$(C_6H_5)_3PAu$–$Co(CO)_4$ indicates a very similar Co environment in this compound. In Cl_3Si–$Co(CO)_4$ the mean axial–equatorial C–C distance is 2.62 A, essentially that found in other compounds where equatorial carbonyl groups are free to move away from axial ones (*e.g.*, $Mn_2(CO)_{10}$[3] and $HMn(CO)_5$[4]). However, shorter nonbonded distances are possible when the equatorial carbonyls are constrained by other structural features (*e.g.*, $((C_6H_5)_2P)H(Mn(CO)_4)_2$[18]).

The $Co(CO)_4$ fragment has idealized symmetry C_{3v}, but not T_d symmetry. It has been pointed out[19] that the infrared spectral data on $HCo(CO)_4$ are consistent with either of these symmetries. We believe it reasonable to assume that the structure of $HCo(CO)_4$ will contain a $Co(CO)_4$ fragment that differs very little from that found here.

The Si atom deviates slightly but significantly from a tetrahedral environment. The mean Co–Si–Cl bond angle is 113.3°, the mean Cl–Si–Cl angle is 105.4°, and the mean $Cl\cdots Cl$ distance is 3.24 A. The Si–Cl distance of 2.03 A found here compares favorably with those usually found, for example with 2.01 A in hexachlorodisilane[20] and silicon tetrachloride.[21]

The Si–Co bond length of 2.254 A represents the first determination of a length for this linkage. If one takes the tetrahedral radius of Si to be 1.17 A and the single bond radius of Co to be 1.16 A,[22] then a "single" Si–Co bond length should be approximately 2.33 A. In view of the approximate nature of this estimate, the Co–Si bond in this structure could be considered a single bond. Yet the radius estimate for Co is probably too short, for "single" Co–Co bonds in a variety of compounds are longer than 2.47 A.[23] Thus a Si–Co bond length of 2.254 A could be interpreted as indicative of some multiple bond character. On the basis of an infrared study Hagen and MacDiarmid[8] have proposed that there is considerable $(d \rightarrow d)\pi$ bonding in this Si–Co bond. If this is the case, then it might manifest itself in differences between the Co–CO apical linkage and the Co–CO equatorial linkages. The apical $Co\cdots O$ distance is possibly significantly longer than the equatorial $Co\cdots O$ distances, but the general variations among Co–C and C–O distances negate this being used as an argument in favor of Si–Co multiple bonding. In short, this study does not in any way refute the conclusions of Hagen and MacDiarmid[8] concerning multiple Si–Co bonding, nor does it corroborate them. Clearly, examination of the Si–Co bond in other substituted silylcobalt carbonyls will provide valuable information on the nature of the bonding. A determination of the structure of $Co(SiF_3)(CO)_4$ is contemplated in the near future.

Acknowledgments.—We are indebted to Professor A. G. MacDiarmid and Mr. A. P. Hagen for supplying samples for this study and for several useful discussions. The support of the National Science Foundation is gratefully acknowledged.

---

(18) R. J. Doedens, W. T. Robinson, and J. A. Ibers, unpublished results.

(19) H. Stammreich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras, and S. Bril, *J. Chem. Phys.*, **32**, 1482 (1960).

(20) Y. Morino and E. Hirota, *ibid.*, **28**, 185 (1958).

(21) M. Iwasaki, A. Kotera, A. Tatematsu, and K. Yamasaki, *J. Chem. Soc. Japan*, **69**, 104 (1948).

(22) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(23) See, for example, J. Lewis, *Pure Appl. Chem.*, **10**, 11 (1965).

CONTRIBUTION FROM THE MALLINCKRODT LABORATORY,
DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

The Crystal and Molecular Structure of a Perfluoropropyl Complex of Molybdenum: π-$C_5H_5Mo(CO)_3C_3F_7$

BY MELVYN R. CHURCHILL AND JAMES P. FENNESSEY

Received November 14, 1966

Tricarbonyl-π-cyclopentadienylheptafluoropropylmolybdenum, π-$C_5H_5Mo(CO)_3C_3F_7$, crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 8.301 \pm 0.007$ A, $b = 15.240 \pm 0.014$ A, $c = 11.249 \pm 0.012$ A, $\beta = 106° 15' \pm 05'$, $Z = 4$. A complete three-dimensional single-crystal X-ray analysis, based on 2172 independent reflections collected with an automated diffractometer, has been completed. The molecular stereochemistry is similar to that in π-$C_5H_5Mo(CO)_3C_2H_5$, but the molybdenum–perfluoropropyl distance is 2.288 A, as compared to a metal–carbon distance of 2.397 A in the molybdenum ethyl. This structure thus provides the first direct measurement of the contraction in metal–carbon bond length which occurs on fluorinating a transition metal alkyl. The factors stabilizing transition metal fluoroalkyls are discussed, and a table of metal–alkyl and metal–fluoroalkyl bond lengths is included.

Both chemical observations and physical measurements[1,2] indicate that the metal–carbon bond strength of transition metal perfluoroalkyls is greater than that of the corresponding nonfluorinated alkyls. While this may, in part, be due to d-orbital contraction on the metal (caused by the high electronegativity of the perfluoroalkyl group), the decrease in the C–F stretching

---

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

(2) (a) F. G. A. Stone, *Endeavour*, **25**, 33 (1966); (b) R. B. King and M. B. Bionette, *J. Organometal. Chem.* (Amsterdam) **2**, 15 (1964).

frequency of $CF_3Mn(CO)_5$ relative to that in CF_3X (X = Cl, Br, I) has been interpreted[3] in terms of back-donation from the molybdenum d orbitals to the C–F antibonding orbitals (*i.e.*, $d\pi$–σ^* bonding). However, both d-orbital contraction *and* $d\pi$–σ^* back-donation will tend to strengthen (and, presumably, shorten) a transition metal–perfluoroalkyl bond. Recent crystallographic studies[4–8] have provided accurate metal–carbon distances for certain transition metal fluoroalkyls, but it is difficult to estimate the corresponding distances in analogous nonfluorinated alkyls since the use of Pauling's covalent radii[9] may be invalid for certain classes of organo-transition metal compounds.[10,11] Furthermore, not one of the fluoroalkyls which has been studied (π-$C_5H_5Rh(CO)(C_2F_5)I$,[4,6] *cis*-$[(HCF_2CF_2)_2Fe(CO)_4]$,[7] and $K_3[Co(CN)_5CF_2CF_2H]$[5]) has an alkyl analog of sufficient stability to enable its molecular parameters to be determined by crystallographic procedures. However, interatomic distances for the molybdenum–ethyl complex, π-$C_5H_5Mo(CO)_3C_2H_5$, *have* been accurately determined[12,13] and the molybdenum–ethyl linkage found to be 2.397 ± 0.019 A in length.[13] This value is consistent with that predicted from the Mo–Mo bond length of 3.222 A in $[\pi\text{-}C_5H_5Mo(CO)_3]_2$[14] (whence $d_{Mo-C} = r_{Mo} + r_{C(sp^3)} = 2.38$ A) and is in good agreement with the Mo–C single-bond distance of 2.39 A proposed by Cotton and Wing[15,16] following their structural studies on *cis*-diethylenetriaminemolybdenum tricarbonyl. In order to make a direct comparison of metal–alkyl and metal–fluoroalkyl bond distances, we decided to examine a perfluoroalkyl complex of molybdenum having a stereochemistry similar to that of π-$C_5H_5Mo(CO)_3C_2H_5$. The perfluoromethyl analog [π-$C_5H_5Mo(CO)_3CF_3$] is expected to show the greatest metal–carbon contraction,[17] but crystals of this complex were found to be X-ray sensitive. Consequently, a sample of the more stable perfluoro*propyl* complex, π-$C_5H_5Mo(CO)_3C_3F_7$, was subjected to an X-ray crystallographic analysis. A preliminary account of this work has been reported.[19]

Collection and Treatment of X-Ray Data.—Bright yellow crystals of π-$C_5H_5Mo(CO)_3C_3F_7$ were supplied by Dr. R. B. King.[2b] The complex is air-stable but slowly darkens in an X-ray beam due to surface decomposition. However, no significant loss in intensity is detectable with a scintillation counter after 4 weeks of data collection. Optical examination and a reciprocal lattice symmetry of C_{2h} indicate that the crystals belong to the monoclinic system. Unit-cell parameters, from aluminum-calibrated ($a_{Al} = 4.049$ A) Weissenberg and precession photographs taken with Cu Kα radiation ($\bar{\lambda}$ 1.5418 A) are $a = 8.301 \pm 0.007$ A, $b = 15.240 \pm 0.014$ A, $c = 11.249 \pm 0.012$ A, and $\beta = 106° 15' \pm 05'$. The unit-cell volume is 1366 A^3. The observed density, obtained by flotation in aqueous zinc iodide solution (ρ_{obsd} 1.98 ± 0.04 g cm^{-3}), is in satisfactory agreement with that calculated for $M = 414$ and $Z = 4$ (ρ_{calcd} 2.01 g cm^{-3}). The observed systematic absences, $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, lead to a unique assignment of the space group as $P2_1/c$ (No. 14).

The crystal used in the analysis was approximately spherical in shape, with a radius of 0.09 mm. Since the absorption coefficient (μ) is 10.47 cm^{-1}, $\mu R = 0.09$ and the variation of transmission factor with θ is negligible.[20] No correction was made for absorption.

The analysis was begun using photographic data; six zones of Weissenberg data ($0kl$–$5kl$) and five zones of precession data ($hk0$, $h0l$–$h3l$) were collected on Ilford Industrial G, B, and C X-ray films using Mo Kα radiation ($\bar{\lambda}$ 0.7107 A). The intensities derived from these eleven zones were corrected for Lorentz and polarization effects and scaled together by a least-squares analysis of common reflections; the resulting 1195 independent $k|F|^2$ were placed on an absolute scale by means of a Wilson plot. After the location of all atoms using this visually-estimated data, a Buerger automated diffractometer became available. In the interest of greater accuracy, the zones $0kl$–$9kl$, representing complete data to $\sin\theta = 0.45$, were collected with the diffractometer (using the equiinclination Weissenberg technique) and the analysis continued using this new counter data. The measurement of diffraction peaks was performed using a background, ω scan, background counting sequence. The angle scanned (ω) is given by $\omega = (2.0 + 1.0/L)°$, where $1/L$ is the Lorentz factor. The scan rate was 2°/min and each background was counted for one-half the time of the appropriate scan. For a reflection having an integrated count C, and backgrounds B_1 and B_2, the following weighting scheme was used

$$\sigma = 0.1[(B_1 + B_2) + C + 2|B_1 - B_2|]$$

Data were corrected for Lorentz and polarization effects and placed on an absolute scale by comparison with the photographically measured data. The total number of electrons per unit cell, $F(000) = 800$.

Solution and Refinement of the Structure.—The position of the molybdenum atom [$X = 0.215$, $Y = 0.105$, $Z = -0.220$] was determined from a three-di-

---

(3) F. A. Cotton and J. A. McCleverty, *J. Organometal. Chem.* (Amsterdam), **4**, 490 (1965).

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

(5) R. Mason and D. R. Russell, *ibid.*, 182 (1965).

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

(7) M. R. Churchill, *ibid.*, **6**, 185 (1967).

(8) M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 125 (1967).

(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(10) M. J. Bennett and R. Mason, *Nature*, **205**, 760 (1965).

(11) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965); see footnote 21 for comments on covalent radii.

(12) M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

(13) M. J. Bennett, Ph.D. Thesis, Sheffield University, England, 1965.

(14) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **37**, 809 (1957).

(15) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965).

(16) It should be emphasized that this value is derived for an octahedral d^6 Mo(0) complex; since covalent radii may be dependent both on oxidation state and stereochemistry,[10] this comparison may not be strictly valid.

(17) Since: (i) the trifluoromethyl group is the most electronegative of the fluoroalkyl ligands and will therefore cause the greatest amount of d-orbital contraction on the metal, and (ii) the presence of three fluorine atoms on the α-carbon atom will lead to a greater lowering of the energy of the α-carbon σ^* orbitals than will be the case with such perfluoroalkyls as $-CF_2CF_3$, etc. (the electronegativity of a $-CF_3$ group being roughly equivalent to that of –Cl).[18]

(18) J. J. Lagowski, *Quart. Rev.* (London), **13**, 233 (1959).

(19) M. R. Churchill and J. P. Fennessey, *Chem. Commun.*, 695 (1966).

(20) "International Tables for X-Ray Crystallography," Vol. 2, The Kynoch Press, Birmingham, England, 1959, p 302.

mensional Patterson synthesis[21] which had been sharpened so that the average intensity was independent of sin θ, and which had the origin peak reduced to the height of a single Mo···Mo interaction.[22]

The initial analysis, based on photographic data, led to the approximate coordinates of the 21 carbon, oxygen, and fluorine atoms after a series of the customary structure-factor[23]–Fourier–structure-factor sequences, additional atoms being located with each successive Fourier synthesis. The analysis was then continued using the previous coordinates and complete three-dimensional counter data. Refinement of positional and isotropic thermal parameters converted to a discrepancy index $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.16$. The extremely high thermal parameters of the terminal CF_3 group and some of the other atoms prompted a difference Fourier, which indicated that the motions of some atoms (in particular, the fluorines and oxygens) were best described in terms of anisotropic thermal parameters, T, given by

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

Owing to a restriction in the number of parameters that may simultaneously be varied, the anisotropic refinement was carried out in stages: first, the molybdenum and perfluoropropyl atoms were refined, then the molybdenum, carbonyl, and π-cyclopentadienyl atoms were refined; this process being repeated four times. Finally, all positional parameters were refined while the anisotropic thermal parameters were held constant. The final suggested shifts are all less than one-twentieth of an estimated standard deviation. The resulting value for the discrepancy index is $R_F = 0.103$ for 2172 independent reflections.

Contributions from hydrogen atoms were not included in the structure factor calculations; it is interesting to note that, while it cannot be claimed that the hydrogen atoms were "found," a positive residual of electron density is present at each of the calculated hydrogen positions.

During the analysis, the scattering factors for neutral fluorine, oxygen, and carbon were used;[24a] the Thomas–Fermi–Dirac values for neutral molybdenum[24b] were corrected for the real part of the dispersion[24c] ($\Delta f' = -1.7$ electrons) but not for the imaginary component ($\Delta f'' = +0.9$ electron). The residual minimized during the analysis was $\Sigma w||F_o|^2 - |F_c|^2|^2$. Final atomic coordinates[25] are shown in Table I; anisotropic thermal parameters[25] are collected in Table II. Observed and calculated structure factors are given in Table III.

TABLE I

FINAL ATOMIC POSITIONAL PARAMETERS FOR π-$C_5H_5Mo(CO)_3C_3F_7$[a,b]

Atom	x/a	y/b	z/c
Mo	0.21381 (10)	0.39365 (6)	0.28094 (8)
F_1	0.4962 (8)	0.3467 (4)	0.5097 (6)
F_2	0.3070 (8)	0.2454 (4)	0.4675 (6)
F_3	0.4361 (10)	0.1951 (6)	0.2744 (7)
F_4	0.6237 (10)	0.2918 (6)	0.3349 (10)
F_5	0.5349 (13)	0.1213 (7)	0.4950 (12)
F_6	0.7241 (10)	0.1350 (6)	0.4168 (8)
F_7	0.7079 (14)	0.2139 (8)	0.5570 (10)
O_1	0.5516 (9)	0.4674 (6)	0.2537 (8)
O_2	0.1418 (10)	0.4285 (6)	−0.0009 (6)
O_3	0.0710 (10)	0.2157 (5)	0.1604 (9)
C_1	0.3953 (11)	0.3009 (6)	0.4124 (9)
C_2	0.5156 (13)	0.2426 (8)	0.3727 (10)
C_3	0.6207 (16)	0.1790 (10)	0.4600 (14)
C_4	0.4353 (11)	0.4379 (6)	0.2637 (9)
C_5	0.1646 (13)	0.4137 (7)	0.0993 (9)
C_6	0.1354 (13)	0.2778 (7)	0.2050 (10)
C_7	0.0826 (16)	0.5230 (8)	0.3038 (12)
C_8	−0.0396 (13)	0.4558 (9)	0.2826 (13)
C_9	0.0127 (13)	0.3955 (9)	0.3905 (11)
C_{10}	0.1594 (14)	0.4302 (8)	0.4708 (10)
C_{11}	0.2032 (14)	0.5072 (8)	0.4195 (10)
H_7	0.0809	0.5771	0.2415
H_8	−0.1477	0.4495	0.2030
H_9	−0.0516	0.3365	0.4047
H_{10}	0.2272	0.4011	0.5580
H_{11}	0.3110	0.5478	0.4608

[a] Numbers in parentheses are the estimated standard deviations of the coordinates and are right-adjusted to the last significant digit of the preceding number. [b] Hydrogen atoms are in calculated positions, assuming a C–H bond length of 1.08 A and normal geometry about the π-cyclopentadienyl carbon atoms.

The Molecular Structure.—Figure 1 pictures the molecule projected down a and shows the system for numbering the atoms; interatomic distances are shown in Table IV and bond angles are in Table V.[26]

The molybdenum is bonded to a π-cyclopentadienyl, three carbonyls, and a perfluoropropyl ligand. If the π-cyclopentadienyl group is considered as a formally tridentate, six-electron donor (*i.e.*, π-$C_5H_5^-$) and the perfluoropropyl group as a $C_3F_7^-$ ligand, the central metal may be regarded as a seven-coordinate d^4 Mo(II) ion having an inert gas (Xe) configuration. Complexes having a molybdenum atom present in a similar environment include: $[\pi$-$C_5H_5Mo(CO)_3]_2$,[14] π-$C_5H_5Mo(CO)_2C_2H_5$,[12,13] and $[\pi$-$C_5H_5Mo(CO)_2]_2\{P(CH_3)_2\}H$.[11] The geometric features of the molybdenum coordination do not conform exactly to any simple steric arrangement. Bennett and Mason[12] compare the molybdenum coordination in π-$C_5H_5Mo(CO)_3C_2H_5$ to that believed present in $[NbOF_6^{3-}]$,[27] but Baird and Dahl[28] interpret a similar metal coordination for $[\pi$-$C_5H_5Mo(CO)_3]_2$ in terms of an $[NbF_7^{2-}]$[29] structure. Suffice to say that an irregular structure may often be interpreted

---

(21) Patterson and Fourier syntheses were calculated 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.

(22) Coefficients for this Patterson synthesis were calculated using an updated version of PASHCO, an IBM 7090 program by B. R. Penfold.

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

(24) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 211; (c) p 216.

(25) Estimated standard deviations (esd's) are derived from the appropriate diagonal elements (a_{jj} of the matrix inverse to the normal equation matrix; the esd of the jth parameter is given by $\sigma(j) = [a_{jj}\Sigma\omega\Delta^2/(m - n)]^{1/2}$, where m is the number of observations, n the number of variables, and $\Sigma\omega\Delta^2$ the summed, weighted, discrepancy between observed and calculated structure factors.

(26) Distances, angles, and corrected bond lengths were calculated using ORFFE, a Fortran crystallographic function and error program by W. R. Busing, K. O. Martin, and H. A. Levy (ORNL-TM-306).

(27) M. B. Williams and J. L. Hoard, *J. Am. Chem. Soc.*, **64**, 1139 (1942).

(28) H. W. Baird and L. F. Dahl, referred to in footnote 36 of ref 11.

(29) J. L. Hoard, *J. Am. Chem. Soc.*, **61**, 1252 (1939).

Table II

Final Anisotropic Thermal Parameters for π-$C_5H_5Mo(CO)_3C_3F_7$ ($\times 10^4$)[a]

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	B_{av}
Mo	162.2 (1.1)	40.0 (0.3)	86.5 (0.7)	−1.3 (0.9)	43.8 (0.7)	−7.9 (0.7)	3.959
F_1	273 (12)	80 (4)	125 (7)	−5 (6)	−11 (8)	−7 (4)	6.73
F_2	288 (12)	63 (3)	139 (6)	14 (5)	98 (8)	22 (3)	6.56
F_3	461 (22)	122 (6)	175 (10)	144 (10)	−2 (12)	−49 (7)	10.42
F_4	465 (22)	108 (6)	478 (21)	83 (10)	364 (19)	104 (10)	14.72
F_5	627 (32)	133 (8)	443 (24)	149 (15)	267 (24)	175 (13)	16.30
F_6	467 (21)	127 (7)	276 (14)	147 (11)	155 (15)	55 (8)	12.17
F_7	553 (29)	167 (11)	268 (17)	153 (16)	−171 (20)	−33 (11)	14.01
O_1	227 (15)	88 (6)	236 (13)	−23 (8)	119 (12)	34 (7)	8.31
O_2	418 (21)	100 (7)	84 (7)	78 (9)	58 (11)	15 (6)	7.93
O_3	348 (21)	63 (5)	236 (14)	−42 (9)	69 (14)	−45 (7)	8.58
C_1	219 (18)	46 (5)	99 (10)	1 (8)	57 (12)	4 (6)	4.83
C_2	237 (20)	68 (7)	120 (13)	13 (10)	60 (14)	5 (8)	5.97
C_3	278 (28)	87 (10)	179 (19)	70 (14)	24 (20)	30 (12)	7.84
C_4	198 (18)	52 (6)	106 (11)	26 (9)	36 (12)	20 (7)	4.94
C_5	306 (24)	58 (8)	109 (12)	42 (10)	44 (14)	−5 (7)	6.08
C_6	226 (20)	60 (7)	139 (14)	−5 (10)	72 (14)	−13 (8)	5.93
C_7	392 (32)	50 (6)	188 (19)	40 (13)	136 (21)	−14 (9)	7.79
C_8	221 (22)	86 (9)	208 (20)	30 (12)	99 (18)	−50 (11)	7.78
C_9	298 (23)	74 (7)	170 (15)	6 (14)	145 (16)	−10 [12]	7.47
C_{10}	297 (25)	79 (8)	125 (13)	22 (12)	117 (16)	−16 (8)	6.90
C_{11}	296 (25)	67 (7)	121 (13)	3 (11)	84 (16)	−37 (8)	6.46

[a] B_{av} is an approximate "equivalent isotropic thermal parameter," obtained by averaging $4b_{11}/a^{*2}$, $4b_{22}/b^{*2}$, and $4b_{33}/c^{*2}$.

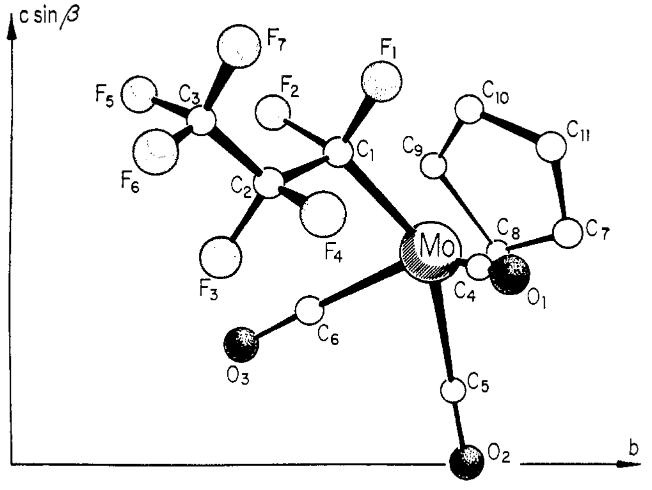

Figure 1.—π-$C_5H_5Mo(CO)_3C_3F_7$ stereochemistry and numbering system for atoms. The molecule is shown projected on 100.

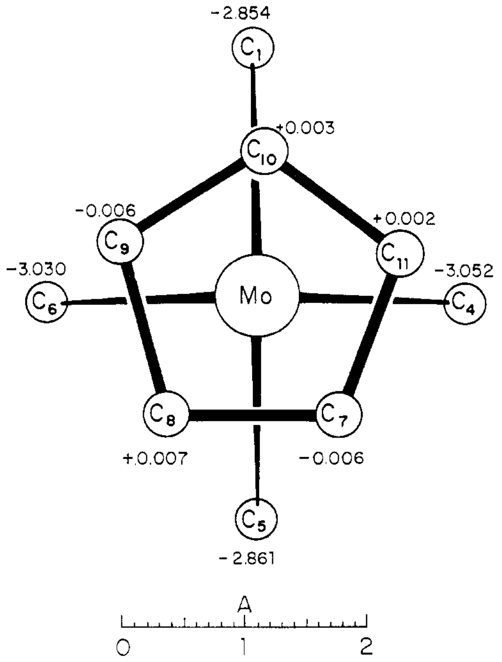

Figure 2.—The molybdenum coordination sphere in π-$C_5H_5Mo(CO)_3C_3F_7$. Numbers represent distances (A) of the atoms from the least-squares plane through the π-cyclopentadienyl ligand.

as a distorted form of a number of more regular shapes; the inability to fix uniquely three points of attachment from the molybdenum atom to the π-cyclopentadienyl ligand can do nothing but enhance this difficulty. The arrangement of ligands around the molybdenum atom in π-$C_5H_5Mo(CO)_3C_3F_7$ can be seen in Figure 2. There is an approximate mirror plane passing through C_1, C_{10}, Mo, and the center of the C_7–C_8 bond. Table VI compares angles around the molybdenum atom in this and analogous[11–14] complexes. All these complexes have the substituent, R, almost directly beneath one carbon atom of the π-cyclopentadienyl ring. (It would be interesting to learn whether the relative orientation of the π-C_5H_5 group and the other four ligands could be altered by introducing appropriate electron-withdrawing or -attracting substituents into the five-membered ring; a scheme of this type has been proposed for simple arenechromium tricarbonyl species,[30–33] and the drawing of π-$C_5H_5Nb(CO)_4$ by Doedens and Dahl[11] indicates a 45° change in orientation of the CO groups relative to their positions in π-C_5H_5-$Mo(CO)_3R$ systems.)

The π-Cyclopentadienyl Ligand.—The π-cyclopentadienyl group is planar (root mean square deviation = 0.005 A), the observed carbon–carbon bond lengths

---

(30) O. L. Carter, A. T. McPhail, and G. A. Sim, *Chem. Commun.*, 212 (1966).

(31) K. S. Muir, G. Ferguson, and G. A. Sim, *ibid.*, 465 (1966).

(32) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1313 (1965).

(33) M. F. Bailey and L. F. Dahl, *ibid.*, **4**, 1298 (1965).

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR π-$C_5H_5Mo(CO)_3C_3F_7$ (IN ELECTRONS)[a]

H	K	FO	FC
***** L= 00 *****			
0	0	*	800
2	0	-47	-48
3	0	-108	-106
4	0	61	58
5	0	57	51
6	0	-15	-4
7	0	-35	-33
8	0	-12	-8
9	0	18	15
2	1	-107	-106
3	1	16	17
4	1	47	47
5	1	-7	-12
6	1	-25	-25
7	1	0	-3
8	1	12	13
9	1	8	7
2	2	-12	-14
3	2	-63	-63
4	2	18	19
5	2	35	35
6	2	0	-3
7	2	-6	-5
8	2	-7	-8
9	2	5	7
1	3	-124	-127
2	3	-71	-70
3	3	87	83
4	3	91	91
5	3	-7	-4
6	3	-48	-49
7	3	4	0
8	3	24	23
9	3	8	6
0	4	-61	-61
1	4	-16	-16
2	4	78	80
3	4	66	66
4	4	-54	-52
5	4	-59	-55
6	4	7	5
7	4	28	30
8	4	5	1
1	5	-32	-34
2	5	0	3
3	5	-3	-1
4	5	-13	-14
5	5	23	19
6	5	19	16
7	5	0	-1
8	5	-6	-4
0	6	-104	-102
1	6	-53	-51
2	6	68	66
3	6	41	40
4	6	-26	-24
5	6	-22	-21
6	6	-10	-4
7	6	14	12
8	6	5	6
1	7	120	121
2	7	53	50
3	7	-54	-55
4	7	-33	-31
5	7	18	17
6	7	42	42
7	7	4	4
8	7	-19	-20
0	8	49	46
1	8	31	12
2	8	-49	-49
3	8	-24	-22
4	8	54	52
5	8	9	8
6	8	2	1
7	8	-17	-18
8	8	-2	-2
1	9	42	40
2	9	28	26
3	9	14	13
4	9	-34	-34
5	9	19	19
6	9	0	4
7	9	-13	9
0	10	66	64
1	10	33	27
2	10	-52	-51
3	10	-24	-24
4	10	12	11
5	10	40	39
6	10	-9	-6
7	10	-23	-22
1	11	-31	-32
2	11	-26	-26
3	11	29	31
5	11	-19	-18
6	11	-29	-26
7	11	18	5
0	12	-19	-12
1	12	-10	0
2	12	-3	-2
3	12	-9	-2
4	12	0	-3
5	12	-4	-3
6	12	13	5
1	13	-28	-29
2	13	-9	-5
3	13	27	28
4	13	7	10
5	13	0	-4
6	13	-15	-13
0	14	-37	-36
1	14	-3	-5
2	14	29	29
3	14	10	13
4	14	-14	-14
5	14	-19	-19
1	15	16	18
2	15	13	2
3	15	-17	-15
4	15	-10	-10
0	16	-16	-8
1	16	-10	-8
2	16	5	3
3	16	0	7
1	17	21	20
2	17	10	12
***** L= 01 *****			
2	1	78	77
-2	1	-67	-69
3	1	-86	-86
-3	1	78	77
4	1	-31	-33
-4	1	75	77
5	1	26	27
-5	1	5	5
6	1	39	37
-6	1	-39	-41
7	1	-12	-12
-7	1	-10	-8
8	1	-19	-19
-8	1	20	21
-9	1	10	12
1	2	-18	-21
2	2	-53	-56
-2	2	131	134
3	2	-44	-46
-3	2	80	78
4	2	51	51
-4	2	-34	-36
5	2	50	49
-5	2	-92	-94
6	2	-14	-15
-6	2	-6	-3
7	2	-28	-29
-7	2	32	35
8	2	-7	-3
-8	2	7	12
-9	2	-16	-17
0	3	31	29
1	3	-34	-35
-1	3	33	36
2	3	-63	-62
-2	3	-17	-13
3	3	63	63
-3	3	-37	-36
4	3	23	21
-4	3	-36	-36
5	3	-13	-12
-5	3	12	13
6	3	-20	-21
-6	3	10	12
7	3	8	5
-7	3	5	9
8	3	10	6
-8	3	-9	-11
-9	3	0	-2
0	4	114	116

---

[a] The table gives h, k, F_o, and F_c in blocks of constant l.

TABLE IV

INTERATOMIC DISTANCES IN π-$C_5H_5Mo(CO)_3C_3F_7$[a]

(a) Bond Distances

	Distance, A			Distance, A	
Atoms	Uncor	Cor[b]	Atoms	Uncor	Cor[b]
Mo–C_1	2.282	2.288	C_2–F_3	1.331	1.397
Mo–C_4	2.018	2.023	C_2–F_4	1.326	1.431
Mo–C_5	1.992	2.010	C_3–F_5	1.263	1.370
Mo–C_6	1.990	2.003	C_3–F_6	1.287	1.345
Mo–C_7	2.301	2.331	C_3–F_7	1.247	1.369
Mo–C_8	2.312	2.342	C_7–C_8	1.414	*c*
Mo–C_9	2.336	2.360	C_8–C_9	1.487	*c*
Mo–C_{10}	2.370	2.390	C_9–C_{10}	1.401	*c*
Mo–C_{11}	2.348	2.367	C_{10}–C_{11}	1.400	*c*
C_1–C_2	1.495	1.507	C_{11}–C_7	1.423	*c*
C_2–C_3	1.478	1.513	C_4–O_1	1.098	1.162
C_1–F_1	1.369	1.405	C_5–O_2	1.113	1.152
C_1–F_2	1.375	1.394	C_6–O_3	1.133	1.188

(b) Distances from Molybdenum Atom (Uncorrected)

Atoms	Distance, A	Atoms	Distance, A
Mo···F_1	3.042	Mo···O_1	3.115
Mo···F_2	3.033	Mo···O_2	3.104
Mo···F_3	3.555	Mo···O_3	3.115
Mo···F_4	3.633	Mo···C_2	3.346

(c) Contacts within the Perfluoropropyl Group (Uncorrected)

Atoms	Dist, A	Atoms	Dist, A	Atoms	Dist, A
F_1···F_2	2.159	F_1···C_3	2.870	F_3···F_7	3.356
F_3···F_4	2.112	F_2···F_3	2.785	F_4···F_5	3.359
F_5···F_6	2.015	F_2···F_4	3.439	F_4···F_6	2.611
F_6···F_7	2.017	F_2···C_3	2.816	F_4···F_7	2.676
F_7···F_5	1.996	F_3···F_5	2.638	F_1···F_7	2.636
F_1···F_3	3.443	F_3···F_6	2.641	F_2···F_5	2.631
F_1···F_4	2.618				

(d) Contacts from π-Cyclopentadienyl Ring to Other Ligands (Uncorrected)

Atoms	Dist, A	Atoms	Dist, A	Atoms	Dist, A
C_7···C_4	3.347	C_9···C_1	3.434	C_{10}···F_2	3.076
C_7···C_5	3.067	C_9···F_2	3.282	C_{11}···C_1	3.537
C_8···C_5	3.081	C_{10}···C_1	2.979	C_{11}···F_1	3.398
C_8···C_6	3.308	C_{10}···F_1	2.990	C_{11}···C_4	3.130
C_9···C_6	3.130				

(e) Contacts Involving Carbonyl Groups and Perfluoropropyl Ligand (Uncorrected)

Atoms	Dist, A	Atoms	Dist, A	Atoms	Dist, A
C_4···C_5	2.506	C_4···C_2	3.217	C_6···C_2	3.236
C_5···C_6	2.435	C_4···F_4	2.710	C_6···F_3	2.709
C_6···C_4	3.416	C_5···C_1	3.906	O_1···F_4	2.837
C_4···C_1	2.754	C_6···C_1	2.721	O_3···F_3	2.959
C_4···F_1	3.011	C_6···F_2	2.939		

[a] Average estimated standard deviations on the uncorrected interatomic distances, as obtained from $\sigma(x)$, $\sigma(y)$, and $\sigma(z)$ in Table I, are: σ(Mo–F) = 0.007 A, σ(Mo–O) = 0.005 A, σ(Mo–C) = 0.009 A, σ(F–F) = 0.010 A, σ(F–O) = 0.009 A, σ(F–C) = 0.011 A, σ(O–O) = 0.006 A, σ(O–C) = 0.010 A, σ(C–C) = 0.013 A. The large difference between some corrected and uncorrected bond lengths makes it extremely difficult to set any standard deviations on the corrected lengths. Where little alteration has occurred, one may anticipate that the σ's for the uncorrected bond lengths may apply; otherwise, internal consistency between chemically equivalent distances is judged to be the best criterion. [b] The function used[26] calculates the interatomic distance averaged over the thermal motion, assuming that the second atom rides over the first. The function is $D_{\text{cor}} = D_0 + (\overline{\Gamma_2^2} - \overline{\xi_2^2} - \overline{\Gamma_1^2} + \overline{\xi_1^2})/2D_0$ where D_0 is the uncorrected distance, $\overline{\Gamma_i^2}$ is the mean square radial thermal displacement of atom i, and $\overline{\xi_i^2}$ is the mean square component of displacement of atom i in the direction defined by the interatomic vector. [c] The correction applied is not considered a reasonable model for these interatomic distances.

TABLE V

BOND ANGLES IN $C_5H_5Mo(CO)_3C_3F_7$

Atoms	Angle, deg	Atoms	Angle, deg
(a) Around Molybdenum Atom			
C_1–Mo–C_4	79.4	C_9–Mo–C_{10}	34.6
C_1–Mo–C_5	131.9	C_{10}–Mo–C_{11}	34.5
C_1–Mo–C_6	78.8	C_{11}–Mo–C_7	35.6
C_4–Mo–C_5	77.3	C_1–Mo–c.o.g.[a]	110.1
C_5–Mo–C_6	75.4	C_4–Mo–c.o.g.[a]	121.1
C_6–Mo–C_4	116.9	C_5–Mo–c.o.g.[a]	118.0
C_7–Mo–C_8	35.7	C_6–Mo–c.o.g.[a]	122.0
C_8–Mo–C_9	37.3		
(b) Carbonyl Groups			
Mo–C_4–O_1	175.3	Mo–C_6–O_3	171.3
Mo–C_5–O_2	176.6		
(c) π-Cyclopentadienyl Ring			
C_7–C_8–C_9	106.1	C_{10}–C_{11}–C_7	108.7
C_8–C_9–C_{10}	107.2	C_{11}–C_7–C_8	108.7
C_9–C_{10}–C_{11}	109.3		
(d) Perfluoropropyl Group			
Mo–C_1–C_2	123.3	F_3–C_2–F_4	105.3
Mo–C_1–F_1	110.3	F_3–C_2–C_3	105.0
Mo–C_1–F_2	109.5	F_4–C_2–C_3	104.9
F_1–C_1–F_2	103.8	C_2–C_3–F_5	112.6
F_1–C_1–C_2	103.4	C_2–C_3–F_6	115.0
F_2–C_1–C_2	104.8	C_2–C_3–F_7	113.1
C_1–C_2–C_3	120.6	F_5–C_3–F_6	104.4
C_1–C_2–F_3	110.7	F_6–C_3–F_7	105.5
C_1–C_2–F_4	109.2	F_7–C_3–F_5	105.3

[a] c.o.g. represents the center of gravity of the π-cyclopentadienyl ligand.

TABLE VI

A COMPARISON OF THE MOLYBDENUM ENVIRONMENT IN SOME SEVEN-COORDINATE COMPLEXES, π-$C_5H_5Mo(CO)_3R$[a]

	I R = C_3F_7	II R = C_2H_5	III R = $(OC)_3Mo$-(π-C_5H_5)	IV R = H[a]
R–Mo–CO (*trans*)	131.9°	131.8°	...	...
R–Mo–CO (*cis*)	79.1°	73.2°	71.6°	...
OC–Mo–CO (*trans*)	116.9°	105.7°	...	112.5°
OC–Mo–CO (*cis*)	76.4°	78.2°	78.1°	77.6°
c.o.g.–Mo–R[b]	110.1°	110.4°	117.6°	...
$\phi(\pi$-$C_5H_5/(CO)_3)$[c]	5.8°	~9.2°	13°	6°
c.o.g.–Mo,[b] A	1.994	~2.04	...	2.00

[a] IV is $[\pi$-$C_5H_5Mo(CO)_2]_2\{P(CH_3)_2\}H$, where a bridging dimethylphosphide ligand occupies a carbonyl site; all measurements are adjusted to allow for this. [b] c.o.g. refers to the center of gravity of the π-cyclopentadienyl ligand. [c] This is the dihedral angle between the π-cyclopentadienyl ligand and the carbon atoms of the carbonyl group.

ranging from 1.400 to 1.487 A (average 1.423 A); the nature of the variation is not in agreement with a simple perturbation removing the degeneracy of the e_1 molecular orbitals of the π-cyclopentadienyl ring[34] and may result from the inability to correct the carbon–carbon distances for the librational motion of the π-cyclopentadienyl ligand. The corrected molybdenum–carbon bond lengths range from 2.331 to 2.390 A, and the variation is symmetrical with respect to the pseudo-mirror plane of the molybdenum coordination sphere. The largest value, 2.390 A, is for the Mo–C_{10} bond, which lies immediately above the perfluoropropyl

(34) M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature*, **201**, 1318 (1964).

group. A survey of the other π-$C_5H_5MoL_4$ molecules which have been crystallographically examined (see Table VII) shows this "tilting" of the π-cyclopentadienyl ring to be a general feature in this class of compounds.

TABLE VII
MOLYBDENUM–π-CYCLOPENTADIENYL DISTANCES (A) IN SOME SEVEN-COORDINATE COMPLEXES[a]

Bond[b]	I[c]	II	III	IV	
Mo–C_{10}	2.390 (2.370)	2.405	2.378	2.389	2.369
Mo–C_{11}	2.367 (2.348)	2.363	2.356	2.356	2.367
Mo–C_7	2.331 (2.301)	2.369	2.320	2.263	2.275
Mo–C_8	2.342 (2.312)	2.369	2.302	2.292	2.276
Mo–C_9	2.350 (2.336)	2.363	2.368	2.344	2.359

[a] I, π-$C_5H_5Mo(CO)_3C_3F_7$; II, π-$C_5H_5Mo(CO)_3C_2H_5$; III, $[\pi$-$C_5H_5Mo(CO)_3]_2$; IV, $[\pi$-$C_5H_5Mo(CO)_2]_2\{P(CH_3)_2\}H$. [b] Metal–carbon distances are given cyclically, the bond directly above the substituent R being given first. [c] Both corrected and uncorrected (in parentheses) values for the molybdenum–carbon distances of π-$C_5H_5Mo(CO)_3C_3F_7$ are given.

The Perfluoropropyl Group.—The molybdenum–perfluoropropyl linkage, Mo–C_1, is 2.288 A in length;[35] other bonds involving the σ-carbon atom (C_1) are normal,[36] C_1–F_1 = 1.405 A, C_1–F_2 = 1.394 A, C_1–C_2 = 1.507 A. The molybdenum–perfluoropropyl linkage is thus ~0.107 A (*i.e.*, some eight standard deviations) shorter than Bennett's final value[13] of 2.397 ± 0.019 A for the molybdenum–ethyl bond in π-$C_5H_5Mo(CO)_3C_2H_5$. According to the molybdenum–carbon bond-order chart of Cotton and Wing,[15] the Mo–C_3F_7 linkage has a bond order of ~1.15–1.17. The contraction in metal–carbon bond length which results on fluorinating a transition metal alkyl can be divided into two components, the first due to strengthened σ bonding (caused by contraction of the metal d orbitals due to the high electronegativity[18] of the perfluoroalkyl group) and the second due to π bonding (back-donation from the metal d_π orbitals[37] to the σ^* orbitals of the C–F bonds on the α-carbon atom). There appears to be no simple way to separate the *relative* contributions of these effects on the basis of the present data. However, one would expect the contraction due to d_π–σ^* back-donation to be dependent on the relative energies of the d_π and σ^* orbitals.[39] Since the energy of the σ^* C–F orbitals is likely to be high, one can anticipate that the energy difference between the C–F σ^* and metal 4d orbitals will probably be smaller than that between the C–F σ^* and metal 3d orbitals. A consideration of the metal–carbon contractions for first- and second-row transition metals may then be indicative of d_π–σ^* back-donation, provided that the contribution from d-orbital contraction remains constant. (There seems, however, to be no way of knowing whether or not this proviso is obeyed.) Although no *precise* comparison of bond lengths in first-row transition metal alkyls and perfluoroalkyls is available, perhaps the most pertinent of the available comparisons is that between *cis*-$[(HCF_2CF_2)_2Fe(CO)_4]$ (Fe^{II}–CF_2 = 2.068 A av)[7] and the nonfluorinated alkyls $(OC)_2Fe(\pi$-$C_5H_4)CH_2Fe(CO)_4$ (Fe^{I}–CH_2 = 2.123 A)[40a] and π-$C_5H_5Fe(CO)_2(\sigma$-$C_5H_5)$[40b] (Fe^{II}–CH = 2.11 ± 0.02 A). These figures would seem to indicate that the contraction caused on fluorinating a first-row transition metal alkyl is probably less than the corresponding figure for a second-row metal; however, since the differing oxidation states or stereochemical environments of the cited iron compounds may cause the comparisons to be invalid, no firm conclusions can be reached. A summary of the available data on transition metal–alkyl and –fluoroalkyl bond lengths is shown in Table VIII.

The perfluoropropyl group in π-$C_5H_5Mo(CO)_3C_3F_7$ has the same approximately eclipsed configuration (see Figure 3) as has been found in previous structural investigations of fluoroalkyls.[4-8] The M–C_α–C_β angle (Mo–C_1–C_2) has a value of 123.3°, which is significantly greater than that for a regular tetrahedral stereochemistry (109° 28′). However, although this tendency is observed for other fluoroalkyls, a similar increase is noted also for nonfluorinated alkyls (120.9° for the Mo–CH_2–CH_3 angle in π-$C_5H_5Mo(CO)_3C_2H_5$[13] and ~130° for the Co–CH_2–C angle in the 5,6-dimethylbenzimidazolylcobamide (DBC) coenzyme[41]).

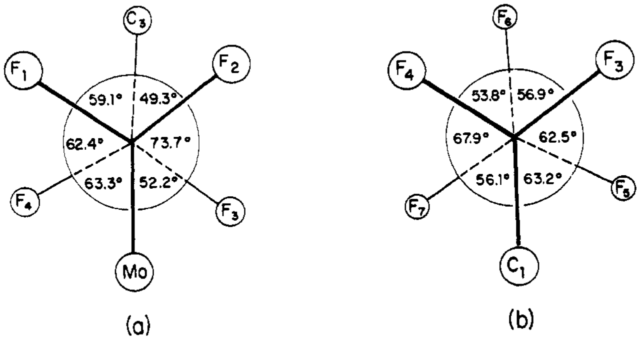

Figure 3.—The conformation of the perfluoropropyl ligand in π-$C_5H_5Mo(CO)_3C_3F_7$: (a) viewed along the C_1–C_2 bond; (b) viewed along the C_2–C_3 bond.

The F–C–F angles in the perfluoropropyl group range from 103.8 to 105.5° (average 104.8°). A similar contraction from the regular tetrahedral value has been observed in $C_6F_8Fe(CO)_3$[42-44] (106.3°), *cis*-$(HCF_2CF_2)_2Fe(CO)_4$[7] (av 104.0°), and a variety of fluorinated ethanes.[36] The carbon–carbon bond lengths in the present complex are each less than 1.54 A (average value 1.51 A); such a contraction is anticipated and

---

(35) Corrected bond lengths (see Table IV) are used where appropriate.

(36) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958; Supplement 1956–1959, Special Publication No. 18, The Chemical Society, London, 1965.

(37) The orbitals available for π bonding in π-$C_5H_5Mo(CO)_3R$ molecules are the d_{xy} and $d_{x^2-y^2}$ orbitals (see ref 38).

(38) M. Randic, *Theoret. Chim. Acta* (Berlin), **2**, 468 (1964).

(39) The C–H σ^* orbitals in nonfluorinated alkyls have the same symmetry properties as C–F σ^* orbitals, but, since the C–H orbitals are of much higher energy, the d_π–σ^*(C–H) overlap is, of course, negligible.

(40) (a) J. Meunier-Piret, P. Piret, and M. van Meerssche, *Acta Cryst.*, **19**, 85 (1965); (b) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

(41) P. G. Lenhert and D. C. Hodgkin, *Nature*, **192**, 937 (1961).

(42) M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 226 (1964).

(43) M. R. Churchill and R. Mason, in press.

(44) M. R. Churchill, Ph.D. Thesis, London, 1964.

TABLE VIII

BOND LENGTHS IN TRANSITION METAL ALKYLS AND FLUOROALKYLS

Complex	Metal coord no.	Bond	Length, A	M–C_α–C_β angle, deg	Ref
$(OC)_2Fe(\pi\text{-}C_5H_4)CH_2Fe(CO_4)$	6	Fe^{I}–CH_2	2.123 ± 0.015	95.1	40a
$\pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}C_5H_5)$	6	Fe^{II}–CH	2.11 ± 0.02	112.5 (av)	40b
$(OC)_4Fe(CF_2CF_2H)_2$	6	Fe^{II}–CF_2	2.068 ± 0.014	121.2 (av)	7
DBC coenzyme	6	Co^{III}–CH_2	2.05 ± 0.05	130	41
$[Co(CN)_5CF_2CF_2H]^{3-}$	6	Co^{III}–CF_2	1.990 ± 0.014	119.7	5
$C_5F_6Co_2(CO)_7$	5	Co^{I}–CF	1.97 ± 0.03	?	[a]
$\pi\text{-}C_5H_5Mo(CO)_3C_2H_5$	7	Mo^{II}–CH_2	2.397 ± 0.019	120.9	13
$\pi\text{-}C_5H_5Mo(CO)_3C_3F_7$	7	Mo^{II}–CF_2	2.288 ± 0.013	123.3	[b]
$\pi\text{-}C_5H_5Rh(CO)(C_2F_5)I$	6	Rh^{III}–CF_2	2.08 ± 0.03	116.4	6
$\pi\text{-}C_5H_5Re(CH_3)_2(C_6H_5CH_3)$	8	Re^{V}–CH_3	2.25 ± 0.03	. . .	[c]

[a] P. B. Hitchcock and R. Mason, *Chem. Commun.*, 503 (1966). [b] This work. [c] N. W. Allcock, *Chem. Commun.*, 177 (1965).

has been explained.[45] In saturated systems, the only fluorinated carbon–carbon bond that may be *longer* than the normal sp^3–sp^3 distance is that in $C_6F_8Fe(CO)_3$ where a $-CF_2-CF_2-$ linkage is forced into the eclipsed configuration due to a metal–"butadiene" interaction.[42–44]

The thermal parameters for the atoms constituting the terminal $-CF_3$ on the perfluoropropyl group indicate that the ligand is affected by substantial librational motions. Previous experience with perfluoromethyl groups[46–50] has indicated that they may often oscillate through a substantial angle. All bond lengths within the C_3F_7 ligand in the present molecule were therefore corrected for thermal motion (see Table IV) in such a way as to assume always that the outer atoms were rolling over the inner atoms. The success of this approximation is shown in the corrected bond lengths, which now are all in substantial agreement with literature values.

Acknowledgments.—We are grateful to Dr. R. B. King for providing the sample. This work has been generously supported by the National Science Foundation (Grant GP-4225) and the Advanced Research Projects Agency (Grant SD-88). J. P. F. acknowledges, with gratitude, the grant of an N.I.H. Predoctoral Fellowship.

---

(45) D. Peters, *J. Chem. Phys.*, **38**, 561 (1963).

(46) C. J. Spencer and W. N. Lipscomb, *Acta Cryst.*, **14**, 250 (1961).

(47) M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 365 (1963).

(48) M. Gerloch and R. Mason, *Proc. Roy. Soc.* (London), **A279**, 170 (1964).

(49) N. A. Bailey and R. Mason, *Acta Cryst.*, **21**, 652 (1966).

(50) M. R. Churchill and R. Mason, *Proc. Roy. Soc.* (London), **A292**, 61 (1966).

CONTRIBUTION FROM THE CYANAMID EUROPEAN RESEARCH INSTITUTE,
COLOGNY, GENEVA, SWITZERLAND

The Pentacarbonyls of Ruthenium and Osmium. I. Infrared Spectra and Reactivity

BY F. CALDERAZZO AND F. L'EPLATTENIER

Received February 3, 1967

The existence of pentacarbonylruthenium and pentacarbonylosmium has been confirmed and their infrared spectra in the carbonyl stretching region have been measured. The two carbonyls have two infrared-active CO stretching vibrations. This suggests a trigonal-bipyramidal configuration of symmetry D_{3h}. The reactions of the two pentacarbonyls with halogens have also been investigated. Pentacarbonylruthenium gives dihalogenotetracarbonyls of the formula $RuX_2(CO)_4$ (X = Br, I) as slightly colored solids, sublimable *in vacuo*. The infrared spectra suggest a *cis* octahedral configuration in solution for the dihalogeno complexes.

Introduction

The monomeric pentacarbonyls of ruthenium[1] and osmium,[2] $Ru(CO)_5$ and $Os(CO)_5$, have been reported in the literature some 30 years ago as volatile, colorless liquids. These compounds, however, were not fully characterized at that time, although their formulas were well established. To the best of our knowledge, no reports, since those of the early discoverers, have appeared concerning the status of these two compounds, their properties, and their structure. This was mainly due to experimental difficulties connected with the high volatility of the compounds and their instability with respect to the corresponding trimers $M_3(CO)_{12}$. It therefore appeared interesting to run some carbonylations of ruthenium and osmium and then investigate the freshly prepared solutions by infrared spectroscopy in order to detect the two penta-

---

(1) W. Manchot and W. J. Manchot, *Z. Anorg. Allgem. Chem.*, **226**, 385 (1936).

(2) W. Hieber and H. Stallmann, *Z. Elektrochem.*, **49**, 288 (1943).