Formation of Nona(ethyl isocyanide)di-iron from Penta(ethyl isocyanide)iron and Reaction of Penta(t-butyl isocyanide)iron with Diphenylacetylene; *X*-Ray Crystal Structures of Nona(ethyl isocyanide)di-iron and Tris(t-butyl isocyanide){1,4-bis-(t-butylimino)-2,3-diphenylbuta-1,3-diene}iron

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Summary U.v. irradiation of [Fe(CNEt)$_5$] in diethyl ether affords [Fe$_2$(CNEt)$_9$], and reaction of diphenylacetylene with [Fe(CNBu^t)$_5$] gives [Fe(CNBu^t)$_3${1–4-η-Bu^{t}N=C=C-(Ph)C(Ph)=C=NBu^t}]; the molecular structures of these complexes are established by single crystal *X*-ray crystallography.

WE report studies with the recently synthesised[1] zerovalent iron complexes [Fe(CNR)$_5$] (R = Bu^t, Et), which have led to a preparation of the potentially important dinuclear complex [Fe$_2$(CNEt)$_9$], and the observation of an interesting cyclisation reaction with diphenylacetylene.

U.v. irradiation (room temperature, 36 h) of a diethyl ether solution of [Fe(CNEt)$_5$] affords (60% yield) orange, air-sensitive crystals of nona(ethyl isocyanide)di-iron [ν_{NC} {tetrahydrofuran (THF)} 2 060vs, 1 920sh, 1 701m(sh), and 1 652vs cm^{-1}]. In contrast with the related [Fe$_2$(CO)$_9$] system,[2,3] no difficulty was experienced in obtaining a suitable crystal for single crystal *X*-ray diffraction studies.

Crystal data: C$_{27}$H$_{45}$Fe$_2$N$_9$, M = 607·4, monoclinic, space group $P2_1/n$, a = 22·193(14), b = 12·762(6), c = 12·332(8), β = 104·60(5), U = 3380·2 Å^3, Z = 4, D_m = 1·23, D_c = 1·19 g cm^{-3}, F(000) = 1288, μ(Mo-K_α) = 9·1 cm^{-1}. Allowing anisotropic thermal parameters for the iron atoms only, and isotropic thermal parameters for the remaining light non-hydrogen atoms, refinement of the structure has reached R = 0·11 for 3054 intensities [223 K, $2\theta \leqslant 50°$, $I \geqslant 2{\cdot}5\,\sigma(I)$, Syntex $P2_1$ diffractometer, Mo-K_α radiation, λ = 0·71069 Å].†

The molecular structure (Figure 1) is related to that established for nonacarbonyldi-iron, each iron atom having an approximately octahedral first co-ordination sphere of carbon atoms, the face defined by atoms C(4), C(5), and C(6) of the three bridging ethyl isocyanide ligands being shared. The Fe–C distances for the terminal isocyanides average to *ca.* 1·84 Å, whereas the bridging ligand Fe–C lengths at *ca.* 1·96 Å are on average *ca.* 0·05 Å shorter than those found in [Fe$_2$(CO)$_9$].[2] A concomitant shortening by 0·06 Å relative to [Fe$_2$(CO)$_9$] is observed in the Fe–Fe distance of 2·462(3) Å. The molecule [Fe$_2$(CNEt)$_9$] lacks the high symmetry of its carbonyl analogue. While the six terminal isocyanide ligands deviate slightly from linearity (mean ∠CNC, 171°), the bridging ligands are considerably bent towards Fe(2) at atoms N(4) and N(5), and towards Fe(1) at atom N(6). The angles at N(4), N(5), and N(6) of 123(1)°, 124(1)°, and 123(1)°, respectively, are significantly smaller than those observed in other structures[4] having bridging isocyanides, and are accompanied by a longer C–N separation [mean 1·26(2) Å] compared with the terminal ligands [mean C–N, 1·17(2) Å].

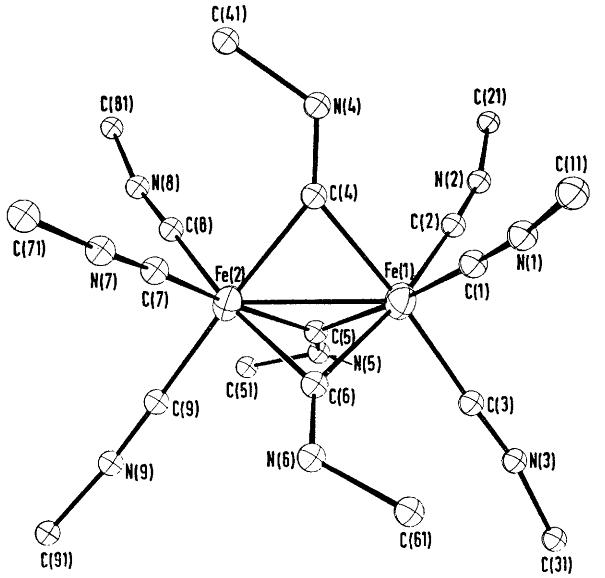

FIGURE 1. Molecular structure of [Fe$_2$(CNEt)$_9$] viewed normal to the Fe–Fe vector, with methyl groups omitted for clarity. Fe(1)–Fe(2), 2·462(3), and C–N (bridging) 1·26(2) Å; mean ∠CNC (bridging) 123(1)°.

Whereas low solubility has precluded low temperature n.m.r. studies with the [Fe$_2$(CO)$_9$] system, thus limiting our knowledge of the nonacarbonyl compound to the solid state, variable temperature ^{1}H and ^{13}C n.m.r. studies‡ with [Fe$_2$(CNEt)$_9$] established an intramolecular exchange process§ in solution involving exchange of bridging and terminal isocyanide ligands with an activation energy of 63·5 ± 1 kJ mol^{-1}. The low temperature data indicate that inversion at the nitrogen atom of the bridging isocyanides is still rapid at −50 °C.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ ^{1}H N.m.r. ([^{2}H$_8$]toluene, −50 °C), τ 5·96 [q, 6H, CH$_2$, ^3J(H–H) 7·1 Hz], 7·14 [q, 12H, CH$_2$, J 7·1 Hz], 8·32 [t, 9H, Me, J 7·1 Hz], and 9·19 [t, 18H, Me, J 7·1 Hz]; ([^{2}H$_8$]toluene, +100 °C), τ 6·61 [q, 18H, CH$_2$, J 7·1 Hz] and 8·76 [t, 27H, Me, J 7·1 Hz]. ^{13}C N.m.r. ([^{2}H$_8$]toluene, −80 °C) 174·5 (CNEt, terminal) and 258·1 (CNEt, bridging) p.p.m.

§ A detailed discussion of this process will be presented in a full paper.

Formation of $[Fe_2(CNEt)_9]$ on u.v. irradiation of $[Fe(CNEt)_5]$ can perhaps be understood in terms of the photochemical generation of $[Fe(CNEt)_4]$ followed by capture with $[Fe(CNEt)_5]$. The easy thermal reactions observed with $[Fe(CNR)_5]$ complexes[1] suggest that access can also be gained to such intermediates *via* a thermal dissociative process.

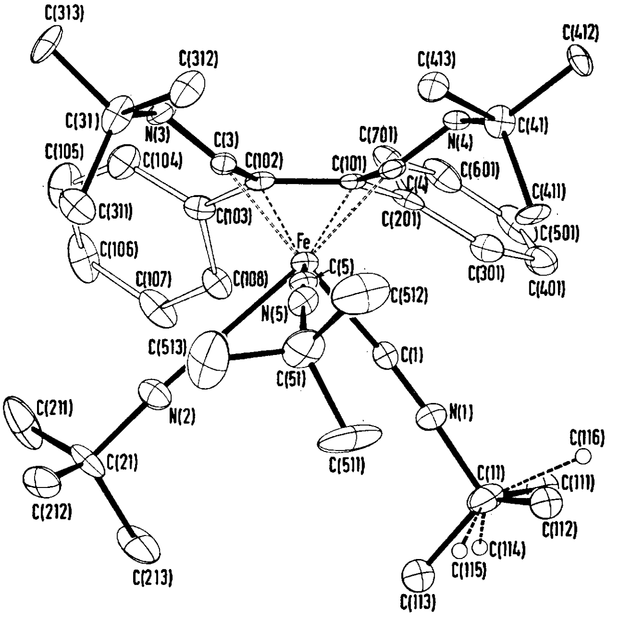

FIGURE 2. Molecular structure of $[Fe(CNBu^t)_3\{1\text{-}4\text{-}\eta\text{-}Bu^tN:C:C(Ph)C(Ph):C:NBu^t\}]$ shown in projection down crystallographic *b*-axis, with the toluene solvent molecule omitted (ORTEP diagram, 30% probability ellipsoids). Important molecular parameters are C(3)–C(102) and C(4)–C(101), 1·44(1); C(101)–C(102), 1·42(1); Fe–C(3), 1·964(11); Fe-C(4), 1·956(7); Fe–C(101), 2·122(8); and Fe–C(102), 2·114(9) Å; ∠N(3)C(3)C(102), 129(1) and ∠N(4)C(4)C(101), 127(1)°.

Reaction of $[Fe(CNBu^t)_5]$ with diphenylacetylene (THF, room temperature, 36 h) affords (72% yield) yellow, air-stable crystals of a complex analysing for $[Fe(PhC_2Ph)(CNBu^t)_5]$. The i.r. and n.m.r. data[¶] did not conclusively establish the structure, and therefore an *X*-ray single crystal structure determination was carried out.

Crystal data: $C_{39}H_{55}N_5Fe$, $M = 649{\cdot}7$, monoclinic, space group $P2_1/c$, $a = 9{\cdot}724(4)$, $b = 42{\cdot}11(3)$, $c = 11{\cdot}330(4)$, $\beta = 113{\cdot}57(5)$, $U = 4252{\cdot}3$ Å^3, $Z = 4$, $D_m = 1{\cdot}07$, $D_c = 1{\cdot}01$ g cm^{-3}, F(000) = 1600, $\mu(\text{Mo-}K_\alpha) = 4{\cdot}0$ cm^{-1}. Refinement of the structure and one disordered toluene molecule (not shown) per asymmetric unit has reached $R = 0{\cdot}09$ for 4327 reflections [193 K, $2\theta \leqslant 50°$, $I \geqslant 2{\cdot}5\sigma(I)$].[†]

The structure (Figure 2) has a pseudo-octahedral first co-ordination sphere, five sites occupied by carbons C(1) to C(5), the sixth occupied by a point midway between atoms C(101) and C(102). The overall geometry is similar to that of tricarbonyl(buta-1,3-diene)iron;[5] atoms C(3), C(102), C(101), and C(4) are ligated co-planar carbon atoms of a *cis*-{bis(t-butylimino)diphenylbuta-1,3-diene} fragment inclined by 16° to the plane containing atoms C(1), C(2), and C(5), and *ca.* 1·5 Å above the iron atom. Thus the bonding mode is different from the related cobalt system[6] described as a substituted cobaltacyclopent-3-ene. The two equivalent isocyanide ligands are linear [mean ∠CNC, 176(1)°], the Fe–C and C–N distances [mean Fe–C, 1·863(10); mean C–N, 1·164(11) Å] suggest only minimal backbonding $[\text{Fe } (3d) \rightarrow (\text{C}{\equiv}\text{N})\ \pi^*]$. In contrast, the unique isocyanide is non-linear [∠C(5)N(5)C(51), 165(1)°], and has a shorter Fe–C distance [Fe–C(5), 1·813(8) Å]. The n.m.r. data show that in solution the molecule is dynamic, the activation energy for isocyanide scrambling being $68{\cdot}3 \pm 1$ kJ mol^{-1}.

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[¶] ν_{NC}(Nujol) 2 115s, 2 080s, and 2 040s; $\nu_{N=C}$ and $\nu_{C=C}$ 1 666m, 1 641m, 1 617sh, and 1 603sh cm^{-1}. ^{1}H N.m.r. (PhCl, 0 °C), τ 8·46 (s, 18H), 8·6 (s, 9H), and 8·93 (s, 18H); (PhCl, 120 °C), τ 8·54 (s, 18H) and 8·73 (s, 27H). ^{13}C N.m.r. ($CDCl_3$) 72·0 [Bu^{t}N=C=*C*-(Ph)*C*(Ph)=C=NBu^t], 167·9, 175·2 (Fe*C*N), and 203·3 [Bu^{t}N=*C*=C(Ph)C(Ph)=*C*=NBu^t] p.p.m.

[1] J-M. Bassett, M. Green, J. A. K. Howard, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1977, 853; J-M. Bassett, D. E. Berry, G. K. Barker, M. Green, J. A. K. Howard, and F. G. A. Stone, *J.C.S. Dalton*, in the press.
[2] F. A. Cotton and J. M. Troup, *J.C.S. Dalton*, 1974, 800.
[3] H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 1939, 286.
[4] M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1509; G. K. Barker, A. M. R. Galas, M. Green, J. A. K. Howard, F. G. A. Stone, T. W. Turney, A. J. Welch, and P. Woodward, *J.C.S. Chem. Comm.*, 1977, 256; W. E. Carroll, A. M. R. Galas, M. Green, M. Murray, T. W. Turney, A. J. Welch, and P. Woodward, *J.C.S. Dalton*, in the press; M. M. Olmstead, H. Hope, L. S. Benner, and A. L. Balch, *J. Amer. Chem. Soc.*, 1977, **99**, 5502; K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Comm.*, 1965, 181.
[5] F. H. Herbstein and M. G. Reisner, *Acta Cryst.*, 1977, **B33**, 3304.
[6] H. Yamazaki, K. Aoki, Y. Yamamoto, and Y. Wakatsuki, *J. Amer. Chem. Soc.*, 1975, **97**, 3546.