Photochemical reactions of $[Re(\eta^5\text{-}C_5R_5)(CO)_3]$ (R = H or Me) with partially fluorinated benzenes: C–H and C–F activation

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UV Irradiation of $[Re(\eta^5\text{-}C_5R_5)(CO)_3]$ (R = Me or H) in the presence of C_6F_5H or $1,2,4,5\text{-}C_6F_4H_2$ effected intramolecular C–H activation, generating the hydrido complexes $trans$-$[Re(\eta^5\text{-}C_5R_5)(CO)_2(Ar)_FH]$ $[(Ar)_F = C_6F_5$ or $2,3,5,6\text{-}C_6F_4H]$ as the principal photochemical products. The identities of the hydrido complexes were confirmed by independent thermal syntheses. The photoreaction of $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ with C_6F_5H also generated the fulvene complex $[Re(\eta^6\text{-}C_5Me_4CH_2)(CO)_2(C_6F_5)]$ **2a** and two bis(aryl) derivatives: cis-$[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)_2]$ **3a** and $[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)(2,3,5,6\text{-}C_6F_4H)]$ **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 $[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)H]$ in C_6F_5H produces **2a**, **3a** and **4a**, while photolysis of **2a** produces only **3a**. The reaction of $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ with $1,2,4,5\text{-}C_6F_4H_2$ gave analogues **2b** and **4b** as minor products. The photoreaction of $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ in C_6F_5H or $1,2,4,5\text{-}C_6F_4H_2$ generated bis(aryl) compounds and the unusual binuclear complexes $[Re_2(\eta^5\text{-}C_5H_5)(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)(CO)_4(Ar)_F]$ as the minor products. The binuclear complex with $(Ar)_F = 2,3,5,6\text{-}C_6F_4H$ 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 $\{Re(CO)_2\}$ 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 C_6F_5H has been achieved with a soluble rhodium complex.[11] In a more complex but related reaction, photolysis of $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ in neat C_6F_6 formed the tetramethylfulvene complex $[Re(\eta^6\text{-}C_5Me_4CH_2)(CO)_2(C_6F_5)]$ 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-$[Ru(dmpe)_2H_2]$ with several fluorinated arenes (C_6F_5H, $1,2,3,4$-$C_6F_4H_2$, and $1,2,3\text{-}C_6F_3H_3$) produces only C–F activation products; an electron-transfer mechanism has been proposed for these reactions.[13] The thermal reaction of $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene) with C_6F_5H, in the presence of triethylphosphine, is close to the $[Ru(dmpe)_2H_2]$ reaction in selectivity for C–F over C–H bond activation.[14] The complex $[Rh(\eta^5\text{-}C_5Me_5)(PMe_3)H_2]$ has also been found to produce a C–F bond activation product selectively in the thermal reaction with C_6F_5H; in this case, a nucleophilic aromatic substitution was indicated as the more plausible mechanism.[15] In contrast, the complexes $[Rh(\eta^5\text{-}C_5Me_5)(PMe_3)(Ph)H]$ and $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(C_2H_4)]$, 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 $\{RhCp'(PMe_3)\}$ (Cp' = $\eta^5\text{-}C_5Me_5$ or $\eta^5\text{-}C_5H_5$) 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 $[Pt(PCy_3)_2]$ (Cy = cyclohexyl) reacts selectively with pentafluorobenzene, $1,3,5\text{-}C_6F_3H_3$ and $1,3\text{-}C_6F_2H_4$ 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, $[Rh(C_5H_5)(PH_3)(\eta^2\text{-}C_6F_2H_4)]$.

In this paper we report that partially fluorinated benzenes (C_6F_5H and $1,2,4,5\text{-}C_6F_4H_2$) react with 16 electron rhenium fragments $[Re(\eta^5\text{-}C_5Me_5)(CO)_2]$ and $[Re(\eta^5\text{-}C_5H_5)(CO)_2]$ (both generated photochemically from the corresponding tricarbonyl complex) to give only the C–H oxidative addition complexes $trans$-$[Re(\eta^5\text{-}C_5R_5)(CO)_2(C_6F_4R')H]$ (R = H or Me; R' = 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 $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ include an unusual dinuclear complex containing a $(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)$ group.

Results

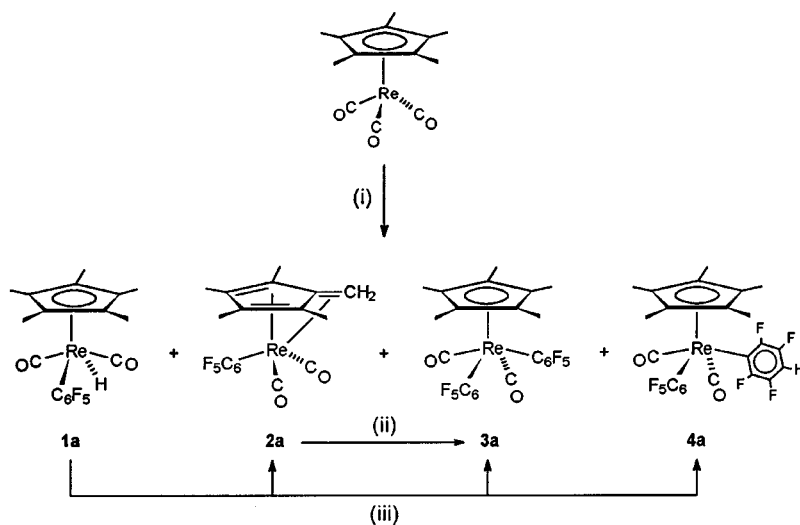### 1 Photoreactions of $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ with pentafluorobenzene and 1,2,4,5-tetrafluorobenzene

UV Irradiation (λ = 300 nm) of $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ in neat C_6F_5H or $1,2,4,5\text{-}C_6F_4H_2$ 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 [Re(η^5-C$_5$Me$_5$)(CO)$_3$] with C$_6$F$_5$H and 1,2,4,5-C$_6$F$_4$H$_2$ ^{a}

Complex	^{1}H	^{19}F
1a (C$_6$D$_6$)	-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$_6$D$_6$)	-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, C$_6$F$_4$H)	-140.05 (m, 2 F, F$_{meta}$), -104.35 (m, 2 F, F$_{ortho}$)
2b	Major isomer	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, C$_6$F$_4$H)	-142.24 (m, 2 F, F$_{meta}$), -106.46 (m, 2 F, F$_{ortho}$)
	Minor isomer	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, C$_6$F$_4$H)	-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, C$_6$F$_4$H)	-162.3 (m), -156.5 (m), -140.01 (m, 2 F, F$_{meta}$ of C$_6$F$_4$H), -104.46 (m, 2 F, F$_{ortho}$ of C$_6$F$_4$H), -102.8 (m)
4b ^{b}	1.70 (s, 15 H, CH$_3$), 6.84–7.00 (m, 2 H, C$_6$F$_4$H, C$_6$F$_3$H$_2$), 7.67 (ddd, J_{HF} 11.5, 9.7, 5.0, 1 H, C$_6$F$_3$H$_2$)	-145.05 (dddd, J_{FF} 20, 14, 13, 6, 1 F, F$_{meta}$ of C$_6$F$_3$H$_2$), -140.06 (m, 2 F, F$_{meta}$ of C$_6$F$_4$H), -138.65 (dddd, J_{FF} 20, 10, 9, 6, 1 F, F$_{para}$ of C$_6$F$_3$H$_2$), -104.12 (br s, 2 F, F$_{ortho}$ of C$_6$F$_4$H), -78.59 (dddd, J_{FF} 14, 8, 6, 5, 1 F, F$_{ortho}$ of C$_6$F$_3$H$_2$)

^{a} All ^{1}H 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} ^{1}H NMR in C$_6$D$_6$ separates overlapping resonances: δ 1.16 (s, 15 H, CH$_3$), 6.40 (tt, J_{HF} 9, 8.8, 1 H, C$_6$F$_4$H), 6.53 (ddd, J_{HF} 10, 8, 7, 1 H, C$_6$F$_3$H$_2$) and 7.40 (ddd, J_{HF} 11.6, 9.7, 5 Hz, 1 H, C$_6$F$_3$H$_2$).

Scheme 1 Products of UV irradiation in C$_6$F$_5$H of (i) [Re(η^5-C$_5$Me$_5$)(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*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)H] **1a**. Careful chromatography of the hexane washings on a neutral alumina column allowed the separation of unchanged [Re(η^5-C$_5$Me$_5$)(CO)$_3$] and three further products, [Re(η^6-C$_5$Me$_4$CH$_2$)(CO)$_2$(C$_6$F$_5$)] **2a** and the mixture of two bis-(fluoroaryl) derivatives: [Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)$_2$] **3a** and [Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)(2,3,5,6-C$_6$F$_4$H)] **4a** (Scheme 1).

The room temperature ^{1}H NMR spectrum of the hydride complex **1a** exhibited a single resonance for the η^5-C$_5$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 ^{1}H 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 [Re(η^6-C$_5$Me$_4$CH$_2$)(CO)$_2$-

[Re(η^5-C$_5$Me$_4$CH$_2$)(CO)$_2$(C$_6$F$_5$)]

2a

(i) NaBH$_4$ (ii) NEt$_4$Br

[NEt$_4$]$^+$ [Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)]$^-$

5

HCl / CH$_2$Cl$_2$

trans-[Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)H]

1a
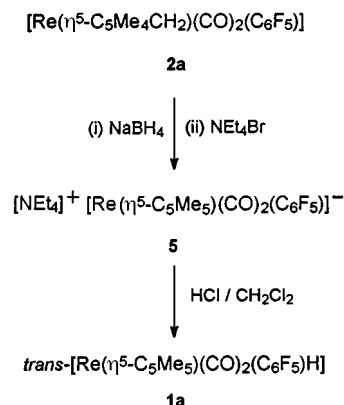
Scheme 2 Thermal synthesis of *trans*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)H].

$(C_6F_5)]$ **2a** was formed in 5.5% yield.[12,19] The presence of a mixture of the bis(aryl)$_F$ complexes $[Re(\eta^5-C_5Me_5)(CO)_2(C_6F_5)_2]$ **3a** and $[Re(\eta^5-C_5Me_5)(CO)_2(C_6F_5)(C_6F_4H)]$ **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 ^{19}F NMR spectrum confirms the conclusion (Table 1). The multiplets at δ −104.5 and −140.0 are assigned to the 2,3,5,6-C_6F_4H ring; similar chemical shifts have been reported for $[Rh(\eta^5-C_5H_5)(PMe_3)(2,3,5,6-C_6F_4H)]$.[16] A further three resonances are almost in the same position as those observed for C_6F_5 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 $[Re(\eta^5-C_5Me_5)(CO)_2X_2]$ (X = Cl or I).[20] The reaction of *trans*-$[Re(\eta^5-C_5Me_5)(CO)_2Cl_2]$ with an excess of $[Cu(C_6F_5)]$ in THF gave complex **3a** in 75% yield as a yellow crystalline solid, eqn. (1).

trans-$(\eta^5$-$C_5R_5)Re(CO)_2Cl_2$ + $2CuC_6F_5$

$\downarrow$ −2CuCl

$(\eta^5$-$C_5R_5)Re(CO)_2(C_6F_5)_2$ (1)

R = Me, *cis* isomer, **3a**

R = H, *trans* isomer, **7a**
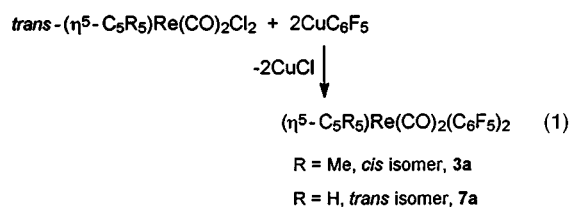
The ^1H and ^{13}C NMR spectra unequivocally indicate the presence of a single compound (Table 1). Even more decisively, the ^{19}F NMR spectrum exhibited only three resonances at δ −162.6, −156.4 and −102.7 which are coincident with those observed in the mixture. A *cis* or lateral orientation of the two CO ligands was assigned on the basis of the relative intensity of the $\nu(CO)$ 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 $[Re(\eta^5-C_5Me_5)(CO)_3]$ in C_6F_5H, the photochemistry of **1a** in pentafluorobenzene was examined. Irradiation ($\lambda = 300$ nm) of a spectroscopically pure sample of **1a** in C_6F_5H 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 $[Re(\eta^5-C_5Me_5)(CO)_3]$ 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 H_2 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 C_6F_5H was photolysed under the same experimental conditions. The IR, ^1H and ^{19}F NMR and the mass spectrum of the product showed, in addition to unchanged starting fulvene, only *cis*-$[Re(\eta^5-C_5Me_5)(CO)_2(C_6F_5)_2]$ **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 C_6F_5H at 150 °C for 2 h. (The complexes did not survive for long at this temperature.)

The products obtained from the reaction of $[Re(\eta^5-C_5Me_5)(CO)_3]$ 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
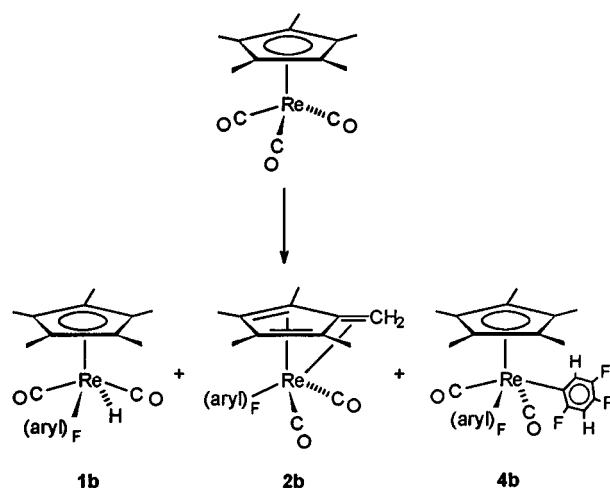
Scheme 3 Products of UV irradiation of $[Re(\eta^5-C_5Me_5)(CO)_3]$ in 1,2,4,5-$C_6F_4H_2$ ((aryl)$_F$ = 2,3,5,6-C_6F_4H).

photolysis was treated directly with bromoform to convert all the hydride complex **1b** into the more stable bromo derivative *trans*-$[Re(\eta^5-C_5Me_5)(CO)_2(C_6F_4H)Br]$. Column chromatography allowed the separation of the bromo complex from the starting tricarbonyl, $[Re(\eta^5-C_5Me_5)(CO)_2(2,3,5,6-C_6F_4H)(2,4,5-C_6F_3H_2)]$ **4b** and the new fulvene complex $[Re(\eta^6-C_5Me_4CH_2)(CO)_2(2,3,5,6-C_6F_4H)]$ **2b**. The symmetric bis(aryl)$_F$ complex $[Re(\eta^5-C_5Me_5)(CO)_2(2,3,5,6-C_6F_4H)_2]$ was not detected.

The hydrido complex **1b** was prepared indirectly in 90% yield by the method shown in Scheme 4. This complex was fully
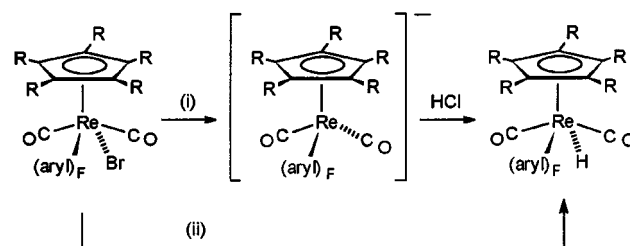
Scheme 4 Thermal syntheses of hydride complexes: (i) AlH_4^-, R = Me, (aryl)$_F$ = 2,3,5,6-C_6F_4H, (ii) BH_4^-, R = H, (aryl)$_F$ = C_6F_5 or 2,3,5,6-C_6F_4H.

characterized by spectroscopy (Table 1 and Experimental section). As expected, it showed a similar intensity pattern for the $\nu(CO)$ bands to those observed for **1a** and a single resonance for the COs in the ^{13}C-$\{^1H\}$ NMR spectrum which is indicative of a *trans* stereochemistry. In addition to the resonances for the hydride and η^5-C_5Me_5 ligands, the ^1H NMR spectrum exhibited the triplet of triplets typical for the aromatic proton in the *para* position. The ^{19}F 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,-C_6F_4H group occupies a position *trans* to the CH_2 group of the fulvene, while in the minor isomer (18.5% in chloroform at 293 K) the η^6-$C_5Me_4CH_2$ ligand is rotated relative to the aromatic group. The presence of the 2,3,5,6-C_6F_4H group in **2b** was clearly established by ^1H and ^{19}F 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 $\nu(CO)$ absorption bands making it difficult to decide between the *cis* and *trans* product. The ^{13}C 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 $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ with C_6F_5H and $1,2,4,5\text{-}C_6F_4H_2$ [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, C_6F_4H)	-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, C_6F_4H) Isomer 2 5.33 (s, 5 H, CH), 7.62 (m, 1 H, C_6F_4H)	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 C_6F_4H), -97.21 (m, 1 F, F_{ortho} of C_6F_4H), -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 C_6F_4H), -151.95 (m, 1 F, F_{meta} of C_6F_4H), -151.47 (tt, J_{FF} 20, 3, 1 F, F_{para} of C_6F_5), -136.70 (m, 1 F, F_{meta} of C_6F_4H), -95.94 (m, 1 F, F_{ortho} of C_6F_4H), -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, C_6F_4H, $C_6F_3H_2$), 7.81 (ddd, J_{HF} 11.3, 9.5, 5.1, 1 H, $C_6F_3H_2$)	-144.50 (m, 1 F, F^5 of $C_6F_3H_2$), -140.11 (m, 2 F, F_{meta} of C_6F_4H), -138.08 (m, 1 F, F^4 of $C_6F_3H_2$), -101.45 (m, 2 F, F_{ortho} of C_6F_4H), -77.20 (m, 1 F, F^2 of $C_6F_3H_2$)
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, C_6F_4H)	-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.
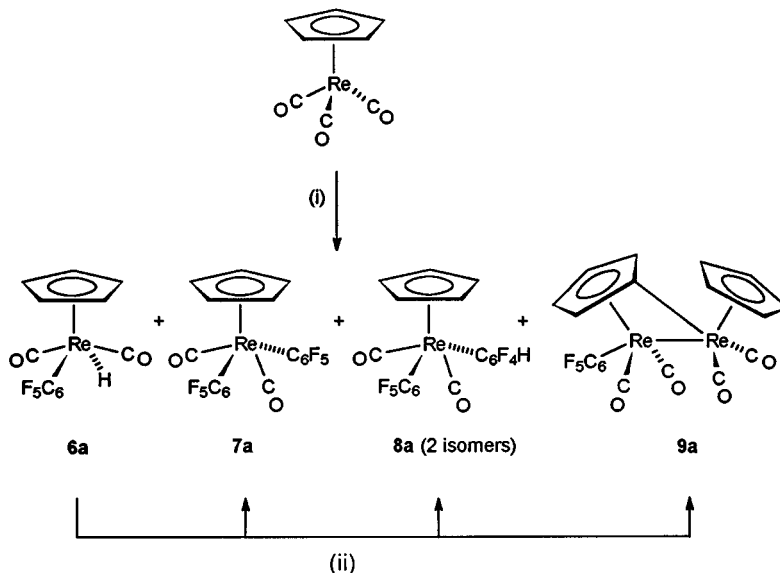
Scheme 5 Products of UV irradiation of (i) $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ and (ii) complex **6a** in C_6F_5H.

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}F} and ^{19}F-{^{19}F} selective decoupling NMR experiments (Table 1).[22]

2 Photolysis of $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ in pentafluorobenzene and 1,2,4,5-tetrafluorobenzene

The reactions of $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ with C_6F_5H and $1,2,4,5\text{-}C_6F_4H_2$ 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 $[Re(\eta^5\text{-}C_5H_4R)(CO)_3]$ (R = H or Me) with hexafluorobenzene.[23]

Five compounds were identified from the reaction mixture on UV irradiation of $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ in neat C_6F_5H at room temperature for 1 h (Scheme 5, Table 2). As in the previous case,

the main reaction product is the hydride complex *trans*-$[Re(\eta^5\text{-}C_5H_5)(CO)_2(C_6F_5)H]$ **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*-$[Re(\eta^5\text{-}C_5H_5)(CO)_2(C_6F_5)Br]$. 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 $[Re(\eta^5\text{-}C_5H_5)(CO)_2(C_6F_5)_2]$ **7a** and the two isomers of $[Re(\eta^5\text{-}C_5H_5)(CO)_2(C_6F_5)(C_6F_4H)]$ **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 ^{1}H 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 penta-fluorobenzene. The presence of traces of **7a** indicated that the intermolecular C–H bond activation of a second molecule of C_6F_5H 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 [Re(η^5-C_5H_5)(CO)$_2$Cl$_2$] with [Cu(C_6F_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 [Re(η^5-C_5H_5)(CO)$_3$] and C_6F_5H (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 M[+] − 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 ^{1}H 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 μ-η^1:η^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 [Re$_2$(η^5-C_5H_5)(μ-η^1:η^5-C_5H_4)(CO)$_4$(C_6F_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 [Re(η^5-C_5H_5)(CO)$_3$] when irradiated in neat 1,2,4,5-$C_6F_4H_2$ (Scheme 6). The major product
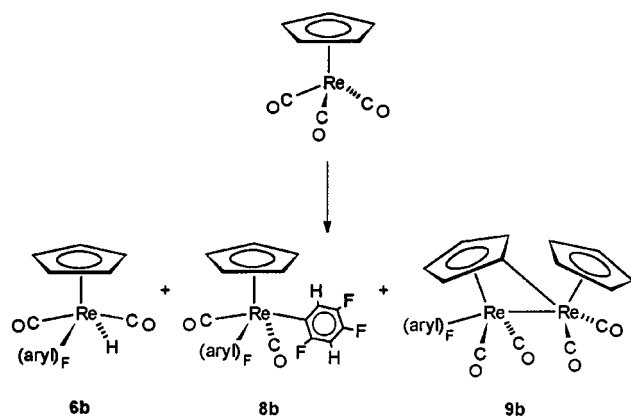
Scheme 6 Products of UV irradiation of [Re(η^5-C_5H_5)(CO)$_3$] in 1,2,4,5-$C_6F_4H_2$, (aryl)$_F$ = 2,3,5,6-C_6F_4H.

was again the hydride complex *trans*-[Re(η^5-C_5H_5)(CO)$_2$-(2,3,5,6-C_6F_4H)H] **6b** (Table 2 and Experimental section). The bis(aryl)$_F$ complex *trans*-[Re(η^5-C_5H_5)(CO)$_2$(2,3,5,6-C_6F_4H)-(2,4,5-$C_6F_3H_2$)] **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-$C_6F_4H_2$. 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 [Re$_2$(η^5-C_5H_5)(μ-η^1:η^5-C_5H_4)(CO)$_4$(2,3,5,6-C_6F_4H)] **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 [Re$_2$(η^5-C_5H_5)(μ-η^1:η^5-C_5H_4)-(CO)$_4$(2,3,5,6-C_6F_4H)] **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(13)
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)
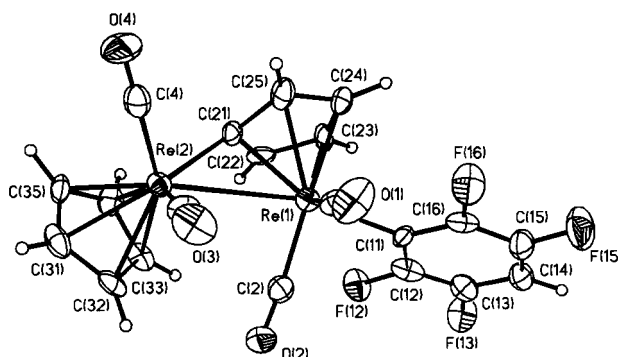
Fig. 1 View of the structure of [Re$_2$(η^5-C_5H_5)(μ-η^1:η^5-C_5H_4)(CO)$_4$-(2,3,5,6-C_6F_4H)] **9b**.

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 [Re$_2$(η^5-C_5H_5)(μ-η^1:η^5-C_5H_4)(CO)$_4$(2,3,5,6-C_6F_4H)] **9b** consists of an Re(η^5-C_5H_4)(CO)$_2$(C_6F_4H) moiety linked to a Re(η^5-C_5H_5)(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 Re(1)–C(21)–Re(2) is close to a right angle [91.2(4)°]. The Re(1)–C(21) distance at 2.16(1) Å is the shortest of those linking the (η^5-C_5H_4) unit to Re(1) but is longer than Re(2)–C(21) [2.07(1) Å] which links the same cyclopentadienyl unit to the second rhenium atom *via* an (η^1-C_5H_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 C_6F_4H unit lies almost in line with the Re–Re bond [Re(2)–Re(1)–C(11) 164.3(3)°]. The two {Re(CO)$_2$} units are twisted with respect to one another: the torsional angles C(1)–Re(1)–Re(2)–C(4) and C(2)–Re(1)–Re(2)–C(3) are 62.7(6) and 85.9(6)°, respectively. If we define the midpoints of the vectors O(1)–O(2) and O(3)–O(4) as X(1A) and X(1B), then the angle between the two {Re(CO)$_2$} units is given approximately by the torsion angle X(1A)–Re(1)–Re(2)–X(1B) which is 73.0°.

Discussion

The $\{Re(\eta^5\text{-}C_5Me_5)(CO)_2\}$ and $\{Re(\eta^5\text{-}C_5H_5)(CO)_2\}$ 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 $[Re(\eta^5\text{-}C_5Me_5)(CO)_2(\eta^2\text{-}C_6H_6)]$ and $[Re_2(\eta^5\text{-}C_5Me_5)_2(CO)_4(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_6)]$ are formed in which the benzene co-ordinates without C–H bond breaking.[27] We have shown earlier that $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ reacts photochemically with hexafluorobenzene to form the fulvene complex **2a** by combined C–F and C–H bond insertion.[12,19] In contrast $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ reacts to form the co-ordination complex $[Re(\eta^5\text{-}C_5H_5)(CO)_2(\eta^2\text{-}C_6F_6)]$.[12,23] In the current paper we have demonstrated that the dominant photochemical reaction of pentafluorobenzene and 1,2,4,5-tetrafluorobenzene with both $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ and $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ is C–H bond activation to form the hydrido complexes $[Re(\eta^5\text{-}C_5R_5)(CO)_2(aryl)_FH]$ **1a**, **1b**, **6a**, **6b** (R = H or Me, $(aryl)_F = C_6F_5$ or $2,3,5,6\text{-}C_6F_4H$). The complex **1a** has also been synthesized independently.

The photochemical conversion of $[Re(\eta^5\text{-}C_5R_5)(CO)_3]$ into $[Re(\eta^5\text{-}C_5R_5)(CO)_2(C_6F_5)H]$ in yields higher than 70% invites questions as to why this reaction is efficient whereas neither the $Re(\eta^2\text{-}C_6F_5H)$ 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 C_6F_5H (477 kJ mol^{-1}) is stronger than that of benzene (460 kJ mol^{-1}),[29] we may expect the $Re\text{-}C_6F_5$ bond to be stronger than the $Re\text{-}C_6H_5$ bond.[28] We therefore postulate that the formation of the C–H activation product rather than $Re(\eta^2\text{-}C_6F_5H)$ 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 $\eta^5\text{-}C_5Me_5$ 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 $[Re(\eta^5\text{-}C_5R_5)(CO)_2(C_6F_5)(C_6F_4H)]$ (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 $[Re(\eta^5\text{-}C_5R_5)(CO)_2(aryl)_FH]$ but not in the reactions of $[Re(\eta^5\text{-}C_5R_5)(CO)_3]$ (R = H or Me). Finally, we note the dinuclear cyclopentadienyl complexes **9a** and **9b**, apparently formed by insertion of a $[Re(\eta^5\text{-}C_5H_5)(CO)_2]$ moiety into a C–H bond of **6a** or **6b** and subsequent elimination of hydrogen. The formation of the bridging $(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)$ ligand is little documented in rhenium chemistry but familiar in the early transition metal chemistry. Wenzel and Bergman[25] described the crystal structure of $[Re_2(\eta^5\text{-}C_5H_5)(\mu\text{-}CH_2PMe_2)(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)(PMe_3)_3H_2]$ formed by decomposition of $[Re(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2PMe_2)(PMe_3)H]$. Pasman and Snel[30] investigated the formation of rhenocene dimers including one assigned as $[Re_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)_2]$. Hoxmeier et al.[31] showed that $[Re(\eta^5\text{-}C_5H_5)_2H]$ reacts with $[Mn(CO)_5(CH_3)]$ to form $[H(\eta^5\text{-}C_5H_5)Re(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)Mn(CO)_4]$. The geometry of Re(2) in complex **9b** is closely mirrored in the molybdenum complex $[(OC)_2(\eta^5\text{-}C_5H_5)Mo(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)Mo(\eta^5\text{-}C_5H_5)(CO)]$.[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 $[Re(\eta^5\text{-}C_5R_5)(CO)_3]$ (R = H or Me) were prepared according to the method of Gladysz and co-workers.[33] The complex trans-$[Re(\eta^5\text{-}C_5Me_5)(CO)_2Cl_2]$ was prepared by photochemical isomerization of the corresponding cis isomer;[21,34] trans-$[Re(\eta^5\text{-}C_5H_5)(CO)_2Cl_2]$ 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, ^{1}H, ^{19}F and ^{13}C NMR spectra on Bruker AC 200, DRX 400 (^{19}F–^{19}F and selective proton/fluorine decoupling experiments) and AMX 500 instruments. All ^{1}H NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances ($CDCl_3$, δ 7.27; C_6D_6, δ 7.13), ^{13}C NMR chemical shifts to solvent peaks ($CDCl_3$, δ 77.0; C_6D_6, δ 128.0) and ^{19}F NMR spectra to internal C_6F_6 at δ −162.9. The assignment of ^{19}F 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 $[Re(\eta^5\text{-}C_5R_5)(CO)_3]$ (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 $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ (300 mg, 0.74 mmol) and $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ (300 mg, 0.89 mmol) in the fluorinated solvent (24 cm^3) were irradiated at 300 nm, for 3 and 1 h, respectively. Irradiation was carried out in a Rayonet RPR-100 photochemical reactor. Reactions with $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ resulted in the formation of yellow solutions, those with $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ 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 $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ in C_6F_5H.

Reaction of photolysed mixtures with bromoform: general procedure

The typical procedure involved dissolution of the photolysis residue in THF (15 cm^3), addition of $CHBr_3$ (0.30 cm^3, 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 $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ in C_6F_5H. 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 cm^3 of hexane. The light brown residue which corresponded to trans-$[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)H]$ **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 $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ (152 mg, 0.38 mmol), 5 mg of a 1.7:1 mixture (by ^{1}H and ^{19}F NMR integration) of cis-$[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)_2]$ **3a**, and $[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)(2,3,5,6\text{-}C_6F_4H)]$ **4a**, and finally the fulvene complex $[Re(\eta^6\text{-}C_5Me_4CH_2)(CO)_2(C_6F_5)]$ **2a** (14 mg, 0.020 mmol, 5.5%).

1a: IR [hexane, $\tilde{v}(CO)/cm^{-1}$] 2024m and 1959s. ^{13}C-{^1H} 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, $\tilde{v}(CO)/cm^{-1}$] 2052s and 1986m. ^{13}C-{^1H} 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, [M]$^+$; and 684, [M − CO]$^+$.

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

[NEt$_4$]$^+$[Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)]$^-$ 5. Tetrahydrofuran (25 cm^3) was added to a solid mixture of the fulvene complex **2a** (100 mg, 0.18 mmol), NaBH$_4$ (35 mg, 0.93 mmol) and NEt$_4$Br (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 CH$_2$Cl$_2$ (10 cm^3) and filtered. The solution was reduced in volume under vacuum to about 3 cm^3. Hexane (50 cm^3) was added with stirring, and the mixture filtered. The pale yellow solid was washed with hexane (5 cm^3) and then dissolved in CH$_2$Cl$_2$ (1.5 cm^3). 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 [CH$_2$Cl$_2$, $\tilde{v}(CO)/cm^{-1}$]: 1849vs and 1769vs. ^1H NMR (CDCl$_3$): δ 1.21 (t, 12 H, CH$_3$ of NEt$_4$$^+$), 1.95 (s, 15 H, CH$_3$) and 3.12 (q, 8 H, CH$_2$ of NEt$_4$$^+$). ^{19}F NMR (CDCl$_3$): δ −168.03 (m, 2F$_{meta}$), −167.18 (m, F$_{para}$) and −104.94 (m, 2F$_{ortho}$). ^{13}C-{^1H} NMR (CDCl$_3$): δ 7.30 (s, CH$_3$ of NEt$_4$$^+$), 10.92 (s, CH$_3$), 52.42 (s, CH$_2$ of NEt$_4$$^+$), 94.78 (s, C_5Me_5), 214.27 (s, CO), and CF aromatic carbons not observed.

***trans*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)H] 1a.** To a solution of complex **5** (100 mg, 0.148 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added HCl solution (1 mol dm^{-3}) in diethyl ether (0.15 cm^3, 0.15 mmol). The mixture was stirred at room temperature for 5 min. The IR spectrum of the solution showed the total disappearence 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 cm^3) 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-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)$_2$] 3a.** To a solution of *trans*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$Cl$_2$] (110 mg, 0.24 mmol) in THF (10 cm^3) was added, *via* syringe, a solution (1.5 cm^3) of [Cu(C$_6$F$_5$)] [prepared from magnesium turnings (0.26 g, 11 mmol), chloropentafluorobenzene (1.3 cm^3, 10 mmol) and CuBr·Me$_2$S (2.47 g, 12 mmol) in THF (12 cm^3)]. 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 C$_{24}$H$_{15}$F$_{10}$O$_2$Re: C, 40.51; H, 2.12%).

[Re(η^5-C$_5$Me$_5$)(CO)$_3$] + 1,2,4,5-C$_6$F$_4$H$_2$ + CHBr$_3$. Following the general procedure, slow elution with hexane moved unchanged [Re(η^5-C$_5$Me$_5$)(CO)$_3$] (153 mg, 0.38 mmol). Hexane–CH$_2$Cl$_2$ (15:1) moved pale yellow *cis*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$-(2,3,5,6-C$_6$F$_4$H)(2,4,5-C$_6$F$_3$H$_2$)] **4b** (yield 13 mg, 0.02 mmol, 5.5%). Hexane–CH$_2$Cl$_2$ (10:1) moved the yellow fulvene complex [Re(η^6-C$_5$Me$_4$CH$_2$)(CO)$_2$(2,3,5,6-C$_6$F$_4$H)] **2b** (yield 11 mg, 0.02 mmol, 6%). Finally, hexane–CH$_2$Cl$_2$ (5:1) moved orange *trans*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$(2,3,5,6-C$_6$F$_4$H)Br] (135 mg, 0.223 mmol, 61%).

2b: IR [hexane, $\tilde{v}(CO)/cm^{-1}$] 2006vs and 1939vs; ^{13}C-{^1H} NMR (CDCl$_3$, major isomer) δ 9.62 (s, CH$_3$), 9.77 (s, CH$_3$), 47.38 (s, CH$_2$), 97.20 (s, $C_5Me_4CH_2$), 107.16 (s, $C_5Me_4CH_2$), 107.38 (s, $C_5Me_4CH_2$), 198.52 (s, CO) and aromatic carbons not observed; mass spectrum (based on ^{187}Re) m/z 526, [M]$^+$; 498, [M − CO]$^+$; and 470, [M − 2CO]$^+$.

4b: IR [hexane, $\tilde{v}(CO)/cm^{-1}$] 2046vs and 1957s. ^{13}C-{^1H} NMR (CDCl$_3$) δ 9.92 (s, CH$_3$), 103.44 (s, C_5Me_5), 104.36 (t, J_{CF} 23, C$_6$F$_4$H), 104.91 (dd, J_{CF} 39, 19, C$_6$F$_3$H$_2$), 107.94 (dm, J_{CF} 34, C$_{ipso}$ of C$_6$F$_3$H$_2$), 108.86 (tm, J_{CF} 39, C$_{ipso}$ of C$_6$F$_4$H), 131.15 (dd, J_{CF} 16, 13, C$_6$F$_3$H$_2$), 145.6 (dm, J_{CF} 235, C$_6$F$_4$H), 147.0 (dm, J_{CF} 258, C$_6$F$_3$H$_2$), 149.14 (dt, J_{CF} 249, 14, C$_6$F$_3$H$_2$), 152.20 (dm, J_{CF} 235, C$_6$F$_4$H), 163.7 (dm, J_{CF} 238 Hz, C$_6$F$_3$H$_2$) and 193.28 (br s, CO); mass spectrum (based on ^{187}Re) m/z 658, [M]$^+$; 630, [M − CO]$^+$; and 602, [M − 2CO]$^+$.

trans-[Re(η^5-C$_5$Me$_5$)(CO)$_2$(2,3,5,6-C$_6$F$_4$H)Br]: mp 180–181 °C (decomp.); IR [CH$_2$Cl$_2$, $\tilde{v}(CO)/cm^{-1}$] 2045s and 1973vs; ^1H NMR (CDCl$_3$) δ 1.88 (s, 15 H, CH$_3$) and 6.88 (tt, 1 H, J_{HF} 9.2, 7.5 Hz, C$_6$F$_4$H); ^{19}F NMR (CDCl$_3$) δ −140.14 (m, 2F$_{ortho}$) and −103.82 (m, 2F$_{meta}$); ^{13}C-{^1H} NMR (CDCl$_3$) δ 10.29 (s, CH$_3$), 104.25 (s, C_5Me_5), 104.36 (t, J_{CF} 23 Hz, CH of C$_6$F$_4$H), 189.66 (s, CO) and the other aromatic carbons not observed; mass spectrum (based on ^{187}Re, ^{79}Br) m/z 606, [M]$^+$; 578, [M − CO]$^+$; and 550, [M − 2CO]$^+$ (Found: C, 35.80; H, 2.70. Calc. for C$_{18}$H$_{16}$BrF$_4$O$_2$Re: C, 35.65; H, 2.66%).

[Re(η^5-C$_5$H$_5$)(CO)$_3$] + C$_6$F$_5$H + CHBr$_3$. Following the general procedure above, slow elution with hexane moved unchanged [Re(η^5-C$_5$H$_5$)(CO)$_3$] (134 mg, 0.40 mmol). Hexane–CH$_2$Cl$_2$ (9:1) moved a 67:26:6 mixture (by ^1H NMR integration) of [Re(η^5-C$_5$H$_5$)(CO)$_2$(C$_6$F$_5$)(2,3,5,6-C$_6$F$_4$H)] **8a** (isomer 1), [Re(η^5-C$_5$H$_5$)(CO)$_2$(C$_6$F$_5$)(2,3,4,5-C$_6$F$_4$H)] **8a** (isomer 2), and [Re(η^5-C$_5$H$_5$)(CO)$_2$(C$_6$F$_5$)$_2$] **7a** (15 mg). Hexane–CH$_2$Cl$_2$ (6:1) moved orange *trans*-[Re(η^5-C$_5$H$_5$)(CO)$_2$(C$_6$F$_5$)Br] (170 mg, 0.31 mmol, 62%). Finally, hexane–CH$_2$Cl$_2$ (2:1) moved dark red [(OC)$_2$(η^5-C$_5$H$_5$)Re(μ-η^1:η^5-C$_5$H$_4$)Re(CO)$_2$-(C$_6$F$_5$)] **9a** (5 mg, 0.006 mmol, 1%).

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

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

9a: IR [CH$_2$Cl$_2$, $\tilde{v}(CO)/cm^{-1}$]: 2014s, 1968s, 1922m and 1918m; mass spectrum (based on ^{187}Re/^{187}Re) m/z 782, [M]$^+$; and 754, [M − CO]$^+$.

trans-[Re(η^5-C$_5$H$_5$)(CO)$_2$(C$_6$F$_5$)Br]: mp 192–194 °C (decomp.); IR [CH$_2$Cl$_2$, $\tilde{v}(CO)/cm^{-1}$] 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-{^1H} NMR (CDCl$_3$) δ 91.70 (s, C$_5$H$_5$), 185.23 (s, CO) and aromatic carbons not observed; mass spectrum (based on ^{187}Re) m/z 554, [M]$^+$; 526, [M − CO]$^+$; 498, [M − 2CO]$^+$; and 475, [M − Br]$^+$ (Found: C, 28.25; H, 1.01. Calc. for C$_{13}$H$_5$-BrF$_5$O$_2$Re: C, 28.17; H, 0.91%).

***trans*-[Re(η^5-C$_5$H$_5$)(CO)$_2$(C$_6$F$_5$)$_2$] 7a.** A procedure similar to that described for the synthesis of complex **3a** was used, except that elution with hexane–CH$_2$Cl$_2$ (4:1) afforded **7a** as a pale yellow solid in 72% yield (Found: C, 35.48; H, 0.77. Calc. for C$_{19}$H$_5$F$_{10}$O$_2$Re: C, 35.58; H, 0.78%).

[Re(η^5-C$_5$H$_5$)(CO)$_3$] + 1,2,4,5-C$_6$F$_4$H$_2$ + CHBr$_3$. Following the general procedure, slow elution with hexane moved unchanged [Re(η^5-C$_5$H$_5$)(CO)$_3$] (153 mg, 0.45 mmol). Hexane–CH$_2$Cl$_2$ (8:1) moved pale yellow *trans*-[Re(η^5-C$_5$H$_5$)(CO)$_2$-(2,3,5,6-C$_6$F$_4$H)(2,4,5-C$_6$F$_3$H$_2$)] **8b** (15 mg, 0.02 mmol, 6%). Hexane–CH$_2$Cl$_2$ (5:1) moved orange *trans*-[Re(η^5-C$_5$H$_5$)(CO)$_2$-(2,3,5,6-C$_6$F$_4$H)Br] (176 mg, 0.33 mmol, 75%). Finally, hexane–

CH$_2$Cl$_2$ (2:1) moved dark red [(OC)$_2$(η^5-C$_5$H$_5$)Re(μ-η^1:η^5-C$_5$H$_4$)Re(CO)$_2$(2,3,5,6-C$_6$F$_4$H)] **9b** (6 mg, 0.008 mmol, 2%).

8b: IR [hexane, $\tilde{v}$(CO)/cm^{-1}] 2058s and 1983vs; ^{13}C-{^{1}H} NMR (CDCl$_3$) δ 90.27 (s, C$_5$H$_5$), 95.84 (dm, J_{CF} 34, C$_{ipso}$ of C$_6$F$_3$H$_2$), 97.22 (tm, J_{CF} 40, C$_{ipso}$ of C$_6$F$_4$H), 104.13 (dd, J_{CF} 38, 20, C$_6$F$_3$H$_2$), 104.97 (t, J_{CF} 23, C$_6$F$_4$H), 132.93 (dd, J_{CF} 17, 12, C$_6$F$_3$H$_2$), 145.3 (dm, J_{CF} 236, C$_6$F$_3$H$_2$), 147.2 (dm, J_{CF} 220, C$_6$F$_3$H$_2$), 149.6 (dt, J_{CF} 250, 14, C$_6$F$_3$H$_2$), 152.07 (dm, J_{CF} 250, C$_6$F$_4$H), 163.78 (ddd, J_{CF} 234, 8, 2, C$_6$F$_3$H$_2$) and 190.23 (pseudo q, J_{CF} 5 Hz, CO). Mass spectrum (based on ^{187}Re): m/z 588, [M]$^+$; 560, [M − CO]$^+$; and 532, [M − 2CO]$^+$ (Found: C, 38.43; H, 1.31. Calc. for C$_{19}$H$_8$F$_7$O$_2$Re: C, 38.85; H, 1.37%).

9b: IR [CH$_2$Cl$_2$, $\tilde{v}$(CO)/cm^{-1}] 2012s, 1966s, 1925m and 1914m; ^{13}C-{^{1}H} NMR (CDCl$_3$) δ 80.11 (s, C$_5$H$_4$), 90.11 (s, C$_5$H$_5$), 99.06 (s, C$_5$H$_4$), 101.37 (s, C$_5$H$_4$), 103.25 (t, J_{CF} 23, C$_{ipso}$ of C$_6$F$_4$H), 105.68 (s, C$_{ipso}$ of C$_5$H$_4$), 106.23 (s, C$_5$H$_4$), 144.94 (d, J_{CF} 250, C$_6$F$_4$H), 151.75 (d, J_{CF} 227 Hz, C$_6$F$_4$H), 156.50 (s, C$_6$F$_4$H), 194.79 (br s, CO), 195.82 (s, CO), 196.78 (br s, CO) and 198.84 (s, CO); mass spectrum (based on ^{187}Re/^{187}Re) m/z 762, [M]$^+$; and 734, [M − CO]$^+$ (Found: C, 31.59; H, 1.34. Calc. for C$_{10}$H$_5$F$_2$O$_2$Re: C, 31.49; H, 1.32%).

trans-[Re(η^5-C$_5$H$_5$)(CO)$_2$(2,3,5,6-C$_6$F$_4$H)Br]: mp 176 °C (decomp.); IR [CH$_2$Cl$_2$, $\tilde{v}$(CO)/cm^{-1}] 2062s and 1994vs; ^{1}H NMR (CDCl$_3$) δ 5.54 (s, 5H, CH) and 6.92 (tt, 1 H, J_{HF} 9.2, 7.6 Hz, C$_6$F$_4$H). ^{19}F NMR (CDCl$_3$) δ −139.90 (m, 2F$_{meta}$) and −101.44 (m, 2F$_{ortho}$); ^{13}C-{^{1}H} NMR (CDCl$_3$) δ 91.83 (s, C$_5$H$_5$), 104.87 (t, J_{CF} 22 Hz, CH of C$_6$F$_4$H), 186.33 (s, CO) and the other aromatic carbons not observed; mass spectrum (based on ^{187}Re, ^{79}Br) m/z 536, [M]$^+$; 508, [M − CO]$^+$; and 480, [M − 2CO]$^+$ (Found: C, 29.18; H, 1.12. Calc. for C$_{13}$H$_6$BrF$_4$O$_2$Re: C, 29.12; H, 1.13%).

Syntheses of hydride complexes

(a) *trans*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$(2,3,5,6-C$_6$F$_4$H)H] 1b. To a solution of the bromo complex *trans*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$-(2,3,5,6-C$_6$F$_4$H)Br] (100 mg, 0.17 mmol) in THF (20 cm^3) was added LiAlH$_4$ (1 M in THF, 0.22 cm^3, 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(η^5-C$_5$Me$_5$)(CO)$_2$(2,3,5,6-C$_6$F$_4$H)]$^−$, as indicated by the absorption bands at 1865 and 1747 cm^{-1}. Hydrochloric acid (1 M in diethyl ether, 0.60 cm^3, 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 cm^3 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, $\tilde{v}$(CO)/cm^{-1}]: 2024m and 1959s. ^{13}C-{^{1}H} NMR (C$_6$D$_6$): δ 11.45 (s, CH$_3$), 100.48 (s, C$_5$Me$_5$), 104.67 (t, J_{CF} 24, CH of C$_6$F$_4$H), 195.77 (s, CO), C$_{ipso}$ and CF aromatic carbons not observed.

(b) (η^5-C$_5$H$_5$) Complexes. For the syntheses of the cyclopentadienyl derivatives **6a** and **6b**, treatment of the corresponding bromo complex with an excess of NaBH$_4$ 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(η^5-C$_5$H$_5$)(CO)$_2$(C$_6$F$_5$)H] **6a**: yield 78%; IR [hexane, $\tilde{v}$(CO)/cm^{-1}] 2040m and 1978s. ^{13}C-{^{1}H} NMR (C$_6$D$_6$) δ 86.09 (s, C$_5$H$_5$), 191.53 (s, CO) and aromatic carbons not observed.

trans-[Re(η^5-C$_5$H$_5$)(CO)$_2$(2,3,5,6-C$_6$F$_4$H)H] **6b**: yield 67%; IR [hexane, $\tilde{v}$(CO)/cm^{-1}] 2040m and 1977s; ^{13}C-{^{1}H} NMR (C$_6$D$_6$) δ 86.09 (s, C$_5$H$_5$), 105.12 (t, J_{CF} 23 Hz, CH of C$_6$F$_4$H), 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 CH$_2$Cl$_2$ solution of complex **9b** with hexanes.

Crystal data and data collection parameters. C$_{20}$H$_{10}$F$_4$O$_4$Re$_2$, M = 762.69, monoclinic, space group $P2_1/n$ a = 7.769(2), b = 19.351(6), c = 12.688(3) Å, β = 104.41(2)°, U = 1847.6 Å^3 (from 42 reflections, 30 < 2θ < 32°, measured at ±ω), T = 220 K, graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), Z = 4, D_c = 2.74 g cm^{-3}, $F(000)$ = 1380.48 (calculated from the scattering factors at 2θ = 0°), red block with dimensions 0.19 × 0.19 × 0.08 mm, μ = 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 = 0.119–0.347).[36] Data were collected to 2θ = 50° 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_{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 Chebychev 3-term polynomial weighting scheme. The final difference map extrema were ±1.4 e Å^{-3}.

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

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