DALTON
FULL PAPER

Boron–boron bond oxidative addition to rhodium(I) and iridium(I) centres

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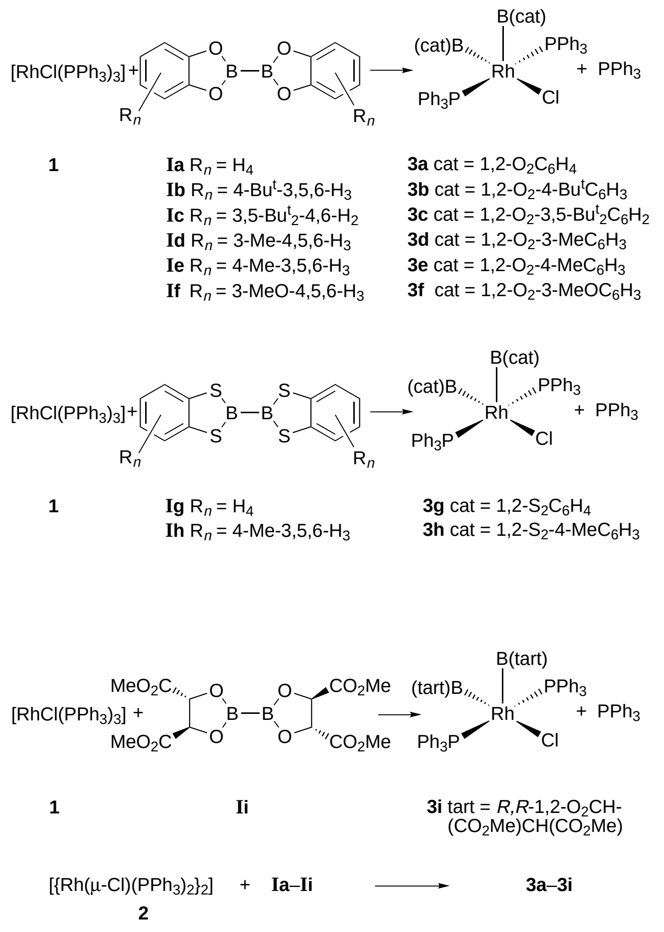
The reaction between the diborane(4) compound $B_2(1,2\text{-}O_2C_6H_4)_2$ and either of the rhodium(I) complexes $[RhCl(PPh_3)_3]$ or $[\{Rh(\mu\text{-}Cl)(PPh_3)_2\}_2]$ afforded the colourless rhodium(III) bis(boryl) species $[RhCl(PPh_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]$. Similar reactions have been carried out with the diborane(4) compounds $B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2$, $B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2C_6H_2)_2$, $B_2(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)_2$, $B_2(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)_2$, $B_2(1,2\text{-}O_2\text{-}3\text{-}MeOC_6H_3)_2$, $B_2(1,2\text{-}S_2C_6H_4)_2$, $B_2(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)_2$ and $B_2[R,R\text{-}1,2\text{-}O_2CH(CO_2Me)CH(CO_2Me)]_2$ affording analogous rhodium complexes all of which have been characterised spectroscopically. The complexes derived from the reactions with $B_2(1,2\text{-}O_2C_6H_4)_2$ and $B_2(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)_2$ have also been characterised by X-ray crystallography, the structures comprising a five-co-ordinate rhodium centre with a square-based-pyramidal geometry in which the apical site is occupied by a boryl group and the phosphines are mutually *trans* in basal positions. Reactivity studies have also been carried out for $[RhCl(PPh_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]$. Hydrolysis or alcoholysis with catechol afforded $[RhH_2Cl(PPh_3)_3]$ and either $B_2(1,2\text{-}O_2C_6H_4)_2(\mu\text{-}O)$ or $B_2(1,2\text{-}O_2C_6H_4)_3$ and addition of the phosphines PMe_3, PEt_3 and PMe_2Ph afforded the new bis(boryl) compounds *cis,mer*-$[RhCl(PMe_3)_3\{B(1,2\text{-}O_2C_6H_4)\}_2]$, $[RhCl(PEt_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]$ and *cis,mer*-$[RhCl(PMe_2Ph)_3\{B(1,2\text{-}O_2C_6H_4)\}_2]$, the PEt_3 complex having been characterised by X-ray crystallography and shown to be similar to the PPh_3 complex. The iridium analogue $[IrCl(PEt_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]$ was also prepared from the reaction between $[IrCl(PEt_3)_3]$ and $B_2(1,2\text{-}O_2C_6H_4)_2$ and shown by X-ray crystallography to be isomorphous with the rhodium complex. Reactions between $[RhCl(PPh_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]$ and the phosphines PPr^i_3, $P(C_6H_{11})_3$, 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) are also described although these do not result in new rhodium boryl complexes. The reaction between $[\{RhCl(dppe)\}_2]$ and $B_2(1,2\text{-}O_2C_6H_4)_2$ afforded a compound tentatively assigned as $[Rh(dppe)_2\{B(1,2\text{-}O_2C_6H_4)\}]$ with analogous compounds being formed with the diborane(4) compounds $B_2(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)_2$ and $B_2(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)_2$. Finally, the reaction between $[Rh(PMe_3)_4]Cl$ and the diborane(4) compound $B_2(1,2\text{-}O_2C_6H_4)_2$ is described which affords *cis,mer*-$[RhCl(PMe_3)_3\{B(1,2\text{-}O_2C_6H_4)\}_2]$. Analogous reactions with $B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2C_6H_2)_2$, $B_2(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)_2$ and $B_2[R,R\text{-}1,2\text{-}O_2CH(CO_2Me)CH(CO_2Me)]_2$ afforded similar products.

Transition-metal-catalysed diborations of alkenes,[1] alkynes[2] and 1,3-dienes[3] are now well established, particularly in the case of alkynes, and an important mechanistic feature is the oxidative addition of the B–B bond in diborane(4) compounds ($R_2B{-}BR_2$) to a low-valent transition-metal centre resulting in metal boryl species, $M{-}BR_2$. These species have also been implicated in the palladium catalysed cross-coupling of diborane(4) compounds with halogenoarenes.[4] Structurally characterised examples of metal boryls deriving from B–B bond oxidative addition to tungsten(II),[5] iron(0),[6] cobalt(0),[7] rhodium(I),[8] iridium(I)[9] and platinum(0)[2b,c,e,f] centres have now been described with additional examples also having been characterised for complexes of tantalum,[10] tungsten,[11] manganese,[12] iron,[13] rhodium[14] and iridium.[15] Herein we describe details of reactions involving the oxidative addition of B–B bonds to rhodium(I) and iridium(I) centres, some of which has been the subject of a preliminary communication,[8a] concentrating on aspects of synthesis, structure and ligand-exchange reactivity. Studies dealing with the rhodium-catalysed diboration of alkenes will be reported separately.

Results and Discussion

In ref. 8(*a*) we described the reactions between the diborane(4) compounds $B_2(1,2\text{-}O_2C_6H_4)_2$ **Ia**, $B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2$ **Ib** and $B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2C_6H_2)_2$ **Ic** and the rhodium(I) complexes $[RhCl(PPh_3)_3]$ **1** or $[\{Rh(\mu\text{-}Cl)(PPh_3)_2\}_2]$ **2** which cleanly afforded the colourless rhodium(III) bis(boryl) species $[RhCl(PPh_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]$ **3a**, $[RhCl(PPh_3)_2\{B(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)\}_2]$ **3b** and $[RhCl(PPh_3)_2\{B(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2C_6H_2)\}_2]$ **3c** as shown in Scheme 1; full experimental details and spectroscopic data are provided here in the Experimental section. Corresponding reactions with the catecholato and dithiocatecholato diborane(4) compounds $B_2(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)_2$ **Id**, $B_2(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)_2$ **Ie**, $B_2(1,2\text{-}O_2\text{-}3\text{-}MeOC_6H_3)_2$ **If**, $B_2(1,2\text{-}S_2C_6H_4)_2$ **Ig** and $B_2(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)_2$ **Ih**[16] afforded the analogous boryl complexes $[RhCl(PPh_3)_2\{B(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)\}_2]$ **3d**, $[RhCl(PPh_3)_2\{B(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)\}_2]$ **3e**, $[RhCl(PPh_3)_2\{B(1,2\text{-}O_2\text{-}3\text{-}MeOC_6H_3)\}_2]$ **3f**, $[RhCl(PPh_3)_2\{B(1,2\text{-}S_2C_6H_4)\}_2]$ **3g** and $[RhCl(PPh_3)_2\{B(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)\}_2]$ **3h** respectively (Scheme 1). The reaction between **1** and the tartrate derivative $B_2\{R,R\text{-}1,2\text{-}O_2CH(CO_2Me)CH(CO_2Me)\}_2$ **Ii**[17] also afforded a bis(boryl) complex, namely $[RhCl(PPh_3)_2\{B[R,R\text{-}1,2\text{-}O_2CH(CO_2Me)CH(CO_2Me)]\}_2]$ **3i**.

Spectroscopic and analytical data for all complexes were consistent with their formulation and the structures of **3a** and **3d** were confirmed by X-ray crystallography, the results of which are shown in Figs. 1 and 2 respectively; selected bond length and angle data are given in Table 1 and crystallographic data are presented in Table 2. Compound **3a** crystallises as the tetra-CH_2Cl_2 solvate **3a**$\cdot 4CH_2Cl_2$ from this solvent with no short intermolecular contacts. Its molecular structure may be



Scheme 1

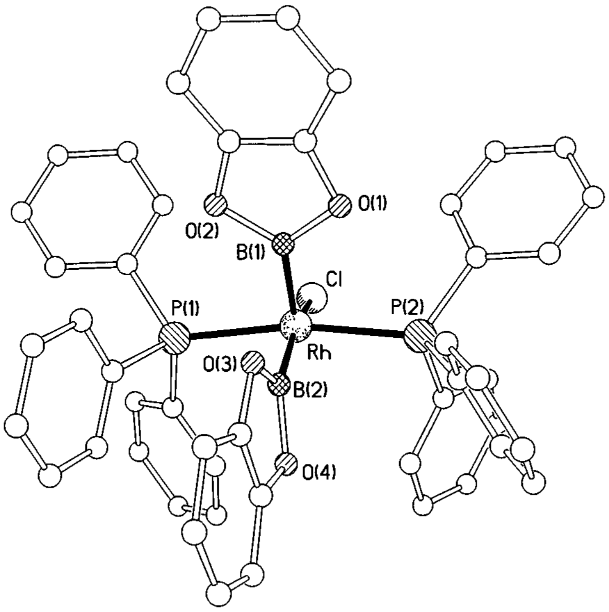


Fig. 1 View of the molecular structure of complex **3a** with key atoms labelled. Hydrogen atoms are omitted for clarity. Atoms are drawn as spheres of arbitrary radius

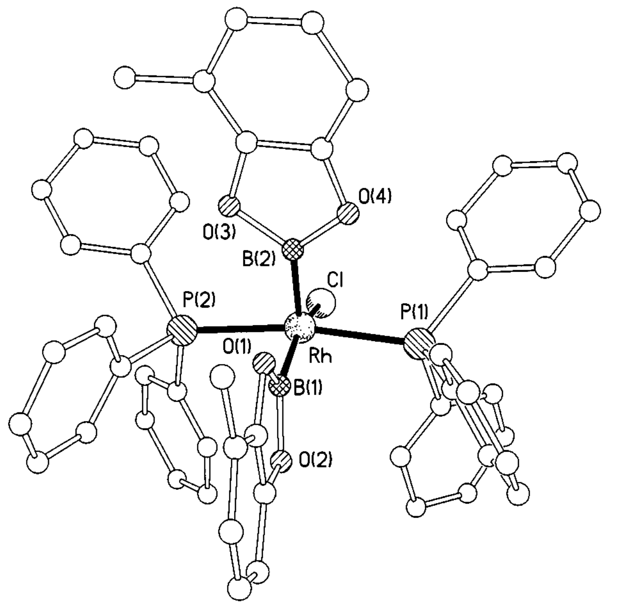
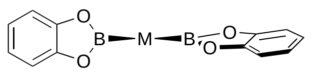
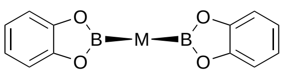


Fig. 2 View of the molecular structure of complex **3d**. Details as in Fig. 1



A



B

described as comprising a five-co-ordinate rhodium centre in a distorted square-based pyramidal environment with one of the boryl groups occupying the apical site and the other in one of the basal sites *trans* to the chlorine; the mutually *trans* PPh_3 ligands occupy the remaining two basal positions. The Rh–B bond distances differ slightly with that to the apical boron [Rh–B(1) 1.954(4) Å] being somewhat shorter than the basal Rh–B bond [Rh–B(2) 2.008(4) Å] although both distances are similar to those of other rhodium(III) boryls.[8c,14,18] Of particular note for comparison, however, is the structure of another crystalline modification of **3a**, which had previously been isolated from a reaction between **1** and $HB(1,2\text{-}O_2C_6H_4)$, as the tris(1,2-dichloroethane) solvate, **3a**·$3C_2H_4Cl_2$-1,2.[8b] The molecular structures of **3a** in the two crystal forms are essentially identical although the present structure is better determined, data for comparison being given in Table 1. The bond angles about the rhodium centre in **3a**·$4CH_2Cl_2$ support the description of the co-ordination geometry as distorted square-based pyramidal with the P(1)–Rh–P(2) and B(2)–Rh–Cl angles being 169.75(3) and 162.07(11)° respectively, *i.e.* both similar and reasonably close to linear [the Rh resides 0.270 Å above the average basal plane towards B(1)], and angles between the apical boron B(1) and the four contact atoms in the basal plane ranging from 78.9(2)° for the B(1)–Rh–B(2) angle to 118.89(11)° for B(1)–Rh–Cl. The acute B–Rh–B angle results in a B···B separation of 2.517 Å, although this is more than 0.8 Å longer than typical values for B–B bonds in bis(catecholate) diborane(4) compounds, which are generally about 1.68 Å.[16b,19] Any residual B···B interaction is therefore necessarily very weak. Moreover, the relative orientations of the boryl ligands are such as to preclude any interaction between the boron p orbitals since the boron catecholate planes are close to orthogonal as shown in **A**. An alternative configuration for two mutually *cis* boryl groups, shown in **B** and observed in, for example, the platinum complexes of general formula *cis*-$[Pt(PR_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]$[2b,c,e,f] and the cobalt compound $[Co(PMe_3)_3\{B(1,2\text{-}O_2C_6H_4)\}_2]$,[7] does allow for the possibility of residual B···B 2p···2p bonding but while any such interaction is still open to question in the platinum compounds[2f,20] the possibility of B···B bonding in the cobalt species has been discussed[7] in view of the short B–B distance (2.185 Å) observed and theoretical studies are in progress to address this issue further.

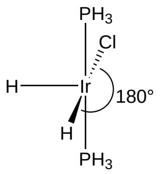
Compound **3d** also crystallises as a solvate with three molecules of CH_2Cl_2 and one half molecule of *n*-hexane per asymmetric unit and with no short intermolecular contacts. The gross molecular structure of **3d** (Fig. 2) is very similar to both those of **3a** including the conformations of the two boryl ligands which are again close to perpendicular as illustrated in **A**. Relevant bond-length data reveal that the apical

Table 1 Selected bond lengths (Å) and angles (°) for compounds **3a**, **3d**, **8** and **9**[a]

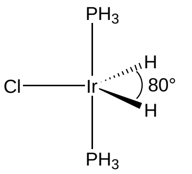
3a·4CH$_2$Cl$_2$		**3a**·3 1,2-Cl$_2$C$_2$H$_4$[b]		**3d**·3CH$_2$Cl$_2$·0.5C$_6$H$_{14}$		**8**		**9**	
B(1)–Rh	1.954(4)	B(2)–Rh	1.956(8)	B(2)–Rh	1.906(13)	B(1)–Rh	1.973(2)	B(1)–Ir	1.991(6)
B(2)–Rh	2.008(4)	B(1)–Rh	2.008(7)	B(1)–Rh	2.034(12)	B(2)–Rh	1.994(2)	B(2)–Ir	2.004(6)
B(1)–Rh–B(2)	78.9(2)	B(1)–Rh–B(2)	79.0(3)	B(2)–Rh–B(1)	80.9(5)	B(1)–Rh–B(2)	75.3(1)	B(1)–Ir–B(2)	76.6(6)
B(1)–Rh–Cl	118.89(11)	B(2)–Rh–Cl	117.5(2)	B(2)–Rh–Cl	118.9(3)	B(1)–Rh–Cl	132.29(7)	B(1)–Ir–Cl	132.9(2)
B(1)–Rh–P(1)	93.90(11)	B(2)–Rh–P(1)	93.5(2)	B(2)–Rh–P(1)	93.4(3)	B(1)–Rh–P(1)	94.91(7)	B(1)–Ir–P(1)	94.5(2)
B(1)–Rh–P(2)	94.45(11)	B(2)–Rh–P(2)	95.8(2)	B(2)–Rh–P(2)	93.8(3)	B(1)–Rh–P(2)	94.69(7)	B(1)–Ir–P(2)	94.8(2)
B(2)–Rh–Cl	162.07(11)	B(1)–Rh–Cl	163.4(2)	B(1)–Rh–Cl	160.2(4)	B(2)–Rh–Cl	152.34(7)	B(2)–Ir–Cl	150.4(2)
B(2)–Rh–P(1)	86.68(10)	B(1)–Rh–P(1)	92.2(2)	B(1)–Rh–P(1)	88.4(4)	B(2)–Rh–P(1)	89.16(7)	B(2)–Ir–P(1)	89.8(2)
B(2)–Rh–P(2)	89.12(10)	B(1)–Rh–P(2)	85.7(2)	B(1)–Rh–P(2)	87.2(4)	B(2)–Rh–P(2)	93.92(7)	B(2)–Ir–P(2)	93.8(2)
Cl–Rh–P(1)	89.38(3)	Cl–Rh–P(1)	88.09(6)	Cl–Rh–P(1)	91.1(1)	Cl–Rh–P(1)	86.52(2)	Cl–Ir–P(1)	86.09(6)
Cl–Rh–P(2)	91.77(3)	Cl–Rh–P(2)	91.14(6)	Cl–Rh–P(2)	90.3(1)	Cl–Rh–P(2)	86.53(2)	Cl–Ir–P(2)	86.53(6)
P(1)–Rh–P(2)	169.75(3)	P(1)–Rh(1)–P(2)	169.88(7)	P(1)–Rh–P(2)	170.8(1)	P(1)–Rh–P(2)	170.37(2)	P(1)–Ir–P(2)	170.56(6)

[a] This table is organised such that comparable bond lengths and angles for the five structures occur in any given line although the atom labelling schemes vary for different structures. [b] Data taken from ref. 8(*b*).

Rh–B bond [Rh–B(2) 1.906(13) Å] is shorter than the corresponding basal bond [Rh–B(1) 2.034(12) Å] as found for **3a**, and the transoid P–Rh–P and B–Rh–Cl angles in the basal plane [170.8(1) and 160.2(4)° respectively] are also consistent with a square-based pyramidal rhodium geometry; the B · · · B distance is 2.56 Å.



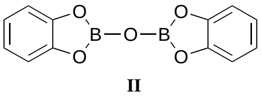
C



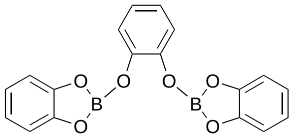
D

An alternative description of the structures of complexes **3a** and **3d** can be given in terms of the discussion presented by Eisenstein and co-workers[21] for d^6 ML$_5$ complexes. In the specific case of one of their model compounds, [IrH$_2$Cl(PH$_3$)$_2$], the so-called T-shaped geometry, shown in **C**, and the alternative Y-shaped geometry (**D**) are calculated to be the lowest-energy structures on the potential-energy surface for this system (the more symmetrical trigonal-bipyramidal geometry is calculated to be a maximum) with the Y-shaped geometry being the actual minimum. The model complex [IrH$_2$Cl(PH$_3$)$_2$] is a particularly apposite example here since it contains two phosphines and a chlorine, as found in **3a**/**3d**, and two high-*trans*-influence hydrides which are probably good models for boryl groups which are also known to exhibit a high *trans* influence.[2*e*,8*c*,9] We will not reiterate here the details of the discussion given by Eisenstein concerning the precise electronic origins of these structural preferences (the reader is referred to the original papers given in ref. 21) but note that the structures of **3a** and **3d** are about midway between the limiting T- and Y-shaped geometries (**C** and **D**) although significantly distorted from a regular trigonal-bipyramidal geometry as expected.[21]

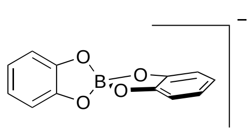
Having established the generality of the reaction between the bis(catecholato) diborane(4) compounds **Ia**–**Ih** and either **1** or **2** affording the rhodium(III) bis(boryls) **3a**–**3h**, we next turned our attention to a study of the reactivity of the rhodium boryl complexes, largely that of **3a**. The first point to note concerns the stability of **3a** in solution. Thus, the reaction to produce **3a** described above using **2** as the rhodium source (and that for the other complexes **3b**–**3i**) was generally carried out in CH$_2$Cl$_2$ solution. Monitoring this reaction by ^{31}P NMR spectroscopy revealed that it was essentially complete within 15 min (somewhat longer in the case of **3c** and **3i**) and that, once formed, **3a** was stable in this solvent for about 1 week, the major phosphorus-containing decomposition product being the rhodium(III) dihydride *cis*,*mer*-[RhH$_2$Cl(PPh$_3$)$_3$] **4**[22,23] for which a doublet was observed at δ 34.0 and a broad singlet at δ 14.6.† In the ^{11}B NMR spectrum signals were observed, in variable ratios depending on the particular reaction, for the species B$_2$(1,2-O$_2$C$_6$H$_4$)$_2$(μ-O) **II** (δ 18.1),[24] B$_2$(1,2-O$_2$C$_6$H$_4$)$_3$ **III** (δ 16.6)[25] and the anion [B(1,2-O$_2$C$_6$H$_4$)$_2$]$^-$ **IV** (δ 12.3).‡,[26]



II



III



IV

If the synthesis of complex **3a** was carried out in the same solvent but using **1** as the rhodium source, decomposition was observed to give the same products but somewhat more quickly with complete disappearance of signals due to **3a** occurring after 2–3 d. A similar set of observations was made when benzene was used as the reaction solvent, but when thf was used complete decomposition of **3a** took place after about 2–3 d if **2** was used as the precursor and after only 24 h if **1** was employed. In all cases the same major decomposition products were produced as evidenced by ^{31}P and ^{11}B NMR spectroscopy. The implication is that **3a** is apparently much less stable in solution in the presence of a two-electron donor such as thf or free PPh$_3$ (produced when **1** is used as the rhodium starting material). The mechanism of these decompositions remains unclear in detail, but the nature of the products indicated that, despite stringent precautions being taken to exclude moisture, some form of hydrolysis was likely especially in (donor) solvents such as thf.§

That compound **3a** was particularly susceptible to hydrolysis was confirmed in a separate experiment wherein it was exposed to small quantities of water. Following the reaction by ^{31}P and ^{11}B NMR spectroscopy revealed exclusive and rapid formation

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† At room temperature the ^{31}P-{^{1}H} NMR spectrum of *cis*,*mer*-[RhH$_2$Cl(PPh$_3$)$_3$] **4**[23*b*] shows a doublet at δ 34.0 (J_{RhP} = 115 Hz) and a broad singlet at δ 14.6 due to rapid intermolecular exchange involving the unique PPh$_3$ ligand. At −60 °C this exchange is essentially frozen out and the spectrum expected for this structure is observed: δ 34.0 (dd, 2 P, PPh$_3$, $^1J_{RhP}$ = 115, $^2J_{PP}$ = 20) and 14.6 (dt, 1 P, PPh$_3$, $^1J_{RhP}$ = 92, $^2J_{PP}$ = 20 Hz).[22]

‡ Chemical shifts for compounds **II**–**IV** are reported for samples in tetrahydrofuran (thf) solution. Values can vary slightly depending on the solvent used.

§ A related degradation of HB(1,2-O$_2$C$_6$H$_4$) in the presence of PPh$_3$ has been described in ref. 22 and refs. therein which affords, as one product **III**, the mechanism for which is also unknown.

of **4** and **II** according to equation (1) (the presence of the PPh_3

$$\underset{\mathbf{3a}}{[RhCl(PPh_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]} + PPh_3 + H_2O \longrightarrow \underset{\mathbf{4}}{[RhH_2Cl(PPh_3)_3]} + \underset{\mathbf{II}}{B_2(1,2\text{-}O_2C_6H_4)_2(\mu\text{-}O)} \quad (1)$$

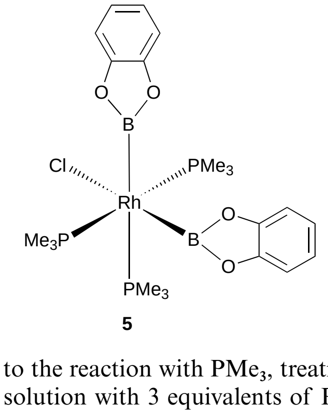
derives from the *in situ* formation of **3a** from **1**), the presence of **II** being confirmed by mass spectrometry. We note that the sensitivity of **3a** to hydrolysis is in contrast to the recently reported ruthenium(II) and osmium(II) boryls described by Roper and co-workers[27] which are stable to hydrolysis.

The susceptibility of the Rh–B bonds in complex **3a** to protolysis was also established from reaction (2) [as with equation

$$\underset{\mathbf{3a}}{[RhCl(PPh_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]} + PPh_3 + 1,2\text{-}(HO)_2C_6H_4 \longrightarrow \underset{\mathbf{4}}{[RhH_2Cl(PPh_3)_3]} + \underset{\mathbf{III}}{B_2(1,2\text{-}O_2C_6H_4)_3} \quad (2)$$

(1), the presence of the PPh_3 in (2) derives from the *in situ* formation of **3a** from **1**] whereby catechol was observed cleanly to afford **4** and **III**; the precise origin of the anion **IV** remains unclear (as does the nature of its associated cation) although it is a very commonly observed decomposition product in all reactions involving metal boryls (see later).

The reactivity of complex **3a** towards phosphine exchange was also investigated with a variety of phosphines. Treatment of **3a** in CH_2Cl_2 solution with 3 equivalents of PMe_3 cleanly afforded a complex formulated as *cis,mer*-$[RhCl(PMe_3)_3\{B(1,2\text{-}O_2C_6H_4)\}_2]$ **5** on the basis of multinuclear NMR data. Thus, the $^{31}P\text{-}\{^1H\}$ NMR spectrum indicated two inequivalent phosphorus environments with a 2:1 occupancy ratio whilst the $^{11}B\text{-}\{^1H\}$ spectrum revealed two boron signals of equal intensity in the metal boryl region indicating a mutually *cis* configuration for the boryl groups (the alternative *cis,fac* isomer would have equivalent boryl groups and hence only one ^{11}B resonance). Further confirmation of the structure of **5** is provided by comparison with the iridium analogue *cis,mer*-$[IrCl(PMe_3)_3\{B(1,2\text{-}O_2C_6H_4)\}_2]$ **6**[9] which has been crystallographically characterised and exhibits almost identical NMR spectra to those of **5** (allowing for the absence of coupling to ^{103}Rh). Compound **5** was also formed quantitatively (and more readily isolated as a pure material) in stoichiometric reactions between either **Ia** and $[RhCl(PMe_3)_3]$ in benzene solution or between **Ia** and $[Rh(PMe_3)_4]Cl$ **7** in thf [further reactions between **7** and diborane(4) compounds will be described later]. Treatment of **3a** with a large excess of PMe_3 resulted in the formation of **7** as the only rhodium–phosphorus containing species as evidenced by ^{31}P NMR spectroscopy, although when carried out in CH_2Cl_2 solution rapid overall decomposition occurred since **7** reacts with this solvent.[28]



5

In contrast to the reaction with PMe_3, treatment of complex **3a** in CH_2Cl_2 solution with 3 equivalents of PEt_3 afforded the colourless crystalline bis(phosphine) complex $[RhCl(PEt_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]$ **8**[8a] rather than a tris(phosphine) species analogous to **5**. The formula of **8** was apparent from multinuclear NMR studies but was confirmed by X-ray crystallography the results of which are shown in Fig. 3; selected bond length and angle data are given in Table 1 and crystallographic data in Table 2. The molecular structure is broadly similar to that of **3a** in that the boryl groups are *cis* with an acute B–Rh–B angle [B(1)–Rh–B(2) 75.3(1)°], a type **A** orientation of the boryl groups (see above), and *trans* phosphines [P(1)–Rh–P(2) 170.37(2)°]. The main difference between **8** and **3a** lies in the angles about the rhodium centre within the plane defined by the atoms Cl, B(1) and B(2). Thus although the B–Rh–B angles are similar in both structures [**8** 75.3(1), **3a**·$4CH_2Cl_2$ 78.9(2)°)], the Cl–Rh–B(1) [**8** 132.29(7), **3a**·$4CH_2Cl_2$ 118.89(11)] and Cl–Rh–B(2) [**8** 152.34(7), **3a**·$4CH_2Cl_2$ 162.07(11)°] angles each differ by about 10–14°, being more nearly equal in **8**. A description of the geometry of **8** as square-based pyramidal is therefore less appropriate here, a better description being in terms of the Y-shaped geometry (**D**) mentioned above in connection with the structures of **3a**/**3d**. However, the fact that the boryl groups are still in different environments (in the sense that the Cl–Rh–B angles still differ by 20°) is reflected in different Rh–B bond lengths [Rh–B(1) 1.973(2), Rh–B(2) 1.994(2) Å]. Furthermore, it is the boryl with the shorter Rh–B bond and the smaller Cl–Rh–B angle [B(1)] which lies parallel to the P(1)–Rh–P(2) vector in **8** as is also the case for **3a**; in the event that the boryl groups were in equivalent environments, *i.e.* the Cl–Rh–B angles were the same, such a distinction would be lost.

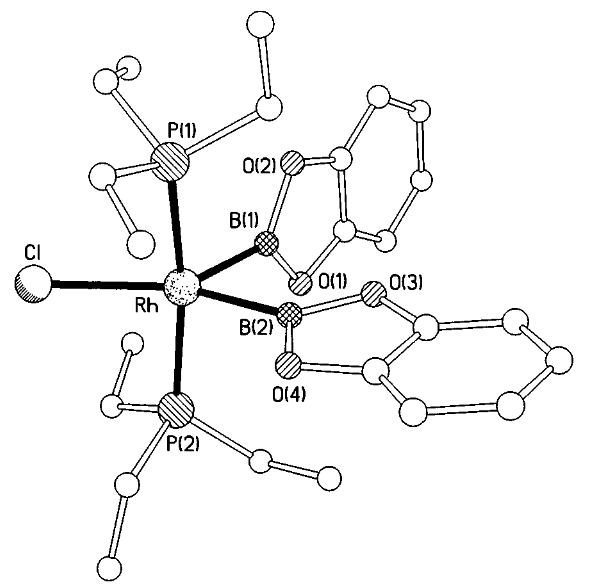


Fig. 3 View of the molecular structure of complex **8**. Details as in Fig. 1

The iridium analogue of complex **8**, $[IrCl(PEt_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]$ **9**, has also been prepared, although by a different route involving the direct reaction between $[IrCl(PEt_3)_3]$ and **Ia**, and structurally characterised and is included here for comparison with **8**; a view of the molecular structure of **9** is shown in Fig. 4 with selected bond length and angle data in Table 1 and crystallographic data in Table 2. In fact the structure of **9** is isomorphous with **8** such that the description given above for **8** is also appropriate for **9**, no further discussion being warranted. In solution, however, the Ir–PEt_3 system differs slightly from the Rh–PEt_3 system. Thus in the rhodium case, as described above, there is no evidence for the presence of a tris(phosphine) derivative analogous to **5** whereas for the iridium example solution NMR studies did indicate the presence of the tris(phosphine) species $[IrCl(PEt_3)_3\{B(1,2\text{-}O_2C_6H_4)\}_2]$ **10**. Thus, at room temperature all ^{31}P NMR resonances were broad but at −55 °C a doublet and triplet spectrum was observed consistent with a *cis,mer*-tris(phosphine) arrangement analogous to **5**. Whether or not the exchange process is intra- or inter-

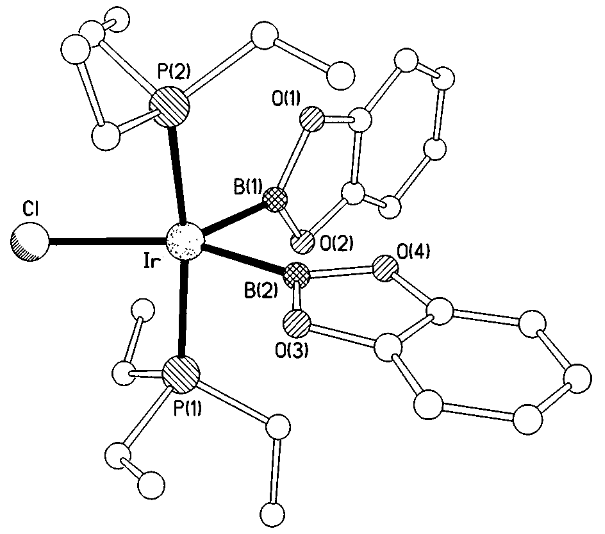
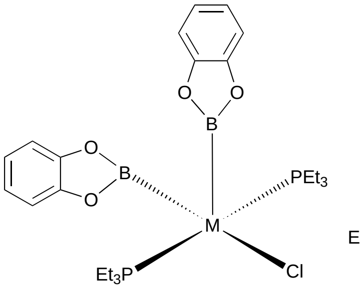
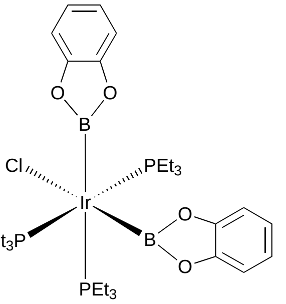


Fig. 4 View of the molecular structure of complex **9**. Details as in Fig. 1



8 M = Rh; **9** M = Ir



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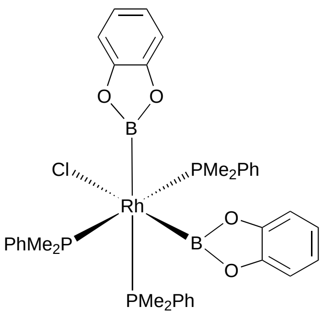
molecular cannot be ascertained from these data but the fact that it is the bis(phosphine) species which was isolated in crystalline form indicates that one of the PEt_3 ligands in **10** is labile, most likely the one *trans* to boron in view of the known high *trans* influence of the boryl group.[2e,8c,9]

The reaction between complex **3a** and 3 equivalents of PMe_2Ph quantitatively afforded the tris(phosphine) complex $[RhCl(PMe_2Ph)_3\{B(1,2\text{-}O_2C_6H_4)\}_2]$ **11** characterised on the basis of multinuclear NMR spectroscopy, and by analogy with the tris-PMe_3 complex **5**; it is also assumed to have the *cis,mer* configuration shown in the diagram. At room temperature the $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a doublet at δ −3.9 ($^1J_{RhP}$ = 101 Hz) for the equivalent, mutually *trans* phosphines and a broad singlet at δ −22.7 for the unique phosphine *trans* to a boryl group. In the latter case broadening of phosphorus signals *trans* to boron is commonly observed [see, for example, ref. 2(*e*)], but some degree of dissociation was also indicated by the fact that the resonance at δ −3.9 showed no phosphorus–phosphorus coupling. Such a dissociation process would be consistent with the known high *trans* influence of boryl groups[2e,8c,9] and this was confirmed by low-temperature $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. Thus at −60 °C the $^{31}P\text{-}\{^1H\}$ spectrum of **11** becomes fully resolved with the mutually *trans* pair of phosphines appearing as a doublet of doublets [δ −3.6 (dd, $^1J_{RhP}$ = 99, $^2J_{PP}$ = 28 Hz)] and the unique phosphine resonating as a doublet of triplets [δ −21.1 (dt, $^1J_{RhP}$ = 69, $^2J_{PP}$ = 28 Hz)], the small value of the $^1J_{RhP}$ coupling constant in the latter case being indicative of the relatively weak Rh–P bond resulting from the aforementioned *trans* influence of the boryl group.[2e,8c,9]



11

The reaction between complex **3a** and the phosphine $PMePh_2$ in CH_2Cl_2 solution proceeded somewhat differently from the reactions described above involving the phosphines PMe_3, PEt_3 and PMe_2Ph. Thus even when a large excess of $PMePh_2$ was added to solutions of **3a** a proportion of **3a** remained unchanged although signals due to unco-ordinated PPh_3 and two new rhodium–phosphine species were observed [δ 19.1 (d, $^1J_{RhP}$ = 109) and 2.8 (d, $^1J_{RhP}$ = 141 Hz)]. The former signal has a chemical shift and rhodium–phosphorus coupling constant consistent with a new bis(boryl) species $[RhCl(PMePh_2)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]$ **12** analogous to **3a** and **8**, but we were not able to isolate this compound as a pure material. The compound giving rise to the signal at δ 2.8 remains unidentified, although the large value of $^1J_{RhP}$ is indicative of a rhodium(I) species, but the fact that the $^{11}B\text{-}\{^1H\}$ NMR spectrum of the reaction mixture showed signals corresponding to compounds **II**–**IV**, indicated that considerable decomposition was occurring. When CH_2Cl_2 solutions of **3a** were treated with an excess of either PPr^i_3 or $P(C_6H_{11})_3$ no reaction took place as evidenced by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy which showed, in both cases, unchanged **3a** and free phosphine even after several days.

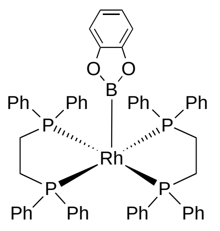
In view of the fact that the structures of the bis(phosphine) complexes **3a**, **3d** and **8** all have mutually *trans* phosphines, we were interested in preparing bis(phosphine) complexes in which the two phosphorus centres were part of a chelating diphosphine. With this in mind we treated CH_2Cl_2 solutions of **3a** with 1 equivalent of either dppe [1,2-bis(diphenylphosphino)ethane] or dcpe [1,2-bis(dicyclohexylphosphino)ethane]. In both cases, however, it was clear from following the reactions by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy that no new metal boryl species were obtained. Rather, in the former case, the only two rhodium–phosphorus containing products formed (in approximately equal amounts) were the rhodium(I) species $[Rh(dppe)_2]Cl$ **13** [δ 58.5 (d, $^1J_{RhP}$ = 133 Hz)][29] and the rhodium(III) species *trans*-$[RhH(Cl)(dppe)_2][B(1,2\text{-}O_2C_6H_4)_2]$ **14** [δ 52.6 (d, $^1J_{RhP}$ = 94 Hz].[30] Compound **14** was characterised by X-ray crystallography, details of which, together with full experimental and spectroscopic data, are reported in ref. 30. The formation of **13** from **3a** can be envisaged as proceeding according to equation (3) but the mechanism of formation of **14** remains unclear

$$\underset{\mathbf{3a}}{[RhCl(PPh_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]} + 2\,\text{dppe} \longrightarrow \underset{\mathbf{13}}{[Rh(dppe)_2]Cl} + 2\,PPh_3 + \underset{\mathbf{Ia}}{B_2(1,2\text{-}O_2C_6H_4)_2} \quad (3)$$

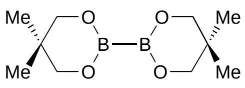
although we note that the reaction was fully reproducible.

The analogous reaction between complex **3a** and dcpe likewise afforded compounds identified as the rhodium(I) species $[Rh(dcpe)_2]Cl$ **15** [δ 67.0 (d, $^1J_{RhP}$ = 129 Hz)][31] and the ionic rhodium(III) species *trans*-$[RhH(Cl)(dcpe)_2][B(1,2\text{-}O_2C_6H_4)_2]$ **16** [δ 61.3 (d, $^1J_{RhP}$ = 90 Hz)].[30] Compound **16** was also characterised by X-ray crystallography, full structural, experimental and spectroscopic data for which are given in ref. 30.

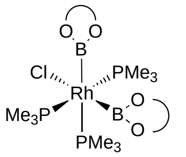
As an alternative route to metal bis(boryls) containing a chelating diphosphine ligand, the compound $[\{RhCl(dppe)\}_2]$ **17** was treated with 1 equivalent of **Ia** in CH_2Cl_2 solution. Monitoring the reaction by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy revealed a quantitative conversion over a period of 24 h into a single new phosphorus-containing species [δ 64.2, $^1J_{RhP}$ = 153 Hz] which was subsequently isolated, albeit in low yield, as a pale yellow crystalline powder. We were not able to obtain



18



Ij



O O = 1,2-O_2-3,5-$Bu^t{}_2C_6H_2$ **21**; 1,2-O_2-3-MeC_6H_3 **22**; tart **23**; $OCH_2CMe_2CH_2O$ **24**

X-ray-quality crystals of this product or satisfactory analytical data, but multinuclear NMR studies were consistent with a formulation as a rhodium(I) mono(boryl) species [Rh(dppe)$_2$-{B(1,2-$O_2C_6H_4$)}] **18**. The ^1H NMR spectrum was particularly informative, the integration of which showed two dppe ligands to one B(1,2-$O_2C_6H_4$) group. Moreover the boryl catecholate resonances had chemical shift values characteristic of rhodium boryls such as **3a**, these resonances being shifted to higher field compared to those of species such as **Ia** and **II**–**IV**. Furthermore, the CH_2 resonances of the dppe ligands were split into two sets consistent with different environments above and below the Rh(dppe)$_2$ plane. The value of $^1J_{RhP}$ is also consistent with a rhodium(I) species although we were not able to observe a resonance for the boryl group in the ^{11}B NMR spectrum. Analogous reactions between **17** and **Id** and **Ie** proceeded in a similar fashion affording complexes formulated as [Rh(dppe)$_2$-{B(1,2-O_2-3-MeC_6H_3)}] **19** and [Rh(dppe)$_2${B(1,2-O_2-4-MeC_6H_3)}] **20**. Clearly the reaction between **17** and the diborane(4) compounds **Ia**, **Id** and **Ie** is complicated and the formulation of the compounds **18**–**20** must be considered as tentative, any mechanistic speculation being unwarranted at this time.

The reaction between compound **Ia** and the cationic rhodium(I) complex [Rh(PMe_3)$_4$]Cl **7** in thf affording **5** has been described above. Compound **7** also reacts cleanly in thf solution with the diborane(4) compounds **Ic**, **Id**, **Ii** and the neopentyl glycolate derivative $B_2(OCH_2CMe_2CH_2O)_2$ **Ij**[16a,b] affording the bis(boryl) complexes *cis,mer*-[RhCl(PMe_3)$_3$-{B(1,2-O_2-3,5-$Bu^t{}_2C_6H_2$)}$_2$] **21**, *cis,mer*-[RhCl(PMe_3)$_3${B(1,2-O_2-3-MeC_6H_3)}$_2$] **22**, *cis,mer*-[RhCl(PMe_3)$_3${B(tart)}$_2$] **23** and *cis,mer*-[RhCl(PMe_3)$_3${B($OCH_2CMe_2CH_2O$)}$_2$] **24** all of which were characterised by multinuclear NMR studies and found to be analogous to **5** described in detail above.

Finally we mention that the reaction between complex **3a** and the isocyanide $CNC_6H_3Me_2$-2,6 proceeds according to equation (4) as described in ref. 8(*b*). An analogous reaction between

$$\underset{\mathbf{3a}}{[RhCl(PPh_3)_2\{B(1,2\text{-}O_2C_6H_4)\}_2]} + CNC_6H_3Me_2\text{-}2,6 \longrightarrow$$
$$[RhCl(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2] + \underset{\mathbf{Ia}}{B_2(1,2\text{-}O_2C_6H_4)_2} \quad (4)$$

3a and CO afforded [RhCl(CO)(PPh_3)$_2$] as the rhodium-containing product although the boron-containing species was not identified. We also note that no reaction was observed between compound **Ia** and the rhodium(I) and iridium(I) complexes [RhCl(PMe_2Ph)$_3$], [RhCl($PMePh_2$)$_3$], [RhCl(CO)-(PPh_3)$_2$], [IrCl(CO)(PMe_2Ph)$_2$] and [IrCl(PPh_3)$_3$].

Experimental

General procedures

All reactions were performed using standard Schlenk or glovebox techniques under an atmosphere of dry, oxygen-free dinitrogen or argon. All solvents were distilled from appropriate drying agents immediately prior to use (sodium–benzophenone for Et_2O, CaH_2 for chlorinated solvents and sodium or sodium–benzophenone for toluene and hexanes). Microanalytical data were obtained at The University of Bristol. The NMR spectra were recorded on JEOL GX 270, GX 400, Lambda 300 and Bruker WP 200 spectrometers and were referenced to $SiMe_4$, $SiMe_4$, 85% H_3PO_4 and $BF_3\cdot Et_2O$ for ^1H, ^{13}C, ^{31}P and ^{11}B nuclei respectively. Mass spectra (high and low resolution) were obtained in electron impact (EI) mode on a Micromass Autospec spectrometer. The compounds **1**,[32] **2**,[32] [RhCl(PMe_3)$_3$],[33] **7**,[33] [IrCl(PEt_3)$_3$][34] and **17**[35] were prepared by literature methods.

Preparations and reactions

[RhCl(PPh$_3$)$_2${B(1,2-O$_2$C$_6$H$_4$)}$_2$] 3a. In a typical preparation CH_2Cl_2 (2–4 cm^3) was added to a mixture of solid complex **2** (0.015 g, 0.011 mmol) and **Ia** (0.005 g, 0.023 mmol) at room temperature resulting in an orange suspension (**2** is only sparingly soluble in this solvent). After stirring for 15 min all of compound **2** had dissolved/reacted and the resulting pale yellow solution was cooled to −78 °C using a solid CO_2–ethanol bath. Addition of *n*-hexane (15 cm^3) resulted in the formation of a white precipitate which was then allowed to settle and the solvent was removed by syringe. The remaining solid was washed with *n*-hexane (2 × 5 cm^3) and finally dried under vacuum affording crude **3a** as a dry white powder (0.015 g, 72%). For any subsequent reactivity studies **3a** was used in this form but analytically pure samples and X-ray-quality crystals were obtained by redissolving the crude product in CH_2Cl_2 (3 cm^3), adding *n*-hexane (10 cm^3) as an overlayer and allowing solvent diffusion to occur over a period of days at −30 °C.

Compound **1** can also be used as a starting rhodium material as described in the text, although this is less desirable since traces of the liberated PPh_3 were sometimes found to contaminate the crude product.

Compounds **3b**–**3e** were prepared in an analogous fashion and with similar yields although in the case of **3b** and **3c** the increased solubility deriving from the Bu^t groups resulted in lower isolated yields. Compounds **3f**–**3h** were characterised on the basis of ^{31}P-{^1H} NMR spectroscopy of their respective reaction mixtures (which indicated quantitative yields in solution as with all other reactions) but were not isolated.

[RhCl(PPh$_3$)$_2${B[*R*,*R*-1,2-O$_2$CH(CO$_2$Me)CH(CO$_2$Me)]}$_2$] 3i. Compound **3i** was prepared and isolated as described for **3a** except that the reaction took much longer to go to completion and was stirred for 2–3 h at room temperature rather than 10–15 min.

Complex **3a**: NMR (CD_2Cl_2) ^1H, δ 7.66 (m, 12 H, PPh_3), 7.15 (m, 18 H, PPh_3), 6.68 (m, 4 H, 1,2-O_2-3,6-C_6H_4) and 6.60 (m, 4 H, 1,2-O_2-4,5-C_6H_4); ^{13}C-{^1H}, δ 149.5 (s, 1,2-O_2-1,2-C_6H_4), 134.9 (t, *o*-C of PPh_3), 132.4 (t, *ipso*-C of PPh_3), 130.4 (s, *p*-C of PPh_3), 128.2 (t, *m*-C of PPh_3), 121.3 (s, 1,2-O_2-3,6-C_6H_4) and 111.1 (s, 1,2-O_2-4,5-C_6H_4); ^{31}P-{^1H}, δ 31.1 (d, PPh_3, $^1J_{RhP}$ = 113 Hz); ^{11}B-{^1H}, δ 38.4 (Found: C, 56.00; H, 3.40. $C_{48}H_{38}B_2ClO_4P_2Rh\cdot 2CH_2Cl_2$ requires C, 56.10; H, 3.95%). The crystal structure reveals the presence of four molecules of CH_2Cl_2 of crystallisation per molecule of **3a**. Some of this solvent is readily lost from the crystals and the best for fit for the analytical data obtained is for two remaining molecules of CH_2Cl_2 per molecule of **3a**.

Complex **3b**: NMR (CD_2Cl_2) ^{1}H, δ 7.74 (m, 12 H, PPh_3), 7.27 (m, 18 H, PPh_3), 6.72 (m, 6 H, 1,2-O_2-4-Bu^t-3,5,6-C_6H_3) and 1.27 (s, 18 H, Bu^t); ^{13}C-{^{1}H}, δ 149.5 and 147.3 (s, 1,2-O_2-4-Bu^t-1,2-C_6H_3), 135.0 (t, *o*-C of PPh_3), 132.6 (t, *ipso*-C of PPh_3), 130.4 (s, *p*-C of PPh_3), 128.3 (t, *m*-C of PPh_3), 145.1, 117.8, 110.0 and 108.8 (s, 1,2-O_2-4-Bu^t-3,4,5,6-C_6H_3), 34.9 (s, *C*Me$_3$) and 31.9 (s, C*Me*$_3$); ^{31}P-{^{1}H}, δ 33.7 (d, PPh_3, $^1J_{RhP}$ = 115 Hz); ^{11}B-{^{1}H}, δ 38.9.

Complex **3c**: NMR (CD_2Cl_2) ^{1}H, δ 7.76 (m, 12 H, PPh_3), 7.28 (m, 18 H, PPh_3), 6.82 (d, 2 H, 1,2-O_2-3,5-Bu$^t_2$-6-C_6H_2, $^4J_{HH}$ = 2), 6.66 (d, 2 H, 1,2-O_2-3,5-Bu$^t_2$-4-C_6H_2, $^4J_{HH}$ = 2 Hz), 1.30 (s, 18 H, Bu^t) and 1.07 (s, 18 H, Bu^t); ^{13}C-{^{1}H}, δ 149.7 and 145.3 (s, 1,2-O_2-3,5-Bu$^t_2$-1,2-C_6H_2), 135.1 (t, *o*-C of PPh_3), 132.6 (t, *ipso*-C of PPh_3), 130.4 (s, *p*-C of PPh_3), 128.4 (t, *m*-C of PPh_3), 144.3, 133.6, 115.2 and 106.7 (s, 1,2-O_2-3,5-Bu$^t_2$-3,4,5,6-C_6H_2), 35.0 and 34.2 (s, *C*Me$_3$), 32.0 and 30.0 (s, C*Me*$_3$); ^{31}P-{^{1}H}, δ 31.9 (d, PPh_3, $^1J_{RhP}$ = 116 Hz); ^{11}B-{^{1}H}, δ 42.6.

Complex **3d**: NMR (CD_2Cl_2) ^{1}H, δ 7.70 (m, 12 H, PPh_3), 7.22 (m, 18 H, PPh_3), 6.64 (t, 2 H, 1,2-O_2-3-Me-5-C_6H_3, $^3J_{HH}$ = 8), 6.58 (d, 2 H, 1,2-O_2-3-Me-6-C_6H_3, $^3J_{HH}$ = 8), 6.52 (d, 2 H, 1,2-O_2-3-Me-4-C_6H_3, $^3J_{HH}$ = 8 Hz) and 1.86 (s, 6 H, Me); ^{13}C-{^{1}H}, δ 149.5 and 148.5 (s, 1,2-O_2-3-Me-1,2-C_6H_3), 135.2 (t, *o*-C of PPh_3), 132.9 (t, *ipso*-C of PPh_3), 130.7 (s, *p*-C of PPh_3), 128.6 (t, *m*-C of PPh_3), 123.0, 121.7, 121.2 and 109.0 (s, 1,2-O_2-3-Me-3,4,5,6-C_6H_3) and 14.6 (s, Me); ^{31}P-{^{1}H}, δ 31.0 (d, PPh_3, $^1J_{RhP}$ = 114 Hz); ^{11}B-{^{1}H}, δ 40.3 (Found: C, 64.60; H, 4.80. $C_{50}H_{42}B_2ClO_4P_2Rh$ requires C, 64.65; H, 4.55%).

Complex **3e**: NMR (CD_2Cl_2) ^{1}H, δ 7.68 (m, 12 H, PPh_3), 7.26 (m, 18 H, PPh_3), 6.54 (m, 6 H, 1,2-O_2-4-Me-3,5,6-C_6H_3) and 2.21 (s, 6 H, Me); ^{13}C-{^{1}H}, δ 149.6 and 147.5 (s, 1,2-O_2-4-Me-1,2-C_6H_3), 135.0 (m, *o*-C of PPh_3), 132.5 (t, *ipso*-C of PPh_3), 130.4 (s, *p*-C of PPh_3), 128.2 (m, *m*-C of PPh_3), 124.2, 121.4, 111.8 and 110.4 (s, 1,2-O_2-4-Me-3,4,5,6-C_6H_3) and 21.3 (s, Me); ^{31}P-{^{1}H}, δ 31.4 (d, PPh_3, $^1J_{RhP}$ = 113 Hz); ^{11}B-{^{1}H}, δ 37.0.

Complex **3f**: NMR (CD_2Cl_2) ^{31}P-{^{1}H}, δ 31.2 (d, PPh_3, $^1J_{RhP}$ = 114 Hz).

Complex **3g**: NMR (CD_2Cl_2) ^{31}P-{^{1}H}, δ 33.8 (d, PPh_3, $^1J_{RhP}$ = 117 Hz); ^{11}B-{^{1}H}, δ 56.1.

Complex **3h**: NMR (CD_2Cl_2) ^{31}P-{^{1}H}, δ 32.8 (d, PPh_3, $^1J_{RhP}$ = 112 Hz).

Complex **3i**: NMR (CD_2Cl_2) ^{1}H, δ 7.68 (m, 12 H, PPh_3), 7.34 (m, 18 H, PPh_3), 4.97 (s, 4 H, C*H*CO$_2$Me) and 3.80 (s, 12 H, CHCO$_2$*Me*); ^{13}C-{^{1}H}, δ 170.0 (s, CH*C*O$_2$Me), 135.2 (m, *o*-C of PPh_3), 130.3 (s, *p*-C of PPh_3), 128.2 (m, *m*-C of PPh_3), 78.1 (s, *C*HCO$_2$Me), 52.8 (s, CHCO$_2$*Me*), *ipso*-C of PPh_3 not observed; ^{31}P-{^{1}H}, δ 32.0 (d, PPh_3, $^1J_{RhP}$ = 117 Hz); ^{11}B-{^{1}H}, δ 36.3.

Satisfactory analytical data for the isolated compounds **3b**, **3c**, **3e** and **3i** were difficult to obtain due to extremely facile loss of some solvent of crystallisation.

Reaction between complex 3a and water. In a typical reaction, complex **1** (0.035 g, 0.038 mmol) and **Ia** (0.009 g, 0.038 mmol) were codissolved in thf (2 cm^3) and the mixture stirred for 20 min. After this time the only product present was **3a** as evidenced by ^{31}P and ^{11}B NMR spectroscopy. A solution of water in thf (0.5 cm^3 of a 0.05 M solution) was then added resulting in an immediate change from pale yellow to orange. The ^{31}P NMR analysis revealed the presence of **4** and free PPh_3 as the sole phosphorus-containing species whilst ^{11}B NMR spectroscopy showed the presence of **II**. The latter was also confirmed by mass spectrometry; *m*/*z* 254 ($C_{12}H_8B_2O_5$, M^+) with the correct isotope pattern.

Reaction between complex 3a and catechol. A sample of complex **3a** was prepared in thf solution as for the analogous hydrolysis experiment. A solution of catechol (0.004 g, 0.036 mmol) in thf (0.5 cm^3) was then added which also resulted in an immediate change from pale yellow to orange. The ^{31}P NMR analysis revealed the presence of **4** and free PPh_3 as the sole phosphorus-containing species whilst ^{11}B NMR spectroscopy showed the presence of **III**. The latter was also confirmed by mass spectrometry; *m*/*z* 346 ($C_{18}H_{12}B_2O_6$, M^+) with the correct isotope pattern.

[RhCl(PMe$_3$)$_3${B(1,2-O$_2$C$_6$H$_4$)}$_2$] 5. *Method A.* Complex **3a** (0.013 g, 0.014 mmol) was dissolved in CD_2Cl_2 (0.6 cm^3) at room temperature affording a pale yellow solution to which PMe_3 (*ca.* 5 μl, 0.045 mmol) was added resulting in an immediate change to bright yellow. Analysis by multinuclear NMR spectroscopy confirmed the formation of **5** in essentially quantitative yield although it was not readily isolated from this particular reaction due to the presence of the PPh_3 produced.

Method B. The compounds [RhCl(PMe_3)$_3$] (0.037 g, 0.100 mmol) and **Ia** (0.024 g, 0.100 mmol) were codissolved in benzene (0.8 cm^3) at room temperature and *n*-hexane (4 cm^3) was then added. This mixture was stirred for 15 min resulting in the formation of a pale yellow precipitate. After removal of the solvent by syringe and drying under vacuum, the crude **5** obtained was recrystallised from toluene–*n*-hexane mixtures affording **5** as a colourless crystalline solid (67%), m.p. 170 °C (decomp.).

Method C. Complex **7** (0.030 g, 0.063 mmol) and **Ia** (0.015 g, 0.063 mmol) were codissolved in thf (5 cm^3) at room temperature and the mixture stirred for 30 min during which time it changed from pale orange to colourless. After this time the solvent volume was reduced by about 50% by vacuum and then cooled by means of a solid CO_2–ethanol bath. Subsequent addition of *n*-pentane (15 cm^3) afforded a white precipitate from which the remaining solvent was removed by syringe. Further washing with pentane (2 × 5 cm^3) and drying by vacuum afforded **5** as a white crystalline solid (0.03 g, 76%). NMR (C_6D_6): ^{1}H, δ 7.21 (m, 4 H, 1,2-O_2-3,6-C_6H_4), 6.96 (m, 4 H, 1,2-O_2-4,5-C_6H_4), 1.52 (t, 18 H, PMe_3, $^2J_{HP}$ = 3) and 1.22 (d, 9 H, PMe_3, $^2J_{HP}$ = 7 Hz); ^{13}C-{^{1}H}, δ 138.0 (s, 1,2-O_2-1,2-C_6H_4), 137.9 (s, 1,2-O_2-1,2-C_6H_4), 134.2 (s, 1,2-O_2-3,6-C_6H_4), 134.0 (s, 1,2-O_2-3,6-C_6H_4), 128.8 (s, 1,2-O_2-4,5-C_6H_4), 128.7 (s, 1,2-O_2-4,5-C_6H_4), 20.0 (t, PMe_3, $^1J_{CP}$ = 16) and 18.0 (d, PMe_3, $^1J_{CP}$ = 18 Hz); ^{31}P-{^{1}H}, δ −9.4 (d, PMe_3, $^1J_{RhP}$ = 100 Hz) and −30.4 (br unresolved m, PMe_3); ^{11}B-{^{1}H}, δ 44.1 and 40.8. NMR (CD_2Cl_2): ^{31}P-{^{1}H}, δ −9.7 (dd, PMe_3, $^1J_{RhP}$ = 101, $^2J_{PP}$ = 30 Hz) and −29.7 (br unresolved m, PMe_3); ^{11}B-{^{1}H}, δ 44.3 and 39.8 (Found: C, 41.60; H, 5.85. $C_{21}H_{35}B_2ClO_4P_3Rh$ requires C, 41.75; H, 5.85%).

[RhCl(PEt$_3$)$_2${B(1,2-O$_2$C$_6$H$_4$)}$_2$] 8. A sample of PEt_3 (0.095 g, 0.81 mmol) was added dropwise to a solution of complex **3a** (0.230 g, 0.26 mmol) in CH_2Cl_2 (5 cm^3). Monitoring the reaction by ^{31}P NMR spectroscopy showed that quantitative conversion into **8** occurred after 30 min. After this time all volatiles were removed by vacuum and the crude product was recrystallised initially from toluene–*n*-hexane mixtures and subsequently from pentane affording **8** as a pale yellow powder (0.043 g, 28%), m.p. 85 °C (decomp.). Colourless, X-ray-quality crystals were obtained by slow evaporation of the solvent from the crude reaction mixture. NMR (C_6D_6): ^{1}H, δ 6.85 (m, 8 H, 1,2-$O_2C_6H_4$), 2.04 [m, 12 H, P(C*H*$_2$CH$_3$)$_3$] and 0.99 [m, 18 H, P(CH$_2$C*H*$_3$)$_3$]; ^{13}C-{^{1}H}, δ 149.8 (s, 1,2-O_2-1,2-C_6H_4), 121.9 (s, 1,2-O_2-3,6-C_6H_4), 111.4 (s, 1,2-O_2-4,5-C_6H_4), 17.1 [t, P(*C*H$_2$CH$_3$)$_3$, $^1J_{CP}$ = 14 Hz] and 8.6 [s, P(CH$_2$*C*H$_3$)$_3$]; ^{31}P-{^{1}H}, δ 29.0 (d, PEt_3, $^1J_{RhP}$ = 106 Hz); ^{11}B-{^{1}H}, δ 39.7 (Found: C, 47.10; H, 6.40. $C_{24}H_{38}B_2ClO_4P_2Rh$ requires C, 47.05; H, 6.25%).

[IrCl(PEt$_3$)$_2${B(1,2-O$_2$C$_6$H$_4$)}$_2$] 9/[IrCl(PEt$_3$)$_3${B(1,2-O$_2$C$_6$H$_4$)}$_2$] 10. Samples of [IrCl(PEt_3)$_3$] (0.058 g, 0.100 mmol) and **Ia** (0.024 g, 0.100 mmol) were codissolved in C_6D_6 (1 cm^3) and stirred for 12 h which resulted in a gradual fading of the solution from red to pale yellow. Multinuclear NMR studies indicated essentially quantitative conversion into complex **10** although colourless, X-ray-quality crystals of **9** were obtained

Table 2 Crystallographic data for complexes **3a**, **3d**, **8** and **9**

	3a·$4CH_2Cl_2$	**3d**·$3CH_2Cl_2$·$0.5C_6H_{14}$	**8**	**9**
Formula	$C_{52}H_{44}B_2Cl_9O_4P_2Rh$	$C_{56}H_{55}B_2Cl_7O_4P_2Rh$	$C_{24}H_{38}B_2ClO_4P_2Rh$	$C_{24}H_{38}B_2ClIrO_4P_2$
M	1238.4	1166.6	612.5	701.8
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	11.2003(6)	10.939(4)	13.9618(14)	13.970(2)
b/Å	13.5606(7)	13.843(6)	10.4578(11)	10.551(2)
c/Å	19.0819(10)	19.916(7)	19.219(2)	19.155(3)
α/°	83.551(2)	80.34(3)		
β/°	83.064(2)	81.99(3)	92.337(3)	92.819(3)
γ/°	79.373(2)	77.63(3)		
U/Å^3	2815.6(3)	2887(2)	2803.8(5)	2819.9(7)
Z	2	2	4	4
D_c/g cm^{-3}	1.461	1.342	1.451	1.653
μ/mm^{-1}	0.83	0.72	0.85	4.97
F(000)	1252	1194	1264	1392
Crystal size/mm	0.62 × 0.20 × 0.18	0.50 × 0.20 × 0.05	0.38 × 0.24 × 0.24	0.50 × 0.44 × 0.12
θ_{max}/°	25.5	27.5	28.4	28.5
Maximum indices h, k, l	12, 16, 22	14, 17, 25	18, 13, 25	17, 13, 24
Reflections measured	24 661	17 737	16 886	17 064
Unique reflections	9306	12 337	6439	6382
R_{int}	0.0385	0.0883	0.0258	0.0644
Transmission factors	0.422–0.502	0.288–0.526	0.739–0.862	0.148–0.408
Number of refined parameters	644	642	314	314
Extinction parameter x	0.0018(2)	0	0.001 33(12)	0.000 12(8)
Weighting parameters a, b	0.0372, 5.1991	0.1355, 8.18	0.0242, 1.7283	0.0336, 11.7717
R' (all data, on F^2)	0.1022	0.3042	0.0646	0.0982
R [data with $F^2 > 2\sigma(F^2)$]	0.0402 (8469)	0.1083 (4356)	0.0289 (5463)	0.0381 (5081)
Goodness of fit on F^2	1.054	0.899	1.042	1.067
Largest difference-map features/e Å^{-3}	+1.00, −0.75	+2.63, −1.84	+0.56, −0.66	+1.44, −1.68

by slow evaporation of the solvent over a period of 18 months; **10** was not isolated. NMR (C_6D_6) for complex **10**: ^{1}H, δ 6.93 (m, 8 H, 1,2-$O_2C_6H_4$), 2.10 and 1.92 [br m, 12 H, P(CH_2CH$_3$)$_3$] and 0.96 [br m, 18 H, P(CH$_2$CH_3)$_3$]; ^{13}C-{^{1}H}, δ 150.6 (s, 1,2-O$_2$-1,2-C$_6$H$_4$), 121.4 (s, 1,2-O$_2$-3,6-C$_6$H$_4$), 111.2 (s, 1,2-O$_2$-4,5-C$_6$H$_4$), 19.2 and 18.4 [t, P(CH$_2$CH$_3$)$_3$, $^1J_{CP} = 14$ Hz], 9.1 and 8.7 [s, P(CH$_2$$CH_3$)$_3$]; ^{11}B-{^{1}H}, δ 30.1; ^{31}P-{^{1}H} (−55 °C), δ −31.2 (t, 1 P, PEt$_3$, $^2J_{PP} = 25$) and −18.4 (d, 2 P, PEt$_3$, $^2J_{PP} = 25$ Hz). Satisfactory analytical data for **9** were not obtained since only a small quantity of crystals were isolated.

[RhCl(PMe$_2$Ph)$_3${B(1,2-O$_2$C$_6$H$_4$)}$_2$] 11. Complex **2** (0.053 g, 0.040 mmol) and **Ia** (0.021 g, 0.088 mmol) were dissolved in CH_2Cl_2 (2 cm^3) and the resulting pale yellow mixture stirred for 1 h after which time the quantitative formation of **3a** was confirmed by ^{31}P-{^{1}H} NMR spectroscopy. A sample of PMe$_2$Ph (0.023 cm^3, 0.16 mmol) was then added, resulting in no colour change, and the mixture stirred for 3 h. Analysis by ^{31}P-{^{1}H} NMR spectroscopy showed essentially quantitative conversion into **11**. In order to isolate a solid sample of **11**, the reaction mixture was cooled in a solid CO$_2$–ethanol bath and *n*-hexane (5 cm^3) added resulting in the formation of a white precipitate. The remaining solution was removed by syringe and the white solid washed with *n*-hexane (3 × 5 cm^3). Difficulties in removing all traces of PPh$_3$ prevented satisfactory analytical data from being obtained. NMR (CD$_2$Cl$_2$) (room temperature): ^{1}H, δ 7.31 (m, 6 H, PMe$_2$$Ph$), 7.20 (m, 9 H, PMe$_2$$Ph$), 7.04 (m, 4 H, 1,2-O$_2$-3,6-C$_6H_4$), 6.90 (m, 4 H, 1,2-O$_2$-4,5-C$_6H_4$), 1.57 (t, 12 H, P$Me_2$Ph, $^2J_{HP} = 4$) and 1.07 (d, 6 H, PMe_2Ph, $^2J_{HP} = 7$ Hz); ^{31}P-{^{1}H}, δ −3.9 (d, 2 P, PMe$_2$Ph, $^1J_{RhP} = 101$ Hz) and −22.7 (br s, 1 P, PMe$_2$Ph); ^{11}B-{^{1}H}, δ 40.3; ^{31}P-{^{1}H} (−60 °C), δ −3.6 (dd, 2 P, PMe$_2$Ph, $^1J_{RhP} = 99$, $^2J_{PP} = 28$) and −21.1 (dt, 1 P, PMe$_2$Ph, $^1J_{RhP} = 69$, $^2J_{PP} = 28$ Hz).

[Rh(dppe)$_2${B(1,2-O$_2$C$_6$H$_4$)}] 18. Complex **17** (0.015 g, 0.014 mmol) and **Ia** (0.007 g, 0.028 mmol) were dissolved in CH$_2$Cl$_2$ (5 cm^3). In fact **17** is not particularly soluble in this solvent such that initially the reaction mixture consisted of an orange suspension but after stirring at room temperature for 12 h all materials had dissolved and the colour had changed to pale yellow. After this time the solvent volume was reduced by about 50% by vacuum and then the solution was cooled using a solid CO$_2$–ethanol bath. On addition of *n*-hexane (15 cm^3) a pale yellow precipitate formed which was allowed to settle. The remaining solvent was removed by syringe and the solid washed with *n*-hexane (2 × 5 cm^3) and then dried under vacuum (0.011 g, 34%). Compounds **19** and **20** were prepared in an analogous manner and in similar yields from **17** and either **Id** or **Ie** respectively.

Complex **18**: NMR (CD$_2$Cl$_2$) ^{1}H, δ 7.95 (m, 16 H, Ph), 7.50 and 7.35 (m, 12 H, Ph), 7.15 and 7.00 (m, 12 H, Ph), 6.96 (m, 2 H, 1,2-O$_2$-3,6-C$_6$H$_4$), 6.55 (m, 2 H, 1,2-O$_2$-4,5-C$_6$H$_4$), 2.87 (br m, 4 H, CH$_2$) and 2.23 (br m, 4 H, CH$_2$); ^{31}P-{^{1}H}, δ 64.2 (d, dppe, $^1J_{RhP} = 153$ Hz).

Complex **19**: NMR (CD$_2$Cl$_2$) ^{1}H, δ 7.90 (m, 16 H, Ph), 7.45 and 7.35 (m, 12 H, Ph), 7.15 and 7.05 (m, 12 H, Ph), 6.70 (m, 1 H, 1,2-O$_2$-3-Me-6-C$_6$$H_3$), 6.60 (m, 2 H, 1,2-O$_2$-3-Me-4,5-C$_6$$H_3$), 2.85 (br m, 4 H, CH$_2$), 2.20 (br m, 4 H, CH$_2$) and 2.15 (s, 3 H, 1,2-O$_2$-3-MeC$_6$H$_3$); ^{31}P-{^{1}H}, δ 66.4 (d, dppe, $^1J_{RhP} = 150$ Hz).

Complex **20**: NMR (CD$_2$Cl$_2$) ^{1}H, δ 7.80 (m, 16 H, Ph), 7.45 and 7.35 (m, 12 H, Ph), 7.05 and 6.95 (m, 12 H, Ph), 6.35 (m, 2 H, 1,2-O$_2$-4-Me-3,6-C$_6$$H_3$), 6.30 (m, 1 H, 1,2-O$_2$-4-Me-5-C$_6$$H_3$), 2.80 (br m, 4 H, CH$_2$), 2.20 (br m, 4 H, CH$_2$) and 2.10 (s, 3 H, 1,2-O$_2$-4-MeC$_6$H$_3$); ^{31}P-{^{1}H}, δ 66.2 (d, dppe, $^1J_{RhP} = 151$ Hz).

***cis,mer*-[RhCl(PMe$_3$)$_3${B(1,2-O$_2$-3,5-Bu$^t_2$C$_6$H$_2$)}$_2$] 21, *cis,mer*-[RhCl(PMe$_3$)$_3${B(1,2-O$_2$-3-MeC$_6$H$_3$)}$_2$] 22, *cis,mer*-[RhCl(PMe$_3$)$_3${B(tart)}$_2$] 23 and *cis,mer*-[RhCl(PMe$_3$)$_3${B(OCH$_2$CMe$_2$CH$_2$O)}$_2$] 24.** Compounds **21**–**24** were prepared from **7** and the corresponding diborane(4) compound **Ic**, **Id**, **Ii** and **Ij** according to method C described above for the preparation of **5** and with similar yields.

Complex **21**: NMR (C$_6$D$_6$) ^{31}P-{^{1}H}, δ −9.8 (dd, PMe$_3$, $^1J_{RhP} = 101$, $^2J_{PP} = 30$ Hz) and −30.3 (br unresolved m, PMe$_3$); ^{11}B-{^{1}H}, δ 42.0.

Complex **22**: NMR ([^{2}H$_8$]toluene) ^{1}H, δ 7.22 (m, 2 H, 1,2-O$_2$-3-Me-6-C$_6$$H_3$), 7.05 (m, 2 H, 1,2-O$_2$-3-Me-5-C$_6H_3$), 6.97 (m, 2 H, 1,2-O$_2$-3-Me-4-C$_6$$H_3$), 2.57 (s, 6 H, 1,2-O$_2$-3-$MeC_6H_3$), 1.69

(t, 18 H, PMe$_3$, $^2J_{HP}$ = 4) and 1.40 (t, 9 H, PMe$_3$, $^2J_{HP}$ = 6 Hz); ^{31}P-{^{1}H}, δ −8.6 (d, PMe$_3$, $^1J_{RhP}$ = 103 Hz) and −30.3 (br unresolved m, PMe$_3$); ^{11}B-{^{1}H}, δ 44.2 and 41.4.

Complex **23**: NMR (C_6D_6) ^{31}P-{^{1}H}, δ −10.9 (d, PMe$_3$, $^1J_{RhP}$ = 93 Hz) and −30.2 (br unresolved m, PMe$_3$); ^{11}B-{^{1}H}, δ 43.3 and 38.2.

Complex **24**: NMR (C_6D_6) ^{31}P-{^{1}H}, δ −8.3 (d, PMe$_3$, $^1J_{RhP}$ = 92 Hz) and −27.0 (br unresolved m, PMe$_3$); ^{11}B-{^{1}H}, δ 39.0.

X-Ray crystallography

Crystallographic data for crystals containing complexes **3a**, **3d**, **8** and **9** are presented in Table 2. Measurements were made at 160 K (173 K for **3d**) on Siemens SMART CCD area-detector diffractometers with Mo-Kα radiation (λ = 0.710 73 Å).[36] Intensities were integrated[36] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being more than a hemisphere in each case. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[37] The structures were solved variously by heavy-atom and direct methods, and refined by least squares on F^2 values for all reflections, with weighting $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. An isotropic extinction parameter x was refined, whereby $F_c' = F_c/[1 + (0.001xF_c^2\lambda^3/\sin 2\theta)]^{\frac{1}{4}}$. The crystal for which data were collected on **3d**·3CH$_2$Cl$_2$·0.5C$_6$H$_{14}$ was the best of many tried but still of poor quality. The sample was prone to solvent loss and whilst this was minimised, the resulting peak profiles were less than ideal making accurate integration difficult. A half molecule of hexane solvent was present in the crystal structure although the third atom was not found in the electron-density difference map. Unresolved disorder was apparent in some of the phenyl rings. Hydrogen atoms were placed in idealised positions.

CCDC reference number 186/769.

See http://www.rsc.org/suppdata/dt/1998/301/ for crystallographic files in .cif format.

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