Nitrogen Derivatives of Iron Carbonyls. Part 5.[1] New Routes in the Mechanism of Reaction of Dodecacarbonyl-*triangulo*-tri-iron with Nitroalkanes, and *X*-Ray Analysis of μ-[Acetone oximato(1—)-*NO*]-μ-isopropylamido-bis(tricarbonyliron) (*Fe–Fe*)

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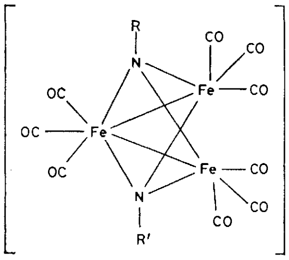
The reaction of $[Fe_3(CO)_{12}]$ with RNO_2 (R = Et or Pr^i) gives, among complexes of well known structures, many other iron–nitrogen–carbonyl complexes which are indicative of novel reaction paths, such as reduction of a nitro- to a nitroso-group, hydrogen abstraction, and N–C bond breakage. The complexes have been fully characterized by means of i.r., mass, and ^1H and ^{13}C n.m.r. spectroscopy. The crystal structure of the title complex has been determined by *X*-ray diffractometry from 2 446 reflections (*R* 0.037). Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 12.008(5)$, $b = 9.827(4)$, $c = 8.580(4)$ Å, $\alpha = 120.53(4)$, $\beta = 99.29(1)$, and $\gamma = 96.80(1)°$. The structure consists of two $Fe(CO)_3$ units linked by an Fe–Fe bond and doubly bridged by the nitrogen of the isopropylamido-ligand and the nitrogen and oxygen of the oximato-ligand. The n.m.r. study shows the presence of a substantial torsional barrier about the N–Fe and N–O bonds and localized carbonyl interchange.

THE reaction between organic nitro-derivatives RNO_2 and iron carbonyls has been considered as a source of nitrene species.[2-4] Even if the isolation of a complex containing a RN fragment is not necessarily evidence for intermediate formation of uncomplexed nitrene, the formation of a nitrene is commonly accepted as the main path for the reduction of a nitro-compound.[5] In subsequent steps the nitrene species can undergo dimerization and H or CO abstraction from the solvent or from the carbonyl. These species can be trapped on the metal, generating complexes such as (1)—(4). When the reaction goes to completion the nitro-compounds are eventually converted into amines (RNH_2), formamides (HCONHR), and ureas $[(RNH)_2CO]$, their precursors being respectively (2) and (3), or (4). In order to rationalize the overall mechanism the identification of the products of the reaction is important, in particular those which are formed *via* the most important reaction paths.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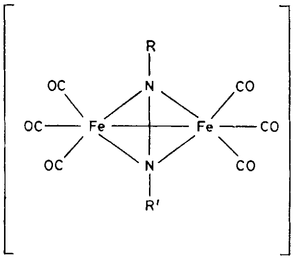
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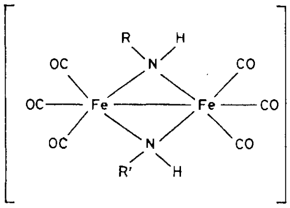
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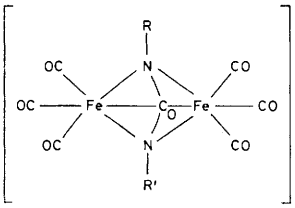
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In a preliminary communication we reported that in the reaction of $[Fe_3(CO)_{12}]$ and nitroethane we were able to isolate several new complexes,[6] some of which have been characterized.[1,6] This suggested that the mechanism of reduction of the nitro-group is more complex than previously indicated. Here we report a complete study of the reactions between $[Fe_3(CO)_{12}]$ and RNO_2 (R = Et or Pr^i), together with the single-crystal *X*-ray analysis of $[Fe_2(CO)_6(NHPr^i)(ONCMe_2)]$.

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[1] Part 4, S. Aime, G. Gervasio, L. Milone, R. Rossetti, and P. L. Stanghellini, *J.C.S. Chem. Comm.*, 1976, 370.

[2] M. Dekker and G. R. Knox, *Chem. Comm.*, 1969, 1243.

[3] H. Alper and J. T. Edward, *Canad. J. Chem.*, 1970, **48**, 1543.

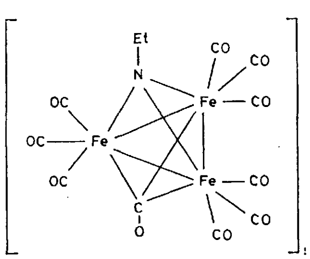
[4] H. Alper, *Inorg. Chem.*, 1972, **11**, 976.

[5] A. J. Carty, *Organometallic Chem. Rev.* 1972, **A7**, 191.

[6] S. Aime, L. Milone, R. Rossetti, and P. L. Stanghellini, *Gazzetta*, 1975, **105**, 617.

RESULTS AND DISCUSSION

The complex $[Fe_3(CO)_{12}]$ reacts with nitroethane to give, among other products, the relatively unstable complex (5) in low yield. Complex (5) crystallizes from n-heptane at -20 °C as red-orange needles which analyzed as $[Fe_3(CO)_{10}(NEt)]$. The mass spectrum shows the stepwise loss of 10 carbonyl groups from the molecular ions. The ^1H n.m.r. pattern is typical of an ethyl group, with a downfield shift for both CH_2 and CH_3 groups as a result of the *N*-co-ordination to the iron atoms. The main feature of the i.r. spectrum in the CO stretching region is the absorption at 1 739 cm^{-1}, which is characteristic of a triply bridging CO group.[7] The high symmetry of the proposed structure is confirmed by the simple pattern of the terminal CO absorption. Iron clusters containing triply bridging CO are well known; however, this is the first example of the isolation of such a species in the case of the reaction with nitro-derivatives. The structure suggests that its formation represents one of the first steps of the reaction, *i.e.* co-ordination of the nitrene to the metal cluster, accompanied by the expulsion of two CO groups and by the promotion of a third CO to a triply bridging position. This mechanism may be similar to that proposed for the formation of $[Fe_3H(CO)_{10}(COMe)]$ from the reaction between $[Fe_3H(CO)_{11}]^-$ and $SFO_2(OMe)$.[8] As further support to this hypothesis we note that (5) is formed immediately on mixing the reactants and its concentration does not increase appreciably but decreases to zero at the end of the reaction suggesting that (5) acts as an intermediate giving rise to other products.



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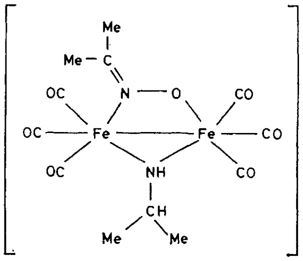

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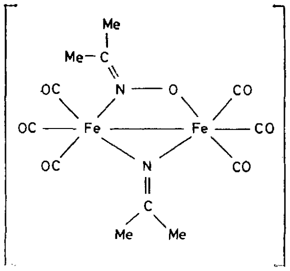
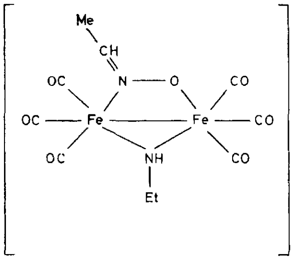


(7)

Complex (6) is the most abundant product of the reaction of $[Fe_3(CO)_{12}]$ with 2-nitropropane. A preliminary account containing the main features of the single-crystal *X*-ray analysis of (6) has been given.[1] We have now completed the structural work and the full details are reported below.

In the same reaction the second most abundant species is complex (7). The six i.r. absorption bands of the terminal CO groups are in agreement with a low symmetry at the metal atoms. The absence of the weak absorption between 3 200 and 3 400 cm^{-1}, as reported for (6), accounts for the loss of the aminic H. The ^1H n.m.r. spectrum shows four singlets of equal intensity; comparison with the spectrum of (6) makes possible the assignment of the two low-field signals to the isopropylideneamino-group. King and Douglas[9] published a different route to (7), from $Na_2[Fe(CO)_4]$ and 2-bromo-2-nitropropane, and more recently Khare and Doedens[10] reported the *X*-ray structure of (7). Complexes (6) and (7) comprise *ca.* 70% of the total yield of the metal carbonyl products: this suggests that the first step of the reduction of the nitro-group is formation of the normally unstable nitrosoalkyl compound which is stabilized by its capture by iron carbonyl.

Further support for this conclusion comes from the isolation of two similar complexes, (8) and (9), from the reaction of $[Fe_3(CO)_{12}]$ with nitroethane. The complexes are isomers and show very similar properties. They are obtained as orange needles by crystallization from n-heptane at -20 °C. In the mass spectra the usual stepwise loss of six carbonyl groups from the molecular ion was observed, together with the loss of oxygen from the nitroso-group. The major peak is the carbonyl- and oxygen-free ion $[C_{10}H_{10}Fe_2N_2]^+$, which successively loses H_2, CH_3, and C_2H_4. The i.r. spectra exhibit, as expected, six bands in the CO stretching region and weak absorption attributable to the N–H (3 200—3 300 cm^{-1}) and C=N (1 600—1 700 cm^{-1}) stretchings. The ^1H n.m.r. peaks were assigned by comparison with the spectra of the other complexes of this series.



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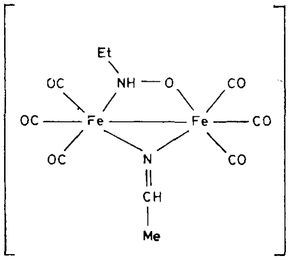

(9)

The structures of the previous complexes, (1)—(9), indicate another interesting feature of the reaction, *i.e.*

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[7] P. Chini, *Inorg. Chim. Acta Rev.*, 1968, **2**, 31; O. Koerner, *Angew. Chem. Internat. Edn.*, 1971, **10**, 910; S. A. Gardner, P. S. Andrews, and M. D. Rausch, *Inorg. Chem.*, 1973, **12**, 2396; E. Sappa and L. Milone, *J. Organometallic Chem.*, 1973, **61**, 383.

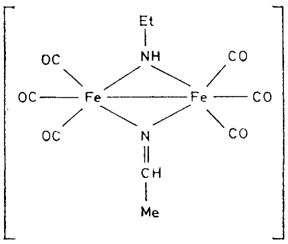
[8] D. S. Shriver, *J. Organometallic Chem.*, 1975, **94**, 259.

[9] R. B. King and W. M. Douglas, *Inorg. Chem.*, 1974, **13**, 1339.

[10] G. P. Khare and R. J. Doedens, *Inorg. Chem.*, 1976, **15**, 86.

the reactivity of the alkyl group of RNO_2. This group has been considered as an unreactive entity bonded to the reactive part of the molecule, since in the previous studies it was unaltered at the end of the reaction both in the metal carbonyl and in the organic system. In contrast, from our results it is clear that the group R can participate in the reaction, mainly by loss of H_2 to form a double CN bond. This feature is evident in the reaction of $[Fe_3(CO)_{12}]$ with 2-nitropropane, where the isopropyl H appears to be particularly reactive. In this context the absence of complexes of the type (3) is noteworthy. The hydrogen abstraction could be the result of an interaction with the metal site to give a carbonylmetal hydride, or of an oxidation by the nitro- or the nitroso-alkyl compound catalyzed by iron carbonyls. The hydrogen abstraction is an important path in the reaction: complexes with at least one CN double bond comprise *ca.* 50% of the total yield in the reaction with nitroethane and >90% in the case of 2-nitropropane.

The most abundant product of the reaction with nitroethane is (10), which has been isolated as a dark red, air-sensitive, viscous oil, totally miscible with organic solvent. Mass, i.r., and n.m.r. spectra are in agreement with the proposed structure. A similar complex is (11), the secondary product of the reaction with 2-nitropropane. It crystallizes from n-heptane as orange-yellow microcrystals of stoicheiometry $C_{12}H_{14}Fe_2N_2O_6$. The mass spectrum exhibits the loss of six carbonyl groups from the molecular ion and the typical fragmentation of the carbonyl-free ion, *i.e.* loss of H_2, CH_3, C_2H_4, *etc.* The ^1H n.m.r. spectrum shows two signals at δ 2.12 and 1.21 p.p.m., attributable to the isopropylidene and isopropyl methyl groups, respectively. A septet (CH) is superimposed on the broad absorption (NH) at δ 2.51 p.p.m. The five i.r. absorption bands of the terminal CO groups, closely related to those of complex (9), are indicative of C_{2v} symmetry for the metal atoms.



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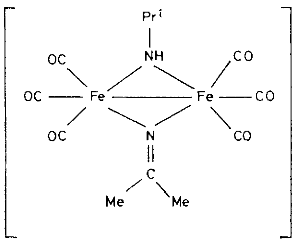

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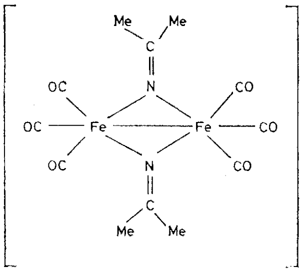

(12)

Dehydrogenation of (11) gives the symmetric complex (12). This complex has been already prepared in a different way,[9] and by Albini and Kisch[11] from 3,3-dimethyldiazirine and $[Fe_2(CO)_9]$. Structure (12) appears to be particularly stable, since it is the result of the arrangement and/or the reduction of different organic ligands on reaction with iron carbonyls. On the other hand, the formation of this complex *via* several independent routes suggests the possibility that the same reactive organic intermediate could be the precursor in all the reactions and so provides indirect evidence of the existence of the nitrene species.

Apart from these complexes, another nitropropane complex (1c; R = Et, R′ = H) was isolated in very low yield. Structure (1c) has not been confirmed crystallographically, but is based on analytical and spectroscopic evidence and by comparison with analogous complexes. The molecular weight was determined by mass spectrometry, which clearly shows the tri-iron composition of the parent ion and the loss of nine carbonyl groups. The presence of the ethyl group and of the NH proton is confirmed by the n.m.r. spectrum; in addition, the N–H stretching appears as an i.r. band at 3 335 cm^{-1}. The pattern of the CO stretching bands is in complete agreement with that of other complexes of type (1).[12] This structure suggests the possibility of another reaction path, *i.e.* breaking of the C–N bond, probably together with hydrogen transfer from C to N. This can be related to the breaking of the $R-N_3$ bond that occurs exceptionally in the reaction of organic azides with organometallic complexes[13] and to the cleavage of the C–N bond of the azirine ring induced by $[Fe_2(CO)_9]$.[14]

Finally, some complexes of well known structure have been obtained. Complex (1a; R = R′ = Et) is one of the major products of the reaction, whereas (1b; R = R′ = Pr^i) has been obtained in low yield, confirming the reactivity of the isopropyl group. In this context, the absence of (2b), (3b), and (4b), it is not surprising. Complex (3a) is also absent, whereas (2a) and (4a) are formed in good yields, as suggested by the greater inertness of the ethyl group.

Dynamic Behaviour.—In complexes (6)—(11) restricted rotation about the N–X bonds (X = O or Fe) is expected to cause non-equivalence of the methyl protons of the isopropyl group or of the methylene protons of the ethyl group.[15] However, the ^1H n.m.r. spectra do not show any clear diastereotopy for these groups. This can be ascribed to accidental or apparent equivalence. In

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[11] A. Albini and H. Kisch, *J. Organometallic Chem.*, 1975, **94**, 75.

[12] P. L. Stanghellini and R. Rossetti, *Atti Accad. Sci. Torino*, 1970—1971, **105**, 391.

[13] S. Cenini and G. La Monica, *Inorg. Chim. Acta*, 1976, **18**, 279.

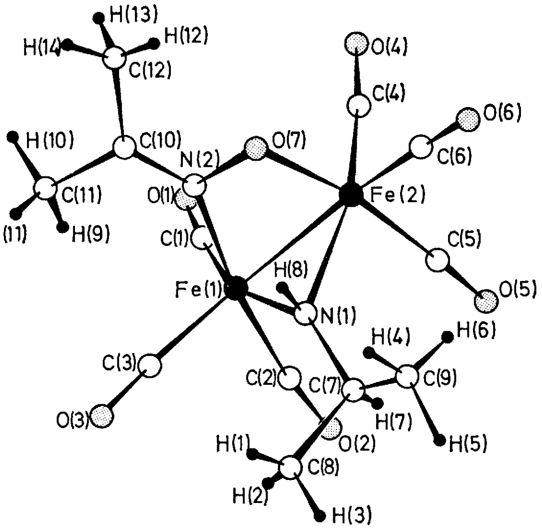
[14] H. Alper and J. Prickett, *J.C.S. Chem. Comm.*, 1976, 191.

[15] 'Dynamic N.M.R. Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, London, 1975, ch. 6.

the ^{13}C n.m.r. spectra of (6) [(11) was not obtained in sufficient quantity for ^{13}C n.m.r. study] two signals at 31.0 and 30.5 p.p.m. were observed for the methyls of the isopropyl group, thus confirming that a substantial torsional barrier is present in these complexes. The signals do not coalesce up to 60 °C, when extensive decomposition occurs.

A second feature is that the carbonyls are engaged in localized interchange at each metal centre. Six resonances having equal integrated intensities are present at 214.8, 214.2, 212.8, 212.2, 205.8, and 204.4 p.p.m. in the spectrum at −10 °C. On increasing the temperature the resonances at 214.8, 212.2, and 205.8 p.p.m. broaden and are partially lost in the noise. At 45 °C these three resonances appear as a single peak, whereas the remaining three resonances are fairly broad.

The Molecular Structure of [Fe$_2$(CO)$_6$(NHPr^i)(ONCMe$_2$)] (6).—The molecular structure of complex (6) (Figure)



A view of one molecule of complex (6) showing the atom-labelling system

contains two Fe(CO)$_3$ groups linked by a Fe–Fe bond and doubly bridged by the nitrogen atom of the isopropylamido-ligand and the nitrogen and oxygen atoms of the acetone oximato-unit. Distances and angles (Tables 1 and 2) within the two bridging ligands are consistent with a single N–C bond in the former ligand and with a double N=C and a single N–O bond in the latter. This structure differs from that found by Khare and Doedens [10] only by two hydrogen atoms of the isopropylamido-ligand.

The Fe(1), N(2), O(7), and Fe(2) atoms do not lie strictly on a plane (Table 3), but the best plane passing through them forms an angle of 13.6° with the O(7),N(2),C(10),C(11),C(12) plane and an angle of 85.4° with the Fe(1),N(1),Fe(2) plane, greater than that found in [Fe$_2$(CO)$_6$(NCMe$_2$)(ONCMe$_2$)] (7) (82.2°).[10] The opening of this angle is due to the presence of a hydrogen atom inserted between the two planes mentioned above; the short N(1) ··· N(2) [2.664(6) Å], N(1) ··· O(7) [2.572(5) Å], H(8) ··· N(2) [2.49(7) Å], and H(8) ··· O(7) [2.26(7) Å] distances reveal the presence of intramolecular short contacts between hydrogen and oxygen and hydrogen and nitrogen. The angles involved in these contacts

TABLE 1

Interatomic distances (Å), with standard deviations in parentheses, for complex (6)

Fe(1)–Fe(2)	2.470(1)	C(7)–N(1)	1.459(7)
Fe(1)–C(1)	1.808(5)	C(7)–H(7)	0.97(7)
Fe(1)–C(2)	1.782(5)	C(8)–H(1)	0.94(7)
Fe(1)–C(3)	1.820(6)	C(8)–H(2)	0.93(7)
Fe(1)–N(1)	1.975(4)	C(8)–H(3)	1.05(8)
Fe(1)–N(2)	1.993(4)	C(9)–H(4)	0.80(7)
Fe(2)–C(4)	1.810(6)	C(9)–H(5)	1.14(8)
Fe(2)–C(5)	1.782(5)	C(9)–H(6)	1.02(8)
Fe(2)–C(6)	1.818(6)	C(10)–C(11)	1.491(8)
Fe(2)–O(7)	1.956(4)	C(10)–C(12)	1.494(8)
Fe(2)–N(1)	1.959(4)	C(10)–N(2)	1.278(7)
C(1)–O(1)	1.135(6)	C(11)–H(9)	0.98(7)
C(2)–O(2)	1.142(7)	C(11)–H(10)	1.09(8)
C(3)–O(3)	1.121(7)	C(11)–H(11)	0.82(8)
C(4)–O(4)	1.129(8)	C(12)–H(12)	0.89(7)
C(5)–O(5)	1.131(6)	C(12)–H(13)	0.84(8)
C(6)–O(6)	1.128(7)	C(12)–H(14)	0.82(8)
C(7)–C(8)	1.517(9)	N(1)–H(8)	0.73(7)
C(7)–C(9)	1.539(8)	N(2)–O(7)	1.371(5)

TABLE 2

Bond angles (°), with estimated standard deviations in parentheses, for complex (6)

Fe(2)–Fe(1)–C(1)	103.5(2)	Fe(2)–C(5)–O(5)	179.6(1)
Fe(2)–Fe(1)–C(2)	98.3(2)	Fe(2)–C(6)–O(6)	177.9(1)
Fe(2)–Fe(1)–C(3)	150.1(2)	C(8)–C(7)–C(9)	109.8(5)
Fe(2)–Fe(1)–N(1)	50.8(1)	C(8)–C(7)–N(1)	112.9(5)
Fe(2)–Fe(1)–N(2)	71.6(1)	C(9)–C(7)–N(1)	110.8(4)
C(1)–Fe(1)–C(2)	89.2(3)	C(8)–C(7)–H(7)	104(4)
C(1)–Fe(1)–C(3)	103.5(2)	C(9)–C(7)–H(7)	108(4)
C(2)–Fe(1)–C(3)	94.6(3)	C(7)–C(8)–H(1)	104(5)
C(1)–Fe(1)–N(1)	154.3(2)	C(7)–C(8)–H(2)	113(5)
C(1)–Fe(1)–N(2)	88.8(2)	C(7)–C(8)–H(3)	107(4)
C(2)–Fe(1)–N(1)	92.8(2)	C(7)–C(9)–H(4)	112(5)
C(2)–Fe(1)–N(2)	168.8(2)	C(7)–C(9)–H(5)	111(4)
C(3)–Fe(1)–N(1)	101.9(2)	C(7)–C(9)–H(6)	111(4)
C(3)–Fe(1)–N(2)	96.5(2)	C(11)–C(10)–C(12)	117.8(5)
Fe(1)–Fe(2)–C(4)	102.1(2)	C(11)–C(10)–N(2)	120.8(5)
Fe(1)–Fe(2)–C(5)	98.1(2)	C(12)–C(10)–N(2)	121.3(5)
Fe(1)–Fe(2)–C(6)	155.0(2)	C(10)–C(11)–H(9)	114(4)
Fe(1)–Fe(2)–N(1)	51.4(1)	C(10)–C(11)–H(10)	105(4)
Fe(1)–Fe(2)–O(7)	75.6(1)	C(10)–C(11)–H(11)	109(5)
C(4)–Fe(2)–C(5)	91.8(3)	C(10)–C(12)–H(12)	107(5)
C(4)–Fe(2)–C(6)	98.8(3)	C(10)–C(12)–H(13)	114(5)
C(5)–Fe(2)–C(6)	94.9(2)	C(10)–C(12)–H(14)	120(5)
C(4)–Fe(2)–N(1)	153.4(2)	Fe(1)–N(1)–Fe(2)	77.8(1)
C(5)–Fe(2)–N(1)	94.6(2)	Fe(1)–N(1)–C(7)	126.1(3)
C(6)–Fe(2)–N(1)	106.4(2)	Fe(1)–N(1)–H(8)	114(6)
C(4)–Fe(2)–O(7)	88.8(2)	Fe(2)–N(1)–C(7)	126.6(3)
C(5)–Fe(2)–O(7)	173.6(2)	Fe(2)–N(1)–H(8)	96(6)
C(6)–Fe(2)–O(7)	91.3(2)	C(7)–N(1)–H(8)	110(6)
N(1)–Fe(2)–O(7)	82.1(2)	Fe(1)–N(2)–C(10)	136.5(3)
Fe(1)–C(1)–O(1)	179.2(1)	Fe(1)–N(2)–O(7)	107.8(3)
Fe(1)–C(2)–O(2)	178.2(1)	C(10)–N(2)–O(7)	115.5(4)
Fe(1)–C(3)–O(3)	178.8(1)	Fe(2)–O(7)–N(2)	103.6(3)
Fe(2)–C(4)–O(4)	178.1(1)		

[N(1)–H(8) · · · N(2) and N(1)–H(8) · · · O(7)] are 95(6) and 107(6)° respectively.

Comparing the structures of (6) and (7), each difference can be ascribed to the isopropylamido-ligand. The Fe–Fe bond [2.470(1) Å] in (6) is slightly shorter than that [2.484(2) Å] found in (7); this shortening, limited by the presence of the Fe–N–O–Fe bridge, may be a consequence of the longer Fe–N bonds of the isopropylamido-ligand [Fe(1)–N(1) 1.975(4), and Fe(2)–N(1) 1.959(4) Å] with respect to the isopropylideneamino-ligand [Fe(1)–N(1) 1.921(4) and Fe(2)–N(1) 1.902(4) Å] as emphasized by Dahl *et al.*[16] Another consequence of the different environments of the Fe–N–Fe bridge is closing of the Fe(1)–N(1)–Fe(2) angle [77.8(1)° in (6) and 81.1(2)° in (7)].

There is no difference between the tricarbonyliron moieties of the two complexes.

EXPERIMENTAL

The complex $[Fe_3(CO)_{12}]$ was prepared according to the known procedure.[17] Iron pentacarbonyl (Alfa Inorganics) was used as received. Nitroethane and 2-nitropropane (reagent grade) were distilled prior to use. Solvents were dried and purified by standard methods. The adsorbent for t.l.c. was silica gel G (E. Merck).

Microanalyses were by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra were recorded on a Beckmann IR 12 spectrometer with grating optics, mass spectra on a Hitachi-Perkin-Elmer RMU-6 spectro-

TABLE 3

Equations of least-squares planes in the form $AX + BY + CZ = D$, in fractional co-ordinates, referred to the cell axes.* Distances (Å × 10^2) of the atoms from the planes are given below the respective atoms

						A	B	C	D	χ^2
Plane (1)	Fe(1)	Fe(2)	Fe(3)			5.64	8.06	−4.89	1.56	
Plane (2)	Fe(1)	Fe(2)	N(2)	O(7)		8.40	−3.34	4.97	3.38	676
	−1.1	1.2	10.5	−9.6						
Plane (3)	O(7)	N(2)	C(10)	C(11)	C(12)	7.97	−1.20	4.61	3.20	1.75
	0.4	−0.6	−0.2	−0.2	0.6					

* $\chi^2 = \Sigma(d/\sigma)^2$ gives the statistical significance of the planarity (D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, 1953, **6**, 698).

TABLE 4

Analytical and spectroscopic data for the complexes

		Analysis (%) [a]						I.r. spectrum (cm^{-1})			
	Complex	C	H	Fe	N	M.p. (θ_c/°C)	M [a,b]	ν(CH) [c]	ν(CO) [d]	Other bands	^1H N.m.r. spectrum (δ/p.p.m.)
(1a)	$[Fe_3(CO)_9(NEt)_2]$	30.4 (30.85)	2.05 (2.00)	33.8 (33.15)	5.30 (5.55)		506 (506)	2 971m, 2 933m, 2 858m	2 048vs, 2 030vs, 2 003s, 1 981m		1.29(3), 3.38(2)
(1b)	$[Fe_3(CO)_9(NPr^i)_2]$	32.9 (33.7)	2.80 (2.65)	31.0 (31.4)	5.30 (5.25)		534 (534)	2 980w, 2 965m, 2 930m, 2 875w	2 044vs, 2 026vs, 1 999s, 1 977m		1.35(6), 3.65(1)
(1c)	$[Fe_3(CO)_9(NH)(NEt)]$	27.5 (27.65)	1.30 (1.25)	34.8 (35.05)	5.70 (5.85)		478 (478)	2 964m, 2 930m, 2 876w, 2 860m	2 051vs, 2 031vs 2 005s, 1 988m	3 335w [ν(NH)]	1.22(3), 3.32(2), 3.77(1)
(2)	$[Fe_2(CO)_6(NEt)_2]$	32.5 (32.8)	2.90 (2.75)	30.4 (30.5)	7.60 (7.65)	97	366 (366)	2 963m, 2 928m, 873(sh), 2 856m 2	2 070m, 2 025vs, 1 992s, 1974s, 1 964m		1.32(3), 3.11(2)
(4)	$[Fe_2(CO)_6\{OC(NEt)_2\}]$	33.4 (33.5)	2.50 (2.55)	28.4 (28.35)	7.00 (7.10)	78	394 (394)	2 963m, 2 929m, 2 876w(sh), 2 858m	2 081m, 2 043vs, 2 001s, 1 988m, 1 730m		1.15(3), 2.9(2)
(5)	$[Fe_3(CO)_{10}(NEt)]$	29.4 (29.4)	1.10 (1.05)	34.3 (34.15)	2.50 (2.85)		491 (491)	2 964m, 2 930m, 2 858w	2 050vs, 2 021s, 2 015m(sh), 1 996m, 1 739s		1.70(3), 4.60(2)
(6)	$[Fe_2(CO)_6(NHPr^i)(ONCMe_2)]$	35.0 (35.15)	3.60 (3.45)	27.0 (27.25)	6.50 (6.50)	78	410 (410)	2 978m, 2 964m, 2 928m, 2 920m, 2 900w, 2 868w	2 071m, 2 030vs, 1 994s, 1 986s, 1 972m,1 964w	3 262w [ν(NH)] 1 737w, 1 601w [ν(C=N)]	1.63(6), 1.75(3), 1.95(3), 2.75(1, CH), 3.25 (1, NH)
(7)	$[Fe_2(CO)_6(NCMe_2)(ONCMe_2)]$	35.5 (35.3)	2.90 (2.95)	27.1 (27.4)	6.70 (6.85)	113	408 (408)	2 970m, 2 926m, 2 864m	2 071m, 2 029vs, 1 999s, 1 988s, 1 972m, 1 965w	1 736w, 1 683w [ν(C=N)]	1.69(1), 1.90(1), 2.55(1), 2.65(1)
(8)	$[Fe_2(CO)_6(NHEt)(ONCHMe)]$	31.8 (31.45)	2.80 (2.65)	29.0 (29.2)	7.30 (7.35)	76	382 (382)	2 964s, 2 931m, 2 874w, 2 860w	2 074m, 2 034vs, 1 997s, 1 990s, 1 979m, 1 964w(sh)	3 280w [ν(NH)] 1 735w [ν(C=N)]	1 57(3), 1 82(3), 3.28(2), 3.58(1, NH), 6.95 (1, CH)
(9)	$[Fe_2(CO)_6(NCHMe)(ONHEt)]$	31.3 (31.45)	2.60 (2.65)	29.2 (29.2)	7.40 (7.35)		382 (382)	2 965s, 2 932m, 2 910w(sh),2861w	2 073m, 2 033vs, 1 994s, 1 987s, 1 975m, 1 965w(sh)	3 284w [ν(NH)] 1 733w [ν(C=N)]	1.42(3), 1.66(3) 2.85(2), 3.83(1, NH), 6.23(1, CH)
(10)	$[Fe_2(CO)_6(NHEt)(NCHMe)]$	32.2 (32.8)	2.90 (2.75)	30.9 (30.5)	7.40 (7.65)		366 (366)	2 965s, 2 937m, 2 913w(sh), 2 874m	2 074m, 2 034vs, 1 998s, 1 989s, 1 978m, 1 968w	3 287w [ν(NH)] 1 731w [ν(C=N)]	1.58(3), 1.63(3) 4.19(3,CH_2 + NH) 6.16(1)
(11)	$[Fe_2(CO)_6(NHPr^i)(NCMe_2)]$	36.8 (36.6)	3.80 (3.60)	28.0 (28.35)	7.20 (7.10)	126	394 (394)	2 978w, 2 965m, 2 930m, 2 870w, 2 860w	2 064m, 2 024vs, 1 986s, 1 974s, 1 964m	3 283w [ν(NH)] 1 675w, 1 660m [ν(C=N)]	1.21(6), 2.12(6), 2.51(2, CH + NH)
(12)	$[Fe_2(CO)_6(NCMe_2)_2]$	36.9 (36.75)	3.10 (3.10)	28.6 (28.5)	7.40 (7.15)	112	392 (382)	3 005w, 2 961m, 2 923s, 2 894w(sh), 2 855m	2 065m, 2 025vs, 1 992s, 1 975s, 1 965m	1 735w, 1 675w, 1 660w [ν(C=N)]	2.15

[a] Calculated values are given in parentheses. [b] By mass spectrometry. [c] In CCl_4. [d] In n-heptane.

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[16] B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, 1975, **14**, 3103.

[17] R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 193.

meter at 70 eV.[*] Hydrogen-1 and ^{13}C n.m.r. spectra for solutions in $CDCl_3$ were obtained on a JEOL JNM-PS-100 spectrometer operating in the Fourier-transform mode at 100 and 25.15 MHz respectively. Chemical shifts are reported as downfield positive with respect to $SiMe_4$. The temperature was monitored by a JEOL JNM-DBT-P-5-H100E temperature-control unit. A Leitz model 350 heating plate was used for melting-point determinations.

Reactions of $[Fe_3(CO)_{12}]$ *with Nitro-derivatives* RNO_2 (R = Et *or* Pr^i).—The reaction was carried out in the same way in both cases. The complex $[Fe_3(CO)_{12}]$ (10 g, *ca.* 20 mmol) was dissolved by a vigorous stirring in boiling benzene (500 cm^3) with continuous bubbling of CO. An equimolar quantity of the nitro-derivative dissolved in benzene was added dropwise and the mixture was allowed to react until it changed from dark green to yellow-brown (*ca.* 2 h). After filtration, the solvent was removed *in vacuo* and the residue, dissolved in light petroleum, was chromatographed by t.l.c. (eluant, light petroleum). The initial chromatography allowed us to separate the products in two fractions: that which moves (fraction A) and that which does not move from the baseline (fraction B). Each fraction was collected and chromatographed again several times until the complexes were well separated. [The eluant for B was light petroleum–diethyl ether (9 : 1).] Finally, each compound was purified by crystallization from n-heptane at −20 °C.

The complexes which were separated on the chromatographic plates, and the colours of their bands, are as follows.

(1) *Reaction with nitroethane.* Fraction A: (1a), red-purple; (2a), lemon-yellow; X [not yet completely identified, analyzes as $Fe_2(CO)_6(N_2C_4H_8)$], yellow; (5), orange; $[Fe_3(CO)_{12}]$ (if still present), dark green; (1c), red-purple; Y [not yet completely identified, analyzes for $Fe_4(CO)_{11}$-(ONEt)(NEt)], green-brown. Fraction B: (8), yellow; (4a), yellow; (10), orange-yellow; (11), yellow.

(2) *Reaction with* 2-*nitropropane.* Fraction A: (1b), red-purple; (11), yellow; (12), yellow; $[Fe_3(CO)_{12}]$; Z (unidentified binuclear carbonyl complex). Fraction B: (6), orange-yellow; (7), orange-yellow.

Analytical and spectroscopic data are given in Table 4.

Crystal Structure Determination for Complex (6).—A crystal of the complex, recrystallized from n-heptane solution at −20 °C, was mounted in a glass capillary under nitrogen. Preliminary Weissenberg photographs indicated a triclinic symmetry. The unit-cell parameters were obtained by carefully centring 25 reflections on a Philips PW 1100 four-circle automatic diffractometer, and were refined by a least-squares procedure.

Structure data. $C_{11}H_{14}Fe_2N_2O_7$, $M = 409.95$, $a = 12.008(5)$, $b = 9.827(4)$, $c = 8.580(4)$ Å, $\alpha = 120.53(4)$, $\beta = 99.29(1)$, $\gamma = 96.80(1)°$, $U = 836.4$ Å^3, $F(000) = 404$, $D_m = 1.64$ g cm^{-3}, $Z = 2$, $D_c = 1.63$ g cm^{-3}, space group $P\bar{1}$, $\mu = 18.14$ cm^{-1}. Integrated intensities were collected up to a 2θ limit of 50° using graphite-monochromatized Mo-K_α radiation and an ω-scan technique (scan range, 1.80°; scan speed, 0.18° s^{-1}); 5 s were spent in taking background measurements on both sides of each peak.

Three standard reflections $(0\bar{4}3)$, $(\bar{2}\bar{2}0)$, and (040) were checked every 350 reflections and no significant variation of the intensity was detected. Of the 2 945 independent reflections collected, 499 were rejected as being unobserved $[I < 3\sigma(I)]$. An absorption correction was not applied because of the low absorption coefficient and of the nearly equidimensional shape of the small crystal. Atomic-scattering factors were taken from Cromer and Waber;[18] the effects of anomalous dispersion of iron were included in structure-factor calculations using Cromer and Liberman's[19] values for $\Delta f'$ and $\Delta f''$.

Solution and refinement of the structure. A three-dimensional Patterson map was interpreted in terms of two independent heavy-atom positions in the centric space group $P\bar{1}$, and confirmed by the subsequent refinement. The other atoms, including those of hydrogen, were revealed by successive difference-Fourier maps. The thermal parameters of iron, carbon, oxygen, and nitrogen were refined anisotropically. For the hydrogen atoms, only the positional parameters were refined during the last anisotropic–isotropic cycles of least squares.[20] The final R value for the 2 446 reflections was 0.037, and R' was 0.040. The weighting scheme was $w = 0.04 + 0.000\,04|F_o|^2$ for $|F_o| \leqslant 152$ or $w = 525/(152 + 2|F_o| + 0.003|F_o|^2)$ for $|F_o| > 152$, where $|F_o| = 7.02$ times the absolute scale.

TABLE 5

Fractional atomic co-ordinates for complex (6), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Fe(1)	0.328 43(5)	0.065 61(8)	0.168 05(9)
Fe(2)	0.259 69(6)	0.270 31(8)	0.426 57(9)
C(1)	0.461 4(4)	0.052 2(6)	0.286 9(7)
C(2)	0.412 2(4)	0.199 1(6)	0.124 8(7)
C(3)	0.298 3(4)	−0.109 8(6)	−0.069 9(7)
C(4)	0.363 7(5)	0.309 8(6)	0.631 0(7)
C(5)	0.334 8(4)	0.446 9(5)	0.443 7(6)
C(6)	0.150 7(4)	0.365 6(6)	0.539 3(7)
C(7)	0.160 4(4)	0.228 0(6)	0.048 7(7)
C(8)	0.137 0(6)	0.109 3(8)	−0.160 7(9)
C(9)	0.054 9(5)	0.301 6(7)	0.093 4(8)
C(10)	0.227 8(4)	−0.182 2(5)	0.252 5(7)
C(11)	0.282 5(5)	−0.310 1(6)	0.126 6(8)
C(12)	0.158 9(5)	−0.219 3(6)	0.362 1(8)
O(1)	0.544 9(3)	0.045 6(5)	0.363 2(5)
O(2)	0.468 4(3)	0.283 5(4)	0.098 3(5)
O(3)	0.278 6(4)	−0.216 5(4)	−0.217 5(5)
O(4)	0.427 3(4)	0.330 2(6)	0.757 2(6)
O(5)	0.382 4(3)	0.558 4(4)	0.453 4(5)
O(6)	0.085 3(4)	0.426 3(5)	0.614 3(7)
O(7)	0.187 1(3)	0.063 0(4)	0.388 0(4)
N(1)	0.190 6(3)	0.154 9(4)	0.156 3(5)
N(2)	0.240 1(3)	−0.045 4(4)	0.266 1(5)
H(1)	0.081(6)	0.021(9)	−0.186(9)
H(2)	0.202(6)	0.074(8)	−0.197(9)
H(3)	0.119(6)	0.174(8)	−0.224(9)
H(4)	−0.001(6)	0.235(8)	0.069(9)
H(5)	0.033(6)	0.363(8)	0.014(9)
H(6)	0.072(6)	0.392(8)	0.230(9)
H(7)	0.224(5)	0.313(7)	0.076(8)
H(8)	0.138(6)	0.108(7)	0.155(9)
H(9)	0.339(6)	−0.271(8)	0.079(9)
H(10)	0.325(6)	−0.352(8)	0.211(9)
H(11)	0.231(6)	−0.384(8)	0.038(9)
H(12)	0.109(6)	−0.154(8)	0.391(9)
H(13)	0.199(6)	−0.226(8)	0.447(9)
H(14)	0.120(6)	−0.312(8)	0.316(9)

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[*] Throughout this paper: 1 eV ≃ 1.60×10^{-19} J.

[18] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[19] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[20] W. R. Busing, K. O. Martin, and H. A. Levy, 'ORFLS, a Fortran Crystallographic Least-Squares Program,' Report ORNL TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.

Observed and calculated structure-factor amplitudes, thermal parameters, and mass-spectral data are available as Supplementary Publication No. SUP 22193 (30 pp.).*

Final fractional co-ordinates are given in Table 5. Least-squares planes were calculated as reported previously.[21]

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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