Cluster Chemistry. Part 20.† Preparation, *X*-Ray Crystal Structures, and some Reactions of $[Fe_3(CO)_{11}(CNBu^t)]$ and $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ ‡

Michael I. Bruce,* Trevor W. Hambley, and Brian K. Nicholson
Jordan Laboratory, Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia, 5001

The reaction between $[Fe_3(CO)_{12}]$ and $CNBu^t$ is initiated by $Ph_2CO^{\cdot -}$ to give $[Fe_3(CO)_{11}(CNBu^t)]$ (1), characterised spectroscopically and by a full *X*-ray crystal structure analysis. Crystals of (1) are monoclinic, space group $P2_1/n$ with $a = 11.586(3)$, $b = 11.819(3)$, $c = 15.949(5)$ Å, $\beta = 72.33(2)°$, and $Z = 4$. The structure was solved by direct methods and refined to $R = 0.025$, $R' = 0.027$ for 1 641 reflections with $I > 2.5\sigma(I)$. The structure is related to that of the C_{2v} isomer of $[Fe_3(CO)_{12}]$ with the $CNBu^t$ ligand occupying an axial position of the unique iron atom. Thermal rearrangement of (1) gives $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ (2) which contains a triply bridging six-electron-donor $CNBu^t$ group. Reaction of (2) with H^- gives $[Fe_3(CO)_9(HC{=}NBu^t)]^-$ which can be protonated to form $[Fe_3H(CO)_9(HC{=}NBu^t)]$.

Although $[Fe_3(CO)_{12}]$ has played an important role in the development of the chemistry of the metal carbonyls, substituted derivatives $[Fe_3(CO)_{12-n}L_n]$ containing simple two-electron Lewis bases have not been studied in great detail. No doubt this is partly due to the poor yields of cluster products obtained [1-4] in thermally induced reactions of $[Fe_3(CO)_{12}]$ with bases in which extensive fragmentation of the Fe_3 unit occurs. As part of a wider study [5] of substitution reactions at metal clusters initiated by $Ph_2CO^{\cdot -}$ under mild conditions, $[Fe_3(CO)_{11}(CNBu^t)]$ (1) became readily available. Only superficial mentions of this compound have previously appeared.[6] Since isocyanide ligands closely mimic the electronic and steric properties of CO we have determined the structure of $[Fe_3(CO)_{11}(CNBu^t)]$ (1) for comparison with that of the parent $[Fe_3(CO)_{12}]$ [7] and with that of the heavier congener $[Ru_3(CO)_{11}(CNBu^t)]$.[8]

Pyrolysis of $[Ru_3(CO)_{11}(CNBu^t)]$ or $[Os_3(CO)_{11}(CNBu^t)]$ has given a variety of higher nuclearity clusters.[9,10] We report herein the thermal rearrangement of $[Fe_3(CO)_{11}(CNBu^t)]$ (1) to give $[Fe_3(CO)_9(CNBu^t)]$ (2) which contains a triply bridging, η^2-isocyanide ligand which is susceptible to nucleophilic attack. Aspects of this work have been communicated.[11]

Experimental

Reactions were carried out under dry nitrogen atmospheres using standard Schlenk techniques. Tetrahydrofuran (thf) was freshly distilled under N_2 from sodium diphenylketyl immediately before use. t-Butyl isocyanide was synthesised by a literature method [12] and $[Fe_3(CO)_{12}]$ (Strem) was purified by Soxhlet extraction with pentane prior to use. Light petroleum is a fraction of b.p. 40—60 °C unless otherwise stated.

Preparation of $[Fe_3(CO)_{11}(CNBu^t)]$ (1).—A mixture of $[Fe_3(CO)_{12}]$ (1.19 g, 2.36 mmol) and $CNBu^t$ (2.6 mmol) in thf (30 cm^3) was treated dropwise from a syringe with a solution of $Ph_2CO^{\cdot -}$ (*ca.* 0.025 mol dm^{-3}) in thf until t.l.c. (silica plates, light petroleum eluant) showed the starting cluster was consumed (0.8—1.5 cm^3 of initiator). Solvent and some $[Fe(CO)_4(CNBu^t)]$ [identified by its characteristic [13] ν(CO) pattern at 2 058s, 1 996s, and 1 967vs cm^{-1}] were pumped off under vacuum and the residue dissolved in light petroleum (50 cm^3). After filtration (**CAUTION**: the residue may be pyrophoric when dry) the filtrate was concentrated to *ca.* 20 cm^3 under vacuum and cooled to −30 °C to give very dark green crystals of $[Fe_3(CO)_{11}(CNBu^t)]$ (1) (0.68 g, 53%), m.p. 117—119 °C [Found: C, 33.95; H, 1.45; N, 2.50%; *M* (mass spectrum), 559. $C_{16}H_9Fe_3NO_{11}$ requires C, 34.40; H, 1.60; N, 2.50%; *M*, 559]. Infrared spectrum (hexane): ν(CN) 2 174m; ν(CO) 2 082m, 2 039s, 2 031s, 2 012s, and 1 996m. I.r. (Nujol): ν(CN) 2 182; ν(CO) 2 082m, 2 034s, 2 028s, 2 010s, 1 966s, 1 848w, and 1 817m cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 1.62 (s, CMe_3). ^{13}C N.m.r. ($CDCl_3$): δ 30.0 (CH_3) and 214.9 (CO).

Preparation of $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ (2).—A solution of $[Fe_3(CO)_{11}(CNBu^t)]$ (1) (0.21 g, 0.38 mmol) in n-heptane (14 cm^3) was gently refluxed (95 °C) for 1—1.5 h until all starting material was consumed (t.l.c.). The red-brown solution was filtered while hot and cooled to −30 °C to give deep red crystals of $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ (2) (0.13 g, 69%), m.p. >120 °C (decomp.) [Found: C, 33.65; H, 1.60; N, 2.80%; *M* (mass spectrum), 503. $C_{14}H_9NO_9Fe_3$ requires C, 33.40; H, 1.80; N, 2.80%; *M*, 503]. I.r. spectrum (hexane): ν(CN) 1 552w; ν(CO) 2 086m, 2 039vs, 2 029vs, 2 017s, 2 000m, 1 993s, 1 981s, and 1 970w cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 1.55 (s, CMe_3). ^{13}C N.m.r. ($CDCl_3$): δ 32.2 (CH_3), 63.87 (CMe_3), 210.1 and 210.4 (CO).

Pyrolysis of $[Fe_3(CO)_{11}(CNBu^t)]$ (1) *at* 125 °C.—A solution of $[Fe_3(CO)_{11}(CNBu^t)]$ (0.30 g) in light petroleum (b.p. 120—160 °C) was heated in an oil bath at 125 °C. After 10 min an i.r. spectrum showed no starting material remained and new bands at 2 086, 2 060, and 1 969 cm^{-1} had appeared. Further heating gave little change to this pattern although an overall decrease in intensity occurred. Solvent was pumped off *in vacuo*, together with traces of $[Fe(CO)_4(CNBu^t)]$, and the residue was chromatographed on silica plates, eluting with 1 : 4 CH_2Cl_2–hexane. Four bands developed. Band 1, $R_f = 0.70$, dark brown, was identified as $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ (2) (0.06 g, 22%) by comparison with an authentic sample. Band 2, $R_f = 0.65$, red-brown, was recrystallised from light petroleum spirit (b.p. 40—60 °C) to give dark red crystals of $[Fe_3(CO)_8(CNBu^t)(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ (0.011 g,

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† For Part 19, see preceding paper.

‡ 3-(t-Butyl isocyanide)-1,2-di-μ-carbonyl-1,1,1,2,2,2,3,3,3-nonacarbonyl-*triangulo*-tri-iron and [μ_3-η^2-t-butyl isocyanide-*C*(Fe^{1-3})-*N*($Fe^{1,2}$)]-1,1,1,2,2,2,3,3,3-nonacarbonyl-*triangulo*-tri-iron respectively.

Supplementary data available (No. SUP 23648, 13 pp.): structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

4%), m.p. 89—91 °C [Found: C, 37.55; H, 3.25; N, 4.90%; *M* (mass spectrum), 558. $C_{18}H_{18}Fe_3N_2O_8$ requires C, 38.75; H, 3.25; N, 5.00%; *M*, 558]. Infrared spectrum (hexane): ν(CN) 2 162m, 1 540w; ν(CO) 2 060(sh), 2 058m, 2 015vs, 1 999w, 1 991m, 1 980s, and 1 968s cm^{-1}. Band 3, $R_f = 0.60$, olive green, low yields, ν(CO) 2 060m, 2 015vs, 1 986s, and 1 970s cm^{-1}. Band 4, $R_f = 0.50$, green, low yields, ν(CN) 2 144m, ν(CO) 2 065s, 2 017vs, 2 005vs, 1 998s, 1 990s, 1 979m, 1 964s, and 1 952w cm^{-1}. Bands 3 and 4 were not identified.

Preparation of $[Fe_3(CO)_9(HC{=}NBu^t)]^-$ (3).—A solution of $[Fe_3(CO)_9(CNBu^t)]$ (1) (0.10 g, 0.2 mmol) in thf (4 cm^3) was treated with a solution of $K[HBBu^s_3]$ in thf (0.40 cm^3 of a 0.5 mol dm^{-3} solution). An immediate colour change to claret occurred. After 5 min $[AsPh_4]Cl$ (0.05 g) was added and the mixture was stirred for 10 min. After removal of thf the residue was extracted with CH_2Cl_2 (3 cm^3) and addition of light petroleum (*ca.* 3 cm^3) precipitated the crude product $[AsPh_4][Fe_3(CO)_9(HC{=}NBu^t)]$ (0.093 g, 53%), m.p. 99—101 °C (Found: C, 51.85; H, 3.55; N, 1.55. $C_{38}H_{30}AsFe_3NO_9$ requires C, 51.45; H, 3.40; N, 1.60%). Infrared spectrum (CH_2Cl_2): ν(CO) 2 055w, 2 033m, 1 972vs, 1 965vs, 1 942s, and 1 919m cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 1.21 (s, CH_3), 9.52 (s, HC=N).

A similar procedure using $[NEt_4]I$ instead of $[AsPh_4]Cl$ gave $[NEt_4][Fe_3(CO)_9(HC{=}NBu^t)]$ as red microcrystals in 48% yield after recrystallisation from $EtOH-H_2O$.

Preparation of $[Fe_3H(CO)_9(HC{=}NBu^t)]$ (4).—A solution of $[Fe_3(CO)_9(CNBu^t)]$ (0.10 g, 0.2 mmol) in thf (4 cm^3) was treated with $K[HBBu^s_3]$ (0.4 cm^3 of a 0.5 mol dm^{-3} solution in thf). After 5 min H_3PO_4 (0.5 cm^3) was added and the mixture stirred for 10 min. Solvent was evaporated and the residue extracted with light petroleum (2 × 5 cm^3). The combined filtered extracts were concentrated to *ca.* 5 cm^3 and cooled to −30 °C to give well formed deep red crystals of $[Fe_3H(CO)_9(HC{=}NBu^t)]$ (4) (0.063 g, 63%), m.p. >70 °C (decomp.) [Found: C, 33.65; H, 2.10; N, 2.75%; *M* (mass spectrum), 505. $C_{14}H_{11}Fe_3NO_9$ requires C, 33.30; H, 2.20; N, 2.75%; *M*, 505]. Infrared spectrum (hexane): ν(CO) 2 088m, 2 052s, 2 025s, 2 017s, 2 003m, 1 998m, 1 973m, and 1 963w cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 1.24 (s, CH_3), 9.21 (s, HC=N), and −25.9 (s, FeH).

Crystal Structure of $[Fe_3(CO)_{11}(CNBu^t)]$ (1).—Deep green crystals suitable for *X*-ray analysis were obtained by recrystallisation from MeOH. A single crystal (0.26 × 0.21 × 0.05 mm) was oriented on a four-circle Enraf-Nonius CAD4 diffractometer and lattice parameters were determined by a least-squares fit to the setting angles of 25 reflections measured using graphite-monochromated Mo-K_α radiation.

Crystal data. $C_{16}H_9Fe_3NO_{11}$, $M = 558.8$, Monoclinic, space group $P2_1/n$, $a = 11.586(3)$, $b = 11.819(3)$, $c = 15.949(5)$ Å, $\beta = 72.33(2)°$, $U = 2\,080$ Å^3, $D_m = 1.74$, $Z = 4$, $D_c = 1.78$ g cm^{-3}, $F(000) = 1\,112$, λ(Mo-K_α) = 0.710 7 Å, μ(Mo-K_α) = 20.9 cm^{-1}, $T = 23$ °C.

Intensity data were collected in the range $1.5 < \theta < 22°$ using an $\omega - \frac{n}{3}\theta$ scan where the optimum value of *n* was found to be 4. ω Scan angles and horizontal counter apertures of $(1.0 + 0.35\tan\theta)°$ and $(2.40 + 0.5\tan\theta)$ mm, respectively, were used. Three standard reflections monitored regularly showed no sign of crystal deterioration. Lorentz, polarisation, and absorption corrections were applied to the data. A total of 2 276 unique reflections were obtained; 1 641 with $I > 2.5\sigma(I)$ were used in the analysis.

Table 1. Positional parameters (× 10^4) for $[Fe_3(CO)_{11}(CNBu^t)]$ (1)

Atom	*x*	*y*	*z*
Fe(1)	9 376(1)	8 536(1)	8 703(1)
Fe(2)	8 840(1)	6 338(1)	8 603(1)
Fe(3)	9 925(1)	7 387(1)	7 175(1)
C(1)	10 906(4)	8 163(4)	8 850(3)
C(2)	12 935(4)	7 694(4)	9 172(3)
C(3)	13 030(5)	6 416(4)	9 215(4)
C(4)	12 865(5)	8 236(5)	10 043(4)
C(5)	13 956(4)	8 173(5)	8 422(4)
N	11 805(3)	7 966(3)	8 978(2)
C(B1) *	8 224(5)	6 713(4)	7 581(3)
C(B2) *	10 586(5)	6 253(4)	7 848(3)
O(B1) *	7 405(3)	6 586(3)	7 331(2)
O(B2) *	11 464(3)	5 784(3)	7 807(2)
C(11)	8 779(4)	8 819(4)	9 849(4)
C(12)	9 888(4)	9 929(5)	8 309(3)
C(13)	7 925(4)	8 762(4)	8 542(3)
C(21)	9 386(4)	6 301(4)	9 555(3)
C(22)	8 772(4)	4 833(4)	8 448(3)
C(23)	7 272(5)	6 527(4)	9 260(3)
C(31)	10 308(4)	6 493(4)	6 230(3)
C(32)	9 301(4)	8 544(5)	6 707(3)
C(33)	11 378(5)	8 069(5)	6 940(3)
O(11)	8 388(4)	9 025(4)	10 583(2)
O(12)	10 171(4)	10 828(3)	8 079(3)
O(13)	7 001(3)	8 993(3)	8 470(2)
O(21)	9 683(3)	6 224(3)	10 166(2)
O(22)	8 765(3)	3 889(3)	8 362(2)
O(23)	6 295(4)	6 581(4)	9 674(3)
O(31)	10 564(3)	5 949(3)	5 606(2)
O(32)	8 980(4)	9 268(4)	6 368(3)
O(33)	12 306(4)	8 481(4)	6 742(3)

* B = bridging.

Solution and refinement. Direct methods (MULTAN) gave the co-ordinates of two of the iron atoms; a difference map phased by these gave the position of the third. A subsequent difference Fourier revealed all other non-hydrogen atoms. In the final cycle of blocked full-matrix least-squares refinement hydrogen atoms were included in their calculated positions (d_{C-H} 0.97 Å) with a common isotropic thermal parameter, while all other atoms were treated anisotropically; convergence gave $R = 0.025$, $R' = 0.027$ with a weighting scheme $w = 1.028[\sigma^2(F_o) + 0.0015F_o^2]^{-1}$. No parameter shifted by more than 0.2σ in the final cycles and a final difference map gave no peaks greater than 0.3 e Å^{-3}. Final positional parameters are given in Table 1, selected bonding parameters in Table 2 and a general view of the molecule in Figure 1. Computing details are given elsewhere.[14]

Crystal Structure of $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ (2).—Main details have been published separately.[11] Crystals of (2) are Triclinic, space group $P\bar{1}$, with $a = 7.749(2)$, $b = 9.310(2)$, $c = 14.038(3)$ Å, $\alpha = 92.49(2)$, $\beta = 90.76(2)$, $\gamma = 108.93(2)°$, $Z = 2$. The structure was refined to $R = 0.028$, $R' = 0.030$ for 1 566 reflections with $I > 2.5\sigma(I)$. Atomic co-ordinates have been previously deposited.[11] A list of bond parameters is given in Table 3 and a view of the molecule is presented in Figure 2.

Results and Discussion

The replacement of one carbonyl group on $[Fe_3(CO)_{12}]$ by $CNBu^t$ is initiated by $Ph_2CO^{\cdot -}$ to give reasonable yields of $[Fe_3(CO)_{11}(CNBu^t)]$ (1). Some fragmentation of the cluster occurs with formation of $[Fe(CO)_4(CNBu^t)]$; this behaviour is typical of substitution reactions of $[Fe_3(CO)_{12}]$ by thermal means[1] and is not unexpected in the $Ph_2CO^{\cdot -}$ induced

Table 2. Selected bond lengths (Å) and angles (°) for $[Fe_3(CO)_{11}(CNBu^t)]$ (1)

Fe(1)–Fe(2)	2.687(1)	Fe(2)–C(B1)	2.018(6)
Fe(1)–Fe(3)	2.691(1)	Fe(3)–C(B1)	2.040(6)
Fe(2)–Fe(3)	2.563(1)	Fe(2)–C(B2)	2.018(5)
Fe(1)–C(1)	1.909(5)	Fe(3)–C(B2)	2.008(5)
C(1)–N	1.145(7)	C(B1)–O(B1)	1.145(7)
N–C(2)	1.469(7)	C(B2)–O(B2)	1.143(6)
C(2)–C(3)	1.517(7)	C(2)–C(5)	1.513(7)
C(2)–C(4)	1.511(8)		

Fe–C(terminal) 1.779(6)—1.814(6), mean 1.799 Å
C–O(terminal) 1.125(7)—1.145(7), mean 1.136 Å

Fe(1)–Fe(2)–Fe(3)	61.6(1)	C(1)–N–C(2)	178.0(4)
Fe(2)–Fe(3)–Fe(1)	61.5(1)	Fe(2)–C(B1)–Fe(3)	78.3(2)
Fe(3)–Fe(1)–Fe(2)	56.9(1)	Fe(2)–C(B2)–Fe(3)	79.1(2)
Fe(1)–C(1)–N	176.6(4)		

Dihedral angles

Fe(1)–Fe(2)–Fe(3) Fe(2)–C(B1)–Fe(3)	114.6°	Fe(2)–C(B1)–Fe(3) Fe(2)–C(B2)–Fe(3)	139.5°
Fe(1)–Fe(2)–Fe(3) Fe(2)–C(B2)–Fe(3	106.1°		

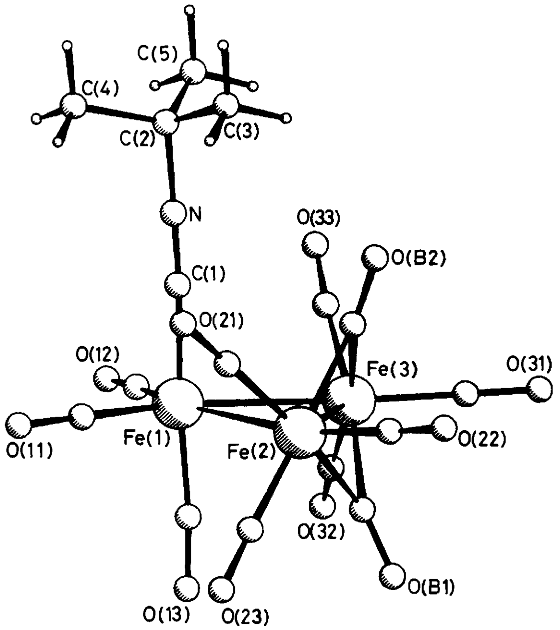

Figure 1. PLUTO plot of the molecular structure of $[Fe_3(CO)_{11}(CNBu^t)]$ (1), showing the atom-numbering scheme

reaction since the radical anion $[Fe_3(CO)_{12}]^{\cdot -}$, the assumed reactive intermediate, is known [15] to give mononuclear fragments readily.*

Attempts to prepare more highly substituted derivatives, $[Fe_3(CO)_{12-n}(CNBu^t)_n]$ ($n = 2$ or 3), by the $Ph_2CO^{\cdot -}$ initiated reaction between $[Fe_3(CO)_{11}(CNBu^t)]$ and excess $CNBu^t$, met with no success; $[Fe(CO)_4(CNBu^t)]$ and $[Fe(CO)_3(CNBu^t)_2]$ were the only products.

Table 3. Selected bond lengths and angles for $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ (2)

Fe(1)–Fe(2)	2.693(1)	Fe(2)–N	2.030(3)
Fe(1)–Fe(3)	2.693(1)	Fe(3)–N	2.033(4)
Fe(2)–Fe(3)	2.482(1)	C(1)–N	1.270(5)
Fe(1)–C(1)	1.754(4)	C(2)–C(3)	1.504(7)
Fe(2)–C(1)	2.006(4)	C(2)–C(4)	1.517(8)
Fe(3)–C(1)	1.998(4)	C(2)–C(5)	1.520(8)
N–C(2)	1.510(6)		

Fe–CO 1.768(5)—1.820(6), mean 1.796 Å
C–O 1.128(7)—1.148(6), mean 1.136 Å

Fe(1)–Fe(2)–Fe(3)	62.6(1)	Fe(1)–C(1)–N	159.8(4)
Fe(2)–Fe(3)–Fe(1)	62.6(1)	C(1)–N–C(2)	132.0(4)
Fe(2)–Fe(1)–Fe(3)	54.9(1)	Fe(2)–C(1)–Fe(3)	76.6(2)
Fe(2)–Fe(1)–C(1)	48.1(1)	Fe(2)–N–Fe(3)	75.3(2)
Fe(3)–Fe(1)–C(1)	47.9(1)		

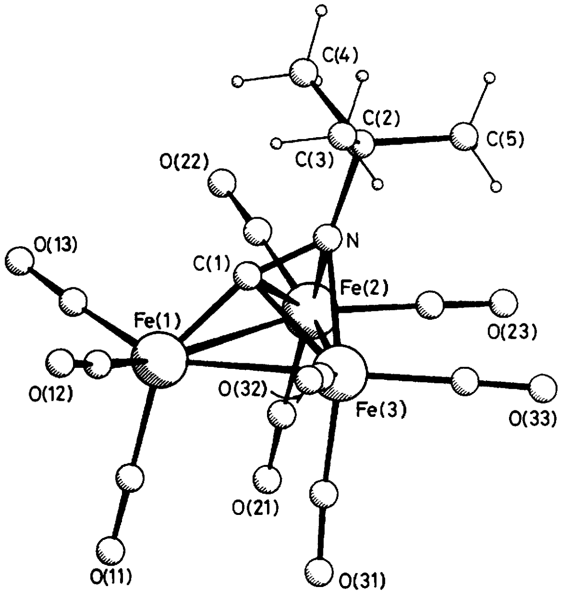

Figure 2. PLUTO plot of the molecular structure of $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ (2), showing the atom-numbering scheme

The deep green, almost black, crystals of $[Fe_3(CO)_{11}(CNBu^t)]$ are readily soluble in organic solvents to give intense green solutions. Neither the solid nor dissolved compound is particularly air-sensitive.

The solution i.r. spectrum of $[Fe_3(CO)_{11}(CNBu^t)]$ shows no detectable absorption in the bridging carbonyl region, although a solid-state spectrum gives two bands assignable to bridging CO groups, consistent with the bridged structure found in the *X*-ray crystallographic analysis (see later). Therefore a non-bridged isomeric form apparently predominates in solution. These observations parallel those made previously for $[Fe_3(CO)_{12}]$.

On heating $[Fe_3(CO)_{11}(CNBu^t)]$ in hydrocarbon solvents at 90—100 °C (see scheme) a smooth transformation occurs to give $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ (2) in which the isocyanide ligand lies across the face of the Fe_3 triangle and is bonded to all three iron atoms in a $\sigma + 2\pi$ fashion. This is the only example of this mode of bonding for an isocyanide although similar complexes are known which contain isomeric cyanide, RCN,[17] or isoelectronic acetylide $RC{\equiv}C^-$ ligands [18] bonded

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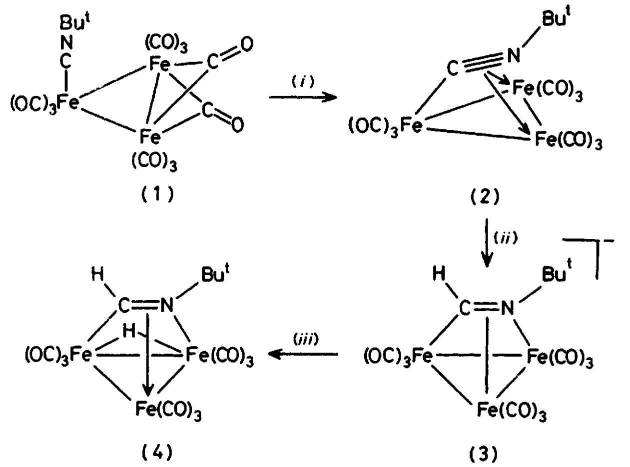
* Recently Simpson and co-workers [16] have found that fragmentation of $[Fe_3(CO)_{12}]$ during $Ph_2CO^{\cdot -}$ induced substitution by $P(OPh)_3$ can be suppressed by working at −30 °C.



Scheme. (*i*) heptane, 95 °C, 1 h; (*ii*) $K[HBBu^s_3]$, thf, 25 °C, 5 min; (*iii*) H_3PO_4, thf, 25 °C, 5 min

through similar $\sigma + 2\pi$ interactions. The extensive involvement of the C≡N π electrons in bonding to the iron triangle in (2) is reflected in the longer C–N distance [1.270(5) Å in (2) *cf.* 1.145(7) Å in (1)] and a lower ν(CN) [1 552 cm^{-1} in (2) *cf.* 2 174 cm^{-1} in (1)].

Thermolysis of $[Fe_3(CO)_{11}(CNBu^t)]$ at higher temperatures, up to 140 °C, gave $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ (2) as the major product, together with small amounts of $[Fe_3(CO)_8(CNBu^t)(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ which contains a terminal, σ-bonded $CNBu^t$ as well as the $\mu_3\text{-}\eta^2\text{-}CNBu^t$ ligand. Two other minor products of the thermolysis at higher temperatures were not identified. Pyrolysis of $[Fe_3(CO)_{11}(CNBu^t)]$ at temperatures above 140 °C led to black insoluble residues showing no ν(CO) bands in their i.r. spectra.

The thermal rearrangement of $[Fe_3(CO)_{11}(CNBu^t)]$ therefore differs from those of the heavier Ru or Os congeners where pentanuclear (Ru) or hexanuclear (Os) clusters were found [9,10] with no species analogous to (2) being observed, while no higher clusters are found for iron.

In view of the unusual co-ordination of the isocyanide ligand in (2) it was of interest to examine the reactivity of the ligand. Terminally bound CNR (R = alkyl or aryl) groups on polynuclear complexes are usually susceptible to attack by electrophiles at the N atom to give bridging carbenoid ligands.[19] However, the $\mu_3\text{-}\eta^2\text{-}CNBu^t$ ligand of (2) does not react with electrophilic H^+ or Et_3O^+ in a similar fashion. Instead, reaction with $[HBBu^s_3]^-$ as a source of nucleophilic H^- proceeded cleanly to give the anion $[Fe_3(CO)_9(HC{=}NBu^t)]^-$ (3). [The addition of ROH to co-ordinated CNR′ to give C(OR)(NR′H) (R = alkyl, R′ = alkyl or aryl) also involves nucleophilic attack.][20] The close similarity between the i.r. spectra of (3) and the isomeric $[Fe_3(CO)_9(RC{=}NH)]^-$ (R = Me, Ph, or Pr^n) clusters reported by Kaesz and co-workers [21] enables a confident assignment of structure to be made. The RC=NH ligand can be regarded as forming two σ bonds *via* the C and N atoms to two of the Fe atoms with the third Fe atom bonding through the C=N π electrons.

Protonation of (3) with H_3PO_4 gives $[Fe_3H(CO)_9(HC{=}NBu^t)]$ (4) (see Scheme). Again the isomeric analogues $[Fe_3H(CO)_9(RC{=}NH)]$ (R = Me, Ph, or Pr^i) are available [21] and more recently Howell and Mathur [22] have prepared related $[Fe_3H(CO)_9(HC{=}NR)]$ complexes by attack of RNC (R = Pr^i) on $[Fe_3H(CO)_{11}]^-$ followed by protonation. The ruthenium analogue of (4) has been obtained by hydrogenation of $[Ru_3(CO)_{11}(CNBu^t)]$,[23] and similar Os clusters are known.[24]

Structure of $[Fe_3(CO)_{11}(CNBu^t)]$ (1).—In the solid state $[Fe_3(CO)_{11}(CNBu^t)]$ (1) adopts a structure derived from the C_{2v} bridged structure found for $[Fe_3(CO)_{12}]$ with one of the axial CO ligands on the non-bridged iron atom replaced by the $CNBu^t$ ligand. This contrasts with other substituted $[Fe_3(CO)_{12}]$ derivatives whose structures are known, namely $[Fe_3(CO)_9(PMe_2Ph)_3]$,[2] $[Fe_3(CO)_{11}(PPh_3)]$ (2 isomers),[3] and $[Fe_3(CO)_{10}(ffars)]$ [4,*] where the ligands occupy equatorial sites. On electronic grounds substitution of CO by a weaker π-acceptor base is expected to favour an axial site *trans* to CO rather than one *trans* to a Fe–Fe bond so that the π bonding to the remaining CO ligands is maximised. On the other hand, steric factors predict bulky ligands would prefer the less crowded equatorial sites. Therefore the observed patterns can be rationalised in terms of a lower steric requirement for $CNBu^t$ allowing occupation of the axial site whereas the bulky phosphine and arsine ligands occupy the least hindered sites. However, too much emphasis should not be placed on these arguments since crystal-packing forces are likely to be similar to the energy difference between isolated axial and equatorial isomers.

A comparison of the structures of $[Fe_3(CO)_{11}(CNBu^t)]$ and $[Fe_3(CO)_{12}]$ shows that the effect of the $CNBu^t$ ligand on the rest of the molecule is slight. Thus the Fe–Fe bond lengths [2.689(1) (unbridged) and 2.563(1) Å (bridged)] are not significantly different from the equivalent ones in $[Fe_3(CO)_{12}]$ [2.680(2) and 2.558(1) Å, respectively] and the Fe–C [1.779(6)—1.814(6) Å] and C–O [1.125(7)—1.145(7) Å] distances involving the terminal CO ligands are normal. However, the individual Fe–C(bridge) distances are not significantly asymmetric, unlike those in $[Fe_3(CO)_{12}]$ where the unsymmetric bridging has occasioned much discussion.[25] For all the $[Fe_3(CO)_{12}]$ derivatives structurally characterised the degree of asymmetry in the CO bridges decreases in the series $[Fe_3(CO)_{12}] > [Fe_3(CO)_{11}(PPh_3)] > [Fe_3(CO)_{10}(ffars)] > [Fe_3(CO)_9(PMe_2Ph)_3] > [Fe_3(CO)_{11}(CNBu^t)]$. The lack of any correlation with size or electronic properties is consistent with the concept of bridging carbonyls occupying a shallow potential-energy well between the terminal extremes so that asymmetry is readily induced by other minor intra- or inter-molecular interactions.[25] A continuum of asymmetry can therefore be expected to arise effectively randomly.

The geometry of the $CNBu^t$ ligand is unremarkable. The Fe–C≡N–C grouping is essentially linear with normal bond lengths.

Attempts have recently been made to explain the structures of cluster carbonyls in terms of packing of the CO ligands to give the lowest energy polyhedron which can accommodate the metal skeleton.[26] The complex $[Fe_3(CO)_{12}]$ and its heavier congeners $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ are important examples in these arguments since the carbonyls of $[Fe_3(CO)_{12}]$ form an icosahedral array whereas in the Ru and Os analogues they are forced to adopt the less favoured anticuboctahedron in order to enclose the larger Ru_3 or Os_3 triangles. This approach rationalises the bridged structure for $[Fe_3(CO)_{12}]$ compared with the non-bridged Ru or Os species. Furthermore the disorder found for $[Fe_3(CO)_{12}]$ can be explained in terms of two equivalent orientations of the Fe_3 triangles within essentially the same CO polyhedron.[26] Recent ^{13}C n.m.r. experiments with $[Fe_3(CO)_{12}]$ have indicated that this molecule is fluxional even in the solid state; a mechanism involving rotation of the Fe_3 moiety within the ligand cage was invoked.[27]

The ligand polyhedron of $[Fe_3(CO)_{11}(CNBu^t)]$ (1), based on the O and N atoms, is essentially icosahedral. The 1 : 5 :

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[*] ffars = 1,2-Bis(dimethylarsino)tetrafluorocyclobut-1-ene.

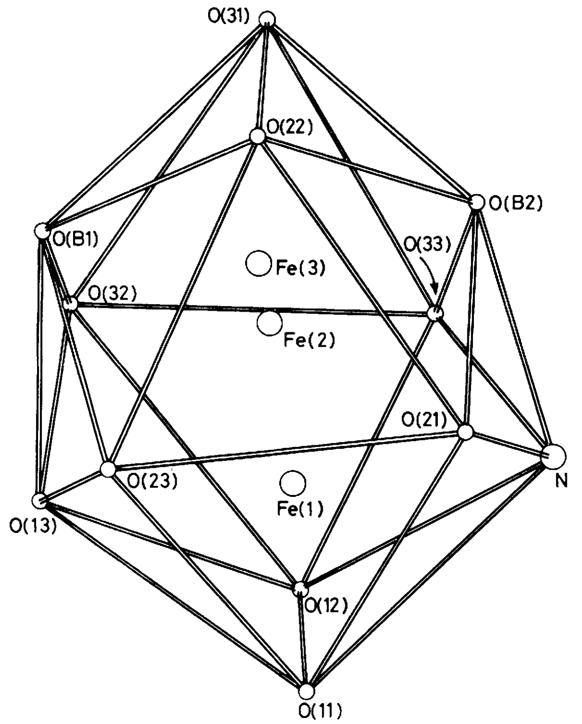


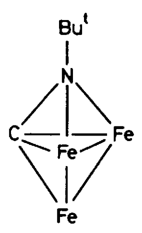
Figure 3. Peripheral atom polyhedron [constructed using O of CO, N of $\mathrm{CNBu^t}$ (*cf.* ref. 34)] for $[\mathrm{Fe_3(CO)_{11}(CNBu^t)}]$ (1)

5 : 1 arrangement illustrated in Figure 3 for the O(31) : [O(22), OB(1), OB(2), O(32), O(33)] : [N, O(12), O(13), O(21), O(23)] : O(11) orientation shows there is some puckering of the pentagonal planes; the dihedral angle between the least-squares planes is 4.4°. The opposite sides O(11)–O(12) and O(22)–O(31) are the longest in the polyhedron (4.5 and 4.9 Å respectively).

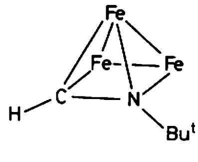
The lack of disorder in $[\mathrm{Fe_3(CO)_{11}(CNBu^t)}]$ is perhaps surprising in view of the similarity between its structure and that of the severely disordered $[\mathrm{Fe_3(CO)_{12}}]$. However because the $\mathrm{CNBu^t}$ ligand occupies an *axial* site on the unique iron atom in (1) a rotation of the plane of the $\mathrm{Fe_3}$ triangle by 60° {the disorder found for $[\mathrm{Fe_3(CO)_{12}}]$} would place the $\mathrm{CNBu^t}$ ligand in a bridging position. Although bridging isocyanide ligands are known [28] they are apparently less favoured than μ-CO; this preference for avoiding a μ-$\mathrm{CNBu^t}$ is apparently sufficient to lock the $\mathrm{Fe_3}$ triangle in one orientation in (1). It is interesting that for $[\mathrm{Ru_3(CO)_{11}(CNBu^t)}]$, where all the ligands are terminal anyway so that similar arguments do not apply, the $\mathrm{Ru_3}$ triangle is disordered.[8]

We have not examined the fluxionality of (1) and (2) in any detail. Nevertheless the single absorption observed in the ^{13}C n.m.r. spectrum of (1) in the CO region shows that at 25 °C all carbonyl ligands are equivalent. In contrast two ^{13}CO singlets are found for (2) at 25 °C; these are assumed to arise from a set of three equivalent CO groups on Fe(1) and from the two identical sets of three equivalent CO groups on Fe(2) and Fe(3). Thus axial–equatorial interchange occurs at each Fe but there is no scrambling between Fe centres on the n.m.r. time-scale.

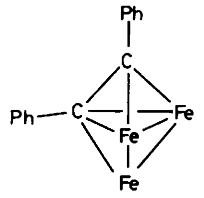
The structures of (2) and (3) can be rationalised in terms of normal σ and π interactions to give 18e counts at each Fe atom. However, a useful alternative analysis is in terms of the skeletal electron-counting rules of Wade.[29] For the 52-electron $[\mathrm{Fe_3(CO)_9}(\mu_3\text{-}\eta^2\text{-}\mathrm{CNBu^t})]$ cluster there are six electron pairs associated with the $\mathrm{Fe_3CN}$ framework; accordingly the structure can be regarded as a *closo* trigonal bipyramid (5) with Fe(1) and N occupying the apical sites below and above the Fe(2)Fe(3)C(1) trigonal plane respectively. Similarly there are seven electron pairs associated with the $\mathrm{Fe_3CN}$ skeleton of the 54e cluster anion $[\mathrm{Fe_3(CO)_9(HC{=}NBu^t)}]^-$ (3) which leads to a prediction of a *nido* structure based on an octahedron with one vertex missing, (6), as found experimentally. It is interesting to analyse in the same fashion the structure of $[\mathrm{Fe_3(CO)_9(PhC{\equiv}CPh)}]$ which was reported some years ago.[30] Electron counting requires the $\mathrm{PhC{\equiv}CPh}$ ligand to act as a six-electron donor to give each Fe an 18e count. However the cluster contains 52 valence electrons, as for $[\mathrm{Fe_3(CO)_9}(\mu_3\text{-}\eta^2\text{-}\mathrm{CNBu^t})]$, hence the observed *closo* trigonal bipyramid (7) is the expected structure, rather than one related to (3) or (6) which might naively be assumed from the similarity between the $\mathrm{PhC{\equiv}CPh}$ and $\mathrm{HC{=}NBu^{t-}}$ ligands. A similar analysis has been very recently published [31] in relation to the structure of $[\mathrm{FeCo_2(CO)_9(EtC{\equiv}CEt)}]$ which is another example of a 54e cluster which also has the *nido* octahedral structure, (6). A more detailed theoretical analysis of the two conformations (6) and (7) is available.[32]



(5)



(6)



(7)

These conclusions lead to two predictions for (6). First, it should be possible to cap the $\mathrm{Fe_2CN}$ face of the cluster with suitable 12e ML_n fragments {*e.g.* $[\mathrm{Rh(CO)_2}]^+$, *cf.* ref. 33} to give octahedral $\mathrm{Fe_3CNM}$ clusters. Second, the two-electron oxidation of $[\mathrm{Fe_3(CO)_9(HC{=}NBu^t)}]^-$ should give a 52e cation $[\mathrm{Fe_3(CO)_9(HC{=}NBu^t)}]^+$ which should rearrange to a trigonal-bipyramidal $\mathrm{Fe_3CN}$ skeleton similar to the $\mathrm{Fe_3C_2}$ core in the $\mathrm{PhC{\equiv}CPh}$ derivative, (7). Both of these conjectures are being tested.

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