Crystal and Molecular Structure of Di-μ-carbonyl-carbonyl(tricarbonylcobalt)-π-indenyliron

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The crystal structure of the title compound has been determined by Patterson and Fourier methods from photographic *X*-ray diffraction data and refined to *R* 0·098, for 1899 unique reflections, by full-matrix least-squares. The monoclinic unit cell, space group $P2_1/c$, has dimensions a = 12·076 ± 0·014, b = 9·905 ± 0·010, c =, 12·683 ± 0·012 Å, β = 97·5 ± 0·1°, for Z = 4. The molecule has the expected non-planar $Fe(CO)_2Co$ bridging system, the angle between the two Fe(CO)Co planes being 148·0°. Distortions within the bridging system are apparent: Fe–C(br) 1·916(13) and 1·838(12), and Co–C(br) 1·960(13) and 2·054(12) Å. Fe ··· Co is 2·552(2) Å.

SPECTROSCOPIC studies of the complexes $(\pi\text{-L})Fe(CO)_2Co(CO)_4$ (L = cyclopentadienyl, methylcyclopentadienyl, and indenyl) have shown them to exist solely as carbonyl-bridged species in the solid state but as mixtures of one non- and two bridged tautomers in solution.[1] It is suggested[1] that in the bridged isomers, the $Fe(CO)_2Co$ bridging systems are puckered with bridge angles[2] *ca.* 140—145° between the two Fe(CO)Co planes, and with ligand distributions about the iron and cobalt atoms similar to those found in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$[2-4] and $Co_2(CO)_8$.[5] To confirm these suggestions the crystal structure of the indenyl compound was undertaken.

EXPERIMENTAL

Crystal Data.—$C_{15}H_7FeO_6Co$, M = 398·0, Monoclinic, a = 12·076 ± 0·014, b = 9·905 ± 0·010, c = 12·683 ± 0·012 Å, β = 97·5 ± 0·1°, U = 1504·1 Å^3, D_m = 1·75 (by flotation), Z = 4, D_c = 1·757, $F(000)$ = 792. Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 21·6 cm^{-1}, for cell dimensions and intensity measurements. Space group $P2_1/c$ (C^5_{2h}, No. 14).

The complex crystallises as brown hexagonally shaped plates lying on the (001) face and with pinacoids {100}, {110}, and {$\bar{1}$10}. Unit-cell parameters were determined from single-crystal precession photographs with Mo-K_α radiation. Intensities were estimated visually from precession photographs for the layers 0—5 precessing about a, c, and [101]. Each reflection was corrected for Lorentz and polarisation effects but no correction for absorption or extinction was applied. A total of 2741 non-zero reflections was recorded and after internal correlation yielded 1899 unique reflections on a common arbitrary scale.

Wilson's method[6] was used to place the data approximately on absolute scale. The scattering factor curves for

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

[2] O. S. Mills, *Acta Cryst.*, 1958, **11**, 62.

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

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

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

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

all atoms are those given in ref. 7, the values for the iron and cobalt atoms being corrected for anomalous dispersion. All calculations were carried out on the Atlas computer at S.R.C. Chilton, with programmes of Hodgson, Mills, and Stephens.

Structure Determination.—The positions of the iron and cobalt atoms were obtained from a three-dimensional Patterson synthesis. A Fourier synthesis, phased by these atoms, gave the positions for all non-hydrogen atoms. Structure factors, calculated with the co-ordinates for all atoms, and an overall thermal parameter of B 3·0 Å^2, gave R 0·21.

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 calculated from the expression $w = (0{\cdot}6|F_o| + 0{\cdot}007|F_o|^2)^{-1}$. For this latter weighting scheme the average values of $w\Delta^2$ for ranges of increasing $|F_o|$ were almost constant. Reflections having $F_c < \frac{1}{3}(F_o)$ were omitted from the least-squares analysis.

Initial refinement, in which 2741 reflections were used, included individual layer scale factors together with positional and individual isotropic thermal parameters for each atom. After two cycles of refinement, at which stage R was 0·126, the positions of the hydrogen atoms on the indenyl ring were calculated assuming C–H 1·00 Å. In subsequent refinement these atoms were included with a thermal parameter of B 5·0 Å^2, but not refined. After a further two cycles of refinement the refined layer scale factors were used to produce a unique set of reflection data which were used in further refinement.

TABLE 1

Atomic co-ordinates with estimated standard deviations in parentheses

	x/a	y/b	z/c	σ_{rms} (Å)
Co	0·3760(1)	0·2266(2)	0·2412(1)	0·0016
Fe	0·1852(1)	0·1118(2)	0·2150(1)	0·0016
O(11)	0·4595(12)	0·3309(15)	0·4534(11)	0·014
O(12)	0·5853(9)	0·1139(12)	0·1847(11)	0·012
O(13)	0·3728(12)	0·4430(13)	0·0828(10)	0·013
O(21)	0·1190(12)	0·0427(13)	0·4199(9)	0·013
O(31)	0·3713(9)	−0·0641(10)	0·2936(12)	0·012
O(32)	0·1825(8)	0·3933(10)	0·2763(9)	0·011
C(11)	0·5042(11)	0·1534(13)	0·2032(12)	0·014
C(12)	0·4236(11)	0·2898(14)	0·3700(12)	0·014
C(13)	0·3717(11)	0·3617(13)	0·1431(13)	0·014
C(21)	0·1476(12)	0·0708(13)	0·3415(11)	0·014
C(31)	0·3304(10)	0·0397(13)	0·2625(12)	0·013
C(32)	0·2159(10)	0·2877(11)	0·2545(11)	0·013
C(1)	0·0259(11)	0·0650(14)	0·1424(14)	0·015
C(2)	0·0667(11)	0·1775(13)	0·0918(11)	0·014
C(3)	0·1654(12)	0·1351(15)	0·0470(13)	0·015
C(4)	0·1773(12)	−0·0057(13)	0·0649(11)	0·014
C(5)	0·0936(10)	−0·0499(13)	0·1247(10)	0·013
C(6)	0·0887(12)	−0·1868(13)	0·1585(12)	0·015
C(7)	0·1654(15)	−0·2733(14)	0·1261(15)	0·017
C(8)	0·2465(15)	−0·2302(17)	0·0621(15)	0·018
C(9)	0·2569(14)	−0·0989(16)	0·0339(14)	0·016
H(1)	−0·040	0·064	0·184	
H(2)	0·031	0·270	0·091	
H(3)	0·215	0·196	0·011	
H(6)	0·032	−0·222	0·203	
H(7)	0·163	−0·374	0·154	
H(8)	0·299	−0·296	0·035	
H(9)	0·316	−0·071	−0·010	

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The refinement was terminated when the maximum shift in any parameters was $<0{\cdot}1\sigma$. Only four reflections were omitted from the final cycle of refinement. Final values for R, based on 1899 reflections, and R' $\{= [\Sigma w\Delta^2/\Sigma w|F_o|^2]\}$ were 0·098 and 0·017.

Final atomic co-ordinate and thermal parameters together with their estimated standard deviations are given in Tables 1 and 2. Calculated and observed structure factors are listed in Supplementary Publication No. SUP 20836 (13 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}
Co	42(1)	70(2)	53(1)	−9(1)	11(1)	−6(1)
Fe	38(1)	67(2)	47(1)	−4(1)	9(1)	−1(1)
O(11)	107(13)	209(20)	78(10)	−25(13)	8(9)	−15(12)
O(12)	68(9)	143(14)	112(11)	35(9)	27(8)	6(11)
O(13)	126(13)	125(14)	99(11)	13(11)	15(10)	47(10)
O(21)	143(15)	162(16)	59(8)	4(12)	39(9)	29(10)
O(31)	67(8)	82(10)	160(14)	16(8)	4(9)	32(10)
O(32)	62(8)	89(10)	107(10)	8(7)	25(7)	−15(8)
C(11)	50(9)	98(14)	56(10)	−19(9)	−5(8)	−31(10)
C(12)	50(9)	82(12)	77(12)	0(9)	4(9)	−10(10)
C(13)	45(8)	86(13)	80(12)	2(8)	8(9)	16(11)
C(21)	71(11)	94(14)	41(9)	−10(10)	−14(9)	−4(9)
C(31)	38(8)	79(12)	81(11)	−2(8)	9(8)	−14(10)
C(32)	50(8)	57(10)	75(10)	7(8)	24(8)	8(9)
C(1)	46(8)	89(14)	102(14)	−5(9)	6(10)	−19(11)
C(2)	60(9)	91(13)	49(9)	13(9)	−7(8)	−4(9)
C(3)	56(9)	119(16)	75(11)	−24(10)	31(9)	−1(11)
C(4)	59(10)	87(13)	56(10)	−11(9)	7(8)	−11(9)
C(5)	45(8)	90(13)	47(8)	−7(8)	2(7)	0(9)
C(6)	68(11)	79(13)	75(12)	−27(9)	10(9)	6(10)
C(7)	94(14)	72(13)	110(16)	−5(12)	15(13)	−6(13)
C(8)	85(14)	120(18)	102(15)	11(13)	17(12)	−37(15)
C(9)	75(11)	118(17)	81(12)	−2(12)	31(10)	−27(13)

For all hydrogen atoms B = 5·0 Å^2.

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

DISCUSSION

Bond distances and angles together with their estimated standard deviations derived directly from the least-squares inverse matrix are given in Table 3. Figure 1 shows the packing of the molecules in the crystal and the labelling of the atoms. The molecules are held in the crystal by van der Waals forces. The closest approach of two atoms involving carbonyl groups is 3·17 Å [O(31) · · · C(12) at $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$] and of two ring atoms is 3·39 Å [C(2) · · · C(5) at $\bar{x}, \bar{y}, \bar{z}$].

The molecular structure corresponds to that postulated,[1] but shows some unusual distortions from the ideal. The molecule is in a *cis*-configuration and the Fe(CO)$_2$Co bridging system is non-planar (see Table 4). The angle between the two Fe(CO)Co planes (148·0°) is intermediate between that (127°) in $Co_2(CO)_8$ [5] and that (164°) in *cis*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$.[4] For comparison Table 5 gives the details for the bridge systems in related compounds. The Fe · · · Co distance of 2·552 Å is in accord with the metal–metal distances given in Table 5.

The indenyl ring is planar within experimental error (see Table 4). The distance of the iron atom to the centroid

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue.

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

of the C_5 ring is 1·76 Å and the angle between the direction of this contact and the Fe–C(21) bond is 127·7°.

TABLE 3

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

(*a*) Distances

	Co · · · Fe	2·552(2)	
Co–C(31)	1·960(13)	Fe–C(31)	1·916(13)
Co–C(32)	2·054(12)	Fe–C(32)	1·838(12)
C(31)–O(31)	1·186(16)	C(32)–O(32)	1·167(14)
Co–C(11)	1·774(14)	C(11)–O(11)	1·163(18)
Co–C(12)	1·830(13)	C(12)–O(12)	1·108(16)
Co–C(13)	1·823(14)	C(13)–O(13)	1·112(16)
Fe–C(21)	1·771(14)	C(21)–O(21)	1·129(16)
Fe–C(1)	2·074(14)	C(5)–C(1)	1·436(18)
Fe–C(2)	2·080(14)	C(1)–C(2)	1·406(20)
Fe–C(3)	2·125(16)	C(2)–C(3)	1·448(18)
Fe–C(4)	2·222(13)	C(3)–C(4)	1·418(19)
Fe–C(5)	2·184(13)	C(4)–C(5)	1·410(17)
C(5)–C(6)	1·425(18)	C(4)–C(9)	1·424(19)
C(6)–C(7)	1·363(22)	C(9)–C(8)	1·359(23)
C(7)–C(8)	1·417(25)		

(*b*) Angles

C(31)–Co–C(32)	89·0(5)	C(31)–Fe–C(32)	97·1(6)
Fe–C(31)–Co	82·4(5)	Fe–C(32)–Co	81·8(4)
Fe–C(31)–O(31)	138·8(11)	Fe–C(32)–O(32)	148·3(11)
Co–C(31)–O(31)	138·8(11)	Co–C(32)–O(32)	129·9(10)
C(31)–Co–C(11)	105·6(7)	C(5)–C(1)–C(2)	108·4(12)
C(31)–Co–C(13)	143·5(7)	C(1)–C(2)–C(3)	107·7(11)
C(11)–Co–C(13)	110·3(7)	C(2)–C(3)–C(4)	107·1(11)
C(32)–Co–C(12)	167·5(6)	C(3)–C(4)–C(5)	109·1(11)
C(32)–Co–C(11)	90·9(6)	C(4)–C(5)–C(1)	107·5(11)
C(32)–Co–C(13)	84·0(5)	C(3)–C(4)–C(9)	130·7(13)
C(12)–Co–C(31)	85·7(5)	C(1)–C(5)–C(6)	131·3(12)
C(12)–Co–C(11)	101·5(6)	C(9)–C(4)–C(5)	120·3(9)
C(12)–Co–C(13)	93·5(6)	C(4)–C(5)–C(6)	121·2(12)
Co–C(11)–O(11)	177·0(13)	C(5)–C(6)–C(7)	116·8(12)
Co–C(12)–O(12)	175·8(14)	C(6)–C(7)–C(8)	122·1(14)
Co–C(13)–O(13)	177·5(13)	C(7)–C(8)–C(9)	122·2(14)
Fe–C(21)–O(21)	176·8(14)	C(8)–C(9)–C(4)	117·3(13)
Fe–Co–C(11)	117·1(4)	Co–Fe–C(21)	108·5(5)
Fe–Co–C(12)	124·1(4)	C(31)–Fe–C(21)	87·8(7)
Fe–Co–C(13)	107·0(4)	C(32)–Fe–C(21)	92·1(6)

The most surprising distortion in the structure is seen in the metal to bridge-carbon distances. It might be expected that two Fe–C_b distances (where C_b = bridge carbon) would be the same, as would the two Co–C_b distances. This type of arrangement has been observed in the structure of $(\pi\text{-}C_7H_8)Co_2(CO)_6$,[8] in which the environments of the two cobalt atoms are different. However, in the present structure the two Fe–C_b distances are not equivalent nor are the two Co–C_b distances. The largest distortion involves the bridge atom C(32). The Fe–C(32) distance (1·84 Å) is intermediate between that (1·91—1·92 Å) for Fe–C_b in related compounds (Table 5) and that (*ca.* 1·75 Å) for iron to terminal-carbonyl carbon.[2-4] As the Fe–C(32) distance is shortened so the Co–C(32) distance (2·04 Å) is lengthened, when compared with the Co–C_b distances observed in related compounds (Table 5). The shortening of the Fe–C(32) distance is accompanied by an opening of the Fe–C(32)–O(32) angle which is tending towards the linear arrangement of a terminal carbonyl group. The planar environment about the carbon atom, C(32), is maintained by an equivalent closure of the Co–C(32)–O(32) angle. From these observations it would seem that this carbonyl group, C(32)–O(32), has both the characteristics of a terminal and of a bridging carbonyl group with the latter probably being predominant. The distances and angles involving the other bridge carbon atom, C(31), are comparable with the values given in Table 5. The Co–C(31) distance (1·96 Å) is longer than that (1·91—1·93 Å) in $Co_2(CO)_8$ [5] and in $[(\pi\text{-diene})Co(CO)_2]_2$,[9,10] but shorter than that (1·987 Å) of the $Co(CO)_3$ moiety in $(\pi\text{-}C_7H_8)Co_2(CO)_6$.[8]

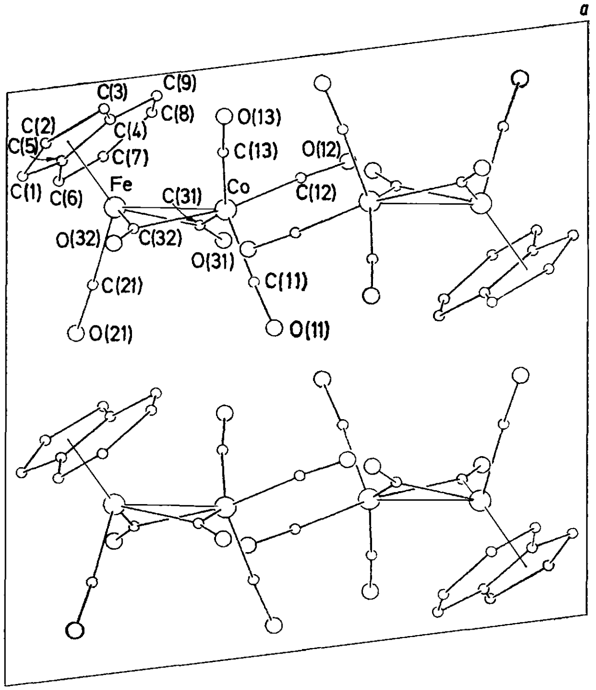

FIGURE 1 The packing of the molecules in the crystal and the labelling of the atoms

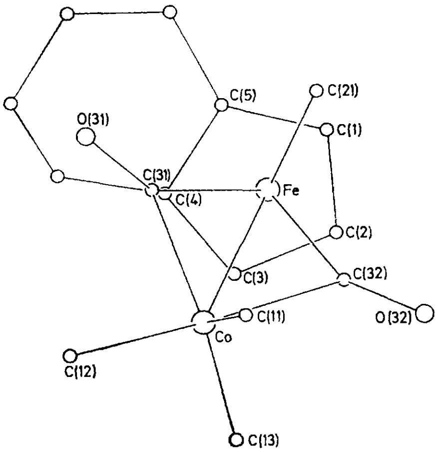

FIGURE 2 The bridging system of the molecule seen projected on the plane of the C_5 ring

Although the arrangement of the carbonyl-carbon atoms bonded to the iron atom, when projected on the place of the C_5 ring, is similar to the corresponding

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

[9] F. S. Stephens, *J. Chem. Soc.* (*A*), 1970, 2745.

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

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: Co, Fe, C(31), O(31) [Co 0·004, Fe 0·004, C(31) −0·016, O(31) 0·009]	−0·1261	0·2261	0·9659	2·3189
Plane 2: Co, Fe, C(32), O(32) [Co −0·001, Fe −0·002, C(32) 0·008, O(32) −0·005]	0·1201	−0·2676	0·9560	2·3000
Plane 3: C(1)—(9) [C(1) −0·01, C(2) −0·04, C(3) 0·04, C(4) 0·01, C(5) <0·01, C(6) 0·03, C(7) 0·01, C(8) 0·04, C(9) 0·01]	0·6071	0·1991	0·7693	1·6862
Plane 4: Co, Fe, C(11) [C(21) 0·48, X * −0·27]	0·4349	−0·8793	0·1942	0·4636
Plane 5: Fe, C(21), X * [Co 0·22, C(11) −0·12]	0·5198	−0·8517	−0·0670	0·0462
Plane 6: C(11), C(12), C(32) [Co 0·03]	0·1957	0·8750	−0·4427	1·7215
Plane 7: C(13), C(12), C(32) [Co 0·21]	0·4369	0·5309	0·7261	4·7388
Plane 8: C(31), C(12), C(32) [Co 0·20]	0·3594	0·1711	0·9174	4·0652

* X is the centroid of the C_5 ring.

TABLE 5

Details of the bridging systems in compounds related to $(\pi\text{-}C_9H_7)FeCo(CO)_6$

	Angle between the two MC_bM planes (°)	M · · · M/Å	$M\text{–}C_b$/Å	$C_b\text{–}M\text{–}C_b$ (°)	$M\text{–}C_b\text{–}M$ (°)
trans-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ [a]	180	2·534(2)	1·914(4)	97·1(4)	82·9(2)
cis-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ [b]	164	2·531(2)	1·917(4)	96·0(2)	82·6(2)
$(OC)_4Fe_2[\pi\text{-}C_5H_4{\cdot}CH(NMe_2)]_2$ [c] (*cis*-configuration)	159·3	2·510(1)	1·925(4)	96·5(2)	81·4(2)
$(C_{10}H_8)_2Fe_4(CO)_{10}{\cdot}C_2H_4Cl_2$ (*cis*-configuration) [d]	154·7	2·508(3)	1·930(4)	95·7(3)	81·0(3)
$(\pi\text{-}C_9H_7)FeCo(CO)_6$ [e]	148·0	2·552(2)	1·92,[f] 1·84(1) 1·96,[g] 2·05(1)	97·1(6) [f] 89·0(5) [f]	82·1(3)
$Co_2(CO)_8$ [h]	127	2·524(2)	1·92(1)	85·0(5)	83·0(5)
$(\pi\text{-}C_7H_8)Co_2(CO)_6$ [i]	135·0	2·531(1)	1·871(3) [j] 1·987(3)	91·1(2) [j] 84·5(1)	82·0(1)
cis-$[(\pi\text{-}C_6H_8)Co(CO)_2]_2$ [k]	175·1	2·559(3)	1·911(10)	95·8(6)	84·1(5)
trans-$[\pi\text{-}C_6H_{10})Co(CO)_2]$ [l]	180	2·549(1)	1·927(3)	97·1(2)	82·9(2)

[a] Ref. 3. [b] Ref. 4. [c] Ref. 11. [d] M. R. Churchill and P. H. Bird, *Inorg. Chem.*, 1969, **8**, 1941. [e] This work. [f] M = Fe. [g] M = Co. [h] Ref. 5. [i] Ref. 8. [j] Involving Co atom bonded to diene. [k] Ref. 10. [l] Ref. 9.

arrangements in *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]$ [3] and for the B-ring in *cis*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]$,[4] some distortions are apparent. The most notable is that involving the bridge atom C(31), which lies almost directly above the ring atom C(4) (see Figure 2); the C(31) · · · C(4) contact is 2·95 Å, and the angle between the direction of this contact and the normal to the plane containing the C_5 ring is 3·6°. Further the centroid of the C_5 ring and the atoms Fe, C(21), Co, C(11) are not coplanar; the dihedral angle between the planes defined by the centroid of the C_5 ring, Fe, C(21) and by Fe, Co, C(11) is 15·9° and the dihedral angles between these planes and the plane of the C_5 ring are 85·4 and 76·8°. These latter values should be compared with those of 89—92° in related compounds.[3,4,9-11]

The environment about the cobalt atom is intermediate between trigonal bipyramidal and square-based pyramidal (Table 6) which is in contrast to the square-based pyramidal environments about the cobalt atoms in $Co_2(CO)_8$ [5] and in $(\pi\text{-}C_7H_8)Co_2(CO)_6$.[8]

TABLE 6

Comparison of trigonal bipyramidal *vs.* square-based pyramidal environment about the Co atom. Planes defined by the ax–eq–ax atoms of a trigonal bipyramid. For the present structure atoms C(12) and C(32) are axial

	Angles between planes (°)				
Eq atoms defining planes	Present structure	$Co_2(CO)_8$ [a]	$(\pi\text{-}C_7H_8)$ $Co_2(CO)_6$ [b]	Trigonal pyramid	Square-based pyramid
C(11) : C(13)	103·1	91·3	94·3	120	90
C(11) : C(31)	100·7	94·4	96·3	120	90
C(13) : C(31)	156·1	174·2	169·3	120	180

[a] Ref. 5. [b] Ref. 8.

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[11] F. S. Stephens, *J. Chem. Soc. (A)*, 1970, 1722.

It is not possible at present to rationalise the distortions in the $Fe(CO)_2Co$ bridging system. Possibly, the position of the indenyl ligand, which may be dictated by packing considerations, creates an asymmetric electron-density distribution about the iron atom and this asymmetry may be, in turn, reflected in the bridge system.

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