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Review

Cluster compounds containing a linear carbon chain derived from polyynediyl and polyynyl complexes, $Fp^*-(C\equiv C)_n-X$ [$X = Fp^*$, H; $Fp^* = Fe(\eta^5\text{-}C_5Me_5)(CO)_2$]☆

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Abstract

Our studies on polynuclear complexes containing a one-dimensional carbon chain derived from polyynyl [$Fp^*-(C\equiv C)_n-H$ **1**^{n}] and polyynediyl complexes [$Fp^*-(C\equiv C)_n-Fp^*$ **2**^{n}; $Fp^* = FeCp^*(CO)_2$] are reviewed. Reaction of **1**^{n} and **2**^{n} with di- and trinuclear metal carbonyl species produces polycarbon–polymetal systems with a variety of coordination structures including η^2-alkyne, μ-acetylide, μ-cumulenylidene, μ_3-alkylidyne and μ_3-propargylidene structures. In addition to the cluster formation reactions as usually observed for acetylide and alkyne cluster compounds, the unique cluster transformations such as valence isomerization of the conjugated carbon chain, metal migration along the carbon rod and C≡C cleavage reaction are observed. These transformations are realized by the flexible electronic structure of the π-conjugated carbon chain (polyynyl↔cumulenic), which fits the electronic structure of the attached metal fragments.

Keywords: Cluster compounds; Linear carbon chain; Polyynediyl complexes

1. Introduction

Polyynediyl, $M-(C\equiv C)_n-M$, and polyynyl complexes, $M-(C\equiv C)_n-H$ [1], are versatile precursors for cluster compounds containing a one-dimensional carbon chain. We have been carrying out synthetic study of polynuclear complexes containing carbon-rich hydrocarbyl fragments as models for intermediates of surface-catalyzed reactions, in particular, catalytic CO hydrogenation (Fischer–Tropsch reaction). One of our projects was synthesis of polynuclear complexes containing $C_2H_xO_y$ (C2) bridge. C2 species should be formed via the first coupling (carbon-chain propagation) of C1 species but little attention had been paid to such species.

Our attention was first focused on heterobimetallic bridging ketene complexes, $M-CH_2-C(=O)-M'$ (a coupling product of methylene and CO species) [2], and subsequently the study was extended to polynuclear complexes containing C_2H and C_2 ligands, which were derived from the ethynyl ($M-C\equiv C-H$) and ethynediyl complexes ($M-C\equiv C-M$). Such types of compounds, which are regarded as parent compounds of metal acetylides, were very rare even in early ’90’s and we succeeded in synthesis of both types of compounds with the $Fe(\eta^5\text{-}C_5Me_5)(CO)_2$ endcap (Fp^*). As a result of our synthetic study, a variety of C_2H and C_2 cluster compounds were obtained and their chemistry was summarized in a review article several years ago [3]. The synthetic study has been further extended to those containing longer carbon chains, which could be accessible from polyynyl [$M-(C\equiv C)_n-H$] and polyynediyl complexes [$M-(C\equiv C)_n-M$] [4,5].

Herein we wish to describe a brief review of our study on cluster compounds containing a linear carbon chain. Although polynuclear complexes with a longer carbon chain may not be viewed as models for surface-bound species, new interest from the viewpoint of material science has appeared. For example, polyynediyl complexes are regarded as molecular wire [6], because the

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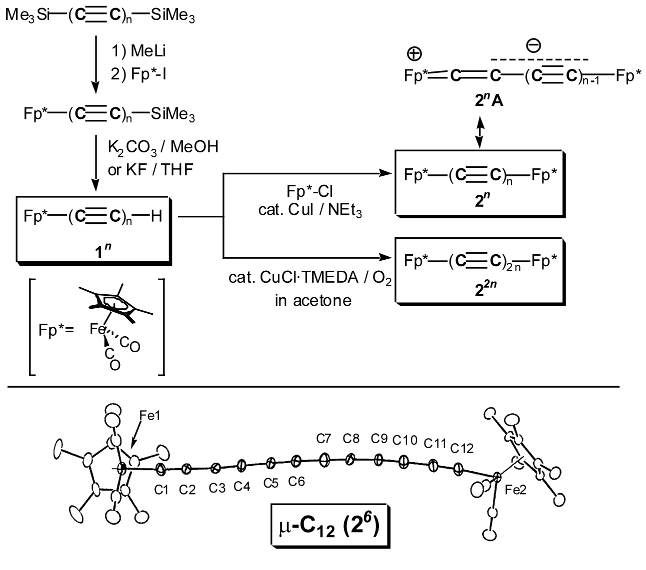
two terminal metal groups can communicate with each other through the π-conjugated systems arising from interaction of p-orbitals of carbon atoms and d orbitals of the terminal metals.

2. Polyynyl and polyynediyl complexes [1f,1g]

Polyynyl and polyynediyl complexes bearing the $FeCp^*(CO)_2$ (Fp*) terminus were prepared by conventional methods (Scheme 1) [1]. Polyynyl complexes, $Fp^*\text{–}(C\equiv C)_n\text{–}H$ ($\mathbf{1}^n$) (The number of the C≡C unit is shown as the italicized superscript.), were readily obtained by alkynylation of Fp*–I with $Li\text{–}(C\equiv C)_n\text{–}SiMe_3$ ($n = 2, 3$) followed by desilylation. Cu-catalyzed metalation of $\mathbf{1}^n$ with Fp*–X gave the polyynediyl complex $\mathbf{2}^n$ with the same carbon chain length, while Cu-catalyzed oxidative dimerization (Hay coupling [7]) of $\mathbf{1}^n$ afforded the polyynediyl complex $\mathbf{2}^{2n}$ with the doubled carbon chain length. Through these reactions a series of $\mathbf{1}^n$ ($n = 1, 2, 3$) and $\mathbf{2}^n$ ($n = 1, 2, 3, 4, 6$) has been prepared and some of them were characterized crystallographically.

Selected spectroscopic and structural data for $\mathbf{1}^n$ and $\mathbf{2}^n$ are summarized in Tables 1 and 2, and the molecular structure of $\mathbf{2}^6$ with the longest carbon chain obtained in our laboratory is shown in Scheme 1. ^{13}C-NMR signals for the carbon chains appear in the range of 50–120 ppm (Tables 1 and 2). Although the signals for the $(C\equiv C)_n\text{–}H$ ligands in $\mathbf{1}^n$ can be assigned on the basis of the magnitude of the $J_{C\text{–}H}$ values, assignment for the $(C\equiv C)_n$ bridge in $\mathbf{2}^n$ can not be made due to lack of coupling information. In addition, as is evident from the data for $\mathbf{1}^n$, the ^{13}C-NMR signals of the carbon chain don't always appear in the descending order, as the carbon atom goes from the metal side to the CH terminus.



Scheme 1.

Similar irregular appearance of the $(C\equiv C)_n$ carbon signals has been noted for those containing FeCp*(dppe), $RuCp(PPh_3)_2$ and $ReCp(NO)(PPh_3)$ fragments [1], for which assignments are made on the basis of the $J_{P\text{–}C}$ values. In Table 1 the carbon signals for the $(C\equiv C)_n$ bridge in $\mathbf{2}^n$ are tentatively assigned following the descending order.

IR data have proven to be more informative. The CO vibrations are shifted to lower energies, as the carbon chain becomes longer. But the shift is saturated as is evident from the same ν_{CO} values for $\mathbf{2}^4$ and $\mathbf{2}^6$. The shift indicates that a longer carbon chain is a better electron-acceptor. Similar tendency has been reported for the $ReCp(NO)(PPh_3)$ complexes [1h,1i,1j,1k,1l]. Lower energy shift is also observed for the C≡C vibrations but the change of the $\nu_{C\equiv C}$ pattern is not monotonic because of coupling of C≡C vibration modes. The lower energy shifts of the $\nu_{C\equiv O}$ and $\nu_{C\equiv C}$ vibrations should be due to contribution of cumulenic structure ($\mathbf{2}^n\mathbf{A}$) and, in accord with this consideration, the Fe–C≡ length becomes shorter, as the carbon chain becomes longer. No systematic change, however, is observed for the C≡C and ≡C–C≡ lengths, which are ca. 1.2 and 1.35 Å, respectively. Although the carbon chain linkage is essentially linear as is evident from the C–C–C angles larger than 172°, it should be noted that the C_{12} carbon chain in $\mathbf{2}^6$ [1g] is slightly twisted (Scheme 1). Similar deformation was later reported by Gladysz for the μ-C_{12} and μ-C_{16} derivatives of the platinum complex [1n,1m,1o].

3. Interaction of butadiynyl complexes $\mathbf{1}^2$ with di- and tri-metallic species leading to polynuclear C_4H complexes

As a typical example of polyynyl complexes $\mathbf{1}^n$, butadiynyl complex $\mathbf{1}^2$ bearing the C_4H ligand was subjected to interaction with di- and tri-nuclear metal carbonyls and was found to readily react with them to afford polynuclear adducts (Scheme 2).

Interaction with homo- and hetero-bimetallic species $[Co_2(CO)_8]$, $[MoCp(CO)_2]_2$, $(OC)_4Co\text{–}MoCp(CO)_3]$ resulted in formation of the adducts with the tetrahedral (μ-η^2:η^2-C_2)MM′ core (**3a**–**c**) [4c] in a manner similar to the adduct formation with alkynes [8], and structural and spectroscopic features of the cores are essentially the same as those of the alkyne-adducts. It is notable that the adduct formation always occurs at the less hindered C≡C–H moiety distal from the bulky Fp* center. Since the M–M′ part in **3** is far from the Fp* terminus for bonding interaction, no attractive interaction between the two metallic moieties leading to a cluster structure is observed. Attempted reaction of $\mathbf{1}^2$ with $Fe_2(CO)_9$ afforded an intractable mixture of products.

While a 1:1 reaction of $\mathbf{1}^2$ and $Co_2(CO)_8$ gave the 1:1 adduct **3a**, addition of an excess amount of $Co_2(CO)_8$

Table 1
Selected spectroscopic data for Fp*–(C≡C)$_n$–H (**1**^{n}) and –Fp* (**2**^{n}) [1f,1g,3]

Complex (ligand)	^{13}C-NMR [a]						IR [b]		
	C_α	C_β	C_γ	C_δ	C_ε	C_ζ	$\nu_{C\equiv C}$	ν_{CO}	ν_{CH}
1^1 (C_2H) [c]	97.0 (55)	97.5 (227)						2022, 1967	3279
1^2 (C_4H) [d]	106.4	92.8 (7)	71.9 (50)	53.5 (252)			2141	2027, 1977	3033
1^3 (C_6H) [e]	114.6	93.7	64.5	48.6 (7)	70.4 (52)	61.7 (255)	2158 2100	2030, 1982	3296
2^1 (μ-C_2)	98.1							1996, 1951	
2^2 (μ-C_4) [f]	98.5	79.8					2150	2020, 1967	
2^3 (μ-C_6) [f]	99.7	94.9	54.0				2094	2020, 1974	
2^4 (μ-C_8) [f]	110.8	94.8	61.6	51.4			2136, 2088	2028, 1981	
2^6 (μ-C_{12}) [f]	118.3	94.6	64.8	62.2	58.9	50.5	2123, 2087	2028, 1981	

[a] Observed in $CDCl_3$ or CD_2Cl_2. Chemical shifts and J_{CH} values shown in parentheses are reported in ppm and Hz, respectively.
[b] CH_2Cl_2 solution samples.
[c] $\delta_H(C_2H)$ 1.99.
[d] $\delta_H(C_4H)$ 1.42.
[e] $\delta_H(C_6H)$ 1.75.
[f] Tentatively assigned in the descending order.

resulted in double addition of the Co_2 fragment to the two C≡C units in **1**^{2} to give **4**, which was also obtained by stepwise addition (**3a** → **4**). Contrastingly, reaction of **3a** with the diiron species, $Fe_2(CO)_9$, did not result in addition to the unreacted C≡C part proximal to the Fe center in **3a** but cluster formation with the C_2Co_2 core to afford the trinuclear μ-η^1(Co):η^2(Fe):η^2(Fe)-acetylide cluster type compound **5** [9] accompanying elimination of a $HCo(CO)_n$ fragment.

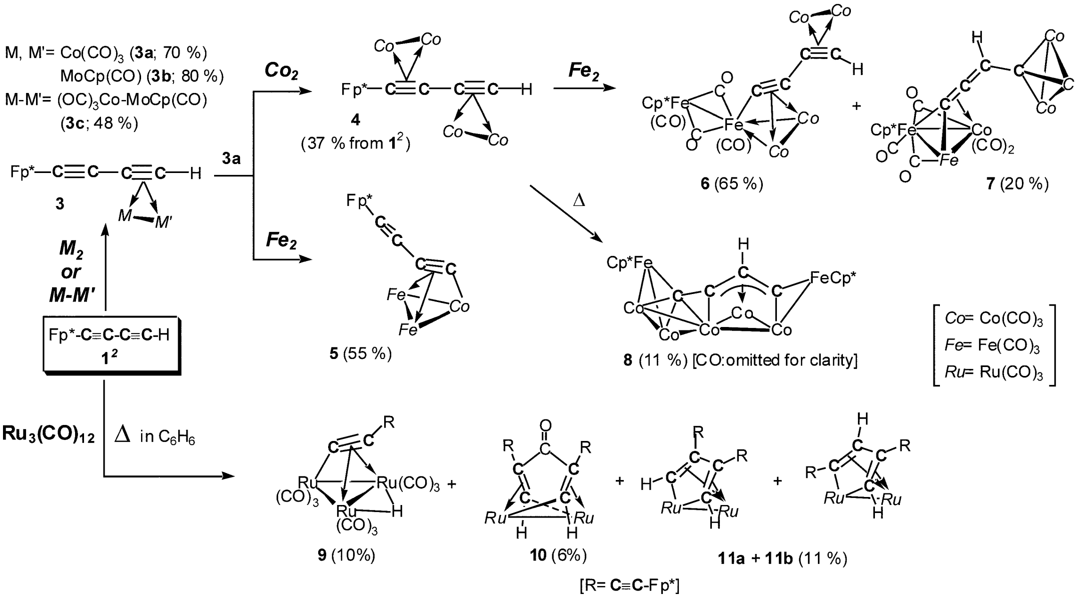
No further addition of $Co_2(CO)_8$ to **4** was observed but **4** further interacted with $Fe_2(CO)_9$ to give **6** and **7**, adducts of an $Fe(CO)_n$ fragment. The major product **6** arises from formal insertion of an $Fe(CO)_n$ fragment into the Cp*Fe–C≡ bond in **4**, and the formation of the minor product **7**, a hybrid of μ_3-allenylidene [10] and μ_3-alkylidyne structures, can be interpreted in terms of a reaction sequence involving (i) interaction of an $Fe(CO)_n$ species with the (μ-η^2:η^2-Fp*–C≡C)Co_2 moiety to give an Fe_2Co_2 core, (ii) formation of the triangular Fe_2Co and Co_3 cores via transfer of a $Co(CO)_n$ unit from the resultant Fe_2Co_2 core to the distal Co_2 moiety, and (iii) 1,2-H migration of the C_4H ligand leading to μ-allenylidene–alkylidyne ligand system. Since (i) the two products are not interconvertible and (ii) **6** and **7** are $(CO)_{16}$ and $(CO)_{17}$ species, respectively, they should be formed via independent reaction pathways. The spiked triangular Fe_2Co_2 linkage in **6** contains two dative Co → Fe bonds.

Thermolysis of the double adduct **4** afforded the heptanuclear Fe_2Co_5 cluster compound **8**, which could be described as a hybrid of a μ_4-acetylide cluster compound with the butterfly M_4 core (**A**), trinucler dimetalloallyl cluster structure (**B**) and the dinuclear μ-vinylidene structure (**C**) (Scheme 3). The unique cluster compound **8** should be formed via addition of a $Cp^*FeCo(CO)_n$ fragment to the distal (C≡C–H)$Co_2(CO)_6$ moiety associated with 1,2-H shift on the C_4H linkage. The $Cp^*FeCo(CO)_n$ fragment should be

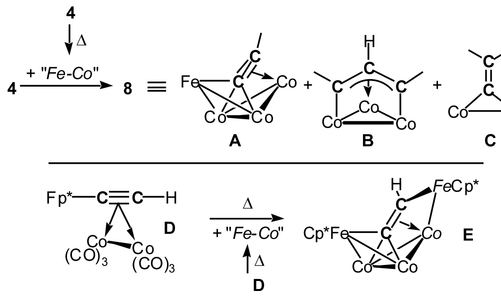
Table 2
Selected structural parameters for Fp*–(C≡C)$_n$–H (**1**^{n}) and –Fp* (**2**^{n}) [1f,1g,3]

Complex	Fe–C	C≡C	C–C	C_ω–Fe	C–C–C, C–C–Fe
1^1 (C_2H) [a]	1.921(3)	1.173(4)			178.7
1^2 (C_4H) [a]	1.907(4)	1.207(5) (C1–C2) 1.153(6) (C3–C4)	1.378(6)		178.0–179.0
2^1 (μ-C_2) [a]	1.939(4)	1.202(5)		1.935(3)	173.0–173.8
2^2 (μ-C_4) [a,b]	1.933(4)	1.197(5) (C1–C2) 1.197(5) (C2*–C1*)	1.398(7)	1.933(4)	178.0
2^2 (Rp) (μ-C_4) [a]	1.90(1) (Fe–C)	1.21(1) (C1–C2) 1.91(1) (C3–C4)	1.40(1)	2.034(9) (C–Ru)	174–178
2^6 (μ-C_{12}) [c]	1.878(9)	1.23(1) (C1–C2) 1.20(1) (C3–C4) 1.22(1) (C5–C6) 1.23(1) (C7–C8) 1.19(1) (C9–C10) 1.20(1) (C11–C12)	1.36(1) (C2–C3) 1.35(1) (C4–C5) 1.35(1) (C6–C7) 1.36(1) (C8–C9) 1.38(1) (C10–C11)	1.888(8)	172.7–178.2

[a] Data collection at room temperature.
[b] Centrosymmetric structure sitting on a crystallographic inversion center.
[c] Data collection at −60 °C.



Scheme 2.



Scheme 3.

formed via partial decomposition of **4**. A similar process [elimination of Cp*FeCo(CO)$_n$ followed by addition to the original structure] was observed for the related C$_2$H complex (**D** → **E**) [3b].

In contrast to the reactions with dinuclear species, in which both of the two C≡C moieties in **1**^{2} took part in bond formation, interaction of **1**^{2} with Ru$_3$(CO)$_{12}$ left the Fp*–C≡C moiety unaffected, i.e. **1**^{2} served as 1-alkyne bearing the Fp*–C≡C substituent [11]. The reaction gave a complicated reaction mixture containing the μ$_3$-acetylide cluster type product **9**, the dinuclear flyover complex **10** and an isomeric mixture of dinuclear metallacyclopentadiene complexes **11a**, **b** (Scheme 2), and the reaction feature was essentially the same as that of the reactions of Ru$_3$(CO)$_{12}$ with 1-alkyne [12].

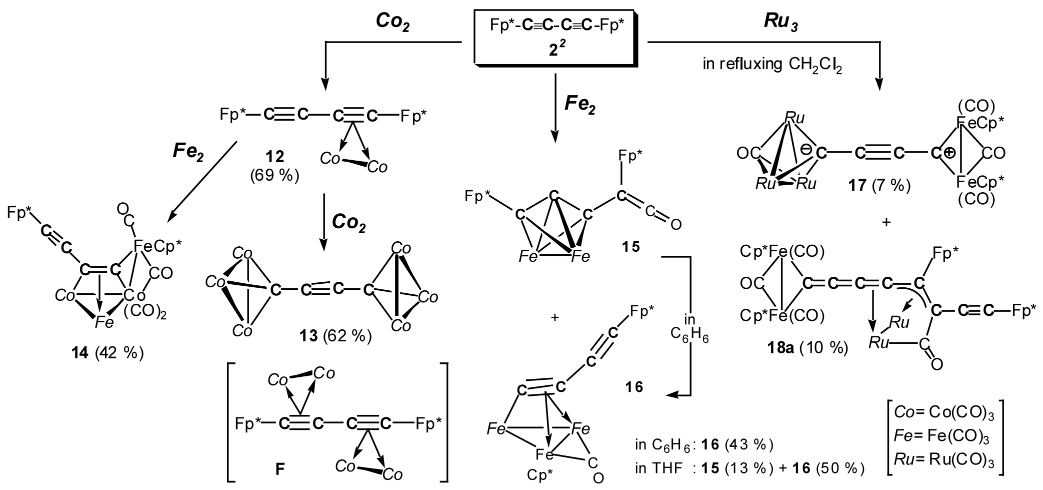
Thus butadiynyl complex **1**^{2} reacts with di- and tri-nuclear species to give adducts **4**–**11**. The adduct formation occurs preferentially at the less hindered distal C≡C–H part. While the reaction with an excess amount of Co$_2$(CO)$_8$ results in addition to the sterically congested Fp*–C≡C part, in the reaction with Ru$_3$(CO)$_{12}$ the butadiynediyl complex **1**^{2} serves as 1-alkyne (R–C≡C–H) bearing the Fp*–C≡C substituent (R), which is left unaffected. Upon treatment with Fe$_2$(CO)$_9$ or thermolysis, the Co$_2$-adducts **3a** and **4** are converted to cluster compounds via decarbonylative metal–metal bond formation (**5**–**7**) or addition of metal species derived from thermal decomposition (**8**).

4. Cluster synthesis from polyynediyl complexes 2^n

Reaction of polyynediyl complexes results in not only cluster formation but also novel transformations of the carbon chain.

4.1. Reactions of butadiynediyl complex 2^2 with dinuclear species: cluster formation and valence isomerization of the C$_4$ bridge

Treatment of the butadiynediyl complex **2**^{2} with an equimolar amount of Co$_2$(CO)$_8$ gave the 1:1 adduct **12** with a tetrahedral (μ-η^2:η^2-C≡C)Co$_2$ core in a manner similar to the reaction of **1**^{2} (Scheme 4) [4d]. The reaction with an excess amount of Co$_2$(CO)$_8$, however, did not afford the 1:2 adduct **F** as observed for **1**^{2} (**4**) but the hexacobalt bis(alkylidyne) cluster compound **13** [13] together with Cp*FeCo(CO)$_5$. The buta-2-yne-1,4-diylidyne C$_4$-linkage in **13** should be formed via valence isomerization of the butadiynediyl linkage in **2**^{2} as shown in Scheme 5. Although the reaction was carefully examined (e.g. addition of Co$_2$(CO)$_8$ in small portions and NMR experiments), only **12**, **13** and Cp*Fe(CO)$_5$ were observed but the 1:2 adduct **F** was not detected at all. This result suggests that, as soon as the adduct **F** is formed, it is converted to **G** (–CO) and then to **13** [+

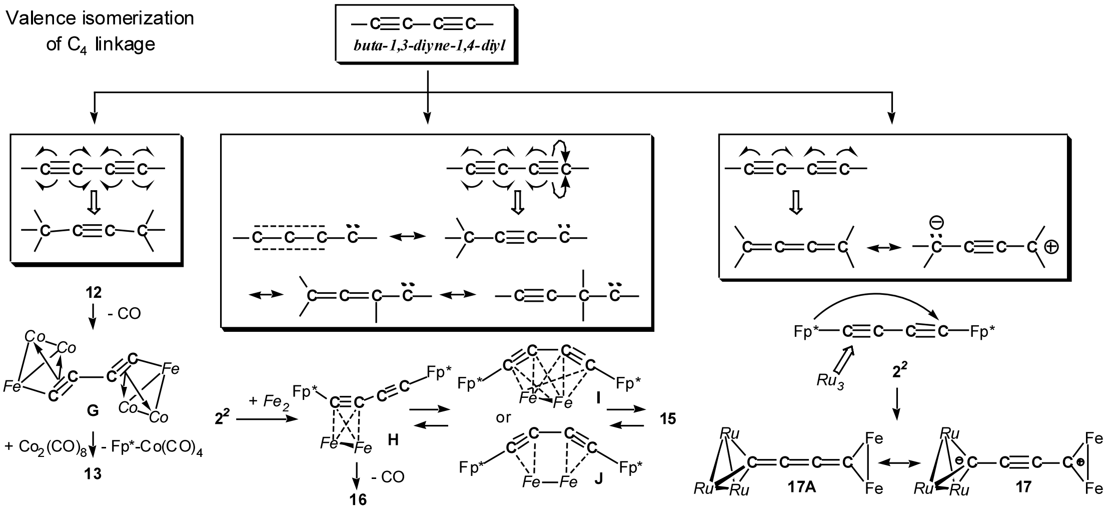


Scheme 4.

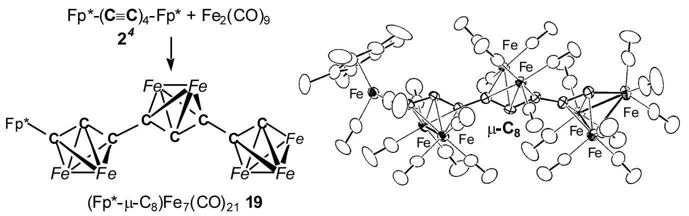
$Co_2(CO)_8$ $-Cp^*FeCo(CO)_5$] in order to release steric congestion of the cluster moieties. Steric congestion of the hexacobalt cluster compound **13** is much released compared with those of the intermediates **F** and **G**. Similar valence isomerization of a C_4 rod was reported by Bruce for $(OC)_3CpMo-(\mu\text{-}C_4)-WCp(CO)_3$ and intermediates corresponding to **G** were isolated [5c,5e].

Further reaction of the 1:1 adduct **12** with the diiron species, $Fe_2(CO)_9$, did not occur at the unreacted Fp*–C≡C moiety but at the $(\mu\text{-}\eta^2:\eta^2\text{-}Fp^*-C\equiv C)Co_2$ moiety to give the tetranuclear acetylide cluster compound with the spiked triangular metal array **14**. Such a reaction feature is the same as that observed for the C_4H complex (**3a**→**5**). The metal array in **14** is formed through addition of a monometallic fragment, $Fe(CO)_n$, to the Co_2 moiety in **12** followed by decarbonylative metal–metal bond formation with the Fp* group.

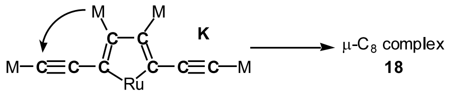
Interaction of $\mathbf{2}^2$ with $Fe_2(CO)_9$ led to formation of a mixture of the unique η^3-propargylidene–ketene complex **15** and the acetylide cluster compound **16** (Scheme 4) [4b]. The product distribution was dependent on the reaction solvent used. The reaction in benzene afforded **16** as a sole product, whereas addition of THF caused formation of **15** in addition to **16**. Furthermore stirring a benzene solution of **16** at ambient temperature caused conversion to **15** via decarbonylation. Formation of the acetylide cluster compound **16** should follow interaction of a diiron fragment with a C≡C moiety in $\mathbf{2}^2$ (**H**; Scheme 5) and subsequent decarbonylative metal–metal bond formation. The structure of the other, unique product **15** can be divided into the C_3 and ketene parts. The former part is described as a dinuclear μ_3-propargylidene structure with the virtually equidistant Fe–C bonds, suggesting the resonance hybrid system involving the propargyl- and allenyl-type contributors as shown in Scheme 5. μ_3-Propargylidene structure is rare [14] but we have encountered an analogous structure **19**, which was obtained upon treatment of the μ-C_8 complex $\mathbf{2}^4$ with $Fe_2(CO)_9$ (Scheme 6) [11]. A plausible formation mechanism of **15** (Scheme 5) involves conversion to a η^4-



Scheme 5.



Scheme 6.



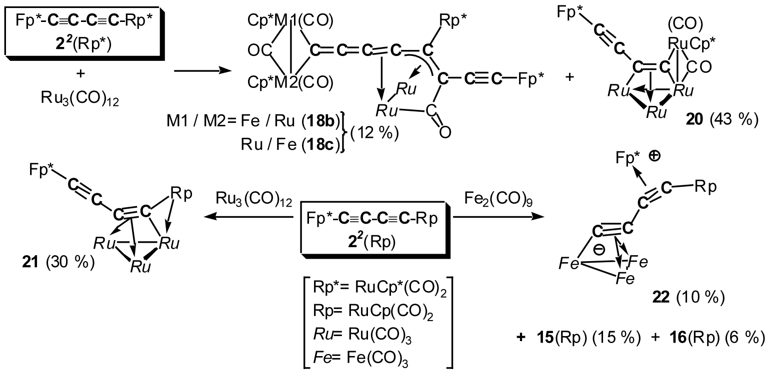
Scheme 7.

bonded intermediate **I** or **J** followed by CO migration to the terminal carbon atom of the C_4 bridge leading to the ketene functional group. An intriguing feature is that the C=CO bond formation process can be reversed as evidenced by the facile conversion of **15** to **16** under ambient conditions.

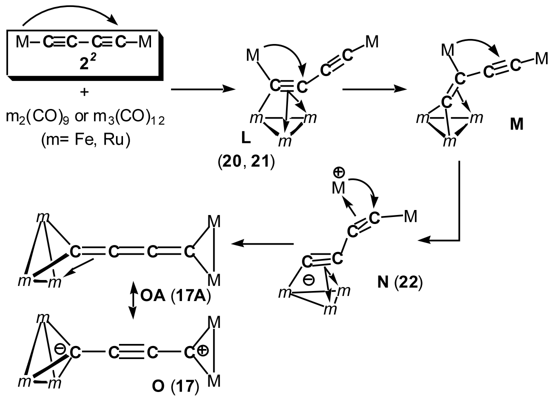
4.2. *Reaction of butadiynediyl complex $\mathbf{2}^2$ with a trinuclear species, $Ru_3(CO)_{12}$: migration of a metal fragment along the C_4 rod [4e]*

Treatment of $\mathbf{2}^2$ with $Ru_3(CO)_{12}$ in heated benzene gave a mixture of products, from which two cluster compounds **17** and **18a** were isolated and characterized (Scheme 4). As for **17**, a single set of Cp*-NMR resonances and the highly deshielded ^{13}C-NMR signal (δ_C 347.1) led to assignment as the mirror-symmetrical cumulenic structure **17A** (Scheme 5). Although a single crystal of **17** could not be obtained, its η^5-C_5Me_4Et analogue $\mathbf{17}^{\#}$ was characterized by X-ray crystallography. The zwitterionic structure $\mathbf{17}^{\#}$ is found to be the dominant resonance contributor as is evident from (i) bond alternation of the C_4 linkage [Ru_3C–C: 1.34(1); C–C: 1.25(1); C–CFe_2: 1.31(1) Å], (ii) the equidistant Ru–C bonds: 2.093–2.120(9) Å], (iii) μ_3-coordination of the bridging CO ligand to the Ru_3 face, and (iv) two of the four μ-C_4 ^{13}C-NMR signals appearing in the region of the C≡C functional group. It should be noted that the structure **17(17A)** results from migration of the Fe(η^5-C_5Me_4R)$(CO)_n$ fragment from one end to the other end along the C_4 rod (Scheme 5). The other isolated product **18a** contains a dimeric structure of $\mathbf{2}^2$ as is indicated by the four sets of Cp* resonances and eight quarternary carbon signals. X-ray crystallography of **18a** reveals the unique hexanuclear structure containing a highly conjugated C_8 carbon chain containing the μ-pentatetraenylidene functional group. It is notable that the C_8–metal conjugated system forms also via 1,4-metal migration on the ruthenacyclopentadiene intermediated **K**, which results from oxidative metallacyclization of $\mathbf{2}^2$ on a ruthenium species (Scheme 7) [15].

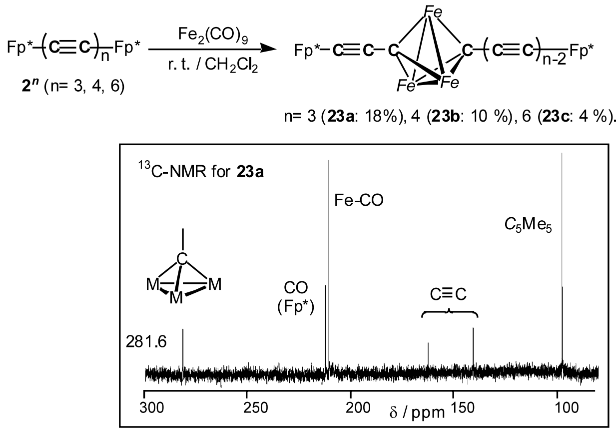
Since these results implicate that metal migration may occur on related systems, heterometallic derivatives of $\mathbf{2}^2$ were subjected to reaction with group 8 metal carbonyls, $Ru_3(CO)_{12}$ and $Fe_2(CO)_9$, and selected results are shown in Scheme 8. Reaction of Fp*–C≡C–C≡C–Rp* $\mathbf{2}^2$(Rp*) [Rp* = RuCp*$(CO)_2$] [16] with $Ru_3(CO)_{12}$ produced an inseparable, isomeric mixture of the dimeric species **18b**, **c** in addition to the acetylide cluster compound **20**. Careful NMR, FDMS and crystallographic analyses of **18b**, **c** revealed that no homodimer (M1 = M2 = Fe or Ru) was formed at all indicating that the metal migration process followed an intramolecular process. On the other hand, reaction of the Rp derivative $\mathbf{2}^2$(Rp) [Rp = RuCp$(CO)_2$] [16] with $Ru_3(CO)_{12}$ produced the adduct **21**, whereas that with $Fe_2(CO)_9$ afforded the zwitterionic complex **22** in addition to **15**(Rp) and **16**(Rp) (see above). The zwitterionic complex **22** can be regarded as a hybrid of a cationic dinuclear μ-η^1:η^2- acetylide complex and an anionic μ-η^1:η^2:η^2-acetylide cluster compound, both of which are coordinatively saturated. As is evident from the structure characterized crystallographically, **22** results from migration of the Fp* fragment along the C_4 rod (Scheme 5). The structure of **21** with the long Ru(Rp)→Ru dative bond [2.965(2) Å] [11] reminds us



Scheme 8.



Scheme 9.



Scheme 10.

of the classical triiron acetylene cluster compound, (μ_3-Ph–C≡C–Ph)$Fe_3(CO)_9$, reported more than 30 years ago [17].

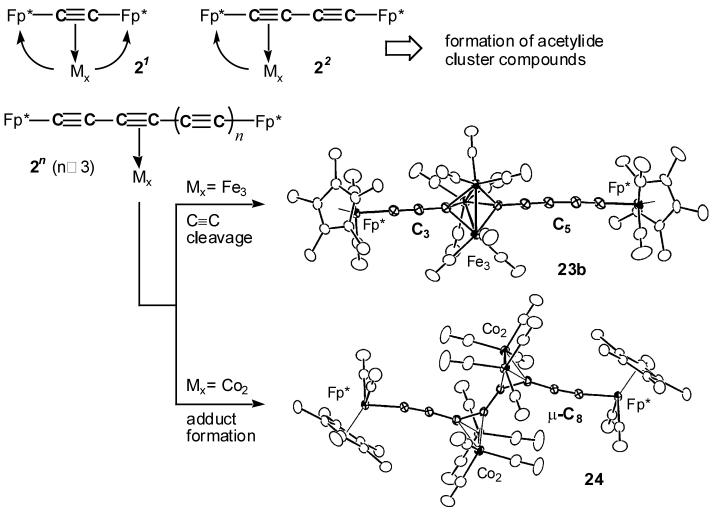
When the results obtained are combined, a plausible migration mechanism involving stepwise migration of the metal fragment along the C_4 rod can be depicted as summarized in Scheme 9, where the related compounds are indicated in parentheses. Initial coordination of **2^2** to the trimetallic species gives rise to the μ-alkyne cluster-type adduct **L**. Subsequent stepwise migration of the metal fragment along the C_4 rod leads to sequential formation of the vinylidene intermediate **M**, the zwitterionic intermediate **N**, and finally to the cumulenic structure **OA**, which is in resonance with the zwitterionic alkyne structure **O**. The vinylidene cluster type intermediate **M** is the only missing link in the reaction sequence. The unique metal migration is realized by the flexible coordination feature of the linear polycarbon linkage, which can adopt either polyynyl or cumulenic resonance structure to fit the electronic structures of the attached metal fragment. Through the processes found in the present study (Schemes 5, 7 and 9) a variety of new conjugated polycarbon–metal systems have been successfully obtained.

4.3. Reaction of polyynediyl complex 2^n ($n \geq 3$) with $Fe_2(CO)_9$: C≡C cleavage reaction [4c]

Interaction of polyynediyl complexes **2^n** bearing a longer carbon chain ($n \geq 3$) with $Fe_2(CO)_9$ gave the orange products **23** completely different from the products **15** and **16** obtained from the butadiynediyl complex **2^2** (Scheme 10). The ^{13}C-NMR spectrum of **23a** obtained from the μ-C_6 complex **2^3** (Scheme 10) is informative; the simple spectral pattern and the highly deshielded signal at δ_C 281.6 suggest formation of a symmetrical structure containing a μ_3-alkylidyne functional group. X-ray crystallography of **23a** reveals the symmetrical, bicapped bis(μ_3-alkylidyne) cluster-type structure resulting from C≡C cleavage at the central C≡C part in **2^3**, and **23b**, **c** also show the deshielded ^{13}C-NMR signals [**23b**: δ_C 270.1, 289.6; **23c**: δ_C 257.0, 297.4]. The C≡C cleavage site (C_γ≡C_δ) in **23b** was also confirmed by X-ray crystallography (see Scheme 11), whereas that in **23c** derived from the μ-C_{12} complex **2^6** could not be determined by spectroscopic methods but should be either of the inner C≡C moieties (C_γ≡C_δ or C_ε≡C_ζ). No evidence for double cleavage of **2^6** leading to Fp*–C≡C–(μ_3-C)[$Fe_3(CO)_9$](μ_3-C)–C≡C–(μ_3-C)[$Fe_3(CO)_9$](μ_3-C)–C≡C–Fp* was obtained.

In order to examine generality of the C≡C cleavage reaction, related compounds, Me_3Si–(C≡C)$_3$–$SiMe_3$ and Fp*–(C≡C)$_3$–$SiMe_3$ (the precursors for **2^3**), were allowed to react with $Fe_2(CO)_9$. As a result, the latter underwent the C≡C cleavage reaction to give Fp*–(C≡C)–(μ_3-C)[$Fe_3(CO)_9$](μ_3-C)–(C≡C)–$SiMe_3$, whereas the former gave a mixture of products, which did not show deshielded ^{13}C-NMR signals in the region below 250 ppm, i.e. C≡C cleavage reaction did not take place. These results indicate that at least one Fp*-substitution is essential for the present C≡C cleavage reaction, in other words, donation of electrons from the Fp* end group to the (C≡C)$_n$ rod should facilitate the cleavage reaction. A similar electronic effect was discussed by Hoffmann and Shapley [17e].

The difference of the reactivities between **2^n** ($n = 1, 2$) and **2^n** ($n \geq 3$) could be ascribed to the location of the reaction site with respect to the terminal Fp* group (Scheme 11). In the case of **2^1** and **2^2** with the shorter carbon chain, the Fp* group is always adjacent to the C≡C part, where the addition occurs, and therefore, formation of simple adducts is always followed by metal–metal bond formation via decarbonylation to lead to acetylide cluster-type products such as **16**. The driving force for the cluster formation should be release of the steric congestion. Contrastingly, in the case of **2^n** ($n \geq 3$), reaction at the inner C≡C moiety should be preferable to that at the Fp*–C≡C moiety due to the steric repulsion with the bulky Fp* group. Since the metal fragment added to the inner part of the polyynediyl linkage is too far from the Fp* terminus to form



Scheme 11.

a metal–metal bond, another reactivity, i.e. C≡C cleavage in the case of the reaction with $Fe_2(CO)_9$, may emerge (Scheme 11). In accord with the consideration on the initial reaction site, treatment of $\mathbf{2}^4$ with $Co_2(CO)_8$ afforded the adduct, Fp*–C≡C–C≡C[$Co_2(CO)_6$]–C≡C[$Co_2(CO)_6$]–C≡C–Fp* (**24**) (Scheme 11), where the central two C≡C groups form the adducts with the tetrahedral (η^2:η^2-C≡C)Co_2 core as observed for **3a** and **4** (Scheme 2).

Carbon–carbon triple bonds are very strong as is evident from the very large bond dissociation energy (~ 200 kcal mol^{-1}) and, therefore, it is not facile to cleave it under mild conditions. $CpML_2$ species (M: group 9 metals) are known to be effective for C≡C cleavage reaction but the reaction requires severe reaction conditions such as flash vacuum pyrolysis and refluxing in a solvent with a high boiling point (e.g. decaline) [18]. In contrast to these systems the present C≡C cleavage reaction proceeds under very mild conditions, i.e. at ambient temperature, due to the promotion effect of the Fp* substituent.

5. Conclusion

Polyynyl ($\mathbf{1}^n$) and polyynediyl complexes ($\mathbf{2}^n$) have proven to be versatile precursors for polynuclear compounds containing a linear carbon chain. Interaction with di- and trinuclear metal carbonyls leads to the formation of adducts with a variety of coordination structures including η^2-alkyne, μ-acetylide, μ-cumulenylidene, μ_3-alkylidyne and μ_3-propargylidene structures. Through these transformations highly conjugated polycarbon–metal systems become accessible.

In addition to the alkyne- and acetylide-cluster type chemistry some novel processes such as valence isomerization of the conjugated carbon chain, metal migration along the carbon rod and C≡C cleavage reaction under ambient conditions have been found for polyynediyl complexes $\mathbf{2}^n$ and these processes are realized by virtue of the steric effects of the bulky terminal metal fragments as well as the flexible electronic structure of the carbon chain (polyynyl↔cumulenic), which fits the electronic structure of the attached metal fragments.

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