The Structure of Nonacarbonyl-μ_3-methylidyne-*triangulo*-tricobalt. X-ray and Neutron Diffraction Studies*

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Abstract

The title compound, $Co_3(CO)_9CH$, crystallizes in space group $P\bar{1}$ ($Z = 2$). The unit-cell dimensions determined from neutron diffraction data at 102 K are $a = 7.936$ (2), $b = 13.656$ (4), $c = 6.856$ (2) Å, $\alpha = 101.60$ (2), $\beta = 109.34$ (2) and $\gamma = 93.96$ (2)°. The structure was solved by Patterson methods with X-ray diffraction data obtained at room temperature, and further refined with low-temperature X-ray and neutron diffraction data. $R(F)$ (neutron) $= 0.037$ for 3781 observations. The molecule possesses an idealized C_{3v} point symmetry. Three $Co(CO)_3$ groups and a CH group form a distorted tetrahedron. The high resolution of the present study reveals significant differences between the axial and equatorial Co—C bond lengths, the average Co—C distances for these being respectively 1.837 (2) and 1.798 (1) Å. The C—H bond distance as determined by neutron diffraction is 1.084 (1) Å. The Co neutron scattering length has been refined to a value of 2.48 (2) fm.

Introduction

Organometallic cluster compounds with a Co_3C core have been known since 1958 (Markby, Wender, Friedel, Cotton & Sternberg, 1958) and have been the subject of a number of review articles (Penfold & Robinson, 1973; Muetterties, 1977; Schmidt, 1978). To gain understanding of the nature of metal–metal and metal–ligand bonding in metal clusters, an electron density study of nonacarbonyl-μ_3-methylidyne-*tri-angulo*-tricobalt has been undertaken. To obtain unbiased nuclear positions, a set of neutron diffraction data was collected to complement the X-ray data. We report here the structural conclusions derived from both neutron and X-ray experiments.

Experimental

The sample was prepared by a procedure described by Seyferth, Hallgren & Hung (1973). The crystals appear black in reflected light and dark red in transmitted light. The density determined by flotation in a mixture of iodoform and chloroform is 2.08 Mg m^{-3}.

X-ray diffraction

Crystals used for X-ray diffraction experiments were prepared by vacuum sublimation at 318 K. Two X-ray diffraction data sets were collected on different crystals, at room temperature and 92 K, respectively.

Room-temperature study. All X-ray measurements were made on a Picker FACS-I four-circle diffractometer using Nb-filtered Mo $K\alpha$ radiation. No systematic absences were observed. The unit-cell parameters and crystal orientation were determined by least-squares refinement based on the setting angles of 30 reflections at $25° < 2\theta < 40°$ (Table 1). A polyhedral crystal, with dimensions $0.20 \times 0.31 \times 0.49$ mm (volume $= 0.080$ mm^3), was used. The intensity data in the range $2\theta < 50°$ were collected in the 2θ–θ step-scan mode.

The step-scan interval was chosen to be $0.04°$ 2θ with a scan range calculated from the expression: scan range (in deg) $= C_1 + C_2 \tan \theta$, where C_1 and C_2 are experimentally determined dispersion constants and θ is the Bragg angle. For $2\theta < 40°$, C_1 and C_2 were 2.8 and $0.8°$, respectively, while in the range $40° < 2\theta < 50°$, C_1 was increased to $2.9°$.

Reflection profiles were analyzed as described by Blessing, Coppens & Becker (1974). Lorentz–polarization corrections and absorption corrections ($\mu = 3.655$ mm^{-1}) were applied, the latter as calculated by Gaussian integration (Coppens, Leiserowitz & Rabinovich, 1965). Symmetry-related reflections and multiple observations were averaged to give structure factors for 2478 independent reflections. Of these, only 1720 with $F_o^2 > 3\sigma(F_o^2)$ were considered significant and

Table 1. *Crystallographic data for* $Co_3(CO)_9CH$ *and* $Co_3(CO)_9CCH_3$

	Co$_3$(CO)$_9$CH			Co$_3$(CO)$_9$CCH$_3$*
	X-ray	X-ray	Neutron	X-ray
Molecular mass		441·91		455·92
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Temperature	298 K	92 K	102 K	Room temperature
Cell dimensions				
a	8·01 (1) Å	7·935 (2) Å	7·936 (2) Å	8·80 Å
b	13·81 (2)	13·662 (2)	13·656 (4)	12·34
c	6·96 (1)	6·855 (1)	6·856 (2)	7·85
α	101·71 (1)°	101·59 (1)°	101·60 (2)°	97·30°
β	108·22 (1)	109·30 (1)	109·34 (2)	112·12
γ	94·89 (1)	93·99 (1)	93·96 (2)	86·70
Z	2	2	2	2
V	707·0 Å^3	680·6 Å^3	679·3 Å^3	783·4 Å^3
$\rho_{calc.}$	2·08 Mg m^{-3}	2·16 Mg m^{-3}	2·16 Mg m^{-3}	1·95 Mg m^{-3}
$\rho_{exp.}$ (room temp.)	2·01 Mg m^{-3}	–	–	1·9 Mg m^{-3}
μ	3·655 mm^{-1}	3·810 mm^{-1}	0·0282 mm^{-1}	–

* The unit-cell parameters of Co$_3$(CO)$_9$CCH$_3$ were transformed to give a reduced cell in the conventional manner. For the original experimental cell, see Sutton & Dahl (1967).

used in the subsequent structure determination. A weighting scheme of $w(F_o^2) = [\sigma^2_{count}(F_o^2) + (0\cdot05F_o^2)^2]^{-1}$ has been applied to all observations used in least-squares refinement of the structural parameters.

The crystal used in this data collection gave a rather wide 2θ spread (2·0–2·4°) and was judged to be of rather poor quality. These data did, however, provide solution of the crystal structure, while better-quality crystals were being prepared for the low-temperature study.

Low-temperature study. The crystal used had dimensions of 0·35 × 0·32 × 0·45 mm and a volume of 0·058 mm^3. The temperature of the crystal was maintained at a nominal value of 92 K by a cold nitrogen stream attachment on the Picker diffractometer. Unit-cell dimensions and crystal orientation were determined as described above, with reflections in the 2θ range of 35–42°. Intensity profile data were collected by the 2θ–θ step-scan technique, with the dispersion constants C_1 and C_2 taken to be 1·8 and 1·4° respectively. The profile analysis, Lp and absorption corrections ($\mu = 3\cdot810$ mm^{-1}) were treated as in the room-temperature study. The observed structure factors were scaled according to the behavior of nine monitor intensities (McCandlish, Stout & Andrews, 1975). An overall intensity variation of 6% for these monitor reflections was observed. The internal agreement between the variation in different standard reflections was about 2% at the beginning of data collection, and diverged toward the end to about 5%. Multiple observations and symmetry-related reflections were averaged. The number of unique reflections is 2359, of which 2159 were considered significant and used in least-squares refinement of the structure parameters. The weighting scheme was chosen to be $w(F_o^2) = [\sigma^2_{count}(F_o^2) + (0\cdot02F_o^2)^2]^{-1}$.

Neutron diffraction

The crystals used for the neutron diffraction experiment were prepared by repeated crystallization from benzene solution. A crystal with optimal ω-scan profile was selected for data collection. Approximate sample dimensions were 1·4 × 2·0 × 2·0 mm along the three principal axes, with a volume of 4·3 mm^3. The diffraction measurements were performed on an automated four-circle diffractometer (McMullan, Andrews, Koetzle, Reidinger, Thomas & Williams, 1976) at the Brookhaven High Flux Beam Reactor. The wavelength of the neutron beam was 1·0013 (2) Å [calibrated with a KBr crystal; $a = 6\cdot6000$ (1) Å, at 298 K] obtained by diffraction from the (002) plane of a Be monochromator. The crystal temperature was maintained at 102 (1) K* with a closed-cycle helium refrigerator;† the operating temperature was chosen by matching the unit-cell volume with that derived from the X-ray data. The unit-cell parameters were determined by least-squares refinement of the $(2\theta)_{obs}$ of 36 reflections in the range 40° < 2θ < 50° (Table 1). The integrated intensities were measured by a 2θ–θ step-scan technique with counts accumulated at each step for a preset monitor count of the incident beam, amounting to approximately 1 s per step. For 2θ < 50°, the scan range in 2θ was 3·0° with a step of 0·04°, while for 2θ > 50°, the scan width was calculated in the same way as for X-ray experiments, with $C_1 = 1\cdot50$° and $C_2 = 3\cdot38$°, and the step interval was adjusted to give at

* The observed temperature was calibrated with reference to a magnetic phase transition in FeF$_2$ at $T_N = 78\cdot38$ (1) K (Hutchings, Schulhof & Guggenheim, 1972). With an FeF$_2$ crystal mounted in the same fashion as the sample, the platinum resistance thermometer used to monitor the temperature indicated $T_N = 76\cdot1$ K. Thus 2 K was added to the recorded value (100 K).

† Air Products and Chemicals, Inc. DISPLEX Model CS-202.

least 61 steps in each scan. The background intensity was examined by scanning over the entire 2θ range at particular φ and χ values chosen to avoid Bragg conditions for the $Co_3(CO)_9CH$ crystal. No distinct features were observed and it therefore was not necessary to take into account the scattering due to the aluminum cryostat for background correction. All unique reflections with $2\theta < 75°$ were measured. Above this value, only 1205 intense reflections (predicted from parameters determined in the X-ray studies) were collected. The upper limit of $2\theta = 104°$ approached the physical limitations of the instrument. The intensities of two reflections were monitored at an interval of 50 reflections. No significant variations in these monitor intensities were observed. Out of a total of 4046 observations only one reflection was rejected for its large negative intensity ($I < -5\sigma$).

The raw intensity data were treated with profile analysis as described previously (McMullan, Epstein, Ruble & Craven, 1979). The linear absorption coefficient was calculated to be 0.0282 mm^{-1}, with the mass absorption coefficient for chemically bonded hydrogen estimated at 0.2364 mm^2 g^{-1} (McMullan & Koetzle, 1979, unpublished). A test run on a set of ψ-scan data for the $1\bar{6}0$ reflection indicated satisfactory results with an absorption correction using measured crystal dimensions. The correction was applied subsequently to all observations. The intensity data were sorted and multiple observations and Friedel pairs, when present, were averaged. Eight observations having $|F_o^2 - \bar{F}_o^2| > 2.5\sigma_{count}(F_o^2)$ were rejected. Further numerical details are given in Table 2. The weighting scheme used in the least-squares refinement was $w(F_o^2) = [\sigma_{count}^2(F_o^2) + (0.01F_o^2)^2]^{-1}$.

Table 2. *Data collection and least-squares refinements*

	X-ray (Mo $K\alpha$)		Neutron [$\lambda = 1.0013$ (2) Å]
	298 K	92 K	102 (1) K
Number of reflections measured	3616	3180	4045
Number of unique reflections	2478	2359	3781
$\sum |F^2 \text{ obs} - \langle F^2 \text{ obs}\rangle|/ \sum F^2 \text{ obs}$	0.057	0.021	0.007
Number of reflections in refinement	1720 (>3σ)	2159 (>3σ)	3781
Number of variables	199	204	210*
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.6	0.6	0.8
$R(F)$	0.088	0.018	0.037
$R(wF)$	0.104	0.025	0.022
$R(F^2)$	0.183	0.034	0.033
$R(wF^2)$	0.200	0.047	0.041
Goodness-of-fit	3.1	1.7	1.1
g (isotropic)†	–	0.24 (1)	0.342 (5)

* The scattering amplitude for Co has been refined and constrained to be equal for all three Co atoms.

† Type I isotropic extinction, Lorentzian distribution.

Solution and refinement of the structure

The crystal structure was solved with the room-temperature X-ray data by the heavy-atom method, assuming symmetry $P\bar{1}$. The successful refinement against the low-temperature X-ray and neutron data confirmed the choice of space group. The structure parameters were refined by full-matrix least-squares procedures in which the quantity minimized was $\sum w|[F_o^2 - (kF_c)^2]|^2$, where the weights ($w$) are as described above. Atomic scattering factors and anomalous scattering terms for the X-ray refinements were taken from *International Tables for X-ray Crystallography* (1974) for Co, O and C, and from Stewart, Davidson & Simpson (1965) for H. The neutron scattering amplitudes (fm) $- 2.8$ for Co, 5.8 for O, 6.65 for C, -3.74 for H $-$ were taken from Bacon (1977). During the final cycles, the Co scattering length was varied in the refinement.

The refinement on the room-temperature data was discontinued at convergence of the anisotropic thermal model (Table 2) without the H atom being located. The use of the 92 K X-ray data in a difference Fourier synthesis, following refinement of the isotropic thermal model, revealed the hydrogen position with a peak density of 0.88 eÅ^{-3}, the highest peak on the map. The parameters varied in the final refinement included 1 scale factor, 69 positional parameters, 133 thermal parameters (isotropic for the hydrogen, anisotropic for the other atoms) and the isotropic extinction parameter for a type I crystal with a Lorentzian distribution of mosaicity (Becker & Coppens, 1974). The indices of fit at convergence listed in Table 2 are for the 2159 observations with $F_o^2/\sigma(F_o^2) > 3.0$ used in the refinement.

The molecular parameters obtained from the above X-ray refinement were adjusted against the neutron data. All recorded independent reflections were included in the refinement. The parameter list here included those above with the addition of anisotropic thermal parameters for the H atom. Convergence was achieved within a few cycles of refinement. Refinement incorporating anisotropic secondary-extinction parameters (type I crystal with Lorentzian distribution) did not improve the fit to the data significantly, so the isotropic model was retained for description of extinction effects. The thermal parameters for the three Co atoms derived from the neutron refinement were *ca* 20% larger than the corresponding values obtained from the X-ray refinement, suggesting significant overweighting of nuclear density at the metal sites. The scattering amplitude of Co at the three sites was therefore refined simultaneously with the other parameters listed above. The error indices then decreased by as much as 10% of their previous values, while the thermal parameters for the Co atom were reduced significantly. The refined scattering amplitude,

Table 3. *Atomic positional parameters for* $Co_3(CO)_9$-CH *as determined in the neutron diffraction study*

Fractional coordinates are given $\times 10^5$. The X-ray (92 K) positional parameters for the cobalt atoms are: Co(1) $x = -4923$ (3), $y = 23167$ (2), $z = -18690$ (4); Co(2) $x = 23567$ (3), $y = 33943$ (2), $z = 5783$ (4) and Co(3) $x = 24084$ (3), $y = 16199$ (2), $z = -10919$ (4).

	x	y	z
Co(1)	−4941 (16)	23144 (10)	−18716 (20)
Co(2)	23567 (16)	33964 (10)	5812 (20)
Co(3)	24074 (16)	16195 (9)	−10908 (20)
C(11)	−6230 (7)	26869 (4)	−43427 (8)
C(12)	−19788 (7)	30730 (4)	−9795 (8)
C(13)	−20160 (7)	11469 (4)	−27361 (10)
C(21)	29556 (7)	40198 (4)	−12942 (9)
C(22)	13490 (7)	43258 (4)	19089 (8)
C(23)	44491 (7)	35736 (4)	27890 (8)
C(31)	31980 (7)	18437 (4)	−32111 (8)
C(32)	44156 (7)	14010 (4)	8704 (9)
C(33)	13436 (7)	3302 (4)	−21046 (9)
C(10)	11818 (6)	21713 (4)	7248 (8)
O(11)	−6663 (10)	29374 (6)	−58390 (11)
O(12)	−29387 (9)	35329 (6)	−4070 (12)
O(13)	−29921 (10)	4195 (6)	−32130 (16)
O(21)	33091 (10)	43776 (5)	−24946 (11)
O(22)	7184 (9)	49072 (5)	27711 (12)
O(23)	57366 (9)	36927 (6)	42359 (11)
O(31)	37239 (10)	19960 (6)	−44921 (11)
O(32)	56579 (10)	12378 (6)	21089 (12)
O(33)	6614 (10)	−4879 (5)	−27377 (13)
H(1)	9814 (17)	19281 (10)	20530 (19)

Table 4. *Interatomic bond lengths* (Å)

	X-ray (298 K)		X-ray (92 K)		Neutron (102 K)	
Co(1)–Co(2)	2·476 (5)	2·488*	2·4769 (6)	2·4808*	2·480 (2)	2·484*
Co(1)–Co(3)	2·498 (4)	2·508	2·4886 (5)	2·4920	2·486 (2)	2·489
Co(2)–Co(3)	2·463 (5)	2·474	2·4729 (5)	2·4760	2·476 (2)	2·479
Ave.	2·479	2·489	2·4795	2·4829	2·481	2·484
Co(1)–C(10)	1·901 (13)	1·910	1·892 (2)	1·895	1·893 (1)	1·896
Co(2)–C(10)	1·873 (13)	1·882	1·889 (2)	1·893	1·895 (1)	1·898
Co(3)–C(10)	1·889 (12)	1·897	1·894 (2)	1·897	1·894 (1)	1·898
Ave.	1·888	1·895	1·892	1·895	1·894	1·897
Co(1)–C(11)	1·817 (16)	1·827	1·835 (2)	1·838	1·838 (1)	1·824
Co(2)–C(21)	1·812 (17)	1·822	1·841 (2)	1·844	1·842 (1)	1·846
Co(3)–C(31)	1·797 (15)	1·807	1·835 (2)	1·838	1·832 (1)	1·836
Ave.	1·809	1·818	1·837	1·840	1·837	1·841
Co(1)–C(12)	1·801 (15)	1·809	1·794 (2)	1·796	1·796 (1)	1·799
Co(1)–C(13)	1·750 (15)	1·758	1·797 (2)	1·800	1·798 (2)	1·801
Co(2)–C(22)	1·802 (15)	1·809	1·799 (2)	1·801	1·799 (1)	1·801
Co(2)–C(23)	1·779 (13)	1·788	1·801 (2)	1·804	1·800 (2)	1·803
Co(3)–C(32)	1·771 (14)	1·779	1·797 (2)	1·799	1·801 (1)	1·804
Co(3)–C(33)	1·732 (15)	1·740	1·789 (2)	1·792	1·792 (2)	1·794
Ave.	1·772	1·780	1·796	1·799	1·798	1·800
C(11)–O(11)	1·111 (15)	1·117	1·137 (3)	1·139	1·136 (1)	1·138
C(21)–O(21)	1·130 (16)	1·136	1·134 (2)	1·136	1·136 (1)	1·138
C(31)–O(31)	1·132 (15)	1·138	1·131 (2)	1·133	1·137 (1)	1·139
Ave.	1·124	1·130	1·134	1·136	1·136	1·138
C(12)–O(12)	1·121 (16)	1·126	1·140 (3)	1·142	1·137 (1)	1·139
C(13)–O(13)	1·126 (18)	1·132	1·133 (3)	1·135	1·135 (1)	1·137
C(22)–O(22)	1·112 (17)	1·117	1·138 (3)	1·139	1·137 (1)	1·138
C(23)–O(23)	1·171 (16)	1·176	1·134 (2)	1·136	1·138 (1)	1·140
C(32)–O(32)	1·173 (16)	1·178	1·137 (3)	1·138	1·138 (1)	1·140
C(33)–O(33)	1·143 (17)	1·149	1·137 (3)	1·138	1·138 (1)	1·140
Ave.	1·141	1·140	1·136	1·138	1·137	1·139
C(10)–H(1)	–	–	0·94 (2)	0·95	1·084 (1)	1·086

* The bond lengths are corrected for thermal motion, with the TL formalism (Cruickshank, 1956). E.s.d.'s are assumed to be the same as the uncorrected bond lengths.

constrained to be identical for the three Co sites, is 2·48 (2) fm, which agrees well with an alternative value of 2·50 (5) fm recommended by Koester (1977). The refinement was terminated when all parameter shifts were less than 0.02σ. The final error indices for each data set are summarized in Table 2. Only the neutron parameters are presented here in Table 3. The interatomic bond lengths and angles for the X-ray and neutron studies (calculated with their respective unit-cell parameters) are presented in Tables 4 and 5* for comparison.

Discussion

The crystal and molecular structure of $Co_3(CO)_9CH$ is similar to that of the methyl-substituted complex (Sutton & Dahl, 1967). No strong intermolecular interactions are observed. All contacts are larger than 3 Å, except in the case of H(1), which lies 2·492 (2),

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* Lists of the observed and calculated structure factors, of the anisotropic thermal parameters and of the interatomic bond angles (Table 5) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35990 (52pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2·529 (2) and 2·613 (2) Å respectively from carbonyl oxygens O(33), O(11) and O(31) of neighboring molecules.

A molecule of $Co_3(CO)_9CH$ consists of three $Co(CO)_3$ units with the three Co atoms and the CH group forming a distorted tetrahedron. Molecular drawings are presented in Fig. 1. The C(10)–H(10) bond distance in the CH group is found to be 1·084 (1) Å in the neutron study, which may be compared to the C–H equilibrium bond lengths of 1·0605 (3) and 1·087 (2) Å determined in the gas phase for acetylene (Fast & Welsh, 1972) and ethylene (Duncan, 1974), respectively. The carbonyl groups can be classified as axial and equatorial. C(11), C(21) and C(31) are the axial ligands, while C(12), C(13), C(22), C(23), C(32), and C(33) are equatorial. Each axial carbonyl occupies a site *trans* to the apical CH group. In the low-temperature studies, the axial and equatorial carbonyls are clearly differentiated in terms of their respective Co–C distances – the average bond lengths from the neutron study being 1·837 (ax.) and 1·798 Å (eq.). With an e.s.d. of the mean of about 0·001 Å the difference of 0·039 Å is statistically highly significant. However, the C–O distances in the carbonyls [1·136 (ax.) and 1·137 Å (eq.)] are not observed to be different, within the experimental e.s.d.'s of 0·001 Å (see Table 4).
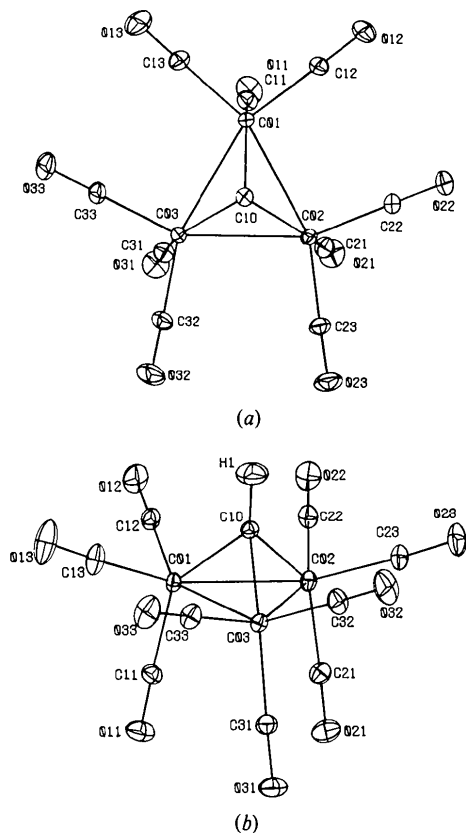
Fig. 1. (a) Top view of $Co_3(CO)_9CH$. 50% probability thermal ellipsoids are shown. The hydrogen is omitted for clarity (Johnson, 1965). (b) Side view of the molecule. 50% probability thermal ellipsoids are shown (Johnson, 1965).

It is interesting to point out that the $Co(1)-Co(3)$ distance is consistently longer than the others in both the X-ray and neutron studies. The differences are marginally significant in the neutron case and very significant in the low-temperature X-ray results (see Table 4). Since the three Co atoms are chemically equivalent, the differences can only be due to crystal-packing forces, indicating that bonds between metal atoms in cluster compounds are more flexible than bonds between first- or second-row atoms. A similar variation in Co—Co bond distances was found in a recent low-temperature neutron diffraction study of

$HFeCo_3(CO)_9[P(OCH_3)_3]_3$ (Teller, Wilson, McMullan, Koetzle & Bau, 1978). Even though the Co—Co bonds are bridged by carbonyl groups in this latter compound, the bond lengths are essentially the same as those in the present study. A listing of selected Co—Co bond lengths in tricobalt carbon cluster compounds is presented in Table 6. The variations of the equivalent Co—Co bond lengths in most of these compounds are of the same order of magnitude as that found in the present study. The precision in the present X-ray work, however, clearly indicates that the differences are beyond experimental error. Similarly, large variations (in relation to e.s.d.'s) are observed in some of the equivalent bond angles such as $Co(1)-Co(3)-C(33)$ [94·06 (6)°] and $Co(2)-Co(3)-C(32)$ [98·88 (7)°] (Table 5, deposited). However, such relative variations are not observed in the $Co-C(10)$, Co—C and C—O bond lengths.

As mentioned above, the crystal and molecular structure of $Co_3(CO)_9CH$ is very similar to that of $Co_3(CO)_9CCH_3$ (Sutton & Dahl, 1967). Hence, the general stereochemical features common to both compounds are not discussed here. A comparison of room-temperature unit-cell dimensions (Table 1) shows that the unit-cell volume increases by 70 $Å^3$ at room temperature as a result of replacing the H atom by a CH_3 group.

Without correction for apparent shortening due to thermal motion, observed bond lengths are slightly shorter at room than at low temperature as may be expected. Application of the correction according to a **TL** rigid-body model (Cruickshank, 1956) reduces this discrepancy (see Table 4). The rigid-body fit gives agreement factors, defined as $[\sum(U_{obs} - U_{calc})^2/\sum U_{obs}^2]^{1/2}$, of 23, 20 and 29%, respectively, for the neutron (102 K) and X-ray 298 K and 92 K parameters.

The equivalent isotropic thermal parameters as derived from the three experiments are compared in Table 7. In general, the r.m.s. amplitudes are smaller for the neutron (at 102 K) than for the X-ray data for which a thermocouple reading of 92 K was obtained. Since the X-ray and neutron unit-cell volumes are equal, the temperatures of the two experiments are considered to be about the same. As mentioned

Table 6. *Selected* Co—Co *bond lengths in tricobalt carbon clusters*

Compound	Co(1)—Co(2)	Co(1)—Co(3)	Co(2)—Co(3)	Reference	Comment	Ave.
$Co_3(CO)_9CH$ (102 K)	2·4766 (6) Å	2·4888 (5) Å	2·4728 (6) Å	This work	Equivalent Co atoms	2·479 (7) Å
$Co_3(CO)_9CCH_3$	2·466 (7)	2·475 (7)	2·462 (7)	Sutton & Dahl (1967)	Equivalent Co atoms	2·468 (5)
$|Co_3(CO)_8PPh_3(C_6H_5)|CCH_3$	2·510 (6)	2·495 (5)	2·490 (6)	Brice, Penfold, Robinson & Taylor (1970)	Co_1-P_{eq}.	2·498 (8)
$Co_5(CO)_{15}C_3H$	2·462 (5)	2·470 (6)	2·485 (4)	Dellaca, Penfold, Robinson Robinson & Spencer (1970)	Equivalent Co atoms	2·472 (10)
$Co_8(CO)_{24}C_6$	2·447 (7)	2·453 (7)	2·462 (7)	Dellaca & Penfold (1971)	Two sets of equivalent	2·454 (6)
	2·490 (7)	2·466 (7)	2·468 (7)		Co atoms	2·475 (11)
$|CCo_3(CO)_9|_2$	2·457 (2)	2·456 (2)	2·457 (1)	Brice & Penfold (1972)	Equivalent Co atoms	2·457 (0·5)
$CH_3CCo_3(CO)_8P(C_6H_{11})_3$	2·52 (1)	2·53 (1)	2·38 (1)	Matheson & Penfold (1977)	Co_1-P_{ax}	2·48 (7)

Table 7. *Equivalent isotropic thermal parameters*

The U_{eq} (Å^2) is defined as the average of the diagonal elements of the thermal parameters (U_{ij}) corresponding to the expression: exp $[-2\pi^2(U_{11} a^{*2} h^2 + U_{22} b^{*2} k^2 + U_{33} c^{*2} l^2 + 2U_{12} a^* b^* hk + 2U_{13} a^* c^* hl + 2U_{23} b^* c^* kl)]$.

	Neutron (102 K)	X-ray (92 K)	X-ray (298 K)
Co(1)	0·0096 (3)	0·0117 (1)	0·0438 (6)
Co(2)	0·0102 (3)	0·0114 (1)	0·0429 (5)
Co(3)	0·0101 (3)	0·0119 (1)	0·0454 (6)
C(11)	0·0149 (1)	0·0164 (6)	0·050 (4)
C(12)	0·0151 (1)	0·0164 (6)	0·060 (5)
C(13)	0·0185 (1)	0·0217 (6)	0·067 (6)
C(21)	0·0155 (1)	0·0160 (6)	0·056 (5)
C(22)	0·0142 (1)	0·0161 (6)	0·058 (5)
C(23)	0·0144 (1)	0·0185 (6)	0·058 (5)
C(31)	0·0151 (1)	0·0155 (6)	0·051 (4)
C(32)	0·0168 (1)	0·0191 (6)	0·063 (5)
C(33)	0·0161 (1)	0·0192 (6)	0·058 (5)
C(10)	0·0114 (1)	0·0134 (5)	0·050 (4)
O(11)	0·0244 (2)	0·0259 (5)	0·079 (4)
O(12)	0·0252 (2)	0·0275 (5)	0·089 (5)
O(13)	0·0333 (2)	0·0362 (6)	0·112 (6)
O(21)	0·0250 (2)	0·0265 (5)	0·088 (5)
O(22)	0·0223 (2)	0·0238 (5)	0·079 (4)
O(23)	0·0220 (2)	0·0238 (5)	0·082 (5)
O(31)	0·0247 (2)	0·0269 (5)	0·098 (5)
O(32)	0·0272 (2)	0·0303 (5)	0·094 (5)
O(33)	0·0257 (2)	0·0282 (7)	0·094 (5)
H(1)	0·0325 (3)	0·0267 (6)†	–

† Isotropic U for H(1) from the X-ray 92 K data.

earlier, the temperature readings for the neutron cryostat have been calibrated, so that the temperature quoted for the neutron study should be more reliable. The differences in thermal parameters can, at least in part, be attributed to bias introduced in the X-ray refinement by the effects of chemical bonding on the electron density distribution.

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