Crystal and Molecular Structure of Di-μ-carbonyl-dicarbonyl(triethylphosphine)cobalt(π-cyclopentadienylnickel)

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The crystal structure of the title compound has been determined by *X*-ray diffraction methods from three-dimensional counter data. The structure was solved by Patterson and Fourier methods and refined by a least-squares procedure to *R* 0·052 for 2853 unique reflections. The monoclinic unit cell, space group $P2_1/c$, has dimensions a = 8·945 ± 0·008, b = 10·462 ± 0·014, c = 20·005 ± 0·025 Å, β = 107·5 ± 0·1° for Z = 4. The molecule has the expected $Ni(CO)_2Co$ bridging system, the angle between the two Ni(CO)Co planes being 133·7°. Distortions within the bridging system are apparent: Ni–C(bridge) 1·825(6) and 1·900(6), Co–C(bridge) 1·956(6) and 1·890(5) Å; Ni · · · Co is 2·4097(8) and Co–P 2·236(1) Å.

SPECTRAL studies[1] of the complexes (π-dienyl)Ni-$[Co(CO)_4L]$ (L = phosphine) have shown them to possess a $Ni(CO)_2Co$ bridging system. The crystal structure of one of these complexes, $(\pi\text{-}C_5H_5)Ni[Co(CO)_4(PEt_3)]$, was undertaken to determine its molecular structure and the relationship of this to those of the parent complexes, $[(\pi\text{-}C_5H_5)NiCO]_2$ and $Co_2(CO)_8$, and of other related complexes.

EXPERIMENTAL

Crystal Data.—$C_{15}H_{20}CoNiO_4P$, M = 412·9, Monoclinic, a = 8·495 ± 0·008, b = 10·462 ± 0·014, c = 20·005 ± 0·025 Å, β = 107·5 ± 0·1°, U = 1785·5 Å^3, D_m = 1·54 (by flotation), Z = 4, D_c = 1·536, $F(000)$ = 848. Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 21·2 cm^{-1}, for cell parameters and intensity measurements. Space group $P2_1/c$ (No. 14, C_{2h}^5).

The complex crystallises as dark red-brown diamond shaped plates lying on the (100) face with pinacoids {011} and $\{0\bar{1}1\}$. Unit-cell parameters were determined from single-crystal precession photographs by use of Mo-K_α radiation. Intensities were measured on a Philips PAILRED diffractometer by use of monochromatised Mo-K_α radiation. Each reflection in the $h0$—$14l$ and $hk0$ layers, to a maximum angle of θ = 30°, was recorded. 3005 Reflections gave counts for which $\sigma(I)/I < 0.5$,[2] which yielded 2853 unique reflections. Intensities were corrected for Lorentz and polarisation effects, but no correction for absorption or extinction was applied.

Wilson's method[3] was used to place the data on approximately absolute scale. Scattering factor curves for all atoms were taken from ref. 4, the values for the nickel and cobalt atoms being corrected for anomalous dispersion.

Structure Determination.—The positions of the nickel and cobalt atoms were obtained from a three-dimensional Patterson synthesis. The complete solution of the structure was obtained by means of a series of Fourier syntheses, each phased on an increasing number of atoms. The structure factors calculated with co-ordinates for all non-hydrogen atoms and an overall thermal parameter B = 3·0 Å^2 gave R 0·18. Refinement of the structure was carried out by use of a least-squares procedure in which the function minimised was $\Sigma w(|F_o| - |F_c|)^2$. The weight for each reflection, w, was unity in the initial refinement and was calculated from the expression $w = (20{\cdot}0 - 0{\cdot}3|F_o| + 0{\cdot}003|F_o|^2)^{-1}$ for the final refinement. For this latter weighting scheme the average values of $w\Delta^2$ for the ranges of increasing $|F_o|$ were almost constant. Reflections for which $|F_c| < \frac{1}{3}|F_o|$ were omitted from the least-squares analysis.

In the initial refinement, a full-matrix technique was used in which positional and individual isotropic thermal parameters for each atom together with an overall scale factor were refined. A difference-Fourier synthesis was calculated when the maximum shift in any parameter was of the order of σ. This map yielded the positions for all the hydrogen atoms and they were included in subsequent calculations with a thermal parameter B 6·0 Å^2. Refinement was continued for all non-hydrogen atoms with

TABLE 1

Atomic co-ordinates (fractional) with estimated standard deviations in parentheses

	x/a	y/b	z/c	σ_{rms}/Å
Ni	0·17589(8)	0·21946(7)	0·02503(3)	0·0007
Co	0·36230(8)	0·26859(6)	0·13687(3)	0·0007
P	0·61798(15)	0·23180(13)	0·15604(6)	0·0013
O(B1)	0·0363(5)	0·3485(6)	0·1149(3)	0·005
O(B2)	0·3715(6)	0·0088(4)	0·0832(2)	0·005
O(T1)	0·3352(7)	0·2157(6)	0·2756(3)	0·006
O(T2)	0·4056(7)	0·5437(4)	0·1232(3)	0·005
C(B1)	0·1368(6)	0·2992(6)	0·0992(3)	0·006
C(B2)	0·3312(7)	0·1139(5)	0·0857(3)	0·006
C(T1)	0·3468(7)	0·2317(6)	0·2216(3)	0·006
C(T2)	0·3898(7)	0·4363(6)	0·1282(3)	0·006
C(11)	0·6893(8)	0·0916(7)	0·2104(4)	0·007
C(12)	0·8625(10)	0·0640(9)	0·2311(4)	0·009
C(21)	0·6774(8)	0·2041(6)	0·0773(3)	0·007
C(22)	0·6332(10)	0·3108(9)	0·0249(4)	0·009
C(31)	0·7468(8)	0·3600(7)	0·2010(3)	0·007
C(32)	0·7318(10)	0·3909(9)	0·2731(4)	0·009
C(1)	−0·0330(9)	0·1914(9)	−0·0544(4)	0·009
C(2)	0·0198(14)	0·3122(9)	−0·0613(4)	0·011
C(3)	0·1644(14)	0·3022(9)	−0·0769(4)	0·010
C(4)	0·1986(11)	0·1698(9)	−0·0757(4)	0·009
C(5)	0·0754(10)	0·1061(8)	−0·0627(3)	0·008
H(1)	−0·119(10)	0·174(9)	−0·045(5)	0·009
H(2)	−0·023(11)	0·375(9)	−0·060(5)	0·10
H(3)	0·214(11)	0·369(9)	−0·083(5)	0·10
H(4)	0·303(10)	0·152(9)	−0·080(4)	0·09
H(5)	0·083(10)	0·007(9)	−0·059(4)	0·09
H(111)	0·654(10)	0·101(9)	0·250(5)	0·09
H(112)	0·610(11)	0·020(9)	0·183(4)	0·09
H(121)	0·908(10)	0·055(8)	0·191(5)	0·09
H(122)	0·923(10)	0·137(9)	0·257(5)	0·09
H(123)	0·890(11)	−0·007(9)	0·256(5)	0·09
H(211)	0·794(10)	0·189(8)	0·095(4)	0·09
H(212)	0·630(10)	0·126(9)	0·061(4)	0·09
H(221)	0·660(10)	0·295(9)	−0·012(5)	0·09
H(222)	0·705(10)	0·392(9)	0·045(4)	0·09
H(223)	0·533(11)	0·348(9)	0·016(4)	0·09
H(311)	0·851(10)	0·333(9)	0·206(4)	0·09
H(312)	0·727(11)	0·428(9)	0·173(5)	0·09
H(321)	0·806(10)	0·455(9)	0·296(5)	0·09
H(322)	0·747(10)	0·315(9)	0·302(5)	0·09
H(323)	0·613(10)	0·420(8)	0·270(4)	0·09

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[1] A. R. Manning, personal communication.

[2] M. Mack, *Norelco Reporter*, 1965, **12**, 40.

[3] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

[4] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

inclusion of individual layer scale factors. After three cycles the refined layer scale factors were used to produce a unique data set which was used in subsequent calculations.

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. However, owing to the large number of parameters being refined it was necessary to refine the parameters in four block matrices. Matrices (1)—(4) contained the parameters for (1) the overall scale and thermal parameter, (2) the nickel and cobalt atoms, and the carbonyl groups, (3) the triethylphosphine group, and (4) the cyclopentadienyl ring. After three cycles of refinement the positional parameters for the hydrogen atoms were included in the refinement in the appropriate matrices. Refinement was terminated when the shift in any parameter was $<0{\cdot}1\ \sigma$. 2818 Reflections were included in the final cycle of refinement. The final values of R, based on 2853 reflections, and R' [$=\Sigma w\Delta^2/\Sigma w|F_o|^2$] were 0·052 and 0·0025, respectively.

Final atomic co-ordinates and thermal parameters together with their estimated standard deviations are given in Tables 1 and 2, respectively. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20919 (18 pp., 1 microfiche).†

TABLE 2

Thermal parameters ($\times 10^4$),* with estimated standard deviations in parentheses

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	119·4(10)	75·5(7)	19·1(2)	−10·7(7)	0·7(3)	−6·2(3)
Co	93·8(8)	56·9(6)	15·2(1)	−6·9(7)	7·5(3)	−1·0(3)
P	94·9(16)	60·0(11)	15·9(3)	3·3(13)	7·7(6)	0·6(5)
O(B1)	115(7)	213(8)	47(2)	12(6)	20(3)	−34(3)
O(B2)	204(9)	62(4)	41(2)	0(5)	5(3)	−9(2)
O(T1)	358(13)	197(8)	31(2)	46(9)	66(4)	27(3)
O(T2)	306(12)	76(5)	39(2)	−8(6)	16(4)	11(2)
C(B1)	96(7)	102(7)	26(2)	−3(6)	8(3)	−8(3)
C(B2)	129(9)	56(5)	27(2)	−6(5)	13(3)	−3(2)
C(T1)	158(9)	81(5)	25(2)	9(6)	24(3)	10(3)
C(T2)	123(9)	80(6)	20(2)	−1(6)	5(3)	−1(2)
C(11)	169(12)	103(7)	29(2)	36(7)	12(4)	14(3)
C(12)	184(14)	159(11)	35(3)	90(10)	2(5)	7(4)
C(21)	139(9)	109(7)	23(2)	15(7)	24(3)	5(3)
C(22)	194(13)	179(12)	28(2)	25(10)	33(4)	22(4)
C(31)	116(9)	106(7)	29(2)	−11(7)	−1(3)	−10(3)
C(32)	205(14)	142(10)	28(2)	−4(10)	−5(4)	−25(4)
C(1)	165(12)	167(12)	32(2)	8(10)	−11(4)	−23(4)
C(2)	323(23)	141(12)	31(3)	106(13)	−35(6)	−9(4)
C(3)	372(25)	154(13)	19(2)	−82(14)	−5(5)	17(4)
C(4)	245(16)	157(10)	22(2)	2(11)	23(4)	−6(4)
C(5)	224(15)	128(9)	23(2)	−36(10)	2(4)	−17(3)

For all hydrogen atoms $B = 6{\cdot}0$ Å^2.

* Anisotropic thermal parameters are given by:

$$\exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23}).$$

All calculations for the structure analysis were carried out on the PDP 10 computer of the University of Essex with programmes written by the author.

TABLE 3

Bond lengths and angles with estimated standard deviations in parentheses

(*a*) Distances (Å)

Ni · · · Co 2·4097(8)

Ni–C(B1)	1·825(6)	Co–C(B1)	1·956(6)
Ni–C(B2)	1·900(6)	Co–C(B2)	1·890(5)
C(B1)–O(B1)	1·158(7)	C(B2)–O(B2)	1·163(6)
Ni–C(1)	2·077(7)	Co–P	2·236(1)
Ni–C(2)	2·103(7)	Co–C(T1)	1·784(6)
Ni–C(3)	2·189(7)	Co–C(T2)	1·788(6)
Ni–C(4)	2·149(7)	C(T1)–O(T1)	1·129(6)
Ni–C(5)	2·085(6)	C(T2)–O(T2)	1·140(7)
C(1)–C(2)	1·371(14)	P–C(11)	1·823(6)
C(2)–C(3)	1·423(15)	P–C(21)	1·831(6)
C(3)–C(4)	1·417(13)	P–C(31)	1·820(6)
C(4)–C(5)	1·379(11)	C(11)–C(12)	1·507(10)
C(5)–C(1)	1·364(11)	C(21)–C(22)	1·500(10)
C(1)–H(1)	0·86(9)	C(31)–C(32)	1·523(10)
C(2)–H(2)	0·77(9)	C(11)–H(111)	0·94(9)
C(3)–H(3)	0·86(9)	C(11)–H(112)	1·06(9)
C(4)–H(4)	0·98(9)	C(12)–H(121)	1·01(9)
C(5)–H(5)	1·04(9)	C(12)–H(122)	0·99(9)
C(21)–H(211)	1·00(9)	C(12)–H(123)	0·90(9)
C(21)–H(212)	0·93(9)	C(31)–H(311)	0·95(9)
C(22)–H(221)	0·86(9)	C(31)–H(312)	0·89(9)
C(22)–H(222)	1·06(9)	C(32)–H(321)	0·96(9)
C(22)–H(223)	0·95(9)	C(32)–H(322)	0·97(9)
		C(32)–H(323)	1·09(9)

(*b*) Angles (°)

C(B1)–Ni–C(B2)	91·6(3)	C(B1)–Co–C(B2)	88·0(2)
Ni–C(B1)–Co	79·1(2)	Ni–C(B2)–Co	79·0(2)
Ni–C(B1)–O(B1)	141·0(5)	Ni–C(B2)–O(B2)	134·3(5)
Co–C(B1)–O(B1)	139·8(5)	Co–C(B2)–O(B2)	146·7(5)
Ni–Co–P	120·60(4)	C(B1)–Co–P	167·9(2)
Ni–Co–C(T1)	127·3(2)	C(B1)–Co–C(T1)	92·0(3)
Ni–Co–C(T2)	101·3(2)	C(B1)–Co–C(T2)	87·6(3)
C(5)–C(1)–C(2)	108·2(9)	C(B2)–Co–P	85·5(2)
C(1)–C(2)–C(3)	108·6(8)	C(B2)–Co–C(T1)	106·8(3)
C(2)–C(3)–C(4)	105·9(8)	C(B2)–Co–C(T2)	142·2(2)
C(3)–C(4)–C(5)	107·2(9)	P–Co–C(T1)	99·7(2)
C(4)–C(5)–C(1)	110·1(8)	P–Co–C(T2)	91·3(2)
Co–P–C(11)	113·4(2)	C(T1)–Co–C(T2)	110·9(3)
Co–P–C(21)	115·2(2)	Co–C(T1)–O(T1)	176·0(6)
Co–P–C(31)	114·9(2)	Co–C(T2)–O(T2)	178·9(6)
C(11)–P–C(21)	104·3(3)	P–C(11)–C(12)	117·7(6)
C(11)–P–C(31)	104·0(3)	P–C(21)–C(22)	113·6(5)
C(21)–P–C(31)	103·7(3)	P–C(31)–C(32)	113·7(6)
C(5)–C(1)–H(1)	125(7)	P–C(11)–H(111)	106(6)
C(2)–C(1)–H(1)	127(7)	P–C(11)–H(112)	102(5)
C(1)–C(2)–H(2)	127(8)	C(12)–C(11)–H(111)	112(5)
C(3)–C(2)–H(2)	124(8)	C(12)–C(11)–H(112)	119(5)
C(2)–C(3)–H(3)	121(7)	H(111)–C(11)–H(112)	99(7)
C(4)–C(3)–H(3)	133(7)	C(11)–C(12)–H(121)	115(5)
C(3)–C(4)–H(4)	113(6)	C(11)–C(12)–H(122)	111(5)
C(5)–C(4)–H(4)	140(6)	C(11)–C(12)–H(123)	114(6)
C(4)–C(5)–H(5)	133(5)	H(121)–C(12)–H(122)	101(7)
C(1)–C(5)–H(5)	117(5)	H(121)–C(12)–H(123)	105(7)
P–C(21)–H(211)	105(5)	H(122)–C(12)–H(123)	109(7)
P–C(21)–H(212)	103(5)	P–C(31)–H(311)	107(5)
C(22)–C(21)–H(211)	113(5)	P–C(31)–H(312)	107(6)
C(22)–C(21)–H(212)	114(5)	C(32)–C(31)–H(311)	109(5)
H(211)–C(21)–H(212)	107(7)	C(32)–C(31)–H(312)	112(6)
C(21)–C(22)–H(221)	112(6)	H(311)–C(31)–H(312)	107(8)
C(21)–C(22)–H(222)	109(5)	C(31)–C(32)–H(321)	111(5)
C(21)–C(22)–H(223)	118(5)	C(31)–C(32)–H(322)	111(5)
H(221)–C(22)–H(222)	101(7)	C(31)–C(32)–H(323)	112(4)
H(221)–C(22)–H(223)	115(8)	H(321)–C(32)–H(322)	110(7)
H(222)–C(22)–H(223)	100(7)	H(321)–C(32)–H(322)	111(7)
		H(322)–C(32)–H(323)	103(7)

DISCUSSION

The Figure shows a perspective drawing of the molecule and the labelling of the atoms. Bond distances and angles, together with their estimated standard deviations derived directly from the least-squares inverse matrices, are given in Table 3. There is a possible error in the values of the bond distances involving the heavier atoms, owing to the uncertainty in the unit-cell parameters, which is greater than the error derived from the structure refinement; a better estimate of the absolute accuracy would be given by raising the σ quoted in Table 3 to 0·003 Å for Ni · · · Co and to 0·004 Å for Co–P. The molecules are held in the crystal lattice by van der Waals forces. The closest approach of two non-hydrogen atoms is 3·25 Å for

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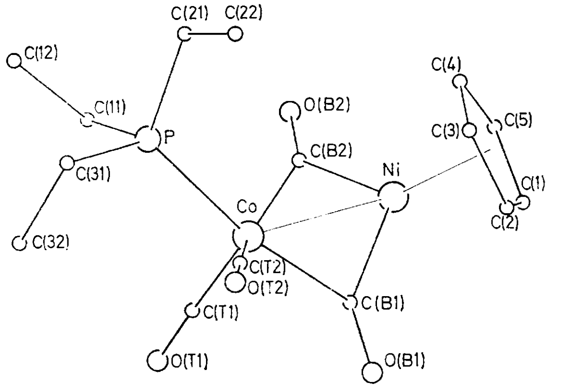
† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

O(T2) ··· C(22) at $1-x$, $1-y$, $\bar{z}$. All other contacts are >3·5 Å.

The compound has the expected non-planar carbonyl bridged structure. The angle (133·7°) between the two Ni(CO)Co planes is intermediate between that (127°) in $Co_2(CO)_8$,[5] and that (142°) in $[(\pi-C_5H_5)Ni(CO)]_2$.[6] The Ni ··· Co distance (2·410 Å) is in accord with that (2·445 Å) derived from the Ni ··· Ni distance (2·365 Å) in $[(\pi-C_5H_5)Ni(CO)]_2$[6] and the Co ··· Co distance (2·524 Å) in $Co_2(CO)_8$.[5]



A perspective drawing of the molecule, showing the labelling of the atoms

TABLE 4

Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$, where X', Y', and Z' are orthogonal co-ordinates related to the atomic co-ordinates X, Y, and Z by $X' = X\sin\beta$, $Y' = Y$, and $Z' = Z + X\cos\beta$. Deviations (Å) of the most relevant atoms from the planes are given in square brackets

	l	m	n	p
Plane (1):				
Ni, Co, C(B1), O(B1)	0·1927	0·8786	−0·4369	2·2894
[Ni 0·005, Co 0·005, C(B1) −0·021, O(B1) 0·012]				
Plane (2):				
Ni, Co, C(B2), O(B2)	0·6585	0·2978	−0·6912	1·6515
[Ni 0·001, Co 0·002, C(B2) −0·006, O(B2) 0·003]				
Plane (3):				
C(1)—(5)	−0·4794	−0·0406	−0·8767	0·9217
[C(1) 0·008, C(2) −0·014, C(3) 0·014, C(4) −0·010, C(5) 0·002]				
Plane (4):				
Ni, Co, C(T1), O(T1), centroid of C_5 ring	−0·4129	0·8994	0·1434	1·4878
[Ni − 0·04, Co 0·02, C(T1) 0·03, O(T1) −0·03, centroid 0·02]				
Plane (5):				
P, C(B2), C(B1)	−0·0341	−0·4033	0·9145	0·1765
[Co 0·20]				
Plane (6):				
P, C(T1), C(B1)	0·1732	0·9650	0·1967	3·5405
[Co 0·05]				
Plane (7):				
P, C(T2), C(B1)	0·0401	0·0104	0·9991	1·6947
[Co 0·22]				

The cyclopentadienyl ring is planar (see Table 4). The distance of the nickel atom from the centroid of the C_5 ring is 1·761 Å, and the angle between this direction and the Ni ··· Co direction is 160·2°.

The most striking distortion in the structure involves the bridging system. It might be expected that the two Ni–C_b distances (b = bridge) be equal and similarly the two Co–C_b distances, but this is not so in either case. The two Ni–C_b–Co angles are equivalent and the mean value (79·0°) agrees well with that (80°) observed in $[(\pi-C_5H_5)Ni(CO)]_2$,[6] but is significantly smaller than that (82—85°) in compounds with Co-$(CO)_2$Co bridging systems.[5,7,8] The environment about the bridge atom C(B1) is as might be expected, the distances Ni–C(B1) (1·825 Å) and Co–C(B1) (1·956 Å) being in accord with corresponding values (1·84 Å) in $[(\pi-C_5H_5)Ni(CO)]_2$,[6] and (1·960 Å) in $(\pi-C_9H_7)FeCo(CO)_6$.[9] However, the environment about the other bridge-carbon atom, C(B2), is distorted, involving a shortening of the Co–C(B2) length to 1·890 Å accompanied by a lengthening of the Ni–C(B2) length to 1·900 Å from expected values observed in related compounds.[5-9] The external angles M–C(B2)–O(B2) are not equivalent, that involving the Co atom opens. However, the planar environment about C(B2) is maintained by an equivalent closure of the Ni–C(B2)–O(B2) angle. The bridging arrangement in the present structure closely resembles that observed in $(\pi-C_9H_7)FeCo(CO)_6$.[9] The similarity in structure of these two compounds is also seen in the cobalt atom environments; in both structures it is intermediate between trigonal-bipyramidal and square-based pyramidal (see Table 5).

TABLE 5

Comparison of trigonal bipyramidal *vs.* square-based pyramidal environment about the Co atom. Planes defined by the axial–equatorial–axial atoms of a trigonal bipyramid. For the present structure atoms P and C(B1) are axial

	Structure				
Atoms[a]	(I)[b]	(II)	(III)	Trig. bipy.	Sq. py.
C(B2) : C(T1)	102·4	100·7	91·3	120	90
C(T2) : C(T1)	102·3	103·2	94·4	120	90
C(T2) : C(B2)	155·2	156·1	174·2	120	180

[a] Equatorial atoms defining planes. [b] (I) Present work; (II) $(\pi-C_9H_7)FeCo(CO)_6$, ref. 9; (III) $Co_2(CO)_8$, ref. 5.

The Co–P distance (2·236 Å) is longer than that in the non-bridged structures $[(Et_3P)Co(CO)_2]_2Hg$ (2·19 Å)[10] and $[(Bu_3P)Co(CO)_3]_2$ (2·18 Å),[11] but shorter than that (2·253 Å) in $(MeC)Co_3(CO)_8(PPh_3)$[12] and (2·267 Å) in $(HCF_2{\cdot}CF_2)Co(CO)_3(PPh_3)$.[13] Steric hindrance prevents the ethyl groups of the triethylphosphine ligand adopting the usual W-shape three-fold symmetry about

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the Co–P direction. The attainment of such an arrangement would bring the methyl group C(12) into close contact with the oxygen atom O(B2) (O · · · C *ca.* 2·1 Å) and the situation is relieved by a rotation of this group about the P–C(11) direction of *ca.* 105° away from O(B2). This rotation gives O(B2) · · · C(12) 4·54 Å, with the methyl group being equally disposed to the methylene groups of the other two ethyl groups.

At present, it is not possible to account for the observed distortion in the bridging system. Clearly, steric factors, such as the close approach of the methylene group C(11) to the oxygen atom O(B2), will be important. On the other hand, the packing of the molecules within the crystal may account for the intermediate geometry about the cobalt atom, which in turn may cause the distortion in the bridging system.

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