Synthesis, molecular structure and NMR spectroscopy of a transition-metal bifluoride complex: formation *via* C–F activation or reaction with $Et_3N{\cdot}3HF$

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The bifluoride complex, *trans*-[Ru(dmpe)$_2$(H)(HF$_2$)] (dmpe = $Me_2PCH_2CH_2PMe_2$), is generated by reaction of *cis*-[Ru(dmpe)$_2$H$_2$] either with fluoroarenes (C_6F_6, C_6F_5H and others) or by reaction with $Et_3N{\cdot}3HF$; its solid-state structure, established crystallographically, reveals a Ru(η^1-FHF) moiety with a long Ru–F bond and an F···F distance close to that in bifluoride salts, while the presence of the same complex in solution is shown by low-temperature NMR spectra.

The C–F activation of hexafluorobenzene with transition-metal complexes may take two forms. Simple oxidative addition yields a metal pentafluorophenyl fluoride.[1,2] In a more puzzling process, several metal hydride complexes yield pentafluorophenyl hydride complexes.[2,3] A strong thermodynamic drive for this reaction is provided by the release of hydrogen fluoride, although its fate has not been determined.[4] We show here that the HF can be trapped as a complex of bifluoride, HF_2, which can also be accessed by reaction with a mild source of HF, $Et_3N{\cdot}3HF$.[5] We have been prompted to publish at this stage by the recent report of [Mo(PMe$_3$)$_4$(H)$_2$F(HF$_2$)].[6]

We demonstrated earlier that the reaction of *cis*-[Ru(dmpe)$_2$-H$_2$] **1** (dmpe = $Me_2PCH_2CH_2PMe_2$) with C_6F_6 at -78 °C generates *trans*-[Ru(dmpe)$_2$(C$_6$F$_5$)H]. Reactions with partially fluorinated arenes yield analogues also arising from C–F activation.[3] In all these reactions, we noted the formation of a second hydride containing species, **2**, which is the subject of this paper. The ^{1}H NMR spectrum (293 K) of **2** formed in the reaction of **1** with a twofold excess of $C_6F_nH_{6-n}$ (n = 6, 5, 4, 3) includes two broad singlet resonances at δ 13.8 and -25.8 in [^{2}H$_8$]thf. It is present in a ratio of *ca.*, 1 : 2 relative to the fluoroaryl hydrides. The ^{31}P{^{1}H} spectrum shows a broad singlet; there are no resonances in the ^{19}F NMR spectrum. Although the spectra of **2** were unaffected by running the reaction in an FEP-lined NMR tube, the formation of **2** was completely suppressed by triethylamine (fivefold excess). These observations suggested that **2** is *trans*-[Ru(dmpe)$_2$-(H)(HF$_2$)] formed from the HF released in the C–F activation reactions. A higher yield route to **2** was provided by the reaction of **1** with triethylamine trihydrofluoride.[7] Amine·HF adducts, $R_3N{\cdot}x$HF, represent mild sources of HF which can be handled in solution without special precautions, and which have been employed to synthesise fluoride complexes.[8]

On addition of $Et_3N{\cdot}3HF$ to **1** (< 1 mol $Et_3N{\cdot}3HF$ per mol of **1**, both reagents dissolved in thf) at room temperature, **2** is formed. Although NMR spectra recorded at 293 K suggest that **2** is the single ruthenium-containing product, low-temperature spectra of recrystallised **2** resolve into two sets of resonances. The major species is indeed identified as *trans*-[Ru-(dmpe)$_2$(H)(HF$_2$)] from the full coupling pattern of ^{1}H, ^{31}P and ^{19}F spectra (Fig. 1, 2).† The NMR spectra are unaffected by heating to 330 K and recooling to *ca.* 200 K. The IR spectrum of **2** (Nujol mull) shows a broad band for the bifluoride ligand at 1690 cm^{-1}, in the range reported for bifluoride ion salts.[9]

A suitable single crystal of **2** was obtained by slow evaporation of a thf solution. The structure determined by X-ray crystallography (Fig. 3)‡ showed a bifluoride group, F–H–F, coordinated to ruthenium and lying *trans* to the hydride ligand. The bifluoride bisects the two chelating dmpe groups and is tilted to give a Ru–F···F bond angle of 129.9(3)°. The F···F distance of 2.276(8) Å is very close to that found in bifluoride salts, MHF$_2$ (M = Na, K, NH$_4^+$),[9] or in pyridine·nHF,[10] and is significantly shorter (9 e.s.d.s) than the F···F separation of 2.351(8) Å found in [Mo(PMe$_3$)$_4$(H)$_2$F(HF$_2$)].[6] The Ru–F bond length [2.284(5) Å] is longer than in any conventional ruthenium–fluoride complexes (2.01–2.04 Å).[11] Indeed, **2** is a rare example of a complex containing M–H and M–F bonds, and is unique in the octahedral stereochemistry of hydride *trans* to fluorine.[12] Formation of platinum bifluoride complexes in solution has been suggested from ^{1}H NMR data.[13] A crystal structure of a niobium dimer with two η^2-HF$_2$ groups has been reported but without evidence for this species in solution.[14] The molybdenum bifluoride complex[6] dissociates completely into [Mo(PMe$_3$)$_4$(H)$_2$F$_2$] and HF in solution.

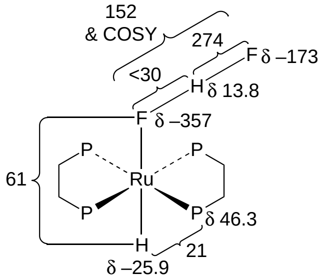

Fig. 1 Coupling pattern (Hz) and chemical shifts in the low-temperature NMR spectra of *trans*-[Ru(dmpe)$_2$(H)(HF$_2$)] **2**

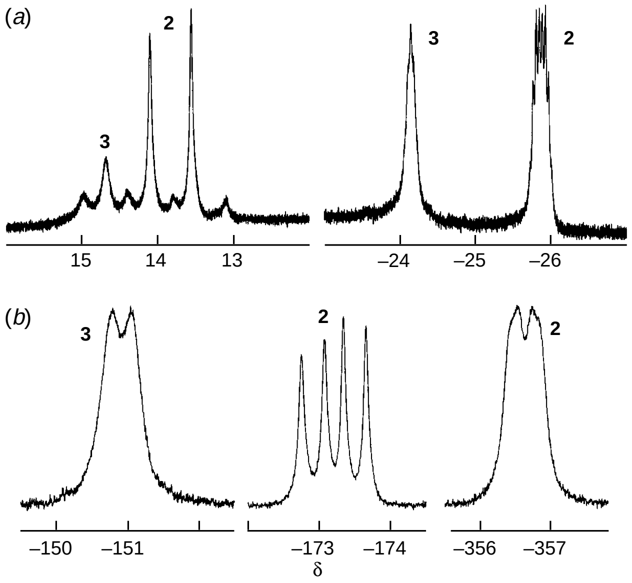

Fig. 2 (*a*) ^{1}H NMR spectrum (500 MHz) of bifluoride and hydride regions of recrystallised **2** in [^{2}H$_8$]thf at 188 K showing the presence of **2** and **3**. (*b*) ^{19}F NMR spectrum (470 MHz) showing the bifluoride and metal–fluoride regions. The spectra in (*a*) and (*b*) are shown on a common scale in Hz cm^{-1}.

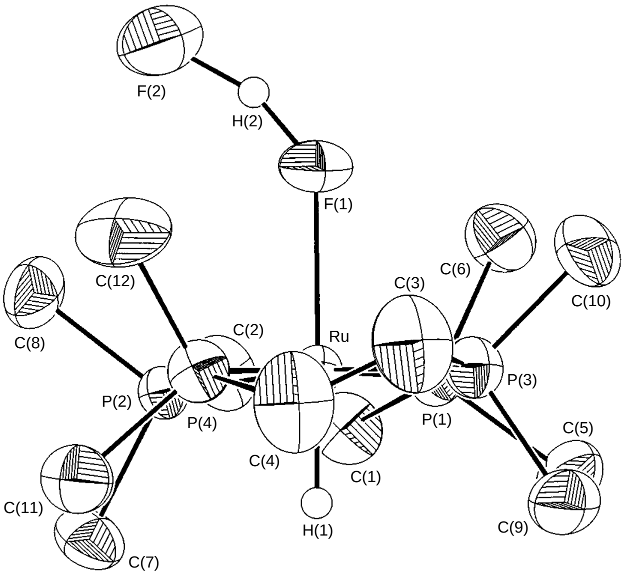

Fig. 3 ORTEP diagram of the molecular structure of **2** (ellipsoids at 50% level). Principal bond lengths (Å), angles and torsional angles (°): Ru–F(1) 2.284(5), F(1)–F(2) 2.276(8), F(2)–F(1)–Ru 129.9(3), F(2)– F(1)–Ru–P(1) 114.9(4), F(2)–F(1)–Ru–P(2) 31.0(4).

The second species, **3**, observed at 188 K, shows a triplet resonance at δ 14.8 (*J* 145 Hz) in the ^{1}H NMR spectrum [Fig. 2(*a*)] and a broad doublet resonance at δ −150.9 [Fig. 2(*b*)] in the ^{19}F NMR spectrum consistent with the HF_2^- anion.[15] It is identified provisionally as [Ru(dmpe)$_2$H$^+$][HF$_2^-$].[16]§

A sequence for the formation of the bifluoride hydride that involves an intermediate dihydrogen hydride complex is shown in eqns. (1) and (2) {[Ru] = Ru(dmpe)$_2$}:

$$[Ru]H_2 + HF \rightarrow [Ru](\eta^2\text{-}H_2)H^+F^- \qquad (1)$$

$$[Ru](\eta^2\text{-}H_2)H^+F^- + HF \rightarrow [Ru](H)(HF_2) + H_2 \qquad (2)$$

The HF originates either in $Et_3N\cdot3HF$ or in reaction of **1** with fluoroarenes. These experiments show that the bifluoride group, HF_2, can be generated in an aprotic organic solvent under mild conditions. The fate of expelled HF in our C–F activation reactions is explained. Taken together with the molybdenum results[6] we may anticipate further bifluoride complexes with the hydrogen atom occupying a range of positions between the two fluorine atoms,¶ which may be probed *via* the values of J_{HF}. Our synthetic methods offer new routes to combination of hard and soft ligands as exemplified by *trans*-[Ru(dmpe)$_2$(OH)H], a complex closely related to **2**.[17] The exchange processes in **2** involving coordinated and free bifluoride are under investigation.

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Footnotes

† *Spectroscopic data* for *trans*-[Ru(dmpe)$_2$(H)(HF$_2$)], **2**: NMR {500 MHz, [^{2}H$_8$]thf, 188 K}: ^{1}H δ −25.86 (dqnt, $^2J_{PH}$ 20.5, $^2J_{FH}$ 61.3 Hz, 1 H, Ru–H), 1.50 (s, 12 H, 4 × CH$_3$), 1.53 (s, 12 H, 4 × CH$_3$), 1.70 (br s, 4 H, 4 × PCH*H*), 1.92 (br s, 4 H, 4 × PC*H*H), 13.83 (d, $^1J_{HF}$ 273.9 Hz, 1 H, HF$_2$). ^{31}P{^{1}H} δ 46.3(s). ^{19}F δ −173.1 (dd, $^1J_{HF}$ 273.9, $^2J_{FF}$ 151.5 Hz, 1 F, Ru–F–H–*F*), −356.8 (br d, $^2J_{FF}$ 151.5 Hz, 1 F, Ru–*F*). IR (Nujol): 1690 cm^{-1} ν(HF$_2$). FABMS, *m/z* 403 [Ru(dmpe)$_2$H]$^+$. The C, H analysis fitted [Ru(dmpe)$_2$(H)(F)], probably because of HF loss in the furnace.

‡ *Crystal data* for *trans*-[Ru(dmpe)$_2$(H)(HF$_2$)] **2**: 0.7 × 0.6 × 0.3 mm, $C_{12}H_{34}F_2P_4Ru$, M = 441.34, monoclinic, space group $P2_1$, a = 9.269(7), b = 11.848(8), c = 10.126(7) Å, β = 114.40(6)°, U = 1012.7(12) Å^3, $F(000)$ = 456, D_c = 1.447 Mg m^{-3}, Z = 2, λ(Mo-Kα) = 0.710 69 Å, μ = 1.095 mm^{-1}, $R_1[I > 2\sigma(I)]$ = 0.0305, wR_2 = 0.0831, GOF = 0.761, T = 293 K, 1873 unique reflections out of 1996 reflections measured. Diffractometer: Rigaku AFC6S, 2θ range 5–50°. After initial solution with the TEXSAN software package[18] by direct methods, SHELXL-93[19] was employed for full-matrix least-squares refinement. The hydride hydrogen atom and the bifluoride hydrogen atom were located from the difference map and refined isotropically. While the location of the hydride was unambiguous, that of the bifluoride hydrogen atom was not. All other hydrogen atoms were refined with a 'riding' model. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to CCDC for this material should quote the full literature citation and reference number 183/328.

§ *NMR data* for [Ru(dmpe)$_2$H]$^+$ **3**: NMR {500 MHz, [^{2}H$_8$]thf, 188 K}: ^{1}H δ −24.14 (br qnt $^2J_{PH}$ 20.4 Hz, 1 H, Ru–H), (1.00 br s, (4 H, 4 × PCH*H*), 1.46 (s 12 H, 4 × CH$_3$), 1.57 (s 12 H, 4 × CH$_3$), 2.07 (br s, 4 H, 4 × PC*H*H). ^{31}P{^{1}H} δ 44.5(s). The spectrum in toluene shows very similar chemical shifts and intensity ratio for **2** and **3**, indicating that **3** is not a solvent adduct.

¶ Preliminary effective core potential *ab initio* calculations by F. Maseras and O. Eisenstein confirm the stability of HF bound to *trans*-[Ru(PH$_3$)$_4$(H)F]. They reproduce the F···F and Ru–F distances satisfactorily and place the bifluoride hydrogen 0.25 Å closer to F(2) than F(1) in agreement with the NMR data.

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