Crystal and Molecular Structure of Di-μ-carbonyl-carbonyl[carbonyl-(2,3-dimethylbuta-1,3-diene)cobalt]-(π-methylcyclopentadienyl)iron

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The crystal structure of the title compound has been determined by *X*-ray diffraction methods by Patterson and Fourier methods from counter data, and refined by least squares to *R* 0·072 for 3066 unique reflections. The monoclinic unit cell, space group *C*2/*c*, has dimensions *a* = 17·700 ± 0·016, *b* = 7·404 ± 0·014, *c* = 23·861 ± 0·040 Å, β = 95·5 ± 0·1°, for *Z* = 8. The dimer molecule has an almost planar $Fe(CO)_2Co$ bridging system; Fe ··· Co is 2·546(1) Å. The metal–bridge-carbon distances are not equivalent [Fe–C 1·897(6) 1·916(6), Co–C 1·966(7) and 1·933(6) Å]. The butadiene is in a *cis*-configuration and is planar. The C–C distances of the butadiene are equal, mean 1·42(1) Å. The cyclopentadienyl ligand is also planar with equal C–C distances round the ring, mean 1·41(1) Å.

It has been established by i.r. spectroscopy that many compounds of the type $[ML(CO)_2]_2$ (M = Fe or Co, L = butadiene or cyclopentadienyl) exist in solution as three tautomeric isomers, two of which have the metal atoms bridged by carbonyl groups, corresponding to the *cis*- and *trans*-isomers with respect to the terminal ligands.[1] The third tautomer is non-bridged. In the solid state, structural evidence shows a predominance of the bridged species, in which the *trans*-isomers have a planar $M{-}(CO)_2{-}M$ bridge arrangement,[2,3] whereas the *cis*-structures deviate from this planarity, more so for M = Fe[4] than for M = Co.[5] The crystal structure analysis of the title compound was undertaken to observe the effect of $[M^1L^1M^2L^2(CO)_4]$ type compounds

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[1] O. S. Mills, *Acta Cryst.*, 1958, **11**, 62; R. B. King and M. B. Bisnett, *J. Organometallic Chem.*, 1967, **8**, 287; A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1319; P. McArdle and A. R. Manning, *ibid.*, 1969, 1498; 1970, 2119, 2123.

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

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

[4] R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc.* (*A*), 1970, 3068; F. S. Stephens, *ibid.*, p. 1722.

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

on the system where M^1 and M^2 are atoms of different metals.

EXPERIMENTAL

Crystal Data.—$C_{16}H_{17}CoFeO_4$, $M = 388{\cdot}1$, Monoclinic, $a = 17{\cdot}700 \pm 0{\cdot}016$, $b = 7{\cdot}404 \pm 0{\cdot}014$, $c = 23{\cdot}861 \pm 0{\cdot}040$ Å, $\beta = 95{\cdot}5 \pm 0{\cdot}1°$, $U = 3112{\cdot}6$ Å^3, $D_m = 1{\cdot}66$ (by flotation), $Z = 8$, $D_c = 1{\cdot}656$, $F(000) = 1584$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, $\mu(\text{Mo-}K_\alpha) = 21{\cdot}6$ cm^{-1} for cell parameters and intensity measurements. Space group Cc (C_s^4, No. 9) or $C2/c$ (C_{2h}^6, No. 15) from systematic absences: hkl for $h + k = 2n + 1$, $h0l$ for $l = 2n + 1$; shown to be the latter by statistical analysis of intensity data [$N(z)$ test],[6] and confirmed by subsequent successful refinement.

The complex was prepared by the substitution of $(MeC_5H_4)FeCo(CO)_6$ with 2,3-dimethylbuta-1,3-diene in heptane solution.[7] The complex crystallises from pentane as brown plates lying on the (100) face with pinacoids {010} and {001}. Unit-cell parameters were determined from single-crystal precession photographs. Intensities were collected on a Philips PAILRED diffractometer for the layers $h0$—$35l$ for $\sin\theta \leqslant 0{\cdot}55$. 3066 Reflections gave counts having $\sigma(I)/I < 0{\cdot}5$ [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.

Scattering factor curves for all atoms were taken from ref. 9, the values for the cobalt and iron atoms being corrected for the effects of anomalous dispersion. Calculations were carried out on the Atlas Computer at S.R.C. Chilton and the PDP 10 Computer of the University of Essex. The *X*-Ray system package of programmes was used for the former computer [10] and for the latter, 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 except those of the butadiene ligand. The complete solution of the structure was obtained from a further Fourier synthesis, 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 $w = (200{\cdot}0 - 2{\cdot}0|F_o| + 0{\cdot}0125|F_o|^2)^{-1}$. For this latter weighting scheme mean values of $w\Delta^2$ for ranges of increasing $|F_o|$ were almost constant. Reflections having $|F_c| < \frac{1}{3}|F_o|$ were omitted from the least-squares analysis.

Initial refinement was by a full-matrix procedure in which positional and individual isotropic thermal parameters for each atom were refined. A difference-Fourier synthesis, calculated when the maximum shift in any parameter was of the order of its σ, showed no unusual features and gave the positions of all the hydrogen atoms. These were included in subsequent calculations with a thermal parameter of B 6·0 Å^2.

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Owing to the large number of parameters (200) being refined it was necessary to refine them in block matrices. The four matrices contained the overall scale and thermal parameter, the metal atoms and carbonyl groups, the cyclopentadienyl ligand, and the butadiene ligand. After several cycles, the positional parameters of the hydrogen atoms were included in appropriate matrices. The refinement was terminated when the maximum shift in a parameter was $<0{\cdot}16\sigma$. 3010 Reflections were included in the final cycle of refinement. The final value for R, based on 3066 reflections, was 0·072, and for R' [$= \Sigma w\Delta^2/\Sigma w|F_o|^2$] was 0·0060.

TABLE 1

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

	x/a	y/b	z/c	σ(r.m.s.)/Å
Fe	0·47817(5)	0·58755(12)	0·36133(4)	0·0009
Co	0·35645(5)	0·64210(12)	0·40764(4)	0·0009
O(T1)	0·3998(4)	0·9088(11)	0·4941(3)	0·007
O(T2)	0·4205(3)	0·3247(8)	0·2780(2)	0·006
O(B1)	0·3792(3)	0·8637(8)	0·3095(2)	0·006
O(B2)	0·4489(3)	0·3391(8)	0·4506(2)	0·006
C(T1)	0·3839(4)	0·8056(11)	0·4601(3)	0·008
C(T2)	0·4425(4)	0·4299(9)	0·3111(3)	0·006
C(B1)	0·3978(4)	0·7524(9)	0·3421(3)	0·007
C(B2)	0·4354(3)	0·4626(9)	0·4211(3)	0·006
C(1)	0·5551(4)	0·8175(9)	0·3643(3)	0·007
C(2)	0·5622(4)	0·7225(11)	0·4159(3)	0·008
C(3)	0·5851(4)	0·5442(11)	0·4051(3)	0·008
C(4)	0·5895(3)	0·5246(11)	0·3479(3)	0·007
C(5)	0·5699(4)	0·6955(11)	0·3213(3)	0·008
C(6)	0·5382(7)	1·0161(14)	0·3564(6)	0·013
C(7)	0·2868(5)	0·4901(15)	0·4573(4)	0·010
C(8)	0·2730(4)	0·4421(10)	0·4004(4)	0·008
C(9)	0·2550(4)	0·5819(10)	0·3603(3)	0·007
C(10)	0·2514(4)	0·7611(12)	0·3819(5)	0·009
C(81)	0·2835(5)	0·2487(13)	0·3816(5)	0·010
C(91)	0·2435(6)	0·5493(16)	0·2989(4)	0·011
H(2)	0·556(7)	0·775(18)	0·448(5)	0·13
H(3)	0·598(7)	0·460(18)	0·433(5)	0·13
H(4)	0·602(7)	0·416(17)	0·326(5)	0·12
H(5)	0·574(7)	0·732(17)	0·282(5)	0·12
H(61)	0·578(7)	0·065(19)	0·360(6)	0·14
H(62)	0·509(7)	0·044(18)	0·389(5)	0·13
H(63)	0·526(8)	0·030(19)	0·319(6)	0·14
H(71)	0·262(7)	0·576(19)	0·473(5)	0·13
H(72)	0·302(7)	0·396(18)	0·480(5)	0·13
H(101)	0·245(7)	0·848(18)	0·356(5)	0·13
H(102)	0·228(7)	0·790(18)	0·422(5)	0·13
H(81)	0·237(8)	0·194(18)	0·373(5)	0·13
H(82)	0·299(8)	0·205(20)	0·405(6)	0·15
H(83)	0·303(7)	0·221(18)	0·340(5)	0·13
H(91)	0·272(8)	0·472(20)	0·286(6)	0·14
H(92)	0·254(8)	0·636(19)	0·276(6)	0·14
H(93)	0·199(8)	0·500(19)	0·287(5)	0·13

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 20956 (18 pp., 1 microfiche).*

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

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

[7] A. R. Manning, *J.C.S. Dalton*, 1972, 821.

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

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

[10] J. M. Stewart, F. A. Kundall, and J. C. Baldwin, *X*-Ray System of Programs, Computer Science Centre Report TR 192, 1970, University of Maryland.

DISCUSSION

The Figure shows a perspective drawing[11] of the molecule and the labelling of the atoms. The bond distances and angles, together with their estimated standard deviations derived directly from the least-squares inverse matrices are given in Table 3. In general the C–H distances are appreciably shorter than accepted values[12] but this is realistic since the hydrogen positions obtained are those of electron-density maxima rather than nuclei.

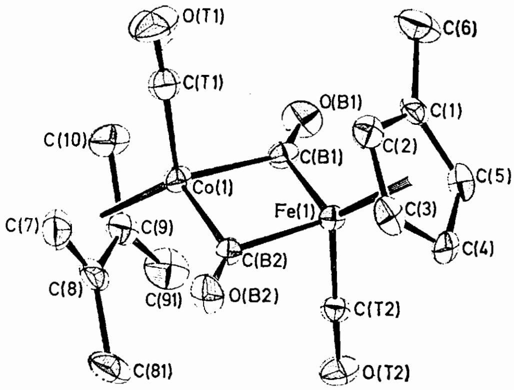
TABLE 2

Thermal parameters ($\times 10^4$),* with estimated standard deviations in parentheses

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Fe	13·3(2)	84·5(14)	8·8(1)	3·9(5)	−0·8(1)	0·8(4)
Co	13·8(2)	108·8(16)	12·3(2)	3·4(5)	−0·1(1)	−8·5(4)
O(T1)	50(3)	261(17)	24(2)	−1(6)	−2(2)	−45(4)
O(T2)	37(2)	155(12)	16(1)	−3(4)	1(1)	−17(3)
O(B1)	29(2)	147(11)	21(1)	22(4)	−3(1)	22(3)
O(B2)	32(2)	166(11)	18(1)	13(4)	5(1)	30(3)
C(T1)	20(2)	147(15)	18(2)	0(5)	2(1)	−6(4)
C(T2)	19(2)	90(11)	12(1)	0(4)	1(1)	0(3)
C(B1)	18(2)	106(11)	12(1)	9(4)	−1(1)	−3(3)
C(B2)	17(2)	103(11)	10(1)	−1(4)	2(1)	−1(3)
C(1)	16(2)	108(13)	18(1)	−15(4)	2(1)	−1(3)
C(2)	19(2)	176(16)	13(1)	−8(5)	−1(1)	−8(4)
C(3)	12(2)	177(17)	19(2)	5(4)	−3(1)	21(4)
C(4)	8(2)	162(15)	19(2)	8(4)	2(1)	−8(4)
C(5)	17(2)	191(17)	13(1)	−7(5)	2(1)	8(4)
C(6)	38(4)	119(17)	41(3)	−9(6)	1(3)	8(6)
C(7)	26(3)	219(22)	22(2)	−1(6)	9(2)	5(5)
C(8)	16(2)	139(15)	23(2)	−14(4)	4(2)	1(4)
C(9)	14(2)	132(13)	20(2)	1(4)	−1(1)	0(4)
C(10)	14(2)	158(17)	32(2)	21(5)	−4(2)	−14(5)
C(81)	27(3)	135(16)	31(3)	−23(6)	−3(2)	−2(5)
C(91)	30(3)	254(26)	22(2)	−6(7)	−9(2)	−4(6)

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

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



A perspective drawing of the molecule and the labelling of the atoms. Thermal ellipsoids are scaled to include 35% probability

The molecule consists of the iron and cobalt atoms bridged by two carbonyl groups with the cyclopentadienyl ligand π-bonded to the iron atom and the butadiene ligand π-bonded to the cobalt atom. The arrangement of the ligands is such to produce a *trans*-configuration of the π-bonded fragments, similar to that found in the isoelectronic complexes *trans*-$[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$ (ref. 3) and *trans*-$[Co(\pi\text{-}C_6H_{10})(CO)_2]_2$ (ref. 2).

TABLE 3

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

(*a*) Distances

Fe···Co	2·5460(10)		
Fe–C(B1)	1·897(6)	Co–C(B1)	1·966(7)
Fe–C(B2)	1·916(6)	Co–C(B2)	1·933(6)
Fe–C(T2)	1·748(7)	Co–C(T1)	1·776(8)
Fe–Cp *	1·747(7)	Co–Bd *	1·674(7)
C(B1)–O(B1)	1·160(8)	C(B2)–O(B2)	1·165(8)
C(T2)–O(T2)	1·150(8)	C(T1)–O(T1)	1·129(9)
Fe–C(1)	2·177(6)	Co–C(7)	2·115(9)
Fe–C(2)	2·129(7)	Co–C(8)	2·086(7)
Fe–C(3)	2·096(6)	Co–C(9)	2·076(7)
Fe–C(4)	2·079(6)	Co–C(10)	2·096(7)
Fe–C(5)	2·118(7)	C(7)–C(8)	1·403(13)
C(1)–C(2)	1·412(10)	C(8)–C(9)	1·424(11)
C(2)–C(3)	1·412(11)	C(9)–C(10)	1·428(11)
C(3)–C(4)	1·382(11)	C(8)–C(81)	1·517(13)
C(4)–C(5)	1·444(11)	C(9)–C(91)	1·480(13)
C(5)–C(1)	1·412(10)	C(7)–H(71)	0·87(13)
C(1)–C(6)	1·510(12)	C(7)–H(72)	0·91(13)
C(2)–H(2)	0·87(12)	C(10)–H(101)	0·90(13)
C(3)–H(3)	0·92(13)	C(10)–H(102)	1·10(12)
C(4)–H(4)	1·00(12)	C(91)–H(91)	0·84(14)
C(5)–H(5)	0·98(12)	C(91)–H(92)	0·87(13)
C(6)–H(61)	0·79(13)	C(91)–H(93)	0·89(13)
C(6)–H(62)	1·00(13)	C(81)–H(81)	0·93(13)
C(6)–H(63)	0·89(13)	C(81)–H(82)	0·68(14)
		C(81)–H(83)	1·10(13)

(*b*) Angles

C(B1)–Fe–C(B2)	98·6(3)	C(B1)–Co–C(B2)	95·7(3)
Fe–C(B1)–Co	82·5(3)	Fe–C(B2)–Co	82·8(3)
Fe–C(B1)–O(B1)	141·1(6)	Fe–C(B2)–O(B2)	139·2(5)
Co–C(B1)–O(B1)	136·5(6)	Co–C(B2)–O(B2)	138·0(5)
Fe–C(T2)–O(T2)	178·6(6)	Co–C(T1)–O(T1)	178·3(7)
Cp–Fe–Co *	136·9(4)	Bd–Co–Fe *	137·5(4)
Cp–Fe–C(T2) *	125·1(4)	Bd–Co–C(T1) *	119·4(4)
C(T2)–Fe–Co	98·0(2)	C(T1)–Co–Fe	103·2(2)
C(T2)–Fe–C(B1)	92·9(3)	C(T1)–Co–C(B1)	100·4(3)
C(T2)–Fe–C(B2)	92·6(3)	C(T1)–Co–C(B2)	102·0(3)
C(1)–C(2)–C(3)	108·1(7)	C(7)–C(8)–C(9)	118·3(8)
C(2)–C(3)–C(4)	108·8(7)	C(7)–C(8)–C(81)	120·7(8)
C(3)–C(4)–C(5)	108·0(7)	C(8)–C(9)–C(10)	116·6(8)
C(4)–C(5)–C(1)	107·1(6)	C(8)–C(9)–C(91)	123·2(8)
C(5)–C(1)–C(2)	108·0(7)	C(9)–C(8)–C(81)	120·9(8)
C(5)–C(1)–C(6)	125·5(4)	C(10)–C(9)–C(91)	120·2(8)
C(2)–C(1)–C(6)	126·5(4)	C(8)–C(7)–H(71)	123(9)
C(1)–C(6)–H(61)	106(10)	C(8)–C(7)–H(72)	114(8)
C(1)–C(6)–H(62)	102(8)	C(9)–C(10)–H(101)	115(9)
C(1)–C(6)–H(63)	105(9)	C(9)–C(10)–H(102)	122(7)
C(1)–C(2)–H(2)	122(9)	C(8)–C(81)–H(81)	110(8)
C(3)–C(2)–H(2)	130(9)	C(8)–C(81)–H(82)	105(13)
C(2)–C(3)–H(3)	124(8)	C(8)–C(81)–H(83)	120(7)
C(4)–C(3)–H(3)	127(8)	C(9)–C(91)–H(91)	116(9)
C(3)–C(4)–H(4)	130(7)	C(9)–C(91)–H(92)	119(9)
C(5)–C(4)–H(4)	122(7)	C(9)–C(91)–H(93)	114(8)
C(4)–C(5)–H(5)	128(8)		
C(1)–C(5)–H(5)	124(8)		

* Cp and Bd are the centroids of the cyclopentadienyl and butadiene fragments respectively.

The Fe···Co distance (2·546 Å) is consistent with metal–metal distances observed in similar iron and cobalt bridged complexes.[2–5]

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[11] 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.

[12] *Chem. Soc. Special Publ.*, No. 11, 1959, and No. 18, 1965.

The methylcyclopentadienyl ligand exhibits the expected planarity (Table 4). The C–C distances within the ligand, mean 1·41 Å, are as expected.[3,4] The iron–ring carbon distances are 2·08—2·18 Å, mean 2·12 Å, and the iron–ring centroid distance is 1·75 Å. The butadiene ligand is in a *cis*-configuration and is planar (Table 4). The two methyl groups lie 0·07—0·09 Å from the butadiene plane and the C–CH_3 bond directions lie towards the $Co(CO)_2Fe$ bridge system. The C–C distances within the butadiene ligand are equal, the mean value (1·42 Å) agreeing well with that (1·417 Å) in *trans*-$[Co(\pi\text{-}C_6H_{10})(CO)_2]_2$.[2] The $Fe(CO)_2Co$ bridging system is almost planar (Table 4). The angle between the planes of the Fe(CO)Co groups is 173·4°. This contrasts with the strict planarity of the bridge observed in *trans*-$[Co(\pi\text{-}C_6H_{10})(CO)_2]_2$ [2] and *trans*-$[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$.[3] The centroids of the π-ligands, the metal atoms, and the terminal carbonyl groups are almost planar (Table 4) and the dihedral angle between this plane and that defined by the $Fe(CO)_2Co$ bridge is 89·5°. The dihedral angles between the last-mentioned plane and those of the π-ligands are 48·8 (cyclopentadienyl) and 64·6° (butadiene).

TABLE 4

Least-squares planes and their equations in the form $lX' + mY' + nZ' - p = 0$ where X', Y', and Z' are orthogonal co-ordinates related to the atomic co-ordinates X, Y, and Z by $X' = X \sin \beta$, $Y' = Y$, and $Z' = Z + X \cos \beta$. Deviations (Å) of the relevant atoms from the planes are given in square brackets

	l	*m*	*n*	*p*
Plane (1): C(1)—(5)	0·9626	0·2690	0·0317	11·2730
[C(1) 0·016, C(2) −0·015, C(3) 0·009, C(4) 0·001, C(5) −0·010, C(6) 0·119]				
Plane (2): C(7)—(10)	0·9712	0·1227	−0·2042	3·2212
[C(7) 0·002, C(8) −0·004, C(9) 0·004, C(10) −0·002, C(81) 0·094, C(91) 0·073]				
Plane (3): Fe, Co, C(B1), O(B1)	0·4682	0·6887	0·5535	11·2642
[Fe, Co, C(B1), O(B1) <0·0005, CB(2) −0·161, O(B2), −0·302]				
Plane (4): Fe, Co, C(B2), O(B2)	0·4959	0·6027	0·6252	11·6834
[Fe −0·001, Co −0·001, C(B2) 0·004, O(B2) −0·003, C(B1) −0·169, O(B1) −0·301]				
Plane (5): Fe, Co, C(B1), O(B1), C(B2), O(B2)	0·4836	0·6469	0·5897	11·4149
[Fe 0·079, Co 0·076, C(B1) −0·006, O(B1) −0·072, C(B2) −0·001, O(B2) −0·075]				
Plane (6): Fe, Co, Cp,* Bd,* C(T1), O(T1), C(T2), O(T2)	0·2368	−0·7389	0·6309	3·7185
[Fe −0·010, Co 0·011, Cp,* 0·025, Bd * 0·018, C(T1) −0·009, O(T1) −0·013, C(T2) −0·015, O(T2) −0·006]				

* See footnote to Table 3.

Within the $Fe(CO)_2Co$ bridging system some distortion is apparent. The environments about the two bridging carbon atoms are equivalent, and the geometry about C(B2) is similar to those in related compounds.[2-5] The distortion about C(B1) involves a lengthening of the Co–C(B1) distance and a shortening of the Fe–C(B1) distance. The angles at this carbon atom are also distorted, Fe–C(B1)–O(B1) opening and Co–C(B1)–O(B1) closing by an equivalent amount, thus maintaining a planar environment about the carbon atom. The cause of this distortion is not readily apparent. Steric factors, such as the nearness of the methyl group on the cyclopentadienyl ligand to this bridge carbonyl group may be dominant. However, there may be a far more general cause involving molecular packing in the crystal.

The molecules are held in the crystal by van der Waals forces. The closest intermolecular contacts are: $O(T2) \cdots O(T2^{I})$ 3·23, $C(2) \cdots O(B2^{II})$ 3·24, and $O(T2) \cdots C(4^{I})$ 3·34 (I at $1 - x, y, \frac{1}{2} - z$; II at $1 - x, 1 - y, 1 - z$). All other contacts are >3·4 Å.

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