Fonction ester $COOCH_3$. Les longueurs de liaison C—O et C=O sont habituelles. A la différence du composé *exo* où le groupe ester est relativement proche du plan moyen, on se rend compte qu'il y a eu une rotation autour de C(12)—C(14) du fait de la cycloaddition. En particulier, la liaison C=O fait un angle de 59,5 (4)° avec le plan du cycle benzénique alors que dans le composé *exo*, la conjugaison avec la double liaison C=C était manifeste, la liaison C=O faisait un angle de 15,1 (4)° avec ce plan et la liaison C=C un angle de 16,9 (4)°.

Lors de la cycloaddition dipolaire sur le diastéréoisomère *exo* (3), le dipôle CH_2N_2 est gêné par deux interactions stériques; celles (*a*) du trépied $Cr(CO)_3$ dans le demi-espace et celle (*b*) du groupe CH_3 axial dans l'autre demi-espace. La première interaction est prédominante si bien que le dipôle attaque le dipolarophile en *exo* du trépied. Lors de cette approche ou après la création du cycle pyrazolinique, l'interaction (*b*) provoque l'effacement du groupe CH_3 en équatorial associé à un basculement de la pointe de l'enveloppe C(11). Le groupe ester semble également se placer pour assurer en particulier une interaction minimum entre le groupe carbonyle C(14)—O(4) et la liaison N(1)—N(2).

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Structure of Tricarbonylbis(methyl isocyanide)iron(0), $Fe(C_2H_3N)(CO)_3$

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Abstract. $M_r = 221{\cdot}99$, monoclinic, $P2_1/c$, $a = 12{\cdot}451$ (6), $b = 6{\cdot}564$ (3), $c = 12{\cdot}087$ (6) Å, $\beta = 92{\cdot}45$ (3)°, $V = 986{\cdot}95$ Å^3, $Z = 4$, $D_x = 1{\cdot}49$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 16·32 cm^{-1}, $F(000) = 447{\cdot}96$, $T = 293$K, $R = 0{\cdot}0680$ for 1335 unique reflections. The molecule exhibits trigonal bipyramidal geometry, with the two methyl isocyanide ligands occupying axial positions. Both the carbonyl and isocyanide ligands show linear coordination.

Introduction. On the basis of electronic arguments (Rossi & Hoffmann, 1975) the geometry of complexes of the type $Fe(CO)_3(CNR)_2$ has been predicted to be trigonal bipyramidal with the isocyanides in axial positions. The IR spectra of this ligand arrangment are predicted to give one ν(NC) and one ν(CO) stretching absorption (Cotton & Parish, 1960), but unexpectedly these complexes typically give one ν(NC) and more than one ν(CO) absorptions in both the solid and solution states (Cotton & Parish, 1960; Albers, Coville & Singleton, 1982). A crystal structure determination of the title compound was thus undertaken to determine whether this result was related to a deviation of the structure from idealized D_{3h} symmetry due to electronic effects, *e.g. via* non-linearity of the C—N—C unit bound to iron. The small size of the isocyanide further limits the possibility that the anomalous IR data result from steric effects (Stainer & Takats, 1982).

Experimental. Compound obtained from the $CoCl_2.2H_2O$ catalysed reaction between $Fe(CO)_5$ and CH_3NC (Albers, Coville & Singleton, 1982). [IR(KBr): 2182(*s*), 2026(*w*), 1935(*sh*), 1919(*s*), 1897(*s*), 1878(*sh*) cm^{-1}.] Since the complex is both air and light sensitive, yellow crystals were grown under nitrogen in the dark from a benzene–hexane solution at 293K. Crystal 0·16 × 0·16 × 0·14 mm, photography established space group $P2_1/c$, Philips PW 1100 four-circle diffractometer, Mo $K\alpha$ graphite-monochromated radiation, ω–2θ scan (scan width 1·60°, scan speed 0·0535° s^{-1}), $3 \le \theta \le 23$°, h −13–13, k 0–7, l 0–13, cell constants from least-squares refinement of the θ

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values of 25 general reflections, 1517 intensities measured, no unobserved reflections with $I < 3\sigma(I)$, 1335 unique reflections after rejection of systematically absent reflections, $R_{\rm int} = 0{\cdot}0$, Lorentz and polarization but no absorption corrections, no crystal deterioration; structure analysis and refinement with *SHELX*82 (Sheldrick, 1982), initial coordinates for iron from Patterson synthesis, other atoms located from difference Fourier syntheses, positional parameters of all atoms and anisotropic temperature factors for non-hydrogen atoms refined by full-matrix least-squares analyses on F until all parameter shifts $< 0{\cdot}5\sigma$, $R = 0{\cdot}0680$, $R_w = 0{\cdot}068$,* unit weights, scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous dispersion corrections for iron from Cromer & Liberman (1970), residual electron density in final difference map within $-0{\cdot}40$ and $+0{\cdot}45$ e Å^{-3}.

Discussion. The stereochemistry of the molecule is illustrated in Fig. 1, which also shows the numbering scheme used in the analysis. Table 1 contains the positional and thermal parameters and Table 2 the bond distances and angles.

As predicted (Rossi & Hoffmann, 1975), the geometry of the complex is trigonal bipyramidal with the methyl isocyanide ligands in axial positions. Further, the *R*NC and CO ligands are linearly coordinated to the central iron atom. The crystal structure determination clearly indicates that idealized D_{3h} symmetry exists in the crystalline state. An alternative explanation will thus be required to account for the anomalous IR spectral data (Cotton & Parish, 1960).

A comparison of the iron—carbonyl (1·79 Å), iron–isocyanide (1·87 Å) and MeN—C (1·15 Å) bond lengths with other iron(0)—isocyanide complexes reported in the literature (Yamamoto, 1980) reveals that all the distances are normal. The iron—isocyanide bond length is longer than found in the only other comparable structure, Fe(CNBu^t)$_5$ [1·824 (8) Å] (Bassett, Berry, Barker, Green, Howard & Stone, 1979), and is consistent with increased electronic density on the iron atom in the pentaisocyanide complex. It is to be noted that in this structure the *R*NC ligands deviate from linearity and that the geometry deviates markedly from D_{3h} symmetry.

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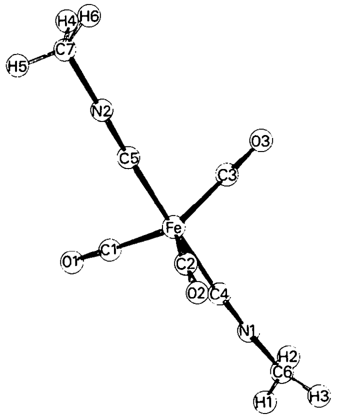

Fig. 1. An *ORTEP* (Johnson, 1965) view of the molecule showing the numbering scheme used.

Table 1. *Final fractional atomic coordinates* (×10^4) *and temperature factors* (Å^2 ×10^3) *for the non-hydrogen atoms*

$U_{\rm eq}$ was obtained by contraction of the dispersion matrix (Hamilton, 1959).

	x	y	z	$U_{\rm eq}$
Fe	2457 (1)	3155 (2)	5729 (1)	46 (1)
N(1)	3692 (5)	696 (10)	4097 (5)	57 (3)
N(2)	1393 (5)	5622 (10)	7472 (5)	60 (4)
O(1)	518 (5)	3058 (11)	4276 (5)	90 (4)
O(2)	2863 (6)	−62 (10)	7371 (5)	93 (4)
O(3)	3977 (6)	6515 (10)	5450 (6)	103 (5)
C(1)	1278 (6)	3069 (12)	4852 (6)	47 (4)
C(2)	2693 (6)	1199 (11)	6743 (6)	54 (4)
C(3)	3384 (7)	5203 (13)	5550 (7)	64 (5)
C(4)	3206 (5)	1614 (11)	4710 (5)	48 (4)
C(5)	1776 (5)	4692 (11)	6785 (6)	52 (4)
C(6)	4352 (8)	−411 (19)	3385 (8)	68 (5)
C(7)	899 (11)	6818 (20)	8298 (10)	87 (7)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Fe—C(1)	1·775 (8)	C(1)—O(1)	1·150 (9)
Fe—C(2)	1·790 (8)	C(2)—O(2)	1·138 (8)
Fe—C(3)	1·791 (9)	C(3)—O(3)	1·144 (9)
Fe—C(4)	1·873 (8)	C(4)—N(1)	1·148 (8)
Fe—C(5)	1·860 (8)	C(5)—N(2)	1·150 (8)
C(6)—N(1)	1·416 (10)	C(7)—N(2)	1·430 (11)
Fe—C(1)—O(1)	178·4 (8)	C(1)—Fe—C(4)	90·7 (3)
Fe—C(2)—O(2)	178·3 (7)	C(2)—Fe—C(4)	89·5 (3)
Fe—C(3)—O(3)	179·2 (8)	C(3)—Fe—C(4)	89·1 (3)
Fe—C(4)—N(1)	178·0 (6)	C(1)—Fe—C(5)	92·2 (3)
Fe—C(5)—N(2)	176·9 (6)	C(2)—Fe—C(5)	89·2 (3)
C(6)—N(1)—C(4)	176·3 (8)	C(3)—Fe—C(5)	89·5 (3)
C(7)—N(2)—C(5)	178·1 (9)	C(4)—Fe—C(5)	177·1 (3)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38597 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dimeric Methyl(diphenylamino)zinc,* $C_{26}H_{26}N_2Zn_2$

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Abstract. $M_r = 497{\cdot}27$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}57\ (2)$, $b = 14{\cdot}95\ (3)$, $c = 20{\cdot}43\ (4)$ Å, $U = 2312{\cdot}09$ Å^3, $Z = 4$, $D_m = 1{\cdot}43\ (2)$, $D_x = 1{\cdot}43$ Mg m^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu(\text{Cu}\ K\alpha) = 2{\cdot}7$ mm^{-1}, $F(000) = 1024$, $T = 295$ K, $R = 0{\cdot}086$ for 2110 observed reflections. The molecule is dimeric in the solid state as in solution, with the MeZn units bridged by two NPh_2 units to give a Zn_2N_2 ring in which all the angles are close to 90° so that the zinc atoms are three-coordinate and the nitrogen atoms are four-coordinate.

Introduction. Reactions between R_2Zn and bases containing acidic hydrogen atoms in 1:1 molar proportions result in the elimination of hydrocarbon, *e.g.*

$$R_2\text{Zn} + R'\text{OH} \rightarrow \tfrac{1}{n}(R\text{ZnO}R')_n + R\text{H}.$$

The product, if monomeric, would contain a coordinatively unsaturated metal atom attached to a donor atom, which because of the dipole $M^{\delta+}$–ligand$^{\delta-}$ would have increased donor properties with the resulting formation of either internal coordination or associated compounds. Because of size and energy constraints, internal coordination has not been observed in Zn compounds and appears to be limited to first-row elements. Degrees of association of two, three, four, five, six and eight have been found for organozinc complexes, formed as above, containing N (Coates & Ridley, 1965; Noltes & Boersma, 1967; Pattison & Wade, 1968), O (Coates & Ridley, 1965, 1966; Schindler, Schmidbaur & Krüger, 1965; Shearer & Spencer, 1980), S (Coates & Ridley, 1965; Adamson & Shearer 1969; Adamson, Bell & Shearer, 1982) and halogen (Boersma & Noltes, 1966; Moseley & Shearer, 1963). Several factors have been considered to influence the degree of association. With alcohols and thiols, the donor atom makes use of both lone pairs of electrons so that many organozinc alkoxides are tetrameric like $(\text{MeZnOMe})_4$ (Shearer & Spencer, 1980) except where bulky organic groups present make the formation of smaller oligomers more favourable (Coates & Ridley, 1965). In contrast, sulphides show larger degrees of association, so that MeZnSPr^i is hexameric in benzene solution (Coates & Ridley, 1965), though octameric in the solid state (Adamson & Shearer, 1969), whereas MeZnSBu^t, and EtZnSBu^t are pentameric in benzene (Coates & Ridley, 1965), the former also in the solid state (Adamson, Bell & Shearer, 1982). In contrast, amino derivatives have only one lone pair of electrons and can only associate to form dimers or cyclic oligomers. This has been particularly noted for organoberyllium amino derivatives, where both entropy factors and steric bulk on the donor atom favour the formation of dimers relative to higher associated products, but dimers involve greater valence-angle deformation which may be relieved by the formation of larger cyclic oligomers (Coates & Fishwick, 1967). Aminozinc alkyls are all dimers in benzene solution (Coates & Ridley 1965), as are the ketimino derivatives RZnN=CPh (Pattison & Wade, 1968), and to confirm the existence of three-coordinate zinc in the solid state we have determined the structure of methyl(diphenylamino)zinc.

Experimental. Preparation by heating freshly sublimed diphenylamine and dimethylzinc under nitrogen in a

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* Bis(μ-diphenylamido)-bis(methylzinc).

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