Mechanism of Carbon−Fluorine Bond Activation by $(C_5Me_5)Rh(PMe_3)H_2$

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Abstract: The complex $Cp^*Rh(PMe_3)H_2$ ($Cp^* = C_5Me_5$) reacts with C_6F_6, C_6F_5H, $C_{12}F_{10}$, or $C_{10}F_8$ in pyridine or 1:1 pyridine/benzene to give the C−F cleavage products $Cp^*Rh(PMe_3)(aryl^F)H$ in high yield. Kinetic studies reveal that the reaction has autocatalytic character, and fluoride ion is shown to be responsible for the catalysis. The anion $[Cp^*Rh(PMe_3)H]^-$ reacts rapidly with $C_{12}F_{10}$ or $C_{10}F_8$ to give the same C−F cleavage products as $Cp^*Rh(PMe_3)H_2$. A mechanism initiated by deprotonation of $Cp^*Rh(PMe_3)H_2$ followed by nucleophilic attack of the resulting anion on the polyfluoroaromatic with subsequent loss of fluoride is proposed. The fluoride ion continues the cycle by deprotonating $Cp^*Rh(PMe_3)H_2$.

Introduction

The activation of carbon−fluorine bonds by metal complexes has proven to be a chemical challenge. The dissociation energy of the C−F bond has been cited as high as 154 kcal mol^{-1} for C_6F_6[1a] (vs 110 kcal mol^{-1} for C_6H_6[1b]). Despite this, numerous examples of C−F bond activation by metal complexes have been cited.[2] Recently, Aizenberg and Milstein have reported homogenous catalytic C−F bond hydrogenation by a late transition metal complex.[3] Catalytic formation of perfluoroaromatic compounds by reductive defluorination of saturated perfluorocarbons by an early transition metal complex has also been achieved.[4]

Our group, in conjunction with Perutz and co-workers, has reported *photochemically* promoted C−F bond cleavage with $(C_5Me_5)Rh(PMe_3)(C_2H_4)$[5] and $(C_5H_5)Ir(PMe_3)H_2$.[5b] Irradiation of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ in C_6F_6 leads to initial formation of $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_6F_6)$, and continued photolysis leads to $(C_5Me_5)Rh(PMe_3)(C_6F_5)F$. Photolysis of $(C_5H_5)Ir(PMe_3)H_2$ in C_6F_6 generated $(C_5H_5)Ir(PMe_3)(C_6F_5)H$ and $(C_5H_5)Ir(PMe_3)(\eta^2\text{-}C_6F_6)$. Neither of these reactions proceeded thermally. Thermal C−F bond cleavage of C_6F_6 by electron rich late transition metal complexes is less common.[6−9] Recently, Perutz and co-workers carried out C−F activation on various polyfluoroaromatics at −78 °C with *cis*-$[Ru(dmpe)_2H_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[10] The reaction with C_6F_6 produced *trans*-$[Ru(dmpe)_2(C_6F_5)H]$ with loss of HF and formation of some $Ru(dmpe)_2(H)(HF_2)$.[11]

Despite the activity in metal-based C−F bond cleavage, little is known about the mechanisms of these reactions. In this paper, we show that $(C_5Me_5)Rh(PMe_3)H_2$ (**1**) is capable of thermal, selective C−F activation with a variety of polyfluoroaromatic compounds (eq 1). The relative reactivity of **1** with different fluoroaromatics is examined, and the high selectivity observed is discussed. In addition, evidence is presented that elucidates the mechanism of C−F cleavage in these polyfluorinated aromatic substrates.

$$\mathbf{1} + aryl^F\text{−}F \rightarrow Cp^*Rh(PMe_3)(aryl^F)H + HF \qquad (1)$$

Results and Discussion

Thermal Reactions of $Cp^*Rh(PMe_3)H_2$ with Polyfluorinated Arenes. The thermolysis of **1** in pyridine-d_5 with 12 equiv of C_6F_6 at 85 °C results in conversion to air-sensitive $(C_5Me_5)Rh(PMe_3)(C_6F_5)H$ (**2**) in good yield (81%, Scheme 1). The ^{1}H NMR spectrum exhibits a hydride resonance at δ −12.664 (ddd, $J_{P-H} = 47.6$, $J_{Rh-H} = 24.4$, $J_{F-H} = 12.5$ Hz, 1 H). The ^{19}F NMR spectrum shows five fluorine resonances of equal area, indicating that there is hindered rotation around the Rh−aryl bond. Two downfield multiplets at δ 95.6 and 90.5 are assigned as belonging to the two ortho fluorines. The ^{31}P-{^{1}H} NMR spectrum shows a doublet of triplets (δ 5.50, $J_{Rh-P} = 142.0$, $J_{F-P} = 10.0$ Hz), indicating coupling of phosphorus to both ortho fluorines.[12] The value of J_{Rh-P} of 142.0 Hz is typical for a $(C_5Me_5)Rh^{III}$ complex.[13] Chlorination of the product with $CHCl_3$ results in the formation of $(C_5Me_5)Rh(PMe_3)(C_6F_5)Cl$ (**2-Cl**), which was confirmed by comparison with an authentic sample.[5b] The ^{31}P{^{1}H} NMR spectrum of this complex shows a doublet of doublets, indicating coupling of phosphorus to only one ortho fluorine with $J_{P-F} = 22$ Hz due to the hindered rotation around the aryl−Rh bond. Compound **2** must similarly only couple to one of the two ortho fluorines at a time, but rotation around the aryl−Rh bond is

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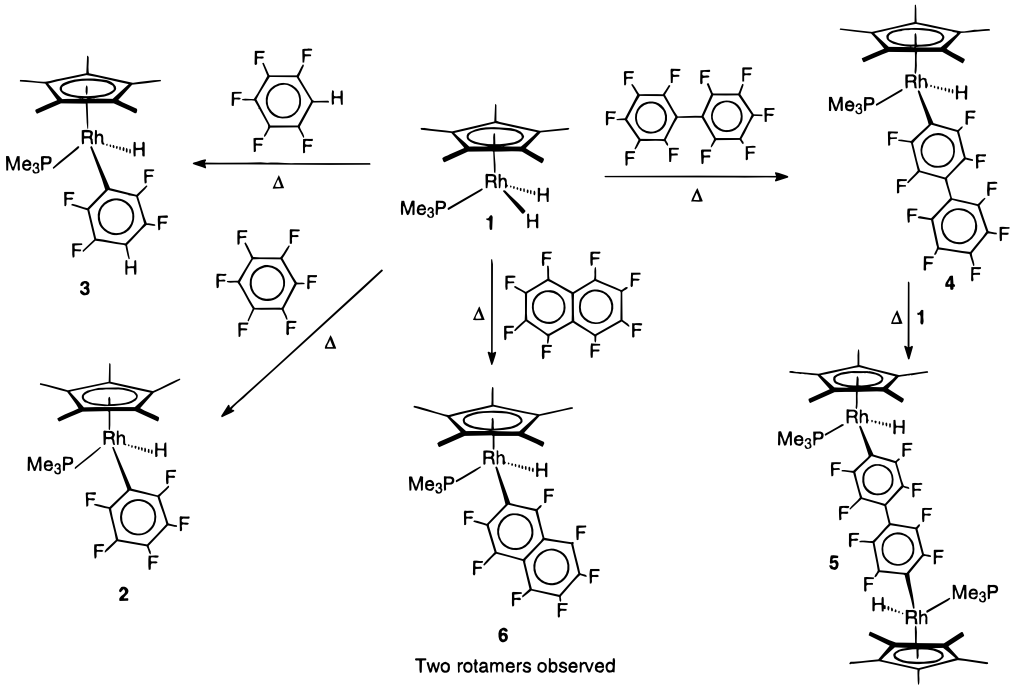
Scheme 1. Reactions of 1 with Polyfluorinated Arenes



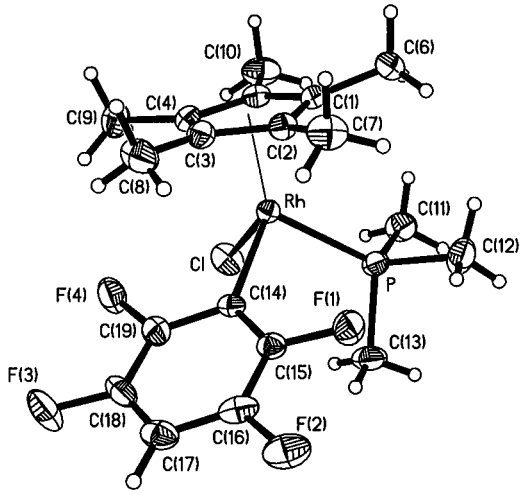


Figure 1. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(C_6F_4H)Cl$, **3-Cl**. Ellipsoids are shown at the 30% probability level.

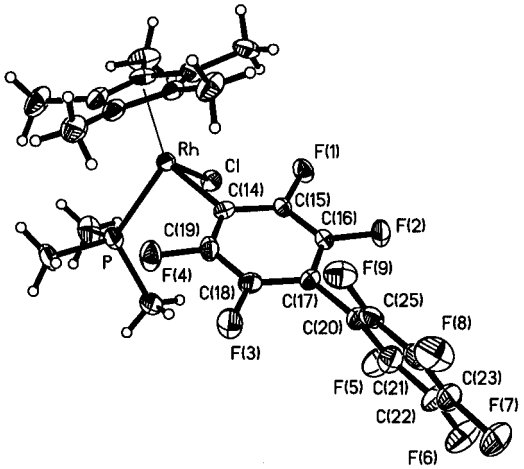


Figure 2. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)$(2-perfluorobiphenyl)-Cl, **4-Cl**. Ellipsoids are shown at the 30% probability level.

rapid enough with the smaller hydride ligand to result in a triplet in the ^{31}P NMR spectrum with an average J_{P-F} of 10 Hz.

The thermal reaction of **1** with C_6F_5H in pyridine produces a single C−F cleavage product in high yield, $(C_5Me_5)Rh(PMe_3)$-$(C_6F_4H)H$ (**3**). The ^1H NMR spectrum shows an aromatic resonance at δ 6.929 (tt, J_{H-F} = 9.6, 6.9 Hz). The triplet of triplet pattern is consistent with a hydrogen coupling to two *ortho* and two *meta* fluorines, indicating that C−F activation occurred exclusively *para* to the hydrogen in C_6F_5H. An X-ray crystal structure of the chloro derivative $(C_5Me_5)Rh(PMe_3)$-$(C_6F_4H)Cl$ (**3-Cl**) (Figure 1) confirmed the site of C−F activation. The ^{19}F NMR of **3** displays four types of fluorine, indicating hindered rotation around the Rh−aryl bond. As in **2**, the ^{31}P NMR spectrum shows a doublet of triplets for **3**, but a doublet of doublets for **3-Cl**. In contrast to the thermal reactions, irradiation of **1** in the presence of C_6F_5H leads only to the C−H activated product, $(C_5Me_5)Rh(PMe_3)(C_6F_5)H$.

Similarly, the thermolysis of **1** in pyridine-d_5 with 12 equiv of perfluorobiphenyl at 85 °C results in near quantitative conversion to $(C_5Me_5)Rh(PMe_3)$(4-perfluorobiphenyl)H (**4**) (Scheme 1). This product displayed ^1H and ^{31}P spectral features similar to those of **2** and **3**. The ^{19}F NMR spectrum showed nine distinct fluorine multiplets. Conversion to the chloro derivative permitted determination of the X-ray structure, indicating that selective C−F activation had occurred at the *para* position to give $(C_5Me_5)Rh(PMe_3)$(4-perfluorobiphenyl)Cl (**4-Cl**) (Figure 2). The aryl−aryl dihedral angle is 62.9°. The ^{19}F NMR spectrum again exhibits nine fluorine resonances, indicating not only hindered rotation about the Rh−aryl bond but also the aryl−aryl bond.

Thermolysis of **1** with 0.5 equiv of perfluorobiphenyl, or thermolysis of **1** with 1 equiv of **4**, gives 4,4′-bis[(C_5Me_5)Rh-(PMe_3)H]perfluorobiphenyl (**5**). While two diastereomers are possible, the ^{19}F NMR spectrum shows only six fluorine resonances rather than the expected eight. The two downfield ortho resonances integrate to two fluorines each while the four upfield resonances integrate to one fluorine each, suggesting that the two ortho fluorines of each diastereomer have coincident chemical shifts. The ^1H NMR spectrum shows only one hydride resonance at δ −12.470 (ddd, J_{P-H} = 44.0 Hz, J_{Rh-H} = 24.0 Hz, J_{F-H} = 16.0 Hz, 1 H) as well as resonances corresponding

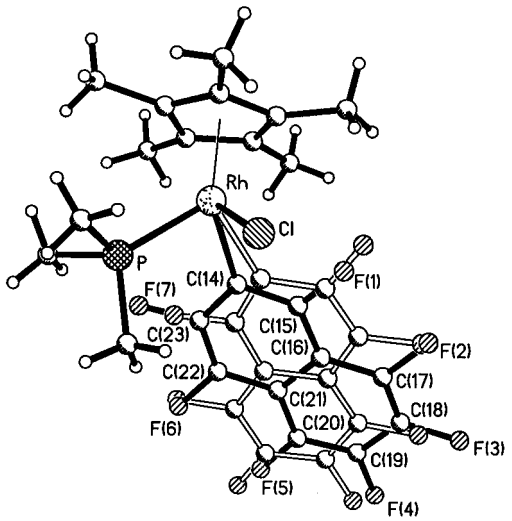


Figure 3. Ball and stick drawing showing both rotomers of $(C_5Me_5)Rh(PMe_3)(C_{10}F_7)Cl$, **6-Cl**.

to a single C_5Me_5 ring and a single PMe_3 group, disguising the fact that two diastereomers are present. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows the characteristic doublet of triplet pattern, indicating coupling of both ortho fluorines to phosphorus. Apparently, the environment around the two halves of the diastereomers is so similar that the ^1H and ^{31}P resonances are coincident. The *meta* ^{19}F resonances, however, experience significantly different environments in the two diastereomers and consequently are distinct. Treatment of **5** with $CHCl_3$ produced chloro derivatives of the two diastereomers. The ^{19}F NMR spectrum shows eight fluorine resonances; in this case the ortho fluorines for each diastereomer were resolved. Integration indicates that one diasteriomer dominates with a ratio of 3:2. The chloro derivative of **5** resisted attempts at forming single crystals, perhaps as it was a mixture of diastereomers.

The selective nature of C−F activation was probed further by reacting **1** with perfluoronaphthalene. ^1H NMR and ^{19}F NMR spectroscopy reveals the presence of two products in a ratio of approximately 1.25:1. The ^1H NMR spectrum consists of one C_5Me_5 group, as well as two overlapping hydrides each of which have a doublet of doublet of doublet splitting pattern. Two distinct trimethylphosphine groups could be assigned. The ^{31}P NMR spectrum shows two doublet of triplet splitting patterns, indicating that C−F activation occurred in the β position. The ^{19}F NMR spectrum shows 14 peaks, and integration allows for the assignment of seven peaks for each product. The NMR data are consistent with the formation of two rotomers of $(C_5Me_5)Rh(PMe_3)(\beta$-perfluoronaphthyl)H (**6**). X-ray crystallography of the chloro derivative **6-Cl** shows a disorder as a result of the presence of the two rotomers. The solid state structure confirms that C−F bond activation occurs only at the β position (Figure 3).

In all of the above reactions, a very broad resonance is observed at $\sim\delta$ 14.3 ppm, assigned as a mixture of pyridine·HF and HF_2^-.[14] Also observed are trace amounts of $[(C_5Me_5)Rh(PMe_3)_2H]^+$.[13] Presumably, the HF produced in the C−F activation reaction reacts with a small portion of the reactant and/or product to generate the byproducts and some fluoride ion, which is trapped as bifluoride. The reactions of **1** with the above fluoroaromatics were also examined in C_6D_6 solvent,

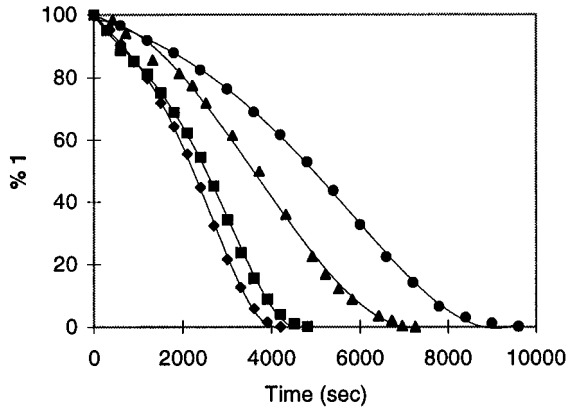


Figure 4. Plot of the disappearance of **1** upon reaction of **1** (0.035 M) with perfluorobiphenyl (◆, 0.66 M; ■, 0.52 M; ▲, 0.36 M; ●, 0.23 M) in a 1:1 pyridine:benzene solvent mixture at 92 °C.

where no added base was present. The same organometallic products, **2**−**6**, were obtained although in lower yields (50−70%). Also observed in these reactions were larger quantities of $[(C_5Me_5)Rh(PMe_3)_2H]^+$ (5−15%) and a trace of aryl^F−H. A small amount of black solid was also formed in these reactions. The higher extent of decomposition can be attributed to the lack of a base to complex the HF produced. Reactions produced slightly higher yields (by about 5%) when run in a 1:1 mixture of benzene/pyridine than in pure pyridine.

Rates of Reaction of 1 with Perfluoroarenes. Several qualitative observations were initially made concerning the reaction of **1** with the perfluoroarenes. First, different arenes react at different rates, spanning a range of a factor of about 25. Second, the rate is dependent on the concentration of perfluoroarene. Third, the reactions are much faster in pyridine than in benzene. And fourth, a plot of [**1**] vs time does not appear to be consistent with either a first- or second-order reaction. Typical plots are shown in Figure 4 for the reaction of **1** with different concentrations of perfluorobiphenyl. The reaction can be seen to *increase* in rate and then slow down only as **1** is nearly depleted. This type of kinetic behavior, while not rare, is not common, and is typical of autocatalytic or product-catalyzed reactions.[15] In this type of reaction, a product of the reaction is capable of reacting with the starting material, thereby increasing the observed rate as the reaction continues. The rate is also seen to increase with substrate concentration.

An obvious product that could be responsible for autocatalysis in the present system is the HF produced (eq 1). As HF is a weak acid in water, it could serve as a proton source in the reactions under study. Protonation of **1** could lead to loss of H_2 to generate an electrophilic metal cation that might be capable of cleaving the C−F bond of the polyfluoroaromatic. To test this possibility, a solution of **1** and perfluorobiphenyl in 1:1 pyridine/benzene was reacted with pyridinium chloride. Reaction occurred rapidly at 92 °C to produce $Cp^*Rh(PMe_3)Cl_2$ and H_2. No C−F activation product was observed. Use of pyridinium tetrafluoroborate as the acid was found to give C−F activation product **4** in ∼50% yield upon heating, but the rate of formation of product is slower than in the absence of added acid under comparable conditions. In addition, a substantial quantity of the decomposition product $[Cp^*Rh(PMe_3)_2H]^+$ is observed. On the basis of these observations, it seems unlikely that protons catalyze the reaction.

(14) An authentic sample of pyridine·HF (Aldrich) in pyridine-d_5 displays a broad singlet at $\sim\delta$ 11.4. Tetrabutylammonium bifluoride, $Bu4N^+HF_2^-$, in pyridine-d_5 displays a sharp triplet (J_{HF} = 120.5 Hz) at δ 18.44. A mixture of pyridine·HF and fluoride ion shows a broad resonance at $\sim\delta$ 14, which moves with the relative amounts of the two components.

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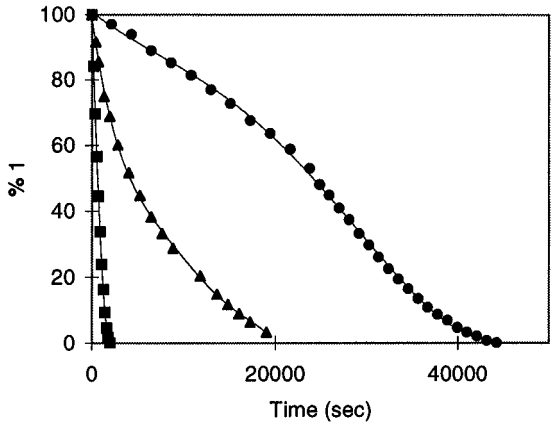

Figure 5. Plot of the disappearance of **1** (0.035 M) upon reaction with perfluorobiphenyl (0.36 M) in a 1:1 pyridine:benzene ratio at 69 °C with 0.21 M fluoride (■), with 0.0077 M fluoride (▲), and without fluoride (●).

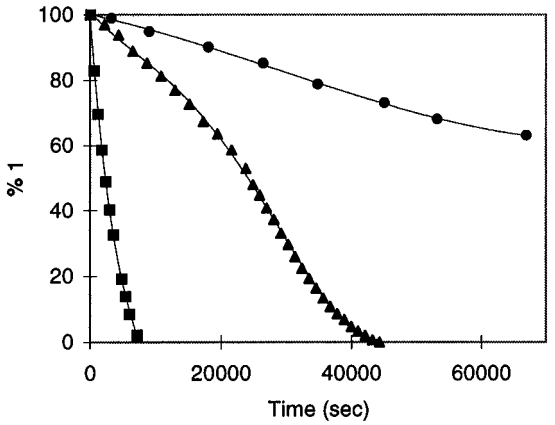

Figure 6. Plot of the disappearance of **1** (0.035 M) upon reaction with perfluorobiphenyl (0.36 M) at 69 °C in 10% pyridine/benzene (●), in 50% pyridine/benzene (▲), and neat pyridine (■).

Another possibility is that the fluoride ion produced catalyzes the reaction. Addition of *n*-Bu_4NF to a mixture of **1** and perfluorobiphenyl in 1:1 pyridine/benzene resulted in rapid reaction at 69 °C to give **4** in high yield. In the absence of added fluoride ion at this temperature the reaction is much slower (Figure 5). Not only does fluoride ion greatly accelerate this reaction, but the behavior of the concentration vs time plots now appears approximately exponential. With fluoride present the reaction now proceeds at moderate rates even at room temperature. The half-life for reaction in pyridine solvent with 0.21 M F^- is ∼14 h, whereas without fluoride the half-life is 96 h. In benzene at room temperature (without added fluoride), only traces of product are seen over this time period.

Reaction of **1** with perfluorobiphenyl in 1:1 pyridine/benzene containing ∼1 equiv of pyridine·HF (but no additional fluoride) did not result in an increase in the rate of reaction. The yield of **4** is only about 50%, and about 25% yield of [Cp*Rh-(PMe_3)$_2$H]$^+$ is observed.

Reaction of the Cp compound CpRh(PMe_3)H_2 with perfluorobiphenyl in pyridine was also examined. The reaction proceeds cleanly at room temperature to give CpRh(PMe_3)-(perfluorobiphenyl)H in good yield. This reaction is about twice as fast as that of **1** under the same conditions (pyridine solvent, no added fluoride).

For comparison, the reaction of **1** with 1 equiv of C_6F_5Cl or C_6F_5Br was examined. In both cases, a rapid reaction ensues at room temperature and (C_5Me_5)Rh(PMe_3)(H)(X) (X = Cl or Br) and C_6F_5H are obtained as the major products. Only trace amounts of (C_5Me_5)Rh(PMe_3)(C_6F_5)H are observed. The formation of these types of products is typical of other metal hydrides reacting with alkyl and aryl halides (halide ≠ F), which are believed to react by a free radical chain mechanism.[16]

Mechanism of C−F Cleavage. Fluoride ion has a clear influence on the rate of reaction of **1** with polyfluoroaromatics. Pyridine as solvent is also found to accelerate the rate of these reactions compared to benzene solvent. Since both pyridine and fluoride ion can act as bases, it seems reasonable to postulate that deprotonation of **1** might be responsible for the reaction with the fluoroaromatic.[17] The resulting metal anion could undergo nucleophilic aromatic substitution to give the products **2**−**6** and (re)generate a fluoride ion. With pyridine as the initial base, the fluoride ion combines with the pyridinium ion to give pyridine·HF, which is largely undissociated. With fluoride as the initial base, the fluoride ion reacts with HF to give bifluoride ion (Scheme 2). Metal carbonyl anions are well-known to undergo nucleophilic aromatic substitutions on polyfluoroaromatics to give metal−aryl complexes, and substitution occurs with the regiochemistry observed in the above reactions.[2,18,19]

Scheme 2

$$\underset{\mathbf{1}}{Cp^*Rh(PMe_3)H_2} + base \underset{}{\overset{fast}{\rightleftharpoons}} [Cp^*Rh(PMe_3)H]^{\ominus} + baseH^{\oplus}$$

(Base = $F^{\ominus}$, pyridine)

$$[Cp^*Rh(PMe_3)H]^{\ominus} + aryl^F\text{-}F \xrightarrow{slow} Cp^*Rh(PMe_3)(aryl^F)H + F^{\ominus}$$

$$F^{\ominus} + baseH^{\oplus} \overset{fast}{\rightleftharpoons} base{\cdot}HF$$

Since the deprotonated anion of **1** is postulated to be the nucleophile that displaces fluoride ion, independent examinations of the reaction of the anion [Cp*Rh(PMe_3)H]$^-$, (**7**), with perfluorobiphenyl and perfluoronaphthylene were examined. Anion **7** was prepared by deprotonation of **1** with *n*-BuLi at −78 °C.[20] Upon treatment of a pyridine-d_5 solution of perfluorobiphenyl with **7**, an instantaneous reaction occurs at room temperature to produce **4** (and also some **5**). Similarly, reaction of **7** with a pyridine solution of perfluoronaphthalene immediately produces **6** (same 1:1.25 ratio of both rotomers).

The effect of pyridine concentration on the rate of reaction also supports a deprotonation mechanism. Figure 6 shows how the rate of reaction increases upon changing the solvent from 10% pyridine in benzene to 50% pyridine in benzene to neat pyridine. The rate increase is dramatic, and is attributable to the shift in the deprotonation equilibrium (first step in Scheme 2). This shift is due in part to the increase in pyridine

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(17) Fluoride is known to be an excellent base in nonprotic solvents, some 12 orders of magnitude better in DMSO than in water. See: Bordwell, F. G. *Acc. Chem. Res*. **1988**, *21*, 456−463.

(18) (a) Smart, B. E. In *Chemistry of Organic Fluorine Compounds II*; Hudlicky, M., Rappoport, Z., Eds.; ACS Monograph 187; American Chemical Society: Washington, DC, 1995; pp 996−997. (b) Rodionov, P. P.; Furin, G. G. *J. Fluorine Chem*. **1990**, *47*, 361−434. (c) Rodionov, P. P.; Osina, O. I.; Platonov, V. E.; Yakobson, G. G. *Bull. Soc. Chim. Fr*. **1986**, *6*, 986−992.

(19) An alternative mechanism for the fluoride ion displacement from the fluorocarbon by the metal anion would involve electron transfer from [Cp*Rh(PMe_3)H$^-$] to the arene generating fluoride ion and an aryl^F radical. This radical could then recombine with the metal radical to generate the observed metal product. Any radicals formed, however, would have to recombine within the radical cage (*vide infra*).

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concentration and in part to the increase in solvent polarity, the latter effect tending to favor the formation of ions.

The enhanced reactivity of the C_5H_5 compound compared to **1** can also be accommodated by an initial deprotonation of the dihydride. One expects the less electron-donating Cp ligand to make $CpRh(PMe_3)H_2$ more acidic, and consequently a higher steady state concentration of anion should be present to react with the fluorocarbon. In addition, the Cp compound will produce a less sterically hindered nucleophile than **1**.

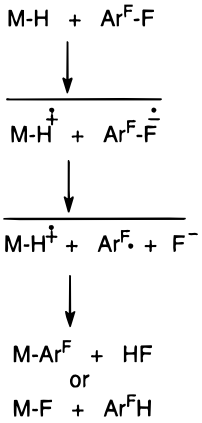
Free radical intermediates can be virtually ruled out in these reactions. When the thermal reaction of **1** with C_6F_6 was carried out in the presence of the radical trap 9,10-dihydroanthracene (10 equiv) in benzene, the rate of reaction and yield of **2** were not affected. ^{1}H NMR spectroscopy and GC-MS showed only a trace of anthracene formation. A similar reaction between **1** and C_6F_6 was performed in neat isopropylbenzene as trap and the reaction monitored by ^{31}P NMR spectroscopy. Again, neither the rate of reaction nor yield of **2** was affected. ^{1}H NMR and GC-MS showed only a trace amount of C_6F_5H in the isopropylbenzene reaction. These results strongly indicate free radicals are not involved.

Earlier C−H and C−C bond cleavage studies involving **1** occur by way of formation of the unsaturated intermediate [Cp*Rh(PMe_3)]. This intermediate can be ruled out in the present C−F bond activations, since reaction with C_6F_5H results in C−F activation rather than C−H activation. Indeed, photoinduced elimination of dihydrogen from **1** or thermolysis of Cp*Rh(PMe_3)PhH in the presence of C_6F_5H produces exclusively Cp*Rh(PMe_3)(C_6F_5)H.[21]

As mentioned earlier, these reactions appear to follow autocatalytic or product-catalyzed behavior. That is, the rate of reaction is observed to increase as the reaction proceeds. The stoichiometric product of the reaction is not fluoride ion, but HF as indicated in eq 1, so that this increase in rate is not expected. As the reaction proceeds, however, some **1** undergoes decomposition by reaction with HF, thereby generating surplus F^-. This additional fluoride can act to increase the rate of reaction by increasing the quantity of strong base, making the reaction appear autocatalytic. In pure benzene solvent, this decomposition is more significant. Also, the reaction could be initiated by adventitious base in the solvent or in the glass wall of the container.[22] Again, once the reaction starts, fluoride ion would be produced which carries the cycle. With added fluoride, decomposition produces little additional fluoride so that the reaction now appears approximately first order in **1**. A detailed kinetic analysis of this system has not proven possible due to the variable small quantity of decomposition that produces fluoride ion.

Comparison with Other C−F Cleavage Reactions. Recently proposed mechanisms for polyfluoroaromatic C−F bond activation by $Rh(PMe_3)_4H$,[3b] $PtH_2(PCy_3)_2$,[23] and $Ru(dmpe)_2H_2$[10] all involve electron transfer from the metal to the fluorocarbon in the first step. This mechanism involves initial outer-sphere electron transfer to form a 17-electron metal cation radical and a fluorinated aromatic anion radical (Scheme 3). Fluoride loss

Scheme 3



M = $Rh(PMe_3)_4$, $Ru(dmpe)_2H$, $Pt(PCy_3)_2H$

occurs readily,[24] and the fluoride ion then removes a proton from the acidic[25] metal cation. Finally, recombination of the resulting radical pair generates the product.

This type of mechanism is inconsistent with the observations made in the reactions of **1** with polyfluoroaromatics. First, free radical intermediates are not involved. Second, the acceleration by fluoride ion is unaccounted for. Third, electrochemical measurements on the oxidation potential of **1** and the reduction potential of the polyfluoroaromatics indicate that the electron transfer is uphill by in excess of 2 V. We have redetermined the polyfluoroarene reduction potentials measured by Pez,[26] and have obtained similar values for the irreversible reductions (−2.4 to −3.0 V vs Fc/Fc^+). While the true reduction potentials might be more positive than this, it is very unlikely that they are off by more than a few hundreds of millivolt. The oxidation of **1** is also irreversible by CV (E_{PA} = −0.336 V), but the true reversible potential is not likely to be far from this value either. The above redox values result in an uphill electron transfer on the order of 2.0 to 2.5 V, which would place a minimum barrier to the reaction of ∼45 kcal/mol. This barrier corresponds to a rate that is over a *billion billion* times slower than the observed rate of reaction of **1** with the slowest substrate, C_6F_5H. Consequently, electron transfer from **1** to the perfluoroarene is extremely unlikely to be involved.

The elucidation of an anionic nucleophilic mechanism in the reaction of **1** with polyfluoroaromatics suggests that a similar mechanism might be considered as an alternative to the electron transfer mechanisms in other similar systems in the literature. This possibility seems even more reasonable in light of the high mismatch of redox potentials between the electron transfer partners (metal complex vs polyfluoroaromatic). In support of this concept, the system reported by Milstein[3b] is considerably more efficient when a base is present (NEt_3, K_2CO_3). Regioselectivities are identical with that observed in the present studies.[27] Systems that have postulated electron transfer from the metal to the polyfluoroaromatic include $Rh(PMe_3)_4H$,[3b] $Ru(dmpe)_2H_2$,[10] $MeIr(PEt_3)_3$ (which cyclometallates before electron transfer),[7] and $PtH_2(PCy_3)_2$.[23] We note that Hughes has recently

(21) This observation appears to also rule out any other oxidative addition pathway involving a 16-electron intermediate, which would be expected to similarly prefer C−H activation. Other possible 16-electron intermediates could arise from $\eta^5 \rightarrow \eta^3$ ring slippage or hydride ligand migration to the C_5Me_5 ring to give an η^4-C_5Me_5H ligand. See: Jones, W. D.; Kuykendall, V. L.; Selmeczy, A. D. *Organometallics* **1991**, *10*, 1577−1586.

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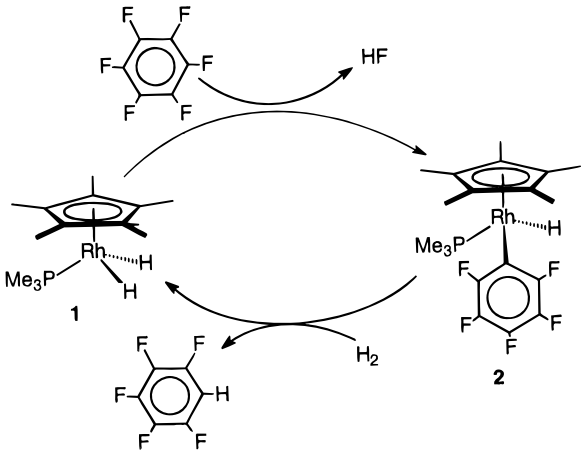
(27) A referee commented that it would be difficult for fluoride ion to deprotonate a species such as $HRh(PMe_3)_4$ or $Ru(dmpe)H_2$. Fluoride ion is an excellent base, however, and the acidities of these transition metal hydrides have not been determined.[17]

Scheme 4



suggested an intramolecular nucleophilic attack on a perfluoroaryl ligand by a deprotonated Cp* methyl group.[22]

Catalytic Reactions. Finally, the reaction of (C_5Me_5)Rh(PMe_3)(C_6F_5)H with excess C_6F_6 was carried out under hydrogen to see if the reaction could be made catalytic by cleavage of the Rh−Aryl^F bond with H_2. A potential catalytic scheme is outlined above (Scheme 4). A solution of **1** and C_6F_6 in C_6D_6 was heated at 135 °C for 25 days under 1 atm of H_2. ^{1}H NMR spectroscopy of the reaction mixture revealed the presence of 1.4 equiv of C_6F_5H based on the starting metal complex. No (C_5Me_5)Rh(PMe_3)(C_6F_5)H or (C_5Me_5)Rh(PMe_3)H_2 was seen. The same reaction performed without H_2 resulted in the formation of 1 equiv of C_6F_5H. Reactions performed under higher pressures of H_2 or in 1:1 pyridine/benzene also showed little evidence for catalysis.

Conclusions

The organometallic complex (C_5Me_5)Rh(PMe_3)H_2 is capable of thermally cleaving C−F bonds of a variety of fluoroaromatics. The cleavage is selective and the rate of C−F activation increases as the number of fluorines increases. The C_5H_5 analog was shown to be able to activate the C−F bond of $C_{12}F_{10}$ more rapidly than the C_5Me_5 species. A mechanism involving nucleophilic aromatic substitution was indicated, with pyridine or fluoride as the base that produces a metal anion that can attack the polyfluoroaromatic compound. This system has the necessary balance between Brönsted acidity of the metal hydride and nucleophilicity of the conjugate base for the reaction to succeed. Our studies suggest that catalytic C−F bond cleavage by a transition metal hydride might be possible in basic solvents containing fluoride ion as a promoter.

Experimental Section

General Considerations. All manipulations were performed under an N_2 atmosphere, either on a high-vacuum line with modified Schlenk techniques or in a Vacuum Atmospheres Corporation Glovebox. Tetrahydrofuran, benzene, and toluene were distilled from dark purple solutions of benzophenone ketyl. Alkane solvents were made olefin-free by stirring over H_2SO_4, washing with aqueous $KMnO_4$ and water, and distilling from dark purple solutions of tetraglyme/benzophenone ketyl. Benzene-d_6, and pyridine-d_5 were purchased from Cambridge Isotope Lab., and distilled under vacuum from dark purple solutions of benzophenone ketyl, and stored in ampules with Teflon sealed vacuum line adapters. The preparations of $[PPN]^+[BH_4]$,[28] (C_5Me_5)Rh(PMe_3)H_2,[29] Li[(C_5Me_5)Rh(PMe_3)H],[20] (C_5H_5)Rh(PMe_3)H_2,[30] pyridinium tetraphenylborate,[31] and (C_5Me_5)Rh(PMe_3)(C_6F_5)Cl[5b] have been previously reported. Isopropyl benzene, chloropentafluorobenzene, bromopentafluorobenzene, 9,10-dihydroanthracene, pyridinium poly(hydrogen fluoride) (~30% pyridine−70% hydrogen fluoride), tetrabutylammonium fluoride hydrate (TBAF·3H_2O), tetra-*n*-butylammonium hexafluorophosphate, and the fluorinated aromatic compounds were purchased from Aldrich Chemical Co. The liquids were stirred over sieves, freeze−pump−thawed three times, and vacuum distilled prior to use. Tetra-*n*-butylammonium hexafluorophosphate was dried at 120 °C under high vacuum for 48 h.

All ^{1}H NMR and ^{31}P NMR spectra were recorded on a Bruker AMX400 spectrometer. All ^{19}F NMR spectra were recorded on a Varian 500 spectrometer. All ^{1}H chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced by using chemical shifts of residual solvent resonances (C_6H_6 δ 7.15, pyridine δ 7.55). ^{19}F NMR spectra were referenced to external $C_6H_5CF_3$ (δ 0.00 with downfield chemical shifts taken to be positive). ^{31}P NMR spectra were referenced to external 30% H_3PO_4 (δ 0.0). GC-MS was conducted on a 5890 Series II gas chromatograph fitted with an HP 5970 Series mass selective detector. Photolysis was done with an Oriel Corp. UV Lamp Model 6137. Analyses were obtained from Desert Analytics. An Enraf-Nonius CAD4 diffractometer and a Siemens SMART system with a CCD area detector were used for X-ray structure determination.

Thermolysis of (C_5Me_5)Rh(PMe_3)H_2 (1) with Various Fluorinated Aromatic Compounds. All reactions were carried out by using the following general procedure. A sample of (C_5Me_5)Rh(PMe_3)H_2 (8.5 mg, 0.027 mmol) was dissolved in 0.60 mL of pyridine-d_5 or benzene-d_6 in a resealable NMR tube along with 12 equiv of the fluoroaromatic compound. Dioxane (or dimethoxyethane) was added as an internal standard. The NMR tube was heated in an oil bath at 85 °C, and the reaction was followed by ^{1}H NMR spectroscopy until the starting material was depleted. NMR spectroscopic data, yields (NMR yields based on an internal standard in pyridine-d_5), and approximate half-lives ($t_{1/2}$) are summarized below. NMR spectroscopic data in C_6D_6 are given in the Supporting Information.

NMR Spectroscopic Data and Yields for (C_5Me_5)Rh(PMe_3)(aryl^F)H Complexes. (C_5Me_5)Rh(PMe_3)(C_6F_5)H. ^{1}H NMR (pyridine-d_5): δ 1.777 (d, J_{Rh-H} = 2.0 Hz, 15 H), 1.101 (d, J_{P-H} = 10.0 Hz, 9 H), −12.664 (ddd, J_{P-H} = 47.6 Hz, J_{Rh-H} = 24.4, J_{F-H} = 12.5 Hz, 1 H). ^{31}P{^{1}H} NMR (pyridine-d_5): δ 5.50 (dt, J_{Rh-P} = 142.0 Hz, J_{F-P} = 10.0 Hz). ^{19}F NMR (C_6D_6): δ 95.6 (m, 1 F_{ortho}), 90.5 (m, 1 F_{ortho}), 38.6 (t, 1 F_{para}), 37.7 (m, 1 F_{meta}), 36.6 (m, 1 F_{meta}). Yield = 81%. $t_{1/2}$ (85 °C) ≅ 12 h.

(C_5Me_5)Rh(PMe_3)(4-perfluorobiphenyl)H. ^{1}H NMR (pyridine-d_5): δ 1.811 (d, J_{Rh-H} = 2.4 Hz, 15 H), 1.143 (d, J_{P-H} = 10.1 Hz, 9 H), −12.483 (ddd, J_{P-H} = 48.9 Hz, J_{Rh-H} = 24.1 Hz, J_{F-H} = 10.8 Hz, 1 H). ^{31}P{^{1}H} NMR (pyridine-d_5): δ 5.39 (dt, J_{Rh-P} = 141.7 Hz, J_{F-P} = 9.7 Hz). ^{19}F NMR (C_6D_6): δ 95.8 (m, 1 F_{ortho}), 90.1 (m, 1 F_{ortho}), 61.5 (m, 1 F_{meta}), 61.1 (m, 1 F_{meta}), 59.5 (m, 1$F_{ortho'}$), 57.9 (m, 1 $F_{ortho'}$), 47.5 (m, 1 F_{para}), 38.4−38.2 (overlapping m, 2 $F_{meta'}$). Yield = 87%. $t_{1/2}$ < 30 min.

(C_5Me_5)Rh(PMe_3)(2,3,5,6-C_6HF_4)H. ^{1}H NMR (pyridine-d_5): δ 6.929 (tt, J_{H-F} = 9.6, 6.9 Hz), δ 1.788 (d, J_{Rh-H} = 2.0 Hz, 15 H), 1.103 (dd, J_{P-H} = 10.0 Hz, J_{Rh-H} = 1.2 Hz, 9 H), −12.634 (ddd, J_{P-H} = 49.0 Hz, J_{Rh-H} = 25.4 Hz, J_{F-H} = 12.9 Hz, 1 H). ^{31}P{^{1}H} NMR (pyridine-d_5): δ 5.03 (dt, J_{Rh-P} = 144.7 Hz, J_{F-P} = 10.2 Hz). ^{19}F NMR (C_6D_6): δ 93.4 (m, 1 F_{ortho}), 88.2 (m, 1 F_{ortho}), 59.9 (t, 1 F_{meta}), 58.4(m, 1 F_{meta}). Yield = 85%. $t_{1/2}$ ≅ 20 h.

(C_5Me_5)Rh(PMe_3)(2-perfluoronaphthalene)H. ^{19}F NMR indicated that rotomer 1 dominated by a ratio of 1.25:1. Rotomer 1: ^{1}H NMR (pyridine-d_5): δ 1.829 (overlaps with Rotomer 2, 15 H), 1.180 (d, J_{P-H} = 9.7 Hz, 9 H), −12.627 (ddd, J_{P-H} = 50.2 Hz, J_{Rh-H} = 26.1 Hz, J_{F-H} = 12.6 Hz, 1 H). ^{31}P{^{1}H} NMR (pyridine-d_5): δ 5.51 (dt, J_{Rh-P} = 141.8 Hz, J_{F-P} = 10.9 Hz). ^{19}F NMR (C_6D_6): 110.7 (m, 1 F), 103.6

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Table 1. Summary of Crystallographic Data for **3-Cl**, **4-Cl**, and **6-Cl**

crystal parameters	**3-Cl**	**4-Cl**	**6-Cl**
chemical formula	$C_{19}H_{25}ClF_4PRh$	$C_{25}H_{24}ClF_9PRh$	$C_{23}H_{24}ClF_7PRh{\cdot}H_2O$
formula wt	498.73	664.78	620.77
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Z	8	4	4
a, Å	14.153(5)	9.139(7)	9.7329(10)
b, Å	9.585(8)	8.082(2)	8.3407(9)
c, Å	30.45(2)	35.903(27)	31.741(3)
β, deg	96.18(4)	93.95(6)	98.026(7)
vol, Å^3	4107(4)	2645.6(2.4)	2551.4(5)
ρ_{calc}, g cm^{-3}	1.61	1.67	1.62
no. of data collected	4011	5374	9459
no. of unique data	3838	5038	3330
no. of params varied	235	334	468
$R_1(F_o)$, $wR_2(F_o^2)$, ($I > 2\sigma(I)$)			0.0725, 0.1901
$R_1(F_o)$, $wR_2(F_o^2)$, all data			0.0813, 0.1964
$R_1(F_o)$, $wR_2(F_o)$, ($I > 3\sigma(I)$)	0.0367, 0.0380	0.0491, 0.0546	
goodness of fit	1.69	1.53	1.23

(m, 1 F), 53.2 (dt, 1 F), 51.9 (dt, 1 F), 48.2(m, 1 F), 39.9 (m, 1 F), 39.2 (m, overlaps with Rotomer 2, 1F). Rotomer 2: ^{1}H NMR (pyridine-d_5): δ 1.829 (overlaps with Rotomer 1, 15 H), 1.154 (d, J_{P-H} = 9.8 Hz, 9 H), −12.451 (ddd, J_{P-H} = 48.1 Hz, J_{Rh-H} = 26.1 Hz, J_{F-H} = 11.0 Hz, 1 H). ^{31}P{^{1}H} NMR (pyridine-d_5): δ 4.98 (dt, J_{Rh-P} = 142.2 Hz, J_{F-P} = 10.7 Hz). ^{19}F NMR (C_6D_6): δ 116.8 (m, 1 F), 98.2 (m, 1 F), 54.7 (dt, 1 F), 51.2 (dt, 1 F), 46.9 (m, 1 F), 40.1(m, 1 F), 39.2 (m, overlaps with Rotomer 1, 1 F). Yield (both rotomers combined) = 90%. $t_{1/2}$ < 30 min.

4,4′-[(C_5Me_5)Rh(PMe_3)H]$_2$perfluorobiphenyl. ^{1}H NMR (C_6D_6): δ 1.684 (s, 15 H), 0.786 (d, J_{P-H} = 10.0 Hz, 9 H), −12.470 (ddd, J_{P-H} = 44.0 Hz, J_{Rh-H} = 24.0, J_{F-H} = 16.0 Hz, 1 H). ^{31}P{^{1}H} NMR (C_6D_6): δ 5.01 (dt, J_{Rh-P} = 143.1, J_{F-P} = 9.2 Hz). ^{19}F NMR (C_6D_6): δ 94.0 (m, 2 F_{ortho}), 89.0 (m, 2 F_{ortho}), 59.6 (dd, 1 F_{meta}), 59.3 (dd, 1 F_{meta}), 58.2 (dd, 1 F_{meta}), 58.0 (dd, 1 F_{meta}).

Chlorination of (C_5Me_5)Rh(PMe_3)(aryl^F)H Compounds. The general procedure employed is described here for (C_5Me_5)Rh(PMe_3)(4-perfluorobiphenyl)H. To an ampule containing a hexane solution of (C_5Me_5)Rh(PMe_3)(4-perfluorobiphenyl)H (50 mg, 0.079 mmol) was added an excess of $CHCl_3$ (12.7 μL, 0.158 mmol) at room temperature. The brown solution turned red/orange immediately along with the formation of a red precipitate. (C_5Me_5)Rh(PMe_3)($C_{12}F_{10}$)Cl was isolated on a thin-layer silica chromatography plate with a 95:5 (v/v) solution of CH_2Cl_2−THF. Elemental analysis and NMR data are summarized below in C_6D_6 solvent.

NMR Spectroscopic Data and Elemental Analysis for (C_5Me_5)Rh(PMe_3)(aryl^F)Cl Complexes. (C_5Me_5)Rh(PMe_3)(4-perfluorobiphenyl)Cl. ^{1}H NMR (C_6D_6): δ 1.264 (d, J_{Rh-H} = 3.2 Hz, 15 H), 1.128 (d, J_{P-H} = 10.8 Hz, 9 H). ^{31}P{^{1}H} NMR (C_6D_6): δ 5.27 (dd, J_{Rh-P} = 140.3 Hz, J_{F-P} = 22.2 Hz). ^{19}F NMR (C_6D_6): δ 93.8 (m, 1 F_{ortho}), 88.0 (m, 1 F_{ortho}), 62.0 (m, 1 F_{meta}), 61.2 (m, 1 F_{meta}), 60.5 (m, 1 $F_{ortho'}$), 58.0 (m, 1 $F_{ortho'}$), 48.0 (m, 1 F_{para}), 39.0 (dt, 1 $F_{meta'}$), 38.7 (dt, 1 $F_{meta'}$). Anal. Calcd for $C_{25}H_{24}ClF_9PRh$: C, 45.17; H, 3.64. Found: C, 45.25; H, 3.52.

(C_5Me_5)Rh(PMe_3)(2,3,5,6-C_6HF_4)Cl. ^{1}H NMR (C_6D_6): δ 6.541 (tt, J_{H-F} = 8.8, 6.8 Hz), δ 1.269 (d, J_{Rh-H} = 3.2 Hz, 15 H), 1.131 (d, J_{P-H} = 10.8 Hz, 9 H). ^{1}P{^{1}H} NMR (C_6D_6): δ 5.41 (dd, J_{Rh-P} = 141.4 Hz, J_{F-P} = 22.8 Hz). ^{19}F NMR (C_6D_6): δ 91.6 (m, 1 F_{ortho}), 86.3 (m, 1 F_{ortho}), 61.0 (m, 1 F_{meta}), 58.5 (m, 1 F_{meta}). Anal. Calcd for $C_{19}H_{25}ClF_4PRh$: C, 45.76; H, 5.05. Found: C, 45.47; H, 4.98.

(C_5Me_5)Rh(PMe_3)(2-perfluoronaphthalene)Cl. Rotomer 1: ^{1}H NMR (C_6D_6): δ 1.297 (d, J_{Rh-H} = 3.2 Hz, 15 H), 1.187(d, J_{P-H} = 10.8 Hz, 9 H). ^{31}P{^{1}H} NMR (C_6D_6): δ 5.87 (dt, J_{Rh-P} = 141.0 Hz, J_{F-P} = 26.7 Hz). ^{19}F NMR (C_6D_6): δ 108.2 (m, 1 F), 100.2 (m, 1 F), 53.0−52.5 (m, 2 F), 49.2 (m, 1 F), 40.2 (m, overlaps with Rotomer 2, 2F). Rotomer 2: ^{1}H NMR (C_6D_6): δ 1.289 (d, J_{P-H} = 3.2 Hz, 15 H), 1.151 (d, J_{P-H} = 10.8 Hz, 9 H). ^{31}P{^{1}H} NMR (C_6D_6): δ 5.13 (dd, J_{Rh-P} = 141.3 Hz, J_{F-P} = 25.5 Hz). ^{19}F NMR (C_6D_6): δ 116.8 (m, 1 F), 95.0 (m, 1 F), 56.2(m, 1 F), 50.9 (m, 1F), 46.9 (m, 1 F), 40.6 (m, 1 F), 40.2 (m, overlaps with Rotomer 1, 1 F). Anal. Calcd for $C_{23}H_{24}ClF_8PRh{\cdot}H_2O$: C, 44.50; H, 4.06. Found: C, 43.98; H, 3.76.

4,4′-[(C_5Me_5)Rh(PMe_3)Cl]$_2$perfluorobiphenyl. ^{1}H NMR ($CDCl_3$): δ 1.657 (d, J_{Rh-H} = 3.6 Hz, 15 H), δ 1.527 (d, J_{P-H} = 10.8 Hz, 9 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 5.26 (dd, J_{Rh-P} = 143.1 Hz, J_{F-P} = 9.2 Hz). ^{19}F NMR indicated that diastereomer 1 dominated by a ratio of 3:2.^{19}F NMR ($CDCl_3$): diasteriomer 1, δ 90.2 (m, 3 F_{ortho}), 86.2 (m, 3 F_{ortho}), 60.4 (m, 3 F_{meta}), 59.0 (m, 3 F_{meta}); diasteriomer 2, δ 89.7 (m, 2 F_{ortho}), 86.8 (m, 2 F_{ortho}), 61.5 (m, 2 F_{meta}), 58.2 (m, 2 F_{meta}). Anal. Calcd for $C_{38}H_{48}Cl_2F_8P_2Rh_2$: C, 45.85; H, 4.86. Found: C, 45.76; H, 4.79.

X-ray Structural Determination of 3-Cl. Orange-red crystals were obtained by layering a CH_2Cl_2 solution of **3-Cl** with hexanes. A single crystal having approximate dimensions of 0.30 × 0.30 × 0.45 mm^3 was mounted on a glass fiber with epoxy. Lattice constants were obtained from 25 centered reflections with values of χ between 5° and 70° on an Enraf Nonius CAD4 diffractometer. Cell reduction revealed a primitive monoclinic crystal system. Data were collected at −20 °C in accord with the parameters found in Table 1. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout the data collection indicating crystal and electronic stability. The Molecular Structure Corporation TEXSAN analysis software package was used for data reduction, solution, and refinement. The space group was assigned as *C2/c* on the basis of systematic absences and a *Z* value of 8. A Patterson map solution of the structure was used to locate the rhodium atom. The structure was expanded with the DIRDIF program to reveal all non-hydrogen atoms. An absorption correction was applied by using the program DIFABS following isotropic refinement. Anisotropic refinement of all non-hydrogen atoms allowed for the use of a difference Fourier map for the location of the hydrogen atoms whose coordinates were subsequently idealized. Full-matrix least-squares anisotropic refinement of the non-hydrogen atoms (with hydrogen atoms attached to carbon atoms in idealized positions) was executed until convergence was achieved. The structure was refined with R_1 = 0.0367 and R_w = 0.0380.[32] Fractional coordinates and thermal parameters are given in the Supporting Information.

X-ray Structural Determination of (C_5Me_5)Rh(PMe_3)(perfluorobiphenyl)Cl (4-Cl). Orange-red crystals were obtained by layering a CH_2Cl_2 solution of **4-Cl** with hexanes. A single crystal of dimensions 0.60 × 0.37 × 0.11 mm^3 was mounted on a glass fiber with epoxy. Lattice constants were obtained from 25 centered reflections with values of χ between 5° and 70° on an Enraf Nonius CAD4 diffractometer. Cell reduction revealed a primitive monoclinic crystal system. Data were collected at −40 °C in accord with the parameters found in Table 1. The space group was uniquely assigned as $P2_1/c$ on the basis of systematic absences. The structure was solved and refined by using

(32) Using the TEXSAN package, $R = (\sum||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\sum w|F_o^2|$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', and f'': Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol IV, Tables 2.2B and 2.3.1.

the TEXSAN software package as described above for **3-Cl**, giving final parameters of $R_1 = 0.0491$ and $R_w = 0.0546$.

X-ray Structural Determination of (C_5Me_5)Rh(PMe_3)(perfluoronaphthyl)Cl (6-Cl). Orange-red crystals were obtained by layering a CH_2Cl_2 solution of **6-Cl** with hexanes. A single crystal of dimensions $0.40 \times 0.35 \times 0.10$ mm^3 was mounted on a glass fiber with epoxy. Data were collected at 20 °C on a Siemens SMART CCD area detector system employing a 3 kW sealed tube X-ray source operating at 1.5 kW; 1.3 hemispheres of data were collected over 7 h, yielding 9459 observed data after integration by using SAINT (see Table 1). Laue symmetry revealed a monoclinic crystal system, and cell parameters were determined from 5832 unique reflections.[33] An absorption correction was applied by using SADABS. The space group was assigned as $P2_1/c$ on the basis of systematic absences by using XPREP, and the structure was solved and refined by using the SHELX95 package. For a Z value of 4 there is one independent molecule within the asymmetric unit. Examination of a difference map following isotropic refinement of the (C_5Me_5)Rh(PMe_3) fragment showed evidence for a rotational disorder of the perfluoronaphthyl group. In the refinement model, the two different orientations were allowed to refine independently while restraining intraring distances to be similar by using the SHELX SAME instruction. The occupancies of the two orientations were fixed at 1:1. In the final model, all non-hydrogen atoms were refined anisotropically (on F^2), with hydrogens included in idealized locations. A water molecule was included in a crystal void. Final agreement factors were $R_1 = 0.0725$ and $wR_2 = 0.1901$.[34] Fractional coordinates and thermal parameters are given in the Supporting Information.

Reaction of (C_5Me_5)Rh(PMe_3)H_2 with Various Concentrations of Perfluorobiphenyl. Four NMR tubes were prepared with varying concentrations of perfluorobiphenyl (0.66, 0.52, 0.36, and 0.23 M) in 1:1 pyridine-d_5/C_6D_6. The concentration of (C_5Me_5)Rh(PMe_3)H_2 in each tube was maintained at 0.035 M. Dioxane (1 μL) was added as an internal standard. The NMR tubes were heated at 92 °C, and the reaction was followed by ^{1}H NMR spectroscopy until the starting material was depleted. The approximate half-lives ($t_{1/2}$) for each concentration was determined: 0.66 M, $t_{1/2} \cong 38$ min; 0.52 M, $t_{1/2} \cong 44$ min; 0.36 M, $t_{1/2} \cong 64$ min; 0.23 M, $t_{1/2} \cong 88$ min.

Reaction of (C_5Me_5)Rh(PMe_3)H_2 with Perfluorobiphenyl and Pyridinium Chloride. A resealable NMR tube containing (C_5Me_5)Rh(PMe_3)H_2 (0.035 M) and perfluorobiphenyl (0.36 M) in 1:1 pyridine-d_5/C_6D_6 was prepared with dioxane as an internal standard. Hydrogen chloride gas (12 equiv based on **1**) was condensed into the tube. The tube was heated in the NMR probe at 92 °C. The reaction was monitored by ^{1}H NMR spectroscopy until the starting material was depleted. The main product was (C_5Me_5)Rh(PMe_3)Cl_2; a singlet at δ 4.37 corresponding to free H_2 was also observed.

Reaction of (C_5Me_5)Rh(PMe_3)H_2 with Perfluorobiphenyl and Pyridinium Tetrafluoroborate. A resealable NMR tube containing (C_5Me_5)Rh(PMe_3)H_2 (0.035 M) and perfluorobiphenyl (0.36 M) and pyridinium tetrafluoroborate (0.14 M) in 1:1 pyridine-d_5/C_6D_6 was prepared with dioxane as an internal standard. The tube was heated in the NMR probe at 92 °C. The reaction was monitored by ^{1}H NMR spectroscopy until the starting material was depleted. The half-life of **1** was ≅65 min and the yield of **4** was 53%. The complex [Cp*Rh(PMe_3)$_2$H]$^+$ was formed in 15% yield.

Reaction of (C_5Me_5)Rh(PMe_3)H_2 with Perfluorobiphenyl and Pyridinium Hydrogen Fluoride. A resealable NMR tube (equipped with a Teflon insert) containing (C_5Me_5)Rh(PMe_3)H_2 (0.035 M), perfluorobiphenyl (0.36 M), and pyridinium poly(hydrogen fluoride) (0.035 M) in 1:1 pyridine-d_5/C_6D_6 was prepared with dimethoxyethane as an internal standard. The tube was heated in the NMR probe at 92 °C The reaction was monitored by ^{1}H NMR until the starting material was depleted. The half-life of **1** was ∼66 min and the yield of **4** was 55%. The complex [Cp*Rh(PMe_3)$_2$H]$^+$ was formed in 23% yield.

Anhydrous TBAF. TBAF·3H_2O was heated under high vacuum with stirring at 40 °C for 48 h.[35] The resulting oil was further dried by dissolving the oil in anhydrous THF and stirring over 4 Å molecular sieves for 24 h. The solvent was removed and the oil stored in dry benzene at −25 °C. A trace of water is always present. This solution loses its potency within several weeks.

Reaction of (C_5Me_5)Rh(PMe_3)H_2 with Perfluorobiphenyl with and without TBAF. Two resealable NMR tubes containing (C_5Me_5)Rh(PMe_3)H_2 (0.035 M) and perfluorobiphenyl (0.36 M) were prepared with dioxane as an internal standard in 1:1 pyridine-d_5/C_6D_6 solvent. TBAF (0.21 M) was added to one of the samples, and the tubes were heated in an NMR probe at 69 °C. Both reactions were monitored by ^{1}H NMR until the starting material was depleted. The approximate half-lives were 460 min (90% yield) in the absence of fluoride and 10 min (93% yield) in the presence of fluoride. Another experiment was performed with 0.0077 M added fluoride ion. Two similar samples were prepared in neat pyridine-d_5 solvent and allowed to react at ambient temperature (21 °C). The approximate half-lives were 90 h (87% yield) in the absence of fluoride and 14 h (93% yield) in the presence of fluoride.

Reaction of (C_5H_5)Rh(PMe_3)H_2 with Perfluorobiphenyl. A resealable NMR tube containing (C_5H_5)Rh(PMe_3)H_2 (0.035 M) and perfluorobiphenyl (0.36 M) in pyridine-d_5 was prepared with dioxane as an internal standard. The tube was left to stand at room temperature (21.5 °C). The reaction was monitored by ^{1}H NMR until the starting material was depleted. The approximate half-live was 48 h (95% yield). ^{1}H NMR (pyridine-d_5): δ 5.680 (s, 5 H), 1.561 (dd, $J_{P-H} = 11.0$ Hz, $J_{P-Rh} = 1.0$ Hz, 9 H), −12.052 (dd, $J_{P-H} = 40.4$ Hz, $J_{Rh-H} = 23.6$ Hz, 1 H). ^{31}P{^{1}H} NMR (pyridine-d_5): δ 14.5 (d, $J_{Rh-P} = 141.7$ Hz).

Photolysis of 1 in the Presence of C_6F_5H. A resealable NMR tube containing a 0.5 mL C_6D_{12} solution of (C_5Me_5)Rh(PMe_3)H_2 (0.0173 mmol) and pentafluorobenzene (0.0865 mmol) was irradiated for ca. 3 h with a water-filtered 200-W Hg Applied Photophysics lamp. The only product formed was (C_5Me_5)Rh(PMe_3)(C_6F_5)H resulting from C−H activation of pentafluorobenzene.

Thermolysis of (C_5Me_5)Rh(PMe_3)H_2 with C_6F_5Cl. A sample of (C_5Me_5)Rh(PMe_3)H_2 (10.7 mg, 0.029 mmol) was dissolved in approximately 0.4 mL of C_6D_6 in a resealable NMR tube along with C_6F_5-Cl (3.74 μL, 0.029 mmol) and 1 μL of dimethoxyethane as an internal standard. The volume was brought to 0.6 mL with C_6D_6. The reaction was monitored by ^{1}H NMR and ^{31}P NMR at ambient temperature. After 380 h ^{1}H NMR and ^{31}P NMR showed the formation of (C_5Me_5)Rh(PMe_3)HCl as the dominant organometallic species along with a small amount of (C_5Me_5)Rh(PMe_3)Cl_2. ^{1}H NMR spectroscopy and GC-MS showed that 1 equiv of C_6F_5H had been formed.

Thermolysis of (C_5Me_5)Rh(PMe_3)H_2 with C_6F_5Br. A sample of (C_5Me_5)Rh(PMe_3)H_2 (10.7 mg, 0.029 mmol) was dissolved in approximately 0.4 mL of C_6D_6 in a resealable NMR tube along with C_6F_5-Br (3.65 μL, 0.029 mmol) and 1 μL of dimethoxyethane as an internal standard. The volume was brought to 0.6 mL with C_6D_6. The reaction was monitored by ^{1}H NMR and ^{31}P NMR at ambient temperature. After 91 h, ^{1}H NMR and ^{31}P NMR showed the formation of (C_5Me_5)Rh(PMe_3)HBr. ^{1}H NMR spectroscopy and GC-MS showed that 1 equiv of C_6F_5H had been formed.

Generation of (C_5Me_5)Rh(PMe_3)HCl. (C_5Me_5)Rh(PMe_3)Cl_2 (6.7 mg, 0.0175 mmol) and [PPN]$^+$[BH_4]$^-$ (14.6 mg, 0.026 mmol) were combined in a Teflon sealed ampule with 2 mL of THF in the drybox. The suspension was stirred at room temperature for 45 min then filtered through cotton with hexanes. The solvent was removed under vacuum and transferred to an NMR tube with C_6D_6. ^{1}H NMR revealed a mixture of compounds: (C_5Me_5)Rh(PMe_3)Cl_2 (ca. 50%), (C_5Me_5)Rh(PMe_3)H_2 (30%), and (C_5Me_5)Rh(PMe_3)HCl (20%). ^{1}H NMR (C_6D_6): δ 1.623 (d, $J_{Rh-H} = 1.6$ Hz, 15 H), δ 1.151 (d, $J_{P-H} = 10.8$ Hz, 9 H), −11.754 (dd, $J_{P-H} = 52.4$, $J_{Rh-H} = 20.0$, 1 H). ^{31}P{Selective ^{1}H} NMR (C_6D_6): δ 8.03 (dd, $J_{Rh-P} = 143.2$ Hz, $J_{H-P} = 47.5$ Hz).

Generation of (C_5Me_5)Rh(PMe_3)HBr. (C_5Me_5)Rh(PMe_3)Br_2 (8.8 mg, 0.0186 mmol) and [PPN]$^+$[BH_4]$^-$ (18.5 mg, 0.033 mmol) were combined in a Teflon sealed ampule with 2 mL of dry THF in the drybox. The suspension was stirred at room temperature for 1 h and then filtered through cotton with hexanes. The solvent was removed under vacuum and transferred to an NMR tube with C_6D_6. ^{1}H NMR

(33) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10× the listed values.

(34) Using the SHELX95 package, $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$, $wR^2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w|F_o^2)^2]\}^{1/2}$, where $w = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and P = [f·(maximum of 0 or F_o^2) + (1 − f)F_c^2].

(35) Cox, D. P.; Terpinski, J.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3216−3219.

spectroscopy revealed a mixture of compounds: $(C_5Me_5)Rh(PMe_3)Br_2$ (ca. 20%), $(C_5Me_5)Rh(PMe_3)H_2$ (20%), and $(C_5Me_5)Rh(PMe_3)HBr$ (60%). ^{1}H NMR (C_6D_6): δ 1.659 (d, $J_{Rh-H} = 1.6$ Hz, 15 H), δ 1.187 (dd, $J_{P-H} = 10.4$ Hz, $J_{Rh-H} = 0.8$ Hz, 9 H), −12.047 (dd, $J_{P-H} = 50.8$, $J_{Rh-H} = 20.0$, 1 H). ^{31}P{Selective ^{1}H} NMR (C_6D_6): δ 6.02 (dd, $J_{Rh-P} = 143.8$ Hz, $J_{H-P} = 48.0$ Hz).

$[(C_5Me_5)Rh(PMe_3)H]_xLi_x$.[20] This orange material was prepared as previously reported. ^{1}H NMR (pyridine-d_5): δ 2.292 (d, $J_{Rh-H} = 1.0$ Hz, 15 H), 1.343 (d, $J_{P-H} = 7.3$ Hz, 9 H), −16.525 (overlapping dd, $J_{P-H} = J_{Rh-H} = 44.6$ Hz, 1H). ^{31}P{^{1}H} NMR (pyridine-d_5): δ −6.258 (d, $J_{Rh-P} = 232.4$).

Reaction of $[(C_5Me_5)Rh(PMe_3)H]_xLi_x$ with Perfluorobiphenyl. A pyridine-d_5 solution of $[(C_5Me_5)Rh(PMe_3)H]_xLi_x$ (10.5 mg, 0.035 mmol) was added to a pyridine-d_5 solution of perfluorobiphenyl (85 mg, 0.254 mmol) at room temperature. ^{1}H and ^{31}P NMR spectroscopy indicated the immediate quantitative formation of **4** and **5** in a ratio of approximately 3 to 1.

Reaction of $[(C_5Me_5)Rh(PMe_3)H]_xLi_x$ with Perfluoronaphthalene. A pyridine-d_5 solution of $[(C_5Me_5)Rh(PMe_3)H]_xLi_x$ (10.5 mg, 0.035 mmol) was added to a pyridine-d_5 solution of perfluoronaphthalene (69 mg, 0.254 mmol) at room temperature. ^{1}H and ^{31}P NMR spectroscopy indicated the immediate quantitative formation of both rotomers of **6** in the same 1.25:1 ratio as the thermal reactions with **1**.

Electrochemical Studies. The cyclic voltametry measurements of $(C_5Me_5)Rh(PMe_3)H_2$ and $(C_5H_5)Rh(PMe_3)H_2$ were carried out under an inert atmosphere with a EG & G PARR Potentiostat/Galvanostat Model 263A in a nitrogen drybox. The polyfluoroaromatic compounds were run under a nitrogen purge in a polarographic cell. The working electrode was a 3 mm diameter platinum disk which was polished prior to each use. A platinum wire served as the auxiliary electrode, and a silver wire served as a pseudoreference electrode. The CV experiments were performed in THF at room temperature with ferrocene as an internal reference, 0.1 M in supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate) and 3.0 mM in the polyfluoroaromatics and 1.0 mM in the metal complexes. The scan rate in all experiments was 0.1 V/s.

All of the species tested displayed irreversible behavior with a scan rate of 0.1 V/s. The peak reduction potentials (E_{PC}) and peak oxidation potentials (E_{PA}) for the polyfluoroaromatics and the metal complexes are reported versus the ferrocene/ferrocenium ion couple (Table 2). The peak reduction potentials for perfluorobenzene and perfluoronaphthalene are in close agreement to those reported by Pez et al.[26]

Table 2. Peak Reduction Potentials (E_{PC}) and Peak Oxidation Potentials (E_{PA}) for Various Polyfluoroaromatics, $(C_5Me_5)Rh(PMe_3)H_2$ and $(C_5H_5)Rh(PMe_3)H_2$ (V vs Ferrocene/Ferrocenium Ion Couple)[a]

perfluoroaromatics	E_{PC} (V)	metal complex	E_{PA} (V)
perfluoronaphthalene	−2.42	$(C_5Me_5)Rh(PMe_3)H_2$	−0.336
perfluorobenzene	−2.45	$(C_5H_5)Rh(PMe_3)H_2$	+0.279
perfluorobiphenyl	−2.61		
pentafluorobenzene	−2.97		

[a] Experimental conditions: [polyfluoroaromatics] = 3.0×10^{-3} M; [metal complex] = 1.0×10^{-3} M; [supporting electrolyte] = 0.1 M tetrabutylammonium hexafluorophosphate; temperature = 23 ± 2 °C, scan rate = 100 mV/s; platinum working electrode, platinum wire auxiliary electrode, and a silver wire reference electrode were used for the measurements. Potentials were referenced to a ferrocene internal standard. Tetrahydrofuran was the solvent used.

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Supporting Information Available: Tables of bond distances and angles, atomic positions, and thermal parameters for **3**, **4**, and **6** as well their NMR spectroscopic data in C_6D_6 (18 pages). See any current masthead page for ordering and Internet access instructions.

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