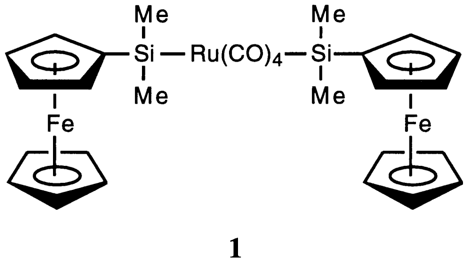
CHEMISTRY LETTERS, pp. 1665-1668, 1994.

Synthesis and Molecular Structure of 1,1'-Ferrocenediyl Bis(dimethylsilylene) Bridged Triruthenium Dihydrido Cluster, $[Ru_3(\mu\text{-}H)_2(\mu\text{-}SiMe_2C_5H_4FeC_5H_4SiMe_2\text{-})(CO)_{10}]$

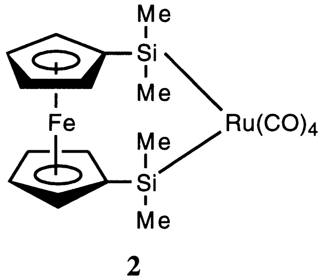
Sonae KOTANI, Tsuneyoshi TANIZAWA, Tomohiro ADACHI,† Toshikatsu YOSHIDA,† and
Kenkichi SONOGASHIRA*
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto,
Sumiyoshi-ku, Osaka 558
† Department of Chemistry, Faculty of Integrated Arts and Sciences, University of
Osaka Prefecture, Sakai, Osaka 591

The reaction between equimolar amounts of 1,1'-bis(dimethylsilyl)ferrocene (**3**) and trirutheniumdodecacarbonyl afforded dihydrido triruthenium cluster (**4**) having an edge-bridge by a 1,1'-ferrocenediyl bis(dimethylsilylene) chelate ligand. This complex was identified by a combination of spectroscopic and X-ray methods. Crystal data for **4**: monoclinic, space group $C2/c$, a = 13.567(4) Å, b = 15.871(3) Å, c = 15.195(5) Å, β = 110.24(2) °, V = 3069(2) Å^3, Z = 4 and $R(R\text{w})$ = 0.041(0.044).

The increasing importance of organosilicon compounds in organic syntheses and applications for new materials[1] has led to considerable interest in the reactivities and the formation of σ-silyl-metal bond which may play an important role in metal-catalyzed reactions of Si-H, such as hydrosilylation[2] and Si-Si bond formation.[3] We have an interest in the chemistry of silyl-metal complexes derived from the reaction of 1- or 1,1'-dimethylsilyl derivatives of ferrocene with a metal carbonyl, since such a compound may contain a silicon-metal bond stabilized with a ferrocenyl group. It is also interesting to see whether there is any direct interaction between the ferrocenyl iron atom and the silyl transition metal group or not.



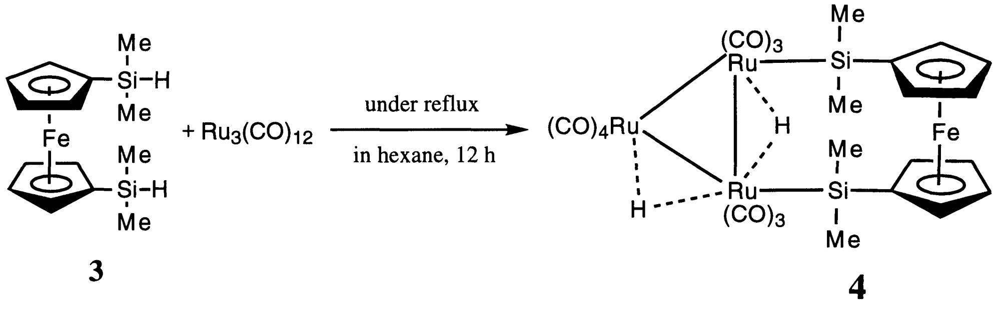
1



2

There are many examples of the syntheses of transition-metal silyl derivatives by the reactions of trirutheniumdodecacarbonyl and hydrosilanes.[4,5] We recently reported the syntheses of σ-ferrocenylsilyl transition-metal complexes, (**1**) and (**2**), having an inter- or an intra-molecular mononuclear ruthenium bridge by the reaction of 1,1'-bis(dimethylsilyl)ferrocene (**3**) with trirutheniumdodecacarbonyl accompanying the cleavage of Ru-Ru bonds.[6)] Herein, we wish to report the synthesis of a new 1,1'-ferrocenediyl-bis(dimethylsilylene)-bridged dihydrido triruthenium cluster without cleavage of Ru-Ru bonds.

The reaction of $Ru_3(CO)_{12}$ with **3** was highly dependent on the ratio of the reactants. Thus, by the reaction of 3 : 1 molar ratio of **3** and $Ru_3(CO)_{12}$, the ferrocenyl complex **2**, having an intramolecular mononuclear ruthenium bridge was obtained. In contrast, $Ru_3(CO)_{12}$ were found to react with equimolar amount of **3** without any cleavage of Ru-Ru bond, affording 1,1'-ferrocenediyl bis(dimethylsilylene) bridged triruthenium dihydrido cluster, $[Ru_3(\mu\text{-}H)_2(\mu\text{-}SiMe_2C_5H_4FeC_5H_4SiMe_2)(CO)_{10}]$. Thus, a solution of 1 : 1 molar ratio of **3** (343 mg, 1.14 mmol) and $Ru_3(CO)_{12}$ (720 mg, 1.13 mmol) in hexane (10 mL) was stirred for 12 h at 70 °C under an atmosphere of argon. After purification by alumina column chromatography (30 mm × 50 mm) with a benzene eluent and recrystallization from hot hexane, diamagnetic red crystals of triruthenium complex (**4**) having an intramolecular 1,1'-ferrocenediyl bis(dimethylsilylene) chelate ligand were obtained in 7% yield (eq. 1). The structure of intramolecular bridged ferrocenediyl derivative **4** has been fully characterized on the basis of their analytical data, IR, ^{1}H-NMR, ^{13}C-NMR, and X-ray diffraction.[7,8)]



eq.1

The IR spectrum of **4** in the carbonyl region is similar to those of dihydorido complexes, $H_2Ru_3(CO)_9X$ (X = S, Se, Te), indicating a low molecular symmetry.[9)] No vibrations due to bridging carbonyls are observed. Mass spectrum (EI) showed the molecular ion and the fragment peaks derived from the stepwise loss of CO groups. In the ^{1}H-NMR spectrum of **4**, the two bridged protons with two ruthenium atoms were detected at -14.78 and -17.04 ppm which are consistent with the presence of two kinds of bridging hydride ligands.[10)] In the ^{13}C-NMR spectrum of **4**, the three carbonyl resonances were detected at 191.45,198.99 and 202.90 ppm. Finally, the structure of **4** has been determined by X-ray diffraction study. The molecular structure of compound **4** is shown with the selected bond distances and angles in Fig. 1. Complex **4** was found as the averaged structure of asymmetric $Ru_3(\mu\text{-}H)_2(\mu\text{-}SiMe_2C_5H_4FeC_5H_4SiMe_2)(CO)_{10}$ on the crystallographic C_2 axis through Ru(1), μ-H(2) and Fe atoms. Existence of the hydride atom bridging either Ru(1)-Ru(2) or Ru(1)-Ru(2)* was supported by the evidence of the statistically disordered equatorial carbonyls coordinated to the Ru(1) atom with respect to the C_2 axis. The cluster consists of a nearly equilateral triangle of ruthenium atoms [Ru(1)-Ru(2), 3.037(4) Å and Ru(2)-Ru(2'), 3.019(7) Å], bonded to ten CO, two μ-hydride and one 1,1'-ferrocenediyl bis(dimethylsilylene) chelate ligands. Both silicon atoms and hydrogen atoms of bridging ligands are coplanar with Ru_3 triangle (Table 1) and the ferrocenyl group has an eclipsed conformation with essentially parallel Cp rings (tilt angle 2.5(3)°).

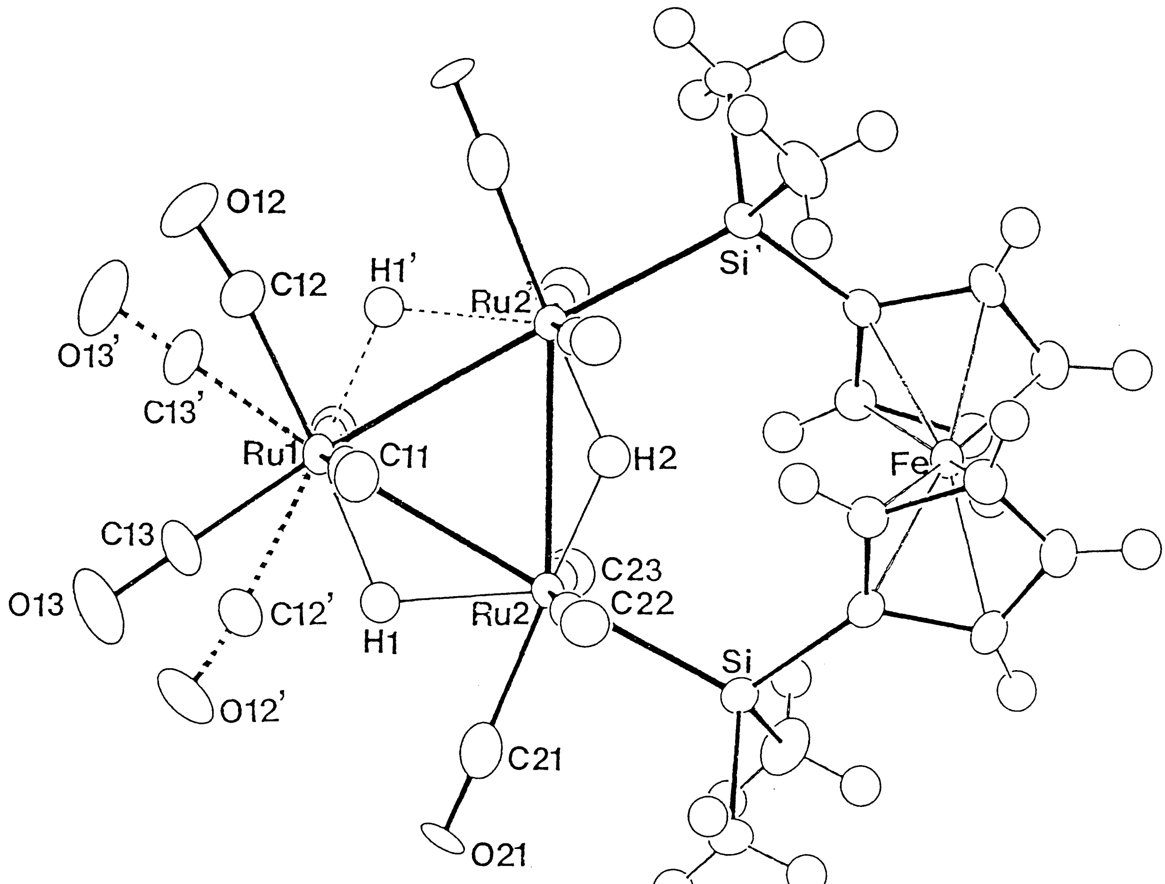


Fig. 1. Molecular structure and numbering scheme for $Ru_3(\mu\text{-}H)_2(\mu\text{-}SiMe_2C_5H_4FeC_5H_4SiMe_2)(CO)_{10}$ (**4**). Selected lengths (Å) and angles (deg): Ru(1)-Ru(2), 3.037(4); Ru(2)-Ru(2'), 3.019 (7); Ru(1)-C(11), 1.931 (8); Ru(1)-C(12), 1.99(2); Ru(1)-C(13), 1.87(2); Ru(2)-C(22), 1.924(7); Ru(2)-C(23), 1.929(7); Ru(1)-H(1), 1.80; Ru(2)-H(1), 1.93; Ru(2)-H(2), 1.66(5); Ru(2)-Si, 2.459(4); Ru(1)-Ru(2)-Ru(2'), 60.20(1); Ru(2)-Ru(1)-Ru(2'), 59.59(3); C(11)-Ru(1)-C(11'), 167.3(4); C(12)-Ru(1)-H(1), 175.5(4); Ru(2')-Ru(1)-C(13), 173.9(5); C(21)-Ru(2)-H(2), 177(3); C(22)-Ru(2)-C(23), 169.3(3); Ru(1)-H(1)-Ru(2), 108.8; Ru(2)-H(2)-Ru(2'), 131(7); Ru(1)-Ru(2)-Si(1), 176.1 (1).

Table 1. Coplanarity of bridging ligands with Ru_3 triangle

Atoms	Deviation from Ru_3 triangle (Å)
Si	+ 0.15(1)
H(1)	+ 0.16
H(2)	0

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics (No. 05236106) from Ministry of Education, Science and Culture, Japan.

References

1) R. West, J. Organomet. Chem., **300**, 327 (1986).

2) J. F. Harrod and A. J. Chalk, "Organic Syntheses via Metal Carbonyl," ed by I. Wender, P. Pino, Wiley, New York (1977), Vol. 2, p.673.

3) C. T. Aitken, J. F. Harrod, and E. Samuel, J. Am. Chem. Soc., **108**, 4059 (1986).

4) W. Fing, Helv. Chim. Acta, **59**, 606 (1976).

5) For reviews, see: K. C. Mackay and B. K. Nicholson, Comprehensive Organometallic Chemistry, 6, 1043; C. S. Cundy, B. M. Kingston M. F. Lappert , Adv. Organomet. Chem., **11**, 253 (1973).

6) S. Kotani, T. Tanizawa, K. Shiina, and K. Sonogashira, Chem. Lett., **1990**, 1889.

7) Red crystals; dec. p. 149-151°C under Ar; Anal. Found: C, 32.50; H, 2.34%. Calcd for $C_{24}H_{22}FeO_{10}Ru_3Si_2$: C, 32.55; H, 2.50%. MS: m/z 888 (M^+); UV/VIS (cyclohexane, nm): λ_{max} (ε) 208 (51000), 250 (36000), 294 (22000), 368 (9000), 455 (3700); ^1H-NMR (C_6D_6, TMS, ppm): -17.04, -14.78 (2H, s, Ru-H), 0.78 (12H, s, Si-CH_3), 3.99, 4.17 (8H, br, Si-C_5H_4); ^{13}C-NMR ($CDCl_3$,TMS, ppm): 8.63 (Si-CH_3), 70.90, 74.51 (Cp), 191.45,198.99, 202.90 (Ru-CO); IR (CCl_4,cm^{-1}): ν_{CO} 2040 (m,sh), 2050 (vs), 2070 (vs), 2100 (w,sh), 2130 (w).

8) Crystals of complex **4** suitable for X-ray analysis were obtained by recrystallization from hexane. Crystallographic data: MF = $C_{24}H_{22}O_{10}Si_2FeRu_3$, Mw 885.7, monoclinic, a = 13.567(4), b = 15.871(3), c = 15.195(5) Å, β = 110.24(2) °,V = 3069(2) $Å^3$, space group $C2/c$, Z = 4, Dc = 1.92 g/cm^3, μ(MoKα) = 9.61 cm^{-1}. Crystal dimensions, 0.4 × 0.4 × 0.2 mm, Tc = 20 °C. Diffraction data were collected on a Rigaku AFC6 diffractometer with graphite monochromated MoKα radiation using the ω-2θ scan mode to a maximum 2θ value of 50°. The structure was solved by Patterson method and refined to R = 0.041 and Rw = 0.044 for 2748 reflections with $|F_0| > 6\sigma(F_0)$.

9) E. Sappa, O. Gambino, and G. Cetini, J. Organomet. Chem., **35**, 375 (1972).

10) K. Burgess, C. Guerin, B. F. G. Johnson, and J. Lewis, J. Organomet. Chem., **295**, C3 (1985).

(Received June 17, 1994)