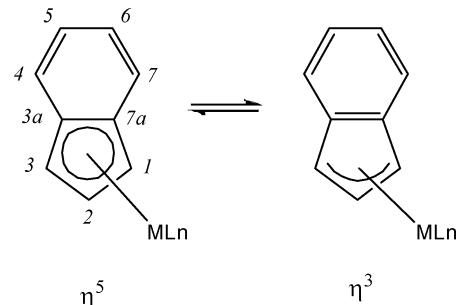
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The indenyl compound ( $\eta^5\text{-C}_9\text{H}_7\text{)}\text{Rh}(\text{coe})_2$  (**1**, coe = *cis*-cyclooctene) has been prepared as a thermally stable alternative to the diethylene derivative ( $\eta^5\text{-C}_9\text{H}_7\text{)}\text{Rh}(\eta^2\text{-H}_2\text{C=CH}_2)_2$ . Compound **1** reacts with unsaturated phosphines Ph<sub>2</sub>PR (R = CH=CH<sub>2</sub>, **2**; CH<sub>2</sub>CH=CH<sub>2</sub>, **3**; and C≡C-*tert*-Bu, **4**) to give complexes of the type ( $\eta^5\text{-C}_9\text{H}_7\text{)}\text{Rh}(\text{Ph}_2\text{PR})_2$ , where bonding occurs through the phosphorus atom. Addition of Ph<sub>2</sub>PC≡CPPh<sub>2</sub> to **1** gave the dimer [ $(\eta^5\text{-C}_9\text{H}_7\text{)}\text{Rh}(\mu\text{-Ph}_2\text{PC≡CPPh}_2)_2$ ] (**5**). Solution and solid state data showed that these new phosphine complexes have only a moderate amount of distortion within the indenyl ring. These compounds were found to catalyse the hydroboration of vinylarenes and the first example of an internal hydroboration of diphenylvinylphosphine has been reported.

## Introduction

There has been considerable interest in the use of late metal indenyl complexes arising from their enhanced catalytic activities, as compared to their cyclopentadienyl analogues, for a number of important organic reactions.<sup>1</sup> This enhanced reactivity has been termed the ‘indenyl effect’ and it is known to occur in both associative (S<sub>N</sub>2) and dissociative (S<sub>N</sub>1) reaction pathways.<sup>2</sup> A low energy barrier associated with an  $\eta^5\rightarrow\eta^3$  ring slippage (Fig. 1) is commonly attributed to the associative reaction pathway, where the metal centre avoids an unfavourable 20-electron transition state. Interestingly, DFT calculations on [ $(\eta^5\text{-C}_9\text{H}_7)\text{MoL}_2(\text{CO})_2$ ]<sup>+</sup> (L = NCR, CNR) show that the indenyl ring starts to slip when the incoming ligand is approaching the metal centre at a distance of *ca.* 400 pm.<sup>2e</sup> This haptotropic rearrangement has also been rationalized *via* a ground state effect where three of the five metal carbon bonds are shorter than the other two to give a distinct  $\eta^3:\eta^2$ -indenyl bonding mode.<sup>3</sup> Recent results by Chirik and co-workers have shown that the indenyl ring can even bind to transition metals through all of the carbon atoms as shown in complexes of the type ( $\eta^9\text{-C}_9\text{H}_5\text{-1,3-R}_2\text{)}(\eta^5\text{-C}_9\text{H}_5\text{-1,3-R}_2\text{)}\text{Zr}$  (R = SiMe<sub>3</sub>, CHMe<sub>2</sub>).<sup>4</sup> A significant amount of research has therefore focussed on examining the structure and bonding in indenyl metal complexes. As part of our ongoing investigation in this area<sup>5</sup> we have prepared a number of ( $\eta^5\text{-C}_9\text{H}_7\text{)}\text{RhL}_2$  complexes and investigated the role the ancillary ligands play in this  $\eta^3:\eta^2$ -indenyl bonding mode.<sup>6</sup> We report herein on the synthesis of indenyl



**Fig. 1** Two of the possible bonding modes in indenyl metal complexes with numbering scheme for the indenyl ring.

rhodium complexes containing unsaturated phosphines and their ability to catalyse the hydroboration of vinylarenes.

## Results and discussion

Although ( $\eta^5\text{-C}_9\text{H}_7\text{)}\text{Rh}(\eta^2\text{-H}_2\text{C=CH}_2)_2$  is frequently used as a starting material in ligand substitution reactions owing to the labile ethylene groups, we have prepared the thermally stable analogue ( $\eta^5\text{-C}_9\text{H}_7\text{)}\text{Rh}(\text{coe})_2$  (**1**, coe = *cis*-cyclooctene) as an alternative to this ethylene precursor. Complex **1** was prepared by the room temperature addition of lithium indenide to [RhCl(coe)<sub>2</sub>]<sub>2</sub> in 66% yield. The <sup>1</sup>H NMR spectrum of **1** shows a distinctive quartet for the indenyl H(2) peak at  $\delta$  6.01 ppm with coupling to H(1,3) and the rhodium metal of  $^3J_{\text{HH}} = J_{\text{RhH}} = 2.2$  Hz. The degree of distortion of the indenyl ring in solution has been measured previously by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy.<sup>2d,s,7</sup> The <sup>13</sup>C{<sup>1</sup>H} NMR data suggest a small distortion away from the  $\eta^5$  bonding mode, as evidenced by the chemical shift of the ring junction carbons C(3a,7a) of 114.5 ppm. For comparison, the analogous ethylene complex ( $\eta^5\text{-C}_9\text{H}_7\text{)}\text{Rh}(\eta^2\text{-H}_2\text{C=CH}_2)_2$  has a chemical shift of 112.2 ppm.<sup>8</sup> Complex **1** has also been characterized by single crystal X-ray diffraction; the molecular structure, selected bond distances and angles, are given in Fig. 2. Details of the data collection, structure solution and refinement are presented in Table 1.

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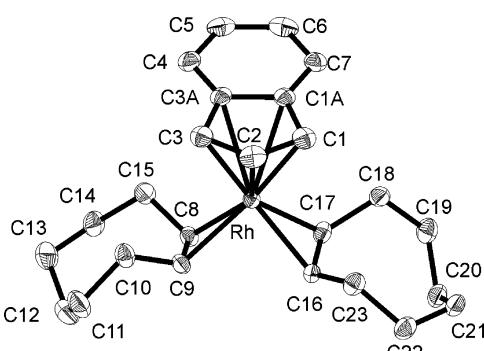
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**Table 1** Crystallographic data collection parameters for **1**, **2**, **4** and **5**

Complex	<b>1</b>	<b>2</b>	<b>4</b>	<b>5</b>
Chemical formula	C <sub>25</sub> H <sub>35</sub> Rh	C <sub>37</sub> H <sub>33</sub> P <sub>2</sub> Rh	C <sub>45</sub> H <sub>45</sub> P <sub>2</sub> Rh	C <sub>70</sub> H <sub>54</sub> P <sub>4</sub> Rh <sub>2</sub>
Formula mass	438.44	642.48	750.66	1224.83
Crystal dimensions (mm <sup>3</sup> )	0.60 × 0.225 × 0.175	0.40 × 0.35 × 0.025	0.40 × 0.275 × 0.20	0.15 × 0.12 × 0.05
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> /c	P-1	P-1
Z	4	4	2	2
a (Å)	7.3306(6)	17.385(4)	11.0600(6)	11.6644(2)
b (Å)	13.4620(12)	10.162(2)	11.8418(7)	13.4814(2)
c (Å)	20.7134(19)	17.492(4)	17.1608(10)	19.1415(3)
α (°)	90	90	108.854(1)	102.0975(5)
β (°)	90	103.055(4)	92.464(1)	92.9700(6)
γ (°)	90	90	112.489(1)	106.4690(5)
Volume (Å <sup>3</sup> )	2044.1(3)	3010.4(12)	1929.21(19)	2802.52(8)
D <sub>calcd</sub> (Mg m <sup>-3</sup> )	1.425	1.418	1.292	1.451
T (K)	173(1)	173(1)	198(1)	120(2)
Radiation	MoK <sub>α</sub> (λ = 0.71073 Å)	MoK <sub>α</sub> (λ = 0.71073 Å)	MoK <sub>α</sub> (λ = 0.71073 Å)	MoK <sub>α</sub> (0.71073 Å)
μ (mm <sup>-1</sup> )	0.841	0.698	0.555	0.746
Total reflections collected	14137	19545	13395	43145
Total unique reflections	4575	6710	8406	12873
No. of variables	235	361	439	685
θ (°)	1.80–27.49	1.20–27.50	1.94–27.50	1.10–27.50
GoF on F <sup>2</sup>	1.038	1.098	1.091	1.021
R <sub>int</sub>	0.0240	0.0580	0.0174	0.0337
R <sub>1</sub> [I > 2σ(I)] <sup>a</sup>	0.0195	0.0477	0.0332	0.0297
wR <sub>2</sub> (all data) <sup>b</sup>	0.0497	0.1374	0.0922	0.0757
Largest diff peak and hole (Å <sup>-3</sup> )	0.795, -0.275	1.514, -1.284	1.473, -0.463	1.261, -0.654

<sup>a</sup> R<sub>1</sub> =  $\sum \|F_o\| - |F_c| / \sum |F_c|$ . <sup>b</sup> wR<sub>2</sub> =  $(\sum [w(F_o^2 - F_c^2)^2] / \sum [F_o^4])^{1/2}$ , where w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0306P)<sup>2</sup> + (0.3037P)] (**1**), 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0447P)<sup>2</sup> + (8.3225P)] (**2**), 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.059P)<sup>2</sup> + (0.2619P)] (**4**) and w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0349P)<sup>2</sup> + (2.0246P)] (**5**), where P = (max(F<sub>o</sub><sup>2</sup>, 0) + 2F<sub>c</sub><sup>2</sup>)/3.

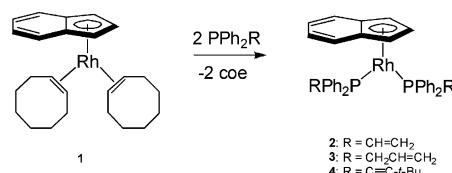


**Fig. 2** Perspective view of molecule **1** with atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Rh–C(9) 2.1495(19), Rh–C(16) 2.1513(19), Rh–C(8) 2.1520(19), Rh–C(17) 2.1659(19), Rh–C(1) 2.230(2), Rh–C(3) 2.2385(19), Rh–C(2) 2.245(2), Rh–C(1A) 2.4126(18), Rh–C(3A) 2.4148(17), C(8)–C(9) 1.408(3), C(16)–C(17) 1.405(3); C(1)–Rh–C(3) 61.76(8), ethene centroid–Rh–ethene centroid 93.2.

The rhodium alkene bond distances of 2.1495(19), 2.1513(19), 2.1520(19), and 2.1659(19) Å (Rh–C<sub>ave</sub> = 2.1547(19) Å) are similar to those reported for related systems<sup>9</sup> and a distinct lengthening of the C=C bonds (C–C<sub>ave</sub> = 1.407(3) Å) of the alkene is also observed, arising from π-back bonding from the metal centre. As expected, there are three ‘short’ (Rh–C(1) 2.230(2), Rh–C(3) 2.2385(19), and Rh–C(2) 2.245(2) Å) and two ‘long’ (Rh–C(1A) 2.4126(18) and Rh–C(3A) 2.4148(17) Å) rhodium–carbon bond distances within the indenyl ring. These values clearly indicate a slip-fold distortion towards an allylic bonding mode, but there is

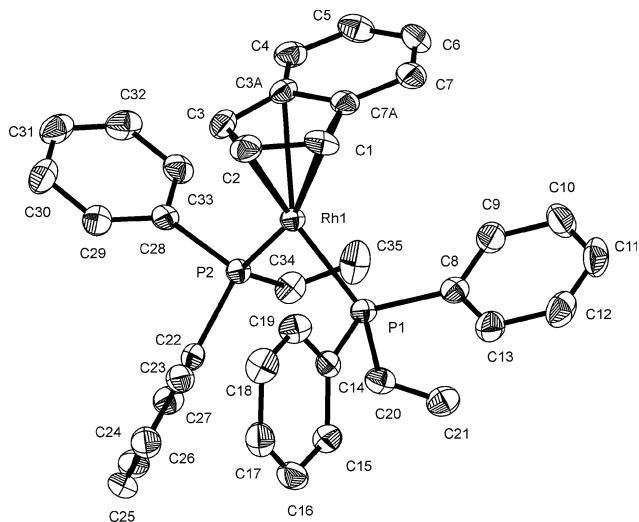
still bonding between the rhodium and ring junction carbons C<sub>3a</sub> and C<sub>1a</sub>, as required to attain an 18 electron configuration at the metal. The value of this slip-distortion is Δ = 0.180(2) Å, where Δ = d(average Rh–C<sub>3a,1a</sub>) – d(average Rh–C<sub>1,3</sub>). The fold angle (FA) of 9.11(8)° is the angle between planes defined by C(1), C(2), C(3) and C(7a), C(7), C(6), C(5), C(4), C(3a), and this also indicates a small distortion towards the allylic bonding mode.

The coordination chemistry of phosphines bearing alkenyl or alkynyl substituents is an area of considerable interest, owing to the use of these ligands in the structural architecture of multinuclear species.<sup>10,11</sup> We therefore decided to examine the reactivity of **1** with such phosphines.<sup>6,l,m</sup> Addition of two equivalents of diphenylvinylphosphine (Ph<sub>2</sub>PCH=CH<sub>2</sub>) to **1** gave (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Rh(Ph<sub>2</sub>PCH=CH<sub>2</sub>)<sub>2</sub> (**2**) in moderate yield (Scheme 1). Compound **2** has been characterized by a number of physical methods including multinuclear NMR spectroscopy. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum for **2** shows a doublet at δ 43.9 ppm with a coupling constant of J<sub>RhP</sub> = 220 Hz, suggesting that the ligands are, not surprisingly, bound to the metal via the soft phosphorus atom. This observation is confirmed by the <sup>1</sup>H NMR data, as no significant change is observed for the vinyl peaks in **2**, as compared to free Ph<sub>2</sub>PCH=CH<sub>2</sub>. The ring junction carbons within



**Scheme 1** Synthesis of indenyl rhodium phosphine complexes **2–4**.

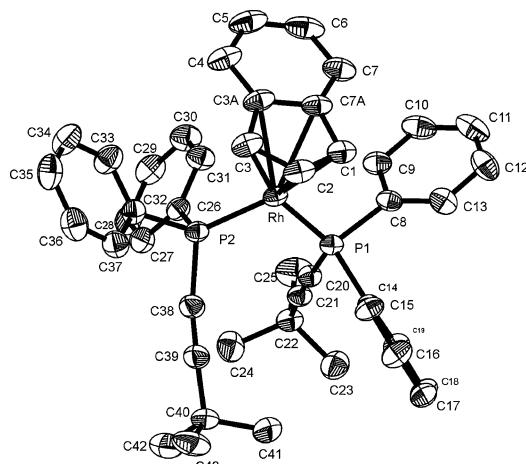
the indenyl ring appear at  $\delta$  118.8 ppm in the  $^{13}\text{C}\{\text{H}\}$  spectrum and again suggest only a moderate amount of slip distortion in solution. Compound **2** has also been characterized by X-ray diffraction, the molecular structure of which is shown in Fig. 3. The ground state slip distortion in **2** is  $\Delta = 0.207(4)$  Å, slightly larger than what is observed in **1**, with a FA of  $10.1(4)^\circ$ . The rhodium phosphorus bond lengths of Rh(1)-P(1) 2.2243(13) and Rh(1)-P(2) 2.2194(13) Å are similar to those observed in other indenyl phosphine systems.<sup>5b,12</sup> For example, rhodium phosphorus bond lengths of 2.213(1) and 2.210(1) Å were reported for the complex ( $\eta^5\text{-C}_9\text{H}_7$ )Rh(PMe<sub>3</sub>)<sub>2</sub>.<sup>5b</sup>



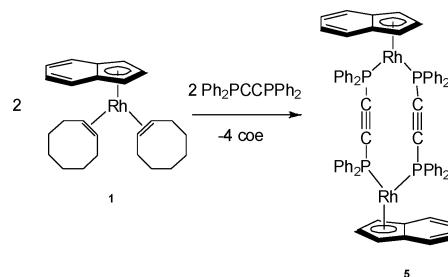
**Fig. 3** Perspective view of molecule of **2** with atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)-P(2) 2.2194(13), Rh(1)-P(1) 2.2243(13), Rh(1)-C(2) 2.228(5), Rh(1)-C(3) 2.230(4), Rh(1)-C(1) 2.235(4), Rh(1)-C(3A) 2.435(4), Rh(1)-C(7A) 2.443(5), C(20)-C(21) 1.315(7), C(34)-C(35) 1.303(8); P(2)-Rh(1)-P(1) 96.10(4), C(3)-Rh(1)-C(1) 62.15(18).

We have also prepared the allyldiphenylphosphine compound **3** and the alkynydiphenylphosphine derivative **4** via a similar route. Both compounds show the characteristic doublet in the  $^{31}\text{P}\{\text{H}\}$  NMR spectra, signifying that bonding is once again occurring through the phosphorus atoms and with coupling to rhodium of  $J_{\text{RhP}} = 220$  Hz and  $J_{\text{RhP}} = 227$  Hz, respectively. The ring junction carbons appear in the  $^{13}\text{C}\{\text{H}\}$  NMR spectra at  $\delta$  120.2 ppm for **3** and  $\delta$  117.7 ppm for **4**. Compound **4** has also been characterized by single crystal X-ray diffraction (Fig. 4). The ground state slip distortion in **4** is unusually small for a bis(phosphine) system with  $\Delta = 0.165(2)$  Å, which is actually less than that observed for **1**. By comparison, a distortion of  $\Delta = 0.201$  Å was observed in the trimethylphosphine analogue ( $\eta^5\text{-C}_9\text{H}_7$ )Rh(PMe<sub>3</sub>)<sub>2</sub>.<sup>5b</sup> A fold angle of  $9.2(3)^\circ$  is also observed for **4**. The rhodium phosphorus bond lengths of Rh-P(1) 2.1938(5) and Rh-P(2) 2.2083(5) Å are again typical for these complexes.

Addition of one equivalent of the linear diphosphine Ph<sub>2</sub>PC≡CPPPh<sub>2</sub> to **1** led to the formation of dimeric **5** in moderate yield (Scheme 2). Compound **5** displays a doublet in the  $^{31}\text{P}\{\text{H}\}$  NMR spectra at  $\delta$  26.1 ppm with  $J_{\text{RhP}} = 220$  Hz. The ring junction carbons appear in the  $^{13}\text{C}\{\text{H}\}$  NMR spectra at  $\delta$  117.9 ppm, suggesting minimal distortion in solution. A single

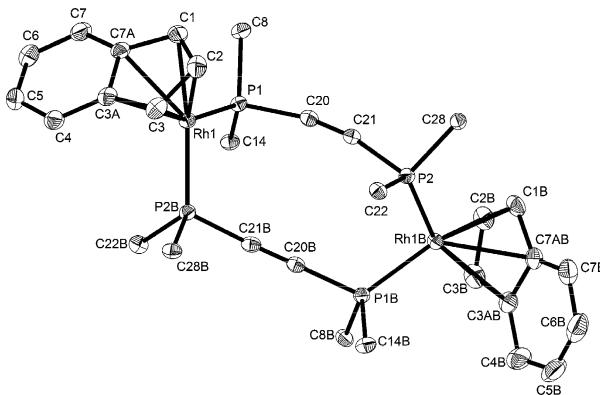


**Fig. 4** Perspective view of molecule of **4** with atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Rh-P(1) 2.1938(5), Rh-P(2) 2.2083(5), Rh-C(1) 2.226(2), Rh-C(2) 2.253(2), Rh-C(3) 2.257(2), Rh-C(7A) 2.390(2), Rh-C(3A) 2.423(2), C(20)-C(21) 1.195(3), C(38)-C(39) 1.195(3); P(1)-Rh-P(2) 94.30(2), C(1)-Rh-C(3) 62.03(9).



**Scheme 2** Synthesis of indenyl rhodium dimer **5**.

crystal X-ray diffraction study confirms the dimeric structure for complex **5** (Fig. 5) with diphosphine ligands coordinating in a P-P' bridging mode. This coordination mode is known for similar complexes of other transition metals.<sup>13,14</sup> In contrast, the only previously characterized rhodium complex of this ligand comprises a polymer.<sup>15</sup> One molecule of **5** constitutes the asymmetric unit showing no molecular symmetry. This is especially apparent in the different rhodium-indenyl bonding situations at Rh(1) and Rh(1B) characterized by values of  $\Delta = 0.146(3)$  Å and a FA of  $9.2(1)^\circ$  for Rh(1) and  $\Delta = 0.185(3)$  Å and a FA of  $8.7(1)^\circ$  for Rh(1B). This is (on average) in good agreement with the results obtained for the related compound **4** with  $\Delta = 0.165(2)$  Å and a FA of  $9.2(3)^\circ$ . The rhodium phosphorus bond length of Rh(1)-P(1) 2.196(1) Å and Rh(1)-P(2B) 2.212(1) Å and Rh(1B)-P(2) 2.192(1) Å, and Rh(1B)-P(1B) 2.208(1) Å respectively, are similar and typical for these complexes. Interestingly, the two alkynydiphenylphosphine moieties in the solid state structure of **5** have different geometries, one is almost linear (P(1B)-C(20B)-C(21B)  $179.0(2)^\circ$  and P(2B)-C(21B)-C(20B)  $175.9(2)^\circ$ ) whilst the other one is considerably bent (P(2)-C(21)-C(20)  $168.5(2)^\circ$  and P(1)-C(20)-C(21)  $165.5(2)^\circ$ ). In both ligands, the carbon-carbon triple bond lengths of 1.205(3) Å (C(20)-C(21)) and 1.202(3) Å (C(20B)-C(21B)) are normal. The bending of one bridging alkynydiphenylphosphine is well documented in related complexes.<sup>14</sup> Additionally compound **5** was studied by

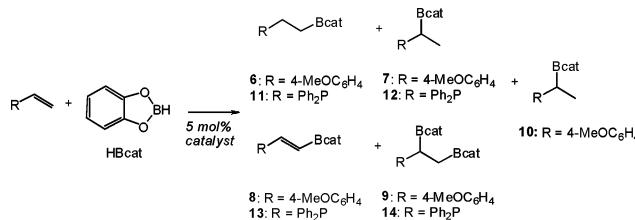


**Fig. 5** Perspective view of molecule of **5** with atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level with hydrogen atoms and non-*ipso* phenyl carbon atoms omitted for clarity. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Rh(1)–P(1) 2.196(1), Rh(1)–P(2B) 2.212(1), Rh(1)–C(1) 2.207(2), Rh(1)–C(2) 2.251(2), Rh(1)–C(3) 2.246(2), Rh(1)–C(7A) 2.368(2), Rh(1)–C(3A) 2.395(2), C(20)–C(21) 1.205(3), Rh(1B)–P(1B) 2.208(1), Rh(1B)–P(2) 2.192(1), Rh(1B)–C(1B) 2.212(2), Rh(1B)–C(2B) 2.234(2), Rh(1B)–C(3B) 2.251(2), Rh(1B)–C(7AB) 2.404(2), Rh(1B)–C(3AB) 2.431(2), C(20B)–C(21B) 1.202(3); P(1)–Rh(1)–P(2B) 95.41(2), C(1)–Rh(1)–C(3) 62.00(9), P(1B)–Rh(1B)–P(2) 94.82(2), C(1B)–Rh(1B)–C(3B) 61.79(9).

mass spectroscopy, but neither ionisation by EI nor by MALDI (in positive and negative ion mode) resulted in helpful data. Interestingly, addition of 2 equivalents of this phosphine to **1** led to an unidentified mixture of rhodium phosphine species.

As indenyl complexes are known to catalyse the addition of catecholborane (HBcat, cat = 1,2-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) to alkenes,<sup>11,k</sup> we have examined complexes **1–5** for their potential to act as catalyst precursors in this important reaction.<sup>16</sup> Although reactions using catalytic amounts of **1** (5 mol%) to facilitate the addition of HBcat to 4-vinylanisole (4-MeOC<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub>) gave a mixture of hydroboration products 4-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>(Bcat) (**6**, 18%) and 4-MeOC<sub>6</sub>H<sub>4</sub>CH(Bcat)CH<sub>3</sub> (**7**, 3%), as ascertained by multinuclear NMR spectroscopy, products derived from a competing dehydrogenative borylation pathway were also observed.<sup>17</sup> Dehydrogenative borylation is believed to proceed *via* initial oxidative addition of the borane to the metal centre, followed by coordination and insertion of the alkene into the Rh–B bond with a subsequent, and selective,  $\beta$ -hydride elimination to give a vinyl boronate product along with an active rhodium dihydride species. Indeed, the vinyl boronate ester 4-MeOC<sub>6</sub>H<sub>4</sub>CH=CH(Bcat) (**8**) was the major boron-containing product observed in 37% yield. Interestingly, the diborated product 4-MeOC<sub>6</sub>H<sub>4</sub>CH(Bcat)CH<sub>2</sub>(Bcat) (**9**) was also generated in this reaction, albeit in minor amounts (2%). This latter product<sup>18b,c,e,19</sup> presumably arises from a selective hydroboration of **8**. A considerable amount (40%) of hydrogenated starting material, 4-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub> (**10**), is also observed in these reactions.

We then examined catalytic hydroboration reactions using the indenyl phosphine complexes **2–5** and found that all gave predominant formation of the internal isomer **7** (*ca.* 95%, Scheme 3) along with only a minor amount (5%) of products derived from the dehydrogenative borylation pathway. The fate of the catalyst system upon completion of these reactions appears to be zwitterionic complexes of the type ( $\eta^6$ -catBcat)RhP<sub>2</sub>, where the



**Scheme 3** Indenyl rhodium catalysed hydroboration of 4-vinylanisole and diphenylvinylphosphine.

indenyl ligand has been borylated, as observed by multinuclear NMR spectroscopy and GC-MS analyses, and replaced by the Bcat<sup>-</sup> anion which has coordinated to the rhodium *via* one of the aryl groups. These zwitterionic systems are remarkably active and selective hydroboration catalysts for a wide range of alkenes, and are well known to give the selective formation of the branched product in hydroborations of vinylarenes using HBcat.<sup>18</sup> As the phosphines also contain a site of unsaturation, it is highly probable that the ligands are also being reduced in these catalytic runs. To test this hypothesis we examined the ability of **2** to add HBcat to Ph<sub>2</sub>PCH=CH<sub>2</sub>. Although conversion of the starting alkene was only 75% using one equivalent of HBcat, we have found that these reactions proceed to give a mixture of the expected linear product Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>(Bcat) (**11**, 20%) along with the unusual branched product Ph<sub>2</sub>PCH(Bcat)CH<sub>3</sub> (**12**, 15%). While derivatives of **11** have recently been prepared and examined for their ability to act as ambiphilic ligands or donor–acceptor systems,<sup>20</sup> the generation of **12** represents the first example of a metal catalysed addition of a borane to diphenylvinylphosphine to give this branched product. The ability to generate **12** selectively and enantiomerically pure will prove to be a valuable method of synthesising chiral monodentate phosphine ligands.<sup>21</sup> While the vinyl boronate ester Ph<sub>2</sub>PCH=CH(Bcat) **13** was not observed to any extent, the corresponding diborated product Ph<sub>2</sub>PCH(Bcat)CH<sub>2</sub>(Bcat) **14** was observed as the major boron containing product (65%). Interestingly, no hydrogenation product was observed in this reaction. We are in the process of examining this reaction further in an effort to improve selectivities and will report our findings in due course.

## Experimental

### General

Reagents and solvents were purchased from Aldrich Chemicals and used as received. Lithium indenide<sup>22</sup> and [RhCl(coc)<sub>2</sub>]<sup>23</sup> were synthesized as previously reported. The phosphines Ph<sub>2</sub>PC≡C-*tert*-butyl and Ph<sub>2</sub>PC≡CPPPh<sub>2</sub><sup>24</sup> were donated as a generous gift from Dr J. F. Corrigan. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR (<sup>1</sup>H 270 MHz; <sup>11</sup>B 87 MHz; <sup>13</sup>C 68 MHz; <sup>31</sup>P 109 MHz) spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm [relative to residual solvent peaks (<sup>1</sup>H and <sup>13</sup>C) or external BF<sub>3</sub>·OEt<sub>2</sub> (<sup>11</sup>B), and H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P)] and coupling constants ( $J$ ) in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), sextet (sext), multiplet (m), broad (br), apparent (app), and overlapping (ov). Melting points were determined using a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Guelph Chemical Laboratories (Guelph, ON). Reactions were performed under an atmosphere of dinitrogen.

**(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Rh(coe)<sub>2</sub> (1).** To a stirred toluene (10 mL) solution of [RhCl(coe)<sub>2</sub>]<sub>2</sub> (1.00 g, 1.39 mmol) was added lithium indenide (0.35 g, 2.86 mmol) as a solid. The reaction was allowed to proceed at RT for 18 h at which point the solution was passed through multiple plugs of silica until the solution became clear orange. The removal of solvent under vacuum afforded **1** as an orange solid. Yield: 0.80 g (66%); m.p.: 120 °C (decomp.) NMR (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H δ 7.13 (s, 4H, H<sub>4-7</sub>), 6.01 (q, J<sub>HH</sub> = J<sub>RhH</sub> = 2.2 Hz, 1H, H<sub>2</sub>), 4.74 (d, J<sub>HH</sub> = 2.2 Hz, 2H, H<sub>1,3</sub>), 2.12–2.08 (ov m, 4H, CH<sub>2</sub>), 1.79–1.51 (ov m, 16H, CH<sub>2</sub> & =CH), 1.40–1.21 (ov m, 8H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} δ 122.9 (s, C<sub>4,7</sub>), 119.3 (s, C<sub>5,6</sub>), 114.5 (d, J<sub>RhC</sub> = 1.9 Hz, C<sub>3a,7a</sub>), 94.9 (d, J<sub>RhC</sub> = 5.4 Hz, C<sub>2</sub>), 83.1 (d, J<sub>RhC</sub> = 4.6 Hz, C<sub>1,3</sub>), 69.9 (d, J<sub>RhC</sub> = 13.7 Hz, C=C), 32.4 (d, J<sub>RhC</sub> = 3.5 Hz, CH<sub>2</sub>), 32.1 (d, J<sub>RhC</sub> = 1.2 Hz, CH<sub>2</sub>), 26.7 (s, CH<sub>2</sub>). Anal. Calcd. (%) for C<sub>25</sub>H<sub>35</sub>Rh (438.50): C, 68.47; H, 8.06. Found: C, 68.38; H, 7.90.

**(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Rh(Ph<sub>2</sub>PCH=CH<sub>2</sub>)<sub>2</sub> (2).** To a stirred THF (5 mL) solution of (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Rh(coe)<sub>2</sub> (0.20 g, 0.46 mmol) was added a THF (3 mL) solution of diphenylvinylphosphine (0.20 g, 0.94 mmol). The reaction was allowed to proceed at RT for 18 h at which point the solvent was removed under vacuum and the resulting orange solid was washed with hexane (2 × 1 mL) to afford **2**. Yield: 0.19 g (65%); m.p.: 110 °C (decomp.). NMR (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H δ 7.46 (br m, 8H, Ar), 7.07–6.99 (ov m, 14H, Ar & H<sub>4,7</sub>), 6.72 (t, J<sub>HH</sub> = 3.0 Hz, 2H, H<sub>5,6</sub>), 6.52 (q, J<sub>HH</sub> = J<sub>RhH</sub> = 2.6 Hz, 1H, H<sub>2</sub>), 6.15 (ov dddd, J<sub>HH</sub> = 17.6, 11.1, Hz, J<sub>PH</sub> = 17.3 Hz, J<sub>RhH</sub> = 2.1 Hz, 2H, RhPCH=CH<sub>2</sub>), 5.41 (d, J<sub>HH</sub> = 17.6 Hz, 2H, CH=CHH), 5.34 (ddd, J<sub>PH</sub> = 29.4 Hz, J<sub>HH</sub> = 11.1 Hz, J<sub>RhH</sub> = 2.2 Hz, 2H, CH=CHH), 4.65 (d, J<sub>HH</sub> = 2.6 Hz, 2H, H<sub>1,3</sub>); <sup>13</sup>C{<sup>1</sup>H} δ 139.0 (t, J = 27.0 Hz, ArCP), 136.8 (t, J = 25.5 Hz, PCH), 133.5 (t, J = 8.2 Hz, Ar) 128.6 (s, Ar), 128.3 (s, CHCH<sub>2</sub>), 127.5 (t, J = 4.6 Hz, Ar), 121.2 (s, C<sub>4,7</sub>), 118.8 (s, C<sub>3a,7a</sub>), 115.8 (s, C<sub>5,6</sub>), 96.1 (d, J<sub>RhC</sub> = 8.6 Hz, C<sub>2</sub>), 76.1 (dt, J<sub>RhC</sub> = 3.8 Hz, J<sub>PC</sub> = 10.6 Hz, C<sub>1,3</sub>); <sup>31</sup>P{<sup>1</sup>H} δ 43.9 (d, J<sub>RhP</sub> = 220 Hz). Anal. Calcd. (%) for C<sub>37</sub>H<sub>53</sub>P<sub>2</sub>Rh (642.55): C, 69.16; H, 5.19. Found: C, 69.46; H, 5.49.

**(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Rh(Ph<sub>2</sub>PCH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub> (3).** To a stirred toluene (5 mL) solution of (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Rh(coe)<sub>2</sub> (0.20 g, 0.46 mmol) was added a toluene (3 mL) solution of allyldiphenylphosphine (0.21 g, 0.94 mmol). The reaction was allowed to proceed at RT for 18 h at which point the solvent was removed under vacuum and the resulting orange solid was dissolved in hexane (10 mL) and stored at –30 °C. An orange precipitate was collected by suction filtration and washed with cold hexane (2 × 1 mL) to afford **3**. Yield: 0.14 g (45%); m.p.: 93–95 °C. NMR (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H δ 7.38 (br m, 8H, Ar), 7.06 (app t, J<sub>HH</sub> = 3.0 Hz, 2H, H<sub>4,7</sub>), 7.02–6.96 (ov m, 12H, Ar), 6.88 (t, J<sub>HH</sub> = 3.0 Hz, 2H, H<sub>5,6</sub>), 6.55 (q, J<sub>HH</sub> = J<sub>RhH</sub> = 2.7 Hz, 1H, H<sub>2</sub>), 5.92 (m, 2H, CH=CH<sub>2</sub>), 4.92 (d, J<sub>HH</sub> = 10.2 Hz, 2H, CH=CHH), 4.81 (d, J<sub>HH</sub> = 13.1 Hz, 2H, CH=CHH), 4.79 (d, J<sub>HH</sub> = 2.7 Hz, 2H, H<sub>1,3</sub>), 2.52 (app t, J<sub>HH</sub> = 7.2 Hz, 4H, PCH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} δ 140.1 (t, J = 18.4 Hz, ArCP), 134.9 (s, CH=CH<sub>2</sub>), 133.1 (t, J = 5.9 Hz, Ar), 128.6 (s, Ar), 127.2 (t, J = 4.6 Hz, Ar), 121.1 (s, C<sub>4,7</sub>), 120.2 (s, C<sub>3a,7a</sub>), 116.5 (t, J = 5.6 Hz, PCH<sub>2</sub>CH), 115.6 (s, C<sub>5,6</sub>), 96.4 (d, J<sub>RhC</sub> = 6.1 Hz, C<sub>2</sub>), 74.8–74.5 (m, C<sub>1,3</sub>), 38.7 (t, J = 11.8 Hz, PCH<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} δ 38.0 (d, J<sub>RhP</sub> = 220 Hz). Anal. Calcd. (%) for C<sub>39</sub>H<sub>57</sub>P<sub>2</sub>Rh (670.66): C, 69.84; H, 5.57. Found: C, 70.11; H, 5.41.

**(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Rh(Ph<sub>2</sub>PC≡C-tert-butyl)<sub>2</sub> (4).** To a stirred THF (5 mL) solution of (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Rh(coe)<sub>2</sub> (0.20 g, 0.46 mmol) was

added a THF (3 mL) solution of Ph<sub>2</sub>PC≡C-tert-butyl (0.25 g, 0.94 mmol). The reaction was allowed to proceed at RT for 18 h at which point the solvent was removed under vacuum and the resulting orange solid was washed with hexane (2 × 2 mL) to afford **4**. Yield: 0.24 g (70%); m.p.: 115 °C (decomp.). NMR (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H δ 7.78 (br m, 8H, Ar), 7.17–7.02 (ov m, 14H, Ar & H<sub>4,7</sub>), 6.74 (t, J<sub>HH</sub> = 3.0 Hz, 2H, H<sub>5,6</sub>), 6.43 (q, J<sub>HH</sub> = J<sub>RhH</sub> = 2.7 Hz, 1H, H<sub>2</sub>), 4.55 (d, J<sub>HH</sub> = 2.7 Hz, 2H, H<sub>1,3</sub>), 0.85 (s, 18H, tert-butyl); <sup>13</sup>C{<sup>1</sup>H} δ 141.0 (t, J = 24.6 Hz, ArCP), 132.7 (t, J = 6.7 Hz, Ar), 128.6 (s, Ar), 127.5 (t, J = 5.1 Hz, Ar), 121.1 (s, C<sub>4,7</sub>), 117.7 (s, C<sub>3a,7a</sub>), 115.8 (s, C<sub>5,6</sub>), 113.5 (t, J = 5.1 Hz, PC≡C), 95.9 (d, J<sub>RhC</sub> = 5.6 Hz, C<sub>2</sub>), 77.9–76.1 (ov m, C<sub>1,3</sub> and PC≡C), 29.9 (s, C(CH<sub>3</sub>)<sub>3</sub>), 28.1 (s, C(CH<sub>3</sub>)<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} δ 25.1 (d, J<sub>RhP</sub> = 227 Hz). Anal. Calcd. (%) for C<sub>45</sub>H<sub>45</sub>P<sub>2</sub>Rh (750.75): C, 71.99; H, 6.05. Found: C, 72.35; H, 6.11.

**[(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Rh(μ-Ph<sub>2</sub>PC≡CPPPh<sub>2</sub>)<sub>2</sub> (5).** To a stirred toluene (5 mL) solution of (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Rh(coe)<sub>2</sub> (0.20 g, 0.46 mmol) was added a toluene (5 mL) solution of Ph<sub>2</sub>PC≡CPPPh<sub>2</sub> (0.18 g, 0.46 mmol). The reaction was allowed to proceed at RT for 18 h at which point an orange precipitate was collected by suction filtration and washed with hexane (2 × 2 mL) to afford **5**. Yield: 0.13 g (46%); m.p.: decomposes above 215 °C. NMR (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H δ 7.48 (br m, 16H, Ar), 7.02–6.92 (ov m, 28H, Ar & H<sub>4,7</sub>), 6.73 (m, 4H, H<sub>5,6</sub>), 6.34 (q, J<sub>HH</sub> = J<sub>RhH</sub> = 2.7 Hz, 2H, H<sub>2</sub>), 4.61 (d, J<sub>HH</sub> = 2.7 Hz, 4H, H<sub>1,3</sub>); <sup>13</sup>C{<sup>1</sup>H} δ 138.6 (t, J = 25.1 Hz, ArCP), 132.0 (t, J = 8.2 Hz, Ar), 128.7 (s, Ar), 127.7 (t, J = 5.1 Hz, Ar), 121.7 (s, C<sub>4,7</sub>), 117.9 (s, C<sub>3a,7a</sub>), 116.0 (s, C<sub>5,6</sub>), 102.8 (app t, J = 31.7 Hz, C≡C), 95.4 (d, J<sub>RhC</sub> = 6.1 Hz, C<sub>2</sub>), 77.3–77.1 (m, C<sub>1,3</sub>); <sup>31</sup>P{<sup>1</sup>H} δ 26.1 (d, J<sub>RhP</sub> = 220 Hz). Anal. Calcd. (%) for C<sub>70</sub>H<sub>54</sub>P<sub>4</sub>Rh<sub>2</sub> (1225.04): C, 68.63; H, 4.45. Found: C, 68.98; H, 4.20.

**General procedure for the hydroboration of 4-vinylanisole.** To a stirred C<sub>6</sub>D<sub>6</sub> (0.5 mL) solution of 4-vinylanisole (50 mg, 0.37 mmol) and the desired catalyst (**1–5**) (5 mol%), was added a C<sub>6</sub>D<sub>6</sub> solution (0.5 mL) catecholborane (44 mg, 0.37 mmol). After 18 h the reaction was monitored by multinuclear NMR spectroscopy. Selected NMR spectroscopic data for: 4-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>(Bcat), **6**: 2.79 (t, J = 7.9 Hz, CH<sub>2</sub>CH<sub>2</sub>(Bcat)), 1.42 (t, J = 7.9 Hz, CH<sub>2</sub>CH<sub>2</sub>(Bcat)); 4-MeOC<sub>6</sub>H<sub>4</sub>CH(Bcat)CH<sub>3</sub>, **7**: 2.74 (q, J = 7.7 Hz, CH(Bcat)CH<sub>3</sub>), 1.48 (d, J = 7.7 Hz, CH(Bcat)CH<sub>3</sub>); 4-MeOC<sub>6</sub>H<sub>4</sub>CH=CH(Bcat), **8**: 7.82 (d, J = 18.3 Hz, CH=CH(Bcat)), 6.34 (d, J = 18.3 Hz, CH=CH(Bcat)); 4-MeOC<sub>6</sub>H<sub>4</sub>CH(Bcat)CH<sub>2</sub>(Bcat), **9**: 2.09 (dd, J = 16.1, 9.1 Hz, CH(Bcat)CHH(Bcat), 1.82 (dd, J = 16.1 Hz, 7.1 Hz, CH(Bcat)CHH(Bcat)); 4-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>, **10**: 2.45 (q, J = 7.7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.10 (t, J = 7.7 Hz, CH<sub>2</sub>CH<sub>3</sub>).

**Hydroboration of diphenylvinylphosphine using **2** as a precatalyst.** To a stirred C<sub>6</sub>D<sub>6</sub> (0.5 mL) solution of diphenylvinylphosphine (50 mg, 0.24 mmol) and the catalyst (**2**) (3 mg, 2 mol%), was added a C<sub>6</sub>D<sub>6</sub> solution (0.5 mL) of catecholborane (31 mg, 0.26 mmol). After 18 h the reaction was monitored by multi-nuclear NMR spectroscopy. Selected NMR spectroscopic data for: Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>(Bcat), **11**: <sup>1</sup>H δ 2.20 (t, J = 8.2 Hz, PCH<sub>2</sub>CH<sub>2</sub>(Bcat)), 1.28 (dt, J<sub>HP</sub> = 12.2 Hz, J<sub>HH</sub> = 8.2 Hz, CH<sub>2</sub>CH<sub>2</sub>(Bcat)); <sup>31</sup>P{<sup>1</sup>H} δ: -10.1; Ph<sub>2</sub>PCH(Bcat)CH<sub>3</sub>, **12**: <sup>1</sup>H δ 2.39 (qd, J<sub>HH</sub> = 7.4, J<sub>HP</sub> = 3.0 Hz, PCH(Bcat)CH<sub>3</sub>), 1.36 (dd, J<sub>HP</sub> = 16.1, J<sub>HH</sub> = 7.4 Hz, PCH(Bcat)CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} δ: -1.2; Ph<sub>2</sub>PCH(Bcat)CH<sub>2</sub>(Bcat), **14**: <sup>1</sup>H δ 2.93 (ddd, J<sub>HH</sub> = 10.6, 5.2, J<sub>HP</sub> = 2.2 Hz, PCH(Bcat)CH<sub>2</sub>(Bcat)), 1.99 (ov ddd, J<sub>HH</sub> = 16.8,

10.6,  $J_{\text{HP}} = 11.8$  Hz, PCH(Bcat)CHH(Bcat)), 1.76 (ddd,  $J_{\text{HH}} = 16.8$ , 5.2,  $J_{\text{HP}} = 11.1$  Hz, PCH(Bcat)CHH(Bcat));  $^{31}\text{P}\{\text{H}\}$  δ: 2.0.

## X-Ray crystallography†

Crystals of **1** were grown from saturated diethyl ether solutions, **2** from saturated  $\text{C}_6\text{D}_6$  solutions at room temperature, and **4** from saturated THF solutions layered with hexanes at  $-30^\circ\text{C}$ . Crystals of **5** were grown by diffusion of *n*-hexane into a solution of **5** in benzene at room temperature. Single crystals were coated with Paratone-N oil or Perfluoropolyether oil, mounted using a glass fibre or human hair and frozen in the cold stream of the goniometer. A hemisphere of data were collected on a Bruker AXS P4/SMART 1000 diffractometer using  $\omega$  and  $\theta$  scans with a scan width of  $0.3^\circ$  and exposure times of 10 s (**1** and **4**) and 30 s (**2**). The detector distances were 5 cm. In the case of **5** more than a hemisphere was collected on a Bruker SMART 6K CCD using  $\omega$  scans ( $0.3^\circ$  width), a detector distance of 4.85 cm and an exposure time of 15 s. The data were reduced (SAINT) and corrected for absorption (SADABS).<sup>25</sup> The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$ (SHELXTL). All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model.

## Conclusions

We have prepared  $(\eta^5\text{-C}_9\text{H}_7)\text{Rh}(\text{coe})_2$  (**1**, coe = *cis*-cyclooctene) as a thermally stable alternative to the diethylenic derivative  $(\eta^5\text{-C}_9\text{H}_7)\text{Rh}(\eta^2\text{-H}_2\text{C=CH}_2)_2$ . Compound **1** reacts with unsaturated phosphines to give complexes of the type  $(\eta^5\text{-C}_9\text{H}_7)\text{RhP}_2$ , where bonding occurs through the phosphorus atom. Solution and solid state data showed that these new phosphine complexes have only a moderate amount of distortion within the indenyl ring. These compounds were found to catalyse the hydroboration of vinylarenes, and the first example of an internal hydroboration of diphenylvinylphosphine has been reported.

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