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Redox-Responsive Recombination of Carbon−Carbon Bonds on Flexible Tetrairon Cores

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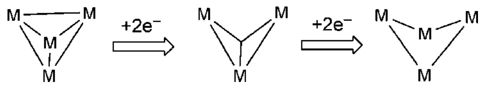
The structures of transition metal clusters in many cases are dependent on the valence electron count.[1] Tetrametallic cores, for example, have the representative structures illustrated in Scheme 1. When all the constituent metal atoms are in the inert gas configuration, the tetrahedron formed by the tetrametallic core involves a total of 60 valence electrons. The addition of two electrons results in scission of one of the metal−metal bonds to afford a butterfly structure, and the addition of another two electrons causes a further metal−metal bond scission to give a butterfly geometry without the hinge metal−metal bond. Although there have been many studies on tetranuclear transition metal clusters, the interconversion between each cluster core structure remains poorly understood. Recently, the present authors reported the reaction of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu\text{-}CO)_4]$ with $LiAlH_4$ to give $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2]$.[2] A survey of the products of this reaction revealed that reductive coupling of carbonyl ligands causes the geometry of the tetrairon core to transition from the tetrahedron to the butterfly structure, and finally to the butterfly structure without the hinge iron−iron bond.[3] The flexibility of the tetrairon core is expected to be crucial to allowing these transformation reactions to proceed.

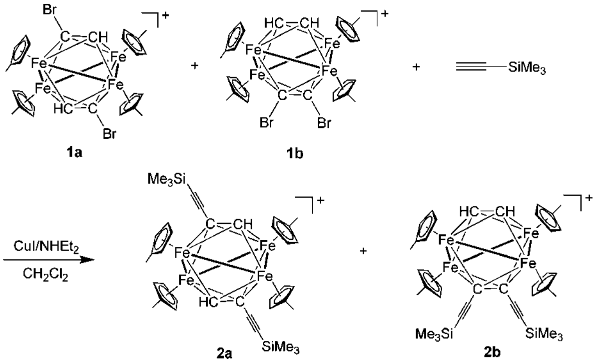
In this communication, two substituents are introduced onto the [4Fe−4C] core of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2](PF_6)$ to probe these transition reactions. Chemical oxidation and reduction of this complex result in interconversion of the tetrairon core between these three structures through recombination of the carbon−carbon bonds. Such a carbon−carbon bond formation reaction on the polymetallic core should be important in relation to Fischer−Tropsch (F−T) reactions.[4]

A 3:1 mixture of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCBr)_2](PF_6)$ (**1a**) and $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)(BrCCBr)](PF_6)$ (**1b**), prepared by reaction of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2](PF_6)$ with 2 equiv of *N*-bromosuccinimide (NBS),[5] was treated with $HC{\equiv}CSiMe_3$ in the presence of CuI and $NHEt_2$ (Scheme 2). After stirring at room temperature for 12 h, insoluble materials were removed by filtration and the filtrate was concentrated to dryness under vacuum. The NMR spectrum of the residue indicates the formation of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCC{-}C{\equiv}CSiMe_3)_2](PF_6)$ (**2a**) and $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)(Me_3SiC{\equiv}C{-}CC{-}C{\equiv}CSiMe_3)](PF_6)$ (**2b**) at a molar ratio of 3:1. As expected from the odd number of cluster electrons, the ^1H NMR signals of **2a** and **2b** exhibit characteristic paramagnetic shifts and line broadening. The broad signals of acetylenic protons are observed at δ −64.4 and −70.8, assignable to those for **2a** and **2b**, respectively. Cluster **2a** was isolated in 33% yield by silica-gel flash chromatography. The ^1H and $^{13}C\{^1H\}$ NMR signals of the two chemically equivalent $SiMe_3$ groups are observed at $\delta(^1H)$ −0.8 and $\delta(^{13}C)$ −8.8, respectively, indicating successful introduction of the silylethynyl groups onto the [4Fe−4C] core. The ^1H NMR spectrum also includes eight signals assigned to the ring proton of the $\eta^5\text{-}C_5H_4Me$ ligands, consistent with the structure of **2a** possessing two sets of chiral iron centers. Accordingly, two ^1H signals with equal intensity (6H × 2) are observed at δ −6.2 and −2.7, assigned to the methyl groups of the $\eta^5\text{-}C_5H_4Me$ ligands.

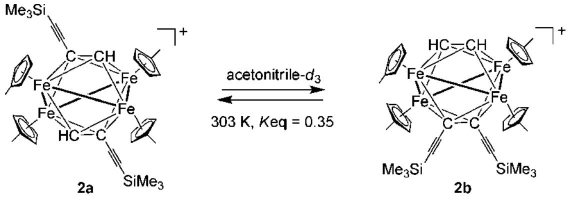
Scheme 1



Scheme 2



Scheme 3



Dissolution of isolated **2a**, a brown powder, in acetonitrile-d_3 resulted in the gradual conversion of **2a** to **2b** (Scheme 3). Equilibrium was reached at a 74:26 molar ratio within 1 week at 303 K. A kinetic study of interconversion between **2a** and **2b** was conducted over a temperature range of 303−343 K. An Eyring plot gives activation parameters of $\Delta H^{\ddagger} = 114(3)$ kJ mol^{-1}, $\Delta S^{\ddagger} = 10(7)$ J mol^{-1} K^{-1}, and $\Delta G^{\ddagger}_{298} = 111(5)$ kJ mol^{-1}. The near-zero value of $\Delta S^{\ddagger}$ indicates that isomerization occurs through an intramolecular and concerted process, as discussed below.

Treatment of **2a** with $[Cp_2Fe](PF_6)$ in acetonitrile to induce one-electron oxidation afforded **3** in 88% yield (Scheme 4). The molecular structure of **3** was unequivocally determined by an X-ray diffraction study (Figure 1). The molecule assumes a butterfly geometry resulting from the formation of one iron−iron bond. The interatomic distances for Fe1−Fe1* (2.494(2) Å), Fe1−Fe2 (2.486(2) Å), and Fe1−Fe2* (2.503(2) Å) represent the five iron−iron bonds, whereas the Fe2···Fe2* distance of 3.390 Å indicates no interaction. Formation of the hinge iron−iron bond leads to scission of the carbon−carbon bonds in the [4Fe−4C] core, as clearly indicated

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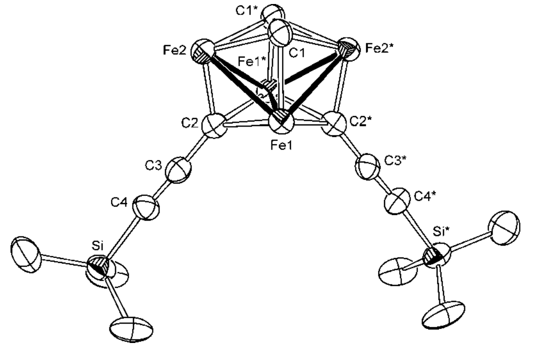
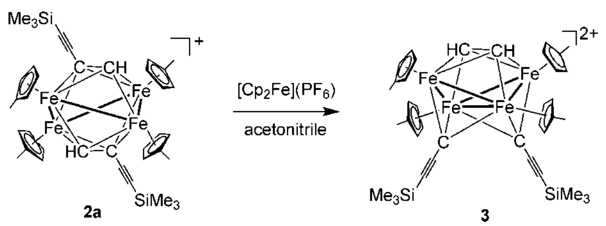
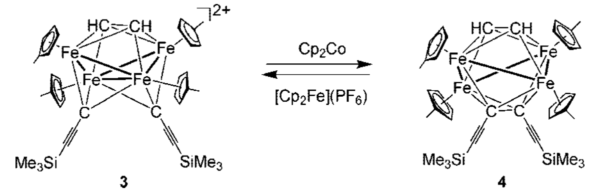


Figure 1. ORTEP drawing of **3**. The η^5-C_5H_4Me ligands and counteranions are omitted for clarity. Asterisks indicate atoms generated by the symmetry operation ($-x$, $-x + y$, $-z + {}^1/_3$).

Scheme 4



Scheme 5



by the increased interatomic distance for C2···C2* (2.852 Å). Based on these structural features, cluster **3** is recognized as an Fe_4C_2 *closo*-octahedron, consistent with Wade−Mingos theory.[6] Importantly, both of the two silylethynyl groups are bonded to the μ_3-carbyne carbon atoms (C2 and C2*), implying recombination of the carbon−carbon bonds through the redox process.[7,8]

Treatment of **3** with excess $[Cp_2Co]$ resulted in two-electron reduction to give the closed form $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)(Me_3SiC{\equiv}C{-}CC{-}C{\equiv}CSiMe_3)]$ (**4**) as a brown solid in 94% yield.[9] The ^{13}C NMR signal of two μ_3-carbyne carbon atoms in **3** is located at δ 341.9, while that for R−*CC*−R (R = $C{\equiv}CSiMe_3$) in **4** appears at δ 187.9. The upfield shift of the signal in **4** strongly supports the contention that the carbon−carbon bond was formed as a result of two-electron reduction. The ^1H NMR spectrum for **4** includes four signals at δ 3.56 (4H), 3.74 (4H), 3.77 (4H), and 3.90 (4H), assigned to the ring protons of the η^5-C_5H_4Me ligands. This feature is consistent with the two sets of achiral iron centers in **4**. The proton signal of the HCCH moiety appears at δ 10.06, very close to the chemical shift in $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2]$ (δ 10.27).[2] Further treatment of **4** with $[Cp_2Fe](PF_6)$ in acetonitrile-d_3 reproduced the open form **3** quantitatively (Scheme 5). These results demonstrate redox-responsive formation and breakage of the carbon−carbon bond in the flexible tetrairon core.[7,8]

For recombination of the carbon−carbon bonds on the tetrairon core, we tentatively propose a concerted mechanism involving a cubane-like transition state, consistent with the kinetic study. A related cubane-type tetrairon cluster $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CH)_2(\mu_3\text{-}CO)_2](PF_6)_2$ has been characterized by the X-ray diffraction study.[3] Andrés and his co-workers also reported the synthesis and structure of $[(\eta^5\text{-}C_5Me_5)_5Ti_4(\mu_3\text{-}CH)_4]$.[10] The electron deficiency resulting from the removal of one electron from **2a** or two electrons from **4** is compensated by the scission of a carbon−carbon bond to afford two μ_3-carbyne ligands, in which one acetylene ligand donates four electrons and two μ_3-carbyne ligands donate six electrons. Cluster **3** can be regarded as being electron-precise based on Wade−Mingos theory.[6] The exclusive formation of isomer **3** can be explained by an electronic factor, where the π-electron of the carbon−carbon triple bond stabilizes the electron-deficient μ_3-carbyne atom.[11]

This dynamic behavior of the [4Fe−4C] core is expected to be useful for developing redox-responsive functional molecules.[12] The silyl groups introduced here are readily removable under basic conditions to afford terminal alkynes.[13] Our redox-active [4Fe−4C] core could thus be incorporated into a wide variety of molecules through well-established organic reactions at the terminal alkynes.

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Supporting Information Available: Experimental procedures, spectroscopic data, and a CIF file for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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