clear band, 4, which was collected. Anal. Calcd for $C_{16}H_{28}O_1Si_3$: C, 59.98; H, 8.80. Found: C, 60.26; H, 8.62.

Thermal Rearrangement of 4. A 100-mL Schlenk flask equipped with a rubber septum and magnetic stir-bar was charged with 0.9 g of 4 and heated under argon for 4 h at 140 °C to give 5 quantitatively (as observed by ^1H and ^{13}C NMR). Anal. Calcd for $C_{16}H_{28}O_1Si_3$: C, 59.98; H, 8.80. Found: C, 60.34; H, 8.75.

Reaction of 2 with Benzonitrile. A solution of 2 was prepared as above by reaction of 4.13 g (0.0183 mol) of 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane with 13 mL of 2.5 M *n*-butyllithium in pentane (0.0325 mol) and 3.9 mL (0.0258 mol) of TMEDA. A 250-mL Schlenk flask was charged with 3.6 mL (0.0353 mol) of benzonitrile and 20 mL of hexane and then cooled to −78 °C in a dry ice/acetone bath. The solution of 2 was added over 5 min with a fine cannula. After the addition was complete, the mixture was warmed to room temperature and stirred for 1 h. Methanol (2 mL, 0.0494 mol) was added dropwise and the solution turned from orange to yellow and a white precipitate formed. The solution was filtered through a Celite-packed Schlenk frit and volatiles were removed by trap-to-trap distillation (room temperature, 30 Torr). GLC analysis showed one major peak (46% yield) and numerous smaller yield products. Separation of the major product was not possible by TLC, and ^1H NMR analysis of the product mixture was too complex for identification of any products. Distillation at 0.03 Torr afforded on fraction between 93 and 96 °C which was determined to be a mixture of isomers 6 and 7. The isomers could not be separated by TLC. However, when the mixture was heated at 160 °C for 3 h, quantitative conversion to 7 was achieved. By careful comparison of the NMR spectral data for the mixture of compounds 6 and 7 with the data obtained for a pure sample of 7, the spectral data for 6 could be determined. Anal. Calcd for $C_{16}H_{29}N_1Si_3$ (7): C, 60.10; H, 9.16. Found: C, 60.42; H, 9.28.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

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Interaction of Iron Ethynyl and Ethynediyl Complexes with $Cp_2Ni_2(CO)_2$: Formation of Tri- and Tetranuclear Adducts with a Multiply Bridging C_2H Ligand[†]

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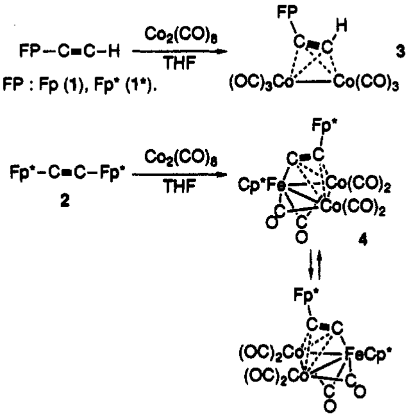
Summary: Reaction of ethynyliron complexes Fp—C≡C—H [FP = Fp (**1**), Fp* (**1***)] with $Cp_2Ni_2(CO)_2$ (**5**) affords the expected adducts $Cp_2Ni_2(\mu\text{-}\eta^2{:}\eta^2\text{-}FP—C≡C—H)$ [FP = Fp (**6**), Fp* (**6***)] with a tetrahedral C_2Ni_2 core together with tetranuclear adducts $(CPFe)(CpNi)_2Ni(CO)_2(\mu\text{-}CO)(\mu_4\text{-}C_2H)$ [CP = CP (**7**), Cp* (**7***)] with a quadruply bridging C_2H ligand. **7** (**7***) is formed by a formal capping reaction of **6** (**6***) with a Ni(CO) fragment. On the other hand, reaction of an ethynediyldiiron complex Fp*—C≡C—Fp* (**2**) with **5** affords a dinuclear complex, $Cp^*FeCpNi(\mu\text{-}CO)_2(CO)$ (**10**), without the C_2 ligand, the fate of which is not known. The molecular structures of **6**, **7**, and **10** have been determined by X-ray crystallography.

Introduction

Coordination structure and chemical properties of C2 species ($C_2H_mO_n$) incorporated in a polymetallic system have attracted much attention in connection with corresponding C2 surface species which may be formed after coupling of C1 species in catalytic CO hydrogenation. We[1] also have been studying chemical properties of polymetallic C_2 and C_2H complexes derived from parent acetylides, i.e. ethynyliron complexes FP—C≡C—H [FP = Fp (1), Fp* (1*)] and an ethynediyldiiron complex Fp*—C≡C—Fp* (2). Treatment of 1–2 with mono- and dinuclear species such as $[Fp^{*+}(THF)]BF_4$[1a] and $Co_2(CO)_8$[1d] successfully produced polynuclear complexes with a multiply bridging C_2H or C_2 ligand, and some of the resulting adducts exhibited unusual properties which had not been observed for analogues containing an organic substituent (e.g. Ph, alkyl, COOR) at the C_2 terminus. For example, interaction of 1 and 1* with $Co_2(CO)_8$ resulted in the formation of the normal expected μ-$\eta^2{:}\eta^2$-adducts 3, whereas the reaction of 2 afforded a rare example of a cluster compound (4) which is fluxional via a reversible metal—metal bond scission and recombination process (Scheme I).

Scheme I



As an extention, herein we wish to report results of interaction of 1–2 with a dinuclear nickel complex $Cp_2Ni_2(CO)_2$ (5), which has been known to react with various alkynes to afford adducts with a tetrahedral C_2Ni_2 core.[2,3]

[†] Abbreviations: Fp = $CpFe(CO)_2$; Cp = η^5-C_5H_5; Fp* = Cp*Fe$(CO)_2$; Cp* = η^5-C_5Me_5.

(1) (a) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1990**, *9*, 816. (b) Akita, M.; Terada, M.; Oyama, S.; Sugimoto, S.; Moro-oka, Y. *Organometallics* **1991**, *10*, 1561. (c) Akita, M.; Terada, M.; Moro-oka, Y. *Organometallics* **1991**, *10*, 2962. (d) Akita, M.; Terada, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1992**, *11*, 1825.

(2) (a) Tilney-Bassett, J. F.; Mills, O. S. *J. Am. Chem. Soc.* **1959**, *81*, 4757. (b) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1974; Vol. 1.

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Table I. Crystallographic Data for 6, 7, and 10

	6	7	10
formula	$C_{19}H_{16}O_2FeNi_2$	$C_{20}H_{16}O_3FeNi_3$	$C_{18}H_{20}O_3FeNi$
fw	449.58	536.29	398.90
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
a/Å	9.219 (7)	17.695 (2)	10.558 (3)
b/Å	28.350 (6)	8.667 (2)	11.083 (4)
c/Å	6.619 (5)	12.548 (2)	15.488 (4)
β/deg		96.03 (1)	108.36 (2)
V/Å^3	1730 (2)	1913.6 (5)	1720.0 (9)
Z	4	4	4
d_{calcd}/g·cm^{-3}	1.73	1.86	1.54
μ/cm^{-1}	30.0	36.85	19.53
temp/°C	25	25	25
2θ/deg	5–50	2–55	5–50
no. of data collcd	3396	4905	3387
no. of data with $F > 3\sigma$	1668	1522	1706
no. of variables	221	248	185
R	0.0267	0.0544	0.0376
R_w	0.0355	0.0398	0.0442

Table II. Structural Parameters for (μ-η^2:η^2-R—C≡C—H)Ni_2Cp_2[a]

	R		
	Fp (6)	H (8)[4]	3[b,1d]
C1–C2	1.313 (7)	1.341 (6)	1.305 (5)
C1-Fe	1.952 (4)		1.954 (3)
C1-Ni1	1.937 (4)	1.884 (4)	2.046 (2)
C1-Ni2	1.936 (5)	1.884 (4)	2.054 (2)
C2-H2	0.99 (6)	0.98 (5)	1.09 (4)
C2-Ni1	1.887 (6)	1.884 (4)	1.943 (3)
C2-Ni2	1.901 (6)	1.884 (4)	1.947 (3)
Ni1-Ni2	2.345 (1)	2.345 (3)	2.481 (1)
Fe-C8	1.766 (6)		1.778 (4)
Fe-C9	1.754 (5)		1.748 (4)
C8-O1	1.144 (6)		1.137 (5)
C9-O2	1.155 (6)		1.141 (5)
∠Fe–C1–C2	147.9 (5)		146.9 (2)
∠C1–C2–H2	142 (3)	148.1 (5)	140 (1)

[a] Bond lengths in Å; bond angles in deg. [b] (μ-η^2:η^2-Fp—C≡C—H)$Co_2(CO)_6$. Corresponding structural parameters are listed.

Table III. Selected Structural Parameters for 7[a]

	Bond Lengths		
C1–C2	1.32 (2)	Fe–C5	1.72 (2)
C1–Fe	1.93 (1)	Ni1–Ni2	2.375 (3)
C1–Ni1	2.03 (1)	Ni1–Ni3	2.581 (3)
C1–Ni2	2.10 (1)	Ni2–Ni3	2.549 (3)
C1–Ni3	1.94 (1)	Ni3–C4	1.70 (2)
C2–Ni1	1.85 (2)	Ni3–C5	1.81 (2)
C2–Ni2	1.85 (2)	C3–O3	1.16 (2)
Fe–Ni3	2.446 (3)	C4–O4	1.24 (2)
Fe–C4	1.87 (2)	C5–O5	1.16 (1)
	Bond Angles		
∠Fe–C1–C2	149 (1)	∠Ni2–Ni3–Fe	97.7 (1)
∠Ni3–C1–C2	132 (1)	∠Ni3–C3–O3	180 (2)
∠Ni2–Ni1–Ni3	61.73 (8)	∠Ni3–C4–O4	138 (1)
∠Ni1–Ni2–Ni3	63.12 (8)	∠Fe–C3–O3	139 (1)
∠Ni1–Ni3–Ni2	55.15 (7)	∠Ni3–C4–Fe	83.4 (7)
∠Ni1–Ni3–Fe	94.86 (9)	∠Fe–C5–O5	177 (1)

[a] Bond lengths in Å; bond angles in deg.

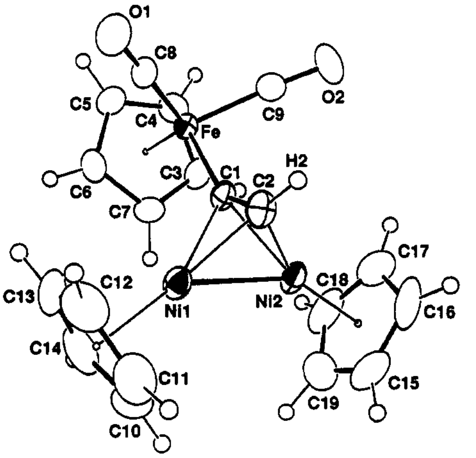


Figure 1. Perspective view of 6 drawn at the 30% probability level.

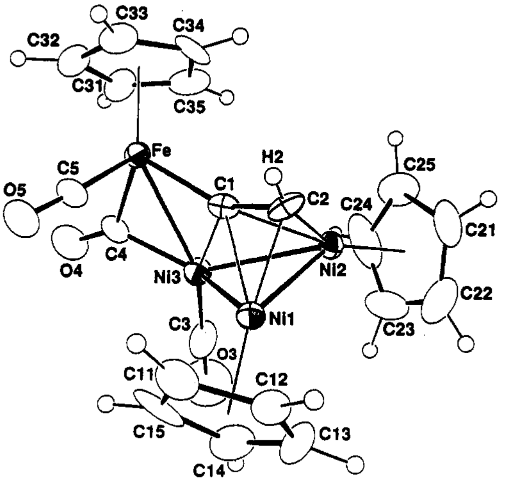
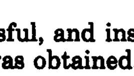


Figure 2. Perspective view of 7 drawn at the 30% probability level.

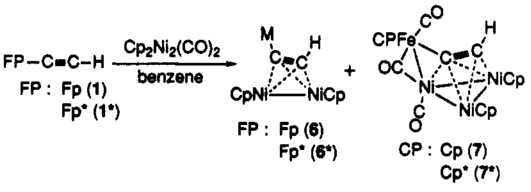
Chart I



9

Results and Discussion

Interaction of Ethynyliron Complexes 1 and 1* with $Cp_2Ni_2(CO)_2$ (5). Reaction of the ethynyliron complexes 1 and 1* with $Cp_2Ni_2(CO)_2$ (5) in heated benzene afforded a mixture of two products, i.e. the expected trinuclear adducts Cp_2Ni_2(μ-η^2:η^2-FP—C≡C—H) (6 and 6*) and tetranuclear adducts (CPFe)$(CpNi)_2Ni(CO)_2$(μ-CO)(μ_4-C_2H) (7 and 7*), respectively (eq 1). The structures of the Cp derivative 6 and 7 were characterized by spectroscopy as well as X-ray crystallography. While 7* was readily isolated and characterized by comparison with 7, formation of 6* was indicated only by ^{1}H NMR (vide infra). Application of another preparative method for (μ-η^2:η^2-R—C≡C—R)$(NiCp)_2$, i.e. treatment with nickelocene,[2] was unsuccessful, and instead, a mixture of unidentified products was obtained.



(1)

The crystallographic data and selected structural parameters of 6 and 7 are summarized in Tables I–III, and perspective views are reproduced in Figures 1 and 2.

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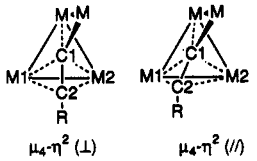
(3) The chemistry of polymetallic alkyne and alkynyl complexes has been studied extensively by Sappa et al., who already published review articles. (a) Alkyne clusters: Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (b) Butterfly clusters: Sappa, E.; Tiripicchio, A.; Carty, A. J.; Toogood, G. E. *Prog. Inorg. Chem.* **1987**, *35*, 437. (c) Ni-containing clusters: Sappa, E.; Tiripicchio, A. *New J. Chem.* **1988**, *12*, 599.

Chart II



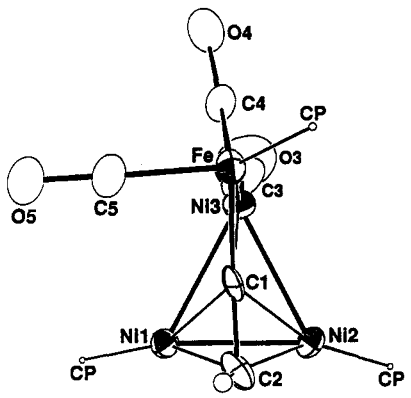
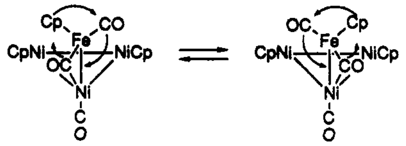


Figure 3. Top view of the core of 7.

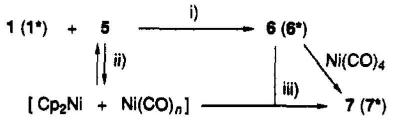
As for 6, the C_2H ligand interacts with the dinickel moiety to form the tetrahedral C_2Ni_2 core and, as a whole, binds the three metal centers together in a μ_3-η^1(Fe):η^2(Ni):η^2(Ni) fashion. The C_2Ni_2 core structure of 6 is very similar to that of the H—C≡C—H adduct (8)[4] except for the following minor differences: (1) The C≡C distance of 6 is shorter than that of 8 by 0.03 Å. (2) C2 lies closer to the Ni atoms by 0.04–0.05 Å than C1 does, whereas, in 8, the ethyne carbon atoms are equidistant from the Ni atoms.[5] These distortions may be interpreted in terms of a vinylidene resonance structure (9, Chart I) or steric hindrance due to the Fp group. This situation is essentially the same as the case of the 1–$Co_2(CO)_8$ adduct (3).[1d] In addition, it should be noted that the structure of the Fe—C—C part of 6 is very close to that of the dicobalt analogue 3[1d] (Table II). 6 (6*) showed ^{1}H and ^{13}C NMR spectra consistent with the crystal structure, and δ_C(C1) resonating in lower field than δ_C(C2) may support the contribution of 9.

The tetranuclear adduct 7 contains the "out-of-plane" spiked triangular metal core,[3] which interacts with the C_2H ligand. Similar $M_4(\mu_4\text{-}C_2R)$ complexes reported so far have been divided into two categories, that is, μ_4-η^2(⊥)- and μ_4-η^2(‖)-coordination modes,[7] which are characterized by terms Δ_1, $\Delta_2 \sim 0$ and Δ_1, $\Delta_2 > 0$, respectively, where $\Delta_1 = |D(\text{M1–C1}) - D(\text{M2–C1})|$ and $\Delta_2 = |D(\text{M1–C2}) - D(\text{M2–C2})|$ (D: distance) (Chart II). The parameters for 7 (Δ_1 = 0.07 Å, Δ_2 = 0.00 Å) fall in the former category, and the situation is evident from a top view of the core (Figure 3). The core structure of 7 is similar to that of $Cp_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4\text{-}C_2Ph)$ (Δ_1 = 0.022 Å, Δ_2 = 0.038 Å) reported by Carty et al.[6] In the NMR spectra of 7 and 7*, even at −80 °C, the two CpNi signals were observed equivalently and the two CO's bonded to Fe (C3–O3 and C4–O4) were observed as a broad signal. The fluxional behavior may be explained by a fast ligands' rotation around the Fe atom, and through this process 7 (7*) is converted to the other enantiomer (Scheme II). The C_2H signals located at δ(C1) 153.3 (7), 163.9 (7*) and δ(C2) 120.3 (7), 117.3 (7*) are unequivocally assigned on the basis of the J_{C-H} values. Similar δ(C) values were reported for $Cp_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4\text{-}C_2Ph)$ [δ(C1) 141.59, δ(C2) 142.61] discussed above.[6] It is noteworthy that the δ(C1)'s of 7, 7*, and Carty's Ni_2Fe_2 complex resonate in considerably higher field compared to previously reported $M_4(\mu_4\text{-}\eta^2\text{-}C_2R)$ compounds: [δ(C1), δ(C2)] = [209.4, 121.9] for $Ru_3Pt(\mu_4\text{-}\eta^2(\perp)\text{-}C_2Bu^t)(\mu\text{-}H)(CO)_9(COD)$;[7a] [228.3, 123.9] for $Ru_3Pt(\mu_4\text{-}\eta^2(\perp)\text{-}C_2Bu^t)(\mu\text{-}H)(CO)_9(dppe)$;[7a] [255.1, 138.9] for $Co_3Fe(\mu_4\text{-}\eta^2(\parallel)\text{-}C_2Ph)Cp_2(CO)_7$;[7b] [252.0, 126.3] for $Co_3Fe(\mu_4\text{-}\eta^2(\parallel)\text{-}C_2CF_3)Cp_2(CO)_7$.[7b]

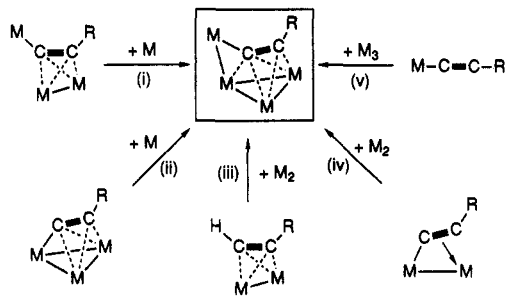
Scheme II



Scheme III



Scheme IV



When the structures of 6 (6*) and 7 (7*) are compared, 7 (7*) apparently results from a capping reaction of 6 (6*) with a Ni(CO) fragment.[8] Actually, the capping reaction was observed by the treatment of 6 with $Ni(CO)_4$. The reaction slowly proceeded even at room temperature, and after heating at 50 °C, 7 was isolated in 70% yield (eq 2).

$$6 + Ni(CO)_4 \xrightarrow[\text{benzene}]{} 7\ (70\%) \qquad (2)$$

In addition, NMR experiments at 40 °C in benzene-d_6 revealed several reaction features: (1) A 1:1 reaction of 1 and 5 produced an equilibrated mixture of 6 and 7 in a 1:5 ratio, and a 2:1 reaction afforded a 2.3:1 mixture of 6 and 7. (2) At an early stage of the 2:1 reaction of 1 and 5, exclusive formation of a small amount of 6 was observed. After prolonged heating 7 was produced with consumption of 6. Thus stepwise formation of 6 and 7 was confirmed. (3) Conversion of 6* to 7* was much faster than that of 6 to 7. Even a 4:1 reaction of 1* and 5 produced a 3:4 mixture of 6* and 7*. This feature and similar solubilities of the Cp* complexes hindered isolation of 6*, which was characterized only by the three singlets [δ (C_6D_6) 1.27 (15

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[4] Wang, Y.; Coppens, P. *Inorg. Chem.* **1976**, *15*, 1122.

[5] This is owing to crystallographic requirement. However, the Ni—C distances of the Ph—C≡C—Ph adduct without such requirement were also the same within experimental errors (Å): C1—Ni1, 1.89 (2); C1—Ni2, 1.89 (2); C2—Ni1, 1.90 (2); C2—Ni2, 1.87 (2). Mills, O. S.; Shaw, B. W. *J. Organomet. Chem.* **1968**, *11*, 595.

[6] Weatherell, C.; Taylor, N. J.; Carty, A. J.; Sappa, E.; Tiripicchio, A. *J. Organomet. Chem.* **1985**, *291*, C9.

[7] (a) Ewing, P.; Farrugia, L. J. *Organometallics* **1989**, *8*, 1246. (b) Rumin, R.; Robin, F.; Pettillon, Y.; Muir, K. W.; Stevenson, I. *Organometallics* **1991**, *10*, 2274.

[8] The formal capping reaction of a Ni(CO) fragment has precedents. See, for example: Fumagalli, A.; Longoni, G.; Chini, P.; Albinati, A.; Bruckner, S. *J. Organomet. Chem.* **1980**, *202*, 329. Capping reactions of an Au$^+$-L fragment which is isolobal with Ni(CO) have been well established. See: Salter, I. *Adv. Organomet. Chem.* **1990**, *29*, 249.

Table IV. Selected Structural Parameters for 10[a]

	Bond Lengths		
Fe–Ni	2.435 (1)	Ni–C3	1.888 (6)
Fe–C1	1.760 (6)	C1–O1	1.152 (7)
Fe–C2	1.897 (6)	C2–O2	1.177 (8)
Fe–C3	1.887 (6)	C3–O3	1.170 (9)
Ni–C2	1.864 (6)		
	Bond Angles		
∠Fe–C1–O1	177.2 (5)	∠Fe–C3–Ni	80.3 (3)
∠Fe–C2–O2	142.5 (5)	∠Ni–C2–O2	136.8 (4)
∠Fe–C3–O3	144.0 (4)	∠Ni–C3–O3	135.5 (4)
∠Fe–C2–Ni	80.7 (3)	∠Ni–Fe–C1	103.7 (2)

[a] Bond lengths in Å; bond angles in deg.

H, Cp*), 5.10 (10 H, Cp × 2), 5.44 (1 H, C_2H)] of the reaction mixtures.

On the basis of the obtained results a plausible reaction sequence leading to the formation of **6** (**6***) and **7** (**7***) is summarized in Scheme III. (i) At first, interaction of **1** (**1***) and **5** gives **6** (**6***). (ii) Under the reaction conditions **5** may be in equilibrium with nickelocene and a $Ni(CO)_n$ species. This is the reverse reaction of formation of **5** from Cp_2Ni and $Ni(CO)_4$ under thermal reaction conditions.[9] In addition, transfer or loss of the Cp ligand in a NiCp fragment in polymetallic complexes is precedented, for example, as reported by Sappa, Tiripicchio, and Carty et al. for $(CpRu)_2Ni(CO)_3(\mu_3\text{-}CO)(C_2Ph_2)$[10a] and $NiRu_4(CO)_9(\mu\text{-}PPh_2)_2(\mu_4\text{-}C_2Pr^i)_2$.[10b] (iii) The liberated $Ni(CO)_n$ species further reacts with **6** (**6***) to give **7** (**7***) via the capping reaction.

Now the $M_4(\mu_4\text{-}C_2R)$ cluster compounds with the "out-of-plane" spiked triangular metal core are available via several reaction routes in addition to the present capping reaction (i) (Scheme IV). Already reported methods involve (ii) the bridging reaction of $M_3(\mu_3\text{-}C_2R)$ complexes[7a,11a] and (iii)–(v) metal-addition reactions to di-[7b] and mononuclear[11b] 1-alkyne or acetylide complexes.

Reaction of Ethynediyldiiron Complex 2 with $Cp_2Ni_2(CO)_2$ (5). Interaction of the ethynediyldiiron complex (**2**) with **5** under similar reaction conditions resulted in the formation of an Fe–Ni mixed-metal complex (**10**) containing only Cp*, Cp, and CO ^{13}C NMR signals (eq 3). Since multiply bridging C_2 ligands often escape detection by ^{13}C NMR,[1d,12] the molecular structure of **10** has been determined by X-ray crystallography (Table IV and Figure 4). As a result, **10** proved to be an Fe–Ni complex without the C_2 ligand, $Cp^*FeCpNi(\mu\text{-}CO)_2(CO)$. Neither intermediate nor byproduct has been detected at all by means of ^1H NMR monitoring of the reaction mixture, and therefore the fate of the C_2 ligand was not clear until now.

$$\underset{\mathbf{2}}{Fp^*\text{—}C{\equiv}C\text{—}Fp^*} \xrightarrow[\text{benzene}]{Cp_2Ni_2(CO)_2} \underset{\mathbf{10}}{Cp^*FeCpNi(\mu\text{-}CO)_2(CO)} \tag{3}$$

The Cp analogue, $Cp_2FeNi(\mu\text{-}CO)_2(CO)$,[13] was prepared by a redistribution reaction between Fp_2 and **5**, but to our knowledge, its molecular structure determination has not been reported. The core structure of **10** is similar to that of $Cp_2Fe_2(\mu\text{-}CO)_2(CO)_2$,[14] where the bridging CO's lie almost equidistant from the two metal centers. The Fe–Ni distance is comparable to that in **7**, and the the Fe–C2–Ni–C3 plane is slightly folded from a planar structure [dihedral angle C2–Fe–Ni–C3 = 156 (3)°] presumably owing to steric hindrance of the Cp* ring.

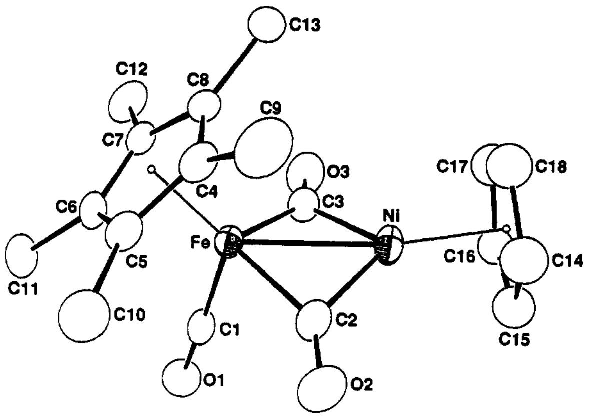

Figure 4. Perspective view of **10** drawn at the 30% probability level.

Concluding Remarks. This note has described the preparation and structure determination of the Fe,Ni-heteropolymetallic C_2H complexes. The results obtained are summarized as follows. (1) The ethynyliron complexes **1** and **1*** are successfully incorporated into $(\mu\text{-}\eta^2{:}\eta^2\text{-}R\text{—}C{\equiv}C\text{—}H)Ni_2Cp_2$-type complexes with a tetrahedral C_2Ni_2 core. However, introduction of the metal substituents (R = FP) does not have a significant influence on the core structure. A similar result has been obtained for the $(\mu\text{-}\eta^2{:}\eta^2\text{-}FP\text{—}C{\equiv}C\text{—}H)Co_2(CO)_6$ system.[1d] (2) Addition of a Ni(CO) fragment to the resultant adducts **6** (**6***) affords the tetranuclear adducts **7** (**7***) with the $\mu_4\text{-}\eta^1(Fe){:}\eta^2(Ni1){:}\eta^2(Ni2){:}\eta^1(Ni3)\text{-}C_2H$ ligand. This reaction serves as a new route to $M_4(\mu_4\text{-}C_2R)$ complexes. (3) Reaction of $Fp^*\text{—}C{\equiv}C\text{—}Fp^*$ (**2**) with $Cp_2Ni_2(CO)_2$ (**5**) results in elimination of the C_2 ligand to give the Fe—Ni dimer **10**.

Experimental Section

General Considerations. All manipulations were carried out under argon atmosphere by using standard Schlenk tube techniques. Benzene, ether, THF, and hexanes were dried over Na–K alloy, distilled, and stored under Ar. **1**, **1***, and **2** were prepared according to the methods described in our previous paper.[1a,b,d] **5** was prepared by the published method.[9] NMR, IR, and MS facilities have been described in our previous paper.[1d]

Interaction of $Fp\text{—}C{\equiv}C\text{—}H$ (1) with $Cp_2Ni_2(CO)_2$ (5). A benzene solution (20 mL) of **1** (266 mg, 1.32 mmol) and **5** (200 mg, 0.66 mmol) was heated for 22 h at 36 °C (in a GLC oven). After evaporation of the volatiles, products were extracted successively with ether (extract A) and THF (extract B). Filtration of extract A through an alumina pad (activity II–IV, Merck Art. 1097) followed by crystallization from ether–hexanes gave **6** (98 mg, 0.22 mmol, 33% yield based on **5**) as very dark red crystals. Filtration of extract B through the alumina pad used for extract A followed by crystallization from THF–hexanes gave **7** (43 mg, 0.08 mmol, 18% based on **5**) as dark brown crystals. **6**: ^1H NMR (C_6D_6) δ 4.23 (5 H, s, CpFe), 5.27 (10 H, s, CpNi × 2), 5.30 (1 H, s, CH); ^{13}C NMR (C_6D_6) δ 87.2 (d, ^1J = 172 Hz, CpNi), 88.2 (d, ^1J = 180 Hz, CpFe), 100.5 (d, ^1J = 206 Hz, CH), 127.5 (s, Fe—C), 215.0 (s, Fe—CO); IR (KBr) 2001, 1960 cm^{-1}. FD-MS m/z 449 (M^+). Anal. Calcd for $C_{19}H_{16}O_2FeNi_2$: C, 50.77; H, 3.56. Found: C, 50.63; H, 3.56. **7**: ^1H NMR (C_6D_6) δ 4.02 (5 H, s, CpFe) 4.99 (10 H, s, CpNi × 2), 7.36 (1 H, s, C_2H); ^{13}C NMR (C_6D_6) δ 86.4 (d, ^1J = 180 Hz, CpFe), 87.0 (d, ^1J = 175 Hz, CpFe), 120.3 (d, ^1J

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= 203 Hz, CH), 153.3 (s, Fe—C), 204.5 (s, Ni—CO), 234 (br, Fe—CO and μ-CO); IR (KBr) 1975, 1957, 1801 cm^{-1}; FD-MS *m/z* 536 (M$^+$). Anal. Calcd for $C_{20}H_{16}O_3FeNi_3$: C, 44.80; H, 2.98. Found: C, 44.54; H, 3.20.

A 1:2 reaction of **1** (301 mg, 1.49 mmol) and **5** (905 mg, 3.00 mmol) in heated benzene (16 mL, for 8 h at 65 °C) gave **7** (208 mg, 0.39 mmol, 28% isolated yield based on **1**).

Interaction of Fp*—C≡C—H (1*) with $Cp_2Ni_2(CO)_2$ (5). A benzene solution (20 mL) of **1*** (170 mg, 0.63 mmol) and **5** (191 mg, 0.63 mmol) was heated for 27 h at 60 °C. Evaporation of the volatiles, extraction with ether, and filtration through an alumina pad followed by crystallization from ether–hexanes gave **7*** (98 mg, 0.22 mmol, 33% yield based on $Cp_2Ni_2(CO)_2$) as brown crystals. **7***: ^{1}H NMR (C_6D_6) δ 1.32 (15 H, s, Cp*Fe) 5.08 (10 H, s, CpNi × 2), 7.73 (1 H, s, C_2H); ^{13}C NMR (C_6D_6) δ 9.6 (q, ^1J = 128 Hz, $C_5\mathit{Me}_5$), 87.1 (d, ^1J = 175 Hz, CpNi), 95.6 (s, C_5Me_5), 117.3 (d, ^1J = 201 Hz, CH), 163.9 (d, ^2J = 14 Hz, Fe—C), 205.9 (s, Ni—CO), 236.2 (Fe—CO and μ-CO); IR (KBr) 1972, 1950, 1788 cm^{-1}; FD-MS *m/z* 606 (M$^+$). Anal. Calcd for $C_{25}H_{26}O_3FeNi_3$: C, 49.53; H, 4.29. Found: C, 49.11; H, 4.29.

Attempts To Isolate 6*. Reactions of **1*** and **5** in <3:1 ratio gave only a very small amount of **6***. While a 4:1 reaction produced a 3:4 mixture of **6*** and **7***, repeated recrystallization resulted in recovery of excess **1*** and the evaporated residue of the final mother liquor contained only small amounts of **6*** and **7***. Attempted separation by column chromatography (alumina and silica gel) resulted in decomposition.

Conversion of 6 into 7 by Treatment with $Ni(CO)_4$. ***Caution***: Due to the extreme toxicity of $Ni(CO)_4$ all the manipulations should be carried out in a well-ventilated place.

A benzene solution (3 mL) of **6** (80 mg, 0.18 mmol) and $Ni(CO)_4$ (~30 μL, 0.23 mmol) was stirred overnight at ambient temperature. A small portion (0.1 mL) of the mixture was taken out and dried. Formation of a considerable amount of **7** was indicated by the bridging CO stretching vibration at 1800 cm^{-1}. Then the remaining solution was heated for 7 h at 50 °C. After evaporation of the volatiles, **7** was isolated from the residue as described above. Recrystallization gave **7** (66 mg, 0.12 mmol) in 70% yield.

Interaction of Fp*—C≡C—Fp* (2) with $Cp_2Ni_2(CO)_2$ (5). A benzene solution (25 mL) of **2** (500 mg, 0.97 mmol) and **5** (290 mg, 0.97 mmol) was heated at 55 °C for 2 days. After consumption of **2** was checked by TLC, the volatiles were removed under reduced pressure. Extraction with hexanes and filtration through a Celite pad followed by crystallization at −20 °C gave **10** (157 mg, 0.39 mmol, 40%) as yellow black crystals: ^{1}H NMR (C_6D_6) δ 1.43 (15 H, s, Cp*Fe) 5.37 (5 H, s, CpNi); ^{13}C NMR (C_6D_6) δ 9.0 ($C_5\mathit{Me}_5$), 93.9 (CpNi), 97.3 (C_5Me_5), 240 (br, CO); IR (KBr) 1986, 1787 cm^{-1}. Anal. Calcd for $C_{18}H_{20}O_3FeNi$: C, 54.22; H, 5.02. Found: C, 53.66; H, 5.19.

X-ray Crystallography of 6, 7, and 10. Single crystals of **6**, **7**, and **10** were obtained by recrystallization from ether–hexanes–toluene and ether–hexanes mixed-solvent systems, respectively, and mounted on glass fibers.

Diffraction measurements were made on a Rigaku AFC-5R (**6** and **10**) and AFC-5 (**7**) automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.710 59 Å). The unit cell was determined and refined by a least-squares method using 24 independent reflections with 19° < 2θ < 21° (**6** and **10**) and 15° < 2θ < 20° (**7**). Data were collected with ω–2θ scan technique. If $\sigma(F)/F$ was more than 0.1, a scan was repeated up to three times and the results were added to the first scan. Three standard reflections were monitored at every 150 (**6** and **10**) and 100 (**7**) measurements. Data processing of **6** and **10** was performed on a Micro Vax II computer by using the TEXSAN structure-solving program system, and data processing of **7** was performed on a FACOM A-70 computer by using the R-CRYSTAN data collection program system. Both systems were obtained from the Rigaku Corp., Tokyo, Japan. Neutral scattering factors were obtained from the standard sources.[15] In the reduction of data, Lorentz and polarization corrections and an empirical absorption correction (ψ scan) were made.

6 crystallized in an orthorhombic system, and **7** and **10** crystallized in monoclinic systems. The structures were solved by using the TEXSAN structure-solving program system. The positions of the metal atoms were located by the direct method (MITHRIL), and the structures were expanded by a combination of the direct method and Fourier synthesis (DIRDIF). For **6** and **7** all the non-hydrogen atoms were refined anisotropically. The hydrogen atoms except $C_2\mathit{H}$ were located at the ideal positions and were not refined, and the position of the $C_2\mathit{H}$ atom was refined with a fixed isotropic thermal parameter [B(H) = 1.2B(C)]. During the refinement of the structure of **10** it became apparent that there was disorder in the Cp part, which was refined isotropically by using a rigid η^5-C_5H_5 model (C–C = 1.40 Å; C–H = 0.95 Å). The occupancy factor of the two components was determined to be C14–18:C14A–18A = 0.648:0.352. The other non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were located at the ideal positions and were not refined [B(H) = 1.2B(C)].

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Supplementary Material Available: Tables of positional and anisotropic thermal parameters and bond lengths and angles for **6**, **7**, and **10** (23 pages). Ordering information is given on any current masthead page.

OM920241I

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Synthesis and Molecular Structure of $Fe_2(CO)_8[\mu\text{-}CuP(t\text{-}Bu)_3]_2$: A Distorted Fe_2Cu_2 Core with a Doubly $Cu(PR_3)$ Bridged Fe–Fe Single Bond

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Summary: Reported here are the synthesis and molecular structure of $Fe_2(CO)_8[\mu\text{-}CuP(t\text{-}Bu)_3]_2$, which contains an Fe_2Cu_2 butterfly metal core with the Fe–Fe single bond doubly bridged by two $CuP(t\text{-}Bu)_3$ fragments. The differences in the Fe–Cu bond distances (ca. 0.1 Å) and the deviation of the metal core from planarity (43.8°) can be attributed to the second-order Jahn–Teller effect and the steric effect imposed by the bulky $P(t\text{-}Bu)_3$ ligands. Crystal data for $Fe_2(CO)_8[\mu\text{-}CuP(t\text{-}Bu)_3]_2$: orthorhombic, space group $P2_12_12_1$, a = 8.881 (3) Å, b = 14.208 (3) Å, c = 31.114 (6) Å, Z = 4, and R = 0.027.

Recently we reported the syntheses and molecular structures of several group 8–group 11 mixed-metal complexes $M_2(CO)_8(\mu\text{-}CuPCy_3)_2$ (M = Fe, Ru; Cy = tricyclohexyl), $[PPh_4][Fe_2(CO)_8(\mu\text{-}CuPCy_3)]$, and $[PPh_4]_2\{[Fe_2(CO)_8]_2[\mu_4,\eta^2\text{-}Cu_2(Cy_2PCH_2CH_2PCy_2)]\}$.[1] The molecular structures of $M_2(CO)_8(\mu\text{-}CuPCy_3)_2$ (M = Fe, Ru) are without precedent in that the metal–metal *single* bond (Fe–Fe or Ru–Ru) is doubly bridged by two $Cu(PCy_3)$ fragments.[1] Two types of structural distortions from a symmetrical D_{2h} four-metal core were recognized in M_2-

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