aqueous MeOH (10 mL) to give a low-melting yellow solid. Purification of the product by column chromatography afforded 0.11 g (55%) of (*p*-(dimethylamino)benzoyl)trimethylsilane: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.33 (s), 4.03 (s), 6.67 and 7.81 (d, AA'BB', J = 9.0 Hz); IR (KBr) 1610 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{19}NOSi$: C, 65.11; H, 8.65; N, 6.33. Found: C, 64.97; H, 8.51; N, 6.35.

Essentially in the same manner as described above, (*m*-(dimethylamino)benzoyl)trimethylsilane was obtained as a yellow oil: ^{1}H NMR δ 0.33 (s), 2.96 (s), 6.55–7.59 (m); IR (neat) 1605 cm^{-1}. Anal. Found: C, 65.08; H, 8.65; N, 6.47.

Measurements of Ultraviolet Spectra. Spectroscopic grade solvents (cyclohexane, hexane, ethanol, and THF) were used as received. UV spectra were recorded on a Shimadzu UV-200 spectrophotometer, concentration for n → π* bands being in a range of $(2.84–7.22) \times 10^{-5}$ mol/L. Solvent effects on the absorption maxima were examined for the parent benzoyltrimethylsilane, and data are shown in Table I.

All data for meta- and para-substituted benzoyltrimethylsilanes measured in cyclohexane are given in Table II.

For an examination of the substituent effect with respect to the observed wavenumbers of the n → π* band, σ values are taken from Jaffe's review[11] and σ_I and $\sigma_R{}^0$ values are from ref 8.

In addition, UV spectral data of other acylsilanes and -germanes, preparation of which was also reported in the preceding paper,[5] are listed in Table III.[4]

Acknowledgment. This work was supported by the Grant-in-Aid from the Ministry of Education, Japan (No. 555341), to which our thanks are due. We thank Prof. Morikawa of this department for the measurements of UV spectra.

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[11] Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.

Fluoroorganometallic Chemistry: Synthesis, Structure, and Chemistry of the Cubane Cluster $[FRh(C_2H_4)(C_2F_4)]_4$†

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Received September 23, 1986

The fluoro-bridged cluster $[FRh(C_2H_4)(C_2F_4)]_4$ was prepared by treatment of $[ClRh(C_2H_4)(C_2F_4)]_2$ with $AgBF_4$, followed by reaction with $[(CH_3)_2N]_3S^+(CH_3)_3SiF_2^-$. The cubanelike structure of the tetrameric complex was established by X-ray crystallography. Reaction of $[FRh(C_2H_4)(C_2F_4)]_4$ with $P(C_6H_5)_3$ yielded the new monometallic complex $FRh(C_2F_4)[P(C_6H_5)_3]_2$. The monometallic rhodium–fluoride complex can undergo reactions involving ligand substitution or fluoride extraction. In a ligand substitution reaction, solutions of $FRh(C_2F_4)[P(C_6H_5)_3]_2$ react with CO to give $FRh(CO)[P(C_6H_5)_3]_2$. Reaction with $(CH_3)_3SiO_3SCF_3$ yielded $CF_3SO_3Rh(C_2F_4)[P(C_6H_5)_3]_2$, derived from the fluoride extraction reaction.

Introduction

Although transition-metal complexes have wide utility in hydrocarbon transformations, the analogous chemistry of metal-bonded fluorocarbons is largely unexplored. Because of the importance of fluorocarbons as specialty chemicals, we have initiated a program aimed at elaborating the similarities and differences between organometallic and fluoroorganometallic chemistry. Hydrido–olefin complexes are cited as important intermediates in a variety of hydrocarbon transformations. We felt that an investigation of analogous fluoro–fluoroolefin complexes, a previously unknown structural type, would be of interest. While common in extended solid-state structures, fluorides are relatively unexplored as ligands in discrete molecular complexes compared to other halides. One reason is the ready solvolysis of the metal–fluorine bond.[1] In those cases where fluoride is observed as a bridging ligand, it is almost exclusively between two metal atoms; fluoride as a face-bridging ligand between three metal atoms is relatively rare.

An obvious route to a metal–fluoride fluoroolefin complex would be the metathesis reaction of fluoride for other halides in preformed fluoroolefin complexes. Many examples of complexes containing π-bonded fluoroolefins are known.[2] We chose to start by addition of fluoride sources to $[ClRh(C_2H_4)(C_2F_4)]_2$, a well-characterized chloro-bridged rhodium complex (1) first synthesized by Cramer.[3] The chemistry encountered in this approach was unexpectedly complex. Herein we report the synthesis and X-ray crystal

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† Contribution No. 4087.

[1] Vaska, L.; Peone, J. *J. Chem. Soc. D* **1971**, 418–419.

[2] Representative examples of simple π complexes of tetrafluoroethylene with transition metals are given below. For Fe, Ru, Os: Cooke, M.; Green, M.; Kuc, T. A.; *J. Chem. Soc. A* **1971**, 1200–1203. Burt, R.; Cooke, M.; Green, M. *J. Chem. Soc. A* **1970**, 2975–2981. Cooke, M.; Green, M. *J. Chem. Soc. A* **1969**, 651–655. For Rh, Ir: Parshall, G. W.; Jones, F. W. *J. Am. Chem. Soc.* **1965**, *87*, 5356–5361. Green, M.; Taylor, S. H. *J. Chem. Soc., Dalton Trans.* **1975**, 1128–1137. Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1165–1169. For Ni, Pd, Pt: Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780–2788. Browning, J.; Cook, D. J.; Cundy, C. S.; Green, M.; Stone, F. G. A. *Chem. Commun.* **1968**, 929–930. Cundy, C. S.; Green, M.; Stone, F. G. A., *J. Chem. Soc. A* **1970**, 1647–1653. Green, M.; Shakshooki, S. K.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2828–2834. Maples, P. K.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 388–392. Mukhedkar, V. A.; Mukhedkar, A. J. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2801–2805. Green, M.; Osborn, R. B. L.; Rest, A. J.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2525–2530. Fornies, J.; Green, M.; Laguna, A.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1515–1518. Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 449–451. Empsall, H. D.; Green, M.; Shakshooki, S. K.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 3472–3476. Maples, P. K.; Green, M.; Stone, F. G. A.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1194–1198. Clark, H. C.; Manzer, L. E. *J. Chem. Soc., Chem. Commun.* **1973**, 870–871. Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1974**, *13*, 1996–2004. See also: Booth, B. L.; Casey, S.; Haszeldine, R. N. *J. Organomet. Chem.* **1982**, *226*, 289–299. Simple π complexes of fluoroolefins of the early transition metal are exceedingly rare.

[3] Cramer, R.; Parshall, G. W. *J. Am. Chem. Soc.* **1965**, *87*, 1392–1393.

0276-7333/87/2306-0982$01.50/0

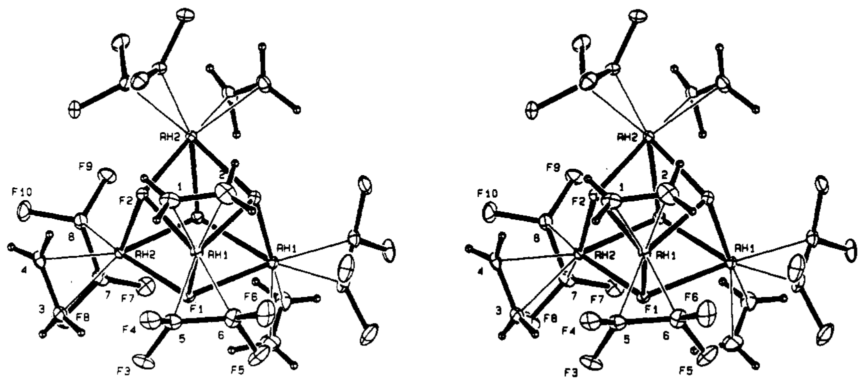


Figure 1. Stereoview of $[FRh(C_2H_4)(C_2F_4)]_4$ revealing the Rh_4F_4 core atoms in a distorted cubanelike framework. In this structure, each fluoride functions as a face-bridging ligand on a Rh_3 face.

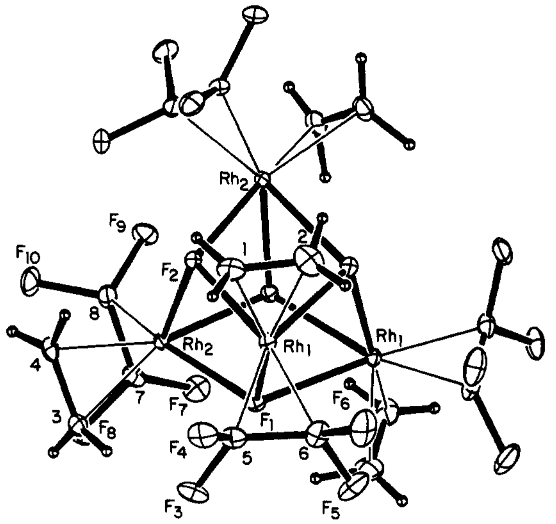
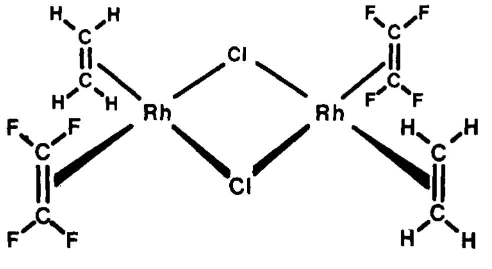


Figure 2. ORTEP view of $[FRh(C_2H_4)(C_2F_4)]_4$. A crystallographic 2-fold symmetry axis through one face of the cubane cluster (Figure 3) reduces the structure to two sets of unique [$FRh(C_2H_4)(C_2F_4)$] moieties.

structure of $[FRh(C_2H_4)(C_2F_4)]_4$, an example of a face-bridging fluoride in a discrete transition-metal–fluoride complex. We also report the reaction chemistry of its phosphine derivative $FRh(C_2F_4)[P(C_6H_5)_3]_2$.



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Results and Discussion

Reaction of $[ClRh(C_2H_4)(C_2F_4)]_2$[3] with 2 equiv of $AgBF_4$ in tetrahydrofuran followed by filtration to remove AgCl and then treatment with 2 equiv of $[(CH_3)_2N]_3S^+$-$(CH_3)_3SiF_2^-$ results in nearly quantitative formation of $[FRh(C_2H_4)(C_2F_4)]_4$ as determined spectroscopically. This product was isolated by removing the solvent by vacuum distillation and then recrystallizing from CH_2Cl_2/ether/pentane mixtures to afford large yellow crystals in an overall isolated yield of 55%.

Table I. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2
Rh(1)	−0.12163 (3)	−0.00268 (3)	0.06617 (1)	1.657 (5)
Rh(2)	0.02232(3)	0.20017 (3)	−0.04107 (2)	1.496 (5)
F(1)	−0.1130 (2)	0.0463 (2)	−0.0300 (1)	1.77 (4)
F(2)	0.0411 (2)	0.1193 (2)	0.0608 (1)	1.68 (4)
F(3)	−0.3331 (2)	0.1209 (3)	0.0248 (1)	3.63 (6)
F(4)	−0.3529 (3)	0.0732 (3)	0.1257 (1)	3.60 (6)
F(5)	−0.3059 (3)	−0.1187 (3)	−0.0046 (1)	4.44 (7)
F(6)	−0.3247 (3)	−0.1662 (3)	0.0964 (2)	4.95 (8)
F(7)	0.0913 (3)	0.1889 (3)	−0.1718 (1)	3.28 (6)
F(8)	0.0033 (3)	0.3628 (3)	−0.1522 (1)	3.82 (6)
F(9)	0.2634 (2)	0.2449 (3)	−0.0789 (1)	2.99 (6)
F(10)	0.1734 (3)	0.4177 (3)	−0.0630 (2)	3.66 (6)
C(1)	−0.1106 (5)	0.0219 (5)	0.1686 (2)	3.2 (1)
C(2)	−0.0892 (6)	−0.0943 (6)	0.1556 (2)	4.2 (1)
C(3)	−0.1282 (4)	0.3240 (4)	−0.0322 (2)	2.77 (9)
C(4)	−0.0406 (4)	0.3570 (4)	0.0107 (2)	2.63 (9)
C(5)	−0.2956 (4)	0.0446 (5)	0.0709 (2)	2.71 (9)
C(6)	−0.2800 (4)	−0.0815 (5)	0.0553 (2)	3.0 (1)
C(7)	0.0654 (4)	0.2709 (4)	−0.1252 (2)	2.48 (9)
C(8)	0.1541 (4)	0.2999 (4)	−0.0776 (2)	2.41 (8)
H(1)A	−0.178 (5)	0.043 (5)	0.186 (2)	5 (1)*
H(1)B	−0.050 (4)	0.078 (4)	0.169 (2)	2 (1)*
H(2)A	−0.008 (5)	−0.111 (5)	0.150 (2)	5 (1)*
H(2)B	−0.141 (4)	−0.152 (4)	0.158 (2)	3 (1)*
H(3)A	−0.197 (4)	0.272 (4)	−0.017 (2)	2 (1)*
H(3)B	−0.134 (5)	0.373 (5)	−0.066 (2)	5 (1)*
H(4)A	0.002 (4)	0.419 (4)	0.006 (2)	3 (1)*
H(4)B	−0.040 (5)	0.318 (5)	0.060 (2)	5 (1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3 + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

A single-crystal X-ray diffraction study revealed the tetrameric nature of this rhodium–fluoride cluster. A stereoview of this structure and an ORTEP drawing of $[FRh(C_2H_4)(C_2F_4)]_4$ are shown in Figures 1 and 2. Positional parameters, bond distances, and bond angles are given in Tables I–III, respectively. The structure consists of a distorted cube defined by interpenetrating tetrahedra of rhodium and fluorine atoms. Each rhodium atom bears one ethylene and one tetrafluoroethylene ligand. The ethylene ligands have a trans stereochemical relationship to a fluorine atom, and the carbon–carbon bond vectors of each pair of ethylene and tetrafluoroethylene ligands are parallel to one another. There is a crystallographically imposed C_2 axis of symmetry which runs perpendicular to one of the faces of the cube (Figure 3). The distortion of the core atoms from the idealized geometry of a cube is manifest by the bond angles within the core framework. All the F–Rh–F angles are in the range 70° to 80°, while the Rh–F–Rh angles are between 98° and 112°. This structure represents to our knowledge the first example

Table II. Bond Distances (Å)

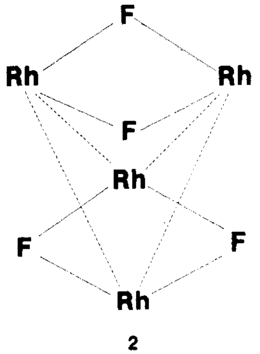
atom 1	atom 2	distance[a]	atom 1	atom 2	distance[a]	atom 1	atom 2	distance[a]
Rh(1)	F(1)	2.073 (2)	Rh(2)	C(8)	1.969 (4)	C(5)	F(3)	1.340 (5)
Rh(1)	F(1)	2.334 (2)	C(1)	C(2)	1.327 (8)	C(5)	F(4)	1.339 (5)
Rh(1)	F(2)	2.238 (2)	C(1)	H(1)A	0.86 (5)	C(5)	C(6)	1.434 (7)
Rh(1)	C(1)	2.152 (4)	C(1)	H(1)B	0.91 (4)	C(6)	F(5)	1.343 (5)
Rh(1)	C(2)	2.145 (5)	C(2)	C(1)	1.327 (8)	C(6)	F(6)	1.356 (5)
Rh(1)	C(5)	1.984 (4)	C(2)	H(2)A	0.92 (6)	C(6)	C(5)	1.434 (7)
Rh(1)	C(6)	1.957 (4)	C(2)	H(2)B	0.86 (5)	C(7)	F(7)	1.354 (5)
Rh(2)	F(1)	2.264 (2)	C(3)	C(4)	1.362 (7)	C(7)	F(8)	1.343 (5)
Rh(2)	F(2)	2.308 (2)	C(3)	H(3)A	0.99 (4)	C(7)	C(8)	1.425 (6)
Rh(2)	F(2)	2.088 (2)	C(3)	H(3)B	0.89 (5)	C(8)	F(9)	1.345 (5)
Rh(2)	C(3)	2.151 (4)	C(4)	C(3)	1.362 (7)	C(8)	F(10)	1.346 (5)
Rh(2)	C(4)	2.146 (4)	C(4)	H(4)A	0.83 (5)	C(8)	C(7)	1.425 (6)
Rh(2)	C(7)	1.972 (4)	C(4)	H(4)B	1.11 (5)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Bond Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
F(1)	Rh(1)	F(1)	77.76 (9)	F(1)	Rh(2)	C(4)	109.7 (2)	C(2)	C(1)	H(1)A	120 (4)
F(1)	Rh(1)	F(2)	76.12 (8)	F(1)	Rh(2)	C(7)	122.9 (1)	C(2)	C(1)	H(1)B	122 (3)
F(1)	Rh(1)	C(1)	157.0 (2)	F(1)	Rh(2)	C(8)	159.8 (1)	H(1)A	C(1)	H(1)B	116 (5)
F(1)	Rh(1)	C(2)	162.0 (2)	F(2)	Rh(2)	F(2)	79.20 (8)	C(1)	C(2)	H(2)A	113 (4)
F(1)	Rh(1)	C(5)	91.4 (1)	F(2)	Rh(2)	C(3)	103.5 (2)	C(1)	C(2)	H(2)B	126 (4)
F(1)	Rh(1)	C(6)	92.6 (2)	F(2)	Rh(2)	C(4)	83.0 (1)	H(2)A	C(2)	H(2)B	120 (5)
F(1)	Rh(1)	F(2)	70.31 (7)	F(2)	Rh(2)	C(7)	160.9 (1)	C(4)	C(3)	H(3)A	119 (3)
F(1)	Rh(1)	C(1)	109.9 (2)	F(2)	Rh(2)	C(8)	120.2 (1)	C(4)	C(3)	H(3)B	114 (4)
F(1)	Rh(1)	C(2)	84.5 (2)	F(2)	Rh(2)	C(3)	160.0 (1)	H(3)A	C(3)	H(3)B	123 (4)
F(1)	Rh(1)	C(5)	156.2 (1)	F(2)	Rh(2)	C(4)	159.3 (1)	C(3)	C(4)	H(4)A	123 (3)
F(1)	Rh(1)	C(6)	115.9 (2)	F(2)	Rh(2)	C(7)	91.9 (1)	C(3)	C(4)	H(4)B	121 (3)
F(2)	Rh(1)	C(1)	85.9 (2)	F(2)	Rh(2)	C(8)	90.8 (1)	H(4)A	C(4)	H(4)B	115 (5)
F(2)	Rh(1)	C(2)	101.0 (2)	C(3)	Rh(2)	C(4)	36.9 (2)	F(3)	C(5)	F(4)	108.5 (4)
F(2)	Rh(1)	C(5)	128.0 (2)	C(3)	Rh(2)	C(7)	90.6 (2)	F(3)	C(5)	C(6)	118.7 (4)
F(2)	Rh(1)	C(6)	166.0 (2)	C(3)	Rh(2)	C(8)	104.3 (2)	F(4)	C(5)	C(6)	118.4 (4)
C(1)	Rh(1)	C(2)	36.0 (2)	C(4)	Rh(2)	C(7)	101.9 (2)	F(5)	C(6)	F(6)	107.4 (4)
C(1)	Rh(1)	C(5)	88.4 (2)	C(4)	Rh(2)	C(8)	89.1 (2)	F(5)	C(6)	C(5)	118.6 (5)
C(1)	Rh(1)	C(6)	102.7 (2)	C(7)	Rh(2)	C(8)	42.4 (2)	F(6)	C(6)	C(5)	118.5 (4)
C(2)	Rh(1)	C(5)	103.9 (2)	Rh(1)	F(1)	Rh(1)	97.42 (9)	F(7)	C(7)	F(8)	107.9 (3)
C(2)	Rh(1)	C(6)	92.3 (3)	Rh(1)	F(1)	Rh(2)	108.80 (9)	F(7)	C(7)	C(8)	120.1 (4)
C(5)	Rh(1)	C(6)	42.7 (2)	Rh(1)	F(1)	Rh(2)	102.50 (8)	F(8)	C(7)	C(8)	118.1 (4)
F(1)	Rh(2)	F(2)	71.18 (7)	Rh(1)	F(2)	Rh(2)	101.82 (8)	F(9)	C(8)	F(10)	107.2 (3)
F(1)	Rh(2)	F(2)	74.34 (8)	Rh(1)	F(2)	Rh(2)	111.92 (9)	F(9)	C(8)	C(7)	119.8 (4)
F(1)	Rh(2)	C(3)	87.6 (2)	Rh(2)	F(2)	Rh(2)	95.20 (8)	F(10)	C(8)	C(7)	118.6 (4)

of a fluoro–fluoroolefin transition-metal complex.[4]



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An instructive analysis is to consider this cubane cluster as a dimer of dimers (**2**) and also to analyze the local coordination geometries about each of the metals. Distances between the rhodium atoms related by the 2-fold symmetry axis are shorter (3.32 and 3.25 Å) than the other two distances between metals (3.53 and 3.59 Å). The rhodium–fluoride distances also group into two classes with two short distances (2.07 and 2.09 Å) and four longer distances (2.24–2.33 Å). The two short distances are in the cube faces through which the 2-fold axis passes, and these fluorine atoms are trans to the ethylene molecules. The Rh–F distances parallel to the 2-fold axis are the longest. These observations suggest that a dimer of dimers is a reasonable initial description of the overall tetrameric structure.

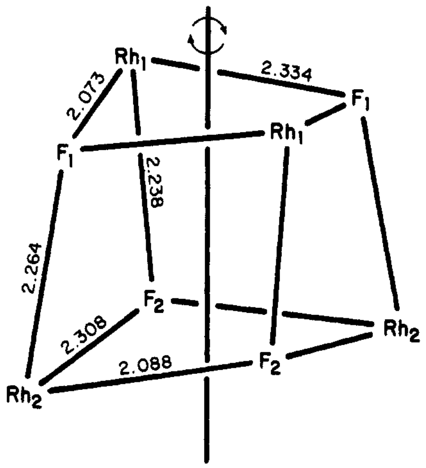

Figure 3. Schematic representation of the core atoms of [FRh(C_2H_4)(C_2F_4)]$_4$ depicting the crystallographically imposed 2-fold symmetry axis through a face of this cubane cluster.

Considering both the ethylene and the tetrafluoroethylene as monodentate ligands, then the local coordi-

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[4] A possible exception is the product of the reaction between FIr(CO)[P(C_6H_5)$_3$]$_2$ and C_2F_4. However, the published work does not allow an assignment of structure or composition. See: Mortimer, C. T.; McNaughton, J. L.; Burgess, J.; Hacker, M. J.; Kemmitt, R. D. W.; Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Organomet. Chem.* **1973**, *47*, 439–441.

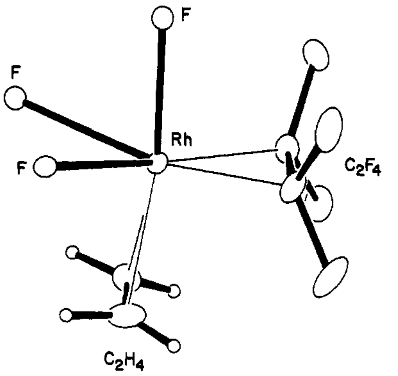

Figure 4. Representation of the local coordination geometry about each Rh in [FRh(C_2H_4)(C_2F_4)]$_4$. This coordination approximates a trigonal bipyramid with one fluoride and one C_2H_4 ligand in axial positions and two fluoride ligands and both carbon atoms of C_2F_4 in the equatorial plane. An equivalent description consistent with the metallocyclopropane model of C_2F_4 bonding to a metal is to consider this structure as an octahedron.

nation geometry about each of the rhodium atoms is trigonal bipyramidal. In this approximation of the structure, the ethylene resides in an axial position while the other axial position is occupied by the highly electronegative fluoride ion in this formally d^8 complex. Both of the carbon atoms of the tetrafluoroethylene ligand and the other two fluorides then reside in the equatorial plane. This representation of the structure can be seen in Figure 4.

Consistent with the crystal structure of (C_5H_5)Rh(C_2H_4)(C_2F_4),[5] the rhodium–carbon bond distances are shorter and the carbon–carbon bond distances are somewhat longer for the tetrafluoroethylene than for the ethylene ligand in the cubane cluster. The average rhodium–carbon bond distance in the tetrafluoroethylene ligand is 1.97 Å vs. 2.15 Å for the ethylene ligand. The carbon–carbon distances are 1.327 (8) and 1.362 (7) Å for the ethylenes compared to 1.425 (6) and 1.434 (7) Å for the tetrafluoroethylene ligands. The F–C–F angles are all in the range 107–109°. These structural characteristics of the individual Rh(C_2H_4)(C_2F_4) fragments are consistent with a metallocyclopropane model of tetrafluoroethylene coordination.[5] Such aspects of fluoroolefin vs. ethylene coordination have been discussed before.[5,6]

While examples of fluoride bridging between two metal atoms are legion,[7] fluoride as a face-bridging ligand is uncommon. Examples include the metal carbonyls of rhenium and manganese, $Mn_4(CO)_{12}F_x(OH)_{4-x}$[8] and $Re_4(CO)_{12}F_4$,[9] as well as the imidazole complexes[10] Co_4F_4(*N*-ethylimidazole)$_{12}^{4+}$ and Cd_4F_4(*N*-ethylimidazole)$_{12}$. All these complexes contain metals in high oxidation states or are of early transition metals for which the metal is relatively hard and fluorophilic. It is likely that hardness of the metal is requisite for effective face-bridging of the relatively hard fluoride ion. On this basis, it is anticipated that investigations of early-transition-metal fluorides will yield many examples of fluorides bonding to three or more metal atoms, but it is also expected that the reactivity of the fluoride in these complexes will be reduced relative to later transition metals for which the metal–fluorine bond strength is much lower.

Figure 5. Scheme summarizing interconversions of [ClRh(C_2H_4)(C_2F_4)]$_2$ and [FRh(C_2H_4)(C_2F_4)]$_4$, and their phosphine derivatives. In general, phosphines effect fragmentation of the tetramer but P(C_6H_5)$_3$ does not displace the C_2F_4 ligand.

At issue is whether the tetrameric framework observed for [FRh(C_2H_4)(C_2F_4)]$_4$ in the solid state is maintained in the solution state or whether the cubane cluster is in equilibrium with two dimers (eq 1). Cryscopic molecular

$$[FRh(C_2H_4)(C_2F_4)]_4 \rightleftharpoons 2[FRh(C_2H_4)(C_2F_4)]_2 \quad (1)$$

weight determinations in tetrahydrofuran suggest that the solution structure is in fact a dimeric compound, [FRh(C_2H_4)(C_2F_4)]$_2$, the direct fluoride analogue of the chloride compound [ClRh(C_2H_4)(C_2F_4)]$_2$. However, analysis of the ^{19}F, ^{13}C, and ^{1}H NMR spectra did not permit a determination of the solution-state structure of the tetrameric complex.

Consistent with the X-ray crystal structure, the ^{1}H NMR spectrum of [FRh(C_2H_4)(C_2F_4)]$_4$ showed a single sharp line at 25 °C for the ethylene ligand. This spectrum was the high-temperature limiting spectrum. This resonance became broader ($\omega_{1/2} \approx 200$ Hz at −65 °C) as the temperature was lowered, but at −65 °C the resonance showed no evidence for approaching the low-temperature limit. The ^{19}F NMR spectrum showed two sets of two equivalent fluorine nuclei for the C_2F_4 resonances and a resonance at −317.6 ppm for the metal–fluoride fluorine nucleus. This resonance was broad but had no resolvable coupling to any of the other NMR active nuclei. Accordingly in this complex, the C_2H_4 ligand is rotating rapidly about the metal olefin bond while the C_2F_4 ligand is static. The static behavior of the C_2F_4 ligand is typical of tetrafluoroethylene ligands and is consistent with the metallocyclopropane model of tetrafluoroethylene coordination.[5] No features of the ^{1}H, ^{19}F, or ^{13}C NMR spectra were suggestive of disruption of the tetrameric framework such as described in eq 1.

Addition of P(C_6H_5)$_3$ to solutions of [FRh(C_2H_4)(C_2F_4)]$_4$ elicits a fragmentation of the cluster to yield the new monometallic complex FRh(C_2F_4)[P(C_6H_5)$_3$]$_2$. This complex is the precise fluoride analogue of the previously known complex ClRh(C_2F_4)[P(C_6H_5)$_3$]$_2$.[11] The monometallic rhodium–fluoride can alternatively be prepared from ClRh(C_2F_4)[P(C_6H_5)$_3$]$_2$ by reaction of that complex with $AgBF_4$, filtration to remove precipitated AgCl, and then treatment of the resulting filtrate with $[(CH_3)_2N]_3S^+(CH_3)_3SiF_2^-$. FRh($C_2F_4$)[P($C_6H_5$)$_3$]$_2$ is then isolated as an analytically pure pale yellow solid by recrystallization from CH_2Cl_2/ether/pentane mixtures.

The rhodium–fluoride FRh(C_2F_4)[P(C_6H_5)$_3$]$_2$ is itself reactive toward simple Lewis bases. Addition of 1 equiv of carbon monoxide to CH_2Cl_2 solutions of FRh(C_2F_4)[P(C_6H_5)$_3$]$_2$ results in nearly instantaneous substitution of the tetrafluoroethylene ligand to yield FRh(CO)[P(C_6H_5)$_3$]$_2$.[1] In a fluoride extraction reaction, CF_3SO_3Rh(C_2F_4)[P(C_6H_5)$_3$]$_2$ was prepared by addition of $(CH_3)_3SiO_3S$-

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CF_3 to CH_2Cl_2 solutions of $FRh(C_2F_4)[P(C_6H_5)_3]_2$. In this triflate complex, the CF_3SO_3 group is oxygen bonded to the central rhodium atom. None of these reactions revealed any evidence for insertion of the tetrafluoroethylene ligand into the metal–fluoride bond. Furthermore, both the cubane cluster $[FRh(C_2H_4)(C_2F_4)]_4$ and the monometallic species $FRh(C_2F_4)[P(C_6H_5)_3]_2$ were unreactive toward added fluoroolefin. This chemistry is summarized in Figure 5.

We are presently extending these studies to include perfluoroalkyl–perfluoroolefin rhodium compounds and are investigating the possibility of a subsequent insertion step of the fluoroolefin into the metal perfluoroalkyl bond.[12]

Experimental Section

All experiments were performed in a nitrogen-filled drybox equipped with a built-in freezer, on a standard Schlenk line with argon source or on a vacuum line. ^{19}F NMR spectra (188 or 282 MHz) are reported relative to $CFCl_3$, $^{31}P\{^1H\}$ NMR spectra (122 MHz) are reported relative to 85% H_3PO_4, and ^1H NMR spectra (300 MHz) are reported relative to $Si(CH_3)_4$. Tetrahydrofuran, ether, pentane, and tetrahydrofuran-d_8 were distilled from sodium benzophenone ketyl. CH_2Cl_2 and CD_2Cl_2 were distilled from P_2O_5. $[(CH_3)_2N]_3S^+(CH_3)_3SiF_2^-$ and $(CH_3)_3SiO_3SCF_3$ were purchased from Aldrich. The starting material $[ClRh(C_2H_4)(C_2F_4)]_2$ was prepared by the literature procedure.[3] **CAUTION**: *C_2F_4 is potentially explosive and should be handled in well-shielded equipment with rigorous exclusion of oxygen. Heating uninhibited C_2F_4 should also be avoided.*

Preparation of $[FRh(C_2H_4)(C_2F_4)]_4$. A 0.75-g (1.41 mmol) portion of $[ClRh(C_2H_4)(C_2F_4)]_2$ was dissolved in approximately 25 mL of tetrahydrofuran. A 0.55-g (2.81 mmol) portion of $AgBF_4$ in approximately 10 mL of tetrahydrofuran was added dropwise with stirring over the course of about 20 min to the solution of the rhodium compound. The solution was stirred an additional hour at room temperature and then the solution was filtered on a fine porosity frit to remove AgCl. The filtrate was treated dropwise with stirring over the course of approximately 30 min with a tetrahydrofuran solution of 0.77 g (2.81 mmol) of $[(CH_3)_2N]_3S^+(CH_3)_3SiF_2^-$. The solution was stirred for an additional hour and then the solution was filtered on a fine porosity frit to remove white solids. The volume was reduced by means of vacuum distillation to a few milliliters and then pentane was added to just induce cloudiness. Cooling to −35 °C for 12 h yielded a yellow powder. The yellow powder was twice recrystallized from CH_2Cl_2/ether/pentane to yield $[FRh(C_2H_4)(C_2F_4)]_4$ as fine yellow crystals. Yield: 0.70 g, 55%. ^1H NMR (CD_2Cl_2, +25 °C): +4.2 ppm (d, J_{Rh-H} = 1.4 Hz). This spectrum was the high temperature limiting spectrum. As the sample was cooled, this resonance broadened but maintained the same chemical shift. At −65 °C the low temperature limiting spectrum was still not obtained. ^{19}F NMR (CD_2Cl_2, +25 °C): −115.2 ppm (mult, 2 F, C_2F_4), −121.6 (mult, 2 F, C_2F_4), −317.6 (br, s, 1 F, Rh-*F*). Each of these multiplet resonances in the C_2F_4 region approximates a doublet of doublets with J_{F-F}(trans) = 88 Hz, J_{F-F}(gem) = 35 Hz ($\omega_{1/2} \cong$ 30 Hz). Presumably, coupling to ^{103}Rh is not resolved. The ^{19}F spectra were temperature invariant but were moderately solvent dependent. ^{19}F NMR (THF-d_8, +25 °C) −121.0 ppm (mult, 2 F, C_2F_4), −123.5 (mult, 2 F, C_2F_4), −298.6 (br, 1 F, Rh-*F*). ^{19}F NMR (toluene-d_8, +25 °C): −119.4 ppm (mult, 2 F, C_2F_4), −122.2 (mult, 2 F, C_2F_4), −298.8 (br, 1 F, Rh-*F*). $[FRh(C_2H_4)(C_2F_4)]_4$ reacted irreversibly with dimethyl-d_6 sulfoxide and acetone-d_6. Anal. Calcd: C, 19.20; H, 1.60. Found: C, 19.70; H, 1.50. Molecular weight (cryoscopy, tetrahydrofuran solution): calcd, 1000; found, 424, 467 (Schwarzkopf).

Preparation of $ClRh(C_2F_4)[P(C_6H_5)_3]_2$. $ClRh(C_2F_4)[P(C_6H_5)_3]_2$ is known from the literature,[11] but a more straightforward synthesis follows. A solution of 1.00 g (1.88 mmol) of $[ClRh(C_2H_4)(C_2F_4)]_2$ in 50 mL of CH_2Cl_2 was treated with a solution of 2.00 g (7.50 mmol) of $P(C_6H_5)_3$ in approximately 20 mL of CH_2Cl_2 dropwise with stirring over the course of 1 h. The solution was stirred an additional 14 h. The solvent volume was reduced to about half by means of vacuum distillation, and then an equal volume of pentane was added, precipitating a yellow powder. The yellow powder was isolated by filtration and dried in vacuo (2.3 g).

Preparation of $FRh(C_2F_4)[P(C_6H_5)_3]_2$. A solution of 2.00 g (2.62 mmol) of $ClRh(C_2F_4)[P(C_6H_5)_3]_2$[11] in approximately 50 mL of tetrahydrofuran was treated dropwise with stirring over the course of about 20 min with a solution of 0.50 g (2.62 mmol) of $AgBF_4$ in 20 mL of tetrahydrofuran. The solution was stirred for an additional 1 h at room temperature. Then it was filtered on a fine porosity frit to remove AgCl and then treated with a tetrahydrofuran solution of 0.72 g (2.62 mmol) of $[(CH_3)_2N]_3S^+(CH_3)_3SiF_2^-$. The solution was stirred for an additional 1 h. The solution was again filtered on a fine porosity frit. The volume was reduced to approximately 20 mL by vacuum distillation, and an equal volume of pentane was added. Cooling the solution to −35 °C for 12 h resulted in a large yield of $FRh(C_2F_4)[P(C_6H_5)_3]_2$ as a fine yellow powder. ^{19}F NMR (CD_2Cl_2, +25 °C): −102.9 ppm (4 F, C_2F_4, six line pattern for the magnetically inequivalent C_2F_4 fluorine nuclei), −190.6 (br, s, $\omega_{1/2}$ = 180 Hz, Rh-*F*). This spectrum of the C_2F_4 region approximates a doublet of doublet of doublets with both J_{P-F} coupling constants approximately equal to 25.4 Hz and J_{Rh-F} = 9.3 Hz.[3] No fluorine–fluorine coupling could be resolved. These spectra in CD_2Cl_2 were temperature dependent. As the temperature was lowered, the resonances for the coordinated tetrafluoroethylene moved slightly upfield, from −102.9 ppm at +25 °C to −103.5 ppm at −65 °C, but the coupling constants for these resonances remained the same. The resonance for the rhodium fluoride moved upfield from −190.6 ppm at +25 °C to −195.2 at −65 °C. As the temperature was lowered, the previously broad resonance for the rhodium fluoride became sharper and at 0 °C was a quartet (*J* = 32 Hz) for the equivalent coupling to two ^{31}P nuclei and one ^{103}Rh nucleus. The magnitude of the coupling constant did not change any further. All these spectral characteristics were fully reversible upon warming the sample. ^{19}F NMR (dimethyl-d_6 sulfoxide, +25 °C): −114 ppm (br, 4 F) and −152 (br, 1 F). ^{19}F NMR (CD_3CN, +25 °C): −118 ppm (mult, 4 F) and −158 (br, 1 F). ^{19}F NMR (acetone-d_6, +25 °C): −150.7 ppm (s, 4 F, for C_2F_4) and −169.5 (br, 1 F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, +25 °C): +35.6 ppm (d, J_{Rh-P} = 142 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −65 °C): −35.5 ppm (d of mult, J_{Rh-P} = 147 Hz). Anal. Calcd: C, 61.11; H, 4.02; P, 8.31. Found: C, 60.24; H, 4.21; P, 8.21. (Carbon analyses are typically low for transition metal complexes of tetrafluoroethylene due to incomplete combustion of fluorocarbons.)

Alternative Preparation of $FRh(C_2F_4)[P(C_6H_5)_3]_2$. A solution of 0.63 g (0.63 mmol of $[FRh(C_2H_4)(C_2F_4)]_4$ in approximately 30 mL of CH_2Cl_2 was treated dropwise with stirring over the course of 30 min with a solution of 1.32 g (5.04 mmol) of $P(C_6H_5)_3$ in approximately 25 mL of CH_2Cl_2. The solution was stirred for an additional 14 h at room temperature. The solvent volume was reduced by means of vacuum distillation to about half the original volume and then 2 mL of ether followed by about 10 mL of pentane were added to precipitate flocculent $FRh(C_2F_4)[P(C_6H_5)_3]_2$ as a yellow powder. The product was isolated by filtration, washed with pentane, and dried in vacuo to afford 0.69 g of product.

Preparation of $FRh(CO)[P(C_6H_5)_3]_2$. A slurry of 0.50 g (0.67 mmol) of $FRh(C_2F_4)[P(C_6H_5)_3]_2$ in 5 mL of CH_2Cl_2 was treated with 17 mL (0.70 mmol) of CO added by means of a gas-tight syringe. Almost within time of mixing, the $FRh(C_2F_4)[P(C_6H_5)_3]_2$ went into solution yielding a clear yellow solution of $FRh(CO)[P(C_6H_5)_3]_2$. The resulting solution was treated with 8 mL of a 1:1 ether/pentane mixture and then cooled to −35 °C for 24 h to afford a 70% isolated yield of $FRh(CO)[P(C_6H_5)_3]_2$. Spectroscopic measurements on the reaction solution showed that the carbonyl compound formed quantitatively and was spectroscopically pure. ^{19}F NMR (CD_2Cl_2, +25 °C): −169.4 ppm (br, $\omega_{1/2}$ = 170 Hz, Rh-*F*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, +25 °C): +24.85 ppm (d, J_{Rh-P} = 137 Hz). ν(CO) infrared (CH_2Cl_2 solution): 1971 cm^{-1}.

Preparation of $CF_3SO_3Rh(C_2F_4)[P(C_6H_5)_3]_2$. A solution of 0.030 g (0.040 mmol) of $FRh(C_2F_4)[P(C_6H_5)_3]_2$ in 0.7 mL of CD_2Cl_2 was treated with 7.7 μL (0.040 mmol) of $(CH_3)_3SiO_3SCF_3$. There

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(12) We have recently prepared $CF_3Rh(C_2F_4)[P(C_6H_5)_3]_2$(solvent). Details of its synthesis and reactivity are forthcoming. Burch, R. R.; Calabrese, J. C., unpublished results.

was a rapid color change from pale yellow to deep yellow. ^{19}F NMR (CD_2Cl_2, +25 °C): −77.8 ppm (s, 3 F, O_3SCF_3) and −97.4 (d of d of d, J_{Rh-F} = 13.3 Hz, and both J_{P-F} coupling constants approximately 27.8 Hz). ^{31}P {^1H} NMR (CD_2Cl_2, +25 °C): +36.7 ppm (d of mult, J_{Rh-P} = 137.5 Hz).

X-ray Data Collection and Structure Solution for $[FRh(C_2H_4)(C_2F_4)]_4$. A single crystal of dimensions 0.20 × 0.13 × 0.25 mm was cut from a large brownish yellow block of $[FRh(C_2H_4)(C_2F_4)]_4$. Data were collected on an Enraf-Nonius CAD4 autodiffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The crystal was tetragonal, space group $P4_12_12$ (no. 92), with a = 10.992 (4) and c = 20.800 (7) Å (at −75 °C). The cell volume, 2513 (2) Å^3, yields a calculated density of 2.643 g cm^{-3} for Z = 4.

Intensity data were collected for 3266 independent reflections (4° < 2θ < 55°), using ω scans at a rate of 5° min^{-1} over a range of 0.8 + 0.35 tan θ deg. Statistical fluctuations were noted in two standard reflections which were monitored every 2 h. Empirical absorption correction factors ranging from 0.825 to 1.000 were applied (μ = 26.96 cm^{-1}). The structure was solved by direct methods and refined by using full-matrix least-squares techniques. The refinement of 213 variables (anisotropic thermal parameters for Rh, F, C; isotropic for H) using 2635 reflections [$I > 2\sigma(I)$] converged at R = 0.025. A refinement of the enantiomorphic structure converged at R = 0.031. In the final difference Fourier map, the four largest peaks, 0.89–1.31 e Å^{-3}, were located near the Rh atom. All computations were carried out with programs supplied by the Enraf-Nonius Corp.

Acknowledgment. The technical assistance of Mrs. G. E. Barkley is gratefully acknowledged.

Supplementary Material Available: Crystal data and tables of thermal parameters and positional parameters (9 pages); tables of structure factors for $[FRh(C_2H_4)(C_2F_4)]_4$ (16 pages). Ordering information is given on any current masthead page.