Crystal and Molecular Structure of Di-μ-carbonyl-tetracarbonyl-(π-norbornadiene)dicobalt

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The crystal structure of the title compound has been determined by *X*-ray diffraction methods by use of counter data, and refined to *R* 0·049 for 2996 unique reflections by a full-matrix least-squares procedure. The triclinic unit cell, space group $P\bar{1}$, has dimensions: $a = 8{\cdot}272, b = 9{\cdot}262, c = 10{\cdot}183$ Å, $\alpha = 112{\cdot}9, \beta = 101{\cdot}7, \gamma = 82{\cdot}3°$, for $Z = 2$. The molecule approximates to *m* symmetry and the Co · · · Co distance is 2·531(1) Å. The norbornadiene ligand bonds to one cobalt atom *via* the carbon–carbon double bonds. The carbon–carbon double bond distance is 1·373(3) Å. The Co(CO)$_2$Co bridging system is non-planar, the angle between the two Co(CO)Co planes being 135·0°. The Co–C distances in the bridge are not equivalent, those to the cobalt atom bonded to the norbornadiene being 1·871(3) Å and those to the other cobalt atom being 1·987(3) Å.

THE replacement of two carbonyl groups per cobalt atom in $Co_2(CO)_8$ by dienes yields complexes of the type {Co(π-diene)(CO)$_2$}$_2$. These have been shown to exhibit tautomeric behaviour [1] similar to that of the isoelectronic {Fe(π-C_5H_5)(CO)$_2$}$_2$ complex.[2] The crystal structure determinations of *trans*-{Co(π-2,3-dimethylbuta-1,3-diene)(CO)$_2$}$_2$ [3] and *cis*-{Co(π-cyclohexa-1,3-diene)(CO)$_2$}$_2$ [4] have shown both to possess a planar Co(CO)$_2$Co bridging system. This arrangement in the latter structure is somewhat surprising particularly as it is a derivative of $Co_2(CO)_8$ which has a non-planar bridging system [5] and also as a similar non-planar bridging system is present in *cis*-{(π-C_5H_5)Fe(CO)$_2$}$_2$.[6]

In an attempt to investigate the effect of diene substitution in $Co_2(CO)_8$ the structure of (π-norbornadiene)-$Co_2(CO)_6$ has been undertaken. The i.r. spectral studies of this complex indicate that it possesses a non-planar bridging system similar to that found in $Co_2(CO)_8$.[7]

EXPERIMENTAL

Crystal Data.—$C_{13}H_8O_6Co_2$, $M = 378{\cdot}1$, Triclinic, $a = 8{\cdot}272 \pm 0{\cdot}009$, $b = 9{\cdot}262 \pm 0{\cdot}010$, $c = 10{\cdot}183 \pm 0{\cdot}012$ Å, $\alpha = 112{\cdot}9 \pm 0{\cdot}1$, $\beta = 101{\cdot}7 \pm 0{\cdot}1$, $\gamma = 82{\cdot}3 \pm 0{\cdot}1°$, $U = 702{\cdot}4$ Å^3, $D_m = 1{\cdot}78$ (by flotation), $Z = 2$, $D_c = 1{\cdot}787$, $F(000) = 376$, Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) $= 24{\cdot}7$ cm^{-1}, for cell dimensions and intensity measurements. Space group $P\bar{1}$ (C_i^1, No. 2).

The complex crystallises from pentane as brown plates. Unit-cell parameters were obtained from single-crystal precession photographs by use of Mo-K_α radiation. Systematic absences indicated the space group to be $P\bar{1}$ or $P1$, the former being indicated from the three-dimensional Patterson synthesis and subsequently confirmed by the refinement. The intensities were collected on a Philips PAILRED diffractometer by use of monochromatic Mo-K_α radiation. Each reflection in the $h0$—$11l$ layers for $\sin\theta \leqslant 0{\cdot}52$ was recorded. 2996 Unique reflections gave counts for which $\sigma(I)/I < 0{\cdot}5$ [8] and these were used for the structure analysis. The intensities were corrected for Lorentz and polarisation effects, but no correction for absorption or extinction was applied.

The scattering factor curves for all atoms were taken from ref. 9, the values for the cobalt atom 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 three-dimensional Patterson synthesis indicated the space group to be centric and yielded the positions of the cobalt atoms. A Fourier synthesis phased by these atoms gave the positions for all non-hydrogen atoms. Structure factors, calculated with the coordinates for all atoms and an overall thermal parameter of *B* 3·0 Å^2, gave *R* 0·197.

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[1] P. McArdle and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2123.

[2] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1319.

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

[4] F. S. Stephens, preceding paper.

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

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

[7] A. R. Manning, unpublished results.

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

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

Refinement of the structure was carried out by a full-matrix 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 $w = (7{\cdot}0—0{\cdot}1|F_o| + 0{\cdot}01\ |F_o|^2)^{-1}$; 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 were $<0{\cdot}33F_o$ were omitted from the least-squares analysis.

TABLE 1

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

	x/a	y/b	z/c	σ_{rms}(Å)
Co(1)	0·18443(7)	0·32836(6)	−0·25078(6)	0·0006
Co(2)	0·14010(8)	0·15386(7)	−0·11922(7)	0·0007
O(31)	−0·0859(5)	0·1288(5)	−0·3896(4)	0·004
O(32)	0·2001(5)	0·4892(4)	0·0563(4)	0·004
O(11)	−0·0590(6)	0·5703(6)	−0·2992(6)	0·005
O(21)	−0·1742(6)	0·1821(6)	−0·0195(6)	0·005
O(22)	0·3963(9)	0·1571(9)	0·1273(8)	0·008
O(23)	0·2031(8)	−0·1744(5)	−0·2952(6)	0·006
C(31)	0·0238(6)	0·1839(5)	−0·3011(5)	0·005
C(32)	0·1803(5)	0·3836(5)	−0·0537(5)	0·005
C(11)	0·0355(6)	0·4769(6)	−0·2784(6)	0·005
C(21)	−0·0508(7)	0·1773(6)	−0·0552(6)	0·006
C(22)	0·3001(9)	0·1552(8)	0·0301(8)	0·007
C(23)	0·1811(8)	−0·0470(7)	−0·2285(7)	0·007
C(1)	0·3758(7)	0·4044(7)	−0·4034(7)	0·006
C(2)	0·3774(6)	0·4682(6)	−0·2401(6)	0·006
C(3)	0·4498(6)	0·3491(6)	−0·1948(5)	0·005
C(4)	0·4980(6)	0·2131(7)	−0·3261(6)	0·006
C(5)	0·3273(6)	0·1610(6)	−0·4098(5)	0·005
C(6)	0·2534(7)	0·2753(7)	−0·4585(6)	0·006
C(7)	0·5406(8)	0·3037(8)	−0·4133(8)	0·007
H(1)	0·357(10)	0·482(10)	−0·450(9)	0·09
H(2)	0·352(10)	0·583(10)	−0·180(9)	0·09
H(3)	0·483(10)	0·358(10)	−0·097(10)	0·09
H(4)	0·581(11)	0·128(10)	−0·302(9)	0·09
H(5)	0·295(10)	0·046(10)	−0·439(9)	0·09
H(6)	0·158(11)	0·284(10)	−0·523(9)	0·09
H(71)	0·549(11)	0·244(11)	−0·514(10)	0·10
H(72)	0·640(11)	0·356(10)	−0·361(9)	0·09

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(1)	86(1)	78(1)	71(1)	−9(1)	7(1)	32(1)
Co(2)	123(1)	83(1)	98(1)	−5(1)	18(1)	45(1)
O(31)	128(6)	154(6)	116(5)	−55(5)	−21(4)	33(4)
O(32)	157(6)	112(5)	88(4)	−25(4)	21(4)	17(4)
O(11)	198(8)	198(8)	197(7)	60(7)	34(6)	132(7)
O(21)	214(9)	183(8)	208(8)	−5(7)	101(7)	93(7)
O(22)	366(16)	308(14)	255(11)	−18(12)	−131(11)	150(11)
O(23)	376(14)	112(7)	181(8)	41(8)	82(8)	52(6)
C(31)	103(6)	95(6)	93(5)	−14(5)	11(5)	32(5)
C(32)	96(6)	88(5)	87(5)	−9(4)	16(4)	35(4)
C(11)	130(7)	117(7)	106(6)	2(6)	16(5)	59(5)
C(21)	178(9)	98(6)	103(6)	−21(6)	42(6)	35(5)
C(22)	214(12)	150(10)	168(10)	−7(8)	−21(9)	85(8)
C(23)	209(11)	120(8)	141(8)	15(7)	44(7)	75(7)
C(1)	158(9)	154(9)	138(7)	−3(7)	47(6)	89(7)
C(2)	113(7)	105(7)	133(7)	−33(5)	25(5)	37(6)
C(3)	104(6)	109(6)	89(5)	−23(5)	7(5)	25(5)
C(4)	111(7)	135(7)	106(6)	3(6)	34(5)	42(6)
C(5)	133(7)	111(7)	90(6)	−7(6)	37(5)	14(5)
C(6)	143(8)	169(9)	85(6)	−17(7)	18(5)	55(6)
C(7)	146(9)	176(10)	159(9)	−20(8)	63(7)	70(8)

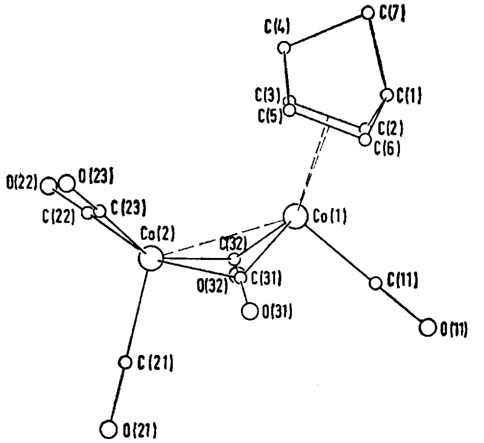
For all hydrogen atoms $B = 5{\cdot}10$ Å^2.

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

After three cycles of refinement, in which positional and individual isotropic thermal parameters for each atom were varied, a difference-Fourier synthesis was calculated. This showed no unusual features and gave the positions of all the hydrogen atoms. They were included in subsequent calculations with a thermal parameter of $B = 5{\cdot}0$ Å^2.

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. After two cycles the positional parameters of the hydrogen atoms were included in the refinement. The refinement was terminated when the maximum shift in a parameter for the heavier atoms was $<0{\cdot}1\sigma$ and for the hydrogen atoms was $<0{\cdot}3\sigma$. 2980 Reflections were included in the final cycle of refinement. The final value for R, based on 2996 reflections, was 0·049 and for R' [$= \Sigma w\Delta^2/\Sigma w|F_o|^2$] was 0·004.

The final atomic co-ordinates and thermal parameters are given together with their estimated deviations in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20446 [18 pp., 1 microfiche].†



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

DISCUSSION

The Figure shows a perspective drawing of the complex and the labelling of the atoms. The bond distances and angles together with their estimated standard deviations derived directly from the least-squares inverse matrix are given in Table 3. There is possible error in the values of the bond distances, other than those involving hydrogen atoms, owing to the uncertainty in the unit cell parameters which is greater than the error from the structure refinement; a better estimate of the absolute accuracy would be given by raising the σ values quoted in Table 3 to 0·004 for Co · · · Co, 0·006 for Co–C, and 0·010 Å for C–O and C–C. The mean C–H distance (0·99 Å) is appreciably shorter than the accepted value [10] but this is not surprising as the hydrogen positions obtained are those of electron-density maxima rather than nuclei. This effect has been observed in other structure determinations.[3,11]

The molecule has m (C_s) symmetry and closely resembles the structure of $Co_2(CO)_8$.[5] The Co · · · Co

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[10] *Chem. Soc. Special Publ.*, No. 11, 1959; No. 18, 1965.

[11] F. S. Stephens, *J. Chem. Soc.* (*A*), 1969, 1723 and references therein.

TABLE 3

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

(*a*) Distances

Co(1) · · · Co(2)	2·531(1)		
C(1)–C(31)	1·867(4)	Co(2)–C(31)	1·993(5)
Co(1)–C(32)	1·875(4)	Co(2)–C(32)	1·980(4)
C(31)–O(31)	1·153(5)	C(32)–O(32)	1·164(5)
Co(1)–C(11)	1·788(5)	C(11)–O(11)	1·140(6)
Co(2)–C(21)	1·790(5)	C(21)–O(21)	1·141(7)
Co(2)–C(22)	1·809(6)	C(22)–O(22)	1·133(8)
Co(2)–C(23)	1·818(6)	C(23)–O(23)	1·120(7)
Co(1)–C(2)	2·147(5)	Co(1)–C(6)	2·157(5)
Co(1)–C(3)	2·168(5)	Co(1)–C(5)	2·180(5)
C(1)–C(2)	1·531(8)	C(1)–C(6)	1·523(8)
C(2)–C(3)	1·376(7)	C(5)–C(6)	1·370(8)
C(3)–C(4)	1·518(7)	C(4)–C(5)	1·526(7)
C(1)–C(7)	1·543(9)	C(4)–C(7)	1·550(8)
C(1)–H(1)	0·98(9)	C(4)–H(4)	1·05(9)
C(2)–H(2)	1·01(9)	C(6)–H(6)	0·93(9)
C(3)–H(3)	0·95(9)	C(5)–H(5)	1·05(9)
C(7)–H(71)	0·97(9)	C(7)–H(72)	0·96(9)

(*b*) Angles

C(31)–Co(1)–C(32)	91·1(2)	C(31)–Co(2)–C(32)	84·5(1)
Co(1)–C(31)–Co(2)	81·9(2)	Co(1)–C(32)–Co(2)	82·0(2)
Co(1)–C(31)–O(31)	142·0(4)	Co(1)–C(32)–O(32)	141·3(4)
Co(2)–C(31)–O(31)	136·1(4)	Co(2)–C(32)–O(32)	136·1(4)
Co(2)–Co(1)–C(11)	123·2(2)	Co(1)–Co(2)–C(21)	120·3(2)
C(31)–Co(1)–C(11)	92·7(2)	Co(1)–Co(2)–C(22)	116·2(2)
C(32)–Co(1)–C(11)	97·4(2)	Co(1)–Co(2)–C(23)	109·5(2)
C(31)–Co(2)–C(21)	91·9(2)	C(32)–Co(2)–C(21)	99·1(2)
C(31)–Co(2)–C(22)	161·5(3)	C(32)–Co(2)–C(22)	85·9(2)
C(31)–Co(2)–C(23)	87·1(2)	C(32)–Co(2)–C(23)	151·5(2)
C(21)–Co(2)–C(22)	105·3(2)	Co(1)–C(11)–O(11)	178·5(5)
C(21)–Co(2)–C(23)	108·4(3)	Co(2)–C(21)–O(21)	176·6(5)
C(22)–Co(2)–C(23)	93·8(3)	Co(2)–C(22)–O(22)	177·2(8)
C(1)–C(7)–C(4)	93·4(4)	Co(2)–C(23)–O(23)	178·4(6)
C(6)–C(1)–C(2)	102·1(4)	C(5)–C(4)–C(3)	100·3(4)
C(6)–C(1)–C(7)	100·4(5)	C(5)–C(4)–C(7)	100·0(5)
C(2)–C(1)–C(7)	100·4(5)	C(3)–C(4)–C(7)	100·4(5)
C(1)–C(2)–C(3)	105·8(5)	C(1)–C(6)–C(5)	106·3(5)
C(2)–C(3)–C(4)	107·5(5)	C(4)–C(5)–C(6)	107·3(5)
H(1)–C(1)–C(2)	117(5)	H(4)–C(4)–C(3)	114(5)
H(1)–C(1)–C(6)	117(5)	H(4)–C(4)–C(5)	117(5)
H(1)–C(1)–C(7)	118(5)	H(4)–C(4)–C(7)	122(5)
H(2)–C(2)–C(1)	124(5)	H(6)–C(6)–C(1)	119(5)
H(2)–C(2)–C(3)	129(5)	H(6)–C(6)–C(5)	134(5)
H(3)–C(3)–C(2)	126(5)	H(5)–C(5)–C(6)	130(5)
H(3)–C(3)–C(4)	126(5)	H(5)–C(5)–C(4)	121(5)
H(71)–C(7)–C(1)	109(5)	H(72)–C(7)–C(1)	118(5)
H(71)–C(7)–C(4)	117(5)	H(72)–C(7)–C(4)	107(5)
H(71)–C(7)–H(72)	112(7)		

distance (2·531) is slightly longer than that (2·524) in $\mathrm{Co_2(CO)_8}$[5] but significantly shorter than that (2·549) in $[\mathrm{Co}(\pi\text{-2,3-dimethylbuta-1,3-diene})(\mathrm{CO})_2]_2$[3] and (2·559 Å) $[\mathrm{Co}(\pi\text{-cyclohexa-1,3-diene})(\mathrm{CO})_2]_2$.[4] The $\mathrm{Co(CO)_2Co}$ bridging system is non-planar (see Table 4) and the angle between the two Co(CO)Co planes of 135·0° is greater than that (127°) found in $\mathrm{Co_2(CO)_8}$.[5] The Co–C bridge distances are not equivalent [means 1·871(3) and 1·987(3) Å for the bridge carbons to Co(1) and to Co(2)], and should be compared with that (*ca.* 1·92 Å) found in $\mathrm{Co_2(CO)_8}$[5] and in $\{\mathrm{Co(diene)(CO)_2}\}_2$ complexes.[3,4] This asymmetry of the bridge is also reflected in the external angles at the bridge carbon atoms, mean values Co(1)–C–O 141·6(3), and Co(2)–C–O 136·3(3)°; however, the internal angle, mean 81·9(1)°, is in good agreement with that (*ca.* 83°) found in $\mathrm{Co_2(CO)_8}$[5] and other similarly bridged structures.[3,4] The angles subtended by the bridge carbon atoms at the cobalt atoms are not equivalent; that at Co(2) of 84·5° is in good agreement with that of 85° observed in $\mathrm{Co_2(CO)_8}$[5] whereas, that at Co(1) of 91·1° tends towards the values of 97·1 and of 95·8° observed in the *trans*-[3] and in the *cis*-bis-diene[4] complexes respectively.

Each cobalt atom is in a square-based pyramidal environment formed about the Co(2) atom by the bridged carbon atoms and the three terminal carbonyl carbon atoms and about the Co(1) atom by the bridge carbon atoms, the terminal carbonyl carbon atom, and the mid-points of the double bonds of the norbornadiene ligand (see Table 4). The cobalt atom in each case lies *ca.* 0·37 Å from the basal plane towards the apical atom and the angle between the two basal planes is 99·8°. This arrangement closely resembles that in $\mathrm{Co_2(CO)_8}$ in which the corresponding values are 0·32 Å and 100°, respectively.* The axial Co–CO distances are equivalent, mean 1·789(4) Å, and are significantly shorter than the equatorial Co–CO distances, mean 1·813(5) Å, which is in accord with the trend shown in $\mathrm{Co_2(CO)_8}$.[5]

TABLE 4

Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where the orthogonalised co-ordinates X', Y', Z' are derived with respect to orthogonal axes a', b', c where b' lies in the bc plane. The deviations (Å) of the relevant atoms are given in square brackets

	l	*m*	*n*	*p*
Plane (1): Co(1), Co(2), C(31), O(31)	0·6188	−0·6846	−0·3884	0·5091
[Co(1), 0·002, Co(2) 0·002, C(31) −0·009, O(31) 0·005]				
Plane (2): Co(1), Co(2), C(32), O(32)	0·9838	−0·1729	0·0480	0·7673
[Co(1) 0·005, Co(2) 0·005, C(32) −0·022, O(32) 0·012]				
Plane (3): C(31), C(32), midpoints C(2)–C(3) and C(5)–C(6)	−0·5583	0·7148	−0·4211	2·5697
[C(31) 0·04, C(32) −0·04, midpoint C(2)–C(3) 0·05, midpoint C(5)–C(6) −0·06, Co(1) 0·37]				
Plane (4): C(31), C(32), C(22), C(23)	0·8029	0·0388	−0·5948	2·5420
[C(31) −0·09, C(32) 0·09, C(22) −0·08, C(23) 0·09, Co(2) −0·38]				

The norbornadiene ligand is bonded to Co(1) *via* the carbon–carbon double bonds. The carbon atoms of the double bonds nearest the other cobalt atom, namely C(3) and C(5), are possibly significantly further from the cobalt atom Co(1), mean Co–C 2·174(4) Å, than are the carbon atoms at the other ends of the double bonds, mean Co–C 2·152(4) Å. The distance of the cobalt atom to the mid-points of the double bonds is 2·05 Å. Although the molecule as a whole has *m* symmetry the norbornadiene ligand, has within experimental error, *mm* (C_{2v}) symmetry. The bond lengths and angles averaged according to *mm* symmetry are given in Table 5. The carbon–carbon double bonds are, as expected,

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* These values were calculated using the atomic parameters given in ref. 5.

lengthened from the value of 1·333 Å in the free ligand[12] to 1·373 Å on co-ordination. The dimensions within the norbornadiene ligand agree well with those found in other similar norbornadiene containing complexes such as $(C_7H_9)PdCl_2$[13] and $\{(C_7H_9)Co(CO)_2\}_2SnR_2$ (R = Cl or Ph).[14]

TABLE 5

Bond lengths (Å) and angles (°) for the norbornadiene ligand averaged according to *mm* (C_{2v}) symmetry with estimated standard deviations in parentheses

(*a*) Distances

C(1)–C(2)	1·525(4)	C(1)–C(7)	1·547(3)
C(2)–C(3)	1·373(3)		

(*b*) Angles

C(2)–C(1)–C(6)	106·7(3)	C(1)–C(2)–C(3)	100·3(3)
C(2)–C(1)–C(7)	101·2(3)	C(1)–C(7)–C(4)	93·4(4)

The molecules are held in the crystal by van der Waals forces. The closest approach of two oxygen atoms is 3·00 Å [O(31) $\cdots$ O(31) at $\bar{x}, \bar{y}, -1-z$], and of an oxygen and carbon atom is 3·24 Å [O(32) $\cdots$ C(2) at $1-x, 1-y, \bar{z}$]. All carbon–carbon atom contacts are >3·75 Å.

The results of the structure analysis indicate that the replacement of two carbonyl groups on a given cobalt atom by a weaker π-acceptor ligand, such as norbornadiene, induces the carbonyl bridge to accept more π-electrons. This has three main effects on the $Co(CO)_2Co$ bridge system; first, the bridge becomes asymmetric, the distances from the bridge carbon atoms to the substituted Co atom are shortened and those to the unsubstituted Co atom are lengthened; secondly, the angle subtended by the bridge carbon atoms at the substituted Co atom increases; and thirdly, the angle between the two Co(CO)Co plane increases, *i.e.* the bridge-system tends towards planarity. It might therefore be suggested that the planarity in the $Co(CO)_2Co$ bridge in *cis*-$\{(\pi$-cyclohexa-1,3-diene$)Co(CO)_2\}_2$[4] results essentially from these effects. Since in this structure each cobalt atom has two carbonyl groups replaced by a diene ligand then π-electrons are accepted by the bridge carbonyls from both cobalt–diene moieties. Therefore no asymmetry in the bridge bond lengths can be envisaged, as is the case in the present structure, and hence the increased electron density on the bridge carbonyl groups tends to cause repulsion of the groups. The net effect is to create a bridging system with the carbonyl groups further apart, the limit being a planar arrangement. This is supported by the observed bridge-carbon–bridge-carbon distances which increase from 2·60 Å in $Co_2(CO)_8$,[5] to 2·67 Å in the present structure, and to 2·84 Å in *cis*-$\{(\pi$-cyclohexa-1,3-diene$)Co(CO)_2\}_2$,[4] this last distance being comparable with that of 2·89 Å in *trans*-$\{(\pi$-2,3-dimethylbuta-1,3-diene$)Co(CO)_2\}_2$[3] which has a strictly planar bridging system.

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