

# Formation of novel conjugated polycarbon–metal systems *via* metal migration on a M–C≡C–C≡C–M linkage

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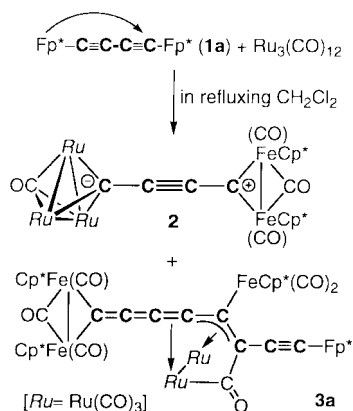
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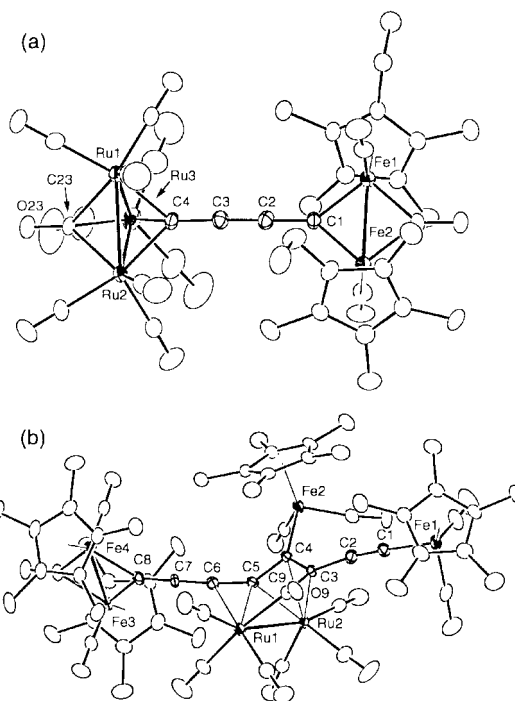
Reactions of butadiynediylmetal complexes,  $\text{Fp}^*\text{-C}\equiv\text{C-C}\equiv\text{C-M}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2$  **1** [M = Fe, Ru; R = Me, H;  $\text{Fp}^* = \text{FeCp}^*(\text{CO})_2$ ], with group 8 metal carbonyls result in migration of a  $\sigma$ -bonded metal fragment along the C<sub>4</sub> rod to form novel highly conjugated polycarbon–metal systems; the zwitterionic  $\mu$ -but-2-yn-1-ylidene-4-ylidyne complex  $\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-C-C}\equiv\text{C-}\mu\text{-C})\text{Fe}_2\text{Cp}^*_2(\text{CO})_3$  **2**, and the dimerized product with a cumulenic  $\mu$ -C<sub>8</sub> ligand  $(\text{Cp}^*\text{Fe})_4\text{-Ru}_2(\text{CO})_{13}[\mu_6\text{-C}_8\text{-C(=O)}]$  **3**, *via* 1,4-migration and the zwitterionic acetylide cluster-type product  $\text{Fp}^{*+}[\text{Cp}(\text{CO})_2\text{Ru}(\eta^2\text{-C}\equiv\text{C})-(\mu_3\text{-C}\equiv\text{C})\text{Fe}_3(\text{CO})_9]^-$  **4**, *via* 1,3-migration.

Increasing attention focused on polycarbon–transition metal complexes stems originally from their relevance to surface bound carbide intermediates<sup>1</sup> and recently from their intriguing chemical and physical properties which are potentially applicable to new molecular devices.<sup>2</sup> However, neither interaction modes nor synthetic methods have been thoroughly exploited. During the course of our synthetic study of polycarbon cluster compounds derived from polyynediylmetal complexes  $\text{M}(\text{C}\equiv\text{C})_n\text{-M}$  [ $n = 1\text{--}6$ ; M = Fe or Ru( $\eta^5\text{-C}_5\text{R}_5$ )(CO)<sub>2</sub>],<sup>3</sup> we observed formation of novel highly conjugated polycarbon–transition metal systems resulting from migration of a  $\sigma$ -bonded metal fragment along the carbon rod. Herein we report results of interaction of butadiynediyl complexes **1** ( $n = 2$ ) with group 8 metal carbonyl species.

Reaction of the butadiynediyliron complex **1a** [Scheme 1,  $\text{Fp}^* = \text{FeCp}^*(\text{CO})_2$ ;  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ]<sup>3b</sup> with  $\text{Ru}_3(\text{CO})_{12}$  in refluxing  $\text{CH}_2\text{Cl}_2$  gave a mixture of products, from which two compounds **2** and **3a** were isolated after TLC separation (silica gel). For the purple red product **2**,<sup>†</sup> the single  $\text{Cp}^*$  NMR signal and the highly deshielded <sup>13</sup>C NMR signal ( $\delta_{\text{C}}$  347.1) suggested formation of a symmetrical cluster compound **2'** bearing a cumulenic  $>\text{C}=\text{C}=\text{C}=\text{Fe}_2$  fragment but X-ray crystallography of its  $\eta^5\text{-C}_5\text{Me}_4\text{Et}$  derivative **2''** [Fig. 1(a)] revealed a mirror symmetrical zwitterionic but-2-yne-1-ylidene-4-ylidyne structure<sup>5</sup> with (i) a C<sub>4</sub> bridge showing long–short–long bond alternation and (ii)  $\mu_3$ -coordination of the C<sub>4</sub> and C<sub>23</sub> atoms. Contribution of the neutral butatrienetetrayl structure **2'**,

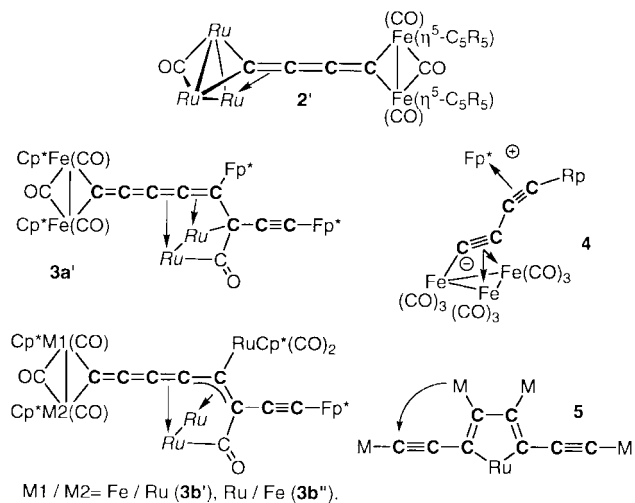


Scheme 1



**Fig. 1** Molecular structures of **2''** (a) and **3a** (b) drawn at the 30% probability level. Selected parameters: **2''**: Fe–C1 1.906(6), 1.885(9), C1–C2 1.31(1), C2–C3 1.25(1), C3–C4 1.34(1), C4–Ru 2.093–2.120(9), Ru–Ru 2.749–2.781(1), Fe1–Fe2 2.530(2) Å; Fe–C1–C2 137.4(6), 138.8(7), C1–C2–C3 179(1), C2–C3–C4 177.4(8), Ru1–C4–C3 133.4(6), Ru2–C4–C3 132.3(7), Ru3–C4–C3 126.0(6)°. **3a**: C1–C2 1.202(8), C2–C3 1.443(8), C3–C4 1.408(7), C3–C9 1.538(8), C4–C5 1.415(7), C5–C6 1.315(8), C6–C7 1.308(7), C7–C8 1.285(7), Fe1–C1 1.912(6), Ru2–C3 2.291(5), Fe2–C4 2.024(5), Ru2–C4 2.279(5), Ru1–C5 2.228(5), Ru2–C5 2.128(5), Ru1–C6 2.458(5), Fe3–C8 1.934(6), Fe4–C8 1.924(6), Ru1–C9 2.118(6), Ru1–Ru2 2.7453(7), Fe3–Fe4 2.542(1) Å; Fe1–C1–C2 176.4(5), C1–C2–C3 168.7(6), C2–C3–C4 128.2(5), C2–C3–C9 114.7(4), C4–C3–C9 113.0(4), C3–C4–C5 112.5(5), C4–C5–C6 144.1(5), Ru1–C5–Ru2 78.1(2), C5–C6–C7 168.4(6), C6–C7–C8 176.4(6), Ru1–C9–C3 110.3(3)°.

however, is evident, since (i) the C<sub>4</sub> rod is slightly tilted toward Ru3 as indicated by the C3–C4–Ru angles and (ii) the C–C distances of the  $\mu$ -C<sub>4</sub>–C≡C moiety are averaged to some extent. It should be noted that the  $(\mu\text{-C}_4)\text{Fe}_2\text{Cp}^*_2(\text{CO})_3$  structure results from 1,4-migration of the iron fragment along the C<sub>4</sub> rod, *i.e.* the  $\text{FeCp}^*(\text{CO})_n$  fragment is shifted from one end of the C<sub>4</sub> bridge to the other upon interaction with  $\text{Ru}_3(\text{CO})_{12}$ . The NMR spectrum of the other deep purple red complex **3a**<sup>†</sup> contained four sets of  $\text{Cp}^*$  signals indicating oligomerization of **1a**, and X-ray crystallography<sup>‡</sup> [Fig. 1(b)] revealed a hexanuclear structure with a dimerized C<sub>8</sub> skeleton. Again, formation of the new C<sub>8</sub> carbon linkage involves 1,4-migration (C5 → C8) of the iron fragment. The migration induces a change of part of the polyene structure into a cumulenic moiety (C8=C7=C6=C5) with similar C–C distances. Although the pentatetraenylidene structure **3a'**  $\pi$ -bonded to the two ruthenium atoms is a possible canonical structure of **3a**, the bent C5–



**Chart 1**

C4–C3 moiety with similar C–C and Ru2–C distances reveals  $\eta^3$ -allyl coordination to Ru2. The linear C3–C2–C1–Fe1 moiety is a normal  $\eta^1$ -acetylide structure. Coordination of the perpendicularly projected, adjacent cumulenenic  $\pi$  orbitals of the C6–C5 and C5–C4 bonds to the two ruthenium atoms connected by a Ru–Ru bond<sup>6</sup> leads to strain, which is relieved by formation of a larger membered ring structure *via* CO-insertion [CO(9)]. The C<sub>8</sub> bridge was also characterized by <sup>13</sup>C NMR spectroscopy.<sup>†</sup> Except for the deshielded C8 signal ( $\delta_C$  254.7), the other signals appeared in a rather narrow range ( $\delta_C$  157–107).

The isostructural C<sub>8</sub> complex **3b**<sup>†</sup> was obtained from the Fe, Ru-mixed metal butadiynediyl complex, Fp\*–C≡C–C≡C–RuCp\*(CO)<sub>2</sub> **1b**,<sup>4</sup> upon treatment with Ru<sub>3</sub>(CO)<sub>12</sub>.§ Complex **3b** consisted of a mixture of two inseparable isomers, **3b'** and **3b''** (Chart 1), as indicated by NMR data containing two sets of signals as well as the successful X-ray structural analysis taking into account a disordered structure containing two components. It should be noted that no homometallic complexes (M1 = M2 = Ru or Fe) were detected by NMR and FD-MS analyses suggesting an intramolecular mechanism for the migration.

Another example of metal migration was observed for reaction of Fp\*–C≡C–C≡C–RuCp(CO)<sub>2</sub> **1c** [Cp( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) derivative of **1b**] with Fe<sub>2</sub>(CO)<sub>9</sub>, a group 8 metal carbonyl.§ The deshielded <sup>13</sup>C NMR signal ( $\delta_C$  193.7) of the resultant purple Fe<sub>3</sub>-adduct **4** (Chart 1)<sup>†</sup> suggested formation of a  $\mu$ -acetylide cluster compound,<sup>7</sup> and X-ray crystallography<sup>‡</sup> revealed a pentanuclear structure consisting of a cationic dinuclear  $\mu$ - $\eta^1$ : $\eta^2$ -acetylide complex part and an anionic trinuclear  $\mu_3$ -acetylide cluster type structure. The structure of each component is normal, and the diamagnetic nature of **4** can be interpreted in terms of the zwitterionic structure, each metal center in which is coordinatively saturated.

In conclusion, interaction of the butadiynediyl complexes **1** with group 8 metal carbonyls results in the formation of novel highly conjugated polycarbon–metal cluster systems. The structures of **2** and **3** suggest the occurrence of stepwise metal migration along the carbon rod, and the C<sub>8</sub> linkage in **4** is formed *via* 1,4-migration on a ruthenacyclopentadiene intermediate **5** resulting from oxidative metallacyclization of **1** (Chart 1).<sup>8</sup> Noteworthy features of the present system are as follows. The formation of zwitterionic structures such as **2** and **4** are regarded as typical of electron transfer through unsaturated carbon rods. Another feature is the flexible coordination mode of the C(sp)<sub>n</sub> system. For example, in the case of interaction with trimetallic species, the C<sub>4</sub> ligand can behave as a three- ( $\mu_3$ - $\eta^1$ -C<sub>4</sub> like C4 in **2**) to seven-electron donor ( $\mu$ - $\eta^3$ -propargylidene-ketene).<sup>3c</sup> When combined with coordination of CO ligands, which can act as either one- or two-electron donors, various intermediates have many opportunities to attain coordinative saturation by switching coordination modes of the C<sub>4</sub> and/or CO ligands.

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## Notes and references

<sup>†</sup> Selected spectroscopic data: **2** (7%):  $\delta_H$ (CD<sub>2</sub>Cl<sub>2</sub>) 1.71 (Cp\*),  $\delta_C$ (CD<sub>2</sub>Cl<sub>2</sub>, –90 °C) 347.1 (C1), 216.7 (C4), 119.0, 118.4 (C3=C4); 269.1 ( $\mu_3$ -CO), 268.3 ( $\mu$ -CO), 211.1 (Fe–CO), 196.9 (Ru–CO). IR(CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (C≡C) 2081;  $\nu$ (CO) 2047, 2008, 1961, 1903;  $\nu$ ( $\mu_3$ -CO) 1801;  $\nu$ ( $\mu_3$ -CO) 1700 cm<sup>–1</sup>. **3a** (10%):  $\delta_H$ (CDCl<sub>3</sub>) 1.92, 1.86, 1.73, 1.68 (Cp\*).  $\delta_C$ (CDCl<sub>3</sub>) 254.7 ( $\mu$ -C=); 157.3, 134.0, 129.0, 128.9, 111.5, 108.8, 106.8 (C1–C7); 274.9 ( $\mu$ -CO); 225.7 (>C=O); 218.0, 216.0, 215.6, 214.5, 213.2, 200.0, 198.6, 197.1, 193.7 (CO). IR(CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (C≡C) 2060;  $\nu$ (CO) 2030, 1801, 2015, 1996, 1961, 1954, 1895,  $\nu$ ( $\mu$ -CO) 1780,  $\nu$ (>C=O) 1575 cm<sup>–1</sup>. **3b** (12%):  $\delta_H$ (CD<sub>2</sub>Cl<sub>2</sub>) 2.04, 1.97, 1.90, 1.88, 1.86, 1.80, 1.75, 1.69 (Cp\*). **5** (11%):  $\delta_H$ (CDCl<sub>3</sub>) 5.56 (Cp), 1.97 (Cp\*).  $\delta_C$ (CDCl<sub>3</sub>) 193.7, 144.0, 123.3, 104.8 (C<sub>4</sub>); 216.0, 215.0, 196.8 (CO). IR(CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (CO) 2047, 2036, 1995, 1982, 1962, 1939;  $\nu$ (C=C) 1606 cm<sup>–1</sup>.

<sup>‡</sup> X-Ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å) at –60 °C. Crystal data: **2**<sup>#</sup>: C<sub>42</sub>H<sub>41</sub>O<sub>13</sub>Fe<sub>2</sub>Ru<sub>3</sub>,  $M = 1168.7$ , monoclinic, space group P2<sub>1</sub>/c,  $a = 15.445(1)$ ,  $b = 16.481(2)$ ,  $c = 18.873(3)$  Å,  $\beta = 112.60(1)^\circ$ ,  $V = 4435.2(10)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.75$  g cm<sup>–3</sup>,  $\mu = 17.0$  cm<sup>–1</sup>,  $R1 = 0.068$  for the 8584 unique data with  $F > 4\sigma(F)$  ( $wR2 = 0.212$  for all 9332 data) and 552 parameters. **3a**: C<sub>68</sub>H<sub>74</sub>O<sub>14</sub>Fe<sub>4</sub>Ru<sub>2</sub>,  $M = 1540.9$ , monoclinic, space group P2<sub>1</sub>/n,  $a = 13.323(2)$ ,  $b = 18.681(9)$ ,  $c = 26.420(4)$  Å,  $\beta = 93.023(7)^\circ$ ,  $V = 6566(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.56$  g cm<sup>–3</sup>,  $\mu = 13.7$  cm<sup>–1</sup>,  $R1 = 0.064$  for the 10696 unique data with  $F > 4\sigma(F)$  ( $wR2 = 0.173$  for all 11815 data) and 815 parameters. Details of **4** are included in the supplementary material. CCDC 182/1669.

§ Other products: from **1b**: Fp\*–C≡C–( $\mu_4$ -C≡C)Ru<sub>4</sub>Cp\*(CO)<sub>11</sub> **6** (43%); from **1c**: Fp\*–C≡C–( $\mu_3$ -C≡C)Fe<sub>2</sub>RuCp\*(CO)<sub>9</sub> **7** (7%) and (CO)<sub>2</sub>Cp\*Ru–( $\mu$ - $\eta^3$ -C<sub>3</sub>)[Fe<sub>2</sub>(CO)<sub>6</sub>]–C(=C=O)–Fp\* **8** (15%). Complexes **6** and **7** are acetylide cluster-type compounds and complex **8** contains a  $\mu$ - $\eta^3$ -propargylidene-ketene ligand.<sup>3c</sup> No characterizable product was obtained from Fp\*–C≡C–C≡C–FeCp(CO)<sub>2</sub>.

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