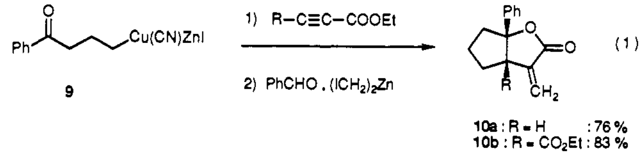

In conclusion, we have developed a new, efficient one-pot synthesis of polyfunctionalized α-methylene-γ-butyrolactones starting from readily available acetylenic esters, ICH$_2$ZnI, (FG-R)Cu(CN)ZnX, and an aldehyde or ketone. Applications to the synthesis of natural products are currently underway.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Spectral data for **1a–k** and **10a,b** and X-ray crystallographic analyses of **1g** and **1j** (52 pages). Ordering information is given on any current masthead page.

Preparation, Characterization, and Sequential Transformation of Dicarbide Cluster Compounds with Permetalated Ethyne, Ethene, and Ethane Structures

Munetaka Akita,* Shuichiro Sugimoto, Masako Tanaka, and Yoshihiko Moro-oka*

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

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The structures and properties of the C$_2$ ligand incorporated in polymetallic systems have been studied as models for elementary species on a heterogeneous catalyst surface, and several coordination modes have been reported.[1] Although ethynediyldimetal complexes (MC≡CM) are expected to serve as versatile starting compounds, this route has been frustrated by their limited accessibility. We[2a,b] and other groups[3] recently developed a preparative method for MC≡CM via deprotonation of [M$_2$(μ-C≡CH)]$^+$. Herein we report the utility of Fp*C≡CFp* (**1**)[2a,b] [Fp* = Cp*Fe(CO)$_2$; Cp* = η^5-C$_5$Me$_5$] as a building block for a series of *dicarbide* cluster compounds.

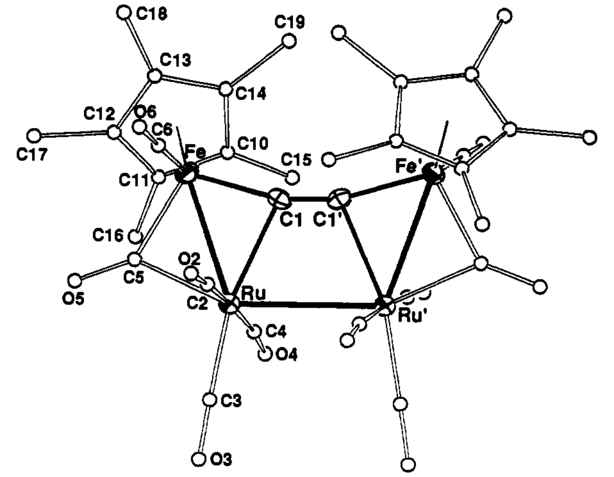


Figure 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Ru-Ru, 2.963 (2); Ru-Fe, 2.733 (2); Ru-C1, 2.204 (7); Fe-C1, 1.946 (7); C1-C1', 1.24 (1); Fe-Ru-Ru', 110.61 (4), C1-Ru-Ru', 66.5 (2); Fe-Ru-C1, 44.9 (2), Ru-Fe-C1, 53.0 (2); Ru-C1-Fe, 82.1 (2); Ru-C1-C1', 112.0 (2); Fe-C1-C1', 165.5 (2).

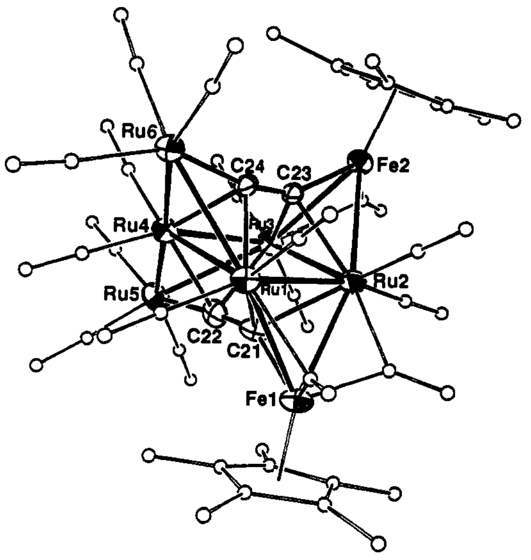
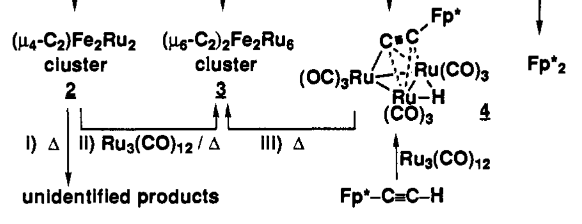


Figure 2. Molecular structure of one of two independent molecules of **3**. Selected bond lengths (Å): Ru-Ru, 2.746 (3)-2.857 (4); Ru-Fe, 2.687 (4)-2.855 (3); C21-C22, 1.35 (4); C23-C24, 1.37 (3); C21-Ru1, 2.25 (2); C21-Ru2, 2.20 (2); C21-Fe1, 1.90 (3); C22-Ru3, 2.15 (2); C22-Ru4, 2.18 (3); C22-Ru5, 1.99 (3); C23-Ru2, 2.18 (2); C23-Ru3, 2.17 (2); C23-Fe2, 1.86 (2); C24-Ru1, 2.15 (2); C24-Ru4, 2.11 (2); Ru6-C24, 2.01 (2).

Scheme I



Treatment of **1** with Ru$_3$(CO)$_{12}$ in refluxing benzene afforded a mixture of products, from which a tetranuclear dicarbide cluster, (μ_4-C$_2$)(Cp*Fe)$_2$Ru$_2$(CO)$_8$(μ-CO)$_2$ (**2**), and an octanuclear bis-

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dicarbide cluster, $(\mu_6\text{-}C_2)_2(Cp^*Fe)_2Ru_6(CO)_{14}(\mu\text{-}CO)_3$ (**3**), were isolated together with another tetranuclear dicarbide cluster, **4**, and Fp^*_2 (Scheme I).[4] Cluster **4**, in which the C_2 ligand is coordinated in a well-established way,[1l,m,2e,5] was also obtained from Fp*C≡CH and $Ru_3(CO)_{12}$.[6]

The tetranuclear cluster **2** (Figure 1), in which the C_2 part lies within the range of bonding interaction of the Fe and Ru atoms, is the first example of a permetalated ethene. However, connection of the two vertices of the rectangular tetrametallic framework distorts the structure, as indicated by (1) the elongated Ru-Ru bond [2.963 (2) Å; cf. **3**, 2.72-2.86 Å], (2) the lesser Ru-C1 interaction [2.198 (9) Å; cf. $Cp_2Ru_2(\mu\text{-}CO)(CO)_2(\mu\text{-}C{=}CH_2)$, 2.026 (7) and 2.033 (7) Å[7]], and (3) the slightly twisted $Fe_2Ru_2(\mu_4\text{-}C_2)$ core (the torsion angle Fe–Ru–Ru′–Fe′ = 24°). In addition, the C1–C1′ length [1.27 (2) Å], which is intermediate between the C–C lengths of **1**[2c] and dinuclear μ-vinylidene complexes [1.30-1.35 Å],[8] suggests triple-bond character still remaining.

The structure of **3** comprises two C_2 ligands and an octametallic framework (Figure 2). Every edge of the Ru_4 square (Ru1-4) is bridged by Fe or Ru, and each C_2 moiety above and below the Ru_4 square interacts with a boat-like hexanuclear array. Such a metal array can be regarded as a finite piece of an fcc or an hcp lattice.[1r] Of the six Ru atoms, Ru5 and Ru6 in the apical positions lie closer to the C_2 ligands. The situation is essentially the same as that in $(\mu_6\text{-}C_2)Co_6(\mu_4\text{-}S)(CO)_{14}$ (**5**),[1r] the only previous example of a $(\mu_6\text{-}C_2)M_6$ cluster with the boat-like metal array. While the C–C distances [C21–C22, 1.35 (4) Å; C23–C24, 1.37 (3) Å] are comparable to that in **5** [1.37 (2) Å], the different sizes of the apical metals cause considerable distortion of the C_2 moieties, as is evident from the M-C-C angles (deg): Fe1-C21-C22 = 149 (2), Ru5-C22-C21 = 175 (2), Fe2-C23-C24 = 150 (2), Ru6–C24–C23 = 166 (2). The PSEP theory[9] predicts that **3** is a coordinatively saturated species with 124 cluster valence electrons, when the $\mu_6\text{-}C_2$ ligand is counted as an 8e donor.

The striking spectroscopic feature of **2** and **3** is the unusual shielding of their C_2 signals when compared with the $\delta(C_\alpha)$'s of μ-vinylidene complexes [$M_2(\mu\text{-}C{=}CR_2)$: $\delta > 230$][8] and μ_3-alkylidyne complexes [$M_3(\mu_3\text{-}CR)$: $\delta > 200$][10] containing their partial structures. Such anomalous properties also may come from the strained structures.

Finally, **3** turned out to be one of the thermodynamically stable species in the reaction system as summarized in Scheme I. Although (i) simple thermolysis of **2** gave unidentified products, (ii) **3** was formed on treatment of **2** with $Ru_3(CO)_{12}$. In addition, (iii) formal dimerization of the $(\mu\text{-}C_2)(Cp^*Fe)Ru_3$ core in **4** leading to **3** was observed.

In marked contrast to the chemistry of C1 species, which has been studied extensively in relation to the CO reduction step of catalytic CO hydrogenation, the properties of the C2 species ($C_2H_xO_y$) that are formed after the first C–C coupling process have remained far less explored. This work reveals the utility of MC≡CM as a versatile starting compound for *C2 chemistry*, in particular, *dicarbide* complexes. Thus the sequential transformation of **1** (permetalated ethyne) into permetalated ethene and ethane [MC≡CM (**1**) → $M_2C{=}CM_2$ (**2**) → M_3CCM_3 (**3**)] has been realized by formal stepwise addition of dimetallic fragments to the C≡C bond in **1**.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters and bond lengths and angles and ORTEP drawings with anisotropic thermal ellipsoids and atomic numbering schemes for **2** and **3** (29 pages); tables of observed and calculated structure factors for **2** and **3** (41 pages). Ordering information is given on any current masthead page.

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(4) A benzene solution (30 mL) of **1** (803 mg, 1.69 mmol) and $Ru_3(CO)_{12}$ (803 mg, 1.26 mmol) was refluxed for 9 h. After removal of $Ru_3(CO)_{12}$ and Fp^*_2 by repeated recrystallization, **2** (192 mg, 0.22 mmol, 13% yield) was isolated by recrystallization from CH_2Cl_2. Preparative TLC of the mother liquor (on alumina, developed with CH_2Cl_2–hexanes = 1:3) afforded **3** (82 mg, 0.05 mmol, 6% yield). **2**: ^{1}H-NMR ($CDCl_3$) δ 1.55 (s, Cp*); ^{13}C-NMR ($CDCl_3$) δ 9.5 (q, J = 128 Hz, C_5Me_5), 98.0 (s, C_5Me_5), 177.2 (s, $\mu_4\text{-}C_2$), 191.1, 196.4, 205.6, 217.8 (s, CO), 262.5 (s, μ-CO); IR (KBr) 2082, 1997, 1981, 1963, 1953, 1775 cm^{-1}. **3**: ^{1}H-NMR ($CDCl_3$) δ 1.62 (s, Cp*); ^{13}C-NMR ($CDCl_3$) δ 9.2 (q, J = 129 Hz, C_5Me_5), 22.7, 31.6 (s, $\mu_6\text{-}C_2$), 98.4 (s, C_5Me_5), 190.5, 190.7, 193.9, 202.8, 208.5, 210.4 (s, CO), 243.4 (s, μ-CO); the simple spectra obtained at room temperature may be explained in terms of local scrambling of the three CO's attached to Ru2; IR (KBr) 2068, 2047, 1997, 1825 cm^{-1}. Crystal data for **2**: $C_{32}H_{30}O_{10}Fe_2Ru_2$, M = 888.42, monoclinic, space group $C2/c$, a = 14.124 (6) Å, b = 11.537 (5) Å, c = 20.142 (5) Å, β = 93.23 (4)°, V = 3277 (4) Å^3, Z = 4, d = 1.80 g·cm^{-3}, μ = 18.09, R (R_w) = 0.0591 (0.0498) for 2668 data with $F > 3\sigma(F)$. Crystal data for **3**: $C_{41}H_{30}O_{17}Fe_2Ru_6$, M = 1512.79, triclinic, space group $P\bar{1}$, a = 16.801 (6) Å, b = 21.402 (8) Å, c = 14.436 (9) Å, α = 101.60 (4)°, β = 93.45 (4)°, γ = 93.50 (3)°, V = 5061 (4) Å^3, Z = 4, d = 1.99 g·cm^{-3}, μ = 23.28, R (R_w) = 0.0780 (0.1119) for 9217 data with $F > 3\sigma(F)$. The structure was solved by using the TEXSAN structure-solving system. A unit cell of **3** contained two independent molecules with essentially the same structure.

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Insertion of Phosphorus into the C–C Bond of Benzene As Observed by Collision-Mass Spectrometry

César A. Muedas, Detlef Schröder, Detlev Sülzle,† and
Helmut Schwarz*

Institut für Organische Chemie der Technischen
Universität Berlin, Strasse des 17. Juni 135
W-1000 Berlin 12, FRG

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The interaction of diverse atomic ions (or neutrals) with neutral (or ionized) benzene has been extensively examined in several studies.[1] There has been, however, no report to date for the phosphorus–benzene case. The results here presented provide evidence of ion–molecule reactions leading to the insertion of a phosphorus atom into the C–C bond of the aromatic ring.

For the generation of the ions $[P,C_6,H_6]^+$ of interest, benzene and PI_3 were reacted in the chemical ionization (CI) source[2] of a modified VG-ZAB tandem mass spectrometer of BEBE configuration.[3] The cations (m/z = 109) were selected under double-focusing conditions using B(1)E(1) and subjected to collisional activation (CA)[4] and neutralization–reionization (NR)[5] experiments. Phenylphosphine, in turn, was used to generate $C_6H_5PH^-$ by deprotonation with $O^{\bullet -}$ under similar CI conditions (abstraction of ring protons by $O^{\bullet -}$ can be excluded on thermo-

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† Present address: Schering AG, Postfach 65 03 11, W-1000 Berlin 65, FRG.

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