C-F Bond Activation of P(C6F5)3 By Ruthenium Dihydride Complexes: Isolation and Reactivity of the ‘Missing’ Ru(PPh3)3H(halide) Complex, Ru(PPh3)3HF
C–F Bond Activation of P(C_6F_5)_3 By Ruthenium Dihydride Complexes: Isolation and Reactivity of the ‘Missing’ Ru(PPh_3)_3H(halide) Complex, Ru(PPh_3)_3HF

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Abstract

The major product of the reaction between Ru(IMe_4)_2(PPh_3)_2H_2 (1; IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene) and P(C_6F_5)_3 (PCF) is the 5-coordinate complex Ru(IMe_4)_2(PF_2{C_6F_5})(C_6F_5)H_2, which is formed via a complex series of C–F/P–C bond cleavage and P–F bond formation steps. In contrast, hydrodefluorination of all six ortho C–F bonds in PCF occurs with Ru(PPh_3)_4H_2 to afford Ru(PPh_3)_3HF 3. NaBAR^F_4 abstracted the fluoride ligand in 3 to give [Ru(\{η^6-C_6H_5\}_2PPh_2)(PPh_3)_2H][BAR^F_4], while B_2pin_2 reacted with 3 in C_6D_6 to yield a mixture of [Ru(\{η^6-C_6D_6\}_2PPh_3)_2H]^+ and Ru(PPh_3)_3H_2. Treatment of 3 with HBpin (5 equiv) and HSiR_3 (R = Et, Ph; 2 equiv) afforded Ru(PPh_3)_3(σ-HBpin)H_2 and Ru(PPh_3)_3(SiR_3)_3H_3 respectively. No stable substitution products were generated when 3 was reacted with Me_3SiX (X = CF_3, C_6F_5).
Introduction

Transition metal hydride complexes have proven to be valuable for effecting the cleavage of carbon-fluorine bonds.\textsuperscript{1-11} In many cases, the precise mechanism(s) underpinning the C–F activation chemistry remain to be fully established.\textsuperscript{12-18} However, based on examples where detailed mechanistic studies have been undertaken, the hydride ligands behave either innocently, for example, in undergoing elimination from the metal (in the case of dihydrides, through either thermally or photochemically induced reductive elimination) to generate coordinatively unsaturated metal species that then perform the C–F activation,\textsuperscript{19,20} or, participate in a more active manner, for example, by undergoing insertion of fluorinated alkenes,\textsuperscript{21,22} or by acting as nucleophiles to displace fluoride from C–F bonds in hydrodefluorination (HDF) reactions.\textsuperscript{9,23-27}

In the last few years, we have reported that the trans-dihydride N-heterocyclic carbene (NHC) complexes Ru(NHC)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}H\textsubscript{2} and Ru(NHC)\textsubscript{4}H\textsubscript{2} (NHC = IMe\textsubscript{4}, IEt\textsubscript{2}Me, IMe\textsubscript{2})\textsuperscript{28} exhibit the latter type of reactivity in the catalytic HDF of aromatic fluorocarbons.\textsuperscript{29-31} In the course of a more general study on the reactivity of the mixed NHC/phosphine complex Ru(IMe\textsubscript{4})\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}H\textsubscript{2} (1, Scheme 1), we observed that both P(C\textsubscript{6}D\textsubscript{3})\textsubscript{3} and P(p-C\textsubscript{6}H\textsubscript{4}Me)\textsubscript{3} readily displaced one or both of the PPh\textsubscript{3} ligands at room temperature.\textsuperscript{32,33} In contrast, the chelating phosphines Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{2}PPh\textsubscript{2} (dppe), Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}PPh\textsubscript{2} (dppp) and Ph\textsubscript{2}PCH\textsubscript{2}PPh\textsubscript{2} (dppm) could only be substituted into 1 at elevated temperatures.\textsuperscript{31} In an attempt to broaden the scope of these substitution reactions, we turned our attention to more electronically diverse phosphines, in particular, the perfluorinated phosphine, P(C\textsubscript{6}F\textsubscript{3})\textsubscript{3} (abbreviated as PCF). While the chemistry of PCF (as well as its derivatives) with transition metal centers has been probed quite
extensively, predominantly with catalytic applications in mind, there are a small number of reports which show that PCF (or derivatives thereof) are susceptible to C–F activation by nucleophilic ligands on metal centers. To the best of our knowledge, these nucleophilic ligands have not included hydrides.

Herein, we report that PCF undergoes a complex series of C–F/P–C bond cleavage and P–F bond formation processes with 1 to yield the unusual PF$_2$(C$_6$F$_5$) complex, Ru(IME$_4$)$_2$(PF$_2${C$_6$F$_5$})(C$_6$F$_5$)H (2). In contrast, hydrodefluorination of all six ortho–C–F bonds takes place with the tetrakis(triphenylphosphine) ruthenium dihydride complex, Ru(PPh$_3$)$_4$H$_2$, to yield Ru(PPh$_3$)$_3$HF (3), the last of the well-known family of Ru(PPh$_3$)$_3$H(halide) complexes to be isolated.

Results and Discussion

Synthesis and Characterization of Ru(IME$_4$)$_2$(PF$_2${C$_6$F$_5$})(C$_6$F$_5$)H (2). The reaction of a C$_6$D$_6$ solution of 1 with 5 equiv PCF resulted in the loss of the Ru-H resonance in the $^1$H NMR spectrum of 1 ($\delta$ = 6.54) over the course of ca. 24 h at room temperature to give one major metal hydride containing product 2 (the yield of 2 was ca. 70% determined by integration of all Ru-H signals in the $^1$H NMR spectrum,), which appeared as a doublet of triplets signal at $\delta$ = -29.62. This was characterized as the unusual 5-coordinate complex, Ru(IME$_4$)$_2$(PF$_2${C$_6$F$_5$})(C$_6$F$_5$)H, (Scheme 1) on the basis of 1- and 2-D NMR experiments using the wealth of spin $\frac{1}{2}$ nuclei in the molecule (Figures S1-S7 in the Supporting Information). Thus, the $^1$H NMR spectrum showed four methyl resonances in a ratio of 6:6:6:6 to 1 for the Ru-H signal, confirming the presence of two IMe$_4$ ligands and a single hydride. The low frequency of the Ru-H resonance was consistent with the hydride
being *trans* to a vacant coordination site, while the magnitude of the coupling constants \( (^2J_{HP} = 46.1 \text{ Hz}, ^3J_{HF} = 6.1 \text{ Hz}) \) placed it *cis* to both the phosphine and ruthenium coordinated \( C_6F_5 \) ligands. The extremely unusual difluoro(pentafluorophenyl)phosphine \( PF_2(C_6F_5) \), which is, to the best of our knowledge, only known as a ligand in a single transition metal complex, displayed a characteristic high frequency phosphorus resonance at 161 ppm. This appeared as a triplet of multiplets with a large one-bond triplet \( J_{PF} \) splitting of >1100 Hz. The \( ^{19}F \) NMR spectrum revealed a similarly diagnostic high frequency (\( \delta = 31 \)) resonance for the \( F_2P \) unit; this appeared as a doublet of triplets with a clearly resolved 1125 Hz doublet splitting to phosphorus. The 16 Hz triplet splitting was shown by \( ^{19}F \) COSY to originate from coupling to the two F atoms at the ortho-positions of the P-bound \( C_6F_5 \) group. The \( ^{19}F \) COSY spectrum allowed the signals for P- and Ru-bound \( C_6F_5 \) groups to be differentiated and fully assigned.

![Scheme 1. Bond activation of PCF with 1](image)

Given the unexpected structure of 2, 1 was reacted with PCF under a range of conditions in an attempt to detect any reaction intermediates. A 1:1 mixture of 1 and PCF resulted in only incomplete conversion to 2 even after standing for 3 weeks at room temperature (after this duration, 1:2 were present in a 1:0.3 integral ratio; Figure S8 in the
Supporting Information). There were no NMR signals of any intermediates. Heating 1
and PCF in a 1:1.5 ratio at 50 °C for ca. 24 h brought about complete loss of 1 and
formation of 2 in ca. 60% yield by NMR spectroscopy; again no intermediate species
were observed. Isolation of the reaction volatiles revealed only the presence of C\textsubscript{6}F\textsubscript{5}H.
The $^{31}$P NMR spectrum of the reaction residue showed signals for 2, free PPh\textsubscript{3} and some
unreacted PCF. Only signals of low intensity were present in the rest of the spectrum.

Despite exhaustive efforts, 2 could not be crystallized. Additionally, efforts to
crystallize either a chloride derivative (by dissolution in CH\textsubscript{2}Cl\textsubscript{2} or CHCl\textsubscript{3}) or
CO/isocyanide trapped derivative also met with failure. It is worth noting that in all of
these reactions, $^{31}$P/$^{19}$F NMR spectra showed that the PF\textsubscript{2}(C\textsubscript{6}F\textsubscript{5}) ligand remained intact.

**Reactivity of 1 with Other Fluorinated Phosphines.** The presence of P(C\textsubscript{6}F\textsubscript{5}) groups
appear to be mandatory for the bond activation steps described above. Neither P(C\textsubscript{6}H\textsubscript{4}-p-
F)\textsubscript{3} nor P(3,4,5-C\textsubscript{6}F\textsubscript{3}H\textsubscript{2})\textsubscript{3} \textsuperscript{35} exhibited reactivity comparable to that of PCF with 1 (Figures
S9 and S10 in the Supporting Information). Thus, addition of 2 equiv of P(C\textsubscript{6}H\textsubscript{4}-p-F)\textsubscript{3} to
a C\textsubscript{6}D\textsubscript{6} solution of 1 resulted in the slow (3 days) formation of two new triplet hydride
resonances at slightly lower frequency ($\delta$ -6.71 and $\delta$ -6.89, both with $^{2}$J\textsubscript{HP} = 20.6 Hz)
from that of 1, which we propose arises from the substitution of one or two PPh\textsubscript{3} ligands
by the fluorinated phosphine (Scheme 2). Over a prolonged period (ca. 3 weeks), further
hydride signals appeared between ca. $\delta$ -8.3 and -9.1 and ca. $\delta$ -11.2 and -11.5. The
similarity of these chemical shifts to those reported previously for isomers of 1, \textsuperscript{32}
suggests that the initial mono- and bis-P(C\textsubscript{6}H\textsubscript{4}-p-F)\textsubscript{3} containing products also undergo
isomerization over longer times.
The reaction between 1 and P(3,4,5-C₆F₃H₂)₃ led to rapid (1 h) and complete conversion to a single new species that exhibited a triplet hydride resonance at δ -6.79 (²J_HP = 20.9 Hz). Over an interval of weeks, this was slowly replaced by a new triplet Ru-H signal at δ -7.13 (²J_HP = 21.1 Hz). Following from the reactivity of P(C₆H₄-p-F)₃ above, these most likely represent mono- and bis-P(3,4,5-C₆F₃H₂)₃ substitution products. No isomerization was seen in this case at longer times.

Scheme 2. Substitution chemistry of 1 with P(C₆H₄-p-F)₃ and P(3,4,5-C₆F₃H₂)₃

Synthesis and Characterization of Ru(PPh₃)₃HF (3). The complex series of C-F and P-C bond cleavage steps, together with P-F and C-H bond formation, necessary to generate Ru-PF₂(C₆F₅) and Ru-C₆F₅ groups and C₆F₅H, in tandem with the lack of any observable intermediates, makes it impossible to propose a credible mechanism to account for the formation of 2. We therefore decided to adopt an alternative approach, to see if PCF displayed related activation chemistry with different ruthenium hydride precursors. Treatment of Ru(PPh₃)₄H₂ with an excess of PCF (4 equiv) led to a change from a yellow suspension to a homogeneous red solution over ca. 2 h at room
temperature. $^{31}$P NMR spectroscopy revealed the presence of unreacted PCF and complete loss of ruthenium starting material, but no obvious new product resonances. However, the low frequency region of the $^1$H NMR spectrum did show the formation of a quartet resonance at δ -22.33, attributable to Ru(PPh$_3$)$_3$HF (3, Scheme 3). The identity of 3, which was isolated in ca. 80% yield as an air-sensitive red-orange solid, was established unequivocally by X-ray diffraction as shown in Figure 1. The P$_{ax}$-Ru-P$_{ax}$ angle of 153.023(17)$^\circ$ is similar to that found in the chloride, bromide and iodide derivatives.$^{54,55}$ In contrast, the P$_{eq}$-Ru-X angle ranged from a value of 133.41(5)$^\circ$ in 3 to 116.428(13)$^\circ$ in Ru(PPh$_3$)$_3$HBr.$^{55}$ The Ru-F bond length (2.0652(12) Å) was comparable to values found in a range of other five- and six-coordinate ruthenium(II) fluoride complexes, such as cis-Ru(dppp)$_2$F$_2$ (2.056(3)/2.069(3) Å),$^{56}$ Ru(PPh$_3$)$_3$(CO)HF (2.0986(15) Å),$^{57}$ Ru($^{t}$Bu$_2$Me)$_2$(CO)(=CF$_2$)HF (2.065(1) Å)$^{58}$ and Ru(Ind)(SIMes)(P(OiPr)$_3$)F$_2$ (2.017(3)/2.035(4); Ind = 3-phenylindenylidene; SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene).$^{59}$
**Figure 1.** Molecular structure of Ru(PPh$_3$)$_3$HF (3). Ellipsoids are shown at 30% probability. Hydrogen atoms, with the exception of the Ru-H ligand are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-F(1) 2.0652(12), Ru(1)-P(1) 2.3423(4), Ru(1)-P(2) 2.1996(5), Ru(1)-P(3) 2.3201(5), P(1)-Ru(1)-F(1) 88.19(4), P(2)-Ru(1)-F(1) 133.51(5), P(1)-Ru(1)-P(3) 153.023(17).

In many respects, 3 bears similarity to the recently reported rhodium fluoride complex Rh(PPh$_3$)$_3$F,$^{51d,e}$ in that they each represent the last member of the well-known families of Ru(PPh$_3$)$_3$H(halide) and Rh(PPh$_3$)$_3$(halide) complexes to be prepared. The solution fluxionality of Ru(PPh$_3$)$_3$HX (X = Cl, Br, I) was apparent in 3. As the complex showed reasonable solubility across a range of solvents, variable temperature $^1$H, $^{31}$P and $^{19}$F NMR spectra were recorded in toluene, THF as well as dichloromethane. Figure 2 shows representative examples of spectra; complete sets of spectra in all solvents are provided in Figures S11-S17 in the Supporting Information. At 298 K, the hydride resonance in 3 appeared as a quartet with $^2$J$_{HP}$ = 28.0 Hz in C$_6$D$_5$CD$_3$, THF-$d_8$ and CD$_2$Cl$_2$ (Figure 2a,b). This became a broad multiplet in CD$_2$Cl$_2$ at 199 K, whereas a more coupled multiplet was observed in both toluene and THF at the same temperature. The best resolved low temperature spectrum was measured in C$_6$D$_5$CD$_3$ at 199 K (Figure 2c); this simplified to a doublet with a $^2$J$_{HF}$ splitting of 16.0 Hz with $^{31}$P decoupling (Figure 2d). While we were unable to observe any $^{31}$P resonance in any solvent at room temperature, the 199 K $^{31}$P($^1$H) NMR spectrum recorded in C$_6$D$_5$CD$_3$ consisted of a 1:2 ratio of a doublet of triplets ($\delta$ 91; $^2$J$_{PF}$ = 84 Hz, $^2$J$_{PP}$ = 23 Hz) and a broadened triplet ($\delta$ 41; $J \approx 21$ Hz) (ESI). In all solvents across the temperature range 298-199 K, the Ru-F
resonance only ever appeared as a broad singlet, ranging in chemical shift from $\delta$ -190 to $\delta$ -205 (Figure 2e).\textsuperscript{61}

![Figure 2.](image)

**Figure 2.** $^1$H NMR spectrum (400 MHz) of Ru-H resonance of Ru(PPh$_3$)$_3$HF 3 in (a) CD$_2$Cl$_2$ (298 K), (b) THF-$d_8$ (298 K), (c) C$_6$D$_5$CD$_3$ (199 K), (d) $^1$H{$^{31}$P} NMR spectrum in C$_6$D$_5$CD$_3$ at 199 K. (e) $^{19}$F NMR spectrum (376 MHz) of Ru-F resonance of 3 in THF-$d_8$ at 298 K.

**Mechanism of Formation of 3.** In contrast to the complex bond activation/formation steps involved in the formation of 2, the formation of 3 arises by hydrodefluorination of PCF. This was probed by monitoring the reaction of different ratios of Ru(PPh$_3$)$_4$H$_2$:PCF by NMR spectroscopy. With sub-stoichiometric ratios of Ru:PCF (i.e. 6:1 and 9:1), we
were able to observe three minor ruthenium containing products (4a, 4b and 5) in addition to 3 (Scheme 3 and Figure S19 in the Supporting Information). Each of these species showed two $^{19}$F NMR signals (a doublet of doublets and a triplet of triplets, relative ratio of 2:1) at much higher frequency than the fluoride resonance of 3, in a region of the spectrum associated with fluoroaromatic groups. A subsequent reaction of Ru(PPh$_3$)$_4$H$_2$ with P(3,4,5-C$_6$F$_3$H$_2$)$_3$ afforded the same three species, but no 3 (Figure S20 in the Supporting Information).$^{62}$ All four Ru species (3, 4a, 4b and 5) can be rationalized by ortho-hydrodefluorination of PCF. The regioselectivity is consistent with a pathway involving substitution of PCF into Ru(PPh$_3$)$_4$H$_2$, followed by intramolecular nucleophilic attack by Ru-H at an ortho-C–F position. An analogous intramolecular attack of a Pt-OME ligand has been proposed to account for the reaction of the ortho-C–F bonds in [Pt(PPh$_2$C$_6$F$_5$)$_2$(THF)Me] with NaOMe to give Pt(PPh$_2${2,6-(OMe)$_2$C$_6$F$_3$})$_2$(OMe)Me.$^{39,40}$ Very recently, Kayaki and co-workers$^{63}$ have reported that Ir-H complexes bearing fluorinated phenylsulfonyl-1,2-diphenylethlyenediamine ligands undergo HDF at the ortho-C–F position to generate iridacycle products.

**Scheme 3.** Synthesis of 3 and proposed structures of 4a, 4b and 5.$^{59}$
The formation of the P(3,4,5-C₆F₃H₂)₃ complexes 4a/4b and 5, together with the lack of any signals for bound or free partially hydrodefluorinated phosphines (e.g. P(3,4,5-C₆F₃H₂)(C₆F₅)₂) implies that the HDF of all six available ortho-C-F sites in a molecule of PCF must be rapid, and certainly faster than the dissociation of any partially hydrodefluorinated phosphine. In the Pt chemistry above, Roundhill suggested that facile free rotation about the Pt-PR₃ bond allows all four ortho-fluorines to be placed very readily in close proximity to the reactive Pt-OMe group.

Scheme 4 shows a possible pathway to 3. Initial intramolecular HDF at an ortho-C-F bond would yield the substituted hydride fluoride complex I (assumed to 5-coordinate like 3), which could then bring about a second HDF step with formation of the difluoride complex II.⁶⁴,⁶⁵ Comproportionation of II and Ru(PPh₃)₄H₂ (known for [Ru(PPh₃)₂I₂]₂ and Ru(PPh₃)₄H₂)⁵⁵ would then generate a reactive Ru-H ligand in III, allowing HDF to propagate until P(3,4,5-C₆F₃H₂)₃ is formed.

Scheme 4. Possible pathway for the intramolecular HDF of PCF to form 3.
Reactivity of Ru(PPh$_3$)$_3$HF. As for other Ru(PPh$_3$)$_3$HX complexes, 3 was stable in solution under inert conditions, but degraded rapidly upon exposure to air to afford green-black solutions. It proved to be relatively thermally robust in solution, with traces of new signals only apparent by $^1$H NMR spectroscopy upon heating at 70 °C in THF-d$_8$ for ca. 7 h. Dissolution of 3 in CD$_2$Cl$_2$ afforded traces of Ru(PPh$_3$)$_3$HCl within hours, although complete conversion required days at room temperature (Figure S23 in the Supporting Information). Ru(PPh$_3$)$_3$HBr was formed in time of mixing upon addition of C$_6$H$_5$CH$_2$Br to 3, whereas reaction with bromodecane only occurred over several days. No reaction took place with PhI either at room temperature or at 70 °C.

Treatment of 3 with NaBAR$_4^+$ in CH$_2$Cl$_2$ (Scheme 5) resulted in an almost near instantaneous disappearance of the starting material and formation of the [BAR$_4^+$] salt 6 of the known cation [Ru($\eta^6$-C$_6$H$_5$PPh$_2$)(PPh$_3$)$_2$H]$^+$, which was identified through the presence of a triplet of doublets Ru-H hydride resonance at δ -8.61, and two $^{31}$P signals at δ 49.0 and -5.2 (Figure S24 in the Supporting Information).$^{66,67}$
Reactivity of 3 with B$_2$pin$_2$ and HBpin. A $^1$H NMR spectrum of a C$_6$D$_6$ solution of 3 recorded 5 min after the addition of 1 equiv B$_2$pin$_2$ showed residual starting material in an integral ratio of 1:0.2:0.4 to two new Ru-H containing products 7 and 8 with resonances at $\delta$ -5.49 and -9.33 respectively (Scheme 5; Figures S25-S27 in the Supporting Information). The chemical shift and coupling constant of 7 are consistent with those of the cation, $[(\eta^6$-arene)Ru(PPPh$_3)_2$H]$^+$ ($\delta$ -9.33; $^2$$J_{HF}$ = 36.7 Hz),$^{68}$ in which the arene is presumably C$_6$D$_6$. The presence of a broad $^{11}$B($^1$H) NMR triplet resonance ($^1J_{BF}$ = ca. 19 Hz) at $\delta$ 6.7, along with a broad $^{19}$F resonance at ca. $\delta$ -141, indicates that [F$_2$Bpin]$^-$ is the accompanying anion.$^{69}$

Within 30 min, an additional second-order hydride signal for Ru(PPPh$_3$)$_4$H$_2$ appeared in the $^1$H NMR spectrum at $\delta$ -10.16. This increased in intensity over time at the expense of 8. After 1 h, 3 had been fully consumed and after ca. 2 h, 8 was also no longer present.
We propose that 8 is the hydride boryl complex, Ru(PPh$_3$)$_3$H(Bpin).$^{70}$ Scheme 6 shows a possible pathway to the products from reaction with B$_2$pin$_2$. Initial formation of 8 releases FBpin, which could be trapped by 3 to give 7. When the reaction was monitored quantitatively in the presence of an internal standard, all of the ruthenium was accounted for by the concentrations of 7 and Ru(PPh$_3$)$_4$H$_2$. However, mass balance of the Ru-H ligands requires some additional source of hydride. The presence of adventitious moisture (in solvent, on glassware, or in the sample of B$_2$pin$_2$) most likely accounts for this and also helps to rationalize the degradation of the boryl ligand in 8.$^{71}$ There were only minor differences in the reaction profile upon changing the stoichiometry of the reaction. Thus, with just 0.5 equiv B$_2$pin$_2$, although 3 (unsurprisingly) took longer to be consumed, formation of 7, Ru(PPh$_3$)$_4$H$_2$ and 8 was still observed at early times in the reaction, and 8 ultimately disappeared to leave just 7 and Ru(PPh$_3$)$_4$H$_2$.$^{72}$

Scheme 6. Possible mechanism for the reaction of 3 and B$_2$pin$_2$.

The reaction of 3 with an equimolar amount of HBpin in toluene-$d_8$ gave the toluene analogue of 7 and Ru(PPh$_3$)$_4$H$_2$, but, in this instance, they were accompanied by formation of both the dihydrogen dihydride complex, Ru(PPh$_3$)$_3$(η$_2$-H$_2$)H$_2$$^{73,74}$ and free FBpin (Scheme 7; Figures S28 and S29 in the Supporting Information). The composition
of the reaction mixture changed over 2 days, to ultimately afford only Ru(PPh$_3$)$_4$H$_2$ and
Ru(PPh$_3$)$_3$(η$^2$-H$_2$)H$_2$. However, when an excess of HBpin (5 equiv) was employed, quite
different chemistry was observed (Scheme 7) with formation of the σ-borane dihydride
complex, Ru(PPh$_3$)$_3$(σ-HBpin)H$_2$ (9), along with a minor species discussed further below
(Figures S30-S32 in the Supporting Information). Crystals of 9 suitable for X-ray
diffraction (Figure 2) were obtained upon layering a C$_6$H$_6$ solution of the complex
containing 10 equiv HBpin with pentane.

![Scheme 7. Reactions of 3 with HBpin as a function of stoichiometry.](attachment:image)

Analysis of key structural metrics in comparison to those of Ru(PCy$_3$)$_2$(η$^2$-H$_2$)(σ-
HBPin)H$_2$ support formulation as a σ-borane dihydride rather than hydroborate species.$^{75}$

$^{77}$ Thus, there is a small, but significant, difference between the B1-H2 (1.36(2) Å) and
B1-H1 (1.57(2) Å) distances, consistent with assignment of the former to σ-B-H and the
latter to Ru-H⋯B. The orientation of the Bpin group (i.e. the [O, O]-B-Ru angle) has
been promoted by Sabo-Etienne as being particularly diagnostic of the B-H coordination
mode. Thus, in Ru(PCy$_3$)$_2$(η$^2$-H$_2$)(σ-HBPin)H$_2$, this angle is 170.0°, while the mixed σ-borane/dihydroborate species, Ru(PCy$_3$)$_2$(σ-HBPin)(η$^2$-H$_2$Bpin)H, has a corresponding angle of 171.5° for the borane and 177.5° for the dihydroborate; in 9, the value is 170.05(16)°. The Ru-B distance of 2.1747(16) Å in 9 is also similar to that in Ru(PCy$_3$)$_2$(η$^2$-H$_2$)(σ-HBPin)H$_2$ (2.173(2) Å).

Figure 2. Molecular structure of Ru(PPh$_3$)$_3$(HBPin)H$_2$ (9). Thermal ellipsoids are shown at 30 % probability. Hydrogen atoms, with the exception those attached to Ru and B are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-B(1) 2.1747(16), Ru(1)-P(1) 2.3337(4), Ru(1)-P(2) 2.3885(4), Ru(1)-P(3) 2.3398(4), P(1)-Ru(1)-P(2) 99.278(13), P(1)-Ru(1)-P(3) 152.859(13), P(2)-Ru(1)-P(3) 97.146(13).

Redissolved crystals of 9 gave a $^1$H NMR spectrum comprising of three broad low frequency signals at δ -5.95, -8.03 and -10.52 in a 1:1:1 ratio at 298 K. At 259 K, the two lowest frequency resonances resolved into a triplet of doublets ($^2$J$_{HP}$ = 27.4, 16.6 Hz) and...
a doublet of triplets \( (^{2}J_{\text{HP}} = 58.7, 17.6 \text{ Hz}) \) respectively. The signal at ca. \( \delta \) -6 remained as a singlet, albeit much sharper. Additional low temperature NMR measurements showed that all three resonances (i) were unchanged in the 211 K \(^{1}\text{H}\{^{11}\text{B}\} \) spectrum, but that they collapsed to singlets in the \(^{1}\text{H}\{^{31}\text{P}\} \) spectrum at the same temperature, (ii) were all in exchange (EXSY, 259 K; Figures S32 in the Supporting Information) and (iii) correlated \((^{1}\text{H}-^{31}\text{P} \text{ HMQC, 211 K})\) to a doublet (\( \delta 52.2, \, ^{2}J_{\text{PP}} = 25 \text{ Hz} \)) and a triplet (\( \delta 50.5, \, ^{2}J_{\text{PP}} = 25 \text{ Hz} \))\(^{78}\) in the \(^{31}\text{P}\{^{1}\text{H}\} \) NMR spectrum. The multiplicities of the proton resonances at low temperature, together with the magnitudes of \( J_{\text{HP}} \), allows clear assignment of the signals at room temperature at ca. \( \delta \) -6, -8 and -10.5 to \( \sigma\)-B-H, Ru-H and Ru-H---B respectively. The respective \( T_{1} \) values of 163 (378), 291 (865) and 191 (447) ms (259 K (values in parentheses measured at 211 K), 500 MHz) support these assignments. The \(^{11}\text{B} \) NMR spectrum showed just single broad resonance at \( \delta 21.9 \); in contrast to complexes described by Sabo-Etienne, this signal is on the lower frequency side of that for free HBpin.\(^{76}\)

Proton NMR spectra of redissolved crystalline \( \textbf{9} \) showed the same minor product noted above that is observed in the initial reaction of \( \text{Ru(PPh}_{3})_{4}\text{H}_{2} \) with HBpin. This species displayed a multiplet Ru-H resonance at \( \delta \) -9.49 (\( T_{1} = 195 \) (259 K), 440 (211 K) ms at 500 MHz)\(^{79}\) that correlated to a sharp \(^{31}\text{P} \) singlet at \( \delta 46 \). The identity of this complex remains unclear. Moreover, unless free HBpin was present in solution, the formation of \( \text{Ru(PPh}_{3})_{3}(\eta^{2}\text{-H}_{2})\text{H}_{2} \) was also observed spectroscopically (Figure S33 in the Supporting Information). After 3 weeks in solution, the dihydrogen dihydride complex was the only remaining ruthenium species observable by \(^{1}\text{H} \) NMR spectroscopy.
A preliminary investigation suggested that 3 reacted with catecholborane (5 equiv) in the same way, although less cleanly. The room temperature $^1$H NMR spectrum featured a number of broad low frequency resonances, which upon cooling to 235 K, sharpened to reveal an obvious 1:1:1 set of signals at ca $\delta$ -4.7, -7.9 and -10.0 assignable to Ru(PPh$_3$)$_3$(σ-HBcat)H$_2$. However, there were also quite a significant number of other low frequency signals; therefore, the reaction was not pursued further.

**Reactivity of 3 with silicon reagents.** 3 reacted rapidly with Me$_3$SiCF$_3$ (1 or 10 equiv, toluene or THF, in the absence and presence of CsF) to bring about complete disappearance of the Ru complex in less than 24 h. The presence of Me$_3$SiF, PPh$_3$, and CF$_3$H (Figures S34 and S35 in the Supporting Information), together with the absence of any new Ru containing species, suggested that conversion of 3 to Ru(PPh$_3$)$_3$H(CF$_3$) may have taken place, but was followed by facile decomposition.$^{80}$ This is consistent with the paucity of Ru-CF$_3$ complexes in the literature.$^{81}$ Indeed, all of the examples that are known contain a $\pi$-accepting CO ligand and display a strong susceptibility to undergo $\alpha$-F elimination to yield difluorocarbene complexes.$^{58,82-84}$ The reaction of 3 with Me$_3$SiC$_6$F$_5$ (again over a range of solvents, in different stoichiometries and in the absence/presence of CsF) was much slower than with Me$_3$SiCF$_3$, but again failed to generate any new Ru-C$_6$F$_5$ containing products. Free C$_6$F$_5$H and Ru(PPh$_3$)$_4$H$_2$ were apparent as a result of decomposition (Scheme 8).

Addition of 2 equiv of R$_3$SiH (R= Et, Ph) to C$_6$D$_6$ solutions of 3 generated Ru(PPh$_3$)$_3$(SiR$_3$)H$_3$ (R= Et 10, Ph 11; Scheme 8) in the time of mixing (Figures S36-S39 in the Supporting Information). Both complexes were initially reported over 40 years ago following reaction of Ru(PPh$_3$)$_4$H$_2$ with the appropriate silane,$^{85,86}$ although their
characterization was limited to $^1$H NMR/IR spectroscopy and elemental analysis. X-ray quality crystals of 10 were isolated upon slow evaporation of a THF solution of the complex, while those of the SiPh$_3$ analogue were isolated from benzene/hexane following the generation of 11 by reaction of Ru(PPh$_3$)$_3$H$_2$ and Ph$_3$SiH. The hydride ligands were located and refined without restraints in the molecular structure of 10, whereas in 11, they were located and refined, subject to being equidistant from Ru1 (Figure 3). As noted for other group 8 metal ML$_3$(SiR$_3$)$_3$H complexes$^{87-92}$ there is an approximately tetrahedral arrangement of the SiP$_3$ units with the hydride ligands capping the SiP$_2$ faces.

Scheme 8. Reactions of 3 with silicon reagents.
Figure 3. Molecular structures of Ru(PPh$_3$)$_3$(SiEt$_3$)H$_3$ (10, left) and Ru(PPh$_3$)$_3$(SiPh$_3$)H$_3$ (11, right). Ellipsoids are shown at 30% probability. Hydrogen atoms (with the exception of those bound to Ru, as well as the disordered component of one phenyl ring attached to Si1 in 11) have been omitted for clarity. Selected bond lengths (Å) and angles (°) for 10:

Ru(1)-Si(1) 2.4114(5), Ru(1)-P(1) 2.3969(4), Ru(1)-P(2) 2.4333(5), Ru(1)-P(3) 2.4043(4), P(1)-Ru(1)-P(2) 105.604(16), P(1)-Ru(1)-P(3) 102.854(15), P(1)-Ru(1)-Si(1) 112.757(17).

11: Ru(1)-Si(1) 2.3682(16), Ru(1)-P(2) 2.4288(5), Ru(1)-P(3) 2.4332(6), Ru(1)-P(4) 2.4404(5), P(2)-Ru(1)-P(3) 104.980(18), P(2)-Ru(1)-P(4) 104.597(17), P(2)-Ru(1)-Si(1) 114.49(2).

Differentiating between silane and silyl hydride coordination modes remains the focus of much debate and discussion. The shortest Si···H contact in 10 involves H1C, and at 2.02(2) Å, it is comparable to the values noted in Ru(PMe$_3$)$_3$(SiMe$_3$)H$_3$ (2.13 Å), Ru(PMe$_3$)$_3$(SiMe$_2$CH$_2$SiMe$_3$)H$_3$ (2.00 Å) and Ru(lMe$_4$)$_2$(PPh$_3$)(SiPh$_3$)H$_3$ (2.075 Å).
Å).\textsuperscript{31} respectively. This suggests that 10 is best considered as a silyl trihydride complex which retains some degree of interaction between Si and H\textsubscript{hydride} centres. In line with this, the \( ^2J_{\text{SiH}} \) splitting (23 Hz) lies between 10 and 65 Hz, values proposed as representing the upper limit for M(Si)H and lower limit for M(\( \sigma \)-Si-H) species respectively.\textsuperscript{77} The \( T_1 \) value of 300 ms (258 K, 400 MHz) for the hydride resonance in 10 rules out any non-classical dihydrogen interactions.\textsuperscript{92}

**Summary and Conclusions**

Two very different products, Ru(IMe\textsubscript{4})\textsubscript{2}(PF\textsubscript{2}{C\textsubscript{6}F\textsubscript{5}})(C\textsubscript{6}F\textsubscript{5})H (2) and Ru(PPh\textsubscript{3})\textsubscript{3}HF (3), result from the reactions of the ruthenium dihydride complexes Ru(IMe\textsubscript{4})\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}H\textsubscript{2} and Ru(PPh\textsubscript{3})\textsubscript{4}H\textsubscript{2} with tris(pentafluorophenyl)phosphine (PCF). The complexity of the C-F/P-C bond cleavage and P-F bond formation steps involved in the formation of 2, together with the lack of observable intermediates on the reaction pathway, provide no obvious clues to the mechanism of the reaction, although it seems likely that the high nucleophilicity of the hydride ligands in Ru(IMe\textsubscript{4})\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}H\textsubscript{2} that results from the \textit{trans} H-Ru-H geometry is an important feature of the overall process. The use of varying ratios of Ru(PPh\textsubscript{3})\textsubscript{4}H\textsubscript{2} and PCF, as well as use of the partially fluorinated phosphine P(3,4,5-C\textsubscript{6}F\textsubscript{5}H\textsubscript{2})\textsubscript{3}, provides good evidence that 3 is formed via an intramolecular attack of the Ru-H ligands to bring about hydrodefluorination of the \textit{ortho}-C-F positions of a coordinated PCF ligand. 3 shows features of the well-known heavier halide analogues, particularly, the highly fluxional behavior in solution. In terms of reactivity, the fluoride ligand in 3 is readily displaced by boranes and silanes. Fifty years after Wilkinson’s seminal report of
Ru(PPh$_3$)$_3$HCl$^{43}$ we are delighted to have completed the family of known
Ru(PPh$_3$)$_3$H(halide) complexes, albeit via an unanticipated reaction.

**Experimental**

**General considerations**

All manipulations were carried out using standard Schlenk, high vacuum and
glovebox techniques using dry and degassed solvents. C$_6$D$_6$, C$_6$D$_5$CD$_3$ and THF-$d_8$ were
vacuum transferred from potassium, while CD$_2$Cl$_2$ was distilled from CaH$_2$. NMR spectra
were recorded at 298 K (unless otherwise stated) on Bruker Avance 400 and 500 MHz
NMR spectrometers and referenced as follows: C$_6$D$_6$ ($^1$H, δ 7.15; $^{13}$C, δ 128.0), C$_6$D$_5$CD$_3$
($^1$H, δ 2.09; $^{13}$C, δ 21.3), THF-$d_8$ ($^1$H, δ 3.58), CD$_2$Cl$_2$ ($^1$H, δ 5.32). $^{31}$P{$^1$H} spectra were
referenced externally to 85% H$_3$PO$_4$ (δ 0.0), $^{19}$F spectra 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(IME$_4$)$_2$(PPh$_3$)$_2$H$_2$ (I)$^{32}$ and Ru(PPh$_3$)$_4$H$_2$$^{98}$ were prepared according to literature
methods.

**Ru(IME$_4$)$_2$(PF$_2$(C$_6$F$_5$))(C$_6$F$_3$)H (2)**. Ru(IME$_4$)$_2$(PPh$_3$)$_2$H$_2$ (17 mg, 0.019 mmol)
and PCF (21 mg, 0.039 mmol) were combined with C$_6$H$_6$ (0.5 mL) in a J. Young’s
resealable NMR tube and the solution heated at 50 °C for 24 h. The deep-red solution
was analysed by NMR spectroscopy and shown to contain 2 as the major product. $^1$H
NMR (C$_6$D$_6$, 500 MHz): δ 3.38 (s, 6H, NCH$_3$), 3.27 (s, 6H, NCH$_3$), 1.31 (s, 6H, NCCH$_3$),
1.24 (s, 6H, NCCH$_3$), -29.63 (dt, $^2$J$_{HF}$ = 46.1 Hz, $^3$J$_{HF}$ = 6.2 Hz, 1H, RuH). $^{31}$P{$^1$H} NMR
(C$_6$D$_6$, 202 MHz): δ 161.5 (tm, $^1$J$_{PF}$ = 1126 Hz). $^{19}$F NMR (C$_6$D$_6$, 470 MHz): δ -31.1 (dt,
$^1J_{FP} = 1126$ Hz, $^4J_{FF} = 16$ Hz, $2F$, PF$_2$, -114.5 (br m, $2F$, Ru-o-C$_6$F$_5$), -137.3 (m, $2F$, P-o-C$_6$F$_5$), -154.4 (t, $^3J_{FF} = 21$ Hz, $1F$, P-p-C$_6$F$_5$), 162.7 (m, $2F$, P-m-C$_6$F$_5$), -163.1 (t, $^3J_{FF} = 20$ Hz, Ru-p-C$_6$F$_5$), -163.4 (m, $2F$, Ru-m-C$_6$F$_5$). Selected $^{13}$C($^1$H) NMR (125 MHz, C$_6$D$_6$): $^\bullet$δ 188.3 (d, $^2J_{CP} = 17$ Hz, NCN), 124.3 (s, NCP$_3$), 124.0 (s, NCP$_3$), 8.7 (s, NCP$_3$), 8.0 (s, NCP$_3$). $^*$Signals from C$_6$F$_5$ groups were not assigned.

**Ru(PPh$_3$)$_3$HF (3).** Ru(PPh$_3$)$_4$H$_2$ (300 mg, 0.26 mmol) and P(C$_6$F$_5$)$_3$ (48 mg, 91.1 µmol) were dissolved in C$_6$H$_6$ (2 mL) and stirred at 298 K overnight to afford a deep red solution. This was filtered by cannula and the filtrate layered with pentane to afford 3 as dark red crystals. Yield 203 mg (79%). $^1$H NMR (THF-$d_8$, 500 MHz): δ 7.27 (t, $^3J_{HH} = 7.8$ Hz, 18H, PC$_6$H$_5$), 7.12 (t, $^3J_{HH} = 7.4$ Hz, 9H, PC$_6$H$_5$), 6.94 (t, $^3J_{HH} = 7.6$ Hz, 18H, PC$_6$H$_5$), 22.33 (q, $^2J_{HH} = 28.0$ Hz, 1H, RuH).

**Reaction of 3 with NaBArF$_4$.** Ru(PPh$_3$)$_3$HF (14 mg, 0.015 mmol) was combined with excess NaBArF$_4$ (34 mg, 0.038 mmol) in CD$_2$Cl$_2$ in a J. Young’s resealable NMR tube. $^1$H and $^{31}$P($^1$H) NMR spectra recorded after ca. 30 min showed formation of [Ru(η$^6$-C$_6$H$_5$PPh$_2$)(PPh$_3$)$_2$H][BArF$_4$] $^\bullet$. Diagnostic $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 6.64 (t, $^3J_{HH} = 5.9$ Hz, 1H, C$_6$H$_5$PPh$_2$), 5.08 (t, $^3J_{HH} = 5.7$ Hz, 2H, C$_6$H$_5$PPh$_2$), 4.41 (m, 2H, C$_6$H$_5$PPh$_2$), -8.61 (td, $^2J_{HH} = 38.6$ Hz, $^3J_{HH} = 8.6$ Hz, 1H, RuH). $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$, 162 MHz): δ 49.0 (s), -5.2 (s).

**Reaction of 3 with B$_2$pin$_2$.** C$_6$D$_6$ solutions of Ru(PPh$_3$)$_3$HF (15 mg, 0.017 mmol) and B$_2$pin$_2$ (4 mg, 0.016 mmol), or Ru(PPh$_3$)$_3$HF (16 mg, 0.018 mmol) and B$_2$pin$_2$ (2 mg, 0.008 mmol), were prepared in J. Youngs NMR tubes and the reactions monitored.
by NMR spectroscopy. Spectra indicated the formation of \([\eta^6-\]
\[\text{C}_6\text{D}_6]\text{Ru}(\text{PPh}_3)_2\text{H}[\text{F}_2\text{Bpin}]\ (7): ^1\text{H} \text{NMR (C}_6\text{D}_6, 500 \text{ MHz}): \delta -9.33 \ (t, \ 2J_{\text{HP}} = 36.7 \text{ Hz,} 1\text{H, RuH}); ^{31}\text{P}\{^1\text{H}\} \text{NMR (C}_6\text{D}_6, 202 \text{ MHz, 298 K): } \delta 51.8 \ (s); ^{11}\text{B}\{^1\text{H}\} \text{NMR (C}_6\text{D}_6, 160} \text{ MHz):} \delta 6.7 \ (br\ t, \ 1J_{\text{BF}} = 19 \text{ Hz}); ^{19}\text{F} \text{NMR (C}_6\text{D}_6, 470 \text{ MHz):} \delta 2141 \ (br\ s)). \text{Ru}(\text{PPh}_3)_4\text{H}_2\ (1^1\text{H} \text{NMR (C}_6\text{D}_6, 500 \text{ MHz):} \delta -10.16 \ (m, 2\text{H, RuH}); ^{31}\text{P}\{^1\text{H}\} \text{NMR (C}_6\text{D}_6, 202 \text{ MHz):} \delta 49.3 \ (t, 2J_{\text{PP}} = 14 \text{ Hz,} 41.1 \ (t, 2J_{\text{PP}} = 14 \text{ Hz})) \text{and 8, which is tentatively assigned as}} \text{Ru}(\text{PPh}_3)_3\text{H(Bpin) (}^1\text{H} \text{NMR (C}_6\text{D}_6, 500 \text{ MHz):} \delta -5.50 \ (dt, 2J_{\text{HP}} = 59.9 \text{ Hz,} 2J_{\text{HP}} = 31.6} \text{Hz, 1H, RuH}); ^{31}\text{P}\{^1\text{H}\} \text{NMR (C}_6\text{D}_6, 202 \text{ MHz):} \delta 55.3 \ (d, 1J_{\text{PP}} = 15 \text{ Hz),} 43.7 \ (t, 1J_{\text{PP}} = 15} \text{Hz}). \text{Ru}(\text{PPh}_3)_3(\text{HBpin})\text{H}_2\ (9). \text{A C}_6\text{H}_6 \text{solution (0.5 ml) of 3 (15 mg, 16.5 \mu mol) and}} \text{HBPin (24.0} \mu \text{L, 0.16 mmol) was layered with pentane to afford a small amount of}} \text{crystals of 9 over a period of ca. 2 weeks. Selected} \text{}^1\text{H} \text{NMR (C}_6\text{D}_5\text{CD}_3, 400 \text{ MHz, 259}} \text{K):} \delta 0.77 \ (s, 12\text{H, Bpin}), -5.95 \ (br\ s, 1\text{H, BH}), -8.04 \ (td, 2J_{\text{HP}} = 27.8 \text{ Hz,} 2J_{\text{HP}} = 16.5 \text{Hz,} 1\text{H, RuH}), -10.46 \ (dt, 2J_{\text{HP}} = 59.6, 2J_{\text{HP}} = 17.5 \text{Hz,} 1\text{H, RuH}···\text{B).} ^{31}\text{P}\{^1\text{H}\} \text{NMR (C}_6\text{D}_5\text{CD}_3, 162 \text{ MHz, 259 K):} \delta 52.2 \ (d, 2J_{\text{PP}} = 25.0 \text{ Hz),} 50.4 \ (t, 2J_{\text{PP}} = 25.0 \text{Hz}). ^{11}\text{B} \text{(C}_6\text{D}_5\text{CD}_3, 128} \text{ MHz, 259 K):} \delta 21.9 \ (br\ s). \text{Consistently high %C values precluded}} \text{satisfactory elemental analysis for 9 from being determined (e.g. anal. calcd (found) for}} \text{C}_{60}\text{H}_{59}\text{BO}_2\text{P}_3\text{Ru: C 70.85 (71.50), H 5.85 (5.75)).} \text{Reaction of 3 with Me}_3\text{SiCF}_3. \text{Reactions were conducted at room temperature in}} \text{J. Youngs resealable NMR tubes using (i) 3 (6.6 mg, 0.007 mmol) and Me}_3\text{SiCF}_3 \ (10.7} \mu \text{L, 0.015 mmol) in C}_6\text{D}_5\text{CD}_3 \text{or THF-}d_8 \text{or (ii) 3 (23 mg, 0.025 mmol) and Me}_3\text{SiCF}_3 \ (7.6} \mu \text{L, 0.051 mmol) in C}_6\text{D}_5\text{CD}_3 \text{or THF-}d_8, \text{both in the absence and presence of CsF (2.3 mg, 0.015 mmol). In all cases,} ^1\text{H} \text{and} ^{19}\text{F} \text{NMR spectroscopy showed formation of}
CF$_3$H ($^1$H NMR (C$_6$D$_2$CD$_3$, 500 MHz): $\delta$ 7.23, q, $^2J_{HF} = 80.0$ Hz; $^{19}$F NMR (C$_6$D$_2$CD$_3$, 470 MHz): $\delta$ -79.2, d, $^2J_{FH} = 79.8$ Hz; THF-$d_8$: $^1$H (500 MHz): $\delta$ 6.89, q, $^2J_{HF} = 79.6$ Hz; $^{19}$F, $\delta$ -79.5, d, $^2J_{FH} = 79.6$ Hz) and Me$_3$SiF (C$_6$D$_2$CD$_3$ (470 MHz) $^{19}$F, $\delta$ 2157.9, m; THF-$d_8$: $^{19}$F, $\delta$ 2158.2, m).

**Ru(PPh$_3$)$_3$(SiEt$_3$)H$_3$ (10).** 3 (34 mg, 0.038 mmol) and Et$_3$SiH (12 µL, 0.076 mmol) were shaken vigorously in THF-$d_8$ in a J. Young’s resealable NMR tube for 2 h to give a pale orange solution. Pale yellow crystals of 10 were obtained upon slow evaporation of solvent. These were washed with pentane (3 x 0.5 mL) and dried in vacuo. Yield 13 mg (34%). $^1$H NMR (THF-$d_8$, 400 MHz): $\delta$ 7.19-7.08 (m, 27H, PC$_6$H$_5$), 6.99-6.89 (m, 18H, PC$_6$H$_3$), 0.61 (t, $^3J_{HH} = 7.4$ Hz, 9H, SiCH$_2$C$_3$H$_3$), 0.43 (q, $^3J_{HH} = 7.4$ Hz, 6H, SiCH$_2$C$_3$H$_3$), -10.58 (m, 3H, RuH$_3$; $^1$H-$^{31}$P NMR: s, $^2J_{SiH} = 22.3$ Hz; $T_1 = 300$ ms (258 K, 400 MHz)). $^{31}$P-$^1$H NMR (THF-$d_8$, 162 MHz): $\delta$ 41.8 (s). $^{29}$Si-$^1$H HMBC (THF-$d_8$, 258 K): $\delta$ 3.3 (br s). Anal. calcd (found) for C$_{60}$H$_{63}$P$_3$SiRu: C 71.61 (71.32), H 6.31 (6.66).

**Ru(PPh$_3$)$_3$(SiPh$_3$)H$_3$ (11).** (a) Ph$_3$SiH (2 mg, 0.008 mmol) was added to a C$_6$D$_6$ solution of 3 (4 mg, 0.004 mmol) in a J. Young's resalable NMR tube. $^1$H and $^{31}$P NMR spectroscopy showed complete conversion to 11 within 40 min. (b) 11 was generated on a preparative scale by slow addition of a C$_6$H$_6$ (2 mL) solution of Ph$_3$SiH (34 mg, 0.13 mmol) to a benzene (5 mL) solution of Ru(PPh$_3$)$_4$H$_2$ (100 mg, 0.087 mmol). The reaction mixture was left to stand overnight, after which time the color had changed from pale yellow to colorless. The solution was layered with hexane, which slowly precipitated at colorless crystals of 11 at room temperature (40 mg, 80% yield). Selected $^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta$ -9.37 (m, 3H, RuH$_3$). $^{31}$P-$^1$H NMR (C$_6$D$_6$, 202 MHz): $\delta$ 37.5 (s). Anal. calcd (found) for C$_{72}$H$_{63}$P$_3$SiRu: C 75.17 (75.16), H 6.31 (6.66).
**X-ray crystallography.** Data for compounds 3, 9, 10 and 11 were obtained using an Agilent SuperNova instrument and a Cu-Kα source. These crystallographic experiments were conducted at 150 K, with the exception of that for 10 (for which data were garnered 200 K). All structures were solved using Olex2 and refined using SHELXL. Refinements were uneventful in the main. The only additional points of note include the fact that the asymmetric units in 3 and 9 each housed one molecule of the ruthenium complex and one guest molecule of benzene. The hydride ligands were located in both cases, and while H1 in 3 was refined at a distance of 1.6 Å from Ru1, those in 9 were refined without restraints. In 10, the asymmetric unit was seen to contain one molecule of the complex, and two molecules of THF. The hydrides in the main feature were readily located and refined without restraints. One of the solvent molecules was treated with the Olex2 solvent mask algorithm, as it is heavily disordered. The second solvent entity exhibited disorder of O1 and C6 therein, in a 50:50 ratio. The assignment of the oxygen is somewhat tentative as, ultimately, fractional occupancy atoms O1 and O1a were restrained to having similar anisotropic displacement parameters (ADPs) in the final least-squares, to assist convergence. The asymmetric unit in 11 was seen to comprise one molecule of the complex and three regions of solvent, which amounted to 2.5 molecules of benzene. The hydride ligands in the main feature were located and refined, subject to being equidistant from Ru1. The phenyl ring based on C13 (attached to Si1) was seen to be disordered in equal proportions over two proximate sites and the associated Si–C13/C13A distances were restrained to being similar in the final least-squares. Two of the solvent regions required disorder modelling. In particular, the one total benzene moiety based on C72 was modelled for disorder over two regions in a 50:50
ratio, while that based on C82 was disordered over three overlapped regions in a 40:40:20 ratio. The arising five, fractional occupancy rings in these 2 regions were refined as rigid hexagons, and ADP restraints were also included, to assist convergence. The half molecule of benzene present, at half occupancy (C88–C90) is located proximate to an inversion center which serves to generate the remainder of that entity.

Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1849162-1849165 for 3, 9, 10 and 11 respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk.

Supporting Information Available: Multinuclear NMR spectra for complexes 2-11. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(61) The addition of alkali metal salts, such as CsF, has been shown in some instances to
sharpen and resolve couplings to transition metal fluoride resonances by scavenging of
trace amounts of HF or water that broadens signals as a result of hydrogen-bonding.51c,57
In the case of 3, addition of CsF had no effect on the appearance of the room temperature
19F NMR spectrum recorded in toluene-d8, but in CD2Cl2, the Ru-F resonance sharpened to yield an obviously coupled, but still unresolvable, broad multiplet. In the 19F{1H} NMR spectrum, this became a broadish quartet with 2JFP = 40 Hz. Interestingly, the CsF also impacted on the appearance of the Ru-H signal in CD2Cl2 (there was no effect in toluene); rather than a quartet, a signal of higher multiplicity was now apparent, which became a broadish doublet with 2JHF = 13.1 Hz upon 31P decoupling (see Figure S18 in Supporting Information). Addition of excess PPh3 to each of these sample made no impact upon the appearance of either the 1H or 19F NMR spectra in dichloromethane, but in toluene, a more coupled (albeit still broad) Ru-H signal was apparent in the proton NMR spectrum, while the Ru-F signal tended towards a broad quartet in the 19F{1H} spectrum.

(62) The presence of three 31P NMR signals (δ 62.1 (br dt, 2JPP = 239 Hz, 2Jpp = 18 Hz), 43.8 (dt, 2Jpp = 239 Hz, 2Jpp = 16 Hz), 38.5 (dd, 2Jpp = 18 Hz, 2Jpp = 16 Hz)), together with a second-order Ru-H resonance (almost coincidental with that for Ru(PPh3)4H2) for 4a suggests it is formed upon substitution of P(3,4,5-C6F3H2)3 into an axial site of Ru(PPh3)4H2. 4b showed two multiplet Ru-H signals (δ -8.8 and -10.8) which simplified to a 1:1 ratio of two doublets (2JHH = 8.4 Hz) upon 31P decoupling, suggestive of an equatorially substituted isomer. 5, which was was only ever observed at very low concentrations, is tentatively assigned as the bis-equatorially substituted complex, Ru(PPh3)2{P(3,4,5-C6F3H2)3}2H2, on the basis that it grows in intensity with time in both of the 9:1 and 6:1 reactions (Figures S20-S22 in the Supporting Information).

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(65) A direct reaction in which F/H exchange takes place between I and Ru(PPh$_3$)$_4$H$_2$ without any need to make the difluoride species II cannot be ruled out.


(70) Ru(PC$_3$)$_2$(η$^2$-C$_2$H$_4$)H(Bpin) exhibits a relatively similar hydride chemical shift of δ -5.77. Caballero, A.; Sabo-Etienne, S. Ruthenium-Catalyzed Hydroboration and Dehydrogentaive Borylation of Linear and Cyclic Alkenes with Pinacolborane. *Organometallics* **2007**, 26, 1191-1195.
(71) In line with this, as \( \textit{8} \) degrades, we observe the formation of a new \( ^{11}\text{B} \) NMR signal at ca. \( \delta \) 22, consistent with the formation of \((\text{Bpin})_2\text{O}\). Bontemps, S.; Vendier, L.; Sabo-Etienne, S. \textit{Angew. Chem. Int. Ed.} \textbf{2012}, \textit{51}, 1671-1674

(72) Hexane precipitation from a benzene solution of \( \textit{7} \) and \( \text{Ru}(\text{PPh}_3)_4\text{H}_2 \) allowed separation of the two components. NMR spectra of the isolated colorless precipitate of \( \textit{7} \) redissolved in \( \text{CD}_2\text{Cl}_2 \) showed the same \( \delta \)-9.08 triplet hydride resonance for the cation, but now the \([\text{F}_2\text{Bpin}]^-\) anion appeared in the \( ^{11}\text{B}\{^1\text{H}\} \) NMR spectrum as a very sharp triplet \( (J_{\text{BF}} = 20.8 \text{ Hz}) \) at \( \delta \)-5.1 and as a 1:1:1:1 quartet with the same coupling at \( \delta \)-144.4. Over a period of 10 days in solution, \([\text{F}_2\text{Bpin}]^-\) appeared to convert into a second, unknown anion, which showed a sharp quartet boron signal at \( \delta \)-0.5 with \( J_{\text{BF}} = 9.6 \text{ Hz} \), the corresponding 1:1:1:1 quartet being at \( \delta \)-146.3 in the \(^{19}\text{F} \) NMR spectrum.


(78) Both phosphorus resonances appeared as broad singlets at 298 K.

(79) This signal was in a ca. 1:1:1:1 ratio with the three low frequency resonances of 8.

(80) $^1$H/$^{19}$F NMR monitoring of a cold (233 K) 1:2 mixture of 3:TMSCF$_3$ showed signals for just the two initial reagents up to 298 K, at which point, CF$_3$H began to appear.


For Table of Contents Use Only

C–F Bond Activation of P(C₆F₅)₃ By Ruthenium Dihydride Complexes: Isolation and Reactivity of the ‘Missing’ Ru(PPh₃)₃H(halide) Complex, Ru(PPh₃)₃HF

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P(C₆F₅)₃ undergoes C–F and P–C activation, as well as P–F bond formation, with the N-heterocyclic carbene complex, Ru(IMe₄)₂(PPh₃)₂H₂, to generate the unusual PF₂(C₆F₅) complex, Ru(IMe₄)₂(PF₂{C₆F₅})(C₆F₅)H, whereas the reaction with Ru(PPh₃)₄H₂ leads to C–F activation and C–H formation to yield Ru(PPh₃)₃HF.