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# Novel rhodium complexes containing a bulky iminophosphine ligand and their use as catalysts for the hydroboration of vinylarenes

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Dedicated to Dr. Brian James in recognition of his outstanding contributions to chemistry and catalysis.

#### Abstract

Addition of o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH=N-2,6<sup>-i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1) to [RhCl(coe)<sub>2</sub>]<sub>2</sub> (coe = *cis*-cycloctene) gave several new iminophosphino rhodium(I) complexes including [Rh( $\kappa^2$ -o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH=N-2,6<sup>-i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)( $\mu$ -Cl)]<sub>2</sub> (2). Addition of 1 to Rh(acac)(coe)<sub>2</sub> (acac = acetylacetonato) gave [Rh(acac)( $\kappa^2$ -o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH=N-2,6<sup>-i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)] (3) in yields of up to 75%. Complex 3 has been examined for its ability to catalyze the hydroboration of a series of vinyl arenes. Reactions using catecholborane and pinacolborane seem to proceed largely through a dehydrogenative borylation mechanism to give a number of boronated products. © 2005 Elsevier B.V. All rights reserved.

Keywords: Borylation; Catalysis; Hydroboration; Iminophosphine; Rhodium compounds

### 1. Introduction

One of the most important synthetic methodologies to emerge from organic chemistry in the last century has been the discovery that boron-hydrogen bonds add to unsaturated organic molecules to form a class of compounds known as organoboranes [1]. Organoboranes possess an incredibly diverse chemistry and are remarkably useful intermediates in organic synthesis. Indeed, organoboranes can be transformed into any number of functional groups. The simplest boron hydride agent is borane, BH<sub>3</sub>, which reacts rapidly with unhindered alkenes to afford initially monoalkylboranes, then dialkylboranes, and finally trialkylboranes. For sterically hindered alkenes, the second and third hydroboration steps become increasingly sluggish. Addition occurs in a controlled *cis*-fashion (*syn*-addition) where the boryl (BR<sub>2</sub>) fragment adds preferentially to the least hindered carbon of the unsymmetrically substituted double bond. While borane adds rapidly to alkenes at -80 °C [2], some hydroborating agents, such as polyhedral boranes, are slow to react even at room temperature. Likewise, addition of H<sub>3</sub>B · THF to catechol affords catecholborane (HBcat, cat = 1,2-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), a relatively stable hydroborating agent which adds to alkenes and alkynes only at elevated temperatures (ca. 100 and 70 °C, respectively) [3]. HBcat decomposes thermally or by addition of nucleophiles to give a number of boron-containing products [4].

That transition metals accelerate the addition of B–H bonds to unsaturated organic moieties was initially reported for catalyzed hydroborations of alkenes and alkynes using polyhedral boranes [5]. Männig and Nöth [6] then demonstrated that rhodium complexes could be used to catalyze the hydroboration of alkenes with HBcat under mild conditions and with *chemoselectivity differing from that of the uncatalyzed reaction*. Indeed, in the catalyzed

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hydroboration of 5-hexen-2-one, addition of HBcat occurred preferentially at the C=C double bond, even in the presence of the more reactive ketone group. Since this seminal discovery, a considerable amount of research has focussed on investigating the mechanism and scope of catalyzed hydroboration reactions [7]. Although other transition metals have been found to catalyze hydroborations with HBcat, rhodium catalysts are usually the most effective for reactions of vinylarenes [8]. The judicious choice of the rhodium complex can be used to effectively generate either the expected linear or the unusual branched hydroboration product (Scheme 1). Unfortunately, these reactions can suffer from poor selectivities or competing pathways (i.e., hydrogenation) and, as a result, a considerable amount of research has focussed on designing new catalyst systems [9]. We report herein on the synthesis and reactivity of rhodium(I) complexes containing a bulky iminophosphine ligand.

### 2. Experimental

Reagents and solvents used were purchased from Aldrich Chemicals. NMR spectra were recorded on a JEOL JNM-GSX270 FT spectrometer. <sup>1</sup>H NMR chemical shifts are reported in ppm and referenced to residual solvent protons in deuterated solvent at 270 MHz. <sup>11</sup>B NMR chemical shifts are reported in ppm and are referenced to  $BF_3 \cdot OEt_2$  as an external standard at 87 MHz. <sup>13</sup>C NMR chemical shifts are referenced to solvent carbon resonances as internal standards at 68 MHz and are reported in ppm. <sup>13</sup>P NMR chemical shifts are reported in ppm and are referenced to H<sub>3</sub>PO<sub>4</sub> as an external standard at 109 MHz. Multiplicities are reported as singlet (s), doublet (d), septet (sept), multiplet (m), and overlapping (ov). Microanalyses for C, H, and N were carried out at Guelph Chemical Laboratories (Guelph, ON). All reactions were carried out under an atmosphere of dinitrogen.

# 2.1. Preparation of $[Rh(\kappa^2-o-Ph_2PC_6H_4CH=N-2,6^{-i}Pr_2C_6H_3)(\mu-Cl)]_2$ (2)

A mixture of **1** (122 mg, 0.29 mmol) and [RhCl(coe)<sub>2</sub>]<sub>2</sub> (100 mg, 0.14 mmol) in toluene (3 mL) was allowed to react for 18 h. Upon removal of solvent the mixture was washed with hexane (2 × 3 mL) and dried under vacuum to afford a dark purple solid (Yield 180 mg, 55%). Selected NMR data (in C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H  $\delta$ : 8.10 (d, 2H,  $J_{RhH}$  = 4 Hz, N=CH), 7.70 (m, 8H, Ar), 7.24–7.02 (ov m, 20H, Ar), 6.87 (m, 6H,

Ar), 3.62 (sept, 4H, J = 7 Hz, C(H)Me<sub>2</sub>), 1.40 (d, 12H, J = 7 Hz, Me), 0.88 (d, 12H, J = 7 Hz, Me); <sup>31</sup>P{<sup>1</sup>H}  $\delta$ : 47.1 (d,  $J_{RhP} = 201$  Hz), 46.1 (d,  $J_{RhP} = 200$  Hz).

# 2.2. Preparation of $[Rh(acac)(\kappa^2-o-Ph_2PC_6H_4CH=N-2,6^{-i}Pr_2C_6H_3)]$ (3)

A mixture of 1 (213 mg, 0.47 mmol) and Rh(acac)(coe)<sub>2</sub> (200 mg, 0.47 mmol) in toluene (3 mL) was heated at reflux for 18 h. Upon removal of solvent the mixture was washed with hexane  $(2 \times 1 \text{ mL})$  and dried under vacuum to afford a dark purple solid (Yield 230 mg, 75%). Spectroscopic NMR data (in C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H  $\delta$ : 8.32 (d, 1 H,  $J_{RhH} = 4$  Hz, N=CH), 7.88 (m, 4H, Ar), 7.40 (d of d, 1H, J = 9 Hz, Ar), 7.25 (t, 1H, J = 9 Hz, Ar), 7.19 (d, 2H, J = 9 Hz, Ar), 7.08 (m, 6H, Ar), 6.98 (m, 3H, Ar), 5.18 (s, 1H, CHC(O)Me), 3.73 (sept, 2H, J = 7 Hz,  $C(H)Me_2$ ), 1.60 (s, 3H, Me(O)C), 1.53 (s, 3H, C(O)Me), 1.42 (d, 6H, J = 7 Hz, Me), 0.98 (d, 6H, J = 7 Hz, Me);  ${}^{31}P{}^{1}H{}\delta$ : 50.7 (d,  $J_{\rm RhP} = 206 \, \text{Hz}$ );  ${}^{13}\text{C}{}^{1}\text{H}$   $\delta$ : 184.2, 183.9, 158.8 (d,  $J_{RhC} = 8$  Hz, C(H)N), 151.4, 141.4, 139.2 (d,  $J_{\rm PC} = 19$  Hz), 135.6 (d,  $J_{\rm PC} = 45$  Hz), 134.0 (d.  $J_{PC} = 13$  Hz), 132.7, 132.3 (d,  $J_{PC} = 9$  Hz), 130.0, 129.3 (d,  $J_{PC} = 6$  Hz), 128.9, 127.6 (d,  $J_{PC} = 9$  Hz), 125.9, 122.4, 99.2, 28.0, 26.6, 26.5, 24.4, 23.6. Anal. Calc. for C<sub>36</sub>H<sub>39</sub>NOPRh: C, 66.35; H, 6.04; N, 2.15. Found: C, 66.98; H, 6.47; N, 1.87%.

2.3. Preparation of  $[Rh(catBcat)(\kappa^2-o-Ph_2PC_6H_4CH=N-2,6^{-i}Pr_2C_6H_3)]$  (4)

A mixture of **3** (140 mg, 0.22 mmol) and B<sub>2</sub>cat<sub>3</sub> (74 mg, 0.22 mmol) in Et<sub>2</sub>O (4 mL) was allowed to react for 18 h. A purple solid was collected by suction filtration and dried under vacuum (Yield 62 mg, 35%). Spectroscopic NMR data (in CDCl<sub>3</sub>): <sup>1</sup>H  $\delta$ : 7.81 (d, 1H,  $J_{RhH} = 5$  Hz, N=CH), 7.57–7.49 (ov m, 5H, Ar), 7.42 (m, 8H, Ar), 7.24–7.13 (ov m, 4H, Ar), 5.24 (m, 4H, Ar), 6.62 (m, 4H, Ar), 3.14 (sept, 2H, J = 7 Hz,  $C(H)Me_2$ ), 1.34 (d, 6H, J = 7 Hz, Me), 0.73 (d, 6H, J = 7 Hz, Me); <sup>11</sup>B{<sup>1</sup>H}  $\delta$ : 13.7 (s); <sup>31</sup>P{<sup>1</sup>H}  $\delta$ : 50.6 (d,  $J_{RhP} = 210$  Hz). Anal. Calc. for C<sub>43</sub>H<sub>40</sub>BNO<sub>4</sub>PRh: C, 66.25; H, 5.18; N, 1.80. Found: C, 66.62; H, 5.35; N, 1.98%.

# 2.4. General procedure for the catalyzed hydroboration of vinylarenes

The appropriate hydroboration reagent (1.2 equivalents), in 0.5 mL of  $C_6D_6$ , was added to a 0.5 mL  $C_6D_6$ solution of **3** and the vinylarene. Reactions were allowed



Scheme 1. The rhodium catalyzed hydroboration of styrene with HBcat.

to proceed for 18 h and then monitored by multinuclear NMR spectroscopy.

# 2.5. X-ray crystallography

Crystals of 1 were grown from saturated MeOH and crystals of 2 and 3 from toluene solutions at -5 °C. Single crystals were coated with Paratone-N oil, mounted using a glass fibre 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 30 s exposure times. The detector distances were 5 (1 and 2) and 6 cm (3). The data were reduced [10a] and corrected for absorption [10b]. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  [10c]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in Fourier difference maps and refined isotropically.

# 3. Results and discussion

### 3.1. Synthesis and structures

There has been recent considerable interest in the synthesis of late metal complexes containing P,N-bidentate ligands as catalysts for the hydroboration of vinylarenes [8,11-13]. For example, rhodium guinap (guinap = 1-(2-diphenylphosphino-1-napthyl)isoquinoline, Fig. 1(a)) complexes have been shown to catalyse the addition of HBcat to 2,4-dimethylstyrene to selectively give the corresponding branched isomer [131]. Similar work with rhodium quinazolinap (Fig. 1(b)) [9a] and pyphos (Fig. 1(c)) [9d] complexes has also been reported and these catalysts show excellent selectivity in favour of the branched products. However, a cationic rhodium system using carbohydrate iminophosphine ligands (Fig. 1(d)) was reported in the catalysed hydroboration of 4-methylstyrene with HBcat to give equimolar amounts of the branched and linear products [13i]. Addition of HBcat to 2,3,4,5-pentafluorostyrene using this iminophosphine catalyst system gave predominant formation of the corresponding terminal product. In order to gain an understanding of the factors that influence selectivities in these reactions we have prepared rhodium complexes containing a bulky hemilabile ligand (Fig. 1(e)) and examined their ability to catalyse the hydroboration of a wide range of vinylarenes.

Ligand 1 [14] (Fig. 1(e)) was prepared as described previously and the molecular structure is shown in Fig. 2. Crystallographic data is provided in Table 1. Bond distances and angles are within the range reported for other iminophosphine ligands [15] and are provided in Table 2. In comparison to the related compound *o*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>OMe-*o* [15c], both iminophosphines have a very similar arrangement with planar C(14)– C(19)=N(20)–C(21) imino units with an *E* configuration



Fig. 1. P,N ligands used in the catalysed hydroboration of vinylarenes.

with respect to the diphenylphosphine group. These structures are in contrast to  $o-Ph_2PC_6H_4CH=NC_6H_4OH-o$ [15d] where the nitrogen is closer to the phosphorus atom as the molecule assumes a Z configuration. The N(20)=C(19) double bond of 1 is 1.267(2) Å is well within the range observed for these types of compounds.

Addition of **1** to  $[RhCl(coe)_2]_2$  (coe = *cis*-cyclooctene) lead to the formation of several new iminophosphinorhodium complexes, as indicated by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and the observation of doublets with  $J_{P-Rh} =$ 200 Hz. While we were not able to isolate these products, dimeric **2** has been characterized by a single crystal X-ray diffraction study. The molecular structure of **2** is shown in Fig. 3, crystallographic data in Table 1, and select bond distances and angles in Table 3. The Rh–P bond distances of Rh(1)–P(3) 2.1543(7) Å and Rh(2)–P(4) 2.1507(7) Å are somewhat shorter than typical donor phosphine Rh–P interactions in related 4-coordinate Rh(I) structures [16]. For instance, the average Rh–P interaction in [Rh(dippe) ( $\mu$ -Cl)]<sub>2</sub> (dippe = 1,2-bis(diisopropylphosphino)ethane) is



Fig. 2. A view of compound **1**, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

Table 1 Crystallographic data collection parameters for 1–3

Complex	1	$2 \cdot 2$ MePh	3
Formula	C <sub>31</sub> H <sub>32</sub> NP	$C_{76}H_{80}Cl_2N_2P_2Rh_2$	C <sub>36</sub> H <sub>39</sub> NO <sub>2</sub> PRh
$F_{\rm w}$	449.55	1360.08	651.56
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\overline{1}$
a (Å)	9.8753(11)	23.4312(17)	11.8139(16)
b (Å)	11.8954(14)	12.9412(10)	12.2718(17)
c (Å)	12.6795(15)	22.3225(16)	14.306(2)
α (°)	66.576(2)	90	75.580(2)
$\beta$ (°)	74.721(2)	93.039(1)	67.240(2)
γ (°)	74.208(2)	90	66.349(2)
$V(\text{\AA}^3)$	1294.6(3)	6759.3(9)	1740.9(4)
Z	2	4	2
$\rho_{\rm calc} ({\rm mg}{\rm m}^{-3})$	1.153	1.337	1.243
Crystal size (mm <sup>3</sup> )	$0.35 \times 0.30 \times 0.20$	$0.40 \times 0.25 \times 0.15$	$0.30 \times 0.15 \times 0.15$
Temperature (K)	213(1)	173(1)	173(1)
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Mo Ka ( $\lambda = 0.71073$ )	Mo K $\alpha$ ( $\lambda = 0.71073$ )
$\mu ({\rm mm}^{-1})$	0.125	0.658	0.566
Total reflections	8400	46142	12725
Total unique reflections	5540	14985	12725
Number of variables	426	811	385
R <sub>int</sub>	0.0175	0.0341	
$\Theta$ range (°)	1.78-27.49	0.87-27.50	1.55-25.00
Largest difference peak/hole (e $Å^{-3}$ )	0.505/-0.168	1.057/-0.564	2.174/-0.633
$S(\text{GoF})$ on $F^2$	1.102	1.038	1.073
$R_1^{a} (I \geq 2\sigma(I))$	0.0463	0.0346	0.0577
$wR_2^{\rm b}$ (all data)	0.1356	0.0883	0.1945

<sup>a</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$ 

 $\frac{1}{w} \frac{1}{w} \frac{1}{2} \frac{1}{w} \frac{1}{v} \frac{1}{v} \frac{1}{v} \frac{1}{2} \frac{1}{v} \frac{1$ 

Table 2 Selected bond lengths (Å) and angles (°) for 1

Selected bold lengths (7) and angles (7) for 1		
P-C(7)	1.8260(17)	
P–C(1)	1.8297(16)	
P-C(13)	1.8363(16)	
C(19)–N(20)	1.2668(19)	
N(20)-C(21)	1.4280(19)	
C(7)–P–C(1)	103.39(7)	
C(7)–P–C(13)	103.07(7)	
C(1)–P–C(13)	101.91(7)	
C(26)-C(21)-N(20)	120.78(13)	
C(22)-C(21)-N(20)	117.26(13)	
N(20)-C(19)-C(14)	121.46(14)	
N(20)-C(19)-H(19)	121.0(9)	
C(19)-N(20)-C(21)	118.68(13)	



2.1821(13) Å [16b]. Furthermore, the Rh–P bond distances in related rhodium(I) cationic complexes containing **1** range from 2.1934(11) to 2.2361(6) Å [17]. Rhodium phosphorus bond distances similar to **2** have been found, however, in related diphosphite complexes [18a,18b] and in [Rh(dfepe)( $\mu$ -Cl)]<sub>2</sub> (dfepe = (C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>) [18c], which contains electron-withdrawing fluoroalkylphosphines. The Rh–N distances of Rh(1)–N(23) 1.996(2) Å and Rh(2)–N(55) 2.005(2) Å are similar to those reported in other rhodium imine complexes [19]. The Rh<sub>2</sub>( $\mu$ -Cl)<sub>2</sub> core is strictly planar with a Rh–Rh distance of 3.4806(3) Å and the metals occupying a distorted square

Fig. 3. A view of complex 2, with displacement ellipsoids drawn at the 30% probability level. H atoms and solvent molecules have been omitted for clarity.

planar environment. Interestingly, cationic diolefin rhodium(I) complexes containing 1 have been shown to undergo conformational change of the iminophosphine ligands in solution, whereby inverting the position of the six-membered chelate ring relative to the N–Rh–P plane [20]. It is possible that this process is responsible for generating isomers of 2 and making isolation problematic.

Table 3 Selected bond lengths (Å) and angles (°) for  ${\bf 2}$ 

6	0		
Rh(1)–N(23)	1.996(2)		
Rh(1) - P(3)	2.1543(7)	N(23)-Rh(1)-P(3)	90.02(6)
Rh(1)-Cl(2)	2.3469(7)	N(23)-Rh(1)-Cl(2)	175.79(6)
Rh(1)-Cl(1)	2.4325(7)	P(3)-Rh(1)-Cl(2)	93.35(2)
Rh(2)–N(55)	2.005(2)	N(23)-Rh(1)-Cl(1)	94.23(6)
Rh(2)–P(4)	2.1507(7)	P(3)-Rh(1)-Cl(1)	175.37(2)
Rh(2)-Cl(1)	2.3490(7)	Cl(2)-Rh(1)-Cl(1)	82.48(2)
Rh(2)-Cl(2)	2.4582(7)	N(55)-Rh(2)-P(4)	89.72(6)
C(22)–N(23)	1.301(3)	N(55)-Rh(2)-Cl(1)	175.76(6)
N(23)-C(24)	1.467(3)	P(4)-Rh(2)-Cl(1)	92.78(3)
C(54)-N(55)	1.300(3)	N(55)-Rh(2)-Cl(2)	95.62(6)
C(54)-H(54)	0.9500	P(4)-Rh(2)-Cl(2)	174.66(3)
N(55)-C(56)	1.454(3)		
Cl(1)-Rh(2)-Cl(2)	81.89(2)	C(48)-P(4)-C(42)	102.50(13)
Rh(2)-Cl(1)-Rh(1)	93.41(2)	C(48)-P(4)-C(36)	103.19(13)
Rh(1)-Cl(2)-Rh(2)	92.80(2)	C(42) - P(4) - C(36)	102.90(13)
C(16)-P(3)-C(4)	102.85(12)	C(48) - P(4) - Rh(2)	113.85(9)
C(16)-P(3)-C(10)	102.51(12)	C(42)-P(4)-Rh(2)	120.75(9)
C(4) - P(3) - C(10)	102.79(12)	C(36) - P(4) - Rh(2)	111.67(9)
C(16) - P(3) - Rh(1)	113.22(8)	C(22)-N(23)-Rh(1)	131.69(17)
C(4) - P(3) - Rh(1)	118.78(9)	C(24)-N(23)-Rh(1)	116.08(15)
C(10)–P(3)–Rh(1)	114.70(8)		

As mentioned previously, rhodium phosphine complexes are versatile and efficient catalysts for the hydroboration of alkenes using catecholborane (HBcat). Among this group, complexes of the type  $Rh(acac)(P_2)$ (acac = acetylacetonato;  $P_2$  = diphosphine) are unique in that they are the only catalyst precursors to have been used in the hydroboration of a tetrasubstituted alkene [7d]. These complexes are also active and selective catalysts for the hydroboration of a wide range of vinylarenes using HBcat, giving predominantly the corresponding branched isomers. In this study, we have prepared the analogous rhodium acetylacetonato complex bearing the bulky iminophosphine ligand 1.

Addition of 1 to Rh(acac)(coe)<sub>2</sub> [21] gave the corre- $[Rh(acac)(\kappa^2-o-Ph_2PC_6H_4CH=N$ complex sponding  $2.6^{-i}Pr_2C_6H_3$ ] (3) in yields of up to 75%. The  ${}^{31}P{}^{1}H{}$ NMR spectra showed a doublet with coupling to rhodium with  $J_{P-Rh} = 206$  Hz. Complex 3 has also been characterized by a single crystal X-ray diffraction study (Fig. 4). The rhodium atom lies in a distorted square planar geometry. While the rhodium oxygen distance of Rh-O(33) of 2.077(3) Å is slightly longer than that found in other rhodium acetylacetonato complexes [22], the Rh–O(37) bond length of 2.018(3) Å is somewhat shorter. This result is presumably due to the steric crowding caused by the bulky imine group, leading to an asymmetry of the steric demand of the iminophosphine ligand. Selected bond distances and angles are provided in Table 4.

Although phosphinorhodium acetylacetonato complexes are active and selective catalysts for the hydroboration of a wide range of alkenes, the catalyst resting state in these systems is believed to be the zwitterionic complexes  $Rh(\eta^6-catBcat)(P_2)$ , arising from the redistribution of substituents on HBcat [7d,23]. Indeed, hydroborations using these zwitterionic complexes give similar selectivities to

Fig. 4. A view of complex **3**, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

Table 4 Selected bond lengths (Å) and angles (°) for **3** 

Rh–N(1)	2.015(3)
Rh–O(37)	2.018(3)
Rh–O(33)	2.077(3)
Rh–P	2.1692(11)
P-C(4)	1.812(4)
P-C(15)	1.823(4)
P-C(9)	1.836(5)
N(1)–C(2)	1.287(5)
N(1)-C(21)	1.486(5)
N(1)-Rh-O(37)	178.37(14)
N(1)-Rh-O(33)	89.96(13)
O(37)–Rh–O(33)	89.57(12)
N(1)-Rh-P	88.07(10)
O(37)–Rh–P	92.43(9)
O(33)-Rh-P	177.66(9)
C(4)–P–C(15)	105.03(18)
C(4)–P–C(9)	101.90(19)
C(15)–P–C(9)	103.06(19)
C(4)–P–Rh	111.08(14)
C(15)–P–Rh	118.81(14)
C(9)–P–Rh	115.14(13)
C(2)-N(1)-C(21)	115.0(3)
C(2)–N(1)–Rh	132.1(3)
C(21)–N(1)–Rh	112.6(3)
N(1)-C(2)-C(3)	127.0(4)

those observed for the acetylacetonato precursors. In an elegant study, Marder and co-workers [23c] found that addition of B<sub>2</sub>cat<sub>3</sub> to Rh(acac)(P<sub>2</sub>) led to the zwitterionic complexes Rh( $\eta^6$ -catBcat)(P<sub>2</sub>) in high yields, along with concomitant formation of acacBcat. In this study we have found that addition of B<sub>2</sub>cat<sub>3</sub> to **3** gave the zwitterionic compound [Rh(catBcat)( $\kappa^2$ -o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH=N-2,6-<sup>i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)] (4). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a doublet with coupling to rhodium at  $J_{P-Rh} = 210$  Hz and the <sup>11</sup>B{<sup>1</sup>H} NMR has a sharp peak at 14 ppm, consistent with the boron atom being four coordinate [23]. All attempts to grow single crystals of **4** suitable for X-ray diffraction stud-

ies proved unsuccessful. Compound **4** rapidly decomposed in chloroform or methylene chloride and as a result, we were unable to obtain useful <sup>13</sup>C{<sup>1</sup>H} NMR data. This result is not surprising as rhodium(I) complexes are well know to activate the C–Cl bond in these solvents [24]. Complexes **2** and **3** also decomposed in chlorinated solvents.

### 3.2. Catalysed hydroborations

The mechanism of the catalyzed hydroboration reaction has been the subject of considerable debate [11]. For reactions using commonly employed RhCl(PPh<sub>3</sub>)<sub>3</sub>, one plausible mechanism has been postulated to occur via initial loss of phosphine to give 'RhCl(PPh<sub>3</sub>)<sub>2</sub>', which in turn oxidatively adds the borane to the metal centre to give an unsaturated hydrido boryl intermediate. This is followed by coordination of the alkene and insertion into either the Rh–H or Rh–B bond [6] with subsequent reductive elimination to afford the corresponding organoboronate ester product (Scheme 2). The unusual regioselectivity observed in hydroborations of vinylarenes is believed to arise when the rhodium centre can best stabilize a benzylic intermediate [10].

In order to compare these new complexes against other rhodium catalysts, we have examined 3 for its ability to catalvze the hydroboration of a series of vinvlarenes. Catalytic studies were not done with the chloride dimer due to difficulties in isolating one discrete complex. Initial studies with 3 were done on 4-vinylanisole using HBcat in C<sub>6</sub>D<sub>6</sub> and this reaction (Scheme 3), surprisingly, gave a mixture of products including the linear hydroboration product 4-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>Bcat (25% by <sup>1</sup>H NMR spectroscopy), the alkenyl boronate ester trans-4-MeOC<sub>6</sub>H<sub>4</sub>CH=CHBcat (25%) and the diborated product 4-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH(B $cat_{2}$  (50%). Interestingly, unlike reactions using other phosphinorhodium acetylacetonato complexes. the branched product 4-MeOC<sub>6</sub>H<sub>4</sub>CH(Bcat)CH<sub>3</sub> was not observed to any significant degree. The diborated product presumably arises from hydroboration of the alkenyl boronate ester, which is generated from a dehydrogenative borylation reaction [25]. Dehydrogenative borylations are generally believed to occur via initial coordination of the alkene to the metal centre followed by insertion into the Rh–B, and not the Rh–H bond, with subsequent  $\beta$ -H elimination to give the corresponding alkenyl boronate ester and an active rhodium dihydride species. Although the linear product could be generated from a traditional catalyzed



Scheme 2. A plausible mechanism for the catalysed hydroboration of alkenes using RhCl(PPh<sub>3</sub>)<sub>3</sub>.



Scheme 3. Catalyzed addition of 4-vinylanisole using HBcat and 3.



Scheme 4. Catalyzed addition of 4-vinylanisole using HBpin and 3.



Scheme 5. Catalyzed addition of 2,3,4,5,6-C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub> using HBpin and 3.

hydroboration reaction, it is also plausible that this product arises from the catalyzed hydrogenation of alkenyl boronate ester via the aforementioned rhodium dihydride intermediate.

Reactions of 4-vinylanisole using pinacolborane (HBpin, pin =  $1,2-O_2C_2Me_4$ ) and 3 gave *exclusive formation* of the corresponding linear 'hydroboration product' 4-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>Bpin after 24 hours (Scheme 4). However, monitoring this addition by <sup>1</sup>H NMR spectroscopy showed the formation of a transient alkenyl boronate ester 4-MeOC<sub>6</sub>H<sub>4</sub>CH=CHBpin at the beginning of the reaction. This observation suggests that reactions using bulky 3 are occurring predominantly through a competing dehydrogenative borylation reaction. Similar chemistry was observed using both HBpin and HBcat for reactions with 2,4,6-trimethylstyrene,  $\alpha$ -methylstyrene and  $\beta$ -methylstyrene. Reactions using preformed zwitterionic 4 also gave similar regioselectivities with both HBcat and HBpin.

Reactions with 4-fluorostyrene, 2,3,4,5,6-perfluorostyrene, and 2-naphthylstyrene and HBcat all gave complicated product distributions, including varying amounts of the corresponding branched hydroboration products. For instance, reactions of highly activated 2,3,4,5,6-perfluorostyrene with HBcat and **3** gave up to 50% of 2,3,4,5,6- $C_6F_5CH(Bcat)CH_3$ . Interestingly, reactions of 2,3,4,5,6perfluorostyrene with HBpin and **3** also gave several products, including the linear hydroboration product, diborated and hydrogenation products and even the branched product 2,3,4,5,6- $C_6F_5CH(Bpin)CH_3$  (50%) (Scheme 5). A recent report [26] describes the formation of similar branched products from hydroborations of vinylarenes using cyclooctadiene rhodium(I) catalysts and HBpin. Reactions with **3**, however, appear to be substrate dependent and further work is therefore needed to understand the factors controlling product selectivities.

# 4. Conclusions

We have found that addition of  $o-Ph_2PC_6H_4CH=$ N-2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1) to [RhCl(coe)<sub>2</sub>]<sub>2</sub> (coe = *cis*-cycloctene) gave several new iminophosphino rhodium(I) complexes including  $[Rh(\kappa^2-o-Ph_2PC_6H_4CH=N-2,6-Pr_2C_6H_3)(\mu-Cl)]_2$ (2). Addition of 1 to  $Rh(acac)(coe)_2(acac = acetylacetonato)$ gave  $[Rh(acac)(\kappa^2 - o - Ph_2PC_6H_4CH = N - 2, 6 - iPr_2C_6H_3)]$  (3), which could be converted to the zwitterionic [Rh(catB $cat)(\kappa^2 - o - Ph_2PC_6H_4CH = N - 2, 6 - iPr_2C_6H_3)]$  (4) by addition of B<sub>2</sub>cat<sub>3</sub>. Complex 3 has been examined for its ability to catalyze the hydroboration of a series of vinyl arenes. Reactions using catecholborane and pinacolborane seem to proceed largely through a dehydrogenative borylation mechanism to give a number of boronated products. Future work will investigate other iminophosphine rhodium complexes for their ability to catalyze the hydroboration of vinylarenes and to gain insight into the steric and electronic requirements needed for the metal to facilitate these unusual dehydrogenative borylation reactions.

#### 5. Supplementary data

Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 285186–285188). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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