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Preliminary communication

SYNTHESES AND X-RAY STRUCTURES OF TWO NITROSYLIRON CLUSTERS $[(Ph_3P)_2N][Fe_6C(CO)_{15}NO]$ AND $[Fe_6C(CO)_{11}(NO)_4]$. FIRST EXAMPLE OF A CARBONYL-NITROSYL CLUSTER WITH FOUR NO LIGANDS

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Summary

$[X]_2[Fe_6C(CO)_{16}]$ ($X = (Ph_3P)_2N$ or Et_4N) reacts with $NOBF_4$ in CH_2Cl_2 to give $[X][Fe_6C(CO)_{15}NO]$. This complex reacts with an excess of $NOBF_4$ to give $[Fe_6C(CO)_{11}(NO)_4]$. The structures of the two new complexes were determined by X-ray crystallography.

Recent interest in nitrosyl-containing clusters stems mainly from their greater reactivity compared with binary carbonyl clusters [1], and from the observations that cluster-bond NO can be reduced [2], *O*-methylated and *O*-protonated [3], or deoxygenated to yield nitrido clusters [4]. However, few nitrosylcarbonyliron clusters are known; we report herein the syntheses of the first carbonylnitrosylhexairon clusters $[Fe_6C(CO)_{15}(NO)]^-$ and $[Fe_6C(CO)_{11}(NO)_4]$.

The salt $[X]_2[Fe_6C(CO)_{16}]$ ($X = (PPh_3)_2N$ and Et_4N) reacts with $NOBF_4$ in CH_2Cl_2 under argon to give the complex $[X][Fe_6C(CO)_{15}(NO)]$ (I)* in 50% yield. The reaction is monitored by infrared spectroscopy and stopped immediately after consumption of the starting cluster. The product is purified by recrystallisation from ethanol/dichloromethane; crystals are obtained from layered hexane/dichloromethane.

The IR spectra** suggest the presence of both bridging and terminal carbonyl

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*Satisfactory elementary analyses were obtained for both complexes.

**Selected IR data in CH_2Cl_2: I: ν(CO) 2070vw, 2020vs, and 1835m, ν(NO) 1750w; II: ν(CO) 2080w, 2040s, 1910w(br) and 1880vw(sh), ν(NO) 1805m(br), and 1610w(br); in KBr disc: II: ν(FeC) 805m, 790m and 760m cm^{-1}.

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ligands and indicate that the NO ligand is terminal. X-ray study* of the $[(PPh_3)_2N]^+$ salt shows (Fig. 1) that the terminal NO group is bonded to one Fe atom, which shares two bridging CO groups with two other Fe atoms of a triangular face. This geometry is very similar to that in $[HRu_6C(CO)_{15}(NO)]$ [5] and in $[Ru_6C(CO)_{15}(NO)(AuPPh_3)]$ [6].

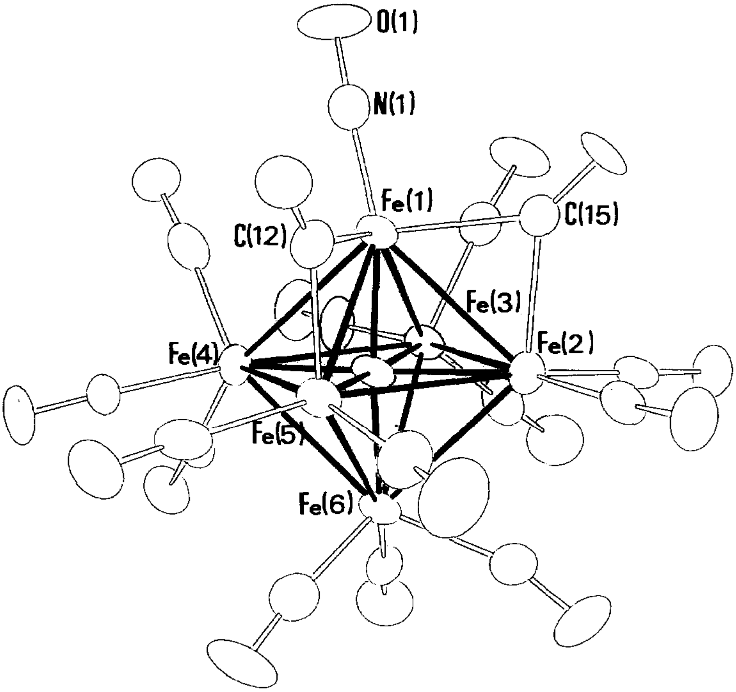

Fig. 1. The structure of the $[Fe_6C(CO)_{15}(NO)]^-$ anion I. Important bond lengths(Å) are: Fe—Fe: (1)—(2) 2.565, (1)—(3) 2.715, (1)—(4) 2.748, (1)—(5) 2.576, (2)—(3) 2.653, (3)—(4) 2.667, (4)—(5) 2.697, (2)—(6) 2.704, (3)—(6) 2.686, (4)—(6) 2.672, (5)—(6) 2.721, max e.s.d. 0.004 Å, Fe(1)—N 1.67(2), mean Fe—C(carbido) 1.89(2) Å.

Addition of an excess of $NOBF_4$ to a CH_2Cl_2 solution of $[X][Fe_6C(CO)_{15}(NO)]$ gives the complex $[Fe_6C(CO)_{11}(NO)_4]$ (II) in low yield (<10% after 2 h). The mechanism of formation of this cluster, which requires an oxidative-reduction step, is not yet clear. The product is extracted with, and recrystallised from dry hexane. The infrared spectrum indicates the presence of both terminal and bridging carbonyl and nitrosyl groups. The X-ray study of a crystal grown by slow cooling of a CH_2Cl_2 solution was carried out, and the molecular structure is shown in Fig. 2. Three terminal nitrosyl ligands are

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*Crystal data for I: $[C_{36}H_{30}NP_2][C_{16}NFe_6O_{16}]$, $M = 1335.85$, orthorhombic, space group $P2_1 2_1 2_1$, a 17.040(9), b 21.014(13), c 14.966(14) Å, U 5359 Å^3, $Z = 4$, D_c 1.66 g cm^{-3}, θ range 2—24°, present R_w-value 0.054 for 3360 reflections with $F>2\sigma(F)$, uncorrected for absorption (Mo-K_α) 17.1 cm^{-1}.

Crystal data for II: $C_{12}Fe_6N_4O_{15}$, $M = 775.2$, orthorhombic, space group $Pnma$, a 17.828(13), b 8.616(4), c 14.331(10) Å, U 2201 Å^3, $Z = 4$, D_c 2.34 g cm^{-3}, θ range 2—24°, present R_w-value 0.063 for 1635 reflections with $F>2\sigma(F)$, uncorrected for absorption, (Mo-K_α) 39.8 cm^{-1}. The nitrogen atom and the two carbon atoms of the three disordered bridging ligands have been refined with the nitrogen scattering factor and an occupation factor of 19/21.

attached to the adjacent iron atoms of one triangular face of the cluster. Two CO and one NO bridge the edges of this face; they were found to be disordered over these 3 positions.

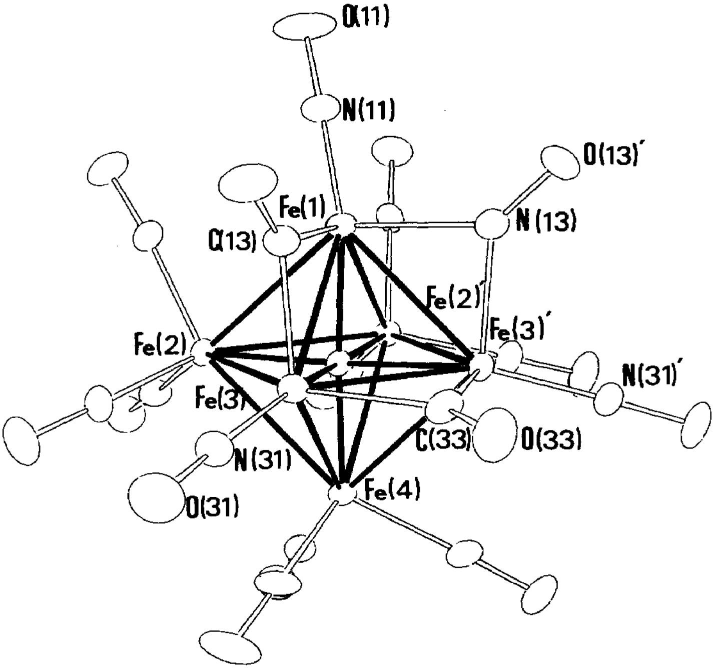

Fig. 2. The structure of the neutral cluster $[Fe_6C(CO)_{11}(NO)_4]$ (II). The atoms with the prime are related to the corresponding atoms without prime by crystallographic mirror symmetry. The bridging NO ligand is shown here in one of the three possible bridging positions. Important bond lengths (Å) are: Fe—Fe: (1)—(2) 2.722, (1)—(3) 2.597, (2)—(2) 2.733, (2)—(3) 2.711, (3)—(3)' 2.590, (2)—(4) 2.706, (3)—(4) 2.708, max e.s.d. 0.003 Å, Fe(1)—N(11) 1.62(2), Fe(3)—N(31) 1.65(1), Fe(3)—X(33) 1.91(1), Fe(1)—X(13) 1.94(1), Fe(3)—X(13) 1.92(1) (X being either C or N), mean Fe—C(carbido) 1.90(2) Å.

In both clusters the FeNO groups are linear and in II the Fe_2NO group is planar. The NO ligands act as 3 electron donors and the clusters follow Wade's rule, with 7 skeleton pairs per 6 iron atoms. The clusters skeletons have C_s symmetry; there is no distorsion from *Oh* to D_3 symmetry such as was observed in the case of Os_6 and Ru_6 clusters [6,7]. The complex $[Fe_6C(CO)_{11}(NO)_4]$ provides the first example of clusters having 4 NO ligands together with 2 CO ligands on one face of the cluster. As noted by others [6,8,9], this may related to the first step of the surface-catalysed reduction of the nitric oxide by carbon monoxide:

$$2NO + CO \rightarrow N_2O + CO_2$$

A study of the reactions of this carbonylnitrosyl cluster is in progress.

Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (U.K.).

References

1 S. Badhuri, B.F.G. Johnson, J. Lewis, D.J. Watson and C. Zucarro, J. Chem. Soc., Dalton Trans., (1979) 557.
2 B.F.G. Johnson, J. Lewis and J.M. Mace, J. Chem. Soc., Chem. Commun., (1984) 186.
3 R.E. Stevens and W.L. Gladfelter, J. Am. Chem. Soc., 104 (1982) 6454.
4 D.E. Fjare and W.L. Gladfelter, J. Am. Chem. Soc., 106 (1984) 4799.
5 B.F.G. Johnson, J. Lewis, W.J.H. Nelson, J. Puga, M. McPartlin and A. Sironi, J. Organomet. Chem., 253 (1983) C5.
6 B.F.G. Johnson, J. Lewis, W.J.H. Nelson, J. Puga, P.R. Raithby, D. Braga, M. McPartlin and W. Clegg, J. Organomet. Chem., 243 (1983) C13.
7 M. McPartlin, C.R. Eady, B.F.G. Johnson, J. Lewis, J. Chem. Soc., Chem. Commun., (1976) 883.
8 D.F. Fjare and W.L. Gladfelter, Inorg. Chem., 20 (1981) 3533.
9 J.A. McCleverty, Chem. Rev., 79 (1979) 53 and ref. therein.