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Multi-substituted isonitrile and mixed ligand derivatives of $Fe_3(CO)_{12}$; the crystal structure of $Fe_3(CO)_{10}(CNBu^t)_2$

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Abstract

Routes to isonitrile complexes $Fe_3(CO)_{12-x}(CNR)_x$ ($R = Bu^t$, Xylyl, $x = 1–3$) are described. The structure of $Fe_3(CO)_{10}(CNBu^t)_2$ has been shown by an X-ray diffraction study to be related to that of $Fe_3(CO)_{12}$, with both isonitrile ligands attached to the unique iron atom, one in an axial and the other in an equatorial, site. The readily prepared $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ complex quantitatively takes up some Lewis bases L to give mixed-ligand derivatives $Fe_3(CO)_9(CNBu^t)L_2$ ($L =$ $CNBu^t$, CNXy, $P(OEt)_3$, PMe_2Ph).

Introduction

One of the aims of cluster chemistry is to be able to use the linked metal atoms to coordinate with reactive species in a specific manner which allows subsequent controlled reactivity. It is therefore important to be able to define the substitution reactions of clusters. For the iron-group clusters $M_3(CO)_{12}$ there are now good synthetic routes to substituted species $M_3(CO)_{12-x}L_x$ [$x = 1–4$] for ruthenium and, to a lesser extent, for osmium using thermally-induced reactions, or by use of electron-transfer catalysts (ETC) such as $Ph_2CO^{-\cdot}$ as initiators [1–3]. Substitution reactions for the heavier element clusters can also be initiated using ionic salts such as $[PPN^+][OAc^-]$ [4], supported metal catalysts such as Pd on C [5], or metal carbonyl dimers [6,7] such as $[Fe(CO)_2Cp]_2$ or $[Fe(CO)_2(PPh_3)(\mu\text{-}SMe)]_2$. These methods also have some limited applications in the substitution reactions of $Fe_3(CO)_{12}$, but with this precursor cluster fragmentation is often observed, leading to relatively poor yields [8]. Fragmentation is also the major process in thermal substitution reactions of $Fe_3(CO)_{12}$ [9,10]. A review and subsequent detailed papers by Bruce and co-workers gives a thorough background to the chemistry of substituted $M_3(CO)_{12}$ complexes [1,2].

We describe below some routes to multi-substituted isonitrile and mixed isonitrile-phosphine derivatives of $Fe_3(CO)_{12}$, and report the crystal structure of

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$Fe_3(CO)_{10}(CNBu^t)_2$, which shows a substitution pattern not previously encountered for $M_3(CO)_{12}$ derivatives.

Experimental

All reactions were carried out under nitrogen by standard Schlenk techniques. Instruments used were a Perkin Elmer 180 (IR), a JEOL FX90Q (NMR) and a Varian CH7 (mass spectra). NMR shifts are from TMS (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). $Fe_3(CO)_{12}$ was purchased from Pressure Chemical Co., while $CNBu^t$ and CNXy (Xy = Xylyl, 2,6-dimethylphenyl) were prepared by published methods [11]. The $Na^+Ph_2CO^{-\cdot}$ solution in thf was ca. 0.025 mol l^{-1}. Unless otherwise specified chromatography was on silica gel plates, with light petroleum (60–80 °C fraction) as eluent.

Reaction of $Fe_3(CO)_{12}$ with $CNBu^t$

(a) without initiators. A solution of $Fe_3(CO)_{12}$ (0.30 g, 0.58 mmol) and $CNBu^t$ (0.7 mmol) in thf (30 ml) was stirred for 90 min at room temperature. The solvent was evaporated, and the residue extracted with CH_2Cl_2. The residue was chromatographed on silica gel plates to give three bands; (i) $Fe_3(CO)_{12}$ (trace); (ii) $Fe_3(CO)_{11}(CNBu^t)$ (0.113 g (34%)) and (iii) $Fe_3(CO)_{10}(CNBu^t)_2$ (0.010 g (3%)).

$Fe_3(CO)_{11}(CNBu^t)$ (**1**) has been previously characterised, and was identified by its infrared spectrum [8].

$Fe_3(CO)_{10}(CNBu^t)_2$ (**2**), m.p. 74 °C. Mass spectrum *m/e* 614 (P^+). IR (cm^{-1}) (hexane): 2168sh, 2152sh, 2141m, (ν(CN)), 2055m, 2024s, 2011s, 2007sh, 1989sh, 1981m, 1832w,br, 1800w; (KBr disc) 2174m, 2152m, 2056m, 2023s, 1991s, 1975sh, 1970sh, 1949m, 1821m, 1785m. NMR ($CDCl_3$); ^1H: δ 1.56 (CH_3); ^{13}C: δ 30.18 (CH_3), 58.53 (CMe_3), 217.85 (CO). It was further characterised by a single crystal X-ray structural study (see below).

The reaction was repeated at −10 °C for 7 days to give, on work-up as above, $Fe_3(CO)_{11}(CNBu^t)$ (0.163 g (48%)), containing only a trace of the di-substituted complex.

(b) with $Ph_2CO^{-\cdot}$ as initiator. 1/1 Ratio: as previously described [8], $Fe_3(CO)_{12}$ (0.30 g, 0.6 mmol) and $CNBu^t$ (0.7 mmol) in thf (30 ml) were treated dropwise with $Ph_2CO^{-\cdot}$ solution until reaction was complete (ca. 1.5 ml of initiator solution). Chromatography gave $Fe_3(CO)_{11}(CNBu^t)$ (0.15 g, 45%) containing a trace of $Fe_3(CO)_{10}(CNBu^t)_2$. 1/2 Ratio: $Fe_3(CO)_{12}$ (0.15 g, 0.3 mmol) and $CNBu^t$ (0.6 mmol) in thf (20 ml) were treated dropwise with $Ph_2CO^{-\cdot}$ solution until no $Fe_3(CO)_{12}$ remained (by tlc). Work-up gave $Fe_3(CO)_{11}(CNBu^t)$ (0.046 g (27%)), $Fe_3(CO)_{10}(CNBu^t)_2$ (0.034g (18%)) and $Fe_3(CO)_9(CNBu^t)_3$ (0.008 g (4%)).

(c) initiated with $[Fe(CO)_2Cp]_2$. 1/1 Ratio: a mixture of $Fe_3(CO)_{12}$ (0.147 g, 0.29 mmol), $CNBu^t$ (0.25 mmol) and $[Fe(CO)_2Cp]_2$ (0.01 g) in thf (20 ml) was stirred under normal laboratory light at room temperature for 1 h, by which time no $Fe_3(CO)_{12}$ was left. Work-up gave $Fe_3(CO)_{11}(CNBu^t)$ 0.061 g (38%)) and $Fe_3(CO)_{10}(CNBu^t)_2$ (0.004 g (2%)).

A similar reaction in the dark gave identical results, while a reaction in direct sunlight gave a red solution from which only traces of $Fe_3(CO)_{11}(CNBu^t)$ could be detected.

1/2 Ratio: $Fe_3(CO)_{12}$ (0.139g, 0.28 mmol), $CNBu^t$ (0.50 mmol) and $[Fe(CO)_2Cp]_2$ (0.01 g) in thf (20 ml) were stirred for 2 h. Work-up gave $Fe_3(CO)_{11}(CNBu^t)$ (0.036 g (23%)) and $Fe_3(CO)_{10}(CNBu^t)_2$ (0.012 g (7%)).

(d) initiated with Pd on C. $Fe_3(CO)_{12}$ (0.195 g, 0.39 mmol) and $CNBu^t$ (0.4 mmol) in thf (30 ml) were stirred with 5% Pd on charcoal for 30 min. Work-up gave $Fe_3(CO)_{11}(CNBu^t)$ (0.076 g (35%)).

(e) initiated with PPN^+OAc^-. As for (d), but with PPN^+OAc^- (5 mg) in place of the Pd on C, gave $Fe_3(CO)_{11}(CNBu^t)$ (35%) and $Fe_3(CO)_{10}(CNBu^t)_2$ (3%).

Reaction of $Fe_3(CO)_{12}$ with CNXy

(a) Without initiators. A solution of $Fe_3(CO)_{12}$ (0.116 g, 0.23 mmol) and CNXy (0.25 mmol) in thf (20 ml) was kept for 90 min. The solvent was evaporated off and the residue extracted with ether. Chromatography of the extract gave $Fe_3(CO)_{11}(CNXy)$ (0.056 g (40%)), $Fe_3(CO)_{10}(CNXy)_2$ (0.010 g (6%)) and $Fe_3(CO)_9(CNXy)_3$ (0.005 g (1%)).

The reaction was also carried out at $-10\,°C$ for 14 d, to give $Fe_3(CO)_{11}(CNXy)$ (60%) along with only traces of higher substituted derivatives.

(b) Initiated with PPN^+OAc^-. 1/1 Ratio: a mixture of $Fe_3(CO)_{12}$ (0.296 g, 0.6 mmol), CNXy (0.084 g, 0.64 mmol) and PPN^+OAc^- (0.005 g) in thf (25 ml) was stirred for 25 min, to give on work up $Fe_3(CO)_{11}(CNXy)$ (0.115 g, 32%), $Fe_3(CO)_{10}(CNXy)_2$ (0.052 g (13%)) and $Fe_3(CO)_9(CNXy)_3$ (0.004 g (1%)).

1/3 Ratio: similarly a mixture of $Fe_3(CO)_{12}$ (0.302 g, 0.6 mmol), CNXy (0.234 g, 1.80 mmol) and PPN^+OAc^- (0.005 g) in thf (25 ml) was stirred for 25 min, to give on work-up $Fe_3(CO)_{11}(CNXy)$ (0.134 g (36%)), $Fe_3(CO)_{10}(CNXy)_2$ (0.062 g (15%)) and $Fe_3(CO)_9(CNXy)_3$ (0.050 g (10%)).

Characterisation of $Fe_3(CO)_{12-x}(CNXy)_x$

$Fe_3(CO)_{11}(CNXy)$. m.p. 89–91 °C. Found: C, 39.52; H, 1.63; N 2.00, $M(P^+)$ 607; $C_{20}H_9Fe_3NO_{11}$ calcd.: C, 39.58; H, 1.50; N, 2.30%, M 607. IR(cm^{-1}) (hexane): 2140m (ν(CN)), 2087m, 2035s, 2029s, 2012m, 1995sh, 1854vw, 1818w; (KBr disc): 2152s, 2078s, 2151sh, 2014vs,br, 1989sh, 1965m, 1844m, 1811m. NMR 9$CDCl_3$) ^1H: δ 2.46 (CH_3), 7.17 (3,4,5-CH); ^{13}C: 18.6 (CH_3), 128.1, 128.5 (2,3,5,6-C), 129.3(4-C), 135.5(1-C), 216.7(CO).

$Fe_3(CO)_{10}(CNXy)_2$. IR(cm^{-1}) (hexane): 2140w, 2118m(ν(CN)), 2054m, 2020sh, 2016s, 2007sh, 2000sh, 1982sh, 1840vw, 1808w; (KBr disc): 2130s, 2111s, 2057m, 2000s, 1983s, 1975sh, 1965sh, 1958w,sh, 1918s, 1828m, 1779m. NMR($CDCl_3$) ^1H: δ 2.30 (CH_3), 7.00 (3,4,5-CH).

$Fe_3(CO)_9(CNXy)_3$. Mass spectrum: m/e 626 (P − CNXy − 2CO). IR(cm^{-1}) (hexane): 2106m(νCN), 2033m, 2001s, 1984m, 1962m, 1794w; (KBr disc): 2119s(ν(CN)) 2020s, 1992sh, 1983s, 1968w, 1961w, 1943m, 1785w, 1729w.

Preparation of $Fe_3(CO)_9(CNBu^t)_3$

A brown solution of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ (0.063g, 0.13 mmol) in hexane (10 ml) was treated with $CNBu^t$ (0.25 mmol). After 3 min the solution was green and reaction was complete (tlc). Removal of the solvent left a quantitative amount of $Fe_3(CO)_9(CNBu^t)_3$, m.p. 76 °C. Mass spectrum: m/e 669 (P^+). IR (cm^{-1}), (hexane): 2164sh, 2132m (ν(CN)), 2037sh, 2030m, 2010sh, 2000sh, 1996s, 1979m, 1961m, 1814vw, 1780w; (KBr disc): 2170sh, 2140s (ν(CN)), 2030s, 1989sh, 1978vs,br, 1820w, 1776m. NMR ($CDCl_3$) ^1H: δ 1.54; ^{13}C: δ 30.37 (CH_3), 57.75 (CCH_3), 158.87(CN), 221.55(CO).

Preparation of $Fe_3(CO)_9(CNBu^t)(CNXy)_2$

Similarly, the addition of 2 mole equivalents of CNXy to a solution of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ in hexane led to a rapid reaction (5 min) to give a quantitative field of $Fe_3(CO)_9(CNBu^t)(CNXy)_2$, m.p. 86–87 °C. Found: C, 49.30; H, 3.46. $C_{32}H_{27}Fe_3N_3O_9$ calcd.: C, 50.23; H, 3.56%. Mass spectrum *m/e* 681 (P – 3CO and/or P – $CNBu^t$). IR (cm^{-1}) (hexane): 2166w, 2118sh, 2103 m (ν(CN)), 2037sh, 2030m, 2002s, 1984m, 1966m, 1827vw, 1790w; (KBr disc): 2160sh, 2121sh, 2105s (ν(CN)), 2030m, 1980vs, br, 1862vw, 1779w. NMR ($CDCl_3$) ^1H: δ 1.59 ($C(CH_3)_3$), 2.41 (Ar-CH_3), 7.07 (3,4,5-CH).

Preparation of $Fe_3(CO)_9(CNBu^t)(PMe_2Ph)_2$

PMe_2Ph (0.035 g, 0.25 mmol) was added to a solution of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ (0.055 g, 0.11 mmol) in thf (2 ml). The reaction was complete after 2 min. Evaporation of solvent gave a quantitative yield of $Fe_3(CO)_9(CNBu^t)(PMe_2Ph)_2$, m.p. 114 °C (dec.). Found: C, 46.29; H, 4.60; N, 2.36; $C_{30}H_{31}Fe_3NO_9P_2$ calcd.: C, 46.26; H, 4.01; N, 1.80%. Mass spectrum *m/e* 723 (P – 2CO). IR (cm^{-1}) (hexane): 2141m (ν(CN)), 2034m, 2026m, 1991s, 1966s, 1806w, 1765w; (KBr disc): 2147m (ν(CN)), 2017s, 1976vs, 1958vs, 1944sh, 1932sh, 1910sh, 1798m, 1761m. NMR ($CDCl_3$) ^1H: δ 1.41 (CCH_3), 1.64 (d, *J* 10 Hz, P–CH_3), 7.36 (m, Ph); ^{13}C: δ 17.01 (d, *J* 27 Hz, P–CH_3), 30.05 (CCH_3), 128.75 (m, Ph); ^{31}P: δ 25.2 (poorly resolved multiplet).

Preparation of $Fe_3(CO)_9(CNBu^t)[P(OEt)_3]_2$

$P(OEt)_3$ (0.049 g, 0.30 mmol) was added to a solution of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ (0.06 g, 0.12 mmol) in thf (2 ml). The reaction was complete after 15 min (tlc). Evaporation of solvent gave a quantitative yield of $Fe_3(CO)_9(CNBu^t)[P(OEt)_3]_2$. IR ($cm^{-1}$) (hexane): 2139m ($\nu$(CN)), 2060m, 2036m, 1996s, 1978s, 1958s, 1944s, 1914s, 1903sh, 1873m, 1814w, 1778m; (KBr disc): 2148m (ν(CN)), 2058w, 2032m, 1990s, 1971s, 1905m, 1896sh, 1812w, 1772m. NMR ($CDCl_3$) ^1H: δ 1.27 (t, *J* 7 Hz, CH_2CH_3), 1.58 $C(CH_3)_3$, 4.01 (q, *J* 7 Hz, OCH_2); ^{13}C: δ 15.94 ($CH_2\mathit{C}H_3$), 30.04 ($C(\mathit{C}H_3)_3$), 61.19 ($O\mathit{C}H_2$); ^{31}P: δ 161.4, 183.9 (two lines of approximately equal amplitude).

X-ray crystal structure of $Fe_3(CO)_{10}(CNBu^t)_2$

Suitable crystals were obtained from hexane. The space group was determined by precession photography and intensity data were collected on an Enraf Nonius CAD4 diffractometer using monochromated Mo-K_α X-rays.

Crystal data. $C_{20}H_{18}Fe_3N_2O_{10}$, *M* 613.91, monoclinic, space group $P2_1/n$, *a* 11.111(4), *b* 23.023(2), *c* 11.366(4) Å, β 114.23(3)°, *U* 2651.2(8) Å^3, D_c 1.54 g cm^{-3}, $Z = 4$, *F*(000) 1240, μ(Mo-K_α) 17.3 cm^{-1}, *T* 23 °C.

A total of 3743 unique reflections were collected in the range $2° < 2\theta < 50°$. After correction for Lorentz, polarisation, and absorption (empirical) effects, 2291 data had $I > 3\sigma(I)$ and were used in all calculations. The structure was solved by direct methods and refined in the usual way. In the final cycles of least-squares refinement all non-hydrogen atoms were assigned anisotropic temperature factors. Refinement converged at $R = 0.0462$, $R_w = 0.0509$, where $w = [\sigma^2(F) +$

Table 1

Final positional parameters for $Fe_3(CO)_{10}(CNBu^t)_2$

Atom	x	y	z
Fe(1)	0.3669(1)	0.0871(1)	0.1187(1)
Fe(2)	0.3276(1)	0.1972(1)	0.1776(1)
Fe(3)	0.1260(1)	0.1344(1)	0.0523(1)
C(1)	0.3753(7)	0.1126(3)	−0.0370(7)
C(2)	0.3955(9)	0.1407(4)	−0.2525(7)
C(3)	0.2589(14)	0.1547(8)	−0.3472(11)
C(4)	0.4574(18)	0.0918(6)	−0.2933(13)
C(5)	0.4865(19)	0.1933(7)	−0.2181(13)
N(1)	0.3848(6)	0.1240(3)	−0.1315(6)
C(6)	0.5495(8)	0.0857(3)	0.2041(6)
C(7)	0.8024(8)	0.0910(5)	0.3494(10)
C(8)	0.8447(14)	0.1445(9)	0.3146(38)
C(9)	0.8763(12)	0.0429(7)	0.3246(14)
C(10)	0.8111(17)	0.0868(15)	0.4829(15)
N(2)	0.6627(6)	0.0853(3)	0.2639(6)
C(11)	0.3583(8)	0.0651(4)	0.2653(8)
C(12)	0.3311(8)	0.0145(4)	0.0536(7)
C(21)	0.4385(8)	0.1830(3)	0.3420(8)
C(22)	0.4572(8)	0.2136(4)	0.1256(7)
C(23)	0.2906(9)	0.2720(4)	0.1985(7)
C(31)	−0.0286(10)	0.1711(4)	0.0172(8)
C(32)	0.0894(8)	0.1053(4)	−0.1062(8)
C(33)	0.0869(8)	0.0679(4)	0.1111(8)
O(11)	0.3611(7)	0.0479(3)	0.3618(6)
O(12)	0.3062(8)	−0.0296(3)	0.0135(7)
O(21)	0.5086(6)	0.1761(3)	0.4468(5)
O(22)	0.5383(7)	0.2261(3)	0.0956(6)
O(23)	0.2723(8)	0.3195(3)	0.2095(6)
O(31)	−0.1231(7)	0.1932(4)	0.0019(7)
O(32)	0.0604(6)	0.0890(3)	−0.2086(6)
O(33)	0.0569(8)	0.0257(3)	0.1444(7)
C(41)	0.1925(8)	0.1641(4)	0.2321(7)
C(42)	0.2033(7)	0.1992(4)	−0.0073(7)
O(41)	0.1648(6)	0.1642(3)	0.3200(5)
O(42)	0.1854(6)	0.2255(2)	−0.1001(5)

Table 2

Selected bond lengths (Å) and angles (°) in $Fe_3(CO)_{10}(CNBu^t)_2$

Bond lengths			
Fe(1)–Fe(2)	2.702(2)	N(1)–C(2)	1.478(9)
Fe(2)–Fe(3)	2.553(1)	N(2)–C(6)	1.159(9)
Fe(1)–Fe(3)	2.696(1)	N(2)–C(7)	1.462(9)
Fe(1)–C(1)	1.902(1)	Fe(2)–C(41)	1.995(8)
Fe(1)–C(6)	1.856(8)	Fe(3)–C(41)	1.987(8)
Fe(1)–C(12)	1.806(10)	Fe(2)–C(42)	1.986(7)
Fe(1)–C(11)	1.782(8)	Fe(3)–C(42)	1.975(8)
N(1)–C(1)	1.152(8)		
Bond angles			
Fe(1)–Fe(2)–Fe(3)	61.7(1)	C(1)–N(1)–C(2)	178.1(8)
Fe(1)–Fe(3)–Fe(2)	61.9(1)	C(6)–N(2)–C(7)	172.3(8)
Fe(2)–Fe(1)–Fe(3)	56.5(1)	C(6)–Fe(1)–C(12)	102.0(4)
C(1)–Fe(1)–C(6)	91.9(3)	C(6)–Fe(1)–C(11)	88.4(3)
Fe(1)–C(1)–N(1)	174.8(7)	C(1)–Fe(1)–C(11)	178.6(4)
Fe(1)–C(6)–N(2)	176.1(6)	C(1)–Fe(1)–C(12)	89.5(4)

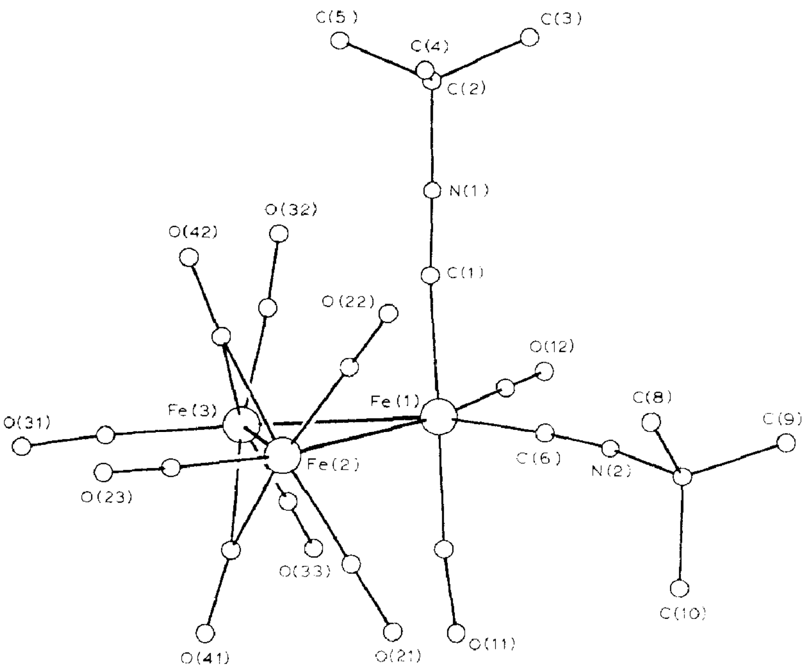


Fig. 1 A PLUTO diagram of the structure of $Fe_3(CO)_{10}(CNBu^t)_2$ (**2**).

$0.0036F^2]^{-1}$. The largest final shift was 0.2σ and the largest feature in a final difference map was 0.6 e $Å^{-3}$. Calculations were performed by use of SHELX-76 [12]. Final positional parameters are given in Table 1 and selected bond lengths and angles in Table 2, and the structure is illustrated in Figure 1. Tables of thermal parameters, a complete table of bond lengths and angles, and a list of observed and calculated structure factors are available from the authors.

Results and discussion

Because of the number of different initiators [1–8] that have been used recently for substitution reactions at $M_3(CO)_{12}$ clusters, a comparison was undertaken of some of these in the reactions of $Fe_3(CO)_{12}$ with an equimolar amount of an isonitrile. A new observation was that in thf solution reactions take place to give reasonable yields of $Fe_3(CO)_{11}(CNR)$ even in the absence of initiators. This is perhaps not unexpected, since it is known [13] that in this ether solvent $Fe_3(CO)_{12}$ spontaneously generates radical ions of the type $[Fe_3(CO)_{11 \text{ or } 12}]^{-\cdot}$, which are assumed to be the intermediates in reactions involving initiators such as $Ph_2CO^{-\cdot}$ and $[Fe(CO)_2Cp]_2$ [1,7]. In the absence of initiators, at room temperature the reactions are complete within 1–2 hours, whereas at −10 °C they take 1–2 weeks but give higher yields of the monosubstituted species. It has been noted previously in the ETC reaction of $Fe_3(CO)_{12}$ with $P(OR)_3$ that use of lower temperatures enhances yields by prolonging the lifetimes of the radical intermediates [14].

All of the initiators used ($Na^+Ph_2CO^{-\cdot}$, PPN^+OAc^-, $[Fe(CO)_2Cp]_2$, Pd on C) in thf increased the reaction rate, and gave significantly larger amounts of higher substituted species, but overall yields were no better than in non-catalysed reactions. Under these conditions the $Na^+Ph_2CO^{-\cdot}$ gave marginally better yields of

$Fe_3(CO)_{11}(CNR)$ than the other initiators, but it is perhaps less convenient to use than the others. We note that much higher yields of $Fe_3(CO)_{11}(CNR)$ have been claimed with $[Fe(CO)_2Cp]_2$ as an initiator [7], but we were unable to reproduce these with thf solutions; a careful reading of the original paper does not indicate which solvent was used in that study and that may account for the differences in our results. Since it is assumed that homolysis of the Fe–Fe bond is a key step for the $[Fe(CO)_2Cp]_2$ initiator, the experiment was repeated under various light intensities; no difference was found between the dark and normal laboratory light reactions, while intense sunlight markedly reduced the yields of $Fe_3(CO)_{11}(CNBu^t)$ through photodegradation of the iron carbonyls in solution.

At higher ratios of $CNR/Fe_3(CO)_{12}$ all of the initiators again gave similar amounts of $Fe_3(CO)_{10}(CNR)_2$ and $Fe_3(CO)_9(CNR)_3$, but only moderate yields of the di-substituted complex could be isolated, and no conditions examined gave more than minor amounts of the tri-substituted species; cluster fragmentation becomes the dominant process at high $CNR/Fe_3(CO)_{12}$ ratios. An alternative route to the higher substituted clusters was therefore sought.

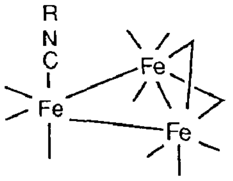
We have shown previously [8] that the cluster $Fe_3(CO)_{11}(CNBu^t)$ undergoes facile decarbonylation to give $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ (**3**), containing a six-electron donor isonitrile ligand. This cluster has now been found to react rapidly and quantitatively with two molar equivalents of $CNBu^t$ to give the cluster $Fe_3(CO)_9(CNBu^t)_3$. Similarly, addition of other Lewis bases L gave $Fe_3(CO)_9(CNBu^t)L_2$. Reactions were rapid and quantitative for L = CNXy, $P(OEt)_3$ or PMe_2Ph and gave rise to the corresponding mixed-ligand substituted clusters, which were stable enough for complete characterisation. Reaction with PBu_3 occurred more slowly and less specifically, to give a product that is thought to be $Fe_3(CO)_9(CNBu^t)(PBu_3)_2$ on the basis of infrared spectral data but which could not be fully characterised. With PPh_3, $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ reacted only slowly, and appeared to give a mixture, including the substituted complex $Fe_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ rather than one containing a η^1-$CNBu^t$ (cf. $Fe_3(CO)_8(\mu_3\text{-}\eta^2\text{-}CNBu^t)(\eta^1\text{-}CNBu^t)$ [8]). Other Lewis bases examined that did not react under moderate conditions with $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ include $AsPh_3$, dppe, dppm, thiophene and PhCCH. The formation of mixed ligand complexes by this route seems to be limited to moderately basic ligands with relatively small steric requirements. A similar route to corresponding mixed ligand species with CNXy has not yet been observed because we have not found conditions which generate the precursor complex $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNXy)$. However, the corresponding nitrile complexes $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}NCR)$ have been reported [15], and we would expect them to provide the analogous mixed ligand complexes.

The solid-state structure of $Fe_3(CO)_{11}(CNBu^t)$ has been shown [8] to be that depicted in **1**, with the basic $Fe_3(CO)_{12}$ structure [16] preserved and the isonitrile occupying an axial site on the unique atom. From the similarity between the infrared spectra of $Fe_3(CO)_{11}(CNXy)$ and $Fe_3(CO)_{11}(CNBu^t)$ we assume that the CNXy ligand is also axially coordinated to the unique iron atom. This is also true for the nitrile ligand in $Fe_3(CO)_{11}(NCPr^i)$ [17], and is probably the electronically preferred site for replacement of one CO by a weaker π-acceptor ligand. In contrast the isonitrile ligand in $Fe_3(CO)_{11}(CNCF_3)$ has been found to have replaced a bridging CO ligand; this can be rationalised in terms of its being a better π-accepting ligand [18]. For larger groups such as PPh_3 the sterically less hindered equatorial sites become favoured [19]. In solution the bridged form is also maintained for $Fe_3(CO)_{11}(CNR)$, since infrared bands assignable to bridging CO groups are observed, but the ^{13}C NMR spectrum shows only a single peak for the CO ligands, suggesting fluxionality at room temperature.

There are no previous reports of structures of $Fe_3(CO)_{10}L_2$ complexes (L = monodentate ligand). The structure of $Fe_3(CO)_{10}(CNBu^t)_2$ (**2**) is shown in Fig. 1. The basic $Fe_3(CO)_{12}$ geometry is retained but somewhat unexpectedly both isonitrile ligands are on the unique iron atom, one in an axial and the other in an equatorial site. This contrasts with the structures assigned to $Fe_3(CO)_{10}L_2$ (L = phosphine) on infrared evidence, for which each L is assumed to be attached to a different iron atom [9], and is also different from the substitution pattern found for $Ru_3(CO)_{10}(CNBu^t)_2$ [20], in which the isonitriles are on different ruthenium atoms. The structure found for $Fe_3(CO)_{10}(CNBu^t)_2$ is presumably favoured because of the low bulk of the $CNBu^t$ ligand and the similarity in bonding interactions for CNR and CO when acting as terminal ligands. Whether the same structure is the lowest energy one in solution is not known; the ^1H and ^{13}C NMR spectra show both $CNBu^t$ ligands to be equivalent and give only one ^{13}CO signal, so the molecule is highly fluxional at room temperature. However the solid state carbonyl-region infrared spectrum of $Fe_3(CO)_{10}(CNXy)_2$ is very similar to that of the $CNBu^t$ analogue. This suggests that the same substitution pattern is followed for both isonitriles, which indicates that the isomer found for $Fe_3(CO)_{10}(CNBu^t)_2$ is the minimum energy one, and is not simply the one of many which is frozen out by crystal packing interactions.

A detailed comparison of the structure of $Fe_3(CO)_{10}(CNBu^t)_2$ with those of $Fe_3(CO)_{11}$ [16] and $Fe_3(CO)_{11}(CNBu^t)$ [8] reveals only small differences. The Fe–Fe bonds involving the unique iron atom increase significantly on going from the unsubstituted to the disubstituted derivative. There is no difference between the lengths of Fe(1)–Fe(2) and Fe(1)–Fe(3) in **2** despite the fact that these bonds are rendered inequivalent by the equatorial $CNBu^t$ ligand. This is unusual for substituted $M_3(CO)_{12}$ complexes for which clear patterns of M–M bond variations have been established [1,2], but undoubtedly reflects the small electronic and steric differences between CO and $CNBu^t$ as ligands. The Fe(1)–C(6) bond involving the equatorial isonitrile ligand (*trans* to an Fe–Fe bond) is shorter than Fe(1)–C(1) involving the $CNBu^t$ in the axial site (*trans* to CO), and the same pattern is observed for the equatorial and axial CO ligands on the same iron atom. The Fe–CO bonds are shorter than the Fe–$CNBu^t$ bonds in each case. These variations reflect the better π-acceptor properties of CO than of $CNBu^t$, and relate to the competition for π-bonding electron density from the ligands in the opposite sites. The bridging carbonyl ligands in **2** are symmetrically situated.

We have been unable to obtain single crystals of $Fe_3(CO)_9(CNR)_3$ derivatives suitable for X-ray analysis, so which of the possible isomeric forms is adopted is unknown. The carbonyl region infrared spectra are simple, indicating high symmetry, which in turn suggests an isomer with one isonitrile axial on the unique iron atom and the other two in equatorial sites on the other iron atoms, as in **4**. The basic $Fe_3(CO)_{12}$ structure is still maintained, as shown by the presence of clear μ-CO bands in the infrared spectra in the solid-state and solution spectra. These trisubstituted derivatives are therefore different from the $Fe_3(CO)_9(P(OEt)_3)_3$ species, which have recently been assigned a non-bridged, $Ru_3(CO)_{12}$-like, structure [21].



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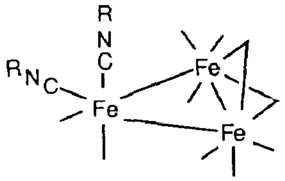

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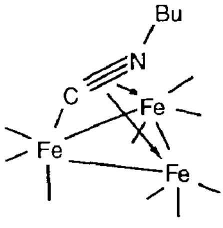

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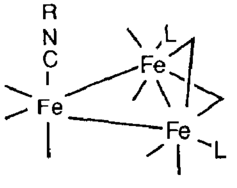

4

There is a clear similarity between the infrared spectrum of the mixed species $Fe_3(CO)_9(CNBu^t)(CNXy)_2$ and the spectra of of $Fe_3(CO)_9(CNR)_3$ (R = Bu^t or Xy) which suggests the same substitution pattern is adopted for all three derivatives.

For the mixed isonitrile-phosphine complexes $Fe_3(CO)_9(CNBu^t)(PR_3)_2$ a number of different isomers are possible. In the absence of crystallographic data we assume a $Fe_3(CO)_{12}$-type structure in which the $CNBu^t$ ligand is axial on the unique atom and the phosphine ligands are equatorial on the other two iron atoms, as in **4**. This would be in accord with the electronic and steric properties of the ligands, and would represent a compromise between the structure of $Fe_3(CO)_{11}(CNBu^t)$ [8] and that of $Fe_3(CO)_9(PMe_2Ph)_3$ [22], in which the three bulky ligands are equatorial on each iron atom. It is clear from the complexity of the ^{31}P NMR spectra of both $Fe_3(CO)_9(CNBu^t)(P(OEt)_3)_2$ and $Fe_3(CO)_9(CNBu^t)(PMe_2Ph)_2$ that more than one isomer is present in solution at room temperature, but nothing definite can be concluded without detailed variable temperature studies of the type performed recently on $Fe_3(CO)_9(P(OR)_3)_3$ [21].

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