

Carbon Compounds of the Transition Metals.

XXIX. Crystal Structure of *trans-anti*-Bis(*pentahapto*-cyclopentadienyl)dicarbonyl-bis(μ -phenylisonitrile)-diiron(*Fe–Fe*), (h^5 -C₅H₅)₂Fe₂(CO)₂(μ -CNPh)₂

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Monoclinic, $P2_1/c$, $a = 10.771$ (2), $b = 14.445$ (2), $c = 7.473$ (1) Å, $\beta = 110.11$ (2)°, C₂₆H₂₀Fe₂N₂O₂, $M_r = 504.16$, $Z = 2$, $U = 1091.8$ Å³. The first reported analysis of a *trans* doubly-bridged isonitrile complex of Fe is presented. The crystallographic centre of symmetry ensures that the bent isonitrile ligands coordinate *anti*.

Introduction

Although isonitrile complexes of transition metals have been known for some time, few structural determinations have been reported, especially where the isonitrile group bridges two metal atoms. For Fe, two examples have been reported. In one (Joshi, Mills, Pauson, Shaw & Stubbs, 1965), the bridging groups are phenylisonitrile and CO and, more recently, a doubly-bridged methylisonitrile complex was published (Cotton & Frenz, 1974). We now report the structure of a doubly-bridged phenylisonitrile complex.

Experimental

Cp₂Fe₂(CO)₂(CNPh)₂ was prepared in small yield by direct substitution of CO in *trans*-Cp₂Fe₂(CO)₄ by PhNC (Howell, 1976). Crystals, obtained from dichloromethane–petroleum spirit, were very thin, dark-red and few. The crystal chosen for structural work was trapezoidal with mean dimensions 0.20 × 0.26 × 0.03 mm. Intensities were collected on a Hilger & Watts Y290 diffractometer (Edwards, Bowden, Standeven & Mills, 1966) with β -filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å, $\mu = 13.9$ cm⁻¹); 2159 reflexions were measured ($\theta \leq 26^\circ$); 1652 with $F_o \geq 3\sigma(F)$ were used in the final refinement. The structure was solved by a combination of direct and Fourier methods and refined by large-block-matrix least squares with weights chosen to give reasonable uniformity in the mean value of $w\Delta F^2$ with distribution of $\sin^2 \theta/\lambda^2$ and with F_o . H atoms were included in the later stages. Scattering factors for H were taken from Stewart, Davidson & Simpson (1965) and for the remaining atoms from Cromer & Waber (1965). A correction was applied for the real component of anomalous scattering of Fe (Cromer, 1965). The final R was 0.041.

Positional parameters are given in Table 1.* Details of molecular geometry are given in Table 2. The numbering scheme is shown in Fig. 1 and a packing diagram in Fig. 2.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32486 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic positional parameters ($\times 10^5$) with estimated standard deviations in parentheses

Hydrogen atoms were assigned to positions 1.05 Å from their bonded carbons with isotropic thermal parameters of 5.0 Å².

	x	y	z
Fe(1)	44553 (4)	53509 (3)	-16306 (6)
C(1)	61463 (30)	47701 (21)	-5306 (39)
C(2)	83558 (31)	42542 (24)	1030 (44)
C(3)	88151 (39)	34552 (27)	-4573 (55)
C(4)	100327 (44)	31038 (29)	6311 (70)
C(5)	108158 (40)	35617 (33)	22101 (63)
C(6)	103835 (36)	43700 (32)	27368 (53)
C(7)	91564 (35)	47256 (28)	16898 (48)
C(8)	36631 (33)	43208 (23)	-26242 (44)
C(9)	31666 (40)	63575 (27)	-33106 (64)
C(10)	39952 (48)	60209 (26)	-42639 (49)
C(11)	52750 (41)	62370 (28)	-31742 (61)
C(12)	52669 (48)	67005 (27)	-15413 (58)
C(13)	39629 (52)	67773 (25)	-16493 (57)
N(1)	70993 (25)	45856 (20)	-10149 (34)
O(8)	31405 (29)	36548 (18)	-33047 (39)
H(3)	82410	31140	-17089
H(4)	103592	24764	2377
H(5)	117466	32939	30167
H(6)	109883	47254	39487
H(7)	88342	53510	20984
H(9)	21323	63005	-37753
H(10)	36910	56681	-55721
H(11)	61191	60792	-35148
H(12)	60978	69460	-4336
H(13)	36323	71009	-6372

Table 2. Molecular geometry with estimated standard deviations in parentheses

(a) Intramolecular distances (Å)

Fe(1)—Fe(1')	2.525 (1)	C(3)—C(4)	1.381 (6)
Fe(1)—C(1)	1.915 (3)	C(4)—C(5)	1.363 (6)
Fe(1)—C(1')	1.944 (3)	C(5)—C(6)	1.364 (6)
Fe(1)—C(8)	1.749 (3)	C(6)—C(7)	1.383 (5)
Fe(1)—C(9)	2.102 (4)	C(7)—C(2)	1.382 (5)
Fe(1)—C(10)	2.094 (3)	C(8)—O(8)	1.142 (4)
Fe(1)—C(11)	2.109 (4)	C(9)—C(10)	1.406 (6)
Fe(1)—C(12)	2.128 (4)	C(10)—C(11)	1.374 (6)
Fe(1)—C(13)	2.127 (4)	C(11)—C(12)	1.395 (6)
C(1)—N(1)	1.229 (4)	C(12)—C(13)	1.383 (6)
N(1)—C(2)	1.408 (4)	C(13)—C(9)	1.383 (6)
C(2)—C(3)	1.376 (5)		

(b) Intramolecular angles (°)

C(1)—Fe(1)—C(1')	98.3 (1)	C(5)—C(6)—C(7)	120.6 (4)
C(1)—Fe(1)—C(8)	93.6 (1)	C(6)—C(7)—C(2)	119.7 (4)
C(1')—Fe(1)—C(8)	91.3 (1)	C(7)—C(2)—C(3)	119.4 (4)
Fe(1)—C(1)—Fe(1')	81.8 (1)	C(7)—C(2)—N(1)	122.1 (3)
Fe(1)—C(1)—N(1)	137.4 (2)	Fe(1)—C(8)—O(8)	178.8 (3)
Fe(1')—C(1)—N(1)	140.9 (2)	C(9)—C(10)—C(11)	107.7 (4)
C(1)—N(1)—C(2)	129.0 (3)	C(10)—C(11)—C(12)	108.7 (4)
N(1)—C(2)—C(3)	118.5 (3)	C(11)—C(12)—C(13)	107.4 (4)
C(2)—C(3)—C(4)	119.8 (4)	C(12)—C(13)—C(9)	108.7 (4)
C(3)—C(4)—C(5)	120.8 (4)	C(13)—C(9)—C(10)	107.5 (4)
C(4)—C(5)—C(6)	119.6 (4)		

(c) Torsion angles (°)

C(8)—Fe(1)—C(1)—N(1)	88	C(7)—C(2)—C(3)—C(4)	4
C(8)—Fe(1)—C(1')—N(1')	-86	C(3)—C(2)—C(7)—C(6)	-3
C(1')—Fe(1)—C(1)—N(1)	-180	C(2)—C(3)—C(4)—(5)	-3
C(1')—Fe(1)—C(1)—Fe(1')	0	C(3)—C(4)—C(5)—C(6)	1
Fe(1)—C(1)—N(1)—C(2)	171	C(4)—C(5)—C(6)—C(7)	0
N(1)—C(2)—C(3)—C(4)	-179	C(5)—C(6)—C(7)—C(2)	0
N(1)—C(2)—C(7)—C(6)	-180	C(9)—C(10)—C(11)—C(12)	0
C(1)—N(1)—C(2)—C(3)	125	C(10)—C(11)—C(12)—C(13)	-1
C(1)—N(1)—C(2)—C(7)	-57	C(11)—C(12)—C(13)—C(9)	1
		C(12)—C(13)—C(9)—C(10)	-1
		C(13)—C(9)—C(10)—C(11)	0

(d) Some least-squares planes and distances of atoms from the planes (Å). x' , y' and z' refer to orthogonal coordinates in Å from right-handed axes such that a' is parallel to a and c' is parallel to c^* .

Plane 1: C(9), C(10), C(11), C(12) and C(13)

$$0.09074x' + 0.87165y' - 0.48166z' - 9.51259 = 0$$

Fe(1) -1.7506; C(9) -0.0021; C(10) -0.0005; C(11) 0.0029; C(12) -0.0043; C(13) 0.0040

Plane 2: C(2), C(3), C(4), C(5), C(6) and C(7)

$$0.64537x' + 0.51825y' - 0.56117z' - 8.95203 = 0$$

C(2) -0.0166; C(3) 0.0181; C(4) -0.0077; C(5) -0.0042; C(6) 0.0056; C(7) 0.0048; N(1) -0.0163; C(1) -0.8117

Plane 3: Fe(1), Fe(1'), C(1), C(1'), N(1) and N(1')

$$-0.30838x' - 0.88567y' - 0.34712z' + 8.05756 = 0$$

Fe(1) 0.0000; C(1) 0.0006; N(1) -0.0003; C(2) -0.1774

Dihedral angles between planes (°)

Plane	1	2
2	38.69	
3	129.26	117.60

Table 2 (cont.)

(e) Intermolecular contacts less than 3.0 Å

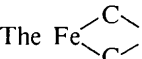
C(5)...H(4 ⁱ)	2.89	O(8)...H(11 ^{iv})	2.78
C(9)...H(3 ⁱⁱ)	2.96	O(8)...H(12 ^{vii})	2.86
C(9)...H(13 ⁱⁱⁱ)	2.97	H(3)...H(9 ^{vi})	2.69
C(10)...H(13 ⁱⁱⁱ)	2.88	H(3)...H(10 ^{iv})	2.94
C(13)...H(3 ⁱⁱ)	2.98	H(3)...H(13 ^{vi})	2.71
N(1)...H(10 ^{iv})	2.42	H(4)...H(5 ^{viii})	2.81
O(8)...H(5 ^v)	2.69	H(6)...H(9 ^{viii})	2.85
O(8)...H(6 ^v)	2.95	H(10)...H(11 ^{iv})	2.64

Equivalent positions

(i)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	(v)	$x - 1, y, z - 1$
(ii)	$1 - x, \frac{1}{2} + y, -\frac{1}{2} - z$	(vi)	$1 - x, y - \frac{1}{2}, -1 - z$
(iii)	$x, 1\frac{1}{2} - y, z - \frac{1}{2}$	(vii)	$x, \frac{1}{2} - y, z - \frac{1}{2}$
(iv)	$1 - x, 1 - y, -1 - z$	(viii)	$1 + x, y, z + 1$

Discussion

From the few structures which have been reported, it appears that the isonitrile group is always non-linear when occupying a bridge position and approximately linear when coordinated as a terminal ligand (Table 3b). In complexes such as the present, the bridging ligands may be disposed *syn* or *anti* whilst the Cp and terminal CO groups may be *cis* or *trans*. Hitherto, only *cis* structures have been reported (Joshi *et al.*, 1965; Cotton & Frenz, 1974). Since the present complex contains a crystallographic centre of symmetry, the ligands are here *anti* and *trans*. Although linear forms of the phenylisonitrile group, which would involve a positively charged N atom with the associated negative charge accommodated on the ring, are possible, the C—N—C angle of 129° shows that this form does not play any dominant role.

The Fe  Fe ring is, of course, accurately planar

(in contrast with the *cis* forms) and the N atoms lie close to that plane; the phenyl group is subjected to two twists, a slight one out of the plane of (FeCN)₂ as shown by the torsion angle Fe(1)—C(1)—N—C(2) (171°) and a further twist about the N—phenyl bond. As a result, the planes of the phenyl group and of (FeCN)₂ are inclined at 62°.

In Table 3(a) we present comparisons of geometric quantities for a number of related carbonyl and isonitrile-bridged complexes of Fe (structures I—V). The Fe—Fe values vary only slightly and do not appear to be simply related to the bridging group or to the kind of isomerism. It is interesting to compare the coordinated CN(R) groups [*R* = phenyl (IV), methyl (V)]. The non-planarity of the Fe₂C₂ ring in (V) is taken up entirely at the angle subtended at the Fe atom [95° in (IV), 98° in

Table 3. Geometric quantities for a number of related complexes of iron

(a) Geometry for complexes of the type: $(h^5-C_5H_5)_2Fe_2(CO)_2(\mu-CX)_2$

Compound	I	II	III*	IV	V
$\mu-CX$	CO	CO	CO/CNPh	CNPh	CNCH ₃
Reference	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
Average bond lengths (Å)					
Fe-Fe	2.534	2.531	2.532	2.525	2.538
Fe- μC	1.914	1.917	1.907/1.899	1.929	1.937
Fe-CO	1.748	1.745	1.734	1.749	1.714
Fe-c.g.	1.754	1.746	1.760	1.751	1.754
Average bond angles (°)					
Fe- μC -Fe	82.9	82.6	83.1/83.6	81.7	81.9
Fe- μC -X	138.6	138.7	138.4/138.0	139.1	139.0
μC -Fe- μC	97.1	96.0	95.3	98.2	95.8
μC -Fe-CO	93.5	90.5	90.1/89.5	92.5	88.0

Key

 μC = bridging carbonc.g. = centroid of C₅H₅(I) = *trans*-($h^5-C_5H_5$)₂Fe₂(CO)₂(μ -CO)₂(II) = *cis*-($h^5-C_5H_5$)₂Fe₂(CO)₂(μ -CO)₂(III) = *cis*-($h^5-C_5H_5$)₂Fe₂(CO)₂(μ -CO)(μ -CNPh)(IV) = *trans*-($h^5-C_5H_5$)₂Fe₂(CO)₂(μ -CNPh)₂(V) = *cis*-($h^5-C_5H_5$)₂Fe₂(CO)₂(μ -CNCH₃)₂(b) Geometry of metal-CN(*R*) systems

Compound	Reference	M-CN(<i>R</i>)	M-C (Å)	C-N (Å)	N-R (Å)	C-N-R (°)
VI	<i>f</i>	Mo-CN	2.17	1.14	—	—
VI	<i>f</i>	Mo-CNCH ₃	2.14	1.13	1.44	174-180
VII	<i>g</i>	Mn-CNPh	1.92	1.12	1.38	171
VIII	<i>h</i>	Co-CNPh	1.85	1.15	1.40	178
IX	<i>i</i>	Pt-CNPh	1.90	1.16	1.37	174
X	<i>c</i>	Fe- μ CNPh	1.90	1.28	1.38	131
XI	<i>e</i>	Fe- μ CNCH ₃	1.94	1.22	1.47	125
XII	<i>d</i>	Fe- μ CNPh	1.93	1.23	1.41	129

Key

(VI) = Mo(CH₃NC)₄(CN)₄(VII) = MnBr(CO)₃(CNPh)₂(VIII) = Co(CNPh)₄I₂(IX) = *cis*-PtCl₂(CNPh)₂(X) = *cis*-($h^5-C_5H_5$)₂Fe₂(CO)₂(μ -CO)(μ -CNPh)(XI) = *cis*-($h^5-C_5H_5$)₂Fe₂(CO)₂(μ -CNCH₃)₂(XII) = *trans*-($h^5-C_5H_5$)₂Fe₂(CO)₂(μ -CNPh)₂

References: (a) Bryan & Greene (1970). (b) Bryan, Greene, Newlands & Field (1970). (c) Shaw & Mills (1963). (d) This work. (e) Cotton & Frenz (1974). (f) Cano & Cruickshank (1971). (g) Bright & Mills (1974). (h) Baumann, Endres, Keller, Nuber & Weiss (1975). (i) Jovanović, Manojlović-Muir & Muir (1972).

* *Note added in proof*:—The structure of this compound has been redetermined with diffractometer data since the submission of this paper. The major change to the table is that the Fe- μC distance should read 1.920/1.928 Å. These values are in close agreement with other entries in the table.

(V)]. That part of the molecule immediately involved in coordination is essentially the same in (IV) and (V) and thus independent of the *R* group, whether alkyl or aryl. The C-N-R angle is slightly larger (129 vs 125°) in the phenyl case. We may therefore extend the comment of Cotton & Frenz (1974) 'in the case of the least sterically demanding isocyanide group CNCH₃' that 'essentially nothing has changed significantly upon

replacing two CO groups by μ -CNCH₃ groups' to cover the bulkier phenyl group as well and to note the innocent nature of the aromatic part in this ligand.

Cotton & Frenz (1974) have also commented with justified caution that, on the basis of two determinations which involve different metal atoms (Ni and Fe), when the metal atoms are doubly bridged by methylisonitrile groups there might be an inequality in

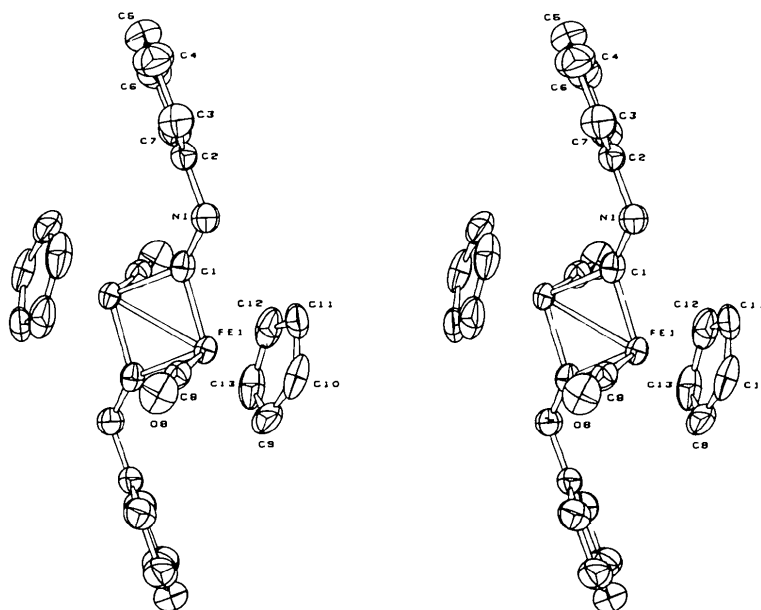


Fig. 1. Stereoscopic view of the molecule showing vibration ellipsoids at the 50% probability level (Johnson, 1965) and the atom-numbering scheme.

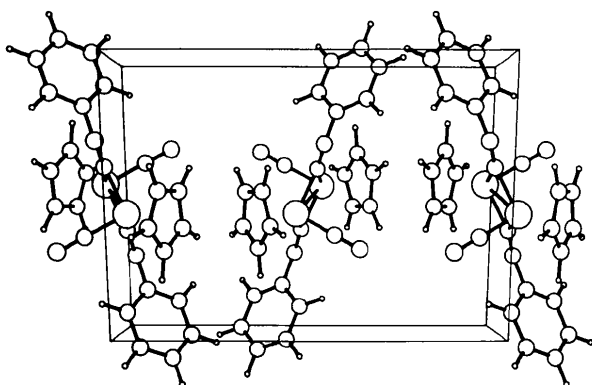


Fig. 2. View showing packing arrangement.

the values of the metal to (bridging) C distances such that the bond *anti* to the substituent on the isonitrile ligand is shorter than that in the *syn* position.

The differences quoted for (V) are 0.010 and 0.031 Å, *i.e.* 1–3 σ . In the present complex this trend is also present; the difference is 0.28 Å (9 σ). Whether this difference be found genuine or not must await still further studies since the calculated values of σ obtained from least squares applied to X-ray intensities must be regarded as underestimates. There are similar variations in bond length elsewhere in the complexes, *e.g.* in the phenyl and cyclopentadienyl groups, although for these the values of σ are somewhat larger.

There are no non-hydrogen contacts less than 3.30 Å. Table 2(e) contains intermolecular contacts less than 3.0 Å.

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