New Cationic Bis(η^3-allyl)ruthenium(IV) Complexes from Allylic C-H Bond Activation of Alkenes

Kenji Itoh,* Katsuyuki Masuda, and Hideaki Ikeda

Department of Materials Science, Toyohashi University of Technology, Tenpaku-cho, Toyohashi, Aichi 441, Japan

Received December 16, 1992

When (allyl)Ru^{IV} complex $CpRuBr_2(\eta^3\text{-}C_3H_5)$ (1) was treated with silver trifluoromethanesulfonate (silver triflate, AgOTf) followed by the reaction with propene (1 atm), new bis-allylic Ru(IV) cationic complex $[CpRu(\eta^3\text{-}C_3H_5)_2]OTf$ (2) was obtained in 95% yield as a mixture of two isomers, in which the allyl ligands had different configurations; exo,endo form **2a** and endo,endo isomer **2b**. The former stereoisomer is predominant (70:30) in dichloromethane, whereas the latter prevails in the presence of alcohols (**2a**:**2b** = 15:85) or catalytic triethylamine (26:74). Interconversion between **2a** and **2b** did not occur in solution at ambient temperatures. 2-Butene gave an allyl-crotyl analogue (**3**; 96% yield), which takes an endo,endo configuration selectively. Such intermolecular allylic C-H bond activation of propene did not occur in the case of pentamethylcyclopentadienyl (Cp*) analogues. Intramolecular allylic C-H bond activation, however, takes place readily in the case of the (η^3-allyl)ruthenium(IV) complex **4**, obtained from 1,5-dimethyl-1,5-cyclooctadiene and $[Cp^*RuCl_2]_2$, to result in the formation of the new bis-allylic complex $[Cp^*Ru(\eta^3,\eta^3\text{-}C_{10}H_{14})]OTf$ (**5**).

Pioneering preparations of bis(η^3-allyl)dichlororuthenium(IV) complexes were reported for the first time in the middle sixties by Shaw, Truter, Allegra, and their coworkers.[1,2] These complexes were obtained from the trimerization of butadiene[1] or from the tail-to-tail dimerization of isoprene with ruthenium trichloride in alcoholic solvents[2] and have been the first organometallic compounds of the ruthenium(IV) oxidation state. Although little attention has been paid to these attractive high-valent organometallic compounds, excepting Nixon's works on the cleavage of the μ,μ-dichloro bridge in the dimeric structure of Allegra's [(1-3-η:6-8-η)-2,7-dimethyloctadiendiyl)$RuCl_2]_2$ with carbon monoxide or several fluorinated phosphines,[3] Allegra's complex has attracted much attention in recent years. Many structure determinations including diastereotopic relationships and dynamic behaviors in solutions have been extensively investigated for a number of derivatives involving several donor ligands, such as pyrazine, semicarbazide, terpyridine, pyridine, quinoline derivatives with hydroxy or thiol substituents, etc.[4-8] Furthermore, Cox and Roulet reported an important finding that the isoprene dimer complex was an excellent precursor to synthesize new allyl or dienyl complexes upon treatment with silver tetrafluoroborate.[9,10]

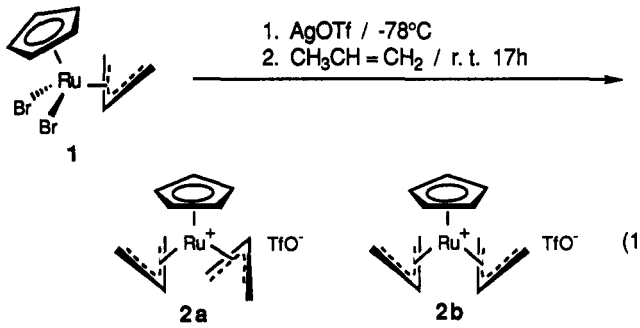
Several years ago, we prepared the first Ru(IV) alkyl-allyl complexes by the alkylation of Shaw and Truter's $RuCl_2[(1\text{-}3\text{-}\eta\text{:}6,7\text{-}\eta\text{:}10\text{-}12\text{-}\eta)\text{-}C_{12}H_{18}]$.[11] It was also found that methylruthenium(IV) halogeno compounds induced facile reductive elimination between the methyl and an allyl ligand regioselectively at the C3 carbon atom of the particular bis-allylic ligand of a butadiene trimer, to result in the formation of Ru(II) monoallyl compounds in the reaction with carbon monoxide, *tert*-butyl isocyanide, or phosphites.[12] Our studies on (allyl)Ru^{IV} complexes have also been focused on much simpler η^3-allyl complexes of Ru(IV), CpRu(allyl)X_2 or Cp*Ru(allyl)X_2 (Cp = $\eta^5\text{-}C_5H_5$; Cp* = $\eta^5\text{-}C_5Me_5$), and their methyl, dimethyl, or (trimethylsilyl)methyl derivatives.[13-21] As an extension of our continuing interest on the organic chemistry of Cp- or Cp*Ru^{IV} allyl derivatives, we describe herein a preparative method of simplest bis-allylic Ru(IV) complexes via allylic C-H bond activation of alkenes by cationic CpRu species.

Results and Discussion

A dichloromethane solution of $CpRuBr_2(\eta^3\text{-}C_3H_5)$ (1) was treated with an ether solution of silver trifluoromethanesulfonate (AgOTf) followed by introducing

(1) (a) Lydon, J. E.; Nicholson, J. K.; Shaw, B. L.; Truter, M. E. *Proc. Chem. Soc.* **1964**, 421. (b) Nicholson, J. K.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 807. (c) Lydon, J. E.; Truter, M. R. *J. Chem. Soc. A* **1968**, 362.
(2) (a) Porri, L.; Gallazzi, M. C.; Colombo, A.; Allegra, G. *Tetrahedron Lett.* **1965**, 4187. (b) Colombo, A.; Allegra, G. *Acta Crystallogr., Sect. B* **1971**, *27*, 1653.
(3) (a) Head, R. A.; Nixon, J. F.; Swain, R.; Woodard, C. M. *J. Organomet. Chem.* **1974**, *76*, 393. (b) Hitchcock, P. B.; Nixon, J. F.; Sinclair, J. *J. Organomet. Chem.* **1975**, *86*, C34.
(4) Cox, D. N.; Roulet, R. J. *Inorg. Chem.* **1990**, *29*, 1360.
(5) Cox, D. N.; Small, R. W. H.; Roulet, R. *J. Chem. Soc., Dalton Trans.* **1991**, 2013.
(6) (a) Toerien, J. G.; van Rooyen, P. H. *J. Chem. Soc., Dalton Trans.* **1991**, 1563. (b) Toerien, J. G.; van Rooyen, P. H. *J. Chem. Soc., Dalton Trans.* **1991**, 2693.
(7) Sommerer, S. O.; Palenik, G. J. *Organometallics* **1991**, *10*, 1223.
(8) (a) Steed, J. W.; Tocher, D. A. *J. Organomet. Chem.* **1991**, *412*, C34. (b) Steed, J. W.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1992**, 459. (c) Steed, J. W.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1992**, 2765. (d) Steed, J. W.; Tocher, D. A. *Inorg. Chim. Acta* **1992**, *191*, 29.
(9) Cox, D. N.; Roulet, R. J. *J. Chem. Soc., Chem. Commun.* **1988**, 951.
(10) Cox, D. N.; Roulet, R. J. *J. Organomet. Chem.* **1988**, *342*, 87.
(11) Nagashima, H.; Ohshima, T.; Itoh, K. *Chem. Lett.* **1984**, 789.
(12) Nagashima, H.; Ohshima, T.; Itoh, K. *Chem. Lett.* **1984**, 793.
(13) Nagashima, H.; Mukai, K.; Itoh, K. *Organometallics* **1984**, *3*, 1314.
(14) Nagashima, H.; Mukai, K.; Shiota, Y.; Ara, K.; Itoh, K.; Suzuki, H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1985**, *4*, 1314.
(15) Nagashima, H.; Yamaguchi, K.; Mukai, K.; Itoh, K. *J. Organomet. Chem.* **1985**, *291*, C20.
(16) Oshima, N.; Suzuki, H.; Moro-oka, Y.; Nagashima, H.; Itoh, K. *J. Organomet. Chem.* **1986**, *314*, C46.
(17) Nagashima, H.; Ara, K.; Itoh, K. *J. Organomet. Chem.* **1987**, *319*, C11.
(18) Itoh, K.; Fukahori, T. *J. Organomet. Chem.* **1988**, *349*, 227.
(19) Nagashima, H.; Michino, Y.; Ara, K.; Fukahori, T.; Itoh, K. *J. Organomet. Chem.* **1991**, *406*, 189.
(20) Nagashima, H.; Mukai, K.; Shiota, Y.; Yamaguchi, K.; Ara, K.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 789.
(21) Itoh, K.; Nagashima, H.; Fukahori, T. *Nippon Kagaku Kaishi* **1991**, 177.

0276-7333/93/2312-2752$04.00/0



(1)

solvent	yield (%)	ratio 2a:2b
CH_2Cl_2	95	70:30
CH_2Cl_2–MeOH (7:3)	70	15:85

propene (1 atm) at −78 °C for 15 min. Then the mixture was allowed to react at room temperature for 17 h under a propene atmosphere. Filtration of silver bromide and the conventional workup afford yellow solids of [CpRu(η^3-C_3H_5)$_2$]OTf (**2**), the composition of which was supported by elemental analysis. Deprotonation of propene has been reported with several electrophilic transition metal complexes. For instance, related to this work, Maitlis et al. reported several years ago that [Cp*Ir(solv)$_3$]$^{2+}$ reacted with propene to give [Cp*Ir(propene)(η^3-C_3H_5)]$^+$.[22] More recently, Wakefield and Stryker determined the X-ray structures of two stereoisomers for *endo*-[Cp*Ir(η^2-C_2H_4)(η^3-C_3H_5)]$^+$ and *exo*-[Cp*Ir(η^2-C_2H_4)(η^3-C_4H_7)]$^+$, as well as the mutual isomerizations of the exo and endo isomers for the former parent allyl complex.[23]

The proton NMR spectrum of **2** indicates the presence of two isomers, **2a** and **2b**, on the basis of the presence of two cyclopentadienyl peaks at δ 5.91 and 6.01 in the ratio 70:30, respectively. The pattern of the spectra was essentially invariant from −50 to +80 °C, indicative of any dynamic behavior being absent in solution. To our regret, however, a number of attempts to separate these two noninterconvertible isomers in pure crystalline forms by fractional recrystallization or chromatography were unsuccessful. Consequently, the elucidation of the structures of **2a** and **2b** had to be made by the following spectroscopic evidence.

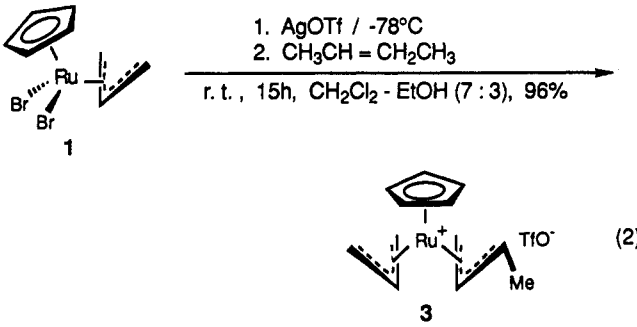
There appeared three kinds of signals due to allylic ligands, and their mutual relationships and the assignments of the individual peaks were unequivocally confirmed by decoupling and COSY experiments, as well as by estimation of their relative intensities to the above two Cp resonances: (A) δ 1.77 (d, anti), 4.23 (d, syn), and 4.84 (tt, central), (B) δ 3.06 (tt, central), 3.62 (d, anti), and 4.04 (d, syn), and (C) δ 3.19 (d, anti), 3.51 (d, syn), and 4.37 (tt, central). Signals due to sets A and B were found to correspond to the stronger Cp proton signal at δ 5.91 and were assigned to the major isomer, **2a**, which involves two allyl ligands in different environments. These assignments are consistent with ^{13}C NMR information. There appeared four allylic resonances for the major isomer (**2a**): two doublets at 88.5 and 96.5 ppm (C2), as well as two triplets at 50.0 and 55.2 ppm (C1 and C3) in the gated ^{13}C NMR spectrum. ^{13}C NMR measurements under selective proton irradiations revealed that signals at 88.5 and 55.2 ppm corresponded to the allylic proton signals of set A, whereas those at 96.5 and 50.0 ppm corresponded to the set B protons. The major isomer (**2a**), therefore, was concluded to contain two different allyl entities, one *endo*- and one *exo*-η^3-allyl ligand, on the basis of the following evidence and considerations. The ^{13}C resonance of the central carbon at 88.5 ppm is substantially in the high field region, which is close to the value (86.3 ppm) of Stryker's *exo*-[Cp*Ir(η^2-C_2H_4)(η^3-C_3H_5)]$^+$ isomer, while the endo-iridium complex showed a resonance at a higher region (97.7 ppm), which is also close to the value, 96.5 ppm, of the present major ruthenium(IV) iomer (**2a**).[23]

More informative results were obtained by NOE experiments. Irradiation of the Cp proton signal of **2a** at δ 5.91 enhances signals of the proton on the central carbon of set A (δ 4.84; +6%) and the anti protons of set B (3.62; +5%), indicating these protons are oriented toward the Cp ring in the major isomer (**2a**). Moreover, irradiation of the anti proton signal of set A at the highest field (δ 1.77) induced an extremely large enhancement (+19%) of the triple triplet proton on the central carbon at δ 3.06. This result strongly suggests the relative position of two different allyl groups in such a manner that anti protons of one allyl group with an exo configuration (set A) are particularly close to the central proton of the other allyl moiety with an endo configuration (set B) in the opposite face to the Cp ligand for **2a**. The anisotropic effect of the *exo*-allyl group may be responsible for the appearance of the central proton of the *endo*-allyl group at an unusually high-field position at δ 3.06. The high-field shift of the anti protons in an *exo*-allyl moiety (set A) is explained in terms of their proximity to the metal center. These assignments are also consistent with the appearance of a small geminal coupling ($J \lesssim 1$ Hz) between the anti and syn protons for an allyl group with an exo configuration. Such geminal coupling has never beeen observed for *endo*-allyl ligands in both **2a** and Stryker's iridium complex.[23] The major configurational isomer (**2a**), therefore, is concluded to be *exo,endo*-[CpRu(η^3-C_3H_5)$_2$]OTf, involving two different allyl configurations on the basis of the above evidence.

On the other hand, the remaining allyl resonances (set C) were found to correspond to the weaker Cp singlet at δ 6.01 and were assigned to the two equivalent η^3-allyl ligands, either *exo,exo*- or *endo,endo*-[CpRu(η^3-C_3H_5)$_2$]-OTf in the minor isomer (**2b**), on the basis of their relative intensities to the minor Cp singlet. Its selective irradiation at δ 6.01 caused an apparent NOE enhancement (+6%) of the anti allyl protons at δ 3.18, whereas no intensity change was observed for the central and syn protons. This NOE evidence suggests that the minor isomer (**2b**) takes an endo,endo configuration. The symmetric structure of **2b** was also supported by ^{13}C NMR spectroscopy, which showed only two allylic resonances at 46.7 (C1 and C3) and 98.9 ppm (C2) together with the related Cp one at 93.1 ppm. The chemical shift of the central carbon of the allyl moiety in the high-field region and the absence of geminal coupling between the anti and syn protons are also consistent with the *endo*-allyl configuration. The above NMR spectroscopic results suggest the two equivalent allyl ligands take endo,endo configurations in the minor isomer (**2b**).

Thermal interconversion between **2a** and **2b** did not occur until decomposition in chloroform or in toluene up to 90 °C. The rotation, flipping, or σ–π interconversion of the allyl ligands, therefore, did not take place in **2**. Such kinetic stability of configurations of an allyl ligand was

(22) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1305.
(23) Wakefield, J. B.; Stryker, J. M. *Organometallics* **1990**, *9*, 2428.



already pointed out by Gibson and co-workers several years ago in the case of $CpRu^{II}(allyl)(CO)$, which was obtained as a mixture of endo and exo isomers, the former of which isomerized slowly under severe conditions to the more stable exo isomer.[24] Faller reported the selective formation of the exo isomer in this Ru(II) system for the first time.[25] The structure determination of unstable *endo*-$CpRu^{II}$(2-methylallyl)(CO) was achieved, since separation of two stereoisomers was feasible in the Ru(II) monoallyl system.[26]

In bis-allylic systems, $CpV(C_3H_5)_2$ and paramagnetic $CpM(C_3H_5)_2$, where M = Cr and Mo, are known.[27-30] Their X-ray structures showed two allylic ligands having endo,-endo configurations. Preferential formation of an *exo,endo*-bis(allyl) complex (**2a**) and the kinetic stability of **2a** and **2b** in the bis(allyl)Ru^{IV} system deserve attention in the transition metal chemistry of the simplest bis-allylic system. In a high oxidation state of ruthenium, preponderant generation of intramolecularly connected *exo,endo*-bis(allyl)dichlororuthenium(IV) complexes is known in the case of ruthenium-mediated dimerization or trimerization of conjugated dienes.[1,2]

The relative ratio of **2a** and **2b** can be controlled to some extent by modification of the preparative conditions. In particular, the presence of nucleophiles was quite important in determining the relative ratios of these two isomers. For instance, the more symmetrical **2b** became the predominant product when the preparation was undertaken in the presence of alcoholic solvents or catalytic quantities of triethylamine to furnish bis-allylic complex mixtures composed of **2a**:**2b** = 15:85 and 26:74, respectively, in slightly lower yield (70–90%), while **2a** was the major product in chlorinated hydrocarbon, THF, or acetone. In the case where **2a** was the major product, extremely weak bases, such as triflate or the oxygen lone pair of the solvent, may attack an allylic C–H bond of the coordinated propene. Consequently, the isomer ratio would depend on the kinetic factors in the C–H bond activation of the coordinated propene by bases present.

An unsymmetrically substituted bis(allyl)ruthenium-(IV) complex, $[CpRu(\eta^3\text{-allyl})(\eta^3\text{-1-methylallyl})]^+OTf^-$ (**3**), was prepared in 96% yield from 2-butene, instead of propene, in the presence of silver triflate and ethanol under similar conditions. The ^1H NMR and ^{13}C NMR spectra of **3** indicated the presence of a single stereoisomer, since only one C_5H_5 proton appeared at δ 5.58. In addition two anti protons, δ 3.09 and 3.22, two syn protons, δ 3.17 and 3.43, and a central proton (δ 4.52) were assigned to the η^3-C_3H_5 ligand, whereas resonances at δ 1.73 (methyl), 2.97 and 4.13 (anti), 3.22 (syn), and 4.27 (central) were ascribed to the η^3-1-methylallyl (crotyl) ligand. The appearance of the central and anti proton signals in a region similar to that in **2b** suggests that both allyl and crotyl ligands are present in endo,endo configurations. The results of ^{13}C NMR are also consistent with the endo,endo structure of **3**, since the allylic central carbon signals appeared in a reasonably low-field, at 98.0 (C_3H_5) and 99.4 (C_4H_7) ppm, values which are consistent with an *endo*-allyl ligand in **2a**, **2b**, or the precedented iridium compounds.[23]

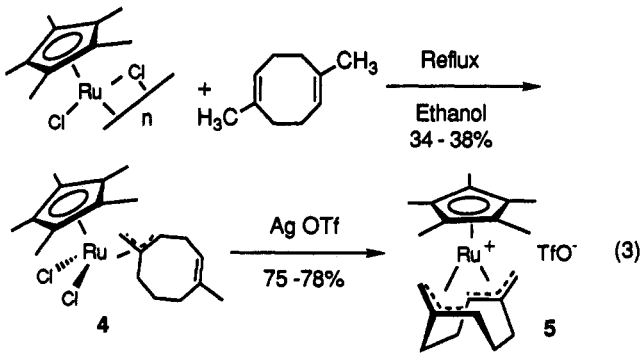
In the preparation of **3**, 1-butene was not an appropriate substrate for the C–H activation and gave a complex mixture of several intractable materials involving a trace amount of **3**. This observation indicates that the allylic methyl group was far more reactive than an allylic methylene C–H bond in the present ruthenium(IV)-mediated allylic activation. This is quite different from the Cp^*Ir^+ system in the reaction with 2-butene or 2-pentene, which affords selectively the corresponding exo isomers, and a secondary C–H bond is preferentially activated in the latter alkene.[23] In the Cp^*Ir^+ system, approach of the triflate ion to an allylic C–H bond encounters severe steric constraint of the Cp* ligand; therefore, coordination of alkene substrates and attack of the triflate ion are only allowed from the side opposite the Cp* ligand. The evolving allyl ligand as so arranged to give the exo configuration. In the case of 2-pentene, the longer ethyl group is considered to be located at the vacant side away from the bulky Cp* ligand, with the smaller methyl group being close to the Cp* ligand, which efficiently blocked the approach of bases. As a consequence, an allylic methylene C–H bond of coordinated 2-pentene was lost selectively to give an *exo*-1,3-dimethylallyl ligand.

Alternatively, in the present ruthenium(IV) system a similar approach of alkene substrates and bases from the side opposite the Cp ligand is substantially interfered with by the *endo*-allyl ligand already present.[20] The coordination site for alkenes is thus restricted to a relatively small area, and the ethyl group of 1-butene cannot be accommodated in the small vacant site, where only a methyl substituent of coordinated alkenes seems to be accessible. Therefore, methyl-substituted alkenes such as propene or 2-butene can be employed for the allylic activation with the present $[CpRu(alkene)(allyl)]^{2+}$ system.

Introduction of the more bulky Cp* auxiliary ligand in the allylruthenium(IV) system is expected to decrease the size of the alkene coordination site to further extent. In fact, a similar reaction of pentamethylcyclopentadienyl complex $Cp^*RuCl_2(\eta^3\text{-}C_3H_5)$ with propene or 2-butene did not give the corresponding bis-allylic complexes in the presence of AgOTf under analogous conditions. The severe steric interference of the $[Cp^*Ru(endo\text{-}\eta^3\text{-}C_3H_5)]^{2+}$ fragment entirely prohibited the coordination of even propene.

For the $[Cp^*Ru(allyl)]^{2+}$ system, we contrived an alternative approach to design an allylic C–H bond

(24) (a) Gibson, D. H.; Hsu, W.-L.; Steinmetz, A. L.; Johnson, B. V. *J. Organomet. Chem.* **1981**, *208*, 89. (b) Worley, S. D.; Gibson, D. H.; Hsu, W.-L. *Organometallics* **1982**, *1*, 134.
(25) (a) Faller, J. W.; Johnson, B. V.; Drya, T. P. *J. Organomet. Chem.* **1974**, *65*, 395. (b) Faller, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211.
(26) Hsu, L.-H.; Nordman, C. E.; Gibson, D. H.; Hsu, W.-L. *Organometallics* **1989**, *8*, 241.
(27) (a) Jonas, K.; Wiskamp, V. *Z. Naturforsch.* **1983**, *B38*, 1113. (b) An excellent review: Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295.
(28) Nieman, J.; Pattiasina, J. W.; Teuben, J. H. *J. Organomet. Chem.* **1984**, *262*, 157.
(29) Ongermund, K.; Dohrig, A.; Jolly, J. W.; Kruger, C.; Romao, C. C. *Organometallics* **1986**, *5*, 1268.
(30) Jolly, P. W.; Kruger, C.; Romao, C. C.; Romao, M. J. *Organometallics* **1984**, *3*, 936.



activation as an *intramolecular* process by means of 1,5-dimethyl-1,5-cyclooctadiene as a substrate in two steps.

The first step of the double allylic C–H activation of the two methyl substituents in 1,5-dimethyl-1,5-cyclooctadiene was achieved by refluxing the diene with $[Cp^*RuCl_2]_2$[31,32] in ethanol. One methyl group of the diene was turned into an η^3-allyl ligand to furnish a new exocyclic η^3-allyl Ru(IV) complex, $Cp^*RuCl_2[\eta^3\text{-}CH_2\text{---}C\text{---}CH\text{---}(CH_2)_2\text{---}C(CH_3)\text{=}CH\text{---}CH_2CH_2]$ (4) in 34–38% isolated yield.

Treatment of 4 with silver triflate induced intramolecular allylic activation of the second methyl substituent of the ligand in dichloromethane at room temperature, to furnish a symmetrical bis-allylic Ru(IV) cationic complex, $[Cp^*Ru(\eta^3,\eta^3\text{-}C_{10}H_{14})]OTf$ (5), in good yield.

The ^1H and ^{13}C NMR spectroscopic results are fully consistent with the depicted symmetric endo,endo structure of 5. It is worthwhile to note that this new bis-allylic ligand was also composed of two isoprene molecules in connectivities and stereochemistries different (*endo,endo*-bis-allyl) from the *exo,endo*-bis-allylic structure of Porri–Allergra's complex.[2] It is important that the intramolecular allylic activation took place quite readily in 4, where the allylic methyl group was present around the $Cp^*Ru^{IV}(allyl)^{2+}$ fragment in the same molecule, while the intermolecular allylic activation did not take place, as mentioned above. The difficulty in the intermolecular allylic activation by $[Cp^*Ru(allyl)]^{2+}$, therefore, is ascribed to the steric inhibition of the approach of alkenes to the coordination sphere of the cationic Cp^*Ru^{IV} species. The present results not only provide a new methodology to prepare simple bis(allyl)ruthenium(IV) complexes other than the oligomerization of conjugated dienes but also suggest the generality of the η^3,η^3-bis(allyl) ligand framework in the Ru(IV) oxidation states.

Experimental Section

Materials and Instrumentation. Complexes $CpRuBr_2(C_3H_5)$[13,20] and $[Cp^*RuCl_2]_2$[31,32] were prepared according to the published procedures. Silver triflate was purchased from Aldrich and used as 0.15 N diethyl ether or 0.2 N acetone solutions. Propene and 1- and 2-butenes were purchased from Tokyo Kasei Co. and used without further purification. 1,5-Dimethyl-1,5-cyclooctadiene was purchased from Aldrich and purified by distillation before use. Dichloromethane was distilled from phosphorus pentoxide before use. Proton and carbon-13 NMR spectra were recorded on a JEOL GX-270 spectrometer. Elemental analyses were achieved at the Microanalysis Center of Kyoto University or determined by a YANACO CHN Corder. IR spectra were measured with a JASCO A-3 spectrometer.

Synthesis of $[CpRu(C_3H_5)_2]OTf$ (2). A dichloromethane (10 mL) solution of $CpRuBr_2(C_3H_5)$ (1) (30 mg, 0.082 mmol) was cooled at −78 °C. An ether solution of silver triflate (1.1 mL of 0.15 N solution, 0.17 mmol) was added with stirring. Precipitation of silver bromide occurred. After the suspension was stirred for 15 min at this temperature, the atmosphere of the flask was substituted by propene (1 atm). The temperature of the mixture was gradually raised to room temperature within 1.5 h. The mixture was reacted at room temperature for 17 h under propene atmosphere. Formed silver bromide was filtered off with a column filled with Celite, and the liquid phase was concentrated under reduced pressure. The obtained yellow solid was redissolved in the least amount of acetone followed by addition of diethyl ether. The bis(allyl)ruthenium triflate 2 (31 mg, 97%) was isolated as a pale yellow amorphous powder. Mp: 158–160 °C dec. Anal. Calcd for $C_{12}H_{15}F_3O_3RuS$: C, 36.27; H, 3.80. Found: C, 36.00; H, 3.62. IR (Nujol): 1257, 1164 (SO_3), 1030 (CF_3) cm^{-1}.

As discussed in the text, complex 2 contains two stereoisomers: **2a** (exo–endo form) and **2b** (endo–endo form) in a 70:30 ratio. **2a**: ^1H NMR (acetone-d_6) δ 1.77 (d, J = 12.2 Hz, anti-exo), 3.06 (tt, center-endo, J = 11.2 and 6.35 Hz), 3.62 (d, J = 12.2 Hz, anti-endo), 4.04 (d, J = 6.4 Hz, syn-endo), 4.27 (d, J = 7.3 Hz, syn-exo), 4.84 (dt, J = 12.2 and 7.8 Hz, center-exo), 5.91 (s, Cp); ^{13}C NMR (acetone-d_6) 50.0 (t, J_{C-H} = 162 Hz, C1 and C3-endo), 55.2 (t, J_{C-H} = 156 Hz, C1 and C3-exo), 88.5 (d, J_{C-H} = 168 Hz, C2-exo), 92.2 (d, J_{C-H} = 184 Hz, Cp), 96.5 (d, J_{C-H} = 164 Hz, C2-endo) ppm. **2b**: ^1H NMR (acetone-d_6) δ 3.19 (d, J = 12.2 Hz, anti), 3.51 (d, J = 7.3 Hz, syn), 4.37 (tt, J = 12.2 and 7.3 Hz, center), 6.01 (s, Cp); ^{13}C NMR (acetone-d_6) 46.7 (t, J_{C-H} = 160 Hz, C1 and C3), 93.1 (d, J_{C-H} = 189 Hz, Cp), 98.9 (d, J_{C-H} = 162 Hz, C2) ppm.

When the preparation was done under similar conditions with the addition of a catalytic quantity (5-10 mol %) of triethylamine, the isomer ratio was reversed in favor of **2b** (**2a**:**2b** = 26:74, in 95% total yield). The predominant formation of **2b** was also observed by employing alcoholic solvents: **2a**:**2b** = 15:85 in ethanol or in a methanol–dichloromethane mixture (3:7 volume ratio), in 70–90% yield, under reaction conditions analogous to the procedures followed in pure dichloromethane. In cases where the contents of **2b** increased, however, the product (2) frequently became a brown semisolid or an oil which gradually turned black at room temperature in several hours. Several attempts to obtain pure crystalline **2a** and **2b** for single crystal X-ray structure determinations have been unsuccessful by means of many combinations of solvent systems and by means of a variety of samples with different isomer ratios.

Synthesis of $[CpRu(C_3H_5)(C_4H_7)]Otf$ (3). Compound 1 (30 mg, 0.082 mmol) was placed in a 30-mL round bottomed flask with a stirring bar under an argon atmosphere. Dichloromethane (7 mL) and ethanol (3 mL) were added, and the flask was cooled to −78 °C. A diethyl ether solution of silver triflate (0.15 N, 1.1 mL, 0.16 mmol) was added via syringe with magnetic stirring. Precipitation of silver bromide took place, and the mixture turned heterogeneous. The mixture was stirred at that temperature for 15 min. The reaction vessel was slightly evacuated, and 2-butene (1 atm; cis–trans mixture) was introduced. The mixture was warmed to room temperature for 1 h and was kept stirring for 15 h. Silver bromide was filtered out with a column packed with Celite. The column was washed with dichloromethane. The liquid phase was concentrated by rotary evaporation to dryness. The residue was dissolved in the least amount of dry acetone. Precipitation was done by adding diethyl ether to give a pale yellow solid (32 mg, 96%). Mp: 167–169 °C. Anal. Calcd for $C_{13}H_{17}F_3O_3RuS$: C, 37.95; H, 4.17. Found: C, 37.75; H, 4.14. ^1H NMR (acetone-d_6): δ 1.73 (d, J = 5.9 Hz, crotyl CH_3), 2.97 (d, J = 11.2 Hz, crotyl-anti at C1), 3.09 (d, J = 11.7 Hz, allyl-anti A), 3.17 (d, J = 6.4 Hz, allyl-syn A), 3.22 (d, J = 8.3 Hz, crotyl-syn), 3.24 (d, J = 10.8 Hz, allyl-anti B), 3.43 (d, J = 7.3 Hz, allyl-syn B), 4.13 (dq, J = 11.2, and 5.9 Hz, crotyl-anti at C3), 4.27 (dt, crotyl at C2), 4.52 (tt, allyl at C2), 5.58 (s, Cp). ^{13}C NMR

(31) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, 3, 274.

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

(acetone-d_6): 19.0 (CH_3), 41.6 and 50.6 (allyl C1 and C3), 45.7 (crotyl C1), 69.2 (crotyl C3), 92.9 (Cp), 98.0 (crotyl C2), 99.4 (allyl C2) ppm. When 1-butene was used instead of 2-butene, the products became extremely complex mixtures of several compounds involving only small amounts of **3**.

Synthesis of Cp*RuCl$_2$(η^3-C$_8$H$_{15}$) (4). An ethanol (20 mL) solution of [Cp*RuCl$_2$]$_2$ (300 mg, 0.978 mmol) and 1,5-dimethyl-1,5-cyclooctadiene (0.45 mL) was refluxed under a dinitrogen atmosphere for 4 h. The mixture was condensed to dryness by rotary evaporation. The residue was chromatographed on a silica gel column in dichloromethane, giving a major red band which was collected. Yellow crystals of **4** were obtained after evaporation of solvent followed by recrystallization from a dichloromethane–hexane mixed solvent in 34% yield (137 mg). Mp: 194–195 °C dec. Anal. Calcd for $C_{20}H_{30}Cl_2Ru$: C, 54.30; H, 6.83. Found: C, 53.71; H, 6.92. ^{1}H NMR ($CDCl_3$): δ 1.56 (s, 15 H, CH_3 of Cp*), 1.58 (s, 3H, CH_3—C═), 2.02 (ddd, 2 H, AA′ part of methylene AA′XX′), 2.22 (s, 1H, anti proton of the exocyclic allylic carbon), 2.41 (dt, 1H, X part of methylene) 2.67–2.89 (m, 5H in total; overlap of an AA′BB′ pattern of two methylene units together with the 1H, br d of the anti proton of the allyl at the ring carbon), 3.48 (ddd, 1H, X′ part of allylic methylene), 3.77 (s, 1H, syn proton of the exocyclic allylic carbon), 5.43 (br t, 1H, C*H*═CMe). ^{13}C NMR ($CDCl_3$): 9.4 (CH_3 of Cp*), 26.9 (CH_3 of CH_3—C═), 26.2, 28.0, 29.5, 34.2 (CH_2 of the eight-membered ring), 65.7 (exocyclic H_2C of the allyl moiety), 81.9 (*C*H of the allylic terminal in the ring), 103.4 (ring carbon of Cp*), 112.9 (H*C*═), 122.6 (allyl central carbon in the ring), 137.2 (CH_3C═) ppm.

Synthesis of [Cp*Ru(η^3,η^3-C$_{10}$H$_{14}$)]OTf (5). Complex **4** (35 mg, 0.086 mmol) was dissolved in dichloromethane (3 mL) in a 30-mL round bottomed flask fitted with a magnetic stirrer under an argon atmosphere. An acetone solution (0.2 N) of silver triflate (0.52 mL, 0.104 mmol) was added by syringe with stirring at room temperature. After stirring for 2 h at room temperature, the formed silver chloride was filtrated out by a Celite column. The liquid was concentrated by rotary evaporation to dryness. Recrystallization of the residue from a dichloromethane–ether mixed solvent furnished yellow crystals of **5** (35 mg, 78% yield). Anal. Calcd for $C_{21}H_{29}O_3RuS$: C, 48.54; H, 5.63. Found: C, 48.23; H, 5.69. ^{1}H NMR ($CDCl_3$): δ 1.61 (s, 2H, anti protons of the exocyclic allyl), 1.80 (s, 15H, CH_3, of Cp*), methylene proton signals appeared at 2.60–2.97 as an AA′BB′ multiplet (4H), 3.06 (br s, 2H, anti proton involved in the eight-membered ring), 3.85 (br d with a small coupling constant, 2H, syn protons of the exocyclic allyl group). ^{13}C NMR ($CDCl_3$): 9.8 (q, CH_3 of Cp*), 32.8 and 32.9 (each t, CH_2 of the ring), 57.5 (t, allylic terminal CH_2 at the exocyclic carbons), 82.1 (d, allylic terminal *C*H in the ring), 102.0 (s, ring carbon of Cp*), 125.2 (s, allyl central carbon) ppm. IR (Nujol): 1260 and 1140 (SO_3), 1025 (CF_3) cm^{-1}.

Acknowledgment. The authors are indebted to the Ministry of Education, Science, and Culture of the Japanese Government (Grant-in-Aid for Scientific Research (6347003) and that for Priority Areas (02247210, 03233212, 042172212, 05236217)) and Mitsubishi Chemical Co. Ltd., for their financial support.

OM920800L