

Intermolecular C–F and Intramolecular C–H Activation Reaction of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ with Hexafluorobenzene: Crystal and Molecular Structure of $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$

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Photochemical reaction of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ with hexafluorobenzene yields $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$ formed by insertion into a C–F bond of C_6F_6 and concomitant insertion into a methyl C–H bond; the reactions of $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$ with PMe_3 and with HCl show that the $(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)$ ligand is subject to both nucleophilic and electrophilic attack.

The last three years have seen major advances in the coordination and intermolecular C–F activation of fluorinated organic molecules by transition metal and lanthanide complexes.^{1–8} Recently, we have demonstrated that hexafluorobenzene can be bound to rhodium⁵ and iridium⁶ complexes in η^2 - and η^4 -coordination modes. We have observed the C–F activation of coordinated C_6F_6 in rhodium and iridium half-sandwich complexes,^{7,8} while others have made parallel observations for square-planar iridium and platinum complexes.^{1,2} Examples of intermolecular C–F oxidative addition of hexafluorobenzene have been confined so far to d^8 and d^{10} metal fragments.^{1,2,7,8} Here, we show that the rhenium complex $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$, can also be used to study the activation of C–F bonds of C_6F_6 although it does not activate C–H bonds of benzene.⁹ Concomitantly, it becomes liable to intramolecular C–H activation.

Photolysis of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ ($\lambda > 285$ nm) in neat C_6F_6 at room temp. produced one major dicarbonyl product. This material was isolated as air-stable orange crystals (8 h irradiation, 60% yield)†,‡ by sublimation of unconverted $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ and subsequent recrystallization from hexane and was identified as $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$ **1**. The C_6F_5 ligand in **1** was characterized by ^{19}F NMR and IR spectroscopy.⁸ Two extreme canonical forms, η^6 -conjugated triene (tetramethylfulvene) **1a** or η^5 -tetramethylcyclopentadienyl σ -alkyl ('tucked-in') **1b** can be considered for the bonding of the $(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)$ ligand (Scheme 1).^{10,11} The chemical shift of the methylene group in the ^1H NMR spectrum (δ 3.46) and the C–H coupling constant (δ 47.5, J_{CH} 162 Hz) observed in the ^{13}C -gated spectrum, imply that the ligand is bound to Re in a η^6 -triolefinic fashion

† Satisfactory elemental analyses have been obtained for **1**, **2** and **3**.

‡ Spectral data for **1**, $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$: NMR (300 MHz). ^1H (C_6D_6): δ 3.46 (s, 2H, CH_2), 1.41 (s, 6H, Me), and 1.07 (s, 6H, Me); $^{13}\text{C}\{^1\text{H}\}$ gated (C_6D_6): δ 47.5 (t, J_{CH} 162 Hz, CH_2), 9.9 (t, J_{CH} 129 Hz, Me) and 9.8 (t, J_{CH} 128 Hz, Me); ^{19}F (C_6D_6): δ –103.6 (d, J_{FF} 20 Hz, *ortho*), –159.0 (t, J_{FF} 20 Hz, *para*) and –163.4 (t, J_{FF} 20 Hz, *meta*). IR (hexane) (ν/cm^{-1}): 2007 vs and 1942 vs [$\nu(\text{CO})$]. MS-EI based on ^{187}Re , m/z : 544 M^+ , 516 $\text{M}^+ - \text{CO}$, 488 $\text{M}^+ - 2\text{CO}$.

1a.§ Nevertheless, the detection of a minor isomer in the NMR spectra suggests restricted rotation about the metal-fulvene bond.¶

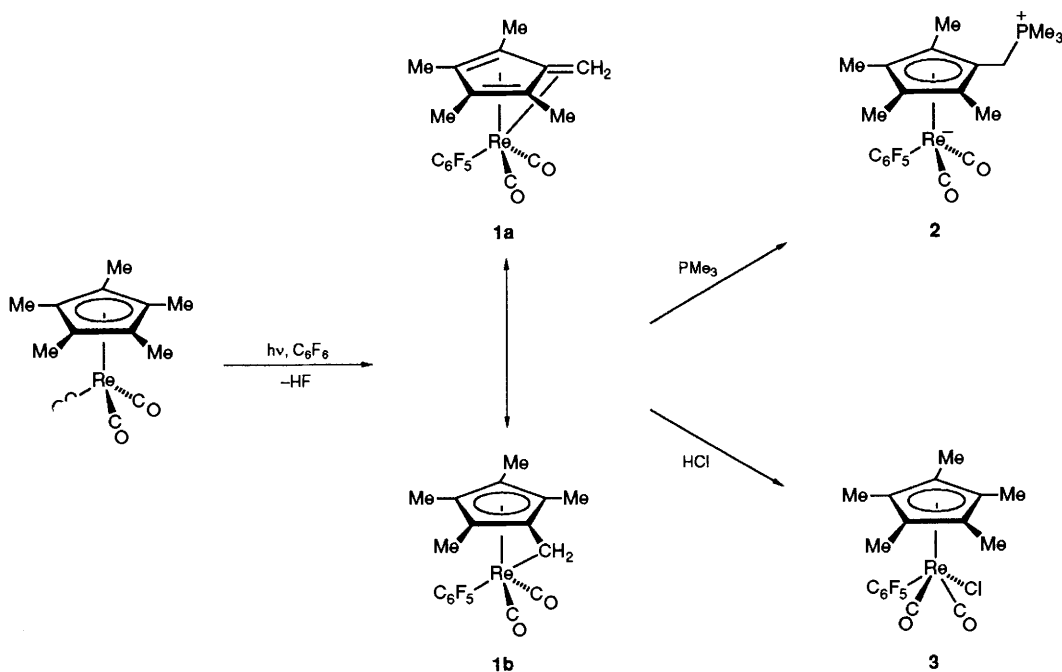
X-Ray crystallographic analysis of **1** (Fig. 1) confirms that the C–F bond of C_6F_6 has been cleaved and that the $\text{C}_5\text{Me}_4\text{CH}_2$ ligand is coordinated to rhenium through six carbon atoms, with the CH_2 group *trans* to the C_6F_5 ligand.¶ The relatively long C–C bond to the CH_2 group [$\text{C}(2) - \text{C}(6) = 1.43(2)$ Å], the bending angle of this bond out of the C_5Me_4 plane (39.6°) and the pattern of Re–C bond lengths are all indicative of the tucked-in structure type, **1b**.¹¹

In a demonstration of the fulvene nature of the $(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)$ ligand,¹² complex **1** undergoes nucleophilic attack by PMe_3 at the methylene carbon leading quantitatively to the zwitterionic complex $[\text{Re}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{PMe}_3)-$

§ Values of $J(\text{CH}) > 150$ Hz for the methylene carbon have been taken to indicate sp^2 -hybridised carbon in several $\eta^6\text{-C}_5\text{R}_4\text{C}_2$ complexes, see ref. 10 and references cited therein.

¶ The ^1H and ^{19}F NMR spectra of **1** show a set of weak resonances in addition to those listed even when a single crystal is used to make up the solution. They are assigned to a minor isomer with the $\eta^6\text{-C}_5\text{Me}_4\text{CH}_2$ ligand rotated relative to the C_6F_5 group so that all methyl groups and the CH_2 protons are inequivalent. The proportion of the minor isomer in toluene is 12% at 296 K and 9% at 203 K.

|| Crystals suitable for X-ray analysis were obtained from toluene-hexane (1:10) at -20°C . Crystal data for $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$, **1**: orange rod, $0.1 \times 0.3 \times 0.4$ mm, $\text{C}_{18}\text{H}_{14}\text{O}_2\text{F}_5\text{Re}$, $M = 543.51$, monoclinic, space group $P2_1/n$, $a = 9.1185(8)$, $b = 13.085(3)$, $c = 14.554(2)$ Å, $\beta = 92.420(10)^\circ$, $U = 1735.0(5)$ Å³, $F(000) = 1032$, $D_c = 2081$ kg m^{-3} , $Z = 4$, $\alpha(\text{Mo-K}\alpha) = 0.71069$ Å, $\mu = 70.67$ cm^{-1} , $T = 296$ K, 3204 unique reflections ($R_{\text{int}} = 2.98$), 2334 reflections [$I > 3.5\sigma(I)$]. Data were collected on a Rigaku AFC6S diffractometer for $5 < 2\theta < 50^\circ$; the structure was solved by direct methods, full-matrix least-squares refinement, $R = 0.030$, $R_w = 0.036$, number of parameters = 236, reflection: parameter ratio = 9.89. The hydrogen atoms were placed in idealised positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.



Scheme 1 Generation, reactions and canonical forms of **1**

(CO)₂(C₆F₅) **2**.** In contrast, the methylene group behaves as a nucleophile itself in the reaction of complex **1** with HCl gas [tetrahydrofuran (thf), 24 h, room temp.], regenerating the (η⁵-C₅Me₅) ligand, to give *cis*-[Re(η⁵-C₅Me₅)(CO)₂(C₆F₅)(Cl)] **3**.†† The protonation occurs at the same position as in [Mo(η⁶-C₅H₄CMe₂)(η⁶-C₆H₆)], but at a different position from [Re(η⁶-C₅Me₄CH₂)(η⁵-C₅Me₅)].^{10,13}

The first step in the formation of **1** should involve the reaction of the unsaturated 16-electron fragment [Re(η⁵-C₅Me₅)(CO)₂] with C₆F₆ to give [Re(η⁵-C₅Me₅)(CO)₂(η²-C₆F₆)] or a C-F oxidative addition product, [Re(η⁵-C₅Me₅)(CO)₂(C₆F₅)F]. However, we could not detect any intermediates in the reaction by IR spectroscopy, and attempts to use C₆F₆ to displace the thf ligand thermally from [Re(η⁵-C₅Me₅)(CO)₂(thf)] failed. The only product isolated was the known [Re₂(η⁵-C₅Me₅)₂(CO)₅] complex.¹⁴ The postulate of [Re(η⁵-C₅Me₅)(CO)₂(η²-C₆F₆)] as an intermediate is supported by the isolation and characterisation of the analogous [Re(η⁵-C₅H₅)(CO)₂(η²-C₆F₆)].¹⁵

The formation of **1** and its reactions are summarised in Scheme 1. Furthermore, these experiments have demonstrated that: (i) intermolecular C-F oxidative addition may occur with a d⁶ metal carbonyl fragment, which is not subject to oxidative addition with C-H bonds; (ii) no clear distinction between fulvene and tucked-in bond types can be made. The

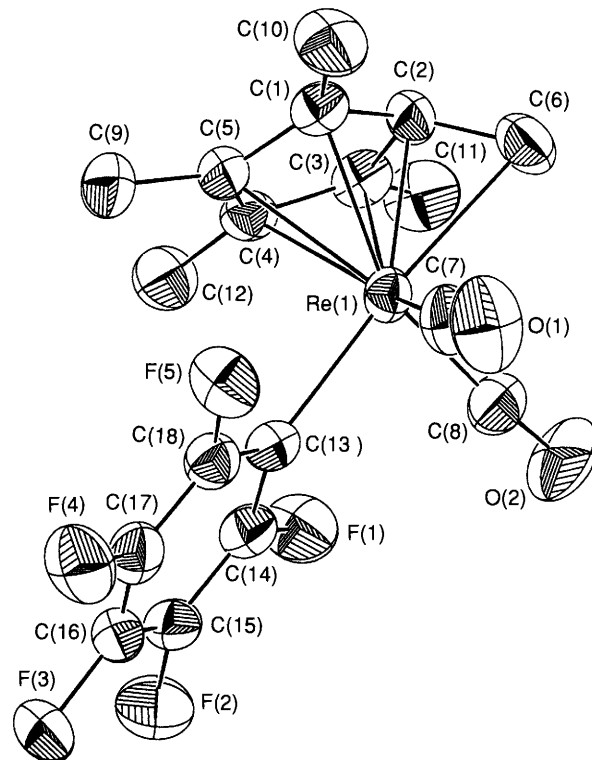


Fig. 1 ORTEP view of the molecular structure of **1** (ellipsoids at the 50% level). Principal bond lengths (Å) and angles (°): Re-C(1) 2.28(1), Re-C(2) 2.14(1), Re-C(3) 2.25(1), Re-C(4) 2.36(1), Re-C(5) 2.35(1), Re-C(6) 2.36(1), Re-C(13) 2.19(1), C(2)-C(6) 1.43(2); C(7)-Re-C(8) 92.1(5), C(8)-Re-C(13) 88.4(6), dihedral of C(1)-C(5) plane-C(2)-C(6) 39.6; dihedral of C(13)-C(18) plane-C(13)-Re 1.4.

** *Spectral data* for **2**, [Re(η⁵-C₅Me₄CH₂PMe₃)(CO)₂(C₆F₅)]: ¹H (CD₃CN): δ 3.42 (d, *J*_{PH} 12 Hz, CH₂), 2.21 (s, 6H, Me), 2.03 (d, *J*_{PH} 4 Hz, 6H, Me), 1.76 (d, *J*_{PH} 14 Hz, 9H, PMe₃). ¹³C{¹H} (DEPT) (CD₃CN): δ 22.5 (d, *J*_{CP} 47 Hz, CH₂), 11.4 (s, Me), 10.3 (s, Me) and 7.5 (d, *J*_{CP} 53 Hz, PMe). ¹⁹F: δ -98.5 (d, *J*_{FF} 26 Hz, *F*_{ortho}), -160.8 (t, *J*_{FF} 20 Hz, *F*_{para}) and -161.3 (t, *J*_{FF} 26 Hz, *F*_{meta}). ³¹P {¹H}: δ 29.1 (s, CH₂-PMe₃). IR (MeCN, ν/cm⁻¹): 1868vs and 1795vs [ν(CO)]. MS-FAB (FAB = fast atom bombardment) (NOPE matrix) *m/z*: 620 M⁺.

†† *Spectral data* for **3**, *cis* [Re(η⁵-C₅Me₅)(CO)₂(C₆F₅)Cl]: ¹H (C₆D₆): δ 1.40 (s, C₅Me₅); ¹⁹F (C₆D₆): δ -85.0 (d, *J*_{FF} 21 Hz, *F*_{ortho}), -136.4 (t, *J*_{FF} 20 Hz, *F*_{para}) and -140.4 (t, *J*_{FF} 20 Hz, *F*_{meta}). IR (CH₂Cl₂, ν/cm⁻¹): 2030vs, 1960s [ν(CO)]. MS-EI (based on ¹⁸⁷Re and ³⁵Cl), *m/z*: 580 M⁺, 552 M⁺ - CO, 524 M⁺ - 2CO.

geometry and protonation point towards one type, NMR evidence and reaction with PMe₃ point to the other. Competition between intermolecular C-F and C-H oxidative addition is under investigation with other fluoroarenes as substrates.

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