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Accounts

Structure and Reactivity of C2 Species on Polymetallic Systems[1)]

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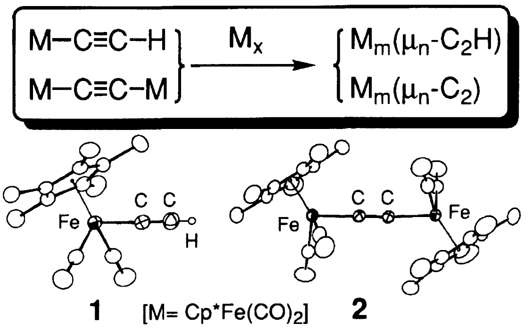
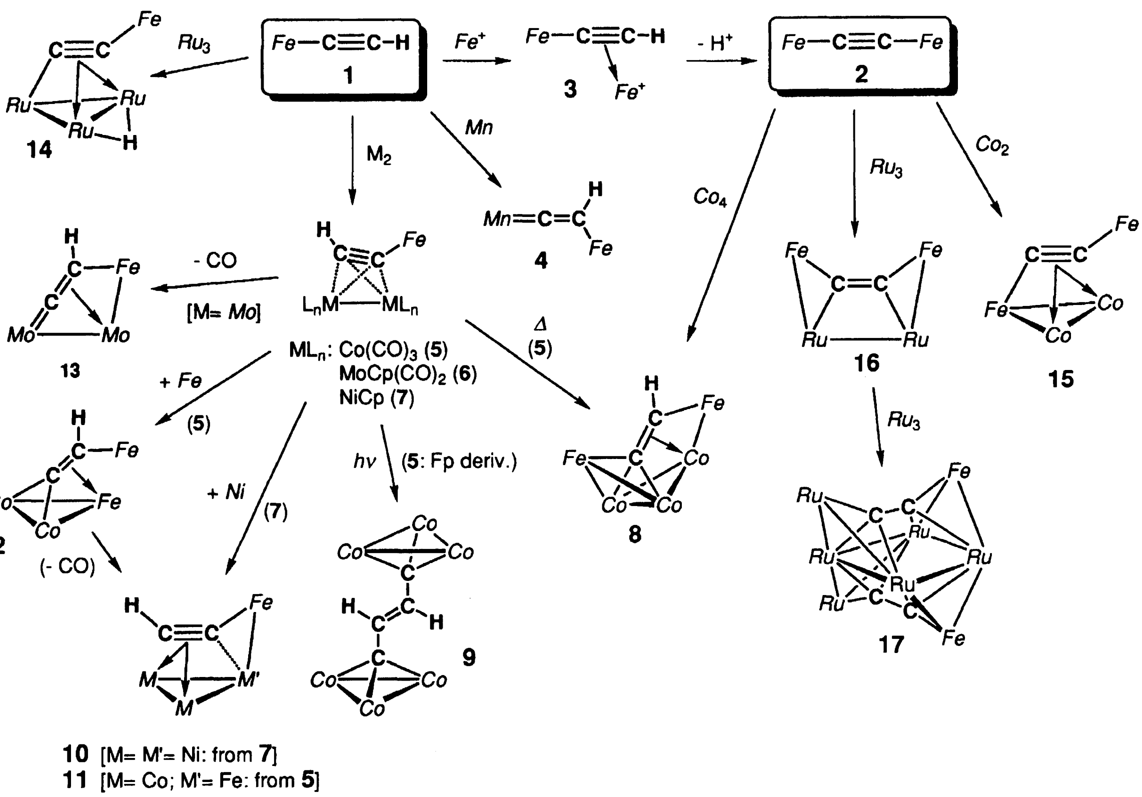
A variety of polymetallic C2 (C_2 and C_2H) complexes are prepared by structure expansion of parent metal acetylide complexes, $Fp^*-C\equiv C-H$ (**1**) and $Fp^*-C\equiv C-Fp^*$ (**2**) [$Fp^* = (\eta^5\text{-}C_5Me_5)Fe(CO)_2$], and their structure and reactivity have been investigated as models for surface-bound C2 species formed during catalytic CO hydrogenation. The results summarized here involve (1) intramolecular 1,2-H shift of the C_2H complexes relevant to the 1-alkyne-to-vinylidene rearrangement within a metal coordination sphere, (2) electronic influence of metal centers on the structure of dinuclear bridging alkynyl complexes, (3) conversion of the C2 moiety into various C2 functional groups, and (4) synthesis of higher nuclearity dicarbide (C_2) cluster compounds with novel coordination structure by sequential addition reactions of metal fragments and direct coupling of a preformed low-nuclearity cluster structure.

Catalytic CO hydrogenation, a series of catalytic reactions that convert syngas (a mixture of CO and H_2) into various useful organic chemicals such as paraffinic and olefinic hydrocarbons and oxygenated compounds,[2)] has been expected to be a new method for exploitation of chemical feedstocks, and the mechanisms of the catalytic reactions have attracted much attention as well. The reactions usually carried out by the action of heterogeneous catalysts contain elementary steps that are hardly realized by means of homogeneous catalysis as well as synthetic organic chemistry. It is generally accepted that the reaction mechanisms of the catalytic reaction involve a combination of elementary steps such as (1) dissociative adsorption of CO forming a carbide species, (2) C–H bond formation giving C1 species (CH_x and CH_xO species), (3) carbon chain elongation via coupling of C1 species, and (4) reductive cleavage of the resulting hydrocarbyl intermediates releasing the products.[2,3)] Among many attempts to get insight into the reaction mechanisms, we have studied structure and reactivity of polymetallic C2 complexes (C2: $C_2H_xO_y$) as models for surface-bound C2 species[4)] which should be formed after the first C–C coupling of C1 species. In contrast to the study on C1 species,[3e,3f)] chemistry of C2 species remains far less explored in the field of not only organometallic chemistry but also surface science.[2e)] Even coordination structure of C2 species has not been studied systematically, though C2 complexes may adopt diverse structures compared to C1 complexes. Following the study on heterobimetallic complexes containing a ketene species [$M-CH_2C(=O)-M$] (a methylene–CO coupling product),[5)] polymetallic carbon-rich C2 (C_2H and C_2) complexes which are derived from parent metal acetylide complexes, i.e. the ethynyl complex $Fp^*-C\equiv C-H$ (**1**) and the ethynediyl complex $Fp^*-C\equiv C-Fp^*$ (**2**) [$Fp^* = Cp^*Fe(CO)_2$; $Cp^* = \eta^5\text{-}C_5Me_5$], have been a subject of our recent study (Scheme 1). As a result, various types of polynuclear C2 complexes were obtained by structure expansion of **1** and **2** as summarized in Scheme 2. Although polymetallic C_2R complexes derived from metal acety-



Scheme 1.



Scheme 2.

lide complexes M–C≡C–R (R=alkyl, aryl etc.) are also studied extensively,[6] it is anticipated that the C_2 and C_2H complexes[7—9] of simple ligand composition should display properties closer to that of the actual surface species and, in fact, some peculiar properties have been revealed. Thus the C_2H and C_2 complexes have been investigated from the viewpoints of model compounds for surface C2 species as well as derivatives of polymetallic acetylide complexes. Herein we summarize the results obtained so far with focus on (1) synthesis of polynuclear C2 compounds with novel coordination modes, (2) intramolecular 1,2-H shift of the C_2H complexes relevant to the 1-alkyne-to-vinylidene rearrangements, and (3) transformation into other C2 species.

Polymetallic C_2H Complexes: Structure, Fluxional Property, and Reactivity

(i) Synthesis of Polymetallic C_2H Complexes (Scheme 2). Polymetallic C_2H complexes were prepared by addition of metal fragments to the C≡C functional group in **1**, the conventional method used for synthesis of polymetallic alkyne and acetylide complexes. The C–C distance and the ^{13}C NMR chemical shifts of the C2 moiety of the C2 complexes are summarized in Table 1.

Treatment of **1** with isolobal 16-electron mononuclear species "Fp^{*+}" and "$Cp'Mn(CO)_2$" produced dinuclear complexes $[Fp_2^*(\mu\text{-}C{\equiv}C\text{-}H)]BF_4$ (**3**)[10] and $Cp'Mn(CO)_2[{=}C{=}C(H)Fp^*]$ (**4**),[11] which were isoelectronic though not isostructural (see below).

Interaction of an acetylenic substrate with dinuclear species giving an adduct with a tetrahedral C_2M_2 core is recognized as one of classical organometallic reactions.[12] As expected, the reaction of **1** with $Co_2(CO)_8$, $Mo_2Cp_2(CO)_4$ and $Ni_2Cp_2(CO)_2$ produced the corresponding adducts $(\mu\text{-}\eta^2:\eta^2\text{-}Fp^*\text{–}C{\equiv}C\text{–}H)(ML_n)_2$ [$ML_n = Co(CO)_3$ (**5**),[13] $MoCp(CO)_2$ (**6**),[14] NiCp (**7**)[15]], respectively. The Mo_2-adduct **6** showed a dynamic behavior via 1,2-H shift as described below, and apparent capping reaction of the FeM_2 triangular face in the Co_2– (**5**)[16] and Ni_2-adducts (**7**)[15] with a mononuclear fragment produced the tetranuclear spiked triangular clusters $(\mu_4\text{-}C_2H)Cp^*FeM_mL_n$ [$M_mL_n = Ni_3Cp(CO)_3$ (**10**), $FeCo_2(CO)_{10}$ (**11**)]. The formation of **11** followed 1,2-H shift of a vinylidene intermediate $[\mu_3\text{-}C{=}C(H)Fp^*]FeCo_2(CO)_9$ **12** as described below. Of the M_2-adducts, the Co_2-derivative **5** exhibited the highest reactivity probably reflecting the lability of the Co–CO part.[17] Thermolysis produced the pentanuclear cluster $Cp_2^*Fe_2Co_3(\mu_5\text{-}C{=}CH)(CO)_{10}$ (**8**) with the spiked butterfly metal frame by formal addition of a $Cp^*FeCo(CO)_x$ species. On the other hand, photolysis of the Fp derivative [$Fp = CpFe(CO)_2$] of **5** afforded the hexacobalt cluster $(\mu\text{-}CH{=}CH)[(\mu_3\text{-}C)Co_3(CO)_9]_2$ (**9**) with a C–CH=CH–C bridge through formal dimerization of the ethynyl ligand, though **5** itself merely produced $Cp^*FeCo(CO)_6$ without the C_2H ligand upon photolysis.

Finally, reaction with a trinuclear species $Ru_3(CO)_{12}$ in refluxing benzene afforded a tetranuclear C_2 cluster

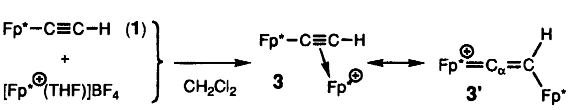
Table 1. Polymetallic C2 Complexes, (μ-C_2H)M_n and (μ-C_2)M_n, Obtained by the Present Study

C_2H complex	n	M_n	Coordination mode		d(C–C)	δ_C(C_α≡C_β-H)		δ_H(C_2H)	Ref.
			η^1	η^2		δ_C(C_α)	δ_C(C_β)		
η^1-C_2H (**1**)	1	Fe	1 (Fe)	0	1.173(4)	97.0	97.5	1.99	10
μ-C_2H (**3**)	2	Fe_2	1 (Fe)	1 (Fe)	1.214(9)	124.2	72.2	3.76	10
μ-C_2H (**4**)	2	FeMn	2 (FeMn)	0	1.269(8)	310.5	91.2	4.62	11
μ_3-C_2H (**5**)	3	$FeCo_2$	1 (Fe)	2 (Co_2)	1.305(5)$^{a)}$	109.5	92.6	6.47	13
μ_3-C_2H (**6**)	3	$FeMo_2$	1 (Fe)	2 (Mo_2)	1.321(9)$^{a)}$	60.8	110.0$^{a)}$	7.06	14
μ_3-C_2H (**7**)	3	$FeNi_2$	1 (Fe)	2 (Ni_2)	1.313(7)$^{a)}$	127.5	100.5$^{a)}$	5.30$^{a)}$	15
μ_3-C_2H (**13**)	3	$FeMo_2$	3 ($FeMo_2$)	0	1.338(9)$^{a)}$	326.2	160.5	8.87	14
μ_4-C_2H (**10**)	4	$FeNi_3$	2 (FeNi)	2 (Ni_2)	1.32(2)$^{a)}$	163.9	117.3	7.73	15
μ_4-C_2H (**11**)	4	Fe_2Co_2	2 (Fe_2)	2 (Co_2)	1.34(1)	192.0	115.7	8.68	16
μ_4-C_2H (**12**)	4	Fe_2Co_2	3 ($FeCo_2$)	1 (Fe)	1.350(9)$^{b)}$	277.5	107.1$^{a)}$	7.18$^{a)}$	16
μ_5-C_2H (**8**)	5	Fe_2Co_3	4 (Fe_2Co_2)	1 (Co)	1.41(1)$^{a)}$	310.0	192.8	11.66	17
μ_5-C_2H (**56**)	5	$FeRu_4$	3 (Ru_3)	2 (FeRu)	1.420(9)$^{a)}$	c)		8.64	39
C_2 complex	n	M_n	Coordination mode		d(C–C)	δ_C(C_2)			Ref.
μ-C_2 (**2**)	2	Fe_2	2 (Fe_2)	0	1.209(4)	98.1			31
μ_4-C_2 (**15**)	4	Fe_2Co_2	2 (Fe_2)	2 (Co_2)	1.34(3)	154.4, 207.7			13
μ_4-C_2 (**14**)	4	$FeRu_3$	2 (FeRu)	2 (Ru_2)	1.30(1)$^{a)}$	96.8, 168.1			18
μ_4-C_2 (**16**)	4	Fe_2Ru_2	4 (Fe_2Ru_2)	0	1.24(1)	177.2			18
μ_5-C_2 (**56**)	5	$FeRu_4$	4 ($FeRu_3$)	1 (Ru)	1.32(2)$^{a)}$	c)			39
μ_5-C_2 (**57**)	5	$FeRu_4$	3 ($FeRu_2$)	2 (Ru_2)	1.334(9)$^{a)}$	c)			39
μ_6-C_2 (**17**)	8	Fe_2Ru_6	6 ($FeRu_5$)	0	1.35(4), 1.37(3)	22.7, 31.6			18

a) Parameters for the CpFe derivative. b) Parameters for the Ru derivative. c) Not recorded.

(μ_3-C≡C–Fp*)(μ-H)$Ru_3(CO)_9$ (**14**) via oxidative addition of the ≡C–H bond.[18)] The coordination structure of **14** can be viewed as an Fp*-substituted analogue of a trinuclear μ_3-acetylide complex where the $C_2R(Fp^*)$ bridge binds the three metal centers together through two π-bonds and one σ-bond.[19)]

(ii) Fluxional Behavior of the Cationic Diiron μ-Ethynyl Complex [Fp_2^*(μ-C≡C–H)]BF_4 via 1,2-H Shift Relevant to 1-Alkyne-to-Vinylidene Ligand Transformation.[10,22)] The cationic *dinuclear* μ-ethynyl complex [Fp_2^*(μ-C≡C–H)]BF_4 (**3**) was obtained by ligand displacement of a labile complex [Fp^{*+}(THF)]BF_4 with **1** (Eq. 1).[10,20)]



(1)

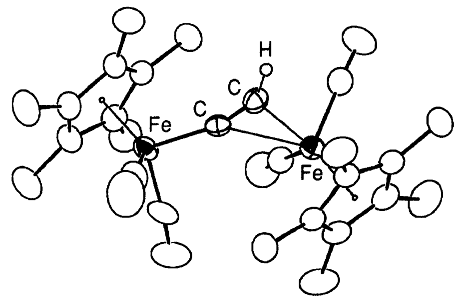


Fig. 1. Molecular structure of **3**. (The BF_4 anion is omitted for clarity.)

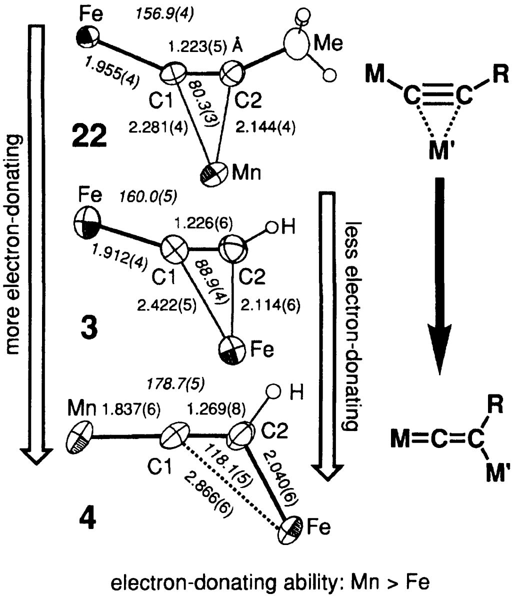
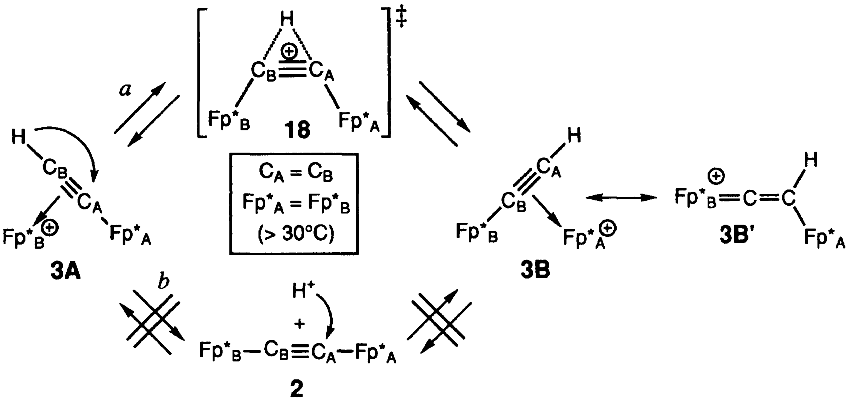
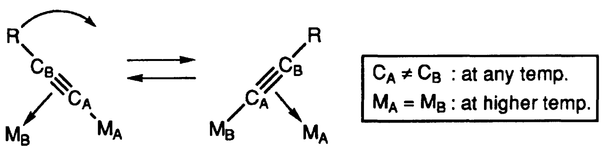


Fig. 2. Core structures of **3**, **4**, and **22**.

The bridging C_2H ligand in the resulting complex **3** is bonded to one of the two iron centers in an η^1-mode (σ-bonded) and to the other metal center in an η^2-mode (π-bonded) as confirmed by X-ray crystallography (Fig. 1). The distortion of the Fe2–C1–C2 moiety from an ideal isosceles triangle structure (Fig. 2) indicates contribution of a vinyldene structure **3'** in addition to the dominant contribution of an η^2-acetylene complex type canonical structure **3**. The deshielded C_α (C1) signal of the C_2H bridge compared to the C_β signal (Table 1) also suggests the contribution of **3'**, since the α-carbon signal of mononuclear vinylidene complexes M=C_α=CR_2 is usually located in very low field



Scheme 3.



Scheme 4.

(δ_C>300).[21]

These structural and spectroscopic features are not peculiar to the C_2H complex but are generally observed for classical C_2R complexes.[20] However, the ethynyl complex **3** exhibits unique fluxional property as shown in Fig. 3. At low temperature (−90 °C) a dynamic motion is frozen out to give a spectrum consistent with the solid state structure. The two metal centers are observed distinctively and the C_α and C_β signals are located at 124.2 and 72.2 ppm, respectively. Upon warming, the two sets of the Fp* signals coalesce into a single set of the signals, whereas the C_2H signals disappears in the temperature range of −60—0 °C and, above 30 °C, a single resonance is detected around the midpoint of the C_α and C_β signals observed at −90 °C. Comparison of the δ_C and J_{C-H} values leads to the conclusion that, at higher temperature, the $\underline{C}_2H$ carbon atom signals coalesce to be observed equivalently. This dynamic behavior has been interpreted in terms of an intramolecular 1,2-shift of the H atom on the C_2 bridge (path *a* in Scheme 3). The C_α atom in one structure (**3A**) migrates to C_β in the other structure (**3B**) through the symmetrical transition state **18**. Therefore, when the H-migration becomes faster than the NMR time scale, the $\underline{C}_2H$ atoms are observed equivalently. Another possible mechanism involves fast deprotonation–reprotonation equilibrium (path *b*), which, *apparently*, is supported by deprotonation by a base giving the ethynediyl complex Fp*–C≡C–Fp* (**2**) (see below). However, this mechanism can be eliminated on the basis of (i) *the absence of an intermolecular H^+-exchange process* confirmed by a mixing experiment with the η^5-C_5Me_4Et ($Cp^\#$) derivative of **3**, $[Fp^\#_2(\mu\text{-C≡C-H})]BF_4$ (**19**)[22] and (ii) *the negative $\Delta S^\ddagger$ value* estimated for the fluxional process of **3**. This unprecedented type of dynamic behavior is in striking contrast with the conventional windshield wiper-like mechanism proposed for dinuclear bridging alkynyl complexes $M_2(\mu\text{-}C_2R)$,[20] the $\underline{C}_2R$ carbon atoms of which are observed separately at any temperature (Scheme 4). The difference should come from the weaker C–H bond compared to C–R bond[23] and the cationic nature of **3** inducing a prototropic migration.

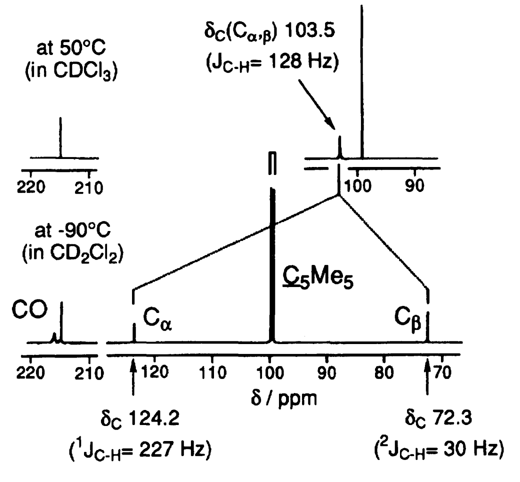
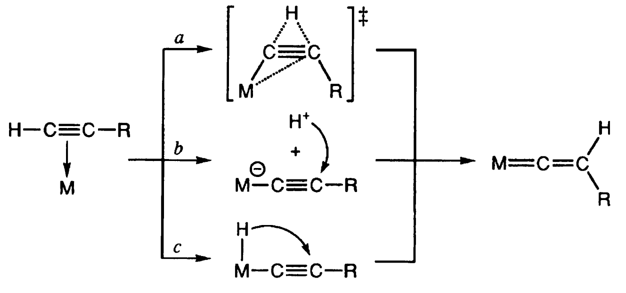
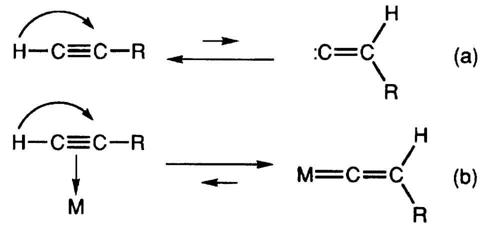


Fig. 3. Variable temperature ^1H NMR spectra of **3**. (The methyl region is omitted for clarity.)

Thus the diiron μ-ethynyl complex **3** *exhibits dynamic behavior by way of the fast intramolecular 1,2-H migration on the C_2 bridge.*[24] A similar dynamic process was proposed for interpretation of a solid state ^{13}C NMR spectrum of a C_2H species resulting from adsorption of ethyne on a Pt–alumina surface.[25] Furthermore, the contribution of the vinylidene structure **3′** is evident as mentioned above. When the metal center (Fp^*_A) σ-bonded to the C_2H bridge in **3A** is replaced by an organic group (R) (Scheme 3), the structural change from **3A** to **3B′** corresponds to *the intramolecular 1,2-H shift mechanism* proposed for transformation of 1-alkyne into a vinylidene species within a transition metal coordination sphere (Scheme 5).[21] This rearrangement is one of typical preparative methods for vinylidene complexes M=C=C(H)R and is involved as a key step in an in-



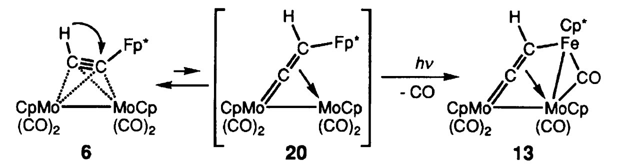
Scheme 5.



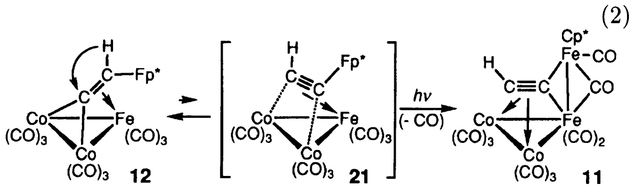
Scheme 6.

creasing number of catalytic reactions of 1-alkynes such as dimerization giving 1,3-butatriene.[26] Three different mechanisms, i.e. (a) intramolecular 1,2-H shift, (b) deprotonation giving an acetylide intermediate followed by reprotonation at C_β, and (c) successive oxidative addition affording M(H)(–C≡C–R) and 1,3-H shift,[27] have been proposed for the transformation. Although the first mechanism is most widely accepted, it was supported so far only by the EHMO calculation studied by Hoffmann et al.[28] Therefore the fluxional process of **3** serves as the first experimental evidence supporting mechanism (a).

Although uncatalyzed 1-alkyne-to-vinylidene tautomerization (path a in Scheme 6) is a highly unfavorable process owing to the thermodynamic instability of the divalent vinylidene species, coordination to a transition metal center results in inversion of the energetics (path b). The inversion results from availability of a vinylidene π^* orbital of suitable symmetry which receives d-electrons from the metal center effectively, as clearly indicated by the EHMO calculation.[28] However, little information on the rearrangements on polynuclear systems has been accumulated so far. In this context, we found that the trinuclear complexes **6** with a tetrahedral C_2Mo_2 core also showed a dynamic behavior by way of 1,2-H shift (**6**⇄**20** in Eq. 2).[14] Although we could not detect the vinylidene intermediate **20**, its intervention was suggested by isolation of the decarbonylated product **13** with the triply bridging vinylidene type-C_2H ligand. Similar reversible 1,2-H shift was also observed for a cluster compound **12** (Eq. 3), which was formed presumably via 1,2-H shift of an alkyne cluster intermediate **21** resulting from a capping reaction of **5** with $Fe_2(CO)_9$ (Scheme 2). Subsequent transformation of **12** to **11** should be initiated by backward 1,2-H shift regenerating the H–C≡C–Fe(Cp*) linkage (**21**) followed by photochemical decarbonylation inducing metal–metal bond formation.



(2)

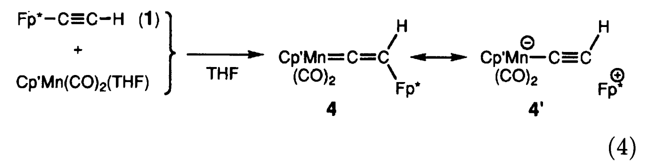


(3)

Thus the 1,2-H shift has proved to be a general process on transition metal complexes. Although limited examples of similar processes were reported for counterparts containing an organic substituent in place of the Fp* group,[29] the activation barrier of the Fe derivatives appears to be much lower than that of the organic counterparts. This phenomenon presumably comes from stabilization of an electron deficient transition state like **18** by donation of electrons from metal centers.[28]

(iii) Electronic Influence of the Metal Centers on the Structures of Dinuclear Bridging Alkynyl Complexes.[11] A number of homo- and heterobimetallic bridging acetylide complexes $MM'(\mu\text{-}C_2R)$ including **3** have been prepared and structurally characterized so far.[20] Although their structure is analyzed as a resonance hybrid of an η^2-structure (like **3**) and a vinylidene structure (like **3′**), electronic influence of the metal centers on the resulting structure has remained unsolved. This is mainly due to (1) lack of synthesis of a series of isoelectronic complexes suitable for an MO analysis and (2) additional interactions between the two metal centers such as M–M bond and other bridging ancillary ligands which obscure the intrinsic electronic interactions among metal centers and the C_2R bridge. Successful synthesis and structural characterization of a series of isoelectronic dinuclear complexes containing a C_2R ligand as a sole bridge provided us with a clue to this problem.

Treatment of **1** with $Cp'Mn(CO)_2(THF)$ [a source of the 16e-$Cp'Mn(CO)_2$ fragment which is isolobal with the Fp^{*+} species] produced a heterobimetallic bridging vinylidene complex $Cp'Mn(CO)_2[C{=}C(H)Fp^*]$ (**4**) (Eq. 4).[11] The reaction appears to proceed via 1,2-H shift of an η^2-intermediate, $CpMn(CO)_2(\eta^2\text{-}Fp^*\text{-}C{\equiv}C\text{-}H)$.



(4)

The complex **4** readily characterized on the basis of the diagnostic C_α signal (δ_C 310.5)[21] is the first example of a dinuclear M=C=C(R)M′-type complex. Small deviations of the structure from mononuclear vinylidene complexes $Cp'Mn(CO)_2(=C=CR_2)$ [(1) shift of C_α toward C_β by 0.05 Å; (2) shielding of the C_α resonance by ca. 70 ppm] are rationalized in terms of contribution of the zwitterionic structure **4′** as confirmed by an EHMO calculation. In contrast to the diiron complex **3**, an η^2-structure like **3** does not contribute to **4** at all. The introduction of the electron-donating Fp* group as the vinylidene substituents ($R_2=Fp^*+H$) causes pushing up the LUMO level of the vinylidene moiety [C=C-(H)Fp*] higher in energy so that back donation from the Mn center to the LUMO becomes less effective. As a result, *the back-donation from the two metal centers activates the* C_2H *bridge as a nucleophile.*

The core structures of the diiron complex **3** and the Fe,Mn–vinylidene complex **4** are reproduced in Fig. 2 together with another heterobimetallic complex $CpMn(CO)_2(\eta^2\text{-}Fp^*\text{-}C\equiv C\text{-}Me)$ **22** (the methylated product of **4**, see below). It is quite interesting that, although the three complexes are isoelectronic ones containing two isolobal 16e $(\eta^5\text{-}C_5R_5)M(CO)_2$ ($M=Fe^+$, Mn) fragments of the first raw elements as metal components and a C_2R ligand as the unique bridge, the resulting structures are considerably different depending on the combination of the metal components. Apparently, the structure of the dinuclear complexes changes from an η^2-structure to a vinylidene structure (**22**→**3**→**4**), as the electron-donating ability of the metal center σ-bonded to the C_2R ligand increases from Fe to Mn and, at the same time, the π-bonded metal center becomes less electron-donating. [The energy levels of the molecular orbitals of the $Cp'Mn(CO)_2$ fragment are higher than those of the isolobal Fp^{*+} fragment.] In order to consider electronic factors determining the structure of the dinuclear complexes, an EHMO calculation[11] has been carried out by using a model where dinuclear complexes $MM'(\mu\text{-}C_2R)$ consist of an interaction between the linear acetylenic moiety M–C≡C–R and the second metal center M′ like the interaction of η^2-alkyne metal complexes (**24**+**28** in Fig. 4). In the case of **22** where (1) the less electron-donating Fe group does not perturb the symmetrical structure of the filled M–C≡C–R's orbital (**23**) significantly and (2) the more electron-donating Mn fragment can back-donate effectively to the LUMO of the acetylenic part (**27**), an η^2-structure results from a typical Dewar–Chatt–Duncanson-type interaction (**24**+**28**) as observed for mononuclear η^2-alkyne complexes. On the other hand, when M is a more electron-donating group like Mn in **4**, the C_β's p orbital becomes bigger than that of C_α owing to electron donation from M (**25**). Then M′ moves to the direction of C_β in order to maximize the interaction with the bigger p orbital (**26**). At the same time, the back-donation from the filled orbital of M′ to the π* orbital of the acetylenic ligand (**30**) is not effective, because the metal-based orbital **29** with less C_2R character is pushed up higher in energy. As a whole, a vinylidene structure results from the **26**-type interaction as observed for **4**. The cationic diiron complex **3** lies between these two extremes.

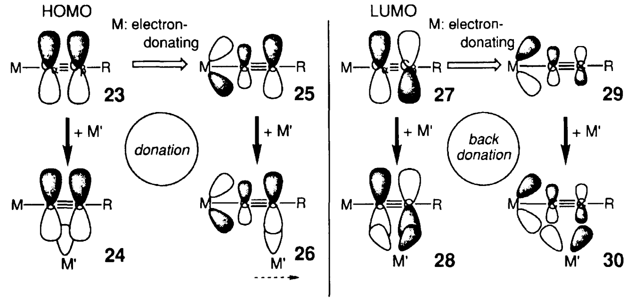


Fig. 4. Orbital interactions of $MM'(\mu\text{-}C_2R)$.

When the positions of M, M′, and R of our complexes (**3**, **4**, and **22**) and related mono- and dinuclear complexes are plotted with respect to the C_2 bridge, we can see a good correlation between the electron-donating ability of the metal centers and structural parameters which may be regarded as indicators of the contribution of the vinylidene structure [e.g. the angle $\angle C_\alpha\text{-}C_\beta\text{-}M'$ and the difference in the distances from M′ to the two carbon atoms $D(C_\alpha\text{-}M')-D(C_\beta\text{-}M')$] [Fig. 5; Mn and Fe stand for $(\eta^5\text{-}C_5R_5)M(CO)_2$ fragments and R′ is an alkyl group.]. *As M becomes more electron-donating* ($R'\rightarrow Fe^+\rightarrow Mn$) *and M′ becomes less so* ($Mn\rightarrow Fe^+\rightarrow R'$), *in other words, as the entry number increases, the structure changes from an* η^2*-structure to a vinylidene structure.* This trend is consistent with the result of the above-mentioned EHMO analysis. Thus the dependence of the structure of dinuclear bridging alkynyl complexes on the electronic properties of the metal centers is revealed for the first time.

Furthermore the structural continuum shown in Fig. 5 reminds us of the reaction pathway calculated for the 1-alkyne-to-vinylidene tautomerization (after the transition state shown by baldfaced characters).[28] In the case of the dinuclear complexes, the intermediate states are stabilized by balancing the back-donation from the two metal centers **26** and **30**, i.e. a struggle of the filled d-electrons of M and M′ toward the vacant C_α's p orbital, whereas, in the case of the 1,2-H shift, the position of the H atom is dependent on the relative size of the C_α and C_β's p orbitals, which is determined by the extent of interaction between the C_α's p orbital and metal d orbital. Anyway, lack of the **28**(**30**)-type interaction causes spontaneous migration to accomplish the ligand transformation after the transition state.

(iv) Transformation of the C_2H Bridge into C2 Species: Stepwise H-addition Leading to C_2H_x Species (x=0—4).[10,11,22,30,31] Reactivity of the dinuclear C_2H complexes has been investigated to explore reaction patterns of C_2H species. As a result, it is found that the isoelectronic complexes **3** and **4** exhibit quite

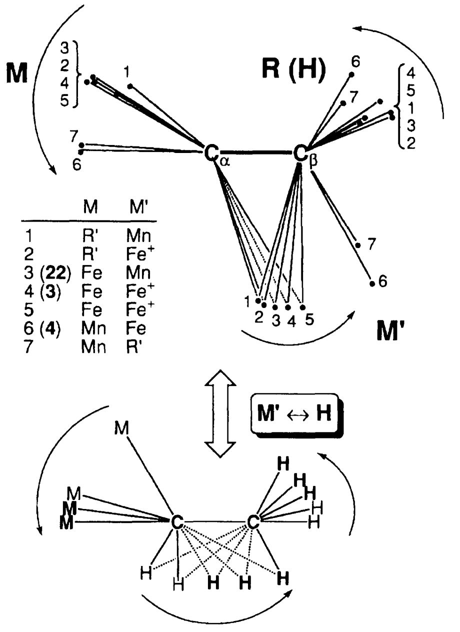


Fig. 5. Structural continuum of MM′(μ-C_2R) and comparison with the reaction pathway calculated for the 1-alkyne-to-vinylidene rearrangement.[28]

similar reactivity as shown in Scheme 7.

The prototropic rearrangement of **3** (Scheme 3) suggests an acidic nature of the $C_2\underline{H}$ atom. As expected, **3** was readily deprotonated by bases such as NEt_3, NaOMe, and alkyllithiums to give the ethynediyl dimetal complex **2**,[20,30] whereas reaction with Superhydride afforded the bridging vinylidene complex (**34**) via nucleophilic addition to C_β.[31,32] The ethynediyl complex **2** belongs to a rather rare class of compounds which have been synthesized mainly by (1) deprotonation of $M_2(\mu\text{-}C_2H)$[10,30,7c,7e] like the formation of **2**, (2) salt elimination from M–C≡C–Li and M′X,[71] and (3) the Cu(I)-catalyzed coupling between M–C≡C–H and M′X,[7d] and has proved to be a good starting complex for dicarbide (C_2) cluster compounds (see below).[7] Electrophilic addition to **2** took place at the C_2 bridge. Protonation regenerated **3** and methylation afforded the propynyl complex **35**.

Similarly, **4** was deprotonated by the action of a base to generate an anionic ethynediyl species **36**.[11,22] The $C_2\underline{H}$ atom in **4** is readily deuterated in the presence of a catalytic amount of NaOEt in EtOD, and is irreversibly deprotonated by BuLi. The latter result contrasts with the nucleophilic addition reaction of mononuclear Mn vinylidene complexes $Mn{=}C{=}CR_2$ where R′Li attacks the electrophilic α-carbon atom to give an anionic carbene intermediate $Mn{=}C(R')\text{–}C\text{–}R_2$.[21,33] In the case of **4**, such C_α attack may be hindered by an increased electron density at C_α owing to the back-donation from the two metal centers as discussed above. The resulting anionic species **36** could be trapped by electrophiles, D^+ and MeI, to give the deuterated starting complex (**4**-*d*) and the methylated η^2-complex **22** through reaction at C_α and C_β, respectively. Although the C_β attack should be the preferable reaction pathway owing to the electron donation from the Mn fragment of higher energy, the methylation at C_α was attributed to the steric repulsion between the Fp* moiety and the electrophile.

Further reaction of the neutral and anionic ethynediyl species **2** and **36** with RLi resulted in nucleophilic addition to CO coordinated to Fe giving acyl intermediates **31** and **37**. Subsequent reductive elimination and Fe-slippage forming a metal–metal bond produced the mono- (**32**) and dianionic dinuclear vinylidene species (**38**), deuterolysis of which afforded the acylated bridging vinylidene (**33**) and vinyl complexes (**39**), respectively.

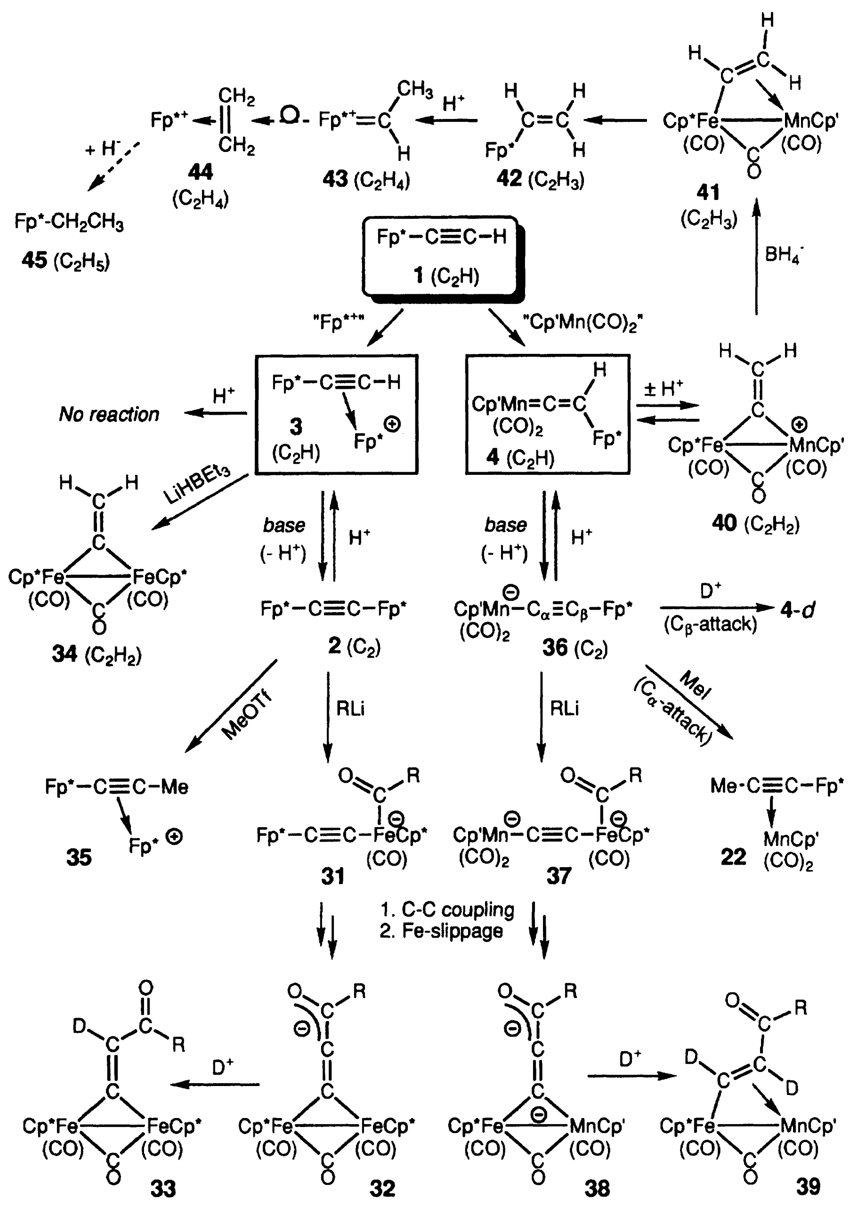
On the other hand, reaction of **4** with H^+ (an electrophile) readily took place at C_β of the electron-rich C_2H bridge to give a cationic bridging vinylidene complex **40** via Fe-slippage, whereas the cationic complex **3** was not affected by H^+ any more. The complex **40** was readily characterized on the basis of the ^{13}C NMR data [$\delta(C_\alpha)=280.1$, $\delta(C_\beta)=132.1$] which is comparable to those of the isoelectronic diiron complex **34** [$\delta(C_\alpha)=295.5$, $\delta(C_\beta)=113.4$].[31] The protonation of **4** was reversible, and a catalytic amount of H^+ induces H–D exchange of **4** in EtOD. Thus *the C_2H bridges function as carbon acids as well as carbon bases.* Subsequent reduction of **40** with a hydride reagent (Et_4NBH_4) produced the vinyl complex **42** by way of an unstable dinuclear μ-vinyl intermediate **41** arising from hydride addition to C_α. The mononuclear vinyl complex **42** would be further converted to ethylidene (**43**) and ethylene species (**44**) by the action of proton and then to the ethyl complex **45** by hydride addition.[3e]

*Thus the C_2H bridge in **3** and **4** is converted to C_2H_x ($x=0$—5) species successfully by a combination of simple addition or abstraction of H^+ and H^-.* This sequential transformation may be realized by stabilization of intermediates (in particular, cationic ones) by electron donation from the two metal centers and serves as a model system for hydrogen-addition steps to a dicarbide species.

Polymetallic C₂ Complexes: Toward Systematic Synthesis of Dicarbide Cluster Compounds

Although the structure and reactivity of carbide cluster compounds (μ-C)M_n were investigated extensively during the last two decades,[34] the homologous complexes with more carbon atoms (μ-C_m)M_n have been targets of recent studies.[35] Some typical coordination modes of polymetallic dicarbide complexes ($m=2$) are summarized in Chart 1 (**46**,[8d,8e] **47**,[8f] **48**,[13,8g] **49**[8j,8k,81]). The C_2 bridge binds 3—6 metal centers together through σ- and π-bonds. More complicated structures **50** and **51** were reported recently by Bruce et al.[8m]

In contrast to the diverse reactivity of the ethynyl



Scheme 7.

complex 1, most of the corresponding reactions of 2 were sluggish probably due to the steric hindrance of the two bulky Fp* groups. In this section a couple of selected structural aspects of the C_2 complexes are discussed.

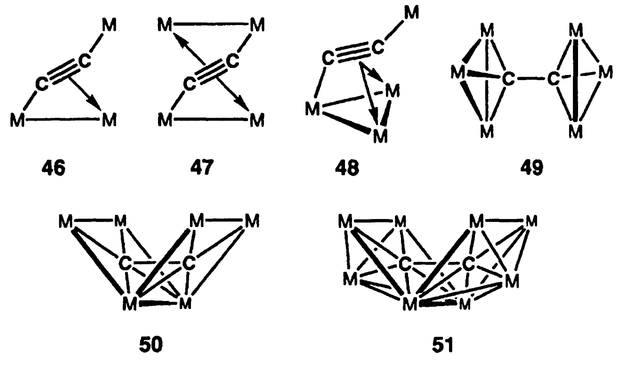
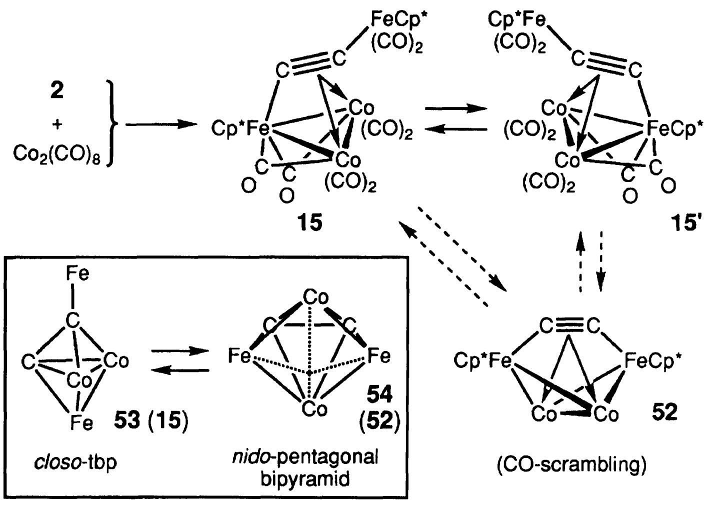


Chart 1.

(i) A Cluster Compound Which Is Fluxional via Reversible Metal–Metal Bond Scission and Recombination Process.13) Of the attempted structure expansion of 2 by interaction with mono- and dinuclear species, only the Co_2-adduct 15 was obtained successfully (Scheme 2).13) Despite of the normal 48-type coordination structure which was viewed as an Fp*-substituted analogue of a trinuclear μ_3-acetylide complex,19) it showed an interesting NMR behavior. While the ^{13}C NMR spectrum recorded at −80°C with the C_2 signals at 154.4 (C–Fp*) and 207.7 ppm (CCo_2Fe) was consistent with the X-ray structure, only a single set of the Fp* signals were observed at room temperature. Thus, at higher temperatures, (1) the two Cp*Fe moieties are observed equivalently, (2) the C_2



Scheme 8.

signals are not located due to a dynamic process, and (3) the CO ligands attached to the $FeCo_2$ cluster part and those bonded to the remote Fp* part exchange at a rate comparable to the NMR time scale. These phenomena can be explained by a combination of cluster skeletal rearrangement and CO scrambling as shown in Scheme 8. The remote Fp* part interacts with the $FeCo_2$ cluster core to form an intermediate **52** with the Fe_2Co_2 butterfly structure. Subsequent extrusion of the Fp* group via metal–metal bond scission regenerates the original structure. If the rate of this reaction sequence as well as CO scrambling at the stage of **52** becomes comparable to the NMR time sale, only one set of the Fp* signals should be observed. The C_2 signals with large separation of the chemical shifts ($\Delta\delta$ 53 ppm) don't reach a fast exchange limit at ambient temperature. This associative mechanism can also be described as an interconversion between the spiked *closo*-trigonal bipyramidal structure **53** and the *nido*-pentagonal bipyramidal structure **54**, both of which have 68 CVE (cluster valence electrons) (Scheme 8). While a number of fluxional cluster compounds have been reported, almost all the examples of the fluxionality originate from fast movement of ligands (e.g. CO) on a metal framework.[36)] The present system is a quite rare example of cluster compounds showing a fluxional property via a reversible M–M bond disruption/recombination process.

The interaction of **2** with a tetracobalt species $Co_4(CO)_{12}$, which is known to react with alkynes to give adducts with an octahedral C_2Co_4 core,[37)] afforded a pentanuclear C_2H cluster **8** via H-pick up and addition of a tricobalt unit resulting from deterioration of the tetranuclear structure (Scheme 2).[17)]

(ii) Sequential Structural Transformation of Dicarbide Cluster Complexes.[17,18,39)] As an extension of the reaction of **2** with polynuclear species, we examined the reaction with a trinuclear species $Ru_3(CO)_{12}$ which was known to react with alkynes to give various types of adducts.[38)] The reaction carried out in refluxing benzene or toluene afforded a complicated mixture of products, from which three polynuclear C_2 complexes **14**, **16**, and **17** were isolated by chromatographic separation (Scheme 9).[18)] One of the tetranuclear cluster **14** was obtained selectively from the ethynyl complex **1** (Scheme 2). The core structure of the novel tetranuclear (**16**) and octanuclear dicarbide cluster compounds (**17**) are reproduced in Fig. 6 together with that of the starting complex (**2**).

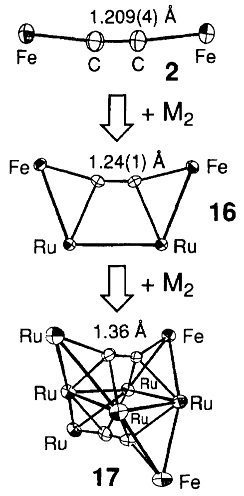


Fig. 6. Sequential transformation of dicarbide complexes.

The tetranuclear complex **16**, in which each carbon atom of the C_2 bridge interacts with the two metal cen-

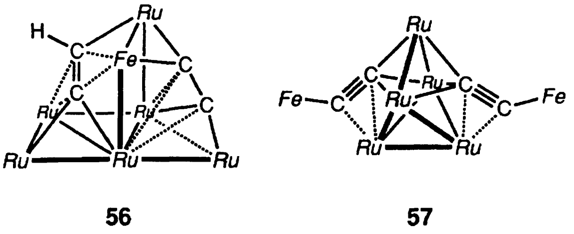
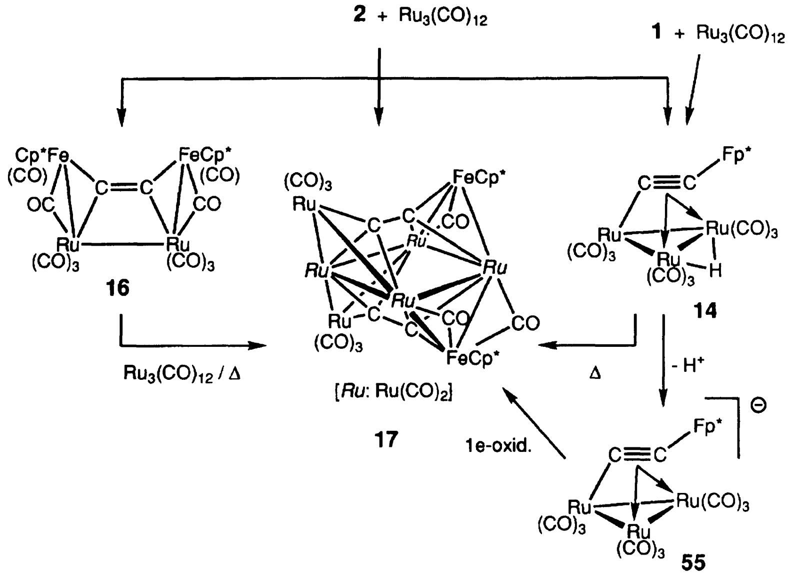


Chart 2.



Scheme 9.

ters (Fe and Ru), is the first example of a permetallated ethene ($M_2C{=}CM_2$), though the structure is distorted considerably owing to the trapezoidal Fe_2Ru_2 framework. The C–C distance [1.27(2) Å], which is slightly longer than that of **2** [1.209(4) Å][18,39] but substantially shorter than the C=C lengths of dinuclear μ-vinylidene complexes $M_2(\mu\text{-}C{=}CR_2)$ (1.30—1.35 Å),[21] indicates triple bond character still remaining. On the other hand, the structure of **17** contains two C_2 bridges coordinated to an octametallic array. Every edge of the central Ru_4 square is bridged by Fe or Ru, and each C_2 moiety interacts with the boat-like hexanuclear $FeRu_5$ partial structure above and below the Ru_4 square. Such a boat-like metal array is found in a finite piece of an *fcc* or an *hcp* lattice. Since each carbon atom of the C_2 bridges lies in a distance of bonding interaction of the three metal centers ($FeRu_2$ or Ru_3), the partial structure of **17** can be viewed as a permetallated ethane like **49**. The electron precise octanuclear dicarbide cluster **17** with 124 CVE (C_2: 8e-donor) is the second example of a dicarbide complex with the boat-like metal array next to the hexacobalt cluster $(\mu_6\text{-}C_2)Co_6(\mu_4\text{-}S)(CO)_{14}$ reported by Stanghellini.[81]

Treatment of an isolated sample of the tetranuclear complex **16** with $Ru_3(CO)_{12}$ in reluxing benzene gave a mixture containing the octanuclear cluster **17**. This result implies that a permetallated ethyne M–C≡C–M (**2**: M=Fp*) can be converted into a permetallated ethene $M_2C{=}CM_2$ (**16**) and then into a permetallated ethane $M_3C\text{–}CM_3$ (**17**) (Fig. 6) by stepwise formal addition of dimetallic fragments to the C≡C triple bond in **2**.

It should be noted that the core composition of **17** $[Fe_2Ru_6(\mu\text{-}C_2)_2]$ is just twice as that of the other tetranuclear product **14** $[FeRu_3(\mu\text{-}C_2)]$ formed in a substantial yield. When **14** was thermolyzed in refluxing toluene or the deprotonated anionic species **55** was treated with a 1e-oxidizing reagent (Cp_2Fe^+), **17** was obtained through dimerization of the cluster core (Scheme 9). The latter process should involve coupling of a radical species. Similar cluster coupling was observed for the Cp derivative of **14** to give heptanuclear clusters $CpFeRu_6(\mu_5\text{-}C_2)(\mu_5\text{-}C_2H)(CO)_{16}$ (**56**) (thermolysis) and $Cp_2Fe_2Ru_5(\mu_5\text{-}C_2)_2(CO)_{17}$ **57** (radical coupling) (Chart 2; CO ligands attached to the Ru atoms are omitted for clarity.) in addition to the octanuclear bis(dicarbide) cluster (the Cp derivative of **17**).[39] The unsymmetrical cluster **56** with the M-shaped basal Ru_5 plane fused with the $FeRu_3$ square contains C_2 and C_2H ligands. The coordination structure of the C_2H part may be viewed as a trimetallated ethene (Ru_3) sandwitched by two metal centers (FeRu), while the $(\mu_5\text{-}C_2)FeRu_5$ moiety corresponds to the partial structure of **16**. A structure similar to the latter one was reported already by Bruce.[8i] Judging from the structure of **56** (The Fe center loses CO ligands completely.), its formation may be initiated by decarbonylation from the more labile Fe center. On the other hand, the C_2-symmetrical arrowhead-shaped cluster **57** with retention of the Fp structure should be formed by condensation of a Ru_3 cluster-centered radical. These type of direct coupling reactions may serve as a pottentially useful synthetic method for higher nuclearity cluster compounds where a bridging ligand (e.g. C≡C) tightly binds the metal centers together to prevent fragmentation of the cluster structure.

Conclusions

A variety of polymetallic C2 (C_2 and C_2H) complexes are prepared successfully by structure expansion of the parent metal acetylides, Fp*–C≡C–H (**1**) and Fp*–C≡C–Fp* (**2**), and their structure and reactivity are investigated as models for surface-bound C2 species. As a result, following aspects have been revealed by the present study. (1) The novel coordination structures of the C2 complexes with 1—8 metal atoms are characterized by X-ray crystallography and spectroscopic methods. (Scheme 2 and Table 1) As can be seen from Table 1, as the number of the metal atoms interacting with the C2 ligand increases, the C–C distance tends to be elongated. The $C_2\underline{H}$ signals are usually located in lower field, and the α-carbon atom of the C_2H complexes resonates in lower field than the β-carbon atom probably owing to contribution of a vinylidene resonance structure. However, no apparent correlation between the ^{13}C NMR data and the coordination structure is established except for the typical vinylidene complexes (**4**, **8**, **12**, and **13**). (2) The 1,2-H shift of the C_2H ligand has proved to be a general process observed for the di-, tri-, and tetranuclear complexes, and the structural and spectroscopic analyses of the dinuclear system have provided us with helpful information concerning the mechanism of the 1-alkyne-to-vinylidene rearrangements within a metal coordination sphere and the electronic factors determining the dinuclear bridging acetylide complexes. (3) The ligand transformation system where C_2H is converted into various C2 functional groups serves as a model system for the reaction pathways of C2 species on a heterogeneous catalyst surface. (4) Higher nuclearity dicarbide cluster compounds with novel coordination modes are prepared by stepwise addition of metal fragments as well as direct coupling of a performed lower-nuclearity cluster structure.

Though the study has not been completed yet, we hope that the results of our study will help understanding of the structure and reactivity of surface C2 species.

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1) Abbreviations used in this paper: Cp = η^5-C_5H_5; Cp′ = η^5-C_5H_4Me; Cp* = η^5-C_5Me_5; Cp$^\#$ = η^5-C_5Me_4Et; Fp=CpFe$(CO)_2$; Fp*=Cp*Fe$(CO)_2$; Fp$^\#$=Cp$^\#$Fe$(CO)_2$.

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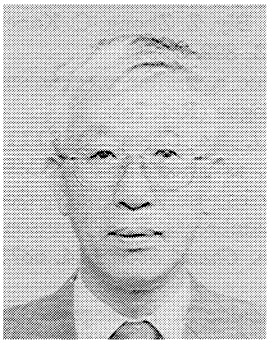

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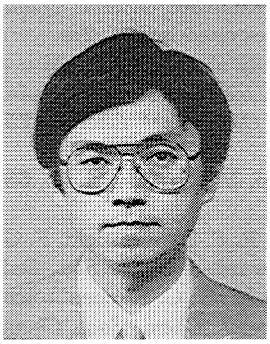

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