Organometallics **2001,** *20,* 4772−4774

Novel Trinuclear Trihydride Complexes of Ruthenium Having a Triply Bridging Borylene Ligand, $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}BX)$ (X = H, CN, OMe, OEt). Synthesis, Structure Determination, and Reaction with Benzothiophene

Rei Okamura, Ken-ichi Tada, Kouki Matsubara, Masato Oshima, and Hiroharu Suzuki*

Department of Applied Chemistry, Graduate School of Science and Engineering,
Tokyo Institute of Technology and CREST, Japan Science and Technology Corporation (JST),
O-okayama, Meguro-ku, Tokyo 152-8552, Japan

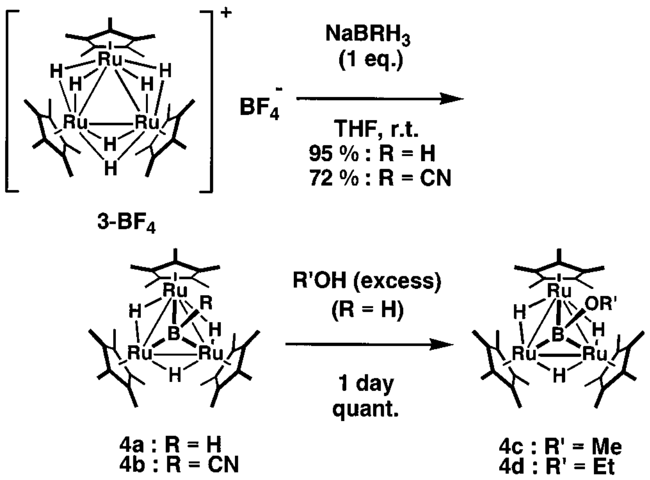
Received July 9, 2001

Summary: The triruthenium hexahydride complex $[\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_6](BF_4)$ *reacted with* $NaBH_3X$ *(X = H, CN) to yield the novel trinuclear* μ_3*-borylene complex* $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}BX)$*, and the* μ_3*-BH derivative was converted into a* μ_3*-B(OR) analogue (R = Me, Et) upon treatment with MeOH and EtOH, respectively. In the reaction of the* μ_3*-BH analogue with benzothiophene, a* μ_3*-thiaruthenacyclohexadiene complex formed via carbon−sulfur bond cleavage was isolated, and its structure was determined by an X-ray diffraction study.*

Cluster complexes have attracted increasing attention due to their promising applicability to organic synthesis.[1] Their ability to multiply coordinate a substrate molecule and to carry out a multielectron transfer to the substrate most certainly distinguishes the reactivity of the cluster complexes from that of mononuclear complexes. We have recently demonstrated the remarkable synergic effect of the adjacent metal centers in the reactions of the polyhydride clusters of ruthenium $\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_4$ (**1**) and $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**2**) with various types of organic substrates such as cyclopentadiene,[2] butadiene,[3] 1,1-disubstituted alkenes,[4] benzothiophene,[5] and alkanes.[6]

Change in the electronic and steric environment of the reaction site via introduction of a triply bridging ligand into the Ru_3 core possibly modifies the reactivity of the parent cluster **2**. We report herein the synthesis of novel trinuclear polyhydride clusters of ruthenium having a triply bridging borylene ligand, $\{(\eta^5\text{-}C_5Me_5)\text{-}Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}BX)$ (**4**: **4a**, X = H; **4b**, X = CN; **4c**, X = OMe; **4d**, X = OEt), and isolation of a benzothiaruthenacyclohexadiene complex formed in the reaction of **4a** with benzothiophene.

Scheme 1



The reaction of the cationic polyhydride cluster $[\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_6](X)$ (X = BF_4 and PF_6) (**3**) with an equimolar amount of $NaBH_4$ at room temperature resulted in the exclusive formation of the neutral polyhydride cluster $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}BH)$ (**4a**), having a μ_3-BH group, which was isolated as a dark red solid in 95% yield (Scheme 1).[7] While treatment of the cationic cluster **3** having a BF_4 or PF_6 group as a counteranion with $NaBH_4$ afforded the same product, the reaction using the triruthenium hexahydride cation derived from the reaction of **1** with sulfuric acid resulted

---

* To whom correspondence should be addressed.

[1] For example: (a) McCann, M. In *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998; Chapter 5, pp 145−166. (b) Suess-Fink, G. In *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998; Chapter 6, pp 167−248. (c) Doyle, M. P. In *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998; Chapter 7, pp 259−282. (d) Ojima, I.; Li, Z. In *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998; Chapter 9, pp 307−343, and references therein.

[2] Suzuki, H.; Takaya, Y.; Takemori, T. *J. Am. Chem. Soc.* **1994**, *116*, 6, 10779.

[3] (a) Takemori, T.; Suzuki, H.; Tanaka, M. *Organometallics* **1996**, *15*, 4346. (b) Suzuki, H.; Takemori, T.; Inagaki, A. *J. Synth. Org. Chem., Jpn.* **1999**, *57*, 935.

[4] Takemori, T.; Inagaki, A.; Suzuki, H. *J. Am. Chem. Soc.* **2001**, *123*, 1762.

[5] Matsubara, K.; Okamura, R.; Tanaka, M.; Suzuki, H. *J. Am. Chem. Soc.* **1998**, *120*, 1108.

[6] (a) Matsubara, K.; Inagaki, A.; Tanaka, M.; Suzuki, H. *J. Am. Chem. Soc.* **1999**, *121*, 7421. (b) Inagaki, A.; Takemori, T.; Tanaka, M.; Suzuki, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 404.

[7] Experimental details for **4a**: THF (10 mL) and **3-BF$_4$** (113 mg, 0.141 mmol) were charged in a 50 mL Schlenk tube. After 5 mg (1 equiv) of $NaBH_4$ was added, the reaction mixture was stirred for 1 h at room temperature. Removal of the solvent under reduced pressure afforded a dark red residual solid. The residue was extracted with 10 mL of pentane, and the combined extract was passed through Celite on a glass filter. Removal of solvent under reduced pressure gave 97 mg (0.134 mmol, 95%) of **4a** as a dark red solid.

10.1021/om010609o CCC: \$20.00

in the formation of the bicapped complex $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_5(\mu_3\text{-}BH)_2$ (**5**).

The new compound **4a** was characterized on the basis of ^1H, ^{13}C, and ^{11}B NMR and IR spectra. In the ^1H NMR spectrum, the resonance signals for both the three C_5Me_5 groups and the three hydrides were observed to be equivalent at δ 1.82 and −1.93 ppm, respectively. This result implies that complex **4a** has a C_3 axis perpendicular to the Ru_3 plane. The X-ray diffraction study on the analogous complex **4d** proved the structure to have a pseudo C_3 axis (vide infra). The resonance of the proton directly bound to the boron atom was observed at δ 8.22 ppm as a broad peak ($w_{1/2} = 238$ Hz) due to the coupling with the ^{11}B nucleus. The ^{11}B NMR spectrum revealed a broad singlet peak with a half-height width of 36.5 Hz at δ 131.3 ppm. The value of δ 131.3 ppm is comparable to the shift of a metal-bound borylene ligand[8] and is much lower than those of a boryl ligand and the borate ions, δ −24.6 ppm for $(C_5Me_5)Mo(CO)_3(BH_2PMe_3)$,[9] δ −27.6 ppm for $(C_5Me_5)W(CO)_3(BH_2PMe_3)$,[9] δ −43 ppm for BH_4^-, and δ −127 ppm for BI_4^-.[10] An absorption due to the B−H stretching vibration appeared at 2428 cm^{-1} in the infrared spectrum.

A complex having a μ_3-BCN ligand, $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}BCN)$ (**4b**), was similarly prepared in 72% yield by the reaction of **3** with the corresponding borate salt, $NaB(CN)H_3$. Treatment of **4a** with alcohols such as methanol and ethanol resulted in replacement of the hydrogen atom bonded to the triply bridging borylene ligand with an alkoxy group to generate $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}BOMe)$ (**4c**) and $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}BOEt)$ (**4d**), respectively. The new complexes **4b**−**d** were characterized by means of ^1H, ^{13}C, and ^{11}B NMR spectroscopy. In the ^{11}B NMR spectra of **4b**−**d**, a broad singlet peak appeared in a relatively low-field region characteristic for the triply bridging borylene ligand: δ 116.9 ppm for **4b**, 77.7 ppm for **4c**, and 87.7 ppm for **4d**, respectively. These values of the ^{11}B chemical shift are also comparable to those reported for borylene ligands.[8] The ^1H resonance for the hydride ligands in **4b**−**d** was observed at significantly low field for transition metal hydrides, δ −0.41 ppm in C_6D_6 and δ −0.78 ppm in THF-d_8, respectively, for **4b**, δ −2.34 ppm (C_6D_6) for **4c**, and δ −2.23 ppm (C_6D_6) for **4d**.

The structure of the triply bridging borylene complex **4** was confirmed by means of an X-ray diffraction study using a red-brown single crystal of **4d** obtained from a mixed solvent of tetrahydrofuran and ethanol at −20 °C. The ORTEP drawing is illustrated in Figure 1 together with the relevant bond lengths and angles.

Compound **4d** consists of a nearly equilateral triangular cluster of three ruthenium atoms with a triply bridging borylene ligand. The average B−Ru distance of 2.154 Å lies in the range of those reported for the transition metal borylene complexes.[8] The EAN rule applied to **4d** requires a formal Ru−Ru bond order of $^5/_3$. The unsaturated nature of the cluster is reflected in the significantly short Ru−Ru distance: average 2.6772 Å.

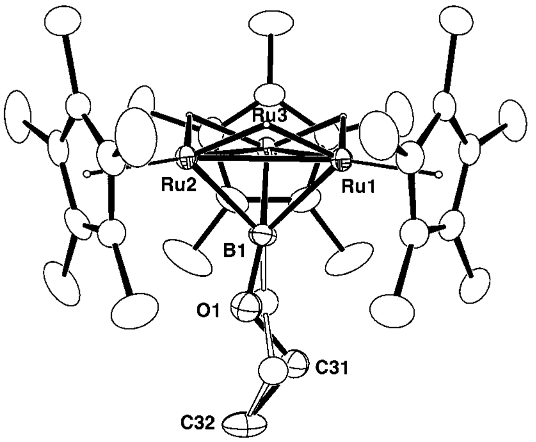


Figure 1. Molecular structure of $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}BOEt)$ (**4d**). The thermal ellipsoids correspond to 30% probability. O1A and C31A show the disorder in the crystal (O1:O1A = 53.4:46.6). Selected bond distances (Å) and angles (deg): Ru1−Ru2 = 2.6770(5), Ru1−Ru3 = 2.6768(5), Ru2−Ru3 = 2.6779(5), Ru1−B1 = 2.177(6), Ru2−B1 = 2.140(7), Ru3−B1 = 2.146(6), B1−O1 = 1.374(13), O1−C31 = 1.43(3), C31−C32 = 1.519(17); Ru2−Ru1−Ru3 = 60.024(14), Ru1−Ru2−Ru3 = 59.985(14), Ru1−Ru3−Ru2 = 59.991(14), Ru1−B1−Ru2 = 76.6(2), Ru1−B1−Ru3 = 76.53(19), Ru2−B1−Ru3 = 77.3(2).

Notably, complexes **4a**−**d** have a spacious reaction site on the reverse side of the μ_3-borylene ligand with respect to the Ru_3 plane. Although there have been, thus far, a few reported examples of the structurally well-defined trinuclear μ_3-borylene cluster, both sides of their triangular frameworks are covered with two triply bridging ligands.[11] Thus, compounds **4a**−**d** are an unprecedented type of a μ_3-borylene cluster, that is, a “single-faced μ_3-borylene cluster”, in which the metal centers most certainly cooperate in the activation of substrates.

The μ_3-borylene ligand introduced into the Ru_3 framework of the cluster likely exerts a considerable effect on the electronic environment of the reaction sites and, consequently, induces changes in reactivity. In addition, the triply bridging ligand most probably prevents cleavage of the metal−metal bond to keep the Ru_3 framework firm.

Previously, we reported desulfurization of benzothiophene by the trinuclear pentahydride cluster **2**.[5] The reaction of **2** with benzothiophene smoothly proceeded under mild conditions to generate the μ_3-sulfido-μ_3-phenethylidyne complex $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu_3\text{-}CCH_2Ph)$ (**6**) by way of the intermediary benzothiaruthenacyclohexadiene **7** (Scheme 2). Although **7** was detected by ^1H and ^{13}C NMR spectroscopy, we were not able to obtain single crystals because of its rapid conversion to **6** in solution as a result of the cleavage of the second carbon−sulfur bond. Application of the μ_3-borylene complex **4a** to the reaction with benzothiophene, however, enabled us to isolate an intermediary benzothiaruthenacyclohexadiene as a stable compound.

---

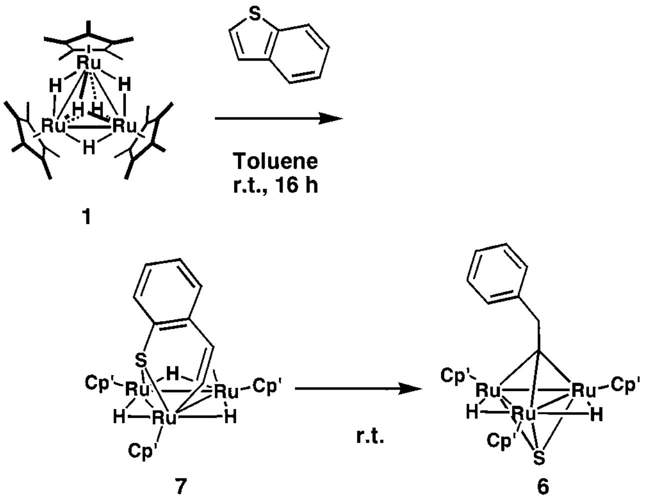
(8) (a) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786 and references therein. (b) Braunschweig, H.; Colling, M. *J. Organomet. Chem.* **2000**, *614*−*615*, 18.

(9) Kawano, Y.; Yasue, T.; Shimoi, M. *J. Am. Chem. Soc.* **1999**, *121*, 11744.

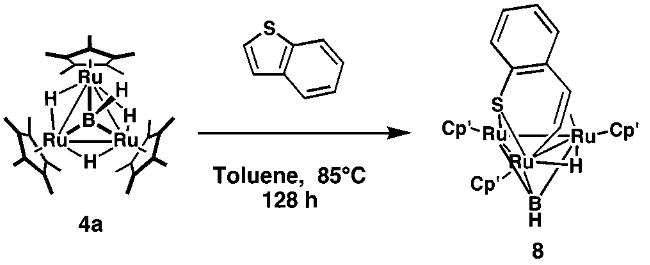
(10) Akitt, J. W.; Mann, B. E. In *NMR and Chemistry. An Introduction to Modern NMR Spectroscopy*, 4th ed.; Stanley Thornes: Glos, 2000; p 35.

(11) (a) Feilong, J.; Fehlner, T. P.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 424 (b) Lei, X.; Shang, M.; Fehlner, T. P. *Inorg. Chem.* **1998**, *37*, 3900.

Scheme 2



The reaction of **4a** with a slight excess of benzothiophene at 85 °C resulted in the predominant formation of the new product **8**, as detected by NMR spectroscopy (eq 1).[12] The new product **8** was isolated as a black-purple solid in 31% yield and assigned as a trinuclear benzothiaruthenacyclohexadiene complex triply bridged by the bolylene ligand on the basis of the ^{1}H and ^{13}C NMR spectra as well as the ^{1}H$-$^{13}C HSC spectrum.



(1)

The remarkable resemblance of the ^{1}H and ^{13}C NMR spectra of **8** to those of **7** strongly indicated the structural similarity between **8** and **7**. The signals characteristic of a μ-σ,π-vinylic fragment of the thiaruthenacycle were observed at δ 7.98 ppm (d, $J = 7.4$ Hz, H on the C$_\alpha$) and δ 4.65 ppm (d, $J = 7.4$ Hz, H on the C$_\beta$) in the ^{1}H NMR spectrum, and δ 178.1 ppm (d, $J_{CH} = 151.3$ Hz, C$_\alpha$) and δ 66.1 ppm (d, $J_{CH} = 144.4$ Hz, C$_\beta$) in the ^{13}C NMR spectrum, respectively.

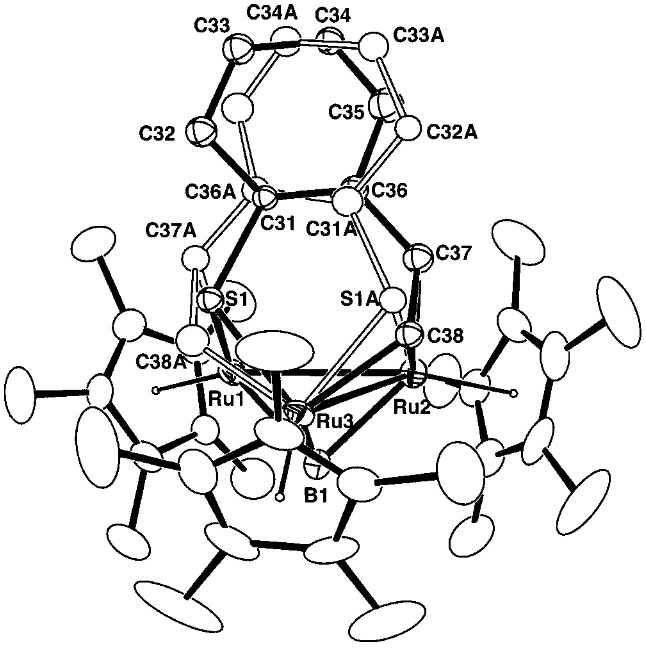


Figure 2. Molecular structure of $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)(\mu_3\text{-}BH)(SC_8H_6)$ (**8**). The thermal ellipsoids correspond to 30% probability. S1A and C31A$-$C38A show the disorder in the crystal (S1:S1A = 59.0:41.0). Selected bond distances (Å) and angles (deg): Ru1$-$Ru2 = 2.9035(8), Ru1$-$Ru3 = 2.7780(9), Ru2$-$Ru3 = 2.7744(9), Ru1$-$B1 = 2.094(9), Ru2$-$B1 = 2.137(8), Ru3$-$B1 = 2.174(9), Ru1$-$S1 = 2.260(4), Ru3$-$S1 = 2.298(4), Ru2$-$C37 = 2.28(1), Ru2$-$C38 = 2.13(2), Ru3$-$C38 = 2.07(1), S1$-$C31 = 1.84(2), C31$-$C36 = 1.36(3), C36$-$C37 = 1.47(3), C37$-$C38 = 1.39(2); Ru2$-$Ru1$-$Ru3 = 58.41(2), Ru1$-$Ru2$-$Ru3 = 58.53(2), Ru1$-$Ru3$-$Ru2 = 63.06(2), Ru1$-$B1$-$Ru2 = 86.7(3), Ru1$-$B1$-$Ru3 = 81.2(3), Ru2$-$B1$-$Ru3 = 80.1(3), Ru3$-$S1$-$C31 = 117.2(6), S1$-$C31$-$C36 = 122(1), C31$-$C36$-$C37 = 125(1), C36$-$C37$-$C38 = 128(1), C37$-$C38$-$Ru3 = 127(1), C38$-$Ru3$-$S1 = 89.8(5).

The proposed structure was confirmed by X-ray crystallography using a single crystal of **8** obtained from Et$_2$O at 5 °C (Figure 2). The structure clearly shows the formation of the benzothiaruthenacycle as a result of oxidative addition of the C(olefinic)$-$S bond to one of the three ruthenium atoms. The triply bridging borylene group coordinated from the back with respect to the Ru$_3$ plane likely inhibits the cleavage of another carbon$-$sulfur bond, C(aromatic)$-$S in the ruthenacycle **8**.

Acknowledgment. This research was partly supported by Fellowships of the Japan Society for the Promotion of Science for Japanese Junior Scientists. We thank JEOL Ltd. for measurement of the ESI-MS spectrum of **4a**. We are also grateful to Kanto Chemical Co., Inc., for a generous supply of pentamethylcyclopentadiene.

Supporting Information Available: Tables of ^{1}H, ^{13}C, and ^{11}B NMR spectral assignments of **4a**$-$**d**, **5**, and **8** and ORTEP diagrams, text describing X-ray procedures, and tables of X-ray data, positional and thermal parameters, and distances and angles for **4d** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010609O

---

[12] Experimental details for **8**: complex **4a** (54.3 mg, 0.075 mmol) and benzothiophene (13.5 mg, 0.101 mmol) were charged in a 50 mL Schlenk tube. After toluene (5 mL) was added, the reaction mixture was stirred for 128 h at 85 °C. After removal of the solvent under reduced pressure, the residue was extracted with pentane and purified by column chromatography. The black-purple fraction was collected, and solvent was removed under reduced pressure to give 20.1 mg (0.024 mmol, 31%) of **8** as a black-purple solid.