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Salts of the bis(catecholato)borate anion with rhodium- and iridium-phosphine complex cations

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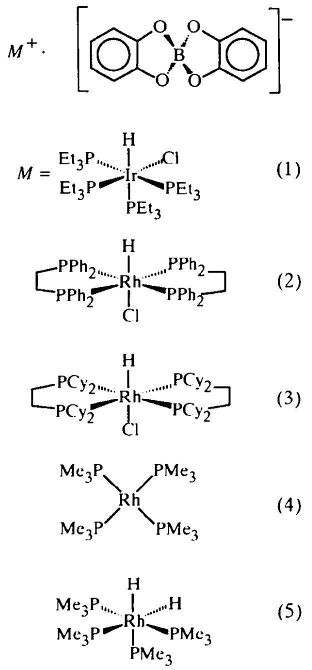
Abstract

In a series of five salts with rhodium- or iridium-phosphine complex cations {*cis*-chlorohydridotetrakis(triethylphosphine)iridium(III) bis(pyrocatecholato-*O*,*O*′)borate, [IrClH($C_6H_{15}P$)$_4$]($C_{12}H_8BO_4$), (1); *trans*-chlorobis[ethylenebis(diphenylphosphine)]hydridorhodium(III) bis(pyrocatecholato-*O*,*O*′)borate dichloromethane solvate, [RhClH($C_{26}H_{24}P_2$)$_2$]($C_{12}H_8BO_4$)·CH_2Cl_2, (2); *trans*-chlorobis[ethylenebis(dicyclohexylphosphine)]hydridorhodium(III) bis(pyrocatecholato-*O*,*O*′)borate tetrakis(dichloromethane) solvate, [RhClH($C_{26}H_{48}P_2$)$_2$]($C_{12}H_8BO_4$)·4CH_2Cl_2, (3); tetrakis(trimethylphosphine)rhodium(I) bis(pyrocatecholato-*O*,*O*′)borate, [Rh(C_3H_9P)$_4$]($C_{12}H_8BO_4$), (4); and *cis*-dihydridotetrakis(trimethylphosphine)rhodium(III) bis(pyrocatecholato-*O*,*O*′)borate, [RhH_2(C_3H_9P)$_4$]($C_{12}H_8BO_4$), (5)}, the bis(catecholato)borate anion has approximate D_{2d} ($\bar{4}2m$) symmetry, with the central spiro-B atom distorted from regular tetrahedral coordination geometry by reduction of the two intra-ring O—B—O bond angles. The two chelate rings show small deviations from planarity by folding about the O···O axis. The hydrido and chloro ligands in the cation of compound (1), which has four monodentate phosphine ligands, are *cis* to each other, but in compounds (2) and (3), each with two chelating diphosphine ligands, they are mutually *trans*. The cation in compound (4) has only four phosphine ligands, which are arranged in a tetragonally distorted square-planar arrangement to minimise steric crowding. Its reaction product with molecular dihydrogen, compound (5), has a *cis* arrangement of the two hydrido ligands in a distorted octahedral cation. The strong *trans* influence of the hydrido ligands is reflected in lengthened bonds to the opposite ligands in each case.

Comment

We have previously reported the structures of a series of salts of the bis(catecholato)borate [bis(benzene-1,2-diolato)borate] anion, $[B(cat)_2]^-$, with organic nitrogen and phosphorus cations (Clegg *et al.*, 1998). This anion seems to be a favoured product in many reactions of catecholborane, HB(cat), and related compounds under a wide variety of conditions, and we have encountered it numerous times in studies of catalytic hydroboration and diboration reactions of $B_2(cat)_2$ and $B_2(cat)_3$, as well as HB(cat). Few crystal structures have been reported of salts of the $[B(cat)_2]^-$ anion with metal-centred cations and of metal complexes of the anion acting as a ligand (He & Hartwig, 1996; Westcott *et al.*, 1991, 1993; Dai *et al.*, 1998). We describe here five structures with iridium- and rhodium-phosphine complex cations, which have been obtained as part of a research programme in synthesis and homogeneous catalysis.



The geometry of the anion is essentially the same in all these structures, and does not differ significantly from that seen previously in its salts with a variety of cations (Clegg *et al.*, 1998, and references therein). In each case, the B atom has a slightly elongated tetrahedral coordination geometry, with the two smallest O—B—O angles opposite each other within the two chelate rings. These rings are close to being planar, with r.m.s. deviations up to 0.045 Å; there is a slight folding about the O···O axis, with a dihedral angle ranging from 0.2 (4) to 11.4 (2)° between BO_2 and O_2C_2 planes (with r.m.s. deviations below 0.01 Å), such that the B atom becomes the flap of an envelope. This folding is only slight and follows no clear pattern in the various structures. Neglecting it, the anion has approximate D_{2d} ($\bar{4}2m$) point-group symmetry, the two chelate rings being perpendicular within 2° in all cases. B—O bond lengths range from 1.468 (12) to 1.504 (13) Å, with a mean of 1.482 Å and a standard deviation of 0.010 Å.

All the cations in these compounds contain iridium or rhodium with four phosphine ligands (either monodentate phosphines, or diphosphines chelating through both P atoms). All but one [in compound (4)] also contain either one hydrido and one chloro ligand, or two hydrido ligands. All the hydrido ligands were located and freely refined. The Rh—H bond in (3) is unusually short at 1.27 (11) Å, compared with 1.578 (3) and 1.583 (3) Å given by Orpen *et al.* (1989), and 1.43 and 1.40 Å found for Rh—D by Nietlispach *et al.* (1993) by spectroscopic methods, but the difference from these latter values is not significant in view of the large uncertainty in the distance as measured by X-ray diffraction. There are no interactions between the cations and anions other than normal electrostatic attraction. This contrasts with previous reports, in which the anion bonds to titanium through two of its O atoms (He & Hartwig, 1996) or is π-bonded to rhodium *via* one of the aromatic rings (Westcott *et al.*, 1991; Dai *et al.*, 1998).

The cation in compound (1) has Ir coordinated by hydrido and chloro ligands in a *cis* geometry in addition to the four triethylphosphine ligands. A similar *cis* arrangement has been found for several other Ir and Rh complexes with four phosphines, one hydrido and one other ligand (Thorn & Tulip, 1982; Milstein *et al.*, 1986; Marder *et al.*, 1987; Stevens *et al.*, 1990). The longest Ir—P bond lies opposite the hydrido ligand, and

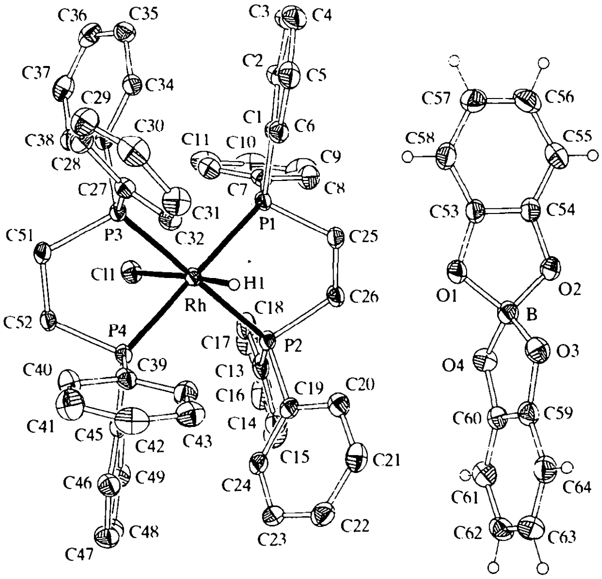


Fig. 2. The molecular structure of compound (2), without the solvent molecule.

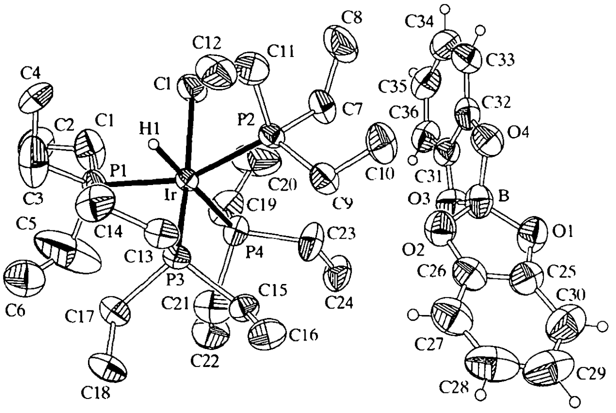


Fig. 1. The molecular structure of compound (1). In this and the other figures, displacement ellipsoids are shown at the 40% probability level, H atoms on phosphine ligands have been omitted, and a small number of unlabelled atoms have numbers which can be deduced from the others. Minor disorder components are not shown.

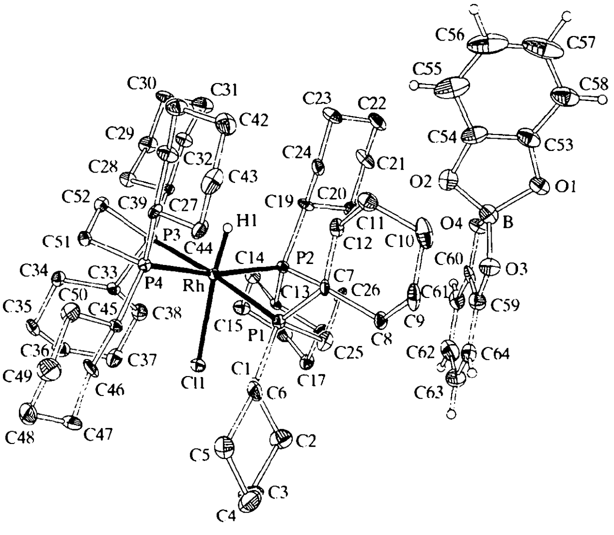


Fig. 3. The molecular structure of compound (3), without solvent molecules.

the shortest opposite chloro, as expected on the basis of the relative *trans* influence of these ligands. The steric bulk of the phosphines forces them apart, with a bond angle for the two mutually *cis* phosphines of 97.91 (5)° and an angle of 158.26 (5)° between the two mutually *trans* phosphines, the angle between hydrido and chloro ligands being closed down to 84 (2)°.

Compounds (2) and (3) have very similar rhodium-centred cations, each with two bidentate diphosphines of the same chelate ring size and bite angle [P—Rh—P angles of 82.80 (3) and 80.84 (3)° for (2), and 83.54 (7) and 82.10 (7)° for (3)]. In both cases, the hydrido and chloro ligands are mutually *trans*, in contrast to the *cis* arrangement in compound (1). All other similar reported complexes with chelating diphosphines also have a *trans* arrangement of one hydrido and one other non-hydrido ligand (Cowie & Dwight, 1979; Behr *et al.*, 1987). The phenyl-substituted diphosphine in compound (2) gives shorter Rh—P bonds than the cyclohexyl-substituted diphosphine in compound (3).

In compound (4), the rhodium(I) cation has only four phosphine ligands and no others. We have obtained this compound in a number of different reactions. It resulted from the reaction of $[\mathrm{Rh(PMe_3)_4Me}]$ with MeB(cat) in hexane solution, probably by methyl abstraction from the starting complex by the MeB(cat), followed by disproportionation of the resulting $[\mathrm{Me_2B(cat)}]$ to $[\mathrm{Me_4B}]^-$ and $[\mathrm{B(cat)_2}]^-$. A more rational and essentially quantitative synthesis involves the stoichiometric reaction of $[\mathrm{Rh(PMe_3)_4Me}]$ with $\mathrm{B_2(cat)_3}$, which gives only MeB(cat) as a by-product, as described in the *Experimental* section. Both compounds (4) and (5) are also formed as components of complex mixtures from reactions of $[\mathrm{Rh(PMe_3)_4H}]$ with HB(cat) (Westcott *et al.*, 1993). Comparison of the geometry of the cation in compound (4) here with that of the chloride salt reported by Jones *et al.* (1980) and the putative *cis*-$[\mathrm{Rh(PMe_3)_4(H)_2}]^+$ cation in its benzene-solvated $[\mathrm{B(cat)_2}]^-$ salt (Westcott *et al.*, 1993), together with the similar orange colour of all three compounds, shows that this last complex was actually $[\mathrm{Rh(PMe_3)_4}]^+[\mathrm{B(cat)_2}]^-\cdot\mathrm{C_6H_6}$ (reductive elimination of dihydrogen having taken place), wrongly described (though not wrongly characterized crystallographically, since the hydrido ligands were not located) as the *cis*-dihydrido complex. The $\mathrm{Rh^I}$ ion in compound (4) has a square-planar coodination geometry which is severely distorted towards tetrahedral because of the steric bulk of the ligands; bond angles between *trans* phosphines are 151.29 (3) and 155.77 (3)°. A similar arrangement has been found for other $\mathrm{Rh^I}$ complexes with four monodentate phosphines (Clark *et al.*, 1975, 1987; Jones *et al.*, 1980; Lundquist *et al.*, 1989; Reibenspies & Darensbourg, 1993). In one complex with substituted phosphabenzene rather than tertiary phosphine ligands, the distortion from square-planar geometry is only very small (Breit *et al.*, 1997), while the cation with four bulky triphenylphosphine ligands lies so far along the distortion pathway that it is actually regular tetrahedral [this structure is in the Cambridge Structural Database (Allen & Kennard, 1993) with refcode KUYTUT; it was deposited as supplementary material for a paper by Burgess *et al.* (1992), but in the final publication this structure is not actually described or even mentioned].

Reaction of compound (4) with dihydrogen gas gives the authentic *cis*-dihydro complex (5), as has also been reported for the chloride salt (Jones *et al.*, 1980). The strong *trans* influence of the hydrido ligands is again reflected in the lengthening of the Rh—P bonds opposite Rh—H relative to the two mutually *trans* phosphines. Several other $[\mathrm{Rh}(\mathrm{P}R_3)_4\mathrm{H_2}]^+$ cations and iridium analogues, including some with two

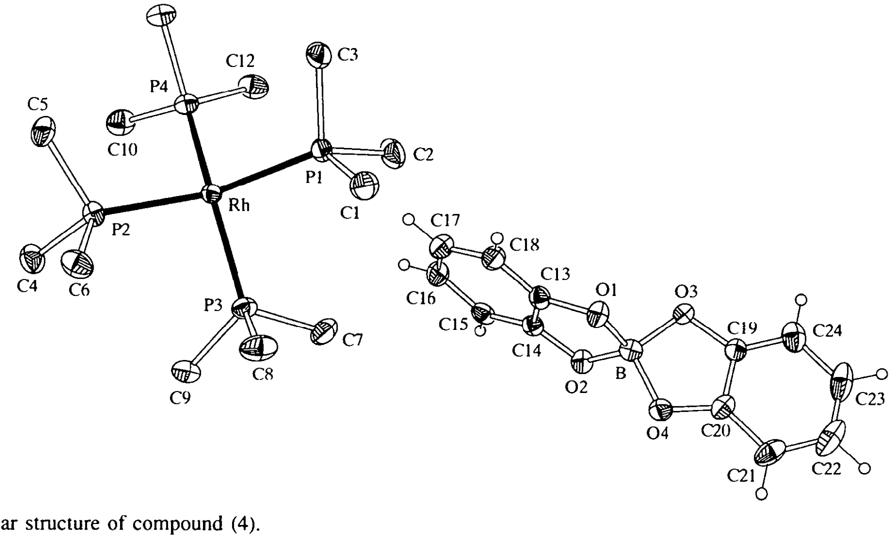


Fig. 4. The molecular structure of compound (4).

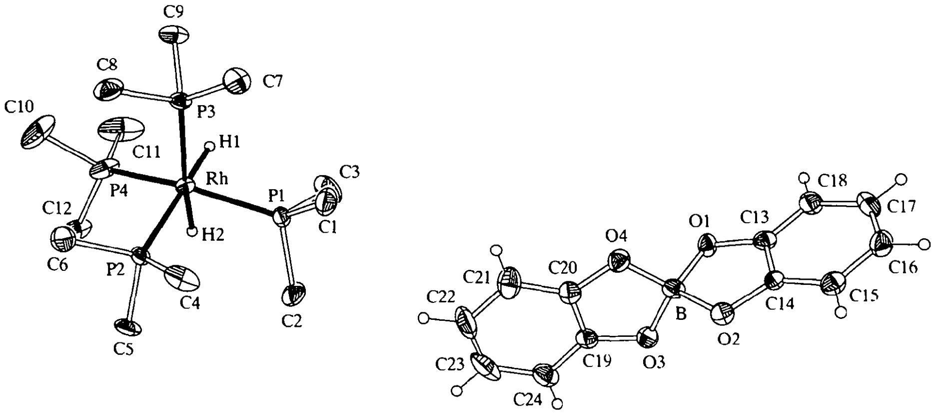


Fig. 5. The molecular structure of compound (5), without minor disorder components.

chelating diphosphines rather than four monodentate phosphines, have been crystallographically characterized (Debaerdemaeker, 1977; Greenwood *et al.*, 1979; Behr *et al.*, 1986, 1987; Ferguson *et al.*, 1988; Brown *et al.*, 1989), and a *cis* arrangement of the hydrido ligands is found in every case.

Experimental

Compounds (1)–(4) were all prepared in reactions of transition metal complexes with either $B_2(cat)_2$ or $B_2(cat)_3$; hydrogenation of compound (4) led to compound (5). For compound (1), a solution of $[IrCl(PEt_3)_3]$ (0.427 g, 0.73 mmol) in THF (1 ml) was added to solid $B_2(cat)_2$ (0.197 g, 0.82 mmol) with stirring, and the mixture was allowed to stand at room temperature for several days, giving crystals of compound (1) by slow solvent evaporation. Satisfactory NMR spectra were obtained, including a doublet of quartets (δ −13.24, J_{H-P} 140.3 and 18.2 Hz; 200 MHz operation, CD_2Cl_2 solvent) for the hydrido ligand; $^{31}P\{^1H\}$ (202.5 MHz, CD_2Cl_2): δ 27.3 (*dt*, P3, $J_{P3-P1/P2}$ 14.2 Hz, J_{P3-P4} 12.1 Hz), 29.9 (*t*, P1/P2, $J_{P1/P2-P3}$ and $J_{P1/P2-P4}$ 14.2 Hz), 37.0 (*m*, P4, J_{P3-P4} 12.1 Hz, $J_{P4-P1/P2}$ 14.2 Hz), with crystallographic atom numbering. For compound (2), $[\{RhCl(PPh_3)_2\}_2]$ (0.061 g, 0.05 mmol) and $B_2(cat)_2$ (0.024 g, 0.10 mmol) were dissolved in CH_2Cl_2 (2 ml) and the solution was stirred for 15 min. A solution of dppe (0.040 g, 0.10 mmol) in CH_2Cl_2 (1 ml) was added slowly by syringe, then a layer of hexanes (3 ml) was added. Solvent diffusion at 243 K over a period of several days afforded crystals of compound (2). Satisfactory NMR spectra were obtained, including a doublet of quintets (δ −16.04, $J_{Rh-H} \sim J_{P-H}$ = 13.0 Hz; 200 MHz, $CDCl_3$) for the hydrido ligand; $^{31}P\{^1H\}$ (36.45 MHz, $CDCl_3$): δ 52.6 (*d*, $J_{Rh\ P}$ 94 Hz). For compound (3), the same procedure was used as for compound (2), but with dcpe (0.042 g, 0.10 mmol) instead of dppe. The coupling for the hydrido ligand (at δ −16.80) was not resolved in the ^1H NMR spectrum; $^{31}P\{^1H\}$ (36.45 MHz, $CDCl_3$): δ 61.3 (*d*, J_{Rh-P} 90 Hz). For compound (4), a solution of $[Rh(PMe_3)_4Me]$ (0.200 g, 0.474 mmol) in heptane (3 ml) was added dropwise with stirring to a solution of $B_2(cat)_3$ (0.164 g, 0.474 mmol) in heptane (100 ml) at 313 K. After stirring for 1 h at 313 K and 1 h at room temperature, the orange precipitate was collected by filtration, washed with toluene and then heptane, and recrystallized from THF to give crystals of compound (4). Satisfactory NMR spectra were obtained; $^{31}P\{^1H\}$ (81 MHz, CD_3CN): δ −14.3 (*d*, J_{Rh-P} 131.6 Hz). For compound (5), hydrogen gas was bubbled into a solution of compound (4) (0.100 g, 0.158 mmol) in THF (10 ml) for 10 min. Crystals were obtained by solvent diffusion of a layer of heptane (15 ml). Satisfactory NMR spectra were obtained, including a second-order splitting pattern which approximates to a doublet of quartets (δ −10.69, $J_{H-P(trans)} \sim$ 136.6 Hz, $J_{H-P(cis)} \sim J_{H-Rh} \sim$ 14.8 Hz) for the hydrido ligands (200 MHz, CD_3CN); $^{31}P\{^1H\}$ (81 MHz, CD_3CN): δ −11.0 [*dt*, 2P(*cis*), J_{Rh-P} 96.4 Hz, J_{P-P} 27.4 Hz], −22.4 [*dt*, 2P(*trans*), J_{Rh-P} 85.7 Hz, J_{P-P} 26.6 Hz].

Compound (1)

Crystal data

$[IrClH(C_6H_{15}P)_4]$-
  $(C_{12}H_8BO_4)$
M_r = 928.25
Monoclinic
$P2_1/n$
a = 14.276 (3) Å
b = 15.290 (3) Å
c = 19.807 (4) Å
β = 102.36 (2)°
V = 4223.3 (15) Å^3
Z = 4
D_x = 1.460 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 29
  reflections
θ = 11.64–12.52°
μ = 3.411 mm^{-1}
T = 298 (2) K
Prism
0.78 × 0.34 × 0.31 mm
Colourless

Data collection

Stoe–Siemens diffractometer
ω/θ scans
Absorption correction:
  multi-scan (Sheldrick,
  1994)
  T_{min} = 0.146, T_{max} = 0.347
8170 measured reflections
7421 independent reflections
5755 reflections with
  $I > 2\sigma(I)$

R_{int} = 0.051
θ_{max} = 25.00°
$h = -16 \rightarrow 16$
$k = -12 \rightarrow 18$
$l = -20 \rightarrow 23$
5 standard reflections
  frequency: 60 min
  intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.080$
$S = 1.020$
7421 reflections
464 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 3.8148P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.019$
$\Delta\rho_{\max} = 0.961$ e Å^{-3}
$\Delta\rho_{\min} = -1.130$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.00010 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Ir—H1	1.52 (5)	Ir—Cl	2.4613 (13)
Ir—P3	2.2979 (12)	B—O1	1.470 (8)
Ir—P2	2.3712 (12)	B—O4	1.474 (9)
Ir—P1	2.3895 (14)	B—O3	1.479 (8)
Ir—P4	2.4439 (14)	B—O2	1.496 (8)
H1—Ir—P3	83 (2)	P3—Ir—Cl	167.00 (5)
H1—Ir—P2	82 (2)	P2—Ir—Cl	79.22 (5)
P3—Ir—P2	95.18 (4)	P1—Ir—Cl	83.70 (5)
H1—Ir—P1	83 (2)	P4—Ir—Cl	94.53 (5)
P3—Ir—P1	98.61 (5)	O1—B—O4	114.1 (5)
P2—Ir—P1	158.26 (5)	O1—B—O3	112.1 (5)
H1—Ir—P4	179 (2)	O4—B—O3	104.7 (5)
P3—Ir—P4	97.91 (5)	O1—B—O2	104.3 (6)
P2—Ir—P4	98.44 (5)	O4—B—O2	111.1 (5)
P1—Ir—P4	96.22 (5)	O3—B—O2	110.7 (5)
H1—Ir—Cl	84 (2)		

Compound (2)

Crystal data

$[\mathrm{RhClH(C_{26}H_{24}P_2)_2}]$-$(\mathrm{C_{12}H_8BO_4})\cdot\mathrm{CH_2Cl_2}$
$M_r = 1248.07$
Triclinic
$P\overline{1}$
$a = 12.5401$ (8) Å
$b = 13.5374$ (9) Å
$c = 16.9310$ (11) Å
$\alpha = 91.937$ (2)°
$\beta = 97.051$ (2)°
$\gamma = 90.121$ (2)°
$V = 2850.8$ (3) Å^3
$Z = 2$
$D_x = 1.454$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 9820 reflections
$\theta = 1.21$–$26.36°$
$\mu = 0.602$ mm^{-1}
$T = 160$ (2) K
Block
0.32 × 0.20 × 0.10 mm
Yellow

Data collection

Bruker SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.764$, $T_{\max} = 0.930$
15 687 measured reflections
10 982 independent reflections
9431 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.030$
$\theta_{\max} = 26.38°$
$h = -15 \rightarrow 14$
$k = -16 \rightarrow 11$
$l = -19 \rightarrow 21$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.104$
$S = 1.139$
10 982 reflections
707 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0119P)^2 + 7.2583P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.025$
$\Delta\rho_{\max} = 1.202$ e Å^{-3}
$\Delta\rho_{\min} = -0.748$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (2)*

Rh—H1	1.59 (5)	Rh—Cl1	2.4875 (9)
Rh—P4	2.3418 (9)	B—O3	1.477 (5)
Rh—P3	2.3473 (9)	B—O1	1.482 (5)
Rh—P1	2.3484 (9)	B—O2	1.483 (5)
Rh—P2	2.3675 (9)	B—O4	1.485 (5)
H1—Rh—P4	92 (2)	P4—Rh—Cl1	85.28 (3)
H1—Rh—P3	96 (2)	P3—Rh—Cl1	85.83 (3)
P4—Rh—P3	80.84 (3)	P1—Rh—Cl1	101.59 (3)
H1—Rh—P1	81 (2)	P2—Rh—Cl1	98.07 (3)
P4—Rh—P1	172.70 (3)	O3—B—O1	110.5 (3)
P3—Rh—P1	97.06 (3)	O3—B—O2	113.2 (3)
H1—Rh—P2	80 (2)	O1—B—O2	104.5 (3)
P4—Rh—P2	98.80 (3)	O3—B—O4	104.8 (3)
P3—Rh—P2	176.05 (3)	O1—B—O4	112.1 (3)
P1—Rh—P2	82.80 (3)	O2—B—O4	112.0 (3)
H1—Rh—Cl1	177 (2)		

Compound (3)

Crystal data

$[\mathrm{RhClH(C_{26}H_{48}P_2)_2}]$-$(\mathrm{C_{12}H_8BO_4})\cdot 4\mathrm{CH_2Cl_2}$
$M_r = 1551.23$
Orthorhombic
$P2_12_12_1$
$a = 13.9320$ (8) Å
$b = 21.2938$ (10) Å
$c = 25.5613$ (14) Å
$V = 7583.1$ (7) Å^3
$Z = 4$
$D_x = 1.359$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14978 reflections
$\theta = 1.66$–$26.34°$
$\mu = 0.671$ mm^{-1}
$T = 160$ (2) K
Needle
0.44 × 0.08 × 0.08 mm
Colourless

Data collection

Bruker SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.791$, $T_{\max} = 0.948$
27 335 measured reflections
14 673 independent reflections
13 157 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.054$
$\theta_{\max} = 26.36°$
$h = -12 \rightarrow 16$
$k = -23 \rightarrow 25$
$l = -25 \rightarrow 31$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.086$
$wR(F^2) = 0.178$
$S = 1.381$
$(\Delta/\sigma)_{\max} = 0.027$
$\Delta\rho_{\max} = 1.082$ e Å^{-3}
$\Delta\rho_{\min} = -2.127$ e Å^{-3}
Extinction correction: none

14 673 reflections
788 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 48.7217P]$ where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.01 (5)

Table 3. *Selected geometric parameters (Å, °) for (3)*

Rh—H1	1.27 (11)	Rh—Cl1	2.513 (2)
Rh—P3	2.377 (2)	B—O4	1.468 (12)
Rh—P4	2.391 (2)	B—O2	1.477 (12)
Rh—P2	2.403 (2)	B—O1	1.479 (11)
Rh—P1	2.408 (2)	B—O3	1.504 (13)
H1—Rh—P3	85 (5)	P3—Rh—Cl1	94.64 (7)
H1—Rh—P4	88 (5)	P4—Rh—Cl1	101.18 (7)
P3—Rh—P4	82.10 (7)	P2—Rh—Cl1	90.24 (7)
H1—Rh—P2	80 (5)	P1—Rh—Cl1	80.32 (7)
P3—Rh—P2	97.69 (7)	O4—B—O2	112.7 (8)
P4—Rh—P2	168.57 (7)	O4—B—O1	111.7 (8)
H1—Rh—P1	100 (5)	O2—B—O1	105.9 (7)
P3—Rh—P1	174.84 (8)	O4—B—O3	104.5 (7)
P4—Rh—P1	97.70 (8)	O2—B—O3	110.8 (8)
P2—Rh—P1	83.54 (7)	O1—B—O3	111.4 (8)
H1—Rh—Cl1	171 (5)		

Compound (4)

Crystal data

$[Rh(C_3H_9P)_4](C_{12}H_8BO_4)$
$M_r = 634.19$
Monoclinic
$P2_1/n$
$a = 9.7315$ (9) Å
$b = 29.559$ (3) Å
$c = 10.8716$ (10) Å
$\beta = 102.541$ (2)°
$V = 3052.7$ (5) Å^3
$Z = 4$
$D_x = 1.380$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8136 reflections
$\theta = 2.25–27.98°$
$\mu = 0.795$ mm^{-1}
$T = 160$ (2) K
Block
0.32 × 0.14 × 0.12 mm
Orange

Data collection

Bruker SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.832$, $T_{\max} = 0.909$
18 627 measured reflections

6970 independent reflections
5320 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\max} = 28.42°$
$h = -12 \rightarrow 12$
$k = -39 \rightarrow 36$
$l = -11 \rightarrow 14$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.082$
$S = 1.053$
6970 reflections
320 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 2.4605P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.625$ e Å^{-3}
$\Delta\rho_{\min} = -0.555$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.00087 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 4. *Selected geometric parameters (Å, °) for (4)*

Rh—P4	2.2929 (8)	B—O1	1.472 (4)
Rh—P2	2.2969 (8)	B—O4	1.475 (4)
Rh—P1	2.3071 (8)	B—O2	1.492 (4)
Rh—P3	2.3083 (8)	B—O3	1.492 (4)
P4—Rh—P2	93.30 (3)	O1—B—O4	113.0 (3)
P4—Rh—P1	92.66 (3)	O1—B—O2	104.8 (2)
P2—Rh—P1	151.29 (3)	O4—B—O2	112.3 (3)
P4—Rh—P3	155.77 (3)	O1—B—O3	112.0 (2)
P2—Rh—P3	93.04 (3)	O4—B—O3	104.8 (2)
P1—Rh—P3	92.93 (3)	O2—B—O3	110.1 (2)

Compound (5)

Crystal data

$[RhH_2(C_3H_9P)_4](C_{12}H_8BO_4)$
$M_r = 636.21$
Orthorhombic
$Pbca$
$a = 13.4442$ (7) Å
$b = 18.7746$ (10) Å
$c = 24.5809$ (12) Å
$V = 6204.5$ (6) Å^3
$Z = 8$
$D_x = 1.362$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27854 reflections
$\theta = 1.98–28.23°$
$\mu = 0.783$ mm^{-1}
$T = 160$ (2) K
Block
0.40 × 0.38 × 0.16 mm
Colourless

Data collection

Bruker SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.714$, $T_{\max} = 0.894$
36 970 measured reflections

7303 independent reflections
5904 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.102$
$\theta_{\max} = 28.39°$
$h = -16 \rightarrow 17$
$k = -24 \rightarrow 18$
$l = -23 \rightarrow 32$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.088$
$wR(F^2) = 0.190$
$S = 1.448$
7303 reflections
359 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 37.8822P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.607$ e Å^{-3}
$\Delta\rho_{\min} = -0.782$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.00012 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 5. *Selected geometric parameters (Å, °) for (5)*

Rh—H1	1.48 (5)	Rh—P3	2.363 (2)
Rh—H2	1.49 (5)	B—O4	1.475 (10)
Rh—P4	2.302 (2)	B—O1	1.476 (10)
Rh—P1	2.304 (2)	B—O3	1.482 (10)
Rh—P2	2.351 (2)	B—O2	1.502 (10)
H1—Rh—H2	88 (4)	H2—Rh—P3	172 (3)
H1—Rh—P4	80 (3)	P4—Rh—P3	99.22 (7)
H2—Rh—P4	80 (3)	P1—Rh—P3	100.92 (7)
H1—Rh—P1	87 (3)	P2—Rh—P3	99.89 (7)

H2—Rh—P1	78 (3)	O4—B—O1	112.9 (6)
P4—Rh—P1	154.56 (9)	O4—B—O3	105.3 (6)
H1—Rh—P2	176 (3)	O1—B—O3	111.9 (6)
H2—Rh—P2	89 (3)	O4—B—O2	110.9 (6)
P4—Rh—P2	96.16 (9)	O1—B—O2	104.0 (6)
P1—Rh—P2	95.53 (8)	O3—B—O2	112.1 (6)
H1—Rh—P3	83 (3)		

For compounds (2)–(5), the data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. Coverage is essentially complete to at least 25° in θ.

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with $U_{\rm iso}$ constrained to be 1.2 (1.5 for methyl groups) × $U_{\rm eq}$ of the carrier atom, except for hydrido ligands, which were freely refined with individual $U_{\rm iso}$ in all cases. The highest residual electron-density peaks were close to metal atoms. The residual electron-density peak with a height > 1 e Å^{-3} in the structure of (2) lies between H1 (1.06 Å) and Cl3 in an adjacent solvent molecule (2.22 Å); in the structure of (3), the highest peak is 0.94 Å from Rh. All other peaks are < 1 e Å^{-3} in height.

In the structure of (1), disorder was resolved for atoms C4, C6 and C12 of the phosphine–ethyl groups, and refinement included alternative positions with relative occupancies of 0.879:0.121 (18), 0.64:0.36 (2) and 0.702:0.298 (15), respectively; because of the low occupancy of the second component of C4 (C4*X*), this atom was refined with an isotropic displacement parameter. The C—C bonds of the disordered groups were weakly restrained to be approximately equal.

In the structure of (5), disorder was refined for the methyl groups of the P3 phosphine (C7, C8 and C9), with relative occupancies of 0.573:0.427 (12) for two alternative orientations. Restraints were not required in the refinement of this disorder, but the two Rh—H bonds were restrained to be approximately equal.

No restraints were applied in the refinement of the other structures, except for an 'approximately isotropic' restraint for atoms C8, C33 and C39 of (3). Elongated displacement ellipsoids for some atoms [particularly C10, C11 and C12 in (5)], some relatively poor geometry within ligands and the rather high refinement residuals for (3) and (5), indicate probable further disorder in the structures of (1), (3) and (5), but this could not be resolved successfully and additional restraints brought no significant improvement.

Data collection: *DIF*4 (Stoe & Cie, 1988) for (1), *SMART* (Siemens, 1995) for all other compounds. Cell refinement: *DIF*4 for (1), local programs for all other compounds. Data Reduction: local programs for (1), *SAINT* (Siemens, 1995) for all other compounds. For all compounds, program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1074). Services for accessing these data are described at the back of the journal.

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