

TaS₂.^[6] Only assumptions can be made about the arrangement of the intercalated molecules in the phases with the smaller interlayer spacing. An undistorted all-*gauche* structure of the C₄F₉ chains is unlikely, because of the size of the fluorine atoms. If, as is assumed, the chains have a twisted *anti* conformation, they must be more strongly tilted at an angle of 40° to the plane of the layers (see Fig. 2b). However, a distorted all-*gauche* conformation or a conformation with *anti* and *gauche* sequences cannot be ruled out. Only one phase was observed for stage 2 as well as stage 1 in the case of the homologous perfluorohexanesulfonic acids. These compounds are not so well ordered; the *d*_i spacings of ca. 2900 pm and 2620 pm, however, are consistent with the *anti* conformation, analogous to those in Figure 2a.

Experimental

Ca. 4–5 mg of Madagascar graphite (>99.5% C, flakes of ca. 2 mm diameter) was packed in a platinum gauze pouch and anodically oxidized in perfluorobutanesulfonic acid (liberated from C₄F₉SO₃K [7] with 100% H₂SO₄). Platinum was used as counter electrode; a relatively large piece of graphite foil (Sigraflex) was used as reference electrode. Upon galvanostatic oxidation well-structured potential/charge curves were obtained only at a very small current density, e.g. 10 µA with 5 mg of graphite, i.e. less than 500 µA per cm² of the prism faces of the graphite flakes. In the potentiodynamic reaction, the current/voltage curves were well-resolved only at a sweep rate below 5–10 µV/s. The use of highly oriented pyrographite (HOPG) gave similar, but not quite so well-structured curves. After a charge transfer corresponding to the selected points of the curves, the oxidation was interrupted and the graphite salt transferred to X-ray capillaries under the acid for taking Debye-Scherrer photographs. For determining the fluorine, the flakes were freed from adhering perfluorobutanesulfonic acid by rinsing with syrupy phosphoric acid and combusted with Na₂O₂/NaOH in a Parr bomb; the fluoride that was formed was determined with an ion-selective electrode by the standard-addition method.

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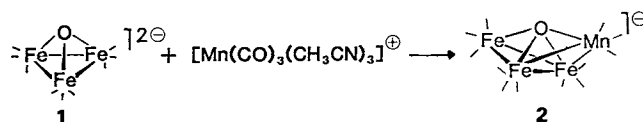
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Synthesis and Structure of [(PPh₃)₂N][Fe₃Mn(CO)₁₂(μ₄-O)]: A Butterfly Oxo Cluster**

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There has been considerable recent interest in the synthesis of clusters that contain substituent-free main-group elements to provide a conceptual bridge between organometallic chemistry and the areas of inorganic solid-state chemistry and surface chemistry.^[1] Among the first-row elements, carbido and nitrido carbonyl clusters are now known which have coordination environments about the main-group atoms ranging from those presumed for sur-

faces to those observed in solid-state compounds.^[2] The synthesis and chemistry of clusters comprised of metal atoms in low oxidation states that contain an oxo ligand is much less well developed. There are only a few examples of clusters containing the μ₃-oxo ligand,^[3] a coordination mode common for oxygen atoms bound to surfaces.^[4] Additionally, to the best of our knowledge, there are no oxo carbonyl clusters belonging to the interesting class of μ₄-L butterfly clusters, which have been intensely studied recently for L=C and N;^[5] nor are there any other higher-nuclearity oxo clusters in which the oxo ligand is bound to more than three metal atoms. We report here on the synthesis and characterization of PPN[Fe₃Mn(CO)₁₂(μ₄-O)] **2** (PPN=[(PPh₃)₂N]⁺), a mixed-metal cluster which represents the first butterfly oxo compound and is a step toward building higher-nuclearity oxo clusters.



Treatment of the orange-red PPN salt of [Fe₃(CO)₉(μ₃-O)]²⁻ **1**^[3] with one equivalent of [Mn(CO)₃(CH₃CN)₃][PF₆]^[6] in acetone followed by crystallization from Et₂O/pentane gives the dark brown butterfly oxo cluster PPN[Fe₃Mn(CO)₁₂(μ₄-O)] **2** in 75% yield.^[7] The structure of **2** is shown in Figure 1 (see also Table 1).^[8] The

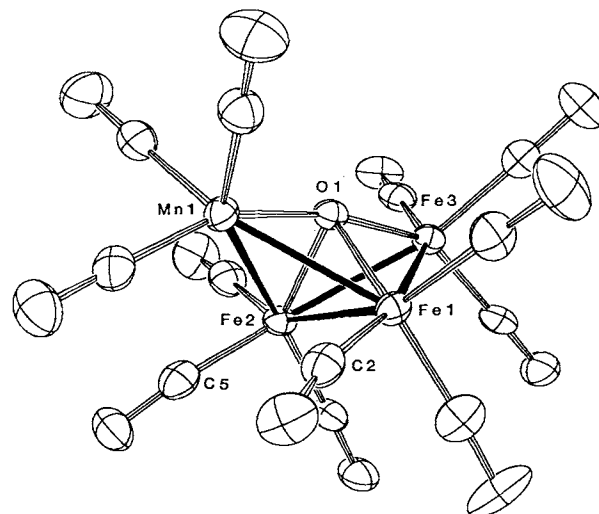


Fig. 1. Crystal structure of **2**. Thermal ellipsoid plot at 40% probability [8].

count of 62 cluster valence electrons, consistent with molecular orbital descriptions of the butterfly carbides,^[9] is achieved by counting the oxo ligand as a six electron donor. All oxygen-metal distances are short (average: 1.89(2) Å). The Mn atom occupies a wingtip position in the butterfly arrangement, in contrast to the analogous carbido cluster, [Fe₃Mn(CO)₁₃(μ₄-C)]⁺, where the Mn atom occupies a hinge site.^[5b] The average Fe-Mn distance (2.61(2) Å) is considerably longer than the average Fe-Fe distance (2.51(1) Å). Two Fe-bound CO ligands form semi-bridges to the Mn atom (Mn1-C2=2.675(5), Mn1-C5=2.736(5) Å), consistent with the preference of manganese for a higher coordination number.



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In the homometallic carbido and nitrido clusters, **3** and **4**, the bond distance from the heteroatom to the hinge metal (M_h) atoms is considerably longer than the distance from the heteroatom to the wingtip metal (M_w) atoms (Table 1). Such a distinct bonding preference is not observed for **2**. Additionally, the elongation of the M_h-M_w distance relative to the M_h-M_h distance in **3** and **4** is not observed in **2**. The Fe-Fe distances in **2** are nearly unperturbed from those seen in **1** (C_{3v} symmetry).^[3] As a consequence of these unique structural features, the M_w-L-M_w angle in **2** is more acute than in the nitrido and carbido clusters, **3** and **4**, respectively, and the dihedral angle between the two wings of the butterfly in **2** is approximately 10° larger than in **3** and **4**.

Table 1. Structural parameters of μ_4 -L butterfly clusters [a].

	2	3	4
M_h-L [Å]	1.902(4)	1.96(3)	1.900(6)
M_w-L [Å]	1.872(3), 1.877(3) [b]	1.80(3)	1.771(5)
M_w-M_h [Å]	2.517(2), 2.612(2) [b]	2.64(1)	2.604(7)
M_h-M_h [Å]	2.499(1)	2.533(2)	2.512(1)
M_w-L-M_w [°]	168.3(1)	176.3(4)	179.0(3)
$M_h-M_h-M_w$ [°]	113	102	102
Ref.	this work	[10]	[11]

[a] M_w , wingtip metal atom; M_h , hinge metal atom. [b] For the first entry, $M = Fe$; for the second entry, $M = Mn$.

The oxo clusters **1** and **2** were characterized by ^{17}O -NMR spectroscopy in acetone solution at room temperature on samples enriched with ^{17}O at the oxo ligand. For **1**, the spectrum consists of a resonance for the CO ligands ($\delta = 356$) and one for the μ_3 -oxo ligand ($\delta = 107$). For **2**, two distinct resonances are seen for the CO ligands ($\delta = 385$ and 370 , intensity ratio 1:3) and the μ_4 -oxo ligand resonance is found at $\delta = 93$. The relative positions of the oxo ligand resonances in **1** and **2** is in qualitative agreement with the correlation observed between the oxygen atom coordination number and the ^{17}O chemical shift of the oxygen atom in polyoxometalate systems.^[12]

Two resonances for the CO ligands of **2** ($\delta = 214.0$; 225.5 ; intensity ratio 3:1) were also observed in the ^{13}C -NMR spectrum ($CD_2Cl_2/CHCl_3$ (1:2), room temperature). These two resonances correspond to the carbonyl ligands bound to the Mn atom and those bound to the Fe atoms. A fluxional process involving equilibration of the hinge and wingtip Fe-bound CO ligands must be occurring at room temperature to account for this pattern. At $-50^\circ C$, this equilibration process is not rapid and distinct resonances are seen for the two types of $Fe(CO)_3$ fragments ($Mn(CO)_3$, $\delta = 225.0$; $Fe(CO)_3$, $\delta = 212.1$ and 214.2 ; intensity ratio 3:3:6).

Unlike the nitrido^[5a] and carbido^[5b] butterfly clusters and the parent cluster **1**, **2** does not display ready reactivity toward Brønsted acids. Addition of one equivalent of CF_3SO_3H to a CH_2Cl_2 solution of **2** results in only negligible protonation.

The rarity of low-valent oxo clusters seems surprising given the vast chemistry that has been developed for the carbido and nitrido clusters. The apparently facile loss of an oxo ligand as CO_2 in carbonyl-containing complexes may, in part, offer an explanation. For instance, **1** decomposes under CO (1 atm) in acetone over a period of several hours to give CO_2 and lower-nuclearity Fe compounds; such a ready decomposition route is not accessible for ni-

trido and carbido clusters. If this route for loss of the oxo ligand can be suppressed, higher-nuclearity oxo clusters of low-oxidation-state metals should be accessible utilizing lower-nuclearity oxo clusters as precursors.

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The Diradical 2,3,5,6-Tetramethylene-1,4-cyclohexanediyl ("1,2,4,5-Tetramethylenebenzene")**

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The title compound **10**, a disjoint diradical with conjugated non-Kekulé structure, is of topical interest in discussing the limits of the Hunds rule.^[1] High-level ab initio SCF-MO-CI calculations lead one to expect a singlet ground state for **10** which lies about 5–7 kcal/mol below the lowest triplet state.^[2] We have now checked this prediction experimentally.

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