from the resistance of the bridging nitrogen atoms to large deformations from a tetrahedral configuration. For compounds which contain an N–N bond, the dihedral angle defined above may provide a means of estimating the limits of deformation of the bridging system. Further structural studies on related compounds are being carried out to determine whether this approach is one of general predictive utility.

Acknowledgments.—The use of the Picker diffractometer at Northwestern University for collection of the intensity data was made possible through the generous hospitality of Professor J. A. Ibers. This work was supported by the National Science Foundation. Computation was supported in part by an NSF institutional grant to the University of California, Irvine, Calif.

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The Crystal and Molecular Structure of Trifluorosilyltetracarbonylcobalt

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Received February 24, 1969

The crystal and molecular structure of trifluorosilyltetracarbonyl cobalt, $Co(SiF_3)(CO)_4$, has been determined from three-dimensional X-ray photographic data. The structure has been solved by symbolic addition and refined by least-squares procedures. The R factor for 375 intensities above background is 7.7%. The material crystallizes in space group Cmca of the orthorhombic system with eight molecules in a cell of dimensions $a = 8.224$ (4), $b = 11.418$ (10), and $c = 18.591$ (7) Å. The Co–Si distance is very slightly shorter than that of the chloro derivative, but there are no other significant differences between the structures of the two molecules.

Introduction

In recent years there has been widespread interest in complexes of nonmetallic second-row donor elements with transition metals and, in particular, the role of $(d \rightarrow d)\ \pi$ bonding in stabilizing such complexes.[1–3] Few comparative data bearing on this question have been available. Recently Robinson and Ibers[1] determined the structure of $Cl_3SiCo(CO)_4$ by X-ray diffraction; the structure of $H_3SiCo(CO)_4$ has been studied by electron diffraction methods.[2] This paper reports the X-ray determination of the structure of a third member of this series, $(F_3Si)Co(CO)_4$. Earlier spectral work indicated that all three molecules had the same basic trigonal-bipyramidal structure, and hence it seemed likely that a comparison of bond lengths in the three compounds would be very useful in assessing the importance of $(d \rightarrow d)\ \pi$ bonding.

Experimental Section

Preparation of Crystals.—A sample of $Co(SiF_3)(CO)_4$, prepared by procedures first outlined by Chalk and Harrod,[4] was kindly supplied by Dr. A. P. Hagen. Crystals were grown by subliming the sample from a break-seal tube into a glass capillary through which the vapor was drawn by a vacuum pump; the capillary was designed so that it could be immersed in liquid nitrogen and easily sealed and removed.

Computations.—Calculations were carried out on an IBM 360/44 computer with 16 K words of core storage and twin 2315-disk drives. The programs used have been footnoted in the text.

Determination of Space Group and Unit Cell Dimensions.—The melting point of the compound is 18°, and therefore capillaries containing the crystals were stored, handled, and photographed in a refrigerated room at temperatures between 0 and 6°. Several different pale yellow transparent crystals were mounted and examined. Only one crystal form was found. Precession and Weissenberg photographs in several different orientations showed that the diffraction symmetry was mmm with extinctions $h + k$ odd for hkl, l odd for $h0l$, and h odd for $hk0$. These absences are consistent with space group Cmca or (with a permutation of axes) Aba2. After the complete set of structure factors had been collected and scaled (*vide infra*), normalized structure factors[5] were calculated using the program SHNORM.[6] The distribution of normalized structure factors was compared with the theoretical distributions for centric and acentric structures;[7] the observed distribution was very close to the theoretical centric distribution. The space group Cmca was therefore chosen for refinement.

Data for unit cell determination were taken from a crystal mounted with the [110] axis parallel to the goniometer axis. Precession photographs of the $hk0$ and hhl zones were taken with Co Kα radiation. All distances greater than 9.0 cm between equivalent spots were measured using a cathetometer which could be read to 0.002 mm. These distances together with the reflection indices were used as input to program CELGLS which uses an iterative least-squares procedure to refine the cell parameters. These were $a = 8.224$ (4), $b = 11.418$ (10), and $c = 18.591$ (7) Å.

Throughout this paper, numbers in parentheses are estimated standard deviations in the least significant digits and are usually derived from the inverse matrix in nonlinear least-squares calculations.

Film shrinkage corrections were not made because the photographs had been collected at one temperature and developed at another. The spots were not especially sharp and the magnitude

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[1] W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, **6**, 1208 (1967).

[2] A. G. Robiette, G. M. Sheldinck, R. N. F. Simpson, B. J. Aylett, and J. A. Campbell, *J. Organometal. Chem.* (Amsterdam), **14**, 279 (1968).

[3] A. P. Hagen and A. G. McDiarmid, *Inorg. Chem.*, **6**, 686 (1967).

[4] A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965).

[5] H. Hauptmann and J. Karle, "Solution of the Phase Problem. I. The Centrosymmetric Crystal," American Crystallographic Association Monograph No. 3, Pittsburgh, Pa., 1953.

[6] SHNORM is a program derived from NRC-4 (S. R. Hall and F. R. Ahmed) to calculate normalized structure factors.

[7] I. L. Karle, K. Britts, and P. Gum, *Acta Cryst.*, **17**, 496 (1964).

of shrinkage errors was judged to be comparable to the measuring errors.

The density of the crystal was not determined experimentally because of its extreme sensitivity to moist air. Eight molecules per unit cell give a calculated density of 1.95 g/cm^3, reasonably close to the value of 1.89 g/cm^3 reported for $Cl_3SiCo(CO)_4$.[1] Thus in this case m crystallographic symmetry must be imposed on the molecule and all atoms except one carbon, one oxygen, and one fluorine must occupy special positions f in the designated space group.

Determination of the Structure.—Intensity data were collected from a second crystal, also mounted about the [110] axis. In this orientation the apparent symmetry is monoclinic and by collecting the full monoclinic data set one can obtain two readings of each intensity, each one from a different layer. This provided an unusually large amount of data for determining layer-to-layer scaling factors. Five layers of integrated data were collected using Co Kα radiation and the Weissenberg equi-inclination technique. Integration was carried out both horizontally and vertically with a Nonius Weissenberg camera to give an approximately square spot. These data were indexed in the monoclinic system, and the plateaus of all integrated spots were measured using a single-beam photometer and a galvanometer calibrated to read intensities directly. Readings were corrected for film background in the vicinity of the spot. After the raw intensities had been corrected for Lorentz and polarization effects, the indices were transformed to the orthorhombic cell, and layer-to-layer scale factors were determined using a linear least-squares procedure described by Rae.[8] The scaled reflections from different layers of data showed consistently good agreement, and the data were therefore placed on the same relative scale for the remainder of the determination, with only a single scale factor refined.

All correlation ratios were equally weighted in the above procedure. Of the 900 reflections in the region $0 \leqslant (\sin \theta)/\lambda \leqslant 0.5$, 375 were observed.

At the end of the data collection the capillary mounting of the crystal was examined with the intent of measuring the crystal dimensions to correct for absorption. However there was no crystal visible in the capillary. Apparently the X-radiation had slowly vaporized it in the course of the data collection. Close examination of the data revealed some evidence that this had been occurring. In the last layer of data collected the integrated spots displayed an odd banded appearance. Correlations between reflections taken early in the data collection and those taken late suggested that the size of the crystal was decreasing. The original size of the crystal was estimated to be 0.2 mm × 0.1 mm × 0.05 mm with the largest dimension being in the direction of the rotation axis. The variation in absorption correction which a crystal of this size could show is of the order of 25%, but this would vary from layer to layer as the crystal diminished in size and also from spot to spot as the shape of the crystal changed during evaporation. To make any absorption correction under these circumstances would have involved much guesswork and very little proper measurement. Moreover, the procedure by which the layers were correlated involved taking averages of correlation factors between early data and late data, and this would tend to reduce the absorption error somewhat. Corrections for absorption and extinction were therefore not made at any stage of the refinement.

The fully correlated data set was then converted to a set of normalized structure factors[5] (hereafter called E's). The 147 largest E's were chosen for sign determination by the symbolic addition procedure.[9] A self-consistent set of signs was obtained with one symbolic sign undetermined. The two possible E maps were plotted, and one clearly revealed the entire molecule.[10] The parameters derived from this map were run through five

TABLE I

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR $F_3SiCo(CO)_4$

K	L	OBS	CALC
**** H = 0 ****			
0	4	104	149
0	6	14	13
0	8	25	25
0	10	32	38
0	12	53	50
0	14	45	42
0	16	18	16
0	18	16	15
2	1	31	29
2	2	10	11
2	3	37	38
2	4	12	9
2	5	49	49
2	6	34	33
2	7	24	25
2	8	21	19
2	9	34	30
2	10	10	10
2	11	13	15
2	12	13	14
2	13	27	30
4	0	106	137
4	1	119	156
4	2	29	30
4	3	59	59
4	4	18	18
4	5	41	41
4	6	35	38
4	7	14	14
4	8	17	19
4	9	21	22
4	11	8	5
4	12	12	11
4	13	38	36
4	15	6	6
4	16	7	8
4	17	16	15
6	0	53	56
6	1	38	39
6	2	5	4
6	3	28	28
6	4	41	42
6	8	47	49
6	9	14	15
6	10	18	17
6	12	28	28
6	13	14	14
6	14	20	21
6	16	7	6
8	0	30	30
8	1	44	42
8	2	22	21
8	3	29	29
8	4	23	21
8	5	7	7
8	6	9	9
8	7	11	11
8	8	18	18
8	9	10	8
8	12	12	12
8	13	8	7
**** H = 1 ****			
1	1	61	68
1	2	71	68
1	3	79	74
1	5	17	14
1	6	94	98
1	7	34	33
1	8	9	9
1	9	10	9
1	10	50	48
1	11	30	27
1	13	13	13
1	14	16	16
1	15	21	21
1	18	12	14
3	1	21	23
3	2	40	43
3	3	17	17
3	4	13	13
3	5	40	43
3	6	24	24
3	7	24	24
3	8	11	13
3	9	19	20
3	10	10	11
3	11	11	11
3	12	13	13
3	15	9	8
3	16	8	7
3	17	10	10
3	19	14	13
5	1	16	15
5	2	74	81
5	3	28	27
5	4	19	19
5	5	25	24
5	6	53	56
5	7	46	47
5	8	18	18
5	9	15	14
5	10	32	31
5	11	29	28
5	12	22	21
5	14	16	15
5	15	9	9
5	16	13	13
5	18	10	11
7	1	17	17
7	2	32	30
7	3	22	22
7	4	9	10
7	5	30	29
7	6	17	16
7	7	30	30
7	9	15	15
7	10	11	10
7	11	15	15
7	14	9	9
7	15	5	6
9	1	15	15
9	2	15	15
9	3	20	19
9	5	10	10
9	6	22	20
9	7	19	18
9	8	12	11
9	9	10	10
9	10	13	13
9	11	15	15
9	12	6	7
**** H = 2 ****			
0	0	150	142
0	2	89	67
0	4	135	111
0	6	22	19
0	8	113	100
0	10	19	18
0	12	49	49
0	14	32	35
0	16	11	15
2	0	3	4
2	1	28	26
2	2	26	26
2	3	66	67
2	4	8	7
2	5	65	64
2	6	5	5
2	7	23	20
2	8	13	12
2	9	30	31
2	10	13	11
2	11	24	23
2	12	12	13
2	13	15	17
4	1	57	67
4	2	26	25
4	3	24	26
4	4	9	10
4	5	41	43
4	6	8	8
4	7	30	31
4	8	21	22
4	9	44	43
4	10	18	17
4	11	13	13
4	12	13	12
4	13	34	34
4	16	9	8
4	17	12	13
6	0	52	50
6	1	12	11
6	2	35	36
6	3	6	5
6	4	41	39
6	5	35	35
6	6	31	32
6	7	13	11
6	8	46	46
6	9	20	20
6	10	16	16
6	12	28	27
6	13	9	8
6	14	13	14
6	16	7	7
8	1	13	13
8	4	15	15
8	7	13	14
8	8	13	12
8	11	12	13
8	12	12	12
8	13	8	8
10	3	10	9
10	4	9	8
10	5	19	18
10	6	9	8
10	8	15	16
10	9	19	19
**** H = 3 ****			
1	1	31	29
1	2	85	74
1	4	16	15
1	5	30	29
1	6	49	40
1	7	40	37
1	8	31	27
1	10	40	37
1	11	47	44
1	12	11	11
1	14	22	22
1	15	15	17
1	18	9	10
1	19	6	7
3	1	23	25
3	2	18	17
3	3	7	8
3	4	19	18
3	5	10	9
3	6	12	14
3	7	14	15
3	8	5	4
3	9	6	8
3	11	26	24
3	12	14	12
3	13	16	15
3	15	12	9
3	16	8	9
3	17	12	12
5	1	22	24
5	2	39	44
5	3	48	51
5	5	9	7
5	6	41	43
5	7	36	34
5	8	28	28
5	10	40	37
5	11	15	15
5	12	24	23
5	14	17	19
5	15	8	9
5	16	5	6
7	1	23	24
7	2	11	11
7	3	28	30
7	6	11	13
7	7	21	22
7	10	13	12
7	11	17	17
7	13	5	6
7	14	9	10
9	4	11	11
9	5	9	10
9	6	15	15
9	7	20	18
9	8	6	5
9	9	7	6
9	11	16	16
**** H = 4 ****			
0	0	104	99
0	4	76	77
0	6	5	4
0	8	68	65
0	10	30	30
0	12	38	35
0	14	21	22
0	16	10	10
0	18	10	10
2	0	17	17
2	1	45	43
2	2	11	12
2	5	21	17
2	9	17	15
2	10	11	9
2	11	13	12
2	12	10	9
2	13	13	14
2	16	6	6
2	17	6	6
4	0	15	15
4	1	34	34
4	2	9	7
4	3	33	34
4	5	30	30
4	6	13	12
4	7	23	25
4	8	10	11
4	9	35	36
4	12	11	11
4	13	24	24
4	17	8	10
6	4	28	31
6	5	13	14
6	6	14	17
6	8	23	23
6	9	14	15
6	12	17	18
**** H = 5 ****			
1	1	16	17
1	2	41	37
1	3	35	33
1	4	11	10
1	5	18	19
1	6	41	38
1	7	31	31
1	8	8	6
1	9	6	4
1	10	23	19
1	11	16	15
1	13	8	8
1	14	7	7
1	15	10	10
1	16	7	7
3	1	8	9
3	2	5	6
3	3	18	19
3	5	19	19
3	7	10	10
3	8	15	14
3	9	19	19
3	12	8	7
3	15	5	7
5	1	16	20
5	2	36	38
5	3	17	19
5	6	35	38
5	7	13	16
5	10	17	16
5	11	15	14
**** H = 6 ****			
0	0	74	75
0	4	53	51
0	6	9	8
0	8	27	25
0	10	16	15
0	12	16	15
0	14	13	13
2	1	14	14
2	3	17	17
2	6	8	9
2	7	13	12
2	13	10	10
4	0	18	17
4	1	34	31
4	3	22	20
4	5	26	24
4	9	16	15
6	0	25	28
6	4	21	22
6	8	14	17
**** H = 7 ****			
1	1	17	17
1	2	20	20
1	3	18	17
1	6	13	14
1	7	15	13
1	10	14	14
1	11	12	12
1	12	5	5
3	1	9	11
3	2	5	5
3	3	6	5
3	4	7	7
3	8	5	2
3	12	6	2
5	2	25	23
5	6	15	13
5	7	10	9
5	8	9	8
5	10	10	12
**** H = 8 ****			
0	0	17	18
0	2	10	10
0	4	18	20
0	6	11	11
0	8	18	19
2	5	12	12
2	7	5	6
2	9	8	10
4	1	9	11
4	2	5	4
4	3	5	5
4	5	13	13
**** H = 9 ****			
1	2	8	8

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(8) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

(9) Symbolic addition was carried out using SAP, a program derived from NRC-4 (S. R. Hall and F. R. Ahmed).

(10) All Fourier summations were carried out using an adapted version of A. Zalkin's FORDAP.

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $F_3SiCo(CO)_4$

Atom	X	Y	Z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.0	0.1662 (2)[b]	0.1308 (1)	0.0151 (4)	0.0064 (3)	0.0031 (1)	0.0	0.0	0.0004 (1)
Si	0.0	−0.0281 (4)	0.1410 (2)	0.0209 (9)	0.0074 (4)	0.0035 (2)	0.0	0.0	0.0006 (2)
F(M)	0.0	−0.0932 (9)	0.0708 (6)	0.1050 (77)	0.0084 (11)	0.0060 (5)	0.0	0.0	−0.0013 (6)
F(G)	0.1454 (12)	−0.0779 (7)	0.1820 (6)	0.0347 (22)	0.0123 (9)	0.0132 (5)	0.0009 (11)	−0.0092 (10)	0.0038 (6)
C(M)	0.0	0.1656 (15)	0.2272 (10)	0.0387 (55)	0.0092 (18)	0.0034 (7)	0.0	0.0	−0.0005 (8)
O(M)	0.0	0.1639 (12)	0.2871 (7)	0.0728 (68)	0.0141 (16)	0.0034 (5)	0.0	0.0	−0.0005 (7)
C(G)	0.1850 (16)	0.1482 (9)	0.0820 (6)	0.0177 (20)	0.0073 (12)	0.0047 (4)	−0.0011 (14)	0.0000 (8)	0.0018 (5)
O(G)	0.3022 (12)	0.1375 (8)	0.0512 (5)	0.0200 (15)	0.0153 (12)	0.0070 (4)	−0.0007 (12)	0.0021 (7)	0.0027 (5)
C(A)	0.0	0.3237 (18)	0.1253 (11)	0.0296 (47)	0.0078 (22)	0.0063 (8)	0.0	0.0	−0.0010 (10)
O(A)	0.0	0.4222 (12)	0.1184 (8)	0.0342 (37)	0.0048 (13)	0.0094 (8)	0.0	0.0	0.0010 (7)

[a] The form of the anisotropic ellipsoid is $\exp-[(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Figures in parentheses are standard deviations computed from the inverse matrix; no deviations are given for symmetry-determined parameters.

TABLE III

SELECTED DISTANCES (Å)

Intramolecular bonded distances[a]		Intramolecular nonbonded distances	
Co–Si	2.226 (5)	Co–O(A)	2.93 (1)
Co–C(A)	1.80 (2)	Co–O(M)	2.89 (1)
Co–C(M)	1.78 (2)	Co–O(G)	2.91 (1)
Co–C(G)	1.78 (1)		
		C(A)–C(M)	2.61 (3)
C(A)–O(A)	1.13 (2)	C(A)–C(G)	2.64 (2)
C(M)–O(M)	1.11 (2)		
C(G)–O(G)	1.13 (1)	Si–C(M)	2.73 (2)
		Si–C(G)	2.75 (1)
Si–F(M)	1.50 (1)		
Si–F(G)	1.53 (1)	F(M)–F(G)	2.39 (1)
		F(G)–F(G)	2.39 (2)
		F(M)–C(G)	3.16 (2)
Intermolecular distances[b]		F(G)–C(M)	3.14 (2)
Co–Co	6.16	F(G)–C(G)	3.19 (1)
O–O	3.20		
O–F	3.14		
F–F	3.05		

[a] Some of these are significantly lengthened by thermal motion. See text. [b] The shortest intermolecular distances of the type specified.

cycles of full-matrix least-squares refinement[11] with all reflections equally weighted. The conventional R factor ($R_1 = \Sigma\Delta/\Sigma|F_o|$ where $\Delta = ||F_o| - |F_c||$) dropped from 32.4 to 14.8% while the weighted R factor ($R_2 = \Sigma w\Delta^2/\Sigma wF_o^2$) dropped from 34.3 to 15.8%.

Least-squares refinement of the structure was then carried out along conventional lines. A weighting scheme of the form

$$\sqrt{w} = (A + BF_o + CF_o^2 + DF_o^3)^{-1}$$

was calculated subject to the condition that $\Sigma w\Delta^2$ be approximately independent of $|F_o|$ and $(\sin\theta)/\lambda$. The constants A, B, C, and D required alterations several times during the refinement. Anisotropic temperature factors were applied to all atoms at an R_1 value of 13.8%. Least-squares refinement converged at R_1 and R_2 values of 7.7 and 8.9%, respectively. In the final cycle of refinement the values of the constants A, B, C, and D in the weighting expression were, respectively, 260.0, −9.20, 0.200, and 0.0100. Three reflections, (004), (040), and (041), are obviously suffering from extinction, but for reasons discussed earlier no such correction was made. The electron density of the highest ten peaks in the final difference Fourier ranged from 0.5 to 0.25 e$^-$/Å^3. These were considered acceptably low values in view of the lack of corrections for absorption and extinction. The final structure factor listing is given in Table I and the atom position and thermal parameters are given in Table II.

TABLE IV

SELECTED ANGLES (DEG)

Bond angles		Dihedral angles[a]	
Co–Si–F(M)	114.9 (5)	Co–Si–F(M) Co–Si–F(G)	120.6 (5)
Co–Si–F(G)	114.4 (4)		
F(M)–Si–F(G)	104.3 (5)	Co–Si–F(G) Co–Si–F(G)	118.8 (10)
F(G)–Si–F(G)	103.2 (8)		
Si–Co–C(M)	84.9 (6)	Si–Co–C(M) Si–Co–C(G)	121.1 (4)
Si–Co–C(G)	85.9 (3)		
C(A)–Co–C(M)	93.5 (8)	Si–Co–C(G) Si–Co–C(G)	117.8 (7)
C(A)–Co–C(G)	94.9 (5)		
C(M)–Co–C(G)	120.5 (4)	Si–Co–O(M) Si–Co–O(G)	121.1 (2)
C(G)–Co–C(G)	117.3 (7)		
C(A)–Co–Si	178.4 (6)	Si–Co–O(G) Si–Co–O(G)	117.9 (4)
Co–C(A)–O(A)	176.8 (18)		
Co–C(M)–O(M)	179.2 (16)		
Co–C(G)–O(G)	179.7 (11)		
		Si–Co–O(G) Co–Si–F(G)	0.45 (52)

[a] Angles are between two planes each defined by three atoms.

Discussion of the Structure

Selected bonded and nonbonded distances are given in Table III, and selected angles are given in Table IV.[12] The crystal consists of discrete molecules, the shortest cobalt–cobalt distance being 6.16 Å. All intermolecular contacts are larger than the sums of the appropriate van der Waals radii. A perspective drawing of the molecule is shown in Figure 1.[13] To simplify the figures, subscript letters have been used instead of the parenthetic letters in the text.

TABLE V

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max
Co	0.203 (4)	0.227 (3)	0.234 (3)
Si	0.214 (6)	0.253 (6)	0.267 (6)
F(M)	0.23 (2)	0.33 (1)	0.60 (2)
F(G)	0.24 (1)	0.32 (1)	0.52 (1)
C(M)	0.23 (2)	0.26 (2)	0.36 (3)
O(M)	0.24 (2)	0.31 (2)	0.50 (2)
C(G)	0.20 (2)	0.25 (1)	0.30 (1)
O(G)	0.24 (1)	0.30 (1)	0.38 (1)
C(A)	0.22 (3)	0.32 (2)	0.33 (2)
O(A)	0.18 (2)	0.34 (2)	0.41 (2)

The rms displacements along the principal axes of the thermal ellipsoids are given in Table V. The aniso-

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[11] Full-matrix least-squares refinements were carried out using CUCILS, a composite program containing elements of ORFLS (W. R. Busing, K. O. Martin, and H. A. Levy), NULS4 (J. A. Ibers), and UCILS (R. J. Doedens).

[12] Distances and angles were calculated using CORFFE, a program derived from ORFFE-II (W. R. Busing, K. O. Martin, and H. A. Levy).

[13] Figures were drawn using CORTEP, adapted from ORTEP (C. K. Johnson).

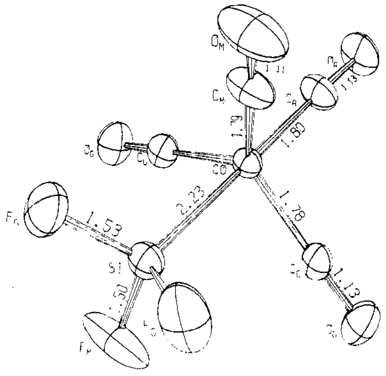

Figure 1.—General view of the $F_3SiCo(CO)_4$ molecule.

tropic motions are large only for the fluorine and oxygen atoms. Orientations of the thermal ellipsoids can be seen in Figures 1 and 2, and all seem physically reasonable.

A detailed comparison of the bonded distances and angles with those determined by Robinson and Ibers[1] for $Cl_3SiCo(CO)_4$ raises several interesting points. The Cl–Si distance of 2.035 (3) Å in the chloro compound is normal, while the F–Si distance of 1.51 (1) Å reported here is significantly shorter than previously reported F–Si distances,[14–18] which range from 1.55 to 1.59 Å. A number of corresponding distances for the two compounds have been listed in Table VI. In this table a parenthetic E indicates an equatorial atom, and the distance given is an average of all the contributing distances.

TABLE VI

A COMPARISON OF SOME BOND DISTANCES (Å) IN $Cl_3SiCo(CO)_4$ AND $F_3SiCo(CO)_4$[a]

Bond	$Cl_3SiCo(CO)_4$	$F_3SiCo(CO)_4$
Co–Si	2.254 (3)	2.226 (5)
Co–C(E)	1.767 (5)	1.78 (1)
C(E)–O(E)	1.15 (1)	1.12 (1)
Co–C(A)	1.797 (9)	1.80 (2)
C(A)–O(A)	1.136 (8)	1.13 (2)

[a] A parenthetic E indicates an average distance for the equatorial groups; a parenthetic A indicates an axial distance.

The shortness of the Si–F distance and the observation that all the C–O distances in the fluoro compound were shorter than the corresponding distances in the chloro compound suggested that the larger thermal motions of the former might be affecting our calculated distances significantly. A calculation of the bond distances of the Si–F bonds and the C–O bonds was made using the riding model.[19] The riding model is undoubtedly a very poor approximation for the thermal correction in the C–O distance, but it is certainly better than the approximation of totally uncorrelated motion. The resulting "corrected" distances are: Si–F, 1.61 (1) Å; C(E)–O(E), 1.17 (2) Å; C(A)–O(A), 1.16 (2) Å. These carbonyl distances do not differ significantly from the corresponding uncorrected ones in the chloro compound. It seems likely that application of this correction to the bond distances in the chloro compound would bring them into even closer agreement.

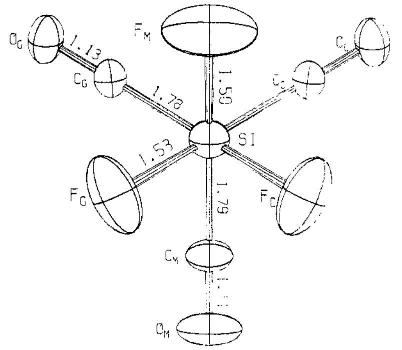

Figure 2.—Molecule viewed down the Co–Si axis showing approximate threefold symmetry.

The change in the Si–F distance on applying a thermal correction is not really surprising when the shape of the thermal ellipsoid for fluorine is considered (see Figure 2). It is, however, a bit unexpected that the Si–F distance should, after thermal correction, be 0.02–0.06 Å longer than previous electron diffraction and microwave determinations of the same distance in other silicon fluorides. Some lengthening of the crystal distance because of lattice vibrations is to be expected, but the magnitude of the observed change is surprising. Since this is the only fluorosilane derivative whose structure has been determined by X-ray diffraction, the authors are reluctant to draw any conclusions from these comparisons. Because of the large thermal motions of fluorine atoms, quoted bond distances in fluorine-containing molecules are very sensitive to thermal corrections, as the above discussion illustrates.

The environment of the Si in the fluoro compound deviates from tetrahedral symmetry in the same way as in its sister compound: the average F–Si–F angle of 103.7° is just slightly smaller than the 105.4° reported by Robinson and Ibers for the chloro derivative. The X–X nonbonded distance in both the chloro and fluoro compounds is approximately 90% of the expected van der Waals distance. The C–X distance from neighboring carbonyl groups exceeds the expected van der Waals distance in both compounds. On this basis it seems reasonable to attribute the X–Si–X angle primarily to X–X nonbonding repulsions rather than to C–X repulsions from the carbonyl groups.

The coordination sphere about the cobalt atom is trigonal bipyramidal, and the bond angles reported here for cobalt do not differ significantly from those reported for the chloro derivative. In both compounds the equatorial carbonyl groups are bent out of the basal plane in the direction of the silyl group. The equatorial carbonyls and the fluorines are staggered, as can be seen in Figure 1.

The Si–Co bond distance in the fluoro derivative is

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shorter than the corresponding distance in the chloro derivative, supporting the hypothesis of a (d → d) π bond between these atoms. The other distances which Robinson and Ibers suggested[1] might provide additional evidence for such a bond were not significantly different in the two compounds.

Acknowledgments.—The authors wish to thank Dr. A. G. McDiarmid for calling their attention to this problem and Dr. A. P. Hagen for providing the sample of $F_3SiCo(CO)_4$. Special thanks are also due to Mr. R. J. Dellaca for his contribution to the computer programs used in this determination.

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The Crystal Structure of Solvated Hydridochloro(trichlorosilyl)bis(triphenylphosphine)rhodium, $RhHCl(SiCl_3)(P(C_6H_5)_3)_2 \cdot xSiHCl_3$

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Received July 25, 1969

The crystal structure of solvated hydridochloro(trichlorosilyl)bis(triphenylphosphine)rhodium, $RhHCl(SiCl_3)(P(C_6H_5)_3)_2 \cdot xSiHCl_3$, has been determined by X-ray diffraction methods. The compound crystallizes in the space group $C_i^1\text{-}P\bar{1}$ of the triclinic system. There are two molecules of $RhHCl(SiCl_3)(P(C_6H_5)_3)_2$ in a unit cell of dimensions $a = 11.727$ (5) Å, $b = 12.952$ (6) Å, $c = 13.365$ (5) Å, $\alpha = 104.65$ (2)°, $\beta = 98.08$ (2)°, $\gamma = 94.43$ (2)°. The structure has been refined by least-squares methods to a conventional R factor of 0.064 over 2485 counter-diffractometric data. It consists of discrete monomeric molecules of $RhHCl(SiCl_3)(P(C_6H_5)_3)_2$ and $SiHCl_3$. The latter are disordered over four different sites; the $SiHCl_3$:Rh ratio is 0.397 (7). The rhodium coordination polyhedron may be described as a highly distorted trigonal bipyramid, with *trans* phosphines at the apices and H, Cl, and $SiCl_3$ in the trigonal plane. Alternatively, the coordination about the formally d^6 Rh(III) ion is distorted octahedral if one chooses to include at the sixth coordination site the contact of 2.79 Å with an *ortho*-hydrogen atom on a phenyl ring of a triphenylphosphine group. The short Rh–Si distance of 2.203 (4) Å is consistent with back-donation of electrons from the metal to the silyl group.

Introduction

The nature of metal–silicon bonding in transition metal–silyl complexes is at present a subject of debate.[1,2] Structural details have been published only for the cobalt complexes $Co(SiR_3)(CO)_4$ (R = F,[3] Cl,[4] H[5]) and for $Mn(Si(CH_3)_3)(CO)_5$.[6] It is our contention that a fruitful discussion of such problems as the relative importance of d_π–d_π back-bonding and electronegativity differences in stabilizing metal–silicon bonds and whether the metal–silicon bond may appropriately be considered as a metal–metal bond will only be possible if adequate structural data are at hand on a sufficient number of representative metal–silyl complexes.

Accordingly, we have determined the crystal structure of the formally d^6 complex hydridochloro(trichlorosilyl)bis(triphenylphosphine)rhodium(III), $RhHCl(SiCl_3)(P(C_6H_5)_3)_2$. This compound was chosen because we believed that back-donation to silicon would be favored by the presence of a second- as opposed to a first-row transition metal and by the absence of strongly π-bonding ligands such as carbonyl. In addition, this compound contains five-coordinate rhodium(III). Five-coordination is much less common in d^6 systems than it is in d^0, d^8, or d^{10} systems;[7] the only d^6 complexes for which structural data are available are the ruthenium(II) complexes $RuXCl(P(C_6H_5)_3)_3$ (X = Cl,[8] H[9]) and $Rh(CH_3)I_2(P(C_6H_5)_3)_2$.[10] Further motives for our interest in this molecule were the presence of a metal–hydrogen bond and the relationship between the structure of the molecule and its postulated role as an intermediate in the catalytic hydrosilation of olefins.

The compound $RhHCl(SiCl_3)(P(C_6H_5)_3)_2$ has been prepared independently by two groups. Haszeldine, Parish, and Parry[11] obtained an unsolvated complex. While this work was underway, de Charentenay, Osborn, and Wilkinson[12] reported a slightly different preparation which yields solvated complexes; these authors suggested that the complexes containing free

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