Chemistry of Low-valent Metal Isocyanide Complexes. Part 2.[1] Oxidative Reactions of Pentakis(t-butyl isocyanide)iron with Alkyl, Allyl, Benzyl, Fluoroalkyl, and Pentafluorophenyl Halides, and with Trimethyloxonium Tetrafluoroborate and Diphenylacetylene. Evidence for Isocyanide Insertion Reactions, and the Molecular Structure of $[Fe(CNBu^t)_3\{1—4\text{-}\eta\text{-}C(=NBu^t)=C(Ph)C(Ph)=C(=NBu^t)\}]$ †

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Reaction of $[Fe(CNBu^t)_5]$ with MeI in thf (tetrahydrofuran) affords $[FeI\{C(=NBu^t)C(Me)=NBu^t\}(CNBu^t)_3]$, whereas with diethyl ether as solvent the salt $[FeMe(CNBu^t)_5]I$ is formed, which on dissolving in thf is transformed into the former product. Cationic complexes $[Fe(CH_2CH=CH_2)(CNBu^t)_5]X$ are formed on reaction of $[Fe(CNBu^t)_5]$ in thf with allyl halides or benzyl bromide. However, EtI, EtBr, Pr^iI, and $[Me_3O][BF_4]$ afford η^2-iminoacyl complexes $[Fe\{C(R)=NBu^t\}(CNBu^t)_4]X$. Reaction of $[Fe(CNC_6H_3Me_2\text{-}2,3)_5]$ with MeI or EtI gives $[FeI\{C(R)=N(C_6H_3Me_2\text{-}2,3)\}(CNC_6H_3Me_2\text{-}2,3)_4]$. n-Heptafluoropropyl iodide and bromopentafluorobenzene readily react with $[Fe(CNBu^t)_5]$ to give $[FeI\{CF(CF_3)_2\}(CNBu^t)_4]$ and $[Fe(C_6F_5)(CNBu^t)_5]Br$ respectively. Diphenylacetylene reacts with $[Fe(CNBu^t)_5]$ to give $[Fe(CNBu^t)_3\{1—4\text{-}\eta\text{-}C(=NBu^t)=C(Ph)C(Ph)=C(=NBu^t)\}]$, which was structurally identified by a single-crystal *X*-ray diffraction study. The crystals are monoclinic, space group $P2_1/c$, $Z = 4$ in a unit cell of dimensions $a = 9.724(4)$, $b = 42.11(3)$, $c = 11.330(4)$ Å, $\beta = 113.57(5)°$. The structure has been refined to $R = 0.092$ ($R' = 0.123$) for 4 327 reflections to $2.9 \leqslant 2\theta \leqslant 50.0°$ at 183 K. The dynamic behaviour of the complex in solution and its mode of formation are discussed.

RECENTLY[1] we described the synthesis and structural characterisation of pentakis(alkyl isocyanide)iron complexes. The *X*-ray crystallographic study of $[Fe(CNBu^t)_5]$ revealed the presence of two highly bent radial isocyanide ligands indicating a build up of electron density at the iron atom, which was being somewhat relieved by back bonding to the isocyanide ligands. This suggested that these zerovalent isocyanide iron complexes would readily undergo oxidative-addition or -elimination reactions with suitable substrates. However, there was the possibility of more complicated reactions ensuing such as electrophilic attack at the isocyanide nitrogen atom[2] and 'insertion' reactions. Previous studies with the compounds $[Ni(CNBu^t)_4]$,[3,4] $[Pd_3(CNBu^t)_6]$,[3-5] and $[Pt_3(CNBu^t)_6]$[6] served to underline the latter possibility. Herein we describe reactions between $[Fe(CNR)_5]$ ($R = Bu^t$ or $CNC_6H_3Me_2\text{-}2,3$) and alkyl, allyl, benzyl, fluoroalkyl, and pentafluorophenyl halides, together with reactions involving trimethyloxonium tetrafluoroborate and diphenylacetylene. Some aspects of this work have been communicated already.[7]

RESULTS AND DISCUSSION

Reaction of methyl iodide with $[Fe(CNBu^t)_5]$ in tetrahydrofuran (thf) afforded a hexane-soluble brown crystalline product (1), which analysed as a 1 : 1 adduct. The i.r. spectrum showed bands at 2 135, 2 090, and 2 045 cm^{-1} assignable to terminally bonded isocyanide ligands, together with weaker bands at 1 631 and 1 571 cm^{-1} in the region for C=N stretching frequencies. The ^1H n.m.r. spectrum revealed the existence of two equivalent and three inequivalent t-butyl environments (relative intensity 18 : 9 : 9 : 9) while the methyl group resonance was downfield at τ 8.05. These observations are consistent with the illustrated static structure (Scheme 1) which incorporates a bis(imino)-group. Carbon-13 n.m.r. studies also support the structure proposed. The ligated carbon atoms [$C^{(c)}$ and $C^{(d)}$] of the isocyanide ligands would be expected to give rise to two signals, with a further two resonances due to $C^{(a)}$ and $C^{(b)}$ of the chelate ligand. At −80 °C four resonances appear in the expected shift region at 170.9, 177.3, 179.3, and 194.5 p.p.m. When the spectrum was recorded at the same temperature but with no ^1H decoupling, the signal at 179.3 p.p.m. broadened and reduced greatly in intensity compared with the others. This band is likely to be due to $C^{(a)}$, broadening resulting from unresolved $^2J(CH)$ coupling. The resonances at 170.9 and 177.3 p.p.m. were of 2 : 1 relative intensity as expected for $C^{(d)}$ and $C^{(c)}$, respectively, leaving the signal at 194.5 p.p.m. to be attributed to $C^{(b)}$. In the room temperature spectrum the resonances at 170.9 and 177.3 p.p.m. were not observed and the bands at 179.3 and 194.5 p.p.m. were weaker, probably due to decreasing relaxation.

It seemed likely that (1) was formed by successive 'insertion' reactions of t-butyl isocyanide ligands into an initially formed iron–methyl σ bond (Scheme 1). Therefore, the reaction of $[Fe(CNBu^t)_5]$ with methyl iodide in diethyl ether was examined in the belief that an ionic product would be precipitated. In agreement, a white microcrystalline product (2) was immediately formed on mixing the reagents. Elemental analysis, the presence of the terminal isocyanide stretching frequencies in the i.r. spectrum at some 60 cm^{-1} to

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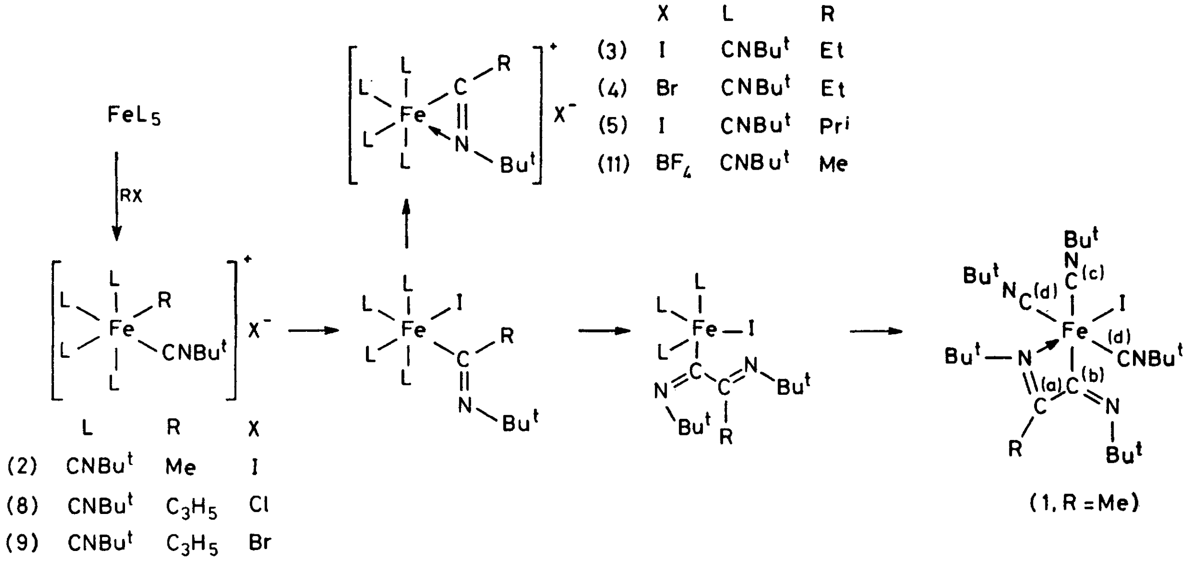
† 1—4-η-(2,3-Diphenyl-*NN'*-di-t-butylbuta-1,3-diene-1,4-diimine)tris(t-butyl isocyanide)iron.

higher wavenumbers than those observed in the spectrum of (1), together with the absence of bands in the region 1 500—2 000 cm^{-1} (C=N) strongly suggested the illustrated cationic structure. When the salt (2) was dissolved in thf, the solution rapidly darkened to brown, and the i.r. spectrum displayed identical absorptions to those found for the neutral complex (1). Thus, as indicated in Scheme 1, initial oxidative addition ($d^8 \rightarrow d^6$) affords (2), the neutral species (1) is then formed *via* successive *cis* migration of the methyl group from iron to the isocyanide contact carbon followed by *cis* migration of the resultant iminoacyl group onto a co-ordinated adjacent isocyanide. The immediate precursor to (1) could collapse to give two possible isomers. The ^{1}H n.m.r. pattern is more consistent with the structure illustrated, where the co-ordinated imino-nitrogen is *trans* to the iron–iodine bond.



Scheme 1

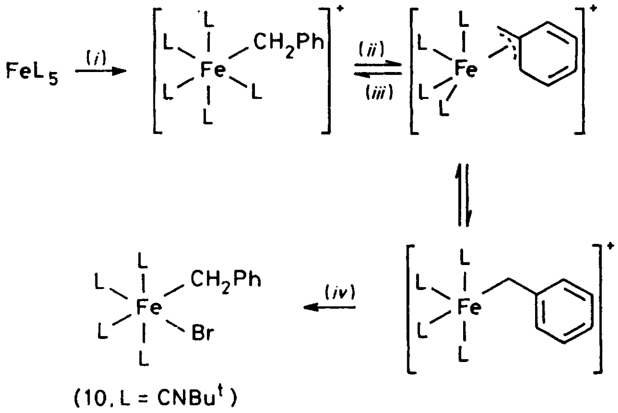
Ethyl iodide or bromide, and isopropyl iodide, also reacted rapidly in tetrahydrofuran solution with [Fe(CNBu^t)$_5$] to give compounds (3), (4), and (5) respectively. However, examination of the analytical and spectroscopic data showed that a different type of complex had been formed from that observed with methyl iodide. Elemental analysis indicated that a 1 : 1 adduct had been produced, but the i.r. spectrum in the 1 500—2 000 cm^{-1} range exhibited only one band attributable to a C=N stretching frequency at 1 750—1 760 cm^{-1}. Comparison of this stretching frequency with that observed [8-10] for the complex [Mo(CO)$_2$(η^2-MeCNPh)(η-C$_5$H$_5$)], which has been shown by *X*-ray crystallography to contain an η^2-bonded iminoacyl group, suggested that a similar bonding arrangement was involved in the iron complexes (3)—(5) (Scheme 1), and examination of the n.m.r. spectra supported this proposal. For example, the ^{1}H spectrum of (4) showed resonances assignable to two equivalent and three inequivalent t-butyl groups along with signals at τ 7.03 [q, 2 H, *J*(HH) 7, FeC(C*H*$_2$CH$_3$)=NBu^t] and 8.38 [t, 3 H, *J*(HH) 7 Hz, FeC(CH$_2$C*H*$_3$)=NBu^t].

Thus it seemed likely that the formation of compounds (3), (4), and (5) involves the intermediacy of a σ-iminoacyl species, which on co-ordination of the *imino*-nitrogen lone pair leads to displacement of halide anion and formation of a η^2-iminoacyl system. In support of this suggestion it was significant that methyl or ethyl iodide reacted in tetrahydrofuran solution with [Fe(CNC$_6$H$_3$Me$_2$-2,3)$_5$] [1] to afford the red-brown crystalline complexes (6) and (7) respectively. Their i.r. spectra displayed bands characteristic of terminally bonded linear isocyanide ligands, but showed only one weak absorption at *ca.* 1 630 cm^{-1} and an aromatic ring absorption at 1 585 cm^{-1}. The position of the latter was at too low a frequency to suggest the existence of an η^2-iminoacyl group, and the absence of any further NC bands discounted the formation of a bis(imino)-complex. This indicated that these products were σ-iminoacyl complexes, [FeI{C(R)=NC$_6$H$_3$Me$_2$-2,6}(CNC$_6$H$_3$Me$_2$-2,6)$_4$] (6,R = Me; 7, R = Et) a suggestion which was supported by both their ^{1}H and ^{13}C n.m.r. spectra. A possible rational for these findings is that in the case of (6) and (7) the lone pair located on the imino-nitrogen atom interacts with the π-electron system of the adjacent phenyl substituent. Support for this suggestion derives from the observation [10] that in the crystalline state the *X*-ray structure of the complex [Mo{σ-C(Me)=NPh}(CO)$_2${P(OMe)$_3$}(η-C$_5$H$_5$)] showed that the phenyl group adopted a conformation such that an interaction of this type could occur. The effect of such an interaction in (6) and (7) would be to decrease the donor ability of the imino-nitrogen lone pair, thereby reducing the tendency to form species like (3).

Further evidence as to the nature of the first step in these oxidative-addition reactions was provided by studying the reaction of [Fe(CNBu^t)$_5$] with 3-chloro- or 3-bromo-propene. The products (8) and (9), air-stable crystalline materials, analysed as 1 : 1 adducts. Infrared spectroscopy failed to reveal the absorption bands associated with the presence of σ- or η^2-iminoacyl groups. However, a sharp band at 1 605 cm^{-1} suggested the presence of a σ-bonded allyl group. The low solubility of the compounds in thf suggested that they were cationic six-co-ordinate species as illustrated, with five terminally bonded CNBu^t ligands and one allyl group σ-bonded to the iron.

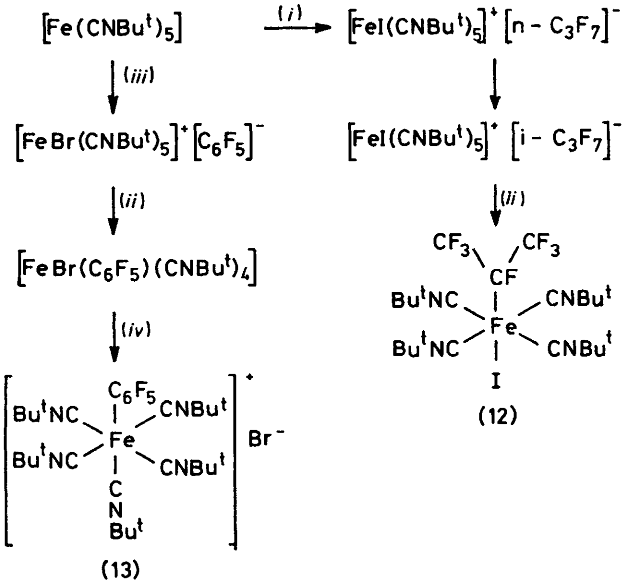
Thus, as in the reaction of [Fe(CNBu^t)$_5$] with MeI in diethyl ether, a carbon–iron σ bond is established by a formal oxidative-addition reaction. It is not possible to comment in detail on the mechanism of this initial step. However, it is interesting to note that in the reaction of *trans*-[Fe(CO)$_3$(PPh$_3$)$_2$] with halogens a reaction path involving a one-electron transfer is indicated.[11]

In contrast with these reactions, benzyl bromide reacted with [Fe(CNBu^t)$_5$] to give a neutral complex (10), which analysed as [FeBr(CH$_2$Ph)(CNBu^t)$_4$]. N.m.r. spectroscopy supported this formulation and the i.r. spectrum with four ν(NC) absorptions suggested a structure in which the σ-bonded benzyl and bromide ligands are in a relative *cis* configuration to one another. The ready loss of an isocyanide ligand is interesting, and possibly arises by the formation of a η^3-bonded benzyl complex (Scheme 2). However, attempts to effect a similar $\sigma \rightarrow \eta^3$ transformation with the σ-allyl complexes (8) and (9) were unsuccessful. By analogy with studies [12,13] on cationic isocyanide–platinum complexes, it might be assumed that the migration of the alkyl group from iron onto a *cis*-co-ordinated t-butyl isocyanide would be promoted by nucleophilic attack on iron by a halide anion. However, an indication that this might not be the case was provided by the observation that reaction of trimethyloxonium tetrafluoroborate with [Fe(CNBu^t)$_5$] afforded the yellow crystalline product (11) which analysed as a 1 : 1 adduct and showed a band in the i.r. at 1 755 cm^{-1} characteristic of the C=N stretching frequency of an η^2-bonded iminoacyl complex. Examination of the ^{1}H and ^{13}C n.m.r. spectra showed a close correspondence to the spectral features exhibited by the η^2-iminoacyl cations (3)—(5), suggesting the structure shown in Scheme 1.



SCHEME 2 (*i*) PhCH$_2$Br, (*ii*) $-$L, (*iii*) $+$L, (*iv*) $+$Br$^-$

This suggests that the methyl group migrates in a unimolecular reaction from iron onto the contact carbon atom of a *cis* isocyanide, as does CO in the carbonyl ‘ insertion ’ reaction.[14] It is interesting that our results show that allyl and benzyl groups do not readily migrate unlike methyl, ethyl, and isopropyl, and suggests a sequence of relative migratory aptitudes Pr^i $\sim$ Et $\sim$ Me $\gg$ C$_3$H$_5$ $\sim$ CH$_2$Ph similar to that found [15] in the carbonyl ‘ insertion ’ reaction.



SCHEME 3 (*i*) CF$_3$CF$_2$CF$_2$I, (*ii*) —CNBu^t, (*iii*) C$_6$F$_5$Br, (*iv*) CNBu^t

The ease with which [Fe(CNBu^t)$_5$] reacted with organic halides suggested that related oxidative reactions might occur with electronegatively substituted halides. A rapid reaction occurred between n-heptafluoropropyl iodide and [Fe(CNBu^t)$_5$] to afford in good yield the green crystalline complex (12), which was assigned the molecular formula [Fe(C$_3$F$_7$I)(CNBu^t)$_4$] on the basis of elemental analysis and a mass spectrum. The i.r. spectrum showed characteristic terminal isocyanide bands of an iron(II) complex, and examination of the ^{1}H and ^{13}C spectra suggested an octahedral structure, in which the C$_3$F$_7$ and iodine ligands have a relative *trans*-stereochemistry. Of considerable interest, and in contrast with the related reaction of [Fe(CO)$_5$],[16] was the observation that the ^{19}F spectrum (see Experimental section) showed resonances characteristic of an i- rather than a n-heptafluoropropyl group. It is suggested that this apparent fluorine migration involves an initial attack by the nucleophile [Fe(CNBu^t)$_5$] on the positive iodine of n-C$_3$F$_7$I affording an ionic species containing n-C$_3$F$_7$$^-$, which has a sufficient lifetime to undergo rearrangement *via* loss of F$^-$ and recombination with C$_3$F$_6$

to give i-$C_3F_7^-$, before undergoing charge collapse to give the product (12) (Scheme 3). Since the cation [FeI-$(CNBu^t)_5]^+$ is an 18-electron species the charge collapse is most likely preceded by dissociative loss of $CNBu^t$ * to give a stereochemically labile five-co-ordinate [FeI-$(CNBu^t)_4]^+$ species.

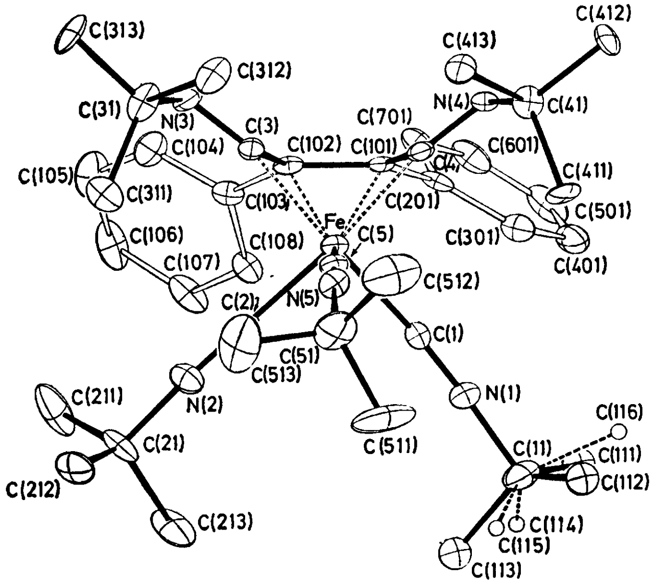


Figure 1 Molecular structure of $[Fe(CNBu^t)_3\{1\text{—}4\text{-}\eta\text{-}C(=NBu^t)=C(Ph)C(Ph)=C(=NBu^t)\}]$ (14)

A similar nucleophilic attack on positive halogen appears to occur in the reaction of $[Fe(CNBu^t)_5]$ with bromopentafluorobenzene (Scheme 3). The product (13) of the reaction was obtained in moderate yield as an orange crystalline material, fully characterised by analysis, and by i.r. and n.m.r. spectroscopy.

Pentafluorohalobenzenes react with simple nucleophiles with displacement of fluoride anion mainly in the *para* position.[17] However, both in the reaction of $[Fe(CNBu^t)_5]$ and $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ (ref. 18) with C_6F_5Br, bromide anion is apparently displaced. These results can be explained if it is assumed that the metal nucleophilic reagents attack the positive halogen as proposed for the isocyanide system.

It has been established that the reaction of isocyanides with low-valent cobalt[19] and platinum[20] acetylene complexes can lead to a formal oxidative reaction, in which the acetylene and one or two isocyanide ligands are incorporated into metalla-ring systems. These reactions are not well understood and it seemed appropriate to complete this initial survey of the oxidative reactions of $[Fe(CNBu^t)_5]$ by studying its possible reactions with acetylenes.

Treatment (room temperature) of $[Fe(CNBu^t)_5]$ with one mol equivalent of diphenylacetylene in thf led to the slow (48 h) formation of a 1 : 1 adduct (14), which was isolated as a yellow crystalline thf solvate. N.m.r. spectroscopy did not distinguish between various pos-

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* An alternative explanation, which avoids the need for this step, is to postulate that $[Fe(CNBu^t)_5]$ dissociates to form the 16-electron species $[Fe(CNBu^t)_4]$ before reaction can occur with the electrophilic reagent.

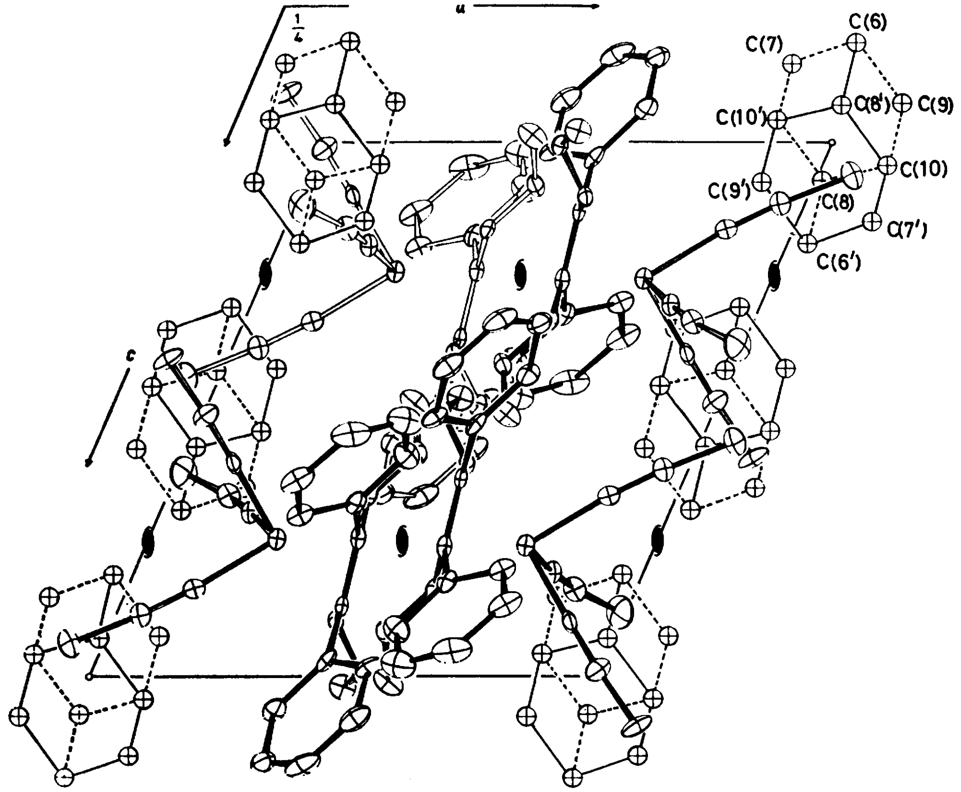


Figure 2 The contents of the unit cell of (14) viewed down the *b* axis towards the origin. Methyl groups omitted for clarity. The toluene solvate molecule is included showing symmetry-related disorder about an inversion centre

sible structures, and therefore a single-crystal *X*-ray diffraction study was undertaken with a suitable crystal of a toluene solvate obtained on crystallisation of (14) from toluene.

The molecular structure of (14) in its toluene solvate is illustrated in Figure 1, which also shows the crystallographic numbering system. The iron atom lies 1.49 Å from the mean plane [C(3),C(4),C(101),C(102)] of the bis(t-butylimino)diphenylbuta-1,3-diene fragment in a distorted-pyramidal arrangement with C(5) at the apex, and C(1), C(2), C(102,3), and C(101,4) [the midpoints of C(3)–C(102) and C(4)–C(101)] forming the base. The iron atom is displaced 0.57 Å from the mean of these basal atoms.

The iron–carbon separations are comparable with those found [21] in other iron–η^4-buta-1,3-diene systems, with two of the carbon atoms significantly closer to the metal, the absolute values varying with the nature of the remainder of the ring. Whereas, normally the ' open ' end of the diene is the furthest from the metal atom this is not the case for complex (14) where the end carbon atoms C(3) and C(4) attached to the nitrogen atoms are the closest to the iron atom [mean Fe–C(3) and Fe–C(4), 1.96 Å; mean Fe–C(101) and Fe–C(102) 2.12 Å]. In the bis(t-butylimino)diphenylbuta-1,3-diene fragment there is some evidence of delocalisation in that C(4)–C(101) 1.44(1) Å, and C(3)–C(102), 1.45(1) Å, are shorter than expected for single σ-bonded carbon–carbon bonds, and the C(101)–C(102) bond [1.42(1) Å], originally the central C–C bond of the diphenylacetylene, is of similar length.

The angles at the distal nitrogen atoms N(3) and N(4) of 123 and 122°, respectively, reflect a dominant sp^2 character in the nitrogen hybridisation. The bending of the normally linear iminoketene illustrated by the angles N(3)C(3)C(102) of 129° and N(4)C(4)C(101) of 127° is a consequence of substantial back donation from the iron to the lowest-lying unfilled π molecular orbital (m.o.) (*a*′ local symmetry) of the butadiene fragment. This compares with a bend-back angle of 130.8° observed with a related co-ordinated ketene [O=C $\underline{\cdot\,\cdot\,\cdot}$ C(Me)–C(Me) $\underline{\cdot\,\cdot\,\cdot}$ C–] complex.[22]

While the bonding distances of the carbon atoms of the two equivalent isocyanide ligands [Fe–C(1), 1.864(11) Å; Fe–C(2), 1.862(8) Å] are consistent with only minimal back donation from the iron atom, the significantly shorter distance for the unique isocyanide [Fe–C(5), 1.813(8) Å] suggests considerable multiple-bond character to this ligand.[1] This is supported by the observation that the angle at N(5) is non-linear [165(1)°] compared with the corresponding angles of the other two isocyanides [C(1)N(1)C(11), 175.4(8)°; C(2)N(2)C(21), 177(1)°]. The packing of the molecule within the monoclinic unit cell is shown in Figure 2, there being no significant short intermolecular contacts.

With the establishment of the solid-state structure of (14) it is possible to discuss the solution n.m.r. spectra of the complex. The asymmetry of the molecule in the crystal is not reflected in any of the n.m.r. spectra, which showed at 0 °C three t-butyl environments. As is shown in Figure 3, the complex exhibits reversible dynamic behaviour, the low-field signal (18 H) being essentially temperature invariant. However, on warming progressively to 120 °C the signals at τ 8.6 (9 H) and 8.93 (18 H) coalesce at 60 °C to give a fully time-averaged spectrum at 120 °C. Although the estimated [23] energy barrier ($\Delta G_{T_c}^{\ddagger}$ 68 ± 1 kJ mol^{-1}, $\Delta V = 47 \pm 2$ Hz, $T_c = 333 \pm 5$ K, $P_A = \frac{2}{3}$, $P_B = \frac{1}{3}$) is considerably higher than those found (*ca.* 35 kJ mol^{-1}) for tricarbonyl-

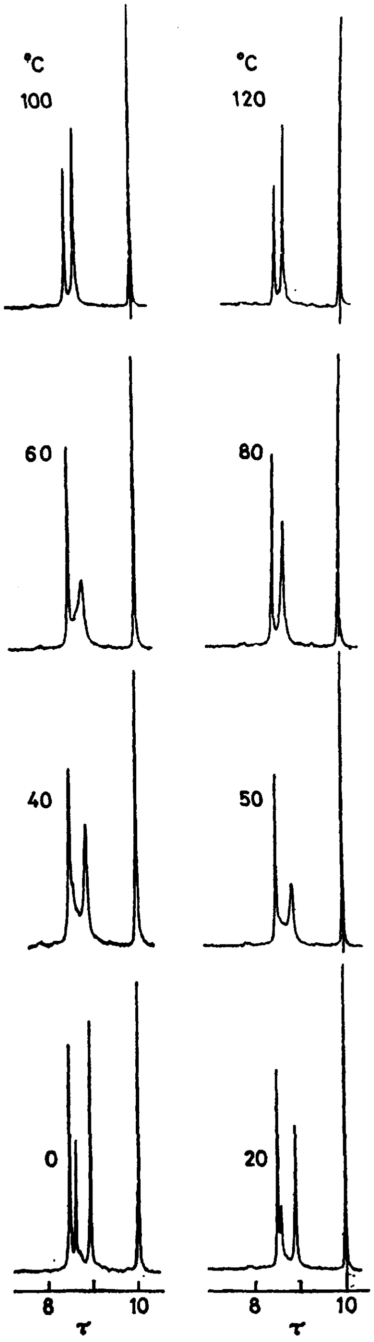
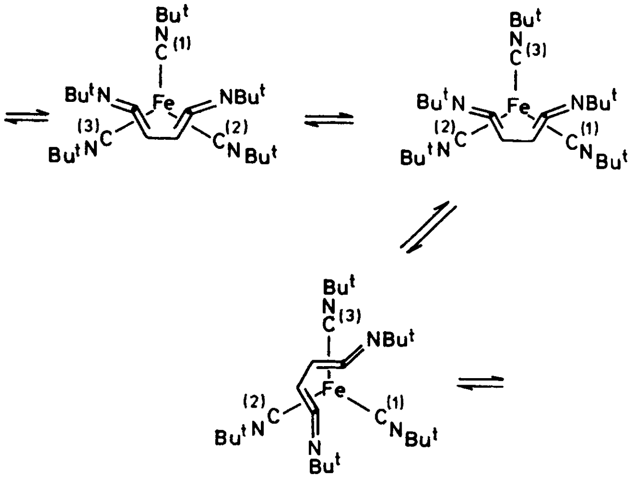


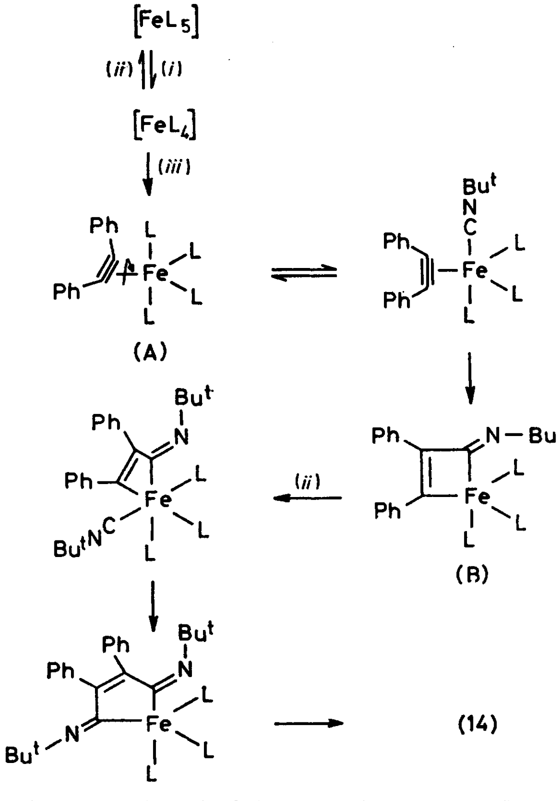
FIGURE 3 Variable-temperature ^1H n.m.r. spectra of [Fe(CNBu^t)$_3${1—4-η-C(=NBu^t)=C(Ph)C(Ph)=C(=NBu^t)}] (14) measured in C_6H_5Cl in the region τ 8—10

(1,3-diene)iron complexes, it is suggested that a similar rotational process occurs with (14) in solution to that postulated[24] for the tricarbonyl complexes (Scheme 4).



SCHEME 4

The formation of the complex (14) may be viewed in its initial stages as one involving an oxidative reaction at the iron centre. Capture of an $[Fe(CNBu^t)_4]$ species



SCHEME 5 L = CNBu^t, (*i*) —L, (*ii*) L, (*iii*) PhC_2Ph

formed in a dissociative process by a molecule of diphenylacetylene results in the formation of a η^2-bonded diphenylacetylene iron(0) complex (A) (Scheme 5). If the η^2-bonded acetylene is now rotated then an oxidative cyclisation reaction can occur analogous to the formation of a metallacyclobutane postulated[25] to be involved in olefin metathesis. The *cis*-isocyanide ligand replaces the isoelectronic co-ordinated carbene and the η^2-diphenylacetylene ligand using only two of its orthogonal π electrons replaces the olefin. Reaction of the resultant 16-electron species (B) with free isocyanide affords an octahedral 18-electron species, which can form (14) by intramolecular migration of the σ-bonded vinyl system from the iron to the adjacent contact carbon atom of a co-ordinated isocyanide. There is precedent for both these reactions in cobalt[19] and platinum[20] chemistry.

EXPERIMENTAL

N.m.r. spectra (^1H, ^{19}F, proton-decoupled ^{13}C) were recorded on Varian Associates HA100 and JEOL PS and PFT spectrometers, with ^{13}C shifts relative to $SiMe_4$ (0.0 p.p.m.) and ^{19}F shifts relative to CCl_3F (0.0 p.p.m.). Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer as Nujol mulls unless otherwise stated. Mass spectra were measured at 70 eV * on an AEI MS 902 spectrometer. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere, with solvents dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction with b.p. 40—60 °C.

Reactions of Pentakis(t-butyl isocyanide)iron.—(a) *With methyl iodide.* To a stirred solution of $[Fe(CNBu^t)_5]$[1] (0.3 g, 0.64 mmol) in dry degassed thf (10 cm^3) was added drop-wise freshly distilled methyl iodide (1 cm^3, 10%, 14 mmol) in the same solvent. After initial discharge of the yellow colour of the starting material, the solution gradually darkened over a period of 3 to 5 min. Stirring was continued for a further 10 min before removing volatile material *in vacuo*. The resultant oil was extracted with light petroleum (8 cm^3), producing a brown solution which was filtered and cooled (—20 °C) to afford orange-brown *crystals* of $[Fe(I)\{C(=NBu^t)C(Me)=NBu^t\}(CNBu^t)_3]$ (1) (0.42 g, 70%) (Found: C, 50.9; H, 8.2; I, 20.7; N, 11.4. $C_{26}H_{48}FeIN_5$ requires C, 50.9; H, 7.8; I, 20.7; N, 11.4%), $\nu_{max.}$ at 2 135m (sh), 2 090s, 2 045s (sh), 1 631m, 1 571m, 1 241m, 1 216s, 946w, and 906m cm^{-1}. N.m.r.: ^1H (C_6D_6, room temperature), τ 8.05 (s, 3 H, Me), 8.33 (s, 9 H, Bu^t), 8.36 (s, 9 H, Bu^t), 8.73 (s, 9 H, Bu^t), and 8.75 (s, 18 H, Bu^t); ^{13}C ($C_6D_5CD_3$, 20 °C), δ 14.1 $[FeC(=NBu^t)C(\mathit{Me})]$, 30.7, 31.1 $(CNC\mathit{Me}_3)$, 55.2, 56.2, 61.9 $(CN\mathit{C}Me_3)$, 179.7 $[FeC(=NBu^t)\mathit{C}(Me)]$, and 194.1 p.p.m. $[Fe\mathit{C}(=NBu^t)C(Me)]$; ^{13}C ($C_6D_5CD_3$, —80 °C), δ 14.1 $[FeC(=NBu^t)C(\mathit{Me})]$, 30.3, 30.7 $(CNC\mathit{Me}_3)$, 55.3, 56.1, 56.3, 62.1 $(CN\mathit{C}Me_3)$, 170.9, 177.3 $(Fe\mathit{C}NBu^t)$, 179.3 $[FeC(=NBu^t)\mathit{C}(Me)]$, and 194.5 p.p.m. $[Fe\mathit{C}(=NBu^t)C(Me)]$.

Freshly distilled MeI (0.3 g, 2 mmol), dissolved in diethyl ether (2 cm^3) was added drop-wise to a stirred solution of $[Fe(CNBu^t)_5]$ (0.5 g, 1.1 mmol) in diethyl ether (10 cm^3). The resulting white precipitate was allowed to settle before removing the supernatant liquid with a syringe. The product was washed with diethyl ether (3 × 5 cm^3), and dried *in vacuo* to give white *microcrystals* of $[FeMe(CNBu^t)_5]I$ (2) (0.55 g, 90%) (Found: C, 50.1; H, 7.9; I, 20.8; N, 11.1. $C_{26}H_{48}FeIN_5$ requires C, 50.9; H, 7.8; I, 20.7;

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

N, 11.4%), $\nu_{max.}$ at 2 190w(sh), 2 130s, 2 055m(sh), 1 236m-(sh), 1 204s, 724w, 589w(sh), and 579m cm^{-1}.

(b) *With ethyl iodide.* Freshly distilled, degassed ethyl iodide (0.5 g, 3 mmol) was added drop-wise to a stirred solution of $[Fe(CNBu^t)_5]$ (0.5 g, 1.1 mmol) in thf. After 15 min, the solution was concentrated *in vacuo* and diethyl ether added to give on cooling (−78 °C) pale yellow *crystals* of $[Fe(CNBu^t)_4(\eta^2\text{-}EtCNBu^t)]I$ (3) (0.45 g, 71%) (Found: C, 51.1; H, 8.2; I, 22.2; N, 10.6. $C_{27}H_{50}FeIN_5$ requires C, 51.5; H, 7.9; I, 20.5; N, 11.1%), $\nu_{max.}$ at 2 170m(sh), 2 145s(sh), 2 125s, 1 761m, 1 329m(sh), 1 201s, 1 098w, 1 041w, 931w, and 838w cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$, room temperature), τ 7.05 [q, 2 H, CH_2, *J*(HH) 7 Hz], 8.35 (s, 9 H, Bu^t), 8.42 [t, 3 H, Me, *J*(HH) 7 Hz], 8.5 (s, 9 H, Bu^t), 8.63 (s, 18 H, Bu^t), and 8.75 (s, 9 H, Bu^t).

(c) *With ethyl bromide.* Ethyl bromide (0.3 g, 2.8 mmol), freshly distilled, was added drop-wise to a stirred solution of $[Fe(CNBu^t)_5]$ (0.5 g, 1.1 mmol) in thf (10 cm^3). After 15 min the solution was concentrated, diethyl ether added, and cooled (−78 °C) to give pale straw coloured *crystals* of $[Fe(CNBu^t)_4(\eta^2\text{-}EtCNBu^t)]Br$ (4) (0.48 g, 69%) (Found: C, 55.4; H, 8.8; N, 11.9. $C_{27}H_{50}BrFeN_5$ requires C, 55.8; H, 8.6; N, 12.1%), $\nu_{max.}$ at 2 170m(sh), 2 120s, 2 045s(sh), 1 761m, 1 233m(sh), 1 196s, 1 105w, 1 090w(sh), 993m, 848m, 740w, 575m, and 555m(sh). N.m.r.: ^{1}H [$(CD_3)_2CO$, room temperature], τ 7.03 [q, 2 H, CH_2, *J*(HH) 7 Hz], 8.32 (s, 9 H, Bu^t), 8.38 [t, 3 H, Me, *J*(HH) 7 Hz], 8.47 (s, 9 H, Bu^t), 8.57 (s, 18 H, Bu^t), and 8.67 (s, 9 H, Bu^t); ^{13}C [$(CD_3)_2CO$, room temperature], δ 12.6 (*Me*), 25.6 ($\mathit{C}H_2$), 29.2, 29.3, 30.7, 31.2 ($CNC\mathit{Me}_3$), 56.9, 57.6, 58.1 ($\mathit{C}Me_3$), and 185.8 p.p.m. [$Fe\mathit{C}(Et)=NBu^t$].

(d) *With isopropyl iodide.* An excess of isopropyl iodide (0.5 cm^3) (freshly distilled) was added drop-wise to a stirred solution of $[Fe(CNBu^t)_5]$ (0.47 g, 1.0 mmol) in thf (15 cm^3). After 20 min, diethyl ether (5 cm^3) was added to give pale yellow *crystals* of $[Fe(CNBu^t)_4(\eta^2\text{-}Pr^iCNBu^t)]I$ (5) (0.35 g, 60%) (Found: C, 51.8; H, 8.4; N, 9.6. $C_{28}H_{52}FeIN_5$ requires C, 52.4; H, 8.1; N, 10.7%), $\nu_{max.}$ at 2 172s, 2 120vs, 2 090(sh), 2 050(sh), 1 750m, 1 230m(sh), 1 195s, 1 118w, 955w, 820w, 740w, 730w, and 720w cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$, room temperature), τ 6.61 [sep., 1 H, CH, *J*(HH) 7 Hz], 8.34 (s, 9 H, Bu^t), 8.5 (s, 9 H, Bu^t), 8.63 (overlapping s and d, 24 H, $CH\mathit{Me}_2$, Bu^t), and 8.75 (s, 9 H, Bu^t); ^{13}C ($CDCl_3$, room temperature), δ 20.1 ($CH\mathit{Me}_2$), 29.2 ($CNC\mathit{Me}_3$), 30.0 ($\mathit{CH}Me_2$), 30.7, 31.2 ($CNC\mathit{Me}_3$), 56.1, 56.7, 57.1 ($C\mathit{Me}_3$), 163.8, 167.6 ($Fe\mathit{C}NBu^t$), and 186.5 p.p.m. [$Fe\mathit{C}(Pr^i)=N$].

(e) *With trimethyloxonium tetrafluoroborate.* To a solution of $[Fe(CNBu^t)_5]$ (0.5 g, 1.1 mmol) in thf (15 cm^3) was added trimethyloxonium tetrafluoroborate (0.16 g, 1.1 mmol). After 15 min, the yellow stirred solution was concentrated *in vacuo*, diethyl ether added, and the mixture cooled (−20 °C) to give yellow *needles* of $[Fe(CNBu^t)_4(\eta^2\text{-}MeCNBu^t)][BF_4]$ (11) (0.49 g, 79%) (Found: C, 54.7; H, 8.3; N, 12.5. $C_{26}H_{48}BF_4FeN_5$ requires C, 54.5; H, 8.4; N, 12.2%), $\nu_{max.}$ ($CHCl_3$) at 2 178s(sh), 2 140vs, 2 130vs, 2 070s(sh), 1 755m, 1 180m, and 1 055s, br cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$, room temperature), τ 7.16 (s, 3 H, Me), 8.35 (s, 9 H, Bu^t), 8.5 (s, 9 H, Bu^t), 8.61 (s, 18 H, Bu^t), and 8.74 (s, 9 H, Bu^t); ^{13}C ($CDCl_3$, room temperature), δ 29.7, 30.1, 30.5, 30.7 ($CNC\mathit{Me}_3$), 56.4, 58.9, 59.2, and 59.5 p.p.m. ($CN\mathit{C}Me_3$).

(f) *With 3-chloropropene.* To a stirred solution of $[Fe(CNBu^t)_5]$ (0.47 g, 1 mmol) in thf (15 cm^3) was added 3-chloropropene (0.2 cm^3). The solution became colourless and on cooling (−78 °C) fine needle crystals were deposited. Recrystallisation (−20 °C) from dichloromethane–diethyl ether (1 : 1) afforded colourless *crystals* of $[Fe(CH_2CH=CH_2)(CNBu^t)_5]Cl$ (8) (0.4 g, 73%) (Found: C, 61.0; H, 9.4; N, 12.6. $C_{28}H_{50}ClFeN_5$ requires C, 61.4; H, 9.1; N, 12.8%), $\nu_{max.}$ at 2 191m(sh), 2 131s, 2 050m(sh), 1 605m, 1 241m, 1 200s, 986w, 860m, and 730w cm^{-1}. N.m.r.: ^{1}H [$(CD_3)_2CO$, room temperature], τ 3.6—4.2 (m, 1 H, CH), 5.2—5.7 (m, 2 H, $C=CH_2$) and 8.45 (m, br, 47 H, CH_2Fe, Bu^t); ^{13}C (CD_3CN, room temperature), δ 14.4 ($Fe\mathit{C}H_2$), 30.9 ($CNC\mathit{Me}_3$), 55.3, 55.8 ($CN\mathit{C}Me_3$), 102.9 ($CH=\mathit{C}H_2$), and 151.4 p.p.m. ($\mathit{C}H=CH_2$).

(g) *With 3-bromopropene.* Similarly, reaction of $[Fe(CNBu^t)_5]$ (0.5 g, 1.1 mmol) with 3-bromopropene (0.5 cm^3) in thf (15 cm^3) gave on cooling (−78 °C) and addition of diethyl ether colourless *microcrystals* of $[Fe(CH_2CH=CH_2)(CNBu^t)_5]Br$ (9) (0.51 g, 80%) (Found: C, 56.1; H, 8.9; N, 10.6. $C_{28}H_{50}BrFeN_5$ requires C, 56.8; H, 8.5; N, 11.8%), $\nu_{max.}$ at 2 185m(sh), 2 160s(sh), 2 120vs, 2 045m(sh), 1 605m, 1 236m, 1 196s, 986w, 856m, and 726w cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$, room temperature), τ 3.7—4.05 (m, 1 H, CH), 5.2—5.6 (m, 2 H, $C=CH_2$), 8.38—8.47 (m, br, 47 H, CH_2Fe, Bu^t); ^{13}C ($CDCl_3$, room temperature), δ 14.0 ($Fe\mathit{C}H_2$), 30.6, 30.9 ($CNC\mathit{Me}_3$), 57.3, 58.9 ($CN\mathit{C}Me_3$), 102.7 ($CH=\mathit{C}H_2$), 150.0 ($\mathit{CH}=CH_2$), 156.8, and 159.9 p.p.m. ($\mathit{C}NCMe_3$).

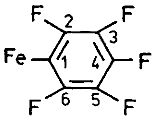
(h) *With benzyl bromide.* To a stirred solution of $[Fe(CNBu^t)_5]$ (0.6 g, 1.3 mmol) in thf (15 cm^3) was added benzyl bromide (0.5 cm^3) drop-wise. The volatile material was removed *in vacuo* and the residue triturated with light petroleum to give crystalline material. Recrystallisation (−20 °C) from thf–light petroleum afforded yellow *crystals* of *cis*-$[FeBr(CNBu^t)_4(\sigma\text{-}CH_2Ph)]$ (10) (0.45 g, 76%) (Found: C, 56.0; H, 7.8; N, 10.4. $C_{17}H_{43}BrFeN_4$ requires C, 56.0; H, 7.7; N, 10.0%), $\nu_{max.}$ (CH_2Cl_2) 2 220m(sh), 2 180vs, 2 150vs, 2 060s(sh), $\nu_{max.}$ at 2 210m(sh), 2 170s(sh), 2 130vs, 2 050m(sh), 1 588m, 1 235m, 1 200s, 745m, 725w, 695m, and 580s cm^{-1}. N.m.r.: ^{1}H [$(CD_3)_2CO$, room temperature], τ 2.85—2.9 (m, 5 H, C_6H_5), 6.5 (s, 2 H, CH_2), 8.38 (s, 18 H, Bu^t), and 8.47 (s, 18 H, Bu^t); ^{13}C ($CDCl_3$, room temperature), δ 14.9 ($Fe\mathit{CH}_2$), 30.6, 30.7 ($CNC\mathit{Me}_3$), 57.4, 58.9 ($CN\mathit{C}Me_3$), 121.9 ($m\text{-}\mathit{C}_6H_5$), 126.1 ($p\text{-}\mathit{C}_6H_5$), 127.9 ($o\text{-}\mathit{C}_6H_5$), 150.4, 155.8, and 159.1 p.p.m. ($\mathit{C}NBu^t$).

Reactions of Pentakis(2,6-*dimethylphenyl isocyanide*)-*iron*.—(a) *With methyl iodide.* An excess of freshly distilled methyl iodide (0.2 cm^3) was added to a stirred solution of $[Fe(CNC_6H_3Me_2\text{-}2,6)_5]$ (0.4 g, 0.6 mmol) in thf (15 cm^3). After 30 min the red-brown solution was concentrated *in vacuo*, diethyl ether (7 cm^3) added, and the mixture cooled (−78 °C) to give fine brown *crystals* of *cis*-$[FeI\{C(Me)=NC_6H_3Me_2\text{-}2,6\}(CNC_6H_3Me_2\text{-}2,6)_4]$ (6) (0.4 g, 84%) (Found: C, 65.5; H, 6.1; N, 8.2. $C_{46}H_{48}FeIN_5$ requires C, 64.7; H, 5.6; N, 8.2%), $\nu_{max.}$ at 2 135m, 2 090vs, 2 075vs, 1 630m, 1 585m, 1 180w, 1 165w, 1 090w, 890m, 820w, 775m, 770(sh), 760(sh), and 720w cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$, room temperature), τ 2.7—3.8 (m, 15 H, $C_6\mathit{H}_3$), 7.32 (s, 12 H, CMe), 7.58 (s, 6 H, CMe), 7.64 (s, 6 H, CMe), 7.98 (s, 6 H, CMe), 8.04 (s, 3 H, Me); ^{13}C ($CDCl_3$, −50 °C), δ 15.1 (*Me*), 18.4, 19.4, 19.5, 20.0 ($C_6H_3\mathit{Me}_2$), 121.9, 122.8, 124.6, 125.8, 126.7, 126.9, 127.6, 128.0, 128.6, 129.3, 133.1, 135.4, 142.2, 149.6 ($\mathit{C}_6H_3Me_2$), 176.7, 178.8, 185.7 ($Fe\mathit{C}N$), and 201.00 p.p.m. [$Fe\mathit{C}(Me)=N$].

(b) *With ethyl iodide.* A similar reaction between ethyl iodide (0.2 g, 1.3 mmol) and $[Fe(CNC_6H_3Me_2\text{-}2,6)_5]$ (0.71 g, 1 mmol) in thf (15 cm^3) afforded orange-brown *needles* of *cis*-$[FeI\{C(Et){=}NC_6H_3Me_2\text{-}2,6\}(CNC_6H_3Me_2\text{-}2,6)_4]$ (7) (0.72 g, 81%) (Found: C, 65.3; H, 6.3; I, 14.2; N, 7.8. $C_{47}H_{50}FeIN_5$ requires C, 65.1; H, 5.7; I, 14.2; N, 8.1%), $\nu_{max.}$ at 2 155m, 2 105vs, 1 633m, 1 585m, 1 166w, 1 086w, 875w, 838w, 781m, and 720w cm^{-1}. N.m.r. resonances: ^1H ($CDCl_3$, room temperature), τ 2.7—3.8 (m, C_6H_3), 7.54 (s, 12 H, Me), 7.63 (s, 6 H, Me), 8.05 (overlapping m, 14 H, Me, CH_2), and 8.68 [t, 3 H, *J*(HH) 7 Hz]; ^{13}C ($CDCl_3$, room temperature), δ 11.5 ($CH_2\mathit{Me}$), 17.9, 18.2, 18.9, 19.4 ($C_6H_3\text{-}\mathit{Me}_2$), 23.9 ($\mathit{C}H_2Me$), 122.9, 124.0, 127.6, 128.4, 128.9, 129.4, 129.7, 130.0, 133.5, 134.7 (C_6H_3), 142.6, 149.1 ($FeCN\mathit{C}$), 172.3 (2 × $Fe\mathit{C}N$), 187.4 ($Fe\mathit{C}N$), and 196.9 p.p.m. [$Fe\mathit{C}\text{-}(Et){=}N$].

Reaction of n*-Heptafluoropropyl Iodide with Pentakis(*t*-butyl isocyanide)iron.*—Freshly distilled n-C_3F_7I (0.2 g, 0.8 mmol) was condensed (−196 °C) into a solution of $[Fe(CNBu^t)_5]$ (0.3 g, 0.6 mmol) in light petroleum (15 cm^3). After 30 min at room temperature the volume of the solvent was reduced *in vacuo* and the solution cooled (−20 °C) to give green *microcrystals* of *trans*-$[FeI\{CF(CF_3)_2\}(CNBu^t)_4]$ (12) (0.3 g, 70%), m.p. 140—141 °C (Found: C, 40.4; H, 5.5; N, 8.1. $C_{23}H_{36}F_7FeIN_5$ requires C, 40.4; H, 5.3; N, 8.2%), $\nu_{max.}$ ($CHCl_3$) at 2 125vs, 2 055m(sh), 1 476w(sh), 1 461m, 1 401w, 1 374m, 1 278m, 1 251m, 1 196m, 1 163s, 1 101m, 1 031w, br, 991m, 931m, 866m, and 571m cm^{-1}. N.m.r.: ^1H ($CDCl_3$, room temperature), τ 8.5 (s, Bu^t); ^{13}C ($CDCl_3$, room temperature), δ 30.5 ($CNC\mathit{Me}_3$), 56.4 ($CN\mathit{C}Me_3$), and 162.5 p.p.m. ($\mathit{C}NBu^t$); ^{19}F [$(CD_3)_2CO$, room temperature], δ 67.8 [d, 6 F, CF_3, ^3J(FF) 11 Hz] and 175 p.p.m. [sep., 1 F, CF, ^3J(FF) 11 Hz]. The mass spectrum showed peaks at *m*/*e* 686, 474, 432, 349, 324, and 241, corresponding to the ions $[FeI\{CF(CF_3)_2\}(CNBu^t)_4]^+$, $[Fe\{CF(CF_3)_2\}(CNBu^t)_3]^+$, $[FeI(CNBu^t)_3]^+$, $[FeI(CNBu^t)_2]^+$, $[FeF(CNBu^t)_3]^+$, and $[FeF(CNBu^t)_2]^+$ respectively.

*Reaction of Bromopentafluorobenzene with Pentakis(*t*-butyl isocyanide)iron.*—Bromopentafluorobenzene (0.25 g, 1 mmol) was added drop-wise with stirring to a solution of $[Fe(CNBu^t)_5]$ (0.47 g, 1 mmol) in thf (20 cm^3). The solvent was removed *in vacuo* and the residue extracted with thf–diethyl ether. The extract was cooled (−20 °C) to give orange *crystals* of $[Fe(C_6F_5)(CNBu^t)_5]Br$ (13) (0.43 g, 60%), m.p. 140—143 °C (Found: C, 51.8; H, 6.7; Br, 11.5; N, 9.8. $C_{31}H_{45}BrF_5FeN_5$ requires C, 51.8; H, 6.3; Br, 11.1; N, 9.7%), $\nu_{max.}$ at 2 185m(sh), 2 130vs, 2 085(sh), 1 575m(sh), 1 565m, 1 505s, 1 395w, 1 355m, 1 275w, 1 230m(sh), 1 215s, 1 200s(sh), 1 085s, 980s, 925w, 850w, 810m, 735m, 595m, 570m, and 440w cm^{-1}. N.m.r.: ^1H ($CDCl_3$, room temperature), τ 8.38 (s, 9 H, Bu^t), 8.5 (s, 36 H, Bu^t); ^{13}C ($CDCl_3$, room temperature), δ 30.4 ($CNC\mathit{Me}_3$), 30.9 ($CNC\mathit{Me}_3$), 58.4 ($CN\mathit{C}Me_3$), 58.9 ($CN\mathit{C}Me_3$), 153.2 p.p.m. ($\mathit{C}NCMe_3$); ^{19}F ($CHCl_3$, room temperature), δ 108.4 (m, 2 F, F^2, F^6), 157.2 (m, 1 F, F^4) and 159.9 p.p.m. (m, 2 F, F^3, F^5), where $J(F^2F^3) = J(F^5F^6)$ 21 Hz, and $J(F^3F^4) = J(F^4F^5)$ 21 Hz.



Reaction of Pentakis(t-butyl isocyanide)iron with Diphenylacetylene.—To a solution of $[Fe(CNBu^t)_5]$ (3.7 g, 7.8 mmol) in degassed thf (20 cm^3) was added diphenylacetylene (1.4 g, 8 mmol). The solution was stirred at room temperature for 48 h. The solvent was removed *in vacuo* and the resultant oil recrystallised (−20 °C) from thf–hexane to afford yellow *crystals* of the thf solvate (14) $[Fe(CNBu^t)_3\{1\text{—}4\text{-}\eta\text{-}C({=}NBu^t)C(Ph)C(Ph){=}C({=}NBu^t)\}]\cdot C_4H_8O$ (4 g, 62%) (Found: C, 71.5; H, 8.7; N, 9.8. $C_{43}H_{63}FeN_5O$ requires C, 71.5; H, 8.7; N, 9.7%), $\nu_{max.}$ at 3 025w, 2 115s, 2 080s, 2 040s, 1 666m, 1 641m, 1 617(sh), 1 603(sh), 1 500w, 1 375w, 1 360m, 1 240(sh), 1 220s, 1 080w, 1 050w, 1 035w, 970w, 930w, 884m, 850w, 795m, 785m, 775m, 767(sh), 749w, 710m, 669w, 568m, 515w, 491w, and 460w cm^{-1}. N.m.r.: ^1H ($CDCl_3$, room temperature), τ 2.5—2.6 (m, 10 H, Ph), 8.48 (s, 9 H, Bu^t), 8.65 (s, 18 H, Bu^t), 8.78 (s, 18 H, Bu^t); ^1H (C_6H_5Cl, 0 °C), τ

TABLE 1

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (14)

Atom	*x*	*y*	*z*
Fe	0.252 85(15)	0.138 20(3)	0.243 67(17)
C(1)	0.133 4(10)	0.132 75(2)	0.336 2(8)
N(1)	0.049 2(9)	0.130 1(2)	0.384 6(7)
C(11)	−0.065 27	0.128 6(3)	0.438 5(11)
C(111) *	−0.003 6(22)	0.102 0(4)	0.549 6(17)
C(112) *	−0.081 3(26)	0.160 3(5)	0.494 7(22)
C(113) *	−0.205 0(26)	0.110 0(5)	0.329 7(22)
C(114) *	−0.130 0(75)	0.101 2(15)	0.434 6(62)
C(115) *	−0.192 8(65)	0.153 6(13)	0.355 8(52)
C(116) *	0.018 8(72)	0.146 9(14)	0.575 6(57)
C(2)	0.101 5(10)	0.119 6(2)	0.102 2(8)
N(2)	0.005 0(10)	0.108 1(2)	0.013 3(7)
C(21)	−0.117 7(11)	0.093 0(2)	0.092 8(10)
C(211)	−0.050 1(16)	0.067 4(3)	−0.147 7(12)
C(212)	−0.199 5(12)	0.119 1(3)	−0.193 9(10)
C(213)	−0.229 0(15)	0.080 2(3)	−0.034 2(11)
C(3)	0.397 1(9)	0.132 7(2)	0.163 6(8)
N(3)	0.455 5(8)	0.139 0(2)	0.082 5(7)
C(31)	0.406 4(12)	0.166 0(2)	−0.009 2(9)
C(311)	0.237 1(13)	0.163 1(2)	−0.095 7(10)
C(312)	0.442 0(13)	0.197 5(2)	0.067 7(11)
C(313)	0.504 3(14)	0.163 1(3)	−0.087 7(11)
C(4)	0.438 8(10)	0.144 7(2)	0.395 8(8)
N(4)	0.532 5(8)	0.159 5(2)	0.492 0(7)
C(41)	0.509 8(11)	0.193 7(2)	0.519 5(9)
C(411)	0.358 1(11)	0.197 9(2)	0.530 4(10)
C(412)	0.637 8(11)	0.201 1(2)	0.649 9(9)
C(413)	0.523 3(12)	0.215 4(2)	0.413 5(9)
C(5)	0.177 4(10)	0.177 6(2)	0.194 3(8)
N(5)	0.119 5(9)	0.202 8(2)	0.161 8(7)
C(51)	0.013 0(13)	0.229 3(3)	0.120 5(12)
C(511)	−0.113 7(16)	0.219 4(3)	0.166 4(17)
C(512)	0.093 3(18)	0.259 5(3)	0.187 8(18)
C(513)	−0.046 6(26)	0.231 3(5)	−0.025 1(14)
C(101)	0.438 2(9)	0.111 3(2)	0.369 4(8)
C(102)	0.410 5(10)	0.104 1(2)	0.239 3(8)
C(103)	0.375 6(10)	0.072 4(2)	0.176 5(8)
C(104)	0.434 7(12)	0.064 0(2)	0.087 9(10)
C(105)	0.401 5(15)	0.035 4(3)	0.023 9(11)
C(106)	0.307 3(16)	0.014 8(2)	0.048 8(10)
C(107)	0.242 7(13)	0.021 8(2)	0.134 1(10)
C(108)	0.277 4(11)	0.051 0(2)	0.198 5(8)
C(201)	0.454 8(9)	0.086 8(2)	0.470 5(8)
C(301)	0.540 8(11)	0.059 8(2)	0.481 7(9)
C(401)	0.561 1(13)	0.037 4(1)	0.579 1(10)
C(501)	0.499 8(14)	0.042 2(3)	0.666 0(11)
C(601)	0.417 5(12)	0.070 0(3)	0.658 7(10)
C(701)	0.395 7(11)	0.092 3(2)	0.561 6(9)
Toluene molecule			
C(6) *	−0.041 1(37)	0.021 2(7)	0.307 7(25)
C(7) *	−0.145 9(53)	0.007 8(13)	0.349 2(52)
C(8) *	0.017 0(46)	−0.009 0(7)	0.570 8(43)
C(9) *	0.103 9(54)	0.021 1(11)	0.426 3(43)
C(10) *	0.130 8(25)	0.005 9(5)	0.545 3(27)

* Disordered, see text.

8.46 (s, 18 H), 8.6 (s, 9 H), 8.93 (s, 18 H); ^{1}H (C_6H_5Cl, 120 °C) τ 8.54 (s, 18 H), 8.73 (s, 27 H); ^{13}C ($CDCl_3$, room temperature), δ 30.4, 30.8, 31.2 (C*Me*$_3$), 55.0, 55.3, 55.6 (*C*Me$_3$), 72.0 [Bu^{t}N=C=*C*(Ph)*C*(Ph)=C=NBu^t], 125.7, 126.6, 131.7, 137.5 (*C*$_6$H$_6$), 167.9, 175.2 (Fe*C*N), and 203.3 p.p.m. [Bu^{t}N= *C*=C(Ph)].

Crystal-structure Determination of Complex (14).—Crystals of (14) were grown as yellow rhombs from toluene (−20 °C); that for study (*ca.* 0.5 mm^3) was sealed in a Lindemann tube and diffracted intensities were recorded at 183 K for $2.9 \leqslant 2\theta < 50.0°$ on a Syntex $P2_1$ four-circle diffractometer.[26] Three reflections [(202), (171), and ($1\bar{2}\bar{2}$)] were used as checks, being remeasured periodically throughout data collection. After 300 h these check reflections did not show other than random fluctuations in intensity. Of the total of 7 404 recorded intensities, 4 372 had $I \geqslant 2.0\sigma(I)$ where $\sigma(I)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure. Corrections were applied for Lorentz and polarisation effects. All the computations were carried out with the ' *X*-Ray ' system of programs [27] available for the CDC 7600 at the London Computing Centre.

Crystal data. $C_{39}H_{55}FeN_5{\cdot}C_7H_8$, $M = 741.8$, Monoclinic, space group $P2_1/c$, $a = 9.724(4)$, $b = 42.11(3)$, $c = 11.330(4)$ Å, $\beta = 113.57(5)°$, $U = 4\,252.3$ Å^3, $D_m = 1.07$ (flotation), $Z = 4$, $D_c = 1.01$ g cm^{-3}, $F(000) = 1\,600$. Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 4.0 cm^{-1}.

Structure solution and refinement. The position of the iron atom was deduced from a Patterson synthesis. A least-squares refinement of the iron atomic positional co-ordinates followed by two electron-density difference syntheses enabled the remaining non-hydrogen atoms in the structure to be found. Allowing all atoms to refine with anisotropic temperature factors resulted in an unstable refinement for atoms C(111), C(112), and C(113). An electron-density difference synthesis, with these atoms being given isotropic thermal motion parameters, revealed peaks of electron density consistent with the t-butyl group being rotationally disordered. Thus a disordered model [atoms C(114), C(115), and C(116)] was introduced into the refinement with site occupation parameters in the ratio 2 : 1. In the same difference map, however, the appearance of strong peaks roughly in the (010) plane suggested the presence of a solvent molecule of crystallisation (see Figure 2). Inspection of this region revealed ten peaks, in symmetry related pairs, disposed around an inversion centre. It was concluded that these peaks represented a toluene molecule, occupying two alternative disordered sites related by inversion through the centre of symmetry. Accordingly,

TABLE 2

Internuclear distances and bond angles with estimated standard deviations in parentheses for the complex [Fe(CNBu^t)$_3${1—4-η-C(=NBu^t)=C(Ph)C(Ph)=C(=NBu^t)}]

(*a*) Distances (Å)

Fe–C(1)	1.864(11)	Fe–C(101)	2.123(8)
Fe–C(2)	1.862(8)	Fe–C(102)	2.115(9)
Fe–C(3)	1.965(11)	Fe–C(102, 3) [a]	1.907
Fe–C(4)	1.955(7)	Fe–C(101, 4)	1.910
Fe–C(5)	1.813(8)	Fe–C(101, 102)	2.037
C(1)–N(1)	1.16(1)	C(2)–N(2)	1.17(1)
N(1)–C(11)	1.47(2)	N(2)–C(21)	1.46(1)
C(11)–C(111)	1.61(2)	N(21)–C(211)	1.52(2)
C(11)–C(112)	1.51(3)	C(21)–C(212)	1.56(1)
C(11)–C(113)	1.63(2)	C(21)–C(213)	1.57(2)
C(11)–C(114)	1.31(7)	C(5)–N(5)	1.18(1)
C(11)–C(115)	1.61(5)	N(5)–C(51)	1.47(1)
C(11)–C(116)	1.63(6)	C(51)–C(511)	1.57(2)
		C(51)–C(512)	1.53(2)
		C(51)–C(513)	1.52(2)
C(101)–C(102)	1.42(1)		
C(3)–C(102)	1.45(1)	C(4)–C(101)	1.44(1)
C(3)–N(3)	1.29(1)	C(4)–N(4)	1.28(1)
N(3)–C(31)	1.48(1)	N(4)–C(41)	1.50(1)
C(31)–C(311)	1.55(1)	C(41)–C(411)	1.54(2)
C(31)–C(312)	1.55(1)	C(41)–C(412)	1.54(1)
C(31)–C(313)	1.54(2)	C(41)–C(413)	1.56(1)
C(102)–C(103)	1.49(1)	C(101)–C(201)	1.50(1)
C(103)–C(104)	1.39(2)	C(201)–C301)	1.39(1)
C(104)–C(105)	1.37(2)	C(301)–C(401)	1.41(1)
C(105)–C(106)	1.37(2)	C(401)–C(501)	1.35(2)
C(106)–C(107)	1.38(2)	C(501–C(601)	1.40(2)
C(107)–C(108)	1.39(1)	C(601)–C(701)	1.39(1)
C(108)–C(103)	1.41(1)	C(701)–C(201)	1.39(2)

TABLE 2 (*Continued*)

(*b*) Angles (°)

C(1)–Fe–C(2)	88.6(4)		
C(1)–Fe–C(3)	164.8(4)	C(2)–Fe–C(4)	162.2(4)
C(1)–Fe–C(4)	94.9(4)	C(2)–Fe–C(3)	91.0(4)
C(1)–Fe–C(5)	91.3(4)	C(2)–Fe–C(5)	92.2(4)
C(1)–Fe–C(101)	96.2(4)	C(2)–Fe–C(102)	91.4(4)
C(1)–Fe–C(102)	123.3(4)	C(2)–Fe–C(101)	121.3(4)
C(3)–Fe–C(4)	81.0(4)	C(101)–Fe–C(102)	39.2(4)
C(3)–Fe–C(5)	103.9(4)	C(4)–Fe–C(5)	105.1(4)
C(3)–Fe–C(101)	71.1(4)	C(4)–Fe–C(102)	72.1(4)
C(3)–Fe–C(102)	41.6(4)	C(4)–Fe–C(101)	41.0(3)
C(5)–Fe–C(102)	145.4(4)	C(5)–Fe–C(101)	145.7(3)
C(102,3) [a]–Fe–C(101,4)	62.6		
C(102,3)–Fe–C(1)	143.2	C(101,4)–Fe–C(2)	140.9
C(102,3)–Fe–C(2)	91.3	C(101,4)–Fe–C(1)	96.0
C(102,3)–Fe–C(5)	125.5	C(101,4)–Fe–C(5)	126.4
Fe–C(1)–N(1)	174.2(7)	Fe–C(2)–N(2)	179.1(9)
C(1)–N(1)–C(11)	175.4(8)	C(2)–N(2)–C(21)	177(1)
N(1)–C(11)–C(111)	104(1)	N(2)–C(21)–C(211)	107.6(9)
N(1)–C(11)–C(112)	111(1)	N(2)–C(21)–C(212)	107.8(8)
N(1)–C(11)–C(113)	104(1)	N(2)–C(21)–C(213)	106.0(9)
N(1)–C(11)–C(114)	117(4)		
N(1)–C(11)–C(115)	105(3)		
N(1)–C(11)–C(116)	101(3)	N(5)–C(51)–C(511)	104(1)
Fe–C(5)–N(5)	175.7(9)	N(5)–C(51)–C(512)	108.6(9)
C(5)–N(5)–C(51)	165(1)	N(5)–C(51)–C(513)	108(1)
Fe–C(3)–C(102)	74.7(6)	Fe–C(4)–C(101)	75.8(4)
Fe–C(3)–N(3)	155.0(7)	Fe–C(4)–N(4)	156.7(6)
C(102)–C(3)–N(3)	129.2(9)	C(101)–C(4)–N(4)	126.9(7)
C(3)–N(3)–C(31)	123.3(9)	C(4)–N(4)–C(41)	121.9(7)
C(3)–C(31)–C(311)	110.3(8)	N(4)–C(41)–C(411)	110.4(8)
N(3)–C(31)–C(312)	108.9(8)	N(4)–C(41)–C(412)	105.1(6)
N(3)–C(31)–C(313)	104.1(8)	N(4)–C(41)–C(413)	110.0(8)
Fe–C(101)–C(4)	63.2(4)	Fe–C(102)–C(3)	63.7(5)
Fe–C(101)–C(102)	70.1(4)	Fe–C(102)–C(101)	70.7(5)
Fe–C(101)–C(201)	133.0(7)	Fe–C(102)–C(103)	126.3(6)
C(102)–C(101)–C(201)	124.2(8)	C(101)–C(102)–C(103)	126.8(8)
C(4)–C(101)–C(201)	121.6(8)	C(3)–C(102)–C(103)	120.8(8)
C(101)–C(201)–C(301)	121(1)	C(102)–C(103)–C(104)	119.6(9)
C(101)–C(201)–C(701)	120.2(8)	C(102)–C(103)–C(108)	122(1)
C(301)–C(201)–C(701)	118.9(9)	C(104)–C(103)–C(108)	118.0(8)
C(201)–C(301)–C(401)	121(1)	C(103)–C(104)–C(105)	122(1)
C(301)–C(401)–C(501)	120(1)	C(104)–C(105)–C(106)	119(1)
C(401)–C(501)–C(601)	119(1)	C(105)–C(106)–C(107)	122(1)
C(501)–C(601)–C(701)	121(1)	C(106)–C(107)–C(108)	118(1)
C(601)–C(701)–C(201)	119.8(9)	C(107)–C(108)–C(103)	121(1)

(*c*) Toluene molecule

C(6)–C(7)	1.40(7)	C(7)–C(6)–C(9)	140(3)
C(6)–C(9)	1.51(5)	C(6)–C(9)–C(10)	127(4)
C(9)–C(10)	1.42(6)	C(9)–C(10)–C(8)	123(3)
C(10)–C(8)	1.40(6)	C(10)–C(8)–C(6′)	122(3)
C(8)–C(10′) [b]	1.52(4)	C(10)–C(8)–C(10′)	110(3)
C(10′)–C(7)	1.28(6)	C(6′)–C(8)–C(10′)	128(4)
C(8)–C(6′)	1.40(6)	C(8)–C(10′)–C(7)	124(3)
		C(10′)–C(7)–C(6)	132(4)

[a] C(*n*,*m*) indicates the midpoint of the line joining atoms C(*n*) and C(*m*). [b] C(*n*′) represents an atom related by the centre of symmetry.

the five unique atomic positions were allocated equal but invariant isotropic temperature factors while their respective populations were allowed to refine. This refinement converged to give unity site occupancy for atoms C(6) and C(10), but half occupancy for atoms C(7), C(8), and C(9). Having established population parameters for these positions, refinement of their fractional positional co-ordinates and anisotropic thermal motion parameters proceeded satisfactorily. While diffuse areas of electron density were indeed present in a difference electron-density synthesis, location of hydrogen atoms was unsuccessful. However, using an average carbon–hydrogen bond length of 0.95 Å, hydrogen atoms for the phenyl groups were introduced in calculated positions, but were not allowed to refine. Individual weights according to the scheme $w^{-1} = \sigma^2(F_o) + 0.095|F_o|$ were applied where $\sigma(F_o)$ is the estimated standard deviation in $|F_o|$ based on counting statistics only, and the final stages of refinement were completed using only those data (4 327 intensities) which satisfied the criterion $I \geqslant 2.5\sigma(I)$. Convergence was reached at $R = 0.092$ ($R' = 0.123$) with the mean and maximum shift-to-error ratios being 0.001 : 1 and 0.022 : 1 respectively, in the last cycle of refinement. The final electron-density difference synthesis showed no peaks >0.5 or < -0.3 e Å^{-3}. Scattering factors were from ref. 28 for C and N, ref. 29 for H, and ref. 30 for Fe, including corrections for the effects of anomalous dispersion for Fe ($\Delta f'$ 0.301, $\Delta f''$ 0.845) Atomic positional parameters are in Table 1, interatomic distances and angles in Table 2, and some least-squares planes in Table 3. Observed and calculated structure factors, all thermal parameters, and positional parameters for hydrogen atoms on the phenyl groups of the ligand, are listed in Supplementary Publication No. SUP 22780 (26 pp.).*

TABLE 3

Some least-squares planes for complex (14) in the form $Ax + By + Cz = D$, where x, y, and z are fractional crystal co-ordinates: distances (Å) of relevant atoms from these planes are given in square brackets

Plane (a): C(3), C(4), C(101), C(102)

$9.415x + 0.511y - 1.792z = 3.504$

[C(3) 0.008, C(4) −0.009, C(101) 0.016, C(102) −0.015, Fe −1.490, C(3) 0.71, N(4) 0.71]

Plane (b): C(101), C(102), C(103), C(201)

$9.450x - 4.551y - 2.230z = 2.841$

[C(101) −0.030, C(102) 0.031, C(103) −0.014, C(201) 0.013, C(3) −0.057, C(4) −0.235]

Plane (c): C(201), C(301), C(401), C(501), C(601), C(701)

$6.312x + 20.194y + 3.192z = 6.145$

[C(201) −0.019, C(301) 0.015, C(401) 0.001, C(501) −0.011, C(601) 0.006, C(701) 0.009]

Plane (d): * C(1), C(2), C(102,3), C(101,4)

$0.970x + 41.142y - 2.408z = 4.774$

[Fe 0.57, C(1) 0.003, C(2) −0.003, C(102,3) 0.004, C(101,4) −0.004]

Plane (e): C(103), C(104), C(105), C(106), C(107), C(108)

$-5.156x + 17.738y - 5.239z = -1.571$

[C(103) −0.007, C(104) 0.003, C(105) 0.004, C(106) −0.007, C(107) 0.003, C(108) 0.003]

Plane (f): C(6), C(7), C(8), C(8), C(10)

$-3.523x + 36.636y + 5.114z = 2.548$

[C(6) −0.052, C(7) 0.037, C(8) −0.019, C(9) 0.037, C(10) −0.003, Fe 2.870]

Angles (°) between the least-squares planes:

(a)—(b) 7.3; (a)—(c) 38.6; (a)—(e) 46.2

* C(*n*,*m*) indicates the midpoint of the line joining atoms C(*n*) and C(*m*).

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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