[PPN][$Ru_3H(CO)_{11}$]/PCy_3-Catalyzed Direct Addition of Formyl Compounds to Alkenes

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Received May 18, 1999

A novel ruthenium catalyst system of [PPN][$Ru_3H(CO)_{11}$]/PCy_3 [PPN = bis(triphenylphosphine)iminium, Cy = cyclohexyl] for the direct hydroamidation and hydroesterification of alkenes with formamides and alkyl formates has been developed. These addition reactions proceeded smoothly under an argon atmosphere, and carbon monoxide is not needed to suppress decarbonylation of formyl compounds or to maintain the catalytic activity.

Introduction

Research on C_1 chemistry, particularly for carbon monoxide-based organic synthesis, has recently aroused a considerable interest in the chemical industry.[1] Among the various C_1 building blocks derived from carbon monoxide, formamides and alkyl formates are of special interest because they can be considered liquid or solid condensates of carbon monoxide with amines or alcohols[2] and as alternative sources of carbamoyl or alkoxycarbonyl moieties via a formyl C−H bond activation.[3]

In this context, several reports have described the addition of formyl compounds to alkenes, especially methyl formate to ethylene, using transition metal catalysts. The homogeneous catalytic hydroesterification of ethylene with methyl formate was originally discovered by Sneeden and co-workers in 1983 using $RuCl_2(PPh_3)_3$ catalyst.[4] Recently, several modified ruthenium-based catalytic systems, such as $RuH_2(PPh_3)_4$,[5] $Ru_3(CO)_{12}$,[6] $Ru_3(CO)_{12}$/P(n-Bu)$_3$,[7] $Ru_3(CO)_{12}$/[PPN]Cl,[8a,b] [PPN][$Ru(CO)_3Cl_3$],[8b,c] $RuCl_3$/Et_4NI,[9] and others,[10] have also been developed. However, the substrates that have been reported thus far are strictly limited to the combination of methyl formate and ethylene, and/or the use of nitrogen[4,6a] or carbon monoxide[6b,10a−d] pressure seems to be generally required. In addition, except for our previous report,[11] transition metal complex-catalyzed hydroamidation of alkenes with formamides has not yet been reported.

On the other hand, in the course of our study on ruthenium catalysis,[12] we independently found that low-valent ruthenium complexes, especially $Ru_3(CO)_{12}$, Ru(cod)(cot) [cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene], and $RuCl_2(PPh_3)_3$, showed high catalytic activity for the activation of the formyl C−H bond, which enables the development of novel catalytic reactions using various formyl compounds such as formamide,[11,13] alkyl formates,[14] and aldehydes.[15] With some exceptions,[13,14b,c,15c] however, our ruthenium-catalyzed addition reactions of formyl compounds to alkenes also required carbon monoxide pressure to suppress the decarbonylation of formyl compounds as well as to maintain high catalytic activity.

Thus, we have been continuing our effort to improve and modify the ruthenium catalyst system for the addition of formyl compounds to alkenes, *which does not*

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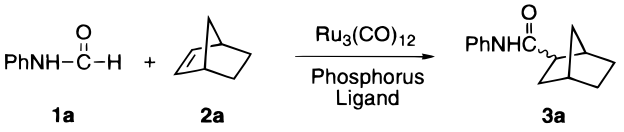
10.1021/om990373c CCC: $15.00
Publication on Web 08/28/1999

Table 1. Effect of Phosphorus Ligands on $Ru_3(CO)_{12}$-Catalyzed Hydroamidation of 2-Norbornene (2a) with Formanilide (1a)[a]



1a 2a 3a

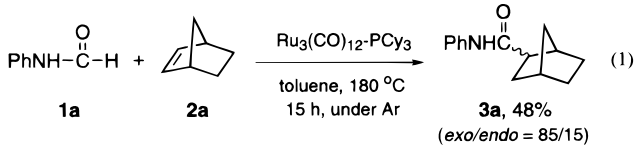
Run	Phosphorus Ligand	Conv. of **1a** (%)[b]	Yield of **3a** (%)[b]	*exo*:*endo*[b]
1	——	20	0	——
2	PCy_3	91	48	85:15
3	PPh_3	67	21	85:15
4	$P(n\text{-}Bu)_3$	64	4	91:9
5	$Ph_2P(CH_2)_2PPh_2$	61	8	88:12
6	$Ph_2P(CH_2)_3PPh_2$	100	31	86:14
7	$Ph_2P(CH_2)_4PPh_2$	89	37	84:16
8	$Et_2P(CH_2)_2PEt_2$	100	0	——

[a] **1a** (5.0 mmol), **2a** (15 mmol), $Ru_3(CO)_{12}$ (0.067 mmol), phosphorus ligand (0.40 mmol as P atom), toluene (3.0 mL) at 180 °C for 15 h under an argon atmosphere. [b] Determined by GLC.

require carbon monoxide. We report here the development of a new and highly active ruthenium catalyst system, $[PPN][Ru_3H(CO)_{11}]/PCy_3$ [PPN = bis(triphenylphosphine)iminium, Cy = cyclohexyl], for both direct hydroamidation and hydroesterification of alkenes with formamides and alkyl formates. These reactions proceeded smoothly under an argon atmosphere with high yield and selectivity of the products.

Results and Discussion

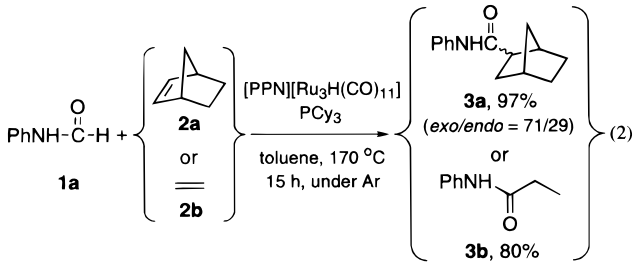
Ruthenium-Catalyzed Hydroamidation of Alkenes with Formamides. Our initial studies examined the reaction of formanilide **1a** with 3 equiv of 2-norbornene **2a** in the presence of 1.34 mol % $Ru_3(CO)_{12}$ in toluene at 180 °C for 15 h under an argon atmosphere, but the conversion of **1a** was low (20%), and no addition product was obtained at all. However, phosphorus ligands have a dramatic effect on the reaction. For example, the catalyst system of 1.34 mol % $Ru_3(CO)_{12}$ with 8.0 mol % PCy_3 gave the desired adduct **3a** in 48% yield (eq 1).



1a 2a (1)

Thus, the effect of phosphorus ligands was examined first, and the results are summarized in Table 1. Among the phosphorus ligands examined, PCy_3 gave the best result. Several mono- and diphosphines such as PPh_3, $Ph_2P(CH_2)_3PPh_2$, and $Ph_2P(CH_2)_4PPh_2$ also increased the catalytic activity, but with phosphines such as $P(n\text{-}Bu)_3$, $Ph_2P(CH_2)_2PPh_2$, and $Et_2P(CH_2)_2PEt_2$, the yield of **3a** drastically decreased, while the conversion of **1a** was still high, due to the formation of a considerable amount of aniline from the decarbonylation of **1a** (*vide infra*).

Even though the best yield of **3a** was obtained by the catalyst system of $Ru_3(CO)_{12}/PCy_3$,[16] the material balance was still low (conversion of **1a**, 91%; yield of **3a**, 48%). Careful analysis of the byproducts in the reaction mixture of run 2 in Table 1 revealed the formation of aniline (from the decarbonylation of **1a**), phenyl isocyanate (from the dehydrogenation of **1a**), and diphenyl urea (from the reaction of aniline with phenyl isocyanate, or from ruthenium-catalyzed dehydrogenative coupling of **1a** with aniline[13a,c]). Thus, further efforts to modify the catalyst system to improve the yield and selectivity of **3a** are required. The IR spectrum of the reaction mixture of run 2 in Table 1 gave important information about the active ruthenium species. After the reaction, two characteristic strong absorption bands at 1934 and 1858 cm^{-1} were observed, which suggests the formation of an anionic ruthenium carbonyl species with a bridging carbonyl ligand. Among the various possible ruthenium complexes, we used $[PPN][Ru_3H(CO)_{11}]$,[17] which is an anionic ruthenium carbonyl cluster with a bridging carbonyl ligand, as the most suitable catalyst precursor. The reaction of formanilide **1a** with 2 equiv of 2-norbornene **2a** in the presence of 1.34 mol % $[PPN][Ru_3H(CO)_{11}]$ and 4.0 mol % PCy_3 at 170 °C for 15 h under an argon atmosphere gave the corresponding adduct **3a** in 97% yield without the formation of any byproducts. Ethylene **2b** also reacted with **1a** under the same reaction conditions to give the adduct **3b** in 80% yield (eq 2).



1a (2)

Next, the catalytic activity of several ruthenium complexes including the reported ruthenium catalyst systems, which are known to be active catalysts for the hydroesterification of ethylene with methyl formate, in the hydroamidation of 2-norbornene **2a** with formanilide **1a** was examined, and the results are summarized in Table 2.

Under the present reaction conditions, the catalytic activities of $Ru_3(CO)_{12}$ and Ru(cod)(cot) were quite low even in the presence of the PCy_3 ligand. The $Ru_3(CO)_{12}$/[PPN]Cl system also showed low catalytic activity, which suggests that the present reaction does not proceed via a $[PPN][Ru_3(\mu_3\text{-}Cl)(CO)_9]$ complex or its analogues[8] and that the hydrido ligand in $[PPN][Ru_3H(CO)_{11}]$ is also essential for high catalytic activity. Furthermore, no **3a** was obtained with the $RuCl_2(PPh_3)_3$ catalyst. The reactions with other ruthenium complexes (runs 9−13) were also in vain. Surprisingly, the catalytic activity of $[Et_4N][Ru_3H(CO)_{11}]$ was quite low, which

(16) Keim and Becker have already reported the low catalytic activity of $Ru_3(CO)_{12}/PCy_3$ for the hydroesterification of ethylene with methyl formate. See ref 6a.

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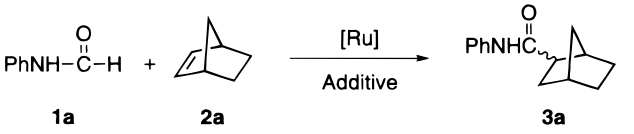
Table 2. Catalytic Activity of Several Ruthenium Complexes on Hydroamidation of 2-Norbornene (2a) with Formanilide (1a)[a]



1a **2a** **3a**

Run	Ruthenium Complex	Additive	Conv. of **1a** (%)[b]	Yield of **3a** (%)[b]	*exo:endo*[b]
1	$[PPN][Ru_3H(CO)_{11}]$	PCy_3	100	97	71:29
2	$[PPN][Ru_3H(CO)_{11}]$	—	100	44	79:21
3	$[Et_4N][Ru_3H(CO)_{11}]$	PCy_3	38	12	79:21
4	$Ru_3(CO)_{12}$	PCy_3	26	18	84:16
5[c]	$Ru_3(CO)_{12}$	PCy_3 + [PPN]Cl	62	26	82:18
6[c]	$Ru_3(CO)_{12}$	[PPN]Cl	57	13	75:25
7	Ru(cod)(cot)	PCy_3	74	16	82:18
8	$RuCl_2(PPh_3)_3$	—	51	0	—
9	$[Ru(CO)_3Cl_2]_2$	PCy_3	68	0	—
10	$[Ru(CO)_2Cl_2]_n$	PCy_3	79	0	—
11	$[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$	PCy_3	91	0	—
12	Cp*RuCl(cod)	PCy_3	26	0	—
13	$[Cp^*Ru(CO)_2]_2$	PCy_3	0	0	—

[a] **1a** (5.0 mmol), **2a** (10 mmol), ruthenium complex (0.20 mmol as Ru atom), PCy_3 (0.20 mmol), toluene (3.0 mL) at 170 °C for 15 h under an argon atmosphere. [b] Determined by GLC. [c] [PPN]Cl (0.20 mmol).

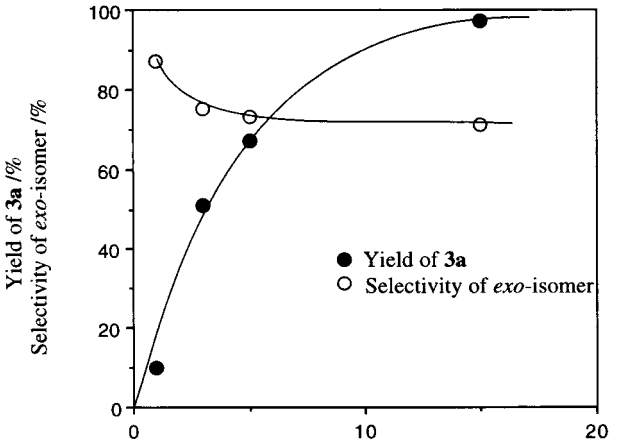


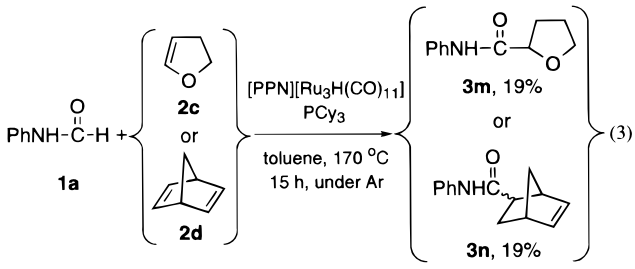
Figure 1. Time-dependence of $[PPN][Ru_3H(CO)_{11}]/PCy_3$-catalyzed hydroamidation of 2-norbornene **2a** with formanilide **1a**.

suggests that the [PPN] cation also influenced the catalytic activity (*vide infra*).

The time-dependence of the hydroamidation of 2-norbornene **2a** with formanilide **1a** is shown in Figure 1. In the early stage of the reaction, the *exo*-isomer of **3a** was predominantly formed. After 5 h, the *exo*- and *endo*-isomers of **3a** seem to reach a thermodynamic equilibrium, and the ratio was constant (*exo*/*endo* = *ca.* 70/30).

The results obtained for the hydroamidation of 2-norbornene **2a** and ethylene **2b** with several *N*-aryl- and *N*-alkyl-substituted formamides (**1a**−**f**) are summarized in Table 3. The substituents on the aromatic ring in **1b**−**d** did not affect the reaction. In all cases, the starting formamides were completely consumed to give the corresponding adducts (**3a**−**l**) in good to high yields. However, formamide (**1g**) *itself* gave an intractable mixture, due to the high reactivity of **1g**, which led to decomposition and/or oligomerization of **1g**. In addition, no reaction occurred with *N*,*N*-disubstituted formamide such as *N*-methylformanilide (**1h**). It appears that *N*,*N*-disubstitution on the formamides may increase the bulkiness of the carbamoyl group in the (hydrido)(carbamoyl)ruthenium intermediate (*vide infra*), which disfavors the process.

As for alkenes, 2,3-dihydrofuran (**2c**) and 2,5-norbornadiene (**2d**) also reacted with **1a** to give the corresponding adducts in 19% yield, respectively (eq 3).



However, no reaction occurred with less reactive alkenes, such as 1-hexene and cyclopentene.

Ruthenium-Catalyzed Hydroesterification of Alkenes with Alkyl Formates. The novel catalyst system, $[PPN][Ru_3H(CO)_{11}]/PCy_3$, can be applied to the direct hydroesterification of 2-norbornene **2a** and ethylene **2b** with alkyl formates (**4a**−**c**) under an argon atmosphere to give the corresponding adducts (**5a**−**e**) in moderate to high yields (Table 4). Unfortunately, the reaction with methyl formate did not give satisfactory results, since decarbonylation of methyl formate mainly proceeded even with the use of this new catalyst system.

Possible Mechanism. Considering the results described above, the most plausible mechanism is illustrated in Scheme 1. First, insertion of an alkene into a hydrido−ruthenium bond occurs to give an (alkyl)ruthenium intermediate. Subsequent oxidative addition of a formyl C−H bond in formamides or alkyl formates to this (alkyl)ruthenium intermediate, followed by reductive elimination between an alkyl and a carbamoyl or an alkoxycarbonyl group on the ruthenium, gives the corresponding hydroamidation and hydroesterification products with regeneration of an active (hydrido)ruthenium species. The use of an anionic ruthenium carbonyl cluster with a hydrido ligand, $[PPN][Ru_3H(CO)_{11}]$, would facilitate both the first insertion of an alkene and the second oxidative addition of a formyl C−H bond to ruthenium.[18] The [PPN] cation also affected the catalytic activity of $[Ru_3H(CO)_{11}]^-$ (*vide supra*), which suggests that the [PPN] cation is present very close to the ruthenium center, and may contribute to increase the catalytic activity. Coordination of PCy_3 to an active ruthenium center is also essential, and PCy_3 could occupy the coordination site for decarbonylation

(18) Enhancement of the rate of the decomposition of methyl formate by $[R_3POH][Ru_3H(CO)_{11}]$ has been reported previously. (a) Warren, B. K.; Dombek, B. D. *J. Catal.* **1983**, *79*, 334. (b) Jenner, G.; Nahmed, E. M.; Libs-Konrath, S. *J. Mol. Catal.* **1991**, *64*, 337.

Table 3. [PPN][$Ru_3H(CO)_{11}$]/PCy_3-Catalyzed Hydroamidation of Alkenes with Formamides[a]

Run	Formamide	Alkene	Product (%)[b]		*exo:endo*[c]
1	PhNH–C(=O)–H **1a**	**2a**	PhNHC(=O)– **3a**	97	71:29
2		**2b**	PhNH–C(=O)– **3b**	80	—
3	4-MePhNH–C(=O)–H **1b**	**2a**	4-MePhNHC(=O)– **3c**	(85)	78:22
4		**2b**	4-MePhNH–C(=O)– **3d**	(87)	—
5	4-MeOPhNH–C(=O)–H **1c**	**2a**	4-MeOPhNHC(=O)– **3e**	(87)	68:32
6		**2b**	4-MeOPhNH–C(=O)– **3f**	(81)	—
7	4-ClPhNH–C(=O)–H **1d**	**2a**	4-ClPhNHC(=O)– **3g**	(82)	72:28
8		**2b**	4-ClPhNH–C(=O)– **3h**	(72)	—
9	$PhCH_2NH$–C(=O)–H **1e**	**2a**	$PhCH_2NHC$(=O)– **3i**	(54)	85:15
10		**2b**	$PhCH_2NH$–C(=O)– **3j**	46	—
11	$n\text{-}C_3H_7NH$–C(=O)–H **1f**	**2a**	$n\text{-}C_3H_7NHC$(=O)– **3k**	50	87:13
12		**2b**	$n\text{-}C_3H_7NH$–C(=O)– **3l**	73	—

[a] Formamide (5.0 mmol), 2-norbornene (10 mmol) or ethylene (20 atm), [PPN][$Ru_3H(CO)_{11}$] (0.067 mmol), PCy_3 (0.20 mmol), toluene (3.0 mL) at 170 °C for 15 h under an argon atmosphere. [b] GLC yield (isolated yield). [c] Determined by GLC.

(and/or dehydrogenation) of formyl compounds (*vide supra*) as well as increase the electron density of ruthenium, which also results in an enhanced rate of oxidative addition.[19] In addition, the choice of alkene substrates in the present reaction is important, and the use of alkenes which have relatively high coordination ability should be required for coordination to a sterically hindered ruthenium center. This may be why only 2-norbornene **2a** and ethylene **2b** gave good results in the present reaction.

In conclusion, we have developed a novel ruthenium catalyst system, [PPN][$Ru_3H(CO)_{11}$]/PCy_3, for both the hydroamidation and hydroesterification of alkenes with formamides and alkyl formates. By this catalyst system, the direct addition of formyl compounds to alkenes under an argon atmosphere is attained, and *no carbon monoxide is required for these reactions*. The reactions developed here offer a simple and practical method for synthesizing carboxamides and esters without the use of carbon monoxide, and formyl compounds can be used as a carbonyl source.

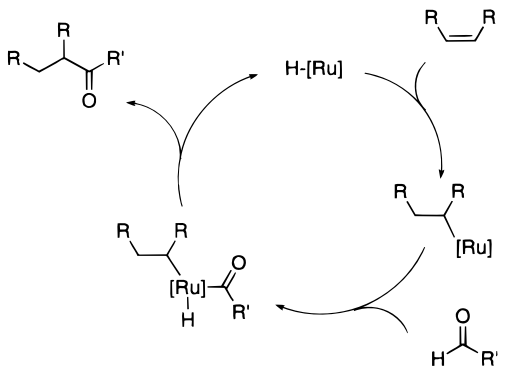
(19) (a) Kubota, M.; Curtis, C. J.; Chappell, T. G. *Inorg. Chim. Acta* **1978**, *27*, 261. (b) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 1802. (c) Jenner, G.; Nahmed, E. M.; Leismann, H. *J. Organomet. Chem.* **1990**, *387*, 315.

Table 4. [PPN][$Ru_3H(CO)_{11}$]/PCy_3-Catalyzed Hydroesterification of Alkenes with Alkyl Formates[a]

Run	Alkyl Formate	Alkene	Product (%)[b]		*exo:endo*[c]
1	$PhCH_2O$–C(=O)–H **4a**	**2a**	$PhCH_2OC$(=O)– **5a**	77	89:11
2		**2b**	$PhCH_2O$–C(=O)– **5b**	80	—
3	$n\text{-}C_3H_7O$–C(=O)–H **4b**	**2a**	$n\text{-}C_3H_7OC$(=O)– **5c**	68	85:15
4		**2b**	$n\text{-}C_3H_7O$–C(=O)– **5d**	37	—
5	CH_3O–C(=O)–H **4c**	**2a**	CH_3OC(=O)– **5e**	(22)	86:14

[a] Alkyl formate (5.0 mmol), 2-norbornene (10 mmol) or ethylene (20 atm), [PPN][$Ru_3H(CO)_{11}$] (0.067 mmol), PCy_3 (0.20 mmol), toluene (3.0 mL) at 170 °C for 15 h under an argon atmosphere. [b] GLC yield (isolated yield). [c] Determined by GLC.

Scheme 1



Experimental Section

General Procedures. GLC analyses were performed on a Shimadzu GC-14A gas chromatograph with a Shimadzu capillary column HiCap-CBP10-S25-050. Recycling preparative HPLC was performed on a LC-908 (Japan Analytical Industry Co. Ltd.) equipped with JAIGEL-1H and 2H columns (GPC) using $CHCl_3$ as an eluent. The ^1H (400 MHz) and ^{13}C NMR spectra (100 MHz) were obtained on a JEOL EX-400 spectrometer. Samples were analyzed in $CDCl_3$, and the

chemical shift values are expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a Nicolet Impact 410 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. The reagents used in this study were dried and purified before use by standard procedures. Formanilide **1a**, 2-norbornene **2a**, phosphines, and [PPN]Cl were obtained commercially and used without further purification. Carbon monoxide (>99.9%) and ethylene (extra-pure grade) were used without further purification. $Ru_3(CO)_{12}$, and $[Ru(CO)_3Cl_2]_2$ were obtained commercially and used without further purification. $[PPN][Ru_3H(CO)_{11}]$,[17] $[Et_4N][Ru_3H(CO)_{11}]$,[17] Ru(cod)(cot),[20] $RuCl_2(PPh_3)_3$,[21] $[Ru(CO)_2Cl_2]_n$,[22] $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$,[23] Cp*RuCl(cod),[24] and $[Cp^*Ru(CO)_2]_2$[25] were prepared as described in the literature. Formamides (**1b**−**f** and **1h**) were prepared as reported previously.[26] Characterization data of **3a** and **5a**, which are representative products, are given below. For other products, see the Supporting Information.

General Procedure for Ruthenium-Catalyzed Hydroamidation of Alkenes with Formamides. A mixture of formamides (5.0 mmol), alkene (10−15 mmol), ruthenium catalyst (0.20 mmol as Ru atom), phosphines (0.20−0.40 mmol as P atom), and toluene (3.0 mL) was placed in a 50 mL stainless steel autoclave equipped with a glass liner and a magnetic stirring bar under an argon atmosphere. When ethylene was used as an olefin, ethylene was pressurized to 20 atm at room temperature. The mixture was then magnetically stirred at 170−180 °C for 15 h. After cooling, the reaction mixture was analyzed by GLC, and the products were isolated by Kugelrohr distillation and/or recycling preparative HPLC.

***exo*-*N*-Phenylbicyclo[2.2.1]heptane-2-carboxamide (3a):** White solid; mp 123−127 °C; IR (KBr) $\nu_{C=O}$ 1657 cm^{-1}, ν_{N-H} 3309 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.13−1.20 (m, 3H, *exo*-H ($C_{5,6}$) and *bridge*-H (C_7)), 1.39 (dd, 1H, J = 11.23, 9.26 Hz, *exo*-H (C_3)), 1.48−1.51 (m, 2H, *endo*-H ($C_{5,6}$)), 1.64 (d, 1H, J = 9.28 Hz, *bridge*-H (C_7)), 1.93 (dd, 1H, J = 11.23, 5.37 Hz, *endo*-H (C_3)), 2.25 (s, 1H, *bridge*-H (C_4)), 2.28 (d, 1H, J = 5.37 Hz, *endo*-H (C_2)), 2.45 (s, 1H, *bridge*-H (C_1)), 7.01−7.54 (m, 5H, Ph), 7.98 (s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 28.5, 29.6, 34.1, 35.8, 36.3, 41.6, 48.6, 119.8, 123.7, 128.7, 138.3, 174.4; MS (EI) *m*/*z* 215 (M^+). Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.83; H, 7.98; N, 6.30.

***endo*-*N*-Phenylbicyclo[2.2.1]heptane-2-carboxamide (3a′):** $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 24.4, 29.1, 31.4, 37.1, 40.7, 41.2, 48.3, 119.6, 123.9, 128.9, 138.3, 172.4; MS (EI) *m*/*z* 215 (M^+).

General Procedure for Ruthenium-Catalyzed Hydroesterification of Alkenes with Alkyl Formates. A mixture of alkyl formates (5.0 mmol), alkene (10 mmol), $[PPN][Ru_3H(CO)_{11}]$ (0.077 g, 0.067 mmol), PCy_3 (0.056 g, 0.20 mmol), and toluene (3.0 mL) was placed in a 50 mL stainless steel autoclave equipped with a glass liner and a magnetic stirring bar under an argon atmosphere. When ethylene was used as an olefin, ethylene was pressurized to 20 atm at room temperature. The mixture was then magnetically stirred at 170 °C for 15 h. After cooling, the reaction mixture was analyzed by GLC, and the products were isolated by Kugelrohr distillation and/or a recycling preparative HPLC.

Benzyl *exo*-Bicyclo[2.2.1]heptane-2-carboxylate (5a): Colorless liquid; bp 135 °C (10 mmHg, Kugelrohr); IR (neat) $\nu_{C=O}$ 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.15 (d, 1H, J = 9.77 Hz, *bridge*-H (C_7)), 1.17−1.34 (m, 2H, *exo*-H ($C_{5,6}$)), 1.40−1.57 (m, 3H, *exo*-H (C_3) and *endo*-H ($C_{5,6}$)), 1.48 (d, 1H, J = 9.77 Hz, *bridge*-H (C_7)), 1.83−1.89 (m, 1H, *endo*-H (C_3)), 2.29 (s, 1H, *bridge*-H (C_4)), 2.37 (dd, 1H, J = 5.13, 8.79 Hz, *endo*-H (C_2)), 2.52 (s, 1H, *bridge*-H (C_1)), 5.09 (s, 2H, $-CH_2O-$), 7.25−7.40 (m, 5H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 28.7, 29.5, 34.2, 36.1, 36.6, 41.0, 46.6, 66.2, 128.1, 128.1, 128.6, 136.5, 175.9; MS (EI) *m*/*z* 230 (M^+). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.33; H, 8.16.

Benzyl *endo*-Bicyclo[2.2.1]heptane-2-carboxylate (5a′): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 24.9, 29.2, 32.0, 37.1, 40.3, 40.6, 46.1, 66.0, 128.10, 128.14, 128.6, 136.5, 174.9; MS (EI) *m*/*z* 230 (M^+).

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. T.O. appreciates Research Fellowships from the Japan Society for the Promotion of Science for Young Scientists.

Supporting Information Available: Complete compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990373C

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