Higher Nuclearity Fe,Ru Mixed-Metal Dicarbide Cluster Compounds Derived from Ethynediyldiiron Complex (η⁵-C₅Me₅)(CO)₂Fe−C≡C−Fe(η⁵-C₅Me₅)(CO)₂

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Reaction of the ethynyliron complexes $FP-C \equiv C-H$ [FP = Fp (1), Fp* (1*); Fp = ($\eta^5-C_5H_5$)-Fe(CO)₂; Fp* = ($\eta^5-C_5Me_5$)Fe(CO)₂] with Ru₃(CO)₁₂ in refluxing benzene affords triruthenium μ - $\eta^1(Ru1)$: $\eta^2(Ru2)$: $\eta^2(Ru3)$ -acetylide cluster type compounds Ru₃(CO)₉[μ_3 - η^1 : η^2 : $\eta^2-C \equiv C-FP$] [FP = Fp (3), Fp* (3*)] in a manner similar to the reaction of 1-alkynes. In contrast to the clean reaction of 1 and 1*, reaction of the ethynediyldiiron complex, Fp*-C \equiv C-Fp* (2*), gives a complicated mixture of products, from which Cp*₂Fe₂Ru₂(μ_4 -C₂)(CO)₁₀ (5*) and Cp*₂-Fe₂Ru₆(μ_6 -C₂)(CO)₁₇ (6*) are isolated and characterized as *permetalated ethene* and *permetalated ethane*, respectively, by X-ray crystallography. It is revealed that the permetalated hydrocarbon structures in 5* and 6* are constructed via formal addition of a dimetallic species to the C-C triple bond in 2*. The octanuclear complexes 6* and 6 (Cp derivative) are also prepared by thermal dimerization of the tetranuclear FeRu₃(μ -C₂) core in 3* and 3. Higher nuclearity cluster compounds including the heptanuclear dicarbide cluster compound CpFeRu₆(μ_5 -C₂)($(CO)_{17}$ (15) are obtained not only by thermolysis but also by one-electron oxidation of the deprotonated anionic form of 3 (13).

Introduction

The C=C functional group can bind metal centers together to form polynuclear compounds. In particular, transition metal acetylide complexes turn out to be versatile starting compounds for cluster compounds because the metal center originally σ -bonded to the acetylide ligand may take part in bond formation with the added metal species to form a three-dimensional metal framework.¹ The resulting structures have been recognized as models for surface-bound hydrocarbyl species,² which occur during conversions of syngas and hydrocarbon effected by heterogeneous catalysts.³ Previous studies have revealed a variety of coordination modes of acetylide cluster compounds, but many of them contain acetylide substituents, which may not be always suitable as surface species (e.g., ester). In this regard, ethynyl (M–C=C–H) and ethynediyl complexes (M– C=C–M)⁴ containing the substituents of the simple composition are expected to display structural and reaction features closer to those of the actual surfacebound species. A polynuclear complex with the C₂ ligand can be recognized as a dicarbide cluster compound, which is a member of transition metal complexes associated with carbon allotropes (C_x) including monocarbon species and fullurenes.^{5,6} We have been carrying out a synthetic study of polynuclear C2⁷ complexes derived from the ethynyl [FP–C=C–H: FP = Fp (1), Fp* (1*); Fp = (η^{5} -C₅H₅)Fe(CO)₂; Fp* = (η^{5} -C₅Me₅)Fe(CO)₂] and ethynediyl iron complexes [Fp*–C=C–Fp* (2*)] (Scheme

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1),^{7,8b,k} and have reported various novel aspects of these systems including H shift on the C_2 bridge, conversion to C_2H_x species, and reversible M–M bond scission.⁸

Herein we disclose details of the results of interaction of the C2 iron complexes $(1, 1^*, \text{and } 2^*)^7$ with $\text{Ru}_3(\text{CO})_{12}$, leading to higher nuclearity Fe,Ru mixed-metal dicarbide cluster compounds. Preliminary reports already appeared,^{8c,h} and studies on the molecular orbital analysis of polynuclear C₂ complexes including the compounds presented herein and related compounds were reported recently by Halet et al.⁹

Reaction of alkynes with $Ru_3(CO)_{12}$ has long been studied extensively (Scheme 1). Previous studies reveal that reaction with 1-alkynes produces the triruthenium acetylide cluster compounds in a selective manner via C-H bond oxidative addition, whereas internal alkynes afford various products depending on the structure of the alkyne substituents and the reaction conditions.¹⁰

Results and Discussion

Interaction of Ethynyliron Complexes FP-C=C-H [FP = Fp (1), Fp* (1*)] with $Ru_3(CO)_{12}$,

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Gladysz, J. A. J. Am. Chem. Soc. **2000**, 122, 810. (7) The term "C2" stands for two carbon systems including C₂ and C₂H species. All Cp* complexes are indicated by asterisks in their compound numbers. Fp: $(\eta^5\text{-}C_5\text{H}_5)\text{Fe}(\text{CO})_2$. Fp*: $(\eta^5\text{-}C_5\text{Me}_5)\text{Fe}(\text{CO})_2$. Cp: $\eta^5\text{-}C_5\text{H}_5$. Cp*: $\eta^5\text{-}C_5\text{Me}_5$. Ru: Ru(CO)₃. **Ru**: Ru(CO)₂.

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Figure 1. Molecular structure of **3** drawn (with displacement ellipsoid amplitudes) at the 30% probability level. Labels without atom names are for CO ligands.

Leading to Acetylide Cluster Type Tetranuclear Dicarbide Cluster Compounds (μ_3 -C=C-FP)(μ -H)-Ru₃(CO)₉ [FP = Fp (3), Fp* (3*)]. Treatment of the ethynyl complexes 1 and 1* with Ru₃(CO)₁₂ in refluxing benzene gave yellow-orange crystals 3 and 3*, respectively, as sole organometallic products (eq 1). The simple



¹H NMR spectra containing the characteristic shielded hydride signals [$\delta_{\rm H}$ -20.05 (**3**), -19.56 (**3***)] in addition to the η^{5} -C₅R₅ resonances [$\delta_{\rm H}$ 3.90 (**3**), 1.25 (**3***)] indicated formation of the acetylide cluster type products analogous to the reaction product of 1-alkyne (Scheme 1).

The cluster compound **3** was characterized by X-ray crystallography, and the molecular structure and selected structural parameters are shown in Figure 1 and Table 1, respectively. Because no bonding interaction is present between the distal Fe center and the Ru₃ triangle, the Fp group simply works as an acetylide substituent. In other words, **3** is better described as a triruthenium μ - $\eta^1(\text{Ru1})$: $\eta^2(\text{Ru2})$: $\eta^2(\text{Ru3})$ -acetylide cluster compound with the Fp–C=C acetylide ligand rather than as a tetranuclear μ - $\eta^1(\text{Fe})$: $\eta^1(\text{Ru1})$: $\eta^2(\text{Ru2})$: $\eta^2(\text{Ru3})$ -dicarbide cluster compound. The core structure of **3** is very similar to that in the previously reported organic

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Table 1. Comparison of Structural Parameters for Acetylide Cluster Type Compounds



			1112	•		
	3	10*	13	4 ^a	14 ^b	16 ^{<i>c</i>}
	M1, M2 = Ru, Ru	M1, M2 = Fe, Ru	M1, M2 = Ru, Ru	M1, M2 = Ru, Ru	M1, M2 = Ru, Ru	M1, M2 = Fe, Fe
	M3, M4 = Ru , Fe	M3, M4 = Ru, Fe	M3, M4 = Ru, Fe	M3, M4 = Ru, Bu ^{t}	M3, M4 = Ru, Bu ^{t}	M3, $M4 = Fe$, Fe
	X = H	X = H	X = none	X = H	none	none
			Bond Lengths (A	Á)		
C1-C2	1.33(2)	1.32(1)	1.271(9)	1.315(3)	1.27(3)	1.288(5)
C1-M4	1.90(1)	1.947(9)	1.984(8)	1.500(3)	1.54(3)	1.959(3)
C1-M2	2.41(1)	2.395(8)	2.347(7)	2.268(3)	2.24(2)	2.190(3)
C1-M3	2.40(1)	2.377(8)	2.349(7)	2.271(3)	2.24(2)	2.212(3)
C2-M1	2.01(1)	1.834(9)	1.984(8)	1.947(3)	1.95(2)	1.839(3)
C2-M2	2.22(1)	2.203(8)	2.189(7)	2.207(3)	2.18(2)	2.020(3)
C2-M3	2.20(1)	2.169(8)	2.199(7)	2.214(3)	2.16(2)	2.021(3)
M1-M2	2.781(2)	2.707(2)	2.7891(9)	2.795(3)	2.800(3)	2.6207(7)
M1-M3	2.774(2)	2.699(1)	2.793(1)	2.799(3)	2.790(3)	2.6252(8)
M2-M3	2.819(2)	2.791(1)	2.6886(9)	2.792(3)	2.665(3)	2.5048(8)
M1-CO	1.89 - 1.94(2)	1.80 - 1.86(1)	1.87 - 1.90(1)	1.898 - 1.931(4)	1.90 - 1.92(2)	1.765 - 1.784(4)
M2-CO	1.96 - 2.00(2)	1.92 - 1.94(1)	1.861 - 1.890(9)	1.910 - 1.938(4)	1.88 - 1.89(2)	1.762 - 1.784(4)
M3-CO	1.90(2)	1.93 - 1.96(1)	1.86 - 1.88(1)	1.910 - 1.944(4)	1.85 - 1.92(2)	1.772 - 1.780(4)
M4-CO	1.80(2)	1.76-1.78(1)	1.744-1.768(9)			1.768-1.772(4)
			Bond Angles (de	g)		
C2-C1-M4	149(1)	147.7(7)	149.3(6)	141.0(2)	141(2)	147.3(3)
C2-C1-M2	65.5(7)	65.5(5)	67.0(4)	70.4(1)	76(1)	d
C2-C1-M3	65.3(8)	64.6(5)	67.4(5)	70.6(1)	77(1)	d
M2-C1-M3	71.7(4)	71.6(2)	69.9(2)	75.9(1)	73(1)	d
M4-C1-M2	135.3(7)	138.9(4)	136.0(3)	135.2(2)	134(1)	d
M4-C1-M3	135.9(7)	134.2(4)	133.1(4)	135.0(2)	138(1)	d
C1-C2-M1	159(1)	161.4(7)	160.1(6)	153.7(2)	156(1)	161.6(3)
M2-C2-M3	79.2(4)	79.3(3)	75.6(2)	78.3(1)	76(1)	d
C1-C2-M2	81.6(8)	81.5(5)	80.7(5)	75.5(1)	76(1)	d
C1-C2-M3	81.6(8)	82.0(5)	80.4(5)	75.3(1)	77(1)	d
M1-C2-M2	82.2(4)	83.7(3)	83.8(3)	84.3(1)	85(1)	d
M1-C2-M3	82.3(4)	84.3(3)	83.7(3)	84.3(1)	85(1)	d
M2-M1-M3	61.00(4)	62.16(4)	57.58(2)	59.9(1)	56.9(1)	57.04(2)
M1-M2-M3	59.38(4)	58.77(3)	61.29(2)	60.1(1)	61.3(1)	61.57(2)
M1-M3-M2	59.62(4)	59.07(4)	61.13(2)	60.0(1)	61.7(1)	61.39(2)
M1-C-O	173-177(2)	178-180(1)	176.9-179.7(8)	176.9-178.3(1)	174-177(2)	178.3-179.4(4)
M2-C-O	176 - 177(2)	174-179(2)	176.2-177.2(8)	176.0-179.0(1)	175-178(2)	176.6-178.3(3)
М3-С-О	176-180(1)	176-179(1)	177-178(1)	175.0-179.9(3)	175 - 178(2)	176.4-177.5(4)
M4-C-O	178(2)	176(1)	175.5 - 177.9(8)			172.9 - 178.0(4)

^{*a*} Ru₃(μ_3 -C=C-Bu⁴)(μ -H)(CO)₉, neutron diffraction, ref 11. ^{*b*} (AsPh₄)[Ru₃(μ_3 -C=C-Bu⁴)(CO)₉], ref 21. ^{*c*} A tetrairon analogue of **13**, (PPN)[Fe₃(μ_3 -C=C-Fp)(CO)₉], ref 5d. ^{*d*} Not reported.

acetylide cluster compound $(\mu_3-C=C-Bu^{\dagger})(\mu-H)Ru_3(CO)_9$ (4) $[\mathbf{R} = \mathbf{Bu}^t$ (Scheme 1); Table 1].¹¹ Upon coordination, the C-C distance [1.33(2) Å] is slightly elongated compared to that of the starting compound [1*: 1.173-(4) Å].^{8k} The Fe-C1 [1.90(1) Å] and Ru1-C2 distances [2.01(1) Å] fall in the range of single bond lengths, and the similar distances between the other two Ru centers and the acetylide carbon atoms [Ru2-C1 2.41(1) Å, Ru3–C1 2.40(1) Å; Ru2–C2 2.22(1) Å, Ru3–C2 2.20(1) Å] typical for π coordination indicate symmetrical coordination of the C2-C1-Fe linkage with respect to the Ru₃ triangle. Although the hydride atom cannot be located, it should be on the Ru2-Ru3 bond, the distance [2.819(2) Å] of which is slightly longer than the other two Ru-Ru distances [2.774(2) and 2.781(2) Å]. In accord with the structure, the C₂ signals [$\delta_{\rm C}$ 79.7, 174.1 (3); $\delta_{\rm C}$ 96.8, 168.1 (3*)] appear in the range analogous to that for trinuclear acetylide cluster compounds of $(\mu_3$ - $C \equiv C - R)M_3$ type,¹ and the deshielded signals are assigned to C2. Details of the structural aspects will be discussed later as compared with related compounds.

Interaction of Ethynediyl Complex Fp*-C=C-Fp* (2*) with Ru₃(CO)₁₂. Sequential Formation of Permetalated Ethene (5*) and Ethane Type Cluster Compounds (6*). In contrast to the clean reaction of 1 and 1*, reaction of 2^* gave a complicated mixture of products in a manner similar to the reaction of internal alkynes (Scheme 1).¹⁰ In addition to the two known compounds (3* and Fp*2), two new compounds **5*** and **6*** showing only one Cp* resonance (¹H NMR) were isolated from the reaction mixture and characterized as *permetalated* ethene and *permetalated* ethane, respectively, by X-ray crystallography (Scheme 2). Molecular structures of 5* and 6* together with expanded views of the core parts are shown in Figures 2 and 3, and selected structural parameters are listed in Tables 2 and 3.

Complex 5^* is found to be a tetranuclear Fe₂Ru₂ complex containing one C₂ ligand and has a C₂-symmetrical structure with respect to the axis passing

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through the midpoints of the C–C and Ru–Ru bonds. The four metal atoms are linked by metal-metal bonds to form an open-rectangular array, which is slightly twisted as can be seen from a top view of the core structure (Figure 3c; Fe-Ru-Ru*-Fe* dihedral angle is 24°). The C₂ ligand interacts with the metal array through σ bonds [Fe–C1, 1.946(7) Å; Ru–C1, 2.204(7)], although the Ru–C1 distance is in the upper limit of **Ru**–**C** σ bond lengths and comparable to π bond lengths [cf. σ bond, 2.026(7) and 2.033(7) Å for Cp₂Ru₂(μ -C=CH₂)(CO)₃;¹² π bond, see, for example, the Ru2,3-C12 lengths (2.2–2.4 Å) for **3** (Table 1)]. The C1–C1* distance [1.24(1) Å] is longer than the C=C distance of the ethynediyl complex $2^{\#}$ [η^5 -C₅Me₄Et derivative of 2^{*} (with two independent molecules): 1.206(6), 1.211(6) Å]^{8k} but substantially shorter than normal $C(sp^2) =$ C(sp²) lengths (1.34 Å).¹³ The C–C linkage, which spans the two iron atoms at both the ends of the openrectangular array, causes distortion of the $Fe_2Ru_2(\mu_4$ - C_2) moiety as judged by the slightly elongated Ru1-Ru1* distance [2.963(2) Å; cf. Ru–Ru lengths (\sim 2.8 Å) in Table 1] and the twisting of the Fe₂Ru₂ array. The two Cp* rings are located in trans configuration with respect to the $Fe_2Ru_2(\mu_4-C_2)$ moiety to avoid steric repulsion between them. NMR data suggesting a symmetrical structure are consistent with the C_2 -symmetrical X-ray structure. The C₂ signal at $\delta_{\rm C}$ 177.2, assigned by comparison with a sample obtained from ¹³CO-enriched Ru₃(CO)₁₂, is highly shielded compared to the α -carbon signals ($\delta_C \sim 300$) of dinuclear μ -vinylidene complexes $[M_2(\mu - C_{\alpha} = CR_2)]$,^{6d} which can be regarded as a partial structure of 5*. Because the five carbonyl ligands are observed separately, they do not exchange at ambient temperature in a solution. Although a number of related complexes including μ -vinylidene complexes^{6d} and alkyne cluster complexes¹ have been reported so far, complex 5* is the first example of a permetalated ethene, $(Cp*Fe)_2Ru_2(\mu_4 C=C)(\mu-CO)_2(CO)_8$. The EHMO calculation done by Halet on the CpRu analogue $(CpRu)_2Ru_2(\mu_4-C=C)(\mu_4-C=C)$ $CO_2(CO)_8$ clearly indicates that it is a permetalated ethene in which the filled out-of-plane π -type p orbitals of the C₂ unit play a minor role in the M-C bonding.^{9a} The p orbitals form a π bond as found in ethene,

although the rather short carbon–carbon double bond should be a result of less effective back-donation due to the distorted structure as discussed above. A formal addition reaction of a diruthenium species to the C \equiv C bond in the ethynediyl complex **2*** should lead to the coordinatively saturated permetalated ethene structure **5*** with 66 cluster valence electrons (CVE) (Scheme 3).

Recently Kousantonis et al. reported the syntheses of the $(\eta^5$ -C₅H₄R)Ru analogues of **5**^{*}, $[(\eta^5$ -C₅H₄R)Ru]₂- $Ru_2(\mu_4-C_2)(CO)_{10}$ (7) [R = H (*cis*-7a), Me (*trans*-7b)], via addition of a mononuclear species, Ru(ethene)(CO)4, to the μ -ethynediyldiruthenium complexes (η^5 -C₅H₄R)(CO)₂- $Ru-C \equiv C-Ru(\eta^5-C_5H_4R)(CO)_2^{-14}$ (cis and trans refer to configuration of the two η^5 -C₅H₄R rings with respect to the Ru₄(μ_4 -C₂) moiety). The features for the M₄(μ_4 -C₂) cores [C-C: 1.258(5) (cis-7a), 1.252(4), 1.258(4) Å (*trans*-7b with two independent molecules); $\delta_{\rm C}$ 154.9 (*cis*-**7a**), 157.1 (*trans*-**7b**)] are essentially the same as those of 5^{*}, and the twisting of the $M_4(\mu_4-C_2)$ core is correlated to the configuration of the cyclopentadienyl rings. The Ru₄C₂ core in *cis*-7a is more closely planar compared to those in trans-7b. The authors proposed that the permetalated ethene structure was formed via sequential addition of a mononuclear species, $Ru(CO)_{n}$, because the reaction afforded both cis and trans isomers, which were not interconverted with each other.

The second product **6*** (Figure 3) has been characterized as an octanuclear compound containing the two C_2 units. The metal array is based on the central Ru_4 square (Ru1–Ru2–Ru3–Ru4), each edge of which is bridged by either the Fe or Ru atom, and the bridging metal atoms are located alternately above and below the Ru_4 square. The C_2 ligand bridges the Fe and Ru centers projected to the same side to interact with the boat-shaped FeRu₅ metal framework. The two C_2 rods above and below the Ru_4 plane are arranged perpendicular to each other, as can be seen from a top view of the core part (Figure 3c).

When the bonding interaction of the C_2 bridge is inspected in detail, the C-C distances [C1-C2, 1.334-(8) Å; C3–C4, 1.354(7) Å] are further longer than the C-C distances in 5^* and $2^{\#}$ but are found to be comparable to C(sp)-C(sp) single bond lengths [cf. butadiyne: 1.384(2) Å].^{13,15} The distances from the C₂ carbon atoms to the out-of-plane metals (Fe1, Fe2, Ru5, Ru6) [C1-Fe1, 1.908(6) Å; C2-Ru5, 1.997(6) Å; C3-Fe2, 1.866(5) Å; C4-Ru6, 1.993(5) Å] are in the ranges of typical σ bond lengths, and the slightly longer C_2 -Ru1-4 distances [2.123-2.205(6) Å] indicate contribution of π -bonding interactions between the C₂ ligand and the Ru₄ square. Although connection of two corners of the two metal triangles by two metal-metal bonds forms the distorted boat-shaped core structure, the C₂-metal bonds are basically σ bonds, and therefore, the C₂M₆ moieties can be described as a *permetalated ethane*. The bis(dicarbide) cluster compound **6*** is found to be coordinatively saturated judging from the number of its cluster valence electrons (124 e).

⁽¹²⁾ Colborn, R. E.; Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Orpen, A. G.; Plaas, D. J. Chem. Soc., Dalton Trans. **1983**, 2661.

⁽¹³⁾ March, J. Advanced Organic Chemistry, 3rd ed.; John Wiley and Sons: New York, 1985.

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 1979, 179, 394.



Figure 2. Molecular structure of **5*** drawn (with displacement ellipsoid amplitudes) at the 30% probability level, where labels without atom names are for CO ligands: (a) overview; (b) side view of the core part; (c) top view of the core part.



Figure 3. Molecular structure of 6^* drawn (with displacement ellipsoid amplitudes) at the 30% probability level, where labels without atom names are for CO ligands: (a) overview; (b) overview of the core part; (c) top view of the core part.

A ¹³C NMR spectrum of **6*** observed at 25 °C (Figure 4a,b) contains one set of Cp* signals and seven quaternary carbon signals, suggesting the occurrence of dynamic behavior. Below -60 °C, 10 quaternary carbon signals are observed in addition to the Cp* signals, for which no apparent change is noted (Figure 4c). First of all, the C₂ signals ($\delta_{\rm C}$ 203.2, 209.0) are assigned by comparison with a sample obtained from ¹³CO-enriched Ru₃(CO)₁₂ (Figure 4d).¹⁶ The remaining eight signals

Table 2. S	Selected	Structural	Parameters	for 5*
	Juiceucu	Suucuiai	1 an ameters	101 0

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	Bond Len	gths (Å)	
C1-C1*	1.24(1)	Ru-C3	1.885(8)
C1–Fe	1.946(7)	Ru-C4	1.905(9)
C1-Ru	2.204(7)	Ru-C5	2.047(8)
Ru-Ru*	2.963(2)	Fe-C5	1.932(8)
Ru–Fe	2.733(2)	Fe-C6	1.740(8)
Ru-C2	1.933(9)		
	Bond Ang	les (deg)	
Ru-C1-C1*	112.0(2)	C2–Ru–C3	88.5(3)
Fe-C1-C1*	165.5(2)	C2-Ru-C4	174.2(3)
Ru-C1-Fe	82.1(2)	C2-Ru-C5	90.0(3)
Ru*-Ru-Fe	110.61(4)	C3-Ru-C4	86.5(4)
Ru*-Ru-C1	66.5(2)	C3-Ru-C5	105.7(4)
Ru*-Ru-C2	92.7(2)	C4-Ru-C5	94.1(3)
Ru*-Ru-C3	98.7(3)	Ru-Fe-C1	53.0(2)
Ru*-Ru-C4	85.3(3)	Ru-Fe-C5	48.4(2)
Ru*-Ru-C5	155.5(2)	Ru-Fe-C6	95.5(3)
Fe-Ru-C1	44.9(2)	C1-Fe-C5	100.9(3)
Fe-Ru-C2	93.0(2)	C1-Fe-C6	90.9(4)
Fe-Ru-C3	150.5(3)	C5-Fe-C6	88.8(4)
Fe-Ru-C4	92.8(3)	Ru-C-O	173.9 –
Fe-Ru-C5	44.9(2)		178.5(9)
C1-Ru-C2	87.5(3)	Ru-C5-Fe	86.7(3)
C1-Ru-C3	164.4(3)	Ru-C5-O5	134.2(7)
C1-Ru-C4	96.7(3)	Fe-C5-O5	139.0(7)
C1-Ru-C5	89.4(3)	Fe-C6-O6	179.3(8)

are, therefore, due to M–CO (seven η^1 -CO and one μ -CO). These spectral features can be interpreted in terms of the mechanism shown in Scheme 4. The inconsistency between the apparent C_2 -symmetrical NMR feature and the X-ray structure with no element of symmetry can be explained by the fast switching of the two bridging carbonyl ligands (indicated as B and B') attached to Ru_A (process a). The switching is not frozen even at -80 °C, and signals for B and B' are not detected in the temperature range 25 to −80 °C because of broadening. The three signals observed at low temperatures (Figure 3c) can be assigned to the CO ligands (F-H) attached to Ru_C, which are not observed at 25 °C because of the Ru_C(CO)₃ rotation (process b) occurring at a rate faster than the NMR time scale. Thus, the seven quaternary signals observed at 25 °C are due to C1, C2, A, C, D, E, and I, and freezing of the

⁽¹⁶⁾ The ¹³C NMR signals for the C₂ ligands of **6*** were reported.^{8c} But careful reexamination of ¹³C NMR measurements revealed that they were due to impurities and the signals could not be located at ambient temperature because of the dynamic processes.

 Table 3. Selected Structural Parameters for 6*

		Bond I	Lengths (Å)		
C1-C2	1.334(8)	C4–Ru6	1.993(5)	C13-Ru1	2.189(7)
C3-C4	1.354(7)	Ru1–Ru2	2.7710(6)	C13-Fe1	1.879(8)
C1-Fe1	1.908(6)	Ru1–Ru4	2.8466(7)	C14-Fe1	1.874(7)
C1-Ru1	2.205(6)	Ru1–Ru6	2.8286(6)	C14-Ru2	2.184(8)
C1-Ru2	2.181(6)	Ru1–Fe1	2.711(1)	C17-Ru3	2.373(8)
C2-Ru3	2.147(6)	Ru2–Ru3	2.8383(7)	C17-Fe2	1.780(8)
C2-Ru4	2.142(6)	Ru2–Fe1	2.7252(9)	Ru-CO	1.866 - 1.968(8)
C2-Ru5	1.997(6)	Ru2–Fe2	2.8442(9)	Fe-C(Cp*)	2.086 - 2.139(7)
C3-Fe2	1.866(5)	Ru3–Ru4	2.8501(6)	C13-O13	1.16(1)
C3-Ru2	2.202(5)	Ru3–Ru5	2.815(1)	C14-O14	1.17(1)
C3-Ru3	2.187(6)	Ru3–Fe2	2.677(1)	C17-O17	1.17(1)
C4-Ru1	2.183(6)	Ru4–Ru5	2.7513(9)	C-O	1.11 - 1.16(1)
C4-Ru4	2.123(6)	Ru4–Ru6	2.7518(7)		
		Bond A	nglas (dag)		
$P_{11} = C_1 = P_{11}$	78 3(9)	$P_{11} = C_1 = C_2$	108.3(4)	$P_{115}-P_{113}-F_{02}$	160 76(3)
Ru1 = C1 = Ru2	82 1(2)	Ru1 C4 C3 Ru4 - C4 - Ru6	83 0(2)	$P_{11} = P_{11} = P_{11} = P_{11}$	01.64(2)
Ru1 = C1 = C2	120 6(4)	$R_{11}/C_{1}/C_{3}$	98 6(A)	Ru1 - Ru4 - Ru5	120 63(2)
$Ru2 - C1 - E_{01}$	83 3(2)	$R_{116} - C_{1} - C_{3}$	166 6(4)	Ru1 - Ru4 - Ru6	60.67(2)
Ru2 = C1 = C2	120 A(A)	$R_{11}2 - R_{11}1 - R_{11}A$	87 99(2)	Ru3 - Ru4 - Ru5	60.31(2)
$F_{01}-C_{1}-C_{2}$	1/85(5)	$R_{11}2 - R_{11}1 - R_{11}6$	115 53(2)	Ru3 - Ru4 - Ru6	121 62(2)
Ru3 - C2 - Ru4	83 3(2)	$R_{11}2 - R_{11}1 - F_{01}1$	59 60(2)	$R_{115} - R_{114} - R_{116}$	177 93(2)
Ru3 - C2 - Ru5	85.5(2)	$R_{11}4 - R_{11}1 - R_{11}6$	58.00(2)	Ru3 - Ru5 - Ru4	61.58(2)
Ru3-C2-C1	100.5(2)	$R_{11}4 - R_{11}1 - Fe1$	106.11(2)	Ru1 - Ru6 - Ru4	61.32(2)
Ru4 - C2 - Ru5	83 3(2)	Ru6-Ru1-Fe1	164 12(3)	$R_{11} - Fe_1 - R_{12}$	61.02(2)
$R_{11}4 - C_{2}^{2} - C_{1}^{2}$	99 8(4)	Ru1 - Ru2 - Ru3	93 48(2)	$R_{11}^2 - Fe^2 - R_{11}^3$	61.20(2)
Ru5 - C2 - C1	173 5(5)	Ru1-Ru2-Fe1	59.10(2)	Ru1 - C13 - O13	132 3(6)
Ru2-C3-Ru3	80.6(2)	Ru1-Ru2-Fe2	110 14(2)	Fe1-C13-O13	144 4(6)
Ru2-C3-Fe2	88.3(2)	Ru3-Ru2-Fe1	105.67(3)	$R_{12}-C_{14}-O_{14}$	132.4(6)
Ru2-C3-C4	108.8(4)	Ru3-Ru2-Fe2	56.20(2)	Fe1-C14-O14	143.5(7)
Ru3-C3-Fe2	82.2(2)	Fe1-Ru2-Fe2	160.08(3)	Ru3-C17-O17	124.9(7)
Ru3-C3-C4	122.1(4)	Ru2-Ru3-Ru4	86.63(2)	Fe2-C17-O17	156.1(8)
Fe2-C3-C4	151.5(5)	Ru2-Ru3-Ru5	119.78(2)	Ru-C-O	173.2 - 178.6(7)
Ru1-C4-Ru4	82.8(2)	Ru4-Ru3-Ru5	58.10(2)		1.0.2 1.0.0(1)
Ru1-C4-Ru6	85.1(2)	Ru4–Ru3–Fe2	104.30(3)		

Scheme 3



(Only pertinent ligands are shown for clarity.)

Ru_C(CO)₃ rotation at low temperatures causes the appearance of 10 signals (C1, C2, A, C, D, E, F, G, H, and I). The C₂ signals are shielded compared to those of **8b** ($\delta_{\rm C}$ 279.4, 285.7) and **8c** ($\delta_{\rm C}$ 285.9, 293.7), the chemical shifts of which are typical for μ_3 -alkylidyne carbon atoms.¹⁷

The first example of a permetalated ethane, $Co_6(\mu_6-C_2)(CO)_{18}$ (**8a**), was isolated from a mixture resulting from thermolysis of the μ_3 -bromomethylidyne tricobalt



Figure 4. ¹³C NMR spectra of **6*** observed at 100 MHz: (a) full spectrum observed at 25 °C; (b) expanded spectrum of (a); (c) expanded spectrum, observed at -60 °C; (d) expended spectrum of a ¹³CO-enriched sample, observed at -60 °C.

cluster compound (μ_3 -BrC)Co₃(CO)₉, as reported by Ercoli in 1966^{5a} and later structurally characterized by Penfold.^{5b} The metal framework consists of two separated Co₃ triangles, which are bridged by the C₂ ligand. Later isoelectronic anionic Fe,Co mixed-metal cluster compounds [Fe₄Co₂(μ_6 -C₂)(CO)₁₈]^{2–} (**8b**) and [Fe₃Co₃(μ_6 -

⁽¹⁷⁾ Mann, B. E.; Taylor, B. F. ¹³C NMR Data for Organometallic Compounds, Academic Press: London, 1981.

Scheme 4



C₂)(CO)₁₈]⁻ (**8c**) were synthesized via a different route (metal addition to an Fe₄-acetylide cluster type C₂ complex) by Shriver.^{5c} A Co₆ cluster compound with the metal framework very similar to the upper half of **6**, Co₆(μ_6 -C₂)(μ_4 -S)(CO)₁₄ (**9**), was isolated from a reaction mixture of Co₂(CO)₈ and CS₂ as reported by Stangellini.^{5e} Their C-C lengths [1.37(1) Å (**8a**), 1.362(8) Å (**8b**), 1.37-(2) Å (**9**)] are comparable to that of **6***.

When the reaction of 2^* with Ru₃(CO)₁₂ was monitored by ¹H NMR, the permetalated ethene 5^* appeared first and subsequently the acetylide 3^* and the permetalated ethane 6^* were gradually formed. In addition, complex 5^* was found to be thermally less stable than 3^* and 6^* . These observations suggest that the permetalated ethane 6^* may be formed by addition of a ruthenium species to 5^* or thermal dimerization of the FeRu₃(μ -C₂) core in 3^* . To confirm these possibilities, reaction of an isolated sample of 5^* with Ru₃(CO)₁ (eq 2) and thermolysis of 3^* (eq 3) were examined. As a

$$\mathbf{5^*} + \operatorname{Ru}_3(\operatorname{CO})_{12} \xrightarrow[\text{refluxing toluene}]{} \mathbf{3^*} (50\%) + \mathbf{6^*} (20\%)$$
(2)

$$3^* \xrightarrow[\text{refluxing toluene]} 6^* (42\%) \tag{3}$$

result, reaction of **5**^{*} with $\operatorname{Ru}_3(\operatorname{CO})_{12}$ in refluxing toluene (eq 2) afforded permetalated ethane **6**^{*} in addition to the acetylide cluster compound **3**^{*} (Scheme 3). Furthermore, **5**^{*} and **6**^{*} were isolated in better yields by carrying out the reactions in refluxing benzene and toluene, respectively (eqs 4 and 5; see Experimental Section). It should be noted that thermolysis of **5**^{*} in

$$2^* + \operatorname{Ru}_3(\operatorname{CO})_{12} \xrightarrow[\text{refluxing toluene}]{} 5^* (59\% \text{ isolated yield})$$

(4)

$$2^* + \operatorname{Ru}_3(\operatorname{CO})_{12} \xrightarrow[\text{refluxing toluene}]{} 6^* (26\% \text{ isolated yield})$$

(5)

the absence of $Ru_3(CO)_{12}$ afforded an intractable mixture of products in which neither **5*** nor **6*** was detected. Furthermore, thermolysis of **3*** in refluxing toluene (eq 3) resulted in dimerization of its $FeRu_3(\mu-C_2)$ core to give the permetalated ethane **6*** with the doubled core composition $Fe_2Ru_6(\mu-C_4)_2$ in 42% yield (eq 3). Thus, the octanuclear permetalated ethane structure **6*** turns out to be a thermodynamic sink in the present reaction system and can be formed via condensation of lower nuclearity C₂ cluster compounds.

Scheme 5



We attempted addition of another group 8 metal carbonyl species, Fe₂(CO)₉, to $5^{*,18}$ The reaction was sluggish, and after the mixture was refluxed in THF for 15 h a small amount of acetylide cluster compound **10**^{*} was obtained (Scheme 5). Complex **10**^{*} showed spectral features (see Experimental Section) essentially the same as those of **3**^{*} and was characterized as an Fe-substituted derivative of **3**^{*} as revealed by X-ray crystallography.¹⁹ In **10**^{*}, the Ru atom σ -bonded to the C₂ ligand in **3**^{*} (Ru1) is replaced by the Fe atom (Fe1). This result suggests that the Ru acetylide cluster compound **3**^{*} is also formed via an analogous addition reaction of an Ru(CO)_n species with **5**^{*}.

We also examined the reaction of **5**^{*} with a proton, a small electrophile, which may directly add to the sterically congested C2 moiety (Scheme 5). Addition of CF₃SO₃H, HBF₄·OEt₂, or CF₃COOH to a CH₂Cl₂ solution of 5* caused an immediate color change from purple to red-purple and a shift of CO vibrations toward the higher energy region, suggesting formation of a cationic species. ¹H NMR spectra of mixtures obtained from CF₃SO₃H and HBF₄·OEt₂ showed one hydride and two Cp* signals [$\delta_{\rm H}$ (CD₂Cl₂) -8.03 (H), 1.91, 1.90 (Cp*)], whereas protonation with CF₃COOH gave a spectrum with a similar pattern but with different chemical shift values $[\delta_{\rm H}({\rm CD}_2{\rm Cl}_2) - 4.13$ (H), 1.94, 1.81 (Cp*)]. These spectral features are consistent with either of the structures 11* shown in Scheme 5, the side-bound bridging hydride complex or the species with an agostic C2····H····Ru interaction. Complex 11* was unstable, and attempted isolation resulted in fragmentation of the

⁽¹⁸⁾ Attempted reactions of **5** with Co₂(CO)₉, Pt(CH₂=CH₂)(PPh₃)₂, [Rh(CH₂=CH₂)₂(μ -Cl)]₂, Cp*Rh(CO)₂, (η ⁵-C₅H₄Me)(CO)₂, and Mn₂(CO)₁₀ afforded a complicated mixture of products from which no characterizable product could be isolated.

⁽¹⁹⁾ An ORTEP view of 10* is included in Supporting Information.

cluster structure to give $[Fp^*-CO]X$ as the only isolable product.

Structure Expansion of Acetylide Cluster Type Tetranuclear Dicarbide Cluster Compounds with Cp Ligand (3) via Thermolysis and Oxidation. Cp derivatives of the higher nuclearity dicarbide cluster compounds would be obtained from the Cp derivative of the ethynediyl complex 2, but synthesis of 2 has been unsuccessful until now. Then the thermal condensation of the FeRu₃(μ -C₂) core observed for the Cp* cluster compound 3* (eqs 2 and 3) prompted us to examine similar coupling reactions of the Cp derivative 3.

(i) **Thermolysis.** Thermolysis of **3** in refluxing toluene followed by silica gel TLC separation afforded two products **6** and **12** resulting from dimerization of the FeRu₃(μ -C₂) core in low yields (eq 6). One was charac-



terized as the dicarbide cluster compound 6 on the basis of FAB-MS and IR data, which are shown in Figure 5. The isotopomer distribution of the molecular ion peaks for **6** is in very good agreement with the calculated one, and fragment peaks due to loss of up to 17 carbonyl ligands are observed (Figure 5a). These data support the composition of **6** to be " $Cp_2Fe_2Ru_2(\mu-C_2)_2(CO)_{17}$ " [cf. **6***: $Cp_2Fe_2Ru_2(\mu-C_2)_2(CO)_{17}$]. Furthermore, the pattern of CO vibrations of 6 (Figure 5b) is very similar to that of 6* and they were shifted toward higher energy region because of less electron-donating ability of the Cp ligands compared to the Cp* ligands in 6*. Although X-ray crystallographic analysis revealed the presence of an $Fe_2Ru_6(\mu_6-C_2)_2$ core similar to that in **6***, the structure could not be refined because of severe disorder of a part of the metal components. Combined with the ¹H NMR data containing only one singlet Cp signal ($\delta_{\rm H}$ 4.71), it is concluded that **6** is the Cp derivative of the bis(dicarbide) cluster compound 6*.

The other product **12** showing the deshielded ¹H NMR signal (δ 8.64) was a heptanuclear FeRu₆ complex containing one C₂ and one C₂H ligand as revealed by X-ray crystallography (Figure 6 and Table 4). The metal core (Figure 6b) consists of the flat W-shaped raftlike Ru₅ framework [Ru(1–5)], which is fused with the FeRu(1,3,6) square. In addition, the Ru(3,4,6) moiety forms a triangular structure, although the Ru4–Ru6 separation [3.056(1) Å] is substantially longer than the other Ru–Ru lengths [2.7575(8)–2.9759(9) Å]. Complex **12** is a coordinatively saturated 104 CVE species when C₂H and C₂ ligands are regarded as five- and sixelectron donors, respectively. The C₂ ligand [C1–C2:



Figure 5. FAB-MS and IR spectra for **6**: (a) FAB-MS spectrum ($[M^+ - nCO]$ region, n = 0-2) and a spectrum calculated for M⁺; (b) comparison of IR spectra of **6** and **6*** (ν_{CO} region).

1.334(9) Å] interacts with the FeRu(1,2,3,6) envelope in the coordination mode, similar to that observed for $(\mu_5-C_2)Ru_5(\mu-SMe)_2(\mu-PPh_2)_2$ [C–C: 1.305(5) Å].^{5h} The C₂H moiety [C3–C4: 1.420(9) Å] can be viewed as a trimetalated [Ru(1,5,6)] ethene, which is sandwiched between Fe and Ru(4) through π interactions. We attempted the determination of the origin of the μ_5 -C₂H atom by conducting the thermolysis in toluene-*d*₈, but it was unsuccessful because of H–D exchange of the bridging hydride in **3** prior to its conversion.

(ii) Oxidation of Anionic Dicarbide Cluster. Redox condensation is another typical synthetic method of higher nuclearity cluster compounds together with the thermolysis discussed above.²⁰ An extended structure may be formed via coupling of a radical species generated by one-electron oxidation of the anionic cluster compound **13**, which was prepared from **3** following the procedure reported for an organic counterpart, PPh₄-[Ru₃(CO)₉(μ -H)(μ_3 -C=C-Bu⁴)] **14**, obtained from **4**.²¹

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Figure 6. Molecular structure of **12** drawn (with displacement ellipsoid amplitudes) at the 30% probability level, where labels without atom names are for CO ligands: (a) overview; (b) overview of the core part.

Scheme 6



Treatment of **13** with 1 equiv of $[Cp_2Fe]PF_6$ gave a mixture of products from which two higher nuclearity cluster compounds **6** and **15** were isolated and characterized (Scheme 6).

One of the products was characterized as the bis-(dicarbide) cluster compound 6 by comparison of its spectral features with those of an authentic sample. The other product 15 characterized by X-ray crystallography turned out to be a heptanuclear bis(dicarbide) cluster compound with the arrowhead-shaped Ru_5 core of C_2 symmetry (Figure 7). A unit cell of 15 contains two crystallographically independent molecules with essentially the same geometry, one of which sits on a crystallographically imposed site. The FpC₂ groups interact with the Ru₄ butterfly parts as acetylide ligands, and the Fe atoms are not incorporated in the central cluster structure. Complex 15 with no Ru(2)...Ru(4) bonding interaction [3.477(2) Å (molecule 1); 3.472(2) Å (molecule 2)] belongs to a rare class of arrowhead M₅ cluster compounds without an encapsulated atom (usu-



Figure 7. Molecular structure of **15** (molecule 1) drawn (with displacement ellipsoid amplitudes) at the 30% probability level, where labels without atom names are for CO ligands: (a) overview; (b) overview of the core part.

ally μ_5 -C),^{20b} and in contrast to the previously reported acetylide clusters where the C=C part interacts with the top metal atom, the dicarbide parts in **5*** are π -coordinated to the bottom-edge Ru atoms.²² The heptanuclear complex **15** is a coordinatively saturated 112 CVE species with two six-electron-donating C₂ ligands. Thus, the (C₂)FeRu₃ cores in **3** and **13** are coupled upon thermolysis and oxidation, respectively, to afford the higher nuclearity cluster compounds **6**, **12**, and **15**.

Comparison of Structures of the $M_3(CO)_9(\mu-X)$ -(μ -C=C-FP) Type Tetranuclear Acetylide Cluster **Compounds** [M = Fe, Ru; X = H, Anion]. Through the present study several $M_3(CO)_9(\mu-X)(\mu-C=C-FP)$ type tetranuclear acetylide cluster compounds 3, 4, 10*, and 13 are obtained, and their structural parameters are compared together with related organic counterparts (4 and 14) and the tetrairon analogue (16) as shown in Table 1. Complex 16 was obtained by nucleophilic replacement of $(PPN)_2[Fe_3(CO)_9(\mu_3-C=C-OAc)]$ by NaFp as reported by Shriver.^{5d} The coordination modes of the M4-C₂ parts and the structure of the $M_3(CO)_9$ core parts in these complexes are very similar; the $C \equiv C - M4$ moiety interacts with M1 and M2,3 through η^1 and η^2 modes, respectively. As for the ruthenium derivatives where M2 and M3 equal Ru, the C=C and M2-M3 distances could be divided into two groups, those in neutral and those in anionic cluster compounds. The C \equiv C distances in the anionic complexes are shorter

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		Bond Len	gths (A)		
C1-C2	1.334(9)	C3–Fe	2.012(7)	Ru1–Ru4	2.8927(8)
C1-Ru1	2.282(7)	C3–Ru4	2.253(6)	Ru1–Ru5	2.8075(9)
C1-Ru6	2.191(6)	C3–Ru5	1.964(7)	Ru1–Fe	2.754(1)
C1-Fe	1.877(7)	C4–Ru4	2.317(7)	Ru2–Ru3	2.7864(8)
C2-Ru1	2.263(7)	C4–Ru6	2.133(7)	Ru3–Ru4	2.7575(8)
C2-Ru2	1.939(6)	C4–Fe	2.031(7)	Ru3–Ru6	2.9759(9)
C2-Ru3	2.180(6)	Ru1–Ru2	2.844(1)	Ru4–Ru5	2.814(1)
C3-C4	1.420(9)	Ru1–Ru2	2.8436(8)	Ru4–Ru6	3.056(1)
C3-Ru1	2.141(6)	Ru1–Ru3	2.7764(9)	Ru6-Fe	2.675(1)
		Bond Ang	les (deg)		
C2-C1- Ru1	72.2(4)	C3-C4-Fe	68.7(4)	Ru4-Ru3-Ru6	64.30(3)
C2-C1-Ru6	134.9(5)	Ru4-C4-Ru6	86.7(3)	C3-Ru4-C4	36.2(2)
C2-C1-Fe	141.7(5)	Ru4-C4-Fe	118.6(3)	C3-Ru4-Ru1	47.2(2)
Ru1-C1-Ru6	116.1(3)	Ru6-C4-Fe	79.9(3)	C3-Ru4-Ru3	95.7(2)
Ru1-C1-Fe	82.3(3)	C2-Ru1-C3	111.6(2)	C3-Ru4-Ru5	43.9(2)
Ru6-C1-Fe	81.9(2)	C2-Ru1-Ru4	100.9(1)	C3-Ru4-Ru6	70.4(2)
C1-C2-Ru1	73.7(4)	C2-Ru1-Ru5	154.6(2)	C4-Ru4-Ru1	74.3(2)
C1-C2-Ru2	158.1(6)	C2-Ru1-Fe	73.8(2)	C4-Ru4-Ru3	96.6(2)
C1-C2-Ru3	86.2(4)	C3-Ru1-Ru5	44.3(2)	C4-Ru4-Ru5	75.3(2)
Ru1-C2-Ru2	84.8(2)	C3-Ru1-Fe	46.5(2)	C4-Ru4-Ru6	44.2(2)
Ru1-C2-Ru3	77.3(2)	C3-Ru1-Ru4	50.5(2)	Ru1-Ru4-Ru3	58.81(2)
Ru2-C2-Ru3	84.9(3)	C2-Ru2-Ru1	52.4(2)	Ru1-Ru4-Ru5	58.93(2)
C4-C3- Ru1	125.2(5)	C2-Ru2-Ru3	51.2(2)	Ru1-Ru4-Ru6	79.22(3)
C4-C3-Ru4	74.4(4)	C2-Ru3-Ru1	52.7(2)	Ru3-Ru4-Ru5	117.01(2)
C4-C3-Ru5	137.2(5)	C2-Ru3-Ru2	43.9(2)	Ru3-Ru4-Ru6	61.32(2)
C4-C3-Fe	70.2(4)	C2-Ru3-Ru4	107.5(2)	Ru5-Ru4-Ru6	114.31(3)
Ru1-C3-Ru4	82.3(2)	C2-Ru3-Ru6	77.1(2)	Ru1-Ru5-Ru4	61.94(2)
Ru1-C3-Ru5	86.2(2)	Ru5-Ru1-Fe	87.33(3)	C3-Ru5-Ru1	49.6(2)
Ru1-C3-Fe	83.0(2)	Ru1-Ru2-Ru3	59.09(2)	C3-Ru5-Ru4	52.7(2)
Ru4-C3-Ru5	83.4(2)	Ru1-Ru3-Ru2	61.48(2)	Ru3-Ru6-Ru4	54.38(2)
Ru4-C3-Fe	122.6(3)	Ru1-Ru3-Ru4	63.03(2)	Ru3-Ru6-Fe	91.09(3)
Ru5-C3-Fe	149.9(3)	Ru1-Ru3-Ru6	82.48(3)	C1-Ru6-Ru3	54.8(2)
C3-C4- Ru4	69.5(4)	Ru2-Ru3-Ru4	122.37(3)	C4-Ru6-Ru3	94.7(2)
C3-C4-Ru6	122.3(5)	Ru2-Ru3-Ru6	120.84(3)	Ru4-Ru6-Fe	81.23(4)
C1-Ru6-C4	80.5(3)	Ru1-Fe-Ru6	88.67(4)	C3 -Fe-C4	41.1(3)
C1-Ru6-Ru4	80.6(2)	C1-Fe-Ru1	55.2(2)	C3-Fe-Ru1	50.5(2)
C1-Ru6-Fe	44.0(2)	C1-Fe-C3	91.1(3)	C3-Fe-Ru6	82.5(2)
C4-Ru6-Ru4	49.2(2)	C1-Fe-C4	91.2(3)	C4-Fe-Ru1	81.7(2)
C4-Ru6-Fe	48.4(2)	C1-Fe-Ru6	54.2(2)	C4-Fe-Ru6	51.7(2)

Scheme 7



than those in the neutral complexes by ca. 0.05 Å, and in contrast, the M2–M3 distances in the anionic complexes are longer than those in the neutral complexes by ca. 0.1 Å. The former feature should be a result of weakened π donations from the acetylide ligand to the anionic trimetallic framework, and the latter is due to lack of the bridging hydride ligand in the anionic complexes. It is notable that no significant influence of the metal substituents (M4) on the C=C moiety is detected when compared with the organic counterparts **4** and **14**. Thus, the M4 groups in **3**, **4**, **10***, **13**, and **16** work simply as acetylide substituents and no apparent communication is present between the M4 group and the triangular cluster part.

Conclusion

The cluster transformations described in the present paper are summarized in Scheme 7. As for the Cp*

Table 5. S	belected	Structural	Parameters	for	15 ^a
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	molecule	1		molecule	2
		Bond Leng	ths (Å)		
C1-C2	1.32(2)	C3-C4	1.34(2)	C5-C6	1.35(2)
C1-Fe1	1.93(2)	C3-Fe2	1.93(1)	C5-Fe11	1.89(1)
C1-Ru3	2.14(1)	C3–Ru5	2.14(1)	C5-Ru13	2.15(1)
C2-Ru1	2.14(1)	C4-Ru1	2.15(1)	C6-Ru11	2.18(1)
C2-Ru2	2.26(1)	C4–Ru2	2.24(1)	C6-Ru12	2.26(1)
C2-Ru3	2.26(1)	C4–Ru5	2.23(1)	C6-Ru13	2.23(1)
C2-Ru4	2.16(1)	C4–Ru4	2.16(1)	C6-Ru12*	2.15(1)
Ru1–Ru2	2.731(2)	Ru1–Ru4	2.708(2)	Ru11-Ru12	2.709(2)
Ru2–Ru3	2.905(2)	Ru4–Ru5	2.885(2)	Ru12-Ru13	2.875(2)
Ru2–Ru5	2.900(2)	Ru3–Ru4	2.916(2)	Ru12-Ru13*	2.944(2)
Ru3–Ru5	2.792(2)			Ru13-Ru13*	2.784(2)
terminal Ru–CO	1.87 - 1.91(2)			terminal Ru–CO	1.85 - 1.90(2)
bridging Ru–CO	1.92 - 2.18(2)			bridging Ru–CO	2.05 - 2.17(2)
terminal Fe–CO	1.70 - 1.78(2)			terminal Fe–CO	1.79(2)
		Bond Angle	es (deg)		
C2-C1-Fe1	144(1)	C4-C3-Fe2	143(1)	C6-C5-Fe11	145(1)
C2-C1-Ru3	78(1)	C4-C3-Ru5	76.1(8)	C6-C5-Ru13	75.3(8)
Fe1-C1-Ru3	138.5(8)	Fe2-C3-Ru5	141.2(7)	Fe11-C5-Ru13	139.9(8)
C1-C2-Ru1	146(1)	C3-C4-Ru1	145(1)	C5-C6-Ru11	144(1)
C1-C2-Ru4	130(1)	C3-C4-Ru4	131(1)	C5-C6-Ru12*	133(1)
C1-C2-Ru2	109.2(9)	C3-C4-Ru2	107.7(9)	C5-C6-Ru12	108(1)
C1-C2-Ru3	67.7(9)	C3-C4-Ru5	68.2(8)	C5-C6-Ru13	68.7(8)
Ru1-C2-Ru4	78.0(4)	Ru1-C4-Ru4	77.9(4)	Ru12-C6-Ru11	77.5(5)
Ru1-C2-Ru2	76.7(5)	Ru1-C4-Ru2	76.9(4)	Ru11-C6-Ru12*	75.2(4)
Ru1-C2-Ru3	144.8(7)	Ru1-C4-Ru5	145.1(7)	Ru11-C6-Ru13	144.2(6)
Ru4-C2-Ru2	103.7(6)	Ru4-C4-Ru2	104.3(5)	Ru12-C6-Ru12*	103.6(5)
Ru4-C2-Ru3	82.4(5)	Ru4-C4-Ru5	82.0(5)	Ru12-C6-Ru13	84.4(5)
Ru2-C2-Ru3	80.0(4)	Ru5-C4-Ru2	80.7(4)	Ru13-C6-Ru12*	79.6(4)
C2-Ru1-C4	74.8(5)			C6-Ru11-C6*	74.7(7)
C4-Ru2-C2	70.6(5)	C4-Ru4-C2	74.0(5)	C6-Ru12-C6*	73.4(5)
C1-Ru3-C2	34.7(5)	C3-Ru5-C4	35.7(5)	C5-Ru13-C6	36.0(5)
Ru4-Ru1-Ru2	79.49(5)			Ru12-Ru11-Ru12*	79.69(7)
Ru1-Ru2-Ru3	96.18(5)	Ru1-Ru2-Ru5	95.75(4)	Ru11-Ru12-Ru13*	95.65(5)
Ru1-Ru4-Ru3	96.44(5)	Ru1-Ru4-Ru5	96.62(5)	Ru11-Ru12-Ru13	97.28(5)
Ru5-Ru2-Ru3	57.50(4)	Ru5-Ru4-Ru3	57.54(4)	Ru13-Ru12-Ru13*	57.15(5)
Ru5-Ru3-Ru2	61.16(5)	Ru3-Ru5-Ru2	61.35(5)	Ru13*-Ru13-Ru12	62.68(4)
Ru5-Ru3-Ru4	60.67(4)	Ru3-Ru5-Ru4	61.79(4)	Ru13*-Ru13-Ru12*	60.17(4)
Ru4-Ru5-Ru2	73.90(4)	Ru2-Ru3-Ru4	73.36(4)	Ru12-Ru13-Ru12*	73.25(5)
terminal M–C–O	176 - 178(2)			terminal M–C–O	177 - 179(2)
Ru2-C1c-O1c	145(1)	Ru4-C1d-O1d	146(1)	Ru12-C11b-O11b	144(1)
Ru1-C1c-O1c	131(1)	Ru1-C1d-O1d	133(1)	Ru11-C11b-O11b	137(1)
Ru1-C1c-Ru2	83.3(7)	Ru1-C1d-Ru4	81.0(5)	Ru11-C11b-Ru12	79.9(6)
Ru3-C3c-O3c	140(1)			Ru13-C13c-O13c	138.9(5)
Ru5-C3c-O3c	136(1)			Ru13-C13c-O13c	138.9(5)
Ru5-C3c-Ru3	83.9(6)			Ru13-C13c-Ru13	82.3(9)

^a With two independent molecules. Molecule 2 sits on a crystallographic C₂-symmetrical site.

system, the present study reveals that permetalated ethene and ethane structures result from formal sequential addition of dimetallic fragments to the $C \equiv C$ triple bond in the ethynediyl complex, a permetalated ethyne (Scheme 3). Although the starting compounds 1, 1^{*}, and 2^{*} are acetylide complexes, the structural features of the obtained permetalated hydrocarbons characterized by X-ray crystallography are totally different from those of previously reported acetylide cluster compounds.¹ The higher nuclearity cluster compounds are also formed by thermal and redox condensation of the FeRu₃(μ -C₂) core in the acetylide cluster compound as revealed by the results of the Cp system. The results obtained would provide insights into the coordination modes of dicarbide species (C_2) on a heterogeneous catalyst surface.² The synthetic study on dicarbide (C₂) cluster compounds is now extended to polycarbon (C_{2n}) cluster compounds derived from related polyynediyl complexes, $M-(C \equiv C)_n - M.^{8k-p}$

Experimental Section

General Methods. All manipulations were carried out under an inert atmosphere by using standard Schlenk tube

techniques. THF, ether, hexanes, benzene, toluene (Na-K alloy), CH₂Cl₂ (P₂O₅), and EtOH [Mg(OEt)₂] were treated with appropriate drying agents, distilled, and stored under argon. ¹H and ¹³C NMR spectra were recorded on JEOL GX-270 (¹H NMR, 270 MHz; ¹³C NMR, 67 MHz) and EX-400 (¹H NMR, 400 MHz; ¹³C NMR, 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 spectra (KBr pellets) and mass spectra (FD) were obtained on a JASCO FT/IR 5300 spectrometer and a Hitachi M-80 mass spectrometer, respectively. Complexes $1,^{8b}$ $1^{*},^{8b}$ $2^{*},^{8k}$ Ru₃(CO)₁₂,²³ Fe₂(CO)₉,²⁴ and [Cp₂Fe]PF₆²⁵ were prepared according to the published methods. ¹³CO-enriched $Ru_3(CO)_{12}$ was prepared by heating a toluene suspension of Ru₃(CO)₁₂ under ¹³CO (4 atm) for 3 days at 120 °C. Other chemicals were purchased and used as received. Chromatography was performed on alumina.

Reaction of 1 with Ru_3(CO)_{12}. A benzene solution (15 mL) of **1** (227 mg, 1.10 mmol) and $Ru_3(CO)_{12}$ (651 mg, 1.00 mmol) was refluxed for 1.5 h. After removal of the volatiles, the

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products were extracted with ether and passed through an alumina plug. Crystallization from ether–hexanes gave **3** (223 mg, 0.29 mmol, 29% yield). **3**. ¹H NMR (CDCl₃): $\delta_{\rm H}$ –20.05 (1H, s, Ru–H), 3.90 (5H, s, Cp). ¹³C NMR (CDCl₃): $\delta_{\rm C}$ 79.7 (s, =C–Fe), 86.7 (d, J = 177 Hz, Cp), 174.1 (s, Ru–C=), 190–194 (br, Ru–CO), 212.6 (s, Fe–CO). IR: 2084, 2036, 1986, 1978, 1963 cm⁻¹. Anal. Calcd for C₁₈H₆O₁₁FeRu₃: C, 28.55; H, 0.80. Found: C, 28.62; H, 0.83.

Reaction of 1* with Ru₃(CO)₁₂. A benzene solution (30 mL) of **1*** (0.58 g, 2.12 mmol) and Ru₃(CO)₁₂ (1.03 g, 1.61 mmol) was refluxed for 4 h. After removal of the volatiles, the resulting solid was washed with hexanes (10 mL \times 3). Extraction with CH₂Cl₂ and filtration through a silica gel pad followed by crystallization from CH₂Cl₂–hexanes gave **3*** (992 mg, 1.20 mmol, 75% yield). **3***. ¹H NMR (CDCl₃): $\delta_{\rm H}$ –19.56 (1H, s, Ru–H), 1.25 (15H, s, Cp*). ¹³C NMR (CDCl₃): $\delta_{\rm C}$ 9.5 (q, *J* = 128 Hz, C₅*Me*₅), 96.8 (s, ≡C–Fe), 97.5 (s, *C*₅Me₅), 168.1 (s, Ru–C≡), 215.1 (s, Fe–CO). IR: 2078, 2050, 2024, 2005, 1996, 1987, 1962 cm⁻¹. Anal. Calcd for C₂₃H₁₆O₁₁FeRu₃: C, 33.39; H, 1.95. Found: C, 33.19; H, 1.80.

Reaction of 2* with Ru₃(CO)₁₂. A benzene solution (40 mL) of 2* (803 mg, 1.69 mmol) and Ru₃(CO)₁₂ (803 mg, 1.26 mmol) was refluxed for 9 h. After removal of the volatiles under reduced pressure, products were extracted with CH₂Cl₂ and passed through a Florisil plug. Concentration followed by cooling at -20 °C gave unreacted Ru₃(CO)₁₂ (177 mg). Further concentration of the filtrate followed by cooling at -20 °C gave 5* (192 mg, 0.22 mmol, 25% yield based on the consumed Ru₃- $(CO)_{12}$) as dark-purple crystals. Further separation of the filtrate by alumina column chromatography (eluted with 1:4 CH₂Cl₂-hexanes) afforded 6* (82 mg, 0.05 mmol, 11% yield) as black crystals. 5^{*}. ¹H NMR (CDCl₃): $\delta_{\rm H}$ 1.55 (30H, s, Cp^{*}). ¹³C NMR (CDCl₃): $\delta_{\rm C}$ 9.5 (q, J = 128 Hz, C₅Me₅), 98.0 (s, C₅Me₅), 177.2 (s, µ₄-C₂), 191.1, 196.4, 205.6 (Ru-CO), 217.8 (Fe-CO), 262.5 (µ-CO). IR: 2082, 2048, 1997, 1981, 1963, 1953, 1775 cm⁻¹. Anal. Calcd for C₃₂H₃₀O₁₀Fe₂Ru₂: C, 43.26; H, 3.40. Found: C, 43.50; H, 3.66. **6***. ¹H NMR (CD₂Cl₂): $\delta_{\rm H}$ 1.61 (30H, s, Cp*). ¹³C NMR (CD₂Cl₂ at 25 °C): $\delta_{\rm C}$ 9.0 (q, J = 128 Hz, C₅Me₅), 98.7 (s, C₅Me₅), 190.1, 191.1, 194.2 (CO), 202.9, 208.4 (C₂), 210.7 (CO), 243.5 (µ-CO). ¹³C NMR (CD₂Cl₂ at -80 °C): $\delta_{\rm C}$ 9.4 (C₅Me₅), 98.6 (C₅Me₅), 190.5, 190.9, 191.4, 194.4, 197.2, 200.8 (CO), 203.2, 209.0 (C2), 210.4 (CO), 244.5 (µ-CO). IR: 2076, 2057, 2016, 1836 cm⁻¹. Anal. Calcd for C₄₂H₃₂O₁₇-Cl₂Fe₂Ru₆: C, 32.55; H, 2.00. Found: C, 32.78; H, 2.06.

Preparation of 5*. A mixture of **2*** (1.01 g, 2.05 mmol) and Ru₃(CO)₁₂ (1.06 g, 2.26 mmol) dissolved in benzene (60 mL) was refluxed for 6 h. After the mixture was left overnight at -30 °C, the frozen mixture was thawed and the supernatant solution was removed via a cannula. The residue was extracted with a CH₂Cl₂-hexane mixture and passed through a short alumina column (5 cm). After Ru₃(CO)₁₂ and Fp*₂ were eluted with CH₂Cl₂-hexane, the product was eluted with ether. Evaporation of the ether solution gave **5*** (1.03 g, 1.20 mmol, 59% yield).

Preparation of 6*. A toluene solution (60 mL) of **2*** (312 mg, 0.60 mmol) and Ru₃(CO)₁₂ (372 mg, 0.58 mmol) was refluxed for 3.5 h. After removal of the volatiles under reduced pressure, the residue was subjected to alumina column chromatography and Ru₃(CO)₁₂ and Fp*₂ were eluted with CH₂-Cl₂-hexane (1:4). A purple-gray band eluted with CH₂Cl₂-hexane (1:3–1:2) was collected. Complex **6*** (0.12 g, 0.08 mmol, 26% yield) was obtained by evaporation of the solvent.

Reaction of 5* with Ru₃(CO)₁₂. A toluene solution (10 mL) of **5*** (35 mg, 0.05 mmol) and Ru₃(CO)₁₂ (32 mg, 0.02 mmol) was refluxed for 3 h. Removal of the volatiles under reduced pressure followed by silica gel TLC separation gave **3*** (17 mg, 0.02 mmol, 50% yield) and **6*** (6 mg, 0.004 mmol, 20% yield), which were characterized by IR and ¹H NMR. Other minor products could not be characterized.

Thermolysis of 3*. A toluene solution of **3*** (78 mg, 0.10 mmol) was refluxed for 11 h. Removal of the volatiles under

reduced pressure followed by silica gel TLC separation gave **6*** (30 mg, 0.021 mmol, 42% yield based on consumed **3***) and **3*** (recovered, 40 mg, 0.05 mmol), which were characterized by IR and ¹H NMR. Other minor products could not be characterized.

Reaction of 3* with Fe₂(CO)₉. A THF solution (10 mL) of **3*** (96.0 mg, 0.112 mmol) and Fe₂(CO)₉ (81 mg, 0.22 mmol) was heated for 15 h at 65 °C. After removal of the volatiles, separation by column chromatography afforded Fp^{*}₂ (6.0 mg, 0.012 mmol), yellow compound **10*** (7.2 mg, 0.092 mmol, 8% yield based on consumed **3***), and **3*** (recovered, 35 mg, 0.041 mmol). **10***. ¹H NMR (CDCl₃): $\delta_{\rm H}$ -20.1 (1H, s, Ru–H), 1.90 (15H, s, Cp*). ¹³C NMR (CDCl₃): $\delta_{\rm C}$ 10.1 (q, J = 128 Hz, C₅*Me*₅), 97.6 (s, C₅Me₅), 100.0 (s, =C–Fe), 182.8 (s, Ru–C=), 213.8, 214.7 (s, Fe–CO). IR: 2085, 2057, 2021, 2005, 1992, 1965, 1943 cm⁻¹. Anal. Calcd for C₂₃H₁₆O₁₁Fe₂Ru₂: C, 35.32; H, 2.06. Found: C, 35.07; H, 2.06.

Protonation of 5*. (i) With CF₃SO₃H or HBF₄·OEt₂. To a CH₂Cl₂ solution of **5*** cooled in an ice bath was added CF₃-SO₃H or HBF₄·OEt₂ (2 equiv), and the resulting mixture was stirred at ambient temperature. IR monitoring indicated a shift of the μ -CO vibration from 1783 cm⁻¹ (**5***) to 1837 cm⁻¹ (**11***). Attempted isolation of the product by addition of hexane gave [Fp*–CO]X. **11***. ¹H NMR data are in the text. IR (CH₂-Cl₂): 2123, 2102, 2061, 2048, 2029, 1837 cm⁻¹.

(ii) With CF₃COOH. Reaction was carried out as described above. ¹H NMR data are in the text. IR (CH₂Cl₂): 2101, 2050, 2026, 1986, 1803 cm⁻¹.

Thermolysis of 3. A toluene solution (10 mL) of **3** (119 mg, 0.16 mmol) was refluxed for 3.5 h. After removal of the volatiles, products were separated by silica gel TLC eluted with 1:2 hexane–CH₂Cl₂. From the top brown band, black product **12** (23 mg, 0.018 mmol, 28% yield based on consumed **3**) was isolated, and from the next yellow band the starting compound **3** (0.031 mmol) was recovered. A trace amount of permetalated ethane **6** was isolated from a middle purple-red band. **6**. ¹H NMR (CDCl₃): $\delta_{\rm H}$ 4.71 (10H, s, Cp). IR (KBr): 2082, 2063, 2022, 1856 cm⁻¹. FAB-MS: *m*/*z* 1373, 1373 – 28*n* (*n* = 1–17). An analytically pure sample could not be obtained despite several attempts. **12**. ¹H NMR (C₆D₆): $\delta_{\rm H}$ 8.64 (1H, s, C₂H), 5.13 (5H, s, Cp). IR: 2071, 2005, 1962, 1824 cm⁻¹. Anal. Calcd for C₂₅H₆O₁₆FeRu₆: C, 24.52; H, 0.49. Found: C, 24.86; H, 0.95. FD-MS: *m*/*z* 1226 (the most intense peak).

Preparation of 13. To a THF solution (50 mL) of 3 (475 mmol, 0.628 mmol) was added an EtOH solution of KOH (53 mg, 0.94 mmol/12 mL) followed by an EtOH solution of PPh₄-Br (364 mg, 0.63 mmol/10 mL), while CO bubbling was maintained. After removal of the volatiles under reduced pressure, the residue was extracted with CH₂Cl₂ and passed through a Celite plug. Addition of ether gave orange solids, crystallization of which from acetone-ethanol afforded 13 as orange crystals (193 mg, 0.176 mmol, 28% yield). 13. ¹H NMR (acetone-d₆): $\delta_{\rm H}$ 8.05–7.84 (20H, m, PPh₄), 5.15 (5H, s, Cp). ¹³C NMR (acetone- d_6): δ_C 215.0 (s, Fe–CO), 203.5 (s, Ru–CO), 187.0 (s, Ru–C=), 136.4 (d, $J_{CP} = 2$ Hz, p-Ph), 135.7 (d, $J_{CP} =$ 10 Hz, *m*-Ph), 131.4 (d, $J_{CP} = 13$ Hz, *o*-Ph), 119.1 (d, $J_{CP} = 90$ Hz, *ipso*-Ph), 88.2 (s, Cp), 74.3 (s, Fe-≡). IR: 2045, 2026, 1993, 1950, 1926 cm⁻¹. Anal. Calcd for C₄₀H₂₅O₉PFeRu₃: C, 46.21; H, 2.42. Found: C, 46.42; H, 2.46.

Oxidation of 11* with [Cp₂Fe]PF₆. A CH₂Cl₂ solution (15 mL) of **11*** (294 mg, 0.268 mmol) and [Cp₂Fe]PF₆ (89 mg, 0.269 mmol) was stirred for 3 h at ambient temperature. After removal of the volatiles, the residue was subjected to silica gel TLC separation (eluted with 1:1 ether–hexane). Products **6** and **15** were isolated from brown and dark-red bands, respectively. Recrystallization gave **6** (43 mg, 0.031 mmol, 23% yield; from CH₂Cl₂-hexane) and **15** (23 mg, 0.018 mmol, 13% yield; from CH₂Cl₂-ether) as black thin plates and black crystals, respectively. **15**. ¹H NMR (CDCl₃): $\delta_{\rm H}$ 4.98 (5H, s, Cp). IR: 2064, 2018, 1986, 1875 cm⁻¹. Anal. Calcd for C₃₁H₁₀O₁₇Fe₂Ru₅: C, 29.28; H, 0.79. Found: C, 29.56; H, 1.06.

Table 6	3. Cr	vstallo	grap	hic	Data
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	complex ^a				
	3	5*	$6^* \cdot CH_2 Cl_2^d$	10*	
formula	C ₁₈ H ₆ O ₁₁ FeRu ₃	$C_{32}H_{30}O_{10}Fe_2Ru_2$	C42H32O17Cl2Fe2Ru6	C23H16O11FeRu3	
fw	757.3	888.42	1597.72	782.2	
diffractometer	AFC5S	AFC5R	R-AXIS IV	AFC5R	
temp (°C)	25	25	-60	25	
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	
space group	pbca	C2/c	C2/c	$P2_1/n$	
a/Å	15.166(2)	14.124(6)	19.545(5)	17.857(4)	
b/Å	21.445(4)	11.537(5)	20.928(2)	10.156(1)	
c/Å	14.025(2)	20.142(5)	23.886(4)	17.162(3)	
β/deg		93.23(4)	96.102(4)	116.81(1)	
/⁄/ų	4561(2)	3277(4)	9714(2)	2777(1)	
Ζ	8	4	8	4	
$d_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	2.21	1.80	2.19	1.87	
μ/cm^{-1}	25.9	18.1	25.7	21.4	
20/deg	55	50	55	55	
no. data collected	5818	6177	10 083	6963	
no. data with $I > 3 \sigma(I)$	2582	2668	8719 ^e	5338	
no. params refined	298	208	632	343	
R^b	0.053	0.059	0.055^{f}	0.053	
$R_{\rm w}{}^c$	0.040	0.050	0.173 ^g	0.073	
			complex ^a		

	$12 \cdot CH_2Cl_2$	13	15 •(H ₂ O) _{2/3}
formula	$C_{26}H_8O_{16}Cl_2FeRu_6$	$C_{42}H_{25}O_{11}PFeRu_3$	C31.67H11.33O17Fe2Ru5
fw	1309.5	1095.7	1283.5
diffractometer	AFC5R	AFC5R	AFC5R
temp (°C)	25	25	25
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	C2/c
a/Å	11.848(5)	10.450(3)	42.215(5)
b/Å	10.812(5)	12.997(7)	15.776(5)
c/Å	27.739(4)	30.117(10)	16.842(4)
β/deg	99.11(2)	99.10(3)	100.06(2)
V/Å ³	3508(4)	4039(3)	11044(5)
Z	4	4	12
$d_{ m calcd}/ m g~cm^{-3}$	2.48	1.80	2.32
μ/cm^{-1}	30.9	15.5	28.4
max 2θ/deg	55	50	50
no. data collected	8880	7894	10 261
no. data with $I > 3 \sigma(I)$	5250	4173	6260
no. params refined	464	523	754
R^b	0.035	0.042	0.052
$R_{ m w}{}^c$	0.039	0.030	0.047

^{*a*} Refined with teXsan²⁶ unless otherwise stated. ^{*b*} $R = [\Sigma||F_0| - |F_c|]/\Sigma|F_0|$. ^{*c*} $R_w = [\Sigma \{ w(|F_0| - |F_c|)^2 \}/\Sigma wF_0^2]^{0.5}; w = 1/\sigma^2(F_0^2)$. ^{*d*} Refined with SHELXS97.^{32b} *e* Number of data with $I > 2 \sigma(I)$. ${}^{f}R1 = [\Sigma||F_0| - |F_c||] \Sigma |F_0|$ (for data with $I > 2 \sigma(I)$). *g* wR2 = $[\Sigma \{w(F_0^2 - F_c^2)\}^2 / \Sigma \{w(F_0^2)^2\}]^{0.5}$; $w = 1/[\sigma^2(F_0^2) + (0.1000P)^2]$ where $P = [2F_c^2 + \max(F_0^2, 0)]/3$ (for all data).

Experimental Procedure for X-ray Crystallography. (i) For 3, 5*, 10*, 12, 13, and 15. Suitable single crystals were mounted on glass fibers. Diffraction measurements were made on Rigaku AFC5S (3) and AFC5R (5*, 10*, 12, 13, and 15) automated four-circle diffractometers at 25 °C by using graphite-monochromated Mo K α radiation ($\lambda = 0.710$ 69 Å). The unit cells were determined and refined by a least-squares method using 20 independent reflections ($2\theta \approx 20^\circ$). Data were collected with $\omega - 2\theta$ (3, 5*, 10*) and ω scan techniques (12, **13**, **15**). 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 every 100 (3) and 150 measurements (the others). The data processing (data collection) was performed on FACOM A-70 (3) and Microvax II computers (the others). In the reduction of data, Lorentz and polarization corrections were made. An empirical absorption correction (Ψ scan) was made.

Crystallographic data and the results of refinements are summarized in Table 6. Structure analysis was performed on a Microvax II computer by using the teXsan structure solving program obtained from the Rigaku Corp., Tokyo, Japan.²⁶ Neutral scattering factors were obtained from the standard source.²⁷ The structures were solved by a combination of direct methods (MITHRIL90²⁸ and SAPI91²⁹) and DIRDIF.³⁰ Unless otherwise stated, non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were fixed at the calculated positions (C-H = 0.95 Å) and were not

⁽²⁶⁾ teXsan, Crystal Structure Analysis Package; Rigaku Corp.: Tokyo, Japan, 1985, 1992, and 1999.

⁽²⁷⁾ International Tables for X-Ray Crystallography; Kynoch Press: Birmingham, 1975; Vol. 4.

⁽²⁸⁾ Gilmore, C. J. MITHRIL, an integrated direct methods computer (29) Fan, H.-F. Structure Analysis Programs with Intelligent Con-

⁽³⁾ Fan, H.-F. Structure Analysis Programs with Intelligent Control: Rigaku Corp.: Tokyo, Japan, 1991.
(30) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system, Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

refined. The C_2H atom in **12** was refined isotropically, and the bridging hydrogen atoms of **3** and **10**^{*} were not included in the refinements.

(ii) For 6*. Diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with Mo K α radiation ($\lambda = 0.710$ 69 Å). All the data collections were carried out at -60 °C. Indexing was performed from these oscillation images, which were exposed for 4 min. The crystal-to-detector distance was 110 mm. Data collection parameters were as follows: detector swing angle, 5°; number of oscillation images, 23; exposed time, 50 min. Readout was performed with a pixel size of 100 μ m × 100 μ m.

Crystallographic data and the results of refinements are summarized in Table 4. The structural analysis was performed on an IRIS O2 computer using the teXsan structure solving program obtained from the Rigaku Corp., Tokyo, Japan. Neutral scattering factors were obtained from the standard source.²⁷ In the reduction of data, Lorentz and polarization corrections were made. An absorption correction was also made.³¹

The structures were solved by a combination of direct methods (SHELXS 86)³² and DIRDIF²⁸ and refined with the

SHELXS97 least-squares refinement program.³² Non-hydrogen atoms were refined with anisotropic thermal parameters. The methyl hydrogen atoms were refined using the riding models, and the other hydrogen atoms were fixed at the calculated positions (C–H = 0.95 Å) and not refined.

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Supporting Information Available: Experimental details for X-ray crystallography and crystallographic results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) (a) Sheldrick, G. M. SHELXS-86: Program for crystal structure

^{(32) (}a) Sheldrick, G. M. SHELXS-86: Program for crystal structure determination; University of Göttingen: Göttingen, Germany, 1986.
(b) Sheldrick, G. M. SHELXL-97: Program for crystal structure refinement; University of Göttingen: Göttingen, Germany, 1997.