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Structure of 1,1,1,2,2,3,3-Heptacarbonyl-1,2,3- μ_3 -ethylidyne-2,3-bis(triphenylphosphite)-triangulo-tricobalt(0)

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Abstract. $[\text{Co}_3(\text{C}_2\text{H}_3)(\text{CO})_7(\text{C}_{18}\text{H}_{15}\text{O}_3\text{P})_2]$, $M_r = 1020.4$, triclinic, $P\bar{1}$, $a = 11.311$ (5), $b = 11.541$ (2), $c = 18.805$ (3) Å, $\alpha = 99.61$ (1), $\beta = 103.21$ (2), $\gamma = 70.93$ (3)°, $V = 2247.3$ Å³, $Z = 2$, $D_x = 1.51$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 12.23$ cm⁻¹, $F(000) = 1036$, $T = 290$ K, $R = 0.056$ for 3828 observed reflections with $F > 4\sigma(F)$. The Co atoms are arranged in a triangle, with Co—Co bond lengths in the range 2.478–2.493 (2) Å. The seven carbonyl ligands are all coordinated terminally, as are the two triphenylphosphite ligands which occupy equatorial positions *trans* to metal–metal bonds. The metal-atom triangle is capped by a μ_3 -ethylidyne (μ_3 -CCH₃) group, whose H atoms, successfully located in the electron-density map, take up staggered conformations with respect to the metal-atom positions.

Introduction. The structures of several μ_3 -ethylidyne triangulo-tricobalt compounds have previously been reported; examples include $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_9$ (Sutton & Dahl, 1967), $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_7\text{dppm}$, where dppm is bisdiphenylphosphinomethane (Balavoine, Collin, Bonnet & Lavigne, 1985), $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_8(\text{PPh}_3)$ (Brice, Penfold, Robinson & Taylor, 1970) and $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_6\text{-}[\text{P}(\text{OMe})_3]_3$ (Dawson, Robinson & Simpson, 1979). In the phosphine- and phosphite-substituted compounds, the ligand has always been

found to be coordinated equatorially and *trans* to a metal–metal bond. In the case of the title compound, $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_7[\text{P}(\text{OPh})_3]_2$, nuclear-magnetic-resonance data had provided conflicting evidence as to whether the ligands were equatorial or axial in solution (Heaton, Johnson & Kernaghan, 1988), and so the structure determination of the compound was undertaken to confirm the ligand positions in the crystal.

Experimental. Very dark red, almost opaque crystals were prepared from solution in heptane; crystals of rectangular cross section. The crystal used for data collection had dimensions 0.50 × 0.25 × 0.15 mm. Intensity data recorded from ω scans on a CAD-4 diffractometer at Queen Mary College, London (SERC service). 25 reflections, $20 < 2\theta < 40^\circ$, used to determine accurate cell parameters. Data collected from $2\theta_{\min} = 3$ to $2\theta_{\max} = 44^\circ$, $0 \leq h \leq 11$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$, using reflections 328, 253 and 0.1, 10 as references. Maximum intensity variation of references < 3%. No absorption correction. Of 5734 reflections measured, 5496 were unique.

Metal-atom positions found by the automatic Patterson search procedure of *SHELX86* (Sheldrick, 1986); these were then used to phase subsequent Fourier syntheses in *SHELX76* (Sheldrick, 1976), in which all other non-H atoms and ethyli-

Table 1. Fractional coordinates of atoms with e.s.d.'s in parentheses

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Co(1)	0-10630 (10)	0-37049 (10)	0-32759 (6)	0-0519 (7)
Co(2)	0-03067 (9)	0-22617 (9)	0-22718 (6)	0-0404 (6)
Co(3)	0-25118 (10)	0-16192 (10)	0-30005 (6)	0-0463 (6)
P(1)	-0-1629 (2)	0-3415 (2)	0-2120 (1)	0-0431 (12)
P(2)	0-3010 (2)	-0-0304 (2)	0-2634 (1)	0-0466 (13)
O(11)	-0-2011 (5)	0-4894 (4)	0-2174 (3)	0-0550 (35)
O(21)	-0-2595 (5)	0-3261 (5)	0-1355 (3)	0-0515 (33)
O(31)	-0-2311 (5)	0-3270 (5)	0-2733 (3)	0-0534 (34)
O(41)	0-2850 (5)	-0-0616 (5)	0-1765 (3)	0-0501 (33)
O(51)	0-2213 (5)	-0-1147 (5)	0-2774 (3)	0-0625 (37)
O(61)	0-4391 (5)	-0-1216 (5)	0-2931 (3)	0-0638 (39)
C(1)	0-1302 (8)	0-4592 (9)	0-2624 (5)	0-0607 (62)
O(1)	0-1460 (6)	0-5114 (6)	0-2218 (4)	0-0854 (51)
C(2)	-0-0325 (10)	0-4634 (9)	0-3642 (5)	0-0754 (71)
O(2)	-0-1126 (7)	0-5204 (7)	0-3925 (4)	0-1053 (60)
C(3)	0-2121 (10)	0-4014 (9)	0-4094 (6)	0-0716 (69)
O(3)	0-2757 (7)	0-4205 (7)	0-4633 (4)	0-0997 (59)
C(4)	0-0772 (8)	0-2447 (7)	0-1448 (5)	0-0544 (56)
O(4)	0-1095 (7)	0-2502 (7)	0-0927 (4)	0-0930 (52)
C(5)	-0-0095 (8)	0-0886 (8)	0-2093 (5)	0-0542 (56)
O(5)	-0-0398 (6)	0-0008 (6)	0-2008 (4)	0-0894 (52)
C(6)	0-3325 (8)	0-2131 (8)	0-2448 (5)	0-0610 (60)
O(6)	0-3810 (7)	0-2487 (7)	0-2094 (4)	0-1048 (56)
C(7)	0-3536 (9)	0-1450 (9)	0-3869 (6)	0-0633 (63)
O(7)	0-4182 (7)	0-1312 (7)	0-4428 (4)	0-0869 (53)
C(8)	0-0891 (7)	0-2121 (7)	0-3294 (4)	0-0507 (21)
C(9)	0-0404 (8)	0-1668 (8)	0-3840 (4)	0-0576 (23)
C(12)	-0-1781 (5)	0-6785 (5)	0-2051 (2)	0-0585 (22)
C(13)	-0-1535 (5)	0-7574 (5)	0-1656 (2)	0-0715 (26)
C(14)	-0-1268 (5)	0-7172 (5)	0-0952 (2)	0-0731 (27)
C(15)	-0-1247 (5)	0-5981 (5)	0-0643 (2)	0-0698 (26)
C(16)	-0-1493 (5)	0-5192 (5)	0-1039 (2)	0-0537 (22)
C(11)	-0-1760 (5)	0-5594 (5)	0-1743 (2)	0-0434 (19)
C(22)	-0-2032 (5)	0-1493 (6)	0-0498 (3)	0-0729 (26)
C(23)	-0-2229 (5)	0-0396 (6)	0-0133 (3)	0-0954 (34)
C(24)	-0-3148 (5)	-0-0032 (6)	0-0294 (3)	0-1023 (37)
C(25)	-0-3870 (5)	0-0637 (6)	0-0821 (3)	0-1091 (38)
C(26)	-0-3673 (5)	0-1733 (6)	0-1186 (3)	0-0829 (30)
C(21)	-0-2754 (5)	0-2161 (6)	0-1025 (3)	0-0529 (21)
C(31)	-0-3454 (5)	0-3936 (5)	0-2954 (3)	0-0468 (20)
C(32)	-0-3608 (5)	0-3627 (5)	0-3606 (3)	0-0742 (26)
C(33)	-0-4706 (5)	0-4258 (5)	0-3892 (3)	0-0876 (32)
C(34)	-0-5649 (5)	0-5199 (5)	0-3527 (3)	0-0724 (26)
C(35)	-0-5494 (5)	0-5508 (5)	0-2875 (3)	0-0822 (30)
C(36)	-0-4397 (5)	0-4876 (5)	0-2588 (3)	0-0742 (27)
C(42)	0-2253 (4)	-0-2447 (6)	0-1273 (4)	0-0798 (28)
C(43)	0-2540 (4)	-0-3639 (6)	0-0917 (4)	0-0991 (36)
C(44)	0-3728 (4)	-0-4194 (6)	0-0716 (4)	0-1039 (37)
C(45)	0-4629 (4)	-0-3556 (6)	0-0872 (4)	0-0968 (34)
C(46)	0-4342 (4)	-0-2364 (6)	0-1228 (4)	0-0739 (27)
C(41)	0-3154 (4)	-0-1810 (6)	0-1429 (4)	0-0546 (22)
C(52)	0-2873 (5)	-0-1352 (5)	0-4100 (3)	0-0603 (22)
C(53)	0-2678 (5)	-0-1769 (5)	0-4706 (3)	0-0681 (25)
C(54)	0-1749 (5)	-0-2358 (5)	0-4621 (3)	0-0775 (28)
C(55)	0-1015 (5)	-0-2531 (5)	0-3930 (3)	0-0727 (26)
C(56)	0-1210 (5)	-0-2114 (5)	0-3324 (3)	0-0611 (23)
C(51)	0-2139 (5)	-0-1525 (5)	0-3409 (3)	0-0516 (21)
C(62)	0-5853 (6)	-0-0211 (5)	0-2748 (3)	0-0780 (28)
C(63)	0-7006 (6)	0-0057 (5)	0-2986 (3)	0-0908 (32)
C(64)	0-7835 (6)	-0-0421 (5)	0-3613 (3)	0-0968 (34)
C(65)	0-7512 (6)	-0-1168 (5)	0-4001 (3)	0-0953 (34)
C(66)	0-6359 (6)	-0-1436 (5)	0-3762 (3)	0-0804 (29)
C(61)	0-5530 (6)	-0-0958 (5)	0-3136 (3)	0-0559 (22)

dyne H atoms were successfully located. Full-matrix least-squares refinement on F converged to $R = 0.056$ for 3828 reflections for which $F > 4\sigma(F)$, $wR = 0.058$, $w = 1/[\sigma^2(F) + 0.000141F^2]$. Cobalt, phosphorus, oxygen and carbonyl carbons allowed anisotropic vibration parameters, all other atoms including phenyl and ethylidyne carbons refined isotropically. All phenyl rings constrained as regular hexagons with C—C = 1.395 Å, with phenyl H atoms in calculated positions. Ethylidyne hydrogens successfully located in electron-density maps, but constrained as a typical methyl group for refinement

Table 2. Selected bond lengths (Å) and angles (°)

Co(1)—Co(2)	2.493 (2)	C(7)—O(7)	1.138 (13)
Co(1)—Co(3)	2.478 (2)	Co(1)—C(8)	1.907 (8)
Co(2)—Co(3)	2.493 (2)	Co(2)—C(8)	1.901 (8)
Co(2)—P(1)	2.141 (2)	Co(3)—C(8)	1.914 (8)
Co(3)—P(2)	2.137 (3)	C(8)—C(9)	1.502 (12)
Co(1)—C(1)	1.837 (10)	P(1)—O(11)	1.610 (6)
Co(1)—C(2)	1.799 (11)	P(1)—O(21)	1.617 (6)
Co(1)—C(3)	1.784 (11)	P(1)—O(31)	1.583 (6)
Co(2)—C(4)	1.811 (9)	P(2)—O(41)	1.595 (6)
Co(2)—C(5)	1.751 (9)	P(2)—O(51)	1.612 (6)
Co(3)—C(6)	1.808 (10)	P(2)—O(61)	1.608 (6)
Co(3)—C(7)	1.772 (10)	O(11)—C(11)	1.366 (8)
C(1)—O(1)	1.125 (12)	O(21)—C(21)	1.365 (8)
C(2)—O(2)	1.118 (13)	O(31)—C(31)	1.387 (8)
C(3)—O(3)	1.135 (13)	O(41)—C(41)	1.384 (8)
C(4)—O(4)	1.140 (11)	O(51)—C(51)	1.365 (8)
C(5)—O(5)	1.148 (11)	O(61)—C(61)	1.372 (9)
C(6)—O(6)	1.148 (12)		
Co(2)—Co(1)—Co(3)	60.21 (4)	Co(3)—C(6)—O(6)	178.0 (9)
Co(1)—Co(2)—Co(3)	59.61 (4)	Co(3)—C(7)—O(7)	177.9 (9)
Co(1)—Co(3)—Co(2)	60.18 (4)	Co(1)—C(8)—C(9)	129.6 (6)
Co(1)—Co(2)—P(1)	93.82 (7)	Co(2)—C(8)—C(9)	131.6 (6)
Co(3)—Co(2)—P(1)	152.07 (8)	Co(3)—C(8)—C(9)	132.2 (6)
Co(1)—Co(3)—P(2)	156.22 (9)	P(1)—O(11)—C(11)	127.8 (4)
Co(2)—Co(3)—P(2)	98.64 (8)	P(1)—O(21)—C(21)	124.2 (5)
Co(1)—C(1)—O(1)	178.6 (9)	P(1)—O(31)—C(31)	123.1 (5)
Co(1)—C(2)—O(2)	174.3 (10)	P(2)—O(41)—C(41)	122.8 (4)
Co(1)—C(3)—O(3)	176.8 (10)	P(2)—O(51)—C(51)	130.6 (5)
Co(2)—C(4)—O(4)	176.6 (8)	P(2)—O(61)—C(61)	128.1 (5)
Co(2)—C(5)—O(5)	176.1 (8)		
H(1)—C(9)—C(8)—Co(2)	61.1 (11)	H(2)—C(9)—C(8)—Co(2)	-58.7 (11)
H(1)—C(9)—C(8)—Co(3)	-61.6 (11)	H(3)—C(9)—C(8)—Co(1)	-59.7 (11)
H(2)—C(9)—C(8)—Co(1)	60.3 (11)	H(3)—C(9)—C(8)—Co(3)	58.4 (12)

with one common refined $U (=0.0507 \text{\AA}^2)$. In the final difference map, the highest peak = $1.0 e \text{\AA}^{-3}$, and is thought to be associated with anisotropic vibration in one of the phenyl rings, lowest minimum = $-0.6 e \text{\AA}^{-3}$. Maximum parameter shift/e.s.d. in final round of refinement = 0.094. Scattering factors and f' and f'' values for Co from *International Tables for X-ray Crystallography* (1974, Vol. IV); all calculations performed on an IBM 3083 computer. Diagram produced by *PLUTO* (Motherwell, 1976).

Discussion. Atom parameters are given in Table 1, and selected bond lengths and angles in Table 2. Fig. 1 shows a view of the molecule, more or less normal to the plane of the Co-atom triangle showing that triangle and its seven coordinated carbonyl groups clearly.

The two triphenylphosphite groups are coordinated equatorially and *trans* to metal-metal bonds, as previously found in related compounds (see above). The μ_3 -CCH₃ group caps one face of the triangle, and the hydrogens on this group are found to be perfectly staggered with respect to the metal-atom positions [e.g. torsion Co(1)—C(8)—C(9)—H(2) = 60.3 (1.1)°]. This is in contrast to the H-atom positions found in CO₃(μ_3 -CCH₃)-(CO)₂dppm (Balavoine, Collin, Bonnet & Lavigne,

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53109 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

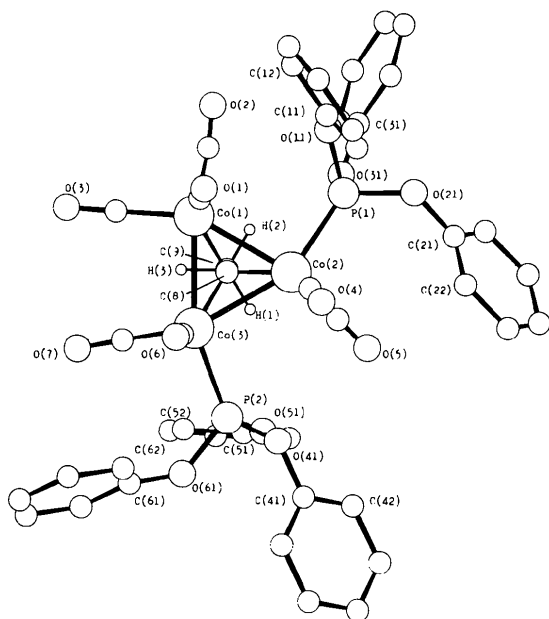


Fig. 1. Structure of the title compound. Phenyl H atoms omitted for clarity. Diagram produced by PLUTO (Motherwell, 1976).

1985), which were found to be intermediate between eclipsed and staggered.

The Co—Co bond lengths [average = 2.488 (2) Å] fall well within the range found for the aforementioned comparable compounds (2.462–2.510 Å). The spread of μ_3 C—Co bond lengths at 1.901 (8) to 1.914 (8) Å is less than previously found, e.g. 1.86 (2) to 1.93 (2) Å in $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_9$

(Sutton & Dahl, 1967). The ethylidyne group is slightly tilted away from the phosphite-coordinated Co atoms; the Co—C(8)—C(9) bond angles are 129.6 (6), 131.6 (6) and 132.2 (6)°, respectively so that the C(8)—C(9) bond is not perfectly normal to the cobalt plane. This effect is also visible in $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_8\text{dppm}$ and $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_8(\text{PPh}_3)$, and is presumably due to the steric effect of the bulky ligands.

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Structure of Sodium Thiosaccharinate Monohydrate*

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Abstract. $\text{Na}[\text{C}_7\text{H}_4\text{NO}_2\text{S}_2]\cdot\text{H}_2\text{O}$, $M_r = 239.25$, orthorhombic, $P2_12_12_1$, $a = 7.499$ (3), $b = 26.895$ (10), $c = 4.705$ (2) Å, $V = 948.93$ Å³, $Z = 4$, D_m (pycnometrically) = 1.64, $D_x = 1.675$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.51$ mm⁻¹, $F(000) = 484$, room tem-

perature, final $R = 0.043$ for 792 independent observed reflections. The crystal structure consists of Na⁺ cations, thiosaccharinate anions and water molecules. Each Na⁺ ion is surrounded by a distorted octahedron composed of two water molecules, three O atoms belonging to the SO₂ groups and one N atom from a thiosaccharinate ion. The Na—O dis-

* Thiosaccharin is 1,2-benzisothiazol-9(2H)-thione 1,1-dioxide.