map, with electron densities ranging from 0·8 to 0·5 e Å^{-3}. A good weighting scheme was $w = w_1 \times w_2$, where $w_1 = 1/\sigma_1^2$, $w_2 = 1/\sigma_2^2$, $\sigma_1 = a + b|F_o|$ and $\sigma_2 = c + d \sin \theta/\lambda$, with coefficients calculated by the program *PESOS* (Martínez-Ripoll & Cano, 1975) (Table 1). After two cycles of least-squares refinement with isotropic temperature factors for the H atoms, the final unweighted and weighted discrepancy indices were $R = 0{\cdot}036$ and $R_w = 0{\cdot}042$, where $R_{w} = (\Sigma w\Delta^2F/\Sigma w|F_o|^2)^{1/2}$. A final difference synthesis had no electron density greater than 0·25 e Å^{-3}. The final positional parameters are given in Table 2.*

Discussion. From infrared spectroscopy it was suggested (Cano Esquivel, 1975) that $Zn(CN)_2.C_{14}H_{12}N_2$ contained six-coordinated Zn. The present investigation was undertaken to establish unequivocally the structure of this compound.

Fig. 1 is a computer-generated perspective drawing of the molecule. Table 3 shows a list of bond angles and bond lengths together with their standard deviations. The Zn atom presents distorted tetrahedral coordination. The bidentate phenanthroline group is almost planar with an average deviation of 0·035 Å and a maximum deviation of 0·086 Å, and forms an angle of 85° with the plane defined by the Zn atom and the two cyanide ligands.

A glance at the bond lengths on both sides of a hypothetical line passing through Zn and the mid-point of the C(5)–C(6) bond suggests the existence of a non-crystallographic twofold axis. This has been tested in terms of a δ_p half-normal probability plot (Abrahams & Keve, 1971), calculated from a comparison of all intramolecular distances less than 3·5 Å on both sides of the above-mentioned line; this shows all the δ_p terms lying on a linear array with a slope of 1·22 (3) and a zero intercept at 0·14 (3). The value of the zero intercept cannot be interpreted as significant for the existence of any bias because the data are not independent. The same can apply to the slope, but in any case the linearity of the plot supports the above-mentioned symmetry of the molecule.

Most of the calculations were carried out using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of the Centro de Proceso de Datos del Ministerio de Educación y Ciencia, Madrid, for the facilities provided on the 1108 Univac computer.

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Bis(μ-diethylimmoniocarbene)-hexacarbonyldiiron(−I)

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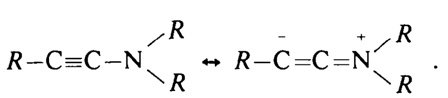
Abstract. $[(C_2H_5)_2NCFe(CO)_3]_2$, FW 448·04, orthorhombic, *Pbca*, $a = 10{\cdot}732$ (4), $b = 14{\cdot}922$ (4), $c = 25{\cdot}721$ (7) Å, $Z = 8$, $D_m = 1{\cdot}43$, $D_c = 1{\cdot}45$ g cm^{-3}, $\mu = 14{\cdot}8$ cm^{-1} (Mo $K\alpha$ radiation), crystal size 0·95 × 0·35 × 0·60 mm. Diffractometer data, 3631 reflections measured, 2449 with $I \geq 3\sigma_I$, $R = 0{\cdot}044$. The molecule consists of two $Fe(CO)_3$ moieties bridged by two $\gt C{=}N(C_2H_5)_2$ units. The Fe–Fe distance is 2·482 (1) Å, and the coordination about each Fe atom is distorted octahedral.

Introduction. About 100 mg of the title compound were kindly supplied by Professor R. B. King. Yellow crystals were grown from an isopentane solution. The unit-cell constants were determined from a least-squares refinement of carefully measured 2θ values for 26 independent reflections. These measurements and subsequent intensity data were obtained with a General Electric XRD-7 quarter-circle manual diffractometer using Mo radiation (Mo $K\alpha$ = 0·71069 Å). Intensity measurements were made by the stationary-crystal/stationary-counter method with balanced Zr and Y filters and the X-ray tube take-off angle set to 5·0°. Measurements were made for a total of 3631 independent reflections [$2\theta_{\max}$ = 50·00°; $(\sin\theta/\lambda)_{\max}$ = 0·5947 Å^{-1}] with 10 s counts being recorded for both the Zr and Y filters. Five reflections were periodically measured during the data collection to monitor crystal alignment and/or deterioration. No significant variation was noted. An absorption correction was made as a function of the diffractometer angles φ and 2θ, and ranged from 1·00 to a maximum of 1·90. The data were reduced by a method reported elsewhere (Pettersen & Levenson, 1976); 2449 reflections were classed as significantly above background.

The structure was solved by conventional heavy-atom methods. The structural parameters were refined using full-matrix least-squares calculations. Scattering factors for neutral atoms and the anomalous-dispersion corrections for Fe were taken from *International Tables for X-ray Crystallography* (1974). In the final cycles of the refinement, the scattering contribution for the 20 H atoms was introduced using calculated positions and isotropic temperature factors of 9·0 Å^2; however, these parameters were not allowed to vary. All the other atoms were refined with anisotropic thermal parameters. The final R value defined as $\Sigma|F_o - |F_c||/\Sigma F_o$ is 0·044 and the weighted R_w defined as $(\Sigma w|F_o - |F_c||^2/\Sigma wF_o^2)^{1/2}$ is 0·059. The goodness of fit $\{= [\Sigma w|F_o - |F_c||^2/(M-S)]^{1/2}\}$ is 2·25 for M = 2449 reflections and S = 235 parameters. All parameter shifts in the last cycle were less than 0·06σ. A final difference map contained four residual density peaks near the two Fe atoms and ranged in value from 0·30–0·43 e Å^{-3}. Other residual peaks were scattered throughout the cell, the largest being 0·16 e Å^{-3}.*

The following computer programs were used: *LSLAT* (cell-parameter refinement); *INCON* (data reduction, Davis, 1965); *NUCLS* (full-matrix least squares); *JIMDAP* (version of Zalkin Fourier program); *ORFFE* (function and error program, Busing, Martin & Levy, 1964); *ORTEP* (Johnson, 1965); *XANADU* (molecular-geometry program, Roberts & Sheldrick, 1973).

Discussion. The reaction chemistry of iron carbonyls with acetylenes has been interesting and productive. A variety of complex products have been characterized and many are summarized (Bowden & Lever, 1968). Recent work has focused on amino-substituted acetylene derivatives as starting materials (King & Harmon, 1976). The reactivity of the amino acetylenes was expected to be altered from that of carbon-substituted acetylenes because the effective bond order of the alkyne is reduced by the resonance structure:



$$R{-}C{\equiv}C{-}N\begin{smallmatrix}R\\R\end{smallmatrix} \leftrightarrow R{-}\overset{-}{C}{=}C{=}\overset{+}{N}\begin{smallmatrix}R\\R\end{smallmatrix}\ .$$

This work is a structure analysis of the complex product resulting from the reaction of iron pentacarbonyl and bis(diethylaminoacetylene), $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$. A preliminary account of this work has been reported (Cash, Pettersen & King, 1977).* Details of the synthesis and spectral analysis can be found in the paper by King & Harmon (1976).

The fractional atomic coordinates and anisotropic thermal parameters are listed in Table 1. Bond lengths and valency angles are listed in Table 2. Fig. 1 presents a stereographic view of the molecular structure and was generated by the *ORTEP* program (Johnson, 1965).

Table 1. *Fractional coordinates* ($\times 10^4$)

Estimated standard deviations are given in parentheses.

	x	y	z
Fe(1)	152 (1)	2580 (1)	1717 (1)
Fe(2)	−441 (1)	2357 (1)	794 (1)
C(1)	816 (4)	2060 (3)	2270 (2)
O(1)	1224 (3)	1723 (3)	2630 (1)
C(2)	1002 (4)	3619 (3)	1712 (1)
O(2)	1532 (4)	4275 (2)	1691 (1)
C(3)	−1228 (4)	3068 (3)	2001 (2)
O(3)	−2103 (3)	3385 (3)	2163 (1)
C(4)	−455 (4)	1584 (3)	267 (2)
O(4)	−469 (4)	1112 (3)	−80 (1)
C(5)	−2027 (5)	2754 (4)	787 (2)
O(5)	−3017 (3)	3003 (3)	807 (1)
C(6)	219 (5)	3282 (3)	441 (2)
O(6)	671 (4)	3852 (3)	219 (1)
C(7)	1105 (3)	2165 (2)	1142 (1)
N(1)	2212 (3)	1892 (2)	1037 (1)
C(8)	3220 (4)	1874 (4)	1432 (2)
C(9)	4087 (6)	2648 (5)	1388 (3)
C(10)	2584 (4)	1597 (4)	518 (2)
C(11)	2544 (7)	602 (5)	481 (3)
C(12)	−788 (3)	1649 (2)	1397 (1)
N(2)	−1326 (3)	912 (2)	1516 (1)
C(13)	−2032 (5)	355 (3)	1139 (2)
C(14)	−3392 (6)	474 (5)	1167 (2)
C(15)	−1242 (4)	520 (3)	2042 (2)
C(16)	−152 (6)	−119 (4)	2082 (3)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32615 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* An incorrect space group for this work was reported at the ACA meeting at Northwestern University in August, 1976. This was due to an error in the c cell dimension (short by a factor of two).

The molecule contains two Fe atoms, which are single-bonded [Fe(1)–Fe(2) = 2·482 (1) Å] and bridged by the C atoms of two diethylimmoniocarbene units [$>C{=}N(C_2H_5)_2$]. A striking result is that formation of this molecule required complete rupture of the C≡C triple bond in the starting material. The distance between the two bridging C atoms [C(7) and C(12)] is 2·27 Å, too large for any significant electronic interaction. Such alkyne rupture is very rare, but has been previously observed (Benn, Wilke & Henneberg, 1973; King & Harmon, 1976).

Table 2. *Bond lengths* (Å) *and valency angles* (°) *for* $[(C_2H_5)_2NCFe(CO)_3]_2$

Fe(1)–Fe(2)	2·482 (1)		
Fe(1)–C(1)	1·769 (6)	Fe(2)–C(4)	1·779 (6)
Fe(1)–C(2)	1·799 (5)	Fe(2)–C(5)	1·802 (6)
Fe(1)–C(3)	1·804 (5)	Fe(2)–C(6)	1·797 (6)
Fe(1)–C(7)	1·902 (5)	Fe(2)–C(7)	1·908 (4)
Fe(1)–C(12)	1·904 (4)	Fe(2)–C(12)	1·914 (5)
C(1)–O(1)	1·140 (6)	C(4)–O(4)	1·137 (6)
C(2)–O(2)	1·133 (6)	C(5)–O(5)	1·127 (6)
C(3)–O(3)	1·131 (5)	C(6)–O(6)	1·132 (6)
C(7)–N(1)	1·285 (5)	C(12)–N(2)	1·280 (5)
N(1)–C(8)	1·484 (6)	N(2)–C(13)	1·486 (7)
N(1)–C(10)	1·463 (6)	N(2)–C(15)	1·475 (7)
C(8)–C(9)	1·487 (9)	C(13)–C(14)	1·473 (9)
C(10)–C(11)	1·488 (11)	C(15)–C(16)	1·513 (8)

C(1)–Fe(1)–C(2)	100·4 (2)	C(4)–Fe(2)–C(5)	101·4 (3)
C(1)–Fe(1)–C(3)	100·6 (2)	C(4)–Fe(2)–C(6)	96·8 (2)
C(1)–Fe(1)–C(7)	105·4 (2)	C(4)–Fe(2)–C(7)	105·5 (2)
C(1)–Fe(1)–C(12)	103·9 (2)	C(4)–Fe(2)–C(12)	104·9 (2)
C(1)–Fe(1)–Fe(2)	144·4 (2)	C(4)–Fe(2)–Fe(1)	144·8 (2)
C(2)–Fe(1)–C(3)	94·1 (2)	C(6)–Fe(2)–C(5)	96·6 (3)
C(2)–Fe(1)–C(7)	90·1 (2)	C(6)–Fe(2)–C(7)	90·6 (2)
C(2)–Fe(1)–C(12)	153·3 (2)	C(6)–Fe(2)–C(12)	155·4 (2)
C(2)–Fe(1)–Fe(2)	103·7 (2)	C(6)–Fe(2)–Fe(1)	106·2 (2)
C(3)–Fe(1)–C(7)	152·5 (2)	C(5)–Fe(2)–C(7)	151·1 (2)
C(3)–Fe(1)–C(12)	92·0 (2)	C(5)–Fe(2)–C(12)	90·3 (2)
C(3)–Fe(1)–Fe(2)	103·3 (2)	C(5)–Fe(2)–Fe(1)	102·0 (2)
C(7)–Fe(1)–C(12)	73·2 (2)	C(7)–Fe(2)–C(12)	72·8 (2)
C(7)–Fe(1)–Fe(2)	49·5 (1)	C(7)–Fe(2)–Fe(1)	49·2 (1)
C(12)–Fe(1)–Fe(2)	49·6 (1)	C(12)–Fe(2)–Fe(1)	49·2 (1)
Fe(1)–C(1)–O(1)	178·8 (5)	Fe(2)–C(4)–O(4)	177·8 (5)
Fe(1)–C(2)–O(2)	177·8 (5)	Fe(2)–C(5)–O(5)	176·8 (5)
Fe(1)–C(3)–O(3)	177·7 (5)	Fe(2)–C(6)–O(6)	177·8 (5)
Fe(1)–C(7)–Fe(2)	81·3 (2)	Fe(2)–C(12)–Fe(1)	81·1 (2)
Fe(1)–C(7)–N(1)	139·8 (4)	Fe(2)–C(12)–N(2)	139·2 (4)
Fe(1)–C(12)–N(2)	139·7 (4)	Fe(2)–C(7)–N(1)	138·9 (4)
C(7)–N(1)–C(8)	122·4 (4)	C(12)–N(2)–C(13)	123·7 (4)
C(7)–N(1)–C(10)	122·7 (4)	C(12)–N(2)–C(15)	122·2 (4)
C(8)–N(1)–C(10)	114·9 (4)	C(13)–N(2)–C(15)	114·1 (4)
N(1)–C(8)–C(9)	113·0 (5)	N(2)–C(13)–C(14)	114·0 (5)
N(1)–C(10)–C(11)	110·6 (6)	N(2)–C(15)–C(16)	111·1 (5)

The average of the two C(bridge)–N distances in the ligands is 1·282 (4) Å, corresponding to a double bond (Kennard *et al.*, 1972). Formally this requires a positive charge on each of the two N atoms and a negative charge on each of the two Fe atoms. This formalism is satisfied if the bridge C atoms each contribute three of their valence electrons to the two Fe atoms and one valence electron to the bond with N. A recent structure, $HRu_3(CO)_{10}(C{=}NMe_2)$ (Churchill, DeBoer & Rotella, 1976), contains a similar bridging ligand. The C=N bond distances for the two independent molecules in the asymmetric unit are 1·280 (6) and 1·279 (5) Å, equivalent to those in the present structure [1·280 (5) and 1·285 (5) Å].

The molecular structure is completed by three carbonyl groups attached to each of the Fe atoms. Although there are no crystallographic symmetry requirements, the molecule has nearly 2 point-group symmetry. The approximate twofold axis bisects the Fe–Fe bond and is perpendicular to the vector between the two bridge C atoms. The five C atoms within the coordination sphere of each Fe atom form square-based pyramids with C(1) and C(4) as the apical positions for Fe(1) and Fe(2) respectively. The two pyramids share an edge along the vector C(7) → C(12). Fe(1) is displaced by 0·40 Å toward the apical C(1) atom from the best least-squares plane containing C(2), C(3), C(7) and C(12). The corresponding displacement for Fe(2) toward C(4) is 0·38 Å from the best least-squares plane containing C(5), C(6), C(7) and C(12). The dihedral angle between the two base planes just defined is 78·9°.

The Fe coordination geometry can also be described as a distorted octahedron. The Fe–Fe bond is considered to be 'bent' and in a *trans* position to the apical C(1) and C(4) atoms. The concept of a 'bent' bond has been proposed elsewhere (Dahl, Martell & Wampler, 1961) and experimental verification by means of electron density studies is also being investigated (Wang & Coppens, 1976). The 'bent' bond angle in this structure is 109·3°, as determined from

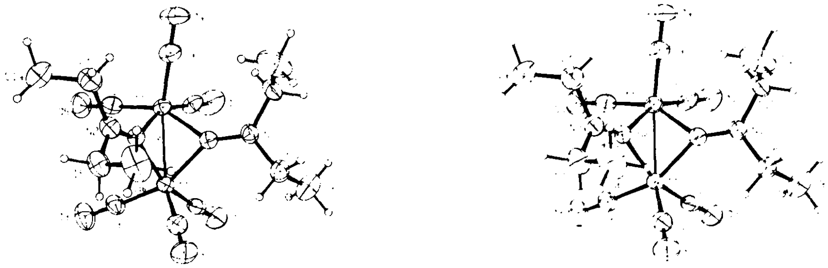

Fig. 1. A stereographic view of $[(C_2H_5)_2NCFe(CO)_3]_2$.

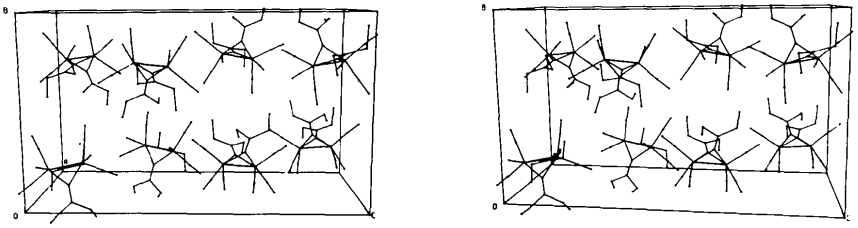

Fig. 2. A stereographic packing diagram showing the contents of one unit cell of $[(C_2H_5)_2NCFe(CO)_3]_2$.

the dot product of the vectors Fe(1) → C(1) and Fe(2) → C(4).

The bond distances from the Fe atoms to the apical carbonyl C atoms are observed to be somewhat shorter [average 1·774 (7) Å] than the four other Fe–carbonyl bonds [average 1·800 (4) Å] by about four standard deviations. This difference is consistent with the reported infrared carbonyl stretching frequencies; ν(CO) at 2054(*s*), 2009(*s*), 1997(*s*), 1976(*s*), 1937(*s*), and 1929(*s*) cm^{-1} (King & Harmon, 1976). The latter two bands probably arise from the apical carbonyl groups because of the increased metal-to-carbon bond strength, and subsequent decrease in the C≡O bond strength. No significant difference is observed for the C≡O bond lengths, but the direction of difference is consistent with the band assignments. The change in the C≡O bond length has been noted to be relatively insensitive to bond order as compared to the change in the metal-to-carbon distance with bond order (Cotton & Wilkinson, 1972). A stereographic view of the unit-cell packing is presented in Fig. 2. The view is approximately along **a**.

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