ELSEVIER

Journal of Organometallic Chemistry 569 (1998) 71–83

Journal of Organometallic Chemistry

Specific C–C coupling of the labile diruthenium bridging methylene complex, $Cp_2Ru_2(\mu\text{-}CH_2)(CO)_2(MeCN)$, with diazoalkanes ($R_2C{=}N_2$) leading to alkenyl complexes, $Cp_2Ru_2(\mu\text{-}CH{=}CR_2)(\mu\text{-}H)(CO)_2$, and alkenes, $CH_2{=}CR_2$[1]

Munetaka Akita *, Ruimao Hua, Selby A.R. Knox[1], Yoshihiko Moro-oka[1], Sadahiro Nakanishi, Michael I. Yates

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

Received 14 March 1998

Abstract

Treatment of the labile μ-methylene species, $Cp_2Ru_2(\mu\text{-}CH_2)(CO)_2(MeCN)$ **1**, with diazoalkanes results in C–C coupling of the alkylidene units. The reaction of monosubstituted diazoalkanes ($N_2{=}CHR$) and 4-*t*-butyldiazocyclohexane gives the μ-alkenyl-μ-hydride complexes, $Cp_2Ru_2(\mu\text{-}CH{=}CR_2)(\mu\text{-}H)(CO)_2$ **2**, as sole products, whereas the reaction of disubstituted aryldiazoalkanes ($N_2{=}CR^1R^2$) produces olefins ($CH_2{=}CR^1R^2$) together with mixtures of unidentified organometallic compounds. Labeling experiments using **1**-d_2 (μ-CD_2) and **1**-^{13}C (μ-$^{13}CH_2$) reveal that the methylene bridge in **1** is converted to the α-CH and μ-H parts in **2** and the alkylidene part of diazoalkane is incorporated into the β-CR_2 part of the alkenyl bridge. The olefinic products should come from a η^2-olefin intermediate, $Cp_2Ru_2(\eta^2CH_2{=}CHR)(CO)_2$ **7**, resulting from coupling of the two alkylidene fragments within the coordination sphere of the diruthenium core. It is notable that C–H oxidative addition in **7** takes place prior to free rotation of the η^2-olefin ligand as judged by the regiospecificity of the labeling experiments. Thus specific coupling of alkylidene units proceeds under mild conditions and this C–C coupling reaction serves as a model system for the carbon chain propagation step of surface-catalyzed reactions such as catalytic CO hydrogenation. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: C–C coupling; Diruthenium; Alkenyl complexes

1. Introduction

During the last two decades much effort has been focused on elucidation of mechanisms of catalytic CO hydrogenation [1] using discrete transition metal complexes [2]. The key features of the proposed mechanisms can be summarized as follows: (1) dissociative adsorption of CO leading to carbide intermediates; (2) formation of CH_X species via H-transfer; (3) C–C bond formation involving the CH_X species; (4) elimination of products. Of the four elementary steps, steps 1, 2 and 4 have been successfully reproduced with model complexes but a limited number of examples have been reported for the third step.

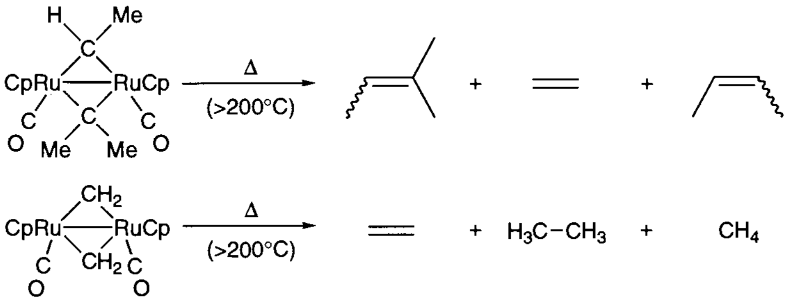
In our laboratories, diruthenium bridging alkylidene complexes, $Cp_2Ru_2(\mu\text{-}CR_2)(CO)_3$ and $Cp_2Ru_2(\mu\text{-}CR_2)_2(CO)_2$, have been the subject of recent research activity [3,4]. In particular, the latter type of compound is a system suitable for examination of the C–C coupling process of alkylidene species. Although intramolecular C–C bond formation was actually observed upon thermolysis (Scheme 1), the selectivity was not high and low yield mixtures of hydrocarbons were obtained ([3]t, [4]a) (Scheme 1).

---

* Corresponding author. Fax: + 81 45 9245226.

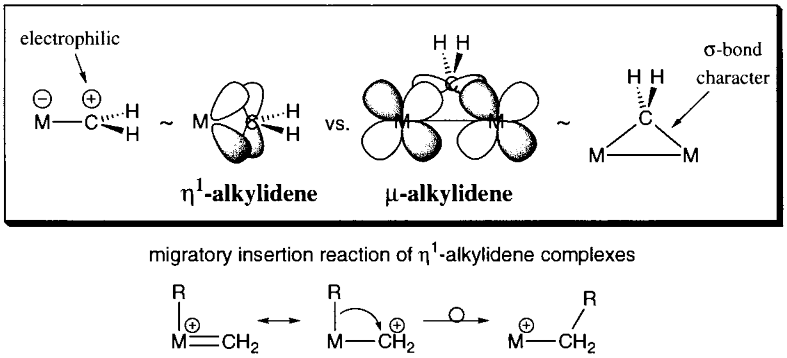
[1] Dedicated to Professor Akira Nakamura in recognition of his important contribution to organometallic chemistry.

PII S0022-328X(98)00775-X



Scheme 1.

Polynuclear bridging alkylidene complexes ($M_n(\mu$-$CR_2)$) are studied extensively as models for surface-bound alkylidene species [5]. As far as the structural aspects are concerned, bridging alkylidene complexes are recognized as better models for the surface-bound species ([1]e) compared to mononuclear alkylidene complexes [$M = CR_2$]. But previous studies revealed that, in general, polynuclear complexes were sluggish with respect to C–C bond formation, whereas mononuclear alkylidene complexes show versatile reactivities such as stoichiometric and catalytic cyclopropanation, olefin metathesis and acetylene polymerization [6].



The difference in the reactivities can be explained in terms of extent of back donation to the vacant p orbital of the CR_2 fragment [7]. As can be seen from the above chart, the overlap with the filled d orbitals is more effective for dinuclear complexes and, therefore, their M–C bonds bear much σ bond character. In contrast, less effective back donation in the mononuclear complexes renders the alkylidene carbon atom electrophilic enough to react with unsaturated hydrocarbons. A typical C–C bond formation reaction of electrophilic bridging methylene complexes is the migratory insertion of a (cationic) alkyl-η^1-alkylidene complex to give a new homologated alkyl complex. This reaction is analyzed as a nucleophilic attack of the metal-bound carbanion (R^-) on the vacant p orbital of the η^1-alkylidene ligand.

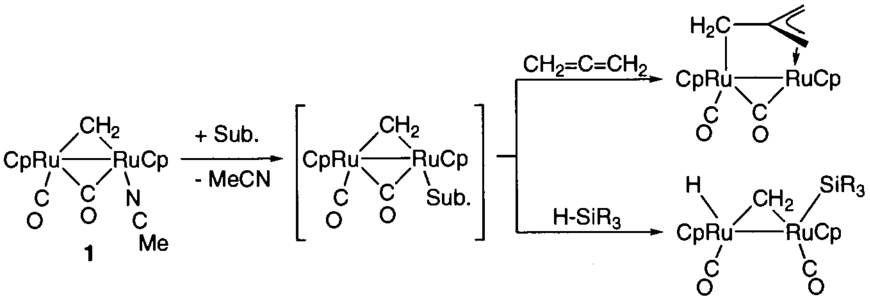
The disadvantages of μ-alkylidene complexes can be overcome through incorporation of a substrate into the transition metal coordination sphere ([3]q). We have reported selective reactions of $Cp_2Ru_2(\mu$-$CH_2)(CO)_2(MeCN)$ **1** bearing the lightly stabilizing MeCN ligand. Addition of a substrate (e.g. allene or hydrosilane) to **1** caused replacement of the MeCN ligand to induce selective transformations (C–C coupling ([3]s) and oxidative addition ([4]e), respectively) (Scheme 2).

Herein we report details of the specific C–C coupling reaction of **1** with diazoalkanes [8]. When a CR_2 species is incorporated into the diruthenium μ-methylene system in this way, the two alkylidenes readily couple with each other to give olefinic products under very mild conditions.

2. Results and discussion

2.1. Reaction of the μ-methylene complex $Cp_2Ru_2(\mu$-$CH_2)(CO)_2(NCMe)$ 1 with diazoalkanes (N_2=CR_2)

Reaction of the mono-μ-methylene complex $Cp_2Ru_2(\mu$-$CH_2)(CO)_2(NCMe)$ **1** with a diazoalkane in CH_2Cl_2 [9] proceeded smoothly at room temperature (r.t.) to give olefinic products as summarized in Scheme 3. Upon addition of the diazoalkane to a CH_2Cl_2 solution of **1**, N_2 gas evolution was observed and the reaction was completed within a few minutes. Separation by preparative TLC afforded three types of prod-



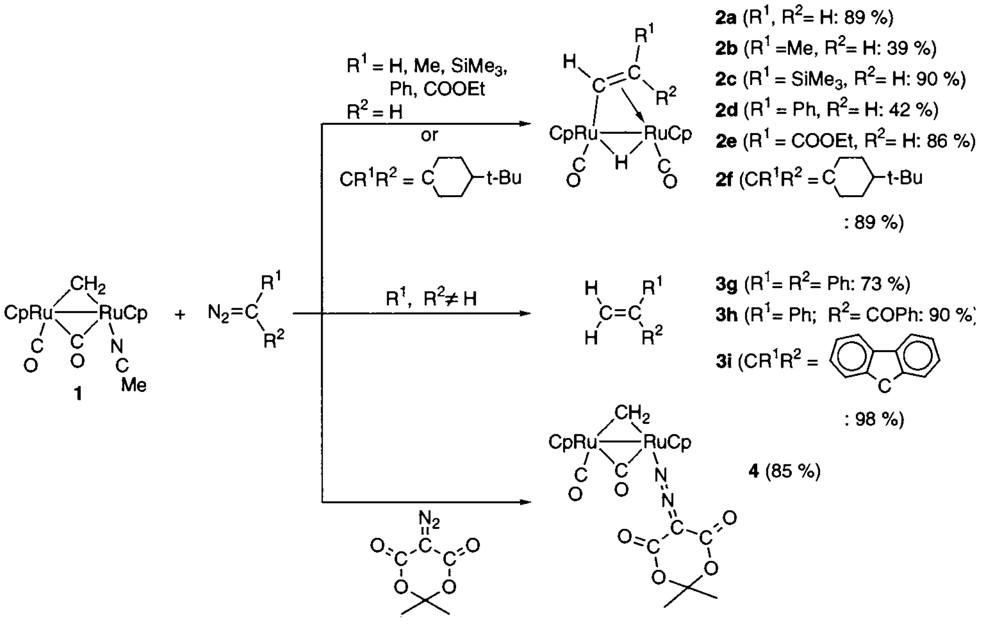
Scheme 2.

ucts: the μ-alkenyl-μ-hydride complex **2** (CR_2: CH_2 (**2a**: 89%), CHMe (**2b**: 39%); $CHSiMe_3$ (**2c**: 90%), CHPh (**2d**: 42%); CHCOOEt (**2e**: 59%); 4-*t*-butylcyclohexylidene (**2f**: 89%)), olefin (CR_2: CPh_2 (**3g**: 73%); CPh–C(=O)Ph: (**3h**: 90%); fluorenylidene (**3i**: 98%)) and the adduct **4** (85%; CR_2: $C(COO)_2CMe_2$ (diazoMeldrum's acid)), depending on the structure of diazoalkane. No other products were detected by ^{1}H-NMR monitoring of reaction mixtures.

The μ-alkenyl-μ-hydride complexes **2** and olefins **3** result from C–C coupling of the methylene unit in **1** and the alkylidene part of external diazoalkane. Monosubstituted diazoalkane (N_2=CHR) and dialkyl-substituted diazoalkane gave **2** in a specific manner, whereas the reaction with diaryl-substituted diazoalkanes (N_2=CR_2) afforded **3** along with a mixture of unidentified organometallic products [10]; no μ-hydride-μ-alkenyl complex **2** could be detected by ^{1}H-NMR analysis of reaction mixtures.

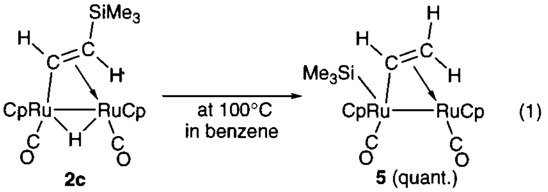
Treatment of **1** with diazoMeldrum's acid, a very stable, commercially available diazoalkane with two electron-withdrawing substituents, produced the brown dinuclear adduct **4** which retained the N_2 moiety, as indicated by elemental analysis. The adduct **4** was formed via replacement of the MeCN ligand. Although it was anticipated that subsequent thermolysis might induce removal of N_2 and then C–C coupling, heating a benzene-d_6 solution of **4** at 60°C resulted in decomposition giving a complicated mixture of unidentified products.

Two notable reactions were observed for **2**. In order to remove the organic part from **2** its thermolysis was examined. When a benzene solution of the $SiMe_3$-derivative **2c** was heated for 2 h at 100°C, quantitative isomerization to the μ-vinyl-silyl complex **5** was observed. Complex **5** was identified by comparison of its spectral data with those of an authentic sample prepared according to our reported method, i.e. interaction of a μ-vinylidene species $Cp_2Ru_2(\mu\text{-}C{=}CH_2)(CO)_2(MeCN)$ with $HSiMe_3$ ([4]f). Although other complexes **2** did not isomerize under similar reaction conditions, thermolysis in the presence of CO or PPh_3 gave a mixture of unidentified dinuclear complexes.

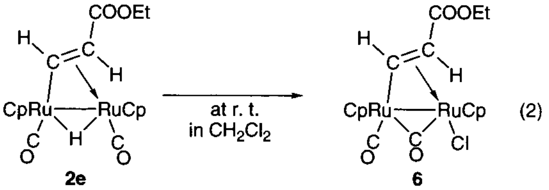


Scheme 3.

The reaction with N_2=CHCOOEt afforded **2e** as the sole organometallic product as mentioned above. However, when the reaction mixture was left in CH_2Cl_2 for 2 days, another μ-CH=CHCOOEt complex **6** (37%), without hydride resonance, was isolated in addition to **2e** (15%).



(1)



(2)

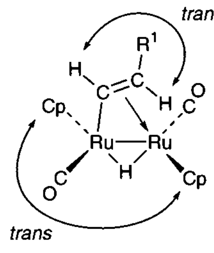
Complex **6** was characterized as the chloride derivative of **2e** as confrmed by X-ray crystallography (see below). The chloride complex **6** is predominantly formed by halogenolysis of the hydride complex **2e** in CH_2Cl_2.

Thus it is found that efficient C–C coupling takes place on the diruthenium system. It should be noted that the reaction conditions of the present C–C coupling are much milder than those of thermolysis of the di-μ-alkylidene complexes $Cp_2Ru_2(\mu\text{-}CR_2)_2(CO)_2$ (Scheme 1).

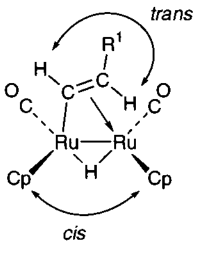
2.2. Characterization of μ-alkenyl-μ-hydride complexes $Cp_2Ru_2(\mu\text{-}CH{=}CR_2)(\mu\text{-}H)(CO)_2$ 2

The μ-alkenyl-μ-hydride complexes **2** were readily characterized on the basis of their NMR and IR spectra (Table 1). As a typical example, a ^{1}H-NMR spectrum of **2a** is reproduced in Fig. 1a. The hydride signal located at δ − 14.42 falls in the range of bridging hydride signals, and the three vinyl protons observed at δ 8.61 (dd), 4.41 (d), and 2.68 (d) are readily assigned to H_a, H_b, and H_c, respectively, on the basis of the coupling constants ($J_{ab} = 7.8$, $J_{ac} = 12.7$ Hz). Separation of the ^{1}H- and ^{13}C-NMR signals is typical for μ-η^1:η^2-alkenyl ligands ([3]h) and IR spectra of **2** containing only terminal CO stretching vibrations (1907–1983 cm^{-1} in CH_2Cl_2) also support the structure. Compound **2b** and related compounds have been already reported by us ([3]i). They were prepared by hydride addition to the corresponding μ-alkenyl cations $[Cp_2Ru_2(\mu\text{-}CR{=}CR_2)(CO)_3]^+$.

With regard to the configuration of the Cp rings, only one isomer was observed for **2c**. However, in the case of **2a,b,d,e**, minor isomers **2a′,b′,d′,e′** with similar spectroscopic features were detected (**2a**:**2a′** = 7:1 (see signals marked with asterisks in Fig. 1); **2b**:**2b′** = 3:1; **2d**:**2d′** = 3:1; **2e**:**2e′** = 3:1). The major component **2** was assigned to the *trans*-isomer



2 (*trans-trans*)

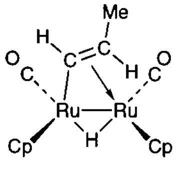


2′ (*cis-trans*)

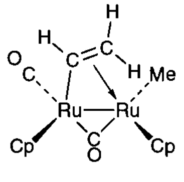
on the basis of the X-ray structure of the major isomer of **2b** (see below), and the minor component **2′** to the *cis*-isomer. No *cis–trans* interconversion was observed for the isolated samples of **2** and **2′** (**a,b,d**-series) even when heated at 100°C, whereas **2e** slowly converted to **2e′** even at r.t. The large proton coupling constants for the substituted alkenyls [11.7–13.6 Hz] lead to assignment of *trans* configuration.

2.3. Molecular structures of μ-alkenyl complexes 2b and 6

The molecular structures of the μ-ethenyl complex **2b** and the chloro complex **6** are presented in Fig. 2 and Fig. 3, and selected structural parameters are summarized in Table 2 and Table 3. The two Ru centers are bridged by the μ-η^1:η^2-alkenyl ligands. One of the structural features is the configuration of the Cp rings with respect to the Ru–Ru bond. Complexes **2b** and **6** adopt *trans*- and *cis*-configurations, respectively. Structural characterization of closely related complexes, a stereoisomer of **2b** with the *cis*-Cp-configuration (**2b′**) ([3]i) and the methyl derivative of **6** ([3]w), have been reported.



2b′ (*cis*)



(*cis*)

They were prepared by very different methods.

In complex **2b** the two CpRu(CO) fragments linked by the Ru–Ru bond [**2b**: 2.830(1); cf. **6**: 2.7815(6) Å] are bridged by a 4e- (μ-alkenyl) and 2e-donor (μ-H) to attain the coordinatively saturated 34e-configuration. Replacement of the μ-H ligand by the Cl ligand (**6**) causes a change in the coordination mode of one of the two terminal CO ligands of **2b** to give a bridging CO. Otherwise, a bridging Cl ligand acting as a 4e-donor would lead to a 36e-configuration.

Table 1
Spectroscopic data for the diruthenium complexes **2** and **6**

Complex	^{1}H-NMR					^{13}C-NMR[a]					IR[b]
(R^1)	α-CH,	β-CH	R^1	μ-H	Cp	α-CH	β-CH	R^1	Cp	CO	
2a	8.61	4.41	2.68	−14.42	4.42	144.4[c]	53.2	—	83.5	202.4	1913
(H)	(dd, 12.7, 7.8)	(d, 7.8)	(d, 12.7)		4.75	(d, 147)	(t, 156)		84.1	203.5	1961
2a′	9.09	4.30	3.09	−15.02	4.20						
(H)	(dd, 11.7, 7.8)	(d, 7.8)	(d, 11.7)		4.60						
2b	8.34	3.54	1.61	−14.44	4.47	145.2	75.9	28.9	84.1	203.6	1954
(Me)	(d, 11.7)	(dq, 11.7, 5.9)	(d, 5.9)		4.76	(d, 153)	(d, 158)	(q, 127)	84.3	206.9	1911
2b′	8.41	3.72	1.64	−14.56	4.49						
(Me)	(d, 11.9)	(dq, 11.9, 6.0)	(d, 6.0)		4.78						
2c	8.78	2.55	0.68	−14.8	4.89	152.1[c]	70.0	−0.14	83.1	202.5	1958
($SiMe_3$)	(d, 13.6)	(d, 13.6)	(9H, s)		5.06	(d, 149)	(d, 137)	(q, 120)	84.8	205.7	1908
2d	9.36	4.64	7.2–7.0	−14.43	4.64	161.9	77.9	146.2	84.5	203.6	1958
(Ph)	(d, 12.5)	(d, 12.5)	(5H, m)		4.80	(d, 162)	(d, 160)	139.0[d]	85.2	206.9	1915
								128.8[d], 126 0[d]			
2d′	9.89	4.74		−14.96	4.65						
(Ph)	(d, 11.9)	(d, 11.9)			4.83						
2e	10.04	3.55	4.18	−15.0	4.91	154.8[c]	58.5	60.0	83.9	202.3	1983
(COOEt)	(d, 11.7)	(d, 11.7)	(2H, q, 6.8)		5.20	(d, 145)	(d, 165)	(t, 147)	84.8	202.5	1919
			1.29 (t, 6.8)					14.5 (q, 127)			1700
2e′	9.27	3.63		−14.6	4.89						1973
(COOEt)	(d, 11.7)	(d, 11.7)			4.97						1923
											1700
2f[e]	8.48	—	2.4–2.1	−13.92	4.95	150.3	78.0	40.2	83.3	203.4	1956
			(5H, m)		4.52	(d, 154)		35.7	85.9	206.7	1907
			1.9–1.0					(d, 119)			
			(4H, m)					33.3 (t, 122)			
			0.92					25.0 (t, 127)			
			(9H, s)					20.1 (q, 125)			
6	10.38	4.30–4.09	1.34–1.29		4.87	163.5[c]	74.3	174.3	87.7	197.6	1996
(COOEt)	(d, 9.8)	(3H, m)	(3H, m)		5.32	(d, 168)	(d, 168)	60.5	91.4	224.9	1842
								(t, 149)			1693
								14.6			
								(q, 127)			

[a] ^{1}H- and ^{13}C-NMR spectra were observed at 400 and 100 MHz, respectively, at room temperature. Spectra were observed in C_6D_6 unless otherwise stated. Chemical shifts are reported in ppm downfield from TMS. Signals unless otherwise stated are singlets, and multiplicity and coupling constants (in Hz) are shown in parentheses.

[b] Recorded in CH_2Cl_2. The wavenumbers are reported in cm^{-1}.

[c] Observed in $CDCl_3$.

[d] Doublet signals with $J =$ ca. 160 Hz.

[e] $CR^1R^2 =$ 4-*t*-butylcyclohexylidene.

As usually observed for dinuclear μ-η^1:η^2-alkenyl complexes, the bridging C1 atom is located almost equidistant from the two Ru centers (**2b**: Ru1–C1: 2.027(5); Ru2–C1: 2.164(5); **6**: Ru1–C1: 2.022(5); Ru2–C1: 2.130(4) Å) and the C1–C2 distances (**2b**: 1.385(7); **6**: 1.412(6) Å) are slightly elongated (normal C=C distance: 1.34 Å upon coordination to Ru2. Other structural parameters fall in the normal ranges. The configuration of the olefinic part in **6** is *trans* in accord with the ^{1}H-NMR analysis, as discussed above.

2.4. Regiospecific C–C coupling revealed by labeling experiments using 1-d_2 (μ-CD_2) and 1-^{13}C (μ-$^{13}CH_2$)

In order to obtain an insight into the mechanism of the C–C coupling, labeling experiments using **1**-d_2 and **1**-^{13}C were conducted (Scheme 4). Treatment of the μ-CD_2 complex (**1**-d_2) with N_2=CH_2 afforded **2a**-d_2, a ^{1}H-NMR spectrum of which is compared with that of **2a** (Fig. 1). Disappearance of the hydride and H_a signals and lack of coupling with the latter proton clearly indicated that the methylene unit in diazomethane was converted to the β-CH_2 part of the bridging ethenyl ligand and the μ-CH_2 moiety in **1** was incorporated into the hydride and the α-CH moiety. The latter feature is confirmed by the ^{13}C-labeling experiment. The ^{13}C-labeled μ-methylene carbon atom in **1**-^{13}C is converted to the α-carbon atom in **2a**-^{13}C. As can be seen from the ^{1}H-NMR spectra (Fig. 1), no other isomer except **2a′** was formed and, therefore, the transformation is found to be specific (Scheme 4).

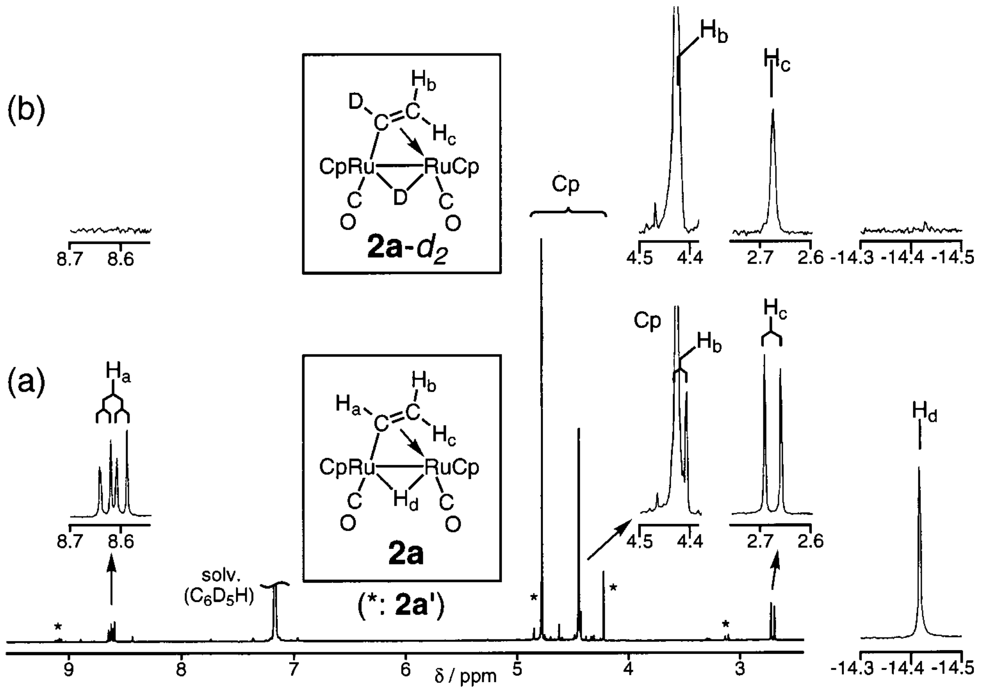


Fig. 1. ^{1}H-NMR spectra of **2a** observed in C_6D_6 (r.t. at 400 MHz). (a) **2a** obtained from **1** (peaks indicated by asterisks are for isomer **2a′**). (b) **2**-d_2 obtained from **1**-d_2.

Similarly, reaction of **1**-d_2 with N_2=CHSiMe$_3$ produced **2c**-d_2 where the hydride and the α-CH sites were completely deuterated. Subsequent thermolysis afforded **5**-d_2 with a β-CD$_2$ group.

Thus the C–C coupling process (Scheme 3), like the thermal isomerization, is a regiospecific transformation. The hydride and the α-CH moieties in **2** come from the μ-CH$_2$ ligand in **1**, and the alkylidene moiety of the diazoalkane is incorporated into the β-CHR part. In addition, thermolysis of **2c** results in the quantitative conversion of the μ-H and α-CH components into β-CH$_2$ in **5**.

2.5. Mechanism of C–C coupling

Plausible reaction pathways for the specific C–C coupling process are summarized in Scheme 5, and explain the following aspects: (1) formation of the olefinic products **2** and **3**; (2) specific transformation of the μ-CH$_2$ moiety of **1** into the μ-H and α-CH parts in **2**; (3) thermal isomerization of **2c** into **5**.

The first aspect suggests that a key intermediate should be the η^2-olefin species **7** arising from coupling of the two CR$_2$ fragments (the μ-methylene ligand in **1** and the CR$_2$ unit from external diazoalkane) within the coordination sphere of the diruthenium unit. In addition, the intermediate in the formation of **7** should have an unsymmetrical structure, because symmetrical ones such as **8′** and **8″** can not explain the specificity of the labeling experiments (the second aspect: Scheme 4). Participation of the di-μ-methylene intermediate **8′** can also be eliminated on the basis of its low reactivity and selectivity with respect to C–C coupling (Scheme 1). Thus we propose the η^1-alkylidene-μ-methylene intermediate **8** as the key intermediate of the transformation. Because a η^1-alkylidene species may be reactive enough to couple with another η^1-bound ligand, migratory insertion of the η^1-alkylidene part into one of the two Ru–CH$_2$ bonds realizes the C–C coupling as discussed in the Section 1 (chart 1).

In the resulting coordinatively unsaturated species **7**, a C–H bond is so closely disposed to the coordinatively unsaturated site of the adjacent ruthenium center that its oxidative addition produces the μ-hydride-μ-alkenyl complex **2**, whereas a bulky olefin ligand (**3**) may be expelled from the coordination sphere due to steric repulsion with the Cp$_2$Ru$_2$(CO)$_2$ residue as observed in the reaction with diaryldiazoalkanes. The labeling experiments suggest that the oxidative addition takes place prior to free rotation of the η^2-CH$_2$=CH$_2$ ligand with respect to the Ru–C=C midpoint axis. Otherwise, a mixture of **2a**-d_2 and its regioisomer Cp$_2$Ru$_2$(μ-H)(μ-CH=CD$_2$)(CO)$_2$ would be formed. This means that the C–H oxidative addition is a very facile process when it is disposed to a reactive site in an appropriate manner. This step can be viewed as an example of 'bimetallic activation' [11],

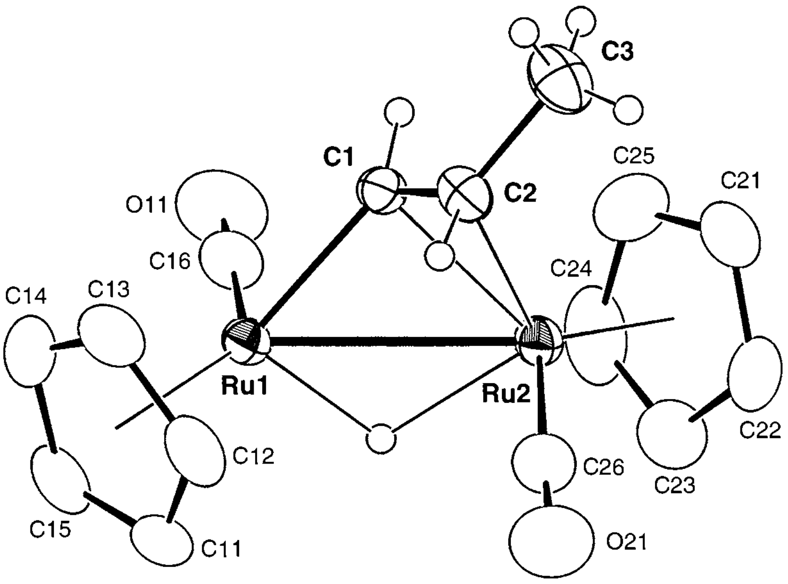


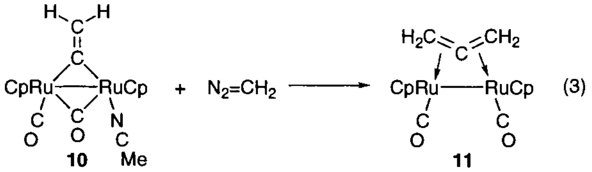
Fig. 2. Molecular structure of **2b** drawn at the 30% probability level.

where one of the metal centers binds the substrate and the other metal center serves as the activation site.

The isomerization of the $SiMe_3$-derivative **2c** into **5** clearly indicates that the C–H oxidative addition is reversible. The reverse reaction (C–H reductive elimination) regenerates the η^2-olefin intermediate **7** [12], which is converted to the silyl complex **5** via C–Si bond cleavage after prolonged heating. These results reveal that the hydride complex resulting from the C–H oxidative addition is the kinetic product and the silyl complex resulting from the C–Si oxidative addition is the thermodynamic product. The kinetic product should arise from oxidative addition of the C–H bond, which is much more facile than that of the sterically congested C–Si bond. The driving force of the isomerization will be the thermodynamic stability of the Ru–Si bond formed by the isomerization. C–Si bond cleavage is not always a facile process [13] but it can be achieved by means of 'bimetallic activation'. We have reported another example of C–Si bond activation in the silyl-μ-methylene species, $Cp_2Ru_2(\mu\text{-}CH_2)(X)(SiR_3)(CO)$ ($X = H$ or SiR_3), where reversible reductive elimination between the methylene carbon atom and the silyl group occurs at ambient temperature ([4]b,c).

A similar coupling of alkylidene species on a polymetallic system has been reported by Shapley and coworkers [14]. Treatment of the labile triosmium μ-methylene species $Os_3(\mu\text{-}CH_2)(CO)_9(\mu\text{-}CO)(MeCN)$ with $N_2{=}CHR$ ($R = H$, $SiMe_3$) furnished the μ-vinyl-μ-hydride complexes $Os_3(\mu\text{-}CH{=}CHR)(\mu\text{-}H)(CO)_{10}$. A labeling experiment using $N_2{=}^{13}CH_2$, however, afforded a mixture of the regioisomers, $\mu\text{-}^{13}CH{=}CH_2$ and $\mu\text{-}CH{=}^{13}CH_2$ species.

A 'vinylidene' version of the present coupling reaction has been reported by us [15]. Reaction of the vinylidene analogue of **1** (**10**) with diazomethane gave the μ-allene complex **11** [11]. Formation of complex **11** is explained in terms of a mechanism similar to Scheme 5 with the intermediate stabilized by coordination of the two π bonds of the allene molecule.



(3)

The isolation of the adduct of diazoMeldrum's acid (**4**) provided an opportunity to consider the interaction modes of the diazoalkane with **1**. Two resonance structures **12A,B** depicted in Scheme 6 are possible for a diazoalkane and both forms can be coordinated to a transition metal center either at the terminal nitrogen atom or the α-carbon atom, where negative charge is developed. In the case of diazoMeldrum's acid, conjugation through the N–N–C(ester)$_2$ π-linkage would reduce the electron-density at the α-carbon atom. Therefore reaction occurs at the N-terminus to give the adduct **4** through the N-bonded form **13A**. Judging from its stability, the coordination of the diazo part of diazoMeldrum's acid appears to be irreversible. In other cases, coordination at the α-carbon atom (**13B**) followed by elimination of N_2 gives the η^1-alkylidene intermediate **8**. If coordination at the N-terminus is reversible, conversion from **13A** to **8** is viable by way of the C-bonded form **13B**. Such bimodal reactivity of diazoalkanes has often been noted [16].

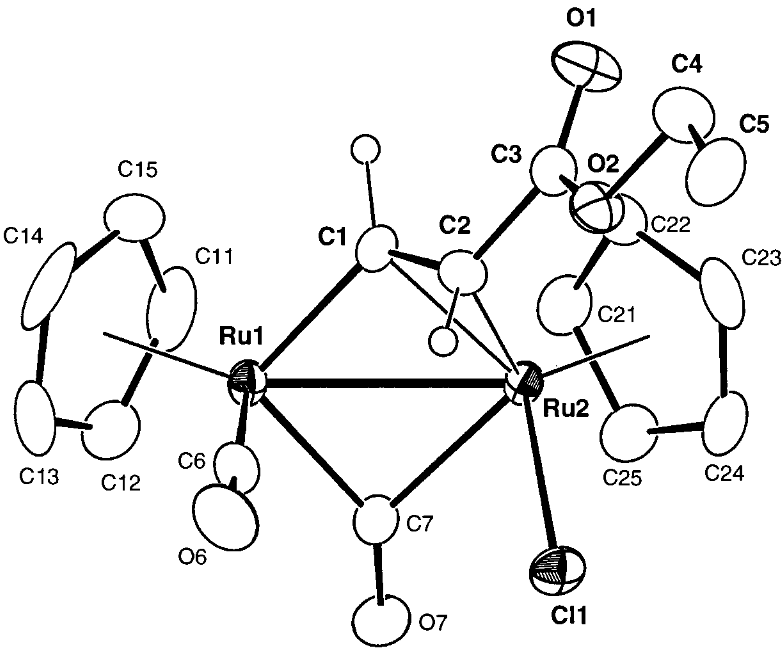


Fig. 3. Molecular structure of **6** drawn at the 30% probability level.

3. Conclusion

The present study has revealed that a bridging methylene complex bearing a labile acetonitrile ligand, $Cp_2Ru_2(\mu\text{-}CH_2)(CO)_2(NCMe)$ **1**, readily reacts with diazoalkane ($N_2{=}CR_2$) to give the olefinic products **2** and **3** via C–C coupling of the bridging CH_2 moiety with the external CR_2 source. Labeling experiments have shown that the μ-CH_2 moiety in **1** is transferred into the μ-H and α-CH parts of the μ-vinyl-μ-hydride complex **2** in a specific manner. It is also notable that the efficiency of C–C coupling depends on the coordination mode of the alkylidene ligand. Although both the (μ-alkylidene)(η^1-alkylidene) intermediate **8** (Scheme 5) and the bis(μ-alkylidene) complex have the same composition '$Cp_2Ru_2(CR_2)_2(CO)_2$', their reactivity has proved to be quite different. Species **8** undergoes C–C specific coupling, whereas the bis(μ-alkylidene) species

Table 2
Selected structural parameters for **2b**[a]

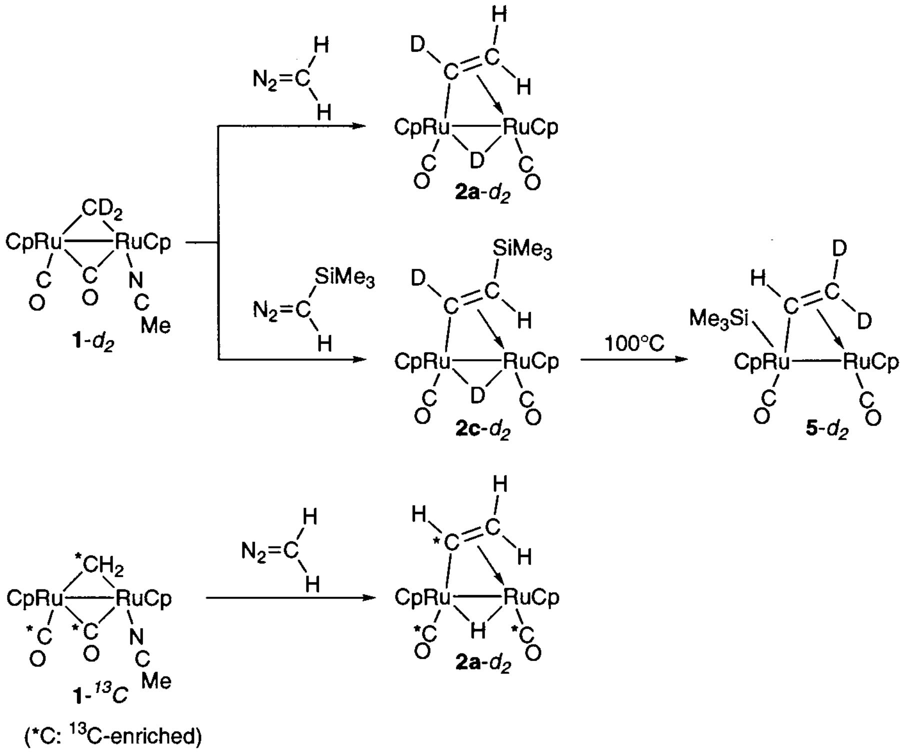
Bond lengths (Å)			
Ru1–Ru2	2.830(1)	Ru1–C11–15	2.205–2.273(6)
Ru1–C1	2.027(5)	Ru2–C21–25	2.201–2.245(6)
Ru2–C1	2.164(5)	Ru1–C16	1.821(6)
Ru2–C2	2.281(5)	Ru2–C26	1.860(6)
C1–C2	1.385(7)	C16–O11	1.160(7)
C2–C3	1.503(7)	C26–O21	1.144(7)
Bond angles (°)			
Ru2–Ru1–C1	49.6(1)	C2–Ru2–C26	81.6(2)
Ru2–Ru1–C16	94.7(2)	Ru1–C1–Ru2	84.9(2)
C1–Ru1–C16	88.4(2)	Ru1–C1–C2	124.3(4)
Ru1–Ru2–C1	45.5(1)	C1–C2–C3	123.1(5)
Ru1–Ru2–C2	71.9(1)	C1–C2–Ru2	67.3(3)
Ru1–Ru2–C26	91.5(2)	C3–C2–Ru2	117.2(3)
C1–Ru2–C2	36.2(2)	Ru1–C16–O11	179.8(6)
C1–Ru2–C26	105.5(2)	Ru2–C26–O21	177.4(6)

[a] Bond lengths in Å and bond angles in degrees.

Table 3
Selected structural parameters for **6**[a]

Bond lengths (Å)			
Ru1–Ru2	2.7815(6)	C3–O2	1.346(6)
Ru1–C1	2.022(5)	C4–O2	1.434(6)
Ru1–C6	1.885(5)	C6–O6	1.129(5)
Ru1–C7	2.007(5)	C7–O7	1.155(5)
Ru2–Cl1	2.431(2)	C1–C2	1.412(6)
Ru2–C1	2.130(4)	C2–C3	1.465(6)
Ru2–C2	2.240(5)	C4–C5	1.484(8)
Ru2–C7	2.133(5)	C1–H1	1.07(4)
C3–O1	1.206(6)	C2–H2	0.93(4)
Bond angles (°)			
Ru2–Ru1–C1	49.6(1)	C3–O2–C4	117.0(4)
Ru2–Ru1–C6	93.3(1)	Ru1–C2–Ru2	84.1(2)
Ru2–Ru1–C7	49.7(1)	Ru1–C1–C2	125.2(4)
C1–Ru1–C6	89.8(2)	Ru2–C1–C2	75.4(3)
C1–Ru1–C7	99.3(2)	Ru2–C2–C1	67.0(3)
C6–Ru1–C7	91.5(2)	Ru2–C2–C3	117.8(3)
Ru1–Ru2–Cl1	97.85(4)	C1–C2–C3	122.6(5))
Ru1–Ru2–C1	46.3(1)	O1–C3–O2	123.1(5)
Ru1–Ru2–C2	74.2(1)	O1–C3–C2	127.4(5)
Ru1–Ru2–C7	45.9(1)	O2–C3–C2	109.4(4)
Cl1–Ru2–C1	110.8(1)	O2–C4–C5	108.5(5)
Cl1–Ru2–C2	84.2(1)	Ru1–C6–06	177.6(5)
Cl1–Ru2–C7	78.0(1)	Ru1–C7–Ru2	84.4(2)
C1–Ru2–C2	37.6(2)	Ru1–C7–O7	142.1(4)
C1–Ru2–C7	92.1(2)	Ru2–C7–O7	133.3(4)
C2–Ru2–C7	112.8(2)		

[a] Bond lengths in Å and bond angles in degrees.



Scheme 4.

produces a low yield mixture of products upon pyrolysis. The C–C bond formation in **1**, however, is viewed as a migratory insertion reaction at a mononuclear center (Chart 1), with the other ruthenium center functioning as a substituent of the μ-methylene ligand to support the dinuclear structure.

On the basis of the present results, a modified mechanism for catalytic CO hydrogenation, involving olefin as a key intermediate, can be proposed. First, the carbon chain can be propagated via coupling of two alkylidene units (divalent carbon species) to give an olefin intermediate. (In the classical Fischer–Tropsch mechanism, alkyl–alkylidene coupling leads to a homologated alkyl). Secondly, olefin can be formed by dissociation of the resulting olefin intermediate. (In the classical mechanism, olefinic products are formed via β-elimination of an alkyl intermediate). Finally, C–H oxidative addition of the olefin species furnishes an alkenyl intermediate, which was recently postulated as an initiator of FT synthesis [17].

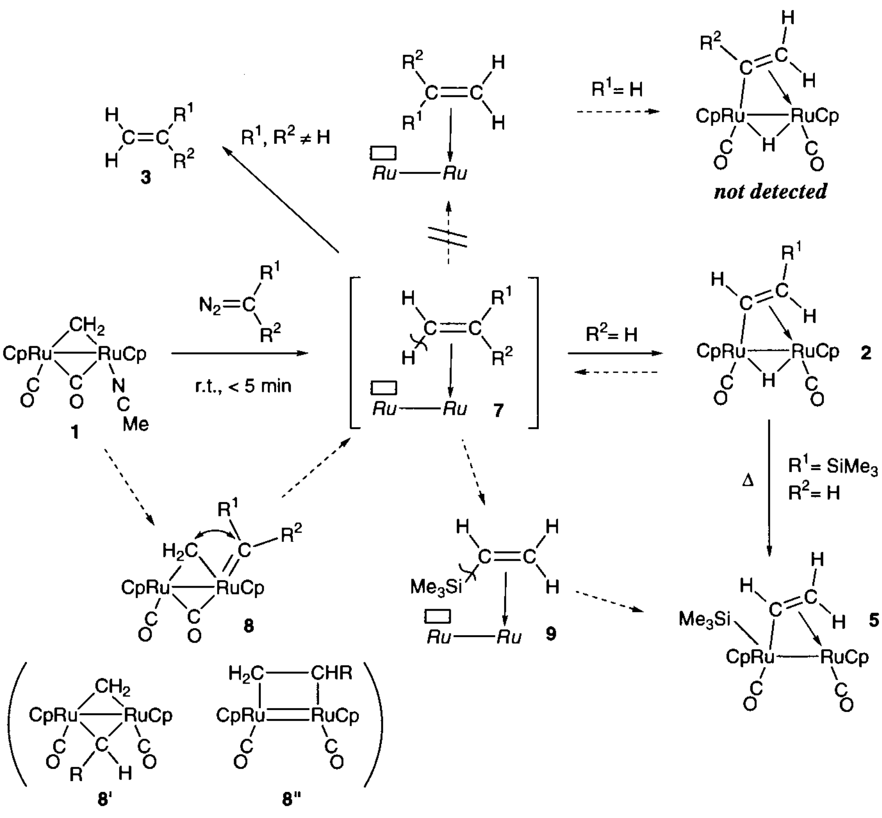
4. Experimental section

4.1. General methods

All manipulations were carried out under an inert atmosphere using standard Schlenk tube techniques. Ether and hexanes (Na–K alloy) and CH_2Cl_2 (P_2O_5) were treated with appropriate drying agents, distilled, and stored under argon. Complex **1** ([3]q) and diazoalkanes (N_2=CR^{1}R^2: CR^{1}R^2= CH$_2$ [18], CHMe [19], CHCOOEt [20], 4-*t*-butylcyclohexylidene [21], CHPh [22], CPh$_2$ [23], CPh(COPh) [23], fluorenylidene [23]) were prepared according to the reported methods. Samples of N_2=CHSiMe$_3$ (10% hexane solution) and diazoMeldrum's acid were purchased from Tokyo Kasei (TCI) and used as received. Preparative TLC was performed on silica gel [silica gel 60 PF$_{254}$ (Merck 1.007747)] and alumina [aluminum oxide 60 PF$_{254}$ (Typ E) (Merck Art. 1103)]. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL EX400 (^{1}H: 400; ^{13}C: 100 MHz) spectrometer. Solvents for NMR measurements containing 0.5% TMS were dried over molecular sieves, degassed, distilled under reduced pressure, and stored under Ar. IR and FD-MS spectra were obtained on a JASCO FT/JR 5300 spectrometer and a Hitachi M80 mass spectrometer, respectively. Elemental analyses were performed in the Elemental Analysis Laboratory of our laboratory.

4.2. Reaction of $Cp_2Ru_2(\mu\text{-}CH_2)(CO)_2(NCMe)$ 1 with diazomethane

To a benzene (2 ml) suspension of **1** (22.3 mg, 0.052 mmol) was added an ethereal (3 ml) solution of CH_2N_2 (ca. 0.50 mmol). After stirring for 20 min at r.t., the reaction mixture was passed through a short alumina

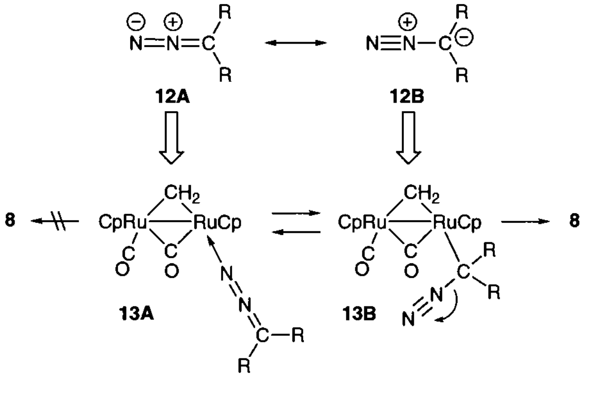


Scheme 5.

pad. The volatiles were removed under reduced pressure and the residue was subjected to preparative TLC separation (silica, eluted with ether:hexane = 1:3). The μ1-ethenyl-μ-hydride complex **2a** (19.3 mg, 0.046 mmol, 89%) was obtained as yellow solid. **2a**: Anal. Calc. for $C_{14}H_{14}O_2Ru_2$: C, 40.38; H, 3.36. Found: C, 40.15; H, 3.31.

*4.3. Reaction of **1** with diazoethane*

An ethereal solution of diazoalkane was prepared by treatment of a cold ethereal solution of *N*-ethyl-*N*-nitrosourea (210 mg, 1.79 mmol) with aqueous KOH solution, and the ether layer was used without further purification. To a THF suspension (2 ml) of **1** (75.7 mg, 0.171 mmol) was added to the ethereal diazoethane solution at ambient temperature. Gas evolution (N_2) was noted and the solution color changed from brown into dark brown. After 10 min of stirring the volatiles were removed under reduced pressure and preparative TLC separation (silica, eluted with hexane:ether = 10:1) gave two isomers: **2b** (28.8 mg, 0.067 mmol, 39% yield) and **2b′** (4.4 mg, 0.010 mmol, 6%). Anal. Calc. for $C_{15}H_{16}O_2Ru_2$: C, 41.85; H, 3.75. Found: C, 41.79; H, 3.69.



Scheme 6.

*4.4. Reaction of **1** with trimethylsilyldiazomethane*

A mixture of **1** (32.0 mg, 0.072 mmol) and Me_3SiCHN_2 (0.4 ml of *n*-hexane solution, ca. 10%, ca. 0.23 mmol) in benzene (2 ml) was stirred for 5 min at r.t. After work up as described for **2a**, complex **2c** (31.8 mg, 0.072 mmol, 91%) was obtained as an orange solid. **2c**: Anal. Calc. for $C_{17}H_{22}O_2Ru_2Si$: C, 41.80; H, 4.50. Found: C, 41.36; H, 4.45.

*4.5. Thermal isomerization of **2b***

Heating a C_6D_6 solution of **2b** for 2 h at 100°C gave the isomer **5** in a quantitative yield. Complex **5** was identified by comparison of a ^{1}H-NMR spectrum with that of an authentic sample prepared according to ref. ([4]f). **5**: δ_H (C_6D_6) 7.82 (1H, dd, $J = 11.7$ and 7.8 Hz, CH), 4.69, 4.60 (5H × 2, s × 2, Cp_2), 3.77 (1H, d, $J = 7.8$ Hz, CH_2), 2.24 (1H, d, $J = 11.7$ Hz, CH_2), IR(CH_2Cl_2): ν(C≡O) 1958, 1908 cm^{-1}.

4.6. Reaction of **1** with ethyl diazoacetate

A sample of ethyl diazoacetate (1.7 ml, O.5 M in CH_2Cl_2, ca. 0.85 mmol) was added to a solution of **1** (126.0 mg, 0.28 mmol) in CH_2Cl_2 (3 ml). The mixture was then stirred for 1 h at r.t. After removal of the volatiles under reduced pressure, the residue was subjected to preparative TLC separation (silica, eluted with acetone:hexane = 1:3). **2c** (81.8 mg, 0.17 mmol, 59%) was obtained as a yellow solid. **2c**: Anal. Calc. for $C_{17}H_{18}O_4Ru_2$: C,4 1.80; H, 3.68. Found: C, 42.10; H, 3.38.

When the reaction was carried under the same conditions for 4 days, **2c** (15%) end the chloride derivative **6** (37%) were obtained. **6**: Anal. Calc. for $C_{17}H_{17}O_4Ru_2Cl$: C, 39.01; H, 3.25. Found: C, 38.43; H, 3.02.

4.7. Reaction of **1** with 4-*t*-butyldiazocyclohexane

To a THF suspension (2 ml) of 1 (25.0 mg, 0.056 mmol) was added a hexane solution of 4-*t*-butyldiazocyclohexane (0.1 M solution, 2 ml, 0.2 mmol). After stirring for 20 min, the mixture was worked up as described for **2b**. **2f** (yellow solid): Anal. Calc. for $C_{23}H_{29}O_2Ru_2$: C, 51.19; H, 5.42. Found: C, 50.87; H, 5.39.

4.8. Reaction of **1** with diphenyldiazomethane

To a benzene (2 ml) suspension of **1** (41.2 mg, 0.093 mmol), 2.5 equivalents of Ph_2CN_2 (0.5 M CH_2Cl_2 solution) was added. The resultant mixture was stirred for 30 min at r.t. After removal of the volatiles, the residue was subjected to preparative TLC separation (silica, eluted with CH_2Cl_2:hexane = 1:2). From the colorless band diphenylethylene **3a** (12.1 mg, 0.067 mmol, 73% yield) was obtained. **3a**: δ_H ($CDCl_3$) 7.37–7.27 (10H, m, Ph), 5.48 (2H, s, CH_2). δ_C ($CDCl_3$) 150.0 (s, =CPh_2), 141.5 (s, *ipso*), 129.2, 128.1, 127.6 (d × 3, $J = 160$ Hz, Ph signals), 114.3 (t, $J = 158$ Hz, CH_2).

4.9. Reaction of **1** with phenylbenzoyldiazomethane

To a mixture of **1** (51.5 mg, 0.12 mmol) and phenylbenzoyldiazomethane (82.5 mg, 0.37 mmol) was added THF (4 ml) and the resultant mixture was stirred for 1 h at r.t. After 1 h the volatiles were removed under reduced pressure, and the product was quantified by ^{1}H-NMR after addition of ferrocene (an internal standard). **3b** [24]: δ_H ($CDCl_3$) 7.9–7.8 (2H, m, Ph), 7.4–7.3 (2H, m, Ph), 7.2–7.0 (6H, m, Ph), 5.63, 5.32 s × 2, =CH_2). δ_C ($CDCl_3$) 150.0 (s, =C), 141.5 (s, *ipso*-Ph), 129.2 (d, $J = 160$ Hz, Ph), 128.1 (d, $J = 160$ Hz, Ph), 127.7 (d, $J = 160$ Hz, Ph). MS (FD) 208 (M^+).

Table 4
Crystallographic data for **2b** and **6**

Compound	**2b**	**6**
Empirical formula	$C_{15}H_{16}O_2Ru_2$	$C_{17}H_{17}O_4Ru_2Cl$
Formula weight	430.43	522.9
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.421(3)	8.794(2)
b (Å)	13.802(5)	13.826(5)
c (Å)	7.353(2)	14.359(5)
α (°)	94.15(3)	
β (°)	98.94(3)	92.90(2)
γ (°)	117.49(2)	
V (Å^3)	739(1)	1744(1)
Z	2	4
$D_{calc.}$ (g cm^{-3})	1.93	1.99
μ (cm^{-1})	20.4	19.0
2θ (°)	3–60	5–50
Number of data collected	4619	3441
Number of unique data with $I > 3\sigma(I)$	3479	2631
Number of parameters refined	172	225
R	0.037	0.026
R_w	0.039	0.025
G-O-F	3.44	2.64

4.10. Reaction of **1** with diazofluorene

The reaction was carried out as described for **3b** starting from **1** (41.1 mg, 0.10 mmol) and diazofluorene (57.0 mg, 0.29 mmol). **3c** [25]: δ_H ($CDCl_3$) 7.5–7.4, 7.3–7.1 (4H × 2, m × 2, aromatic protons), 5.78 (2H, s, =CH_2).

4.11. Reaction of **1** with 5-diazoMeldrum's acid

To a benzene (2 ml) suspension of **1** (42.3 mg, 0.095 mmol) was added diazoMeldrum's acid (16.5 mg, 0.097 mmol). The solids dissolved to give a brown solution and the resultant mixture was stirred for 30 min at r.t. After removal of the volatiles under reduced pressure, the residue was dissolved in acetone and subjected to preparative TLC separation (alumina, eluted with acetone:hexane = 1:2). 4 (46.2 mg, 0.08 mmol, 85%) was obtained as a brown solid. (the major isomer) δ_H ($CDCl_3$) 9.94, 9.13 (1H × 2, s × 2, μ-CH_2), 5.41, 5.39 (SH × 2, s × 2, Cp_2), 1.64 (6H, s, CH_3). δ_C ($CDCl_3$) 230.9 (s, μ-CO), 197.8 (s, CO), 160.1 (s, CO), 129.1 (t, $J = 151$ Hz, μ-CH_2), 103.5 (s, N–C), 92.7 (d, $J = 180$ Hz, Cp), 91.2 (d, $J = 180$ Hz, Cp). 68.7 (s, C), 26.4 (q, $J = 132$ Hz). IR(CH_2Cl_2): ν(C–O) 1987, 1834, 1674 cm^{-1}. Anal. Calc. for $C_{19}H_{10}N_2O_6Ru_2$: C, 39.86; H, 3.15; N, 4.89. Found: C, 39.75; H,3.43, N, 4.34.

4.12. X-ray crystallography

Single crystals of **2b** and **6** were obtained by recrystallization from THF-hexanes and CH_2Cl_2-hexane, respectively, and mounted on glass fibers.

Diffraction measurements of **2b** and **6** were made on a Rigaku AFC5R automated fourcircle diffractometer by using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71059$ Å). The unit cells were determined and refined by a least-squares method using 20 independent reflections (2θ ca. 20°). Data were collected with a 2θ-ω scan technique. If $\sigma(F)/F$ was more than 0.1, a scan was repeated up to three times and the results were added to the first scan. Three standard reflections were monitored at every 150 measurements. The data processing (data collection) was performed on a microvax II computer. In the reduction of data, Lorentz and polarization corrections were made. Empirical absorption corrections (Ψ scan) were made. Crystallographic data and the results of refinements are summarized in Table 4.

Structure analysis was performed on an IRIS Indigo computer by using the teXsan structure solving program system obtained from the Rigaku Corporation, Tokyo, Japan. Neutral scattering factors were obtained from the standard source [26]. The function minimized was $\Sigma_w(|F_o|-|F_c|)^2$ where $w=[\sigma^2(F_o)]^{-1}=4F_o^2\cdot[\sigma^2(F_o^2)]^{-1}$. The schemes for unweighted and weighed agreement factors were as follows: $R=\Sigma\||F_o|-|F_c\|/\Sigma|F_o|$; $Rw=[(\Sigma_w(|F_o|-F_c\|)^2/\Sigma_w F_o^2)]^{\frac{1}{2}}$. The structures were solved by a combination of the direct methods (SAPI91 and SHELXL 87) and Fourier synthesis (DIRDIF). Unless otherwise stated, non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms except H1 and H2 of **6** (refined isotropically) were fixed at the calculated positions (C–H = 0.95 Å) and were not refined.

Acknowledgements

We are grateful to the Ministry of Education, Science, Sports and Culture of the Japanese Government for financial support of this research. M. Akita thanks the Royal Society of Chemistry for Journals Grants for International Authors.

References

[1] (a) J. Falbe, New Synthesis with Carbon Monoxide, Springer, Berlin, 1980. (b) W. Keim, Catalysis in C1 Chemistry, D. Reidel, Dordrecht, 1983. (c) R.B. Anderson, The Fischer-Tropsch Synthesis, Academic Press, London, 1984. (d) H. Pines, The Chemistry of Catalytic Hydrocarbon Conversions, Academic Press, London, 1981. (e) G.A. Somorjai, Introduction to Surface Chemistry and Catalysis, Wiley, New York, 1994.

[2] (a) C. Masters, Adv. Organomet. Chem. 19 (1979) 63. (b) E.L. Muetterties, T.N. Rhodin, E. Band, C.F. Brucker, W.R. Pretzer, Chem. Rev. 79 (1979) 79. (c) C.K. Roofer-DePoorter, Chem. Rev. 81 (1981) 447. (d) W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 117. (e) A.R. Cutler, P.K. Hanna, J.C. Vites, Chem. Rev. 88 (1988) 1363 and references cited therein. For carbide complexes, (f) M. Tachikawa, E.L. Muetterties, Prog. Inorg. Chem. 28 (1981) 203. (g) J.S. Bradley, Adv. Organomet. Chem. 22 (1983) 1. (h) D.F. Shriver, M.J. Sailor, Acc. Chem. Res. 21 (1988) 374. See also (i) W. Beck, B. Niemer, M. Wieser, Angew. Chem. Int. Ed. Engl. 32 (1993) 923.

[3] (a) A.F. Dyke, S.A.R. Knox, P.J. Naish, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1980) 441. (b) A.F. Dyke, S.A.R. Knox, P.J. Naish, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1980) 804. (c) D.L. Davies, A.F. Dyke, A. Endesfelder, et al., J. Organomet. Chem. 198 (1980) C43. (d) A.F. Dyke, S.A.R. Knox, K.A. Mead, P. Woodward, J. Chem. Soc. Chem. Commun. (1981) 861. (e) M. Cooke, D.L. Davies, J.E. Guerchais, S.A.R. Knox, K.A. Mead, J. Roué, P. Woodward, J. Chem. Soc. Chem. Commun. (1981) 862. (f) P.Q. Adams, D.L. Davies, A.F. Dyke, S.A.R. Knox, K.A. Mead, P. Woodward, J. Chem. Soc. Chem. Commun. (1983) 222. (g) N.J. Ferrow, S.A.R. Knox, M.J. Morris, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1983) 234. (h) A.F. Dyke, S.A.R. Knox, M.J. Morris, P.J. Naish, J. Chem. Chem. Soc. Dalton Trans. (1983) 1417. (i) R.E. Colborn, A.F. Dyke, S.A.R. Knox, K.A. Mead, P. Woodward, J. Chem. Chem. Soc. Dalton Trans. (1983) 2099. (j) R.E. Colborn, D.L. Davies, A.F. Dyke, A. Endesfelder, et al., J. Chem. Soc. Dalton Trans. (1983) 2661. (k) S.A.R. Knox, Pure Appl. Chem. 56 (1984) 81. (l) N.J. Ferrow, S.A.R. Knox, J. Chem. Soc. Chem. Commun. (1984) 679. (m) D.L. Davis, B.P. Gracey, V. Guerchais, S.A.R. Knox, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1984) 841. (n) D.L. Davies, S.A.R. Knox, K.A. Mead, M.J. Morris, P. Woodward, J. Chem. Soc. Dalton Trans. (1984) 2293. (o) N.G. Connelly, N.J. Ferrow, B.P. Gracey, S.A.R. Knox, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1985) 14. (p) N.G. Connelly, N.J. Ferrow, S.A.R. Knox, K.A. Macpherson, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1985) 16. (q) N.M. Doherty, J.A.K. Howard, S.A.R. Knox, N.J. Terrill, M.I. Yates, J. Chem. Soc. Chem. Commun. (1989) 638. (r) J.A.K. Howard, S.A.R. Knox, N.J. Terrill, M.I. Yates, J. Chem. Soc. Chem. Commun. (1989) 640. (s) M.J. Fildes, S.A.R. Knox, A.G. Orpen, M.L. Turner, M.I. Yates, J. Chem. Soc. Chem. Commun. (1989) 1680. (t) R.E. Colborn, D.L. Davies, A.F. Dyke, S.A.R. Knox, K.A. Mead, A.G. Orpen, J. Chem. Soc. Dalton Trans. (1989) 1799. (u) S.A.R. Knox, K.A. Macpherson, A.G. Orpen, M.C. Rendle, J. Chem. Soc. Dalton Trans. (1989) 1807. (v) G.C. Bruce, S.A.R. Knox, A.J. Phillips, J. Chem. Soc. Chem. Commun. (1990) 716. (w) G.C. Bruce, B. Gangnus, S.E. Garbar, S.A.R. Knox, A.G. Orpen, A.J. Philiiips, J. Chem. Soc. Chem. Commun. (1990) 1360. (x) R.E. Colborn, A.F. Dyke, B.P. Gracey, et al., J. Chem. Soc. Dalton Trans. (1990) 761. (y) S.A.R. Knox, J. Organomet. Chem. 400 (1990) 255.

[4] (a) M. Akita, T. Oku, Y. Moro-oka, J. Chem. Soc. Chem. Commun. (1992) 1031. (b) M. Akita, T. Oku, R. Hua, Y. Moro-oka, J. Chem. Soc. Chem. Commun. (1993) 1670. (c) M. Akita, R. Hua, Y. Moro-oka, J. Chem. Soc. Chem. Commun. (1996) 541. (d) M. Akita, R. Hua, T. Oku, Y. Moro-oka, Organometallics 15 (1996) 2548. (e) M. Akita, R. Hua, T. Oku, M. Tanaka, Y. Moro-oka, Organometallics 15 (1996) 4162. (f) R. Hua, M. Akita, Y. Moro-oka, Inorg. Chim. Acta 250 (1996) 177. (g) M. Akita, R. Hua, Y. Moro-oka, J. Organomet. Chem. 539 (1997) 205. (h) M. Akita, R. Hua, S. Nakanishi, M. Tanaka, Y. Moro-oka, Organometallics 16 (1997) 5572.

[5] (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.

[6] (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, 1987. (b) M. Brookhart and W. B. Studabaker, Chem. Rev. 87 (1987) 411. (c) E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, ch. 5.1–5.5. (d) B. Cornils, W.A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds (2 vols.), VCH, Weinheim, 1996. (e) G.W. Parshal, S.D. Ittel, Homogeneous Catalysis, 2nd ed., Wiley-Interscience, New York, 1992.

[7] (a) H. Berke, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 7224. (b) B.E.R. Schilling, R. Hoffmann, D.L. Lichtenberger, J. Am. Chem. Soc. 101 (1979) 585. (c) N.M. Kostic, R.F. Fenske, J. Am. Chem. Soc. 104 (1982) 3879.

[8] A part of the results were already reported in a preliminary communication. M. Akita, R. Hua, S.A.R. Knox, Y. Moro-oka, S. Nakanishi, M.I. Yates, J. Chem. Soc. Chem. Commun. (1997) 51.

[9] Complex **1** is soluble in CH_2Cl_2 but insoluble in other organic solvents such as benzene and ether. However, the reaction with diazoalkane is so fast that it makes the system homogeneous within a few minutes.

[10] One of the organometallic products was tentatively assigned to a dinitrogen complex $Cp_2Ru_2(\mu\text{-}N_2)(CO)_2$ on the basis of its spectral data [δ_H 4.27, ν(CO): 1953 cm^{-1}, $m/e = 316$ (for $Cp_2^{101}Ru_2(N_2)(CO)_2$)] but it could not be fully characterized due to its thermal instability. It should arise from the trapping of an eliminated highly coordinatively unsaturated species by the evolved N_2.

[11] See, for example, T. Takao, S. Yoshida, S. Suzuki, M. Tanaka, Organometallics 14 (1995) 3856 and references cited therein.

[12] The ease of the C–H reductive elimination (**2** → **7**) is dependent on the substituent of the μ-alkenyl part. The interconversion between **2e** and **2e′** is explained in terms of free rotation of the Ru–Ru bond in **7**.

[13] See 4 (c,h) and references cited therein.

[14] J.R. Shapley, A.C. Sievert, M.R. Churchill, H.J. Wassermann, J. Am. Chem. Soc. 103 (1981) 6975.

[15] G.S. Lewandos, N.M. Doherty, S.A.R. Knox, K.A. Macpherson, A.G. Orpen, Polyhedron 7 (1988) 837.

[16] See, for example, (a) K.D. Schramm, J.A. Ibers, J. Am. Chem. Soc. 100 (1978) 2932. (b) G.L. Hillhouse, B.L. Haymore, W.A. Herrmann, Inorg. Chem. 18 (1979) 2423. (c) L. Messerle, M.D. Curtis, J. Am. Chem. Soc. 104 (1982) 889. (d) M.D. Curtis, L. Messerle, J.J. D'Errico, W.M. Butler, M.S. Hay, Organometallics 5 (1986) 2283. (e) A. Nakamura, T. Yoshida, M. Cowie, S. Otsuka, J.A. Ibers, J. Am. Chem. Soc. 99 (1977) 2108.

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

[18] T.J. DeBoer, H.J. Backer, Org. Synth. Collect. 4 (1963) 250.

[19] A.F. Mckay, W.L. Ott, G.W. Taylor, M.N. Buchanan, J.F. Crooker, Can. J. Res. Sect. B 28 (1950) 683.

[20] N.E. Searle, Org. Synth. Collect. vol. 4 (1963) 424.

[21] T.L. Holton, H. Shechter, J. Org. Chem. 60 (1995) 4725.

[22] D.G. Farnum, J. Org. Chem. 28 (1963) 870.

[23] C.D. Nenitzescu, E. Solomonica, Org. Synth. Collect. 2 (1943) 496.

[24] R.P. Kopinski, J. Pinhey, Aust. J. Chem. 36 (1983) 311.

[25] M. Neuenschwander, H.P. Farrni, H. Lehmann, R. Vögeli, Chimia 28 (1974) 115.

[26] International Tables for X-Ray Crystallography, vol. 4, Kynoch Press, Birmingham, 1975.