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μ_3-Benzylidyne-tris(tricarbonylcobalt)(3*Co*–*Co*)

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Abstract. $[Co_3(C_7H_5)(CO)_9]$, $M_r = 518{\cdot}01$, triclinic, $P\bar{1}$, $a = 15{\cdot}771$ (3), $b = 15{\cdot}930$ (3), $c = 8{\cdot}051$ (3) Å, $\alpha = 100{\cdot}97$ (2), $\beta = 100{\cdot}02$ (2), $\gamma = 101{\cdot}10$ (1)°, $V = 1901{\cdot}4$ Å^3, $Z = 4$, $D_m = 1{\cdot}83$, $D_x = 1{\cdot}81$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}523$ mm^{-1}, $F(000) = 1016$, $T = 293$ (1) K, final $R = 0{\cdot}0466$ for 4027 observed $[I > 3\sigma(I)]$ reflections. There are two independent molecules in the asymmetric unit. The three Co atoms form an equilateral triangle, symmetrically capped by the C atom of the μ_3-carbyne ligand, to form a tetrahedral cluster core. The phenyl substituent of the carbyne is displaced slightly from a totally symmetrical orientation towards one of the Co atoms.

Introduction. Clusters of the type $YCCo_3(CO)_9$ (Y = alkyl, aryl, halo *etc.*) are well known (Penfold & Robinson, 1973; Seyferth, 1976; Schmid, 1978) and interest in their chemistry stems from the unusual stability afforded by the clamping effect of the bridging carbyne and the potential of these systems in catalysis (Masters, 1979). The title compound has been the subject of investigation in our laboratories since the discovery that its one-electron reduction leads to the formation of a particularly stable radical anion (Peake, Robinson, Simpson & Watson, 1977; Bond, Peake, Robinson, Simpson & Watson, 1977). This, in turn, provides an effective substrate for electron-transfer-catalyzed substitution (Bezems, Rieger & Visco, 1981; Arewgoda, Robinson & Simpson, 1983) and metal-exchange reactions (Jensen, Robinson & Simpson, 1983). The work reported here was undertaken to determine the detailed structure of the $PhCCo_3(CO)_9$ molecule.

Experimental. Crystals were grown from hexane as brown-black plates. Crystal dimensions 0·94 × 0·38 × 0·08 mm. D_m by flotation (aqueous $ZnBr_2$). Preliminary precession photography (Cu $K\alpha$) indicated a triclinic space group which was confirmed as $P\bar{1}$ by the success of the refinement. Nicolet $P\bar{3}$ diffractometer, Mo $K\alpha$ radiation (graphite monochromator). Cell dimensions determined by least squares from settings of 24 strong reflections in the range $28{\cdot}2 < 2\theta < 30{\cdot}8°$. 5220 reflections measured. Range of hkl: ±17, ±18, 9. $2\theta_{max} = 45°$. Three standard reflections measured after every 100 reflections; no significant variation. Intensities corrected for Lorentz and polarization effects and empirical absorption corrections applied using *SHELXTL* (Sheldrick, 1980); transmission factors 0·529–0·924. Of 5001 unique reflections ($R_{int} = 0{\cdot}0172$), 4027 were considered observed with $I > 3\sigma(I)$. Structure determined by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The two independent molecules were refined in alternating blocked-matrix cycles minimizing $\sum w(|F_o| - |F_c|)^2$, using *SHELX*76 (Sheldrick, 1976). Neutral-atom scattering factors taken from Cromer & Mann (1968); real and imaginary anomalous-dispersion coefficients from Cromer & Liberman (1970). The phenyl substituents

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for both molecules were refined as rigid groups (C—C = 1·40 Å).

A difference map computed following the location of all non-hydrogen atoms revealed a disorder component in the phenyl substituent of molecule (2). Two orientations of the phenyl ring could be identified with the planes defining the alternative rings inclined at an angle of 79°. The C atoms for both components were input in calculated positions and the occupancy factor refined to $f = 0{\cdot}483\ (8)$ $(f' = 1 - f)$. All non-hydrogen atoms, except the C atoms of the disordered rings, were assigned anisotropic thermal parameters and H atoms were included in calculated positions [C–H = 1·08 Å, $U_{\rm iso}(H_i) = 0{\cdot}10$ Å^2]. Refinement of this model converged with $R = 0{\cdot}0466$ and $wR = 0{\cdot}0766$ [$w^{-1} = \sigma^2(F_o) + 0{\cdot}0031(F_o)^2$] for the 4027 observed reflections. 225 parameters were refined for molecule (1) and 243 for molecule (2), to include the disorder of the phenyl substituent. $(\Delta/\sigma)_{\rm max} = 0{\cdot}4$. The final difference map showed a number of peaks, 0·88–0·50 e Å^{-3}, in the vicinity of the disordered phenyl rings of molecule (2), possibly indicating some additional non-resolvable disorder; remaining peaks <0·47 e Å^{-3}; max. negative $\Delta\rho$ −0·52 e Å^{-3}.

Discussion. Atomic positional parameters are listed in Table 1,* with bond distances and angles in Table 2. The overall molecular geometry is illustrated for molecule (1) in Fig. 1. Molecular parameters for molecule (1) will be used in the subsequent discussion; small differences in bond lengths and angles between the two independent molecules can best be assigned to crystal-packing effects, but the positional disorder in the phenyl ring of the μ_3-carbyne moiety is limited to molecule (2).

The structure of the $CCo_3(CO)_9$ unit varies little from the idealized C_{3v} geometry of the capped triangular cluster (Sutton & Dahl, 1967; Penfold & Robinson, 1973; Raithby, 1980). The Co—Co bonds are equal within experimental error and the Co atoms are equidistant from the capping C atom [Cap(1)] which is symmetrically located 1·266 (6) Å above the centroid of the Co_3 triangle. The phenyl ring is tilted in the direction of Co(11) such that the Cap(1)—C(115)—*R*(*c*) angle is 178 (1)°, while the angle C(115)—Cap(1)—*T*(*c*) is 176·3 (8)° [*R*(*c*) and *T*(*c*) are the centroids of the phenyl ring and the Co_3 triangle respectively]. The dihedral angle between the Co_3 plane and that of the phenyl ring is 91·5 (5)°. The six equatorial carbonyl groups are bent out of the Co_3 plane towards the apical phenyl substituent such that each CoC(eq)-C(eq) plane is inclined at approximately 30° to the plane of the Co atoms. These values correspond well to those found in other tricobalt–carbon clusters. Furthermore, non-bonded contacts between the atoms of the equatorial carbonyl ligands and the C atoms C(110),

Table 1. *Positional and isotropic thermal parameters*

Occupancy factor for C(210), C(211), C(212), C(213), C(214) and C(215): $f = 0{\cdot}483\ (8)$; occupancy factor for corresponding primed atoms: $f' = 1 - f$.

	x	*y*	*z*	$U_{\rm eq}$ or $U_{\rm iso}$(Å^2)
Molecule (I)				
Co(11)	1·1252 (1)	0·8294 (1)	0·4736 (1)	0·045
Co(12)	1·0131 (1)	0·8454 (1)	0·2337 (1)	0·048
Co(13)	1·1112 (1)	0·7450 (1)	0·1750 (1)	0·057
Cap(1)	1·0272 (4)	0·7442 (4)	0·3184 (7)	0·048
C(110)†	0·9680 (3)	0·5850 (3)	0·3017 (7)	0·109
C(111)†	0·9114 (3)	0·5179 (3)	0·3450 (1)	0·153
C(112)†	0·8512 (3)	0·5381 (3)	0·4456 (7)	0·102
C(113)†	0·8476 (3)	0·6254 (3)	0·5027 (7)	0·133
C(114)†	0·9042 (3)	0·6926 (3)	0·4594 (7)	0·107
C(115)†	0·9644 (3)	0·6724 (3)	0·3589 (7)	0·055
C(11)	1·0788 (4)	0·8753 (4)	0·6456 (8)	0·057
O(11)	1·0487 (3)	0·9025 (4)	0·7584 (6)	0·093
C(12)	1·1784 (4)	0·7610 (5)	0·5858 (8)	0·064
O(12)	1·2105 (4)	0·7171 (4)	0·6630 (8)	0·106
C(13)	1·2154 (4)	0·9237 (4)	0·4825 (8)	0·058
O(13)	1·2703 (3)	0·9806 (4)	0·4826 (7)	0·089
C(14)	0·9326 (5)	0·8022 (5)	0·0337 (9)	0·070
O(14)	0·8814 (4)	0·7783 (4)	−0·0957 (7)	0·112
C(15)	0·9415 (4)	0·8890 (4)	0·3588 (8)	0·060
O(15)	0·8954 (3)	0·9179 (3)	0·4334 (7)	0·083
C(16)	1·0764 (5)	0·9471 (5)	0·1858 (9)	0·066
O(16)	1·1139 (4)	1·0067 (3)	0·1597 (7)	0·087
C(17)	1·0415 (7)	0·6758 (7)	−0·0187 (11)	0·119
O(17)	0·9961 (6)	0·6305 (7)	−0·1324 (10)	0·213
C(18)	1·1748 (5)	0·6680 (5)	0·2336 (10)	0·073
O(18)	1·2133 (4)	0·6202 (4)	0·2656 (8)	0·111
C(19)	1·1905 (6)	0·8178 (6)	0·0998 (10)	0·079
O(19)	1·2420 (5)	0·8634 (5)	0·0544 (8)	0·120
Molecule (2)				
Co(21)	0·5147 (1)	0·2758 (1)	0·3829 (1)	0·050
Co(22)	0·5111 (1)	0·2011 (1)	0·0824 (1)	0·048
Co(23)	0·3868 (1)	0·1550 (1)	0·2183 (1)	0·046
Cap(2)	0·4324 (3)	0·2663 (3)	0·1729 (7)	0·043
C(210)†	0·3055 (8)	0·3342 (7)	0·124 (2)	0·109 (6)*
C(211)†	0·2680 (8)	0·4023 (7)	0·084 (2)	0·142 (9)*
C(212)†	0·3179 (8)	0·4712 (7)	0·033 (2)	0·131 (9)*
C(213)†	0·4055 (8)	0·4720 (7)	0·022 (2)	0·081 (5)*
C(214)†	0·4430 (8)	0·4040 (7)	0·063 (2)	0·093 (5)*
C(215)†	0·3930 (8)	0·3351 (7)	0·114 (2)	0·036 (6)*
C(210′)†	0·3253 (8)	0·3031 (6)	−0·054 (1)	0·087 (5)*
C(211′)†	0·2815 (8)	0·3629 (6)	−0·116 (1)	0·103 (6)*
C(212′)†	0·2927 (8)	0·4468 (6)	−0·012 (1)	0·074 (4)*
C(213′)†	0·3477 (8)	0·4708 (6)	0·153 (1)	0·141 (8)*
C(214′)†	0·3914 (8)	0·4110 (6)	0·215 (1)	0·116 (6)*
C(215′)†	0·3802 (8)	0·3271 (6)	0·111 (1)	0·063 (8)*
C(21)	0·5934 (5)	0·3731 (6)	0·393 (1)	0·083
O(21)	0·6404 (5)	0·4384 (4)	0·393 (1)	0·136
C(22)	0·4626 (5)	0·3251 (6)	0·542 (1)	0·087
O(22)	0·4295 (5)	0·3595 (6)	0·6396 (9)	0·151
C(23)	0·5808 (4)	0·2149 (5)	0·5074 (9)	0·066
O(23)	0·6223 (4)	0·1783 (4)	0·5811 (7)	0·095
C(24)	0·4521 (4)	0·1572 (5)	−0·1385 (9)	0·062
O(24)	0·4176 (4)	0·1316 (4)	−0·2804 (7)	0·097
C(25)	0·5946 (5)	0·2792 (5)	0·0360 (9)	0·071
O(25)	0·6509 (4)	0·3275 (4)	0·0039 (9)	0·123
C(26)	0·5728 (4)	0·1189 (4)	0·1247 (8)	0·060
O(26)	0·6118 (3)	0·0679 (4)	0·1562 (7)	0·091
C(27)	0·3025 (4)	0·1006 (5)	0·0221 (9)	0·066
O(27)	0·2483 (3)	0·0681 (4)	−0·0939 (7)	0·101
C(28)	0·3127 (4)	0·1788 (4)	0·3556 (9)	0·058
O(28)	0·2648 (4)	0·1932 (4)	0·4390 (7)	0·098
C(29)	0·4211 (4)	0·0606 (4)	0·2857 (8)	0·060
O(29)	0·4431 (3)	0·0017 (3)	0·3242 (7)	0·090

* Refined isotropic temperature factor.
† Atom of rigid phenyl group.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, mean-plane data, and additional bond lengths and angles, and a figure showing molecule (2) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42314 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(114) and C(115) of the phenyl ring (3·35–3·54 Å) are significantly greater than those between the C atoms of adjacent CO ligands (2·73–2·94 Å), suggesting that an overall balance of non-bonded contacts has been achieved over the cluster polyhedron.

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

Molecule (1)		Molecule (2)	
Co(11)–Co(12)	2·469 (1)	Co(21)–Co(22)	2·470 (1)
Co(11)–Co(13)	2·471 (1)	Co(21)–Co(23)	2·476 (1)
Co(11)–Cap(1)	1·915 (5)	Co(21)–Cap(2)	1·905 (5)
Co(11)–C(11)	1·779 (7)	Co(21)–C(21)	1·768 (8)
Co(11)–C(12)	1·780 (8)	Co(21)–C(22)	1·781 (9)
Co(11)–C(13)	1·840 (6)	Co(21)–C(23)	1·852 (8)
Co(12)–Co(13)	2·469 (1)	Co(22)–Co(23)	2·466 (1)
Co(12)–Cap(1)	1·903 (6)	Co(22)–Cap(2)	1·916 (6)
Co(12)–C(14)	1·791 (6)	Co(22)–C(24)	1·794 (6)
Co(12)–C(15)	1·789 (7)	Co(22)–C(25)	1·771 (8)
Co(12)–C(16)	1·876 (8)	Co(22)–C(26)	1·822 (7)
Co(13)–Cap(1)	1·904 (6)	Co(23)–Cap(2)	1·909 (6)
Co(13)–C(17)	1·772 (8)	Co(23)–C(27)	1·822 (6)
Co(13)–C(18)	1·806 (9)	Co(23)–C(28)	1·786 (7)
Co(13)–C(19)	1·801 (9)	Co(23)–C(29)	1·835 (8)
Cap(1)–C(115)	1·487 (8)	Cap(2)–C(215)	1·474 (14)
		Cap(2)–C(215′)	1·486 (15)
C(11)–O(11)	1·147 (9)	C(21)–O(21)	1·154 (11)
C(12)–O(12)	1·150 (10)	C(22)–O(22)	1·130 (12)
C(13)–O(13)	1·125 (8)	C(23)–O(23)	1·124 (10)
C(14)–O(14)	1·149 (8)	C(24)–O(24)	1·135 (8)
C(15)–O(15)	1·132 (9)	C(25)–O(25)	1·157 (10)
C(16)–O(16)	1·094 (10)	C(26)–O(26)	1·148 (9)
C(17)–O(17)	1·093 (11)	C(27)–O(27)	1·113 (7)
C(18)–O(18)	1·102 (11)	C(28)–O(28)	1·123 (10)
C(19)–O(19)	1·140 (11)	C(29)–O(29)	1·138 (10)
Co(12)–Co(11)–Co(13)	60·0 (1)	Co(22)–Co(21)–Co(23)	59·8 (1)
Co(12)–Co(11)–Cap(1)	49·5 (2)	Co(22)–Co(21)–Cap(2)	49·9 (2)
Co(13)–Co(11)–Cap(1)	49·5 (2)	Co(23)–Co(21)–Cap(2)	49·6 (2)
C(11)–Co(11)–C(12)	96·5 (3)	C(21)–Co(21)–C(22)	95·5 (4)
C(11)–Co(11)–C(13)	100·0 (3)	C(21)–Co(21)–C(23)	102·8 (3)
C(12)–Co(11)–C(13)	104·2 (3)	C(22)–Co(21)–C(23)	101·3 (4)
Co(11)–Co(12)–Co(13)	60·0 (1)	Co(21)–Co(22)–Co(23)	60·2 (1)
Co(11)–Co(12)–Cap(1)	49·9 (1)	Co(21)–Co(22)–Cap(2)	49·5 (1)
Co(13)–Co(12)–Cap(1)	49·6 (2)	Co(23)–Co(22)–Cap(2)	49·7 (2)
C(14)–Co(12)–C(15)	97·1 (3)	C(24)–Co(22)–C(25)	95·6 (3)
C(14)–Co(12)–C(16)	100·2 (3)	C(24)–Co(22)–C(26)	103·1 (3)
C(15)–Co(12)–C(16)	101·7 (3)	C(25)–Co(22)–C(26)	100·0 (3)
Co(11)–Co(13)–Co(12)	60·0 (1)	Co(21)–Co(23)–Co(22)	60·0 (1)
Co(11)–Co(13)–Cap(1)	49·9 (1)	Co(21)–Co(23)–Cap(2)	49·5 (1)
Co(12)–Co(13)–Cap(1)	49·5 (2)	Co(22)–Co(23)–Cap(2)	50·0 (2)
C(17)–Co(13)–C(18)	97·8 (4)	C(27)–Co(23)–C(28)	96·9 (3)
C(17)–Co(13)–C(19)	103·7 (4)	C(27)–Co(23)–C(29)	101·3 (3)
C(18)–Co(13)–C(19)	101·1 (4)	C(28)–Co(23)–C(29)	102·3 (3)
Co(11)–Cap(1)–Co(12)	80·6 (2)	Co(21)–Cap(2)–Co(22)	80·5 (2)
Co(11)–Cap(1)–Co(13)	80·6 (2)	Co(21)–Cap(2)–Co(23)	81·0 (2)
Co(12)–Cap(1)–Co(13)	80·9 (2)	Co(22)–Cap(2)–Co(23)	80·3 (2)
Co(11)–Cap(1)–C(115)	128·2 (4)	Co(21)–Cap(2)–C(215)	128·7 (5)
Co(12)–Cap(1)–C(115)	113·4 (4)	Co(22)–Cap(2)–C(215)	131·3 (6)
Co(13)–Cap(1)–C(115)	133·1 (4)	Co(23)–Cap(2)–C(215)	134·9 (6)
		Co(21)–Cap(2)–C(215′)	132·8 (5)
		Co(22)–Cap(2)–C(215′)	135·2 (6)
		Co(23)–Cap(2)–C(215′)	126·7 (5)
Co(11)–C(11)–O(11)	177·8 (7)	Co(21)–C(21)–O(21)	175·6 (8)
Co(11)–C(12)–O(12)	177·2 (7)	Co(21)–C(22)–O(22)	176·8 (9)
Co(11)–C(13)–O(13)	177·9 (6)	Co(21)–C(23)–O(23)	178·5 (7)
Co(12)–C(14)–O(14)	176·9 (7)	Co(22)–C(24)–O(24)	177·1 (7)
Co(12)–C(15)–O(15)	177·6 (7)	Co(22)–C(25)–O(25)	177·3 (7)
Co(12)–C(16)–O(16)	179·2 (6)	Co(22)–C(26)–O(26)	178·1 (6)
Co(13)–C(17)–O(17)	175·9 (10)	Co(23)–C(27)–O(27)	177·0 (7)
Co(13)–C(18)–O(18)	178·4 (7)	Co(23)–C(28)–O(28)	178·6 (6)
Co(13)–C(19)–O(19)	178·6 (8)	Co(23)–C(29)–O(29)	178·5 (6)

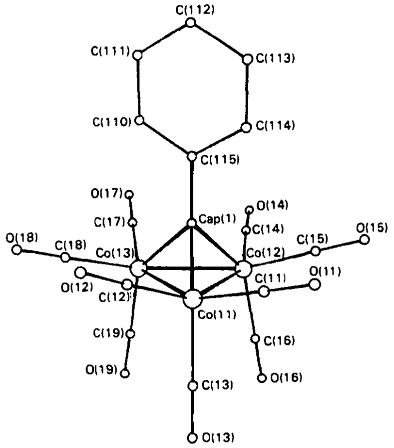

Fig. 1. Molecule (1) of the title compound showing the atomic numbering scheme; H atoms have been omitted.

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