ogous bis-diamine complexes, where the diacido ligands are not axially symmetric, there can exist a further source of asymmetry in the molecule which may contribute to the observed optical activity.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Structural Studies of Derivatives of Methinyltricobalt Enneacarbonyls.
V.[1] Crystal Structure of Bis(methinyltricobalt enneacarbonyl), $[CCo_3(CO)_9]_2$

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The crystal and molecular structure of bis(methinyltricobalt enneacarbonyl), $[CCo_3(CO)_9]_2$, has been determined by three-dimensional X-ray analysis. The crystals are monoclinic, space group C_{2h}^6-$C2/c$, with four molecules in a unit cell of dimensions $a = 16.368$ (3), $b = 9.450$ (2), $c = 18.906$ (4) Å, and $\beta = 106.79$ (2)°. X-Ray data were collected by counter methods using Mo Kα radiation. Full-matrix least-squares refinement with Co atoms treated anisotropically led to a final value of the conventional R factor of 0.054 for the 1650 independent reflections having $F^2 > \sigma(F^2)$. The crystal structure consists of discrete dimeric molecular units each with a crystallographic dyad axis and with idealized symmetry D_3-32. These are derived from the parent compound $CH_3CCo_3(CO)_9$ by elimination of the terminal methyl group and direct linkage of the triply bridging carbon atoms. The central formally single C–C bond is extremely short at 1.37 (1) Å. The two Co_3 triangles are semieclipsed to minimize nonbonded repulsions and the mean Co–Co bond length is 2.456 (2) Å.

Introduction

The compound $Co_6(CO)_{18}C_2$ was first reported by Allegra, Peronaci, and Ercoli,[2] who prepared it by warming bromomethinyltricobalt enneacarbonyl, $BrCCo_3(CO)_9$, in anhydrous toluene. They assumed that it was a dimer containing two connected $-CCo_3(CO)_9$ units of the type first characterized in $CH_3CCo_3(CO)_9$.[3]

A number of further products of the reaction between $YCCo_3(CO)_9$ (Y = Cl, Br) and arenes have been isolated[4,5] and structurally characterized[1,5–7] and all have proved to be based on the $-CCo_3(CO)_9$ structural entitity containing a CCo_3 tetrahedron. Study of the detailed geometries of these molecules pointed to the desirability of a precise structure determination of $[CCo_3(CO)_9]_2$, a preliminary account of which we have reported.[8]

Experimental Section

Preparation of $[CCo_3(CO)_9]_2$.—The compound was prepared by Dr. B. H. Robinson, University of Otago, from $BrCCo_3(CO)_9$ and toluene using the method previously reported.[2] Dark brown air-stable irregularly shaped crystals were obtained by recrystallization from the solvent.

Crystallographic Data.[9]—$Co_6C_{20}O_{18}$, mol wt 881.8, is monoclinic with $a = 16.368$ (3), $b = 9.450$ (2), $c = 18.906$ (4) Å, $\beta = 106.79$ (2)°; $V = 2801$ Å^3; $d_{\text{obsd}} = 2.10$ (2) g/cm^3; $Z = 4$; $d_{\text{calcd}} = 2.09$ g/cm^3; μ(Mo Kα) = 13.5 cm^{-1}. Systematic absences occurred for hkl reflections when $(h + k)$ was odd and for $00l$ reflections when l was odd. Possible space groups are therefore C_{2h}^6-$C2/c$ or C_s^4-Cc. The centrosymmetrical space group $C2/c$ was indicated both by intensity statistics of the full data set and a by the distribution of peaks in a three-dimensional Patterson map and was confirmed by the subsequent successful structure solution and refinement. This space group requires molecular symmetry C_i-$\bar{1}$ or C_2-2.

Unit cell dimensions and their estimated standard deviations were obtained at room temperature (23 ± 2°) with Mo Kα_1 radiation (λ 0.7093 Å) using the least-squares procedure described below. The experimental density was determined using a calibrated density gradient column containing a mixture of bromoform and m-xylene.

Diffraction data were obtained from a crystal fragment whose shape approximated to that of a parallelepiped with faces defined by the forms {001}, {010}, and {20$\bar{1}$}. Crystal cross sections normal to these faces were 0.15, 0.25, and 0.32 mm, respectively. All quantitative data were obtained from a Hilger-Watts four-circle diffractometer controlled by a PDP-8I computer using Zr-filtered Mo Kα radiation. A preliminary mosaicity check of the crystal by means of open-counter ω scans showed that the width at half-height of intense low-angle reflections was acceptably low at 0.10°. The crystal was mounted on a goniometer head in random orientation and 12 strong high-angle reflections were accurately centered through a circular 1.0-mm diameter diffracted-beam collimator. The setting angles so obtained formed the basis for a least-squares refinement of lattice constants and an orientation matrix. The method was as outlined by Busing[10] and adapted to our own system.

Intensity data were collected by use of an X-ray beam takeoff angle of 3° and in the bisecting mode ($\omega = \theta$). A diffracted beam collimator of circular cross section, diameter 5 mm, was positioned 23 cm from the crystal. The θ–2θ scan technique was used, counts being recorded at equal steps of 0.01° in θ. Scans were symmetric about the Mo K$\bar{\alpha}$ counter setting and 15-sec stationary-crystal, stationary-counter background counts were recorded at each end of the scan. For reflections in the range $0.1° < \theta < 18°$, the θ-scan range was 0.4° with counting for 1.5 sec at each step. For reflections in the range $18° < \theta < 23°$ the scan range was 0.6° with counting for 1 sec at each step, so that the total scan counting time was 60 sec in each case. Attenuators were automatically inserted in the primary beam if the total scan count exceeded 150,000. The intensities of three

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[1] Part IV: R. J. Dellaca and B. R. Penfold, *Inorg. Chem.*, **10**, 1269 (1971).

[2] G. Allegra, E. M. Peronaci, and R. Ercoli, *Chem. Commun.*, 549 (1966).

[3] P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 261 (1967).

[4] B. H. Robinson, J. L. Spencer, and R. Hodges, *Chem. Commun.*, 1480 (1968).

[5] R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, **9**, 2204 (1970).

[6] G. Allegra and S. Valle, *Acta Crystallogr., Sect. B*, **25**, 107 (1969).

[7] R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, **9**, 2197 (1970).

[8] M. D. Brice, R. J. Dellaca, B. R. Penfold, and J. L. Spencer, *J. Chem. Soc. D*, 72 (1971).

[9] Here and throughout this paper, the figures given in parentheses are estimated standard deviations in the least significant digits quoted.

[10] W. R. Busing in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 319.

standard reflections were monitored throughout the data collection and showed no significant variation. The data were scaled only to allow for the different scan widths. A standard deviation was assigned to each measured intensity using the expression

$$\sigma(I) = [C + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where C is the scan count, B_1 and B_2 are background counts, t_c and t_b are scan and background times, respectively, and p is an empirical coefficient[11] of the net count I, an initial value of 0.05 being assigned to p. Of the total of 1947 independent reflections recorded within the range $\theta < 23°$, 297 had intensities I less than $\sigma(I)$. Absorption corrections were applied before final refinement using a gaussian integration method, the transmission factors ranging from 0.68 to 0.83.

Structure Solution and Refinement.—A unique set of signs for structure factors was obtained by a standard symbolic addition procedure and the resultant Fourier E map contained three predominant peaks which proved to be the sites of the three independent Co atoms. Preliminary least-squares refinement of their positions led to values of R_1 and R_2[12] of 0.26 and 0.33, respectively.

At this stage a novel method was used to locate the carbon and oxygen atoms. In the five tricobalt enneacarbonyl derivatives previously determined in this laboratory the conformations of the $CCo_3(CO)_9$ moieties were closely similar. The same relative positions of carbon and oxygen atoms found for one of these compounds $[C_2Co_3(CO)_9]_2$[5] were therefore assumed. These positions were sufficiently close approximations for the refinement to proceed as described below.

In all least-squares calculations the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, the weight w being taken as $4F_o^2/[\sigma(F_o^2)]^2$. The usual tabulations of atomic scattering factors[13] for Co, C, and O were used, those for Co only being corrected for anomalous dispersion; values for $\Delta f'$ and $\Delta f''$ were interpolated from Cromer's tables.[14]

Refinement of positional and isotropic thermal parameters for all 22 atoms converged at $R_1 = 0.08$ and $R_2 = 0.09$. Further refinement with anisotropic thermal parameters for Co atoms only (suggested by difference electron density maps) lowered R_1 to 0.066 and R_2 to 0.076. There was no evidence of pronounced thermal anisotropy of the carbonyl groups.

Examination of average values of the minimized function over ranges of $|F_o|$ and $(\sin \theta)/\lambda$ showed that the most intense reflections were being overweighted. The data were therefore reprocessed with an increased value of 0.07 for the parameter p in the expression for $\sigma(I)$. Absorption corrections were then applied and the structure factors for the equivalent forms (hkl) and $(\bar{h}\bar{k}\bar{l})$ were averaged. All parameters were then refined to convergence, the maximum parameter shift on the last cycle being less than one-tenth of its estimated standard deviation. The minimized function now showed very little systematic dependence on $|F_o|$ or $\sin \theta$. Examination of intense low-angle data did however indicate that secondary extinction was appreciable. This effect was corrected for, assuming the angularly dependent extinction function derived by Zachariasen[15] and incorporating this into the least-squares equations in a manner similar to that as suggested by Larson.[16]

Final positional and thermal parameters for all atoms are listed in Tables I and II and observed and calculated structure factors for all 1650 reflections used in the refinement (those for which $F_o^2 \geq \sigma(F_o^2)$ are compared in Table III.[17]

TABLE I

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR $[CCo_3(CO)_9]_2$

Atom	x	y	z	B, Å^2
Co(1)	0.40066 (6)	0.14473 (10)	0.13720 (5)	2.3[a]
Co(2)	0.54594 (7)	0.20994 (10)	0.13718 (6)	2.3[a]
Co(3)	0.44062 (7)	0.39521 (10)	0.13716 (6)	2.3[a]
C(1)	0.4868 (4)	0.2492 (7)	0.2121 (4)	1.8 (2)
C(11)	0.3060 (5)	0.1738 (9)	0.1651 (5)	2.9 (2)
C(12)	0.3528 (6)	0.1228 (9)	0.0403 (5)	3.5 (2)
C(13)	0.4148 (5)	−0.0375 (10)	0.1620 (5)	3.2 (2)
C(21)	0.6424 (6)	0.3117 (9)	0.1618 (5)	3.3 (2)
C(22)	0.5925 (5)	0.0406 (9)	0.1649 (4)	2.9 (2)
C(23)	0.5318 (6)	0.1966 (9)	0.0402 (5)	3.6 (2)
C(31)	0.5161 (5)	0.5359 (9)	0.1656 (4)	2.8 (2)
C(32)	0.3544 (6)	0.4764 (9)	0.1625 (5)	3.3 (2)
C(33)	0.4061 (6)	0.4283 (10)	0.0396 (5)	3.7 (2)
O(11)	0.2464 (4)	0.1899 (7)	0.1832 (4)	4.7 (1)
O(12)	0.4208 (5)	−0.1563 (8)	0.1754 (4)	5.0 (2)
O(13)	0.3217 (5)	0.1106 (8)	−0.0217 (4)	6.1 (2)
O(21)	0.7047 (5)	0.3707 (8)	0.1749 (4)	5.1 (2)
O(22)	0.6239 (4)	−0.0660 (8)	0.1842 (4)	4.7 (1)
O(23)	0.5225 (5)	0.1880 (9)	−0.0232 (5)	6.4 (2)
O(31)	0.5626 (4)	0.6274 (7)	0.1829 (4)	4.7 (1)
O(32)	0.2990 (5)	0.5336 (8)	0.1750 (4)	5.1 (2)
O(33)	0.3820 (5)	0.4522 (9)	−0.0232 (4)	6.1 (2)

[a] Equivalent isotropic parameter for atom refined anisotropically.

TABLE II

	Co(1)	Co(2)	Co(3)
Anisotropic Thermal Parameters for Cobalt Atoms, Å^2			
U_{11}[a]	0.03168	0.03318	0.03410
U_{22}	0.02697	0.02888	0.02479
U_{33}	0.02774	0.02866	0.02881
U_{12}	−0.00354	0.00144	0.00271
U_{13}	0.00797	0.01446	0.00989
U_{23}	−0.00290	−0.00065	0.00351
Rms Amplitudes of Vibration, Å			
Min	0.154 (2)	0.149 (2)	0.151 (2)
Intermed	0.171 (2)	0.171 (2)	0.172 (2)
Max	0.183 (2)	0.189 (2)	0.187 (2)

[a] The expression for the atomic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

All calculations were carried out on an IBM 360/44 computer with 32K words of core storage. The program HILGOUT to process diffractometer paper tape output was written in this laboratory by Dr. R. J. Dellaca. Other programs used were local modifications of DATAPH by P. Coppens for absorption correction by gaussian integration; NRC-4 by S. R. Hall and F. R. Ahmed for symbolic addition; ORFLS for full-matrix least-squares refinement and ORFFE for interatomic distances and angles and thermal vibration analysis, both by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP by A. Zalkin for Fourier summations; ORTEP by C. K. Johnson for interatomic distance and angle calculations and for production of structure diagrams on an incremental plotter. Among the most significant modifications were those of ORFLS to allow for the application of geometric constraints to a group of atoms and those of ORTEP to allow for the rapid presentation of different views of a structure on a line printer.

Description of Structure and Discussion

The crystal structure consists of well-separated molecules of $[CCo_3(CO)_9]_2$; the closest intermolecular contact is 3.07 Å. General perspective 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 IV and V, respectively, and Table VI contains selected intramolecular nonbonded distances

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(11) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

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

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

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

(15) W. H. Zachariasen, *ibid.*, **23**, 558 (1967).

(16) A. C. Larson in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 291. The actual function minimized at this point was $[\Sigma w(|F_o| - |F_c|/Z)]^2$ where $Z = \{g\beta I_c + [1 + (g\beta I_o)^2]^{1/2}\}^{1/2}$. In this expression, β is Zachariasen's polarization correction term, $(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)^2$, and the final value of the extinction parameter g was 0.4 (1) × 10^{-6}.

(17) Table III containing structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1381. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

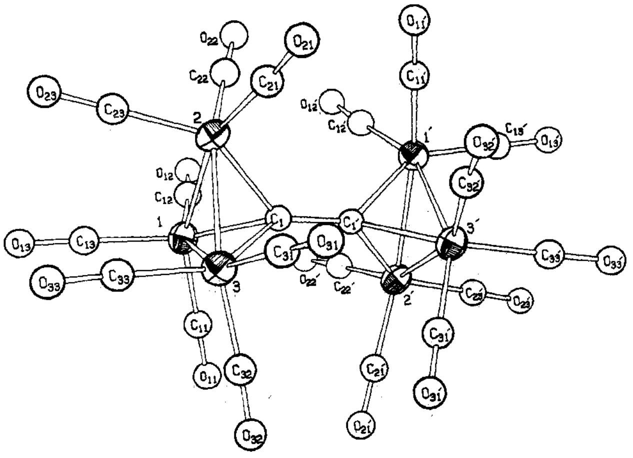


Figure 1.—A general view of one molecule of $[CCo_3(CO)_9]_2$ chosen to show all atoms resolved.

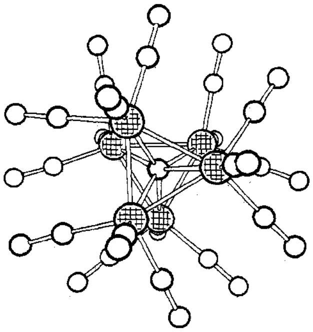


Figure 2.—One molecule of $[CCo_3(CO)_9]_2$ viewed down the pseudo threefold axis.

Table IV

Bond Distances (Å)[a]

Co(1)–Co(2)	2.457 (2)	Co(3)–C(31)	1.79 (1)
Co(1)–Co(3)	2.456 (2)	Co(3)–C(32)	1.79 (1)
Co(2)–Co(3)	2.457 (1)	Co–CO(equatorial)	*1.79 (1)*
	2.457 (1)	C(1)–C(1′)	1.37 (1)
Co(1)–C(1)	1.95 (1)	C(13)–O(13)	1.15 (1)
Co(2)–C(1)	1.97(1)	C(23)–O(23)	1.15 (1)
Co(3)–C(1)	1.97 (1)	C(33)–O(33)	1.15 (1)
Co–C(bridge)	*1.96 (1)*	C–O(axial)	*1.15 (1)*
Co(1)–C(13)	1.78 (1)	C(11)–O(11)	1.13 (1)
Co(2)–C(23)	1.79 (1)	C(12)–O(12)	1.14 (1)
Co(3)–C(33)	1.79 (1)	C(21)–O(21)	1.12 (1)
Co–CO(axial)	*1.79 (1)*	C(22)–O(22)	1.14 (1)
Co(1)–C(11)	1.80 (1)	C(31)–O(31)	1.13 (1)
Co(1)–C(12)	1.78 (1)	C(32)–O(32)	1.14 (1)
Co(2)–C(21)	1.79 (1)	C–O(equatorial)	*1.13 (1)*
Co(2)–C(22)	1.78 (1)		

[a] Mean values of bonds assumed to be chemically equivalent are italicized 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. The estimated standard deviations of individual bonds were calulated using variances and covariances in positional parameters and variances only in cell parameters.

Table V

Bond Angles (deg)[a]

Co(1)–Co(2)–Co(3)	60.0 (1)	C(11)–Co(1)–C(12)	97.4 (4)
Co(2)–Co(3)–Co(1)	60.0 (1)	C(21)–Co(2)–C(22)	97.8 (4)
Co(3)–Co(1)–Co(2)	60.0 (1)	C(31)–Co(3)–C(32)	97.5 (4)
	60.0		*97.6*
C(1)–Co(1)–Co(2)	51.5 (2)	Co(1)–Co(2)–C(23)	98.3 (3)
C(1)–Co(1)–Co(3)	51.4 (2)	Co(1)–Co(3)–C(33)	99.4 (3)
C(1)–Co(2)–Co(3)	51.3 (2)	Co(2)–Co(3)–C(33)	97.9 (3)
C(1)–Co(2)–Co(1)	50.9 (2)	Co(2)–Co(1)–C(13)	99.6 (3)
C(1)–Co(3)–Co(1)	51.0 (2)	Co(3)–Co(1)–C(13)	98.6 (3)
C(1)–Co(3)–Co(2)	51.4 (2)	Co(3)–Co(2)–C(23)	99.6 (3)
	51.3		*98.9*
C(1′)–C(1)–Co(1)	134.5 (4)	Co(1)–Co(2)–C(22)	96.1 (3)
C(1′)–C(1)–Co(2)	133.8 (4)	Co(1)-Co(3)–C(32)	100.5 (3)
C(1′)–C(1)–Co(3)	132.9 (4)	Co(2)–Co(3)–C(31)	96.1 (3)
	133.7	Co(2)–Co(1)–C(12)	101.0 (3)
C(1)–Co(1)–C(11)	102.3 (3)	Co(3)–Co(1)–C(11)	96.0 (3)
C(1)–Co(1)–C(12)	106.6 (3)	Co(3)–Co(2)–C(21)	100.6 (3)
C(1)–Co(2)–C(21)	107.0 (3)		*98.4*
C(1)–Co(2)–C(22)	102.4 (3)	Co(1)–Co(2)–C(21)	156.3 (3)
C(1)–Co(3)–C(31)	102.5 (3)	Co(1)–Co(3)–C(31)	151.3 (3)
C(1)–Co(3)–C(32)	106.1 (3)	Co(2)–Co(3)–C(32)	156.0 (3)
	106.6	Co(2)–Co(1)–C(11)	151.5 (3)
C(1)–Co(1)–C(13)	144.5 (4)	Co(3)–Co(1)–C(12)	156.5 (3)
C(1)–Co(2)–C(23)	143.9 (4)	Co(3)–Co(2)–C(22)	151.5 (3)
C(1)–Co(3)–C(33)	143.6 (4)		*153.8*
	144.0	Co(1)–C(11)–O(11)	178.7 (8)
C(11)–Co(1)–C(13)	99.1 (4)	Co(1)–C(12)–O(12)	177.0 (8)
C(12)–Co(1)–C(13)	98.2 (4)	Co(1)–C(13)–O(13)	179.1 (8)
C(21)–Co(2)–C(23)	98.4 (4)	Co(2)–C(21)–O(21)	176.2 (8)
C(22)–Co(2)–C(23)	99.0 (4)	Co(2)–C(22)–O(22)	178.1 (8)
C(31)–Co(3)–C(33)	99.4 (4)	Co(2)–C(23)–O(23)	179.9 (8)
C(32)–Co(3)–C(33)	99.3 (4)	Co(3)–C(31)–O(31)	178.5 (8)
	98.9	Co(3)–C(32)–O(32)	175.7 (8)
Co(1)–C(1)–Co(2)	77.6 (2)	Co(3)–C(33)–O(33)	178.0 (8)
Co(1)–C(1)–Co(3)	77.6 (2)		*177.9*
Co(2)–C(1)–Co(3)	77.3 (2)		
	77.5		

[a] See footnote *a* of Table IV. Rms deviations are not given for mean values of angles assumed to be chemically equivalent because these usually far exceed the esd's of individual values.

Table VI

Selected Intramolecular Nonbonded Distances (Å)

Those within One Asymmetric Unit

C(11)···C(12)	2.69	C(31)···C(32)	2.69
C(11)···C(13)	2.73	C(31)···C(33)	2.74
C(12)···C(13)	2.70	C(32)···C(33)	2.73
C(21)···C(22)	2.70	C(11)···C(32)	2.98
C(21)···C(23)	2.71	C(12)···C(22)	2.99
C(22)···C(23)	2.72	C(21)···C(31)	2.99
		C(13)···C(23)	3.01
		C(13)···C(33)	3.02
		C(23)···C(33)	3.00

Those between the Two Parts of the Dimer

		Calcd	
	Obsd	Assuming molecular mirror plane	Assuming molecular center of symmetry
O(11)···O(21′)	3.09	*a*	2.64
O(12)···O(22′)	3.08	*a*	3.39
O(31)···O(32′)	3.10	*a*	*a*
O(11)···O(11′)	*a*	2.42	*a*
O(12)···O(12′)	*a*	2.70	*a*
O(21)···O(21′)	*a*	2.72	*a*
O(22)···O(22′)	*a*	2.38	*a*
O(31)···O(31′)	*a*	2.42	*a*
O(32)···O(32′)	*a*	2.72	*a*
O(12)···O(31′)	*a*	*a*	2.63
O(22)···O(32′)	*a*	*a*	2.61

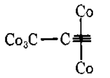
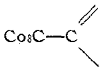
[a] Distances over 3.5 Å.

both as observed and also as calculated for two hypothetical molecules of higher symmetry.

The molecule consists of two $CCo_3(CO)_9$ units linked by direct bonding of the bridging carbon atoms, the crystallographic dyad axis bisecting the central carbon–carbon bond so formed. The two Co_3 triangles are neither fully staggered as in the centrosymmetric $[C_2Co_3(CO)_9]_2$[5] nor eclipsed, so that the potential D_{3d} or D_{3h} symmetry of the whole molecule is reduced in fact to an idealized D_3-32. The departures from this ideal-

TABLE VII

CARBON–CARBON BOND LENGTHS INVOLVING THE BRIDGING CARBON ATOM IN DERIVATIVES OF $YCCo_3(CO)_9$[a]

	$Co_3C{-}C{\equiv}$			$Co_3C{-}CH_3$
	$[Co_3(CO)_9C_2]_2$ 1.37 (1)	$Co_5(CO)_{15}C_3H$ 1.46 (2)	$C_6H_5CCo_3(CO)_6$ (mesitylene) 1.48 (2)	$CH_3CCo_3(CO)_9$ 1.53 (3)
	$Co_8(CO)_{24}C_6$ 1.36 (3)	$Co_8(CO)_{24}C_6$ 1.44 (3)	$C_6H_5CCo_3(CO)_6$ (*c*-octatetraene) 1.47 (3)	$CH_3CCo_3(CO)_8P(C_6H_5)_3$ 1.50 (2)
	$[Co_3(CO)_9C]_2$ (this analysis) 1.37 (1)			
Mean value obsd	1.37	1.45	1.48	1.51
Obsd for ref compds	1.37 $C_{sp}{-}C_{sp}$	1.45 $C_{sp}{-}C_{sp^2}$	1.45 $C_{sp}{-}C_{sp^2}$	1.46 $C_{sp}{-}C_{sp^3}$

[a] Data for $YCCo_3(CO)_9$ compounds obtained from ref 1. Data for reference compounds obtained from ref 20.

ized state are however quite small and each $CCo_3(CO)_9$ group retains its idealized C_{3v}-$3m$ symmetry. As may be deduced from Figures 1 and 2, the twisting of the rigid $CCo_3(CO)_9$ groups about their connecting bond is such as to minimize nonbonded repulsions between carbonyl groups. This is illustrated quantitatively in Table VI where actual nonbonded distances between CO groups from the two parts of the dimer are compared with those that would apply if the dimer were either eclipsed or fully staggered but with the dimensions of each $CCo_3(CO)_9$ group unchanged. Although the CO nonbonded repulsions have been minimized by the angle of twist, a further bending apart of the Co–CO bonds has been required. Thus the dihedral angles between the Co_3 triangle and the planes formed by each Co atom and its associated equatorial CO groups have an average value of only 24.0° compared with the values of 28° in $[C_2Co_3(CO)_9]_2$,[5] 29° in $CH_3CCo_3(CO)_9$,[3] and 32° in $Co_3(CO)_{10}BH_2N(C_2H_5)_3$,[18] in all of which compounds no such nonbonded repulsions may occur.

The bond lengths and angles of the individual $CCo_3(CO)_9$ groups are with one exception in good agreement with those in other compounds.[1] The exception is the set of Co–C(bridge) bonds whose average value of 1.96 (1) Å observed here compares with an average value of 1.915 Å (range 1.90–1.93 Å) observed for seven other compounds, and this must be considered a significant difference. This indication of a weakening of the Co–C bonds is supported by the fact that these bonds are much more easily ruptured by electron impact in the mass spectrometer than are those of $Co_5(CO)_{15}C_3H$.[19]

Of greatest significance however in the molecular structure is the central formally single C–C bond of length 1.37 (1) Å. In all cases where CCo_3 groups are linked through a conjugated carbon chain, there is a marked shortening of the C–C bond formed by the bridging carbon atom relative to that expected of an sp^3-hybridized carbon forming a single bond.[1] In this case however where there is no intervening carbon chain, we have the bond, as it were, in isolation and may hope to reach firmer conclusions as to its nature and, hence, the nature of the Co–C bridging bonds themselves. Carbon–carbon single bonds as short as 1.371 (5) Å have previously been observed only in such molecules as diacetylene[20] where both atoms concerned are formally sp hybridized. We therefore assume that the p character of the outwardly directed orbitals of the bridging carbon atoms has been reduced approximately to this level. Making the same assumption for the other compounds containing linked CCo_3 groups we find that there is excellent agreement between the observed bond lengths and those calculated for single bonds (see Table VII). The agreement is less good where the bridging carbon is bonded directly to a terminal group but is still within limits of error. Consistent with this assumption is the observation that the ^{1}H nmr signal for the terminal $-CH_3$ group in $CH_3CCo_3(CO)_9$ and a number of its derivatives is typically at about τ 6.5[21] indicating a considerable deshielding relative to ethane (τ 9.1 and midway between ethylene (τ 4.7) and acetylene and methylacetylene (τ 8.2).

The weight of evidence is that the outwardly directed orbital used by the bridging carbon atom in forming a σ bond is much reduced in p character relative to sp^3. The bridging carbon is then left with three electrons in predominantly p orbitals available for bonding to the three cobalt atoms. In a localized bonding description such as given by Sutton and Dahl[3] the interorbital angle will be reduced toward 90° to coincide more nearly with Co–C–Co interatomic angles of 80°. Alternatively however a delocalized bonding description for the CCo_3 cluster may be more appropriate.

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