4346 *Organometallics* **1996,** *15,* 4346−4348

Formation of Novel Trinuclear μ_3-*s*-*cis*-η^2:η^2-1,3-Diene Complexes of Ruthenium Having an Agostic Ru−H−C Interaction. Direct Evidence for Diene Activation in Cooperation with the Three Metal Centers

Toshifumi Takemori and Hiroharu Suzuki*

Department of Chemical Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

Masako Tanaka

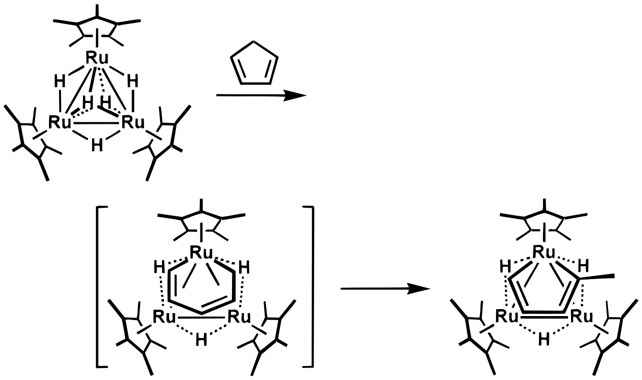
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan

Received March 29, 1996[⊗]

Summary: Trinuclear pentahydride complex $[(C_5Me_5)Ru]_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**1**) *reacts with 1,3-butadiene or isoprene to form a 1,3-dimetalloallyl complex* $[(C_5Me_5)Ru]_3(H)_4(\mu_3\text{-}\eta^3\text{-}C(Me)CHC(R))$.

In the reaction field provided by a cluster complex, substrates may be activated in an effective and somewhat different manner from that observed for the mononuclear complex due to the cooperative action of the metal centers. It has been well established that a mononuclear polyhydride complex gives rise to a coordinatively unsaturated site upon thermal excitation, UV irradiation, or hydrogen transfer to an olefin.[1] The multinuclear polyhydride complex can, therefore, be considered as one of the suitable precursors for *multimetallic activation*, which is a distinctive manner of substrate activation achieved by the concerted action of many metal centers. Although coordinatively unsaturated species can also be generated from transition metal polycarbonyl or polyhydrido−carbonyl complexes, the presence of electron-withdrawing carbonyl ligands in the unsaturated species decreases the rate of the C−H or C−C oxidative addition. We therefore decided to employ multinuclear polyhydride complexes having no carbonyl ligands as the precursors. Thus far there have been few studies of the reactivities of trinuclear transition metal polyhydride complexes having no carbonyl ligands[2] while there is a vast chemistry of hydrido−carbonyl clusters.

In the preceding communication we demonstrated a typical example of trimetallic activation of unsaturated hydrocarbons through the reaction of a trinuclear ruthenium pentahydride, $[(\eta^5\text{-}C_5Me_5)Ru]_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**1**), with cyclopentadiene.[3] The reaction proceeds smoothly at ambient temperature to form a trinuclear 2-methylruthenacyclopentadiene (**3**) by way of an intermediate ruthenacyclohexadiene (**2**) as a result of the C−C bond cleavage of cyclopentadiene. However, an intermediary diene complex having a three-center two-electron Ru−C−C interaction, formed in the initial stage of the reaction, could not be detected by ^1H NMR in spite of a detailed analysis of the reaction at low temperature.



During the course of investigating the activation of acyclic conjugated dienes with the trinuclear complex **1**, we have successfully been able to obtain definitive evidence of the cooperation of three metal centers. Here we report the detection of an agostic intermediate in which three ruthenium centers concertedly activate a 1,3-diene by taking the role of a coordination site or an activation site.

---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

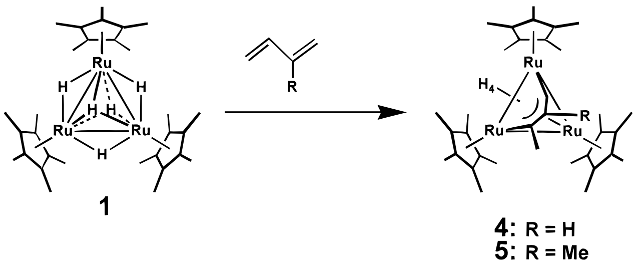
[1] (a) Sponsler, M. B.; Weiller, B. H.; Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 6841. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (c) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (e) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433. (f) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7436. (g) Crabtree, R. H.; Parnell, C. P. *Organometallics* **1984**, *3*, 1727. (h) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738. (i) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (j) Crabtree, R. H.; Holt, E. N.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986. (k) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260. (l) Baudry, D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 788. (m) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243. (n) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1982**, 606. (o) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* **1982**, *224*, 363. (p) Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Yingrui, L. *Tetrahedron Lett.* **1985**, *26*, 1999.

[2] (a) Kersten, J. L.; Rheingold, A. L.; Theopold, K. H.; Casey, C. P.; Wiedenhoefer, R. A.; Hop, C. E. C. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1341. (b) Casey, C. P.; Widenhoefer, R. A.; Hallenbeck, S. L. *Organometallics* **1993**, *12*, 3788. (c) Casey, C. P.; Widenhoefer, R. A.; Hallenbeck, S. L.; Gavney, J. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1692. (d) Casey, C. P.; Widenhoefer, R. A.; Hayashi, R. K. *Inorg. Chim. Acta* **1993**, *212*, 81. (e) Casey, C. P.; Wiedenhoefer, R. A.; Hallenbeck, S. L.; Hayashi, R. K. *Inorg. Chem.* **1994**, *33*, 2639. (f) Casey, C. P.; Widenhoefer, R. A.; Hallenbeck, S. L.; Hayashi, R. K.; Gavney, J. A. *Organometallics* **1994**, *13*, 4720. (g) Casey, C. P.; Hallenbeck, S. L.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 4607.

[3] Suzuki, H.; Takaya, Y.; Takemori, T.; Tanaka, M. *J. Am. Chem. Soc.* **1994**, *116*, 10779.

S0276-7333(96)00246-4 CCC: $12.00

Treatment of **1** with excess butadiene (1 atm) in tetrahydrofuran at room temperature for 12 h led to the formation of a trinuclear 1-methyl-1,3-dimetalloallyl complex $[(C_5Me_5)Ru]_3(H)_4[\mu_3\text{-}\eta^3\text{-}C(Me)CHCH]$ (**4**), which was isolated in 70% yields as dark green crystalline solids.[4] The reaction of **1** with isoprene proceeded in a similar manner at ambient temperature to form a corresponding μ-dimetalloallyl complex **5** (eq 1).



(1)

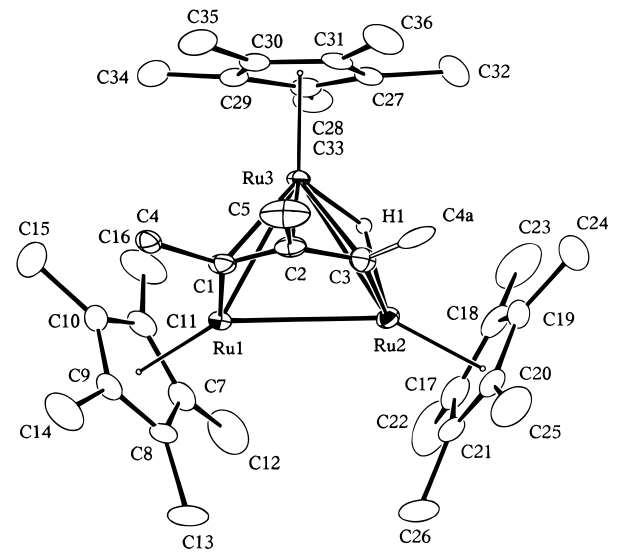


Figure 1. Molecular structure of $[(C_5Me_5)Ru]_3[\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(Me)C(Me)CH](H)_4$ (**5**). The thermal ellipsoids correspond to 30% probability. C4a shows the disorder in the crystal. Selected bond lengths (Å) and angles (deg) are as follows: Ru1−Ru2 2.883(1), Ru1−Ru3 2.8455(9), Ru2−Ru3 2.8528(9), Ru1−C1 2.039(6), Ru2−C3 2.027(6), Ru3−C1 2.261(6), Ru3−C2 2.244(5), Ru3−C3 2.214(6), Ru2−H1 1.73, Ru3−H1 1.73, C1−C2 1.427(9), C1−C4 1.51(1), C2−C3 1.391(9), C2−C5 1.526(9), C3−C4a 1.35(2); Ru2−Ru1−Ru3 59.73(2), Ru1−Ru2−Ru3 59.48(3), Ru1−Ru3−Ru2 60.79(2), Ru1−C1−Ru3 82.7(2), Ru2−C3−Ru3 84.4(2), Ru1−C1−C4 122.6(5), Ru1−C1−C2 126.1(4), C2−C1−C4 111.1(6), C1−C2−C3 117.9(5), C1−C2−C5 121.7(6), C3−C2−C5 120.4(6), Ru2−C3−C2 128.4(4), Ru2−C3−C4a 124.3(9), C2−C3−C4a 106.6(10), Ru3−C1−C4 124.5(5), Ru3−C2−C5 127.0(4), Ru3−C3−C4a 124.3(9).

The products were characterized on the basis of ^1H and ^{13}C NMR spectral data. The ^{13}C resonances for the terminal carbons of the allylic moiety bridging among the three rutheniums appeared in the range of δ 160−180 while those for the central carbons were observed in a much higher field (δ 100−115). Downfield shifts of the resonances for the terminal carbons of the allylic ligands may be regarded in terms of the contribution of a μ-carbene-like resonance hybrid. Such downfield shifts are also observed in the analgous trinuclear μ_3-1,3-dimetalloallyl complexes, $M_3(\mu_3\text{-}\eta^3\text{-}C_3)L_n$ (M = Fe, Ru, or Os).[5] The ^1H resonances for the hydrides in **5** appeared at δ −18.32 (2H) and −13.33 (2H) as two broad singlets at 298 K due to the fluxional averaging, while they were observed as inequivalent broad singlets at δ −18.95, −17.88, −16.06, and −11.67 at 233 K. We tentatively assigned them to four inequivalent bridging hydrides as the IR spectrum did not exhibit any band assignable to the terminal hydride in the 2100−1900 cm^{-1} range. The molecular structure of **5** was definitely proven by X-ray crystallography[6] and is illustrated in Figure 1. The allyl skeleton is disordered between two orientations (64:36).

Monitoring the reaction of **1** with 1 equiv of isoprene in benzene-d_6 at room temperature by ^1H and ^{13}C NMR spectrometry showed the formation of an intermediary trinuclear μ-η^2:η^2-*s-cis*-isoprene complex **6** which involved agostic interaction among terminal carbon and hydrogen atoms and one of the ruthenium atoms. After 10 h, the yield of **6** reached its maximum value (65%), and the reaction was completed after standing for 1 week at room temperature to generate the dimetalloallyl complex **5**. Although **6** could not be isolated, it was definitely characterized on the basis of the ^1H and ^{13}C NMR, $^1H-^1H$ COSY, and $^1H-^{13}C$ HSC spectra. The ^1H NMR spectrum displayed a singlet at δ 1.18 (3H) and five multiplet resonances at δ −9.33 (1H), 0.59 (1H), 1.26 (1H), 1.54 (1H), and 3.91 (1H) assignable to the methyl group, four methylene protons, and a methine proton, respectively, of the coordinated isoprene. The ^{13}C resonances for the isoprene in **6** have undergone

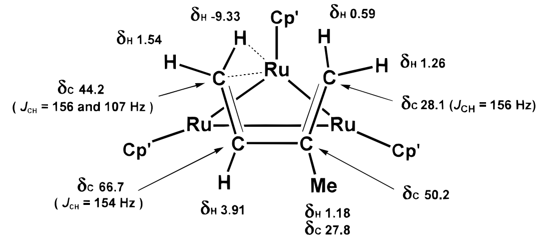
---

(4) Experimental details for **4**: A 50-mL Schlenk tube was charged with 0.400 g (0.56 mmol) of **1** and 20 mL of toluene. The Schlenk tube was evacuated after the solvent was frozen by using liquid nitrogen. Then the solution was warmed to room temperature, and a rubber balloon filled with 1 atm of butadiene was connected to the Schlenk tube. The mixture was stirred at room temperature for 14 h. Removal of the solvent under reduced pressure followed by purification by column chromatography on alumina with toluene/THF (20/1) afforded 0.300 g (70%) of **4** as a dark-green crystalline solid. Recrystallization from pentane gave dark-green prisms.

(5) (a) Evans, M.; Hursthouse, M.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Chem. Commun.* **1972**, 545. (b) Bruce, M. I.; Cairns, M. A.; Green, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1293. (c) Gambino, O.; Valle, M.; Aime, S.; Vaglio, G. A. *Inorg. Chim. Acta* **1974**, *8*, 71. (d) Nuel, D.; Mathieu, R. *Organometallics* **1988**, *7*, 16. (e) Beanan, L. R.; Rahman, Z. A.; Keister, J. B. *Organometallics* **1983**, *2*, 1062. (f) Aime, S.; Jannon, G.; Osella, D.; Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1987. (g) Dalton, D. M.; Keister, J. B. *J. Organomet. Chem.* **1985**, *290*, C37. (h) Beanan, L. A.; Keister, J. B. *Organometallics* **1985**, *4*, 1713. (i) Keister, J. B. *Polyhedron* **1988**, *7*, 847. (j) Ziller, J. W.; Bower, D. K.; Dalton, D. M.; Keister, J. B.; Churchill, M. R. *Organometallics* **1989**, *8*, 492. (k) Churchill, M. R.; Buttrey, L. A.; Keister, J. B.; Ziller, J. W.; Janik, T. S.; Striejewske, W. S. *Organometallics* **1990**, *9*, 766. (l) Clauss, A. D.; Shapley, J. R.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 7387. (m) Yeh, W.-Y.; Chen, S.-L.; Peng, S.-M.; Lee, G.-H. *J. Organomet. Chem.* **1993**, *461*, 207.

(6) Complex_**5** crystallized from pentane in the monoclinic system, space group $P\bar{1}$ (No. 2), with $a = 11.101(4)$ Å, $b = 17.564(7)$ Å, $c = 8.583(2)$ Å, $\alpha = 94.88(3)°$, $\beta = 90.76(3)°$, $\gamma = 89.45(4)°$, $V = 1667(1)$ Å^3, $Z = 2$, and $D_{calc} = 1.554$ g cm^{-3}. Intensity data were collected on a Rigaku AFC-5R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) in the $5° < 2\theta < 50°$ range. The data were processed using the TEXSAN crystal structure analysis package operated on an IRIS Indigo computer. Neutral atom scattering factors were obtained from the standard sources.[8] 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 direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The position of only one hydrogen atom (H1) bonded to the Ru atoms was located by sequential difference Fourier synthesis but was not refined. The final cycle of full-matrix least-squares refinement was based on 4354 observed reflections ($I > 3.00\sigma(I)$) and 390 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.040$ and $R_w = 0.044$.

Chart 1[a]



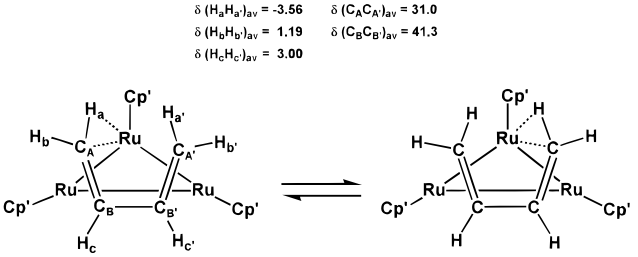
[a] Bridging hydrides are neglected for clarity.

substantial upfield shifts as a result of coordination. The assignment of these resonances is shown in Chart 1.

Notable features of the NMR spectra are the resonances appearing at δ 44.2 (J_{CH} = 156 and 107 Hz) in the ^{13}C NMR spectrum and that observed at δ −9.33 in the ^{1}H NMR spectrum. The C(sp^2)−H coupling constant of 107 Hz lie within the range of those of structurally well-established agostic complexes.[7] The small C(sp^2)−H coupling constant and the upfield shift of the resonance for the terminal methylene proton to the hydride region unambiguously indicates the presence of a three-center two-electron Ru−H−C interaction.

In the reaction of **1** with butadiene, an intermediary agostic complex **7** was similarly detected by means of NMR spectroscopy. The reaction of **1** with 1.5 equiv of butadiene in toluene-d_8 for 5 min at 243 K brought the complete consumption of **1** to give the 95/5 mixture of **7** and **4**. The ^{1}H resonances attributable to the intermediate **7** consisted of three multiplets at δ −3.55 (2H), 1.19 (2H), and 3.00 (2H) for the coordinated butadiene besides two singlets for the C_5Me_5 groups and two hydride signals at δ 1.72 (30H), 1.79 (15H), −21.79 (2H), and −16.44 (2H), respectively. The ^{13}C NMR spectrum for the mixture exhibited two resonances for the butadiene coordinated in **7** at δ 31.0 (dd, J_{CH} = 154.7 and 131.9 Hz) and 49.3 (d, J_{CH} = 151.1 Hz). The assignment of these resonances is shown in Chart 2.

Chart 2[a]



7

[a] Bridging hydrides are neglected for clarity.

The resonance for methylene proton of the butadiene ligand in **7** (δ −3.55) shifts downfield compared to that in the isoprene analogue **6** (δ −9.33), and the δ value of −3.55 ppm is close to the average value of the shifts for the methylene protons, δ −9.33 and 0.59 in **6**. In addition, the J_{CH} value of 131.9 Hz is very close to the averaged value of those for the agostic C(sp^2)−H (J = 107.0 Hz) and nonagostic C(sp^2)−H (J = 156.0 Hz) bonds observed for **6**. These findings strongly indicate that complex **7** is a fluxional agostic complex. The dynamic process was so rapid that the ^{1}H NMR spectrum measured at 190 K was essentially the same as that measured at 243 K.

The intermediates **6** and **7** undergo activation of the agostic C−H bond to ultimately form the dimetalloallyl complexes **5** and **4**, respectively. These results evidently show that two of three ruthenium centers in **1** act as coordination sites and the third metal takes the role of an activation site via the agostic interaction in the reaction with 1,3-diene. This is a typical example showing the activation process performed by the concerted action of three metal centers.

Acknowledgment. This research was financially supported by a grant from the Asahi Glass Foundation and a Grant for Scientific Research on Priority Areas (Nos. 05236104 and 07242227) from the Ministry of Education, Science, and Culture. The authors are grateful to Kanto Chemical Co., Inc., for the generous supply of pentamethylcyclopentadiene.

Supporting Information Available: A table of ^{1}H and ^{13}C NMR spectral assignments of **4**−**7** and an ORTEP diagram, text describing X-ray procedures, and tables of X-ray data, positional and thermal parameters, and distances and angles for **5** (46 pages). Ordering information is given on any current masthead page.

OM9602466

---

(7) (a) Erker, G.; Frömberg, W.; Angermund, K.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1629. (b) Kryspin, I.-H.; Gleiter, R.; Krüger, C.; Zwettler, R.; Erker, G. *Organometallics* **1990**, *9*, 517. (c) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466. (d) He, Z.; Plasseraud, L.; Moldes, I.; Dahan, F.; Neibecker, D.; Etienne, M.; Mathieu, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 916. (e) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(8) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1975; Vol. 4.