

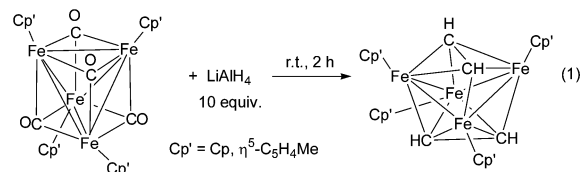
Reversible Cleavage and Recombination of an Acetylenic Carbon–Carbon Bond on a Tetrairon Cluster Coupled with a Two-Electron Redox Reaction

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Over the last few decades, considerable attention has been paid to the reduction of carbonyl ligands in transition-metal complexes and clusters^{1–3} to understand the heterogeneous reduction of CO (i.e., the Fischer–Tropsch reaction).⁴ The reduction of carbonyl ligands on dinuclear complexes has been reported by Atwood et al.,^{1b–d} where the treatment of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ with LiAlH_4 was shown to give a mixture of CH_4 , C_2H_4 , C_3H_6 , C_3H_8 , C_4H_8 , and C_4H_{10} , in which no iron moiety was present. Recently, our group reported that the reaction of $\text{Cp}'_4\text{Fe}_4(\mu_3\text{-CO})_4$ ($\text{Cp}' = \text{Cp}, \eta^5\text{-C}_5\text{H}_4\text{Me}$) with LiAlH_4 causes reductive coupling of four carbon monoxide molecules to give bis(acetylene) clusters $\text{Cp}'_4\text{Fe}_4(\text{HCCH})_2$ (eq 1).⁵ The present report shows the successful isolation of an intermediate as a cationic form, bis(methyldiyne) cluster $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\mu_3\text{-CH})_2(\mu_3\text{-CO})_2](\text{PF}_6)_2$ (**1**). The two-electron reduction of **1** is also shown to result in the coupling of two methyldiyne ligands to afford $(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{HCCH})(\mu_3\text{-CO})_2$ (**2**), the two-electron oxidation of which reproduces **1**.



Our previous paper revealed that treatment of $(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{CO})_4$ with LiAlH_4 (10 equiv) in THF gave $(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{HCCH})_2$ in 77% yield.^{5b} The intermediates obtained depended on the reaction conditions, and **1** was obtained with smaller amounts of LiAlH_4 and shorter reaction times (eq 2). A typical synthetic procedure is as follows: A THF suspension of $(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{CO})_4$ and ca. 2-fold excess of LiAlH_4 is stirred for 5 min at room temperature, following which ethyl acetate is added to the reaction mixture to decompose unreacted LiAlH_4 . After the addition of NH_4PF_6 , the mixture is bubbled through with air. Volatiles are then removed in vacuo, and the residue is washed sequentially with water, toluene, and finally THF to remove NH_4PF_6 , $(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{CO})_4$ (37%), and any unidentified products, respectively. Extraction of the residue with acetonitrile, followed by evaporation in vacuo, gives $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{CH})_2(\text{CO})_2](\text{PF}_6)_2$ (**1**) as a brown solid in 14% yield.

Recrystallization of **1** from acetonitrile/diethyl ether gave brown crystals. X-ray diffraction study revealed that cluster **1** takes an Fe_4C_2 bicapped tetrahedral geometry with mirror plane defined by Fe2, Fe3, C1, and C2 atoms (Figure 1). The C1–C2 interatomic distance (2.85(2) Å) indicates an absence of the interaction between the two carbon atoms. Although the two hydrogen atoms on C1 and C2 were not located crystallographically, ¹H and ¹³C nuclear

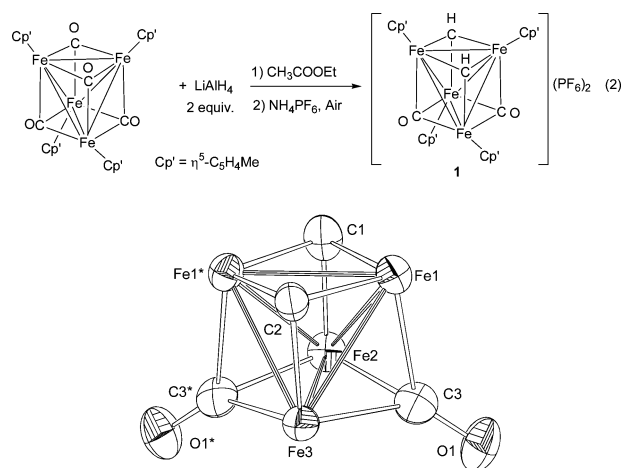
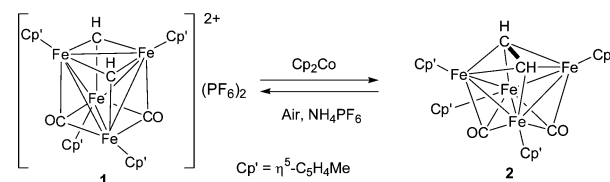


Figure 1. ORTEP drawing for the cationic moiety in **1**. The $\text{C}_5\text{H}_4\text{Me}$ ligands are omitted for clarity. Asterisks indicate atoms generated by the symmetry operation ($x, 1/2 - y, z$).

Scheme 1



magnetic resonance (NMR) data (vide infra) clearly showed the existence of two chemically equivalent $\mu_3\text{-CH}$ ligands. Thus, cluster **1** can be characterized as a bis(methyldiyne) cluster formulated as $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\mu_3\text{-CH})_2(\mu_3\text{-CO})_2](\text{PF}_6)_2$, in which two carbon monoxide molecules are reduced to give two μ_3 -methyldiyne ligands. The tetrairon core is slightly distorted from the ideal tetrahedral structure, with interatomic distances of 2.462(3) (Fe1–Fe1*), 2.510(3) (Fe1–Fe2), 2.506(3) (Fe1–Fe3), and 2.542(3) Å (Fe2–Fe3). These bond distances are typical for the expected iron–iron single bonds in cationic cubane-type clusters.⁶ Assuming that each methyldiyne ligand donates three electrons, cluster **1** can be viewed as a 60e species, consistent with the existence of six iron–iron bonds. The Cambridge Structural Database contains only one example of a cluster of the form $\text{M}_4(\mu_3\text{-CR})_2(\mu_3\text{-CO})_2$. Shaposhnikova et al. reported the reaction between $\text{Cp}_2\text{Ni}_2(\text{Ph}_2\text{C}_2)$ and $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ to form $\text{Cp}_4\text{Ni}_2\text{Mo}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CO})_2$, in which two alkylidyne ligands bridge the butterfly-type Mo_2Ni_2 wing.⁷ Product **1** represents the first X-ray structurally characterized example of a $\text{M}_4(\text{CH})_2(\text{CO})_2$ cubane-type cluster.

It is notable that ¹H and ¹³C NMR signals were observed at $\delta(^1\text{H})$ 17.26 and $\delta(^{13}\text{C})$ 377.5. These very low-field chemical shifts suggest the presence of methyldiyne ligands.⁸ The existence of two $\mu_3\text{-CO}$ ligands was confirmed by ¹³C NMR (δ 266.8) and infrared (IR)

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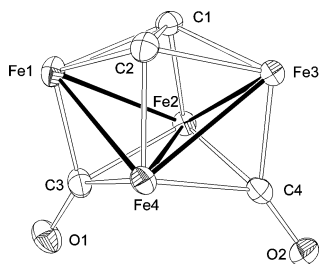


Figure 2. ORTEP drawing of **2**. The C_5H_4Me ligands are omitted for clarity.

[1726 cm^{-1} (ν_{CO})] spectral data. These spectroscopic features are consistent with the solid-state structure.

Treatment of **1** with Cp_2Co in acetonitrile resulted in the formation of the neutral cluster $(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(\mu_3-CO)_2$ (**2**) in 70% yield (Scheme 1). Cooling of the diethyl ether solution of **2** at $-30\text{ }^\circ C$ allowed the growth of brown crystals suitable for X-ray diffraction study (Figure 2). The asymmetric unit consists of two independent molecules of **2**, with no major differences between the two. The molecule assumes a butterfly geometry resulting from the scission of one of the iron–iron bonds of the tetrahedron in **1**. Surprisingly, the bond length of C1–C2 at 1.504(6) Å demonstrates the coupling of two methylidyne fragments in **1** to form the acetylene ligand that bridges four iron atoms in $\mu_4-\eta^2:\eta^2:\eta^1:\eta^1$ -fashion. The interatomic distances of Fe1–Fe2 (2.5119(8) Å), Fe1–Fe4 (2.4792(9) Å), Fe2–Fe3 (2.5025(8) Å), Fe2–Fe4 (2.5837(8) Å), and Fe3–Fe4 (2.4995(8) Å) indicate that these represent the five iron–iron bonds, whereas that of Fe1...Fe3 (3.4385(8) Å) indicates that there is no interaction on this bond.⁹ According to these structural features, cluster **2** is recognized as an Fe_4C_2 *closo*-octahedron, consistent with Wade–Mingos theory.^{10,11}

The dramatic structural changes from the bis(methylidyne) cluster **1** to the acetylene cluster **2** are reflected in the NMR spectral data. The 1H and ^{13}C NMR signals of the acetylene ligand in **2**, $\delta(^1H)$ 11.52 and $\delta(^{13}C)$ 206.5, are considerably highfield-shifted as compared to those of the methylidyne ligands in **1** and are in fact comparable to those of the acetylene ligands in $(\eta^5-C_5H_4Me)_4Fe_4(HCCH)_2$ [$\delta(^1H)$ 10.27 and $\delta(^{13}C)$ 212.6].^{5a}

The point we wish to stress is that formation and cleavage of the carbon–carbon bond can be controlled on the tetrairon core by two-electron reduction and oxidation as illustrated in Scheme 1. Treatment of **2** with air in the presence of NH_4PF_6 led to the cleavage of the carbon–carbon bond in the acetylene ligand to reproduce **1** in 51% yield.

It is reasonable to consider that supersaturation¹² resulting from the two-electron reduction of **1** is released by the coupling of two methylidyne ligands to give an acetylene ligand in which two methylidyne ligands donate six electrons and the acetylene ligand donates four. Electron-induced carbon–carbon bond formation has been reported by several groups.¹³ Yeh and Shapley reported the electron-induced coupling of two alkylidyne units: treatment of $Os_5(CO)_9(\mu_3-CPh)(\mu_3-COMe)$ with sodium benzophenone ketyl followed by protonation gave $(\mu-H)Os_5(CO)_9(\mu_3,\eta^2-CCPh)$ and MeOH.^{13c} Mathieu reported a similar observation for two-electron reduction of $Fe_3(CO)_9(\mu_3-CCH_2R)(\mu_3-COC_2H_5)$ ($R = n-C_3H_7, Ph$), which induced alkylidyne–alkylidyne coupling with subsequent rearrangement to acetylidyne to give $[Fe_3(CO)_9(\mu_3-\eta^2-CCCH_2R)]^-$ by

dissociation of the ethoxide anion.^{13d} To the authors' knowledge, the present results are the first example of reversible carbon–carbon bond cleavage and formation between acetylene and two methylidyne fragments via two-electron oxidation and reduction.

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Supporting Information Available: Experimental details of the synthesis and characterization of all compounds (PDF), and full details of the X-ray analysis in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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