JOC*Article*

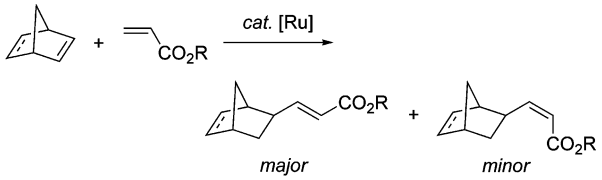
Ruthenium-Complex-Catalyzed Regio- and Stereoselective Linear Codimerization of 2-Norbornenes with Acrylic Compounds

Yasuyuki Ura, Hiroshi Tsujita, Kenji Wada, Teruyuki Kondo, and Take-aki Mitsudo*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

mitsudo@scl.kyoto-u.ac.jp

Received March 4, 2005



A linear codimerization of 2-norbornenes with acrylic compounds such as acrylates and an acrylamide proceeded efficiently by ruthenium catalyst systems, $RuCl_3$(tpy)/Zn (tpy = 2,2′:6′,2″-terpyridine) or $[RuCl_2(C_6H_6)]_2$/Zn in a primary or secondary alcoholic solvent, to afford the corresponding *exo-trans*-2-norbornylacrylates as major products regio- and stereoselectively along with a small amount of *cis* isomers. The reaction of 2,5-norbornadiene with methyl acrylate also gave the linear *exo-trans* codimer, which was effectively catalyzed by the addition of triarylphosphines to the $RuCl_3$(tpy)/Zn catalyst system.

Introduction

Linear codimerization of unsaturated hydrocarbons affording valuable chemicals has been receiving considerable attention due to industrial aspects.[1] Hydrovinylation of alkenes and dienes (addition of *ethylene* to alkenes and dienes), which originated from the research by Alderson et al., appeared in 1965 in the open literature.[2] This is one of the most successfully developed reactions among the codimerizations known to date and is known to be preeminently catalyzed by several late transition metal complexes such as Ni and Pd, with high enantioselectivity.[3−6] On the other hand, although linear codimerization of alkenes and/or dienes except hydrovinylation also has been intensively investigated, the scope of substrates is still rather limited, and most of the reactions suffer from difficulty in controlling the cross-coupling selectivity as well as the regio- and stereoselectivity.[2,7−28] In the course of our investigation on the low-valent ruthenium-catalyzed selective dimerization reactions of unsaturated hydrocarbons,[28,29] we found a linear codimerization of a novel combination of substrates, 2-norbornenes and acrylic compounds. The reaction proceeds regio- and stereoselectively by ruthenium catalyst systems involving neutral tridentate ligands,

* To whom correspondence should be addressed. Phone: +81 75 383 2506. Fax: +81 75 383 2507.

(1) Olivier-Bourbigou, H.; Saussine, L. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Colins, B., Herrmann, W. A., Eds.; Wiley-VCH: New York, 2002; Vol. 1, p 253.

(2) Alderson, T.; Jenner, E. L.; Lindsey, R. V., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 5638.

(3) (a) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185. (b) Bogdanović, B.; Spliethoff, B.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 622. (c) Bogdanović, B. *Adv. Organomet. Chem.* **1979**, *17*, 105. See also ref 1.

(4) (a) RajanBabu, T. V. *Chem. Rev.* **2003**, *103*, 2845. (b) RajanBabu, T. V.; Casalnuovo, A. L.; Ayers, T. A.; Nomura, N.; Jin, J.; Park, H.; Nandi, M. *Curr. Org. Chem.* **2003**, *7*, 301. (c) RajanBabu, T. V.; Nomura, N.; Jin, J.; Nandi, M.; Park, H.; Sun, X. *J. Org. Chem.* **2003**, *68*, 8431. (d) Kumareswaran, R.; Nandi, M.; RajanBabu, T. V. *Org. Lett.* **2003**, *5*, 4345. (e) RajanBabu, T. V. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Vol. 1, Chapter 12. (f) RajanBabu, T. V.; Nomura, N.; Jin, J.; Radetich, B.; Park, H.; Nandi, M. *Chem. Eur. J.* **1999**, *5*, 1963.

(5) Goossen, L. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3775.

(6) Hahn, C.; Cucciolito, M. E.; Vitagliano, A. *J. Am. Chem. Soc.* **2002**, *124*, 9038.

(7) Faissner, R.; Huttner, G. *Eur. J. Inorg. Chem.* **2003**, 2239.

(8) Marciniec, B.; Kownacki, I.; Kubicki, M. *Organometallics* **2002**, *21*, 3263.

(9) Hilt, G.; du Mesnil, F.; Lüers, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 387.

(10) Jin, J.; RajanBabu, T. V. *Tetrahedron* **2000**, *56*, 2145.

(11) Fujiwhara, M.; Nishikawa, T.; Hori, Y. *Org. Lett.* **1999**, *1*, 1635.

(12) Kretschmer, W. P.; Troyanov, S. I.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 284.

(13) (a) Sato, T.; Kakiuchi, F.; Chatani, N.; Murai, S. *Chem. Lett.* **1998**, 893. (b) Kakiuchi, F.; Tanaka, Y.; Sato, T.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 679.

(14) Trost, B. M.; Imi, K.; Davies, I. W. *J. Am. Chem. Soc.* **1995**, *117*, 5371.

(15) Masuda, K.; Ohkita, H.; Kurumatani, S.; Itoh, K. *J. Organomet. Chem.* **1993**, *454*, C13.

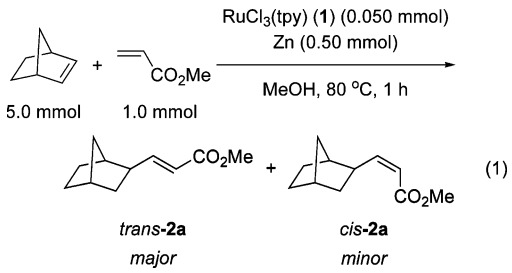
(16) Nikishin, G. I.; Klimova, T. E.; Ignatenko, A. V.; Kovalev, I. P. *Tetrahedron Lett.* **1991**, *32*, 1077.

10.1021/jo050413o CCC: $30.25
Published on Web 07/20/2005

$RuCl_3$(tpy) (tpy = 2,2′:6′,2″-terpyridine) (**1**) or $[RuCl_2(C_6H_6)]_2$ (**3**) in the presence of Zn in an alcoholic solvent.

Results and Discussion

First, complex **1**, which can be reduced by an appropriate reductant to generate an electron-rich low-valent species in situ, was used as a catalyst. The reaction of 2-norbornene (5.0 mmol) with methyl acrylate (1.0 mmol) in the presence of 5 mol % of complex **1** and Zn powder (0.50 mmol) in MeOH under reflux gave the corresponding *exo-trans* codimer *trans*-**2a** as a major product along with a small amount of *cis*-**2a** (eq 1).



(1)

Catalytic activity of several ruthenium and group 9 complexes in the presence of Zn was surveyed in the codimerization of 2-norbornene with methyl acrylate (Table 1). Complex **1** gave the best result (87% yield, *trans*:*cis* ratio > 40:1) among ruthenium polypyridyl complexes (runs 1, 3, and 4). In the absence of Zn, **1** did not show catalytic activity (run 2). In place of **1**, $RuCl_2(PPh_3)_3$ showed a certain activity, whereas $[RuCl_2(CO)_3]_2$ was ineffective (runs 5 and 6). $[RuCl_2(C_6H_6)]_2$ (**3**) was found to be also effective, and the activity is comparable to that of **1** (run 7). However, other η^6-substituted arene complexes such as $[RuCl_2(p\text{-cymene})]_2$ and $[RuCl_2(C_6Me_6)]_2$ were not efficient (runs 8 and 9). No dissociation of these arenes was observed during the codimerization according to the GC−MS analysis, indicating that the arenes stay on ruthenium and work as spectator ligands. Thus, the bulky arene ligands seem to lower the catalytic activity by steric hindrance against the substrates. $RuH_2(PPh_3)_4$, Ru(cod)(cot) (cot = 1,3,5-cyclooctatriene), and $Ru(CO)_3(PPh_3)_2$, which are zerovalent or can be reduced to zerovalent in situ, were examined without Zn, and the former two complexes were somewhat effective (runs 10 and 11), but the latter was almost ineffective (run 12). Rhodium and iridium complexes with a tpy ligand have no catalytic activity (runs 13 and 14).

TABLE 1. Catalytic Activity of Several Complexes on the Linear Codimerization of 2-Norbornene with Methyl Acrylate[a]

run	catalyst	yield/% (*trans*:*cis*)[b]
1	**1**	87 (>40:1)
2	**1** (without Zn)	0
3[c]	$RuCl_3$(tbtpy)	8
4[d]	$RuCl_4$(bpy)	20
5	$RuCl_2(PPh_3)_3$	20
6	$[RuCl_2(CO)_3]_2$	0
7	$[RuCl_2(C_6H_6)]_2$ (**3**)	87 (>40:1)
8	$[RuCl_2(p\text{-cymene})]_2$	19
9	$[RuCl_2(C_6Me_6)]_2$	7
10[e]	$RuH_2(PPh_3)_4$	12
11[e,f,g]	Ru(cod)(cot)	26 (12:1)
12[e,f]	$Ru(CO)_3(PPh_3)_2$	<5
13	$RhCl_3$(tpy)	0
14	$IrCl_3$(tpy)	0

[a] 2-Norbornene (5.0 mmol), methyl acrylate (1.0 mmol), catalyst (0.050 mmol as a metal atom), Zn (0.50 mmol) in MeOH (1.0 mL) at 80 °C for 1 h. [b] Determined by GLC. [c] tbtpy = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine. [d] bpy = 2,2′-bipyridine. [e] Without Zn. [f] In toluene. [g] cot = 1,3,5-cyclooctatriene.

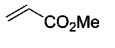
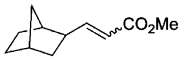
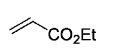
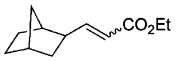
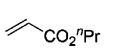
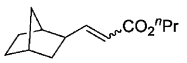
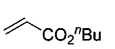
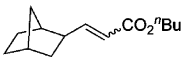
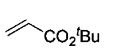
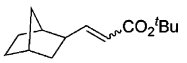
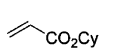
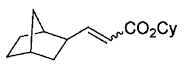
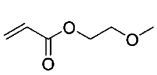
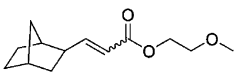
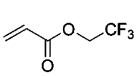
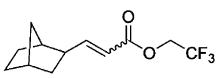
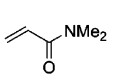
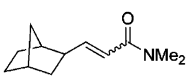
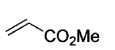
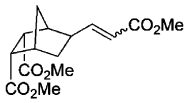
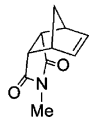
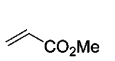
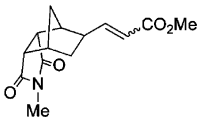
Several metals were examined as reducing agents instead of Zn under the same reaction conditions shown in run 1. A Zn−Cu couple gave a moderate yield of the codimers (75%), whereas others such as Al, Fe, and Mg afforded 7%, 4%, and 0% yield, respectively. When sodium and potassium carbonates were used in place of metals, only trace amounts of the codimers with byproducts were obtained.

The effect of solvents was also found to be critical in the **1**/Zn-catalyzed codimerization under the same reaction conditions as shown in eq 1. MeOH was the best solvent (87%), whereas in a secondary alcohol, *i*-PrOH, the reaction was rather slow at 80 °C and the yield of the product was 28% after 1 h. In *t*-BuOH or nonalcoholic solvents such as toluene and THF the codimerization did not proceed at all, probably because no reduction of the ruthenium species occurred in these solvents.

The **1**- or **3**-catalyzed linear codimerization was applied to diverse substrates (Table 2). By the use of ethyl acrylate in EtOH, the *exo* codimers were obtained in 82% total yield with a *trans*:*cis* ratio of 20:1 (run 2). Other acrylates having primary, secondary, and tertiary hydrocarbyl substituents at the ester moiety afforded the corresponding *exo-trans* and *cis* codimers in good yields, respectively (runs 3−6). Acrylates with heteroatom(s) at the ester moiety are also applicable (runs 7 and 8). In the case of *N*,*N*-dimethyl acrylamide, however, **1** could not catalyze the codimerization. Instead, **3** worked as a catalyst moderately to afford the codimers (run 9).

(17) El Amrani, M. A.; Mortreux, A.; Petit, F. *Tetrahedron Lett.* **1989**, *30*, 6515.
(18) Cros, P.; Triantaphylides, C.; Buono, G. *J. Org. Chem.* **1988**, *53*, 185.
(19) Oehme, G.; Grassert, I.; Mennenga, H.; Baudisch, H. *J. Mol. Catal.* **1986**, *37*, 53.
(20) Bochmann, M.; Thomas, M. *J. Mol. Catal.* **1984**, *26*, 79.
(21) Grenouillet, P.; Neibecker, D.; Tkatchenko, I. *J. Chem. Soc., Chem. Commun.* **1983**, 542.
(22) Ito, T.; Takami, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1220.
(23) (a) Ito, T.; Takahashi, K.; Takami, Y. *Tetrahedron Lett.* **1973**, *14*, 5049. (b) Ito, T.; Kawai, T.; Takami, Y. *Tetrahedron Lett.* **1972**, *13*, 4775.
(24) Saegusa, T.; Ito, Y.; Tomita, S.; Kinoshita, H. *J. Org. Chem.* **1970**, *35*, 670.
(25) Barlow, M. G.; Bryant, M. J.; Haszeldine, R. N.; Mackie, A. G. *J. Organomet. Chem.* **1970**, *21*, 215.
(26) Kawakami, K.; Kawata, N.; Maruya, K.; Mizoroki, T.; Ozaki, A. *J. Catal.* **1975**, *39*, 134.
(27) (a) Umezawa, H.; Fujiwara, Y.; Sawara, K.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2230. (b) Kawamoto, K.; Tatani, A.; Imanaka, T.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1239.
(28) Mitsudo, T.; Zhang, S.-W.; Kondo, T.; Watanabe, Y. *Tetrahedron Lett.* **1992**, *33*, 341.
(29) (a) Mitsudo, T.; Kondo, T. *Synlett* **2001**, 309. (b) 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. (c) Shiotsuki, M.; Suzuki, T.; Kondo, T.; Wada, K.; Mitsudo, T. *Organometallics* **2000**, *19*, 5733. (d) Mitsudo, T.; Zhang, S.-W.; Nagao, M.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 598. (e) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580. (f) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Organomet. Chem.* **1987**, *334*, 157. (g) Mitsudo, T.; Kokuryo, K.; Shinsugi, T.; Nakagawa, Y.; Watanabe, Y.; Takegami, Y. *J. Org. Chem.* **1979**, *44*, 4492. (h) Mitsudo, T.; Kokuryo, K.; Takegami, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 722.

TABLE 2. Ruthenium-Catalyzed Linear Codimerization of 2-Norbornenes with Acrylic Compounds[a]

run	substrates: 2-norbornenes	substrates: acrylic compounds	products		reaction conditions	yield / % (*trans*:*cis*)[b]
1				**2a**	MeOH 80 °C, 1 h	87 (> 40:1)
2				**2b**	EtOH 90 °C, 1 h	82 (20:1)
3				**2c**	*n*-PrOH 100 °C, 1 h	62 (20:1)
4				**2d**	*n*-BuOH 100 °C, 1 h	76 (8.5:1)
5				**2e**	*n*-BuOH 100 °C, 1 h	62 (11:1)
6				**2f**	*i*-PrOH 90 °C, 6 h	75 (12:1)
7				**2g**	*i*-PrOH 90 °C, 4 h	52 (16:1)
8				**2h**	*i*-PrOH 90 °C, 1 h	44 (10:1)
9[c]				**2i**	*i*-PrOH 80 °C, 24 h	45 (8.0:1)
10[c]				**2j**	*i*-PrOH 80 °C, 24 h	45 (10:1)
11[c]				**2k**	*i*-PrOH 80 °C, 24 h	66 (5.6:1)

[a] 2-Norbornenes (5.0 mmol), acrylic compounds (1.0 mmol), **1** (0.050 mmol), Zn (0.50 mmol). [b] Determined by GLC. [c] **3** (0.025 mmol) was used instead of **1**.

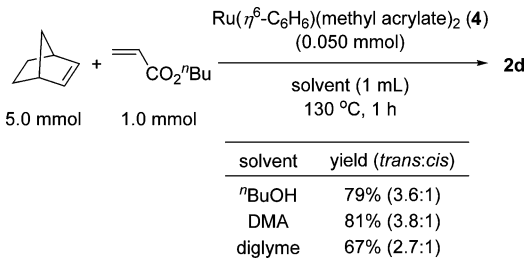
Substituted 2-norbornenes also reacted with methyl acrylate in the presence of **3** (runs 10 and 11). The scope of the catalytic activity of **3** seems to be wider than that of **1**. Reactions with unsymmetrical norbornene derivatives such as dicyclopentadiene and 5-vinyl-2-norbornene resulted in the formation of a complex mixture of codimers. While *N*-methyl-7-oxa-5-norbornene-2,3-dicarboximide as a heteroatom bridged norbornene and benzonorbornadiene were also employed in the reaction with methyl acrylate, no conversion of the substrates occurred. The use of other electron-deficient alkenes such as acrylonitrile and vinyl ketones resulted in either no formation or formation of a trace amount of the products under the present reaction conditions.

In Table 2, the results under various reaction conditions were summarized. EtOH, *n*-PrOH, *i*-PrOH and *n*-BuOH were used instead of MeOH (runs 2−8) to avoid the transesterification reaction. In runs 9−11, *i*-PrOH seems to be better than MeOH in the **3**/Zn catalytic system. When these reactions were conducted in MeOH, the yields of the corresponding codimers **2i**, **2j**, and **2k** were 18%, 6% and 52%, respectively. As for the reaction temperature, for example in runs 2−4, the reactions at 80 °C were also examined, but the yields were slightly lower than those shown in Table 2 (78%, 53%, and 44%). Thus, in some cases higher temperature is required to obtain higher yields of the products.

To elucidate a possible mechanism, a zerovalent ruthenium complex having a benzene ligand, Ru(η^6-C_6H_6)-(methyl acrylate)$_2$ (**4**), which is known to catalyze the homodimerization of methyl acrylate in the presence of sodium naphthalenide,[30] was examined as a catalyst. Complex **4** was prepared by treatment of **3** with methyl acrylate and Zn in MeOH. 2-Norbornene reacted with *n*-butyl acrylate in the presence of 5 mol % of **4** in *n*-BuOH at 130 °C, affording the codimer **2d** in 79% (Scheme 1). Moreover, the codimerization proceeded smoothly even in an aprotic solvent such as *N*,*N*-dimethylacetamide (DMA) or diglyme. This suggests that in the **1** or **3**/Zn catalytic system, alcohol is not necessarily

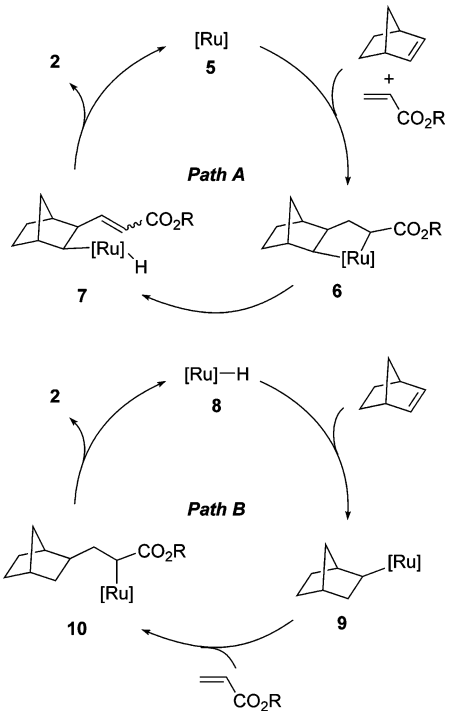
(30) McKinney, R. J. *Organometallics* **1986**, *5*, 1752.

SCHEME 1



solvent	yield (*trans*:*cis*)
^{n}BuOH	79% (3.6:1)
DMA	81% (3.8:1)
diglyme	67% (2.7:1)

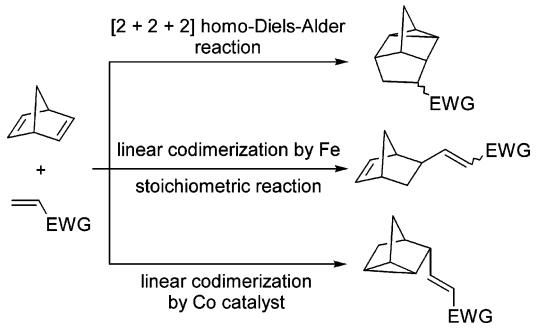
SCHEME 2. Possible Mechanisms



required as a solvent for the codimerization process but is needed at the initial reduction step of ruthenium by Zn.

Two possible reaction pathways for the linear codimerization of 2-norbornene with an acrylate are illustrated in Scheme 2. In path A, coordination of 2-norbornene and an acrylate to zerovalent ruthenium active species **5**, followed by oxidative cyclization gives ruthenacyclopentane intermediate **6**. This step seems to be reasonable according to the results described in Scheme 1. β-Hydrogen elimination to form **7** and successive reductive elimination would give **2** along with the regeneration of **5**. This metallacycle mechanism is proposed in the Fe(CO)$_5$-mediated photoassisted reaction,[31] and in addition, the β-hydrogen elimination from the ruthenacyclopentane (**6** → **7**) is plausible, which is supported by DFT calculation (the energy barrier for the β-hydrogen elimination from nonsubstituted ruthenacyclopentane with a benzene ligand is estimated at 2.7 kcal/mol).[32] On the other hand, in path B, ruthenium hydride species **8** is generated in situ initially, and 2-norbornene inserts into the Ru−H bond of **8** to give **9**. Subsequent insertion of

SCHEME 3



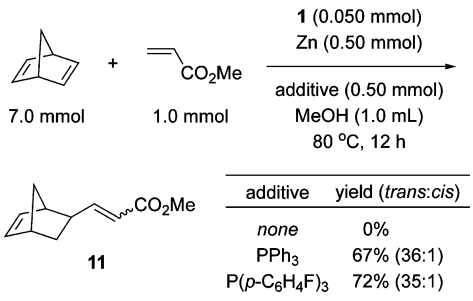
acrylate to the Ru−C bond affords **10**. β-Hydrogen elimination from **10** would give **2** and ruthenium hydride **8** again. The mechanism involving successive insertion of alkenes via a metal hydride species has been well investigated by Brookhart et al. in the homodimerization of alkenes catalyzed by Rh and Pd.[33] The result in Scheme 1 using aprotic solvents indicates that the hydride in **8** should be derived from the acrylate, if the reaction proceeds via path B. As another mechanism, insertion of norbornene to a Ru−H bond formed by sp^2 C−H activation of acrylate and successive reductive elimination would give *cis*-**2**,[13,14] whereas the predominant formation of *trans* isomers cannot be explained. Time dependence of the codimerization of 2-norbornene with methyl acrylate under the reaction conditions shown in Table 1, run 1 was examined by GLC, and the *trans*:*cis* ratio of **2a** was revealed to be approximately constant (>40:1) during the reaction, suggesting that no isomerization from the *cis* to the *trans* isomer occurs. Moreover, if the reaction proceeds via this pathway, acrylates having a substituent at the α- or β-position should react with 2-norbornene; actually no reaction occurred, and thus this pathway seems unlikely.

In the reactions of 2,5-norbornadiene with an electron-deficient alkene, the [2 + 2 + 2] homo-Diels−Alder reaction is well-known to proceed thermally or catalytically by several transition metal complexes.[34−36] In contrast, linear codimerization is comparatively rare; only Fe-mediated photoreaction mentioned above[31] and Co(I)-catalyzed reaction[9] have been reported, which give the corresponding codimers as depicted in Scheme 3. The reaction of 2,5-norbornadiene with methyl acrylate under the optimized conditions for 2-norbornene, however, did not afford the codimers. Further investigation revealed that the **1**/Zn/PPh$_3$ system promotes linear codimerization to give the *exo-trans* codimer **11** regio- and stereoselectively as a major isomer in good yield along with no formation of [2 + 2 + 2] cycloadducts (Scheme 4). P(*p*-C$_6$H$_4$F)$_3$ also worked efficiently, whereas other additives such as arylalkylphosphines, trialkylphosphines, biden-

(31) Schmid, H.; Naab, P.; Hayakawa, K. *Helv. Chim. Acta* **1978**, *61*, 1427.
(32) Huang, X.; Zhu, J.; Lin, Z. *Organometallics* **2004**, *23*, 4154.

(33) (a) Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2777. (b) Brookhart, M.; Hauptman, E. *J. Am. Chem. Soc.* **1992**, *114*, 4437. (c) Hauptman, E.; Sabo-Etienne, S.; White, P. S.; Brookhart, M.; Garner, J. M.; Fagan, P. J.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 8038. (d) DiRenzo, G. M.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 6225.
(34) (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49 and references therein. (b) Lautens, M.; Edwards, L. G.; Tam, W.; Lough, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 10276.
(35) Pardigon, O.; Tenaglia, A.; Buono, G. *Tetrahedron Lett.* **2000**, *41*, 4089.
(36) Gugelchuk, M. M.; Doherty-Kirby, A. L. *J. Org. Chem.* **1996**, *61*, 3490.

SCHEME 4



additive	yield (*trans*:*cis*)
none	0%
PPh_3	67% (36:1)
$P(p\text{-}C_6H_4F)_3$	72% (35:1)

tate phosphines, phosphites, and amines were almost ineffective. The combination of **3**/Zn/PPh_3 showed no catalytic activity. The addition of phosphine probably prevents the coordination of norbornadiene to the ruthenium in a bidentate manner to deactivate the catalyst.

In summary, we have developed a novel ruthenium-catalyzed linear codimerization of 2-norbornenes with acrylic compounds. This reaction provides a straightforward method to introduce a series of norbornyl substituents on the terminal sp^2 carbon of acrylic compounds. The obtained codimers are potentially expected as monomers with a bulky substituent for materials such as high-resolution photoregists.

Experimental Section

All solvents were distilled under Ar over appropriate drying reagents (Na or CaH_2). $[RuCl_2(CO)_3]_2$ was obtained commercially and used without further purification. $RuCl_3$(tpy),[37] $RuCl_3$(tbtpy),[38] $RuCl_4$(bpy),[39] $RuCl_2(PPh_3)_3$,[40] $[RuCl_2(C_6H_6)]_2$,[41] $RuH_2(PPh_3)_4$,[42] Ru(cod)(cot),[43] $Ru(CO)_3(PPh_3)_2$,[44] $RhCl_3$(tpy),[45] and $IrCl_3$(tpy)[46] were prepared as described in the literature. Methyl acrylate and 2,5-norbornadiene were obtained commercially and distilled before use. Other reagents (norbornenes, acrylates, and phosphines) were obtained commercially and used without further purification. Compounds **2d**, **2e**, and **2g**−**k** were purified on a recycling preparative HPLC using $CHCl_3$ as an eluent. The codimers obtained here are all new compounds except **2b**, the ^1H NMR data of which were compared with the data reported previously.[47]

General Procedure for Ruthenium-Catalyzed Codimerizaition of 2-Norbornenes with Acrylates. The reaction of 2-norbornene with methyl acrylate is representative. 2-Norbornene (470 mg, 5.0 mmol), methyl acrylate (86 mg, 1.0 mmol), complex **1** (22 mg, 0.050 mmol), Zn powder (33 mg, 0.50 mmol), and MeOH (1.0 mL) were placed into a 20-mL Pyrex glass reactor equipped with a magnetic stirring bar and a three-way cock under Ar. The mixture was stirred under reflux (bath temp 80 °C) for 1 h. After the reaction mixture was cooled to room temperature, the volatile materials were evaporated under vacuum. Kugelrohr distillation at 110−120 °C (10 mmHg) and flash column chromatography on silica gel (hexane/EtOAc = 50/1) gave 129 mg of codimer **2a** (0.70 mmol, 70%). The structure of **2a** was confirmed by GC−MS, ^1H and ^{13}C NMR, IR, and elemental analysis. The *trans*:*cis* ratio was determined by GLC.

***exo*-Methyl 3-Bicyclo[2.2.1]hept-2-ylprop-2-enoate (2a).** Colorless liquid, GC yield 87% (*trans*:*cis* = 40:1), isolated yield 70%. IR spectrum (neat): 1727, 1652 cm^{-1}. ^1H NMR for *trans*-**2a** ($CDCl_3$, 400 MHz): δ 6.85 (dd, J = 7.8, 15.7 Hz, 1H), 5.72 (dd, J = 1.0, 15.7 Hz, 1H), 3.71 (s, 3H), 2.29−2.22 (m, 2H), 2.15 (br s, 1H), 1.60−1.43 (m, 4H), 1.40−1.32 (m, 2H), 1.28−1.15 (m, 2H). ^{13}C NMR for *trans*-**2a** ($CDCl_3$, 100 MHz): δ 167.3, 153.9, 118.1, 51.4, 44.7, 41.9, 37.0, 36.7, 35.9, 29.7, 29.0. MS (EI) *m*/*z* 180 (M^+). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.15; H, 9.16.

***exo*-Ethyl 3-Bicyclo[2.2.1]hept-2-ylprop-2-enoate (2b).** Colorless liquid, GC yield 82% (*trans*:*cis* = 20:1), isolated yield 63%. IR spectrum (neat): 1720, 1649 cm^{-1}. ^1H NMR for *trans*-**2b** ($CDCl_3$, 400 MHz): δ 6.85 (dd, J = 7.6, 15.6 Hz, 1H), 5.71 (dd, J = 1.0, 15.6 Hz, 1H), 4.17 (q, J = 6.8 Hz, 2H), 2.28−2.22 (m, 2H), 2.15 (br s, 1H), 1.60−1.50 (m, 4H), 1.40−1.32 (m, 2H), 1.28 (t, J = 6.8 Hz, 3H), 1.25−1.15 (m, 2H). ^{13}C NMR for *trans*-**2b** ($CDCl_3$, 100 MHz): δ 167.3, 153.8, 118.7, 60.1, 44.6, 41.8, 36.9, 36.6, 35.8, 29.6, 28.9, 14.3. MS (EI) *m*/*z* 194 (M^+). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.15; H, 9.16.

***exo-n*-Propyl 3-Bicyclo[2.2.1]hept-2-ylprop-2-enoate (2c).** Colorless liquid, GC yield 62% (*trans*:*cis* = 20:1), isolated yield 43%. IR spectrum (neat): 1720, 1650 cm^{-1}. ^1H NMR for *trans*-**2c** ($CDCl_3$, 400 MHz): δ 6.78 (dd, J = 7.8, 15.6 Hz, 1H), 5.65 (dd, J = 1.4, 15.6 Hz, 1H), 4.00 (t, J = 6.8 Hz, 2H), 2.22−2.15 (m, 2H), 2.09 (br s, 1H), 1.60 (m, 2H), 1.55−1.40 (m, 4H), 1.34−1.25 (m, 2H), 1.21−1.07 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR for *trans*-**2c** ($CDCl_3$, 100 MHz): δ 167.0, 153.6, 118.6, 65.8, 44.7, 41.9, 37.0, 36.7, 35.9, 29.8, 29.0, 22.2, 10.6. MS (EI) *m*/*z* 208 (M^+). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.03; H, 9.93.

***exo-n*-Butyl 3-Bicyclo[2.2.1]hept-2-ylprop-2-enoate (2d).** Colorless liquid, GC yield 76% (*trans*:*cis* = 8.5:1), isolated yield 42%. IR spectrum (neat): 1720, 1649 cm^{-1}. ^1H NMR for *trans*-**2d** ($CDCl_3$, 400 MHz): δ 6.78 (dd, J = 8.3, 15.7 Hz, 1H), 5.65 (d, J = 15.7 Hz, 1H), 4.12 (t, J = 6.8 Hz, 2H), 2.28−2.23 (m, 2H), 2.15 (br s, 1H), 1.67−1.15 (m, 12H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR for *trans*-**2d** ($CDCl_3$, 100 MHz): δ 167.0, 153.5, 118.6, 64.1, 44.7, 41.9, 37.0, 36.7, 35.9, 30.9, 29.8, 29.0, 19.3, 13.9. ^1H NMR for *cis*-**2d** ($CDCl_3$, 400 MHz): δ 6.07 (dd, J = 11.3, 11.7 Hz, 1H), 5.61 (dd, J = 1.5, 11.7 Hz, 1H), 4.11 (t, J = 6.8 Hz, 2H), 3.29 (m, 1H), 2.26 (br s, 1H), 2.06 (br s, 1H), 1.73−1.18 (m, 12H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR for *cis*-**2d** ($CDCl_3$, 100 MHz): δ 166.5, 155.6, 116.8, 63.8, 43.0, 41.0, 38.9, 36.6, 36.1, 30.8, 29.6, 28.9, 19.3, 13.8. MS (EI) *m*/*z* 222 (M^+). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.60; H, 10.16.

***exo-t*-Butyl 3-Bicyclo[2.2.1]hept-2-ylprop-2-enoate (2e).** Colorless liquid, GC yield 62% (*trans*:*cis* = 11:1), isolated yield 31%. IR spectrum (neat): 1720, 1650 cm^{-1}. ^1H NMR for *trans*-**2e** ($CDCl_3$, 400 MHz): δ 6.67 (dd, J = 7.7, 15.7 Hz, 1H), 5.57 (dd, J = 1.4, 15.7 Hz, 1H), 2.20−2.14 (m, 2H), 2.07 (br s, 1H), 1.52−1.44 (m, 2H), 1.41 (s, 9H), 1.37−1.36 (m, 1H), 1.32−1.25 (m, 2H), 1.19−1.07 (m, 3H). ^{13}C NMR for *trans*-**2e** ($CDCl_3$, 100 MHz): δ 166.3, 152.4, 120.3, 79.9, 44.6, 42.0, 37.0, 36.7, 35.9, 29.8, 29.0, 28.3 (3C). MS (EI) *m*/*z* 222 (M^+). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.60; H, 10.16.

***exo*-Cyclohexyl 3-Bicyclo[2.2.1]hept-2-ylprop-2-enoate (2f).** Colorless liquid, GC yield 75% (*trans*:*cis* = 12:1), isolated yield 60%. IR spectrum (neat): 1716, 1648 cm^{-1}. ^1H NMR for *trans*-**2f** ($CDCl_3$, 400 MHz): δ 6.83 (dd, J = 8.3, 15.6 Hz, 1H), 5.71 (d, J = 15.6 Hz, 1H), 4.79 (m, 1H), 2.28−2.21 (m, 2H), 2.15 (br s, 1H), 1.87−1.85 (m, 2H), 1.74−1.72 (m, 2H), 1.61−1.14 (m, 14H). ^{13}C NMR for *trans*-**2f** ($CDCl_3$, 100 MHz): δ

(37) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.
(38) Hadda, T. B.; Bozec, H. L. *Polyhedron* **1988**, *7*, 575.
(39) Stoessel, S. J.; Elliott, C. M.; Stille, J. K. *Chem. Mater.* **1989**, *2*, 259.
(40) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12,* 237.
(41) Bennett, B. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, *24*, 233.
(42) Young, R.; Wilkinson, G. *Inorg. Synth.* **1977**, *17*, 75.
(43) Itoh, K.; Nagashima, H.; Oshima, T.; Oshima, N.; Nishiyama, H. *J. Organomet. Chem.* **1984**, *272*, 179.
(44) Wonchoba, E. R.; Parshall, G. W. *Inorg. Synth.* **1974**, *15*, 50.
(45) Pruchnik, P. F.; Jakimowicz, P.; Ciunik, Z.; Zakrzewska-Czerwinska, J.; Opolski, A.; Wietrzyk, J.; Wojdat, E. *Inorg. Chim. Acta* **2002**, *334*, 59.
(46) Collin, J.-P.; Dixon, I. M.; Sauvage, J.-P.; Williams, J. A. G.; Barigelletti, F.; Flamigni, L. *J. Am. Chem. Soc.* **1999**, *121*, 5009.
(47) Negishi, E.; Lew, G.; Yoshida, T. *J. Org. Chem.* **1974**, *39*, 2321.

166.4, 153.2, 119.1, 72.3, 44.7, 41.9, 37.0, 36.7, 35.9, 31.8 (2C), 29.8, 29.0, 25.6, 23.9 (2C). MS (EI) *m/z* 248 (M^+). Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.34; H, 9.54.

***exo*-2-Methoxyethyl 3-Bicyclo[2.2.1]hept-2-ylprop-2-enoate (2g).** Colorless liquid, GC yield 52% (*trans*:*cis* = 16:1), isolated yield 38%. IR spectrum (neat): 1719, 1648 cm^{-1}. ^1H NMR for *trans*-**2g** ($CDCl_3$, 400 MHz): δ 6.88 (dd, J = 8.3, 15.6 Hz, 1H), 5.57 (d, J = 15.6 Hz, 1H), 4.28 (t, J = 4.4 Hz, 2H), 3.62 (t, J = 4.4 Hz, 2H), 3.40 (s, 3H), 2.28−2.22 (m, 2H), 2.15 (br s, 1H), 1.59−1.50 (m, 3H), 1.39−1.34 (m, 2H), 1.27−1.15 (m, 3H). ^{13}C NMR for *trans*-**2g** ($CDCl_3$, 100 MHz): δ 166.9, 154.3, 118.2, 70.6, 63.2, 59.0, 44.7, 41.8, 36.9, 36.6, 35.8, 29.7, 28.9. MS (EI) *m/z* 224 (M^+). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.33; H, 8.92.

***exo*-2,2,2-Trifluoroethyl 3-Bicyclo[2.2.1]hept-2-ylprop-2-enoate (2h).** Colorless liquid, GC yield 44% (*trans*:*cis* = 10:1), isolated yield 27%. IR spectrum (neat): 1741, 1649 cm^{-1}. ^1H NMR for *trans*-**2h** ($CDCl_3$, 400 MHz): δ 6.98 (dd, J = 8.3, 15.6 Hz, 1H), 5.79 (dd, J = 1.5, 15.6 Hz, 1H), 4.51 (q, J_{H-F} = 8.8 Hz, 2H), 2.31−2.26 (m, 2H), 2.18 (br s, 1H), 1.62−1.50 (m, 3H), 1.40−1.34 (m, 2H), 1.29−1.18 (m, 3H). ^{13}C NMR for *trans*-**2h** ($CDCl_3$, 100 MHz): δ 165.1, 156.7, 123.0 (q, $^1J_{C-F}$ = 277 Hz), 117.7, 60.1 (q, $^2J_{C-F}$ = 36.5 Hz), 44.9, 41.8, 36.8, 36.6, 35.9, 29.7, 28.9. MS (EI) *m/z* 248 (M^+). HR-MS (EI) *m/z* 248.1029 (M^+), calcd for $C_{12}H_{15}F_3O_2$ 248.1024.

***exo*-3-Bicyclo[2.2.1]hept-2-yl-*N*,*N*-dimethylprop-2-enamide (2i).** Colorless liquid, GC yield 45% (*trans*:*cis* = 8.0:1), isolated yield 18%. IR spectrum (neat): 1659, 1620 cm^{-1}. ^1H NMR for *trans*-**2i** ($CDCl_3$, 400 MHz): δ 6.76 (dd, J = 7.7, 15.2 Hz, 1H), 6.15 (d, J = 15.2 Hz, 1H), 3.07 (s, 3H), 3.00 (s, 3H), 2.28−2.25 (m, 2H), 2.13 (br s, 1H), 1.55−1.13 (m, 8H). ^{13}C NMR for *trans*-**2i** ($CDCl_3$, 100 MHz): δ 167.0, 150.8, 117.4, 45.0, 42.2, 37.4, 37.3, 36.6, 35.8, 35.7, 29.7, 29.0. MS (EI) *m/z* 193 (M^+). HR-MS (FAB-*m*NBA) *m/z* 194.1548 ($M + H^+$), calcd for $C_{12}H_{20}NO$ 194.1545.

***exo*-Methyl 3-[5,6-Bis(methoxycarbonyl)bicyclo[2.2.1]-hept-2-yl]prop-2-enoate (2j).** Colorless liquid, GC yield 45% (*trans*:*cis* = 10:1), isolated yield 18%. IR spectrum (neat): 1738, 1731, 1716, 1651 cm^{-1}. ^1H NMR for *trans*-**2j** ($CDCl_3$, 400 MHz): δ 6.90 (dd, J = 7.8, 15.6 Hz, 1H), 5.81 (dd, J = 1.0, 15.6 Hz, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 3.12−3.03 (m, 2H), 2.95 (dd, J = 3.9, 11.7 Hz, 1H), 2.63 (br s, 1H) 2.47 (d, J = 2.5 Hz, 1H) 2.05−1.96 (m, 1H), 1.62−1.58 (m, 1H), 1.40−1.19 (m, 2H). ^{13}C NMR for *trans*-**2j** ($CDCl_3$, 100 MHz): δ 172.5, 172.1, 167.1, 152.6, 119.3, 51.7, 51.5, 51.5, 47.0, 46.0, 44.8, 41.1, 37.7, 37.4, 32.0. MS (EI) *m/z* 296 (M^+). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.82; H, 6.80.

***exo*-Methyl 3-(4-Aza-4-methyl-3,5-dioxotricyclo[5.2.1.$0^{2,6}$]-dec-8-yl)prop-2-enoate (2k).** White solid, GC yield 66% (*trans*:*cis* = 5.6:1), isolated yield 52%, mp 104−105 °C. IR spectrum (KBr): 1765, 1724, 1692, 1658 cm^{-1}. ^1H NMR for *trans*-**2k** ($CDCl_3$, 400 MHz): δ 6.79 (dd, J = 7.3, 15.6 Hz, 1H), 5.76 (dd, J = 1.5, 15.6 Hz, 1H), 3.72 (s, 3H), 3.20−3.11 (m, 2H), 2.99 (s, 3H), 2.85 (m, 1H), 2.70 (d, J = 4.4 Hz, 1H), 2.25 (m, 1H), 1.78−1.76 (m, 1H), 1.62−1.54 (m, 2H), 1.49−1.45 (m, 1H). ^{13}C NMR for *trans*-**2k** ($CDCl_3$, 100 MHz): δ 177.4, 177.4, 166.6, 150.7, 120.2, 51.7, 48.7, 48.4, 44.2, 39.6, 39.3, 39.2, 32.0, 24.6. MS (EI) *m/z* 263 (M^+). Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.58; H, 6.50; N, 5.31.

Synthesis of Ru(η^6-C_6H_6)(methyl acrylate)$_2$ (4). To a MeOH suspension (20 mL) of $[RuCl_2(C_6H_6)]_2$ (0.55 g, 1.0 mmol) were added methyl acrylate (1.55 g, 18 mmol) and Zn (0.65 g, 10 mmol), and the mixture was stirred at room temperature for 16 h under Ar. After removal of the solvent under vacuum, the residue was dissolved in $CHCl_3$ (5 mL) and was chromatographed on alumina under Ar. Elution with $CHCl_3$ gave a yellow solution, from which the solvent was removed under vacuum. The obtained yellow solid was recrystallized from $CHCl_3$/pentane to give **4** (0.21 g, 28% yield), which contained two minor isomers. Only the major isomer could be fully characterized by ^1H and ^{13}C NMR as shown below. Mp 144−145 °C (decomp). IR spectrum (KBr): 2985, 2944, 1693, 1464, 1453, 1438, 1386 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 5.48 (s, 6H), 3.61 (s, 6H), 2.99 (d, J = 10.7 Hz, 2H), 1.97 (d, J = 7.8 Hz, 2H), 0.85 (dd, J = 7.8, 10.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.5 (2C), 93.4 (6C), 51.1 (2C), 46.2 (2C), 34.4 (2C). Anal. Calcd for $C_{14}H_{18}O_4Ru$: C, 47.86; H, 5.16. Found: C, 47.58; H, 5.03.

Codimerization of 2-Norbornene with *n*-Butyl Acrylate Catalyzed by Complex 4. 2-Norbornene (470 mg, 5.0 mmol), *n*-butyl acrylate (128 mg, 1.0 mmol), complex **4** (18 mg, 0.050 mmol), and a solvent (1.0 mL) were placed in a 20-mL Pyrex glass reactor equipped with a magnetic stirring bar and a three-way cock under Ar. The mixture was stirred at 130 °C for 1 h. Yield and *trans*:*cis* ratio were determined by GLC with naphthalene as an internal standard.

Ruthenium-Catalyzed Linear Codimerization of 2,5-Norbornadiene with Methyl Acrylate. 2,5-Norbornadiene (645 mg, 7.0 mmol), methyl acrylate (86 mg, 1.0 mmol), complex **1** (22 mg, 0.050 mmol), Zn powder (33 mg, 0.50 mmol), P(*p*-C_6H_4F)$_3$ (158 mg, 0.50 mmol), and MeOH (1.0 mL) were placed in a 20-mL Pyrex glass reactor equipped with a magnetic stirring bar and a three-way cock under Ar. The mixture was stirred under reflux (bath temp 80 °C) for 12 h. After the reaction mixture was cooled to room temperature, the volatile materials were evaporated under vacuum. Kugelrohr distillation at 120−130 °C (10 mmHg) and flash column chromatography on silica gel (hexane/EtOAc = 50/1) gave 103 mg of codimer **11** (0.58 mmol, 58%). The *trans*:*cis* ratio was determined by GLC.

***exo*-Methyl 3-Bicyclo[2.2.1]hept-5-en-2-ylprop-2-enoate (11).** Colorless liquid, GC yield 72% (*trans*:*cis* = 35:1), isolated yield 58%. IR spectrum (neat): 1724, 1652 cm^{-1}. ^1H NMR for *trans*-**11** ($CDCl_3$, 400 MHz): δ 6.98 (dd, J = 8.8, 15.6 Hz, 1H), 6.12 (t, J = 2.0 Hz, 2H), 5.83 (dd, J = 1.0, 15.6 Hz, 1H), 3.73 (s, 3H), 2.93 (br s, 1H), 2.70 (d, J = 1.4 Hz, 1H), 2.17 (ddd, J = 4.4, 8.8, 13.2 Hz, 1H), 1.47−1.36 (m, 4H), ^{13}C NMR for *trans*-**11** ($CDCl_3$, 100 MHz): δ 167.0, 154.1, 137.4, 135.8, 119.4, 51.4, 47.8, 45.6, 42.4, 41.5, 32.6. MS (EI) *m/z* 178 (M^+). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13: H, 7.92. Found: C, 74.23; H, 7.96.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **2h** and **2i**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050413O