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# Reactivity of nitrido-carbonyl clusters: synthesis and solid state structure of $[Fe_5MnN(CO)_{16}]^{2-}$ and $[Fe_6N(CO)_{14}NO]^{2-}$; oxidation of a cluster-coordinated nitride

**Roberto Della Pergola,***[a] **Luigi Garlaschelli,**[b] **Mario Manassero,***[c] **Mirella Sansoni,**[c] **Donatella Strumolo,**[b] **Fabrizia Fabrizi de Biani**[d] **and Piero Zanello**[d]

[a] *Dipartimento di Scienze dell' Ambiente e del Territorio, Università di Milano Bicocca, piazza della Scienza 1, 20126 Milano, Italy. E-mail: roberto.dellapergola@unimib.it*
[b] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica and centro CSSMTBO del CNR, Università di Milano, via G. Venezian 21, 20133 Milano, Italy*
[c] *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, via G. Venezian 21, 20133 Milano, Italy. E-mail: m.manassero@csmtbo.mi.cnr.it*
[d] *Dipartimento di Chimica dell' Università, via A. Moro, 53100 Siena, Italy*

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The cluster $[Fe_5MnN(CO)_{16}]^{2-}$ (**1**) was synthesized from $[Fe_6N(CO)_{15}]^{3-}$ and $Mn_2(CO)_{10}$, in refluxing EtCN, or $[Fe_4N(CO)_{12}]^-$ and $[FeMn(CO)_9]^-$. Its solid state structure was determined on the $[Me_3NCH_2Ph]^+$ salt, and consists of an octahedral metal cage, enclosing a six-coordinated nitrido ligand. The position of the manganese atom in the solid state could be established, despite some crystallographic disorder, by considering the local stereochemistry of the ligands. The cluster $[Fe_6N(CO)_{14}NO]^{2-}$ (**2**) was obtained in moderate yields by the reaction of $[Fe_4N(CO_{12}]^-$ with $Mo(CO)_3(EtCN)_3$. The nitrosyl is formed by oxidation of the starting nitride, and the source of the oxygen is presumably a carbonyl, whose splitting is mediated by the molybdenum complex. This process is the first example of an oxidation of a nitride in a carbonyl cluster. The solid state structure of the iron cluster is also octahedral, and the linear nitrosyl ligand was unambiguously located from the short Fe–N bond distance, and from dishomogeneous distribution of ligands. Cyclic voltammetric studies have shown that electron transfer processes are followed by chemical reactions thus testifying that no stable redox congeners exist for these two nitride clusters.

## Introduction

Recently we described the synthesis and the chemical characterization of octahedral mixed metal clusters, containing an interstitial nitride, iron, and a different metal of Groups 6 (Mo and W)[1] or 9 (Rh and Ir).[2] The former are obtained in poor yields (5–20%) but the latter can be prepared much more selectively, and have been used to relate spectroscopic, electrochemical and catalytic behavior with the number of heterometallic centers.[2]

In order to expand this type of chemistry as much as possible, we shifted our investigations to the metals of Group 7 and obtained **1**, a new Fe–Mn nitrido cluster, which is described here. To our knowledge, **1** is the first example of a nitrido cluster containing an atom of a Group 7 element.[3,4]

The reactivity of exposed carbide atoms in butterfly iron clusters is well documented, and is believed to mimic the behavior of carbon atoms adsorbed on metallic surfaces.[5,6] By way of contrast exposed nitride ligands in clusters are much less reactive, and even protonation can only be achieved under forcing conditions, with disruption of the metallic frame.[7] In this paper we report a peculiar reaction between $[Fe_4N(CO)_{12}]^-$ and $Mo(CO)_3(EtCN)_3$, which yields **2**, a nitrido–nitrosyl iron cluster, reproducibly. This represents a new type of reaction whose mechanism is not yet fully understood.

## Results

### (A) The synthesis

**$[Fe_5MnN(CO)_{16}]^{2-}$.** The nitrido Fe–Mn cluster **1** was prepared by three different routes, all comparable with respect to complexity, yields and purity of the final product. While attempting the synthesis of heterometallic species, containing rhodium, molybdenum or tungsten, we obtained the best results by condensation of $[Fe_4N(CO)_{12}]^-$ with nucleophilic anionic metal complexes, such as $[Rh(CO)_4]^-$, $[M_2(CO)_{10}]^{2-}$ or $[M(CO)_3(C_5H_5)]^-$ (M = Mo or W).[1,2] However, the reaction of $[Fe_4N(CO)_{12}]^-$ with $[Mn(CO)_5]^-$ proved unsuccessful, and the first results in this field were obtained by condensation of the more reduced cluster $[Fe_6N(CO)_{15}]^{3-}$ with $Mn_2(CO)_{10}$ in refluxing EtCN. The process is not a simple metal substitution in the octahedral frame of the cluster, and cannot be described by a balanced chemical equation; therefore the best experimental conditions were empirically determined to achieve maximum yields, easy purification and short reaction time. The two reagents were mixed in the molar ratio $[Fe_6N(CO)_{15}]^{3-} : Mn_2(CO)_{10} = 1 : 3$, and allowed to react for 4 h. The excess of neutral dimer can be easily eliminated by extraction with toluene, and the anionic products were dissolved in methanol. Fairly pure salts of **1**, such as $[PPh_4]_2$**1** or $[Me_3NCH_2Ph]_2$**1** can be precipitated after addition of the suitable ammonium or phosphonium halide, and recovered by filtration. The reaction of $[Fe_6N(CO)_{15}]^{3-}$ and $[Mn(CO)_5Br]$ in refluxing MeCN was also tested, and found to lead to similar results but after longer reaction times (usually 10 hours).

The binuclear $[FeMn(CO)_9]^-$ was expected to react with $[Fe_4N(CO)_{12}]^-$ more smoothly, since iron, manganese, nitrogen and negative charge are all in the correct ratio, according to eqn. (1):

$$[Fe_4N(CO)_{12}]^- + [FeMn(CO)_9]^- \rightarrow [Fe_5MnN(CO)_{16}]^{2-} + 5CO \quad (1)$$

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Contrary to expectations, the reaction does not represent any improvement, possibly because of the poor reactivity of $[Fe_4N(CO)_{12}]^-$ with low-charged species, and the yields are not higher than 15%. Moreover, the synthesis of the binuclear species[8] appears to be less straightforward than the synthesis of $[Fe_6N(CO)_{15}]^{3-}$, and this method was not considered further.

**$[Fe_6N(CO)_{14}NO]^{2-}$.** The nitrido–nitrosyl cluster **2** was unexpectedly observed by reacting equimolar amounts of $[Fe_4N(CO)_{12}]^-$ and $Mo(CO)_3(NCEt)_3$. The reaction is very slow, taking more than 12 h to convert all the starting $[Fe_4N(CO)_{12}]^-$ nitride in refluxing MeCN. After this time, the solution contains a small amount of **2**, together with the unreacted molybdenum complex; the main product of this reaction is $[Fe_6N(CO)_{15}]^{3-}$.[9] We progressively increased the molar ratio $[Fe_4N(CO)_{12}]^-$ : $Mo(CO)_3(NCEt)_3$ to 2 : 1, obtaining identical results. The presence of the NO group in **2** can be easily established from the IR spectrum, which shows a band at 1723 $cm^{-1}$, typical for a linear nitrosyl ligand, and from excellent elemental analysis. It is evident that the NO ligand is formed upon oxidation of the exposed nitride, but the origin of the oxygen atom could not be fully established. The source of the oxygen atom could be (i) adventitious atmospheric oxygen, (ii) an oxo-containing unidentified impurity, (iii) wet solvent, or (iv) a CO ligand of the metal complexes.

The first two possibilities cannot be completely excluded but are quite unlikely considering that the reaction is fairly reproducible, even with deliberately crystallized reagents, and the yields are constant, independent of the precautions taken. Moreover, the presence of large amounts of $[Fe_6N(CO)_{15}]^{3-}$ are only consistent with a reducing reaction medium.[9]

To rule out the intervention of wet solvent, increasing amounts of water were added, without detectable modification of the course of the reaction or of the yields. When labeled $H_2{}^{18}O$ was added, the unlabeled $[Fe_6N(CO)_{14}N^{16}O]^{2-}$ was formed.

The only remaining possibility is an oxygen transfer between CO and N, mediated by molybdenum:

$$\text{M–CO} + \text{Fe–}(\mu_4\text{-N}) \rightarrow \text{M–C} + \text{Fe–NO} \qquad (2)$$

This process would also produce a "naked" carbon atom, possibly in the form of a carbide cluster, a bulk metal carbide or a ketenylidene[6,10] complex; all attempts to detect such a species have so far failed.

The splitting of a carbonyl ligand by thermal activation or by a Lewis acid has been extensively employed to yield several carbide clusters;[11] the ability of molybdenum to promote such a splitting is also well documented.[12] Nevertheless the reaction here described is quite unusual because the oxygen atom eventually binds to the nitride and is neither transferred to a second carbonyl ligand (with formation of $CO_2$) nor coordinated by the Lewis acid.

In the meantime, the exposed nitride of $[Fe_4N(CO)_{12}]^-$ becomes a fully interstitial nitride in **2**. This transformation can be conceived as a reduction, since the oxidation state of the entire cluster framework becomes more negative. Therefore, the whole process can be classified as a disproportionation of the nitride, leading to two nitrogen atoms in different oxidation states and different chemical environments, both coordinated to the same iron cage. Whatever the mechanism, this is one of the very few examples of a nitrido ligand undergoing a chemical reaction within a metal cluster.[3]

**Table 1** Selected interatomic distances (Å) and angles (°) for $[Fe_5MnN(CO)_{16}]^{2-}$ **1**, with estimated standard deviations (e.s.d.s) in parentheses. See text for a discussion about the composition of Mn and Fe(1)

| | | | |
|---|---|---|---|
| Mn–Fe(1) | 2.698(1) | Mn–C(1) | 1.783(2) |
| Mn–Fe(2) | 2.674(1) | Mn–C(2) | 1.787(3) |
| Mn–Fe(3) | 2.704(1) | Mn–C(3) | 1.847(3) |
| Mn–Fe(4) | 2.686(1) | Fe(1)–C(4) | 1.776(3) |
| Fe(1)–Fe(2) | 2.707(1) | Fe(1)–C(5) | 1.764(4) |
| Fe(1)–Fe(3) | 2.677(1) | Fe(1)–C(6) | 1.844(3) |
| Fe(1)–Fe(5) | 2.641(1) | Fe(2)–C(7) | 1.753(3) |
| Fe(2)–Fe(4) | 2.601(1) | Fe(2)–C(8) | 1.772(3) |
| Fe(2)–Fe(5) | 2.675(1) | Fe(2)–C(15) | 2.109(3) |
| Fe(3)–Fe(4) | 2.661(1) | Fe(3)–C(9) | 1.763(3) |
| Fe(3)–Fe(5) | 2.586(1) | Fe(3)–C(10) | 1.757(3) |
| Fe(4)–Fe(5) | 2.680(1) | Fe(3)–C(16) | 2.031(3) |
| | | Fe(4)–C(11) | 1.782(2) |
| Mn–N | 1.887(2) | Fe(4)–C(12) | 1.753(3) |
| Fe(1)–N | 1.894(2) | Fe(4)–C(15) | 1.930(3) |
| Fe(2)–N | 1.866(2) | Fe(5)–C(13) | 1.763(2) |
| Fe(3)–N | 1.876(2) | Fe(5)–C(14) | 1.758(3) |
| Fe(4)–N | 1.893(2) | Fe(5)–C(16) | 1.929(3) |
| Fe(5)–N | 1.895(2) | | |
| Fe(2)–C(15)–O(15) | 134.9(2) | Fe(3)–C(16)–O(16) | 136.2(2) |
| Fe(4)–C(15)–O(15) | 145.0(2) | Fe(5)–C(16)–O(16) | 142.3(2) |

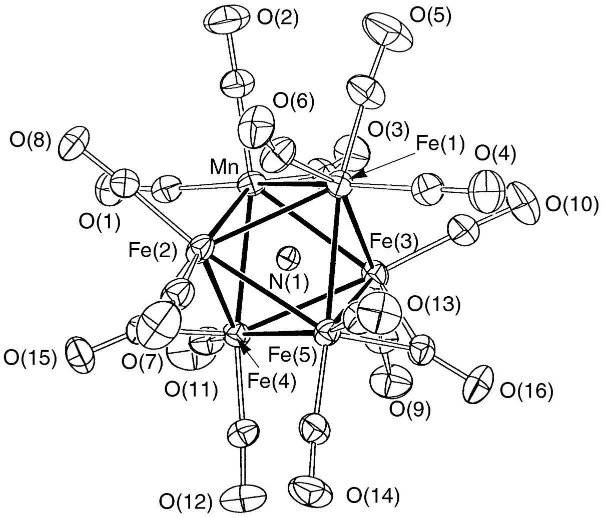

**Fig. 1** The solid state structure of $[Fe_5MnN(CO)_{16}]^{2-}$. Carbon atoms are labeled as the oxygen to which they are attached.

## (B) The solid state structure

**$[Fe_5MnN(CO)_{16}]^{2-}$.** The crystal structure of the cluster **1** was determined on the $[Me_3NCH_2Ph]_2$**1** salt, and the geometry of the anion is shown in Fig. 1; significant structural parameters are reported in Table 1. The six metal atoms define an octahedron, centered by an interstitial nitride. The sixteen carbonyl groups are not homogeneously distributed and, as already observed for this type of octahedral cluster, the metals with fewer electrons bind preferentially to terminal ligands.[1,2] In the structure of **1** four vertices, carrying two terminal and one bridging ligand, can be unambiguously labeled iron; the other two metal sites, related by an idealised twofold axis, have three terminal CO. At first sight, the two vertices are different and they have been labeled Fe(1) and Mn. Metal–metal and metal–ligand bond distances for the two crystallographic sites are appreciably different: the average values, in Å, are 2.674 [Fe(1)–Fe], 2.698 (Mn–Fe), 1.795 [Fe(1)–CO], 1.806 (Mn–CO), 1.894(2) [Fe(1)–N], 1.887(2) (Mn–N). However, the refinement of the occupancy factors (see the Experimental section) suggests that iron and manganese equally populate these two positions. Several Fe–Mn mixed-metal clusters have been reported,[8,13] and some of them contain an exposed main group atom;[14,15] however, their solid state structures are rarely reported in detail,[14,16] and can not help in distinguishing the two elements. A criterion for discriminating between metals which differ by only one electron was also proposed, which relies on the asymmetry of μ-CO.[17] This approach is not useful for this heterometallic compound, since bridging ligands are not bound to Mn: CO(3) and CO(6), bound respectively to Mn and Fe(1),

**Table 2** Average interatomic distances (Å) in the clusters **1** and **2**; (t = terminal, br = bridging)

| | **1** (M = Mn or Fe) | **2** (M = Fe) |
|---|---|---|
| Fe–Mn | 2.698(1) | |
| Fe–M (unbridged) | 2.679 | 2.679 |
| Fe–Fe (bridged) | 2.594 | 2.590 |
| M–N | 1.885 | 1.879 |
| M–CO$_t$ | 1.78 | 1.76 |
| M–CO$_{br}$ | 2.00 | 2.00 |
| C$_t$–O$_t$ | 1.15 | 1.16 |
| C$_{br}$–O$_{br}$ | 1.16 | 1.16 |

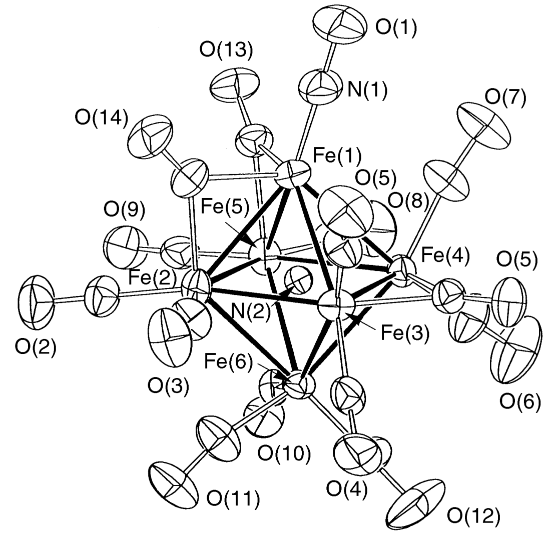

**Fig. 2** The solid state structure of [Fe$_6$N(CO)$_{14}$NO]$^{2-}$. Carbon atoms are labeled as the oxygen to which they are attached. Relevant bond lengths and angles: Fe(1)–N(1) 1.677(3) Å, N(1)–O(1) 1.175(4) Å; Fe(1)–N(1)–O(1) 176.4(3)°.

deviate slightly from linearity to the same extent. Even if the two distinct labels appear to be arbitrarily assigned they have been maintained, because the resulting figures reproduce exactly the topological relationships within the cluster. Relevant bond distances for anions **1** and **2** are collected and compared in Table 2.

**[Fe$_6$N(CO)$_{14}$NO]$^{2-}$.** The solid state structure of the nitrosyl–nitrido cluster **2** was determined on the [PPh$_4$]$_2$**2**·C$_4$H$_8$O salt. The anion is shown in Fig. 2; significant structural parameters are listed in Table 3. Also in this case, the six metal atoms define an octahedron, centered by the interstitial nitride and also in **2** all metal vertices carry three ligands. The NO group is linear [with a Fe(1)–N(1)–O(1) angle of 176.4(3)°], and should be considered as a three-electron donor. Therefore, Fe(1) binds preferentially to bridging CO. The uneven distribution of fifteen ligands, perturbed by an excess of one electron, has already been observed in [Ir$_6$(CO)$_{14}$NO]$^-$ and was compared to the homogenous architecture of [Ir$_6$(CO)$_{15}$]$^{2-}$.[18] The same effect can be brought about by an electron rich metal center, as already observed in [Fe$_5$MN(CO)$_{15}$]$^{2-}$ (M = Rh or Ir),[2] when compared to [Fe$_6$N(CO)$_{15}$]$^{3-}$. Final evidence for the labeling of the NO group stems from the Fe(1)–N(1) bond distance [1.677(3) Å], which is significantly shorter than any reported Fe–C bond length.[4]

The cluster **2** can be conceived as the third member of a series of compounds of general formula [Fe$_5$(ML)N(CO)$_{14}$]$^{2-}$, which are formed by capping an unmodified [Fe$_5$N(CO)$_{14}$]$^{2-}$ moiety with three different isoelectronic fragments (ML = Rh–CO, Mo–Cp and Fe–NO).

## (C) Electrochemistry

**[Fe$_5$MnN(CO)$_{16}$]$^{2-}$.** Cyclic voltammetry of the dianion **1** in acetonitrile solution shows two close spaced one-electron reductions (checked by controlled potential coulometry) and an irreversible oxidation ($E_p$ = + 0.10 V). The first reduction step is complicated by fast chemical reactions ($E_{pc}$ = −1.45 V), whereas the second one possesses features of partial chemical reversibility ($E°'$ = − 1.50 V, $\Delta E_p$ = 108 mV at a scan rate of 0.2 V s$^{-1}$). Even if the two processes tend to overlap with the scan rate, substantially the same profile is maintained at high scan rates (2.0 V s$^{-1}$), thus seemingly ruling out the possibility that the second reduction might arise from the decomposition species produced in the first one-electron addition.

**Table 3** Selected interatomic distances (Å) and angles (°) for [Fe$_6$N(CO)$_{14}$NO]$^{2-}$ **2** with estimated standard deviations (e.s.d.s) in parentheses

| | | | |
|---|---|---|---|
| Fe(1)–Fe(2) | 2.599(1) | Fe(1)–N(1) | 1.677(3) |
| Fe(1)–Fe(3) | 2.746(1) | Fe(1)–C(13) | 1.936(3) |
| Fe(1)–Fe(4) | 2.681(1) | Fe(1)–C(14) | 1.983(3) |
| Fe(1)–Fe(5) | 2.601(1) | Fe(2)–C(2) | 1.712(4) |
| Fe(2)–Fe(3) | 2.642(1) | Fe(2)–C(3) | 1.783(3) |
| Fe(2)–Fe(5) | 2.729(1) | Fe(2)–C(14) | 2.000(3) |
| Fe(2)–Fe(6) | 2.678(1) | Fe(3)–C(4) | 1.756(3) |
| Fe(3)–Fe(4) | 2.569(1) | Fe(3)–C(5) | 1.753(3) |
| Fe(3)–Fe(6) | 2.670(1) | Fe(3)–C(15) | 2.009(3) |
| Fe(4)–Fe(5) | 2.681(1) | Fe(4)–C(6) | 1.708(3) |
| Fe(4)–Fe(6) | 2.666(1) | Fe(4)–C(7) | 1.752(4) |
| Fe(5)–Fe(6) | 2.620(1) | Fe(4)–C(15) | 1.995(3) |
| | | Fe(5)–C(8) | 1.773(4) |
| Fe(1)–N(2) | 1.885(2) | Fe(5)–C(9) | 1.749(4) |
| Fe(2)–N(2) | 1.875(2) | Fe(5)–C(13) | 2.060(3) |
| Fe(3)–N(2) | 1.876(2) | Fe(6)–C(10) | 1.822(3) |
| Fe(4)–N(2) | 1.873(2) | Fe(6)–C(11) | 1.791(4) |
| Fe(5)–N(2) | 1.888(2) | Fe(6)–C(12) | 1.741(3) |
| Fe(6)–N(2) | 1.875(2) | N(1)–O(1) | 1.175(4) |
| Fe(1)–N(1)–O(1) | 176.4(3) | Fe(2)–C(14)–O(14) | 140.8(3) |
| Fe(1)–C(13)–O(13) | 141.3(3) | Fe(3)–C(15)–O(15) | 139.6(3) |
| Fe(5)–C(13)–O(13) | 137.6(3) | Fe(4)–C(15)–O(15) | 140.6(3) |
| Fe(1)–C(14)–O(14) | 137.6(3) | | |

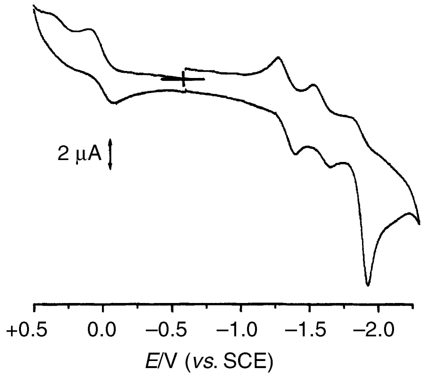

**Fig. 3** Cyclic voltammogram of [PPh$_4$]$_2$[Fe$_6$N(CO)$_{14}$NO] (0.6 × 10$^{-3}$ mol dm$^{-3}$) recorded at a platinum electrode in MeCN solution. Supporting electrolyte [NEt$_4$][ClO$_4$] (0.1 mol dm$^{-3}$), scan rate 0.2 V s$^{-1}$.

This picture delineates a redox flexibility poorer than that exhibited by the isoelectronic dianions [Fe$_5$MN(CO)$_{15}$]$^{2-}$ (M = Rh, Ir), which displayed either a one-electron reduction or a one-electron oxidation, both chemically reversible (on the cyclic voltammetric timescale), in addition to an irreversible second oxidation.[2]

**[Fe$_6$N(CO)$_{14}$NO]$^{2-}$.** Fig. 3 shows the cyclic voltammetric behavior of [PPh$_4$]$_2$**2** in acetonitrile solution. Apart from the irreversible reduction at very negative potential values ($E_p$ = − 1.9 V), which is assigned to the [PPh$_4$]$^+$ counter ion, it exhibits a series of reversible electron transfer processes, namely a first (coulometrically measured) one-electron oxidation ($E°'$ = +0.02 V) and two one-electron reductions ($E°'$ = −1.36 V and −1.59 V, respectively). All the processes are complicated by degradation of the respective electrogenerated congeners in

**Table 4** Crystallographic data and collection parameters for compounds $[\mathrm{Me_3NCH_2Ph}]_2$**1** and $[\mathrm{PPh_4}]_2$**2**·$\mathrm{C_4H_8O}$

| Compound | $[\mathrm{Me_3NCH_2Ph}]_2$**1** | $[\mathrm{PPh_4}]_2$**2**·$\mathrm{C_4H_8O}$ |
|---|---|---|
| Formula | $\mathrm{C_{36}H_{32}Fe_5MnN_3O_{16}}$ | $\mathrm{C_{66}H_{48}Fe_6N_2O_{16}P_2}$ |
| $M$ | 1096.84 | 1522.15 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) |
| $a$/Å | 10.656(1) | 11.887(1) |
| $b$/Å | 13.845(2) | 12.549(1) |
| $c$/Å | 16.216(2) | 23.621(2) |
| $\alpha$/° | 89.34(1) | 90.73(1) |
| $\beta$/° | 71.18(1) | 93.89(1) |
| $\gamma$/° | 71.05(1) | 106.59(1) |
| $U$/Å$^3$ | 2130.1(5) | 3367.2(6) |
| $Z$ | 2 | 2 |
| $T$/K | 293 | 293 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$ | 20.0 | 13.7 |
| Reciprocal space explored | Full sphere | Full sphere |
| Measured reflections (total; independent) | 23533; 9339 | 38085; 14927 |
| $R_{\mathrm{int}}$ | 0.032 | 0.035 |
| Final $R_2$ and $R_{2w}$ indices ($F^2$, all reflections) | 0.048, 0.076 | 0.061, 0.101 |
| Conventional $R_1$ index | ($I > 2\sigma(I)$, 6200 refls.) 0.031 | ($I > 2\sigma(I)$, 8781 refls.) 0.054 |

that the current ratio $i_{\mathrm{p(reverse)}}/i_{\mathrm{p(direct)}}$ is always significantly lower than unity at low scan rates. In confirmation, cyclic voltammetric tests after stepwise controlled potential coulometric reductions reveal the disappearance of the original voltammetric profiles. In addition to the first, partially reversible oxidation shown in Fig. 3, the nitrosyl dianion exhibits further irreversible anodic processes ($E_{\mathrm{p}} = +0.30$ V and $+0.59$ V, respectively), which are somewhat reminiscent, from a qualitative viewpoint, of the voltammetric behavior of the trianion $[\mathrm{Fe_6N(CO)_{15}}]^{3-}$. In fact, the isoelectronic (86 CVE) $[\mathrm{Fe_6N(CO)_{15}}]^{3-}$ exhibits three one-electron oxidations, only the first of which exhibits features of partial chemical reversibility.[9]

In an attempt to assign the extra reduction processes observed for $[\mathrm{Fe_6N(CO)_{14}NO}]^{2-}$, it must be taken into account that, in acetonitrile solution, the free nitrosonium cation $\mathrm{NO^+}$ is reversibly reduced to nitric oxide $\mathrm{NO^{\bullet}}$ at quite positive potential values ($E^{\circ\prime} = +1.28$ V),[19] but, upon coordination to metal fragments, its one-electron reduction shifts towards negative potential values. For instance, in $[(\mathrm{bpy})_2\mathrm{M(NO)Cl}]^{2+}$ the reduction occurs at $E^{\circ\prime} = +0.19$ V for M = Ru, and at $E^{\circ\prime} = -0.30$ V for M = Os.[20] In $[\mathrm{Os(CN)_5(NO)}]^{2-}$ the reduction step is localized at $E^{\circ\prime} = -1.03$ V.[21] It must however also be noted that it has been recently reported that in $[\mathrm{Ru^{II}(hedta)(NO)}]$ [hedta$^{3-}$ = *N*-(hydroxyethyl)ethylenediaminetriacetate] the $\mathrm{NO^+/NO^{\bullet}}$ redox change is followed by the reduction of $\mathrm{NO^{\bullet}}$ to $\mathrm{NO^-}$.[22]

On this basis, it could be proposed that in the nitrosyl cluster **2**, both of the two reduction processes correspond to the sequential conversion $\mathrm{NO^+/NO^{\bullet}/NO^-}$, accompanied by the shift between linear and bent coordination modes. Thus, if the two added electrons are localized as a lone pair on NO, the transient $[\mathrm{Fe_6N(CO)_{14}NO}]^{4-}$ would still possess 86 CVE. Unfortunately, on the basis of this evidence alone we cannot rule out that one of the two steps might be centered on the metal–carbonyl residue. Finally, it has to be noted that while exhaustive (three-electron) oxidation of $[\mathrm{Fe_6N(CO)_{15}}]^{3-}$ afforded $[\mathrm{Fe_5N(CO)_{14}}]^-$,[9] exhaustive oxidation of **2** leads to complete decomposition of the cluster assembly.

## Experimental

All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under oxygen-free nitrogen atmospheres using the Schlenk-tube technique.[23] $[\mathrm{NEt_4}][\mathrm{Fe_4N(CO)_{12}}]$,[24] $[\mathrm{Mo(CO)_3(EtCN)_3}]$,[25] $[\mathrm{FeMn(CO)_9}]^-$ [8] and $[\mathrm{Mn(CO)_5Br}]$[26] were prepared by literature methods. Infrared spectra in solution were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, using calcium fluoride cells previously purged with $\mathrm{N_2}$. Elemental analyses were carried out by the staff of Laboratorio di Analisi of the Dipartimento di Chimica Inorganica, Metallorganica e Analitica. Yields are calculated as moles of product/moles of $[\mathrm{Fe_4N(CO)_{12}}]^-$. The materials and apparatus for the electrochemistry have been described elsewhere. All the potential values are referenced to the saturated calomel electrode (SCE).[2]

### Synthesis of $[\mathrm{Fe_5MnN(CO)_{16}}]^{2-}$

**Method a: From $[\mathrm{Fe_6N(CO)_{15}}]^{3-}$ and $\mathrm{Mn_2(CO)_{10}}$.** $[\mathrm{NEt_4}]_3[\mathrm{Fe_6N(CO)_{15}}]$ (0.60 g, 0.52 mmol) and $\mathrm{Mn_2(CO)_{10}}$ (0.68 g, 1.74 mol) were dissolved in EtCN (20 mL) and refluxed, while monitoring by IR. After about 4 h, the starting $[\mathrm{Fe_6N(CO)_{15}}]^{3-}$ was completely consumed, and the solution was cooled at room temperature. The solvent was removed under vacuum, the residue was washed with toluene (2 × 10 cm$^3$), and dissolved with methanol. Addition of $[\mathrm{PPh_4}]$Br caused precipitation of microcrystalline $[\mathrm{PPh_4}]_2$**1**, which was filtered off, washed with 2-propanol and dried. It was then dissolved in the minimum amount of THF, and the solution layered with 2-propanol. Crystals of the salt $[\mathrm{PPh_4}]_2$**1** were used for chemical characterization but were unsuitable for single crystal X-ray analysis. The crystals of $[\mathrm{Me_3NCH_2Ph}]_2$**1** were obtained similarly, but, after the addition of $[\mathrm{Me_3NCH_2Ph}]$Br, water was added to complete precipitation. Yield 21%. IR (THF, cm$^{-1}$)$\nu$(CO): 2015w, 1955vs, 1785m. Elemental analysis: Calc. for $\mathrm{C_{54}H_{48}Fe_5MnNO_{16}P_2}$: C 52.11, H 2.73, N 0.95%. Found: C 52.36, H 3.16, N 0.50%.

**Method b: From $[\mathrm{Fe_6N(CO)_{15}}]^{3-}$ and $[\mathrm{Mn(CO)_5Br}]$.** $[\mathrm{NEt_4}]_3[\mathrm{Fe_6N(CO)_{15}}]$ (0.59 g, 0.51 mmol) and $[\mathrm{Mn(CO)_5Br}]$ (0.42 g, 1.51 mmol) were dissolved in EtCN (20 mL) and refluxed for 12 h. The solvent was then removed under vacuum and the residue treated as above.

**Method c: From $[\mathrm{Fe_4N(CO)_{12}}]^-$ and $[\mathrm{FeMn(CO)_9}]^-$.** $[\mathrm{NEt_4}][\mathrm{Fe_4N(CO)_{12}}]$ (0.16 g; 0.22 mmol) and $[\mathrm{PPh_4}][\mathrm{FeMn(CO)_9}]$ (0.15 g, 0.21 mmol) were dissolved in EtCN (20 mL) and refluxed for 2 h. The solvent was then removed under vacuum and the residue treated as above. Yield 15%.

### Synthesis of $[\mathrm{Fe_6N(CO)_{14}NO}]^{2-}$

$[\mathrm{NEt_4}][\mathrm{Fe_4N(CO)_{12}}]$ (0.76 g, 1.07 mmol) and $\mathrm{Mo(CO)_3(EtCN)_3}$ (0.175 g, 0.51 mmol) were dissolved in MeCN (40 mL) and refluxed, while monitoring by IR the disappearence of the bands for $[\mathrm{Fe_4N(CO)_{12}}]^-$. After 12 h the reaction was complete and the mixture was cooled to room temperature. The solvent was then removed under vacuum, and the solid was repeatedly washed with toluene. The dark residue was then suspended in methanol and the insoluble $[NEt_4]_3[Fe_6N(CO)_{15}]$ was filtered and eliminated. $[PPh_4]Br$ was added to the dark solution, inducing precipitation of microcrystalline $[PPh_4]_2$**2**. The solid was collected by filtration, washed with 2-propanol, and dried. It was then dissolved with the minimum amount of THF and the solution was layered with 2-propanol. Yield 0.17 g of $(PPh)_4$**2**$\cdot C_4H_8O$ (11%). IR (THF, $cm^{-1}$) $\nu$(CO): 2016w, 1954vs, 1814m, 1781m; $\nu$(NO) 1723w. Elemental analysis (in keeping with the presence of co-crystallized THF): Calc. for $C_{66}H_{48}Fe_6N_2O_{16}P_2$: C 52.08, H 3.18, N 1.84%. Found: C 52.4, H 3.23, N 1.75%.

### X-Ray data collection and structure determinations

Crystal data and other experimental details are summarized in Table 4. The diffraction experiments were carried out on a Siemens SMART CCD area-detector diffractometer at room temperature. The structures were solved by direct methods and refined by full-matrix least-squares, minimizing the function $\Sigma\omega(F_o^2 - k|F_c|^2)^2$ (refinement on $F^2$). Anisotropic thermal factors were refined for all the non-hydrogen atoms. Hydrogen atoms were placed in their ideal positions and not refined. In anion **1**, refinement of the occupancy factors of the two atoms labeled Mn and Fe(1) suggests that these two crystallographic sites are equally occupied by Mn and Fe atoms, in a fifty-fifty disorder.

CCDC reference numbers 155801 and 155802.

See http://www.rsc.org/suppdata/dt/b1/b100148p/ for crystallographic data in CIF or other electronic format.

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