The U atom is η^5 covalently bonded to the planar [within 0·06 (2) Å] indenyl ring. The slight lengthening of U—C(8) and U—C(9) in comparison with U—C(2) and U—C(3) may result from the fact that the negative charge of the indenyl anion primarily resides on the three non-bridging C atoms. Examination of short interligand contacts reveals that it cannot be attributed to steric effects.

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Structure of 1,1,2,2,3,3-Hexacarbonyl-1,2;2,3;3,1-tris(μ-diphenylphosphido)-*triangulo*-tricobalt(I)(3*Co—Co*) Acetonitrile Solvate, $[Co_3\{P(C_6H_5)_2\}_3(CO)_6].C_2H_3N$

By M. K. Markiewicz, M. E. Fraser, R. K. Ungar, S. Fortier* and M. C. Baird*

Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6

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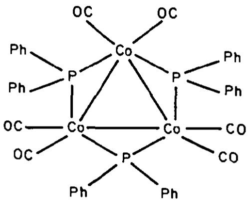
Abstract. $M_r = 941{\cdot}5$, triclinic, $P\bar{1}$, $a = 12{\cdot}448\ (2)$, $b = 16{\cdot}234\ (4)$, $c = 11{\cdot}656\ (4)$ Å, $\alpha = 98{\cdot}34\ (3)$, $\beta = 110{\cdot}19\ (2)$, $\gamma = 103{\cdot}54\ (2)$°, $V = 2082{\cdot}2$ Å^3, $Z = 2$, $D_x = 1{\cdot}502$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54184$ Å, $\mu = 112{\cdot}3$ cm^{-1}, $F(000) = 956$, $T = 293$ K, final $R = 0{\cdot}043$ for 2749 observed reflections. The cobalt atoms form an approximate equilateral triangle with each edge being bridged by a diphenylphosphido ligand. Each of the cobalt atoms is, in addition, coordinated to two terminal carbonyl groups. The mean values for the Co—Co, Co—P, Co—C and C≡O bond lengths are 2·60 (3), 2·172 (3), 1·75 (1) and 1·148 (8) Å respectively.

Introduction. During an investigation of the chemistry of cobalt complexes of the cationic tertiary phosphine $Ph_2PCH_2CH_2NMe_3^+$ (as the iodide salt) (Smith, Ungar, Sanderson & Baird, 1983), green crystals of the title compound (I) were obtained. A similar compound, $[Co_3(\mu\text{-}PMe_2)_3(CO)_6]$, was known (Keller & Vahrenkamp, 1978, 1979) to contain non-equivalent dimethylphosphido ligands. Since such compounds are currently of considerable interest because of their potential catalytic properties (Harley, Guskey & Geoffroy, 1983), it was decided to investigate the structure of the diphenylphosphido analogue for purposes of comparison. It was later discovered that a single-crystal X-ray diffraction study had previously been carried out on the title compound (Huntsman, 1973), for which, to our knowledge, the results have not been published.



(I)

Experimental. Dark-green crystal, specimen 0·17 × 0·17 × 0·06 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$; cell parameters from least squares applied to 25 reflections with $5{\cdot}7 \leq \theta \leq 27{\cdot}2°$; 4673 unique reflections, 2749 considered observed at $3\sigma(I)$ level, h 0→12, k −16→16, l −11→10, $\theta \leq 52°$, θ–2θ scans, three standard reflections monitored after every 7200 s of exposure, max. variation in intensity −7·6%, Lp correction, decay correction, numerical absorption correction, min., max. and av. transmission 0·3308, 0·6562 and 0·5258. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and Fourier methods. Full-matrix least-squares refinement minimizing $\sum w||F_o| - |F_c||^2$, where $w = 4F^2/[\sigma^2(F^2) + (0{\cdot}06\,F^2)^2]$, anisotropic temperature factors for non-hydrogen atoms. Acetonitrile molecule located from difference Fourier map, atoms refined with isotropic temperature factors. Hydrogen atoms, calculated and assigned isotropic temperature factor equal to 1·2 times equivalent isotropic value of parent atom, included in calculations but not refined. Scattering factors those of Cromer & Waber (1974), anomalous-dispersion coefficients from Cromer (1974).

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* Authors to whom correspondence should be addressed.

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Correction for isotropic secondary-extinction effect included in refinement, $g = 0{\cdot}503 \times 10^{-6}$. Final $R = 0{\cdot}043$, $R_w = 0{\cdot}051$, $S = 1{\cdot}195$ for all observed reflections. Final max. Δ/σ 0·13, final max. and min. $\Delta\rho$ excursions 0·526 and −0·407 e Å^{-3} found in vicinity of solvent molecule; calculations performed on a PDP 11/23 computer using Enraf–Nonius *SDP* (Frenz, 1979) and *ORTEP* (Johnson, 1965).

Discussion. The atomic parameters are given in Table 1,* and a view of the molecule is shown in Fig. 1. Bond lengths and angles pertaining to the cobalt atoms' coordination polyhedra are given in Table 2. The cobalt atoms form an approximate equilateral triangle with each edge being bridged by a diphenylphosphido ligand. Two of the phosphorus atoms are on opposite sides of the plane of the cobalt atoms while the third one lies close to the Co_3 plane. Each of the cobalt atoms is, in addition, coordinated to two terminal carbonyl groups which are approximately linear. Thus the gross features of the structure are very similar to those of the dimethylphosphido analogue. Indeed, the averages of the Co—Co, Co—P, Co—C and C≡O bond lengths of the two compounds are not significantly different.

Major differences are observed, however, on comparing the orientations of the phosphido bridges of the two compounds. For the diphenylphosphido compound, the angles between the Co_3 plane and the planes defined by Co(1)/Co(2)/P(1), Co(1)/Co(3)/P(3) and Co(2)/Co(3)/P(2) are 168·5 (2), 113·3 (2) and 119·6 (2)°, respectively. For the dimethylphosphido compound, in contrast, the corresponding angles are 156·3, 110·0 and 137·0°.

The differences, while significant, probably do not imply differences in the bonding of the two compounds. In both cases, solution NMR spectroscopy demonstrates clearly that the compounds are fluxional, undergoing a facile process in which the phosphido bridges exchange positions (Keller & Vahrenkamp, 1978; Harley *et al.*, 1983). Thus the barriers to movement of the phosphido bridges in and out of the Co_3 planes are small, and the conformations in the crystalline state are likely to be determined by crystal packing forces.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq}(Å^2)
Co(1)	0·3540 (1)	0·32646 (7)	0·5341 (1)	3·33 (3)
Co(2)	0·2082 (1)	0·17342 (7)	0·5220 (1)	3·00 (3)
Co(3)	0·4202 (1)	0·18766 (7)	0·5269 (1)	3·34 (3)
P(1)	0·1863 (2)	0·3014 (1)	0·5610 (2)	3·45 (5)
P(2)	0·2526 (2)	0·1054 (1)	0·3776 (2)	3·22 (5)
P(3)	0·4962 (2)	0·3019 (1)	0·6848 (2)	3·49 (5)
O(1*A*)	0·3073 (6)	0·3312 (4)	0·2712 (5)	7·0 (2)
O(1*B*)	0·5528 (5)	0·4866 (3)	0·3631 (6)	7·1 (2)
O(2*B*)	0·7428 (5)	0·8860 (3)	0·2474 (5)	5·9 (2)
O(2*A*)	0·9609 (5)	0·0702 (4)	0·3834 (5)	7·0 (2)
O(3*A*)	0·5730 (5)	0·2253 (4)	0·3900 (5)	8·1 (2)
O(3*B*)	0·4906 (5)	0·0507 (3)	0·6425 (6)	7·0 (2)
N(1*S*)*	0·327 (1)	0·9240 (9)	−0·003 (1)	18·8 (5)
C(1*B*)	0·5895 (6)	0·5610 (5)	0·4053 (7)	4·1 (2)
C(1*S*)*	0·671 (1)	0·0737 (9)	0·214 (1)	12·3 (4)
C(1*A*)	0·3207 (6)	0·3237 (4)	0·3710 (7)	3·7 (2)
C(2*B*)	0·7563 (6)	0·8574 (5)	0·3355 (6)	3·8 (2)
C(2*A*)	0·0590 (6)	0·1136 (5)	0·4398 (7)	4·1 (2)
C(2*S*)*	0·675 (1)	0·068 (1)	0·100 (1)	16·2 (6)
C(3*A*)	0·5133 (7)	0·2108 (5)	0·4445 (7)	5·0 (2)
C(3*B*)	0·4651 (7)	0·1052 (5)	0·5983 (7)	4·5 (2)
C(11)	0·0553 (7)	0·3207 (5)	0·4504 (7)	4·5 (2)
C(12)	0·0298 (7)	0·2953 (5)	0·3220 (8)	5·9 (3)
C(13)	0·9288 (9)	0·3044 (6)	0·2332 (9)	7·9 (3)
C(14)	0·8494 (9)	0·3353 (6)	0·268 (1)	9·6 (4)
C(15)	0·8722 (8)	0·3591 (7)	0·392 (1)	9·3 (4)
C(16)	0·0252 (7)	0·6473 (6)	0·5148 (9)	6·7 (3)
C(21)	0·8151 (6)	0·6505 (4)	0·2891 (6)	3·5 (2)
C(22)	0·8532 (7)	0·7028 (5)	0·2186 (7)	5·1 (2)
C(23)	0·8491 (8)	0·6668 (5)	0·1020 (8)	6·2 (3)
C(24)	0·8065 (7)	0·5775 (5)	0·0536 (8)	6·0 (3)
C(25)	0·7712 (7)	0·5244 (5)	0·1223 (8)	5·9 (3)
C(26)	0·7750 (7)	0·5593 (5)	0·2386 (7)	4·7 (2)
C(31)	0·1982 (6)	0·1154 (4)	0·2159 (6)	3·5 (2)
C(32)	0·2708 (8)	0·1244 (6)	0·1496 (7)	5·9 (3)
C(33)	0·2231 (8)	0·1265 (6)	0·0222 (7)	7·0 (3)
C(34)	0·1026 (9)	0·1201 (6)	0·9646 (8)	6·7 (3)
C(35)	0·9650 (8)	0·8877 (6)	0·9702 (8)	7·3 (3)
C(36)	0·0799 (7)	0·1105 (5)	0·1549 (7)	5·3 (3)
C(41)	0·2210 (6)	−0·0128 (4)	0·3548 (6)	3·0 (2)
C(42)	0·1955 (7)	−0·0526 (5)	0·4414 (7)	5·2 (2)
C(43)	0·1761 (7)	0·8578 (5)	0·4302 (7)	6·0 (3)
C(44)	0·1860 (7)	0·8086 (5)	0·3298 (8)	5·3 (3)
C(45)	0·2116 (7)	0·8468 (5)	0·2429 (7)	5·0 (2)
C(46)	0·2301 (7)	−0·0641 (5)	0·2544 (7)	4·6 (2)
C(51)	0·3489 (6)	0·6327 (4)	0·2754 (7)	3·8 (2)
C(52)	0·3226 (7)	0·5878 (5)	0·3575 (8)	5·7 (3)
C(53)	0·2034 (7)	0·5405 (5)	0·3317 (9)	6·7 (3)
C(54)	0·1127 (7)	0·5427 (5)	0·2256 (9)	6·7 (3)
C(55)	0·1386 (7)	0·5870 (5)	0·1432 (8)	6·0 (3)
C(56)	0·2562 (7)	0·6319 (5)	0·1657 (7)	4·8 (2)
C(61)	0·4974 (6)	0·3008 (4)	0·8402 (6)	3·6 (2)
C(62)	0·5245 (7)	0·2365 (5)	0·9018 (8)	5·6 (3)
C(63)	0·5255 (8)	0·2398 (6)	1·0216 (8)	6·6 (3)
C(64)	0·4988 (8)	0·3074 (6)	0·0816 (7)	6·1 (3)
C(65)	0·4740 (7)	0·3715 (5)	1·0224 (8)	5·6 (3)
C(66)	0·4717 (7)	0·3677 (5)	0·9047 (7)	4·7 (2)

* Solvent molecule.

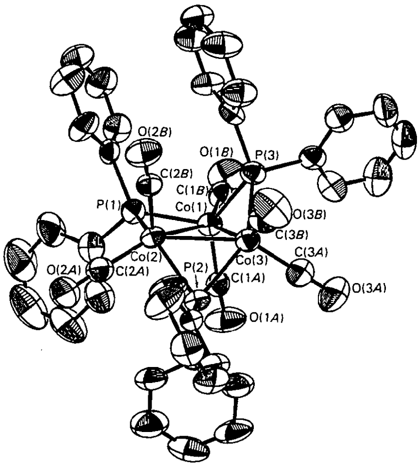

Fig. 1. *ORTEP* diagram (Johnson, 1965) and atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom parameters and complete bond length and angle data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39843 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Co(1)–Co(2)	2·664 (2)	Co(2)–C(2*A*)	1·722 (9)
Co(1)–Co(3)	2·574 (2)	Co(2)–C(2*B*)	1·745 (9)
Co(2)–Co(3)	2·575 (2)	Co(3)–C(3*A*)	1·753 (10)
Co(1)–P(1)	2·172 (2)	Co(3)–C(3*B*)	1·775 (9)
Co(2)–P(1)	2·161 (2)	C(1*A*)–O(1*A*)	1·146 (8)
Co(2)–P(2)	2·179 (2)	C(1*B*)–O(1*B*)	1·150 (8)
Co(3)–P(2)	2·164 (2)	C(2*A*)–O(2*A*)	1·152 (8)
Co(1)–P(3)	2·183 (2)	C(2*B*)–O(2*B*)	1·163 (8)
Co(3)–P(3)	2·170 (2)	C(3*A*)–O(3*A*)	1·139 (9)
Co(1)–C(1*A*)	1·791 (9)	C(3*B*)–O(3*B*)	1·139 (9)
Co(1)–C(1*B*)	1·736 (9)		
Co(2)–Co(1)–Co(3)	58·86 (4)	P(1)–Co(1)–P(3)	112·46 (9)
Co(1)–Co(2)–Co(3)	58·83 (4)	P(1)–Co(2)–P(2)	133·06 (9)
Co(1)–Co(3)–Co(2)	62·32 (4)	P(2)–Co(3)–P(3)	142·7 (1)
Co(2)–Co(1)–P(1)	51·89 (6)	P(1)–Co(1)–C(1*A*)	108·1 (3)
Co(3)–Co(1)–P(1)	109·92 (7)	P(1)–Co(1)–C(1*B*)	99·7 (3)
Co(2)–Co(1)–P(3)	88·00 (7)	P(3)–Co(1)–C(1*A*)	135·0 (3)
Co(3)–Co(1)–P(3)	53·50 (6)	P(3)–Co(1)–C(1*B*)	93·3 (3)
Co(1)–Co(2)–P(1)	52·23 (6)	P(1)–Co(2)–C(2*A*)	98·5 (3)
Co(3)–Co(2)–P(1)	110·22 (7)	P(1)–Co(2)–C(2*B*)	105·9 (3)
Co(1)–Co(2)–P(2)	91·72 (7)	P(2)–Co(2)–C(2*A*)	89·7 (3)
Co(3)–Co(2)–P(2)	53·36 (6)	P(2)–Co(2)–C(2*B*)	117·1 (3)
Co(1)–Co(3)–P(2)	94·56 (7)	P(2)–Co(3)–C(3*A*)	102·0 (3)
Co(2)–Co(3)–P(2)	53·91 (6)	P(2)–Co(3)–C(3*B*)	98·2 (3)
Co(1)–Co(3)–P(3)	54·00 (6)	P(3)–Co(3)–C(3*A*)	102·6 (3)
Co(2)–Co(3)–P(3)	90·61 (7)	P(3)–Co(3)–C(3*B*)	102·9 (3)
Co(2)–Co(1)–C(1*A*)	102·4 (2)	C(1*B*)–Co(1)–C(1*A*)	98·5 (4)
Co(2)–Co(1)–C(1*B*)	148·9 (3)	C(2*B*)–Co(2)–C(2*A*)	102·9 (4)
Co(3)–Co(1)–C(1*A*)	94·8 (2)	C(3*A*)–Co(3)–C(3*B*)	103·4 (4)
Co(3)–Co(1)–C(1*B*)	141·7 (3)		
Co(1)–Co(2)–C(2*A*)	137·3 (3)	Co(1)–C(1*A*)–O(1*A*)	172·5 (7)
Co(1)–Co(2)–C(2*B*)	114·1 (3)	Co(1)–C(1*B*)–O(1*B*)	178·6 (8)
Co(3)–Co(2)–C(2*A*)	142·7 (3)	Co(2)–C(2*A*)–O(2*A*)	176·8 (8)
Co(3)–Co(2)–C(2*B*)	91·8 (3)	Co(2)–C(2*B*)–O(2*B*)	172·8 (7)
Co(1)–Co(3)–C(3*A*)	99·2 (3)	Co(3)–C(3*A*)–O(3*A*)	179·4 (8)
Co(1)–Co(3)–C(3*B*)	151·0 (3)	Co(3)–C(3*B*)–O(3*B*)	178·0 (9)
Co(2)–Co(3)–C(3*A*)	144·5 (3)		
Co(2)–Co(3)–C(3*B*)	105·5 (3)		

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Synthèse et Structure d'un Complexe Trinucléaire du Cobalt(II) à Multiples Coordinats Chélatant et Ponteur: μ_3-Chloro-tris(diméthoxy-1,2 éthane)-μ_3-sulfato-tris-(μ-trifluoroacétato-*O,O'*)-tricobalt(II), $[Co_3Cl(C_2F_3O_2)_3(SO_4)(C_4H_{10}O_2)_3]$

PAR JACQUES ESTIENNE

Laboratoire de Chimie Organique Structurale, Université de Provence, Centre de Saint-Jérôme, 13397 *Marseille CEDEX* 13, *France*

(*Reçu le* 15 *mai* 1984, *accepté le* 20 *septembre* 1984)

Abstract. $M_r = 917{\cdot}7$, rhombohedral, $R3$, $a = 9{\cdot}654$ (3) Å, $\alpha = 84{\cdot}06$ (3)°, $V = 886{\cdot}1$ (8) Å^3, $Z = 1$, $D_x = 1{\cdot}70$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 16{\cdot}2$ cm^{-1}, $F(000) = 461$, $T = 298$ K, $R = 0{\cdot}058$, $R_w = 0{\cdot}068$ for 3957 non-zero diffractometer data. The reaction of cobalt trifluoroacetate in a 1,2-dimethoxyethane solution with thionyl chloride, at room temperature and under nitrogen, results in the formation of an air-sensitive crystalline complex whose composition has been defined by this X-ray crystallographic study. The structure consists of a discrete trimeric complex lying on a threefold axis of the crystal with nearly C_{3v} molecular symmetry. The cobalt atoms, which occupy the corners of an equilateral triangle [Co—Co distance 3·786 (1) Å], are bridged by three different anions. The trifluoroacetato ligands approximately in the plane of the metal atoms act as bidentate bridging groups. A sulphate moiety acting as a tripod ligand and a chlorine atom located 2·481 (1) Å from the three cobalt atoms are respectively above and below the metal plane. The two oxygen atoms of a dimethoxyethane molecule in a *gauche* conformation complete the distorted octahedral environment of each cobalt atom acting as a bidentate chelating group.

Introduction. Le chlorure de thionyle s'est avéré un agent chlorurant efficace dans la synthèse de complexes trifluroacétates de cobalt et de nickel susceptibles de

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