Reductive Coupling of Carbonyl Ligands on a Cubane-Type Tetrairon Cluster [$Cp_4Fe_4(CO)_4$] or [$(MeC_5H_4)_4Fe_4(CO)_4$] To Give an Acetylene-Coordinated Cluster [$Cp_4Fe_4(HC{\equiv}CH)_2$] or [$(MeC_5H_4)_4Fe_4(HC{\equiv}CH)_2$]

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Abstract: Treatment of [$Cp_4Fe_4(CO)_4$] with $LiAlH_4$ in tetrahydrofuran (THF) resulted in the reductive coupling of carbonyl ligands to produce a nonsubstituted acetylene-coordinated cluster [$Cp_4Fe_4(HC{\equiv}CH)_2$]. X-ray structure analysis revealed that the cluster consists of a puckered rhombus of four iron atoms. The coordination mode of the acetylene ligands was determined to be μ_4-η^2:η^2:η^1:η^1-HC≡CH. The cyclic voltammogram of the acetylene-coordinated cluster exhibits three reversible or quasireversible one-electron oxidation waves and one irreversible one-electron reduction wave, corresponding to +3/+2, +2/+1, +1/0, and 0/−1 charged couples, respectively. Similarly, [$(MeC_5H_4)_4Fe_4(CO)_4$] reacts with $LiAlH_4$ in THF to give [$(MeC_5H_4)_4Fe_4(HC{\equiv}CH)_2$].

Introduction

Transition-metal-mediated transformation of C_1 precursors such as carbon monoxide to valuable organic compounds is an important subject in organometallic chemistry.[1] To our knowledge, however, there are only a few known examples of the coupling of two carbon monoxide molecules to give an alkyne molecule. Lippard et al. reported that treatment of [$M(CO)_2(dmpe)_2Cl$] (M = Nb, Ta) with sodium amalgam, followed by addition of R_3SiCl, produced a substituted acetylene-coordinated complex [$M\{R_3SiOC{\equiv}COSiR_3\}(dmpe)_2Cl$].[2]

Reduction of carbonyl ligands on an iron complex has been reported by Wong and Atwood.[3] Treatment of the diiron complex [$Cp_2Fe_2(CO)_4$] (Cp = η^5-C_5H_5) with $LiAlH_4$ in THF resulted in the formation of CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8, and C_4H_{10}. However, no iron moiety was characterized. These results led us to examine the reaction of the cubane-type tetrairon cluster [$Cp_4Fe_4(CO)_4$] (**1**) with hydride-transfer reagents to characterize the iron moiety. In this paper, we report for the first time the formation of nonsubstituted acetylene ligands by the reductive coupling of carbonyl ligands on the cubane-type tetrairon clusters [$Cp_4Fe_4(CO)_4$] and [$(MeC_5H_4)_4Fe_4(CO)_4$].

Experimental Section

General. All manipulations were carried out under a dry nitrogen or argon atmosphere. Reagent-grade THF, toluene, and hexane were distilled from sodium−benzophenone immediately before use. Acetonitrile and dichloromethane were distilled from CaH_2. Benzene-d_6 was dried over 4A molecular sieves. The compounds [$Cp_4Fe_4(CO)_4$] (**1**)[4a] and [$(MeC_5H_4)_4Fe_4(CO)_4$] (**2**)[4b] were prepared according to published procedures. All other chemicals were used as received. All NMR spectra were recorded on a Bruker ARX-300 spectrometer. The IR spectra were recorded on a Bruker IFS66v spectrometer. Mass spectra were obtained with a JEOL JMS-HX110 spectrometer. Cyclic voltammetry was carried out with a Bioanalytical System BAS-100BW electrochemical analyzer. Measurements were made in 0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate (TBAB)/acetonitrile solutions with a three-electrode system with a Pt rod working electrode, a Pt coil auxiliary electrode, and an Ag/AgCl reference electrode.

[$Cp_4Fe_4(HC{\equiv}CH)_2$] (3). A THF solution (150 mL) of [$Cp_4Fe_4(CO)_4$] (**1**) (870 mg, 1.46 mmol) was stirred with excess $LiAlH_4$ (309 mg, 8.14 mmol) at room temperature. Disappearance of **1** within 30 min was confirmed by using silica gel TLC (toluene:hexane = 4:1). Volatiles were then removed under reduced pressure and the greenish black residue was extracted with toluene (100 mL). The extract was filtered through a Celite pad and the solvent was removed under reduced pressure. Recrystallization of the residue from dichloromethane−hexane (1:3) at −30 °C afforded air-stable brown crystals of **3** (71 mg) in 9% isolated yield. Data for **3**: ^{1}H NMR (benzene-d_6) δ 3.95 (s, 20H, 4Cp), 10.78 (s, 4H, HC≡CH). ^{13}C NMR (benzene-d_6) δ 85.1 (Cp), 209.2 (HC≡CH, ^1J(CH) = 160 Hz). Anal. Calcd for $C_{24}H_{24}Fe_4$: C, 53.80; H, 4.51. Found: C, 53.70; H, 4.57. Mass (FAB, Xe, *m*-nitrobenzyl alcohol matrix) *m*/*z* 536 (M^+, 100) and 471 (M^+ − Cp, 5). IR (KBr) $\tilde{\nu}_{max}$/cm^{-1} 3074 (w), 2927 (m), 2908 (m), 1421 (m), 1113 (m), 1057 (w), 1003 (m), 903 (m), 822 (s), 795 (s), 694 (w), 615 (m), 540 (m), 441 (m); Raman $\tilde{\nu}_{max}$/cm^{-1} 1118. Mp > 280 °C.

[$(MeC_5H_4)_4Fe_4(HC{\equiv}CH)_2$] (4). $LiAlH_4$ powder (154 mg, 4.05 mmol) was added to a THF solution (80 mL) of [$(MeC_5H_4)_4Fe_4(CO)_4$] (**2**) (202 mg, 0.309 mmol) with stirring at room temperature. The reaction was monitored by TLC (toluene:hexane = 4:1). After the TLC spot of **2** had disappeared in the TLC (40 min), volatiles were evaporated under reduced pressure. The residue was extracted with toluene (80 mL), filtered through a Celite pad, and concentrated under reduced pressure. Recrystallization of the residue from hexane at −30

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Table 1. Crystallographic Data for [$Cp_4Fe_4(HC{\equiv}CH)_2$] (**3**)

formula	$C_{24}H_{24}Fe_4$
formula wt	535.84
cystal system	orthorhombic
space group	*Pbca*
color of crystal	brown
unit cell dimensions	
a, Å	17.765(3)
b, Å	17.662(7)
c, Å	12.461(3)
V, Å^3	3909(3)
Z	8
no. of unique data	4995
total with $I > 3\sigma(I)$	2281
R^a	0.056
$R_w{}^b$	0.085
goodness of fit	0.81

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

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for [$Cp_4Fe_4(HC{\equiv}CH)_2$] (**3**)

Fe1−Fe2	2.491(2)	Fe1···Fe3	3.302(2)
Fe1−Fe4	2.500(2)	Fe2−Fe3	2.490(2)
Fe2···Fe4	3.300(2)	Fe3−Fe4	2.504(2)
Fe1−C1	1.93(1)	Fe1−C2	1.996(9)
Fe1−C4	1.978(8)	Fe2−C1	1.974(9)
Fe2−C2	1.93(1)	Fe2−C3	1.974(9)
Fe3−C2	1.989(9)	Fe3−C3	1.93(1)
Fe3−C4	1.989(9)	Fe4−C1	1.995(9)
Fe4−C3	2.004(9)	Fe4−C4	1.935(9)
C1−C3	1.49(1)	C2−C4	1.49(1)
Fe2−Fe1−Fe4	82.78(6)	Fe1−Fe2−Fe3	83.06(6)
Fe2−Fe3−Fe4	82.71(6)	Fe1−Fe4−Fe3	82.59(6)

°C provided pure **4** (20 mg) in 11% isolated yield. Data for **4**: ^{1}H NMR (benzene-d_6) δ 1.54 (s, 12H, *Me*C_5H_4), 3.77, 3.75 (m, 16H, MeC_5H_4), 10.27 (s, 4H, HC≡CH). ^{13}C NMR (benzene-d_6) δ 19.1 (*Me*C_5H_4), 83.2, 86.5, 98.8 (MeC_5H_4), 212.6 (HC≡CH, ^1J(CH) = 157 Hz). Anal. Calcd for $C_{28}H_{32}Fe_4$: C, 56.81; H, 5.45. Found: C, 56.57; H, 5.33. Mass (FAB, Xe, *m*-nitrobenzyl alcohol matrix) *m/z* 592 (M$^+$, 100) and 513 (M$^+$ − MeC_5H_4, 4). IR (KBr) $\tilde{\nu}_{max}$/cm^{-1} 3088 (w), 2918 (m), 2900 (m), 1483 (m), 1446 (m), 1367 (m), 1259 (w), 1230 (w), 1026 (m), 924 (w), 901 (m), 858 (w), 845 (w), 814 (s), 793 (s), 692 (w), 602 (w), 536 (m), 446 (m), 434 (w), 420 (w), 409 (w). Raman $\tilde{\nu}_{max}$/cm^{-1} 1234. Mp 114 °C.

Reaction of [$(MeC_5H_4)_4Fe_4(CO)_4$] (2) with $NaBH_4$. A solution of [$(MeC_5H_4)_4Fe_4(CO)_4$] (**2**) (101 mg, 0.155 mol) in THF (10 mL) and ethanol (50 mL) was treated with $NaBH_4$ (199 mg, 5.26 mmol) and stirred at room temperature. The reaction was monitored by silica gel TLC. No reaction took place even after 5 days. Recovered **2**: 87 mg (86%).

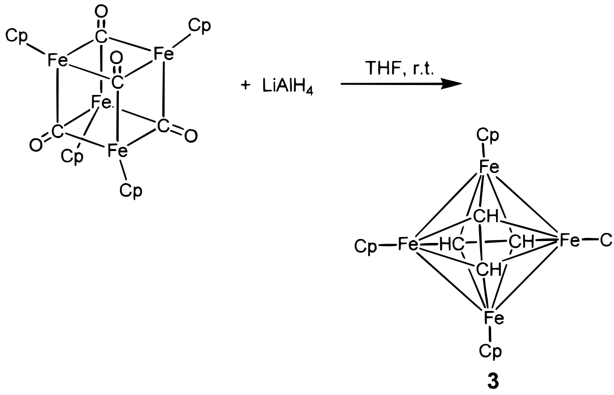
Reaction of [$(MeC_5H_4)_4Fe_4(CO)_4$] (2) with KH. A solution of [$(MeC_5H_4)_4Fe_4(CO)_4$] (**2**) (42 mg, 0.064 mol) in THF (50 mL) was treated with KH (450 mg, 11.2 mmol) and stirred at room temperature. The reaction was monitored by silica gel TLC. No reaction took place even after 8 days. Recovered **2**: 36 mg (85%).

Cross Reaction of [$Cp_4Fe_4(CO)_4$] (1) and [$(MeC_5H_4)_4Fe_4(CO)_4$] (2) with $LiAlH_4$. A solution of [$Cp_4Fe_4(CO)_4$] (**1**) (30.0 mg, 0.050 mmol) and [$(MeC_5H_4)_4Fe_4(CO)_4$] (**2**) (33.2 mg, 0.051 mol) in THF (30 mL) was treated with $LiAlH_4$ (52.4 mg, 1.38 mmol) and stirred at room temperature for 30 min. The resulting mixture was evaporated to dryness, and the residue was extracted with toluene (50 mL). Concentration of the extract *in vacuo* afforded a greenish brown solid that contained **3** and **4** in the molar ratio of 5:2. No crossover products such as [$Cp_2(MeC_5H_4)_2Fe_4(HC{\equiv}CH)_2$] were observed.

Crystallographic Analysis of [$Cp_4Fe_4(HC{\equiv}CH)_2$] (3). Brown crystals of **3** were obtained upon recrystallization from CH_2Cl_2/hexane at −30 °C. Diffraction data for **3** were collected on a Rigaku AFC-6S four-cycle diffractometer with graphite-monochromated Mo Kα radiation with use of the $\omega - 2\theta$ scan technique. The reflection data were corrected for Lorentz−polarization effects and for absorption. The unit cell dimensions were determined by the least-squares method with 20 reflections in the range of $25.1° < 2\theta < 27.8°$. The structure of **3** was solved by direct methods (SIR92), expanded with the Fourier technique (DIRDIF94), and refined by full-matrix least squares with the crystal structure analysis package teXsan on a Silicon Graphics Indy computer. The crystal data are summarized in Table 1, and selected interatomic distances and angles are listed in Table 2.

Results and Discussion

Treatment of [$Cp_4Fe_4(CO)_4$] (**1**) with $LiAlH_4$ in THF afforded brown crystals of **3** in 9% isolated yield (eq 1). Cluster **3** is air-stable in the solid state as well as in solution. Elemental analysis and mass spectral data support the formula [$Cp_4Fe_4(HC{\equiv}CH)_2$]. The infrared spectrum of **3** exhibits no band in the CO stretching frequency region, and instead, a new band assigned to the C−H stretching vibration appears at 3074 cm^{-1}. The Raman spectrum of **3** shows a medium-intensity band at 1118 cm^{-1} assignable to the C−C stretching vibration in the acetylene ligands. The remarkable low-frequency shift of the C−C stretching vibration compared to free acetylene (1974 cm^{-1}) is consistent with the coordination mode of acetylene (μ_4-η^2:η^2:η^1:η^1-HC≡CH) and is close to the single C−C bond stretching frequency of hydrocarbons (800−1200 cm^{-1}). Gervasio et al. measured the IR spectrum of [$(\mu_4\text{-}\eta^2\text{-}C_2H_2)Co_4(CO)_8(\mu\text{-}CO)_2$] and assigned a band at 1199 cm^{-1} to the C−C stretching mode of acetylene based on the ^{13}C isotopic shift.[5] In the ^{1}H NMR spectrum, two singlet signals appear at 3.95 and 10.78 ppm, which are assignable to four cyclopentadienyl ligands and two acetylene ligands, respectively. The ^{1}H-nondecoupled ^{13}C NMR spectrum shows a doublet signal assignable to the acetylenic carbons at 209.2 ppm (^1J(CH) = 160 Hz).



(1)

The MeC_5H_4 analogue [$(\eta^5\text{-}MeC_5H_4)_4Fe_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}HC{\equiv}CH)_2$] (**4**) was synthesized by the reaction of [$(MeC_5H_4)_4Fe_4(CO)_4$] (**2**) with $LiAlH_4$ in THF. The ^{1}H NMR spectrum indicates the existence of four chemically equivalent MeC_5H_4 ligands. The ^{1}H NMR signal of two acetylene ligands appears as a singlet at 10.27 ppm. The ^{13}C{^{1}H} NMR spectrum exhibits a singlet at 212.6 ppm assignable to acetylenic carbons.

It was found that the hydride-transfer reagents $NaBH_4$ and KH did not reduce the μ_3-CO ligands on the Fe_4 core of **2** and resulted in almost quantitative recovery of **2**.

The structure of **3** was unequivocally determined to be [$Cp_4Fe_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}HC{\equiv}CH)_2$] by a single-crystal X-ray diffraction analysis. An ORTEP drawing of **3** is shown in Figure 1. The cluster consists of a puckered rhombus of four iron atoms. The dihedral angle between the plane of Fe1−Fe2−Fe3 and Fe1−Fe4−Fe3 is 123.6°. The four iron−iron bond

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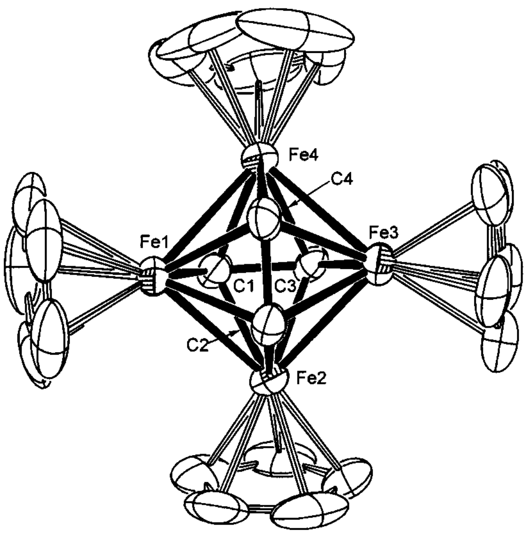
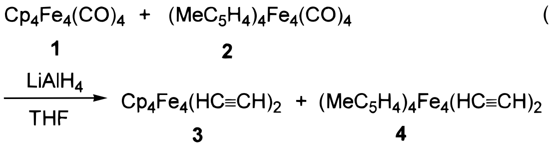


Figure 1. Molecular structure of [$Cp_4Fe_4(HC{\equiv}CH)_2$] (**3**) (ORTEP, thermal ellipsoids at the 30% probability level).

lengths of Fe1−Fe2, Fe2−Fe3, Fe3−Fe4, and Fe4−Fe1 (2.49−2.50 Å) are considerably shorter than those usually expected for typical iron−iron single bonds (2.55−2.70 Å).[6] The interatomic distances of Fe1−Fe3 and Fe2−Fe4 are 3.302(2) and 3.300(2) Å, respectively, which indicates that no iron−iron bonds exist between them. The bond lengths of C1−C3 (1.49(1) Å) and C2−C4 (1.49(1) Å) in the acetylene ligands are close to that of a typical C−C single bond in hydrocarbons (1.54 Å). The torsion angle between the vectors of C1−C3 and C2−C4 is 84.7(6)°. Wadepohl et al. reported the synthesis and characterization of acetylene-coordinated tetracobalt cluster [$Cp_4Co_4(RC{\equiv}CR)$] where the C−C bond distance of the alkyne in the cluster (1.499(5) Å) is similar to that of **3**.[7] The elongation of the carbon−carbon bonds observed in the two acetylene ligands of **3** is attributable to electron donation from the C−C π-bonding orbitals to the Fe_4 core and back-donation from the Fe_4 core to the empty C−C π^*-bonding orbitals. The coordination of one acetylene ligand to the four iron atoms consists of end-on type Fe−C σ-bonds and side-on type π-bonds delocalized over two carbon and two iron atoms. In agreement with this picture, the Fe−C bond distances of the former (1.93 Å (average)) are much shorter than those of the latter (1.99 Å (average)). Assuming that each acetylene ligand donates four electrons, cluster **3** is a 60 e^- species. This requires the presence of six iron−iron bonds rather than the four normally expected for a puckered rhombic arrangement of four metals.[8] The extra two iron−iron bonds can be considered to be delocalized over the Fe_4 framework, resulting in the shortening of each iron−iron bond.

The coordination mode of acetylene ligands μ_4-η^2:η^2:η^1:η^1-RC≡CR in M_4 clusters is well documented,[9] though our clusters **3** and **4** are the first examples of M_4 clusters containing two μ_4-η^2:η^2:η^1:η^1-HC≡CH ligands. The M_4 core of the clusters usually takes a butterfly structure having five metal−metal bonds. In contrast, cluster **3** has a puckered rhombus without the "hinge" metal−metal bond.

The cross-reaction of a 1:1 molar mixture of **1** and **2** with $LiAlH_4$ gave **3** and **4** in the molar ratio of 5:2. No crossover products such as [$Cp_2(MeC_5H_4)_2Fe_4(HC{\equiv}CH)_2$] were detected, which indicates that clusters **3** and **4** are formed intramolecularly.



$$\underset{\mathbf{1}}{Cp_4Fe_4(CO)_4} + \underset{\mathbf{2}}{(MeC_5H_4)_4Fe_4(CO)_4} \xrightarrow[\text{THF}]{LiAlH_4} \underset{\mathbf{3}}{Cp_4Fe_4(HC{\equiv}CH)_2} + \underset{\mathbf{4}}{(MeC_5H_4)_4Fe_4(HC{\equiv}CH)_2} \tag{2}$$

Formation of acetylene-coordinated clusters **3** and **4** may involve the reduction of carbonyl ligands by $LiAlH_4$ to give bis(carbyne) species which undergo C−C coupling to produce an acetylene ligand. Nuel et al. reported that the bis(μ_3-carbyne)iron cluster [$Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COEt)$] reacts with CO to bring about the coupling of the two bridging carbyne groups to give an acetylene cluster [$Fe_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}MeC{\equiv}COEt)$].[10] The paper establishes the feasibility of carbyne−carbyne coupling on iron clusters to form acetylene. Other mechanisms for the formation of **3** and **4** could be considered. For example, carbon−carbon bond formation could occur via coupling of carbonyl and carbyne ligands. According to Churchill's paper, [$W(CH)(Cl)(PMe_3)_4$] reacts with CO in the presence of AlX_3 (X = Cl, Me) to give a carbonyl−carbyne coupling product [$W(\eta^2\text{-}HC{\equiv}COAlX_3)(CO)(PMe_3)_3Cl$].[11] The aluminum reagent seems to play an important role in activating CO toward coupling with the carbyne.

Very recently, Rauchfuss et al. reported the reactions of [$Cp_4Fe_4(CO)_4$] (**1**) with nucleophiles such as *n*-BuLi, PhLi, NaH, and KH.[12] In no case was reduction of carbonyl ligands observed. In the cases of KH and NaH, though, some decomposition of **1** was observed. Reaction of **1** with organolithium reagents resulted in the reduction of cluster **1** itself to generate [$Cp_4Fe_4(CO)_4$]$^-$, instead of reducing the CO ligands.

Thermolysis of [Cp^*TiMe_3] in toluene resulted in elimination of methane to give [$Cp^*_4Ti_4(CH)_4$], which was characterized as a carbyne-bridged cubane-type cluster [$Cp^*_4Ti_4(\mu_3\text{-}CH)_4$].[13] The dramatic structural difference between the titanium and iron clusters [(Cp or $Cp^*)_4M_4(C_4H_4)$] is of great interest.

Finally, cyclic voltammetric data for **3** and **4** are summarized in Table 3. The cyclic voltammogram of **3** exhibits three reversible or quasireversible one-electron oxidation waves and an irreversible one-electron reduction wave. The electrochemical behavior of cluster **4** is quite similar to that of **3**, but all the redox potentials of **4** are shifted to the negative side by 70−80 mV compared with those of **3**. This is attributable to the

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Table 3. Cyclic Voltammetric Data of **3** and **4** in 0.1 M TBAB−Acetonitrile[a]

redox couple	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V	ΔE_p/mV
$[\mathbf{3}]^{3+}/[\mathbf{3}]^{2+}$	+1.08	+0.99	+1.04	90
$[\mathbf{3}]^{2+}/[\mathbf{3}]^{1+}$	+0.27	+0.20	+0.24	70
$[\mathbf{3}]^{1+}/[\mathbf{3}]^{0}$	−0.62	−0.70	−0.66	80
$[\mathbf{3}]^{0}/[\mathbf{3}]^{1-}$		−1.32		
$[\mathbf{4}]^{3+}/[\mathbf{4}]^{2+}$	+1.00	+0.91	+0.96	90
$[\mathbf{4}]^{2+}/[\mathbf{4}]^{1+}$	+0.20	+0.13	+0.17	70
$[\mathbf{4}]^{1+}/[\mathbf{4}]^{0}$	−0.69	−0.77	−0.73	80
$[\mathbf{4}]^{0}/[\mathbf{4}]^{1-}$		−1.38		

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

stronger electron-releasing effect of the MeC_5H_4 ligands compared to the Cp ligands.

Conclusion

The main finding in this work is that two carbon monoxide molecules can be converted to a nonsubstituted acetylene on an Fe_4 cluster core. Reduction of carbonyl ligands is achieved with use of the hydride-transfer reagent $LiAlH_4$. The resulting acetylene-coordinated cluster $[Cp_4Fe_4(HC{\equiv}CH)_2]$ (**3**) consists of a puckered rhombus of four iron atoms with two μ_4-η^2:η^2:η^1:η^1-HC≡CH ligands. The X-ray structure analysis and Raman spectral data establish that the C−C bond order of the coordinated acetylene is reduced to nearly unity.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering information and Web access instructions.

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