only 1466 cm.$^{-1}$ in $Co_2S_8C_8(CF_3)_8$ as compared to 1515 cm.$^{-1}$ in $CoS_4C_4(CF_3)_4^{-2}$. On the subject of other distances we note that the average Co–S distance of 1.69 ± 0.02 Å. compares on the lower side with the average M–S distances of 1.72, 1.72, and 1.75 Å., respectively, in the anions. Other distances and angles agree within experimental error where they can be compared among these four structures.

Finally, the packing of dimers in the crystal is largely determined by the bulky CF_3 groups, but there are no abnormally short intermolecular contacts between dimer units. The F atoms are 3.5 Å. or greater from Co and S atoms.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS

The Crystal and Molecular Structure of Racemic Iodocarbonyl-π-cyclopentadienyl-pentafluoroethylrhodium

BY MELVYN R. CHURCHILL

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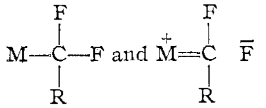
Iodocarbonyl-π-cyclopentadienyl-pentafluoroethylrhodium, π-$C_5H_5Rh(CO)(C_2F_5)I$, crystallizes as an ordered racemate in space group $P2_1/c$, with $a = 12.410 \pm 0.010$, $b = 7.823 \pm 0.008$, $c = 12.632 \pm 0.010$ Å.; $\beta = 109.86 \pm 0.05°$. A three-dimensional single-crystal X-ray analysis, based on 960 independent reflections, using conventional Patterson, Fourier, and least-squares refinement techniques has led to the location of all atoms except hydrogens, with estimated standard deviations ranging from 0.003 Å. for the rhodium–iodine vector to 0.04 Å. for carbon–carbon distances. The final value for the discrepancy index, R_1, is 6.98%. An interesting result of the analysis is that the rhodium–carbon bond distance for the perfluoroethyl group is only 0.11 Å. longer than the rhodium–carbonyl bond length. On allowing for the 0.07 Å. difference in the radii of sp^3 and sp hybridized carbon atoms, the effective difference in rhodium–carbon bond lengths decreases to only 0.04 Å. ($\sim$1.3 σ). This, coupled with the distortion of the α carbon atom of the perfluoroethyl group from a regular tetrahedral environment, gives some weight to the proposal that the perfluoroethyl group participates in metal–ligand (d_π–σ^*) back donation. A comparison with known metal–carbon bond lengths suggests that for certain transition metal complexes, the metal–perfluoroalkyl linkage may be some 0.2–0.3 Å. shorter than the metal–carbon bond in an analogous nonfluorinated metal–alkyl.

Introduction

One of the remarkable features of transition metal perfluoroalkyl complexes (as compared to the corresponding alkyl derivatives) is their great thermal and aerobic stability. Although it is possible that this may, in part, be a result of the slightly greater size, and concomitantly greater mechanical shielding effect, of the perfluoroalkyl group, Jaffé and Doak's calculations[1] on simple σ-bonded first-row transition metal alkyls indicated that the metal–carbon bonds were inherently unstable. Chatt and Shaw,[2] likewise, conclude that transition metal alkyls will not exist for metals with filled (or partially filled) d orbitals, unless there is considerable ligand-field stabilization. It seems likely, therefore, that the intrinsically greater stability of perfluoroalkyl compounds owes its origin to an electronic, rather than to a steric, effect. From an electrostatic viewpoint, the stabilization of the metal–perfluoroalkyl bond may be considered the result of metal orbital contraction (due to the high electronegativity of the perfluoroalkyl group); alternatively, in valence bond terms, one can consider stabilization of the perfluoroethyl group as a result of the contribution of such canonical structures[3] as



$$M{-}\overset{\displaystyle F}{\underset{\displaystyle R}{C}}{-}F \text{ and } \overset{+}{M}{=}\overset{\displaystyle F}{\underset{\displaystyle R}{C}}\ \overline{F}$$

A more detailed theory of the metal–perfluoroalkyl bonding has recently been proposed[4] in order to explain anomalies in the infrared spectra of some perfluoromethyl compounds. The carbon–fluorine stretching modes of $CF_3Mn(CO)_5$ occur some 100 cm.$^{-1}$ lower than those in simple perfluoromethyl compounds such as CF_3Cl. This is interpreted[4] as a result of electrons drifting from the d_π orbitals of the manganese into some carbon–fluorine antibonding orbitals of appropriate (*i.e.*, "quasi-E") symmetry.

For each description, the net result is that the metal–carbon bond of a transition metal perfluoroalkyl is predicted to be stronger (and, presumably, shorter) than that of an analogous alkyl complex. The present investigation was undertaken to determine whether the

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[1] H. H. Jaffé and G. O. Doak, *J. Chem. Phys.*, **21**, 196 (1953).

[2] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

[3] R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 34 (1964); J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

[4] F. A. Cotton and J. A. McCleverty, *J. Organometal. Chem.*, in press.

stronger bonding of the perfluoroalkyl (*vis à vis* the alkyl) ligand would lead to any crystallographically significant shortening of the metal–carbon bond. A preliminary account of this work has been published.[5]

Experimental

The compound, prepared from π-cyclopentadienylrhodium dicarbonyl and pentafluoroethyl iodide,[6] was recrystallized from 40–60° petroleum ether–dichloromethane. Hexagonal plates, of maximum dimension 0.20 mm. and thickness approximately 0.05 mm., were used in collecting eight zones of Weissenberg data, $h0l$ through $h4l$ and $hk0$ through $hk2$. Molybdenum Kα radiation (λ = 0.7107 Å.) was used throughout the analysis and all data were recorded on Ilford Industrial 'G' X-ray film. No correction was made for absorption.

The unit cell dimensions were obtained by a least-squares analysis of axial Weissenberg data taken with copper (Kα) radiation and calibrated with aluminum. A total of 960 independent reflections were estimated visually using a standard (linear) calibrated wedge made from the crystal under investigation. The observed intensities were corrected for Lorentz and polarization effects and placed on a single scale by comparison of common reflections. All data were initially placed on the absolute scale suggested by a Wilson plot, which also indicated the average over-all temperature factor, $\bar{B}$ = 3.58 Å.^{2}. The final scale was obtained by allowing each zone to refine its scale-factor independently by a least-squares procedure during the course of the structure refinement. At the end of this procedure it was encouraging to note that the maximum deviation of any zone from the mean scale factor was less than 7%.

Unit Cell and Space Group

Monoclinic crystals of π-$C_5H_5Rh(CO)(C_2F_5)I$ are isolated as red plates with well-developed 100 and small (but characteristic) 001, 011, and 01$\bar{1}$ faces. The systematic absences $\{h0l\}$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ uniquely assign the space group as $P2_1/c$ (C_{2h}^5; no. 14), which requires that the crystal be racemic. The unit cell dimensions are a = 12.410 ± 0.010 Å., b = 7.823 ± 0.008 Å.; c = 12.632 ± 0.010 Å., β = 109.86 ± 0.05°. The volume of the unit cell is 1153.2 (±3.1) Å.^{3}.

The observed density, ρ_{obsd} = 2.50 ± 0.05 g. cm.$^{-3}$, is in satisfactory agreement with the calculated value, ρ_{calcd} = 2.543 g. cm.$^{-3}$ (Z = 4 and M = 442 for $RhC_8H_5F_5OI$). The total number of electrons per unit cell, $F(000)$ = 816.

TABLE I

FINAL POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS. CALCULATED POSITIONS FOR HYDROGEN ATOMS ARE INCLUDED

Atom	X	$10^3\sigma(X)$	Y	$10^3\sigma(Y)$	Z	$10^3\sigma(Z)$
Rh	0.23249	0.15	0.42302	0.27	−0.04362	0.15
I	0.10381	0.15	0.16244	0.27	−0.02388	0.15
F-1	0.2154	1.3	0.5173	2.5	0.1678	1.2
F-2	0.3289	1.3	0.3066	2.4	0.1859	1.1
F-3	0.3730	1.7	0.7281	2.5	0.1415	1.6
F-4	0.4868	1.2	0.5164	2.5	0.1485	1.3
F-5	0.4312	1.4	0.5753	2.8	0.2868	1.2
O	0.4231	2.2	0.1720	3.1	−0.0217	1.8
C-1	0.2960	2.0	0.4522	3.3	0.1305	1.6
C-2	0.4005	2.2	0.5758	5.2	0.1787	2.3
C-3	0.3598	2.6	0.2634	4.2	−0.0271	2.0
C-4	0.2279	2.8	0.5389	3.8	−0.2093	2.0
C-5	0.1174	2.2	0.4785	4.2	−0.2215	2.0
C-6	0.0796	2.1	0.5759	3.8	−0.1378	2.3
C-7	0.1684	2.9	0.6913	4.0	−0.0790	2.2
C-8	0.2628	2.3	0.6724	4.2	−0.1187	2.6
H-4	0.2783		0.4930		−0.2583	
H-5	0.0705		0.3816		−0.2800	
H-6	−0.0016		0.5613		−0.1249	
H-7	0.1664		0.7788		−0.0135	
H-8	0.3424		0.7428		−0.0892	

Determination of the Structure.—The three-dimensional Patterson map[7] $P(UVW)$ revealed a set of vectors consistent with two independent heavy atoms at X_1 = 0.107, Y_1 = 0.163, Z_1 = −0.022; X_2 = 0.232, Y_2 = 0.423, Z_2 = −0.045. The first position, giving rise to the smaller internal peaks, was originally attributed to the rhodium atom (Z = 45) and the second to the iodine atom (Z = 53). A three-dimensional Fourier[7] synthesis (R = 29.8%), based on this assumption, immediately showed well-defined peaks consistent with the carbonyl group and with all seven atoms of the perfluoroethyl group and indicated that the original assignment of rhodium and iodine atoms should be reversed. Structure factor calculations,[8] phased now by the rhodium, iodine, oxygen, three carbon, and five fluorine atoms, had an initial discrepancy index R = 24%, which reduced to 15.1% after a single cycle of refinement. A difference Fourier at this stage showed clearly the positions of the five carbon atoms of the π-cyclopentadienyl system. Structure factors, phased now by all atoms other than hydrogen (initial R = 12.9%), converged after two cycles of positional and isotropic thermal parameter refinement to a value R = 11.2%. Refinement was continued using anisotropic thermal parameters (T), defined by

$$T = -\exp[b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl]$$

A further six cycles of positional and anisotropic thermal parameter refinement led to a reduction in the discrepancy index to the final value

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 6.98\%$$

The least-squares refinement was based on a unit weighting system; the maximum coordinate shift indicated by the last cycle of refinement was less than one-tenth of the average atomic standard deviation. Throughout the analysis, the scattering factors compiled by Ibers[9] were used.

Dispersion corrections are small and were ignored. Although hydrogen atom positions have been estimated for the sake of completeness (see Table I), they were not included in the structure-factor calculations, nor were they evident from a final difference-Fourier synthesis.

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(5) M. R. Churchill, *Chem. Commun.* (London), 86 (1965).

(6) J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4200 (1964).

(7) Patterson and Fourier maps were all computed using ERFR-2, a two- and three-dimensional Fourier program for the IBM 709/7090 by W. G. Sly, D. P. Shoemaker, and J. H. van der Hende.

(8) Structure factor calculations and full-matrix refinement of positional and thermal parameters were carried out using OR-FLS, a Fortran least-squares program by W. R. Busing, K. O. Martin, and H. A. Levy.

(9) "International Tables for X Ray Crystallography," Vol 3, The Kynoch Press, Birmingham, England. Scattering factors for iodine and rhodium are taken from p. 211; those for carbon, oxygen, and fluorine from p. 202.

TABLE II

π-$C_5H_5Rh(CO)(C_2F_5)I$: FINAL ANISOTROPIC THERMAL PARAMETERS

Atom	10^4b_{11}	10^4b_{22}	10^4b_{33}	10^4b_{12}	10^4b_{13}	10^4b_{23}	B, Å.^{2} [a]
Rh	85.7(1.5)	140.4(4.9)	64.4(1.5)	5.6(2.1)	20.3(1.1)	0.3(2.4)	3.91
I	120.8(1.9)	187.4(5.4)	103.5(1.9)	−42.7(2.3)	28.4(1.3)	−7.4(2.5)	5.66
F-1	144(15)	414(56)	102(14)	−42(22)	65(12)	−94(22)	7.9
F-2	143(16)	309(48)	67(12)	−6(23)	23(11)	18(21)	6.4
F-3	219(25)	149(36)	119(18)	−24(23)	−3(16)	−34(24)	7.4
F-4	87(14)	394(53)	113(14)	−48(20)	33(11)	−40(22)	6.9
F-5	157(18)	496(65)	65(13)	−37(28)	−1(11)	−75(24)	8.1
O	224(31)	267(57)	116(21)	163(35)	64(21)	49(31)	8.4
C-1	97(21)	123(51)	24(14)	−25(27)	−2(14)	16(27)	3.2
C-2	82(24)	311(91)	87(26)	−40(41)	23(19)	−58(46)	5.7
C-3	143(31)	203(70)	37(18)	20(37)	3(19)	73(33)	4.9
C-4	185(37)	164(65)	49(19)	44(38)	46(21)	38(32)	5.6
C-5	86(24)	309(85)	82(22)	47(35)	41(19)	38(36)	5.6
C-6	85(21)	190(60)	106(24)	37(33)	0(19)	24(40)	5.1
C-7	193(36)	164(67)	77(24)	15(42)	−19(25)	114(39)	6.3
C-8	110(27)	226(71)	136(31)	56(37)	55(24)	73(45)	6.4

[a] B, the "equivalent" isotropic temperature factor is obtained by a straight average of $4b_{11}/a^{*2}$, $4b_{22}/b^{*2}$, and $4b_{33}/c^{*2}$.

TABLE III

π-$C_5H_5Rh(CO)(C_2F_5)I$: OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	F_o	F_c
0	0	4	158.	146.
0	0	6	117.	120.
0	0	10	-46.	-45.
0	0	12	-52.	-53.
0	1	3	121.	111.
0	1	4	162.	148.
0	1	5	18.	24.
0	1	6	116.	112.
0	1	7	18.	25.
0	1	8	121.	114.
0	1	9	59.	60.
0	1	10	52.	57.
0	1	11	40.	41.
0	2	0	36.	37.
0	2	2	-88.	-84.
0	2	3	12.	15.
0	2	5	-22.	-19.
0	2	10	-27.	-27.
0	2	11	28.	29.
0	3	1	-163.	-169.
0	3	2	40.	42.
0	3	3	-126.	-117.
0	3	4	111.	102.
0	3	5	-100.	-94.
0	3	6	101.	91.
0	3	7	-41.	-40.
0	3	9	58.	56.
0	4	0	-51.	-60.
0	4	1	-59.	-63.
0	4	2	-100.	-106.
0	4	3	-96.	-101.
0	4	4	-73.	-71.
0	4	5	-133.	-130.
0	4	7	-112.	-106.
0	4	9	-50.	-46.
0	4	11	-23.	-20.
0	5	1	68.	77.
0	5	2	10.	15.
0	7	1	63.	88.
0	8	0	-44.	-45.
0	8	1	9.	17.
0	8	2	-33.	-32.
0	9	1	-14.	-13.
1	0	2	245.	250.
1	0	4	314.	315.
1	0	-4	-141.	-128.
1	0	6	196.	188.
1	0	-6	-188.	-180.
1	0	8	85.	87.
1	0	-8	-59.	-64.
1	0	10	54.	56.
1	0	-10	-67.	-74.
1	0	-10	-67.	-74.
1	1	3	-22.	-26.
1	1	-3	89.	101.
1	1	4	-93.	-87.
1	1	-4	-188.	-175.
1	1	5	-87.	-80.
1	1	-5	113.	126.
1	1	6	20.	24.
1	1	-6	-123.	-122.
1	1	7	8.	13.
1	1	-7	77.	76.
1	1	8	43.	42.
1	1	10	44.	41.
1	1	-11	11.	6.
1	2	0	-27.	-31.
1	2	1	30.	40.
1	2	-1	-48.	-49.
1	2	2	-19.	-17.
1	2	-2	-49.	-52.
1	2	3	35.	33.
1	2	-3	-26.	-29.
1	2	4	-12.	-14.
1	2	-4	-30.	-31.
1	2	5	18.	19.
1	2	-5	-48.	-50.
1	2	6	26.	28.
1	2	-6	-61.	-61.
1	2	7	-12.	-16.
1	2	-7	-94.	-93.
1	2	8	-7.	-2.
1	2	9	-7.	-11.
1	2	-9	-81.	-75.
1	2	-11	-60.	-57.
1	3	0	-109.	-117.
1	3	1	-112.	-112.
1	3	-1	-79.	-79.
1	3	2	-110.	-111.
1	3	-2	-123.	-138.
1	3	3	-91.	-85.
1	3	-3	-54.	-61.
1	3	4	-21.	-21.
1	3	-4	-51.	-55.
1	3	5	-136.	-126.
1	3	6	35.	34.
1	3	7	-68.	-68.
1	3	-7	38.	36.
1	3	8	25.	26.
1	3	-8	17.	21.
1	3	9	-38.	-34.
1	3	-9	17.	20.
1	3	10	51.	55.
1	3	-10	35.	34.
1	3	-11	21.	22.
1	3	12	28.	26.
1	3	-12	32.	33.
1	4	0	-65.	-71.
1	4	1	156.	158.
1	4	-1	149.	154.
1	4	2	-94.	-105.
1	4	3	68.	67.
1	4	-3	146.	158.
1	4	4	-46.	-50.
1	4	-4	16.	18.
1	4	5	-28.	-25.
1	4	-5	64.	70.
1	4	6	-55.	-56.
1	4	7	-36.	-34.
1	4	-7	28.	26.
1	4	8	-50.	-48.
1	4	-8	28.	27.
1	4	9	-55.	-52.
1	4	-10	16.	17.
1	4	11	-51.	-46.
1	4	-11	-26.	-28.
1	5	1	59.	65.
1	5	2	-29.	-30.
1	5	-2	13.	16.
1	6	0	47.	48.
1	6	1	27.	24.
1	6	2	27.	22.
1	6	-2	51.	53.
1	7	1	39.	37.
1	7	-1	14.	15.
1	7	-2	-16.	-19.
1	8	0	-10.	-13.
1	8	1	-44.	-41.
1	8	-1	-51.	-43.
1	8	2	-29.	-29.
1	9	0	17.	19.
1	9	-1	-17.	-17.
1	9	2	10.	13.
1	11	0	18.	17.
2	0	2	63.	65.
2	0	4	62.	51.
2	0	-4	-70.	-66.
2	0	6	85.	87.
2	0	-6	-52.	-56.
2	0	8	118.	115.
2	0	10	63.	70.
2	0	12	42.	44.
2	1	0	-145.	-133.
2	1	1	95.	95.
2	1	2	-91.	-91.
2	1	3	102.	97.
2	1	-3	46.	49.
2	1	4	-108.	-99.
2	1	-4	-37.	-46.
2	1	5	66.	66.
2	1	-5	32.	38.
2	1	6	-57.	-62.
2	1	-6	-17.	-19.
2	1	7	-17.	-16.
2	1	-7	-52.	-58.
2	1	8	-31.	-32.
2	1	-8	-15.	-15.
2	1	9	-8.	-10.
2	1	-9	-58.	-59.
2	1	11	-22.	-26.
2	1	-11	-52.	-51.
2	2	0	-86.	-86.
2	2	1	-124.	-117.
2	2	-1	-117.	-112.
2	2	2	-114.	-113.
2	2	-2	-59.	-62.
2	2	3	20.	22.
2	2	5	30.	34.
2	2	-5	-161.	-179.
2	2	6	-12.	-18.
2	2	7	48.	44.
2	2	-7	-118.	-118.
2	2	9	20.	18.
2	2	-9	-88.	-79.
2	2	10	18.	22.
2	3	0	-45.	-48.
2	3	1	-49.	-51.
2	3	-1	-33.	-34.
2	3	2	-86.	-85.
2	3	-2	36.	34.
2	3	3	-56.	-56.
2	3	-3	14.	14.
2	3	4	-142.	-134.
2	3	-4	30.	35.
2	3	5	-72.	-69.
2	3	-5	57.	63.
2	3	6	-89.	-81.
2	3	-6	85.	88.
2	3	7	-58.	-58.
2	3	-7	35.	31.
2	3	8	-25.	-24.
2	3	-8	82.	75.
2	3	9	-44.	-46.
2	3	-9	38.	42.
2	3	-10	10.	17.
2	3	11	-27.	-32.
2	3	-11	30.	28.
2	4	0	13.	14.
2	4	1	100.	107.
2	4	-1	76.	79.
2	4	2	13.	12.
2	4	-2	32.	34.
2	4	3	137.	136.
2	4	-3	16.	22.
2	4	4	-43.	-39.
2	4	-4	41.	41.
2	4	5	98.	93.
2	4	6	-41.	-38.
2	4	-6	30.	31.
2	4	7	43.	39.
2	4	-7	-30.	-36.
2	4	8	-41.	-37.
2	4	-8	28.	27.
2	4	-9	-23.	-22.
2	5	0	52.	54.
2	5	1	-30.	-29.
2	5	-1	-29.	-30.
2	5	2	31.	33.
2	5	-2	103.	101.
2	6	0	66.	72.
2	6	-1	14.	15.
2	6	2	75.	73.
2	6	-2	70.	69.
2	7	0	-20.	-21.
2	7	1	-25.	-26.
2	7	-1	-59.	-58.
2	7	-2	-53.	-48.
2	8	0	23.	22.
2	8	1	-48.	-43.
2	8	-1	-25.	-25.
2	8	-2	26.	25.
2	9	0	-10.	-2.
2	9	1	-17.	-20.
2	9	-1	-14.	-14.
3	0	0	-120.	-116.
3	0	2	-91.	-91.
3	0	-2	-78.	-74.
3	0	4	-92.	-91.
3	0	-4	-29.	-28.
3	0	-6	-18.	-18.
3	0	10	29.	36.
3	0	-10	-10.	-15.
3	0	-10	-10.	-15.
3	0	12	23.	24.
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9	3	-3	-44.	-48.
9	3	4	14.	15.
9	3	-4	-50.	-54.
9	3	5	-14.	-11.
9	3	-5	-40.	-37.
9	3	6	14.	17.
9	3	-6	-38.	-40.
9	3	-7	-21.	-19.
9	3	-8	-21.	-19.
9	3	-9	-17.	-17.
9	3	-12	17.	14.
9	4	0	-31.	-32.
9	4	1	-14.	-12.
9	4	-1	17.	18.
9	4	2	-35.	-32.
9	4	-2	-29.	-33.
9	4	3	-26.	-26.
9	4	-3	26.	27.
9	4	5	-30.	-31.
9	4	7	-26.	-28.
9	4	-7	30.	33.
9	5	0	-26.	-23.
9	5	1	33.	29.
9	5	-1	-39.	20.
9	5	-2	-21.	-26.
9	6	-1	19.	15.
9	7	0	12.	16.
9	7	1	36.	28.
9	7	-1	33.	25.
10	0	2	23.	27.
10	0	-2	-13.	-9.
10	0	4	25.	31.
10	0	-4	-25.	-28.
10	0	6	29.	38.
10	1	0	-34.	-32.
10	1	1	21.	20.
10	1	-1	41.	37.
10	1	-2	-29.	-30.
10	1	-3	67.	67.
10	1	-4	-11.	-16.
10	1	-5	48.	47.
10	1	-6	-11.	-20.
10	1	-7	17.	18.
10	2	0	-16.	-15.
10	2	1	27.	26.
10	2	-1	15.	18.
10	2	-2	-44.	-45.
10	2	3	23.	22.
10	2	-3	-19.	-22.
10	2	-4	-42.	-44.
10	2	-5	-39.	-40.
10	2	-6	-25.	-26.
10	2	-7	-48.	-49.
10	2	-11	-38.	-36.
10	3	0	-39.	-40.
10	3	1	-42.	-36.
10	3	-1	-28.	-27.
10	3	2	-40.	-38.
10	3	-2	-34.	-33.
10	3	3	-17.	-18.
10	3	4	-21.	-25.
10	3	5	-10.	-17.
10	3	-5	-14.	-13.
10	3	-8	23.	22.
10	3	-10	28.	28.
10	3	-12	14.	16.
10	4	1	31.	25.
10	4	-1	27.	27.
10	4	2	-13.	-16.
10	4	3	20.	19.
10	4	-3	16.	18.
10	5	-2	10.	8.
10	6	0	32.	26.
10	6	-1	17.	14.
10	6	-2	44.	37.
10	8	-1	-19.	-14.
11	0	2	-15.	-15.
11	0	-8	25.	32.
11	0	-10	10.	14.
11	1	0	-8.	-11.
11	1	1	46.	42.
11	1	-1	27.	28.
11	1	3	29.	30.
11	1	-7	-28.	-30.
11	1	-9	-41.	-41.
11	1	-10	-11.	-10.
11	1	-11	-24.	-21.
11	2	0	-35.	-35.
11	2	1	-13.	-15.
11	2	-1	-42.	-39.
11	2	-2	-12.	-12.
11	2	-3	-51.	-52.
11	2	-5	-58.	-54.
11	2	-7	-37.	-37.
11	2	-8	20.	24.
11	2	-9	-23.	-17.
11	3	-1	-5.	-8.
11	3	2	-13.	-12.
11	3	-2	25.	24.
11	3	4	-17.	-16.
11	3	-5	10.	7.
11	3	-6	27.	29.
11	3	-8	21.	18.
11	5	0	20.	19.
11	5	-2	33.	31.
11	6	0	29.	23.
11	6	-2	19.	18.
11	7	1	-14.	-12.
11	7	-1	-14.	-11.
12	0	-4	21.	21.
12	1	3	8.	12.
12	1	-3	-28.	-29.
12	1	-4	-11.	-17.
12	1	-5	-38.	-37.
12	1	-6	-11.	-18.
12	1	-7	-31.	-29.
12	1	-8	-11.	-15.
12	2	1	-39.	-31.
12	2	-1	-43.	-38.
12	2	-2	9.	10.
12	2	3	-28.	-24.
12	2	-3	-33.	-31.
12	2	-4	22.	22.
12	2	-6	19.	19.
12	2	-8	18.	14.
12	2	-9	14.	13.
12	2	-11	14.	16.
12	3	0	25.	18.
12	3	2	13.	17.
12	3	-2	19.	21.
12	5	0	24.	19.
12	5	-2	21.	20.
12	6	0	-7.	-2.
13	1	0	-12.	-10.
13	1	1	-26.	-21.
13	1	-1	-30.	-25.
13	1	-2	-11.	-14.
13	1	3	-11.	-12.
13	1	-3	-18.	-18.
13	1	-4	-15.	-16.
13	2	1	-15.	-11.
13	2	-2	11.	15.
13	6	0	-18.	-17.
14	2	1	-11.	-10.
14	3	0	-13.	-11.

Final atomic coordinates are collected in Table I and thermal parameters in Table II. In each table the standard deviations, $\sigma(j)$, were estimated by the least-squares program OR-FLS,[8] using the formula $\sigma(j) = [a_{jj}(\Sigma\omega\Delta^2)/(m - n)]^{1/2}$ where a_{jj} is the appropriate (diagonal) element of the matrix inverse to the normal equation matrix, m the number of observations, n the number of variables in the refinement, and $\Sigma\omega\Delta^2$ the standard crystallographic residue. Observed and calculated structure factors are shown in Table III.

TABLE IV

π-$C_5H_5Rh(CO)(C_2F_5)I$: INTERATOMIC DISTANCES AND ANGLES[a]

(i) From Rhodium Atom

Atoms	Distance, Å.	Atoms	Angle, deg.
Rh–I	2.653	I–Rh–C-1	90.5
Rh–C-1	2.08	I–Rh–C-3	89.4
Rh–C-3	1.97	C-1–Rh–C-3	87.4
Rh–C-4	2.26	C-4–Rh–C-5	36.3
Rh–C-5	2.26	C-5–Rh–C-6	39.3
Rh–C-6	2.22	C-6–Rh–C-7	37.3
Rh–C-7	2.23	C-7–Rh–C-8	37.1
Rh–C-8	2.26	C-8–Rh–C-4	38.8

(ii) In Perfluoroalkyl Group

Atoms	Distance, Å.	Atoms	Angle, deg.
C-1–C-2	1.57	Rh–C-1–C-2	116.4
C-1–F-1	1.34	Rh–C-1–F-1	110.6
C-1–F-2	1.33	Rh–C-1–F-2	113.6
C-2–F-3	1.28	C-2–C-1–F-1	104.4
C-2–F-4	1.34	C-2–C-1–F-2	105.1
C-2–F-5	1.29	F-1–C-1–F-2	105.8
F-1–F-2	2.13	C-1–C-2–F-3	110.5
F-3–F-4	2.16	C-1–C-2–F-4	108.3
F-4–F-5	2.14	C-1–C-2–F-5	108.6
F-5–F-3	2.10	F-3–C-2–F-4	111.0
		F-3–C-2–F-5	109.6
		F-4–C-2–F-5	108.9

(iii) In Cyclopentadienyl Ring

Atoms	Distance, Å.	Atoms	Angle, deg.
C-4–C-5	1.41	C-8–C-4–C-5	109.6
C-5–C-6	1.50	C-4–C-5–C-6	106.1
C-6–C-7	1.42	C-5–C-6–C-7	108.6
C-7–C-8	1.43	C-6–C-7–C-8	109.5
C-8–C-4	1.50	C-7–C-8–C-4	106.3

(iv) Others

Atoms	Distance, Å.	Atoms	Angle, deg.
C-3–O	1.05	Rh–C-3–O	175.8
I–C-1	3.39	F-4–F-3–F-5	60.1
I–C-3	3.29	F-3–F-4–F-5	58.6
I–C-4	4.36	F-3–F-5–F-4	61.3
I–C-5	3.56		
I–C-6	3.51		
I–C-7	4.31		
C-1–C-6	3.67		
C-1–C-7	3.19		
C-1–C-8	3.49		
C-3–C-7	4.03		
C-3–C-8	3.48		
C-3–C-4	3.17		
C-3–C-5	3.59		

[a] Average estimated standard deviations are as follows: 0.003 Å. for Rh–I, 0.018 Å. for Rh–F and I–F, 0.025 Å. for Rh–O and I–O, 0.030 Å. for Rh–C and I–C, 0.025 Å. for F–F, 0.034 Å. for C–F, 0.035 Å. for C–O, and 0.041 Å. for C–C distances. These values do not include any contribution from errors in unit cell constants.

The Molecular Structure

Intramolecular bond lengths, bond angles, and important intramolecular vectors are listed in Table IV. The essential geometry of the molecule, and the numbering of atoms, is shown in Figure 1.

The molecule may be regarded as an octahedral complex of a d^6 Rh(III) ion. The angles between the carbonyl, iodide, and perfluoroethyl ligands are all very close to the ideal value of 90°; the formally tridentate π-cyclopentadienyl group completes the sixfold coordination of the metal. The over-all stereochemistry about the metal is similar to that in π-cyclopentadienylmanganese tricarbonyl,[10] except that the rhodium atom in the present complex is at an asymmetric center.[6]

The orientation of the π-cyclopentadienyl ring with respect to the three ligands opposite (see Figure 2) appears to be sterically fixed due to the large size of the iodine atom. The contacts I–C-5 and I–C-6 are approximately equal ($\sim$3.5 Å.), indicating that the iodine atom lies below and between these two atoms. The perfluoroethyl and carbonyl ligands are thus forced into positions with no particular symmetry with respect to the π-cyclopentadienyl ring. The α carbon of the perfluoroethyl group (*i.e.*, C-1) lies approximately below C-7, but is displaced slightly toward C-8; the carbon of the carbonyl group (C-3) lies almost below C-4 and is also displaced slightly toward C-8. The carbon–carbon bond lengths within the π-cyclopentadienyl ring vary in the range 1.41–1.50 Å. Although this variation is not statistically significant (0.09 Å. $\simeq 2.2\sigma$), the nature of the variation around the ring is consistent with a perturbation toward the "allyl-ene" structure[11] which might be expected to result from the totally asymmetric ligand field (see Figure 2).

The Perfluoroethyl Group

The perfluoroethyl group is in the expected staggered conformation, the Rh–C_α distance being 2.08 Å. compared to the rhodium–carbonyl distance of 1.97 Å. Since the difference between the covalent radii of sp^3 and sp hybridized carbon atoms is 0.07 Å., the excess π-character in the rhodium–carbonyl bond results in a decrease of only 0.04 Å. ($\sim 1.3\sigma$) relative to the rhodium–perfluoroethyl linkage. A similarly small difference is found for the Co–CF_2 and Co–CN bonds in $K_3[Co(CN)_5CF_2CF_2H]$[12]; for transition metal (*nonfluorinated*) alkyls,[13–15] however, the difference (Δ) in metal–carbon bond lengths for the alkyl and carbonyl groups is significantly greater (see Table V).

These comparisons suggest that the rhodium–perfluoroalkyl bond in π-$C_5H_5Rh(CO)(C_2F_5)I$ is considerably shorter than might be expected for a simple metal–carbon σ bond. However, evidence of bond shortening does not permit us to differentiate between orbital contraction on the rhodium atom (due to the high electronegativity[16] of the perfluoroethyl group) and the alternative of π donation from the metal d_π orbitals (in this case, d_{xy}, $d_{x^2-y^2}$) into C–F antibonding orbitals. Although the C_α–C_β bond length (1.57 ± 0.04 Å.) is not significantly different from a simple single bond, a detailed survey of the bond angles around the α carbon of the perfluoroethyl does give some support for

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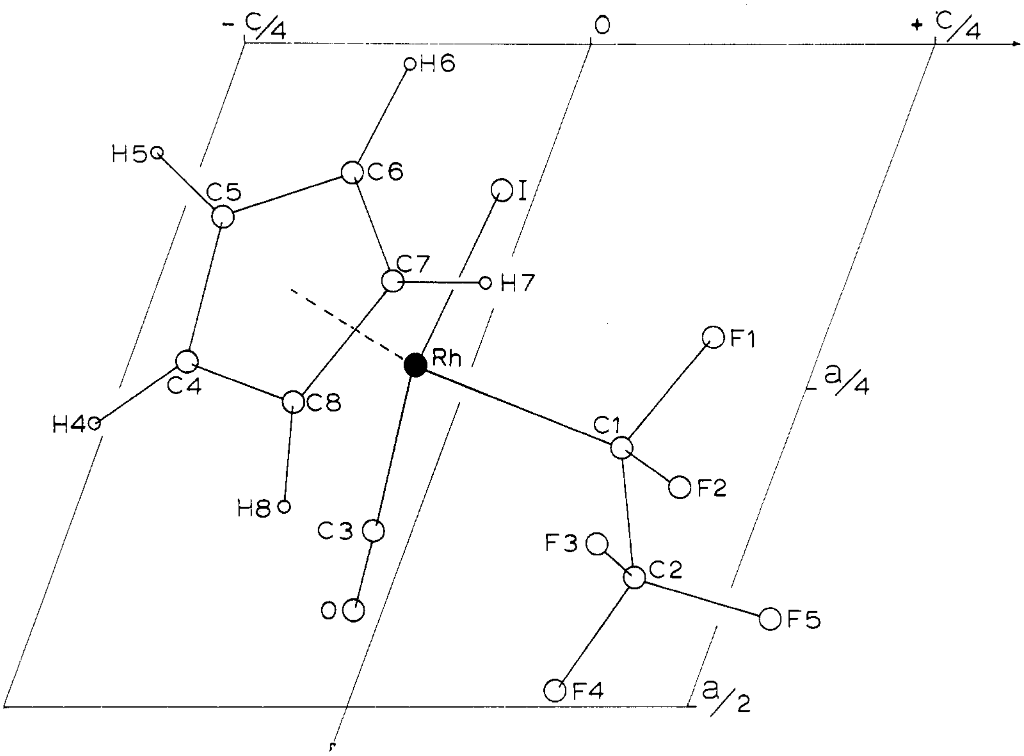

Figure 1.—π-$C_5H_5Rh(CO)(C_2F_5)I$: the molecule projected down *b*.

TABLE V

A COMPARISON OF METAL–CARBON BOND LENGTHS IN SOME TRANSITION METAL FLUOROALKYLS AND ALKYLS

Complex	Bond	d_{m-c} (with e.s.d.), Å.	Δ,[a] Å.
π-$C_5H_5Rh(CO)(C_2F_5)I$	Rh–CF_2	2.08 (±0.03)	
	Rh–CO	1.97 (±0.03)	0.04
$K_3[Co(CN)_5CF_2CF_2H]$[12]	Co–CF_2	1.990 (±0.014)	
	Co–CN (*trans*)	1.927 (±0.014)	(−)0.007
π-$C_5H_5Mo(CO)_3C_2H_5$[13]	Mo–CH_2	2.38 (±0.03)	
	Mo–CO	1.97 (±0.03)	0.34
$(OC)_2\overline{Fe(\pi\text{-}C_5H_4)\text{–}CH_2Fe}^*(CO)_4$[14]	Fe*–CH_2	2.123 (±0.015)	
	Fe*–CO (*trans*)	1.809 (±0.015)	0.244
π-$C_5H_5Re(CH_3)_2C_5H_5CH_3$[15]	Re–CH_3 (av.)	2.25 (±0.03)	
	Re–CO[b]	<2.00	>0.18

[a] Δ is the contraction of the metal–carbonyl (or cyanide) bond length relative to the metal–alkyl (or fluoroalkyl) distance, after correction has been made for the different hybridization states of the carbon atoms (see text). [b] Structural studies on the series $M_2(CO)_{10}$ (M = Mn,[c] Tc,[d] Re[e]) suggest a Re^0–CO distance of ~2.00 Å. The Re^V–CO distance, required for comparison with the observed Re^V–CH_3 bond length, is expected to be significantly lower than 2.00 Å. [c] L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963). [d] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1140 (1965). [e] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

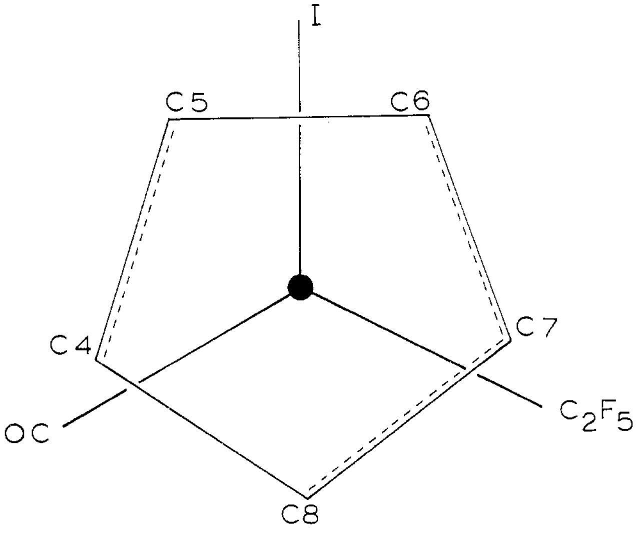

Figure 2.—π-$C_5H_5Rh(CO)(C_2F_5)I$: orientation of ligands with respect to the π-cyclopentadienyl ring.

d_π–σ^* back donation. As back donation increases the double-bond character in the rhodium–perfluoroethyl linkage, the angles Rh–C_α–C_β, Rh–C_α–F_1, Rh–C_α–F_2 are expected to increase from the regular tetrahedral value (due to the increasing repulsion of the electrons in the Rh–C_α bond from those in the C_α–C_β, C_α–F_1, and C_α–F_2 bonds[17]). Such distortions do, in fact, occur (Rh–C_α–C_β = 116.4°, Rh–C_α–F_1 110.6°, Rh–C_α–F_2 = 113.6°). Confirmatory evidence for the generality of these observations has been obtained by Mason and Russell,[12] whose study of $K_3[Co(CN)_5CF_2CF_2H]$ shows a Co–C_α–C_β angle of 119.7 ± 0.9°.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KANSAS, LAWRENCE, KANSAS

Association of Alkali Metal Ions with Anions of β-Diketones in Methanol and Ethanol

BY DEAN C. LUEHRS, REYNOLD T. IWAMOTO, AND JACOB KLEINBERG

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The pK_a values of a number of β-diketones (acetylacetone, benzoylacetone, dibenzoylmethane, 2-thenoyltrifluoroacetone, and dimedone) in anhydrous methanol and ethanol have been determined, and, in addition, the interaction of the anions of these diketones with alkali metal cations in the same solvents has been studied. The pK_a values in these solvents for each of the diketones are similar and much higher than the corresponding value in water. For the anion of any of the diketones studied except dimedone, the pK values for the dissociation of the complexes with alkali metal ions generally decrease, as expected, with increasing cationic size. Values for pK are higher in ethanol than in methanol. No clear correlation was found between the pK_a values of the diketones and the dissociation constants of the complexes in either solvent.

Introduction

Although a large number of complexes of alkali metal ions with anions of β-diketones have been prepared, little quantitative data exist on the dissociative stability of such complexes. Van Uitert, Haas, Fernelius, and Douglas[1] found that in aqueous dioxane β-diketones containing two aromatic rings, such as dibenzoylmethane, gave the strongest complexes with sodium ion, β-diketones containing methyl groups formed complexes of lesser stability, and dimedone (1,1-dimethyl-3,5-cyclohexanedione) did not appear to complex at all. Dimedone differs from the other diketones studied in that steric factors do not permit simultaneous bonding of both oxygens to the metal ion. Fernelius and Van Uitert[2] found that the stability of alkali metal ion complexes with the anion of dibenzoylmethane in 75% dioxane–25% water decreases with increasing cationic size. The stability constants reported seemed surprisingly large in view of the high water content of the solvent mixture. Thus log K values ranging from 5.95 (for Li^+) to 3.42 (for Cs^+) were obtained.

In the present communication we report the results of a study of the stability of complexes of alkali metal ions with the anions of a variety of β-diketones in essentially anhydrous methanol and ethanol. It was expected that the relative absence of water in these solvents would enhance markedly the extent of complex formation over that exhibited in the dioxane–water medium cited above.

Experimental

Materials.—Methanol and ethanol were purified by treatment with calcium hydride and potassium borohydride, followed by fractional distillation through a 4-ft. column packed with glass helices. The fraction collected for each solvent boiled within a 0.3° range. Analysis by the Karl Fischer method showed the water content of each solvent to be less than 2×10^{-2} *M*. Practical grade acetylacetone (Fisher Scientific Co.) was purified according to the method of Steinbach and Freiser.[3] Benzoylacetone and dibenzoylmethane, both Eastman White Label, were used without further purification. The former, after being dried *in vacuo* at room temperature, melted at 57–58°, and the latter, after drying *in vacuo* at 65°, melted at 77–78.5°. 2-Thenoyltrifluoroacetone, Fisher Certified Reagent, dried *in vacuo*, melted at 44–45° and was used without further purification. Dimedone, obtained from Matheson Coleman and Bell, was purified by sublimation *in vacuo* at 100°; m.p., 148–149°. All melting points are uncorrected and agree well with literature values.[4] Tetrabutylammonium hydroxide titrant, purchased from Southwestern Analytical Chemicals, was 1 *M* Titration Grade in methanol. This was diluted to 0.1 *M* concentration with methanol or ethanol and the resulting solution was standardized by titration of primary standard potassium acid phthalate to a phenolphthalein end point. Reagent grade lithium perchlorate, sodium perchlorate, potassium iodide, potassium thiocyanate, sodium benzoate, and benzoic acid were all dried at 110° just prior to use. Tetraethylammonium bromide (Eastman White Label) was recrystallized three times from acetonitrile before use. Lithium salicylate, obtained by neutralization of lithium hydroxide with salicylic acid and evaporation to dryness, was dried at 110° before use. Tetrabutylammonium perchlorate was precipitated by the addition of perchloric acid to tetrabutylammonium iodide (Eastman White Label) in water. The crude salt was filtered, washed with water, and dissolved in acetone. The resulting solution was treated with silver perchlorate to remove iodide impurity. After filtration of silver iodide, a small amount of water was added to the acetone solution and excess silver ion removed by controlled potential electrolysis at −0.2 v. *vs.* s.c.e. The solution was then evaporated almost to dryness, and the tetrabutylammonium perchlorate was

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