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Article

Synthesis and Structures of One- and Two-Electron Oxidized Forms of Bis(acetylene)tetrairon Clusters $Cp'_4Fe_4(HCCH)_2$ ($Cp' = Cp$, η^5-C_5H_4Me)

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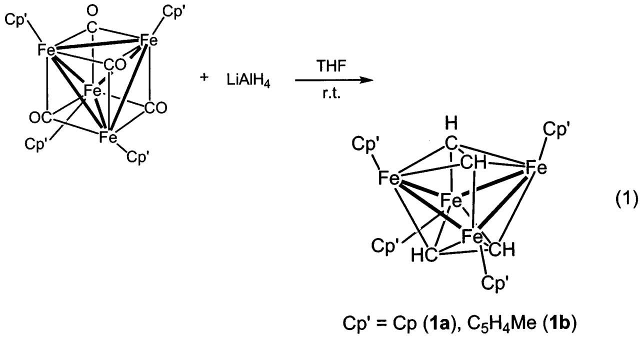
Air-oxidation of $Cp'_4Fe_4(HCCH)_2$ ($Cp' = Cp$ (**1a**), C_5H_4Me (**1b**)) in an NH_4PF_6/CH_3CN solution afforded the one-electron oxidized clusters $[Cp'_4Fe_4(HCCH)_2](PF_6)$. Oxidation of **1a** with excess $AgBF_4$ in THF afforded [**1a**](BF_4), while that of **1b** with excess $AgBF_4$ gave [**1b**]$(BF_4)_2$. The X-ray crystal structure analysis of [**1a**](BF_4) revealed that the monocationic cluster retains the butterfly-type $Fe_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}HCCH)_2$ framework similar to that of the neutral cluster. The average Fe–Fe bond length is shorter by 0.029 Å than that in the neutral cluster. Electrochemical oxidation of **1a** and **1b** in 0.1 M NH_4PF_6/CH_3CN solution at +0.30 and +0.25 V versus Ag/10 mM $AgNO_3$, respectively, afforded the two-electron oxidized clusters [**1a**]$(PF_6)_2$ and [**1b**]$(PF_6)_2$. The X-ray crystal structure analysis for [**1b**]$(BF_4)_2$ shows that the butterfly-type cluster core is retained but shrinks more of those of neutral and monocationic clusters. The four Fe–Fe bonds in [**1b**]$(BF_4)_2$ are unequivalent: one Fe–Fe bond (2.397(1) Å) is apparently shorter than the others (2.439(2)–2.461(2) Å).

Introduction

Over the last few decades, increasing attention has been focused on the reduction of coordinated carbon monoxide in transition metal complexes and clusters to further understand the heterogeneous reduction of CO such as the Fischer–Tropsch reaction and, if possible, to develop homogeneous catalysts for the reduction of CO.[1] The cubane-type tetrairon cluster $Cp'_4Fe_4(\mu_3\text{-}CO)_4$ ($Cp' = Cp$, η^5-C_5H_4-Me) can be regarded as a model for the metal surface that absorbs carbon monoxide. In the previous paper, we reported that treatment of $Cp'_4Fe_4(\mu_3\text{-}CO)_4$ with $LiAlH_4$ leads to the reductive coupling of carbonyl ligands to give butterfly-type acetylene-coordinated clusters $Cp'_4Fe_4(HCCH)_2$ ($Cp' = Cp$ (**1a**), η^5-C_5H_4Me (**1b**)) (eq 1).[2] If the acetylene ligands in **1** are substituted by carbon monoxide to give the original cubane-type carbonyl clusters or $Cp'_4Fe_4(HCCH)_2(CO)_2$ and free acetylene,[3] a conversion cycle of carbon monoxide to acetylene can be constructed. It is very interesting to examine the change of reactivity of the cluster toward ligand substitu-



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(3) This type of reaction indeed occurs, but very slowly. The details will be reported elsewhere.

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Table 1. Cyclic Voltammetric Data of **1a** and **1b** in 0.1 M (n-Bu_4N)(PF_6)- Acetonitrile[a]

redox couple	E_{pa}, V	E_{pc}, V	$E_{1/2}$, V	ΔE_p, mV
$[\mathbf{1a}]^{3+}/[\mathbf{1a}]^{2+}$	+1.08	+0.99	+1.04	90
$[\mathbf{1a}]^{2+}/[\mathbf{1a}]^{1+}$	+0.27	+0.20	+0.24	70
$[\mathbf{1a}]^{1+}/[\mathbf{1a}]^{0}$	−0.62	−0.70	−0.66	80
$[\mathbf{1a}]^{0}/[\mathbf{1a}]^{1-}$		−1.32		
$[\mathbf{1b}]^{3+}/[\mathbf{1b}]^{2+}$	+1.00	+0.91	+0.96	90
$[\mathbf{1b}]^{2+}/[\mathbf{1b}]^{1+}$	+0.20	+0.13	+0.17	70
$[\mathbf{1b}]^{1+}/[\mathbf{1b}]^{0}$	−0.69	−0.77	−0.73	80
$[\mathbf{1b}]^{0}/[\mathbf{1b}]^{1-}$		−1.38		

[a] Sweep rate: 50 mV s^{-1}. Potentials are given in V vs Ag/10 mM $AgNO_3$.

tion accompanied by oxidation or reduction since one-electron oxidized or reduced complexes undergo more facile substitution than the original complexes do.[4] This paper describes the synthesis and structures of the one- and two-electron oxidized clusters of **1**. In the previous paper,[2] we reported that the cyclic voltammogram of the acetylene clusters **1a** and **1b** exhibit three reversible or quasireversible one-electron oxidation waves and an irreversible one-electron reduction wave. The electrochemical data are summarized in Table 1. On the basis of the redox data for **1**, oxidation of **1** was carried out.

Experimental Section

General Comments. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with appropriate reagents. The compounds $Cp_4Fe_4(CO)_4$[5a] and $(MeC_5H_4)_4$-$Fe_4(CO)_4$[5b] were prepared according to the literature procedures. All other chemicals were used as received. NMR spectra were recorded on a Bruker ARX-300 spectrometer. IR spectra were recorded on a Horiba FT-200 spectrometer. Mass spectra were obtained with a JEOL JMS-HX110 spectrometer. Bulk electrolysis was carried out using a Bioanaytical System BAS-100BW. A platinum net was used as a working electrode; a carbon rod was used as a counter electrode, which was separated from the electrolysis solution by a sintered glass filter; and an Ag/10 mM $AgNO_3$ electrode was used as a reference electrode.

Improved Synthesis of $Cp_4Fe_4(HCCH)_2$ (1a). A THF solution (40 mL) of $Cp_4Fe_4(CO)_4$ (500 mg, 0.84 mmol) was stirred with excess $LiAlH_4$ (318 mg, 8.38 mmol) at room temperature. Immediately, the color of the solution changed from green to brown. After being stirred for 2 h, volatiles were removed under reduced pressure. To the greenish black residue was added a mixture of toluene and ethanol (16:1, 60 mL) at room temperature to deactivate the hydride-transfer reagent. The insoluble materials were removed using the Celite pad. The filtrate was evaporated to dryness, and then the resulting residue was extracted with toluene (80 mL) through the Celite pad. Removal of volatiles under reduced pressure afforded a brown solid of **1a** (151 mg) in 33% yield.

Improved Synthesis of $(C_5H_4Me)_4Fe_4(HCCH)_2$ (1b). Cluster **1b** (351 mg) was synthesized in 77% yield by a method similar to that for **1a**, using $(C_5H_4Me)_4Fe_4(CO)_4$ (500 mg, 0.77 mmol) and excess $LiAlH_4$ (290 mg, 7.64 mmol).

Synthesis of [1a](PF_6) by Air-Oxidation. Cluster **1a** (35 mg, 0.065 mmol) was dissolved in 0.1 M NH_4PF_6 solution of acetonitrile (10 mL). The solution was exposed to air with stirring for 1 h at room temperature. After filtration, volatiles were removed under reduced pressure. The residue was washed first with water (30 mL) to remove excess NH_4PF_6 and finally with ether (30 mL). The brown solid was extracted with acetonitrile, and the solvent was removed in vacuo to give [**1a**](PF_6) (34 mg, 76%) as a brown solid. Anal. Calcd for $C_{24}H_{24}F_6Fe_4P$: C, 42.34; H, 3.55. Found: C, 42.07; H, 3.60. Mass (FAB, *m*-nitrobenzyl alcohol, Xe) m/z: 681 (M^+, 3), 536 ($M^+ - PF_6$, 100). IR (KBr, $\tilde{\nu}/cm^{-1}$): 3107 (w), 2941 (w), 1421 (m), 1115 (w), 1061 (w), 1009 (w), 847 (vs), 557 (m). ^1H NMR (300 MHz, CD_3CN): δ −75.40 (br, $W_{1/2}$ = 50 Hz, 4H, 2HCCH), 8.10 (br, $W_{1/2}$ = 25 Hz, 20H, 4Cp).

Synthesis of [1b](PF_6) by Air-Oxidation. Cluster **1b** (54 mg, 0.091 mmol) was treated in a manner similar to the synthesis of [**1a**](PF_6) mentioned above. [**1b**](PF_6) (53 mg, 79%) was obtained as a brown solid. Anal. Calcd for $C_{28}H_{32}F_6Fe_4P$: C, 45.64; H, 4.38. Found: C, 45.43; H, 4.63. Mass (FAB, *m*-nitrobenzyl alcohol, Xe) m/z: 737 (M^+, 2), 592 ($M^+ - PF_6$, 100). IR (KBr, $\tilde{\nu}/cm^{-1}$): 3111 (w), 2926 (w), 1483 (m), 1373 (w), 1031 (w), 842 (vs), 829 (vs), 557 (m). ^1H NMR (300 MHz, CD_3CN): δ −76.53 (br, $W_{1/2}$ = 55 Hz, 4H, HCCH), −1.49 (br, $W_{1/2}$ = 14 Hz, 12H, $4C_5H_4\mathit{Me}$), 6.00 (br, $W_{1/2}$ = 22 Hz, 8H, $4C_5\mathit{H}_4Me$), 8.87 (br, $W_{1/2}$ = 25 Hz, 8H, $4C_5\mathit{H}_4Me$).

Electrochemical Oxidation of 1a to a Dicationic Cluster. (A) Synthesis of [1a](PF_6)$_2$. A 0.1 M NH_4PF_6 solution of CH_3CN (40 mL) containing **1a** (42 mg, 0.078 mmol) was electrolyzed at +0.30 V versus Ag/$AgNO_3$. After the current decreased to almost zero, the solution was filtered. The filtrate was evaporated to dryness under reduced pressure. The greenish brown residue was washed with water (50 mL) and ether (30 mL) and then extracted with acetonitrile. Removal of the solvent in vacuo afforded a greenish brown solid that was recrystallized from acetonitrile/ether to give brown crystals of [**1a**](PF_6)$_2$. Yield: 44 mg, 68%. Anal. Calcd for $C_{24}H_{24}F_{12}Fe_4P_2$: C, 34.91; H, 2.93. Found: C, 35.48; H, 3.20. Mass (FAB, *m*-nitrobenzyl alcohol, Xe) m/z: 536 ($M^+ - 2PF_6$, 100). IR (KBr, $\tilde{\nu}/cm^{-1}$): 3120 (w), 1429 (m), 1425 (w), 1068 (w), 1016 (w), 1012 (w), 862 (vs), 829 (vs), 762 (w), 557 (s), 534 (vs). ^1H NMR (300 MHz, CD_3CN) δ fraction showing sharp signals: 4.92 (s, 10H, 2Cp), 5.62 (s, 10H, 2Cp), 14.81 (s, 2H, 2*H*CCH), 17.99 (s, 2H, 2*H*CCH); fraction showing broad signals: 56.6 (br, $W_{1/2}$ = 980 Hz, 20H, 4Cp), −154.9 (br, $W_{1/2}$ = 1000 Hz, 4H, 2HCCH). ^{13}C NMR (75.5 MHz, CD_3CN) δ fraction showing sharp signals: 90.1, 91.5 (Cp).

(B) Synthesis of [1b](PF_6)$_2$. A 0.1 M NH_4PF_6 solution (40 mL) of CH_3CN containing **1b** (37 mg, 0.063 mmol) was electrolyzed at +0.25 V versus Ag/$AgNO_3$. Then, the solution was treated with a procedure similar to the synthesis of [**1a**](PF_6)$_2$ mentioned above. [**1b**](PF_6)$_2$ was obtained as brown crystals. Yield: 30 mg, 54%. Anal. Calcd for $C_{28}H_{32}F_{12}Fe_4P_2$: C, 38.14; H, 3.66. Found: C, 38.44; H, 3.93. Mass (FAB, *m*-nitrobenzyl alcohol, Xe) m/z: 737 ($M^+ - PF_6$, 2), 592 ($M^+ - 2PF_6$, 100), 532 ($M^+ - 2PF_6 - 4Me$, 2). IR (KBr, $\tilde{\nu}/cm^{-1}$): 3120 (w), 1483 (m), 1454 (w), 1404 (w), 1390 (w), 1240 (w), 1032 (w), 829 (vs), 557 (s). ^1H NMR (300 MHz, CD_3CN) δ fraction showing sharp signals: 1.77, 2.09 (s, 6H × 2, $4(C_5H_4\mathit{Me})$), 4.50, 4.98, 5.27, 5.56 (m, 4H × 4, $4(C_5\mathit{H}_4$-Me)), 14.27 (s, 2H, 2*H*CCH), 17.67 (s, 2H, 2*H*CCH); fraction showing broad signals: −154.1 (br, $W_{1/2}$ = 720 Hz, 4H, HCCH), −10.7 (br, $W_{1/2}$ = 25 Hz, 12H, $4(C_5H_4\mathit{Me})$), 52.1, 56.8 (br, $W_{1/2}$ = 260 Hz, 8H × 2, $C_5\mathit{H}_4Me$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN) δ fraction showing sharp signals: 13.1, 13.7 ($C_5H_4\mathit{Me}$), 88.1, 89.6, 89.7, 91.4, 109.6, 110.3 (C_5H_4Me), 186.4, 258.0 (HCCH).

Synthesis of [1a](BF_4) by Oxidation with $AgBF_4$. To a THF solution (50 mL) of **1a** (29 mg, 0.054 mmol) was added $AgBF_4$

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(209 mg, 1.07 mmol), and the mixture was stirred at room temperature for 14 h. The insoluble materials were collected by filtration and extracted with acetonitrile. The solvent was evaporated in vacuo to give a brown solid of [**1a**](BF_4). Yield: 30 mg, 89%. Anal. Calcd for $C_{24}H_{24}BF_4Fe_4$: C, 46.30; H, 3.89. Found: C, 45.73; H, 3.83. Mass (FAB, *m*-nitrobenzyl alcohol, Xe) *m*/*z*: 536 ($M^+ - BF_4$, 100). IR (KBr, $\tilde{\nu}$/cm^{-1}): 1080 (vs), 1041 (vs), 856 (s), 829 (s). ^{1}H NMR (300 MHz, CD_3CN): δ −73.93 (br, $W_{1/2}$ = 80 Hz, 4H, 2HCCH), 8.09 (br, $W_{1/2}$ = 40 Hz, 20H, 4Cp).

Synthesis of [1b](BF_4)$_2$ by Oxidation with $AgBF_4$. To a THF solution (50 mL) of **1b** (47 mg, 0.079 mmol) was added $AgBF_4$ (155 mg, 0.796 mmol), and the mixture was stirred at room temperature for 3 h. The insoluble materials were collected by filtration and washed with THF and CH_2Cl_2. Extraction with acetonitrile and subsequent removal of the solvent afforded a greenish brown solid of [**1b**](BF_4)$_2$ (55 mg, 90%). Anal. Calcd for $C_{28}H_{32}B_2F_8Fe_4$: C, 43.93; H, 4.21. Found: C, 43.14; H, 4.12. Mass (FAB, *m*-nitrobenzyl alcohol, Xe) *m*/*z*: 592 ($M^+ - 2(BF_4)$, 100). IR (KBr, $\tilde{\nu}$/cm^{-1}): 1479 (m), 1462 (w), 1448 (w), 1392 (w), 1389 (w), 1371 (w), 1367 (w), 1350 (w), 1232 (w), 1055 (vs), 847 (m), 534 (w), 521 (w). ^{1}H NMR (300 MHz, CD_3CN) δ fraction showing sharp signals: 1.78, 2.08 (s, 6H × 2, 4(C_5H_4*Me*)), 4.51, 4.99, 5.28, 5.57 (m, 4H × 4, 4(C_5*H_4*Me)), 14.28 (s, 2H, 2*H*CCH), 17.69 (s, 2H, 2*H*CCH); fraction showing broad signals: −155.4 (br, $W_{1/2}$ = 403 Hz, 4H, HCCH), −10.5 (br, $W_{1/2}$ = 196 Hz, 12H, 4(C_5H_4*Me*)), 53.4, 58.0 (br, $W_{1/2}$ = 280 Hz, 8H × 2, C_5*H_4*Me). ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN): δ 13.2, 13.8, 88.2, 89.6, 89.7, 91.5.

Reaction of 1b with 1 Equiv of HOTf. To a CH_2Cl_2 solution (30 mL) of **1b** (200 mg, 0.34 mmol) was added HOTf (40 μL, 0.44 mmol) at room temperature. After the solution was stirred overnight, volatiles were removed under reduced pressure. The residue was washed with water and ether in this order and extracted with acetonitrile (50 mL). The extract was filtered through the Celite pad. Evaporation of the solvent from the filtrate gave a greenish brown solid of [**1b**](OTf). Yield: 201 mg, 80%. Anal. Calcd for $C_{29}H_{32}F_3Fe_4O_3S$: 47.01; H, 4.35. Found: C, 46.71; H, 4.31. Mass (FAB, *m*-nitrobenzyl alcohol, Xe) *m*/*z*: 592 (M^+ − OTf, 100). IR (KBr, $\tilde{\nu}$/cm^{-1}): 3089 (w), 2925 (w), 1724 (br), 1481 (w), 1371 (m), 1269 (vs), 1220 (s), 1145 (s), 1027 (s), 821 (m), 636 (s), 569 (w), 515 (w). ^{1}H NMR (300 MHz, CD_3CN): δ −75.01 (br, $W_{1/2}$ = 42 Hz, 4H, HCCH), −1.38 (br, $W_{1/2}$ = 6 Hz, 12H, 4C_5H_4*Me*), 6.00 (br, $W_{1/2}$ = 16 Hz, 8H, 4C_5*H_4*Me), 8.85 (br, $W_{1/2}$ = 16 Hz, 8H, 4C_5*H_4*Me).

Reaction of 1b with Excess HOTf. To a CH_2Cl_2 solution (30 mL) of **1b** (200 mg, 0.34 mmol) was added HOTf (300 μL, 3.4 mmol) at room temperature. The solution was treated with a procedure similar to that employed in the reaction of **1b** with 1 equiv of HOTf. A greenish brown solid of [**1b**](OTf)$_2$ was obtained. Yield: 227 mg, 75%. Anal. Calcd for $C_{30}H_{32}F_6Fe_4O_6S_2$: C, 40.48; H, 3.62. Found: C, 39.77; H, 3.56. Mass (FAB, *m*-nitrobenzyl alcohol, Xe) *m*/*z*: 592 (M^+ − 2(OTf), 100). IR (KBr, $\tilde{\nu}$/cm^{-1}): 3091 (w), 2927 (w), 1708 (br), 1481 (m), 1452 (m), 1371 (m), 1265 (vs), 1155 (s), 1030 (vs), 847 (m), 638 (vs), 573 (w), 517 (w). ^{1}H NMR (300 MHz, CD_3CN) δ fraction showing sharp signals: 1.78, 2.37 (s, 6H × 2, 4(C_5H_4*Me*)), 4.52, 5.01, 5.21, 5.58 (m, 4H × 4, 4(C_5*H_4*Me)), 14.30 (s, 2H, 2*H*CCH), 17.73 (s, 2H, 2*H*CCH); fraction showing broad signals: −155.1 (br, $W_{1/2}$ = 156 Hz, 4H, HCCH), −10.72 (br, $W_{1/2}$ = 16 Hz, 12H, 4(C_5H_4*Me*)), 52.10, 56.78 (br, $W_{1/2}$ = 51 Hz, 8H × 2, C_5*H_4*Me).

X-ray Crystal Structure Determination. Crystals of [**1a**](BF_4) and [**1b**](BF_4)$_2$ for X-ray analysis were grown by placing a layer of diethyl ether over an acetonitrile solution of the cationic clusters at room temperature. Diffraction data of [**1a**](BF_4) were collected at room temperature on a Rigaku AFC-6S four-circle diffractometer with graphite-monochromated Mo Kα radiation using the $\omega - 2\theta$ scan technique (3° < 2θ < 55°). Diffraction data of [**1b**](BF_4)$_2$ were collected at −123 °C on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo Kα radiation using the $\omega - 2\theta$ scan technique (3° < 2θ < 52°). An empirical absorption correction based on azimuthal scans was applied; maximum and minimum factors were shown in Table 2. The data were corrected for Lorentz and polarization effects. Crystallographic data of [**1a**](BF_4) and [**1b**](BF_4)$_2$ are listed in Table 2.

Table 2. Crystallographic Data of [**1a**](BF_4) and [**1b**](BF_4)$_2$

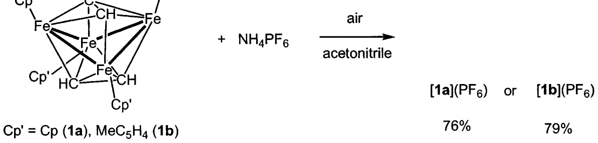
complex	[**1a**](BF_4)	[**1b**](BF_4)$_2$
formula	$C_{24}H_{24}BF_4Fe_4$	$C_{28}H_{32}B_2F_8Fe_4$
fw	622.65	765.56
cryst syst	orthorhombic	orthorhombic
space group	*Pbcn* (No. 60)	*Pbca* (No. 61)
a, Å	11.975(7)	18.678(2)
b, Å	16.442(7)	17.604(2)
c, Å	11.655(7)	17.072(3)
V, Å^3	2294(1)	5613(2)
Z	4	8
d_{calcd}, g cm^{-3}	1.802	1.811
F_{000}	1252.00	3088.00
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
μ(Mo Kα), cm^{-1}	25.19	20.97
trans factor range	1.00−0.88	1.00−0.85
T, K	293	150
cryst size, mm	0.40 × 0.30 × 0.30	0.50 × 0.20 × 0.20
μ(Mo Kα), cm^{-1}	25.19	20.97
$2\theta_{max}$, deg	55.0	52.0
no. of unique data collected	2648	5502
no. of data used	1284 ($I > 3\sigma(I)$)	3445 ($I > 3\sigma(I)$)
no. of variables	158	395
R^a, R_w^b	0.059, 0.085	0.055, 0.058
GOF	1.20	2.23
Δe, Å^{-3}	0.72, −0.50	1.37, −0.69

[a] $R = \Sigma F_o^2 - F_c^2)/\Sigma F_o^2$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Results and Discussion

Improved Synthesis of Acetylene-Coordinated Clusters 1a and 1b. In the previous paper,[2] we reported the synthesis of $Cp'_4Fe_4(HCCH)_2$ (Cp′ = Cp (**1a**), C_5H_4Me (**1b**)) by the reaction of $Cp'_4Fe_4(\mu_3\text{-CO})_4$ with $LiAlH_4$ (eq 1). After volatiles were removed from the reaction mixture, the residue was extracted with toluene. The isolated yields were low (9% for **1a**, 11% for **1b**). In the present paper, toluene is replaced by a mixture of toluene and ethanol, which carries out decomposition of excess $LiAlH_4$ and extraction of the cluster simultaneously. By this change in the experimental procedure, the isolated yields were dramatically improved (9 vs 33% for **1a**, 11 vs 77% for **1b**).

Air-Oxidation of 1 in the Presence of NH_4PF_6. When the acetonitrile solutions of **1a** and **1b** were exposed to air in the presence of NH_4PF_6, the monocationic salts [**1a**](PF_6) and [**1b**](PF_6) were formed (eq 2). Workup of the mixture



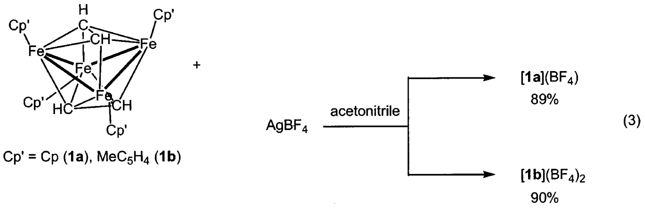
(2)

afforded brown solids of [**1a**](PF_6) and [**1b**](PF_6) in 76 and 79% yields, respectively. As expected from an odd number of electrons, [**1a**](PF_6) and [**1b**](PF_6) are paramagnetic. The ^{1}H NMR signals of [**1a**](PF_6) and [**1b**](PF_6) exhibit the characteristic paramagnetic shifts and line broadening. The ^{1}H NMR spectrum of [**1a**](PF_6) in CD_3CN shows two broad singlets at 8.10 ($W_{1/2}$ = 25 Hz) and −75.40 ppm ($W_{1/2}$ = 50 Hz) assignable to four Cp and two HCCH ligands, respectively. Elemental analysis and mass spectral data of [**1a**](PF_6) and [**1b**](PF_6) are consistent with the formulas.

Electrochemical Oxidation of 1. To synthesize [**1**]$(PF_6)_2$, bulk electrolyses of **1a** and **1b** were carried out in a 0.1 M NH_4PF_6/CH_3CN solution at 0.30 and 0.25 V versus Ag/$AgNO_3$, respectively. Workup of the reaction mixtures and recrystallization of the residues afforded brown crystals of [**1**]$(PF_6)_2$. The results of elemental analysis and mass spectroscopic data are in good agreement with the formulas.

The neutral clusters **1** are diamagnetic; thus, the dicationic clusters were also expected to be diamagnetic. However, this was not the case. The ^{1}H NMR spectrum of analytically pure samples of [**1a**]$(PF_6)_2$ in CD_3CN shows two types of signals; sharp (A) and broad (B) signals (Figure 3). The two sharp singlet signals at 17.99 and 14.81 ppm with equal intensity are assignable to acetylene ligands. The two signals of the corresponding Cp ligands are found at 5.62 and 4.92 ppm. In addition to these sharp signals, two broad signals were observed at −154.9 and 56.6 ppm. Spectroscopic features of [**1b**]$(PF_6)_2$, [**1b**]$(BF_4)_2$, and [**1b**]$(OTf)_2$ are quite similar to that of [**1a**]$(PF_6)_2$. Details of this spectroscopic behavior will be reported elsewhere.

Oxidation of $Cp'_4Fe_4(HCCH)_2$ (Cp′ = Cp (1a), C_5H_4Me (1b)) by $AgBF_4$. Treatment of **1a** with excess $AgBF_4$ gave the one-electron oxidation product [**1a**](BF_4) in 89% yield (eq 3). In contrast, treatment of **1b** with excess $AgBF_4$ did not give [**1b**](BF_4) but did give a two-electron oxidation product [**1b**]$(BF_4)_2$ in 90% yield (eq 3). The spectroscopic features of [**1a**](BF_4) and [**1b**]$(BF_4)_2$ are quite similar to those of [**1a**](PF_6) and [**1b**]$(PF_6)_2$, respectively. The difference in the products between the Cp (**1a**) and the C_5H_4Me (**1b**) analogues can be understood by the difference in the redox potentials of **1a** and **1b**. The redox potentials of **1b** shift to the negative side by 70−80 mV as compared with those of **1a** as shown in Table 1. This may come from the stronger electron-releasing character of the C_5H_4Me ligand than that of the Cp ligand.



(3)

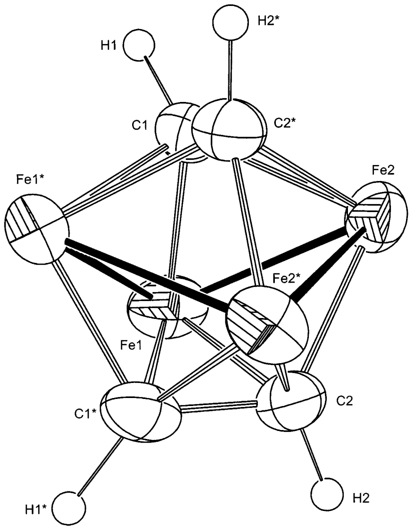


Figure 1. ORTEP drawing of the cation in [**1a**](BF_4). The Cp ligands are omitted for clarity. Asterisks indicate atoms generated by the symmetry operation ($-x$, y, $1/2 - z$).

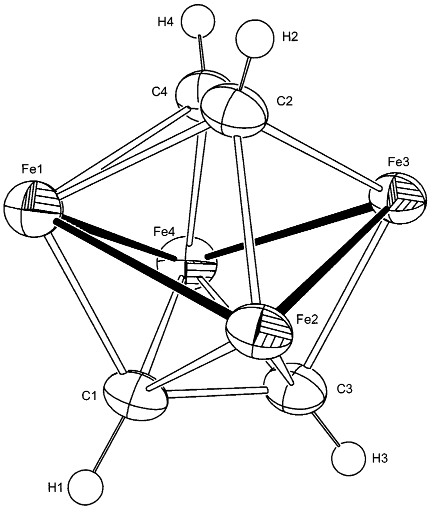
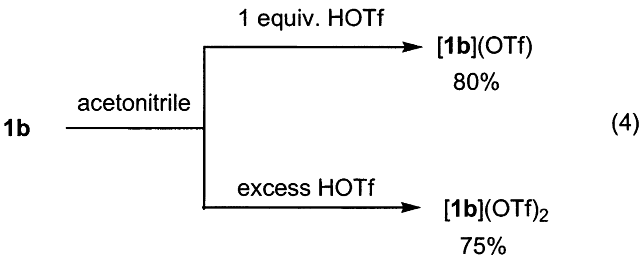


Figure 2. ORTEP drawing of the cation in [**1b**]$(BF_4)_2$. The C_5H_4Me ligands are omitted for clarity.

Reaction of 1b with HOTf. Treatment of **1b** with 1 equiv of HOTf caused oxidation of **1b** to give the one-electron oxidized product [**1b**](OTf) in 80% yield (eq 4). When **1b** was allowed to react with excess HOTf, the two-electron oxidized cluster [**1b**]$(OTf)_2$ was obtained in 75% yield (eq 4).



(4)

It has been reported that hydrocarbon fragments bridging over metal cores can be released upon treatment with a Brönsted acid.[1e,6] In our system, elimination of the acetylene

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[6] (a) Whitmire, K.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 1456−1457. (b) Drezdzon, M. A.; Whitmire, K. H.; Bhattacharyya, A. A.; Hsu, W.-L.; Nagel, C. C.; Shore, S. G.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5630−5633. (c) Shriver, D. F.; Sailor, M. J. *Acc. Chem. Res.* **1988**, *21*, 374−379.

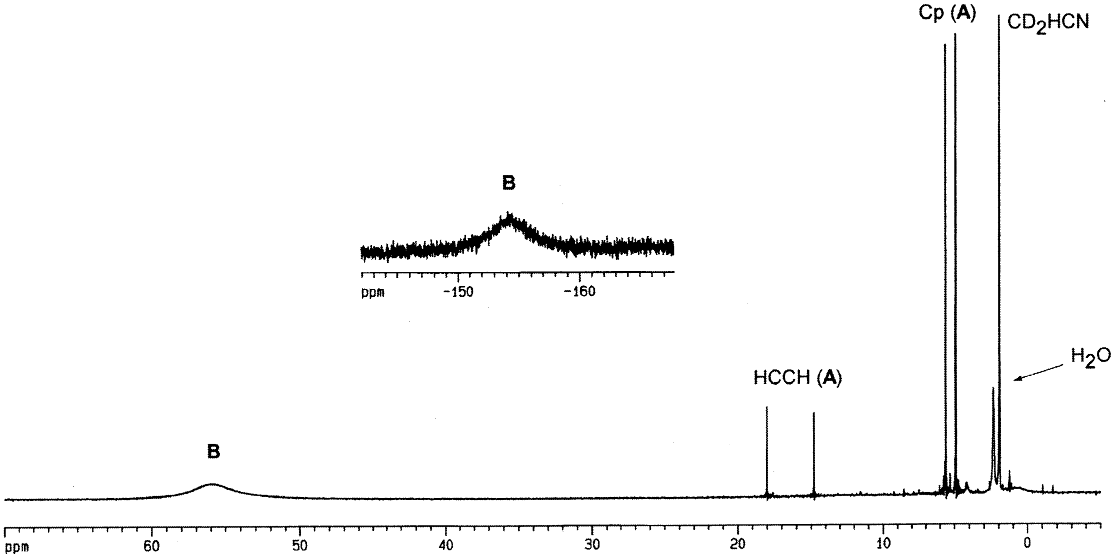

Figure 3. ^{1}H NMR spectrum of [**1a**](PF_6)$_2$.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) in [**1a**](BF_4)

		Interatomic Distances			
Fe1	Fe1*[a]	2.465(3)	Fe1	Fe2	2.475(2)
Fe2	Fe2*[a]	2.461(3)	Fe1	Fe2*[a]	3.272(2)
Fe1	C1	1.959(9)	Fe1	C1*[a]	1.982(9)
Fe1	C2	1.975(9)	Fe2	C1	1.993(9)
Fe2	C2	1.932(9)	Fe2	C2*[a]	1.996(9)
C1	C2*[a]	1.46(1)			
C1	H1	1.1(1)	C2	H2	1.0(1)

			Bond Angles				
Fe1	Fe1*[a]	Fe2*[a]	82.96(5)	Fe1	Fe2	Fe2*[a]	83.05(5)

[a] Asterisks indicate atoms generated by the symmetry operation ($-x$, y, $1/2 - z$).

Table 4. Selected Interatomic Distances (Å) and Bond Angles (deg) in [**1b**](BF_4)$_2$ (Å)

		Interatomic Distances			
Fe1	Fe2	2.461(2)	Fe1	Fe3	3.243(2)
Fe1	Fe4	2.439(2)	Fe2	Fe3	2.397(1)
Fe2	Fe4	3.243(2)	Fe3	Fe4	2.443(2)
Fe1	C1	1.930(8)	Fe1	C2	1.975(8)
Fe1	C4	1.995(8)	Fe2	C1	1.995(8)
Fe2	C2	1.933(8)	Fe2	C3	2.016(8)
Fe3	C2	1.999(8)	Fe3	C3	1.943(8)
Fe3	C4	1.985(8)	Fe4	C1	1.993(8)
Fe4	C3	1.963(9)	Fe4	C4	1.921(8)
C1	C3	1.46(1)	C2	C4	1.46(1)
C1	H1	0.93(9)	C2	H2	0.72(10)
C3	H3	0.84(7)	C4	H4	0.82(9)

			Bond Angles				
Fe2	Fe1	Fe4	82.89(5)	Fe1	Fe2	Fe3	83.77(5)
Fe2	Fe3	Fe4	84.16(5)	Fe1	Fe4	Fe3	83.26(5)

or its derivatives was not observed at all, but oxidation of the cluster cores takes place to give the one- and two-electron oxidized products, depending on the amount of HOTf.

Crystal structure of [1a](BF_4) and [1b](BF_4)$_2$. The structures of [**1a**](BF_4) and [**1b**](BF_4)$_2$ were determined by the single-crystal X-ray diffraction study. ORTEP drawings of the cationic parts of [**1a**](BF_4) and [**1b**](BF_4)$_2$ are illustrated in Figures 1 and 2, respectively, in which Cp and C_5H_4Me ligands are omitted for clarity. Hydrogen atoms on acetylene ligands were located crystallographically and refined isotropically. Selected interatomic distances and angles of [**1a**](BF_4) and [**1b**](BF_4)$_2$ are listed in Tables 3 and 4, respectively. In both mono- and dicationic clusters, two acetylene ligands bridge over four iron atoms in a μ_4-η^2:η^2:η^1:η^1 fashion that is similar to that of the neutral cluster.[2] All of the neutral, mono-, and dicationic forms exhibit the butterfly-type Fe_4 cores in which four Fe−Fe bonds are formed. The average of the Fe−Fe bond distances in **1a**, [**1a**]$^+$, and [**1b**]$^{2+}$ are 2.50, 2.47, and 2.44 Å, respectively. As the cluster is oxidized from 0 to +2, the average bond length of Fe−Fe decreases successively. The stepwise shortening is most likely due to the removal of electrons from the Fe−Fe antibonding MO by oxidation.[7] Thus, the total bond order of four Fe−Fe bonds in [**1a**]$^+$ and [**1b**]$^{2+}$ increases by 0.5 and 1.0, respectively, from the neutral cluster. The C−C bond lengths of acetylene ligands remain almost unchanged with oxidation. In each structure of **1a**[2] and [**1a**]$^+$, all four Fe−Fe bond lengths are almost identical. However, in [**1b**]$^{2+}$, one Fe−Fe bond (Fe2−Fe3, 2.397(1) Å) is shorter than the others (2.439(2)−2.461(2) Å).

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Inomata, S.; Hitomi, K.; Tobita, H.; Ogino, H. *Inorg. Chim. Acta* **1994**, *225*, 229−238.