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# The reaction of the unsaturated rhenium fragment {Re($\eta^5$-$C_5Me_5$)-$(CO)_2$} with 1,4-difluorobenzene. Thermal intramolecular conversion of a rhenium (difluorophenyl)(hydride) to Re($\eta^2$-$C_6H_4F_2$) and a [1,4]-metallotropic shift

**Jorge J. Carbó,[a] Odile Eisenstein,[b] Catherine L. Higgitt,[c] A. Hugo Klahn,*[d] Feliu Maseras,[a] Beatriz Oelckers[d] and Robin N. Perutz*[c]**

[a] *Unitat de Química Física, Edifici C.n, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain*
[b] *Laboratoire de Structure et Dynamique des Systèmes Moléculaires et Solides (UMR 5636), Case Courrier 14, Université de Montpellier 2, 34095 Montpellier Cedex 5, France*
[c] *Department of Chemistry, University of York, York, UK YO10 5DD. E-mail: rnp1@york.ac.uk*
[d] *Instituto de Química, Universidad Católica de Valparaiso, Casilla 4059, Valparaiso, Chile*

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UV irradiation of [($\eta^5$-$C_5Me_5$)Re$(CO)_2N_2$] in neat 1,4-$C_6H_4F_2$ generates a mixture of the C–H activation product *trans*-[($\eta^5$-$C_5Me_5$)Re$(CO)_2$(2,5-$C_6H_3F_2$)H] **1a** and the $\eta^2$-arene complex [($\eta^5$-$C_5Me_5$)Re$(CO)_2$(2,3-$\eta^2$-1,4-$C_6H_4F_2$)] **2a**, identified on the basis of their IR and NMR spectra. Reaction of the mixture with $CHBr_3$ allowed the isolation of *trans*-[($\eta^5$-$C_5Me_5$)Re$(CO)_2$(2,5-$C_6H_3F_2$)Br] **1a–Br**; subsequent reaction with $LiBEt_3H$ followed by HCl at low temperature provided an independent route to **1a** free of **2a**. Nevertheless, complex **1a** converts to **2a** above 213 K. NOESY/EXSY spectroscopy of mixtures of **1a** and **2a** at low temperature shows that a conformer of **2a** is populated at low temperature in which the hydrogen atoms on the coordinated carbons point towards the $\eta^5$-$C_5Me_5$ ring. Rapid exchange occurs between the hydrogen atoms on the coordinated carbons in **2a** and those on the uncoordinated carbons *via* an unusual [1,4]-metallotropic shift with $\Delta H^\ddagger = 59 \pm 8$ kJ mol$^{-1}$ and $\Delta S^\ddagger \approx 0$. There is no evidence from NMR spectroscopy for intermolecular exchange between **1a** and **2a** or between these complexes and free 1,4-$C_6H_4F_2$. It is postulated that photolysis initially generates **2a** which is converted to **1a** in a secondary photochemical step. The ratio of **1a** to **2a** is controlled by the photochemical conditions and the thermal conversion of **1a** to **2a**. Thermal reaction of a mixture of **1a** and **2a** yields two dimers, [($\eta^5$-$C_5Me_5$)$_2$Re$_2$(CO)$_5$)] and [{($\eta^5$-$C_5Me_5$)Re$(CO)_2$}$_2$($\mu$-2,3-$\eta^2$-4,5-$\eta^2$-1,4-$C_6H_4F_2$)] **3**. Complex **3** was isolated in low yield and shown to contain the first example of coordination to a CH=CF bond as well as a CH=CH bond. DFT calculations were carried out on [($\eta^5$-$C_5H_5$)Re$(CO)_2$(2,5-$C_6H_3F_2$)H] **1b**, [($\eta^5$-$C_5H_5$)Re$(CO)_2$(2,3-$\eta^2$-1,4-$C_6H_4F_2$)] **2b** and [($\eta^5$-$C_5H_5$)Re$(CO)_2$(1,2-$\eta^2$-1,4-$C_6H_4F_2$)] **4b**. Two minima were located for each of **2b** and **4b** corresponding to the two conformations of the arene ring with respect to the cyclopentadienyl group. The most stable complex was **2b**, followed by **1b** and then by **4b**, successfully reproducing the stability of **2a** compared to **1a** and the absence of experimental evidence for **4a**. Theoretical investigations of the [1,4]-metallotropic shift show that it occurs *via* three sequential [1,2]-shifts. The rate determining step is predicted to be the shift across the C–F moiety. In the transition states, the rhenium atom has a short bond to a single carbon atom and extended bonds to two neighbouring carbon atoms.

## Introduction

Reactions of organotransition metal complexes with partially fluorinated arenes have been shown to induce both C–H and C–F activation, as well as coordination of the aromatic molecule to the metal centre.[1] For instance, the complexes *cis*-[Ru(dmpe)$_2H_2$] and [Ni$(COD)_2$]/$PEt_3$ (dmpe = bis(dimethylphosphino)ethane, COD = 1,5-cyclooctadiene) react thermally with several fluorobenzenes (or fluoroheteroaromatics) to produce only C–F activation products.[2,3] In contrast, the platinum complexes [Pt$(PCy_3)_2$] (Cy = cyclohexyl) and [Pt(dmpe)$_2$Me-($O_2CCF_3$)] have been proven to react thermally with fluorobenzenes to give C–H activation products.[4,5] Cyclopentadienyl rhodium complexes [Cp′Rh($PMe_3$)LL′] (Cp′ = $\eta^5$-$C_5H_5$, $\eta^5$-$C_5Me_5$; L = Ph, L′ = H; L = L′ = H; L = $C_2H_4$) are more versatile: coordination, C–H bond activation and C–F activation of several fluoroaromatics have been reported, depending on the cyclopentadienyl and ancillary L and L′ ligands, and also on the reaction conditions (thermal or photochemical).[6–8] The reactivity of these rhodium systems towards hydrogenated and fluorinated aromatics has been particularly important for elucidating the factors affecting the outcome of reaction, and has demonstrated that, at least for rhodium, $\eta^2$-coordination precedes C–H or C–F oxidative addition.[9–11] Recently, a theoretical calculation for the reaction of the unsaturated rhodium fragment {($\eta^5$-$C_5H_5$)Rh($PH_3$)} with a partially fluorinated benzene such as 1,4-difluorobenzene has revealed that the corresponding C–H and C–F oxidative addition products could proceed from a common $\eta^2$-bound species.[12] However, the coordination of partially fluorinated benzenes is far less common than the coordination to metal centres of the fully fluorinated $C_6F_6$. As far as we can ascertain, the only example reported is the rhodium complex [($\eta^5$-$C_5H_5$)Rh-($PMe_3$)($\eta^2$-$C_6F_5OMe$)].[7] Related to this are the rhodium complexes of 1,4- and 1,3-bis(trifluoromethyl)benzene [($\eta^5$-$C_5H_5$)Rh($PMe_3$)($\eta^2$-$C_6H_4(CF_3)_2$)].[10]

For several years, we have been interested in the insertion reactions of the photogenerated fragments {($\eta^5$-$C_5R_5$)Re$(CO)_2$}

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**Table 1** $^1H$ (500 MHz) and $^{19}F$ (470 MHz) data for products from the reaction of $[(\eta^5\text{-}C_5R_5)Re(CO)_2(N_2)]$ with 1,4-difluorobenzene (R = Me, H)[a]

| | $^1H$ | $^{19}F$ |
|---|---|---|
| **1a**[b] | −8.81 (s br, 1 H, ReH) | −122.11 (m, $1F_{meta}$) |
| 293 K | 1.58 (s, 15 H, $C_5Me_5$) | −83.83 (dm, $J_{FF} \approx 20$, $1F_{ortho}$) |
| | 6.56 (dt, $J = 9.2, 3.3$, 1 H, $C_6H_3F_2$) | |
| | 6.70 (m, 1 H, $C_6H_3F_2$) | |
| | 7.59 (m, 1 H, $C_6H_3F_2$) | |
| **1b**[c] | −8.86 (d, $J_{HF} = 2.1$, ReH) | −122.22 (m, $1F_{meta}$) |
| 300 K | 4.97 (s, $C_5H_5$)[d] | −83.21 (m, $1F_{ortho}$) |
| **2a**[b] | 1.53 (s) | −108.11 (m)[e] |
| 293 K | 3.20 (br, coordinated CH, $C_6H_4F_2$) | |
| | 5.51 (br, uncoordinated CH, $C_6H_4F_2$) | |
| **2a** | 1.41 (s, 15 H, $C_5Me_5$) | |
| 210 K | 3.11 (vt, $J_{HF} \approx 3$, 2 H, $C_6H_4F_2$) | |
| | 5.54 (vt, $J_{HF} = 6.5$, 2 H, $C_6H_4F_2$) | |
| **2b**[c] | 4.93 (s, $C_5H_5$)[f] | −109.35 (m)[e] |
| **3**[g] | 1.61 (s, 15 H, $C_5Me_5$) | −115.53 (m, 1F) |
| 293 K | 1.69 (s, 15 H, $C_5Me_5$) | −111.68 (dm, $J_{FF}$ 18, 1F) |
| | 2.83 (m, 1 H, $\eta^2$-CH=CH) | |
| | 2.86 (m, 1 H, $\eta^2$-CH=CH) | |
| | 4.18 (m, 1 H, $\eta^2$-CH=CF) | |
| | 5.48 (m, 1 H, non-coordinated CH) | |

[a] $\delta$ values reported in ppm and $J$ values in hertz. [b] $^1H$ and $^{19}F$ NMR spectra in $[^2H_8]$-toluene. [c] $^1H$ and $^{19}F$ NMR spectra in a 1 : 1 mixture of $[^2H_{12}]$-cyclohexane and 1,4-$C_6H_4F_2$. [d] Aromatic protons obscured by the presence of excess free 1,4-$C_6F_2H_4$ ($\delta \approx 6.4$, vt, apparent $J_{HF} = 6.0$ Hz). [e] Second order pattern (1 : 3 : 4 : 3 : 1 quintet) as in the free ligand. [f] $\eta^2$-$C_6F_2H_4$ protons obscured or too broad to detect. [g] $^1H$ and $^{19}F$ NMR spectra in $C_6D_6$.

(R = Me, H) into the C–H, C–F and C–Cl bonds of halogenoarenes. We have previously reported that both C–F activation and coordination to rhenium are possible in the case of $C_6F_6$. The product of reaction of $\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}$ with $C_6F_6$ is $[(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(C_6F_5)]$, while $\{(\eta^5\text{-}C_5H_5)Re(CO)_2\}$ yields $[(\eta^5\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-}C_6F_6)]$.[13,14] Very recently, we have demonstrated that these fragments react with the partially fluorinated benzenes $C_6HF_5$ and 1,2,4,5-$C_6H_2F_4$ to yield only the C–H oxidative addition products.[15] In contrast the partially chlorinated benzenes $C_6HCl_5$, 1,2,4,5-$C_6H_2Cl_4$ and 1,3,5-$C_6H_3Cl_3$, react preferentially by cleavage of C–Cl bonds.[16] In this paper, we report the photochemical reactions of $[(\eta^5\text{-}C_5R_5)Re(CO)_2L]$ (R = Me, L = CO, $N_2$; R = H, L = CO) with 1,4-difluorobenzene to produce both coordination and C–H activation products. In addition, we demonstrate that the hydride complex $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(2,5\text{-}C_6H_3F_2)H]$ **1a** converts thermally to the 1,4-difluorobenzene $\eta^2$-bound complex $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(2,3\text{-}\eta^2\text{-}1,4\text{-}C_6H_4F_2)]$ **2a**. The thermal conversion of **2a** to the binuclear complex $[\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}_2(\mu\text{-}2,3\text{-}\eta^2\text{-}4,5\text{-}\eta^2\text{-}C_6H_4F_2)]$ **3** is also described. The coordination preferences of 1,4-difluorobenzene at $\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}$ are compared with those predicted by density functional calculations on the $C_5H_5$ analogues. The unusual [1,4]-metallotropic shifts of **2a** are traced *via* DFT calculations to a series of [1,2]-shifts.

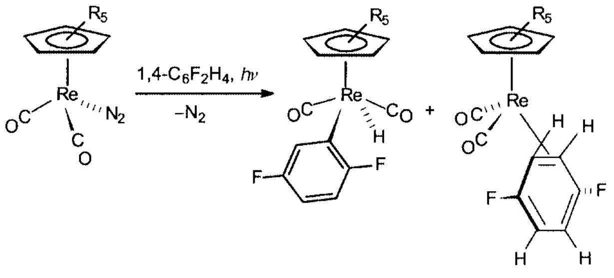
## Results

### Reaction of $[(\eta^5\text{-}C_5Me_5)Re(CO)_2L]$ (L = CO, $N_2$) with 1,4-difluorobenzene

UV irradiation of $[(\eta^5\text{-}C_5Me_5)Re(CO)_3]$ in a quartz tube in neat 1,4-difluorobenzene at room temperature for 3 h produced a yellow solution. An IR spectrum in hexane of an evaporated sample of this solution showed, in addition to strong absorption bands due to the carbonyl groups of the starting complex, small absorptions at 1970, 1944 and 1908 $cm^{-1}$. An increase in the irradiation time to 7 h did not improve the yield of products, and the solution darkened.

To overcome the low photochemical reactivity of $[(\eta^5\text{-}C_5Me_5)Re(CO)_3]$ toward 1,4-$C_6H_4F_2$, we decided to use the photochemical precursor $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(N_2)]$.[17] Dinitrogen complexes of rhenium $[(\eta^5\text{-}C_5Me_5)Re(CO)(L)(N_2)]$ (L = phosphines and phosphites) are known to lose $N_2$ very efficiently upon UV irradiation.[18,19] UV irradiation of a solution of $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(N_2)]$ in neat 1,4-$C_6H_4F_2$, for 1 h and under the same conditions as described for the tricarbonyl complex, resulted in a faster reaction: strong carbonyl bands are observed in the IR spectrum (hexane solution) consistent with the formation of one product with absorptions at 1970, 1908 (major) and a second product at 2018, 1944 $cm^{-1}$ (minor). The only other significant IR absorption bands in the carbonyl region were due to a small amount of unreacted $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(N_2)]$ and some $[(\eta^5\text{-}C_5Me_5)Re(CO)_3]$. On the basis of previous IR data for complexes *trans*-$[(\eta^5\text{-}C_5Me_5)Re(CO)_2(aryl_F)H]$ ($aryl_F = C_6F_5$, 2,3,5,6-$C_6HF_4$),[15] the $\nu$(CO) bands for the minor species at 2018 and 1944 $cm^{-1}$ were assigned to the C–H activation product *trans*-$[(\eta^5\text{-}C_5Me_5)Re(CO)_2(2,5\text{-}C_6H_3F_2)H]$ **1a**. The structure of the major product could not be inferred from the IR data alone, although CO absorption bands of almost equal intensity at 1970 and 1908 $cm^{-1}$ suggested the formation of an $\eta^2$-bound difluorobenzene complex.

When $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(N_2)]$ was irradiated in a 1 : 1 mixture of 1,4-$C_6H_4F_2$ and $[^2H_{12}]$-cyclohexane, and the reaction followed by $^1H$ and $^{19}F$ NMR spectroscopy, two products were formed in a 9 : 5 ratio after 75 min. The same two products were observed after removal of the solvent and redissolving in $[^2H_8]$-toluene. On the basis of the NMR data (Table 1), the products were assigned conclusively as *trans*-$[(\eta^5\text{-}C_5Me_5)Re(CO)_2(2,5\text{-}C_6H_3F_2)H]$ **1a** (minor species) and $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(2,3\text{-}\eta^2\text{-}1,4\text{-}C_6H_4F_2)]$ **2a** (major species, Scheme 1).



**1a** **2a** R = Me
**1b** **2b** R = H

**Scheme 1** UV irradiation products of $[(\eta^5\text{-}C_5R_5)Re(CO)_2(N_2)]$ (R = Me, H) in 1,4-$C_6H_4F_2$.

The $^1$H NMR spectrum for complex **1a** showed a broadened resonance for the hydride proton, probably due to long range couplings to fluorine nuclei,[20] as observed previously for the related complexes *trans*-[(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(aryl$_F$)H] (aryl$_F$ = C$_6$F$_5$, 2,3,5,6-C$_6$HF$_4$).[15] The hydride resonance was unaffected by cooling the sample to 210 K.

For complex **2a**, the symmetric coordination mode of the 1,4-difluorobenzene molecule was evident from both the $^1$H and $^{19}$F NMR spectra (Table 1). The $^1$H NMR spectrum at room temperature showed two broad resonances at δ 3.20 and 5.51 for protons bound to the coordinated and non-coordinated carbons, respectively; on cooling, these proton resonances sharpened and at 210 K are seen as virtual triplets with distinct $J_{HF}$ couplings. The $^{19}$F NMR spectrum showed only one second-order multiplet which was temperature independent, indicating the presence of two equivalent fluorine nuclei. Their splitting pattern was the same as in the free ligand, consistent with couplings to four hydrogen atoms. The temperature dependence of the $^1$H resonances suggests the occurrence of an exchange process (see below).

Complex **2a** represents the first example of an η$^2$-bound difluorobenzene metal complex. There are three other known examples of cyclopentadienyl rhenium complexes with η$^2$-coordinated benzene derivatives: [(η$^5$-C$_5$H$_5$)Re(CO)$_2$(η$^2$-C$_6$F$_6$)],[14] [(η$^5$-C$_5$H$_5$)Re(CO)(NO){η$^2$-C$_6$H$_5$(CHPh$_2$)}]$^+$,[21] and [(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(η$^2$-C$_6$H$_6$)].[22]

An interesting question concerning the possibility of an equilibrium between the hydride complex **1a** and the η$^2$-difluorobenzene complex **2a** arose when variable temperature NMR studies (see below) showed small changes in the ratio between the two species. Complexation of arenes in the η$^2$-mode has been demonstrated to occur prior to C–H and C–F oxidative additions for the unsaturated [(η$^5$-C$_5$Me$_5$)Rh(PMe$_3$)] system,[9–11] and equilibria between η$^2$-arene and aryl hydride rhodium complexes were observed with a variety of fused polycyclic arenes, and also with 1,4-C$_6$H$_4$(CF$_3$)$_2$.[10] However, the hypothesis of an equilibrium between complexes **1a** and **2a** was discarded on the basis of $^1$H–$^1$H-EXSY studies (see below) and because a change of solvent from [$^2$H$_8$]-toluene to [$^2$H$_8$]-THF did not cause a change in the observed ratio of **1a** to **2a**. Moreover, careful IR monitoring of the photoreaction of [(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(N$_2$)] with 1,4-difluorobenzene, showed that the ratio of the two products was not constant, suggesting that there is an appreciable barrier to their interconversion.

With the aim of gaining more insight into the relationship between the difluorophenyl hydride **1a** and η$^2$-difluorobenzene complex **2a**, we decided to prepare the hydride **1a** thermally. This should allow us to study its chemical and photochemical reactivity. [(η$^5$-C$_5$Me$_5$)Re(CO)$_3$] was photolysed in 1,4-difluorobenzene and the solvent removed. *trans*-[(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(2,5-C$_6$H$_3$F$_2$)Br] **1a-Br** was isolated in *ca.* 20% yield by bromoform-treatment of the residue. When [(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(N$_2$)] was used as photo-precursor, yields of **1a-Br** up to 33% were obtained. Reduction of **1a-Br** with an excess of 'super-hydride' in THF at low temperature resulted in the formation of the anionic complex [*trans*-(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(2,5-C$_6$H$_3$F$_2$)]$^-$, as shown by two CO absorption bands at 1854 and 1737 cm$^{-1}$. Protonation with HCl at room temperature was expected to yield the fluorophenyl hydride **1a**; however, an IR spectrum run immediately after the addition of the acid showed four CO absorption bands, consistent with the formation of both complexes **1a** and **2a** (Scheme 2). The ratio of **1a** to **2a** was approximately 1 : 1, which was very different from that obtained in the photochemical reaction of [(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(N$_2$)] with 1,4-difluorobenzene. This reaction provided the highest quality IR spectra of **1a** and **2a**: they showed that at least 90% of **2a** was present as a single conformer, in contrast to the two equally populated conformers of [(η$^5$-C$_5$H$_5$)Re(CO)$_2$(η$^2$-C$_6$F$_6$)].[14]

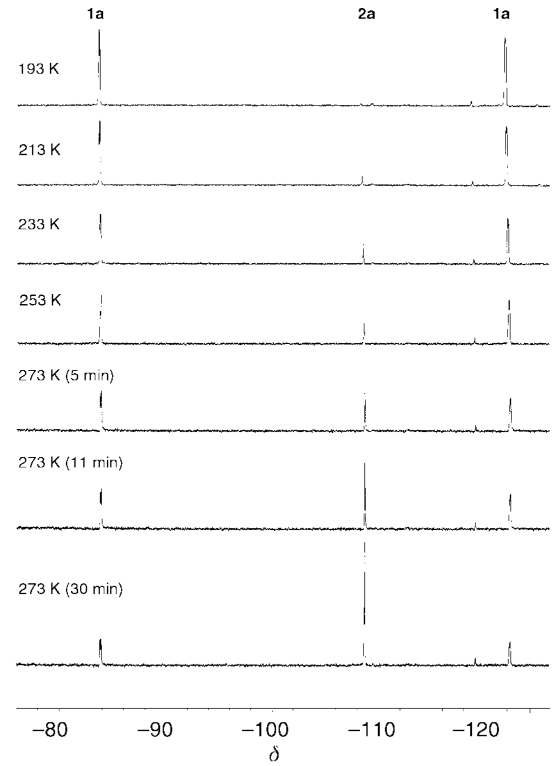
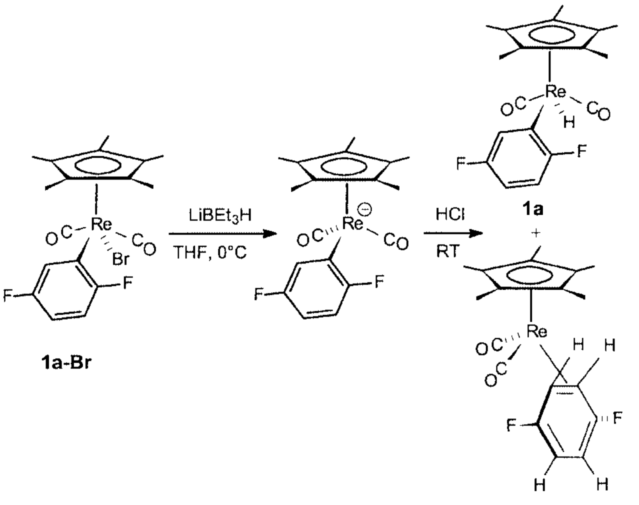


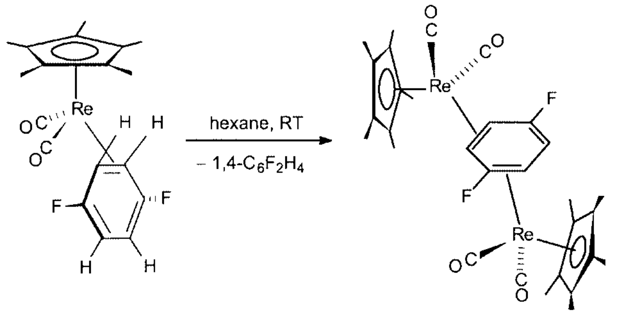
**Fig. 1** $^{19}$F-NMR spectra of the thermal conversion of *trans*-[(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(2,5-C$_6$H$_3$F$_2$)H] **1a** to [(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(2,3-η$^2$-1,4-C$_6$H$_4$F$_2$)] **2a**.



**Scheme 2** Reduction of [(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(2,5-C$_6$H$_3$F$_2$)Br] **1a-Br**.

Since the room-temperature protonation of the anionic complex *trans*-[(η$^5$-C$_5$Me$_5$)Re(CO)$_2$(2,5-C$_6$H$_3$F$_2$)]$^-$ yielded a mixture of **1a** and **2a**, we repeated the reaction at low temperature in [$^2$H$_8$]-THF and followed it by $^{19}$F NMR spectroscopy. From Fig. 1, it is clear that the kinetic product was the hydride complex **1a**, as shown by two fluorine resonances at ≈δ −84 and −122. The hydride complex starts to convert to the more stable η$^2$-difluorobenzene complex at 213 K. The reaction can be monitored conveniently at 273 K, and after 30 min, a 1 : 1 ratio of **1a** to **2a** was determined by $^{19}$F NMR integration (Fig. 1). This ratio represents the maximum amount of η$^2$-difluorobenzene complex that it is possible to obtain under these conditions. After this time, decomposition of the hydride **1a** is evident both from the decrease of **1a** relative to **2a** and the increasing amount of free ligand, which appears in the $^{19}$F NMR spectrum at ≈δ −119. Complex **2a** survives for a longer time. The hydride complex **1a** decomposed thermally in a similar way to the photochemical decomposition of the analogous hydride complexes *trans*-[($\eta^5$-$C_5Me_5$)Re(CO)$_2$(aryl$_F$)H] (aryl$_F$ = $C_6F_5$, 2,3,5,6-$C_6HF_4$),[15] yielding [($\eta^5$-$C_5Me_5$)$_2$Re$_2$(CO)$_5$][22] as one of the decomposition products.

Although the mixture of **1a** and **2a** was moderately stable under dinitrogen atmosphere at room temperature in 1,4-difluorobenzene solution, attempts to isolate any of the complexes failed, whether using the thermal or the photochemical route. After photolysis of [($\eta^5$-$C_5Me_5$)Re(CO)$_2$(N$_2$)] in 1,4-$C_6H_4F_2$ and removal of the solvent, the residue was dissolved in hexane and stirred under $N_2$ for 6 h, allowing thermal dimerization to occur, and a precipitate to form. The precipitate was filtered off and washed with hexanes; the dimer [($\eta^5$-$C_5Me_5$)$_2$Re$_2$(CO)$_5$] was separated chromatographically from the washings. The remaining material was recrystallized from toluene yielding complex **3** as a pale yellow crystalline powder in low yield (13%). This material is thermally stable in benzene or toluene but not in THF. The IR spectrum of **3** in benzene showed CO absorption bands at 1963, 1948, 1891 and 1881 cm$^{-1}$, consistent with a dimeric structure without bridging carbonyls. Compound **3** was identified by multinuclear NMR spectroscopy and its mass spectrum as the bridged binuclear complex [{($\eta^5$-$C_5Me_5$)Re(CO)$_2$}$_2$($\mu$-2,3-$\eta^2$-4,5-$\eta^2$-1,4-$C_6H_4F_2$)] as shown in Scheme 3. It was not possible to obtain crystals of **3** suitable for X-ray diffraction.

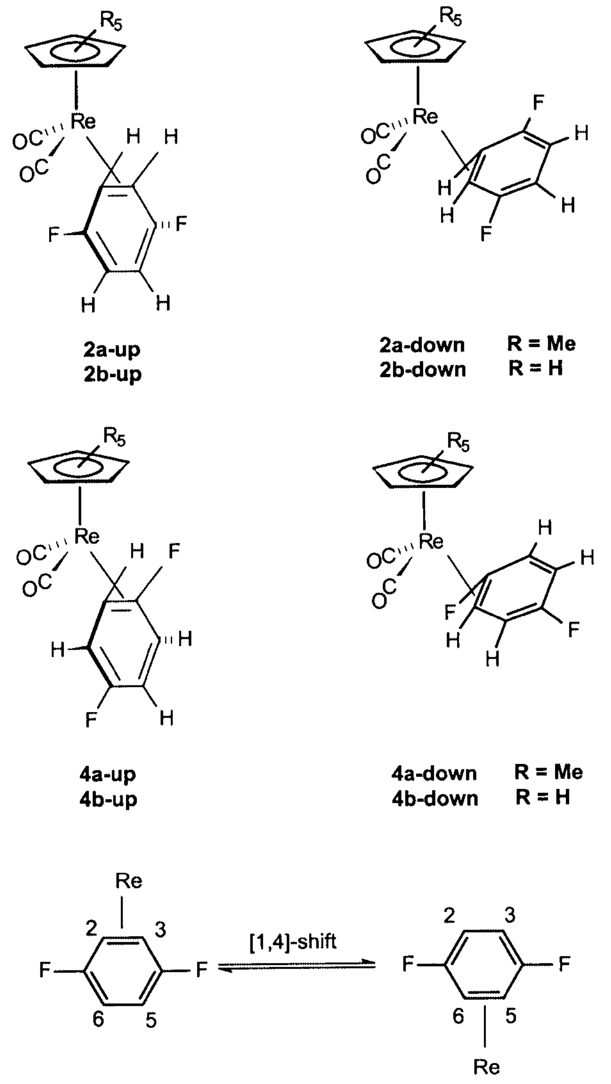


**Scheme 3** Thermal decomposition of [($\eta^5$-$C_5Me_5$)Re(CO)$_2$(2,3-$\eta^2$-1,4-$C_6H_4F_2$)] **2a**.

The $^1$H NMR spectrum of **3** in $C_6D_6$ is consistent with the non-symmetrical bonding of the two {($\eta^5$-$C_5Me_5$)Re(CO)$_2$} moieties to the 1,4-difluorobenzene molecule: two distinct resonances for the methyl protons are seen, and four resonances for the aromatic protons are observed as multiplets at $\delta$ 2.83, 2.86, 4.18 and 5.48. Similarly, the $^{19}$F NMR spectrum showed two resonances for the inequivalent fluorine nuclei at $\delta$ −115.53 and −111.68 (Table 1). Complex **3** is analogous to [{($\eta^5$-$C_5Me_5$)Re(CO)$_2$}$_2$($\mu$-$\eta^2$ : $\eta^2$-$C_6H_6$)], obtained by Pasman *et al.* as the thermal decomposition product of [($\eta^5$-$C_5Me_5$)Re(CO)$_2$($\eta^2$-$C_6H_6$)].[23] There was no evidence for any thermal exchange of the coordinated 1,4-$C_6H_4F_2$ for $C_6D_6$ in the binuclear complex.

## EXSY and NOESY study of exchange and conformation in 1a and 2a

The observation of broadening at high temperature in the aromatic resonances of [($\eta^5$-$C_5Me_5$)Re(CO)$_2$(2,3-$\eta^2$-1,4-$C_6H_4F_2$)] **2a** is suggestive of dynamic behaviour. There are also possibilities for interconversion of **1a** and **2a**. In addition, **2a** is capable of adopting two conformations (Scheme 4), one with the hydrogen atoms of the coordinated C=C bond deflected towards the carbonyl groups, the other with these hydrogen atoms deflected towards the $\eta^5$-$C_5Me_5$ ligand. At the same time, the plane of the benzene ring will be canted in the opposite direction. These questions of exchange and conformation may be answered by NOESY/EXSY measurements. In such small molecules as **2a**, exchange manifests itself through off-diagonal peaks phased positive with respect to the diagonal in the NOESY/EXSY spectrum, while NOE–distance interactions appear negative.[24]



**Scheme 4** Conformers of **2**, **4** and [1,4]-shift of preferred conformer **2a-up**.

A NOESY/EXSY spectrum measured at 190 K (mixing time $\tau_m$ = 0.9 s, recycle delay $d_1$ = 14 s) of a mixture of **1a** and **2a** in [$^2$H$_8$]-toluene, shows no exchange peaks. The only NOE interaction occurs between the protons of the coordinated C=C bond of **2a** at $\delta$ 3.1 and the ($\eta^5$-$C_5Me_5$) protons (Fig. 2a). This spectrum provides clear evidence that the *up* conformer of **2a** is populated (Scheme 4). Taken together with the IR results above, we deduce that the *up* conformer of **2a** is most probably dominant. Rapid exchange between *up* and *down* conformers at 190 K cannot be excluded (compare [($\eta^5$-$C_5H_5$)Re(CO)$_2$($\eta^2$-$C_6F_6$)]).[14] On warming the sample to higher temperatures, exchange cross-peaks appear between the two sets of aromatic resonances of **2a**. When the temperature is raised as far as 250 K, the dominant cross-peak arises from this process (Fig. 2b). In addition, NOE cross-peaks can be seen between both aromatic resonances of **2a** and the $\eta^5$-$C_5Me_5$ protons, and between the aromatic resonance of **1a** at $\delta$ 7.59 and the corresponding $C_5Me_5$ resonance. The NOE peaks linking the hydrogens on the uncoordinated carbon atoms and the $C_5Me_5$ probably arise by a combination of exchange and cross-relaxation. There is no evidence for exchange between the hydride resonance of **1a** and the $\eta^2$-arene resonances of **2a**, or between the free ligand and **1a** or **2a**.

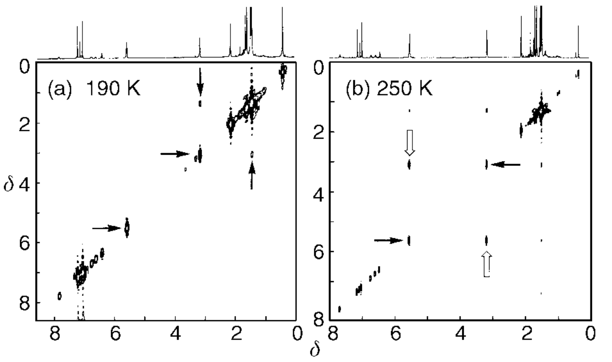


**Fig. 2** NOESY/EXSY spectra of a mixture of **1a** and **2a** in [$^2H_8$]-toluene (a) at 191 K, (b) at 250 K. The off-diagonal peaks marked with a filled-in arrow are NOE peaks (→), while those marked with an open arrow (⇒) are exchange peaks. The diagonal peaks marked with an arrow (→) arise from the protons of the $C_6H_4F_2$ group.

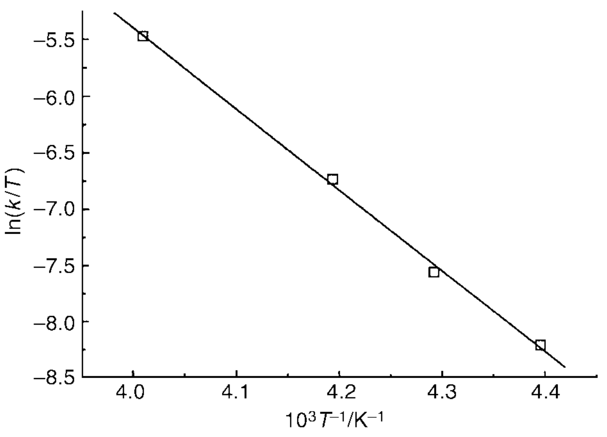


**Fig. 3** Eyring plot for the [1,4]-exchange process in **2a**, derived from EXSY data.

These experiments establish that **2a** undergoes a [1,4]-metallotropic shift resulting in exchange of the two sets of aromatic protons. The rate of this process may be determined by measuring the volume of the cross-peaks ($I_{AB}$) relative to those of the the diagonal peaks ($I_{AA}$) and solving eqn. (1) for the

$$\frac{I_{AA}}{I_{AB}} = \frac{1 + \exp(-2k\tau_m)}{1 - \exp(-2k\tau_m)} \qquad (1)$$

exchange rate constant $k$ (Table 2).[24] An Eyring plot of the temperature dependence of the rate constants (Fig. 3) yielded $\Delta H^{\ddagger} = 59 \pm 8$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -5 \pm 33$ J K$^{-1}$ mol$^{-1}$. Since the value of $\Delta S^{\ddagger}$ is close to zero and poorly determined, corrections for the rate of the actual chemical exchange have a negligible effect.[25]

### Reaction of [($\eta^5$-$C_5H_5$)Re(CO)$_2$($N_2$)] with 1,4-difluorobenzene

UV irradiation (70 min) of [($\eta^5$-$C_5H_5$)Re(CO)$_2$($N_2$)] in a 1 : 1 mixture of 1,4-difluorobenzene and [$^2H_{12}$]-cyclohexane produced a brown solution. $^1$H and $^{19}$F NMR spectra (Table 1) showed the presence of both the C–H activation product [($\eta^5$-$C_5H_5$)Re(CO)$_2$(2,5-$C_6H_3F_2$)H] **1b**, and the $\eta^2$-difluorobenzene complex [($\eta^5$-$C_5H_5$)Re(CO)$_2$(2,3-$\eta^2$-1,4-$C_6H_4F_2$)] **2b** (Scheme 1). In this case, a 1 : 16 ratio between the hydride and the $\eta^2$-difluorobenzene complex was determined by $^{19}$F-NMR integration. As expected, $^{19}$F resonance patterns for **1b** and **2b** are similar to those observed for the related complexes **1a** and **2a**. Attempts to isolate any of the products from the reaction mixture failed, since removal of the excess of 1,4-$C_6H_4F_2$ led to decomposition of both species. If the reaction is followed by IR spectroscopy in hexane, CO absorption bands assigned to the $\eta^2$-difluorobenzene complex **2b** are observed at 1981 and 1919 cm$^{-1}$ (the latter overlaps with the starting material), but the hydride **1b** could not be detected.

**Table 2** Rate constants for [1,4]-metallotropic exchange in **2a** derived from EXSY data

| Temperature/K | Rate constant, $k$/s$^{-1}$ |
|---|---|
| 228 | 0.0623 |
| 233 | 0.122 |
| 239 | 0.285 |
| 250 | 1.05 |

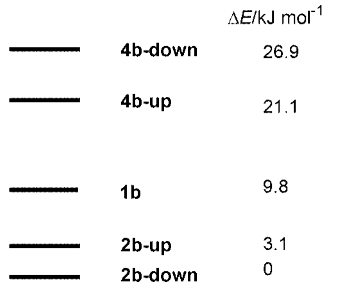


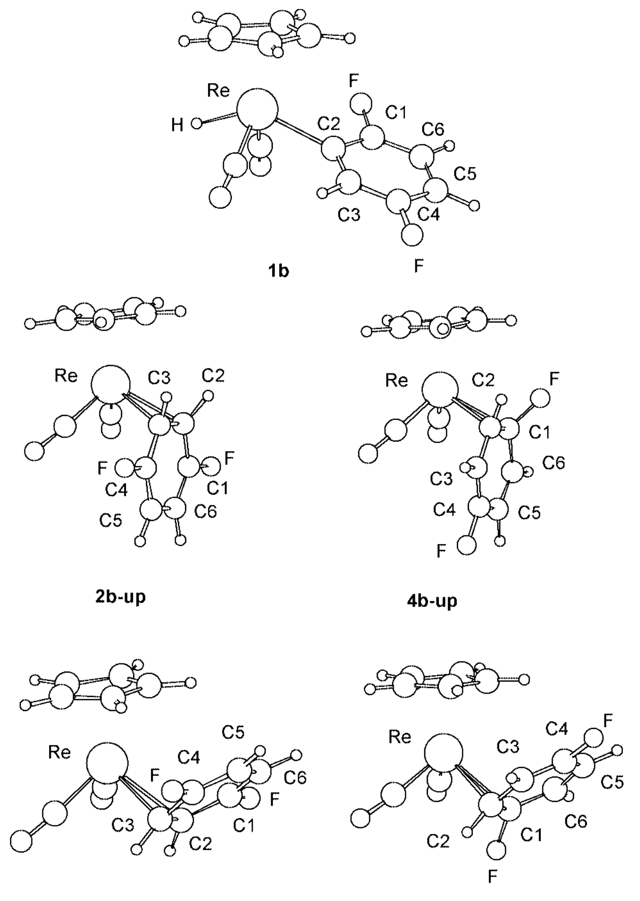
**Fig. 4** Calculated energies of **1b**, **2b** and **4b**.

## Computational studies

**Coordination or C–H activation of 1,4-difluorobenzene at {($\eta^5$-$C_5H_5$)Re(CO)$_2$}.** The 1,4-disubstituted arene can coordinate in an $\eta^2$ manner to the metal fragment through either the CH=CF or the CH=CH bond. It might be expected that the σ-acceptor/π-donor fluorine centre would favour coordination to the CH=CF bond but this is conspicuously not the case. It is also by no means obvious that coordination of 1,4-$C_6H_4F_2$ should be favoured over C–H bond activation. To gain a better understanding of the bonding and dynamic properties of **1a** and **2a** we carried out DFT (B3LYP) calculations on the models [($\eta^5$-$C_5H_5$)Re(CO)$_2$(2,5-$C_6H_3F_2$)H] **1b** and [($\eta^5$-$C_5H_5$)Re(CO)$_2$-(2,3-$\eta^2$-1,4-$C_6H_4F_2$)] **2b** and its isomers.

The difluorophenyl hydride complex [($\eta^5$-$C_5H_5$)Re(CO)$_2$(2,5-$C_6H_3F_2$)H] **1b** was located as a minimum. Its energy lies 9.8 kJ mol$^{-1}$ above the global minimum (see Fig. 4) in agreement with the greater thermodynamic stability for **2** suggested by the experimental results. The optimized geometry of **1b** shows a transoid arrangement of the phenyl and hydride ligands (Fig. 5), as indicated by experimental data on **1a**. The corresponding cisoid species has not been searched for. The difluorophenyl group is $\eta^1$-bonded as shown by the coplanar geometry of the rhenium atom and the phenyl ring. Furthermore, only C(2) lies within bonding distance of rhenium [Re–C(2) 2.203 Å].

Four isomers of [($\eta^5$-$C_5H_5$)Re(CO)$_2$($\eta^2$-1,4-$C_6H_4F_2$)] have been considered (Scheme 4, Fig. 5). In **2b**, the CH=CH bond is coordinated to the metal centre (2,3-$\eta^2$-1,4-$C_6H_4F_2$) whereas in **4b** the CH=CF bond is coordinated to the metal (1,2-$\eta^2$-1,4-$C_6H_4F_2$). Each coordination mode can occur with the substituents on the coordinated carbon atoms deflected towards the cyclopentadienyl ring (**-up**) or towards the CO ligands (**-down**). Four different local minima have been located. The most stable structure is **2b-down** (energy zero) followed by **2b-up** (3.1 kJ mol$^{-1}$). At higher energy is **4b-up** (21.1 kJ mol$^{-1}$) followed by **4b-down** (26.9 kJ mol$^{-1}$, Fig. 4). There is thus a clear preference for the coordination to CH=CH (**2b**) over the coordination to CH=CF (**4b**) in good agreement with the experiment. What does not agree so well is that calculations show a small energy preference for the **down** orientation, while the combination of IR and NOESY experiments indicate a preference for the **up** structure (see Discussion section). The analysis below will therefore concentrate on the **up** isomers.



**1b**

**2b-up**

**4b-up**

**2b-down**

**4b-down**

**Fig. 5** B3LYP optimized geometries of local minima **1b**, **2b-up** and **4b-up**. See text for geometrical parameters.

Fig. 5 shows the optimized geometries of **2b-up** and **4b-up**. The arene is $\eta^2$-bonded almost symmetrically in the isomer **2b-up**. The computed Re–C(2) and Re–C(3) bond distances (2.378 and 2.376 Å) are clearly in the bonding range, although longer than experimental values for related complexes such as $[(\eta^5\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-}C_6F_6)]$.[14] The other Re–C distances are well out of bonding range, [Re–C(1) 3.311, Re–C(4) 3.321, Re–C(5) 4.024, Re–C(6) 4.016 Å]. In **2b-up**, the calculated C(2)–C(3) distance is 1.430 Å. The $\eta^2$-coordination of the metal to the benzene ring causes a localization of the remaining $\pi$ electrons resulting in an elongation of C(3)–C(4) (1.434 Å) and a shortening of C(1)–C(6) (1.362 Å). The higher energy isomer, **4b-up**, has a similar geometry. Interestingly, the presence of the fluorine atom on the coordinated double bond shortens the distance of these carbon atoms to the metal centre [Re–C(1) 2.364 Å, Re–C(2) = 2.362 Å]. The C(1)–C(2) distance (1.429 Å) is no longer than that in **2b-up**.

The difficulty in reproducing the X-ray values for Re–C distances by computation has been reported previously for other systems.[26] In order to test our methods, we computed the geometry of $[(\eta^5\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-}C_6F_6)]$. The calculated Re–CF bond length (2.257 Å) for the latter is sufficiently close to the experimental values (2.165 and 2.205 Å)[14] to validate the long Re–C distance in **2b-up**.

In order to understand better the preference for coordination to the CH=CH bond, we carried out calculations on $[(\eta^5\text{-}C_5H_5)Re(CO)_2(C_2H_4)]$ **5b** and $[(\eta^5\text{-}C_5H_5)Re(CO)_2(C_2H_3F)]$ **6b** (eqn. (2)). This reaction is endothermic by 9.7 kJ mol$^{-1}$, which

$$\mathbf{5b} + CH_2{=}CHF \longrightarrow \mathbf{6b} + CH_2{=}CH_2 \qquad \Delta E = 9.7\ \text{kJ mol}^{-1} \quad (2)$$

confirms the preference for coordinating $CH_2{=}CH_2$ over the fluorinated olefin, but indicates that the fluorine does not influence the binding energy of the alkene very much. The weak effect of substituents on the binding energy of alkenes to other metal fragments has been reported previously.[27] Our calculations also provided the opportunity to compare the binding energy of 1,4-$C_6H_4F_2$ and $C_6F_6$ *via* the isodesmic reaction in eqn. (3). The reaction is calculated to be exothermic by 4.0 kJ mol$^{-1}$ (see Discussion section).

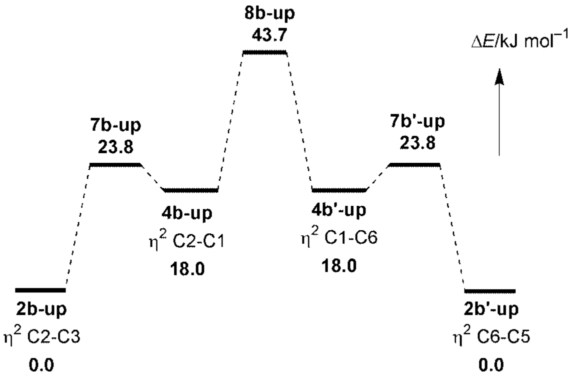
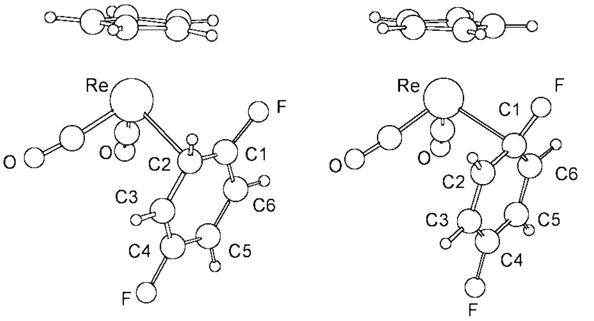


**Fig. 6** Energy profile of the succession of [1,2]-shifts leading to the overall [1,4]-shift. Energies are indicated in kJ mol$^{-1}$.



**7b-up**

**8b-up**

**Fig. 7** B3LYP optimized geometries of transition states **7b-up** and **8b-up**. See text for geometrical parameters.

$$\mathbf{2b\text{-}up} + C_6F_6 \longrightarrow [(\eta^5\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-}C_6F_6)] + 1{,}4\text{-}C_6H_4F_2 \qquad \Delta E = -4.0\ \text{kJ mol}^{-1} \quad (3)$$

**The [1,4]-metallotropic shift.** The EXSY data inform of an exchange between all the hydrogen atoms of the arene ring in **2a** which necessarily requires the existence of a [1,4]-metallotropic shift. However, the experimental data do not provide information on the detailed mechanism of this process. It could take place in a single step, or in a multi-step process, provided that the kinetics are satisfied.

Our theoretical calculations suggest that the [1,4]-shift takes place through a succession of [1,2]-shifts, as shown in Fig. 6. The first step shifts the point of $\eta^2$-coordination from the C(3)–C(2) bond to the C(2)–C(1) bond, transforming **2b-up** into **4b-up**. The associated transition state (eigenvalue 72i cm$^{-1}$) labelled **7b-up** (Fig. 6) lies 23.8 kJ mol$^{-1}$ above **2b-up**. The metal in **7b-up** is close to C(2) alone and the Re–C(2) distance (2.485 Å) is only 0.1 Å longer than in **2b-up** (Fig. 7). In contrast, the Re–C(3) and Re–C(1) distances are significantly longer than in **2b-up** (3.176 and 2.760 Å). Thus this transition state clearly describes the motion of the metal from C(3) to C(1). In agreement with the Hammond principle, the geometry of the transition state is closer to **4b-up** so that Re–C(1) is shorter than Re–C(3). In the transition state for this [1,2]-shift, the metal can be described as $\eta^3$-bonded to the arene ring (although only weakly to the outside carbon atoms). The

**Table 3** Reactivity trends of fluorinated benzenes at $\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}$

| Substrate | Reaction type | Ref. |
|---|---|---|
| $C_6F_6$ | C–F and C–H activation | 13 |
| $C_6HF_5$ | C–H activation | 15 |
| $1,2,4,5\text{-}C_6H_2F_4$ | C–H activation | 15 |
| $1,4\text{-}C_6H_4F_2$ | C–H activation and $\eta^2$-coordination | This work |
| $C_6H_6$ | $\eta^2$-coordination | 23 |

fluorine atom lies on one of the outside carbons of the $\eta^3$-bonded fragment.

A further [1,2]-metallotropic shift moves the point of $\eta^2$-coordination from C(2)–C(1), **4b-up**, to C(1)–C(6), generating an isoenergetic isomer, **4b′-up**. This is accomplished *via* transition state **8b-up** (eigenvalue 137i cm$^{-1}$, Fig. 7). The arene is also bonded in an $\eta^3$-manner in this transition state and it is the central bond of this three-carbon unit that carries the fluorine substituent. At 2.515 Å, the Re–C(1) is the shortest bond, but slightly longer than Re–C(2) in **7b-up**. The Re–C(2) and Re–C(6) distances in **8b-up** are identical (2.968 Å) and are longer than the corresponding distances in **7b-up**. The increase in the Re–arene distances is reflected in the energy of this transition state which lies 43.7 kJ mol$^{-1}$ above **2b-up**. The final step of the [1,4]-shift mirrors the first step. It transforms **4b′-up** into **2b′-up** (C(6)–C(5) coordinated to Re) *via* transition state **7b′-up** which is isoenergetic to **7b-up**. The highest transition state for the [1,4]-shift is thus **8b-up**. The energy difference between **2b-up** and **8b-up** compares very favourably to the experimental enthalpy of activation ($\Delta H^‡ = 59$ kJ mol$^{-1}$). The EXSY spectra can be understood if the first and third stages of the [1,4]-shift occur far more rapidly than the second stage as predicted by the theoretical activation energies (Fig. 6).

## Discussion

### Trends in reactivity

The $\{(\eta^5\text{-}C_5R_5)Re(CO)_2\}$ (R = Me, H) systems have been shown to effect both C–H activation of 1,4-difluorobenzene and coordination in the $\eta^2$-mode. Comparison with previous studies of the reaction of these rhenium moieties with several fluorobenzenes reveals trends in reactivity. With $C_6F_6$, the permethylated rhenium fragment $\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}$ reacts by combined C–F and C–H activation,[13] while the less electron-rich $\{(\eta^5\text{-}C_5H_5)Re(CO)_2\}$ forms only the $\eta^2$-coordination complex.[14] With the less fluorinated benzenes $C_6HF_5$ and $1,2,4,5\text{-}C_6H_2F_4$ both rhenium fragments react to form C–H activation products in high yields.[15] The primary reaction product of $\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}$ with $C_6H_6$ is $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(\eta^2\text{-}C_6H_6)]$,[23] but the more electron rich fragment $\{(\eta^5\text{-}C_5Me_5)Re(CO)(PMe_3)\}$ reacts with $C_6H_6$ to yield the C–H activation product $[(\eta^5\text{-}C_5Me_5)Re(CO)(PMe_3)(C_6H_5)H]$.[18]

The results obtained with fluorinated benzenes clearly show that for a given electron density at the metal centre, the $\eta^2$-complex will become preferred over the C–H activation product as the number of electron withdrawing groups (*i.e.* fluorine atoms) in the benzene ring decreases. As expected, the reactivity of $\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}$ with 1,4-difluorobenzene lies between that with $C_6HF_5$ or $C_6H_2F_4$ and that observed with $C_6H_6$ (Table 3).

The study of the ratio of the difluorophenyl hydride and $\eta^2$-1,4-difluorobenzene complexes **1a** and **2a** allowed us to discard the possibility of a thermal equilibrium between them. The protonation of *trans*-$[(\eta^5\text{-}C_5Me_5)Re(CO)_2(2,5\text{-}C_6H_3F_2)]^-$ showed that the hydride complex **1a** converts *thermally* to the more stable $\eta^2$-complex **2a**, so the question can now be turned to the reason for the presence of both species in the photochemically induced reaction of $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(N_2)]$ with 1,4-difluorobenzene. Attempts to perform the irradiation under more selective conditions in order to examine the origin of these species were unsuccessful. However, it is reasonable to postulate that the primary product of the reaction is the $\eta^2$-complex **2a**, which converts *photochemically*, and not thermally, to the hydride complex **1a**. A similar transformation has been described by one of us for the prolonged irradiation of $[(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(C_2H_4)]$ in $C_6F_6$: the C–F insertion product $[(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(C_6F_5)F]$ is formed upon irradiation of the primary photoproduct $[(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_6F_6)]$.[9]

The NMR data for complexes **2a** and **2b** show unambiguously that the $\eta^2$-coordination of the 1,4-difluorobenzene ring occurs at the CH=CH bond in preference to the CH=CF bond in agreement with theory. The theoretical energy gap of *ca.* 21 kJ mol$^{-1}$ would give an equilibrium constant between **2** and **4** of *ca.* $10^{-4}$. The *up*/*down* conformer preference is illuminated by NOESY measurements in combination with the IR spectra which show that the ratio of **2a-up** to **2a-down** is at least 9 : 1 at room temperature (*i.e.* $\Delta G_{(\text{down-up})} > 5.5$ kJ mol$^{-1}$). The theoretical calculations predict that **2b** should adopt a *down* conformation ($\Delta E_{(\text{down-up})} = -3$ kJ mol$^{-1}$). In contrast to **2a**, $[(\eta^5\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-}C_6F_6)]$ shows approximately equal populations of the two possible conformers, as is evident from the two sets of equally intense *v*(CO) bands.[14] In the case of $[(\eta^5\text{-}C_5R_5)Ir(C_2H_4)(\eta^2\text{-}C_6F_6)]$ (R = H, Me), both rotamers are present in solution, but the *down*-form is the major isomer for the $C_5H_5$ complex.[28] The *down*/*up* ratio of the $Ir(C_5H_5)$ complex is affected appreciably by solvent (2.2 in cyclohexane to 4.8 in $CD_3CN$). The conformer ratio in the $Ir(C_5Me_5)$ analogue is close to unity in toluene solution. The differences between theory and experiment in the conformer distribution of **2** are likely to be very small in energy terms and may be associated with the simplicity of the DFT model which attempts to model neither the effect of the methyl groups nor the solvent.

The complexes **2a** and **2b** are not sufficiently stable to allow isolation. Complex **2a** decomposed slowly in hydrocarbon solvents to the thermodynamically more stable binuclear complex $[\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}_2(2,3\text{-}\eta^2\text{-}4,5\text{-}\eta^2\text{-}C_6H_4F_2)]$ **3**, in a similar way to that reported for $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(\eta^2\text{-}C_6H_6)]$,[23] $[(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(\eta^2\text{-naphthalene})]$,[10] $[(d^tbpe)Ni(\eta^2\text{-}C_6H_6)]$,[29] and the closely related $[TpRe(CO)_2(\eta^2\text{-}L)]$ ($d^tbpe = {}^tBu_2PCH_2CH_2P^tBu_2$; Tp = hydridotris(pyrazolyl)borate; L = furan, naphthalene or *N*-methylpyrrole).[30] In complex **3**, there is $\eta^2$-coordination to both CH=CH and CH=CF bonds, which suggests that there is indeed little preference for $\eta^2$-coordination to the CH=CH bond of the 1,4-difluorobenzene molecule. As Pörschke *et al.* have noted,[29] the $\eta^2$-coordination of the first $\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}$ moiety leads to the localization of the benzene ring $\pi$ electron density, leaving one C=C bond coordinated to rhenium and the other two as a conjugated diene moiety. Under these conditions, coordination of the second rhenium is expected to proceed more readily than the first one.

The DFT calculations support the preference for the coordination of 1,4-difluorobenzene to the CH=CH bond but show that the coordination to the CH=CF bond is energetically accessible. Thus they account for the fact that coordination to the CH=CF bond occurs if the CH=CH bond is no longer available (as when coordinated to two metal fragments in **3**) or in a dynamic process (as in exchange between the CH=CH bonds). In addition, the difluorophenyl hydride isomer is only slightly higher in energy than the most stable CH=CH $\eta^2$-bonded species indicating a marginal preference for Re(I) over Re(III).

### Dynamic exchange processes

The EXSY data show that **2a** undergoes a [1,4]-metallotropic shift with activation parameters very close to those for the [1,2]-shift observed for [($\eta^5$-$C_5H_5$)Re(CO)$_2$($\eta^2$-$C_6F_6$)]. Whereas [1,2]-shifts are common and [1,3]-shifts occur frequently for coordinated polycyclic aromatics,[31] we are not aware of any other [1,4]-shifts. The EXSY data suggest that any exchange between **1a** and **2a** or between the complexes and free ligand occurs at a negligible rate compared to the relaxation timescale ($\leqslant 0.1\ s^{-1}$). The computational study of the dynamic process shows that, as intuitively expected, the exchange between the two CH=CH bonds does not go through the centre of the benzene ring in a one-step process. This would have required the cyclopentadienyl ring to decrease its hapticity to avoid a 22-electron transition state. Instead, the exchange takes place through a rotation of the Re fragment around the periphery of the benzene. The full exchange is a multistep process involving three transition states in which the metal fragment interacts strongly with one carbon of the benzene ring and more weakly with the carbon atoms either side in an $\eta^3$-bonded fashion. The rate determining step of the exchange process corresponds to the transition state in which the central carbon of the $\eta^3$ fragment carries a fluorine substituent. Swinging over the C–F bond is the most energy-demanding step. The similarity of the enthalpy of activation for the [1,4]-shift of **2a** to the [1,2]-shift of [($\eta^5$-$C_5H_5$)Re(CO)$_2$($\eta^2$-$C_6F_6$)] is thus explained. The geometries of **2b**, **4b** and the transition states for the haptotropic shifts make interesting comparison with the calculated structure of [($\eta^5$-$C_5H_5$)Rh(PH$_3$)($\eta^2$-1,4-$C_6H_4F_2$)] and the transition state for C–F activation at rhodium.[12]

### Energetic effects of fluorination

The calculations suggest that it is energetically unfavourable to bring the fluorine atoms into the proximity of the metal. This feature appears in the preference for the coordination of the CH=CH bond of 1,4-$C_6H_4F_2$ and in the lower energy of the $\eta^3$-type transition state when the fluorine is further away from the metal centre (**7b-up** *vs.* **8b-up**). It is also apparent in eqn. (2) where ethene is exchanged for fluoroethene. However, hexafluorobenzene is bonded more tightly to the metal than the 1,4-difluorobenzene as shown by eqn. (3).

Photoelectron spectra show that the ionization energy of 1,4-$C_6H_4F_2$ (9.33 eV) is only slightly different from that of benzene (9.24 eV).[32] Thus the introduction of fluorine should have little effect on the donor ability of the ligand. Nevertheless, fluorine appears to have two other opposing effects. On the one hand, it lowers the LUMO of the arene and makes the fluorinated arene a much better acceptor of electrons. This has a favourable effect on the bonding. On the other hand, the through-space Re···F interaction is destabilizing because of the repulsion between occupied rhenium orbitals and the electron density around fluorine. In the case of fluoroethene, the destabilization dominates, but for hexafluorobenzene the stabilizing effect dominates due to the presence of six fluorine atoms, four of them distant from the metal. These opposing effects explain why the coordination to the CH=CH bond is preferred for 1,4-difluorobenzene.

## Conclusions

Photolysis of [($\eta^5$-$C_5Me_5$)Re(CO)$_2$(N$_2$)] in the presence of 1,4-$C_6H_4F_2$ yields a mixture of [($\eta^5$-$C_5Me_5$)Re(CO)$_2$(2,5-$C_6H_3F_2$)H] **1a** and [($\eta^5$-$C_5Me_5$)Re(CO)$_2$(2,3-$\eta^2$-1,4-$C_6H_4F_2$)] **2a**. Thermal synthesis of **1a** at low temperature demonstrates that **1a** is unstable with respect to **2a**. It is likely that **2a** is the primary photochemical product, but is partially converted into **1a** in a secondary photochemical reaction. The energetic preference for CH=CH coordination over C–H activation or CH=CF coordination is confirmed theoretically. EXSY/NOESY experiments combined with IR evidence show that **2a** preferentially adopts the conformation with the hydrogen atoms on the coordinated C=C bond close to the $\eta^5$-$C_5Me_5$ group. The hydrogen atoms on the coordinated C=C bond exchange with those on the uncoordinated C=C bond in an unusual [1,4]-metallotropic shift. Theoretical examination of this pathway shows that it consists of a series of [1,2]-shifts. The second step in which the rhenium atom passes across the CF moiety is the rate determining step. Complex **2a** decomposes thermally into a dinuclear complex [{($\eta^5$-$C_5Me_5$)Re(CO)$_2$}$_2$-($\mu$-2,3-$\eta^2$-4,5-$\eta^2$-1,4-$C_6H_4F_2$)] **3** in which the $C_6H_4F_2$ ligand is coordinated to the rhenium atoms both through a CH=CH bond and through a CH=CF bond.

## Experimental

### General methods

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 dinitrogen complexes [($\eta^5$-$C_5R_5$)Re(CO)$_2$(N$_2$)] (R = Me, H), were prepared according to Sutton's procedure.[17] The complexes [($\eta^5$-$C_5R_5$)Re(CO)$_3$] were prepared according to Gladysz *et al.*[33] 1,4-Difluorobenzene (99%) from Aldrich was used as received. Infrared spectra were recorded in solution (CaF$_2$ cell) on a Perkin-Elmer FT-1605 spectrometer. $^1$H, $^{19}$F and $^{13}$C NMR spectra were recorded on a Bruker AMX 500 instrument. All $^1$H NMR chemical shifts are referenced using the chemical shifts of residual solvent resonances (THF, $\delta$ 3.58 and 1.78; toluene, $\delta$ 2.10; cyclohexane, $\delta$ 1.38). $^{13}$C NMR chemical shifts were referenced to solvent peaks. $^{19}$F-NMR spectra were referenced to external $C_6F_6$ at $\delta$ −162.90. Coupling assignments are indicated, where known. Mass spectra were run on a VG Autospec.

EXSY/NOESY spectra were recorded on a Bruker AMX 500 spectrometer with the noesytp pulse programme. The $\pi/2$ pulse length was calibrated before each spectrum. Spectra were typically acquired with 256 or 512 slices in the F$_1$ domain, and 4k or 6k points in F$_2$. Spectra were usually processed with zero filling in the F$_1$ domain to double the number of slices. A window function was applied and the baseline was corrected. $T_1$ values were measured with a standard inversion–recovery experiment employing a recycle delay of 30 s. Data were analysed with Bruker software yielding a value of $T_1$, for the arene protons of **2a** of 3 s. Samples for $T_1$ and NOESY measurements were degassed prior to acquisition by freeze–pump–thaw methods. Mixing times and recycle times are given in the Results section.

### Photolysis of [($\eta^5$-$C_5R_5$)Re(CO)$_2$(N$_2$)] with 1,4-difluorobenzene (R = Me, H)

Two different experimental procedures were used depending on the mode of monitoring the photoreaction. The procedure described for [($\eta^5$-$C_5H_5$)Re(CO)$_2$(N$_2$)] is analogous to that described here for the permethylated analogue except where otherwise indicated.

**(a) IR monitoring.** [($\eta^5$-$C_5Me_5$)Re(CO)$_2$(N$_2$)] (94 mg, 0.23 mmol) was dissolved in 1,4-difluorobenzene (12 mL) in a quartz tube. The tube was fitted with a rubber septum. The solution was degassed by three freeze–pump–thaw cycles and the pressure was then restored with N$_2$. The solution was irradiated at 30 °C ($\lambda$ = 300 nm) for 1 h using a Rayonet RPR photochemical reactor. The solution turned golden yellow (dark red for the $C_5H_5$ complex). Samples were taken every 10 min, evaporated to dryness and redissolved in hexanes. IR spectra of the resulting solutions showed the continuing disappearance of the CO absorptions bands due to the starting material (2125(w), 1923(s) and 1901(s) cm$^{-1}$), and the increase in the intensity of new CO absorption bands at 2017, 1970, 1944 and 1908 cm$^{-1}$. (For the $C_5H_5$ complex, IR spectra were recorded in 1,4-difluorobenzene due to rapid decomposition in other solvents, and showed only two new absorption bands at 1980 and 1919 cm$^{-1}$.)

**(b) NMR monitoring.** [($\eta^5$-$C_5Me_5$)Re(CO)$_2$($N_2$)] (10 mg, 0.025 mmol) was added to a Pyrex NMR tube fitted with a teflon Young's stopcock. Previously degassed 1,4-difluorobenzene (≈0.5 mL) and [$^2H_{12}$]-cyclohexane (≈0.5 mL) were condensed into the NMR tube. The solution was then irradiated at room temperature with an Applied Photophysics 250 W high-pressure mercury arc fitted with a water filter. The reaction was followed by monitoring the intensity decrease for the ($\eta^5$-$C_5Me_5$) methyl protons resonance of the starting material, until no significant changes were observed (≈75 min).

### Preparation of *trans*-[($\eta^5$-$C_5Me_5$)Re(CO)$_2$(2,5-$C_6H_3F_2$)Br] (1a-Br)

A solution of ($\eta^5$-$C_5Me_5$)Re(CO)$_3$ (450 mg, 1.1 mmol) in 1,4-difluorobenzene (45 mL) in a quartz tube was degassed with three freeze–pump–thaw cycles. The solution was irradiated for 4 h ($\lambda$ = 300 nm) at 30 °C using a Rayonet RPR 100 photochemical reactor. The solution turned light yellow. An IR spectrum in hexane showed CO absorption bands due to the starting carbonyl complex and new ones at 1970, 1944 and 1908 cm$^{-1}$. The solvent was removed under vacuum and the yellow residue was dissolved in THF (25 mL). $CHBr_3$ (0.3 mL; 3.4 mmol) was added. The solution was stirred at room temperature for 7 h. The solvent was removed under vacuum, and the reddish residue was chromatographed on neutral alumina. Slow elution with hexane moved unchanged [($\eta^5$-$C_5Me_5$)Re(CO)$_3$] (250 mg; 0.62 mmol). Elution with hexane/$CH_2Cl_2$ 6 : 1 moved a yellow band, from which *trans*-[($\eta^5$-$C_5Me_5$)Re(CO)$_2$(2,5-$C_6H_3F_2$)Br] **1a-Br** was isolated as an orange microcrystalline solid (60 mg; 0.11 mmol; 22%). IR ($CH_2Cl_2$, $\nu$(CO), cm$^{-1}$): 2038(m), 1959(s). $^1$H-NMR ($CDCl_3$) $\delta$: 1.82 (s, 15H); 6.79 (m, 1H); 6.94 (m, 1H); 7.35 (m, 1H). $^{13}$C{$^1$H}-NMR ($CDCl_3$) $\delta$: 9.88 (s, $C_5\mathit{Me}_5$), 103.49 (s, $\mathit{C}_5Me_5$), 112.95 (dd, $J_{CF}$ 36, 5 Hz, $C_{ipso}$-$C_6F_2H_3$), 113.86 (dd, $J_{CF}$ 24, 10 Hz, $\mathit{C}_6F_3H_2$), 115.22 (dd, $J_{CF}$ 36, 8 Hz, $\mathit{C}_6F_3H_2$), 131.62 (dd, $J_{CF}$ 20, 11 Hz, $\mathit{C}_6F_3H_2$), 158.46 (d, $J_{CF}$ 247 Hz, $\mathit{C}_6F_3H_2$), 164.54 (d, $J_{CF}$ 224 Hz, $\mathit{C}_6F_3H_2$), 193.27 (s br, CO). $^{19}$F-NMR ($CDCl_3$) $\delta$: −122.14 (m, 1$F_{meta}$); −83.57 (m, 1$F_{ortho}$). Mass spectrum (EI, based on $^{187}$Re, $^{79}$Br) *m*/*z*: 570 [M]$^+$, 542 [M − CO]$^+$, 514 [M − 2CO]$^+$. Calcd. for $C_{18}H_{18}F_2O_2BrRe$: C, 37.90; H, 3.18. Found: C, 38.00; H, 3.22%.

### Reduction of *trans*-[($\eta^5$-$C_5Me_5$)Re(CO)$_2$(2,5-$C_6H_3F_2$)Br] (1a-Br)

To a stirred solution of *trans*-[($\eta^5$-$C_5Me_5$)Re(CO)$_2$(2,5-$C_6H_3F_2$)Br] (40 mg; 0.070 mmol) in THF (7 mL) at −78 °C, was added a solution of $LiBEt_3H$ (1.0 M in THF solution, 0.1 mL). The solution turned light yellow and an IR spectrum at room temperature showed the disappearance of the starting complex and new bands at 1854 and 1737 cm$^{-1}$. The solvent was removed under vacuum, and the oily dark yellow residue obtained was kept at 0 °C and dried under high vacuum for 2 h. It was then dissolved in [$^2H_8$]-THF and cooled to −100 °C. HCl was added (1.0 mol dm$^{-3}$ in diethyl ether solution, 0.15 mL), and the reaction was followed by $^{19}$F-NMR spectroscopy. All spectra were run with 32 pulses and 60 s delay for fluorine relaxation.

### Synthesis of [{($\eta^5$-$C_5Me_5$)Re(CO)$_2$}$_2$($\mu$-2,3-$\eta^2$-4,5-$\eta^2$-$C_6H_4F_2$)] (3)

[($\eta^5$-$C_5Me_5$)Re(CO)$_2$($N_2$)] (125 mg, 0.31 mmol) in a quartz tube was dissolved in 1,4-difluorobenzene (15 mL). The solution was degassed with three freeze–pump–thaw cycles, and was then irradiated at room temperature ($\lambda$ = 300 nm) for 90 min using a Rayonet RPR 100 photochemical reactor equipped with only eight UV lamps. The solution turned yellow. The solvent was removed under vacuum, and the golden residue was dissolved in the minimum amount of hexane (≈10–12 mL). The mixture was stirred under nitrogen at room temperature for 6 h. The solution turned dark brown and a pale yellow solid was formed. The mixture was filtered and the solid was washed twice with 2 mL of hexane. The washings were transferred to a column of neutral alumina. Elution with hexane/$CH_2Cl_2$ (5 : 1) yielded [($\eta^5$-$C_5Me_5$)$_2$Re$_2$(CO)$_5$] (45 mg; 0.058 mmol; 19%). The solid residue was redissolved in toluene (7–10 mL), and the solution was quickly filtered through a thin layer of neutral alumina (≈2 mm thick). The colourless filtrate was concentrated under vacuum to one half of the volume. Hexane (15 mL) was carefully poured down the walls of the flask. After five days at 4 °C, complex **3** was isolated as a pale yellow microcrystalline solid (35 mg; 0.040 mmol; 13%). **3**: IR ($C_6H_6$, $\nu$(CO), cm$^{-1}$): 1963(m), 1948(s), 1891(s), 1881(m). Mass spectrum (EI, based on $^{187}$Re/$^{187}$Re) *m*/*z*: 870 [M]$^+$, 842 [M − CO]$^+$, 756 [M − $C_6H_4F_2$]$^+$, 728 [M − CO − $C_6H_4F_2$]$^+$, 700 [M − $C_6H_4F_2$ − 2CO]$^+$. $^{13}$C{$^1$H}-NMR acquired with a series of $^1$H–$^{13}$C HMQC gradient experiments optimized for long-range couplings ([$^2H_8$]-toluene) $\delta$: 10.25 (s, $C_5\mathit{Me}_5$), 10.89 (s, $C_5\mathit{Me}_5$), 29.02 (s, $\eta^2$-coordinated CH=CH), 36.88 (s, $\eta^2$-coordinated CH=CH), 48.80 (s, $\eta^2$-coordinated CH=CF), 98.23 (s, $\mathit{C}_5Me_5$), 99.48 (s, $\mathit{C}_5Me_5$), 104.88 (s, non-coordinated CH), 122.42 (d, $J_{CF}$ 233 Hz, $\eta^2$-coordinated CF), 163.75 (d, $J_{CF}$ 238 Hz, non-coordinated CF), carbonyl resonances were not observed.

### Computational details

All calculations were carried out with the Gaussian 98 package of programs[34] at the B3LYP computational level.[35,36] An effective core potential was used to replace the 60 innermost electrons of rhenium.[37] The basis set was of double ζ quality[37–39] with polarization functions on all atoms except rhenium. All geometries were fully optimized without any symmetry constraints. The nature of the transition states was ascertained by analytical calculations of frequencies.

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