

## Stepwise Bromination of Two Acetylene Molecules on a Butterfly-Type Tetrairon Core and Reactivity of the Resulting Bromoacetylene Fragment toward Nucleophiles

Masato Takano, Masaaki Okazaki,\* and Hiromi Tobita\*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

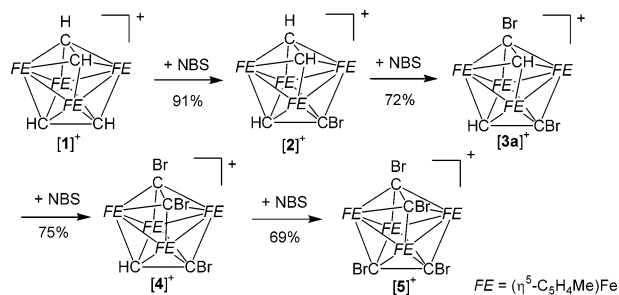
Received April 27, 2004; E-mail: mokazaki@mail.tains.tohoku.ac.jp; tobita@mail.tains.tohoku.ac.jp

Treatment of  $\text{Cp}'_4\text{Fe}_4(\mu_3\text{-CO})_4$  ( $\text{Cp}' = \text{Cp}, \text{C}_5\text{H}_4\text{Me}$ ) with  $\text{LiAlH}_4$  has been shown to promote the reductive coupling of two carbonyl ligands to yield  $\text{Cp}'_4\text{Fe}_4(\text{HCCH})_2$ .<sup>1</sup> To functionalize the resulting acetylene moieties, we attempted to convert the moieties to haloacetylene and dihaloacetylene, which are recognized as useful  $\text{C}_2$  synthetic intermediates in organic chemistry.<sup>2</sup> The present report shows the stepwise bromination of two acetylene ligands in  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{HCCH})_2]^+$  using *N*-bromosuccinimide (NBS) to form  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{C}_4\text{H}_4\text{-}n\text{Br}_n)]^+$  ( $n = 1\text{--}4$ ). The reactivity of  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{HCCBr})(\text{HCCH})]^+$  toward water, pyridine, and  $\text{ZnMe}_2$  is also investigated.

Treatment of  $(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{HCCH})_2$  (**1**) with 1 equiv of NBS resulted in one-electron oxidation of **1** to give  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{HCCH})_2]\text{Br}$  (**[1]Br**) in 83% yield. Complex **[1]Br** was characterized by comparison of the nuclear magnetic resonance (NMR) data with the data for  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{HCCH})_2](\text{OTf})$  reported previously.<sup>1b</sup> In this reaction, bromination of acetylene ligands was not observed.

Treatment of **[1](OTf)** with 1 equiv of NBS gave  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{HCCBr})(\text{HCCH})](\text{OTf})$  (**[2](OTf)**) in 91% isolated yield. It should be noted that further treatment of NBS led to the stepwise bromination of two acetylene ligands, as illustrated in Scheme 1.

### Scheme 1. Stepwise Bromination of the Acetylene Ligands



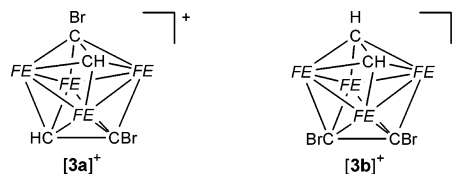
All clusters were isolated in moderate yields. The formulas for clusters **[2]<sup>+</sup>**–**[5]<sup>+</sup>** were established by elemental analysis. As expected from the odd number of cluster electrons, the <sup>1</sup>H NMR signals of clusters **[2]<sup>+</sup>**–**[5]<sup>+</sup>** exhibited characteristic paramagnetic shifts and line broadening. The NMR data for the acetylenic protons are listed in Table 1. The increase in the number of bromines leads to a downfield shift of the acetylenic protons, explainable as due to the diamagnetic deshielding effect of bromine.

For the clusters with formula  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\text{C}_4\text{H}_2\text{Br}_2)]^+$ , two isomers, **[3a]<sup>+</sup>** and **[3b]<sup>+</sup>**, can be considered, as illustrated in Scheme 2. Although both possess two sets of chemically equivalent iron centers, the two isomers can be distinguished by NMR spectroscopy on the basis of the chirality of the iron center. The <sup>1</sup>H NMR spectrum of the isolated product displays eight signals assigned to the ring proton of the  $\eta^5\text{-C}_5\text{H}_4\text{Me}$  ligands, in good agreement with the structure of **[3a]<sup>+</sup>** with two sets of chiral iron centers.

**Table 1.** <sup>1</sup>H NMR Data ( $\text{CD}_3\text{CN}$ ) of the Acetylene Ligands in **[1]<sup>+</sup>**–**[4]<sup>+</sup>**

	<b>[1]<sup>+</sup></b>	<b>[2]<sup>+</sup></b>	<b>[3a]<sup>+</sup></b>	<b>[3b]<sup>+</sup></b>	<b>[4]<sup>+</sup></b>
HCCH $\delta$	−75.2	−70.6	—	−67.4	—
HCCBr $\delta$	—	−61.0	−57.2	—	−54.0

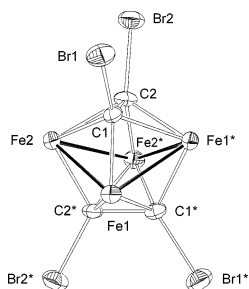
### Scheme 2. Structural Features of Isomers **[3a]<sup>+</sup>** and **[3b]<sup>+</sup>**



When the reaction of **[2]<sup>+</sup>** with 1 equiv of NBS was monitored by <sup>1</sup>H NMR spectroscopy, the formation of **[3b]<sup>+</sup>** was observed as a minor product. The molar ratio of **[3a]<sup>+</sup>** to **[3b]<sup>+</sup>**, determined by NMR, was 3:1. Besides the signals of **[3a]<sup>+</sup>**, the <sup>1</sup>H NMR spectrum of the mixture displayed four signals assigned to  $\text{C}_5\text{H}_4\text{Me}$  ring protons, supporting the **[3b]<sup>+</sup>** structure with two sets of achiral iron centers. A singlet signal was observed at  $\delta$  −67.4, assigned to protons of the nonsubstituted acetylene ligand in **[3b]<sup>+</sup>** (Table 1).

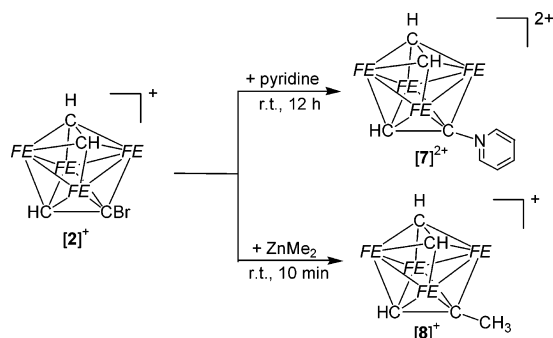
Single crystals of **[5]<sup>+</sup>** suitable for X-ray diffraction analysis were prepared by replacing the counteranion with tetrakis[bis(3,5-trifluoromethyl)phenyl]borate (TFPB). An ORTEP drawing of the cationic part in **[5](TFPB)** is illustrated in Figure 1. Four acetylenic protons were substituted with bromine atoms. The structural features of the  $\text{Fe}_4\text{C}_2$  core are similar to those of **[1](TFPB)**.<sup>1d</sup> Two chemically equivalent dibromoacetylene ligands bridge four iron atoms in a  $\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1$  fashion. The interatomic distances of  $\text{Fe1}^*-\text{Fe1}^*$  (2.472(2) Å),  $\text{Fe1}^*-\text{Fe2}^*$  (2.510(1) Å), and  $\text{Fe2}^*-\text{Fe2}^*$  (2.475(2) Å) indicate the existence of four iron–iron bonds, whereas the distances of  $\text{Fe1}^*\cdots\text{Fe2}^*$  and  $\text{Fe1}^*\cdots\text{Fe2}^*$  (3.296(1) Å) indicate that there is no interaction between these pairs.<sup>1</sup> The distance  $\text{C1}-\text{C2}$  (1.491(10) Å) is comparable to that in the nonsubstituted acetylene-coordinated cluster  $[\text{Cp}'_4\text{Fe}_4(\text{HCCH})_2]^{n+}$  ( $\text{Cp}' = \text{Cp}, \eta^5\text{-C}_5\text{H}_4\text{Me}; n = 0, 1, 2$ ; average 1.48 Å).<sup>1</sup>

Cluster **[1]<sup>+</sup>** is air-stable even in solution, in sharp contrast to the case for **[2]<sup>+</sup>**. Treatment of the acetonitrile solution of **[2](PF<sub>6</sub>)** with water resulted in carbon–carbon bond cleavage of the bromoacetylene ligand to form  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_4\text{Fe}_4(\mu_3\text{-CH})(\mu_3\text{-CO})(\text{HCCH})](\text{PF}_6)$  (**[6](PF<sub>6</sub>)**),<sup>1d</sup> accompanied by the minor formation of **[1](PF<sub>6</sub>)**.<sup>1b</sup> Treatment of the mixture with  $\text{Cp}_2\text{Co}$  led to one-electron reduction of **[1](PF<sub>6</sub>)**, whereas **[6](PF<sub>6</sub>)** remained intact.<sup>3</sup> The residue was extracted with hexane and dichloromethane in this order, and evaporation of the two extracts gave **1** and **[6](PF<sub>6</sub>)** in 33% and 54% isolated yields, respectively. Experiments using  $\text{H}_2^{18}\text{O}$  or  $\text{D}_2\text{O}$  revealed that the oxygen atom of CO in **[6](PF<sub>6</sub>)** and one of the hydrogen atoms of HCCH in **[1](PF<sub>6</sub>)** are derived from water. As an explanation for the formation of **[6](PF<sub>6</sub>)**, we tentatively

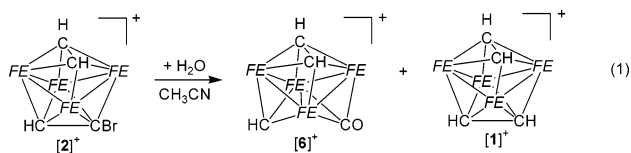


**Figure 1.** ORTEP drawing of the cationic part in [5](TFPB). The  $C_5H_4Me$  ligands are omitted for clarity. Asterisks indicate atoms generated by the symmetry operation  $(-x, y, 1/2 - z)$ .

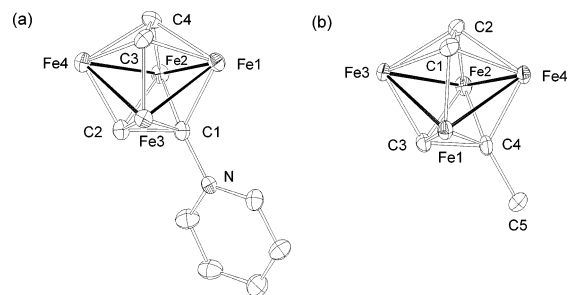
**Scheme 3.** Reactivity of [2]<sup>+</sup> toward Pyridine and  $ZnMe_2$



propose a mechanism involving the transient formation of the ethynol-coordinated cluster  $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(HCCOH)](PF_6)$  via nucleophilic attack of water toward the acetylenic carbon with a bromo group. Boyar et al. reported the isomerization of an ethynol cluster  $Os_3H_2(\mu_3-HCCOH)(CO)_9$  to the corresponding keto form  $Os_3H_3(\mu_3-HCCO)(CO)_9$ , resulting in decarbonylation to give the methylidyne cluster  $Os_3H_3(\mu_3-CH)(CO)_9$ .<sup>4</sup> Vollhardt and Wolfgruber synthesized and structurally characterized an ethynol-coordinated tricobalt cluster  $[Cp_3Co_3(\mu_3-CH)(\mu_3-HCCOH)]^+$ , which caused decarbonylation and coupling of two methylidyne ligands to give  $[Cp_3Co_3(\mu-H)(\mu-CO)(\mu_3-HCCH)]^+$ .<sup>5</sup> It should be noted that haloalkynes are considerably stable toward water. Thus, the reactivity discovered here is characteristic of the bromoacetylene fragment coordinated to the tetrairon core.<sup>2</sup>



The bromo group on the acetylene ligand was easily substituted with pyridine to give cluster [7](PF<sub>6</sub>)<sub>2</sub> in 90% yield (Scheme 3). The structure of [7](PF<sub>6</sub>)<sub>2</sub> was unambiguously determined by X-ray diffraction study (Figure 2a). Product [7](PF<sub>6</sub>)<sub>2</sub> can be best described as a cluster coordinated with a pyridinium-substituted acetylene, in which one of the positive charges is localized on the coordinated pyridinium nitrogen atom. The structure of the Fe<sub>4</sub>C<sub>2</sub> core is essentially the same as that in [1](TFPB).<sup>1d</sup> The N–C1 bond distance (1.492(9) Å) is in the normal range expected for the pyridinium nitrogen–carbon bonds.<sup>6</sup> Boyar et al. have reported the



**Figure 2.** ORTEP drawings of the cationic parts in [7](PF<sub>6</sub>)<sub>2</sub> (a) and [8](BPh<sub>4</sub>) (b). The  $C_5H_4Me$  ligands are omitted for clarity.

synthesis of  $Os_3H(\mu_3-HCCPy)(CO)_9$ , which is a rare example of a pyridinium-substituted acetylene cluster.<sup>4</sup>

Treatment of [2](TFPB) with  $ZnMe_2$  in diethyl ether led to elongation of the carbon–carbon chain to give [8](TFPB) in 78% yield (Scheme 3). Successful introduction of the methyl group to form the propyne ligand was confirmed by X-ray diffraction study (Figure 2b).

There have been limited examples of haloalkyne-coordinated complexes and clusters to date, probably due to the relative inaccessibility of haloalkynes,<sup>7–9</sup> and most complexes have been synthesized by reactions of transition metal complexes with haloalkynes. The reactivity of these complexes remains largely unknown. For  $M_n$  transition-metal clusters ( $n > 2$ ), there is only one example, reported by Lentz and Michael, who obtained  $Cp^*CoFe_3(CO)_9(\mu_4-\eta^2-FC\equiv CF)$  by irradiating a mixture of  $Fe_3(CO)_9(\mu_3-CF)_2$  and  $Cp^*Co(CO)_2$ .<sup>9</sup>

**Supporting Information Available:** Experimental details and characterization data (PDF); X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

**References**

- (1) (a) Okazaki, M.; Ohtani, T.; Inomata, S.; Tagaki, N.; Ogino, H. *J. Am. Chem. Soc.* **1998**, *120*, 9135. (b) Okazaki, M.; Ohtani, T.; Takano, M.; Ogino, H. *Inorg. Chem.* **2002**, *41*, 6726. (c) Okazaki, M.; Ohtani, T.; Ogino, H. *J. Am. Chem. Soc.* **2004**, *126*, 4104. (d) Okazaki, M.; Ohtani, T.; Takano, M.; Ogino, H. *Organometallics*, in press.
- (2) (a) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier Publishing Co.: New York 1971. (b) Patai, S. *Supplement C2: The Chemistry of Triple-bonded Functional Groups*; John Wiley & Sons: New York, 1991; Chapter 6. (c) Wagner, A.; Heitz, M. P.; Mioskowski, C. *Tetrahedron Lett.* **1990**, *31*, 3141. (d) Vinczer, P.; Struhar, S.; Novak, L.; Szantay, C. *Tetrahedron Lett.* **1992**, *33*, 683. (e) Nishiguchi, I.; Kanbe, O.; Itoh, K.; Maekawa, H. *Synlett* **2000**, 89 and references cited therein.
- (3) Cyclic voltammograms of [1]<sup>+</sup> and [6]<sup>+</sup> displayed one-electron reduction waves at  $E_{1/2} = -0.73$  and  $-1.32$  V vs Ag/AgNO<sub>3</sub>, respectively. The electrochemistry of the clusters will be reported elsewhere.
- (4) Boyar, E.; Deeming, A. J.; Kabir, S. E. *J. Chem. Soc., Chem. Commun.* **1986**, 577.
- (5) Vollhardt, K. P. C.; Wolfgruber, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 929.
- (6) Kiviniemi, S.; Nissinen, M.; Alaviuhkola, T.; Rissanen, K.; Pursiainen, J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2364.
- (7) Mononuclear complexes: (a) Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1319. (b) Sünkel, K. *J. Organomet. Chem.* **1988**, *348*, C12. (c) Löwe, C.; Hund, H.-U.; Berke, H. *J. Organomet. Chem.* **1989**, *371*, 311. (d) Sünkel, K.; Birk, U.; Robl, C. *Organometallics* **1994**, *13*, 1679. (e) Sünkel, K.; Birk, U. *Polyhedron* **1999**, *18*, 3187.
- (8) Dinuclear complexes: (a) Stahl, K.; El-Kholi, A.; Müller, U.; Dehnicke, K. *J. Organomet. Chem.* **1986**, *316*, 95. (b) Lang, H.; Rheinwald, G.; Lay, U.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **2001**, *634*, 74.
- (9) Tetranuclear cluster: Lentz, D.; Michael, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 845.

JA047569A