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BIS(1–3:5–6-η-CYCLOOCTADIENYL)RUTHENIUM: PREPARATION, NMR SPECTROSCOPY, AND ISOMERIZATION TO (η^6-1,3,5-CYCLOOCTATRIENE)(1–2:5–6-η-1,5-CYCLOOCTADIENE)RUTHENIUM VIA THE ACTIVATION OF A C–H BOND *

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Summary

The complex Ru(1–3:5–6-η-C_8H_{11})$_2$ (II) was prepared by the reduction of ruthenium trichloride hydrate with zinc in the presence of 1,5-cyclooctadiene at room temperature. Complex II, isomerized to Ru(η^6-C_8H_{10})(1–2:5–6-η-C_8H_{12}) (I) at 70 °C by the migration of a hydrogen atom from one 1–3:5–6-η-C_8H_{11} ligand to the other. The ^1H and ^{13}C NMR spectral evidence including selective irradiation studies suggests unsymmetrical coordination of the olefinic moiety of the 1–3:5–6-η-C_8H_{11} ligand in the complex II.

Introduction

Activation of C–H bonds by means of several transition metal complexes has attracted much attention in recent years [1a–1c]. Among a number of examples including the C–H bond activation of simple alkanes [1–4], the formation of (η^6-1,3,5-cyclooctatriene)(1–2:5–6-η-cyclooctadiene)ruthenium(0) (I) from 1,5-cyclooctadiene (COD) and reduced ruthenium species [2,3] seems to us a good model system for understanding the mechanism of allylic C–H bond activation processes. The Pertici's direct preparation of I involved formally a double activation of two allylic C–H bonds of a COD molecule to yield a 1,3,5-cyclooctatriene ligand in the final product I. In this context, the author reported a linked-norbornadiene Ru^{II} complex containing three molecular units of the diene and a coordinated C–H bond, when norbornadiene was employed as the diene component in a similar system [5,6]. The activation of any C–H bond did not occur in the case of norbornadiene because

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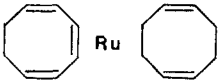
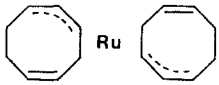
* Dedicated to Prof. Sei Otsuka on his 65th birthday.

the formally allylic C–H bonds are located at the bridgehead position. As a consequence, an alternative stepwise insertion of two norbornadienes took place from a ruthenium hydride intermediate [6].

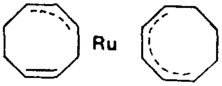
In this paper, we report that the title complex, $Ru(1-3:5-6-\eta-C_8H_{11})_2$ (II) is the key primary intermediate for the formation of the Ru^0 complex I. The thermal isomerization of II to I is a formal reduction process, Ru^{II} to Ru^0, induced by the hydrogen shift from one $1-3:5-6-\eta-C_8H_{11}$ ligand of II to the other one present in the same molecule. Secondly, the presence of unsymmetrical coordination of the η^2-olefin moiety is shown based on careful NMR spectroscopic evidence. Finally, we show some spectoscopic evidence for another $C_{16}H_{22}Ru$ isomer, $Ru(1-5-\eta-C_8H_{11})(1-3:5-6-\eta-C_8H_{11})$ (III), as well as the interrelation between the following four $C_{16}H_{22}Ru$ isomers, I–IV.



(I)



(II)



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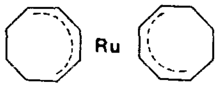


(IV)

Results and discussion

Although the first preparation of I was undertaken by Müller and Fischer several years ago by Grignard reduction of $[RuCl_2(COD)]_n$ in the presence of 1,3,5-cyclooctatriene under UV irradiation in poor yield [7], Pertici et al. reported its more direct preparation from ruthenium chloride hydrate, zinc powder, and the less expensive COD, all of which are readily available [2,3]. The author found that the Pertici's procedure frequently gave complex mixtures of isomeric products, the isomer ratio of which was dependent on reaction temperatures. When an ethanol solution of ruthenium chloride hydrate was added to an ethanol suspension of COD and zinc powder at room temperature, the crystalline mononuclear complex with the same composition as I, $C_{16}H_{22}Ru$, was isolated as the main product after chromatographic separation followed by repeated recrystallization from pentane. However, the ^1H and ^{13}C NMR spectra of this new isomer were completely different from either known Ru^0 complex I or its Ru^{II} isomer, bis(1–5-η-cyclooctadienyl)ruthenium(II), (IV) [2,3]. The ^{13}C NMR spectrum of this new isomer showed only eight carbon resonances at δ 22.5, 27.3, 36.7, 35.3, 38.9, 62.4, 76.7, and 87.6 ppm under complete proton decoupling in C_6D_6. The gated ^{13}C NMR spectrum showed that the former three resonances were split into triplets due to methylene units, while the remaining five resonances were split into doublets assignable to the methine units. These data are consistent with the presence of two equivalent C_8H_{11}

ligands being present in this new $C_{16}H_{22}Ru$ isomer. Since we eliminated the fully conjugated isomer IV from NMR spectral evidence, the most reasonable coordination mode of the η-C_8H_{11} ligand in the present isomer is 1–3:5–6-η-C_8H_{11}. In fact, the spectral patterns of the new isomer were similar to those of several reported cationic 1–3:5–6-C_8H_{11} complexes, $[Ru(1\text{–}3{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})(CO)_3]^+$ BF_4 [8,9] and $[Ir(\eta^5\text{-}C_5Me_5)(1\text{–}3{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})]^+$ $^-PF_6$ [10], or those of well-defined zwitter-ionic ruthenium complexes, $Ru(\eta^6\text{-}C_6H_5\bar{B}X_3)(1\text{–}3{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})$, $X = F$ or C_6H_5 [11]. The comparison of ^{13}C NMR data for these known complexes with those for the present $C_{16}H_{22}Ru$ isomer is shown in Table 1. We thus concluded that the new isomer was reasonably formulated as bis(1–3:5–6-η-cyclooctadienyl)ruthenium (II), ($Ru(1\text{–}3{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})_2$) based on the above ^{13}C NMR results, elemental analyses, molecular weight determination, and ^1H NMR data which are discussed in more detail below. The complex II to our knowledge is the first neutral 1–3:5–6-η-C_8H_{11} complex with a symmetrical coordination mode.

The GLC examination of the liquid phase of the preparation suggested the presence of cyclooctene. Therefore, one molecule of COD behaved as the hydrogen acceptor of two allylic hydrogen atoms from each COD molecule, which was converted to two-coordinated 1–3:5–6-η-C_8H_{11} in II.

The ^1H NMR spectrum of $Ru(1\text{–}3{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})$ (II) showed extremely complex patterns for a wide range between δ 1–5 ppm in C_6D_6 (Fig. 1; A). We undertook several decoupling experiments of II, since previous spectroscopic studies on cationic or zwitter-ionic complexes used less common solvents such as SO_2 or CD_3NO_2, and some assignments were ambiguous for this particular ligand system.

The most characteristic feature of the ^1H NMR spectrum was the highest field quartet at δ 1.12 ppm, which was unexpectedly found to correspond to the sp^2 carbon resonance appeared at 38.9 ppm. This signal was perturbed by the selective proton irradiation of the lowest field multiplet at δ 4.71 ppm and vice versa (Fig. 1; B and D), and of overlapping multiplets around δ 2.8 ppm (H(1)) based on $^1H\ \{^1H\}$ (Fig. 1; C, F, and G) and $^{13}C\ \{^1H\}$ selective irradiations. The two proton signals attached to the sp^2 carbon atoms at highest and lowest fields, δ 1.12 and 4.71 ppm should be assigned to the η^2-olefin moiety (H(5) and H(6)). The former was assigned to H(5), because it was perturbed into a doublet (Fig. 1; C) on the irradiation of the dienyl proton signal around δ 2.8 ppm (2H). The final assignment together with its correspondence to the ^{13}C NMR data for II are shown in Fig. 2. The ^1H NMR data for several 1–3:5–6-η-C_8H_{11} complexes are summarized in Table 2.

(Continued on p. 184)

TABLE 1

^{13}C NMR DATA FOR SEVERAL 1–3:5–6-η-C_8H_{11} COMPLEXES

Compound	Chemical shifts (ppm)								Ref.
	$\delta(CH_2)$			$\delta(CH)$					
$Ru(1\text{–}3{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})_2$ (II)	22.5	27.3	36.7	35.3	38.9	62.4	76.7	87.6	this work [a]
$Ru(1\text{–}3{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})(\eta^6\text{-}C_6H_5BF_3)$	17.4	26.3	33.6	24.6	29.6	69.9	77.3	80.7	12 [b]
$[Ir(1\text{–}3{:}5\text{–}6\text{-}\eta\text{-}C_8H_{11})(\eta^5\text{-}C_5Me_5)]PF_6$	19.5	30.8	36.8	29.4	34.6	71.5	81.4	84.3	10 [b]

[a] Measured in C_6D_6. Assignments of each signal are shown in Fig. 2. [b] Measured in CD_3NO_2. Assignments were interchangable in each set.

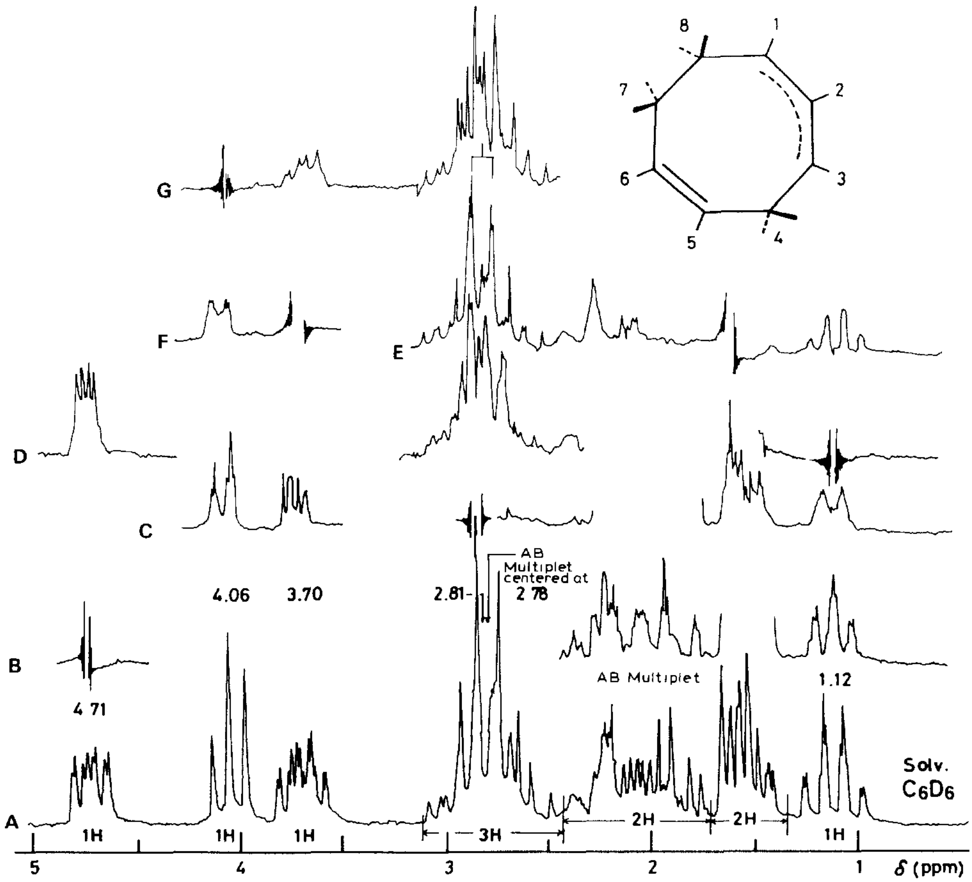
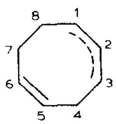


Fig. 1. ^1H NMR spectrum of Ru(1–3:5–6-η-C_8H_{11})$_2$ (II) and its ^1H-{^1H} decoupling results in C_6D_6 at 25 °C.

TABLE 2

1H NMR SPECTRAL DATA OF SEVERAL 1–3:5–6-η-C_8H_{11} COMPLEXES

Compound	Chemical shifts (δ, ppm)								Solvent	Ref.
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)		
Ru(1–3:5–6-η-C_8H_{11})$_2$ (II)	2.81	4.06	3.70	2.78	1.12	4.78	2.07	2.0	C_6D_6	this work
[Ru(1–3:5–6-η-C_8H_{11})-(CO)$_3$]$^+$ BF_4^-	5.16	5.03	4.68	3.4	4.04	5.74	2.8–3.1		SO_2	9
[M(1–3:5–6-η-C_8H_{11})-(η^5-C_5Me_5)]$^+$ PF_6^-										
M = Rh	4.99	4.28	4.53	3.25		4.11	2.6		CD_3NO_2	10
M = Ir	4.93	4.05	4.29	3.44 3.32	3.22	3.93	2.44 2.88	1.85 2.35	CD_3NO_2	10

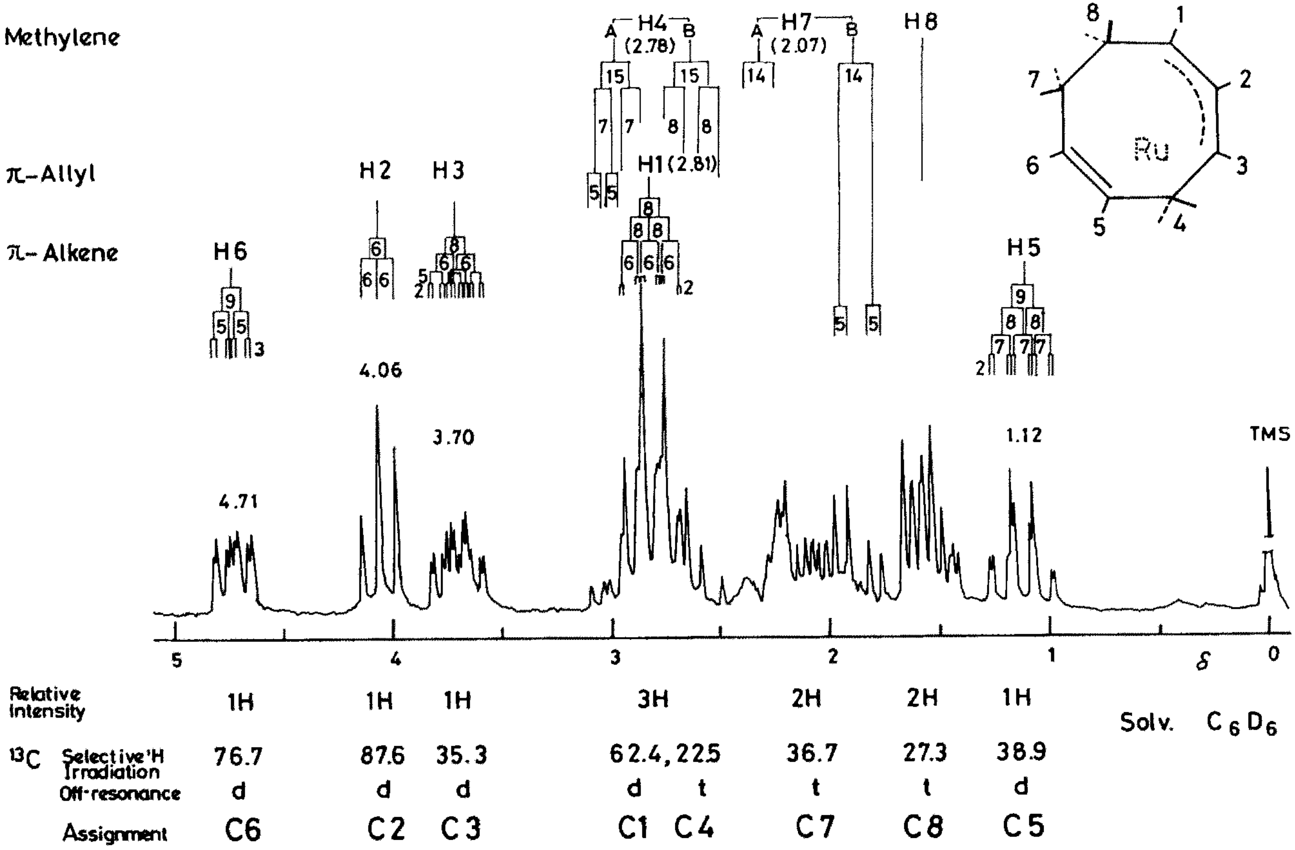
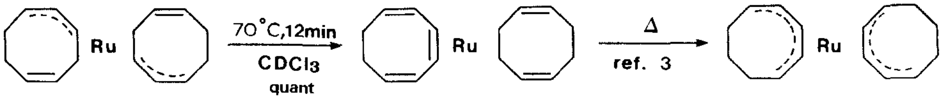


Fig. 2. Assignments of ^1H and ^{13}C NMR spectral data of Ru(1–3:5–6-η-C_8H_{11})$_2$ (II).

The unexpectedly large chemical shift difference between two olefinic signals (5 and 6) is quite unusual, and can be ascribed to the unsymmetrical coordination mode which is present in this particular complex II. The stronger metal–carbon interaction at C(5) compared with that at C(6) makes the ruthenium atom to approach to the C(4–5) region. As a consequence, one of the dienylic C–H bonds (H(4)) becomes accessible to the C–H bond activation by the ruthenium atom.

In fact, II was found to isomerize readily to the Ru^0 complex I. When a $CDCl_3$ solution of II was heated under an argon atmosphere at 70 °C for 12 min, I was formed quantitatively without any incorporation of the deuterium atom from the solvent. This finding suggests that the hydrogen atom at the dienylic position (H(4) in II) in one 1–3:5–6-η-C_8H_{11} ligand migrates regioselectively to the C(3) position of the other one. The net result of this isomerization is a formal reduction of the Ru^{II} state in II to the Ru^0 state in the final product I.



(II) (I) (IV)

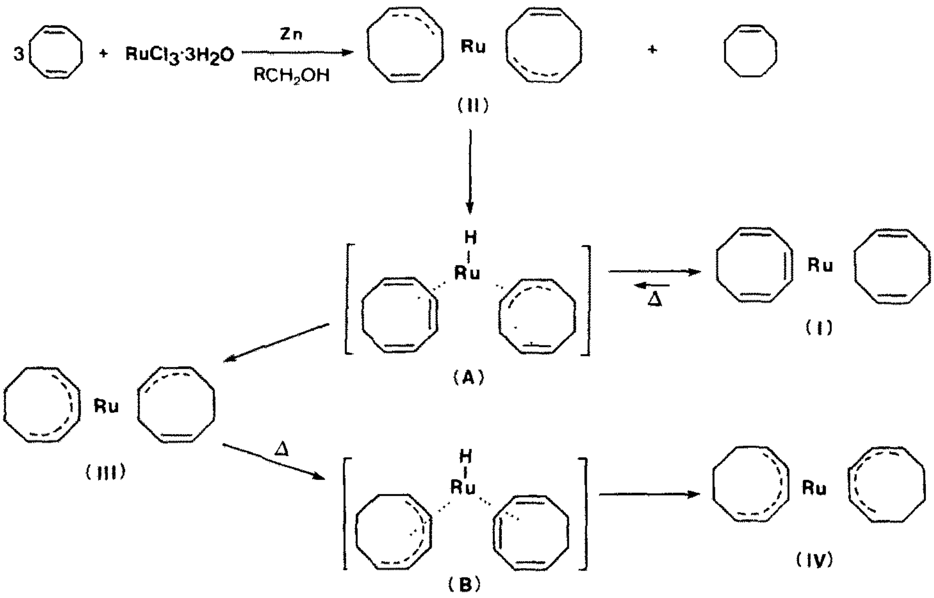
The regioselective capture of the hydrogen atom at the C(3) carbon atom to regenerate a 1–2:5–6-η-C_8H_{12} ligand in I is well consistent with the Maitlis' observation that the cationic 1–3:5–6-η-C_8H_{11} iridium(III) complex was converted to a neutral COD complex on metal hydride reduction [10].

A reversal formal oxidation induced by the migration of a hydrogen atom, Ru^0 to Ru^{II} states, was already found by Pertici et al. in the case of the thermal isomerization of I to form IV at elevated temperature [2,3].

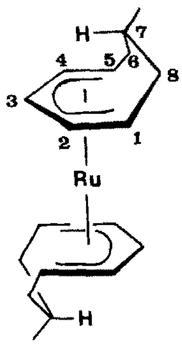
We obtained some ^1H NMR evidence for another $C_{16}H_{22}Ru$ isomer, Ru(1–5-η-C_8H_{11})(1–3:5–6-η-C_8H_{11}) (III), which was formed in 30–45% yields when a similar reduction was undertaken at 33–70 °C in ethanol. When the filtrate of the preparation of either I or II in ethanol was carefully separated by chromatography, III was obtained as an extremely air-sensitive colorless oil, which decomposed gradually to metallic ruthenium and a complex mixture of several cyclic C_8 hydrocarbons. Any attempts to isolate III in pure form were unsuccessful. However, the ^1H NMR spectrum of slightly contaminated III showed unequivocally the presence of characteristic signals due to both 1–5-η-C_8H_{11} and 1–3:5–6-η-C_8H_{11} ligands. The formation of III is explained in terms of a competitive "intra-ring" hydrogen shift from II by way of the hydride intermediate, Ru(H)(η^4-C_8H_{10})(1–3:5–6-η-C_8H_{11}) (**A**), to recombine with the same C_8 ring. Consequently, the hydride intermediate **A** is a common intermediate for the formation of either Ru^0 complex I via "inter-ring" hydrogen migration, or of III via an "intra-ring" one.

When a mixture of I, II, and III was heated in refluxing toluene, all three isomers were converted irreversibly to the most thermodynamically stable isomer IV. The thermal isomerization of I to IV [3], that of II to I, and that of III to IV, suggest that three $C_{16}H_{22}Ru$ isomers, I, II, and III are kinetic products, whereas IV is the thermodynamic product. The formation of IV from III is explained by another hydride intermediate, Ru(H)(1–5-η-C_8H_{11})(1–4-η-C_8H_{10}) (**B**), which may be generated by the C–H bond activation of the dienyl C–H bond present in III. The interrelationship between these four $C_{16}H_{22}Ru$ isomers are depicted in Scheme 1.

SCHEME 1



The extremely high thermodynamic stability of IV is ascribed both to an extensive delocalization of π-electrons within the planar "open-ruthenocene" η^5-ligand and to the minimun ring–ring steric repulsion. The latter effect is partly supported by the re-examination of the ^{1}H NMR of IV in $CDCl_3$. One proton signal of the 1–5-η-C_8H_{11} ligand in IV appeared at an extremely high-field region (δ 0.18 ppm as a quartet of triplets). Such a high field shift is interpreted reasonably by the magnetic anisotropy of the η^5-pentadienyl plane. The presence of one sp^3 C–H bond in the anisotropic region requires the flipping-out of three methylene bridges (C(6,7) and C(8)) to the outside of the π-system. As the most stable conformation of IV, two C_8H_{11} ligands become staggered as shown below.



(IV)

In this conformation, the *endo*-H(7) proton is located on the π-system and therefore shows a high-field shift.

The relative stability between four isomers are estimated in the order; II < I ≤ III < IV. The order unfortunately makes difficult the highly selective preparation of I which is the kinetic product with reduced thermodynamic stability, which was also close in stability to undesirable III. The Ru^0 complex I, however, is an attractive precursor for preparations of several ruthenium complexes [12–16] as well as a useful template for [$\pi 6s + \pi 2s$] cycloadditions in the reaction of 1-alkynes [16,17] to give bicyclo[4.2.2]decatrieneruthenium(0) complexes. Consequently, we slightly modified the original preparation by Pertici et al. by means of ultra-sound activation in refluxing methanol as shown in the Experimental.

Experimental

Commercially available reagents were used without further purification excepting COD, which was distilled under reduced pressure before use. NMR spectra were recorded on a JEOL FX-90Q Fourier Transform spectrometer. Elemental analyses were achieved at the Microanalysis Center of Kyoto University.

Preparation of bis(1–3:5–6-η-cyclooctadienyl)ruthenium (II)

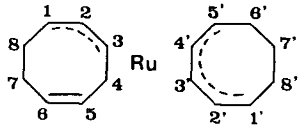
An ethanol (20 ml) solution of $RuCl_3 \cdot 3H_2O$ (Engelhardt; 624 mg) was added slowly for 30 min to a stirred suspension of ethanol (5 ml), COD (11 ml), and zinc powder (Kanto Chemical Co., 7 g) under an argon atmosphere at room temperature. After the addition was complete, the mixture was stirred at room temperature for 2 h, followed by filtration under dinitrogen. The filtrate was concentrated on a vacuum line to remove solvent, excess COD, and cyclooctene. The remaining brown oil was placed on the top of the alumina column (Merck 1097, hexane) which was flushed with dinitrogen. The pale yellow band on elution with hexane was collected and was concentrated in vacuo. Addition of few drops of pentane to dissolve the remaining yellow oil and cooling the flask at $-78\,^\circ C$ for several hours, result in the formation of almost colorless, pale yellow crystalls of II (283 mg, 35%). II, M.p. 113–114 °C, Anal. Found; C, 60.68; H, 7.09. $C_{16}H_{22}Ru$ calcd.; C, 60.92, H, 7.03%. Cryoscopic M.W. Found: 346, calcd. 315.

Thermal isomerization of II to (η^6-1,3,5-cyclooctatrene)(η-1,5-cyclooctadiene)ruthenium (I)

A $CDCl_3$ (0.5 ml) solution of II (75 mg) was placed in a NMR sample tube (Ø 5 mm) filled with argon. After the tube was sealed the mixture was heated at 70 °C for 12 min. The ^1H NMR spectrum of the mixture showed the spectrum which was identical with reported and authentic I [3]. When the mixture was evaporated and purified by chromatography on alumina (Merck 1097, hexane), I was recovered as yellow orange crystals in over 85% yield. The ^1H NMR spectrum of the isolated I showed correct signal intensities indicative of the absence of deuterium incorporation from the solvent. The thermal isomerization of II was extremely slow in C_6D_6 and gave a mixture of I, II, and III at 70 °C for 5 h.

Attempted isolation of (1–5-η-cyclooctadienyl)(1–3:5–6-η-cyclooctadienyl)ruthenium (III)

An ethanol (10 ml) solution of ruthenium chloride hydrate (801 mg) was added to a suspension of COD (12 ml), zinc powder (13 g), and ethanol (2 ml) for 30 min under argon atmosphere at room temperature. The mixture was stirred at room temperature for 2 days. A similar work-up of the mixture as described for II gave a yellow oily mixture of $C_{16}H_{22}Ru$ isomers in 48% yield (540 mg), in which I and III were present in 58/42 ratio based on the NMR spectrum. Most of the former isomer I was separated by recrystallization from pentane at $-78\,^{\circ}C$ and the liquid layer was quickly removed by means of syringe. This liquid phase was stirred at room temperature for few minutes under dihydrogen (1 atom) to decompose I, and was subjected to chromatographic separation on alumina with pentane. The central part of the pale yellow band was collected under dinitrogen. On evaporation of volatiles in vacuo, almost pure III (contaminated with I) was obtained as colorless air-sensitive oil. ^1H NMR ($CDCl_3$): δ 5.93 (1H, t, J 6 Hz, H(3′)), 4.58 (1H, dd, J 6 and 7 Hz, H(6)), 2.90 (3H, t, J 7 Hz, H(4) corresponding to 2H and accompanied 1H overlapping multiplet underneath, H(1)), 3.3–4.2 (6H, m, H(2,3, 1′, 2′, 4, and 5′)), 0.5–2.4 (11H, m, H(6′, 7′(*exo*), 8) and H(5–8)), and 0.17 ppm (1H, quartet of t, J 3 and 10 Hz, H(7′(*endo*))).



(III)

Modified preparation of (η^6-1,3,5-cyclooctatriene)(η-1,5-cyclooctadiene)ruthenium(0) (I)

Zinc dust (6 g) was placed in a 50 ml flask fitted with condenser and pressure equalizing dropping funnel, and the system was filled with argon. Freshly distilled COD (12.5 ml) and methanol (5 ml) was added to the flask, which was placed in the ultrasound apparatus (Branson, Model Bransonic B220). The bath temperature was kept at $70\,^{\circ}C$ with a thermostat. A methanol (12 ml) solution of $RuCl_3 \cdot 3H_2O$ (Engelhardt; 530 mg) was added through the dropping funnel slowly for 20 min to the refluxing mixture under dinitrogen flow under ultrasound. After the addition was complete, the mixture was kept under ultrasonic vibration for additional 2 h at $70\,^{\circ}C$. After the precipitate was separated by filtration, the filtrate was evaporated with a vacuum line. The residual deep brown oil was extracted with minimum amounts of hexane three times, and the extracts were placed on an alumina column (Merck 1097) under dinitrogen. Chromatographic separation was done with hexane as an eluent, and the yellow band was collected. Evaporation of hexane and C_8 hydrocarbons in vacuo resulted in the formation of orange crystals of crude I (590 mg, 93%). M.p., ^1H, and ^{13}C NMR spectra were identical with the reported I after recrystallization from pentane with 75–85% recovery. Yields based on the used ruthenium chloride were in the range of 70–93%.

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