

Structure of Bis{[2-(dimethylarsino)-3,3,4,4-tetrafluorocyclobut-1-enyl]-diphenylphosphine}hexacarbonyldicobalt, [(Ph₂P)C=C(Me₂As)CF₂CF₂Co(CO)₃]₂

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Abstract. C₄₂H₃₂As₂F₈Co₂O₆P₂, *M_r* = 1113.06, monoclinic, *P*2₁/*n*, *a* = 10.102 (1), *b* = 20.188 (3), *c* = 11.596 (2) Å, β = 105.26 (2)°, *V* = 2277.2 Å³, ρ_o = 1.60 (KI flotation), *Z* = 2, ρ_c = 1.62 g cm⁻³; Mo *K*α radiation, λ = 0.70926 Å, μ(Mo *K*α) = 9.24 cm⁻¹, *F*(000) = 1108, *t* = 24.5°C. For 1854 observed reflections the final *R* = 0.052. The crystallographically centrosymmetric molecule is comprised of two linked Co atoms [Co–Co' 2.663 (2) Å], each having an irregular trigonal-bipyramidal environment. A trigonal plane is formed by the three carbonyl groups. The ligand coordinates with the P atom occupying an axial position [Co(1)–P(3) 2.173 (2) Å], while the As atom lies above an adjacent phenyl ring (As···C contacts ranging from 3.51 to 4.25 Å).

Introduction. Crystals of the title compound were dark red, irregular in shape ranging from plates to needles, and showed the greatest elongation along *c*. A Weissenberg photograph of the *hk*0 zone and precession photographs of the *0kl* and *h0l*–*h2l* layers were taken using Cu *K*α radiation (λ = 1.5418 Å). The systematic absences of *h0l* when *h* + *l* = 2*n* + 1 and *0k0* when *k* = 2*n* + 1 indicated the space group as *P*2₁/*n* (a non-standard orientation of *P*2₁/*c*).

A crystal was ground to an approximate sphere of diameter 0.28 mm and was used to determine cell dimensions and intensity data. It was mounted with a general orientation in order to minimize intrinsic multiple reflections. Cell dimensions were obtained by a least-squares analysis of the 2θ values of 19 reflections which had been accurately centred on a computer-controlled four-circle Picker diffractometer. The radiation used was Mo *K*α₁, with a take-off angle of 2.6° at 24°C; the errors in cell dimensions are those determined by the least-squares process.

Intensity data were collected by the θ–2θ scan technique using Mo *K*α radiation (Nb filter) and a scintillation counter equipped with a pulse-height analyser. The take-off angle was 3.6°. Each reflection was scanned for 1° (extended for spectral dispersion) at a scan rate of 2° min⁻¹. A stationary background count was taken for 10 s at each end of the scan range. After

every 70 reflections, two standards were measured and the maximum deviation of any standard from the mean

Table 1. Atomic coordinates (× 10⁴)

	<i>x</i>	<i>y</i>	<i>z</i>
As (1)	5025 (1)	2267 (1)	686 (8)
Co(2)	684 (1)	435 (1)	801 (1)
P(3)	1845 (2)	1110 (1)	2153 (2)
C(4)	7010 (10)	2251 (6)	2275 (10)
C(5)	4813 (13)	2082 (6)	140 (10)
C(6)	4739 (8)	1352 (4)	2225 (7)
C(7)	3664 (8)	982 (4)	2373 (7)
C(8)	4507 (9)	355 (5)	2644 (8)
C(9)	5731 (10)	774 (5)	2541 (9)
F(10)	6346 (6)	582 (3)	1719 (7)
F(11)	6715 (5)	841 (3)	3581 (6)
F(12)	4169 (5)	–145 (3)	1851 (5)
F(13)	4604 (6)	81 (3)	3717 (5)
C(14)	–864 (10)	896 (5)	488 (8)
O(15)	–1841 (7)	1203 (4)	284 (6)
C(16)	1746 (9)	546 (5)	–181 (8)
O(17)	2438 (7)	649 (3)	–807 (6)
C(18)	962 (9)	–230 (4)	1813 (8)
O(19)	1130 (6)	–657 (3)	2502 (6)
C(20)	1598 (8)	1991 (4)	1842 (7)
C(21)	1220 (9)	2201 (5)	667 (8)
C(22)	1057 (10)	2877 (5)	403 (9)
C(23)	1265 (10)	3328 (5)	1298 (9)
C(24)	1632 (10)	3129 (5)	2452 (9)
C(25)	1825 (9)	2460 (5)	2744 (8)
C(26)	1627 (8)	1025 (4)	3661 (7)
C(27)	2725 (9)	1078 (4)	4673 (8)
C(28)	2500 (9)	1017 (5)	5797 (8)
C(29)	1220 (10)	928 (5)	5915 (9)
C(30)	121 (10)	884 (5)	4935 (9)
C(31)	352 (9)	921 (5)	3799 (8)
H(21)	1051	1886	47
H(22)	813	3015	–407
H(23)	1188	3783	1119
H(24)	1738	3444	3059
H(25)	2109	2325	3549
H(27)	3611	1153	4597
H(28)	3252	1033	6473
H(29)	1095	895	6721
H(30)	–810	817	5012
H(31)	–371	873	3122
H(4A)	7414	1866	2164
H(4B)	7264	2373	3086
H(4C)	7279	2592	1822
H(5A)	5397	2404	–85
H(5B)	3887	2226	–227
H(5C)	4946	1691	–147

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was 4.8%. In this manner, intensities for 3341 reflections with $2\theta < 45^\circ$ were measured.

Intensities were corrected for background (normalized to the scan time) and for the Lorentz-polarization factor. An absorption correction was applied by assuming the crystal to be a sphere, $\mu r = 0.15$. For each reflection, the e.s.d. in the intensity, σ_I , was determined from $\sigma_I = [(T_C) + (T_S/T_B)^2(B_1 + B_2) + (KI)^2]^{1/2}$, where T_C = total count, B_1 and B_2 are the backgrounds at each end of the scan range, T_S = scan time, T_B = background count time and K is a constant set to 0.03. If $I < 3.0\sigma_I$ (where I = net intensity) the reflection was considered unobserved. The number of observed reflections was 1854.

From a three-dimensional Patterson map, the position of the Co was determined. This, followed by a

series of structure factor calculations and electron density syntheses, allowed the positions of all non-hydrogen atoms to be located. Full-matrix least-squares refinement of positional and isotropic temperature

Table 3. *Least-squares planes and deviations of atoms*

	A	B	C	D	χ^2
Plane I: C(20)–C(25)	0.9979	0.0645	–0.0005	–1.3139	2.3
Plane II: C(26)–C(31)	0.1430	–0.9896	–0.0147	2.0310	6.6
Plane III: C(14), C(16), C(18)	–0.3409	–0.6552	–0.6742	1.2052	0.0
[Co 0.12, O(15)–0.06, O(17)–0.03, O(19) 0.06 Å]					
Plane IV: C(6)–C(9)	0.0373	–0.2340	–0.9715	2.9186	14.1
[C(6), 0.014, C(7)–0.013, C(8) 0.017, C(9)–0.021 Å]					

Dihedral angles between planes

(I)/(II)	85.5°	(II)/(III)	52.4°
(I)/(III)	112.5	(II)/(IV)	75.5
(I)/(IV)	88.7	(III)/(IV)	37.3

Table 2. *Interatomic distances (Å) and angles (°)*

Asterisks indicate values corrected for riding motion. (The second atom is assumed to ride on the first.)

As(1)–C(4)	1.93 (1)	C(8)–F(12)	1.35 (1)
	[1.94 (1)]*	C(8)–F(13)	1.34 (1)
As(1)–C(5)	1.93 (1)	C(9)–F(10)	1.33 (1)
	[1.95 (1)]*	C(9)–F(11)	1.35 (1)
As(1)–C(16)	1.95 (1)	C(20)–C(21)	1.38 (1)
Co(2)–Co'(2)	2.663 (2)	C(21)–C(22)	1.40 (1)
Co(2)–P(3)	2.173 (2)	C(22)–C(23)	1.36 (1)
Co(2)–C(14)	1.77 (1)	C(23)–C(24)	1.35 (1)
Co(2)–C(16)	1.77 (1)	C(24)–C(25)	1.39 (1)
Co(2)–C(18)	1.76 (1)	C(25)–C(26)	1.39 (1)
C(14)–O(15)	1.14 (1)	C(26)–C(27)	1.39 (1)
C(16)–O(17)	1.15 (1)	C(27)–C(28)	1.39 (1)
C(18)–O(19)	1.16 (1)	C(28)–C(29)	1.35 (1)
P(3)–C(7)	1.81 (1)	C(29)–C(30)	1.37 (1)
P(3)–C(20)	1.82 (1)	C(30)–C(31)	1.40 (1)
P(3)–C(26)	1.83 (1)	C(31)–C(26)	1.36 (1)
C(6)–C(7)	1.37 (1)	As(1)···C(20)	3.51
C(7)–C(8)	1.51 (1)	As(1)···C(21)	3.73
C(8)–C(9)	1.53 (1)	As(1)···C(22)	4.10
C(9)–C(6)	1.52 (1)	As(1)···C(23)	4.25
		As(1)···C(24)	4.08
		As(1)···C(25)	3.68

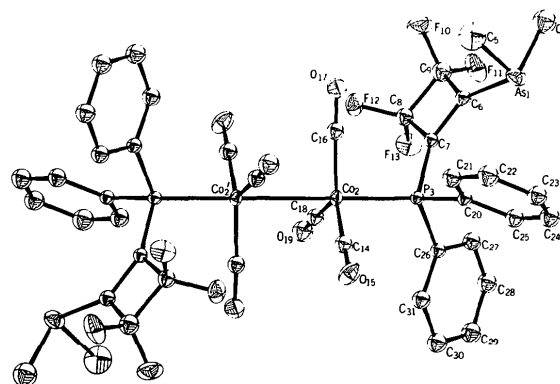


Fig. 1. The molecular structure of $[(\text{Ph}_2\text{P})\text{C}=\text{C}(\text{Me}_2\text{As})\text{CF}_2\text{CF}_2\text{Co}(\text{CO})_3]_2$.

Table 2 (cont.)

C(4)–As(1)–C(5)	96.4 (5)	Co(2)–P(3)–C(7)	103.6 (4)	P(3)–C(26)–C(27)	122.0 (6)
C(4)–As(1)–C(6)	94.6 (4)	Co(2)–P(3)–C(20)	116.8 (3)	P(3)–C(26)–C(31)	118.9 (6)
C(5)–As(1)–C(6)	97.1 (4)	Co(2)–P(3)–C(26)	117.0 (3)	C(31)–C(26)–C(27)	119.0 (8)
Co'(2)–Co(2)–P(3)	177.6 (2)	C(7)–P(3)–C(20)	104.4 (4)	C(26)–C(27)–C(28)	119.7 (8)
Co'(2)–Co(2)–C(14)	86.3 (3)	C(7)–P(3)–C(26)	103.1 (4)	C(27)–C(28)–C(29)	120.4 (9)
Co'(2)–Co(2)–C(16)	85.8 (3)	C(20)–P(3)–C(26)	103.6 (4)	C(28)–C(29)–C(30)	121.0 (1.0)
Co'(2)–Co(2)–C(18)	85.7 (3)	P(3)–C(20)–C(21)	118.9 (6)	C(29)–C(30)–C(31)	118.6 (9)
P(3)–Co(2)–C(14)	95.6 (3)	P(3)–C(20)–C(25)	122.2 (6)	C(30)–C(31)–C(26)	121.2 (8)
P(3)–Co(2)–C(16)	94.7 (3)	C(6)–C(9)–F(10)	117.1 (8)	C(9)–C(6)–C(7)	92.5 (7)
P(3)–Co(2)–C(18)	92.1 (3)	C(6)–C(9)–F(11)	114.9 (6)	C(6)–C(7)–C(8)	93.5 (7)
C(14)–Co(2)–C(16)	116.9 (4)	C(8)–C(9)–F(10)	115.9 (9)	C(7)–C(8)–C(9)	86.8 (7)
C(14)–Co(2)–C(18)	120.2 (4)	C(8)–C(9)–F(11)	113.9 (8)	C(8)–C(9)–C(6)	87.1 (7)
C(16)–Co(2)–C(18)	120.6 (4)	F(10)–C(9)–F(11)	107.2 (9)	C(7)–C(8)–F(12)	117.2 (7)
Co(2)–C(14)–O(15)	178.5 (9)	C(25)–C(20)–C(21)	118.9 (8)	C(7)–C(8)–F(13)	116.0 (7)
Co(2)–C(16)–O(17)	176.8 (8)	C(20)–C(21)–C(22)	120.1 (9)	C(9)–C(8)–F(12)	115.2 (8)
Co(2)–C(18)–O(19)	177.9 (9)	C(21)–C(22)–C(23)	120.2 (9)	C(9)–C(8)–F(13)	116.0 (8)
		C(22)–C(23)–C(24)	120.0 (1.0)	F(12)–C(8)–F(13)	105.5 (8)
		C(23)–C(24)–C(25)	120.9 (9)		
		C(24)–C(25)–C(20)	119.6 (8)		

Table 4. Comparison of distances and angles in (F₄AsP)₂Co₂(CO)₆, [Co(CO)₃Bu₃P]₂, and Co₂(CO)₆[P(C₆H₅)₃]₂

	(F ₄ AsP) ₂ Co ₂ (CO) ₆	[Co(CO) ₃ Bu ₃ P] ₂	Co ₂ (CO) ₆ [P(C ₆ H ₅) ₃] ₂
Co—Co'	2.663 (2) Å	2.665 (14) Å	2.661 (3) Å
Co—P	2.173 (2)	2.178 (15)	2.191 (4)
Co—C	1.77 (1)	1.753 (33)	1.78 (1)
C—O	1.15 (1)	1.12 (3)	1.13 (1)
P—Co—C	94.5 (3)°	92.3 (10)°	94.2 (2)°
Co—C—O	177.1 (9)	178 (3)	178.2 (7)
Co'—Co—P	177.6 (2)	180	180

parameters of these atoms reduced R to 0.117. (Unobserved reflections were not included in the refinement.) A series of difference Fourier syntheses showed that As(1), Co(2), F(10), F(11), F(12), F(13), O(15) and O(17) were all undergoing anisotropic thermal motion. When the refinement was carried out with anisotropic temperature parameters for these atoms R was reduced to 0.066.

An electron-density difference map showed C(4) and C(5) also to be undergoing anisotropic motion; changes were made to allow for this and the methyl and phenyl H atoms were included at calculated positions. Subsequent least-squares refinement gave an R of 0.052 and an R' of 0.052.* The weighting scheme used was $w = 1/\sigma_F^2$, where $\sigma_F = \sigma_I/Lp^2F_o$ and Lp is the Lorentz-polarization factor. Scattering factors for non-hydrogen atoms were those given by Cromer & Waber (1965), while for the H atoms those of Stewart, Davidson & Simpson (1965) were used. Anomalous-dispersion corrections for the As and Co atoms were obtained from *International Tables for X-ray Crystallography* (1962). Computer programs described by Einstein & Jones (1972) were used in this study.

Final parameters for all atoms are listed in Table 1. Table 2 contains interatomic distances and angles, while Table 3 lists some selected planar groups. Errors are those from the variance-covariance matrix and the errors in the cell dimensions. Fig. 1 is an illustration of the molecule and has been drawn with the plot program *ORTEP* (Johnson, 1965).

Discussion. A trigonal-bipyramidal environment has been found to exist around the Co atoms. Carbonyl groups occupy the equatorial positions while a P atom and the complementary Co atom fill the axial positions. Similar situations were found with respect to the crystal structures of [Co(CO)₃Bu₃P]₂ (Ibers, 1968), and

Co₂(CO)₆[P(C₆H₅)₃]₂ (Foust, 1970). Table 4 gives a comparison of the basic skeletal features of the three structures. In the title compound it can be seen that the carbonyl groups deviate from equatorial positioning. This suggests that the Co—P bond is of a higher order than the Co—Co' bond.

Irregular tetrahedral coordination is present around the P atoms, as expected, with bond angles varying from 103.1 (1) to 117.0 (3)°. The P—C bonds, however, are not significantly different in length, being 1.81 (1), 1.82 (1) and 1.83 (1) Å.

In the title compound the F₄AsP ligand {[2-(dimethylarsino)-3,3,4,4-tetrafluorocyclobut-1-enyl]-diphenylphosphine} is monodentate, although it has two possible donor sites. While consideration of the effects of electron donation and steric interactions might lead one to favour coordination through the As, the P atoms coordinate to the metal. This may be attributed to the presence of the two electron-withdrawing phenyl groups. These would increase the π bonding from filled d orbitals on the metal to empty d orbitals on the P. In contrast, the As has two electron-donating methyl groups.

The As does have 'long contacts', though, with a phenyl ring (3.51–4.25 Å).

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33310 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.