Crystal and Molecular Structure of *cis*-(Isobutyl isocyanide)di-μ-carbonylcarbonylbis(π-cyclopentadienyl)di-iron

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The crystal structure of the title compound has been determined by the heavy-atom method from *X*-ray diffraction counter data and refined to *R* 0·072 for 1447 unique reflections by a full-matrix least-squares procedure. The orthorhombic unit cell, space group $P2_12_12_1$, has dimensions a = 6·649 ± 0·011, b = 13·062 ± 0·035, c = 20·553 ± 0·052 Å, for Z = 4. The complex has a *cis*-configuration with a non-planar $Fe(CO)_2Fe$ bridging system, the angle between the two Fe(CO)Fe planes being 165·6°. The isocyanide ligand is terminal to one Fe, and has a linear Fe–C–N–C grouping. The distances from the iron atoms to the bridge-carbon atoms are equivalent, mean 1·91 Å. The distance of the iron atom to the terminal carbonyl carbon atom is 1·745(16) Å and to the isocyanide carbon atom 1·846(15) Å, Fe ··· Fe 2·524(3) Å.

COMPLEXES of the type $[(\pi\text{-}C_5H_5)_2Fe_2(CNR)_n(CO)_{4-n}]$ can exist in solution as equilibrium mixtures of several tautomeric forms, which arise from the relative positions of the cyclopentadienyl rings (*cis* or *trans*) and also the positions of the isocyanide ligand(s) (terminal or bridging). For the latter case the C–N–C bond of the ligand bends,

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leading to *syn*- and *anti*-positions for the group R.[1,2] Solution i.r. studies [3] for the series [4] of compounds having R = Me, Et, Bu^i, Cy, Bu^t and $n = 1$ or 2 * have shown a trend from bridging to terminal positions of the isocyanide ligands, so that there is no evidence for the bridged tautomer when R is Bu^t. This has been attributed to steric effects arising from the bulkiness of the ligands.[3] Recently the crystal structures of the two complexes $[\{(\pi\text{-}C_5H_5)Fe(CO)(CNMe)\}_2]$ [2] and $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ [4] have been reported and these are in accord with the results from the i.r. studies, the former having only bridging and the latter terminal isocyanide groups.

The solution i.r. studies of the title compound indicate the presence of species containing bridging and terminal isocyanide groups,[5] with the latter predominating. The *X*-ray crystal analysis was undertaken to determine which isomer was present and to establish the molecular geometry.

EXPERIMENTAL

Crystal Data.—$C_{18}H_{19}Fe_2NO_3$, $M = 409\cdot0$, Orthorhombic, $a = 6\cdot649 \pm 0\cdot011$, $b = 13\cdot062 \pm 0\cdot035$, $c = 20\cdot553 \pm 0\cdot052$ Å, $U = 1785\cdot0$ Å^3, $D_m = 1\cdot50$ (by flotation), $Z = 4$, $D_c = 1\cdot521$, $F(000) = 840$. Mo-K_α radiation, $\lambda = 0\cdot71069$ Å; μ(Mo-K_α) = 16·8 cm^{-1}, for cell dimensions and intensity measurements. Space group $P2_12_12_1$ (D_2^4, No. 19) from systematic absences.

The complex crystallises in a tabular form elongated along *a* with pinacoids {100}, {010}, and {001}. Unit-cell parameters were determined from single-crystal precession photographs by use of Mo-K_α radiation. Intensities were collected by use of a Philips PAILRED diffractometer with monochromatised Mo-K_α radiation. Each reflection in the 0—9*kl* layers for $\sin\theta < 0\cdot53$ was recorded. After averaging equivalent reflections 1447 unique reflections having $\sigma(I)/I < 0\cdot5$ were obtained,[6] and these were used for the structure analysis. Intensities were corrected for Lorentz and polarisation effects, but not for absorption or extinction. Scattering factor curves for all atoms were taken from ref. 7, the values for the iron atoms being corrected for the effects of 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 yielded two distinct solutions for the iron atoms: (i) (0·116, 0·205, 0·155) and (0·116, 0·383, 0·136), and (ii) (0·384, 0·295, 0·345) and (0·384, 0·117, 0·364). These two solutions are related by a transformation of $\frac{1}{2} - x$, $\frac{1}{2} - y$, $\frac{1}{2} - z$, and each was used to phase a Fourier synthesis. For the first solution the map yielded positions of only some of the lighter atoms and a subsequent Fourier synthesis phased by the increased number of atoms yielded no further atom positions. On the other hand, the Fourier map derived from the alternative solution readily yielded the positions of the non-hydrogen atoms except for those of the isobutyl group, which were obtained from a difference synthesis phased by the atoms already located.

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 $w = (3\cdot5 - 0\cdot1|F_o| + 0\cdot0015|F_o|^2)^{-1}$. 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.

For the initial refinement positional and individual isotropic thermal parameters for each atom were varied. A difference-Fourier synthesis was calculated when the maximum shift in any parameter was of the order of its σ. This map showed no unusual features, and gave the positions of all the hydrogen atoms, which were included in subsequent calculations with a thermal parameter of $B = 5\cdot0$ Å^2, but were at no point refined.

TABLE 1

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

	x/a	*y/b*	*z/c*
Fe(1)	0·3841(4)	0·2934(1)	0·3382(1)
Fe(2)	0·3842(4)	0·1047(1)	0·3647(1)
O(B1)	0·0708(14)	0·2263(8)	0·4271(5)
O(B2)	0·6276(21)	0·1658(9)	0·2542(5)
O(T2)	0·0694(18)	0·0338(9)	0·2778(5)
N	0·1031(24)	0·2880(11)	0·2258(6)
C(B1)	0·2103(23)	0·2144(12)	0·3918(6)
C(B2)	0·5155(21)	0·1813(11)	0·2976(7)
C(T1)	0·2062(23)	0·2903(12)	0·2693(6)
C(T2)	0·1953(23)	0·0628(10)	0·3121(7)
C(3)	−0·0189(28)	0·2792(13)	0·1684(8)
C(4)	0·0351(38)	0·1903(19)	0·1268(10)
C(5)	−0·1036(46)	0·1903(20)	0·0697(10)
C(6)	0·2421(37)	0·1768(26)	0·1107(13)
C(11)	0·5774(50)	0·4144(16)	0·3153(10)
C(12)	0·4020(53)	0·4545(11)	0·3344(11)
C(13)	0·3625(47)	0·4242(18)	0·3938(14)
C(14)	0·5102(55)	0·3680(19)	0·4181(10)
C(15)	0·6562(30)	0·3597(14)	0·3683(19)
C(21)	0·4566(39)	−0·0442(11)	0·3931(13)
C(22)	0·6278(43)	0·0068(20)	0·3786(10)
C(23)	0·6467(35)	0·0865(19)	0·4228(15)
C(24)	0·4778(45)	0·0802(18)	0·4627(10)
C(25)	0·3620(37)	0·0035(18)	0·4431(11)
H(31)	−0·001	0·344	0·142
H(32)	−0·163	0·274	0·182
H(4)	0·014	0·128	0·155
H(51)	−0·064	0·245	0·039
H(52)	−0·091	0·122	0·046
H(53)	−0·244	0·199	0·084
H(61)	0·257	0·108	0·088
H(62)	0·284	0·232	0·081
H(63)	0·324	0·177	0·151
H(11)	0·653	0·416	0·272
H(12)	0·330	0·496	0·303
H(13)	0·231	0·447	0·415
H(14)	0·507	0·340	0·462
H(15)	0·785	0·322	0·379
H(21)	0·404	−0·106	0·370
H(22)	0·718	−0·010	0·342
H(23)	0·763	0·136	0·425
H(24)	0·451	0·129	0·500
H(25)	0·231	−0·016	0·464

Final refinement, carried out with anisotropic thermal parameters for all non-hydrogen atoms, was terminated when the maximum shift in a parameter was $< 0\cdot13\sigma$.

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* Cy = cyclohexyl.

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[2] F. A. Cotton and B. A. Frenz, *Inorg. Chem.*, 1974, **13**, 253.

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[4] R. D. Adams, F. A. Cotton, and J. M. Troup, *Inorg. Chem.*, 1974, **13**, 257.

[5] A. R. Manning, personal communication.

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

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

1446 Reflections were included in the final cycle of refinement. The final value for R, based on 1447 reflections, was 0·072, and for R' [$= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] was 0·085.

Final atomic 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 21268 (12 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}
Fe(1)	164(4)	34(1)	10(1)	−6(3)	3(2)	1(1)
Fe(2)	127(4)	31(1)	15(1)	1(3)	0(2)	2(1)
O(B1)	96(23)	67(8)	24(3)	0(11)	15(7)	−19(5)
O(B2)	225(32)	78(9)	27(3)	30(17)	42(10)	6(7)
O(T2)	193(34)	84(9)	26(3)	−47(15)	−23(8)	−16(6)
N	241(35)	76(10)	15(3)	10(25)	−20(11)	3(7)
C(B1)	216(38)	40(8)	13(3)	31(18)	−24(10)	−20(6)
C(B2)	125(31)	50(10)	16(3)	2(15)	21(10)	14(6)
C(T1)	197(35)	43(9)	9(3)	−25(18)	12(10)	−1(7)
C(T2)	152(33)	20(7)	20(4)	−9(14)	19(10)	4(6)
C(3)	293(50)	70(13)	16(4)	39(22)	−8(13)	0(9)
C(4)	489(80)	87(17)	24(6)	−2(32)	−40(19)	−2(11)
C(5)	539(88)	140(20)	34(6)	61(51)	−70(26)	−44(12)
C(6)	310(72)	177(32)	45(9)	83(42)	12(22)	−28(19)
C(11)	651(119)	51(12)	35(6)	−99(36)	83(23)	−24(9)
C(12)	664(106)	18(8)	33(5)	43(31)	−49(28)	−1(8)
C(13)	442(88)	76(14)	49(7)	−66(35)	63(26)	−42(10)
C(14)	724(126)	92(19)	29(6)	−196(40)	−75(21)	26(11)
C(15)	171(53)	41(11)	102(15)	−48(19)	−62(24)	−5(15)
C(21)	445(85)	16(9)	57(9)	−32(22)	−78(22)	9(10)
C(22)	332(67)	125(21)	32(6)	101(42)	11(21)	7(13)
C(23)	233(62)	102(17)	65(9)	−73(29)	−89(21)	53(12)
C(24)	578(103)	88(17)	25(5)	114(35)	−68(19)	−18(10)
C(25)	274(59)	90(15)	34(6)	−5(31)	21(18)	26(10)

For all hydrogen atoms $B = 5{\cdot}0$ 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 (I) and the atom labelling, and Figure 2 the packing of the molecules in the crystal.[8] The molecules are held in the crystal by van der Waals forces. The closest intermolecular contacts are O(B2) $\cdots$ C(3) at $1 + x, y, z$ (3·29), O(B2) $\cdots$ C(12) at $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ (3·31),

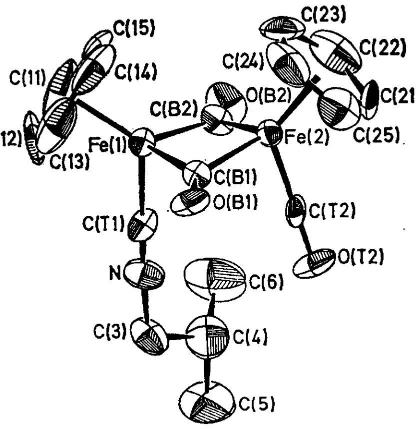

FIGURE 1 A perspective drawing of the molecule and the atom labelling system. Thermal ellipsoids are scaled to include 50% probability

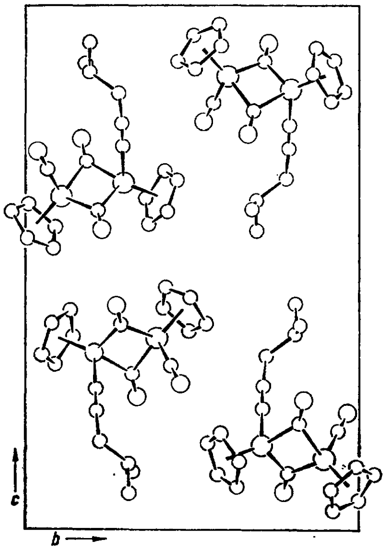

FIGURE 2 The packing of the molecules in the crystal

TABLE 3

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

(a) Distances

	Fe(1) $\cdots$ Fe(2)	2·524(3)	
Fe(1)–C(B1)	1·901(17)	Fe(2)–C(B1)	1·924(14)
Fe(1)–C(B2)	1·899(15)	Fe(2)–C(B2)	1·915(13)
Fe(1)–C(T1)	1·846(15)	Fe(2)–C(T2)	1·745(16)
Fe(1)–Cp(1)*	1·741(17)	Fe(2)–Cp(2)*	1·755(18)
Fe(1)–C(11)	2·091(21)	Fe(2)–C(21)	2·086(15)
Fe(1)–C(12)	2·110(15)	Fe(2)–C(22)	2·082(23)
Fe(1)–C(13)	2·060(17)	Fe(2)–C(23)	2·128(18)
Fe(1)–C(14)	2·086(20)	Fe(2)–C(24)	2·133(18)
Fe(1)–C(15)	2·099(18)	Fe(2)–C(25)	2·088(17)
C(B1)–O(B1)	1·187(16)	C(B2)–O(B2)	1·180(16)
C(T1)–N	1·126(18)	C(T2)–O(T2)	1·158(17)
C(11)–C(12)	1·338(40)	C(21)–C(22)	1·352(33)
C(12)–C(13)	1·311(31)	C(22)–C(23)	1·387(33)
C(13)–C(14)	1·323(37)	C(23)–C(24)	1·393(33)
C(14)–C(15)	1·415(37)	C(24)–C(25)	1·326(31)
C(15)–C(11)	1·404(34)	C(25)–C(21)	1·356(30)
N–C(3)	1·437(20)	C(3)–C(4)	1·486(28)
C(4)–C(5)	1·494(29)	C(4)–C(6)	1·426(32)

(b) Angles

Fe(2)–Fe(1)–C(B1)	49·1(4)	Fe(1)–Fe(2)–C(B1)	48·3(5)
Fe(2)–Fe(1)–C(B2)	48·8(4)	Fe(1)–Fe(2)–C(B2)	48·3(5)
C(B1)–Fe(1)–C(B2)	96·7(6)	C(B1)–Fe(2)–C(B2)	95·4(7)
Cp(1)*–Fe(1)–C(B1)	122·3(6)	Cp(2)*–Fe(2)–C(B1)	122·7(6)
Cp(1)*–Fe(1)–C(B2)	125·4(7)	Cp(2)*–Fe(2)–C(B2)	123·1(6)
Cp(1)*–Fe(1)–C(T1)	123·9(6)	Cp(2)*–Fe(2)–C(T2)	125·0(6)
C(T1)–Fe(1)–C(B1)	92·5(6)	C(T2)–Fe(2)–C(B1)	88·9(6)
C(T1)–Fe(1)–C(B2)	86·6(7)	C(T2)–Fe(2)–C(B2)	92·6(6)
Fe(1)–C(B1)–Fe(2)	82·6(6)	Fe(1)–C(B2)–Fe(2)	82·9(5)
Fe(1)–C(B1)–O(B1)	139·3(13)	Fe(1)–C(B2)–O(B2)	139·1(12)
Fe(2)–C(B1)–O(B1)	138·1(14)	Fe(2)–C(B2)–O(B2)	138·0(13)
C(15)–C(11)–C(12)	107·3(20)	C(25)–C(21)–C(22)	109·3(18)
C(11)–C(12)–C(13)	109·2(24)	C(21)–C(22)–C(23)	107·5(22)
C(12)–C(13)–C(14)	111·8(27)	C(22)–C(23)–C(24)	105·6(19)
C(13)–C(14)–C(15)	106·2(18)	C(23)–C(24)–C(25)	109·5(20)
C(14)–C(15)–C(11)	105·5(20)	C(24)–C(25)–C(21)	108·0(21)
Fe(1)–C(T1)–N	177·6(13)	Fe(2)–C(T2)–O(T2)	179·0(13)
C(T1)–N–C(3)	175·7(17)	N–C(3)–C(4)	113·5(15)
C(3)–C(4)–C(5)	107·7(19)	C(3)–C(4)–C(6)	117·6(23)
C(5)–C(4)–C(6)	114·4(23)		

* Cp(1) and Cp(2) are the centroids of C(11)–C(15) and C(21)–C(25) respectively.

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[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.

and O(B1) · · · C(23) at $-1 + x, y, z$ (3·36 Å). All other non-hydrogen contacts are >3·4 Å. The bond distances and angles, together with their estimated standard deviations derived directly from the least-squares inverse matrix, are given in Table 3.

The structure has the expected $Fe(CO)_2Fe$ bridging system with the cyclopentadienyl rings in a *cis*-configuration and the isocyanide ligand in a terminal position. The angle between the two Fe(CO)Fe planes is 165·6° (Table 4). The molecular dimensions do not differ significantly from those of the parent compound (II) *cis*-$[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2]$ [9] and of the analogous $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$ (III).[4] A comparison of all three structures is given in Table 5.

TABLE 4

Least-squares planes and their equations in the form: $lX + mY + nZ - p = 0$ where X, Y, and Z are co-ordinates in Å. Deviations (Å) of relevant atoms from the planes are given in square brackets

	l	m	n	p
Plane (1): C(11)—(15)	0·4561	0·8222	0·3404	8·4227
[C(11) −0·02, C(12) 0·02, C(13) −0·01, C(14) <0·01, C(15) 0·01]				
Plane (2): C(21)—(25)	0·4920	−0·6010	0·6298	6·9109
[C(21) 0·02, C(22) −0·01, C(23) <0·01, C(24) 0·01, C(25) −0·02]				
Plane (3): Fe(1), Fe(2), C(B1), O(B1)	0·6059	0·1716	0·7768	7·6014
[Fe(1) 0·004, Fe(2) 0·004, C(B1) −0·018, C(B2) 0·010]				
Plane (4): Fe(1), Fe(2), C(B2), O(B2)	0·7852	0·1336	0·6047	6·7181
[Fe(1) 0·003, Fe(2) 0·003, C(B2) −0·013, O(B2) 0·007]				

The cyclopentadienyl rings are both planar (Table 4) and the angle between the two planes is 93·2°. The C–C distances in each ring are not significantly different, mean 1·37 Å, which compares well with that observed in (II).[9] The isocyanide ligand has the expected geometry, with a linear Fe–C–N–C grouping.

TABLE 5

Comparison of structural data for compounds closely related to (I); distances in Å, angles in °

	(II) [a]	(III) [b]	(I) [c]
Fe · · · Fe	2·531(2)	2·523(2)	2·524(3)
Fe–$(CO)_t$	1·745(21)	1·73(1)	1·745(16)
Fe–$(CN)_t$		1·81(1)	1·846(15)
Fe–C_b	1·917(7)	1·90(1)	1·91(1)
Fe–Cp [d]	1·746(5)	1·749(7)	1·75(2)
Fe–C_b–Fe	82·6(3)	83·1(4)	82·8(5)
C_b–Fe–C_t	90·5(25)	89·5(6)	90·2(6)
C_b–Fe–C_b	96·0(3)	95·4(7)	96·1(7)
Dihedral angle	164	162·3	165·6

[a] *cis*-$[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2]$, ref. 9. [b] $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu^t)]$, ref. 4. [c] This work. [d] Centroid of C_5H_5 ring.

The results from this structural determination indicate that the replacement of one carbonyl ligand of the parent compound by an isocyanide ligand does not affect the overall geometry of the molecule but does apparently preferentially stabilise the *cis*-isomer in the solid state. Obviously the factors affecting the relative stabilities of the different isomers are complex and further structural information for the series of compounds $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_n(CNMe)_{4-n}]$ for $n = 0$—3,[10] will enable us to study the mechanism of interconversion between isomers.

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[10] R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 1973, **95**, 6589.