Bis(allyl) Ruthenium(IV) Complexes. Part 2.[1] Ruthenium Complexes containing σ- and μ-Pyrazine and σ- and μ-Bis(diphenylphosphino)methane (dppm) Ligands. Crystal Structures of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-dppm})]\cdot Me_2CO\cdot CH_2Cl_2$ and $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}(\mu\text{-dppm})]\cdot 1.5CHCl_3$†

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Reaction of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1** ($C_{10}H_{16}$ = 2,7-dimethyloctadienediyl) with one equivalent of pyrazine (pyz) or bis(diphenylphosphino)methane (dppm) leads to the formation of the neutral dimeric products $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-pyz})]$ **2a** and $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-dppm})]$ **2b** respectively. The neutral monomeric complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(\sigma\text{-pyz})]$ **3a** and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(\sigma\text{-dppm})]$ **3b** are obtained by reacting **1** with two equivalents of pyz and dppm respectively. The mixed valence diruthenium complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}(\mu\text{-dppm})]$ **5** is readily obtained from the reaction of **3b** with $[\{Ru(\eta^6\text{-}C_6H_6)(\mu\text{-}Cl)Cl\}_2]$ **4**. The X-ray structures of complex **2b** [space group $P\bar{1}$ (no. 2), a = 11.914(1), b = 11.943(2), c = 19.524(2) Å, α = 105.79(1), β = 107.64(1), γ = 91.01(1)°, Z = 2], and complex **5** [space group $P2_1$ (no.4), a = 10.259(1), b = 21.284(2), c = 21.058(3) Å, β = 94.48(1)°, Z = 4] are reported.

Cleavage of the dimeric chloro-bridged complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1** ($C_{10}H_{16}$ = 2,7-dimethyloctadienediyl) by monodentate ligands,[2–4] bidentate ligands,[1] and co-ordinating solvents[5] to form neutral monomeric complexes of the type $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})LCl_2]$ and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(L\frown S)Cl]$ is now well established. In addition to the neutral complexes, we have found that the cationic complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(L\frown S)(NCMe)][X]$ ($L\frown S$ = benzothiazole-2-thiolate, X = BF_4^-; $L\frown S$ = pyridine-2-thiolate, X = PF_6^-) are readily formed.[1] However, to date there have been no reports on the formation of dimeric ruthenium(IV) complexes from **1**.

The synthesis and study of binuclear complexes often has as motivating factor the possible role co-operative effects, brought about by the close proximity of two metal centres, might play in substrate activation and catalysis.[6–9] However, not many synthetic routes exist (mainly because of the unavailability of suitable starting materials) for the rational preparation of either homo- or hetero-bimetallic complexes. One attractive synthetic route involves the use of the free phosphorus atom in σ-dppm [dppm = bis(diphenylphosphino)methane] complexes to co-ordinate to a second metal centre, and so form dimeric complexes.[10,11]

The dppm chemistry of ruthenium is surprisingly sparse and mainly restricted to mononuclear complexes,[12,13] and to our knowledge is non-existent for ruthenium in the +4 oxidation state. As noted by Shaw and co-workers,[11] dimeric complexes containing single dppm bridges, in the absence of other bridging ligands or metal–metal bonds, are exceptionally rare. Examples include a ruthenium(II) dimer,[14] and a metal–metal bonded ruthenium(I) dimer.[15]

The use of pyrazine as a bridging ligand in binuclear ruthenium complexes has, by and large, been restricted to the well known Creutz–Taube type complexes in which the ruthenium atoms are present as $Ru^{II}Ru^{II}$ or $Ru^{III}Ru^{III}$ species, or as mixed valence $Ru^{II}Ru^{III}$ species.[16]

In this paper we report the synthesis and characterisation of the first dimeric ruthenium(IV) complexes in which pyrazine and dppm act as single bridging ligands. In addition to the dimeric complexes $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-}L\frown L)]$ ($L\frown L$ = pyz **2a** or dppm **2b**), we have prepared the corresponding monomeric complexes, $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(\sigma\text{-}L\frown L)]$ ($L\frown L$ = pyz **3a** or dppm **3b**), in which the pyrazine and dppm are co-ordinated as pendulous monodentate ligands. The σ-dppm complex **3b** is shown to be a useful synthetic precursor for the rational synthesis of the mixed-valence ruthenium dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}(\mu\text{-dppm})]$ **5**. The X-ray structures of complexes **2b** and **5** are reported.

Results and Discussion

Reaction of the dimeric complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1** with one equivalent of either pyrazine or dppm in CH_2Cl_2 (Scheme 1) rapidly leads to quantitative formation of the dimeric products $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-pyz})]$ **2a** and $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-dppm})]$ **2b** respectively. Both complexes are stable to air in solutions of polar non-co-ordinating solvents (*e.g.* CH_2Cl_2 or $CHCl_3$), and in the solid state.

Although the dimeric nature of these complexes is readily deduced from the relative intensities of the octadienediyl groups and the bridging ligands (2:1) in the ^1H NMR spectra (Table 1), closer examination of these spectra together with the $^{13}C\text{-}\{^1H\}$ spectra, and the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2b** (Table 2) reveals an underlying complexity.

The ^1H NMR spectrum of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-pyz})]$ **2a** recorded at 303 K has two separate sets of resonances of approximately equal intensity for the pyrazine protons, and,

† μ-Bis(diphenylphosphino)methane-bis{dichloro[(1,2,3,6,7,8-η)-2,7-dimethylocta-2,6-diene-1,8-diyl]ruthenium}–acetone–dichloromethane (1/1/1) and 1(η⁶)-Benzene-μ-bis(diphenylphosphino)methane-tetrachloro-1κ²*Cl*,2κ²*Cl*-[2(1,2,3,6,7,8-η)-2,7-dimethylocta-2,6-diene-1,8-diyl]-diruthenium–chloroform(2/3).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

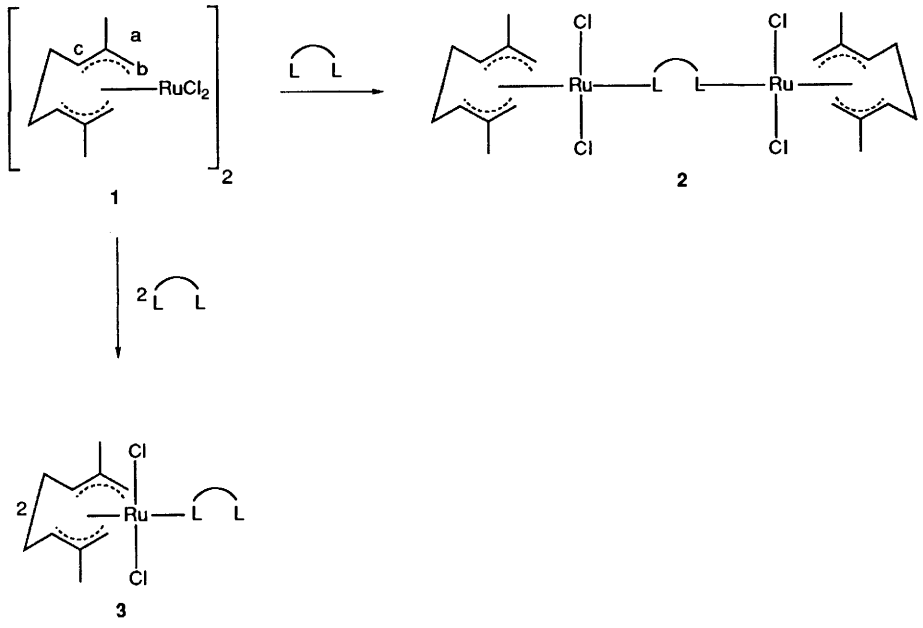


Fig. 1 Schematic representation of the proposed isomeric forms of **2a** (L⌒L = pyz) and **2b** (L⌒L = dppm)

with the exception of the H_c protons, all the octadienediyl protons also show a doubling of resonances. Similarly, with the exception of the aliphatic methylene and methyl groups of the octadienediyl moiety, and the pyrazine ligand itself, the ^{13}C-$\{^1H\}$ NMR spectrum of **2a** shows a doubling of all the octadienediyl carbon resonances. These observations suggest either some form of asymmetry within the dimer, or the presence of two different isomers in solution.

Based on NMR evidence, Cox and Roulet[5] have proposed that, in solutions of non-co-ordinating solvents, the parent dimer **1** exists in two diastereoisomeric forms, the so-called C_i and C_2 isomers. Their observation that these isomers of **1** are present in an approximate 1:1 ratio in non-co-ordinating solvents has subsequently been confirmed by us.[1] It thus seems likely that the product obtained from the reaction of **1** with a bridging ligand should, in similar fashion to complex **1** itself, exist as a mixture of two isomers (Fig. 1).

Because of the planarity of the pyrazine ligand,[16] one would expect complex **2a** to be a linear molecule in which *cis–trans* isomerism of the $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2]$ units about the pyrazine N ··· N axis is not possible. Thus, the pyrazine ligand can bridge two $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2]$ groups in which either (*i*) the octadienediyl groups are related by a centre of inversion (*i.e.* a pyrazine-bridged C_i dimer), or (*ii*) by a C_2 axis of symmetry (*i.e.* a pyrazine bridged C_2 dimer). The presence of approximately equimolar amounts of the proposed isomeric forms of complex **2a** would explain both the observed doubling of the ^1H and ^{13}C-$\{^1H\}$ NMR resonances, and the relative intensities of the ^1H resonances at 303 K.

The ^1H NMR spectrum of complex **2a** in $CDCl_3$ was further investigated over the temperature range 303–323 K. As the temperature is increased, so the pyrazine and octadienediyl resonances which show doubling at 303 K begin to merge into single resonances. Although the Me resonances are completely merged into a single resonance (δ 2.39) at 323 K, the resonances due to the pyrazine and relevant octadienediyl protons are not completely coalesced at this temperature.

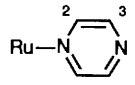
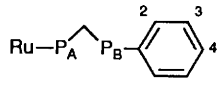
These results suggest that (*i*) in solution at 303 K, complex **2a** exists as an approximately equimolar mixture of the proposed isomers (Fig. 1), (*ii*) at 303 K the $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2]$ groups in the respective isomers adopt similar orientations with respect to the plane of the pyrazine ligand, with little or no rotation about the Ru–N bonds; the presence of, say, two different rotamers per isomer would lead to four sets of resonances instead of the two sets observed, and (*iii*) at elevated temperatures the barrier to rotation about the Ru–N bonds is overcome, and the resulting increased rotation about these bonds leads to an averaged spectrum for the two isomers.

As with complex **2a**, the compound $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-dppm})]$ **2b** shows a similar doubling of NMR resonances. In the ^1H spectrum recorded at 303 K, the terminal allyl protons, H_a, and the internal allyl protons, H_c, appear as broad multiplets while the remaining octadienediyl protons give rise to two sets of resonances. In addition, the methylene protons of the dppm ligand give rise to two resonances at δ 4.88 and 4.68. Selective decoupling of either resonance has no effect on the multiplicity of the remaining resonance. This clearly shows the presence of two distinctly different molecules in solution which, from the relative intensities of the proton resonances, are present in an approximately equimolar amount.

Although the phenyl region of the ^{13}C-$\{^1H\}$ NMR spectrum (303 K) of **2b** is complex, all the octadienediyl carbons give rise to two sets of resonances, as does the methylene carbon of the dppm ligand. The presence of two different molecules in solution is further illustrated by the ^{31}P-$\{^1H\}$ NMR spectrum of **2b** which consists of two distinct singlets 1.1 ppm apart when recorded at 303 K.

The variable-temperature ^1H NMR study of complex **2b** reveals that, unlike **2a**, the spectrum remains unchanged over the temperature range 303–323 K. However, when **2b** is cooled below 303 K, the proton spectrum shows an initial broadening of all the resonances, with the exception of the CH_2 resonance at δ 2.58 which remained essentially unchanged over the entire temperature range studied. At 233 K the methyl resonances had merged to give a single broad peak at δ 2.11, while the H_b protons had merged to give a single broad resonance at δ 3.29. At this temperature the phenyl protons give rise to three broad resonances at δ 7.39, 7.16 and 6.98. The merging of peaks continued up to 216 K, at which point significant broadening of the peaks occurred due to partial precipitation of **2b** from solution. However, it was clear that the P–CH_2–P protons had merged sufficiently to give rise to a broad resonance at δ 4.68. In addition, at 216 K, the ^{31}P-$\{^1H\}$ spectrum of **2b** reveals the presence of a single relatively sharp peak at δ 23.42. Furthermore, it is important to note that where merging of peaks occurred (in both the ^1H and ^{31}P-$\{^1H\}$ NMR), the

Table 1 Proton NMR data for the new complexes[a]

Complex	Octadienediyl[b] H_a	H_b	H_c	CH_2	Me	Other[c]
2a	4.65 (s, 4 H) 4.61 (s, 4 H)	4.39 (s, 4 H) 4.34 (s, 4 H)	5.29 (m, 8 H)	3.06 (m, 8 H) 2.45 (m, 8 H)	2.39 (s, 12 H) 2.38 (s, 12 H)	9.33 (s, 4 H, pyz-H) 9.25 (s, 4 H, pyz-H)
2b	4.19 (m, 8 H)	3.31 (s, 4 H) 3.15 (s, 4 H)	5.22 (m, 8 H)	3.37 (m, 8 H) 2.58 (m, 8 H)	2.14 (s, 12 H) 2.11 (s, 12 H)	7.61 (m, 4 H, Ph), 7.52–7.39 (m, 14 H, Ph), 7.24–7.12 (m, 8 H, Ph), 7.09–6.93 (m, 14 H, Ph), 4.88 [br t, 2 H, J(H–P) 7.00, PCH_2P], 4.68 [merged dt, 2 H, J(HH) 16.2, J(H–P) 8.10, PCH_2P] 
3a	4.58 (s, 2 H)	4.40 (s, 2 H)	5.29 (m, 2 H)	3.06 (m, 2 H) 2.45 (m, 2 H)	2.38 (s, 6 H)	9.27 [dd, 2 H, $^3J(H^2H^3)$ 3.25, $^5J(H^2H^3)$ 0.85, H^2], 8.60 [dd, 2 H, $^3J(H^3H^2)$ 3.25, $^5J(H^3H^2)$ 0.85, H^3] 
3b[d]	4.20 [d, 2 H, J(H–P_a) 9.25]	3.30 [d, 2 H, J(H–P_a) 3.54]	5.14 (br m, 2 H)	3.41 (m, 2 H) 2.62 (m, 2 H)	2.13 (s, 6 H)	7.61 (m, 4 H, H^4), 7.3–7.1 (m, 16 H, H^2 and H^3), 3.71 [ddd, 1 H, J(HH) 15.26, J(H–P_a or H–P_b) 8.72, J(H–P_b or H–P_a) 2.27, PCH_2P], 3.41 (m, 1 H, PCH_2P)
5[e]	4.01 [d, 2 H, J(H–P) 9.49]	2.97 [d, 2 H, J(H–P) 3.47]	5.10 (m, 2 H)	3.33 (m, 2 H) 2.52 (m, 2 H)	2.08 (s, 6 H)	7.70 (m, 2 H, H^4), 7.57 (m, 2 H, H^4), 7.48–7.14 (m, 8 H, Ph), 7.09 (m, 4 H, Ph), 6.98 (m, 2 H, Ph), 6.87 (m, 2 H, Ph), 5.16 (s, 6 H, Ru–arene), 4.98 [merged ddd, 1 H, J(HH) 16.0, J(H–P) 8.10, J(H–P′) 7.48, PCH_2P], 4.59 [merged ddd, 1 H, J(HH) 16.0, J(H–P) 10.95, J(H–P′) 5.50, PCH_2P]

[a] All spectra recorded at 303 K in $CDCl_3$. Chemical shift (δ) in ppm. [b] Numbering shown in Scheme 1. [c] Given as: chemical shift (δ) in ppm, multiplicity, relative intensity, J/Hz, assignment. pyz = pyrazine. [d] Accidental overlap of octadienediyl CH_2 and PCH_2P observed in two-dimensional ^1H–^{13}C HETCOR (heteronuclear correlation) spectrum. [e] Numbering of dppm phenyl protons as for complex **3b**.

position of the corresponding low-temperature resonance is in close agreement with that found for one of the sets of resonances at 303 K.

In complex **2b**, the two $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2]$ units are bridged by a flexible, yet sterically demanding, dppm ligand. Thus in **2b**, unlike complex **2a** which is certainly a linear molecule due to the rigidity of the pyrazine ligand,[16] it is conceivable that certain conformations (*e.g. cis* or *trans* with respect to the orientation of the phenyl groups, or the metal centres, about the P • • • P axis) might be energetically favoured and hence predominate in solution. Consequently one could envisage at least four different isomers for complex **2b** namely the *cis* and *trans* C_i isomers, and the *cis* and *trans* C_2 isomers (Fig. 1). Naturally, each of these isomers would give rise to a distinct set of NMR resonances. However, since a maximum of only two sets of resonances are observed over the temperature range studied, it follows that only two of the possible isomers are present in solution at temperatures above 233 K, and that at temperatures below this value there is a conversion to only one isomeric form of **2b**.

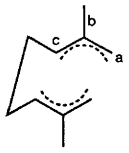
Should complex **2b** be present in solution as a mixture of the C_i and C_2 isomers at high temperatures, one would not expect selective conversion to either isomer at low temperatures since this process would require breakage of the Ru–P bonds (see ref. 5). It would thus appear that, in solution, complex **2b** is present as either the C_i or the C_2 dimer, but not both. Evidence for this is provided by the X-ray structure of **2b** which clearly shows that the complex is present as the C_i dimer only, and that in the solid state an approximate *cis* conformation is adopted (see below). It thus seems reasonable to assume that, in solution, complex **2b** exists only as the C_i dimer, and that at relatively high temperatures (>233 K) it is the presence of approximately equimolar amounts of the *cis* and *trans* C_i isomers which give rise to the doubling of the spectrum. At relatively low temperatures (<233 K) the molecule adopts a lower-energy conformation (it is not clear whether this is the *cis* or *trans* conformation in solution) which leads to the presence of a single isomer, and hence a simplified spectrum.

In the case of complex **2b** the selective formation of the C_i dimer from $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1**, which is itself present as a mixture of the C_i and C_2 isomers,[5] is most likely due to the steric requirements of the bridging dppm ligand. The fact that the complex $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\sigma\text{-dppm})]$ is stable (see discussion of complex **3b**), suggests that the reaction is probably a stepwise process in which the σ complex is the first product formed. In the second step the remaining parent dimers would then be selectively cleaved to give the final product which consists solely of C_i dimers.

The NMR data for **2a** and **2b** are consistent with a trigonal bipyramidal geometry about the ruthenium centres in which the octadienediyl groups, together with the pyrazine or dppm ligands, occupy equatorial positions, while the chloride ligands occupy the axial positions. This co-ordination geometry is confirmed by the X-ray structural analyses of **2b** and **5** (see below).

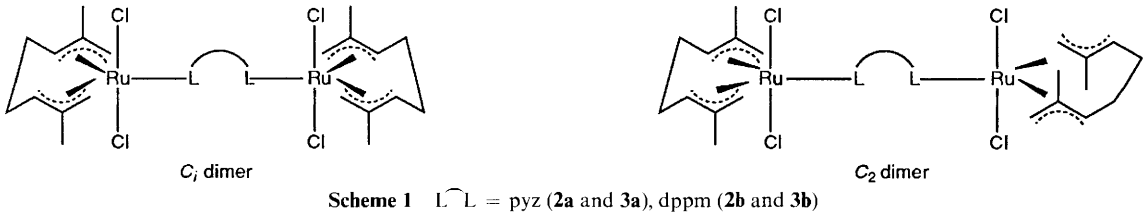
By treating complex **1** with two equivalents of pyrazine or dppm in CH_2Cl_2 (Scheme 1), it is possible to form the corresponding monomeric complexes $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\sigma\text{-pyz})]$ **3a** and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\sigma\text{-dppm})]$ **3b** in which the second donor atom of the pyrazine and dppm ligands is

Table 2 ^{13}C-{^1H} and ^{31}P-{^1H} NMR data for the new complexes[a]



	Octadienediyl						
Complex	C_a	C_b	C_c	CH_2	Me	Other[b]	^{31}P-{^1H}[c]
2a	79.7 79.5	132.0 131.9	96.6 96.0	36.1	21.1	149.4 (pyz-C)	
2b[d,e]	68.6 68.5	124.9 124.5	106.2 [dd, ^2J(C–P) 16.2, ^4J(C–P) 4.83], 106.1 [dd, ^2J(C–P) 16.1, ^4J(C–P) 4.83]	36.3 36.25	20.8 20.7	134.5 [br d, J(C–P) 10.8, C^2], 133.5 [br d, J(C–P) 11.1, C^2], 129.8, 129.4, 129.2 (C^4 or C^3), 126.5, 126.4, 126.35, 126.3 (C^3 or C^4), 125.9 [d, J(C–P) 6.79, C^3], 21.6 [t, J(C–P) 8.00, P–C–P], 21.2 [t, J(C–P) 8.04, P–C–P]	23.48, 22.38
3a	79.4	131.8	95.7	36.1	21.1	149.2 (C^2), 145.2 (C^3)	
3b[e]	67.2	124.3	107.0	36.2	20.4	Phenyls at P_a: 139.2 [dd, J(C–P_a) 14.3, J(C–P_b) 7.25, C^1], 134.3 [d, J(C–P_a) 7.40, C^4], 132.8 [d, J(C–P_a) 22.0, C^2], 132.0 [d, J(C–P_a) 20.2, C^2], 128.0 [pseudo t, J(C–P_a) 6.8, C^3]. Phenyls at P_b: 137.9 [dd, J(C–P_b) 14.6, J(C–P_a) 3.32, C^1], 132.7 [d, J(C–P_b) 7.17, C^4], 129.6 [d, J(C–P_b) 18.7, C^2], 128.2 [d, J(C–P_b) 20.4, C^2], 127.2 [d, J(C–P_b) 9.21, C^3], 126.9 [d, J(C–P_b) 9.89, C^3], 25.9 [dd, J(C–P_a or C–P_b) 33.6, J(C–P_b or C–P_a) 25.6, P–C–P]	20.28 [d, J(P_a–P_b) 39.4, P_a], −25.43 [d, J(P_b–P_a) 39.4, P_b]
5[d,f]	68.3 [d, J(C–P) 4.38]	126.7	105.9 [d, J(C–P) 9.43]	36.5	20.8	135.0 [d, J(C–P) 9.58, C^2], 134.2 [d, J(C–P) 7.25, C^2], 133.1 [d, J(C–P) 7.62, C^2], 132.6 [d, J(C–P) 8.60, C^2], 131.0, 130.6, 129.3 (C^4), 127.9–127.6 (C^3), 126.5–126.1 (C^3), 20.8 (P–C–P)	21.87 (AB system)

[a] All spectra recorded at 303 K in $CDCl_3$. Chemical shift (δ) in ppm. [b] Where coupling to phosphorus occurs, data given as: chemical shift (δ), multiplicity, J/Hz, assignment. pyz = pyrazine. [c] Relative to 85% H_3PO_4. [d] Quaternary carbons, C^1, obscured by other phenyl resonances. [e] Assigned with the aid of two-dimensional ^1H–^{13}C HETCOR spectrum. [f] Accidental overlap of Me and P–C–P resonances. Number of phenyl carbons as for **2b**.



C_i dimer C_2 dimer

Scheme 1 L⌒L = pyz (**2a** and **3a**), dppm (**2b** and **3b**)

unco-ordinated. Interestingly, complex **3b** is obtained in quantitative yield while complex **3a** cannot be isolated in pure form as it exists in equilibrium with the dimer **2a** in solution. The equilibrium, **2a** + pyrazine ⇌ 2(**3a**), is proposed on the basis of the NMR data which indicate that all three species are present in solution. Furthermore, at high temperature (323 K) the resonances due to the σ- and μ-pyrazine protons, the free pyrazine protons (δ 8.57), and the H_a, H_b and Me protons of both complexes are broad, which clearly indicates a dynamic process. From the relative intensities of the three species in the ^1H NMR spectrum ($CDCl_3$ at 303 K) the equilibrium constant is estimated to be $K \approx 6.8$.

Although sufficiently stable for most laboratory manipulations, complex **3b** does decompose slowly in solution (days) to form a mixture of products which could not be identified. Presumably the decomposition pathway involves, in part, chelation of the dppm and dimer formation. However, complex **3b** is stable in the solid state and samples have been kept for several weeks, in air at room temperature, with no apparent decomposition.

Table 3 Selected bond lengths (Å) and angles (°)

(*a*) For **2b**

Ru(1)–Cl(1)	2.429(2)	Ru(2)–Cl(3)	2.400(2)
Ru(1)–Cl(2)	2.407(3)	Ru(2)–Cl(4)	2.419(2)
Ru(1)–P(1)	2.449(2)	Ru(2)–P(2)	2.451(2)
Ru(1)–C(2)	2.211(6)	Ru(2)–C(37)	2.212(8)
Ru(1)–C(3)	2.296(8)	Ru(2)–C(38)	2.276(9)
Ru(1)–C(4)	2.294(9)	Ru(2)–C(39)	2.308(7)
Ru(1)–C(7)	2.272(8)	Ru(2)–C(42)	2.263(8)
Ru(1)–C(8)	2.288(7)	Ru(2)–C(43)	2.262(9)
Ru(1)–C(9)	2.270(6)	Ru(2)–C(44)	2.243(8)
P(1)–C(23)	1.850(8)	P(2)–C(23)	1.845(8)
P(1)–C(arene, av.)	1.824(6,7)	P(2)–C(arene, av.)	1.827(7,8)
Cl(1)–Ru(1)–Cl(2)	175.6(1)	Cl(3)–Ru(2)–Cl(4)	173.2(1)
Cl(1)–Ru(1)–P(1)	84.8(1)	Cl(3)–Ru(2)–P(2)	90.3(1)
C(3)–Ru(1)–C(8)	130.0(3)	C(38)–Ru(2)–C(43)	128.8(3)
Cl(1)–Ru(1)–C(3)	100.9(3)	Cl(3)–Ru(2)–C(38)	80.7(2)
Cl(1)–Ru(1)–C(8)	84.4(3)	Cl(3)–Ru(2)–C(43)	98.8(3)
Ru(1)–P(1)–C(23)	109.0(2)	Ru(2)–P(2)–C(23)	108.6(2)
P(1)–C(23)–P(2)	133.5(4)		

(*b*) For **5**

Molecule A		Molecule B	
Ru(1)–Cl(1)	2.409(2)	Ru(1)–Cl(1)	2.435(3)
Ru(1)–Cl(2)	2.432(2)	Ru(1)–Cl(2)	2.418(3)
Ru(1)–P(1)	2.447(2)	Ru(1)–P(1)	2.425(2)
Ru(1)–C(3)	2.309(10)	Ru(1)–C(3)	2.301(12)
Ru(1)–C(8)	2.251(9)	Ru(1)–C(8)	2.282(11)
Ru(2)–Cl(3)	2.403(2)	Ru(2)–Cl(3)	2.413(2)
Ru(2)–Cl(4)	2.401(2)	Ru(2)–Cl(4)	2.412(3)
Ru(2)–P(2)	2.363(2)	Ru(2)–P(2)	2.367(2)
Ru(2)–C(arene, av.)	2.195(8,9)	Ru(2)–C(arene, av.)	2.178(11,14)
P(1)–C(23)	1.816(8)	P(1)–C(23)	1.797(8)
P(2)–C(23)	1.841(7)	P(2)–C(23)	1.850(7)
P–C(arene, av.)	1.830(8)	P–C(arene, av.)	1.845(8,9)
Cl(1)–Ru(1)–Cl(2)	175.2(1)	Cl(1)–Ru(1)–Cl(2)	174.4(1)
Cl(1)–Ru(1)–P(1)	90.2(1)	Cl(1)–Ru(1)–P(1)	84.3(1)
C(3)–Ru(1)–C(8)	131.1(3)	C(3)–Ru(1)–C(8)	130.0(4)
Cl(1)–Ru(1)–C(3)	99.0(2)	Cl(1)–Ru(1)–C(3)	84.6(3)
Cl(1)–Ru(1)–C(8)	81.8(2)	Cl(1)–Ru(1)–C(8)	99.9(3)
Ru(1)–P(1)–C(23)	109.1(2)	Ru(1)–P(1)–C(23)	110.8(2)
Cl(3)–Ru(2)–Cl(4)	87.7(1)	Cl(3)–Ru(2)–Cl(4)	87.5(1)
P(2)–Ru(2)–Cl(3)	86.8(1)	P(2)–Ru(2)–Cl(3)	87.1(1)
P(1)–C(23)–P(2)	132.4(4)		

The NMR spectra of these monomeric complexes are simplified since isomers similar to those proposed for the dimeric complexes are not possible. Nevertheless, depending on the arrangement of the octadienediyl ligand about the ruthenium, it is possible to have chiral isomers. Such chiral monomeric complexes would, however, give rise to identical NMR spectra and would thus be indistinguishable by this technique. However, the existence of such chiral isomers can be inferred from the X-ray structure of complex **5** which reveals the presence of chiral $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2]$ units.

With the exception of the aliphatic methylene protons in **3a**, the ^1H NMR spectra of **3a** and **3b**, recorded at 303 K, show single resonances for the chemically equivalent protons. Similarly, the $^{13}C\text{-}\{^1H\}$ NMR spectra (303 K) of **3a** and **3b** show single resonances for like carbons in the octadienediyl groups. This implies that the two halves of the octadienediyl ligand are in equivalent environments in complexes **3a** and **3b**, and that at 303 K there is free rotation about the Ru–N and Ru–P bonds in the respective complexes. A trigonal bipyramidal geometry about the ruthenium atoms in which the octadienediyl moieties and the pyrazine, or dppm, ligands are co-ordinated in the equatorial plane is consistent with the NMR data for complexes **3a** and **3b** respectively.

Monodentate co-ordination of the pyrazine ligand in $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(\sigma\text{-pyz})]$ **3a** is reflected by the ^1H NMR spectrum in which the pyrazine protons give rise to two doublets of doublets 0.7 ppm apart. The asymmetry imparted on the pyrazine ligand due to this mode of co-ordination is also reflected in the $^{13}C\text{-}\{^1H\}$ NMR spectrum in which the two carbons attached to the co-ordinated N atom are shifted 4 ppm downfield with respect to the carbons which are attached to the free N atom.

The clearest indication for monodentate co-ordination of the dppm ligand in $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(\sigma\text{-dppm})]$ **3b** is provided by the $^{31}P\text{-}\{^1H\}$ NMR spectrum. The co-ordinated phosphorus gives rise to a doublet which is shifted 46 ppm downfield from the doublet of the unco-ordinated phosphorus atom. This mode of co-ordination is confirmed by the $^{13}C\text{-}\{^1H\}$ NMR spectrum in which the methylene carbon of the dppm ligand gives rise to a doublet of doublets as a result of coupling to the two non-equivalent phosphorus atoms.

Synthetic interest in $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(\sigma\text{-dppm})]$ **3b** lies in the unco-ordinated phosphorus atom which is available for co-ordination to a second metal centre. In this sense, complex **3b** could be regarded as an exotically substituted phosphine which could serve as a useful synthon for the rational preparation of asymmetric dimers. We investigated this possibility by treating a freshly prepared solution of **3b** with one equivalent of the known[17] ruthenium(II) arene dimer $[\{Ru(\eta^6\text{-}C_6H_6)(\mu\text{-Cl})Cl\}_2]$ **4** [equation (1)]. The chloro bridges in **4** are readily cleaved,

$$\mathbf{3b} + [\{Ru(\eta^6\text{-}C_6H_6)(\mu\text{-Cl})Cl\}_2] \longrightarrow [\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}(\mu\text{-dppm})] \quad (1)$$

leading to the formation of the dppm bridged $Ru^{IV}Ru^{II}$ mixed valence dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}(\mu\text{-dppm})]$ **5**. Complex **5** is obtained in good yield, and is stable to air in both the solid and in solution.

Naturally, depending on the conformation of the octadienediyl group about the ruthenium(IV) centre, it is once again possible to have chiral isomers. Although the existence of such isomers in solution cannot be determined by NMR spectroscopy, the X-ray structure of **5** reveals that in the solid state such chiral isomers do indeed exist (see below).

The NMR data of complex **5** indicate that the integrity of the molecule is retained in solution; we found no evidence of any redox processes, or other forms of decomposition during spectral acquisition. Although the proton resonances of the octadienediyl group in **5** are shifted to slightly higher field, this part of the ^1H NMR spectrum closely resembles that found for complex **3b**, and for the respective isomers of complex **2b**. As a result of having two different metal centres co-ordinated at either end of the dppm ligand, the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **5** gives rise to a distinct AB splitting pattern centred at δ 21.87 with $J(P\text{–}P') = 53.54$ Hz, and $\Delta\delta(P\text{–}P') = 242.6$ Hz.

Crystal Structure Determinations.—Diffraction quality crystals of **2b** were obtained by recrystallisation from acetone–dichloromethane mixtures. The molecular structure of **2b** is shown in Fig. 2. Selected bond lengths and angles are presented in Table 3, with the fractional coordinates given in Table 4.

The X-ray structural analysis of complex **2b** reveals the presence of one acetone and one dichloromethane molecule per molecule of **2b**. The geometry about the respective ruthenium atoms is best described as a trigonal bipyramid with the bridging dppm ligand occupying an equatorial position at both ruthenium centres. In similar fashion to that reported[18] for the X-ray structure of the dimeric parent compound **1**, the two octadiendiyl groups in the $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2]$ sub-units of **2b** each have local C_2 symmetry, but have opposite chirality with respect to each other. The presence of only the C_i isomer is possibly due to the steric requirements of the dppm ligand, as discussed above.

The X-ray structure of complex **5** was also determined. Dif-

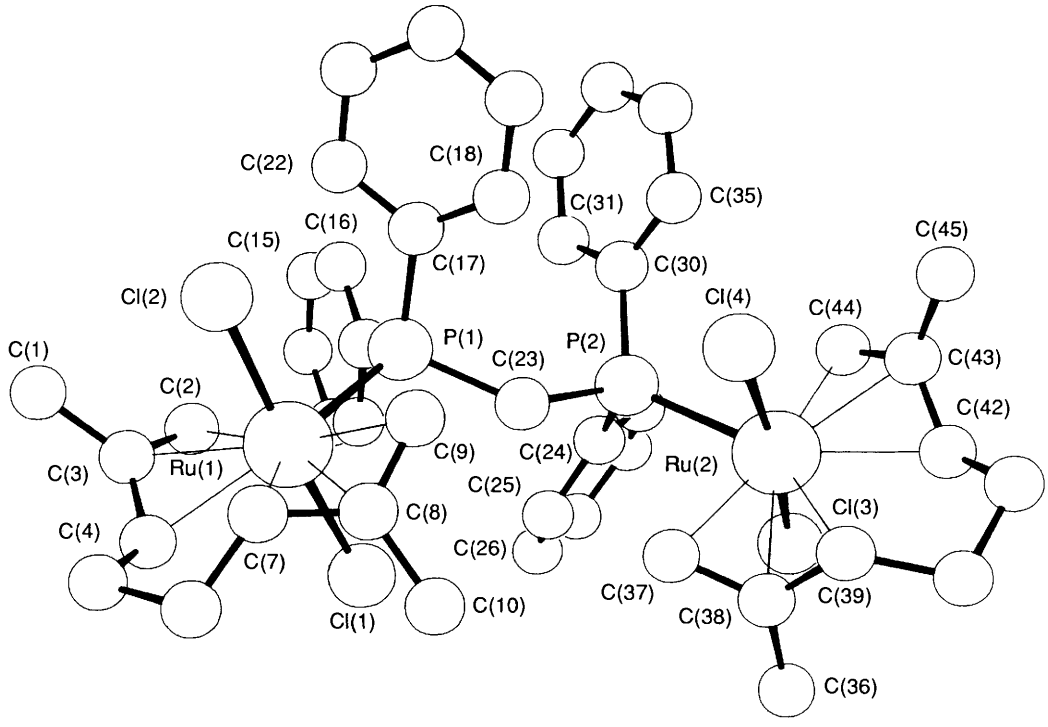


Fig. 2 Molecular structure of complex **2b** showing the atom numbering

Table 4 Fractional coordinates ($\times 10^4$) for complex **2b**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ru(1)	3343(1)	3440(1)	1052(1)	C(26)	−183(8)	−348(9)	1690(5)
Cl(1)	1416(2)	3128(2)	1201(1)	C(27)	−233(9)	−1411(10)	1841(6)
Cl(2)	5291(2)	3616(2)	933(1)	C(28)	720(9)	−1727(8)	2327(6)
C(1)	3659(9)	3093(9)	−682(5)	C(29)	1752(8)	−965(7)	2664(5)
C(2)	2695(7)	2020(7)	20(4)	C(30)	4350(7)	169(6)	3015(4)
C(3)	2825(8)	3031(8)	−232(4)	C(31)	4214(8)	−850(7)	2422(4)
C(4)	2204(8)	3935(8)	17(4)	C(32)	5143(10)	−1526(8)	2416(5)
C(5)	2398(9)	5195(8)	8(5)	C(33)	6201(9)	−1222(9)	2962(6)
C(6)	2560(10)	5915(7)	802(5)	C(34)	6347(8)	−237(8)	3532(5)
C(7)	3543(9)	5420(7)	1288(5)	C(35)	5454(7)	461(7)	3566(5)
C(8)	3522(8)	5187(7)	1951(5)	Ru(2)	3015(1)	2380(1)	4207(1)
C(9)	4354(8)	4500(6)	2252(4)	Cl(3)	1139(2)	1321(2)	3981(1)
C(10)	2600(9)	5607(7)	2303(5)	Cl(4)	4871(2)	3347(2)	4277(1)
P(1)	3850(2)	1827(2)	1609(1)	C(36)	585(7)	3809(8)	4146(5)
C(11)	3168(8)	362(6)	982(4)	C(37)	2162(7)	3512(6)	3510(4)
C(12)	1925(7)	171(7)	712(4)	C(38)	1843(8)	3865(7)	4162(5)
C(13)	1318(8)	−869(7)	218(5)	C(39)	2786(8)	4258(6)	4834(5)
C(14)	1930(9)	−1739(7)	−45(5)	C(40)	2672(8)	4506(8)	5602(5)
C(15)	3157(10)	−1588(7)	209(5)	C(41)	3531(9)	3774(8)	5984(5)
C(16)	3820(8)	−534(7)	738(4)	C(42)	3258(8)	2568(8)	5432(4)
C(17)	5429(6)	1741(6)	1944(4)	C(43)	4095(9)	1850(8)	5222(5)
C(18)	6087(7)	2153(7)	2696(5)	C(44)	3675(7)	839(6)	4603(4)
C(19)	7299(8)	2108(8)	2941(5)	C(45)	5409(8)	2229(8)	5620(5)
C(20)	7875(8)	1652(8)	2426(6)	Cl(5)	664(4)	5719(4)	7966(2)
C(21)	7241(9)	1290(8)	1670(6)	C(46)	1836(11)	5264(11)	7632(8)
C(22)	6019(8)	1354(7)	1423(5)	Cl(6)	2033(4)	3954(4)	7669(3)
C(23)	3314(6)	2053(5)	2429(3)	C(47)	9645(4)	2480(4)	5726(3)
P(2)	3160(2)	1120(2)	3020(1)	C(48)	−1709(4)	2412(4)	5252(3)
C(24)	1811(7)	108(6)	2504(4)	C(49)	545(4)	1655(4)	6011(3)
C(25)	834(7)	425(7)	2026(4)	O	287(4)	3365(4)	5849(3)

fraction-quality crystals were obtained by recrystallisation from methanol–chloroform mixtures. The crystal structure of **5** reveals the presence of two independent molecules in the asymmetric unit, labelled A and B respectively. The asymmetric unit also contains three chloroform molecules which co-crystallised from the solvent mixture used. The molecular structure of molecule A of complex **5** is shown in Fig. 3. Selected bond lengths and angles are given in Table 3, and the fractional coordinates are given in Table 5.

In complex **5** the dppm ligand acts as a single bridging ligand between a ruthenium(IV) [labelled Ru(1A) and Ru(1B) in the respective molecules] and a ruthenium(II) centre [labelled Ru(2A) and Ru(2B) in the respective molecules]. As with complex **2b**, the ruthenium(IV) unit in **5** has trigonal bipyramidal geometry with the dppm ligand co-ordinated to the ruthenium(IV) centre *via* an equatorial position. The octadienediyl groups in the respective molecules also occupy equatorial positions, and like **2b** have local C_2 symmetry. In both molecules the ruth-

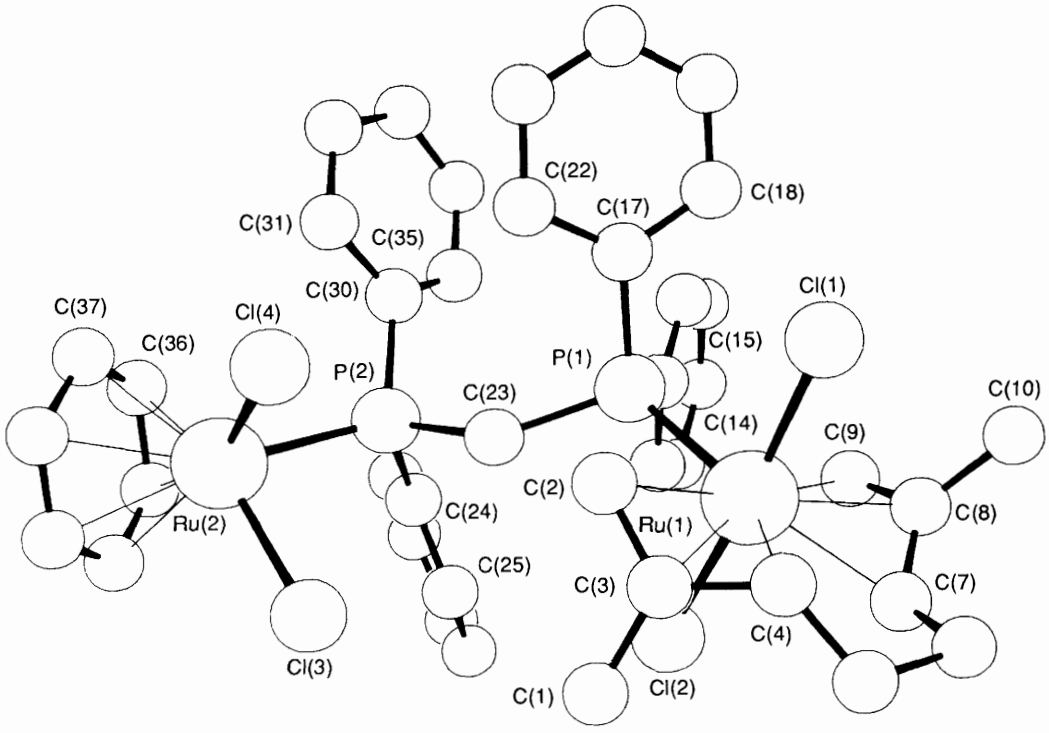


Fig. 3 Molecular structure of molecule A of complex **5** showing the atom numbering

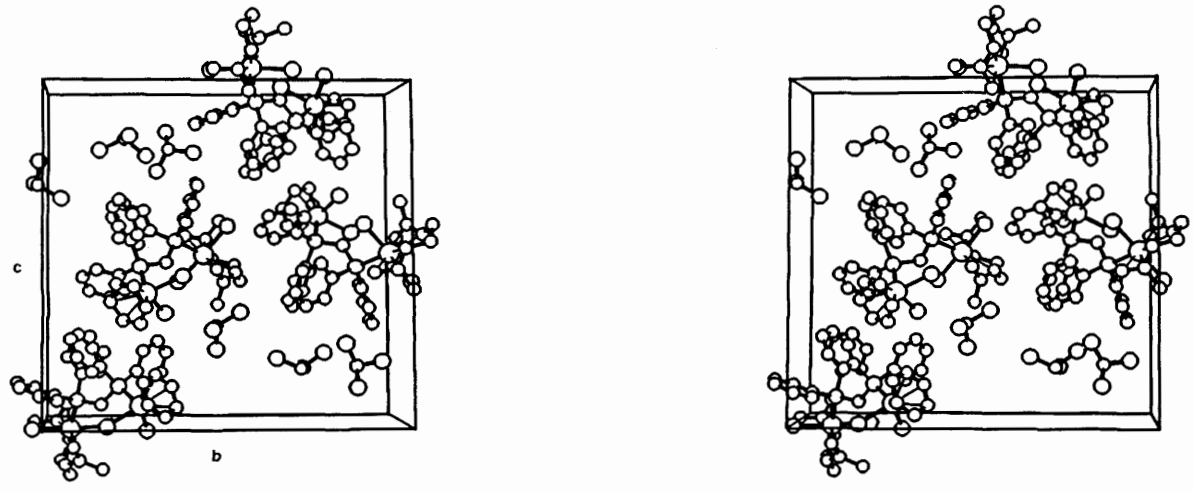


Fig. 4 Stereodiagram of the unit cell of complex **5** viewed along the *a* axis

enium(II) centre has the usual octahedral co-ordination geometry with the η^6-co-ordinated benzene approximately perpendicular to the P · · · P axis.

An important result arising from the X-ray structural analysis of **5** is the difference in chirality between the two ruthenium(IV) centres [Ru(1A) and Ru(1B)] of molecules A and B in the asymmetric unit. The difference in chirality, which is simply brought about by the arrangement of the octadienediyl groups about the respective ruthenium(IV) centres, is most readily seen in the stereodiagram of the unit cell of complex **5** (Fig. 4). This result represents the first conclusive evidence for the existence of chiral isomers in complexes of this type *i.e.* complexes containing a single [Ru(η^3:η^3-$C_{10}H_{16}$)] unit. Furthermore, as would be expected, the chiral isomers are present in a 1:1 ratio.

Another difference between molecules A and B of complex **5** is the relative orientation of the respective ruthenium(II) and ruthenium(IV) units about the P · · · P axis. Viewed along the P(1) · · · P(2) vector, molecule A has a Ru(1A)–P(1A) · · · P(2A)–Ru(2A) dihedral angle of 49.8(2)°, while molecule B is twisted in the opposite sense and has a Ru(1B)–P(1B) · · · P(2B)–Ru(2B) dihedral angle of −47.6(2)°.

Some striking features common to both complexes **2b** and **5** are (*i*) the very long Ru · · · Ru non-bonded distances of 6.718 (**2b**) and 6.735 Å (average) (**5**), (*ii*) the relatively large P–C–P bond angles of 133.5(4) (**2b**) and 132.3(4)° (average) (**5**), and (*iii*) the approximate *cis* arrangement of the metal centres (or the phenyl groups of the dppm ligand) about the respective P · · · P axes of molecules **2b** and **5**, as illustrated by the absolute values of the Ru(1)–P(1) · · · P(2)–Ru(2) dihedral angles of 38.2(2) (**2b**) and 48.7(2)° (average) (**5**). These features are similar to those reported for the dimeric ruthenium(II) cationic complex [{Ru(η^5-C_5H_5)(phen)}$_2$(μ-dppm)][PF_6]$_2$ (phen = 1,10-phenanthroline).[14]

Experimental

Materials.—All reagents and solvents used are commercially available, and were used without further purification. Commercial $RuCl_3 \cdot xH_2O$ was purchased from Fluka and Strem Chemicals. Due to the stability of the compounds studied, all reactions and manipulations were carried out in the presence of

Table 5 Fractional coordinates ($\times 10^4$) for complex **5**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ru(1A)	2357(1)	4526	4986(1)	Ru(1B)	374(1)	663(1)	−362(1)
Cl(1A)	3170(3)	5195(1)	5850(1)	Cl(1B)	−126(3)	1777(1)	−283(1)
Cl(2A)	1688(2)	3792(1)	4137(1)	Cl(2B)	995(3)	−433(1)	−341(1)
C(1A)	2935(12)	4888(5)	3473(4)	C(1B)	1171(14)	1623(5)	−1556(5)
C(2A)	4204(9)	4853(4)	4544(5)	C(2B)	2309(9)	752(5)	−828(4)
C(3A)	3135(10)	5077(4)	4150(5)	C(3B)	1295(13)	946(6)	−1282(5)
C(4A)	2193(9)	5454(4)	4440(5)	C(4B)	289(12)	511(6)	−1437(5)
C(5A)	882(11)	5635(5)	4168(5)	C(5B)	−967(12)	653(7)	−1812(5)
C(6A)	−88(9)	5491(4)	4662(5)	C(6B)	−2033(11)	372(6)	−1434(6)
C(7A)	235(8)	4819(4)	4853(5)	C(7B)	−1794(9)	602(6)	−761(5)
C(8A)	491(9)	4622(4)	5472(5)	C(8B)	−1633(10)	247(5)	−224(6)
C(9A)	943(8)	4016(4)	5548(5)	C(9B)	−1105(9)	549(5)	355(5)
C(10A)	325(10)	5032(5)	6042(5)	C(10B)	−1976(12)	−427(6)	−229(6)
P(1A)	3818(2)	3683(1)	5389(1)	P(1B)	1866(2)	858(1)	569(1)
C(11A)	3059(8)	2975(3)	5712(3)	C(11B)	1124(8)	983(4)	1328(4)
C(12A)	2205(8)	2626(4)	5298(4)	C(12B)	1277(10)	591(5)	1858(4)
C(13A)	1587(9)	2086(4)	5504(5)	C(13B)	650(10)	712(5)	2396(4)
C(14A)	1828(10)	1894(4)	6129(5)	C(14B)	−70(9)	1224(5)	2447(4)
C(15A)	2674(10)	2228(4)	6533(4)	C(15B)	−217(9)	1642(5)	1957(5)
C(16A)	3279(9)	2774(4)	6323(4)	C(16B)	327(9)	1509(4)	1383(4)
C(17A)	5006(8)	3915(3)	6032(4)	C(17B)	3078(8)	244(4)	751(3)
C(18A)	4617(9)	4083(4)	6614(4)	C(18B)	2638(10)	−331(4)	978(4)
C(19A)	5508(11)	4244(4)	7106(4)	C(19B)	3560(13)	−805(5)	1153(5)
C(20A)	6777(12)	4245(5)	7028(5)	C(20B)	4866(12)	−713(5)	1064(6)
C(21A)	7212(12)	4110(5)	6468(6)	C(21B)	5258(11)	−155(5)	814(5)
C(22A)	6345(9)	3939(4)	5937(4)	C(22B)	4376(9)	321(4)	645(4)
C(23A)	4746(7)	3399(3)	4747(3)	C(23B)	2792(7)	1563(3)	471(3)
P(2A)	5637(2)	2662(1)	4633(1)	P(2B)	3801(2)	2055(1)	1043(1)
C(24A)	4437(8)	2077(4)	4369(3)	C(24B)	4625(9)	1524(4)	1653(4)
C(25A)	3394(9)	2243(4)	3929(4)	C(25B)	4009(9)	1327(4)	2187(4)
C(26A)	2447(9)	1820(4)	3700(4)	C(26B)	4667(11)	918(4)	2604(4)
C(27A)	2518(10)	1217(5)	3896(5)	C(27B)	5871(10)	703(5)	2502(4)
C(28A)	3567(11)	1036(4)	4321(5)	C(28B)	6466(10)	894(4)	1984(5)
C(29A)	4490(9)	1448(4)	4547(4)	C(29B)	5847(9)	1303(4)	1546(4)
C(30A)	6363(9)	2400(4)	5416(4)	C(30B)	2690(8)	2581(4)	1442(4)
C(31A)	7668(9)	2578(5)	5568(4)	C(31B)	1669(9)	2864(4)	1068(4)
C(32A)	8270(12)	2434(5)	6154(5)	C(32B)	878(10)	3302(4)	1344(5)
C(33A)	7547(14)	2073(6)	6595(5)	C(33B)	1080(11)	3448(5)	1961(6)
C(34A)	6294(14)	1904(6)	6398(6)	C(34B)	2133(11)	3195(4)	2329(5)
C(35A)	5702(10)	2063(4)	5826(4)	C(35B)	2924(9)	2757(4)	2061(4)
Ru(2A)	7133(1)	2818(1)	3850(1)	Ru(2B)	5329(1)	2665(1)	524(1)
Cl(3A)	5392(2)	3353(1)	3240(1)	Cl(3B)	3599(2)	2863(1)	−295(1)
Cl(4A)	7686(2)	3807(1)	4350(1)	Cl(4B)	5832(3)	1729(1)	−54(1)
C(36A)	8239(10)	1985(4)	4128(5)	C(36B)	6973(12)	2729(6)	1231(6)
C(37A)	9131(9)	2463(5)	4063(5)	C(37B)	5951(13)	3075(6)	1430(6)
C(38A)	9101(9)	2776(5)	3471(4)	C(38B)	5405(14)	3535(6)	1064(7)
C(39A)	8183(9)	2641(4)	2981(4)	C(39B)	5815(16)	3656(6)	479(9)
C(40A)	7241(9)	2166(4)	3065(4)	C(40B)	6865(15)	3333(8)	248(7)
C(41A)	7295(10)	1822(4)	3615(5)	C(41B)	7424(10)	2853(7)	629(7)
Cl(1S)	5006(4)	6515(2)	1883(2)	Cl(6S)	6786(6)	5419(2)	3293(3)
Cl(2S)	2881(4)	7340(2)	1531(2)	C(2S)	6933(17)	4751(6)	2893(6)
Cl(3S)	5292(5)	7824(2)	2052(2)	Cl(7S)	8366(7)	9250(3)	1873(3)
C(1S)	4550(11)	7231(5)	1585(5)	Cl(8S)	9950(8)	8470(3)	1187(4)
Cl(4S)	6125(9)	4776(3)	2185(2)	Cl(9S)	9570(10)	8190(3)	2418(3)
Cl(5S)	8592(7)	4618(3)	2811(3)	C(3S)	8763(17)	8521(8)	1767(11)

air. Complex **1**, $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$, was prepared as described previously.[1]

Characterisation.—Proton, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra were, unless otherwise indicated, recorded at 303 K using a Bruker AC 300 spectrometer operating at 300.13, 75.47 and 121.5 MHz for the respective nuclei. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra were referenced relative to $SiMe_4$ (δ 0) using the residual signal from the deuteriated solvents. The $^{31}P\text{-}\{^1H\}$ NMR spectra were referenced externally relative to 85% H_3PO_4 (δ 0). The two-dimensional spectra were recorded using standard Bruker software, and use was made of the Aspect 3000 computer to process the raw data. Elemental analyses were carried out by the Division of Energy Technology, Council for Scientific and Industrial Research, South Africa. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.

Preparations.—$[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-pyz})]$ **2a**. To compound **1** (154 mg, 0.25 mmol) dissolved in dichloromethane (20 cm^3) was added pyrazine (20 mg, 0.25 mmol) which had been dissolved in dichloromethane (5 cm^3). After addition of the pyrazine, the purple solution rapidly turned orange. After stirring for 30 min at room temperature, the dichloromethane was removed *in vacuo* and complex **2a** was obtained as a dry orange solid. Recrystallisation from dichloromethane–hexane

Table 6 Crystal data, collection and refinement details for complexes **2b** and **5**

	2b	**5**
Formula	$C_{45}H_{54}Cl_4P_2Ru_2 \cdot CH_2Cl_2 \cdot C_3H_6O$	$C_{41}H_{44}Cl_4P_2Ru_2 \cdot 1.5CHCl_3$
M	1131.8	2243.5
Crystal system	Triclinic	Monoclinic
a/Å	11.914(1)	10.259(1)
b/Å	11.943(2)	21.284(2)
c/Å	19.524(2)	21.058(3)
α/°	105.79(1)	90
β/°	107.64(1)	94.48(1)
γ/°	91.01(1)	90
U/Å^3	2532(1)	4584(1)
Space group	$P\bar{1}$	$P2_1$
Z	2	4
D_c/Mg m^{-3}	1.49	1.63
$F(000)$	1168	2252
Radiation	Mo-Kα	Mo-Kα
λ/Å	0.7107	0.7107
μ/cm^{-1}	9.19	11.42
Crystal size/mm	0.19 × 0.20 × 0.35	0.27 × 0.27 × 0.32
Colour	Dark orange	Orange
θ_{max}/°	31	30
Scan type/ω:2θ	1:1	3:2
Scan angle/°	0.62 + 0.34 tanθ	0.60 + 0.34 tanθ
Horizontal aperture/mm	4.0	4.0
Zone collected: h	0, +17	0, +14
k	±17	0, +30
l	±28	±29
Decay(%)	8.6 (corrected)	1.4 (uncorrected)
Absorption (min., max.)	0.96, 1.00	0.95, 1.00
No. measured reflections	16 095	14 322
No. used reflections	8889, $I > 3\sigma(I)$	9884, $I > 2\sigma(I)$
No. of parameters	554	1015
R^a	0.067	0.058
R'^b [$w = \sigma(F_o)^{-2}$]	0.053	0.034

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

mixtures gave small orange crystals of **2a**. Yield: 163 mg (94%), m.p. 190–195 °C (decomp.) (Found: C, 41.25; H, 5.25; N, 4.05. $C_{24}H_{36}Cl_4N_2Ru_2$ required C, 41.40; H, 5.20; N, 4.00%).

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-dppm)] **2b**. Using the above procedure for **2a**, the dimer **1** (154 mg, 0.25 mmol) was treated with bis(diphenylphosphino)methane (96 mg, 0.25 mmol). As with **2a**, the purple solution rapidly turned orange. Recrystallisation from dichloromethane–acetone mixtures gave dark orange crystals of complex **2b**. Yield: 242 mg (97%), m.p. 155–156 °C (Found: C, 53.45; H, 5.40; Cl, 14.65. $C_{45}H_{54}Cl_4P_2Ru_2$ requires C, 54.00; H, 5.45; Cl, 14.15%).

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(σ-pyz)] **3a**. Using the above procedure for **2a**, the dimer **1** (154 mg, 0.25 mmol) was treated with pyrazine (40 mg, 0.50 mmol). After addition of the pyrazine the purple solution rapidly turned red-orange. Removal of the solvent gave a dry red-orange solid. The product was found to be a mixture of complexes **3a** and **2a**; see Results and Discussion.

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(σ-dppm)] **3b**. Using the above procedure for **2a**, the dimer **1** (154 mg, 0.25 mmol) was treated with bis(diphenylphosphino)methane (192 mg, 0.50 mmol). The solution immediately turned from purple to orange. The solvent was removed *in vacuo*, and complex **3b** was obtained as a dry orange blistered solid in quantitative yield. Compound **3b** was used without further purification. M.p. 120–121 °C (Found: C, 60.60; H, 5.45. $C_{35}H_{38}Cl_2P_2Ru$ requires C, 60.70; H, 5.55%).

[{Ru(η^6-C_6H_6)(μ-Cl)Cl}$_2$] **4**. A modified method of that reported by Zelonka and Baird[17] was used to prepare compound **4**. To a solution of $RuCl_3 \cdot xH_2O$ (350 mg) in ethanol (2 cm^3), was added cyclohexa-1,3-diene (5 cm^3). The mixture was heated, without stirring, in a sealed tube at 100 °C for 16 h. The microcrystalline product was collected on a sintered glass frit and washed consecutively with ethanol and dichloromethane, and dried under vacuum. The colour of the products obtained in separate preparations ranged from yellow to dark orange. Compound **4** was used without further purification. Yield: 332 mg (*ca.* 98%), m.p. 255–260 °C (decomp.).

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}{Ru(η^6-C_6H_6)Cl_2}(μ-dppm)] **5**. To a solution of compound **3b** (150 mg, 0.22 mmol) in dichloromethane (20 cm^3) was added compound **4** (50 mg, 0.22 mmol). The mixture was stirred for 90 min at room temperature during which time the dimer **4** dissolved upon reaction with **3b**. The orange solution was filtered through a short column of Celite filter aid, and the solvent removed *in vacuo*. Recrystallisation of the product from acetone or chloroform–methanol mixtures gave orange crystals of complex **5**. Yield: 192 mg (96%), m.p. 180–181 °C (decomp.) (Found: C, 51.55; H, 4.80. $C_{41}H_{44}Cl_4P_2Ru_2$ requires C, 52.25; H, 4.70%).

Crystal Structure Determinations.—Crystal data and processing parameters are given in Table 6.

Data collection and processing. Unit cell dimensions were obtained by least-squares methods from the positions of 25 centred reflections for each sealed crystal (25 with $\theta > 18°$ for **2b**; 10 with $\theta > 15°$ for **5**), on an Enraf-Nonius CAD4 diffractometer at 24 °C. Lorentz polarization corrections and an empirical method for absorption correction[19] were applied to both data sets, as well as decay correction for **2b**.

Structure analyses and refinement. Structure **2b** was solved by Patterson and Fourier methods, and structure **5** by direct methods (SHELX 86).[20] Refinement was by blocked matrix least-squares methods (SHELX 76).[21] Atomic scattering factors were taken from the literature.[22]

For complex **2b**, the molecule cocrystallised with one molecule of dichloromethane and one molecule of acetone in the

asymmetric unit. The acetone molecule was finally fixed in the position obtained from the difference maps, after numerous attempts to refine the atoms and also modelling the solvent using the different conformations obtained. Refining the structure with isotropic thermal parameters for the atoms of this solvent yielded satisfactory results (maximum positional shift/e.s.d. < 1; residual electron density < 1 e Å^{-3}). All the other non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were placed in calculated positions with a common isotropic thermal parameter that refined to $U_{iso} = 0.150(7)$ Å^2.

For complex **5**, two molecules cocrystallised with three chloroform solvent molecules in the asymmetric unit. All non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included in calculated positions with a common isotropic thermal parameter that refined to $U_{iso} = 0.093(5)$ Å^2. At convergence the maximum positional shift/e.s.d. was < 1 and the residual electron density < 1 e Å^{-3}.

Fractional atomic coordinates for **2b** and **5** are given in Tables 4 and 5 respectively.

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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