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Stoichiometric and catalytic C–F bond activation by the *trans*-dihydride NHC complex [Ru(IEt$_2$Me$_2$)$_2$(PPh$_3$)$_2$H$_2$] (IEt$_2$Me$_2$ = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene)†

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The room temperature reaction of C_6F_6 or C_6F_5H with [Ru(IEt$_2$Me$_2$)$_2$(PPh$_3$)$_2$H$_2$] (**1**; IEt$_2$Me$_2$ = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene) generated a mixture of the *trans*-hydride fluoride complex [Ru(IEt$_2$Me$_2$)$_2$(PPh$_3$)$_2$HF] (**2**) and the bis-carbene pentafluorophenyl species [Ru(IEt$_2$Me$_2$)$_2$(PPh$_3$)(C$_6$F$_5$)H] (**3**). The formation of **3** resulted from C–H activation of C_6F_5H (formed from C_6F_6 *via* stoichiometric hydrodefluorination), a process which could be reversed by working under 4 atm H_2. Upon heating **1** with C_6F_5H, the bis-phosphine derivative [Ru(IEt$_2$Me$_2$)(PPh$_3$)$_2$(C$_6$F$_5$)H] (**4**) was isolated. A more efficient route to **2** involved treatment of **1** with 0.33 eq. of TREAT-HF (Et$_3$N·3HF); excess reagent gave instead the $[H_2F_3]^-$ salt (**5**) of the known cation [Ru(IEt$_2$Me$_2$)$_2$(PPh$_3$)$_2$H]$^+$. Under catalytic conditions, **1** proved to be an active precursor for hydrodefluorination, converting C_6F_6 to a mixture of tri, di and monofluorobenzenes (TON = 37) at 363 K with 10 mol% **1** and Et$_3$SiH as the reductant.

Introduction

Recent years have witnessed increasing evidence for the valuable role of N-heterocyclic carbenes (NHCs) and their derivatives in catalytic transformations involving organofluorine substrates.[1] Thus, organocarbene catalysts have been employed for the formation of both C–F and C–CF$_3$ bonds,[2,3] as well as enantioselective transformations of fluorine containing substrates.[4] Transition metal NHC complexes have also been employed for C–F bond formation through hydrofluorination,[5–7] but have perhaps received more attention in processes in which C–F bonds are broken (Scheme 1), either through cross-coupling[8] or, of particular relevance to the work reported in this manuscript, hydrodefluorination (HDF).[9–11]

Prompted by our studies over a number of years on catalytic HDF of fluoroaromatic substrates using ruthenium NHC hydride precursors and the elucidation by DFT calculations of a mechanism involving nucleophilic hydride attack,[10–13] we have set out to investigate the catalytic effectiveness of Ru NHC species containing increasingly more nucleophilic Ru–H ligands. Very recently, we reported an example of such a species in the form of the mixed carbene-phosphine complex [Ru(IEt$_2$Me$_2$)$_2$(PPh$_3$)$_2$H$_2$] (**1**; IEt$_2$Me$_2$ = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene).[14] The unusual *trans*-arrangement of the two hydride ligands imparts highly nucleophilic character to Ru–H, as evidenced by the formation of methane and [Ru(IEt$_2$Me$_2$)$_2$(PPh$_3$)$_2$HI] upon addition of the electrophile MeI. We now report our initial findings on both the stoichiometric and catalytic reactivity of **1** towards aromatic fluorocarbons. As hoped for, the complex displays high activity for the catalytic HDF of C_6F_6, undergoing up to five HDF steps in generating fluorobenzene.

Results and discussion

Stoichiometric C–F and C–H activation of C_6F_6 and C_6F_5H by 1

Monitoring by $^{31}P\{^1H\}$ NMR spectroscopy the room temperature reaction of [Ru(IEt$_2$Me$_2$)$_2$(PPh$_3$)$_2$H$_2$] (**1**) with 10 eq. of either C_6F_6 or C_6F_5H in C_6H_6 solution[15] showed, over the course of *ca.* 5 h, complete loss of starting material and the appearance of two new product peaks at δ 45 and 59. These were assigned to the hydride fluoride complex [Ru(IEt$_2$Me$_2$)$_2$(PPh$_3$)$_2$HF] (**2**) and the pentafluorophenyl complex [Ru(IEt$_2$Me$_2$)$_2$(PPh$_3$)(C$_6$F$_5$)H] (**3**) respectively (Scheme 2). The formation of the two products, which were present after 5 h in an

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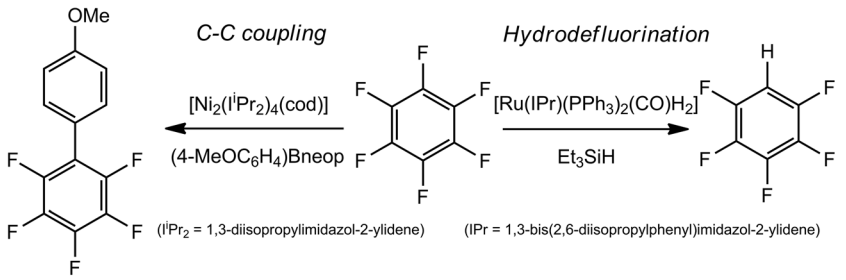
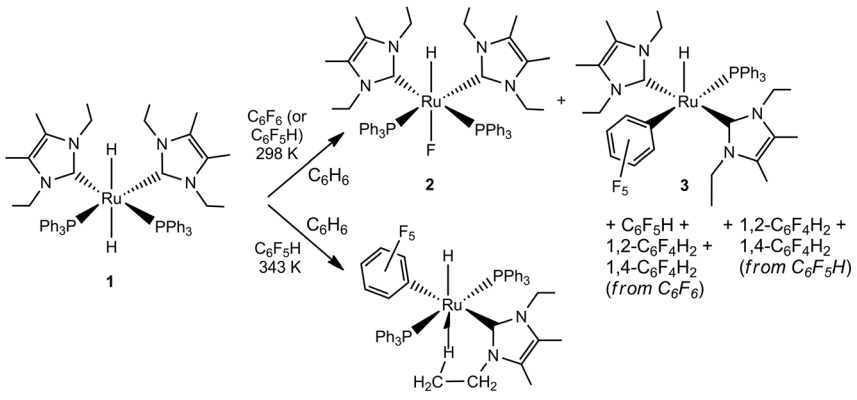


Scheme 1



Scheme 2

approximate ratio (by $^{31}P\{^{1}H\}$ NMR spectroscopy) of 1 : 0.2 from C_6F_6 and 1 : 0.5 from C_6F_5H, arise from competing C–F and C–H activation respectively. C–H activation proved to be reversible. Thus, addition of H_2 (4 atm) to an *in situ* generated mixture of **2**, **3** and PPh_3 led to the complete disappearance of **3** over 4 h at room temperature. In a more controlled experiment, addition of 4 atm H_2 to a solution containing an isolated, crystalline sample of **3** (*vide infra*) and an equivalent of PPh_3 led to the complete conversion of the former to a mixture of **1** and **2** within 4 h at 298 K. Generation of the latter could be rationalised following analysis of the ^{1}H and ^{19}F NMR spectra of the volatile materials from the C_6F_6 reaction. This revealed the presence of the hydrodefluorination products C_6F_5H (major species) and both 1,2,3,4- and 1,2,4,5-$C_6F_4H_2$, indicating that **1** must initially activate the C–F bond in C_6F_6 to give **2** and C_6F_5H, which then proved to be at least as reactive a substrate as C_6F_6, undergoing C–F activation to give the tetrafluorobenzene isomers (and additional **2**), as well as C–H activation to produce **3**. The competitive nature of C–H activation is clearly shown by the higher ratio of **3** : **2** formed in the reaction of **1** with C_6F_5H.[16]

Both **2** and **3** could be isolated from the reaction mixture following removal of the volatile components and recrystallization of the residue. The X-ray structure of **2** (Fig. 1) revealed retention of the *cis* arrangement of the two NHC ligands and

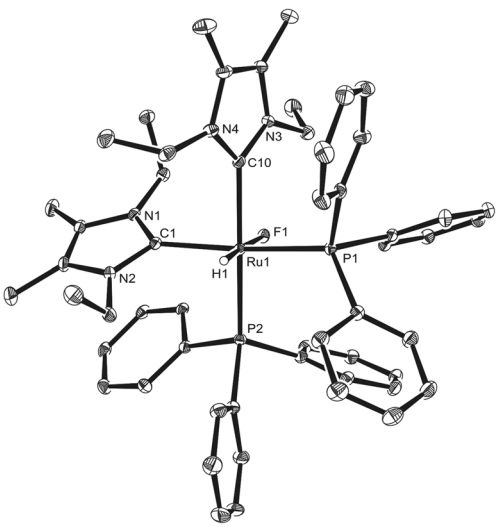


Fig. 1 Molecular structure of **2**. Solvent, minor disordered component and hydrogen atoms (with the exception of the hydride ligand) have been omitted for clarity. Ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.115(2), Ru(1)–C(10) 2.109(2), Ru(1)–P(1) 2.3343(6), Ru(1)–P(2) 2.3493(6), Ru(1)–F(1) 2.264(2), P(1)–Ru(1)–P(2) 98.66(2), C(1)–Ru(1)–P(1) 170.54(6), C(10)–Ru(1)–F(1) 91.64(8).

two PPh_3 groups from **1** and, as a result, very little change in either Ru–C/Ru–P distances and angles. Of particular interest was the long Ru–F distance of 2.264(2) Å. This is comparable to the value (2.284(5) Å) in [Ru(dmpe)$_2$H(FHF)] (dmpe = 1,2-bis(dimethylphosphino)ethane), which is the only other *trans* H–Ru–F complex we could find that has been structurally verified.[17] Surprisingly, crystallographically characterised examples of Ru(L)$_4$H(halide) (L = PR_3 or NHC) species with *trans* H–Ru–halide geometries in general are not that common,[18] despite complexes of this type being known for over 50 years.[19] Elongation in the Ru-F distance in both **2** and [Ru(dmpe)$_2$H(FHF)] compared to those in *cis*-[Ru(dppp)$_2$F$_2$] (dppp = 1,4-bis-(diphenylphosphino)ethane) and *trans*-[Ru(dppe)$_2$F$_2$] (dppe = 1,2-bis(diphenylphosphino)ethane) (2.056(3)/2.069(3) and 2.1729(18) Å respectively)[20] presumably results from the presence of a *trans*-labilising hydride ligand.

A very clear low frequency doublet of triplets Ru–H signal was apparent for **2** in the room temperature ^{1}H NMR spectrum in toluene-d_8 at δ −21.7 (with diagnostic J_{HF} and J_{HP} values of 52.0 and 19.7 Hz respectively). The IEt_2Me_2 signals were broad and overlapping, but resolved upon cooling to 228 K into eight sets of N–CH_2 and four sets N–CH$_2$CH_3 signals respectively. The hydride signal at 228 K now appeared as a doublet of doublet of doublets (J_{HF} = 51.6 Hz, J_{HP} = 25.6 Hz, J_{HP} = 14.1 Hz), indicating that the two PPh_3 ligands became inequivalent at low temperature. In line with this, the ^{31}P{^{1}H} spectrum changed from a broad singlet at room temperature to what is best described as two very broad, overlapping multiplets spread over *ca.* 1 ppm at 228 K. We were unable to resolve J_{PP} or J_{PF} splittings even at this low temperature. The ^{19}F NMR spectrum showed a broad fluoride resonance at δ −354 in both THF-d_8 and toluene-d_8 at room temperature, although the doublet hydride splitting of *ca.* 52 Hz was partially resolved in the THF case. Altering the temperature over the range 248–318 K failed to resolve any further couplings, while the addition of CsF also made no effect.[21]

The X-ray structure of the second product, the bis-IEt_2Me_2 pentafluorophenyl complex [Ru(IEt_2Me_2)$_2$(PPh_3)(C_6F_5)H] (**3**), revealed the anticipated square based pyramidal geometry, with the hydride *trans* to the vacant site (Fig. 2). The two carbenes were now oriented *trans* to one another, forcing the PPh_3 and fluoroaryl ring also to be *trans*. The combination of (i) the nature of the *trans* ligand and (ii) the coordinative unsaturation of the metal centre impacted upon the Ru-$C_{fluoroaryl}$ bond length, which was shorter (2.136(4) Å) than that found in related systems.[11,12]

The positioning of the hydride opposite a vacant site reflected in the solution spectroscopic properties of the compound, in particular, the very low frequency hydride chemical shift of δ −33.0. This appeared as a doublet of triplets, with a typical *cis*-^{31}P doublet splitting of 30.6 Hz, and a triplet splitting of 7.2 Hz arising from interaction with the two *ortho*-fluorine atoms of the C_6F_5 ring.

Efforts to accelerate the reaction of **1** with C_6F_5H using higher temperatures resulted instead in the isolation of the bis-phosphine pentafluorophenyl complex [Ru(IEt_2Me_2)-(PPh_3)$_2$(C_6F_5)H] (**4**, Scheme 2) as the major ruthenium containing product of the reaction following overnight heating at 343 K. It was found that **4** could also be formed at room temperature, although very much as the minor partner alongside **2** and **3** if a sample of **1** and C_6F_6 (10 eq.) was left at room temperature for *ca.* 100 h (ratio **2** : **3** : **4** = 1 : 0.4 : 0.1). Heating an isolated sample of **3** with PPh_3 (2 eq.) at 343–363 K in C_6H_6 for 5 h failed to give **4**, implying (unsurprisingly)[22] that simple substitution of NHC by phosphine does not account for the formation of **4**.

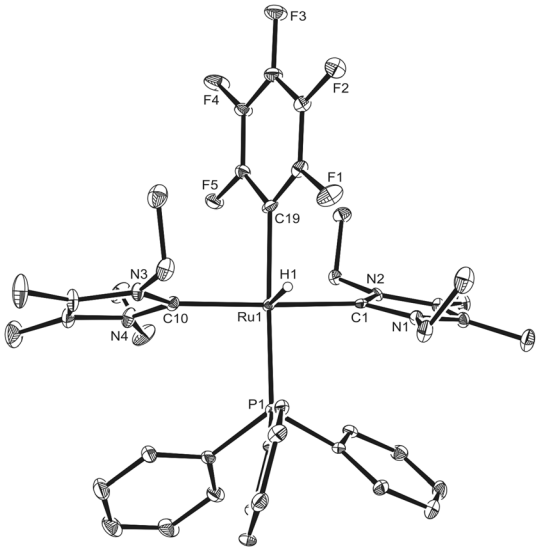


Fig. 2 Molecular structure of **3**. All hydrogen atoms, except for Ru–H, are omitted for clarity. Ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.090(3), Ru(1)–C(10) 2.088(3), Ru(1)–C(19) 2.136(4), Ru(1)–P(1) 2.2783(11), C(1)–Ru(1)–C(10) 173.39(15), C(1)–Ru(1)–C(19) 88.43(14).

Crystals of the red compound **4** suitable for X-ray crystallography were isolated from benzene/hexane and displayed the structure shown in Fig. 3. Most noticeable was the distorted octahedral geometry now present that resulted from an agostic interaction involving one of the NHC-Et groups occupying the site opposite the Ru–H. The need for the agostic stabilisation must reflect the instability of the five-coordinate 16e Ru(II) species upon replacing the strongly donating IEt_2Me_2 ligand in **3** for PPh_3 in forming **4**. The agostic distances (Ru···C(5), 2.752 Å; Ru···H(5A), 2.052 Å) lie in between those in the related NHC complexes [Ru($I^iPr_2Me_2$)$_2$($I^iPr_2Me_2$)′Cl] and [Ru(IEt_2Me_2)-(PPh_3)$_2$HCl] previously described by our group[23] and are within the range considered to be strong interactions.[24] The Ru–C distance to the pentafluorophenyl ligand was 2.160(2) Å.

Evidence for the agostic interaction being retained in solution was apparent from small, but very clear, doublet ^{19}F splittings on low frequency resonances for Ru···H–C at δ 0.5 and δ 6.4 in the ^{1}H and ^{13}C{^{1}H} NMR spectra respectively. Use of ^{1}H-^{19}F HMBC spectroscopy established that the coupling resulted from the *ortho*-F signal at δ −112 (see ESI†). The hydride resonance in **4** (δ −24.7) resonated to higher frequency

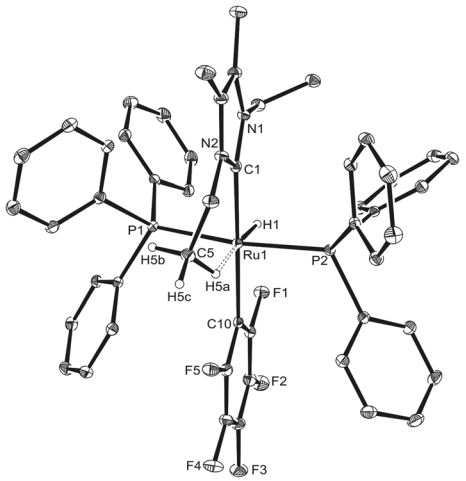
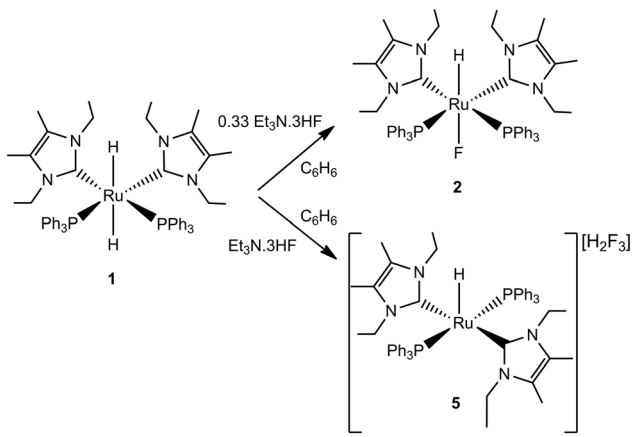


Fig. 3 Molecular structure of **4**. All hydrogen atoms, except Ru–H and those in the agostic methyl group, are omitted. Ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.060(2), Ru(1)–C(10) 2.160(2), Ru(1)–P(1) 2.3452(6), Ru(1)–P(2) 2.3188(6), P(1)–Ru(1)–P(2) 168.093(19), C(10)–Ru(1)–P(1) 91.56(6), C(1)–Ru(1)–P(2) 89.41(6).

of that in five-coordinate (non-agostic) **3**, and appeared as triplet of doublets, the doublet splitting now arising from coupling to the other *ortho*-F signal at δ −106 (see ESI†). These couplings help to emphasise the restricted rotation of the C_6F_5 ring suggested by the steric crowding in the crystal structure and proven by the presence of five different ^{19}F NMR resonances.

Formation of 2 *via* reaction of 1 with 'HF'

In an effort to find a higher yielding route to the hydride fluoride complex **2**, the reaction of **1** with $Et_3N{\cdot}3HF$ (TREAT-HF) was investigated. This reagent has become quite commonplace for the formation of transition metal bifluoride ($[FHF]^-$) complexes,[25] but has, on occasion, also produced metal fluoride species.[26] As shown in Scheme 3, **2** was formed as the sole Ru containing product upon reaction of **1** with $Et_3N{\cdot}3HF$ in a precise 1 : 1 ratio (*i.e.* 0.33 eq. TREAT-HF). However, increasing the stoichiometry to 1 : 3 Ru : HF gave instead the previously reported cation $[Ru(IEt_2Me_2)_2(PPh_3)_2H]^+$,[14] which was shown crystallographically to be formed as the relatively unusual $[H_2F_3]^-$ salt, **5** (see ESI†).[27]



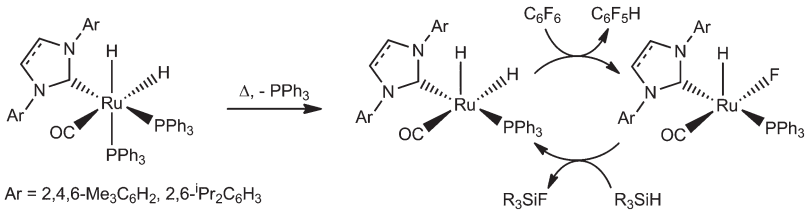
Scheme 3

Catalytic HDF using 1

Initial catalytic studies have shown that **1** is far more active for HDF than our previously reported $[Ru(NHC)(PPh_3)_2(CO)H_2]$ system[10,11] bearing unsaturated or saturated *N*-aryl substituted carbenes. As shown in Scheme 4, this reacted *via* initial phosphine loss to give 16-electron $[Ru(NHC)(PPh_3)(CO)H_2]$, which was converted to the hydride fluoride complex $[Ru(NHC)(PPh_3)(CO)HF]$ following hydrodefluorination. Back reaction with the alkysilane reductant regenerated the dihydride complex, forming a strong Si–F bond in R_3SiF in the process which provides the driving force for the reaction.

The mixture of C–F and C–H activation products formed in the stoichiometric reaction of **1** and C_6F_6 suggests that the first step of a comparable catalytic cycle with **1** might be more complex, and so the individual stoichiometric reactions of **2**, **3** and **4** with Et_3SiH were investigated to establish the viability of the return reduction steps necessary to complete the catalytic cycle. It was found that: (i) Treatment of the hydride fluoride complex **2** with 1 eq. Et_3SiH led to the instantaneous reformation of **1**, along with Et_3SiF; (ii) There was no reaction between **3** and Et_3SiH (1.5 eq.) at room temperature over 6 h, or even upon heating at 343 K for 4 h; (iii) No reaction occurred between the bis-phosphine fluoroaryl complex **4** and silane (1.5 eq.) at room temperature overnight, although following addition of IEt_2Me_2 (5 eq.), both $C_6F_4H_2$ and Et_3SiF appeared very quickly in the ^{19}F NMR spectrum. Over the course of *ca.* 2 h, however, the sample began to decompose, shown by the deposition of black solid material.

Fig. 4 shows the product distribution from the HDF of C_6F_6 with 10 mol% **1** carried out with Et_3SiH as reductant (80 eq.) in C_6H_6 at 363 K. The elevated temperature was adopted in an effort to both push catalysis through at a reasonable rate and also to try to drive HDF through to lower fluorine containing products, which are typically more difficult to obtain.[28] Remarkably, **1** proved capable of bringing about three and four HDF steps to a significant extent, affording 96% of the reaction mixture as isomers of tri- and difluorobenzenes over 72 h.[29] Doubling the reaction time increased the amount of 1,2- and 1,4-$C_6F_2H_4$ and even generated a small amount of fluorobenzene through completion of five HDF steps, giving an overall turnover number of 37. While an in-depth study of the regioselectivity of HDF remains to be carried out, the presence of both 1,2,4,5- and 1,2,3,4-isomers of $C_6F_4H_2$ after 72 h suggests that the very high *ortho*-regioselectivity found with $[Ru(NHC)(PPh_3)_2(CO)H_2]$ (which converted C_6F_5H overwhelmingly to 1,2,3,4-$C_6F_4H_2$) is less apparent with **1**. When HDF of C_6F_6 was repeated but now under 4 atm H_2, the amount of difluorobenzene products increased (TON = 38), while the relative ratio of the 1,2 : 1,3 : 1,4 difluorobenzene isomers also altered. Interestingly, no turnover of the reaction between C_6F_6



Scheme 4

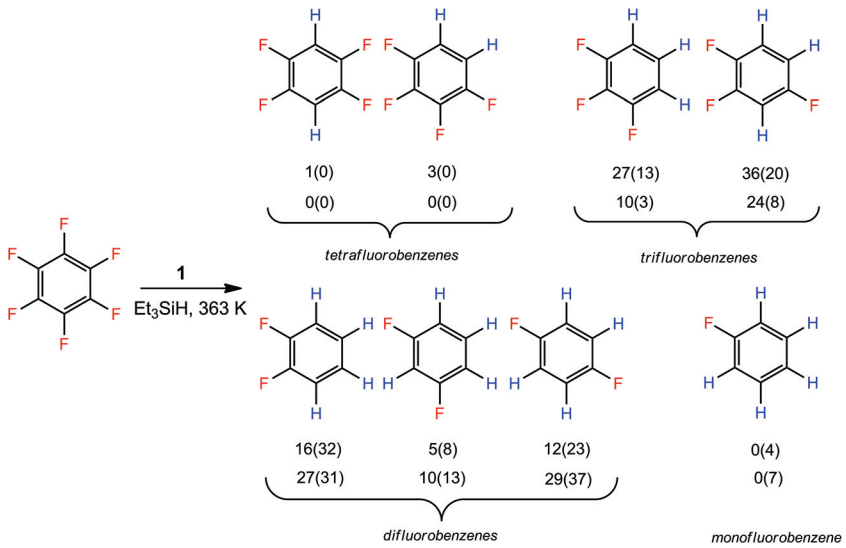


Fig. 4 Product distribution from the catalytic HDF of C_6F_6 using 10 mol% **1** with 80 eq. Et_3SiH in C_6H_6 at 363 K. Reactions run under (top line) Ar (1 atm) and (bottom line) H_2 (4 atm) with percentage of products (average of 3 runs) shown after 72 h and (in parentheses) 144 h. HDF products were assigned by ^{19}F NMR spectroscopy.

and 10 mol% **1** took place under 4 atm H_2/excess NEt_3 (80 equivalents)[30] in the absence of the silane.

Conclusions

In conclusion, we have shown that $[Ru(IEt_2Me_2)_2(PPh_3)_2H_2]$ (**1**) is a far more active catalyst for the hydrodefluorination of C_6F_6 than the previously reported $[Ru(NHC)(PPh_3)(CO)H_2]$ systems, as reflected in the reduction of C_6F_6 down as far as fluorobenzene. Given the previous mechanistic studies on Ru–H catalysed HDF, this enhanced activity most likely arises from the greater nucleophilicity of the hydride ligands in **1**, arising as a result of their *trans* H–Ru–H geometry. A mechanistic study of **1** is ongoing to confirm the role of the Ru–H bond, and also to help rationalise the lower regioselectivity compared to $[Ru(NHC)(PPh_3)(CO)H_2]$. Moreover, we hope to be able to explain why **1** is so catalytically competent in spite of appearing, at least on the basis of stoichiometric experiments, to be far more prone than $[Ru(NHC)(PPh_3)(CO)H_2]$ to unfavourable C–H activation reactions with partially fluorinated substrates like C_6F_5H. Given that the catalysis was run under high temperature conditions where C–H activated products like $[Ru(IEt_2Me_2)(PPh_3)_2(C_6F_5)H]$ (**4**) are observed, one possibility is that such species are not dead-ends, but can be recycled into the catalytic cycle, allowing propagation of HDF to continue. While this may help to explain the bias towards more of the lower fluorine containing products with a moderate pressure of H_2 shown in Fig. 4, it fails to explain the change in isomer distribution. We hope to present answers to these questions in the near future.

Experimental

General considerations

All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques. Solvents were purified using an MBraun SPS solvent system (hexane, Et_2O) or under a nitrogen atmosphere from sodium benzophenone ketyl (benzene). C_6D_6 and $C_6D_5CD_3$ were vacuum transferred from potassium. NMR spectra were recorded on Bruker Avance 400/500 and Avance III 500 MHz NMR spectrometers and referenced as follows: ^1H, δ 7.15 (C_6D_5H), δ 2.09 ($C_6D_5CD_2H$) and δ 3.58 (THF-d_7); $^{13}C\{^1H\}$, δ 128.0 (C_6D_6) and δ 21.3 ($C_6D_5CD_3$); $^{31}P\{^1H\}$, externally to 85% H_3PO_4 (δ 0.0); ^{19}F, externally to

$CFCl_3$ (δ 0.0). PPh_3 resonances are excluded unless they could be assigned unequivocally. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon. $[Ru(PPh_3)_4H_2]$[31] and IEt_2Me_2 [32] were prepared according to literature methods.

$[Ru(IEt_2Me_2)_2(PPh_3)_2H_2]$ (1). An alternative synthesis of **1** carried out in benzene rather than as previously described[14] in THF is reported here. This new approach afforded **1** in shorter time and in higher yield. $[Ru(PPh_3)_4H_2]$ (500 mg, 0.43 mmol) and IEt_2Me_2 (130 mg, 0.86 mmol) were dissolved in benzene (5 mL) and stirred in an ampoule sealed with a J. Youngs PTFE tap for 5 min at 298 K. The solution was filtered by cannula into a fresh ampoule and the volatiles were removed *in vacuo* to leave a sticky orange residue. This was washed with hexane (2 × 2 mL) to afford **1** as pale yellow solid. Yield: 279 mg, 70%. Spectroscopic data matched those in the original report.[14]

$[Ru(IEt_2Me_2)_2(PPh_3)_2HF]$ (2). C_6F_6 (50 μL, 0.45 mmol) was added to a benzene (5 mL) solution of **1** (140 mg, 0.15 mmol) in an ampoule fitted with J. Youngs PTFE tap. The reaction mixture was stirred vigorously for 24 h, filtered by cannula and evaporated to dryness to afford an oily red residue. Addition of hexane (1 mL) under the action of vigorous stirring resulted in a formation of a deep orange suspension (of **3**), which was filtered by cannula. Leaving the hexane filtrate at room temperature for few days afforded yellow crystals of **2**, which were manually separated from red needles of residual **3**. Yield of **2**: 43 mg, 30%. A more efficient route to **2** involved treatment of **1** with $Et_3N{\cdot}3HF$ (TREAT-HF). Thus, TREAT-HF (6.1 μL, 0.037 mmol) was added by syringe to a benzene solution (5 mL) of **1** (100 mg, 0.11 mmol) in an ampoule fitted with a J. Youngs PTFE tap. The reaction mixture was stirred for 30 min, the volatiles then removed under vacuum and the sticky yellow solid washed with hexane (2 mL) to afford **2** as a pale yellow solid. Yield: 75 mg, 72%. ^{1}H NMR: δ_H ($C_6D_5CD_3$, 400 MHz, 228 K) −21.58 (ddd, 1H, J_{HF} = 51.6 Hz, J_{HP} = 25.0 Hz, J_{HP} = 14.1 Hz, Ru–*H*), 0.26 (t, 3H, J_{HH} = 6.8 Hz, NCH_2CH_3), 0.34 (t, 3H, J_{HH} = 6.8 Hz, NCH_2CH_3), 1.10 (t, 3H, J_{HH} = 6.8 Hz, NCH_2CH_3), 1.16 (s, 3H, $NCCH_3$), 1.21 (s, 3H, $NCCH_3$), 1.39 (t, 3H, J_{HH} = 6.8 Hz, NCH_2CH_3), 1.49 (s, 3H, $NCCH_3$), 1.56 (s, 3H, $NCCH_3$), 2.32 (m, 1H, J_{HH} = 6.8 Hz, $NCHHCH_3$), 2.61 (m, 1H, J_{HH} = 6.8 Hz, $NCHHCH_3$), 3.13 (m, 1H, J_{HH} = 6.8 Hz, $NCHHCH_3$), 3.36 (m, 1H, J_{HH} = 6.8 Hz, $NCHHCH_3$), 5.60 (br m, 1H, J_{HH} = 6.8 Hz, $NCHHCH_3$), 5.83 (br m, 1H, J_{HH} = 6.8 Hz, $NCHHCH_3$), 6.45 (br s, 1H, $NCHHCH_3$), 6.80 (br s, 1H, $NCHHCH_3$)*.

* = chemical shift established by ^{1}H COSY.

$^{31}P\{^1H\}$ NMR: δ_P ($C_6D_5CD_3$, 121.5 MHz, 298 K): 43.1 (br s). $^{13}C\{^1H\}$ NMR: δ_C ($C_6D_5CD_3$, 100 MHz, 228 K) 8.7 (s, $NCCH_3$), 8.8 (s, $NCCH_3$), 9.1 (s, $NCCH_3$), 9.4 (s, $NCCH_3$), 13.6 (s, NCH_2CH_3), 14.2 (s, NCH_2CH_3), 15.0 (s, NCH_2CH_3), 16.2 (s, NCH_2CH_3), 40.5 (d, J_{CP} or J_{CF} = 32.2 Hz, NCH_2CH_3), 42.0 (d, J_{CP} or J_{CF} = 16.4 Hz, NCH_2CH_3), 43.2 (s, NCH_2CH_3), 122.3 (s, $NCCH_3$), 122.9 (s, $NCCH_3$), 123.5 (s, $NCCH_3$), 124.4 (s, $NCCH_3$), 191.4 (m, Ru–C_{NHC}). ^{19}F NMR (THF-d_8, 470 MHz, 298 K): δ −354.4 (br d, J_{FH} = 51.6 Hz). Analysis found: C, 68.99; H, 7.15; N, 5.62%. $C_{57}H_{63}N_4FP_2Ru{\cdot}0.5C_6H_{14}$ requires: C, 68.93; H, 7.10; N, 5.64%.

$[Ru(IEt_2Me_2)_2(PPh_3)(C_6F_5)H]$ (3). C_6F_5H (120 μL, 1.1 mmol) was syringed into a J. Youngs resealable ampoule containing a hexane suspension (5 mL) of **1** (100 mg, 0.11 mmol). The reaction mixture was stirred vigorously at room temperature for 24 h to give a dark orange solid, which was isolated by cannula filtration, washed with hexane (2 × 5 mL) and dried *in vacuo*. Yield 53 mg, 58%. ^{1}H NMR: δ_H (C_6D_6, 500 MHz, 298 K) −32.95 (dt, 1H, J_{HP} = 30.6 Hz, J_{HF} = 7.2 Hz, Ru–*H*), 0.98 (t, 6H, J_{HH} = 7.3 Hz, NCH_2CH_3), 1.02 (t, 6H, J_{HH} = 7.3 Hz, NCH_2CH_3), 1.45 (s, 6H, $NCCH_3$), 1.48 (s, 6H, $NCCH_3$), 3.05 (m, 2H, NCH_2CH_3), 3.60 (m, 4H, NCH_2CH_3), 4.77 (m, 2H, NCH_2CH_3), 6.90–7.05 (br m, 9H, PC_6H_5), 7.43–7.49 (m, 6H, PC_6H_5). $^{31}P\{^1H\}$ NMR: δ_P (C_6D_6, 121.5 MHz, 298 K) 59.5 (tt, J_{PF} = 20.7 Hz, J_{PF} = 9.7 Hz). $^{13}C\{^1H\}$ NMR: δ_C (C_6D_6, 126 MHz, 298 K) 9.0 (s, NCH_2CH_3), 9.2 (s, NCH_2CH_3), 15.3 (s, $NCCH_3$), 15.4 (s, $NCCH_3$), 42.4 (s, NCH_2CH_3), 43.2 (s, NCH_2CH_3), 123.2 (s, $NCCH_3$), 123.6 (s, $NCCH_3$), 127.1 (d, J_{CP} = 7.3 Hz, PC_6H_5), 127.4 (s, PC_6H_5), 133.6 (d, J_{CP} = 11.0 Hz, PC_6H_5), 142.8 (d, J_{CP} = 26.7 Hz, PC_6H_5), 195.9 (d, J_{CP} = 12.1 Hz, Ru–C_{NHC}). ^{19}F NMR: δ_F (C_6D_6, 470 MHz, 298 K) −166.4 (1F, t, J_{FF} = 20.3 Hz, *p*-C_6F_5), −165.6 (2F, m, *m*-C_6F_5), −111.5 (2F, br s, *o*-C_6F_5). Analysis found: C, 60.36; H, 5.74; N, 6.72. $C_{42}H_{48}N_4F_5PRu$ requires: C, 60.34; H, 5.79; N, 6.70.

$[Ru(IEt_2Me_2)(PPh_3)_2(C_6F_5)H]$ (4). A J. Young NMR tube containing **1** (45 mg, 48 μmol) and C_6F_5H (16 μL, 145 μmol) was heated in C_6H_6 (0.5 mL) at 343 K overnight to afford a deep red solution. This was filtered by cannula and the filtrate evaporated to dryness. After washing with hexane (3 × 0.5 mL), the residue was redissolved in a minimal amount of THF and layered with hexane to afford deep red crystals of **4**. Yield: 13 mg, 28%. ^{1}H NMR: δ_H (THF-d_8, 500 MHz, 298 K) −24.66 (1H, td, J_{PH} = 23.5 Hz, J_{HF} = 6.9 Hz, Ru–*H*), 0.34 (3H, t, J_{HH} = 7.3 Hz, NCH_2CH_3), 0.48 (3H, td, J_{HH} = 7.3 Hz, J_{HF} = 1.5 Hz, NCH_2CH_3), 1.92 (s, 3H, $NCCH_3$), 1.96 (s, 3H, $NCCH_3$), 2.90 (2H, q, J_{HH} = 7.3 Hz, NCH_2CH_3), 3.38 (2H, q, J_{HH} = 7.3 Hz, NCH_2CH_3), 7.02–7.24 (30H, br m, PC_6H_5). $^{31}P\{^1H\}$ NMR: δ_P (THF-d_8, 202 MHz, 298 K) 52.3 (s). $^{13}C\{^1H\}$ NMR: δ_C (THF-d_8, 126 MHz, 298 K) 6.4 (d, J_{CF} = 7.5 Hz, NCH_2CH_3), 9.4 (s, $NCCH_3$), 9.8 (s, $NCCH_3$), 14.5 (s, NCH_2CH_3), 42.5 (s, NCH_2CH_3), 44.0 (s, NCH_2CH_3), 124.7 (s, $NCCH_3$), 126.2 (s, $NCCH_3$), 127.9 (virtual triplet ('vt'), J = 4 Hz, PC_6H_5), 129.0 (s, PC_6H_5), 134.6 ('vt', J = 6 Hz, PC_6H_5), 139.0 ('vt', J = 17 Hz, PC_6H_5), 194.0 (m, Ru–C_{NHC}). ^{19}F NMR: δ_F (THF-d_8, 470 MHz, 298 K) −171.5 (1F, t, J_{FF} = 20.2 Hz, *p*-C_6F_5), −170.1 (1F, m, *p*-C_6F_5), −168.9 (1F, m, *m*-C_6F_5), −111.8 (1F, m, *o*-C_6F_5), −105.5 (1F, m, *o*-C_6F_5). Analysis found: C, 64.89; H, 4.98; N, 3.01. $C_{51}H_{47}N_2F_5P_2Ru$ requires: C, 64.75; H, 5.01; N, 2.96.

$[Ru(IEt_2Me_2)_2(PPh_3)_2H][H_2F_3]$ (5). TREAT-HF (17.5 μL, 0.11 mmol) was added to a benzene (5 mL) solution of **1** (100 mg, 0.11 mmol) in a J. Youngs resealable ampoule. The reaction mixture was stirred at room temperature for 30 min at 298 K, before the sample was reduced to dryness. The sticky orange/red residue was washed with hexane (2 × 2 mL) and Et_2O (2 × 2 mL) and then redissolved in THF (5 mL). Addition of Et_2O resulted in the precipitation of **5** as an orange solid, which was washed further with Et_2O (2 × 5 mL) and then dried

Table 1 Crystal data and structure refinement details for compounds **2**, **3** and **4**

Compound reference	**2**	**3**	**4**
Chemical formula	$C_{57}H_{70}N_4FP_2Ru$	$C_{42}H_{48}N_4F_5PRu$	$C_{51}H_{47}N_2F_5P_2Ru$
Formula mass	993.18	835.88	945.92
Crystal system	Monoclinic	Orthorhombic	Triclinic
a/Å	16.7400(1)	31.0451(7)	12.6690(2)
b/Å	16.5550(1)	8.9768(2)	13.1530(2)
c/Å	19.4760(1)	14.4306(3)	15.5900(3)
α/°	90.00	90.0	96.300(1)
β/°	109.727(1)	90.0	105.626(1)
γ/°	90.00	90.0	116.893(1)
Unit cell volume/Å^3	5080.63(5)	4021.62(17)	2148.63(6)
Space group	$P2_1/a$	$Pna2_1$	$P\bar{1}$
No. of formula units per unit cell, Z	4	4	2
No. of reflections measured	94 717	22 071	40 103
No. of independent reflections	11 623	7401	9725
R_{int}	0.0678	0.0684	0.0478
Final R_1 values ($I > 2\sigma(I)$)	0.0370	0.0402	0.0338
Final w$R(F^2)$ values ($I > 2\sigma(I)$)	0.0767	0.0877	0.0685
Final R_1 values (all data)	0.0582	0.0502	0.0516
Final w$R(F^2)$ values (all data)	0.0851	0.0942	0.0746

in vacuo. Yield: 76 mg, 69%. Crystals suitable for X-ray diffraction were obtained upon layering a concentrated THF-d_8 solution with hexane. ^{1}H NMR: δ_H (THF-d_8, 500 MHz, 298 K) −29.65 (1H, t, J_{HP} = 24.0 Hz, Ru–*H*), 0.44 (6H, t, J_{HH} = 7.3 Hz, NCH_2CH_3), 0.88 (6H, t, J_{HH} = 7.3 Hz, NCH_2CH_3), 1.81 (6H, s, $NCCH_3$), 2.01 (6H, s, $NCCH_3$), 2.75 (4H, q, J_{HH} = 7.3 Hz, NCH_2CH_3), 3.36 (4H, q, J_{HH} = 7.3 Hz, NCH_2CH_3), 7.16–7.34 (30H, m, $P(C_6H_5)_3$), 13.68 (2H, br s, $[H_2F_3]^-$). ^{31}P{^{1}H} NMR: δ_P (THF-d_8, 202 MHz, 298 K) 46.1 (s). ^{19}F NMR: δ_F (THF-d_8, 470 MHz, 298 K) −115.2 (br s). Analysis found: C, 64.38; H, 5.69; N, 4.84. $C_{54}H_{65}N_4F_3P_2Ru{\cdot}2C_4D_8O$ requires C, 64.73; H, 5.70; N, 4.87.

Procedures for catalytic HDF

A stock solution of **1** was prepared by dissolving 0.0184 g (0.02 mmol) of the complex in 2 mL C_6H_6 in the glovebox. 0.5 mL aliquots of this solution was syringed into three J. Young's resealable NMR tubes, and C_6F_6 (5.8 μL, 0.05 mmol) and Et_3SiH (63 μL, 0.4 mmol) added to each tube. These were then placed in a pre-heated oil bath at 363 K and monitored by ^{19}F NMR spectroscopy after 72 and 144 h. For reactions performed under H_2, a C_6H_6 (0.3 mL) sample of **1** (0.0046 g, 0.005 mmol) was placed into a medium-walled NMR tube fitted with a resealable valve and freeze–pump–thaw degassed (3 cycles). A mixture of C_6F_6 (5.8 μL, 0.05 mmol), Et_3SiH (63 μL, 0.4 mmol) and C_6H_6 (0.1 mL) was vacuum transferred into the pressure tube, which was then put under 4 atm H_2 and placed in a pre-heated oil bath at 363 K. The reaction was monitored by ^{19}F NMR spectroscopy after 72 and 144 h.

X-ray crystallography

Data for **2** and **4** were obtained using a Nonius Kappa CCD diffractometer, while those for **3** and **5** (see ESI†) were collected using Agilent SuperNova and Agilent Excaliber diffractometers, respectively. Details of the data collections, solutions and refinements are given in Table 1. All diffraction measurements were conducted at 150 K using Mo(Kα) radiation and hydride ligands were uniformly refined subject to being a distance of 1.6 Å from the relevant metal centre. Convergence was straightforward in all cases, and only exceptional details merit note. In particular, the asymmetric unit in **2** was seen to comprise one bis-carbene complex and half of a hexane molecule. The latter is proximate to an inversion centre which serves to generate the remainder. The fluoride and hydride ligands were modelled subject to being disordered with each other in a 53 : 47 ratio. Fractional occupancy hydride atoms were refined with a common isotropic displacement parameter. In **3**, H5A, H5B and H5C were readily located and refined with the single restraint of being at a distance of 0.98 Å from C5. The structures were solved using SHELXS-97[33] and refined using full-matrix least squares in SHELXL-97.[33] Crystallographic data for compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1400863–1400866.

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