

## Cluster Chemistry. Synthesis and X-Ray Crystal Structure of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CNBu}^\dagger)]$ ,<sup>†</sup> a Trinuclear Cluster Complex containing an Isocyanide Ligand acting as a Six-electron Donor

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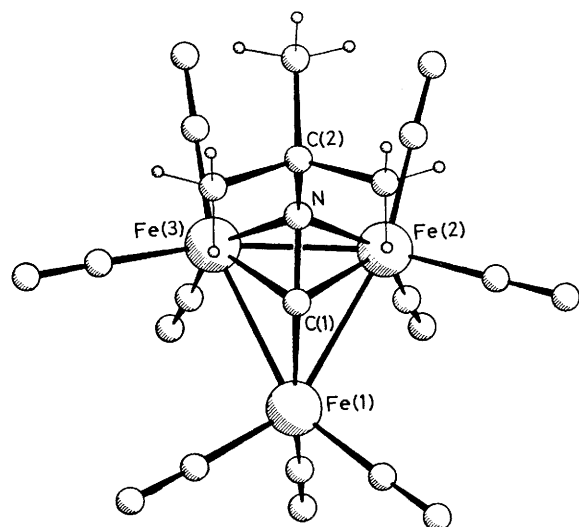
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Mild thermolysis of  $[\text{Fe}_3(\text{CO})_{11}(\text{CNBu}^\dagger)]$  gives  $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CNBu}^\dagger)]$  (**1**) in which the isocyanide ligand is bonded to all metal atoms in a  $(1\sigma + 2\pi)$  manner, lying across the  $\text{Fe}_3$  triangle; reaction of  $\text{H}^-$  with (**1**) gives  $[\text{Fe}_3(\text{CO})_9(\text{HC}=\text{NBu}^\dagger)]^-$  (**2**), which forms  $[\text{HFe}_3(\text{CO})_9(\text{HC}=\text{NBu}^\dagger)]$  (**3**) with  $\text{H}^+$ .

There is much current interest in the extended interactions that occur between small unsaturated molecules and metal clusters, which are not possible in mononuclear complexes.

Such systems can often be prepared by simple thermal rearrangements; examples include the pyrolysis of  $[\text{M}_3(\text{CO})_{11}(\text{CNBu}^\dagger)]$  to give pentanuclear ( $\text{M} = \text{Ru}$ )<sup>2</sup> or hexanuclear ( $\text{M} = \text{Os}$ )<sup>3</sup> clusters, the former containing a  $\mu_3$ -isocyanide ligand acting as a 6e donor. We now describe a three-atom cluster which also contains an isocyanide ligand giving six electrons to the cluster, but with a geometry different from that found in the  $\text{Ru}_5$  complex.

<sup>†</sup> Following the nomenclature suggestions in ref. 1, the bridging isocyanide ligand in this complex would be described as  $[\eta^2-(\mu_3\text{-C}, \mu_2\text{-N})\text{-CNBu}^\dagger]$ .

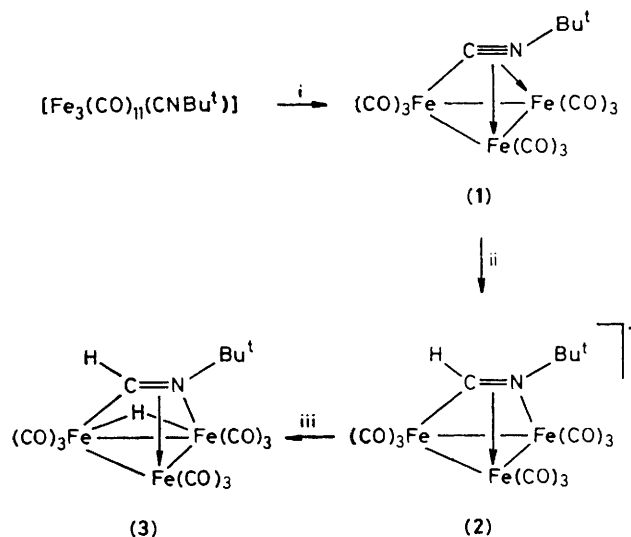


**Figure 1.** The structure of  $[\text{Fe}_3(\text{CO})_9(\text{CNBU}^t)]$  showing the (non-crystallographic) mirror symmetry of the molecule. Bond lengths: Fe(1)–Fe(2) 2.693(1); Fe(1)–Fe(3) 2.693(1); Fe(2)–Fe(3) 2.482(1); Fe(1)–C(1) 1.754(4); Fe(2)–C(1) 2.006(4); Fe(3)–C(1) 1.998(4); Fe(2)–N 2.030(3); Fe(3)–N 2.033(4); C(1)–N 1.270(5); N–C(2) 1.510(6) Å; bond angles: Fe(1)–C(1)–N 159.8(4); C(1)–N–C(2) 132.0(4)°.

After heating a green heptane solution of  $[\text{Fe}_3(\text{CO})_{11}(\text{CNBU}^t)]$  under reflux (45 min), a brown solution was obtained, which on cooling ( $-30^\circ\text{C}$ ) afforded deep red-brown crystals of  $[\text{Fe}_3(\text{CO})_9(\text{CNBU}^t)]$  (1) in 70% yield [ $\nu(\text{CO})$  (hexane) 2086m, 2038s, 2029s, 2018s, 2000w, 1992s, and 1981s  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  1.55s;  $^{13}\text{C}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  32.2s ( $\text{CMe}_3$ ), 63.8s ( $\text{CMe}_3$ ), and 210.0s and 210.4s p.p.m. (CO);  $M^+$  at  $m/e$  503].<sup>‡</sup> The usual 18e requirement suggests that the isocyanide ligand in (1) acts as a six-electron donor, so we have carried out an X-ray structure analysis to determine the geometry of this unusual arrangement.

**Crystal data:**  $\text{C}_{14}\text{H}_9\text{Fe}_3\text{NO}_9$ ,  $M = 502.8$ , triclinic, space group  $P\bar{1}$ ,  $a = 7.749(2)$ ,  $b = 9.310(2)$ ,  $c = 14.038(3)$  Å;  $\alpha = 92.49(2)$ ,  $\beta = 90.76(2)$ ,  $\gamma = 108.93(2)^\circ$ ;  $U = 956.6$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.77$ ,  $D_c = 1.75$   $\text{g cm}^{-3}$ ;  $F(000) = 500$ ,  $\lambda(\text{Mo-K}\alpha) = 0.7107$  Å,  $\mu(\text{Mo-K}\alpha) = 22.6$   $\text{cm}^{-1}$ . Refinement gave  $R = 0.028$  ( $R^1 = 0.030$ ) for 1566 absorption-corrected intensities [ $277\text{ K}$ ,  $3 \leq 2\theta \leq 44^\circ$ ,  $I > 2.5\sigma(I)$ , Enraf-Nonius CAD 4].<sup>§</sup>

The structure of (1) is shown in Figure 1, and important bond distances and angles are given in the caption. The complex contains an isosceles triangle of iron atoms, each co-ordinated to one axial and two equatorial CO ligands. The CNBU<sup>t</sup> group lies across the triangular face so that the C atom is bonded to the unique Fe(1) while the C≡N moiety lies symmetrically above the Fe(2)–Fe(3) bond. The bonding of the CNBU<sup>t</sup> to the cluster involves donation of the lone pair on C(1) to Fe(1) through a 'bent'  $\sigma$ -interaction and



**Scheme 1.** Reagents and conditions: i, heptane,  $100^\circ\text{C}$ , 1 h; ii,  $\text{K}[\text{HBBu}^t_3]$ , tetrahydrofuran (THF), 2 min,  $25^\circ\text{C}$ ; iii,  $\text{H}_3\text{PO}_4$ , THF, 5 min,  $25^\circ\text{C}$ .

formation of two orthogonal  $\pi$ -bonds from C≡N to Fe(2) and Fe(3). That the double  $\pi$  bridge is efficient is confirmed by the short Fe(2)–Fe(3) distance [2.482(1) Å] which is appreciably shorter than the corresponding doubly CO-bridged bond in  $[\text{Fe}_3(\text{CO})_{12}]$  [2.558(1) Å].<sup>4</sup> The extensive removal of  $\pi$ -electron density from the C≡N bond is shown by both the lengthening of this bond [1.270(5) Å] and the lowering of the  $\nu(\text{CN})$  mode (1553  $\text{cm}^{-1}$ ) compared with values for terminal RNC ligands (*ca.* 1.15 Å and *ca.* 2170  $\text{cm}^{-1}$  respectively).

The 6e-interaction of the isocyanide ligand with the three metal atoms found in (1) completes a series of structurally characterised complexes containing the iso-electronic ligands CO [in  $[\text{Nb}_3(\text{CO})_9(\eta\text{-C}_5\text{H}_5)_3]$ ],<sup>1</sup> CNBU<sup>t</sup> [in (1)], NCPr [in  $[\text{Fe}_3(\text{CO})_9(\text{NCPr})]$ ],<sup>5</sup> and  $\text{C}\equiv\text{CR}^-$  [in  $[\text{Fe}_3(\text{C}\equiv\text{CPh})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$ ]<sup>6</sup> and  $[\text{Ru}_3(\text{C}\equiv\text{CR})(\mu\text{-PPh}_2)(\text{CO})_8]$ .<sup>7</sup> Two other examples of two-atom 6e-donor groups in clusters are CNBU<sup>t</sup> in  $[\text{Ru}_5(\text{CO})_{14}(\text{CNBU}^t)_2]$ <sup>2</sup> and CS in  $[\text{Fe}_5(\mu_4\text{-CS})(\mu_3\text{-S})_2(\text{CO})_{13}]$ .<sup>8</sup> All provide further evidence for the lengthening (and hence weakening) of C–X multiple bonds on co-ordination to clusters of metal atoms, and their reactivity may help the understanding of the chemistry of these and related molecules on metal surfaces.

Not surprisingly, the isocyanide ligand in (1) is inert towards  $\text{HPF}_6$  or  $\text{Et}_3\text{O}^+\text{BF}_4^-$ , but readily undergoes nucleophilic attack by  $\text{H}^-$  at the carbon atom (Scheme 1) to give  $[\text{Fe}_3(\text{CO})_9(\text{HC}=\text{NBU}^t)]^-$  (2), which can be isolated as claret-coloured  $[\text{AsPh}_4]^+$  or  $[\text{NEt}_4]^+$  salts [ $\nu(\text{CO})$  (tetrahydrofuran) 2031m, 1970vs, 1963s, 1943s, and 1919m  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  1.21s (9H,  $\text{CMe}_3$ ) and 9.52s (1H, =CH)]. Protonation ( $\text{H}_3\text{PO}_4$ ) of (2) gives red  $[\text{HFe}_3(\text{CO})_9(\text{HC}=\text{NBU}^t)]$  (3) [ $\nu(\text{CO})$  (hexane) 2088m, 2052s, 2025s, 2017s, 2003m, 1998m, 1973m, and 1963m  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$   $-15.9$ s (1H, FeH), 1.24s (9H,  $\text{CMe}_3$ ), and 9.21s (1H =CH); ( $M - \text{CO}$ )<sup>+</sup> at  $m/e$  477]. Ruthenium<sup>9</sup> and osmium<sup>10</sup> analogues of (3) have been described, and identification of (3) was facilitated by comparison with them; the Pr<sup>t</sup> analogue of (3) has been obtained<sup>11</sup> by protonating the product of the prolonged reaction between  $[\text{HFe}_3(\text{CO})_{11}]^-$  and CNPr<sup>t</sup>. The spectral properties of (2) and (3) also strongly resemble those of the isomeric complexes  $[\text{Fe}_3(\text{CO})_9(\text{HN}=\text{CR})]^-$  and  $[\text{HFe}_3(\text{CO})_9(\text{HN}=\text{CR})]$ , respectively, prepared by transformations of nitrile ligands on  $\text{Fe}_3$  carbonyl clusters.<sup>12</sup>

<sup>‡</sup> Satisfactory analytical data were also obtained for complexes (1), (3), and the  $\text{AsPh}_4^+$  salt of anion (2).

<sup>§</sup> 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.

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