

Octacarbonyl(tricyclohexylphosphine)methylmethynyltricobalt Containing the Co₃C Tetrahedral Cluster

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Abstract. [CH₃CCO₃(CO)₈(C₆H₁₁)₃P], C₂₈H₃₆O₈PCO₃, triclinic, $P\bar{1}$, $a = 10.851(3)$, $b = 14.852(3)$, $c = 9.990(3)$ Å, $\alpha = 104.62(2)$, $\beta = 94.63(2)$, $\gamma = 97.97(2)^\circ$, $V = 1534.7$ Å³, $M_r = 708.4$, $Z = 2$, $D_m = 1.50(3)$, $D_c = 1.53$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 17.43$ cm⁻¹. One *axial* carbonyl of the parent CCo₃(CO)₉ unit has been replaced by P(C₆H₁₁)₃ and the *equatorial* carbonyls have been rearranged so that three of them are no longer terminal but form bridges across each of the sides of the Co₃ triangle.

Introduction. Reaction of alkyl- and arylphosphines and -arsines with YCCO₃(CO)₉ ($Y = \text{CH}_3, \text{C}_6\text{H}_5, \text{F}$ or Cl) gives a range of complexes YCCO₃(CO)_{9-n}L_n (Matheson, Robinson & Tham, 1971; Robinson & Tham, 1969). Two distinct structural types are suggested by the IR spectra, one in which the CCo₃ unit (Penfold & Robinson, 1973) has only terminal CO groups as has been established for CH₃CCO₃(CO)₈-PPh₃ (Brice, Penfold, Robinson & Taylor, 1970), and one in which there are both bridging and terminal CO groups. An example of the latter type has been reported for a diarsine substituent (Einstein & Jones, 1972). The present analysis establishes structural features for a compound of the second type arising from substitution of a monophosphine.

The compound was prepared by reacting CH₃CCO₃(CO)₉ and P(C₆H₁₁)₃ under reflux followed by separation from other products on silica HF₂₅₄ plates. Recrystallization from petroleum spirit (b.p. 30–40°) gave small red plates of CH₃CCO₃(CO)₈-P(C₆H₁₁)₃. X-ray intensities were obtained from a rectangular plate of mean cross-section 0.20 mm and thickness 0.01 mm, with a Hilger & Watts four-circle diffractometer and Zr-filtered Mo *K* radiation. The crystal was a poor diffractor and of 2380 independent reflexions for $2\theta \leq 36^\circ$, only 673 had $|F|^2 \geq 2\sigma|F|^2$ and these were used in the structure determination. The detailed procedures for data collection and assignment of errors are described by Countryman & Penfold (1972). Absorption corrections (calculated by Gaussian integration) were applied and transmission factors ranged from 0.82 to 0.96.

The structure was solved by conventional heavy-atom procedures, with all three Co atoms, located from

the Patterson function, used for phasing. In the full-matrix least-squares refinement individual isotropic thermal parameters were assigned to each atom (the number of observations was insufficient to permit additional anisotropic parameters); the function minimized was $\sum w||F_o| - |F_c||^2$ and the weights w

Table 1. Atomic coordinates ($\times 10^3$) and thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Co(1)	67.1 (7)	258.2 (5)	295.7 (7)	3.5 (2)
Co(2)	19.1 (8)	376.5 (5)	164.3 (8)	4.6 (2)
Co(3)	-73.2 (7)	215.5 (5)	68.2 (7)	4.3 (2)
P	261 (1)	212.0 (8)	332 (1)	2.7 (3)
O(1)	-146 (4)	349 (3)	-96 (4)	9 (1)
O(2)	-11 (3)	58 (2)	169 (3)	6 (1)
O(3)	220 (3)	446 (2)	401 (3)	5 (1)
O(4)	-26 (3)	252 (2)	545 (3)	5 (1)
O(5)	207 (3)	439 (2)	-2 (3)	6 (1)
O(6)	-71 (4)	544 (3)	295 (4)	9 (1)
O(7)	-318 (4)	115 (3)	35 (4)	9 (1)
O(8)	29 (3)	148 (2)	-187 (4)	7 (1)
C(1)	-110 (5)	329 (3)	-1 (6)	7 (2)
C(2)	8 (4)	143 (3)	174 (4)	4 (1)
C(3)	143 (5)	388 (3)	328 (5)	5 (1)
C(4)	20 (5)	254 (3)	443 (5)	4 (1)
C(5)	128 (5)	417 (3)	82 (6)	6 (1)
C(6)	-28 (5)	488 (4)	242 (5)	6 (2)
C(7)	-211 (7)	164 (4)	45 (6)	8 (2)
C(8)	-13 (5)	166 (3)	-84 (6)	6 (1)
C(9)	-90 (4)	303 (3)	244 (4)	3 (1)
C(10)	-198 (5)	316 (5)	325 (5)	6 (1)
C(11)	369 (4)	302 (3)	466 (4)	3 (1)
C(12)	314 (4)	338 (3)	606 (4)	4 (1)
C(13)	408 (4)	425 (3)	693 (4)	4 (1)
C(14)	532 (4)	406 (3)	730 (4)	5 (1)
C(15)	590 (4)	366 (3)	592 (5)	5 (1)
C(16)	501 (4)	279 (3)	502 (5)	4 (1)
C(21)	249 (4)	95 (2)	364 (4)	2 (1)
C(22)	207 (4)	97 (3)	507 (4)	3 (1)
C(23)	175 (4)	-9 (3)	523 (4)	4 (1)
C(24)	289 (5)	-58 (3)	495 (5)	5 (1)
C(25)	334 (4)	-58 (3)	361 (4)	4 (1)
C(26)	365 (4)	47 (3)	347 (4)	3 (1)
C(31)	363 (4)	200 (2)	188 (4)	2 (1)
C(32)	283 (5)	127 (3)	58 (5)	5 (1)
C(33)	360 (4)	116 (3)	-69 (4)	4 (1)
C(34)	394 (5)	211 (3)	-101 (5)	7 (1)
C(35)	471 (5)	284 (3)	25 (6)	7 (2)
C(36)	388 (5)	299 (3)	151 (5)	6 (1)

were $4|F_o|^2/(\sigma|F_o|^2)$. Before the final cycle, the 36 H atoms were included in calculated positions with a thermal parameter, B , of 8 \AA^2 . Scattering factors of Co, P, C and O were from Cromer & Waber (1965), those for H from Stewart, Davidson & Simpson (1965); anomalous dispersion corrections for Co only were from Cromer (1965). The final R for the 673 reflexions was 0.065. Final values of atom coordinates and thermal parameters are given in Table 1.*

Discussion. A general view of one molecule with all atoms labelled is shown in Fig. 1 and a view parallel to the Co_3 triangle, with cyclohexane rings omitted, in Fig. 2. The molecules are well separated; the closest intermolecular contact is 3.1 \AA . Because of the severe

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32490 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

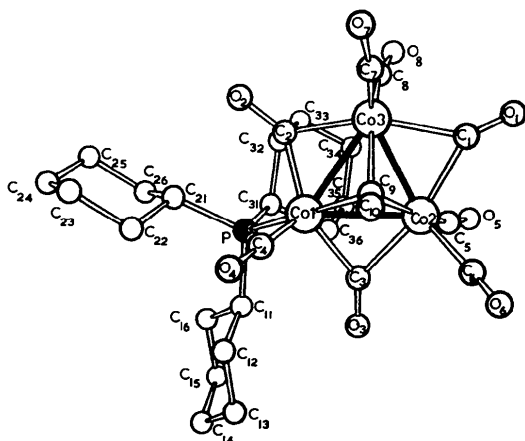


Fig. 1. One molecule of $\text{CH}_3\text{CCo}_3(\text{CO})_8\text{P}(\text{C}_6\text{H}_{11})_3$ viewed approximately normal to the Co_3 triangle showing all atoms labelled.

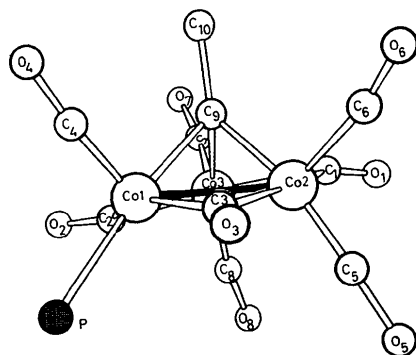


Fig. 2. The molecule viewed parallel to the Co_3 triangle to illustrate the detailed conformation of the $\text{Co}_3(\text{CO})_8$ core. The three cyclohexane rings are omitted.

limitation on the number of diffraction data, errors in atomic coordinates and derived bond lengths and angles are high. In Table 2, therefore, individual distances and angles are given only for the Co_3C tetrahedral unit and the Co-P bond. Mean values are given for other chemically similar sets of bonds.

The two essential features of the molecular structure are that first, one *axial* CO group of the parent $-\text{CCo}_3(\text{CO})_9$ unit has been replaced by $(\text{C}_6\text{H}_{11})_3\text{P}$ and, second, three of the original six *equatorial* CO groups have moved into bridging positions across each side of the Co_3 triangle. These arrangements change the coordination of the Co atoms from six to seven. The molecule has an approximate plane of symmetry passing through $\text{Co}(1)$, P, C(1), and O(1) perpendicular to the Co_3 triangle.

So far as direct comparisons may be made, conformational features are very similar to those observed in the arsine derivative $\text{CH}_3\text{CCo}_3(\text{CO})_7$, ffars (Einstein & Jones, 1972). Thus the bridging CO groups are in the plane of the Co_3 triangle, the *equatorial* terminal CO groups have been substantially displaced towards the apical methyl group [the angle between the terminal Co-C-O bonds and the Co_3 triangle is $\sim 50^\circ$ compared with 30° in the unbridged cases (Penfold & Robinson, 1973)] and the remaining *axial* CO groups

Table 2. Bond lengths and angles

Mean values of chemically similar lengths and angles are italicized. The uncertainties in parentheses for mean values of bond lengths are r.m.s. deviations from the mean value. No such uncertainties are given for mean values of bond angles as members of most groups are less strictly comparable because of the non-equivalence of the Co atoms.

(a) Bond lengths (\AA)

Co(1)—Co(2)	2.52 (1)	Co—CO(bridge)	<i>1.95 (8)</i>
Co(1)—Co(3)	2.53 (1)	Co—CO(terminal)	<i>1.66 (9)</i>
Co(2)—Co(3)	2.38 (1)	C—O(bridge)	<i>1.18 (5)</i>
Co(1)—P	2.33 (1)	C—O(terminal)	<i>1.19 (9)</i>
Co(1)—C(9)	1.99 (4)	P—C	1.85 (2)
Co(2)—C(9)	1.86 (4)	C—C(cyclohexyl)	<i>1.55 (3)</i>
Co(3)—C(9)	1.94 (4)		
Co—C(apical)	<i>1.93 (5)</i>		
C(9)—C(10)	1.48 (6)		

(b) Bond angles ($^\circ$)

Co(1)—Co(2)—Co(3)	61.6 (3)	Co—C(bridge)—Co	79
Co(2)—Co(3)—Co(1)	62.1 (3)	Co—C(9)—Co	80
Co(3)—Co(1)—Co(2)	56.3 (3)	C(10)—C(9)—Co	132
C(9)—Co(1)—Co(2)	47 (1)	C(9)—Co—C(ax.)	163
C(9)—Co(2)—Co(1)	51 (1)	C(9)—Co(1)—P	173
C(9)—Co(2)—Co(3)	53 (1)	C(9)—Co—C(eq.)	94
C(9)—Co(3)—Co(1)	51 (1)	C(ax.)—Co—C(eq.)	100
C(9)—Co(3)—Co(2)	50 (1)	C(4)—Co(1)—P	98
C(9)—Co(1)—Co(3)	49 (1)	C(ring)—P—C(ring)	104
C(apical)—Co—Co	50	C—C—C(ring)	110
Co(1)—P—C(11)	112 (1)		
Co(1)—P—C(21)	114 (1)		
Co(1)—P—C(31)	118 (1)		
Co—P—C(ring)	115		

have been splayed out by 15–20° relative to unbridged structures. These adjustments are all consistent with the need to accommodate the very bulky $P(C_6H_{11})_3$ ligand.

The unique Co(2)—Co(3) bond opposite the phosphine ligand is 0.14 (1) Å shorter than the mean of the other two. In $CH_3CCO_3(CO)_7$, the unique Co—Co bond (in that case bridged by the ffars ligand) is also significantly shortened [by 0.035 (3) Å] but in the non-bridged $CH_3CCO_3(CO)_7P(C_6H_5)_3$ (Brice, Penfold, Robinson & Taylor, 1970) no such differences are observed.

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3,4,5,6-Tetrahydro-2,9-dimethyl-7-hydroxy-5-isopropyl-2,6-methano-2H-1-benzoxocin

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Abstract. $C_{17}H_{24}O_2$, $M_r = 260.38$, triclinic, $P\bar{1}$, $a = 10.619$ (4), $b = 10.734$ (4), $c = 15.028$ (4) Å, $\alpha = 101.11$ (2), $\beta = 107.58$ (2), $\gamma = 102.90$ (2)°, $U = 1528$ Å³, $Z = 4$, D_m (floatation) = 1.12, $D_x = 1.132$ g cm⁻³, $\mu = 4.9$ cm⁻¹. There are two independent molecules in the asymmetric unit. The structure was refined to an R of 0.057 for 3970 independent reflexions.

Introduction. The title compound (an isocannabinoid) was prepared, as part of the synthesis of a series of terpenophenols with central nervous system activity, by the reaction of α -pinene with orcinol in dry benzene in the presence of $POCl_3$; large crystals were obtained from petroleum spirit/diethyl ether (R. Mechoulam, private communication). The analogous preparation of the 9-pentyl derivative has been described (Houry, Mechoulam, Fowler, Macko & Loev, 1974; Houry, Mechoulam & Loev, 1975), as has a similar preparation of the title compound (Stevens, Jurd & Manners, 1974). Intensities were measured on an

automated Syntex $P2_1$ four-circle diffractometer with Cu $K\alpha$ radiation and graphite monochromator, with a crystal $0.9 \times 0.4 \times 0.4$ mm. Accurate cell dimensions were obtained by least squares from 15 strong reflexions. The cell used was both the Dirichlet and Delaunay cell; no cell of higher symmetry could be found with the lattice-geometry program *XCELL* written by Dr R. Taylor. 4443 reflexions were measured in the range $0 < 2\theta < 116^\circ$; averaging equivalent reflexions (Lp but no absorption corrections were applied) gave 3970 reflexions with $F > 4\sigma(F)$.

Multiresolution Σ_2 sign expansion with the program *SHELX* generated E maps containing multiple images, which we could not interpret. With the program *XCSO*, which incorporates a pseudo-tangent refinement to select the starting set (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973), and the negative quartet test NQUEST (De Titta, Edmonds, Langs & Hauptman, 1975) the best E map established positions for all 38 heavy atoms in the asymmetric unit: only 7 small peaks in the top 45 were false. Figures of merit were NQUEST -0.685 , R_A (a point-atom R index based on observed

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