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Synthesis, characterisation and reactivity of ruthenium bis-bifluoride, ruthenium hydride bifluoride and ruthenium hydride fluoride complexes

Naseralla A. Jasim, Robin N. Perutz,* Simon P. Foxon and Paul H. Walton

Department of Chemistry, University of York, Heslington, York, UK YO10 5DD.
E-mail: rnp1@york.ac.uk

Received 30th January 2001, Accepted 15th April 2001
First published as an Advance Article on the web 10th May 2001

Published on 10 May 2001. Downloaded by University of Chicago on 30/10/2014 13:10:02.

Bifluoride complexes, *trans*-[Ru(depe)$_2$H(FHF)] (**1**), *trans*-[Ru(dppe)$_2$H(FHF)] (**2**), *trans*-[Ru(dppp)$_2$H(FHF)] (**3**) and *cis*-[Ru(PMe$_3$)$_4$(FHF)$_2$] (**4**) (depe = Et$_2$PCH$_2$CH$_2$PEt$_2$, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$, dppp = Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$) were synthesised from the reactions of the corresponding *cis*-dihydride complexes with NEt$_3$·3HF in THF. The characteristic features of the low temperature NMR spectra of the bifluoride complexes include ^{19}F resonances at *ca.* δ −300 for the proximal fluorine and *ca.* δ −165 for the distal fluorine. The acidic protons resonate at *ca.* δ 13. The value of J(HF) for the distal fluorine lies in the range 300–400 Hz. The bifluoride ligands exhibit characteristic vibrations at *ca.* 2300 cm^{-1} and *ca.* 2430 cm^{-1} in the IR spectrum. All the complexes exhibit dynamic exchange processes, probably due to dissociation of FHF$^-$. In addition, complex **3** undergoes a ring flipping process that is suppressed at low temperature. The X-ray crystal structure of **3** has been obtained. The bifluoride ligand is disordered over two positions about the inversion centre. The Ru–F distance is 2.351(5) Å and the F · · · F distance is 2.290(8) Å, the Ru–F · · · F angle is 149.7°. The X-ray crystal structure for **4** reveals that the Ru–F distances are 2.149(5) Å and 2.150(4) Å, the F · · · F bond lengths are 2.323(8) Å and 2.329(8) Å, with Ru–F · · · F angles of 128.5(3)° and 138.4(3)°. The two bifluoride ligands are *cis* to each other. Reaction of **1** and **3** with [NMe$_4$]F yields *trans*-[Ru(depe)$_2$(H)F] **5** and *trans*-[Ru(dppp)$_2$(H)F] **6**. Reaction of **2** with Me$_3$SiX (X = N$_3$, OTf) yields *trans*-[Ru(dppe)$_2$(H)N$_3$] and [Ru(dppe)$_2$(H)]OTf. Reactions with several halo-organic compounds yields *trans*-[Ru(dppe)$_2$(H)X] (X = Cl, Br and I). The organic products from CH$_3$I, CH$_3$COCl and C$_6$H$_5$COCl were identified as CH$_3$F, CH$_3$COF and C$_6$H$_5$COF respectively.

Introduction

Doherty and Hoffman have reviewed a wide range of examples of low-valent fluoro-organometallic species with carbonyl, phosphine and stilbene ligands.[1] Roesky *et al.* described transition-metal complexes containing fluorine–metal and carbon–metal bonds.[2] The combination of "soft" metals with "hard" ligands is well established and known to yield interesting and often unusual synthetic chemistry and many potential catalytic applications.[3,4] Recently, Togni *et al.* reported the synthesis and crystal structure of five-coordinate [Ru(dppp)$_2$F]PF$_6$, *trans*-[Ru(dppp)$_2$F(CO)] and *cis*-[Ru(dppp)$_2$F$_2$] complexes.[5] The coordinatively unsaturated complex [Ru(dppp)$_2$F]PF$_6$ reacts with activated haloalkenes R–X (X = Cl, Br) in a 1 : 1 molar ratio to give fluorinated organic derivatives.[6] Bergman *et al.* reported the synthesis and the crystal structure of [(η^5-C$_5$H$_5$)Ir(PMe$_3$)(Ph)F].[7] The syntheses of ruthenium fluorides such as [(η^5-C$_5$H$_5$)RuF(CO)(PCy$_3$)][8] and [(η^5-C$_5$H$_5$)RuF(AsPh$_3$)(PPh$_3$)] have been reported, as have bis-(chelating-phosphine)fluoro complexes of the form [RuF(CO)L$_2$]X, (L = dppm, dppe and X = BF$_4$, PF$_6$) in which the fluoro ligand is *trans* to the CO.[9] Hope *et al.* have shown that XeF$_2$ can be used to introduce fluorine oxidatively into low-valent Ru, Os and Ir complexes or *via* reaction of Ru(II) and Os(II) hydrides with anhydrous HF.[10] A related trifluoro-bridged diruthenium cation [Ru$_2$F$_3$(PMe$_2$Ph)$_6$]$^+$ has also been reported.[11]

Holloway and Hope have shown that the reactivity of organometallic fluorides is controlled by the metal–fluorine bond (the addition of Lewis bases results in either addition reactions or ligand substitution reactions).[12] Weaker metal–fluorine bonds allow reaction at the fluoride ligand, either F–Cl exchange or Lewis acid abstraction of fluoride, to form coordinatively unsaturated metal complexes.[13] Insertion of small organic molecules, such as C$_2$F$_4$ or CS$_2$, into metal–fluorine bonds has also been detected.[14] The Ir(III) hydride fluoride [Ir(H)$_2$F(P^{t}BuPh)$_2$] complex reacts with trimethylsilyl compounds (TMS–X) to give a quantitative transfer of the X-group to Ir (X = OTf, NCS, NCO, OCOCH$_3$, OCOCF$_3$, N$_3$, SPh).[15]

The F–H–F ligand has now been established at a variety of metals: Mo, W, Ru, Ni, Pd and Pt.[16] We have reported the synthesis and reactivity of *trans*-[Pt(PR$_3$)$_2$H(FHF)] (R = Cy or ^{i}Pr). At ambient temperature, fluxional behaviour is observed which is principally associated with intermolecular exchange of HF between platinum centres. The distal fluoride of the bifluoride ligand undergoes exchange between two platinum centres and exchange of HF between platinum centres occurs similarly. (We refer to the fluorine bound directly to the metal as proximal and the fluorine bound *via* the hydrogen bond as distal.) The bifluoride ligand can be replaced easily by anionic ligands (*e.g.* OTf$^-$) or neutral ligands such as PPh$_3$ or pyridine. Parkin *et al.* reported the bifluoride complexes, [M(PMe$_3$)$_4$H$_2$F(FHF)] M = Mo and W, synthesised with aqueous HF.[17] Earlier studies of bifluoride complexes[17–20] are summarised in ref. 16.

Of particular relevance to this paper is the ruthenium bifluoride complex, *trans*-[Ru(dmpe)$_2$H(FHF)], that we characterised in solution and solid state.[20] This complex was prepared by the reaction of *cis*-[Ru(dmpe)$_2$H$_2$] either with fluoroarenes (C$_6$F$_6$, C$_5$F$_5$H or others), or by reaction with NEt$_3$·3HF. The ^{1}H NMR spectrum of the ruthenium complex shows coupling constants J(HF$_{\text{distal}}$) = 274 Hz while J(HF$_{\text{proximal}}$) < 30 Hz. The NMR and IR parameters suggest the presence of an asymmetric bifluoride ligand with predominant M–F · · · H–F character. It was proposed that the reaction of the transition metal dihydride with C$_6$F$_6$ yields *trans*-[Ru(dmpe)$_2$(C$_6$F$_5$)H] with release of HF

DOI: 10.1039/b101007g

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Table 1 NMR data for complexes **1–6** and *trans*-[Ru(dmpe)$_2$H(FHF)] in [$^2H_8$]-THF at room temperature (δ, J/Hz)

Complex	δ (^{1}H) acidic	δ (^{1}H) hydride	δ (^{19}F)	δ (^{31}P)	J(PF)	J(PH)	J(H$_{hydride}$F)
1	13.3	−24.3 quin	−352 −167	65.0	—	21.5	—
2	12.0	−25.8 quin	−326 −167.5	65.1	—	20	—
3	12.0	−22.8 quin	−355 −162	20.8	—	20	—
4	13.2	—	−291 −160.3	3.5 t 25.4 dt	25	—	—
5	—	−23.6 dquin	−416	65.1 d	13	20	57
6	—	−20.8 dquin	−415	18	—	19	46
trans-[Ru(dmpe)$_2$H(FHF)][20]	13.8	−25.9 quin		46.3	—	21	—

which reacts with *cis*-[Ru(dmpe)$_2$H$_2$] to form the bifluoride complex.

Crystal structures of bifluoride complexes show that the bifluoride ligand is not coordinated linearly to the metal centre but exhibits an M–F ··· F angle of 128–156° (see Table 8).[17,19,20] The F ··· F separation in each of these complexes is considerably less than twice the van der Waals radius of fluorine (1.4 Å).[21] The metal–fluorine bond lengths are long, probably as a result of weakening through the hydrogen bond to the distal fluorine. In *trans*-[Ru(dmpe)$_2$H(FHF)] the lengthening is accentuated by the hydride ligand *trans* to bifluoride.

We report the synthesis of a series of ruthenium bifluoride complexes and examine their structures, spectroscopy, reactivity and dynamics.

Results

The dihydrides, *cis*-[Ru(PP)$_2$H$_2$] (PP = depe, dppe, dppp) and *cis*-[Ru(PMe$_3$)$_4$H$_2$] react immediately with NEt$_3$·3HF in THF solution at room temperature to give hydrogen, *trans*-[Ru(PP)$_2$H(FHF)] **1–3** and *cis*-[Ru(PMe$_3$)$_4$(FHF)$_2$] **4** respectively. Effervescence in the first few minutes provides evidence for the evolution of hydrogen from the reactions. This method was satisfactory for **2–4**, but gave an impure product with **1**. The dmpe analogue had originally been made by the C–F activation method (see above). Reaction of *cis*-[Ru(depe)$_2$H$_2$] with C$_6$F$_5$H yielded *trans*-[Ru(depe)$_2$(4-C$_6$F$_4$H)H] and *trans*-[Ru(depe)$_2$H(FHF)] **1**. The C–F activation product was separated by fractional crystallisation and is not discussed further here. It is analogous to the dmpe species described in ref. 20. There was no evidence for aromatic C–H bond activation. By this method we were able to obtain satisfactory samples of **1**, but corresponding attempts at C–F activation with the other ruthenium hydrides did not yield any reaction at all. All products were characterised by ^{1}H, ^{19}F and ^{31}P NMR spectroscopy, IR spectroscopy, mass spectrometry and elemental analysis (C,H). Complexes **3** and **4** were also characterised by X-ray crystallography.

NMR spectroscopy

The ^{1}H NMR spectra of **1–3** are similar to each other. A resonance at δ *ca.* −24 appears as a quintet (J(PH) = *ca.* 20 Hz) at room temperature and is assigned to the hydride ligand (Fig. 1a). The NMR spectrum is very similar to that of *trans*-[Ru(dmpe)$_2$H(FHF)].[20] On cooling, the hydride resonance resolves into a doublet of quintets (Fig. 1b), which collapses into a doublet on phosphorus decoupling with J(HF) *ca.* 60 Hz (Fig. 1c). The coupling between the proximal fluorine and the hydride proton in **1–3** was not observed at room temperature in the ruthenium bifluoride complexes, because of exchange processes (see below). Complex **4** exhibits no hydride resonance in this region.

A broad, low-field resonance found at δ 12.0–13.3 splits into a doublet resonance and shifts up to 0.6 ppm to lower field on cooling with unresolved shoulders on the inside, J(HF) = 392 Hz for **1**, J(HF) = 306 Hz for **2**, J(HF) = 317 Hz for **3** and J(HF) = 339 Hz for **4** and J(HF) < 40 Hz for the small coupling. This resonance is assigned to the hydrogen of the FHF ligand. The large coupling is associated with the distal fluorine of the bifluoride ligand (Fig. 2). The magnitude of this coupling provides additional evidence to support the suggestion of weakened hydrogen bonding relative to that of the bifluoride anion. For comparison, the ^{1}H NMR spectrum of the free bifluoride anion shows a triplet with J(HF) = 120 Hz. The value of J(HF) for free HF is solvent dependent; in MeCN J(HF) = 479 Hz, in DMSO J(HF) = 440 Hz and in the liquid phase J(HF) = 529 Hz. Thus, the value of J(HF) in the ruthenium complexes (306–392 Hz), lies between those for the bifluoride anion and HF.[22] The NMR parameters are listed in Tables 1 and 2.

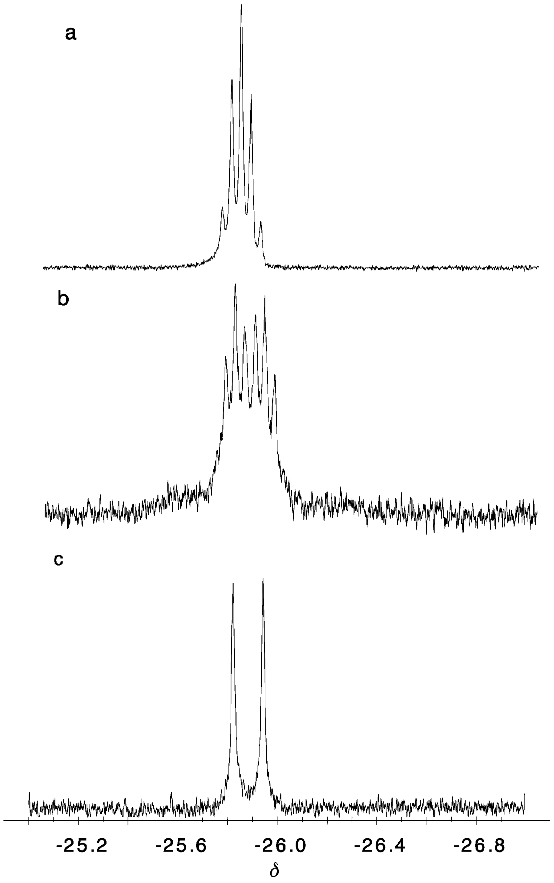

Fig. 1 ^{1}H NMR spectra (500.13 MHz) of the hydride region of *trans*-[Ru(dppe)$_2$H(FHF)] **2** in [$^2H_8$]-THF (a) at room temperature, (b) at 193 K, (c) at 193 K with ^{31}P broad band decoupling.

The ^{31}P{^{1}H} NMR spectrum shows a singlet at δ 67.0 for **1** which is unresolved at low temperature. A singlet at δ 65.1 at room temperature for **2** is resolved into a doublet at low temperature (J(PF) = 17 Hz). However the singlet at δ 20.8 for

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Table 2 NMR data for complexes **1–6** and *trans*-[Ru(dmpe)$_2$H(FHF)] in [$^2H_8$]-THF at low temperature (δ, *J*/Hz)

Complex	δ (^{1}H) acidic	δ (^{1}H) hydride	δ (^{19}F)	δ (^{31}P)	J(PF)	J(PH$_{hydride}$)	J(H$_{hydride}$F)	J(H$_{acidic}$F)	J(H$_{acidic}$F)	J(FF)
1	13.3 dd	−24.3 dquin	−352 s, br −167 dd	67.0 s	10	20	64	392	36	162
2	12.6 d	−25.8 dquin	−326 s, br −168 dd	65.1 d	17	20	62	306	<30	125
3	12.6 d	−22.9 dquin	−355 d −162 dd	13.8 t^a 27.1 td^a	— 10	21	62	317	<30	164
4	13.2 d	—	−291 d −160 dd	3.5 tt^b 27.5 dt^b	25 189	—	—	339	—	153
6	—	−20.8 dquin	−415 s, br	12.4^c 23.9^c	13	19	46	—	—	—
trans-[Ru(dmpe)$_2$ H(FHF)]	13.8	−25.9	−357 −173	46.3	—	21	61	274	<30	152

^{a} J(PP) = 42. ^{b} J(PP) = 32. ^{c} J(PP) = 43 Hz.

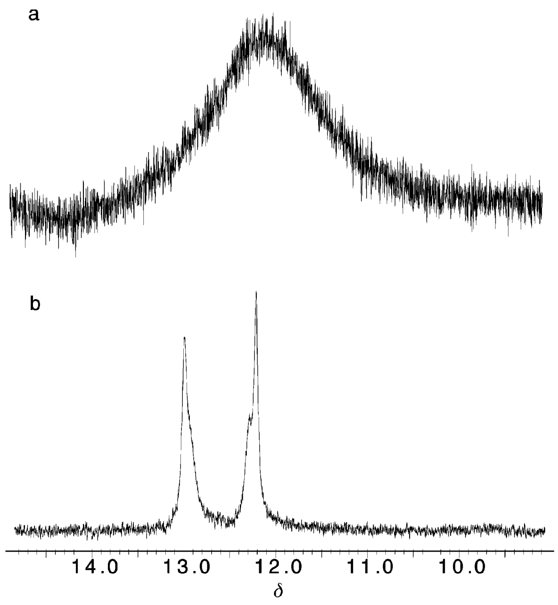

Fig. 2 ^{1}H NMR spectra (500.13 MHz) of the acidic region of *trans*-[Ru(dppe)$_2$H(FHF)] **2** in [$^2H_8$]-THF (a) at room temperature, (b) at 193 K.

3 resolves into a sharp triplet at δ 13.8 and a triplet of doublets at δ 27.1 (J(PP) = 42, J(PF) = 10 Hz) at low temperature (Fig. 3). It is proposed that the ^{31}P{^{1}H} NMR spectrum splits into two inequivalent resonances at low temperature because the two six-membered rings are locked in different conformations, one pointing up to the bifluoride, the other pointing down to the hydride (see crystal structure). Each of these two phosphorus nuclei will be coupled to the other two phosphorus nuclei to give an [AX]$_2$ system which simplifies to yield apparent triplets with a splitting of 42 Hz.

The room temperature ^{31}P{^{1}H} NMR spectrum for complex **4** shows two resonances, a triplet at δ 3.5 and a doublet of triplets at δ 25.4. At low temperature, the former splits into a triplet of triplets. The two mutually *cis* phosphorus atoms are magnetically inequivalent. Low temperature ^{31}P{^{1}H} *J*-resolved NMR experiments showed that J(PF) = 25 Hz for the mutually *trans* phosphine ligands, and $|J(PF_{cis}) + J(PF_{trans})|$ = 189 Hz for the mutually *cis* phosphine ligands, while J(PP) = 32 Hz.

The ^{19}F NMR spectra at room temperature of **1–3** contain two resonances. The broad resonance at *ca.* δ −350 is assigned to the proximal fluorine. On cooling, this resonance broadens for complexes **1** and **2** and splits into a doublet for **3** and **4**.

The second resonance at *ca.* δ −165 is broad at room temperature. On cooling this resonance sharpens to a doublet of doublets, *e.g.* J(FF) = 164 Hz and J(HF) = 317 Hz for **3** (Fig. 4). The observation of matching values of J(HF) in the proton and fluorine NMR spectra supports the proposal that HF is hydrogen bonded in the FHF ligand. The coupling constant networks are summarised in Fig. 5 and Tables 1 and 2.

^{31}P{^{1}H} NMR spectra of *trans*-[Ru(dppp)$_2$H(FHF)] **3** were recorded over a temperature range of 178–253 K in CD_2Cl_2. The rate constant *k* for the ring flipping dynamic process was calculated by simulation using the program g-NMR.[23] Fig. 3 shows an overlay of the experimental and the calculated variable temperature ^{31}P{H} NMR spectra; Fig. 6 shows the Eyring plot. The resulting kinetic data are listed in Table 3, yielding $\Delta H^{\ddagger} = 30 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -48 \pm 9$ J K^{-1} mol^{-1} and $\Delta G^{\ddagger} = 41 \pm 3$ kJ mol^{-1} at 233 K.

Infrared spectroscopy

IR spectra of the dihydride and the bifluoride complexes were recorded over the range 4000–200 cm^{-1} as Nujol mulls, (samples were prepared under argon). The ν(M–H) bands for the dihydride starting materials at 1700–1872 cm^{-1} were

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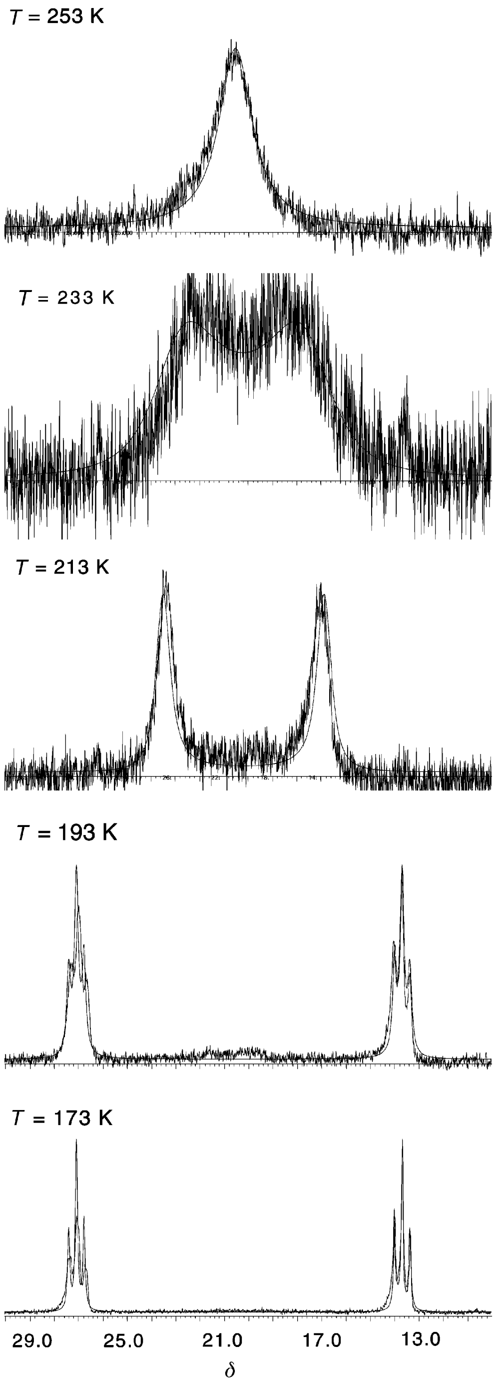

Fig. 3 Variable temperature $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2 (121.49 MHz) overlaid with simulated spectra for *trans*-[Ru(dppp)$_2$H(FHF)] **3**.

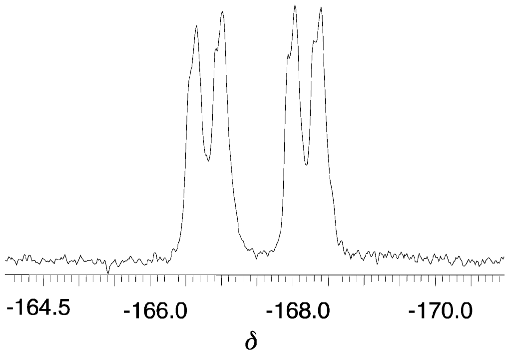

Fig. 4 ^{19}F NMR spectra (470.4 MHz) for *trans*-[Ru(dppe)$_2$H(FHF)] in [$^2H_8$]-THF showing the distal fluorine resonance at 193 K.

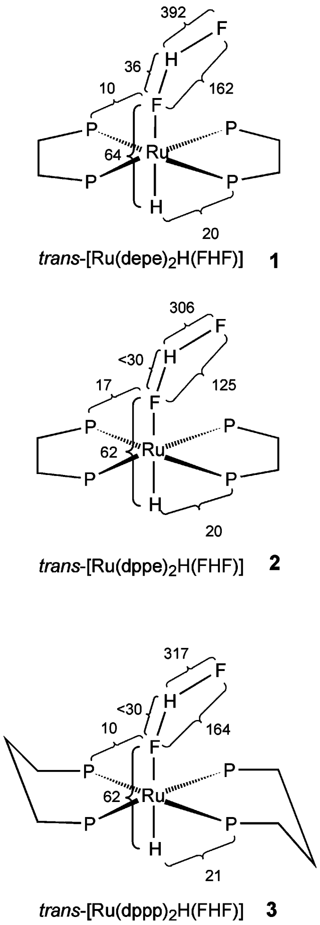

Fig. 5 Coupling constants and postulated structures of *trans*-[Ru(depe)$_2$H(FHF)] **1**, *trans*-[Ru(dppe)$_2$H(FHF)] **2** and *trans*-[Ru(dppp)$_2$H(FHF)] **3** at low temperature.

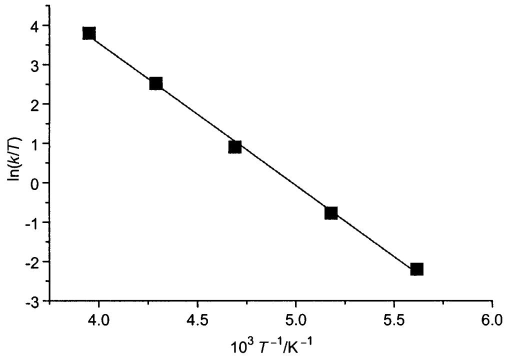

Fig. 6 Eyring plot for ring flipping of *trans*-[Ru(dppp)$_2$H(FHF)] **3**.

Table 3 Simulated rate constants for ring flipping of **3** at low temperature

T/K	k/s^{-1}
178	1.97×10^1
193	8.96×10^1
213	5.26×10^2
233	2.90×10^3
253	1.13×10^4

replaced by new bands on formation of the bifluoride complexes. The complexes **1–3** show three absorption bands (Table 4); for instance, for **2** there are two broad bands at 2315 cm^{-1} and 2450 cm^{-1}, assigned to ν(HF) of the bifluoride (Fig. 7). These values are higher than that of the bifluoride ion in its various salts (ν(HF) = 1250–1750 cm^{-1}).[24] The third sharper absorption of **2** at 1893 cm^{-1} was assigned as the ν(Ru–H)

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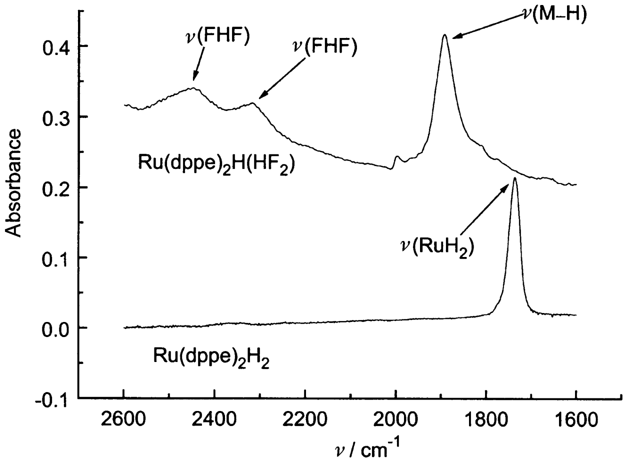

Fig. 7 IR spectra (Nujol mull) of *trans*-[Ru(dppe)$_2$H(FHF)] **2** and *cis*-[Ru(dppe)$_2$H$_2$].

Table 4 IR data (ν/cm^{-1}) for **1–4** and for corresponding dihydride complexes

Complexes	Vibration mode	1	2	3	4
MH$_2$	ν(M–H)	1868	1872	1870	1822
M(H)(FHF)	ν(M–H)	1889	1893	1900	—
	ν(HF)	2310	2315	2316	2290
	ν(HF)	2450	2450	2463	2399

vibration. In general, as the hydrogen bond interaction increases, ν(HF) is reduced from the value observed for free HF (gas phase 3960 cm^{-1}).[25] Complexes of HF with a variety of non-metal bases have been studied by IR spectroscopy in matrices. For the majority of bases, the HF stretching mode lies above 3000 cm^{-1}, even with strong bases such as NMe$_2$H it lies no lower than 2760 cm^{-1}.[26] Our observed bands for the HF stretching modes of the coordinated bifluoride complex lie in an intermediate region and are indicative of a weakened hydrogen bonding interaction. The position of the lower frequency band in each case was found to be close to that observed for ν(RuH) in *trans*-[Ru(PR$_3$)$_4$(H)Cl].[27]

Complex **4** shows two broad absorption bands at 2290 cm^{-1} and 2399 cm^{-1} which are close to the values of ν(HF) for the ruthenium hydride bifluoride complexes and assigned to the ν(HF) of the bifluoride. No hydride band was seen in the IR for this complex.

Crystal structure of complex 3

The crystal structure of **3**·2THF was determined by single crystal X-ray crystallography. The bifluoride complex **3** was crystallised from THF at −20 °C. During the refinement, the ruthenium ion was automatically constrained to lie on the inversion centre. The asymmetric unit contains exactly one half of the molecule. Applying the symmetry operator of $P\bar{1}$ (about the centre of inversion) reveals the full structure, but results in disorder of the bifluoride (FHF) unit over two positions about the metal centre. Refinement of the site occupation factor of each bifluoride unit against a free variable reveals that the occupation of both sites is equal to *ca.* 0.5, excluding the alternative formulation, [Ru(dppp)$_2$(FHF)$_2$]. The hydrogen atoms in the bifluoride, hydride and solvent of crystallisation were not located.

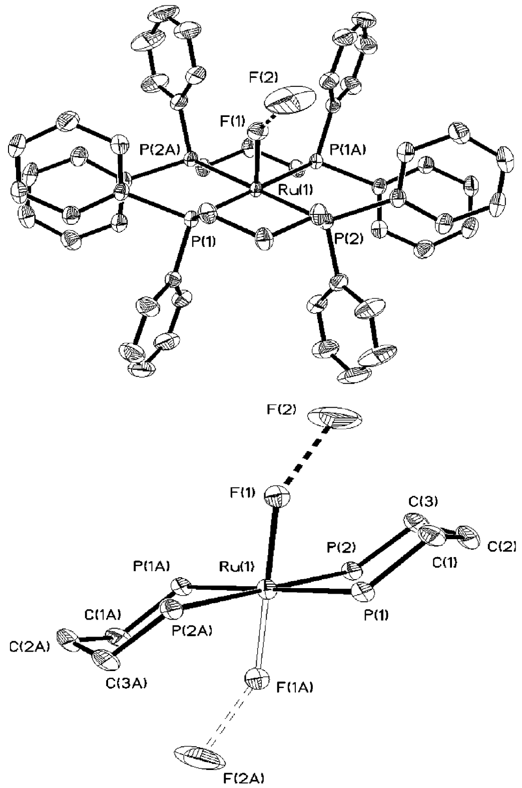

Fig. 8 Top: the crystal structure (ORTEP[28] diagram) of *trans*-[Ru(dppp)$_2$H(FHF)] **3**·2THF (thermal ellipsoids at the 50% probability level). Hydrogen atoms and THF are not shown. Bottom: with the phenyl groups removed, but with the second disordered bifluoride shown pale. Each bifluoride site has 50% occupancy.

Table 5 Selected bond distances (Å) and angles (°) for **3**

Ru(1)–F(1)	2.351(5)	F(1) ··· F(2)	2.290(8)
Ru(1)–P(1A)	2.3653(14)	P(1A)–Ru(1)–P(1)	180.00
Ru(1)–P(1)	2.3653(14)	P(1A)–Ru(1)–P(2)	93.72(5)
Ru(1)–P(2A)	2.3798(14)	P(1)–Ru(1)–P(2)	86.28(5)
Ru(1)–P(2)	2.3798(14)	Ru(1)–F(1) ··· F(2)	149.7(3)

ORTEP[28] diagrams of the crystal structure are shown in Fig. 8. The structure (Table 5) shows the presence of bifluoride, F–H–F, coordinated to ruthenium lying *trans* to the hydride (which was not located). The Ru–F ··· F angle, 149.7(3)°, is larger than that of *trans*-[Ru(dmpe)$_2$H(FHF)].[20] The F ··· F distance of 2.290(8) Å is similar to those found in the bifluoride salts, MFHF (M = Na$^+$, K$^+$, NH$_4^+$),[29] pyridine(HF)$_n$,[30] and in *trans*-[Ru(dmpe)$_2$H(FHF)], but significantly shorter than the F ··· F separation (2.352(8) Å) found for [Mo(PMe$_3$)$_4$H$_2$F-(FHF)]. The F ··· F separation in *trans*-[Ru(dppp)$_2$H(FHF)] is considerably less than twice the van der Waals radius (1.4 Å).[21]

The Ru–F bond length, 2.351(5) Å, is even longer than that (2.284(5) Å) found for *trans*-[Ru(dmpe)$_2$H(FHF)] and is substantially longer than found in any conventional ruthenium fluoride complexes, typically 2.01–2.07 Å.[3,5,6,20] The long Ru–F bond probably results from a combination of the *trans* influence of the hydride and the hydrogen bonding in the FHF unit.

The crystal structure helps to understand the variable temperature ^{31}P{^{1}H} NMR behaviour. The six-membered rings are locked in different conformations, one pointing up to the bifluoride, the other pointing down to the hydride. In solution, the two rings will be flipping and the bifluoride ligand rotating about the Ru–F bond faster than the NMR time scale.

Crystal structure of complex 4

Complex **4** was crystallised from THF at −20 °C. The structure (Fig. 9, Table 6) shows the presence of two bifluoride ligands coordinated to the ruthenium centre and lying *cis* to each other in two different planes. The Ru–F ··· F angles of 128.5(3)° and 138.4(3)° are comparable to the values of 129.9(3)° reported for *trans*-[Ru(dmpe)$_2$H(FHF)].[20] The F ··· F bond lengths, 2.323(8) Å and 2.329(8) Å, are longer than those of *trans*-[Ru(dppp)H(FHF)] **3** (2.290(8) Å) but the difference is on the borderlines of significance. The Ru–F bond lengths of 2.149(4)

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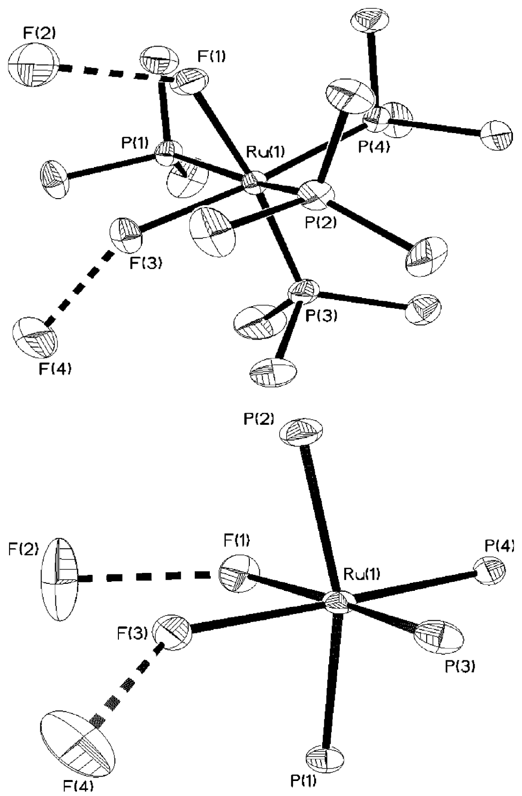

Fig. 9 Top: the crystal structure (ORTEP[28] diagram) of *cis*-$[Ru(PMe_3)_4(FHF)_2]$ **4**. Hydrogen atoms have been omitted. The thermal ellipsoids are shown at the 50% probability level. Bottom: with the methyl groups removed.

Table 6 Selected bond distances (Å) and angles (°) for **4**

Ru(1)–F(1)	2.150(5)	Ru(1)–F(1) ··· F(2)	128.5(3)
Ru(1)–F(3)	2.149(4)	Ru(1)–F(3) ··· F(4)	138.4(3)
Ru(1)–P(1)	2.394(3)	P(3)–Ru(1)–P(1)	98.59(11)
Ru(1)–P(2)	2.370(4)	P(1)–Ru(1)–P(2)	163.16(7)
Ru(1)–P(3)	2.258(3)	P(3)–Ru(1)–P(4)	96.68(8)
Ru(1)–P(4)	2.264(2)	F(1)–Ru(1)–P(1)	82.75(17)
F(1) ··· F(2)	2.323(8)	F(3)–Ru(1)–P(3)	89.02(15)
F(3) ··· F(4)	2.329(8)	F(1)–Ru(1)–P(4)	91.52(15)
		F(3)–Ru(1)–P(1)	85.23(15)

Å and 2.150(5) Å lie between those in conventional ruthenium fluoride complexes (2.01–2.07 Å)[14] and those of *trans*-$[Ru(dmpe)_2H(FHF)]$ and complex **3**. The absence of a strong *trans* directing ligand evidently results in a much shorter Ru–F bond.

The angle between the plane containing the F(2) ··· F(1)–Ru unit and the P(3)–P(4)–Ru plane is 1.9°, the angle between the F(4) ··· F(3)–Ru plane and the P(3)–P(4)–Ru plane is 29.1°. Thus, the bifluoride ligand F(1) ··· F(2) is in approximately the same plane as the two phosphine ligands P(3) and P(4), while the second bifluoride ligand F(3) ··· F(4) lies in a different plane.

The F ··· F separation in both **3** and **4** indicates that the bifluoride ligand is involved in a weaker hydrogen bonding interaction than that of the free bifluoride anion, which can be described as hydrogen bonding of HF to the proximal fluorine Ru–F ··· HF. The low temperature NMR spectra support this description. *cis*-$[Ru(PMe_3)_4(FHF)_2]$ is the first ruthenium bis-bifluoride complex to be characterised in solution and in the solid state.

Reactivity of bifluoride complexes

(a) Conversion of bifluoride to fluoride complexes. Parkin *et al.* extracted HF from $[Mo(PMe_3)_4H_2F_2](HF)_2$ by adding 1/3 of an equivalent of $[Mo(PMe_3)_5N_2]$ which reacts with HF to yield $[Mo(PMe_3)_4H_2F(FHF)]$.[17] It was suggested above that the interaction between HF and RuF in the bifluoride complexes consisted of a normal hydrogen bond between Ru–F and HF.

Table 7 NMR data for complexes *trans*-$[Ru(dppe)_2(H)X]$ (X = Cl, Br, I, N_3) and $[Ru(depe)_2H]OTf$ in $[^2H_8]$-THF

Complex	δ (^{1}H)	δ (^{31}P)	J(PH)/Hz
trans-$[Ru(dppe)_2(H)Cl]$	−18.9	63.4	20
trans-$[Ru(dppe)_2(H)Br]$	−17.6	62.7	20
trans-$[Ru(dppe)_2(H)I]$	−15.6	62.5	20
$[Ru(dppe)_2H]OTf$	−11.9	52.6	20
trans-$[Ru(dppe)_2(H)(N_3)]$	−18.7	65.7	19

Attempts to remove HF from the ruthenium bifluoride complexes with pyridine, triethylamine and lithium diisopropylamide gave new products which have not been characterised. However, reaction of **1** and **3** with dry $[NMe_4]F$ in THF under argon was more successful. The products **5** and **6** were studied by IR and NMR spectroscopy and identified as *trans*-$[Ru(depe)_2(H)F]$ **5** and *trans*-$[Ru(dppp)_2(H)F]$ **6**. The IR spectrum from the reaction of **3** no longer contained the ν(HF) bands belonging to the bifluoride complex of **3** at 2316 cm^{-1} and 2463 cm^{-1} and the hydride band shifted from 1900 cm^{-1} to 1925 cm^{-1}.

The ^{1}H NMR spectrum shows a resonance at δ −23.6 for **5** and at δ −20.8 for **6**. Both show a doublet of quintets pattern that simplifies to a doublet when phosphorus decoupled (J(HF) = 46 Hz and J(PH) = 19 Hz) for **6**. No resonances due to the acidic proton were seen at low field, providing evidence that the compound is not a bifluoride complex. The HF coupling is very clear in the proton NMR spectra at room temperature.

The $^{31}P\{^1H\}$ NMR spectrum for complex **5** shows a doublet resonance at δ 65.1 (J = 13 Hz) at room temperature. Complex **6** shows a singlet resonance at δ 18. On cooling, this resonance splits into two resonances, a triplet at δ 12.4 (J(PP) = 43 Hz) and a triplet of doublets at δ 23.9 (J(PF) = 13 Hz and J(PP) = 43 Hz), in a similar way to the bifluoride complex with the same phosphine. Notice that P–F coupling is only detected to one pair of ^{31}P nuclei.

The ^{19}F NMR spectrum of **6** shows only one broad resonance at δ −415 at room temperature which broadens at low temperature. The lack of a resonance at *ca.* δ −167 due to the distal fluorine of the bifluoride ligand gives further evidence that the ligand is a fluoride and that the reaction products are *trans*-$[Ru(dppp)_2(H)F]$ and *trans*-$[Ru(depe)_2(H)F]$ (eqns. (1) and (2)). It should be noted that we cannot distinguish whether the reaction involves replacement of bifluoride by fluoride, or removal of HF.

$$[Ru(PP)_2H_2] + NEt_3{\cdot}3HF \xrightarrow{THF} \textit{trans}\text{-}[Ru(PP)_2H(FHF)] \qquad (1)$$

$$(PP = depe, dppp)$$

$$\textit{trans}\text{-}[Ru(PP)_2H(FHF)] \xrightarrow[{[Me_4N]F}]{THF} \textit{trans}\text{-}[Ru(PP)_2(H)F] \qquad (2)$$

(b) Replacement of bifluoride. In the ruthenium bifluoride complexes, the bifluoride ligand can also be replaced easily by other halides or cyanide. The bifluoride ligand of **2** exchanges rapidly with X^- in aqueous MX (X^- = Cl^-, Br^-, I^- and CN^-) to give *trans*-$[Ru(dppe)_2(H)X]$ (Scheme 1) in low yield. The NMR parameters of *trans*-$[Ru(dppe)_2(H)X]$ are listed in Table 7.

The bifluoride complex *trans*-$[Ru(dppe)_2H(FHF)]$ abstracts halides from the reaction with halo-organic compounds (CH_3I, $CHCl_3$, $CHBr_3$, CH_2Cl_2, 2-bromopyridine, C_6H_5X [X = Cl, Br and I], CH_3COCl, C_6H_5COCl) in THF to yield the corresponding *trans*-$[Ru(dppe)_2(H)X]$ complex (X = Cl, Br and I) in good yields. The bifluoride complex can also fluorinate some halo-

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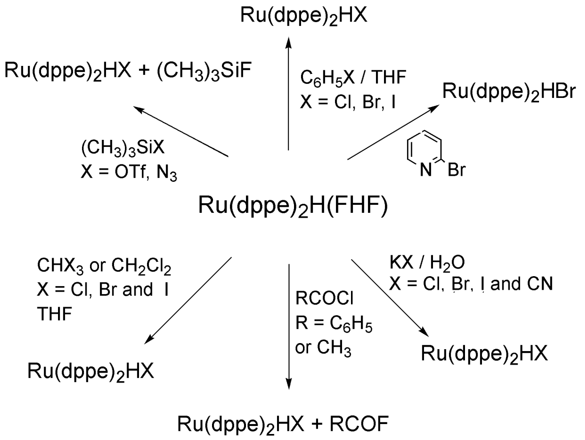

Scheme 1 Ligand replacement and reactivity of *trans*-[Ru(dppe)$_2$-H(FHF)].

organics (CH_3I, CH_3COCl and C_6H_5COCl to produce CH_3F, CH_3COF and C_6H_5COF) (Scheme 1). The ^{19}F NMR spectra show the disappearance of the distal and the terminal fluorine resonances of the bifluoride ligand. In the reaction of the bifluoride complex with CH_3I and CH_3COCl the fluorine resonances for CH_3F and CH_3COF were observed. NMR data are summarised in Table 7.

Ruthenium bifluoride complexes can also react with Me_3SiX ($X = N_3$ or OTf) in THF, to produce $[Ru(dppe)_2(H)X]$ in good yield. These reactions were initially carried out in an NMR tube, then scaled up. The ν(HF) band of the bifluoride was absent from the IR spectrum of all these products. In the azide complex, two bands were found; a sharp band at 2036 cm^{-1} assigned to the $\nu(N_3)$ stretching vibration and a shoulder at 2013 cm^{-1} assigned to ν(Ru–H). In the triflate complex a strong and sharp band located at 2147 cm^{-1} was assigned to the ν(Ru–H) stretching vibration and two bands found at 1261 cm^{-1} and 1161 cm^{-1} were assigned to $\nu(SO_3)$ and $\nu(CF_3)$ of the OTf respectively. The hydride resonance of the triflate lies at δ −11.9, compared with *ca.* δ −17 to −18 for most of the other *trans*-$[Ru(dppe)_2(H)X]$ complexes (Table 7). The ν(Ru–H) mode in the IR spectrum and the hydride resonance in the NMR spectrum for the triflate complex are quite distant from those of other complexes. The IR spectra of five-coordinate ruthenium hydride salts show ν(Ru–H) vibrations at higher frequencies than for other hydride complexes.[31] Five-coordinate salts have been reported in which the hydride resonates between δ −8.02 and −11.62,[32] close to the hydride resonance observed for the triflate complex. It is suggested that the triflate complex is a five-coordinate salt $[RuH(dppe)_2](OTf)$, while the azide complex is six-coordinate *trans*-$[Ru(dppe)_2(H)(N_3)]$.

Exchange with free bifluoride and dynamic behaviour of bifluoride complexes

The fluxionality is very clear in the variable temperature NMR spectra of all the bifluoride complexes. The extraction of HF from these complexes suggests that the HF in the bifluoride ligand might dissociate HF in solution (eqn. (3)), but the lack of etching on the glass, even on prolonged standing, excludes this mechanism.

$$\text{M–F–H–F} \rightleftharpoons \text{MF} + \text{H–F} \qquad (3)$$

Free bifluoride anion was detected during the synthesis which indicates that the bifluoride complex may also dissociate FHF^- in solution (eqn. (4)).

$$\text{M–F–H–F} \rightleftharpoons \text{M}^+ + \text{F–H–F}^- \qquad (4)$$

We now turn to the effect of cooling on the NMR spectra of **2**. The acidic proton resonance appears as a broad singlet at δ 12.0 at room temperature. On cooling, this resonance separates and sharpens into a doublet at (T_c *ca.* 253 K). The hydride resonance is a quintet at room temperature, which changes into a doublet of quintets at low temperature. In the ^{19}F NMR spectra, the resonance of the proximal fluorine at *ca.* δ −326 is broad at room temperature and broadens further on cooling. The resonance of the distal fluorine is broad at room temperature and resolves into a doublet of doublets on cooling. A similar observation was found in all the other ruthenium bifluoride complexes. The change in the hydride resonance is different from that in the platinum bifluoride complex reported in our previous work in which coupling to the proximal fluorine was retained at room temperature.[16] The proximal fluorine coupling is very clear in the hydride resonance of the ruthenium complex at low temperature, but disappeared at room temperature. The disappearance of the hydride–fluorine coupling suggests that the bifluoride ligand is dissociating from the complex at room temperature, but remains bound at low temperature (eqn. (4)). This behaviour would also account for the change in chemical shift of the acidic proton on cooling.

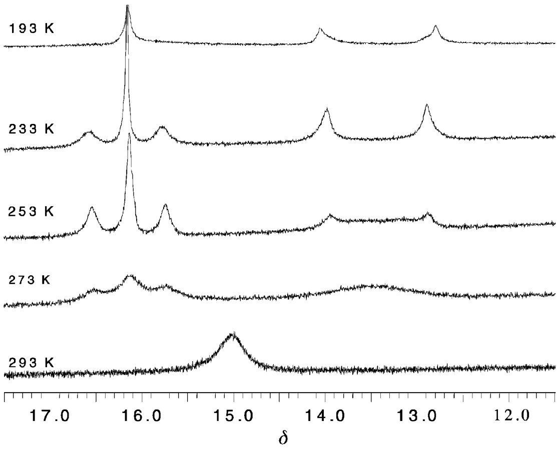

Fig. 10 Variable temperature ^1H NMR spectra (300.13 MHz) of a mixture of $[NBu_4]FHF$ and *trans*-$[Ru(dppe)_2H(FHF)]$ in $[^2H_8]$-THF.

The complexes **1**, **2** and **4** show identical dynamic behaviour in the ^1H and ^{19}F NMR spectra and may therefore undergo the same exchange processes. However, the poor resolution of the spectra and the complexity of the system prevent us from carrying out additional kinetic analysis.

Dynamic behaviour was observed on addition of $[NBu_4]FHF$. The behaviour of solutions of $[NBu_4]FHF$ alone was described in ref. 16. At room temperature, the bifluoride proton is observed as the expected triplet at δ 16.1 ($J(HF) = 120$ Hz), but on cooling the outer resonances of the triplet broaden and weaken without change in frequency. This behaviour probably originates in ion-pair formation. A spectrum of a mixture of $[NBu_4]FHF$ and **2** at 193 K corresponded simply to the spectra measured for the components alone. However, warming caused the resonances of the bifluoride complex and free bifluoride to coalesce into one resonance at δ 15.0 (Fig. 10). The exchange process is shown in eqn. (5).

$$\text{M–F–H–F} + \text{F*–H*–F*}^- \rightleftharpoons \text{M–F*–H*–F*} + \text{F–H–F}^- \qquad (5)$$

Discussion

Spectroscopic analysis has enabled us to characterise four ruthenium bifluoride complexes. These complexes illustrate the scope for direct hydrogen bonding to metal-bound fluorine—the importance of hydrogen bonding in the metal coordination sphere is recognised for its influence on bonding, structure and reactivity.[33] The crystal structures for **3** and **4** were also determined. The spectroscopic and X-ray data make it evident that the hydrogen bond is far from symmetric and could be

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Table 8 Low temperature coupling constants, bond lengths and angles of bifluoride complexes

Complex	*J*(FF)/Hz	*J*(M*FH*F)/Hz	*J*(MF*HF*)/Hz	F ··· F distance/Å	M–F distance/Å	M–F ··· F angle/°
trans-[Ru(depe)$_2$H(FHF)] **1**	162	36	392	—	—	—
trans-[Ru(dppe)$_2$H(FHF)] **2**	125	<30	306	—	—	—
trans-[Ru(dppp)$_2$H(FHF)] **3**	164	<30	317	2.290(8)	2.351(5)	149.7(3)
trans-[Ru(dmpe)$_2$H(FHF)][20]	152	<30	274	2.276(8)	2.2846(5)	129.9(3)
cis-[Ru(PMe$_3$)$_4$(FHF)$_2$] **4**	153	—	339	2.323(8) 2.329(8)	2.149(5) 2.150(5)	128.5(3) 138.4(3)
trans-[Pt(PCy$_3$)$_2$H(FHF)][16]	103	48	412	—	—	—
trans-[Pt(P^{i}Pr$_3$)$_2$H(FHF)][16]	103	43	393	—	—	—
[MoF(PMe$_3$)$_4$(H)$_2$(FHF)][17]	—	—	410	2.351(8)	2.124(3)	134
[W(PMe$_3$)$_4$F(H)$_2$(FHF)][17]	—	—	430	2.389(6)	2.117(5)	156
[Ni(C$_4$N$_2$F$_2$H)(PEt$_3$)$_2$(FHF)][19]	—	—	427	2.404(5)	1.909(3)	—
[Ni(C$_5$NF$_4$)(PEt$_3$)$_2$(FHF)][19]	≈85	41	424	—	—	—
HF	—	410–530	—	—	—	—
FHF$^-$	—	120		2.24–2.28	—	—

described as containing a Ru–F ··· H–F moiety. The appearance of the hydride–fluorine coupling at low temperature and its disappearance at room temperature suggests that the bifluoride ligand dissociates from the complex at room temperature, but remains bound at low temperature. The weakly bound bifluoride ligand in *trans*-[Ru(dppe)$_2$H(FHF)] exchanges with free bifluoride anion in [^{2}H$_8$]-THF solution at low temperature. We also found that the FHF$^-$ ligand is weakly coordinated and can be replaced with X$^-$ (X$^-$ = Cl$^-$, Br$^-$, I$^-$, N$_3^-$ and OTf$^-$). It can also be used to fluorinate some organic compounds (CH$_3$Cl, CH$_3$COCl and C$_6$H$_5$COCl yielding CH$_3$F, CH$_3$COF and C$_6$H$_5$COF respectively). The overall reaction is a halide metathesis that yields *trans*-[Ru(PP)$_2$(H)X]. The preparative methods described in this paper can also be used to introduce the fluoride ligand selectively under mild conditions by sequential reaction with NEt$_3$·3HF and [NMe$_4$]F.

Table 8 summarises the HF coupling constants of the distal fluorine for the bifluoride and key geometric parameters reported in our previous paper,[16] the current work and some bifluoride complexes from the literature. The F ··· F distance in the bifluoride complexes ranges from 2.276(8) to 2.404(5) Å, appreciably longer than the F ··· F distance in the bifluoride anion (2.24–2.28 Å). There is good correlation (correlation coefficient 0.96) between the F ··· F distance and *J*(HF) for the distal fluorine, suggesting that the magnitude of *J*(HF) increases as the hydrogen bond weakens.

Brammer *et al.* have shown that hydrogen bonds at metal fluoride complexes are shorter than for other metal halide complexes. They have also found that M–F ··· H angles lie in the range 130–160° compared to 90–130° for their analogues with other halides.[34] Our bond angles Ru–F ··· F fall within the range suggested by Brammer, but as yet we cannot compare our geometric parameters for those with analogues in which fluorine is replaced by other halogens.

In this paper, we have characterised a bis-bifluoride complex in which the bifluoride ligand lies *trans* to one PMe$_3$ and *cis* to another. In the remainder of the ruthenium bifluoride complexes, the bifluoride lies *trans* to hydride. It is now apparent that the complexes of type *trans*-[Ru(PP)$_2$(H)(FHF)] have a Ru–F bond length between 0.13 and 0.2 Å longer than that in *cis*-[Ru(PMe$_3$)$_4$(FHF)$_2$]. The magnitude of *J*(PF) increases from 10–20 Hz with a *cis*-disposition of phosphines and bifluoride to *ca.* 190 Hz for a *trans*-disposition.

Experimental

All syntheses and manipulations were carried out under argon using standard Schlenk (vacuum 10^{-2} mbar) and high vacuum techniques (vacuum 10^{-4} mbar), or in a glove box. Diethyl ether, toluene, benzene, hexane, tetrahydrofuran (Fison AR or HPLC grade) were dried over sodium–benzophenone and distilled under argon. The dried solvents were stored under argon in ampoules fitted with a Young's ptfe tap. All deuterated, [^{2}H$_6$]-benzene, [^{2}H$_8$]-toluene and [^{2}H$_8$]-tetrahydrofuran solvents (Goss Scientific) were dried over potassium and vacuum distilled prior to use. All NMR tubes (Wilmad 528-PP) were either fitted with a Young's tap to allow sealing under argon atmosphere, or were flame sealed under vacuum.

Most NMR spectra were recorded on a Bruker MSL300 (^{1}H recorded at 300.13 MHz, ^{19}F at 282.35 MHz, ^{31}P at 121.49 MHz) or Bruker AMX500 spectrometers (^{1}H recorded at 500.13 MHz, ^{19}F at 470.4 MHz, ^{31}P at 202.46 MHz). ^{19}F NMR spectra with ^{1}H decoupling were recorded on a Bruker DRX400 spectrometer, as were ^{1}H spectra with ^{19}F decoupling. Simulations were carried out with g-NMR.[23] Mass spectra were recorded on a VG Autospec instrument and are quoted for ^{102}Ru. IR spectra were measured on a Mattson-Unicam Research Series instrument fitted with a CsI beamsplitter.

Chemicals were obtained from the following sources RuCl$_3$·*x*H$_2$O (Aldrich), trimethylphosphine (PMe$_3$) (Strem); bis(dimethylphosphino)methane (dmpe), bis(diethylphosphino)ethane (depe), bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)propane (dppp) (Aldrich or Lancaster). [NMe$_4$]F and NEt$_3$·3HF were supplied by Aldrich, Me$_3$SiOTf was obtained from Gelest and Me$_3$SiN$_3$ was synthesised by standard methods. KCl, KBr, KI, NaOH, KPF$_6$, KOH, KCN, Mg, MgSO$_4$, P$_2$O$_5$ and iodine were supplied by Fisons and sodium dispersion by Strem. [NMe$_4$]F was dried and dry [NBu$_4$](FHF) was synthesised according to the literature.[16] The dihydrides Ru(depe)$_2$H$_2$,[35] Ru(dppe)$_2$H$_2$,[35] Ru(dppp)$_2$H$_2$[36] and Ru(PMe$_3$)$_4$H$_2$[37] were synthesised by standard methods.

Syntheses

Synthesis of *trans*-[Ru(depe)$_2$H(FHF)] (1). *cis*-[Ru(depe)$_2$H$_2$] (0.2 g, 0.361 mmol) was dissolved in THF (30 mL) in a Schlenk tube and a two-fold excess of C$_6$F$_5$H (0.13 g, 0.773 mmol) was added to the solution. The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum. The residue was extracted with hexane, and the extract filtered through a cannula. The filtrate was reduced to 3 mL and cooled to −30 °C to form crystals of *trans*-[Ru(depe)$_2$H(C$_6$F$_5$)]. The supernatant was filtered off and the solvent removed under vacuum to yield yellow *trans*-[Ru(depe)$_2$H(FHF)]. (Found: C, 44.06; H, 9.7. Calc. for C$_{20}$F$_2$H$_{50}$P$_4$Ru: C, 43.39; H, 9.10%). The C,H analysis figures are slightly higher than calculated which is consistent with some loss of HF as was observed with the dmpe analogue.

IR (Nujol, cm^{-1}): 2450 (m, b), 2310 (m, b), 1889 (m), 1567 (w), 1372 (w), 1259 (s), 1043 (s), 1028 (s), 939 (m), 808 (m), 788 (m), 738 (w), 721 (w), 532 (w), 481 (m), 391 (w), 352 (vw).

Mass spectra (FAB-MS): *m*/*z* 514 (100%, M$^+$ − 2HF).

Synthesis of *trans*-[Ru(dppe)$_2$H(FHF)] (2). *cis*-[Ru(dppe)$_2$H$_2$] (1.0 g, 1.11 mmol) was dissolved in THF (50 mL) in a Schlenk tube and a three-fold excess of NEt$_3$·3HF (0.537 g, 3.33 mmol)

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was added to the solution. The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum. The residue was extracted with benzene, filtered through a cannula, and pumped to dryness. Recrystallisation from THF–hexane at −30 °C afforded yellow crystals (yield 85%). (Found: C, 66.03; H, 5.57. Calc. for $C_{52}F_2H_{50}P_4Ru$: C, 66.58; H, 5.37%).

IR (Nujol, cm^{-1}): 2450 (m, b), 2315 (m, b), 1893 (m), 1233 (vw), 1190 (w), 884 (vw), 877 (w), 751 (s), 664 (m), 646 (m), 520 (s), 452 (m), 425 (w), 355 (w), 327 (vw).

Mass spectra (FAB-MS): *m*/*z* 898 (100%, $M^+ - 2HF$).

Synthesis of *trans*-[Ru(dppp)$_2$H(FHF)] (3). This complex was prepared in an identical fashion to *trans*-[Ru(dppe)$_2$H(FHF)]. The product was recrystallised from THF at −30 °C to afford yellow crystals (yield 82%). (Found: C, 66.72; H, 5.89. Calc. for $C_{54}F_2H_{54}P_4Ru$: C, 67.14; H, 5.63%).

IR (Nujol cm^{-1}): 2463 (b, m), 2316 (b, m), 1900 (s), 1124 (w), 1072 (m), 984 (w), 949 (m), 917 (m), 843 (s), 795 (w), 759 (w), 739 (s), 645 (w), 545 (m), 513 (s), 498 (s), 465 (w), 422 (m), 379 (vw), 330 (w).

Mass spectra (FAB-MS): *m*/*z* 927 ($M^+ -$ FHF).

Synthesis of *cis*-[Ru(PMe$_3$)$_4$(FHF)$_2$] (4). *cis*-[Ru(PMe$_3$)$_4$H$_2$] (0.50 g, 1.04 mmol) was dissolved in THF (50 mL) in a Schlenk tube. The solution was cooled to 0 °C and a two-fold excess of $NEt_3 \cdot 3HF$ (0.335 g, 2.07 mmol) added. The mixture was stirred for 1 h until yellow crystals formed. The solvent was removed under vacuum. The residue was extracted with benzene, filtered through a cannula, and dried under vacuum. The product was recrystallised from THF at −30 °C to afford yellow crystals (yield 85%). (Found: C, 29.76; H, 7.90. Calc. for $C_{12}F_4H_{38}P_4Ru$: C, 29.75; H, 7.91%).

IR (Nujol, cm^{-1}): 2399 (m, b), 2290 (m, b), 1313 (w), 1255 (w), 955 (m), 940 (m), 865 (w), 723 (s), 670 (w), 635 (w), 471 (vw), 380 (w), 360 (w).

Mass spectra (FAB-MAS): *m*/*z* 425 ($M^+ - HF_3$).

Abstraction of HF from bifluoride complexes. *trans*-[Ru(depe)$_2$(H)(FHF)] (0.1 g, 0.11 mmol) or *trans*-[Ru(dppp)$_2$(H)(FHF)] (0.1 g, 0.106 mmol) was dissolved in THF (50 mL) in a Schlenk tube. The solution was added to excess solid [NMe$_4$]F (0.1 g, 1.1 mmol) under argon. The resulting suspension was stirred at room temperature for 2 h and the solvent was then removed under vacuum. The product was extracted with benzene (60 mL) and then dried under vacuum to yield a yellow product.

Synthesis of *trans*-[Ru(dppe)$_2$(H)N$_3$]. *cis*-[Ru(dppe)$_2$H(FHF)] (0.1 g, 0.106 mmol) was dissolved in THF (20 mL) in a Schlenk tube and $(CH_3)_3SiN_3$ (0.012 g, 0.106 mmol) was added to the solution. The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum and the solid residue was extracted with benzene and dried under vacuum. Recrystallisation from THF–hexane at −30 °C afforded yellow crystals (yield 78%). (Found: C, 66.97; H, 5.5; N: 4.1. Calc. for $C_{52}H_{49}N_3P_4Ru$: C: 66.31; H, 5.23; N, 4.46%).

IR (Nujol, cm^{-1}): 2036 (s), 2014 (m), 1172 (vw), 880 (w), 693 (m), 508 (m), 484 (m), 427 (w), 419 (w), 383 (vw), 347 (vw).

Synthesis of [Ru(dppe)$_2$(H)]OTf. This complex was synthesised using the same method as described for *trans*-[Ru(dppe)$_2$(H)N$_3$].

IR (Nujol, cm^{-1}): 2174 (s), 1261 (m), 1161(m), 895 (vw), 888 (vw), 783 (w sh), 722 (m), 640 (w), 580 (vw), 514 (w).

Structure determination for complex 3

Yellow block-shaped crystals of **3**·2THF were obtained from a solution of **3** in THF at −20 °C. Diffraction data were collected for a crystal with dimensions 0.4 × 0.3 × 0.2 mm.

Crystal data. $C_{62}H_{70}F_2P_4O_2Ru$, $M = 1110.13$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.812(5)$, $b = 12.060(6)$, $c = 11.379(5)$ Å, $\alpha = 112.51(3)$, $\beta = 96.17(4)$, $\gamma = 109.18(3)°$, $U = 1362.9(10)$ Å^3, $T = 150$ K, $Z = 1$, $\mu(\text{MoK}\alpha) = 0.455$ mm^{-1}, 5371/5062 measured/unique data, $R_{int} = 0.0518$. The structure was solved by direct methods using SAPI,[38] and expanded using Fourier techniques with DIRDIF,[39] and refined against F^2 (SHELXL 97).[40] Hydrogen atoms on the phosphine ligands were placed in idealised positions, but hydrogen atoms on the bifluoride, the hydride position and the THF were not included. The ruthenium atom sits on the centre of symmetry. The bifluoride was disordered about the two positions generated by the crystallographic inversion operation. When the site occupations of the two fluorine atoms were allowed to refine freely, they converged to 52%, clearly excluding the structure [Ru(dppp)$_2$(FHF)$_2$]. This formula was also excluded as follows. When the site occupation factors of F(1) and F(2) were set at 100% and the structure allowed to refine, the U_{iso} values for F(1) and F(2) increased significantly, the *R* values were raised and a hole formed close to F(1). Final *R*1, *wR*2 on all data 0.0710, 0.1279; *R*1, *wR*2 on $[I_o > 2\sigma(I_o)]$ 0.0445, 0.1162.

Structure determination for complex 4

Yellow block-shaped crystals were obtained from a solution of **4** in THF at −20 °C. Diffraction data were collected for a crystal with dimensions 0.5 × 0.5 × 0.5 mm.

Crystal data. $C_{12}H_{38}F_4P_4Ru$, $M = 483.37$, monoclinic, space group *Cc* (no. 9), $a = 16.435(14)$, $b = 8.819(3)$, $c = 17.826(18)$ Å, $\beta = 123.46(5)°$, $U = 2155(3)$ Å^3, $T = 150$ K, $Z = 4$, $\mu(\text{MoK}\alpha) = 1.408$ mm^{-1}, 2379/1761 measured/unique data, $R_{int} = 0.0294$. The structure was solved by direct methods using SAPI,[38] and expanded using Fourier techniques with DIRDIF,[39] and refined against F^2 (SHELXL 97).[40] Hydrogen atoms on the phosphine ligands were placed in idealised positions, but hydrogen atoms on the bifluoride were not included. Final *R*1, *wR*2 on all data 0.0396, 0.1024, *R*1, *wR*2 on $[I > 2\sigma(I)]$, 0.0368, 0.0990.

CCDC reference numbers 157681 and 157682.

See http://www.rsc.org/suppdata/dt/b1/b101007g/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We would like to acknowledge discussions and experimental assistance from Dr S. B. Duckett and Prof. W. Levason, and the University of York and the EPSRC for financial assistance.

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