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Triply-bridged diruthenium(II) 1,4-bis(diphenylphosphino)butane (dppb) and (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap) complexes, including structural characterisation of [(dppb)ClRu(μ-D_2O)(μ-Cl)$_2$RuCl(dppb)], [(η^2-H_2)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] and the [(dppb)ClRu(μ-Cl)$_3$RuCl(dppb)]$^-$ anion [1]

Kenneth S. MacFarlane, Ian S. Thorburn, Paul W. Cyr, Daniel E.K.-Y. Chau, Steven J. Rettig, Brian R. James *

Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1, Canada

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Abstract

Several triply-bridged diruthenium(II) (1,4-bis(diphenylphosphino)butane) complexes were synthesised and characterised by elemental analysis, UV–Vis, NMR and IR spectroscopies. The solid-state structures of [(dppb)ClRu(μ-D_2O)(μ-Cl)$_2$RuCl(dppb)] (**1**), [(η^2-H_2)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] (**2**) and [TMP][(dppb)ClRu(μ-Cl)$_3$RuCl(dppb)] (**3**) were established by X-ray crystallographic analyses (TMP = 1,1,3-trimethyl-2,3-dihydroperimidinium; dppb = $Ph_2P(CH_2)_4PPh_2$). Crystals of **1**·1.5C_6D_6, **2**·1.5C_7D_8 and **3**·2Me_2CO·2H_2O are all monoclinic, space groups $P2_1/c$, $P2_1/n$ and $C2/c$, respectively, with $Z=4$; $a=16.8681(6)$, $b=13.3542(4)$, $c=26.4966(7)$ Å, $\beta=91.877(1)°$ for **1**·1.5C_6D_6; $a=19.8123(1)$, $b=14.5246(2)$, $c=22.1803(1)$ Å, $\beta=106.58(1)°$ for **2**·1.5C_7D_8; $a=21.596(2)$, $b=16.019(2)$, $c=22.317(2)$ Å, $\beta=106.15(1)°$ for **3**·2Me_2CO·2H_2O. The structures of **1** and **2** were solved by direct methods while **3** was solved by heavy atom methods and all were refined by full-matrix least-squares procedures to $R_1=0.0433$, 0.0612 and $R=0.039$ ($wR_2=0.0709$ (**1**), 0.1178 (**2**)) for 7751, 6757 and 5237 reflections with $I\geq 2\sigma(I)$ for **1** and **2** and $I\geq 3\sigma(I)$ for **3**, respectively. Complex **1** was also studied in the solid-state by ^{31}P CP/MAS NMR spectroscopy. The bromo- and iodo-analogues of **1** were prepared, and these three species were screened as catalysts for hydrogenation of aldimines. The complexes [H_2NR_2][{RuCl(P–P)}$_2$(μ-Cl)$_3$] were synthesised by the addition of NR_3 or [H_2NR_2]Cl to $RuCl_2$(P–P)(PPh_3), where P–P = dppb or (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap) and R = Et, n-Bu or n-Oct. The syntheses of [(DMA)$_2$H][(PPh_3)$_2$ClRu(μ-Cl)$_3$RuCl(PPh_3)$_2$], [(py)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] and [(C_2H_4)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] were also accomplished (DMA = *N*,*N*-dimethylacetamide; py = pyridine).

Keywords: Crystal structures; Ruthenium complexes; Triply-bridged complexes; Diphosphine complexes

1. Introduction

The long term interest in Ru/H_2 chemistry at the University of British Columbia (UBC) stems from studies that Jack Halpern initiated during his years on faculty at UBC (1950–1962), and particularly during my* postdoctoral years (1960–1962) within the Halpern group. There has always been a 'continuum' of Ph.D. students doing Ru/H_2 chemistry under my supervision since 1964, and the most recent seven Ph.D. dissertations (1978–1995) in this area are listed in the references of this current paper. The number of complications and extent of remarkable chemistry within the Ru/H_2/phosphine area continue to grow as the field progresses! This paper illustrates a few of our more recent findings, and the subject matter is considered particularly appropriate for a volume honouring Jack Halpern.

We have previously published several papers on ruthenium(II) ditertiaryphosphine complexes and their reactivity with small molecules e.g., [1–4]. For example, the syntheses of doubly-chloro-bridged complexes with achiral and chiral diphosphines have been reported, along with the reactivity of the [RuCl(dppb)]$_2$(μ-Cl)$_2$ complex with a variety of neutral

* Corresponding author. E-mail: brj@chem.ubc.ca

[1] In honour of Professor Jack Halpern.

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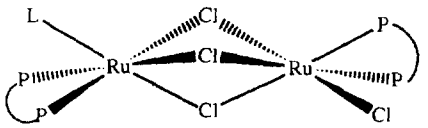
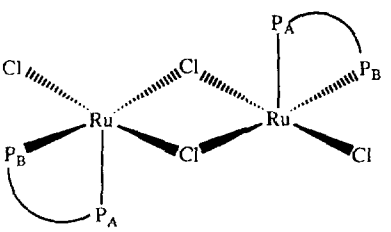
two-electron ligands L; the products were the triply-chloro-bridged species [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] (structure **I**) [1]. The molecular hydrogen (L = η^2-H_2) complex was characterised in solution by NMR techniques including T_1 measurements and the determination of the ^1J(HD) coupling constant of the HD-isotopomer [1]. We now report the X-ray structure of this [(η^2-H_2)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] complex (**2**).



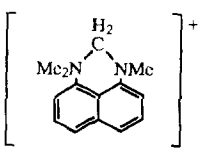
I

The complex [RuCl(dppb)]$_2$(μ-Cl)$_2$, first prepared by the H_2-reduction of the mixed-valence species [RuCl(dppb)]$_2$(μ-Cl)$_3$ [1,5–7], consistently showed (via elemental analysis) a mol of H_2O to be present [1,5–9]. Solution $^{31}P\{^1H\}$ NMR spectral measurements showed an AB pattern consistent with structure **II**, suggesting that H_2O is not coordinated in solution [1,5–9]. In this paper, we report a new synthesis of '[RuCl(dppb)]$_2$(μ-Cl)$_2$' and X-ray and ^{31}P CP/MAS NMR data that show this species is actually [RuCl(dppb)]$_2$(μ-H_2O)(μ-Cl)$_2$ (**1**) in the solid state. In solution, **1** dissociates to give [RuCl(dppb)]$_2$(μ-Cl)$_2$ (**1′**) (see Section 3). The bromo- and iodo-analogues of **1** are also described here.

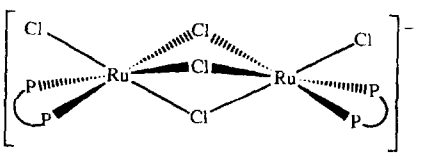


II

The H_2-reduction of [RuCl(dppb)]$_2$(μ-Cl)$_3$ in DMA gives the isolable, ionic species [(DMA)H][Ru$_2$Cl$_5$(dppb)$_2$] [7], which can be converted, by 'washing out' [(DMA)H]Cl with MeOH, to '[RuCl(dppb)]$_2$(μ-Cl)$_2$' [1]. The anionic portion of [(DMA)H][Ru$_2$Cl$_5$(dppb)$_2$] has been observed in a number of different reactions (several of which will be discussed here) and in one case, where the cation is 1,1,3-trimethyl-2,3-dihydroperimidinium (TMP), an X-ray crystal structure has been obtained (complex **3**, structure **III**) [10]. As only the structural details of the TMP cation were reported [10], at that time because of its interesting formation by hydride loss from Proton Sponge (1,8-bis(dimethylamino)naphthalene), we now include details on the anion because of its relevance to the chemistry presented here.



TMP present in 3



III

The reactions of tertiary amines with RuCl$_2$(dppb)(PPh$_3$) to produce the ionic species [H_2NR_2][Ru$_2$Cl$_5$(dppb)$_2$] are presented in this paper, and are important, as the binap analogues are useful catalysts for the asymmetric hydrogenation of ketones and olefins [11–13]. Kawano et al. have reported on a key asymmetric catalyst Ru$_2$Cl$_4$(binap)$_2$·NEt$_3$ [14], formulated as a neutral complex (structure **I** (L = NEt$_3$)), while we have reported the synthesis of the achiral analogue Ru$_2$Cl$_4$(dppb)$_2$(NEt$_3$) [1]. However, King et al. [15] and Ohta et al. [16] have recently reported the isolation of ionic species [H_2NEt_2][Ru$_2$Cl$_5$(P–P)$_2$] using preparative conditions (i.e., [RuCl$_2$(COD)]$_x$ + (P–P) + NEt$_3$ in refluxing toluene) similar to those used by Kawano et al. [14] for the isolation of the neutral complex. Ohta et al. have reported the X-ray crystal structure of [H_2NEt_2][Ru$_2$Cl$_5$((*R*)-*p*-MeO-binap)$_2$], the anion having the same geometry as structure **III** [16]. Reported in the present paper is a new route to the ionic species [H_2NEt_2][Ru$_2$Cl$_5$(P–P)$_2$], where P–P is dppb or binap, and this involves the addition of [H_2NEt_2]Cl to the five-coordinate complex RuCl$_2$(P–P)(PPh$_3$). The chemistry is described in terms of the known solution equilibrium between RuCl$_2$(P–P)(PPh$_3$) and the dinuclear complexes Ru$_2$Cl$_4$(P–P)$_2$ (Eq. (1)) [1,2].

$$2RuCl_2(P-P)(PPh_3) \rightleftharpoons [RuCl(P-P)]_2(\mu-Cl)_2 + 2PPh_3 \quad (1)$$

Also presented here is the synthesis of [(DMA)$_2$H]-[(PPh$_3$)$_2$ClRu(μ-Cl)$_3$RuCl(PPh$_3$)$_2$] (**13**), the anion being analogous to the anion of **3** (cf. **III**). The synthesis and characterisation of [(py)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] (**12**) and [(C_2H_4)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] (**14**) are discussed here, and the solution chemistry compared with that of other [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] complexes, including the L = η^2-H_2 complex (**2**).

2. Experimental

2.1. General procedures and materials

Reagent grade solvents (supplied by Fisher) were distilled under N_2 from CaH_2 (CH_2Cl_2), Na (C_6H_6, diethyl ether and hexanes), or Mg/I_2 (ethanol and methanol). DMA was vacuum distilled at 35–40°C from CaH_2 prior to use. Purified Ar and N_2 (Praxair Canada Inc.) were used without further purification, while H_2 (Praxair) was passed through an Engelhard Deoxo catalytic hydrogen purifier to remove traces of O_2. The amines, N^{n}Bu$_3$ (Anachemia), N^{n}Oct$_3$ (Aldrich) and py (BDH) were used as supplied. [H_2NEt_2]Cl, [$HNEt_3$]Cl and [$H_2N^nBu_2$]Cl were prepared from Et_2NH, Et_3N, and $^nBu_2NH$ and aqueous HCl, respectively, and were characterised by elemental analysis and ^1H NMR. The diphosphines, dppb (Aldrich) and (*R*)-binap (a gift from S.A. King at Merck), were used as supplied. Me_3SiBr (Aldrich) was stored under Ar and used as supplied.

Ruthenium was obtained as $RuCl_3 \cdot 3H_2O$ on loan from Johnson Matthey Ltd. (41.4–44% Ru) or Colonial Metals (39.1% Ru). Manipulations were carried out under Ar using standard Schlenk techniques.

$RuCl_3(PPh_3)_2DMA \cdot DMA$ solvate [17], $RuCl_2(PPh_3)_3$ [18], $RuBr_2(PPh_3)_3$ [18–20], $RuCl_2(P(p\text{-tolyl})_3)_3$ [19,21,22], $RuCl_2(dppb)(PPh_3)$ [1,23], $RuCl_2(dppb)(P(p\text{-tolyl})_3)$ [2], $RuBr_2(dppb)(PPh_3)$ [2], $RuCl_2((R)\text{-binap})(PPh_3)$ [1] and $[TMP][Ru_2Cl_5(dppb)_2]$ [10] were prepared according to published procedures. These complexes were analytically pure and the spectroscopic data (UV–Vis and/or NMR) agreed with those in the literature [1,2,17,23]. The preparation of $Ru(dppb)(\eta^3\text{-Me-allyl})_2$ follows procedures described by Gênet et al. [24], and will be described elsewhere.

Table 1
$^{31}P\{^1H\}$ NMR data (121.42 MHz, 20°C) for $Ru_2X_4(dppb)_2$ complexes

Complex [a]	Solvent	Chemical shift, δ	$^2J(PP)$ (Hz)
$Ru_2Cl_4(dppb)_2$ (**1**)	C_6D_6	$\delta_A = 64.7$, $\delta_B = 55.6$ [b]	47.3
	$CDCl_3$	$\delta_A = 63.5$, $\delta_B = 54.3$	46.9
	CD_2Cl_2	$\delta_A = 64.2$, $\delta_B = 56.0$	46.8
	C_7D_8	$\delta_A = 64.7$, $\delta_B = 55.5$	46.9
$Ru_2Br_4(dppb)_2$ (**4**)	C_6D_6	$\delta_A = 66.4$, $\delta_B = 56.8$	43.7
	$CDCl_3$	$\delta_A = 65.2$, $\delta_B = 55.6$	44.3
	CD_2Cl_2	$\delta_A = 66.0$, $\delta_B = 57.3$	44.6
	C_7D_8	$\delta_A = 66.7$, $\delta_B = 57.0$	45.2
$Ru_2I_4(dppb)_2$ (**5**) [c]	$CDCl_3$	$\delta_A = 70.1$, $\delta_B = 55.6$	39.9

[a] Complexes **1**, **4** and **5** are actually $[RuX(dppb)]_2(\mu\text{-}H_2O)(\mu\text{-}X)_2$ in the solid state but dissociate H_2O in solution giving $Ru_2X_4(dppb)_2$ (Section 3.1).
[b] Slight differences in δ values from the previously reported values [1] result from different methods of referencing.
[c] Formed in situ (Section 2.5).

2.2. Instrumentation

Solution NMR spectra were recorded on a Varian XL300 spectrometer, using the residual proton of the solvent (^1H) or external $P(OMe)_3$ ($^{31}P\{^1H\}$: 141.00 ppm with respect to 85% external H_3PO_4) as the reference. The ^1H NMR data for complexes **1, 4, 6–13** are presented in this Experimental section for purposes of characterisation; the data are straightforward and are not discussed. The $^{31}P\{^1H\}$ NMR data for complexes **1**, **4** and **5** are listed in Table 1, and those for **2**, **3**, **6–12** and **14** in Table 2. The UV–Vis spectra were recorded on a Hewlett Packard 8452A spectrophotometer and are given as λ_{max} (nm), [ϵ_{max} ($M^{-1}\,cm^{-1}$)], (sh) indicates a shoulder. The $^{31}P\{^1H\}$ solid-state cross polarisation, magic angle spinning (CP/MAS) NMR spectra were recorded (with the kind help of Dr H. Meyer zu Altenshildesche of this department) on a Bruker MSL400 instrument (161.97 MHz for ^{31}P). All ^{31}P chemical shifts (solid-state and solution) are reported with respect to external 85% H_3PO_4. The solid samples were packed as powders in 7 mm o.d. zirconia rotors. High-resolution, solid-state ^{31}P NMR spectra were obtained, by combining high-power proton decoupling with ^1H–^{31}P cross polarisation (CP) (2.0 μs 90° ^1H pulse, 3 ms contact time, 10 s recycle time) and magic-angle spinning (MAS) at ~2.5–4.0 kHz. Liquid secondary ion mass spectrometry

Table 2
$^{31}P\{^1H\}$ NMR data (121.42 MHz, 20°C) for the [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] and [cation][(P–P)ClRu(μ-Cl)$_3$RuCl(P–P)] complexes

Complex	Solvent	Chemical shift, δ	$^2J(PP)$ (Hz)
[(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)]			
L = η^2-H_2 (**2**)	$CDCl_3$	$\delta_A = 54.4$, $\delta_B = 39.0$	33.3
		$\delta_C = 53.8$, $\delta_D = 53.3$	46.6
	CD_2Cl_2	$\delta_A = 54.6$, $\delta_B = 39.1$	33.9
		$\delta_C = 53.1$, $\delta_D = 52.4$	44.8
L = η^2-C_2H_4 (**14**)	C_6D_6	$\delta_A = 54.4$, $\delta_B = 53.8$	44.1
		$\delta_C = 46.8$, $\delta_D = 35.6$	34.7
L = py (**12**)	$CDCl_3$	$\delta_A = 54.3$, $\delta_B = 45.0$	36.4
		$\delta_C = 52.6$, $\delta_D = 51.6$	42.7
[cation][(P–P)ClRu(μ-Cl)$_3$RuCl(P–P)]			
[cation] = TMP, P–P = dppb (**3**)	CD_2Cl_2 [a]	53.6, s	
[cation] = H_2NOct_2, P–P = dppb (**6**)	$CDCl_3$	48.9, s	
	C_6D_6	49.2, s	
[cation] = H_2NBu_2, P–P = dppb (**7**)	$CDCl_3$	48.8, s	
	CD_2Cl_2 [b]	48.8, s	
[cation] = H_2NBu_2, P–P = binap (**8**)	$CDCl_3$	$\delta_A = 55.1$, $\delta_B = 51.6$	37.6
	C_6D_6	$\delta_A = 54.9$, $\delta_B = 51.9$	38.5
[cation] = H_2NEt_2, P–P = binap (**9**)	$CDCl_3$	$\delta_A = 54.2$, $\delta_B = 51.5$	37.5 [c]
[cation] = H_2NEt_2, P–P = dppb (**10**)	$CDCl_3$	48.9, s	
[cation] = $HNEt_3$, P–P = dppb (**11**)	$CDCl_3$	49.0, s	

[a] Ref. [10].
[b] Data at −98°C.
[c] The data agree well with those given (in CD_2Cl_2) in Ref. [15a].

(−ve LSIMS) was carried out on a Kratos Concept IIHQ hybrid mass spectrometer operating at 8 kV, using samples in a thioglycerol/$CHCl_3$ matrix. Elemental analyses were performed by Mr P. Borda of this department.

2.3. *[(dppb)ClRu(μ-H_2O)(μ-Cl)$_2$RuCl(dppb)] (1)*

Complex **1** was prepared from $RuCl_2$(dppb)(PPh_3) or $RuCl_2$(dppb)(P(*p*-tolyl)$_3$). A C_6H_6 solution (5 ml) of $RuCl_2$(dppb)(PPh_3) (0.19 g, 0.22 mmol) with added H_2O (5 ml) was refluxed under Ar. The dark green, two-layer mixture became orange after 1 h. Hexanes (10 ml) were added to precipitate a bright orange solid that was collected by vacuum filtration, washed with MeOH (2×5 ml) and hexanes (5×5 ml), and dried under vacuum. Yield: 0.099 g (75%). *Anal.* Calc. for **1** ($C_{56}H_{58}Cl_4OP_4Ru_2$): C, 55.36; H, 4.81. Found: C, 55.43; H, 4.89%. The solid turned brown after being dried under vacuum at 78°C for 24 h. *Anal.* Calc. for Ru_2Cl_4(dppb)$_2$ (**1′**) ($C_{56}H_{56}Cl_4P_4Ru_2$): C, 56.20; H, 4.72. Found: C, 56.08; H, 4.78%. The product is hygroscopic [1,5,6,8]. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 1.35 (br m, 4H, CH_2), 1.61 (s, 2H, free H_2O), 1.65–2.60 (br m, 10H, CH_2), 3.41 (br m, 2H, CH_2), 7.2–7.9 (m, 40H, Ph). UV–Vis (C_6H_6): 454 (sh) [1270], 678 [800]. The NMR spectroscopic data agree with those for the dimer isolated by an alternative preparation from Ru_2Cl_5(dppb)$_2$ [1]. Orange crystals of **1** suitable for X-ray diffraction were isolated from an NMR tube containing $RuCl_2$(dppb)(PPh_3) (20 mg, 0.023 mmol) and D_2O (1.0 μl, 0.055 mmol) in C_6D_6 (~1 ml).

2.4. *[(dppb)BrRu(μ-H_2O)(μ-Br)$_2$RuBr(dppb)] (4)·2H_2O*

2.4.1. *Method 1*

The title complex was prepared by the same method as for **1**, but using $RuBr_2$(dppb)(PPh_3) (0.20 g, 0.21 mmol) as the starting material. An orange–brown solid was isolated. Yield: 0.12 g (86%). *Anal.* Calc. for Ru_2Br_4(dppb)$_2$·3H_2O ($C_{56}H_{56}Br_4P_4Ru_2$·3H_2O): C, 47.07; H, 4.37. Found: C, 47.02; H, 4.20%. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 1.01–1.40 (br m, 8H, CH_2), 1.60 (s, 6H, free H_2O), 2.02–2.54 (br m, 6H, CH_2), 3.82 (br m, 2H, CH_2), 6.78–8.25 (m, 40H, Ph).

2.4.2. *Method 2*

Alternatively, **4** could be prepared by metathesis of **1**. To a C_6H_6 solution (5 ml) of **1** (81 mg, 0.068 mmol) was added Me_3SiBr (200 μl, 1.52 mmol) under a flow of Ar, when the originally pale orange solution became dark orange. After being stirred for 18 h at room temperature (r.t.), the resulting red–brown solution was pumped to dryness. The brown residue was washed with hexanes (2×5 ml) and dried under vacuum. Yield: 0.050 g (54%). The spectroscopic data were the same as those recorded for the solid isolated by method 1.

2.5. *[(dppb)IRu(μ-I)$_2$RuI(dppb)] (5)*

The title complex was prepared in situ. To an initial yellow $CDCl_3$, 'NMR solution' of Ru(dppb)(η^3-Me-allyl)$_2$ (~47 mM) was added 2.2 equiv. of HI (0.17 ml of a 0.30 M aq. MeOH solution) at r.t. The red–brown product formed as a suspension, and was not very soluble in the $CDCl_3$/MeOH; however an in situ $^{31}P\{^1H\}$ NMR spectrum could be recorded (see Table 1). The complex is even less soluble in C_6D_6.

2.6. *[(η^2-H_2)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] (2)*

Complex **1** was dissolved in toluene-d_8 in an NMR tube, and the system evacuated and placed under 2 atm of H_2. The NMR tube was sealed and left at r.t. in the dark for several months over which period orange crystals deposited. **2** has been observed previously in equilibrium in solution with **1** and the in situ spectroscopic data reported (Table 2) [1].

2.7. *[H_2N(n-Oct)$_2$]$^+$[(dppb)ClRu(μ-Cl)$_3$RuCl(dppb)]$^-$ (6)*

An excess of N^nOct_3 (5 ml, 11 mmol) was added to a dark green suspension of $RuCl_2$(dppb)(PPh_3) (0.19 g, 0.22 mmol) in C_6H_6 (5 ml). After the solution was refluxed for 16 h under a flow of Ar, the volume of the orange suspension was reduced to ~5 ml, and hexanes (30 ml) were added to precipitate more product. This was collected, washed with EtOH (2×5 ml) and hexanes (5×5 ml), and dried under vacuum. Yield: 0.063 g (40%). *Anal.* Calc. for **6** ($C_{72}H_{92}NCl_5P_4Ru_2$): C, 58.64; H, 6.29; N, 0.95; Cl, 12.02. Found: C, 58.55; H, 6.17; N, 0.90; Cl, 12.20%. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 0.97 (t, 6H, J = 8.8 Hz, –CH_2CH_3), 1.40 (m, 24H, 20H for –CH_2(CH_2)$_5$$CH_3$ and 4H for CH_2 of dppb), 1.70 (m, 8H, 4 each of CH_2 of dppb and $H_2NCH_2CH_2CH_2$–), 2.15 (br m, 4H, CH_2 of dppb), 2.90 (m, 4H, $H_2NCH_2CH_2$–), 2.95 (br m, 4H, CH_2 of dppb), 6.9–7.6 (m, 40H, Ph), 7.9 (br s, 2H, H_2NCH_2–). UV–Vis (CH_2Cl_2): 316 [5080], 374 [3190], 486 [590].

2.8. *[H_2N(n-Bu)$_2$]$^+$[(dppb)ClRu(μ-Cl)$_3$RuCl(dppb)]$^-$ (7)*

The title complex was prepared as an orange solid in the same manner as **6**, except that N^nBu_3 (5 ml, 21 mmol) was used. Yield: 0.070 g (44%). *Anal.* Calc. for **7** ($C_{64}H_{76}NCl_5P_4Ru_2$): C, 56.41; H, 5.62; N, 1.03; Cl, 13.01. Found: C, 56.47; H, 5.59; N, 0.98; Cl, 13.29%. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 0.97 (t, 6H, –CH_2CH_3), 1.35 (m, 4H, –$CH_2CH_2CH_3$), 1.40 (m, 4H, CH_2 of dppb), 1.65 (m, 4H, $H_2NCH_2CH_2CH_2$–), 1.75 (br m, 4H, CH_2 of dppb), 2.15 (br m, 4H, CH_2 of dppb), 2.90 (m, 4H, $H_2NCH_2CH_2$–), 2.95 (br m, 4H, CH_2 of dppb), 6.9–7.6 (m, 40H, Ph), 7.9 (br s, 2H, H_2NCH_2–). UV–Vis (toluene): 372 [3300], 484 [590]; (CH_2Cl_2): 316 [5330], 374 [3250], 484 [590].

2.9. $[H_2N(n\text{-}Bu)_2]^+$ $[(binap)ClRu(\mu\text{-}Cl)_3RuCl(binap)]^-$ (8)·$2H_2O$

2.9.1. Method 1

An excess of N^nBu_3 (5 ml, 21 mmol) was added to an orange suspension of $RuCl_2$((*R*)-binap)(PPh_3) (0.13 g, 0.12 mmol) in C_6H_6 (5 ml). After the solution was refluxed for 20 h under a flow of Ar, the solution volume was reduced to ~5 ml, and hexanes (10 ml) were added to precipitate the orange product, which was collected, washed with hexanes (4×5 ml), and dried under vacuum. Yield: 0.067 g (60%). *Anal.* Calc. for **8**·$2H_2O$ ($C_{96}H_{88}NCl_5O_2P_4Ru_2$): C, 64.38; H, 4.95; N, 0.78. Found: C, 64.24; H, 4.78; N, 0.68%. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 1.05 (t, 6H, J=8.8 Hz, $-CH_2CH_3$), 1.45 (m, 4H, $-CH_2CH_2CH_3$), 1.87 (m, 4H, $NCH_2CH_2CH_2-$), 2.40 (br m, 1H, $H_2NCH_2CH_2-$), 2.95 (br m, 2H, $H_2NCH_2CH_2-$), 3.25 (br m, 1H, $H_2NCH_2CH_2-$), 6.1–8.1 (m, 64H, aromatic protons), 8.5 (br s, 2H, H_2NCH_2-). H_2O was observed at δ 1.5. UV–Vis (CH_2Cl_2): 334 (sh) [13700], 400 (sh) [4700].

2.9.2. Method 2

Complex **8** could also be prepared by stirring [$H_2N^nBu_2$]Cl (0.023 g, 0.14 mmol) with $RuCl_2$(binap)(PPh_3) (0.13 g, 0.13 mmol) in CH_2Cl_2 (10 ml) at r.t. for 18 h. The volume of the resulting dark orange solution was reduced to ~1 ml and C_6H_6 (5 ml) was added, and the solution filtered through Celite. The filtrate was reduced in volume to ~1 ml, and hexanes (30 ml) added to precipitate the brown product, which was collected, washed with hexanes (3×4 ml), and dried under vacuum. Yield: 0.099 g (82%). The analytical and spectroscopic data were as given above.

2.10. $[H_2NEt_2]^+$ $[(binap)ClRu(\mu\text{-}Cl)_3RuCl(binap)]^-$ (9)

Excess [H_2NEt_2]Cl (0.017 g, 0.16 mmol) was added to a CH_2Cl_2 solution (15 ml) of $RuCl_2$((*R*)-binap)(PPh_3) (0.17 g, 0.16 mmol) and the resulting mixture stirred at r.t. for 18 h. The volume of the solution was reduced to ~3 ml and C_6H_6 (10 ml) was added, and the solution was filtered through Celite. The dark brown filtrate was reduced in volume to ~2 ml, and hexanes (10 ml) added to precipitate the light brown product, which was collected, washed with hexanes (2 ml), and dried under vacuum. Yield: 0.084 g (63%). *Anal.* Calc. for $C_{92}H_{76}NCl_5P_4Ru_2$: C, 65.04; H, 4.51; N, 0.82; Cl, 10.43. Found: C, 65.09; H, 4.57; N, 0.97; Cl, 10.64%. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 1.47 (br m, 6H, J=8.8 Hz, $-CH_2CH_3$), 3.12 (br m, 4H, $-CH_2-$), 6.4–8.0 (m, 64H, aromatic protons), 8.68 (2H, H_2NEt_2). UV–Vis (CH_2Cl_2): 404 [4160], 480 (sh) [940]. In situ NMR experiments show this reaction to be complete within 30 min.

2.11. $[H_2NEt_2]^+$ $[(dppb)ClRu(\mu\text{-}Cl)_3RuCl(dppb)]^-$ (10)

10 was prepared in the same manner as the binap analogue **9**, with $RuCl_2$(dppb)(PPh_3) (0.89 g, 0.10 mmol) and [H_2NEt_2]Cl (0.011 g, 0.10 mmol) being stirred in CH_2Cl_2 (10 ml). Yield of the light orange–brown solid: 0.042 g (64%). *Anal.* Calc. for $C_{60}H_{68}NCl_5P_4Ru_2$: C, 55.16; H, 5.25; N, 1.07. Found: C, 55.66; H, 5.14; N, 0.98%. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): 1.26 (br s, 6H, CH_3 of H_2NEt_2), 1.38 (br m, 4H, CH_2), 1.70 (br m, 4H, CH_2), 2.12 (br m, 4H, CH_2), 2.91 (br m, 4H, CH_2), 3.00 (br m, 4H, CH_2 of H_2NEt_2), 5.9–7.7 (m, 40H, Ph), 8.0 (br s, 2H, NH_2). One sample of **10** analysed as containing a hexanes solvate. *Anal.* Calc. for $C_{66}H_{82}NP_4Cl_5Ru_2$: C, 56.92; H, 5.93; N, 1.01. Found: C, 56.99; H, 5.72; N, 1.05%, and ^{1}H NMR confirmed the presence of hexanes. UV–Vis (CH_2Cl_2): 314 [5390], 374 (sh) [3270], 482 [620].

2.12. $[HNEt_3]^+$ $[(dppb)ClRu(\mu\text{-}Cl)_3RuCl(dppb)]^-$ (11)

[$HNEt_3$]Cl (1.7 mg, 0.012 mmol) was added to a $CDCl_3$ solution of [RuCl(dppb)]$_2$(μ-H_2O)(μ-Cl)$_2$ (13 mg, 0.011 mmol). Hexanes (2 ml) was added to precipitate the orange product, which was collected, washed with hexanes (2×1 ml), and dried under vacuum. *Anal.* Calc. for $C_{62}H_{72}NCl_5P_4Ru_2$: C, 55.80; H, 5.44; N, 1.05; Cl, 13.28. Found: C, 55.73; H, 5.49; N, 0.97; Cl 12.95%. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 1.05 (br m, 9H, CH_3 of $HNEt_3$), 1.36 (br m, 4H, CH_2), 1.72 (br m, 4H, CH_2), 2.15 (br m, 4H, CH_2), 3.01 (br m, 4H, CH_2), 3.15 (br m, 6H, CH_2 of $HNEt_3$), 6.8–7.7 (m, 40H, Ph), 8.02 (br s, 1H, $HNEt_3$). LSIMS (−ve, m/z): 1232 [anion molecular weight − 1].

2.13. [(py)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] (12)

Complex **12** was prepared in situ by the addition of 1 equiv. of py (3.2 μl, 39 μmol) to a CH_2Cl_2 solution (2.0 ml) of [RuCl(dppb)]$_2$(μ-H_2O)(μ-Cl)$_2$ (47 mg, 39 μmol). The initially clear orange solution became darker upon the addition of py. The reaction mixture was stirred at r.t. for 1.5 h and then Et_2O (5 ml) was added to precipitate an orange solid, which was collected, washed with Et_2O (3×2 ml), and dried under vacuum. Yield: 33 mg (66%). *Anal.* Calc. for $C_{61}H_{61}NCl_4P_4Ru_2$: C, 57.42; H, 4.82; N, 1.10. Found: C, 57.14; H, 5.01; N, 1.13%. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 1.2–3.1 (m, 15H, CH_2 of dppb), 3.98 (m, 1H, CHH), 6.33–8.67 (m, 45H, 40H of Ph of dppb and 5H of py). UV–Vis (CH_2Cl_2): 480 [571], 682 [191].

2.14. $[(DMA)_2H]^+$ $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3RuCl(PPh_3)_2]^-$ (13)

The title complex, which has been observed previously in solution but never isolated [17,19,25], was prepared by modification of a route reported for [$Ru_2Cl_4(PPh_3)_4$] [19,25,26]. As in the preparation of [$Ru_2Cl_4(PPh_3)_4$], a green suspension of $RuCl_3(PPh_3)_2$DMA·DMA (0.19 g, 0.21 mmol) was stirred at r.t. under 1 atm H_2 in DMA (10 ml) for 5 days to generate a deep red solution. In the original preparation of orange [$Ru_2Cl_4(PPh_3)_4$], the solution was then reduced in volume to ~5 ml, and MeOH (75 ml) was added to 'break up' the ionic species that exists in solution. In this present preparation for **13**, the solution was reduced in volume to ~5 ml, and Et_2O (20 ml) was added to precipitate slowly (overnight stirring under H_2) an orange solid, which was collected, washed with Et_2O (3×5 ml), and dried under vacuum.

Yield: 0.13 g (78%). *Anal.* Calc. for **13** ($C_{80}H_{79}N_2Cl_5O_2P_4Ru_2$): C, 59.91; H, 4.96; N, 1.75; Cl, 11.05. Found: C, 59.64; H, 5.00; N, 1.70; Cl, 10.90%. $^{31}P\{^1H\}$ NMR (121.42 MHz, C_7D_8): δ 44.6, s from −85 to 20°C. ^1H NMR (300 MHz, C_7D_8, −40°C): δ 2.02 (br s, 6H, CH_3), 2.25 (br s, 6H, CH_3), 2.68 (br s, 6H, CH_3), 6.8–7.9 (m, 60H, Ph), 8.0 (br s, 1H, $(DMA)_2H^+$).

2.15. X-ray crystallographic analyses of [(dppb)ClRu(μ-D_2O)(μ-Cl)$_2$RuCl(dppb)] (1), [(η^2-H_2)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] (2) and [TMP][(dppb)ClRu(μ-Cl)$_3$RuCl(dppb)] (3)

Crystallographic data for complexes **1** and **2** appear in Table 3. For crystallographic data for complex **3** see Section 5.

Crystals of **1** and **2** were mounted on the Siemens SMART system for data collection at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced orientation matrices determined from 143 and 115 reflections for **1** and **2**, respectively. Final cell constants were calculated from a set of 6009 and 8192 strong reflections from the actual data collection for **1** and **2**, respectively. The data collection technique for these crystals is known as a hemisphere collection. Here, a randomly oriented region of reciprocal space is surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames are collected with 0.30° steps in ω.

The space groups $P2_1/c$ and $P2_1/n$ were determined on systematic absences and intensity statistics for **1** and **2**, respectively [27]. Successful direct-methods solutions were calculated which provided most non-hydrogen atoms from the E-map; several full-matrix least-squares/difference Fou-

Table 3
Crystallographic data for **1** and **2**

Compound	(dppb)ClRu(μ-D_2O)(μ-Cl)$_2$RuCl(dppb)·1.5 C_6D_6 (**1**)	(η^2-H_2)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)·1.5 C_7D_8 (**2**)
Formula	$C_{65}H_{67}Cl_4OP_4Ru_2$	$C_{66.50}H_{70}Cl_4P_4Ru_2$
Formula weight	1332.01	1337.05
Crystal habit, colour	block, orange	block, orange
Crystal size (mm)	0.28×0.15×0.09	0.30×0.11×0.06
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	16.8681(6)	19.8123(1)
b (Å)	13.3543(4)	14.5246(2)
c (Å)	26.4966(7)	22.1803(1)
β (°)	91.877(1)	106.58(1)
V (Å^3)	5965.5(3)	6117.38(9)
Z	4	4
ρ_{calc} (g cm^{-3})	1.483	1.452
F(000)	2724	2740
T (K)	173(2)	173(2)
Radiation	Mo	Mo
λ (Å)	0.71073	0.71073
μ (mm^{-1})	0.835	0.813
Transmission factors (max., min.)	0.93, 0.79	1.000, 0.803
Scan type	area detector	area detector
Scan range (°) in ω	0.30 deg frames	0.30 deg frames
Frame duration (s)	20	30
Data collected	hemisphere	hemisphere
$2\theta_{max}$ (°)	50.06	50.06
Crystal decay (%)	negligible	negligible
Total reflections	28778	29331
Unique reflections	10407	10635
R_{merge}	0.0535	0.0535
Reflections with $I>2\sigma(I)$	7751	6757
R_1 [a] ($I>2\sigma(I)$)	0.0433	0.0612
wR_2 [b] ($I>2\sigma(I)$)	0.0709	0.1178
R_1 (all data)	0.0742	0.1162
wR_2 (all data)	0.0940	0.1397
GOF [c]	1.026	1.005
Max. Δ/σ (last cycle)	0.001	0.002
Residual density (e Å^{-3})	−0.529, +0.444	−1.395, +0.709

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = q/(\sigma^2(F_o^2) + (aP)^2 + bP)$, $P = (F_o^2 + 2F_c^2)/3$, $a = 0.0181$ and $b = 7.1759$ for **1**, and $a = 0.0604$ and $b = 0.0$ for **2**. Values given for R_1 and wR_2 are based on those reflections with $I>2\sigma(I)$.
[c] GOF $= S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$.

rier cycles were performed which located the remainder of the non-hydrogen atoms [27]. All non-hydrogen atoms were refined with anisotropic displacement parameters except for the disordered toluene in **2**. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative ($1.2(U_{iso})$ host for CH_2 and aryl) isotropic displacement parameters. For **2**, the individual hydrogen atoms of the η^2-H_2 moiety were not located, although the electron density was observed and therefore the occupancy of H(1) was doubled and refined isotropically. The asymmetric unit contains one complex along with 1.5 toluene solvates. The half-occupied toluene is located on an inversion center and was refined isotropically. Distance and U_{ij} restraints were applied to both toluenes to keep these more regular.

For **1**, the asymmetric unit contains one complex along with 1.5 benzene solvents of crystallisation. The 1/2 benzene is found on an inversion center.

Final atomic coordinates and equivalent isotropic thermal parameters, and selected bond lengths and angles appear in Tables 4 and 5, respectively. See also Section 5.

3. Results and discussion

3.1. Reactivity of $RuCl_2(dppb)(PPh_3)$ with H_2O

The isolated product from the reaction between $RuX_2(dppb)(PAr_3)$ (X = Br, Cl; Ar = Ph or *p*-tolyl) and H_2O in the a two-phase H_2O/C_6H_6 mixture is now known to be $[RuX(dppb)]_2(\mu\text{-}H_2O)(\mu\text{-}X)_2$ (**1**) (see Section 3.5). The previously formulated complex $Ru_2Cl_4(dppb)_2$, prepared by the H_2-reduction of $Ru_2Cl_5(dppb)_2$ [1,5–7], is indeed **1**. Refluxing a C_6H_6 solution (with no H_2O) of $RuCl_2(dppb)(PPh_3)$ does not produce '$Ru_2Cl_4(dppb)_2$' according to reaction (1); H_2O is needed and the product is generated as **1**. Heating the orange complex **1** under vacuo leads to isolation of the 'dehydrated' brown solid $Ru_2Cl_4(dppb)_2$ (**1′**). The solution $^{31}P\{^1H\}$ NMR spectra of **1** and **1′** are identical, and show a single AB quartet pattern (Table 1); this, coupled with the fact that the ^1H NMR spectrum of **1** (but not **1′**) in dry $CDCl_3$ shows a free water signal at δ 1.6 (assigned by addition of H_2O, or its removal by adding molecular sieves (4 Å)), establishes that in solution the μ-H_2O dissociates from **1** and generates the five-coordinate **1′** (cf. structure **II**), (Eq. (2)).

$$\underset{\mathbf{1}}{[(dppb)ClRu(\mu-H_2O)(\mu-Cl)_2RuCl(dppb)]} \rightarrow \underset{\mathbf{1'}}{[RuCl(dppb)]_2(\mu-Cl)_2} + H_2O \quad (2)$$

Further support favouring the dissociation of H_2O in solution is the reversible binding reactivity of **1** with H_2 and N_2 to form species of type **I** [1]; this process requires ligand dissociation from the six-coordinate centre(s) of precursor **1**. Of note, the relatively long Ru–O bond lengths observed

Table 4
Fractional atomic coordinates and U_{eq} values (Å^2) with e.s.d.s in parentheses

Atom	x	y	z	U_{eq} [a]
(dppb)ClRu(μ-D_2O)(μ-Cl)$_2$RuCl(dppb)·1.5C_6D_6 (**1**)				
Ru(1)	0.1750(1)	0.6131(1)	0.1195(1)	0.018(1)
Ru(2)	0.2469(1)	0.6581(1)	0.2342(1)	0.017(1)
Cl(1)	0.0712(1)	0.4912(1)	0.1175(1)	0.028(1)
Cl(2)	0.2837(1)	0.7174(1)	0.1487(1)	0.021(1)
Cl(3)	0.1154(1)	0.6877(1)	0.1974(1)	0.022(1)
Cl(4)	0.3765(1)	0.5917(1)	0.2479(1)	0.028(1)
P(1)	0.1224(1)	0.7184(1)	0.0622(1)	0.021(1)
P(2)	0.2400(1)	0.5227(1)	0.0615(1)	0.023(1)
P(3)	0.2808(1)	0.8008(1)	0.2732(1)	0.021(1)
P(4)	0.2080(1)	0.5795(1)	0.3043(1)	0.021(1)
O(1)	0.2256(2)	0.5195(2)	0.1849(1)	0.022(1)
C(1)	0.0161(2)	0.7514(3)	0.0658(2)	0.022(1)
C(2)	−0.0181(3)	0.8136(3)	0.0293(2)	0.040(1)
C(3)	−0.0971(3)	0.8407(4)	0.0304(2)	0.044(1)
C(4)	−0.1432(2)	0.8078(3)	0.0697(2)	0.034(1)
C(5)	−0.1094(2)	0.7491(3)	0.1068(2)	0.032(1)
C(6)	−0.0300(2)	0.7200(3)	0.1053(2)	0.027(1)
C(7)	0.1663(2)	0.8445(3)	0.0636(2)	0.022(1)
C(8)	0.2221(2)	0.8742(3)	0.0294(2)	0.032(1)
C(9)	0.2572(3)	0.9679(3)	0.0326(2)	0.039(1)
C(10)	0.2375(3)	1.0334(3)	0.0702(2)	0.037(1)
C(11)	0.1810(3)	1.0057(3)	0.1040(2)	0.035(1)
C(12)	0.1456(2)	0.9124(3)	0.1008(2)	0.029(1)
C(13)	0.3176(2)	0.5755(3)	0.0222(2)	0.027(1)
C(14)	0.3529(3)	0.5173(3)	−0.0144(2)	0.037(1)
C(15)	0.4135(3)	0.5550(4)	−0.0426(2)	0.043(1)
C(16)	0.4386(3)	0.6524(4)	−0.0358(2)	0.043(1)
C(17)	0.4038(3)	0.7110(3)	−0.0003(2)	0.034(1)
C(18)	0.3436(2)	0.6733(3)	0.0291(2)	0.028(1)
C(19)	0.2977(2)	0.4262(3)	0.0962(2)	0.027(1)
C(20)	0.2639(3)	0.3348(3)	0.1100(2)	0.037(1)
C(21)	0.3067(3)	0.2681(3)	0.1407(2)	0.044(1)
C(22)	0.3826(3)	0.2906(4)	0.1577(2)	0.046(1)
C(23)	0.4161(3)	0.3816(4)	0.1447(2)	0.042(1)
C(24)	0.3742(3)	0.4485(3)	0.1143(2)	0.033(1)
C(25)	0.1278(2)	0.6838(3)	−0.0042(2)	0.025(1)
C(26)	0.0852(3)	0.5845(3)	−0.0180(2)	0.034(1)
C(27)	0.1405(3)	0.4981(3)	−0.0294(2)	0.034(1)
C(28)	0.1803(3)	0.4462(3)	0.0162(2)	0.030(1)
C(29)	0.3584(2)	0.8676(3)	0.2399(2)	0.024(1)
C(30)	0.3420(3)	0.9454(3)	0.2061(2)	0.037(1)
C(31)	0.4013(3)	0.9911(4)	0.1795(2)	0.046(1)
C(32)	0.4789(3)	0.9611(4)	0.1869(2)	0.042(1)
C(33)	0.4961(3)	0.8841(4)	0.2196(2)	0.041(1)
C(34)	0.4368(2)	0.8370(3)	0.2460(2)	0.035(1)
C(35)	0.2024(2)	0.8955(3)	0.2779(2)	0.022(1)
C(36)	0.1558(2)	0.9146(3)	0.2351(2)	0.026(1)
C(37)	0.0919(2)	0.9808(3)	0.2360(2)	0.028(1)
C(38)	0.0723(3)	1.0257(3)	0.2810(2)	0.035(1)
C(39)	0.1186(2)	1.0073(3)	0.3240(2)	0.032(1)
C(40)	0.1841(2)	0.9449(3)	0.3227(2)	0.027(1)
C(41)	0.1927(2)	0.4473(3)	0.2883(1)	0.022(1)
C(42)	0.1183(3)	0.4117(3)	0.2719(2)	0.035(1)
C(43)	0.1090(3)	0.3136(4)	0.2555(2)	0.050(1)
C(44)	0.1740(4)	0.2513(4)	0.2538(2)	0.054(2)
C(45)	0.2478(3)	0.2852(3)	0.2689(2)	0.047(1)
C(46)	0.2571(3)	0.3822(3)	0.2867(2)	0.034(1)
C(47)	0.1165(2)	0.6129(3)	0.3356(1)	0.023(1)
C(48)	0.0776(2)	0.7024(3)	0.3250(2)	0.026(1)
C(49)	0.0135(2)	0.7331(3)	0.3531(2)	0.033(1)

(*continued*)

Table 4 (*continued*)

Atom	x	y	z	U_{eq} [a]
C(50)	−0.0133(3)	0.6725(3)	0.3907(2)	0.036(1)
C(51)	0.0234(3)	0.5818(3)	0.4016(2)	0.035(1)
C(52)	0.0878(2)	0.5522(3)	0.3739(2)	0.030(1)
C(53)	0.3254(2)	0.7929(3)	0.3375(1)	0.024(1)
C(54)	0.2690(2)	0.7591(3)	0.3788(2)	0.028(1)
C(55)	0.2792(3)	0.6519(3)	0.3978(2)	0.034(1)
C(56)	0.2808(2)	0.5696(3)	0.3575(2)	0.029(1)
C(57)	0.4863(3)	0.1645(4)	0.3516(2)	0.049(1)
C(58)	0.4395(3)	0.1029(3)	0.3219(2)	0.044(1)
C(59)	0.3606(3)	0.0915(3)	0.3318(2)	0.045(1)
C(60)	0.3284(3)	0.1404(4)	0.3720(2)	0.049(1)
C(61)	0.3744(3)	0.2025(4)	0.4013(2)	0.053(1)
C(62)	0.4547(3)	0.2145(4)	0.3916(2)	0.056(2)
C(63)	0.4900(8)	0.4507(10)	0.5446(4)	0.146(5)
C(64)	0.4494(5)	0.4196(7)	0.5009(5)	0.123(4)
C(65)	0.4600(7)	0.4683(10)	0.4569(4)	0.135(5)
$(\eta^2\text{-}H_2)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)\cdot 1.5C_7D_8$ (**2**) [b]				
Ru(1)	0.3628(1)	0.2361(1)	0.0991(1)	0.020(1)
Ru(2)	0.2037(1)	0.2455(1)	0.1155(1)	0.019(1)
Cl(1)	0.2481(1)	0.2111(1)	0.0241(1)	0.024(1)
Cl(2)	0.3037(1)	0.1412(1)	0.1634(1)	0.024(1)
Cl(3)	0.2925(1)	0.3626(1)	0.1312(1)	0.023(1)
Cl(4)	0.4573(1)	0.2727(1)	0.1925(1)	0.027(1)
P(1)	0.4103(1)	0.1086(1)	0.0715(1)	0.025(1)
C(1)	0.4818(3)	0.1220(4)	0.0355(3)	0.030(2)
C(2)	0.5469(3)	0.1743(4)	0.0789(3)	0.033(2)
C(3)	0.5562(3)	0.2702(4)	0.0556(3)	0.033(2)
C(4)	0.5089(3)	0.3457(4)	0.0697(3)	0.028(2)
P(2)	0.4119(1)	0.3313(1)	0.0420(1)	0.023(1)
C(5)	0.3463(3)	0.0365(4)	0.0130(3)	0.030(2)
C(6)	0.3422(4)	0.0378(4)	−0.0508(4)	0.041(2)
C(7)	0.2898(4)	−0.0132(6)	−0.0931(4)	0.059(2)
C(8)	0.2445(4)	−0.0657(6)	−0.0717(5)	0.067(3)
C(9)	0.2483(4)	−0.0690(5)	−0.0095(5)	0.058(2)
C(10)	0.2987(4)	−0.0173(5)	0.0336(4)	0.043(2)
C(11)	0.4503(3)	0.0203(4)	0.1306(3)	0.027(2)
C(12)	0.4657(4)	−0.0656(5)	0.1101(4)	0.042(2)
C(13)	0.5019(4)	−0.1317(5)	0.1523(4)	0.052(2)
C(14)	0.5228(4)	−0.1115(5)	0.2157(4)	0.045(2)
C(15)	0.5079(4)	−0.0287(5)	0.2368(4)	0.043(2)
C(16)	0.4722(3)	0.0376(4)	0.1951(3)	0.029(2)
C(17)	0.3960(3)	0.3195(4)	−0.0435(3)	0.022(1)
C(18)	0.3398(3)	0.2682(4)	−0.0794(3)	0.031(2)
C(19)	0.3248(3)	0.2654(5)	−0.1448(3)	0.036(2)
C(20)	0.3655(4)	0.3149(5)	−0.1744(3)	0.038(2)
C(21)	0.4215(3)	0.3670(4)	−0.1390(3)	0.032(2)
C(22)	0.4369(3)	0.3689(4)	−0.0743(3)	0.032(2)
C(23)	0.3861(3)	0.4521(4)	0.0455(3)	0.021(1)
C(24)	0.4085(3)	0.4997(4)	0.1025(3)	0.026(2)
C(25)	0.3920(3)	0.5908(4)	0.1070(3)	0.036(2)
C(26)	0.3516(3)	0.6373(4)	0.0551(3)	0.035(2)
C(27)	0.3268(3)	0.5916(5)	−0.0022(3)	0.035(2)
C(28)	0.3443(3)	0.5005(4)	−0.0071(3)	0.030(2)
P(3)	0.1771(1)	0.2613(1)	0.2082(1)	0.021(1)
C(29)	0.1312(3)	0.3655(4)	0.2209(3)	0.028(2)
C(30)	0.1694(3)	0.4546(4)	0.2122(3)	0.031(2)
C(31)	0.1310(4)	0.5075(4)	0.1528(3)	0.037(2)
C(32)	0.1356(3)	0.4706(4)	0.0893(3)	0.026(2)
P(4)	0.1187(1)	0.3492(1)	0.0656(1)	0.022(1)
C(33)	0.1211(3)	0.1670(4)	0.2206(3)	0.021(1)
C(34)	0.1499(4)	0.0791(4)	0.2316(3)	0.033(2)
C(35)	0.1088(4)	0.0053(4)	0.2376(3)	0.036(2)
C(36)	0.0382(4)	0.0176(5)	0.2310(3)	0.041(2)
C(37)	0.0077(4)	0.1035(5)	0.2194(3)	0.037(2)
C(38)	0.0494(3)	0.1789(4)	0.2150(3)	0.028(2)
C(39)	0.2506(3)	0.2582(4)	0.2811(3)	0.024(1)
C(40)	0.2356(3)	0.2389(5)	0.3374(3)	0.039(2)
C(41)	0.2900(4)	0.2420(5)	0.3943(3)	0.048(2)
C(42)	0.3580(3)	0.2631(5)	0.3942(3)	0.040(2)
C(43)	0.3729(3)	0.2813(4)	0.3385(3)	0.032(2)
C(44)	0.3190(3)	0.2784(4)	0.2823(3)	0.027(2)
C(45)	0.1113(3)	0.3596(4)	−0.0183(3)	0.026(2)
C(46)	0.1695(3)	0.3901(4)	−0.0361(3)	0.032(2)
C(47)	0.1693(4)	0.3944(5)	−0.0982(3)	0.038(2)
C(48)	0.1099(4)	0.3663(5)	−0.1452(3)	0.045(2)
C(49)	0.0524(4)	0.3365(5)	−0.1287(3)	0.046(2)
C(50)	0.0515(3)	0.3326(5)	−0.0661(3)	0.038(2)
C(51)	0.0269(3)	0.3260(4)	0.0649(3)	0.026(2)
C(52)	0.0023(3)	0.2370(4)	0.0649(3)	0.023(1)
C(53)	−0.0662(3)	0.2193(5)	0.0645(3)	0.032(2)
C(54)	−0.1114(3)	0.2906(5)	0.0645(3)	0.035(2)
C(55)	−0.0890(3)	0.3796(5)	0.0639(3)	0.038(2)
C(56)	−0.0195(3)	0.3973(5)	0.0642(3)	0.035(2)
C(101)	0.8195(5)	−0.1129(7)	0.2683(4)	0.076(3)
C(102)	0.7637(5)	−0.0641(8)	0.2820(5)	0.094(3)
C(103)	0.7196(5)	−0.1102(9)	0.3108(5)	0.098(4)
C(104)	0.7288(6)	−0.1995(9)	0.3227(5)	0.097(4)
C(105)	0.7813(6)	−0.2477(8)	0.3128(5)	0.094(3)
C(106)	0.8268(5)	−0.2059(7)	0.2851(4)	0.073(2)
C(107)	0.8669(6)	−0.0727(10)	0.2384(6)	0.153(6)
C(201)	−0.0276(8)	−0.0300(14)	0.0284(8)	0.068(6)
C(202)	0.0432(6)	−0.0256(9)	0.0580(6)	0.029(3)
C(203)	0.0909(7)	0.0079(11)	0.0283(7)	0.053(4)
C(204)	0.0699(10)	0.0436(16)	−0.0296(9)	0.085(7)
C(205)	−0.0003(10)	0.0439(14)	−0.0588(9)	0.081(6)
C(206)	−0.0500(9)	0.0094(14)	−0.0329(8)	0.072(6)
C(207)	−0.0771(10)	−0.0655(19)	0.0594(11)	0.122(10)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
[b] SOF is 1.0 for all the atoms except for C(201)–C(207) where the value is 0.50.

in the solid-state of **1** (see Section 3.5) also suggest weak coordination of H_2O.

Reaction (2) does not seem to be established as a rapid, reversible equilibrium, as the $^{31}P\{^1H\}$ NMR spectrum is well resolved (not broad), and also −70°C spectra of solutions of $RuCl_2(dppb)(PPh_3)$ which show some **1′** to be present (via equilibrium (1)) are identical to the room temperature spectra [1].

Complex **1** does not contain a C_2-axis in the solid-state because of distortions from octahedral geometry at the Ru centres (Section 3.5), but in solution thermal motion could make the pairs of P atoms equivalent, and a single AB quartet would be anticipated in a $^{31}P\{^1H\}$ NMR spectrum — however, its position would perhaps be different to that of the AB pattern of **1′** (but see below). We had thought that coordination of H_2O would be terminal within the well-documented structure type **I** which generally leads to two AB quartets.

The ^{31}P CP/MAS NMR spectrum of **1** shows three isotropic resonances at δ 55.9, 62.2 and 64.6 integrating in a ratio

Table 5
Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

(dppb)ClRu(μ-D_2O)(μ-Cl)$_2$RuCl(dppb)·1.5C_6D_6 (**1**)			
Ru(1)–P(1)	2.2333(11)	Ru(1)–P(2)	2.2647(11)
Ru(1)–O(1)	2.280(3)	Ru(1)–Cl(1)	2.3895(10)
Ru(1)–Cl(2)	2.4099(10)	Ru(1)–Cl(3)	2.5296(10)
Ru(2)–P(3)	2.2334(11)	Ru(2)–P(4)	2.2492(11)
Ru(2)–O(1)	2.286(2)	Ru(2)–Cl(4)	2.3760(10)
Ru(2)–Cl(3)	2.4270(10)	Ru(2)–Cl(2)	2.4969(10)
P(1)–C(25)	1.824(4)	P(1)–C(7)	1.839(4)
P(1)–C(1)	1.852(4)	P(2)–C(13)	1.839(4)
P(2)–C(19)	1.842(4)	P(2)–C(28)	1.848(4)
P(3)–C(29)	1.835(4)	P(3)–C(35)	1.838(4)
P(3)–C(53)	1.841(4)	P(4)–C(47)	1.832(4)
P(4)–C(41)	1.833(4)	P(4)–C(56)	1.845(4)
P(1)–Ru(1)–P(2)	93.71(4)	P(1)–Ru(1)–O(1)	173.25(7)
P(2)–Ru(1)–O(1)	92.67(7)	P(1)–Ru(1)–Cl(1)	97.99(4)
P(2)–Ru(1)–Cl(1)	89.58(4)	O(1)–Ru(1)–Cl(1)	84.26(7)
P(1)–Ru(1)–Cl(2)	97.76(4)	P(2)–Ru(1)–Cl(2)	98.41(4)
O(1)–Ru(1)–Cl(2)	79.10(7)	Cl(1)–Ru(1)–Cl(2)	161.82(4)
P(1)–Ru(1)–Cl(3)	98.42(4)	P(2)–Ru(1)–Cl(3)	167.87(4)
O(1)–Ru(1)–Cl(3)	75.22(7)	Cl(1)–Ru(1)–Cl(3)	88.62(3)
Cl(2)–Ru(1)–Cl(3)	80.14(3)	P(3)–Ru(2)–P(4)	95.32(4)
P(3)–Ru(2)–O(1)	171.11(7)	P(4)–Ru(2)–O(1)	92.81(7)
P(3)–Ru(2)–Cl(4)	91.55(4)	P(4)–Ru(2)–Cl(4)	89.50(4)
O(1)–Ru(2)–Cl(4)	84.93(7)	P(3)–Ru(2)–Cl(3)	105.32(4)
P(4)–Ru(2)–Cl(3)	96.91(4)	O(1)–Ru(2)–Cl(3)	77.18(7)
Cl(4)–Ru(2)–Cl(3)	161.23(4)	P(3)–Ru(2)–Cl(2)	94.71(4)
P(4)–Ru(2)–Cl(2)	169.97(4)	O(1)–Ru(2)–Cl(2)	77.17(6)
Cl(4)–Ru(2)–Cl(2)	90.17(3)	Cl(3)–Ru(2)–Cl(2)	80.47(3)
Ru(1)–Cl(2)–Ru(2)	84.20(3)	Ru(2)–Cl(3)–Ru(1)	83.16(3)
C(25)–P(1)–C(7)	102.6(2)	C(25)–P(1)–C(1)	100.9(2)
C(7)–P(1)–C(1)	99.9(2)	C(25)–P(1)–Ru(1)	117.70(14)
C(7)–P(1)–Ru(1)	114.33(13)	C(1)–P(1)–Ru(1)	118.61(13)
C(13)–P(2)–C(19)	100.1(2)	C(13)–P(2)–C(28)	103.1(2)
C(19)–P(2)–C(28)	101.8(2)	C(13)–P(2)–Ru(1)	123.31(14)
C(19)–P(2)–Ru(1)	107.11(13)	C(28)–P(2)–Ru(1)	118.00(14)
C(29)–P(3)–C(35)	102.9(2)	C(29)–P(3)–C(53)	101.4(2)
C(35)–P(3)–C(53)	104.5(2)	C(29)–P(3)–Ru(2)	111.58(13)
C(35)–P(3)–Ru(2)	116.36(13)	C(53)–P(3)–Ru(2)	118.05(14)
C(47)–P(4)–C(41)	103.0(2)	C(47)–P(4)–C(56)	102.8(2)
C(41)–P(4)–C(56)	101.1(2)	C(47)–P(4)–Ru(2)	122.23(13)
C(41)–P(4)–Ru(2)	107.57(12)	C(56)–P(4)–Ru(2)	117.39(14)
Ru(1)–O(1)–Ru(2)	92.20(9)		
(η^2-H_2)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)·1.5C_7D_8 (**2**)			
Ru(1)–P(1)	2.240(2)	Ru(1)–P(2)	2.272(2)
Ru(1)–Cl(4)	2.422(2)	Ru(1)–Cl(1)	2.431(2)
Ru(1)–Cl(2)	2.502(2)	Ru(1)–Cl(3)	2.527(2)
Ru(2)–P(3)	2.277(2)	Ru(2)–P(4)	2.295(2)
Ru(2)–Cl(3)	2.401(2)	Ru(2)–Cl(1)	2.479(2)
Ru(2)–Cl(2)	2.480(2)	Ru(2)–H(1)	1.75(3)
P(1)–C(1)	1.825(6)	P(1)–C(11)	1.844(6)
P(1)–C(5)	1.857(7)	P(2)–C(23)	1.836(6)
P(2)–C(4)	1.855(6)	P(2)–C(17)	1.841(6)
P(3)–C(29)	1.828(6)	P(3)–C(33)	1.833(6)
P(3)–C(39)	1.841(6)	P(4)–C(45)	1.831(6)
P(4)–C(32)	1.844(6)	P(4)–C(51)	1.845(6)
P(1)–Ru(1)–P(2)	94.09(6)	P(1)–Ru(1)–Cl(4)	97.65(6)
P(2)–Ru(1)–Cl(4)	89.67(6)	P(1)–Ru(1)–Cl(1)	94.20(6)
P(2)–Ru(1)–Cl(1)	100.09(6)	Cl(4)–Ru(1)–Cl(1)	164.08(6)
P(1)–Ru(1)–Cl(2)	90.07(6)	P(2)–Ru(1)–Cl(2)	175.80(6)
Cl(4)–Ru(1)–Cl(2)	90.34(5)	Cl(1)–Ru(1)–Cl(2)	79.01(5)
P(1)–Ru(1)–Cl(3)	170.41(6)	P(2)–Ru(1)–Cl(3)	94.17(5)
Cl(4)–Ru(1)–Cl(3)	87.27(5)	Cl(1)–Ru(1)–Cl(3)	79.55(5)
Cl(2)–Ru(1)–Cl(3)	81.64(5)	P(3)–Ru(2)–P(4)	92.42(6)
P(3)–Ru(2)–Cl(3)	98.38(6)	P(4)–Ru(2)–Cl(3)	90.67(5)
P(3)–Ru(2)–Cl(1)	170.64(5)	P(4)–Ru(2)–Cl(1)	96.93(6)
Cl(3)–Ru(2)–Cl(1)	81.11(5)	P(3)–Ru(2)–Cl(2)	92.11(5)
P(4)–Ru(2)–Cl(2)	173.93(6)	Cl(3)–Ru(2)–Cl(2)	84.68(5)
Cl(1)–Ru(2)–Cl(2)	78.53(5)	P(3)–Ru(2)–H(1)	90.9(10)
P(4)–Ru(2)–H(1)	96.9(10)	Cl(3)–Ru(2)–H(1)	167.8(9)
Cl(1)–Ru(2)–H(1)	88.5(10)	Cl(2)–Ru(2)–H(1)	87.1(10)
Ru(1)–Cl(1)–Ru(2)	83.76(5)	Ru(2)–Cl(2)–Ru(1)	82.28(5)
Ru(2)–Cl(3)–Ru(1)	83.33(5)	C(1)–P(1)–Ru(1)	118.1(2)
C(11)–P(1)–Ru(1)	120.7(2)	C(5)–P(1)–Ru(1)	113.7(2)
C(23)–P(2)–Ru(1)	112.9(2)	C(17)–P(2)–Ru(1)	122.9(2)
C(4)–P(2)–Ru(1)	116.9(2)	C(29)–P(3)–Ru(2)	118.4(2)
C(33)–P(3)–Ru(2)	111.5(2)	C(39)–P(3)–Ru(2)	117.5(2)
C(45)–P(4)–Ru(2)	112.3(2)	C(32)–P(4)–Ru(2)	116.2(2)
C(51)–P(4)–Ru(2)	118.0(2)		
[TMP][(dppb)ClRu(μ-Cl)$_3$RuCl(dppb)]·2Me_2CO·2H_2O (**3**)			
Ru–Cl(1)	2.4269(10)	P(1)–C(1)	1.858(4)
Ru–Cl(2)	2.4968(10)	P(1)–C(5)	1.840(5)
Ru–Cl(3)	2.4136(10)	P(1)–C(11)	1.841(5)
Ru–P(1)	2.2650(12)	P(2)–C(4)	1.841(4)
Ru–P(2)	2.2642(10)	P(2)–C(17)	1.841(4)
Ru–Cl(2)′	2.5007(9)	P(2)–C(23)	1.840(4)
Cl(1)–Ru–Cl(2)	78.85(3)	Cl(3)–Ru–P(1)	88.12(4)
Cl(1)–Ru–Cl(3)	167.71(3)	Cl(3)–Ru–P(2)	86.67(4)
Cl(1)–Ru–P(1)	97.50(3)	Cl(3)–Ru–Cl(2)′	90.02(4)
Cl(1)–Ru–P(2)	103.41(3)	P(1)–Ru–P(2)	96.74(4)
Cl(1)–Ru–Cl(2)′	78.77(3)	P(1)–Ru–Cl(2)′	93.52(4)
Cl(2)–Ru–Cl(3)	94.16(4)	P(2)–Ru–Cl(2)′	169.10(4)
Cl(2)–Ru–P(1)	172.04(4)	Ru–Cl(1)–Ru′	87.77(5)
Cl(2)–Ru–P(2)	91.01(4)	Ru–Cl(2)–Ru′	84.64(3)
Cl(2)–Ru–Cl(2)′	78.87(4)	Ru–P(1)–C(1)	118.8(2)
Ru–P(1)–C(5)	122.69(15)	Ru–P(1)–C(11)	111.15(15)

of 2:1:1 (Fig. 1). In the structure of **1** (Fig. 2, Section 3.5), the two P-atoms that are *trans* to the μ-H_2O ligand have identical Ru–P bond lengths, and presumably give rise to the resonance at δ 55.9, while the remaining two P-atoms that are *trans* to two different μ-Cl ligands have slightly different Ru–P bond lengths which perhaps explains their non-equivalence in the solid-state spectrum. The solid-state chemical shifts listed are in the same region as observed in the $^{31}P\{^1H\}$ solution spectra, which is somewhat surprising, as the latter refer to **1′**; as expected the CP/MAS spectrum shows broad, featureless resonances with no observable *cis* P coupling.

The preparation of **1** from $RuCl_2(dppb)(PPh_3)$ is more convenient than the synthetic route originally reported [1,5–7], because of much shorter reaction times in each of the three required steps (Scheme 1). The short reaction time from the air-stable $RuCl_2(dppb)(PPh_3)$ allows for easy preparation of relatively small samples of air-sensitive **1**; $[RuCl(dppb)]_2(\mu\text{-}Cl)_2$ (**1′**) is even more air-sensitive than **1**.

It should be noted that of the many $[RuCl(P\text{–}P)]_2(\mu\text{-}Cl)_2$ complexes reported in Refs. [1] and [7], only the dppp (1,3-(bis)diphenylphosphino)propane), and dppb complexes analysed for formulation with a mol of H_2O. The isolated

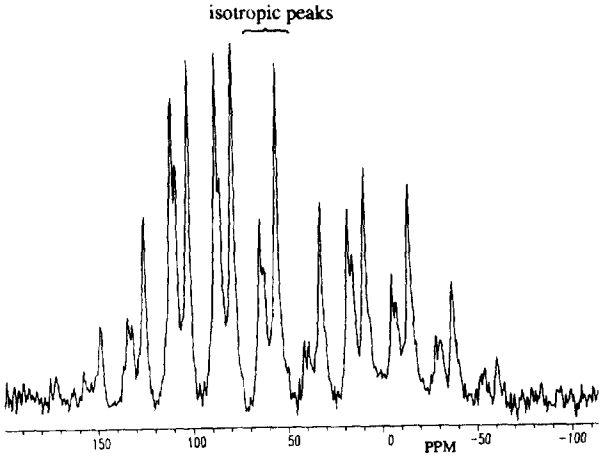


Fig. 1. 161.97 MHz ^{31}P CP/MAS NMR spectrum of **1**.

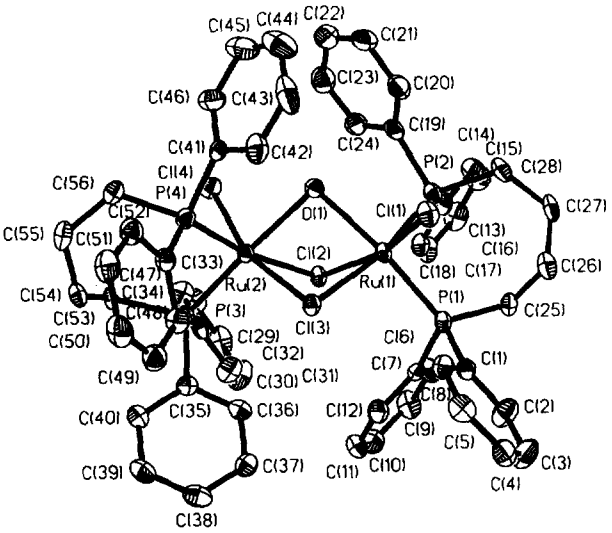
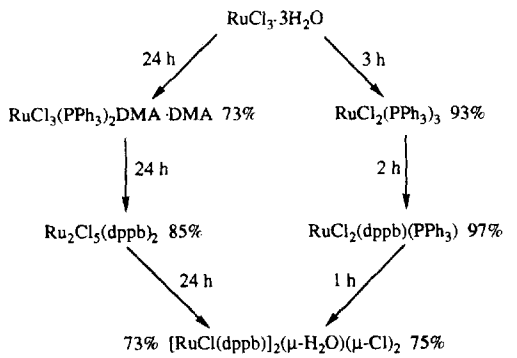


Fig. 2. ORTEP view of **1** with 50% probability thermal ellipsoids.



Scheme 1. Comparison of the yields and reaction times of two synthetic routes to $[RuCl(dppb)]_2(\mu\text{-}H_2O)(\mu\text{-}Cl)_2$ (**1**); the left-hand-side shows the earlier synthesis (Refs. [1,5–7]).

dpppt (1,5-bis(diphenylphosphino)pentane), diop, chiraphos, binap and bdpp (skewphos) analogues (the structures of these diphosphines are given in Ref. [1]) contain no H_2O by microanalysis. Initial attempts to isolate $[((R)\text{-binap})ClRu(\mu\text{-}H_2O)(\mu\text{-}Cl)_2RuCl((R)\text{-binap})]$ from $RuCl_2(binap)(PPh_3)$ following the right-hand-side route shown in Scheme 1 have not been successful, although partial conversions are evident from the in situ (C_6D_6) $^{31}P\{^1H\}$ NMR data [1a]; also seen is a singlet at δ 49.5 which corresponds closely to that reported for the trinuclear $[Ru_3Cl_5(binap)_3]Cl$ [28].

3.2. The bromo- and iodo-analogues $[RuX(dppb)]_2(\mu\text{-}H_2O)(\mu\text{-}X)_2$ (X = Br (4), I (5))

Complex **4** can also be conveniently prepared from 'aquation' of $RuBr_2(dppb)(PPh_3)$. It should be noted that $RuBr_3(PPh_3)_2$ could not be prepared pure [2] and so this necessitates the use of the right-hand-side route in Scheme 1 for synthesis of **4**. The $^{31}P\{^1H\}$ NMR shifts of **4** (Table 1) are slightly downfield (1–2 ppm), and the $^2J(PP)$ coupling constant is somewhat smaller, compared to corresponding data for the chloro-analogue, **1**.

Complex **4** was also prepared directly from **1** by metathesis with Me_3SiBr, a method used by Andersen in hafnium chemistry [29]. The use of this silane is convenient as both the product Me_3SiCl (b.p. 57°C) and any excess Me_3SiBr (b.p. 79°C) are easily removed under dynamic vacuum.

The iodo-analogue **5** was prepared in situ by addition of 2.2 equiv. of HI to a $CDCl_3$ solution of $Ru(dppb)(\eta^3\text{-Me-allyl})_2$. The Me-allyl group is presumably removed by protonation as 2-methylpropene giving $[RuI(dppb)]_2(\mu\text{-}I)_2$ (**5**) in solution. The $^{31}P\{^1H\}$ AB quartet is now shifted somewhat downfield from that of the bromo-analogue, and a regular trend is seen also in the $^2J(PP)$ values that decrease in the order **1** (Cl) > **4** (Br) > **5** (I) (Table 1).

3.3. Reactivity of tertiary amines with $RuCl_2(P\text{–}P)(PPh_3)$

The tertiary amines N^nBu_3 and N^nOct_3 react with $RuCl_2(P\text{–}P)(PPh_3)$ in refluxing C_6H_6 to give $[H_2NR_2][Ru_2Cl_5(P\text{–}P)_2]$ species, where P–P = dppb or binap, with net 'dealkylation' of the amine. The $^{31}P\{^1H\}$ NMR spectra of the dppb-containing ionic complexes **6**, **7**, **10** and **11** (Table 2) all show singlets at $\delta \sim 49$, indicating that the Ru centres (and consequently all four P-atoms) are equivalent on the NMR time-scale and that the structure of the anion is the same as that determined for $[TMP][Ru_2Cl_5(dppb)_2]$ (**3**) by X-ray diffraction (Fig. 3, C_{2v} symmetry, see structure **III**) [10]. $^{31}P\{^1H\}$ NMR spectroscopy on **7** in CD_2Cl_2 at −98°C still shows a singlet at δ 48.8, ruling out an exchange process that would produce an averaged signal (amine exchange has been suggested within the neutral complex $[(NEt_3)(dppb)\text{-}Ru(\mu\text{-}Cl)_3RuCl(dppb)]$, which also gives a singlet at $\delta \sim 49$, while two AB quartets would be expected for a static structure like **I** [1,3]). The complex $[(DMA)_2H][Ru_2Cl_5(PPh_3)_4]$ (**13**) is an analogous ionic species and gives a $^{31}P\{^1H\}$ singlet (δ 44.6) at −85°C, again suggesting that the anion has C_{2v} symmetry. The anion $[Ru_2Cl_5(binap)_2]^-$ within complexes **8** and **9** reveals an AB pattern in the

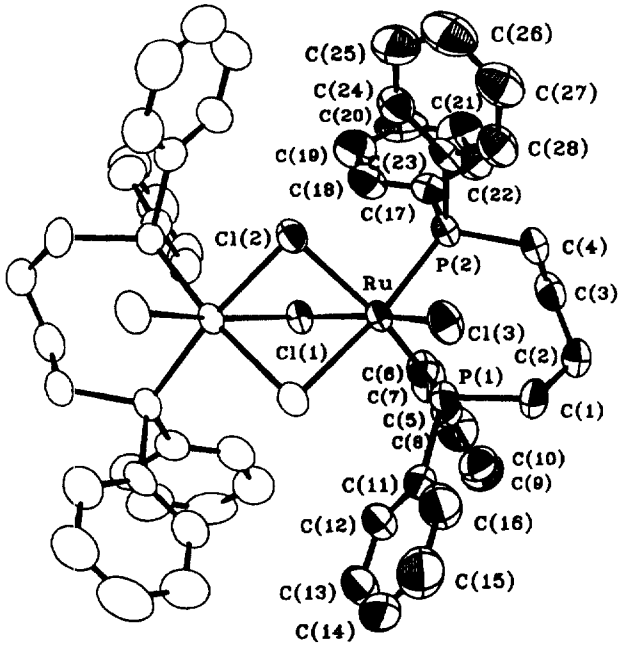


Fig. 3. ORTEP view of the anion of **3** with 50% probability thermal ellipsoids.

$^{31}P\{^1H\}$ NMR spectrum (Table 2), because the chirality in the diphosphine backbone removes the C_{2v} symmetry [15,16]. Complexes **6** and **7** were isolated in 40% based on the Ru content, and the fates of the other 60% Ru and the organic co-product from the amine dealkylation remain to be established. The dioctylammonium derivative **6** was synthesised in an attempt to characterise the 'missing' R group, as the boiling points of the possible organic products would be higher than those derived from the butyl analogue **7**. However, by ^1H NMR no identifiable organic fragments were observed. Our group has recently reported on the degradation of dibenzylamine to benzylamine derivatives using solutions containing $Ru_2Cl_4(dppb)_2$ (**1'**), via established dehydrogenation/hydrolysis pathways, Eq. (3) [3]. Related is the dehydrogenation of an alkyl group of NEt_3 by $RhCl_3(dmso)_3$ to give initially $RhCl_3(dmso)_2(\eta^1\text{-}CH_2CH{=}NEt_2)$, the net H_2 being consumed in generation of an unidentified Rh^ICl co-product and HCl; the η^1-ylidic enamine complex was readily hydrolysed in the presence of HCl and H_2O to give $[H_2NEt_2][RhCl_4(dmso)_4]$ and CH_3CHO [30]. However, in the present Ru systems there are no protons detected by NMR in the region expected for aldehydes, or coordinated η^1-ylidic enamines or imines. $RuCl_2(PPh_3)_3$, a complex very similar to $RuCl_2(dppb)(PPh_3)$ [2], can catalyse the conversion of primary to secondary amines via an amine dehydrogenation step in the overall catalytic cycle and, because all steps are potentially reversible, this cycle may also account for net dealkylation [31]. The unusual TMP cation of complex **3** is produced by hydride loss from Proton Sponge [10]. So there is precedence for alkyl group re-arrangement or loss within amine systems; the Introduction of Ref. [3] can be consulted for further examples.

$$\mathbf{1'} + NH(CH_2Ph)_2 \longrightarrow Ru_2Cl_4(dppb)_2[NH(CH_2Ph)_2]$$

$$\xrightarrow{-H_2} Ru_2Cl_4(dppb)_2[PhCH_2N{=}CHPh] \xrightarrow{H_2O} Ru_2Cl_4(dppb)_2[NH_2CH_2Ph] + PhCHO \quad (3)$$

The NR_3 amines are thought to react with $RuCl_2(P\text{–}P)(PPh_3)$ initially through some dehydrogenation/protonation processes to give $[H_2NR_2]Cl$ and some reduced Ru species; the secondary amine salt is then thought to react with $Ru_2Cl_4(P\text{–}P)_2$, which is present in solution via the equilibrium with $RuCl_2(P\text{–}P)(PPh_3)$ (Eq. (1)). The direct reaction of $[HNEt_3]Cl$ with $Ru_2Cl_4(dppb)_2$ (**1'**) (or $[RuCl(dppb)]_2(\mu\text{-}H_2O)(\mu\text{-}Cl)_2$) (**1**) has been shown to produce $[HNEt_3][Ru_2Cl_5(dppb)_2]$ (**11**). The ^1H NMR spectrum of **11** (see Section 2.12) shows a broad singlet at δ 8.02 for the $[HNEt_3]^+$ proton, and this disappears due to exchange on addition of D_2O to the sample. The same is true for all the dialkylammonium species (**6–10**); for example, addition of D_2O to a $CDCl_3$ solution of the binap species **8** causes the $[H_2NBu_2]^+$ protons at δ 8.5 to disappear.

Further evidence for the initial production of dialkylammonium chloride salts and the subsequent reaction with $Ru_2Cl_4(P\text{–}P)_2$ comes from direct addition of $[H_2NEt_2]Cl$ to $RuCl_2(P\text{–}P)(PPh_3)$ that generates $[H_2NEt_2][Ru_2Cl_5(P\text{–}P)_2]$ in good yields, where P–P = binap (**9**) or dppb (**10**). This provides for a convenient and high yield, three-step synthesis (from $RuCl_3 \cdot 3H_2O$) of these ionic complexes; the binap derivative (**9**) has been reported by King et al. to effect the catalytic asymmetric hydrogenation of methyl acetoacetate [15], but **9** could not be prepared by the addition of $[H_2NEt_2]Cl$ to a precursor $[RuCl_2(COD)]_x$/binap mixture [15].

The reaction of NEt_3 with $RuCl_2(dppb)(PPh_3)$ in refluxing C_6H_6, although giving in situ products with the characteristic δ_P 49 singlet of $[Ru_2Cl_5(dppb)_2]^-$, is more complex than the NBu_3 or $NOct_3$ reactions, and gives a mixture of products. The C, H, N analysis consistently falls between that expected for the ionic complex $[H_2NEt_2][Ru_2Cl_5(dppb)_2]$ and the neutral complex $[(NEt_3)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)]$, previously isolated and characterised (including the key Cl analysis) from a room temperature reaction of NEt_3 with **1** [1,3a]. Both the neutral and ionic species give $^{31}P\{^1H\}$ singlets at $\delta \sim 49$ in solution, and chlorine analysis is one simple method for distinguishing between the two species. Solid-state $^{31}P\{^1H\}$ data for $Ru_2Cl_4(dppb)_2(NEt_3)$ do show four resonances (δ 56.4, 54.1, 47.1, 40.7); line broadening ($\omega_{1/2} \sim 162$ Hz) causes each of these signals to appear as a singlet rather than the doublet expected for a structure such as **III** (L = NEt_3). Investigations are underway to examine the role of the α- and β-hydrogens of the tertiary amines, by using for example NPh_3 and NMe_3 as reagents.

3.4. Reaction of H_2, C_2H_4 and py with $[RuCl(dppb)]_2(\mu\text{-}H_2O)(\mu\text{-}Cl)_2$

The reaction of H_2 with $Ru_2Cl_4(dppb)_2$ (or $[RuCl(dppb)]_2(\mu\text{-}H_2O)(\mu\text{-}Cl)_2$) to give $[(\eta^2\text{-}H_2)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)]$ (**2**) has been studied in some detail [1,32]. The crystallographically determined structure of **2** (Fig. 4) is discussed in Section 3.5. Of interest here, is the $^{31}P\{^1H\}$ NMR spectrum and its comparison with those of other $[(L)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)]$ species (L = py (**12**), C_2H_4 (**14**); Table 2).

The addition of 1 atm C_2H_4 to a C_6D_6 solution of **1** ($\sim 10^{-2}$ M Ru_2) resulted in ~85% conversion to the η^2-ethylene adduct **14** as evidenced by two AB quartets in the $^{31}P\{^1H\}$ NMR spectrum; the reaction is reversible, as shown by replacing the C_2H_4 with Ar. Of interest, addition of 100 equiv. of styrene to **1** in C_6D_6 showed no formation of the corresponding styrene adduct, presumably for steric reasons; we have reported previously on the kinetics and mechanism of the H_2-hydrogenation of styrene using **1** as the catalyst in DMA solutions, where the only spectroscopically observed species was the η^2-H_2 complex **2** [33].

Complex **12** was prepared by addition of 1 equiv. of py directly to **1**; previous attempts to prepare **12** from $RuCl_2(dppb)(PPh_3)$ by addition of excess py resulted in the isolation of *trans*-$RuCl_2(dppb)(py)_2$ [4], although addition of excess ligand L (L = sulfoxides, thioethers) to $RuCl_2(dppb)(PPh_3)$ had been successful in synthesising $[(L)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)]$ complexes [1,2]. Titration of **1** with 1, 2, 4 and 10 equiv. of py is shown in Fig. 5 as followed by $^{31}P\{^1H\}$ NMR spectroscopy. Addition of 1 equiv. shows almost complete loss of the AB pattern due to **1**, and the appearance of two AB patterns due to **12**; with the second equivalent of py, the δ_C, δ_D resonances (pertaining to the Ru^2 centre) become a broad multiplet, while the δ_A, δ_B resonances remain unchanged. The second py is thought to

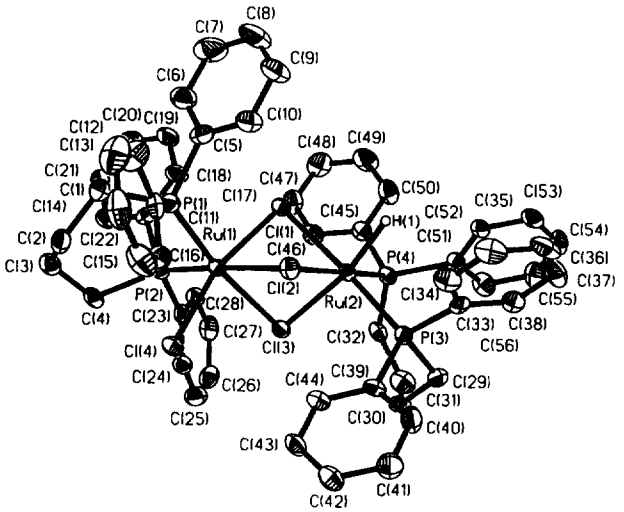


Fig. 4. ORTEP view of **2** with 50% probability thermal ellipsoids (H(1) indicates the electron density observed between the two H atoms of the η^2-H_2 moiety).

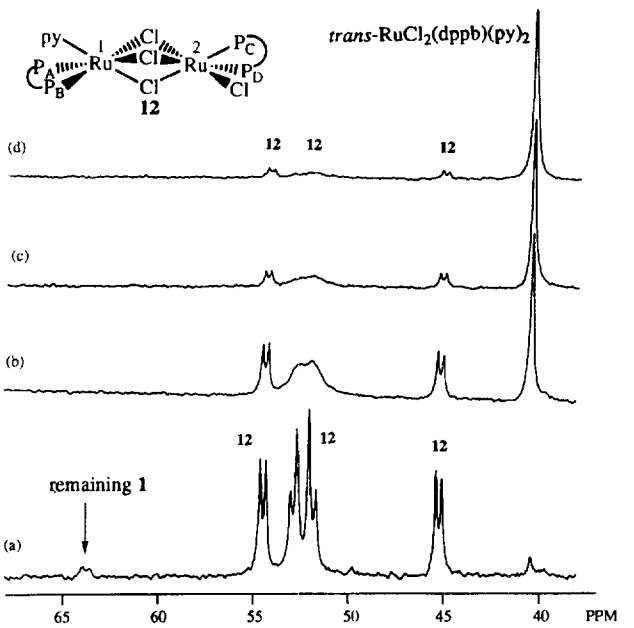


Fig. 5. $^{31}P\{^1H\}$ NMR spectra (121.42 MHz, $CDCl_3$, 20°C) of **1** plus (a) 1 equiv. of py, (b) 2 equiv. of py, (c) 4 equiv. of py, and (d) 10 equiv. of py; the spectra are time-independent and are measured immediately after the additions of py.

coordinate to Ru^2, and generate a $[RuCl(dppb)py]_2(\mu\text{-}Cl)_2$ intermediate en route to *trans*-$RuCl_2(dppb)(py)_2$ (observed as a singlet at δ 40.4). The rapid equilibrium shown in Eq. (4) would account for the non-detection of the $(\mu\text{-}Cl)_2$ species and the broadening of the resonances at the Ru^2 end, while the resonances at the Ru^1 end remain resolved (spectrum Fig. 5(b)). At 4 equiv. of py the $(\mu\text{-}Cl)_2$ intermediate is mostly converted to *trans*-$RuCl_2(dppb)(py)_2$ (spectrum Fig. 5(c)). Interestingly, complex **12** can be observed in situ by addition of 0.5 equiv. of py to $RuCl_2(dppb)(PPh_3)$ in $CDCl_3$.

$$[RuCl(dppb)py]_2(\mu\text{-}Cl)_2 \rightleftharpoons \underset{\mathbf{12}}{[(py)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)]} + py \quad (4)$$

The $^{31}P\{^1H\}$ NMR spectra of the $[(L)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)]$ complexes consist of two AB quartets (Table 2), except when L is an aliphatic amine (see above and Refs. [1a,2]); a characteristic pattern consists of one 'tight' quartet centred at δ_{AB} 52 ± 2 ($^2J(AB) = 43 \pm 2$ Hz) and a second, more widely separated quartet centred at higher field which varies considerably on the nature of L [1,2]. The latter δ_{CD} resonance is thus assigned to the L(P–P)Ru fragment, while the invariance of the downfield signal is attributed to the locked conformation of the (P–P)ClRu(μ-Cl)$_3$ unit, which is essentially independent of the nature of the ligand coordinated at the other Ru. It should be noted that the complexes **2** and **12** are 'slight' exceptions to the above rule: one AB quartet is still centred near δ 52 with $^2J = \sim 43$ Hz, but the second AB quartet is no longer upfield. Thus, for **2** (L = η^2-H_2) and **12** (L = py), the AB and CD designations

by convention are reversed from those of the other [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] complexes (i.e., the most downfield resonance is labelled A; see Fig. 5 and Table 2, where the L = C_2H_4 complex (**14**) can be used for comparison).

3.5. Molecular structures of 1, 2 and 3

The molecular structures of complexes **1**, **2** and the anion of **3** are shown in Figs. 2, 4 and 3, respectively. All three structures are face-sharing, triply-bridged diruthenium(II,II) complexes with Ru–Ru internuclear distances, of 3.290 (**1**), 3.278 (**2**) and 3.367 Å (**3**), well outside of the range generally found for a Ru–Ru single bond (2.632–3.034 Å) [34]. The Ru–Ru distances for **1**–**3** are very similar to the range (3.25–3.35 Å) found for other Ru(μ-Cl)$_3$Ru species such as [H_2NEt_2][Ru_2Cl_5((*R*)-*p*-MeO–binap)$_2$] [16], Ru_2Cl_4(dppb)$_2$(dmso) [1], Ru_2Cl_5(chiraphos)$_2$ [35] and Ru_2Cl_4(PPh_3)$_4$(CS) [36]. Cotton and Torralba [37] have characterised a series of Ru(II,II), Ru(II,III) and Ru(III,III) complexes with face-sharing bioctahedra of the general formula [$Ru_2Cl_3(PR_3)_6$][X] (X is a mono-anion), [$Ru_2Cl_5(PR_3)_4$] and [$Ru_2Cl_6(PR_3)_4$], respectively, and have demonstrated that longer Ru–Ru distances (3.28–3.44 Å) result in enlarged Ru–Cl_b–Ru angles (82.9–87.9°) and contracted Cl_b–Ru–Cl_b angles (77.2–80.9°), where Cl_b is a bridging chloride. Complex **1** shows Ru–Cl_b–Ru angles of 83.16 and 84.20°, and Cl_b–Ru–Cl_b angles of 80.14 and 80.47°, while **3** has Ru–Cl_b–Ru angles of 84.64 and 87.77° and Cl_b–Ru–Cl_b angles of 78.77 and 78.85°, all within the suggested ranges [37]. However, **2** has Ru–Cl_b–Ru angles of 82.28–83.56° and Cl_b–Ru–Cl_b angles of 78.53–84.68°, which contain one Ru–Cl_b–Ru angle below and three Cl_b–Ru–Cl_b angles above the suggested ranges [37], and these 'anomalies' must be due to the presence of the small η^2-H_2 ligand.

The Ru–P (2.24–2.295 Å), Ru–$Cl_{terminal}$ (2.376–2.422 Å), and Ru–Cl_b (2.401–2.530 Å) bond lengths for complexes **1**–**3** are all within the usual ranges for Ru(II) complexes [1,38]. The *trans* influence [34,39] can be observed in all three complexes. For example in **1**, within the (μ-Cl)$_2$ moiety, the Ru–Cl_b bond distances *trans* to phosphine are longer than those *trans* to Cl; also the stronger *trans* influence of Cl compared with H_2O results in longer Ru(1)–P(2) and Ru(2)–P(4) bonds versus Ru(1)–P(1) and Ru(2)–P(3), respectively, while the Ru–Cl_b bond lengths in **2** increase in the order *trans* to η^2-H_2, Cl and P, and in **3** the Ru–Cl(2) bond *trans* to phosphine is longer than Ru–Cl(1), *trans* to Cl. In contrast to this trend, η^2-H_2 within an Os(II) complex is shown to exert a relatively high *trans* influence when *trans* to Cl [40].

Complex **1** is one of the few structurally characterised dinuclear Ru(II) complexes bridged by an aqua (D_2O) ligand and the first, to our knowledge, where the μ-H_2O is not stabilied by H-bonding (in this discussion, D_2O is not distinguished from H_2O). A Cambridge database search revealed five Ru(II)–Ru(II) [41], one Ru(II)–Ru(III) [42] and one Ru(III)–Ru(III) [43] complexes containing a μ-H_2O ligand, and all show intramolecular H-bonding to other O-containing ligands. The Ru–O bond lengths in the complexes reported to date range from 2.107–2.173 Å [41–43] while for **1** the values are 2.280 and 2.286 Å (the H_2O is symmetrically situated between the two Ru atoms); the significantly longer bonds presumably result from the absence of any H-bonding and the strong *trans* influence of the phosphine ligands, although some of the other structurally characterised μ-H_2O complexes also have phosphines *trans* to H_2O [41–43].

Although the hydrogens of the μ-H_2O were not located, the ligand is undoubtedly H_2O (and not OH^- or O^{2-}) as the Ru–O bond lengths would be much shorter for either the μ-OH or μ-O species [38]. Also, the complex is diamagnetic (NMR evidence), again supporting a Ru_2(II,II) formulation. The long Ru–O bond lengths in **1** are also consistent with the ready dissociation of the μ-H_2O ligand in solution and in the solid-state (Section 3.1).

Complex **2** confirms the structure we had suggested previously based on NMR data [1], and, although the individual H atoms in the η^2-H_2 moiety were not located, the electron density between the two H atoms was observed 1.75 Å from a Ru centre. The structure of **2** is of the same basic arrangement observed previously for the analogous [(dmso)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] (see structure **I**, where L = dmso) [1] and [(CS)(PPh_3)$_2$Ru(μ-Cl)$_3$RuCl(PPh_3)$_2$] [36] complexes but is different to that determined for the mixed-valence complex Ru_2Cl_5(*S*,*S*-chiraphos)$_2$ [35] and **3**, the latter having a two-fold axis through a μ-Cl (see structure **III**). Compared to **3**, complex **2** essentially has one of the octahedra rotated by ± 120° about the Ru–Ru vector, and an η^2-H_2 instead of a Cl ligand.

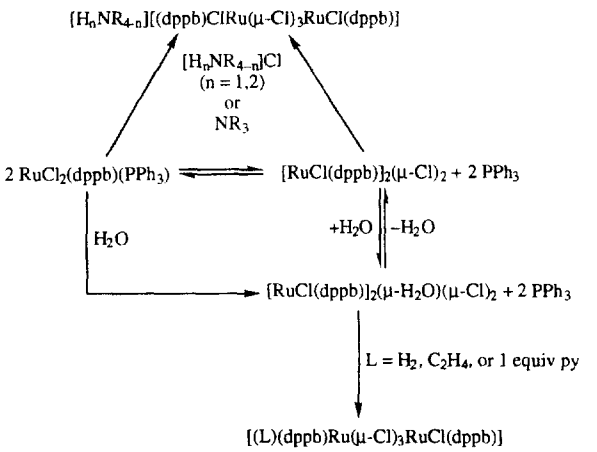
3.6. Preliminary catalytic hydrogenation results

This group has previously reported on the catalytic hydrogenation of imines using '$RuCl_2$(dppb)' complexes including complex **1** and the [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] species [44]. One goal was to synthesise bromo-analogues such as **4**, and examine the role of halide, which is known to be important in many catalysed imine hydrogenations [45,46]. Under the conditions used by Fogg et al. [44] (i.e., 1000 psi H_2, r.t., 10 ml MeOH, 0.77 mM Ru, [imine] = 0.153 M), complex [RuBr(dppb)]$_2$(μ-H_2O)(μ-Br)$_2$ (**4**), for example, catalysed the hydrogenation of $PhCH_2N$=C(H)Ph to dibenzylamine with 66% conversion in 1 h, compared to 87% when the chloro analogue **1** was used as catalyst [44]; however, **4** catalysed the hydrogenation of PhN=C(H)Ph to $PhNHCH_2Ph$ in 74% in 3 h, while **1** gave only 24% conversion. The iodo analogue **5**, generated in situ from Ru(dppb)(η^3-Me-allyl)$_2$ and 2 equiv. of HI, gave 100% conversion of PhN=C(H)Ph to the amine in only 1 h. Clearly, the role of halide is important but reactivity trends can clearly be dependent on the substrate. The absence of halide completely inhibits the catalysis; for example,

$Ru(dppb)(\eta^3\text{-Me-allyl})_2$ in the absence of added HX gives zero conversion of $PhCH_2N{=}C(H)Ph$. The relative insolubility of the bromo- and iodo-analogues (for example, **4** and **5**) makes their characterisation somewhat more difficult than the chloro-derivatives, but the general chemistry of these systems seems similar [47]. More complete data on the catalyses will be published elsewhere [48].

4. Conclusions

Scheme 2 summarises the chemistry described in this paper. The reactivity of $RuCl_2(dppb)(PPh_3)$ is dominated by the equilibria involving $[RuCl(dppb)]_2(\mu\text{-}Cl)_2$ (**1′**), with much of the chemistry occurring through dinuclear species. The $\mu\text{-}H_2O$ ligand in **1** is not stabilised by H-bonding interactions as found in other $Ru(\mu\text{-}H_2O)Ru$ systems, and is labile; for example, $[(L)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)]$ products, $L = \eta^2\text{-}H_2$ (**2**), C_2H_4 and py, are readily formed by reaction of **1** with L, and **2** is characterised by X-ray diffrac-



Scheme 2. Summary of the reaction pathways.

tion. Tertiary amines and di- and trialkylammonium chloride salts react with $RuCl_2(dppb)(PPh_3)$ to produce [cation]-$[(dppb)ClRu(\mu\text{-}Cl)_3RuCl(dppb)]$ species, and the structure of the anion within the TMP salt is described. Synthetic routes to the bromo- (**4**) and iodo-analogues (**5**) of **1** are established, and preliminary data on their relative reactivity as catalysts for the hydrogenation of aldimines are reported.

5. Supplementary material

Tables of hydrogen atom parameters, anisotropic thermal parameters, complete lists of bond lengths and angles, and measured and calculated structure factor amplitudes for the structures of **1** and **2** are available on request from the authors. Crystallographic data for complex **3** along with the atomic coordinates, bond lengths and angles, and thermal parameters have been deposited previously at the Cambridge Crystallographic Data Centre, when this group reported previously on the structural details of the cation [10].

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