ORGANOMETALLICS

Reactions of Bromoacetylene with Primary Amine on a Butterfly-Type Tetrairon Core to Give Isonitrile and Methyne through Oxidation and Deprotonation

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Supporting Information

ABSTRACT: Reaction of $[(\eta^{5}-C_{5}H_{4}Me)_{4}Fe_{4}(HCCH)(HCC-Br)]$ -(PF₆) with ^tBuNH₂ forms $[(\eta^{5}-C_{5}H_{4}Me)_{4}Fe_{4}(HCCH)(HCC-NH^{t}Bu)](PF_{6})$, of which one electron oxidation leads to carbon–carbon bond cleavage to give $[(\eta^{5}-C_{5}H_{4}Me)_{4}Fe_{4}(HCCH)(\mu_{3}-CH)-(\mu_{3}-CNH^{t}Bu)](PF_{6})_{2}$, and further treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) affords $[(\eta^{5}-C_{5}H_{4}Me)_{4}Fe_{4}(HCCH)(\mu_{3}-CH)(\mu_{3}-\eta^{1}-CN^{t}Bu)](PF_{6})$. Thus, the HCCBr group is converted to ^tBuNC and CH groups on the redox-responsive tetrairon core.

The structures and electronic properties of transition-metal L clusters can be altered through multiredox processes at the metal centers.¹ Tetrametallic cores, for example, change their structures as illustrated in Scheme 1. According to the effective atomic number (EAN) rule, the electron-precise tetrahedral structure involves 60 valence electrons. Addition of electrons causes the successive scission of metal-metal bonds to give the butterfly geometry without the hinge metal-metal bond.² Oxidation and reduction of metal clusters sometimes enhance the skeletal rearrangement of hydrocarbyl ligands through carbon-carbon bond formation and breaking.^{2,3} Thus, a redox-responsive tetrametallic core would act as an active reaction site for the electroninduced transformation of chemically inert substrates to valuable compounds. On the basis of these features characteristic of polymetallic cores, we have succeeded in the reductive coupling of four carbon monoxide molecules to give two acetylene molecules on the tetrairon core: treatment of $[(\eta^5-C_5H_4Me)_4Fe_4(\mu_3 (O)_4$ with LiAlH₄ afforded $[(\eta^5 - C_5 H_4 M e)_4 Fe_4 (HCCH)_2]$ (1), the structure of which has been determined by X-ray diffraction study.⁴ The one-electron oxidation of 1, followed by treatment with N-bromosuccinimide (NBS), resulted in stepwise and selective bromination of the four acetylenic carbons depending on the amount of NBS employed.⁵ Herein, we report the reaction of $[(\eta^5 - C_5 H_4 Me)_4 Fe_4 (HCCH) (HCC - Br)] (PF_6)$ $([2](PF_6))$ with ^tBuNH₂ as a primary amine. Further reactions involving one-electron oxidation and deprotonation at the nitrogen atom allowed the formation of the μ_3 -CH and μ_3 isonitrile moieties, where the role of the redox-responsive tetrairon core should be crucial.

Treatment of $[2](PF_6)$ with ^tBuNH₂ (3 equiv) in acetonitrile with effective stirring, followed by crystallization from CH₂Cl₂/ hexane, allowed the isolation of $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)-$



(HCC–NH^tBu)](PF₆) ([3](PF₆)) in 95% yield. When the reaction was carried out with 1 equiv of ^tBuNH₂, half the amount of [2](PF₆) remained intact, which indicates that excess ^tBuNH₂ is necessary for deprotonation. The [3](PF₆) cluster exhibits 59 electrons; the ¹H NMR spectrum exhibits characteristic paramagnetic shifts and line broadening. NMR signals of the NH^tBu group protons appear at δ 1.1 (9H, ^tBu) and -13.0 (1H, NH). NMR signals of the acetylenic protons were observed at δ –63.0 (2H, HCCH) and –78.0 (1H, HCCN).



One-electron oxidation of [3](PF₆) was achieved by $[Cp_2Fe](PF_6)$ in acetonitrile. Workup of the reaction mixture and crystallization from CH₃CN/CH₂Cl₂ gave greenish-brown crystals of $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(\mu_3-CH)(\mu_3-CNH^tBu)]$ -(PF₆)₂ ([4](PF₆)₂) in 53% yield. Although the structure of [4](PF₆)₂ was not determined by X-ray diffraction analysis, due to the poor quality of the crystals, the butterfly structure with two μ_3 -carbyne ligands is strongly supported by the electron count rule. The compound [4](PF₆)₂ contains 62 electrons as a whole, which is an appropriate number of electrons for a butterfly-type cluster with the hinge metal—metal bond (EAN rule).¹ With respect to the Wade—Mingos theory, [4](PF₆)₂ exhibits 14

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        Received:
        June 8, 2011

        Published:
        June 20, 2011
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Scheme 1



skeletal electrons and 7 electron pairs, consistent with an Fe_4C_2 closo-octahedron.⁶ As expected from the even numbers of cluster electrons, $[4](PF_6)_2$ is diamagnetic. The ¹H NMR signal of the HCCH ligand appears at δ 13.61 (2H).⁴ The presence of two μ_3 carbyne ligands is confirmed by ¹H and ¹³C{¹H} NMR spectroscopic data. In the ¹H NMR spectrum, the signal of the μ_3 -CH ligand is observed at δ 19.40. In the low-field region of the $^{13}C{^{1}H}$ NMR spectrum, two signals are observed at δ 342.3 (μ_3 -CH) and 333.7 (μ_3 -CN). The assignment is based on the ${}^{13}C{}^{1}H{}$ NMR spectroscopic data using DEPT pulse sequence. It should be noted that the formation of $[(\eta^5-C_5H_4Me)_4Fe_4 (HCC-NH^{t}Bu)(\mu_{3}-CH)_{2}](PF_{6})_{2}$ was not confirmed by NMR spectroscopy. The exclusive formation of $[4](PF_6)_2$ can be explained by an electronic factor, where π -donation from the amino group stabilizes the electron-deficient μ_3 -carbyne carbon atom.²



Further treatment of [4](PF₆)₂ with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile, followed by crystallization from CH₂Cl₂/diethyl ether, afforded greenish-brown crystals of [(η^5 -C₅H₄Me)₄Fe₄(HCCH)(μ_3 -CH)(μ_3 - η^1 -CN^tBu)](PF₆) ([5](PF₆)) in quantitative yield. Compound [5](PF₆) is stable even in solution. In accordance with deprotonation, the ¹H signal of NH (δ 7.90) disappeared. In the low-field region of the ¹H NMR spectrum, two singlet signals are observed at δ 21.68 (1H) and 12.45 (2H), the chemical shifts of which are characteristic of the μ_3 -CH and HCCH ligands, respectively.^{2,4}



X-ray crystallography confirmed the formation of [**5**](PF₆), which includes a μ_3 - η^1 -isonitrile ligand (Figure 1). The interatomic distances of Fe1–Fe3 (2.5245(7) Å), Fe1–Fe4 (2.5415(8) Å), Fe2–Fe3 (2.4767(8) Å), Fe2–Fe4 (2.4670(8) Å), and Fe3–Fe4 (2.5958(8) Å) indicate the existence of five iron–iron bonds, whereas the distance of Fe1···Fe2 (3.433 Å) indicates that there is no interaction between the pair. The average of the iron–iron bond distances (2.521 Å) is similar to that in the μ_3 -CO analogue [(η^5 -C₅H₄Me)₄Fe₄(HCCH)(μ_3 -CH)(μ_3 -CO)](PF₆) ([6](PF₆), av Fe–Fe bond: 2.500 Å).^{2b} The C3–C4 bond length (1.492(5) Å) is comparable to that in [1](BF₄) (1.46(1) Å) and [6](PF₆) (1.54(1) Å).^{2b,8} The distance of C1···C2 is 2.989 Å, which indicates no bonding



Figure 1. ORTEP drawing of [5](PF₆) shown with 50% probability ellipsoids. Four methyl groups on the cyclopentadienyl rings and the counteranion are omitted for clarity.

interaction between them. The hydrogen atoms on C2, C3, and C4 were located by differential Fourier map and refined isotropically. The μ_3 - η^1 -briding isonitrile is slightly distorted from linear with a C1–N–C5 angle of 161.4(4)°. The angle is similar to those in [Pd₃(μ_3 -CNXy)(μ -dppm)₃]²⁺ (167(1)°),^{9a} [Ni₃(μ_3 -CNMe)(μ_3 -I)(CNMe)₂(dppm)₂]⁺ (170(1)°),^{9b} and [(Cp*Co)₃-(μ_3 -CNMe)(μ_3 -CMe)(μ_2 -H)] (165(1)°),^{9c} which are closer to the geometry expected for sp hybridization than for the alternative sp² bent structure reported for [(CpCo)₃(μ_3 -CNR)-(μ_3 -S)] [R = C₆H₁₁ (two independent molecules: 141°, 129°),^{10a} C₂H₅ (130.6(6)°),^{10b P}Tol (130.8(5)°)^{10c}]. The C1–N distance (1.178(5) Å) lies in the range of slightly bent structures previously reported (1.16–1.19 Å)⁹ and is close to the carbon–nitrogen triple bond (1.157(5) Å).

The $\nu(NC)$ frequency is useful as an indication of the binding mode of an isonitrile ligand. Note that $\nu(NC)$ for free isonitrile occurs at 2121 cm⁻¹. The IR spectrum of [5](PF₆) exhibits a strong-intensity band at 1912 cm⁻¹, attributable to the C–N stretching vibration mode of μ_3 -isonitrile. A much greater shift to lower energy (300–600 cm⁻¹) is observed for $\nu(NC)$ in sp²-like bent structures.¹⁰ For [5](PF₆), a relatively small shift (209 cm⁻¹) compared to the free isonitrile is consistent with the almost linear μ_3 - η^1 -CNR ligand.⁹

Proton-induced carbyne—isonitrile coupling at the tungsten atom has been reported by Filippou, where treatment of *cis*-[Cp*Cl₂(^tBuNC)-W=CNEt₂] with HCl yielded the aminoalkyne complex [Cp*Cl₃W(η^2 -^tBu(H)NC=CNEt₂].¹¹ This reaction is the reverse process of our transformation from [**3**]⁺ to [**5**]⁺. In view of C1 chemistry, two carbon monoxide molecules are totally transformed to isonitrile and methyne via successive formation of acetylene, bromoacetylene, aminoacetylene, and aminocarbyne on the redox-responsive tetrairon reaction sites.²

In a previous communication, we reported the reaction of $[2](PF_6)$ with excess water. The reaction proceeded at room temperature to give $[6](PF_6)$ as a major product.^{5a} Although the transient formation of $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(HCC-OH)]$ -(PF₆) can be easily considered, such a compound was not detected spectroscopically. In sharp contrast, for the reaction of $[2](PF_6)$ with primary amine, the aminoacetylene-coordinated cluster $[3](PF_6)$ can be isolated as a thermally stable form.¹² Cluster $[3](PF_6)$ is sensitive to moisture in solution and transformed to $[6](PF_6)$ quantitatively via cleavage of C–C and C–N bonds (eq 4). Elimination of ^tBuNH₂ was confirmed by ¹H NMR spectrum. Aminoalkynes are stable toward moisture;

therefore, the reactivity observed here is characteristic of the aminoacetylene moiety bound to the redox-responsive tetrairon core.¹³ Transformation would be driven by thermodynamically favorable formation of the μ_3 -CO moiety, although the reaction mechanism concerning the nucleophilic substitution is not yet certain.



ASSOCIATED CONTENT

Supporting Information. Experimental procedures, spectroscopic data, and a CIF file for [**5**](PF₆). This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This work was supported by the Collaborative Research Program of Institute for Chemical Research, Kyoto University (grant 2010-6). M.O. acknowledges the funding program for Next Generation World-Leading Researchers.

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