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The synthesis and characterisation of a dirhodium(II) compound with bridging orthometallated dimethylphenylphosphine ligands

Elizabeth C. Morrison and Derek A. Tocher *

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ (UK)

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Abstract

The reaction of $[Rh_2(O_2CMe)_4]$ with PMe_2Ph in Me_3CCO_2H gives the purple compound $[Rh_2(O_2CCMe_3)_2\{PMe_2(C_6H_4)\}_2(Me_3CCO_2H)_2]$. Recrystallization from aqueous methanol yields the corresponding bis-aquo adduct, which has been characterised crystallographically. That compound has a Rh–Rh bond length of 2.492(1) Å, and forms infinite hydrogen bonded chains in the solid state. Although compounds of this type with bridging triarylphosphine ligands have been characterised previously this is the first report of a fully characterised compound containing a tertiary phosphine ligand with both alkyl and aryl substituent groups.

Introduction

The first report of orthometallation reactions involving tertiary phosphine ligands occurring across the single bond in dirhodium(II) compounds appeared in 1984 [1]. Since that time a number of further reports have appeared. These reports detail the results of crystallographic determinations, electrochemical studies, and reactivity/mechanistic investigations [2–11]. A common theme running through this series of papers has been the exclusive use of triarylphosphine ligands. We have previously reported preliminary results on the synthesis and structure of the compound $[Rh_2(O_2CCMe_3)_2\{PMePh(C_6H_4)\}_2(C_5H_5N)_2]$, which contained the first example of a mixed alkyl/aryl orthometallated bridging tertiary phosphine ligand [12] on a dirhodium(II) centre. Unfortunately problems with the low quality of the crystallographic data, and with disorder, prevented us from reporting the full details of the crystal and molecular structure of that compound. We have now prepared alternative derivatives, $[Rh_2(O_2CCMe_3)_2\{PMe_2(C_6H_4)\}_2L_2]$, and wish to report the full details of their characterisation by spectroscopic, electrochemical, and crystallographic techniques.

Results and discussion

The four bridging acetate ligands in the compound $[Rh_2(O_2CMe)_4]$ can be replaced in a one-step synthesis using a refluxing solution of dimethylphenylphosphine in pivalic acid. The reaction proceeds smoothly to give a purple solution after approximately one hour. The solvent was removed *in vacuo* and the crude product purified by column chromatography. The ^1H NMR spectrum of the new compound showed two singlet resonances which were attributed to the methyl groups of neutral and anionic pivalate ligands, as well as signals from the coordinated phosphine ligands. Although the NMR spectrum did not contain a resonance which could be readily assigned to the acidic protons of the neutral pivalic acid molecules the infrared spectrum did contain an absorption band at 3240 cm^{-1} which can be tentatively assigned to an O–H stretching mode. The rather low wavenumber is not unreasonable given that molecules of carboxylic acids in the axial positions of several related compounds of this type have been shown to hydrogen bond relatively strongly to the oxygen atoms of the bridging carboxylate ligands [2,10,11]. The $^{31}P\{^1H\}$ NMR spectrum consisted of a single AA′XX′ pattern centred at δ 6.9 ppm. This pattern has been observed previously and is known to be characteristic of a head-to-tail arrangement for two bridging orthometallated phosphine ligands [10,12]. It should be noted in passing that these ^{31}P NMR signals are sharp even at 25 ° C. This of course contrasts with the observations made on the ^{31}P NMR spectra of a range of axial phosphine and phosphite adducts of $[Rh_2(O_2CR)_4]$ molecules, which at ambient temperature are characterised by the broad unresolved signals typical of highly labile systems [13].

Cyclic voltammetry was used to investigate the redox behaviour of this molecule. Metal–metal bonded dirhodium(II)tetracarboxylate compounds generally undergo a reversible one-electron oxidation [14] and those orthometallated dirhodium(II) compounds which have been studied so far are also known to undergo a similar redox reaction [2–4,9,10,12]. In dichloromethane solution this compound undergoes an oxidation reaction at +0.93 V (vs. Ag/AgCl). The voltammetric wave exhibits the characteristics typical of a one-electron reversible process [15,16]. The potential is similar to that reported for the closely related compound $[Rh_2(O_2CMe)_2\{Ph_2P(C_6H_4)\}_2(HO_2CMe)_2]$, in which the metal centres are also bonded to axially coordinated carboxylic acid molecules [2]. Addition of pyridine to the electrochemical solution results in a shift in the position of the oxidation wave to +0.63 V and is indicative of the replacement of the axially coordinated pivalic acid molecules by the better donor ligand, pyridine. This shift of potential, to more cathodic values, with increasing donor ability is an indication that the HOMO levels are destabilised with increasing binding ability of the axial ligand. The analytical, spectroscopy, and electrochemical data collected on this compound are completely consistent with the proposed formulation, i.e. $[Rh_2(O_2CCMe_3)_2\{PMe_2(C_6H_4)\}_2(Me_3CCO_2H)_2]$. Our inability to obtain crystals of this compound suitable for X-ray crystallographic analysis meant we were unable to conclusively establish that this new compound, which we strongly believed had bridging orthometallated dimethylphenylphosphine ligands, had an analogous structure to that previously found for a number of triarylphosphine complexes with closely related stoichiometries.

Recrystallisation of $[Rh_2(O_2CCMe_3)_2\{PMe_2(C_6H_4)\}_2(Me_3CCO_2H)_2]$ from aqueous methanol gave a homogeneous mass of red crystals. Analytical and spectroscopic data (see Experimental) on these crystals was consistent with the formulation $[Rh_2(O_2CCMe_3)_2\{PMe_2(C_6H_4)\}_2(H_2O)_2]$, i.e. the axial pivalic acid molecules have been replaced by water molecules. This has been confirmed by X-ray structural analysis.

X-Ray crystallographic results

The structure consists of a dinuclear $[Rh_2]^{4+}$ unit with two bridging pivalate ligands and two bridging orthometallated phosphine ligands (Fig. 1). The bridging orthometallated phosphines are in a *cisoid* arrangement and are coordinated in a head-to-tail fashion, i.e. each rhodium is coordinated by only one phosphorus atom.

The Rh(1)–Rh(2) bond length, 2.492(1) Å, is shorter than that reported for other rhodium compounds of this type with two axially coordinated oxygen donor atoms [1,2,10]. It is of course longer than any of the Rh–Rh bond distances observed in dirhodium tetraacetate with O-donor molecules in the axial sites. In addition it is unsurprisingly longer than the Rh–Rh distance in the compound $[Rh_2(O_2CMe)_3\{PPh_2(C_6H_4)\}(HO_2CMe)_2]$, 2.430(2) Å, which contains only one bridging metallated phosphine ligand [11]. The metal–metal bond length in this compound is significantly less than that reported for the only other compound with mixed alkyl/aryl phosphine bridging ligands, $[Rh_2(O_2CCMe_3)_2\{PMePh(C_6H_4)\}_2(C_5H_5N)_2]$, 2.535(5) Å, but in that case the axially coordinated ligands are the stronger pyridine donors [12].

The two sites trans to the metal–metal bond are occupied by water molecules. The Rh–O distances, 2.360(9) and 2.351(9) Å, are indistinguishable from each other but are significantly longer than those observed in $[Rh_2(O_2CCMe_3)_4(H_2O)_2]$, 2.295(2) Å [17]. The only other compound to have a similar core geometry and a water molecule in the axial site of a rhodium ion is $[Rh_2(O_2CMe)_2\{P(C_6H_4)(C_6H_5)$-

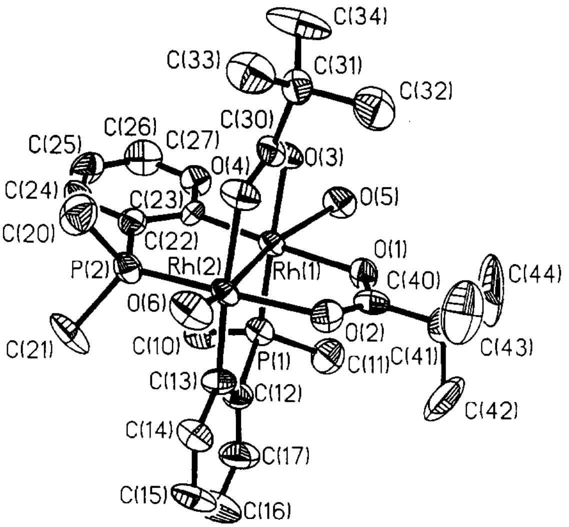

Fig. 1. The molecular structure of $[Rh_2(O_2CCMe_3)_2\{PMe_2(C_6H_4)\}_2(H_2O)_2]$. Atoms are represented by thermal vibration ellipsoids at the 50% confidence level, and the atomic labelling scheme is defined.

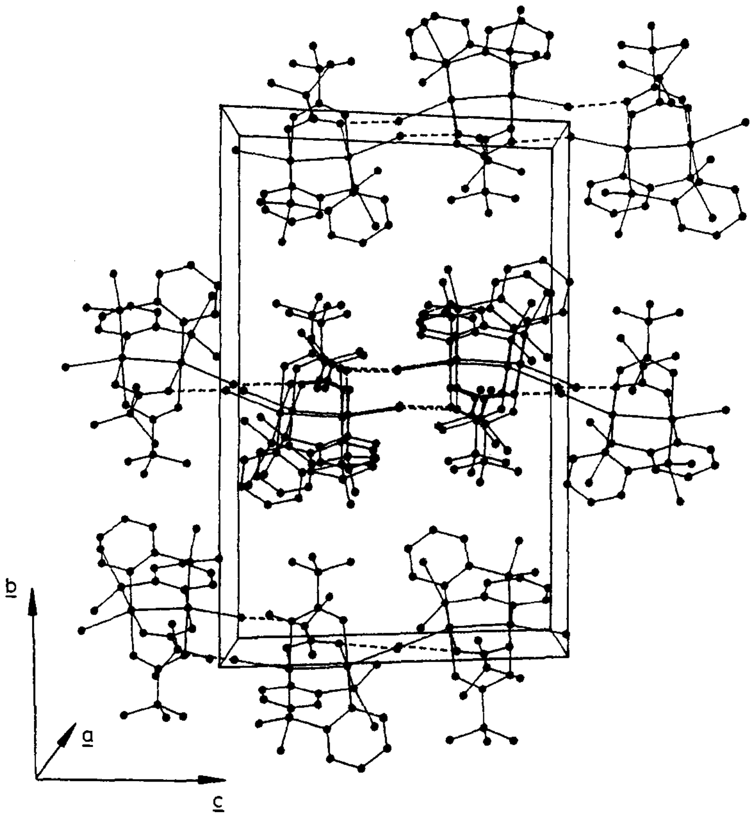

Fig. 2. A cell packing diagram viewed down the *a* axis illustrating the chain of hydrogen bonded dimers.

$(C_6F_4Br)\}_2(H_2O)]$. This compound [5] has only a single axially coordinated water molecule, with a Rh–OH_2 bond length of 2.296(2) Å. The likely cause of the greater Rh–O distances in $[Rh_2(O_2CCMe_3)_2\{PMe_2(C_6H_4)\}_2(H_2O)_2]$ is revealed when the crystal packing diagram is examined (Fig. 2). Each of the axially coordinated water molecules is involved in hydrogen bonding to a carboxylate oxygen atom on a bridging ligand of an adjacent molecule in the crystal lattice. The two independent O · · · O distances are 2.81 and 2.75 Å, consistent with an interaction of moderate strength. Thus in the solid state the dimers are arranged in infinite hydrogen bonded chains running approximately parallel to the crystallographic *c* axis.

The geometry about each metal ion is pseudo octahedral. The angles around each rhodium atom range from 76.0(3)° to 96.3(3)° for the *cis* bonds. The Rh–OH_2 bonds are not colinear with the Rh–Rh bonds, the two Rh–Rh–OH_2 angles being 162.1(2)° and 160.9(3)°. Substantial deviations from colinearity are a common feature of this type of compound, and the phenomenon is usually attributed to a combination of the steric effects of the phosphine ligands and the different "bite" angles of the two different types of bridging ligand [1,2,10,12]. Despite this observation, however, the torsion angles about the Rh–Rh bond are remarkably small [O(3)–Rh(1)–Rh(2)–O(4), 2.2°; O(1)–Rh(1)–Rh(2)–O(2), 2.1°; C(23)–Rh(1)–Rh(2)–P(2), 6.0°; P(1)–Rh(1)–Rh(2)–C(13), 5.6°]. The corresponding angles found for the other examples of this type of compound typically falling in the range 12° to

25° [2,10,12]. The $Rh-O_{carboxylate}$ distances show very little variation (2.154(9) to 2.187(9) Å), in contrast to some previous reports [2,10]. This implies that the *trans* influences of the M–P and M–C bonds in this particular compound are essentially indistinguishable. This can only be a consequence of the two methyl substituent groups on these particular phosphine ligands.

The Rh(1)–C(23) and Rh(2)–C(13) bond distances are crystallographically indistinguishable, at 1.99(1) Å, and are closely similar to those found in related structures; $Rh^{II}-C(sp^2)$ [18,19]. Similarly the rhodium–phosphorus bond lengths, 2.192(4) and 2.190(4) Å, are unremarkable.

In conclusion we have now unequivocally established that the orthometallation reactions which occur across the single metal–metal bond in dirhodium(II) com-

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)
Rh(1)	1852(1)	4455(1)	6640(1)	29(1)
Rh(2)	2835(1)	4531(1)	8444(1)	31(1)
P(1)	2882(4)	3562(2)	6667(2)	36(1)
P(2)	1158(4)	3979(2)	8620(3)	39(1)
O(1)	3626(9)	4977(4)	6612(6)	41(4)
O(2)	4467(9)	5079(5)	8207(6)	43(4)
O(3)	932(9)	5367(4)	6684(6)	38(3)
O(4)	1756(10)	5400(4)	8296(6)	44(4)
O(5)	1389(10)	4645(5)	4960(6)	49(4)
O(6)	3517(10)	4944(5)	10029(6)	52(4)
C(10)	1846(16)	2850(7)	6385(13)	62(7)
C(11)	3869(19)	3531(9)	5812(13)	69(8)
C(12)	4070(15)	3394(6)	7848(10)	40(5)
C(13)	3988(14)	3774(6)	8600(9)	38(5)
C(14)	4882(17)	3622(7)	9562(11)	57(7)
C(15)	5770(19)	3107(8)	9692(12)	66(7)
C(16)	5858(21)	2752(8)	8922(12)	73(8)
C(17)	5020(19)	2902(9)	7973(13)	71(8)
C(20)	259(18)	4402(9)	9334(12)	67(7)
C(21)	1507(20)	3218(7)	9270(12)	70(8)
C(22)	−125(15)	3817(6)	7487(9)	40(5)
C(23)	168(13)	4010(6)	6635(9)	33(5)
C(24)	−1346(18)	3512(7)	7439(11)	59(7)
C(25)	−2301(15)	3386(8)	6532(13)	60(7)
C(26)	−2066(18)	3601(8)	5702(11)	60(7)
C(27)	−848(15)	3880(7)	5708(10)	45(5)
C(30)	1169(13)	5640(5)	7499(9)	34(5)
C(31)	773(16)	6341(6)	7480(10)	43(6)
C(32)	2047(21)	6692(8)	7327(14)	75(9)
C(33)	625(20)	6520(8)	8486(12)	67(8)
C(34)	−525(22)	6498(8)	6631(12)	88(9)
C(40)	4494(14)	5159(6)	7364(9)	39(5)
C(41)	5723(13)	5501(8)	7232(10)	53(6)
C(42)	6865(21)	5009(11)	7485(22)	131(16)
C(43)	6118(24)	6069(10)	7957(15)	95(10)
C(44)	5470(25)	5712(16)	6193(16)	175(17)

Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

pounds are not restricted to triaryl phosphine ligands, but can also occur with phosphine ligands containing only a single aryl ring. As a consequence of this development renewed interest in this area is likely.

Experimental

Microanalyses were carried out in the Chemistry Department of University College London. NMR spectra (^1H, ^{31}P) were obtained on a Varian XL200 spectrometer. Cyclic voltammetry was performed using a Metrohm E506 potentiostat and Metrohm E612 VA Scanner. The working electrode was a platinum wire electrode (Metrohm EA285), the reference an Ag, $AgCl/Cl^-$, CH_2Cl_2 electrode (against which ferrocene was oxidised at a potential of 0.60 V), and the auxiliary electrode a massive platinum wire.

Dirhodium(II)tetraacetate was prepared via a literature method [20]. All other reagents were obtained from commercial suppliers.

$[Rh_2(O_2CCMe_3)_2\{PMe_2(C_6H_4)\}_2(Me_3CCO_2H)_2]$

To a solution of PMe_2Ph (0.1 cm^3) in Me_3CCO_2H (10 cm^3) was added $[Rh_2(O_2CMe)_4]$ (0.20 g). The mixture was refluxed for one hour in which time it became purple in colour. The solvent was removed *in vacuo*. The red gum was dissolved in CH_2Cl_2 and loaded on column of silca gel (60–120 mesh). A mauve band was eluted with CH_2Cl_2. The solvent was removed for a second time and the resulting solid washed with water to remove any remaining pivalic acid. The solid was filtered from the aqueous suspension and dried at ca. 325 K for eight hours. Yield 0.19 g, 47%. (Found: C, 48.2; H, 6.7; P, 6.8. $C_{36}H_{58}O_8P_2Rh_2$ calc.: C, 48.8; H,

Table 2

Bond lengths (Å)

Rh(1)–Rh(2)	2.492(1)	Rh(1)–P(1)	2.192(4)
Rh(1)–O(1)	2.172(10)	Rh(1)–O(3)	2.187(9)
Rh(1)–O(5)	2.360(9)	Rh(1)–C(23)	1.995(14)
Rh(2)–P(2)	2.190(4)	Rh(2)–O(2)	2.181(10)
Rh(2)–O(4)	2.154(9)	Rh(2)–O(6)	2.351(9)
Rh(2)–C(13)	1.990(14)	P(1)–C(10)	1.839(16)
P(1)–C(11)	1.840(22)	P(1)–C(12)	1.804(13)
P(2)–C(20)	1.836(20)	P(2)–C(21)	1.863(16)
P(2)–C(22)	1.795(12)	O(1)–C(40)	1.239(14)
O(2)–C(40)	1.240(17)	O(3)–C(30)	1.270(15)
O(4)–C(30)	1.235(14)	C(12)–C(13)	1.383(20)
C(12)–C(17)	1.421(23)	C(13)–C(14)	1.448(18)
C(14)–C(15)	1.415(24)	C(15)–C(16)	1.376(26)
C(16)–C(17)	1.413(23)	C(22)–C(23)	1.420(21)
C(22)–C(24)	1.412(24)	C(23)–C(27)	1.452(17)
C(24)–C(25)	1.402(21)	C(25)–C(26)	1.378(27)
C(26)–C(27)	1.401(25)	C(30)–C(31)	1.558(18)
C(31)–C(32)	1.599(27)	C(31)–C(33)	1.559(24)
C(31)–C(34)	1.553(22)	C(40)–C(41)	1.539(22)
C(41)–C(42)	1.546(27)	C(41)–C(43)	1.575(27)
C(41)–C(44)	1.512(28)		

6.6: P, 7.0%). ^{1}H NMR ($CDCl_3$): δ 0.56 (s, 18H, $[O_2CCMe_3]^-$), δ 1.29 (s, 18H, HO_2CCMe_3), δ 2.65 (d, 12H, $[Me_2P(C_6H_4)]^-$), δ 6.9–7.6 (m, 8H, $[Me_2P(C_6H_4)]^-$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 6.59 ppm (AA′XX′). Cyclic voltammogram: $E_{1/2}$ + 0.93 V, ΔE_p 70 mV (reversible oxidation).

$[Rh_2(O_2CCMe_3)_2\{PMe_2(C_6H_4)\}_2(H_2O)_2]$

The di-aquo adduct was obtained from the compound described above by recrystallisation from aqueous methanol. (Found: C, 44.1; H, 6.1; P, 7.4.

Table 3

Bond angles (°)

Rh(2)–Rh(1)–P(1)	90.0(1)	Rh(2)–Rh(1)–O(1)	85.0(2)
P(1)–Rh(1)–O(1)	92.1(3)	Rh(2)–Rh(1)–O(3)	87.2(2)
P(1)–Rh(1)–O(3)	176.5(2)	O(1)–Rh(1)–O(3)	85.6(4)
Rh(2)–Rh(1)–O(5)	162.1(2)	P(1)–Rh(1)–O(5)	96.3(3)
O(1)–Rh(1)–O(5)	78.0(3)	O(3)–Rh(1)–O(5)	85.8(3)
Rh(2)–Rh(1)–C(23)	96.2(4)	P(1)–Rh(1)–C(23)	90.3(4)
O(1)–Rh(1)–C(23)	177.3(4)	O(3)–Rh(1)–C(23)	92.1(5)
O(5)–Rh(1)–C(23)	100.5(4)	Rh(1)–Rh(2)–P(2)	90.3(1)
Rh(1)–Rh(2)–O(2)	87.4(2)	P(2)–Rh(2)–O(2)	177.8(2)
Rh(1)–Rh(2)–O(4)	85.5(2)	P(2)–Rh(2)–O(4)	94.0(3)
O(2)–Rh(2)–O(4)	85.7(4)	Rh(1)–Rh(2)–O(6)	160.9(3)
P(2)–Rh(2)–O(6)	95.7(3)	O(2)–Rh(2)–O(6)	86.4(4)
O(4)–Rh(2)–O(6)	76.0(3)	Rh(1)–Rh(2)–C(13)	95.8(4)
P(2)–Rh(2)–C(13)	91.2(4)	O(2)–Rh(2)–C(13)	89.2(5)
O(4)–Rh(2)–C(13)	174.6(5)	O(6)–Rh(2)–C(13)	102.1(4)
Rh(1)–P(1)–C(10)	118.2(5)	Rh(1)–P(1)–C(11)	113.1(6)
C(10)–P(1)–C(11)	103.5(9)	Rh(1)–P(1)–C(12)	112.2(5)
C(10)–P(1)–C(12)	103.1(7)	C(11)–P(1)–C(12)	105.5(8)
Rh(2)–P(2)–C(20)	111.3(6)	Rh(2)–P(2)–C(21)	119.7(7)
C(20)–P(2)–C(21)	101.7(9)	Rh(2)–P(2)–C(22)	113.0(5)
C(20)–P(2)–C(22)	104.1(7)	C(21)–P(2)–C(22)	105.3(7)
Rh(1)–O(1)–C(40)	122.5(10)	Rh(2)–O(2)–C(40)	119.2(8)
Rh(1)–O(3)–C(30)	118.7(7)	Rh(2)–O(4)–C(30)	123.0(9)
P(1)–C(12)–C(13)	115.8(10)	P(1)–C(12)–C(17)	120.8(12)
C(13)–C(12)–C(17)	123.3(13)	Rh(2)–C(13)–C(12)	125.1(9)
Rh(2)–C(13)–C(14)	118.4(11)	C(12)–C(13)–C(14)	116.4(13)
C(13)–C(14)–C(15)	120.0(14)	C(14)–C(15)–C(16)	122.1(14)
C(15)–C(16)–C(17)	118.9(17)	C(12)–C(17)–C(16)	119.1(17)
P(2)–C(22)–C(23)	115.8(10)	P(2)–C(22)–C(24)	122.4(11)
C(23)–C(22)–C(24)	121.8(12)	Rh(1)–C(23)–C(22)	124.3(9)
Rh(1)–C(23)–C(27)	118.7(11)	C(22)–C(23)–C(27)	117.0(12)
C(22)–C(24)–C(25)	120.0(16)	C(24)–C(25)–C(26)	118.9(16)
C(25)–C(26)–C(27)	123.0(13)	C(23)–C(27)–C(26)	119.0(14)
O(3)–C(30)–O(4)	124.7(11)	O(3)–C(30)–C(31)	117.1(10)
O(4)–C(30)–C(31)	118.0(11)	C(30)–C(31)–C(32)	103.3(13)
C(30)–C(31)–C(33)	109.0(12)	C(32)–C(31)–C(33)	110.0(12)
C(30)–C(31)–C(34)	112.6(11)	C(32)–C(31)–C(34)	110.1(13)
C(33)–C(31)–C(34)	111.6(15)	O(1)–C(40)–O(2)	125.8(14)
O(1)–C(40)–C(41)	116.6(12)	O(2)–C(40)–C(41)	117.6(11)
C(40)–C(41)–C(42)	104.6(15)	C(40)–C(41)–C(43)	110.0(15)
C(42)–C(41)–C(43)	110.4(14)	C(40)–C(41)–C(44)	111.9(13)
C(42)–C(41)–C(44)	108.7(19)	C(43)–C(41)–C(44)	111.0(18)

$C_{26}H_{42}O_6P_2Rh_2$ calc.: C, 43.6; H, 5.6; P, 8.5%). ^1H NMR δ 0.75 (s, 18H, $[O_2CCMe_3]^-$), δ 2.86 (d, 12H, $[Me_2P(C_6H_4)]^-$), δ 3.05 (s, broad, 4H, H_2O), δ 6.7–7.6 (m, 8H, $[Me_2P(C_6H_4)]^-$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -2.94 ppm (AA′XX′). Cyclic voltammogram: $E_{1/2}$ $+0.90$ V, ΔE_p 75 mV (reversible oxidation).

Crystal structure determination of $[Rh_2(O_2CCMe_3)_2\{PMe_2(C_6H_4)\}_2(H_2O)_2]$

Crystal data: $C_{26}H_{42}O_6P_2Rh_2$, $M = 718.44$, monoclinic, a 10.414(3), b 21.459(6), c 14.463(3) Å, β 108.23°, V 3070(1) Å^3, D_c 1.55 g cm^{-1}, $Z = 4$, μ(Mo-K_α) 12.0 cm^{-1}, $F(000)$ 1464, λ(Mo-K_α) 0.71073 Å, space group $P2_1/c$ from systematic absences.

A crystal of approximate dimensions $0.65 \times 0.26 \times 0.10$ mm^3 was used to collect 5283 unique data in the range $5° \leq 2\theta \leq 50°$, on a Nicolet R3mV diffractometer equipped with a molybdenum X-ray tube and graphite monochromator.

The asymmetric unit contains one complete molecule. The unique rhodium atoms were found by interpretation of a Patterson map and the remaining non-hydrogen atoms found by iterative application of least-squares refinement and difference-Fourier synthesis. The hydrogen atoms were not located and have not been included in the refinement. In the latter stages all the non-hydrogen atoms were refined anisotropically. At the end of the refinement $R = 0.0581$ ($R_w = 0.0596$), based on the 2744 absorption corrected data with $I \geq 3\sigma(I)$. The largest shift/esd was 0.03, and the largest peak in the final difference-Fourier synthesis was 0.75 e Å^{-3}, close to one of the metal atoms. Crystallographic calculations used the SHELXTL PLUS program package [21]. Final fractional coordinates are given in Table 1, while bond lengths and angles are presented in Tables 2 and 3 respectively. The molecular structure is shown in Fig. 1, and the hydrogen bonded chains in Fig. 2. Tables of anisotropic thermal parameters and lists of structure factors are available from the authors.

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