

Four-membered Chelate Rings in Complexes with 2,2-Bis(diphenylphosphino)propane. Crystal and Molecular Structures of *trans*-[RuCl₂{Me₂C(PPh₂)₂}₂], [RuCl{Me₂C(PPh₂)₂}(η-C₅H₅)] and [(η-C₅H₅)Ru(μ-CO)₂-{μ-Me₂C(PPh₂)₂}RhCl₂](*Rh-Ru*)[†]

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The compound Me₂C(PPh₂)₂ (2,2-dppp) reacted with 0.5 equivalent of [Rh₂Cl₂(CO)₄] to afford monomeric [RhCl(CO)(2,2-dppp-*P,P'*)] **1**. Metathesis with LiBr afforded [RhBr(CO)(2,2-dppp-*P,P'*)] **2**. With 0.25 equivalent of [Rh₂Cl₂(CO)₄] the rigid, square-planar [Rh(2,2-dppp)₂]Cl **3** was formed. These results are in sharp contrast to the chemistry seen with H₂C(PPh₂)₂ and H(Me)C(PPh₂)₂. With 0.5 equivalent of [RuCl₂(PPh₃)₃], 2,2-dppp reacted to give brown-orange *trans*-[RuCl₂(2,2-dppp)₂] **4a**. In solution this is in equilibrium with a green five-co-ordinate species [RuCl(2,2-dppp)₂]Cl **4b**, the first such complex to be observed with a four-membered chelating diphosphine. With [RuCl(PPh₃)₂(η-C₅H₅)], 2,2-dppp reacted to form [RuCl(2,2-dppp)(η-C₅H₅)] **5**. Although its rhodium(I) chemistry suggests that 2,2-dppp favours chelation rather than bridging modes of co-ordination, when **5** was treated with 0.5 equivalent of [Rh₂Cl₂(CO)₄] it readily formed [(η-C₅H₅)Ru(μ-CO)₂(μ-2,2-dppp)RhCl₂](*Rh-Ru*) **6**. The structures of **4-6** have been determined by X-ray diffraction.

Ligands of the type R₂PXPR₂ (R = alkyl, alkoxy, or aryl; X = CH₂, C=CH₂, NR or O) exhibit a highly versatile co-ordination chemistry. The archetypal example Ph₂PCH₂PPh₂ (dppm) can chelate, behave as monodentate, or bridge two metal atoms in a variety of co-ordination geometries.¹ Owing to the strain inherent in a four-membered chelate ring there is often a fine balance between these types of behaviours, and routes to heterobimetallic complexes bridged by dppm have been developed which exploit the tendency of mononuclear complexes [M(dppm-*P*)_n] or [M(dppm-*P,P'*)_n] to react with a labile source of a second metal ion to afford species [M(μ-dppm)_nM']^{1,2}

Although the compound Ph₂PCH(Me)PPh₂ (1,1-dppe) has not been extensively investigated, its chemistry seems similar to that of dppm. In particular, it readily forms complexes containing M(μ-1,1-dppe)_nM' moieties. For example, with [Rh₂Cl₂(CO)₄] both dppm and 1,1-dppe (2 equivalents) react to give dimers, *trans*-[Rh₂Cl₂(CO)₂(μ-dppm)₂] and [Rh₂Cl(CO)₂(1,1-dppe)₂]⁺ respectively.^{3,4} On treatment of [Pd(PPh₃)₄] with either dppm or 1,1-dppe, and an excess of Cl₂C=CH₂ (in refluxing benzene) high yields of 'A-frames' [Pd₂Cl₂(μ-L-L)₂(μ-C=CH₂)] are obtained.⁵ There is some evidence that 1,1-dppe has less tendency to bridge than does dppm. For instance, comproportionation of substitution-labile complexes of Pd⁰ and Pd^{II} in the presence of dppm affords [Pd₂Cl₂(μ-dppm)₂](*Pd-Pd*) cleanly. However, with 1,1-dppe a mixture of palladium(I) dimer and [PdCl₂(1,1-dppe-*P,P'*)] is obtained.⁶ The additional steric demands of the methyl groups can affect the reactivities of the complexes in an interesting way, and introduces the possibility of *syn* and *anti* isomerism in

bimetallic species. For example, whereas [Pd₂Cl₂(μ-dppm)₂] reacts with CO to give the 'A-frame' [Pd₂Cl₂(μ-dppm)₂(μ-CO)], *anti*-[Pd₂Cl₂(μ-1,1-dppe)₂] does not. The corresponding *syn* isomer binds CO, but much more weakly than does [Pd₂Cl₂(μ-dppm)₂].⁷

Although Ph₂PCMe₂PPh₂ (2,2-dppp) was first described by Hewertson and Watson⁸ in 1962, little co-ordination chemistry involving it has so far been published. The complex [(AuCl)₂(2,2-dppp)] has been described; this can be oxidised by X₂ (X = Cl or Br), first to [{Au^{III}Cl(X)}₂(2,2-dppp)](*Au-Au*), then [(Au^{III}ClX)₂(2,2-dppp)].⁹ Complexes of 1,1-dppe and 2,2-dppp with Group 6 metal carbonyls and with Pd^{II} and Pt^{II} have been made indirectly, by successive deprotonation and alkylation (MeI) of [M(CO)₄(dppm)]¹⁰ (M = Cr, Mo or W) or [MX₂(dppm)]¹¹ (M = Pd or Pt; X = Cl, Br or I). The complexes *fac*-[MnMe(CO)₃(L-L)] and [Mn(CO)₃(CO)₃(L-L)] (L-L = dppm, 1,1-dppe or 2,2-dppp) have been synthesised.¹² Interestingly, while other diphosphines and diarsines gave only the *fac* acetyl complex, dppm and 1,1-dppe gave a mixture of *fac* and *mer* and 2,2-dppp gave exclusively the *mer* isomer.

We anticipated that complete substitution by methyl groups for hydrogen at the methylene carbon would greatly enhance the stability of chelate rings because of the Thorpe-Ingold (*gem*-dimethyl) effect.¹³ The stereoelectronic effects of employing four-membered rings in homogeneous catalysis have been little studied since such rings are usually unstable under the reaction conditions typically employed in these processes. As a first step towards a study of this area, we have examined the co-ordination chemistry of Ru^{II} and Rh^I with 2,2-dppp, and have observed that it does indeed have a significantly greater tendency to chelate than that of dppm. Nevertheless, we have also made a bimetallic 2,2-dppp-bridged Ru^{II}-Rh^I complex; we report these results here.

[†] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv-xxx.

Table 1 Analytical, mass spectrometric and infrared data

Complex	Analysis (%)			FAB mass spectrum data ^a (<i>m/z</i>)	IR ^b /cm ⁻¹	
	C	H	X		v(CO)	Other
1	56.7 (56.7)	4.1 (4.45)	6.3 (6.4)	996 (<i>M</i> ⁺), 961 (<i>[M - Cl]</i> ⁺) 614 (<i>M</i> ⁺ , 100%), 579 (<i>[M - Cl]</i> ⁺ , 45), 428 (<i>[M - PPh₂ - H]</i> ⁺ , 11%) 773 (<i>[M - Cl]</i> ⁺ , 21%)	1998vs	300s [v(Rh-Cl)]
2	52.5 (53.5)	4.1 (4.1)	13.5 (13.8)		1990vs	240m [v(Rh-Br)]
3	67.1 (67.3)	5.4 (5.4)	3.8 (3.7)			
4	64.4 (65.1)	5.15 (5.2)	n.d.			
5	62.75 (62.6)	5.1 (5.1)	n.d.			
6·0.5CH ₂ Cl ₂	48.7 (48.7)	3.8 (3.8)	n.d.		1818s 1792s	

n.d. = Not determined. ^a Recorded in 3-nitrobenzyl alcohol. ^b Nujol mulls, NaCl or polystyrene plates.

Table 2 NMR Spectroscopic data

Complex	³¹ P-{ ¹ H}(δ) ^a	Selected ¹ H NMR (δ) ^a
1	22.6 [dd, <i>J</i> (RhP) 137, <i>J</i> (PP) 88, P <i>trans</i> to Cl], -11.4 [dd, <i>J</i> (RhP) 108, <i>J</i> (PP) 88, P <i>trans</i> to P]	1.34 [t, <i>J</i> (PH) 15.7, C(CH ₃) ₂]
2	20.9 [dd, <i>J</i> (RhP) 142, <i>J</i> (PP) 104, P <i>trans</i> to Br], -12.0 [dd, <i>J</i> (RhP) 108, <i>J</i> (PP) 104, P <i>trans</i> to P]	1.34 [t, <i>J</i> (PH) 15.7, C(CH ₃) ₂]
3	11.7 [d, <i>J</i> (RhP) 120] ^b	1.43 [qnt, <i>J</i> (PH) 7.4, C(CH ₃) ₂] ^b
4a	24.3 (s)	1.61 [qnt, <i>J</i> (PH) 6.5, C(CH ₃) ₂]
4b	14.2 [t, <i>J</i> (PP) 27], 34.2 [t, <i>J</i> (PP) 27]	
5	43.5 (s)	1.34 [t, 3 H, <i>J</i> (PH) 16.5, C(CH ₃) ₂], 1.73 [t, 3 H, <i>J</i> (PH) 12.6, C(CH ₃) ₂], 4.52 (s, 5 H, C ₅ H ₅)
6	84.8 (A), 68.4 (B) [ABX; <i>J</i> (RhP _A) 9, <i>J</i> (RhP _B) 123, <i>J</i> (P _A P _B) 105]	0.45 [t, <i>J</i> (PH) 26, C(CH ₃) ₂], 5.05 (s, C ₅ H ₅)

^a In CDCl₃ except where noted; *J* in Hz. ^b In (CD₃)₂CO.

Results and Discussion

Synthesis and Spectroscopic Data.—The compound Me₂C(PPh₂)₂ (2,2-dppp) was prepared by the literature method, that is treatment of an ammonia solution of NaPPh₂ (generated by cleavage of PPh₃ by Na, followed by quenching of NaPh with anhydrous NH₄Br) with 2,2-dichloropropane.⁹ In contrast to dpmp and 1,1-dppe it is somewhat air-sensitive in solution, or as an impure solid. After recrystallisation from propan-1-ol and thorough drying *in vacuo*, however, it may be stored in air. It was characterised by microanalyses (C and H), mass spectrometry (electron impact, EI) and NMR spectroscopy. The ³¹P-{¹H} NMR spectrum showed a single peak at δ +12.6. There is a progressive shift upfield, therefore, from dpmp (δ -22.1) to 1,1-dppe (δ -6.4) to 2,2-dppp, presumably since the P-C-P angle becomes more constricted.

Treatment of [Rh₂Cl₂(CO)₄] in acetone with 2 equivalents of 2,2-dppp gave a yellow complex, microanalytical data for which were consistent with the formula [RhCl(CO)(2,2-dppp)] **1** (Table 1). The infrared spectrum showed a single metal-carbonyl band, in the terminal region, and a strong band at 300 cm⁻¹. The latter was absent from the spectrum of the corresponding bromide and is therefore assigned as v(Rh-Cl). The ³¹P-{¹H} NMR spectrum of **1** (Table 2) showed an AMX pattern, with one ¹*J*(RhP) value typical of P *trans* to Cl and the other of P *trans* to P.¹⁴ Metathesis of **1** with LiBr afforded the corresponding bromide **2**, with similar analytical and NMR spectroscopic properties to those of **1**. The data show that **1** and **2** are monomeric, with chelating 2,2-dppp. In contrast, when [Rh₂Cl₂(CO)₄] is treated under similar conditions with dpmp or 1,1-dppe, it affords, exclusively, binuclear complexes with bridging diphosphine ligands;^{3,4} these have subsequently been extensively investigated.¹

On treatment of [Rh₂Cl₂(CO)₄] with 4 equivalents of 2,2-dppp in benzene orange [Rh(2,2-dppp)₂]Cl **3** is formed. That this is a non-fluxional square-planar complex is confirmed by the microanalytical data and the absence of a carbonyl-stretching mode in the infrared spectrum (Table 1), and, further, by the fact that the ³¹P-{¹H} NMR spectrum shows a

temperature-invariant singlet. Whereas [Rh(dpmp)₂]BF₄ reacts with CO readily to form the fluxional [Rh(CO)(dpmp)₂]BF₄, [Rh(dppe)₂]⁺ is unreactive towards CO, even at elevated pressure.¹⁵ It is interesting, therefore, that the reactions of 2,2-dppp with [Rh₂Cl₂(CO)₄] closely mirror those of the strongly chelating ligand Ph₂P(CH₂)₂PPh₂ (dppe), which forms [RhCl(CO)(dppe-*P, P'*)] or [Rh(dppe)₂]Cl depending on the mole ratio.¹⁶

Treatment of [RuCl₂(PPh₃)₃] with 2 equivalents of 2,2-dppp in dichloromethane afforded a dull brown precipitate, analytical and FAB mass spectral data for which were consistent with the formula [RuCl₂(2,2-dppp)₂] **4**. The ³¹P-{¹H} NMR spectrum of a freshly prepared orange solution of this, in CDCl₃, showed a sharp singlet at δ 24.3 (Table 2), indicating *trans* geometry (**4a**). The co-ordination chemical shift [δ(complex) - δ(ligand)] for the ³¹P NMR resonances for this complex (+12.2 ppm) is similar to that of dpmp in *trans*-[RuCl₂(dpmp)₂] (+15.9 ppm).¹⁷ The ¹H NMR spectrum at room temperature showed a rather broad resonance at δ 1.61, due to the methyl groups; strong P-*trans*-P coupling gives rise to the 'virtual' quintet pattern seen.¹⁴ To obtain information about the effect of the *gem*-dimethyl groups on the chelate ring, we performed a crystal structure determination on **4a** (see later).

When left overnight at room temperature the saturated solution used for the ³¹P NMR experiment turned dark green. The ³¹P-{¹H} NMR spectrum showed, in addition to a singlet due to residual *trans*-[RuCl₂(2,2'-dppp)₂] (*ca.* 25% total signal), two triplets at δ 14.2 and 34.2 [²*J*(PP) 27 Hz] (**4b**). In principle there are three possible explanations for this change. The first is oxidation to Ru^{III}. Although there are examples of dark green ruthenium(III) complexes {including [RuCl₂(dpmp)₂]BF₄,¹⁸ Table 3}, the observation of sharp NMR spectra precludes this; other ruthenium(III) complexes of this type are low-spin d⁵, and attempts to observe ³¹P NMR signals failed.¹⁸ Two possibilities suggested by the ³¹P-{¹H} NMR spectrum are isomerisation to *cis*-[RuCl₂(2,2-dppp)₂], and formation of pseudo-trigonal-bipyramidal [RuCl(2,2-dppp)₂]Cl.

Table 3 Electronic spectral data

Complex ^a	$10^{-3}\lambda/\text{cm}^{-1}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) ^b
4 (orange form)	15.4 (60), 20.6 (sh) (200), 23.3 (sh) (340), 30.9 (3400)
(green form)	15.3 (1), 19.5 (1.21), 23.6 (sh) (1.77), 28.6 (sh) (3.15) ^c
[RuCl ₂ (dppp) ₂] ^d	20.9 (355), 26.0 (sh) ^e
[RuCl(dppp) ₂]PF ₆ ^d	18.2 (640), 23.3 (2440), 27.0 (sh) ^e
[RuCl ₂ (dppm) ₂] ^f	20.7, 23.0
[RuCl ₂ (dppm) ₂] ^{f,g}	24.0, 27.8
[RuCl ₂ (dppm) ₂]BF ₄ ^h	14.2 (420), 21.4 (530), 25.0 (550)
[RuCl ₂ (dppb) _{1.5}] ⁱ	14.7 (420), 21.7 (1440), 27.0 (sh) ^e

^a All *trans* except where noted. ^b In CH₂Cl₂ except where noted. ^c Relative peak heights in parentheses; a faint precipitate prevented calculation of absorption coefficients. Spectrum recorded on a concentrated solution in CDCl₃, in a 0.1 mm pathlength cell. ^d Ref. 21. ^e In ClCH₂CH₂Cl. ^f Ref. 19; absorption coefficients not reported. ^g *cis* isomer. ^h Ref. 18. ⁱ Refs. 17 and 20.

Since the *cis* isomers of complexes [RuX₂(diphosphine)₂] invariably have higher-energy electronic transitions than do the *trans* isomers {see, for example, [RuCl₂(dppm)₂];¹⁹ Table 3}, and are therefore pale yellow,¹⁹ we favour the formation of [RuCl(2,2-dppp)₂]Cl as the explanation. Although such complexes are generally red or brown²⁰⁻²³ {for example, [RuCl(dppp)₂]⁺ [dppp = Ph₂P(CH₂)₃PPh₂];^{21,23} Table 3}, there are two examples of green, apparently five-co-ordinate ruthenium(II)-diphosphine complexes, [RuCl₂(PPh₃)(dppb)]²⁴ and [RuCl₂(dppb)_{1.5}]⁺ [dppb = Ph₂P(CH₂)₄PPh₂].^{17,20,24} The electronic spectrum of a freshly prepared solution of [RuCl₂(2,2-dppp)₂] **4a** in CH₂Cl₂ (Table 3) was very similar to those reported for other *trans*-[RuCl₂(diphosphine)₂] complexes,^{20,25} except for the presence of a weak absorption at 15 400 cm⁻¹. Following literature precedent, the bands at 20 600 and 23 300 cm⁻¹ are assigned to ¹A_{1g} → ¹E_g¹ and ¹A_{1g} → ¹A_{2g} transitions respectively (assuming approximate D_{4h} symmetry). The highest-energy band is probably ligand-to-metal charge transfer in nature. When re-recorded after 12 h the intensity of the band at 15 400 cm⁻¹ had increased and some change in the intensities of the other bands had occurred, but there was no significant shift in their position. The colour of this dilute (1.62 mmol dm⁻³) solution was yellow-green. The spectrum of the concentrated, green solution in CDCl₃ employed for NMR spectroscopy was also recorded, using 0.1 cm pathlength cells (Table 3), although reliable absorption coefficients could not be obtained as the solution was cloudy. The peak positions and relative intensities are consistent with five-co-ordination. Attempts to isolate the green complex are continuing.

Five-co-ordinate complexes [RuCl(diphosphine)₂]⁺ form readily when the diphosphine forms six-membered chelate rings {for example, [RuCl(Ph₂PCH₂CH₂CH₂PRR')₂]⁺; R,R' = Ph or Me}.^{23,24} Five-membered chelate ring diphosphines give five-co-ordinate complexes readily only if they have bulky substituents (for example, [RuCl{(C₆H₁₁)₂PCH₂CH₂P(C₆H₁₁)₂}]⁺).²¹ Although [RuCl(dppe)₂]PF₆ has been isolated,²⁶ it is substitution labile and reverts to six-co-ordination in donor solvents.²⁷ The complex **4b** appears to be the first example of a four-membered chelate ligand promoting five-co-ordination at Ru^{II}.

We have attempted a considerable number of ring-opening reactions on Ni^{II}-, Pd^{II}- and Pt^{II}-2,2-dppp chelate complexes, of the kind known to work with the corresponding dpmp complexes, but none has yet been successful; the chelate rings in these complexes are remarkably robust.²⁸ We have previously shown that whereas [RuCl₂(dppm)₂] is unreactive to ring-opening reactions with [Rh₂Cl₂(CO)₄],²⁹ [RuCl(dppm)(η-C₅H₅)] does react, to give the heterobimetallic [(η-C₅H₅)Ru(μ-CO)₂(μ-dppm)RhCl₂](*Rh-Ru*).³⁰ Furthermore, analogous

complexes can be made with other four-membered ring diphosphines having markedly different bite angles, such as dppen [dppen = (Ph₂P)₂C=CH₂] and (Ph₂P)₂NH.^{30,31} We therefore wished to examine this reaction using 2,2-dppp.

Whereas the ligand-exchange reaction of [RuCl(PPh₃)₂(η-C₅H₅)] with dppen proceeds in high (85%) yield,³⁰ we found that treatment of [RuCl(PPh₃)₂(η-C₅H₅)] with 1 equivalent of 2,2-dppp in refluxing toluene for 5 h afforded a mixture. The products were separated by preparative TLC [silica plates, CH₂Cl₂-toluene (2:1)]. The band with the highest R_f was yellow. Its ³¹P-{¹H} NMR spectrum showed a pair of doublets at δ 45 and -81 [*J*(PP) = 48 Hz] and a singlet at δ -5. This product decomposed on isolation and we have not yet succeeded in characterising it further. The middle band was unreacted [RuCl(PPh₃)₂(η-C₅H₅)]. The band with the lowest R_f value was bright orange. It was identified as [RuCl(2,2-dppp)(η-C₅H₅)] **5**, obtained pure in 45% yield, by (i) microanalytical and FAB mass spectral data consistent with this formula (Table 1), (ii) its ³¹P-{¹H} NMR spectrum, which showed a singlet at δ 43.5 and (iii) a crystal structure determination (see later). The ³¹P-{¹H} co-ordination chemical shift for **5** (31.5 ppm) is very similar to those observed for the related complexes [RuCl(dppm)(η-C₅H₅)] (33.4 ppm),³⁰ [RuCl(Ph₂PNHPPPh₂)(η-C₅H₅)] (28.8 ppm)³¹ and [RuCl(dppen)(η-C₅H₅)] (35.3 ppm).³⁰ Interestingly, the ¹H NMR spectrum showed that the two methyl groups are inequivalent at room temperature (Table 2); this has been observed previously for the complexes *fac*-[MnX(CO)₃(2,2-dppp)] (X = Me, H, Cl, Br or I).¹²

Treatment of a toluene solution of complex **5** with [RhCl₂(CO)₂]₂ (1:1 Rh:Ru) afforded the heterobimetallic [(η-C₅H₅)Ru(μ-CO)₂(μ-2,2-dppp)RhCl₂](*Rh-Ru*) **6** in good yield. This was characterised by microanalyses, and by its FAB mass spectrum, which showed a cluster of peaks centred at *m/z* 773, corresponding to [M - Cl]⁺ (calc. for C₃₄H₃₁ClO₂P₂Rh¹⁰²Ru: 773). Interestingly, although there are also peaks centred at *m/z* 752 {corresponding to [M - (CO)₂]⁺} and 717 {corresponding to [M - Cl - (CO)₂]⁺}, there is no significant peak at *m/z* 745 {corresponding to [M - Cl - CO]⁺}. The infrared spectrum showed bands in the CO stretching region at 1818 and 1792 cm⁻¹, indicative of bridging carbonyls; these are at rather lower energies than the corresponding bands for [(η-C₅H₅)Ru(μ-CO)₂(μ-L-L)RhCl₂](*Rh-Ru*) (L-L = dppen, 1859, 1820; L-L = dppm, 1855, 1818 cm⁻¹). The ³¹P-{¹H} NMR spectrum showed an ABX pattern (Table 2). We assign the downfield portion, centred at δ 84.8, to phosphorus co-ordinated to ruthenium because of its small (9 Hz) coupling to the rhodium atom, and the upfield portion, centred at δ 68.4, to phosphorus co-ordinated to rhodium [*J*(RhP) 123 Hz]. The co-ordination chemical shifts (72.8, 56.4 ppm respectively) are similar to those for [(η⁵-C₅H₅)Ru(μ-CO)₂(μ-dppen)RhCl₂](*Rh-Ru*) (77.9, 67.5 ppm respectively). The ¹H NMR spectrum showed a broad triplet at δ 0.45, due to the ligand methyl groups, indicating that both the chemical environments of the methyl groups, and the different phosphorus-proton coupling constants, are similar. The upfield shift from the values found for these methyl groups when the ligand chelates to a single metal centre (Table 2) is noteworthy.

Structural Studies.—(i) **Complex 4.** On recrystallisation of complex **4** from CH₂Cl₂-hexane orange crystals were obtained, which proved to be the six-co-ordinate **4a**. The molecular structure is shown in Fig. 1, fractional coordinates are given in Table 4 and selected bond lengths and angles in Table 5. The structure confirms the *trans* geometry assigned spectroscopically. There is a crystallographically imposed centre of symmetry, as also found for the analogous complexes *trans*-[RuCl₂(dppm)₂] **7**,³² *trans*-[RuCl₂(dppen)₂] **8**³³ and *trans*-[RuCl₂{(Ph₂P)₂CHCH₂NH(CH₂)₃NH₂}]₂ **9**.³⁴ Looking at the four-membered chelate rings, there is a general lengthening

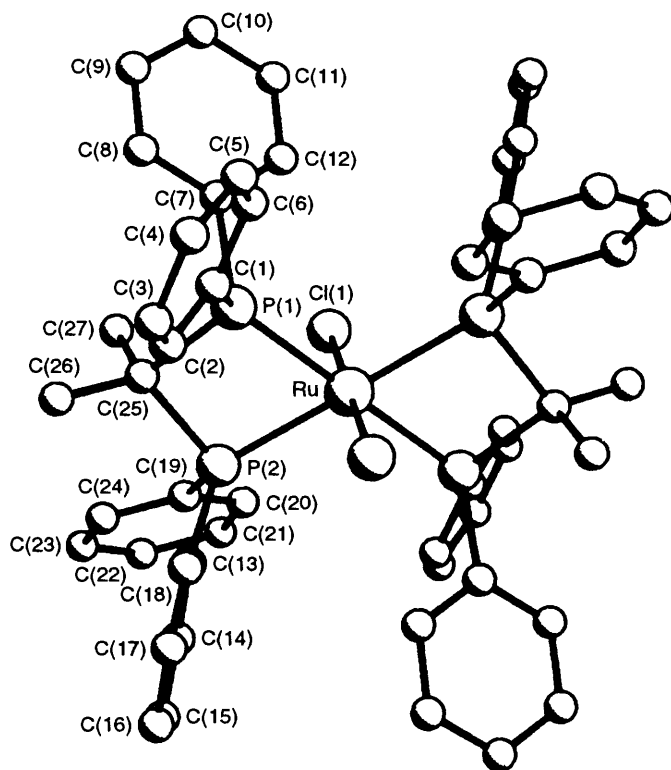


Fig. 1 Molecular structure of $[\text{RuCl}_2(2,2\text{-dppp})_2]$ **4a**

Table 4 Final positional parameters with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of $[\text{RuCl}_2(2,2\text{-dppp})_2]$ **4a**. The Ru atom has occupancy 0.5, all other atoms occupancy 1

Atom	x	y	z
Ru	1.0	0	1.0
Cl(1)	1.098 50(6)	0.097 28(5)	1.147 51(6)
P(1)	0.897 06(6)	0.116 18(5)	0.895 05(6)
P(2)	1.116 29(6)	0.058 52(5)	0.897 44(6)
C(1)	0.765 1(2)	0.101 9(2)	0.778 4(2)
C(2)	0.762 5(3)	0.079 6(2)	0.671 8(2)
C(3)	0.658 1(3)	0.070 2(2)	0.589 6(2)
C(4)	0.554 5(3)	0.081 2(2)	0.612 3(3)
C(5)	0.554 7(3)	0.101 2(2)	0.717 6(3)
C(6)	0.658 8(3)	0.111 6(2)	0.799 3(3)
C(7)	0.845 1(2)	0.207 4(2)	0.959 1(2)
C(8)	0.796 1(3)	0.280 9(2)	0.898 8(3)
C(9)	0.748 8(3)	0.345 9(2)	0.945 8(3)
C(10)	0.747 9(3)	0.338 4(2)	1.054 5(3)
C(11)	0.795 3(3)	0.266 1(2)	1.114 2(3)
C(12)	0.844 5(3)	0.201 2(2)	1.066 8(2)
C(13)	1.137 5(2)	0.000 1(2)	0.778 2(2)
C(14)	1.247 4(3)	-0.025 9(2)	0.776 4(2)
C(15)	1.261 5(3)	-0.076 4(2)	0.690 7(3)
C(16)	1.167 7(3)	-0.101 5(2)	0.605 5(2)
C(17)	1.057 9(3)	-0.077 8(2)	0.607 2(2)
C(18)	1.043 1(3)	-0.028 2(2)	0.692 6(2)
C(19)	1.264 1(2)	0.098 4(2)	0.957 6(2)
C(20)	1.327 8(3)	0.070 1(2)	1.060 4(2)
C(21)	1.444 1(3)	0.091 6(3)	1.102 0(3)
C(22)	1.496 2(3)	0.144 3(2)	1.041 3(3)
C(23)	1.431 8(3)	0.174 7(2)	0.939 6(3)
C(24)	1.317 2(3)	0.151 1(2)	0.898 3(3)
C(25)	1.023 0(2)	0.158 4(2)	0.847 3(2)
C(26)	1.003 5(3)	0.187 1(2)	0.728 4(3)
C(27)	1.075 8(3)	0.234 9(2)	0.922 4(3)

of all ring bonds compared with the latter complexes. Thus, the P-C(25) bond lengths [1.912(3), 1.911(3) Å] in **4a** compare with

Table 5 Selected bond lengths (Å) and bond angles (°) with e.s.d.s in parentheses for $[\text{RuCl}_2(2,2\text{-dppp})_2]$ **4a**

Ru-Cl(1)	2.4311(9)	P(2)-C(13)	1.849(3)
Ru-P(1)	2.3668(9)	P(2)-C(19)	1.832(3)
Ru-P(2)	2.3614(9)	P(2)-C(25)	1.911(3)
P(1)-C(1)	1.847(3)	C(25)-C(26)	1.529(4)
P(1)-C(7)	1.832(3)	C(25)-C(27)	1.540(4)
P(1)-C(25)	1.912(3)		
Cl(1)-Ru-Cl(1)	180.00	Ru-P(2)-C(19)	124.26(9)
Cl(1)-Ru-P(1)	91.31(4)	Ru-P(2)-C(25)	96.19(9)
Cl(1)-Ru-P(2)	87.33(3)	C(13)-P(2)-C(19)	99.0(1)
P(1)-Ru-P(2)	72.25(3)	C(13)-P(2)-C(25)	109.4(1)
Ru-P(1)-C(1)	123.4(1)	C(19)-P(2)-C(25)	105.9(1)
Ru-P(1)-C(7)	121.8(1)	P(1)-C(25)-P(2)	93.6(1)
Ru-P(1)-C(25)	95.97(9)	P(1)-C(25)-C(26)	120.5(2)
C(1)-P(1)-C(7)	97.1(1)	P(1)-C(25)-C(27)	106.8(2)
C(1)-P(1)-C(25)	111.4(1)	P(2)-C(25)-C(26)	118.2(2)
C(7)-P(1)-C(25)	106.6(1)	P(2)-C(25)-C(27)	108.6(2)
Ru-P(2)-C(13)	121.0(1)	C(26)-C(25)-C(27)	107.9(2)

corresponding average bond lengths of 1.849(5) Å for **7**, 1.837(3) Å for **8** and 1.855(10) Å for **9**, and the average Ru-P bond length in **4a**, 2.3641(9) Å, compares with 2.3535(10) Å for **7**, 2.3375(10) Å for **8** and 2.357(1) Å for **9**. Also of note is that there is significantly less difference between individual Ru-P [and P-C (central)] distances within **4a** than within **7-9** [for the Ru-P bonds, 0.0054(9) Å in **4a** compared with, respectively, 0.027(1), 0.013(1) and 0.016(4) Å]. Turning to the bond angles, the presence of the *gem*-dimethyl groups considerably distorts the bond angles at C(25) (Table 4). Comparing **4a** with the dppm complex **7**, the P-C(25)-P bond angle is somewhat smaller for **4a** [93.6(1)°] than for **7** [95.9(2)°]. The two C(25)-P-Ru angles in **4a** are significantly greater than for **7-9**. There is a small but distinct trend in the P-Ru-P angles from **7** and **9** [71.39(4) and 71.5(1)° respectively] to **4a** [72.25(3)°] to **8** [73.13(2)°]. Clearly, the presence of the *gem*-dimethyl group opens out this angle, but not to the same extent as the presence of an sp^2 -hybridised carbon atom in the ring. There is no obvious clue in the structure as to why this complex, but none of the others, dissociates in solution. The Ru-Cl bond length is normal for complexes of this type.

(ii) **Complex 5**. Crystals of complex **5** were obtained from toluene-heptane by diffusion. There were two different molecules in the unit cell, differing significantly in bond lengths, but not in general arrangement; one is shown in Fig. 2. Fractional coordinates for both are given in Table 6 and bond lengths and angles in Table 7. Detailed comparison with analogous complexes is not worthwhile because of the high *R* factor, a consequence of disorder of one of the phenyl rings in one molecule. In gross terms, the structure is similar to that of $[\text{RuCl}(\text{dppen})(\eta\text{-C}_5\text{H}_5)]^{30}$ and $[\text{RuCl}(\text{dppm})(\eta\text{-C}_5\text{H}_5)]^{35}$.

(iii) **Complex 6**. The structure of $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-2,2-dppp})\text{RhCl}_2](\text{Rh-Ru})$ **6** is shown in Fig. 3. Fractional coordinates are in Table 8 and selected bond lengths and angles in Table 9. The structure is very similar to that of the analogous complex $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-dppen})\text{RhCl}_2](\text{Rh-Ru})^{30}$. The Rh-Ru bond is bridged by the 2,2-dppp ligand and by two semibridging carbonyl ligands. The carbonyl ligands are more strongly bound to the Ru atom [Ru-C(1)-O(1) 151(2), Rh-C(1)-O(1) 126(1); Ru-C(2)-O(2) 148(1), Rh-C(2)-O(2) 124(1)°]. The estimated standard deviations (e.s.d.s) are too high to allow us to determine whether there is a correlation between the observed lower CO stretching frequencies in this complex and CO or M-C bond lengths, compared with the corresponding dppen complex. The Rh-Cl bond *trans* to phosphorus [Rh-Cl(2) 2.393(4) Å] is significantly longer than that *trans* to the metal-metal bond [Rh-Cl(1) 2.330(4) Å]. While the formal oxidation states of the metal atoms are Rh^{I} and Ru^{II} ,

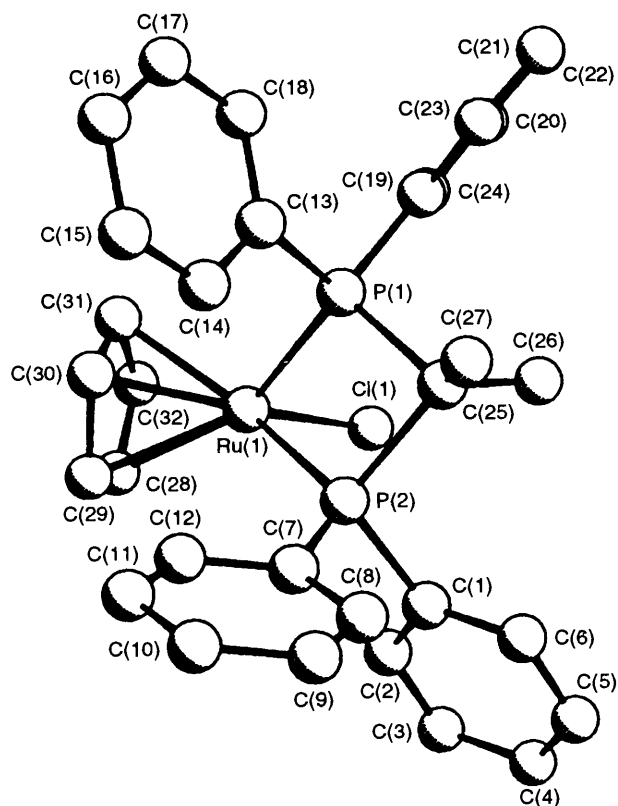


Fig. 2 Molecular structure of one of the molecules of $[\text{RuCl}(2,2\text{-dppm})(\eta\text{-C}_5\text{H}_5)]$ **5** (two independent molecules in the asymmetric unit)

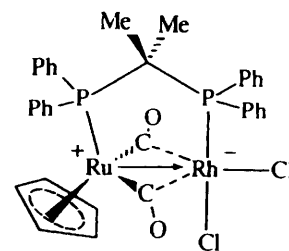


Fig. 4 Representation of a likely bonding mode for complex **6**

presence of the two methyl groups in 2,2-dppp again compresses this bond angle significantly. As observed on comparing the chelate ring in complex **4** with analogous complexes of dppen and dppm, both the metal-phosphorus bonds [$\text{Rh-P}(2)$ 2.271(4), $\text{Ru-P}(1)$ 2.329(4) Å] and the carbon-phosphorus bonds [$\text{P}(1)\text{-C}(3) = \text{P}(2)\text{-C}(3)$ 1.91(1) Å] in the dimetal-diphosphine unit of **6** are longer than the corresponding bonds in $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-dppen})\text{RhCl}_2]$ [Rh-P 2.259(3), Ru-P 2.301(3), $\text{P-C}(=\text{CH}_2)$ 1.823(9), 1.831(9) Å]³⁰ and $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-dppm})\text{RhCl}_2]$ [Rh-P 2.259(4), Ru-P 2.295(4), P-CH_2 1.84(1), 1.85(1) Å].³⁷

Experimental

Methods and Reagents.—General methods were as described in previous papers from this laboratory.^{30,38} The compound $\text{Me}_2\text{C}(\text{PPh}_2)_2$ was prepared from Me_2CCl_2 (Aldrich Chemical Co.) and NaPPh_2 in liquid ammonia by a modification of the literature method,⁸ and recrystallised from propan-1-ol. All reactions were performed using standard Schlenk techniques except where noted. The following complexes were prepared by literature methods: $[\text{RuCl}_2(\text{PPh}_3)_3]$,³⁹ $[\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]$,⁴⁰ and $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$.⁴¹

Synthesis of Complexes.— $[\text{RhCl}(\text{CO})(2,2\text{-dppp})]$ **1**. To a solution of $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ (0.1 g, 0.25 mmol) in acetone (2.5 cm³) was added the diphosphine (0.206 g, 0.50 mmol) with stirring, at room temperature. After 3 h the yellow-orange precipitate was filtered off and dried *in vacuo*. Yield 0.19 g, 67%. The addition of diethyl ether (10 cm³) to the mother-liquor precipitated $[\text{Rh}(2,2\text{-dppp})_2]\text{Cl}$ **3** (0.04 g).

$[\text{RhBr}(\text{CO})(2,2\text{-dppp})]$ **2**. A mixture of solid complex **1** (0.15 g, 0.26 mmol) and LiBr (0.13 g, 1.5 mmol) was taken up in CO-saturated acetone (20 cm³). The solution was refluxed under CO for 2 h, giving a light yellow solution. This was evaporated to dryness. The product was extracted into CH_2Cl_2 (10 cm³) and precipitated by slow addition of heptane. It was filtered off and dried *in vacuo*. Yield 0.12 g, 74%.

$[\text{Rh}(2,2\text{-dppp})_2]\text{Cl}$ **3**. A solution of $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ (0.1 g, 0.25 mmol) in benzene (20 cm³) was treated with the diphosphine (0.43 g, 1.04 mmol) with stirring, at room temperature. Gas was evolved and the solution turned dark orange. After 30 min a light orange precipitate began to appear. After 5 h this was filtered off and dried *in vacuo*. Yield 0.37 g, 78%. A further quantity could be recovered from the mother-liquor by precipitation with heptane.

trans- $[\text{RuCl}_2(2,2\text{-dppm})_2]$ **4**. To $[\text{RuCl}_2(\text{PPh}_3)_3]$ (2.0 g, 2.09 mmol) in CH_2Cl_2 (25 cm³) was added the diphosphine (1.7 g, 4.13 mmol) in CH_2Cl_2 (5 cm³). The mixture was stirred for 2 h, yielding a light brown precipitate. This was filtered off, washed briefly with diethyl ether and dried *in vacuo*. Yield 1.62 g, 82%. A small additional amount of product could be obtained from the mother-liquor by precipitation with ethanol.

$[\text{RuCl}(2,2\text{-dppp})(\eta\text{-C}_5\text{H}_5)]$ **5**. To $[\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]$ (0.20 g, 0.28 mmol) in toluene (100 cm³) was added 2,2-dppp (0.115 g, 0.28 mmol). The solution was refluxed for 5 h. The volume was then reduced to ca. 15 cm³ *in vacuo* and degassed hexane (50 cm³) added. The mixture was set aside at -20°C for 24 h, whereupon an orange precipitate was observed. This was

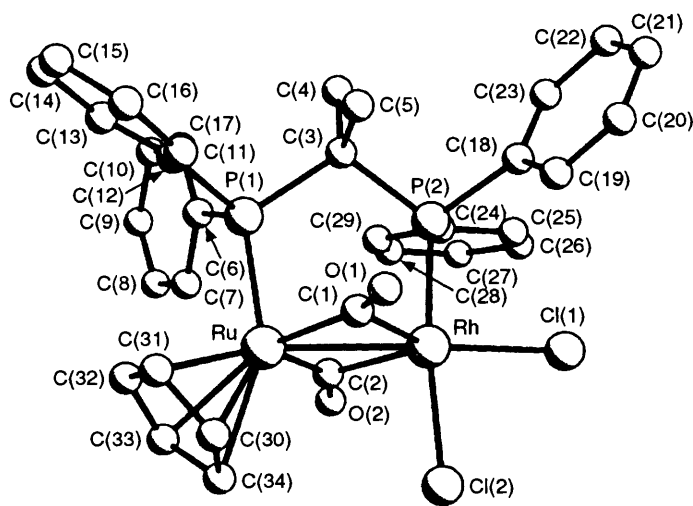


Fig. 3 Molecular structure of $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-}2,2\text{-dppp})\text{RhCl}_2](\text{Rh-Ru})$ **6**

a better representation of the structure may be that shown in Fig. 4, where a ruthenium(II) cation is bonded to a rhodium(I) anion *via* a donor bond. This representation is supported by evidence from the reactivity of $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-dppen})\text{RhCl}_2]$ with CO, when heterolytic Rh-Ru bond cleavage occurs to give a ruthenium cation and a rhodium anion.³⁶ The Rh-Ru bond length in **6** [Rh-Ru 2.697(2)°] is the same as in $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-dppen})\text{RhCl}_2]$ [Rh-Ru 2.697(1)°], whereas in $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-dppm})\text{RhCl}_2]$ the Rh-Ru bond length is significantly longer [2.715(2) Å].³⁷ The $\text{P}(1)\text{-C}(3)\text{-P}(2)$ bond angle [109.9(7)°] in **6** is significantly smaller than the corresponding angle in both the dppen complex [115.1(5)°]³⁰ (where the central carbon is sp² hybridised) and the dppm complex [112.9(6)°].³⁷ Thus the

Table 6 Final positional parameters with e.s.d.s in parentheses for the non-hydrogen atoms of the two independent molecules of $[\text{RuCl}_2(2,2\text{-dppp})(\eta\text{-C}_5\text{H}_5)]$ **5**

Atom	x	y	z	Atom	x	y	z
Ru(1)	0.2457(2)	0.0254(4)	0.0774(1)	C(19)	0.198(1)	-0.044(2)	0.1987(7)
Ru(2)	0.7514(2)	0.0351(4)	0.4112(1)	C(20)	0.205(1)	-0.110(2)	0.2430(8)
Cl(1)	0.2279(7)	0.218(1)	0.1105(4)	C(21)	0.163(1)	-0.083(2)	0.2786(6)
Cl(2)	0.7668(6)	0.232(1)	0.3772(4)	C(22)	0.116(1)	0.010(2)	0.2699(7)
P(2)	0.3581(6)	0.024(1)	0.1186(3)	C(23)	0.110(1)	0.076(2)	0.2255(8)
P(1)	0.2491(6)	-0.072(1)	0.1521(4)	C(24)	0.151(1)	0.048(2)	0.1899(6)
P(3)	0.6421(6)	0.016(1)	0.3658(3)	C(13)	0.244(2)	-0.232(2)	0.144(1)
P(4)	0.7595(6)	-0.064(1)	0.3398(3)	C(14)	0.293(1)	-0.289(3)	0.121(1)
C(30)	0.215(2)	-0.112(4)	0.024(2)	C(15)	0.286(1)	-0.409(3)	0.1089(9)
C(31)	0.155(2)	-0.058(4)	0.032(1)	C(16)	0.229(2)	-0.472(2)	0.120(1)
C(32)	0.157(2)	0.055(4)	0.015(2)	C(17)	0.180(1)	-0.415(3)	0.143(1)
C(28)	0.214(3)	0.067(4)	-0.005(2)	C(18)	0.187(1)	-0.295(3)	0.1550(9)
C(29)	0.253(3)	-0.033(5)	-0.001(2)	C(33)	0.584(1)	0.144(2)	0.3560(8)
C(25)	0.340(2)	-0.029(4)	0.186(1)	C(34)	0.530(1)	0.154(2)	0.3156(7)
C(26)	0.333(2)	0.075(4)	0.219(1)	C(35)	0.488(1)	0.255(2)	0.3107(7)
C(27)	0.382(2)	-0.134(4)	0.212(1)	C(36)	0.502(1)	0.346(2)	0.3461(8)
C(57)	0.851(2)	-0.006(4)	0.465(1)	C(37)	0.556(1)	0.336(2)	0.3865(7)
C(58)	0.821(2)	0.096(3)	0.483(1)	C(38)	0.598(1)	0.234(2)	0.3914(7)
C(59)	0.755(2)	0.075(3)	0.492(1)	C(39)	0.587(1)	-0.104(2)	0.3805(8)
C(60)	0.742(2)	-0.049(3)	0.483(1)	C(40)	0.6187(8)	-0.206(2)	0.4029(8)
C(61)	0.798(2)	-0.101(4)	0.467(1)	C(41)	0.579(1)	-0.305(2)	0.4091(8)
C(62)	0.670(2)	-0.031(4)	0.307(1)	C(42)	0.507(1)	-0.302(2)	0.3929(8)
C(63)	0.625(2)	-0.116(4)	0.272(1)	C(43)	0.4759(8)	-0.200(2)	0.3705(8)
C(64)	0.677(2)	0.078(4)	0.275(1)	C(44)	0.516(1)	-0.101(2)	0.3643(8)
C(1)	0.409(1)	0.161(2)	0.128(1)	C(45)	0.778(1)	-0.223(1)	0.3513(8)
C(2)	0.392(1)	0.247(2)	0.0911(8)	C(46)	0.848(1)	-0.244(2)	0.3711(8)
C(3)	0.429(1)	0.354(2)	0.0945(8)	C(47)	0.8692(8)	-0.358(2)	0.3866(7)
C(7)	0.424(2)	-0.064(3)	0.101(2)	C(48)	0.821(1)	-0.450(1)	0.3824(7)
C(8)	0.488(2)	-0.079(3)	0.132(1)	C(49)	0.752(1)	-0.429(2)	0.3626(8)
C(9)	0.532(2)	-0.168(4)	0.121(1)	C(50)	0.7305(8)	-0.315(2)	0.3471(7)
C(10)	0.512(2)	-0.244(3)	0.080(2)	C(51)	0.821(1)	-0.031(2)	0.2980(8)
C(11)	0.447(2)	-0.229(3)	0.050(1)	C(52)	0.821(1)	-0.099(2)	0.2550(8)
C(12)	0.403(2)	-0.140(4)	0.061(1)	C(53)	0.869(1)	-0.074(2)	0.2236(7)
C(4)	0.483(1)	0.373(2)	0.135(1)	C(54)	0.916(1)	0.019(2)	0.2351(7)
C(5)	0.500(1)	0.287(2)	0.1718(7)	C(55)	0.915(1)	0.087(2)	0.2781(8)
C(6)	0.463(1)	0.180(2)	0.1684(8)	C(56)	0.867(1)	0.062(2)	0.3095(7)

Table 7 Selected bond lengths (Å) and bond angles (°) with e.s.d.s in parentheses for the two independent molecules of $[\text{RuCl}_2(2,2\text{-dppp})(\eta\text{-C}_5\text{H}_5)]$ **5**

Ru(1)–Cl(1)	2.42(1)	Ru(2)–Cl(2)	2.43(1)
Ru(1)–P(1)	2.31(1)	Ru(2)–P(3)	2.27(1)
Ru(1)–P(2)	2.288(9)	Ru(2)–P(4)	2.260(9)
Ru(1)–($\eta\text{-C}_5\text{H}_5$) (mean)	2.18(4)	Ru(1)–($\eta\text{-C}_5\text{H}_5$) (mean)	2.26(3)
P(1)–C(30)	2.09(3)	P(3)–C(62)	1.73(3)
P(2)–C(30)	1.87(3)	P(4)–C(62)	1.89(3)
Cl(1)–Ru(1)–P(1)	91.3(4)	Cl(2)–Ru(2)–P(3)	92.5(3)
Cl(1)–Ru(1)–P(2)	95.1(3)	Cl(2)–Ru(2)–P(4)	95.9(3)
P(1)–Ru(1)–P(2)	72.5(3)	P(3)–Ru(2)–P(4)	71.3(3)
Ru(1)–P(1)–C(30)	95(1)	Ru(2)–P(3)–C(62)	98(1)
Ru(1)–P(2)–C(30)	103(1)	Ru(2)–P(4)–C(62)	94(1)
P(1)–C(30)–P(2)	86(1)	P(3)–C(62)–P(4)	93(1)

filtered off and dried *in vacuo*, affording 0.13 g of impure material ($^3\text{P}\text{-}\{^1\text{H}\}$ NMR evidence; see Results and Discussion). Preparative TLC (silica plates, 2:1 CH_2Cl_2 -toluene) afforded three bands. The third band was pure complex **5**, which was extracted into CH_2Cl_2 , evaporated to dryness and dried further *in vacuo* (45%).

$[\eta^5\text{-C}_5\text{H}_5]\text{Ru}(\mu\text{-CO})_2(\mu\text{-}2,2\text{-dppp})\text{RhCl}_2$ (*Rh*-*Ru*) **6**. To a solution of complex **5** (0.126 g, 0.205 mmol) in toluene (20 cm^3) was added a solution of $[\text{RhCl}_2(\text{CO})_4]$ (0.04 g, 0.103 mmol) in toluene (10 cm^3). The mixture was stirred at room temperature for 0.5 h. On addition of heptane (25 cm^3) a yellow solid was formed. This was filtered off and dried *in vacuo*. An analytically pure sample was obtained by recrystallisation from CH_2Cl_2 -heptane. Yield 0.149 g, 90%.

Crystal Structure Determinations.— $[\text{RuCl}_2(2,2\text{-dppp})_2]$ **4a**. Crystals of complex **4a** were grown from CH_2Cl_2 -hexane and a suitable orange crystal of dimensions 0.20 × 0.10 × 0.20 mm was mounted on a glass fibre.

Crystal data. $\text{C}_{54}\text{H}_{52}\text{Cl}_2\text{P}_4\text{Ru}$, $M = 997$, monoclinic, space group $P2_1/n$, $a = 12.084(2)$, $b = 15.492(5)$, $c = 12.737(4)$ Å, $\beta = 106.99(2)^\circ$, $U = 2280(1)$ Å³ (by least-squares refinement of angles from 25 reflections), Mo-K α radiation, $\lambda = 0.71069$ Å, $Z = 2$, $D_c = 1.452$ g cm^{-3} , $F(000) = 1028$, $\mu = 6.30$ cm^{-1} .

Data collection and processing. Rigaku AFC6S diffractometer, ω - 2θ scan mode with ω scan width = $1.15 + 0.30 \tan \theta^\circ$, graphite-monochromated Mo-K α radiation. 4168 Unique reflections recorded ($\theta_{\text{max}} = 25^\circ$, $0 \leq h \leq 14$, $0 \leq k \leq 18$, $-15 \leq l \leq 15$) of which 3292 with $I > 3\sigma(I)$ were used in refinement. Temperature 153 K. Empirical absorption correction based on azimuthal scans applied. Three standard reflections showed no significant variation during data collection.

Structure analysis and refinement. The structure was solved by direct methods using the TEXSAN structure-analysis package.⁴² All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and were not refined.* Final unweighted and weighted agreement factors $\{R = \sum |F_o| - |F_c| / \sum |F_o|$, $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ were 0.029 and 0.037 respectively. A weighting scheme [$w = 1/\sigma^2(F_o)$] including a factor ($p = 0.03$) to downweight intense reflections was used. The final electron-

* The molecule lies on a centre of symmetry with the Ru atom at the origin.

Table 8 Final positional parameters with e.s.d.s in parentheses for the non-hydrogen atoms of $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-2,2-dppp})\text{RhCl}_2](\text{Rh-Ru})$ **6**. Atoms marked * have occupancy 0.5

Atom	x	y	z	Atom	x	y	z
Rh	-0.142 57(6)	0.252 5(1)	0.890 16(6)	C(16)	0.224(2)	-0.002(1)	0.930(1)
Ru	0.011 57(6)	0.246 9(1)	0.984 05(6)	C(17)	0.159(1)	0.068(1)	0.918(1)
Cl(2)	-0.220 4(2)	0.255 0(4)	1.010 1(2)	C(18)	-0.140(1)	0.171(1)	0.693(1)
Cl(1)	-0.275 2(2)	0.272 9(3)	0.810 4(3)	C(19)	-0.183(1)	0.095(1)	0.722(1)
P(1)	0.096 7(2)	0.243 4(4)	0.873 8(2)	C(20)	-0.217(1)	0.031(1)	0.668(1)
P(2)	-0.083 7(2)	0.251 8(4)	0.767 8(2)	C(21)	-0.210(1)	0.035(1)	0.586(1)
O(1)	-0.080 4(8)	0.065 4(8)	0.933 5(8)	C(22)	-0.171(1)	0.111(1)	0.556(1)
O(2)	-0.068 5(8)	0.432 8(8)	0.933 5(8)	C(23)	-0.136(1)	0.180(1)	0.609(1)
C(1)	-0.063(1)	0.143(1)	0.937(1)	C(24)	-0.091(1)	0.371(1)	0.718 8(9)
C(2)	-0.055(1)	0.348(1)	0.936(1)	C(25)	-0.170(1)	0.391(1)	0.671(1)
C(3)	0.035(1)	0.211(1)	0.770(1)	C(26)	-0.180(1)	0.482(1)	0.642(1)
C(4)	0.073 6(8)	0.250(2)	0.695 3(8)	C(27)	-0.118(1)	0.550(1)	0.660(1)
C(5)	0.034(1)	0.106(1)	0.764(1)	C(28)	-0.044(1)	0.527(1)	0.709(1)
C(6)	0.157(1)	0.353(1)	0.855(1)	C(29)	-0.031(1)	0.438(1)	0.740(1)
C(7)	0.142(1)	0.431(1)	0.902(1)	C(30)	0.008(2)	0.180(2)	1.107(1)
C(8)	0.181(1)	0.516(1)	0.894(1)	C(31)	0.086(2)	0.171(2)	1.085(1)
C(9)	0.234(2)	0.523(1)	0.838(1)	C(32)	0.123(1)	0.261(2)	1.081(1)
C(10)	0.253(1)	0.448(2)	0.786(1)	C(33)	0.066(2)	0.322(1)	1.098(1)
C(11)	0.212(1)	0.363(1)	0.795(1)	C(34)	-0.009(1)	0.272(2)	1.116(1)
C(12)	0.181(1)	0.156(1)	0.892(1)	Cl(3)*	0.526 8(8)	0.235(1)	0.967 7(8)
C(13)	0.271(1)	0.174(1)	0.888(1)	Cl(4)*	0.477(1)	0.341(1)	0.845(1)
C(14)	0.333(1)	0.103(2)	0.902(1)	Cl(35)*	0.557(3)	0.347(3)	0.941(3)
C(15)	0.311(1)	0.016(2)	0.924(1)				

Table 9 Selected bond lengths (Å) and bond angles (°) with e.s.d.s in parentheses for $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-2,2-dppp})\text{RhCl}_2](\text{Rh-Ru})$ **6**

Rh-Ru	2.697(2)	P(1)-C(3)	1.91(1)
Rh-Cl(1)	2.330(4)	P(1)-C(6)	1.86(2)
Rh-Cl(2)	2.393(4)	P(1)-C(12)	1.81(2)
Rh-P(2)	2.271(4)	P(2)-C(3)	1.91(1)
Rh-C(1)	2.09(2)	P(2)-C(18)	1.84(2)
Rh-C(2)	2.01(2)	P(2)-C(24)	1.88(2)
Ru-P(1)	2.329(4)	O(1)-C(1)	1.14(2)
Ru-C(1)	1.98(2)	O(2)-C(2)	1.22(2)
Ru-C(2)	1.90(2)	C(3)-C(4)	1.52(2)
Ru-($\eta\text{-C}_5\text{H}_5$)(mean)	2.22(2)	C(3)-C(5)	1.51(2)
Ru-Rh-Cl(2)	91.5(1)	C(3)-P(1)-C(6)	106.1(7)
Ru-Rh-Cl(1)	174.5(1)	C(3)-P(1)-C(12)	105.2(7)
Ru-Rh-P(2)	95.07(9)	C(6)-P(1)-C(12)	104.4(7)
Ru-Rh-C(1)	46.8(5)	Rh-P(2)-C(3)	116.6(5)
Ru-Rh-C(2)	44.7(6)	Rh-P(2)-C(18)	112.3(6)
Cl(2)-Rh-Cl(1)	88.1(2)	Rh-P(2)-C(24)	110.8(5)
Cl(2)-Rh-P(2)	173.5(1)	C(3)-P(2)-C(18)	102.3(7)
Cl(2)-Rh-C(1)	92.1(5)	C(3)-P(2)-C(24)	107.7(7)
Cl(2)-Rh-C(2)	93.4(6)	C(18)-P(2)-C(24)	106.5(7)
Cl(1)-Rh-P(2)	85.4(1)	Rh-C(1)-Ru	83.0(6)
Cl(1)-Rh-C(1)	138.7(5)	Rh-C(1)-O(1)	126(1)
Cl(1)-Rh-C(2)	129.8(6)	Ru-C(1)-O(1)	151(2)
P(2)-Rh-C(1)	92.7(5)	Rh-C(2)-Ru	87.1(8)
P(2)-Rh-C(2)	91.0(6)	Rh-C(2)-O(2)	124(1)
C(1)-Rh-C(2)	91.5(6)	Ru-C(2)-O(2)	148(1)
Rh-Ru-P(1)	95.7(1)	P(1)-C(3)-P(2)	109.9(7)
P(1)-Ru-C(1)	92.3(5)	P(1)-C(3)-C(4)	115(1)
P(1)-Ru-C(2)	91.5(7)	P(1)-C(3)-C(5)	108(1)
C(1)-Ru-C(2)	98.2(5)	P(2)-C(3)-C(4)	109(1)
Ru-P(1)-C(3)	114.3(5)	P(2)-C(3)-C(5)	108(1)
Ru-P(1)-C(6)	115.8(6)	C(4)-C(3)-C(5)	108(1)
Ru-P(1)-C(12)	110.1(5)		

density difference map showed no peaks >0.41 or <-0.33 $\text{e} \text{ \AA}^{-3}$.

$[\text{RuCl}_2(2,2\text{-dppp})(\eta\text{-C}_5\text{H}_5)]$ **5**. Crystals of complex **5** were grown from a toluene-heptane solution and a suitable orange crystal of dimensions $0.20 \times 0.10 \times 0.35$ mm was mounted on a glass fibre.

Crystal data. $\text{C}_{32}\text{H}_{31}\text{ClP}_2\text{Ru}$, $M = 614$, monoclinic, space group $P2_1/n$, $a = 19.64(1)$, $b = 11.29(1)$, $c = 27.006(8)$ Å, $\beta =$

$100.04(3)^\circ$, $U = 5898(8)$ Å³ (by least-squares refinement of angles from 18 reflections), Mo-K α radiation, $\lambda = 0.710 69$ Å, $Z = 8$, $D_c = 1.383$ g cm⁻³, $F(000) = 2512$, $\mu = 7.37$ cm⁻¹.

Data collection and processing. Diffractometer and radiation as for complex **4a**, ω scan mode with ω scan width = $0.76 + 0.30 \tan \theta^\circ$. 10 230 Reflections recorded ($\theta_{\text{max}} = 25^\circ$, $0 \leq h \leq 21$, $0 \leq k \leq 13$, $-31 \leq l \leq 31$) of which 2194 with $I > 4\sigma(I)$ were used in refinement. Temperature 296 K. Other details as for **4a**.

Structure analysis and refinement. Direct methods as for complex **4a**. The Ru, Cl and P atoms were refined anisotropically, all other non-hydrogen atoms were refined isotropically. The phenyl groups were treated as rigid bodies (C-C 1.40 Å). Hydrogen atoms treated as for **4a**. There are two molecules in the asymmetric unit which show some differences in bond lengths and angles but the general molecular arrangement is the same. Refinement was hampered by disorder of one of the phenyl rings in one molecule [C(7)-C(12)] which could not be satisfactorily modelled. Final R and R' 0.078 and 0.099 respectively. The final electron-density difference map showed no peaks >1.32 or <-0.70 $\text{e} \text{ \AA}^{-3}$.

$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-2,2-dppp})\text{RhCl}_2] \cdot 0.5\text{CH}_2\text{Cl}_2$ **6**. Crystals of complex **6** were grown from a CH_2Cl_2 -heptane solution and a suitable yellow crystal of dimensions $0.4 \times 0.1 \times 0.3$ mm was mounted on a glass fibre.

Crystal data. $\text{C}_{34}\text{H}_{31}\text{Cl}_2\text{O}_2\text{P}_2\text{RhRu} \cdot 0.5\text{CH}_2\text{Cl}_2$, $M = 851$, monoclinic, space group $P2_1/n$, $a = 15.441(7)$, $b = 14.278(4)$, $c = 16.273(6)$ Å, $\beta = 95.76(3)^\circ$, $U = 3570(2)$ Å³ (by least-squares refinement of angles from 16 reflections), Mo-K α radiation, $\lambda = 0.710 69$ Å, $Z = 4$, $D_c = 1.587$ g cm⁻³, $F(000) = 1706$, $\mu = 12.14$ cm⁻¹.

Data collection and processing. Diffractometer radiation and scan mode as for complex **4a**; ω scan width = $1.57 + 0.30 \tan \theta^\circ$. 6558 Unique reflections recorded ($\theta_{\text{max}} = 25^\circ$, $0 \leq h \leq 17$, $0 \leq k \leq 16$, $-19 \leq l \leq 19$) of which 2543 with $I > 3\sigma(I)$ were used in refinement. Other details as for **4a**.

Structure analysis and refinement. Direct methods as for complex **4a**. All non-hydrogen atoms were refined anisotropically except for those of the solvent molecule which was refined isotropically. The hydrogen atoms were placed in calculated positions and assigned isotropic thermal parameters 20% greater than the B_{equiv} value of the atom to which they were bonded. Final R and R' 0.050 and 0.062 respectively. The final

electron-density difference map showed no peaks > 1.66 or $< -0.89 \text{ e } \text{\AA}^{-3}$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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