

cis–*trans* Isomerisation of $\text{CpRe}(\text{CO})_2(\text{H})(\text{Ar}_F)$ ($\text{Ar}_F = \text{C}_6\text{F}_n\text{H}_{5-n}$; $n = 0$ – 5) is the rate determining step in C–H activation of fluoroarenes: a DFT study †

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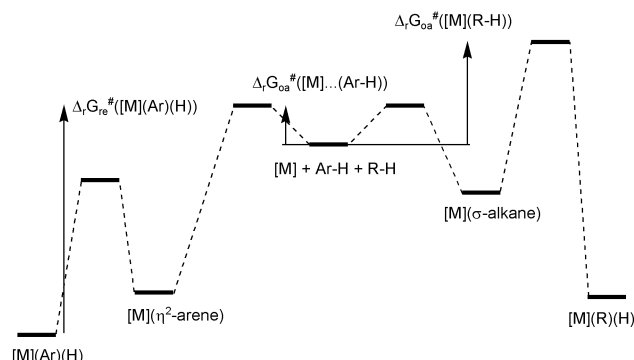
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Density functional calculations have been used to examine the reaction of $\{\text{CpRe}(\text{CO})_2\}$ with fluorobenzenes $\text{C}_6\text{F}_n\text{H}_{6-n}$ ($n = 0$ – 5). Two classes of product have been observed experimentally (using Cp or Cp*): (a) coordination of the arene in an η^2 fashion and (b) C–H activation to form a hydrido–aryl complex. Increasing the number of fluorines on the arene ring was shown to favour C–H activation. The thermodynamic and kinetic (reaction path) aspects of these transformations have been examined with DFT (B3PW91) calculations. For a given arene, the rhenium moiety is shown to exhibit the following order of thermodynamic preference for coordination: $\text{HC}=\text{CH}$ site $>$ $\text{HC}=\text{CF}$ site $>$ $\text{FC}=\text{CF}$ site. Binding energies to the different arenes do not follow a clear trend and span ca. 20 kJ mol^{−1}. The Re–C bond energies in $\text{CpRe}(\text{CO})(\text{H})(\text{C}_6\text{F}_n\text{H}_{5-n})$ span 55 kJ mol^{−1}. Calculated structural parameters agree with the crystal structure of coordination of C_6H_6 and C_6F_6 . Likewise the binding energy of C_6H_6 is in good agreement with experimental data. The calculated free energy difference between $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{F}_n\text{H}_{6-n})$ and $\text{CpRe}(\text{CO})_2(\text{H})(\text{C}_6\text{F}_n\text{H}_{5-n})$ shows that preference for the hydrido–aryl complex is determined principally by the bond dissociation energy of the C–H bond of the free arene. The binding energy to the η^2 -arene appears to be only a secondary factor. Three families of complexes are apparent. If there is no F on the carbon *ortho* to the Re–C bond that is formed, the η^2 -arene complex is energetically preferred. If there is one F at the *ortho* position, the energies of the products are similar. In the case of two *ortho* F substituents, the product of oxidative addition is significantly favoured. In agreement with the calculations, experimental evidence shows that benzene only coordinates to $\text{Cp}^*\text{Re}(\text{CO})_2$, 1,4- $\text{C}_6\text{F}_2\text{H}_4$ gives a mixture of products and 1,3- $\text{C}_6\text{F}_2\text{H}_4$ gives only the hydrido–aryl complex. The arene with the stronger C–H bond is the one which gives more oxidative addition product because the Re–C bond energy increases with F substitution (and in particular with *ortho* F) more than twice as fast as the C–H bond dissociation energy. The reaction path for the overall transformation has been determined. The σ C–H complex is identified as an intermediate on the pathway for the oxidative addition. The initial product of oxidative addition is the *cis* hydrido–aryl isomer which subsequently isomerizes to the *trans* isomer. The rate determining step has been found to be the *cis*–*trans* isomerisation process and not the oxidative addition step. The *cis*–*trans* isomerisation proceeds via an unconventional concerted motion of H and the two COs. The variation of the Re–C bond energy is the dominant factor in determining the changes in the energy barrier between the different fluoroarenes, resulting in strong correlation between the thermodynamics and kinetics of reaction. The activation barriers are therefore also grouped in three families (0 F *ortho*, 1 F *ortho*, 2 F *ortho*).

Introduction

Transition-metal-mediated activation of aromatic or aliphatic carbon–hydrogen bonds is a fundamental process in homogeneous catalysis and has been the subject of numerous studies.¹ Organometallic complexes have been shown to promote the cleavage of the strong C–H bond in arenes very selectively relative to the weaker C–H bond in alkanes because substantially stronger metal–carbon bonds are formed with aryl than with alkyl groups, *i.e.* thermodynamics dominate the reactions.² Arene C–H bond activation has been shown to be slightly favoured kinetically through η^2 -coordination of the arene to the metal centre prior to C–H bond cleavage.³ For the reverse reaction, reductive elimination of Ar–H, decoordination of the arene is the rate determining step because of the stable η^2 -arene intermediate on the pathway (Scheme 1). There is a growing body of evidence that the pathway for oxidative addition for aliphatic C–H bonds involves precoordination with an alkane σ -complex intermediate prior to bond cleavage (Scheme 1).^{3m,4}

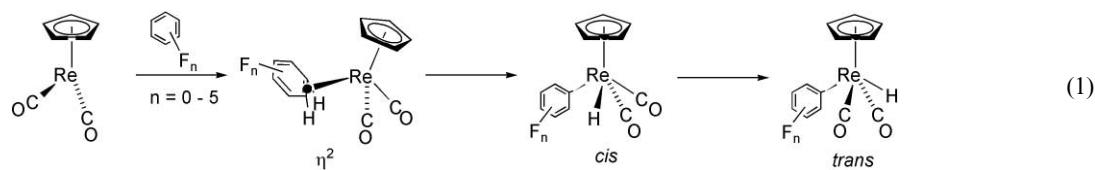


Scheme 1

It has also been proposed that there is a σ -complex intermediate on the pathway to C–H activation of arenes.^{3f–i,4m}

For several years, we have been interested in the reactions of the photo-generated fragments $\{(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_2\}$ ($\text{R} = \text{H}, \text{Me}$) with fluoroarenes.⁵ With C_6F_6 , only η^2 -coordination of the arene is observed and the dynamics both of the exchange

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between rotamers and of the ring whizzing process were studied.^{5a} With C_6F_5H and 1,2,4,5- $C_6F_4H_2$, C–H activation is observed, generating the hydrido–aryl complexes *trans*-[(η^5 - C_5R_5)Re(CO)₂(H)(Ar_F)] (Ar_F = C_6F_5 or 2,3,5,6- C_6F_4H) as the principal photochemical products.^{5b} UV irradiation of Cp*Re(CO)₂(N₂) (Cp = η^5 -C₅H₅, Cp* = η^5 -C₅Me₅) in neat 1,4- $C_6F_4H_2$ generates a mixture of the C–H activation product *trans*-[Cp*Re(CO)₂(H)(2,5- $C_6F_4H_3$)] and the η^2 -arene complex Cp*Re(CO)₂(2,3- η^2 -1,4- $C_6F_4H_2$).^{5c} Reaction with benzene was shown by Van der Heijden *et al.* to give Cp*Re(CO)₂(η^2 -C₆H₆),⁶ and the activation parameters for dissociation of C₆H₆ were determined by Bengali and Leicht ($\Delta_r H^\ddagger$ = 87.1 kJ mol⁻¹).⁷ No C–H activation products were detected with C₆H₆. These observations led us to write that “the results obtained with fluorinated benzenes clearly show that for a given electron density at the metal centre the η^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”.^{5c}

Recently, we have shown that a better understanding of the substituent influence can be obtained through M–C/H–C bond energy correlations.⁸ The Re–C bond dissociation energies (BDE) for *trans*-[CpRe(CO)₂(H)(C₆F_{*n*}H_{5-*n*})] (*n* = 0–5) were computed with DFT calculations and were plotted against the calculated H–C BDE for the organic counterpart H–C₆F_{*n*}H_{5-*n*} (*n* = 0–5). A very good linear correlation was obtained with a slope of 2.25, indicating a great sensitivity of the M–C bond strength to substitution of the phenyl ring with fluorine atoms. Unexpectedly, the calculations showed that the position of the fluorine atoms, but not their total number, has a critical influence. The Re–C BDE is increased most by fluorine-substitution at the position *ortho* to the Re–C bond. The strengthening of the Re–C bond is associated with increased negative charge on the aryl ring as the number of *ortho* fluorine substituents increases. Our evidence suggests that σ -effects dominate this polarisation of the Re–C bond which can be compared to the Pauling analysis of the change in bond strength with electronegativity. The theoretical study led us to predict that the reaction with 1,3-difluorobenzene should yield the 2,6 C–H activation product since this species would benefit from the stabilisation by two *ortho* fluorines. This was confirmed by a subsequent experiment in which irradiation of Cp*Re(CO)₂(N₂) in liquid 1,3- $C_6F_4H_2$ yielded exclusively *trans*-[Cp*Re(CO)₂(H)(2,6- $C_6F_4H_3$)].⁸

These calculations demonstrate that thermodynamics favour the C–H activation product when both *ortho* positions are substituted by fluorine atoms. However, the kinetics of the reaction might be influenced differently by the substitution pattern of the arene ring. For example, it was shown that, when under thermodynamic control, C–H activation of 1,3-difluorobenzene by the rhodium fragment {Cp*Rh(PMe₃)} yields Cp*Rh(PMe₃)(H)(2,6- $C_6F_4H_3$), the isomer with the maximum number of *ortho*-fluorine atoms.⁹ Under kinetic control, the products observed are Cp*Rh(PMe₃)(H)(2,4- $C_6F_4H_3$) and Cp*Rh(PMe₃)(H)(3,5- $C_6F_4H_3$) in a 5 : 1 ratio. The major kinetic isomer has one fluorine atom in an *ortho* position corresponding to a stronger Rh–C bond. These two kinetic isomers should originate from the same η^2 -arene complex, Cp*Rh(PMe₃)(H)(4,5- η^2 -1,3- $C_6F_4H_2$). The different species along the pathway for oxidative addition are not influenced in the same manner by F-substitution. In the case of CpRe(CO)₂(η^2 - $C_6F_4H_2$), the η^2 -arene complexes of fluorarenes were shown theoretically and experimentally to be more stable when no F

atom is present on the coordinated C=C bond,^{5c} whereas the C–H activation products show a strong preference for *ortho*-F substitution.

There is one notable difference in stereochemistry between the rhodium and the rhenium complexes. In the case of the unsaturated d⁸ fragment {Cp*Rh(PMe₃)}, the H and aryl groups resulting from the C–H activation product are necessarily *cis*; this corresponds to the least motion outcome of the cleavage of the C–H bond. However, for the d⁶ {CpRe(CO)₂} fragment under study, the thermodynamic product is the *trans* isomer *trans*-[CpRe(CO)₂(H)(C₆F_{*n*}H_{5-*n*})], and *cis* to *trans* isomerisation from the C–H activation product is necessary in addition to C–H activation.

In this paper, we describe a theoretical study of the mechanism of C–H activation of fluoroarenes H–C₆F_{*n*}H_{5-*n*} by {CpRe(CO)₂} to yield *trans*-[CpRe(CO)₂(H)(C₆F_{*n*}H_{5-*n*})] (eqn. (1)). All the substitution patterns have been considered (*n* = 0–5, 20 independent reaction paths) in order to evaluate the influence of the substitution by F atoms on every step of the reaction. Coordination of the fluoroarenes is shown to be thermodynamically preferred over C–H activation when no F atoms are present on the coordinated C=C bond. The rate determining step is found to be the *cis* to *trans* isomerisation within CpRe(CO)₂(H)(C₆F_{*n*}H_{5-*n*}), where the Re–C bond is already formed. Consequently the overall C–H activation reaction is favoured thermodynamically and kinetically for strong Re–C bonds, *i.e.* when both *ortho* positions of the phenyl ring are substituted with fluorine.

Results

Coordination of C₆F_{*n*}H_{6-*n*}

Arene molecules coordinated to transition metal centres in an η^2 -fashion have now been isolated and characterized crystallographically.^{3e,5a,c,10} The arene ligand is generally folded at the coordinated C=C bond as shown by crystal structures of complexes of C₆H₆ and C₆F₆ and as illustrated by the calculated geometry for CpRe(CO)₂(η^2 -C₆H₆) (Fig. 1). Two rotamers have been located on the potential energy surface differing by the orientation of the C₆H₄ unit with respect to the carbonyl ligands. When the hydrogen atoms on the coordinated double bond are tipped toward the Cp ring, the rotamer is defined as the up isomer. The other rotamer, with the hydrogen atoms tipped toward the carbonyl ligands, is called the down isomer.

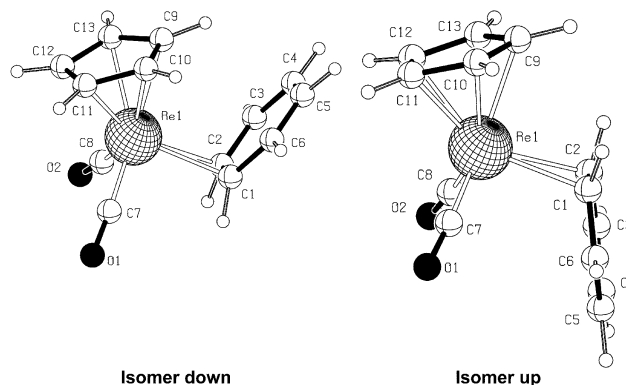


Fig. 1 Optimized geometry (B3PW91) for the two rotamers of CpRe(CO)₂(η^2 -C₆H₆). H(1) and H(2) are the hydrogen atoms bonded to C(1) and C(2), respectively.

Table 1 Comparison of selected geometrical parameters (bond distances in Å, angles in °) for the experimental structures of $[\{\text{Cp}^*\text{Re}(\text{CO})_2\}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)]$ (A),⁶ and $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{F}_6)$ (C),^{5a} with the optimized geometry of $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_6)$ (**B_{up}** and **B_{down}**), and $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{F}_5\text{H})$ (D), respectively. See Fig. 1 and text for definitions of atoms labels and up and down isomers

	A Dimer (exptl.)	B _{up} ($\eta^2\text{-C}_6\text{H}_6$) (calc.)	B _{down} ($\eta^2\text{-C}_6\text{H}_6$) (calc.)	C ($\eta^2\text{-C}_6\text{F}_6$) (exptl.)	D ($\eta^2\text{-C}_6\text{F}_5\text{H}$) (calc.)
Re–D(1)	1.955	1.962	1.960	1.946	1.968
Re–D(2)	2.158	2.265	2.261	2.057	2.100
Re–C(1)	2.263	2.374	2.368	2.166	2.205
Re–C(2)	2.275	2.320	2.376	2.204	2.241
C(1)–C(2)	1.400	1.428	1.431	1.475	1.455
Re–Cp (av.)	2.290	2.308	2.306	2.285	2.312
Re–CO (av.)	1.901	1.902	1.902	1.912	1.922
C–O (av.)	1.143	1.168	1.167	1.152	1.158
D(1)–Re–D(2)	121.3	120.0	126.5	130.0	133.2
C(7)–Re–C(8)	85.5	87.6	87.7	86.4	84.3
Re–D(2)–C(2)–C(3)	65.4	65.8	70.5	64.9	71.0
D(2)–C(2)–C(3)–X(2) ^a		23.5	25.9	42.2	40.9

^a X(2) is the atom bonded to C(2): H or F.

The calculated geometry of the up isomer of $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_6)$ is in good agreement with the crystal structure of $[\{\text{Cp}^*\text{Re}(\text{CO})_2\}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)]$ determined by Van der Heijden *et al.*⁶ (Table 1). The atoms of the C_6H_4 unit are almost coplanar and tipped toward the carbonyl ligands. In the calculated structure, the atoms C(1), C(2), H(1) and H(2) form the second plane, bent at 23.5° to the first one and lying adjacent to the Cp ring. The Re atom lies at 2.265 Å from the mid-point of C(1)–C(2) (labelled D(2)) and 1.962 Å from the centroid of the Cp ring (labelled D(1)). The D(1)–Re–D(2) angle is 120.0°. The influence of F-substitution on the arene coordination is also properly reproduced. Table 1 shows a comparison between the experimental structure of $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{F}_6)$ and the calculated geometry for $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{F}_5\text{H})$, where the hydrogen atom on $\text{C}_6\text{F}_5\text{H}$ is in position 4 with respect to the coordinated FC=CF bond, and should not influence the coordination of the arene significantly. The calculated geometrical parameters are in good agreement with the experimental data. The trends are correctly reproduced with increased back-donation from the metal when fluorine atoms are on the coordinated C=C bond. The Re–C(1) and Re–C(2) bonds are shorter (compared to coordination of C_6H_6) and the C(1)–C(2) bond is longer. Additionally, the fold angle of the atoms at the coordinated bond is larger with FC=CF (40.9°) than with HC=CH (25.9°).

The coordination mode of the down isomer with $\eta^2\text{-C}_6\text{H}_6$, is similar to the up isomer with the C_6H_4 unit now tipped toward the Cp ring (Fig. 1, isomer down). The latter is 1.9 kJ mol⁻¹ more stable than the up isomer. Experimentally, the preference for the up or down isomer depends on the level of fluorine substitution and also on the substitution of the cyclopentadienyl ring (C_5H_5 vs. C_5Me_5). With $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{F}_6)$, the up and down isomers are almost isoenergetic according to experiment ($\Delta G^\circ_{300} = 0.7$ kJ mol⁻¹) and they interconvert very easily ($\Delta G^\ddagger_{184} = 36.7$ kJ mol⁻¹).^{5a} For $\text{Cp}^*\text{Re}(\text{CO})_2(2,3\text{-}\eta^2\text{-}1,4\text{-C}_6\text{F}_2\text{H}_4)$ the up isomer is populated preferentially at room temperature (ratio 9 : 1).^{5c} The calculated energy difference between the two rotamers in $\text{CpRe}(\text{CO})_2(2,3\text{-}\eta^2\text{-}1,4\text{-C}_6\text{F}_2\text{H}_4)$ is 5.5 kJ mol⁻¹ in favour of the down isomer. The difference between the calculated and the experimental result could originate from steric repulsion between the phenyl ring and methyl groups on Cp* in the down rotamer. For 1,2,3,4- $\text{C}_6\text{F}_4\text{H}_2$, the down rotamer is also calculated to be more stable, with a difference in energy of 5.3 kJ mol⁻¹ with respect to the up isomer. As the majority of structures determined crystallographically exhibit the down geometry,^{5a} and given the very small energy separation between the two rotamers, we have only considered the down geometry in all subsequent calculations on η^2 -coordinated fluoroarenes.

To further test the quality of the theoretical approach, we compared experimental and calculated ν_{CO} vibrational frequencies (Table 2). Although shifted to higher values, the trend is reproduced remarkably as illustrated by the excellent linear correlation between calculated and experimental values (Fig. 2). Electron density at a Re^I centre is higher than at a Re^{III} centre as reflected by the lower carbonyl vibrational frequencies for the η^2 -arene complexes. Comparison between $\text{Cp}^*\text{Re}(\text{CO})_3$ and $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-arene})$ indicates that the arenes are not as good π -acceptor ligands as CO even with several F-substituents. The higher carbonyl vibrational frequencies show that 1,4-difluorobenzene is a better π -acceptor than benzene as expected for a less electron-rich benzene ring. Even the trend between the 2,6 and 2,5 isomers of $(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_2(\text{H})(\text{C}_6\text{F}_3\text{H}_2)$ is faithfully reproduced.

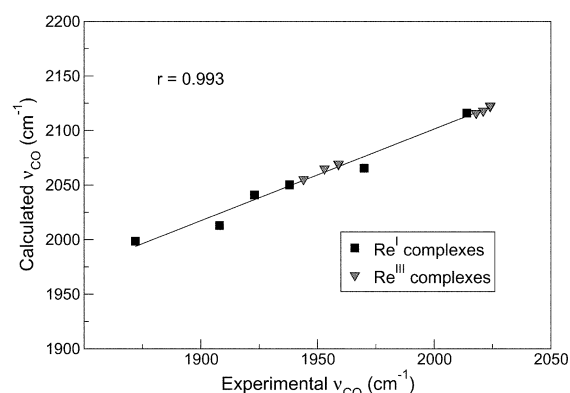


Fig. 2 Correlation between experimental and calculated ν_{CO} vibrational frequencies (cm^{-1}) for $\text{Cp}^*\text{Re}^{\text{I}}(\text{CO})_3$, $\text{Cp}^*\text{Re}^{\text{I}}(\text{CO})_2(\eta^2\text{-arene})$ and $\text{Cp}^*\text{Re}^{\text{III}}(\text{CO})_2(\text{H})(\text{aryl})$ (see Table 2).

The binding energy of C_6H_6 in $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_6)$ is computed to be 88.6 kJ mol⁻¹, which is close to the experimental value of 87.1 kJ mol⁻¹ obtained by Bengali and Leicht on $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_6)$.⁷ The experimental value is a lower limit to the Re– C_6H_6 bond strength because the study is performed in heptane solution. This leads to the formation of a weak heptane adduct in place of the naked $\{\text{Cp}^*\text{Re}(\text{CO})_2\}$.

In fluoroarenes, there are six potential sites for η^2 -coordination (omitting symmetry arguments). The regioselectivity and the energetics of the coordination are important to consider, because the η^2 -arene may be formed prior to C–H activation. The effect of fluorination can be considered by analogy to alkenes. Electron deficient alkenes are known to bind strongly to electron rich transition metal fragments, because substitution of the C=C π -bond by electron-withdraw-

Table 2 Comparison between experimental and calculated ν_{CO} (cm^{-1}) for complexes with different levels of fluorine substitution

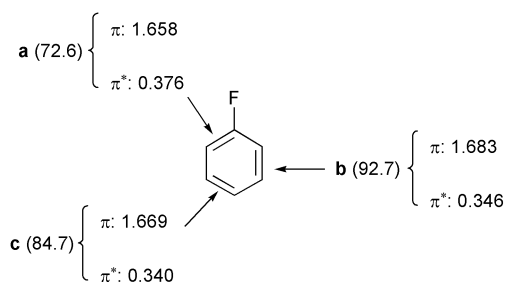
	Exptl. (R = Me)		Calc. (R = H)	
$(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_3$ ¹¹	2014	1923	2116.0	2041.0
$(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_6)$ ⁷	1938	1872	2050.2	1998.5
$(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_2(2,3\text{-}\eta^2\text{-1,4-C}_6\text{F}_2\text{H}_4)$ ^{5c}	1970	1908	2065.5	2012.9
$(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_2(\text{H})(2,6\text{-C}_6\text{F}_2\text{H}_3)$ ⁸	2021	1953	2118.0	2065.0
$(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_2(\text{H})(2,5\text{-C}_6\text{F}_2\text{H}_3)$ ^{5c}	2018	1944	2115.9	2055.2
$(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_2(\text{H})(2,3,5,6\text{-C}_6\text{F}_4\text{H})$ ^{5b}	2024	1959	2122.1	2068.9
$(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_2(\text{H})(\text{C}_6\text{F}_5)$ ^{5b}	2024	1959	2122.6	2069.5

Table 3 Comparison between $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{F}_2\text{H}_4)$ complexes showing the binding energy, E_b , of the arene to the metallic fragment and the relative energy, ΔE , for coordination to the other sites (kJ mol^{-1})

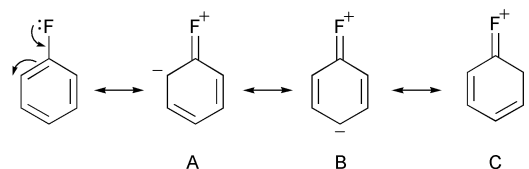
$E_b/\text{kJ mol}^{-1}$	1,2-C ₆ F ₂ H ₄				1,3-C ₆ F ₂ H ₄			1,4-C ₆ F ₂ H ₄	
	87.0								
Coord. Site	1,2	2,3	3,4	4,5	1,2	3,4	4,5	1,2	2,3
$\Delta E/\text{kJ mol}^{-1}$	19.6	3.2	0.0	3.0	11.9	20.1	0.0	27.2	0.0
Pop. π^a	1.641	1.682	1.681	1.687	1.678	1.662	1.689	1.662	1.698
$r(\text{C-F})/\text{\AA}$	1.370	1.371	1.343	1.340	1.373	1.369	1.345	1.376	1.348
	1.365	1.338	1.339	1.340	1.342	1.345	1.340	1.346	1.344

^a The population of the π orbitals of the free arene as a function of the position with respect to the fluorine atoms were obtained through a NBO analysis.

ing groups (e.g. F) lowers the energy of $\pi^*(\text{C}=\text{C})$, and increases back-donation from the transition metal centre. Substitution by electron-withdrawing groups also lowers the energy of $\pi(\text{C}=\text{C})$ and donation from the alkene is thus less efficient. The final outcome of the bonding of electron deficient alkenes results from a subtle balance between two opposing effects. For fluorobenzene, calculations show that the F-substituted double bond (a in Fig. 3) is the least favoured site for η^2 -coordination to $\{\text{CpRe}(\text{CO})_2\}$ and the 2,3-position (site b) is preferred by 20.1 kJ mol^{-1} . Coordination to the 3,4-position (site c) is intermediate with a destabilization of 8.0 kJ mol^{-1} with respect to site b. The binding energy of C_6FH_5 to $\{\text{CpRe}(\text{CO})_2\}$ is slightly larger (92.7 kJ mol^{-1}) than that of C_6H_6 (88.6 kJ mol^{-1}).

**Fig. 3** Binding energy (in parenthesis, kJ mol^{-1}) of C_6FH_5 to $\{\text{CpRe}(\text{CO})_2\}$ as a function of the site of η^2 -coordination. Population of the $\pi(\text{C}=\text{C})$ and $\pi^*(\text{C}=\text{C})$ natural bonding orbitals, as deduced from an NBO analysis on free C_6FH_5 , is given for each site of coordination.

A Natural Bond Orbital (NBO) analysis¹² on C_6FH_5 demonstrates that the $\text{C}=\text{C}$ bonds are not equivalent in the free arene. The NBO scheme seeks a Lewis structure that allows for the most efficient partition of the wavefunction in terms of localized bonds. For free C_6FH_5 the procedure yielded three $\text{C}=\text{C}$ π -bonds and the corresponding π^* antibonds whose populations are given in Fig. 3 for the three different sites of coordination. The relatively high population in π^* indicates that a strictly localized description of the π -cloud in three distinct $\text{C}=\text{C}$ bonds is not possible. However, we can estimate the donating power of each $\text{C}=\text{C}$ bond from the population of $\pi(\text{C}=\text{C})$. The double bond character is higher between C(2) and C(3) (high population in π and low population in π^*). The relative values of π occupancy of the $\text{C}=\text{C}$ double bonds in the arene ring can be obtained qualitatively from the mesomeric

**Scheme 2**

forms in which F is a π donor (Scheme 2). The double bond in site b is present in all resonance forms (A–C), whereas the double bond at site a is lost (see Fig. 3). Therefore conjugation with F reduces the olefinic character at the $\text{C}=\text{C}$ bonds carrying F [C(1)–C(2) or C(1)–C(6)] more significantly than those without fluorine. From this analysis, donation from the arene is more efficient at site b in agreement with the relative energies of the various $\eta^2\text{-C}_6\text{FH}_5$ adducts.

The η^2 -coordination of an arene to a transition metal fragment induces a loss in resonance energy in the aromatic ring.¹³ If maximum conjugation is preserved in the η^2 -arene, coordination should be energetically favoured. The regioselectivity of the complexation to a transition metal centre is thus influenced by the stability, in terms of conjugation, of the remaining butadiene-type moiety on the ring. Our results with coordination of difluorobenzenes illustrate the critical influence exerted by the position of the F-substituents on the ring (Table 3).

Inspection of Table 3 clearly shows that η^2 -coordination of an F-substituted $\text{C}=\text{C}$ bond is energetically less favourable. In fluoroarenes, the fluorine atoms are involved in the π conjugation and significant energy is lost if the π conjugation of F is not possible in the η^2 -adduct, as occurs when F is on the coordinated $\text{C}=\text{C}$ bond. The worst situation is met when the bond is substituted by two fluorine atoms with a binding energy of only 67.4 kJ mol^{-1} to $\{\text{CpRe}(\text{CO})_2\}$ (coordination site 1,2 for 1,2-C₆F₂H₄, Table 3). The loss of conjugation between F and the ring is illustrated by the significant lengthening of the C–F bond (Table 3) because resonance forms of type A–C (see Scheme 2) are lost. The C–F bond is also extended due to the allowed mixing of the $\sigma^*(\text{C-F})$ orbital with the $\pi^*(\text{C}=\text{C})$ orbital upon coordination. It should be noted that the coordinated $\text{HC}=\text{CH}$ bond is associated with the largest $\pi(\text{C}=\text{C})$ population in the free arene (1.689 and 1.698 for 1,3-C₆F₂H₄ and 1,4-C₆F₂H₄, respectively).

Fig. 4 presents the best site for coordination to $\{\text{CpRe}(\text{CO})_2\}$ schematically for the various fluoroarenes $\text{C}_6\text{F}_n\text{H}_{6-n}$. Our results for C_6FH_5 and $\text{C}_6\text{F}_2\text{H}_4$ have shown that there is a marked preference for formation of an η^2 -adduct at a $\text{HC}=\text{CH}$ bond. The regioselectivity of coordination is thus governed by the loss of resonance energy within the aromatic ring. For the remaining butadiene moiety, a 1,4-substitution pattern is preferred over other patterns as is shown by the difluorobenzenes. This behaviour is also observed when three to five F atoms are present on the ring, with the limitation that, in some cases, a “ $\text{HC}=\text{CF}$ ” bond is involved in the best coordination site.

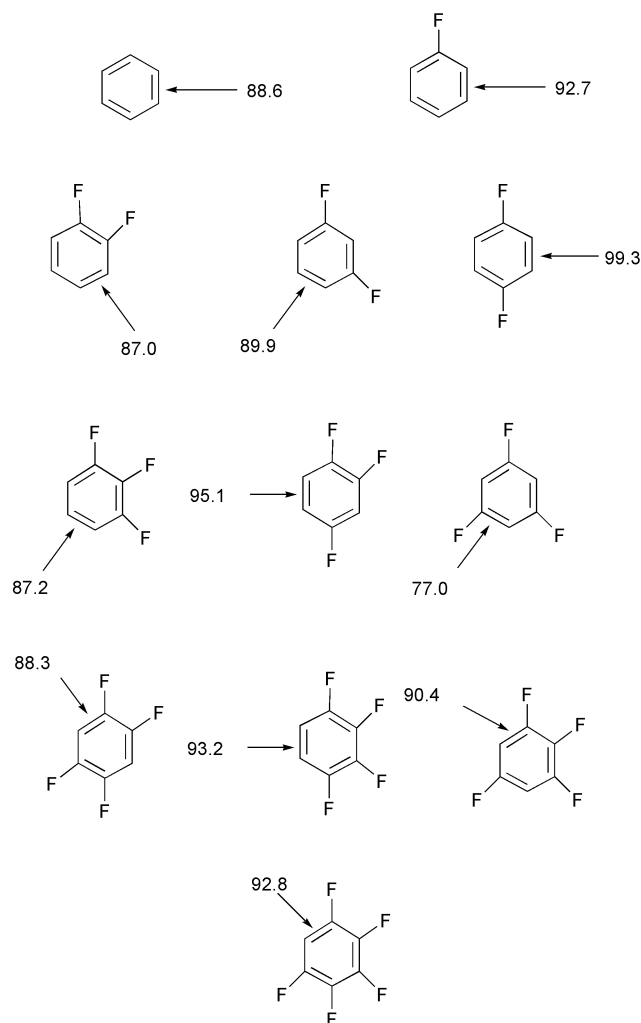


Fig. 4 Binding energy of $\text{C}_6\text{F}_n\text{H}_{6-n}$ to $\text{CpRe}(\text{CO})_2$ (kJ mol^{-1}) for $n = 0$ –5. Only the preferred coordination site (largest binding energy) is given.

We might have expected that the observation of C–H activation when there is a high degree of substitution could have resulted from a destabilization of the η^2 -arene complex as coordination to a $\text{FC}=\text{CH}$ bond is required. This is clearly not the case as the binding energy to $\{\text{CpRe}(\text{CO})_2\}$ of C_6FH_5 is the same as that of $\text{C}_6\text{F}_5\text{H}$ (Fig. 4, 92.7 vs. 92.8 kJ mol^{-1}). Moreover, there is no steady variation of the binding energy with increased fluorine substitution, and the binding energy spans a range of 22.3 kJ mol^{-1} with coordination to 1,3,5- $\text{C}_6\text{F}_3\text{H}_3$ being the weakest and that to 1,4- $\text{C}_6\text{F}_2\text{H}_4$ the strongest (Fig. 4). We conclude that the binding energy of the arene modulates the preferred products of reaction in an irregular but predictable way.

Competition between η^2 -coordination and oxidative addition

Competition between η^2 -coordination and oxidative addition depends on the stability of the oxidative addition product as well as the η^2 -complex (eqn. (2)). The range spanned by the Re–

Table 4 Relative energies of $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{F}_n\text{H}_{6-n})$ and all possible resulting isomers of $\text{trans-CpRe}(\text{CO})_2(\text{H})(\text{C}_6\text{F}_n\text{H}_{5-n})$ ($n = 0$ –5); see eqn. (2)

Arene	Aryl	ΔE^a	ΔG^b	$D(\text{C}-\text{H})^c$
C_6H_6	C_6H_5	22.3	13.0	489.8
C_6FH_5	2- C_6FH_4	11.9	3.5	500.5
	3- C_6FH_4	25.5	13.7	490.6
	4- C_6FH_4	27.4	18.1	494.3
1,2- $\text{C}_6\text{F}_2\text{H}_4$	2,3- $\text{C}_6\text{F}_2\text{H}_3$	4.9	–5.5	500.3
	3,4- $\text{C}_6\text{F}_2\text{H}_3$	21.1	10.8	494.5
1,3- $\text{C}_6\text{F}_2\text{H}_4$	2,4- $\text{C}_6\text{F}_2\text{H}_3$	10.3	4.3	504.6
	2,6- $\text{C}_6\text{F}_2\text{H}_3$	–2.5	–5.2	512.0
	3,5- $\text{C}_6\text{F}_2\text{H}_3$	22.2	15.2	492.0
1,4- $\text{C}_6\text{F}_2\text{H}_4$	2,5- $\text{C}_6\text{F}_2\text{H}_3$	17.5	6.1	501.2
	2,3,4- $\text{C}_6\text{F}_3\text{H}_2$	5.7	1.7	503.6
1,2,3- $\text{C}_6\text{F}_3\text{H}_3$	3,4,5- $\text{C}_6\text{F}_3\text{H}_2$	20.6	10.7	495.0
	2,3,5- $\text{C}_6\text{F}_3\text{H}_2$	11.8	1.5	501.7
	2,4,5- $\text{C}_6\text{F}_3\text{H}_2$	14.3	4.0	504.8
1,2,4- $\text{C}_6\text{F}_3\text{H}_3$	2,3,6- $\text{C}_6\text{F}_3\text{H}_2$	1.4	–6.4	511.8
	2,4,6- $\text{C}_6\text{F}_3\text{H}_2$	–14.5	–21.0	515.5
1,3,5- $\text{C}_6\text{F}_3\text{H}_3$	2,3,4,5- $\text{C}_6\text{F}_4\text{H}$	10.3	0.0	504.4
1,2,3,4- $\text{C}_6\text{F}_4\text{H}_2$	2,3,5,6- $\text{C}_6\text{F}_4\text{H}$	–6.4	–13.8	512.4
1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$	2,3,4,6- $\text{C}_6\text{F}_4\text{H}$	–5.0	–13.7	514.7
1,2,3,6- $\text{C}_6\text{F}_4\text{H}_2$	C_6F_5	–3.5	–12.7	514.7

^a ΔE (kJ mol^{-1}) is the electronic energy difference. ^b ΔG (kJ mol^{-1}) is the corresponding free energy difference computed within the harmonic oscillator approximation. ^c $D(\text{C}-\text{H})$ is the calculated C–H bond dissociation energy (kJ mol^{-1}) in free $\text{C}_6\text{F}_n\text{H}_{6-n}$.

C BDE in $\text{trans-}[\text{CpRe}(\text{CO})(\text{H})(\text{aryl})]$ is larger (54.7 kJ mol^{-1})⁸ than the range of arene binding energies and is associated with an increase of the BDE upon fluorine substitution. The strength of the Re–aryl bond is therefore a key parameter in accounting for the products of reaction. The differences in electronic energy (ΔE) and Gibbs free energy (ΔG) between $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{F}_n\text{H}_{6-n})$ and $\text{CpRe}(\text{CO})_2(\text{H})(\text{C}_6\text{F}_n\text{H}_{5-n})$ are reported in Table 4. The value of ΔG is lower than that of ΔE because a C–H bond is broken during the reaction (lower zero point energy in the hydrido–aryl complex). The variation in ΔG , as a function of the C–H bond dissociation energy in $\text{H}-\text{C}_6\text{F}_n\text{H}_{5-n}$ is illustrated in Fig. 5. In every case, ΔG is calculated with respect to the most stable η^2 -arene complex (as shown in Fig. 4) and is positive when the arene complex is preferred. There is a decrease of ΔG with increasing H–C organic BDE, indicative of greater stabilization of the oxidative addition product. The complexes are grouped in a fashion already found in our study of Re–C/H–C bond energy correlation.⁸ There are three distinct families, depending on the number of F atoms at the *ortho* position in the C–H activation product.

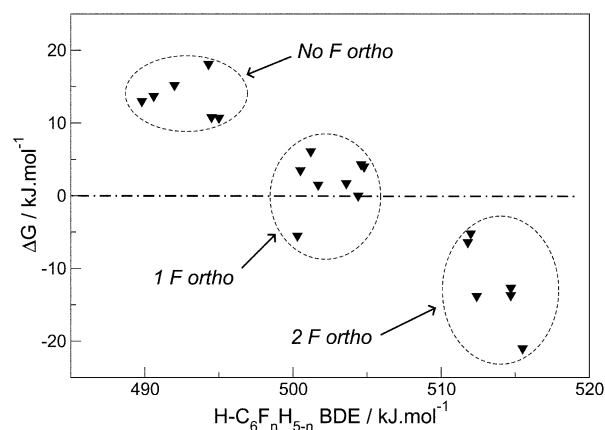


Fig. 5 Free energy difference, ΔG (kJ mol^{-1}), between $\text{CpRe}(\text{CO})_2(\eta^2\text{-arene})$ and $\text{CpRe}(\text{CO})_2(\text{H})(\text{aryl})$ as a function of calculated C–H BDE (kJ mol^{-1}) in the free arene (See Table 4). A positive ΔG indicates that the η^2 -arene complex is favoured.



If no F is present at an *ortho* position, the reaction is endothermic by 10–20 kJ mol⁻¹ and no hydrido–aryl complex is obtained. This is in agreement with the observations by Van der Heijden *et al.*⁶ and by Bengali and Leicht,⁷ where only coordination of C₆H₆ to {Cp*Re(CO)₂} is obtained. With one *ortho* fluorine, the reaction is essentially thermoneutral and both products can be observed simultaneously in solution. This is experimentally the case for 1,4-C₆F₂H₄, which yields a mixture of the C–H activation product, CpRe(CO)₂(H)(2,5-C₆F₂H₃), and the η²-difluorobenzene, CpRe(CO)₂(2,3-η²-1,4-C₆F₂H₃), in a 1 : 16 ratio.^{5c} This ratio translates to a Gibbs free energy difference of 6.9 kJ mol⁻¹ at 298 K. The exceptional closeness of the calculated values of 6.1 kJ mol⁻¹ (Table 4) is probably accidental but shows that DFT calculations represent the bonding in these systems very well.

The results with 1,2-C₆F₂H₄ and 1,2,3-C₆F₃H₃ deserve special comment because the CpRe(CO)₂(H)(2,3-C₆F₂H₃) and CpRe(CO)₂(H)(2,3,4-C₆F₃H₂) complexes are significantly more stable than the other members of the one *ortho* F family (ΔE = 4.9 and 5.7 kJ mol⁻¹, respectively). The weaker binding energies of the arenes (87.0 and 87.2 kJ mol⁻¹, see Fig. 4) offer an explanation of the increased stability of the hydrido–aryl complexes. This example illustrates the need for two parameters, with the Re–C BDE as the leading one and the η²-coordination binding energy responsible for the scatter within each family in Fig. 5.

Finally, when the two *ortho* positions are occupied by fluorine, ΔG is negative and only the oxidative addition product should be observed. The reaction is particularly favoured for 1,3,5-C₆F₃H₃ because the η²-coordination product is destabilized (Fig. 4). Experimentally, oxidative addition is indeed the sole outcome for C₆F₅H, 1,2,4,5-C₆F₄H₂ and 1,3-C₆F₂H₄.^{5b,8}

In general, the competition between η²-coordination of the arene and C–H oxidative addition is governed mainly by the thermodynamic stability of the hydrido–aryl product with modulation originating from the η²-coordination process. The counter-intuitive result is that the strongest C–H bonds are cleaved preferentially because Re–aryl bond strengths increase twice as fast as H–C BDEs.⁸

Reaction mechanism

We have studied the reaction path connecting the η²-complex and the *trans*-hydrido–aryl complex with two goals in mind. First, we wished to find out how the activation energies varied with fluorine-substitution. Secondly, we wished to understand the reaction of Cp*Re(CO)₂(N₂) with 1,4-C₆F₂H₄ which revealed that Cp*Re(CO)₂(2,3-η²-1,4-C₆F₂H₄) and Cp*Re(CO)₂(H)(2,5-C₆F₂H₃) are both present in solution but they are not at thermal equilibrium with each other. It was proposed that the primary product of the reaction is the η²-complex, which converts photochemically, and not thermally, to the hydride complex. The succession of elementary steps along the reaction path from CpRe(CO)₂(η²-C₆H₆) to CpRe(CO)₂(H)(C₆H₅) is represented in Fig. 6 and Table 5 collects variation of selected geometrical parameters along the path. The rate determining step is not the cleavage of the C–H bond, but the isomerisation from the *cis*-hydrido–aryl to the *trans* isomer with a maximum activation energy of 143.0 kJ mol⁻¹ above the η²-arene adduct.

After coordination of the arene, an η²-C–H complex is identified as a minimum 17.9 kJ mol⁻¹ above the η²-arene complex. Despite all attempts, we could not locate a transition state

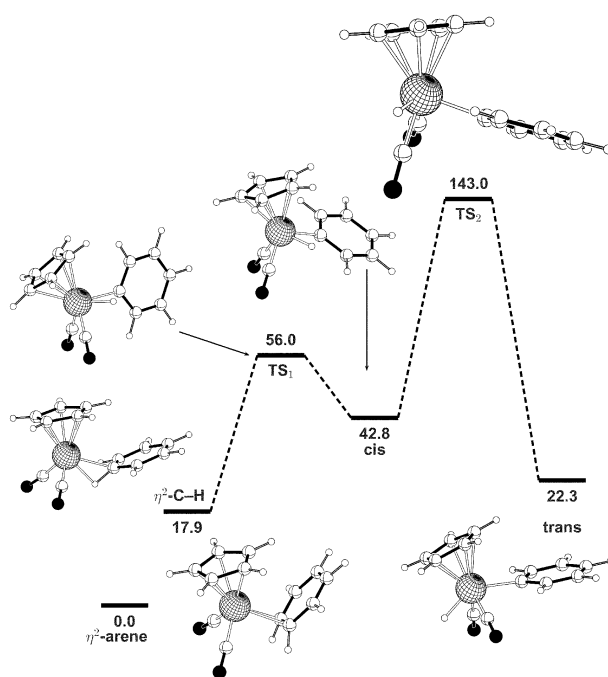
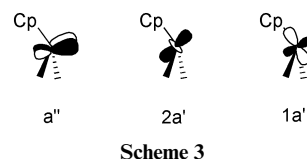


Fig. 6 Reaction path for the transformation of CpRe(CO)₂(η²-C₆H₆) into *trans*-CpRe(CO)₂(H)(C₆H₅). Electronic energies (ΔE) in kJ mol⁻¹.

connecting these two complexes. However, the Re–C(1) bond distance is very similar in the two complexes (Table 5) and the transition state should be very close in energy to the η²-C–H complex. In contrast to the geometry of the η²-arene complex where the C=C bond is perpendicular to the mirror plane of the {CpRe(CO)₂} moiety, the coordinated C–H bond of the η²-C–H complex lies in this mirror plane with the phenyl ring almost parallel to the Cp ring (Fig. 6). There is a slight elongation of the C–H bond (1.147 Å) due to back-donation from the d⁶ {CpRe(CO)₂} fragment. The occupied valence molecular orbitals (MO) of {CpRe(CO)₂} are represented schematically in Scheme 3 and it has been shown that the a'' MO is the highest occupied MO.¹³ The two a' orbitals, 1a' and 2a', have the correct symmetry to back-donate into σ*(C–H) of the η²-C–H adduct, but the overlap is weak and the MOs are low in energy leading to only weak electron transfer from the Re d orbitals to the σ*(C–H) orbital.



To cleave the C–H bond, the electron transfer into σ*(C–H) has to be more efficient and thus must involve the best π-electron donating MO of the metallic fragment, *i.e.* the a'' MO. In the transition state for C–H oxidative addition, TS₁, the phenyl ring has rotated by 90° to allow interaction between the a'' and the σ*(C–H) MOs. The activation energy from the η²-C–H complex, is 38.1 kJ mol⁻¹ and is typical for C–H activation at a transition metal centre. The C–H bond has elongated significantly (1.670 Å) and is now similar in length to the incipient Re–H bond (1.669 Å). The Re–C bond is almost formed in TS₁, which raises the question of the nature of the migrating H atom, proton or hydride. The carbonyl vibrational frequencies have increased in the transition state (1993.6 and 2042.4 cm⁻¹ in η²-C–H vs. 2031.8 and 2080.2 cm⁻¹ in TS₁), indicating a lower electron density available at the metal centre, in agreement with an oxidised Re d⁴ centre. This transition state leads to a *cis*-hydrido–aryl intermediate lying 42.8 kJ mol⁻¹ above the η²-C₆H₆ complex. Isomerisation from the *cis* to

Table 5 Evolution of selected geometrical parameters (distances in Å, angles in °) along the reaction path for the transformation of $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_6)$ to *trans*- $\text{CpRe}(\text{CO})_2(\text{H})(\text{C}_6\text{H}_5)$. TS_1 corresponds to the transition state associated with the C–H bond cleaving process, while TS_2 is the transition state for the *cis* to *trans* isomerisation. The atoms are labelled as in Fig. 1, the extrema as in Fig. 6. D(1) is the Cp ring centroid

	$\eta^2\text{-C}_6\text{H}_6$	$\eta^2\text{-C-H}$	TS_1	<i>cis</i>	TS_2	<i>trans</i>
Re–C(1)	2.374	2.377	2.225	2.195	2.145	2.204
C(1)–H(1)	1.084	1.147	1.670	2.220	2.802	3.633
Re–H(1)	2.843	1.940	1.669	1.652	1.684	1.672
C(7)–Re–C(8)	87.9	91.4	84.9	82.0	78.7	98.0
C(7)–Re–D(1)	123.9	123.7	124.8	124.7	154.6	129.1
C(8)–Re–D(1)	122.3	125.7	124.1	128.5	114.2	131.8
C(1)–Re–D(1)	120.4	114.5	121.2	117.4	114.0	110.6
H(1)–Re–D(1)	132.5	143.6	122.8	113.2	107.5	110.6

the *trans* isomer is then necessary to obtain the more stable product. This situation contrasts markedly with the case of oxidative addition by d^8 {CpML} fragments (M = Ir or Rh, L = PMe_3 or CO),^{1c,3b} where the *cis* isomer is the only possible product. Thus, the oxidative addition process is the rate-limiting step in these systems.

A pathway leading directly to the *trans* isomer from the $\eta^2\text{-C-H}$ complex was also searched. Cleaving the C–H bond without rotating the phenyl ring would have put the migrating hydride *trans* to the Cp ring and could have led to the *trans* isomer directly. All attempts to locate such a pathway failed and TS_1 was always obtained. In the case of $\text{C}_6\text{F}_5\text{H}$ we could optimize a TS with the target geometry but this TS connects to the *cis* isomer. If the hydride moves in the mirror plane of {CpRe(CO)₂}, it is not far from being *trans* to Cp, a geometry that appears to be energetically unfavourable. Recently Lesnard *et al.*¹⁴ have shown that in $\text{CpW}(\text{H})_2(\text{CO})_3^+$, the geometry with H *trans* to Cp is accessible, but in their case the *trans* hydride could be seen as a proton H^+ occupying the electron rich site in $\text{CpW}(\text{H})(\text{CO})_3$.

The transition state TS_2 for the isomerisation process has been located $143.0 \text{ kJ mol}^{-1}$ above the $\eta^2\text{-C}_6\text{H}_6$ complex on the potential energy surface. The barrier to *cis*–*trans* isomerisation is calculated as $100.2 \text{ kJ mol}^{-1}$. The transition state motion corresponds to an in-plane transfer of the hydride in the basal plane made by the four ligands (H, CO, CO and aryl) in the piano stool structure. This is illustrated by the variation of the angles between the basal ligands and the centroid of the Cp ring, D(1) (Table 5). The C(1)–Re–D(1) and H(1)–Re–D(1) angles do not change significantly upon *cis* to *trans* isomerisation and remain close to 110° . In contrast, there is a marked alteration of the carbonyl–Re–D(1) angles with one angle getting larger (154.6°) and the other smaller (114.2°). Thus, the transition state motion can be described as a transfer of the hydride in the basal plane, while both CO ligands experience a concerted motion away from the basal plane. Related piano-stool rearrangements have been noted.¹⁵ The high energy of TS_2 could result from two factors. The increased *trans* effect exerted by the Cp ring on one carbonyl (C(7)–Re–D(1) 154.6°) is not favoured energetically; and the migration of both carbonyl groups reduces the overlap with the a'' orbital (Scheme 3), thus leading to less efficient back-donation.

In the case of $\text{CpRe}(\text{CO})_2(\text{H})_2$, both *cis* and *trans* isomers have been observed by Casey *et al.*^{16a} The equilibrium ratio between the two isomers is 2 : 98 at 24°C , corresponding to a $\Delta G = 9.6 \text{ kJ mol}^{-1}$ in favour of the *trans* isomer. This is in the same range of energy as that calculated with phenyl group in place of hydrogen (20.5 kJ mol^{-1} , Fig. 6). The experimental activation energy for *cis* to *trans* isomerisation was estimated to be 99.0 kJ mol^{-1} , close to our calculated value of $100.2 \text{ kJ mol}^{-1}$ with $\text{CpRe}(\text{CO})_2(\text{H})(\text{C}_6\text{H}_5)$. The *cis*–*trans* isomerization of $(\text{C}_5\text{H}_4\text{Me})\text{Re}(\text{CO})(\text{P}(\text{OPh})_3)\text{Br}_2$ has been studied in the solid state and has been shown to involve the exchange between CO and Br.^{16b,c}

Influence of F-substitution on the kinetics of the reaction

For all the fluoroarenes considered, the reaction mechanism is the same as the one discussed for C_6H_6 and the energies of each intermediate and transition state are reported in Table 6. The rate-determining step is the isomerisation process from the *cis* isomer to the thermodynamic *trans* product. In this crucial step, the Re–aryl bond is already formed and we may expect significant influence of the F-substitution pattern on the activation barrier. Because the unsaturated fragment {CpRe(CO)₂} is generated photochemically *in situ*, the energy origin has been taken as that of separated {CpRe(CO)₂} and $\text{C}_6\text{F}_n\text{H}_{5-n}$. Inspection of Table 6 shows that the only step that is endothermic with respect to the entry channel is the isomerisation process and this corresponds to the true activation barrier. Fig. 7 represents the variation of the activation barrier (energy of TS_2 relative to separated reactants) with the Re– $\text{C}_6\text{F}_n\text{H}_{5-n}$ bond energy in the *trans* product. This bond is chosen since it is already formed in the *cis* isomer. It is important to note that the experimental samples are irradiated with a UV source and the energetic barrier may therefore be overcome photochemically.

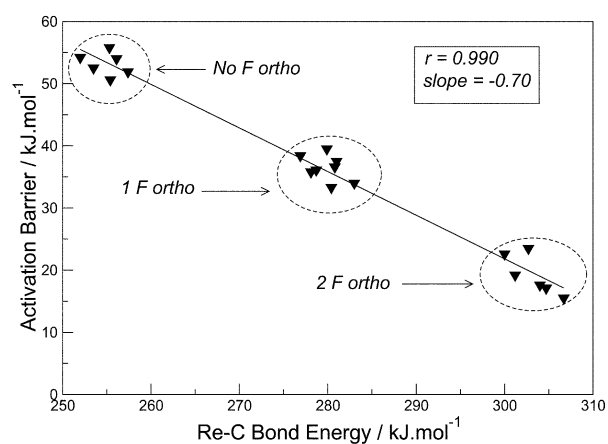


Fig. 7 Variation of the electronic energy (kJ mol^{-1}) of the transition state for *cis* to *trans* isomerisation in $\text{CpRe}(\text{CO})_2(\text{H})(\text{C}_6\text{F}_n\text{H}_{5-n})$, TS_2 , as a function of the BDE D(Re–H) in *trans* $\text{CpRe}(\text{CO})_2(\text{H})(\text{C}_6\text{F}_n\text{H}_{5-n})$ (see Table 6).

There is a decrease of the activation barrier from 55 to 15 kJ mol^{-1} above the entry channel as the Re–C BDE increases. Again three distinct families of points are obtained, depending on the number of fluorines at an *ortho* position. The Re–C bond is present in both the *cis* and *trans* isomers and is the sole parameter in the process that varies with F-substitution so the points in Fig. 7 are not scattered as in Fig. 5. The *cis* to *trans* isomerisation is easiest when two *ortho* F are present: the activation barrier of less than 20 kJ mol^{-1} is easy to overcome at room temperature and the oxidative addition products are obtained. For the subset with one *ortho* F, the barrier is higher ($30\text{--}40 \text{ kJ mol}^{-1}$) leading to a significant amount of the

Table 6 Electronic energy difference (kJ mol⁻¹) between the various extrema along the path for formation of *trans*-CpRe(CO)₂(H)(C₆F_nH_{5-n}) from the separated reactants {CpRe(CO)₂} and C₆F_nH_{6-n}. Negative values indicate extrema more stable than separated reactants. The bond energy, *D*(Re–C) (kJ mol⁻¹), in CpRe(CO)₂(H)(C₆F_nH_{5-n}) is also given

Arene	Aryl	η ² -C–H	TS ₁	<i>cis</i>	TS ₂	<i>trans</i>	<i>D</i> (Re–C)
C ₆ H ₆	C ₆ H ₅	-70.9	-32.8	-46.0	54.2	-66.5	252.0
C ₆ FH ₅	2-C ₆ FH ₄	-68.7	-40.0	-61.2	38.4	-80.8	276.9
	3-C ₆ FH ₄	-65.4	-30.4	-44.4	52.5	-67.2	253.5
	4-C ₆ FH ₄	-69.1	-30.4	-44.3	55.8	-65.3	255.3
1,2-C ₆ F ₂ H ₄	2,3-C ₆ F ₂ H ₃	-64.6	-45.4	-63.2	35.8	-82.1	278.1
	3,4-C ₆ F ₂ H ₃	-63.9	-31.0	-63.9	54.0	-65.9	256.1
1,3-C ₆ F ₂ H ₄	2,4-C ₆ F ₂ H ₃	-66.9	-41.5	-59.5	39.5	-79.6	279.9
	2,6-C ₆ F ₂ H ₃	-66.5	-51.4	-73.3	22.7	-92.4	300.0
	3,5-C ₆ F ₂ H ₃	-60.0	-33.2	-48.0	50.6	-67.7	255.4
1,4-C ₆ F ₂ H ₄	2,5-C ₆ F ₂ H ₃	-63.8	-44.6	-62.6	36.1	-81.8	278.7
1,2,3-C ₆ F ₃ H ₃	2,3,4-C ₆ F ₃ H ₂	-63.2	-42.9	-62.0	36.6	-81.5	280.8
	3,4,5-C ₆ F ₃ H ₂	-58.8	-30.7	-46.6	51.9	-66.6	257.4
1,2,4-C ₆ F ₃ H ₃	2,3,5-C ₆ F ₃ H ₂	-60.2	-45.3	-65.0	33.3	-83.3	280.4
	2,4,5-C ₆ F ₃ H ₂	-62.4	-42.1	-61.3	37.5	-80.8	281.0
	2,3,6-C ₆ F ₃ H ₂	-63.0	-52.8	-76.2	19.2	-93.7	301.2
1,3,5-C ₆ F ₃ H ₃	2,4,6-C ₆ F ₃ H ₂	-64.7	-48.8	-72.2	23.5	-92.5	302.7
1,2,3,4-C ₆ F ₄ H ₂	2,3,4,5-C ₆ F ₄ H	-59.1	-43.2	-64.0	34.0	-82.9	283.0
1,2,4,5-C ₆ F ₄ H ₂	2,3,5,6-C ₆ F ₄ H	-58.6	-51.4	-77.1	17.1	-94.7	304.7
1,2,3,6-C ₆ F ₄ H ₂	2,3,4,6-C ₆ F ₄ H	-63.8	-51.7	-77.2	17.6	-95.4	304.0
C ₆ F ₅ H	C ₆ F ₅	-59.1	-51.2	-75.8	15.5	-96.3	306.7

η²-arene complex. However, once the latter is at thermal equilibrium with its surrounding solvent, the barrier that must be overcome to form the *trans*-hydrido-aryl complex is high (>100 kJ mol⁻¹). Consequently, there is no thermal equilibrium between the two products. When no *ortho* F is present, the *cis* to *trans* isomerisation step is highly disfavoured thermodynamically and kinetically and only the η²-arene is obtained.

Discussion

Our computational studies show that several factors control the preference for η²-coordination vs. oxidative addition in the reaction of fluoroarenes with {CpRe(CO)₂}. Geometries are well reproduced as is shown for CpRe(CO)₂(η²-C₆H₆) and CpRe(CO)₂(η²-C₆F₅H) (Fig. 1 and Table 1), our models for [(Cp*Re(CO)₂)₂(μ-η²:η²-C₆H₆)] and CpRe(CO)₂(η²-C₆F₆). The calculated binding energy of benzene in CpRe(CO)₂(η²-C₆H₆) is also in good agreement with the experimental value determined for Cp*Re(CO)₂(η²-C₆H₆). However, as can be expected, significantly different binding energies have been measured for complexes of (η²-C₆H₆) with other metal–ligand fragments. Bond dissociation enthalpies of 47.7 and 59.4 kJ mol⁻¹ have been measured for (CO)₅Cr(η²-C₆H₆)^{10f} and CpMn(CO)₂(η²-toluene)^{10c} respectively. The binding energy in this work cannot be transferred to other complexes but the trends calculated with F substitution are likely to be maintained with other neutral metal fragments.

For all C₆F_nH_{6-n} systems, the η²-arene complex is a stable minimum. For a given arene, coordination preference decreases in the order HC=CH > HC=CF > FC=CF. The preference for coordination at CH=CH over CH=CF is consistent with a previous calculation^{5c} comparing the binding of ethene and vinyl fluoride to {CpRe(CO)₂}. In that case, we found a preference for binding ethene of 9 kJ mol⁻¹. The preference has been established here for the {CpRe(CO)₂} fragment and should not be assumed to be valid for other transition metal fragments. The calculations also show that the slight localisation of the π electrons caused by F in the uncoordinated arene makes some bonds more electron rich and better candidates for coordinating to the unsaturated metal fragment. The double bond with the highest π-electron density gives the preferred coordination site without exception. Back-donation certainly plays a role in the overall bonding of the arene to the metal but its influence on the regioselectivity of the coordination is not clear.

The binding energy of the arene at its preferred site of coordination varies from 77 to 99.3 kJ mol⁻¹. Within an arene, the preference HC=CH > HC=CF > FC=CF sees no exception but there is no clear trend in the binding energy values between arenes. The presence of fluorine on the coordinated bond does not decrease the binding energy of the arene systematically. Weak binding energy is calculated for 1,3,5-C₆F₃H₃ with the record low of 77 kJ mol⁻¹. However, binding the HC=CF bond in arenes like C₆F₅H can lead to binding energy not far from the record high found for coordination to the HC=CH bond in 1,4-C₆F₂H₄ (Fig. 4). It should be noted that coordination of rhenium to the preferred double bond allows the metal to reach a C–H bond *ortho* to an F centre without ring whizzing for all possible fluorinated arenes (Fig. 4). In the case of 1,3-C₆F₂H₄ and 1,2,4-C₆F₃H₃, the initial coordination should lead to a product with one *ortho* F and not two *ortho* F, if no change of the coordination site to the metal fragment occurs. However, ring whizzing has been shown experimentally^{5a,c} and theoretically^{5c} to be easy when shifts occur over a C–H bond but to have a higher barrier for going over a C–F bond. In the rhodium analogues, this accounts for the formation of Cp*Rh(PMe₃)(H)(2,4-C₆F₂H₃) and Cp*Rh(PMe₃)(H)(3,5-C₆F₂H₃) in a 5 : 1 ratio at low temperature, which rearranges to Cp*Rh(PMe₃)(H)(2,6-C₆F₂H₃) upon warming.⁹

The calculated free energy difference between η²-arene and the hydrido-aryl complex correlates with the homolytic C–H bond dissociation energy. The calculations indicate the presence of three domains defined by the number of fluorines at an *ortho* position on the aryl in the final product. The free energy is positive in the case of no *ortho*-F, borderline in the case of one *ortho* F and negative in the case of two *ortho* F. The case of no *ortho* F is only represented by benzene which indeed does not form the hydrido-phenyl derivative. As soon as the six-membered ring is substituted with F, the calculations show that, if a product of oxidative addition is to be formed, it will always have one F at an *ortho* position. Thus only two of the families are significant, those with one F and with two F. With two *ortho* F, oxidative addition should always occur. It has been found experimentally that 1,3-C₆F₂H₄ does indeed give oxidative addition exclusively, although it is predicted to have one of the least negative energies of reaction in this family (Table 4).

The challenging situation for prediction is that of the family with one *ortho* F since calculations indicate this group to be borderline. Comparison with experimental values is almost

too good. In the case of 1,4-C₆F₂H₄ the calculated free energy is 6.1 kJ mol⁻¹ in favour of the η²-arene complex. The ratio of η²-coordination and hydrido-aryl complex translates into a difference of free energy of 6.9 kJ mol⁻¹. It is probably safe to predict that the group with one *ortho* F will lead to a mixture of coordination and oxidative addition products. Of this family, the 1,2-C₆F₂H₄ system is the arene which is most likely to give the oxidative addition as the major product.

A reaction mechanism for the transformation of the η²-arene into the *trans* hydrido-aryl complex is proposed. The transition state linking the η²-arene and the σ C-H complex could not be located but the latter is the starting point for the oxidative addition as demonstrated by the connection of the transition state to the σ C-H complex. The difficulty could arise because of the technical demands of locating a TS very near the σ-complex. It should be noted that no transition state for a transformation from the η²-arene to the oxidative addition product has been located to our knowledge.

Oxidative addition leads to a *cis* product first, followed by an isomerisation to the *trans* product. In this isomerisation the hydride does not reach the *trans* position by going in between the two CO ligands but by rotating around the latter. This movement of H is made possible by the concerted shift of the two carbonyls away from the migrating hydride, one carbonyl getting closer to the position *trans* to the Cp ring (see Table 5). In this motion, all groups avoid alignment *trans* to the Cp ring. In contrast, previous authors have postulated a trigonal bipyramidal intermediate in related isomerisations with one ligand *trans* to Cp.¹⁵ The transition state from the *cis* to the *trans* isomer is the highest point in the path for all fluoroarenes. This barrier correlates with the Re-C BDEs so the calculated activation energies fall into three groups according to the number of F *ortho* to the metal in the product. The lowest barrier corresponds to products with two *ortho* F. The variation of the Re-C bond energy is the dominant factor in determining the changes in the energy barrier between the different fluoroarenes; since the Re-C bond is fully formed in the transition state, the energies of the *cis*, *trans* and TS are similarly affected by fluorination. The development of the three families can be visualised in Fig. 8 which shows that the three families of complex remain rigorously distinct from *cis*, through TS₂ to the *trans* product with the exception of only one of the 20 complexes (CpRe(CO)₂(H)(3,4-C₆F₂H₄)). The families begin to form already in TS₁. Therefore, it appears that the thermodynamic and kinetic aspects of this reaction favour cleavage of the strongest C-H bond.

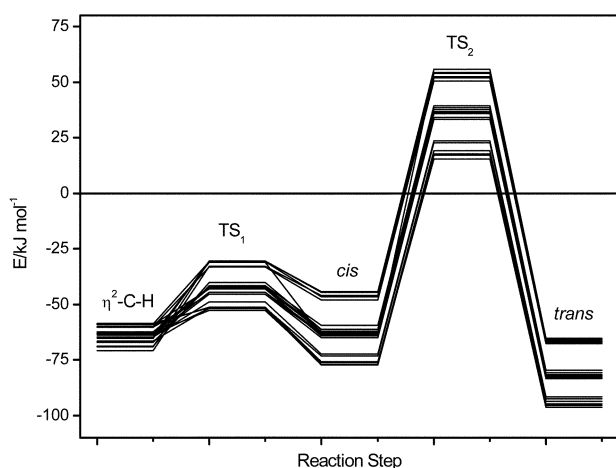


Fig. 8 Calculated electronic energies (kJ mol⁻¹) of steps in reaction pathway from CpRe(CO)₂(η²-C-H-C₆F_nH_{6-n}). Each line represents the pathway for one of the 20 complexes. The energy zero is taken as {CpRe(CO)₂ + C₆F_nH_{6-n}}.

At present, there is a shortage of experimental kinetic data to compare with the calculated barriers. Here we point to two recent unpublished experimental observations.¹⁷ The predicted decrease in overall activation energy with increasing Re-C BDE is consistent with a competition reaction that we carried out under kinetic control. {Cp*Re(CO)₂} was generated photochemically from Cp*Re(CO)₂(N₂) at 243 K in a 1 : 1 mixture of 1,3-C₆F₂H₄ and 1,4-C₆F₂H₄ (see ref. 8). The product distribution indicates that the kinetically preferred product arose from C-H activation of the 1,3-isomer [product distribution: Re(2,6-C₆F₂H₃)H : Re(2,3-η²-1,4-C₆F₂H₄) : Re(2,5-C₆F₂H₃)-H = 18 : 3.5 : 1]. The predicted barrier height for the Cp analogue of the preferred product is 22.7 kJ mol⁻¹ whereas that for the disfavoured product is 36.1 kJ mol⁻¹ (Table 6).

In an earlier paper we reported the isomerisation of trans-Cp*Re(CO)₂(2,6-C₆F₂H₃)H to Cp*Re(CO)₂(2,3-η²-1,4-C₆F₂H₄).^{5c} We have now followed this reaction at 263 K by NMR spectroscopy in order to obtain kinetic data. Although the reaction did not yield high quality data over a long period (and was therefore unsuitable for full kinetic analysis), we were able to obtain an estimate of the barrier to the process analogous to that shown in Fig. 6 but in the direction moving from right to left. The initial rate of decay of the hydride was ca. 4 × 10⁻⁴ s⁻¹, yielding ΔG[#] of ca. 81 kJ mol⁻¹. This compares with a calculated ΔE[#] of 117.9 kJ mol⁻¹. Although the comparison is limited by the lack of enthalpy of activation, we are satisfied that the barrier is in the appropriate range.

The computational studies rationalize all known experimental observations:^{5b,c,8} the lack of C-H activation in the case of benzene, the mixture of products in the case of 1,4-C₆F₂H₄ and the exclusive observation of the hydrido-aryl complexes with 1,2,4,5-C₆F₄H₂, C₆F₅H and 1,3-C₆F₂H₄. We have set ourselves the challenge of predicting the outcome of the reaction with reactants that have not yet been studied. Oxidative addition should occur exclusively with 1,3,5-C₆F₃H₃, 1,2,4-C₆F₃H₃ and 1,2,3,5-C₆F₄H₂. Mixtures of coordination and oxidative addition products should be obtained for C₆F₅H, 1,2-C₆F₂H₄, 1,2,3-C₆F₃H₃ and 1,2,3,4-C₆F₄H₂. These predictions, if realised, will confirm the key role of the *ortho* position in the aromatic C-H bond activation and the relative lack of importance of the other fluorines.

Conclusions

1. The leading parameter affecting the outcome of the reaction of {CpRe(CO)₂} with fluoroarenes (*i.e.* coordination *v.s.* activation) is the C-H bond dissociation energy. As this bond increases in strength, so the Re-C bond strengthens even more and the balance tips further towards the oxidative addition product. As a consequence, the free energy difference between coordination and activation is predicted to fall into three families according to the number of *ortho* fluorine atoms in the final product (Fig. 5). With no *ortho* fluorine, coordination is favoured, with two *ortho* fluorines activation is favoured and with one *ortho* fluorine both products may be observed.

2. The binding energy of the arene is a less important factor than the C-H bond dissociation energy and shows its significance in the dispersion within the three families along the vertical coordinate in Fig. 5. It does not vary systematically with the number of fluorine substituents.

3. When coordinating to an arene such as 1,2-difluorobenzene, the preferred site of coordination follows the order: HC=CH > HC=CF > FC=CF.

4. The rate determining step in oxidative addition is the *cis*-*trans* isomerisation of the Re(III) product. The barrier decreases with the number of *ortho* fluorine atoms (Fig. 6).

5. The σ-C-H complex has been identified as a minimum on the pathway to C-H activation.

6. Both thermodynamic and kinetic factors favour cleavage of the strongest C-H bonds.

Experimental

Computational details

All calculations were performed with the Gaussian 98 set of programs¹⁸ within the framework of hybrid DFT (B3PW91).¹⁹ The rhenium atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group (17 valence electrons) and its associated (8s7p5d)/[6s5p3d] basis set,²⁰ augmented by an f polarization function ($\alpha = 0.869$).²¹ A 6-31G(d,p) basis set²² was used for all the remaining atoms. Full optimizations of geometry without any constraint were performed, followed by analytical computation of the Hessian matrix to confirm the nature of the located extrema as minima or transition states on the potential energy surface. The thermodynamic quantities, ΔG and ΔS , were computed within the harmonic oscillator approximation as implemented in Gaussian 98. The NBO analysis¹² was performed using the keywords 3CBONDS and RESONANCE.

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