Mono- and Bi-nuclear Complexes of Rhodium with Functionalised Diphosphine Ligands†

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Treatment of [RhCl(PPh$_3$)$_3$] with R$_2$PCH$_2$CH$_2$PR$_2$ (R = C$_6$H$_4$SMe-2 or C$_6$H$_4$SPr^i-2) gives the ionic complexes [Rh(R$_2$PCH$_2$CH$_2$PR$_2$)]Cl **A**. When R = C$_7$H$_4$NS (benzothiazolyl) or C$_8$H$_7$N$_2$ (*N*-methylbenzimidazolyl), however, the partially substituted complexes [RhCl(PPh$_3$)(R$_2$PCH$_2$CH$_2$PR$_2$)] **B** result. Treatment of **B** (R = C$_7$H$_4$NS) with CHCl$_3$ results in oxidation and disproportionation to the salt [(RhCl)$_2$(μ-dbtpe)$_2$][RhCl$_4$(dbtpe)]$_2$ **C** [dbtpe = (C$_7$H$_4$NS)$_2$PCH$_2$CH$_2$P(SNC$_7$H$_4$)$_2$]. X-Ray diffraction analysis of **C** shows the cation to have a structure with a P–P chelated dbtpe ligand on each RhCl unit spanning the two metals by P,N ligation. The anion has regular octahedral co-ordination. Reaction of dbtpe with [{RhCl(cod)}$_2$] (cod = cycloocta-1,5-diene) or [{RhCl(CO)$_2$}$_2$] gives [(RhCl)$_2$(μ-dbtpe)$_2$] **D** which also has two P–P chelated RhCl units linked by P,N ligation, as shown by an X-ray crystal structure analysis. Full spectroscopic details are given for these compounds and their possible inter-relationship is discussed.

Phosphine ligands have a long history of use in stabilising metal complexes containing ligands of catalytic interest such as dinitrogen, hydrides and unsaturated hydrocarbons.[1–3] There is much current interest in multimetal systems, clusters or arrays, which might provide multiple sites for reactions or multiple redox processes. We have prepared a series of diphosphines which carry functional groups capable of additional ligation *via* N- or S-donor groups[4] and are exploring their chemistry in the expectation that polynuclear complexes can be produced *via* mixed ligation from the relatively 'soft' P- and S-donors together with the relatively 'hard' N-donor atoms. We also expected some variation in behaviour of these ligands as compared to non-functionalised diphosphines such as Ph$_2$PCH$_2$CH$_2$PPh$_2$, because of the varying steric and electronic requirements of the functional groups at phosphorus.

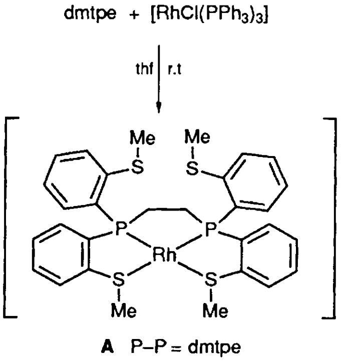
Here we describe some of our results for rhodium, where both 'regular' P–P ligation (apparently modified by electronic/steric factors) and multifunctional ligation are displayed. Some of these data have been communicated in a brief form.[4]

Results and Discussion

Diphosphine Nomenclature.—For simplicity we define the functionalised diphosphines (R$_2$PCH$_2$CH$_2$PR$_2$) that we have used as follows: R = C$_6$H$_4$SMe-2, dmtpe; C$_6$H$_4$SPr^i-2, ditpe; C$_7$H$_4$NS (benzothiazolyl), dbtpe; and C$_8$H$_7$N$_2$ (*N*-methylbenzimidazolyl), dmbpe.

Preparation of [Rh(P–P)]Cl **A** (P–P = dmtpe or ditpe).—Reaction of dmtpe with [RhCl(PPh$_3$)$_3$] in tetrahydrofuran (thf) or benzene resulted in the precipitation of a yellow-orange, air-stable complex [Rh(dmtpe)]Cl **A**, [reaction (1), r.t. = room temperature]. Reaction of ditpe under the same conditions produced the analogue **A** (P–P = ditpe). These compounds, which are 1 : 1 electrolytes in MeNO$_2$, are formulated as shown on the basis of elemental analysis and spectroscopic data.

Both complexes have a simple doublet in their ^{31}P-{^{1}H} NMR spectra, showing that the phosphorus atoms are magnetically equivalent and coupled to rhodium (Experimental section). The chemical shift of **A** (P–P = ditpe) is some 45 ppm to low field of that of **A** (P–P = dmtpe) presumably as a result of inductive release of electron density by the isopropyl groups, or a slight distortion caused by their size, or both of these effects.



(1)

A P–P = dmtpe

The ^{1}H NMR spectrum of **A** (P–P = dmtpe) shows a broad singlet at δ 1.6 assigned to the methyl protons, a multiplet between δ 2.5 and 3.0 assigned to the CH$_2$ protons and a phenyl-proton multiplet at δ 7.5. The structure shown is the simplest which is consistent with these data and conforms to the expected square-planar geometry of the Rh^I. The ^{31}P NMR spectrum of **A** (P–P = ditpe) is also consistent with this structure (Experimental section) and in addition the fast atom bombardment (FAB) mass spectrum shows (M^+ – Cl) at m/z = 797 as expected.

Preparations of the Complexes [RhCl(PPh$_3$)(P–P)] **B** (P–P = dbtpe *or* dmbpe).—In general, reaction of the diphosphines Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1, 2 or 3) with [RhCl(PPh$_3$)$_3$] leads to complete loss of PPh$_3$ from Rh and formation of [Rh(P–P)$_2$]Cl[5] without isolation of any intermediate compounds. The analogous reaction of dmtpe and ditpe, to give [Rh(P–P)]Cl has been described above.

In contrast, reaction of dbtpe and dmbpe with [RhCl(PPh$_3$)$_3$] leads to the formation of orange, diamagnetic, uncharged complexes [RhCl(PPh$_3$)(P–P)] **B**, the first examples of this class of intermediate complex, shown for **B** (P–P =

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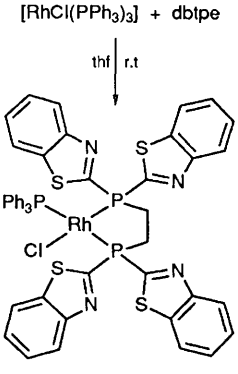
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



B P–P = dbtpe

(2)

dbtpe) in reaction (2). The formulation of compounds **B** follows from analytical data and their spectroscopic properties.

The ^{31}P-{^{1}H} NMR spectrum of **B** (P–P = dbtpe) in dichloromethane is assigned to an ABCX spin system, where A, B, C = ^{31}P and X = ^{103}Rh, consistent with the proposed structure as in Fig. 1, which shows the spectral parameters and the successful computer simulation using those parameters. The ^{1}H NMR spectrum shows multiplets for the CH_2 protons (δ 2.65) and the phenyl protons (δ 7.0–8.2). The molecular formula was confirmed by the FAB mass spectrum, which gave the molecular ion at m/z = 1026 and the molecular ion minus chlorine at m/z = 991. Complex **B** (P–P = dmbpe) was prepared by an analogous reaction and also has an ABCX ^{31}P-{^{1}H} NMR spectrum which was successfully simulated using the parameters shown in the Experimental section.

Complexes **B** may be regarded as intermediates on the route to the [Rh(P–P)$_2$]Cl complexes from [RhCl(PPh$_3$)$_3$], the electronic/steric properties of dbtpe and dmbpe in **B** being such that attack by a second molecule of diphosphine is prevented. They may also be regarded as intermediates on the route to **A**, but intramolecular displacement of PPh$_3$ does not occur, presumably because further ligation by dbtpe and dmbpe would involve formation of an energetically unfavoured four-membered metallocycle.

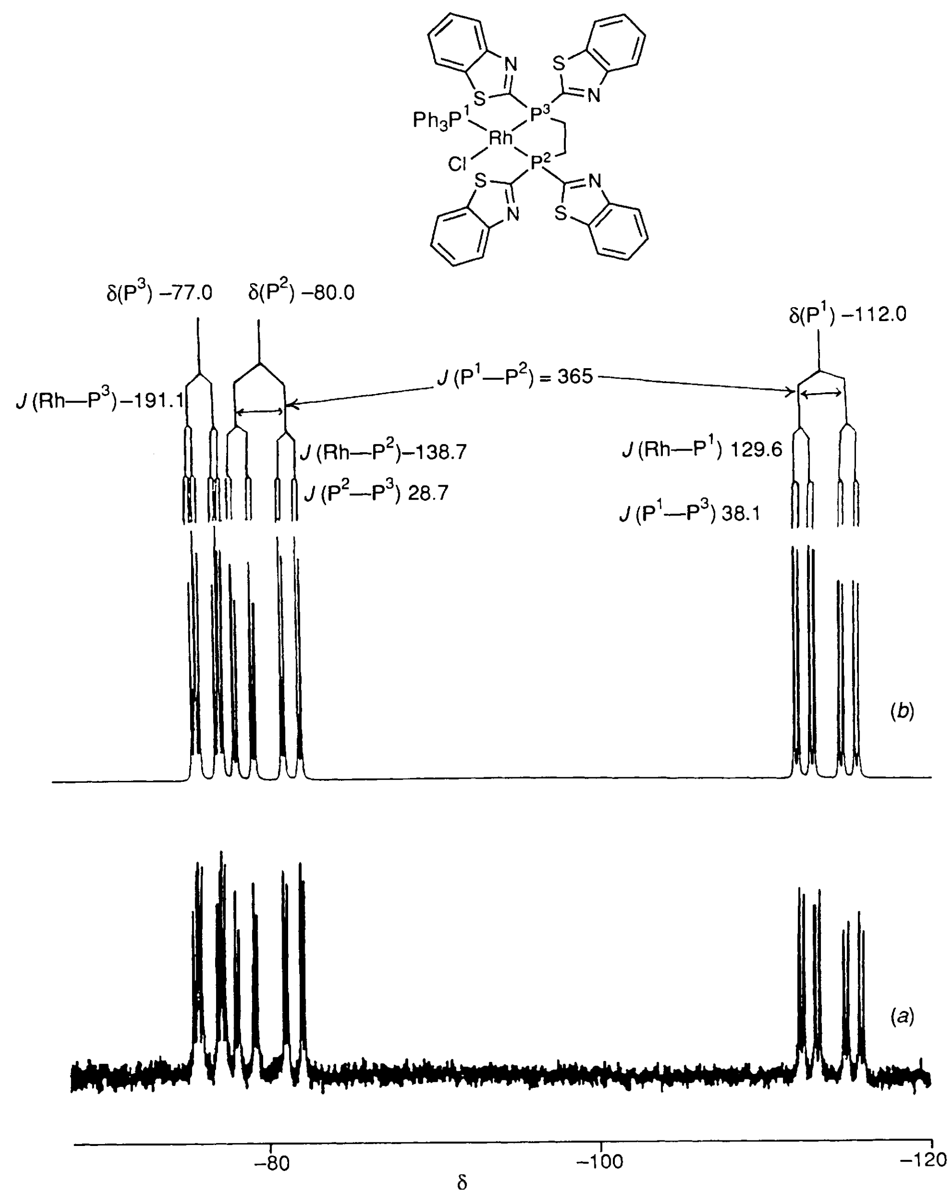
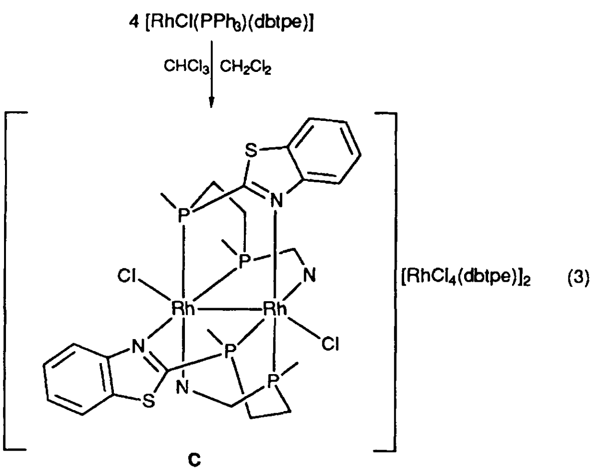


Fig. 1 ^{31}P-{^{1}H} NMR spectrum (J/Hz) of [RhCl(PPh$_3$)(dbtpe)] **B** in CH_2Cl_2: (a) real spectrum; (b) simulated spectrum



(3)

Preparation and Structure of $[(RhCl)_2(\mu\text{-dbtpe})_2][RhCl_4(dbtpe)]_2$ **C**.—On standing in CH_2Cl_2–$CHCl_3$ solution, $[RhCl(PPh_3)(dbtpe)]$ undergoes a slow reaction, with loss of PPh_3, to give red crystals of the complex $[\{RhCl(dbtpe)\}_2][RhCl_4(dbtpe)]_2$ **C** [reaction (3)]. The molecular structure of **C** was established by an X-ray structure determination; however, crystal instability associated with solvent loss led to a low-resolution data set being obtained. As a consequence the molecular structure is of unusually low precision and only the gross features of the geometry can be relied upon. The structures of the cation and anion are shown in Figs. 2 and 3 respectively.[4]

The complex contains a novel binuclear centrosymmetric cation (Fig. 2) with the dbtpe ligands spanning two metals. Each rhodium in the cation carries a dbtpe ligand chelating through the phosphorus atoms, and one benzothiazolyl group from each phosphorus ligates the second rhodium through nitrogen to give a 'double-A-frame' geometry such as is observed in carboxylate complexes.[6] The Rh–Rh distance of 2.723(8) Å is within the range associated with a single bond.[7]

Clearly the Cl(5)–Rh(2)–Rh(2′)–Cl(5′) atoms are not collinear. The chlorine atom bends towards the phosphorus atom P(4) by *ca.* 20° from the Rh–Rh vector. The angle Cl(5)–Rh(2)–Rh(2′) is 160.3(5)° (Figs. 2 and 4 and Table 1).

The anion contains rhodium involved in classical diphosphine chelation in an approximately octahedral configuration (Fig. 3), with the diphosphine and two Cl atoms forming a plane and the other two chlorine atoms situated above and below the plane. The angle Cl(3)–Rh(1)–Cl(2) is 176.0(6)° which is almost linear. All principal distances are similar to corresponding ones in the cation and are listed in Table 1. Atomic co-ordinates are given in Table 2.

Preparation and Structure of $[(RhCl)_2(\mu\text{-dbtpe})_2]$ **D**.—The reaction of 2 mol equivalents of dbtpe with either $[\{RhCl(cod)\}_2]$ (cod = cycloocta-1,5-diene) or $[\{RhCl(CO)_2\}_2]$ in thf gave a deep purple crystalline complex, whose $^{31}P\text{-}\{^1H\}$ NMR spectrum in dichloromethane was obtained with the best resolution at −70 °C. The spectrum has been successfully analysed and simulated as an ABX spin system as shown in Fig. 5. The ^1H NMR spectrum of **D** at −70 °C shows five multiplets in the methylene region between δ 2.8 and 4.2, indicating the presence of several different methylene groups. The phenyl region of the ligand becomes more complicated on ligation, indicating the presence of different benzothiazolyl groups in the complex.

Conductivity measurements of the complex in dichloromethane show that it is non-conducting. The FAB mass spectrometric analysis shows a molecular ion corresponding to a dimer (m/z = 1529) and other fragments at m/z 1494 (M^+ − Cl) and 1458 (M^+ − 2Cl). The molecular ion has a lower relative intensity than that of the M^+ − Cl ion.

In accord with the above discussion, the complex was formulated as $[Rh_2Cl_2(dbtpe)_2]$ **D** [reaction (4)], with each metal carrying one dbtpe ligand chelated through the phosphorus atoms with a benzothiazolyl group ligating the other metal.

Loss of resolution occurs in the $^{31}P\text{-}\{^1H\}$ NMR spectrum at higher temperature, which could be due to the rapid exchange of the free and co-ordinated benzothiazolyl groups. Complex **D**

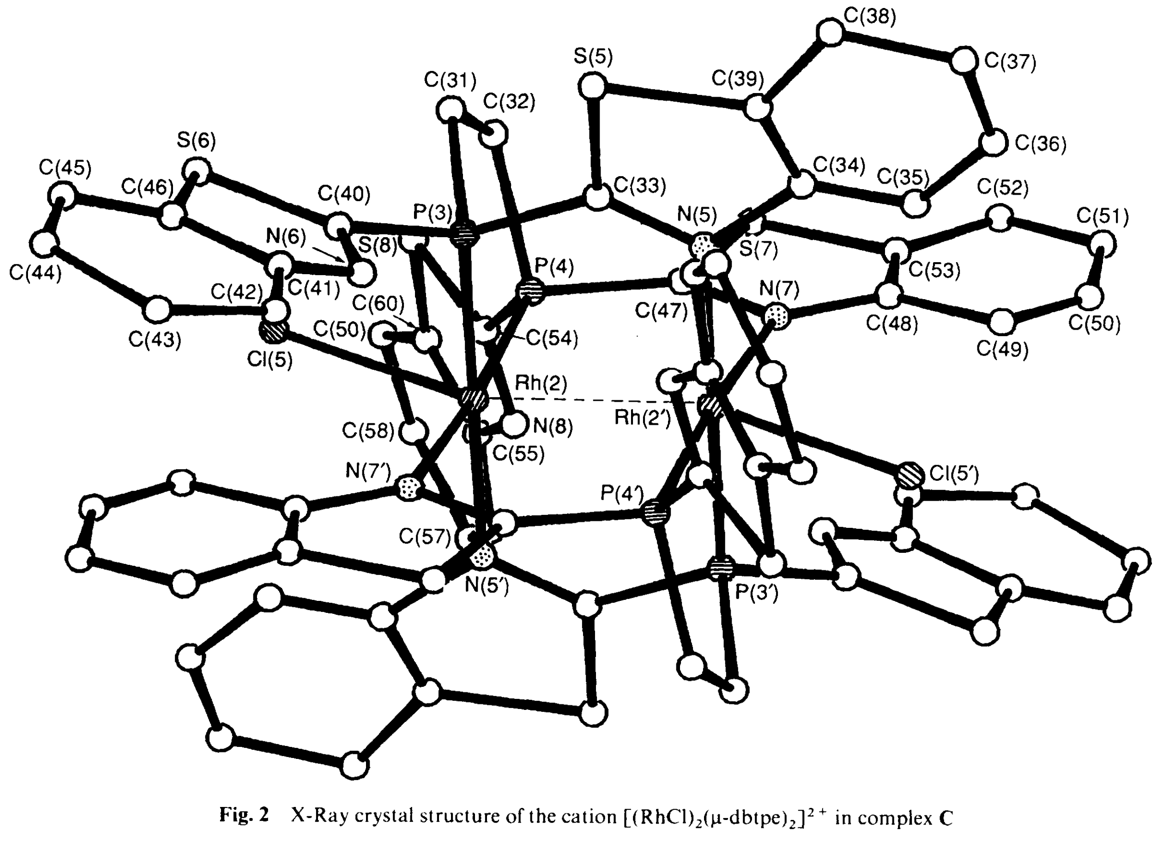


Fig. 2 X-Ray crystal structure of the cation $[(RhCl)_2(\mu\text{-dbtpe})_2]^{2+}$ in complex **C**

Table 1 Selected intramolecular distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses, for complex **C**

Rh(1)–Cl(1)	2.45(2)	Rh(1)–Cl(2)	2.33(2)
Rh(1)–Cl(3)	2.36(2)	Rh(1)–Cl(4)	2.39(2)
Rh(1)–P(1)	2.22(2)	Rh(1)–P(2)	2.18(2)
Rh(2)–Rh(2′)	2.723(8)	Rh(2)–Cl(5)	2.54(2)
Rh(2)–P(3)	2.21(2)	Rh(2)–P(4)	2.22(2)
Rh(2)–N(5′)	2.16(5)	Rh(2)–N(7′)	2.25(5)
Cl(1)–Rh(1)–Cl(2)	91.0(6)	Cl(1)–Rh(1)–Cl(3)	92.1(6)
Cl(1)–Rh(1)–Cl(4)	96.7(6)	Cl(1)–Rh(1)–P(1)	169.9(7)
Cl(1)–Rh(1)–P(2)	85.6(7)	Cl(1)–Rh(1)–Cl(3)	176.0(6)
Cl(2)–Rh(1)–Cl(4)	91.4(6)	Cl(2)–Rh(1)–P(1)	83.8(7)
Cl(2)–Rh(1)–P(2)	92.3(6)	Cl(3)–Rh(1)–Cl(4)	90.7(6)
Cl(3)–Rh(1)–P(1)	92.7(7)	Cl(3)–Rh(1)–P(2)	85.4(6)
Cl(4)–Rh(1)–P(1)	92.0(7)	Cl(4)–Rh(1)–P(2)	175.5(5)
P(1)–Rh(1)–P(2)	86.0(7)	Rh(2′)–Rh(1)–Cl(5)	160.3(5)
Rh(2′)–Rh(2)–P(3)	86.6(5)	Rh(2′)–Rh(2)–P(4)	86.6(5)
Rh(2′)–Rh(2)–N(5′)	94(1)	Rh(2′)–Rh(2)–N(7′)	94(1)
Cl(5)–Rh(2)–P(3)	83.4(7)	Cl(5)–Rh(2)–P(4)	75.7(6)
Cl(5)–Rh(2)–N(5′)	96(1)	Cl(5)–Rh(2)–N(7′)	102(1)
P(3)–Rh(2)–P(4)	84.6(7)	P(3)–Rh(2)–N(5′)	179(1)
P(3)–Rh(2)–N(7′)	89(2)	P(4)–Rh(2)–N(5′)	95(1)
P(4)–Rh(2)–N(7′)	173(2)	N(5′)–Rh(2)–N(7′)	92(2)

Primed atoms are related to unprimed ones by the symmetry element $1 - x, -y, -z$

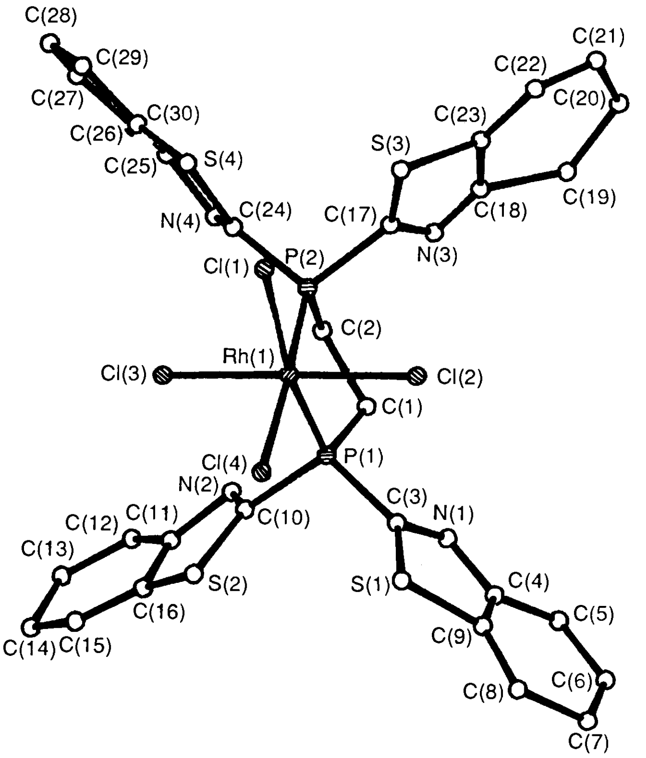


Fig. 3 X-Ray crystal structure of the anion $[RhCl_4(dbtpe)]^-$ in **C**

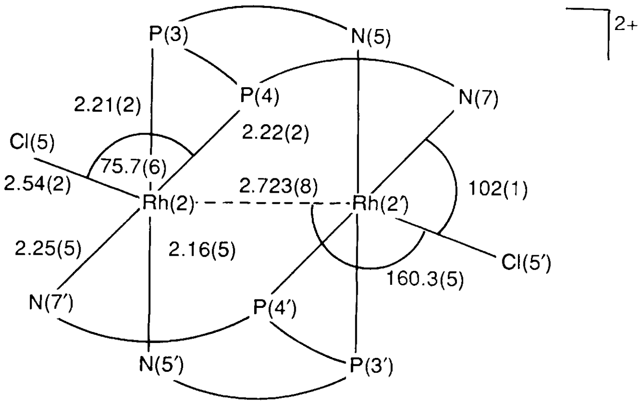


Fig. 4 Bond distances (Å) and angles (°) in the immediate co-ordination sphere of the centrosymmetric dication $[(RhCl)_2(\mu\text{-dbtpe})_2]^{2+}$ in **C**

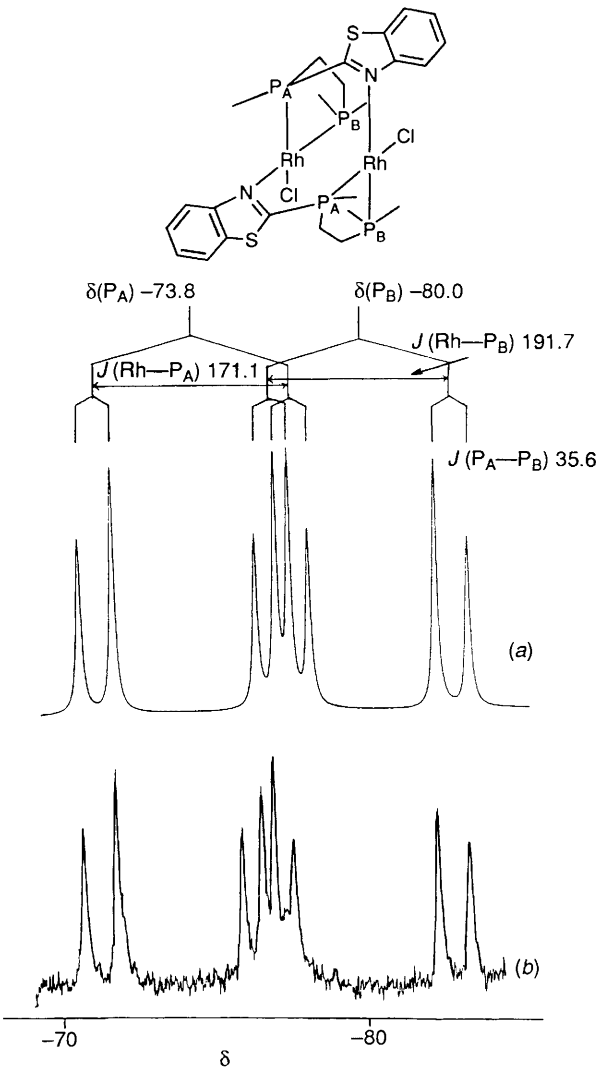


Fig. 5 $^{31}P\text{-}\{^1H\}$ NMR spectrum (*J*/Hz) of $[(RhCl)_2(\mu\text{-dbtpe})_2]$ **D** at −70 °C: (*a*) simulated spectrum; (*b*) real spectrum

is air-stable in the solid state, but in solution in the presence of air it changes to a brown material, presumably by oxidation to Rh^{III} (see later).

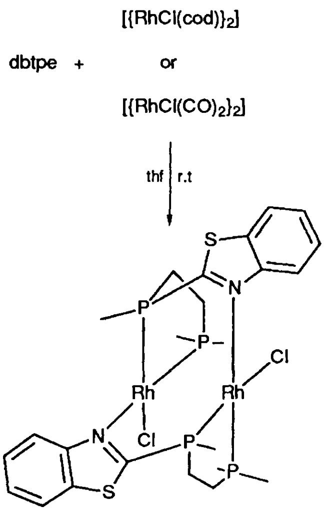
An X-ray crystal structure determination of $[Rh_2Cl_2(dbtpe)_2]$, crystallised from thf–hexane, confirmed the predicted bimetallic structure (Fig. 6). The metal atoms are co-ordinated in square-planar patterns. Each dbtpe ligand chelates to one rhodium through the phosphorus atoms, and only one benzothiazolyl group of each dbtpe ligand forms a bridge to the second rhodium atom through nitrogen. Each metal is also co-ordinated to a chlorine atom. There appears to be only slight interaction between the two metals, since the Rh ··· Rh distance of 3.073(2) Å is longer than the normal Rh–Rh single bond {*e.g.* 2.7838(8) Å in $[Rh_2Cl_2(\mu\text{-}SO_2)(dppm)_2]$[8] (dppm = $Ph_2PCH_2PPh_2$) and 2.936(2) Å in $[Rh_2(Hdmg)_4(PPh_3)_2]$[9] (Hdmg = dimethylglyoximate)} but somewhat less than the non-bonded Rh ··· Rh separation of 3.152(1) and 3.155(4) Å observed in $[Rh_2(CO)_2(\mu\text{-}Cl)(dppm)_2]BF_4$[10] and $[Rh_2(CO)_2(\mu\text{-}S)(dppm)_2]$[11] respectively. To accommodate the bridging benzothiazolyl ligands, the two co-ordination square planes are virtually eclipsed with the two chlorine atoms showing a torsion

Table 2 Fractional atomic co-ordinates (× 10^4 for Rh; × 10^3 for others) for complex **C** with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Rh(1)	2894(4)	3875(3)	2420(3)	P(1)	317(1)	511(1)	256(1)	C(13)	384(4)	713(4)	−16(3)	C(37)	944(5)	104(4)	43(4)
Rh(2)	4120(4)	44(3)	384(3)	P(2)	131(1)	448(1)	245(1)	C(14)	471(5)	662(4)	−33(3)	C(38)	868(5)	110(4)	102(3)
Cl(1)	232(1)	260(1)	239(1)	P(3)	478(1)	65(1)	114(1)	C(15)	503(5)	595(4)	19(3)	C(39)	772(4)	91(4)	88(3)
Cl(2)	287(1)	379(1)	359(1)	P(4)	364(1)	130(1)	−4(1)	C(16)	461(4)	586(3)	81(3)	C(40)	473(5)	18(4)	200(3)
Cl(3)	288(1)	406(1)	124(1)	N(1)	366(4)	593(3)	353(2)	C(17)	47(5)	435(4)	319(3)	C(41)	537(5)	−72(4)	266(3)
Cl(4)	465(1)	328(1)	231(1)	N(2)	305(4)	618(3)	153(2)	C(18)	−31(5)	468(4)	393(3)	C(42)	590(6)	−136(5)	287(4)
Cl(5)	248(1)	64(1)	106(1)	N(3)	16(4)	493(3)	349(3)	C(19)	−82	500	465	C(43)	569(6)	−174(5)	359(4)
Cl(6)	822(3)	682(3)	225(2)	N(4)	7(4)	501(3)	149(3)	C(20)	−159(5)	470(4)	514(3)	C(44)	464(6)	−116(5)	397(4)
Cl(7)	727(4)	626(3)	326(3)	N(5)	654(3)	54(3)	36(2)	C(21)	−154	376	509	C(45)	404(6)	−41(5)	362(4)
Cl(8)	377(4)	158(3)	431(3)	N(6)	548(4)	−48(3)	214(2)	C(22)	−92	346	460	C(46)	440(5)	−28(4)	301(3)
Cl(9)	765(4)	293(3)	184(3)	N(7)	535(4)	116(3)	−92(3)	C(23)	−49(6)	395(5)	405(4)	C(47)	442(4)	155(4)	−67(3)
Cl(10)	778(4)	368(4)	298(3)	N(8)	240(3)	113(3)	−85(2)	C(24)	60(5)	439(4)	177(3)	C(48)	580(5)	152(4)	−143(3)
Cl(11)	793(3)	745(3)	493(2)	C(1)	202(4)	580(4)	279(3)	C(25)	−58(6)	474(5)	107(4)	C(49)	685(4)	119(4)	−174(3)
Cl(12)	67(5)	38(4)	238(3)	C(2)	111(4)	564(3)	239(3)	C(26)	−134(6)	538(5)	66(4)	C(50)	701(5)	164(4)	−222(3)
Cl(13)	−22(4)	151(3)	274(3)	C(3)	396(4)	522(3)	320(3)	C(27)	−181(6)	510(5)	16(4)	C(51)	645(5)	238(4)	−249(3)
Cl(14)	183(4)	136(4)	426(3)	C(4)	435(5)	598(4)	396(3)	C(28)	−163(6)	420(5)	7(4)	C(52)	547(4)	270(3)	−222(3)
Cl(15)	708(5)	585(5)	218(4)	C(5)	421(6)	661(5)	443(4)	C(29)	−101(6)	368(5)	46(4)	C(53)	525(5)	216(4)	−168(3)
S(1)	510(2)	463(1)	336(1)	C(6)	502(5)	652(4)	489(4)	C(30)	−46(5)	398(4)	93(3)	C(54)	251(4)	155(3)	−39(3)
S(2)	481(1)	520(1)	138(1)	C(7)	598(6)	591(5)	485(4)	C(31)	416(4)	175(3)	116(3)	C(55)	155(5)	144(4)	−106(3)
S(3)	35(2)	337(1)	344(1)	C(8)	604(5)	525(4)	433(3)	C(32)	363(4)	212(4)	54(3)	C(56)	106(5)	117(4)	−161(4)
S(4)	40(2)	341(1)	150(1)	C(9)	514(5)	539(4)	397(4)	C(33)	609(5)	65(4)	97(3)	C(57)	10(5)	162(4)	−198(3)
S(5)	679(2)	89(1)	159(1)	C(10)	362(5)	563(4)	176(3)	C(34)	753(4)	74(3)	31(3)	C(58)	−43(6)	241(5)	−164(4)
S(6)	378(2)	49(1)	260(1)	C(11)	361(5)	638(4)	96(3)	C(35)	815(4)	73(4)	−20(3)	C(59)	−10(5)	270(4)	−105(4)
S(7)	409(2)	243(1)	−121(1)	C(12)	319(5)	703(4)	49(3)	C(36)	910(6)	87(5)	−13(4)	C(60)	97(5)	219(4)	−81(3)
S(8)	154(1)	242(1)	−21(1)												

Table 3 Selected bond dimensions (lengths in Å, angles in °) for $[(RhCl)_2(\mu\text{-dbtpe})_2]\cdot 4thf$ **D** with e.s.d.s in parentheses

(*a*) In the rhodium co-ordination spheres			
Rh(1) ··· Rh(2)	3.073(2)		
Rh(1)–Cl(1)	2.371(4)	Rh(2)–Cl(2)	2.365(4)
Rh(1)–P(1ab)	2.162(4)	Rh(2)–P(2ab)	2.169(4)
Rh(1)–P(1cd)	2.144(4)	Rh(2)–P(2cd)	2.162(4)
Rh(1)–N(2c)	2.147(11)	Rh(2)–N(1c)	2.145(11)
Cl(1)–Rh(1)–P(1ab)	91.6(1)	Cl(2)–Rh(2)–P(2ab)	92.3(2)
Cl(1)–Rh(1)–P(1cd)	174.3(2)	Cl(2)–Rh(2)–P(2cd)	175.5(2)
Cl(1)–Rh(1)–N(2c)	89.5(3)	Cl(2)–Rh(2)–N(1c)	85.5(3)
P(1ab)–Rh(1)–P(1cd)	84.3(2)	P(2ab)–Rh(2)–P(2cd)	83.7(2)
P(1ab)–Rh(1)–N(2c)	166.7(3)	N(1c)–Rh(2)–P(2ab)	172.6(3)
P(1cd)–Rh(1)–N(2c)	93.6(3)	N(1c)–Rh(2)–P(2cd)	98.2(3)
(*b*) In the phosphine ligands			
P(1ab)–C(1a1)	1.824(14)	P(1cd)–C(1c1)	1.799(14)
P(1ab)–C(1b1)	1.867(16)	P(1cd)–C(1d1)	1.841(15)
P(1ab)–C(1ab)	1.823(13)	P(1cd)–C(1cd)	1.823(16)
P(2ab)–C(2a1)	1.869(14)	P(2cd)–C(2c1)	1.825(14)
P(2ab)–C(2b1)	1.828(13)	P(2cd)–C(2d1)	1.819(14)
P(2ab)–C(2ab)	1.823(14)	P(2cd)–C(2cd)	1.833(15)



(4)

D

angle of *ca.* 90° about the Rh ··· Rh vector. Bond lengths and angles are summarised in Table 3. Atomic co-ordinates are in Table 4.

Inter-relationship between Complexes **A**–**D**.—It appears that the sequence of the reaction of dbtpe with $[RhCl(PPh_3)_3]$ and oxidation of rhodium-(I) to -(III) is in principle as illustrated in Scheme 1. The first step involves the replacement of triphenylphosphine molecules to form a neutral intermediate **B** (P–P = dbtpe), which then loses the remaining PPh_3 to form the bimetallic neutral complex **D**. The reaction then passes through several steps, some of which involve oxidation, to form the dicationic complex ion **C** in which a Rh–Rh bond has formed and a second benzothiazolyl group, arising from the 'spectator' phosphorus of the ligand on one rhodium, binds to the second rhodium through nitrogen.

Compounds **B** also represent intermediates on the route to **A** from $[RhCl(PPh_3)_3]$ as discussed above. We have attempted to establish Scheme 1 further by probing the final oxidation step electrochemically, but the process is clearly very complicated with a number of electrochemically irreversible steps and no reliable conclusions could be drawn, except that the first step appears to be a one-electron oxidation of **D** which then goes through several further steps.

The ligands used in this study have shown the capacity, as we had hoped, for P–X ligation in mono- and bi-nuclear complexes. It appears, as might be expected, that P–N is favoured over P–S ligation to rhodium, particularly when the oxidation state of the metal is relatively high as in **C**.

The complexes we have obtained show interconvertability, isolation of intermediate steps being achieved by an adventitious combination of steric and electronic properties of the functional groups at phosphorus. In several compounds, the functional groups remain unco-ordinated and this raises the possibility of using these compounds as ligands to bind at further metal sites; this will be explored in the future.

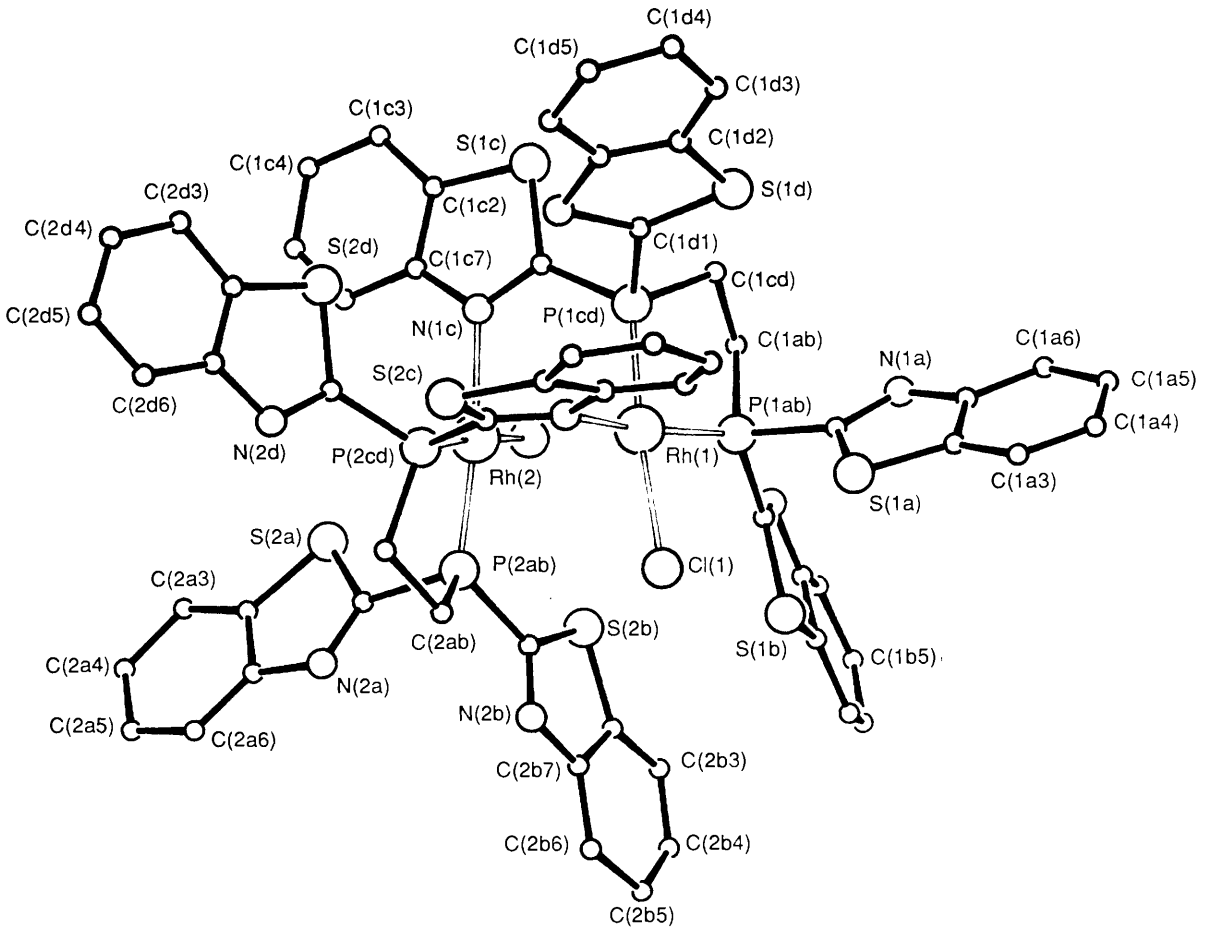
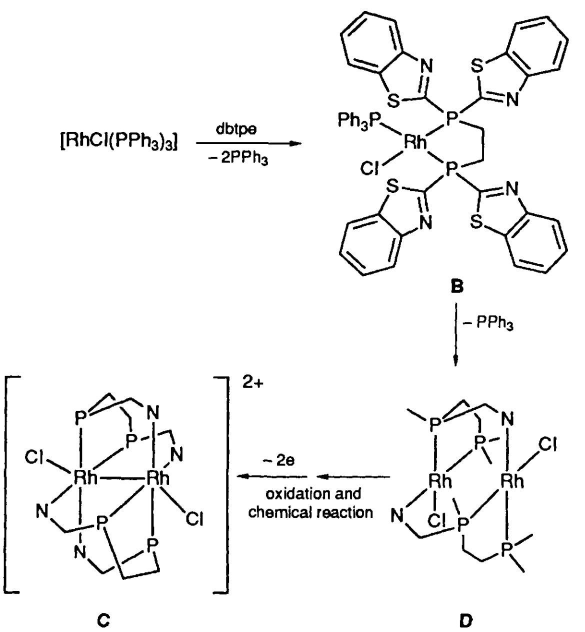


Fig. 6 X-Ray crystal structure of $[(RhCl)_2(\mu\text{-dbtpe})_2]$ **D**



Scheme 1 Reaction sequence of dbtpe with $[RhCl(PPh_3)_3]$ and oxidation to Rh^{III}

Experimental

All manipulations were carried out under an atmosphere of pure dinitrogen using standard Schlenk, glove-box and vacuum techniques. All solvents were dried by standard methods and distilled under pure dinitrogen before use.

The NMR spectra were measured using JEOL FX90Q, GSX270, or Bruker WP80 or WM360 instruments [^{1}H relative to $SiMe_4$, ^{31}P to $P(OMe)_3$]. Mass spectrometry was carried out with a Kratos MS80RF instrument, IR spectra were obtained using Perkin-Elmer 598 or 883 spectrometers and conductivities using a Portland Electronics conductivity bridge. Microanalyses were by Mr. C. J. Macdonald of the Nitrogen Fixation Laboratory or Ms. K. Plowman of the University of Sussex.

The compounds $[RhCl(PPh_3)_3]$, $[\{RhCl(cod)\}_2]$ and $[\{RhCl(CO)_2\}_2]$ were prepared by published methods.[12]

Preparation of [Rh(dmtpe)]Cl **A** (P–P = dmtpe).—A mixture of $[RhCl(PPh_3)_3]$ (0.34 g, 0.37 mmol) and dmtpe (0.23 g, 0.39 mmol) in thf (40 cm^3) was stirred at room temperature for 2.5 h. The orange solid *product* was filtered off, washed with thf (10 cm^3) then diethyl ether (2 × 15 cm^3) and dried under vacuum. Yield 0.2 g, 77%. Found: C, 49.65; H, 4.30. Calc. for $C_{30}H_{32}ClP_2RhS_4$: C, 49.90; H, 4.45%). Molar conductance ($MeNO_2$): 70 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). ^{31}P-{^{1}H} NMR (CH_2Cl_2): δ −85, J(Rh–P) = 156 Hz.

Preparation of [Rh(ditpe)]Cl **A** (P–P = ditpe).—To a solution of $[\{RhCl(cod)\}_2]$ (0.25 g, 0.5 mmol) in thf (25 cm^3) was added ditpe (0.7 g, 1.0 mmol) at room temperature. The yellow-orange mixture was stirred under dinitrogen for 48 h, during which time it changed first to a clear red solution, then an orange solid gradually precipitated. This was filtered off, washed with thf (10 cm^3) then ether (2 × 10 cm^3) and dried under vacuum. Yield: 0.5 g, 60% (Found: C, 54.75; H, 5.95. Calc. for

Table 4 Final atomic co-ordinates (fractional × 10^4) for $[(RhCl)_2(\mu\text{-dbtpe})_2]\cdot 4thf$ **D** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Rh(1)	1401.4(8)	2122.0(6)	1528.7(8)
Rh(2)	3391.2(8)	3225.1(6)	2596.3(8)
Cl(1)	2004(3)	1107(2)	1657(3)
Cl(2)	3256(3)	3857(2)	4172(3)
C(1a1)	−465(10)	1684(7)	2051(10)
S(1a)	−619(3)	812(2)	1149(3)
C(1a2)	−1805(11)	651(8)	1145(11)
C(1a3)	−2542(11)	24(8)	544(11)
C(1a4)	−3449(13)	3(9)	662(15)
C(1a5)	−3664(13)	625(9)	1311(14)
C(1a6)	−2956(13)	1269(8)	1894(13)
C(1a7)	−2020(11)	1279(8)	1793(11)
N(1a)	−1244(9)	1858(6)	2331(10)
C(1b1)	1244(11)	2236(8)	3813(12)
S(1b)	1565(4)	1415(2)	3732(3)
C(1b2)	1722(13)	1776(10)	4977(12)
C(1b3)	1984(15)	1458(11)	5617(14)
C(1b4)	2147(17)	1836(15)	6564(12)
C(1b5)	1986(16)	2532(15)	6954(16)
C(1b6)	1751(18)	2867(12)	6331(13)
C(1b7)	1596(13)	2475(9)	5339(13)
N(1b)	1304(10)	2739(7)	4634(9)
P(1ab)	734(3)	2312(2)	2629(3)
C(1ab)	331(11)	3180(7)	3053(11)
C(1cd)	−124(11)	3289(8)	2104(12)
P(1cd)	718(3)	3001(2)	1412(3)
C(1c1)	1507(10)	3827(8)	1795(10)
S(1c)	1037(3)	4588(2)	1783(4)
C(1c2)	2300(11)	5083(8)	2368(11)
C(1c3)	2624(14)	5793(8)	2632(12)
C(1c4)	3638(14)	6061(9)	3077(13)
C(1c5)	4286(12)	5617(8)	3242(12)
C(1c6)	4002(10)	4912(7)	2956(10)
C(1c7)	2986(10)	4643(6)	2519(9)
N(1c)	2509(8)	3949(6)	2202(7)
C(1d1)	−120(10)	2859(7)	158(11)
S(1d)	−1404(4)	2563(3)	−287(4)
C(1d2)	−1434(13)	2520(9)	−1397(12)
C(1d3)	−2332(18)	2329(11)	−2238(16)
C(1d4)	−2327(19)	2363(13)	−3040(14)
C(1d5)	−1343(20)	2505(11)	−3034(15)
C(1d6)	−444(19)	2745(12)	−2168(17)
C(1d7)	−524(13)	2737(9)	−1344(14)
N(1d)	414(10)	2931(7)	−519(9)
C(2a1)	5788(10)	3117(8)	3836(10)
S(2a)	5976(3)	4039(2)	4513(3)
C(2a2)	7273(9)	4016(8)	4850(10)
C(2a3)	8068(13)	4597(9)	5470(12)
C(2a4)	9054(12)	4461(8)	5620(13)
C(2a5)	9227(12)	3757(10)	5179(14)
C(2a6)	8432(10)	3198(9)	4565(13)
C(2a7)	7461(11)	3322(7)	4420(11)
N(2a)	6548(9)	2805(6)	3798(9)
C(2b1)	4390(10)	2248(7)	3950(9)
S(2b)	3992(3)	2691(2)	4931(3)
C(2b2)	4400(12)	2084(8)	5360(12)
C(2b3)	4379(14)	2067(11)	6214(13)
C(2b4)	4770(17)	1519(11)	6327(15)
C(2b5)	5141(18)	1005(11)	5753(18)
C(2b6)	5190(16)	1043(12)	4892(15)
C(2b7)	4781(11)	1593(8)	4702(13)
N(2b)	4772(10)	1696(6)	3902(10)
P(2ab)	4446(3)	2609(2)	3113(3)
C(2ab)	4594(10)	1829(7)	2092(10)
C(2cd)	4610(11)	2075(8)	1309(11)
P(2cd)	3632(3)	2637(2)	1217(3)
C(2c1)	2529(10)	2025(7)	123(10)
S(2c)	2486(3)	1681(3)	−1086(3)
C(2c2)	1277(12)	1220(9)	−1519(11)
C(2c3)	603(15)	784(10)	−2503(12)
C(2c4)	−343(14)	466(9)	−2697(12)
C(2c5)	−596(12)	548(8)	−1888(13)
C(2c6)	29(10)	985(7)	−942(12)
C(2c7)	937(12)	1330(7)	−760(10)
N(2c)	1713(8)	1802(6)	194(8)
C(2d1)	4041(11)	3048(7)	575(10)
S(2d)	3475(4)	3731(3)	355(4)
C(2d2)	4211(11)	3701(9)	−306(11)
C(2d3)	4248(15)	4097(10)	−806(14)
C(2d4)	4900(16)	3983(12)	−1297(14)
C(2d5)	5554(15)	3514(13)	−1294(15)
C(2d6)	5483(15)	3113(11)	−833(14)
C(2d7)	4841(12)	3210(8)	−327(11)
N(2d)	4724(9)	2840(6)	183(9)
In the thf molecules			
C(30)	8379(20)	4622(14)	−31(20)
C(31)	8099(21)	4562(15)	766(21)
C(32)	8578(26)	5320(19)	1627(26)
C(33)	8493(23)	5732(16)	1199(22)
C(34)	8932(22)	5378(16)	524(22)
C(40)	8169(19)	4440(13)	2911(18)
C(41)	8024(21)	5115(15)	3549(20)
C(42)	6928(20)	5186(15)	3180(20)
C(43)	6474(23)	4427(16)	2328(22)
C(44)	7168(24)	3943(18)	2388(24)
C(50)	8572(16)	195(12)	4618(16)
C(51)	9199(20)	795(14)	4862(20)
C(52)	8740(22)	1148(16)	4280(22)
C(53)	7670(25)	970(18)	4046(24)
C(54)	7644(26)	249(18)	4139(25)
C(60)	4321(26)	8892(19)	1003(26)
C(61)	4687(28)	9492(20)	2050(27)
C(62)	3679(29)	9750(21)	2000(29)
C(63)	3076(27)	9161(20)	1478(27)
C(64)	3608(25)	8585(18)	1297(24)

$C_{38}H_{48}ClP_2RhS_4$: C, 54.80; H, 5.75%). Molar conductance ($MeNO_2$): 51.3 Ω^{-1} cm^2 mol^{-1} (1 : 1 electrolyte). $^{31}P\text{-}\{^1H\}$ NMR (CH_2Cl_2): δ −40, *J*(Rh–P) = 162 Hz. Mass spectrum: *m/z* = 797 (M^+ − Cl).

Preparation of [RhCl(PPh$_3$)(dbtpe)] **B** (P–P = dbtpe).—A mixture of [RhCl(PPh$_3$)$_3$] (0.52 g, 0.56 mmol) and dbtpe (0.35 g, 0.56 mmol) in thf (50 cm^3) was stirred for 48 h to give a clear red solution. This was concentrated to *ca.* 25 cm^3, then hexane was added slowly until a trace of solid formed. The solution was filtered and the filtrate kept overnight to give orange *crystals* of [RhCl(PPh$_3$)(dbtpe)]. These were filtered off, washed with ether (2 × 10 cm^3) and dried under vacuum. Yield 0.35 g, 60% (Found: C, 56.45, H, 3.65; N, 5.45. Calc. for $C_{48}H_{35}ClN_4P_3RhS_4$: C, 56.15; H, 3.40; N, 5.45%). Mass spectrum: *m/z* = 1026. $^{31}P\text{-}\{^1H\}$ NMR discussed in the text.

Preparation of [RhCl(PPh$_3$)(dmbpe)] **B** (P–P = dmbpe).—A mixture of [RhCl(PPh$_3$)$_3$] (0.45 g, 0.48 mmol) and dmbpe (0.3 g, 0.48 mmol) in thf (50 cm^3) was stirred at room temperature for 24 h, during which time all the solid dissolved to give a clear red-orange solution. This was filtered from the trace of solid and the filtrate layered with hexane. The orange-red *crystals* of [RhCl(PPh$_3$)(dmbpe)] which precipitated were filtered off and dried under vacuum. Yield 0.3 g, 60% (Found: C, 61.40; H, 4.35; N, 11.00. Calc. for $C_{52}H_{47}ClN_8P_3Rh$: C, 61.55; H, 4.65; N, 11.05%).

The $^{31}P\text{-}\{^1H\}$ NMR spectrum is similar to that of complex **B** (P–P = dbtpe), showing three types of phosphorus atom (ABCX spin system where A, B, C = ^{31}P and X = ^{103}Rh). The complex is proposed to have a square-planar configuration with two phosphorus atoms *trans* to each other, to satisfy the high value of *J*(P^1–P^3) (365.0 Hz). The chemical shifts are δ (P^1)

-112.48, $\delta(P^2)$ -94.84 and $\delta(P^3)$ -95.17 and the coupling constants, $J(Rh-P^1) = 132.96$, $J(Rh-P^2) = 182.87$, $J(Rh-P^3) = 139.29$, $J(P^1-P^2)$ -33.86, $J(P^1-P^3) = 356.1$, and $J(P^2-P^3) = -23.5$ Hz, The spectrum was successfully replicated by computer simulation using the above parameters. The ^1H NMR spectrum showed a multiplet between δ 2.0 and 3.1 assigned to the methylene protons, two singlets at δ 3.8 and 4.0 assigned to the methyl protons and a multiplet between δ 6.7 and 7.7 assigned to the phenyl protons.

Oxidation of $[RhCl(PPh_3)(dbtpe)]$.—A solution of $[RhCl(PPh_3)(dbtpe)]$ (0.05 g, 0.045 mmol) in $CHCl_3$ (5 cm^3) was left to stand for 2 weeks. The yellow-orange solution slowly changed to red with the formation of red *crystals* of $[\{RhCl(dbtpe)\}_2][RhCl_4(dbtpe)]_2$ **C**, which was subsequently identified by X-ray analysis as a 'double-A-frame' complex.

X-Ray Structure Analysis of $[\{RhCl(dbtpe)\}_2][RhCl_4(dbtpe)]_2\cdot xCHCl_3$ **C**.—*Crystal data.* $C_{120}H_{80}Cl_{10}N_{16}P_8Rh_4S_{16}\cdot xCHCl_3$, $M = 3273.1$ (for $x = 0$, see below), triclinic, space group $P\bar{1}$ (no. 2), $a = 13.684(3)$, $b = 16.764(5)$, $c = 19.977(4)$ Å, $\alpha = 87.99(2)$, $\beta = 85.22(2)$, $\gamma = 77.08(2)°$, $U = 4450.5$ Å^3, $Z = 1$, $D_c = 1.22$ g cm^{-3}, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,69$ Å, $\mu = 8.0$ cm^{-1}.

The translucent red crystals are stable only when immersed in mother-liquor; on removal they turn cloudy and cease to diffract within seconds, presumably due to loss of occluded solvent. The crystal used for data collection, *ca.* 0.5 × 0.3 × 0.3 mm, was sealed in a capillary with some mother-liquor, but even so it gave diffraction data only to fairly low angle. An Enraf-Nonius CAD4 diffractometer was used in θ–2θ mode, with $\Delta\theta = (0.8 + 0.35 \tan\theta)°$ and a maximum scan time of 1 min. A total of 3759 reflections was measured, with $+h \pm k \pm l$ and $2 < \theta < 15°$, and 2462 unique reflections with $I > \sigma(I)$ were used in the refinement. Two standard reflections measured every 30 min showed a decrease of 10% during the data collection and a correction for this was applied. No absorption correction was made.

The structure was solved by routine heavy-atom methods. In one benzothiazole group of the anion three carbon atoms, C(19), C(21), C(22), were poorly defined and were placed at calculated positions. There were a large number of residual peaks not attached to the anion or cation, which were assumed to be the Cl atoms from $CHCl_3$ solvent molecules and included at half occupancy. The total number of such solvent molecules present is not clear and they have been omitted from the calculation of the formula weight in the crystal data. Refinement was by block-diagonal least squares with only the Rh, Cl, S and P atoms anisotropic, owing to lack of data. Hydrogen atoms were not included. The weighting scheme was $w = \sigma^{-2}(F)$ and the final residuals were $R = 0.138$, $R' = 0.184$. The structure analysis was done using programs from the Enraf-Nonius SDP-plus package[13] run on a PDP 11/34 computer.

Preparation of $[(RhCl)_2(\mu\text{-dbtpe})_2]$ **D**.—A mixture of $[\{RhCl(cod)\}_2]$ (0.43 g, 0.87 mmol) and dbtpe (1.1 g, 1.76 mmol) in thf (50 cm^3) was stirred at room temperature for 24 h. Initially a deep purple solution was formed; subsequently, deep purple *crystals* appeared. These were filtered off, washed with thf (2 × 15 cm^3) and dried under vacuum. The combined filtrate (deep purple) was concentrated to *ca.* 30 cm^3 under vacuum and layered with hexane to give large crystals which were used for X-ray analysis. Total yield (1.0 g, 75%) (Found: C, 47.30; H, 2.75; N, 7.10. Calc. for $C_{60}H_{40}Cl_2N_8P_4Rh_2S_8$: C, 47.10; H, 2.60; N, 7.35%). Mass spectrum (FAB): $m/z = 1529$. $^{31}P\text{-}\{^1H\}$ NMR discussed in text.

X-Ray Structure Analysis of $[(RhCl)_2(\mu\text{-dbpte})_2]\cdot 4thf$ **D**.—*Crystal data.* $C_{76}H_{72}Cl_2N_8O_4P_4Rh_2S_8$, $M = 1818.6$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.115(2)$, $b = 21.075(4)$, $c = 16.027(2)$, $\alpha = 115.75(1)$, $\beta = 109.80(1)$, $\gamma = 90.29(1)°$, $U = 3975$, $Z = 2$, $D_c = 1.52$ g cm^{-3}, $F(000) = 1856$, $\mu(Mo\text{-}K\alpha) = 8.1$ cm^{-1}, $\lambda(Mo\text{-}K\bar{\alpha}) = 0.710\,69$ Å.

The compound forms small, purple-brown prisms. One, *ca.* 0.24 × 0.24 × 0.12 mm, was sealed in a capillary which had previously been wetted with thf to prevent solvent loss. After preliminary photographic examination, the crystal was transferred to an Enraf-Nonius CAD4 diffractometer, equipped with monochromated Mo-Kα radiation. Accurate cell dimensions were determined from goniometer settings for 25 strong reflections, with $10 < \theta < 11°$, and intensity data were then measured to $\theta_{max} = 20°$.

After correction for Lorentz and polarisation effects and for negative intensities (no absorption correction was considered necessary and there was no observed deterioration of the crystal), 7378 unique reflections were entered into the SHELX program system.[14] The locations of the rhodium atoms were found from a Patterson synthesis and all other non-hydrogen atoms were located in subsequent electron-density Fourier difference syntheses. Hydrogen atoms of the rhodium complex were placed in ideal positions, and set to ride on their bonded C atoms; all non-hydrogen atoms in the complex were refined anisotropically. The oxygen atoms of the solvent molecule were not identified; each thf molecule was refined as an unconstrained, five-membered ring of isotropic carbon atoms (no hydrogen atoms were included).

The structure was refined by block-diagonal least-squares methods[15] to convergence at $R = 0.118$, $R' = 0.117$,[14] using $w = (\sigma_F^2 + 0.005\ F^2)^{-1}$, for all data; for the 3983 reflections with $I > \sigma_I$, $R = 0.065$ and $R' = 0.070$. A final difference map showed peaks *ca.* 1.0 e Å^{-3} in the neighbourhood of the thf solvent molecules.

Scattering factors for neutral atoms were used.[16] All computer programs, including those of refs. 14 and 15 and those listed in Table 4 of ref. 17, were run on a MicroVAX II computer.

Additional material available for both structures comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

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