Crystal and Molecular Structure of Di-μ-carbonyl-dicarbonyl[cyclohexyl(diphenyl)phosphine](π-methylcylopentadienylnickelio)cobalt

By **Ian L. C. Campbell** and **Frederick S. Stephens**,*† Department of Chemistry, University of Essex, Colchester CO4 3SQ

The crystal structure of the title compound has been determined by *X*-ray diffraction methods using counter data. Refinement to *R* 0·084 for 3661 reflections was carried out by a least-squares procedure. The monoclinic unit cell, space group $P2_1/c$, has dimensions $a = 14{\cdot}261 \pm 0{\cdot}022$, $b = 10{\cdot}034 \pm 0{\cdot}017$, $c = 18{\cdot}508 \pm 0{\cdot}032$ Å, $\beta = 98{\cdot}5 \pm 0{\cdot}1°$, for $Z = 4$. The dimer molecule has a non-planar $Ni(CO)_2Co$ bridging system, the angle between the two Ni(CO)Co planes being 133·9°. Metal to bridge-carbon distances are Ni–C 1·85, Co–C 1·93 Å; Ni ··· Co is 2·418(2) and Co–P 2·269 Å. The cobalt atom is in a square-based pyramidal environment. The methylcyclopentadienyl ligand and the phenyl rings are planar, and the cyclohexyl ring is in a chair conformation.

SPECTRAL studies of the complexes [(π-dienyl)-$NiCo(CO)_4L$] where L is a phosphine indicate the presence of a non-planar $Ni(CO)_2Co$ bridging system.[1] The crystal structure analysis of one of these compounds, $[(\pi\text{-}C_5H_5)NiCo(CO)_4(PEt_3)]$,[2] has shown distortions in the carbonyl-bridging system which could not be readily explained. The crystal-structure analysis of the title compound was undertaken to determine its molecular structure and its relationship to other similar compounds.

EXPERIMENTAL

Crystal Data.—$C_{28}H_{28}CoNiO_4P$, $M = 577{\cdot}1$, Monoclinic, $a = 14{\cdot}261 \pm 0{\cdot}022$, $b = 10{\cdot}034 \pm 0{\cdot}017$, $c = 18{\cdot}508 \pm 0{\cdot}032$ Å, $\beta = 98{\cdot}5 \pm 0{\cdot}1°$, $U = 2619{\cdot}3$ Å^3, $D_m = 1{\cdot}47$ (by flotation), $Z = 4$, $D_c = 1{\cdot}463$, $F(000) = 1192$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, for cell dimensions and intensity measurements; μ(Mo-K_α) = 14·7 cm^{-1}. Space group $P2_1/c$ (No. 14, C^5_{2h}).

The complex crystallises in a tabular form on (100) with pinacoids {010} and {001}. Unit-cell parameters were determined from single-crystal precession photographs. Since crystals of the compound decompose slowly in air the crystal used for the collection of intensity data was coated with an adhesive. The intensities were collected on a Philips PAILRED diffractometer. Each reflection in the $h0$—$14l$ layers was recorded for $\sin\theta < 0{\cdot}54$. 3661 unique reflections giving counts[3] for which $\sigma(I)/I < 0{\cdot}5$ were used for the structure analysis. Intensities were corrected for Lorentz and polarisation effects but not for absorption or extinction. Scattering-factor curves for all atoms were taken from ref. 4, the values for the nickel and cobalt being corrected for anomalous dispersion. All calculations were carried out on a PDP 10 computer at the University of Essex with programmes written by one of us (F. S. S.).

Structure Determination.—The positions of the two metal atoms were obtained from a three-dimensional Patterson synthesis. The complete solution of the structure was obtained from a series of Fourier syntheses, each phased by the increased number of atoms. Refinement of the structure was carried out by a least-squares procedure in which the function minimised was $\Sigma w\Delta^2$. The weight for each reflection, w, was initially unity and in the final refinement given by $w = (10{\cdot}0 - 0{\cdot}1|F_o| + 0{\cdot}0015|F_o|^2)^{-1}$. For this latter weighting scheme the average values of $w\Delta^2$ for 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.

Initial refinement used a full-matrix procedure in which positional and individual isotropic thermal parameters for each atom were refined. A difference-Fourier synthesis was calculated when the maximum shift in a parameter was of the order of its σ. This map showed no unusual features and yielded the approximate positions for all hydrogen atoms. In subsequent calculations the contributions for the hydrogen atoms were included with the positions calculated, assuming C–H 1·0 Å, and with thermal parameters of B 6·0 Å^2. Refinement was continued for all non-hydrogen atoms with inclusion of individual-layer scale factors. After two 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. Owing to the large number of parameters being refined (317) it was necessary to refine the parameters in block matrices; the six matrices contained the parameters for (1) the overall scale and thermal parameters, (2) the nickel, cobalt, and phosphorus atoms, and carbonyl groups, (3) the cyclopentadienyl ligand, (4) the cyclohexyl ring, and (5) and (6) the two phenyl rings. Refinement was terminated when the maximum shift in a parameter was $<0{\cdot}1\sigma$. 3589 reflections were included in the final cycle of refinement. The final value for R, based on 3661 reflections, was 0·084 and for R' [= $(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] was 0·093.

Final atomic co-ordinates and thermal parameters are given together with their estimated standard deviations in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21177 (22 pp., 1 microfiche).‡

DISCUSSION

Figure 1 shows a perspective drawing of the molecule and the labelling of the atoms.[5] Figure 2 shows the packing of the molecules in the crystal.[5] The molecules are held in the crystal by van der Waals forces. The closest intermolecular carbon–oxygen contacts are O(B2) ··· C(36) at $-x, \frac{1}{2}+y, \frac{1}{2}-z$ 3·35 and O(B1) ··· C(24) at $x, -\frac{1}{2}-y, -\frac{1}{2}+z$ 3·39 Å. All C ··· C contact distances are >3·6 Å. The bond distances and angles, together with their estimated

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† *Present address:* School of Chemistry, Macquarie University, North Ryde, New South Wales 2113, Australia.

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

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

[2] F. S. Stephens, *J.C.S. Dalton*, 1974, 1067.

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

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

[5] C. K. Johnson, ORTEP: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL 3794, 1965, Revised 1971, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

TABLE 1

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

	x/a	y/b	z/c	σ_{rms}/Å
Ni	0·28523(9)	0·28338(12)	0·16101(6)	0·0012
Co	0·20786(8)	0·08709(11)	0·19983(6)	0·0011
P	0·21622(14)	0·07851(20)	0·32313(10)	0·0020
O(B1)	0·2573(9)	0·0816(9)	0·0534(4)	0·010
O(B2)	0·1268(6)	0·3472(7)	0·2296(5)	0·010
O(T1)	0·0217(6)	0·0071(10)	0·1279(5)	0·010
O(T2)	0·3321(7)	−0·1454(11)	0·1988(6)	0·011
C(B1)	0·2505(9)	0·1307(11)	0·1085(6)	0·011
C(B2)	0·1793(7)	0·2736(10)	0·2088(5)	0·010
C(T1)	0·0916(8)	0·0367(9)	0·1581(6)	0·010
C(T2)	0·2853(8)	−0·0557(11)	0·2029(6)	0·011
C(1)	0·4322(8)	0·3172(11)	0·1513(7)	0·011
C(2)	0·4152(8)	0·3768(12)	0·2162(6)	0·012
C(3)	0·3408(9)	0·4694(12)	0·1984(7)	0·013
C(4)	0·3140(9)	0·4719(11)	0·1213(6)	0·012
C(5)	0·3704(8)	0·3740(10)	0·0935(5)	0·010
C(6)	0·5023(10)	0·2078(15)	0·1451(9)	0·015
C(11)	0·3186(5)	0·1699(8)	0·3678(4)	0·008
C(12)	0·4086(6)	0·1141(9)	0·3730(6)	0·010
C(13)	0·4887(7)	0·1887(12)	0·4005(7)	0·011
C(14)	0·4806(8)	0·3167(11)	0·4226(6)	0·011
C(15)	0·3929(7)	0·3757(10)	0·4170(6)	0·010
C(16)	0·3112(6)	0·3036(9)	0·3888(5)	0·010
C(21)	0·2286(6)	−0·0898(8)	0·3611(4)	0·010
C(22)	0·2687(8)	−0·1140(9)	0·4337(5)	0·010
C(23)	0·2692(7)	−0·2457(10)	0·4614(5)	0·010
C(24)	0·2138(9)	−0·3432(10)	0·4232(6)	0·011
C(25)	0·1758(8)	−0·3219(10)	0·3506(6)	0·011
C(26)	0·1714(7)	−0·1902(9)	0·3227(6)	0·010
C(31)	0·1162(6)	0·1460(9)	0·3640(4)	0·010
C(32)	0·1262(7)	0·1478(12)	0·4450(5)	0·011
C(33)	0·0422(9)	0·2078(13)	0·4742(6)	0·012
C(34)	−0·0489(8)	0·1615(15)	0·4380(7)	0·013
C(35)	−0·0599(7)	0·1532(12)	0·3573(7)	0·012
C(36)	0·0229(6)	0·0963(10)	0·3273(5)	0·010
H(2)	0·449	0·358	0·267	
H(3)	0·314	0·525	0·236	
H(4)	0·264	0·529	0·092	
H(5)	0·368	0·353	0·041	
H(61)	0·555	0·246	0·147	
H(62)	0·507	0·138	0·179	
H(63)	0·493	0·174	0·093	
H(12)	0·418	0·018	0·358	
H(13)	0·555	0·145	0·407	
H(14)	0·540	0·372	0·443	
H(15)	0·386	0·469	0·435	
H(16)	0·249	0·350	0·383	
H(22)	0·297	−0·038	0·464	
H(23)	0·310	−0·268	0·510	
H(24)	0·200	−0·432	0·446	
H(25)	0·148	−0·401	0·319	
H(26)	0·132	−0·165	0·275	
H(31)	0·114	0·242	0·351	
H(321)	0·187	0·194	0·466	
H(322)	0·134	0·051	0·463	
H(331)	0·046	0·310	0·469	
H(332)	0·043	0·195	0·528	
H(341)	−0·061	0·071	0·460	
H(342)	−0·102	0·214	0·454	
H(351)	−0·074	0·246	0·336	
H(352)	−0·120	0·102	0·338	
H(361)	0·022	0·111	0·274	
H(362)	0·018	−0·004	0·332	

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	48·4(7)	73·3(11)	20·1(3)	−21·7(8)	12·5(4)	2·3(6)
Co	33·7(6)	62·8(10)	16·9(3)	−9·5(7)	7·8(4)	1·6(5)
P	23·0(9)	46·7(17)	15·1(3)	−3·3(12)	6·9(6)	−0·6(9)
O(B1)	192(11)	152(12)	30(3)	−84(10)	48(5)	−21(5)
O(B2)	68(5)	89(8)	52(4)	27(6)	26(4)	16(4)
O(T1)	51(5)	179(13)	62(4)	−21(7)	−10(4)	−30(6)
O(T2)	100(8)	191(14)	65(5)	79(9)	34(5)	−7(7)
C(B1)	85(8)	98(12)	24(3)	−45(8)	20(4)	−1(5)
C(B2)	47(6)	78(9)	25(3)	0(6)	10(3)	19(5)
C(T1)	48(6)	64(9)	34(4)	−9(6)	3(4)	−12(5)
C(T2)	64(7)	118(13)	27(3)	8(8)	21(4)	7(5)
C(1)	48(6)	99(12)	43(4)	−23(7)	21(4)	4(6)
C(2)	54(7)	126(14)	34(4)	−33(8)	17(4)	−9(6)
C(3)	72(8)	111(13)	50(5)	−42(9)	36(6)	−26(7)
C(4)	73(8)	84(11)	39(4)	−7(8)	19(5)	14(6)
C(5)	55(6)	94(11)	24(3)	−11(7)	17(4)	14(5)
C(6)	71(9)	148(18)	74(7)	10(11)	30(7)	8(10)
C(11)	20(4)	65(7)	14(2)	−5(4)	8(2)	−6(3)
C(12)	26(4)	60(9)	46(4)	8(5)	7(3)	−6(5)
C(13)	31(5)	119(14)	48(5)	−9(7)	5(4)	−12(7)
C(14)	49(6)	100(12)	32(4)	−8(7)	10(4)	−8(5)
C(15)	41(6)	87(10)	36(4)	−18(6)	12(4)	−19(5)
C(16)	35(5)	75(9)	22(3)	2(5)	14(3)	−2(4)
C(21)	33(4)	60(8)	21(2)	−7(5)	7(3)	7(4)
C(22)	63(7)	69(9)	19(3)	5(6)	−4(3)	6(4)
C(23)	44(5)	100(11)	23(3)	15(6)	8(3)	8(5)
C(24)	74(8)	59(9)	36(4)	11(7)	13(5)	10(5)
C(25)	67(7)	74(10)	39(4)	−27(7)	6(5)	14(5)
C(26)	48(6)	63(9)	31(3)	−13(6)	4(3)	6(4)
C(31)	23(4)	83(9)	19(2)	−1(5)	7(3)	−3(4)
C(32)	47(6)	169(16)	20(3)	30(8)	12(3)	−11(6)
C(33)	69(8)	162(16)	24(3)	38(10)	17(4)	6(6)
C(34)	48(7)	221(22)	39(4)	46(10)	19(5)	18(8)
C(35)	35(6)	141(15)	44(5)	4(7)	18(4)	1(7)
C(36)	28(4)	109(11)	30(3)	13(6)	12(3)	3(5)

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

* Anisotropic thermal parameters are in the form: $\exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$.

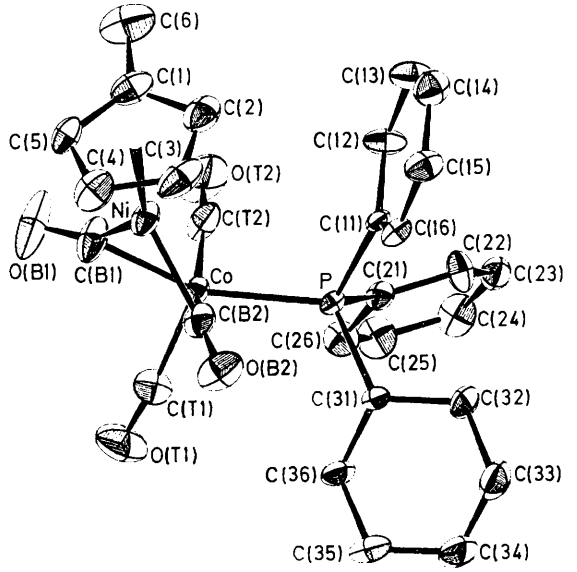

FIGURE 1 A perspective drawing of the molecule and the labelling of the atoms. Thermal ellipsoids are scaled to include 36% probability

standard deviations derived directly from the least-squares inverse matrices, are given in Table 3. The molecule consists of the nickel and cobalt atoms bridged by two carbonyl groups, with the methylcyclopentadienyl ligand π-bonded to the nickel atom and the phosphine ligand co-ordinated to the cobalt atom. The Co–P distance (2·269 Å) is similar to that observed for the non-bridged structure $[(HCF_2{\cdot}CF_2)Co(CO)_3(PPh_3)]$ (2·267 Å),[6] but longer than that in $[\{Bu_3PCo(CO)_3\}_2]$ (2·18 Å),[7] $[(C_5H_5)NiCo(CO)_4(PEt_3)]$ (2·236 Å),[2] and

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[6] J. B. Wilford and H. M. Powell, *J. Chem. Soc.* (*A*), 1967, 2092.

[7] J. A. Ibers, *J. Organometallic Chem.*, 1968, **14**, 423.

$[(C_5H_5)FeCo(CO)_4(PPh_2Me)]$ (2·221 Å).[8] The carbon atoms bound to the phosphorus atom exhibit the expected trigonal symmetry about the Co–P direction.

TABLE 3

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances *			
Ni · · · Co	2·418(2)		
Ni–C(B1)	1·842(11)	Co–C(B1)	1·929(10)
Ni–C(B2)	1·863(9)	Co–C(B2)	1·928(10)
Ni–Cp	1·754(9)	Co–P	2·269(2)
Ni–C(1)	2·156(10)	Co–C(T1)	1·795(11)
Ni–C(2)	2·191(11)	Co–C(T2)	1·805(12)
Ni–C(3)	2·104(11)	P–C(11)	1·817(8)
Ni–C(4)	2·092(10)	P–C(21)	1·827(8)
Ni–C(5)	2·077(8)	P–C(31)	1·839(8)
C(B1)–O(B1)	1·150(12)	C(T1)–O(T1)	1·109(12)
C(B2)–O(B2)	1·157(11)	C(T2)–O(T2)	1·130(13)
C(1)–C(2)	1·395(15)	C(31)–C(32)	1·486(12)
C(2)–C(3)	1·412(17)	C(32)–C(33)	1·511(14)
C(3)–C(4)	1·422(17)	C(33)–C(34)	1·447(18)
C(4)–C(5)	1·414(15)	C(34)–C(35)	1·482(16)
C(5)–C(1)	1·402(15)	C(35)–C(36)	1·491(13)
C(1)–C(6)	1·501(17)	C(36)–C(31)	1·488(12)
C(11)–C(12)	1·390(11)	C(21)–C(22)	1·402(12)
C(12)–C(13)	1·397(13)	C(22)–C(23)	1·417(13)
C(13)–C(14)	1·359(15)	C(23)–C(24)	1·385(15)
C(14)–C(15)	1·373(14)	C(24)–C(25)	1·388(15)
C(15)–C(16)	1·405(13)	C(25)–C(26)	1·417(13)
C(16)–C(11)	1·405(11)	C(26)–C(21)	1·419(22)
(*b*) Angles			
C(B1)–Ni–C(B2)	91·9(5)	C(B1)–Co–C(B2)	87·3(4)
Co–Ni–Cp	159·1(3)	Ni–Co–P	111·8(1)
C(B1)–Ni–Cp	132·7(6)	Ni–Co–C(T1)	122·3(3)
C(B2)–Ni–Cp	134·9(6)	Ni–Co–C(T2)	110·6(3)
P–Co–C(T1)	109·3(3)	P–Co–C(T2)	89·9(3)
C(6)–C(1)–C(2)	125·6(12)	C(T1)–Co–C(T2)	108·2(5)
C(6)–C(1)–C(5)	126·1(11)	Co–P–C(11)	111·0(2)
C(5)–C(1)–C(2)	108·3(10)	Co–P–C(21)	114·2(3)
C(1)–C(2)–C(3)	107·5(11)	Co–P–C(31)	118·1(3)
C(2)–C(3)–C(4)	109·2(10)	C(11)–P–C(21)	105·4(4)
C(3)–C(4)–C(5)	105·6(10)	C(11)–P–C(31)	104·3(4)
C(4)–C(5)–C(1)	109·4(9)	C(21)–P–C(31)	102·7(4)
Ni–C(B1)–Co	79·7(4)	Ni–C(B2)–Co	79·3(4)
Ni–C(B1)–O(B1)	140·5(8)	Ni–C(B2)–O(B2)	137·2(8)
Co–C(B1)–O(B1)	139·3(9)	Co–C(B2)–O(B2)	143·5(8)
Co–C(T1)–O(T1)	175·3(11)	Co–C(T2)–O(T2)	174·4(11)
P–C(11)–C(12)	120·0(6)	P–C(21)–C(22)	122·1(7)
P–C(11)–C(16)	121·3(6)	P–C(21)–C(26)	116·7(6)
C(16)–C(11)–C(12)	118·2(8)	C(26)–C(21)–C(22)	118·7(8)
C(11)–C(12)–C(13)	120·4(8)	C(21)–C(22)–C(23)	119·2(8)
C(12)–C(13)–C(14)	120·9(10)	C(22)–C(23)–C(24)	120·2(9)
C(13)–C(14)–C(15)	120·1(10)	C(23)–C(24)–C(25)	119·8(9)
C(14)–C(15)–C(16)	120·2(9)	C(24)–C(25)–C(26)	119·1(10)
C(15)–C(16)–C(11)	120·1(8)	C(25)–C(26)–C(21)	119·3(9)
P–C(31)–C(32)	117·1(6)	C(32)–C(33)–C(34)	114·3(10)
P–C(31)–C(36)	112·7(6)	C(33)–C(34)–C(35)	116·0(10)
C(36)–C(31)–C(32)	114·2(8)	C(34)–C(35)–C(36)	115·2(10)
C(31)–C(32)–C(33)	113·8(9)	C(35)–C(36)–C(31)	114·0(9)

* Cp is the centroid of the cyclopentadienyl fragment.

The two phenyl rings of the phosphine ligand are planar (Table 4) and the cyclohexyl ring is in a chair conformation.

The methylcyclopentadienyl ligand exhibits the expected planarity (Table 5). The C–C distances within the ligand are in accord with those previously reported,[2,8] mean 1·41 Å. The nickel to ring-carbon distances are 2·08—2·18 Å, mean 2·12 Å. The nickel to ring-centroid distance is 1·75 Å, and the angle between this direction and the Ni · · · Co direction is 159·1°. The Ni · · · Co distance (2·418 Å) is in good agreement with that found (2·410 Å) in $[(C_5H_5)NiCo(CO)_4(PEt_3)]$,[2] and is consistent with the metal–metal distance derived from the parent compounds. The $Ni(CO)_2Co$ bridging system exhibits the expected non-planarity. The angle between the two Ni(CO)Co planes (133·9°) agrees well with that (133·7°) in $[(C_5H_5)NiCo(CO)_4(PEt_3)]$,[2] being

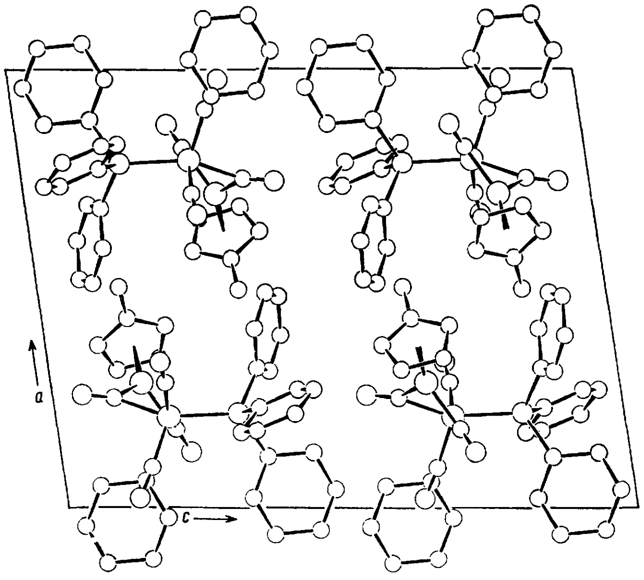

FIGURE 2 Unit-cell contents projected on the *ac* plane

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 $X' = X \sin \beta$, $Y' = Y$, $Z' = Z + X \cos \beta$. Deviations (Å) of the most relevant atoms from the planes are given in square brackets

	l	*m*	*n*	*p*
Plane (1): C(1)—(5)	0·6821	0·7041	−0·1976	6·0271
[C(1) −0·002, C(2) 0·012, C(3) −0·016, C(4) 0·015, C(5) −0·008, C(6) −0·046]				
Plane (2): C(11)—(16)	−0·0822	−0·3097	0·9473	4·9014
[C(11) 0·014, C(12) −0·005, C(13) −0·006, C(14) 0·008, C(15) 0·001, C(16) −0·012, P −0·16]				
Plane (3): C(21)—(26)	−0·8290	0·2551	0·4978	0·2367
[C(21) −0·053, C(22) 0·043, C(23) −0·046, C(24) 0·059, C(25) −0·068, C(26) 0·065, P 0·19]				
Plane (4): Ni, Co, C(B1), O(B1)	0·8916	−0·3932	0·2246	2·9962
[Ni 0·007, Co 0·007, C(B1) −0·030, O(B1) 0·017]				
Plane (5): Ni, Co, C(B2), O(B2)	0·5898	0·0343	0·8068	4·3913
[Ni −0·001, Co −0·002, C(B2) 0·007, O(B2) −0·004]				
Plane (6): P(1), C(B1), C(B2)	0·8995	0·4065	0·1602	3·9484
[Co −0·43, C(T1) −2·20, C(T2) −0·05]				
Plane (7): P(1), C(B1), C(T1)	−0·3494	0·9336	0·0796	0·1095
[Co −0·06, C(B2) 1·85, C(T2) −1·79]				
Plane (8): P(1), C(B1), C(T2)	0·9110	0·3808	0·1583	3·9525
[Co −0·43, C(B2) −0·05, C(T1) −2·20]				

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[8] G. Davey and F. S. Stephens, *J.C.S. Dalton*, 1974, 698.

intermediate between the values for the parent compounds $[Co_2(CO)_8]$ (127°) [9] and $[\{(C_5H_5)NiCO\}_2]$ (142°).[10]

The distortion in the bridge distances observed for $[(C_5H_5)NiCo(CO)_4(PEt_3)]$ [2] is not apparent in this complex. As might be expected the two Ni–C$_b$ (b = bridge) distances are equivalent (1·85 Å) as are the two Co–C$_b$ distances (1·93 Å). However some distortion in the angles around one of the bridge-carbon atoms is evident. The two Ni–C$_b$–Co angles are equivalent (mean 79·5°) as are the two M–C(B1)–O(B1) angles (mean 139·9°). The distortion about C(B2) involves an opening of the angle to the cobalt atom (143·5°) with a corresponding closing of the angle to nickel (137·2°), thus maintaining the planar environment of C(B2). This angular distortion is also present in $[(C_5H_5)NiCo(CO)_4(PEt_3)]$.[2] A probable explanation in this instance is the close proximity of H(31) on the cyclohexyl ring causing a steric repulsion to take place.

TABLE 5

Comparison of trigonal bipyramidal *vs.* square-based pyramidal environment about the cobalt atom, and of the Co–P and Co–C$_b$ (*trans* to P) distances (Å). Planes are defined by the axial–equatorial–axial atoms of a trigonal bipyramid. In the present structure atoms P and C(B1) are axial

			Equatorial atoms defining plane		
Compound	Co–P	Co–C$_b$	C(B2)⋮C(T1)	C(T2)⋮C(T1)	C(T2)⋮C(B2)
$(MeC_5H_4)NiCo(CO)_4[PPh_2(C_6H_{11})]$ [a]	2·269	1·929	92·9	94·5	178·4
$(C_5H_5)NiCo(CO)_4(PEt_3)$ [b]	2·236	1·956	102·3	102·4	155·2
$(C_5H_5)FeCo(CO)_5[PPh_2(Me))]$ [c]	2·221	2·027	103·1	107·6	149·3
Trigonal bipyramid			120	120	120
Square-based pyramid			90	90	180

[a] This work. [b] Ref. 2. [c] Ref. 8.

The cobalt is in a square-based pyramidal environment as can be demonstrated by the angles between the mean planes of the axial–equatorial–axial atoms which would define a trigonal bipyramid (Tables 4 and 5). This contrasts with the intermediate geometry shown by $[(C_5H_5)NiCo(CO)_4(PEt_3)]$ [2] and $[(C_5H_5)FeC(CO)_4(PPh_2Me)]$ [8] (Table 5). Comparing the Co–P and Co–C$_b$ bond-lengths in these two compounds with those in the present structure, it is apparent that as the Co–P bond becomes shorter, the Co–C$_b$ distance *trans* to the phosphine ligand increases. This further correlates with the geometry round the cobalt; the nearer the geometry to a square-based pyramidal arrangement the longer the Co–P bond (Table 5). Thus the suggested [8] *trans*-influence of the phosphine ligand *via* the axial–axial bonds of a trigonal-bipyramidal cobalt atom in these complexes appears to be substantiated. However, it is still not clear what factors govern the particular cobalt atom environment. Intramolecular contacts, particularly those involving the bulky phosphine ligand, will be important, but an over-riding factor may be the intermolecular forces arising from the packing of the molecules in the crystal.

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[9] G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, 1964, **17**, 732.

[10] J. P. Nice, Ph.D. Thesis, University of Manchester, 1966.