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Articles

Synthesis and Characterization of Fe,Co-Mixed Metal Polynuclear Complexes with C_4H and C_4 Ligands Derived from Butadiynyl (X = H) and Butadiynediyl Iron Complexes (X = Fp*), Fp*−C≡C−C≡C−X [Fp* = (η^5-C_5Me_5)Fe$(CO)_2$]: Transformation of the C_4(H) Cluster Frameworks via Valence Isomerization and 1,2-H Shift of the Carbon Linkages

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Sequential addition of $Co_2(CO)_8$ and $Fe_2(CO)_9$ to Fp*−C≡C−C≡C−X (X = H (**1**), Fp* (**2**)) affords a variety of Fe,Co mixed metal cluster compounds resulting from a combination of (1) addition of a Co_2 fragment to the C≡C bonds, (2) reorganization of the cluster framework including metal−metal bond formation, (3) replacement of metal fragments and transfer of metal fragments, (4) valence isomerization of the C_4(H) linkage, and (5) 1,2-H shift of the C_4H ligand.

Polynuclear metal complexes bearing linear carbon allotropes (C_n) as a ligand[1−4] have been a subject of our recent research activities.[2,3] Such synthetic studies should provide information on structural aspects of carbide (C_n) species adsorbed on a heterogeneous metal catalyst surface. The carbide intermediate, which should be formed at an early stage of catalytic transformation of carbon monoxide and hydrocarbons, is a key species for not only construction of carbon skeletons but also deactivation of the catalyst.[5] In previous papers, we reported synthesis and properties of polymetallic C_2H_x complexes (x = 0, 1) derived from the ethynyl (Fp*−C≡C−H) and ethynediyl complexes (Fp*−C≡C−Fp*).[3] In addition to features common to those of polynuclear acetylide cluster compounds, notable features peculiar to the simple C_2H_x system have been observed. Recently our research targets are extended to polymetallic systems with longer carbon rods.[2i,j,3h] Herein we disclose the results of classical cluster formation reactions of the butadiynyl and butadiynediyl iron complexes, Fp*−C≡C−C≡C−H (**1**) and Fp*−C≡C−C≡C−Fp* (**2**),

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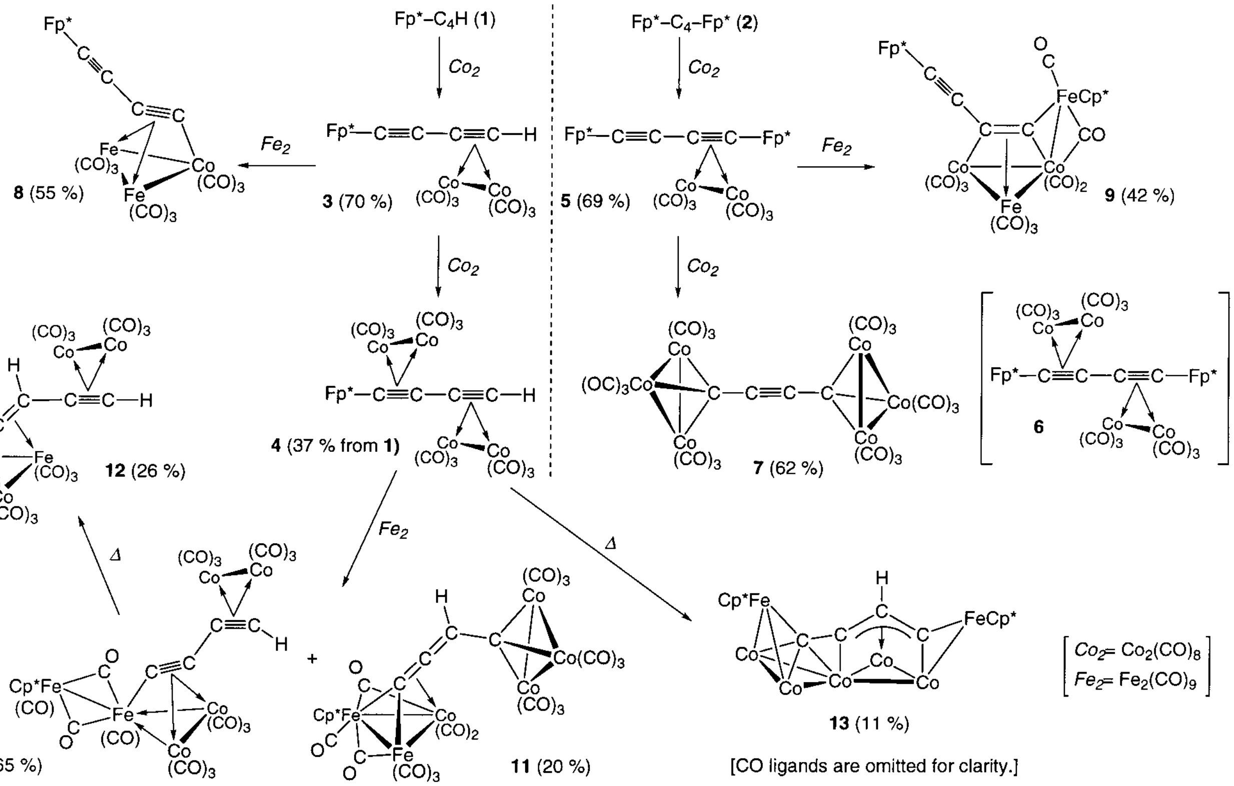
10.1021/om990494c CCC: $18.00

Scheme 1



[Co_2= $Co_2(CO)_8$, Fe_2= $Fe_2(CO)_9$]

[CO ligands are omitted for clarity.]

with $Co_2(CO)_8$ leading to adducts with the tetrahedral C_2Co_2 core. Simple adduct formation with the tetrahedral C_2Co_2 core[6] is followed by formation of a variety of Fe,Co mixed metal cluster compounds via a combination of (i) metal fragment addition and (ii) 1,2-H shift and valence isomerization of the carbon linkages upon further treatment with $Fe_2(CO)_9$ and thermolysis. A few reactions with molybdenum species[7] will be also described.

Results and Discussion

Adduct Formation with $Co_2(CO)_8$. Adducts obtained by interaction of **1** and **2** with $Co_2(CO)_8$ are summarized in Scheme 1. Reaction of the butadiynyl complex **1** with $Co_2(CO)_8$ readily proceeded with gas evolution (CO) to give adducts **3** and **4** in a stepwise manner. The reaction sites were readily determined by the change of the ≡C−H coupling constants. Upon coordination of 1 equiv of the dicobalt species, the $^1J_{C-H}$ value decreased from 252 Hz (**1**) to 224 Hz (**3**; cf. **4**: 219 Hz), indicating a considerable change of the hybridization of the terminal ≡CH carbon atom, and a significant shift of the ≡CH ^{1}H NMR signal (δ_H 1.42 (**1**) → 6.02 (**3**)) was also noted. Thus the initial reaction took place at the less sterically congested C≡C−H moiety. However, the ^{13}C NMR chemical shifts of the C_4H bridge could not be assigned completely, because they appeared in the similar, rather narrow range (δ_C 79−132 (**3**); 81−129 (**4**); cf. 53−107 (**1**)). The structures of **3** and **4** were characterized by X-ray crystallography (see below).

A 1:1 reaction of the butadiynediyl complex **2** with $Co_2(CO)_8$ also afforded the 1:1 adduct **5**, which was readily characterized by (1) inequivalent Cp* signals (δ_H 1.86, 1.94 in $CDCl_3$) and (2) the presence of only terminal CO stretching vibrations. The structure with the tetrahedral C_2Co_2 core was determined by X-ray crystallography (see below). In contrast to the reaction of the ethynediyl complex, Fp*−C≡C−Fp*, leading to an μ_3-acetylide cluster-type compound,[3a] **5** did not undergo decarbonylation to give an analogous cluster compound. The steric congestion in the ethynediyl complex bearing the bulky Fp* groups at both ends of the C_2 bridge should be released by decarbonylation associated with metal−metal bond formation to form a compact cluster compound. But, in the case of **5** bearing the less bulky C≡C−Fp* group as a substituent, no severe steric congestion was present so as to induce decarbonylation. Attempted thermal and photochemical decarbonylation of **5** resulted in the formation of an intractable mixture of products.

In contrast to the reaction of **1**, treatment of **2** with an excess amount of $Co_2(CO)_8$ or treatment of an isolated sample of **5** with $Co_2(CO)_8$ did not afford a 1:2 adduct analogous to **4** (**6**) but orange product **7** with no ^{1}H NMR signal. The simple ^{13}C NMR spectrum of **7** indicated a symmetrical structure, and the hexacobalt buta-2-yne-1,4-diylidyne structure[8] was characterized by its spectroscopic data (FD-MS and IR) and comparison of its crystallographic parameters with those of the previously reported data for an authentic sample.[9] In accord with the formulation, the residual part was isolated as Fp*−Co(CO)$_4$,[3e] a sole detectable organometallic byproduct. Although we also examined reaction of **1** with a slight excess amount of $Co_2(CO)_8$, no evidence

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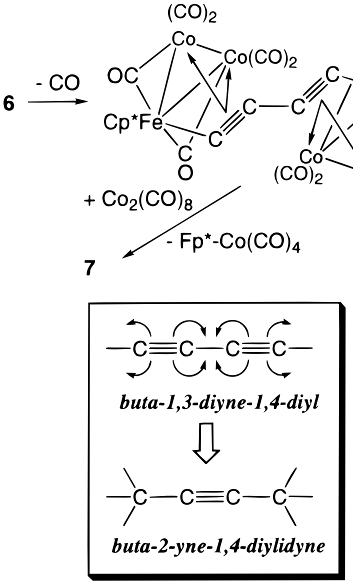
Scheme 2



for **6** was obtained even by ^{1}H NMR monitoring of a reaction mixture. This means that, as soon as **6** is formed, it is trapped by $\mathrm{Co_2(CO)_8}$ to give **7** probably by way of an acetylide cluster type intermediate **A** (Scheme 2).[25] Because the sum of the number of carbonyl ligands in the products (30: $\mathbf{7} + 2 \times \mathrm{Fp^*{-}Co(CO)_4}$) is larger than that in the adduct (28: $\mathbf{A} + 2 \times \mathrm{Co_2(CO)_8}$), **7** should be formed by a multistep process involving CO transfer in addition to adduct formation with a $\mathrm{Co_2}$ fragment and elimination of $\mathrm{Fp^*{-}Co(CO)_4}$. The structural change of the $\mathrm{C_4}$ bridge can be viewed as valence isomerization from a "buta-1,3-diyne-1,4-diyl" species (**2**) to a "buta-2-yne-1,4-diylidyne" species (**7**) induced by addition of two dicobalt species and elimination of Fe−Co species, which occur at both the ends of the $\mathrm{C_4}$ bridge in a simultaneous manner. Although adduct formation and subsequent acetylide cluster formation may be possible for related diynyl complexes, M−C≡C−C≡C−R,[10] this type of valence isomerization is not feasible for them. This is a reactivity peculiar to polyynediyl complexes

Molecular structures of adducts **3**, **4**, and **5** were determined by X-ray crystallography.[11] As generally observed for (μ-η^2:η^2-R−C≡C−R)$\mathrm{Co_2(CO)_6}$-type compounds, (1) they contain tetrahedral $\mathrm{C_2Co_2}$ cores with C≡C interatomic distances of 1.35(1) (**3**), 1.336(5) (Fe−C≡C), 1.331(5) (C≡C−H) (**4**), and 1.332(5) Å (**5**), C−Co distances of 1.94−2.06 Å, and Co−Co distances of 2.46−2.48 Å and (2) the linear Fe−C≡C−C≡C−H(or Fe) linkages are bent away from the dicobalt moiety with the C≡C−C(Fe) angles of 138−150°. The parameters are comparable to those reported for a typical organic analogue: (μ-Bu^t−C≡C−Bu^t)$\mathrm{Co_2(CO)_6}$ (C≡C, 1.341(3) Å; C−Co, 1.982−1.988(2) Å; ∠C≡C−C: 144.1(2)°, 144.8(2)°).[12] Upon coordination, the C≡C bonds are elongated by ca. 0.13−0.20 Å when compared with those in **1** (Fe−C≡C, 1.207(5); C≡C−H, 1.153(6) Å) and **2** (1.197(4) Å).[3i] In addition, the Fe−C≡ bonds in the Fe−(C≡C)$\mathrm{Co_2}$ parts in **4** (1.996(4) Å) and **5** (1.990(4) Å) are longer than

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(11) Due to the limitation of the space, details of crystallographic results of **3**−**5**, **8**−**11**, **13**, **14**, and **15** are included in the Supporting Information. Cell parameters were as follows. **3**: monoclinic, $a = 6.772(2)$ Å, $b = 14.443(2)$ Å, $c = 12.077(2)$ Å, $\beta = 91.920(1)°$, $V = 1180.6(4)$ Å^3. **4**: triclinic, $a = 11.157(2)$ Å, $b = 16.808(3)$ Å, $c = 9.152(3)$ Å, $\alpha = 91.48(2)°$, $\beta = 111.65(2)°$, $\gamma = 91.23(2)°$, $V = 1593(1)$ Å^3. **5**: triclinic, $a = 11.983(2)$ Å, $b = 14.399(4)$ Å, $c = 11.912(3)$ Å, $\alpha = 114.04(2)°$, $\beta = 91.45(2)°$, $\gamma = 73.71(2)°$, $V = 1792.5(8)$ Å^3. **8**: monoclinic, $a = 7.864(2)$ Å, $b = 27.080(3)$ Å, $c = 13.436(2)$ Å, $\beta = 103.84(2)°$, $V = 2778.1(8)$ Å^3. **9**: orthorhombic, $a = 17.700(7)$ Å, $b = 33.617(3)$ Å, $c = 12.877(1)$ Å, $V = 7663(2)$ Å^3. **10**: monoclinic, $a = 9.827(2)$ Å, $b = 20.945(18)$ Å, $c = 17.389(4)$ Å, $\beta = 102.46(2)°$, $V = 3495(2)$ Å^3. **11**: monoclinic, $a = 15.270(2)$ Å, $b = 9.133(2)$ Å, $c = 29.328(6)$ Å, $\beta = 100.74(1)°$, $V = 4019(1)$ Å^3. **13**: orthorhombic, $a = 11.918(2)$ Å, $b = 19.139(4)$ Å, $c = 20.204(3)$ Å, $V = 4609(5)$ Å^3. **14**: monoclinic, $a = 8.889(6)$ Å, $b = 20.99(5)$ Å, $c = 14.98(2)$ Å, $\beta = 95.41(7)°$, $V = 2782(5)$ Å^3. **15**: triclinic, $a = 12.802(7)$ Å, $b = 15.657(6)$ Å, $c = 6.976(2)$ Å, $\alpha = 98.27(4)°$, $\beta = 91.25(4)°$, $\gamma = 67.84(3)°$, $V = 1280(1)$ Å^3.

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those in the free Fe−C≡C moieties (1.907(4) (**1**), 1.933(4) (**2**), 1.902(9) (**3**), and 1.908(4) Å (**5**)) by ca. 0.08 Å, presumably because the η^1-acetylide ligand is replaced by a ligand with poor π-accepting ability (the C_2Co_2 core). The noncoordinated −C≡C− parts in **3** and **5** retain the linear structures.

Cluster Structure Expansion by Treatment with $Fe_2(CO)_9$. The resulting adducts **3**−**5** were further subjected to reaction with $Fe_2(CO)_9$ in the hope of forming higher nuclearity cluster compounds.[13]

(i) 1:1 Adducts 3 and 5. Reaction of **3** afforded a cluster compound **8** containing single sets of Cp* signals (^1H and ^{13}C NMR). The ^{13}C NMR signals for the C_4 linkage (δ_C 200.0, 163.3, 137.6, 101.6) in the lower field indicated that **8** was an acetylide cluster, and its molecular structure was confirmed by X-ray crystallography.[11] The acetylide part, C4≡C3−C2≡C1−Fp*(Fe1) (C4−C3, 1.28(1); C3−C2, 1.370(9); C2−C1, 1.19(1); C1−Fe1, 1.936(8) Å), interacts with the Fe_2Co triangle (Co1−Fe2, 2.625(2); Co1−Fe3, 2.627(1); Fe2−Fe3, 2.474(2) Å) in an essentially symmetrical manner as indicated by the C3−C4 part located almost equidistant from Fe2 and Fe3 (C3−Fe2, 2.127(6); C3−Fe3, 2.143(8); C4−Fe2, 2.020(7); C4−Fe3, 1.995(7) Å), and the coordination mode can be described as "μ_3-η^1(Co1):η^2(Fe2):η^2(Fe3)", a typical coordination mode of trinuclear μ_3-acetylide cluster compounds where the C≡C vector is located perpendicular to the M−M vector π-bonded to the acetylide ligand.[14,15] A μ-C≡C−$SiMe_3$ derivative was reported and structurally characterized by Seyferth.[14b] Formation of **8** can be explained in terms of a sequence of reactions: (i) addition of a mononuclear species $Fe(CO)_n$ leading to an intermediate with an $FeCo_2$ triangle, (ii) elimination of $HCo(CO)_n$, leaving a dinuclear μ-acetylide complex, (μ-η^1:η^2-C≡C−C≡C−Fp*)$FeCo(CO)_7$, and (iii) further addition of an $Fe(CO)_n$ species, giving rise to the trinuclear cluster core of **8**. A similar mechanism was proposed for a tetranuclear dicarbide cluster compound.[16]

In contrast to the reaction of the μ-C_4H complex **3** mentioned above, treatment of **5** with $Fe_2(CO)_9$ resulted in formation of tetranuclear "spiked triangular" cluster compound **9** (Co1−Fe3, 2.543(1); Co1−Co2, 2.606(1); Co1−Fe1, 2.5795(9); Co2−Fe3, 2.4744(9) Å) with the −C≡C−Fp* pendant moiety (C2−C1−Fe1). The structure of **9** was determined by X-ray crystallography.[11] Structures of tetranuclear μ-acetylide cluster compounds with the spiked triangular metal array are divided into parallel (||) and perpendicular (⊥) types on the basis of the relative orientation of the acetylide C≡C bond with respect to the basal M_3 triangle.[17] Because in complex **9** the C1−C2 bond is arranged almost parallel to the Co1−Co2 vector, the coordination structure of the core part is described as a ||-type structure. A closely related tetranuclear C_2H complex, $(Cp^*Fe)Co_2Ru(CO)_{10}(\mu_4(||)\text{-}C_2H)$,[3f] was reported by us, and its parameters for the Fe−C≡C part involved in the cluster part (Fe−C≡, 1.917(5); C≡C, 1.340(6) Å) are comparable to those in **9** (C1−Fe1, 1.957(4); C1−C2, 1.338(6) Å).

(ii) 1:2 Adduct 4. Treatment of the μ-C_4 complex **4** with $Fe_2(CO)_9$ in benzene at room temperature afforded two products **10** and **11** after fractional crystallization.

The yellow major product **10** contained a (μ-C≡C−H)-$Co_2(CO)_6$ partial structure as suggested by the characteristic ^{13}C NMR signal for the ≡C−H moiety (δ_C 77.2 (d, J = 223 Hz)). The molecular structure of **10** was determined by X-ray crystallography (Figure 1a and Table 1). As a result, complex **10** turned out to arise from formal oxidative addition of the Fe1−C1≡ bond in **4** to an $Fe(CO)_n$ species. The tetrametallic Fe_2Co_2 part constitutes a spiked triangular metal array, and the $FeCo_2$ triangle contains two Co-to-Fe dative bonds as judged by the electron counting at Fe2. No significant difference in the bond lengths are observed between the covalent and dative Co−Fe bonds (cf. **8** Co1−Fe2, 2.625(2); Co1−Fe3, 2.627(1) Å; and **9** Co1−Fe1, 2.5795(9); Co1−Fe3, 2.543(1) Å). The C≡C− ligand with the C−C separation of 1.32(1) Å interacts only with the $FeCo_2$ triangular part just like an acetylide ligand in trinuclear μ_3-acetylide cluster compounds, and the Fe1−C1 separation (3.48(1) Å) indicates a nonbonding interaction between them. All metal centers are coordinatively saturated, when the dative bonds are taken into account.

The minor product **11** was not soluble in organic solvents enough to afford a satisfactory ^{13}C NMR spectrum and was then characterized by X-ray crystallography (Figure 1b and Table 1). The composition, $Cp^*Fe_2Co_4(\mu\text{-}C_4H)(CO)_{16}$, is the same as that of the major product **10**, but the structure is completely different from **10**. Complex **11** consists of two trinuclear Fe_2Co and Co_3 cluster parts, which are bridged by an isomeric C_4H bridge formed via 1,2-H shift of the butadiynyl linkage. The resulting C_4H linkage interacts with the Fe_2Co part as a μ_3-η^1(Fe1):η^1(Fe2):η^2(Co1)-allenylidene ligand, and the C4 atom is incorporated as a part of the μ_3-alkylidynetricobalt structure.[8] In accord with this description, (1) the C1−C2 and C2−C3 lengths fall in the range of C(sp)=C(sp^2) bond lengths and the C3−C4 length (1.45(2) Å) indicates its single bond character, (2) the Fe1−Fe2−C1−C2 plane is located perpendicular to the C2−C3−C4−H1 plane in a manner similar to the situation in an organic allene molecule, (3) the C4 atom is located almost equidistant from the three cobalt atoms (C4−Co2−4, 2.45−2.48 Å), and (4) the =C−H ^1H NMR signal is observed in the olefinic proton region. Thus complex **11** can be described as a hexanuclear μ_4-buta-1,2-dien-1-yliden-4-ylidyne complex.

Both of complexes **10** and **11** result from formal addition of an $Fe(CO)_2$ fragment to **4**, but they are not interconverted with each other under the conditions when they are formed. A plausible formation mechanism (Scheme 3) involves a common intermediate **B** with a spiked triangular metal array, which should be

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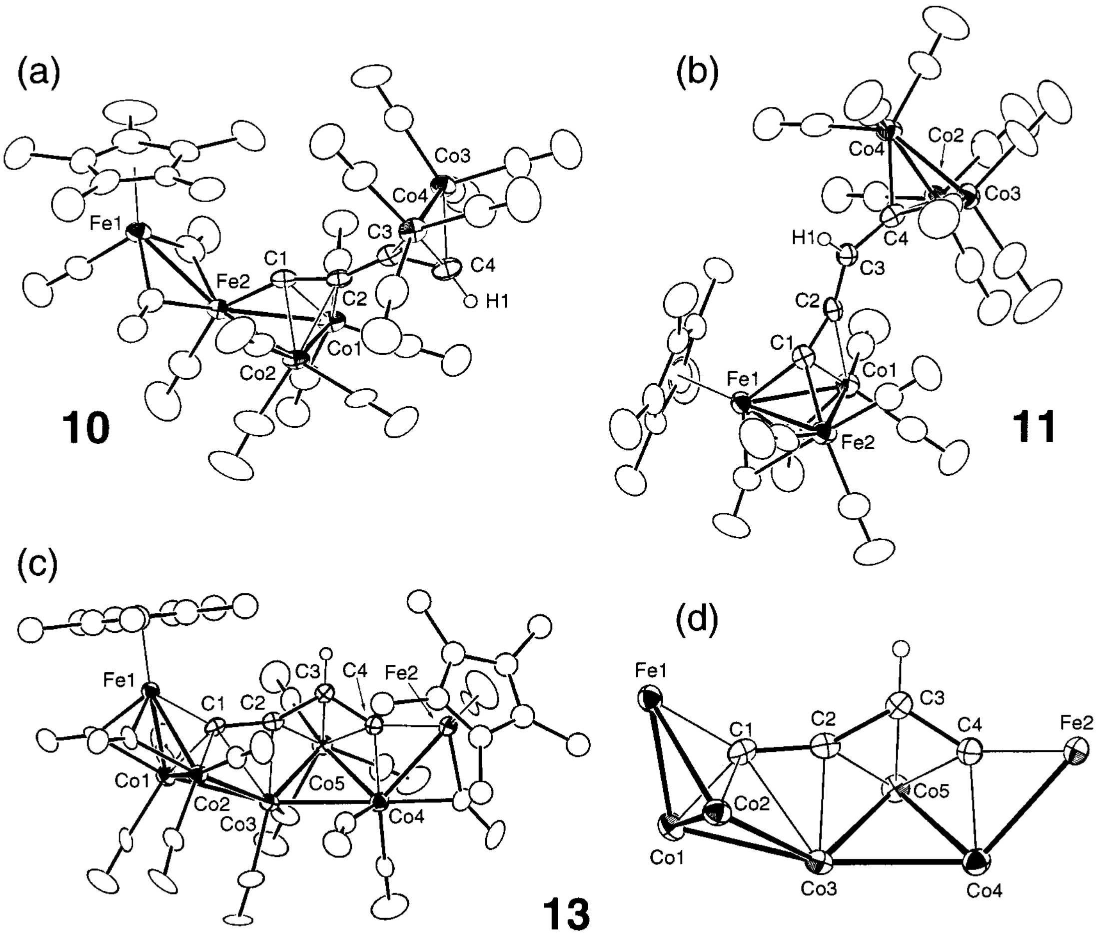
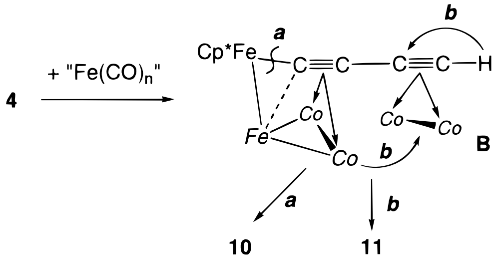


Figure 1. Molecular structures of (a) **10** and (b) **11** and (c) an overview and (d) an expanded view of the core part of **13** drawn at the 30% probability level.

Table 1. Selected Interatomic Distances (in Å) for 10, 11, and 13

		10			
Fe2–C1	1.81(1)	C2–Co1	2.088(9)	C4–H1	0.9(1)
C1–C2	1.32(1)	C2–Co2	2.089(8)	Co1–Co2	2.518(2)
C2–C3	1.42(1)	C3–Co3	1.989(9)	Co1–Fe2	2.618(2)
C3–C4	1.34(1)	C3–Co4	1.98(1)	Co2–Fe2	2.653(2)
C1–Co1	2.009(9)	C4–Co3	1.953(9)	Co3–Co4	2.458(2)
C1–Co2	2.018(7)	C4–Co4	1.97(1)	Fe1–Fe2	2.513(2)
		11			
C1–Fe1	1.96(1)	C3– H1	0.94(9)	Co1–Fe2	2.586(2)
C1–Co1	1.95(1)	C2–Co1	2.19(1)	Co2–Co3	2.483(2)
C1–Fe2	1.92(1)	C4–Co2	1.88(1)	Co2–Co4	2.456(3)
C1–C2	1.29(2)	C4–Co3	1.94(1)	Co3–Co4	2.464(3)
C2–C3	1.35(2)	C4–Co4	1.93(1)	Fe1–Fe2	2.554(3)
C3–C4	1.45(2)	Co1–Fe1	2.501(3)		
		13			
Fe1–C1	1.84(2)	Co3–C2	1.98(2)	Co2–Fe1	2.506(4)
C1–C2	1.46(3)	Co5–C2	2.14(2)	Co3–Co4	2.650(4)
C2–C3	1.43(3)	Co5–C3	2.16(2)	Co3–Co5	2.472(4)
C3–C4	1.43(2)	Co5–C4	2.15(2)	Co4–Co5	2.509(4)
Fe2–C4	1.84(2)	Co1–Co2	2.463(4)	Co4–Fe2	2.554(4)
C1–Co1	1.91(2)	Co1–Co3	2.609(4)	Co4–C4	1.89(2)
C1–Co2	1.88(2)	Co1–Fe1	2.507(4)		
C1–Co3	2.31(2)	Co2–Co3	2.658(4)		

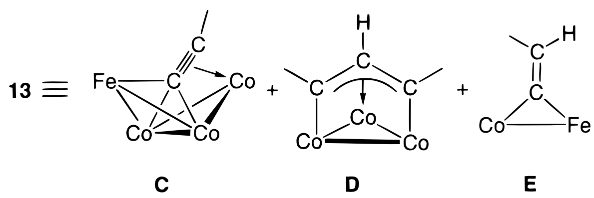
Scheme 3



formed by interaction of an Fe(CO)$_n$ species with the Co1–Co2 part and the terminal Fp* group in **4**. Fe1–C1 bond cleavage would lead to the μ_3-acetylide cluster **10**, a formal oxidative addition product, whereas Co transfer from the Fe$_2$Co$_2$ part to the Co$_2$ part associated with 1,2-H shift would produce complex **11**.

Complex **10** turned out to decompose under thermal conditions (in refluxing benzene). When a benzene solution of **10** was refluxed for 1 h, purple complex **12** was isolated from a reaction mixture. The reaction of **4** with Fe$_2$(CO)$_9$ in refluxing benzene also produced **12**. The characterization of **12** as a trinuclear μ_3-vinylidene cluster is based on the two ^{13}C NMR signals, δ_C 73.2 (d, J = 219 Hz) and δ_C 271.6 (s), which indicates the presence of a (μ-C≡C–H)Co$_2$(CO)$_6$ partial structure and a quarternary μ_3-vinylidene carbon atom, respectively. The ^{1}H NMR signals at δ_H 6.58 and 7.40 can be assigned to the ≡CH and =CH protons. The structure was also confirmed by preliminary X-ray crystallography, although the structure could not be refined satisfactorily owing to the low quality of the crystal. Complex **12**

Chart 1



should be formed by homolysis of the Fe−Fe bond in **10** followed by H-abstraction at C2.

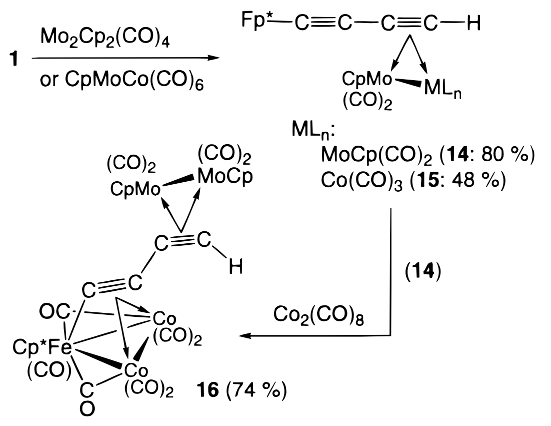
Formation of Heptanuclear μ-C_4H Cluster Compound 13 by Thermolysis of 4. To attempt further functionalization of the C_4(H) bridge, the resulting Co_2 adducts **3**, **4**, and **5** were subjected to thermolysis and photolysis. Although most of the reactions gave an inseparable, complicated mixture of products, thermolysis of **4** produced a dark yellow complex **13** (Scheme 1). A ^{1}H NMR spectrum of **13** contained a deshielded signal (δ_H 9.31) in addition to a pair of Cp* signals indicating formation of a higher nuclearity cluster compound with two Cp*Fe units. Because no characterizable ^{13}C NMR spectrum was obtained due to its low solubility in organic solvents, it was subjected to X-ray crystallography (Figure 1c,d), which revealed a heptanuclear structure with the C_4H bridge, $Cp^*_2Fe_2Co_5(\mu\text{-}C_4H)(CO)_{14}$.

The overall structure can be viewed as a fused form of three partial structures: a tetranuclear acetylide cluster structure with the butterfly metal array (**C**),[18] a trinuclear dimetallo-π-allyl structure (**D**),[19] and a dinuclear μ-vinylidene structure (**E**) [20] (Chart 1). As for the **C**-type structure, examples of acetylide cluster compounds are rather limited compared to vinylidene complexes.[21] One of characteristic features is migration of the terminal hydrogen atom to the β-carbon atom, and its ^{1}H NMR signal was located in a lower field (δ_C 9.31). Similar deshielding was reported for related compounds.[18] In accord with the analysis of the structure, the C−C distances are comparable to those in typical examples of each component (Chart 1), although the C3−C4 distance is slightly longer than the C=C distance of dinuclear μ-vinylidene complexes due to π-conjugation with the adjacent unsaturated system (**D**). Complex **13** is a coordinatively saturated species with 108 CVE.

Comparison of the compositions of **4** and **13** suggests that **13** may be formed by interaction of **4** with $Cp^*FeCo(CO)_n$ species, which arises from thermal decomposition of **4**. But treatment of an isolated sample of **4** with $Fp^*\text{-}Co(CO)_4$ did not afford **13**.

Interaction with Molybdenum Species (Scheme 4). Reaction of the butadiynyl complex **1** with the coordinatively unsaturated dimolybdenum species, $Mo_2Cp_2(CO)_4$, afforded the adduct **14** with the tetrahedral C_2Mo_2 core in a manner similar to the reactions with alkynes[7] and the ethynyl complex, $Fp^*−C≡C−H$.[3d] The reaction of the butadiynediyl complex **2** with $Mo_2Cp_2(CO)_4$ also gave the same product **14** after replacement of the Fp* group by a hydrogen atom probably due to the steric repulsion between the Fp* group and the dimolybdenum fragment. The structural parameters of the C_2Mo_2 core characterized by X-ray crystallography [11] (C−C, 1.32(1); C−Mo, 2.161−2.234(9); Mo−Mo, 2.963(2) Å; Mo−C−O angle and Mo···CO distance for the semibridging CO: 168.8(8)° (the other angles, 166−178.4(10)°) and 2.859(9) Å, respectively) are similar to the above-mentioned derivatives.[3d,7] Treatment of **1** with the heterobimetallic species, $CpMoCo(CO)_7$, also produced the adduct **15**. The structural parameters for the coordinated acetylide part are 1.41(1) Å (C≡C), 2.01(1), and 2.02(1) Å (≡C−Co) and 2.14(1) and 2.20(1) Å (≡C−Mo).

Scheme 4



Although the Mo_2 adduct **14** did not further react with an excess amount of $Mo_2Cp_2(CO)_4$ due to the congestion around the free C≡C part, reaction with $Co_2(CO)_8$ resulted in adduct formation to give the acetylide cluster type compound **16**. The steric congestion around the C_2Co_2 moiety is released by decarbonylation associated with metal−metal bond formation.

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere by using standard Schlenk tube techniques. THF and benzene (Na−K alloy) and CH_2Cl_2 (CaH_2) were treated with appropriate drying agents, distilled, and stored under argon. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 (^{1}H, 200 MHz) and JEOL EX400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometers. Solvents for NMR measurements containing 0.5% TMS were dried over molecular sieves, degassed, distilled under reduced pressure, and stored under Ar. IR and FD-MS spectra were obtained on a JASCO FT/IR 5300 spectrometer and a Hitachi M80 mass spectrometer, respectively. Complexes **1** and **2** were prepared according to the published procedures.[2i] $Co_2(CO)_8$ was purchased and used as received, and $Fe_2(CO)_9$,[22] $Mo_2Cp_2(CO)_4$,[23] and $CpMoCo(CO)_7$[24] were prepared by the established methods.

Interaction of 1 with $Co_2(CO)_8$: (i) Synthesis of 3. A THF solution (35 mL) of **1** (399 mg, 1.35 mmol) and $Co_2(CO)_8$ (448 mg, 1.31 mmol) was stirred for 1 h at room temperature. Upon dissolution, the mixture turned dark green with gas evolution. The volatiles were removed under reduced pressure, and the residue was extracted with CH_2Cl_2 and passed through an alumina plug. Crystallization from CH_2Cl_2−hexane gave **3** (592 mg, 1.01 mmol, 70% yield) as dark green crystals. ^{1}H NMR ($CDCl_3$): δ_H 6.02 (1H, s, ≡CH), 1.85 (15H, s, Cp*). ^{13}C NMR ($CDCl_3$): δ_C 213.8 (s, Fe−CO), 200.3 (br s, Co−CO), 132.2, 106.7 (s × 2, Fe−C≡C), 97.5 (s, C_5Me$_5$), 78.9 (d, ^2J = 32 Hz, *C*≡CH), 70.2 (d, J = 224 Hz, C≡*C*H), 9.8 (q, J = 128 Hz, C_5Me_5). IR (KBr): 2086, 2053, 2013, 1999, 1967 cm^{-1}; (CH_2Cl_2) 2088, 2048, 2019, 1973 cm^{-1}. Anal. Calcd for $C_{22}H_{16}O_8FeCo_2$: C, 45.40; H, 2.77. Found: C, 45.45; H, 2.95.

(ii) Synthesis of 4. Reaction of **1** (264 mg, 0.89 mmol) and $Co_2(CO)_8$ (834 mg, 2,45 mmol; 2.75 equiv) in THF (35 mL) as described for **3** gave **4** (238 mg, 0.32 mmol, 37% yield) as dark green crystals. ^{1}H NMR ($CDCl_3$): δ_H 6.86 (1H, s, ≡CH), 1.80 (15H, s, Cp*). ^{13}C NMR ($CDCl_3$): δ_C 215.2 (s, Fe−CO), 201.9, 199.3 (br s × 2, Co−CO), 129.5, 115.4, 90.0 (s × 3, Fe−C≡C−C≡), 97.9 (s, *C*$_5$Me$_5$), 81.3 (d, J = 219 Hz, C≡*C*H), 9.3 (q, J = 128 Hz, C$_5$*Me*$_5$). IR (KBr): 2095, 2056, 2024, 2007, 1994, 1970, 1957 cm^{-1}. Anal. Calcd for $C_{28}H_{16}O_{14}FeCo_4$: C, 38.74; H, 1.86. Found: C, 38.20; H, 2.00.

Interaction of 2 with $Co_2(CO)_8$: (i) Synthesis of 5. Reaction of **2** (91 mg, 0.17 mmol) with $Co_2(CO)_8$ (58 mg, 0.17 mmol) in THF (10 mL) for 2 h at room temperature followed by workup as described above afforded **5** (96 mg, 0.12 mmol, 69% yield) as dark yellow powders. ^{1}H NMR ($CDCl_3$): δ_H 1.86, 1.94 (15H × 2, s × 2, Cp*). ^{13}C NMR ($CDCl_3$): δ_C 215.7, 214.4 (s × 2, Fe−CO), 203.0 (br s, Co−CO), 118.2, 110.7, 105.8, 100.2 (s × 4, Fe−C≡C−C≡C−Fe), 97.7, 97.2 (s × 2, *C*$_5$Me$_5$), 10.0, 9.9 (q × 2, J = 129 Hz, C$_5$*Me*$_5$). IR (KBr): 2059, 2013, 1988, 1967 cm^{-1}. Anal. Calcd for $C_{34}H_{30}O_{10}Fe_2Co_2$: C, 49.31; H, 3.65. Found: C, 48.96; H, 3.26.

(ii) Formation of 7. Treatment of a THF solution (10 mL) of **2** (94 mg, 0.17 mmol) with $Co_2(CO)_8$ (408 mg, 1.19 mmol) for 1.5 h at room temperature gave **7** (97 mg, 0.11 mmol, 62% yield) as orange crystals, which were characterized by X-ray crystallography. Chromatographic separation of the supernatant gave Fp*−$Co(CO)_4$.

Reaction of 3 with $Fe_2(CO)_9$ To Give 8. A THF solution (30 mL) of **3** (132 mg, 0.23 mmol) and $Fe_2(CO)_9$ (412 mg, 1.13 mmol) was stirred for 19 h at ambient temperature. The mixture gradually turned brown. Then the volatiles were removed under reduced pressure, and the resultant residue was extracted with CH_2Cl_2 and passed through an alumina plug. Crystallization from CH_2Cl_2−hexanes gave **8** as brown crystals (90 mg, 0.13 mmol, 55% yield). ^{1}H NMR ($CDCl_3$): δ_H 1.89 (15H, s, Cp*). ^{13}C NMR (CD_2Cl_2): δ_C 213.7, 212.5, 211.8 (s × 3, M−CO), 200.0, 163.3, 137.6, 101.6 (s × 4, Fe−C≡C−C≡C−Co), 98.5 (s, *C*$_5$Me$_5$), 10.0 (q, J = 129 Hz, C$_5$*Me*$_5$). IR (CH_2Cl_2): 2047, 2037, 2019 cm^{-1}. FD-MS: m/z = 718 (M$^+$). Anal. Calcd for $C_{25}H_{15}O_{11}Fe_3Co$: C, 41.83; H, 2.09. Found: C, 41.75; H, 2.11.

Reaction of 5 with $Fe_2(CO)_9$ To Give 9. A mixture of **5** (110 mg, 0.13 mmol) and $Fe_2(CO)_9$ (509 mg, 1.39 mmol) dissolved in THF (20 mL) was stirred for 55 h at room temperature. The reaction mixture turned orange with gas evolution. Workup as described above (extraction with ether) gave **9** as orange crystals (64 mg, 0.055 mmol, 42% yield). ^{1}H NMR ($CDCl_3$): δ_H 1.90, 1.95 (15H × 2, s × 2, Cp*). ^{13}C NMR ($CDCl_3$): δ_C 214.4, 214.0, 211.9 (s × 3, M−CO), 126.4, 112.2, 102.5, 98.8 (s × 4, Fe−C≡C−C≡C−Fe), 97.8, 97.4 (s × 2, *C*$_5$Me$_5$), 9.89, 9.95 (q × 2, J = 129 Hz, C$_5$*Me*$_5$). IR (KBr): 2065, 2016, 1970, 1940, 1821 cm^{-1}. Anal. Calcd for $C_{42}H_{30}O_{12}Fe_2Co_2$: C, 45.97; H, 3.62. Found: C, 45.98; H, 3.33.

Reaction of 4 with $Fe_2(CO)_9$ To Give 10 and 11. A benzene solution (30 mL) of **4** (366 mg, 0.43 mmol) and $Fe_2(CO)_9$ (459 mg, 0.97 mmol) was stirred for 30 min at room temperature. Workup as described above gave **10** as yellow crystals (269 mg, 0.27 mmol, 65% yield). Concentration and cooling of the supernatant solution gave **11** (83 mg, 0.084 mmol, 20% yield) as purple crystals. **10**: ^{1}H NMR ($CDCl_3$): δ_H 6.70 (1H, s, CH), 1.87 (15H, s, Cp*). ^{13}C NMR ($CDCl_3$): δ_C 250.6 (μ-CO), 208.8 (s, Fe−CO), 201.0, 198.8 (br s, Co−CO), 175.1, 103.6 (s, C_4H), 97.8 (s, *C*$_5$Me$_5$), 81.5 (s, C_4H), 77.2 (d, J = 223 Hz, ≡CH), 10.0 (q, J = 129 Hz, C$_5$*Me*$_5$). IR (KBr): 2098, 2061, 2027, 2016, 2007, 1954, 1820 cm^{-1}; (CH_2Cl_2) 2096, 2086, 2063, 2032, 1976, 1819 cm^{-1}. FD-MS: m/z = 980 (M$^+$). Anal. Calcd for $C_{30}H_{16}O_{16}Fe_2Co_4$: C, 36.77; H, 1.65. Found: C, 36.46; H, 1.96. **11**: ^{1}H NMR ($CDCl_3$): δ_H 8.83 (1H, s, CH), 1.76 (15H, s, Cp*). IR (KBr): 2097, 2054, 2006, 1956, 1859, 1809 cm^{-1}. FD-MS: m/z = 980 (M$^+$).

Formation of 12. (i) Thermolysis of 4 in the Presence of $Fe_2(CO)_9$. A benzene solution (25 mL) of **4** (196 mg, 0.23 mmol) and $Fe_2(CO)_9$ (240 mg, 0.66 mmol) was refluxed for 1 h. Removal of the volatiles, extraction with CH_2Cl_2, filtration through an alumina pad, and crystallization from CH_2Cl_2−hexane gave **12** (45 mg, 0.059 mmol, 26% yield) as purple brown crystals.

(ii) Thermolysis of 10. Refluxing a benzene solution (15 mL) of **10** (50 mg, 0.051 mmol) for 1 h followed by workup as described above gave **12** (10 mg, 0.013 mmol, 26% yield). **12**: ^{1}H NMR ($CDCl_3$): δ_H 7.33 (1H, s), 6.58 (1H, s). ^{13}C NMR ($CDCl_3$): δ_C 271.6 (s, C=), 210.2 (s, Fe−CO), ~200 (br, Co−CO), 166.4 (s, *C*≡CH), 131.2 (d, J = 166 Hz, =CH), 73.2 (d, J = 219 Hz, ≡CH). IR (KBr): 2106, 2090, 2043, 1988, 1636 cm^{-1}. FD-MS: m/z = 762 (M$^+$). Anal. Calcd for $C_{19}H_4O_{15}Cl_2FeCo_4$ (**12**·CH_2Cl_2): C, 28.36; H, 0.63. Found: C, 28.37; H, 0.26.

Thermolysis of 4 To Give 13. A benzene solution (50 mL) of **4** (864 mg, 1.00 mmol) was refluxed for 3 h. Workup as described above gave **13** as dark yellow crystals (119 mg, 0.11 mmol, 11% yield). ^{1}H NMR ($CDCl_3$): δ_H 9.31 (1H, s, CH), 1.97, 1.82 (15H × 2, s × 2, Cp*). IR (KBr): 2056, 2014, 1831 cm^{-1}; (CH_2Cl_2) 2059, 2014, 1831 cm^{-1}. FD-MS: m/z = 1118 (M$^+$). Anal. Calcd for $C_{39}H_{33}O_{14}Cl_2Fe_2Co_5$ (**13**·CH_2Cl_2): C, 38.94; H, 2.77; Cl, 5.89. Found: C, 38.71; H, 2.71; Cl, 5.24.

Reaction of 1 with $Mo_2Cp_2(CO)_4$ To Give 14. A CH_2Cl_2 solution (25 mL) of **1** (304 mg, 1.03 mmol) and $Mo_2Cp_2(CO)_4$ (418 mg, 0.963 mmol) was stirred for 3 h at ambient temperature. After removal of the volatiles the residue was subjected to chromatographic separation on alumina. Elution with 1:3 CH_2Cl_2−hexanes gave Fp*$_2$, **1**, and then a brick red band, from which **14** was isolated after removal of the eluent. **14** (563 mg, 0.77 mmol, 80% yield): ^{1}H NMR ($CDCl_3$): δ_H 5.27 (10H, s, Cp_2), 4.83 (1H, s, C_4H), 1.84 (15H, s, Cp*). ^{13}C NMR ($CDCl_3$): δ_C 231.1, 230.6, 214.9 (CO), 110.2, 109.8 (s × 2, Fe−C≡C), 96.9 (s, *C*$_5$Me$_5$), 92.8 (d, J = 178 Hz, Cp), 68.3 (d, ^{2}J = 5 Hz, *C*≡CH), 62.1 (d, J = 211 Hz, C≡*C*H), 10.0 (q, J = 129 Hz, C$_5$*Me*$_5$). IR (KBr): 2079, 2008, 1969, 1964, 1918, 1910, 1834, 1817 cm^{-1}. FD-MS: m/z = 732 (M$^+$). Anal. Calcd for $C_{30}H_{26}O_6FeMo_2$: C, 49.34; H, 3.59. Found: C, 49.20; H, 3.59.

Reaction of 1 with $CpMoCo(CO)_7$ To Give 15. A benzene solution (10 mL) of **1** (72 mg, 0.24 mmol) and $CpMoCo(CO)_7$ (84 mg, 0.20 mmol) was stirred for 1 h at 50 °C. After removal of the volatiles under reduced pressure, the residue was extracted with CH_2Cl_2 and filtered through an alumina pad. Chromatographic separation on alumina (eluted with CH_2Cl_2−hexanes, 1:3) gave Fp*$_2$, $CpMoCo(CO)_7$, and then a red brown band, from which **15** was isolated after removal of the eluent. **15** (64 mg, 0.098 mmol, 48% yield): ^{1}H NMR ($CDCl_3$): δ_H 5.51 (1H, s, C_4H), 5.36 (5H, s, Cp), 1.84 (15H, s, Cp*). ^{13}C NMR ($CDCl_3$): δ_C 228.5, 227.1 (s, Mo−CO), 214.5, 214.3 (s, Fe−CO), 120.9, 108.0 (s × 2, Fe−C≡C), 97.2 (s, *C*$_5$Me$_5$), 92.6 (d, J = 178 Hz, Cp), 77.8 (d, ^{2}J = 9 Hz, *C*≡CH), 70.6 (d, J = 217 Hz, C≡*C*H), 9.8 (q, J = 128 Hz, C$_5$*Me*$_5$). IR (KBr) 2076, 2045, 2010, 1980, 1955, 1920 cm^{-1}. FD-MS: m/z = 656 (M$^+$). Anal. Calcd for $C_{26}H_{21}O_9FeCoMo$: C, 47.59; H, 3.23. Found: C, 47.28; H, 3.43.

Reaction of 14 with $Co_2(CO)_8$ To Give 16. A THF solution (15 mL) of **14** (100 mg, 0.137 mmol) and $Co_2(CO)_8$ (260 mg, 0.76 mmol) was stirred for 4 h at ambient temperature. After removal of the volatiles the residue was extracted with CH_2Cl_2 and passed through an alumina pad. Crystallization from CH_2Cl_2−hexane gave **16** (97 mg, 0.101 mmol, 74% yield) as red-gray plates. Despite several attempts, an analytically pure sample was not obtained. ^{1}H NMR ($CDCl_3$): δ_H 5.55 (1H, s, C_4H), 5.36 (10H, s, Cp_2), 1.84 (15H, s, Cp*). ^{13}C NMR ($CDCl_3$): δ_C 244.6 (m-CO), 231.4 (s, Mo−CO), 206.0 (s, Fe−CO), 201.3 (br s, Co−CO), 169.3, 122.2 (s, Fe−C≡C), 96.9 (s, *C*$_5$Me$_5$), 92.8 (d, J = 180 Hz, Cp), 88.7 (d, J = 210 Hz, C≡*C*H), 44.4 (d, ^{2}J = 4 Hz, *C*≡CH), 9.4 (q, J = 129 Hz, C$_5$*Me*$_5$). IR (KBr): 2029, 2000, 1979, 1926, 1834, 1809 cm^{-1}. FD-MS: m/z = 960 (M$^+$).

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Note Added in Proof. After submission of our manuscript, a paper that reported valence isomerization of a C_4 linkage similar to the process **2** → **7** was published.[25]

Supporting Information Available: Details for crystal structure determination of complexes **3**−**5**, **8**−**11**, and **13**−**15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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