

# Photochemical intermolecular C–H and C–F insertion of rhodium into pentafluoroanisole to generate a metallacycle; conversion to a cyclic carbene complex

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**Irradiation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{PMe}_3)(\text{C}_2\text{H}_4)]$  in pentafluoroanisole generates the metallacycle  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)\text{RhCH}_2\text{OC}_6\text{F}_4]$ ; reaction of this complex with 1 equiv. of  $\text{Ph}_3\text{C}^+\text{PF}_6^-$  at 220 K generates  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)\text{Rh}=\text{C}(\text{H})\text{OC}_6\text{F}_4]\text{PF}_6^-$ .**

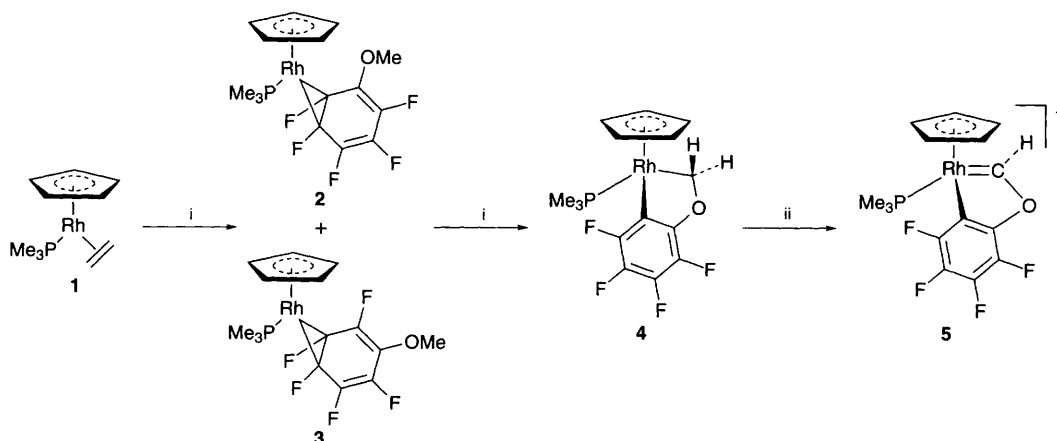
Hexafluorobenzene can form a variety of products upon reaction with transition-metal complexes:<sup>1</sup> coordination as  $\text{M}(\eta^2\text{-C}_6\text{F}_6)$  or  $\text{M}(\eta^4\text{-C}_6\text{F}_6)$  has been observed from the photoreactions of half-sandwich rhodium and iridium ethene complexes.<sup>2,3</sup> Sandwich complexes containing  $\text{M}(\eta^4\text{-C}_6\text{F}_6)$  ( $\text{M} = \text{Ru}, \text{Os}$ ) and  $\text{M}(\eta^6\text{-C}_6\text{F}_6)$  ( $\text{M} = \text{Mo}, \text{W}$ ) units have been isolated by metal-vapour synthesis.<sup>4</sup> In a few cases, cleavage of a C–F bond has been observed. Thermal and photochemical routes to C–F activation products,  $\text{M}(\text{C}_6\text{F}_5)\text{F}$  ( $\text{M} = \text{Rh}, \text{Pt}$ ) have been reported.<sup>2,5</sup> Metal dihydride complexes react to give products of the form  $\text{M}(\text{C}_6\text{F}_5)\text{H}$ , via the elimination of HF.<sup>2,6</sup> In a more complex but related reaction, photolysis of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3]$  formed  $[(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{Re}(\text{CO})_2(\text{C}_6\text{F}_5)]$ .<sup>7</sup> Catalytic conversion of  $\text{C}_6\text{F}_6$  to  $\text{C}_6\text{F}_5\text{H}$  has been achieved with a rhodium complex.<sup>8</sup>

If these reactions are to find application, it is important to understand the effect of substituents on the fluoroarene. In this paper, we show that pentafluoroanisole,  $\text{C}_6\text{F}_5\text{OMe}$ , undergoes intermolecular C–H and C–F bond activation when reacted photochemically with  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{PMe}_3)(\text{C}_2\text{H}_4)]$  **1**. The photochemistry of **1** has already been explored extensively at room temperature; it reacts with benzene to yield  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{H}_5)\text{H}]$  via a short-lived  $\eta^2$ -arene complex.<sup>9</sup> Photolysis with  $\text{C}_6\text{F}_6$  results in the isolation of a stable  $\eta^2$ -hexafluorobenzene complex,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{F}_6)]$ .<sup>2</sup> Importantly, **1** has not been observed previously to undergo either C–F or aliphatic C–H activation at ambient temperature, although such processes have been observed in low-temperature matrices.<sup>2,10</sup>

The irradiation of **1** in pentafluoroanisole ( $\lambda > 325 \text{ nm}$ , 6 d) generates the metallacycle,  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)\text{RhCH}_2\text{OC}_6\text{F}_4]$  **4**, quantitatively, as an isolable air-stable orange solid which was characterised by multinuclear NMR spectroscopy.<sup>†</sup> The  $^1\text{H}$  NMR spectrum shows the  $\text{CH}_2$  group to be diastereotopic and the two resonances appear at  $\delta$  6.82 as a triplet of doublets and  $\delta$  5.24 as a doublet of doublet of doublets, with very different P–H coupling constants. This very low-field chemical shift compares with shifts of  $\delta$  5.67 (ddd) and 5.17 (ddd) for the diastereotopic protons of the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_2\text{OMe})\text{I}]$  and similar shifts for a related iridium complex.<sup>11,12</sup> The  $^{13}\text{C}$  DEPT spectrum of **4** confirms the group as  $\text{CH}_2$  (at  $\delta$  69.2) with a doublet of doublets coupling ( $^1J_{\text{CRh}}$  29.2  $^2J_{\text{CP}}$  14.3 Hz); the value of  $J_{\text{CH}}$  is determined as 151 Hz from the fully coupled  $^{13}\text{C}$  spectrum.

Spectra measured after short irradiation times show the presence of the metallacycle **4** and two isomers of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{PMe}_3)(\eta^2\text{-C}_6\text{F}_5\text{OMe})]$ , **2** and **3**, which show characteristic doublet of quartet (due to equal coupling to rhodium and two fluorine nuclei) resonances for the  $\text{PMe}_3$  group in the  $^1\text{H}$  NMR spectrum and doublet of doublet of doublet resonances in the  $^{31}\text{P}$  NMR spectrum, indicative of coupling to rhodium and two inequivalent fluorine nuclei. The identity of the isomers was further confirmed by a  $^{19}\text{F}$ – $^{19}\text{F}$  COSY NMR spectrum. An  $(\eta^2\text{-fluoroarene})$  complex has been observed previously as an intermediate which undergoes secondary photolysis to yield a C–F activation product upon photolysis of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_2\text{H}_4)]$  in  $\text{C}_6\text{F}_6$ .<sup>13</sup> The two isomers **2** and **3** must be converted to **4** photochemically and not thermally since no change is observed on heating a mixture of **2**, **3** and **4** to 80 °C for 46 h.

Loss of HF and the formation of the five-membered ring presumably provide the driving forces for the formation of **4** (Scheme 1). Previously we have shown that the reactive fragment  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{PMe}_3)$  is capable of inserting into a C–F



**Scheme 1** Reagents and conditions:  $h\nu$ ,  $\text{C}_6\text{F}_5\text{OMe}$ ,  $-\text{HF}$ ,  $-\text{C}_2\text{H}_4$ , 300 K; ii,  $\text{CD}_2\text{Cl}_2$ ,  $\text{Ph}_3\text{C}^+\text{PF}_6^-$ , 220 K

bond of  $\text{C}_6\text{F}_6$  and the C–H bonds of methane<sup>10</sup> at low temperature in matrices. These reactions do not yield stable products at room temperature in solution. In remarkable contrast, the reaction with  $\text{C}_6\text{F}_5\text{OMe}$  involves both insertion into a C–F bond and insertion into a C–H bond of a methyl group to form a stable product.<sup>‡</sup> The metallacycle **4** is set up to undergo hydride abstraction with  $\text{Ph}_3\text{C}^+\text{PF}_6^-$  to yield a carbene as has been reported by Brookhart and co-workers for  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})_2\text{W}(\text{CH}_2\text{R})]$ .<sup>14</sup> The addition of 1 equiv. of  $\text{Ph}_3\text{C}^+\text{PF}_6^-$  to a  $\text{CD}_2\text{Cl}_2$  solution of **4** at 220 K generates  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)\text{Rh}=\text{C}(\text{H})\text{OC}_6\text{F}_4]\text{PF}_6$  **5** quantitatively (Scheme 1). The complex was fully characterised by multinuclear NMR spectroscopy.<sup>†</sup> The carbene proton resonance appears at  $\delta$  13.09 in the  $^1\text{H}$  NMR spectrum while the carbene carbon is found at  $\delta$  308.6 in the  $^{13}\text{C}\{^1\text{H}\}$  spectrum. The complex decomposes on warming to room temperature.

Overall, these reactions provide an unusual entry to a carbene complex in addition to the C–F/C–H bond activation process. This carbene complex can also be considered as one of the few examples of a metallafuran complex and is the first representative for rhodium.<sup>15</sup>

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## Footnotes

<sup>†</sup> *Spectroscopic data*: NMR in  $\text{CD}_2\text{Cl}_2$ .  $^1\text{H}$  (500.13 MHz) and  $^{13}\text{C}$  spectra (125.76 MHz) relative to  $\text{CD}_2\text{Cl}_2$  at  $\delta$  5.30 and  $\delta$  54.2 respectively,  $^{31}\text{P}$  spectra (202.45 MHz) relative to  $\text{P}(\text{OMe})_3$  at  $\delta$  +140.85,  $^{19}\text{F}$  spectra (470.59 MHz) relative to  $\text{CFCl}_3$  at  $\delta$  0; coupling constants in Hz.

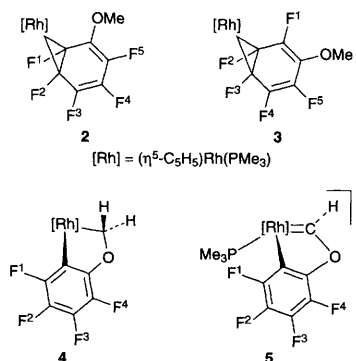
$[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{PMe}_3)(\eta^2\text{-C}_6\text{F}_5\text{OMe})]$  **2**:  $^1\text{H}$ ,  $\delta$  4.86 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 3.82 (d, 3 H,  $J_{\text{HF}}$  1.4,  $\text{OCH}_3$ ), 1.40 (dq, 9 H,  $J_{\text{HP}}$  10.5,  $J_{\text{HRh}} = J_{\text{HF}}$  0.9,  $\text{PMe}_3$ );  $^{19}\text{F}$ ,  $\delta$  –150.74 (m, 1 F,  $\text{F}^3$ ), –157.15 (m, 1 F,  $\text{F}^1$ ), –157.80 (m, 1 F,  $\text{F}^2$ ), –171.47 (m,  $\text{F}^{4/5}$ ), –171.50 (m,  $\text{F}^{5/4}$ ). **3**:  $^1\text{H}$ ,  $\delta$  4.87 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 4.28 (t, 3 H,  $J_{\text{HF}}$  1.1,  $\text{OCH}_3$ ), 1.40 (dq, 9 H,  $J_{\text{HP}}$  10.5,  $J_{\text{HRh}} = J_{\text{HF}}$  0.9,  $\text{PMe}_3$ );  $^{19}\text{F}$ ,  $\delta$  –141.37 (m, 1 F,  $\text{F}^1$ ), –148.05 (m, 1 F,  $\text{F}^4$ ), –159.65 (m, 1 F,  $\text{F}^2$ ), –160.76 (m, 1 F,  $\text{F}^3$ ), –167.64 (m, 1 F,  $\text{F}^5$ ). **2** and **3**:  $^{31}\text{P}$   $\{^1\text{H}\}$ ,  $\delta$  5.06 (ddd,  $J_{\text{PRh}}$  195,  $J_{\text{PF}}$  63, 56,  $\text{PMe}_3$ ), 4.74 (ddd,  $J_{\text{PRh}}$  195,  $J_{\text{PF}}$  64, 56,  $\text{PMe}_3$ ).

$[(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)\text{RhCH}_2\text{OC}_6\text{F}_4]$  **4**:  $^1\text{H}$ ,  $\delta$  6.82 (td, 1 H,  $J_{\text{HRh}} = J_{\text{HH}}$  4.9,  $J_{\text{HP}}$  1.9,  $\text{CH}^a$ ), 5.31 (dd, 5 H,  $J_{\text{HP}}$  1.5,  $J_{\text{HRh}}$  0.5,  $\text{C}_5\text{H}_5$ ), 5.24 (ddd, 1 H,  $J_{\text{HP}}$  16.9,  $J_{\text{HH}}$  4.9,  $J_{\text{HRh}}$  1.5,  $\text{CH}^b$ ), 1.30 (dd, 9 H,  $J_{\text{HP}}$  10.7,  $J_{\text{HRh}}$  1.1,  $\text{PMe}_3$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$ ,  $\delta$  90.3 (td,  $J$  3.2, 1.0,  $\text{C}_5\text{H}_5$ ), 69.2 (dd,  $J$  29.2, 14.3  $\text{CH}_2$ ), 19.4 (dd,  $J_{\text{PC}}$  34.0,  $J_{\text{RhC}}$  1.30,  $\text{PMe}_3$ ).  $^{19}\text{F}$ ,  $\delta$  –121.80 (ddd, 1 F,  $J$  31.5, 12.4, 3.8,  $\text{F}^1$ ), –164.95 (t, 1 F,  $J$  20.0,  $\text{F}^3$ ), –165.07 (m, 1 F,  $\text{F}^4$ ), –171.76 (ddd, 1 F,  $J$  30.5, 19.1, 7.6,  $\text{F}^2$ ).  $^{31}\text{P}$   $\{^1\text{H}\}$ ,  $\delta$  15.40 (d,  $J_{\text{PRh}}$  157,  $\text{PMe}_3$ ). IR (KBr,  $\nu/\text{cm}^{-1}$ ; 1500–550  $\text{cm}^{-1}$  region): 1488s, 1470s, 1439m, 1420m, 1287m, 1262m, 1217w, 1105m, 1097m, 1046m, 965s, 896m, 803s, 771m, 736w, 683w, 558vw. MS:  $m/z$  422 ( $\text{M}^+$ ), 244 ( $\text{M} - \text{C}_6\text{F}_4\text{OCH}_2$ ) $^+$ . HRMS: calc.  $m/z$  421.9931, experimental 421.9930. Satisfactory elemental analysis (C, H) was obtained.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)\text{Rh}=\text{C}(\text{H})\text{OC}_6\text{F}_4]\text{PF}_6$  **5**. NMR at 220 K:  $^1\text{H}$ ,  $\delta$  13.09 (d, 1 H,  $J$  3.3,  $\text{Rh}=\text{CH}$ ), 5.88 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 1.34 (d, 9 H,  $J_{\text{HP}}$  12.1,  $\text{PMe}_3$ );  $^{13}\text{C}$   $\{^1\text{H}\}$ ,  $\delta$  308.6 (d,  $J_{\text{CRh}}$  43.5,  $\text{Rh}=\text{C}$ ), 94.2 (s,  $\text{C}_5\text{H}_5$ ), 18.9 (d,  $J_{\text{CP}}$  38.1,  $\text{PMe}_3$ );  $^{19}\text{F}$ ,  $\delta$  –75.75 (d, 6 F,  $J_{\text{FP}}$  712,  $\text{PF}_6^-$ ), –119.96 (dd, 1 F,  $J$  28, 13,

$\text{F}^1$ ), –150.05 (dd, 1 F,  $J$  21, 14,  $\text{F}^4$ ), –154.92 (dd, 1 F,  $J$  29, 20,  $\text{F}^2$ ), –156.90 (t, 1 F,  $J$  20,  $\text{F}^3$ );  $^{31}\text{P}$   $\{^1\text{H}\}$ , 9.55 (d,  $J_{\text{PRh}}$  122.5,  $\text{PMe}_3$ ), –145.04 (spt,  $J_{\text{PF}}$  712,  $\text{PF}_6^-$ ).

<sup>‡</sup> The analogous reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{PPh}_3)(\text{C}_2\text{H}_4)]$  with pentafluoroanisole generates  $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{RhCH}_2\text{OC}_6\text{F}_4]$ , but not the  $\eta^2\text{-C}_6\text{F}_5\text{OMe}$  complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{PPh}_3)(\eta^2\text{-C}_6\text{F}_5\text{OMe})]$ .



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