Crystal and Molecular Structure of Di-μ-carbonyl-dicarbonyl(π-cyclopentadienylnickelio)(tris-*p*-fluorophenylphosphine)cobalt

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The crystal structure of the title compound has been determined by *X*-ray diffraction methods from counter data. Refinement to R 0·071 for 2464 reflections was carried out by a least-squares procedure. The monoclinic unit cell, space group $I2/a$, has dimensions $a = 16{\cdot}396 \pm 0{\cdot}042$, $b = 10{\cdot}663 \pm 0{\cdot}058$, $c = 29{\cdot}260 \pm 0{\cdot}084$ Å, $\beta = 91{\cdot}1 \pm 0{\cdot}1°$, for $Z = 8$. The dimer molecule has a non-planar $Ni(CO)_2Co$ bridging system, the angle between the two Ni(CO)Co planes being 133·9°. The metal to bridge-carbon distances are not equivalent: $Co-C_b$ 1·90(1) and 2·03(1), and $Ni-C_b$ 1·89(1) and 1·82(1) Å. Ni · · · Co is 2·425(2) and Co–P is 2·243 Å.

INFRARED spectral studies of complexes of the type (π-dienyl)$MCo(CO)_4L$ [M = Fe(CO) or Ni, L = phosphine] have shown them to contain bridging-carbonyl groups.[1] *X*-Ray structural analyses of several of these compounds [2-3] have shown that a distortion in the cobalt to bridge-carbon distances appears to be related to the Co–P distance, and to the geometry around the cobalt atom. The crystal structure of the title compound was undertaken to determine the effect on the bridging system of a modified electronic and steric environment of the cobalt atom, and to enable the relationships of an extended series to be assessed.

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[1] A. R. Manning, *J. Organometallic Chem.*, 1972, **37**, C41; **40**, C73.

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

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

EXPERIMENTAL

Crystal Data.—$C_{27}H_{17}CoF_3NiO_4P$, $M = 611{\cdot}0$, Monoclinic, $a = 16{\cdot}396 \pm 0{\cdot}042$, $b = 10{\cdot}663 \pm 0{\cdot}058$, $c = 29{\cdot}260 \pm 0{\cdot}084$ Å, $\beta = 91{\cdot}1 \pm 0{\cdot}1°$, $U = 5114{\cdot}5$ Å^3, $D_m = 1{\cdot}62$ (by flotation), $Z = 8$, $D_c = 1{\cdot}587$, $F(000) = 2464$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, for cell dimensions and intensity measurements; μ(Mo-K_α) = 15·3 cm^{-1}. Systematic absences: hkl for $h + h + l = 2n + 1$, $h0l$ for $h(l) = 2n + 1$. Space group Ia or $I2/a$ [non-standard forms of C_c (No. 9) and $C2/c$ (No. 15)].

The complex crystallises in a tabular form on (001) elongated along the b axis with pinacoids {010} and {001}. Unit-cell parameters were determined from single-crystal precession photographs by use of Mo-K_α radiation. Systematic absences showed the space group to be Ia or $I2/a$, the latter being indicated by a statistical analysis of the intensity data [$N(Z)$ test [5]] and subsequently confirmed by the successful refinement. Intensities were measured on a Philips PAILRED diffractometer. Each reflection in the h 0—15 l layers for $\sin\theta < 0{\cdot}53$ was recorded and 2464 reflections having counts for which $\sigma(I)/(I) < 0{\cdot}5$ were used for the structure analysis.[6] Intensities were corrected for Lorentz and polarisation effects, but not for absorption or extinction. The intensities of several reflections chosen as standards and measured between the collection of each layer showed a steady decrease in intensity due to slow decomposition of the crystal. The intensities of the standards were used to obtain a scale factor for each layer and these were used to put each layer onto a common arbitrary scale.

Scattering factor curves for all atoms were taken from ref. 7, the values for the nickel and cobalt atoms being corrected for anomalous dispersion. Calculations were carried out on a PDP 10 computer at the University of Essex with programmes written by F. S. S.

Structure Determination.—The three-dimensional Patterson synthesis indicated the space group to be centric and yielded the positions of the two metal atoms. A Fourier synthesis phased by these atoms gave the positions for all non-hydrogen 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 $w = (92{\cdot}5 - 0{\cdot}3|F_o| + 0{\cdot}0013|F_o|^2)^{-1}$. For this latter weighting scheme mean 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. When the maximum shift in any parameter was of the order of its σ a difference-Fourier synthesis was calculated which gave the approximate positions of all hydrogen atoms. In further calculations the hydrogen atom contributions were included using positions calculated assuming C–H 1·0 Å and a thermal parameter of B 6·0 Å^2, but at no time were their parameters refined.

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The large number of parameters (335) necessitated this refinement being carried out in five block matrices: (1) the overall scale and thermal parameter, (2) the metals, phosphorus atom, carbonyl groups, and cyclopentadienyl ligand, and (3)—(5) each fluorophenyl group. Refinement was terminated when the maximum shift in a parameter was $<0{\cdot}1\sigma$. 2459 reflections were included in the final cycle of refinement. The final value for R, based on 2464 reflections, was 0·071 and for R' [$= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] was 0·076.

TABLE 1

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

	x/a	y/b	z/c	σ_{rms}/Å
Ni	0·27493(8)	0·27762(14)	0·12942(5)	0·0014
Co	0·40422(9)	0·35705(13)	0·10283(5)	0·0014
P	0·5194(2)	0·2496(3)	0·1173(1)	0·0026
F(1)	0·6866(5)	0·1681(9)	−0·0577(2)	0·008
F(2)	0·7751(5)	0·4705(10)	0·2394(3)	0·009
F(3)	0·4577(5)	−0·2423(7)	0·2034(3)	0·008
O(B1)	0·3930(5)	0·3030(10)	0·2013(3)	0·009
O(B2)	0·2525(6)	0·4837(10)	0·0696(4)	0·010
O(T1)	0·3960(8)	0·2687(14)	0·0071(3)	0·013
O(T2)	0·4631(7)	0·6124(10)	0·1043(4)	0·011
C(B1)	0·3712(7)	0·3173(11)	0·1632(4)	0·011
C(B2)	0·2872(7)	0·4120(12)	0·0917(5)	0·013
C(T1)	0·4001(8)	0·3014(12)	0·0438(5)	0·013
C(T2)	0·4396(8)	0·5108(13)	0·1056(4)	0·013
C(1)	0·2414(8)	0·1056(14)	0·1597(6)	0·015
C(2)	0·2200(9)	0·0941(14)	0·1152(5)	0·015
C(3)	0·1659(9)	0·1917(14)	0·1032(5)	0·014
C(4)	0·1508(7)	0·2600(15)	0·1456(6)	0·015
C(5)	0·2005(8)	0·2025(16)	0·1780(5)	0·015
C(11)	0·5746(6)	0·2195(11)	0·0649(3)	0·010
C(12)	0·6034(7)	0·3199(11)	0·0399(4)	0·012
C(13)	0·6423(6)	0·3028(13)	−0·0003(4)	0·012
C(14)	0·6497(6)	0·1855(14)	−0·0176(3)	0·012
C(15)	0·6211(8)	0·0794(14)	0·0051(4)	0·013
C(16)	0·5838(7)	0·0969(11)	0·0468(4)	0·011
C(21)	0·5991(6)	0·3224(10)	0·1534(3)	0·010
C(22)	0·5787(7)	0·4100(12)	0·1861(4)	0·012
C(23)	0·6391(8)	0·4613(13)	0·2157(4)	0·012
C(24)	0·7176(8)	0·4189(14)	0·2104(4)	0·013
C(25)	0·7404(8)	0·3376(15)	0·1790(5)	0·014
C(26)	0·6800(6)	0·2847(14)	0·1496(4)	0·013
C(31)	0·5046(6)	0·0977(10)	0·1444(3)	0·010
C(32)	0·4463(7)	0·0171(12)	0·1257(4)	0·012
C(33)	0·4310(8)	−0·0978(12)	0·1445(5)	0·013
C(34)	0·4747(7)	−0·1316(11)	0·1846(4)	0·012
C(35)	0·5302(8)	−0·0543(13)	0·2038(4)	0·013
C(36)	0·5466(6)	0·0616(12)	0·1838(4)	0·011
H(1)	0·281	0·050	0·176	
H(2)	0·239	0·027	0·094	
H(3)	0·142	0·211	0·072	
H(4)	0·113	0·332	0·150	
H(5)	0·206	0·229	0·211	
H(12)	0·595	0·407	0·052	
H(13)	0·665	0·376	−0·017	
H(15)	0·627	−0·006	−0·008	
H(16)	0·563	0·023	0·064	
H(22)	0·521	0·438	0·189	
H(23)	0·625	0·526	0·239	
H(25)	0·799	0·314	0·176	
H(26)	0·695	0·221	0·126	
H(32)	0·415	0·044	0·098	
H(33)	0·390	−0·156	0·130	
H(35)	0·560	−0·080	0·232	
H(36)	0·588	0·119	0·198	

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 **21183** (15 pp., 1 microfiche).*

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

[4] I. L. C. Campbell and F. S. Stephens, preceding paper.

[5] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.

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

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

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	26·0(5)	81·4(14)	8·6(2)	−5·3(8)	−3·9(2)	2·5(4)
Co	25·1(5)	58·6(13)	7·6(2)	0·7(8)	−3·3(2)	−2·2(4)
P	25·2(10)	58·2(26)	4·8(3)	−2·7(13)	−3·2(4)	−1·8(7)
F(1)	55(4)	247(14)	8(1)	−1(6)	5(2)	−11(3)
F(2)	52(4)	286(17)	16(1)	−46(7)	−14(2)	−24(4)
F(3)	86(5)	104(9)	16(1)	11(6)	−2(2)	23(3)
O(B1)	45(4)	213(15)	6(1)	−10(6)	−2(2)	−6(3)
O(B2)	44(5)	144(13)	26(2)	24(6)	−3(2)	35(4)
O(T1)	102(8)	309(24)	10(1)	58(11)	−15(3)	−27(5)
O(T2)	76(7)	70(10)	33(2)	−12(8)	−12(3)	4(4)
C(B1)	38(5)	93(12)	7(1)	−21(7)	−1(2)	−5(3)
C(B2)	31(5)	81(13)	18(2)	9(7)	−2(3)	−4(5)
C(T1)	46(6)	75(13)	16(2)	7(7)	−7(3)	−5(4)
C(T2)	38(6)	95(14)	13(2)	7(8)	−6(3)	4(4)
C(1)	33(6)	104(15)	22(3)	5(8)	1(3)	4(5)
C(2)	52(7)	115(17)	17(2)	−28(9)	−1(3)	−14(5)
C(3)	52(7)	125(17)	13(2)	−32(9)	−11(3)	12(5)
C(4)	18(4)	141(19)	25(3)	−3(8)	−3(3)	5(6)
C(5)	38(6)	177(21)	13(2)	−34(10)	0(3)	6(6)
C(11)	23(4)	101(12)	5(1)	11(6)	−1(2)	−13(3)
C(12)	32(5)	86(13)	13(2)	−17(7)	1(2)	5(4)
C(13)	27(5)	137(16)	7(1)	−22(7)	3(2)	−3(4)
C(14)	21(4)	180(20)	5(1)	10(7)	3(2)	−9(4)
C(15)	45(6)	137(17)	8(1)	0(8)	3(2)	−1(4)
C(16)	44(5)	73(11)	6(1)	4(7)	0(2)	−4(3)
C(21)	28(4)	80(11)	6(1)	−21(6)	−5(2)	−7(3)
C(22)	36(5)	108(14)	9(2)	−10(7)	0(2)	−2(4)
C(23)	39(6)	129(17)	8(1)	−26(8)	−2(2)	−14(4)
C(24)	39(6)	157(18)	9(2)	−47(9)	−10(2)	−8(2)
C(25)	36(6)	177(20)	14(2)	−10(9)	−13(3)	−12(6)
C(26)	15(4)	167(18)	16(2)	−18(7)	−4(2)	−16(5)
C(31)	25(4)	64(10)	5(1)	10(5)	−6(2)	2(3)
C(32)	37(5)	86(13)	11(2)	2(7)	−5(2)	2(4)
C(33)	45(6)	72(12)	16(2)	5(7)	−2(3)	0(4)
C(34)	43(6)	73(12)	11(2)	6(7)	−1(2)	18(4)
C(35)	51(7)	118(16)	8(2)	11(9)	0(3)	11(4)
C(36)	24(4)	111(14)	8(1)	8(6)	−2(2)	−1(4)

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

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

DISCUSSION

Figure 1 shows a perspective drawing of the molecule and the labelling of the atoms.[8] Figure 2 shows the packing of the molecules in the crystal.[8] The molecules are held in the crystal by van der Waals forces. Closest intermolecular contacts are: O(T2) ··· F(3) at x, $1 + y, z$ (3·29 Å) and F(1) ··· C(33) at $1 - x$, $-y$, $-z$ (3·25 Å). All other intermolecular contacts are >3·3 Å.

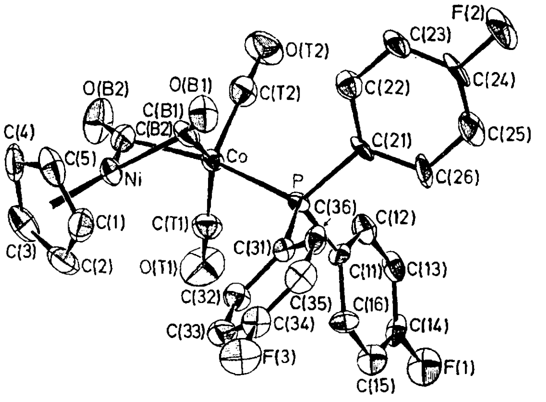

FIGURE 1 A perspective drawing of the molecule and the labelling of the atoms. Thermal ellipsoids are scaled to include 36% probability

Bond distances and angles, together with their estimated standard deviations derived directly from the least-squares inverse matrices, are given in Table 3.

TABLE 3

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

(*a*) Distances *

Ni ··· Co 2·425(2)

Ni–C(B1)	1·894(11)	Co–C(B1)	1·904(11)
Ni–C(B2)	1·823(14)	Co–C(B2)	2·026(12)
Ni–Cp	1·761(12)	Co–P	2·242(3)
Ni–C(1)	2·115(14)	Co–C(T1)	1·827(14)
Ni–C(2)	2·191(13)	Co–C(T2)	1·740(15)
Ni–C(3)	2·138(12)	P–C(11)	1·824(10)
Ni–C(4)	2·107(12)	P–C(21)	1·836(9)
Ni–C(5)	2·054(13)	P–C(31)	1·822(10)
C(B1)–O(B1)	1·176(12)	C(B2)–O(B2)	1·145(14)
C(T1)–O(T1)	1·130(14)	C(T2)–O(T2)	1·150(15)
C(1)–C(2)	1·349(19)	C(21)–C(22)	1·383(15)
C(2)–C(3)	1·408(20)	C(22)–C(23)	1·413(15)
C(3)–C(4)	1·464(20)	C(23)–C(24)	1·376(18)
C(4)–C(5)	1·381(19)	C(24)–C(25)	1·323(18)
C(5)–C(1)	1·349(20)	C(25)–C(26)	1·416(15)
C(11)–C(12)	1·384(15)	C(26)–C(21)	1·392(15)
C(12)–C(13)	1·361(15)	C(31)–C(32)	1·390(14)
C(13)–C(14)	1·356(17)	C(32)–C(33)	1·368(16)
C(14)–C(15)	1·397(18)	C(33)–C(34)	1·409(16)
C(15)–C(16)	1·388(15)	C(34)–C(35)	1·343(17)
C(16)–C(11)	1·420(15)	C(35)–C(36)	1·396(17)
C(14)–F(1)	1·343(11)	C(36)–C(31)	1·384(13)
C(24)–F(2)	1·370(11)	C(34)–F(3)	1·334(13)

(*b*) Angles

C(B1)–Ni–C(B2)	92·3(5)	C(B1)–Co–C(B2)	85·9(5)
Co–Ni–C(B1)	50·5(3)	Ni–Co–C(B1)	50·1(3)
Co–Ni–C(B2)	54·8(4)	Ni–Co–C(B2)	47·3(4)
Co–Ni–Cp *	159·5(4)	P–Co–C(B1)	88·0(4)
C(B1)–Ni–Cp *	131·3(6)	P–Co–C(B2)	165·8(4)
C(B2)–Ni–Cp *	135·2(6)	P–Co–C(T1)	91·7(4)
Co–P–C(11)	111·2(3)	P–Co–C(T2)	101·2(4)
Co–P–C(21)	118·7(4)	C(B1)–Co–C(T1)	143·0(5)
Co–P–C(31)	114·7(3)	C(B1)–Co–C(T2)	105·5(5)
C(11)–P–C(21)	101·4(5)	C(B2)–Co–C(T1)	85·6(6)
C(11)–P–C(31)	106·4(5)	C(B2)–Co–C(T2)	92·8(5)
C(21)–P–C(31)	103·0(4)	C(T1)–Co–C(T2)	110·9(6)
Ni–C(B1)–Co	79·4(4)	Ni–C(B2)–Co	77·9(5)
Ni–C(B1)–O(B1)	134·5(9)	Ni–C(B2)–O(B2)	143·8(11)
Co–C(B1)–O(B1)	145·4(10)	Co–C(B2)–O(B2)	138·0(11)
Co–C(T1)–O(T1)	178·4(12)	Co–C(T2)–O(T2)	175·3(13)
C(5)–C(1)–C(2)	109·3(14)	P–C(21)–C(22)	120·3(8)
C(1)–C(2)–C(3)	108·9(13)	P–C(21)–C(26)	120·1(8)
C(2)–C(3)–C(4)	105·9(11)	C(26)–C(21)–C(22)	119·6(9)
C(3)–C(4)–C(5)	104·7(13)	C(21)–C(22)–C(23)	120·7(11)
C(4)–C(5)–C(1)	111·1(14)	C(22)–C(23)–C(24)	116·7(11)
P–C(11)–C(12)	119·2(9)	C(23)–C(24)–C(25)	124·8(10)
P–C(11)–C(16)	122·3(9)	C(23)–C(24)–F(2)	115·7(12)
C(16)–C(11)–C(12)	118·3(9)	C(25)–C(24)–F(2)	119·5(12)
C(11)–C(12)–C(13)	121·6(11)	C(24)–C(25)–C(26)	118·7(12)
C(12)–C(13)–C(14)	119·5(11)	C(25)–C(26)–C(21)	119·5(12)
C(13)–C(14)–C(15)	122·5(10)	C(31)–C(32)–C(33)	121·7(10)
C(13)–C(14)–F(1)	119·9(12)	C(32)–C(33)–C(34)	118·0(12)
C(15)–C(14)–F(1)	117·7(12)	C(33)–C(34)–C(35)	121·3(11)
C(14)–C(15)–C(16)	117·8(12)	C(33)–C(34)–F(3)	117·6(11)
C(15)–C(16)–C(11)	120·2(11)	C(35)–C(34)–F(3)	121·1(10)
P–C(31)–C(32)	118·4(7)	C(34)–C(35)–C(36)	120·3(10)
P–C(31)–C(36)	122·8(8)	C(35)–C(36)–C(31)	119·9(11)
C(36)–C(31)–C(32)	118·8(10)		

* Cp is the centroid of the cyclopentadienyl ring.

The compound crystallises as discrete molecules, with the nickel and cobalt atoms bridged by two carbonyl groups. The cyclopentadienyl ligand is π-bonded to the

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[8] 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 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): Ni, Co, C(B1), O(B1)	−0·3128	0·9359	0·1621	1·9698
[Ni −0·009, Co −0·012, C(B1) 0·048, O(B1) −0·027]				
Plane (2): Ni, Co, C(B2), O(B2)	0·0531	0·6230	0·7804	4·9786
[Ni −0·008, Co −0·006, C(B2) 0·032, O(B2) −0·018]				
Plane (3): C(1)—(5)	0·7559	0·6100	−0·2375	2·5756
[C(1) 0·011, C(2) −0·021, C(3) 0·022, C(4) −0·016, C(5) 0·004]				
Plane (4): C(11)—(16)	0·8825	−0·0878	0·4620	8·8964
[C(11) 0·005, C(12) −0·015, C(13) 0·015, C(14) −0·004, C(15) −0·007, C(16) −0·007, F(1) −0·001, P −0·106]				
Plane (5): C(21)—(26)	0·1545	0·7384	−0·6564	1·2349
[C(21) −0·003, C(22) 0·004, C(23) 0·004, C(24) −0·013, C(25) 0·013, C(26) −0·005, F(2) −0·006, P −0·100]				
Plane (6): C(31)—(36)	0·7075	−0·4174	−0·5703	3·3093
[C(31) 0·005, C(32) −0·010, C(33) 0·007, C(34) 0·002, C(35) −0·006, C(36) 0·003, F(3) −0·019, P −0·044]				
Plane (7): P, C(B2), C(B1)	0·3782	0·9058	0·1910	6·2550
[Co 0·25]				
Plane (8): P, C(B2), C(T1)	0·4329	0·8854	−0·1692	5·4892
[Co 0·26]				
Plane (9): P, C(B2), C(T2)	−0·1578	0·0383	0·9867	1·9834
[Co −0·04]				

nickel and the phosphine co-ordinated to the cobalt. The molecule was the expected non-planar carbonyl-bridged structure. The value of the angle between the two Ni(CO)Co planes (**133·9°**) lies between those of the parent compounds $Co_2(CO)_8$ (127°) [9] and [{(π-C_5H_5)-Ni(CO)}$_2$] (142°),[10] and is not significantly different from that found in other similar compounds: [(π-C_5H_5)NiCo(CO)$_4${$PPh_2(C_6H_{11})$}] (133·9°) [4] and [(π-C_5H_5)-NiCo(CO)$_4$(PEt$_3$)] (132·4°).[2] The Ni · · · Co distance (**2·425 Å**) is in accord with those previously reported for similar complexes.[2,4] 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 **159·5°**.

As has been observed for other similar compounds,[2,3] there is a striking distortion present in the bridging system. The metal to bridge-carbon distances are not equivalent [Ni–C(B1) **1·894(11)**, Ni–C(B2) **1·823(14)**, Co–C(B1) **1·904(11)**, and Co–C(B2) **2·026(12)**], C(B2) being *trans* to the phosphine ligand about the cobalt atom. Also, the angles around C(B1) are not regular. The Co–C(B1)–O(B1) angle has opened to **145·4°**, but the planar environment about C(B1) has been maintained by a corresponding closure of the angle to nickel.

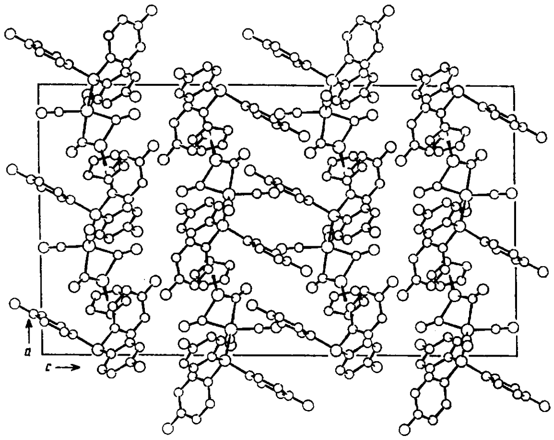

FIGURE 2 The packing of the molecules in the crystal

The three fluorophenyl rings are each planar (Table 4) with the fluorine atoms in the *para*-position. The carbon atoms bound to the phosphorus atom exhibit the expected trigonal symmetry about the Co–P direction but this three-fold symmetry is not maintained by the orientation of the phenyl rings. Ring C(21)—(26) is rotated such that the contacts between C(22) and H(22) to the carbonyl groups (B1) and (T2) are approximately equivalent.

TABLE 5

Comparison of trigonal bipyramidal *vs.* square-based pyramidal cobalt atom environment, and of Co–P and Co–C_b (*trans* to P) distances (Å) for compounds closely related to the present complex. Planes are defined by the axial–equatorial–axial atoms of a trigonal bipyramid, and in the present structure atoms P and C(B2) are axial

	Distances *		Equatorial atoms defining planes		
Compound	Co–P	Co–C	C(B1)⁚C(T2)	C(T1)⁚C(T2)	C(B1)⁚C(T1)
[(π-MeC_5H_4)NiCo(CO)$_4${$PPh_2(C_6H_{11})$}] [a]	2·269(2)	1·929(10)	92·9	94·5	178·4
[(π-C_5H_5)NiCo(CO)$_4${P(*p*-FC_6H_4)$_3$}] [b]	2·242(3)	2·026(12)	99·4	101·6	159·0
[(π-C_5H_5)NiCo(CO)$_4$(PEt$_3$)] [c]	2·236(1)	1·956(6)	102·3	102·4	155·2
[(π-C_5H_5)FeCo(CO)$_5$(PPh$_2$Me)] [d]	2·221(6)	2·027(20)	103·1	107·6	149·3
Trigonal-bipyramid			120	120	120
Square-based pyramid			90	90	180

* Estimated standard deviations in parentheses. [a] Ref. 4. [b] Present work. [c] Ref. 2. [d] Ref. 3.

The environment about the cobalt atom is intermediate between trigonal bipyramidal and square-based pyramidal (Table 5). This is similar to that found in [(π-C_5H_5)NiCo(CO)$_4$(PEt$_3$)] [2] and in [(π-C_5H_5)-FeCo(CO)$_5$(PPh$_2$Me)],[3] but contrasts with the square-based pyramidal environment of the cobalt in [(π-MeC_5H_4)NiCo(CO)$_4${$PPh_2(C_6H_{11})$}].[4] The Co · · · P distance (**2·242 Å**) lies between that in [(π-C_5H_5)NiCo(CO)$_4$-(PEt$_3$)] (**2·236 Å**) [2] and in [(π-MeC_5H_4)NiCo(CO)$_4${PPh$_2$-(C_6H_{11})}] (**2·269 Å**).[4]

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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.

The study of similar compounds has shown a possible relationship between the length of the cobalt to carbon-bridge bond *trans* to the phosphine ligand and the Co–P distance.[3,4] It has been suggested, from structural studies of similar compounds, that the phosphine ligand exerts a *trans*-effect causing a distortion in the carbonyl-bridging system. This effect seems to be nullified by a change from a trigonal bipyramidal to a square-based pyramidal environment about the cobalt atom.[4] In the present structure the relationship of the Co–P distance with the cobalt atom geometry is consistent with previous observations [2-4] (Table 5). However the Co–C(B2) distance is longer than might have been predicted. Whilst the suggested hypothesis seems to be a good working model, it is obvious that the situation is more complex, and that other factors, such as the packing of the molecules in the crystal, need to be considered. The determination of other similar structures is necessary to enable this to be attempted.

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