Stepwise Reduction of Four Carbonyl Ligands in $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_4$ To Produce Clusters Containing μ_3-Methylidyne and/or Acetylene Ligands

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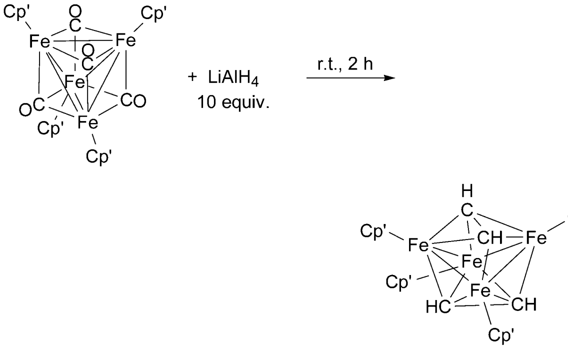
Treatment of $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_4$ with $LiAlH_4$, followed by air-oxidation in the presence of NH_4PF_6, led to stepwise reduction of the four carbonyl ligands to afford $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_3(\mu_3\text{-}CH)](PF_6)$, $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2](PF_6)_2$, $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)(\mu_3\text{-}CH)(HCCH)](PF_6)$, and $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2](PF_6)$. Two-electron reduction of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2](PF_6)_2$ resulted in coupling of two methylidyne ligands to form the acetylene-coordinated cluster $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(HCCH)$, two-electron oxidation of which regenerated $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2](PF_6)_2$. Further treatment of isolated $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(HCCH)$ with $LiAlH_4$ produced $(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2$. All clusters were fully characterized by X-ray diffraction studies.

Introduction

Reduction of coordinated carbon monoxide molecules in transition-metal complexes and clusters, followed by carbon−carbon bond formation, have attracted considerable attention.[1,2] It is well-known that reduction of the terminal carbonyl ligands, in many cases, results in the initial formation of formyl ligands.[3] Reductive coupling of two terminal carbonyl ligands to form acetylene ligands with use of sodium amalgam as a reducing agent has been extensively examined by Lippard and co-workers.[4] In the case of μ-carbonyl ligands, Wong and Atwood reported the reaction of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ with $LiAlH_4$ to produce CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8, and C_4H_{10}, for which no products containing iron have been characterized.[5a,b] Ortaggi and Paolesse reported that reduction of the same iron complex by $Ca[Al(O^iPr)_2H_2]_2$ led to the successful isolation of the μ-CH_2 complex $Cp_2Fe_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}CO)$.[5g] Treatment of the iron−ruthenium or diruthenium complexes $Cp_2M_2(CO)_2(\mu\text{-}CO)_2$ (M_2 = FeRu, Ru_2) with $LiBEt_3H$ followed by hydrolysis also produced the μ-CH_2 complexes.[5e] However, little is known about reduction of the μ_3-carbonyl ligands on transition-metal clusters. Recently, we reported for the first time the formation of nonsubstituted acetylene ligands by reductive coupling of the μ_3-carbonyl ligands on the cubane-type tetrairon clusters $Cp'_4Fe_4(\mu_3\text{-}CO)_4$ (Cp' = Cp, η^5-C_5H_4Me) (eq 1).[6] Our recent interest has been focused on the product survey in the reaction of $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_4$ with $LiAlH_4$.[7] The present paper describes the successful isolation and X-ray structural characterization of the products, which are salts containing $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_3(\mu_3\text{-}CH)]^+$,



(1)

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Cp' = η^5-C_5H_4Me

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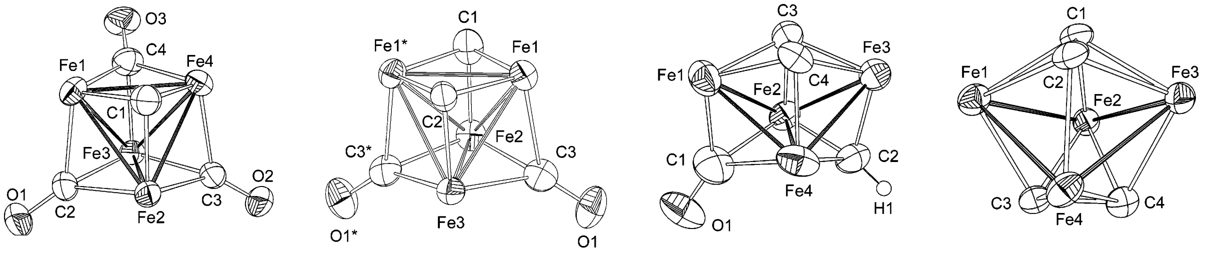
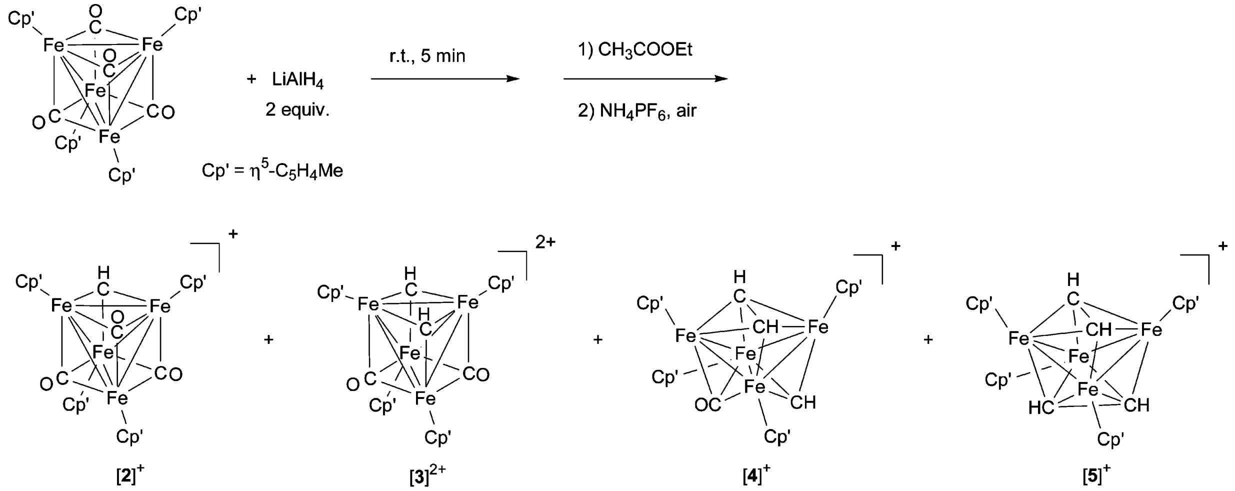


$[\mathbf{2}]^+$ $[\mathbf{3}]^{2+}$ $[\mathbf{4}]^+$ $[\mathbf{5}]^+$

$[Cp'_4Fe_4(CO)_3(CH)]^+$ $[Cp'_4Fe_4(CO)_2(CH)_2]^{2+}$ $[Cp'_4Fe_4(CO)(HCCH)(CH)]^+$ $[Cp'_4Fe_4(HCCH)_2]^+$

Figure 1. ORTEP drawings for the cationic moieties in [**2**](PF$_6$), [**3**](PF$_6$), [**4**](PF$_6$), and [**5**](TFPB) (Cp′ = η^5-C$_5$H$_4$Me). The C$_5$H$_4$Me ligands are omitted for clarity. Asterisks indicate atoms generated by the symmetry operation (x, $^1/_2 - y$, z).

Scheme 1



[(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_2$(μ_3-CH)$_2$]$^{2+}$, [(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)(μ_3-CH)(HCCH)]$^+$, and [(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(HCCH)$_2$]$^+$. Additionally, the two-electron reduction of [(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_2$(μ_3-CH)$_2$]$^{2+}$ results in the coupling of two μ_3-methylidyne ligands to afford (η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_2$(HCCH)$_2$, the two-electron oxidation of which reproduces [(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_2$(μ_3-CH)$_2$]$^{2+}$. On the basis of the experimental results, we have proposed a formation mechanism for (η^5-C$_5$H$_4$Me)$_4$Fe$_4$(HCCH)$_2$ involving the stepwise reduction of four carbonyl ligands. Some of the results reported here have appeared previously in a preliminary form.[7]

Results and Discussion

Product Survey in the Reaction of (η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_4$ with LiAlH$_4$. Previous research by our group revealed that treatment of Cp$_4$Fe$_4$(μ_3-CO)$_4$ or (η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_4$ with LiAlH$_4$ (10 equiv) led to the reductive coupling of four carbonyl ligands to yield the bis(acetylene) cluster Cp$_4$Fe$_4$(HCCH)$_2$ (33%) or (η^5-C$_5$H$_4$Me)$_4$Fe$_4$(HCCH)$_2$ (**1**) (77%). The reaction conditions were modified in order to isolate intermediates produced before the formation of **1**. The cationic clusters [(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_3$(μ_3-CH)](PF$_6$) ([**2**](PF$_6$)), [(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_2$(μ_3-CH)$_2$](PF$_6$)$_2$ ([**3**](PF$_6$)$_2$), [(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)(μ_3-CH)(HCCH)](PF$_6$) ([**4**](PF$_6$)), and [(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(HCCH)$_2$](PF$_6$) ([**5**](PF$_6$)) were obtained with smaller additions of LiAlH$_4$ (2 equiv) and a shorter reaction time (5 min), followed by air oxidation in the presence of NH$_4$PF$_6$ (Scheme 1). As described in the Experimental Section, the clusters [**2**](PF$_6$), [**3**](PF$_6$)$_2$, and [**4**](PF$_6$) were isolated in 2%, 14%, and 3% yields, respectively, and 37% of the starting material, (η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_4$, was recovered. The cluster [**5**](PF$_6$) was identified by comparison with NMR data we previously reported.[6b] To obtain single crystals for X-ray structure analysis, the counteranion of [**5**]$^+$ was replaced with [B(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_4$]$^-$ (TFPB). The structures of [**2**](PF$_6$), [**3**](PF$_6$)$_2$, [**4**](PF$_6$), and [**5**](TFPB) were all unequivocally determined by X-ray diffraction studies. ORTEP drawings of the cationic moieties are depicted in Figure 1.

Structure of [(η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_3$(μ_3-CH)](PF$_6$) ([2](PF$_6$)). Selected interatomic distances and angles of [**2**](PF$_6$) are listed in Table 1. As in the starting material (η^5-C$_5$H$_4$Me)$_4$Fe$_4$(μ_3-CO)$_4$, cluster [**2**](PF$_6$) maintains a cubane-type Fe$_4$C$_4$ core, in which one of the carbonyl ligands has been reduced to a methylidyne ligand. Although the hydrogen atom on C1 cannot be located by difference Fourier synthesis, the ^{1}H and ^{13}C NMR data strongly support the existence of the μ_3-methylidyne ligand: ^{1}H and ^{13}C NMR signals were observed at δ 18.10 and 365.9, respectively, which are characteristic for the μ_3-methylidyne ligand.[8] A ^{13}C NMR signal of three chemically equivalent carbonyl ligands was observed at δ 280.1. The four iron metals exist in a tetrahedron with interatomic distances of 2.507(1) Å (Fe1−Fe2), 2.5294(9) Å (Fe1−Fe3), 2.5064-

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Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_3(\mu_3\text{-}CH)](PF_6)$ ([2](PF_6))

Distances			
Fe1−Fe2	2.507(1)	Fe1−Fe3	2.5294(9)
Fe1−Fe4	2.5064(9)	Fe2−Fe3	2.535(1)
Fe2−Fe4	2.520(2)	Fe3−Fe4	2.5335(9)
Fe1−C1	1.875(5)	Fe1−C2	2.006(5)
Fe1−C4	2.020(5)	Fe2−C1	1.883(5)
Fe2−C2	2.012(5)	Fe2−C3	2.008(5)
Fe3−C2	1.976(5)	Fe3−C3	1.983(5)
Fe3−C4	1.980(6)	Fe4−C1	1.877(4)
Fe4−C3	2.010(5)	Fe4−C4	2.009(5)
O1−C2	1.190(6)	O2−C3	1.186(6)
O3−C4	1.184(6)		
C1···C2	2.959(7)	C1···C3	2.948(7)
C1···C4	2.962(7)	C2···C3	3.053(7)
C2···C4	3.057(8)	C3···C4	3.055(7)
Angles			
Fe2−Fe1−Fe3	60.44(3)	Fe2−Fe1−Fe4	60.34(3)
Fe3−Fe1−Fe4	60.41(3)	Fe1−Fe2−Fe3	60.22(3)
Fe1−Fe2−Fe4	59.81(3)	Fe3−Fe2−Fe4	60.16(3)
Fe1−Fe3−Fe2	59.35(3)	Fe1−Fe3−Fe4	59.35(3)
Fe2−Fe3−Fe4	59.62(3)	Fe1−Fe4−Fe2	59.84(3)
Fe1−Fe4−Fe3	60.25(3)	Fe2−Fe4−Fe3	60.22(3)

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2](PF_6)_2$ ([3](PF_6)$_2$)

Distances			
Fe1−Fe1*	2.462(3)	Fe1−Fe2	2.510(3)
Fe1−Fe3	2.506(3)	Fe2−Fe3	2.542(3)
Fe1−C1	1.88(1)	Fe1−C2	1.89(1)
Fe1−C3	2.05(1)	Fe2−C1	1.87(2)
Fe2−C3	2.02(1)	Fe3−C2	1.89(2)
Fe3−C3	2.00(1)		
O−C3	1.18(1)		
C1···C2	2.85(2)	C1···C3	2.98(2)
C2···C3	2.99(2)	C3···C3*	3.07(3)
Angles			
Fe1*-Fe1−Fe2	60.63(4)	Fe1*-Fe1−Fe3	60.59(4)
Fe2−Fe1−Fe3	60.90(8)	Fe1−Fe2−Fe1*	58.74(9)
Fe1−Fe2−Fe3	59.48(8)	Fe1−Fe3−Fe1*	58.83(9)
Fe1−Fe3−Fe2	59.62(7)		

(9) Å (Fe1−Fe4), 2.535(1) Å (Fe2−Fe3), 2.520(2) Å (Fe2−Fe4), and 2.5335(9) Å (Fe3−Fe4). These bond lengths are typically observed for cationic tetrairon cubane-type clusters.[9] Assuming that a methylidyne ligand donates 3e to the tetrairon core, the cluster [**2**](PF_6) can be viewed as a 60e species, consistent with the existence of the six iron−iron bonds. The infrared spectrum shows a strong band at 1676 cm^{-1}, which is typical for μ_3-carbonyl ligands. Formation of the μ_3-methylidyne ligand via reduction of the terminal carbonyl ligand was demonstrated by Akita et al. Reaction of $Cp_2Mo_2(CO)_4$ with $HSiMe_2Ph$ resulted in the formation of $[CpMo(CO)_2]_3(\mu_3\text{-}CH)$.[10] We succeeded for the first time in the direct conversion of the μ_3-carbonyl ligand to the μ_3-methylidyne ligand. The resulting cubane-type species $M_4(\mu_3\text{-}CO)_3(\mu_3\text{-}CH)$ is unprecedented.

Structure of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2](PF_6)_2$ ([3](PF_6)$_2$). Selected interatomic distances and angles of [**3**](PF_6)$_2$ are listed in Table 2. The geometry of [**3**](PF_6)$_2$ can be regarded as an Fe_4C_2 bicapped tetrahedron with a mirror plane defined by the Fe2, Fe3, C1, and C2 atoms. The C1···C2 interatomic distance is 2.85(2) Å, indicating no interaction between the two bridging carbon atoms. Taking into account the considerably low-field-shifted signals of ^{1}H and ^{13}C NMR (δ_H 17.26, δ_C 377.5),[8] the product [**3**](PF_6)$_2$ is described as a bis(methylidyne) cluster formulated as $Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2$, in which two carbonyl ligands were converted to μ_3-methylidyne ligands on the tetrairon core. In accordance with the electron count (60e), the cluster [**3**](PF_6)$_2$ possesses six iron−iron bonds with typical bond distances of 2.462(3) Å (Fe1−Fe1*), 2.510(3) Å (Fe1−Fe2), 2.506(3) Å (Fe1−Fe3), and 2.542(3) Å (Fe2−Fe3).[11] The Cambridge Structural Database contains only one example of a cluster of the form $M_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CR)_2$. Shaposhinikova et al. reported a reaction between $Cp_2Ni_2(Ph_2C_2)$ and $Cp_2Mo_2(CO)_6$ to form $Cp_4Ni_2Mo_2(\mu_3\text{-}CO)_2(\mu_3\text{-}CPh)_2$, in which two alkylidyne ligands bridge the butterfly-type Mo_2Ni_2 wing.[12] The core structure of the four transition metals is in sharp contrast with [**3**](PF_6)$_2$ (tetrahedron). The cluster [**3**](PF_6)$_2$ represents the first example of a $M_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2$ cubane-type cluster characterized by an X-ray diffraction study.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)(\mu_3\text{-}CH)(HCCH)](PF_6)$ ([4](PF_6))

Distances			
Fe1−Fe2	2.498(2)	Fe1···Fe3	3.414(2)
Fe1−Fe4	2.508(2)	Fe2−Fe3	2.477(2)
Fe2−Fe4	2.548(2)	Fe3−Fe4	2.468(2)
Fe1−C1	1.861(10)	Fe1−C3	1.974(8)
Fe1−C4	1.982(8)	Fe2−C1	2.12(1)
Fe2−C2	1.892(8)	Fe2−C3	1.971(8)
Fe3−C2	1.844(8)	Fe3−C3	1.961(8)
Fe3−C4	1.966(8)	Fe4−C1	2.111(10)
Fe4−C2	1.893(9)	Fe4−C4	1.965(8)
O1−C1	1.19(1)	C1···C2	2.89(1)
C1···C3	3.03(1)	C1···C4	3.03(1)
C2···C3	2.86(1)	C2···C4	2.86(1)
C3−C4	1.54(1)		
C2−H1	0.95(8)		
Angles			
Fe2−Fe1−Fe4	61.20(5)	Fe1−Fe2−Fe3	86.68(5)
Fe1−Fe2−Fe4	59.60(5)	Fe3−Fe2−Fe4	58.82(5)
Fe2−Fe3−Fe4	62.03(5)	Fe1−Fe4−Fe2	59.20(4)
Fe1−Fe4−Fe3	86.63(5)	Fe2−Fe4−Fe3	59.15(5)

Structure of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)(\mu_3\text{-}CH)(HCCH)](PF_6)$ ([4](PF_6)). Selected interatomic distances and angles of [**4**](PF_6) are listed in Table 3. In contrast to $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_4$, [**2**]($PF_6$), and [**3**]($PF_6$)$_2$, the cluster [**4**]($PF_6$) exhibits a tetrairon butterfly core with five iron−iron bonds. The existence of the five iron−iron bonds is confirmed from the interatomic distances: Fe1−Fe2 (2.498(2) Å), Fe1−Fe4 (2.508(2) Å), Fe2−Fe3 (2.477(2) Å), Fe2−Fe4 (2.548(2) Å), and Fe3−Fe4 (2.468(2) Å).[6] The interatomic distance of Fe1···Fe3 (3.414(2) Å) indicates no interaction between them. The C3−C4 length (1.54(1) Å) is comparable to that in **1** (1.51(1) and 1.48(2) Å) and [**5**](TFPB) (1.46(2) and 1.45(1) Å), indicating the coupling of two methylidyne ligands to form the acetylene ligand. The interatomic

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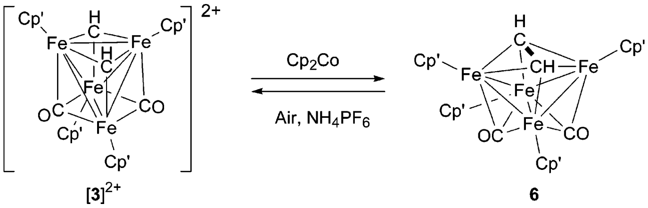
Table 4. Selected Interatomic Distances (Å) and Angles (deg) for [(η^5-$C_5H_4Me)_4Fe_4(HCCH)_2$](TFPB) ([5](TFPB))

Distances			
Fe1−Fe2	2.489(2)	Fe1−Fe4	2.453(2)
Fe2−Fe3	2.458(2)	Fe3−Fe4	2.503(2)
Fe1···Fe3	3.254(2)	Fe2···Fe4	3.303(2)
C1−C2	1.46(2)	C3−C4	1.45(1)
Angles			
Fe2−Fe1−Fe4	83.86(6)	Fe1−Fe2−Fe3	82.26(7)
Fe2−Fe3−Fe4	83.48(7)	Fe1−Fe4−Fe3	82.08(6)

Scheme 2



$[3]^{2+}$ 6

distance of C1···C2 (2.89(1) Å) showed that there is no interaction between the two carbon atoms.

In the low-field region of the ^{1}H NMR spectrum, two signals were observed at δ 12.97 and 20.28, unequivocally assigned to the acetylene and μ_3-methylidyne ligands, respectively. In the low-field region of the ^{13}C NMR spectrum, three signals were observed: δ 230.4 (HCCH), 276.6 (μ_3-CO), and 392.4 (μ_3-CH). The existence of the μ_3-carbonyl ligands is also confirmed by the IR spectrum, which shows a strong band at 1718 cm^{-1}.

Since the cluster [**4**](PF_6) includes three different types of organic fragments, i.e., CO, CH, and HCCH, it is expected to be a good model of the metal surface in which the Fischer−Tropsch reaction proceeds.[1,2] The reactivity of the cluster [**4**](PF_6) concerning coupling reactions of the organic fragments is of great interest.

[(η^5-$C_5H_4Me)_4Fe_4(HCCH)_2$](TFPB) ([5](TFPB)). An ORTEP drawing of [**5**](TFPB) is illustrated in Figure 1. Selected interatomic distances and angles are listed in Table 4. In [**5**](TFPB), two acetylene ligands bridge the butterfly-type four-iron core in a μ_4-η^2:η^2:η^1:η^1 fashion that is similar to that of **1**. However, the average iron−iron bond length in [**5**](TFPB) (2.476(2) Å) is significantly shorter than that in **1** (2.493(2) Å), reflecting the removal of an electron from the iron−iron antibonding MO by one-electron oxidation.[6b,13]

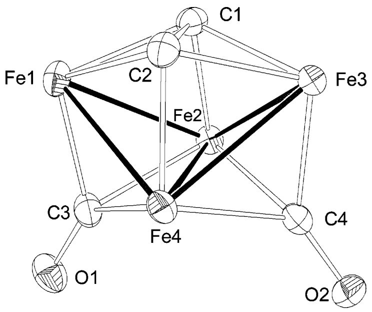


Figure 2. ORTEP drawing of (η^5-$C_5H_4Me)_4Fe_4(\mu_3$-$CO)_2$(HCCH) (**6**). The C_5H_4Me ligands are omitted for clarity.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for (η^5-$C_5H_4Me)_4Fe_4(\mu_3$-$CO)_2$(HCCH) (6) (Molecule A)

Distances			
Fe1−Fe2	2.5119(8)	Fe1···Fe3	3.4385(8)
Fe1−Fe4	2.4792(9)	Fe2−Fe3	2.5025(8)
Fe2−Fe4	2.5837(8)	Fe3−Fe4	2.4995(8)
Fe1−C1	1.969(4)	Fe1−C2	1.965(4)
Fe1−C3	1.899(4)	Fe2−C1	1.937(4)
Fe2−C3	2.048(4)	Fe2−C4	2.065(4)
Fe3−C1	1.971(4)	Fe3−C2	1.964(4)
Fe3−C4	1.909(4)	Fe4−C2	1.941(4)
Fe4−C3	2.047(4)	Fe4−C4	2.042(4)
O1−C3	1.201(5)	O2−C4	1.201(5)
C1−C2	1.504(6)		
Angles			
Fe2−Fe1−Fe4	62.35(2)	Fe1−Fe2−Fe3	86.58(3)
Fe1−Fe2−Fe4	58.21(2)	Fe3−Fe2−Fe4	58.84(2)
Fe2−Fe3−Fe4	62.20(2)	Fe1−Fe4−Fe2	59.45(2)
Fe1−Fe4−Fe3	87.36(3)		

Two-Electron Reduction of [3]($PF_6)_2$. Treatment of [**3**]($PF_6)_2$ with Cp_2Co in acetonitrile led to the formation of the neutral cluster (η^5-$C_5H_4Me)_4Fe_4(\mu_3$-$CO)_2$(HCCH) (**6**) in 70% yield (Scheme 2). Cooling of the diethyl ether solution of **6** to −30 °C allowed the growth of brown crystals suitable for an X-ray diffraction study (Figure 2). Selected interatomic distances and angles are listed in Table 5. The asymmetric unit consists of two independent molecules of **6**, 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 [**3**]($PF_6)_2$. The bond length of C1−C2 at 1.504(6) Å reveals that, surprisingly, two of the methylidyne fragments in [**3**]($PF_6)_2$ have coupled to form the acetylene ligand that bridges the four iron atoms in μ_4-η^2:η^2:η^1:η^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 the value of Fe1···Fe3 (3.4385(8) Å) indicates that there is no interaction for these atoms.[11] According to the structural features described, cluster **6** is recognized as an Fe_4C_2 closo octahedron, consistent with Wade−Mingos theory.[14,15]

The dramatic structural changes which occur from the bis(methylidyne) cluster [**3**]($PF_6)_2$ to the acetylene cluster **6** are reflected in the NMR spectral data. The ^{1}H and ^{13}C NMR signals of the acetylene ligand in **6** (δ(^{1}H) 11.52 and δ(^{13}C) 206.5) are considerably shifted to high field compared to those of the methylidyne ligands in [**2**](PF_6) (δ(^{1}H) 18.10 and δ(^{13}C) 365.9), [**3**]($PF_6)_2$ (δ(^{1}H) 17.26 and δ(^{13}C) 377.5) and [**4**](PF_6) (δ(^{1}H) 20.28 and δ(^{13}C) 392.4) and are in fact comparable to those of the acetylene ligands in **1** (δ(^{1}H) 10.27 and δ(^{13}C) 212.6) and [**4**](PF_6) (δ(^{1}H) 12.97 and δ(^{13}C) 230.4).

Two-Electron Oxidation of 6. We wish to stress 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 2. Treatment of **6** with air in the presence of NH_4PF_6 led to cleavage of the carbon−carbon bond in the acetylene ligand to reproduce [**3**]($PF_6)_2$ in 51% yield. Electron-induced carbon−carbon bond formation has been reported by several groups.[16] Yeh and Shapley reported

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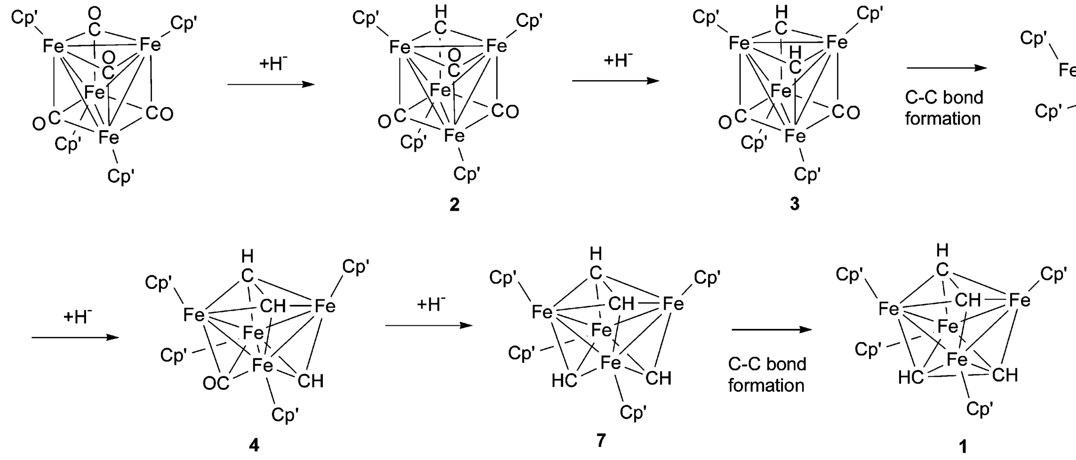
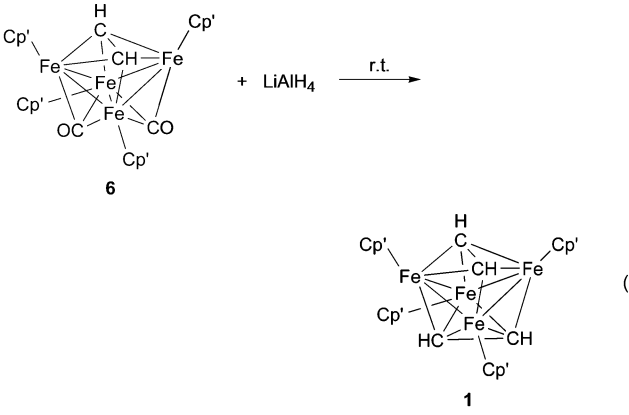
Scheme 3



the electron-induced coupling of two alkylidyne units: treatment of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ with sodium benzophenone ketyl followed by protonation produced $(\mu\text{-}H)Os_3(CO)_9(\mu_3,\eta^2\text{-}CCPh)$ and MeOH.[16c] Mathieu et al. reported a similar observation for two-electron reduction of $Fe_3(CO)_9(\mu_3\text{-}CCH_2R)(\mu_3\text{-}COC_2H_5)$ (R = n-C_3H_7, Ph), which induced alkylidyne−alkylidyne coupling with subsequent rearrangement of the acetylide to yield $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CCCH_2R)]^-$ after dissociation of the ethoxide anion.[16d] They also described the reaction of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ with CO (20 atm) to form $Fe_3(CO)_{10}(\mu_3\text{-}CH_3C{\equiv}COC_2H_5)$, in which coordination of carbon monoxide plays essentially the same role as two-electron reduction.[16e] To our 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.

Reduction of $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(HCCH)$ (6). Treatment of the isolated $(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)(\mu_3\text{-}CO)_2$ (**6**) with $LiAlH_4$ also produced **1** in 39% isolated yield (eq 2), supporting the transient formation of **6** in the course of the reaction between $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_4$ and $LiAlH_4$ to yield **1**.



(2)

Formation Mechanism of $(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2$ by the Reaction of $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_4$ with $LiAlH_4$. On the basis of the experimental results, we propose a mechanism for the formation of **1** involving the stepwise reduction of four carbonyl ligands on the tetrairon core (Scheme 3). Initial reduction of a μ_3-carbonyl ligand forms $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_3(\mu_3\text{-}CH)$ (**2**), in which the Fe_4C_2 cubane-type core is maintained. Reduction of the second carbonyl ligand leads to the transient formation of $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2$ (**3**), which undergoes the coupling of two methylidyne ligands to form **6**. During the conversion from **3** to **6**, the tetrairon core structure changes from tetrahedron to butterfly, accompanied by the scission of one iron−iron bond. To understand the instability of **3**, it is useful to consider the cluster electron count. Tetrahedral geometry is commonly observed in cubane-type clusters and is associated with a total of 60 valence electrons. The "supersaturation"[17] of cluster **3** (62e) is released by the coupling of the two μ_3-methylidyne ligands to give an acetylene ligand in which the two methylidyne ligands donate six electrons and the acetylene ligand donates four. Accordingly, the two-electron-oxidized form, that is $[\mathbf{3}](PF_6)_2$ (60e), can exist in a stable form and takes an Fe_4 tetrahedral geometry. Reduction of one of the carbonyl ligands in **6** gives $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)(\mu_3\text{-}CH)(HCCH)$ (**4**), also with the Fe_4 butterfly core. Further reduction of the final carbonyl ligand in **4** generates the bis(μ_3-methylidyne) cluster $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CH)_2(HCCH)$ (**7**), resulting in the coupling of two μ_3-methylidyne ligands to produce the bis(acetylene) cluster **1**.

Oxygen atoms from the carbonyl ligands would likely be abstracted by the aluminum, although no aluminum- and oxygen-containing products were identified. Shriver et al. reported that when $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ and $Cp_4Fe_4(\mu_3\text{-}CO)_4$ were treated with $AlEt_3$, $Cp_2Fe_2(CO)_2(\mu\text{-}COAlEt_3)_2$ and $Cp_4Fe_4(\mu_3\text{-}COAlEt_3)_4$ were formed, respectively, with $AlEt_3$ coordinated to the bridging carbonyl ligands.[18] Churchill and Schrock reported the reaction of $W(CH)(PMe_3)_4Cl$ and CO in the presence of $AlCl_3$ to yield $W(\eta^2\text{-}HCCOAlCl_3)(CO)(PMe)_3Cl$, in which $AlCl_3$ induces methylidyne−carbonyl coupling.[19]

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Andrés et al. successfully synthesized $Cp^*_4Ti_4(CH)_4$ by thermal reaction of Cp^*TiMe_3 in toluene.[20] According to an X-ray diffraction study, the complex was determined to be $Cp^*_4Ti_4(\mu_3\text{-}CH)_4$, which is the first and, to date, only example of the tetrakis(μ_3-methylidyne) cubane-type cluster. The structure seems to reflect the relative electron deficiency of titanium compared with iron.

Experimental Section

General Information and Materials. Infrared spectra were recorded on a Horiba FT-200 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX-300 instrument. Mass spectra were recorded on a JEOL-HX110 instrument operating in the fast atom bombardment mode (FAB). All reactions were performed under dry nitrogen using deoxygenated solvents dried with appropriate reagents. The compounds $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_4$,[21] $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2]Br$,[22] and Na(TFPB) (TFPB = $B(3,5\text{-}C_6H_3(CF_3)_2)_4^-$)[23] were prepared by published procedures. All other chemicals were used without further purification.

Synthesis of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_3(\mu_3\text{-}CH)](PF_6)$ ([2](PF$_6$)), $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2](PF_6)_2$ ([3](PF$_6$)$_2$), $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)(\mu_3\text{-}CH)(HCCH)](PF_6)$ ([4](PF$_6$)), and $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2](PF_6)$ ([5](PF$_6$)). A THF (80 mL) solution of $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_4$ (398 mg, 0.611 mmol) and $LiAlH_4$ (52 mg, 1.4 mmol) was stirred at room temperature for 5 min. The reaction mixture was treated with ethyl acetate (5 mL) to decompose excess $LiAlH_4$. After NH_4PF_6 was added, air was bubbled through the mixture for 1 h. Volatiles were removed under reduced pressure, and the residue was washed with water and then diethyl ether. Extraction of the residue with acetonitrile and evaporation of the extract in vacuo gave a greenish solid, from which $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_4$ (148 mg, 37%) was recovered by extraction with toluene. The insoluble material was extracted with THF (extract **A**) and acetonitrile (extract **B**) in this order. Evaporation of extract **A** in vacuo gave a brown solid containing $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_3(\mu_3\text{-}CH)](PF_6)$ ([**2**](PF$_6$)), $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)(\mu_3\text{-}CH)(HCCH)](PF_6)$ ([**4**](PF$_6$)), and $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2](PF_6)$ ([**5**](PF$_6$)). The brown solid was dissolved in acetonitrile and charged into a silica gel flash column (silica gel 50 g). Elution with a toluene/THF mixture (7/2) and then with THF afforded a greenish brown band and a brown band. The former eluate was concentrated to dryness to give [**2**](PF$_6$) (9 mg, 2%). The latter eluate was concentrated to dryness and the residue dissolved in acetonitrile. The solution was treated with Cp_2Co (10 mg, 0.053 mmol) and stirred for 2 h at room temperature. Volatiles were removed under reduced pressure, and the residue was washed with toluene to remove $(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2$ (**1**) and then extracted with acetonitrile. The extract was concentrated in vacuo and charged into a silica gel flash column (silica gel, 50 g). Elution with THF afforded a brown band, which was collected and evaporated to dryness to yield [**4**](PF$_6$) (16 mg, 3%). Concentration of extract **B** to dryness gave a brown solid of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2](PF_6)_2$ ([**3**](PF$_6$)$_2$) (80 mg, 14%). Data for [**2**](PF$_6$): ^1H NMR (300 MHz, CD_3CN) δ 2.00 (s, 9H, C_5H_4Me), 2.23 (s, 3H, C_5H_4Me), 4.65, 4.82 (t, J = 2.0 Hz, 4Hx3, C_5H_4Me), 4.98, 5.29 (t, J = 2.0 Hz, 4H, C_5H_4Me), 18.10 (s, 1H, μ_3-CH); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN) δ 13.4, 13.7 (C_5H_4Me), 97.3, 98.9, 100.2, 109.4, 110.0, 110.6 (C_5H_4Me), 280.1 (μ_3-CO), 365.9 (μ_3-CH); $^{13}C\{\text{non-}^1H\}$ NMR (75.5 MHz, benzene-d_6) δ 365.8 (d, $^1J_{CH}$ = 185 Hz, μ_3-CH); IR (KBr) $\tilde{\nu}$ 3112 (w), 2924 (w), 1676 (vs, ν_{CO}), 1487 (m), 1446 (m), 1373 (m), 1026 (m), 827 (vs, PF$_6$), 611 (m), 555 (vs, PF$_6$); mass (FAB) m/z 637 ($M^+ - PF_6$, 100), 581 ($M^+ - PF_6 - 2CO$, 18), 553 ($M^+ - PF_6 - 3CO$, 13). Anal. Calcd for $C_{28}H_{29}F_6Fe_4O_3P$: C, 43.01; H, 3.74. Found: C, 43.09; H, 3.69. Data for [**3**](PF$_6$)$_2$: ^1H NMR (300 MHz, CD_3CN) δ 2.00, 2.16 (s, 6H × 2, C_5H_4Me), 4.96, 5.20, 5.50, 5.58 (t, J = 2.0 Hz, 4H × 4, C_5H_4Me), 17.26 (s, 2H, μ_3-CH); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN) δ 13.4, 13.5 (C_5H_4Me), 95.5, 97.0, 98.5, 102.6, 115.2, 115.5 (C_5H_4Me), 266.8 (μ_3-CO), 377.5 (μ_3-CH); $^{13}C\{\text{non-}^1H\}$ NMR (75.5 MHz, CD_3CN) δ 377.5 (d, $^1J_{CH}$ = 185 Hz, μ_3-CH); IR (KBr) $\tilde{\nu}$ 3122 (w), 1726 (vs, ν_{CO}), 1485 (m), 1456 (m), 1446 (m), 1375 (m), 1238 (w), 1024 (m), 827 (vs, PF$_6$), 584 (s), 555 (vs, PF$_6$); mass (FAB) m/z 767 ($M^+ - PF_6$, 54), 737 ($M^+ - PF_6 - 2Me$, 4), 622 ($M^+ - 2PF_6$, 82), 607 ($M^+ - 2PF_6 - Me$, 87), 592 ($M^+ - 2PF_6 - 2Me$, 100), 579 ($M^+ - 2PF_6 - 2Me - CH$, 15), 566 ($M^+ - 2PF_6 - 2CO$, 14). Anal. Calcd for $C_{28}H_{30}F_{12}Fe_4O_2P_2$: C, 36.88; H, 3.32. Found: C, 37.14; H, 3.73. Data for [**4**](PF$_6$): ^1H NMR (300 MHz, CD_3CN) δ 1.80 (s, 6H, C_5H_4Me), 2.02 (s, 3H, C_5H_4Me), 2.21 (s, 3H, C_5H_4Me), 3.59 (m, 2H, C_5H_4Me), 4.16 (m, 2H, C_5H_4Me), 4.52 (m, 2H, C_5H_4Me), 4.66 (m, 2H, C_5H_4Me), 4.78 (m, 2H, C_5H_4Me), 4.90 (m, 2H, C_5H_4Me), 5.07 (m, 4H, C_5H_4Me), 12.97 (s, 2H, HCCH), 20.28 (s, 1H, μ_3-CH); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN) δ 12.6, 13.4, 13.5 (C_5H_4Me), 84.5, 86.2, 86.6, 86.9, 87.1, 88.0, 88.9, 93.5, 103.5, 104.3, 104.8 (C_5H_4Me), 230.4 (HCCH), 276.6 (μ_3−CO), 392.4 (μ_3-CH); $^{13}C\{\text{non-}^1H\}$ NMR (75.5 MHz, CD_3CN) δ 230.4 (d, $^1J_{CH}$ = 171 Hz, HCCH), 392.4 (d, $^1J_{CH}$ = 171 Hz, μ_3-CH); IR (KBr) $\tilde{\nu}$ 1718 (vs, ν_{CO}), 1028 (w), 847 (vs, PF$_6$), 829 (vs, PF$_6$), 557 (s, PF$_6$), 430 (s); mass (FAB) m/z 752 (M^+, 3), 607 ($M^+ - PF_6$, 100), 579 ($M^+ - PF_6 - CO$, 16). Anal. Calcd for $C_{28}H_{29}F_6Fe_4O_3P$: C, 44.73; H, 4.16. Found: C, 44.47; H, 4.10.

Synthesis of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2](TFPB)$ ([5](TFPB)). An acetonitrile solution of $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(HCCH)_2]Br$ (38 mg, 0.057 mmol) was treated with Na(TFPB) (55 mg, 0.062 mmol). Volatiles were removed under reduced pressure and the residue was extracted twice with diethyl ether (10 mL × 2). The extract was concentrated to dryness and the residue extracted with dichloromethane (10 mL). Removal of the solvent afforded [**5**](TFPB) (73 mg, 88%).

Synthesis of $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(HCCH)$ (6). An acetonitrile solution of [**3**](PF$_6$)$_2$ (297 mg, 0.326 mmol) and Cp_2Co (200 mg, 1.06 mmol) was stirred for 2 h at room temperature. Volatiles were removed under reduced pressure, and the residue was extracted with THF. The extract was charged into a silica gel flash column. Elution with toluene and then with THF afforded a purple band of Cp_2Co and a greenish brown band. The latter eluate was concentrated to dryness to give $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(HCCH)$ (**6**) as a brown solid (141 mg (70%)). ^1H NMR (300 MHz, benzene-d_6): δ 1.85, 1.90 (s, 6H × 2, C_5H_4Me), 3.64, 4.08, 4.28, 4.33 (s, 4H × 4, C_5H_4Me), 11.52 (s, 2H, HCCH); $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6) δ 11.5, 13.3 (C_5H_4Me), 83.3, 84.3, 84.7, 94.1, 97.5, 99.3 (C_5H_4Me), 206.5 (HCCH), 297.5 (μ_3-CO). $^{13}C\{\text{non-}^1H\}$ NMR (75.5 MHz, benzene-d_6): δ 206.5 (d, $^1J_{CH}$ = 163 Hz, HCCH). IR (KBr): $\tilde{\nu}$ 2915 (w), 1659 (vs, ν_{CO}), 1626 (vs, ν_{CO}), 1032 (w), 1022 (w), 897 (w), 885 (w), 825 (w), 814 (w), 611 (w), 519 (w), 447 (w), 436 (w), 424 (w). Mass (FAB) m/z 622 (M^+, 100), 566 ($M^+ - 2CO$, 20). Anal. Calcd for $C_{28}H_{30}Fe_4O_2$: C, 54.07; H, 4.86. Found: C, 54.43; H, 4.82.

Oxidation of 6 to [3](PF$_6$)$_2$. Complex **6** (24 mg, 0.039 mmol) was dissolved in an acetonitrile solution (10 mL) containing 0.1 M NH_4PF_6. Air was bubbled through the solution for 1 h with stirring. After evaporation in vacuo, the residue was washed with water to remove excess NH_4PF_6 and then extracted with acetonitrile. Removal of the solvent from the extract in vacuo gave [**3**](PF$_6$)$_2$ as a brown solid (18 mg (51%)).

Reaction of 6 with $LiAlH_4$. A solution of $(\eta^5\text{-}C_5H_4Me)_4Fe_4(\mu_3\text{-}CO)_2(HCCH)$ (**6**; 35 mg, 0.056 mmol) in THF (20 mL) was treated with $LiAlH_4$ (34 mg, 0.90 mmol). After the mixture

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[23] Bahr, S. R.; Boudjouk, P. *J. Org. Chem.* **1992**, *57*, 5545.

was stirred at room temperature for 5 min, volatiles were removed under reduced pressure. The residue was extracted with toluene, and the extract was filtered through a Celite pad. Evaporation of the filtrate to dryness yielded (η^5-$C_5H_4Me)_4Fe_4$-$(HCCH)_2$ (**1**; 13 mg, 39%).

X-ray Diffraction Studies. Recrystallization of **1** from hexane at −30 °C gave single crystals of **1**. Crystals of [**2**](PF_6) and [**3**]$(PF_6)_2$ were grown by placing a layer of diethyl ether over an acetonitrile solution of the clusters at room temperature. Crystals of [**4**](PF_6) and [**5**](TFPB) were grown by placing a layer of hexane over a dichloromethane solution of the clusters. Crystals of **6** were grown by cooling a diethyl ether solution of **6** at −30 °C. Diffraction data of **1**, [**2**](PF_6), [**3**]$(PF_6)_2$, [**4**](PF_6), and **6** were collected at room temperature on a Rigaku AFC-6S four-cycle diffractometer with graphite-monochromated Mo Kα radiation using the $\omega-2\theta$ scan technique ($3° < 2\theta < 55°$). Diffraction data for [**5**](TFPB) were collected at −123 °C on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation to a maximum 2θ value of 55°. A total of 44 images, corresponding to 220.0° oscillation angles, were collected at two different goniometer settings. The exposure time was 5.00 min/deg. The camera radius was 127.40 nm. The readout was performed in the 0.100 mm pixel mode. All calculations were performed using the teXsan crystallographic package of Molecular Structure Corp. For further details, see the CIF files in the Supporting Information. An ORTEP drawing and selected interatomic distances and angles of **1** are also shown in the Supporting Information.

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Supporting Information Available: An ORTEP drawing and table giving interatomic distances and angles for **1**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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