Carbon–carbon bond cleavage and skeletal rearrangement of coordinated norbornadiene. Preparation of a η^6-6-methylfulvene complex $[(C_5Me_5)Ru(C_5H_4CHCH_3)]BF_4$

Hiroharu Suzuki [a], Takeaki Kakigano [b], Hideno Fukui [b], Masako Tanaka [a] and Yoshihiko Moro-oka [b]

[a] *Department of Chemical Engineering, Faculty of Engineering;* [b] *Research Laboratory of Resources Utilization; Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152 (Japan)*

(Received December 8, 1993; in revised form February 9, 1994)

Abstract

The reaction of $(C_5Me_5)Ru(nbd)Cl$ (**1**) (nbd = norbornadiene) with $AgBF_4$ in ethanol yields $[(C_5Me_5)Ru(nbd)](BF_4)$ (**2a**), which undergoes skeletal rearrangement of the coordinated norbornadiene initiated by C(1)–C(2) bond cleavage to form a 6-methylfulvene complex $[(C_5Me_5)Ru(C_5H_4CHCH_3)](BF_4)$ (**3**) upon stirring in dichloromethane. Complex **3** is directly derived from **1** by the treatment with $AgBF_4$ in non-coordinating solvent such as CH_2Cl_2. Treatment of **3** with t-BuOOLi followed by pyrolysis affords an acetylruthenocene complex $(C_5Me_5)Ru(C_5H_4COCH_3)$ (**5**) by way of $(C_5Me_5)Ru[C_5H_4CH(OOtBu)CH_3]$ (**4**). The molecular structure of **2b** is determined by an X-ray diffraction study.

Key words: Ruthenium; Bond cleavage; Norbornadiene

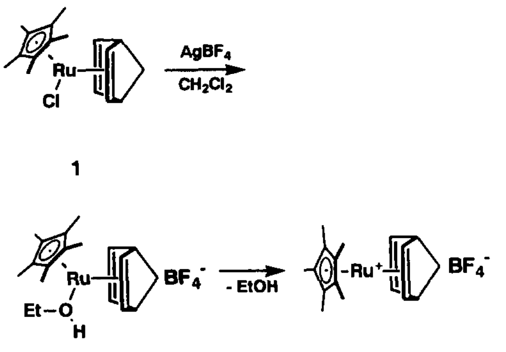
1. Introduction

While there have been numbers of reported examples of alkane C–H activation by transition metal complexes [1], relatively few examples of C–C bond cleavage have been reported [2]. Most common examples of C–C bond cleavage are caused by 5,5-dialkylated cyclopentadienes or highly-strained hydrocarbons such as cyclopropanes or cubane, which add extra stability to the products owing to the formation of an aromatic ring or the strain release of breaking the C–C bond. Here, we describe a novel skeletal rearrangement of a coordinated norbornadiene to 6-methylfulvene induced by coordinative unsaturation at the ruthenium centre.

2. Results and discussion

2.1. Preparation and molecular structure of $[(C_5Me_5)Ru(nbd)](BF_4)$ (2a)

Treatment of $(C_5Me_5)Ru(nbd)Cl$ (**1**) (nbd = norbornadiene) [3] with one equivalent of $AgBF_4$ in ethanol at ambient temperature for a day gives yellowish orange suspension. Filtration through a column packed with Celite followed by removal of solvent from the filtrate under reduced pressure yields a cationic complex **2a** having C_5Me_5 and norbornadiene ligands as orange crystalline solid (eqn. (1)).



1

2a

(1)

The ^1H-NMR spectra of **2a**, measured in $CDCl_3$, reveals only four signals, one for the C_5Me_5 ligand at δ 1.56 and three for the norbornadiene ligand at δ 2.05 (2H, bridge), 4.20 (2H, bridgehead), and 4.27 (4H,

---

Correspondence to: Dr. H. Suzuki.

SSDI 0022-328X(94)24639-Z

olefinic). If **2a** has an octahedral configuration, five resonance signals (two non-equivalent sets of olefinic protons, two non-equivalent bridgehead protons, and equivalent bridge protons) should be observed for the coordinated norbornadiene. The NMR data for **2a** strongly suggest that **2a** has two pseudo mirror planes, one of them bisects the carbon–carbon double bonds of the norbornadiene ligand and the other contains bridge and bridgehead carbons. Complex **2a** is, therefore, unsaturated (16e) in chloroform. In ethanol solution, **2a** would be stabilized by the coordination of the solvent molecule. Recrystallization from the mixed solvent of ethanol and diethyl ether affords yellow prismatic single crystals of $[(C_5Me_5)Ru(nbd)(H_2O)](BF_4)$ (**2b**) which is saturated and stabilized by the coordination of a water molecule instead of ethanol. The water molecule coordinated in **2b** originates in the moisture included in diethyl ether. The structure of **2b** was assigned on the basis of ^{1}H-NMR, ^{13}C-NMR, IR spectroscopy and elemental analysis. The ^{1}H-NMR spectrum measured in $CDCl_3$ reveals magnetically equivalent protons bound to a bridge carbon (δ 1.50) and two nonequivalent sets of bridgehead protons (δ 3.82 and 3.92) and olefinic protons (δ 4.21 and 4.71). These results show that complex **2b** has an octahedral configuration and the water molecule is coordinated to the ruthenium centre even in $CDCl_3$. The resonance signal of the coordinated water overlaps with that of olefinic protons at δ 4.71.

A coordinatively saturated cationic complex $[(C_5Me_5)Ru(nbd)(CH_3CN)](BF_4)$ (**2c**) is prepared by the reaction of **1** with $AgBF_4$ in CH_3CN. Complex **2c** is obtained via an alternative route. The weakly coordinated solvent molecule in **2b** can be readily exchanged with CH_3CN to form **2c** by dissolving **2b** in CH_3CN.

The molecular structure of **2b** was confirmed by single crystal X-ray diffraction. The results are displayed in Fig. 1 using a numbering scheme; Table 1 lists some of the relevant bond distances and angles.

The crystal structure reveals the presence of eight molecules in the unit cell; they are two kinds of crystallographically independent, chemically identical molecules. These molecules showed the expected structure, in that they contained a water molecule coordinated to the ruthenium centre. The Ru–O distance of 2.238(5) Å is somewhat longer than that observed in $[C_5Me_5)Ru(CO)_2(H_2O)](CF_3SO_3)$ (2.173(3) Å) [4], but is comparable with the values of 2.234(11) and 2.246(7) Å found in $(C_5Me_5)Ru[(\mu\text{-}CH(CO_2Me)CH(CO_2Me))(\mu\text{-}C(CO_2Me)CH(CO_2Me))](\mu\text{-}H)Ru(C_5Me_5)$ [5] and $(Ph_3P)_3RuH[CH{=}C(CH_3)\text{-}CO_2C_4H_9]$ [6], respectively, where the oxygen atom is coordinated to ruthenium through lone-pair electrons. The average bond distance of 2.201(8) Å between Ru and olefinic carbon of norbornadiene is similar to those in $(PPh_3)_2Ru(nbd)Cl_2$ (2.205 Å) [7] and $[(C_5H_5)Ru(nbd)(PPh_3)](ClO_4)$ (2.235 Å) [8] and is consistent with the values between Ru and π-bonded carbon atoms. The BF_4 anions are omitted

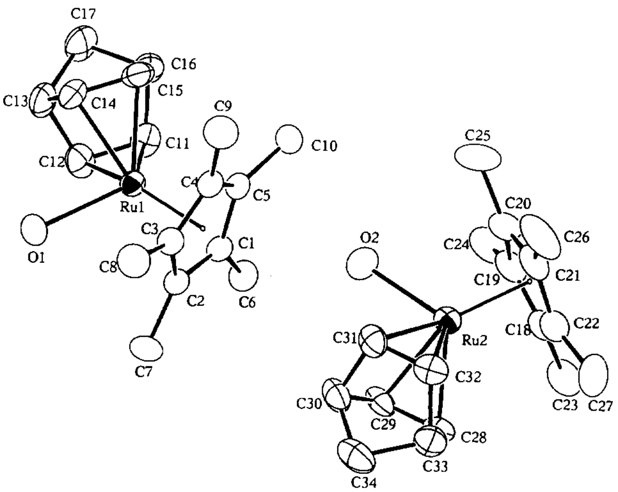
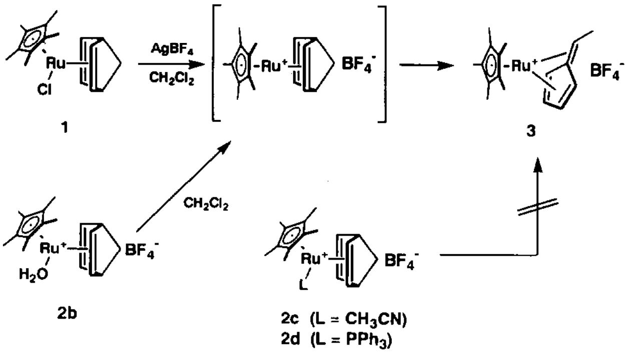


Fig. 1. Molecular structure of $[(C_5Me_5)Ru(nbd)(H_2O)](BF_4)$ (**2b**). The BF_4 anions are omitted for clarity. The thermal elipsoids correspond to 30% probability.

TABLE 1. Selected bond distances (Å) and angles (°) for **2b**

Ru1–C1	2.223(7)	Ru2–C18	2.218(9)
Ru1–C2	2.217(8)	Ru2–C19	2.210(8)
Ru1–C3	2.217(8)	Ru2–C20	2.206(8)
Ru1–C4	2.218(8)	Ru2–C21	2.218(8)
Ru1–C5	2.148(8)	Ru2–C22	2.161(8)
Ru1–C11	2.217(8)	Ru2–C28	2.217(8)
Ru1–C12	2.192(8)	Ru2–C29	2.178(8)
Ru1–C14	2.187(8)	Ru2–C31	2.199(8)
Ru1–C15	2.208(8)	Ru2–C32	2.209(8)
Ru1–O1	2.248(4)	Ru2–O2	2.227(5)
C11–C12	1.39(1)	C28–C29	1.38(1)
C12–C13	1.53(1)	C29–C30	1.53(1)
C13–C14	1.51(1)	C30–C31	1.53(1)
C14–C15	1.39(1)	C31–C32	1.37(1)
C15–C16	1.50(1)	C32–C33	1.52(1)
C16–C11	1.50(1)	C33–C28	1.52(1)
C13–C17	1.57(1)	C30–C34	1.52(1)
C16–C17	1.53(1)	C33–C34	1.52(1)
O1–Ru1–C11	118.1(3)	O2–Ru2–C28	116.3(3)
O1–Ru1–C12	81.4(3)	O2–Ru2–C29	79.8(3)
O1–Ru1–C14	80.9(3)	O2–Ru2–C31	80.0(3)
O1–Ru1–C15	117.6(3)	O2–Ru2–C32	116.1(3)
C11–C12–C13	105.5(8)	C28–C29–C30	105.7(8)
C12–C13–C14	100.3(7)	C29–C30–C31	100.8(7)
C13–C14–C15	105.7(8)	C30–C31–C32	105.5(8)
C14–C15–C16	107.5(8)	C31–C32–C33	107.1(8)
C15–C16–C11	98.9(7)	C32–C33–C28	99.1(7)
C16–C11–C12	107.4(8)	C33–C28–C29	106.6(8)
C13–C17–C16	92.9(7)	C30–C34–C33	94.2(7)



Scheme 1.

from Fig. 1 for clarity although one of the two independent BF_4 anions is disordered.

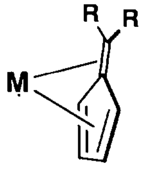
2.2. Skeletal rearrangement of [$(C_5Me_5)Ru(nbd)$](BF_4) (2a)

As mentioned above, the reaction of **1** with $AgBF_4$ in coordinating solvent affords a stable coordinatively saturated (18e) cationic complex [$(C_5Me_5)Ru(nbd)(sol)$](BF_4). If the reaction of **1** with $AgBF_4$ is conducted in non-coordinating or poorly coordinating solvent, the generation of an unsaturated (16e) cationic species [$(C_5Me_5)Ru(nbd)$](BF_4) is expected. Such a cationic species would undergo skeletal rearrangement, initiated by the C–C bond cleavage, to form a stable complex with 18e configuration since the cleavage of a bridgehead C–H bond of norbornadiene coordinated in **2** is prohibited according to "Bredt's rule". Treatment of **1** with $AgBF_4$ in dichloromethane at room temperature for 12 h yields a cationic fulvene complex [$(C_5Me_5)Ru(\eta^6\text{-}C_5H_4{=}CHCH_3)$]$(BF_4)$ (**3**) in 54% yield (Scheme 1).

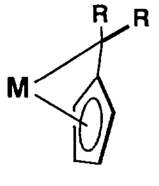
Complex **3** is also derived from the cationic complex **2b** in which a water molecule is weakly coordinated to the ruthenium centre. When the cationic complex **2b** is dissolved and stirred for a day in non-coordinating solvent, e.g. CH_2Cl_2 or $CHCl_3$, the fulvene complex **3** is formed from a coordinatively unsaturated (16e) species [$(C_5Me_5)Ru(nbd)$](BF_4) which is generated by a partial dissociation of a coordinated water molecule.

Complex **3** was characterized on the basis of ^1H-NMR, ^{13}C-NMR, IR spectral data and elemental analysis. The ^1H-NMR spectrum of **3** reveals one set of doublet and quartet, with a coupling constant of 6.6 Hz, ascribed to the ethylidene group of coordinated fulvene at δ 1.89 and 5.62. Signals for ring protons of the fulvene ligand appear at δ 4.81, 5.24, 5.75, and 5.86. In the ^{13}C-NMR spectrum, resonance signals for methyl and methine carbons of ethylidene group are observed at δ 15.2 (q, $J = 127.8$ Hz) and 100.1 (d, $J = 163.6$ Hz), respectively.

The importance of a "fulvene-like" π-bonded type (**A**) *vs.* a σ,η^5-cyclopentadienyl-type (**B**) description is proposed to account for the structural and spectral features of the η^6-C_5H_4CRR' transition metal complexes.



[A]

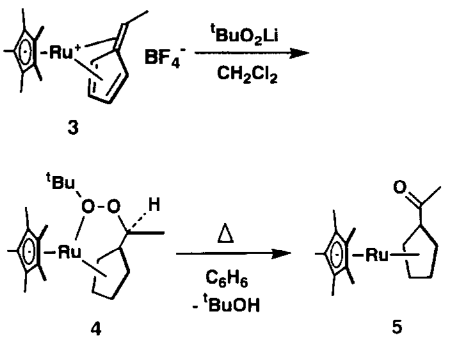


[B]

From the standpoint of the **A** ↔ **B** description, the ^{13}C-NMR parameters, δ ($^{13}C(a)$) and $J_{C(\alpha)-H}$ should be most informative [9]. The olefinic carbon atoms generally exhibit an upfield chemical shift upon coordination. For the η^6-fulvene-type complex **A**, the ^{13}C signal of α-carbon appears in the ordinary region of olefin π-bonded to the metal centre, and the $J_{C(\alpha)-H}$ value is comparable with that observed for olefin. However, the δ ($^{13}C(\alpha)$) for the σ,η^5-cyclopentadienyl-type complex **B** shifts to a higher magnetic field than that observed for complex **A** owing to the increase in the σ-bond character between the α-carbon and metal centre. The δ ($^{13}C(\alpha)$) value of δ 100.1 and the $J_{C(\alpha)-H}$ value of 163.6 Hz are indicative of the "η^6-fulvene-type" coordination of the "$C_5H_4CHCH_3$" ligand in **3**.

Rearrangement of norbornadiene to 6-methylfulvene is induced by coordinative unsaturation generated on the ruthenium centre. Such a skeletal rearrangement of the ligand is, therefore, expected to be depressed in the presence of donor ligands. When the cationic norbornadiene–ruthenium complexes **2c** and **2d** [3] were stirred in dichloromethane for 50 h, no reaction proceeded and the starting complexes were completely recovered.

The cleavage of carbon–carbon bonds of the coordinated bicyclic olefins initiated by protonation has been reported by Bennett *et al.* [10] and Bly *et al.* [11]. We examined the participation of HBF_4 in the rearrangement of **1** to **3**. The reaction of cationic complexes of **2b**, **2c**, and **2d** in dichloromethane in the presence of 0.1 equiv. HBF_4 was monitored using ^1H-NMR spectroscopy. In spite of addition of the acid to the dichloromethane solution of the complexes **2c** and **2d**, rearrangement of norbornadiene ligand was not observed, and **2c** and **2d** were recovered quantitatively. Furthermore, addition of HBF_4 to a solution of **2b** neither accelerated the rate of the rearrangement nor changed the reaction product. From these results, it can be concluded that coordinative unsaturation of the metal centre is the most dominant driving force of the



Scheme 2.

skeletal rearrangement of the coordinated norbornadiene to 6-methylfulvene.

An attempt to obtain a X-ray grade single crystal of the fulvene complex **3** was, unfortunately, unsuccessful. Therefore, we decided to convert **3** to a structurally well-established compound to confirm the structure of **3**.

We previously reported that t-butylperoxide anion nucleophilically attacked the olefinic ligand in the reaction of saturated (18e) cationic olefin–transition metal complexes with lithium t-butylperoxide, whereas the anion directly attacked cationic metal centre to form a t-butylperoxo–metal complex in the reaction of a cationic complex with 16-electron configuration [12]. Since the fulvene complex **3** is saturated, nucleophilic attack of t-BuOO$^-$ at the α-carbon of the coordinated 6-methylfulvene forming a substituted ruthenocene would be expected. Treatment of **3** with 1.2 equiv. lithium t-butylperoxide in dichloromethane at -35°C afforded a novel α-*t*-butylperoxyethylruthenocene $(C_5Me_5)Ru[\eta^5\text{-}C_5H_4CH(OO^tBu)CH_3]$ (**4**) in 74% yield (Scheme 2).

The spectral data for **4** are consistent with the structure shown in Scheme 2. In the IR spectrum of **4** characteristic bands assigned to the stretching vibration of C–O and O–O bonds appear at 1199 and 860 cm^{-1}, respectively. The ^{1}H-NMR spectrum for **4** exhibits a substantial upfield chemical shift compared with the fulvene complex **3**. The signals of methine and methyl protons attached to α-carbon are observed at δ 4.80 (q, $J = 6.3$ Hz) and 1.53 ppm; whereas those for **3** appear δ 5.62 and 1.89 ppm, respectively. The values of δ 4.80 and 1.53 ppm are comparable with those reported for the α-hydroxyethylferrocene $(C_5H_5)Fe[C_5H_4CH(OH)\text{-}CH_3]$ (δ 4.48 and 1.42 ppm) [13]. The resonances for ring protons are also higher than those for **3** by *ca.* 1.15 (av.) ppm.

Complex **4** is fairly stable both in solid state and in solution, but slowly decomposes to form 1,2,3,4,5-pentamethyl-1′-acetylruthenocene $(C_5Me_5)Ru(C_5H_4CO\text{-}CH_3)$ (**5**) and t-butanol upon heating in benzene. The pyrolysis was monitored using ^{1}H-NMR spectroscopy. When a solution of **4** in C_6D_6 was heated at 80°C, singlet peaks at δ 1.86 and 1.24 ascribed to the signals for the C_5Me_5 and t-butyl groups in **4** significantly decrease in the intensity. With increasing reaction time, a progressive increase in the intensity of the new signals for acetylruthenocene **5** at δ 1.72 (C_5Me_5) and 1.96 ($-COCH_3$) as well as that for t-butanol at δ 1.12 was observed. The reaction completed after 15 h. Acetylruthenocene **5** formed in this reaction was isolated by column chromatography and identified by direct comparison with an authentic sample which was derived from $(C_5Me_5)Ru(C_5H_5)$ according to the reported method for iron analogues [14]. Formation of t-butanol was also confirmed by GLC analysis. These observations as well as the spectral data warrant the structures of the complexes **4** and **3**.

Further mechanistic studies pertaining to the formation of **3** will be reported in due course.

3. Experimental details

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. IR spectra were recorded on a Hitachi 260-50 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL GX-270 and GX-500 instruments Elemental analysis was performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology.

$(C_5Me_5)Ru(nbd)Cl$ [3] and $(C_5Me_5)Ru(C_5H_5)$ [15] were prepared according to previously published methods.

3.1. *[(C$_5$Me$_5$)Ru(norbornadiene)](BF$_4$)* (2a)

A 50-ml Schlenk tube was filled with 0.364 g (1 mmol) of $(C_5Me_5)Ru(nbd)Cl$ (**1**), 0.195 g (1 mmol) of $AgBF_4$, and 10 ml of ethanol. After stirring at ambient temperature for 15 h, the resulting mixture was filtered. Solvent was removed from the filtrate under reduced pressure to leave an orange solid (**2a**) which was washed with three portions of 10 ml of diethyl ether and dried *in vacuo*. Yield was 0.609 g (91%); Mp. 238.5–240°C. IR (KBr, cm^{-1}): 3064, 3009, 2952, 2915, 1409, 1301, 1183, 1071, 1029, and 754. ^{1}H-NMR ($CDCl_3$): δ 1.56 (15H, s, C_5Me_5), 2.05 (2H, m, bridge–H), 4.20 (2H, m, bridgehead–H), 4.72 (4H, m, olefinic–H).

3.2. *[(C$_5$Me$_5$)Ru(norbornadiene)(H$_2$O)](BF$_4$)* (2b)

A 50-ml Schlenk tube was filled with 0.475 g (1.30 mmol) of **1**, 0.253 g (1.30 mmol) of $AgBF_4$, and 10 ml of ethanol. The mixture was stirred at ambient temperature for 12 h. Precipitated AgCl was removed by filtration. The orange–yellow filtrate was concentrated and diethyl ether was added. Cooling the solution at −20°C afforded 0.259 g (46%) of **2b** as yellow prisms. Mp. 248–248.5°C. IR (KBr, cm^{-1}): 3430, 3062, 3000, 2949, 2910, 1620, 1509, 1483, 1448, 1416, 1407, 1383, 1307, 1180, 1158, 1052, 870, 795, 760, 611, and 525. ^1H-NMR ($CDCl_3$): δ 1.50 (2H, br, bridge–H), 1.56 (15H, s, C_5Me_5), 3.82 (1H, br, bridgehead–H), 3.92 (1H, br, bridgehead–H), 4.21 (2H, t, $J = 4.0$ Hz, olefinic–H), 4.71 (4H, t, $J = 4.0$ Hz, olefinic–H and H_2O). ^{13}C-NMR ($CDCl_3$): δ 9.3 (q, $J = 128.0$ Hz, $C_5\mathit{Me}_5$), 48.2 (d, $J = 153.8$ Hz, bridgehead), 51.6 (d, $J = 158.1$ Hz, bridgehead), 64.2 (t, $J = 132.5$ Hz, bridge), 64.8 (d, $J = 183.7$ Hz, olefinic), 78.4 (d, $J = 186.8$ Hz, olefinic), 94.4 (s, C_5Me_5). Anal. found: C, 47.12; H, 5.93. $C_{17}H_{25}BOF_4Ru$ calcd. (Mw 433.3): C, 47.13; H, 5.82.

3.3. *[(C_5Me_5)Ru(norbornadiene)(CH_3CN)](BF_4) (2c)*

A 50-ml Schlenk tube was filled with 0.238 g (0.66 mmol) of **1**, 0.128 g (0.66 mmol) of $AgBF_4$, and 10 ml of CH_3CN. After the mixture was stirred at room temperature for 15 h, the precipitate of AgCl was removed by filtration. Removal of solvent from the filtrate *in vacuo* gave a yield yellow–orange solid, **2c**. Crystallization from the mixed solvent of CH_2Cl_2 and Et_2O gave 0.220 g (73%) of **2c** as orange prisms. Mp. 145–146°C. IR (KBr, cm^{-1}): 3086, 3063, 2995, 2956, 2913, 1504, 1455, 1423, 1384, 1305, 1184, 1155, 1032, 870, 767, 538, and 527. ^1H-NMR ($CDCl_3$) δ 1.40 (2H, t, $J = 0.15$ Hz, bridge–H), 1.65 (15H, s, C_5Me_5), 2.79 (3H, s, CH_3CN), 3.65 (1H, m, bridgehead–H), 3.91 (1H, m, bridgehead–H), 3.98 (2H, t, $J = 3.6$ Hz, olefinic–H), 4.43 (2H, t, $J = 3.6$ Hz, olefinic–H). ^{13}C-NMR ($CDCl_3$): δ 4.6 (q, $J = 137.9$ Hz, $\mathit{C}H_3CN$), 9.9 (q, $J = 128.1$ Hz, $C_5\mathit{Me}_5$), 46.4 (d, $J = 153.2$ Hz, bridgehead), 50.0 (d, $J = 145.8$ Hz, bridgehead), 61.9 (d, $J = 179.0$ Hz, olefinic), 63.4 (t, $J = 134.0$ Hz, bridge), 74.1 (d, $J = 180.0$ Hz, olefinic), 94.2 (s, C_5Me_5), 130.4 (s, $CH_3\mathit{C}N$). Anal. found: C, 49.91; H, 5.80; N, 2.97. $C_{19}H_{26}BNF_4Ru$ calcd. (Mw. 456.3): C, 50.01; H, 5.74; N, 3.07.

3.4. *[(C_5Me_5)Ru(η^6-6-methylfulvene)](BF_4) (3)*

A 50-ml Schlenk tube was filled with 0.601 g (1.65 mmol) of **1**, 0.479 g (2.39 mmol) of $AgBF_4$, and 10 ml of dichloromethane. After stirring at ambient temperature for 12 h, the mixture was filtered. Solvent was removed from the filtrate under reduced pressure to leave a pale yellow solid, **3**, which was washed with two portions of 10 ml of diethyl ether and dried *in vacuo*. Crystallization from dichloromethane afforded 0.371 g (54%) of **3** as pale yellow prismatic solid. Mp. 244–245°C. IR (KBr, cm^{-1}): 3108, 2969, 2816, 1479, 1431, 1392, 1059, 1031, 882, 851, 527, 393, and 348. ^1H-NMR ($CDCl_3$): δ 1.89 (3H, d, $J = 6.6$ Hz, $= CHC\mathit{H}_3$), 1.99 (15H, s, $C_5\mathit{Me}_5$), 4.81 (1H, m, $C_5\mathit{H}_4{=}CHCH_3$), 5.24 (1H, m, $C_5\mathit{H}_4{=}CHCH_3$), 5.62 (1H, q, $J = 6.6$ Hz, $={C\mathit{H}}CH_3$), 5.75 (1H, m, $={C\mathit{H}}CH_3$), 5.86 (1H, m, $={C\mathit{H}}CH_3$). ^{13}C-NMR ($CDCl_3$): δ 9.5 (q, $J = 128.8$ Hz, $C_5\mathit{Me}_5$), 15.2 (q, $J = 127.8$ Hz, $=CH\mathit{C}H_3$), 79.5 (d, $J = 189.6$ Hz, $\mathit{C}_5H_4{=}CHCH_3$), 82.3 (d, $J = 185.6$ Hz, $\mathit{C}_5H_4{=}CHCH_3$), 94.9 (d, $J = 183.0$ Hz, $\mathit{C}_5H_4{=}CHCH_3$), 95.4 (d, $J = 183.0$ Hz, $\mathit{C}_5H_4{=}CHCH_3$), 97.6 (s, C_5Me_5), 100.1 (d, $J = 163.5$ Hz, $C_5H_4{=}\mathit{C}HCH_3$), 105.0 (s, $C_4H_4\mathit{C}{=}CCH_3$). Anal. found: C, 48.87; C, 5.49. $C_{17}H_{23}BF_4Ru$ calcd. (Mw 415.2): C, 49.17; H, 5.58.

3.5. *(C_5Me_5)Ru[η-$C_5H_4CH(OO^tBu)CH_3$] (4)*

Potassium *t*-butylperoxide (0.349 g, 2.72 mmol) was added to a stirred solution of **3** (0.125 g, 0.30 mmol) in dichloromethane (5 ml) at −35°C. After being stirred at −35°C for 0.5 h, solvent was removed under reduced pressure to leave a brown solid. Extraction with three portions of 10 ml of pentane from the residual solid and removal of solvent from the combined extract *in vacuo* afforded a yield of 0.093 g (74%) of **4** as yellow oily substance. IR (C_6H_6, cm^{-1}): 3093, 2973, 2903, 1476, 1456, 1381, 1363, 1309, 1261, 1239, 1199, 1069, 1031, 860, 808, and 447. ^1H-NMR (C_6D_6): δ 1.24 (9H, s, $-C\mathit{Me}_3$), 1.53 (3H, d, $J = 6.3$ Hz, $-CH(O_2{}^tBu)\mathit{Me}$), 1.85 (15H, s, $C_5\mathit{Me}_5$), 4.08 (2H, m, $C_5\mathit{H}_4$–$CH(O_2{}^tBu)Me$), 4.29 (1H, m, $C_5\mathit{H}_4$–$CH(O_2{}^tBu)Me$), 4.41 (1H, m, $C_5\mathit{H}_4$–$CH(O_2{}^tBu)Me$), 4.80 (1H, q, $J = 6.3$ Hz, $-C\mathit{H}(O_2{}^tBu)Me$). Anal. found: C, 59.92; H, 7.70. $C_{21}H_{32}O_2Ru$ calcd. (Mw 417.6): C, 60.41; H, 7.72.

3.6. *Pyrolysis of (C_5Me_5)Ru[η^5-$C_5H_4CH(OO^tBu)CH_3$] (4)*

(C_5Me_5)Ru[η^5-$C_5H_4CH(OO^tBu)CH_3$] (**4**) (0.036 g, 0.086 mmol) and benzene-d_6 (0.4 ml) were placed in a 5 m/m NMR sample tube filled with argon. Just after the NMR sample tube was sealed, a ^1H-NMR spectrum was taken at 25°C. The sample was then heated at 80°C, and ^1H-NMR spectra were taken three times at 4-h intervals, and additionally, once at 3-h intervals at 80°C. With the reaction time, a progressive increase in the intensity of the signals for acetylruthenocene **5** and a significant decrease in those for **4** were observed. Signals for the starting compound **4** disappeared after 15 h, and the yield of **5** reached over 90% (by ^1H-NMR). The solution was analysed using GLC after completion of the pyrolysis, and GLC analysis showed the formation of *t*-butanol. Complex **5** was isolated by column chromatography on alumina and identified by direct comparison with an authentic acetylruthenocene **5** derived from (C_5Me_5)Ru(C_5H_5) (see below).

3.7. $(C_5Me_5)Ru[\eta^5\text{-}C_5H_4COCH_3]$ (5)

To a stirred solution of $AlCl_3$ (0.634 g, 4.76 mmol) and acetyl chloride (0.45 ml, 6.30 mmol) dichloromethane (15 ml) was added 1,2,3,4,5-pentamethylruthenocene $(C_5Me_5)(C_5H_5)Ru$ (0.918 g, 3.05 mmol) at 0°C. After stirring at ambient temperature for 36 h, the reaction mixture was poured into cooled (0°C) water. Products were extracted with three portions of 10 ml of dichloromethane. The combined organic phase was washed three times with 10 ml of aqueous $NaHCO_3$ (1N), and dried over $MgSO_4$. Purification by column chromatography on alumina (Merck, Art. 1097) with n-hexane/Et_2O (6/1) and by thin-layer chromatography on alumina (Merck, Art. 5788) with n-hexane/Et_2O (6/1) gave $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4COCH_3)$ (**5**) (0.310 g, 30%), $(C_5Me_5)Ru[(\eta^5\text{-}C_5H_3(COCH_3)_2]$ (**6**) (0.121 g, 10%), and recovered $(C_5Me_5)(C_5H_5)Ru$ (0.360 g, 39%). **5**: Mp. 115–115.2°C. IR (KBr, cm^{-1}): 3097, 3083, 2964, 2889, 1664, 1472, 1450, 1418, 1395, 1377, 1363, 1348, 1335, 1273, 1107, 1069, 1055, 1032, 1010, 952, 888, 834, 814, 653, 618, and 516. ^{1}H-NMR ($CDCl_3$): δ 1.72 (15H, s, C_5Me_5), 1.96 (3H, s, $-COMe$), 4.20 (2H, t, $J = 1.8$ Hz, C_5H_4COMe), 4.63 (2H, t, C_5H_4COMe). ^{13}C-NMR ($CDCl_3$): δ 11.3 (q, $J = 126.5$ Hz, C_5Me_5), 26.4 (q, $J = 126.4$ Hz, $-COMe$), 73.1 (d, $J = 175.8$ Hz, C_5H_4COMe), 76.3 (d, $J = 177.6$ Hz, C_5H_4COMe), 86.0 (s, C_5Me_5), 196.0 (s, $-COMe$). Anal. found: C, 59.79; H, 6.66. $C_{17}H_{22}ORu$ calcd. (Mw 343.4): C, 59.45; H, 6.46. **6**: Mp. 126.5–127°C. IR (KBr, cm^{-1}): 3080, 2970, 2962, 2895, 1663, 1654, 1470, 1437, 1400, 1380, 1352, 1342, 1264, 1233, 1154, 1109, 1070, 1055, 1033, 1014, 969, 923, 870, 840, 648, 631, 577, 537, 488, 451, and 408. ^{1}H-NMR ($CDCl_3$): δ 1.61 (15H, s, C_5Me_5), 2.26 (6H, s, $-COMe$), 4.13 (1H, t, $J = 2.6$ Hz, $C_5H_3(COMe)_2$), 4.65 (2H, d, $J = 2.6$ Hz, $C_5H_3(COMe)_2$). ^{13}C-NMR ($CDCl_3$): δ 10.6 (C_5Me_5), 29.4 ($-COMe$), 76.6 ($C_5H_3(COMe)_2$), 79.5 ($C_5H_3(COMe)_2$), 86.0 ($C_5H_3(COMe)_2$), 87.2 (C_5Me_5), 197.8 ($-COMe$). Anal. found: C, 59.21; H, 6.42. $C_{19}H_{24}O_2Ru$ calcd. (Mw 385.5): C, 59.20; H, 6.28. In the ^{13}C-NMR spectra of **5** and **6**, the signals for ring carbons attached to the acetyl groups could not be detected because of long relaxation time of the carbons.

3.8. X-ray structure determination of $[(C_5Me_5)Ru(norbornadiene)(H_2O)](BF_4)$ (2b)

3.8.1. Data collection and reduction

An X-ray quality crystal of **2b** was obtained from the mixed solvent of ethanol and diethyl ether, and mounted on a glass fibre. Diffraction experiment was performed on a Rigaku AFC-5 four-circle diffractometer equipped with graphite-monochromated Mo-Kα radiation. The lattice parameters and orientation matrices were obtained and refined from 25 machine-centred reflections with $20° < \theta < 30°$. The compound crystallizes in the monoclinic space group $P2_1/a$ (No. 14) with $a = 16.456(1)$, $b = 16.815(2)$, $c = 13.349(4)$ Å, and $\beta = 92.70(1)°$; $V = 3689.7(9)$ Å^3; $Z = 8$; $D_{calc} = 1.560$ g cm^{-3}, μ(Mo-Kα) = 8.88 cm^{-1}. A total of 11550 reflections were collected using a ω–2θ scan technique to a maximum 2θ of 60°, and three standard reflections were recorded every 100 reflections. The data were processed using the TEXSAN crystal solution package operating on an Iris indigo computer. Neutral atom scattering factors were obtained from the standard sources [16]. In the reduction of the data, Lorentz/polarization corrections and empirical absorption correction based on azimuthal scans were applied to the data for structure.

3.8.2. Structure solution and refinement

The Ru atom positions were determined by heavy atom Patterson methods. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations, and refined anisotropically by using full-matrix least-squares techniques on F. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4047 observed reflections ($I > 5.00s(I)$) and 424 variable parameters and converged (largest parameter was 0.29 times its esd) with unweighted and weighted agreement factors of

$$R = \sum \| F_o - F_c \| / \sum | F_o | = 0.048$$

$$R_w = \sqrt{\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2} = 0.041$$

Acknowledgement

This research was supported by a Grant-in-Aid for Scientific Research on Priority Area (No. 05225210 and 05236104) from the Ministry of Education, Science, and Culture, Japan. The authors are grateful to Kanto Chemical Co., Inc. for a generous gift of pentamethylcyclopentadiene.

References

1 For examples, see: (a) A.E. Shirov, *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Reidel, Dordrecht, 1984; (b) R.H. Crabtree, *Chem. Rev., 85* (1985) 245; (c) M.L.H. Green and D. O'Hare, *Pure Appl. Chem., 57* (1985) 1987; (d) J. Halpern, *Inorg. Chim. Acta, 100* (1985) 41. and references cited therein.

2 For example, (a) C.F.H. Tipper, *J. Chem. Soc.*, (1955) 2043; (b) H. Hogeveen and H.C. Volger, *J. Am. Chem. Soc., 89* (1967) 2486; (c) J.W. Kang, R. Moseley and P.M. Maitlis, *J. Am. Chem.*

Soc., 91 (1969) 5970; (d) L. Cassar, P.E. Eaton and J. Halpern, *J. Am. Chem. Soc., 92* (1970) 6366; (e) L. Cassar and J. Halpern, *J. Chem. Soc. D,* (1971) 1082; (f) R.B. King and A. Efraty, *J. Am. Chem. Soc., 94* (1972) 3773; (g) F.W.S. Benfield and M.L.H. Green, *J. Chem. Soc., Dalton Trans.,* (1974) 1324; (h) K.C. Bishop, *Chem. Rev., 76* (1976) 461; (i) P. Eilbracht and P. Dahler, *Chem. Ber., 113* (1980) 542; (j) P. Eilbracht, P. Dahler, U. Mayser and E. Henkes, *Chem. Ber., 113* (1980) 1033; (k) P. Eilbracht, U. Mayser and G. Tiedtke, *Chem. Ber., 113* (1980) 1420; (l) P. Eilbracht and U. Mayser, *Chem. Ber., 113* (1980) 2211; (m) J.W. Suggs and S.D. Cox, *J. Organomet. Chem., 221* (1981) 199; (n) J.W. Suggs and C-H. Jun, *J. Am. Chem. Soc., 106* (1984) 3054; (o) T.C. Flood and J.A. Statler, *Organometallics, 3* (1984) 1794; (p) J.W. Suggs and C-H. Jun, *J. Chem. Soc., Chem. Commun.,* (1985) 92; (q) R.C. Hemond, R.P. Hughes and H.B. Locker, *Organometallics, 5* (1986) 2391; (r) J.W. Suggs and C-H. Jun, *J. Am. Chem. Soc., 108* (1986) 4679; (s) R.H. Crabtree, R.P. Dion, D.V. McGrath and E.M. Holt, *J. Am. Chem. Soc., 108* (1986) 7222.

3 N. Oshima, H. Suzuki and Y. Moro-oka, *Chem. Lett.,* (1984) 1161.

4 A. Thiri, V. Guerchais, L. Toupet and C. Lapinte, *J. Organomet. Chem., 381* (1990) C47.

5 H. Suzuki, H. Omori, D.H. Lee, Y. Yoshida, M. Fukushima, M. Tanaka and Y. Moro-oka, *Organometallics, in press.*

6 S. Komiya, T. Ito, M. Cowie, A. Yamamoto, J.A. Ibers, *J. Am. Chem. Soc., 98* (1976) 3874.

7 D.E. Bergbreiter, B.E. Bursten, M.S. Bursten and F.A. Cotton, *J. Organomet. Chem., 205* (1981) 407.

8 R. Uson, L.A. Oro, M.A. Ciriano, M.M. Naval, M.C. Apreda, C. Foces-foces, F.H. Cano and S. Garcia-Blanco, *J. Organomet. Chem., 256* (1983) 331.

9 (a) O. Koch, F. Edelmann and U. Behrens, *Chem. Ber., 115* (1982) 1313; (b) B. Lubke, F. Edelmann and U. Behrens, *Chem. Ber., 116* (1983) 11; (c) J.A. Bandy, V.S.B. Mtetwa, K. Prout, J.C. Green, C.E. Davies, M.L.H. Green, N.J. Hazel, A. Iszquierdo and J.J. Martin-Polo, *J. Chem. Soc., Dalton Trans.,* (1985) 2037; (d) U. Behrens, *J. Organomet. Chem., 182* (1979) 89; (e) V.G. Andiranov, Yu.T. Struchkov, V.N. Setkina, V.I. Zdanovich, A.Zh. Zhakaeva and D.N. Kursanov, *J. Chem. Soc., Chem. Commun.,* (1975) 117; (f) V.G. Andiranov and Yu. T. Struchkov, *J. Struct. Chem. (Engl. Transl.), 18* (1977) 251; (g) A.Z. Kreindlin, P.V. Petrovskii, M.I. Rybinskaya, A.I. Yanovskii and Yu. T. Struchkov, *J. Organomet. Chem., 319* (1987) 229; (h) M.I. Rybinskaya, A.Z. Kreindlin, Yu.T. Struchkov and A.I. Yanovsky, *J. Organomet. Chem., 359* (1989) 233; (i) L.E. Schock, C.P. Brock and T.J. Marks, *Organometallics, 6* (1987) 232.

10 M.A. Bennett, J.C. Nicholls, A.K.F. Rahman, A.D. Redhouse, J.L. Spencer and A.C. Willis, *J. Chem. Soc., Chem. Commun.,* (1989) 1328.

11 R.S. Bly, R.K. Bly, M.M. Hossain, L. Lebioda and M. Raja, *J. Am. Chem. Soc., 110* (1988) 7723.

12 (a) R. Sugimoto, H. Suzuki, Y. Moro-oka and T. Ikawa, *Chem. Lett.,* (1982) 1863; (b) N. Oshima, Y. Hamatani, H. Fukui, H. Suzuki and Y. Moro-oka, *J. Organomet. Chem., 303* (1986) C21.

13 G. Cerichelli, B. Floris and G. Ortaggi, *J. Organomet. Chem., 78* (1974) 241.

14 A.N. Nesmeyanov, M.I. Rybinskaya, G.B. Shul'pin and A.A. Pogrebnyak, *J. Organomet. Chem., 92* (1975) 341.

15 M.O. Albers, D.C. Liles, D.J. Robinson, A. Shaver, E. Singleton, M.B. Wiege, J.C.A. Boeyens and D.C. Levendis, *Organometallics, 5* (1986) 2321.

16 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch Press, Birmingham, 1975.