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Photochemical C–H bond activation of the diruthenium bridging methylene complex, $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)_2$: insertion of norbornadienes into the methylene C–H bond and unprecedented intramolecular H–D exchange between the two methylene units

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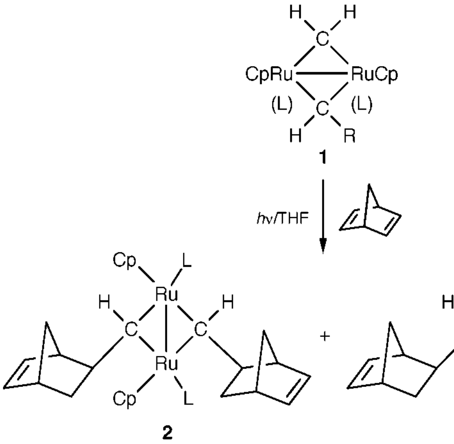
Two photochemical reactions of the diruthenium bis-μ-methylene complex $(\eta^5\text{-}C_5H_5)_2Ru_2(\mu\text{-}CH_2)_2(CO)_2$ are described: (i) insertion reaction of norbornadiene into the methylene C–H bonds leading to $(\eta^5\text{-}C_5H_5)_2Ru_2(\mu\text{-}CHR')_2(CO)_2$ (R′ = 5-*exo*-norbornenyl) and (ii) H exchange between the two methylene units, involve μ-methylidyne intermediates generated *via* C–H bond activation of the μ-methylene ligand.

C1 species (CH_x) are pivotal intermediates in surface catalyzed reactions, such as catalytic conversion of CO and hydrocarbons,[1] and organometallic compounds containing the CH_x ligands have been studied extensively as model compounds for surface-bound species.[2] Although C–C coupling of C1 species is a key step of the carbon chain propagation during the catalytic processes, only a limited number of successful C–C coupling reactions of bridging hydrocarbyl complexes, in particular, μ-CH_2 complexes, have been reported so far, and most of the C–C coupling processes involve coordination of an unsaturated C–C bond (or alkylidene species) to the metal vacant site followed by insertion into the M–μ-CR_x bond.[3,4d] During the course of our studies of the photochemical reactions of the diruthenium di-μ-methylene complex $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)_2$ **1a**,[4] we found an unusual C–C coupling reaction at the bridging methylene carbon atom and unprecedented H exchange between the two methylene carbon atoms, which should involve μ-methylidyne species as a key intermediate.

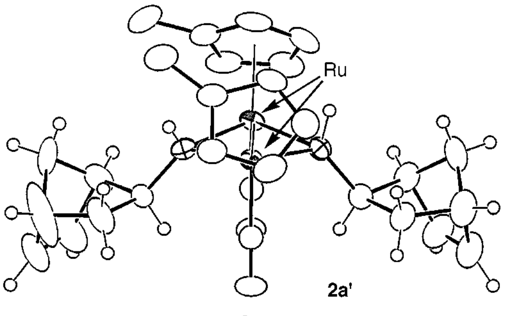
Irradiation of a THF solution of the di-μ-methylene complex **1a**[4a] in the presence of an excess of norbornadiene (nbd) for 5 h gave a yellow isomeric mixture of products (**2a**; 89% yield) after TLC separation (Scheme 1). The significant change in the ^1H NMR signals of the μ-CH_x part compared to **1a** [(i) intensity: 2H (from 4H); (ii) ^3J = 11.7 Hz for μ-CH (from ^2J = 0.6 Hz for μ-CH_2)]† suggested the occurrence of a C–C coupling reaction at the μ-methylene carbon atom. The molecular structure of the $\eta^5\text{-}C_5H_4Me$ derivative (**2a′**) was determined by X-ray crystallography,‡ which revealed (i) insertion of the C=C bond in nbd into the C–H bonds of both of the μ-methylene ligands, and (ii) C–C coupling from the less sterically congested *exo*-side of nbd. Reaction of the μ-methylene-μ-ethylidene complex **1b** resulted in exclusive insertion into the μ-methylene part to give the 1:1 adduct **3b**, as indicated by a similar change in the μ-CH_2 signals and the unchanged μ-$CHCH_3$ pattern.† Furthermore, the photochemical C–C coupling reaction was also observed for the cyclohexyl isocyanide complex **1c**, while the dppe derivative **1d** remained unreacted.§ We also attempted the C–C coupling of **1a** with a variety of unsaturated hydrocarbons such as 2- or 7-substituted nbd, norbornene, cyclohexa-1,4-diene, butadiene, quadricyclene, ethyl acrylate and 1,1-diphenylethylene. However, only a few 2-substituted nbds (Me and Me_3Si derivatives) afforded 1:1 adducts **3** (R = H); the others did not give any C–C coupling product.[5]

For elucidation of the reaction mechanism, a labeling experiment using **1a**-d_4 [(μ-CD_2)$_2$] was carried out and the distribution of the deuterium atoms was determined by ^1H and ^{13}C NMR, as illustrated in Scheme 2. The D distribution over the moiety originating from the C=C bond in nbd clearly indicated that the C–C coupling process was not a simple insertion reaction into the C–D bonds, but consisted of a multi-step reaction sequence. The result may be interpreted in terms of a μ-methylidyne intermediate **4** as summarized in Scheme 2. Possible candidates for **4** are the decarbonylated μ-methylidyne species $Cp_2Ru_2(\mu\text{-}CH)(H)(\mu\text{-}CH_2)(CO)$ **4′**, suggested by the H–D exchange reaction (see below)[6] and the radical species **4″**, generated by H abstraction. Addition of **4′** or **4″** to the π-

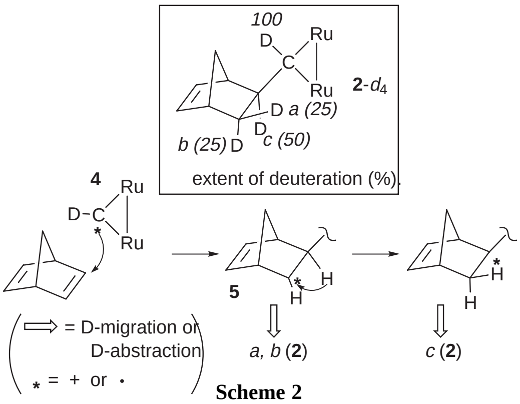


	R	L	products
1a	H	CO	**2a** (89 %)
1a′	H	CO	**2a′** (80 %)
1b	CH_3	CO	**3b** (38 %)
1c	H	CNCy	**2c** (23 %)
1d	H	dppe	–

(**1a′**, **2a′**: $\eta^5\text{-}C_5H_4CH_3$ derivatives)



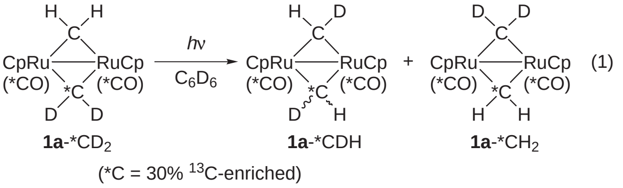
Scheme 1



Scheme 2

electrons of nbd should form intermediate **5**. Direct H recombination gives **2**-d_4 deuterated at either of sites *a* or *b*, whereas a 1,2-H shift finally leads to deuteration at the site *c*, and the driving force for the 1,2-H migration should be formation of the tertiary cation (or radical), which is more stable than the secondary one (**5**). Subsequently, the C–C coupling reaction will be completed by either intramolecular H(D) migration (**4′**) or intermolecular H(D) abstraction [**4″**: from **2**-d_2 (radical chain reaction)]. Although the mechanism involving H migration can account for the D distribution, the reaction is not retarded by addition of cation and radical quenchers (*e.g.* MeOH and hydroquinones, respectively) and intermediate **4** cannot be trapped by diphenylethylene and ethyl acrylate (cation and radical trapping agents).

In order to obtain further information on the properties of the μ-methylene complexes, a benzene-d_6 solution of the labeled compound $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}{}^*CD_2)({}^*CO)_2$ (**1a**-*CD$_2$; *C = *ca.* 30% ^{13}C-enriched) was subjected to irradiation *in the absence of nbd* (Scheme 3). As a result, the intensity of the quintet μ-*CD$_2$ signals of **1a**-*CD$_2$ [δ_C 107.4 (*cis* isomer), 108.8 (*trans* isomer)] diminished and instead there appeared the triplet (*cis*-**1a**-*CDH: δ_C 107.7) and then the singlet signals (*cis*-**1a**-*CH$_2$: δ_C 108.8) as shown in Fig. 1.¶ An equilibrated mixture of the isotopomers was obtained after 40 h irradiation. The spectral changes unequivocally indicates that the hydrogen atoms attached to the two methylene carbon atoms exchange with each other. Similar isomerization was also observed for $Cp_2Ru_2(\mu\text{-}CD_2)(\mu\text{-}CHCH_3)(CO)_2$ **1b**-d_2, which was converted to $Cp_2Ru_2(\mu\text{-}CDH)(\mu\text{-}CDCH_3)(CO)_2$. A plausible intermediate for the exchange reaction of **1a** is the μ-methylidyne species $Cp_2Ru_2(\mu\text{-}CH)(\mu\text{-}CH_2)(H)(CO)$ **4′** formed by decarbonylation followed by H migration from the bridging carbon atom to the ruthenium center; the H–D exchange reaction would be completed by a 1,3-H(D) shift, reversed H(D) migration and CO recombination.



Scheme 3

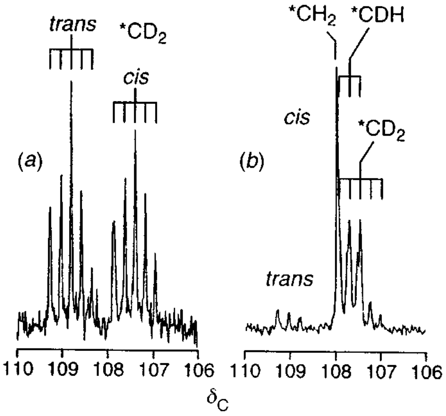


Fig. 1 ^{1}H decoupled ^{13}C NMR spectra of **1a**-*CD$_2$:expanded views of the μ-CH$_2$ region (*a*) before and (*b*) after irradiation for 40 h.

In summary, we have reported the two photochemical C–H bond cleavage reactions of the bridging alkylidene complexes **1**; the present work reveals a new type of functionalization of bridging alkylidene complexes by way of μ-alkylidyne intermediates. In addition, combined with our previous results of the $CH_3 \leftrightarrow CH_2\text{–}H$[4b] and $CH_2 \leftrightarrow CH\text{–}H$ interconversions[4c] on diruthenium systems, our results suggest the occurrence of analogous interconversions of CH_x species (x = 1–3) on a catalyst surface.

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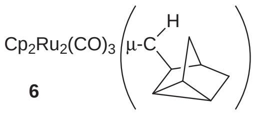
Notes and references

† *Selected data* for **2a**: $\delta_H(C_6D_6)$ 9.26 (d, *J* 11.7, μ-CH), 6.40, 6.15 (m, =CH), 4.71, 4.67 (Cp$_2$); $\nu(CH_2Cl_2)/cm^{-1}$ 1946, 1913 (CO). For **2b**: $\delta_H(C_6D_6)$ 9.60 (d, *J* 7.3, μ-C*H*CH$_3$), 9.25 (q, $^3J_{HH}$ 11.7, μ-CH), 6.42, 6.16 (m, =CH), 4.62, 4.60 (Cp$_2$), 3.10 (d, $^3J_{HH}$ 11.7, CHCH$_3$); $\nu(CH_2Cl_2)/cm^{-1}$ 1949, 1914 (CO). For **6**: $\delta_H(C_6D_6)$ 10.03 (d, $^3J_{HH}$ 11.2, μ-CH), 4.70 (Cp$_2$); $\nu(CH_2Cl_2)/cm^{-1}$ 1974, 1934, 1779 (CO).

‡ X-Ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo-Kα radiation. The structure was solved by using the SHELXL-93 least-squares program (refined on F^2) linked to the teXsan crystal structure analysis package. *Crystal data* for **2a′**: $C_{30}H_{34}O_2Ru_2$, M = 628.7, T = −60 °C, orthorhombic, space group *Pbca*, a = 17.621(2), b = 18.267(2), c = 16.085(4) Å, V = 1552(1) Å^3, Z = 8, D_c = 1.61 g cm^{-3}, μ = 11.92 cm^{-1}, R_1 = 0.072 for the 4828 data with $F_o > 4\sigma(F_o)$ and 317 parameters. CCDC 182/1094.

§ Similar reaction of the mono-μ-methylene complex, $Cp_2Ru_2(\mu\text{-}CH_2)(CO)_3$, also resulted in C–C coupling to give $Cp_2Ru_2(\mu\text{-}CH\text{-}nortricyclyl)(CO)_3$ **6**.



¶ Irradiation of **1a** initially brought about the *trans*-to-*cis* isomerization (within 1 h) as can be seen from the spectral change. Similar isomerization is usually observed for the related $Cp_2M_2(\mu\text{-}X)_2(CO)_2$ systems (M = Ru, Fe) (ref. 7).

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