Organometallics **2001,** *20,* 10−12

Synthesis, Characterization, and Structure Determination of the Heterobimetallic Polyhydride Complexes $(C_5Me_5)Ru(\mu\text{-}H)_3MH_3(C_5Me_5)$ (M = Mo, W) Containing Group VI and Group VIII Metals

Takanori Shima, Jun-ichi Ito, 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

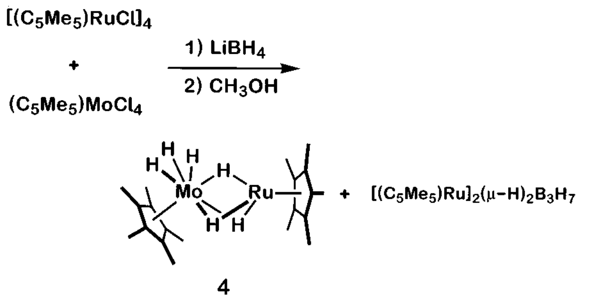
Received September 7, 2000

Summary: $(C_5Me_5)Ru(\mu\text{-}H)_3MH_3(C_5Me_5)$ *(**4**, M = Mo; **5**, M = W), the first heterobimetallic polyhydride complexes containing ruthenium and group VI metals, were synthesized, and those structures were determined by X-ray studies. The reactions of **4** and **5** with phosphines, amine, and acetylacetone were examined.*

Multinuclear complexes having strong interactions among metals have attracted attention due to their remarkable reactivity, originating in the ability of multielectron transfer between a substrate and the complex, and of coordination of a substrate at the multiple metal centers. As a part of our early efforts directed toward "*multimetallic activation*", we reported the synthesis and reactions of di- and triruthenium polyhydride complexes, $(C_5Me_5)Ru(\mu\text{-}H)_4Ru(C_5Me_5)$ (**1**) and $[(C_5Me_5)Ru]_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**2**), and demonstrated that they acted as precursors of the active species for *multimetallic activation*.[1] As an extension of the chemistry of homometallic clusters, we focused our attention on the synthesis of a heterometallic polyhydrido cluster to render the reaction site electronically anisotropic. In such a heterometallic reaction site, a polar substrate would interact anisotropically with each metal center and regio- and chemoselective activation of the substrate would, therefore, be achieved.

We have recently reported the synthesis of the novel heterobimetallic trihydride complex $(C_5Me_5)Ru(\mu\text{-}H)_3\text{-}Ir(C_5Me_5)$ (**3**), containing both group VIII and group IX metals, in a molecule and demonstrated the selective cleavage of the $C(sp^2)-H$ bond at the iridium site through reactions with ethylene, 1-phenylpropyne, and diphenylacetylene.[2] Enhancement of the anisotropic character of the reaction site would improve the regioselectivity in the stage of substrate activation, because the regioselectivity is likely responsible for the difference in the electronic properties between the two metal centers. As the next stage of our study, we tackled the synthesis of a new class of heterometallic polyhydrido complexes containing ruthenium and an electron-deficient metal. In this paper, we report the first synthesis, the structure, and the reaction of novel heterobimetallic polyhydride complexes, $(C_5Me_5)Ru(\mu\text{-}H)_3MH_3(C_5Me_5)$ (**4**, M = Mo; **5**, M = W).

A suspension of a 1/1 mixture of $[(C_5Me_5)RuCl]_4$[3] and $(C_5Me_5)MoCl_4$[4] in diethyl ether was treated with excess $LiBH_4$ at ambient temperature for 12 h. Workup with methanol at −78 °C resulted in the formation of the new heterobimetallic complex $(C_5Me_5)Ru(\mu\text{-}H)_3MoH_3(C_5Me_5)$ (**4**) together with a dinuclear ruthenium complex containing a triborane ligand, *nido*-1,2-$[(C_5Me_5)Ru]_2(\mu\text{-}H)_2B_3H_7$ (eq 1).[5] The new compound **4** was isolated as a brown-yellow solid in 34% yield and assigned as a dinuclear hexahydrido complex on the basis of ^1H NMR spectroscopy.



(1)

The ^1H NMR spectrum of **4** measured at ambient temperature exhibited two singlet peaks at δ 1.94 (15H) and 1.91 (15H) for the C_5Me_5 ligands bound to ruthenium and molybdenum, respectively. These signals were unequivocally assigned in comparison with those of $(C_5Me_4Et)Ru(\mu\text{-}H)_3MoH_3(C_5Me_5)$ (**4′**) derived from $\{(C_5Me_4Et)RuCl\}_4$ and $(C_5Me_5)MoCl_4$. The signals for the hydrides were observed to be equivalent at δ −5.99 (6H) due to a rapid exchange of the hydride ligands among the terminal sites on molybdenum and the bridging sites. The ^1H NMR spectra depend on the temperature

---

* To whom correspondence should be addressed.

[1] (a) Omori, H.; Suzuki, H.; Kakigano, T.; Moro-oka, Y. *Organometallics* **1992**, *11*, 989. (b) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 1129. (c) Takao, T.; Yoshida, S.; Suzuki, H.; Tanaka, M. *Organometallics* **1995**, *14*, 3855. (d) Tada, K.; Oishi, M.; Suzuki, H.; Tanaka, M. *Organometallics* **1996**, *15*, 2422. (e) Suzuki, H.; Takaya, Y.; Takemori, T.; Tanaka, M. *J. Am. Chem. Soc.* **1994**, *116*, 10779. (f) Takemori, T.; Suzuki, H.; Tanaka, M. *Organometallics* **1996**, *15*, 4346. (g) Inagaki, A.; Takaya, Y.; Takemori, T.; Suzuki, H.; Tanaka, M.; Haga, M. *J. Am. Chem. Soc.* **1997**, *119*, 625. (h) Matsubara, K.; Okamura, R.; Tanaka, M.; Suzuki, H. *J. Am. Chem. Soc.* **1998**, *120*, 1108. (i) Matsubara, K.; Inagaki, A.; Tanaka, M.; Suzuki, H. *J. Am. Chem. Soc.* **1999**, *121*, 7421.

[2] Shima, T.; Suzuki, H. *Organometallics* **2000**, *19*, 2420.

[3] Fagan, P. J.; Michael, D. W.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

[4] Murray, R. C.; Blum, L.; Liu, A. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 953.

[5] Lei, X.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1999**, *121*, 1275.

10.1021/om000769k CCC: $20.00
Publication on Web 12/09/2000

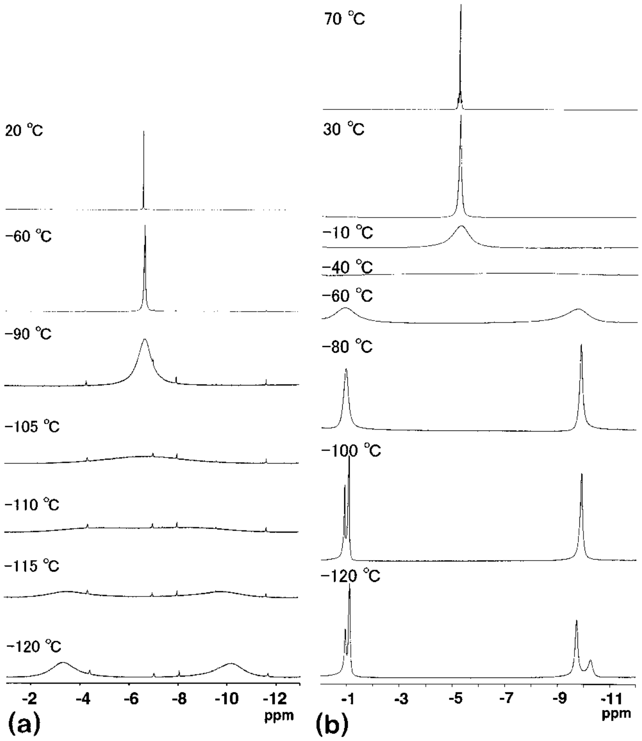


Figure 1. Variable-temperature 400 MHz ^1H NMR spectra (THF-d_8) of **4** (a) and **5** (b) showing the hydride resonances.

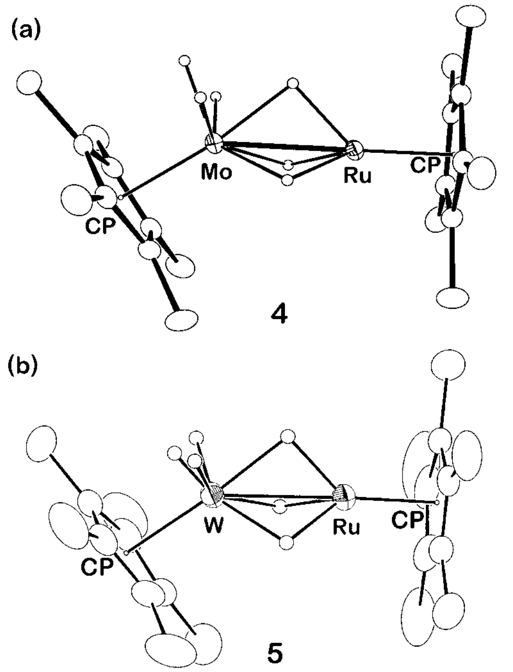


Figure 2. Molecular structures of (a) $(C_5Me_5)Ru(\mu\text{-}H)_3MoH_3(C_5Me_5)$ (**4**) and (b) $(C_5Me_5)Ru(\mu\text{-}H)_3WH_3(C_5Me_5)$ (**5**). Selected bond distances (Å) and angles (deg): (a) Ru−Mo = 2.5255(7), CP−Mo−Ru = 145.6, CP−Ru−Mo = 179.6; (b) Ru−W = 2.5176(8), CP−W−Ru = 140.0, CP−Ru−W = 177.3 (CP = C_5Me_5 centroid).

and are illustrated in Figure 1a. A sharp singlet observed at δ −6.60 at room temperature broadened with a decrease in temperature and flattened at −105 °C. Below this temperature, the signal decoalesced into two broad peaks with the same intensity. At −120 °C, two broad signals appeared at δ −3.36 (3H) and −10.23 (3H). The former was assigned to the resonance of the terminal hydrides bound to molybdenum on the basis of a comparison with that of the structurally well-defined molybdenum hydride complex, δ −3.17 for $(C_5Me_5)MoH_5(PMe_3)$[6] and δ −5.27 for $(C_5Me_5)MoH_3(dppe)$.[7] The latter signal was most likely assigned to that of the bridging hydrides because the value of δ −10.23 was comparable with those for the bridging hydrides in $(C_5H_5)Mo(CO)_2(\mu\text{-}H)(\mu\text{-}I)Mo(CO)_2(C_5H_5)$ (δ −11.45)[8] and in **1** (δ −13.99).

The tungsten analogue of **4**, $(C_5Me_5)Ru(\mu\text{-}H)_3WH_3(C_5Me_5)$ (**5**), was prepared in a similar manner. Treatment of a 1/1 mixture of $[(C_5Me_5)RuCl]_4$ and $(C_5Me_5)WCl_4$[4] with excess $LiBH_4$ resulted in the formation of the heterobimetallic complex $(C_5Me_5)Ru(\mu\text{-}H)_3WH_3(C_5Me_5)$ (**5**) together with the formation of homometallic dimers **1** and *nido*-1,2-$[(C_5Me_5)Ru]_2(\mu\text{-}H)_2B_3H_7$. The heterobimetallic cluster **5** can be isolated by means of column chromatography as brown solids in 40% yield. The ^1H NMR spectra shown in Figure 1b clearly establishes the fluxionality of the hydrides in **5** as observed for the mixed-metal cluster **4**. A singlet peak for the hydrides observed at δ −5.21 (J_{HW} = 57.2 Hz, 6H) at 70 °C broadened and split into two signals with a decrease in temperature. At −80 °C, broad signals for the terminal hydrides and the bridging hydrides appeared at δ −0.92 (3H) and δ −9.86 (3H), respectively. Both of the two broad signals again split into two singlets. Although the two sets of peaks were observed at δ −0.94 (1H) and −1.09 (2H) and δ −9.71 (2H) and −10.25 (1H) at −120 °C, the spectrum was not yet a sharp low-temperature limiting one. The split pattern of the resonance signal for the hydride ligands is fully consistent with the X-ray structure, which has a pseudo-symmetry plane with one of the terminal hydrides, one of the bridging hydrides, and the two metal atoms.

The X-ray diffraction study of **4** and **5** clearly establishes the dinuclear structure bridged by three hydrides. The ORTEP drawings are displayed in parts a and b of Figure 2, along with some of the relevant bond distances and angles.[9] The Ru−Mo and Ru−W distances of 2.5255(7) and 2.5176(8) Å, respectively, are significantly shorter than the sum of the covalent radii (about 2.75 Å) but longer than that of the isoelectronic (30e), structurally well-defined bimetallic complex triply bridged by three carbonyl groups, $(C_5Me_5)Ru(\mu\text{-}CO)_3W(C_5Me_4Et)$ (d_{Ru-W} = 2.410(1) Å).[10]

On the heterometallic reaction sites of the newly synthesized dinuclear complexes **4** and **5**, the substrates most probably interact with each metal center anisotropically due to an incline of the electron density at the metal centers. We, therefore, examined the site selectivity of the heterobimetallic complexes **4** and **5** in the reaction with several types of substrates such as phosphines, amines, and acetylacetone (Scheme 1). Treatment of **4** with an excess amount of trimethylphosphine in toluene at room temperature led to the exclusive formation of $(C_5Me_5)Ru(\mu\text{-}H)_3MoH(PMe_3)(C_5Me_5)$ (**6a**), in which the phosphine was coordinated to

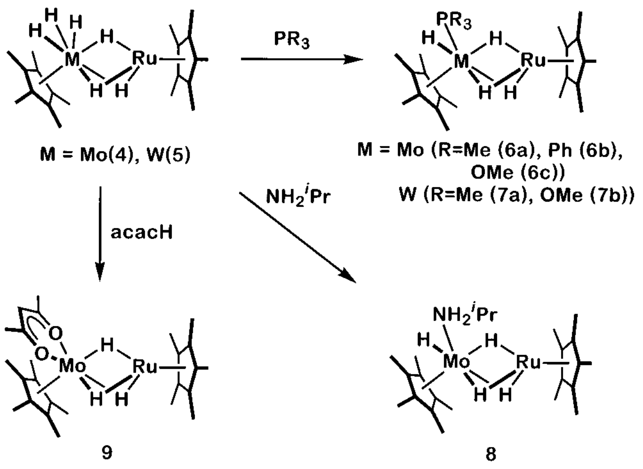
---

(6) Abugideiri, F.; Kelland, M. A.; Poli, R. *Organometallics* **1993**, *12*, 2388.

(7) Pleune, B.; Poli, R.; Fettinger, J. C. *Organometallics* **1997**, *16*, 1581.

(8) Curtis, M. D.; Fotinos, N. A.; Han, K. R.; Butler, W. M. *J. Am. Chem. Soc.* **1983**, *105*, 2686.

Scheme 1



the molybdenum atom as a terminal ligand. Complex **4** reacted with PPh_3 or $P(OMe)_3$ in a similar manner to give the corresponding phosphine complex, **6b** or **6c**, in reasonable yields. Liberation of dihydrogen originating from two of the three terminal hydrides bonded to the molybdenum was confirmed by the observation of a resonance signal around δ 4.5 ppm in the ^1H NMR spectrum. Coordination of the phosphine ligand at the molybdenum center was proved on the basis of the ^1H NMR spectrum of **6a**, which exhibited a doublets of quartets signal at δ −5.88 (J_{PH} = 29.2 Hz, J_{HH} = 4.8 Hz) for the terminal hydride bound to the molybdenum. The tungsten complex **5** also reacted with phosphines to produce the tungsten analogue of **6**, $(C_5Me_5)Ru(\mu\text{-}H)_3WH(PR_3)(C_5Me_5)$ (**7a**, R = Me; **7b**, R = OMe). Evidence for the coordination of the phosphine ligand to the tungsten atom was obtained by ^{31}P NMR spectroscopy. A singlet signal of the phosphine ligand in **7a** was observed at δ −31.4 with satellite peaks due to the ^{183}W nucleus (J_{PW} = 250 Hz). The reaction of **4** with isopropylamine smoothly proceeded in toluene at room temperature to form the amine complex $(C_5Me_5)Ru(\mu\text{-}H)_3MoH(NH_2{}^iPr)(C_5Me_5)$ (**8**). Coordination of the amine ligand to the molybdenum atom in **8** was confirmed by means of a single-crystal X-ray diffraction study.[11] These results clearly showed that the σ-donor ligand had a tendency to be coordinated to the electron-deficient group VI metal rather than the ruthenium atom.

In the reaction of **4** with acetylacetone, the dinuclear η^2-acetylacetonato−μ-trihydrido complex **9** was generated by way of C−H cleavage at a methylene carbon.[12]

In summary, we were able to synthesize the first dinuclear polyhydride-bridged complexes containing ruthenium and a group VI metal that had only C_5Me_5 groups as ancillary ligands. The reaction chemistry of the heterobimetallic clusters with a series of polar organic substrates is under study, and the results will be reported in due course.

Acknowledgment. This research was partly supported by Fellowships of the Japan Society for the Promotion of Science for Japanese Junior Scientists. We are also grateful to Kanto Chemical Co., Inc., for a generous supply of pentamethylcyclopentadiene.

Supporting Information Available: Table of ^1H and ^{13}C NMR spectral assignments of **4**−**9** and ORTEP diagrams, text describing X-ray procedures, and tables of X-ray data, positional and thermal parameters, and distances and angles for **4**, **5**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000769K

---

(9) (a) Complex **4** crystallized from pentane at −33 °C in the monoclinic system, space group $P2_1/n$ (No. 14), with a = 11.004(4) Å, b = 14.024(4) Å, c = 14.149(4) Å, β = 107.64(2)°, V = 2080.3(10) Å^3, Z = 4, and d(calcd) = 1.511 g/cm^3. The data were collected at −50 °C on a Rigaku AFC-7R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) in the 5° < 2θ < 55° range. The data were processed using the TEXSAN crystal structure analysis package operating on an IRIS Indigo computer. At the early stages of the refinement, the atomic scattering factors were obtained from the standard sources. In the reduction of the data, Lorentz/polarization corrections and empirical absorption corrections based on azimuthal scans were applied to the data. The structure was solved by Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined on full-matrix least squares on F^2 using the SHELXL-97 program systems. The final cycle of refinement was based on 4560 observed reflections ($I > 2.00\sigma(I)$) and 212 variable parameters and converged with unweighted and weighted agreement factors of R1 = 0.0366 and wR2 = 0.0904. (b) Complex **5** crystallized from pentane at −35 °C in the monoclinic system, space group $P2_1/n$ (No. 14), with a = 8.070(3) Å, b = 19.196(5) Å, c = 14.320(4) Å, β = 101.14(3)°, V = 2176(1) Å^3, Z = 4, and d(calcd) = 1.713 g/cm^3. Data collection and solution were carried out as in ref 9a. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3595 observed reflections ($I > 3.00\sigma(I)$) and 200 variable parameters and converged with unweighted and weighted agreement factors of R = 0.039 and R_w = 0.046.

(10) Amevor, S. F.; Hund, H. U.; Salzer, A. *J. Organomet. Chem.* **1996**, *520*, 79.

(11) Complex **8** crystallized from pentane at −33 °C in the monoclinic system, space group $P2_1/n$ (No. 14), with a = 11.3161(17) Å, b = 16.979(6) Å, c = 15.643(2) Å, β = 108.104(9)°, V = 2856.9(11) Å^3, Z = 4, d(calcd) = 1.234 g/cm^3, R1 = 0.1127, and wR2 = 0.3044. See the ORTEP diagram and tables of X-ray data and distances and angles in the Supporting Information.

(12) The structure of **9** was determined by means of X-ray diffraction study. Complex **9** crystallized from pentane at −33 °C in the monoclinic system, space group $P2/a$ (No. 13), with a = 13.7947(15) Å, b = 12.491(5) Å, c = 15.5681(16) Å, β = 109.855(10)°, V = 2523.1(10) Å^3, Z = 4, d(calcd) = 1.499 g/cm^3, R1 = 0.0402, and wR2 = 0.1010. See the ORTEP diagram and tables of X-ray data and distances and angles in the Supporting Information.