Reactions of Catecholatoborane with Phosphinorhodium Complexes: Molecular Structures of $[RhHCl(Bcat)(PPr^i_3)_2]$ and $[\{(Pr^i_2PCH_2)_2\}Rh\{(\eta^6\text{-cat})Bcat\}]$ (cat = $1,2\text{-}O_2C_6H_4$)

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Addition of catecholatoborane (HBcat), **1**, to $[RhCl(N_2)(PPr^i_3)_2]$ gives the first structurally characterised, unsaturated boryl complex, $[RhHCl(Bcat)(PPr^i_3)_2]$, whereas reaction of $[\{(Pr^i_2PCH_2)_2\}Rh(\eta^3\text{-2-Me-allyl})]$ with 2 equiv. of **1** affords $[\{(Pr^i_2PCH_2)_2Rh\{(\eta^6\text{-cat})Bcat\}]$ *via* B-substituent redistribution; both complexes catalyse the hydroboration of oct-1-ene with **1**

The transition metal catalysed addition of catecholatoborane, **1**, to alkenes[1] often gives complementary stereochemistry[2] to conventional hydroboration (*i.e.* with 9-borabicyclo[3.3.1]-nonane, 9-BBN)[3] and, in some cases, allows efficient transfer of chirality from the bis(phosphine) metal centre to the substrate.[4] A plausible mechanism for the $[RhCl(PPh_3)_3]$ catalysed alkene hydroboration, put forth by Mannig and Nöth,[1] involves oxidative addition of **1** to give $[RhHCl(Bcat)(PPh_3)_2]$[5] which binds and inserts the alkene $CH_2{=}CHR$ into the Rh–H bond, followed by reductive elimination of RCH_2CH_2Bcat with formation of $[RhCl(PPh_3)_2]_2$. A similar mechanism was proposed[6] for the $[Rh(PPh_3)_2]^+$ catalysed hydroboration of n-butyl acrylate by carborane anions, and a related pathway presumably operates for the cationic $[(P\text{–}P^*)Rh(diene)]^+$ ($P\text{–}P^*$ = chiral bidentate phosphine) catalysts employed for asymmetric hydroborations. In the latter case, rapid hydroboration of the coordinated diene ligand is observed.[7] We report herein the first structural characterisation of a coordinatively unsaturated [Rh(H)(Bcat)] complex[8] and of a new zwitterionic hydroboration catalyst precursor.

The reaction of **1** with $[RhCl(PPh_3)_3]$ leads to a mixture of products which, at −40 °C, consists primarily of $[RhHCl(Bcat)(PPh_3)_2]$[5] and $[RhH_2Cl(PPh_3)_3]$[9] (the latter is presumably the source of competing alkene hydrogenation during hydroboration catalysis). As we were unable to obtain suitable crystals of $[RhHCl(Bcat)(PPh_3)_2]$ for X-ray diffraction, we prepared the analogous PPr^i_3 complex. Addition of one equivalent of **1** to $[RhCl(N_2)(PPr^i_3)_2]$[10] yields golden crystals of $[RhHCl(Bcat)(PPr^i_3)_2]$ **2** in 90% yield. The molecular structure† of **2** (Fig. 1) consists of a 16 electron

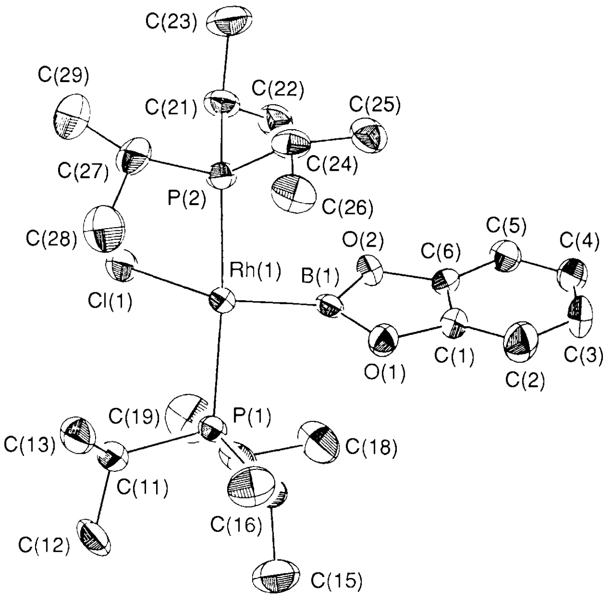

Fig. 1 Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Rh(1)–P(1) 2.334(2), Rh(1)–P(2) 2.338(2), Rh(1)–Cl(1) 2.418(2), Rh(1)–B(1) 1.961(7), B(1)–O(1) 1.401(7), B(1)–O(2) 1.430(6), P(1)–Rh(1)–P(2) 172.32(5), Cl(1)–Rh(1)–B(1) 137.5(2), Cl(1)–Rh(1)–P(1) 92.69(6), Cl(1)–Rh(1)–P(2) 87.78(6), P(1)–Rh(1)–B(1) 91.1(2), P(2)–Rh(1)–B(1) 93.8(2), Rh(1)–B(1)–O(1) 132.8(4), Rh(1)–B(1)–O(2) 119.3(4), O(1)–B(1)–O(2) 107.9(5).

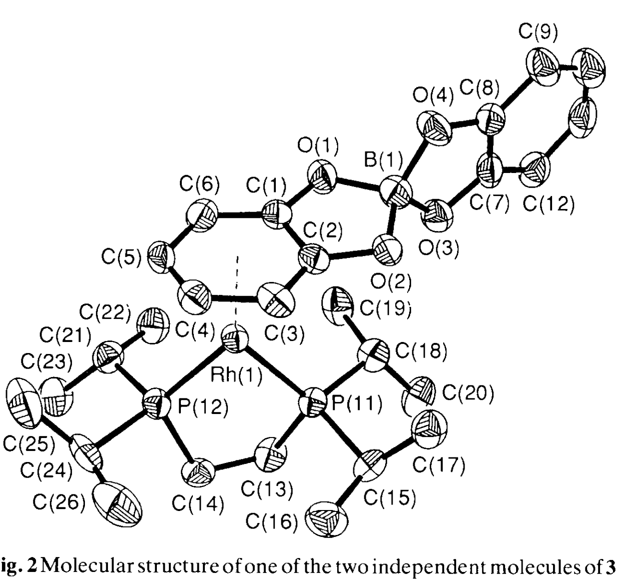

Fig. 2 Molecular structure of one of the two independent molecules of **3**. Hydrogen atoms are omitted for clarity.

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† *Crystal data* for **2** (from hexane): $C_{24}H_{47}BClO_2P_2Rh$, M = 578.76, monoclinic, space group $P2_1/c$ (No. 14), a = 11.243(4), b = 11.140(2), c = 23.570(10) Å, β = 102.15(2)°, U = 2885.9 Å^3, $F(000)$ = 1216, Z = 4, D_c = 1.332 g cm^{-3}, μ(Mo-Kα) = 8.02 cm^{-1}, T = 203 K. Anisotropic refinement of all non-hydrogen atoms (Hs fixed; 280 variables) using 3291 reflections with $I > 3\sigma(I)$, from 7108 unique data collected on an Enraf-Nonius CAD4 diffractometer by the ω scan method ($1.8° \leqslant 2\theta \leqslant 55.0°$), gave R = 0.045, R_w = 0.037. The hydride on Rh could not be located or successfully refined in a calculated position.

For **3** (from toluene): $C_{26}H_{40}BO_4P_2Rh$, M = 592.2, orthorhombic, space group $Pca2_1$, a = 14.480(5), b = 17.743(5), c = 21.773(5) Å, U = 5594(3) Å^3, Z = 8, $F(000)$ = 2464, D_c = 1.406 g cm^{-3}, μ(Mo-Kα) = 7.40 cm^{-1}, T = 220 K. With Z = 8, we initially collected data in the setting for the centric space group *Pbcm*. However, solution was not possible in this space group, and a consistent solution was achieved in $Pca2_1$ with two molecules per asymmetric unit. The choice of the acentric space group was supported throughout the refinement. Anisotropic refinement of all non-hydrogen atoms and isotropic refinement of Hs with a riding model (691 variables), using 4896 reflections with $F > 6\sigma(F)$ from 6594 unique data collected on a Siemens R3m/v diffractometer by the ω scan method ($3.5° \leqslant 2\theta \leqslant 55.0°$), gave R = 0.032, R_w = 0.037. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

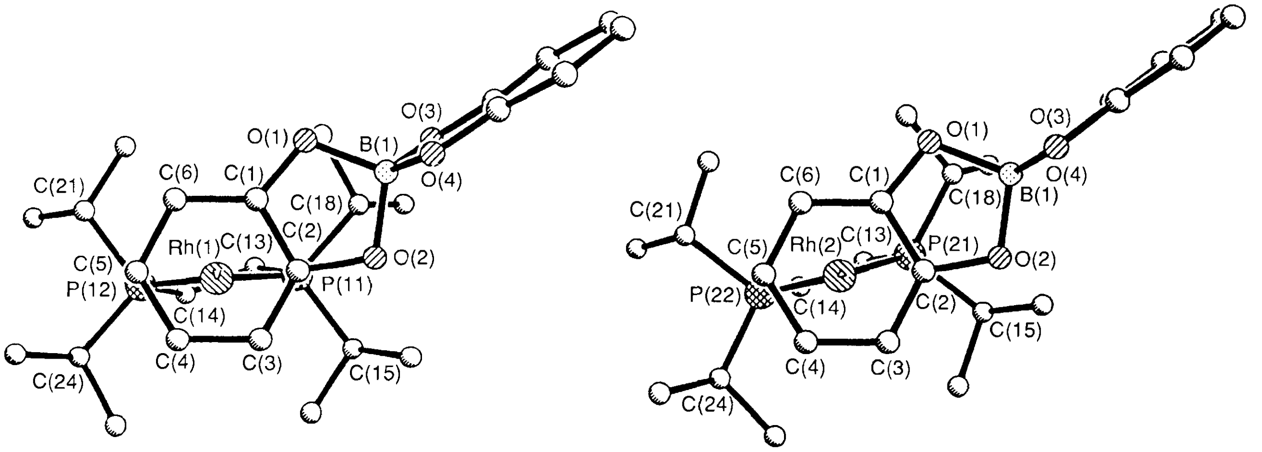

Fig. 3 Ball and stick diagram of the molecular structure of the two independent molecules of **3** viewed perpendicular to the π-bound arene rings. Selected bond distances (Å) and angles (°) for molecule 1: Rh(1)–P(11) 2.222(2), Rh(1)–P(12) 2.223(2), Rh(1)–C(1) 2.516(6), Rh(1)–C(2) 2.372(6), Rh(1)–C(3) 2.307(6), Rh(1)–C(4) 2.262(6), Rh(1)–C(5) 2.256(6), Rh(1)–C(6) 2.435(7), P(11)–Rh(1)–P(12) 85.6(1). For molecule 2: Rh(2)–P(21) 2.230(2), Rh(2)–P(22) 2.223(2), Rh(2)–C(1) 2.458(6), Rh(2)–C(2) 2.426(7), Rh(2)–C(3) 2.379(6), Rh(2)–C(4) 2.269(6), Rh(2)–C(5) 2.241(7), Rh(2)–C(6) 2.377(6), P(21)–Rh(2)–P(22) 85.5(1).

distorted trigonal-bipyramidal Rh^{III} centre with apical PPr^i_3 ligands and a planar catecholatoboryl ligand. The BO_2 plane is rotated through 14.9° with respect to the RhBCl plane. Although the rhodium hydride ligand was not located in the X-ray study, its presence is clearly indicated by the B–Rh–Cl angle of 138.5°, and from solution NMR data.‡

In an attempt to prepare a d^8[Rh(Bcat)] complex, we investigated the reaction of $[\{(Pr^i_2PCH_2)_2\}Rh(\eta^3\text{-2-Me-allyl})]$[11] with **1**. The sole metal-containing product,§ however, was the zwitterion $[\{(Pr^i_2PCH_2)_2\}Rh\{(\eta^6\text{-cat})Bcat\}]$ **3**. The molecular structure† of **3** (Fig. 2) consists of a chelated bis(phosphine)rhodium cation unsymmetrically coordinated to one of the arene rings of the $[B(cat)_2]^-$ anion. There are two unique molecules in the crystallographic asymmetric unit which differ in the rotational orientation and slippage of the P_2Rh moiety with respect to the π-bonded arene ring (Fig. 3). Presumably, the potential surface for such distortions is quite shallow. Significant differences in the Rh–arene carbon bond distances were also observed in the molecular structure of $[\{P(OMe)_3\}_2Rh(\eta^6\text{-}BPh_4)]$.[12] The formation of **3** involves the redistribution of catecholato groups, which has been observed in reactions of **1** with $NaBH_4$[13] and PMe_3.[7]

The reactivity and catalytic alkene hydroboration activity of **2** are similar to that of the PPh_3 analogue, except that **2** has an enhanced tendency to decarbonylate aldehydes. Complex **3** is a novel hydroboration catalyst precursor, and is a possible model for the resting state of the $[(P\text{–}P^*)Rh(diene)]^+$ chiral hydroboration catalysts. Experiments are underway to evaluate the catalytic activity of aryl phosphine analogues of **3**, as the activity of **3** is limited presumably by the basicity of the phosphine. Interestingly, the related zwitterion, $[(\eta^4\text{-1,5-}C_8H_{12})Rh(\eta^6\text{-}BPh_4)]$, has recently been shown[14] to catalyse alkene hydroformylation, and the salt $[(\eta^3\text{-}C_3H_5)Ni(\eta^4\text{-1,5-}C_8H_{12})]^+[Bcat_2]^-$ catalyses[15] 1,4-*trans*-polymerisation of butadiene.

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‡ *Selected NMR spectroscopic data* for **2** (in $[^2H_8]$toluene at 25 °C): $^{31}P\{^1H\}$ δ 51.7 (d, $J_{P\text{-}Rh}$ 109 Hz); $^{11}B\{^1H\}$ δ 37.7 (br); ^1H δ −17.08 (d t, $J_{H\text{-}Rh}$ 28, $^2J_{H\text{-}P}$ 14 Hz, 1H, Rh–H). *For* **3**: $^{31}P\{^1H\}$ δ 106.9 (d, $J_{P\text{-}Rh}$ 209 Hz); $^{11}B\{^1H\}$ δ 15.1 (s); ^1H δ 6.6–6.4 (ov m, 4H), 6.26 (m, 2H), 5.16 (m, 2H), 1.94 (d sept, $^3J_{H\text{-}H} = {^3J_{P\text{-}H}}$ = 7 Hz, 4H, $CHMe_2$), 1.16 (ov m, 4H, PCH_2CH_2P), 0.95 (dd, $^3J_{H\text{-}H}$ 7, $^3J_{P\text{-}H}$ 13 Hz, 12 H, CH_3), 0.83 (dd, $^3J_{H\text{-}H}$ 7, $^3J_{P\text{-}H}$ 13 Hz, 12H, CH_3).

§ An incompletely characterised mixture of boranes is formed from the interaction of the allyl ligand with HBcat and with BH_3·tetrahydrofuran (the latter is a product of B-substituent redistribution).