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Facile C≡C bond cleavage of polyynediyldiiron complexes, Fp*–(C≡C)$_n$–Fp* [Fp* = Fe(η^5-C_5Me_5)$(CO)_2$; n = 3, 4], with $Fe_2(CO)_9$ leading to bis(μ_3-alkylidyne) complexes, Fp*–C≡C-μ_3-C–$Fe_3(CO)_9$–μ_3-C–(C≡C)$_{n-2}$–Fp*

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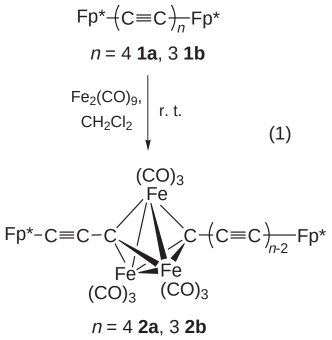
Reaction of the polyynediyldiiron complexes, Fp*–(C≡C)$_n$–Fp* [Fp* = Fe(η^5-C_5Me_5)$(CO)_2$; n = 3, 4], with $Fe_2(CO)_9$ at room temperature results in C≡C bond cleavage to give the bis(μ_3-alkylidyne) complexes, Fp*–C≡C-μ_3-C–$Fe_3(CO)_9$–μ_3-C–(C≡C)$_{n-2}$–Fp*, a trinuclear cluster complex sandwiched by the two conjugated (C≡C)$_x$–Fe systems.

Carbon–carbon bond cleavage reaction on transition metal species has for a long time been an intriguing subject in the field of organotransition metal chemistry[1] since such studies should provide new strategies for activation and functionalization of hydrocarbons. C(sp)–C(sp) (C≡C) bond cleavage and coupling reactions on polynuclear systems have had several precedents over the last three decades and the group 9 metal systems [M(η_5-C_5R_5): M = Co, Rh, Ir] have been studied most extensively.[2] Previously reported C≡C cleavage reactions, however, require vigorous reaction conditions such as pyrolytic reactions. During the course of the synthetic study of polynuclear C_{2n} complexes (2n = 2, 4, 6, 8) derived from the corresponding polyynediyldiiron complexes, Fp*–(C≡C)$_n$–Fp* **1** [Fp* = Fe(η^5-C_5Me_5)$(CO)_2$],[3] we observed C≡C bond cleavage reaction of **1** under very mild reaction conditions.

Reaction of the octatetraynediyldiiron complex **1a** with $Fe_2(CO)_9$ in CH_2Cl_2 (or THF, benzene) for 7 h at ambient temperature afforded orange complex **2a** (18% yield)† as a single product after removal of insoluble materials by filtration [eqn. (1)]. Complex **2a** was also obtained by reaction with $Fe_3(CO)_{12}$. The ^{1}H NMR spectrum of **2a** contains two Cp* signals indicating an unsymmetrical structure and only η^1-CO ligands are detected by IR. The most characteristic spectroscopic feature of **2a** is the highly deshielded quaternary carbon signals [δ_C ($CDCl_3$) 270.1, 289.6], which suggest formation of a complex bearing two μ_3-alkylidyne functional groups, *i.e.* a C≡C bond in the C_8 linkage is cleaved by the action of the iron carbonyls. The C≡C bond cleavage position is definitely confirmed to be the inner C3≡C4 bond as revealed by X-ray crystallography [Fig. 1(a)].‡ The (μ_3-C)$_2$$Fe_3(CO)_9$ unit adopts a typical bicapped μ3-alkylidyne structure as indicated by its structural parameters: (i) the Fe_3 moiety is virtually an equilateral triangle with Fe–Fe separations of Fe31–Fe41 2.498(2), Fe31–Fe51 2.514(2), Fe41–Fe51 2.518(2) Å; (ii) the μ_3-alkylidyne carbon atoms are located almost equidistant from the three iron centers [Fe–μ_3-C: C3–Fe31: 1.955(5), C3–Fe41 1.981(8), C3–Fe51 1.972(8), C4–Fe31 1.962(9), C4–Fe41 1.962(7), C4–Fe51 1.942(5) Å]. These parameters are comparable to those of previously reported μ_3-alkylidyne triiron cluster compounds.[4] The acetylenic moiety is essentially linear and clear bond alternation is observed: [Fe11-C1 1.900(6), C1≡C2 1.228(9), C2–C3 1.389(9), C4–C5 1.39(1), C5≡C6 1.21(1), C6–C7 1.38(1), C7≡C8 1.19(1), C8–Fe21 1.904(7) Å; C–C–C(or Fe11,21) 173.9–179.1(8)°]. The absence of **2b** (see below) in the reaction mixture indicates that the present C≡C cleavage reaction involves an intramolecular process.



C≡C cleavage was also observed for an analogue, the hexatriynediyl complex **1b** (10% yield)[5] [eqn. (1)]. Spectroscopic and crystallographic analyses of the product **2b**† reveal cleavage between the central C3≡C4 bond, and the structural parameters for the Fe–C≡C–(μ_3–C)Fe_3(μ_3–C)–C≡C–Fe moiety [Fe–Fe 2.503–2.538(4), C–Fe_3 1.92–2.00(1) Å, Fe1–C1 1.87(1), C1≡C2 1.26(1), C2–C3 1.38(1), C4–C5 1.37(1), C5≡C6 1.23(1), C6–Fe2 1.88(1) Å; C–C–C(or Fe1,2) 172–176(1)°] are similar to those of **2a**.

The present C≡C cleavage reaction of **1a**,**b** is in sharp contrast to the results of the reactions of the lower congeners, the butadiynediyl (**1c**: n = 2) and ethynediyl complexes (**1d**: n = 1), which afford other types of products (**4**–**6**)[3b] The C≡C units

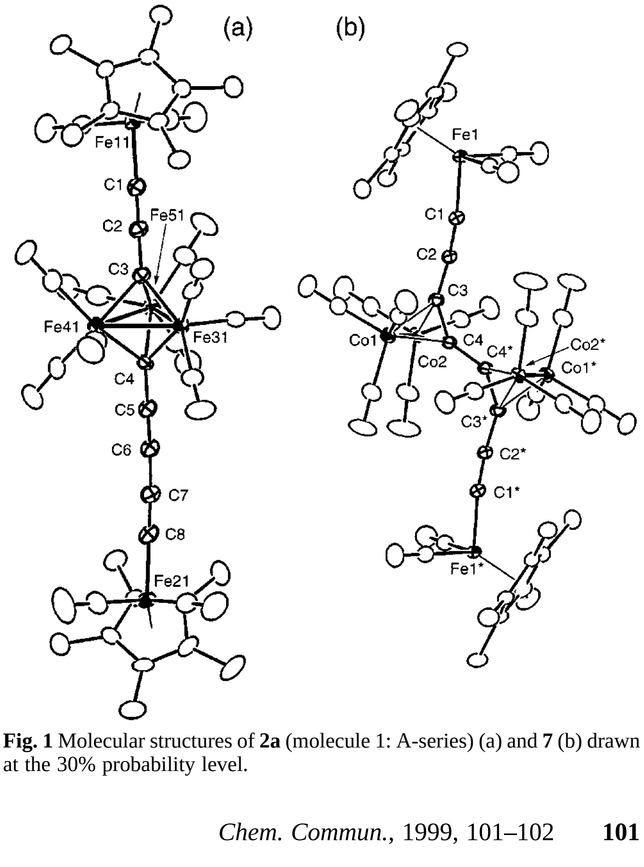
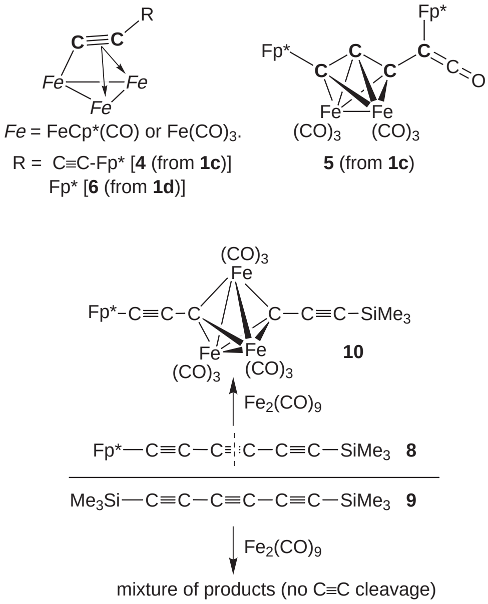


Fig. 1 Molecular structures of **2a** (molecule 1: A-series) (a) and **7** (b) drawn at the 30% probability level.



Scheme 1

in **1c**,**d** are directly bonded to the iron atoms, and their formation mechanism should involve reaction of the C≡C moiety with a diironcarbonyl species, $\mathrm{Fe_2(CO)}_x$, followed by interaction with either of the adjacent atoms, Fe or C, associated with decarbonylation (M–M bond formation) and/or CO-migration.[6] In contrast, **1a**,**b** contain two kinds of C≡C functional groups; one directly bonded to the Fp* group and the other sandwiched by the two C≡C groups. Because the latter can avoid steric repulsion with the bulky Fp* group, the ironcarbonyl species would first interact with the central C≡C moiety to induce the cleavage reaction. In accord with this consideration, reaction of **1a** with $\mathrm{Co_2(CO)_8}$ gave adduct **7** with tetrahedral $\mathrm{C_2Co_2}$ cores (55% yield),§ where the central C≡C bonds interact with the dicobalt species [Fig. 1(b)].

In order to examine the effect of the substituents at the C_x termini, C_6-silyl derivatives (the precursors for **1b**),[5] Fp*–C≡C–SiMe3 **8** and Me3Si–(C≡C)–SiMe3 **9**, were subjected to reaction with $\mathrm{Fe_2(CO)_9}$ (Scheme 1). The reaction of **8** resulted in C≡C cleavage at the C3≡C4 bond to give the bis-μ_3-alkylidyne complex **10** (22% yield)§ analogous to **2**, whereas **9** gave a mixture of products, which did not show any ^{13}C NMR resonances > δ250 indicating absence of C≡C cleavage. Thus at least one Fp* substitution at the C_x termini is crucial for C≡C bond cleavage. The details of the mechanism of C≡C cleavage, however, is not clear at present. Interaction with diironcarbonyl species would give an adduct with a tetrahedral $\mathrm{C_2Fe_2}$ core[7] analogous to the structure of **7** and subsequent addition of a third iron atom would induce C≡C bond cleavage and formation of an $\mathrm{Fe_3}$ triangle. Electron-donating groups such as Fp* may stabilize the electron-deficient intermediate, which should be formed prior to C≡C cleavage.[2e]

Thus the present study reveals the possibility of C≡C bond cleavage of a polyyne linkage under very mild conditions. The obtained bis(μ_3-alkylidyne) complexes **2** belong to a new class of compounds, where the trinuclear cluster core containing d electrons is sandwiched by two π-conjugated $(\mathrm{C{\equiv}C})_x$–M systems. Interaction of M–$(\mathrm{C{\equiv}C})_n$–M′ with various metal species is now under further study and results will be reported in due course.

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Notes and references

† *Selected spectroscopic data*: **2a**: ν(C≡C) 2095, 2068, ν(CO) 2037, 2011, 1981 cm^{-1} ($\mathrm{CH_2Cl_2}$); δ_H($\mathrm{CDCl_3}$) 1.91, 1.95 (Cp* × 2); δ_C($\mathrm{CDCl_3}$) 83.8, 96.6, 116.5, 143.4, 144.4, 172.1, 270.1, 289.6 (C_8). **2b**: ν(CO) 2037, 2028, 2002, 1992, 1979 cm^{-1}; δ_H 1.94 (Cp*); δ_C 141.4, 163.2, 281.6 (C_6). **7**: ν(C≡C) 2092, ν(CO) 2073, 2053, 2014, 1973 cm-1; δ_H 1.84 (Cp*); δ_C 87.7, 93.7, 109.0, 135.0 (C_8). **10**: ν(CO) 2041, 2015, 1983 cm^{-1}; δ_H 1.96 (Cp*), 0.37 ($\mathrm{SiMe_3}$); δ_C 122.7, 127.8, 144.3, 269.9, 296.9 (C_6: one of the C_6 signals could not be located).

‡ X-Ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo-Kα radiation. The triiron cluster moieties in **2a**,**b** and **10** were found to be disordered with respect to the C≡C–C···C–C≡C axis and refined taking into account minor components. *Crystal data*: for **2a**: $\mathrm{C_{41}H_{30}O_{13}Fe_5}$, M = 1009.9, T = −60 °C, triclinic, space group $P\bar{1}$, a = 15.287(5), b = 24.814(3), c = 13.540(3), α = 102.56(2)°, β = 115.10(3)°, γ = 102.68(2)°, V = 4247(2) Å^3, Z = 4, D_c = 1.58 g cm^{-3}, μ = 17.3 cm^{-1}, $R(R_\mathrm{w})$ = 0.062 (0.084) for 10185 unique data with $I > 3\sigma(I)$ and 1357 parameters. The unit cell contained two independent molecules. For **2b**: $\mathrm{C_{39}H_{30}O_{13}Fe_5}$, M = 985.9, T = −60 °C, monoclinic, space group $P2_1/n$, a = 13.520(4), b = 38.03(1), c = 8.136(2) Å, β = 91.67(2)°, V = 4181(1) Å^3, Z = 4, D_c = 1.57 g cm^{-3}, μ = 17.5 cm^{-1}, $R(R_\mathrm{w})$ = 0.079 (0.086) for 3614 unique data with $I > 3\sigma(I)$ and 551 parameters. For **7**: $\mathrm{C_{44}H_{30}O_{16}Fe_2Co_4}$, M = 1162.1, T = −60 °C, monoclinic, space group $P2_1/c$, a = 8.890(4), b = 18.890(5), c = 14.10(2) Å, β = 99.22(5)°, V = 2337(2) Å^3, Z = 2, D_c = 1.65 g cm^{-3}, μ = 20.6 cm^{-1}, $R(R_\mathrm{w})$ = 0.047 (0.060) for 4035 unique data with $I > 3\sigma(I)$ and 358 parameters. For **10**: $\mathrm{C_{30}H_{24}O_{11}SiFe_5}$, M = 812.0, T = −60 °C, monoclinic, space group $P2_1/n$, a = 11.929(3), b = 14.071(2), c = 21.55(1) Å, β= 99.691(3)°, V = 3564(1) Å$^{3[}$, Z = 4, D_c = 1.51 g cm^{-3}, μ = 16.8 cm^{-1}, $R(R_\mathrm{w})$ = 0.080 (0.100) for 4041 unique data with $I > 3\sigma(I)$ and 532 parameters. CCDC 182/1103.

§ Complexes **7** and **10** were characterized by X-ray crystallography.‡ *Selected structural parameters*: for **7**: Fe1–C1 1.898(3), C1–C2 1.219(4), C3–C4 1.362(4), C4–C4* 1.408(6), Co1–Co2: 2.4696(8), Co–C 1.953–1.984(4) Å, Fe1–C1–C2 173.2(3), C1–C2–C3 173.7(3), C2–C3–C4 144.1(3), C3–C4–C4* 141.6(3)°. For **10**: Fe2–Fe3 2.507(3), Fe2–Fe4 2.501(3), Fe3–Fe4 2.504(3), C3–Fe2 1.978(7), C3–Fe3 1.936(8), C3–Fe4 1.991(7), C4–Fe2 1.966(8), C4-Fe3: 1.949(8), C4-Fe4: 1.929(8), Fe1-C1 1.890(6) , C1≡C2 1.236(9), C2–C3 1.376(9), C4–C5 1.39(1), C5≡C6 1.22(1), C6–Si1 1.829(9) Å; C–C–C(or Fe1,2) 171.1–178.8(9)°.

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5 Complex **1b** was prepared by Cu-catalyzed coupling between Fp*–C_6H and Fp*–Cl analogous to the synthesis of **1a**.[3a] A. Sakurai, M. Akita and Y. Moro-oka, to be reported.

6 The interaction of the attached diiron part with the Fe atom σ-bonded to the C_{2n} group leads to the stable trinuclear μ-acetylide cluster structure (**4**, **6**) and, in the formation of **5**, the interaction with the adjacent carbon atom (C3) would leave the carbene carbon atom (C4), which may be stabilized by interaction with the Fp*-group at the other terminus and finally couples with CO to give the ketene structure.[3b]

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