Ruthenium-Catalyzed Allylic Substitution of Cyclic Allyl Carbonates with Nucleophiles. Stereoselectivity and Scope of the Reaction

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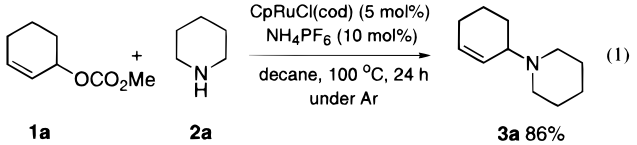
$CpRuCl(cod)/NH_4PF_6$ (Cp = cyclopentadienyl, cod = 1,5-cyclooctadiene) is an effective catalyst system for the allylic substitution of cyclic allyl carbonates with nucleophiles. This catalyst system enables the first investigation of the stereochemical course of the ruthenium-catalyzed allylic substitution reaction, in which the reaction proceeds with an overall retention of configuration. The stoichiometric reaction of *trans*-5-(methoxycarbonyl)cyclohex-2-enyl chloride with Cp*RuCl(cod) (Cp* = pentamethylcyclopentadienyl) gave the unexpected complex $Cp^*Ru(\eta^6\text{-}C_6H_5CO_2Me)^+$ by the rapid dehydrohalogenation/dehydrogenation of the desired $Cp^*RuCl_2(\eta^3\text{-}C_6H_8CO_2Me)$ complex.

Introduction

The transition-metal-complex-catalyzed substitution reaction of allylic alcohol derivatives with nucleophilic reagents is now a well-established methodology in organic synthesis and is widely used to construct complex organic molecules.[1] Most of the work in this field has been devoted to palladium complexes for the design of chemo-, regio-, stereo-, and enantioselective catalyst systems,[2] and a wide range of transition-metal complexes has recently been used for the reaction.[3] However, a general use of ruthenium catalysts has not been forthcoming,[4] and examples are strictly limited to our reports on the ruthenium-catalyzed highly regioselective allylic substitution of acyclic allyl carbonates with carbon[5] and nitrogen nucleophiles,[6] in which substitution exclusively occurred at the more-substituted allylic terminus in η^3-allylruthenium intermediates. Essential to the use of this process in organic synthesis is control of the stereochemical course of the reaction, as well as the regiochemistry. Although ruthenium complexes often show interesting catalytic activity and product selectivity, which are quite different from those with palladium and other transition-metal complexes,[7] the appropriate matching and tuning of the ruthenium catalysts with the substrates, ligands, and solvents used are always important.[6,8] For example, catalysts such as Ru(cod)(cot)[5] (cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene) and Cp*RuCl(cod)[6] (Cp* = pentamethylcyclopentadienyl), which were highly active for the allylic substitution of *acyclic* allyl carbonates, were totally ineffective for the allylic substitution of *cyclic* allyl carbonates. Thus, we have been continuing our efforts to improve and modify the ruthenium catalyst system. After many trials, we finally found that $CpRuCl(cod)/NH_4PF_6$ (Cp = cyclopentadienyl) is a highly effective catalyst system for the allylic substitution of *cyclic* allyl carbonates (eq 1). We report here the development of this new catalyst system, which has enabled the first investigation of the stereochemical course of the ruthenium-catalyzed allylic substitution reaction.



1a **2a** **3a** 86% (1)

(1) (a) Harrington, P. J. In *Transition Metals in Total Synthesis*; Wiley: New York, 1990; p 25. (b) Godleski, S. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, U.K., 1991; Vol. 4, p 585. (c) Hegedus, L. S. In *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994; p 261. (d) Tsuji, J. In *Palladium Reagents and Catalysts*; Wiley: New York, 1995; p 290. (e) Harrington, P. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, p 797. (f) Heumann, A. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: New York, 1998; Vol. 1, p 251. For a review, see: (g) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. (h) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (i) Tsuji, J. *Pure Appl. Chem.* **1982**, *54*, 197. (j) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140.

(2) (a) Trost, B. M. *Pure Appl. Chem.* **1981**, *53*, 2357. (b) Bäckvall, J.-E. *Acc. Chem. Res.* **1983**, *16*, 335. (c) Bäckvall, J.-E. *Pure Appl. Chem.* **1983**, *55*, 1669. (d) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (e) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173. (f) Consiglio, G.; Waymouth, R. *Chem. Rev.* **1989**, *89*, 257. (g) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (h) Trost, B. M. *Pure Appl. Chem.* **1996**, *68*, 779. (i) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (j) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689.

(3) For lead references, see the following. (a) Fe: Enders, D.; Jandeleit, B.; Raabe, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1949. (b) Co: Bhatia, B.; Reddy, M. M.; Iqbal, J. *Tetrahedron Lett.* **1993**, *34*, 6301. (c) Ni: Bricout, H.; Carpentier, J.-F.; Mortreux, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1863. (d) Rh: Evans, P. A.; Nelson, J. D. *J. Am. Chem. Soc.* **1998**, *120*, 5581. (e) Ir: Takeuchi, R.; Kashio, M. *J. Am. Chem. Soc.* **1998**, *120*, 8647. (f) Pt: Brown, J. M.; MacIntyre, J. E. *J. Chem. Soc., Perkin Trans. 2* **1985**, 961. (g) Mo: Trost, B. M.; Hachiya, I. *J. Am. Chem. Soc.* **1998**, *120*, 1104. (h) W: Lloyd-Jones, G. C.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 462 and pertinent references therein.

(4) The catalytic activity of $RuH_2(PPh_3)_4$ for the allylic alkylation reaction has been reported briefly: Minami, I.; Shimizu, I, Tsuji, J. *J. Organomet. Chem.* **1985**, *296*, 269.

(5) Zhang, S.-W.; Mitsudo, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1993**, *450*, 197.

(6) Kondo, T.; Ono, H.; Satake, N.; Mitsudo, T.; Watanabe, Y. *Organometallics* **1995**, *14*, 1945.

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Table 1. Effects of the Catalyst and the Solvent on the Synthesis of 3a by the Reaction of 1a with 2a[a]

catalyst	additive[b]	solvent	yield (%)[c]
Ru(cod)(cot)		decane	4
$Ru_3(CO)_{12}$		decane	0
$RuH_2(PPh_3)_4$		decane	8
$RuCl_2(PPh_3)_3$		decane	10
Cp*RuCl(cod)		decane	0
CpRuCl(cod)		decane	27
CpRuCl(cod)	NH_4PF_6	decane	86
CpRuCl(cod)	NH_4PF_6	*N*-methylpiperidine	75
CpRuCl(cod)	NH_4PF_6	1,4-dioxane	18
CpRuCl(cod)	NH_4PF_6	mesitylene	15
$CpRuCl(PPh_3)_2$	NH_4PF_6	decane	55

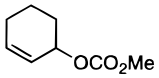
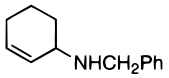
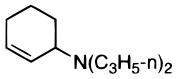
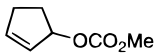
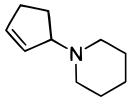
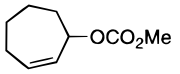
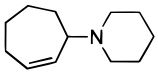
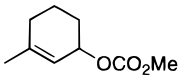
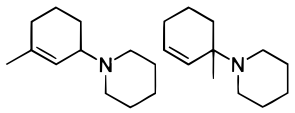
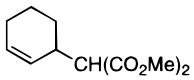
[a] A mixture of **1a** (1.0 mmol), **2a** (2.0 mmol), Ru complex (0.050 mmol), and solvent (2.0 mL) in a 20-mL Pyrex flask was heated at 100 °C for 24 h under an argon atmosphere. [b] NH_4PF_6 (0.10 mmol) was used. [c] GLC yield based on the amount of **1a** charged.

Results and Discussion

We initially examined the catalytic activity of several ruthenium complexes in the reaction of cyclohex-2-enyl methyl carbonate (**1a**) with piperidine (**2a**), and the results are summarized in Table 1. The reaction of **1a** (1.0 mmol) with **2a** (2.0 mmol) in the presence of a catalytic amount of CpRuCl(cod) (5 mol %) and NH_4PF_6 (10 mol %) in decane (2.0 mL) at 100 °C for 24 h under an argon atmosphere gave the corresponding cyclic allylamine, *N*-(cyclohex-2-enyl)piperidine (**3a**), in 86% yield. Other ruthenium catalysts, such as Ru(cod)(cot),[5] $Ru_3(CO)_{12}$, $RuH_2(PPh_3)_4$,[4] $RuCl_2(PPh_3)_3$, and Cp*RuCl(cod),[6] were totally ineffective in the present reaction. Although the catalytic activity of CpRuCl(cod) *itself* was low, the concomitant use of NH_4PF_6 dramatically increased the catalytic activity, probably due to the formation of a coordinatively unsaturated cationic ruthenium species,[9] which is needed to overcome the steric hindrance of cyclic allyl carbonates. The PPh_3 ligand showed a negative effect in the reaction using the catalyst system of $CpRuCl(PPh_3)_2/NH_4PF_6$. The present reaction was also affected by the solvent, and the yield of **3a** drastically decreased in mesitylene and 1,4-dioxane. The best result was obtained in decane.

The results obtained from the $CpRuCl(cod)/NH_4PF_6$-catalyzed allylic substitution of several cyclic allyl carbonates with nucleophiles are summarized in Table 2. Both acyclic primary and secondary amines, represented by benzylamine (**2b**) and dipropylamine (**2c**), were smoothly allylated with **1a** to give the corresponding cyclic allylamines, **3b** and **3c**, in high isolated yields. Five-membered and seven-membered cyclic allyl carbonates, **1b** and **1c**, also reacted with **2a** to give the corresponding cyclic allylamines, **3d** and **3e**, in good yields. In the case of **1d**, substitution predominantly occurred at the less-substituted allylic carbon to give a mixture of regioisomers, **3f** and **3f′**, in a total isolated yield of 88% with a ratio of 77:23. The regiochemistry is quite different from that observed in our previous study on acyclic allyl carbonates,[5,6] probably due to the higher steric hindrance of **1d** and relatively severe reaction conditions. Allylic alkylation of a stabilized *C*-nucleophile, dimethyl sodiomalonate (**4a**), with **1a** also proceeded smoothly to give **5a** in an isolated yield of 92%.

Table 2. $CpRuCl(cod)/NH_4PF_6$-Catalyzed Allylic Substitution of Cyclic Allyl Carbonates with Nucleophiles[a]

cyclic allylic carbonate	nucleophile	product	isolated yield (%)[b]
 **1a**	$PhCH_2NH_2$ **2b**	 **3b**	65
1a	$(n\text{-}C_3H_5)_2NH$ **2c**	 **3c**	83
 **1b**	 **2a**	 **3d**	75
 **1c**	**2a**	 **3e**	65
 **1d**	**2a**	 **3f** **3f'**	88[c]
1a	$NaCH(CO_2Me)_2$ **4a**	 **5a**	92

[a] Conditions: cyclic allylic carbonate (1.0 mmol), nucleophile (2.0 mmol), CpRuCl(cod) (0.050 mmol), NH_4PF_6 (0.10 mmol), decane (2.0 mL) at 100 °C for 24 h under an argon atmosphere. [b] Based on the amount of allyl carbonate charged. [c] **3f**/**3f′** = 77:23.

The development of this new catalyst system enables the first investigation of the stereochemical course of the ruthenium-catalyzed allylic substitution reaction. First, we chose *cis*-5-(methoxycarbonyl)cyclohex-2-enyl methyl carbonate (*cis*-**1e**) as a substrate because it has been extensively used to examine the stereochemical course of palladium-[10] and molybdenum-catalyzed[11] allylic substitution reactions. Treatment of *cis*-**1e** with piperidine (**2a**) in the presence of 5 mol % CpRuCl(cod)

(7) For a recent example, see: (a) Kondo, T.; Suzuki, N.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **1997**, *119*, 6187. (b) Suzuki, N.; Kondo, T.; Mitsudo, T. *Organometallics* **1998**, *17*, 766. (c) Kondo, T.; Uenoyama, S.; Fujita, K.; Mitsudo, T. *J. Am. Chem. Soc.* **1999**, *121*, 482. (d) Mitsudo, T.; Suzuki, T.; Zhang, S.-W.; Imai, D.; Fujita, K.; Manabe, T.; Shiotsuki, M.; Watanabe, Y.; Wada, K.; Kondo, T. *J. Am. Chem. Soc.* **1999**, *121*, 1839 and references therein. For a review, see: Naota, T.; Takaya, H.; Murahashi, S. *Chem. Rev.* **1998**, *98*, 2599.

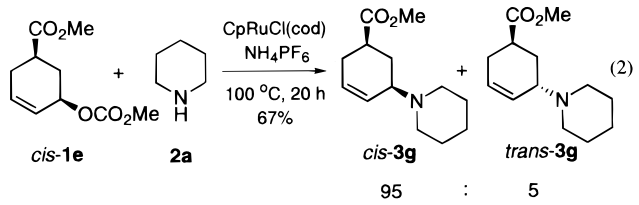
(8) For example, see: (a) Kondo, T.; Hiraishi, N.; Morisaki, Y.; Wada, K.; Watanabe, Y.; Mitsudo, T. *Organometallics* **1998**, *17*, 2131. (b) Kondo, T.; Kodoi, K.; Nishinaga, E.; Okada, T.; Morisaki, Y.; Watanabe, Y.; Mitsudo, T. *J. Am. Chem. Soc.* **1998**, *120*, 5587.

(9) (a) Davies, S. D.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1. (b) For catalytic reactions, see: Trost, B. M. *Chem. Ber.* **1996**, *129*, 1313 and references therein.

(10) (a) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730. (b) Granberg, K. L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1992**, *114*, 6858.

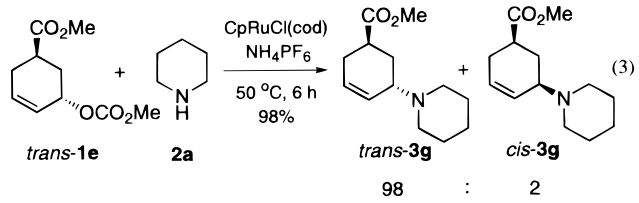
(11) (a) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1987**, *109*, 1469. (b) Trost, B. M.; Merlic, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 9590.

and 10 mol % NH_4PF_6 in decane at 100 °C for 20 h predominantly gave *cis*-**3g** (total yield of **3g** 67%, *cis*-**3g**:*trans*-**3g** = 95:5) (eq 2).[12] The reactivity of *trans*-5-



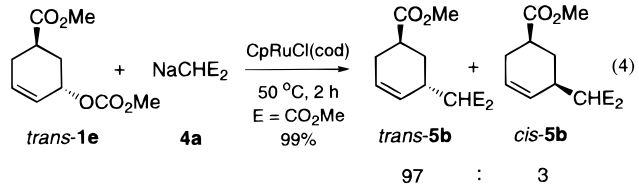
(2)

(methoxycarbonyl)cyclohex-2-enyl methyl carbonate (*trans*-**1e**) was higher than that of *cis*-**1e**, and the reaction of *trans*-**1e** with **2a** at 50 °C for 6 h gave *trans*-**3g** almost exclusively (total yield of **3g** 98%, *trans*-**3g**:*cis*-**3g** = 98:2) (eq 3). The selective formation of *trans*-



(3)

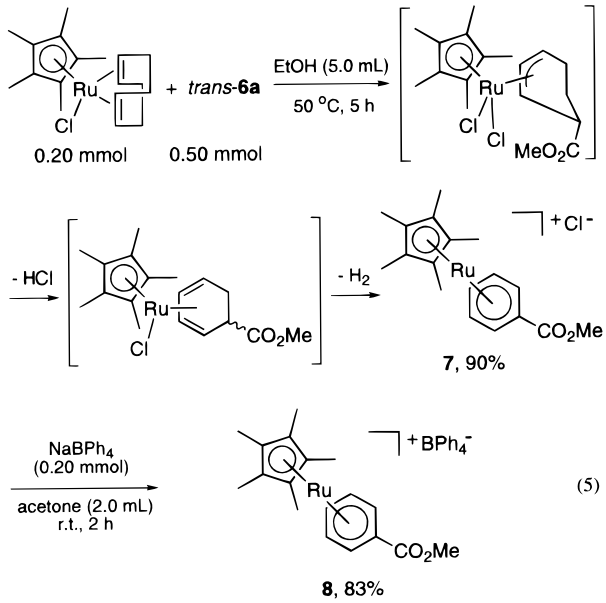
5b from the reaction of *trans*-**1e** with a stabilized *C*-nucleophile (**4a**) was also observed (total yield of **5b** 99%, *trans*-**5b**:*cis*-**5b** = 97:3), where the addition of NH_4PF_6 as a cocatalyst was not needed (eq 4). Consequently,



(4)

the ruthenium-catalyzed allylic substitution proceeded with an overall retention of configuration, since interconversion of *cis*-**3g** and *trans*-**3g** was not observed in any of these reactions.

To investigate the stereochemistry of the first oxidative-addition step of allylic compounds to ruthenium, a stoichiometric reaction of Cp*RuCl(cod) with *trans*-**6a** was examined.[13] The reaction proceeded smoothly in ethanol at 50 °C for 5 h to give an unexpected [Cp*Ru(η^6-$C_6H_5CO_2Me$)]$^+Cl^-$ complex (**7**) as the sole product, which would be obtained by rapid dehydrohalogenation/dehydrogenation[14] of the desired $Cp^*RuCl_2(\eta^3$-$C_6H_8CO_2$-Me) complex (eq 5). The molecular structure of **7** was established by X-ray structure analysis of the anion-



(5)

exchanged complex [Cp*Ru(η^6-$C_6H_5CO_2Me$)]$^+$[BPh_4]$^-$ (**8**) (Figure 1).[15] A similar reaction sequence has already been reported in the reaction of CpRuBr(cod) with 3-bromocyclohexene by Singleton and co-workers.[16] Thus, our attempt to determine the stereochemistry of the oxidative addition of allylic compounds to ruthenium was in vain.

Although little work has been done to determine the stereochemical course of the reaction of (η^3-allyl)ruthenium complexes with nucleophiles, Harman and co-workers recently reported that the reaction with soft nucleophiles exclusively proceeded via an anti mechanism,[17] as in the reaction of most (η^3-allyl)palladium complexes.[10,18] The observations described here together with information in the literature allow us to suggest that the ruthenium-catalyzed allylic substitution reaction proceeds via a double-inversion (anti−anti) mechanism.[19,20] The higher reactivity of *trans*-**1e** compared to that of *cis*-**1e** in the present reaction was explained

(12) The effect of the concentration of CpRuCl(cod) catalyst (5, 10, 25, and 50 mol %) was also examined in the reaction of *cis*-**1e** with **2a**. The best stereoselectivity of product **3g** was observed in eq 2 (5 mol % CpRuCl(cod), *cis*-**3g**/*trans*-**3g** = 95/5). While the increase of the concentration of CpRuCl(cod) catalyst slightly decreased the stereoselectivity of **3g**, the stereoselectivity was constant in the range from 10 mol % to 50 mol % CpRuCl(cod) catalyst (10 mol %, *cis*-**3g**/*trans*-**3g** = 86/14; 25 mol %, *cis*-**3g**/*trans*-**3g** = 88/12; 50 mol %, cis-**3g**/*trans*-**3g** = 87/13). For a related reference, see: Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 897.

(13) Since no reaction occurred between Cp*RuCl(cod) and an allylic carbonate, *trans*-**1e**, under the stoichiometric reaction conditions, the reaction with a more reactive allylic halide, *trans*-**6a**, was examined.

(14) The formation of (η^6-arene)ruthenium(II) complexes by dehydrogenation of cyclohexadienes with ruthenium(III) trichloride has been reported: Bennet, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

(15) Crystal data for **8**: $C_{42}H_{43}O_2BRu$, mol wt = 691.68, yellow crystals, prismatic (0.10 × 0.10 × 0.20 mm), orthorhombic, space group $P2_12_12_1$ (No. 19), a = 14.82(1) Å, b = 14.96(1) Å, c = 31.85(1) Å, V = 7061(7) Å^3, Z = 8, D_{calcd} = 2.602 g/cm^3, F_{000} = 5760.00, μ(Mo Kα) = 9.57 cm^{-1}, data collection temperature 23.0 °C, scan type ω (8.0°/min), $2\theta_{max}$ = 55.0°, 8864 reflections measured, 4708 reflections observed ($I > 3.00\sigma(I)$), R = 0.056, R_w = 0.060, GOF = 1.04.

(16) (a) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1986**, 645. (b) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2347.

(17) Spera, M. L.; Chin, R. M.; Winemiller, M. D.; Lopez, K. W.; Sabat, M.; Harman, W. D. *Organometallics* **1996**, *15*, 5447.

(18) (a) Trost, B. M.; Weber, L. *J. Am. Chem. Soc.* **1975**, *97*, 1611. (b) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416. (c) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 3435. (d) Collins, D. J.; Jackson, W. R.; Timms, R. N. *Aust. J. Chem.* **1977**, *30*, 2167. (e) Åkermark, B.; Bäckvall, J.-E.; Löwenborg, A.; Zetterberg, K. *J. Organomet. Chem.* **1979**, *166*, C33. (f) Åkermark, B.; Jutand, A. *J. Organomet. Chem.* **1981**, *217*, C41.

(19) For a mechanism with double inversion of configuration in palladium-catalyzed allylic alkylation reactions, see: (a) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767. (b) Hayashi, T.; Konishi, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1984**, 107. (c) Hayashi, T.; Yamamoto, A.; Hagihara, T. *J. Org. Chem.* **1986**, *51*, 723. (d) Fiaud, J.-C.; Legros, J.-Y. *J. Org. Chem.* **1987**, *52*, 1907.

(20) A mechanism with double retention of configuration is unlikely in the present reaction, but cannot be completely ruled out: (a) Faller, J. W.; Linebarrier, D. *Organometallics* **1988**, *7*, 1670. (b) Dvořák, D.; Starý, I.; Kočovský, P. *J. Am. Chem. Soc.* **1995**, *117*, 6130.

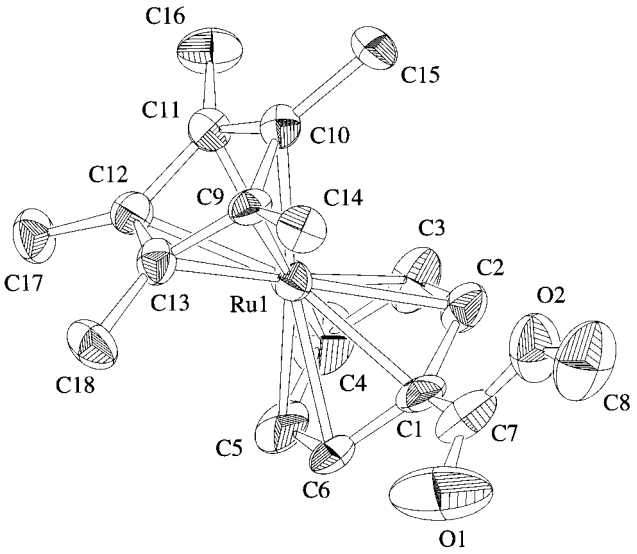


Figure 1. ORTEP drawing of **8** with 30% thermal ellipsoids. Only one of the two independent molecules is shown for clarity. Hydrogen atoms and the counterion (BPh_4^-) are also omitted for clarity.

as follows. *trans*-**1e** should always react faster, since the leaving group is pseudoaxial, so that the alignment of the π system with the σ^* orbital is easily attained in contrast to *cis*-**1e**, where the leaving group is pseudoequatorial.[21]

In conclusion, we developed a novel ruthenium catalyst system for allylic substitution of *cyclic* allyl carbonates. The development of this new catalyst system provides some insight into the stereochemistry of the ruthenium-catalyzed allylic substitution reaction, and we believe that this finding broadens the applicability of the ruthenium catalyst to organic synthesis using a transition-metal-catalyzed allylic substitution reaction.

Experimental Section

General Considerations. GLC analyses were performed on a Shimadzu GC-8A gas chromatograph with a glass column (3 mm i.d. × 3 m) packed with Silicone SE-30 (5% on Chromosorb W(AW-DMCS), 80−100 mesh) and a Shimadzu GC-14A gas chromatograph with a capillary column (Shimadzu capillary column HiCap-CBP10-M25-025 (polarity similar to OV-1701): 0.22 mm i.d. × 25 m). The ^{1}H (270, 300, and 400 MHz) and ^{13}C NMR spectra (67.5, 75, and 100 MHz) were obtained on JEOL GSX-270, AL-300, and EX-400 spectrometers, respectively. Samples were analyzed in $CDCl_3$, and the chemical shift values are expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a Nicolet Impact 410 spectrometer. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. The reagents used in this study were dried and purified before use by standard procedures. Cyclic allyl carbonates (**1a**−**e**) were prepared from the corresponding alcohols and methyl chloroformate according to the reported procedure.[22] *cis*- and *trans*-5-(Methoxycarbonyl)cyclohex-2-en-1-ol and *trans*-5-(methoxycarbonyl)cyclohex-2-enyl chloride (*trans*-**6a**) were prepared as described in the literature.[23] NH_4PF_6 and $Ru_3(CO)_{12}$ were obtained commercially and used without further purification. Ru(cod)(cot),[24] $RuH_2(PPh_3)_4$,[25] $RuCl_2(PPh_3)_3$,[26] Cp*RuCl(cod),[27] CpRuCl(cod),[28] and CpRuCl-$(PPh_3)_2$[29] were prepared as described in the literature.

General Procedure. A mixture of cyclic allylic carbonate (**1**) (1.0 mmol), *N*-nucleophile (**2**) or *C*-nucleophile (**4a**) (2.0 mmol), CpRuCl(cod) (15.5 mg, 0.050 mmol), NH_4PF_6 (16.3 mg, 0.10 mmol), and decane (2.0 mL) was placed in a two-necked 20-mL Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under a flow of argon. The mixture was magnetically stirred at 100 °C for 24 h. After the reaction mixture was cooled, the products were analyzed by GLC and isolated by column chromatography (Florisil (60−100 mesh), eluent Et_2O), followed by Kugelrohr distillation.

The spectral and analytical data of **3a**,[30] **3c**,[31] **3d**,[32] **5a**,[33] *trans*-**5b**,[10] and *cis*-**5b**[10] have already been reported. All of the new compounds are characterized below.

3-Methylcyclohex-2-enyl Methyl Carbonate (1d). Colorless liquid. Bp: 60−65 °C (1.0 mmHg, Kugelrohr). IR (neat): 1672, 1749 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 1.61−1.64 (m, 1H), 1.71 (s, 3H), 1.75−1.79 (m, 3H), 1.94−1.96 (m, 2H), 3.77 (s, 3H), 5.08 (br, 1H), 5.53 (br, 1H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 18.4, 23.3, 27.6, 29.6, 54.0, 72.2, 119.1, 141.3, 155.2. MS (EI): *m*/*z* 170 (M^+). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.75; H, 8.49.

***N*-(Cyclohex-2-enyl)dipropylamine (3b).** Colorless liquid. Bp: 50−55 °C (1.0 mmHg, Kugelrohr). IR (neat): 724, 1656 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.85 (t, 3H, J = 7.34 Hz), 1.26 (br, 2H), 1.42 (m, 4H), 1.76−1.80 (m, 2H), 1.95 (br, 2H), 2.27−2.46 (m, 4H), 3.34 (br, 1H), 5.59−5.62 (m, 1H), 5.70−5.80 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.9, 22.0, 22.4, 23.9, 25.4, 53.0, 57.1, 129.2, 131.3. MS (EI): *m*/*z* 181 (M^+). Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.78. Found: C, 79.36; H, 12.88.

***N*-(Cyclohept-2-enyl)piperidine (3e).** Colorless liquid. Bp: 60−70 °C (1.0 mmHg, Kugelrohr). IR (neat): 1650 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.24−1.34 (m, 2H), 1.34−1.47 (m, 3H), 1.50−1.63 (m, 4H), 1.63−1.70 (m, 1H), 1.82−1.86 (m, 1H), 1.90−2.20 (m, 3H), 2.42−2.55 (m, 4H), 3.20 (br, 1H), 5.72−5.85 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.7, 26.4, 26.6, 28.3, 28.9, 29.2, 49.5, 65.4, 130.4, 135.1. MS (EI): *m*/*z* 179 (M^+). Anal. Calcd for $C_{12}H_{21}N$: C, 80.38; H, 11.80. Found: C, 80.10; H, 11.65.

***N*-(3-Methylcyclohex-2-enyl)piperidine (3f).** Colorless liquid. Bp: 60−70 °C (1.0 mmHg, Kugelrohr). IR (neat): 1687 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.35−1.50 (m, 2H), 1.50−1.61 (m, 6H), 1.67 (s, 3H), 1.71−1.82 (m, 2H), 1.82−1.95 (m, 2H), 2.42−2.61 (m, 4H), 3.12 (m, 1H), 5.38 (br, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.4, 23.7, 24.8, 25.0, 26.5, 30.1, 49.7, 61.3, 124.3, 136.6. MS (EI): *m*/*z* 179 (M^+). Exact mass: calcd for $C_{12}H_{21}N$, 179.1675; found, 179.1673.

***N*-(1-Methylcyclohex-2-enyl)piperidine (3f′).** Colorless liquid. Bp: 60−70 °C (1.0 mmHg, Kugelrohr). IR (neat): 737, 1673 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.17 (s, 3H), 1.35−1.50 (m, 2H), 1.50−1.61 (m, 6H), 1.71−1.82 (m, 2H), 1.82−1.95 (m, 2H), 2.42−2.61 (m, 4H), 5.50 (d, J = 10.28 Hz, 1H), 5.67 (dt, J = 10.28, 3.76 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz):

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δ 20.4, 21.9, 24.9, 25.5, 26.8, 28.0, 46.9, 56.7, 126.7, 135.5. MS (EI): *m*/*z* 179 (M^+). These spectral data were obtained for a 77:23 mixture of **3f** and **3f′**.

Methyl *cis*-5-Piperidinylcyclohex-3-enecarboxylate (*cis*-3g). Colorless liquid. Bp: 100−110 °C (1.0 mmHg, Kugelrohr). IR (neat): 1736 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.41−1.46 (m, 2H), 1.54−1.60 (m, 4H), 1.63 (q, J = 7.81 Hz, 1H), 2.08−2.11 (m, 1H), 2.19−2.23 (m, 2H), 2.47−2.50 (m, 2H), 2.54−2.62 (m, 3H), 3.36 (m, 1H), 3.70 (s, 3H), 5.66−5.69 (m, 1H), 5.75−5.77 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.7, 25.0, 26.5, 27.9, 39.4, 49.5, 51.7, 61.3, 127.1, 130.6, 175.9. MS (EI): *m*/*z* 223 (M^+). Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48. Found: C, 69.87; H, 9.26.

Methyl *trans*-5-Piperidinylcyclohex-3-enecarboxylate (*trans*-3g). Colorless liquid. Bp: 100−110 °C (1.0 mmHg, Kugelrohr). IR (neat): 1736 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz); δ 1.41−1.46 (m, 2H), 1.51−1.62 (m, 4H), 1.76 (ddd, J = 5.86, 9.72, 13.67 Hz, 1H), 2.06 (td, J = 4.40, 13.67 Hz, 1H), 2.22−2.26 (m, 2H), 2.43−2.50 (m, 2H), 2.54−2.61 (m, 2H), 2.72−2.79 (m, 1H), 3.13−3.14 (m, 1H), 3.69 (s, 3H), 5.68−5.75 (m, 1H), 5.82−5.87 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.6, 25.0, 26.4, 27.1, 36.9, 49.2, 50.5, 57.5, 127.5, 128.4, 175.6. MS (EI): *m*/*z* 223 (M^+). Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48. Found: C, 69.85; H, 9.21.

Preparation of [Cp*Ru(η^6-$C_6H_5CO_2Me$)]$^+$[Cl]$^-$ (7) and [Cp*Ru(η^6-$C_6H_5CO_2Me$)]$^+$[BPh_4]$^-$ (8). A mixture of Cp*RuCl(cod) (75.9 mg, 0.20 mmol), *trans*-**6a** (0.50 mmol), and ethanol (5.0 mL) was placed in a two-necked 20-mL Pyrex flask equipped with a magnetic stirring bar under a flow of argon. The mixture was magnetically stirred at 50 °C for 5 h. After the mixture was cooled, the solvent was evaporated and the orange residue was washed with pentane (10 mL × 2), followed by drying in vacuo to give 73.4 mg (0.18 mmol, 90%) of [Cp*Ru(η^6-$C_6H_5CO_2Me$)]$^+$[Cl]$^-$ (**7**) as an orange powder. Mp: 277.2−279.5 °C dec. IR (KBr): 1726 cm^{-1}. ^1H NMR (270 MHz, CD_2Cl_2): δ 2.16 (s, 15H), 4.06 (s, 3H), 6.72 (br, 2H), 7.26−7.31 (br, 2H), 7.70−7.71 (br, 1H).

A mixture of complex **7** (73.4 mg, 0.18 mmol), $NaBPh_4$ (68.4 mg, 0.20 mmol), and acetone (2.0 mL) was placed in a two-necked 20-mL Pyrex flask equipped with a magnetic stirring bar under a flow of argon. The mixture was magnetically stirred at room temperature. After 2 h, the white precipitate (NaCl) was filtered off and washed with acetone (5 mL × 2). The combined filtrate was evaporated, and the orange residue was recrystallized from CH_2Cl_2/Et_2O to give 103.2 mg (0.15 mmol, 83%) of [Cp*Ru(η^6-$C_6H_5CO_2Me$)]$^+$[BPh_4]$^-$ (**8**) as orange crystals. Mp: 175.6−179.0 °C dec. IR (KBr): 1730 cm^{-1}. ^1H NMR (270 MHz, CD_2Cl_2): δ 1.83 (s, 15H), 3.96 (s, 3H), 5.49−5.54 (m, 3H), 6.14 (d, J = 6.24 Hz, 2H), 6.87 (t, J = 7.16 Hz, 4H), 7.02 (t, J = 7.43 Hz, 8H), 7.31 (m, 8 H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 10.5, 53.9, 87.1, 87.9, 88.6, 98.4, 122.2, 125.9, 126.0, 136.3, 163.3, 164.0, 164.6, 164.7, 165.4.

X-ray Structural Determination of [Cp*Ru(η^6-$C_6H_5CO_2Me$)]$^+$[BPh_4]$^-$ (8). Crystal data, data collection, and refinement parameters for [Cp*Ru(η^6-$C_6H_5CO_2Me$)]$^+$[BPh_4]$^-$ (**8**) are summarized in the X-ray structure report (see the Supporting Information). A single crystal of [Cp*Ru(η^6-$C_6H_5CO_2Me$)]$^+$[BPh_4]$^-$ (**8**) was mounted and placed on a Rigaku AFC-7R diffractometer. The unit cell was determined by the automatic indexing of 20 centered reflections and confirmed by the examination of axial photographs. Intensity data were collected using graphite-monochromated Mo Kα X-radiation (λ = 0.710 69 Å). Check reflections were measured every 150 reflections; the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was determined using Patterson and standard difference map techniques on an O2 computer using SHELX97.[34] Systematic absences were uniquely consistent with the space group $P2_12_12_1$ (No. 19).

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Supporting Information Available: Tables giving crystal data and refinement details, positional and thermal parameters, and bond distances and angles for [Cp*Ru(η^6-$C_6H_5CO_2Me$)]$^+$[BPh_4]$^-$ (**8**). This material is available free of charge via the Internet at http://pubs.acs.org.

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