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C–F bond activation of perfluoroalkenes by ruthenium phosphine hydride complexes: X-ray crystal structures of *cis*-Ru(dmpe)$_2$F(F···HF) and [Ru(dcpe)$_2$H]$^+$[(CF$_3$)$_2$C=C(O)CF$_2$CF$_3$]$^-$

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The reaction of $(CF_3)_2C{=}C(F)CF_2CF_3$ or $CF_3CF{=}CF_2$ with $Ru(dmpe)_2H_2$ affords the bifluoride fluoride complex *cis*-Ru(dmpe)$_2$F(F···HF), whereas reaction with $Ru(dcpe)_2H_2$ yields the cation $[Ru(dcpe)_2H]^+$ with $[(CF_3)_2C{=}C(O)CF_2CF_3]^-$ as the anion.

Considerable advances have been made in the past few years on the activation of carbon–fluorine bonds and there is now a wide range of both early and late transition metal complexes available that can be employed in this regard.[1] Among these studies, several metal hydride complexes stand out due to their ability to cleave both saturated and unsaturated perfluorocarbons under very mild conditions.[2] Indeed, $Rh(PMe_3)_4H$ has proved sufficiently active to bring about the catalytic hydrogenation of C_6F_6 to C_6F_5H with only very mild heating.[3] In most of these cases, C–F activation is accompanied by elimination of HF, which provides a strong thermodynamic driving force for the reaction, to give metal hydride products.

We have previously reported that *cis*-Ru(dmpe)$_2$H$_2$ (**1**, dmpe = $Me_2PCH_2CH_2PMe_2$) activates the C–F bond in C_6F_6 at −78 °C to give *trans*-Ru(dmpe)$_2$(C$_6$F$_5$)H, thus releasing HF, which subsequently reacts with **1** to form the bifluoride hydride complex *trans*-Ru(dmpe)$_2$H(FHF), **2**.[4] This facile C–F activation by $Ru(dmpe)_2H_2$ prompted us to investigate its reactivity with other unsaturated fluorocarbons. Thus, we now report that **1** reacts with $(CF_3)_2C{=}C(F)CF_2CF_3$ or $CF_3CF{=}CF_2$ to give the bifluoride fluoride complex, *cis*-Ru(dmpe)$_2$F(F···HF), **3**, in preference to a hydride product. In contrast, $Ru(dcpe)_2H_2$ [dcpe = $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$] reacts with the same perfluoroalkenes to give the 16-electron hydride species $[Ru(dcpe)_2H]^+$ and a perfluoroenolate anion.

Treatment of a benzene or THF solution of **1** with $(CF_3)_2C{=}C(F)CF_2CF_3$ (ratio 1 : 1) at room temperature results in the rapid formation of **2** and *cis*-Ru(dmpe)$_2$F(F···HF) **3** (ratio *ca.* 1 : 4) as shown by multinuclear NMR spectroscopy.† The ^{1}H NMR spectrum of **3** in C_6D_6 exhibited a doublet at δ 14.2 with a $^1J_{HF}$ coupling constant of 328 Hz. The corresponding ^{19}F NMR spectrum displayed a doublet at δ −174 with the same coupling constant and two broad multiplets at δ −343 and −362 corresponding to the two types of Ru–F bond. The $^{31}P\{^1H\}$ NMR spectrum of **3** showed a complex multiplet at δ 57 and an 'apparent' quintet signal at δ 42. The latter was assigned to the mutually *trans* P atoms which show similar couplings to both *cis*-P and *cis*-F atoms. GC–MS analysis of the fluoro-organic products showed that a mixture of four compounds with *m*/*z* 246 [*i.e.* replacement of 3F by 3H in $(CF_3)_2C{=}C(F)CF_2CF_3$] was formed, although it has not proved possible to characterise this mixture any further using multinuclear NMR.

When the same reaction was conducted in the presence of ten equivalents of Et_3N, the formation of **2** was completely suppressed, allowing the isolation of **3**. The X-ray crystal structure determination of **3**‡ (Fig. 1) shows the *cis* disposition of the two fluoride ligands and a strong hydrogen bonding interaction between one of them and the HF moiety. The Ru–FHF bond length is significantly lengthened [2.168(3) Å] compared to the unperturbed Ru–F bond [2.101(3) Å]. Both Ru–F distances are noticeably longer than those found in the difluoride complex *cis*-Ru(dppp)$_2$F$_2$ (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) (average 2.06 Å), which is the only other well characterised ruthenium fluoride complex that is not stabilised by carbonyl ligands.[5] A comparison of the F···F distance in **3** and related complexes reveals that the value of 2.292(8) Å is slightly longer than that in the bifluoride complex **2** [2.276(8) Å][4] but considerably shorter than the corresponding distances in M(PMe$_3$)$_4$H$_2$F(FHF)[6] [M = Mo, 2.351(8) Å; M = W, 2.390(13) Å] or Pd(PPh$_3$)$_2$(Ph)FHF (2.36 Å).[7] The M–F···F unit is bent in all of these cases with an angle at the metal-bound fluorine in the range 129–157°. The Ru–F···F angle in **3** is 142°. These data suggest that Ru(dmpe)$_2$F(F···HF) is most accurately described as a bifluoride fluoride complex in the solid state, although in solution the magnitude of J_{HF} points to a weakening of the Ru–F···H–-F interaction.

A change of the chelating phosphine from dmpe to dcpe results in a dramatic change in the reactivity at the metal centre which allows the fate of the fluorocarbon to be more accurately determined. Although $Ru(dcpe)_2H_2$ shows no reaction towards C_6F_6, even upon heating to 80 °C, addition of an equimolar amount of $(CF_3)_2C{=}C(F)CF_2CF_3$ in benzene gives orange crystals in 31% yield at room temperature overnight. A single crystal X-ray diffraction study confirmed these crystals to be $[Ru(dcpe)_2H]^+[(CF_3)_2C{=}C(O)CF_2CF_3]^-$, **4**, (Fig. 2).‡ While the gross structure is similar to that reported by Winter and Hornung for the [BPh$_4$] salt,[8] there are some differences between the structural parameters in our structure which we attribute to crystal packing effects. In the perfluoroenolate anion, lengthening of the C=C bond [1.426(9) Å] and shortening of the C–O bond [1.228(7) Å] suggest delocalisation of charge across the C=C–O unit.[9] Formation of $[(CF_3)_2C{=}C(O)CF_2CF_3]^-$ arises from hydrolysis by adventitious water, since addition of excess water (10 equivalents) to a

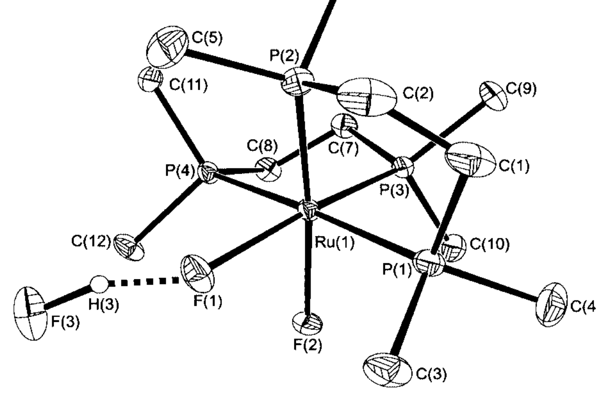

Fig. 1 ORTEX view of the molecular structure of **3**. Ellipsoids are shown at the 30% level. Principal bond lengths (Å) and angles (°): Ru–F(1) 2.168(3), Ru–F(2) 2.101(3), F(1)–F(3) 2.292(8); F(3)–F(1)–Ru 141.8(2), F(1)–Ru–F(2) 85.4(1).

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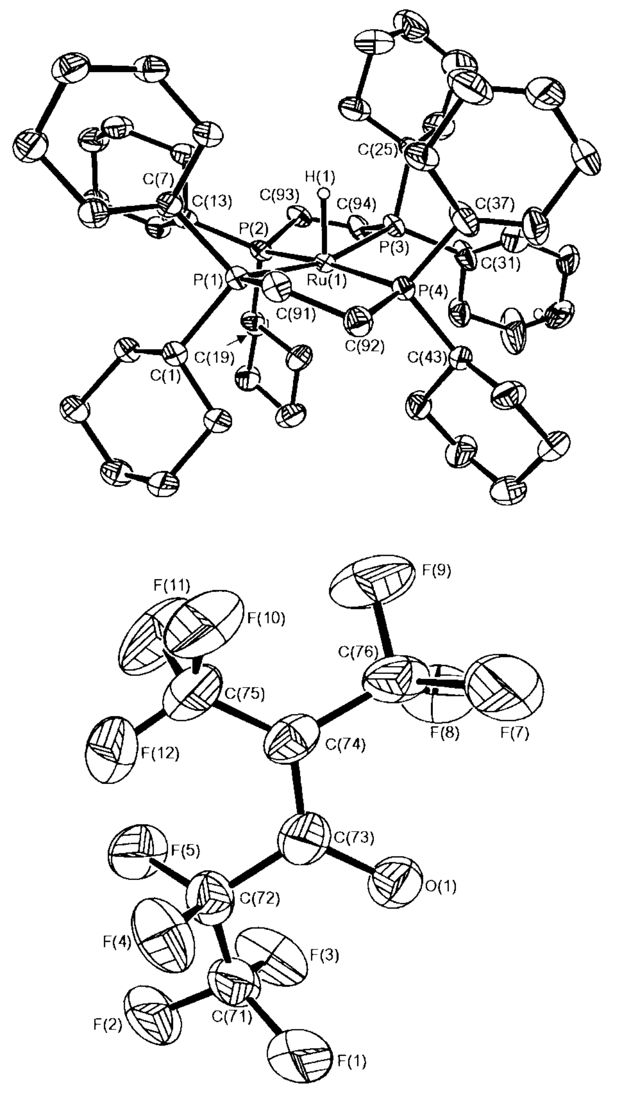

Fig. 2 ORTEX view of the molecular structure of **4**. Ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (°): C(72)–C(73) 1.514(10), C(73)–C(74) 1.426(9), C(73)–O(1) 1.228(7); P(2)–Ru–P(3) 81.62(4), P(1)–Ru–P(4) 83.56(4).

1 : 1 mixture of Ru(dcpe)$_2$H$_2$ and (CF$_3$)$_2$C=C(F)CF$_2$CF$_3$ affords **4** in quantitative yield in 12 hours. The ^{31}P{^{1}H} NMR spectrum† of **4** in d$_8$-THF displayed a singlet at δ 73.4 whereas the proton NMR showed a high field quintet at δ −31.9 (J 19.22 Hz), in agreement with the reported values for [Ru(dcpe)$_2$H]$^+$.[8] The ^{19}F NMR spectrum of **4** showed the expected four resonances for the anion.[10]

Addition of hexafluoropropene to the dihydride complexes resulted in very similar reactivity to that seen with (CF$_3$)$_2$C=C(F)CF$_2$CF$_3$. Addition of 1 atmosphere of CF$_3$CF=CF$_2$ to a THF solution of **1** resulted in the formation of **3** as the only inorganic product. Analysis of the fluoro-organic products by ^{19}F NMR revealed the presence of both *Z*- and *E*-CF$_3$CF=CFH and CF$_3$CF=CH$_2$ in a ratio 4 : 1 : 3. Addition of CF$_3$CF=CF$_2$ to a THF solution of Ru(dcpe)$_2$H$_2$ gave [Ru(dcpe)$_2$H]$^+$ with [(CF$_3$)$_2$C=C(O)CF$_2$CF$_3$]$^-$ unexpectedly present as the anion.

In summary, we have shown that the pathways for C–F bond activation of perfluoroalkenes by Ru(P–P)$_2$H$_2$ is highly dependent upon the phosphine substituents. The mechanism(s) surrounding the formation of **3** and **4** are presently under investigation.

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Notes and references

† *Selected spectroscopic data* for **3**: NMR (400 MHz, d$_6$-benzene, 298 K): ^{1}H, δ 14.20 (d, J_{HF} 328 Hz, 1H, HF). ^{31}P{^{1}H}, δ 56.8 (m), 42.2 (quin, $J_{\mathrm{PP}} = J_{\mathrm{PF}}$ 23 Hz). ^{19}F, δ −342.75 (m, RuF), −362.42 (m, RuF). IR (C$_6$D$_6$, cm^{-1}) 2452, 1915 (ν FHF). C, H analysis fitted Ru(dmpe)$_2$F$_2$, probably due to facile loss of HF upon heating. Anal. calc. for C$_{12}$H$_{32}$F$_2$P$_4$Ru: C, 32.80; H, 7.34. Found: C, 32.55; H, 7.28%. For **4**: NMR (400 MHz, d$_8$-THF, 298 K): ^{1}H, δ −31.87 (quin, J_{HP} 19.22 Hz, 1H, Ru–H). ^{31}P{^{1}H}, δ 73.4 (s). ^{19}F, δ −45.5 (qt, J_{FF} 10.73, J_{FF} 19.57, 3F, CF$_3$), −51.3 (q, J_{FF} = 10.73, 3F, CF$_3$), −77.8 (s, 3F, CF$_3$), −113.6 (q, J_{FF} 19.57, 2F, CF$_2$). FAB-MS: *m*/*z* 947 ([Ru(dcpe)$_2$H]$^+$). Anal. calc. for C$_{58}$H$_{97}$F$_{11}$OP$_4$Ru: C, 55.98; H, 7.86. Found: C, 56.10; H, 8.12%.

‡ *Crystal data*: for [Ru(dmpe)$_2$F(F···HF)] **3**: C$_{12}$H$_{33}$F$_3$P$_4$Ru, M = 459.33, monoclinic, space group Cc, a = 9.071(1), b = 17.621(2), c = 13.805(2) Å, β = 106.061(2)°, U = 1965.2(4) Å^3, T = 133 K, Z = 4, μ(Mo-Kα) = 0.71073 mm^{-1}, 5399 data were collected on a Bruker SMART 1000 CCD diffractometer of which 4105 were unique (R_{int} = 0.0221), 3938 had $F_{\mathrm{o}} > 4\sigma(F_{\mathrm{o}})$, $5.22 < 2\theta < 56.64°$, no absorption correction was applied. Structure solved by direct methods using SHELXS[11] and all non-hydrogen atoms refined anisotropically using full-matrix least squares on F^2 (SHELXL-97).[12] Hydrogen atoms included at calculated positions throughout except for H(3) which was located and positionally refined. R_1 = 0.0322 (for 4σ data), wR_2 = 0.0775, S = 1.005 (for all data).

For [Ru(dcpe)$_2$H]$^+$[(CF$_3$)$_2$C=C(O)CF$_2$CF$_3$]$^-$·2C$_6$H$_6$ **4**: C$_{70}$H$_{109}$F$_{11}$OP$_4$Ru, M = 1400.52, triclinic, space group $P\bar{1}$, a = 12.386(3), b = 13.661(4), c = 21.907(6) Å, α = 106.14(2), β = 93.17(2), γ = 93.83(2)°, U = 3542.23(17) Å^3, T = 170 K, Z = 2, μ(Mo-Kα) = 0.838 mm^{-1}, 33863 data were collected on a Nonius Kappa CCD area detector of which 10742 were unique (R_{int} = 0.0441), 8993 had $F_{\mathrm{o}} > 4\sigma(F_{\mathrm{o}})$, $7.04 < 2\theta < 47.64°$, no absorption correction was applied. Structure solved by direct methods using SHELXS[11] and all non-hydrogen atoms refined anisotropically using full-matrix least squares on F^2 (SHELXL-97).[12] Hydrogen atoms included at calculated positions throughout except for H(1) which was located and positionally refined. R_1 = 0.0571 (for 4σ data), wR_2 = 0.1511, S = 1.041 (for all data).

CCDC 154917 and 154918. See http://www.rsc.org/suppdata/cc/b0/b009862k/ for crystallographic data in .cif or other electronic format.

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