Organometallics **1993,** *12,* 3109–3117 3109

Transition-Metal Chemistry of Hexafluorobutadiene. Facile Hydrolysis of (Hexafluoro-1-metalla-3-cyclopentene)rhodium Complexes To Give Tetrafluoro-1-metalla-3-cyclopenten-2-one and Tetrafluoro-1-metalla-2-cyclopenten-4-one Complexes. Crystal and Molecular Structures of *trans*-$[(\overline{\mathrm{Rh{-}CF_2CF{=}CF{-}C}}\mathrm{O})\mathrm{Cl(PPh_3)_2}]$, *mer*-$[(\overline{\mathrm{Rh{-}CF_2CF{=}CF{-}C}}\mathrm{F_2})\mathrm{Cl(PMe_3)_3}]$, and *mer*-$[(\overline{\mathrm{Rh{-}CF{=}CF{-}CO{-}C}}\mathrm{F_2})\mathrm{Cl(PMe_3)_3}]$

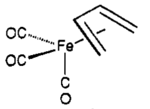
Russell P. Hughes,*[,1a] Peter R. Rose,[1a] and Arnold L. Rheingold[1b]

Departments of Chemistry, Burke Chemistry Laboratory, Dartmouth College, Hanover, New Hampshire 03755-3564, and University of Delaware, Newark, Delaware 19716

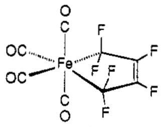
Received March 22, 1993

Hexafluorobutadiene reacts with $[\mathrm{RhCl(PPh_3)_3}]$ in hot benzene to afford the 5-coordinate tetrafluorometallacyclopentenone (η^2-tetrafluorovinylketene) complex **7**, in which a CF_2 group has been hydrolyzed to a ketone by adventitious water. Complex **7** has been characterized by spectroscopic means and by an X-ray crystallographic study of its acetone solvate: $C_{43}H_{36}F_4O_2P_2ClRh$, monoclinic, $P2_1/n$, $a = 18.5706(33)$ Å, $b = 10.2670(12)$ Å, $c = 21.8591(31)$ Å, $\beta = 107.793(13)°$, $V = 3968.3(10)$ Å^3, $Z = 4$. The corresponding 6-coordinate derivatives **9** and **10** can be prepared by treatment of **7** with thallium acetylacetonate and trimethylphosphine, respectively. The initial reaction of hexafluorobutadiene with $[\mathrm{RhCl(PPh_3)_3}]$ is shown to proceed via the intermediacy of a 5-coordinate hexafluorometallacyclopentene complex **11** in which one α-CF_2 group is remarkably sensitive to hydrolysis. Complex **12**, a coordinatively saturated analogue of **11**, can be isolated from the reaction of hexafluorobutadiene with the trimethylphosphine complex $[\mathrm{RhCl(PMe_3)_3}]$ and has also been characterized by X-ray crystallography: $C_{13}H_{27}F_6P_3ClRh$, monoclinic, $Pbca$, $a = 17.951(4)$ Å, $b = 18.619(3)$ Å, $c = 25.466(4)$ Å, $V = 8512.1(29)$ Å^3, $Z \doteq 16$. Compound **12** is far less moisture sensitive than its coordinatively unsaturated analogue **11** but does not undergo reaction with water under more forcing conditions, or upon chromatography, to give an isomeric metallacyclopentenone ligand in complex **13**, which has also been characterized by X-ray crystallography: $C_{13}H_{27}F_4OP_3ClRh$, monoclinic, $P2_1/n$, $a = 8.688(3)$ Å, $b = 14.712(4)$ Å, $c = 16.129(5)$ Å, $\beta = 92.12(2)°$, $V = 2060.3(12)$ Å^3, $Z = 4$. The crystal of **13** chosen for study was contaminated with a solid solution impurity, most probably **15**, which is a proposed intermediate in the hydrolysis reaction. Mechanisms are proposed to account for the observed α- and β-hydrolysis pathways.

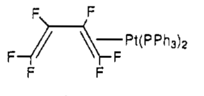
Introduction



1



2



3

The differences in bonding, structure, and chemistry of fluorinated organic ligands as compared to their more thoroughly studied hydrocarbon analogues continue to provide surprises and intriguing chemistry.[2] For example, compared to the abundant organometallic chemistry of its hydrocarbon analogue, 1,3-butadiene, that of hexafluorobutadiene is remarkably sparse, and only two well characterized complexes containing this ligand have been reported prior to our work. In contrast to butadiene itself, which binds to the tricarbonyliron fragment to give the well-known η^4-diene complex **1**,[3] hexafluorobutadiene reacts with iron carbonyl to afford the fluorinated 1-metalla-3-cyclopentene complex **2**,[4] which has been characterized unambiguously by X-ray crystallography.[5] The driving force for this mode of reactivity may well be the formation of stronger metal–carbon σ-bonds to fluorinated carbon atoms and the *gem*-difluoro effect which arises from the exothermicity associated with the pyramidalization of a planar CF_2 group.[6] In addition to **2** the only

---

[1] (a) Dartmouth College. (b) University of Delaware.

[2] Hughes, R. P. *Adv. Organomet. Chem.* **1990,** *31,* 183.

[3] The preparation of complex **1** was first reported in: Reihlen, H.; Gruhl, A.; von Hessling, G.; Pfrengle, O. *Liebigs Ann. Chem.* **1930,** *482,* 161. The correct structure of **1** was first formulated by: Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1958,** 642.

[4] Hunt, R. L.; Roundhill, D. M.; Wilkinson, G. *J. Chem. Soc. A* **1967,** 982.

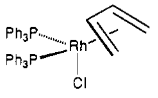
[5] Hitchcock, P. B.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1967,** 242.

[6] Smart, B. E. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1983; Chapter 14.

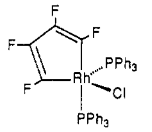
0276-7333/93/2312-3109$04.00/0

other transition metal complex of hexafluorobutadiene appears to be the η^2-complex of platinum(0), **3**, which has been characterized spectroscopically.[7] Examples of reaction chemistry of hexafluorobutadiene are also few: the insertion of hexafluorobutadiene into a Co–H bond to give allylic complexes of cobalt has been reported,[8] and some early reports of defluorination reactions involving rhodium are reexamined in this work.

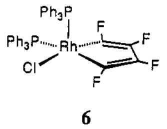
We were intrigued by an early report that, while reaction of butadiene with Wilkinson's compound, [RhCl(PPh$_3$)$_3$], afforded an η^4-butadiene complex **4**, reaction of hexafluorobutadiene with the same compound in hot benzene solution afforded a tetrafluorometallacyclopentadiene complex, with apparent loss of one PPh$_3$ ligand and two fluorines![9] The assignment of the suggested structure **5** or **6** was based on solution ^{19}F NMR and solution IR spectra, but there were some inconsistencies between the reported data and the suggested structures. Structure **5** or **6** would require four different fluorine and two different phosphorus environments, but the ^{19}F NMR spectrum of this compound showed only three ^{19}F resonances in a 2:1:1 ratio, leading to the assumption that two fluorines in the ring were accidentally isochronous. These structures would also require symmetrically inequivalent phosphorus environments, but unfortunately no ^{31}P NMR data were available. The IR spectrum showed two bands at 1739 and 1672 cm^{-1}, which were attributed to the two fluorinated double bonds in the ring.[9]



4



5



6

The apparently facile cleavage of two strong C–F bonds and loss of two fluorines to a nebulous fate intrigued us and stimulated a reinvestigation of this reaction. The results and some new rhodium chemistry of hexafluorobutadiene are described herein.

Results and Discussion

Repetition of the reaction of hexafluorobutadiene with [RhCl(PPh$_3$)$_3$] under the literature conditions (sealed glass tube; benzene solution; 65 °C) afforded 60–70% yields of yellow crystalline material with ^{19}F NMR and IR data almost identical to those reported in the literature. The ^{19}F NMR (benzene-d_6) spectrum of this material exhibited three resonances at δ −49.9, −123.1, and −132.2 ppm (relative to CFCl$_3$) in a 2:1:1 ratio, and the solution infrared spectrum (CH$_2$Cl$_2$) of the yellow compound matched closely that reported by Wilkinson.[9] Subjection of single crystals of this compound, as an acetone solvate, to X-ray crystallographic analysis revealed the true structure of the compound as **7**, in which the hexafluorobutadiene had been converted into a tetrafluorometallacyclopentenone ligand. The interpretation of the 1:1:2 pattern in the ^{19}F NMR spectrum is now clear (see below), and the IR bands can be reassigned as 1672 ($\nu_{C=O}$) and 1734 ($\nu_{C=C}$) cm^{-1}. An ORTEP diagram of the structure of **7** is shown in Figure 1, details of the crystallographic determination are provided in Table I, fractional atomic coordinates are in Table II, and some selected angles and distances are listed in Table III.

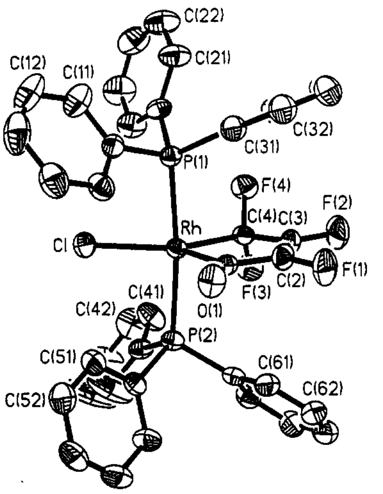
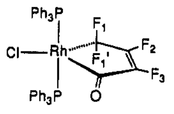
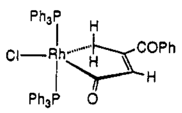


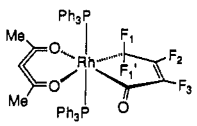
Figure 1. ORTEP drawing and labeling scheme for **7**. Ellipsoids are drawn at 35% probability. Hydrogens have been omitted for clarity.



7



8



9

The coordination geometry around the rhodium atom can be described as approximately trigonal bipyramidal, and many precedents for this kind of coordination exist. A closely analogous structure is that of **8**, which has been described as an η^2-vinylketene complex.[10] By analogy, complex **7** is the first example of an η^2-tetrafluorovinylketene complex, but for purposes of common nomenclature, with compounds described below we will refer to it as a metallacyclopentenone compound. As observed in the structure of **8**,[10] the metallacyclic ring in **7** occupies two adjacent equatorial sites on the metal center and is planar, with no significant puckering of C(2) and C(3) out of the C(1)–Rh–C(2) plane. The P(1)–Rh–P(2) angle for **7** is 172.3(1)°, demonstrating slightly distorted *trans* phosphines, and the Rh–P bond distances for phosphines P(1) and P(2) are identical at 2.371(2) and 2.375(2) Å, respectively. Comparison of the Rh–C bond distances with those in **8** shows an identical value for the ketone carbon [Rh–C(1) = 1.968(5) Å (**7**); 1.973(6) Å (**8**)], but a significantly shorter bond from Rh to the CF$_2$ in **7** compared to the CH$_2$ in **8** [Rh–C(4) = 2.013(5) Å (**7**), 2.064 (9) Å (**8**)]. The shorter σ-bond to the fluorinated carbon is consistent with other literature data on hydrocarbon and fluorocarbon alkyl compounds.[11]

The assignments for the ^{19}F NMR resonances in **7** were made on the basis of ^{19}F NMR, ^{19}F{^{19}F} NMR, ^{19}F{^{31}P} NMR, and ^{31}P{^{1}H} NMR data, and full details are given in the experimental section. The signals at δ −123.1 and −132.2, assigned to fluorines F$_2$ and F$_3$, displayed observable coupling only to each other and the sp^3 fluorines. The signal at δ −49.9, which is assigned to geminal fluorines

---

(7) Green, M.; Osborn, R. B. L.; Rest, A. J.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2525.

(8) Sasaoka, S.-I.; Joh, T.; Tahara, T.; Takahashi, S. *Chem. Lett.* **1989**, 1163.

(9) Roundhill, D. M.; Lawson, D. N.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 845–849.

(10) Huffman, M. A.; Liebeskind, L. S.; Pennington, W. T. *Organometallics* **1992**, *11*, 255–266.

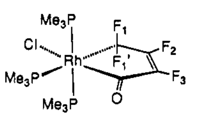
(11) Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1967**, *6*, 1213. Bennett, M. J.; Mason, R. *Proc. Chem. Soc. London* **1963**, 273. Bennett, M. A.; Chee, H.-K.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1061.

Table I. Crystallographic Data for Complexes 7, 12, and 13

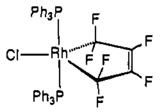
	(a) Crystal Parameters		
formula	$C_{43}H_{36}F_4O_2P_2ClRh$	$C_{13}H_{27}F_6P_3ClRh$	$C_{13}H_{27}F_4OP_3ClRh$
fw	861.06	528.63	506.63
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	*Pbca*	$P2_1/n$
a, Å	18.5706(33)	17.951(4)	8.688(3)
b, Å	10.2670(12)	18.619(3)	14.712(4)
c, Å	21.8591(31)	25.466(4)	16.129(5)
β, deg	107.793(13)		92.12(2)
V, Å^3	3968.3 (10)	8512.1(29)	2060.3(12)
Z	4	16	4
cryst dimens, mm	0.18 × 0.40 × 0.43	0.12 × 0.32 × 0.36	0.11 × 0.23 × 0.46
cryst color	yellow	yellow	yellow
D(calc), g cm^{-3}	1.441	1.650	1.633
μ(Mo Kα), cm^{-1}	6.33	11.98	12.13
temp, K	296	296	296
T(max)/*T*(min)	1.152	1.178	1.166
	(b) Data Collection		
diffractometer	Siemens *P*4		Nicolet R3m
monochromator	graphite		graphite
radiation (λ, Å)	Mo Kα (0.710 73)		Mo Kα (0.710 73)
2θ scan range, deg	4–52	4–52	4–60
data collected (*h*,*k*,*l*)	±23,+13,+27	+23,+23,+32	±12,+20,+22
no. of rflns collcd	8469	9116	6298
no. of indpt rflns	7788	8351	5900
R(merg), %	2.77		5.35
no. of indpt obsvd rflns $F_o \geq n\sigma(F_o)$	4703 (n = 5)	5222 (n = 4)	4030 (n = 5)
no. of std rflns	3 std/197 rflns	3 std/197 rflns	3 std/197 rflns
var in stds	<1	<1	~6
	(c) Refinement		
R(*F*), %	4.03	4.28	4.14
R(*wF*), %	4.26	4.15	4.30
$\Delta(\rho)$, e Å^{-3}	0.826	0.488	0.539
N_o/N_v	16.5	12.0	17.2
GOF	1.095	0.980	1.108

F_1 and $F_{1'}$ displayed additional coupling to phosphorus and to ^{103}Rh. The two sp^3 bound fluorines are symmetrically equivalent, but magnetically inequivalent, and spectral simulation was required to determine the geminal fluorine–fluorine coupling constant ($J_{F_1-F_{1'}}$ = 165 Hz). The ^{31}P NMR spectrum of complex 7 exhibited a single resonance at δ 29.3 characterized by large coupling to the rhodium and the sp^3 bound fluorines [J_{F_1-P} = 54.2 Hz and J_{P-Rh} = 121.5 Hz]. The Rh–P coupling is very similar to those of related trigonal bipyramidal complexes with *trans* phosphine ligands.[12] The large coupling between the two magnetically inequivalent *trans* phosphines was determined using spectral simulation to be $J_{P-P'}$ = 295 Hz.

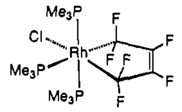
The 5-coordinate, 16-electron complex 7 was converted to two 6-coordinate, 18-electron derivatives. Complex 9 was obtained by treatment of 7 with thallium acetylacetonate (acac), and complex 10 by treatment with an excess of trimethylphosphine. The solution infrared spectrum of 9 revealed stretching frequencies at 1723 and 1649 cm^{-1}, consistent with $\nu_{C=C}$ and $\nu_{C=O}$ stretches for the metallacyclic ring, and its ^{1}H NMR spectrum revealed the expected two methyl resonances at δ 1.60 and 1.08 ppm and a methine resonance at δ 4.42 for the acac ligand. The ^{31}P NMR spectrum exhibits a single resonance at δ 25.3, indicative of mutually *trans* phosphines, and characterized by a large coupling to rhodium and to the CF_2 fluorines. Simulation allowed the determination of the expected large phosphorus—phosphorus coupling constant [$J_{P-P'}$ = 295 Hz]. The assignments for the ^{19}F NMR resonances in 9 were made on the basis of those for 7; the resonance of F_1 and $F_{1'}$ appears at δ −69.2 and is coupled to both the other fluorines and the rhodium and phosphorus atoms. Resonances at δ −133.0 and −135.1 are assigned to F_2 and F_3, respectively; in contrast to the corresponding resonance in 7, F_3 displays an additional 3-Hz coupling to ^{103}Rh.



10



11



12

The structure of the tris(trimethylphosphine) derivative 10 was also established spectroscopically. ^{19}F NMR spectroscopy revealed the expected three resonances at δ −69.1, −132.2, and −139.5 ppm, characteristic of the fluorinated metallacycle. The ^{31}P NMR spectrum of 10 displayed two complex multiplets in a 2:1 ratio at δ −2.6 and −19.2 ppm, and its ^{1}H NMR spectrum displayed a doublet and a virtual triplet in the methyl region, characteristic of a meridional tris(phosphine) complex.[13] Clearly there are two possible meridional isomers, with Cl *trans* to CF_2 or to C=O, but only one is observed in solution. We are not able to provide definitive arguments as to which is formed in this case.

Thus, in the reaction of hexafluorobutadiene with $[RhCl(PPh_3)_3]$, a PPh_3 ligand is lost and one CF_2 undergoes hydrolysis to a ketone. We regarded adventitious water as the most likely reagent for this latter transformation, with formation of C=O and 2 equiv of HF providing the

---

(12) Verkade, J. G.; Mosbo, J. A. *Phosphorus-31 NMR Spectroscopy Analysis*; VCH: New York, 1987; Vol. 8, Chapter 13.

(13) Jenkins, J. M.; Moss, J. R.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 2796–2800.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 7

	x	y	z	U(eq)[a]
Rh	9934(1)	2629(1)	2462(1)	38(1)
P(1)	9813(1)	1797(1)	3437(1)	40(1)
P(2)	9957(1)	3705(1)	1506(1)	42(1)
Cl	10357(1)	4641(1)	3017(1)	63(1)
O(1)	8389(2)	2239(4)	1877(2)	64(2)
F(1)	8500(2)	−288(3)	1442(2)	82(2)
F(2)	10005(2)	−1160(3)	1768(2)	84(2)
F(3)	10870(2)	1140(3)	1895(2)	68(1)
F(4)	10863(2)	381(3)	2809(2)	65(1)
C(1)	8991(3)	1739(5)	1984(2)	40(2)
C(2)	9097(3)	422(6)	1774(3)	54(2)
C(3)	9794(3)	14(5)	1917(3)	52(2)
C(4)	10389(3)	961(5)	2265(3)	44(2)
C(11)	9496(4)	3214(7)	4422(3)	76(3)
C(12)	9064(5)	4115(9)	4651(4)	99(4)
C(13)	8450(5)	4706(7)	4232(5)	92(4)
C(14)	8243(4)	4437(6)	3596(4)	75(3)
C(15)	8668(3)	3580(6)	3361(3)	57(2)
C(16)	9290(3)	2938(5)	3770(3)	46(2)
C(21)	10717(4)	593(7)	4565(3)	72(3)
C(22)	11362(4)	458(9)	5086(3)	93(4)
C(23)	11965(4)	1260(9)	5141(3)	87(3)
C(24)	11939(3)	2158(8)	4669(4)	87(3)
C(25)	11306(3)	2280(7)	4142(3)	70(3)
C(26)	10681(3)	1511(6)	4085(3)	48(2)
C(31)	8503(3)	307(6)	3265(3)	54(2)
C(32)	8095(4)	−834(7)	3170(3)	68(3)
C(33)	8428(4)	−1999(7)	3160(3)	78(3)
C(34)	9199(4)	−2060(6)	3249(3)	76(3)
C(35)	9622(4)	−915(6)	3340(3)	63(3)
C(36)	9282(3)	283(5)	3359(2)	43(2)
C(41)	11519(3)	3994(7)	1924(3)	75(3)
C(42)	12204(4)	4593(8)	1982(4)	86(3)
C(43)	12215(4)	5759(10)	1714(4)	119(5)
C(44)	11558(5)	6341(11)	1392(5)	181(6)
C(45)	10876(4)	5748(8)	1334(5)	126(4)
C(46)	10846(3)	4570(6)	1603(3)	50(2)
C(51)	8911(3)	5560(5)	1670(3)	59(2)
C(52)	8354(4)	6484(6)	1457(3)	71(3)
C(53)	8069(3)	6802(6)	827(4)	67(3)
C(54)	8352(3)	6187(7)	392(3)	69(3)
C(55)	8920(3)	5245(6)	592(3)	60(2)
C(56)	9205(3)	4936(5)	1238(3)	45(2)
C(61)	9119(3)	2078(6)	522(3)	55(2)
C(62)	8991(4)	1333(6)	−25(3)	66(3)
C(63)	9533(4)	1246(6)	−329(3)	70(3)
C(64)	10201(4)	1884(6)	−93(3)	71(3)
C(65)	10351(3)	2604(6)	461(3)	61(2)
C(66)	9808(3)	2721(5)	781(3)	46(2)
O(2)	12445(6)	5855(10)	4568(4)	195(6)
C(5)	12192(5)	6318(10)	4031(5)	102(4)
C(6)	11632(6)	7329(10)	3920(6)	147(6)
C(7)	12382(6)	5793(13)	3525(5)	176(8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances and Bond Angles for 7

	Bond Distances (Å)		
Rh–Cl	2.403(2)	Rh–P(1)	2.371(2)
Rh–P(2)	2.375(2)	Rh–C(1)	1.968(5)
Rh–C(4)	2.013(5)	C(1)–C(2)	1.460(8)
C(1)–O(1)	1.188(6)	C(2)–C(3)	1.305(8)
C(2)–F(1)	1.339(6)	C(3)–C(4)	1.494(7)
C(3)–F(2)	1.338(7)	C(4)–F(3)	1.389(7)
C(4)–F(4)	1.379(6)		
	Bond Angles (deg)		
Cl–Rh–P(1)	87.8(1)	Cl–Rh–P(2)	87.3(1)
P(1)–Rh–P(2)	172.3(1)	Cl–Rh–C(1)	140.2(2)
Cl–Rh–C(4)	138.2(1)	P(1)–Rh–C(1)	89.8(2)
P(1)–Rh–C(4)	92.7(2)	P(2)–Rh–C(1)	90.1(2)
P(2)–Rh–C(4)	95.0(2)	C(1)–Rh–C(4)	81.6(2)
Rh–C(1)–C(2)	114.5(4)	Rh–C(4)–C(3)	113.5(3)
C(1)–C(2)–C(3)	116.1(5)	C(2)–C(3)–C(4)	116.0(5)
Rh–C(1)–O(1)	122.4(4)	C(1)–C(2)–F(1)	120.3(5)
O(1)–C(1)–C(2)	123.2(5)	C(2)–C(3)–F(2)	125.0(3)
C(3)–C(2)–F(1)	123.5(5)	C(3)–C(4)–F(3)	107.2(5)
C(3)–C(4)–F(4)	109.6(4)	F(3)–C(4)–F(4)	101.8(4)
C(4)–C(3)–F(2)	119.0(5)	Rh–C(4)–F(3)	113.5(3)
Rh–C(4)–F(4)	112.5(3)		

thermodynamic compensation for cleavage of two C—F bonds, but careful drying of solvents and reagents still resulted in formation of good yields (60%) of 7 under the original conditions reported in the literature. However, when the reaction of hexafluorobutadiene with [RhCl(PPh$_3$)$_3$] was allowed to proceed at room temperature for extended periods of time in a sealed glass tube in which the internal surfaces had been silylated, a yellow solid 11 precipitated. Characterization of 11 was accomplished spectroscopically using ^{19}F and ^{31}P NMR, but we could not obtain satisfactory microanalysis data, due to its sensitivity to moisture (see below). However, the preparation of a stable analogue (see below) gives us additional confidence in the structural assignment for 11. The solution ^{19}F NMR spectrum of 11 showed two resonances at δ −50.3 and −140.1 ppm in a 2:1 ratio, consistent with two pairs of equivalent geminal fluorines and two equivalent vinyl fluorines required by the proposed metallacyclopentene structure, and is similar to that of the analogous iron complex 2.[4] The ^{31}P NMR spectrum of 11 comprises a single complex multiplet at δ 32.8 ppm, similar to those observed for 7 and 8 and consistent with the proposed structure.

In solution, compound 11 is extremely sensitive to adventitious moisture, rapidly converting to 7. Only when the internal glass surfaces of the reaction vessel were silylated was formation of 7 suppressed at higher reaction temperatures, allowing 11 to be observed spectroscopically. When solutions of 11 were transferred to unsilylated glass vessels, or when water was added to dry solutions of 11, conversion to 7 was rapid. Clearly, 11 is sufficiently aquaphilic to react with surface moisture on unpassivated glassware.

We reasoned that the loss of the third triphenylphosphine originally present in [RhCl(PPh$_3$)$_3$] might be sterically driven and that the presence of a vacant coordination site in 11 might be important in facilitating its conversion to 7. In an attempt to prepare a coordinatively saturated analogue of 11 which might be less reactive, we carried out the corresponding reaction of hexafluorobutadiene with the rhodium complex [RhCl(PMe$_3$)$_3$]. In this reaction a clean conversion to the metallacyclic complex 12 was observed. This product was characterized by a single crystal X-ray diffraction study. An ORTEP representation is shown in Figure 2, details of the structure determination are provided in Table I, fractional atomic coordinates are in Table IV, and selected bond distances and angles are in Table V. There are two independent molecules in the unit cell, labeled 12 and 12′, but there are no significant structural differences between them; subsequent discussion is limited to molecule 12. The complex contains a metallacyclopentene ring analogous to that found in 2, and proposed for 11, but with pseudooctahedral coordination around rhodium and retention of all three PMe$_3$ ligands meridionally bound in the coordination sphere. The structure is unremarkable in many ways. Notably, the Rh–P(2) distance trans to C(1) is longer than the two other Rh–P distances, as expected considering the different *trans* influences involved.[14] In view of previous discussions concerning possible π-acceptor properties associated with the σ^*-

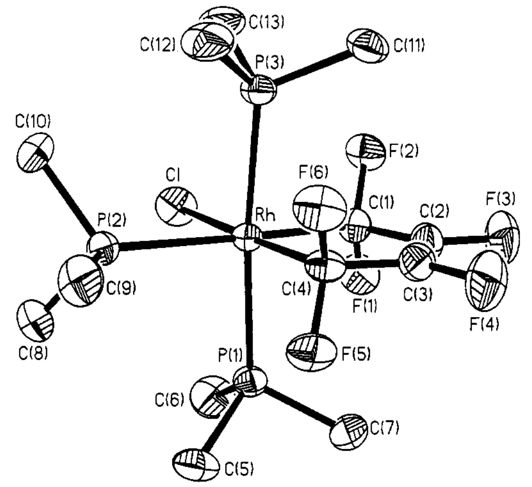


Figure 2. ORTEP drawing and labeling scheme for **12**. Ellipsoids are drawn at 35% probability. Hydrogens have been omitted for clarity.

orbitals of C–F bonds in fluoroalkyl substituents bound to transition metals,[15] it is worth noting that complex **12** provides a direct comparison of two CF_2 groups, one *trans* to a π-acceptor ligand [P(2)] and one trans to a π-donor ligand [Cl]. While the Rh–C(1) distance *trans* to P(2) is significantly longer than that *trans* to Cl [Rh–C(1) = 2.075(6) Å; Rh–C(4) = 2.024(6) Å], the C–F distances and F–C–F and Rh–CF_2–C angles for the two CF_2 groups are identical, within experimental error, an observation inconsistent with any π-acceptor properties for the CF_2 group. The *trans* phosphines are tipped toward the metallacyclic ring, with the angle P(1)–Rh–P(3) = 173.8(1)°.

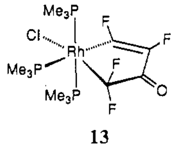
The solution structure of **12** is clearly analogous to that observed in the solid state. The IR spectrum displayed a band at 1741 cm^{-1}, characteristic of $\nu_{C=C}$ for a fluorinated olefin.[16] The ^{19}F NMR spectrum displayed four resonances in a 2:2:1:1 ratio at δ –67.5, –81.2, –140.2, and –142.0 ppm. Clearly, there is a plane of symmetry which includes the metallacyclic ring, but not one perpendicular to it. The ^{31}P NMR spectrum exhibited two complex multiplets in a 2:1 ratio at δ –5.8 and –21.9 ppm, respectively, and the meridional disposition of the PMe_3 ligands is confirmed by the ^1H NMR spectrum which contains the expected doublet and virtual triplet.[13]

In contrast to coordinatively unsaturated complex **11**, complex **12** shows no tendency to react with water at room temperature but, on heating with water, or on chromatography on alumina, hydrolysis did occur to give a complex which clearly contained a metallacycle composed of CF_2, CF=CF, and C=O fragments, but which not was the previously prepared compound **10**. All of the spectroscopic evidence points to structure **13**, containing a metallacyclic ring isomeric with that observed in compounds **7**, **9**, and **10**, with the ketone function in a position β to the metal rather than α. The IR spectrum displayed two peaks at 1694 and 1606 cm^{-1}, characteristic of $\nu_{C=C}$ and $\nu_{C=O}$, the ^{19}F NMR spectrum exhibited the expected three peaks in a 1:2:1 ratio at δ –46.6, –59.0, and –140.5 ppm, the ^1H NMR spectrum revealed the doublet and virtual triplet phosphorus–methyl pattern expected for a meridional isomer,[13] and the ^{31}P NMR spectrum revealed two resonances at δ –5.1 and –17.4 ppm in a 2:1 ratio, all consistent with the proposed structure **13**. In addition each NMR spectrum revealed a second set of small resonances which we have tentatively assigned to the presence of small amounts of the other possible meridional isomer **14** in the sample.

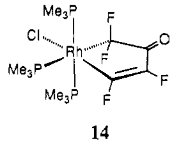
Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for the Two Independent Molecules 12 and 12′

	x	*y*	*z*	*U*(eq)[a]
Rh	2499(1)	2371(1)	5094(1)	31(1)
Rh′	5153(1)	289(1)	2674(1)	30(1)
P(1)	1822(1)	3194(1)	4558(1)	43(1)
P(2)	3192(1)	3324(1)	5499(1)	43(1)
P(3)	3047(1)	1495(1)	5654(1)	42(1)
P(1′)	5795(1)	–394(1)	2017(1)	44(1)
P(2′)	5809(1)	1371(1)	2451(1)	44(1)
P(3′)	4417(1)	902(1)	3311(1)	42(1)
Cl	3554(1)	2357(1)	4489(1)	60(1)
Cl′	6177(1)	142(1)	3299(1)	50(1)
F(1)	1868(3)	1683(2)	4149(1)	63(2)
F(2)	2414(2)	907(2)	4641(2)	59(1)
F(3)	846(3)	845(3)	4730(2)	84(2)
F(4)	437(3)	1617(3)	5596(2)	87(2)
F(5)	1165(2)	2942(2)	5594(2)	58(1)
F(6)	1703(2)	2159(2)	6082(1)	62(2)
F(1′)	5129(2)	–1269(2)	2886(2)	63(2)
F(2′)	4498(2)	–692(2)	3462(1)	58(1)
F(3′)	3578(3)	–1380(2)	2717(2)	79(2)
F(4′)	3184(2)	–380(3)	1968(2)	89(2)
F(5′)	4447(2)	359(2)	1644(1)	57(1)
F(6′)	3817(2)	934(2)	2224(2)	65(2)
C(1)	1995(4)	1544(3)	4679(2)	43(2)
C(2)	1279(4)	1374(4)	4932(3)	54(3)
C(3)	1076(4)	1735(4)	5344(3)	50(3)
C(4)	1579(4)	2310(3)	5552(2)	42(2)
C(5)	1587(4)	4081(3)	4821(3)	69(3)
C(6)	2259(5)	3391(5)	3936(3)	79(4)
C(7)	884(4)	2940(4)	4360(3)	63(3)
C(8)	3451(4)	4071(4)	5077(3)	71(3)
C(9)	2792(4)	3759(4)	6075(3)	67(3)
C(10)	4140(4)	3100(4)	5703(4)	82(4)
C(11)	2492(4)	693(3)	5790(3)	58(3)
C(12)	3253(5)	1739(4)	6333(3)	73(3)
C(13)	3905(4)	1103(4)	5410(3)	72(3)
C(1′)	4675(4)	–661(3)	2929(2)	43(2)
C(2′)	3992(4)	–782(4)	2616(3)	50(2)
C(3′)	3798(4)	–311(4)	2267(3)	54(3)
C(4′)	4268(4)	338(3)	2180(3)	45(2)
C(5′)	6061(5)	45(4)	1401(3)	73(3)
C(6′)	6652(4)	–799(5)	2241(3)	84(4)
C(7′)	5309(5)	–1156(4)	1731(3)	75(3)
C(8′)	6777(4)	1270(5)	2245(4)	86(4)
C(9′)	5420(5)	1944(4)	1947(3)	79(3)
C(10′)	5992(5)	1993(4)	2990(3)	67(3)
C(11′)	3489(4)	545(4)	3454(3)	69(3)
C(12′)	4134(5)	1826(4)	3176(3)	75(3)
C(13′)	4828(4)	939(4)	3965(3)	68(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.



13



14

Attempts to grow single crystals of **13** resulted in one useable crystal which unfortunately contained a solid

---

[14] Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. *Concepts and Models of Inorganic Chemistry*, 2nd ed.; John Wiley & Son: New York, 1983.

[15] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15. Cotton, F. A.; McCleverty, J. A. *Ibid.* **1965**, *4*, 490. Cotton, F. A.; Wing, R. M. *Ibid.* **1967**, *9*, 511. Clark, H. C.; Tsai, J. H. *Ibid.* **1967**, *7*, 515. Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315. Hall, M. B.; Fenske, R. F. *Ibid.* **1972**, *11*, 768. Bennett, M. A.; Chee, H.-K.; Jeffery, J. C.; Robertson, G. B. *Ibid.* **1979**, *18*, 1071.

[16] Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*; McGraw Hill: New York, 1980; Chapter 2.

Table V. Selected Bond Distances and Bond Angles for the Two Independent Molecules 12 and 12′

	12	**12′**
	Bond Distances (Å)	
Rh–Cl	2.443(2)	2.446(2)
Rh–P(1)	2.386(2)	2.397(2)
Rh–P(2)	2.400(2)	2.403(2)
Rh–P(3)	2.378(2)	2.383(2)
Rh–C(1)	2.075(6)	2.070(6)
Rh–C(4)	2.024(6)	2.029(7)
C(1)–C(2)	1.472(10)	1.479(10)
C(2)–C(3)	1.299(10)	1.296(10)
C(3)–C(4)	1.497(9)	1.490(10)
C(1)–F(1)	1.394(7)	1.399(7)
C(1)–F(2)	1.406(7)	1.396(7)
C(2)–F(3)	1.355(8)	1.364(8)
C(3)–F(4)	1.322(8)	1.346(8)
C(4)–F(5)	1.395(7)	1.404(7)
C(4)–F(6)	1.396(7)	1.380(8)
	Bond Angles (deg)	
P(1)–Rh–P(2)	92.0(1)	92.5(1)
P(1)–Rh–Cl	92.3(1)	92.0(1)
P(2)–Rh–P(3)	92.0(1)	91.7(1)
P(2)–Rh–Cl	82.9(1)	83.1(1)
P(3)–Rh–Cl	92.9(1)	91.5(1)
P(1)–Rh–C(1)	87.9(2)	88.0(2)
P(1)–Rh–C(4)	87.1(2)	88.1(2)
P(2)–Rh–C(1)	173.4(2)	173.8(2)
P(2)–Rh–C(4)	102.6(2)	101.5(2)
P(3)–Rh–C(1)	88.6(2)	88.1(2)
P(3)–Rh–C(4)	87.4(2)	88.1(2)
Cl–Rh–C(1)	90.5(2)	90.7(2)
Cl–Rh–C(4)	174.5(2)	175.4(2)
C(1)–Rh–C(4)	84.0(3)	84.7(3)
Rh–C(1)–C(2)	108.6(4)	107.8(4)
Rh–C(1)–F(1)	115.2(4)	115.2(4)
Rh–C(1)–F(2)	115.3(4)	115.7(4)
Rh–C(4)–C(3)	109.2(4)	108.4(4)
Rh–C(4)–F(5)	115.5(4)	115.2(4)
Rh–C(4)–F(6)	115.9(4)	116.5(4)
C(1)–C(2)–C(3)	119.1(6)	119.3(6)
F(1)–C(1)–F(2)	100.2(5)	100.1(4)
C(1)–C(2)–F(3)	119.4(6)	118.4(6)
F(1)–C(1)–C(2)	108.6(6)	108.5(6)
F(2)–C(1)–C(2)	108.4(5)	109.2(4)
C(2)–C(3)–C(4)	119.1(6)	119.9(6)
F(3)–C(2)–C(3)	121.5(7)	122.3(6)
C(2)–C(3)–F(4)	123.1(7)	122.9(7)
F(4)–C(3)–C(4)	117.8(6)	117.2(6)
C(3)–C(4)–F(5)	108.0(5)	107.3(5)
C(3)–C(4)–F(6)	107.1(5)	107.9(5)
F(5)–C(4)–F(6)	100.4(5)	100.9(5)

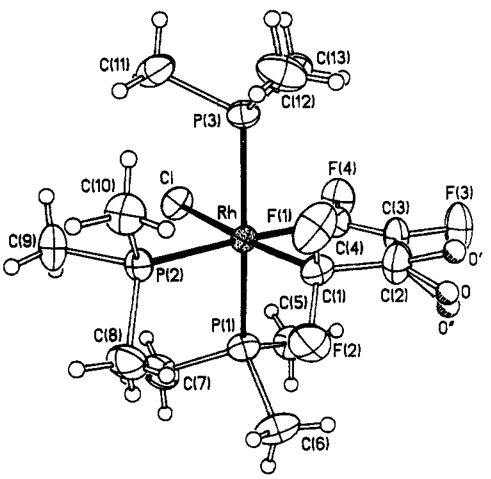


Figure 3. ORTEP drawing and labeling scheme for **13**. Ellipsoids are drawn at 35% probability. Hydrogens have been omitted for clarity. The substitution at C(2) is mixed; O is a 60% occupancy carbonyl oxygen atom, consistent with a C(=O) group, and O′ and O″ are 40% occupancy O/F composite sites, appropriate for a CF(OH) group.

Table VI. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for 13

	x	*y*	*z*	*U*[a]
Rh	510(1)	2329(1)	3549(1)	31(1)
Cl	−1569(1)	1213(1)	3753(1)	53(1)
P(1)	−1545(1)	3302(1)	3142(1)	47(1)
P(2)	996(1)	1840(1)	2177(1)	42(1)
P(3)	2125(1)	1201(1)	4163(1)	45(1)
F(1)	3628(3)	2981(2)	3403(3)	84(1)
F(2)	1991(4)	3920(2)	2890(2)	80(1)
F(3)	1210(4)	3978(3)	5670(2)	92(2)
F(4)	−659(4)	2568(2)	5270(2)	69(1)
O	3096(29)	4544(22)	4300(21)	71(9)
O′	3612(21)	4234(20)	4555(14)	115(11)
O″	2591(32)	4664(24)	4369(23)	103(11)
C(1)	2161(5)	3306(3)	3519(3)	45(1)
C(2)	2301(7)	3861(4)	4331(4)	68(2)
C(3)	1231(6)	3551(4)	4919(3)	56(2)
C(4)	332(5)	2870(3)	4703(3)	45(1)
C(5)	−2741(6)	3608(4)	3997(3)	65(2)
C(6)	−1183(7)	4405(4)	2682(4)	77(2)
C(7)	−2954(6)	2791(4)	2413(4)	71(2)
C(8)	796(7)	2682(4)	1353(3)	72(2)
C(9)	−151(7)	902(4)	1778(4)	71(2)
C(10)	2930(5)	1458(4)	1976(3)	63(2)
C(11)	1851(7)	56(4)	3757(4)	71(2)
C(12)	4219(6)	1309(5)	4220(4)	84(3)
C(13)	1717(7)	1034(4)	5244(3)	70(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

solution impurity, as revealed by an X-ray crystallographic study. The resultant ORTEP representation is shown in Figure 3, details of the crystallographic determination are provided in Table I, fractional atomic coordinates are in Table VI, and selected bond distances and angles are in Table VII. Various models were tested to resolve the disorder that is clearly evident at C(2). The most chemically and crystallographically reasonable model contained a 60% occupancy oxygen atom in the ring plane, corresponding to the spectroscopically defined structure **13**, and roughly equal populations (40% each) of sites above and below the ring plane (O′ and O″) which were treated as O/F composite atoms appropriate to a CF(OH) group in complex **15**, which is a reasonable intermediate en route to **13** (see below). The occupancies were refined with constraints appropriate to the assumption that C(2) was either C(=O) or CF(OH) substituted.

Curiously, the Rh–C bond distances in **13** are identical, even though C(4) is sp^2 and C(1) is sp^3; presumably, the fact that C(4) is *trans* to the stronger *trans* influence ligand PMe$_3$ and C(1) is *trans* to Cl acts to offset the expected shorter distance from Rh to C(4). The P(1)–Rh–P(3) bond angle of 166.3(1)° shows a tipping of the *trans* phosphines opposite that observed in **12**, with the phosphines leaning away from the metallacycle ring.

No evidence was obtained for intermediate **15** in the spectroscopy of the bulk sample of this reaction product, and it appears that the crystal chosen for crystallography was not representative of the bulk. It is clear that the impurity peaks observed in the spectroscopy of the bulk sample are not due to the highly unsymmetrical **15** but probably correspond to the meridional complex **14** (vide supra) which contains a plane of symmetry.

Concluding Remarks

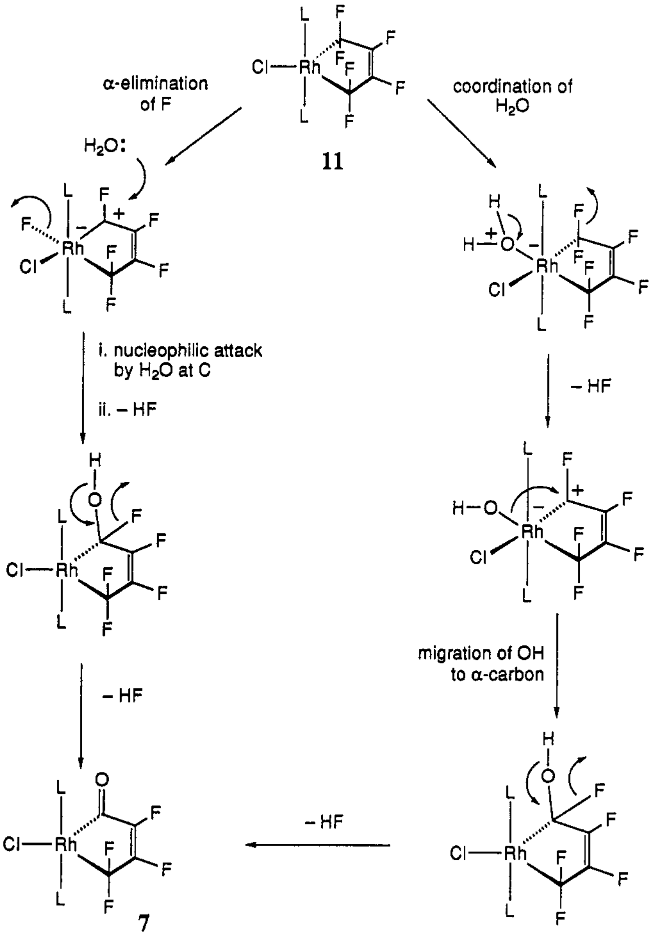
We conclude from these observations that hexafluorobutadiene prefers to bind to rhodium via a formal

Table VII. Selected Bond Distances and Bond Angles for 13

	Bond Distances (Å)		
Rh–Cl	2.471(1)	Rh–P(1)	2.362(1)
Rh–P(2)	2.379(1)	Rh–P(3)	2.367(1)
Rh–C(1)	2.034(4)	Rh–C(4)	2.036(4)
C(1)–C(2)	1.544(7)	C(2)–C(3)	1.426(8)
C(3)–C(4)	1.310(7)	C(1)–F(1)	1.380(5)
C(1)–F(2)	1.362(6)	C(3)–F(3)	1.365(6)
C(4)–F(4)	1.354(6)	C(2)–O	1.22(3)
C(2)–O′	1.30(2)	C(2)–O″	1.21(4)
	Bond Angles (deg)		
Cl–Rh–P(1)	83.8(1)	Cl–Rh–P(2)	94.5(1)
Cl–Rh–P(3)	84.5(1)	P(1)–Rh–P(2)	94.8(1)
P(1)–Rh–P(3)	166.3(1)	P(2)–Rh–P(3)	93.1(1)
Cl–Rh–C(1)	173.0(1)	Cl–Rh–C(4)	93.3(1)
P(1)–Rh–C(1)	95.2(1)	P(1)–Rh–C(4)	86.3(1)
P(2)–Rh–C(1)	92.4(1)	P(2)–Rh–C(4)	172.2(1)
P(3)–Rh–C(1)	95.6(1)	P(3)–Rh–C(4)	87.4(1)
C(1)–Rh–C(4)	79.8(2)	Rh–C(1)–C(2)	112.7(3)
C(1)–C(2)–C(3)	111.3(5)	C(2)–C(3)–C(4)	117.7(5)
Rh–C(4)–C(3)	118.6(4)	Rh–C(1)–F(1)	114.5(3)
Rh–C(1)–F(2)	115.5(3)	F(1)–C(1)–F(2)	101.8(4)
C(2)–C(1)–F(1)	104.7(4)	C(2)–C(1)–F(2)	106.6(4)
C(2)–C(3)–F(3)	118.2(5)	C(3)–C(4)–F(4)	117.3(4)
C(4)–C(3)–F(3)	124.1(5)	Rh–C(4)–F(4)	124.1(3)

oxidative addition reaction, to give a metallacyclopentene ring, analogous to that previously reported for complex 2.[4,5] When triphenylphosphine ligands are present on the rhodium center, steric effects preclude coordination of three PPh_3 ligands, and a 5-coordinate complex **11** is formed. In this coordinatively unsaturated compound hydrolysis of an α-CF_2 in the metallacycle is extraordinarily facile, but notably, subsequent hydrolysis of the second α-CF_2 group does not occur at 60 °C. In the 6-coordinate trimethylphosphine analogue **12** the additional phosphine on the metal shuts down facile hydrolysis of an α-CF_2 in the hexafluorometallacyclopentene ring, but under more forcing conditions with H_2O, or upon chromatography, hydrolysis occurs via attack at the β-position.

Scheme I



^{a} L = PPh_3.

There are many examples of hydrolysis of $[M{-}CF_3]$ moieties to give $[M{-}CO]^+$ that can be found in the literature,[24] but they usually require the presence of a Lewis acid as F^- acceptor to generate the $[^+M{=}CF_2] \leftrightarrow [M{-}CF_2{}^+]$ species which is thereby activated toward nucleophilic attack at carbon by H_2O and subsequent elimination of HF. For example, while $[FeCp(CO)_2CF_3]$ is hydrolytically stable, treatment with BF_3 affords the isolable cationic derivative $[FeCp(CO)_2CF_2]^+BF_4{}^-$ which is easily hydrolyzed to give $[FeCp(CO)_3]^+BF_4{}^-$.[17] Similar reactivity is observed for $[MoCp(CO)_3CF_3]$,[18] $[Mn(CO)_5CF_3]$,[17] and $[Pt(PPh_3)_2(H)(CF_3)]$,[19] although in the last example H^+ appears to be the initial fluoride acceptor. The neutral electrophilic difluorocarbene complex $[Ru(PPh_3)_2(CO)Cl_2(CF_2)]$ also exhibits hydrolytic reactivity at the CF_2 group.[20] It is unclear whether the change in reaction pathway is solely the result of a change in coordination number at the metal, but some mechanistic speculation as to the possible role of a vacant coordination site on rhodium is presented in Scheme I. Two pathways can be envisaged whereby the vacant coordination site in **11** can participate in activation of the α-CF_2 group toward hydrolysis. The rhodium center could act as an internal Lewis acid in an α-elimination of fluoride, thereby activating the α-carbon to attack by H_2O, with subsequent elimination of HF. Alternatively, coordination of H_2O would enhance its acidity and assist in loss of HF; subsequent migration of OH to the α-carbon followed by elimination of a second HF molecule would afford the observed product **7**. When the vacant site on the metal is blocked, as in **12**, activation of the α-C—F bond by these pathways is shut down, and nucleophilic attack by H_2O is forced to occur at the β-carbon by the well established S_N2' pathway shown in Scheme II.[21] Intermediate **15** is the most likely contaminant in the crystal of **13** that was subjected to X-ray crystallographic analysis (vide supra).

What still remains unclear is why the α-CF_2 group in **11** is so sensitive to water whereas that in **7** is not. It is, however, quite clear that the transition metal chemistry of hexafluorobutadiene is significantly different from that of its hydrocarbon analogue, and it is under continuing investigation in our group.

Experimental Procedures

General Considerations. Infrared spectra were recorded on a Bio-Rad Digilab FTS-40 Fourier transform infrared spectro-

---

(17) Richmond, T. G.; Crespi, A. M.; Shriver, D. F. *Organometallics* **1984**, *3*, 314. Crespi, A. M.; Shriver, D. F. *Ibid.* **1985**, *4*, 1830.

(18) Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1978**, *153*, 67.

(19) Michelin, R. A.; Ros, R.; Guadalupi, G.; Bombieri, G.; Benetollo, F.; Chapius, G. *Inorg. Chem.* **1989**, *28*, 840–846.

(20) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293.

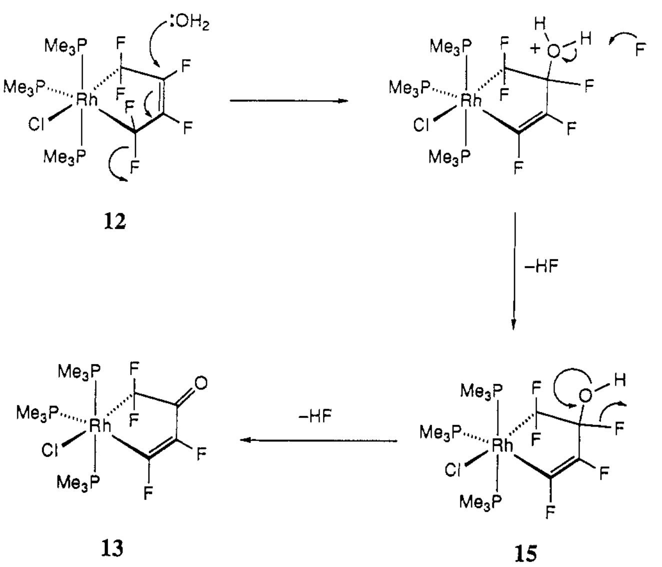
(21) Olah, G. A., Chambers, R. D., Prakash, G. K. S., Eds. *Synthetic Fluorine Chemistry*; John Wiley & Son: New York, 1992.

(22) Wilkinson, G.; Osborn, J. A. *Inorg. Synth.* **1967**, *10*, 67–69.

(23) Price, R. T.; Anderson, R. A.; Muetterties, E. L. *J. Organomet. Chem.* **1989**, *376*, 407–417. Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511–518.

(24) The first reports of elimination of fluoride from metal–fluoroalkyl complexes appear to be by: Treichel, P. M.; Pitcher, E.; Stone, F. G. A. *Inorg. Chem.* **1962**, *1*, 511.

Scheme II



photometer, calibrated against the 1601-cm^{-1} peak of polystyrene. ^{1}H NMR (300 MHz), ^{19}F NMR (282 MHz), and ^{31}P{^{1}H or ^{19}F} NMR (121.4 MHz) spectra were recorded at 25 °C unless otherwise noted. ^{1}H shifts were recorded as ppm downfield from tetramethylsilane, and ^{19}F NMR shifts as ppm upfield from internal $CFCl_3$. Chemical shifts for ^{31}P{^{1}H} NMR spectra were referenced to the deuterium resonance of the solvent by using the internal frequency lock of the spectrometer so that the resonance from a 5-mm NMR tube of 85% H_3PO_4 appeared at 0.0 ppm at 20 °C. Melting points were determined using an Electrothermal capillary melting point apparatus and are uncorrected. Microanalyses were completed at Galbraith Laboratories, Inc., Knoxville, TN.

All solvents were dinitrogen saturated and distilled over a variety of drying agents: tetrahydrofuran (THF) and toluene were dried over potassium; hexanes, diethyl ether, petroleum ether, and benzene were dried over sodium–potassium alloy; methylene chloride, pentane, and heptane were dried over calcium hydride. All reactions were run in oven dried glassware using conventional Schlenk techniques, under an atmosphere of dinitrogen which was deoxygenated over BASF catalyst and dried using Aquasorb, or in a Vacuum Atmospheres drybox equipped with an HE-492 gas purification system.

Alumina (activity III) was obtained from ICN Pharmaceuticals, Inc. $RhCl_3 \cdot xH_2O$ was obtained from Johnson Matthey Aesar/Alfa. Hexafluorobutadiene was obtained from PCR Research Chemicals, Gainesville, FL. Triphenylphosphine was obtained from Aldrich Chemical Co. and recrystallized from diethyl ether/ethanol before use. Trimethylphosphine was obtained from Strem Chemical Co. and was vacuum distilled before use. Carbon monoxide was obtained from Matheson. $[RhCl(PPh_3)_3]$[22] and $[RhCl(PMe_3)_3]$[23] were prepared by literature procedures.

Reaction of $[RhCl(PPh_3)_3]$ with Hexafluorobutadiene at 65 °C. A pressure tube (125 mL) was charged with $[Rh(PPh_3)_3(Cl)]$ (1.00 g, 1.08 mmol) and benzene (20 mL). The contents were degassed using the freeze–pump–thaw method and cooled to −196 °C. Hexafluorobutadiene (600 Torr, 19.3 mmol) was collected in a gas manifold (600 mL) and condensed into the pressure tube. The tube was warmed to room temperature and heated to 65 °C in an oil bath for 12 h. The resulting clear yellow solution was pumped to dryness, yielding an oily yellow solid. The yellow product was crystallized from ethanol/CH_2Cl_2, yielding pale yellow crystals of complex 7 (0.53 g, 1.069 mmol, 62%). Mp: 175 °C dec. ^{1}H NMR: δ 7.05 (br), 8.0 (br) ppm. ^{19}F NMR (acetone-d_6): δ −49.9 [ddddd, $J_{F_1-F_{1'}} = 165$ Hz, $J_{F_1-F_2} = 21.6$ Hz, $J_{F_1-F_3} = 5.6$ Hz, $J_{F_1-P} = 54.2$ Hz, $J_{F_1-Rh} = 13$ Hz, $F_1{=}F_{1'}$], −123.1 [dt, $J_{F_1-F_2} = 21.6$ Hz, $J_{F_2-F_3} = 12.6$ Hz, F_2], −132.2 [dt, $J_{F_1-F_3} = 5.6$ Hz, $J_{F_2-F_3} = 12.6$ Hz, F_3] ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ 29.3 [ddd, $^3J_{F_1-P} = 54.2$ Hz, $J_{P-P} = 295$ Hz, $J_{P-Rh} = 121.5$ Hz] ppm. IR (CH_2Cl_2): $\nu_{C=C} = 1734$, $\nu_{C=O} = 1672$ cm^{-1}. The ^{19}F NMR and infrared spectra were consistent with those reported by Wilkinson.[9] Elemental composition was confirmed by an X-ray diffraction study (see below).

Room Temperature Reaction of $[RhCl(PPh_3)_3]$ with Hexafluorobutadiene. An oven dried Schlenk flask (50 mL) was charged with $[RhCl(PPh_3)_3]$ (0.65 g, 0.71 mmol) and toluene (15 mL). Hexafluorobutadiene (50 Torr, 1.6 mmol) was collected in a gas manifold (600 mL) and condensed into the Schlenk flask cooled to −196 °C. The flask was warmed to room temperature and stirred for 48 h. The resulting solution was filtered *via* cannula to give an orange-yellow filtrate. The filtrate was treated with petroleum ether (35 mL) and filtered *via* cannula to give 11 as a pale yellow solid (244 mg, 42%). Mp: 170 °C dec. ^{19}F NMR (benzene-d_6): δ −50.3 (4F, m, CF_2), −141.1 (2F, m, CF) ppm. ^{31}P{^{1}H} NMR (benzene-d_6): δ 32.8 (m) ppm. ^{1}H NMR (benzene-d_6): δ 8.1–6.9 (br mult) ppm. Upon standing, solutions of complex 11 rapidly converted to 7. Satisfactory microanalysis results could not be obtained for 11. Due to the complexity of the spin system AA′A″A‴GG′MM′X (A = CF_2, G = CF, M = P, X = Rh) the ^{19}F spectrum could not be simulated satisfactorily and *J* values could not be obtained.

NMR Tube Reaction of $[RhCl(PPh_3)_3]$ with Hexafluorobutadiene. An NMR tube (5 mm) was flame dried under vacuum. Bis(trimethylsilyl)acetamide (1–2 mL) was added to the NMR tube under a positive dinitrogen pressure and heated to reflux with a Bünsen burner for 10 min until the walls of the tube appeared waxy. The NMR tube was cooled under positive dinitrogen pressure, rinsed with acetone (3 × 3 mL), and pumped until dry (1 h). $[RhCl(PPh_3)_3]$ (26 mg, 2.69×10^{-5} mol) and benzene-d_6 (1 mL) were added to the silylated tube. The brick red slurry was degassed using the freeze–pump–thaw technique (2×). Hexafluorobutadiene (~1.8×10^{-5} mol) was collected in a gas bulb and condensed into the frozen NMR tube (−196 °C). The frozen NMR tube was sealed under vacuum and carefully warmed to room temperature. The ^{19}F NMR spectrum of the initial reaction solution displayed starting material and a small amount of 11. The NMR tube was inverted so that the contents were contained in the pointy end of the tube and heated in an oil bath at 66 °C. The reaction was monitored periodically by ^{19}F NMR by carefully inverting the tube to prevent the solid $[RhCl(PPh_3)_3]$ from washing into the NMR quality end of the tube. The ^{19}F NMR spectrum indicated virtually quantitative formation of 11.

On transfer to nonsilylated glassware the solution of 11 rapidly converted to 7. A drop of distilled, deoxygenated H_2O was added to a silylated NMR tube containing a toluene (0.6 mL) solution of 11 (20 mg). The sample was agitated for 5 min. The ^{19}F NMR spectrum of the mixture showed slow conversion to 7, which was rapidly accelerated by heating the tube with a heat gun.

Reaction of 7 with Tl(acac). A Schlenk flask was charged with 7 (0.196 g, 0.25 mmol), Tl(acac) (0.090 g, 0.25 mmol), and CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 18 h. The resulting pale yellow suspension was filtered *via* cannula to give a pale yellow supernatant and fine white solid (TlCl). The supernatant was evaporated to dryness giving an off white solid that was crystallized from toluene/petroleum ether at −20 °C to give off white crystals of 9 (92 mg, 42%). Mp: 185 °C dec. ^{19}F NMR (acetone-d_6): δ −69.2 [ddddd, $J_{F_1-F_{1'}} = 200$ Hz, $J_{F_1-F_2} = 16.4$ Hz, $J_{F_1-F_3} = 7.5$ Hz, $J_{F_1-P} = 43.5$ Hz, $J_{F_1-Rh} = 8.2$ Hz, F_1, $F_{1'}$], −133.0 [dt, $J_{F_1-F_2} = 16.4$ Hz, $J_{F_2-F_3} = 6.7$ Hz, F_2], −135.1 [ddt, $J_{F_1-F_3} = 7.5$ Hz, $J_{F_2-F_3} = 6.7$ Hz, $J_{F_3-P} = 2.9$ Hz, F_3] ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ 25.3 (dddd, $J_{F_1-P} = 43.5$ Hz, $J_{F_3-P} = 2.9$ Hz, $J_{P-Rh} = 121.1$ Hz, $J_{P-P} = 295$ Hz) ppm. ^{1}H NMR (acetone-d_6): δ 7.9–6.9 (30H, mult), 4.42 (1H, s, CH), 1.60 (3H, s, CH_3), 1.08 (3H, s, CH_3) ppm. Anal. Calcd for $C_{45}H_{37}F_4O_3P_2Rh$: C, 62.67; H, 4.30. Found: C, 62.40; H; 4.37.

Reaction of 7 with PMe_3. PMe_3 (110 μL, 1.06 mmol) was added to a stirred solution of 7 (0.213 g, 0.265 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 2 h at room temperature, and the solvent was removed under reduced pressure. The residue was crystallized from methanol to give **10** (53 mg, 39%). Mp: 180 °C dec. ^{1}H NMR (benzene-d_6): δ 1.01 (overlapping doublet and virtual triplet, *J* = 7.3, 3.7 Hz) ppm. ^{19}F NMR (benzene-d_6): δ −69.1 (2F, m, F_1 and $F_{1'}$), −132.2 (1F, dt, *J* = 9.2 Hz, *J* = 16.1 Hz, F_2), −139.5 (1F, dt, *J* = 9.4 Hz, F_3) ppm. ^{31}P{^{1}H} NMR (benzene-d_6): −8.4 (2P, m), −24.9 (1P, m) ppm. IR (CH_2Cl_2): $\nu_{C=C}$ = 1720, $\nu_{C=O}$ = 1668 cm^{-1}. Anal. Calcd for $C_{13}H_{27}ClF_4OP_3Rh$: C, 30.82; H, 5.37. Found: C, 30.50; H; 5.27.

Reaction of [RhCl(PMe$_3$)$_3$] with Hexafluorobutadiene. A flame dried Schlenk flask (50 mL) was charged with [RhCl(PMe$_3$)$_3$] (0.511 g, 1.39 mmol) and toluene (15 mL). Hexafluorobutadiene (600 Torr, 1.96 mmol) was collected in a gas bulb (60 mL) and condensed into the Schlenk flask at −196 °C. The mixture was warmed to −78 °C and stirred for 1 h. The resulting amber solution was warmed to room temperature and stirred for 18 h. The solution was cannula filtered, and the solvent and excess hexafluorobutadiene were removed under reduced pressure. The residue was crystallized from methylene chloride/petroleum ether to afford **12** (0.447 g, 61%). Mp: 193 °C dec. ^{19}F NMR (acetone-d_6): δ −67.5 (2F, m, CF_2), −81.2 (2F, m, CF_2), −140.2 (1F, m, CF), −142.0 (1F, m, CF) ppm. ^{31}P{^{1}H} NMR (benzene-d_6): δ −5.8 (2P, m), −21.9 (1P, m) ppm. ^{1}H NMR (acetone-d_6): δ 1.58 (d, *J* = 8.2 Hz), 1.48 (virtual t, *J* = 7.0 Hz) ppm. Anal. Calcd for $C_{13}H_{27}F_6P_3Rh$: C, 29.65; H, 5.17. Found: C, 29.53; H, 5.16. Complex **12** was air and moisture stable as a solid and in solution.

Chromatography of 12 on Alumina. A solution of **12** (60 mg) was subjected to column chromatography on neutral alumina with toluene as the initial eluant. Elution gave traces of a pale yellow eluate that displayed no ^{19}F NMR spectrum. Washing the column with methylene chloride afforded a yellow eluate which, upon solvent evaporation, crystallized to give **13** as pale yellow blocks (50 mg). ^{19}F NMR ($CDCl_3$): δ −46.6 (1F, m), −59.0 (2F, m), −140.5 (1F, m) ppm. (Resonances for an isomer thought to be **14** were observed at δ −61.3 (2F, m), −96.0 (1F, m), −102.2 (1F, m) ppm.) ^{31}P{^{1}H} NMR ($CDCl_3$): δ −5.1 (2P, m), −17.4 (1P, m) ppm. ^{1}H NMR ($CDCl_3$): δ 1.15 (virtual t), 0.97 (d, *J* = 7.35 Hz) [isomer **14** δ 1.01 (virtual t), 0.96 (d, *J* = 7.42 Hz)]. Anal. Calcd for $C_{13}H_{27}ClF_4OP_3Rh$: C, 30.82; H, 5.37. Found: C, 30.71; H, 5.21.

X-ray Crystallographic Determinations. Crystal, data collection, and refinement parameters are collected in Table I. Yellow crystals of **13**, **7** (as an acetone solvate), and **12** were each mounted on a glass fiber with epoxy cement. The unit cell parameters were obtained from the least squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic characterizations showed 2/*m* Laue symmetry for both **13** and **7** and *mmm* Laue symmetry for **12**. Systematic absences in the diffraction data of **13** and **7** uniquely established their space group as $P2_1/n$, and the systematic absences in the diffraction data for **12** uniquely established the space group as *Pbca*. No absorption correction was required for the data sets (low μ, T_{max}/T_{min} = 1.166, 1.152, and 1.178 for **13**, **7**, and **12**, respectively).

The structures of **13** and **7** were each solved by direct methods which located the Rh atoms; that of **12** was solved by a Patterson map which located the Rh atom. Compound **12** contains two independent molecules in the unit cell. The remaining nonhydrogen atoms for all compounds were located by subsequent least squares and difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions [d_{CH} = 0.960 Å, *U* = 1.2*U* for attached C for **13**, *U* is fixed (0.08 Å^3) for **7** and **12**]. All phenyl rings of **7** were fixed as rigid planar hexagons [d_{CC} = 1.396 Å]. For all compounds all non-hydrogen atoms were refined with anisotropic thermal parameters. The substituents on C(2) are chemically and positionally disordered in **13**. Various models were tested. The most chemically and crystallographically reasonable model contained a 60% occupancy oxygen atom in the ring plane and roughly equal populations (40% each) of sites above and below the ring plane (O′ and O″) which were treated as O/F composite atoms. The occupancies were refined with constraints appropriate to the assumption that C(2) was either C(=O) or CF(OH) substituted.

For **13**, all computer programs and the sources of the scattering factors are contained in the SHELXTL program library (5.1) [G. Sheldrick, Nicolet (Siemens)]. For **7** and **12** all computer programs and the sources of all the scattering factors are contained in the SHELXTLPLUS program library (4.11) [G. Sheldrick, Siemens, Madison, WI].

Acknowledgment. R.P.H. acknowledges the U.S. Air Force Office of Scientific Research for generous financial support, and Johnson Matthey Aesar/Alfa for a loan of precious metal salts.

Supplementary Material Available: Tables of crystal data, bond lengths and angles, thermal parameters, and atomic coordinates for **7** and **12** and tables of bond lengths and angles, thermal parameters, and atomic coordinates for **13** (19 pages). Ordering information is given on any current masthead page.

OM930172N