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 [(η^5-C_5H_5)Rh(PMe_3)(C_2H_4)] in pentafluoroanisole generates the metallacycle [(η^5-C_5H_5)(PMe_3)$RhCH_2OC_6F_4$]; reaction of this complex with 1 equiv. of $Ph_3C^+PF_6^-$ at 220 K generates [(η^5-C_5H_5)(PMe_3)Rh=C(H)OC_6F_4]PF_6.

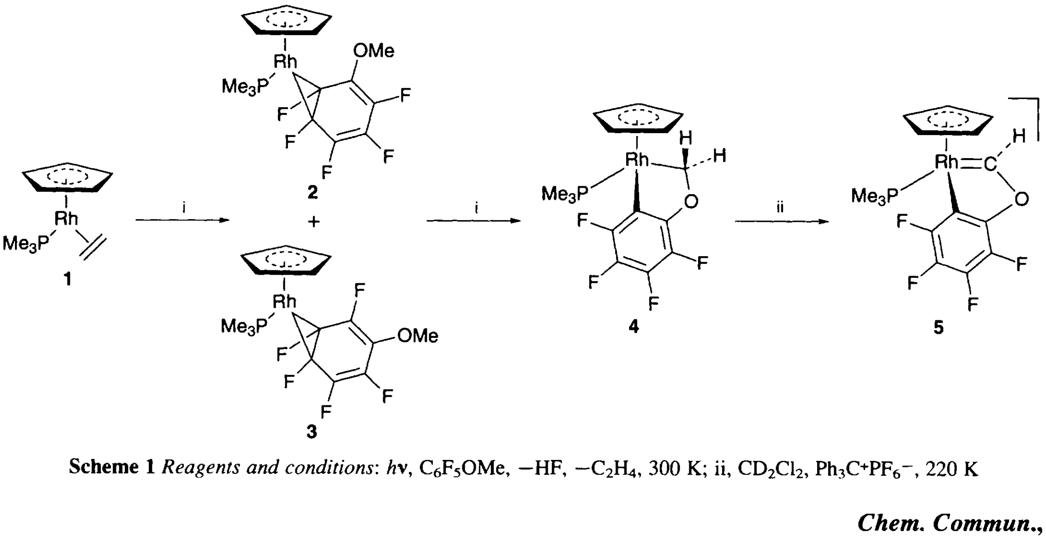
Hexafluorobenzene can form a variety of products upon reaction with transition-metal complexes:[1] coordination as M(η^2-C_6F_6) or M(η^4-C_6F_6) has been observed from the photoreactions of half-sandwich rhodium and iridium ethene complexes.[2,3] Sandwich complexes containing M(η^4-C_6F_6) (M = Ru, Os) and M(η^6-C_6F_6) (M = Mo, W) units have been isolated by metal-vapour synthesis.[4] In a few cases, cleavage of a C–F bond has been observed. Thermal and photochemical routes to C–F activation products, M(C_6F_5)F (M = Rh, Pt) have been reported.[2,5] Metal dihydride complexes react to give products of the form M(C_6F_5)H, *via* the elimination of HF.[2,6] In a more complex but related reaction, photolysis of [(η^5-C_5Me_5)Re(CO)$_3$] formed [(η^6-$C_5Me_4CH_2$)Re(CO)$_2$(C_6F_5)].[7] Catalytic conversion of C_6F_6 to C_6F_5H has been achieved with a rhodium complex.[8]

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, C_6F_5OMe, undergoes intermolecular C–H and C–F bond activation when reacted photochemically with [(η^5-C_5H_5)Rh(PMe_3)(C_2H_4)] **1**. The photochemistry of **1** has already been explored extensively at room temperature; it reacts with benzene to yield [(η^5-C_5H_5)Rh(PMe_3)(C_6H_5)H] *via* a short-lived η^2-arene complex.[9] Photolysis with C_6F_6 results in the isolation of a stable η^2-hexafluorobenzene complex, [(η^5-C_5H_5)Rh(PMe_3)(C_6F_6)].[2] 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.[2,10]

The irradiation of **1** in pentafluoroanisole (λ > 325 nm, 6 d) generates the metallacycle, [(η^5-C_5H_5)(PMe_3)$RhCH_2OC_6F_4$] **4**, quantitatively, as an isolable air-stable orange solid which was characterised by multinuclear NMR spectroscopy.† The ^1H NMR spectrum shows the CH_2 group to be diastereotopic and the two resonances appear at δ 6.82 as a triplet of doublets and δ 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 δ 5.67 (ddd) and 5.17 (ddd) for the diastereotopic protons of the complex [(η^5-C_5H_5)Rh(PMe_3)(CH_2OMe)I] and similar shifts for a related iridium complex.[11,12] The ^{13}C DEPT spectrum of **4** confirms the group as CH_2 (at δ 69.2) with a doublet of doublets coupling ($^1J_{CRh}$ 29.2 $^2J_{CP}$ 14.3 Hz); the value of J_{CH} is determined as 151 Hz from the fully coupled ^{13}C spectrum.

Spectra measured after short irradiation times show the presence of the metallacycle **4** and two isomers of [(η^5-C_5H_5)Rh(PMe_3)(η^2-C_6F_5OMe)], **2** and **3**, which show characteristic doublet of quartet (due to equal coupling to rhodium and two fluorine nuclei) resonances for the PMe_3 group in the ^1H NMR spectrum and doublet of doublet of doublet resonances in the ^{31}P NMR spectrum, indicative of coupling to rhodium and two inequivalent fluorine nuclei. The identity of the isomers was further confirmed by a ^{19}F–^{19}F COSY NMR spectrum. An (η^2-fluoroarene) complex has been observed previously as an intermediate which undergoes secondary photolysis to yield a C–F activation product upon photolysis of [(η^5-C_5Me_5)Rh(PMe_3)(C_2H_4)] in C_6F_6.[13] 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 (η^5-C_5H_5)Rh(PMe_3) is capable of inserting into a C–F



Scheme 1 *Reagents and conditions*: *hv*, C_6F_5OMe, –HF, –C_2H_4, 300 K; ii, CD_2Cl_2, $Ph_3C^+PF_6^-$, 220 K

bond of C_6F_6[2] and the C–H bonds of methane [10] at low temperature in matrices. These reactions do not yield stable products at room temperature in solution. In remarkable contrast, the reaction with C_6F_5OMe involves both insertion into a C–F bond and insertion into a C–H bond of a methyl group to form a stable product.‡ The metallacycle **4** is set up to undergo hydride abstraction with $Ph_3C^+PF_6^-$ to yield a carbene as has been reported by Brookhart and co-workers for $[(\eta^5\text{-}C_5H_5)(PPh_3)(CO)_2W(CH_2R)]$.[14] The addition of 1 equiv. of $Ph_3C^+PF_6^-$ to a CD_2Cl_2 solution of **4** at 220 K generates $[(\eta^5\text{-}C_5H_5)(PMe_3)\overline{Rh{=}C(H)OC}_6F_4]PF_6$ **5** quantitatively (Scheme 1). The complex was fully characterised by multinuclear NMR spectroscopy.† The carbene proton resonance appears at δ 13.09 in the ^1H NMR spectrum while the carbene carbon is found at δ 308.6 in the $^{13}C\{^1H\}$ 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.[15]

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Footnotes

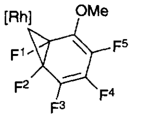
† *Spectroscopic data*: NMR in CD_2Cl_2. ^1H (500.13 MHz) and ^{13}C spectra (125.76 MHz) relative to CD_2Cl_2 at δ 5.30 and δ 54.2 respectively, ^{31}P spectra (202.45 MHz) relative to $P(OMe)_3$ at δ +140.85, ^{19}F spectra (470.59 MHz) relative to $CFCl_3$ at δ 0; coupling constants in Hz.

$[(\eta^5\text{-}C_5H_5)Rh(PMe_3)(\eta^2\text{-}C_6F_5OMe)]$ **2**: ^1H, δ 4.86 (s, 5 H, C_5H_5), 3.82 (d, 3 H, J_{HF} 1.4, OCH_3), 1.40 (dq, 9 H, J_{HP} 10.5, $J_{HRh} = J_{HF}$ 0.9, PMe_3); ^{19}F, δ −150.74 (m, 1 F, F^3), −157.15 (m, 1 F, F^1), −157.80 (m, 1 F, F^2), −171.47 (m, $F^{4/5}$), −171.50 (m, $F^{5/4}$). **3**: ^1H, δ 4.87 (s, 5 H, C_5H_5), 4.28 (t, 3 H, J_{HF} 1.1, OCH_3), 1.40 (dq, 9 H, J_{HP} 10.5, $J_{HRh} = J_{HF}$ 0.9, PMe_3); ^{19}F, δ −141.37 (m, 1 F, F^1), −148.05 (m, 1 F, F^4), −159.65 (m, 1 F, F^2), −160.76 (m, 1 F, F^3), −167.64 (m, 1 F, F^5). **2** and **3**: $^{31}P\{^1H\}$, δ 5.06 (ddd, J_{PRh} 195, J_{PF} 63, 56, PMe_3), 4.74 (ddd, J_{PRh} 195, J_{PF} 64, 56, PMe_3).

$[(\eta^5\text{-}C_5H_5)(PMe_3)\overline{RhCH_2OC}_6F_4]$ **4**: ^1H, δ 6.82 (td, 1 H, $J_{HRh} = J_{HH}$ 4.9, J_{HP} 1.9, CH^a), 5.31 (dd, 5 H, J_{HP} 1.5, J_{HRh} 0.5, C_5H_5), 5.24 (ddd, 1 H, J_{HP} 16.9, J_{HH} 4.9, J_{HRh} 1.5, CH^b), 1.30 (dd, 9 H, J_{HP} 10.7, J_{HRh} 1.1, PMe_3). $^{13}C\{^1H\}$, δ 90.3 (td, *J* 3.2, 1.0, C_5H_5), 69.2 (dd, *J* 29.2, 14.3 CH_2), 19.4 (dd, J_{PC} 34.0, J_{RhC} 1.30, PMe_3). ^{19}F, δ −121.80 (ddd, 1 F, *J* 31.5, 12.4, 3.8, F^1), −164.95 (t, 1 F, *J* 20.0, F^3), −165.07 (m, 1 F, F^4), −171.76 (ddd, 1 F, *J* 30.5, 19.1, 7.6, F^2). $^{31}P\{^1H\}$, δ 15.40 (d, J_{PRh} 157, PMe_3). IR (KBr, ν/cm^{-1}; 1500–550 cm^{-1} region): 1488s, 1470s, 1439m, 1420m, 1287m, 1262m, 1217w, 1105m, 1097m, 1046m, 965s, 896m, 803s, 771m, 736w, 683w, 558vw. MS: *m*/*z* 422 (M^+), 244 $(M - C_6F_4OCH_2)^+$. HRMS: calc. *m*/*z* 421.9931, experimental 421.9930. Satisfactory elemental analysis (C, H) was obtained.

$[(\eta^5\text{-}C_5H_5)(PMe)\overline{Rh{=}C(H)OC}_6F_4]PF_6$ **5**. NMR at 220 K; ^1H, δ 13.09 (d, 1 H, *J* 3.3, Rh=CH), 5.88 (s, 5 H, C_5H_5), 1.34 (d, 9 H, J_{HP} 12.1, PMe_3); $^{13}C\{^1H\}$, δ 308.6 (d, J_{CRh} 43.5, Rh=C), 94.2 (s, C_5H_5), 18.9 (d, J_{CP} 38.1, PMe_3); ^{19}F, δ −75.75 (d, 6 F, J_{FP} 712, PF_6^-), −119.96 (dd, 1 F, *J* 28, 13, F^1), −150.05 (dd, 1 F, *J* 21, 14, F^4), −154.92 (dd, 1 F, *J* 29, 20, F^2), −156.90 (t, 1 F, *J* 20, F^3); $^{31}P\{^1H\}$, 9.55 (d, J_{PRh} 122.5, PMe_3), −145.04 (spt, J_{PF} 712, PF_6^-).

‡ The analogous reaction of $[(\eta^5\text{-}C_5H_5)Rh(PPh_3)(C_2H_4)]$ with pentafluoroanisole generates $[(\eta^5\text{-}C_5H_5)(PPh_3)\overline{RhCH_2OC}_6F_4]$, but not the η^2-C_6F_5OMe complexes $[(\eta^5\text{-}C_5H_5)Rh(PPh_3)(\eta^2\text{-}C_6F_5OMe)]$.



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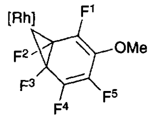

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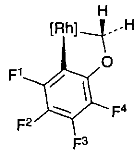
[Rh] = $(\eta^5\text{-}C_5H_5)Rh(PMe_3)$



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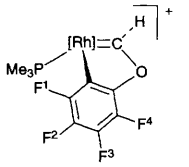

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