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Inertness of the Aryl−F Bond toward Oxidative Addition to Osmium and Rhodium Complexes: Thermodynamic or Kinetic Origin?

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Abstract: Quantum calculations with the density functional theory (B3LYP) have been carried out to compare the reactivity of aryl-H and aryl-F bonds toward oxidative addition and to understand the high degree of inertness of the latter. The thermodynamic energy patterns for oxidative addition of 1,4-difluorobenzene toward two very different metal fragments have been examined. In one of them the final product of oxidative addition could be a 16-electron unsaturated complex of the type $Os(H)(CO)(C_6F_2H_3)(PH_3)_2$ and/or $Os(F)(CO)(C_6FH_4)(PH_3)_2$. In the other system the final product of oxidative addition could be an 18-electron saturated complex $CpRh(PH_3)(H)(C_6F_2H_3)$ or $CpRh(PH_3)(F)(C_6FH_4)$. These two systems are models for experimental complexes which prefer the C−H to the C−F oxidative addition. The calculations reveal that, for both systems, the C−F oxidative addition is thermodynamically preferred, especially in the 16-electron case. The activation energy has been determined in the case of Rh, and it is shown that the activation energy for C−F activation is considerably higher than that for C−H activation. This clearly shows that the inertness of the C−F bond has a kinetic origin.

Introduction

Compounds containing aromatic C−F bonds have considerable interest as solvents, agrochemicals, pharmaceuticals, and dyes.[1] However, their extensive use is constrained in part by the difficulty in eliminating them from the environment.[2,3] The selective cleavage of C−F bonds, or C−F bond activation, offers potential both in synthesis and disposal of fluorocarbons and has therefore become an important goal in the chemical community. Two thorough reviews of C−F bond activation have appeared recently[4,5] as well as reviews of the interaction of C−F bonds with metal centers[6] and of metal−fluoride complexes.[7,8] In this paper we are concerned with homogeneous activation of aromatic C−F bonds and will not consider heterogeneous processes or activation of aliphatic C−F bonds. Intramolecular activation of the C−F bond has been carried out with Pt(II) and W(0) complexes,[9,10] and it has been demonstrated that the C−F bond is cleaved selectively in the presence of weaker C−H or C−X (X = Cl, Br) bonds if the ligands are designed with steric constraints;[10] otherwise, C−H attack is preferred. The kinetic analysis of these reactions supports a conventional oxidative addition mechanism.[10] The first record of intermolecular C−F activation of hexafluorobenzene involved oxidative addition at $Ni(PEt_3)_2$ to yield *trans*-$Ni(PEt_3)_2(C_6F_5)F$:[11] this sketchy report was recently confirmed in a much more detailed study.[12] Related nickel and platinum complexes with chelating phosphines also undergo oxidative addition with hexafluorobenzene.[13] Another successful approach, but not involving simple oxidative addition, has been the photolysis of $Re(\eta^5\text{-}C_5Me_5)(CO)_3$ with C_6F_6: intramolecular C−H activation and intermolecular C−F activation combine with HF elimination to yield the product.[14]

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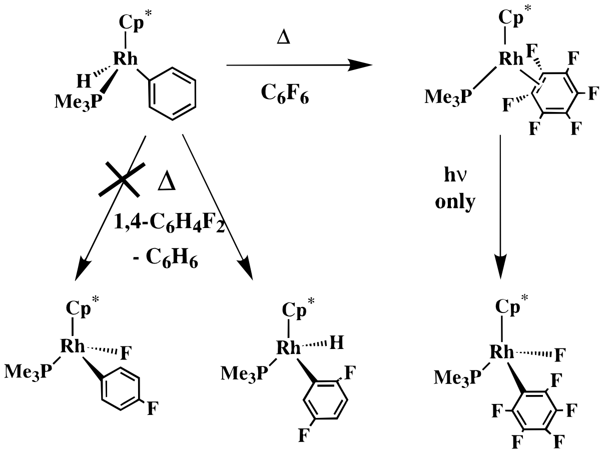
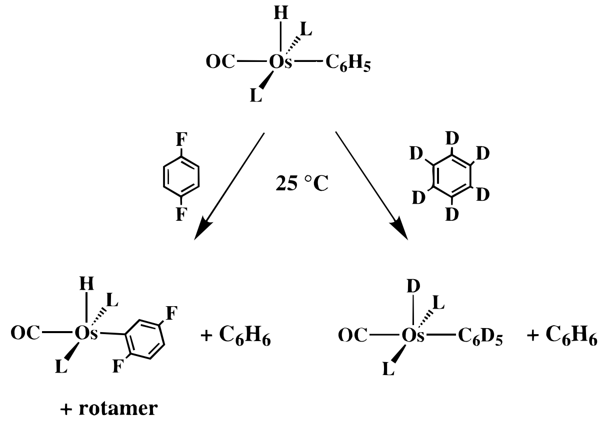
Scheme 1



Scheme 2



An attractive approach is to target reaction intermediates which have proved effective in cleaving C−H and H−H bonds. As the strength of C−H bonds increases, so do the bond energies of the corresponding metal−carbon bonds, leading to more stable products of C−H activation. Similarly the strength of C−F bonds might not prohibit C−F activation (CF_4 130 kcal·mol^{-1}, C_2F_6 127 kcal·mol^{-1}, C_6F_6 ca. 150 kcal·mol^{-1}).[15] One typical method of C−H bond activation involves photodissociation of H_2 from metal dihydrides to yield 16-electron d^8 fragments which react with hydrocarbons. Recently, it has emerged that some of these dihydride precursors react with hexafluorobenzene *without* photolysis to give metal pentafluorophenyl hydride complexes, either by electron transfer or base-catalyzed mechanisms: examples are $Ru(dmpe)_2H_2$ and $(\eta^5$-$C_5Me_5)Rh(PMe_3)(H)_2$.[2,16,17] These reactions certainly do not proceed by the simple oxidative addition mechanism characteristic of C−H activation. Aizenberg and Milstein have demonstrated that $Rh(PMe_3)_4H$ or $Rh(PMe_3)_3(C_6F_5)$ catalyze the conversion of C_6F_6 to C_6F_5H in the presence of H_2 and base.[18] It is not yet clear whether this reaction ever involves a direct oxidative addition product $[Rh](C_6F_5)F$ or resembles the stoichiometric reactions above.

Reductive elimination of alkane (or arene) from a suitable metal alkyl hydride (or aryl hydride) provides a thermal method of generating C−H activating intermediates. For instance, $(\eta^5$-$C_5Me_5)Rh(PMe_3)(R)H$ (R = alkyl, phenyl) acts as an effective source of $(\eta^5$-$C_5Me_5)Rh(PMe_3)$, which will then attack other hydrocarbons.[19] However, when these compounds are reacted thermally with hexafluorobenzene, the η^2-C_6F_6 adduct is formed but not the C−F activation product (Scheme 1).[20,21] Interaction with partially fluorinated arenes invariably yields carbon−*hydrogen* activation products.[22] The adducts $(\eta^5$-$C_5Me_5)Rh(PMe_3)(\eta^2$-$C_6F_6)$ (R = H, Me) can be converted to the oxidative addition product, $(\eta^5$-$C_5Me_5)Rh(PMe_3)(C_6F_5)F$, but only by photochemical means (Scheme 1).[20,23] We recently encountered a related example involving a 14-electron intermediate. The complex $OsH(Ph)(CO)L_2$ (L = P^tBu_2Me) undergoes exchange of intact C_6H_6 in the presence of added C_6D_6. However, reaction with partially fluorinated arenes $C_6F_nH_{6-n}$ (n = 1, 5) invariably yields aryl *hydride* complexes $Os(H)(C_6F_nH_{5-n})(CO)L_2$ (Scheme 2). There is no reaction between $OsH(Ph)(CO)L_2$ and hexafluorobenzene.[24] It is tempting to postulate that these failures to effect C−F activation can be explained by it being thermodynamically unfavorable and to point to the observation that C−F bonds are about 30 kcal·mol^{-1} stronger than the C−H bonds being formed in these arene exchange reactions. However, the validity of this argument is questionable since the metal−fluorine bond energies are unknown. Furthermore, there are no experimental investigations of the kinetics of intermolecular C−F activation and hence no knowledge of the kinetic factors which affect the reactivity.

Su and Chu reported one of the first theoretical studies of C−F activation recently.[25] They showed that oxidative addition of the C−F bond of CH_3−F to 3-coordinated 14-electron $M(X)(PH_3)_2$ (M = Rh, Ir; X = CH_3, H, Cl) is thermodynamically favorable. The reaction was most favorable and had the smallest activation barrier for $Ir(Cl)(PH_3)_2$. However, the C−F bond of CH_3F is exceptionally weak:[15] indeed, it is weaker than an aromatic C−H bond. Similar studies were carried out by Krogh-Jespersen et al.[26]

In this paper, we present the results of DFT (B3LYP) calculations of thermodynamic and kinetic aspects of the reactions of a partially fluorinated benzene (1,4-difluorobenzene) to give 16-electron Os^{II} and 18-electron Rh^{III} complexes, respectively. The purpose of our calculations is to understand why only the C−H activation product is observed. These two systems have been chosen since they lead to products in which the interaction between the metal and the fluoride in the final product could be very different since one metal center is unsaturated while the other is saturated. The results reported here reverse the conventional wisdom that C−H scission is thermodynamically preferred over C−F scission and show that the preference for C−H oxidative addition is of kinetic origin.

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Computational Details

All calculations were carried out with the Gaussian 94 package of programs[27] at the B3LYP computational level.[28] Effective core potentials were used for replacing the 60 innermost electrons of Os,[29] 28 innermost electrons of Rh [29] and the 10 innermost electrons of P.[30] Preliminary calculations showed that the addition of polarization functions on C and F was mandatory. Consequently, the basis set was of valence double-ζ quality[29−31] with polarization functions on all atoms[32,33] except the metal centers and the hydrogen atoms in the case of osmium complex.

All geometries presented were characterized as zero gradient stationary points through the analytical computation of gradients. Transition states were located with the use of approximate Hessians and synchronous transit-guided quasi-Newton methods.[34] No symmetry restrictions were introduced unless otherwise mentioned.

Results

Thermodynamic Preference for M−F vs M−H in 16-Electron Pentacoordinated Os^{II} Complexes. The complex $OsH(Ph)(CO)L_2$ ($L = P^tBu_2Me$) has been shown to exchange C_6H_6 in the presence of C_6D_6.[24] In the specific case of partially fluorinated benzene rings $C_6F_nH_{6-n}$ ($n = 1-5$), $OsH(C_6F_nH_{5-n})(CO)L_2$ complexes are formed exclusively. In addition, C_6F_6 does not react with $OsH(Ph)(CO)L_2$. These results indicate that the metal reacts preferentially with a C−H bond over a C−F bond. One reason for this selectivity could be that $OsH(C_6F_nH_{5-n})(CO)L_2$ is thermodynamically favored over $OsF(C_6F_{n-1}H_{6-n})(CO)L_2$. To check these ideas, we have undertaken the study of the thermodynamic energy pattern in the case of 1,4-difluorobenzene. This particular reagent (also used experimentally) has been chosen as the fluoroarene because the ring is significantly (i.e. doubly) fluorinated, because all hydrogens are equivalent, and because the hydrogens are sterically accessible (i.e. no major steric hindrance from F, as there would be in ($1,3,5-C_6H_3F_3$)) for any direction of approach by the metal reagent.

The nonfluorinated $OsH(Ph)(CO)(PH_3)_2$ complex has been optimized within C_s symmetry constraint and it takes the expected square-pyramidal structure with apical hydride and transoid basal CO and phenyl ring. The PH_3 groups were related by the mirror plane. The best conformation of the phenyl ring is calculated to be coplanar with the Os−H bond. The same overall structure is adopted by the fluoro derivatives, and the six possible isomers (within C_s constraint) with H (or F) and cis phenyl ligands are shown in Figure 1. The six isomers are labeled according to the site occupancy (apical or basal) of H or F and the conformational (cisoid or transoid) relationship of the ortho F substituent on the six-membered ring with respect to the hydride. All six isomers are calculated to be minima on the potential energy surface. In contrast to all expectations based on experimental precedent, *the most stable isomer (basal F) contains an Os−F bond and not an Os−H bond*. This absolute minimum has the aryl ligand trans to the empty site and the fluoride trans to CO. The next minimum (*apical H transoid*), which is significantly higher in energy (16.2 kcal·mol^{-1}), has the hydride at the apical site, the phenyl group trans to CO, and the ortho fluorine of the phenyl group in the vicinity of the metal empty site. Putting the ortho fluorine near the hydride (apical H, cisoid) is less favorable by 3.8 kcal·mol^{-1}. All other isomers are higher in energy for various combinations of reasons: lack of push−pull interaction (H trans to CO) and electronegative ligand (F) trans to the empty site.

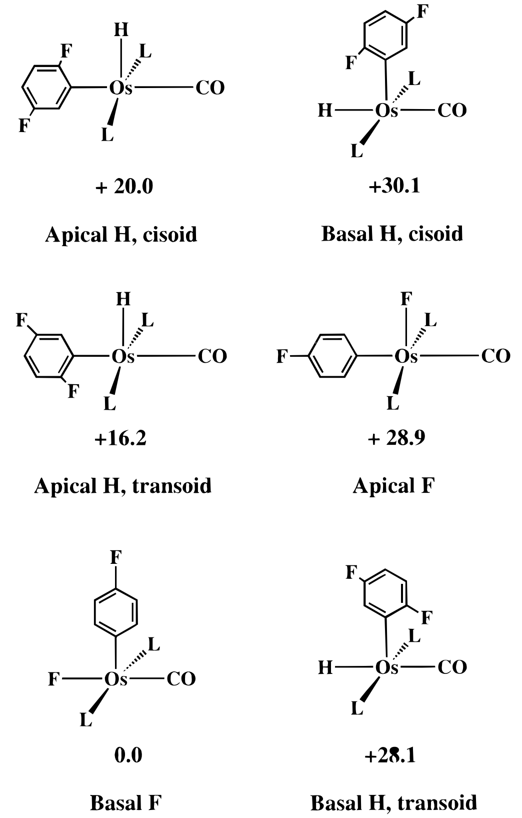

Figure 1. Schematic representation of the 6 isomers for $Os(H)(CO)(2,5-C_6F_2H_3)(PH_3)_2$ and $Os(F)(CO)(4-C_6FH_4)(PH_3)_2$. Relative B3LYP energies (kcal·mol^{-1}) of the optimized structures are given with respect to the most stable isomer basal F.

The two lower minima, *basal F* and *apical H transoid*, have no remarkable geometrical features (Figure 2). The angles between basal and apical ligands vary from 87.3° and 101.0° and are thus reasonably close to 90°, showing that these species are essentially pieces of an octahedron with one missing ligand. As expected from the lack of a trans ligand in *basal F*, the Os−C(phenyl) distance is shorter (2.077 Å) than in the *apical H transoid* (2.152 Å). The lesser σ donating ability and the larger π donation of F compared to that of the aryl ligand results in a shorter Os−C(O) bond length (1.867 Å) in *basal F* than in *apical H* (1.912 Å). The significant energy preference for *basal F* is due to a combination of factors. The aryl ligand is a reasonably good σ donor and, although not as good as hydride, it is a likely ligand for the apical site of the square pyramid. There is also a strong energy gain in having a ligand like F trans to CO since it is not a very strong σ donor and has thus a reasonably weak trans influence. Furthermore, the good π donor effect of F creates a good push−pull effect into CO.[35]

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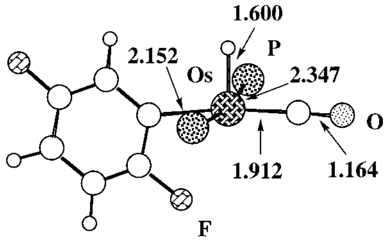
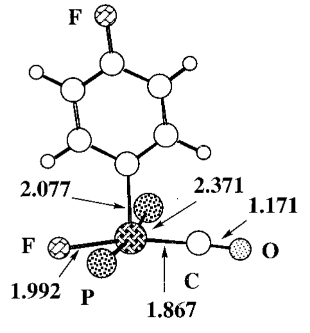


Apical H, transoid



Basal F

Figure 2. Optimized geometries (B3LYP) of the two most stable isomers *basal F* and *apical H transoid* (see Figure 1).

The nature of the preferred isomer could be influenced by the metal within group 8 since the chemistry of Os and Ru was sometimes found to be different.[36] The two most stable isomers, *basal F* and *apical H transoid*, were thus calculated with Ru in place of Os, giving essentially the same results with a change of only 0.3 kcal·mol^{-1} for the difference in energies between the two isomers.

The surprising, but yet firmly established, thermodynamic preference for the M−F containing isomer in these specific 16-electron five-coordinate species raises the question of the origin of this result. In a square pyramid, the two sites (basal and apical) are each preferred by ligands with specific electronic properties.[37] Thus the isomer with an apical Os−F bond is 29 kcal·mol^{-1} less stable than the isomer with the equatorial Os−F bond, and the general question of whether Os−F is "preferred" or "disfavored" with respect to Os−H has no meaning in this complex. Instead, Os−F is preferred at the basal site and Os−H is preferred at the apical site of the square-pyramidal complex; the coordination site strongly influences thermodynamics. *This is a case where the traditionally defined bond dissociation energy may be of little use for determining reaction thermodynamics.*

Thermodynamic Preference for Rh−F vs Rh−H in 18-Electron Rh^{III} Complexes. Analysis of the thermodynamic preference in these systems complements the study of the 16-electron complexes of ruthenium and osmium since (i) there are no possible "site preferences" in the products which are best viewed as slightly distorted octahedral complexes and (ii) the lack of unsaturation and of a CO ligand eliminates any push−pull interaction and means that the metal−F bond is exclusively a single bond.[35] In addition, one should keep in mind that 4-electron repulsion between the metal and halide lone pairs in a saturated complex could also weaken the metal−F bond.

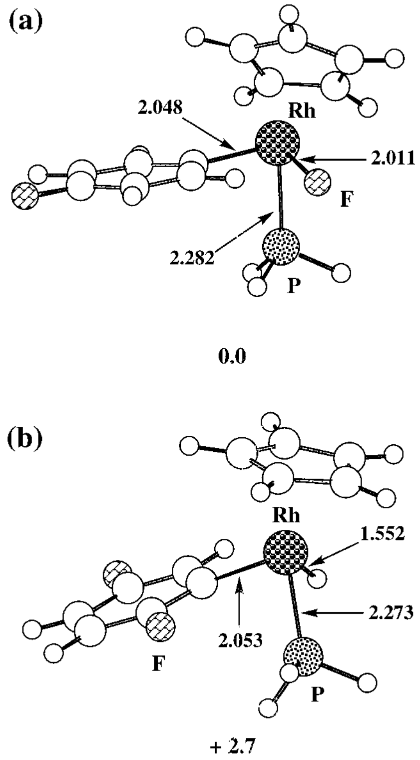


Figure 3. Optimized geometries (B3LYP) of the most stable isomers of (a) CpRh(F)(4-C_6FH_4)(PH_3) and (b) CpRh(2,5-$C_6F_2H_3$)(PH_3). Relative B3LYP energies (kcal·mol^{-1}) of the optimized structures are given with respect to the most stable isomer.

The thermodynamic pattern associated with the products of reaction of CpRh(PH_3) with 1,4-difluorobenzene to form either CpRh(H)(2,5-$C_6F_2H_3$)(PH_3) or CpRh(F)(4-C_6FH_5)(PH_3) was calculated. These three-legged piano-stool complexes have no opportunity for site preference and the only isomers for CpRh(H)(2,5-$C_6F_2H_3$)(PH_3) are associated with the cisoid or transoid conformational orientation of the ortho C−F bond with respect to the Rh−H bond. Full optimization of these two conformations of CpRh(H)(2,5-$C_6F_2H_3$)(PH_3) shows that their energies differ by only 1.8 kcal·mol^{-1}.

The optimized structures of CpRh(F)(4-C_6FH_5)(PH_3) and of CpRh(H)(2,5-$C_6F_2H_3$)(PH_3) in their most stable conformation are shown in Figure 3. The isomer containing the Rh−F bond is calculated to be the more stable although the difference in energy between the two isomers is only 2.7 kcal·mol^{-1}. The geometries of CpRh(F)(4-C_6FH_5)(PH_3) and CpRh(H)(2,5-$C_6F_2H_3$)(PH_3) are unremarkable and are in good agreement with the crystal structures of similar systems. Thus the Rh−C bond length is around 2.05 Å in both isomers, which is very close to the 2.07 Å distance found in Cp*Rh(PMe_3)(C_6F_5)Cl[20] and Cp*Rh(PMe_3)(C_6H_5)Br.[22] The lack of variation in the *calculated* Rh−C(phenyl) and Rh−P distance between the two isomers illustrates the lack of site preference and the lack of influence of the change of H for F on bond lengths for these two cis ligands. The two isomers are thus of comparable energies, and this result is unlikely to be significantly changed when Cp is replaced by Cp* or PH_3 by PMe_3.

This is an ideal case where the relative energies of CpRh(F)(4-C_6FH_5)(PH_3) and CpRh(H)(2,5-$C_6F_2H_3$)(PH_3), which differ most significantly by the interchange of one F and one H center between Rh and C, should reflect in great part the relative intrinsic metal−ligand bond energies. Since the energies of these two species are similar and since the binding energy of C−F exceeds that of C−H by about 30 kcal·mol^{-1}, it can be concluded that the bond dissociation energy of Rh−F exceeds that of Rh−H by about the same amount.

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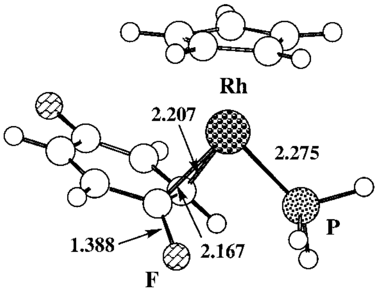

Figure 4. Optimized geometry (B3LYP) of CpRh(η^2-$C_6F_2H_4$)(PH_3). The coordinated CC bond is substituted by H and F.

The outcome for the calculations of the thermodynamic pattern associated with the activation of the C−H bond versus the C−F bond reveals the unexpected result that there is no thermodynamic preference for forming the metal−H over the metal−F products. There is therefore no thermodynamic preference for activating the C−H bond over the C−F bond. The lack of activation of the C−F bond thus must have a kinetic origin. We have therefore carried out a study of the relative activation energies of C−H and C−F in 1,4-difluorobenzene by the CpRh(PH_3) fragment.

Activation Energies for Oxidative Addition of C−H and C−F to the CpRh(PH$_3$) Fragment. The mechanism for oxidative addition of C−H and C−S bonds by CpRh(L) has been investigated by theoretical methods.[39] While theoretical studies of the activation of C−F bonds by a few other metal fragments have been carried out,[25,26] there is not, to our knowledge, a theoretical study of the activation of C−F and arenes with CpRh^{I}(L).

According to experimental studies, the reaction of the 16-electron fragment CpRhL with an arene starts with coordination of the metal to the arene to make an η^2 complex CpRh(L)(η^2-arene).[40] Since the σ bonds that are activated by the metal are those involving the carbons of the coordinated C═C double bond, we have chosen to study an η^2 complex that could lead to either C−H or C−F bond activation and then locate the transition states for activating each bond. We have thus optimized the structure of the (η^2-1,4-$C_6F_2H_4$) intermediate in which the C═C bond carries both F and H.[41] The geometry of this intermediate is shown in Figure 4. Its energy is *only* 5.6 kcal•mol^{-1} above the final fluoride product and 2.9 kcal•mol^{-1} above the most stable hydride complex. This close proximity in energy is in good agreement with the experimental observation that the CpRhL(η^2-arene) complex and CpRhL(H)(aryl) are close in energy.[40] For instance, equilibria between two such species are observed for arene = 1,4-$C_6H_4(CF_3)_2$.

The geometry of CpRh(PH_3)(η^2-$C_6F_2H_4$) shown in Figure 4 clearly illustrates the η^2-nature of the coordination of the benzene ring in which the metal is bonded to only one π bond of the six-membered ring. No crystal structure of η^2 coordinated partially fluorinated benzene is available, but the calculated structure can be advantageously compared to the η^2-C_6F_6 complex.[21] The calculated Rh−C bond distances are similar with that to the F-substituted carbon 0.04 Å shorter. The calculations reveal that the $C_6F_2H_4$ ring is folded along the coordinated C═C bond, as in the experimental structures of η^2-C_6F_6 or η^2-arene complexes. Thus the angle made by the arene and the Rh−CC planes is calculated to be 107° for η^2-$C_6F_2H_4$, compared to 114.3° for the experimental structure of Cp*Rh(PMe$_3$)($\eta^{2-}C_6F_6$).[21] The coordination of the metal to one of the CC bonds of the arene causes a diene pattern of the four noncoordinated carbons which are all out of bonding interaction from the metal (more than 3 Å from Rh). The Rh−C(F) and Rh−C(H) distances to coordinated $C_6F_2H_4$, calculated to be equal to 2.167 and 2.207 Å, respectively, are longer than the single Rh−C bond length (ca. 2.05 Å) in the final phenyl complex but well within the range of bonding interaction.

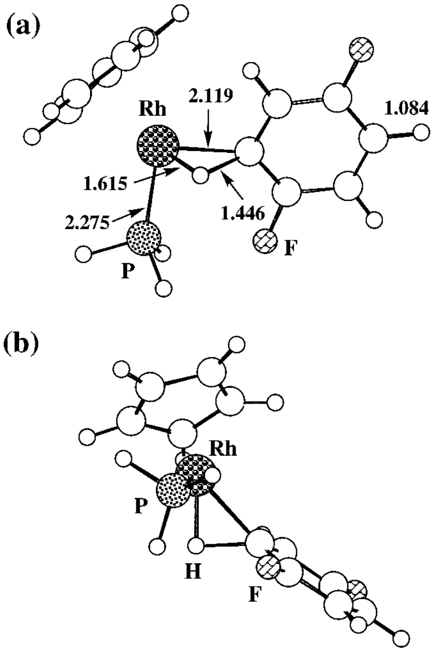

Figure 5. Two views of the optimized geometry (B3LYP) of the transition states for C−H cleavage by CpRh(η^2-$C_6F_2H_4$)(PH_3).

The transition states corresponding to the insertion into the C−H and C−F bonds are shown in Figures 5 and 6, respectively. The transition state leading to the C−H activation is calculated to be 9.4 kcal•mol^{-1} above the η^2-arene intermediate while the transition state leading to the C−F activation is 33.3 kcal•mol^{-1} above the same intermediate (Figure 7). This difference of 23.9 kcal•mol^{-1} between the two activation energies is immense and accounts for the kinetic selectivity of activation for the C−H bond. Interestingly this indicates that the microscopic reverse, the reductive elimination of aryl-F, would also be much more difficult than that of aryl-H. Thus the calculated activation energy for C−H reductive elimination from CpRh(H)(2,5-$C_6F_2H_3$)(PH_3) is only 12.3 kcal•mol^{-1} while the activation energy for concerted C−F reductive elimination from CpRh(F)(4-C_6FH_5)(PH_3) is very high (38.9 kcal•mol^{-1}). Thus while the C−F bond is very difficult to activate, it would also be very difficult to make a C−F bond through reductive elimination.

What is the origin of the large difference in activation energy in the geometries of the two transition states? While the metal is closest to C and H (or F) but not very far from the adjacent carbons of the six-membered ring, atomic motion at the transition state (TS) toward reactant or products (i.e. the

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[38] Ziegler, T.; Tschinke, V.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177. Siegbahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *J. Phys. Chem.* **1993**, *97*, 2564, Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1995**, *117*, 799.

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[40] Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685.

[41] We feel it is sufficient to consider only the first of the two possible η^2-arene isomers (coordination to C(H)═C(F) and C(H)═C(H)) since it shows a much lower activation energy for cleaving the C−H bond. Thus, regardless of how high or low the activation energy is for C−H activation from the second η^2-arene isomer, the greater ease of cleaving the C−H bond has already been demonstrated.

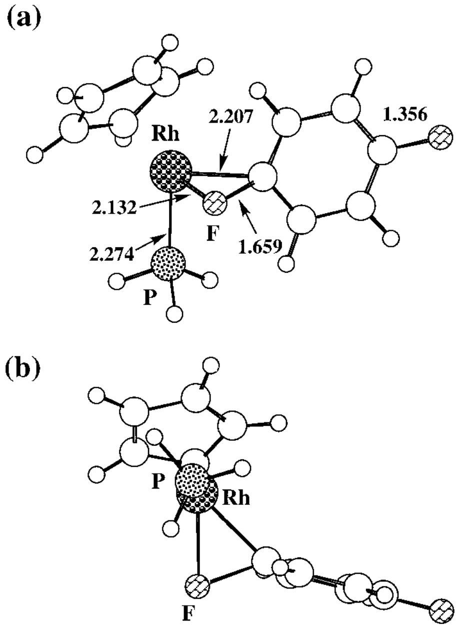


Figure 6. Two views of the optimized geometry (B3LYP) of the transition states for C−F cleavage by CpRh(η^2-$C_6F_2H_4$)(PH_3).

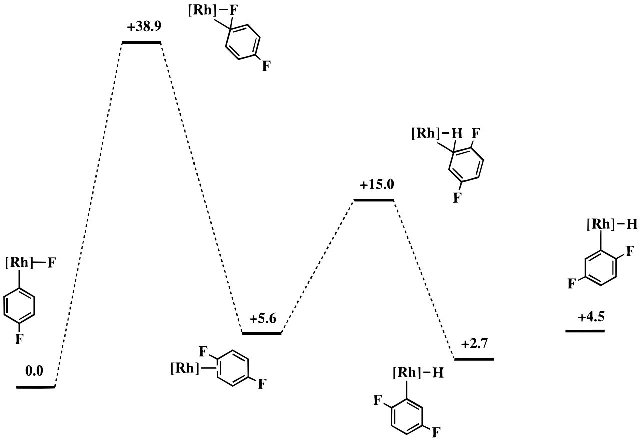
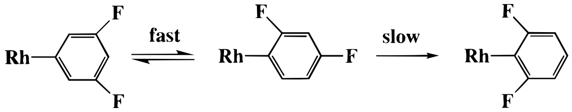


Figure 7. Energy diagram (kcal·mol^{-1}) for the oxidative addition to C−H and C−F bonds of (1,4-difluorobenzene). [Rh] = (η^5-C_5H_5)Rh-(PH_3). The (η^2-$C_6F_2H_2$) intermediate in which a C(H)=C(F) bond is coordinated to the metal is considered as a common reactant.

Chart 1



eigenvector corresponding to the negative eigenvalue at the TS) involves also mostly Rh, C, and H (or F). It is thus a three-center process in which the C−H or C−F bonds are cleaved while the Rh−C and Rh−H or Rh−F bonds are made. The extent to which these bonds are cleaved or made may be informative of the origin of the difference in the relative height of the activation barriers. In the TS for C−H cleavage, the C−H bond is significantly cleaved (1.446 Å in the TS vs 1.085 Å in the η^2-complex). Simultaneously, the Rh−H bond is significantly made (1.615 Å in the TS vs 1.552 Å in the product) as well as the Rh−C bond (2.119 Å in the TS vs 2.053 Å in the product). In the TS for C−F cleavage, the C−F bond is also significantly stretched (1.659 Å in the TS vs 1.388 in the η^2-complex), the F center already well bonded to the metal (2.132 Å vs 2.011 Å in the product) but the Rh−C bond not much formed (2.207 vs 2.048 Å in the product). While the TS is not purely a F →Rh σ complex, the Rh−C distance at the TS is longer than in the (η^2-$C_6H_4F_2$) intermediate. The orientation of the phenyl ring with respect to the metal fragment is also indicative of a Rh−C bond that is already well-made in the case of C−H activation and of a poorer bonding interaction in the case of C−F activation. As shown in Figure 5 (C−H activation), the phenyl ring is orientated to have the sp^2 hybrid of C(ipso) pointing toward Rh and not toward H any more. In contrast in Figure 6 (C−F activation) the corresponding hybrid is more toward F than toward the metal. Therefore, in the case of C−H activation, the geometry of the TS reveals that the C−H bond cleavage is compensated by synchronous formation of both Rh−H and Rh−C, which keeps the TS at low energy. In the case of C−F activation, bond cleavage is less compensated by formation of all new bonds. The Rh−F bond is well advanced, probably due to the availability of lone pairs on F for interacting with the metal, but the formation of the Rh−C bond is far from complete. This diminished degree of bonding within the transition state for C−F activation in comparison to C−H activation certainly lies at the origin of its high energy.

Discussion and Conclusion

The inertness of the C−F bond is not due to a thermodynamic factor but is entirely of kinetic origin. A similar suggestion recently has been made to interpret the selective cleavage of a C−C bond in an aryl-CF_3 group in preference to the C−F bond.[42] In fact, our study shows that the oxidative addition to the C−F bond would be either slightly (rhodium case) or even strongly (osmium case) favored. While the C−F bond is strong, the M−F bond formed, as shown by the two representative systems investigated here, is also probably strong for a large number of metal centers. This is not surprising in fact. A parallel has been made for trends in binding energies for M−X and H−X with binding energies for pure organic species.[43] It is thus only to be expected that a strong C−F bond may also mean a strong M−F bond.

The high activation energy of the concerted oxidative addition of a C−F bond cannot be understood solely in terms of the strong energy of the bond to be cleaved. If bond cleavage and bond formation were more synchronous as it is in C−H activation, formation of the new M−C and M−F bonds could have compensated the loss of bonding in the C−F bond. The geometry of the TS that has been located in the case of rhodium reveals that formation of the Rh−C bond is not sufficiently advanced while F is already close to the metal, perhaps because the lone pairs of F could be used by the metal to create the partial M···F bond in the TS while not reaching the electron density of the σ C−F bond. However, we could not locate any precoordinated adduct between the metal fragment and the C−F bond or even the F center. This could account for the fact that fluoroalkanes are used as noncoordinating solvents. Similarly, the possible repulsion between the metal center and F could explain the rather large difference in rate of rearrengement Cp*Rh(PMe3)($C_6H_3F_2$)H (Chart 1).[22] This can be interpreted in terms of a higher barrier for Rh^I "migrating past" a C−F than past a C−H bond. Another reason for the difficulty in cleaving the C−F bond may be related to the high polarity of the bond where the positively charged carbon is not well

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prepared to make a metal−carbon as shown by the increased Rh···C separation in the TS.

We believe that the high activation energy which we found for C−F bond activation in the case of Rh^I complexes would also apply to the Os complexes. In an approximate manner, if the transition states still differ by around 24 kcal·mol^{-1} in favor of C−H activation, the stronger thermodynamic preference for making the Os−F complex should not be able to invert the preference since there is only 16 kcal·mol^{-1} in favor of making the Os−F final complex.

If the concerted oxidative addition to a C−F bond is kinetically unfavorable, the reductive elimination of R−F is even more unfavorable because of microscopic-reversibility. However, the strong ionic character of the M−F bond may offer other routes to remove R and F.

In summary, this work shows that some of the late transition metal complexes which are best adapted for C−H activation turn out to be kinetically protected to C−F oxidative addition despite the thermodynamic preference for the (M)(F)(aryl) product. This rationalizes the general inertness of fluorocarbon solvents and the resistance of fully fluorinated arenes to C−F oxidative addition.

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