ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 617–618 (2001) 254–260

Journal of Organo metallic Chemistry

Photochemical C–H bond activation of diruthenium bridging alkylidene complexes: Interligand H-exchange on $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CHR)(CO)_2$ (R = H, Me)

Munetaka Akita *, Hideki Musashi, Sadahiro Nakanishi, Yoshihiko Moro-oka

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received 2 June 2000

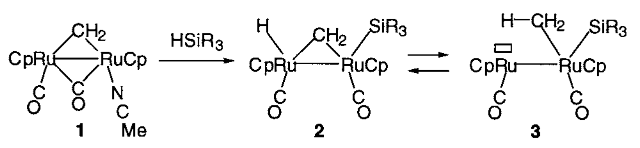
Abstract

Irradiation of a double labeled diruthenium di-μ-methylene complex, $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}{}^*CD_2)(CO)_2$ (**5**-$^{13}C,d_2$) (*C: ^{13}C-enriched), caused H–D exchange between the two bridging methylene ligands to give an isomeric mixture of $Cp_2Ru_2(\mu\text{-}CHD)(\mu\text{-}{}^*CDH)(CO)_2$ and $Cp_2Ru_2(\mu\text{-}CD_2)(\mu\text{-}{}^*CH_2)(CO)_2$. In contrast to the photochemical hydrogen migration of **5**-$^{13}C,d_2$, irradiation of a deuterated μ-methylene-μ-ethylidene complex, $Cp_2Ru_2(\mu\text{-}CD_2)(\mu\text{-}CHCH_3)(CO)_2$ (**7**-d_2), resulted in interligand exchange between β-hydrogen atoms of the ethylidene ligand and methylene hydrogen atoms to afford a mixture of $Cp_2Ru_2(\mu\text{-}CHD)(\mu\text{-}CHCH_2D)(CO)_2$ and $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CHCHD_2)(CO)_2$. These exchange reactions can be interpreted in terms of μ-methylidyne, $CpRu(CO)(\mu\text{-}CH)(\mu\text{-}CH_2)Ru(H)Cp$, and μ-alkenyl intermediates, $CpRu(CO)(\mu\text{-}CH)(\mu\text{-}CH{=}CH_2)Ru(H)Cp$, respectively. These species may be formed photochemical decarbonylation followed by migration of α- and β-hydrogen atoms of the bridging ligands to the coordinatively unsaturated ruthenium center. Subsequent CH_2–H reductive elimination and free rotation of the resulting Ru–CH_3 bond would cause the interligand H-exchange. Similar processes may be viable on a heterogeneous catalyst surface. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photochemical C–H bond activation; Diruthenium bridging alkylidene complexes; Interligand H-exchange

1. Introduction

Bridging alkylidene complexes are versatile probes for investigation of structure and properties of surface-bound methylene species [1]. They could reproduce various aspects of functions of catalytic CO hydrogenation and hydrocarbon transformations [2]. In particular, previous studies on bridging alkylidene complexes provided us with information on key elementary steps of the catalytic reactions such as interconversion with related hydrocarbyl species and C–C bond formation. We reported intriguing interplay between diruthenium bridging methylene species and hydrosilanes [3]. For example, treatment of the labile diruthenium-μ-methylene complex **1** with hydrosilane affords the hydrido-silyl-μ-methylene complex **2** (Scheme 1) [3f,k,m]. A labeling experiment using deuterosilane reveals that the hydrido hydrogen atom and the methylene hydrogen atom exchange via a methyl intermediate **3**. Since complex **1** is obtained via a reaction sequence involving deoxygenative reduction of the carbonyl complex $Cp_2Ru_2(CO)_4$ (**4**), the whole reaction sequence 'CO (**4**) → CH_2 (**1**) → CH_2–H (**2**) → CH_3 (**3**) → → CH_4' corresponding to a mechanism proposed for methanation has been successfully reproduced on a diruthenium system by using hydrosilanes as a H_2-equivalent.



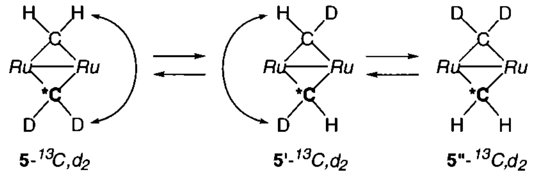
Scheme 1.

During the course of our study we found that irradiation of the diruthenium-di-μ-methylene complex **5** in the presence of norbornadiene caused insertion of the

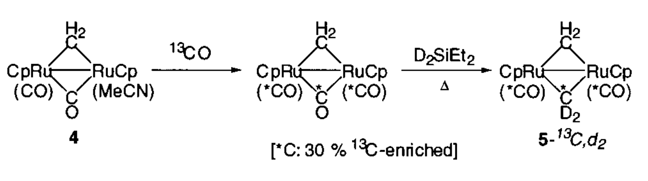
---

* Corresponding author. Tel./fax: + 81-45-9245230.
E-mail address: makita@res.titech.ac.jp (M. Akita).

PII: S0022-328X(00)00538-6



Scheme 2.



Scheme 3.

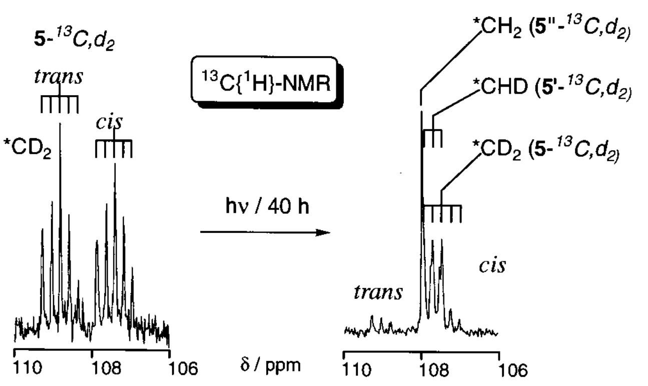
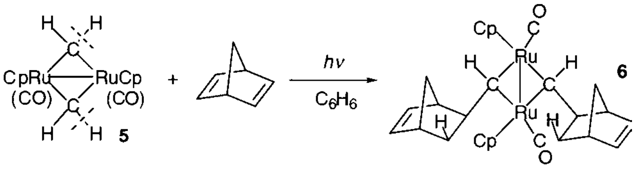


Fig. 1. Change of ^{1}H-decoupled ^{13}C-NMR spectra of 5-$^{13}C,d_2$ (μ-CH_2 region; observed at 100 MHz in C_6D_6) induced by irradiation.

C=C bond into C–H bonds in the bridging methylene group (Eq. (1)) [3p].



(1)

The formation of the product **6** suggests that C–H bond activation may take place even in the absence of norbornadiene. Herein we disclose detailed results of labeling experiments, which were carried out to examine the possibility of C–H activation on the bridging alkylidene ligands.[1]

2. Results and discussion

2.1. Photochemical H-exchange on the diruthenium-di-μ-methylene complex 5

In order to examine H-exchange between the two bridging methylene groups a double labeling experiment using $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}{*CD_2})({*CO})_2$ (**5**-$^{13}C,d_2$) (*C: ^{13}C-enriched) was carried out. If the expected process occurs, the exchange may be readily detected by the change of the coupling pattern of the ^{13}C-NMR signal for the *C atom (Scheme 2).

The desired isotopomer of **5**-$^{13}C,d_2$ was prepared in a specific manner according to Scheme 3, which involved deoxygenative CO-reduction developed by our group [3j]. Treatment of the labile MeCN derivative **4** [5] with ^{13}CO resulted in not only replacement of the MeCN ligand but also subsequent intramolecular scrambling of the carbonyl ligands. Thermolysis of the resultant mono-μ-methylene complex, $Cp_2Ru_2(\mu\text{-}CH_2)({*CO})_3$, in the presence of D_2SiEt_2 afforded a ^{13}C,D-double labeled sample **5**-$^{13}C,d_2$, in which the *CD_2 part was > 95% D- and ca. 30% ^{13}C-enriched as revealed by ^{1}H- and ^{13}C-NMR analyses (see also Fig. 1).

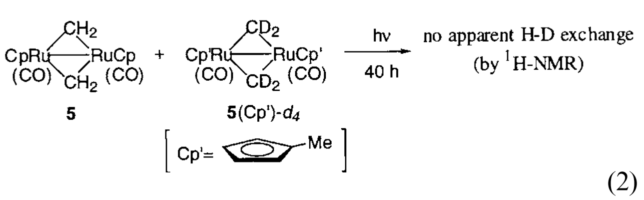
A C_6D_6 solution of **5**-$^{13}C,d_2$ sealed in an NMR tube was irradiated by a high-pressure mercury lamp and the change was monitored by ^{13}C-NMR. Spectra before and after irradiation for 40 h are compared in Fig. 1. Synthesis of the di-μ-methylene complex **5** following Scheme 3 gave an almost equimolar mixture of the *trans*- and *cis*-isomers originating from the different arrangements of the two Cp rings with respect to the central $Ru_2(\mu\text{-}CH_2)_2$ square, as we reported previously [3j]. Thus in the initial spectrum (Fig. 1(a)) the two methylene carbon signals corresponding to each isomer were observed as two quintets due to coupling with two deuterium nuclei with $I = 1$ attached to the bridging methylene carbon atom. The most apparent change induced by the irradiation was *trans*-to-*cis* isomerization, which has been observed for related $Cp_2M_2(\mu\text{-}X)(\mu\text{-}Y)(L)_n$-type dinuclear complex (X, Y = CO, CR_2, SiR_2, etc.) [6]. The isomerization attained an equilibrium after irradiation for 30 min. The most significant change induced by the irradiation was the coupling pattern of the *cis*-isomer. As irradiation of the sample was continued, the triplet and singlet signals appeared successively in slightly lower field with consumption of the quintet CD_2 signal. The triplet and singlet signals were assigned to the *CDH moiety in **5**′-$^{13}C,d_2$ and the *CH_2 moiety in **5**″-$^{13}C,d_2$, respectively. These spectral changes revealed that isotropic *CHD and *CH_2 groups were generated by irradiation of **5**-$^{13}C,d_2$ containing $^{12}CH_2$ and *CD_2 groups and suggested that the methylene hydrogen atoms exchanged between the two methylene groups. The isomerization processes could be also followed by ^{1}H-NMR. Appearance of new peaks

---

[1] A part of the results was already reported as a preliminary communication [3p].

assignable to **5**′-$^{13}C,d_2$ and **5**″-$^{13}C,d_2$ and changes of peak shapes could be observed. But it was difficult to get definite conclusion, because peak separations were not always sufficient and the incomplete ^{13}C-enrichment (ca. 30%) caused complicated peak appearance of some of the signals. For example, one of the methylene hydrogen atom of the starting complex **5**-$^{13}C,d_2$ ($\delta \sim 7.4$) was observed as an apparent triplet due to overlap of a doublet signal [$^3J_{CH}$ due to the ^{13}C nucleus in the opposite $^{13}CD_2$ ligand (ca. 30%)] and a singlet signal [no coupling with the opposite $^{12}CD_2$ ligand (ca. 70%)].

In order to discriminate intra- and intermolecular mechanisms another labeling experiment was carried out (Eq. (2)).



(2)

When a C_6D_6 solution of a mixture of **5** and **5**(Cp′)-d_4 bearing η^5-C_5H_4Me ligands and CD_2 bridges was irradiated for 40 h, no apparent ^{1}H-NMR spectral change except the *trans*-to-*cis* isomerization was noted establishing an intramolecular mechanism for the present H-exchange reaction. This experiment also confirmed that H–D exchange process was localized on the $Ru_2(\mu\text{-}CH_2)_2$ moiety in **5**.

The results described above reveal that irradiation of **5** induces intramolecular H-exchange between the two methylene bridges. The exchange did not occur under thermal conditions (150°C).

2.2. Photochemical H-exchange on the diruthenium-μ-methylene-μ-ethylidene complex 7

Possibility of occurrence of an analogous process on a related compound was examined using the μ-methylene-μ-ethylidene complex **7**, $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CHCH_3)(CO)_2$. A deuterated sample, $Cp_2Ru_2(\mu\text{-}CD_2)(\mu\text{-}CHCH_3)(CO)_2$ (**7**-d_2), was also prepared by deoxygenative reduction of the μ-ethylidene complex, $Cp_2Ru_2(\mu\text{-}CHCH_3)(\mu\text{-}CO)(CO)_2$, with D_2SiEt_2 as described in our previous paper [3j]. Irradiation of **7**-d_2 also caused a change of the ^{1}H-NMR pattern of the bridging alkylidene signals.

Fig. 2(a) shows a ^{1}H-NMR spectrum of **7**-d_2 before irradiation. Although three stereoisomers, *trans*-**7**, *cis*-

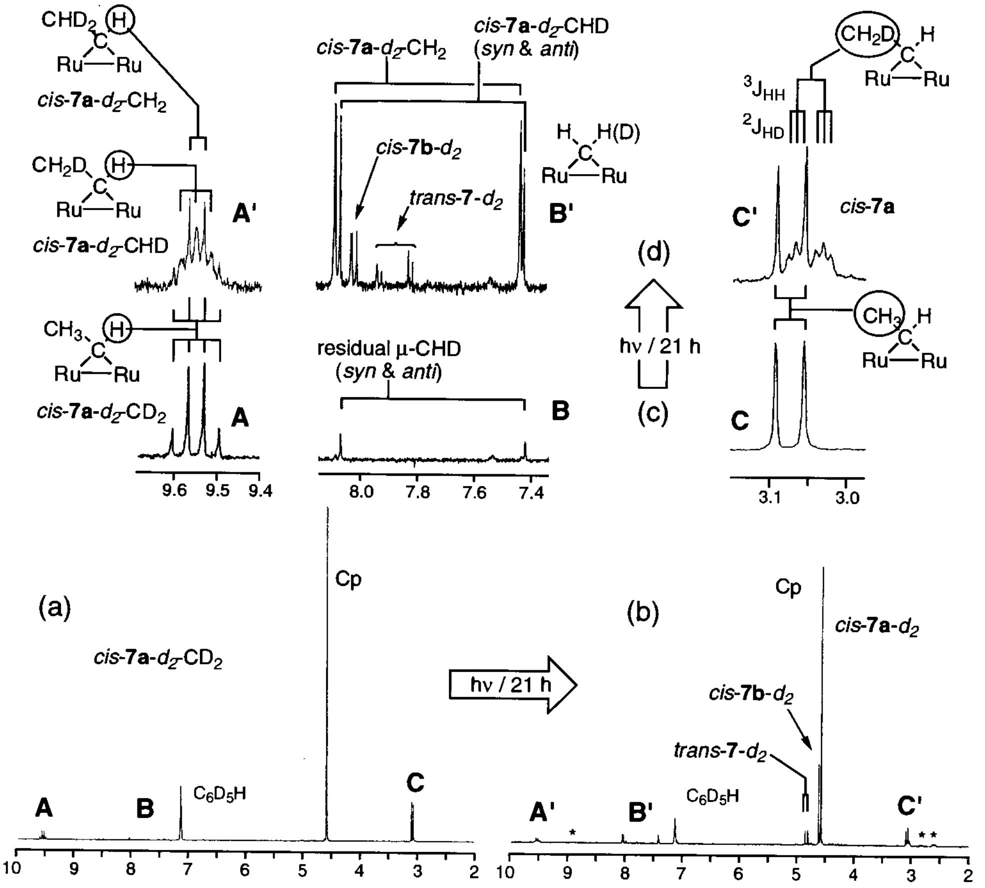


Fig. 2. Change of ^{1}H-NMR spectra of **7**-d_2 (observed at 200 MHz in C_6D_6) induced by irradiation. Full spectra before (a) and after irradiation for 21 h (b) and their expanded views (c) and (d). Peaks indicated by asterisks in (b) are due to *cis*-**7b** and *trans*-**7** isomers.

7a and *cis*-**7b**, are possible for **7** (Chart 1), only one isomer is present in the solution as is also evident from the expanded charts (Fig. 2(c)).

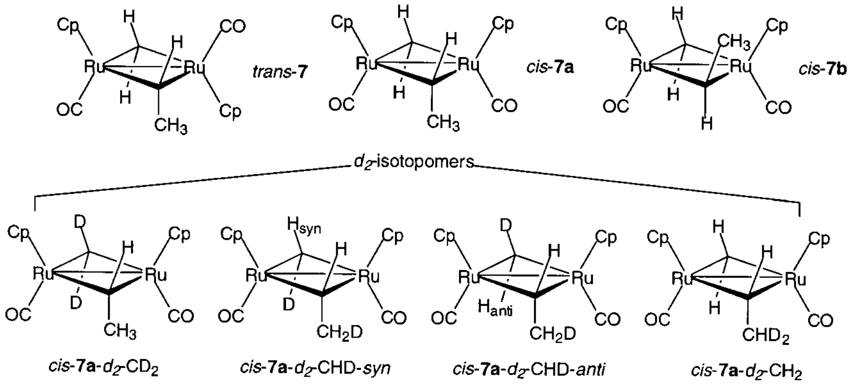


Chart 1.

Because the two Cp rings are equivalent, *trans*-**7** can be eliminated. Of the two *cis*-isomers **7a**,**b**, the species in the solution was assigned to *cis*-**7a** taking into account steric repulsion between the Cp rings and the methyl group in the ethylidene bridge. In the starting complex *cis*-**7a**, no deuterium atom was incorporated into the ethylidene group, which appeared as the quartet (δ 9.56, CH) and doublet signals (δ 3.08, CH_3), as can be seen from Fig. 2(c). On the basis of the residual CHD signals at δ 7.45 and 8.07, the extent of deuteration of the bridging methylene hydrogen atoms was estimated to be about 95%.

Fig. 2(b) shows a ^{1}H-NMR spectrum recorded after irradiation for 21 h and Fig. 2(d) is its expanded views. The most remarkable change is an increase of intensity of the μ-CH_2 signals in the range of δ 7.4–8.1 indicating replacements of the μ-CD_2-deuterium atoms with hydrogen atoms. In this case, too, photochemical isomerization led to the formation of a mixture of the three possible isomers *cis*-**7a**,**b** and *trans*-**7** (75:16:9) which were assigned by comparison with authentic samples as shown in Fig. 2(d). In every case, signals for D-containing ligands appear in slightly higher field and their shapes become complicated due to overlap and coupling with D. In addition, because all peaks could be assigned to isomers shown in Chart 1, it was concluded that photochemical deterioration was negligible. In Fig. 3 the intensities of the μ-CH (δ ~ 9.56), μ-CH_2 (δ 7.4–8.1), and CH_3 signals (δ ~ 3.08) were plotted against the irradiation time in order to check distribution of deuterium atoms. The intensities of the signals were calculated with respect to the deuterated solvent residue (C_6D_5H). During the irradiation over 24 h the intensity of the CH_3 signal monotonically decreased, whereas that of the μ-CH_2 signals increased. Because sum of the intensities of the CH_3 and μ-CH_2 signals did not change significantly, the μ-CH_2 signal increased with the consumption of the CH_3 signal suggesting H-exchange. As for the μ-CH signal, its intensity did not change for initial 12 h within the range of experimental errors indicating that the μ-CH moiety did not take part in the present H–D exchange at an early stage of the reaction. Prolonged irradiation ($>$ 21 h), however, caused a slight decrease of the intensity of the μ-CH signal (~ 0.88 H) suggesting occurrence of slow H-exchange analogous to the exchange observed for 5.

From these ^{1}H-NMR changes it was concluded that irradiation of **7** caused H-exchange between methylene hydrogen atoms of the μ-CH_2 group and methyl hydrogen atoms (β-hydrogen atoms) of the other bridging μ-$CHCH_3$ group. This exchange reaction also did not proceed under thermal conditions. It is notable that exchange with the β-hydrogen atoms of the ethylidene group takes place in preference to that with the α-hydrogen atom, presumably because β-hydride elimination is more facile than α-hydride elimination as usually observed for mononuclear alkyl complexes [4].

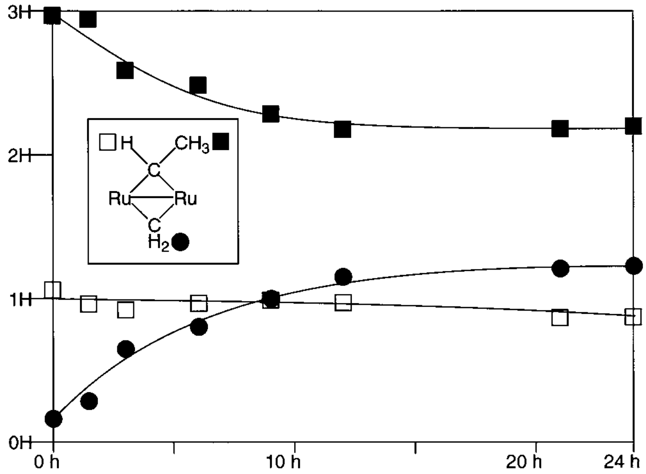


Fig. 3. Plots of intensities of ^{1}H-NMR signals for the bridging alkylidene ligands in **7**-d_2 against irradiation time (observed at 200 MHz in C_6D_6).

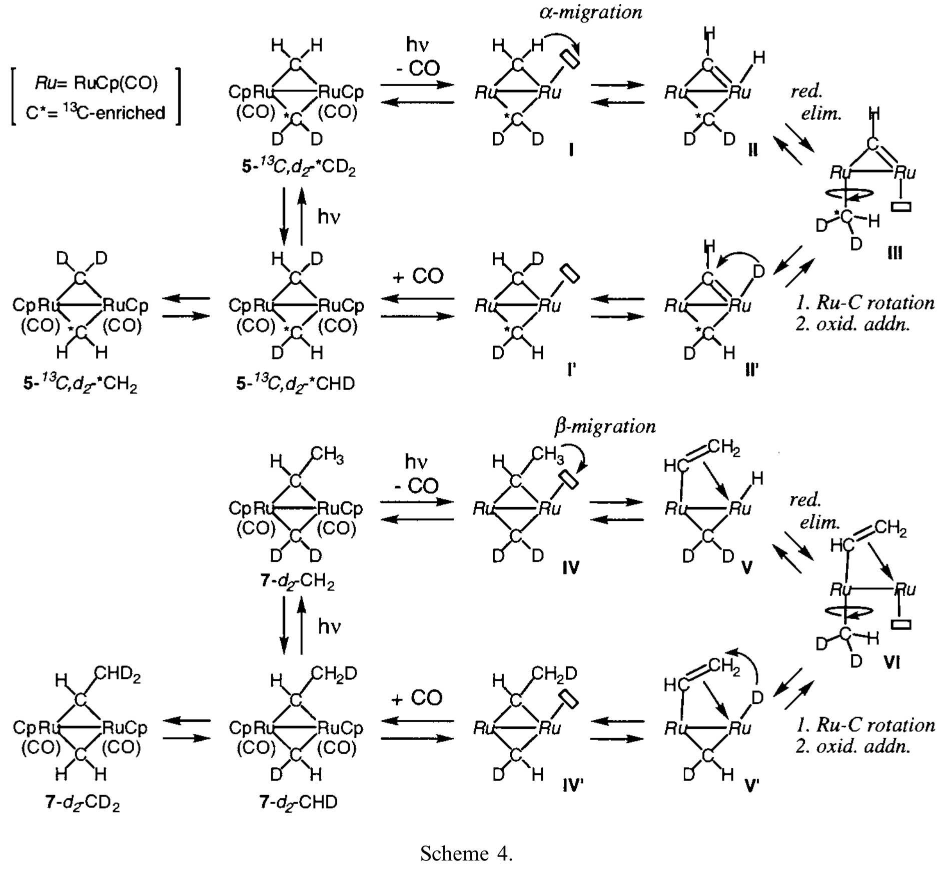
2.3. H–D exchange mechanisms

The observations presented in this paper can be explained in terms of mechanisms summarized in Scheme 4. In both systems the H–D exchange reactions should be initiated by photochemical decarbonylation. In the presence of a coordinating substrate, the resulting coordinatively unsaturated species **I** could be trapped. As we reported previously, photolysis of a MeCN solution of **5** gave the adduct $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$ via **I** [3m]. But in the absence of such a donor a methylene hydrogen atom may migrate to the coordinatively unsaturated site (α-hydride migration) to form the coordinatively saturated hydrido-μ-methylidyne species **II** [7], which is supported by the structure of the photolysis product in the presence of norbornadiene (Eq. (1)). Because the resultant species contains the $Ru(\mu\text{-}CH_2)Ru\text{–}H$ moiety similar to that in **2** (Scheme 3), C–H reductive elimination would give the coordinatively unsaturated methyl species **III** [8]. Free rotation of the CH_3–Ru bond followed by C–H oxidative addition results in H–D scrambling. Subsequent reversed H-migration and carbonylation would furnish **5**-$^{13}C,d_2$-*CHD and further reaction would lead to **5**-$^{13}C,d_2$-*CH_2. Thus the H–D exchange on **5** can be explained on the basis of the equilibrium between the hydrido-μ-methylidyne species (**II**, **II′**) and the methyl species (**III**). Coupling reaction with norbornadiene (Eq. (1)) may also be explained in terms of the methylidyne intermediate **II**. The methylidyne carbon atom may be electrophilic enough to react with a strained olefinic substrate [7], although further study is needed to clarify the coupling reaction mechanism.

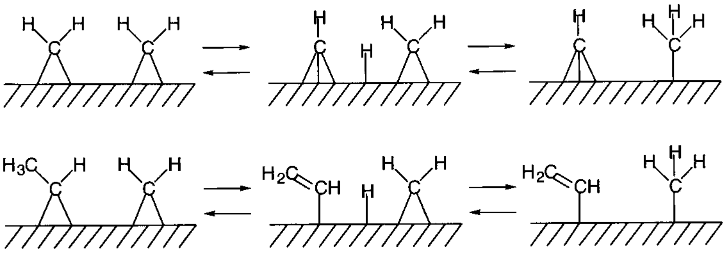
A reaction scheme analogous to the above-discussed mechanisms can be depicted for the μ-ethylidene-μ-methylene complex **7**. In this case, however, the coordinatively unsaturated species **IV** resulting from photochemical decarbonylation undergoes β-hydride migration rather than α-hydride migration to give the μ-alkenyl-hydride intermediate **V**. H–D scrambling should occur also at the stage of the coordinatively unsaturated methyl species **VI** formed by C–H reductive elimination of **V**. For the di-μ-methylene complex **5** it required more than 24 h to attain an equilibrium, whereas the H-exchange between the μ-$CHCH_3$ and μ-CH_2 moieties in **7** reached an equilibrium within 12 h. In addition, the exchange process involving the α-hydrogen atom (μ-$CHCH_3$) in **7** also occurred but the exchange rate was much slower than that of β-hydrogen atom, as mentioned above.

3. Conclusion

The present study reveals interconversion of C_1 and C_2 species on a diruthenium system. Hydride migration



Scheme 4.



Scheme 5.

form bridging methylene (α-migration) and ethylidene ligands (β-migration) forms the methylidyne and vinyl species, respectively, together with hydride intermediate, which couples with the remaining methylene moiety to give a methyl group. H–D exchange proceeds repeating these reversible H-migrations.

Analogous H-migration has been reported for cluster systems [8] and may be possible on a heterogeneous catalyst surface (Scheme 5), i.e. (i) interconversion of CH_x species via H-migration, i.e. hydrogenation of methylidyne species to methylene and methyl species, and (ii) formation of a vinyl species, which was recently proposed as an effective initiator in the chain propagation step of catalytic CO hydrogenation [9].

4. Experimental

4.1. General methods

All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques. CH_2Cl_2 was dried over P_4O_{10}, distilled, and stored under argon. ^1H- and ^{13}C-NMR were recorded on Bruker AC-200 (^1H: 200 MHz) and JEOL EX-400 spectrometers (^{13}C: 100 MHz), respectively. Complexes **4** and **7**-d_2 were prepared according to the established methods [3j]. Benzene-d_6 for NMR measurements were dried over molecular sieves, distilled under reduced pressure and kept under argon atmosphere. D_2SiEt_2 was prepared by reduction of Cl_2SiEt_2 by $LiAlD_4$ in dibutyl ether or diglyme.

4.2. Preparation of **5**-$^{13}C,d_2$

$Cp_2Ru_2(\mu\text{-}CH_2)(^*CO)_3$ was prepared by treatment of a CH_2Cl_2 solution of **4** with ^{13}CO (> 95% ^{13}C-enriched; 2 atm) in a glass autoclave. Subsequent deoxygenative reduction with D_2SiEt_2 following Ref. [3j] gave **5**-$^{13}C,d_2$. ^{13}C-NMR data for the μ-CH_2 moieties in **5**-$^{13}C,d_2$ (in C_6D_6): 107.7 ($J_{C-D}=22$ Hz: *cis*-isomer), 109.0 ($J_{C-D}=$ 22 Hz: *trans*-isomer).

4.3. Photochemical reaction of **5**-$^{13}C,d_2$ and **7**-d_2

Complex **5**-$^{13}C,d_2$ or **7**-d_2 (ca. 20 mg) was weighed in an NMR tube, which was evacuated and filled with argon. C_6D_6 (ca. 0.4 ml) was added to the tube, which was sealed by a torch. The C_6D_6 solution was then irradiated by a high-pressure mercury lamp (Ushio UM-452) and the reaction was monitored by ^1H- or ^{13}C-NMR.

^1H-NMR data for **7** (in C_6D_6) *cis*-**7a**: 9.56 (1H, q, $J=7.0$ Hz, μ-CHCH$_3$), 8.07, 7.45 (1H × 2, s × 2, μ-CH_2), 4.58 (10H, s, Cp × 2), 3.08 (3H, d, $J=7.0$ Hz, μ-CHCH_3); *cis*-**7b**: 9.50 (1H, q, $J=7.6$ Hz, μ-CHCH$_3$), 8.02 (1H, s, μ-CH_2; the other H-atom overlaps with the C_6D_5H signal, 4.61 (10H, s, Cp × 2), 2.61 (3H, d, $J=7.6$ Hz, μ-CHCH_3); *trans*-7: 9.51 (1H, q, $J=7.2$ Hz, μ-CHCH$_3$), 7.94, 7.83 (1H × 2, s × 2, μ-CH_2), 4.86, 4.82 (5H × 2, s × 2, Cp × 2), 2.85 (3H, d, $J=7.2$ Hz, μ-CHCH_3).

4.4. Labeling experiment (Eq. (2))

Each 0.025 mmol amount of **5** and **5**(Cp′)-d_4 was weighed in an NMR tube. After Ar-replacement C_6D_6 (0.5 ml) was added and sealed by a torch. Irradiation with a high pressure Hg lamp caused *trans*-to-*cis* isomerization but no increase of the intensity of the residual μ-CHD signals was observed at all after irradiation for 40 h.

Acknowledgements

We are grateful to the Ministry of Education, Science, Sports and Culture of the Japanese Government for financial support of this research.

References

[1] (a) W.A. Herrmann, Adv. Organomet. Chem. 20 (1982) 159. (b) W.A. Herrmann, J. Organomet. Chem. 250 (1983) 319. (c) I.M. Saez, D.G. Andrews, P.M. Maitlis, Polyhedron 7 (1988) 827. (d) R.J. Puddephatt, Polyhedron 7 (1988) 767. (e) S.A.R. Knox, J. Organomet. Chem. 250 (1990) 255. (f) M.J. Hostetler, M.D. Butts, R.B. Bergman, J. Am. Chem. Soc. 115 (1993) 2743. (g) M.D. Butts, R.B. Bergman, Organometallics 13 (1994) 2668.

[2] (a) J. Falbe, New Synthesis with Carbon Monoxide, Springer, Berlin, 1980. (b) H. Pines, The Chemistry of Catalytic Hydrocarbon Conversions, Academic Press, London, 1981. (c) W. Keim, Catalysis in C_1 Chemistry, D. Reidel, Dordrecht, 1983. (d) R.B. Anderson, The Fischer–Tropsch Synthesis, Academic Press, London, 1984. (e) G.A. Somorjai, Introduction to Surface Chemistry and Catalysis, John Wiley & Sons, New York, 1994.

[3] (a) M. Akita, O. Mitani, Y. Moro-oka, J. Chem. Soc. Chem. Commun. (1989) 527. (b) M. Akita, T. Oku, Y. Moro-oka, J. Chem. Soc. Chem. Commun. (1990) 1790. (c) M. Akita, O. Mitani, M. Sayama, Y. Moro-oka, Organometallics 10 (1991) 1394. (d) M. Akita, T. Oku, M. Tanaka, Y.Moro-oka, Organometallics 10 (1991) 3080. (e) M. Akita, T. Oku, Y. Moro-oka, J. Chem. Soc. Chem. Commun. (1992) 1031. (f) M. Akita, T. Oku, R. Hua, Y. Moro-oka, J. Chem. Soc. Chem. Commun. (1993) 1670. (g) M. Akita, K. Noda, Y. Moro-oka, Organometallics 13 (1994) 4145. (h) M. Akita, Y. Moro-oka, Stud. Surf. Sci. Catal. 92 (1995) 137. (i) M. Akita, K. Noda, Y. Takahashi, Y. Moro-oka, Organometallics 14 (1995) 5209. (j) M. Akita, T. Oku, R. Hua, Y. Moro-oka, Organometallics 15 (1996) 2548. (k) M. Akita, T. Oku, R. Hua, M. Tanaka, Y. Moro-oka, Organometallics 15 (1996) 4162. (l) R. Hua, M. Akita, Y. Moro-oka, Inorg. Chim. Acta 250 (1996) 177. (m) M. Akita, R. Hua, S. Nakanishi, M. Tanaka, Y. Moro-oka, Organometallics 16 (1997) 5572. (n) M. Akita, R. Hua, S.A.R. Knox, Y. Moro-oka, S. Nakanishi, M.I. Yates, J. Chem. Soc. Chem. Commun. (1997) 52. (o) M. Akita, R. Hua, S.A.R. Knox, Y. Moro-oka, S. Nakanishi, M.I. Yates, J. Organomet. Chem. 569 (1998) 71. (p) M. Akita, S. Nakanishi, H. Musashi, Y. Moro-oka, J. Chem. Soc. Chem. Commun. (1999) 145. (q) M. Akita, Applied Cat. A: General 200 (2000) 153.

[4] (a) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987. (b) A. Yamamoto, Organotransition Metal Chemistry, John Wiley & Sons, New York, 1986.

[5] N.M. Doherty, J.A.K. Howard, S.A.R. Knox, N.J. Terril, M.I. Yates, J. Chem. Soc. Chem. Commun. (1989) 638.

[6] H. Ogino, H. Tobita, Adv. Organomet. Chem. 42 (1998) 223.

[7] For dinuclear μ-methylidyne species, see for example: $[Cp_2Ru_2(\mu\text{-}CH)(CO)(dppe)]^+$: (a) D.L. Davies, B.P. Gracy, V. Guerchais, S.A.R. Knox, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1984) 841. (b) N. Connelly, N.J. Forrow, B.P. Gracey, S.A.R. Knox, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1985) 14. $[Cp_2Fe_2(\mu\text{-}CH)(CO)_3]^+$: (c) C.P. Casey, P.J. Fagan, W.H. Miles, J. Am. Chem. Soc. 104 (1982) 1134. (d) C.P. Casey, P.J. Fagan, J. Am. Chem. Soc. 104 (1982) 4950. (e) C.P. Casey, P.J. Fagan, W.H. Miles, S.R. Marder, J. Mol. Cat. 21 (1983) 173.

[8] (a) R.B. Calvert, J.R. Shapley, J. Am. Chem. Soc. 99 (1977) 5525. (b) R.B. Calvert, J.R. Shapley, J. Am. Chem. Soc. 100 (1978) 7726. (c) J.R. Shapley, D.S. Strickland, G.M. St. George, M.R. Churchill, C. Bueno, Organometallics 2 (1983) 185. (d) J.C. Vites, G. Jacobsen, T.K. Dutta, T.P. Fehlner, J. Am. Chem. Soc. 107 (1985) 5563. (e) T.K. Dutta, J.C. Vites, G. Jacobsen, T.P. Fehlner, Organometallics 6 (1987) 842.

[9] P.M. Maitlis, H.C. Long, R. Quyoum, M.L. Turner, and Z.-Q. Wang, J. Chem. Soc. Chem. Comm. (1996) 1.