Formation of Difluoromethylene−Arenium Complexes by Consecutive Aryl−CF_3 C−C Bond Activation and C−F Bond Cleavage

Milko E. van der Boom, Yehoshoa Ben-David, and David Milstein*

Contribution from the Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel

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Abstract: Oxidative addition of one of the strongest C−C bonds, Aryl−CF_3, to Rh(I) takes place upon treating 1-CF_3-2,6-$(CH_2P^tBu_2)_2$-C_6H_3 (**1**, PCP) with $[RhClL_2]_2$ (L = C_2H_4 or C_8H_{14}) in dioxane or toluene at elevated temperatures leading to quantitative formation of Rh(CF_3)(2,6-$(CH_2P^tBu_2)_2$-C_6H_3)Cl (**2**-Cl). The iodide analogue **2**-I was prepared by reacting Rh(η^1-N_2)(2,6-$(CH_2P^tBu_2)_2$-C_6H_3) (**3**) with CF_3I at room temperature. ArCF_2−F bond cleavage was not observed in parallel to the C−C bond activation. Treating a dioxane solution of the thermally stable Rh^{III}−CF_3 complexes **2**-Cl,I with excess trifluoromethanesulfonic acid (HOTf) at room temperature resulted in C−F bond cleavage and selective formation of the unique difluoromethylene−arenium complexes [Rh(1-CF_2-2,6-$(CH_2P^tBu_2)_2$-C_6H_3)X][OTf] (**4**; X = Cl, I) which were characterized spectroscopically by NMR, UV/vis, and FD-MS. No reaction was observed with HCl. Reaction of **2**-Cl with BF_3 or Ph_3CBF_4 (trityl cation) also resulted in C−F bond cleavage to give [Rh(1-CF_2-2,6-$(CH_2P^tBu_2)_2$-C_6H_3)Cl]BF_4 (**10**).

Introduction

The design of well-defined soluble transition-metal complexes capable of selective activation and functionalization of strong single bonds under mild conditions is a highly desirable goal of considerable current interest.[1] Homogeneous activation of strong, unstrained C−C and C−F bonds by the insertion of platinum group metal complexes in solution is a major recent topic.[2−5] In continuation of our interest in C−C and C−F bond activation,[3,5] we now report on the consecutive C−C activation and C−F cleavage in one system. The process involves selective metal insertion into a very strong aryl−CF_3 C−C bond, followed by reaction of the resulting Rh^{III}−CF_3 complex with protonic or Lewis acids to form unique difluoromethylene−arenium complexes by C−F cleavage and C−C bond formation. Part of this study has been communicated.[3i] Arenium or Wheland complexes are transient intermediates in electrophilic aromatic substitution reactions,[7] and a few stable arenium metal complexes have been reported.[1f,8,9] The first methylene−arenium compounds were reported very recently.[9] Difluoromethylene−arenium complexes are unknown.

* To whom correspondence should be addressed. Fax: +972-8-9344142. E-mail: comilst@wiccmail.weizmann.ac.il.

(1) For some reviews regarding bond activation see: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1048. (c) Saunders, G. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2615. (d) Burdeniuc, J.; Jedlicak, B.; Crabtree, R. H. *Chem. Ber./Recueil* **1997**, *130*, 145. (e) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, 373. (f) Steenwinkel, P.; Gossage, R. A.; van Koten, G. *Chem. Eur. J.* **1998**, *4*, 759. (g) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (h) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2180. (i) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 870.

(2) (a) Suzuki, H.; Takaya, Y.; Takemori, T. *J. Am. Chem. Soc.* **1994**, *116*, 10779. (b) Nicholls, J. C.; Spencer, J. L. *Organometallics* **1994**, *13*, 1781. (c) For a recent theoretical study on C−C bond activation see: Holthausen, M. C.; Koch, W. *J. Am. Chem. Soc.* **1996**, *118*, 9932.

(3) (a) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699. (b) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42. (c) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774. (d) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1965. (e) van der Boom, M. E.; Kraatz, H.-B.; Ben-David, Y.; Milstein, D. *Chem. Commun.* **1996**, 2167. (f) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406. (g) Gandelman, M.; Vigalok, A.; Shimon, L. J. W.; Milstein, D. *Organometallics* **1997**, *16*, 3981. (h) Liou, S.-Y.; van der Boom, M. E.; Milstein, D. *Chem. Commun.* **1998**, 687. (i) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *Chem. Commun.* **1998**, 917. (j) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 13415. (k) Rybtchinski, B.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 4528.

(4) For some examples of intermolecular C−F activation by platinum metals see: (a) Whittlesy, M. K.; Perutz, R. N.; Greener, B.; Moore, M. H. *Chem. Commun.* **1997**, 187. (b) Edelbach, B. L.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 7734. (c) Hofmann, P.; Unfried, G. *Chem. Ber.* **1992**, *125*, 659. (d) Hughes, R. P.; Linder, D. C.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 5678. (e) Lopez, O.; Crespo, M.; Font-Bardia, M.; Solans, X. *Organometallics* **1997**, *16*, 1233. (f) Burdeniuc, J.; Crabtree, R. H. *Organometallics* **1998**, *17*, 1582. (g) Hintermann, S.; Pregosin, P. S.; Ruegger, H.; Clark, H. C. *J. Organomet. Chem.* **1992**, *435*, 225. (h) For a recent theoretical study on C−F bond activation see: Su, M.-D.; Chu, S.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 10178.

(5) (a) Blum, O.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1991**, 258. (b) Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359. (c) Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 8674.

(6) (a) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Vigalok, A.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 625. (b) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531.

(7) Taylor, R. *Electrophilic Aromatic Substitution*; John Wiley & Sons: New York, 1990.

(8) (a) van Koten, G.; Timmer, K.; Noltes, J. G.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 250. (b) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (c) Grove, D. M.; van Koten, G.; Ubbels, H. J. C. *Organometallics* **1982**, *1*, 1366. (d) Terheijden, J.; van Koten, G.; Vinke, I. C.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 2891. (e) Steenwinkel, P.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1998**, *17*, 5411. (f) For a theorectical study on the formation of $[PtI(MeC_6H_3$-$(CH_2NMe_2)_2$-*o*,*o*′$)]BF_4$ see: Ortiz, J. V.; Havlas, Z.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1.

(9) (a) Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 7873. (b) Vigalok, A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 477. (c) Vigalok, A.; Rybtchinski, B.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *Organometallics* **1999**, *18*, 895.

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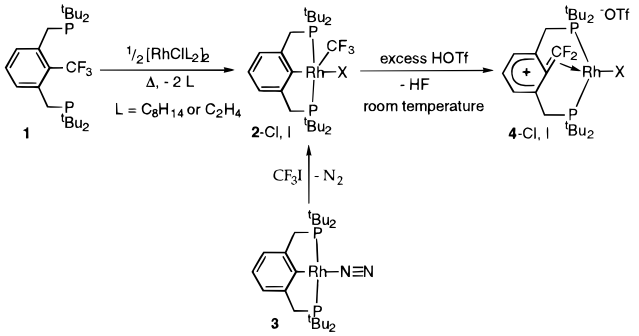
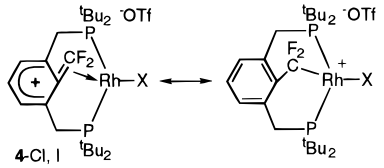
Scheme 1



Results and Discussion

Reaction of $[RhClL_2]_2$ (L = C_2H_4 or C_8H_{14}) with 2 equiv of 1-CF_3-2,6-$(CH_2P^tBu_2)_2$-C_6H_3 (**1**) in a toluene or dioxane solution at 160 °C in a sealed pressure vessel resulted in oxidative addition of the Ar−CF_3 bond to Rh(I) yielding the complex Rh(CF_3)(2,6-$(CH_2P^tBu_2)_2$-C_6H_3)Cl (**2**-Cl) quantitatively. This compound was unambiguously characterized by various NMR techniques, FD-MS, and independent preparation of its iodide analogue **2**-I (Scheme 1). Complex **2**-I was prepared by oxidative addition of CF_3I to the known Rh(I) complex Rh(η^1-N_2)(2,6-$(CH_2P^tBu_2)_2$-C_6H_3) (**3**) in THF at room temperature.[3i,j,10a,b] Interestingly, although one C−C and three benzylic C−F bonds are available, only metal insertion into the unstrained sp^2−sp^3 C−C bond is observed.[11] Products indicative of an $ArCF_2$−F bond cleavage process were not detected upon monitoring the reaction by $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR at room temperature. Direct sp^2−sp^3 Ar−CH_3, Ar−CH_2CH_3, and Ar−OCH_3 oxidative addition to Rh(I) was reported by us recently.[3,6] In the Ar−C oxidative addition, competitive C−H bond activation was observed,[3] whereas in the Ar−OCH_3 bond activation processes only Ar−O bond cleavage occurred with Rh(I).[6] To our knowledge, metal insertion into a strong, unstrained C−C single bond of a fluorocarbon in solution is unprecedented. This unique bond activation process may proceed via a concerted three-centered transition state as recently elucidated for oxidative addition of Rh(I) and Ir(I) to an Ar−CH_3 bond.[3f] However, the strongly electron withdrawing nature of the CF_3 group may make a nucleophilic attack on the arene by the electron-rich metal center possible. It is noteworthy that Bergman et al. observed C−C bond cleavage in hexafluoroacetone with $(Me_2PCH_2CH_2PMe_2)_2$Ru(H)(OH) to afford $(Me_2PCH_2CH_2PMe_2)_2$-Ru(H)($OC(O)CF_3$) and CF_3H.[12]

Remarkably, reaction of complexes **2**-Cl,I with excess HOTf (∼70 equiv) in dioxane or CH_2Cl_2 at room temperature resulted in the immediate formation of the novel green arenium complexes **4**-Cl,I by an unusual organometallic sequence involving C−F, M−C, and M−Ar bond cleavage, and C−C bond formation. Moreover, this intriguing transformation also involves a mild dearomatization process. No reaction was observed with **2**-Cl when HCl was used. The spectroscopic data are fully in agreement with the formation of difluoromethylene−arenium complexes (vide infra),[9] the resonance form of a difluorobenzyl cation.[13] Prolonged standing of **4**-I resulted in some halide dissociation giving a complex formulated as **4**-(dioxane)$(OTf)_2$ (10−15%) as indicated by ^1H, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR and FD-MS of the reaction solution. The latter shows a signal at M = 667.1, suggesting the presence of [Rh((CF_2)(2,6-$(CH_2P^tBu_2)_2$-C_6H_3)-$(C_4H_4O_2)$]$^{2+}$ in the reaction mixture. Dicationic PCP type Rh(I) complexes have been reported previously.[9]



To probe the possibility of converting the Rh−CF_3 group to a carbonyl moiety,[1e] complex **2**-Cl was reacted with excess HOTf in a dioxane/H_2O (95:5 v/v) solution at room temperature. However, only **4**-Cl was formed as judged by $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR, which is stable in these acidic reaction conditions for at least 24 h. The known Rh(CO)(2,6-$(CH_2P^tBu_2)_2$-C_6H_3) was not observed by IR and $^{31}P\{^1H\}$ NMR analysis of the product solution.[1e,10c] Noteworthy, treatment of benzylic PCP type Rh(I) and Pt(II) complexes with HCl or HOTf resulted in sp^2−sp^3 C−C bond activation.[3c,e]

Complexes **4**-Cl,I were characterized spectroscopically by ^1H, ^{31}P, ^{19}F, and ^{13}C NMR, FD-MS, and UV/vis. Assignments in the NMR spectra were made with use of $^1H\{^{31}P\}$ and ^{13}C DEPT135 NMR. Complexes **4**-Cl,I exhibit almost identical spectroscopic properties. The ^1H NMR spectrum of the latter shows two characteristic 1:2:1 triplets for the inequivalent ^{t}Bu groups at δ 1.01 and 1.13 ($^3J_{PH}$ = 5.9 and 7.1 Hz), respectively, which collapse to singlets upon phosphorus decoupling. The occurrence of the ^{t}Bu triplet patterns testifies that the ligand maintained a trans configuration.[3f,i,j,5,9,10] The four protons of the two diastereotopic CH_2P groups appear as a typical AB pattern at δ 2.77 (ΔABq = 88 Hz, $^2J_{HH}$ = 15.7 Hz). The two meta protons appear as a doublet at δ 7.31 ($^3J_{HH}$ = 7.5 Hz) and the para proton is observed at δ 8.24 as a double triplet ($^3J_{HH}$ = 7.5 Hz, $^5J_{RhH}$ = 2.8 Hz), which is clearly not in the normal region for aryl protons.[8,9,12] The $^{31}P\{^1H\}$ NMR spectrum of **4**-I displayed a doublet of triplets at δ 25.1 ($^1J_{RhP}$ = 97.4 Hz, $^3J_{PF}$ = 18.4 Hz) for the two magnetically equivalent trans phosphorus atoms which are coupled to rhodium and to two fluoride nuclei. The large $\Delta\delta$(**4**−**2**) = − 38 ppm and the relatively small rhodium−phosphorus coupling constants ($^1J_{RhP}$ ∼ 100 Hz) are indicative of the formation of methylene−arenium PCP−Rh(I) complexes.[9] The new CF_2 moiety is clearly observed by $^{19}F\{^1H\}$ NMR as a double triplet at δ −44.9 ($^2J_{RhF}$ = 19.6 Hz, $^3J_{PF}$ = 18.2 Hz), and is markedly shifted ($\Delta\delta$ >30 ppm) in comparison to the signal of the Rh−CF_3 group of the starting compound. The FD-MS spectra of **4**-Cl,I show the M^+ − OTf (581.1, **4**-Cl; 673.1, **4**-I) and a correct isotope pattern. Four new distinctly different bands are seen in the UV/vis spectrum of **4**-I at λ 600, 370 (sh), 320, and 260 nm, while no starting material **2**-I remained (λ 430 and 280 nm).[14] Analogous

(10) (a) [Ir(2,6-$(CH_2P^tBu_2)_2$-C_6H_3)]$_2$(μ^2-N_2) was very recently structurally characterized. Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1. (b) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442. (c) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc.* **1976**, 1020.

(11) For a report on C−F versus C−C bond activation with lanthanide cations in the gas phase see: Schwarz, H.; Hornung, G.; Cornehl, H. H. *J. Am. Chem. Soc.* **1996**, *118*, 9960.

(12) (a) Kaplan, A. W.; Bergman, R. G. *Organometallics* **1997**, *16*, 1106. (b) Kaplan, A. W.; Bergman, R. G. *Organometallics* **1998**, *17*, 5072.

(13) (a) $ArCF_2^+$ species have been studied by Olah et al.: Olah, G. A.; Mo, Y. K. *J. Org. Chem.* **1973**, *38*, 2686. (b) For C−F bond activation by $ArCF_2^+$ species see: Ferraris, D.; Cox, C.; Anand, R.; Lectka, T. *J. Am. Chem. Soc.* **1997**, *119*, 4319.

(14) Arene carbonium ions generated in acidic media exhibit similar spectroscopic properties; cyclohexadienyl cations exhibit an absorption band in the UV/vis spectrum at λ ∼ 400 nm. Brouwer, D. M.; Mack, E. L.; Maclean, L. In *Carbonium Ions*; Olah, G. A., Scheyer, P. V., Eds.; Wiley-Interscience: New York, 1970; Vol. 11

Scheme 2

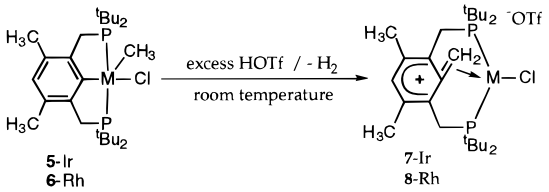


Table 1. Comparison of ^{1}H NMR Data of Methylene **7**−**9**[9] and Difluoromethylene−Arenium PCP Complexes **4**-Cl,I

complex	M	X	δ, *p*-H (ppm)	$\Delta\delta$(complex − ligand) (ppm)
7	Ir	Cl	9.20	2.4
8	Rh	Cl	8.60	1.8
9	Rh	CO	7.98	1.18
4-Cl	Rh	Cl	8.31	1.11
4-I	Rh	I	8.24	1.04

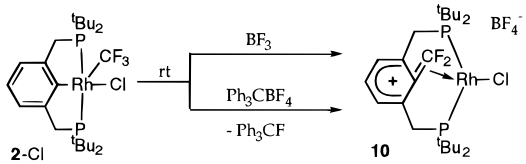
methylene−arenium PCP−Rh(I) complexes have virtually identical UV/vis spectra.[9]

As recently reported, the chloro(methyl) PCP metal(III) complexes **5** and **6** react with HOTf affording the methylene−arenium complexes **7** and **8** (Scheme 2),[9b,c] which have almost identical spectroscopic properties as **4**-Cl,I.

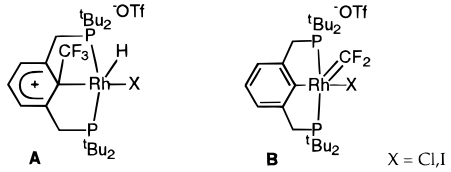
The dicationic carbonyl analogue [Rh(CH$_2$)(2,6-(CH$_2$P^{t}Bu$_2$)$_2$-C$_6$H$_3$)(CO)]$^{2+}$ (**9**) was obtained by treatment of **8** with AgOTf and CO.[9c] NMR and X-ray analysis revealed that the positive charge on the aromatic ring decreases in the order **9** < **8** < **7**, and it seems that the chemical shift δ and $\Delta\delta$(complex − free ligand) of the *p*-H is a good probe for the extent of the positive charge localized on the aromatic ring (Table 1). Therefore, we may conclude that the amount of positive charge distributed in the ring of complex **4**-Cl,I is comparable to that of complex **9**, with the difluoromethylene−arenium resonance form being dominant. Van Koten and co-workers reported a stable arenium complex [PtI(MeC$_6$H$_3$-(CH$_2$NMe$_2$)$_2$-*o*,*o*′)]BF$_4$, which was obtained by reaction of a cationic Pt(II) complex with MeI.[1f,8] The ^{1}H NMR spectrum of this interesting complex shows the para and meta protons at δ 8.70 and 7.60 ppm, respectively.[8b]

As reported, it is likely that protonation of complexes **5** and **6** results in a 1,2-migration of the methyl group to the aromatic ring, followed by β-H elimination to give complexes **7**, **8**, and H$_2$.[9c] Complex **5** undergoes a 1,2-methyl shift between the metal center and the ipso carbon of the aromatic group upon treatment with AgBF$_4$ and CO in THF at room temperature.[9b,c] In contrast to that, the CF$_3$ group does not migrate upon reacting **2**-I with AgBF$_4$ and CO under identical reaction conditions as indicated by ^{31}P{^{1}H} and ^{19}F{^{1}H} NMR.[15a] Reductive elimination of an alkyl group is more favorable than that of a trifluoromethyl group.[15b] We do not believe that a pathway involving protonation of the metal center and an unprecedented 1,2-migration of the trifluoroalkyl group to the aromatic ring giving complex **A**, followed by a rarely observed β-F elimination process, is operative with **2**-Cl,I.[1e] Although speculative, we suggest that the formation of **4**-Cl,I might proceed via an electrophilic attack by H$^+$ on the trifluoromethyl ligand, giving an unobserved Rh═CF$_2$ species **B** and HF, which is followed by a migratory insertion of the aryl group to the difluorocarbene ligand. The α C−F bonds of fluorinated ligands are activated toward electrophiles due to π back-bonding of the metal center, and therefore might react with strong acids to afford cationic

Scheme 3



difluorocarbene species and HF.[1e,16] The aryl−M σ bond in PCP type complexes is relatively inert in comparison to regular σ aryl−M and alkyl−M bonds.[17] However, insertion of terminal acetylenes into the strong σ aryl−Ru(II) bond of a PCP complex, which probably proceeds via intermediacy of unobserved carbene species, was recently reported.[18] Cleavage of aryl−Rh-(I) and −Ru(II) σ bonds involving PCP ligand exchange[3h,19] and insertion of a methylene group into the σ aryl−Rh(I) bond of a PCP type complex upon reaction with MeI are also known.[3b]



In support of our proposed carbene mechanism involving species such as **B**, reaction of complex **2**-Cl with 1 equiv of BF$_3$·OEt$_2$ in CD$_2$Cl$_2$ resulted in the selective formation of [Rh-(1-CF$_2$-2,6-(CH$_2$P^{t}Bu$_2$)$_2$-C$_6$H$_3$)Cl]BF$_4$ (**10**) as judged by ^{1}H, ^{31}P, and ^{19}F NMR and UV/vis analysis of the green product solution (Scheme 3). No starting material remained. The FAB-MS spectrum of **10** shows the M$^+$ − BF$_4$ (581.1) and a correct isotopic pattern. It is known that Lewis acids such as BF$_3$ can abstract fluorides from carbon to afford a M═CF$_2$ species.[1e,16,20] Moreover, complex **10** was prepared independently by reaction of **2**-Cl with 1 equiv of Ph$_3$CBF$_4$ overnight at room temperature in CD$_2$Cl$_2$. Formation of Ph$_3$CF was observed by ^{19}F NMR and GC-MS. The C−F bond cleavage process cannot be reversed by reaction of **10** with ^{n}Bu$_4$NF.

Summary

A number of unprecedented transformations have been presented here. Selective oxidative addition of one of the strongest C−C bonds, Ar−CF$_3$, was demonstrated. This reaction is selective and does not involve C−F activation. The Rh^{III}−

(15) (a) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417. (b) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

(16) (a) For a review on formation and reactivity of transition-metal dihalocarbene complexes see: Brothers, J. P.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293. (b) Anderson, S.; Hill, A. F.; Clark, G. R. *Organometallics* **1992**, *11*, 1988. (c) Michelin, R. A.; Ros, R.; Guadalupi, G.; Bombieri, G.; Benetollo, F.; Chapuis, G. *Inorg, Chem.* **1989**, *28*, 840. (d) Burch, R. R.; Calabrese, J. C.; Ittel, S. D. *Organometallics* **1988**, *7*, 1642. (e) Richmond, T. G.; Shriver, D. F. *Organometallics* **1983**, *2*, 1061. (f) Richmond, T. G.; Shriver, D. F. *Organometallics* **1984**, *3*, 305. (g) Richmond, T. G.; Crespi, A. M.; Shriver, D. F. *Organometallics* **1984**, *3*, 314. (h) Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1978**, *153*, 67. (i) Clark, B. R.; Hoskins, S. V.; Roper, W. R. *J. Organomet. Chem.* **1982**, *234*, C9.

(17) (a) Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1992**, *114*, 7085. (b) Milstein, D. Unpublished results.

(18) (a) Jia, G.; Lee, H. M.; Xia, H. P.; Williams, I. D. *Organometallics* **1996**, *15*, 5453. (b) Lee, H. M.; Yao, J.; Jia, G. *Organometallics* **1997**, *16*, 3927.

(19) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317.

(20) (a) For a report on the formation of a Ru═CF$_2$ species by α C−F migration see: Huang, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 3185. (b) It is known that H$^+$ or BF$_3$ might act as F$^-$ scavengers by formation of a relatively strong bond (B.D.E. H−F = 135.9 kcal·mol^{-1}, B−F = 183 ± 3 kcal·mol^{-1}).[1e,16] *Handbook of Chemistry and Physics*, 57th ed.; CRC Press: Boca Raton, FL, 1976−1977.

CF_3 complex reacts with electrophiles to produce the unique difluoromethylene−arenium complexes. This unusual dearomatization process probably proceeds via a Rh=CF_2 intermediate. Interestingly, isostructural fluoro- and hydrocarbon methylene−arenium complexes were obtained, although the mechanism involved is distinctly different.[3f,9] Formation of these arenium compounds seems surprising, since the electron-withdrawing CF_2 group is expected to destabilize such unusual structures. However, it was shown that the CH_2 group of analogous methylene−arenium complexes **7**−**9** is hardly involved in delocalization of the positive charge on the aromatic ring.[9] Stable arenium compounds are rare,[1f,8,9] and moreover, the difluoromethylene−arenium resonance form of a difluorobenzyl complex was thus far unknown. Interestingly, the overall process involves cleavage of a sp^3 C−F bond of a fluorocarbon in solution promoted by prior metal insertion into an Ar−CF_3 C−C bond.

Experimental Section

General Procedures. The procedures and spectroscopic analyses are similar to those previously reported.[3,6] $CFCl_3$ was used as an external reference at $\delta = 0.0$ in the ^{19}F NMR. All reactions were carried under an inert atmosphere in a nitrogen-filled drybox or by using standard Schlenk techniques. Solvents were dried, distilled, and degassed before use. Rh(η^1-N_2)(2,6-($CH_2P^tBu_2$)$_2$-C_6H_3) and [RhClL$_2$]$_2$ (L = C_2H_4 or C_8H_{14}) were prepared according to published procedures.[3i,j,21] BF_3·OEt_2 was purchased from Merck. CF_3I, Ph_3CBF_4, $^nBu_4NF$ (1.0 M in THF), HCl (4.0 M in dioxane), HOTF, and DOTf were purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker AMX 400 or an Bruker DPX 250 spectrometer. Ph_3PO was used as an internal standard for integration. FD-MS analyses were performed at the University of Amsterdam.

Formation of 1-CF_3-2,6-($CH_2P^tBu_2$)$_2$-C_6H_3 (1). Compound **1** was prepared from 2-bromo-*m*-xylene by trifluoromethylation,[22] bromination, and phosphination with di-*tert*-butylphosphine.[10c] **(a) Preparation of trifluoromethyl-*m*-xylene:** A mixture of sodium trifluoracetate (27.2 g, 200 mmol), CuI (19.1 g, 100 mmol), *N*-methylpyrrolidone (400 mL), and 2-bromo-*m*-xylene (9.25 g, 50 mmol) was stirred in a 1 L flask and heated at 160 °C for 60 h. After the oil bath was cooled to 100 °C, the reaction flask was connected to a vacuum system with a trap immersed in liquid N_2 to condense the product. The material in the trap was collected with ether and washed once with an aqueous HCl solution (10%) and twice with water. The ether layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was distilled under water vacuum (bp 65 °C, yield 87%). ^1H NMR ($CDCl_3$) δ 7.09 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-ArH), 7.92 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-ArH), 2.33 (q, 6H, J_{FH} = 3.3 Hz, CH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −53.0 (s, CF_3). $^{13}C\{^1H\}$ NMR δ 137.37 (q, J_{CF} = 2.1 Hz, Ar), 130.8 (s, Ar), 130.13 (s, Ar), 127.53 (q, J_{CF} = 28.4 Hz, Ar), 126.01 (q, J_{CF} = 276.28, CF_3), 21.38 (q, J_{CF} = 4.1 Hz, CH_3). **(b) Bromomethylation:** A mixture of trifluoromethyl-*m*-xylene (9.3 g, 53.3 mmol), NBS (19.2 g, 108 mmol), and AIBN (0.3 g) in CCl_4 (150 mL) was refluxed for 2 h under lamp light. The mixture was cooled, filtered, and concentrated in vacuo. The product was purified by column chromatography (dry silica; eluent: hexane/ether = 95/5) and recrystallized from methanol at − 30 °C (yield 8.9 g, 50%, mp 64 °C). ^1H NMR ($CDCl_3$) δ 7.48 (m, 3H, ArH), 4.63 (q, 4H, J_{FH} = 1.5 Hz, $ArCH_2Br$). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −52.7 (s, CF_3). $^{13}C\{^1H\}$ NMR δ 137.4 (q, J_{CF} = 1.8 Hz, Ar), 133.36 (s, Ar), 132.23 (s, Ar), 125.5 (q, J_{CF} = 30 Hz, Ar), 124.5 (q, J_{CF} = 277, CF_3), 30.02 (q, J_{CF} = 4.8 Hz, $ArCH_2Br$). **(c) Phosphination:** An acetone solution of di-*tert*-butylphosphine (3.25 g, 22.3 mmol, 20% excess) was added to an acetone solution (25 mL) of α,α′-dibromo-2-trifluoromethyl-*m*-xylene (3.06 g, 9.2 mmol) and the mixture was refluxed for 2 h. Upon heating a white solid precipitated from the clear reaction solution, which was collected and washed with degassed pentane (2 × 250 mL). Degassed H_2O (50 mL) was added to the white solid, followed by an aqueous solution of NaOAc (16 g, 50 mL). The resulting solution was extracted twice with ether (2 × 250 mL). The combined ether layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was dissolved in pentane and filtered; white crystals were obtained at − 30 °C (3.23 g, 76%). For **1**: ^1H NMR ($CDCl_3$) δ 7.61 (d, 2H, $^3J_{HH}$ = 7.8 Hz, ArH), 7.20 (t, 1H, $^3J_{HH}$ = 7.8 Hz, ArH), 3.01 (s, 4H, CH_2P), 1.02 (d, 36H, $^3J_{PH}$ = 10.9 Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 38.9 (q, $^5J_{FP}$ = 7.3 Hz). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ − 49.8 (t, $^5J_{PF}$ = 7.4 Hz, $ArCF_3$). $^{13}C\{^1H\}$ NMR δ 141.30 (d, J_{CF} = 13.5 Hz, Ar), 130.41 (s, J_{CF} = 21.4 Hz, Ar), 129.89 (s, Ar), 127.1 (q, J_{CF} = 27.1 Hz,), 126.0 (q, J_{CF} = 277 Hz, Ar), 31.93 (d, J_{CF} = 22.2 Hz, $C(CH_3)_3$), 29.60 (d, J_{CF} = 13.3 Hz, $C(CH_3)_3$), 26.47 (dq, J_{CF} = 2.7 Hz, $ArCH_2P$). MS: 463 ($M^+ + 1$).

Ar−CF_3 C−C Bond Activation. Formation of 2-Cl,I. A toluene or dioxane solution (10 mL) of **1** (24 mg; 0.040 mmol) and [RhCl(L)$_2$]$_2$ (L = C_2H_4 or C_8H_{14}) (0.020 mmol) was loaded into a high-pressure vessel and heated for 9 h at 160 °C. The resulting yellow solution was analyzed by $^1H\{^{31}P\}$ and $^{19}F\{^1H\}$ NMR indicating the quantitative formation of **2**-Cl. Removal of the volatiles in vacuo afforded complex **2**-Cl as a yellow solid in quantitative yield. Traces of ligand impurities and C_8H_{14} can be removed by washing the residue with cold pentane (−30 °C). The reaction can be run at lower temperatures when a 5-fold excess of **1** is used, leading to the quantitative formation of **2**-Cl after heating at 120 °C overnight. No other complexes were found. No C−C or C−F activation were indicated by NMR upon reaction of **1** with other metal precursors such as [{IrCl(C$_8$H$_{14}$)$_2$}$_2$], (PhCN)$_2$PtCl$_2$, or Pd(CF_3CO_2)$_2$. The iodide analogue of **2**-Cl was obtained by reaction of CF_3I with **3** under similar reaction conditions as for the reaction of **3** with EtI.[3j] For **2**-Cl: ^1H NMR (C_6D_6) δ 7.0 (m, 3H, ArH), 3.37 (dvt, 2H left part of ABq, $^2J_{HH}$ = 17.0 Hz, $^2J_{PH}$ = 4.2 Hz, CH_2P), 2.82 (dvt, 2H right part of ABq, $^2J_{HH}$ = 17.0 Hz, $^2J_{PH}$ = 4.4 Hz, CH_2P), 1.42 (vt, 18H, $^2J_{PH}$ = 7.0 Hz, $C(CH_3)_3$), 1.05 (vt, 18H, $^2J_{PH}$ = 6.0 Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 62.6 (dq, $^1J_{RhP}$ = 116.7 Hz, $^3J_{FP}$ = 16.3 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6) δ 9.0 (dt, $^2J_{RhF}$ = 21.3 Hz, $^3J_{PF}$ = 16.5 Hz, $RhCF_3$). FD-MS: M^+ 600 (correct isotope pattern). For **2**-I: ^1H NMR (C_6D_6) δ 7.0 (m, 3H, ArH), 3.42 (dvt, 2H left part of ABq, $^2J_{HH}$ = 17.0 Hz, $^2J_{PH}$ = 4.8 Hz, CH_2P), 2.99 (dvt, 2H right part of ABq, $^2J_{HH}$ = 17.0 Hz, $^2J_{PH}$ = 4.4 Hz, CH_2P), 1.49 (vt, 18H, $^2J_{PH}$ = 6.9 Hz, $C(CH_3)_3$), 1.03 (vt, 18H, $^2J_{PH}$ = 6.1 Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 62.4 (dq, $^1J_{RhP}$ = 115.6 Hz, $^3J_{FP}$ = 15.7 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6) δ 10.9 (dt, $^2J_{RhF}$ = 21.5 Hz, $^3J_{PF}$ = 15.6 Hz, $RhCF_3$). Anal. Calcd for $C_{25}H_{43}I_1F_3P_2Rh_1$: C, 43.37; H 6.26. Found: C, 42.72; H, 6.01.

Reaction of 2-Cl,I with HOTf. Formation of Complexes 4-Cl,I. A yellowish dioxane solution (1 mL) of complex **2**-Cl,I (10 mg; 0.017, 0.015 mmol, respectively) was loaded into a 5 mm screwcap NMR tube and treated with excess HOTf (0.1 mL, ∼70 equiv). The reaction solution turned immediately green upon addition of the acid, indicative of the formation of a methylene−arenium complex.[9] $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR analysis after approximately 15 min indicated the quantitative formation of **4**-Cl,I (>95%), no starting material remaining. Subsequently, the reaction solution was dried under high vacuum yielding complex **4**-Cl,I as a green powder. The reaction of **2**-Cl with HOTf proceeds also smoothly in the presence of H_2O (50 μL), and no formation of Rh(CO)(2,6-($CH_2P^tBu_2$)$_2$-C_6H_3) was observed by IR and $^{31}P\{^1H\}$ NMR.[10c] No deuterium incorporation in **4**-Cl,I was observed when DOTf was used. No reaction was observed when HCl was used instead of HOTf. Complexes **4**-Cl,I have similar spectroscopic properties. ^1H NMR of **4**-Cl (CD_2Cl_2) δ 8.31 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-ArH), 7.40 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-ArH), 3.18 (ABq, 4H, ΔABq = 140 Hz, $^2J_{HH}$ = 16.9 Hz, CH_2P), 1.46 (vt, 18H, $^3J_{PH}$ = 7.1, $C(CH_3)_3$), 1.27 (vt, 18H, $^3J_{PH}$ = 7.1, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR of **4**-Cl (dioxane-d_8) δ 23.5 (dt, $^1J_{RhP}$ = 96.0 Hz, $^3J_{PF}$ = 17.7 Hz). $^{19}F\{^1H\}$ NMR of **4**-Cl (dioxane-d_8) δ −46.6 (vq, $^1J_{RhP}$ = $^3J_{PF}$ = 18.3 Hz, CF_2; this signal is observed as a dt in CD_2Cl_2; $^1J_{RhP}$ = 19.3 Hz, $^3J_{PF}$ = 18.3 Hz), −78.7 (s, O_3SCF_3). FD-MS of **4**-Cl: M^+ − OTf 581.1 (correct isotope pattern). ^1H NMR of **4**-I (C_6D_6) δ 8.24 (dt, 1H, $^3J_{HH}$ = 7.5 Hz, $^5J_{RhH}$ = 2.8 Hz, *p*-ArH), 7.31 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *m*-ArH)), 2.77 (ABq, 4H, ΔABq = 88 Hz, $^2J_{HH}$ = 15.7 Hz, CH_2P), 1.13 (vt, 18H, $^3J_{PH}$ = 5.9, $C(CH_3)_3$), 1.01 (vt, 18H, $^3J_{PH}$ = 7.1, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR of **4**-I (C_6D_6) δ 25.1 (dt, $^1J_{RhP}$ = 97.4 Hz, $^3J_{PF}$ = 18.4 Hz). $^{19}F\{^1H\}$ NMR of **4**-I (C_6D_6)

(21) van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92.
(22) Carr, G. E.; Chambers, R. D.; Holmes, T. F.; Parker, D. G. *J. Chem. Soc., Perkin Trans. 1* **1988**, 921.

δ −44.9 (dt, $^1J_{RhP}$ = 19.6 Hz, $^3J_{PF}$ = 18.2 Hz, CF_2), −78.7 (s, O_3SCF_3). $^{13}C\{^1H\}$ NMR of **4**-I (C_6D_6) δ 163.26 (vt, $^{2+4}J_{PC}$ = 6.7 Hz, *o*-C), 146.8 (s, *p*-C), 134.03 (vt, $^{3+5}J_{PC}$ = 10.0 Hz, *m*-C), 120.19 (q, $^1J_{FC}$ = 317.6 Hz, O_3SCF_3), 38.65 (t, $^{1+3}J_{PC}$ = 14.8 Hz, $C(CH_3)_3$), 36.39 (t, J_{PC} = 13.8 Hz, $C(CH_3)_3$), 30.96 (t, $^{2+4}J_{PC}$ = 3.8 Hz, $C(CH_3)_3$), ≈30.0 (br, CH_2P), 29.44 (t, $^{2+4}J_{PC}$ = 3.34 Hz, $C(CH_3)_3$). UV/vis of **4**-I (0.03 mM in CH_2Cl_2): λ (ϵ) 600 (5600), 370 (sh, ∼33000), 320 (66000), 260 (75000). For comparison, UV/vis of **2**-I (0.03 mM in CH_2Cl_2): λ (ϵ) 430 (27000), 280 (75000). FD-MS of **4**-I: M^+ − OTf 673.1 (correct isotope pattern). Prolonged standing of the product solution of **4**-I at room temperature for 3 days resulted probably in formation of **4**-$(OTf)_2$ (10−15%). The compounds **4**-I and **4**-$(OTf)_2$ were not separated. Selected spectroscopic data: ^1H NMR of **4**-$(OTf)_2$ 8.05 (dt, 1H, $^3J_{HH}$ = 7.4 Hz, $^5J_{RhH}$ ≈ 3.0 Hz, *p*-ArH). $^{31}P\{^1H\}$ NMR of **4**-$(OTf)_2$ (C_6D_6) δ 21.5 (dt, $^1J_{RhP}$ = 96.2 Hz, $^3J_{PF}$ = 19.1 Hz). $^{19}F\{^1H\}$ NMR of **4**-$(OTf)_2$ (C_6D_6) δ −47.9 (vq, $^1J_{RhP}$ = $^3J_{PF}$ = 20.4 Hz, CF_2). FD-MS of **4**-$(OTf)_2$: [M + (dioxane) − $(OTf)_2$] 667.1 (correct isotope pattern).

Reaction of 2-Cl with BF_3 and Ph_3CBF_4. Formation of Complex 10. A cold yellowish CD_2Cl_2 solution (1 mL, − 30 °C) of complex **2**-Cl (10 mg, 0.017 mmol) was treated with 1 equiv of BF_3 in ether using a microsyringe and was loaded into a 5 mm screwcap NMR tube. An excess of BF_3 (10 equiv) can be used as well. The reaction solution was left at room temperature and turned green within 5 min. ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ analysis after 1 h showed disappearance of the starting material and the selective formation of complex **10**. Removal of the volatiles in vacuo afforded complex **10** as a green solid in quantitative yield. Treatment of a yellowish CD_2Cl_2 solution (1 mL) of complex **2**-Cl (10 mg, 0.017 mmol) with 1 equiv of Ph_3CBF_4 (6 mg, 0.018 mmol) at room temperature overnight resulted also in the quantitative formation of **10**. Formation of Ph_3CF was observed by ^{19}F and GC-MS of the product solution. This reaction proceeds relatively slowly: 55% conversion was observed after approximately 2 h at room temperature by ^{19}F and ^{31}P NMR. Treatment of a green CD_2Cl_2 solution (1 mL) of complex **10** (10 mg, 0.017 mmol) with 1 equiv of $^nBu_4NF$ (17 μL, 1 M solution in THF) at room temperature resulted in an immediate color change to yellow. ^{19}F and $^{31}P\{^1H\}$ NMR showed a mixture of unknown composition. No starting material remained and no formation of a Rh−CF_3 species was indicated. Complex **10**: ^1H ($CDCl_3$) δ 8.41 (t, $^3J_{HH}$ = 7.7 Hz), 7.41 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *m*-ArH), 3.24 (ABq, 4H, ΔAB_q = 142 Hz, $^2J_{HH}$ = 17.2 Hz, CH_2P), 1.47 (vt, 18H, $^3J_{PH}$ = 7.6 Hz, $C(CH_3)_3$), 1.29 (vt, 18H, $^3J_{PH}$ = 7.3 Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ ($CDCl_3$) δ 25.77 (dt, $^1J_{RhP}$ = 97.7 Hz, $^3J_{PF}$ = 18.1 Hz). $^{19}F\{^1H\}$ ($CDCl_3$) δ −44.9 (dt, $^1J_{RhP}$ = 19.6 Hz, $^3J_{PF}$ = 16.3 Hz), 149.9 (br, BF_4^-). UV/vis ($CDCl_3$): λ 585, 355, 309, 275. Anal. Calcd for $C_{25}H_{43}Cl_1B_1F_6P_2Rh_1 \cdot CHCl_3$: C, 39.63; H 5.63. Found: C, 40.24; H, 5.57. FAB-MS: M^+ − BF_4^- 581.1 (correct isotope pattern).

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