Novel Ruthenium Complex-Catalyzed Dimerization of 2,5-Norbornadiene to Pentacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradeca-4,11-diene Involving Carbon−Carbon Bond Cleavage

Take-aki Mitsudo,* Toshiaki Suzuki, Shi-Wei Zhang,† Daisuke Imai, Ken-ichi Fujita,‡ Takao Manabe, Masashi Shiotsuki, Yoshihisa Watanabe, Kenji Wada, and Teruyuki Kondo

Contribution from the Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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Abstract: Bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene) dimerizes in the presence of a catalytic amount of Ru(1-2:5-6-η-cyclooctadiene)(1-6-η-cyclooctatriene) (Ru(cod)(cot)) and an electron-deficient olefin such as *N*,*N*-dimethylacrylamide, dimethyl fumarate, or dimethyl maleate in toluene or tetrahydrofuran (THF) to give a new compound, pentacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradeca-4,11-diene (PCTD), in high yield along with a small amount of a known *endo*−*endo* dimer, heptacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{4,11}$.$0^{5,9}$.$0^{10,14}$]tetradecane (HCTD), which is a major product in the reaction in DMSO. Ru(cod)(cot)-dimethyl fumarate in THF was the most efficient catalyst, and the yield of PCTD was 96% even at 40 °C. The structure of PCTD was determined by X-ray analysis of its derivative, $[AgOTf(PCTD)]_n$. PCTD was found to be derived via *endo*−*endo* dimerization of 2,5-norbornadiene. Formation of PCTD from two molecules of 2,5-norbornadiene involves the cleavage of two carbon−carbon bonds. Dimerization of 7-*tert*-butoxy-2,5-norbornadiene gave the corresponding *exo*- and *endo*-4,9-disubstituted PCTD derivatives. Ru(cod)(cot) reacts with dimethyl fumarate to give a novel complex, $Ru(cot)(dmfm)_2$ (dmfm = dimethyl fumarate), in high yield. The structure of the complex was determined by X-ray analysis. At 40 °C in toluene, $Ru(cot)(dmfm)_2$ itself catalyzes the dimerization of 2,5-norbornadiene to give PCTD in excellent yield in the absence of olefinic additives. The mechanisms of the formation of PCTD are discussed.

Introduction

Recently, transition metal complex-catalyzed organic syntheses involving carbon−carbon bond cleavage[1−16] have received much attention. Some of these reactions involve the oxidative addition of a carbon−carbon single bond to low-valent metal complexes,[2−10] and β-alkyl elimination[11−14] to give the products. These reactions often provide versatile, novel methods to prepare useful compounds. Most of the catalytic carbon−carbon bond cleavage reactions that have been reported so far, except for the metathesis of olefins, have been due to ring strain,[2−5,11] prearomaticity,[12] intramolecular addition in which the carbon−carbon bond is forced into close proximity to the metal,[6−8,13] or combinations of these phenomena.[9,10,14] The first ruthenium[15] and tin[16] complex-catalyzed deallylations of tertiary homoallyl alcohols have been reported quite recently.

On the other hand, highly selective ruthenium complex-catalyzed carbon−carbon bond-forming reactions have been

* To whom correspondence should be addressed.

† Present address: The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567.

‡ Present address: Faculty of Integrated Human Studies and Graduated School of Human and Environmental Studies, Kyoto University, Yoshida, Kyoto 606-8501.

(1) For reviews, see: (a) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241.

(2) (a) Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780. (b) Noyori, R.; Kumagai, Y.; Umeda, I.; Takaya, H. *J. Am. Chem. Soc.* **1972**, *94*, 4018.

(3) (a) Aoki, S.; Fujimura, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1988**, *110*, 3296. (b) Fujimura, T.; Aoki, S.; Nakamura, E. *J. Org. Chem.* **1991**, *56*, 2809.

(4) (a) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2013. (b) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843.

(5) Lautens, M.; Ren, Y. *J. Am. Chem. Soc.* **1996**, *118*, 10668.

(6) Kaneda, K.; Azuma, H.; Wayaku, M.; Teranisi, S. *Chem. Lett.* **1974**, 215.

(7) Suggs, J. W.; Jun, C.-H. *Chem. Commun.* **1985**, 92.

(8) Lieu, S.-Y.; van der Boom, M.; Milstein, D. *Chem. Commun.* **1998**, 687.

(9) (a) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1991**, *113*, 2771. (b) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 4895.

(10) (a) Murakami, M.; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540. (b) Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285. (c) Murakami, M.; Takahashi, K.; Amii, H.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 9307. (d) Murakami, M.; Itami, K.; Ubukata, M.; Tsuji, I.; Ito, Y. *J. Org. Chem.* **1998**, *63*, 4.

(11) Hayashi, M.; Ohmatsu, T.; Meng, Y.-P.; Saigo, K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 837.

(12) (a) Rondon, D.; Chaudret, B.; He, X.-D.; Labroue, D. *J. Am. Chem. Soc.* **1991**, *113*, 5671. (b) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647.

(13) Harayama, H.; Kuroki, T.; Kimura, M.; Tanaka, S.; Tamaru, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2352.

(14) Tsukada, N.; Shibuya, A.; Nakamura, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 8123.

(15) Kondo, T.; Kodoi, K.; Nishinaga, E.; Okada, T.; Morisaki, Y.; Watanabe, Y.; Mitsudo, T. *J. Am. Chem. Soc.* **1998**, *120*, 5587.

(16) Nokami, J.; Yoshizane, K.; Matsuura, H.; Sumida, S. *J. Am. Chem. Soc.* **1998**, *120*, 6609.

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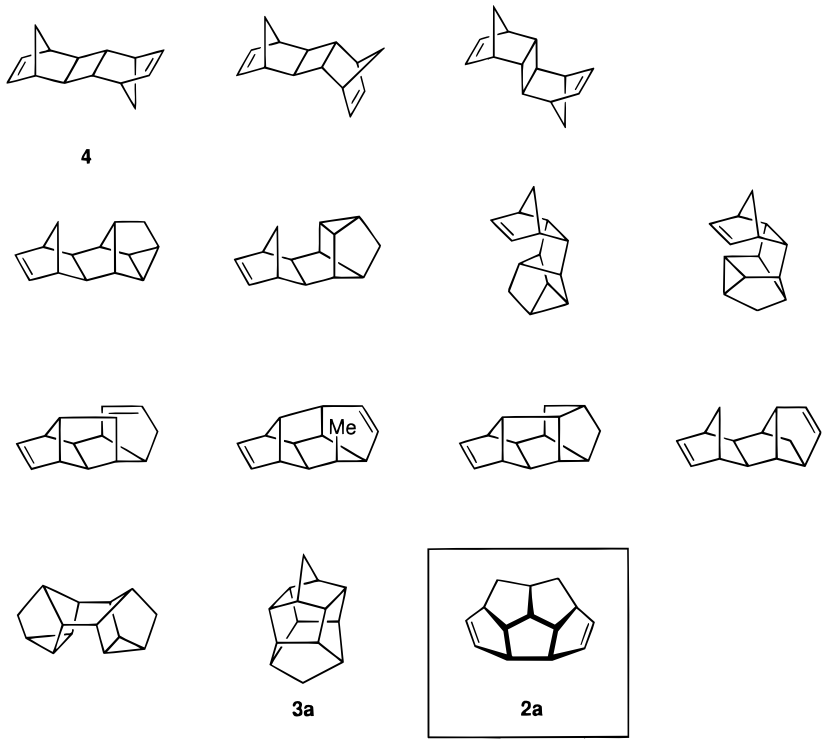
Chart 1. Reported Dimers of 2,5-Norbornadiene



intensively developed.[17−27] We have previously reported the highly selective ruthenium complex-catalyzed codimerization of olefins or dienes with acetylenes.[24,25] In the course of our study on the codimerization of bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadienes, **1a**) with electron-deficient olefins, we observed the unexpected dimerization of **1a**, rather than codimerization, to form pentacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradeca-4,11-diene (PCTD, **2a**).[28]

Several dimerization reactions of **1a** have been reported to give various dimers, as shown in Chart 1. It has been reported that dimerization of **1a** is effectively catalyzed by a variety of metal complexes such as $Fe(CO)_5$,[29,30] $Fe_2(CO)_9$,[30] $Fe_3(CO)_{12}$,[30] $Fe(CO)_2(NO)_2$,[31] $Fe_2(AsMe_2)(CO)_6(NO)$,[32] $Co_2(CO)_8$,[30,33] Zn-

(17) Bennett, M. A.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U. K., 1982; Vol. 4, p 931.

(18) (a) Trost, B. M.; Krause, L.; Portnoy, M. *J. Am. Chem. Soc.* **1997**, *119*, 11319. (b) Trost, B. M.; Portnoy, M.; Kurihara, H. *J. Am. Chem. Soc.* **1997**, *119*, 836. (c) Trost, B. M.; Imi, K.; Davies, I. W. *J. Am. Chem. Soc.* **1995**, *117*, 5371. (d) Trost, B. M.; Mueller. T. J. J.; Martines, J. *J. Am. Chem. Soc.* **1995**, *117*, 1888. (e) Trost, B. M.; Indolese, A. F.; Mueller. T. J. J.; Treptow, B. *J. Am. Chem. Soc.* **1995**, *117*, 615. (f) Trost, B. M.; Mueller. T. J. J. *J. Am. Chem. Soc.* **1994**, *116*, 4985. (g) Trost, B. M.; Flygare, J. A. *J. Org. Chem.* **1994**, *59*, 1078. (h) Trost, B. M.; Martines, J.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 10402. (i) Trost, B. M.; Imi, K.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 8831. (j) Trost, B. M.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 4361.

(19) (a) Chatani, N.; Morimoto, T.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **1998**, *120*, 5335. (b) Fukuyama, T.; Chatani, N.; Kakiuchi, F.; Murai, S. *J. Org. Chem.* **1997**, *62*, 5647. (c) Morimoto, T.; Chatani, N.; Fukumoto, Y.; Murai, S. *J. Org. Chem.* **1997**, *62*, 3762. (d) Chatani, N.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Org. Chem.* **1997**, *62*, 2604. (e) Chatani, N.; Fukuyama, T.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **1996**, *118*, 493. (f) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049. (g) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529.

(20) (a) Yamamoto, Y.; Kitahara, H.; Hattori, R.; Itoh, K. *Organometallics* **1998**, *17*, 1910. (b) Itoh, K.; Masuda, K.; Fukahori. T.; Nakano, K.; Aoki, K.; Nagashima, H. *Organometallics* **1994**, *13*, 1020. (c) Masuda, K.; Ohkita, H.; Kurumatani, S.; Itoh, K. *J. Organomet. Chem.* **1993**, *454*, C13. (d) Masuda, K.; Ohkita, H.; Kurumatani, S.; Itoh, K.. *Organometallics* **1993**, *12*, 2221.

(21) (a) Doyle, M. P.; Peterson, C. S.; Zhou, Q.-L.; Nishiyama, H. *Chem. Comuun.* **1997**, 211. (b) Park, S.-B.; Murata, K.; Matsumoto. H.; Nishiyama, H. *Tetrahedron: Assym.* **1995**, *6*, 2487. (c) Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223.

(22) (a) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887. (b) Kim, S. H.; Zuercher, W. J.; Bowden, N. B.; Grubbs, R. H. *J. Org. Chem.* **1996**, *61*, 1073. (c) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (d) Fu, G. C.; Grubbs, R. H.; Nguyen, S. T. *J. Am. Chem. Soc.* **1993**, *115*, 9856. (e) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858.

(23) (a) Kinoshita, A.; Mori, M. *Heterocycles* **1997**, *46*, 287. (b) Kinoshita, A.; Sakakibara, N.; Mori, M. *J. Am. Chem. Soc.* **1997**, *119*, 12388. (c) Kinoshita, A.; Mori, M. *J. Org. Chem.* **1996**, *61*, 8356. (d) Kinoshita, A.; Mori, M. *Synlett.* **1994**, *12*, 1020.

(24) (a) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580. (b) Mitsudo, T.; Nakagawa, Y.; Watanabe, K.; Hori, Y.; Masawa, H.; Watanabe, H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 565. (c) Mitsudo, T.; Nakagawa, Y.; Watanabe, H.; Watanabe, K.; Masawa, H.; Watanabe, Y. *Chem. Commun.* **1981**, 496.

(25) (a) Mitsudo, T.; Zhang, S.-W.; Nagao, M.; Watanabe, Y. *Chem. Commun.* **1991**, 598. (b) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Organomet. Chem.* **1987**, *334*, 157. (c) Mitsudo, T.; Hori, Y.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3201. (d) Mitsudo, T.; Kokuryo, K.; Shinsugi, T.; Nakagawa, Y.; Watanabe, Y.; Takegami, Y. *J. Org. Chem.* **1979**, *44*, 4492.

(26) (a) Zhang, S.-W.; Mitsudo, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1995**, *485*, 55. (b) Zhang, S.-W.; Mitsudo, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1993**, *450*, 197. (c) Mitsudo, T.; Zhang, S.-W.; Kondo, T.; Watanabe, Y. *Tetrahedron Lett.* **1992**, *33*, 341. (d) Mitsudo, T.; Zhang, S.-W.; Satake, N.; Kondo, T.; Watanabe, Y. *Tetrahedron Lett.* **1992**, *33*, 5533. (e) Mitsudo, T.; Takagi, M.; Zhang, S.-W.; Watanabe, Y. *J. Organomet. Chem.* **1992**, *423*, 405.

(27) (a) Suzuki, N.; Kondo, T.; Mitsudo, T. *Organometallics* **1998**, *17*, 766. (b) Kondo, T.; Suzuki, N.; Okada, T. Mitsudo, T. *J. Am. Chem. Soc.* **1997**, *119*, 6187.

(28) Mitsudo, T.; Zhang, S.-W.; Watanabe, Y. *Chem. Commun.* **1994**, 435.

(29) Lemal, D. M.; Shim, K. S. *Tetrahedron Lett.* **1961**, *11*, 368.

(30) Bird, C. W.; Colinese, D. L.; Cookson, R. C.; Hudec, J.; Williams, R. O. *Tetrahedron Lett.* **1961**, *11*, 373.

(31) Jolly, P. W.; Stone, F. G. A.; Mackenzie, K. *J. Chem. Soc.* **1965**, 6416.

(32) Langenbach, H. J.; Keller, E.; Vahrenkamp, H. *Angew. Chem., Int Ed. Engl.* **1977**, *16*, 188.

(33) (a) Ennis, M.; Manning, A. R. *J. Organomet. Chem.* **1976**, *116*, C31. (b) Ennis, M.; Foley, R. M.; Manning, A. R. *J. Organomet. Chem.* **1979**, *166*, C18.

Table 1. Ruthenium Complex-Catalyzed Dimerization of **1a** in the Presence of *N,N*-Dimethylacrylamide or Dimethyl Fumarate[a]

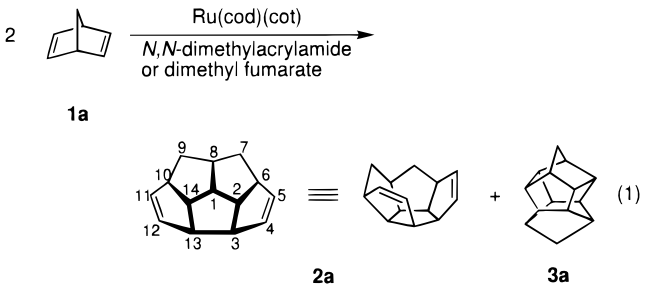
						yield, %[d]		
run	catalyst	olefinic additive[b]	solvent[c]	temp., °C	time, h	**2a**	**3a**	**4**
1	Ru(cod)(cot)	DMAc	NMP	80	10	83	2	0
2	Ru(cod)(cot)	DMAc	NMP	120	15	82	6	0
3	Ru(cod)(cot)	DMAc	toluene	120	15	93	5	0
4	Ru(cod)(cot)	DMFm	THF	40	1	96	2	0
5	Ru(1-5-η-cyclooctadienyl)$_2$	DMFm	toluene	120	2	92	2	0
6	Ru(1-5-η-cyclooctadienyl)$_2$	DMFm	THF	40	24	1	trace	0
7	$Ru_3(CO)_{12}$	DMFm	toluene	120	2	73	9	3
8	$Ru_3(CO)_{12}$[e]	DMAc	NMP[f]	80	10	2	0	63

[a] 2,5-Norbornadiene, 5.0 mmol; catalyst, 2.0 mol % as metal; olefinic additive, 20 mol %; solvent, 3.0 mL in a sealed glass tube at 80 or 120 °C, or in a 20 mL two-necked flask at 40 °C. [b] DMAc, *N,N*-dimethylacrylamide; DMFm, dimethyl fumarate. [c] NMP, *N*-methylpiperidine; THF, tetrahydrofuran. [d] GC yield. [e] 6.0 mol % as Ru atom. [f] 0.30 mL.

$[Co(CO)_4]_2$,[34] $Co_2(CO)_6(PPh_3)_2$,[35] $CoBr(PPh_3)_3$,[36] Rh/C,[37] $RhCl(PPh_3)_3$,[37c] $RhCl(cyclooctene)_2$,[38] $Ni(CO)_4$,[39,40] $Ni(acrylonitrile)_2$,[41] and $Mo(CO)_6$.[42] In most cases, more than five isomeric dimers and/or their carbonylated compounds are produced simultaneously. In all of these products, except for **2a**, the structure of **1a** is retained. The dimerization of **1a** to **2a** is a novel type of reaction that involves the cleavage of at least two carbon−carbon bonds to give a new carbon skeleton. In this study, the details of the ruthenium complex-catalyzed dimerization of **1a** were examined, and we found that the products dramatically depend on the ruthenium complexes, additives, and solvents. When Ru(cod)(cot)-dimethyl fumarate was used as a catalyst in tetrahydrofuran (THF), **2a** was obtained in excellent yield. Thus, the ruthenium complex can catalyze carbon−carbon bond cleavage and reconstruction of a novel carbon skeleton under very mild conditions. Preliminary results have been reported in a communication.[28]

Results and Discussion

2,5-Norbornadiene (**1a**) dimerized in the presence of a catalytic amount of ruthenium complexes such as Ru(1-2:5-6-η-cyclooctadiene)(1-6-η-cyclooctatriene), [Ru(cod)(cot)], together with electron-deficient olefins under mild reaction conditions to give a novel dimer **2a** in excellent-to-high yield along with a small amount of a known dimer, heptacyclo-[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{4,11}$.$0^{5,9}$.$0^{10,14}$]tetradecane (HCTD,[42] **3a**) as a byproduct (eq 1).



Catalysts, Additives, and Solvents. The catalytic activities of various ruthenium complexes were examined with regard to the dimerization of **1a** in the presence of an electron-deficient olefin such as *N,N*-dimethylacrylamide or dimethyl fumarate, and the results are summarized in Table 1. The zerovalent ruthenium complex, Ru(cod)(cot), was the best catalyst for this reaction (runs 1−4). In *N*-methylpiperidine, Ru(cod)(cot)-*N,N*-dimethylacrylamide catalyzed the dimerization of **1a** at 80 °C to give **2a** in 83% yield (run 1), and a higher temperature (120 °C) decreased the selectivity for **2a** (run 2). In toluene at 120 °C, the yield of **2a** increased to 93% (run 3). Ru(cod)(cot) in the presence of dimethyl fumarate in THF catalyzed the reaction even at 40 °C to give **2a** in 96% yield (run 4). The presence of an electron-deficient olefinic additive was essential. In the absence of electron-deficient olefins, **2a** was still formed, but the amount corresponded to the amount of the catalyst (yield ca. 2%). A divalent ruthenium complex, Ru(1-5-η-cyclooctadienyl)$_2$, which is an isomer of Ru(cod)(cot), catalyzed the dimerization at 120 °C (run 5). In THF at 40 °C, however, Ru(1-5-η-cyclooctadienyl)$_2$ did not show catalytic activity (run 6). This suggests that a higher temperature is required to generate the catalytically active species from Ru(1-5-η-cyclooctadienyl)$_2$ for the dimerization of **1a**. $Ru_3(CO)_{12}$ with dimethyl fumarate gave **2a** in good yield in toluene (run 7), while $Ru_3(CO)_{12}$ with *N,N*-dimethylacrylamide in *N*-methylpiperidine at 80 °C gave only 2% of **2a**, and the *exo-trans-exo* dimer of **1a**, pentacyclo-[8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]tetradeca-5,11-diene (**4**),[35] in 63% yield (run 8).

The catalytic activities of various ruthenium complexes and other transition metal complexes for the dimerization of **1a** in the presence of dimethyl fumarate were examined. A ruthenium hydride complex, $RuH_2(PPh_3)_4$, and trinuclear ruthenium anion complexes, $[PPN][Ru_3H(CO)_{11}]$ and $[PPN][Ru_3Cl(CO)_{10}]$ ([PPN] = bis(triphenylphosphine)iminium cation), were effective in producing **2a** in moderate yield in the presence of dimethyl fumarate (43−55%). Other ruthenium complexes such as $[RuCl_2(cod)]_n$, $[RuCl_2(CO)_3]_2$, $[RuCp(CO)_2]_2$ (Cp = cyclopentadienyl), $[RuCp^*(CO)_2]_2$, $[RuCp^*Cl_2]_2$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl), and $Ru(acac)_3$ (acac = acetylacetonato anion) showed no catalytic activity under these reaction conditions. Other metal complexes such as $Pd(PPh_3)_4$,

(34) (a) Schrauzer, G. N.; Bastian, B. N.; Fosselius, G. A. *J. Am. Chem, Soc.* **1966**, *88*, 4890. (b) Schrauzer, G. N.; Ho, R. K. Y.; Schlesinger, G. *Tetrahedron Lett.* **1970**, 543.

(35) Arnold, D. R.; Trecker, D. J.; Whipple, E. B. *J. Am. Chem. Soc.* **1965**, *87*, 2596.

(36) Kanai, H.; Watabe, Y.; Nakayama. T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1277.

(37) (a) Mrowca, J. J.; Katz, T. J. *J. Am. Chem. Soc.* **1966**, *88*, 4012. (b) Katz, T. J.; Carnahan Jr., J. C.; Boecke, R. *J. Org. Chem.* **1967**, *32*, 1301. (c) Acton, N.; Roth, R. J.; Katz, T. J.; Frank, J. K.; Maier, C. A.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 5446.

(38) Kiji, J.; Nishimura, S.; Yoshikawa, S.; Sasakawa. E.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2523.

(39) (a) Bird, C. W.; Cookson, R. C.; Hudec, J. *Chem. Ind.* **1960**, 20. (b) Doyle, M. J.; McMeeking, J.; Binger, P. *Chem. Commun.* **1976**, 376.

(40) Voecks, G. E.; Jennings, P. W.; Smith, G. D.; Caughlan, C. N. *J. Org. Chem.* **1972**, *37*, 1460.

(41) Yoshikawa, S.; Kiji, J.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1093.

(42) (a) Chow, T. J.; Chao, Y.-S.; Liu, L.-K. *J. Am. Chem. Soc.* **1987**, *109*, 797. (b) Chow, T. J.; Chao, Y.-S. *J. Chem. Commun.* **1985**, 700. (c) Chow, T. J.; Chao, Y.-S. *J. Organomet. Chem.* **1985**, *296*, C23. (d) Chow, T. J.; Wu, M.-Y.; Liu, L.-K. *J. Organomet. Chem.* **1985**, *281*, C33.

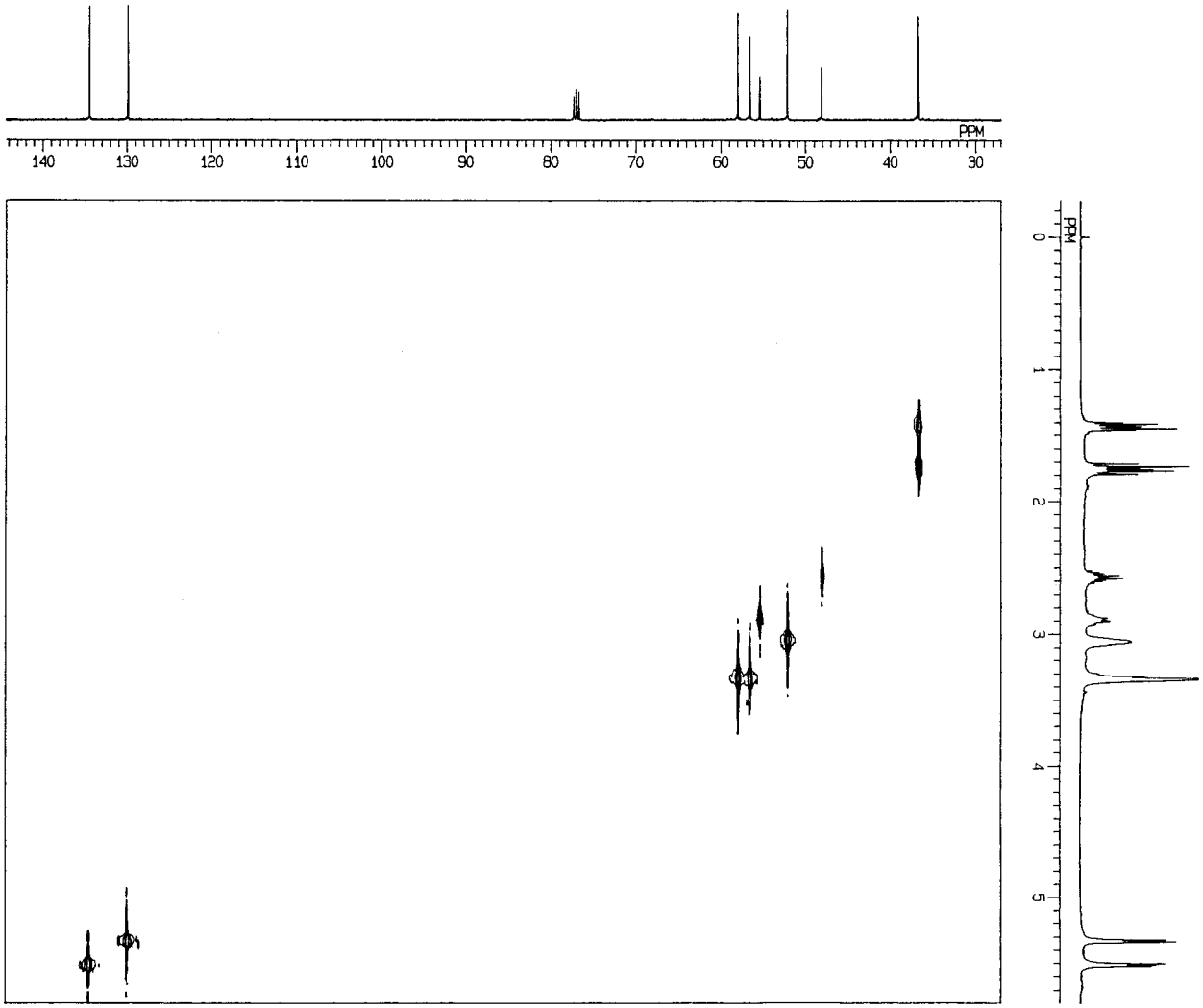


Figure 1. $^{1}H/^{13}C$ $\sigma-\sigma$ heteronuclear correlation NMR spectrum of **2a** ($CDCl_3$; ^{1}H, 400 MHz; ^{13}C, 100 MHz).

Table 2. Effects of Olefinic Additives and Solvents on the Ruthenium Complex-Catalyzed Dimerization of **1a**[a]

						yield, %[d]	
run	catalyst	olefinic additive[b]	solvent[c]	temp., °C	time, h	**2a**	**3a**
9	Ru(cod)(cot)	DMMl	THF	40	1	96	2
10	Ru(cod)(cot)	MAc	toluene	120	2	48	7
11	Ru(cod)(cot)	MVK	toluene	120	2	76	6
12	Ru(cod)(cot)	DMAc	*n*-hexane	80	10	81	4
13	Ru(cod)(cot)	DMAc	pyridine	120	2	50	2
14	Ru(cod)(cot)	DMAc	DMI	120	2	78	5
15	Ru(cod)(cot)	DMAc	DMF	120	15	71	3
16	Ru(cod)(cot)	DMFm	DMF	40	1	91	1
17	Ru(cod)(cot)	DMFm	NMP	120	2	13	trace
18	Ru(cod)(cot)	DMAc	DMSO	120	2	23	70
19	Ru(cod)(cot)	DMFm	DMSO	120	2	26	66
20	$Ru_3(CO)_{12}$	DMAc	DMSO	120	2	11	26
21	$Ru_3(CO)_{12}$	DMFm	DMSO	120	2	25	66

[a] 2,5-Norbornadiene, 5.0 mmol; catalyst, 2.0 mol % as metal; olefinic additive, 20 mol %; solvent, 3.0 mL in a sealed glass tube at 80 or 120 °C, or in a 20 mL two-necked flask at 40 °C. [b] DMAc, *N*,*N*-dimethylacrylamide; DMFm, dimethyl fumarate; DMMl, dimethyl maleate; MAc, methyl acrylate; MVK, methyl vinyl ketone. [c] NMP, *N*-methylpiperidine; THF, tetrahydrofuran; DMI, *N*,*N*-dimethylimidazolidone; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide. [d] GC yield.

$Pd(OAc)_2$, $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$, and $RhCp^*(C_2H_4)_2$ showed no catalytic activity. Thus, the reaction was characteristic of ruthenium complexes.

For high catalytic activity, the combination of a ruthenium complex with an electron-deficient olefin and a solvent turned out to be very important. The effects of olefinic additives and solvents are summarized in Tables 1 and 2. The Ru(cod)(cot)-catalyzed dimerization of **1a** was performed in the presence of various olefinic additives. When dimethyl fumarate or dimethyl maleate was used in THF (runs 4 and 9), the yield of **2a** increased to 96% even at 40 °C for 1 h. (**Caution!** *This reaction sometimes occurs violently even at 40 °C in THF. The reaction should be performed behind a heavy wall.*) Methyl acrylate and methyl vinyl ketone were also effective (runs 10 and 11). *N*,*N*-Dimethylacrylamide was effective (runs 1−3); however, methyl-substituted *N*,*N*-dimethylacrylamide gave lower yields (2−11%).

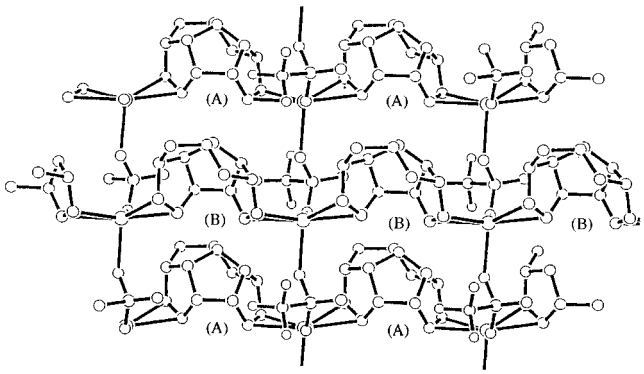
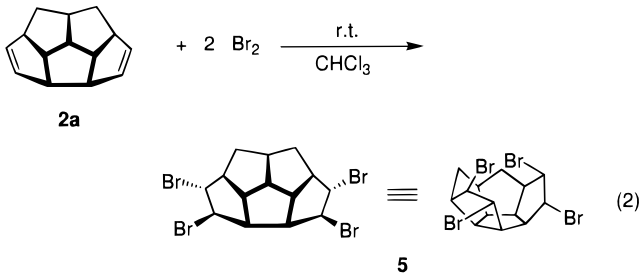


Figure 2. ORTEP drawing of polymeric complex **6**.

The effects of the solvent on the Ru(cod)(cot)-catalyzed dimerization reaction of **1a** were examined. The reaction proceeded in both nonpolar and polar solvents such as *n*-hexane, pyridine, *N*,*N*-dimethylformamide (DMF), and 1,3-dimethylimidazolidone (DMI) (runs 12−16), as well as in THF or in toluene. *N*-Methylpiperidine (NMP) was a good solvent for *N*,*N*-dimethylacrylamide (runs 1 and 2), but not for dimethyl fumarate (run 17). Interestingly, in dimethyl sulfoxide (DMSO), **3a** was obtained as a major product in place of **2a** (runs 18 and 19). Similarly, in the case of $Ru_3(CO)_{12}$ with *N*,*N*-dimethylacrylamide or dimethyl fumarate in DMSO, **3a** was formed as a major product in moderate yield (runs 20 and 21).

Spectroscopic Data of Dimer 2a. The ^{1}H-^{13}C COSY spectrum of **2a** is shown in Figure 1. These data together with the DEPT spectrum show that **2a** has C_s symmetry in solution, and the structure was inferred to be pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]-tetradeca-4,11-diene. The high-resolution solid-state ^{13}C NMR (CPMAS) spectrum was measured. The chemical shifts were almost the same as those in solution, and two methylene carbons were equivalent (see below).

Structure of 2a. The structure of **2a** inferred from its spectral data was confirmed by X-ray analyses of two derivatives. One derivative was a tetrabromide of PCTD, the structure of which was previously confirmed by X-ray analysis.[28] Dimer **2a** reacted with an excess of bromine to give the corresponding tetrabromide, 4,5,11,12-tetrabromopentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane **5**, in 72% yield selectively (eq 2). The addition of bromine is *trans*, and the bromines at the 4 and 12 positions are oriented *exo* to reduce steric hindrance. Since we could not completely rule out the possibility that **5** may be derived via cationic rearrangement from some bromonium ion, another derivative of **2a** was prepared.



The reaction of **2a** with silver triflate in THF gave a colorless complex, polymeric [AgOTf(PCTD)]$_n$ (**6**) (eq 3). ^{1}H and ^{13}C NMR spectra of **6** were slightly shifted from those of **2a**, showing that this silver complex has a coordinated PCTD. Recrystallization from THF gave single crystals, the structure of which was determined by X-ray analysis. The results are shown in Figures 2 and 3. Crystal data and the details of the data collection are given in Table 3, while a list of selected

Table 3. Summary of Crystal Data, Collection Data, and Refinement of **6** and **7**

	6	**7**
formula	$C_{15}H_{16}F_3O_3SAg$	$C_{20}H_{26}O_8Ru$
formula weight	442.21	495.49
crystal system	orthorhombic	monoclinic
space group	$Pca2_1$	$P2_1/c$
color of crystal	colorless	yellow
habit	needle	prismatic
a, Å	19.708(4)	7.816(5)
b, Å	7.742(4)	25.190(5)
c, Å	9.858(4)	11.050(6)
α, deg	90	90
β, deg	90	109.01(4)
γ, deg	90	90
V, Å^3	1504(1)	2056(1)
Z	4	4
D (calcd), g cm^{-3}	1.948	1.600
crystal size, mm	0.10 × 0.10 × 0.40	0.10 × 0.10 × 0.05
data collection temp, °C	23.0	23.0
diffractmeter	Rigaku AFC7R	Rigaku AFC7R
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)	
μ (Mo Kα), cm^{-1}	15.19	8.06
scan mode	ω−2θ	ω
scan width, deg	0.79 + 0.30 tanθ	0.52 + 0.30 tanθ
scan speed, deg min^{-1}	8.0	16
2θ range, deg	28.2−29.8	29.4−30.0
no. of measd reflections	2015	4967
no. of obsd reflections	1499 ($I > 2.00\sigma(I)$)	2892 ($I > 3.00\sigma(I)$)
no. of parameters refined	225	288
R, %[a]	2.9	4.0
R_w, %[a]	3.0	4.1
GOF	1.28	0.66

[a] $R = \sum||F_o| - |F_c||/\sum|F_o^2|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

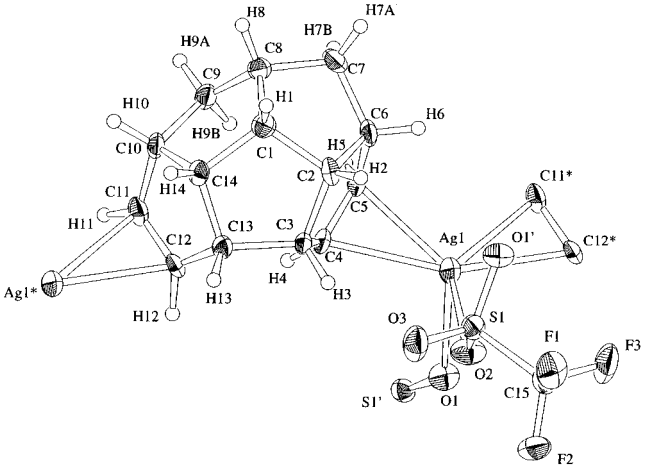


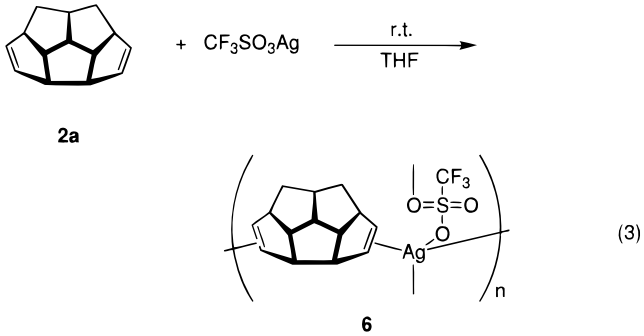
Figure 3. ORTEP drawing of the partial structure of **6**. Thermal ellipsoids are shown at the 30% probability level.

bond lengths and angles is provided in Table 4. The inferred structure of PCTD was confirmed. It has five five-membered rings with two olefinic groups on both sides at the 4 and 11 positions. The coordination around the silver ion is highly distorted from a tetrahedral coordination. Both olefinic moieties of the PCTD coordinate to two silver atoms, so PCTD bridges two silver atoms, and the triflate ligand forms another bridge between two silver atoms. Consequently, **6** is a two-dimensional gridiron-like polymer. A characteristic structure of the complex is the alternative orientation of PCTD. The open side of the cage structure of PCTD (A) in Figure 2 is oriented to the backside, and that of PCTD (B) is oriented to the front side. The PCTD molecule in **6** is not symmetric (Figure 3). The two five-membered rings C8−C1−C2−C6−C7 and C8−C1−C14−C10−C9 are envelope-shaped. One of the two methylene groups (C7) is oriented *exo* and the other (C9) is oriented *endo*. The

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for **6**

Bond Distances			
Ag(1)−O(1)	2.448(5)	Ag(1)−O(2)	2.346(4)
Ag(1)−C(4)	2.509(5)	Ag(1)−C(5)	2.435(6)
Ag(1)−C(11)	2.459(6)	Ag(1)−C(12)	2.474(5)
C(1)−C(2)	1.564(8)	C(1)−C(8)	1.552(9)
C(1)−C(14)	1.519(9)	C(2)−C(3)	1.556(9)
C(2)−C(6)	1.554(8)	C(3)−C(4)	1.513(9)
C(3)−C(13)	1.568(8)	C(4)−C(5)	1.341(9)
C(5)−C(6)	1.52(1)	C(6)−C(7)	1.527(9)
C(7)−C(8)	1.530(9)	C(8)−C(9)	1.534(9)
C(9)−C(10)	1.538(8)	C(10)−C(11)	1.494(9)
C(10)−C(14)	1.551(8)	C(11)−C(12)	1.339(8)
C(12)−C(13)	1.47(1)	C(13)−C(14)	1.539(9)
Bond Angles			
O(1)−Ag(1)−O(2)	85.0(2)	O(1)−Ag(1)−C(4)	102.7(2)
O(1)−Ag(1)−C(5)	121.9(2)	O(1)−Ag(1)−C(11)	101.3(2)
O(1)−Ag(1)−C(12)	88.7(3)	O(2)−Ag(1)−C(4)	100.5(2)
O(2)−Ag(1)−C(5)	123.6(2)	O(2)−Ag(1)−C(11)	129.5(2)
O(2)−Ag(1)−C(12)	100.1(2)	C(4)−Ag(1)−C(5)	31.4(2)
C(4)−Ag(1)−C(11)	125.8(2)	C(4)−Ag(1)−C(12)	157.2(2)
C(5)−Ag(1)−C(11)	95.5(2)	C(5)−Ag(1)−C(12)	126.1(2)
C(11)−Ag(1)−C(12)	31.5(2)	C(2)−C(1)−C(8)	106.7(5)
C(2)−C(1)−C(14)	108.4(5)	C(8)−C(1)−C(14)	108.1(5)
C(1)−C(2)−C(3)	106.8(4)	C(1)−C(2)−C(6)	105.7(5)
C(3)−C(2)−C(6)	108.0(5)	C(2)−C(3)−C(4)	103.1(4)
C(2)−C(3)−C(13)	106.7(5)	C(4)−C(3)−C(13)	116.4(5)
Ag(1)−C(4)−C(5)	71.2(3)	C(3)−C(4)−C(5)	113.0(6)
Ag(1)−C(5)−C(4)	77.3(4)	C(4)−C(5)−C(6)	112.6(6)
C(2)−C(6)−C(5)	103.2(6)	C(2)−C(6)−C(7)	107.0(6)
C(5)−C(6)−C(7)	115.4(6)	C(6)−C(7)−C(8)	105.8(5)
C(1)−C(8)−C(7)	105.1(5)	C(1)−C(8)−C(9)	105.2(5)
C(7)−C(8)−C(9)	115.1(6)	C(8)−C(9)−C(10)	106.1(5)
C(9)−C(10)−C(11)	112.4(5)	C(9)−C(10)−C(14)	106.2(5)
C(11)−C(10)−C(14)	103.7(5)	Ag(1)−C(11)−C(12)	74.9(3)
C(10)−C(11)−C(12)	110.7(7)	Ag(1)−C(12)−C(11)	73.6(3)
C(11)−C(12)−C(13)	113.7(8)	C(3)−C(13)−C(12)	115.5(6)
C(3)−C(13)−C(14)	107.4(5)	C(12)−C(13)−C(14)	103.3(5)
C(1)−C(14)−C(10)	107.0(5)	C(1)−C(14)−C(13)	108.7(5)
C(10)−C(14)−C(13)	105.3(5)		

dihedral angle between planes C8/C1/C2/C6 and C6/C7/C8 is 150.3°, and that between planes C8/C1/C14/C10 and C10/C9/C8 is −153.1°. The structure of **6** was fully consistent with the spectral data described above. Although the two methylene groups of coordinated PCTD in silver complex **6** are nonequivalent, the CPMAS spectrum of free PCTD did not indicate nonequivalency of the two methylene groups.



(3)

Reaction of Ru(cod)(cot) with Dimethyl Fumarate. The reaction of Ru(cod)(cot) with dimethyl fumarate in toluene generated yellow microcrystals of Ru(cot)(dmfm)$_2$ (dmfm = dimethyl fumarate) **7** in 76% yield (eq 4). The reaction of Ru(cod)(cot) with dimethyl maleate gave the same complex **7**. ^{1}H- and ^{13}C NMR spectra of **7** showed that the cyclooctadiene in Ru(cod)(cot) was replaced by two molecules of dimethyl fumarate and that none of the protons of the cyclooctatriene

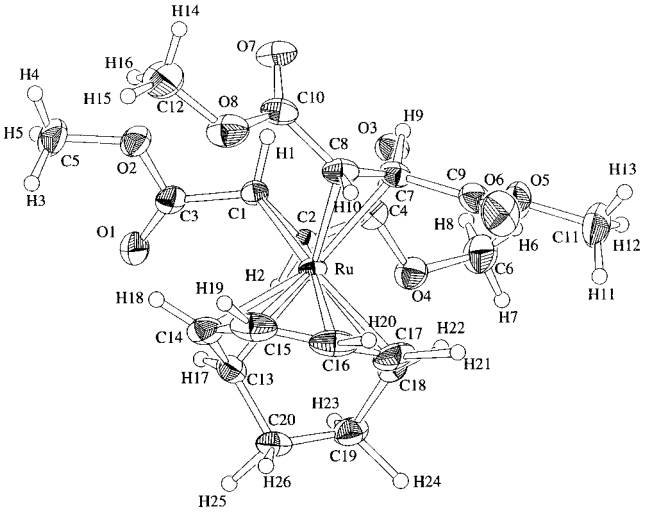
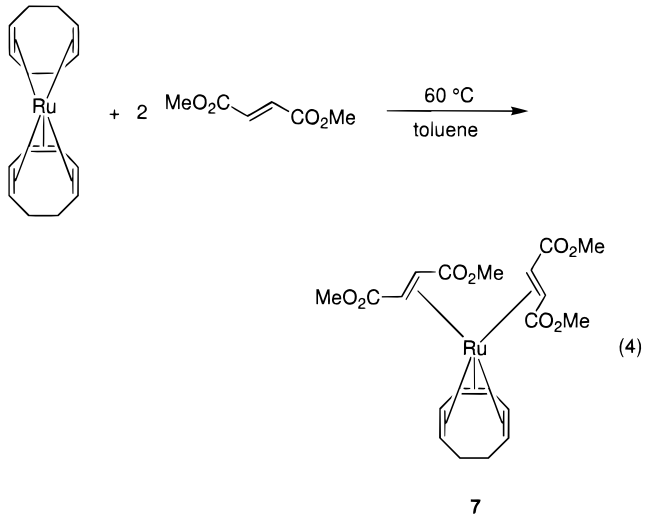


Figure 4. ORTEP drawing of the structure of **7**. Thermal ellipsoids are shown at the 30% probability level.

ligand are equivalent, which indicates that the structure of Ru(cot)(dmfm)$_2$ is **7**. The structure of **7** was confirmed by X-ray analysis (Figure 4).



(4)

Crystal data and the details of data collection are given in Table 3, and a list of selected bond lengths and angles is provided in Table 5. The structure is represented by a highly distorted trigonal bipyramid or a highly distorted square pyramid. The molecule does not have a symmetry plane. In the molecular structure of **7**, the coordinated triene moiety of the η^6-C_8H_{10} ligand is characterized by C−C bond lengths that do not significantly differ from each other. A similar bonding pattern indicating substantial electron delocalization within the conjugated π-system has previously been observed for the triene fragment of Ru(cod)(cot), which likewise does not exhibit a marked C−C/C=C change in its carbon−carbon bond lengths.[43] In the (1-6-η-C_8H_{10})Ru moiety in **7**, the metal-to-carbon distances are between 2.229(6) and 2.285(6) Å and are slightly longer than those in Ru(cod)(cot) (2.196(5) and 2.259(8) Å). The distances between ruthenium and the olefinic carbons of dimethyl fumarate ligands in **7** are shorter than those betweenRu and the olefinic carbons of the cyclooctatriene ligand because of the enhanced back-donation from ruthenium to electron-deficient olefins.

It has been reported that the cyclooctatriene ligand in Ru(cod)(cot) is often replaced by appropriate ligands to give

(43) Frosin, K.-M.; Dahlenburg, L. *Inorg. Chim. Acta* **1990**, *167*, 83.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for **7**

Bond Distances			
Ru(1)−C(1)	2.155(5)	Ru(1)−C(2)	2.169(5)
Ru(1)−C(7)	2.204(5)	Ru(1)−C(8)	2.190(5)
Ru(1)−C(13)	2.261(6)	Ru(1)−C(14)	2.256(6)
Ru(1)−C(15)	2.274(6)	Ru(1)−C(16)	2.256(6)
Ru(1)−C(17)	2.229(6)	Ru(1)−C(18)	2.285(6)
C(1)−C(2)	1.431(7)	C(7)−C(8)	1.408(8)
C(13)−C(14)	1.407(9)	C(13)−C(20)	1.498(9)
C(14)−C(15)	1.43(1)	C(15)−C(16)	1.42(1)
C(16)−C(17)	1.42(1)	C(17)−C(18)	1.401(8)
C(18)−C(19)	1.513(8)	C(19)−C(20)	1.503(9)
Bond Angles			
C(1)−Ru(1)−C(2)	38.7(2)	C(1)−Ru(1)−C(7)	89.4(2)
C(1)−Ru(1)−C(8)	114.8(2)	C(1)−Ru(1)−C(13)	89.4(2)
C(1)−Ru(1)−C(14)	124.9(2)	C(1)−Ru(1)−C(15)	157.1(2)
C(1)−Ru(1)−C(16)	145.1(3)	C(1)−Ru(1)−C(17)	108.2(2)
C(1)−Ru(1)−C(18)	83.7(2)	C(2)−Ru(1)−C(7)	84.6(2)
C(2)−Ru(1)−C(8)	89.5(2)	C(2)−Ru(1)−C(13)	128.0 (2)
C(2)−Ru(1)−C(14)	163.2(3)	C(2)−Ru(1)−C(15)	159.6(3)
C(2)−Ru(1)−C(16)	123.7(3)	C(2)−Ru(1)−C(17)	94.6(2)
C(2)−Ru(1)−C(18)	91.8(2)	C(7)−Ru(1)−C(8)	37.4 (2)
C(7)−Ru(1)−C(13)	101.1(2)	C(7)−Ru(1)−C(14)	92.9(2)
C(7)−Ru(1)−C(15)	103.3(2)	C(7)−Ru(1)−C(16)	122.7(2)
C(7)−Ru(1)−C(17)	150.2(2)	C(7)−Ru(1)−C(18)	172.5 (2)
C(8)−Ru(1)−C(13)	125.6(2)	C(8)−Ru(1)−C(14)	98.5(2)
C(8)−Ru(1)−C(15)	85.9(2)	C(8)−Ru(1)−C(16)	89.4(2)
C(8)−Ru(1)−C(17)	113.4(3)	C(8)−Ru(1)−C(18)	149.5 (2)
C(13)−Ru(1)−C(14)	36.3(2)	C(13)−Ru(1)−C(15)	69.6(3)
C(13)−Ru(1)−C(16)	96.5(3)	C(13)−Ru(1)−C(17)	102.3(2)
C(13)−Ru(1)−C(18)	75.9(2)	C(14)−Ru(1)−C(15)	36.8 (3)
C(14)−Ru(1)−C(16)	71.4(3)	C(14)−Ru(1)−C(17)	95.6(3)
C(14)−Ru(1)−C(18)	88.7(2)	C(15)−Ru(1)−C(16)	36.5(3)
C(15)−Ru(1)−C(17)	69.2(3)	C(15)−Ru(1)−C(18)	82.3 (2)
C(16)−Ru(1)−C(17)	36.9(3)	C(16)−Ru(1)−C(18)	64.7(2)
C(17)−Ru(1)−C(18)	36.1(2)	Ru(1)−C(1)−C(2)	71.2(3)
C(2)−C(1)−C(3)	121.7(5)	Ru(1)−C(2)−C(1)	70.1 (3)
C(1)−C(2)−C(4)	120.9(5)	Ru(1)−C(7)−C(8)	70.8 (3)
C(8)−C(7)−C(9)	119.7(5)	Ru(1)−C(8)−C(7)	71.9 (3)
C(7)−C(8)−C(10)	123.2(5)	Ru(1)−C(13)−C(14)	71.7 (4)
Ru(1)−C(13)−C(20)	111.4(4)	C(14)−C(13)−C(20)	125.3(6)
Ru(1)−C(14)−C(13)	72.1 (3)	Ru(1)−C(14)−C(15)	72.3(4)
C(13)−C(14)−C(15)	131.5(6)	Ru(1)−C(15)−C(14)	70.9 (3)
Ru(1)−C(15)−C(16)	71.0(3)	C(13)−C(14)−C(15)	134.9(6)
Ru(1)−C(16)−C(15)	72.4 (4)	Ru(1)−C(16)−C(17)	70.5(3)
C(15)−C(16)−C(17)	128.6(6)	Ru(1)−C(17)−C(16)	72.6 (4)
Ru(1)−C(17)−C(18)	74.1(4)	C(16)−C(17)−C(18)	119.1(6)
Ru(1)−C(18)−C(17)	69.7 (4)	Ru(1)−C(18)−C(19)	110.8(4)
C(17)−C(18)−C(19)	124.5(6)	C(18)−C(19)−C(20)	107.6 (5)
C(13)−C(20)−C(19)	101.4(6)		

reactive species in the early stage of catalytic reactions. Cyclooctatriene ligands are replaced by arenes in the reaction under hydrogen to give Ru(arene)(cod).[44] Ru(cod)(cot) reacts with an excess of CO to yield $Ru(cod)(CO)_3$,[45] and with tertiary phosphine ligands (P) to give complexes of the type $Ru(cod)P_3$, such as Ru(cod)(η^1-dppm)(η^2-dppm) [dppm = 1,2-bis(diphenylphosphino)methane].[46,47] The preferential liberation of the cyclooctatriene ligand in Ru(cod)(cot) is believed to occur in all of the reactions of Ru(cod)(cot). Recently, S. Komiya and co-workers reported the first example of the selective displacement of cyclooctadiene from Ru(cod)(cot) by trimethylphosphine to give Ru(II)(6-η^1:1-3-η^3-C_8H_{10})(PMe_3)$_3$, but in this complex, the Ru(II) atom is coordinated by the 6-η^1:1-3-η^3-C_8H_{10} ligand, not by the conjugated η^6-cyclooctatriene ligand.[48] Thus, complex **7** is the first example that is derived from Ru(cod)(cot) by replacement of the cyclooctadiene ligand by 2 mol of an olefin, and retaining the 1-6-η-cyclooctatriene ligand.

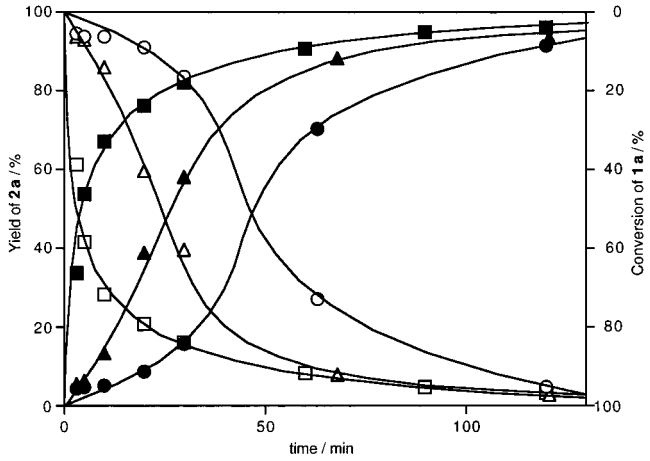


Figure 5. Time dependence of the dimerization of **1a** catalyzed by Ru complexes. Reaction conditions: (a) 5.0 mmol **1a**, 2.0 mol % Ru(cod)(cot), 10 mol % dimethyl maleate, 3.0 mL THF; ○ and ● represent the conversion of **1a** and the yield of **2a**, respectively. (b) 5.0 mmol **1a**, 2.0 mol % Ru(cod)(cot), 10 mol % dimethyl fumarate, 3.0 mL THF; △ and ▲ represent the conversion of **1a** and the yield of **2a**, respectively. (c) 5.0 mmol **1a**, 2.0 mol % Ru(cot)(dimethyl fumarate)$_2$ (**7**), 6 mol % dimethyl fumarate, 3.0 mL THF; □ and ■ represent the conversion of **1a** and the yield of **2a**, respectively.

Complex **7** itself has catalytic activity for the dimerization of **1a**. At 40 °C in toluene in the presence of 2 mol % of **7**, the yield of **2a** was about 40%. The addition of dimethyl fumarate dramatically increased the yield of **2a** to 96%. When the amount of **7** was increased to 5 mol %, the product was obtained in 96% yield at 40 °C even in the absence of dimethyl fumarate.

Time courses of the catalytic reaction using Ru(cod)(cot)/dimethyl fumarate or dimethyl maleate, or Ru(cot)(dmfm)$_2$ (**7**)/dimethyl fumarate are shown in Figure 5. Complex **7**/dimethyl fumarate showed very high activity without an induction period. Ru(cod)(cot)/dimethyl fumarate was also very active; however, a short induction period was observed. Ru(cod)(cot)/dimethyl maleate showed a longer induction period, but the yield of the product was 91% after 120 min. This strongly suggests that dimethyl maleate is isomerized to dimethyl fumarate during the reaction.

Relationship between the Structures of 2a and 3a. The relationship between the structures of **2a** and **3a** should be examined. Although these structures look very different, they are actually quite closely related. If the two carbon−carbon bonds in **3a** are cleaved and a hydrogen H* is transferred as shown in eq 5, **3a** would be transformed into **2a**. This means that **2a** is a derivative of an *endo*−*endo* dimer of **1a**, and the two bridge carbons in **1a** come into the 4 and 9 positions or 7 and 12 positions in **2a**. This strongly suggests that during the dimerization of **1a** to **2a**, at least two carbon−carbon bonds are cleaved. However, this does not mean that **3a** is a precursor

(44) (a) Pertici, P.; Vitulli, G.; Lazzaroni, R.; Salvadori, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1019. (b) Vitulli, G.; Pertici, P.; Salvadori, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2255. (c) Vitulli, G.; Pertici, P.; Bigelli, C. *Gazzetta Chim. Ital.* **1985**, *115*, 79. (d) Vitulli, G.; Bertozzi, S.; Lazzaroni, R. *Inorg. Chim. Acta* **1988**, *149*, 235.

(45) Deganello, G.; Mantovani, A.; Sandrini, P. L.; Pertici, P.; Vitulli, G.*J. Organomet. Chem.* **1977**, *135*, 215.

(46) (a) Chaudret, B.; Commenges, G.; Poilblanc, R. *Chem. Commun.* **1982**, 1388. (b) Chaudret, B.; Commenges, G.; Poilbanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.

(47) Pertici, P.; Vitulli, G.; Porzio, W.; Zocchi, M.; Barili, P. L.; Deganello, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1553.

(48) Hirano, M.; Marumo, T.; Miyasaka, T.; Fukuoka, A.; Komiya, S. *Chem. Lett.* **1997**, 297.

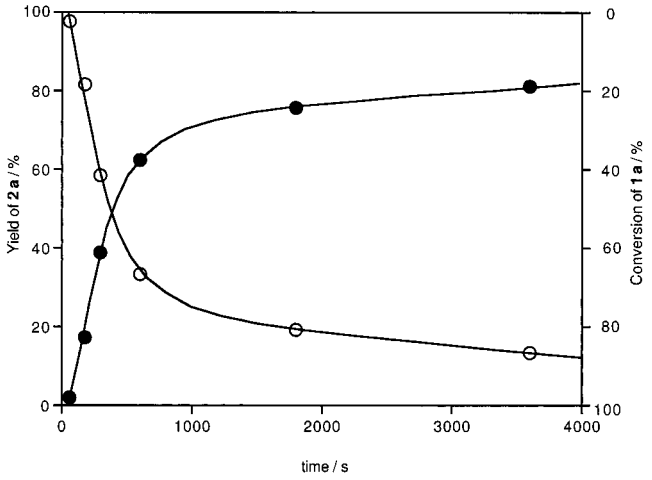
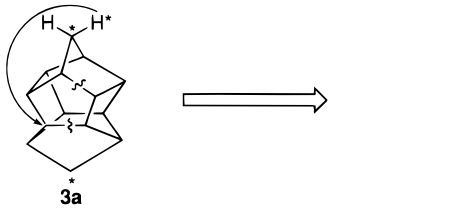
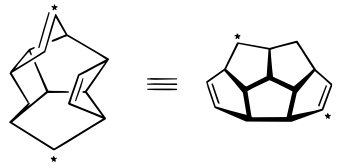


Figure 6. Representative plots of conversion of **1a** and yield of **2a**. The reaction was carried out at 120 °C in sealed tubes, where the amounts of **1a**, Ru(cod)(cot), *N*,*N*-dimethylacrylamide, and toluene were 5.0 mmol, 0.10 mmol, 1.0 mmol, and 3.0 mL, respectively. ○ and ● represent the conversion of **1a** and yield of **2a**, respectively.

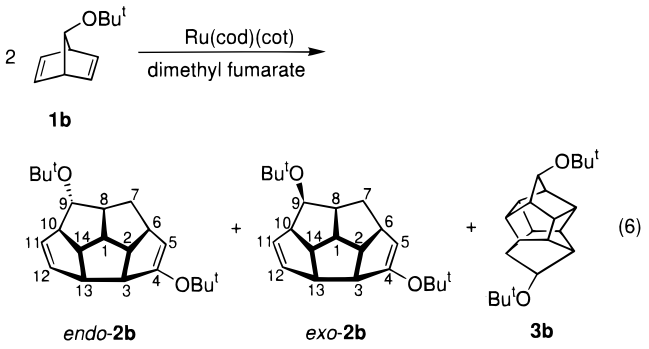
of **2a**. When **2a** and **3a** were treated under the catalytic reaction conditions, they were not interconverted into each other.





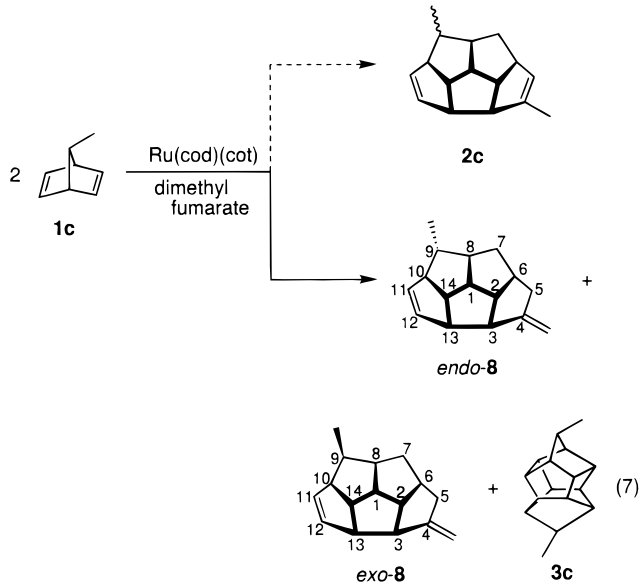
(5)

The reaction of 7-*tert*-butoxynorbornadiene (**1b**) in the presence of Ru(cod)(cot)/dimethyl fumarate gave a mixture of *exo*- and *endo*-4,9-di-*tert*-butoxypentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]-tetradeca-4,11-diene (**2b**) and 7,12-di-*tert*-butoxyheptacyclo-[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (**3b**)[49] in a total of 40% yield (eq 6, **2b**/**3b** = 4:1). Treatment of the mixture by GPC (gel permeation chromatography) gave pure *endo*-**2b** (9%) and a mixture of *exo*-**2b** and **3b** (18%, ca. 2:1 ratio). Separation of *exo*-**2b** and **3b** was unsuccessful. The substituents, *tert*-butoxy groups, were found at the expected positions. ^{1}H and ^{13}C NMR, DEPT, ^{1}H-^{1}H COSY, and ^{1}H-^{13}C COSY spectra showed that in **2b** two *tert*-butoxy groups are located at the 4 and 9 positions.



(6)

The reaction of 7-methylbicyclo[2.2.1]hepta-2,5-diene **1c** did not give the corresponding product **2c**. In this case, a mixture of isomers of 12-methylene compounds, *endo*- and *exo*-7-methyl-12-methylenepentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradec-4-ene, *endo*- and *exo*-**8** was obtained in a total 90% yield (*endo*/*exo* = 1:1.1) along with 2% of 7,12-dimethyl heptacyclo-[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (**3c**) (eq 7). Treating the mixture by GPC for separation gave pure *endo*-**8** (38%) and a mixture of *exo*-**8** and its unidentified isomer (50%, ca. 10:1 ratio).



(7)

Kinetics of the Dimerization of 1a to 2a. A kinetic study was performed on the dimerization of **1a** to **2a** in the presence of Ru(cod)(cot)/*N*,*N*-dimethylacrylamide in toluene. The Ru(cod)(cot)/dimethyl fumarate catalyst was too active, and the reproducibility was unsatisfactory. The time course of this reaction is shown in Figure 6, and the rate of formation of **2a** was revealed to be first-order for the concentration of Ru(cod)(cot), [Ru], and third-order for [**1a**], i.e. d[**2a**]/dt = k_{obs}[Ru][**1a**]^3 (see Supporting Information for the linear plot of (1/[**1a**]^2 − 1/[**1a**]$_0^2$) vs. time and dependence of [Ru(cod)(cot)]$_0$ on d[**2a**]/dt).

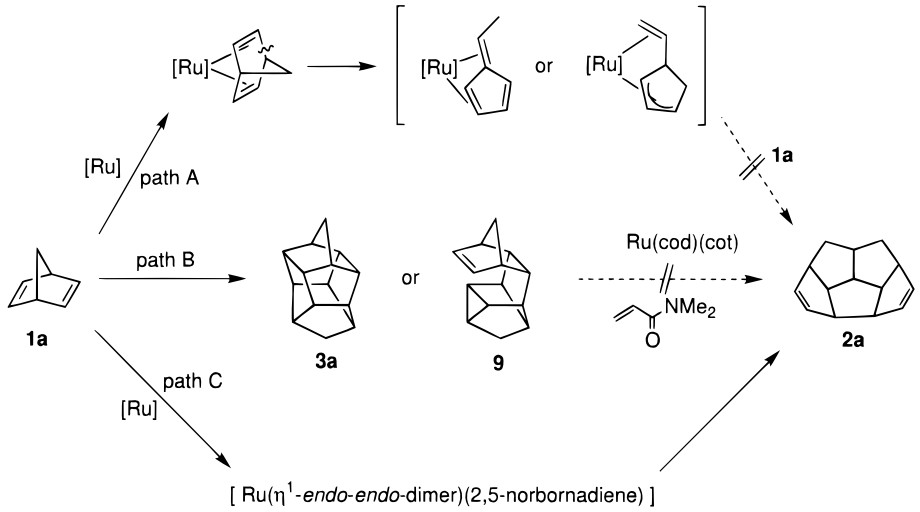
Mechanism of the Dimerization of 1a to 2a. The mechanism of the formation of **2a** is not yet clear. The three reaction pathways summarized in Scheme 1 should be considered. The first involves the cleavage of a carbon−carbon bond of 2,5-norbornadiene on the ruthenium complex followed by building up of the PCTD skeleton (path A). Examples of the cleavage of a carbon−carbon bond in 2,5-norbornadiene on a metal complex have been reported previously,[50,51] however, once the cleavage occurs, building up the PCTD structure requires so many steps that this pathway seems unlikely. The second pathway is the formation of an *endo*−*endo* dimer and subsequent carbon−carbon bond cleavage to give PCTD (path B). Several *endo*−*endo* dimers, such as **3a** or **9**,[37] prepared by other methods were treated under the catalytic reaction conditions for the preparation of **2a** and did not give any PCTD. Thus, path B

(49) (a) Marchand, A. P. *J. Org. Chem.* **1984**, *49*, 1660. (b) Marchand, A. P.; Hayes, B. R. *Tetrahedron Lett.* **1977**, 1027.

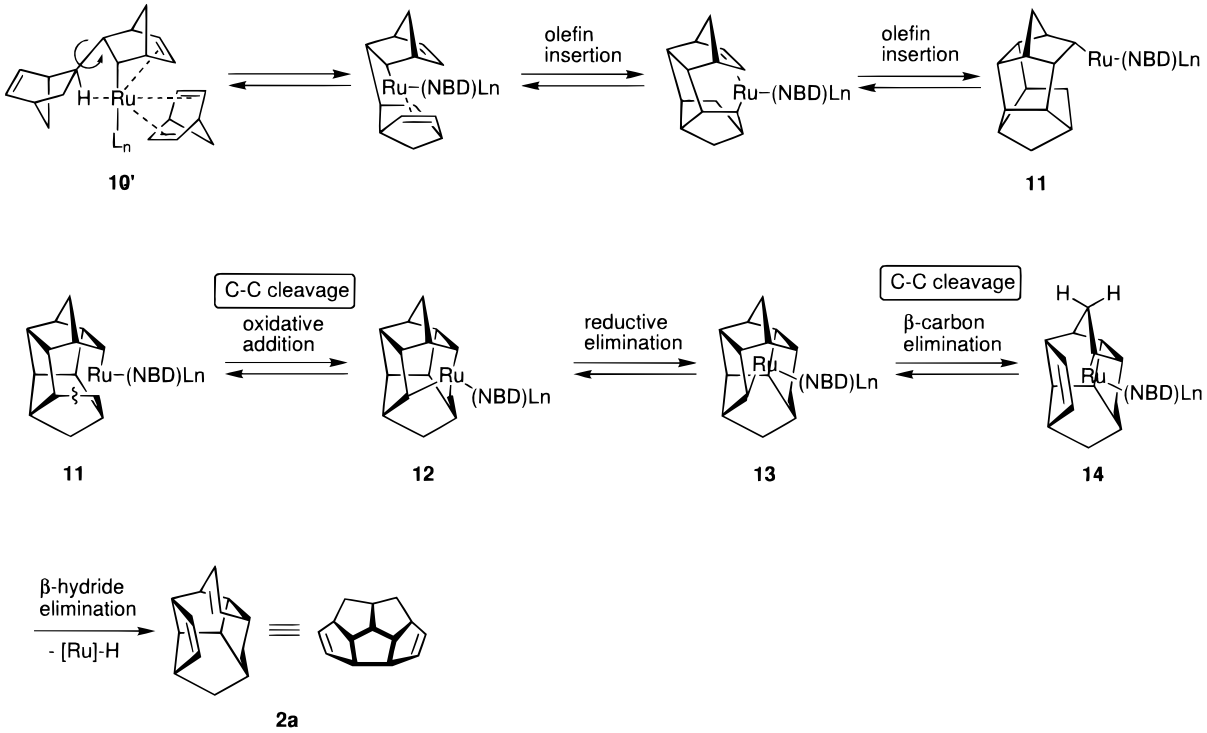
(50) (a) Suzuki, H.; Kakigano, T.; Fukui, H.; Tanaka, M.; Moro-oka, Y. *J. Organomet. Chem.* **1994**, *473*, 295. (b) Kakigano, T.; Suzuki, H.; Igarashi, M.; Moro-oka, Y. *Organometallics* **1990**, *9*, 2192.

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

Scheme 1. Three Pathways for the Formation of **2a**

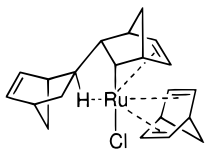


Scheme 2. Plausible Mechanism of the Formation of **2a**



also appears to be unlikely. The last pathway involves Ru(η^1-*endo*−*endo* dimer) (path C).

Concerning the *endo*−*endo* dimerization of **1a**, K. Itoh and co-workers reported the reaction of **1a** with a [$RuCl_2$(2,5-norbornadiene)]$_n$ in the presence of zinc powder and alumina. They isolated several Ru(η^1-*endo*−*endo* dimer) complexes which have further coordinated **1a**, such as **10**.[52] Complex **10**[53]



10

is closely related to the key intermediate of our reaction and seems to be consistent with the results of the kinetic study described above. The results of the kinetic study strongly suggest that the rate-determining step of the reaction is the coordination of the three molecules of **1a** on the ruthenium center, and path C is much more plausible than paths A and B.

A hypothetical reaction pathway for the formation of **2a** which involves the cleavage of two carbon−carbon bonds via oxidative addition of a carbon−carbon bond and β-alkyl elimination on a ruthenium η^1-dimer complex is illustrated in Scheme 2. First, (η^1-*endo*−*endo* dimer) ruthenium complex **10′**, which is an analogue of **10**, may be formed, followed by the insertion of two olefinic groups of 2,5-norbornadienes to form complex **11**. In complex **11**, oxidative addition of a closely located carbon−carbon bond occurs to give **12**, and reductive elimination gives **13**. β-Carbon elimination in complex **13** gives **14**, which has a β-hydrogen that can be eliminated. Once **14** is formed, β-hydrogen elimination occurs to give **2a** irreversibly. Several attempts were made to isolate the reaction intermediates

(52) Ito, K.; Oshima, N.; Jameson, G. B.; Lewis, H. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 3014.

to confirm the hypothetical mechanism, but they have not yet been successful.

Conclusions

Ru(cod)(cot) is widely used as one of the most versatile zerovalent ruthenium complexes. The combination of Ru(cod)(cot) with suitable ligands provides many useful catalytic systems.[26,27,54,55] The catalytically active complex consisting of Ru(cod)(cot)/electron-deficient olefin, such as dimethyl fumarate, dimethyl maleate or *N*,*N*-dimethylacrylamide, can cleave the C−C bond of 2,5-norbornadiene to give a novel compound, pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene (PCTD). PCTD has five five-membered rings with two olefinic groups on both sides. It may be possible to introduce functional groups to the olefinic groups, which would make PCTD a useful monomer for new polymers.

A novel complex, Ru(cot)(dmfm)$_2$, which possesses a 1,3,5-cyclooctatriene and two electron-deficient olefinic ligands, is considered to be a catalyst precursor for the dimerization of 2,5-norbornadiene. It has excellent activity and selectivity for the formation of PCTD under mild reaction conditions.

In conclusion, ruthenium complexes catalyze carbon−carbon bond cleavage and this represents a novel tool for organic syntheses.

Experimental Section

Materials or Methods. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Ru(cod)(cot),[56] Ru(1-5-η-cyclooctadienyl)$_2$,[56b] $RuCl_2(PPh_3)_3$,[57] $RuH_2(PPh_3)_4$,[58] $RuH_2(CO)(PPh_3)_3$,[59] RuCp*Cl(cod),[60] $[RuCp^*Cl_2]_2$,[60] $[RuCp^*(CO)_2]_2$,[61] $[RuCp(CO)_2]_2$,[62] $[RuCl_2(CO)_3]_2$,[63] $[RuCl_2(cod)]_n$,[64] $[PPN][Ru_3H(CO)_{11}]$,[65] $[PPN][Ru_3Cl(CO)_{10}]$,[66] $Pd(PPh_3)_4$,[67] $RhCl(PPh_3)_3$,[68] $RhH(PPh_3)_4$,[69] and $RhCp^*(C_2H_4)_2$[70] were synthesized as described in the literature. 2,5-Norbornadiene and all solvents were distilled under argon over appropriate drying reagents (sodium, calcium hydride, or sodium benzophenone ketyl). 7-*tert*-Butoxy-2,5-norbornadiene (**1b**)[71] and 7-methyl-2,5-norbornadiene (**1c**)[72] were prepared as described in the literature. Methyl acrylate, methyl vinyl ketone, and dimethyl maleate were distilled just before use. $RuCl_3 \cdot nH_2O$, $Ru_3(CO)_{12}$, $Ru(acac)_3$, $Pd(OAc)_2$, *N*,*N*-dimethylacrylamide, dimethyl fumarate, bromine, and silver triflate were obtained commercially and used without further purification. *N*,*N*-Dimethyl-2-methylacrylamide and *N*,*N*-dimethylbut-2-enamide were prepared from methyl-substituted acryloyl chloride and dimethylamine. All new compounds are characterized below.

Physical and Analytical Measurements. Analytical gas chromatography was performed on a Shimadzu GC-14A gas chromatograph with FID detection and a Shimadzu C-R6A Chromatopac recorder/integrator using a 3.2-mm i.d. column with 2% w/w silicone OV-17 liquid phase on a Chromosorb WAW DMCS support in 60/80 mesh. GPC was performed on a JAI (Japan Analytical Industry) Recycling Preparative HPLC LC-908 with a UV and RI detector and a JAI SS-250F2 recorder using JAIGEL-1H (20 mm i.d., 600 mm) and JAIGEL-2H (20 mm i.d., 600 mm) columns. NMR spectra were recorded on either a JEOL GSX-270 (FT, 270 MHz (^{1}H), 68 MHz (^{13}C)) a JEOL EX-400 (FT, 400 MHz (^{1}H), 100 MHz (^{13}C)) instrument. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. A solid-state ^{13}C NMR spectrum was recorded on a GSX-270. IR spectra were recorded using a Nicolet Impact 410 FT-IR spectrometer. GC-MS studies were conducted on a Shimadzu GCMS-QP5000 instrument with 70-eV electron impact ionization. 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.

Synthesis of Pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene (2a). To a 20-mL, two-necked flask with a stirring bar, Ru(cod)(cot) [32 mg (0.10 mmol)] and dimethyl fumarate [0.14 g (1.0 mmol)] were added in an argon atmosphere. THF (3.0 mL) and 2,5-norbornadiene (**1a**) [0.46 g (0.51 mL), 5.0 mmol] were then added. The mixture was stirred at 40 °C for 1 h. GC analysis of the reaction mixture showed the formation of **2a** in 96% yield. The resulting solution was evaporated in vacuo, and Kugelrohr distillation gave **2a** as a white solid (0.40 g, 88% yield). Since dimer **2a** was sensitive to air and a satisfactory elemental analysis was not obtained, the HRMS spectrum was measured.

2a. Colorless solid, mp 102−104 °C. MS (*m*/*z*): 184 (M^+). HRMS (EI) *m*/*z* calcd for $C_{14}H_{16}$ 184.1252, found 184.1248. IR spectrum (KBr) 3041, 2931, 2896, 1605, 1450, 1346, 847, 723, cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (dd, 2H, 4- and 12-H, J = 5.6, 2.2 Hz), 5.34 (d, 2H, 5- and 11-H, J = 5.6 Hz), 3.35 (m, 4H, 2-, 3-, 13- and 14-H), 3.05 (m, 2H, 6- and 10-H), 2.89 (m, 1H, 1-H), 2.57 (qt, 1H, 8-H, J = 8.6, 5.6 Hz), 1.75 (dt, 2H, 7- and 9-*exo*-H, J = 13.2, 8.6 Hz), 1.43 (dt, 2H, 7- and 9-*endo*-H, J = 13.2, 5.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5 (C4 and C12), 129.9 (C5 and C11), 58.0 and 56.6 (C2, C3, C13 and C14), 55.5 (C1), 52.2 (C6 and C10), 48.2 (C8), 36.8 (C7 and C9). ^{13}C NMR (68 MHz, solid): δ 134.8 (C4 and C12), 130.4 (C5 and C11), 59.0 and 57.6 (C2, C3, C13 and C14), 53.1 (C1), 51.8 (C6 and C10), 49.1 (C8), 37.8 (C7 and C9).

Transition Metal Complex-Catalyzed Dimerization of 1a. A solution of 0.46 g (0.51 mL, 5.0 mmol) of **1a**, 0.10 mmol of transition metal complex, and 1.0 mmol of *N*,*N*-dimethylacrylamide or dimethyl fumarate in 3.0 mL of toluene, THF, or *N*-methylpiperidine was stirred at 40−120 °C for 1−11 h in a heavy-walled glass ampule, or in a 20-mL, two-necked flask under an argon atmosphere. Conversion of

(53) Complex **10** or its cationic derivative formed by the treatment of **10** with AgOTf in CH_3CN (ref 52) was not an active catalyst for the dimerization of **1a** to **2a**. These facts suggest that a neutral complex without a halogen ligand is a catalytically active species.

(54) (a) Kondo, T.; Hiraishi, N.; Morisaki, Y.; Wada, K.; Watanabe, Y.; Mitsudo, T. *Organometallics* **1998**, *17*, 2131. (b) Watanabe, Y.; Morisaki, Y.; Kondo, T.; Mitsudo, T. *J. Org. Chem.* **1996**, *61*, 4214. (c) Mitsudo, T.; Suzuki, N.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1994**, *59*, 7759. (d) Kondo, T.; Akazome, M.; Tsuji, Y.; Watanabe, Y. *J. Org. Chem.* **1990**, *55*, 1286. (e) Hori, Y.; Mitsudo, T.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3011. (f) Hori, Y.; Mitsudo, T.; Yamakawa, Y.; Watanabe, Y. *J. Organomet. Chem.* **1987**, *321*, 397. (g) Kondo, T.; Tsuji, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 6229. (h) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 4417. (i) Tsuji, Y.; Huh, Keun Tae; Ohsugi, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1365.

(55) (a) Fukuoka, A.; Nagano, T.; Furuta, S.; Yoshizawa, M.; Hirano, M.; Komiya, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1409. (b) Ohgomori, Y.; Ichikawa, S.; Sumitani, N. *Organometallics* **1994**, *13*, 3758. (c) Maruyama, Y.; Sezaki, T.; Tekawa, M.; Sakamoto, T.; Shimizu, I.; Yamamoto, A. *J. Organomet. Chem.* **1994**, *473*, 257. (d) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604. (e) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Johar, P. S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 987. (f) Airoldi, M.; Deganello, G.; Dia, G.; Gennaro, G. *Inorg. Chim Acta* **1983**, *68*, 179. (g) Pertici, P.; Vitulli, G.; Carlini, C. *J. Mol. Catal.* **1981**, *11*, 353. (h) Airoldi, M.; Deganello, G.; Dia, G.; Gennaro, G. *J. Organomet. Chem.* **1980**, *187*, 391.

(56) (a) Itoh, K.; Nagashima, H.; Ohshima, T.; Oshima, N.; Nishiyama, H. *J. Organomet. Chem.* **1984**, *272*, 179. (b) Pertici, P.; Vitulli, G. *J. Chem. Soc., Dalton Trans.* **1980**, 1961.

(57) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg, Synth.* **1970**, *12*, 237.

(58) Young, R.; Wilkinson, G. *Inorg, Synth.* **1977**, *17*, 75.

(59) Parshall, G. W. *Inorg, Synth.* **1974**, *15*, 48.

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

(61) Nelson, G. O.; Summer, C. E. *Organometallics* **1986**, *5*, 1983.

(62) Humphries, A.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710.

(63) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1976**, *16*, 51.

(64) Bennett, M. A.; Wilkinson, G. *Chem. Ind.* **1959**, 1516.

(65) Keister, J. B.; Shapley, J. B.; Strickland, D. A. *Inorg. Synth.* **1990**, *27*, 196.

(66) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647.

(67) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(68) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

(69) Burch, R. R.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *1*, 188.

(70) Maitlis, P. M.; Kang, J. W.; Moseley, K. J. *J. Chem Soc. A* **1970**, 2875.

(71) Story, P. R. *J. Org. Chem.* **1961**, *26*, 287.

(72) Story, P. R.; Fahrenholtz, S. R. *J. Org. Chem.* **1963**, *28*, 1716.

1a and the yields of **2a**, **3a**, and **4** were determined by GC analysis of the reaction mixture, using *n*-tetradecane or mesitylene as an internal standard.

Selective Ru(cod)(cot)-Catalyzed Preparation of Heptacyclo-[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (3a). A solution of 0.49 g (0.54 mL, 5.3 mmol) of **1a**, 32 mg (0.10 mmol) of Ru(cod)(cot), and 99 mg (0.10 mL, 1.0 mmol) of *N*,*N*-dimethylacrylamide in 3.0 mL of DMSO was stirred at 120 °C for 15 h in a sealed, heavy-walled glass ampule under argon. After cooling to room temperature, the resulting white precipitate was filtered off and washed with DMSO. Kugelrohr distillation gave **3a** as a white solid (220 mg, 45% yield), which was identified by ^{1}H and ^{13}C NMR.[42]

Selective Ru$_3$(CO)$_{12}$-Catalyzed Preparation of the *exo*-*trans*-*exo* Dimer of 1a, Pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene (4). A solution of 0.46 g (0.51 mL, 5.0 mmol) of **1a**, 64 mg (0.10 mmol) of Ru$_3$(CO)$_{12}$, and 99 mg (0.10 mL, 1.0 mmol) of *N*,*N*-dimethylacrylamide in 0.30 mL of *N*-methylpiperidine was stirred at 80 °C for 10 h in a sealed, heavy-walled glass ampule under argon. Kugelrohr distillation gave **4** as a white solid (0.24 g, 51% yield), which was identified by ^{1}H and ^{13}C NMR.[35]

Ru(cod)(cot)-Catalyzed Dimerization of 7-*tert*-Butoxy-2,5-norbornadiene, 1b. To a 20-mL, two-necked flask equipped with a reflux condenser and a stirring bar, Ru(cod)(cot) [64 mg (0.20 mmol)] and dimethyl fumarate [0.29 g (2.0 mmol)] were added in an argon atmosphere. THF (6.0 mL) and 7-*tert*-butoxy-2,5-norbornadiene (**1b**) [1.67 g (1.78 mL), 10.2 mmol] were then added. The mixture was refluxed with stirring for 12 h. Kugelrohr distillation of the reaction mixture gave 675.4 mg of white solid (40% yield), which was a mixture of three isomers. The isomers were separated by GPC to give pure *endo*-4,9-di-*tert*-butoxypentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene (*endo*-**2b**, 151 mg, yield 9%) and a mixture of *exo*-4,9-di-*tert*-butoxypentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene (*exo*-**2b**) and 7,12-di-*tert*-butoxyheptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (**3b**) (303 mg, yield 18%) in a ratio of ca. 2:1.

endo-**2b**. Colorless solid, mp 99−100 °C. MS (*m*/*z*): 328 (M$^+$), 272 (M$^+$ − 56), 216 (M$^+$ − 112). HRMS (EI) *m*/*z* calcd for $C_{22}H_{32}O_2$ 328.2402, found 328.2403. IR spectrum (KBr): 3049, 2974, 2933, 2900, 1458, 1389, 1365, 1181, 1096, 713 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (dt, 1H, 12-H, J = 5.4, 2.2 Hz), 5.50 (dt, 1H, 11-H, J = 5.4, 2.2 Hz), 4.42 (d, 1H, 5-H, J = 2.4 Hz), 4.06 (t, 1H, 9-H, J = 7.3 Hz), 3.40 (dt, 1H, 13-H, J = 9.8, 2.2 Hz), 3.25 (q, 1H, 2-H, J = 9.3 Hz), 3.15 (dd, 1H, 3-H, J = 9.8, 9.3 Hz), 3.10 (dd, 1H, 10-H, J = 7.3, 2.2 Hz), 3.08 (td, 1H,14-H, J = 9.8, 7.3 Hz), 2.89 (dtd, 1H, 6-H, J = 9.8, 9.3, 2.4 Hz), 2.67 (dt, 1H, 1-H, J = 9.8, 9.3 Hz), 2.47 (dtd, 1H, 8-H, J = 10.3, 9.3, 7.3 Hz), 1.69 (ddd, 1H, 7-*exo*-H, J = 13.7, 10.3, 9.8 Hz), 1.60 (dt, 1H, 7-*endo*-H, J = 13.7, 9.3 Hz), 1.37 (s, 9H, Me), 1.19 (s, 9H, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7 (C4), 132.3 (C11), 132.0 (C12), 102.9 (C5), 76.7 (CMe_3), 76.0 (C9), 72.6 (CMe_3), 57.7 (C3), 56.0 (C13), 55.9 (C10), 55.1 (C2), 52.7 (C14), 51.7 (C8), 50.6 (C1), 49.1 (C6), 35.1 (C7), 28.4 (Me), 28.0 (Me).

The mixture of *exo*-**2b** and **3b**. Colorless solid, mp 86−88 °C. Anal. Calcd. for $C_{22}H_{32}O_2$: C, 80.44; H, 9.82. Found: C, 80.16; H, 9.98. IR spectrum (KBr): 3056, 2971, 2965, 2933, 1629, 1458, 1385, 1362, 1195, 1182, 1086, 1060, 1023, 719 cm^{-1}.

exo-**2b**. MS (*m*/*z*): 328 (M$^+$), 272 (M$^+$ − 56), 216 (M$^+$ − 112). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.64 (dt, 1H, 12-H, J = 5.8, 2.0 Hz), 5.58 (dt, 1H, 11-H, J = 5.8, 2.0 Hz), 4.40 (br d, 1H, 5-H, J = 2.4 Hz), 3.82 (dd, 1H, 9-H, J = 3.4, 2.9 Hz), 3.48 (dt, 1H, 14-H, J = 10.3, 9.3 Hz), 3.32 (ddd, 1H, 13-H, J = 9.8, 9.3, 2.0 Hz), 3.24 (td, 1H, 2-H, J = 9.8, 9.3 Hz), 3.14 (dd, 1H, 3-H, J = 9.8, 9.3 Hz), 3.03 (dt, 1H,1-H, J = 10.3, 9.8 Hz), 2.97 (dd, 1H, 10-H, J = 9.3, 2.9 Hz), 2.95 (qd, 1H, 6-H, J = 8.3, 2.4 Hz), 2.44 (dddd, 1H, 8-H, J = 9.3, 8.8, 6.3, 3.4 Hz), 1.84 (dt, 1H, 7-*exo*-H, J = 13.2, 8.8 Hz), 1.54 (dt, 1H, 7-*endo*-H, J = 13.2, 6.3 Hz), 1.36 (s, 9H, Me), 1.16 (s, 9H, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2 (C4), 132.4 (C11), 131.8 (C12), 103.5 (C5), 83.8 (C9), 76.8 (CMe_3),72.9 (CMe_3), 61.4 (C10), 57.2 (C8), 57.1 (C3), 56.3 (C13 and C14), 55.2 (C2), 53.4 (C1), 48.2 (C6), 37.2 (C7), 29.8 (Me), 28.0 (Me).

3b.[49] MS (*m*/*z*): 328 (M$^+$), 313 (M$^+$ − Me), 255 (M$^+$ − Bu^t). HRMS (EI) *m*/*z* calcd for $C_{22}H_{32}O_2$ 328.2402, found 328.2396. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27 (br s, 2H), 2.74 (br s, 4H), 2.33 (br s, 6H), 2.16 (br s, 2H), 1.17 (d, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.0 (OCH), 72.7 (CMe3), 55.7 (CH), 53.2 (CH), 51.8 (CH), 51.2 (CH), 48.9 (CH), 48.3 (CH), 28.6 (Me).

Ru(cod)(cot)-Catalyzed Dimerization of 7-Methyl-2,5-norbornadiene (1c). To a 20-mL, two-necked flask equipped with a reflux condenser and a stirring bar, Ru(cod)(cot) [32 mg (0.10 mmol)] and dimethyl fumarate [0.14 g (1.0 mmol)] were added in an argon atmosphere. Benzene (3.0 mL) and 7-methyl-2,5-norbornadiene (**1c**) [0.54 g (0.58 mL), 5.1 mmol] were then added. The mixture was refluxed with stirring for 10 h. The reaction mixture was concentrated in vacuo and chromatographed on Florisil and on alumina with hexane as an eluent. After concentration of the eluted solution at room temperature in vacuo, the resulting isomers were separated by GPC to give pure *endo*-7-methyl-12-methylenepentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]-tetradec-4-ene (*endo*-**8**, 206 mg, yield 38%) and a mixture of *exo*-7-methyl-12-methylenepentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradec-4-ene (*exo*-**8**) and an unidentified isomer (272 mg, yield 50%) in a ratio of ca. 10:1. Although 7,12-dimethylheptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]-tetradecane (**3c**) could not be isolated, GPC analysis of the reaction mixture showed the formation of **3c** in ca. 2% yield. **3c** was identified using GCMS by comparison with an authentic sample which was synthesized by the Ru(cod)(cot)-catalyzed dimerization of **1c** in the presence of *N*,*N*-dimethylacrylamide in DMSO.

endo-**8**. (The atomic numbering is different from that according to IUPAC. See eq 7.) Colorless liquid, bp 80 °C/0.5 mmHg. MS (*m*/*z*): 212 (M$^+$), 197 (M$^+$ − Me). HRMS (EI) *m*/*z* calcd for $C_{16}H_{20}$ 212.1565, found 212.1555. IR spectrum (neat): 3063, 3041, 2934, 2874, 1708, 1647, 1453, 1431, 1374, 881, 863, 741, 718 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.72 (dt, 1H, 12-H, J = 5.7, 2.2 Hz), 5.62 (dt, 1H, 11-H, J = 5.7, 2.2 Hz), 4.99 (br s, 1H, =CH), 4.80 (br s, 1H, =CH), 3.46 (dd, 1H, 3-H, J = 11.2, 9.8 Hz), 3.43 (ddq, 1H, 13-H, J = 11.2, 10.7, 2.2 Hz), 3.33 (ddd, 1H, 14-H, J = 10.7, 8.8, 8.3 Hz), 3.14 (dt, 1H, 2-H, J = 9.8, 8.8 Hz), 3.00 (ddq, 1H, 10-H, J = 8.3, 7.8, 2.2 Hz), 2.91 (dt, 1H, 1-H, J = 10.3, 8.8 Hz), 2.51 (ddt, 1H,5-*exo*-H, J = 16.6, 7.3, 2.7 Hz), 2.35 (m, 1H, 6-H), 2.32 (dddd, 1H, 8-H, J = 11.7, 10.3, 8.3, 7.8 Hz), 2.22 (d, 1H, 5-*endo*-H, J = 16.6 Hz), 2.17 (tq, 1H, 9-H, J = 7.8, 7.3 Hz), 1.42 (ddd, 1H, 7-H, J = 13.2, 8.3, 7.8 Hz), 1.29 (ddd, 1H, 7-H, J = 13.2, 11.7,8.8 Hz), 1.01 (d, 3H, Me, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2 (C4), 132.3 (C11), 132.1 (C12), 107.8 (=CH_2), 58.8 (C2), 56.9 (C14), 56.8 (C10), 56.1 (C1), 56.0 (C3), 55.3 (C13), 53.3 (C8), 45.2 (C6), 41.7 (C5), 41.3 (C9), 34.2 (C7), 14.1 (Me).

The mixture of *exo*-**8** and its unidentified isomer. Colorless liquid, bp 80 °C/0.5 mmHg. IR spectrum (neat): 3064, 3036, 2947, 2885, 1648, 1454, 1373, 880, 742, 717 cm^{-1}.

exo-**8**. (The atomic numbering is different from that according to IUPAC. See eq 7.) MS (*m*/*z*): 212 (M$^+$), 197 (M$^+$ − Me). HRMS (EI) *m*/*z* calcd for $C_{16}H_{20}$ 212.1565, found 212.1567. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.58 (d, 1H, 11-H, J = 5.4 Hz), 5.54 (d, 1H, 12-H, J = 5.4 Hz), 4.97 (br s, 1H, =CH), 4.79 (br s, 1H, =CH), 3.43 (m, 3H, 3-, 13- and 14-H), 3.14 (dt, 1H, 2-H, J = 8.8, 8.3 Hz), 3.08 (q, 1H, 1-H, J = 8.3 Hz), 2.83 (m, 1H, 10-H), 2.49 (ddt, 1H,5-*exo*-H, J = 16.6, 8.3, 2.7 Hz), 2.34 (dq, 1H, 6-H, J = 8.8, 8.3 Hz), 2.20 (d, 1H, 5-*endo*-H, J = 16.6 Hz), 2.11 (dt, 1H, 8-H, J = 11.2, 8.3 Hz), 2.08 (q, 1H, 9-H, J = 7.3 Hz), 1.68 (dt, 1H, 7-H, J = 13.2, 8.3 Hz), 1.34 (ddd, 1H, 7-H, J = 13.2, 11.1, 8.8 Hz), 0.91 (d, 3H, Me, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3 (C4), 135.0 (C11), 130.6 (C12), 107.6 (=CH_2), 61.0 (C10), 58.8 (C2), 56.7, 56.4 and 55.5 (C3, C13 and C14), 56.4 (C8), 55.3 (C1), 44.8 (C6), 44.1 (C9), 41.6 (C5), 38.9 (C7), 23.5 (Me).

Ru(cod)(cot)-Catalyzed Preparation of 7,12-Dimethylheptacyclo-[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (3c). A solution of 0.53 g (0.57 mL, 5.0 mmol) of 7-methyl-2,5-norbornadiene (**1c**), 32 mg (0.10 mmol) of Ru(cod)(cot) and 99 mg (0.10 mL, 1.0 mmol) of *N*,*N*-dimethylacrylamide in 3.0 mL of DMSO was stirred at 120 °C for 20 h in a sealed, heavy-walled glass ampule under argon. After cooling to room temperature, 7,12-dimethylheptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]-tetradecane (**3c**) was isolated by Kugelrohr distillation (82 mg, 15% yield) and identified by ^{1}H and ^{13}C NMR.

3c. Colorless liquid, bp 80 °C/0.5 mmHg. HRMS (EI) *m*/*z* calcd for $C_{16}H_{20}$: 212.1565. Found: 212.1562. MS (*m*/*z*): 212 (M$^+$), 197 (M$^+$ − Me). IR spectrum (neat): 2943, 2883, 2871, 1455, 1452, 1375 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.57 (m, 4H), 2.41 (m, 4H), d 2.34 (q,

2H, J = 6.8), 2.19 (br s, 2H), 2.11 (br s, 2H), 0.91 (d, 6H, J = 6.8, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.5, 55.4, 53.1, 53.0, 50.6 (CMe), 50.4, 15.5 (Me).

Preparation of [AgOTf(PCTD)]$_n$ (6). PCTD (94.6 mg, 0.513 mmol) and 251.1 mg (0.977 mmol) of silver triflate were dissolved in THF (15 mL) in a 100-mL, two-necked flask under argon, and the resulting solution was allowed to stand for 48 h. To this solution was added 50 mL of *n*-pentane to give a white solid, which was filtered off, washed twice with 10 mL of *n*-pentane and three times with 10 mL of diethyl ether, and then dried in vacuo at room temperature to give 179.2 mg of **6**. Single crystals for X-ray analysis were obtained from THF−pentane solution, and they were dried under a stream of argon.

Complex **6**. Colorless solid, mp (dec) 165−167 °C. ^{1}H NMR (400 MHz, THF): δ 5.79 (d, 2H, 4- and 12-H, J = 3.9 Hz), 5.36 (d, 2H, 5- and 11-H, J = 5.4 Hz), 3.39 (m, 4H, 2-, 3-, 13- and 14-H), 3.12 (m, 2H, 6- and 10-H), 2.95 (q, 1H, 1-H, J = 9.3 Hz), 2.61 (qt, 1H, 8-H, J = 9.3, 5.4 Hz), 1.78 (dt, 2H, 7- and 9-*exo*-H, J = 13.2, 8.8 Hz), 1.48 (dt, 2H, 7- and 9-*endo*-H, J = 13.2, 5.4 Hz). ^{13}C NMR (100 MHz, THF): δ 134.0 (C4 and C12), 129.4 (C5 and C11), 58.8 and 57.8 (C2, C3, C13 and C14), 56.6 (C1), 53.3 (C6 and C10), 49.1 (C8), 37.5 (C7 and C9). Anal. Calcd for $C_{136}H_{144}Ag_{10}F_{30}O_{30}S_{10}$ as a AgOTf-(PCTD-AgOTf)$_9$: C, 38.64; H, 3.43; F, 13.48. Found: C, 38.65; H, 3.47; F, 13.34. Yield of **6** was 72% based on the amount of **2a**.

Synthesis of Ru(cot)(dimethyl fumarate)$_2$ 7. To a 20-mL, two-necked flask was added a solution of 2.09 g (6.6 mmol) of Ru(cod)(cot) and 1.91 g (13.2 mmol) of dimethyl fumarate in 7.0 mL of toluene, and the mixture was stirred at 60 °C. A yellow powder precipitated immediately. After 2 h, the product was separated by filtration, washed with toluene, and dried under vacuum to give **7** (2.50 g, yield 76%). An elemental analysis gave satisfactory data without recrystallization.

Complex **7**. Yellow solid, mp (dec) 177−178 °C. Anal. Calcd for $C_{20}H_{26}O_8Ru$: C, 48.48; H, 5.29. Found: C, 48.22; H, 5.23. IR spectrum (KBr disk): 1706, 1695, 1307, 1166, 1028 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.75 (ddd, 1H, 4-H of cot, J = 8.3, 5.9, 1.0 Hz), 5.84 (dq, 1H, 1-H of cot, J = 9.8, 2.0 Hz), 5.58 (dd, 1H, 3-H of cot, J = 9.8, 8.3 Hz), 4.97 (dd, 1H, 5-H of cot, J = 7.3, 5.9 Hz), 4.33 (t, 1H, 2-H of cot, J = 9.8 Hz), 4.21 (d, 1H, ═CH of fumarate, J = 9.8 Hz), 3.88 (dtd, 1H, 6-H of cot, J = 10.7, 7.3, 1.0 Hz), 3.76 (s, 3H, Me), 3.62 (s, 3H, Me), 3.57 (d, 1H, ═CH of fumarate, J = 10.7 Hz), 3.544 (s, 3H, Me), 3.538 (s, 3H, Me), 3.23 (tdd, 1H, 8-H of cot, J = 15.1, 5.4, 2.0 Hz), 2.64 (br d, 1H, 8-H of cot, J = 15.1 Hz), 2.31 (d, 1H, ═CH of fumarate, J = 9.8 Hz), 2.15 (d, 1H, ═CH of fumarate, J = 10.7 Hz), 1.16 (ddd, 1H, 7-H of cot, J = 12.7, 7.3, 5.4 Hz), −0.46 (dddd, 1H, 7-H of cot, J = 15.1, 12.7, 10.7, 2.0 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 175.8 (C═O), 175.1 (C═O), 174.4 (C═O), 171.9 (C═O), 114.4 (C2 of cot), 106.5 (C3 of cot), 102.3 (C5 of cot), 100.6 (C1 of cot), 99.5 (C4 of cot), 92.7 (C6 of cot), 56.1 (═CH of fumarate), 51.8 (Me), 51.7 (Me), 51.3 (Me), 51.2 (Me), 49.8 (═CH of fumarate), 48.8 (═CH of fumarate), 46.8 (═CH of fumarate), 40.8 (C8 of cot), 22.5 (C7 of cot).

Crystallographic Study of 6 and 7. The crystal data and experimental details for **6** and **7** are summarized in Table 3. Diffraction data were obtained with a Rigaku AFC-7R. The reflection intensities were monitored by three standard reflections at every 150 measurements. No decay correction was applied. Reflection data were corrected for Lorentz and polarization effects. Azimuthal scans of several reflections indicated no need for an absorption correction. The structures were determined by direct methods using SHELX86[73] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[74] No hydrogen atoms were refined except for the four hydrogens on C(1), C(2), C(7), and C(8) of **7**, which was refined isotropically. The final R and Rw values were 0.029 and 0.030 for **6** and 0.040 and 0.041 for **7**, respectively. The calculations were performed on IRIS Indigo and O_2 computer using the program system teXsan.[75]

The final atomic parameters for non-hydrogen atoms of **6** and **7** are given in the Supporting Information, and selected bond lengths and angles are summarized in Tables 4 and 5, respectively.

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Supporting Information Available: Description of the X-ray procedures, tables of X-ray data, positional and thermal parameters, bond lengths and angles, and an ORTEP diagram for compounds **5**, **6**, and **7**; the linear plot of $(1/[\mathbf{1a}]^2 - 1/[\mathbf{1a}]_0^2)$ vs. time and dependence of $[Ru(cod)(cot)]_0$ on d[**2a**]/dt (68 pages, print/PDF). See any current masthead page for ordering information and Web access information.

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(73) SHELX86: Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M.; Kruger, C.; Goddard, R.; Eds.; Oxford University Press: Oxford, U. K., 1985; pp 175−189.

(74) (a) Cromer, D. T.; Waber, G. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV. (b) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781. (c) Creagh, D. C.; McAuley, W. J. *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C.

(75) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985, 1992.