Selectivity in the Activation of Fluorinated Aromatic Hydrocarbons by [(C_5H_5)Rh(PMe_3)] and [(C_5Me_5)Rh(PMe_3)]

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Thermolysis of (C_5Me_5)Rh(PMe_3)(Ph)H (1) in neat fluorobenzene, *o*-difluorobenzene, *p*-difluorobenzene, or 1,3,5-trifluorobenzene results in the formation of the new aryl hydride complexes (C_5Me_5)Rh(PMe_3)($aryl_F$)H ($aryl_F$ = 2-C_6H_4F, 2,3-$C_6H_3F_2$, 2,5-$C_6H_3F_2$, or 2,4,6-$C_6H_2F_3$). Short term thermolysis of 1 in *m*-difluorobenzene produces a kinetic mixture of products resulting from activation of all possible C–H bond positions. Continued thermolysis of this mixture results in exclusive formation of the thermodynamic product (C_5Me_5)Rh(PMe_3)(2,6-$C_6H_3F_2$)H. Irradiation of (C_5Me_5)Rh(PMe_3)H_2 in *o*-difluorobenzene at −30 °C gives both (C_5Me_5)-Rh(PMe_3)(2,3-$C_6H_3F_2$)H and (C_5Me_5)Rh(PMe_3)(3,4-$C_6H_3F_2$)H as the kinetic products. Thermolysis of this mixture results in exclusive formation of the thermodynamic product (C_5Me_5)-Rh(PMe_3)(2,3-$C_6H_3F_2$)H. These aryl hydrides are readily converted to their bromo derivatives by reaction with bromoform. Photochemical reaction of (C_5H_5)Rh(PMe_3)(C_2H_4) (2) with *o*-, *m*-, and *p*-difluorobenzene, 1,3,5-trifluorobenzene, 1,2,4,5-tetrafluorobenzene, or pentafluorobenzene at room temperature gives single aryl hydride products (C_5H_5)Rh(PMe_3)($aryl_F$)H ($aryl_F$ = 2,3-$C_6H_3F_2$, 2,6-$C_6H_3F_2$, 2,5-$C_6H_3F_2$, 2,4,6-$C_6H_2F_3$, 2,3,5,6-C_6HF_4, or C_6F_5) in which C–H insertion occurs adjacent to a fluorine. Photochemical reaction of 2 with α,α,α-trifluorotoluene gives both *m*- and *p*-trifluorotolyl insertion products. These compounds are also converted to their bromo derivatives by reaction with bromoform. Photochemical reaction of 2 with 2,3,4,5,6-pentafluorotoluene gives an η^2-arene complex with metal coordination in the 3,4 positions. The (C_5Me_5)Rh(PMe_3)($aryl_F$)Br complexes were structurally characterized. (C_5Me_5)Rh(PMe_3)(2,3-$C_6F_2H_3$) crystallizes in monoclinic space group $C2/c$ (No. 15) with $Z = 8$, $a = 14.071(9)$ Å, $b = 9.640(5)$ Å, $c = 30.774(12)$ Å, $\beta = 97.48(4)°$, and $V = 4139(7)$ Å^3. (C_5Me_5)Rh(PMe_3)(2,4-$C_6F_2H_3$) crystallizes in monoclinic space group $C2/c$ (No. 15) with $Z = 8$, $a = 14.073(8)$ Å, $b = 9.505(3)$ Å, $c = 30.910(10)$ Å, $\beta = 97.30(5)°$, and $V = 4101(5)$ Å^3, and also in monoclinic space group $P2_1/c$ (No. 14) with $Z = 4$, $a = 9.401(6)$ Å, $b = 11.595(4)$ Å, $c = 18.809(8)$ Å, $\beta = 91.38(4)°$, and $V = 2049(3)$ Å^3. (C_5Me_5)Rh(PMe_3)(2,4,6-$C_6F_3H_3$) crystallizes in monoclinic space group $C2/c$ (No. 15) with $Z = 8$, $a = 14.263(9)$ Å, $b = 9.492(2)$ Å, $c = 30.917(17)$ Å, $\beta = 97.99(2)°$, and $V = 4145(6)$ Å^3.

Introduction

A number of transition metal compounds are capable of activation of aromatic and aliphatic C–H bonds in homogeneous solution.[1] Some of these metal complexes are in high oxidation states and act through an electrophilic σ-metathesis pathway, while others are in low oxidation states and react by oxidative addition of the C–H bond.[2] Of the latter variety, the reactive fragments [(C_5Me_5)-Rh(PMe_3)] and [(C_5H_5)Rh(PMe_3)] have been studied in detail.

These fragments react with the primary and secondary C–H bonds of alkanes R–H to give unstable oxidative addition adducts of the type (C_5R_5)Rh(PMe_3)(R)H.[3] Benzene activation proceeds through the η^2-arene intermediate (C_5R_5)Rh(PMe_3)(η^2-C_6H_6), which can be observed directly in laser flash photolysis experiments.[4,5] Other arenes also react via η^2-arene complexes, giving either C–H oxidative addition products or stable, isolable η^2-arene complexes, or equilibria between the two. Isolable η^2-arene complexes include those of electron deficient arenes, such as (C_5R_5)Rh(PMe_3)(η^2-C_6F_6),[5] and those with fused polycyclic aromatics such as (C_5H_5)Rh(PMe_3)(η^2-naphthalene), (C_5Me_5)Rh(PMe_3)(η^2-phenanthrene),[6] and (C_5-Me_5)Rh(PMe_3)(η^2-perylene).[7] Equilibria between η^2-arene and aryl hydride complexes are observed for [(C_5H_5)Rh-(PMe_3)] + 1,4-$C_6H_4(CF_3)_2$, [(C_5H_5)Rh(PMe_3)] + 1,3-$C_6H_4(CF_3)_2$,[7] and for [(C_5Me_5)Rh(PMe_3)] + naphthalene.

The observation of η^2-arene complex formation with hexafluorobenzene and 1,4-$C_6H_4(CF_3)_2$ led us to investigate the reactions of the reactive fragments [(C_5H_5)Rh(PMe_3)]

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(1) See, for example: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245-269. (b) Bergman, R. *Science* **1984**, *223*, 902-908. (c) Hill, C. L. *Activation and Functionalization of Alkanes*; Wiley: New York, 1989. (d) Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A. *Selective Hydrocarbon Activation*; VCH Publishers, Inc.: New York, 1990. (e) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91-100.

(2) For a recent summary of references, see: Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32*, 131-144.

(3) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650-1663. Periana, R. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332-7346.

(4) Belt, S. T.; Duckett, S. B.; Helliwell, M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1989**, 928-930.

(5) Belt, S. T.; Dong, L.; Duckett, S. B.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 266-269.

(6) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722-8723.

(7) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685-7695.

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and $[(C_5Me_5)Rh(PMe_3)]$ with fluorinated aromatic hydrocarbons. In addition to the possibility of either C–H insertion and/or η^2-complex formation, we also considered insertion into the C–F bond as a reasonable possibility. On the basis of the observation of the photochemically promoted C–F bond cleavage in $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_6F_6)$ and $(C_5H_5)Ir(PMe_3)H_2$, C–F activation would require photoinitiation.[8] In this paper we show that partially fluorinated benzenes $C_6H_{6-x}F_x$ react with sources of $[(C_5H_5)Rh(PMe_3)]$ and $[(C_5Me_5)Rh(PMe_3)]$ to give C–H activation products only. However, there is considerable regioselectivity in the product distribution. In addition we report a new η^2-arene complex derived from the reaction of $(C_5H_5)Rh(PMe_3)(C_2H_4) + C_6F_5CH_3$.

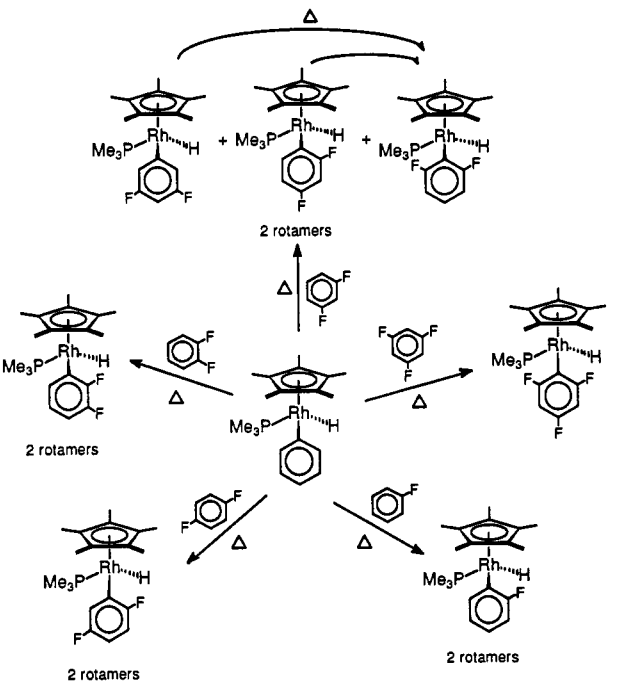
Results

Thermal Reactions of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with Polyfluorinated Arenes. In all cases studied, C–H activation products of the type $(C_5Me_5)Rh(PMe_3)(aryl_F)H$ were formed. Thermolysis of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (1) in neat fluoroarene overnight at 67 °C led to loss of benzene and formation of the 16 electron fragment $[(C_5Me_5)Rh(PMe_3)]$, which then reacted rapidly with the fluorinated solvent. The reactions were monitored by $^{31}P\{^1H\}$ NMR spectroscopy to ensure that complete reaction had occurred. Removal of the volatile components left yellow-tan oils in all cases, which were then dissolved in deuterated solvent and analyzed by room temperature or low temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

The products of thermolysis of 1 with fluorobenzene, *o*-difluorobenzene, and *p*-difluorobenzene gave similar results. Room temperature NMR spectra of the resulting mixtures exhibited two broad hydride resonances by ^1H NMR spectroscopy and a single broad $^{31}P\{^1H\}$ NMR resonance. Low temperature (−40 °C) ^1H NMR spectroscopy for the fluorobenzene reaction revealed two products, with one hydride showing a normal doublet of doublets (dd) resonance due to rhodium and phosphorus coupling at δ −13.685 (J_{P-H} = 48.0 Hz, J_{Rh-H} = 32.0 Hz). The other resonance appeared as a doublet of doublet of doublets (ddd) at δ −12.869 (J_{P-H} = 47.3, J_{Rh-H} = 29.5, J_{F-H} = 7.9 Hz) with the additional 7.9-Hz splitting attributed to coupling to the *o*-fluorine substituent on the phenyl ring. $^{31}P\{^1H\}$ NMR spectroscopy at −40 °C confirmed the existence of two products, each a dd pattern, at δ 7.71 (J_{Rh-P} = 148.4, J_{F-P} = 9.9 Hz) and δ 7.12 (J_{Rh-P} = 147.9, J_{F-P} = 10.2 Hz). Very similar NMR spectra were obtained at −40 °C from the reactions of 1 with *o*-difluorobenzene and *p*-difluorobenzene, each giving two products with similar coupling patterns (see Experimental Section). Since only one possible C–H activation site is available for *p*-difluorobenzene, the two products observed for this reaction were assigned as rotamers of the complex $(C_5Me_5)Rh(PMe_3)(2,5\text{-}C_6H_3F_2)H$. Due to the nearly identical nature of the low temperature ^1H NMR spectra for these three reactions, and the observation of P–F coupling in the low temperature $^{31}P\{^1H\}$ NMR spectrum for both of the products with fluorobenzene and *o*-difluorobenzene, it appears in each case that C–H insertion occurs specifically at the C–H bond ortho to a fluorine substituent, yielding $(C_5Me_5)Rh(PMe_3)(2\text{-}C_6H_4F)H$ and $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$ regiospecifically (see Scheme 1).

(8) Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 264–265. Belt, S. T.; Helliwell, M.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1429–1441.

Scheme 1. Products of the Reaction of 1 with Fluoroarenes



The photochemical reaction of $(C_5Me_5)Rh(PMe_3)H_2$ with *o*-difluorobenzene at −30 °C in THF-d_8 solvent, however, showed the formation of an additional C–H activation product. Resonances were now observed for both the 2,3-isomer (as in the thermal reaction) and the 3,4-isomer $(C_5Me_5)Rh(PMe_3)(3,4\text{-}C_6H_3F_2)H$ in a 2:1 ratio. When the sample was warmed to 25 °C, the 3,4-isomer was observed to convert completely to the 2,3-isomer over a period of 1 h.

Reaction of the mixture from the thermolysis reactions with bromoform followed by thin-layer chromatography led to the isolation of only one product in each case, identified as the corresponding aryl bromide complex $(C_5Me_5)Rh(PMe_3)(aryl_F)Br$ with $aryl_F$ = 2-C_6H_4F, 2,3-$C_6H_3F_2$, and 2,5-$C_6H_3F_2$. ^1H NMR spectra showed signals for aromatic, C_5Me_5, and PMe_3 resonances, and $^{31}P\{^1H\}$ NMR spectra showed a dd resonance for each complex (see Experimental Section).

The reaction of 1 with *m*-difluorobenzene overnight at 67 °C gave different results. Room temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy again showed spectra indicative of fluxional behavior, and low temperature NMR spectroscopy was required to fully identify and characterize the products. ^1H NMR spectra obtained at room temperature showed the presence of several products, but with broad unresolved hydride, PMe_3, and C_5Me_5 resonances. Room temperature $^{31}P\{^1H\}$ NMR displayed broad phosphorus resonances that did not show P–F coupling. Cooling a toluene-d_8 or THF-d_8 solution of the reaction mixture to −40 °C resulted in a slowing of the fluxional process, with the slow-exchange limiting spectrum for this mixture revealing the existence of four products. Four hydride resonances were observed at δ −12.470, −12.540, −13.286, and −13.405 (see Figure 1). The two resonances at higher field exhibited the normal dd pattern (J_{P-H} = ca. 48 Hz, J_{Rh-H} = ca. 32 Hz), but the two at lower field displayed a ddd pattern with an additional $H\text{–}F_{ortho}$ coupling (J_{F-H} = 8–9 Hz). These four products were assigned as $(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)H$, $(C_5Me_5)Rh$-

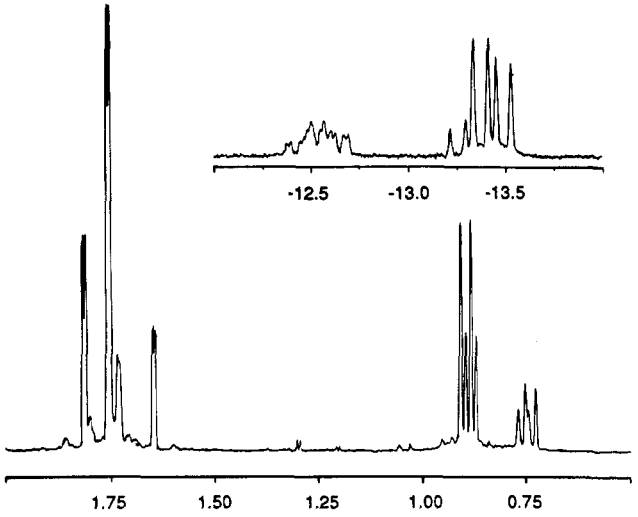


Figure 1. ^{1}H NMR spectrum (400 MHz) showing the hydride and aliphatic regions for the reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with *m*-difluorobenzene at 60 °C.

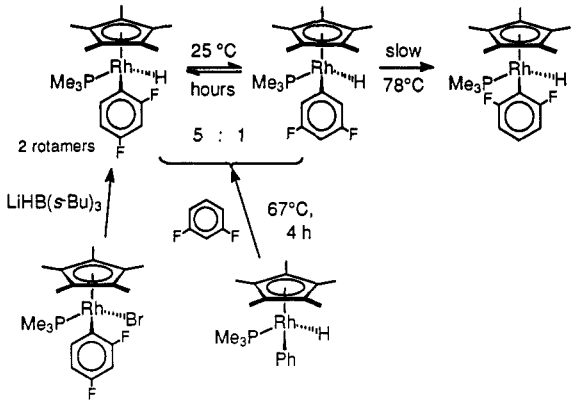
$(PMe_3)(2,4\text{-}C_6H_3F_2)H$ (two rotameric isomers), and $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)H$. Consistent with this, the low temperature $^{31}P\{^1H\}$ NMR spectrum (−60 °C) also showed P–F coupling, giving rise to dd resonances for the 2,4-disubstituted isomers at δ 8.57 (J = 147.7, 9.3 Hz) and 10.52 (J = 155.2, 7.4 Hz) and a doublet of triplets (dt) for the 2,6-disubstituted isomer at δ 8.52 (J = 145.3, 9.6 Hz). The $^{31}P\{^1H\}$ NMR spectrum of the 3,5-disubstituted isomer showed a simple doublet due to rhodium coupling at δ 10.00 (J = 148.4 Hz).

In an effort to determine whether the above mixture represented a kinetic or thermodynamic product distribution, the reaction was repeated using a shorter thermolysis time. After heating a solution of 1 in *m*-difluorobenzene for 4 h at 67 °C, low temperature ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy revealed the presence of only $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)H$ and $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)H$ in a 5:1 ratio, with no evidence of $(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)H$. Continued thermolysis of these products in *m*-difluorobenzene at 78 °C for 20 h resulted in exclusive formation of $(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)H$, demonstrating that while formation of the 2,4- and 3,5-isomers is kinetically favored, the formation of the 2,6-isomer is thermodynamically favored.

Reaction of the mixture from the thermolysis with $m\text{-}C_6H_4F_2$ at 67 °C with $CHBr_3$ led to the formation of three new materials, identified as the difluorophenyl bromide complexes $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)Br$, $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)Br$, and $(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)Br$. Chromatography on silica plates using a 10:4:1 hexanes/CH_2Cl_2/THF mixture allowed the separation of the 2,4-disubstituted isomer from the 3,5- and 2,6-disubstituted isomers (see Experimental Section).

In order to examine the interconversion of the meta-disubstituted difluorophenyl complexes (*via* an η^2-arene complex[9]), $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)Br$ was converted to the corresponding hydride complex by treatment with $LiHB(s\text{-}Bu)_3$ at room temperature (see Experimental Section). Low temperature (−40 °C) ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy showed initial formation of only $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)H$ along with some $(C_5Me_5)Rh(PMe_3)H_2$ (~20%). After several hours at 25 °C, the 3,5-$C_6H_3F_2$ isomer grows in to the extent of ~20% of the 2,4-isomer. No spectroscopic evidence for $(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)$ was seen after 48 h at room temperature. Heating the solution at 67 °C overnight led to formation of a mixture of all four metal hydride products (Scheme 2), as seen in the thermal reaction of 1 with *m*-difluorobenzene.

Scheme 2. Isomerization of $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)H$



In order to reinforce the NMR assignments of the products for *o*-difluorobenzene and *m*-difluorobenzene, phenyl hydride 1 was reacted with 1,3,5-trifluorobenzene. Room temperature ^{1}H NMR spectra showed inequivalent aromatic hydrogens at δ 6.658 (t, $J_{F\text{-}H}$ = 7.9 Hz, 1 H) and δ 6.569 (t, $J_{F\text{-}H}$ = 7.9 Hz, 1 H), each coupled to two fluorine atoms, and the hydride resonance appeared as a ddd pattern at δ −12.734 ($J_{P\text{-}H}$ = 51.2, $J_{Rh\text{-}H}$ = 25.6 Hz, $J_{F\text{-}H}$ = 7.9 Hz). A $^{31}P\{^1H\}$ NMR spectrum revealed a doublet of triplets at δ 5.18 ($J_{Rh\text{-}P}$ = 146.1, $J_{F\text{-}P}$ = 10.2 Hz), demonstrating that the PMe_3 ligand is coupled to both *o*-fluorines. This observation is consistent with the assignments made for the low temperature spectrum of $(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)H$ from the *m*-difluorobenzene reaction (*vide supra*).

Reaction of the product mixture with $CHBr_3$ gave the bromide complex $(C_5Me_5)Rh(PMe_3)(2,4,6\text{-}C_6H_2F_3)Br$ which again showed inequivalent aromatic ^{1}H NMR resonances at δ 6.628 (t, $J_{F\text{-}H}$ = 8.6 Hz, 1 H) and δ 6.500 (t, $J_{F\text{-}H}$ = 8.6 Hz, 1 H). Only one P–F coupling was seen in the $^{31}P\{^1H\}$ NMR spectrum, giving a dd resonance at δ 2.56 ($J_{Rh\text{-}P}$ = 144.7, $J_{F\text{-}P}$ = 24.5 Hz).

In an attempt to measure the barrier for loss of $aryl_F$ from $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$, the complex was dissolved in C_6D_6 and the rate of formation of $(C_5Me_5)Rh(PMe_3)(C_6D_5)D$ monitored by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy at 74 °C. $^{31}P\{^1H\}$ NMR spectra obtained from 23–115 h showed the expected formation of $(C_5Me_5)Rh(PMe_3)(C_6D_5)D$ at δ 7.42 (dt, $J_{Rh\text{-}P}$ = 155, $J_{D\text{-}P}$ = 7 Hz) and a concomitant decrease in the concentration of $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$ (see Figure 2). However, spectra obtained after longer reaction times revealed the growth of additional products, identified as metal deuterides by the characteristic small 1:1:1 triplet coupling ($J_{D\text{-}P}$ = 7 Hz). In addition, ^{1}H NMR spectroscopy showed a decrease in the relative intensity of the product C_5Me_5 resonance at δ 1.736 (s) compared to the product PMe_3 resonance at δ 0.881 (br d, $J_{P\text{-}H}$ = 9 Hz). ^{2}H NMR spectroscopy confirmed the presence of deuterated C_5Me_5 material at δ 1.70 (s). After 700 h a family of resonances could be identified, each successively shifted by ~34 Hz to higher field, all exhibiting the same dt pattern and identical coupling constants. These products were

(9) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 686–687.

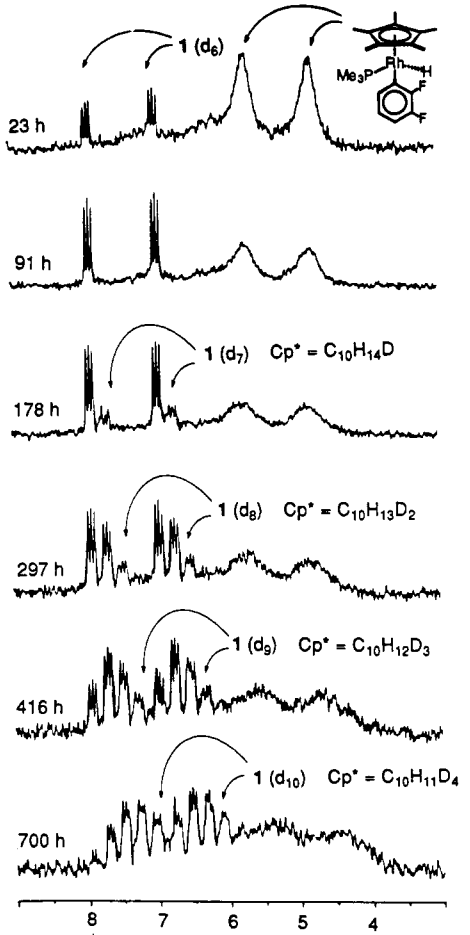


Figure 2. ^{31}P NMR spectrum (162 MHz) for the reaction of $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$ with C_6D_6 at 74 °C.

assigned as isotopomers of $(C_5Me_5)Rh(PMe_3)(C_6D_5)D$ which had undergone progressive H/D exchange at the C_5Me_5 methyl groups. The mechanism by which deuterium exchange takes place is not yet known.[10] In addition, the broad resonance observed in the $^{31}P\{^1H\}$ NMR spectrum for $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$ became even broader and was also shifted to slightly higher field (by ~0.3 ppm), presumably also due to deuterium incorporation in the C_5Me_5 ligand.

X-ray Structures of $(C_5Me_5)Rh(PMe_3)(aryl_F)Br$ Derivatives. Crystal structures of the bromide complexes $(C_5Me_5)Rh(PMe_3)(aryl_F)Br$ were obtained for the 2,3-$C_6H_3F_2$, 2,4-$C_6H_3F_2$, and 2,4,6-$C_6H_2F_3$ derivatives (Figures 3–5). All three materials crystallized in the monoclinic space group $C2/c$, with the 2,4-difluoro derivative also producing crystals in the monoclinic space group $P2_1/c$. For the trio of $C2/c$ structures, nearly identical unit cells and isomorphous packing were found (see Tables 1–5), indicating that fluorine substituents on the phenyl ring do not significantly affect the packing for molecules of this type. Comparison of the $P2_1/c$ crystal data for $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)Br$ with the parent phenyl bromide complex $(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$[11] also shows

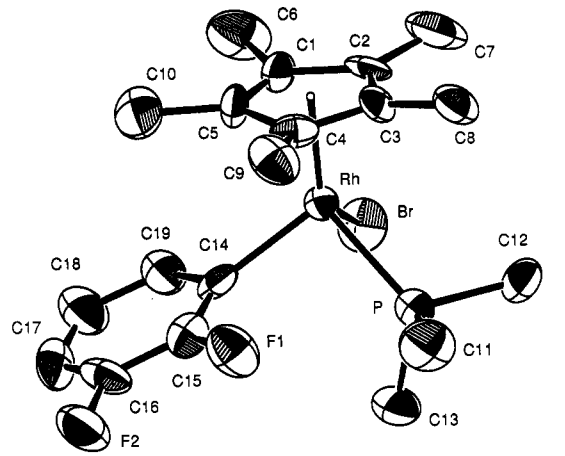


Figure 3. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)Br$, space group $C2/c$. Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

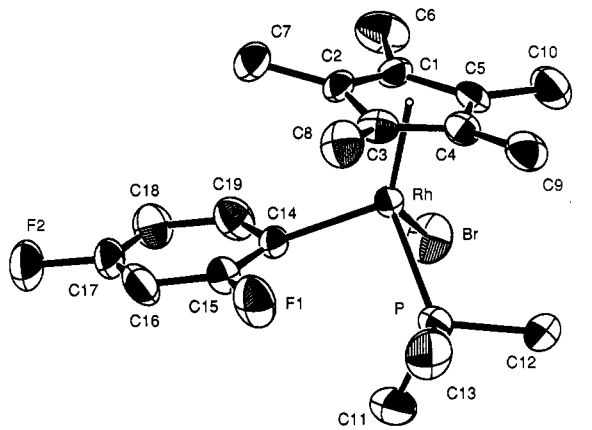


Figure 4. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)Br$, space group $C2/c$. Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

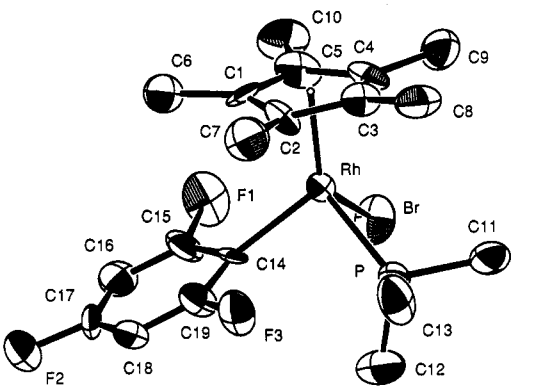


Figure 5. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(2,4,6\text{-}C_6H_2F_3)Br$, space group $C2/c$. Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

similar cell constants and isomorphous packing. Apparently, the crystal packing energies in the two space groups observed for $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)Br$ are comparable, allowing both forms to crystallize from the same solution. Comparison of the $C2/c$ structures with that of $(C_5Me_5)Rh(PMe_3)(C_6F_5)Cl$ shows that they too have similar cell constants and isomorphous packing.[8]

Structural features of the three compounds are not unusual (Table 6). The Rh–C_{ipso} bond length varies

(10) A similar observation was made on prolonged irradiation of either $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ or $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ in C_6D_6. The incorporation of deuterium into the C_5Me_5 ligand in the product $(C_5Me_5)Rh(PMe_3)(C_6D_5)D$ was demonstrated by ^1H and ^2H NMR spectroscopy, and by mass spectrometry of the brominated product, which showed ^2H incorporation only into the $(C_5Me_5)Rh(PMe_3)^+$ fragment.

(11) Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376–2388.

(12) Perutz, R. N.; Belt, S. T.; McCamley, A.; Whittlesey, M. K. *Pure Appl. Chem.* **1990**, *62*, 1539–1545.

Table 1. Summary of Crystallographic Data for $(C_5Me_5)Rh(PMe_3)$(polyfluorophenyl)Br Compounds

cryst param	2,3-difluoro	2,4-difluoro	2,4-difluoro	2,4,6-trifluoro
chemical formula	$RhBrPF_2C_{19}H_{27}$	$RhBrPF_2C_{19}H_{27}$	$RhBrPF_2C_{19}H_{27}$	$RhBrPF_3C_{19}H_{26}$
fw	507.2	507.2	507.2	525.2
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group (No.)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
Z	8	8	4	8
a, Å	14.071(9)	14.073(8)	9.401(6)	14.263(9)
b, Å	9.640(5)	9.505(3)	11.595(4)	9.492(2)
c, Å	30.774(12)	30.910(10)	18.809(8)	30.917(17)
β, deg	97.48(4)	97.30(5)	91.38(4)	97.99(2)
vol, Å^3	4139(7)	4101(5)	2049(3)	4145(6)
ρ_{calc}, g cm^{-3}	1.63	1.54	1.64	1.68
cryst dimens, mm				
temp, °C	−20	−20	−20	−20
	Measurement of Intensity Data			
$2\theta/\omega$ scan range, deg	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
2θ range, deg	4–44	4–44	4–44	4–44
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of data collected	2845	2818	2860	2852
no. of unique data $F^2 > 3\sigma(F^2)$	1393	2051	1500	1751
no. of params varied	217	217	217	226
μ, cm^{-1}	28.16	28.42	28.43	28.22
systematic absences	hkl, $h+k$ odd $h0l$, l odd	hkl, $h+k$ odd $h0l$, l odd	$0k0$, k odd $h0l$, l odd	hkl, $h+k$ odd $h0l$, l odd
abs cor	differential	differential	differential	differential
range of transm factors	0.75–1.16	0.84–1.34	0.68–1.22	0.80–1.33
equiv data	$0kl = 0k\bar{l}$	$0kl = 0k\bar{l}$	$0kl = 0k\bar{l}$	$0kl = 0k\bar{l}$
agreement between equiv data (F_o)	0.175	0.097	0.046	0.25
$R(F_o)$	0.0465	0.0429	0.0590	0.0710
$R_w(F_o)$	0.0488	0.0602	0.0645	0.0851
goodness of fit	1.35	2.73	2.09	3.28

Table 2. Positional Parameters and B_{eq} for $(C_5Me_5)Rh(PMe_3)$(2,3-difluorophenyl)Br ($C2/c$)

atom	x	y	z	B_{eq} (Å^2)
Rh	0.26512(7)	0.0588(1)	0.13089(4)	2.57(5)
Br	0.1633(1)	−0.0842(2)	0.17697(5)	4.80(9)
P	0.2855(3)	0.2116(4)	0.1877(1)	3.5(2)
F(1)	0.2141(6)	0.3830(9)	0.0985(3)	5.3(5)
F(2)	0.0675(6)	0.482(1)	0.0457(3)	6.2(5)
C(1)	0.299(1)	−0.119(2)	0.0905(5)	3.4(7)
C(2)	0.373(1)	−0.112(1)	0.1280(5)	3.2(7)
C(3)	0.4198(8)	0.018(2)	0.1258(4)	3.0(7)
C(4)	0.3731(9)	0.093(1)	0.0883(5)	3.2(7)
C(5)	0.302(1)	−0.000(2)	0.0663(5)	3.3(7)
C(6)	0.237(1)	−0.245(2)	0.0782(6)	6(1)
C(7)	0.398(1)	−0.223(2)	0.1606(6)	6(1)
C(8)	0.5087(8)	0.067(2)	0.1536(5)	3.9(7)
C(9)	0.410(1)	0.227(2)	0.0708(5)	4.8(8)
C(10)	0.246(1)	0.031(2)	0.0222(5)	6(1)
C(11)	0.352(1)	0.372(2)	0.1835(5)	5.6(9)
C(12)	0.3456(9)	0.132(2)	0.2360(4)	4.3(7)
C(13)	0.176(1)	0.273(2)	0.2054(5)	5.4(9)
C(14)	0.144(1)	0.155(2)	0.0997(4)	3.3(7)
C(15)	0.141(1)	0.291(2)	0.0862(5)	3.7(8)
C(16)	0.062(1)	0.344(2)	0.0570(5)	4.4(9)
C(17)	−0.013(1)	0.263(2)	0.0421(5)	5(1)
C(18)	−0.011(1)	0.127(2)	0.0549(6)	6(1)
C(19)	0.065(1)	0.076(2)	0.0839(5)	4.2(7)

Table 3. Positional Parameters and B_{eq} for $(C_5Me_5)Rh(PMe_3)$(2,4-difluorophenyl)Br ($C2/c$)

atom	x	y	z	B_{eq} (Å^2)
Rh	0.26796(4)	0.06430(6)	0.13152(2)	2.10(3)
Br	0.16725(7)	−0.0768(1)	0.17785(3)	4.62(5)
P	0.2880(2)	0.2222(2)	0.18708(7)	3.2(1)
F(1)	0.2152(4)	0.3904(5)	0.0974(2)	5.0(3)
F(2)	−0.0772(4)	0.3148(7)	0.0116(2)	6.4(3)
C(1)	0.3036(5)	−0.1187(8)	0.0925(2)	2.6(3)
C(2)	0.3055(5)	0.0013(9)	0.0668(2)	2.5(3)
C(3)	0.3748(6)	0.0976(8)	0.0886(3)	3.0(4)
C(4)	0.4224(5)	0.0244(8)	0.1262(3)	2.7(4)
C(5)	0.3790(5)	−0.1053(8)	0.1290(3)	2.6(3)
C(6)	0.2433(7)	−0.248(1)	0.0833(4)	4.9(5)
C(7)	0.2465(6)	0.025(1)	0.0233(3)	4.0(4)
C(8)	0.4072(7)	0.232(1)	0.0702(3)	4.4(5)
C(9)	0.5112(6)	0.0766(9)	0.1528(3)	3.9(4)
C(10)	0.4060(7)	−0.2159(9)	0.1630(3)	4.4(4)
C(11)	0.1783(7)	0.287(1)	0.2047(3)	5.2(5)
C(12)	0.3499(7)	0.143(1)	0.2362(3)	4.4(4)
C(13)	0.3581(8)	0.382(1)	0.1822(3)	5.8(5)
C(14)	0.1472(5)	0.1647(8)	0.1005(2)	2.6(4)
C(15)	0.1420(6)	0.2988(8)	0.0846(3)	3.1(4)
C(16)	0.0679(7)	0.353(1)	0.0550(3)	4.2(5)
C(17)	−0.0040(7)	0.264(1)	0.0419(3)	4.4(5)
C(18)	−0.0084(6)	0.130(1)	0.0559(3)	4.7(5)
C(19)	0.0677(6)	0.0831(9)	0.0848(3)	4.1(4)

between 2.02 and 2.08 Å, and the plane of the phenyl ring is tilted roughly 12° from the Rh–C vector in the direction away from the phosphine ligand. Packing diagrams reveal no apparent interactions between independent molecules in the unit cell. The orientation of the Rh–Br vector for the 2,3-$C_6H_3F_2$ and 2,4-$C_6H_3F_2$ derivatives is roughly antiperiplanar to the *o*-fluorine substituent, with dihedral angles for the planes defined by the phenyl ring and (Br, Rh, C_{14}) of ~137°.

Photochemical Reactions of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ with Polyfluorinated Arenes. In this series of studies, solutions of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ (**2**) in fluorinated arene solvent were irradiated with Pyrex filtered light for 40 h. **2** is known to lose ethylene under these conditions, and consequently, this procedure served as a convenient method for generating the coordinatively unsaturated species $[(C_5H_5)Rh(PMe_3)]$ which reacted rapidly with the fluoroarene.[12] In all cases in which the arene contains an aryl C–H bond, oxidative addition of the bond was shown to generate polyfluorophenyl hydride products by ^1H, $^{31}P\{^1H\}$, ^{19}F, and $^{13}C\{^1H\}$ NMR spectroscopies (see Scheme 3). The products were further characterized by conversion to the bromo derivatives by reaction with bromoform and observation of the expected parent ion for $(C_5H_5)Rh(PMe_3)(aryl_F)Br$ in the mass spectrum (see Experimental Section).

Table 4. Positional Parameters and B_{eq} for $(C_5Me_5)Rh(PMe_3)(2,4\text{-difluorophenyl})Br$ ($P2_1/c$)

atom	x	y	z	B_{eq} (Å^2)
Rh	0.1614(1)	−0.2276(1)	−0.13587(6)	2.86(6)
Br	0.0195(2)	−0.2826(2)	−0.2462(1)	6.9(1)
P	0.3286(5)	−0.1664(4)	−0.2115(2)	4.5(2)
F(1)	0.474(1)	−0.325(1)	−0.0839(5)	6.4(6)
F(2)	0.403(1)	−0.722(1)	−0.0890(5)	6.9(6)
C(1)	−0.017(2)	−0.226(2)	−0.0647(8)	4.0(8)
C(2)	−0.012(2)	−0.114(1)	−0.0964(8)	3.6(9)
C(3)	0.118(2)	−0.066(1)	−0.0780(7)	3.0(8)
C(4)	0.196(2)	−0.147(2)	−0.0349(9)	4(1)
C(5)	0.106(2)	−0.241(2)	−0.0228(7)	4(1)
C(6)	−0.147(2)	−0.303(2)	−0.069(1)	6(1)
C(7)	−0.127(2)	−0.061(2)	−0.143(1)	6(1)
C(8)	0.165(2)	0.057(1)	−0.0923(9)	5(1)
C(9)	0.334(2)	−0.124(2)	0.0066(9)	7(1)
C(10)	0.132(2)	−0.341(2)	0.028(1)	6(1)
C(11)	0.264(2)	−0.057(2)	−0.273(1)	6(1)
C(12)	0.397(2)	−0.277(2)	−0.270(1)	8(1)
C(13)	0.487(2)	−0.099(2)	−0.172(1)	8(1)
C(14)	0.248(1)	−0.387(1)	−0.1301(7)	3.1(8)
C(15)	0.387(2)	−0.415(2)	−0.1007(9)	4(1)
C(16)	0.443(2)	−0.522(2)	−0.0865(9)	4(1)
C(17)	0.356(2)	−0.613(2)	−0.103(1)	5(1)
C(18)	0.224(2)	−0.599(2)	−0.132(1)	5(1)
C(19)	0.177(2)	−0.488(2)	−0.1447(9)	5(1)

Table 5. Positional Parameters and B_{eq} for $(C_5Me_5)Rh(PMe_3)(2,4,6\text{-difluorophenyl})Br$ ($C2/c$)

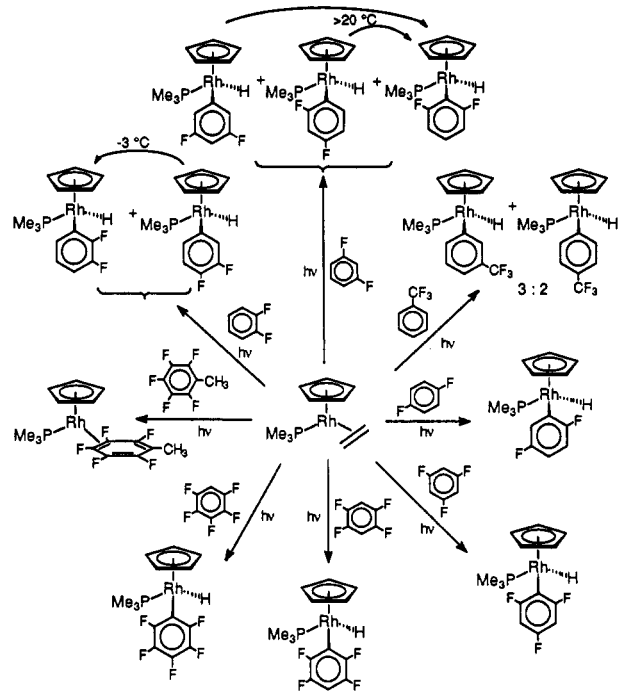
atom	x	y	z	B_{eq} (Å^2)
Rh	0.26903(8)	0.0625(1)	0.13097(4)	2.15(5)
Br	0.1743(1)	−0.0690(2)	0.18180(7)	4.8(1)
P	0.2935(3)	0.2276(4)	0.1852(2)	3.2(2)
F(1)	0.0726(7)	−0.059(1)	0.0867(4)	5.6(6)
F(2)	−0.0740(7)	0.322(1)	0.0108(4)	6.4(7)
F(3)	0.2132(7)	0.3900(9)	0.1017(4)	4.6(5)
C(1)	0.299(1)	−0.020(1)	0.0664(6)	2.7(8)
C(2)	0.3673(9)	0.089(1)	0.0846(6)	2.6(7)
C(3)	0.423(1)	0.029(2)	0.1242(6)	3.0(8)
C(4)	0.380(1)	−0.101(2)	0.1317(7)	3.5(9)
C(5)	0.311(1)	−0.130(2)	0.0961(7)	4(1)
C(6)	0.240(1)	−0.009(2)	0.0239(7)	4(1)
C(7)	0.390(2)	0.220(2)	0.0621(7)	6(1)
C(8)	0.509(1)	0.093(2)	0.1486(7)	4(1)
C(9)	0.417(1)	−0.200(2)	0.1683(7)	5(1)
C(10)	0.254(1)	−0.270(2)	0.0905(8)	5(1)
C(11)	0.355(1)	0.151(2)	0.2342(7)	4(1)
C(12)	0.186(1)	0.301(2)	0.2025(8)	6(1)
C(13)	0.364(1)	0.383(2)	0.1798(8)	6(1)
C(14)	0.152(1)	0.164(1)	0.1000(5)	2.3(7)
C(15)	0.073(1)	0.083(2)	0.0790(6)	3.7(9)
C(16)	−0.002(1)	0.133(2)	0.0517(7)	4(1)
C(17)	−0.003(1)	0.271(2)	0.0406(6)	5(1)
C(18)	0.069(1)	0.360(2)	0.0572(6)	4(1)
C(19)	0.142(1)	0.301(2)	0.0851(6)	3.5(9)

Table 6. Selected Distances (Å) and Angles (deg) for $(C_5Me_5)Rh(PMe_3)(aryl_F)Br$ Complexes

	$aryl_F$			
	2,3-$C_6H_3F_2$	2,4-$C_6H_3F_2$ ($C2/c$)	2,4-$C_6H_3F_2$ ($P2_1/c$)	2,4,6-$C_6H_2F_3$
		Distances		
Rh–C14	2.07(1)	2.076(7)	2.02(2)	2.05(1)
Rh–Br	2.548(2)	2.525(2)	2.522(3)	2.539(2)
Rh–P	2.275(4)	2.271(2)	2.259(5)	2.285(5)
		Angles		
P–Rh–Br	86.9(1)	86.97(7)	85.6(1)	85.6(1)
P–Rh–C14	94.6(4)	93.5(2)	92.1(4)	93.0(4)
Br–Rh–C14	90.6(4)	91.2(2)	90.9(4)	92.8(4)
Rh–C14–C15	124(1)	126.8(6)	126(1)	120(1)
Rh–C14–C19	119(1)	118.5(6)	125(1)	130(1)

Irradiation of **2** in pentafluorobenzene at ambient temperature gave a single product $(C_5H_5)Rh(PMe_3)(C_6F_5)H$ whose ^{19}F NMR spectrum showed a downfield

Scheme 3. Photochemical Reaction of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ with Fluoroarenes at Room Temperature



resonance at δ −104.42 (d, J_{F-F} = 33.0 Hz, 2 F_{ortho}) that could be assigned to the ortho fluorines. Two upfield resonances were detected at δ −164.40 (t, J_{F-F} = 19.1 Hz, 1 F_{para}) and −165.30 (m, 2 F_{meta}). The $^{31}P\{^1H\}$ NMR spectrum showed a doublet of binomial sextets (δ 14.30, J_{Rh-P} = 141.1, $J_{F-P,\ app}$ = 1.6 Hz). The sextet can be understood as an effect of virtual coupling to all five fluorine nuclei since $J_{F-F} \gg J_{P-F}$. The ^1H NMR spectrum showed a hydride at −12.80 (dd, J_{P-H} = 40.7, J_{Rh-H} = 23.7 Hz, 1 H). On cooling a solution in toluene-d_8 to −83 °C, the ^{19}F NMR spectra reveal that the rotation of the C_6F_5 ring is frozen out and the *o*-fluorine resonances are split into two sets centered at δ −104.95 and −107.64 ($\Delta\nu$ = 763 Hz, ν_0 = 282.4 MHz). Similarly, the *m*-fluorine resonances split into two sets centered at δ −164.95 and −166.23 ($\Delta\nu$ = 356 Hz). The coalescence temperature for the *o*-fluorine resonances is estimated as −33 °C and for the *m*-fluorine resonances as −45 °C.

Reaction of **2** with 1,2,4,5-tetrafluorobenzene also gave a single product identified as $(C_5H_5)Rh(PMe_3)(2,3,5,6\text{-}C_6F_4H)H$. The ^{19}F NMR spectrum showed a downfield resonance at δ −106.31 (dt, J_{app} = 31, 11 Hz, 2 F_{ortho}) and an upfield resonance at δ −142.58 (t, J_{app} = 12 Hz, F_{meta}). The $^{31}P\{^1H\}$ NMR spectrum showed a doublet of quintets at δ 14.17 (J_{Rh-P} = 142.1, $J_{F-P,\ app}$ = 1.3 Hz), again revealing the effects of virtual coupling.

Reaction of **2** with 1,3,5-trifluorobenzene again gave just one product, $(C_5H_5)Rh(PMe_3)(2,4,6\text{-}C_6H_2F_3)H$. Similarly, reaction with *p*-difluorobenzene gave $(C_5H_5)Rh(PMe_3)(2,5\text{-}C_6H_3F_2)H$; with *o*-$C_6H_4F_2$ $(C_5H_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$ was obtained, and with *m*-$C_6H_4F_2$ the product was $(C_5H_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)H$. The origin of the stereoselectivity of the last two reactions was investigated by photolysis at −28 °C (*o*-$C_6H_4F_2$) and −38 °C (*m*-$C_6H_4F_2$), followed by the acquisition of ^{31}P NMR spectra in the neat arene solvent at those temperatures. The reaction with *o*-$C_6H_4F_2$ yielded two Rh(III) products in a ratio of 3.3:1 (δ 15.24 and 15.14). On warming, the minor product

converts to the major one between −8 and −3 °C. The minor product is assigned as the Rh(3,4-$C_6H_3F_2$)H isomer, the major one as Rh(2,3-$C_6H_3F_2$)H. The low temperature reaction with *m*-$C_6H_4F_2$ yielded three Rh(III) products in the ratios 2.2:2.2:1 (δ 15.44, 15.36, and 14.85). The products with resonances at δ 15.36 and 14.85 convert over hours to the third product at ca. 20 °C. The unstable products are assigned as the Rh(2,4-$C_6H_3F_2$)H and Rh(3,5-$C_6H_3F_2$)H isomers; the stable one is Rh(2,6-$C_6H_3F_2$)H.

The photolysis of **2** in (trifluoromethyl)benzene showed the formation of two of the three possible C–H insertion products in a 3:2 ratio. The ^{19}F NMR spectrum showed two singlets at δ −61.69 and −62.12. The ^1H NMR spectrum of the major isomer showed aromatic resonances at δ 8.03 (s), 7.68 (d, J_{H-H} = 7.4 Hz), 7.23 (d, J_{H-H} = 6.8 Hz), and 6.83 (t, J_{H-H} = 7.6 Hz) of area 1 H each, plus C_5H_5, PMe_3, and hydride resonances. The minor isomer was more symmetrical, displaying aromatic resonances at δ 7.57 (d, J_{H-H} = 7.6 Hz, 2 H) and 7.21 (d, J_{H-H} = 6.5 Hz, 2 H). Consequently, the major and minor products were assigned as the *m*- and *p*-C–H insertion adducts (C_5H_5)Rh(PMe_3)(3-$C_6H_4CF_3$)H and (C_5H_5)Rh(PMe_3)(4-$C_6H_4CF_3$)H, respectively.

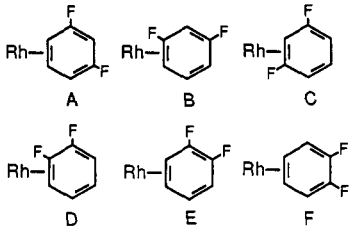
Insertion into the benzylic C–H bonds of pentafluorotoluene is expected to yield thermally unstable products,[3] but this ligand should be capable of forming η^2-arene complexes like C_6F_6,[4,7] or less likely of undergoing C–F activation reactions. On irradiation of a solution of **2** in pentafluorotoluene, no metal hydride resonances were observed in the ^1H NMR spectrum, although a single new product was formed with a C_5H_5 resonance at δ 4.51, a PMe_3 resonance at 0.90 (dq, J_{P-H} = 10.4 Hz, J_{Rh-H} = J_{F-H} = 0.9 Hz), and a methyl resonance at 1.64 (m). The ^{19}F NMR spectrum showed five distinct multiplet resonances of equal area at δ −134.48, −159.91, −160.83, −161.14, and −161.72, indicating an asymmetric binding of the arene. The $^{31}P\{^1H\}$ NMR spectrum showed a doublet of triplets at δ 3.51 with a large Rh–P coupling constant (J_{Rh-P} = 198 Hz, J_{F-P} = 56 Hz) consistent with a Rh(I) complex. The above data support the formulation of the product as an η^2-$C_6F_5CH_3$ complex with the arene bound through the 3,4 double bond (C_5H_5)Rh(PMe_3)(3,4-η^2-$C_6F_5CH_3$) (see Scheme 3, compare with (C_5H_5)Rh(PMe_3)(η^2-C_6F_6)[4] and (C_5Me_5)Rh(PMe_3)(η^2-C_6F_6)[8]).

Discussion

It is revealing to compare the behavior of the [(C_5H_5)Rh(PMe_3)] and [(C_5Me_5)Rh(PMe_3)] fragments. Both react with fluorobenzenes $C_6H_{6-x}F_x$ (x = 1–5) to yield C–H activation products. Spectral features for the two sets of $aryl_F$ hydride derivatives display effects attributable to hindered rotation about the Rh–aryl bond when the bulkier C_5Me_5 ligand is employed. For the C_5H_5 series of compounds, the fast-exchange limit is observed at room temperature in all cases, as is evidenced by the observation of single resonances for F_{ortho}, F_{meta}, C_{ortho}, C_{meta}, H_{ortho}, and H_{meta} by ^{19}F, $^{13}C\{^1H\}$, and ^1H NMR spectroscopies. Whereas some of the C_5Me_5 complexes exhibited hydride H–F and P–F couplings of ca. 10 Hz in the NMR spectra, H–F splittings were absent from the C_5H_5 complexes and P–F couplings were reduced to 1–2 Hz. Since J_{F-F} now greatly exceeds J_{P-F}, virtual coupling effects determine that the ^{31}P resonances appear to be coupled equally to several fluorine nuclei.

The C_5Me_5 derivatives are all close to the coalescence temperature (T_c) at 0 °C and display broad room temperature ^1H and $^{31}P\{^1H\}$ NMR spectra due to hindered rotation about the Rh–C_{ipso} bond. Cooling the solutions to −40 °C freezes out this rotational process and allows the observation of (hydride) H–F_{ortho} and P–F_{ortho} couplings. On the basis of the ^1H NMR hydride chemical shift differences ($\Delta\nu$) and coalescence temperatures ($T_c \sim 0$ °C), barriers to rotation $\Delta G^{\ddagger}_{rot}$ for (C_5Me_5)Rh(PMe_3)(2,3-$C_6H_3F_2$)H, (C_5Me_5)Rh(PMe_3)(2,4-$C_6H_3F_2$)H and (C_5Me_5)Rh(PMe_3)(2,5-$C_6H_3F_2$)H were calculated. All fall within the range 13.3–13.5 kcal/mol, demonstrating that the electronic effect on rotational barriers for a second fluorine in the 3-, 4-, or 5-position of the phenyl ring is minimal. Interestingly, when two *o*-fluorine substituents are present, as in the 2,6-difluorophenyl and 2,4,6-trifluorophenyl derivatives, the hydride shows an observable coupling to one F_{ortho} nucleus, while the P nucleus shows coupling to both F_{ortho} nuclei. In contrast, the halide complexes (C_5Me_5)Rh(PMe_3)($aryl_F$)X (X = Br, Cl, F) show coupling of the ^{31}P nucleus to only one F_{ortho} nucleus (see also ref 8). The internal rotation of the fluoroarene may also be frozen out for the C_5H_5 complexes. ^{19}F NMR spectra of (C_5H_5)Rh(PMe_3)(C_6F_5)H allow independent estimates of the barrier to rotation to be obtained from the coalescence of the *o*-fluorine resonances (10.4 kcal/mol) and *m*-fluorine resonances (10.2 kcal/mol).

Chart 1



A common feature to both fragments is their thermodynamic selectivity for activation of the C–H bond adjacent to the aryl–F bond. With 1,2-difluorobenzene both [(C_5H_5)Rh(PMe_3)] and [(C_5Me_5)Rh(PMe_3)] have a thermodynamic preference to activate the C–H bond adjacent to fluorine, giving (C_5R_5)Rh(PMe_3)(2,3-$C_6H_3F_2$)H. Both fragments also give (C_5R_5)Rh(PMe_3)(2,6-$C_6H_3F_2$)H as the thermodynamic product upon reaction with *m*-difluorobenzene. Similarly, the reaction of **1** with fluorobenzene results in the preferred activation of the ortho C–H bond. (Reactions of the other arenes can give only one possible C–H insertion product.) The basis for the thermodynamic selectivity of the reactions appears to be an inductive effect of the adjacent C–F bond. Selectivity for the ortho C–H bond has already been observed by Tolman *et al.* on thermolysis of Fe(dmpe)$_2$(naphthyl)H with fluorobenzene.[13] This observation may also have been based on thermodynamic selection.

The kinetic selectivity of these fragments is lower, however, giving a mixture of all possible C–H insertion products in the cases examined. Assuming η^2-coordination to precede C–H oxidative addition,[4,5] these observations suggest that there are only minor preferences for forming different η^2-complexes with the arene ring. For example, the observation of both (C_5Me_5)Rh(PMe_3)(2,4-$C_6H_3F_2$)H and (C_5Me_5)Rh(PMe_3)(3,5-$C_6H_3F_2$)H as kinetic products in the reaction of *m*-difluorobenzene with **1** would indicate that η^2-coordination as indicated by A or B in Chart 1 is

(13) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742–1751.

preferred over C. On the basis of the known stabilization effects of fluorine substitution on the formation of (η^2-C_6F_6) and (3,4-η^2-$C_6F_5CH_3$) complexes, one might have anticipated a preference for coordination at site B or C, as such complexes are thought to derive their stability from their resemblance to electron-withdrawing alkenes with some additional stablization from interaction between F and C–H bonds of the PMe_3 ligand [see structure of $(C_5H_5)Rh(PMe_3)(\eta^2\text{-}C_6F_6)$].[8] No such kinetic preference is observed, however. Similarly, reaction of either [(C_5Me_5)Rh(PMe_3)] or [(C_5H_5)Rh(PMe_3)] with *o*-difluorobenzene at low temperature gives both possible C–H insertion products as kinetic products, again indicating that η^2-coordination can occur at either sites D, E, or F.

Reduction of $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)Br$ with $LiHB(s\text{-}Bu)_3$ at 25 °C gives initially only $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)H$. Equilibration with $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)H$ occurs slowly over several hours at 25 °C, indicating that these isomers are of comparable free energy. Heating to 78 °C is required to effect migration past the fluorine to give the thermodynamically preferred 2,6-isomer. The observation of an equilibrium between $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)H$ and $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)H$ can be interpreted in terms of comparable inductive effects of 3,5 substitution vs 2,4 substitution.

There is no evidence that precoordination through a fluorine lone pair plays any role in these reactions. The notion that F-coordination directs the site of activation is in accord with the observation of several cases of F-coordinated fluoroaryl groups[14] but seems less convincing considering the known stability of η^2-arene complexes of [(C_5R_5)Rh(PMe_3)].

We have now described stable η^2-arene complexes with $C_6F_5CH_3$ and C_6F_6 as well as polycyclic arenes.[4-8] In addition, equilibrium mixtures of aryl hydrides and η^2-arene complexes are formed with $p\text{-}C_6H_4(CF_3)_2$ and $m\text{-}C_6H_4(CF_3)_2$.[7] Considering these results, it might be thought surprising that no η^2-arene complexes are observed, even with C_6F_5H. On closer inspection, however, it fits well with the generalization made previously that the product distribution is determined by product bond strengths.[1d] The C–H bonds of fluoroarenes are considerably stronger than those of benzene;[15] it follows from Bryndza's correlation[16] that Rh–$aryl_F$ bonds must be considerably stronger than Rh–phenyl bonds. Thus, any stabilization of the η^2-arene complexes for fluoroarenes relative to benzene may be more than matched by stabilization of the fluoroaryl hydride relative to the phenyl hydride.

In the case of $C_6F_5CH_3$ only benzylic C–H bonds are present and the lability of the corresponding benzylic C–H activation products precludes their observation at ambient temperature. We do not yet know whether they are formed reversibly but convert to the thermodynamic product $(C_5H_5)Rh(PMe_3)(3,4\text{-}\eta^2\text{-}C_6F_5CH_3)$.

The H/D exchange reaction of the C_5Me_5 ring observed while attempting to measure the free energy barrier for loss of H–$aryl_F$ from $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$ was unexpected. This complication of a competitive reaction pathway rendered rate measurements unreliable. A rough estimate of $\Delta G^\ddagger$ for loss of H–$aryl_F$ based on the approximate half-life $t_{1/2} \sim 200$ h gives $\Delta G^\ddagger \sim 32.3$ kcal/mol. This value correlates well with kinetic measurements of reductive elimination for other disubstituted aryl hydride complexes.[17]

Conclusions

The thermally generated fragment [(C_5Me_5)Rh(PMe_3)] and the photochemically generated fragment [(C_5H_5)Rh(PMe_3)] both react with fluorinated aromatic hydrocarbons $aryl_F$ to yield the C–H activated products (C_5R_5)Rh(PMe_3)($aryl_F$)H when an aromatic C–H bond is present. Both systems show regiospecific formation of (C_5R_5)Rh(PMe_3)(2,3-$C_6H_3F_2$)H from the reaction with *o*-difluorobenzene. [(C_5Me_5)Rh(PMe_3)] also reacts regiospecifically with fluorobenzene to yield $(C_5Me_5)Rh(PMe_3)(2\text{-}C_6H_4F)H$. The reaction of **1** with *m*-difluorobenzene at 67 °C results in a kinetic mixture of all C–H activation products. More severe conditions are required to drive this reaction to the thermodynamic product of C–H activation ortho to both fluorine atoms. Isomerization of $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)H$ to $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)H$ is facile, while migration across the fluorine substituent to form $(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)H$ is much slower.

The C_5H_5 derivatives all show fast-exchange limit behavior by NMR spectroscopy at room temperature, while the C_5Me_5 analogs are near coalescence at room temperature and the fluxional process of Rh–$aryl_F$ ring rotation can be frozen out below −40 °C. The barrier to rotation, $\Delta G^\ddagger_{rot}$, is 10.3 kcal/mol for $(C_5H_5)Rh(PMe_3)(C_6F_5)H$. The corresponding barrier for the C_5Me_5 complex is ~13.5 kcal/mol and is not influenced by fluorine substituents in the 3-, 4-, or 5- position of the ring. Reaction with *m*-difluorobenzene gives only the 2,6-difluorophenyl C–H insertion product, with no other isomers being observed. Reaction of $(C_5H_5)Rh(PMe_3)$ with $C_6F_5CH_3$ yields an η^2-arene product, $(C_5H_5)Rh(PMe_3)(3,4\text{-}\eta^2\text{-}C_6F_5CH_3)$.

An unexpected H/D exchange reaction was encountered while attempting to measure the rate of arene loss from $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$ in C_6D_6 which progressively deuterates the methyl groups of the C_5Me_5 ligand by an as yet undetermined mechanism. Further studies are necessary in order to probe the mechanism of this unusual process.

Experimental Section

General Considerations. All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. Dri-lab. 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, THF-d_8, toluene-d_8, and cyclohexane-d_{12} were distilled under vacuum from dark purple solutions of benzophenone ketyl and stored in ampules with Teflon sealed vacuum line adapters. The preparations of (C_5Me_5)Rh(PMe_3)(Ph)H[3] and (C_5H_5)Rh(PMe_3)(C_2H_4)[18] have been previously reported. The fluorinated aromatic compounds were

(14) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89.
(15) Smart, B. E. *Mol. Struct. Energ.* **1986**, *3*, 141.
(16) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.
(17) Selmeczy, A. D.; Jones, W. D.; Osman, R.; Perutz, R. N. Manuscript in preparation.
(18) Werner, H.; Feser, R. *J. Organomet. Chem.* **1982**, *232*, 351–370.

purchased from Aldrich Chemical Co. and were stirred over sieves and vacuum distilled prior to use.

All ^1H NMR spectra were recorded on Bruker AMX400, MSL300, or WP200 NMR spectrometers. All ^1H and ^{13}C chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced using the chemical shifts of residual solvent resonances (benzene, δ 7.15; chloroform, δ 7.24; acetone, δ 2.04; THF, δ 3.58 and 1.78; toluene, δ 2.10; cyclohexane, δ 1.38). ^{19}F NMR spectra were referenced to external $CFCl_3$. ^{31}P NMR spectra were referenced to external H_3PO_4. ^1H spectra recorded at 400 MHz are reported to three decimal places, since 0.001 ppm corresponds to a resolution of 0.4 Hz, which represents the precision of the measurement rather than the accuracy obtained from sample to sample. Coupling assignments are indicated, where known. Other couplings are the apparent separations of the lines. All temperatures for variable temperature NMR spectroscopy were calibrated relative to the chemical shift differences in the NMR spectra of known standards (25–113 °C, 80% ethylene glycol in DMSO-d_6 −45 to +25 °C, 4% methanol in methanol-d_4). Analyses were obtained from Desert Analytics.

Photolysis of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ in Fluorinated Arene Solvents. All reactions were carried out using the following general procedure. A solution of $(C_5H_5)Rh(PMe_3)(C_2H_4)$ (20–30 mg, 0.073–0.11 mmol) in 1.0–2.0 mL of fluorinated arene solvent was irradiated in a Pyrex ampule fitted with a PTFE stopcock for ca. 40 h using a water filtered 200-W Hg Applied Photophysics lamp. The solvent was removed under vacuum and the residue taken up in CD_3CN and placed in an NMR tube. ^1H, ^{19}F, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker MSL 300 spectrometer in order to determine products. NMR data are summarized below in CD_3CN solvent.

Bromination of $(C_5H_5)Rh(PMe_3)(aryl_F)H$ Compounds. The general procedure employed is described here for $(C_5H_5)Rh(PMe_3)(C_6H_4CF_3)H$. A sample of $(C_5H_5)Rh(PMe_3)(C_6H_4CF_3)H$ was dissolved in 2 mL of THF and cooled to −78 °C. To this solution, 1 mL of a 25% solution of $CHBr_3$/THF was added dropwise down the side of the ampule to allow the solution to cool prior to reaction. The solution was allowed to warm slowly, resulting in a color change from dark brown to orange. The volatiles were removed under vacuum, and the red oily residue was dissolved in CH_2Cl_2, layered with hexane, and allowed to stand. The crystalline brominated product $(C_5H_5)Rh(PMe_3)(C_6H_4CF_3)Br$ was obtained by filtration and analyzed by mass spectroscopy, as summarized below.

NMR Spectroscopic Data for Complexes $(C_5H_5)Rh(PMe_3)(aryl_F)H$ and Mass Spectrometric Data for the Bromo Complexes. $(C_5H_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$. ^1H NMR (CD_3CN): δ 7.30 (m, 1 H), 6.70 (m, 2 H), 5.35 (s, 5 H), 1.38 (dd, J_{P-H} = 11.0 Hz, J_{Rh-H} = 0.9 Hz, 9 H), −13.47 (dd, J_{P-H} = 41.1, J_{Rh-H} = 28.3 Hz, 1 H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 142.48 (C_{ortho}), 121.99 (C_{meta}), 110.12 (C_{para}), 87.25 (t, J_{P-C} = J_{Rh-C} = 2.4 Hz, C_5H_5), 21.22 (d, J_{P-C} = 35.2 Hz, $P(CH_3)_3$). ^{19}F NMR (CD_3CN): δ −106.70 (d, J_{F-F} = 30.8 Hz, 1 F_{ortho}), −140.80 (d, J_{F-F} = 30.8 Hz, 1 F_{meta}). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 16.30 (δ, J_{Rh-P} = 148.0 Hz). Mass spec (quoted for ^{81}Br derivatives) (70 eV, *m/e*): 438 (M^+), 357 (M^+ − Br), 244 (M^+ − Br − $aryl_F$).

$(C_5H_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)H$. ^1H NMR (C_6D_6): δ 6.77 (m, 3 H), 5.10 (m, 5 H), 0.90 (dd, J_{P-H} = 10.9 Hz, J_{Rh-H} = 1.3 Hz, 9 H), −12.63 (dd, J_{P-H} = 42.2 Hz, J_{Rh-H} = 24.4 Hz, 1 H). ^{19}F NMR (C_6D_6): δ −76.64 (s, F_{ortho}). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 15.67 (dt, J_{Rh-P} = 147 Hz, J_{F-P} = 1.6 Hz).

$(C_5H_5)Rh(PMe_3)(2,5\text{-}C_6H_3F_2)H$. ^1H NMR (CD_3CN): δ 7.25 (m, 1 H), 6.69–6.57 (m, 2 H), 5.33 (s, 5 H) 1.40 (dd, J_{P-H} = 11.1 Hz, J_{Rh-H} = 1.1 Hz, 9 H), −13.57 (dd, J = 41.2, 28.4 Hz, 1 H). $^{13}C\{^1H\}$ NMR: δ 87.30 (s, C_5H_5), 21.2 (d, J_{P-C} = 35.7 Hz, $P(CH_3)_3$). ^{19}F NMR (CD_3CN): δ −88.10 (d, J_{F-F} = 13.8 Hz, 1 F_{ortho}), −124.57 (d, J_{F-F} = 10.7 Hz, 1 F_{meta}). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 14.56 (d, J_{Rh-P} = 148.0 Hz). Mass spec (70 eV, *m/e*): 438 (M^+), 357 (M^+ − Br), 244 (M^+ − Br − $aryl_F$).

$(C_5H_5)Rh(PMe_3)(2,4,6\text{-}C_6H_2F_3)H$. ^1H NMR (CD_3CN): δ 6.54 (m, 2 H), 5.35 (s, 5 H), 1.37 (dd, J_{P-H} = 11.0 Hz, J_{Rh-H} = 0.9 Hz, 9 H), −13.03 (dd, J_{P-H} = 41.7 Hz, J_{Rh-H} = 24.6 Hz, 1 H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 86.91 (d, J_{Rh-C} = 2.5 Hz, C_5H_5), 21.44 (dd, J_{P-C} = 34.2 Hz, J_{Rh-C} = 1.2 Hz, $P(CH_3)_3$). ^{19}F NMR (CD_3CN): δ −73.61 (s, 2 F_{ortho}), −121.07 (s, 1 F_{para}). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 14.73 (d, J_{Rh-P} = 144.0 Hz). Mass spec (70 eV, *m/e*): 456 (M^+), 375 (M^+ − Br), 244 (M^+ − Br − $aryl_F$).

$(C_5H_5)Rh(PMe_3)(2,3,5,6\text{-}C_6HF_4)H$. ^1H NMR (CD_3CN): δ 6.61 (m, 1 H), 5.39 (quin, J_{app} = 0.6 Hz, 5 H), 1.39 (dd, J_{P-H} = 11.2 Hz, J_{Rh-H} = 1.2 Hz, 9 H), −12.78 (dd, J_{P-H} = 41.0 Hz, J_{Rh-H} = 24.3 Hz, 1 H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 87.05 (t, J_{P-C} = J_{Rh-C} = 2.1 Hz, C_5H_5), 21.42 (d, J_{P-C} = 35.6 Hz, $P(CH_3)_3$). ^{19}F NMR (CD_3CN): δ −106.31 (dt, J_{app} = 31.4 Hz, 10.7 Hz, 1 F_{ortho}), −142.58 (t, J_{app} = 11.7 Hz, 1 F_{meta}). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 14.17 (dquin, J_{Rh-P} = 142.1 Hz, $J_{F-P,\ app}$ = 1.3 Hz). Mass spec (70 eV, *m/e*): 474 (M^+), 393 (M^+ − Br), 244 (M^+ − Br − $aryl_F$).

$(C_5H_5)Rh(PMe_3)(C_6F_5)H$. ^1H NMR (CD_3CN): δ 5.39 (q, J_{Rh-H} = J_{F-H} = 0.8 Hz, 5 H), 1.39 (dd, J_{P-H} = 11.2 Hz, J_{Rh-H} = 1.2 Hz, 9 H), −12.80 (dd, J_{P-H} = 40.7 Hz, J_{Rh-H} = 23.7 Hz, 1 H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 86.90 (t, J_{Rh-C} = J_{P-C} = 2.8 Hz, C_5H_5), 21.30 (dd, J_{P-C} = 35.5 Hz, J_{Rh-C} = 1.5 Hz, $P(CH_3)_3$). ^{19}F NMR (CD_3CN): δ −104.42 (d, J_{F-F} = 33.0 Hz, 2 F_{ortho}), −164.40 (t, J_{F-F} = 19.1 Hz, 1 F_{para}), −165.30 (m, 2 F_{meta}). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 14.30 (dsextets, J_{Rh-P} = 141.1 Hz, $J_{F-P,\ app}$ = 1.6 Hz). Mass spec (70 eV, *m/e*): 492 (M^+), 411 (M^+ − Br), 244 (M^+ − Br − $aryl_F$).

$(C_5H_5)Rh(PMe_3)(3\text{-}C_6H_4CF_3)H$. ^1H NMR (C_6D_6): δ 8.03 (s, 1 H), 7.68 (d, J_{H-H} = 7.4 Hz, 1 H), 7.23 (d, J_{H-H} = 6.8 Hz, 1 H), 6.83 (t, J_{H-H} = 7.6 Hz, 1 H), 4.96 (d, J_{Rh-H} = 1.2 Hz, 5 H), 0.78 (dd, J_{P-H} = 10.5 Hz, J_{Rh-H} = 1.2 Hz, 9 H), −13.74 (dd, J_{P-H} = 42.2 Hz, J_{Rh-H} = 30.8 Hz, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 88.03 (t, J_{Rh-C} = J_{P-C} = 2.8 Hz, C_5H_5), 21.50 (dd, J_{Rh-C} = 34.6 Hz, J_{P-C} = 1.9 Hz, $P(CH_3)_3$). ^{19}F NMR (C_6D_6): δ −61.69 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 13.20 (d, J_{Rh-P} = 154.1 Hz). Mass spec (70 eV, *m/e*, mixture of 3- and 4-isomers): 470 (M^+), 389 (M^+ − Br), 244 (M^+ − Br − $aryl_F$).

$(C_5H_5)Rh(PMe_3)(4\text{-}C_6H_4CF_3)H$. ^1H NMR (C_6D_6): δ 7.57 (d, J_{H-H} = 7.6 Hz, 2 H), 7.21 (d, J_{H-H} = 6.5 Hz, 1 H), 4.98 (d, J_{Rh-H} = 1.2 Hz, 5 H), 0.77 (dd, J_{P-H} = 10.5 Hz, J_{Rh-H} = 1.2 Hz, 9 H), −13.76 (dd, J_{P-H} = 42.2 Hz, J_{Rh-H} = 31.1 Hz, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 88.13 (t, J_{P-C} = J_{Rh-C} = 2.9 Hz, C_5H_5), 21.50 (dd, J_{P-C} = 34.6 Hz, J_{Rh-C} = 1.9 Hz, $P(CH_3)_3$). ^{19}F NMR (C_6D_6): δ −62.12 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 13.00 (d, J_{Rh-P} = 154.5 Hz).

NMR Spectroscopic Data for $(C_5H_5)Rh(PMe_3)(3,4\text{-}\eta^2\text{-}C_6F_5CH_3)$. ^1H NMR (C_6D_6): δ 4.51 (s, 5 H), 1.64 (m, 3 H), 0.90 (dq, J_{P-H} = 10.4, J_{Rh-H} = J_{F-H} = 0.9 Hz, 9 H). ^{19}F NMR (C_6D_6): δ −134.48 (m, 1 F), −159.91 (m, 1 F), −160.83 (m, 1 F), −161.14 (m, 1 F), −161.72 (m, 1 F). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 3.51 (dt, J_{Rh-P} = 198.1, J_{F-P} = 55.7 Hz).

Preparation of Fluorinated Aryl Hydride Complexes $(C_5Me_5)Rh(PMe_3)(aryl_F)H$. In a typical experiment, 25 mg of $(C_5Me_5)Rh(PMe_3)(Ph)Br$ (0.053 mmol) was converted to the phenyl hydride $(C_5Me_5)Rh(PMe_3)(Ph)H$ by a previously described procedure.[3] The phenyl hydride was isolated as a yellow oil and dissolved in 0.6–0.8 mL of fluorinated arene and heated at 67 °C overnight. The solutions darkened slightly to a golden color. Removal of the fluorinated solvent left a tan oil. Difficulty in crystallization of the small quantities of oil precluded obtaining elemental analyses.

Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with *m*-Difluorobenzene. $(C_5Me_5)Rh(PMe_3)(Ph)Br$ (25 mg, 0.053 mmol) was converted to the phenyl hydride $(C_5Me_5)Rh(PMe_3)(Ph)H$ by a previously described procedure.[3] The phenyl hydride was isolated as a yellow oil and dissolved in 0.8 mL of *m*-difluorobenzene and heated to 67 °C for 4 h. The volatiles were removed under vacuum, and toluene-d_8 was introduced. Low temperature ^1H and $^{31}P\{^1H\}$ NMR showed the presence of $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)H$ and $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)H$. The volatiles were removed under vacuum and the solid redissolved in 0.8 mL of *m*-difluorobenzene. The solution was heated to 78 °C for 20 h. The volatiles were removed under vacuum and the solid was dissolved in toluene-d_8. Low temperature ^1H and $^{31}P\{^1H\}$ NMR showed exclusive formation of $(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)H$.

Photolysis of $(C_5Me_5)Rh(PMe_3)H_2$ in *o*-Difluorobenzene at Low *T*. $(C_5Me_5)Rh(PMe_3)Br_2$ (25 mg, 0.053 mmol) was

converted to $(C_5Me_5)Rh(PMe_3)H_2$ using a previously published procedure.[3] The dihydride was dissolved in 0.37 mL of *o*-difluorobenzene and transferred into a resealable NMR tube. An additional 0.33 mL of THF-d_8 was introduced. Photolysis using a Pyrex filter for 400 min at −30 °C showed the formation of a 2:1 mixture of $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$/$(C_5Me_5)Rh(PMe_3)(3,4\text{-}C_6H_3F_2)H$ by low temperature NMR spectroscopy. When the sample was allowed to warm to room temperature, the 3,4-$C_6H_3F_2$ isomer was seen to disappear, leaving only the 2,3-isomer.

Spectroscopic Data for Complexes $(C_5Me_5)Rh(PMe_3)(Ar)H$. $(C_5Me_5)Rh(PMe_3)(2\text{-}C_6H_4F)H$. Rotamer 1: ^1H NMR (THF-d_8, −40 °C) δ 1.839 (s, 15 H), 1.205 (d, J_{P-H} = 11.2 Hz, 9 H), −13.685 (dd, J_{P-H} = 48.0, J_{Rh-H} = 32.0 Hz, 1 H); ^{31}P NMR (THF-d_8, −40 °C) δ 7.71 (dd, J_{Rh-P} = 148.4, J_{F-P} = 9.9 Hz). Rotamer 2: ^1H NMR (THF-d_8, −40 °C) δ 1.565 (s), 1.163 (d, J_{P-H} = 10.9 Hz, 9 H), −12.869 (ddd, J_{P-H} = 47.3, J_{Rh-H} = 29.5, J_{F-H} = 7.9 Hz, 1 H); ^{31}P NMR (THF-d_8, −40 °C) δ 7.12 (dd, J_{Rh-P} = 147.9, J_{F-P} = 10.2 Hz).

$(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$. Rotamer 1: ^1H NMR (toluene-d_8, −40 °C): δ 7.559 (d, J_{H-H} = 6.3 Hz, 1 H), 6.781 (m, 1 H), 6.714 (m, 1 H), 1.745 (d, J_{Rh-H} = 1.7 Hz, 15 H), 0.873 (d, J_{P-H} = 9.9 Hz, 9 H), −13.305 (dd, J_{P-H} = 48.0, J_{Rh-H} = 30.4 Hz, 1 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, −40 °C) δ 6.43 (dd, J_{Rh-P} = 147.6, J_{F-P} = 10.5 Hz). Rotamer 2: ^1H NMR (toluene-d_8, 233 K) δ 6.8–7.2 (obscured), 1.720 (s, 15 H), 0.732 (d, J_{P-H} = 9.9 Hz, 9 H), −12.373 (ddd, J_{P-H} = 51.4, J_{Rh-H} = 28.3, J_{F-H} = 10.4 Hz, 1 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, −40 °C) δ 8.19 (dd, J_{Rh-P} = 149.6, J_{F-P} = 10.5 Hz).

$(C_5Me_5)Rh(PMe_3)(3,4\text{-}C_6H_3F_2)H$. ^1H NMR (THF-d_8): δ 1.709 (s, 15 H), 1.040 (d, J_{P-H} = 8.8 Hz, 9 H), −13.528 (dd, J_{P-H} = 49.2, J_{Rh-H} = 25.6 Hz, 1 H). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 12.03, (d, J_{Rh-P} = 152.1 Hz).

$(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)H$. Rotamer 1: ^1H NMR (toluene-d_8, −40 °C): δ 7.656 (q, J = 6.0 Hz, 1 H), 6.6–6.9 (obscured), 1.751 (s, 15 H), 0.877 (d, J_{P-H} = 10.4 Hz, 9 H), −13.405 (dd, J_{P-H} = 47.6, J_{Rh-H} = 31.3 Hz, 1 H). $^{31}P\{^1H\}$ NMR (toluene-d_8, 213 K) δ 8.57 (dd, J_{Rh-P} = 147.7, J_{F-P} = 9.3 Hz). Rotamer 2: ^1H NMR (toluene-d_8) δ 6.6–6.9 (obscured), 1.725 (s, 15 H), 0.732 (d, J_{P-H} = 8.9 Hz, 9 H), −12.470 (ddd, J_{P-H} = 51.4, J_{Rh-H} = 28.6, J_{F-H} = 8.6 Hz, 1 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, −60 °C) δ 10.52 (dd, J_{Rh-P} = 155.2, J_{F-P} = 7.4 Hz).

$(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)H$. ^1H NMR (toluene-d_8) δ 6.6–6.9 (obscured), 1.636 (s, 15 H), 0.710 (d, J_{P-H} = 8.9 Hz, 9 H), −13.286 (dd, J_{P-H} = 47.6, J_{Rh-H} = 32.7 Hz, 1 H). $^{31}P\{^1H\}$ NMR (toluene-d_8, 213 K): δ 10.00 (d, J_{Rh-P} = 148.4 Hz).

$(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)H$. ^1H NMR (toluene-d_8, 233 K): δ 6.6–6.9 (obscured), 6.517 (t, J_{H-H} = 8.9 Hz, 1 H), 1.807 (s, 15 H), 0.862 (d, J_{P-H} = 10.4 Hz, 9 H), −12.540 (ddd, J_{P-H} = 50.6, J_{Rh-H} = 26.4, J_{F-H} = 8.9 Hz, 1 H). $^{31}P\{^1H\}$ NMR: (C_6D_6) δ 11.47 (dt, J_{Rh-P} = 145.8, J_{F-P} = 10.2 Hz); (toluene-d_8,) δ 8.52 (dt, J_{Rh-P} = 145.3, J_{F-P} = 9.6 Hz).

$(C_5Me_5)Rh(PMe_3)(2,5\text{-}C_6H_3F_2)H$. Rotamer 1: ^1H NMR (toluene-d_8, −40 °C) δ 7.622 (br d, J = 9.1 Hz, 1 H), 6.674 (m, 1 H), 6.568 (m, 1 H), 1.731 (s, 15 H), 0.895 (d, J = 10.2 Hz, 9 H), −13.489 (dd, 48.6, 30.9 Hz, 1 H). Rotamer 2: ^1H NMR (toluene-d_8, −40 °C) δ 7.2 (br, 1 H), 6.789 (br, 1 H), 6.433, (t, J = 6.1 Hz, 1 H), 1.770 (s, 15 H), 0.760 (d, J_{P-H} = 9.7 Hz), −12.432 (ddd, J_{P-H} = 45.8, J_{Rh-H} = 27.9 Hz, J_{F-H} = 8.6 Hz, 1 H).

$(C_5Me_5)Rh(PMe_3)(2,4,6\text{-}C_6H_2F_3)H$. ^1H NMR (C_6D_6) δ 6.658 (t, J_{F-H} = 7.9 Hz, 1 H), 6.569 (t, J_{F-H} = 7.9 Hz, 1 H), 1.777 (s, 15 H), 0.860 (d, J_{P-H} = 10.1 Hz, 9 H), −12.734 (ddd, J_{P-H} = 51.2, J_{Rh-H} = 25.6, J_{F-H} = 7.9 Hz, 1 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 5.18 (dt, J_{Rh-P} = 146.1, J_{F-P} = 10.2 Hz).

Preparation of Fluorinated Aryl Bromide Complexes $(C_5Me_5)Rh(PMe_3)(aryl_F)Br$. This procedure was used to convert the aryl hydride complexes to the air-stable bromo derivatives. To a benzene solution of $(C_5Me_5)Rh(PMe_3)(aryl_F)H$ was added several drops of $CHBr_3$. The solution immediately turned red. Removal of volatiles left an orange-red solid. Thin-layer chromatography on silica plates with 4% THF in CH_2Cl_2 led to isolation of the complexes $(C_5Me_5)Rh(PMe_3)(aryl_F)Br$ in moderate yields (20–60%).

Separation of Products from the *m*-Difluorobenzene Reaction. The mixture of products obtained from the reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with *m*-difluorobenzene was isolated as described above. Thin-layer chromatography of the mixture on silica plates with 1:4:10 THF/CH_2Cl_2/hexanes solution led to two orange bands. Scraping the leading edge of the first band and extracting with CH_2Cl_2 allowed isolation of $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)Br$. Scraping the second band and extracting with CH_2Cl_2 allowed isolation of a mixture of $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)Br$ and $(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)Br$.

Spectroscopic Data for Complexes $(C_5Me_5)Rh(PMe_3)(aryl_F)Br$. $(C_5Me_5)Rh(PMe_3)(2\text{-}C_6H_4F)Br$. ^1H NMR (C_6D_6): δ 8.576 (tq, J = 6.5, 1.7 Hz, 1 H), 6.981 (qt, J = 6.5, 1.7 Hz, 1 H), 6.940 (m, 1 H), 6.904 (qd, J = 7.6, 1.7 Hz, 1 H), 1.408 (d, J_{Rh-H} = 2.8 Hz, 15 H), 1.197 (d, J_{P-H} = 10.5 Hz, 9 H). ^{31}P NMR (C_6D_6): δ 2.29 (dd, J_{Rh-P} = 149.4, J_{F-P} = 12.5 Hz).

$(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)Br$. ^1H NMR ($CDCl_3$): δ 7.66 (m, 1 H), 6.71 (m, 2 H), 1.585 (d, J_{Rh-H} = 2.8 Hz, 15 H), 1.420 (d, J_{P-H} = 10.5 Hz, 9 H). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 7.81 (dd, J_{Rh-P} = 147.5, J_{F-P} = 11.7 Hz).

$(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)Br$. ^1H NMR (C_6D_6): δ 8.400 (q, J = 7.5 Hz, 1 H), 6.781 (dt, J = 8.6, 2.6 Hz, 1 H), 6.704 (dt, J = 8.8, 2.6 Hz, 1 H), 1.366 (d, J_{Rh-H} = 2.9 Hz, 15 H), 1.143 (d, J_{P-H} = 10.5 Hz, 9 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 2.12 (dd, J_{Rh-P} = 148.2, J_{F-P} = 11.5 Hz).

$(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)Br$. ^1H NMR (C_6D_6): δ 6.815 (q, J = 7.6 Hz, 2 H), 6.68 (buried m, 1 H), 1.277 (d, J_{Rh-H} = 2.2 Hz, 15 H), 0.959 (d, J_{P-H} = 10.5 Hz, 9 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.48 (d, J_{Rh-P} = 148.9 Hz).

$(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)Br$. ^1H NMR (C_6D_6): δ 6.804 (q, J = 6.5 Hz, 2 H), 6.550 (tt, J = 9.2, 2.4 Hz, 1 H), 1.431 (d, J_{Rh-H} = 2.9 Hz, 15 H), 1.298 (d, J_{P-H} = 10.8 Hz, 9 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 3.21 (dd, J_{Rh-P} = 145.8, J_{F-P} = 25.6 Hz).

$(C_5Me_5)Rh(PMe_3)(2,4,6\text{-}C_6H_2F_3)Br$. ^1H NMR (C_6D_6): δ 6.628 (t, J = 8.6 Hz, 1 H), 6.500 (t, J_{F-H} = 8.6 Hz, 1 H), 1.377 (d, J_{Rh-H} = 2.8 Hz, 15 H), 1.250 (d, J_{P-H} = 10.5 Hz, 9 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 2.56 (dd, J_{Rh-P} = 144.7, J_{F-P} = 24.5 Hz).

Preparation of $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)H$. $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)Br$ (10 mg, 0.02 mmol) was dissolved in 5 mL of THF. Then 0.5 mL of 1 M l-selectride (0.5 mmol) was added under a nitrogen atmosphere and the volatiles were removed under vacuum, leaving a gummy oil. The gum was allowed to stand for 1 h. Flash chromatography on silica gel using 3:1 hexanes/THF led to the isolation of a yellow solution. Removal of the solvent left a yellow oil. The oil was dissolved in THF-d_8 and examined by low temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, revealing $(C_5Me_5)Rh(PMe_3)(2,4\text{-}C_6H_3F_2)H$, $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3F_2)H$, and some $(C_5Me_5)Rh(PMe_3)H_2$. No spectroscopic evidence for $(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3F_2)$ was observed.

Kinetic Measurement of Reductive Elimination for $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)H$. $(C_5Me_5)Rh(PMe_3)(Ph)Br$ (20 mg, 0.042 mmol) was converted to the phenyl hydride 1 by a known procedure.[3] The yellow oil was dissolved in *o*-difluorobenzene and heated at 67 °C overnight. The solvent was removed under vacuum and the remaining tan oil redissolved in 0.7 mL of C_6D_6. The sample was placed in a sealed NMR tube and heated to 74 °C. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at appropriate intervals.

X-ray Structural Determination of $(C_5Me_5)Rh(PMe_3)(2,3\text{-}C_6H_3F_2)Br$. A small red crystal of the complex was mounted on a glass fiber with epoxy and placed in the cold stream (−20 °C) of the diffractometer. A total of 25 reflections with values of χ between 5 and 70° (to ensure sampling of different regions of *hkl* space) were centered and used for cell determination. Data were collected in a *C*-centered monoclinic crystal system, and data reduction showed absences consistent with space group *C*2/*c*. Solution of the Patterson map allowed placement of the rhodium atom, and use of the program DIRDIF allowed location of all remaining atoms. An absorption correction was applied

following isotropic refinement with the program DIFABS.[19] In the final model, hydrogens were placed in idealized positions and all non-hydrogen atoms were refined anisotropically. Data collection and refinement parameters are given in Table 1.

X-ray Structural Determination of (C_5Me_5)Rh(PMe_3)-(2,4-$C_6H_3F_2$)Br. A small red crystal of the complex was used for the structure determination using the procedure described above. In the final model, hydrogens were placed in idealized positions and all non-hydrogen atoms were refined anisotropically. Data collection and refinement parameters are given in Table 1.

A second crystal was mounted and found to crystallize in a different space group. Since the crystal was believed to be the 3,5- or 2,6-difluorophenyl isomer, the structural analysis was carried out by mounting a red crystal on a glass fiber with epoxy and placing in the cold stream (−20 °C) of the diffractometer. Cell reduction now showed a primitive monoclinic crystal system, and systematic absences were consistent with space group $P2_1/c$. Data collection and structural refinement were carried out as for the $C2/c$ molecule. In the final model, hydrogens were placed in idealized positions and all non-hydrogen atoms were refined anisotropically. The molecule was found to be the same 2,4-difluorophenyl complex, which had crystallized in a different space group. Data collection and refinement parameters are given in Table 1. The atom labeling scheme for this structure is the same as that used for the $C2/c$ solution.

X-ray Structural Determination of (C_5Me_5)Rh(PMe_3)-(2,4,6-$C_6H_3F_2$)Br. A small red crystal of the complex was used for structure determination as described above. In the final model, hydrogens were placed in idealized positions and all non-hydrogen atoms were refined anisotropically. Data collection and refinement parameters are given in Table 1.

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Supplementary Material Available: Tables of crystal data, bond distances and angles, positional parameters, and thermal parameters (29 pages). Ordering information is given on any current masthead page.

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