

Preliminary communication

Structure expansion of the mixed-metal dicarbide cluster core
in $[(\mu_3\text{-C}\equiv\text{C-Fp})\text{Ru}_3(\mu\text{-H})(\text{CO})_9]$ via direct radical and thermal coupling
reactions leading to higher-nuclearity $(\mu\text{-C}_2\text{H}_x)\text{M}_y$ cluster compounds
($x = 0, 1; y = 7, 8$), $\text{CpFeRu}_6(\mu_5\text{-C}_2)(\mu_5\text{-C}_2\text{H})(\text{CO})_{16}$,
 $\text{Cp}_2\text{Fe}_2\text{Ru}_5(\mu_5\text{-C}_2)_2(\text{CO})_{17}$ and $\text{Cp}_2\text{Fe}_2\text{Ru}_6(\mu_6\text{-C}_2)_2(\text{CO})_{17}$

Munetaka Akita*, Hideki Hirakawa, Masako Tanaka, Yoshihiko Moro-oka*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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Abstract

Thermolysis of the mixed-metal tetranuclear dicarbide cluster $[(\mu_3\text{-C}\equiv\text{C-Fp})\text{Ru}_3(\mu\text{-H})(\text{CO})_9]$ (**2**) and one-electron oxidation of the anion $(\text{PPh}_4)[(\mu_3\text{-C}\equiv\text{C-Fp})\text{Ru}_3(\text{CO})_9]$ (**3**) derived from **2** lead to coupling of the $(\text{C}_2)\text{FeRu}_3$ core to give the novel heptanuclear $\text{Cp}_2\text{Fe}_2\text{Ru}_5(\mu_5\text{-C}_2)_2(\text{CO})_{17}$ (**5**), $\text{CpFeRu}_6(\mu_5\text{-C}_2)(\mu_5\text{-C}_2\text{H})(\text{CO})_{16}$ (**6**), and the octanuclear cluster compound $\text{Cp}_2\text{Fe}_2\text{Ru}_6(\mu_6\text{-C}_2)_2(\text{CO})_{17}$ (**4**) with the multiply-bridging C_2 and C_2H ligand.

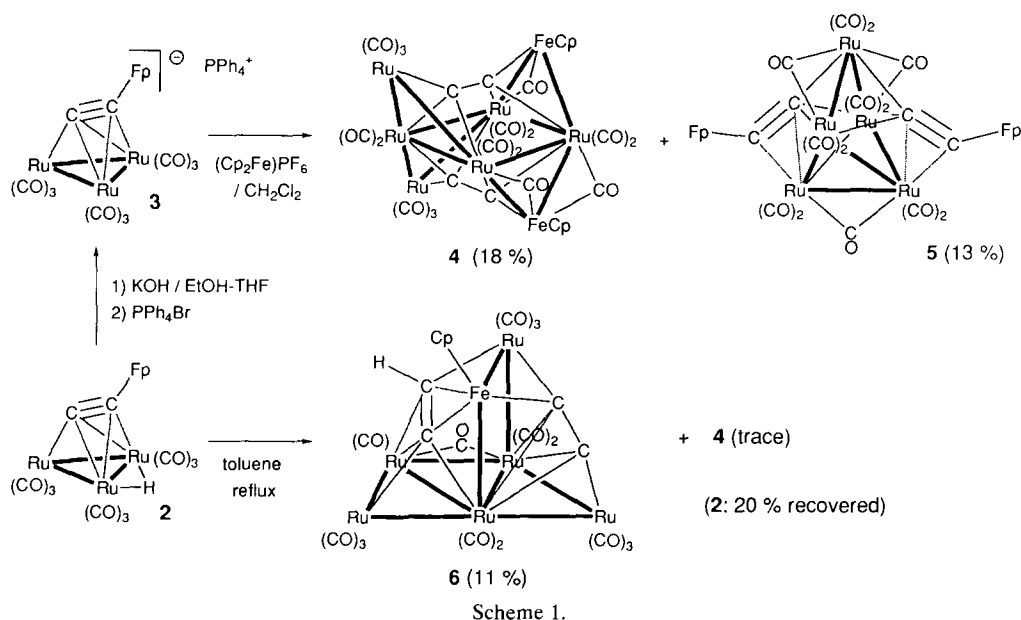
Keywords: Iron; Ruthenium; Dicarbide; Cluster; Acetylide(alkynyl); Coupling

Structure and chemical properties of polymetallic complexes containing C_2 ligands ($\text{C}_2\text{H}_m\text{O}_n$) have attracted much attention as models for the surface-bound C_2 species [1] which are formed at an early stage of catalytic CO hydrogenation; i.e. after the first C–C coupling of the C1 species. Of the C_2 model compounds, hydrogen-poor C_2H_x ($x = 0, 1$) complexes relevant to the dicarbide (C_2) species have been the subject of our recent study [2] and, in a previous paper, we reported synthesis of the tetra- and octanuclear dicarbide cluster compounds $(\text{Cp}^*\text{Fe})_2\text{Ru}_2(\mu_4\text{-C}_2)(\text{CO})_{10}$ and $(\text{Cp}^*\text{Fe})_2\text{Ru}_6(\mu_6\text{-C}_2)_2(\text{CO})_{17}$ (**1**) by sequential addition of dimetallic fragments to $\text{Fp}^*\text{-C}\equiv\text{C-Fp}^*$ [2a,3]. In this article we discuss alternative methods of preparation of higher-nuclearity $(\text{C}_2\text{H}_x)\text{M}_y$ cluster compounds ($x = 0, 1; y = 7, 8$) via direct radical and thermal coupling of the $(\text{C}_2)\text{FeRu}_3$ core in the mixed-metal dicarbide cluster $[(\mu_3\text{-C}\equiv\text{C-Fp})\text{Ru}_3(\mu\text{-H})(\text{CO})_9]$ (**2**) [4,5].

Abbreviations used in this paper: $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{Fp} = \text{CpFe}(\text{CO})_2$; $\text{Fp}^* = \text{Cp}^*\text{Fe}(\text{CO})_2$.

* Corresponding authors.

When a radical species was generated by treatment of the anionic mixed-metal dicarbide complex $(\text{PPh}_4)[(\mu_3\text{-C}\equiv\text{C-Fp})\text{Ru}_3(\text{CO})_9]$ (**3**) (the deprotonated form of **2**) [6] with a typical one-electron oxidant $[(\text{Cp}_2\text{Fe})\text{PF}_6]$ at room temperature, two products (**4** and **5**) containing only $^1\text{H-NMR}$ Cp signals were isolated together with a trace amount of **2** after TLC separation (silica gel eluted with CH_2Cl_2 :hexanes = 1:3) (Scheme 1) [7]. One of the products (**4**) was assigned to the Cp derivative of the octanuclear bis(dicarbide) cluster (**1**) with the permetalated ethane structure [2a] on the basis of the similar $\nu(\text{CO})$ pattern, the FAB-MS result and the preliminary X-ray analysis [8]. The structure of the other product (**5**) was determined, by X-ray crystallography [9], to be the heptanuclear bis(dicarbide) cluster with the arrowhead-shaped Ru_5 core of C_2 symmetry (Fig. 1) [10]. The FpC_2 groups interact with the Ru_4 butterfly parts as acetylide ligands, and the Fe atoms are not incorporated in the central cluster structure. The complex **5** with no $\text{Ru}(2) \cdots \text{Ru}(4)$ bonding interaction (3.477(2) Å, molecule 1; 3.472(2) Å, molecule 2) [8] belongs to a rare class of arrowhead M_5 cluster compounds without an encapsulated atom (usually $\mu_5\text{-C}$) [10] and, in con-



trast to the previously reported acetylide clusters [11] where the C≡C part interacts with the top metal atom, the dicarbide parts in **5** are π -coordinated to the bottom-edge Ru atoms. Thus, the (C₂)FeRu₃ core in **3** couples to afford the higher-nuclearity clusters via

dimerization of a radical intermediate under mild conditions.

Thermolysis of the neutral tetranuclear dicarbide cluster compound (**2**) in refluxing toluene for 3.5 h afforded a mixture of a new cluster compound (**6**) and

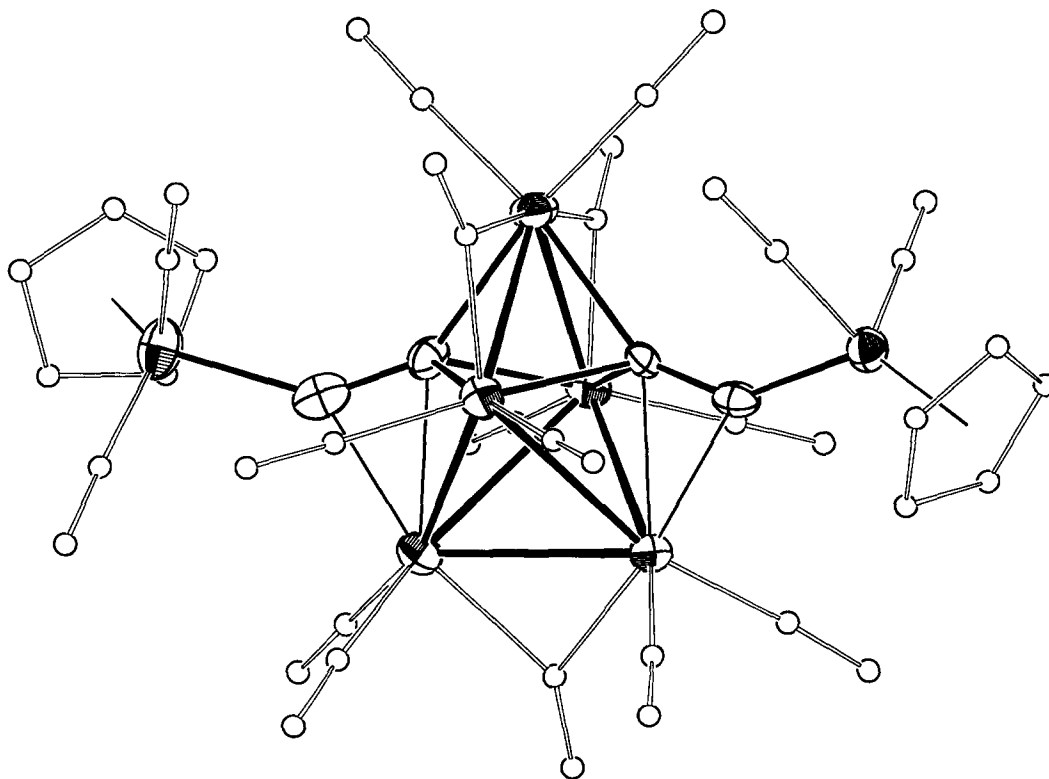


Fig. 1. Molecular structure of **5** (one of the independent molecules). Selected bond lengths (Å): Ru(1)–Ru(2) = 2.731(2); Ru(1)–Ru(4) = 2.708(2); Ru(2)–Ru(3) = 2.905(2); Ru(2)–Ru(5) = 2.900(2); Ru(3)–Ru(4) = 2.916(2); Ru(3)–Ru(5) = 2.792(2); Ru(4)–Ru(5) = 2.885(2); C(1)–C(2) = 1.32(2); C(1)–Fe(1) = 1.93(2); C(1)–Ru(3) = 2.14(1); C(2)–Ru(1) = 2.14(1); C(2)–Ru(2) = 2.26(1); C(2)–Ru(3) = 2.26(1); C(2)–Ru(4) = 2.16(1); C(3)–C(4) = 1.34(2); C(3)–Fe(2) = 1.93(1); C(3)–Ru(5) = 2.14(1); C(4)–Ru(1) = 2.15(1); C(4)–Ru(2) = 2.24(1); C(4)–Ru(4) = 2.16(1); C(4)–Ru(5) = 2.23(1).

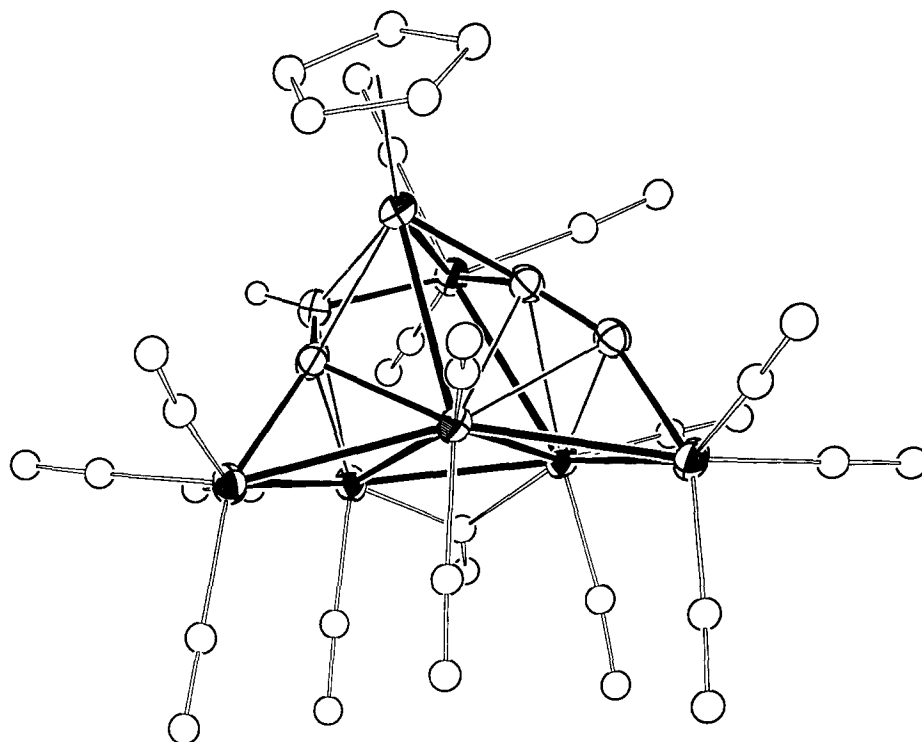


Fig. 2. Molecular structure of **6**. Selected bond lengths (Å): Ru(1)–Ru(2) = 2.844(1); Ru(1)–Ru(3) = 2.776(1); Ru(1)–Ru(4) = 2.8927(9); Ru(1)–Ru(5) = 2.8075(9); Ru(1)–Fe = 2.754(1); Ru(2)–Ru(3) = 2.786(1); Ru(3)–Ru(4) = 2.7574(9); Ru(3)–Ru(6) = 2.976(1); Ru(4)–Ru(5) = 2.814(1); Ru(6)–Fe = 2.675(1); C(1)–C(2) = 1.334(9); C(1)–Ru(1) = 2.282(7); C(1)–Ru(3) = 2.478(7); C(1)–Fe = 1.877(7); C(2)–Ru(1) = 2.263(6); C(2)–Ru(2) = 1.939(7); C(2)–Ru(3) = 2.180(6); C(3)–C(4) = 1.420(9); C(3)–Ru(1) = 2.141(6); C(3)–Ru(4) = 2.253(7); C(3)–Ru(5) = 1.964(7); C(3)–Fe = 2.012(6); C(4)–Ru(4) = 2.317(7); C(4)–Ru(6) = 2.133(7); C(4)–Fe = 2.031(7).

a trace amount of the octanuclear cluster (**4**), which was separated by TLC (silica gel eluted with CH_2Cl_2 : hexanes = 1:1) (Scheme 1) [7]. The deshielded $^1\text{H-NMR}$ signal (δ 8.64) of **6** indicated the formation of a polymetallic C_nH complex, which was characterized by X-ray crystallography [9] to be the heptanuclear FeRu_6 cluster (**6**) bearing the $\mu_5\text{-C}_2$ and $\mu_5\text{-C}_2\text{H}$ ligands (Fig. 2). The metal core consists of the flat W-shaped raft-like Ru_5 framework [Ru(1–5)], which is fused with the $\text{FeRu}(1,3,6)$ square [10]. The C_2 ligand interacts with the $\text{FeRu}(1,2,3,6)$ envelop in essentially the same coordination mode as that observed for $(\mu_5\text{-C}_2)\text{Ru}_5(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2$ [12], though the structure becomes asymmetric owing to the Fe atom of the smaller atomic size. The C_2H moiety [13] can be viewed as a trimetalated [Ru(1,5,6)] ethylene which is sandwiched by Fe and Ru(4) through π -interactions.

Thus, the tetranuclear dicarbide cluster cores in **2** and **3** are expanded directly to the hepta- and octanuclear cluster skeletons (**4**–**6**) through the one-step radical and thermal processes. It is noteworthy that the Fe parts in **5** retain the original Fp structure and, on the contrary, the Fe center in **6** loses CO completely. These observations suggest that (i) the former process follows dimerization of a Ru_3 cluster-centered radical species and that (ii) the thermolysis of **2** causes CO-dis-

sociation from the more labile Fe center and subsequent attack of the resulting unsaturated species to another **2** molecule may finally give **6**. The successful synthesis of the higher-nuclearity clusters **4**–**6** has been realized by the dicarbide ligands, which bind the metal centers tightly through σ - and π -bonds and, as a result, prevent fragmentation of the cluster structure. The present direct coupling methods are potentially useful as synthetic methods for higher-nuclearity cluster compounds with a tightly binding ligand.

Acknowledgments

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References and Notes

- [1] See for example, J. Silvestre and R. Hoffmann, *Langmuir*, **1** (1985) 621 and references cited therein.
- [2] (a) M. Akita, S. Sugimoto, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.*, **114** (1992) 7581; (b) M. Akita, M. Terada and Y.

- Moro-oka, *Organometallics*, 11 (1992) 1825; (c) M. Akita, S. Sugimoto, M. Tanaka and Y. Moro-oka, *Organometallics*, 11 (1992) 3468; (d) M. Akita, S. Sugimoto, A. Takabuchi, M. Tanaka and Y. Moro-oka, *Organometallics*, 12 (1993) 2925; (e) M. Akita, N. Ishii, A. Takabuchi, M. Tanaka and Y. Moro-oka, *Organometallics*, 13 (1994) 258; (f) see also references cited in [2a.e].
- [3] Structure expansion of dicarbide clusters by addition of metal fragments has also been studied by Bruce et al. C.J. Adams, M.I. Bruce, B.W. Skelton and A.H. White, *J. Chem. Soc., Chem. Comm.*, (1993), 446 and references cited therein.
- [4] Starting complex **2** was prepared by reaction of $\text{Fp-C}\equiv\text{C-H}$ with $\text{Ru}_3(\text{CO})_{12}$. See, E. Sappa, O. Gambino, L. Milone and G. Cetini, *J. Organomet. Chem.*, 39 (1972) 169.
- [5] Thermal coupling of the Fp^* analogue of **2** was mentioned briefly in ref. [2a].
- [6] Complex **3** was prepared according to the following literature. C. Barner-Thorsen, K.I. Hardcastle, E. Rosenberg, J. Siegel, A.M.M. Lanfredi, A. Tiripicchio and M.T. Camerini, *Inorg. Chem.*, 20 (1981) 4306.
- [7] Selected spectral data, **2**: $^1\text{H-NMR}$ (CDCl_3) δ 3.90 (5H, s, Cp), -20.05 (1H, s, $\mu\text{-H}$); IR (CH_2Cl_2) 2086(m), 2057(vs), 2042(vs), 2035(sh), 2007(vs), 1968(br w) cm^{-1} . **3**: $^1\text{H-NMR}$ (acetone- d_6) δ 8.05–7.84 (20H, m, PPh_4), 5.15 (5H, s, Cp); IR (CH_2Cl_2) 2045(s), 2026(s), 1993(vs), 1950(s), 1926(m) cm^{-1} . **4**: $^1\text{H-NMR}$ (CDCl_3) δ 4.71 (10H, s, Cp); IR (CH_2Cl_2) 2081(m), 2063(vs), 2022(vs), 1858(br) cm^{-1} ; FAB-MS 1373 (the most intense peak). **5**: $^1\text{H-NMR}$ (CDCl_3) δ 4.98 (5H, s, Cp); IR (CH_2Cl_2) 2064(m), 2018(vs), 1986(sh), 1875(br w), 1855(br w) cm^{-1} . **6**: $^1\text{H-NMR}$ (C_6D_6) δ 8.64 (1H, s, C_2H), 5.13 (5H, s, Cp); IR (KBr) 2071(vs), 2005(vs), 1962(sh), 1824(m) cm^{-1} ; FD-MS 1226 (the most intense peak).
- [8] The FAB-MS spectrum contained the M^+ and $\text{M}^+-n(\text{CO})$ ($n = 1-17$) peaks with the bell-shaped isotopomer distribution consistent with the composition. Although X-ray crystallographic analysis revealed the presence of the $\text{Fe}_2\text{Ru}_6(\mu_6\text{-C}_2)_2$ core similar to that in **1**, the structure could not be refined because of the severe disorder of a part of the metal components.
- [9] Crystal data, **5**: $\text{C}_{31}\text{H}_{10}\text{O}_{17}\text{Fe}_2\text{Ru}_5 \cdot (\text{H}_2\text{O})_{2/3}$, $M = 1283.5$, monoclinic space group $C2/c$; $a = 42.215(5)$, $b = 15.776(5)$, $c = 16.842(4)$ Å; $\beta = 100.06(2)^\circ$; $V = 11044(5)$ Å³, $Z = 12$; $d_{\text{calc}} = 2.32$, $\mu = 28.4$ cm^{-1} ; $R(R_w) = 0.050(0.047)$ for 6032 data with $I > 3\sigma(I)$. **6**: $\text{C}_{25}\text{H}_6\text{O}_{16}\text{FeRu}_6 \cdot \text{CH}_2\text{Cl}_2$, $M = 1309.5$, monoclinic space group $P2_1/c$; $a = 11.848(5)$, $b = 10.812(5)$, $c = 27.739(4)$ Å; $\beta = 99.11(2)^\circ$; $V = 3508(4)$ Å³, $Z = 4$; $d_{\text{calc}} = 2.48$; $\mu = 30.9$ cm^{-1} , $R(R_w) = 0.0346(0.0386)$ for 5250 data with $I > 3\sigma(I)$. Data collections were made on a Rigaku-AFC5R diffractometer by using monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71059$ Å). The structure was solved by the TEXSAN structure solving system. All the non-hydrogen atoms were refined anisotropically. The position of H(4) in **6** was confirmed by using the isotropic thermal parameter and the remaining H atoms attached to the Cp ring and the solvent were fixed at the calculated positions and not refined. The unit cell of **5** contained two independent molecules, one of which possessed a crystallographic C_2 symmetry. Their structures were essentially the same except for the orientation of the Fp parts.
- [10] (a) M.I. Bruce, *J. Organomet. Chem.*, 394 (1990) 265; (b) D.F. Shriver, H.D. Kaesz and R.D. Adams, *The Chemistry of Metal Cluster Complexes*, VCH, New York, 1990, chap. 2.
- [11] (a) D.H. Farrar, G.R. John, B.F.G. Johnson, J. Lewis, P.R. Raithby and M.J. Rosales, *J. Chem. Soc., Chem. Comm.*, (1981) 886; (b) M. Lanfranchi, A. Tiripicchio, E. Sappa, A. MacLaughlin and A.J. Carty, *J. Chem. Soc., Chem. Comm.*, (1982) 538. Condensation of a trinuclear Ru_3 acetylide cluster with $\text{Cp}_2\text{Ni}_2(\text{CO})_2$ giving a pentanuclear bis(acetylide) cluster $[\text{Ni-Ru}_4(\mu_4\text{-C}\equiv\text{C-Pr}^i)_2(\mu\text{-PPh}_2)(\text{CO})_9]$ was reported in this paper.
- [12] C.J. Adams, M. I. Bruce, B.W. Skelton and A.H. White, *J. Chem. Soc., Chem. Comm.*, (1992) 26.
- [13] Although we attempted determination of the origin of the $\mu_5\text{-C}_2\text{H}$ atom by conducting the thermolysis in toluene- d_8 H-D exchange of the bridging hydride in **2** was evident before formation of **4**.