

Photochemical reactions of $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3]$ ($\text{R} = \text{H}$ or Me) with partially fluorinated benzenes: C–H and C–F activation

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Received 30th March 1999, Accepted 28th April 1999

UV Irradiation of $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3]$ ($\text{R} = \text{Me}$ or H) in the presence of $\text{C}_6\text{F}_5\text{H}$ or 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ effected intramolecular C–H activation, generating the hydrido complexes *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2(\text{Ar})_F\text{H}]$ [$(\text{Ar})_F = \text{C}_6\text{F}_5$ or 2,3,5,6- $\text{C}_6\text{F}_4\text{H}$] as the principal photochemical products. The identities of the hydrido complexes were confirmed by independent thermal syntheses. The photoreaction of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ with $\text{C}_6\text{F}_5\text{H}$ also generated the fulvene complex $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$ **2a** and two bis(aryl) derivatives: *cis*- $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)_2]$ **3a** and $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)(2,3,5,6\text{-C}_6\text{F}_4\text{H})]$ **4a** in low yield. Complex **2a** results from an intramolecular C–H activation, while **3a** and **4a** derive from a C–H and a C–F activation of a second molecule of pentafluorobenzene, respectively. The origin of the minor products was elucidated by showing that UV irradiation of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)\text{H}]$ in $\text{C}_6\text{F}_5\text{H}$ produces **2a**, **3a** and **4a**, while photolysis of **2a** produces only **3a**. The reaction of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ with 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ gave analogues **2b** and **4b** as minor products. The photoreaction of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ in $\text{C}_6\text{F}_5\text{H}$ or 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ generated bis(aryl) compounds and the unusual binuclear complexes $[\text{Re}_2(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\text{CO})_4(\text{Ar})_F]$ as the minor products. The binuclear complex with $(\text{Ar})_F = 2,3,5,6\text{-C}_6\text{F}_4\text{H}$ has been characterized by X-ray crystallography. The Re–Re bond [3.0258(7) Å] is close to collinear with the Re–C (aryl) bond. One $\{\text{Re}(\text{CO})_2\}$ unit is twisted by about 73.0° with respect to the other.

Introduction

Many of the studies dealing with intermolecular C–F bond activation by transition metal complexes are limited to perfluoro aromatic molecules.^{1–6} Remarkable results have been achieved in the field by using hexafluorobenzene. For instance, η^2 and η^4 co-ordination modes at rhodium and iridium complexes have been reported; some of these are proposed as intermediates in the oxidative addition of aromatic C–F bonds to transition metals.^{7,8} Several thermal and photochemical routes to C–F activation products have been discovered in the last decade, which are conveniently summarized in two thorough reviews.^{9,10} More recently, the catalytic conversion of C_6F_6 into $\text{C}_6\text{F}_5\text{H}$ has been achieved with a soluble rhodium complex.¹¹ In a more complex but related reaction, photolysis of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ in neat C_6F_6 formed the tetramethylfulvene complex $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$ *via* intermolecular C–F and intramolecular C–H activation.¹²

At partially fluorinated arenes, both C–F and C–H activation have been reported. For instance, the thermal reaction of *cis*- $[\text{Ru}(\text{dmpe})_2\text{H}_2]$ with several fluorinated arenes ($\text{C}_6\text{F}_5\text{H}$, 1,2,3,4- $\text{C}_6\text{F}_4\text{H}_2$, and 1,2,3- $\text{C}_6\text{F}_3\text{H}_3$) produces only C–F activation products; an electron-transfer mechanism has been proposed for these reactions.¹³ The thermal reaction of $[\text{Ni}(\text{COD})_2]$ ($\text{COD} = 1,5\text{-cyclooctadiene}$) with $\text{C}_6\text{F}_5\text{H}$, in the presence of triethylphosphine, is close to the $[\text{Ru}(\text{dmpe})_2\text{H}_2]$ reaction in selectivity for C–F over C–H bond activation.¹⁴ The complex $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)_2\text{H}_2]$ has also been found to produce a C–F bond activation product selectively in the thermal reaction with $\text{C}_6\text{F}_5\text{H}$; in this case, a nucleophilic aromatic substitution was indicated as the more plausible mechanism.¹⁵ In contrast, the complexes $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\text{Ph})\text{H}]$ and $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{C}_2\text{H}_4)]$, the former in thermal and the latter in photochemical reactions, have proved to activate the C–H bonds rather than the C–F bonds in mono-, di- and tri-

fluorobenzenes; it was proposed that the reactive fragment $\{\text{RhCp}'(\text{PMe}_3)\}$ ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ or $\eta^5\text{-C}_5\text{H}_5$) co-ordinates the fluoroarene by an η^2 mode before the C–H bond insertion.¹⁶ Similarly, it has been shown that the unsaturated complex $[\text{Pt}(\text{PCy}_3)_2]$ ($\text{Cy} = \text{cyclohexyl}$) reacts selectively with pentafluorobenzene, 1,3,5- $\text{C}_6\text{F}_3\text{H}_3$ and 1,3- $\text{C}_6\text{F}_2\text{H}_4$ to give the corresponding hydrido complexes.¹⁷ Very recently, a theoretical approach to the inertness of the aryl–fluorine bond toward oxidative addition to osmium and rhodium complexes has been reported.¹⁸ DFT Calculations showed that the barrier to C–F activation of 1,4-difluorobenzene far exceeds the barrier to C–H activation although the energies of the products are similar. The two types of bond activation reaction proceed from a common intermediate, $[\text{Rh}(\text{C}_5\text{H}_5)(\text{PH}_3)(\eta^2\text{-C}_6\text{F}_2\text{H}_4)]$.

In this paper we report that partially fluorinated benzenes ($\text{C}_6\text{F}_5\text{H}$ and 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$) react with 16 electron rhenium fragments $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$ and $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ (both generated photochemically from the corresponding tricarbonyl complex) to give only the C–H oxidative addition complexes *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2(\text{C}_6\text{F}_4\text{R}')\text{H}]$ ($\text{R} = \text{H}$ or Me ; $\text{R}' = \text{F}$ or H). Secondary UV irradiation of the hydride derivatives in the corresponding fluorinated benzene is shown to produce both C–H and C–F activation products. The secondary products from $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ include an unusual dinuclear complex containing a $(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)$ group.

Results

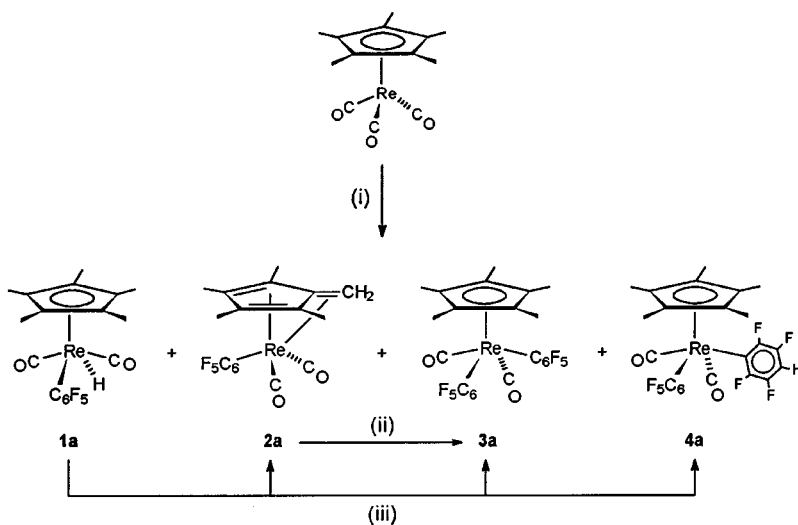
1 Photoreactions of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ with pentafluorobenzene and 1,2,4,5-tetrafluorobenzene

UV Irradiation ($\lambda = 300$ nm) of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ in neat $\text{C}_6\text{F}_5\text{H}$ or 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ at room temperature for 3 h produced yellow solutions which, after removal of the solvent under vacuum, left a yellow-brown solid. The solid obtained from the

Table 1 Proton and ^{19}F NMR data for products from reaction of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ with $\text{C}_6\text{F}_5\text{H}$ and 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ ^a

Complex	^1H	^{19}F
1a (C_6D_6)	-8.98 (br s, 1 H, ReH), 1.48 (s, 15 H, CH_3)	-162.64 (m, 2 F, F_{meta}), -157.80 (t, J_{FF} 21, 1 F, F_{para}), -102.86 (m, 2 F, F_{ortho})
1b (C_6D_6)	-8.99 (br s, 1 H, ReH), 1.50 (s, 15 H, CH_3), 6.42 (tt, J_{HF} 9.4, 7.5, 1 H, $\text{C}_6\text{F}_4\text{H}$)	-140.05 (m, 2 F, F_{meta}), -104.35 (m, 2 F, F_{ortho})
2b	Major isomer 1.72 (s, 6 H, CH_3), 2.05 (s, 6 H, CH_3), 4.11 (s, 2 H, CH_2), 6.77 (tt, J_{HF} 9.4, 7.4, 1 H, $\text{C}_6\text{F}_4\text{H}$) Minor isomer 1.50 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 4.03 (d, J_{CH} 1.6, 1 H, CH_2), 4.82 (d, J_{CH} 1.6, 1 H, CH_2), 6.65 (tt, J_{HF} 9.5, 7.3, 1 H, $\text{C}_6\text{F}_4\text{H}$)	Major isomer -142.24 (m, 2 F, F_{meta}), -106.46 (m, 2 F, F_{ortho}) Minor isomer -143.32 (m, 2 F, F_{meta}), F_{ortho} not observed
3a	1.76 (s, CH_3)	-162.60 (m, 2 F, F_{meta}), -156.43 (t, J_{FF} 20, 1 F, F_{para}), -102.70 (m, 2 F, F_{ortho})
4a	1.75 (s, 15 H, CH_3), 6.96 (tt, J_{HF} 9.1, 7.5, 1 H, $\text{C}_6\text{F}_4\text{H}$)	-162.3 (m), -156.5 (m), -140.01 (m, 2 F, F_{meta} of $\text{C}_6\text{F}_4\text{H}$), -104.46 (m, 2 F, F_{ortho} of $\text{C}_6\text{F}_4\text{H}$), -102.8 (m)
4b ^b	1.70 (s, 15 H, CH_3), 6.84–7.00 (m, 2 H, $\text{C}_6\text{F}_4\text{H}$, $\text{C}_6\text{F}_3\text{H}_2$), 7.67 (ddd, J_{HF} 11.5, 9.7, 5.0, 1 H, $\text{C}_6\text{F}_3\text{H}_2$)	-145.05 (dddd, J_{FF} 20, 14, 13, 6, 1 F, F_{meta} of $\text{C}_6\text{F}_3\text{H}_2$), -140.06 (m, 2 F, F_{meta} of $\text{C}_6\text{F}_4\text{H}$), -138.65 (dddd, J_{FF} 20, 10, 9, 6, 1 F, F_{para} of $\text{C}_6\text{F}_3\text{H}_2$), -104.12 (br s, 2 F, F_{ortho} of $\text{C}_6\text{F}_4\text{H}$), -78.59 (dddd, J_{FF} 14, 8, 6, 5, 1 F, F_{ortho} of $\text{C}_6\text{F}_3\text{H}_2$)

^a All ^1H and ^{19}F NMR spectra at 298 K in CDCl_3 , except where indicated; δ values reported in ppm and J values in Hertz. The spectra for complexes **2b** and **3a** were recorded on a Bruker AMX 500 spectrometer; those for **1a**, **1b** and **4a**, **4b** on a Bruker AC 200 spectrometer. ^b ^1H NMR in C_6D_6 separates overlapping resonances: δ 1.16 (s, 15 H, CH_3), 6.40 (tt, J_{HF} 9, 8.8, 1 H, $\text{C}_6\text{F}_4\text{H}$), 6.53 (ddd, J_{HF} 10, 8, 7, 1 H, $\text{C}_6\text{F}_3\text{H}_2$) and 7.40 (ddd, J_{HF} 11.6, 9.7, 5 Hz, 1 H, $\text{C}_6\text{F}_3\text{H}_2$).

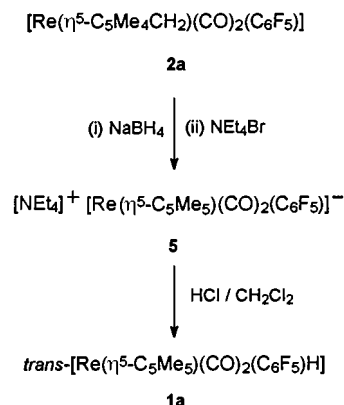
**Scheme 1** Products of UV irradiation in $\text{C}_6\text{F}_5\text{H}$ of (i) $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$, (ii) **2a**, (iii) **1a**.

reaction with pentafluorobenzene was washed with several portions of cold hexane leaving a brown residue which was crystallized from hexane at low temperature to produce a light brown solid identified as *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)\text{H}]$ **1a**. Careful chromatography of the hexane washings on a neutral alumina column allowed the separation of unchanged $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ and three further products, $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$ **2a** and the mixture of two bis-(fluoroaryl) derivatives: $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)_2]$ **3a** and $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)(2,3,5,6\text{-C}_6\text{F}_4\text{H})]$ **4a** (Scheme 1).

The room temperature ^1H NMR spectrum of the hydride complex **1a** exhibited a single resonance for the $\eta^5\text{-C}_5\text{Me}_5$ ligand and a broad hydride resonance. The latter remained unchanged even at 233 K. Similar phenomena have previously been observed for hydrido complexes of rhodium containing fluoroaryl ligands and have been explained in terms of unresolved coupling with the *ortho* fluoro substituent of the aromatic ligand.¹⁶ The ^{19}F and ^{13}C NMR spectra showed the expected resonances for a single compound (Table 1 gives ^1H and ^{19}F NMR data for all complexes, ^{13}C NMR data are given in the Experimental section). The mass spectrum of **1a** showed neither the molecular ion nor the loss of CO, but the presence of the fulvene complex. Attempts to obtain an analytically pure

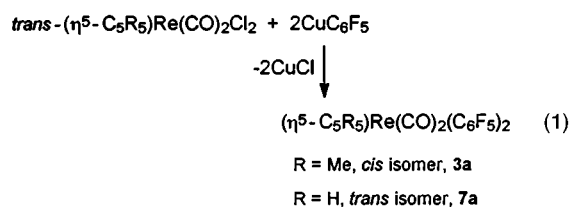
sample of this complex by this method were unsuccessful due to the formation of an unidentified light brown solid during the crystallization. To dispel any doubt about the identification of **1a**, a pure sample of this complex was synthesized in 83% overall yield by the method shown in Scheme 2.

The tetramethylfulvene complex $[\text{Re}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$

**Scheme 2** Thermal synthesis of *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)\text{H}]$.

(C₆F₅)] **2a** was formed in 5.5% yield.^{12,19} The presence of a mixture of the bis(aryl)_F complexes [Re(η⁵-C₅Me₅)(CO)₂(C₆F₅)₂] **3a** and [Re(η⁵-C₅Me₅)(CO)₂(C₆F₅)(C₆F₄H)] **4a** in low yield was also unexpected (Scheme 1). They could not be separated and were characterized in the mixture. The mass spectrum showed peaks corresponding to the parent ions of **3a** and **4a** and the loss of one CO group. The ¹H NMR spectrum also showed the presence of two species; the two resonances at δ 1.76 and 1.75 in a ratio 1.7: 1.0 are assigned to **3a** and **4a**, respectively. The latter complex showed a triplet of triplets at δ 6.96, as expected for a hydrogen in the *para* position of the fluoroaryl ligand. The ¹⁹F NMR spectrum confirms the conclusion (Table 1). The multiplets at δ -104.5 and -140.0 are assigned to the 2,3,5,6-C₆F₄H ring; similar chemical shifts have been reported for [Rh(η⁵-C₅H₅)(PMe₃)(2,3,5,6-C₆F₄H)].¹⁶ A further three resonances are almost in the same position as those observed for C₆F₅ ligands in complex **3a** (see below).

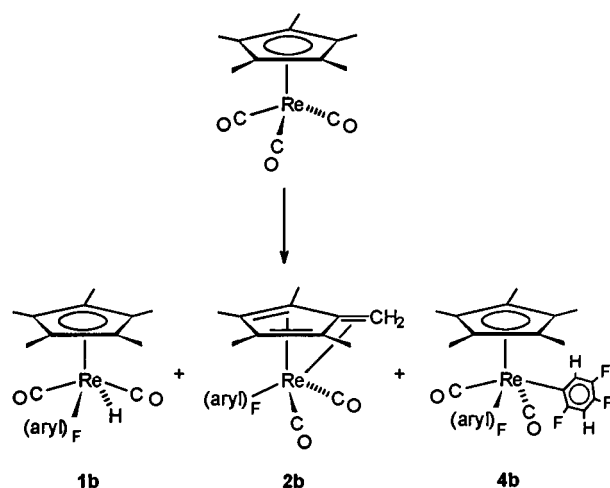
In order to confirm the assignment and stereochemistry of these bis(aryl)_F derivatives, complex **3a** was synthesized independently, following the methodology reported for the halide substitution of the dicarbonyldihalide complexes [Re(η⁵-C₅Me₅)(CO)₂X₂] (X = Cl or I).²⁰ The reaction of *trans*-[Re(η⁵-C₅Me₅)(CO)₂Cl₂] with an excess of [Cu(C₆F₅)] in THF gave complex **3a** in 75% yield as a yellow crystalline solid, eqn. (1).



The ¹H and ¹³C NMR spectra unequivocally indicate the presence of a single compound (Table 1). Even more decisively, the ¹⁹F NMR spectrum exhibited only three resonances at δ -162.6, -156.4 and -102.7 which are coincident with those observed in the mixture. A *cis* or lateral orientation of the two CO ligands was assigned on the basis of the relative intensity of the ν(CO) absorption bands.²¹

With the aim of obtaining insight into the origin of the fulvene complex **2a** and the origin of the two bis(aryl) derivatives **3a** and **4a** in the photolysis of [Re(η⁵-C₅Me₅)(CO)₃] in C₆F₅H, the photochemistry of **1a** in pentafluorobenzene was examined. Irradiation (λ = 300 nm) of a spectroscopically pure sample of **1a** in C₆F₅H at room temperature for 5 h resulted in the formation of **2a**, **3a** and **4a** in about the same ratio as that found in the photolysis of the parent [Re(η⁵-C₅Me₅)(CO)₃] in the same solvent (Scheme 1). This result indicates that, of the three products, at least the fulvene complex **2a** is formed from **1a**, presumably by H₂ elimination. At this stage, we could not distinguish whether the bis(aryl)_F derivatives **3a** and **4a** derived from the photoreaction of **1a** or **2a**. To answer this question, a pure sample of the fulvene complex in C₆F₅H was photolysed under the same experimental conditions. The IR, ¹H and ¹⁹F NMR and the mass spectrum of the product showed, in addition to unchanged starting fulvene, only *cis*-[Re(η⁵-C₅Me₅)(CO)₂(C₆F₅)₂] **3a** (Scheme 1). We can therefore conclude that the second bis(aryl)_F complex **4a** is formed photochemically from the hydrido complex **1a**. A thermal reaction can be ruled out since no new absorption bands were observed in the IR spectra after treatment of either **1a** or **2a** with C₆F₅H at 150 °C for 2 h. (The complexes did not survive for long at this temperature.)

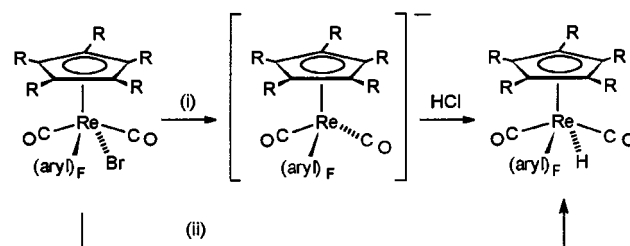
The products obtained from the reaction of [Re(η⁵-C₅Me₅)(CO)₃] with 1,2,4,5-tetrafluorobenzene are shown in Scheme 3. Like in the previous case, the major product observed (by IR) after UV irradiation was the hydrido complex **1b**, but it could not be separated from the reaction mixture by extraction with hexane as in the case of **1a**. The residual solid obtained after



Scheme 3 Products of UV irradiation of [Re(η⁵-C₅Me₅)(CO)₃] in 1,2,4,5-C₆F₄H₂ ((aryl)_F = 2,3,5,6-C₆F₄H).

photolysis was treated directly with bromoform to convert all the hydride complex **1b** into the more stable bromo derivative *trans*-[Re(η⁵-C₅Me₅)(CO)₂(C₆F₄H)Br]. Column chromatography allowed the separation of the bromo complex from the starting tricarbonyl, [Re(η⁵-C₅Me₅)(CO)₂(2,3,5,6-C₆F₄H)(2,4,5-C₆F₃H₂)] **4b** and the new fulvene complex [Re(η⁶-C₅Me₄CH₂)(CO)₂(2,3,5,6-C₆F₄H)] **2b**. The symmetric bis(aryl)_F complex [Re(η⁵-C₅Me₅)(CO)₂(2,3,5,6-C₆F₄H)₂] was not detected.

The hydrido complex **1b** was prepared indirectly in 90% yield by the method shown in Scheme 4. This complex was fully



Scheme 4 Thermal syntheses of hydride complexes: (i) AlH₄⁻, R = Me, (aryl)_F = 2,3,5,6-C₆F₄H, (ii) BH₄⁻, R = H, (aryl)_F = C₆F₅ or 2,3,5,6-C₆F₄H.

characterized by spectroscopy (Table 1 and Experimental section). As expected, it showed a similar intensity pattern for the ν(CO) bands to those observed for **1a** and a single resonance for the COs in the ¹³C-¹H NMR spectrum which is indicative of a *trans* stereochemistry. In addition to the resonances for the hydride and η⁵-C₅Me₅ ligands, the ¹H NMR spectrum exhibited the triplet of triplets typical for the aromatic proton in the *para* position. The ¹⁹F NMR spectrum showed only two resonances at δ -140.05 and -104.35 due to the aromatic fluoro substituents in the *meta* and *ortho* positions, respectively.

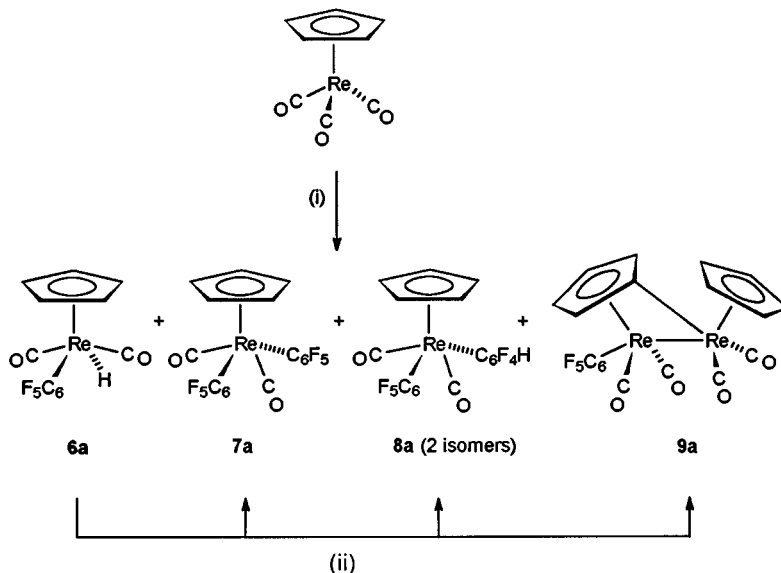
The fulvene complex **2b** exhibited similar spectroscopic parameters to those reported for **2a** (Table 1 and Experimental section).^{12,19} Like **2a**, it is present in two isomeric forms: in the major isomer the 2,3,5,6-C₆F₄H group occupies a position *trans* to the CH₂ group of the fulvene, while in the minor isomer (18.5% in chloroform at 293 K) the η⁶-C₅Me₄CH₂ ligand is rotated relative to the aromatic group. The presence of the 2,3,5,6-C₆F₄H group in **2b** was clearly established by ¹H and ¹⁹F NMR spectra.

The bis(aryl)_F complex **4b** was isolated in about 5% yield as a single compound but its characterization is complicated. The IR spectrum is ambiguous, showing equally intense ν(CO) absorption bands making it difficult to decide between the *cis* and *trans* product. The ¹³C NMR spectrum showed only one broad resonance in the carbonyl region (δ 193.3) which suggests a *trans* geometry. Considering that the fluoroaryl ligands are

Table 2 Proton and ^{19}F NMR data for products from reaction of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ with $\text{C}_6\text{F}_5\text{H}$ and 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ ^a

Complex	^1H	^{19}F
6a (C_6D_6)	-9.18 (t, J_{HF} 2.4, 1 H, ReH), 4.18 (s, 5 H, CH)	-162.84 (m, 2 F, F_{meta}), -157.83 (t, J_{FF} 21, 1 F, F_{para}), -99.74 (m, 2 F, F_{ortho})
6b (C_6D_6)	-9.13 (t, J_{HF} 2.5, 1 H, ReH), 4.23 (s, 5 H, CH), 6.44 (tt, J_{HF} 9.4, 7.5, 1 H, $\text{C}_6\text{F}_4\text{H}$)	-140.24 (m, 2 F, F_{meta}), -101.14 (m, 2 F, F_{ortho})
7a	5.31 (s, CH)	-157.6 (m, 2 F, F_{meta}), -151.7 (tt, J_{FF} 20, 3, 1 F, F_{para}), -95.6 (m, 2 F, F_{ortho})
8a	Isomer 1 5.33 (s, 5 H, CH), 7.01 (tt, J_{HF} 9.2, 7.2, 1 H, $\text{C}_6\text{F}_4\text{H}$) Isomer 2 5.33 (s, 5 H, CH), 7.62 (m, 1 H, $\text{C}_6\text{F}_4\text{H}$)	Isomer 1 -157.55 (m, 2 F, F_{meta} of C_6F_5), -151.70 (tt, J_{FF} 20, 3, 1 F, F_{para} of C_6F_5), -135.16 (m, 2 F, F_{meta} of $\text{C}_6\text{F}_4\text{H}$), -97.21 (m, 1 F, F_{ortho} of $\text{C}_6\text{F}_4\text{H}$), -95.56 (m, 2 F, F_{ortho} of C_6F_5) Isomer 2 -157.39 (m, 2 F, F_{meta} of C_6F_5), -154.21 (m, 1 F, F_{para} of $\text{C}_6\text{F}_4\text{H}$), -151.95 (m, 1 F, F_{meta} of $\text{C}_6\text{F}_4\text{H}$), -151.47 (tt, J_{FF} 20, 3, 1 F, F_{para} of C_6F_5), -136.70 (m, 1 F, F_{meta} of $\text{C}_6\text{F}_4\text{H}$), -95.94 (m, 1 F, F_{ortho} of $\text{C}_6\text{F}_4\text{H}$), -95.21 (m, 2 F, F_{ortho} of C_6F_5)
8b	5.27 (s, 5 H, CH), 6.88–6.99 (m, 2 H, $\text{C}_6\text{F}_4\text{H}$, $\text{C}_6\text{F}_3\text{H}_2$), 7.81 (ddd, J_{HF} 11.3, 9.5, 5.1, 1 H, $\text{C}_6\text{F}_3\text{H}_2$)	-144.50 (m, 1 F, F^5 of $\text{C}_6\text{F}_3\text{H}_2$), -140.11 (m, 2 F, F_{meta} of $\text{C}_6\text{F}_4\text{H}$), -138.08 (m, 1 F, F^4 of $\text{C}_6\text{F}_3\text{H}_2$), -101.45 (m, 2 F, F_{ortho} of $\text{C}_6\text{F}_4\text{H}$), -77.20 (m, 1 F, F^2 of $\text{C}_6\text{F}_3\text{H}_2$)
9a	4.86 (br s, 1 H, CH), 4.97 (br s, 1 H, CH), 5.28 (br s, 1 H, CH), 5.74 (br s, 1 H, CH), 5.75 (s, 5 H, CH)	-164.56 (m, 2 F, F_{meta}), -159.51 (t, J_{FF} 20, 1 F, F_{para}), -100.43 (m, 2 F, F_{ortho})
9b	4.87 (br s, 1 H, CH), 4.99 (br s, 1 H, CH), 5.28 (br s, 1 H, CH), 5.74 (br s, 1 H, CH), 5.76 (s, 5 H, CH), 6.85 (tt, J_{HF} 9.4, 7.4, 1 H, $\text{C}_6\text{F}_4\text{H}$)	-142.41 (m, 2 F, F_{meta}), -102.38 (m, 2 F, F_{ortho})

^a All ^1H and ^{19}F NMR spectra at 298 K in CDCl_3 , except where indicated. Spectra for complexes **7a**, **7b** and **8a**, **8b** recorded on a Bruker AMX 500 spectrometer; those for **6a**, **6b** and **9a**, **9b** on a Bruker AC 200 spectrometer.

**Scheme 5** Products of UV irradiation of (i) $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ and (ii) complex **6a** in $\text{C}_6\text{F}_5\text{H}$.

very similar, it is possible nevertheless that the two CO resonances expected for the *cis* isomer are almost coincident. A full assignment of the H, F and C nuclei of the fluoroaryl groups was achieved by a combination of multinuclear NMR, ^{19}F - ^{19}F COSY, ^1H - $\{^{19}\text{F}\}$ and ^{19}F - $\{^{19}\text{F}\}$ selective decoupling NMR experiments (Table 1).²²

2 Photolysis of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ in pentafluorobenzene and 1,2,4,5-tetrafluorobenzene

The reactions of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ with $\text{C}_6\text{F}_5\text{H}$ and 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ were carried out in order to test whether, instead of the activation of C–H or C–F bonds, the η^2 co-ordination of the partially fluorinated arene can occur in the way that we have found for the reaction of $[\text{Re}(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})_3]$ (R = H or Me) with hexafluorobenzene.²³

Five compounds were identified from the reaction mixture on UV irradiation of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ in neat $\text{C}_6\text{F}_5\text{H}$ at room temperature for 1 h (Scheme 5, Table 2). As in the previous case,

the main reaction product is the hydride complex *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}_6\text{F}_5)\text{H}]$ **6a**. Since it could not be separated efficiently from the unchanged tricarbonyl complex, the reaction mixture was treated with CHBr_3 in order to transform the hydride **6a** into *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}_6\text{F}_5)\text{Br}]$. This compound was separated by column chromatography from the other reaction products and isolated as an analytically pure sample and characterized by spectroscopy (Experimental section) and X-ray crystallography.²⁴ The reaction of the bromo complex with NaBH_4 yielded the hydride **6a** directly in good yield (Scheme 4). The hydride resonance of complex **6a** in the ^1H NMR spectrum yields a triplet at δ -9.18, due to coupling of the hydride to the *ortho* fluorine atoms of the C_6F_5 ligand. Once again, the *trans* orientation of the CO groups was demonstrated from the IR and ^{13}C NMR spectra.

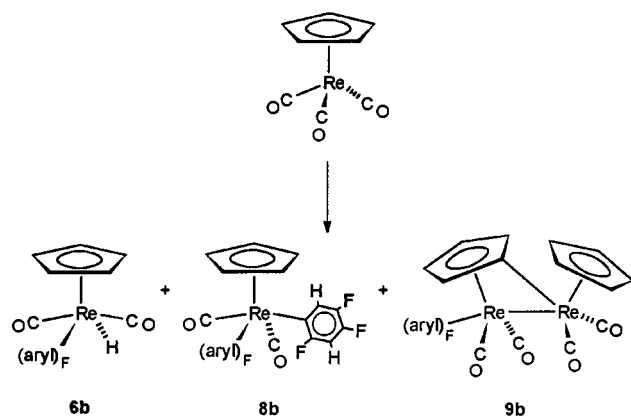
Minor products in this reaction were the bis(aryl)_F derivative $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}_6\text{F}_5)_2]$ **7a** and the two isomers of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_4\text{H})]$ **8a**, which could not be separated. A full assignment of the aromatic proton and fluorine nuclei of **7a**

and **8a** was achieved by selective proton and ^{19}F decoupling of ^{19}F NMR spectra and ^{19}F - ^{19}F COSY spectroscopy (Table 2).²² A ratio of 67:27:6 estimated from ^1H and ^{19}F NMR for **8a** (isomer 1):**8a** (isomer 2):**7a** indicates that the intermolecular activation of a C–F bond in the *para* position (isomer 1) is more favourable than in the *ortho* position (isomer 2) of the pentafluorobenzene. The presence of traces of **7a** indicated that the intermolecular C–H bond activation of a second molecule of $\text{C}_6\text{F}_5\text{H}$ also occurs but to a much lesser extent.

As in the case of **3a**, complex **7a** was prepared as an analytically and spectroscopically pure sample by treating $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}_2]$ with $[\text{Cu}(\text{C}_6\text{F}_5)]$, eqn. (1). The stereochemistry of **7a** was assigned as *trans* since the higher wavenumber CO absorption in the IR spectrum is now the less intense of the pair. Based on this result, we believe that **8a** also adopts a *trans* orientation of the CO groups.

The last product, formed in the reaction of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ and $\text{C}_6\text{F}_5\text{H}$ (Scheme 5), could be isolated with care as a dark red, air-stable solid in very low yield (about 1%). The mass spectrum of this compound exhibited peaks at m/z 782 and 754 (molecular ion M^+ and $\text{M}^+ - \text{CO}$, respectively) with their pattern consistent with the presence of two rhenium atoms. The IR spectrum of this air-stable compound, in THF solution, is complex, suggesting the presence of at least four terminal CO groups (Experimental section). The ^1H NMR spectrum showed five singlets in the δ 4.80–5.80 region (Table 2), which are consistent with one cyclopentadienyl ligand co-ordinated in an η^5 fashion, and a second cyclopentadienyl co-ordinated in an unusual $\mu\text{-}\eta^1\text{:}\eta^5$ form.²⁵ The ^{19}F NMR spectrum showed the resonances expected for a C_6F_5 ligand. These features allow us to assign the product as the complex $[\text{Re}_2(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\text{CO})_4(\text{C}_6\text{F}_5)]$ **9a**. The small amount (5 mg) of this complex available precludes us from measuring the ^{13}C NMR spectrum or obtaining elemental analysis.

Very similar photochemical behaviour to that already described was observed for $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ when irradiated in neat 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ (Scheme 6). The major product



Scheme 6 Products of UV irradiation of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ in 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$, $(\text{aryl})_{\text{F}} = 2,3,5,6\text{-C}_6\text{F}_4\text{H}$.

was again the hydride complex *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(2,3,5,6\text{-C}_6\text{F}_4\text{H})\text{H}]$ **6b** (Table 2 and Experimental section). The bis(aryl)_F complex *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(2,3,5,6\text{-C}_6\text{F}_4\text{H})(2,4,5\text{-C}_6\text{F}_3\text{H}_2)]$ **8b** was formed as a result of a C–F bond activation of a second molecule of tetrafluorobenzene; this is the only isomer possible due to the symmetry of 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$. However, the bis(aryl)_F derivative produced by the C–H bond activation of a second molecule of tetrafluorobenzene was not detected.

The dark red binuclear complex $[\text{Re}_2(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\text{CO})_4(2,3,5,6\text{-C}_6\text{F}_4\text{H})]$ **9b** could be isolated in 2% yield in this case and was fully characterized by spectroscopy, elemental analysis (Table 2 and Experimental section) and X-ray crystallography (see below).

Table 3 Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[\text{Re}_2(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\text{CO})_4(2,3,5,6\text{-C}_6\text{F}_4\text{H})]$ **9b**

Re(1)–Re(2)	3.0258(7)	Re(2)–Re(1)–C(1)	96.9(4)
Re(1)–C(1)	1.91(1)	Re(2)–Re(1)–C(2)	80.9(4)
Re(1)–C(2)	1.95(2)	C(1)–Re(1)–C(2)	100.2(6)
Re(1)–C(11)	2.19(1)	Re(2)–Re(1)–C(11)	164.3(3)
Re(1)–C(21)	2.16(1)	C(1)–Re(1)–C(11)	88.9(5)
Re(1)–C(22)	2.31(1)	C(2)–Re(1)–C(11)	83.7(5)
Re(1)–C(23)	2.33(1)	Re(2)–Re(1)–C(21)	43.2(3)
Re(1)–C(24)	2.29(1)	C(1)–Re(1)–C(21)	118.2(5)
Re(1)–C(25)	2.23(1)	C(2)–Re(1)–C(21)	111.9(5)
Re(2)–C(3)	1.91(1)	C(11)–Re(1)–C(21)	143.8(4)
Re(2)–C(4)	1.90(1)	Re(1)–Re(2)–C(3)	78.0(4)
Re(2)–C(21)	2.07(1)	Re(1)–Re(2)–C(4)	110.3(4)
Re(2)–C(31)	2.31(1)	C(3)–Re(2)–C(4)	81.3(6)
Re(2)–C(32)	2.29(1)	Re(1)–Re(2)–C(21)	45.6(3)
Re(2)–C(33)	2.33(1)	C(3)–Re(2)–C(21)	111.8(5)
Re(2)–C(34)	2.31(1)	C(4)–Re(2)–C(21)	85.8(5)
Re(2)–C(35)	2.27(1)	Re(1)–C(1)–O(1)	176.0(12)
C(21)–C(22)	1.46(2)	Re(1)–C(2)–O(2)	176.3(12)
C(21)–C(25)	1.45(2)	Re(2)–C(3)–O(3)	173.0(13)
C(22)–C(23)	1.40(2)	Re(2)–C(4)–O(4)	178.4(10)
C(23)–C(24)	1.43(2)	Re(1)–C(11)–C(12)	121.4(9)
C(24)–C(25)	1.44(2)	Re(1)–C(11)–C(16)	124.0(9)
		Re(1)–C(21)–Re(2)	91.2(4)

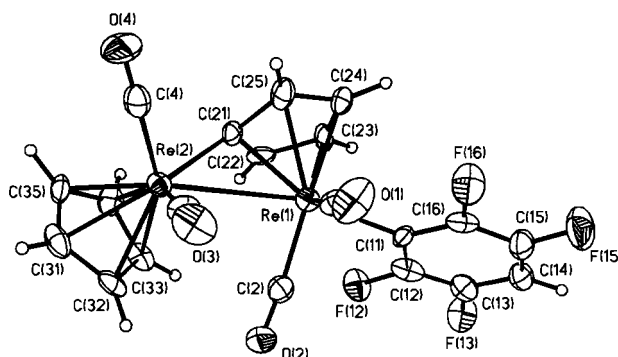


Fig. 1 View of the structure of $[\text{Re}_2(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\text{CO})_4(2,3,5,6\text{-C}_6\text{F}_4\text{H})]$ **9b**.

Since UV irradiation of a pure sample of the hydrido complexes **6a** and **6b** in the corresponding partially fluorinated benzene produces the same minor products as those already described, we conclude that the bis(aryl)_F complexes **7a**, **8a** and **8b**, and the binuclear species **9a** and **9b**, are secondary photoproducts.

3 Crystal and molecular structure of complex **9b**

The structure of $[\text{Re}_2(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\text{CO})_4(2,3,5,6\text{-C}_6\text{F}_4\text{H})]$ **9b** consists of an $\text{Re}(\eta^5\text{-C}_5\text{H}_4)(\text{CO})_2(\text{C}_6\text{F}_4\text{H})$ moiety linked to a $\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ unit via an Re–Re bond of 3.0258(7) Å and a cyclopentadienyl group which is bonded η^5 to Re(1) and η^1 to Re(2) (Fig. 1, Table 3). The bridging cyclopentadienyl unit is tilted such that $\text{Re}(1)\text{--}C(21)\text{--}Re(2)$ is close to a right angle [91.2(4)°]. The $\text{Re}(1)\text{--}C(21)$ distance at 2.16(1) Å is the shortest of those linking the ($\eta^5\text{-C}_5\text{H}_4$) unit to Re(1) but is longer than $\text{Re}(2)\text{--}C(21)$ [2.07(1) Å] which links the same cyclopentadienyl unit to the second rhenium atom via an ($\eta^1\text{-C}_5\text{H}_4$) interaction. The bond angles at both Re(1) and Re(2) are considerably distorted from those typical of a four-legged piano-stool (Table 3). For instance, the $\text{C}_6\text{F}_4\text{H}$ unit lies almost in line with the Re–Re bond [$\text{Re}(2)\text{--}Re(1)\text{--}C(11)$ 164.3(3)°]. The two $\{\text{Re}(\text{CO})_2\}$ units are twisted with respect to one another: the torsional angles $C(1)\text{--}Re(1)\text{--}Re(2)\text{--}C(4)$ and $C(2)\text{--}Re(1)\text{--}Re(2)\text{--}C(3)$ are 62.7(6) and 85.9(6)°, respectively. If we define the midpoints of the vectors $O(1)\text{--}O(2)$ and $O(3)\text{--}O(4)$ as X(1A) and X(1B), then the angle between the two $\{\text{Re}(\text{CO})_2\}$ units is given approximately by the torsion angle $X(1A)\text{--}Re(1)\text{--}Re(2)\text{--}X(1B)$ which is 73.0°.

Discussion

The $\{\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\}$ and $\{\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}$ fragments are often generated photochemically from the corresponding tricarbonyl or dicarbonyl(dinitrogen) complexes.²⁶ None of these dicarbonyl moieties undergoes C–H activation reactions with benzene. Instead, complexes such as $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\eta^2\text{-C}_6\text{H}_6)]$ and $[\text{Re}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\text{CO})_4(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ are formed in which the benzene co-ordinates without C–H bond breaking.²⁷ We have shown earlier that $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ reacts photochemically with hexafluorobenzene to form the fulvene complex **2a** by combined C–F and C–H bond insertion.^{12,19} In contrast $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ reacts to form the coordination complex $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\eta^2\text{-C}_6\text{F}_6)]$.^{12,23} In the current paper we have demonstrated that the dominant photochemical reaction of pentafluorobenzene and 1,2,4,5-tetrafluorobenzene with both $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ and $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ is C–H bond activation to form the hydrido complexes $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2(\text{aryl})_F\text{H}]$ **1a**, **1b**, **6a**, **6b** (R = H or Me, $(\text{aryl})_F = \text{C}_6\text{F}_5$ or 2,3,5,6- $\text{C}_6\text{F}_4\text{H}$). The complex **1a** has also been synthesized independently.

The photochemical conversion of $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3]$ into $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2(\text{C}_6\text{F}_5)\text{H}]$ in yields higher than 70% invites questions as to why this reaction is efficient whereas neither the $\text{Re}(\eta^2\text{-C}_6\text{F}_5\text{H})$ product nor the C–F activation product is formed. As indicated above the corresponding reactions of benzene do not result in C–H activation. According to Bryndza *et al.*²⁸ the strengths of metal–carbon bonds correlate with the strengths of the corresponding C–H bonds. Since the C–H bond of $\text{C}_6\text{F}_5\text{H}$ (477 kJ mol⁻¹) is stronger than that of benzene (460 kJ mol⁻¹),²⁹ we may expect the Re– C_6F_5 bond to be stronger than the Re– C_6H_5 bond.²⁸ We therefore postulate that the formation of the C–H activation product rather than $\text{Re}(\eta^2\text{-C}_6\text{F}_5\text{H})$ complex may be assisted by the thermodynamic stability of the product. Recent calculations on rhodium and osmium complexes suggest that C–F activation products may have comparable or greater stability than C–H activation products, but that there may be a much higher barrier to their formation.¹⁸

In addition to the hydride complexes, several other minor products are formed. Secondary photolysis of the $\eta^5\text{-C}_5\text{Me}_5$ complexes **1a** and **1b** generates the fulvene complexes **2a** and **2b** by loss of hydrogen. The bis(pentafluorophenyl) complex **3a** is formed by photochemical reaction of the fulvene complex **2a** with pentafluorobenzene in a second C–H activation step. Small quantities of a series of C–F bond activation products of the type $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_4\text{H})]$ (R = H **8a** or Me **4a**) are formed by secondary reaction of the hydrides, **6a** and **1a**, respectively, with pentafluorobenzene. Similarly, the C–F bond activation products **4b** and **8b** are formed from the hydrides **1b** and **6b** with symmetric tetrafluorobenzene. It is intriguing that C–F bond activation is competitive with C–H bond activation in the reaction of $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2(\text{aryl})_F\text{H}]$ but not in the reactions of $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3]$ (R = H or Me). Finally, we note the dinuclear cyclopentadienyl complexes **9a** and **9b**, apparently formed by insertion of a $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ moiety into a C–H bond of **6a** or **6b** and subsequent elimination of hydrogen. The formation of the bridging $(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)$ ligand is little documented in rhenium chemistry but familiar in the early transition metal chemistry. Wenzel and Bergman²⁵ described the crystal structure of $[\text{Re}_2(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-CH}_2\text{PMe}_2)(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\text{PMe}_3)_3\text{H}_2]$ formed by decomposition of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_3)\text{H}]$. Pasman and Snel³⁰ investigated the formation of rhenocene dimers including one assigned as $[\text{Re}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)_2]$. Hoxmeier *et al.*³¹ showed that $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}]$ reacts with $[\text{Mn}(\text{CO})_5(\text{CH}_3)]$ to form $[\text{H}(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_4]$. The geometry of Re(2) in complex **9b** is closely mirrored in the molybdenum complex $[(\text{OC})_2(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]$.³²

Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. All solvents were purified and dried by conventional methods, and distilled under nitrogen prior to use. The precursors $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3]$ (R = H or Me) were prepared according to the method of Gladysz and co-workers.³³ The complex *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Cl}_2]$ was prepared by photochemical isomerization of the corresponding *cis* isomer;^{21,34} *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}_2]$ was prepared using an analogous procedure. Pentafluorobenzene (99%) and 1,2,4,5-tetrafluorobenzene (99%) from Aldrich were degassed with three freeze–pump–thaw cycles prior to use and stored under nitrogen. Infrared spectra were recorded in solution (NaCl cell) on a Perkin-Elmer FT-1605 spectrophotometer, ¹H, ¹⁹F and ¹³C NMR spectra on Bruker AC 200, DRX 400 (¹⁹F–¹⁹F and selective proton/fluorine decoupling experiments) and AMX 500 instruments. All ¹H NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances (CDCl_3 , δ 7.27; C_6D_6 , δ 7.13), ¹³C NMR chemical shifts to solvent peaks (CDCl_3 , δ 77.0; C_6D_6 , δ 128.0) and ¹⁹F NMR spectra to internal C_6F_6 at δ –162.9. The assignment of ¹⁹F resonances and F–F and F–H coupling constants was assisted by compilations of data for fluoroaromatic compounds.³⁵ Coupling assignments are indicated, where known. Mass spectra (EI, 70 eV) were obtained at the Centro de Instrumentación, Universidad de Santiago, Santiago, Chile, and the Chemistry Department of the University of York (VG Autospec). Elemental analyses were obtained at the Centro de Instrumentación, Pontificia Universidad Católica de Chile, Santiago, Chile.

Photolysis of $[\text{Re}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3]$ (R = H or Me) in fluorinated arene solvents: general procedure

All reactions were carried out under nitrogen at room temperature in a quartz tube (20 cm long, 1.5 cm external diameter) fitted with a rubber septum. Solutions of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ (300 mg, 0.74 mmol) and $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ (300 mg, 0.89 mmol) in the fluorinated solvent (24 cm³) were irradiated at 300 nm, for 3 and 1 h, respectively. Irradiation was carried out in a Rayonet RPR-100 photochemical reactor. Reactions with $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ resulted in the formation of yellow solutions, those with $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ resulted in dark orange solutions. After irradiation, the solvent was removed under vacuum to afford yellow and dark red solids, respectively. The residues were treated with CHBr_3 using the procedure described below, with the exception of the residue obtained after irradiation of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ in $\text{C}_6\text{F}_5\text{H}$.

Reaction of photolysed mixtures with bromoform: general procedure

The typical procedure involved dissolution of the photolysis residue in THF (15 cm³), addition of CHBr_3 (0.30 cm³, 0.87 g, 3.4 mmol) and stirring under nitrogen at room temperature for 5–8 h. Solvent was removed under vacuum, and the resulting orange-red solid chromatographed on neutral alumina.

Photolysis of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ in $\text{C}_6\text{F}_5\text{H}$. After irradiation, the solvent was transferred under vacuum, and the resulting yellow solid carefully extracted at 4 °C with successive portions of 5, 5, 2, 2 and 1 cm³ of hexane. The light brown residue which corresponded to *trans*- $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)\text{H}]$ **1a** was crystallized from hexane at –10 °C (yield 92 mg, 0.117 mmol, 46%). The hexane extract was chromatographed on neutral alumina. Slow elution with hexane moved unchanged $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ (152 mg, 0.38 mmol), 5 mg of a 1.7:1 mixture (by ¹H and ¹⁹F NMR integration) of *cis*- $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)_2]$ **3a**, and $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)(2,3,5,6\text{-C}_6\text{F}_4\text{H})]$ **4a**, and finally the fulvene complex $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$ **2a** (14 mg, 0.020 mmol, 5.5%).

1a: IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2024m and 1959s. ^{13}C - $\{^1\text{H}\}$ NMR (C_6D_6) δ 11.40 (s, CH_3), 100.55 (s, C_5Me_5), 195.62 (s, CO), C_{ipso} and CF aromatic carbons not observed.

3a: IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2052s and 1986m. ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3) δ 10.41 (s, CH_3), 98.37 (tm, J_{CF} 39, C_{ipso}), 104.35 (s, C_5Me_5), 137.17 (dm, J_{CF} 256, C_6F_5), 139.38 (dm, J_{CF} 251, C_6F_5), 152.26 (dm, J_{CF} 236, C_6F_5) and 188.02 (tm, J_{CF} 5 Hz, CO); mass spectrum (based on ^{187}Re) m/z 712, $[\text{M}]^+$; and 684, $[\text{M} - \text{CO}]^+$.

4a: IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] obscured; mass spectrum (based on ^{187}Re) m/z 694, $[\text{M}]^+$; and 666, $[\text{M} - \text{CO}]^+$.

[NEt₄]⁺[Re(η^5 -C₅Me₅)(CO)₂(C₆F₅)⁻ 5. Tetrahydrofuran (25 cm³) was added to a solid mixture of the fulvene complex **2a** (100 mg, 0.18 mmol), NaBH₄ (35 mg, 0.93 mmol) and NEt₄Br (39 mg, 0.18 mmol). Evolution of gas was immediate. The suspension was stirred at room temperature until the IR of the solution showed no evidence for the starting complex and new CO bands were detected at 1860 and 1783 cm⁻¹ (30 min). Solvent was removed under vacuum, and the pale yellow solid dissolved in CH₂Cl₂ (10 cm³) and filtered. The solution was reduced in volume under vacuum to about 3 cm³. Hexane (50 cm³) was added with stirring, and the mixture filtered. The pale yellow solid was washed with hexane (5 cm³) and then dissolved in CH₂Cl₂ (1.5 cm³). A layer of hexanes was slowly poured into the flask. Complex **5** (108 mg, 0.16 mmol, 87%) was isolated as pale yellow scales. IR [CH₂Cl₂, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$]: 1849vs and 1769vs. ^1H NMR (CDCl_3): δ 1.21 (t, 12 H, CH₃ of NEt₄⁺), 1.95 (s, 15 H, CH₃) and 3.12 (q, 8 H, CH₂ of NEt₄⁺). ^{19}F NMR (CDCl_3): δ -168.03 (m, 2F_{meta}), -167.18 (m, F_{para}) and -104.94 (m, 2F_{ortho}). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 7.30 (s, CH₃ of NEt₄⁺), 10.92 (s, CH₃), 52.42 (s, CH₂ of NEt₄⁺), 94.78 (s, C₅Me₅), 214.27 (s, CO), and CF aromatic carbons not observed.

trans-[Re(η^5 -C₅Me₅)(CO)₂(C₆F₅)H] 1a. To a solution of complex **5** (100 mg, 0.148 mmol) in CH₂Cl₂ (10 cm³) was added HCl solution (1 mol dm⁻³) in diethyl ether (0.15 cm³, 0.15 mmol). The mixture was stirred at room temperature for 5 min. The IR spectrum of the solution showed the total disappearance of complex **5** and the presence of absorptions due to **1a** at 2014 and 1940 cm⁻¹. The solvent was removed under vacuum. Diethyl ether (10 cm³) was added to the residue, and the mixture filtered. The solvent was pumped off to afford **1a** as a pale yellow solid in 95% yield (77 mg, 0.14 mmol).

cis-[Re(η^5 -C₅Me₅)(CO)₂(C₆F₅)₂] 3a. To a solution of **trans**-[Re(η^5 -C₅Me₅)(CO)₂Cl₂] (110 mg, 0.24 mmol) in THF (10 cm³) was added, *via* syringe, a solution (1.5 cm³) of [Cu(C₆F₅)₂] [prepared from magnesium turnings (0.26 g, 11 mmol), chloropentafluorobenzene (1.3 cm³, 10 mmol) and CuBr·Me₂S (2.47 g, 12 mmol) in THF (12 cm³)]. After 2 h of stirring at room temperature the IR spectrum of the mixture showed no starting material and new CO absorptions bands at 2047 and 1980 cm⁻¹. Solvent was removed under vacuum, and the residue chromatographed on neutral alumina. Elution with hexane afforded complex **3a** as a pale yellow solid after pumping off the solvent (131 mg, 0.184 mmol, 77%) (Found: C, 40.67; H, 2.06. Calc. for C₂₄H₁₅F₁₀O₂Re: C, 40.51; H, 2.12%).

[Re(η^5 -C₅Me₅)(CO)₃] + 1,2,4,5-C₆F₄H₂ + CHBr₃. Following the general procedure, slow elution with hexane moved unchanged [Re(η^5 -C₅Me₅)(CO)₃] (153 mg, 0.38 mmol). Hexane-CH₂Cl₂ (15:1) moved pale yellow *cis*-[Re(η^5 -C₅Me₅)(CO)₂(2,3,5,6-C₆F₄H)(2,4,5-C₆F₃H₂)] **4b** (yield 13 mg, 0.02 mmol, 5.5%). Hexane-CH₂Cl₂ (10:1) moved the yellow fulvene complex [Re(η^6 -C₅Me₄CH₂)(CO)₂(2,3,5,6-C₆F₄H)] **2b** (yield 11 mg, 0.02 mmol, 6%). Finally, hexane-CH₂Cl₂ (5:1) moved orange *trans*-[Re(η^5 -C₅Me₅)(CO)₂(2,3,5,6-C₆F₄H)Br] (135 mg, 0.223 mmol, 61%).

2b: IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2006vs and 1939vs; ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3 , major isomer) δ 9.62 (s, CH₃), 9.77 (s, CH₃), 47.38 (s, CH₂), 97.20 (s, C₅Me₄CH₂), 107.16 (s, C₅Me₄CH₂), 107.38 (s, C₅Me₄CH₂), 198.52 (s, CO) and aromatic carbons not observed; mass spectrum (based on ^{187}Re) m/z 526, $[\text{M}]^+$; 498, $[\text{M} - \text{CO}]^+$; and 470, $[\text{M} - 2\text{CO}]^+$.

4b: IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2046vs and 1957s. ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3) δ 9.92 (s, CH₃), 103.44 (s, C₅Me₅), 104.36 (t, J_{CF} 23, C₆F₄H), 104.91 (dd, J_{CF} 39, 19, C₆F₃H₂), 107.94 (dm, J_{CF} 34, C_{ipso} of C₆F₃H₂), 108.86 (tm, J_{CF} 39, C_{ipso} of C₆F₄H), 131.15 (dd, J_{CF} 16, 13, C₆F₃H₂), 145.6 (dm, J_{CF} 235, C₆F₄H), 147.0 (dm, J_{CF} 258, C₆F₃H₂), 149.14 (dt, J_{CF} 249, 14, C₆F₃H₂), 152.20 (dm, J_{CF} 235, C₆F₄H), 163.7 (dm, J_{CF} 238 Hz, C₆F₃H₂) and 193.28 (br s, CO); mass spectrum (based on ^{187}Re) m/z 658, $[\text{M}]^+$; 630, $[\text{M} - \text{CO}]^+$; and 602, $[\text{M} - 2\text{CO}]^+$.

trans-[Re(η^5 -C₅Me₅)(CO)₂(2,3,5,6-C₆F₄H)Br]: mp 180–181 °C (decomp.); IR [CH₂Cl₂, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2045s and 1973vs; ^1H NMR (CDCl_3) δ 1.88 (s, 15 H, CH₃) and 6.88 (tt, 1 H, J_{HF} 9.2, 7.5 Hz, C₆F₄H); ^{19}F NMR (CDCl_3) δ -140.14 (m, 2F_{ortho}) and -103.82 (m, 2F_{meta}); ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3) δ 10.29 (s, CH₃), 104.25 (s, C₅Me₅), 104.36 (t, J_{CF} 23 Hz, CH of C₆F₄H), 189.66 (s, CO) and the other aromatic carbons not observed; mass spectrum (based on ^{187}Re , ^{79}Br) m/z 606, $[\text{M}]^+$; 578, $[\text{M} - \text{CO}]^+$; and 550, $[\text{M} - 2\text{CO}]^+$ (Found: C, 35.80; H, 2.70. Calc. for C₁₈H₁₆BrF₄O₂Re: C, 35.65; H, 2.66%).

[Re(η^5 -C₅H₅)(CO)₃] + C₆F₅H + CHBr₃. Following the general procedure above, slow elution with hexane moved unchanged [Re(η^5 -C₅H₅)(CO)₃] (134 mg, 0.40 mmol). Hexane-CH₂Cl₂ (9:1) moved a 67:26:6 mixture (by ^1H NMR integration) of [Re(η^5 -C₅H₅)(CO)₂(C₆F₅)(2,3,5,6-C₆F₄H)] **8a** (isomer 1), [Re(η^5 -C₅H₅)(CO)₂(C₆F₅)(2,3,4,5-C₆F₄H)] **8a** (isomer 2), and [Re(η^5 -C₅H₅)(CO)₂(C₆F₅)₂] **7a** (15 mg). Hexane-CH₂Cl₂ (6:1) moved orange *trans*-[Re(η^5 -C₅H₅)(CO)₂(C₆F₅)Br] (170 mg, 0.31 mmol, 62%). Finally, hexane-CH₂Cl₂ (2:1) moved dark red [(OC)₂(η^5 -C₅H₅)Re(μ - η^1 : η^5 -C₅H₄)Re(CO)₂(C₆F₅)₂] **9a** (5 mg, 0.006 mmol, 1%).

7a: IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] obscured; mass spectrum (based on ^{187}Re) m/z 642, $[\text{M}]^+$; 614, $[\text{M} - \text{CO}]^+$; and 586, $[\text{M} - 2\text{CO}]^+$.

8a (isomer 1 + isomer 2): IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2066m and 2004s; mass spectrum (based on ^{187}Re) m/z 624, $[\text{M}]^+$; 596, $[\text{M} - \text{CO}]^+$; and 568, $[\text{M} - 2\text{CO}]^+$.

9a: IR [CH₂Cl₂, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$]: 2014s, 1968s, 1922m and 1918m; mass spectrum (based on $^{187}\text{Re}/^{187}\text{Re}$) m/z 782, $[\text{M}]^+$; and 754, $[\text{M} - \text{CO}]^+$.

trans-[Re(η^5 -C₅H₅)(CO)₂(C₆F₅)Br]: mp 192–194 °C (decomp.); IR [CH₂Cl₂, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2063s and 1997vs; ^1H NMR (CDCl_3) δ 5.54 (s, CH); ^{19}F NMR (CDCl_3) δ -162.13 (m, 2F_{meta}), -156.05 (tt, J_{FF} 20, 3 Hz, 1F_{para}) and -99.89 (m, 2F_{ortho}); ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3) δ 91.70 (s, C₅H₅), 185.23 (s, CO) and aromatic carbons not observed; mass spectrum (based on ^{187}Re) m/z 554, $[\text{M}]^+$; 526, $[\text{M} - \text{CO}]^+$; 498, $[\text{M} - 2\text{CO}]^+$; and 475, $[\text{M} - \text{Br}]^+$ (Found: C, 28.25; H, 1.01. Calc. for C₁₃H₅BrF₅O₂Re: C, 28.17; H, 0.91%).

trans-[Re(η^5 -C₅H₅)(CO)₂(C₆F₅)₂] **7a.** A procedure similar to that described for the synthesis of complex **3a** was used, except that elution with hexane-CH₂Cl₂ (4:1) afforded **7a** as a pale yellow solid in 72% yield (Found: C, 35.48; H, 0.77. Calc. for C₁₉H₅F₁₀O₂Re: C, 35.58; H, 0.78%).

[Re(η^5 -C₅H₅)(CO)₃] + 1,2,4,5-C₆F₄H₂ + CHBr₃. Following the general procedure, slow elution with hexane moved unchanged [Re(η^5 -C₅H₅)(CO)₃] (153 mg, 0.45 mmol). Hexane-CH₂Cl₂ (8:1) moved pale yellow *trans*-[Re(η^5 -C₅H₅)(CO)₂(2,3,5,6-C₆F₄H)(2,4,5-C₆F₃H₂)] **8b** (15 mg, 0.02 mmol, 6%). Hexane-CH₂Cl₂ (5:1) moved orange *trans*-[Re(η^5 -C₅H₅)(CO)₂(2,3,5,6-C₆F₄H)Br] (176 mg, 0.33 mmol, 75%). Finally, hexane-

CH₂Cl₂ (2:1) moved dark red [(OC)₂(η⁵-C₅H₅)Re(μ-η¹:η⁵-C₅H₄)Re(CO)₂(2,3,5,6-C₆F₄H)] **9b** (6 mg, 0.008 mmol, 2%).

8b: IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2058s and 1983vs; ¹³C-¹H} NMR (CDCl₃) δ 90.27 (s, C₅H₅), 95.84 (dm, J_{CF} 34, C_{ipso} of C₆F₃H₂), 97.22 (tm, J_{CF} 40, C_{ipso} of C₆F₄H), 104.13 (dd, J_{CF} 38, 20, C₆F₃H₂), 104.97 (t, J_{CF} 23, C₆F₄H), 132.93 (dd, J_{CF} 17, 12, C₆F₃H₂), 145.3 (dm, J_{CF} 236, C₆F₄H), 147.2 (dm, J_{CF} 220, C₆F₃H₂), 149.6 (dt, J_{CF} 250, 14, C₆F₃H₂), 152.07 (dm, J_{CF} 250, C₆F₄H), 163.78 (ddd, J_{CF} 234, 8, 2, C₆F₃H₂) and 190.23 (pseudo q, J_{CF} 5 Hz, CO). Mass spectrum (based on ¹⁸⁷Re): m/z 588, [M]⁺; 560, [M - CO]⁺; and 532, [M - 2CO]⁺ (Found: C, 38.43; H, 1.31. Calc. for C₁₉H₈F₇O₂Re: C, 38.85; H, 1.37%).

9b: IR [CH₂Cl₂, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2012s, 1966s, 1925m and 1914m; ¹³C-¹H} NMR (CDCl₃) δ 80.11 (s, C₅H₄), 90.11 (s, C₅H₅), 99.06 (s, C₅H₄), 101.37 (s, C₅H₄), 103.25 (t, J_{CF} 23, C_{ipso} of C₆F₄H), 105.68 (s, C_{ipso} of C₅H₄), 106.23 (s, C₅H₄), 144.94 (d, J_{CF} 250, C₆F₄H), 151.75 (d, J_{CF} 227 Hz, C₆F₄H), 156.50 (s, C₆F₄H), 194.79 (br s, CO), 195.82 (s, CO), 196.78 (br s, CO) and 198.84 (s, CO); mass spectrum (based on ¹⁸⁷Re/¹⁸⁷Re) m/z 762, [M]⁺; and 734, [M - CO]⁺ (Found: C, 31.59; H, 1.34. Calc. for C₁₀H₅F₂O₂Re: C, 31.49; H, 1.32%).

trans-[Re(η⁵-C₅H₅)(CO)₂(2,3,5,6-C₆F₄H)Br]: mp 176 °C (decomp.); IR [CH₂Cl₂, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2062s and 1994vs; ¹H NMR (CDCl₃) δ 5.54 (s, 5H, CH) and 6.92 (tt, 1 H, J_{HF} 9.2, 7.6 Hz, C₆F₄H). ¹⁹F NMR (CDCl₃) δ -139.90 (m, 2F_{meta}) and -101.44 (m, 2F_{ortho}); ¹³C-¹H} NMR (CDCl₃) δ 91.83 (s, C₅H₅), 104.87 (t, J_{CF} 22 Hz, CH of C₆F₄H), 186.33 (s, CO) and the other aromatic carbons not observed; mass spectrum (based on ¹⁸⁷Re, ⁷⁹Br) m/z 536, [M]⁺; 508, [M - CO]⁺; and 480, [M - 2CO]⁺ (Found: C, 29.18; H, 1.12. Calc. for C₁₃H₆BrF₄O₂Re: C, 29.12; H, 1.13%).

Syntheses of hydride complexes

(a) *trans*-[Re(η⁵-C₅Me₅)(CO)₂(2,3,5,6-C₆F₄H)H] **1b**. To a solution of the bromo complex *trans*-[Re(η⁵-C₅Me₅)(CO)₂(2,3,5,6-C₆F₄H)Br] (100 mg, 0.17 mmol) in THF (20 cm³) was added LiAlH₄ (1 M in THF, 0.22 cm³, 0.22 mmol). The mixture was stirred until decolouration was complete (10 min). An IR spectrum recorded at this time showed the disappearance of the starting complex, and the formation of the anionic [Re(η⁵-C₅Me₅)(CO)₂(2,3,5,6-C₆F₄H)]⁻, as indicated by the absorption bands at 1865 and 1747 cm⁻¹. Hydrochloric acid (1 M in diethyl ether, 0.60 cm³, 0.60 mmol) was added, and after 5 min of stirring the IR spectrum showed no evidence for the anionic complex and new bands appeared at 2014 and 1944 cm⁻¹. Solvent was removed under vacuum, and the residue extracted twice with 5 cm³ of hexane-THF (5:1) and filtered. The solvent was pumped off to afford **1b** as a pale yellow solid (78 mg, 0.15 mmol, 90%). IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2024m and 1959s. ¹³C-¹H} NMR (C₆D₆): δ 11.45 (s, CH₃), 100.48 (s, C₅Me₅), 104.67 (t, J_{CF} 24 Hz, CH of C₆F₄H), 195.77 (s, CO), C_{ipso} and CF aromatic carbons not observed.

(b) (η⁵-C₅H₅) Complexes. For the syntheses of the cyclopentadienyl derivatives **6a** and **6b**, treatment of the corresponding bromo complex with an excess of NaBH₄ in THF yielded directly the hydrido complex after a few hours of stirring at room temperature. The reaction was carefully monitored by IR. The solvent was pumped off and the residue extracted several times with hexanes and filtered. The corresponding hydride was isolated as a light yellow microcrystalline solid after evaporation of the filtrate under vacuum.

trans-[Re(η⁵-C₅H₅)(CO)₂(C₆F₅H)] **6a**: yield 78%; IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2040m and 1978s. ¹³C-¹H} NMR (C₆D₆) δ 86.09 (s, C₅H₅), 191.53 (s, CO) and aromatic carbons not observed.

trans-[Re(η⁵-C₅H₅)(CO)₂(2,3,5,6-C₆F₄H)H] **6b**: yield 67%; IR [hexane, $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$] 2040m and 1977s; ¹³C-¹H} NMR (C₆D₆) δ 86.09 (s, C₅H₅), 105.12 (t, J_{CF} 23 Hz, CH of C₆F₄H), 191.83 (s, CO), C_{ipso} and CF aromatic carbons not observed.

Structure determination for complex 9b

Dark red crystals were obtained by layering a CH₂Cl₂ solution of complex **9b** with hexanes.

Crystal data and data collection parameters. C₂₀H₁₀F₄O₄Re₂, $M = 762.69$, monoclinic, space group $P2_1/n$ $a = 7.769(2)$, $b = 19.351(6)$, $c = 12.688(3)$ Å, $\beta = 104.41(2)^\circ$, $U = 1847.6$ Å³ (from 42 reflections, $30 < 2\theta < 32^\circ$, measured at $\pm\omega$), $T = 220$ K, graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å), $Z = 4$, $D_c = 2.74$ g cm⁻³, $F(000) = 1380.48$ (calculated from the scattering factors at $2\theta = 0^\circ$), red block with dimensions $0.19 \times 0.19 \times 0.08$ mm, $\mu = 13.34$ mm⁻¹. An absorption correction was performed by Gaussian integration after refinement of the crystal dimensions and morphology against a set of ψ scans ($T = 0.119\text{--}0.347$).³⁶ Data were collected to $2\theta = 50^\circ$ in ω - θ mode on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device (4171 data, $-9 < h < 8$, $-1 < k < 23$, $0 < l < 15$ comprising 3256 unique data, $R_{\text{int}} = 3\%$).

Structure solution and refinement. The structure was solved by Patterson methods (DIRDIF)³⁷ and refined against F using 2307 data with $F > 4\sigma(F)$ (CRYSTALS).³⁸ Hydrogen atoms were clearly visible in difference maps, but were placed in idealized positions during refinement. All non-H atoms were modelled with anisotropic displacement parameters. At convergence $R = 3.95\%$, $R' = 4.00\%$ and $S = 1.15$ with 272 parameters and a Chebyshev 3-term polynomial weighting scheme. The final difference map extrema were ± 1.4 e Å⁻³.

CCDC reference number 186/1444.

See <http://www.rsc.org/suppdata/dt/1999/2039/> for crystallographic files in .cif format.

Acknowledgements

We would like to thank Universidad Católica de Valparaíso (DGIP 125/782-97) and Fondo Nacional de Ciencias y Tecnología (FONDECYT)-Chile for financial support (grants 1960383 and 7960007). B. O. acknowledges Fundacion Andes for a doctoral fellowship. We also acknowledge the support of EPSRC.

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