Structure of an Iron–Cobalt Organometallic Complex. Crystal and Molecular Structure of Di-μ-carbonyl-carbonyl[dicarbonyl(methyldiphenylphosphine)cobaltio]-π-cyclopentadienyliron

By **Geoffrey Davey**, Inland Waters Directorate, Environment Canada, 562 Booth St., Ottawa, Ontario, Canada
Frederick S. Stephens,* Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex

The crystal structure of the title compound has been determined by three-dimensional photographic X-ray diffraction methods and refined to R 0·085 for 1466 unique reflections by least-squares procedures. The triclinic unit cell, space group $P\bar{1}$, has dimensions: a = 6·948 ± 0·009, b = 11·551 ± 0·018, c = 14·618 ± 0·019 Å, α = 100·9, β = 86·9, γ = 104·3° (all ±0·1°), for Z = 2. The molecule shows no overall symmetry and possesses two bridging carbonyl groups, with Fe · · · Co 2·540 (4) Å. The Fe(CO)$_2$Co bridging system is non-planar with the π-cyclopentadienyl ring *trans* to the puckering. The angle between the two bridging Fe–C–Co planes is 25·4°. The carbon atoms of the π-cyclopentadienyl ring are displaced equally from the Fe atom, mean distance 2·11 Å. The Fe–C and Co–C distances in the carbonyl bridge are not equivalent: Fe–C(1) 1·797(16), Fe–C(2) 1·967(19), Co–C(1) 2·027(20), Co–C(2) 1·907(17) Å, and indicate a *trans*-influence of the methyl(diphenyl)phosphine group. Co–P is 2·221(6) Å.

THE structures of several binuclear Fe–Fe and Co–Co carbonyl compounds with π-cyclopentadienyl and similar π-bonding ligands have been investigated. However, a series of mixed binuclear Fe–Co complexes, (π-ring)-COFe·(CO)$_2$·Co(CO)$_3$ (ring = C$_5$H$_5$, MeC$_5$H$_4$, and C$_9$H$_7$) has also been studied by i.r. spectroscopy.[1] Results indicate a non-planar dicarbonyl bridging system in the solid state, but it was not possible to determine whether the π-cyclopentadienyl ring is *cis* or *trans* to the puckering of the bridging system.[1] We have undertaken the structural determination of (π-C$_5$H$_5$)COFe·(CO)$_2$·Co-(CO)$_2$(PMePh$_2$), which is derived from (π-C$_5$H$_5$)COFe·-(CO)$_2$·Co(CO)$_3$, to determine the nature of the carbonyl bridging system. Further interest in this and related complexes lies in the effect on the overall molecular structure and on the ' local ' molecular environments of the Fe and Co atoms of replacing a carbonyl group on the Co atom with a phosphine group.

EXPERIMENTAL

Crystal Data.—C$_{23}$H$_{18}$CoFeO$_5$P, M = 520·2, Triclinic, a = 6·948 ± 0·009, b = 11·551 ± 0·018, c = 14·618 ± 0·019 Å, α = 100·9 ± 0·1, β = 86·9 ± 0·1, γ = 104·3 ± 0·1°, U = 1116·5 Å^3, D_m = 1·54 (by flotation), Z = 2, D_c = 1·547, F(000) = 528. Space group, $P\bar{1}$ (C_i, No. 2). Mo-K_α (λ = 0·71069 Å) radiation for cell dimensions and intensity measurements; μ(Mo-K_α) = 15·35 cm^{-1}.

Unit-cell parameters were determined from single-crystal precession photographs. Intensities were estimated visually from precession photographs for the layers 0—3, 0—4, 0—4, and 0—2, precessing about b, c, [011], and [0$\bar{1}$1] respectively. Each reflection was corrected for Lorentz and polarisation effects but no correction for absorption or extinction was applied. A total of 2332 non-zero reflections was recorded and after internal correlation yielded 1480 unique reflections on a common arbitrary scale.

Wilson's method[2] was used to place the data on an approximately absolute scale. The scattering factors used for neutral atoms were taken from refs. 3 and 4, and for Fe$^+$ from ref. 5, the values for cobalt and iron being corrected for anomalous dispersion. Most calculations in this analysis were carried out with the ' X-Ray ' system[6] of crystallographic programs.

Structure Determination.—Statistical tests on intensity data, to determine whether the space group is $P1$ or $P\bar{1}$, were inconclusive. Thus, with two molecules in the triclinic unit cell, the space group was assumed to be centrosymmetric and taken as $P\bar{1}$. This was later confirmed by the structure analysis. The positions of the cobalt and iron atoms were deduced from a three-dimensional sharpened Patterson synthesis. Subsequently, two Fourier syntheses were sufficient to locate all the non-hydrogen atoms. The structure factors, calculated with the co-ordinates for all atoms (excluding hydrogens) and thermal parameters of U = 0·038 for cobalt, 0·044 for iron, and 0·057 Å^2 for phosphorus and for the remaining atoms, gave R 0·24.

Refinement of the structure was carried out by a full-matrix least-squares procedure in which the function minimised was $\Sigma w(|F_o| - |F_c|)^2$. The weight for each reflection, w, was initially unity and in the final refinement was given by $w = (8 + |F_o| + 0{\cdot}013|F_o|^2)^{-1}$.

In the initial refinement, in which 2332 reflections were used, individual layer scale-factors together with positional and isotropic thermal parameters for each atom were refined. After two cycles of refinement, at which stage the maximum shift in any parameter was of the order of its estimated standard deviation and R was 0·149, a difference-Fourier synthesis was calculated. This map showed no unusual features and indicated the approximate positions of the hydrogen atoms except those of the methyl group. The positions of the found hydrogen atoms were optimised (assuming C–H 1·0 Å), and in subsequent refinement they were included with an isotropic thermal parameter of U 0·082 Å^2 but not refined. After a further cycle of refinement the refined layer scale factors were used to produce a unique set of reflection data which was used in subsequent refinement.

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Owing to the large number of parameters (281) being refined it was necessary to divide these into three block matrices. Matrices (1)—(3) contained the following: (1) overall scale factor,

---

[1] A. R. Manning, *J. Chem. Soc.* (*A*), 1971, 2321.

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

[3] P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 390.

[4] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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

[6] J. M. Stewart, G. J. Kruger, H. L. Ammon, and S. R. Hall, 1972, Computer Sci. Centre Report, University of Maryland Technical Report TR 192.

overall temperature factor, atoms Co, Fe, P,O(1)—(5), and C(1)—(5); (2) atoms C(6)—(10); and (3) atoms C(11)—C(23). The final refinement was terminated when the maximum shift in any parameter was 0·25σ and the average shift was 0·04σ. Fourteen high-order, and low-intensity, reflections were considered to be poorly defined and were omitted from the final cycle of refinement. The final value of R was 0·085, based on 1466 reflections and R' 0·013 [$= \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$). The structure was confirmed by a difference Fourier map, which showed maximum positive electron densities of 0·7 eÅ^{-3}, located around the iron and cobalt atoms.

TABLE 1

Final atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

	x/a	y/b	z/c	σ_{rms}/Å $\times 10^3$
Co	2142(3)	3093(2)	2542(2)	25 *
Fe	1916(4)	2950(2)	795(2)	27 *
P	1239(4)	1652(4)	3401(3)	44 *
O(1)	4221(21)	5214(12)	1757(9)	14
O(2)	−1289(19)	1333(12)	1616(10)	14
O(3)	−1100(26)	4281(18)	725(15)	20
O(4)	456(23)	4960(13)	3702(12)	16
O(5)	6314(21)	3371(14)	2973(14)	17
C(1)	3169(26)	4229(15)	1629(14)	19
C(2)	184(27)	2084(16)	1684(14)	19
C(3)	77(31)	3791(22)	740(15)	23
C(4)	1078(25)	4187(17)	3241(13)	19
C(5)	4729(31)	3289(17)	2824(16)	22
C(6)	2485(41)	1228(21)	136(16)	25
C(7)	4279(29)	2138(21)	341(15)	22
C(8)	4406(32)	3112(16)	−131(14)	20
C(9)	2628(35)	2844(19)	−625(11)	21
C(10)	1570(39)	1680(16)	−445(18)	24
C(11)	−1399(23)	1356(17)	3788(15)	19
C(12)	2541(23)	2053(14)	4503(11)	16
C(13)	3750(31)	1377(19)	4734(14)	21
C(14)	4811(32)	1797(18)	5572(16)	22
C(15)	4636(32)	2812(22)	6159(14)	23
C(16)	3346(41)	3437(23)	5953(17)	27
C(17)	2379(39)	3117(21)	5112(16)	25
C(18)	1700(26)	150(15)	2890(12)	18
C(19)	3325(26)	129(16)	2313(13)	19
C(20)	3729(35)	−959(25)	1930(16)	26
C(21)	2524(40)	−2030(20)	2104(15)	20
C(22)	898(35)	−2013(16)	2664(17)	23
C(23)	458(26)	−896(16)	3056(15)	20
H(6) †	249	56	47	
H(7)	552	232	72	
H(8)	524	391	−25	
H(9)	184	314	−105	
H(10)	27	109	−64	
H(13)	387	59	432	
H(14)	573	132	574	
H(15)	546	311	674	
H(16)	310	414	642	
H(17)	157	366	493	
H(19)	421	91	217	
H(20)	493	−99	152	
H(21)	281	−282	181	
H(22)	2	−279	281	
H(23)	−77	−88	346	

* σ_{rms} for Co, Fe, and P all $\times 10^4$. † Hydrogen atom co-ordinates $\times 10^3$.

Final atomic co-ordinates and thermal parameters together with their estimated standard deviations are given in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20909 (3 pp., 1 microfiche).*

TABLE 2

Thermal parameters ($\times 10^3$),* with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	50(2)	56(2)	57(2)	19(1)	1(1)	10(1)
Co	67(2)	69(2)	54(2)	16(2)	−41(1)	14(1)
P	52(3)	56(3)	55(3)	22(2)	2(2)	5(2)
O(1)	108(10)	72(9)	76(9)	16(8)	9(8)	21(8)
O(2)	74(8)	91(10)	87(10)	−7(7)	−13(8)	30(8)
O(3)	115(13)	191(19)	187(20)	88(14)	3(13)	99(16)
O(4)	118(12)	98(11)	112(12)	70(10)	5(10)	−5(9)
O(5)	54(8)	107(12)	178(18)	25(8)	−17(10)	18(11)
C(1)	73(11)	56(11)	88(14)	26(9)	13(10)	51(10)
C(2)	71(11)	55(11)	74(13)	0(9)	−6(10)	22(10)
C(3)	83(14)	135(20)	71(14)	33(14)	−3(12)	47(15)
C(4)	61(11)	82(13)	56(11)	13(10)	12(9)	15(11)
C(5)	65(12)	57(12)	97(16)	8(10)	5(12)	5(11)
C(6)	148(23)	75(15)	70(15)	50(16)	−1(15)	9(13)
C(7)	68(12)	86(15)	73(15)	14(12)	−5(11)	−26(13)
C(8)	106(16)	50(11)	68(14)	14(11)	10(13)	23(11)
C(9)	129(18)	105(16)	22(9)	50(14)	−11(11)	23(11)
C(10)	136(20)	39(11)	123(22)	−34(12)	37(17)	42(13)
C(11)	44(9)	81(13)	102(16)	22(9)	25(10)	31(12)
C(12)	63(10)	52(10)	38(10)	30(8)	3(8)	21(9)
C(13)	91(14)	94(15)	52(12)	33(12)	−9(11)	6(12)
C(14)	108(16)	58(12)	77(15)	38(12)	3(13)	19(12)
C(15)	97(16)	106(17)	61(14)	43(14)	−24(12)	8(14)
C(16)	139(21)	106(18)	80(18)	56(17)	−28(17)	−29(15)
C(17)	145(21)	96(17)	78(16)	69(16)	−47(15)	−9(14)
C(18)	68(11)	54(11)	48(11)	9(9)	−8(9)	−19(10)
C(19)	70(11)	62(12)	53(12)	18(10)	20(10)	−1(10)
C(20)	98(16)	126(21)	70(16)	63(16)	13(13)	−5(16)
C(21)	123(18)	74(15)	52(13)	37(14)	7(13)	22(11)
C(22)	107(17)	49(12)	97(18)	−3(12)	−11(15)	32(12)
C(23)	70(11)	55(11)	92(15)	12(9)	2(11)	16(10)

For all hydrogen atoms $U = 0{\cdot}082$ Å^2.

* The anisotropic temperature factors are given by: exp-$[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos\gamma^* + 2U_{13}hla^*c^* \cos\beta^* + 2U_{23}klb^*c^* \cos\alpha^*)]$.

DISCUSSION

Bond lengths and angles together with their estimated standard deviations are given in Table 3. Figure 1 shows a perspective drawing of the complex and the labelling of the atoms. The crystal consists of discrete binuclear (π-C_5H_5)(CO)Fe·(CO)$_2$·Co(CO)$_2$(PMePh$_2$) molecules. The shortest intermolecular contact is 3·05 Å between O(3) and O(3) at ($-x$, $1 - y$, $1 - z$). All other intermolecular contacts are >3·15 Å and the molecules are held in the crystal by van der Waals forces. Figure 2 shows the molecular packing in the crystal.

The molecule is in a *cis*-configuration and the Fe(CO)$_2$-Co bridging system is non-planar (Table 4). The dihedral angle between the two FeCCo planes (25·4°) is intermediate between those in *cis*-[(π-C_5H_5)Fe(CO)$_2$]$_2$ (16°),[7] {π-C_5H_4·CH(NMe$_2$)}$_2$Fe$_2$(CO)$_4$ (20·7°),[8] [(π-C_5H_5)$_2$-Fe$_2$(CO)$_3$](Ph$_2$PC)$_2$ (20°),[9] and in Co$_2$(CO)$_8$ (52·5 and 54·9°).[10] This is in agreement with the conclusions of the i.r. spectral studies.[1] The bridging carbonyl group C(2)O(2) is almost symmetrical with metal–carbon distances [Fe–C(2) 1·967, Co–C(2) 1·907 Å] comparable to those found in similar organometallic binuclear Fe [7,11]

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

[7] R. F. Bryan, P. T. Greene, D. S. Field, and M. J. Newlands, *Chem. Comm.*, 1969, 1477; *J. Chem. Soc.* (*A*), 1970, 3068.

[8] P. McArdle, A. R. Manning, and F. S. Stephens, *Chem. Comm.*, 1969, 1310; F. S. Stephens, *J. Chem. Soc.* (*A*), 1970, 1722.

[9] A. J. Carty, T. W. Ng, W. Carter, G. J. Palenik, and T. Birchall, *Chem. Comm.*, 1969, 1101.

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

[11] R. F. Bryan and P. T. Greene, *J. Chem. Soc.* (*A*), 1970, 3064.

TABLE 3

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

Fe · · · Co 2·540(4)

Fe–C(1)	1·797(16)	Co–C(1)	2·027(20)
Fe–C(2)	1·967(19)	Co–C(2)	1·907(17)
Fe–C(3)	1·798(26)	Co–C(4)	1·753(19)
Fe–C(6)	2·159(25)	Co–C(5)	1·817(22)
Fe–C(7)	2·102(23)	Co–P	2·221(6)
Fe–C(8)	2·130(21)	C(1)–O(1)	1·178(19)
Fe–C(9)	2·094(17)	C(2)–O(2)	1·163(20)
Fe–C(10)	2·088(22)	C(3)–O(3)	1·106(34)
P–C(11)	1·856(17)	C(4)–O(4)	1·170(25)
P–C(12)	1·817(16)	C(5)–O(5)	1·112(27)
P–C(18)	1·851(18)	C(12)–C(13)	1·372(31)
C(6)–C(7)	1·422(30)	C(13)–C(14)	1·406(30)
C(7)–C(8)	1·410(33)	C(14)–C(15)	1·344(30)
C(8)–C(9)	1·403(32)	C(15)–C(16)	1·359(41)
C(9)–C(10)	1·429(29)	C(16)–C(17)	1·378(35)
C(10)–C(6)	1·336(40)	C(17)–C(12)	1·399(28)
C(18)–C(19)	1·374(25)	C(19)–C(20)	1·364(25)
C(20)–C(21)	1·372(34)	C(21)–C(22)	1·360(35)
C(22)–C(23)	1·408(28)	C(23)–C(18)	1·357(24)
C(1)–Fe–C(2)	97·1(8)	C(1)–Co–C(2)	91·7(8)
C(1)–Fe–C(3)	86·6(9)	C(1)–Co–C(4)	90·9(8)
C(2)–Fe–C(3)	88·5(9)	C(1)–Co–C(5)	86·1(9)
Fe–C(1)–Co	83·0(7)	C(1)–Co–P	171·3(5)
Fe–C(2)–Co	81·9(6)	C(2)–Co–P	85·8(6)
Fe–C(1)–O(1)	147·1(17)	C(2)–Co–C(4)	108·1(8)
Fe–C(2)–O(2)	134·0(16)	C(2)–Co–C(5)	139·8(9)
Co–C(1)–O(1)	129·6(15)	Fe–C(3)–O(3)	177·3(21)
Co–C(2)–O(2)	144·1(17)	Co–C(4)–O(4)	176·6(15)
C(7)–C(6)–C(10)	102·9(21)	Co–C(5)–O(5)	177·4(18)
C(6)–C(7)–C(8)	111·8(21)	C(7)–C(8)–C(9)	106·9(17)
C(8)–C(9)–C(10)	104·9(21)	C(9)–C(10)–C(6)	114·4(22)
C(17)–C(12)–C(13)	119·3(16)	C(12)–C(13)–C(14)	118·3(18)
C(13)–C(14)–C(15)	122·3(23)	C(14)–C(15)–C(16)	119·1(21)
C(15)–C(16)–C(17)	120·9(23)	C(16)–C(17)–C(12)	119·8(25)
C(23)–C(18)–C(19)	120·9(17)	C(18)–C(19)–C(20)	119·4(18)
C(19)–C(20)–C(21)	121·0(21)	C(20)–C(21)–C(22)	119·8(22)
C(21)–C(22)–C(23)	119·7(18)	C(22)–C(23)–C(18)	119·2(18)

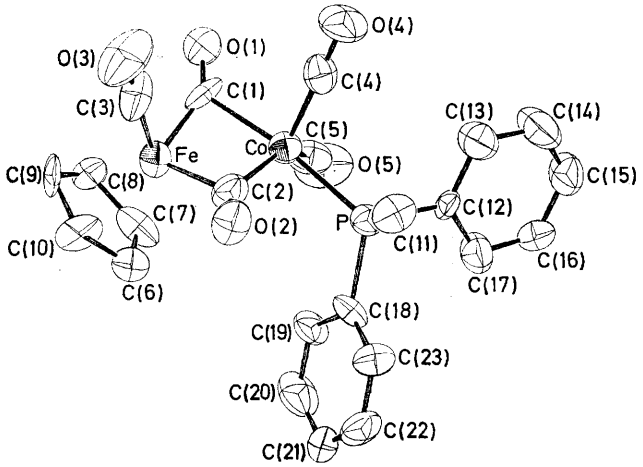

FIGURE 1 ORTEP drawing of the molecule viewed along *a*, showing the atom labelling; thermal ellipsoids represent 50% probability

and Co[10,12] compounds. However, the bridging carbonyl group C(1)O(1) is asymmetric, with metal–carbon distances [Fe–C(1) 1·797, Co–C(1) 2·027 Å] significantly different from those found in similar compounds.[7,10-12] Further the difference in the two Fe–C_b distances (C_b = bridge carbon) is significant, as is that between the two Co–C_b distances. The asymmetry is due probably to a *trans*-influence of the phosphine ligand, which is *trans* to

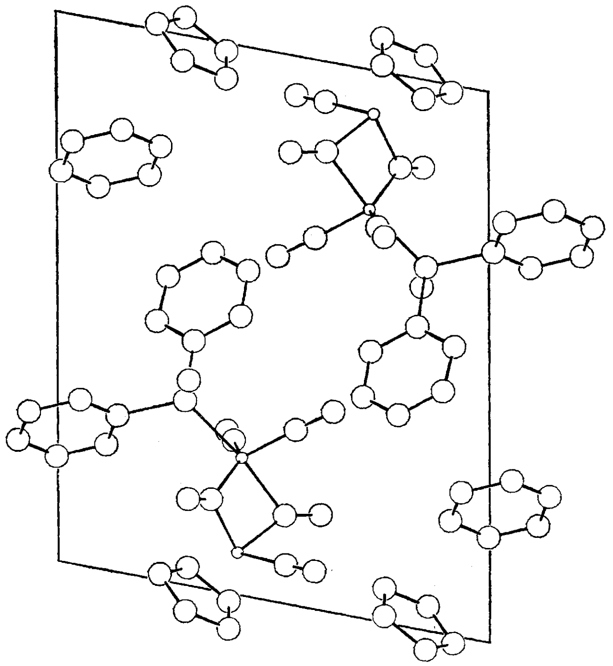

FIGURE 2 Unit-cell contents projected on the *bc* plane

TABLE 4

Equations of the planes of best fit in the form $lX' + mY' + nZ' - p = 0$ where the orthogonalised co-ordinates X', Y', Z' are derived with respect to the orthogonal axes *a*, *b′*, *c′* where *c′* lies in the *ac* plane. Deviations (Å) of relevant atoms are given in square brackets

	l	*m*	*n*	*p*
Plane (1): Co, Fe, C(1) [O(1) 0·074]	0·9402	−0·3323	−0·0748	−0·5984
Plane (2): Co, Fe, C(2) [O(2) −0·002]	−0·7101	0·7036	0·0283	1·9062
Plane (3): C(6)—(10) [C(6) 0·001, C(7) 0·008, C(8) − 0·013, C(9) 0·014, C(10) −0·010]	−0·5313	0·4576	0·7130	−0·1567
Plane (4): C(12)—(17) [C(12) 0·001, C (13) 0·020, C(14) 0·009, C(15) −0·020, C(16) −0·040, C(17) −0·028]	−0·6195	−0·5421	0·5678	1·3155
Plane (5): C(18)—(23) [C(18) 0·013, C(19) −0·006, C(20) −0·003, C(21) 0·004, C(22) 0·003, C(23) −0·012]	0·5984	0·0508	0·7800	4·1634
Plane (6): P, C(1), C(2) [Co 0·16]	−0·7454	0·5444	0·3848	2·2802
Plane (7): P, C(1), C(5) [Co 0·15]	−0·3053	0·7259	0·6163	3·9714
Plane (8): P, C(1), C(4) [Co −0·003]	0·8093	0·3686	0·4573	3·3119

---

[12] F. S. Stephens, *J.C.S. Dalton*, 1972, 1752.

C(1). The weakening of a metal–ligand bond, with a subsequent increase in bond length, *trans* to a phosphorus ligand has been observed with other transition metals.[13] The weakening of the Co–C(1) bond is accompanied by a corresponding strengthening of the Fe–C(1) bond. It is unlikely that this situation arises from the influence of the π-cyclopentadienyl ligand since both Fe–C_b bonds should be equally affected. The values of C_b–Fe–C_b angle (97·1°) is in good agreement with that observed in *cis*- and *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (96·0, 97·1).[7,11] The C_b–Co–C_b angle (91·7°) is comparable to the corresponding angle observed in $[(\pi\text{-}C_7H_8)Co(CO)\cdot(CO)_2\cdot Co(CO)_2]$ (91·1°)[14] and in $[(\pi\text{-}C_6H_8)Co(CO)_2]_2$ (95·8°).[15] Thus, the overall stereochemistry of the bridging system in this complex is similar to those observed in both Fe–Fe and Co–Co carbonyl-bridged complexes.

The eighteen-electron rule, which is known to apply particularly well to organometallic compounds,[16] indicates a two-electron Fe · · · Co metal–metal interaction. The Fe · · · Co distance (2·540 Å) is similar to Fe · · · Fe distances {2·531 in *cis*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$[7] and 2·540 Å in *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$[11]} and Co · · · Co distances {ranging from 2·524 in $Co_2(CO)_8$[10] to 2·559 Å in $[(\pi\text{-}C_6H_8)Co(CO)_2]_2$[15]} observed in related compounds where two-electron metal–metal interactions are also expected.

The stereochemistry of the five-co-ordinate Co atom is intermediate between trigonal-bipyramidal and square-based pyramidal. This is demonstrated by a consideration of the angles between the three planes defined by the axial–equatorial–axial atoms of a trigonal bipyramid, since for the former all will be 120°, whereas for the latter two will be 90° and the other 180°. In the present structure P–C(1) is the pseudo-trigonal axis and the angles between the planes [planes (6)—(8), Table 4] are 149·3, 103·1, and 107·6°. The co-ordination of the Fe atom is similar to that observed in both *cis*- and *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]$.[7,11] If the Fe–C(1), Fe–C(2), and Fe–C(3) directions are considered to define the axes of an octahedron then the cyclopentadienyl ring lies parallel to the $(\bar{1}\bar{1}\bar{1})$ face of the defined octahedron. The angles between the direction of the Fe atom to the centroid of the cyclopentadienyl ring and the 'axial' directions Fe–C(1), Fe–C(2), and Fe–C(3) are 127·5, 125·6, and 125·3°, values in good agreement with that (125·3°) for the dihedral angle between [100] and $[\bar{1}\bar{1}\bar{1}]$ of a regular octahedron.

The electronic environment of the five-co-ordinate Co atoms in $Co_2(CO)_8$ have been interpreted on the basis of an octahedron,[10] similar to the Fe environments in $Fe_2(CO)_9$, with one position having a very small overlap integral. If, in the present structure, the 'local' molecular axes of the Co atom are defined as Co–C(1), Co–C(2), and Co–C(4) on the basis of an octahedron and assuming the pseudo-octahedral environment of the Fe atom, then a usually non-bonding Fe(d_π) and a non-bonding Co(d_π) orbital would lie along the Fe · · · Co direction. Since both these orbitals would be of t_2 symmetry in this much simplified scheme, a bond of π-symmetry with respect to the 'local' molecular axes and of σ-symmetry with respect to the Fe · · · Co direction would be formed. Such a bond may account for the expected two-electron metal–metal interaction and for the intermediate geometry about the Co atom, the latter arising from an attempt to align the molecular axes to obtain maximum overlap of the d_π orbitals.

The cyclopentadienyl ring and the two phenyl rings exhibit the expected planarity (Table 4). The bond lengths and angles within the rings are in good agreement with previously reported values.[17] The Fe atom is 1·813 Å from the centroid of the C_5 ring.

We thank Dr. A. R. Manning for supplying a sample of the complex.

[3/1955 *Received*, 24*th September*, 1973]

---

[13] G. G. Mather and A. Pidcock, *J.C.S. Dalton*, 1973, 560.

[14] F. S. Stephens, *J.C.S. Dalton*, 1972, 1754.

[15] F. S. Stephens, *J.C.S. Dalton*, 1972, 1752.

[16] R. Krishnamurthy and W. B. Schaap, *J. Chem. Ed.*, 1970, **6**, 47, 433.

[17] *Chem. Soc. Special Publ.*, (*a*) No. 11, 1958; (*b*) No. 18, 1965.