# Rhodium(I) acetylacetonato complexes containing phosphinoalkynes as catalysts for the hydroboration of vinylarenes[1]

**Christopher M. Vogels, Andreas Decken, and Stephen A. Westcott**

**Abstract:** Three novel rhodium(I) acetylacetonato (acac) complexes bearing phosphinoalkynes ($Ph_2PC{\equiv}C$-*t*-Bu, $Ph_2PC{\equiv}CPPh_2$, and $Ph_2PC{\equiv}CC{\equiv}CPPh_2$) have been prepared and characterized fully. Addition of $B_2cat_3$ (cat = 1,2-$O_2C_6H_4$) to Rh(acac)($Ph_2PC{\equiv}C$-*t*-Bu)$_2$ (**1a**) led to zwitterionic Rh($\eta^6$-catBcat)($Ph_2PC{\equiv}C$-*t*-Bu)$_2$ (**2a**), the first example of this type of compound to contain monodentate phosphine ligands. All new rhodium complexes have been investigated for their ability to catalyse the hydroboration of vinylarenes.

*Key words:* catalysis, hydroboration, phosphinoalkynes, regioselectivity, rhodium.

**Résumé :** On a préparé et complètement caractérisé trois nouveaux complexes acétylacétonato du rhodium(I) portant des phosphinoalcynes ($Ph_2PC{\equiv}C$-*t*-Bu; $Ph_2PC{\equiv}CPPh_2$ et $Ph_2PC{\equiv}CC{\equiv}CPPh_2$). L'addition de $B_2cat_3$ (cat = 1,2-$O_2C_6H_4$) au Rh(acac)($Ph_2PC{\equiv}C$-*t*-Bu)$_2$ (**1a**) conduit à la formation du composé zwitterionique Rh($\eta^6$-catBcat)($Ph_2PC{\equiv}C$-*t*-Bu)$_2$ (**2a**), le premier exemple de ce type de composé à contenir des ligands phosphines monodentates. On a examiné l'utilité potentielle de tous les nouveaux complexes du rhodium comme catalyseurs pour l'hydroboration de vinylarènes.

*Mots clés :* catalyse, hydroboration, phosphinoalcynes, régiosélectivité, rhodium.

[Traduit par la Rédaction]

## 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 today. Indeed, organoboranes can be transformed into any number of functional groups. The simplest boron hydride agent is borane, $BH_3$, 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 ($BR_2$) 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 $H_3B{\cdot}THF$ to catechol affords catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$), a relatively stable hydroborating agent, which adds to alkenes and alkynes only at elevated temperatures (ca. 100 and 70 °C, respectively) (3). Catecholborane 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 catalysed hydroborations of alkenes and alkynes using polyhedral boranes (5). Männig and Nöth (6) then demonstrated that rhodium complexes could be used to catalyse the hydroboration of alkenes with HBcat under mild conditions and with *chemoselectivity differing from that of the uncatalysed reaction* (Scheme 1). Indeed, in the catalysed 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 focused on investigating the mechanism and scope of late metal catalysed hydroboration reactions (7). Although other metals have been found to catalyse hydroborations with HBcat, rhodium-based catalyst systems are usually the most effective for reactions of vinylarenes (8). Unfortunately, these reactions often suffer from poor selectivities or competing pathways (i.e., hydrogenation), and as a result, a considerable amount of research has focused on designing new catalyst systems (9). We report herein on the synthesis and hydroboration of rhodium(I) acetylacetonato complexes containing phosphinoalkyne ligands.

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*Dedicated to Dr. A.J. Carty in recognition of his outstanding contributions to chemistry and for being an exceptional and encouraging teacher and mentor.*

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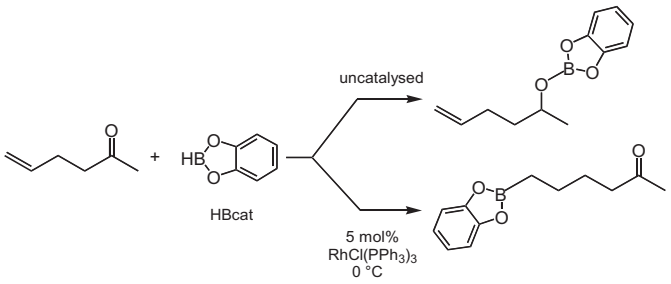
**Scheme 1.** Hydroboration of 5-hexen-2-one.




## Experimental

### General

Reagents and solvents used were purchased from Aldrich Chemicals. NMR spectra were recorded on a JEOL JNM-GSX270 FT spectrometer. $^{1}$H NMR chemical shifts are reported in parts per million (ppm) and referenced to residual solvent protons in deuterated solvent at 270 MHz. $^{11}$B NMR chemical shifts are reported in ppm and are referenced to $BF_3{\cdot}OEt_2$ as an external standard at 87 MHz. $^{13}$C NMR chemical shifts are referenced to solvent carbon resonances as internal standards at 68 MHz and are reported in ppm. $^{31}$P NMR chemical shifts are reported in ppm and are referenced to $H_3PO_4$ as an external standard at 109 MHz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m), broad (br), and overlapping (ov). All reactions were carried out under an atmosphere of dinitrogen. Microanalyses for C and H were carried out at Guelph Chemical Laboratories (Guelph, Ontario). Phosphines were prepared as described previously and donated as a generous gift from Dr. J.F. Corrigan (10). Rh(acac)(coe)$_2$ was prepared as described previously (11).

### Rh(acac)(Ph$_2$PC≡C-*t*-Bu)$_2$ (1a)

A solution of Ph$_2$PC≡C-*t*-Bu (0.25 g, 0.95 mmol) in toluene (1 mL) was added to a solution of Rh(acac)(coe)$_2$ (0.20 g, 0.47 mmol) in toluene (2 mL), and the mixture was stirred for 18 h. The removal of solvent under vacuum afforded an orange solid, which was washed with hexane (3 × 3 mL) and collected by suction filtration to give **1a** (0.31 g, 88%). Spectroscopic NMR data (in $C_6D_6$): $^{1}$H δ: 8.25–8.18 (ov m, 8H, Ar), 7.17–7.04 (ov m, 12H, Ar), 5.20 (s, 1H, C=C*H*), 1.53 (s, 6H, C(O)*Me*), 0.93 (s, 18H, *tert*-butyl). $^{13}$C{$^{1}$H} δ: 184.3, 137.0 (app. quint, $J_{C\text{-}P\text{-}Rh}$ = 26 Hz), 133.9 (t, $J_{C\text{-}P}$ = 6 Hz), 128.7, 127.3 (t, $J_{C\text{-}P}$ = 5 Hz), 114.4 (t, $J_{C\text{-}P}$ = 6 Hz, PC*C*), 99.6, 75.7 (td, $J_{C\text{-}P}$ = 153, 46 Hz, P*C*C), 29.9, 28.2, 26.8. $^{31}$P{$^{1}$H} δ: 31.4 (d, $J_{P\text{-}Rh}$ = 196 Hz). Anal. calcd. for $C_{41}H_{45}O_2P_2Rh$ (%): C 67.02, H 6.19; found: C 66.79, H 6.45.

### [{Rh(acac)}$_2$(μ-Ph$_2$PC≡CPPh$_2$-κ$^2$*P*)$_2$] (1b)

A solution of Ph$_2$PC≡CPPh$_2$ (0.14 g, 0.36 mmol) in toluene (1 mL) was added to a solution of Rh(acac)(coe)$_2$ (0.15 g, 0.36 mmol) in toluene (2 mL), and the mixture was stirred for 18 h. The solvent was removed under vacuum, and the resulting orange precipitate was washed with hexane (3 × 3 mL) and collected by suction filtration to give **1b** (0.18 g, 82%). Spectroscopic NMR data (in $C_6D_6$): $^{1}$H δ: 7.95–7.88 (ov m, 16H, Ar), 7.01–6.89 (ov m, 24H, Ar), 5.26 (s, 2H, C=C*H*), 1.57 (s, 12H, C(O)*Me*). $^{13}$C{$^{1}$H} δ: 184.6, 134.1 (app. quint, $J_{C\text{-}P\text{-}Rh}$ = 27 Hz), 133.4 (t, $J_{C\text{-}P}$ = 6 Hz), 128.9, 127.5 (t, $J_{C\text{-}P}$ = 5.2 Hz), 102.4 (td, $J_{C\text{-}P}$ = 109, 36 Hz, P*C*C), 99.8, 26.9. $^{31}$P{$^{1}$H} δ: 32.1 (d, $J_{P\text{-}Rh}$ = 191 Hz). Anal. calcd. for $C_{62}H_{54}O_4P_4Rh_2$ (%): C 62.42, H 4.57; found: C 62.26, H 4.25.

### [{Rh(acac)}$_2$(μ-Ph$_2$PC≡CC≡CPPh$_2$-κ$^2$*P*)$_2$] (1c)

A solution of Ph$_2$PC≡CC≡CPPh$_2$ (0.22 g, 0.52 mmol) in THF (1 mL) was added to a solution of Rh(acac)(coe)$_2$ (0.20 g, 0.47 mmol) in THF (2 mL), and the mixture was stirred for 1 h. The resulting orange precipitate was collected by suction filtration and washed with hexane (3 × 3 mL) to give **3** (0.28 g, 95%). Spectroscopic NMR data (in $C_6D_6$): $^{1}$H δ: 7.94–7.90 (ov m, 16H, Ar), 6.98–6.90 (ov m, 24H, Ar), 5.25 (s, 2H, C=C*H*), 1.52 (s, 12H, C(O)*Me*). $^{31}$P{$^{1}$H} δ: 35.5 (d, $J_{P\text{-}Rh}$ = 193 Hz). Anal. calcd. for $C_{66}H_{54}O_4P_4Rh_2$ (%): C 63.87, H 4.39; found: C 63.42, H 4.49.

### Rh(η$^6$-Bcat$_2$)(Ph$_2$PC≡C-*t*-Bu)$_2$ (2a)

A solution of $B_2cat_3$ (0.05 g, 0.14 mmol) in toluene (0.5 mL) was added to a solution of Rh(acac)(Ph$_2$PC≡C-*t*-Bu)$_2$ (0.10 g, 0.14 mmol) in toluene (2 mL), and the mixture was stirred for 18 h. The precipitate that formed was removed by suction filtration, and hexane (3 mL) was added to the filtrate, and the solution was stored at –25 °C for 3 days. The resulting red precipitate was collected by suction filtration to afford **2a** (0.080 g, 66%). Spectroscopic NMR data (in $C_6D_6$): $^{1}$H δ: 7.89–7.81 (ov m, 8H, Ar), 7.15–6.96 (ov m, 16H, Ar), 4.83 (m, 4H, η$^6$-cat), 0.80 (s, 18H, *tert*-butyl). $^{11}$B δ: 15.0. $^{31}$P{$^{1}$H} δ: 23.6 (d, $J_{P\text{-}Rh}$ = 213 Hz). Anal. calcd. for $C_{48}H_{46}BO_4P_2Rh$ (%): C 66.83, H 5.39; found: C 67.17, H 5.62.

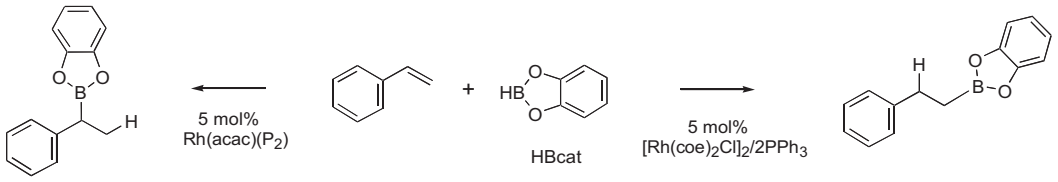
### General procedure for the hydroboration of vinylarenes

Under an atmosphere of dinitrogen, 1 equiv. of catecholborane in 0.5 mL of $C_6D_6$ was added to a 0.5 mL $C_6D_6$ solution of the appropriate catalyst and vinylarene. The reactions were allowed to proceed for 18 h, at which point NMR data were collected. Product distributions were confirmed by GC–MS.

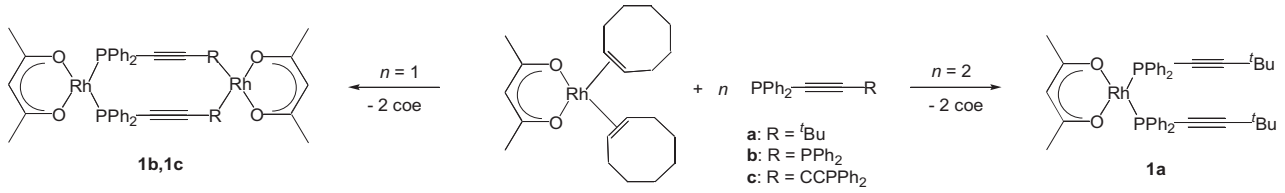
### X-ray crystallography

Crystals of **1a** and **2a** were grown from satd. $Et_2O$ and toluene–hexane (1:1) solutions, respectively, at –30 °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 ω and θ scans with a scan width of 0.3° and exposure times of 30 s (**1a**) and 10 s (**2a**). The detector distances were 5 cm (**2a**) and 6 cm (**1a**). Crystals of **1a** were multiple twins; however, only the data for the major isomer lead to a successful structure refinement. The data were reduced (12*a*) and corrected for absorption (12*b*). The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$ (12*c*). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in Fourier difference maps and refined isotropically.

**Scheme 2.** The rhodium-catalysed hydroboration of styrene with HBcat.




**Scheme 3.** Synthesis of rhodium complexes **1a**–**1c**.



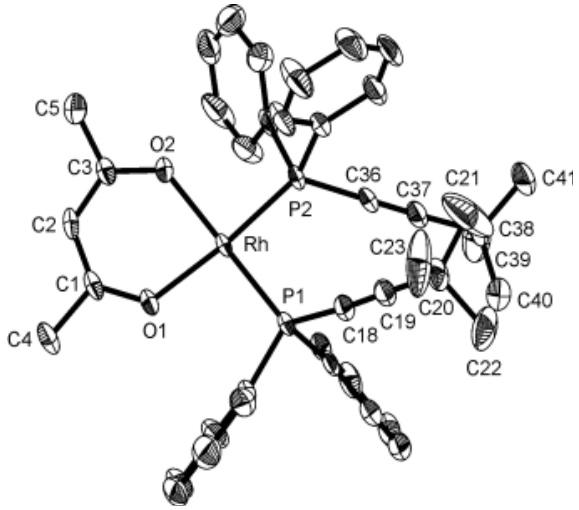

## Results and discussion

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 (13*a*). 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 (Scheme 2). Although a considerable amount of research has focused on using these complexes as catalysts for this reaction (13), all examples have used chelating bidentate phosphines. In this study, we have prepared the analogous rhodium acetylacetonato complexes bearing monodentate phosphinoalkynes and examined their ability to catalyze the hydroboration of vinylarenes.

### Rhodium complexes

The coordination chemistry of bis(diphenylphosphino)acetylene and related alkynyl phosphines is an area of considerable interest (14–17). Although the normal mode of coordination is via the phosphine groups, examples where the alkyne unit is bound to a metal in a $\eta^2$-$\pi$ fashion are also known (15*i*). We have found that alkynyl phosphines **a**–**c** add to $Rh(acac)(coe)_2$ (coe = *cis*-cyclooctene) to give $Rh(acac)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ (**1a**), $[\{Rh(acac)\}_2(\mu\text{-}Ph_2PC{\equiv}CPPh_2\text{-}\kappa^2P)_2]$ (**1b**), and $[\{Rh(acac)\}_2(\mu\text{-}Ph_2PC{\equiv}CC{\equiv}CPPh_2\text{-}\kappa^2P)_2]$ (**1c**), respectively (Scheme 3). All new complexes have been characterized by a number of physical methods, including multinuclear NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra all showed doublets with coupling to rhodium with ca. $J_{P\text{-}Rh}$ = 195 Hz. Complex **1a** has also been characterized by a single crystal X-ray diffraction study (Fig. 1),[3] confirming that ligand **a** is bound to the metal centre via the phosphine groups. The rhodium atom lies in a distorted square-planar geometry with typical rhodium–oxygen distances of Rh—O(1) 2.057(3) and Rh—O(2) 2.061(3) Å

**Fig. 1.** The molecular structure of **1a** showing probability ellipsoids at 30% and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Rh—O(1) 2.057(3), Rh—O(2) 2.061(3), Rh—P(1) 2.173(1), Rh—P(2) 2.182(1), C(18)—C(19) 1.186(6), C(36)—C(37) 1.180(6); O(1)-Rh-O(2) 88.3(1), O(1)-Rh-P(1) 90.98(8), O(2)-Rh-P(1) 176.24(9), O(1)-Rh-P(2) 174.28(8), O(2)-Rh-P(2) 86.04(9), P(1)-Rh-P(2) 94.72(4), P(1)-C(18)-C(19) 174.2(4), P(2)-C(36)-C(37) 178.8(4).




found in other rhodium acetylacetonato complexes (18). Likewise, bond distances and angles within the phosphine ligands are similar to those reported previously, with C≡C bond lengths of C(18)—C(19) 1.186(6) and C(36)—C(37) 1.180(6) Å (17). Crystallographic data are given in Table 1. For complexes **1b** and **1c**, coordination of both phosphine groups to rhodium is observed by $^{31}P$ NMR spectroscopy.

As mentioned previously, phosphinorhodium acetylacetonato complexes are active and selective catalysts for the hydroboration of a wide range of alkenes. However, the catalyst resting state in these systems is believed to be the zwit-

[3] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 4088. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 275010 and 275011 contain the crystallographic data for this manuscript. These 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).

**Table 1.** Crystallographic data collection parameters for **1a** and **2a**.

| | **1a** | **2a** |
|---|---|---|
| Formula | $C_{41}H_{45}O_2P_2Rh$ | $C_{48}H_{46}BO_4P_2Rh$ |
| fw | 734.62 | 862.51 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| a (Å) | 12.151(3) | 11.749 9(9) |
| *b* (Å) | 12.820(3) | 14.204 1(11) |
| *c* (Å) | 13.875(3) | 14.348 2(11) |
| α (°) | 97.010(3) | 85.954(1) |
| β (°) | 96.656(4) | 70.850(1) |
| γ (°) | 117.772(3) | 71.777(1) |
| *V* (Å$^3$) | 1861.0(7) | 2 147.3(3) |
| *Z* | 2 | 2 |
| $\rho_{calcd}$ (mg m$^{-3}$) | 1.311 | 1.334 |
| Crystal size (mm$^3$) | 0.225×0.2×0.05 | 0.40×0.35×0.15 |
| Temperature (K) | 173(1) | 173(1) |
| Radiation | Mo Kα (λ = 0.710 73 Å) | Mo Kα (λ = 0.710 73 Å) |
| μ (mm$^{-1}$) | 0.578 | 0.515 |
| Total reflections | 8835 | 15 025 |
| Total unique reflections | 5824 | 9 365 |
| No. of variables | 454 | 541 |
| $R_{int}$ | 0.034 1 | 0.015 7 |
| θ Range (°) | 1.83–24.99 | 1.50–27.49 |
| Largest difference peak/hole (e Å$^{-3}$) | 2.529/–2.163 | 0.887/–0.239 |
| *S* (GoF) on $F^2$ | 1.013 | 1.067 |
| $R_1$[a] ($I>2\sigma(I)$) | 0.060 1 | 0.028 6 |
| $wR_2$[b] (all data) | 0.156 4 | 0.077 9 |

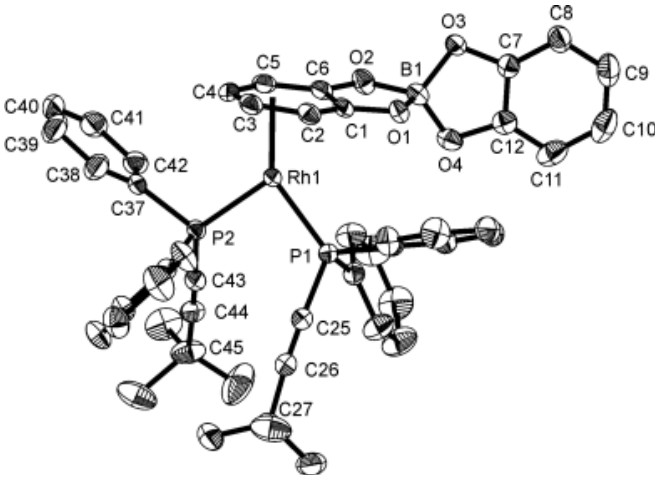
[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.1223P)^2]$ (**1a**) and $w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + (0.6575P)]$ (**2a**), where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

terionic complexes Rh(η$^6$-catBcat)($P_2$), arising from the redistribution of substituents on HBcat. Indeed, hydroborations using these zwitterionic complexes give similar selectivities to those observed for the acetylacetonato precursors (13). In an elegant study, Marder and co-workers (13*d*) found that addition of $B_2cat_3$ to Rh(acac)($P_2$) led to the zwitterionic complexes Rh(η$^6$-catBcat)($P_2$) in high yields, along with concomitant formation of acacBcat. The diboron species $B_2cat_3$ is generated as an unwanted decomposition product in nucleophilic reactions with HBcat or when HBcat is heated to elevated temperatures (7*f*). We have found that addition of $B_2cat_3$ to **1a** gave the corresponding zwitterionic complex Rh(η$^6$-catBcat)($Ph_2PC{\equiv}C$-*t*-Bu)$_2$ (**2a**), which represents the first example of this type of compound to bear monodentate phosphine ligands (13*d*) to be structurally characterized by X-ray diffraction. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet with coupling to rhodium at $J_{P\text{-}Rh}$ = 213 Hz and the $^{11}B$ NMR has a sharp peak at 15 ppm, consistent with the boron atom being four coordinate (19, 20). The molecular structure of **2a** has been confirmed by a single crystal X-ray diffraction study (Fig. 2) and shows that the $P_2Rh$ fragment is bound to the catBcat$^-$ anion via one of the catecholato groups in a η$^6$ fashion. As with related systems (19), there appears to be considerable slippage of the $P_2Rh$ group with respect to the π-bound arene ring. Indeed, two bond distances, Rh(1)—C(4) and Rh(1)—C(3), are considerably shorter (2.254(2) and 2.275(2) Å) than the remaining Rh—C bonds (ranging from 2.336(2) to 2.497(2) Å). The potential surface for such distortions is reputably quite shallow. Initial attempts to prepare **1b** and **1c** via this route were complicated by considerable degradation to give rhodium metal and a number of unidentified rhodium phosphine complexes. Interestingly, the reactivity of related rhodium β-diketonate diphosphine complexes with chlorinated solvents has been reported previously (21).

## Hydroboration studies

To compare complexes **1a**–**1c** against other rhodium catalysts, we have examined their ability to catalyse the hydroboration of a series of vinylarenes. Initial studies were done on 4-vinylanisole in $C_6D_6$ (**3**, Table 2), and as with many other rhodium catalysts, all new phosphinoalkyne complexes gave selective formation of the branched isomer **3a**. Interestingly, hydroborations with isolated **2a** also gave exclusive formation of this product. In reactions of 4-fluorostyrene (**4**), however, complexes **1a** and **1c** gave small amounts of diboration product **4c** and hydrogenation product **4d**. Diborated product **4c** presumably arises from hydroboration of the transient vinyl boronate ester 4-F-$C_6H_4$CH=CHBcat, which is generated from a competing dehydrogenative borylation reaction (22). The vinyl boronate ester products are not observed to any extent, via $^1H$ NMR spectroscopy, in reactions using these relatively unhindered alkenes. 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

**Fig. 2.** The molecular structure of **2a** showing probability ellipsoids at 30% and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)—P(2) 2.2129(5), Rh(1)—P(1) 2.2260(5), Rh(1)—C(4) 2.254(2), Rh(1)—C(3) 2.275(2), Rh(1)—C(2) 2.336(2), Rh(1)—C(1) 2.392(2), Rh(1)—C(5) 2.429(2), Rh(1)—C(6) 2.497(2), B(1)—O(4) 1.461(3), B(1)—O(3) 1.469(2), B(1)—O(2) 1.494(3), B(1)—O(1) 1.511(2), C(25)—C(26) 1.193(3), C(43)—C(44) 1.185(3); P(2)-Rh(1)-P(1) 91.85(2), O(4)-B(1)-O(3) 106.1(2), O(4)-B(1)-O(2) 112.7(2), O(3)-B(1)-O(2) 113.8(2), O(4)-B(1)-O(1) 111.5(2), O(3)-B(1)-O(1) 109.8(2), O(2)-B(1)-O(1) 103.2(2).



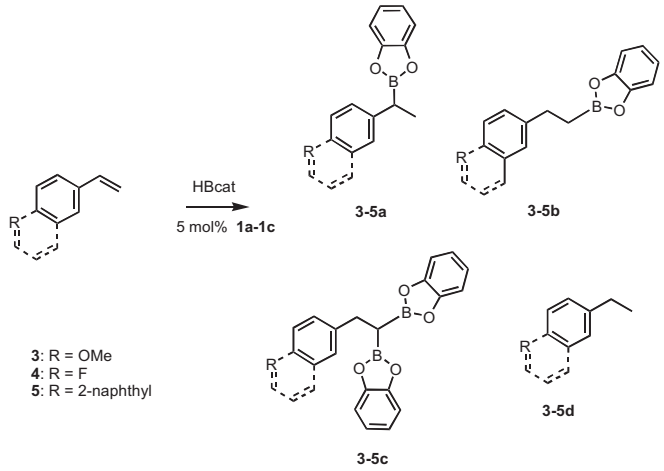

β-H elimination to give the corresponding vinyl boronate ester and an active rhodium dihydride species. This latter dihydride is presumably responsible for the hydrogenation of the starting alkene to give **4d**. Similar selectivities were observed in hydroborations of 2-vinylnaphthylene (**5**). Interestingly, dirhodium complex **1b** gave the best selectivities of the three new rhodium complexes examined for these reactions. Ratios of products were determined by multinuclear NMR spectroscopy and confirmed by GC–MS (7*e*, 13*a*).

Hydroborations of electron-deficient 2,3,4,5,6-pentafluorostyrene (**6**) were also examined, and selectivities are similar to that observed in reactions with 4-vinylanisole (Table 3). These results suggest the electronic nature of the arene group does not play a significant role in these hydroborations. Increasing the steric bulk around the alkene group by addition of fluorine groups in the 2 and 6 positions also did not seem to affect selectivities.

We then decided to investigate reactions of 2,4,6-trimethylstyrene (**7**), where the methyl groups further increase the steric crowding around the vinyl group. As expected, catalysed hydroborations of this bulkier vinylarene gave a mixture of branched (**7a**) and linear product (**7b**), along with a considerable amount of diborated product (**7c**), when complex **1a** was used (Table 4). Minor amounts of vinyl boronate ester product are observed by $^1$H NMR spectroscopy (<1%). Rhodium complex **1c**, containing the dialkyne units, gave a significant amount of the linear product **7b**. It is plausible that reactions using **1b** and **1c** are complicated by addition of HBcat to the sterically uncongested dialkyne unit. Indeed, severe degradation of the starting rhodium complex is often observed in these reactions.

While results with vinylarene **7** show that steric hindrance caused by methyl groups ortho to the arene ring can alter

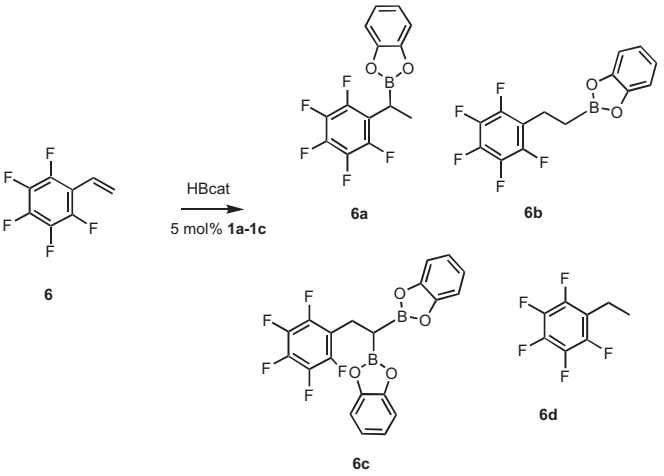
**Table 2.** Rhodium catalysed hydroboration of vinylarenes **3–5** using 1.1HBcat.




| Catalyst | a | b | c | d |
|---|---|---|---|---|
| 4-Vinylanisole | **3a** | **3b** | **3c** | **3d** |
| **1a** | >98 | — | — | — |
| **1b** | >98 | — | — | — |
| **1c** | >98 | — | — | — |
| 4-Fluorostyrene | **4a** | **4c** | **4c** | **4d** |
| **1a** | 95 | — | 2 | 3 |
| **1b** | >98 | — | — | — |
| **1c** | 98 | — | 2 | — |
| 2-Vinylnaphthalene | **5a** | **5b** | **5c** | **5d** |
| **1a** | 90 | — | — | 10 |
| **1b** | >98 | — | — | — |
| **1c** | 97 | — | — | 3 |

**Note:** Ratios were determined by $^1$H NMR spectroscopy.

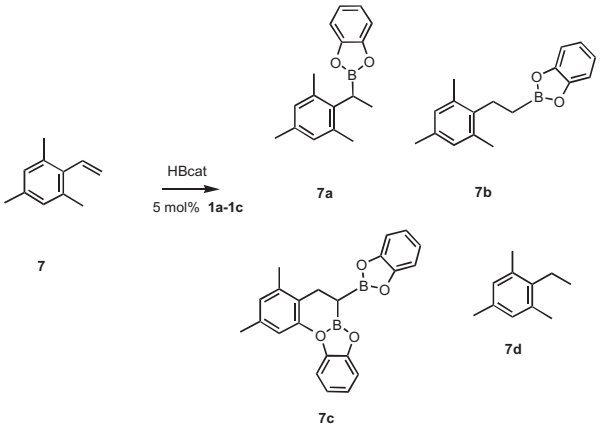
**Table 3.** Rhodium catalysed hydroboration of **6** using 1.1HBcat.




| Catalyst | 6a | 6b | 6c | 6d |
|---|---|---|---|---|
| **1a** | 96 | — | 2 | 2 |
| **1b** | 96 | — | 2 | 2 |
| **1c** | 96 | — | 2 | 2 |

**Note:** Ratios were determined by $^1$H NMR spectroscopy.

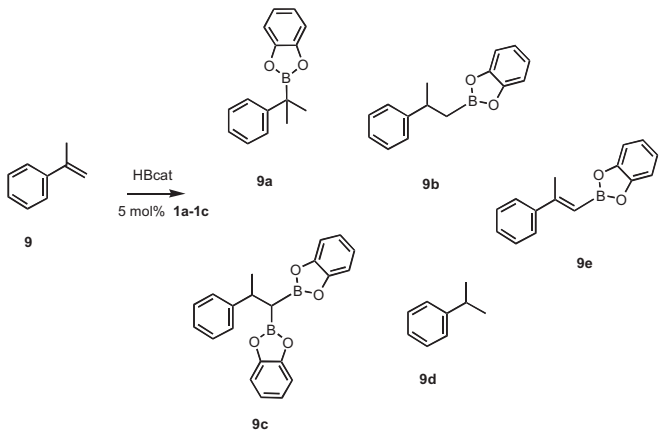
**Table 4.** Rhodium catalysed hydroboration of **7** using 1.1HBcat.




| Catalyst | 7a | 7b | 7c | 7d |
|---|---|---|---|---|
| **1a** | 40 | 40 | 15 | 5 |
| **1b** | 40 | 55 | — | 5 |
| **1c** | 5 | 85 | 10 | — |

**Note:** Ratios were determined by $^1$H NMR spectroscopy.

**Table 5.** Rhodium catalysed hydroboration of **9** using 1.1HBcat.




| Catalyst | 9a | 9b | 9c | 9d | 9e |
|---|---|---|---|---|---|
| **1a** | 40 | 30 | 20 | 5 | 5 |
| **1b** | 50 | 25 | 10 | 5 | 10 |
| **1c** | 40 | 30 | 15 | 10 | 5 |

**Note:** Ratios were determined by $^1$H NMR spectroscopy.

hydroboration selectivities, reactions with *trans*-β-methylstyrene (**8**), where a methyl group is substituted for a hydrogen in the β position of the vinyl group, gave selective formation of $C_6H_5CH(Bcat)CH_2CH_3$ (**8a**) regardless of the choice of catalyst used to affect this transformation. The other isomer ($C_6H_5CH_2CH(Bcat)CH_3$, **8b**) was not observed to any significant extent. Reactions with α-methylstyrene (**9**), however, where substitution occurs in the α position, gave extremely complicated product distributions (Table 5). The corresponding vinyl boronate ester ($C_6H_5CMe{=}CH(Bcat)$, **9e**) was also observed to a considerable extent in these reactions, especially when complex **1b** was used to catalyse this reaction. Although linear product **9b** could be generated from a traditional catalysed hydroboration reaction, it is also plausible that this product arises from the catalysed hydrogenation of vinyl boronate ester **9e**.

## Conclusions

Three novel rhodium(I) acetylacetonato (acac) complexes bearing phosphinoalkynes ($Ph_2PC{\equiv}C$-*t*-Bu, $Ph_2PC{\equiv}CPPh_2$, and $Ph_2PC{\equiv}CC{\equiv}CPPh_2$) have been prepared and characterized fully, including an X-ray diffraction study for $Rh(acac)(Ph_2PC{\equiv}C$-*t*-$Bu)_2$ (**1a**). Addition of $B_2cat_3$ (cat = 1,2-$O_2C_6H_4$) to $Rh(acac)(Ph_2PC{\equiv}C$-*t*-$Bu)_2$ (**1a**) led to zwitterionic $Rh(\eta^6$-catBcat$)(Ph_2PC{\equiv}C$-*t*-$Bu)_2$ (**2a**), which was also characterized by an X-ray diffraction study. This represents a novel zwitterionic rhodium complex bearing monodentate phosphine ligands. All new rhodium complexes are active catalysts for the hydroboration of a wide range of vinylarenes. Selectivities are excellent for reactions using unhindered vinylarenes (including *trans*-β-methylstyrene) and favour the formation of the corresponding branched hydroboration products. Reactions with hindered vinylarenes, however, give complicated product distributions, arising from a competing dehydrogenative borylation reaction.

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