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Structural Studies of Derivatives of Methinyltricobalt Enneacarbonyls. II.[1] The Crystal Structure and Spectra of $Co_5(CO)_{15}C_3H$

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$Co_5(CO)_{15}C_3H$ is one product of the reaction of $ClCCo_3(CO)_9$ with mesitylene. Its crystal and molecular structure has been determined by three-dimensional X-ray analysis. Crystals are triclinic, space group $P\bar{1}$ with two molecules in a cell of dimensions $a = 9.67$ (1), $b = 15.02$ (2), $c = 9.421$ (8) Å; $\alpha = 95.2$ (1), $\beta = 113.3$ (1), $\gamma = 98.8$ (2)°. X-Ray data were collected by conventional film techniques using Co $K\alpha$ radiation and the intensities of 1392 reflections above background were measured photometrically. The structure was refined isotropically by modified full-matrix least-squares procedures to a conventional R factor of 0.067. The $-CCo_3(CO)_9$ structural unit of the parent compound is retained and is linked to a Co_2-$(CO)_8$ unit through an acetylene bridge. This bridge and the Co_2 pair form a tetrahedral grouping. The five Co-Co bonds in the molecule range in length from 2.447 (4) (in the $-Co_2(CO)_8$ unit) to 2.485 (4) Å. The hydrogen atom has not been located directly but its presence is confirmed by the molecular weight obtained from the mass spectrum. Infrared and mass spectral results are reported and discussed.

Introduction

Among the products of the reactions of chloromethinyltricobalt enneacarbonyl, $ClCCo_3(CO)_9$, with mesitylene[5] are a number of carbonyls[6,7] possessing additional carbon atoms, the simplest of which was formulated as $Co_5(CO)_{15}C_3H$ on the basis of complete analytical data, molecular weight, and mass spectrum. In the infrared spectrum there were no bands due to bridging CO groups, an observation which suggested that there had been retention of the $-CCo_3(CO)_9$ unit of the parent compound in which all CO groups are terminal. (The structural details of the $-CCo_3(CO)_9$ group were earlier determined by Sutton and Dahl[8] in the structure determination of $CH_3CCo_3(CO)_9$.) The indications were that a novel structure had been formed by linkage of a $-CCo_3(CO)_9$ unit to further Co atoms.

Experimental Section

Preparation of $Co_5(CO)_{15}C_3H$.—Chloromethinyltricobalt ennea-

carbonyl[9-11] (2.16 g) and mesitylene (15 ml) were heated at 130° for 30 min under an atmosphere of carbon monoxide. The resulting dark brown solution was rapidly cooled and the mesitylene removed *in vacuo*. The solid residue was then extracted with five 12-ml portions of petroleum ether (bp 30-40°) and the extract applied to four 20 cm × 20 cm × 1.25 mm silica HF_{254} plates. Development of the plates with pentane gave the following four bands (in order of increasing retention time): (1) purple, unreacted $ClCCo_3(CO)_9$ (and possibly $HCCo_3(CO)_9$); (2) grayish brown; (3) orange brown $(Co_6(CO)_{18}C_4)$; (4) dark brown $(Co_8(CO)_{24}C_6)$. Band 2 was removed and eluted with acetone-pentane. The black solid obtained by removing the solvent was recrystallized from petroleum ether (bp 30-40°) to give small dark needles of $Co_5(CO)_{15}C_3H$: yield 15 mg. *Anal.* Calcd for $C_{18}HCo_5O_{15}$: C, 28.76; H, 0.13; Co, 39.19. Found: C, 28.53; H, 0.19; Co, 39.60.

The compound is air stable, soluble without decomposition in most organic solvents, but insoluble in water. Solutions of the compound are only moderately stable in air at room temperature. A satisfactory melting point could not be obtained as the solid decomposes above 100°. Sublimation with considerable decomposition occurs at 60° (0.05 mm).

Infrared Spectra.—Solution and mull spectra were obtained in the region 5000-200 cm^{-1} on a Perkin-Elmer 225 spectrophotometer using, where appropriate, sodium chloride, potassium bromide, and polythene cells. Spectra from 200 to 50 cm^{-1} were recorded on a RIIC interferometer.

Mass Spectra.[12]—Mass spectra were obtained on an AEI MS9 mass spectrometer with an ionizing energy of 70 eV using a direct

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(7) A full discussion of reactions leading to the formation of $Co_5(CO)_{15}C_3H$ and other carbonyl carbides is given in part III of this series: R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, **9**, 2204 (1970).

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(12) We thank Dr. R. Hodges, Massey University, Palmerston North, New Zealand, for running these spectra.

inlet system. However some difficulty was experienced in obtaining a satisfactory spectrum owing to the low thermal stability of the compound.

Nmr Spectra.—Hydrogen-1 nmr spectra were recorded on a Varian HA-100 spectrometer using $CDCl_3$ as solvent and TMS internal reference.

Crystallographic Data.[13]—$Co_5(CO)_{15}C_3H$, mol wt 751.5, is triclinic with $a = 9.667$ (11), $b = 15.023$ (15), $c = 9.421$ (8) Å; $\alpha = 95.2$ (1), $\beta = 113.3$ (1), $\gamma = 98.8$ (2)°; $V = 1225$ Å³; $d_{obsd} = 2.05$ (2) g/cm³; $Z = 2$; $d_{calcd} = 2.038$ (4) g/cm³; μ(Co Kα) = 64.5 cm⁻¹. With two molecules per unit cell in space group P1 or P$\bar{1}$, no crystallographic symmetry conditions are imposed on the molecule. The structure has been refined successfully in space group P$\bar{1}$ with all atoms occupying the general twofold set of equivalent positions.

Unit cell dimensions and their estimated standard deviations were obtained from a least-squares refinement on $\sin^2 \theta$. Input data were the distances between Friedel pairs of reflections on calibrated zero-level precession photographs taken with Polaroid film and Mo Kα radiation (λ 0.7107 Å) at room temperature (20°). The experimental density was obtained using a suitably calibrated density gradient tube with CH_3I and CCl_4 as media.

All X-ray intensity data were obtained from one rectangular prismatic crystal of approximate dimensions $0.2 \times 0.1 \times 0.1$ mm, with the longest dimension along the a axis. Using Co Kα radiation, three-dimensional data were collected with a two-dimensionally integrating equiinclination Weissenberg camera at room temperature. The plateaus of the integrated spots and adjacent background areas were measured using a single-beam photometer and a galvanometer calibrated to read intensities directly. The levels (nkl), with $n = 0$–6, were investigated, and within these, intensities were assigned to 1392 independent reflections judged to be above the threshold of observation. Complete coverage of the reciprocal lattice required measurements to be obtained from both halves of the Weissenberg films for nonzero levels. Corrections for spot extension were applied to measurements on one half but it was considered that the integration process had obviated the need for correction to measurements in the other half where the spots are normally contracted. Absorption corrections were applied using the Gaussian quadrature method with accurately measured crystal dimensions. Transmission factors varied between 0.53 and 0.67. Only observed reflections were used in the refinement process and no attempt was made to place the data on a common scale using correlating data from a crystal mounted about a second axis. Following final refinement, structure factor calculations for the 594 "unobserved" reflections in the reciprocal lattice region investigated showed that there were 50 F_c values greater than F_{min} but none greater than $2F_{min}$.

All calculations were performed on an IBM 360/44 computer with 16K words of core storage and twin 2315 disk drives. The principal programs used have been described in part I of this series.

Structure Determination and Refinement

The presence of a center of symmetry, hence space group P$\bar{1}$, was strongly indicated by the distribution of vectors in a computed three-dimensional Patterson function. Trial coordinates for the five Co atoms were obtained from the vector map, one initial misplacement being corrected following a preliminary electron density difference map phased by Co atoms alone. Several subsequent difference maps followed by intermediate least-squares refinement revealed all carbon and oxygen atoms.

With seven scale factors and parameters for 38 iso-

(13) Here and throughout this paper, the uncertainties given in parentheses are estimated standard deviations in the least significant digits quoted.

TABLE I
POSITIONAL AND THERMAL PARAMETERS
FOR $Co_5(CO)_{15}C_3H$

Atom	x	y	z	B^a
Co(1)	0.4098 (3)	0.1884 (2)	−0.1055 (3)	3.60 (7)
Co(2)	0.2973 (3)	0.1845 (2)	0.0893 (3)	3.39 (6)
Co(3)	0.0904 (3)	0.3852 (2)	−0.2253 (3)	3.13 (6)
Co(4)	−0.0166 (3)	0.2530 (2)	−0.4387 (3)	3.25 (6)
Co(5)	−0.1099 (3)	0.2606 (2)	−0.2280 (3)	3.47 (7)
C(1)	0.218 (2)	0.117 (1)	−0.122 (2)	3.0 (3)
C(2)	0.198 (2)	0.203 (1)	−0.132 (2)	3.1 (3)
C(3)	0.094 (2)	0.261 (1)	−0.216 (2)	2.5 (3)
C(11)	0.387 (2)	0.154 (1)	−0.298 (2)	5.7 (5)
C(12)	0.519 (2)	0.304 (1)	−0.054 (2)	3.9 (4)
C(13)	0.555 (3)	0.126 (1)	−0.018 (2)	6.2 (5)
C(21)	0.365 (2)	0.301 (1)	0.196 (2)	4.2 (4)
C(22)	0.140 (2)	0.144 (1)	0.130 (2)	5.1 (4)
C(23)	0.426 (2)	0.127 (1)	0.221 (2)	5.2 (4)
C(31)	0.150 (2)	0.441 (1)	−0.032 (2)	4.3 (4)
C(32)	0.258 (2)	0.426 (1)	−0.248 (2)	4.3 (4)
C(33)	−0.028 (2)	0.458 (1)	−0.327 (2)	4.5 (4)
C(41)	0.125 (2)	0.274 (1)	−0.504 (2)	4.2 (4)
C(42)	−0.074 (2)	0.136 (1)	−0.509 (2)	5.9 (5)
C(43)	−0.164 (2)	0.295 (1)	−0.583 (2)	4.5 (4)
C(51)	−0.182 (2)	0.142 (1)	−0.247 (2)	6.1 (5)
C(52)	−0.084 (2)	0.292 (1)	−0.034 (2)	4.2 (4)
C(53)	−0.283 (2)	0.303 (1)	−0.332 (2)	4.9 (4)
O(11)	0.368 (2)	0.130 (1)	−0.426 (2)	7.8 (4)
O(12)	0.585 (2)	0.378 (1)	−0.012 (2)	6.1 (3)
O(13)	0.655 (2)	0.089 (1)	0.044 (2)	8.1 (4)
O(21)	0.410 (2)	0.375 (1)	0.262 (2)	6.5 (3)
O(22)	0.033 (2)	0.113 (1)	0.156 (2)	7.3 (4)
O(23)	0.514 (2)	0.090 (1)	0.307 (2)	7.2 (4)
O(31)	0.188 (1)	0.484 (1)	0.093 (2)	5.7 (3)
O(32)	0.368 (2)	0.457 (1)	−0.267 (2)	6.9 (4)
O(33)	−0.108 (2)	0.507 (1)	−0.397 (2)	5.9 (3)
O(41)	0.223 (2)	0.290 (1)	−0.550 (2)	6.6 (3)
O(42)	−0.117 (2)	0.058 (1)	−0.554 (2)	7.5 (4)
O(43)	−0.258 (2)	0.325 (1)	−0.681 (2)	6.4 (3)
O(51)	−0.221 (2)	0.065 (1)	−0.258 (2)	8.8 (4)
O(52)	−0.066 (2)	0.312 (1)	0.095 (2)	6.4 (3)
O(53)	−0.393 (2)	0.331 (1)	−0.395 (2)	7.4 (4)

^{a} Isotropic thermal parameter (in Å²).

tropic atoms to be refined, the total number of variables was 159 whereas core storage limitations in our computer at the time restricted to 81 the number we could vary simultaneously. The variables in the least-squares process were therefore split into three blocks with the scale factors, parameters for the five cobalt atoms, and parameters for as many carbon and oxygen atoms as could be accommodated being varied in each block. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weight w was determined by the empirical formula of Cruickshank,[14] $w = (A + B|F_o| + C|F_o|^2 + D|F_o|^3)^{-1}$. Coefficients which gave best constancy of average values of the minimized function over the full F_o range were $A = 11.4$, $B = 0.23$, $C = -6.3 \times 10^{-3}$, and $D = 6.0 \times 10^{-5}$. The usual tabulations of atomic scattering factors[15] for Co, O, and C were used, those for Co only being corrected for anomalous dispersion and values for $\Delta f'$ and $\Delta f''$ of -2.19 and 0.74 electrons, respectively, being interpolated from Cromer's tables.[16]

(14) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, Oxford, 1965, p 114.

(15) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

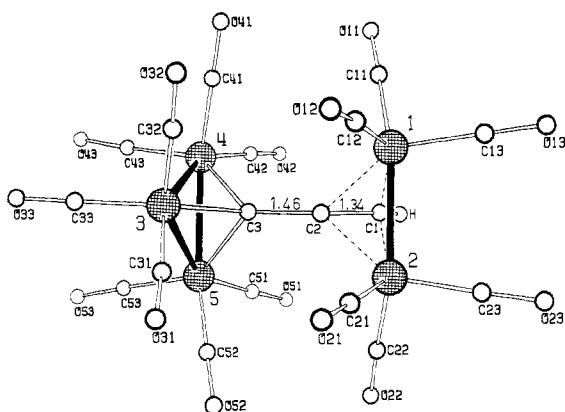(16) D. T. Cromer, *Acta Crystallogr.*, **18**, 511 (1965).

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $Co_5(CO)_{15}C_3H$

K	L	OBS	CALC
**** H = 0 ****			
2	0	179	174
3	0	[illegible]	53
4	0	[illegible]	16
5	0	[illegible]	46
6	0	[illegible]	17
7	0	[illegible]	19
8	0	[illegible]	16
9	0	[illegible]	59
11	0	[illegible]	39
14	0	[illegible]	33
0	1	[illegible]	59
1	1	[illegible]	120
2	1	[illegible]	52
3	1	[illegible]	101
4	1	[illegible]	110
5	1	[illegible]	124
6	1	[illegible]	66
7	1	[illegible]	68
8	1	[illegible]	21
9	1	[illegible]	26
10	1	[illegible]	21
-1	1	[illegible]	81
-2	1	[illegible]	38
-3	1	[illegible]	54
-4	1	[illegible]	12
-5	1	[illegible]	10
-6	1	[illegible]	38
-7	1	[illegible]	28
-8	1	81	84
-9	1	41	42
-10	1	[illegible]	75
-11	1	[illegible]	36
-12	1	[illegible]	23
-13	1	[illegible]	19
0	2	[illegible]	20
1	2	[illegible]	31
2	2	[illegible]	51
[illegible]	2	[illegible]	29
4	2	[illegible]	38
5	2	[illegible]	14
6	2	[illegible]	63
[illegible]	2	[illegible]	29
13	2	21	21
-1	2	54	54
-2	2	[illegible]	12
-3	2	15	33
-4	2	12	35
-5	2	31	28
-8	2	43	42
-9	2	37	36
-10	2	23	19
-11	2	23	21
0	3	45	45
1	3	62	58
2	3	79	79
3	3	12	10
4	3	15	13
5	3	38	37
6	3	19	18
8	3	44	47
10	3	25	29
-2	3	40	41
-3	3	58	59
-4	3	29	25
-6	3	25	24
-9	3	28	26
-10	3	36	36
-13	3	21	18
-14	3	13	12
-15	3	12	12
0	4	25	28
1	4	82	83
2	4	15	17
3	4	87	87
5	4	24	24
6	4	80	87
7	4	58	60
8	4	40	46
9	4	37	37
-1	4	18	15
-3	4	42	41
-4	4	21	20
-6	4	54	52
-7	4	24	21
-8	4	67	61
-10	4	57	51
-11	4	22	22
-13	4	49	49
2	5	21	19
3	5	41	43
6	5	57	54
7	5	32	28
8	5	54	61
10	5	16	19
[illegible]	5	15	22
-1	5	76	82
-2	5	37	35
-3	5	77	75
-5	5	61	58
[illegible]	5	43	42
[illegible]	5	71	68
-9	5	51	47
[illegible]	5	48	45
-10	5	18	17
0	6	72	74
1	6	16	16
3	6	33	29
5	6	23	21
9	6	20	22
-2	6	80	74
-4	6	42	39
-5	6	23	24
[illegible]	6	30	25
[illegible]	[illegible]	20	19
[illegible]	[illegible]	27	21
-11	[illegible]	25	21
[illegible]	[illegible]	17	15
-1	7	24	23
[illegible]	7	19	15
[illegible]	7	16	13
[illegible]	7	15	13
-11	7	10	7
-12	7	10	7
2	8	20	17
4	8	17	13
-5	8	27	21
-7	8	31	27
0	9	37	35
2	9	19	20
-2	9	23	21
-5	9	14	13
-6	9	11	11
-7	9	8	7
**** H = 1 ****			
0	0	91	78
1	0	126	116
2	0	70	66
3	0	25	22
4	0	251	237
6	0	108	113
8	0	69	74
10	0	18	13
11	0	37	35
-3	0	74	75
-4	0	53	52
-5	0	79	83
-6	0	62	65
-7	0	61	63
-8	0	86	93
-9	0	55	56
-10	0	61	65
-11	0	26	27
-12	0	31	32
0	1	100	101
1	1	37	37
2	1	11	6
3	1	34	36
5	1	57	63
7	1	97	106
8	1	19	15
9	1	73	79
11	1	21	26
12	1	26	29
13	1	16	18
14	1	15	18
-1	1	50	53
-2	1	172	168
-3	1	44	40
-4	1	159	160
-5	1	44	46
-6	1	17	21
-7	1	145	140
-8	1	38	40
-9	1	22	18
-10	1	35	36
-11	1	17	14
-13	1	19	20
0	2	26	26
1	2	46	45
2	2	47	47
3	2	87	86
4	2	49	48
5	2	58	58
7	2	21	21
9	2	29	30
12	2	18	19
13	2	13	13
14	2	16	21
-1	2	41	38
-2	2	77	77
-3	2	71	68
-4	2	20	21
-5	2	13	7
-6	2	32	30
-7	2	26	26
-8	2	23	21
-9	2	25	24
-10	2	17	14
-11	2	36	34
-12	2	30	28
-13	2	18	19
-15	2	13	15
0	3	82	79
1	3	23	21
2	3	23	23
3	3	33	28
4	3	18	20
8	3	36	36
-1	3	52	56
-3	3	24	22
-4	3	25	21
-5	3	26	24
-6	3	19	19
-8	3	24	21
-9	3	37	34
-10	3	21	18
0	4	34	34
1	4	21	17
2	4	33	32
3	4	34	35
5	4	15	12
6	4	21	18
7	4	49	43
9	4	25	28
-1	4	17	15
-2	4	152	148
-4	4	46	43
-5	4	31	30
-6	4	27	25
-7	4	34	32
-8	4	28	25
-9	4	21	17
0	5	31	33
1	5	67	64
2	5	22	22
3	5	47	46
4	5	32	30
5	5	39	37
7	5	19	20
10	5	17	17
-1	5	98	96
-2	5	22	20
-3	5	38	36
-4	5	36	32
-5	5	17	16
-6	5	40	35
-8	5	17	14
-9	5	36	31
-10	5	46	41
-11	5	27	24
-12	5	26	24
-13	5	15	17
0	6	23	21
1	6	37	37
2	6	24	21
4	6	47	50
6	6	30	33
-1	6	31	31
-2	6	21	18
-3	6	40	36
-5	6	54	45
-7	6	25	22
-8	6	42	36
-9	6	29	26
-10	6	35	32
-11	6	17	16
-12	6	19	16
1	7	25	24
3	7	20	16
-4	7	32	31
-7	7	27	25
-9	7	27	22
0	-1	71	71
1	-1	132	118
2	-1	32	35
3	-1	42	39
4	-1	43	44
5	-1	87	83
6	-1	38	33
7	-1	47	49
10	-1	27	28
14	-1	17	19
-1	-1	139	128
-3	-1	17	16
-4	-1	41	42
-5	-1	33	35
-6	-1	69	67
-7	-1	17	13
-8	-1	22	19
-9	-1	21	17
-10	-1	43	44
-13	-1	17	19
-15	-1	24	28
0	-2	11	6
1	-2	35	39
2	-2	9	8
3	-2	10	10
5	-2	50	49
6	-2	39	40
8	-2	39	37
10	-2	20	19
-1	-2	19	20
-2	-2	27	21
-3	-2	70	72
-4	-2	56	56
-5	-2	35	33
-7	-2	39	41
-10	-2	26	25
-11	-2	15	15
-12	-2	16	21
0	-3	74	75
1	-3	61	60
2	-3	16	16
3	-3	11	11
4	-3	62	57
5	-3	15	17
6	-3	85	85
8	-3	35	35
9	-3	26	29
11	-3	49	49
-1	-3	222	212
-2	-3	66	66
-3	-3	70	69
-5	-3	94	101
-6	-3	44	51
-7	-3	17	16
-8	-3	54	56
-9	-3	21	22
-10	-3	46	40
-11	-3	30	36
0	-4	42	45
1	-4	100	105
3	-4	86	54
4	-4	35	35
5	-4	82	85
6	-4	21	19
-1	-4	78	83
-2	-4	80	88
-3	-4	59	62
-4	-4	27	29
-5	-4	38	43
-6	-4	17	15
-9	-4	47	50
-10	-4	29	31
-11	-4	24	26
-13	-4	18	22
0	-5	67	68
2	-5	22	20
3	-5	27	27
-1	-5	29	28
-2	-5	103	107
-3	-5	20	21
-4	-5	60	63
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2	-3	23	23
3	-3	79	78
4	-3	33	32
6	-3	73	73
7	-3	34	33
9	-3	22	24
10	-3	14	13
-1	-3	70	77
-3	-3	24	20
-4	-3	44	46
-5	-3	16	15
-8	-3	50	52
-10	-3	49	53
-12	-3	20	25
-13	-3	25	29
0	-4	52	51
1	-4	39	37
2	-4	46	48
3	-4	18	18
5	-4	19	19
8	-4	34	30
-1	-4	29	28
-2	-4	47	45
-4	-4	40	42
-5	-4	26	23
-6	-4	44	44
-10	-4	22	22
-13	-4	13	16
-14	-4	8	10
1	-5	34	35
2	-5	30	33
4	-5	17	15
-1	-5	21	22
-5	-5	18	14
-7	-5	20	18
-8	-5	20	25
-9	-5	22	21
-11	-5	19	19
1	-6	80	79
3	-6	29	24
4	-6	39	37
-1	-6	79	78
-8	-6	30	28
-10	-6	24	30
0	-7	86	84
1	-7	17	12
2	-7	20	17
4	-7	17	16
-1	-7	33	33
-2	-7	73	70
-4	-7	35	33
-5	-7	27	27
-6	-7	31	31
-8	-7	20	20
2	-8	32	35
4	-8	34	34
-1	-8	19	19
-2	-8	23	27
-5	-8	22	21
-7	-8	33	37
-8	-8	12	12
1	-9	22	19
3	-9	19	20
-4	-9	14	13
-2	-10	13	13
**** H = 6 ****			
0	0	39	40
1	0	16	17
2	0	11	9
5	0	31	26
6	0	13	9
7	0	11	10
9	0	11	12
-1	0	17	15
-2	0	16	13
-3	0	16	16
-4	0	49	54
-5	0	19	20
-6	0	37	34
-9	0	22	26
1	1	23	22
2	1	16	17
5	1	16	16
7	1	23	23
8	1	12	13
-1	1	39	36
-2	1	11	9
-3	1	26	25
-6	1	25	25
-7	1	25	25
-10	1	13	14
0	2	62	57
2	2	40	38
3	2	15	12
4	2	23	19
5	2	24	23
6	2	25	26
-2	2	34	31
-3	2	15	16
-9	2	16	19
-10	2	14	13
-11	2	29	28
0	3	13	14
1	3	14	15
2	3	14	14
3	3	20	17
4	3	13	13
5	3	30	32
-2	3	29	26
-3	3	18	17
-4	3	36	38
-6	3	21	22
-7	3	20	21
-8	3	26	26
-9	3	28	22
-10	3	30	26
-11	3	16	14
2	4	23	24
-1	4	25	23
-3	4	31	31
-5	4	17	12
-6	4	17	15
-8	4	27	25
0	-1	45	44
1	-1	21	18
2	-1	57	56
3	-1	38	37
4	-1	46	40
5	-1	32	30
6	-1	30	28
10	-1	15	16
-1	-1	40	41
-2	-1	50	54
-6	-1	27	27
-7	-1	19	18
-8	-1	23	25
-9	-1	42	42
-10	-1	29	31
-11	-1	29	34
-12	-1	13	13
-13	-1	13	15
1	-2	36	33
2	-2	32	31
3	-2	14	14
4	-2	28	26
5	-2	15	16
6	-2	28	24
8	-2	36	38
10	-2	24	25
-2	-2	7	9
-3	-2	72	82
-4	-2	26	29
-5	-2	33	34
-6	-2	39	41
-7	-2	14	16
-8	-2	36	39
-9	-2	21	24
-10	-2	22	20
-12	-2	19	23
1	-3	29	30
2	-3	37	38
3	-3	27	25
4	-3	11	9
5	-3	42	36
6	-3	32	33
7	-3	47	49
9	-3	20	23
10	-3	14	14
-2	-3	43	40
-3	-3	10	8
-4	-3	50	54
-5	-3	12	10
-6	-3	47	47
-7	-3	42	39
-8	-3	49	49
-9	-3	28	27
-10	-3	25	29
0	-4	57	59
2	-4	62	63
3	-4	12	16
6	-4	21	19
8	-4	23	23
-1	-4	11	11
-2	-4	15	13
-3	-4	28	27
-4	-4	23	23
-5	-4	15	19
-6	-4	13	13
-9	-4	27	30
2	-5	43	43
3	-5	25	24
-1	-5	33	33
-2	-5	14	16
-3	-5	36	36
-5	-5	14	11
-8	-5	18	16
-11	-5	14	17
0	-6	15	10
2	-6	34	30
3	-6	22	17
-1	-6	15	13
-2	-6	49	51
-4	-6	58	56
-6	-6	30	26
-7	-6	29	30
-8	-6	26	26
-9	-6	27	29
-10	-6	19	23
-11	-6	8	10
0	-7	57	57
1	-7	32	30
2	-7	47	45
3	-7	21	18
4	-7	48	45
-1	-7	28	26
-2	-7	23	22
-7	-7	16	19
-8	-7	14	15
-9	-7	18	25
-10	-7	12	14
1	-8	14	14
4	-8	27	26
-1	-8	35	38
-3	-8	16	17
-4	-8	23	24
-5	-8	12	11
-6	-8	27	28
-8	-8	11	13
0	-9	15	15
-2	-9	13	12
-3	-9	12	13

The initial refinement converged at values for R_1 and R_2[17] of 0.082 and 0.098. Corrections for absorption and for extension of spot size followed by further refinement reduced R_1 and R_2 to 0.072 and 0.082, respectively. At this stage it was observed that a number of low-angle reflections with high raw intensities showed large discrepancies, F_o invariably being less than F_c. With this evidence for secondary extinction, the approximate correction suggested by Zachariasen[18] was applied. The form of the correction was $F(\text{corrected}) = F_o(1 + CI)$ where C was a variable in the least-squares process and I was the raw intensity. Refinement with inclusion of this correction reduced R_1 and R_2 to their final values of 0.067 and 0.077. The value obtained for the extinction parameter C was 5.1 (5) × 10^{-6} on an absolute scale. Final positional and thermal parameters, with esd's are listed in Table I, and observed and calculated structure factors are compared in Table II.

In a final electron density difference map there were peaks of height up to 1.2 $e^-/Å^3$ close to the Co atoms. The highest peak not within 0.8 Å of a Co atom was 0.6 $e^-/Å^3$, or approximately one-sixth of the height of a carbon atom in the structure. Attempts to locate the hydrogen atom proved fruitless. Presumably the situation would be more favorable if any anisotropy of the Co atoms was accommodated by the inclusion of more thermal parameters. However we regard the presence of the hydrogen atom as definitely established by the

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[17] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

[18] W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

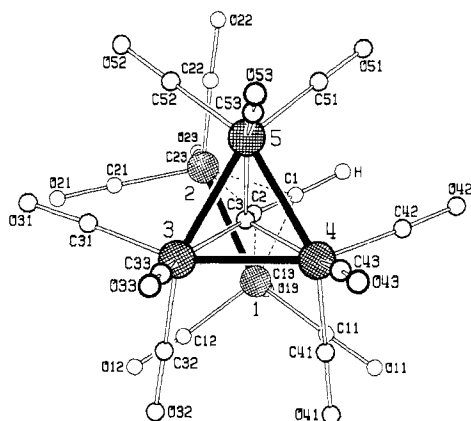Figure 1.—One molecule of $Co_5(CO)_{15}C_3H$ with the Co_3 triangle nearly edge on.

Figure 2.—One molecule of $Co_5(CO)_{15}C_3H$ viewed normal to the Co_3 triangle.

mass spectral evidence presented below. Further attempts to find it using the existing data set were therefore considered unjustifiable.

Description of Structure and Discussion

The crystal structure consists of well-separated monomeric molecules of $Co_5(CO)_{15}C_3H$, no intermolecular contact being shorter than 3.0 Å. Views of the whole molecule are shown in Figures 1 and 2. (Parentheses have been omitted from atom labels in order to simplify the diagrams but the numbering scheme is the same as in Table I.) Bond lengths and angles are listed in Tables III and IV with intramolecular nonbonded contacts in Table V.

In the molecule the $-CCo_3(CO)_9$ unit of the parent compound is retained with its idealized C_{3v}-3m symmetry and is linked to a hexacarbonyldicobalt unit by means of an acetylene bridge. The $Co_2(CO)_6C_2H_2$ group has idealized symmetry C_s-m. Similar arrangements have previously been found in complexes of Co_2-$(CO)_6$ with diphenylacetylene[19] and with the cyclic acetylene C_6F_6[20] and also in a related complex of $Ni_2(C_5H_5)_2$ with diphenylacetylene.[21] However, the linkage of such units to other metal clusters has not previously been found.

(19) W. G. Sly, *J. Amer. Chem. Soc.*, **81**, 18 (1959); revised bond lengths reported as personal communication by D. A. Brown, *J. Chem. Phys.*, **33**, 1057 (1960).
(20) N. A. Bailey and R. Mason, *J. Chem. Soc. A*, 1293 (1968).
(21) O. S. Mills and B. W. Shaw, *J. Organometal. Chem.*, **11**, 595 (1968).

TABLE III
BOND DISTANCES (Å)[a]

Co(1)-Co(2)	2.447 (4)	Co(3)-C(31)	1.76 (2)
		Co(3)-C(32)	1.75 (2)
Co(3)-Co(4)	2.462 (5)	Co(4)-C(41)	1.71 (2)
Co(3)-Co(5)	2.470 (6)	Co(4)-C(42)	1.75 (2)
Co(4)-Co(5)	2.485 (4)	Co(5)-C(51)	1.78 (2)
Av	2.472 (10)	Co(5)-C(52)	1.75 (2)
		Av	1.75 (2)
Co(1)-C(11)	1.75 (2)		
Co(2)-C(22)	1.75 (2)	Co(3)-C(33)	1.77 (2)
Av	1.75 (1)	Co(4)-C(43)	1.78 (2)
		Co(5)-C(53)	1.82 (2)
Co(1)-C(12)	1.80 (2)	Av	1.79 (2)
Co(1)-C(13)	1.78 (2)		
Co(2)-C(21)	1.81 (2)	Co(3)-C(3)	1.89 (1)
Co(2)-C(23)	1.77 (2)	Co(4)-C(3)	1.93 (1)
Av	1.79 (2)	Co(5)-C(3)	1.93 (2)
		Av	1.92 (2)
Co(1)-C(1)	1.94 (2)		
Co(2)-C(1)	1.95 (1)		
		C(1)-C(2)	1.34 (2)
		C(2)-C(3)	1.46 (2)
Co(1)-C(2)	2.01 (2)		
Co(2)-C(2)	1.99 (2)	C-O	1.14 (2)-1.19 (2)
		Mean of 15 values	1.17 (2)

[a] Estimated standard deviations for individual bonds were calculated using variances and covariances in positional parameters and variances only in cell parameters. They may be underestimates because of the neglect of anisotropic thermal motion. Mean values of bonds assumed chemically equivalent are indicated and their associated uncertainties are rms deviations given by the expression $(\Sigma^n(x_i - \bar{x})^2/n)^{1/2}$, where there are n observations.

From the view shown in Figure 2 it can be seen that the whole molecule possesses approximate symmetry C_s-m, exact symmetry being destroyed by a significant (6.2°) rotation of the Co(1)-Co(2) bond (with its associated carbonyls) away from its idealized orientation parallel to the Co(4)-Co(5) edge of the Co_3 triangle. There are a number of close nonbonded contacts between CO groups in the two parts of the molecule and most of the distortions from normal bond angle values can be related to the repulsions arising from these close contacts. Thus, of the equatorial CO groups attached to the Co_3 triangle, those which are involved in the closest contacts with the $Co_2(CO)_6$ unit are displaced toward the Co_3 plane. This displacement is reflected in the values of the dihedral angles between the Co_3 triangle and the planes formed by each Co atom and its associated equatorial CO groups. (All of the angles quoted below relate to mean planes involving Co, C, and O atoms; they are within 0.2° of the values obtained by considering instead the exact CoOO planes.) For Co(3), both of whose O atoms are within 3.0 Å of O atoms in the $Co_2(CO)_6$ unit, this dihedral angle is 22°. The corresponding angle for Co(4) is 27°, while for Co(5), whose equatorial O atoms are least involved in contacts with the $Co_2(CO)_6$ unit, the value is 30°. By comparison, in $CH_3CCo_3(CO)_9$[8] and $Co_3(CO)_{10}BH_2N$-$(C_2H_5)_3$[22] where there are no such contacts, the average values are 29 and 32°, respectively.

(22) F. Klanberg, W. B. Askew, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2265 (1968).

Table IV

Bond Angles (deg)[a]

Co(3)-Co(4)-Co(5)	59.9 (1)		C(2)-C(3)-Co(3)	140 (1)
Co(3)-Co(5)-Co(4)	59.6 (1)		C(2)-C(3)-Co(4)	128 (1)
Co(4)-Co(3)-Co(5)	60.5 (2)		C(2)-C(3)-Co(5)	126 (1)
Av	60.0			
			C(31)-Co(3)-Co(4)	155.3 (6)
Co(3)-C(3)-Co(4)	80.4 (6)		C(32)-Co(3)-Co(5)	152.6 (6)
Co(3)-C(3)-Co(5)	80.6 (6)		C(41)-Co(4)-Co(5)	151.7 (6)
Co(4)-C(3)-Co(5)	80.2 (5)		C(42)-Co(4)-Co(3)	152.2 (7)
Av	80.4		C(51)-Co(5)-Co(3)	149.6 (7)
			C(52)-Co(5)-Co(4)	152.6 (6)
C(3)-Co(3)-Co(4)	50.5 (4)		Av	152.3
C(3)-Co(3)-Co(5)	50.5 (5)			
C(3)-Co(4)-Co(5)	50.0 (5)		C(11)-Co(1)-C(12)	104.1 (8)
C(3)-Co(4)-Co(3)	49.1 (4)		C(12)-Co(1)-C(13)	102.2 (9)
C(3)-Co(5)-Co(3)	48.9 (4)		C(21)-Co(2)-C(23)	101.4 (8)
C(3)-Co(5)-Co(4)	49.9 (4)		C(22)-Co(2)-C(21)	102.7 (8)
Av	49.8		Av	102.6
C(3)-Co(3)-C(33)	141.7 (7)		C(11)-Co(1)-C(13)	95.0 (9)
C(3)-Co(4)-C(43)	142.7 (7)		C(22)-Co(2)-C(23)	96.0 (9)
C(3)-Co(5)-C(53)	142.1 (7)			
Av	142.2		C(11)-Co(1)-Co(2)	148.1 (7)
			C(22)-Co(2)-Co(1)	147.6 (6)
C(31)-Co(3)-C(32)	97.6 (8)			
C(41)-Co(4)-C(42)	97.3 (9)		C(12)-Co(1)-Co(2)	101.6 (5)
C(51)-Co(5)-C(52)	97.5 (9)		C(21)-Co(2)-Co(1)	102.8 (6)
Av	97.5			
			C(11)-Co(1)-C(1)	97.8 (8)
C(3)-Co(3)-C(31)	107.1 (7)		C(22)-Co(2)-C(1)	97.5 (8)
C(3)-Co(3)-C(32)	103.2 (7)		C(11)-Co(1)-C(2)	103.6 (8)
C(3)-Co(4)-C(41)	103.9 (7)		C(22)-Co(2)-C(2)	102.6 (8)
C(3)-Co(4)-C(42)	103.8 (8)			
C(3)-Co(5)-C(51)	101.3 (8)		C(13)-Co(1)-C(1)	106.7 (8)
C(3)-Co(5)-C(52)	105.0 (7)		C(23)-Co(2)-C(1)	109.2 (7)
Av	104.1			
			C(1)-C(2)-Co(1)	67.2 (9)
C(31)-Co(3)-C(33)	99.1 (8)		C(1)-C(2)-Co(2)	68.4 (9)
C(32)-Co(3)-C(33)	100.3 (8)			
C(41)-Co(4)-C(43)	99.9 (8)		C(1)-Co(1)-C(2)	39.7 (6)
C(42)-Co(4)-C(43)	101.2 (9)		C(1)-Co(2)-C(2)	39.9 (6)
C(51)-Co(5)-C(53)	102.8 (9)			
C(52)-Co(5)-C(53)	100.4 (9)		C(1)-Co(1)-Co(2)	50.5 (4)
Av	100.6		C(1)-Co(2)-Co(1)	50.3 (5)
C(31)-Co(3)-Co(5)	98.1 (6)		C(13)-Co(1)-Co(2)	97.8 (7)
C(32)-Co(3)-Co(4)	98.2 (6)		C(23)-Co(2)-Co(1)	98.1 (6)
C(41)-Co(4)-Co(3)	95.9 (6)			
C(42)-Co(4)-Co(5)	99.5 (7)		C(12)-Co(1)-C(2)	104.0 (7)
C(51)-Co(5)-Co(4)	98.3 (7)		C(21)-Co(2)-C(2)	102.7 (7)
C(52)-Co(5)-Co(3)	96.7 (6)			
Av	97.8		C(12)-Co(1)-C(1)	141.8 (7)
			C(21)-Co(2)-C(1)	141.1 (7)
C(33)-Co(3)-Co(4)	96.7 (6)		C(13)-Co(1)-C(2)	142.8 (8)
C(33)-Co(3)-Co(5)	99.2 (6)		C(23)-Co(2)-C(2)	145.3 (8)
C(43)-Co(4)-Co(3)	100.5 (6)			
C(43)-Co(4)-Co(5)	98.9 (6)		C(2)-C(1)-Co(1)	73.2 (10)
C(53)-Co(5)-Co(3)	100.9 (6)		C(2)-C(1)-Co(2)	71.8 (9)
C(53)-Co(5)-Co(4)	97.7 (6)			
Av	99.0		C(3)-C(2)-Co(1)	133.6 (12)
			C(3)-C(2)-Co(2)	135.3 (10)
Co-C-O	177-180			
Mean of 15 values	177.5		C(2)-Co(1)-Co(2)	51.3 (4)
			C(2)-Co(2)-Co(1)	52.2 (5)
C(1)-C(2)-C(3)	145.6 (14)			
			Co(1)-C(1)-Co(2)	79.2 (6)
			Co(1)-C(2)-Co(2)	76.5 (5)

[a] See footnote to Table III. Rms deviations of mean values are not given because in general these far exceed esd's of individual angles.

Table V

Selected Intramolecular Nonbonded Distances (Å)

C(31)···C(32)	2.64		C(31)···C(33)	2.69
C(41)···C(42)	2.60		C(32)···C(33)	2.70
C(51)···C(52)	2.65		C(41)···C(43)	2.67
			C(42)···C(43)	2.73
C(31)···C(52)	2.92		C(51)···C(53)	2.81
C(32)···C(41)	2.89		C(52)···C(53)	2.74
C(42)···C(51)	3.03			
			C(13)···C(23)	2.97
C(33)···C(43)	3.00			
C(53)···C(33)	3.09		C(12)···C(21)	3.24
C(43)···C(53)	3.01			
			O(11)···O(41)	3.06
C(11)···C(12)	2.81		O(12)···O(32)	2.98
C(11)···C(13)	2.61		O(21)···O(31)	2.95
C(12)···C(13)	2.79		O(22)···O(52)	3.24
C(21)···C(22)	2.79			
C(21)···C(23)	2.78			
C(22)···C(23)	2.62			

Of considerable interest are the dimensions of the carbon chain. The value of 1.34 (2) Å for the C(1)–C(2) acetylene bridge and the angle of 146 (1)° it makes with C(2)–C(3) may be compared with values observed in the closely related compounds Co₂(CO)₆C₆H₅C₂C₆H₅[19] (1.37 Å, 138°) and Ni₂(C₅H₅)₂C₆H₅C₂C₆H₅[21] (1.35 Å). Corresponding bond lengths in other examples, where the acetylene bridge is associated with a cluster of at least three metal atoms, are Co₄(CO)₁₀C₂H₅C₂C₂H₅[23] (1.44 (2) Å), Fe₃(CO)₉C₆H₅C₂C₆H₅[24] (1.41 (2) Å, 124°), and Fe₃(CO)₈(C₆H₅C₂C₆H₅)₂[25] (1.38 (3) Å). These dimensions indicate that the bond in the acetylene bridge is more nearly a double than a triple bond (the C–C lengths in acetylene and ethylene are 1.20 and 1.34 Å, respectively). Whatever detailed description of the bonding is preferred, there must therefore be considerable delocalization of the π orbitals of the acetylene into the available Co orbitals. The acetylene bonds are systematically longer in the compounds containing clusters of three or four atoms in all of which compounds the acetylene group itself is associated with more than two metal atoms, and hence there may be even greater delocalization of the π electrons. The limited information available from these studies on the C≡C—C angles indicates a general reduction in size as the acetylene bond lengthens, consistent with increasing p character in the outwardly directed carbon atomic orbitals.

The C(2)–C(3) bond length of 1.46 (2) Å agrees with other values found for bonds linking four-coordinate and two-coordinate carbon atoms.[26] The C(2)–C(3) bond departs significantly from its ideal orientation normal to the Co₃ plane, as can be observed from the inequality of the angles C(2)–C(3)–Co(3) (140 (1)°), C(2)–C(3)–Co(4) (128 (1)°), and C(2)–C(3)–Co(5) (126 (1)°). This distortion can be related to the general state of strain of the whole molecule caused by the close nonbonded approaches of the carbonyl groups.

(23) L. F. Dahl and D. L. Smith, *J. Amer. Chem. Soc.*, **84**, 2450 (1962).
(24) J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *ibid.*, **88**, 292 (1966).
(25) R. P. Dodge and V. Schomaker, *J. Organometal. Chem.*, **3**, 274 (1965).
(26) "Tables of Interatomic Distances," Special Publication No. 18, The Chemical Society, London, 1965.

The remaining bond lengths are normal with the axial Co–C bonds in the $Co_3(CO)_9$ unit systematically longer than the equatorial bonds as previously observed.[1,22]

Infrared and Nmr Spectra.—Infrared spectral data are presented in Table VI. Of particular importance

TABLE VI

INFRARED SPECTRUM (CM^{-1}) OF $Co_5(CO)_{15}C_3H^{a,b}$

4189 vw		1465 w	$\nu(C=C)$
4169 vw		1046 w	$\nu(C—C)$
4164 vw			
4136 vw	$\nu(CO)$	870 w	$\gamma(CH), \delta(CCC)$
4129 vw	overtone and	784 w	
4123 vw	combination bands		
4113 vw, sh		640 m	
4085 vw		610 w	
4058 vw		583 w	
4010 vw		554 m	
		529 s	
3076 w	$\nu(CH)$	517 s	
		496 s	$\nu(Co—C)$ and
		460 w	$\delta(Co—C—O)$
2515 vw		447 w	
2473 vw		431 w	
2290 vw		414 w	
2108.7 ms		406 w	
2084.1 s		401 w	
2064.8 vs			
2058.4 vs		385 w	
2049.5 ms		377 w, sh	
2043.5 ms	$\nu(CO)$	360 vw	$\delta(CCC) + ?$
2033.8 s		357 vw	
2029.9s			
2021 w			
2016 w			
1981 w			

^{a} From 4200 to 800 cm^{-1} in CCl$_4$ or n-octane (2200–1900 cm^{-1}); from 800 to 200 cm^{-1} in Nujol mull. ^{b} Frequencies in the range 2200–1900 cm^{-1} are accurate to ±0.2 cm^{-1}; the remainder, to ±1 cm^{-1}.

is the evidence for the presence of a C–H bond involving C(1). A weak band at 3076 cm^{-1} attributable to a (C–H) stretching mode was observed in both the mull and solution spectra. Similar bands are found in $Co_2(CO)_6C_2H_2$[27] at 3118 and 3087 cm^{-1}, positions characteristic of an *ethylenic* C–H bond.

Recent work has shown that the highest $\nu(CO)$ mode (probably the totally symmetrical "breathing" mode) in $YCCo_3(CO)_9$ compounds rarely occurs above 2103 cm^{-1} unless the apical substituent Y is a strong electron-withdrawing group.[28] As this band in $Co_5(CO)_{15}C_3H$ is found at 2108.7 cm^{-1} (cf. 2110 cm^{-1} in $ClCCo_3(CO)_9$), it may be inferred that the $Co_2(CO)_6C_2$ group is electron withdrawing.

It has been suggested that the highest frequency bands in the region 650–600 cm^{-1} in $YCCo_3(CO)_9$ compounds are due to Co–C stretching absorptions associated with Co–C σ bonds as distinct from the Co–C-(carbonyl) absorptions.[9] Thus we assign the bands at 640 and 610 cm^{-1} to $\nu(Co–C_\sigma)$; the comparable band in $ClCCo_3(CO)_9$ occurs at 601 cm^{-1}. Further discussion of the infrared data will be deferred to a later paper in this series when comparisons with other compounds will be made.

Further evidence for the presence of a proton comes

(27) H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby, and I. Wender, *J. Amer. Chem. Soc.*, **78**, 120 (1956); Y. Iwashita, F. Tamura, and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969); B. H. Robinson and J. L. Spencer, unpublished results.
(28) B. H. Robinson and J. L. Spencer, unpublished results.

from the ^{1}H nmr spectrum where a weak singlet was observed at τ 3.12. This may be compared with the singlet at τ 4.18 found in $Co_2(CO)_6C_2H_2$. This relative deshielding in $Co_5(CO)_{15}C_3H$ together with the shifts in CO stretching frequencies mentioned above are indicative of electron delocalization in the Co_3C_3 unit.

Mass Spectrum.—Details of the mass spectrum are given in Table VII. Perhaps the best evidence for the

TABLE VII

MASS SPECTRUM OF $Co_5(CO)_{15}C_3H^a$

Ion	A	Ion	A
$Co_5(CO)_{15}C_3H^{+\,b}$	18	$Co_5(CO)C_3H^+$	14
$Co_5(CO)_{14}C_3H^+$	15	$Co_5(CO)C_3^+$	0.7
$Co_5(CO)_{13}C_3H^+$	31	$Co_4(CO)_3C_3H^+$	1.5
$Co_5(CO)_{12}C_3H^+$	10	$Co_5C_3H^{+\,c}$	40
$Co_5(CO)_{11}C_3H^+$	6	$Co_5C_3^{+\,b}$	3.8
$Co_5(CO)_{10}C_3H^+$	15	$Co_4(CO)_2C_3H^+$	1.4
$Co_5(CO)_9C_3H^+$	100	$Co_4(CO)C_3H^+$	1.8
$Co_5(CO)_8C_3H^+$	55	$Co_4(CO)C_3^+$	0.2
$Co_4(CO)_{10}C_3H^+$	0.2	$Co_4C_3H^{+\,b}$	18
$Co_5(CO)_7C_3H^+$	41	$Co_4C_3^+$	4.3
$Co_4(CO)_9C_3H^+$	0.3	Co_4C^+	0.5
$Co_5(CO)_6C_3H^+$	35	$Co_3C_3H^+$	0.8
$Co_4(CO)_8C_3H^+$	0.2	$Co_3C_3^+$	4.3
$Co_5(CO)_5C_3H^+$	31	$Co_3C_2^+$	0.9
$Co_4(CO)_7C_3H^+$	1.7	Co_3C^+	0.9
$Co_5(CO)_4C_3H^+$	30	$Co_2C_3H^+$	3.1
$Co_4(CO)_6C_3H^+$	2	$Co_2C_3^+$	3.8
$Co_5(CO)_3C_3H^+$	26	$Co_2C_2H^+$	0.4
$Co_4(CO)_5C_3H^+$	1.7	$Co_2C_2^+$	0.6
$Co_5(CO)_2C_3H^+$	20	Co_2C^+	0.3
$Co_5(CO)_2C_3^+$	0.5	Co_2^+	0.2
$Co_4(CO)_4C_3H^+$	1.7		

^{a} Metastable peaks were not observed except for the successive loss of carbonyl fragments. ^{b} Doubly charged species Co_5-$(CO)_{15}C_3H^{2+} \rightarrow Co_5C_3H^{2+}$ also $Co_5C_3^{2+}$ and $Co_4C_3H^{2+}$ were observed. ^{c} Mass measured, 331.6732; calcd for Co_5C_3H, 331.6733.

existence of a hydrogen atom in $Co_5(CO)_{15}C_3H$ is the presence of the parent molecular ion $Co_5(CO)_{15}C_3H^+$ and the ion $Co_5C_3H^+$. The latter ion has been mass measured.

As expected,[29] the initial fragmentation process involves the progressive loss of carbon monoxide with retention of the $Co_5C_3H^+$ unit

$$Co_5(CO)_{15}C_3H^+ \longrightarrow Co_5(CO)_{15-n}C_3H^+ + nCO$$
$$(n = 0 \longrightarrow 15)$$
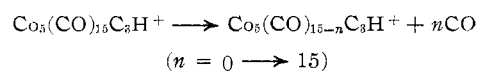
Appropriate metastable peaks for this breakdown were observed.

A totally unexpected fragmentation series arising from an ion $Co_4(CO)_{10}C_3H^+$ was noted

$$Co_4(CO)_{10}C_3H^+ \longrightarrow Co_4(CO)_{10-n}C_3H^+ + nCO$$
$$(n = 0 \longrightarrow 10)$$
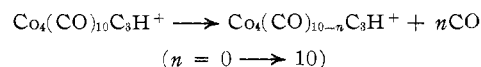
These ions do not arise from an impurity as they appeared in the same relative abundance with different samples. It is difficult to account for this fragmentation in terms of the molecular structure of $Co_5(CO)_{15}$-C_3H. A fragmentation series beginning with the ions $Co_3(CO)_9C_3H^+$ or $Co_2(CO)_6C_2H^+$ would be reasonable (no such ions were ever observed) but there seems no

(29) M. I. Bruce, *Advan. Organometal. Chem.*, **6**, 275 (1968).

reason why one cobalt atom or a $Co(CO)_5$ group should be easily lost. Although acetylene derivatives of the type $Co_4(CO)_{10}C_2R_2$ are known,[23,30] the ion $Co_4(CO)_{10}$-C_3H^+ does not have the correct composition or fragmentation pattern to indicate that a species $Co_4(CO)_{10}$-C_2H or $Co_4(CO)_{10}HC_2CH_3$ is formed in the mass spectrometer. Nevertheless it is apparent that the predominant secondary fragmentation process from the $Co_5C_3H^+$ ion is one of successive removal of cobalt from the cluster, as in the case of the parent $YCCo_3(CO)_9$ compounds[31]

$$Co_5C_3H^+ \xrightarrow{-Co} Co_4C_3H^+ \xrightarrow{-Co} Co_3C_3H^+ \xrightarrow{-Co} Co_2C_3H^+$$

$$\left\downarrow{-H} \quad\quad \right\downarrow{-H} \quad\quad \left\downarrow{-H} \quad\quad \right\downarrow{-H}$$

$$Co_5C_3{}^+ \xrightarrow{-Co} Co_4C_3{}^+ \xrightarrow{-Co} Co_3C_3{}^+ \xrightarrow{-Co} Co_2C_3{}^+$$
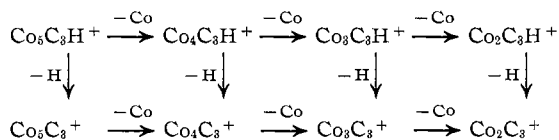
Notably absent from the spectrum are rearrangement ions of the type Co_3H^+ which are in relatively high abundance in the spectra of $CH_3CCo_3(CO)_9$, C_6H_5-$CCo_3(CO)_9$, and $HCCo_3(CO)_9$. This provides further confirmation that the hydrogen is indeed bonded to the terminal carbon atom C(1).

An important feature of the spectrum is the presence in reasonable abundance of doubly charged ions

$$Co_5(CO)_{15}C_3H^{2+} \longrightarrow Co_5(CO)_{15-n}C_3H^{2+} + nCO$$

$$(n = 0 \longrightarrow 15)$$
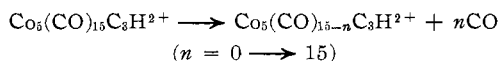
It is well known that doubly charged species are found in the mass spectra of very stable carbonyl clusters only, generally those of the heavier transition elements,[29,32] and they may therefore be taken as a guide to

the overall stability of the cluster. Moreover such species were found only in $C_6H_5CCo_3(CO)_9$ of the parent clusters.[31] It would seem that carbide clusters of the type investigated here are particularly stable units, especially to electron impact, and that it is the tetravalent carbon atoms rather than strong cobalt–cobalt bonding which impart unusual stability to these clusters. In this regard the absence of fragments $Co_n{}^+$, $Co_5C_2{}^+$, Co_5C^+, and $Co_4C_2{}^+$ is significant as is also the fact that singly charged pentacobalt carbide ions account for 90.8% of the metal-containing ions.

Pure samples of the analogous compounds $Co_5(CO)_{15}$-C_3F and $Co_5(CO)_{15}C_3CH_3$ have not yet been prepared. However they have appeared as impurities in several mass spectra[33] of $Co_5(CO)_{15}C_3H$. Besides confirming the presence of an additional group in these molecules, the breakdown patterns follow exactly those discussed above.

An Attempted Preparation.—After the crystal structure had been determined, it seemed that a possible alternative method of preparing the compound might be to treat a $Co_2(CO)_6C_2H_2$ complex with the parent cluster compound. Consequently $Co_2(CO)_6C_2H_2$[34] was mixed with $BrCCo_3(CO)_9$ in different solvents and at various temperatures but there was never any indication of a reaction between the two Co complexes.

(30) U. Kruerk and W. Hubel, *Chem. Ber.*, **94**, 2829 (1961).

(31) B. H. Robinson and W. S. Tham, *J. Chem. Soc. A*, 1784 (1968).

(32) B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, *ibid., A*, 341 (1967).

(33) B. H. Robinson, R. Hodges, and J. L. Spencer, to be submitted for publication.

(34) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. H. Wotiz, R. Markby, and I. Wender, *J. Amer. Chem. Soc.*, **76**, 1457 (1954).