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Synthesis and reactions of the rhenium fulvene complexes $[Re(\eta^6\text{-}C_5Me_4CH_2)(CO)_2(C_6F_4R)]$ (R = F or CF_3): products derived from initial C–F activation

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Received 17th April 1998, Accepted 8th July 1998

The UV irradiation of $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ in the presence of C_6F_6 effected intermolecular C–F and intramolecular C–H activation generating $[Re(\eta^6\text{-}C_5Me_4CH_2)(CO)_2(C_6F_5)]$ **1a** in two isomeric forms. In the major isomer the CH_2 group lies *trans* to the C_6F_5 group both in solution and in the crystal. In the minor isomer the CH_2 lies *cis* to the C_6F_5 group. A similar reaction with $C_6F_5CF_3$ generates $[Re(\eta^6\text{-}C_5Me_4CH_2)(CO)_2(C_6F_4CF_3)]$ **1b** in four isomeric forms. In the major form the CF_3 group is in the 4 position and the CH_2 group lies *trans* to the $C_6F_4CF_3$ group. The other three isomers are formed by rotation of the $\eta^6\text{-}C_5Me_4CH_2$ ligand as above, by placing the CF_3 at the 3 position, and by a combination of the two. Complex **1a** reacted with PMe_3 to form the zwitterionic complex $[Re(\eta^5\text{-}C_5Me_4CH_2PMe_3)(CO)_2(C_6F_5)]$ and with MeO^- to form the anion $[Re(\eta^5\text{-}C_5Me_4CH_2OMe)(CO)_2(C_6F_5)]^-$, isolable as the NEt_4^+ salt. The reaction of **1a** with HX (X = Cl or Br) generated *cis*-$[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)X]$ initially. More prolonged reaction led to the *trans* isomers. On reaction with HI, only the *trans* isomer was formed. Reaction of **1a** with HBF_4 in Et_2O in the presence of MeCN led to formation of the salt $[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)(NCMe)]^+[BF_4]^-$. The halogens Cl_2, Br_2 and I_2 reacted to form (halogenomethyl)tetramethylcyclopentadienyl complexes *trans*-$[Re(\eta^5\text{-}C_5Me_4CH_2X)(CO)_2(C_6F_5)X]$ (X = Cl, Br or I). The bromo complex has been characterized crystallographically.

The C–H bond activation of methyl groups in metal-bound pentamethylcyclopentadienyl complexes, leading to the formation of a tetramethylfulvene ligand, has been the source of much recent interest. This transformation has been shown to occur thermally, photochemically or under the influence of strong bases with complexes of Ru,[1,2] Rh,[3,4] Ir,[4,5] Os,[6] Ti[7] and Zr.[8]

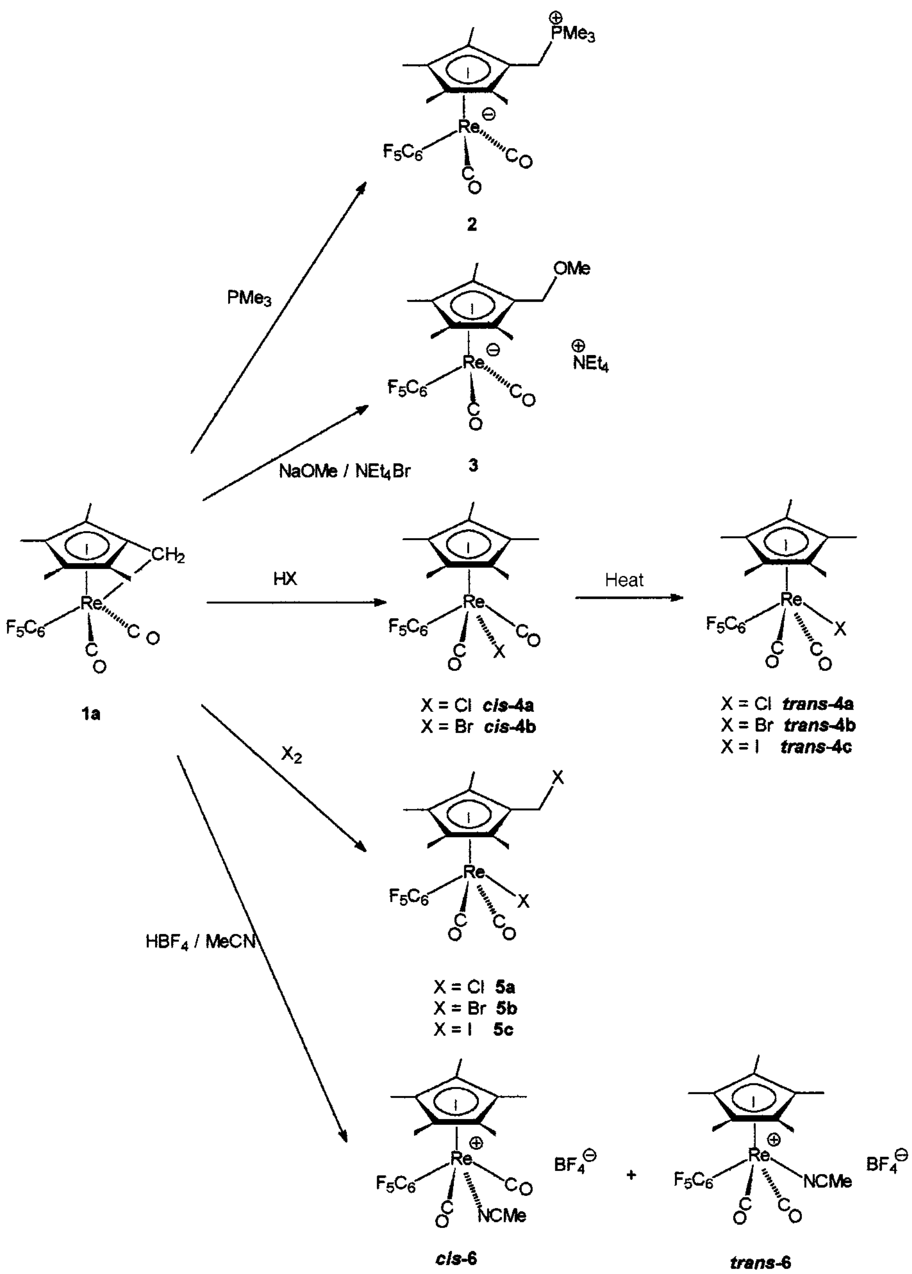
In recent years there has also been considerable interest in using co-ordinated or unco-ordinated fulvene molecules in the preparation of organometallic complexes bearing substituted cyclopentadienyl ligands, C_5H_4R or C_5Me_4R, where R is a pendant arm which may or may not contain a functional group. For instance, Behrens and co-workers[9] reported the reaction of the complex $[Cr(\eta^6\text{-fulvene})(CO)_3]$ (fulvene = 6,6-dimethyl- or 1,2,3,4-tetraphenylfulvene) with tertiary phosphines to produce the zwitterionic addition products $[Cr(\eta^5\text{-}C_5R_4CR'_2PR''_3)(CO)_3]$ (R = H or Ph; R′ = H or Me; R″ = Me, Et or Ph), in a demonstration of the electrophilic nature of the exocyclic methylene carbon. By contrast, the reaction of $[Zr(\eta^6\text{-}C_5Me_4CH_2)(\eta^5\text{-}C_5Me_5)(Ph)]$ with iodine to produce the ring-substituted cyclopentadienyl phenyl iodide complex, $[Zr(\eta^5\text{-}C_5Me_4CH_2I)(\eta^5\text{-}C_5Me_5)(Ph)]$, has also been reported.[8] Maitlis and co-workers[1] reported that the complex $[Ru(\eta^5\text{-}C_5H_4CH_2Cl)(CO)_2Cl]$ can be produced in high yield by treating the dimeric fulvene complex $[\{Ru(\eta^6\text{-}C_5H_4CH_2)Cl_2\}_2]$ with carbon monoxide. More recently, Koelle and co-workers[10] reported the reactions of several cationic tetramethylfulvene ruthenium complexes $[Ru(\eta^6\text{-}C_5Me_4CH_2)Cp^{pc}]^+$ (Cp^{pc} = prochiral cyclopentadienyl ligand) with optically active phenylethylamine to produce diastereomeric ruthenocene complexes.

In a preliminary communication we have described the synthesis of the fulvene complex $[Re(\eta^6\text{-}C_5Me_4CH_2)(CO)_2(C_6F_5)]$ **1a** and its reactions with PMe_3 and HCl to give the zwitterionic complex $[Re(\eta^5\text{-}C_5Me_4CH_2PMe_3)(CO)_2(C_6F_5)]$ **2** and *cis*-$[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)Cl]$ **4a** respectively.[11] Here full details are given of the synthesis of **1a** and its CF_3-aryl substituted analogue $[Re(\eta^6\text{-}C_5Me_4CH_2)(CO)_2(C_6F_4CF_3)]$ **1b** *via* C–F bond activation of C_6F_6 and $C_6F_5CF_3$ respectively. Also included in this work are the reactions of **1a** with methoxide to form the anion $[Re(\eta^5\text{-}C_5Me_4CH_2OMe)(CO)_2(C_6F_5)]^-$ **3**, with HX to give $[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)X]$ (X = Cl **4a** or Br **4b**), as well as the reactions of **1a** with X_2, leading to the complexes *trans*-$[Re(\eta^5\text{-}C_5Me_4CH_2X)(CO)_2(C_6F_5)X]$ (X = Cl **5a**, Br **5b** or I **5c**). The proposed structure of **5b** is supported by X-ray crystallography. The protonation reaction of **1a** with HBF_4 to produce the cationic complex $[Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_6F_5)(NCMe)]^+$ **6** is also described. These reactions are summarized in Scheme 1.

Results

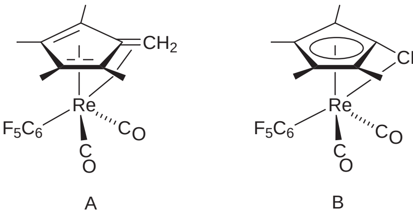
1. Tetramethylfulvene complexes $[Re(\eta^6\text{-}C_5Me_4CH_2)(CO)_2(C_6F_4R)]$, R = F 1a or CF_3 1b

Photolysis of $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ (λ = 300 nm) in a quartz tube in neat C_6F_6 or $C_6F_5CF_3$ at room temperature gave, in both cases, one major dicarbonyl product. These compounds, isolated as air stable orange crystals in good yield, were identified as the tetramethylfulvene complexes, $[Re(\eta^6\text{-}C_5Me_4CH_2)(CO)_2(C_6F_4CF_3R)]$ (R = F or CF_3). In each case, however, the product was present in more than one form (see below). The crystal structure of **1a**, described in a previous communication,[11] shows that the C_6F_5 group occupies a position '*trans*' to the CH_2 group of the fulvene. The C–C bond to the CH_2 group is relatively long [1.43(2) Å] and is bent out of the C_5Me_4 plane by 39.6°.



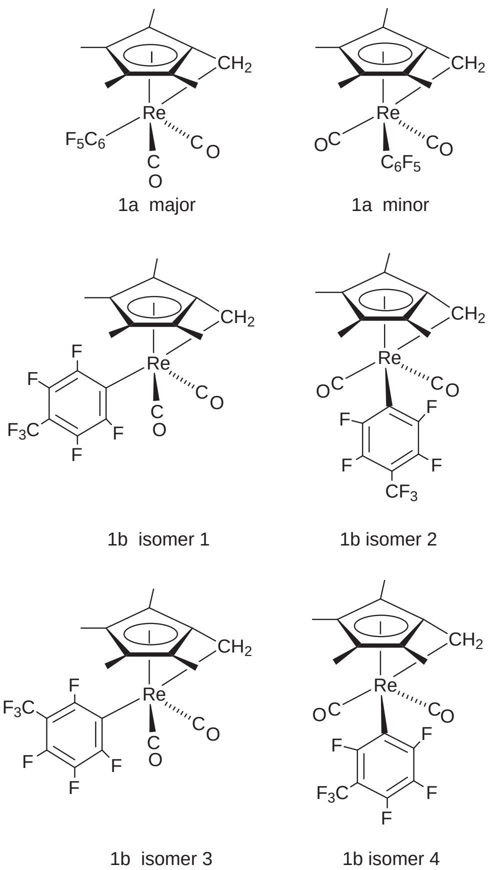
Scheme 1 Reactions of the fulvene complex **1a**.

Two extreme canonical forms can be envisaged for the bonding of a η6-conjugated triene ligand, η6-tetramethylfulvene **A** or η5-tetramethylcyclopentadienyl-σ-alkyl ("tucked-in") **B**. The crystal structure is close to expectations for a "tucked-in" complex.[11,12]



An assessment of the bonding can also be obtained from the NMR spectra. For the major isomer of each complex (Scheme 2) both ^{1}H chemical shifts of the methylene group (*δ* 4.10 **1a** and 4.17 **1b**) and the C–H coupling constants measured in the ^{13}C-gated spectrum for each CH_2 triplet (J_{CH} 162 **1a** and 163 Hz **1b**) suggest that the $C_5Me_4CH_2$ ligand is bound to the rhenium in a η6-triolefinic fashion, form **A**.[13] The separate observation of two isomers is more easily understood if there is an appreciable contribution from the tucked-in canonical form, **B**, generating a barrier to internal rotation. The equivalence of the CH_2 protons and the presence of two resonances for the C_5Me_4 protons show that the major isomer in solution is the same as that revealed by the crystal structure. In addition to the resonances of the major species, the ^{1}H and ^{19}F NMR spectra of **1a** showed a set of weak resonances which are assigned to a minor isomer with the η6-$C_5Me_4CH_2$ ligand rotated relative to the C_6F_5 group (Scheme 2). The proportion of the minor isomer is 14% in chloroform at 293 K. For the minor isomer, as expected, all methyl groups and the CH_2 protons are inequivalent in the ^{1}H NMR spectrum, as are the CO groups in the ^{13}C NMR spectrum. The EXSY experiments for **1a** revealed no evidence for interconversion of the two isomers on the NMR timescale at 300 K. Complex ^{1}H and ^{13}C NMR spectra resulting from the presence of several isomers have also been reported for the dimeric tetramethylfulvene complex [{Ru(η6-$C_5Me_4CH_2$)Cl_2}$_2$].[14]

In contrast to complex **1a**, the ^{1}H NMR spectrum of **1b** shows the presence of four species. The major isomer (isomer 1, 66%) has a "*trans*" orientation of the methylene group with a



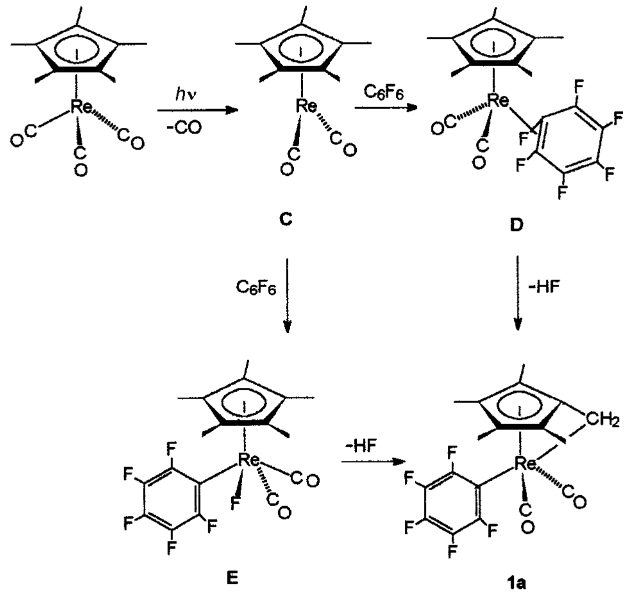
Scheme 2 Isomers of complexes **1a** and **1b**.

4-$C_6F_4CF_3$ ligand. Consequently, two singlets are observed for the methyl protons and one singlet for the CH_2 protons. The second isomer (isomer 2, 24.4%) possesses a "*cis*" conformation of the CH_2 and 4-$C_6F_4CF_3$, similar to that found for the minor isomer of **1a**. Isomer 3 (12.2%) contains the CH_2 group "*trans*" to a 3-$C_6F_4CF_3$ ligand and shows a similar ^1H NMR pattern to those previously described. However, the ^{19}F NMR spectrum of this isomer shows, as expected, three different resonances for the fluorine atoms bound to the aryl ring. The assignment of these resonances was made by using selective ^{19}F–^{19}F NMR decoupling techniques. The "*cis*" arrangement of the CH_2 and 3-$C_6F_4CF_3$ groups for isomer 4 was assigned on the basis of the inequivalent resonances for the methyl and CH_2 protons in the ^1H NMR spectrum. The ^{19}F NMR spectrum shows resonances which support the presence of the *meta* substituted aromatic ligand. The low abundance of this isomer (2.4%) precludes us from observing the ^{13}C NMR spectrum.

The formation of complex **1a** (Scheme 3) should involve an unsaturated 16-electron fragment [Re(η^5-C_5Me_5)(CO)$_2$] **C**, by photodissociation of CO from [Re(η^5-C_5Me_5)(CO)$_3$], which reacts with the fluorinated arene to give the intermediate [Re(η^5-C_5Me_5)(CO)$_2$(η^2-C_6F_6)] **D**, and/or the C–F oxidative addition intermediate [Re(η^5-C_5Me_5)(CO)$_2$(C_6F_5)F] **E**. However, we could not detect any intermediates in these reactions by IR spectroscopy. The postulated η^2 co-ordination of the perfluoroarene in an intermediate stage **D** is supported by the isolation and characterization of the analogous [Re(η^5-C_5H_4R)(CO)$_2$(η^2-C_6F_6)], R = H or Me.[15] The final stage of the reaction involves release of HF. Rather than attacking the product in an analogous way to HCl (see below), the HF attacks the glassware.

2. Reactions of [Re(η^6-$C_5Me_4CH_2$)(CO)$_2$(C_6F_5)] 1a with nucleophiles

Complex **1a** underwent facile reactions with PMe_3 and OMe^- at the methylene CH_2 group of the tetramethylfulvene ligand, to



Scheme 3 Possible mechanisms for formation of complex **1a**.

produce the zwitterionic complex [Re(η^5-$C_5Me_4CH_2PMe_3$)-(CO)$_2$(C_6F_5)] **2** and the anion [Re(η^5-$C_5Me_4CH_2OMe$)(CO)$_2$-(C_6F_5)]$^-$ **3**, respectively. Both complexes were isolated as white microcrystalline solids, the latter as the NEt_4^+ salt. They are insoluble in non-polar organic solvents, but **3** dissolves in CH_2Cl_2 and $CHCl_3$, while **2** only dissolves in MeCN. The anionic nature of these complexes at rhenium was easily recognized from the large frequency shift of the ν(CO) bands when compared with the uncharged precursor **1a** [$\Delta\nu$ = 122 (MeCN) and 142 cm^{-1} (CH_2Cl_2), for **2** and **3**, respectively]. The formal negative charge at the metal centre shifted δ(CO) by about 10 ppm to lower field in the ^{13}C NMR spectrum, when compared to **1a**. Both the ν(CO) bands and ^{13}C chemical shifts of the carbonyls of **2** and **3** are in the same region as those observed for the three legged anion [Re(η^5-C_5Me_5)(CO)$_2$Br]$^-$ [ν(CO) (CH_2Cl_2): 1860s and 1718s cm^{-1}; ^{13}C-{^1H} NMR (CD_2Cl_2) δ 213.1].[16]

The presence of the PMe_3 and methoxy groups bound to the CH_2 was deduced from ^1H and ^{13}C NMR spectra. For instance, the CH_2 groups were observed in the proton spectra as a doublet (J_{PH} 12 Hz) at δ 3.42 for **2** and a singlet at δ 4.11 for **3**. A similar pattern was observed in the ^{13}C NMR spectra: a doublet at δ 22.73 (J_{CP} 47 Hz) for **2** and a singlet at δ 67.09 for **3**.

3. Reaction of complex 1a with hydrogen halides

The reaction of the fulvene complex **1a** with aqueous HX (X = Cl, or Br) in diethyl ether or thf occurs in a similar manner to that previously reported for HCl gas, in the same solvent.[11] In both cases only a single product, formulated as *cis*-[Re(η^5-C_5Me_5)(CO)$_2$(C_6F_5)X], *cis*-**4a** and *cis*-**4b**, is formed in good yield. Under similar conditions aqueous HF does not react with **1a**.

The *cis*-[Re(η^5-C_5Me_5)(CO)$_2$(C_6F_5)X] (X = Cl or Br) complexes, isolated as red microcrystalline solids, exhibit mass spectra which show M^+, [M−CO]$^+$ and [M−2CO]$^+$ peaks. The ^1H and ^{19}F NMR spectra just exhibit resonances expected for a single isomer. In addition to the resonances of the η^5-C_5Me_5 carbons, the ^{13}C NMR spectra in the carbonyl region clearly show two resonances due to the non-equivalent CO ligands in a *cis* or lateral arrangement. Similarly, the IR spectra (CH_2Cl_2 solution) in each case consist of only two ν(CO) absorptions in the region 1953–2052 cm^{-1}, of which the higher wavenumber one is much more intense. A similar pattern of intensities is observed for other *cis*-dicarbonyl complexes of this type for which the structure is known by X-ray crystallography.[17]

From the reaction of the fulvene complex **1a** with aqueous HI in thf, under similar conditions to those used for the preparation of *cis*-**4a** and *cis*-**4b**, only *trans*-[Re(η^5-C_5Me_5)(CO)$_2$-(C_6F_5)I], *trans*-**4c**, could be isolated in good yield. At an early stage of the reaction the IR spectrum of the mixture showed, in addition to the absorptions of the final product at 2034 and 1968 cm^{-1} (CH_2Cl_2 solution), the presence of two weak bands at 2028 and 1953 cm^{-1} which are probably due to the *cis* isomer. These bands quickly disappear at room temperature, producing an increase in intensity of the bands of the isolated product. When the reaction was carried out at 0 °C the *cis*:*trans* ratio was estimated to be 2:1, but all attempts to separate the mixture by column chromatography were unsuccessful due to rapid *cis* $\longrightarrow$ *trans* isomerization on the silica gel. The chloro and bromo complexes *cis*-**4a** and *cis*-**4b** also proved unstable with respect to the thermal isomerization in solution. Both compounds can be converted into the corresponding *trans* isomers *trans*-**4a** and *trans*-**4b** in thf solution at room temperature. The conversion of the chloro derivative (18 h) is slower than that of the bromo derivative (5 h). This trend can be explained on the basis of steric arguments: the two bulkiest ligands in the iodo derivative (C_6F_5 and I) will adopt the *trans* or diagonal position more easily than in the smaller chloro and bromo analogues. Thermal *cis* $\rightarrow$ *trans* isomerization in solution of organic solvents is a well known process in four-legged piano stool complexes of rhenium.[18,19]

The *trans*-**4a**–**4c** isomers, obtained as orange-red solids after column purification, show considerably greater solubility than the *cis* isomers, especially in hydrocarbon solvents. These compounds are recognizable by their two IR ν(CO) absorptions in which the higher wavenumber one [$\nu(CO)_{sym}$] is now the less intense of the pair. Both bands are also shifted to higher wavenumber by comparison with the corresponding *cis* isomer by amounts which increase in the order I < Br < Cl. Almost exactly the same trend was observed previously for *cis*- and *trans*-[Re(η^5-C_5Me_5)(CO)$_2$X$_2$] (X = Cl, Br or I) and explained in terms of the increased competition for rhenium d electrons between the carbonyl groups when they are mutually *trans*.[17] All of these complexes exhibit a single ^{13}CO resonance for equivalent CO groups in the ^{13}C NMR spectrum. Accordingly, we are confident that all adopt the *trans* geometry, that is the geometry which places the bulky C_6F_5 and halogen ligands in a less hindered position. Furthermore, very recently we reported the synthesis and characterization of the closely related complex *trans*-[Re(η^5-C_5Me_5)(CO)$_2$(Ph)I] which was shown to have a *trans* orientation of the CO ligands by X-ray crystallography.[20]

The reaction of complex **1a** with HBF_4 in the presence of MeCN, at room temperature, also regenerates the η^5-C_5Me_5 ligand and yields the orange cationic complex [Re(η^5-C_5Me_5)(CO)$_2$(C_6F_5)(NCMe)]$^+$ which could be isolated as the BF_4^- salt in excellent yield. This solid is air stable and insoluble in most of the organic solvents but soluble in MeCN. By IR and NMR spectroscopy, it was identified as a mixture of *cis* and *trans* isomers in a proportion of 2:1. Since attempts to separate the isomers were unsuccessful, they were characterized in solution. As expected, a large shift to high energy was observed for the ν(CO) bands, when compared to those of the other dicarbonyl complexes, *i.e.* **5a**–**5c** (see below). These absorption bands are in the same region as those of *cis*- and *trans*-[Re(η^5-C_5Me_5)(CO)$_2${P(OMe)$_3$}X]$^+$ (X = Cl, Br or I).[18] The presence of the two isomers was clearly shown by ^{1}H, ^{13}C and ^{19}F NMR (see Experimental section).

4. (Halogenomethyl)tetramethylcyclopentadienyl complexes *trans*-[Re(η^5-$C_5Me_4CH_2X$)(CO)$_2$(C_6F_5)X] 5a–5c (X = Cl, Br or I)

The fulvene complex [Re(η^6-$C_5Me_4CH_2$)(CO)$_2$(C_6F_5)] **1a** reacts readily with halogens X_2 (X = Cl, Br or I) in hexanes at room temperature to produce the (halogenomethyl)tetramethylcyclopentadienyl halide complexes *trans*-[Re(η^5-$C_5Me_4CH_2X$)-(CO)$_2$(C_6F_5)X] **5a**–**5c** as orange-yellow or red crystalline solids. The bromo and iodo derivatives were obtained in almost quantitative yield. The lower yield of the chloro analogue is associated with the formation of a green-brown material that is devoid of carbonyl ligands and that has resisted purification *via* chromatography as it is irreversibly adsorbed onto neutral alumina.

The presence of the (halogenomethyl)tetramethylcyclopentadienyl ligand in these complexes was easily detected by ^{1}H and ^{13}C NMR spectroscopy. Two distinct methyl groups and a lower field resonance for the methylene group are observed for the chloro and bromo derivatives **5a** and **5b** by both techniques. In contrast, the ^{13}C NMR spectrum for the iodo complex **5c** shows the methylene group resonance at high field (δ −3.06 in $CDCl_3$), as a consequence of the "heavy atom effect". Similar patterns to those described here have been reported for the related compounds [Ru(η^5-$C_5Me_4CH_2Cl$)(CO)$_2$Cl],[1] [Rh(η^5-$C_5Me_4CH_2X$)-(η^5-C_5H_5)]$^+$ (X = Cl or I),[3] [Zr(η^5-$C_5Me_4CH_2I$)(η^5-C_5Me_5)-(Ph)I],[8] [Re(η^5-$C_5Me_4CH_2PMe_3$)(CO)$_2$(C_6F_5)],[11] and [Fe(η^6-$C_6Me_5CH_2X$)(η^5-C_5H_5)]$^+$ (X = Cl, Br or I).[21]

The presence of the C_6F_5 ligand in complexes **5a**–**5c** was clearly established by the three multiplets observed in the ^{19}F NMR spectrum (see Experimental section). The ^{13}C NMR spectra show a single resonance for the CO group for each of these compounds. The IR spectrum (CH_2Cl_2 solution) in each case consists of only two ν(CO) absorptions in the 2060–1970 cm^{-1} region, of which the higher wavenumber band is much less intense, implying a *trans* or diagonal orientation of the CO ligands.

5. Crystal structure of *trans*-[Re(η^5-$C_5Me_4CH_2Br$)(CO)$_2$(C_6F_5)-Br] 5b

The structure of *trans*-[Re(η^5-$C_5Me_4CH_2Br$)(CO)$_2$(C_6F_5)Br] **5b** confirms the presence of the (bromomethyl)tetramethylcyclopentadienyl ligand (Fig. 1; Tables 1, 2). The complex exists as discrete molecules in the unit cell, with no unusually short intermolecular contacts. The rhenium atom is formally in the III oxidation state and is seven-co-ordinated if the η^5-$C_5Me_4CH_2Br$ group is considered as three-co-ordinate. The Re–C (CO) bond lengths are in the range 1.89–2.03 Å reported for *trans*-[Re-(η^5-C_5Me_5)(CO)$_2$Br$_2$],[17] *trans*-[Re(η^5-C_5Me_5)(CO)$_2$(Ph)I],[20] *trans*-[Re(η^5-C_5Me_5)(CO)$_2$Et$_2$],[22] *trans*-[Re(η^5-C_5Me_5)(CO)$_2$H$_2$],[23] *trans*-[Re(η^5-C_5H_5)(CO)$_2$(COMe)Me][24] and *trans*-[Re(η^5-C_5H_5)-(CO)$_2$(SnPh$_3$)$_2$].[25] The interbond angle relating the carbonyl groups C(17)–Re–C(18) of 100.5(5)° is in the range for the complexes mentioned above, for which the *trans* orientation of the CO ligands has been confirmed by X-ray crystallography. The Re–C (C_6F_5) bond length of 2.203(10) Å is almost identical, in terms of the achieved precision, to that reported for the parent fulvene complex **1a**.[11] The angle relating the C_6F_5 group and Br(1) C(11)–Re–Br(1) of 142.6(3)° is greater than that reported for *trans*-[Re(η^5-C_5Me_5)(CO)$_2$(Ph)I] [140.8(2)°].[20] Other bond lengths and angles are unexceptional.

Discussion

The photoreactions of [Re(η^5-C_5Me_5)(CO)$_3$] with C_6F_6 and $C_6F_5CF_3$ result in combined C–H and C–F bond activation (Schemes 2, 3). This method provides a route to introduce a fluoroaryl group at rhenium and, simultaneously, activate one of the ring methyl groups. Since our initial report of this reaction many more intermolecular C–F bond activation reactions have been discovered.[26–28] Another one which occurs in combination with C–H activation is the photoreaction of [Rh(η^5-C_5H_5)(PMe$_3$)(C_2H_4)] with C_6F_5OMe which leads to the metallacycle [Rh(η^5-C_5H_5)(PMe$_3$)($C_6F_4OCH_2$)].[28] The thermodynamic driving force for these reactions is provided by the release of HF. In the present reactions HF is scavenged by

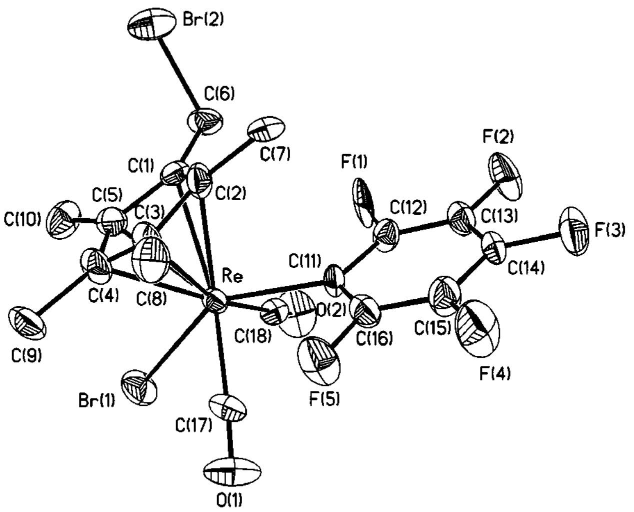


Fig. 1 Thermal ellipsoid diagram (50% probability) of *trans*-[Re(η^5-$C_5Me_4CH_2Br$)$(CO)_2$(C_6F_5)Br] **5b**.

Table 1 Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for *trans*-[Re(η^5-$C_5Me_4CH_2Br$)-$(CO)_2$(C_6F_5)Br] **5b**

Re–C(1)	2.332(10)	Re–C(11)	2.203(10)
Re–C(2)	2.356(12)	Re–C(17)	1.970(12)
Re–C(3)	2.334(14)	Re–C(18)	2.032(10)
Re–C(4)	2.246(12)	Re–Br(1)	2.6254(13)
Re–C(5)	2.298(11)	Br(2)–C(6)	1.965(11)
C(17)–Re–C(18)	100.5(5)	C(17)–Re–C(11)	83.9(5)
C(18)–Re–C(11)	80.8(4)	C(1)–C(6)–Br(2)	108.9(8)
C(11)–Re–Br(1)	142.6(3)		

Table 2 Crystallographic parameters for *trans*-[Re(η^5-$C_5Me_4CH_2Br$)-$(CO)_2$(C_6F_5)Br] **5b**

Empirical formula	$C_{18}H_{14}Br_2F_5O_2Re$
M	703.31
Colour, crystal size/mm	Orange, 0.28 × 0.16 × 0.06
Crystal system, space group	Triclinic, $P\bar{1}$
a/Å	8.372(1)
b/Å	9.246(1)
c/Å	14.570(2)
α/°	79.56(1)
β/°	75.29(1)
γ/°	63.33(1)
U/Å^3	971.9(2)
Z	2
D_c/g cm^{-3}	2.40
μ/mm^{-1}	10.42
F(000)	656
θ Range for data collection/°	2.47–25.05
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 10$, $0 \le l \le 17$
Reflections collected/independent	3627/3343 (R_{int} = 0.054)
Observed reflections	2952 [$I > 2\sigma(I)$]
Data/restraints/parameters	3343/6/253
Goodness of fit on F^2	0.923
Final *R*1, *wR*2, [$I > 2\sigma(I)$]	0.038, 0.124
(all data)	0.048, 0.131
Largest difference peak, hole/e Å^{-3}	1.70, −1.82

$R1 = \Sigma(|F_o - F_c|/|F_o|)$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$, $a = 0.08$, $b = 23.44$.

the quartz glassware rather than reacting with the products or precursors. The formation of **1a** and **1b** contrasts with the reactions of [Re(η^5-C_5H_4R)$(CO)_3$] (R = H or Me) with C_6F_6 which simply give rise to the substitution products [Re(η^5-C_5H_4R)$(CO)_2$(η^2-C_6F_6)].[15]

The formation of the tetramethylfulvene group in complex **1a** offers considerable opportunities for generating ring-functionalized cyclopentadienyl complexes. In this paper we have shown that this method can be used to form η^5-C_5Me_4-CH_2R ligands with R = PMe_3, OMe, Cl, Br or I (Scheme 1).

The reactions of the fulvene complex **1a** with PMe_3 and with MeO^- demonstrate the electrophilic character of the methylene group. In the light of these reactions, it seems unlikely that acids HX (X = Cl, Br or I) and HBF_4 attack directly at the methylene group. An alternative pathway could involve initial attack of H^+ at the metal followed by migration to the CH_2 group.

The reactions of the fulvene complex with X_2 could proceed by one of two routes. In the first, primary electrophilic addition of the halogen to the CH_2 group gives the unstable cation [Re(η^5-$C_5Me_4CH_2X$)$(CO)_2$(C_6F_5)]$^+$, which then co-ordinates X^-. Analogous reactions have been reported for the complexes [Rh(η^4-$C_5Me_4CH_2$)(η^5-C_5H_5)] and [Fe(η^5-$C_6Me_5{=}CH_2$)(η^5-C_5H_5)] with an excess of iodine, and in both cases the corresponding cations could be isolated.[3,21] However, this mechanism conflicts with the electrophilic character of the CH_2 group shown above. Another possible reaction pathway involves direct attack of the halogen molecule at the metal centre, leading to the intermediate species [Re(η^6-$C_5Me_4CH_2$)$(CO)_2$(C_6F_5)X]$^+$, which then could react at the methylene group with X^-. Support for this suggestion is given by the reactions of the parent carbonyl complex [Re(η^5-C_5Me_5)$(CO)_3$] with halogens, which yield the cationic complexes [Re(η^5-C_5Me_5)$(CO)_3$X]$^+$.[29,30] The mechanism of the reaction and reason for the production of only one of the two possible isomers remain as unanswered questions for future study.

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 precursor, [Re(η^5-C_5Me_5)$(CO)_3$], was prepared according to Gladysz and co-workers.[31] Hexafluorobenzene (99%) and octafluorotoluene (98%) from Aldrich were used as received. 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 (complexes **3**, **4a**–**4c** and **5a**–**5c**), DRX 400 (^{19}F–^{19}F decoupling experiments) and AMX 500 instruments (complexes **1a**–**1b**, **2** and **6**). All ^{1}H NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances ($CDCl_3$, δ 7.27; CD_3CN, δ 2.00), ^{13}C NMR chemical shifts to solvent peaks ($CDCl_3$, δ 77.0; CD_3CN, δ 0.3, 117.2) and ^{19}F NMR spectra to external C_6F_6 at δ −162.90. Coupling assignments are indicated, where known. Mass spectra and elemental analyses were obtained at the Microanalysis Department of Simon Fraser University, Canada, and the Centro de Instrumentación of Pontificia Universidad Católica de Chile, Santiago, Chile.

Preparations

[Re(η^6-$C_5Me_4CH_2$)$(CO)_2$(C_6F_5)] 1a. The complex [Re(η^5-C_5Me_5)$(CO)_3$] (150 mg, 0.37 mmol) was dissolved in hexafluorobenzene (12 cm^3) in a quartz tube. The solution was degassed with three freeze–pump–thaw cycles, and irradiated for 6 h (λ = 300 nm) at room temperature using a Rayonet RPR-100 photochemical reactor. The solution turned yellowish brown, and an IR spectrum showed, in addition to the CO bands corresponding to the parent complex, two bands at 2007 and 1940 cm^{-1}. Corrosion of the quartz tube was observed. The solvent was removed under vacuum, and the resulting brown residue purified by chromatography on a neutral alumina column. Elution with hexanes moved unchanged [Re(η^5-C_5Me_5)$(CO)_3$] (43 mg, 0.11 mmol) and then the fulvene complex **1a**, which was obtained as a yellow solid after evaporation of the solvent (93 mg, 65%). Recrystallisation of **1a** from hexanes yielded orange crystals. IR [hexanes, $\tilde{\nu}$(CO)/cm^{-1}]: 2007vs and 1940vs. Mass spectrum (EI, based on ^{187}Re): *m*/*z* 544 (M^+), 516 (M^+ − CO) and 488 ($M^+ - 2CO$) (Found: C, 39.70; H, 2.55. Calc. for $C_{18}H_{14}F_5O_2Re$: C, 39.78; H, 2.60%).

Major isomer (trans CH_2 and C_6F_5). ^1H NMR ($CDCl_3$): δ 1.72 (s, 6 H, CH_3), 2.05 (s, 6 H, CH_3) and 4.10 (s, 2 H, CH_2). ^{19}F NMR ($CDCl_3$): δ −164.37 (m, $2F_{meta}$), −160.10 (t, J_{FF} 20 Hz, F_{para}) and −104.66 (m, $2F_{ortho}$). ^{13}C-{^1H}NMR ($CDCl_3$): δ 9.62 (s, CH_3), 9.75 (s CH_3), 47.37 (s, CH_2), 96.95 (s, C_5Me_4), 107.36 (s, C_5Me_4), 107.43 (s, C_5Me_4), 109.93 (t, J_{CF} 51, C_{ipso} C_6F_5), 136.14 (d, J_{CF} 253, C_6F_5), 138.20 (d, J_{CF} 226, C_6F_5), 150.39 (d, J_{CF} 225, C_6F_5) and 198.27 (t, J_{CF} 5.1 Hz, CO). Gated ^{13}C-{^1H}NMR ($CDCl_3$): δ 9.62 (t, J_{CH} 128, CH_3), 9.75 (t, J_{CH} 127, CH_3) and 47.37 (t, J_{CH} 161 Hz, CH_2).

Minor isomer, (cis CH_2 and C_6F_5). ^1H NMR ($CDCl_3$): δ 1.50 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 4.00 (d, J_{HH} 1.5, 1 H, CH_2) and 4.80 (d, J_{HH} 1.5 Hz, 1 H, CH_2). ^{19}F NMR ($CDCl_3$): δ −165.35 (m, $2F_{meta}$), −162.86 (t, J_{FF} 20 Hz, F_{para}) and −105 (broad, $2F_{ortho}$). ^{13}C-{^1H}NMR ($CDCl_3$): δ 8.61 (s, CH_3), 10.19 (s, CH_3), 10.72 (s, CH_3), 11.34 (s, CH_3), 64.80 (s, CH_2), 94.05 (s, C_5Me_4), 98.70 (s, C_5Me_4), 106.91 (s, C_5Me_4), 109.25 (s, C_5Me_4), 114.02 (s, C_5Me_4), 112.3 (m, C_{ipso} C_6F_5), 198.01 (s, CO) and 200.75 (s, CO).

[Re(η^6-$C_5Me_4CH_2$)$(CO)_2$($C_6F_4CF_3$)] 1b. This complex was prepared in a similar manner to that of **1a** but using octafluorotoluene. Yield 52%. IR [hexane, $\tilde{\nu}$(CO)/cm^{-1}]: 2006vs and 1942vs. Mass spectrum (EI, based on ^{187}Re): *m/z* 594 (M^+), 566 ($M^+ - CO$) and 538 ($M^+ - 2CO$) (Found: C, 38.39; H, 2.36. Calc. for $C_{19}H_{14}F_7O_2Re$: C, 38.45; H, 2.38%).

Isomer 1, [Re(η^6-$C_5Me_4CH_2$)$(CO)_2$(4-$C_6F_4CF_3$)], trans CH_2 and 4-$CF_3C_6F_4$. ^1H NMR ($CDCl_3$): δ 1.75 (s, 6 H, CH_3), 2.06 (s, 6 H, CH_3) and 4.17 (s, 2 H, CH_2). ^{19}F NMR ($CDCl_3$): δ −144.58 (m, $2F_{meta}$), −104.12 (m, $2F_{ortho}$) and −56.97 (t, J_{FF} 21 Hz, 3F, CF_3). ^{13}C-{^1H}NMR ($CDCl_3$): δ 9.70 (s, CH_3), 9.75 (s, CH_3), 48.82 (s, CH_2), 97.79 (s, C_5Me_4), 107.26 (s, C_5Me_4), 107.39 (s, C_5Me_4), 121.57 (q, J_{CF} 270, CF_3), 126.17 [t, J_{CF} 50, C_{ipso} $C_6F_4(CF_3)$], 142.52 [d, J_{CF} 260, $C_6F_4(CF_3)$], 149.51 [d, J_{CF} 230, $C_6F_4(CF_3)$], 161.30 [d, J_{CF} 220, $C_6F_4(CF_3)$] and 197.80 (t, J_{CF} 6 Hz, CO).

Isomer 2, [Re(η^6-$C_5Me_4CH_2$)$(CO)_2$(4-$C_6F_4CF_3$)], cis CH_2 and 4-$CF_3C_6F_4$. ^1H NMR ($CDCl_3$): δ 1.52 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 4.02 (d, J_{HH} 1.7, 1 H, CH_2) and 4.83 (d, J_{HH} 1.7 Hz, 1 H, CH_2). ^{19}F NMR ($CDCl_3$): δ −145.85 (m, F_{meta}), −105 (broad, F_{ortho}) and −56.79 (t, J_{FF} 21 Hz, CF_3). ^{13}C-{^1H}NMR ($CDCl_3$): δ 8.64 (s, CH_3), 10.18 (s, CH_3), 10.76 (s, CH_3), 11.30 (s, CH_3), 64.99 (s, CH_2), 94.46 (s, C_5Me_4), 98.98 (s, C_5Me_4), 106.76 (s, C_5Me_4), 109.04 (s, C_5Me_4), 113.95 (s, C_5Me_4), 129.77 [t, J_{CF} 50 Hz, C_{ipso} $C_6F_4(CF_3)$], 197.38 (s, CO), 199.85 (s, CO), and CF aromatic groups not observed.

Isomer 3, [Re(η^6-$C_5Me_4CH_2$)$(CO)_2$(3-$C_6F_4CF_3$)], trans CH_2 and 3-$CF_3C_6F_4$. ^1H NMR ($CDCl_3$): 1.71 (s, 6 H, CH_3), 2.05 (s, 6 H, CH_3) and 4.12 (s, 2 H, CH_2). ^{19}F NMR ($CDCl_3$): δ −166.07 (m, F_{meta}), −140.36 (m, F_{para}), −90.72 (m, F_{ortho}), −78.12 (m, F_{ortho}) and −57.31 (ddd, J_{FF} 25, 21, 1 Hz, CF_3). ^{13}C-{^1H}NMR ($CDCl_3$): δ 9.57 (s, CH_3), 9.74 (s, CH_3), 47.71 (s, CH_2), 97.01 (s, C_5Me_4), 107.48 (s, C_5Me_4), 107.35 (s, C_5Me_4), 198.08 (s, CO), and aromatic carbons not observed.

Isomer 4, [Re(η^6-$C_5Me_4CH_2$)$(CO)_2$(3-$C_6F_4CF_3$)], cis CH_2 and 3-$CF_3C_6F_4$. ^1H NMR ($CDCl_3$): δ 1.50 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 3.95 (d, J_{HH} 1.7, 1 H, CH_2), 4.79 (d, J_{HH} 1.7 Hz, 1 H, CH_2) and one methyl group not observed. ^{19}F NMR ($CDCl_3$): δ −167.17 (m, F_{meta}), −143.24 (m, F_{para}), −57.19 (ddd, J_{FF} 25, 21, 1 Hz, CF_3) and the two F_{ortho} not observed.

[Re(η^5-$C_5Me_4CH_2PMe_3$)$(CO)_2$(C_6F_5)] 2. To a solution of complex **1a** (60 mg, 0.11 mmol) in thf (10 cm^3) at 0 °C was added an excess of PMe_3 (0.05 cm^3), with stirring. The solution immediately changed from yellow to colourless. At this point, the IR spectrum (in thf) showed the complete disappearance of **1a** and new strong bands at 1880 and 1812 cm^{-1}. After 15 min of stirring at 0 °C a white precipitate appeared. The volume of thf was reduced to about one third under vacuum and Et_2O (5 cm^3) was added to complete the precipitation. The white solid was washed twice with Et_2O (5 cm^3) and then recrystallized from acetonitrile–diethyl ether at 4 °C. A colourless microcrystalline solid was isolated (66 mg, 97% yield), which decomposed over 90 °C. IR [MeCN, $\tilde{\nu}$(CO)/cm^{-1}]: 1868vs and 1795vs. ^1H NMR (CD_3CN): δ 1.76 (d, J_{PH} 14 Hz, PMe_3), 2.03 (s, CH_3), 2.04 (s, CH_3) and 3.42 (d, J_{PH} 12 Hz, CH_2). ^{13}C-{^1H}NMR (CD_3CN): δ 7.69 (d, J_{CP} 53, PMe_3), 10.38 (s, CH_3), 11.56 (s, CH_3), 22.73 (d, J_{CP} 47, CH_2), 81.21 (s, C_5Me_4), 95.59 (s, C_5Me_4), 95.81 (d, J_{CP} 1, C_5Me_4), 121.71 (t, J_{CF} 59, C_{ipso} C_6F_5), 134.42 (d, J_{CF} 230, C_6F_5), 135.32 (d, J_{CF} 245, C_6F_5), 150.53 (d, J_{CF} 210 Hz, C_6F_5) and 210.38 (s, CO). ^{19}F NMR (CD_3CN): δ −161.3 (t, J_{FF} 26 Hz, $2F_{meta}$), −160.8 (t, J_{FF} 20 Hz, F_{para}), −98.5 (d, J_{FF} 26 Hz, $2F_{ortho}$). ^{31}P-{^1H}NMR (CD_3CN): δ 29.1 (s, CH_2PMe_3). Mass spectrum (FAB, based on ^{187}Re): *m/z* 620 (M^+) (Found: C, 40.33; H, 4.02. Calc. for $C_{21}H_{23}F_5O_2PRe$: C, 40.65; H, 3.72%).

$[NEt_4]^+$[Re(η^5-$C_5Me_4CH_2OMe$)$(CO)_2$(C_6F_5)]$^-$ 3. To a solution of the fulvene complex **1a** (60 mg, 0.11 mmol) in CH_2Cl_2 (15 cm^3) was added tetraethylammonium bromide (23 mg, 0.11 mmol) and sodium methoxide (12 mg, 0.22 mmol). After 15 min of stirring at room temperature the solution turned colourless, and the IR spectrum only showed CO absorptions at 1855 and 1775 cm^{-1}. The mixture was filtered, and the white solid washed twice with CH_2Cl_2 (2 cm^3). The filtrate was reduced in volume to ≈5 cm^3, and then a layer of diethyl ether was slowly poured into the flask. After 24 h complex **3** was isolated as a white crystalline solid (58 mg, 75%). IR [CH_2Cl_2, $\tilde{\nu}$(CO)/cm^{-1}]: 1855vs and 1775vs. ^1H NMR ($CDCl_3$): δ 1.19 (t, 12 H, CH_3 NEt_4^+), 1.92 (s, 6 H, CH_3), 1.95 (s, 6 H, CH_3), 2.40 (q, 8 H, CH_2 NEt_4^+), 3.31 (s, 3 H, OCH_3) and 4.11 (s, 2 H, CH_2). ^{19}F NMR ($CDCl_3$): δ −167.50 (m, $2F_{meta}$), −166.93 (tt, J_{FF} 20.3, 2.3 Hz, F_{para}) and −104.42 (m, F_{ortho}). ^{13}C-{^1H}NMR ($CDCl_3$): δ 7.32 (s, CH_3 NEt_4^+), 10.59 (s, CH_3), 10.79 (s, CH_3), 52.45 (s, CH_2 NEt_4^+), 57.74 (s, CH_2OCH_3), 67.09 (s, CH_2OCH_3), 89.42 (s, C_5Me_4), 95.50 (s, C_5Me_4), 98.66 (s, C_5Me_4) and 212.89 (s, CO) (Found: C, 45.85; H, 5.22. Calc. for $C_{27}H_{37}F_5NO_3Re$: C, 46.01; H, 5.29%).

***cis*-[Re(η^5-C_5Me_5)$(CO)_2$(C_6F_5)Cl] *cis*-4a.** A solution of complex **1a** (50 mg, 0.092 mmol) in HCl (1.0 M solution in diethyl ether, 6 cm^3) was stirred at room temperature for 8 h. The mixture changed from yellow to red, and the IR spectrum showed no evidence for the starting material. Solvent was removed under vacuum, and the residual reddish oil was dissolved in CH_2Cl_2 (5 cm^3) dried over anhydrous Na_2SO_4, and filtered. A layer of hexanes was slowly poured into a flask, and after 2 d at room temperature *cis*-**4a** was isolated as red crystals in 90% yield (48 mg), mp 179 °C (decomp.). IR [CH_2Cl_2, $\tilde{\nu}$(CO)/cm^{-1}]: 2033vs and 1959s. ^1H NMR ($CDCl_3$): δ 2.06 (s, CH_3). ^{19}F NMR ($CDCl_3$): δ −163.94 (m, $2F_{meta}$), −160.06 (t, J_{FF} 20.1 Hz, F_{para}) and −108.82 (m, $2F_{ortho}$). ^{13}C-{^1H}NMR ($CDCl_3$): δ 10.83 (s, CH_3), 108.49 (s, C_5Me_5), 199.75 (s, CO) and 202.20 (s, CO). Mass spectrum (EI, based on ^{187}Re and ^{35}Cl): *m/z* 580 (M^+), 552 ($M^+ - CO$) and 524 ($M^+ - 2CO$) (Found: C, 37.64; H, 2.74. Calc. for $C_{18}H_{15}ClF_5O_2Re$: C, 37.28; H, 2.61%).

***trans*-[Re(η^5-C_5Me_5)$(CO)_2$(C_6F_5)Cl] *trans*-4a.** This complex was prepared following the same procedure as that used for *cis*-**4a**, but the stirring at room temperature was maintained for 18 h. The yellow-orange solid obtained after evaporation of the solvent was dissolved in the minimum amount of hexanes, and crystallized at −18 °C as yellow-orange needles (45 mg, 70%), mp 175 °C (decomp.). IR [CH_2Cl_2, $\tilde{\nu}$(CO)/cm^{-1}]: 2054s and 1979vs. ^1H NMR ($CDCl_3$): δ 1.83 (s, CH_3). ^{19}F NMR ($CDCl_3$): δ −162.36 (m, $2F_{meta}$), −156.69 (t, J_{FF} 20.3 Hz, F_{para}) and

−101.76 (m, 2F$_{ortho}$). ^{13}C-{^{1}H}NMR ($CDCl_3$): δ 9.80 (s, CH_3), 104.78 (s, C_5Me$_5$) and 190.58 (s, CO). Mass spectrum (EI, based on ^{187}Re and ^{35}Cl): *m*/*z* 580 (M^+), 552 (M^+ − CO) and 524 (M^+ − 2CO) (Found: C, 37.40; H, 2.71. Calc. for $C_{18}H_{15}ClF_5O_2Re$: C, 37.28; H, 2.61%).

***cis*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)Br] *cis*-4b.** The fulvene complex **1a** (60 mg, 0.110 mmol) in thf (15 cm^3) was stirred at 5 °C with an excess of aqueous HBr (47%, 0.4 cm^3, 3.48 mmol). The reaction was followed by IR spectroscopy until all the fulvene complex had reacted (*ca.* 2.5 h). The thf was pumped off and the reddish oily residue was dissolved in CH_2Cl_2 (5 cm^3) and treated with a 5% aqueous solution (10 cm^3) of Na_2CO_3. The organic layer was separated, dried over anhydrous Na_2SO_4 and filtered. The solution was reduced to about 3 cm^3 under vacuum and a layer of hexanes poured slowly into the flask. The complex *cis*-**4b** (56 mg, 81%) was isolated as red crystals, mp 194 °C (decomp.). IR [CH_2Cl_2, $\tilde{\nu}$(CO)/cm^{-1}]: 2032vs and 1958s. ^{1}H NMR ($CDCl_3$): δ 2.12 (s, CH_3). ^{19}F NMR ($CDCl_3$): δ −163.96 (m, 2F$_{meta}$), −160.24 (t, J_{FF} 20.1 Hz, F$_{para}$) and −107.46 (br s, 2F$_{ortho}$). ^{13}C-{^{1}H}NMR ($CDCl_3$): δ 11.01 (s, CH_3), 107.70 (s, C_5Me$_5$), 198.13 (s, CO) and 201.40 (s, CO). Mass spectrum (EI, based on ^{187}Re and ^{79}Br): *m*/*z* 624 (M^+), 596 (M^+ − CO) and 568 (M^+ − 2CO) (Found: C, 34.82; H, 2.48. Calc. for $C_{18}H_{15}BrF_5O_2Re$: C, 34.62; H, 2.42%).

***trans*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)Br] *trans*-4b.** This complex was prepared using a similar procedure to that used for *cis*-**4b**, but the reaction mixture was stirred at room temperature for 4.5 h. The complex *trans*-**4b** (60 mg, 87%) was isolated as orange-reddish needles after crystallization from hexanes at −18 °C, mp 174 °C (decomp.). IR [CH_2Cl_2, $\tilde{\nu}$(CO)/cm^{-1}]: 2045s and 1974vs. ^{1}H NMR ($CDCl_3$): δ 1.89 (s, CH_3). ^{19}F NMR ($CDCl_3$): δ −162.42 (m, 2F$_{meta}$), −156.78 (t, J_{FF} 20.3 Hz, F$_{para}$) and −102.29 (m, 2F$_{ortho}$). ^{13}C-{^{1}H}NMR ($CDCl_3$): δ 10.30 (s, CH_3), 104.24 (s, C_5Me$_5$) and 189.04 (s, CO). Mass spectrum (EI, based on ^{187}Re and ^{79}Br): *m*/*z* 624 (M^+), 596 (M^+ − CO) and 568 (M^+ − 2CO) (Found: C, 34.83; H, 2.40. Calc. for $C_{18}H_{15}BrF_5O_2Re$: C, 34.62; H, 2.42%).

***trans*-[Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)I] *trans*-4c.** To a solution of the fulvene complex **1a** (60 mg, 0.11 mmol) in thf (15 cm^3) was added an aqueous HI solution (67%, *d* = 1.97 g cm^{-3}; 0.4 cm^3, 4.12 mmol). The mixture was stirred at room temperature for 3 h in the dark. Following the same purification procedures to those described previously, *trans*-**4c** (60 mg, 81%) was isolated as red needles, mp 203 °C (decomp.). IR [CH_2Cl_2, $\tilde{\nu}$(CO)/cm^{-1}]: 2034s and 1968vs. ^{1}H NMR ($CDCl_3$): δ 2.01 (s, CH_3). ^{19}F NMR ($CDCl_3$): δ −162.51 (m, 2F$_{meta}$), −156.97 (tt, J_{FF} 20.2, J_{FF} 2.0 Hz, F$_{para}$) and −103.24 (m 2F$_{ortho}$). ^{13}C-{^{1}H}NMR ($CDCl_3$): δ 11.33 (s, CH_3), 103.38 (s, C_5Me$_5$) and 187.61 (s CO). Mass spectrum (EI, based on ^{187}Re): *m*/*z* 672 (M^+), 644 (M^+ − CO) and 616 (M^+ − 2CO) (Found: C, 32.68; H, 2.03. Calc. for $C_{18}H_{15}F_5IO_2Re$: C, 32.20; H, 2.25%).

***trans*-[Re(η^5-C$_5$Me$_4$CH$_2$Cl)(CO)$_2$(C$_6$F$_5$)Cl] 5a.** To a solution of the fulvene complex **1a** (60 mg, 0.11 mmol) in hexanes (25 cm^3) were added 5 drops of a saturated solution of Cl_2 in hexanes and the mixture stirred at room temperature for 5 min. After this time the IR spectrum showed the complete disappearance of the starting complex. The resulting solution was evaporated to dryness under vacuum and the yellow greenish residue was chromatographed on neutral alumina. A yellow band was eluted with hexane–CH_2Cl_2 (9:1) from which **5a**, an orange yellowish solid, was obtained after solvent evaporation (39 mg, 57% yield, mp 171 °C (decomp.)). A greenish brown material remained irreversibly adsorbed on the top of the column. IR [CH_2Cl_2, $\tilde{\nu}$(CO)/cm^{-1}]: 2060vs and 1992vs. ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 6 H, CH_3), 1.88 (s, 6 H, CH_3) and 4.18 (s, 2 H, CH_2). ^{19}F NMR ($CDCl_3$): δ −161.51 (m, 2F$_{meta}$), −155.52 (t, J_{FF} 20.1 Hz, F$_{para}$) and −101.39 (m, 2F$_{ortho}$). ^{13}C-{^{1}H}NMR ($CDCl_3$): δ 9.51 (s, CH_3), 10.09 (CH_3), 37.17 (s, CH_2), 97.56 (s, C_5Me$_4$CH$_2$Cl), 105.78 (s, C_5Me$_4$CH$_2$Cl), 107.37 (s, C_5Me$_4$CH$_2$Cl) and 188.81 (s, CO). Mass spectrum (EI, based on ^{187}Re and ^{35}Cl): *m*/*z* 614 (M^+), 586 (M^+ − CO) and 558 (M^+ − 2CO) (Found: C, 34.66; H, 2.22. Calc. for $C_{18}H_{14}Cl_2F_5O_2Re$: C, 35.19; H, 2.30%).

***trans*-[Re(η^5-C$_5$Me$_4$CH$_2$Br)(CO)$_2$(C$_6$F$_5$)Br] 5b.** To a solution of the fulvene complex **1a** (70 mg, 0.128 mmol) in hexanes (30 cm^3) was added a solution (6.6 cm^3) prepared by dissolving Br_2 (0.1 cm^3) in hexanes (10 cm^3). After 5 min of stirring at room temperature an orange precipitate started to form, and an IR spectrum of the supernatant showed only the presence of the product. The solution was evaporated to dryness under vacuum, and the residual orange solid was dissolved in the minimum amount of CH_2Cl_2 and crystallized by layer diffusion of hexanes into this solution. Complex **5b** was obtained as a red crystalline solid (89 mg, 98%), mp 178 °C (decomp.). IR [CH_2Cl_2, $\tilde{\nu}$(CO)/cm^{-1}]: 2053vs and 1986vs. ^{1}H NMR ($CDCl_3$): δ 1.89 (s, 6 H, CH_3), 1.93 (s, 6 H, CH_3) and 4.07 (s, 2 H, CH_2). ^{19}F NMR ($CDCl_3$): δ −161.60 (m, 2F$_{meta}$), −155.64 (t, J_{FF} 20.3 Hz, F$_{para}$) and −101.95 (m, 2F$_{ortho}$). ^{13}C-{^{1}H}NMR ($CDCl_3$): δ 10.10 (s, CH_3), 10.48 (s, CH_3), 24.36 (s, CH_2), 97.24 (s, C_5Me$_4$CH$_2$Br), 104.86 (s, C_5Me$_4$CH$_2$Br), 106.86 (s, C_5Me$_4$CH$_2$Br) and 187.14 (s, CO). Mass spectrum (EI, based on ^{187}Re and ^{79}Br): *m*/*z* 704 (M^+), 676 (M^+ − CO) and 648 (M^+ − 2CO) (Found: C, 30.60; H, 1.98. Calc. for $C_{18}H_{14}Br_2F_5O_2Re$: C, 30.73; H, 1.99%).

***trans*-[Re(η^5-C$_5$Me$_4$CH$_2$I)(CO)$_2$(C$_6$F$_5$)I] 5c.** This complex was prepared in a similar way to that of **5b**, adding I_2 (23.3 mg, 0.092 mmol) to a solution of the fulvene complex **1a** (50 mg, 0.092 mmol), but the resulting solution was stirred at room temperature for 2 h. Complex **5c** was isolated as dark red crystals in 95% yield, mp 192 °C (decomp.). IR [CH_2Cl_2, $\tilde{\nu}$(CO)/cm^{-1}]: 2038vs and 1973vs. ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 6 H, CH_3), 2.02 (s, 6 H, CH_3) and 3.99 (s, 2 H, CH_2). ^{19}F NMR ($CDCl_3$): δ −161.77 (m, 2F$_{meta}$), −155.94 (tt, J_{FF} 20.4, 2.3 Hz, F$_{para}$) and −103.14 (m, 2F$_{ortho}$). ^{13}C-{^{1}H}NMR ($CDCl_3$): δ −3.06 (s, CH_2), 11.25 (s, CH_3), 11.44 (s, CH_3), 98.41 (s, C_5Me$_4$CH$_2$I), 102.89 (s, C_5Me$_4$CH$_2$I), 105.80 (s, C_5Me$_4$CH$_2$I) and 185.80 (s, CO). Mass spectrum (EI, based on ^{187}Re): *m*/*z* 798 (M^+), 770 (M^+ − CO) and 671 (M^+ − I) (Found: C, 27.17; H, 1.71. Calc. for $C_{18}H_{14}F_5I_2O_2Re$: C, 27.10; H, 1.76%).

[Re(η^5-C$_5$Me$_5$)(CO)$_2$(C$_6$F$_5$)(NCMe)]$^+$[BF$_4$]$^-$ 6. To a solution of complex **1a** (117 mg, 0.215 mmol) in MeCN (12 cm^3), was added HBF_4 (1.7 cm^3, 0.215 mmol) in MeCN [prepared by dilution of 0.25 cm^3 of HBF_4 in Et_2O (54%, *d* = 1.19 g cm^{-3})]. The mixture was stirred at room temperature for 7 h. After this time it had changed from yellow to orange and the IR spectrum, in MeCN, showed only the presence of two strong absorptions at 2062 and 1982 cm^{-1}, a shoulder at about 2075 cm^{-1} and a medium intensity band at 2006 cm^{-1}. The solvent was pumped off and the residual orange solid crystallized from MeCN–Et_2O at −10 °C to give a 2:1 mixture of *cis* and *trans* isomers of **6** as orange needles (82%) (Found: C, 34.15; H, 2.65. Calc. for $C_{20}H_{18}BF_9NO_2Re$: C, 34.10; H, 2.58%). Mass spectrum [FAB(+), based on ^{187}Re]: *m*/*z* 586.

cis-**6**. IR [MeCN, $\tilde{\nu}$(CO)/cm^{-1}]: 2062vs and 1982vs. ^{1}H NMR (CD_3CN): δ 2.23 (s, 15 H, CH_3) and 2.67 (s, 3 H, CH_3CN). ^{19}F NMR (CD_3CN): δ −161.55 (m, 2F$_{meta}$), −156.54 (tt, J_{FF} 19.5, 1.8 Hz, F$_{para}$), −149.81, (s, BF_4^-) and −106.50 (m, 2F$_{ortho}$). ^{13}C-{^{1}H} NMR (CD_3CN): δ 4.48 (s, *C*H$_3$CN), 10.00 (s, CH_3), 105.12 (t, J_{CF} 40, C$_{ipso}$ C$_6$F$_5$), 110.77 (s, C_5Me$_5$), 133.72 (s, CH$_3$*C*N), 139.80 (d, J_{CF} 250, C$_6$F$_5$), 149.20 (d, J_{CF} 228, C$_6$F$_5$), 151.00 (d, J_{CF} 234, C$_6$F$_5$), 194.64 (s, CO) and 196.61 (t, J_{CF} 3.3 Hz, CO).

trans-**6**. IR [MeCN, $\tilde{\nu}$(CO)/cm^{-1}]: 2074m and 2006s. ^{1}H

NMR (CD_3CN): δ 2.01 (s, 15 H, CH_3) and 3.00 (s, 3 H, CH_3CN). ^{19}F NMR (CD_3CN): δ −160.03 (m, $2F_{meta}$), −154.34 (tt, J_{FF} 19.6, 2.9 Hz, F_{para}), −149.81, (s, BF_4^-) and −99.83 (m, $2F_{ortho}$). $^{13}C-\{^1H\}$NMR (CD_3CN): δ 5.35 (s, CH_3CN), 9.46 (s, C_5Me_5), 96.61 (t, J_{CF} 38, C_{ipso} C_6F_5), 107.98 (s, C_5Me_5), 137.43 (s, MeCN), 188.83 (t, J_{CF} 6.4 Hz, CO), and CF aromatic groups not observed.

Crystallography

Small orange crystals of *trans*-[Re(η^5-$C_5Me_4CH_2Br$)$(CO)_2$-(C_6F_5)Br] **5b** suitable for X-ray diffraction were obtained by recrystallization from hexane at 273 K. A single crystal was mounted on a glass fiber in epoxy cement. Intensity data were collected at 293(2) K on a Siemens R3m diffractometer equipped with a graphite monochromator and Mo-Kα (λ = 0.71073 Å) radiation, by the ω–2θ scan technique. The unit cell parameters were determined by least-squares refinement of 25 centred reflections. Intensities were corrected for Lorentz-polarization effects, and a semiempirical absorption correction (ψ scan) was also applied. Two standard reflections were monitored every 98, and showed no systematic changes. The structure was solved by direct methods and subsequent Fourier difference syntheses. It was refined by full-matrix least squares on F^2, with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed in ideal positions [d(C−H) = 0.96 Å] and allowed to ride on their corresponding carbon atoms. In all cases an isotropic displacement parameter 1.3 times larger than that of the host was used. The largest peak of 1.7 e $Å^{-3}$ was located at 1.5 Å from the rhenium atom, and has no chemical significance.

Computer programs used in this study were SHELXL 97 and SHELXLTL PC software packages.[32,33] Table 2 summarizes the crystal data and data collection conditions.

CCDC reference number 186/1082.

See http://www.rsc.org/suppdata/dt/1998/3079/ for crystallographic files in .cif format.

Acknowledgements

We would like to thank Universidad Catolica de Valparaiso (DGIP 125782-97) and FONDECYT-Chile for financial support (grants 1960383 and 7960007). The York group acknowledges the support of EPSRC. B. O. acknowledges Fundacion Andes for a Doctoral fellowship.

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