Coupling of Ethylidyne and Carbonyl Ligands leading to a μ_3,η^2 bonded Propynolate Anion induced by One-electron Reduction of [Fe₃(CO)₉(μ_3-CO)(μ_3-CMe)] [PPh₄]: X-Ray Crystal Structure of [Fe₃(CO)₉(μ_3, η^2-MeC≡CO)] [PPh₄]₂

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The electrochemical one-electron reduction of [Fe₃(CO)₉(μ_3-CO)(μ_3-CMe)][PPh₄] leads to a product containing a μ_3, η^2 bonded propynolate anion, [Fe₃(CO)₉(μ_3, η^2-MeC≡CO)] [PPh₄]₂.

We recently reported[1] that the electrochemical one-electron reduction of [Fe₃(CO)₉(μ_3-CO)(μ_3-CMe)] [PPh₄] and the subsequent treatment of the resulting product with methanol or weak acids led to the cluster [Fe₃(CO)₉(μ_3-C≡CMe)]-[PPh₄], a product formally resulting from carbon–oxygen scission and coupling of the generated carbide with the ethylidyne ligand.

The paramagnetic intermediate, [Fe₃(CO)₁₀CMe] [PPh₄]₂, was not then fully characterized and on the basis of i.r. data we assumed that the structure of the starting anion, [Fe₃(CO)₉(μ_3-CO)(μ_3-CMe)]⁻, was preserved.

Nevertheless, the possibility of a coupling of carbon monoxide with ethylidyne ligands at this stage of the reaction was also a plausible hypothesis as some examples of carbon monoxide–alkylidyne coupling are known.[2] We have now succeeded in the isolation of such an intermediate and its structure has been fully characterized by a single crystal X-ray study (Figure 1).

Crystal data:† Fe₃O₁₀P₂C₆₀H₄₃, M = 1152.5, monoclinic,

space group $P2_1/n$, a = 12.538(2), b = 18.658(2), c = 23.195(3) Å, β = 100.00(1)°, U = 5343.7 Å³, Z = 4, D_c = 1.432 g cm⁻³, μ(Mo-K_α) = 9.2 cm⁻¹, R = 0.049 for 2499 observed data with $I > 3\sigma(I)$ and 1.5 < θ < 21°. Intensities were collected by the θ–2θ scan mode using graphite monochromatized Mo-K_α radiation, λ = 0.71069 Å (Enraf-Nonius CAD4 diffractometer) and corrected for standard linear decrease. The structure was solved by conventional heavy-atom methods and refined by full-matrix least-squares techniques, treating non-hydrogen atoms anisotropically, except phenyl rings which were treated as isotropic rigid groups.

The most salient feature of the structure is the occurrence of an MeCCO group bonded in a μ_3, η^2 mode. Examination of bond angles and bond distances in the O(10)C(10)C(11)C(12) unit clearly shows that this group can be described as a propynolate anion, MeC≡CO⁻, bonded in the same way as alkynes in trinuclear clusters, *i.e.* in the $\mu(\eta^2, \parallel)$ mode.[3] Moreover, the C(10)–O(10) bond distance, 1.447(16) Å, is characteristic of a C–O single bond.[4]

The Fe(3)C(10)O(10)C(11)C(12) group is nearly planar and the Fe(1) and Fe(2) atoms are displaced from this plane by 1.82 and −0.15 Å, respectively. The C(10)–C(11) distance and the Fe–C(10) and Fe–C(11) distances have values similar to those found in similar complexes.[3]

The iron triangle is nearly isosceles, the longer distance being Fe(2)–Fe(3). Each iron is surrounded by three carbonyl groups and the iron–carbon distances are normal (mean value 1.744 Å) except Fe(3)–C(9) which is longer [1.815(14) Å]. This could be attributed to the fact that this carbonyl group is nearly *trans* to C(10); C(9)Fe(3)C(10) 155.3(5)°.

It should be mentioned that this cluster has only 47 valence-electrons but there is no visible effect on the bond lengths, in the metal frame, nor in the organic part of the molecule. This could be due to the fact that the lack of one electron is not fully localized. The knowledge of this structure gives some insight into the mechanism of the carbon–oxygen scission we have observed.
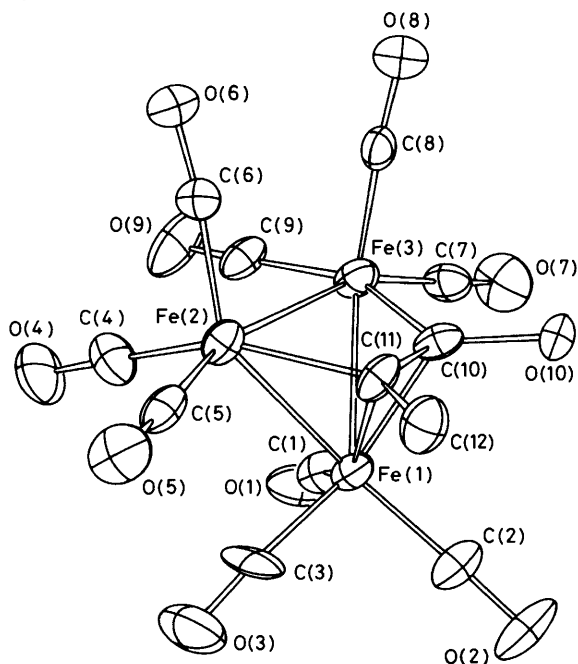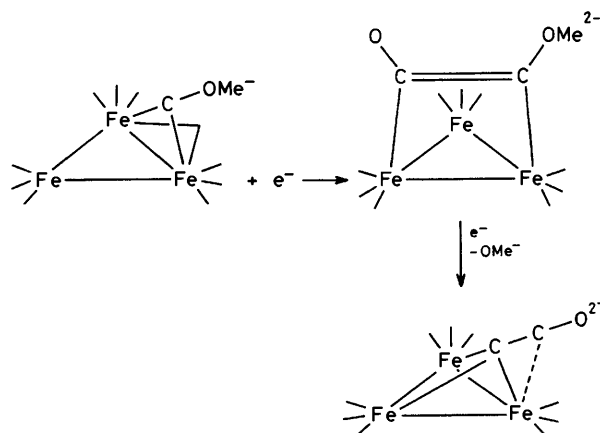

Figure 1. Structure of the dianion. Some important bond lengths (Å) and angles (°) are: Fe(1)–Fe(2) 2.520(3), Fe(1)–Fe(3) 2.545(2), Fe(2)–Fe(3) 2.693(2), Fe(1)–C(10) 2.054(11), Fe(1)–C(11) 2.076(10), Fe(2)–C(11) 1.994(12), Fe(3)–C(10) 1.916(12), C(10)–C(11) 1.358(16), C(10)–O(10) 1.447(16), C(11)–C(12) 1.521(16), C(10)–C(11)–C(12) 126.2(11), C(11)–C(10)–O(10) 118.4(10), Fe(2)–C(11)–C(10) 105.8(9), Fe(3)–C(10)–C(11) 114.3(10).

Scheme 1

As a first step, the one-electron reduction could generate an oxo-carbyne which then would be coupled with the ethylidyne ligand. As a second step, the oxygen of the propynolate anion would be protonated (H^+), leading to an unstable propynol complex evolving as $[Fe_3(CO)_9(\mu_3\text{-}MeC{\equiv}C)]\,[PPh_4]$.

The same type of intermediate could also be invoked for the recently published synthesis of carbide clusters implicating the reduction of alkylidyne clusters containing bridging carbon monoxide[5] (Scheme 1).

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