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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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6 **C–F Bond Activation of P(C₆F₅)₃ By Ruthenium Dihydride Complexes: Isolation**
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8 **and Reactivity of the ‘Missing’ Ru(PPh₃)₃H(halide) Complex, Ru(PPh₃)₃HF**
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13 Mateusz K. Cybulski, Caroline J. E. Davies, John P. Lowe, Mary F. Mahon and Michael

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20
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22

23
24 **Abstract**

25
26 The major product of the reaction between Ru(IME₄)₂(PPh₃)₂H₂ (**1**; IME₄ = 1,3,4,5-
27 tetramethylimidazol-2-ylidene) and P(C₆F₅)₃ (PCF) is the 5-coordinate complex
28
29 Ru(IME₄)₂(PF₂{C₆F₅})(C₆F₅)H **2**, which is formed via a complex series of C–F/P–C bond
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31 cleavage and P–F bond formation steps. In contrast, hydrodefluorination of all six *ortho*
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33 C–F bonds in PCF occurs with Ru(PPh₃)₄H₂ to afford Ru(PPh₃)₃HF **3**. NaBAR^F₄
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35 abstracted the fluoride ligand in **3** to give [Ru({η⁶-C₆H₅})PPh₂](PPh₃)₂H][BAR^F₄], while
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37 B₂pin₂ reacted with **3** in C₆D₆ to yield a mixture of [Ru({η⁶-C₆D₆})(PPh₃)₂H]⁺ and
38
39 Ru(PPh₃)₄H₂. Treatment of **3** with HBpin (5 equiv) and HSiR₃ (R = Et, Ph; 2 equiv)
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41 afforded Ru(PPh₃)₃(σ-HBpin)H₂ and Ru(PPh₃)₃(SiR₃)₃H₃ respectively. No stable
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43 substitution products were generated when **3** was reacted with Me₃SiX (X = CF₃, C₆F₅).
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Introduction

Transition metal hydride complexes have proven to be valuable for effecting the cleavage of carbon-fluorine bonds.¹⁻¹¹ In many cases, the precise mechanism(s) underpinning the C–F activation chemistry remain to be fully established.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,^{19,20} or, participate in a more active manner, for example, by undergoing insertion of fluorinated alkenes,^{21,22} or by acting as nucleophiles to displace fluoride from C–F bonds in hydrodefluorination (HDF) reactions.^{9,23-27}

In the last few years, we have reported that the *trans*-dihydride N-heterocyclic carbene (NHC) complexes Ru(NHC)₂(PPh₃)₂H₂ and Ru(NHC)₄H₂ (NHC = IMe₄, IEt₂Me₂, IMe₂)²⁸ exhibit the latter type of reactivity in the catalytic HDF of aromatic fluorocarbons.²⁹⁻³¹ In the course of a more general study on the reactivity of the mixed NHC/phosphine complex Ru(IMe₄)₂(PPh₃)₂H₂ (**1**, Scheme 1), we observed that both P(C₆D₅)₃ and P(*p*-C₆H₄Me)₃ readily displaced one or both of the PPh₃ ligands at room temperature.^{32,33} In contrast, the chelating phosphines Ph₂P(CH₂)₂PPh₂ (dppe), Ph₂P(CH₂)₃PPh₂ (dppp) and Ph₂PCH₂PPh₂ (dppm) could only be substituted into **1** at elevated temperatures.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(C₆F₅)₃ (abbreviated as PCF). While the chemistry of PCF (as well as its derivatives) with transition metal centers has been probed quite

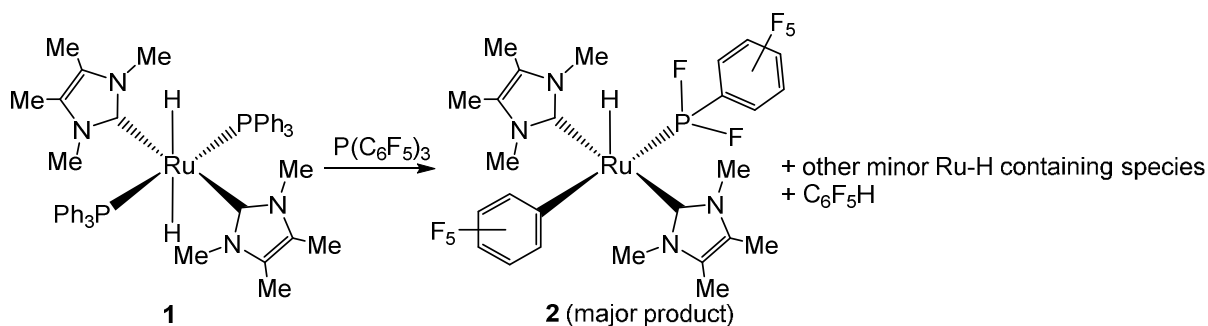
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3 extensively, predominantly with catalytic applications in mind,³⁴⁻³⁸ there are a small
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5 number of reports which show that PCF (or derivatives thereof) are susceptible to C–F
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7 activation by nucleophilic ligands on metal centers.³⁹⁻⁴² To the best of our knowledge,
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9 these nucleophilic ligands have not included hydrides.
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12 Herein, we report that PCF undergoes a complex series of C–F/P–C bond
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14 cleavage and P–F bond formation processes with **1** to yield the unusual PF₂(C₆F₅)
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16 complex, Ru(IMe₄)₂(PF₂{C₆F₅})(C₆F₅)H (**2**). In contrast, hydrodefluorination of all six
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18 *ortho*-C-F bonds takes place with the tetrakis(triphenylphosphine) ruthenium dihydride
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20 complex, Ru(PPh₃)₄H₂, to yield Ru(PPh₃)₃HF (**3**), the last of the well-known family of
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22 Ru(PPh₃)₃H(halide) complexes to be isolated.⁴³
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29 Results and Discussion

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31 **Synthesis and Characterization of Ru(IMe₄)₂(PF₂{C₆F₅})(C₆F₅)H (**2**).** The reaction
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33 of a C₆D₆ solution of **1** with 5 equiv PCF resulted in the loss of the Ru-H resonance in the
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35 ¹H NMR spectrum of **1** (δ - 6.54) over the course of ca. 24 h at room temperature to give
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37 one major metal hydride containing product **2** (the yield of **2** was ca. 70% determined by
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39 integration of all Ru-H signals in the ¹H NMR spectrum,), which appeared as a doublet of
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41 triplets signal at δ -29.62. This was characterized as the unusual 5-coordinate complex,
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43 Ru(IMe₄)₂(PF₂{C₆F₅})(C₆F₅)H, (Scheme 1) on the basis of 1- and 2-D NMR experiments
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45 using the wealth of spin ½ nuclei in the molecule (Figures S1-S7 in the Supporting
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47 Information). Thus, the ¹H NMR spectrum showed four methyl resonances in a ratio of
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49 6:6:6:6 to 1 for the Ru-H signal, confirming the presence of two IMe₄ ligands and a
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51 single hydride. The low frequency of the Ru-H resonance was consistent with the hydride
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being *trans* to a vacant coordination site, while the magnitude of the coupling constants (${}^2J_{\text{HP}} = 46.1 \text{ Hz}$, ${}^3J_{\text{HF}} = 6.1 \text{ Hz}$) placed it *cis* to both the phosphine and ruthenium coordinated C_6F_5 ligands. The extremely unusual difluoro(pentafluorophenyl)phosphine $\text{PF}_2(\text{C}_6\text{F}_5)$,⁴⁴⁻⁴⁶ which is, to the best of our knowledge, only known as a ligand in a single transition metal complex,⁴⁷ 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 $>1100 \text{ Hz}$.⁴⁸ The ${}^{19}\text{F}$ 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 ${}^{19}\text{F}$ COSY to originate from coupling to the two F atoms at the *ortho*-positions of the P-bound C_6F_5 group. The ${}^{19}\text{F}$ 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**

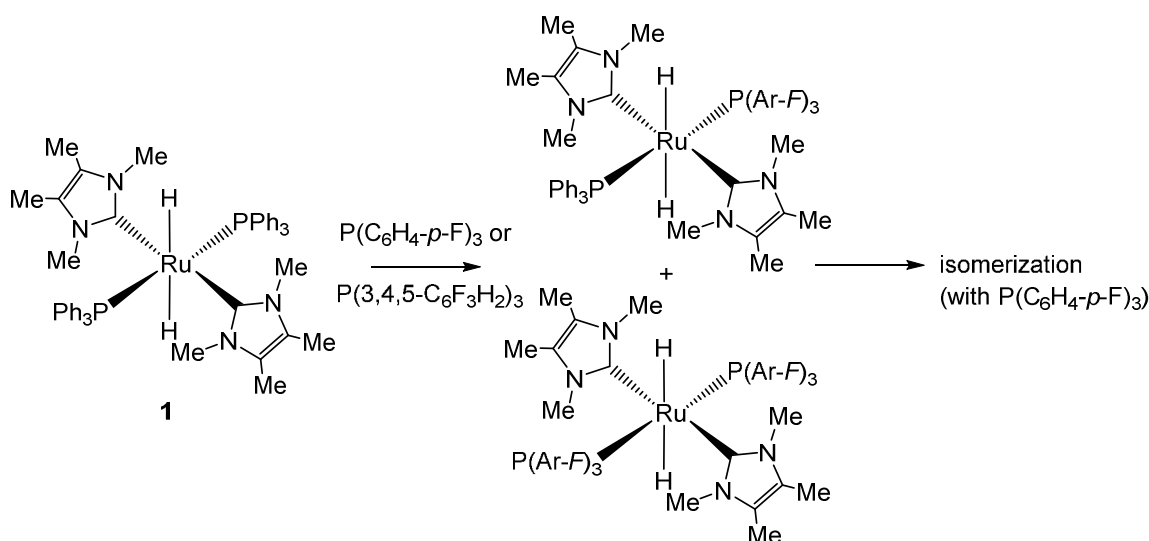
Given the unexpected structure of **2**, **1** was reacted with PCF under a range of conditions in an attempt to detect any reaction intermediates. A 1:1 mixture of **1** and PCF resulted in only incomplete conversion to **2** even after standing for 3 weeks at room temperature (after this duration, **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 C₆F₅H. The ³¹P NMR spectrum of the reaction residue showed signals for **2**, free PPh₃ 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 CH₂Cl₂ or CHCl₃) or CO/isocyanide trapped derivative also met with failure. It is worth noting that in all of these reactions, ³¹P/¹⁹F NMR spectra showed that the PF₂(C₆F₅) ligand remained intact.

Reactivity of 1 with Other Fluorinated Phosphines. The presence of P(C₆F₅) groups appear to be mandatory for the bond activation steps described above. Neither P(C₆H₄-*p*-F)₃ nor P(3,4,5-C₆F₃H₂)₃³⁵ exhibited reactivity comparable to that of PCF with **1** (Figures S9 and S10 in the Supporting Information). Thus, addition of 2 equiv of P(C₆H₄-*p*-F)₃ to a C₆D₆ solution of **1** resulted in the slow (3 days) formation of two new triplet hydride resonances at slightly lower frequency (δ -6.71 and δ -6.89, both with ²J_{HP} = 20.6 Hz) from that of **1**, which we propose arises from the substitution of one or two PPh₃ ligands by the fluorinated phosphine (Scheme 2). Over a prolonged period (ca. 3 weeks), further hydride signals appeared between ca. δ -8.3 and -9.1 and ca. δ -11.2 and -11.5. The similarity of these chemical shifts to those reported previously for isomers of **1**,³² suggests that the initial mono- and bis-P(C₆H₄-*p*-F)₃ containing products also undergo isomerization over longer times.

The reaction between **1** and $P(3,4,5\text{-C}_6\text{F}_3\text{H}_2)_3$ led to rapid (1 h) and complete conversion to a single new species that exhibited a triplet hydride resonance at δ -6.79 ($^2J_{\text{HP}} = 20.9$ Hz). Over an interval of weeks, this was slowly replaced by a new triplet Ru-H signal at δ -7.13 ($^2J_{\text{HP}} = 21.1$ Hz). Following from the reactivity of $P(\text{C}_6\text{H}_4\text{-}p\text{-F})_3$ above, these most likely represent mono- and bis- $P(3,4,5\text{-C}_6\text{F}_3\text{H}_2)_3$ substitution products. No isomerization was seen in this case at longer times.



Scheme 2. Substitution chemistry of **1** with $P(\text{C}_6\text{H}_4\text{-}p\text{-F})_3$ and $P(3,4,5\text{-C}_6\text{F}_3\text{H}_2)_3$

Synthesis and Characterization of $\text{Ru}(\text{PPh}_3)_3\text{HF}$ (3**).** The complex series of C-F and P-C bond cleavage steps, together with P-F and C-H bond formation,⁴⁹⁻⁵³ necessary to generate $\text{Ru-PF}_2(\text{C}_6\text{F}_5)$ and $\text{Ru-C}_6\text{F}_5$ groups and $\text{C}_6\text{F}_5\text{H}$, 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 $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ 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

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3 temperature. ^{31}P NMR spectroscopy revealed the presence of unreacted PCF and
4 complete loss of ruthenium starting material, but no obvious new product resonances.
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6 However, the low frequency region of the ^1H NMR spectrum did show the formation of a
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8 quartet resonance at δ -22.33, attributable to $\text{Ru}(\text{PPh}_3)_3\text{HF}$ (**3**, Scheme 3). The identity of
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10 **3**, which was isolated in ca. 80% yield as an air-sensitive red-orange solid, was
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12 established unequivocally by X-ray diffraction as shown in Figure 1. The $\text{P}_{\text{ax}}\text{-Ru-P}_{\text{ax}}$
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14 angle of $153.023(17)^\circ$ is similar to that found in the chloride, bromide and iodide
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16 derivatives.^{54,55} In contrast, the $\text{P}_{\text{eq}}\text{-Ru-X}$ angle ranged from a value of $133.41(5)^\circ$ in **3** to
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18 $116.428(13)^\circ$ in $\text{Ru}(\text{PPh}_3)_3\text{HBr}$.⁵⁵ The Ru-F bond length ($2.0652(12)$ Å) was comparable
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20 to values found in a range of other five- and six-coordinate ruthenium(II) fluoride
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22 complexes, such as *cis*- $\text{Ru}(\text{dppp})_2\text{F}_2$ ($2.056(3)/2.069(3)$ Å),⁵⁶ $\text{Ru}(\text{PPh}_3)_3(\text{CO})\text{HF}$
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24 ($2.0986(15)$ Å),⁵⁷ $\text{Ru}(\text{P}^t\text{Bu}_2\text{Me})_2(\text{CO})(=\text{CF}_2)\text{HF}$ ($2.065(1)$ Å)⁵⁸ and
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26 $\text{Ru}(\text{Ind})(\text{SIMes})(\text{P}(\text{O}^i\text{Pr})_3)_2\text{F}_2$ ($2.017(3)/2.035(4)$; Ind = 3-phenylindenylidene; SIMes =
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28 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene).⁵⁹
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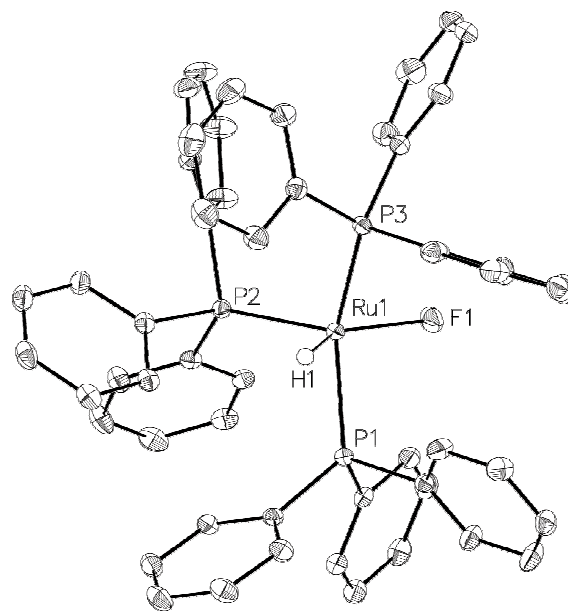
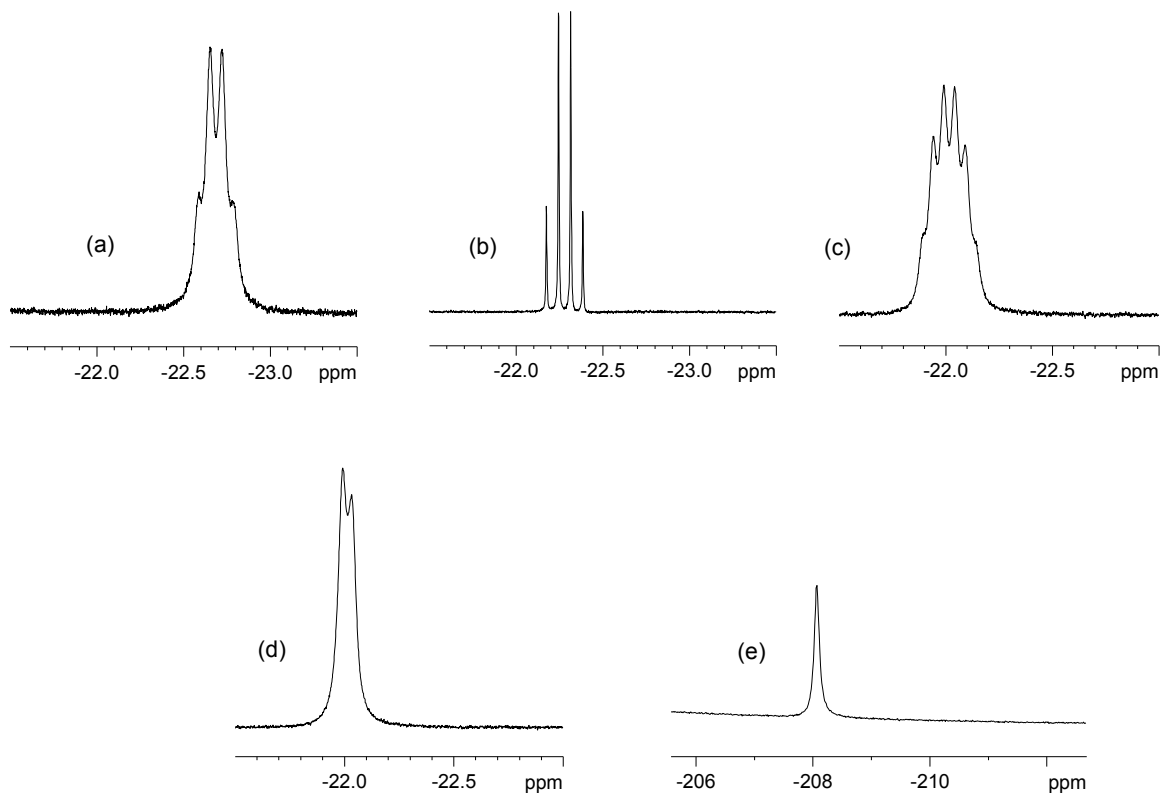


Figure 1. Molecular structure of Ru(PPh₃)₃HF (**3**). Ellipsoids are shown at 30 % probability. Hydrogen atoms, with the exception of the Ru-H ligand are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-F(1) 2.0652(12), Ru(1)-P(1) 2.3423(4), Ru(1)-P(2) 2.1996(5), Ru(1)-P(3) 2.3201(5), 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(PPh₃)₃F,^{51,d,e} in that they each represent the last member of the well-known families of Ru(PPh₃)₃H(halide) and Rh(PPh₃)₃(halide) complexes to be prepared. The solution fluxionality of Ru(PPh₃)₃HX (X = Cl, Br, I)^{43,60} was apparent in **3**. As the complex showed reasonable solubility across a range of solvents, variable temperature ¹H, ³¹P and ¹⁹F 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 ²J_{HP} = 28.0 Hz in C₆D₅CD₃, THF-*d*₈ and CD₂Cl₂ (Figure 2a,b). This became a broad multiplet in CD₂Cl₂ 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 C₆D₅CD₃ at 199 K (Figure 2c); this simplified to a doublet with a ²J_{HF} splitting of 16.0 Hz with ³¹P decoupling (Figure 2d). While we were unable to observe any ³¹P resonance in any solvent at room temperature, the 199 K ³¹P {¹H} NMR spectrum recorded in C₆D₅CD₃ consisted of a 1:2 ratio of a doublet of triplets (δ 91; ²J_{PF} = 84 Hz, ²J_{PP} = 23 Hz) and a broadened triplet (δ 41; *J* ≈ 21 Hz) (ESI). In all solvents across the temperature range 298-199 K, the Ru-F

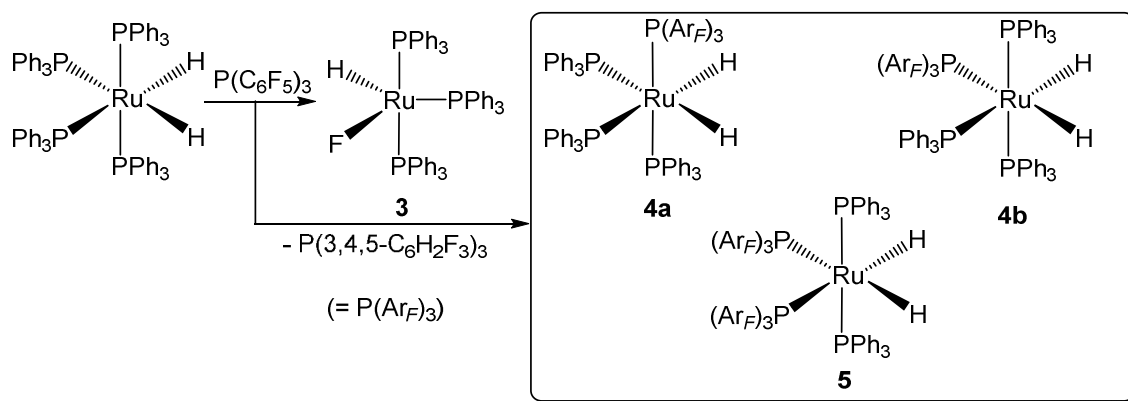
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3 resonance only ever appeared as a broad singlet, ranging in chemical shift from δ -190 to
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5 δ -205 (Figure 2e).⁶¹
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36 **Figure 2.** ¹H NMR spectrum (400 MHz) of Ru-H resonance of Ru(PPh₃)₃HF **3** in (a)
37 CD₂Cl₂ (298 K), (b) THF-*d*₈ (298 K), (c) C₆D₅CD₃ (199 K), (d) ¹H{³¹P} NMR spectrum
38 in C₆D₅CD₃ at 199 K. (e) ¹⁹F NMR spectrum (376 MHz) of Ru-F resonance of **3** in THF-
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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(PPh₃)₄H₂:PCF by NMR spectroscopy. With sub-stoichiometric ratios of Ru:PCF (i.e. 6:1 and 9:1), we

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3 were able to observe three minor ruthenium containing products (**4a**, **4b** and **5**) in
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5 addition to **3** (Scheme 3 and Figure S19 in the Supporting Information). Each of these
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7 species showed two ^{19}F NMR signals (a doublet of doublets and a triplet of triplets,
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9 relative ratio of 2:1) at much higher frequency than the fluoride resonance of **3**, in a
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11 region of the spectrum associated with fluoroaromatic groups. A subsequent reaction of
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13 $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ with $\text{P}(3,4,5\text{-C}_6\text{F}_3\text{H}_2)_3$ afforded the same three species, but no **3** (Figure S20
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15 in the Supporting Information).⁶² All four Ru species (**3**, **4a**, **4b** and **5**) can be rationalized
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17 by *ortho*-hydrodefluorination of PCF. The regioselectivity is consistent with a pathway
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19 involving substitution of PCF into $\text{Ru}(\text{PPh}_3)_4\text{H}_2$, followed by intramolecular nucleophilic
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21 attack by Ru-H at an *ortho*-C-F position. An analogous intramolecular attack of a Pt-
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23 OMe ligand has been proposed to account for the reaction of the *ortho*-C-F bonds in
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25 $[\text{Pt}(\text{PPh}_2\text{C}_6\text{F}_5)_2(\text{THF})\text{Me}]$ with NaOMe to give $\text{Pt}(\text{PPh}_2\{2,6\text{-}$
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27 $(\text{OMe})_2\text{C}_6\text{F}_3\})_2(\text{OMe})\text{Me}$.^{39,40} Very recently, Kayaki and co-workers⁶³ have reported that
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29 Ir-H complexes bearing fluorinated phenylsulfonyl-1,2-diphenylethylenediamine ligands
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31 undergo HDF at the *ortho*-C-F position to generate iridacycle products.
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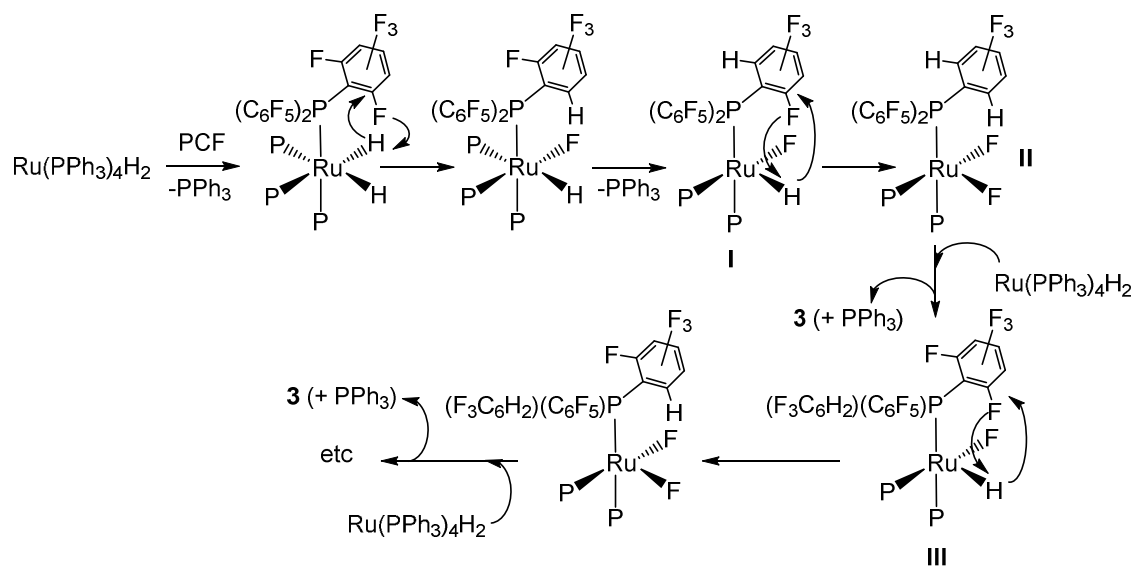


53 **Scheme 3.** Synthesis of **3** and proposed structures of **4a**, **4b** and **5**.⁵⁹

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The formation of the $P(3,4,5-C_6F_3H_2)_3$ complexes **4a/4b** and **5**, together with the lack of any signals for bound or free partially hydrodefluorinated phosphines (e.g. $P(3,4,5-C_6F_3H_2)(C_6F_5)_2$) 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- PR_3 bond allows all four *ortho*-fluorines to be placed very readily in close proximity to the reactive Pt-OMe group.

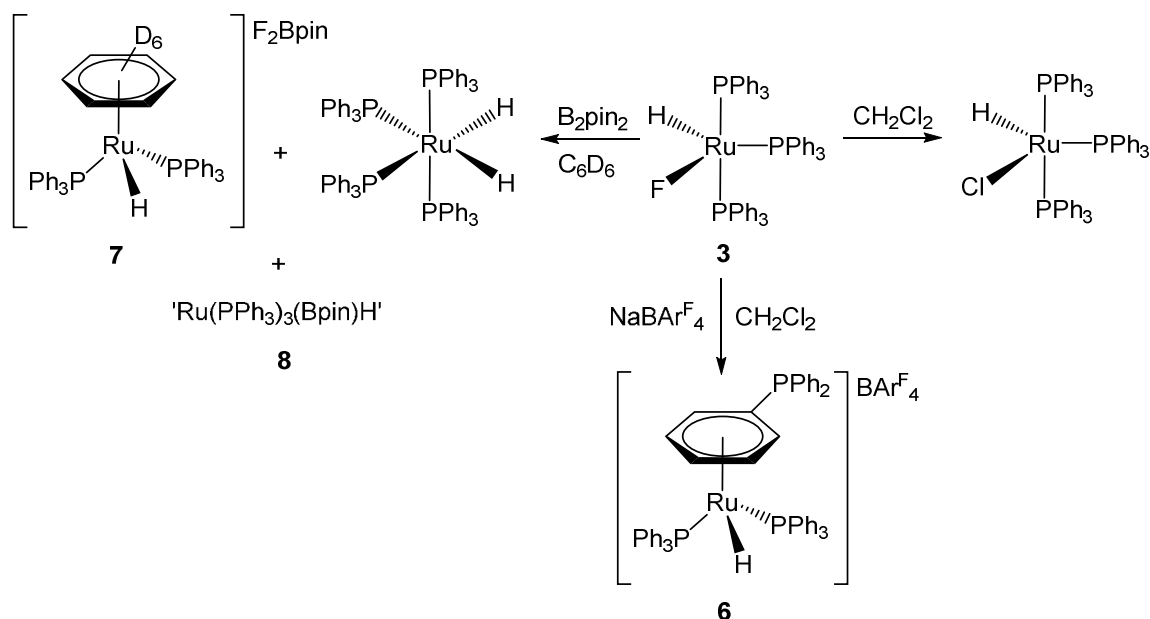
Scheme 4 shows a possible pathway to **3**. Initial intramolecular HDF at an *ortho*-C-F bond would yield the substituted hydride fluoride complex **I** (assumed to 5-coordinate like **3**), which could then bring about a second HDF step with formation of the difluoride complex **II**.^{64,65} Comproportionation of **II** and $Ru(PPh_3)_4H_2$ (known for $[Ru(PPh_3)_2I_2]_2$ and $Ru(PPh_3)_4H_2$)⁵⁵ would then generate a reactive Ru-H ligand in **III**, allowing HDF to propagate until $P(3,4,5-C_6F_3H_2)_3$ is formed.



Scheme 4. Possible pathway for the intramolecular HDF of PCF to form **3**.

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3 **Reactivity of Ru(PPh₃)₃HF.** As for other Ru(PPh₃)₃HX complexes, **3** was stable in
4 solution under inert conditions, but degraded rapidly upon exposure to air to afford green-
5 black solutions. It proved to be relatively thermally robust in solution, with traces of new
6 signals only apparent by ¹H NMR spectroscopy upon heating at 70 °C in THF-*d*₈ for ca. 7
7 h. Dissolution of **3** in CD₂Cl₂ afforded traces of Ru(PPh₃)₃HCl within hours, although
8 complete conversion required days at room temperature (Figure S23 in the Supporting
9 Information). Ru(PPh₃)₃HBr was formed in time of mixing upon addition of C₆H₅CH₂Br
10 to **3**, whereas reaction with bromodecane only occurred over several days. No reaction
11 took place with PhI either at room temperature or at 70 °C.
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24 Treatment of **3** with NaBAR^F₄ in CH₂Cl₂ (Scheme 5) resulted in an almost near
25 instantaneous disappearance of the starting material and formation of the [BAR^F₄] salt **6** of
26 the known cation [Ru(η⁶-C₆H₅PPh₂)(PPh₃)₂H]⁺, which was identified through the
27 presence of a triplet of doublets Ru-H hydride resonance at δ -8.61, and two ³¹P signals at
28 δ 49.0 and -5.2 (Figure S24 in the Supporting Information).^{66,67}
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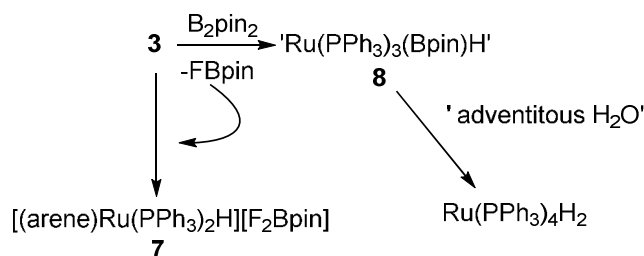


Scheme 5. Reactivity of **3**.

Reactivity of 3 with B₂pin₂ and HBpin. A ¹H NMR spectrum of a C₆D₆ solution of **3** recorded 5 min after the addition of 1 equiv B₂pin₂ 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 δ -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, [(η⁶-arene)Ru(PPh₃)₂H]⁺ (δ -9.33; t, ²J_{HP} = 36.7 Hz),⁶⁸ in which the arene is presumably C₆D₆. The presence of a broad ¹¹B{¹H} NMR triplet resonance (¹J_{BF} = ca. 19 Hz) at δ 6.7, along with a broad ¹⁹F resonance at ca. δ -141, indicates that [F₂Bpin]⁻ is the accompanying anion.⁶⁹

Within 30 min, an additional second-order hydride signal for Ru(PPh₃)₄H₂ appeared in the ¹H NMR spectrum at δ -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.

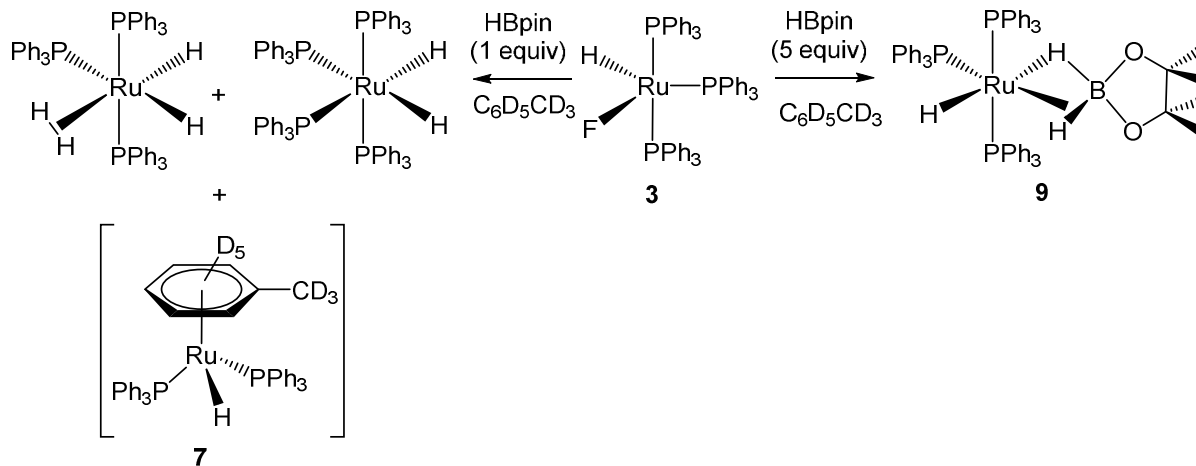
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3 We propose that **8** is the hydride boryl complex, $\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Bpin})$.⁷⁰ Scheme 6 shows
4 a possible pathway to the products from reaction with B_2pin_2 . Initial formation of **8**
5 releases FBpin, which could be trapped by **3** to give **7**. When the reaction was monitored
6 quantitatively in the presence of an internal standard, all of the ruthenium was accounted
7 for by the concentrations of **7** and $\text{Ru}(\text{PPh}_3)_4\text{H}_2$. However, mass balance of the Ru-H
8 ligands requires some additional source of hydride. The presence of adventitious
9 moisture (in solvent, on glassware, or in the sample of B_2pin_2) most likely accounts for
10 this and also helps to rationalize the degradation of the boryl ligand in **8**.⁷¹ There were
11 only minor differences in the reaction profile upon changing the stoichiometry of the
12 reaction. Thus, with just 0.5 equiv B_2pin_2 , although **3** (unsurprisingly) took longer to be
13 consumed, formation of **7**, $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ and **8** was still observed at early times in the
14 reaction, and **8** ultimately disappeared to leave just **7** and $\text{Ru}(\text{PPh}_3)_4\text{H}_2$.⁷²
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Scheme 6. Possible mechanism for the reaction of **3** and B_2pin_2 .

The reaction of **3** with an equimolar amount of HBpin in toluene- d_8 gave the toluene analogue of **7** and $\text{Ru}(\text{PPh}_3)_4\text{H}_2$, but, in this instance, they were accompanied by formation of both the dihydrogen dihydride complex, $\text{Ru}(\text{PPh}_3)_3(\eta^2\text{-H}_2)\text{H}_2$ ^{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 $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ and $\text{Ru}(\text{PPh}_3)_3(\eta^2\text{-H}_2)\text{H}_2$. 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, $\text{Ru}(\text{PPh}_3)_3(\sigma\text{-HBpin})\text{H}_2$ (**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_6H_6 solution of the complex containing 10 equiv HBpin with pentane.



Scheme 7. Reactions of **3** with HBpin as a function of stoichiometry.

Analysis of key structural metrics in comparison to those of $\text{Ru}(\text{PCy}_3)_2(\eta^2\text{-H}_2)(\sigma\text{-HBpin})\text{H}_2$ 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 \cdots 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.⁷⁶ Thus, in $\text{Ru}(\text{PCy}_3)_2(\eta^2\text{-H}_2)(\sigma\text{-HBPin})\text{H}_2$, this angle is 170.0° , while the mixed σ -borane/dihydroborate species, $\text{Ru}(\text{PCy}_3)_2(\sigma\text{-HBPin})(\eta^2\text{-H}_2\text{Bpin})\text{H}$, has a corresponding angle of 171.5° for the borane and 177.5° for the dihydroborate; in **9**, the value is $170.05(16)^\circ$. The Ru-B distance of $2.1747(16)$ Å in **9** is also similar to that in $\text{Ru}(\text{PCy}_3)_2(\eta^2\text{-H}_2)(\sigma\text{-HBPin})\text{H}_2$ ($2.173(2)$ Å).

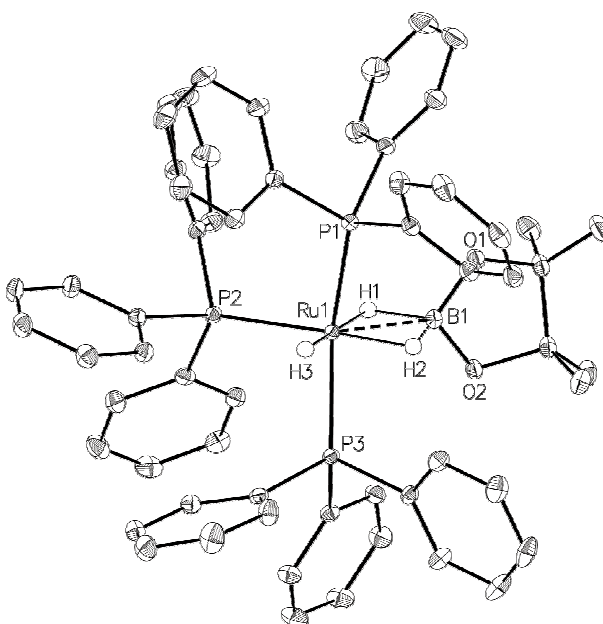


Figure 2. Molecular structure of $\text{Ru}(\text{PPh}_3)_3(\text{HBPin})\text{H}_2$ (**9**). Thermal ellipsoids are shown at 30 % probability. Hydrogen atoms, with the exception those attached to Ru and B are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ru(1)-B(1) $2.1747(16)$, 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 ^1H 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 ($^2J_{\text{HP}} = 27.4, 16.6$ Hz) and

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3 a doublet of triplets ($^2J_{\text{HP}} = 58.7, 17.6$ Hz) respectively. The signal at ca. $\delta -6$ remained as
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5 a singlet, albeit much sharper. Additional low temperature NMR measurements showed
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7 that all three resonances (i) were unchanged in the 211 K $^1\text{H}\{^{11}\text{B}\}$ spectrum, but that they
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9 collapsed to singlets in the $^1\text{H}\{^{31}\text{P}\}$ spectrum at the same temperature, (ii) were all in
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11 exchange (EXSY, 259 K; Figures S32 in the Supporting Information) and (iii) correlated
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13 (^1H - ^{31}P HMQC, 211 K) to a doublet ($\delta 52.2, ^2J_{\text{PP}} = 25$ Hz) and a triplet ($\delta 50.5, ^2J_{\text{PP}} = 25$
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15 Hz)⁷⁸ in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The multiplicities of the proton resonances at low
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17 temperature, together with the magnitudes of J_{HP} , allows clear assignment of the signals
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19 at room temperature at ca. $\delta -6, -8$ and -10.5 to σ -B-H, Ru-H and Ru-H \cdots B respectively.
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21 The respective T_1 values of 163 (378), 291 (865) and 191 (447) ms (259 K (values in
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23 parentheses measured at 211 K), 500 MHz) support these assignments. The ^{11}B NMR
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25 spectrum showed just single broad resonance at $\delta 21.9$; in contrast to complexes
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27 described by Sabo-Etienne, this signal is on the lower frequency side of that for free
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29 HBpin.⁷⁶
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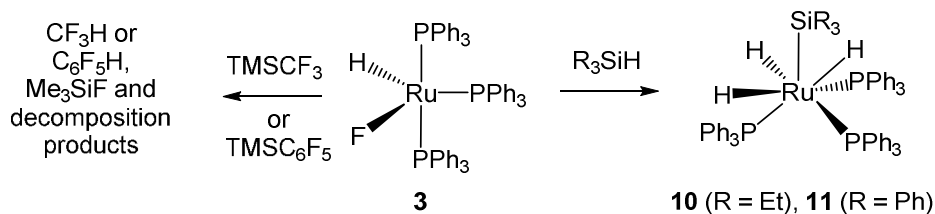
36 Proton NMR spectra of redissolved crystalline **9** showed the same minor product
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38 noted above that is observed in the initial reaction of $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ with HBpin. This
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40 species displayed a multiplet Ru-H resonance at $\delta -9.49$ ($T_1 = 195$ (259 K), 440 (211 K)
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42 ms at 500 MHz)⁷⁹ that correlated to a sharp ^{31}P singlet at $\delta 46$. The identity of this
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44 complex remains unclear. Moreover, unless free HBpin was present in solution, the
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46 formation of $\text{Ru}(\text{PPh}_3)_3(\eta^2\text{-H}_2)\text{H}_2$ was also observed spectroscopically (Figure S33 in the
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48 Supporting Information). After 3 weeks in solution, the dihydrogen dihydride complex
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50 was the only remaining ruthenium species observable by ^1H NMR spectroscopy.
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3 A preliminary investigation suggested that **3** reacted with catecholborane (5
4 equiv) in the same way, although less cleanly. The room temperature ^1H NMR spectrum
5 featured a number of broad low frequency resonances, which upon cooling to 235 K,
6 sharpened to reveal an obvious 1:1:1 set of signals at ca δ -4.7, -7.9 and -10.0 assignable
7 to $\text{Ru}(\text{PPh}_3)_3(\sigma\text{-HBcat})\text{H}_2$. However, there were also quite a significant number of other
8 low frequency signals; therefore, the reaction was not pursued further.
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17 **Reactivity of **3** with silicon reagents.** **3** reacted rapidly with Me_3SiCF_3 (1 or 10
18 equiv, toluene or THF, in the absence and presence of CsF) to bring about complete
19 disappearance of the Ru complex in less than 24 h. The presence of Me_3SiF , PPh_3 , and
20 CF_3H (Figures S34 and S35 in the Supporting Information), together with the absence of
21 any new Ru containing species, suggested that conversion of **3** to $\text{Ru}(\text{PPh}_3)_3\text{H}(\text{CF}_3)$ may
22 have taken place, but was followed by facile decomposition.⁸⁰ This is consistent with the
23 paucity of Ru- CF_3 complexes in the literature.⁸¹ Indeed, all of the examples that are
24 known contain a π -accepting CO ligand and display a strong susceptibility to undergo α -
25 F elimination to yield difluorocarbene complexes.^{58, 82-84} The reaction of **3** with
26 $\text{Me}_3\text{SiC}_6\text{F}_5$ (again over a range of solvents, in different stoichiometries and in the
27 absence/presence of CsF) was much slower than with Me_3SiCF_3 , but again failed to
28 generate any new Ru- C_6F_5 containing products. Free $\text{C}_6\text{F}_5\text{H}$ and $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ were
29 apparent as a result of decomposition (Scheme 8).
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47 Addition of 2 equiv of R_3SiH (R= Et, Ph) to C_6D_6 solutions of **3** generated
48 $\text{Ru}(\text{PPh}_3)_3(\text{SiR}_3)\text{H}_3$ (R= Et **10**, Ph **11**; Scheme 8) in the time of mixing (Figures S36-S39
49 in the Supporting Information). Both complexes were initially reported over 40 years ago
50 following reaction of $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ with the appropriate silane,^{85,86} although their
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3 characterization was limited to ^1H NMR/IR spectroscopy and elemental analysis. X-ray
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5 quality crystals of **10** were isolated upon slow evaporation of a THF solution of the
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7 complex, while those of the SiPh_3 analogue were isolated from benzene/hexane following
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9 the generation of **11** by reaction of $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ and Ph_3SiH . The hydride ligands were
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11 located and refined without restraints in the molecular structure of **10**, whereas in **11**,
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13 they were located and refined, subject to being equidistant from Ru1 (Figure 3). As noted
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15 for other group 8 metal $\text{ML}_3(\text{SiR}_3)\text{H}_3$ complexes⁸⁷⁻⁹² there is an approximately tetrahedral
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17 arrangement of the SiP_3 units with the hydride ligands capping the SiP_2 faces.
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34 **Scheme 8.** Reactions of **3** with silicon reagents.
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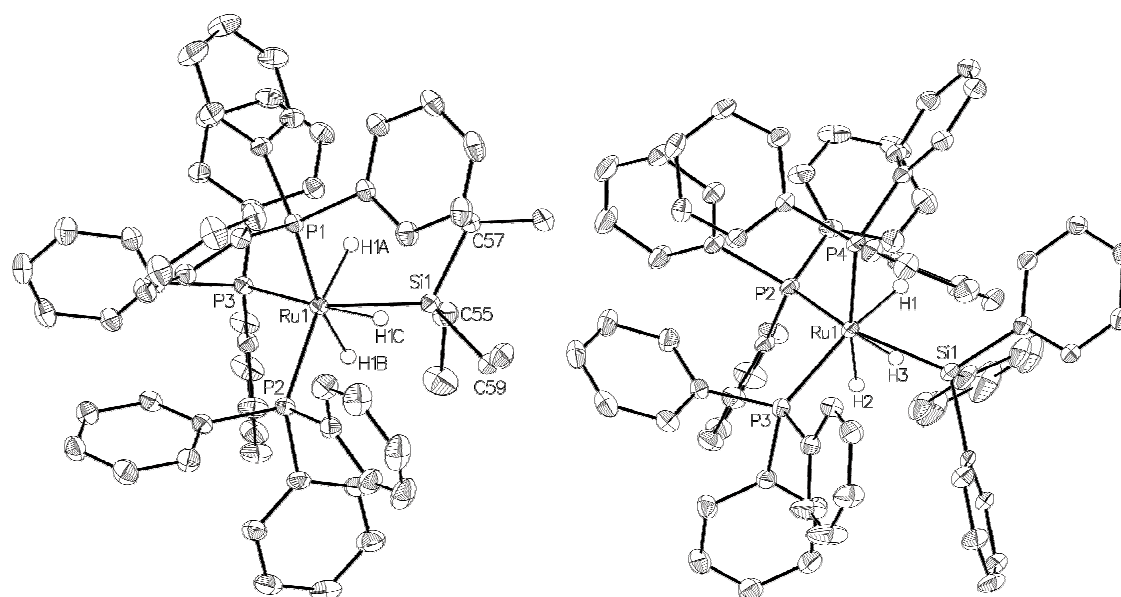


Figure 3. Molecular structures of $\text{Ru}(\text{PPh}_3)_3(\text{SiEt}_3)\text{H}_3$ (**10**, left) and $\text{Ru}(\text{PPh}_3)_3(\text{SiPh}_3)\text{H}_3$ (**11**, right). Ellipsoids are shown at 30 % probability. Hydrogen atoms (with the exception of those bound to Ru, as well as the disordered 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.^{77,93-95} The shortest Si...H contact in **10** involves H1C, and at 2.02(2) Å, it is comparable to the values noted in $\text{Ru}(\text{PMe}_3)_3(\text{SiMe}_3)\text{H}_3$ (2.13 Å),⁹⁶ $\text{Ru}(\text{PMe}_3)_3(\text{SiMe}_2\text{CH}_2\text{SiMe}_3)\text{H}_3$ (2.00 Å)⁹⁷ and $\text{Ru}(\text{IME}_4)_2(\text{PPh}_3)(\text{SiPh}_3)\text{H}_3$ (2.075

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3 Å).³¹ respectively. This suggests that **10** is best considered as a silyl trihydride complex
4 which retains some degree of interaction between Si and H_{hydride} centres. In line with this,
5 the ²J_{SiH} splitting (23 Hz) lies between 10 and 65 Hz, values proposed as representing the
6 upper limit for M(Si)H and lower limit for M(σ-Si-H) species respectively.⁷⁷ The T₁
7 value of 300 ms (258 K, 400 MHz) for the hydride resonance in **10** rules out any non-
8 classical dihydrogen interactions.⁹²

19 Summary and Conclusions

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22 Two very different products, Ru(Ime₄)₂(PF₂{C₆F₅})(C₆F₅)H (**2**) and Ru(PPh₃)₃HF
23 (**3**), result from the reactions of the ruthenium dihydride complexes Ru(Ime₄)₂(PPh₃)₂H₂
24 and Ru(PPh₃)₄H₂ with tris(pentafluorophenyl)phosphine (PCF). The complexity of the C-
25 F/P-C bond cleavage and P-F bond formation steps involved in the formation of **2**,
26 together with the lack of observable intermediates on the reaction pathway, provide no
27 obvious clues to the mechanism of the reaction, although it seems likely that the high
28 nucleophilicity of the hydride ligands in Ru(Ime₄)₂(PPh₃)₂H₂ that results from the *trans*
29 H-Ru-H geometry is an important feature of the overall process. The use of varying ratios
30 of Ru(PPh₃)₄H₂ and PCF, as well as use of the partially fluorinated phosphine P(3,4,5-
31 C₆F₃H₂)₃, provides good evidence that **3** is formed via an intramolecular attack of the Ru-
32 H ligands to bring about hydrodefluorination of the *ortho*-C-F positions of a coordinated
33 PCF ligand. **3** shows features of the well-known heavier halide analogues, particularly,
34 the highly fluxional behavior in solution. In terms of reactivity, the fluoride ligand in **3** is
35 readily displaced by boranes and silanes. Fifty years after Wilkinson's seminal report of
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Ru(PPh₃)₃HCl,⁴³ we are delighted to have completed the family of known Ru(PPh₃)₃H(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. C₆D₆, C₆D₅CD₃ and THF-*d*₈ were vacuum transferred from potassium, while CD₂Cl₂ was distilled from CaH₂. NMR spectra were recorded at 298 K (unless otherwise stated) on Bruker Avance 400 and 500 MHz NMR spectrometers and referenced as follows: C₆D₆ (¹H, δ 7.15; ¹³C, δ 128.0), C₆D₅CD₃ (¹H, δ 2.09; ¹³C, δ 21.3), THF-*d*₈ (¹H, δ 3.58), CD₂Cl₂ (¹H, δ 5.32). ³¹P{¹H} spectra were referenced externally to 85% H₃PO₄ (δ 0.0), ¹⁹F spectra externally to CFCl₃ (δ 0.0). PPh₃ resonances are excluded unless they could be assigned unequivocally. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon.

Ru(IME₄)₂(PPh₃)₂H₂ (**1**)³² and Ru(PPh₃)₄H₂⁹⁸ were prepared according to literature methods.

Ru(IME₄)₂(PF₂{C₆F₅})(C₆F₅)H (2**).** Ru(IME₄)₂(PPh₃)₂H₂ (17 mg, 0.019 mmol) and PCF (21 mg, 0.039 mmol) were combined with C₆H₆ (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. ¹H NMR (C₆D₆, 500 MHz): δ 3.38 (s, 6H, NCH₃), 3.27 (s, 6H, NCH₃), 1.31 (s, 6H, NCCH₃), 1.24 (s, 6H, NCCH₃), -29.63 (dt, ²J_{HP} = 46.1 Hz, ³J_{HF} = 6.2 Hz, 1H, RuH). ³¹P{¹H} NMR (C₆D₆, 202 MHz): δ 161.5 (tm, ¹J_{PF} = 1126 Hz). ¹⁹F NMR (C₆D₆, 470 MHz): δ -31.1 (dt,

$^1J_{\text{FP}} = 1126$ Hz, $^4J_{\text{FF}} = 16$ Hz, 2F, PF₂), -114.5 (br m, 2F, Ru-*o*-C₆F₅), -137.3 (m, 2F, P-*o*-C₆F₅), -154.4 (t, $^3J_{\text{FF}} = 21$ Hz, 1F, P-*p*-C₆F₅), 162.7 (m, 2F, P-*m*-C₆F₅), -163.1 (t, $^3J_{\text{FF}} = 20$ Hz, Ru-*p*-C₆F₅), -163.4 (m, 2F, Ru-*m*-C₆F₅). Selected $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C₆D₆): * δ 188.3 (d, $^2J_{\text{CP}} = 17$ Hz, NCN), 124.3 (s, NCCH₃), 124.0 (s, NCCH₃), 34.5 (s, NCH₃), 33.4 (s, NCH₃), 8.7 (s, (s, NCCH₃), 8.0 (s, NCCH₃). *Signals from C₆F₅ groups were not assigned.

Ru(PPh₃)₃HF (3). Ru(PPh₃)₄H₂ (300 mg, 0.26 mmol) and P(C₆F₅)₃ (48 mg, 91.1 μmol) were dissolved in C₆H₆ (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%). ^1H NMR (THF-*d*₈, 500 MHz): δ 7.27 (t, $J_{\text{HP}} = 7.8$ Hz, 18H, PC₆H₅), 7.12 (t, $J_{\text{HP}} = 7.4$ Hz, 9H, PC₆H₅), 6.94 (t, $J_{\text{HP}} = 7.6$ Hz, 18H, PC₆H₅), -22.33 (q, $^2J_{\text{HP}} = 28.0$ Hz, 1H, RuH). ^{19}F NMR (THF-*d*₈, 376 MHz): δ -208.1 Anal. calcd (found) for C₅₄H₄₆P₃Ru: C 71.42 (71.80), H 5.11 (5.24).

Reaction of 3 with NaBAR^F₄. Ru(PPh₃)₃HF (14 mg, 0.015 mmol) was combined with excess NaBAR^F₄ (34 mg, 0.038 mmol) in CD₂Cl₂ in a J. Young's resealable NMR tube. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded after ca. 30 min showed formation of [Ru(η^6 -C₆H₅PPh₂)(PPh₃)₂H][BAR^F₄] **6**. Diagnostic ^1H NMR (400 MHz, CD₂Cl₂): δ 6.64 (t, $^3J_{\text{HH}} = 5.9$ Hz, 1H, C₆H₅PPh₂), 5.08 (t, $^3J_{\text{HH}} = 5.7$ Hz, 2H, C₆H₅PPh₂), 4.41 (m, 2H, C₆H₅PPh₂), -8.61 (td, $^2J_{\text{HP}} = 38.6$ Hz, $^3J_{\text{HP}} = 8.6$ Hz, 1H, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, 162 MHz): δ . 49.0 (s), -5.2 (s).

Reaction of 3 with B₂pin₂. C₆D₆ solutions of Ru(PPh₃)₃HF (15 mg, 0.017 mmol) and B₂pin₂ (4 mg, 0.016 mmol), or Ru(PPh₃)₃HF (16 mg, 0.018 mmol) and B₂pin₂ (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**): ^1H NMR (C_6D_6 , 500 MHz): δ -9.33 (t, $^2J_{\text{HP}} = 36.7$ Hz, 1H, RuH); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz, 298 K): δ 51.8 (s); $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 160 MHz): δ 6.7 (br t, $^1J_{\text{BF}} = 19$ Hz); ^{19}F NMR (C_6D_6 , 470 MHz): δ -141 (br s), $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ (^1H NMR (C_6D_6 , 500 MHz): δ -10.16 (m, 2H, RuH); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz): δ 49.3 (t, $^2J_{\text{PP}} = 14$ Hz), 41.1 (t, $^2J_{\text{PP}} = 14$ Hz)) and **8**, which is tentatively assigned as $\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Bpin})$ (^1H NMR (C_6D_6 , 500 MHz): δ -5.50 (dt, $^2J_{\text{HP}} = 59.9$ Hz, $^2J_{\text{HP}} = 31.6$ Hz, 1H, RuH); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz): δ 55.3 (d, $J_{\text{PP}} = 15$ Hz), 43.7 (t, $J_{\text{PP}} = 15$ Hz)).

$\text{Ru}(\text{PPh}_3)_3(\text{HBpin})\text{H}_2$ (9**)**. A C_6H_6 solution (0.5 ml) of **3** (15 mg, 16.5 μmol) and HBPin (24.0 μL , 0.16 mmol) was layered with pentane to afford a small amount of crystals of **9** over a period of ca. 2 weeks. Selected ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 400 MHz, 259 K): δ 0.77 (s, 12H, Bpin), -5.95 (br s, 1H, BH), -8.04 (td, $^2J_{\text{HP}} = 27.8$ Hz, $^2J_{\text{HP}} = 16.5$ Hz, 1H, RuH), -10.46 (dt, $^2J_{\text{HP}} = 59.6$, $^2J_{\text{HP}} = 17.5$ Hz, 1H, RuH...B). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 162 MHz, 259 K): δ 52.2 (d, $^2J_{\text{PP}} = 25.0$ Hz), 50.4 (t, $^2J_{\text{PP}} = 25.0$ Hz). ^{11}B ($\text{C}_6\text{D}_5\text{CD}_3$, 128 MHz, 259 K): δ 21.9 (br s). Consistently high %C values precluded 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)).

Reaction of **3 with Me_3SiCF_3** . Reactions were conducted at room temperature in J. Youngs resealable NMR tubes using (i) **3** (6.6 mg, 0.007 mmol) and Me_3SiCF_3 (10.7 μL , 0.015 mmol) in $\text{C}_6\text{D}_5\text{CD}_3$ or THF- d_8 or (ii) **3** (23 mg, 0.025 mmol) and Me_3SiCF_3 (7.6 μL , 0.051 mmol) in $\text{C}_6\text{D}_5\text{CD}_3$ or THF- d_8 , both in the absence and presence of CsF (2.3 mg, 0.015 mmol). In all cases, ^1H and ^{19}F NMR spectroscopy showed formation of

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3 CF₃H (¹H NMR (C₆D₅CD₃, 500 MHz): δ 7.23, q, ²J_{HF} = 80.0 Hz; ¹⁹F NMR (C₆D₅CD₃,
4 470 MHz): δ -79.2, d, ²J_{FH} = 79.8 Hz; THF-*d*₈: ¹H (500 MHz): δ 6.89, q, ²J_{HF} = 79.6 Hz;
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6 ¹⁹F, δ -79.5, d, ²J_{FH} = 79.6 Hz) and Me₃SiF (C₆D₅CD₃ (470 MHz) ¹⁹F, δ -157.9, m; THF-
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8 *d*₈: ¹⁹F, δ -158.2, m).
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12 **Ru(PPh₃)₃(SiEt₃)H₃ (10). 3** (34 mg, 0.038 mmol) and Et₃SiH (12 μL, 0.076
13 mmol) were shaken vigorously in THF-*d*₈ in a J. Young's resealable NMR tube for 2 h to
14 give a pale orange solution. Pale yellow crystals of **10** were obtained upon slow
15 evaporation of solvent. These were washed with pentane (3 x 0.5 mL) and dried in vacuo.
16 Yield 13 mg (34%). ¹H NMR (THF-*d*₈, 400 MHz): δ 7.19-7.08 (m, 27H, PC₆H₅), 6.99-
17 6.89 (m, 18H, PC₆H₅), 0.61 (t, ³J_{HH} = 7.4 Hz, 9H, SiCH₂CH₃), 0.43 (q, ³J_{HH} = 7.4 Hz, 6H,
18 SiCH₂CH₃), -10.58 (m, 3H, RuH₃; ¹H{³¹P} NMR: s, ²J_{SiH} = 22.3 Hz; T₁ = 300 ms (258 K,
19 400 MHz)). ³¹P{¹H} NMR (THF-*d*₈, 162 MHz): δ 41.8 (s). ²⁹Si-¹H HMBC (THF-*d*₈, 258
20 K): δ 3.3 (br s). Anal. calcd (found) for C₆₀H₆₃P₃SiRu: C 71.61 (71.32), H 6.31 (6.66).
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33 **Ru(PPh₃)₃(SiPh₃)H₃ (11).** (a) Ph₃SiH (2 mg, 0.008 mmol) was added to a C₆D₆
34 solution of **3** (4 mg, 0.004 mmol) in a J. Youngs resalable NMR tube. ¹H and ³¹P NMR
35 spectroscopy showed complete conversion to **11** within 40 min. (b) **11** was generated on
36 a preparative scale by slow addition of a C₆H₆ (2 mL) solution of Ph₃SiH (34 mg, 0.13
37 mmol) to a benzene (5 mL) solution of Ru(PPh₃)₄H₂ (100 mg, 0.087 mmol). The reaction
38 mixture was left to stand overnight, after which time the color had changed from pale
39 yellow to colorless. The solution was layered with hexane, which slowly precipitated at
40 colorless crystals of **11** at room temperature (40 mg, 80% yield). Selected ¹H NMR
41 (C₆D₆, 500 MHz): δ -9.37 (m, 3H, RuH₃). ³¹P{¹H} NMR (C₆D₆, 202 MHz): δ 37.5 (s).
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43 Anal. calcd (found) for C₇₂H₆₃P₃SiRu: C 75.17 (75.16), H 5.52 (5.82).
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X-ray crystallography. Data for compounds **3**, **9**, **10** and **11** were obtained using an Agilent SuperNova instrument and a Cu-K α 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 Olex2⁹⁹ and refined using SHELXL.¹⁰⁰ 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

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3 ratio, while that based on C82 was disordered over three overlapped regions in a 40:40:20
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5 ratio. The arising five, fractional occupancy rings in these 2 regions were refined as rigid
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7 hexagons, and ADP restraints were also included, to assist convergence. The half
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9 molecule of benzene present, at half occupancy (C88–C90) is located proximate to an
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11 inversion center which serves to generate the remainder of that entity.
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15 Crystallographic data for all compounds have been deposited with the Cambridge
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17 Crystallographic Data Centre as supplementary publications CCDC 1849162-1849165
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19 for **3**, **9**, **10** and **11** respectively. Copies of these data can be obtained free of charge on
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21 application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033,
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23 e-mail: deposit@ccdc.cam.ac.uk.
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27 **Supporting Information Available:** Multinuclear NMR spectra for complexes **2-**
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29 **11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.
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35 **Notes**

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 $[\text{Pt}(\text{SRf})_2(1,2\text{-C}_6\text{F}_4(\text{SRf})\text{-}(\text{PPh}_2))]$ and Chiral $[\text{Pt}(\text{SRf})_2(1,2\text{-C}_6\text{F}_4(\text{SRf})(\text{PPh}(\text{C}_6\text{F}_5)))]$.
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51 trace amounts of HF or water that broadens signals as a result of hydrogen-bonding.^{51e,57}
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54 In the case of **3**, addition of CsF had no effect on the appearance of the room temperature
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¹⁹F NMR spectrum recorded in toluene-*d*₈, 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 ²J_{FP} = 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 ²J_{HF} = 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, ²J_{PP} = 239 Hz, ²J_{PP} = 18 Hz), 43.8 (dt, ²J_{PP} = 239 Hz, ²J_{PP} = 16 Hz), 38.5 (dd, ²J_{PP} = 18 Hz, ²J_{PP} = 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 (²J_{HH} = 8.4 Hz) upon ³¹P decoupling, suggestive of an equatorially substituted isomer. **5**, which 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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10 unsuccessful, with unreacted **3** remaining in all cases.

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11 separation of the two components. NMR spectra of the isolated colorless precipitate of **7**
12 redissolved in CD_2Cl_2 showed the same δ -9.08 triplet hydride resonance for the cation ,
13 but now the $[\text{F}_2\text{Bpin}]^-$ anion appeared in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum as a very sharp
14 triplet ($^1J_{\text{BF}} = 20.8$ Hz) at δ -5.1 and as a 1:1:1:1 quartet with the same coupling at δ -
15 144.4. Over a period of 10 days in solution, $[\text{F}_2\text{Bpin}]^-$ appeared to convert into a second,
16 unknown anion, which showed a sharp quartet boron signal at δ -0.5 with $J_{\text{BF}} = 9.6$ Hz,
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3 *For Table of Contents Use Only*
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6 C–F Bond Activation of P(C₆F₅)₃ By Ruthenium Dihydride Complexes: Isolation and
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8 Reactivity of the ‘Missing’ Ru(PPh₃)₃H(halide) Complex, Ru(PPh₃)₃HF
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13 Mateusz K. Cybulski, Caroline J. E. Davies, John P. Lowe, Mary F. Mahon and Michael
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15 K. Whittlesey
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19 P(C₆F₅)₃ undergoes C–F and P–C activation, as well as P–F bond formation, with the N-
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21 heterocyclic carbene complex, Ru(IMe₄)₂(PPh₃)₂H₂, to generate the unusual PF₂(C₆F₅)
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23 complex, Ru(IMe₄)₂(PF₂{C₆F₅})(C₆F₅)H, whereas the reaction with Ru(PPh₃)₄H₂ leads to
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25 C–F activation and C–H formation to yield Ru(PPh₃)₃HF.
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