to those of similar unsubstituted cyclopentadienylmetal carbonyl derivatives[25] with the added possibility (particularly noticeable in $(CH_3)_5C_5Mn(CO)_3$) of competitive successive losses of methyl groups from the pentamethylcyclopentadienyl ring. The decamethylferrocene ion $[(CH_3)_5C_5]_2Fe^+$ was observed as a pyrolysis product in the mass spectrum of $CH_3COFe(CO)_2C_5(CH_3)_5$ similar to the observation of the ferrocene ion $(C_5H_5)_2Fe^+$ as a pyrolysis product in the mass spectra of numerous cyclopentadienyliron carbonyl derivatives.[25]

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(25) R. B. King, *J. Amer. Chem. Soc.*, **90**, 1417 (1968).

Crystal Structure of $(C_5H_5)Rh(C_2F_4)(C_2H_4)$. A Comparison of Rhodium–Ethylene and Rhodium–Tetrafluoroethylene Bonding

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Abstract: The molecular and crystal structures of π-cyclopentadienylethylenetetrafluoroethylenerhodium, $(C_5H_5)Rh(C_2F_4)(C_2H_4)$, have been determined from room-temperature X-ray diffractometer data. The molecule has idealized $C_s(m)$ symmetry with the rhodium atom coordinated to a cyclopentadienyl ring, an ethylene ligand, and a tetrafluoroethylene ligand. The rhodium to C_5H_5 ring plane distance is 1.899 Å. The ethylene ligand distances are 2.167 (2) Å for Rh–C and 1.358 (9) Å for C–C; the tetrafluoroethylene distances are 2.024 (2) Å for Rh–C and 1.405 (7) Å for C–C. The dihedral angle between the fluorine atom substituents is 74.3°, greater than for any observed metal–olefin substituent angles and close to the positions expected for "tetrahedral" geometry. The ethylene hydrogen atoms were located and refined, establishing the nonplanar geometry of the coordinated ethylene. The carbon atom geometry found for the ethylene ligand is nearly identical with that in ethylene oxide, C_2H_4O. The stereochemical implications with respect to bonding are examined; the large differences in rhodium–olefin distances are discussed in terms of increased π bonding to the tetrafluoroethylene ligand which exerts a significant trans influence (0.07 Å) on the cyclopentadienyl ring. Crystals of $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ are monoclinic, space group $P2_1/c$, with four molecules per cell of dimensions a = 7.262 (4), b = 9.101 (4), c = 16.879 (9) Å, and β = 118.49 (9)°. The structure was solved by Patterson and Fourier techniques and refined by least squares to a conventional R of 0.031.

In recent years a great many metal–olefin complexes have been prepared and much has been inferred about the metal–olefin geometry from spectral evidence,[1] but there have been few systematic studies of the influence of olefin substitution on the metal–olefin stereochemistry. We report here the molecular and crystal structures of π-cyclopentadienylethylenetetrafluoroethylenerhodium, $(C_5H_5)Rh(C_2F_4)(C_2H_4)$, which is ideal for assessing the effects of fluoro substitution on rhodium–olefin geometry, since it contains both the substituted and unsubstituted olefins. The very electronegative fluorine substituents provide a valuable comparison with the available metal–olefin structural data on cyano-substituted olefins. Differences might be anticipated in view of the nature of the inductive and π-acceptor characteristics of the substituents. Of particular interest is the comparison of the geometries of the olefin carbon atoms and its relation to the σ–π *vs.* "metallocyclopropane" metal–olefin bonding models.

The preparation and interpretation of the nmr spectrum of $(C_2H_5)Rh(C_2F_4)(C_2H_4)$ were reported earlier.[2] The nmr spectrum in particular suggested a significant difference in metal–olefin bonding between the unsubstituted and tetrafluoro-substituted olefins. The coupling constants of the ethylene protons change little on coordination to rhodium, but the fluorine–fluorine couplings of tetrafluoroethylene change significantly following coordination to rhodium.

The structure of $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ is compared with the available data from the recent structure determination of acetylacetonatoethylenetetrafluoroethylenerhodium, $(C_5H_7O_2)Rh(C_2F_4)(C_2H_4)$.[3]

Crystal Data and Structure Determination

Crystals of π-cyclopentadienylethylenetetrafluoroethylenerhodium, $(C_5H_5)Rh(C_2F_4)(C_2H_4)$, are monoclinic, space group $P2_1/c$, with cell dimensions of a = 7.262 (4), b = 9.101 (4), c = 16.879 (9) Å, and β = 118.49 (9)°. These parameters resulted from the least-squares refinement of 11 carefully measured reflections on the diffractometer. The observed and calculated densities for four molecules per cell are 1.94 and 2.01 g/cm³, respectively. There is no space group imposed molecular symmetry. All atoms were placed in the general positions $\pm(x, y, z; x, \frac{1}{2} - y, \frac{1}{2} + z)$.[4]

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(1) F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969), and references therein for work on platinum and palladium complexes.

(2) R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 2519 (1969).

(3) J. A. Evans and D. R. Russell, *Chem. Commun.*, 197 (1971).

(4) "International Tables for X-ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 99.

A prismatic crystal of dimensions 0.20 × 0.24 × 0.32 mm was chosen for this investigation. The crystal was mounted on a Picker four-circle automatic diffractometer with the 010 axis coincident with the diffractometer ϕ axis. Data were measured out to a 2θ of 50° using Zr-filtered Mo Kα radiation (λ 0.7107 Å) and the θ–2θ scan technique. The scan range used was 1.5° (1°/min) plus the angular separation of Kα_1 and Kα_2 with individual backgrounds of 10 sec recorded before and after each scan. A total of 1637 reflections was measured including check reflections and *hk*0 and $\bar{h}k0$ data which were averaged.

The data were corrected in the usual way for Lorentz and polarization effects and for absorption using the program ACACA.[5] The linear absorption coefficient for Mo Kα radiation is 17.2 cm^{-1}. The crystal was approximated by six plane faces for the absorption correction. The minimum and maximum calculated transmission factors are 0.66 and 0.72, respectively. The structure factor errors were estimated as previously described.[6] Structure factors which were less than their estimated standard deviations were called "unobserved" and given zero weight in the refinement.

The rhodium atom position was determined from the regular Patterson synthesis. The remaining nonhydrogen atoms were found in two steps on electron density difference maps. The $R(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.082 with anisotropic thermal parameters for the Rh atom and isotropic thermal parameters for the remaining nonhydrogen atoms. The R was 0.038 after allowing all the atoms to have anisotropic thermal parameters. The large decrease in R reflects the considerable anisotropic behavior of the fluorine and cyclopentadienyl carbon atoms.

An electron density difference map was examined for the locations of the ethylene hydrogen atoms. There was clear evidence for all four ethylene hydrogen atoms (0.4–0.6-e/Å^3 peaks). The hydrogen atom positional parameters were varied in further refinements but not their thermal parameters which were set at 5.0 Å^2. The wR values, $\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, before and after inclusion of the hydrogen atoms were 0.053 and 0.050, respectively, indicating statistical significance.[7] The cyclopentadienyl hydrogen atoms were placed in their calculated positions with isotropic thermal parameters of 9.0 Å^2. No attempt was made to refine these positions in view of the large anisotropic thermal motion of the ring carbon atoms.

The large thermal motion of the cyclopentadienyl ring is in the ring plane in a fashion typical of librational motion. The following two questions in particular were considered in view of the thermal motion and the variation in C–C ring distances observed: (a) whether the C_5H_5 ring is disordered between several conformations, and (b) whether a rigid group refinement would be more appropriate than an individual atom refinement. Separate refinements were done with the C_5H_5 ring disordered between conformations related by a twofold axis (180° rotational disorder). The higher R factors obtained confirmed that this was not occurring here. Small static conformational disorder which is difficult to separate from dynamic librational motion cannot be excluded, but it is usually adequately described by individual thermal parameters. A rigid group refinement was not done because of the systematic nature of the bond lengths observed and their possible correlation with trans effects (*vide infra*). Thus the individual atom refinement seemed to be the best way to handle the C_5H_5 ring here.

The refinement converged after several more cycles of refinement. The final parameter shifts were on the order of 0.1 of their standard deviations. The final R values for the 1465 observed reflections were 0.031 for R and 0.041 for wR. The standard deviation of an observation of unit weight is 1.379. An examination of $w\Delta^2$ averages as a function of F_o, and $(\sin\theta)/\lambda$ indicated that the estimated errors in the weak reflections were somewhat underestimated, but no weighting scheme modification was made.

The least-squares minimized the function $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors for the neutral atoms were used.[8] The real and imaginary parts[9] of the anomalous scattering of rhodium were included in the calculated structure factors.

The final positional parameters are given in Table I and the thermal parameters in Table II. The observed and calculated structure factors (× 3) are available.[10]

Table I. Positional Parameters for $(C_5H_5)Rh(C_2F_4)(C_2H_4)$[a]

Atom	*x*	*y*	*z*
Rh	0.47900 (5)	0.20908 (4)	0.12618 (2)
F(1)	0.3696 (5)	0.5112 (3)	0.0690 (2)
F(2)	0.1421 (5)	0.4213 (4)	0.1035 (2)
F(3)	0.2647 (6)	0.3055 (4)	−0.0608 (2)
F(4)	0.0400 (5)	0.2140 (4)	−0.0242 (2)
C(1)	0.3347 (9)	0.1491 (8)	0.2083 (4)
C(2)	0.2879 (10)	0.0440 (8)	0.1444 (5)
C(3)	0.2854 (7)	0.3846 (5)	0.0771 (3)
C(4)	0.2315 (7)	0.2767 (6)	0.0101 (3)
C(5)	0.7204 (9)	0.1183 (14)	0.0944 (6)
C(6)	0.7399 (9)	0.2706 (13)	0.1042 (7)
C(7)	0.8045 (10)	0.2986 (9)	0.1972 (8)
C(8)	0.8109 (10)	0.1656 (16)	0.2331 (5)
C(9)	0.7599 (11)	0.0633 (10)	0.1737 (9)
H(1)C(1)	0.4501 (102)	0.1410 (76)	0.2719 (44)
H(2)C(1)	0.2304 (123)	0.2121 (71)	0.2036 (46)
H(3)C(2)	0.3688 (103)	−0.0472 (77)	0.1644 (43)
H(4)C(2)	0.1576 (99)	0.0417 (76)	0.0939 (43)
H(5)C(5)	0.6843	0.0521	0.0318
H(6)C(6)	0.7128	0.3581	0.0503
H(7)C(7)	0.8393	0.4106	0.2374
H(8)C(8)	0.8485	0.1405	0.3001
H(9)C(9)	0.7472	−0.0519	0.1828

[a] The standard deviations of the least significant digits are given in parentheses.

Structure Description

The crystal structure of $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ consists of the packing of discrete molecules. The molecular structure illustrating the numbering system used

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(5) The programs used here, in addition to various local programs, include Prewitt's absorption correction program ACACA and least-squares program SFLS5, the Busing–Levy error function program ORFFE, the Johnson plotting program ORTEP, and the Fourier program FOUR written in part by C. J. Fritchie, Jr.

(6) L. J. Guggenberger, *Inorg. Chem.*, 7, 2260 (1968).

(7) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(8) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *ibid.*, 17, 1040 (1964).

(9) D. H. Templeton in ref 4, Vol. III, 1962, p 215.

(10) This table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-3779. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

Table II. Thermal Parameters (× 10^4) for $(C_5H_5)Rh(C_2F_4)(C_2H_4)$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	164.7 (11)	120.8 (6)	41.4 (2)	−11.7 (5)	32.2 (3)	2.3 (2)
F(1)	397 (10)	141 (4)	88 (2)	−26 (5)	57 (4)	20 (2)
F(2)	352 (10)	222 (5)	90 (2)	87 (6)	98 (4)	6 (3)
F(3)	430 (12)	279 (7)	46 (2)	32 (6)	43 (3)	10 (2)
F(4)	223 (8)	228 (6)	90 (2)	−51 (5)	0 (3)	−15 (3)
C(1)	321 (17)	257 (11)	79 (4)	3 (12)	97 (7)	47 (6)
C(2)	364 (19)	199 (10)	120 (5)	−59 (12)	116 (9)	33 (6)
C(3)	233 (12)	126 (6)	56 (3)	−1 (7)	47 (5)	7 (3)
C(4)	203 (12)	180 (8)	45 (3)	0 (8)	20 (4)	1 (4)
C(5)	241 (17)	433 (22)	96 (5)	−2 (17)	74 (8)	−88 (9)
C(6)	218 (16)	403 (19)	120 (6)	97 (15)	107 (9)	127 (9)
C(7)	211 (16)	238 (13)	157 (9)	−96 (11)	104 (10)	−90 (8)
C(8)	199 (17)	507 (27)	61 (4)	24 (18)	21 (6)	25 (8)
C(9)	280 (21)	220 (13)	172 (9)	57 (13)	76 (13)	47 (9)

[a] The standard deviations of the least significant digits are given in parentheses. The hydrogen atom thermal parameters were fixed at 5.0 Å^2 for H(1)–H(4) and 9.0 Å^2 for H(5)–H(9). The anisotropic thermal ellipsoid is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Selected Interatomic Distances for $(C_5H_5)Rh(C_2F_4)(C_2H_4)$[a]

Rh–C(1)	2.169 (5)	C(3)–F(1)	1.342 (5)
Rh–C(2)	2.165 (6)	C(3)–F(2)	1.355 (5)
	2.167 (2)	C(4)–F(3)	1.356 (6)
Rh–C(3)	2.026 (5)	C(4)–F(4)	1.351 (6)
Rh–C(4)	2.022 (5)		1.351 (3)
	2.024 (2)	C(1)–H(1)	1.001 (56)
Rh–C(5)	2.222 (6)	C(1)–H(2)	0.922 (84)
Rh–C(6)	2.171 (6)	C(2)–H(3)	0.979 (68)
Rh–C(7)	2.233 (6)	C(2)–H(4)	0.923 (53)
Rh–C(8)	2.252 (6)		0.956 (20)
Rh–C(9)	2.237 (7)	C(1)–C(3)	2.978 (8)
Rh–F(1)	2.897 (3)	C(1)–F(2)	2.977 (8)
Rh–F(2)	2.995 (3)	C(1)–C(8)	3.283 (9)
Rh–F(3)	2.910 (4)	C(2)–C(4)	2.984 (9)
Rh–F(4)	2.982 (4)	C(2)–F(4)	2.975 (8)
Rh–H(1)	2.640 (83)	C(2)–C(9)	3.227 (10)
Rh–H(2)	2.686 (102)	C(3)–C(6)	3.278 (8)
Rh–H(3)	2.644 (75)	C(3)–H(2)	2.827 (86)
Rh–H(4)	2.618 (71)	C(4)–C(6)	3.251 (8)
C(1)–C(2)	1.358 (9)	C(4)–H(4)	2.755 (76)
C(3)–C(4)	1.405 (7)	F(1)–C(6)	3.295 (9)
C(5)–C(6)	1.395 (13)	F(3)–C(6)	3.256 (8)
C(6)–C(7)	1.432 (12)	F(2)–H(2)	2.419 (68)
C(7)–C(8)	1.344 (12)	F(4)–H(4)	2.354 (67)
C(8)–C(9)	1.286 (12)		
C(9)–C(5)	1.324 (12)		

[a] The standard deviations of the least significant figures are given in parentheses. Mean distances are given where meaningful; the estimated error of the mean was calculated according to $[\sum_1^n(d_i - \bar{d})^2/n(n-1)]^{1/2}$ where d_i and $\bar{d}$ are the distance and mean distance, respectively.

here is shown in Figure 1. The rhodium atom is coordinated to an ethylene ligand, a tetrafluoroethylene ligand, and a cyclopentadienyl ring. The molecule has idealized $C_s(m)$ molecular symmetry, where the idealized mirror plane contains the atoms Rh, C(6), and H-(6) and the C(1)–C(2) and C(3)–C(4) midpoints. A view normal to the molecular plane (idealized mirror plane) is shown in Figure 2, which shows the overall trigonal ligand geometry about the Rh atom.

A selected set of interatomic distances is given in Table III and a set of interatomic angles in Table IV. Some pertinent vector and dihedral angles are given in Table V. The angle between the three-membered metal olefin rings is 97.7°, with both equally disposed about the cyclopentadienyl ring (140.4 and 137.3°). The olefin bonds are nearly parallel (1.5°) and both are nearly perpendicular to the C_5H_5 ring and parallel to the molecular plane normal. The dihedral angles also show that there is a steric effect operating on the olefin substituents, where the substituents on the side adjacent to the other olefin are bent back further than those on the C_5H_5 side (Figure 2).

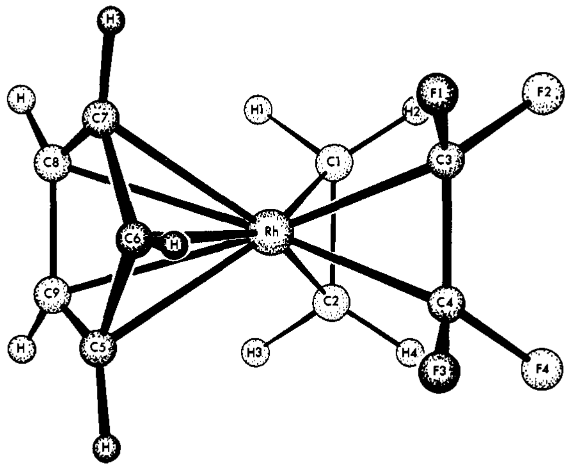

Figure 1. The molecular structure of $(C_5H_5)Rh(C_2F_4)$ (C_2H_4).

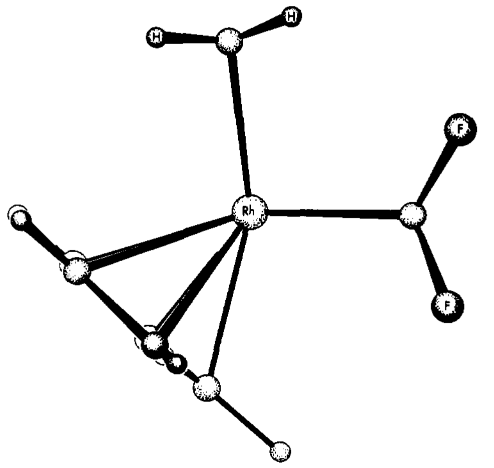

Figure 2. The molecular structure of $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ viewed in the direction of the normal to the molecular plane (idealized mirror plane).

Table IV. Selected Interatomic Angles for $(C_5H_5)Rh(C_2F_4)(C_2H_4)$[a]

C(1)–Rh–C(2)	36.5 (3)	F(1)–C(3)–F(2)	106.3 (4)
C(3)–Rh–C(4)	40.6 (2)	F(3)–C(4)–F(4)	106.4 (4)
C(5)–Rh–C(6)	37.0 (4)		106.4 (1)
C(6)–Rh–C(7)	37.9 (3)	H(1)–C(1)–H(2)	111.9 (52)
C(7)–Rh–C(8)	34.9 (3)	H(4)–C(2)–H(4)	118.8 (54)
C(8)–Rh–C(9)	33.3 (3)		115.4 (34)
C(9)–Rh–C(5)	34.6 (3)	C(9)–C(5)–C(6)	107.2 (7)
Rh–C(1)–C(2)	71.6 (3)	C(5)–C(6)–C(7)	105.5 (7)
Rh–C(2)–C(1)	71.9 (3)	C(6)–C(7)–C(8)	104.9 (7)
	71.8 (2)	C(7)–C(8)–C(9)	111.4 (8)
Rh–C(3)–C(4)	69.6 (3)	C(8)–C(9)–C(5)	110.9 (8)
Rh–C(4)–C(3)	69.8 (3)	Rh–C(3)–F(1)	117.3 (3)
	69.7 (1)	Rh–C(4)–F(3)	117.7 (4)
C(4)–C(3)–F(1)	118.9 (5)		117.5 (2)
C(4)–C(3)–F(2)	118.3 (4)	Rh–C(3)–F(2)	123.5 (3)
C(3)–C(4)–F(3)	118.5 (5)	Rh–C(4)–F(4)	123.0 (4)
C(3)–C(4)–F(4)	118.4 (5)		123.2 (3)
	118.5 (1)	Rh–C(1)–H(1)	106.9 (30)
C(2)–C(1)–H(1)	124.4 (38)	Rh–C(2)–H(3)	108.5 (33)
C(2)–C(1)–H(2)	119.0 (41)		107.7 (8)
C(1)–C(2)–H(3)	116.2 (39)	Rh–C(1)–H(2)	114.5 (37)
C(1)–C(2)–H(4)	120.5 (39)	Rh–C(2)–H(4)	109.2 (35)
	120.0 (17)		111.8 (27)

[a] The footnote from Table III applies here.

Table V. Vector–Vector, Vector–Plane, and Dihedral Angles for $(C_5H_5)Rh(C_2F_4)(C_2H_4)$[a]

	C_2F_4 Ligand			C_2H_4 Ligand	
β[b]	C(4)–C(3) C(4)–F(3)–F(4)	52.7	β	C(2)–C(1) C(2)–H(4)–H(3)	68.7
β	C(3)–C(4) C(3)–F(2)–F(1)	52.9	β	C(1)–C(2) C(1)–H(1)–H(2)	69.6
α	C(3)–F(2)–F(1) C(4)–F(3)–F(4)	74.3	α	C(1)–H(1)–H(2) C(2)–H(4)–H(3)	42.4
	Rh–C(3)–C(4) C(3)–C(4)–F(1)	110.6		Rh–C(1)–C(2) C(1)–C(2)–H(1)	98.3
	Rh–C(3)–C(4) C(3)–C(4)–F(2)	118.0		Rh–C(1)–C(2) C(1)–C(2)–H(2)	108.3
	Rh–C(3)–C(4) C(3)–C(4)–F(3)	111.3		Rh–C(1)–C(2) C(1)–C(2)–H(3)	102.3
	Rh–C(3)–C(4) C(3)–C(4)–F(4)	117.4		Rh–C(1)–C(2) C(1)–C(2)–H(4)	102.1
			General		
	Rh–C(1)–C(2) Rh–C(3)–C(4)	97.7		C(3)–C(4) C_5H_5 ring	89.9
	Rh–C(2)–C(1) C_5H_5 ring	140.4		C(1)–C(2) C(3)–C(4)	1.5
	Rh–C(3)–C(4) C_5H_5 ring	137.3		C(1)–C(2) Molecular plane	177.4
	C(1)–C(2) C_5H_5 ring	88.4		C(3)–C(4) Molecular plane	178.9
				C_5H_5 ring Molecular plane	89.1

[a] A–B here means the vector from atom A to atom B. A–B–C denotes the plane normal which is in the direction of (A–B) × (A–C), where A–B and A–C are again vectors. The C_5H_5 ring plane and the molecular plane are the least-squares planes (Table VI). The angle here is the angle between the two implied directions. [b] See the text for the definition of α and β.

Table VI. Least-Squares Planes for $(C_5H_5)Rh(C_2F_4)(C_2H_4)$[a]

1. Molecular plane $-0.0895X + 0.6927Y + 0.7156Z - 2.415 = 0$
2. Cyclopentadienyl plane $0.9695X - 0.0891Y + 0.2285Z - 4.543 = 0$

Atom	Plane 1	Plane 2
Rh	0.022*[b]	−1.898
F(1)	1.350	−2.661
F(2)	1.322	−4.342
F(3)	−1.351	−2.659
F(4)	−1.367	−4.328
C(1)	0.669	−3.228
C(2)	−0.688	−3.190
C(3)	0.699	−3.187
C(4)	−0.706	−3.183
C(5)	−1.066	0.016*
C(6)	−0.009*	−0.014*
C(7)	1.180	0.007*
C(8)	0.744	0.002*
C(9)	−0.541	−0.011*
H(1)	1.26	−2.69
H(2)	1.08	−3.99
H(3)	−1.09	−2.64
H(4)	−1.19	−3.88
⟨C(1)–C(2)⟩	−0.009*	−3.209
⟨C(3)–C(4)⟩	−0.004*	−3.185

[a] The planes are based on the Cartesian coordinate system (*a*, *b*, *c**). [b] The asterisks identify the atoms included in the plane calculation.

The Rh–C(C_2H_4) distance of 2.167 (2) Å may be compared with 2.19 (1) Å in $(C_5H_7O_2)Rh(C_2F_4)(C_2H_4)$,[3] 2.12 (3) Å in $[(C_8H_{12})RhCl]_2$,[11] and 2.08 Å in $(C_5H_5)RhC_6(CF_3)_6$.[12] The Rh–C(C_2F_4) distance of 2.024 (2) Å may be compared with 2.01 (1) Å in $(C_5H_7O_2)Rh(C_2F_4)(C_2H_4)$[3] and 2.01 Å in $[(C_6H_5)_3P]_2Rh(C_2F_4)Cl$.[13] The perpendicular metal to C_5H_5 ring distance of 1.899 Å here compares with 1.85 Å in $(C_5H_5)RhC_6(CF_3)_6$,[12] 1.87 Å in $(C_5H_5)Rh(CO)(C_2F_5)I$,[14] and 1.90 Å in $[(C_5H_5)RhCO]_3$[15] and $(C_5H_5)Rh_2(CO)_3$.[16] The individual Rh–C(C_5H_5) distances are in the range of observed distances.[12,14–16] A Rh–C distance of 1.98 (1) Å was found for a rhodium-substituted cyclopentadiene ring in $RhCl[(C_6H_5)_3Sb]_2C_4(CF_3)_4 \cdot CH_2Cl_2$.[17]

The C–C distance of 1.405 (7) Å in the C_2F_4 ligand compares directly with 1.40 (2) Å in $(C_5H_7O_2)Rh(C_2F_4)(C_2H_4)$[3] and 1.41 Å in $[(C_6H_5)_3P]_2Rh(C_2F_4)Cl$.[13] Other C–C distances in tetrasubstituted metal-coordinated olefins are 1.42 (3) Å in $[(C_6H_5)_3P]_2Pt[Cl_2CC(CN)_2]$,[18] 1.476 (5) Å in $(C_4H_9NC)_2Ni[C_2(CN)_4]$,[19] 1.49 (5) Å in $[(C_6H_5)_3P]_2Pt[C_2(CN)_4]$,[20] 1.506 (15) Å in $[(C_6H_5)_3P]_2IrBr(CO)[C_2(CN)_4]$,[21] and 1.526 (12) Å in $[(C_6H_5)_3P]_2Ir(C_6N_4H)(CO)[C_2(CN)_4]$.[22] The C–C distance in uncoordinated C_2F_4 is 1.313 (35) Å.[23] The average C–F distance of 1.351 (3) Å here is similar to the 1.333 (5) Å value frequently found in olefinic and polyfluoro compounds.[24]

The C_5H_5 ring is planar with substantial differences in C–C bond lengths. The least-squares planes and the

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(11) J. A. Ibers and R. G. Snyder, *Acta Crystallogr.*, **15**, 923 (1962).

(12) M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A*, **292**, 61 (1966).

(13) P. B. Hitchcock, M. McPartlin, and R. Mason, *Chem. Commun.*, 1367 (1969).

(14) M. R. Churchill, *Inorg. Chem.*, 4, 1734 (1965).

(15) Von E. F. Paulus, *Acta Crystallogr., Sect. B*, **25**, 2206 (1969).

(16) O. S. Mills and J. P. Nice, *J. Organometal. Chem.*, **10**, 337 (1967).

(17) J. T. Mague, *Inorg. Chem.*, **9**, 1610 (1970).

(18) A. McAdam, J. N. Francis, and J. A. Ibers, *J. Organometal. Chem.*, **29**, 149 (1971).

(19) J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, **92**, 5333 (1970).

(20) G. Bombieri, E. Forsellini, C. Panattoni, R. Graziani, and G. Bandoli, *J. Chem. Soc. A*, 1313 (1970).

(21) L. M. Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, **No. 47**, 84 (1969).

(22) J. S. Ricci and J. A. Ibers, *J. Amer. Chem. Soc.*, **93**, 2391 (1971).

(23) I. L. Karle and J. Karle, *J. Chem. Phys.*, **18**, 963 (1950).

(24) L. E. Sutton, Ed., *Chem. Soc. Spec. Publ.*, **No. 18**, S17s (1965).

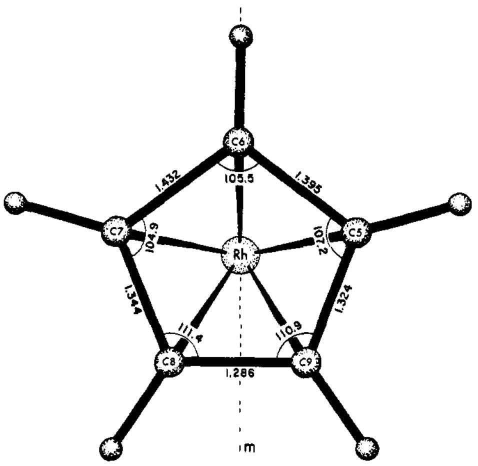

Figure 3. The local geometry of the cyclopentadienyl ring in $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ showing the idealized mirror plane.

deviations from these planes are given in Table VI for the C_5H_5 plane and the molecular plane (idealized mirror plane). We believe there are significant differences in the C–C ring bond lengths, but perhaps they are not as pronounced as these results indicate. The large librational effects encountered here, as in other C_5H_5 complexes,[25] preclude the determination of accurate C–C distances in this group, and our errors here are consequently underestimated. The rms amplitudes of vibration are summarized in Table VII. The geometry of the C_5H_5 ring is shown in Figure 3. The ring has the idealized $C_s(m)$ symmetry of the molecule. The lack of axial symmetry (removing the degeneracy of the d orbitals) allows the C_5H_5 ring to distort to accommodate the local bonding requirements.[26,27] The C(8)–C(9) distance of 1.286 (12) Å appears to be the shortest cyclopentadienyl distance observed. It is reasonable that this should be shortened somewhat in view of the trans influence (*vide infra*) of the C_2F_4 ligand. The longer Rh–C(8) and Rh–C(9) might be associated with a localization of electron density in the C(8)–C(9) bond.

Table VII. Root-Mean-Square Amplitudes of Vibration (Å) for $(C_5H_5)Rh(C_2F_4)(C_2H_4)$

	Minimum	Intermediate	Maximum
Rh	0.183 (1)	0.217 (1)	0.234 (1)
C(1)	0.208 (7)	0.271 (7)	0.364 (8)
C(2)	0.206 (8)	0.308 (8)	0.386 (9)
C(3)	0.219 (6)	0.225 (6)	0.263 (6)
C(4)	0.192 (6)	0.265 (6)	0.275 (6)
F(1)	0.229 (4)	0.278 (4)	0.359 (4)
F(2)	0.222 (4)	0.315 (4)	0.332 (4)
F(3)	0.223 (4)	0.319 (4)	0.347 (4)
F(4)	0.190 (4)	0.316 (4)	0.387 (5)
C(5)	0.211 (8)	0.272 (8)	0.472 (12)
C(6)	0.179 (8)	0.251 (8)	0.492 (11)
C(7)	0.176 (8)	0.271 (8)	0.465 (11)
C(8)	0.195 (8)	0.299 (8)	0.464 (12)
C(9)	0.226 (8)	0.304 (9)	0.477 (12)

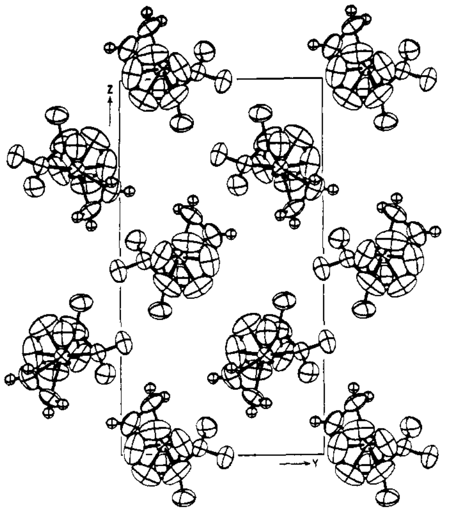

Figure 4. The 100 projection of the crystal structure of $(C_5H_5)Rh(C_2F_4)(C_2H_4)$. The cyclopentadienyl hydrogen atoms have been omitted.

A rigid-body thermal motion analysis was done on the C_5H_5 ring after the method of Cruickshank.[28] The principal axis of libration was in the direction of the C_5H_5 ring, with an rms amplitude of 19°. The bond distances corrected for librational motion[29] are 1.46 Å for C(5)–C(6), 1.51 Å for C(6)–C(7), 1.40 Å for C(7)–C(8), 1.32 Å for C(8)–C(9), and 1.38 Å for C(9)–C(5). These are in the range of observed C_5H_5 distances.[25] The differences between the corrected and uncorrected distances point out the uncertainties involved here. Fortunately, these uncertainties are in the C_5H_5 plane and do not seriously affect the Rh–C(C_5H_5) distances.

The 100 projection of the crystal structure is shown in Figure 4. This view illustrates the anisotropic nature of the C_5H_5 thermal parameters (Table VII). All of the intermolecular contacts were calculated. There are no nonhydrogen atom contacts less than 3.0 Å. The shortest contacts are 2.163 Å for F(1)–H(6) and 2.554 Å for F(2)–H(8), where the second atoms are on adjacent molecules.

The rhodium–ethylene geometry is remarkably well determined in view of the fact that the "heavy" rhodium atom dominates the scattering. This is the first example of an X-ray determination of the coordinated metal–ethylene geometry. There is a neutron diffraction study of Zeise's salt, $[KPtCl_3(C_2H_4)\cdot H_2O]$,[30] but this work was done in the wrong space group.[31] A recent X-ray refinement of Zeise's salt[31] in the correct space group gave distances of 2.127 (19) Å for Pt–C(C_2H_4) and 1.37 (3) Å for C–C(C_2H_4). The molecular geometry did not change much from earlier refinements in the wrong space group, so the neutron diffraction study is probably meaningful in spite of the space group problem. The neutron study gave distances of 1.354 (15) Å for C–C and 1.10 (5) Å for C–H and angles

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(25) P. J. Wheatley in "Perspectives in Structural Chemistry," Vol. I, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1967, p 9.

(26) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 713 (1963).

(27) M. J. Bennett, M. R. Churchill, M. Gerlock, and R. Mason, *Nature (London)*, **201**, 1318 (1964).

(28) D. W. J. Cruickshank, *Acta Crystallogr.*, **9**, 754 (1956).

(29) D. W. J. Cruickshank, *ibid.*, **14**, 896 (1961); D. W. J. Cruickshank, *ibid.*, **9**, 757 (1956).

(30) W. C. Hamilton, K. A. Klanderman, and R. Spratley, *ibid.*, *Sect. A*, **25**, S172 (1969).

(31) There have been several X-ray studies of Zeise's salt, $KPtCl_3(C_2H_4)\cdot H_2O$, none of which has located hydrogen atoms. For references to these and an explanation of the space group problem, see J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *ibid.*, *Sect. B*, **27**, 366 (1971).

Table VIII. Comparison of the $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ and $(C_5H_7O_2)Rh(C_2F_4)(C_2H_4)$ Structures

	$(C_5H_5)Rh$-$(C_2F_4)(C_2H_4)$	$(C_5H_7O_2)Rh$-$(C_2F_4)(C_2H_4)$
Rh–C(C_2F_4), Å	2.024 (2)	2.01 (1)
Rh–C(C_2H_4), Å	2.167 (2)	2.19 (1)
C–C(C_2F_4), Å	1.405 (7)	1.40 (2)
C–C(C_2H_4), Å	1.358 (9)	1.42 (2)
Trans ligand	π-C_5H_5	Oxygen
Rh–ligand trans to (C_2F_4), Å	2.244 (7)	2.047 (8)
Rh–ligand trans to (C_2H_4), Å	2.171 (6)	2.027 (8)

Table IX. Olefin Geometries on Metal–Olefin Coordination

Compound	Ligand	α	β
$KPtCl_3(C_2H_4)\cdot H_2O$[a]	C_2H_4	34.7	72.7
$(C_5H_5)Rh(C_2F_4)(C_2H_4)$	C_2H_4	42.4	69.1
$(C_4H_9NC)_2Ni[C_2(CN)_4]$[b]	$C_2(CN)_4$	56.8	61.6
$[(C_6H_5)_3P]_2Pt[Cl_2CC(CN)_2]$[c]	$Cl_2CC(CN)_2$	62.0	69.9 $C(CN)_2$ 48.4 $C(Cl)_2$
$[(C_6H_5)_3P]_2Pt[C_2(CN)_4]$[d]	$C_2(CN)_4$	63.8	58.1
$[(C_6H_5)_3P]_2Ir(C_6N_4H)(CO)[C_2(CN)_4]$[e]	$C_2(CN)_4$	67.4	56.3
$[(C_6H_5)_3P]_2IrBr(CO)[C_2(CN)_4]$[f]	$C_2(CN)_4$	70.7	54.8
$(C_5H_5)Rh(C_2F_4)(C_2H_4)$	C_2F_4	74.3	52.8
$-M(C_2X_4)$	C_2X_4 sp^2 carbon	0	90
	C_2X_4 sp^3 carbon	109.5	35.3
$(C_5H_5)Rh(C_2F_4)(C_2H_4)$	C_2F_4 idealized[g]	69.7	55.1
	C_2H_4 idealized	71.7	54.1

[a] Reference 30. [b] Reference 19. [c] Reference 18. [d] Reference 20. [e] Reference 22. [f] Reference 21. [g] Idealized geometry is defined in the text.

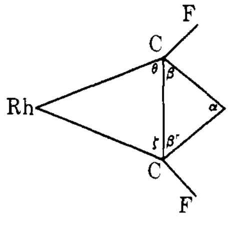
of 114 (3)° for H–C–H and 121 (3)° for C–C–H. The values found here are 1.358 (9) Å for C–C and 0.96 (2) Å for C–H and angles of 115 (3)° for H–C–H and 120 (2)° for C–C–H. Clearly, the geometry determined here by X-rays is identical with that found by neutrons with the exception of the usual forshortening of the C–H distance in the X-ray study. The C–C distance in uncoordinated ethylene is 1.337 (2) Å.[32]

The $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ and $(C_5H_7O_2)Rh(C_2F_4)$-(C_2H_4)[3] structures have some common features which are compared in Table VIII. Generally the features are similar, the biggest difference being the increased C–C(C_2H_4) distance in the $(C_5H_7O_2)Rh$-$(C_2F_4)(C_2H_4)$ structure. However, this is only of borderline significance in view of the estimated error involved. This may be rationalized in terms of trans effects. The O atom trans to C_2H_4 in $(C_5H_7O_2)Rh$-$(C_2F_4)(C_2H_4)$ is not as effective a π acceptor as C_5H_5 in $(C_5H_5)Rh(C_2F_4)(C_2H_4)$, and hence cannot compete as well for the C_2H_4 π density, increasing the C–C bond length in $(C_5H_7O_2)Rh(C_2F_4)(C_2H_4)$ through population of the olefin π^* orbital. There is a trans effect in $(C_5H_7O_2)Rh(C_2F_4)(C_2H_4)$, but it is not as pronounced as in $(C_5H_5)Rh(C_2F_4)(C_2H_4)$.

The Rh–C_2F_4 geometry in $[(C_6H_5)_3P]_2Rh(C_2F_4)Cl$[13] (Rh–C = 2.01 Å, C–C = 1.41 Å) is also similar to that reported here based on the limited available data. In that structure the *cis*-Rh–P bonds are about 0.05 Å longer than those in the $[(C_6H_5)_3P]_3RhCl$ structure,[13] consistent with increased π character in the Rh–C_2F_4 bond. The angle data will probably also compare closely, since the carbon atoms are 0.44 Å from the fluorine atom plane in $[(C_6H_5)_3P]_2Rh(C_2F_4)Cl$. In $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ the carbon atoms are 0.489 Å from the fluorine atom plane; the Rh atom is 2.384 Å from this plane. The C_2H_4 carbon atoms and Rh atom are 0.18 Å and 2.24 Å, respectively, from the hydrogen atom plane.

Metal–Olefin Bonding

The angles involving the coordinated olefins are important in inferring something about the nature of the metal–olefin bonding. Of particular importance is the degree to which the substituents on the olefins are bent back. There are a number of interatomic angles or dihedral angles which can be used to describe the bending back of the olefin substituents, but we will follow the convention of Ibers and coworkers[19] in order to facilitate meaningful comparisons between structural results. The pertinent angles for $(C_5H_5)Rh(C_2F_4)$-(C_2H_4) are presented in Table V. The α angle is the angle between the plane normals, where the planes are defined by the olefin atoms and their substituents; β is the angle between the olefin bond and the plane normal (Table V). The α and β angles are not independent.



For increasing bending back of the substituents, α increases from 0° and β decreases from 90°.

A comparison is given in Table IX for the structures where the substituent positions are reported. The data have been ordered according to increasing bending back of the olefin substituents, *i.e.*, increasing α. The F atoms in the C_2F_4 ligand here are bent back further than any other substituents. However, even the H atoms in the C_2H_4 ligand are bent back, but to a much smaller extent.

The fundamental question is the nature of the correspondence between the metal–olefin geometry and the metal–olefin bonding. Is the bonding more appropriately discussed in terms of the familiar σ–π model[33,34] or a "metallocyclopropane" model? The

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(32) L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, Jr., *J. Chem. Phys.*, 42, 2683 (1965).

metal–olefin geometry is usually discussed in terms of the σ–π model on the premise that the olefin carbon geometry is not tetrahedral. However, it seems clear that there will never be a metal-coordinated olefin where the carbon atom geometry is tetrahedral because of the severe nontetrahedral (steric and electronic) constraints. So we must establish what "tetrahedral" geometry is under these constraints. As a first-order approximation, we might get the expected "tetrahedral" geometry by bisecting the interior Rh–C–C angle and placing two atoms on the other side in tetrahedral fashion. We have done this calculation placing two F atoms (C–F = 1.351 Å and F–C–F = 109.47°) out from C(3) in a plane normal to the RhC(3)C(4) plane bisecting the Rh–C(3)–C(4) angle. The results are given in Table IX under idealized C_2F_4 ligand. The resulting α and β angles are close to those observed here for the C_2F_4 geometry ($\Delta\alpha = 4.6°$, $\Delta\beta = 2.3°$). We conclude that the Rh–C_2F_4 geometry here is close to what could be expected for "tetrahedral" carbon atom geometry. The bending back here for C_2F_4 might be close to the limit of what can be found for this type of metal–olefin bonding (with minimum substituent steric constraints). We note that possibly a metal–Cl_2CCCl_2 geometry could be bent back further based on the 48.4° β for $Cl_2CC(CN)_2$ in $[(C_6H_5)_3P]_2Pt[Cl_2CC(CN)_2]$ (Table IX). We have also computed the idealized tetrahedral geometry for C_2H_4 and find $\alpha = 71.7°$ and $\beta = 54.1°$ (Table IX), far from the values observed here, confirming the fact that the C_2H_4 is more nearly planar.

If we accept the idea of what "tetrahedral" geometry might be, we can postulate a simple criterion for assessing distortions from "tetrahedral" geometry. If θ is one of the interior Rh–C–C angles and ζ is the other Rh–C–C angle (to allow for different substituents), then for "tetrahedral" carbon geometry

$$\alpha_T = \theta/2 + \zeta/2$$

$$\beta_T = 90 - (\theta/2)$$

$$\beta_T' = 90 - (\zeta/2)$$

These angles then are the approximate calculated angles for "tetrahedral" geometry. The α_T and β_T values for C_2F_4 in $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ are 69.7 and 55.2°, respectively, compared to the observed values of 74.3° for α and 52.8° for β. Actually, the F atoms here are bent back slightly more than calculated for "tetrahedral" geometry. We have not included a C–C distance criterion in assessing C-atom geometry because of the uncertainties involved, especially the lack of generality between different metal–olefin combinations.

A test of our assumption of "tetrahedral" geometry is the structure of ethylene oxide, C_2H_4O, where the C_2H_4 geometry is similar to that found here and there is no π bonding. The ethylene oxide geometry[35] has 1.470 Å for C–C, 1.435 Å for C–O, 1.08 Å for C–H, and an H_2C–C dihedral angle of 158.6°, giving an observed β of 68.6°. The interior O–C–C angle is then 59.2°, giving a β_T of 60.4°, not far from the observed value. The hydrogen atoms in C_2H_4O are bent less than our criterion dictates in the direction of minimizing nonbonded contacts. Another useful test of our criterion is the structure of tetracyanoethylene oxide, but all the necessary data are not yet available.[36,36a]

A recent interpretation of the spectral data from Zeise's salt[37,38] suggested the similarity between metal–ethylene and ethylene oxide geometry and postulated a nonplanar ethylene ligand in metal–ethylene complexes. The crystal structure here confirms the nonplanarity of the ethylene ligand and establishes the magnitude of the nonplanarity. In fact, the geometry of Rh–C_2H_4 here is nearly identical with the geometry of C_2H_4 in C_2H_4O ($\Delta\alpha = 0.4°$, $\Delta\beta = 0.5°$).

A comparison of the ethylene and tetrafluoroethylene ligand geometries is significant, since differences should be due primarily to the effect of F-atom substitution. We believe the usual metal–ethylene bonding description applies here for Rh–C_2H_4. This description calls for approximately equal olefin to metal σ bonding and metal to olefin π bonding (based on calculations for Zeise's salt).[39] The populations of the π^* olefin orbitals decrease the C–C bond orders[40] and can account for the C(1)–C(2) distance here being about 0.02 longer than in uncoordinated ethylene. In addition to the angular differences between the Rh–C_2H_4 and Rh–C_2F_4 geometries (*vide supra*), the C_2F_4 is significantly closer to the Rh atom (2.167 (2) Å *vs.* 2.024 (2) Å for Rh–C). The implication is that there is a significant shift in electron density from the Rh d_π to the olefin π^* orbital. By analogy with metal–tetracyanoolefin complexes, we would expect a longer C(3)–C(4) distance than 1.405 (7) Å if the π^* ligand orbital has an appreciable population. However, it does not seem unreasonable that the C–C bond order in M–C_2F_4 would be greater than in M–$C_2(CN)_4$ complexes where the π density is more delocalized.

It is interesting that in $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ we may be approaching the situation where we have a more or less pure π bond between Rh and C_2F_4. This is equivalent to the valence-bond "rhodiacyclopropane" model.[41,42] This description would be consistent with the bending back of the substituents and the ^{13}C nmr work, which indicate appreciable amounts of s character in olefin–rhodium bonds.[43] Also, the inductive effect of the F atoms seems to be as effective as the excellent π-accepting CN's (inductive and resonance) in promoting the bending back of olefin substituents.

Another effect sometimes used to explain shortened metal–carbon bonds where the carbon atoms have fluorine substituents is contraction of the metal d orbitals due to the high electronegativity of the fluorine atoms.[44,45] We cannot totally exclude this effect here

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(33) M. J. S. Dewar, *Bull. Chem. Soc. Jap.*, **18**, 279 (1951).

(34) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(35) T. E. Turner and J. A. Howe, *J. Chem. Phys.*, 24, 924 (1956).

(36) D. A. Matthews, J. Swanson, and G. D. Stucky, American Crystallographic Association Meeting, Tulane University, New Orleans, La., March 1970, Abstract K6.

(36a) NOTE ADDED IN PROOF. The pertinent data are $\alpha = 52.2°$ and $\beta = 63.9°$ with $\alpha_T = 58.3°$ and $\beta_T = 60.7°$: D. A. Matthews, J. Swanson, M. H. Mueller, and G. D. Stucky, *J. Amer. Chem. Soc.*, **93**, 5945 (1971).

(37) J. Hiraishi, *Spectrochim. Acta*, *Part A*, **25**, 749 (1969).

(38) J. Hiraishi, D. Finseth, and F. A. Miller, *ibid.*, *Part A*, **25**, 1657 (1969).

(39) J. W. Moore, *Acta Chem. Scand.*, 20, 1154 (1966).

(40) B. R. Penfold and W. N. Lipscomb, *Acta Crystallogr.*, 14, 589 (1961).

(41) C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 798 (1968).

(42) J. A. Pople, *Quart. Rev., Chem. Soc.*, 11, 273 (1957).

(43) G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *Chem. Commun.*, 1530 (1970).

in the Rh–C_2F_4 bonding, but we tend to discount it because it is not necessary to rationalize the observed stereochemistry and there is no evidence for it in the other Rh–ligand bonding, although it is not strictly necessary that such contraction be reflected in the remaining bonds.

There is a significant ground-state trans influence here, as the C_5H_5 group is 0.074 Å further from the Rh atom on the side trans to C_2F_4 (trans throughout is taken in a general connotation, since the ligands are not perfectly trans as seen in Figure 2). Both C_2H_4 and C_2F_4 have the potential for exerting a π-trans influence because of their inherent π-acceptor abilities coupled with the presence of a good π-bonding trans ligand (C_5H_5). The C_2F_4 ligand exerts the larger trans influence, indicating that the C_2F_4 ligand withdraws appreciably more electron density from the Rh atom *via* the $d_\pi-\pi^*$ route than the C_2H_4 ligand, entirely consistent with our bonding description above.

The metal–ethylene geometry here is reminiscent of suggestions that ligand geometries in metal complexes may correspond to a superposition of the electronic ground-state and low-lying excited-state geometries of uncoordinated ligands.[46] However, the nature, or even existence, of this type of superposition is as yet unclear. It is not certain whether C_2H_4 has an excited state geometry close to that observed here.[47]

The structure found here confirms what was inferred from the nmr, namely, that the coordinated C_2F_4 was quite distorted from noncoordinated C_2F_4. The short Rh–C_2F_4 bond with its high π-bond order is consistent with the chemistry of this and related Rh–ethylene systems in the sense that fluorine substitution stabilizes rhodium–olefin complexes.[48] Also the higher π-bond order in Rh–C_2F_4 (*vs.* Rh–C_2H_4) is entirely consistent with its higher barrier to rotation.[2]

(44) P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, 1, 143 (1964).

(45) F. G. A. Stone, *Endeavour*, **25**, 33 (1966).

(46) R. Mason, *Nature (London)*, 217, 543 (1968), and references therein.

(47) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 533.

(48) R. Cramer, *J. Amer. Chem. Soc.*, **89**, 4621 (1967).

Reaction of Azidopentaammineiridium(III) Cation with Acid. Intermediate Formation of Coordinated Nitrene

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Abstract: The acid decomposition of $[Ir(NH_3)_5N_3]^{2+}$ salts occurs by a mechanism involving an intermediate complex of coordinated nitrene, $[Ir(NH_3)_5NH]^{3+}$. This intermediate behaves as a powerful electrophile, reacting with HSO_4^- and Cl^- to yield $[Ir(NH_3)_5NH_2OSO_3]^{2+}$ and $[Ir(NH_3)_5NH_2Cl]^{3+}$, respectively. The characterization of these complexes is described and a study has been made of their interconversion and their reactions to form $[Ir(NH_3)_5NH_2OH]^{3+}$. Kinetic data have been obtained for the acid decomposition of $[Ir(NH_3)_5N_3]^{2+}$ salts in an attempt to elucidate the mechanism of the formation and reactions of metal nitrenes.

It has been proposed[1] that acid-catalyzed decomposition of Ru(III) azides proceeds by a mechanism involving an intermediate coordinated nitrene,[2] Ru(III)–NH, which then reacts *via* two separate pathways to yield dinitrogen complexes of Ru(II), $[Ru(NH_3)_5N_2]^{2+}$, and $[(NH_3)_5Ru–N_2–Ru(NH_3)_5]^{4+}$.

The facile reduction of Ru(III) to Ru(II) makes possible the internal redox reactions which yield these products. Several other easily reduced metal ions (Ce(IV),[3] Co(III),[4] Mn(III)[5]) react with N_3^- liberating 1.5 mol of N_2/mol of metal ion. As in the case of Ru(III), these metal ions undergo a one-electron reduction in the reaction.

Azido complexes of metal ions which readily lose one electron (Cr(II),[6] Ti(III),[7] Co(II),[8] Ni(I)[8]) show different behavior. For example, 1 mol of azide ion reacts with 2 mol of $[Cr(H_2O)_6]^{2+}$ producing 1 mol of N_2, $[Cr(H_2O)_6]^{3+}$, and $[CrNH_3(H_2O)_5]^{3+}$. A small amount of the imido-bridged complex, $[(H_2O)_5Cr–NH–Cr(H_2O)_5]^{4+}$, is also produced and the presence of this species suggests that a coordinated nitrene intermediate might also be involved in these reactions.

We were interested in studying the reactions of coordinated nitrenes where these redox reactions are not possible. The absence of Ir(II) and Ir(IV) amine complexes[9] indicated that decomposition of Ir(III) azides (where N_2 evolution has previously been observed[10])

(1) L. A. P. Kane-McGuire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **92**, 5865 (1970).

(2) The term nitrene throughout this paper refers to the molecule NH.

(3) C. F. Wells and M. Husain, *J. Chem. Soc. A*, 2891 (1969).

(4) C. F. Wells and D. Mays, *ibid.*, 2175 (1969); A. Hamm and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963); R. K. Murmann, J. C. Sullivan, and R. C. Thompson, *ibid.*, 7, 1876 (1968); **9**, 1590 (1970).

(5) M. A. Suwyn and R. E. Hamm, *ibid.*, **6**, 2150 (1967); G. Davies, L. I. Kirschenbaum, and K. Kustin, *ibid.*, **8**, 663 (1969).

(6) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962); R. G. Linck, *Inorg. Chem.*, 11, 61, (1972).

(7) R. S. P. Coutts and J. R. Surtees, *Aust. J. Chem.*, **19**, 387 (1966).

(8) W. C. Kaska, C. Sutton, and E. Serros, *Chem. Commun.*, 100 (1970).

(9) W. P. Griffith, "The Chemistry of the Rare Platinum Metals," Interscience, New York, N. Y., 1967, p 269.

(10) R. A. Bauer and F. Basolo, *Inorg. Chem.*, **8**, 2231 (1969).