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Chiral Ruthenium(II)–Bis(2-oxazolin-2-yl)pyridine Complexes. Asymmetric Catalytic Cyclopropanation of Olefins and Diazoacetates

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A chiral ruthenium(II)–bis(2-oxazolin-2-yl)pyridine catalyst prepared in situ from optically active bis(2-oxazolin-2-yl)pyridine (Pybox-*ip*) (**2**) and $[RuCl_2(p\text{-cymene})]_2$ (**1**) exhibited efficient activity for the asymmetric cyclopropanation (ACP) of styrene and several diazoacetates to give the corresponding *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates (**3** and **4**) in good yields (66—87%). A mixture of **1** and **2** in an atmosphere of ethylene produced the *trans*-$RuCl_2$(Pybox-*ip*)(ethylene) complex (**5**), which also proved to be a powerful catalyst for ACP. The stereoselectivity of the *trans*- and *cis*-cyclopropanes were from 90 : 10 up to 98 : 2, and their enantioselectivities reached 97%. A catalytic system with **5** could be used for several olefins and internal olefins. A concerted mechanism of ACP with the Ru–Pybox catalyst was postulated on the basis of the stereospecificity with deuterated styrene. Other substituents, such as ethyl, *s*-butyl, benzyl, and phenyl on the oxazoline rings of Pybox in place of the isopropyl group were also examined, and were found to exhibit a similar high *trans*-stereoselection and a high enantioselectivity of the cyclopropane products; ex. with Ru–Pybox-*ethyl* 91 : 9 of **3** : **4** and 82% ee for **3**. The non-chiral Ru–Pybox-*dihydro* catalyst exhibited asymmetric induction with 39% ees of **3** with *d*- and *l*-menthyl diazoacetates, and kept a high *trans*- and *cis*-stereoselection of 97 : 3.

The asymmetric catalytic cyclopropanation of olefins with diazoacetates has been intensively studied for three decades, since Nozaki and his co-workers initiated it in 1966.[1)] Noteworthy achievements include the chiral camphorquinone-dioxime cobalt catalysts by Nakamura[2)] and chiral shiff-base copper catalysts by Aratani[3)] used for the industrial synthesis of pyrethroides. Very recently, a further refinement of its enantioselectivity has been attained by the development of chiral nitrogen-base ligands in combination with copper and rhodium complexes.[4—7)] For example, *semicorrin* **A**,[4)] *bis*(*oxazoline*) **B**[5a)] and **C**[5b)], and other nitrogen ligands such as **D**[6a)], **E**[6c)], and **F**[7b,7e)] were highlighted to provide an extremely high level of enantioselectivity (>90% ee) (Chart 1).[8)]

We have developed a C_2-symmetric 2,6-bis(2-oxazolin-2-yl)pyridine (Pybox) as a chiral ligand for the enantioselective hydrosilylation of ketones with its rhodium complex.[9)] We have been strongly intrigued by the application of the Pybox ligand to the asymmetric cyclopropanation of olefins and diazoacetates. However, we could not find any expected results for the stereoselection and enantioselection with catalysts of CuOTf–Pybox and $Rh_2(OAc)_4$–Pybox.[10)] After screening candidate metal complexes, we discovered a combination of ruthenium(II) chloride and Pybox that exhibited a powerful catalytic activity.[11)] It has been reported that some ruthenium complexes show catalytic activity for cyclopropanation comparable to, or less than, those of copper and rhodium catalysts.[12)] However, ruthenium metal has not yet been used for asymmetric cyclopropanation. We report here on a new asymmetric cyclopropanation of olefins and diazoacetates by using ruthenium(II)–Pybox catalysts that possess a high stereoselectivity and enantioselectivity, together with the intramolecular cyclopropanation and substituent effect of Pybox derivatives.

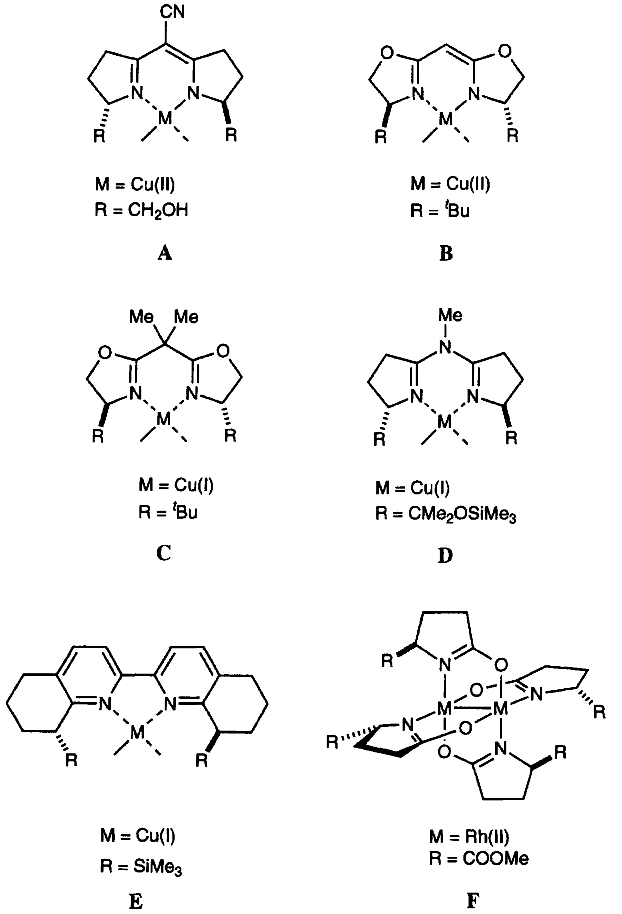
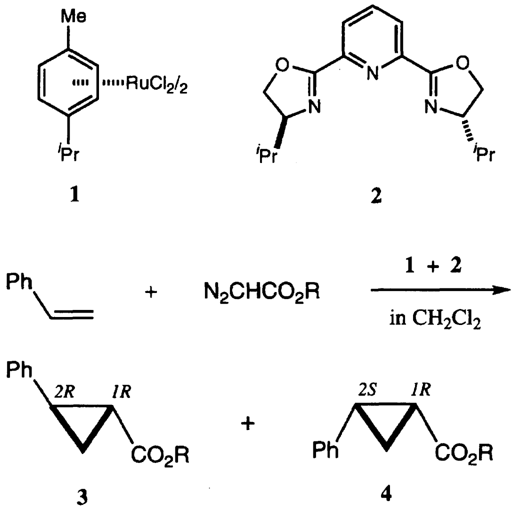


Chart 1.

Results and Discussion

Ru–Pybox-*ip* Catalyst. The addition of $[RuCl_2(p\text{-cymene})]_2$ (**1**)[13] to a solution of Pybox-*ip*-(*S*,*S*) (**2**) in dichloromethane gave a dark-red solution which exhibited catalytic activity for the asymmetric cyclopropanation of styrene and diazoacetates (Scheme 1). For example, ethyl diazoacetate (3.0 mmol, ca. 1 M CH_2Cl_2, 1 M=1 mol dm^{-3}) was slowly added to a dichloromethane solution of the ruthenium complex **1** (1 mol%) and Pybox-*ip* **2** (2 molar amounts to Ru) in the presence of styrene (5 molar amounts to the diazoacetate) at 20—25 °C. A mixture of the corresponding *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates **3** and **4** was isolated in 66% yield (ratio of **3** and **4**=92:8) by column chromatography (Table 1). The cyclopropanes were converted to the corresponding methyl esters for a chiral GLPC analysis to show high enantioselectivities of 88% ee for the (1*R*,2*R*)-*trans*-isomer **3** and 78% ee for the (1*R*,2*S*)-*cis*-isomer **4**. The increase in bulkiness of the ester moiety from ethyl to *t*-butyl and menthyl groups lead us to attain a high *trans*: *cis* selectivity of up to 97:3 and enantioselectivity of up to 95% ee (Runs 3—5).

By a treatment of the solution of the ruthenium complex **1** and Pybox-*ip* **2** in an ethylene atmosphere (1 atm), we could successfully isolate an ethylene-complex, *trans*-$RuCl_2$(Pybox-*ip*)(ethylene) **5**, in 93% yield as the sole product (Scheme 2). The C_2-symmetric structure of **5** was confirmed on the basis of an NMR study. The ethylene-complex **5** can be purified by silica-gel column chromatography and is stable in solution. Complex **5** also exhibited the same catalytic activity of the asymmetric cyclopropanation (Table 1, Runs 6—12). It is quite noteworthy that complex **5** gave high selectivities by itself with no complement addition of Pybox-*ip* **2**, compared to the in-situ system employed with an excess of **2**. The high enantioselectivity of 96% ee for the *trans*-product **3** was attained by *l*-menthyl diazoacetate (Run 10). In contrast, the highest %ee for the *cis*-cyclopropane **4** (97% ee) was observed due to a better stereochemical matching with the *d*-menthyl group (Run 9). Furthermore, the *trans*: *cis* ratio increased to 98:2 (Run 11). The extra addition of Pybox-*ip* **2** to **5** caused no significant improvement (Run 11). The catalytic efficiency of **5** did not decrease, even when 1 mol% of **5** (*ton*=100) was used (Run 12). Other halogen derivatives, such as the bromo-complex **6** and the iodo-complex **7**, were examined, but gave almost parallel or somewhat lower yields and selectivities (Runs 13—15).



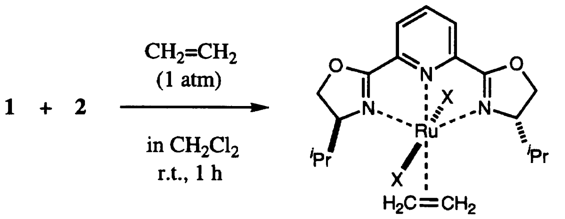
Scheme 1.

We have thus obtained the high stereoselective and enantioselective cyclopropanation of styrene. It has been investigated and shown in detail that not only the *trans*: *cis* selectivity, but also the enantioselectivity, strongly depend on the bulkiness and the shapes of the ester moiety of the diazoacetates.[1b,1e,14] In general, an increase in the bulkiness of the ester groups can improve both selectivities. However, we can insist in our case that the octahedral circumstance around the active metal-site of $RuCl_2$–Pybox, rather than the bulkiness of the ester groups, is strongly related to such high *trans*: *cis* selectivity as the main factor. We describe it again in a later section based on *trans*-selectivity with

Table 1. Asymmetric Cyclopropanation of Styrene and Diazoacetates with Ru(Pybox-*ip*) Catalysts[a)]

Run	Catalyst	N_2CHCO_2R R=	Product: **3** (*trans*) and **4** (*cis*)			
			Yield	Ratio	% ee (abs config)	
			%	**3**:**4**	**3**	**4**
1	**1**+**2**[b)]	Et	69	92:8	89 (1*R*,2*R*)	78 (1*R*,2*S*)
2	**1**+**2**[c)]	Et	66	92:8	89 (1*R*,2*R*)	75 (1*R*,2*S*)
3	**1**+**2**[c)]	*t*-Bu	81	97:3	94 (1*R*,2*R*)	85 (1*R*,2*S*)
4	**1**+**2**[c)]	*d*-Ment	85	95:5	86 (1*R*,2*R*)	95 (1*R*,2*S*)
5	**1**+**2**[c)]	*l*-Ment	87	95:5	95 (1*R*,2*R*)	76 (1*R*,2*S*)
6	**5**	Me	74	90:10	88 (1*R*,2*R*)	70 (1*R*,2*S*)
7	**5**	Et	73	91:9	89 (1*R*,2*R*)	79 (1*R*,2*S*)
8	**5**	*t*-Bu	65	97:3	94 (1*R*,2*R*)	87 (1*R*,2*S*)
9	**5**	*d*-Ment	82	97:3	87 (1*R*,2*R*)	97 (1*R*,2*S*)
10	**5**	*l*-Ment	83	97:3	96 (1*R*,2*R*)	80 (1*R*,2*S*)
11	**5**+**2**[d)]	*l*-Ment	84	98:2	96 (1*R*,2*R*)	84 (1*R*,2*S*)
12	**5**[e)]	*l*-Ment	82	97:3	96 (1*R*,2*R*)	80 (1*R*,2*S*)
13	**6**	Me	47	88:12	88 (1*R*,2*R*)	79 (1*R*,2*S*)
14	**6**[f)]	*l*-Ment	83	95:5	95 (1*R*,2*R*)	79 (1*R*,2*S*)
15	**7**[f)]	*l*-Ment	69	94:6	90 (1*R*,2*R*)	56 (1*R*,2*S*)

a) Styrene (15 mmol), diazoacetate (3.0 mmol), cat. **1**+**2**: $[RuCl_2(p\text{-cymene})]_2$ (**1**) (0.03 mmol) and Pybox-*ip* (**2**) (2 or 4 molar amounts to Ru), cat. **5**—**7** (0.06 mmol), solvent: CH_2Cl_2 (2 mL), 20—25 °C, ca. 8 h for addition of diazoacetate then stirring for 4—12 h. Isolated yields. The ratios by ^1H NMR. The % ee's by chiral capillary GLPC (column: Astec B-DA, 30 m) with the corresponding methyl ester. b) **2** (2 molar amounts to Ru). c) **2** (4 molar amounts to Ru). d) **2** (3 molar amounts to **5**). e) **5** (0.03 mmol, *ton*=100). f) 30 °C.



5 X = Cl 93 %
(**6** X = Br, **7** X = I)

Scheme 2.

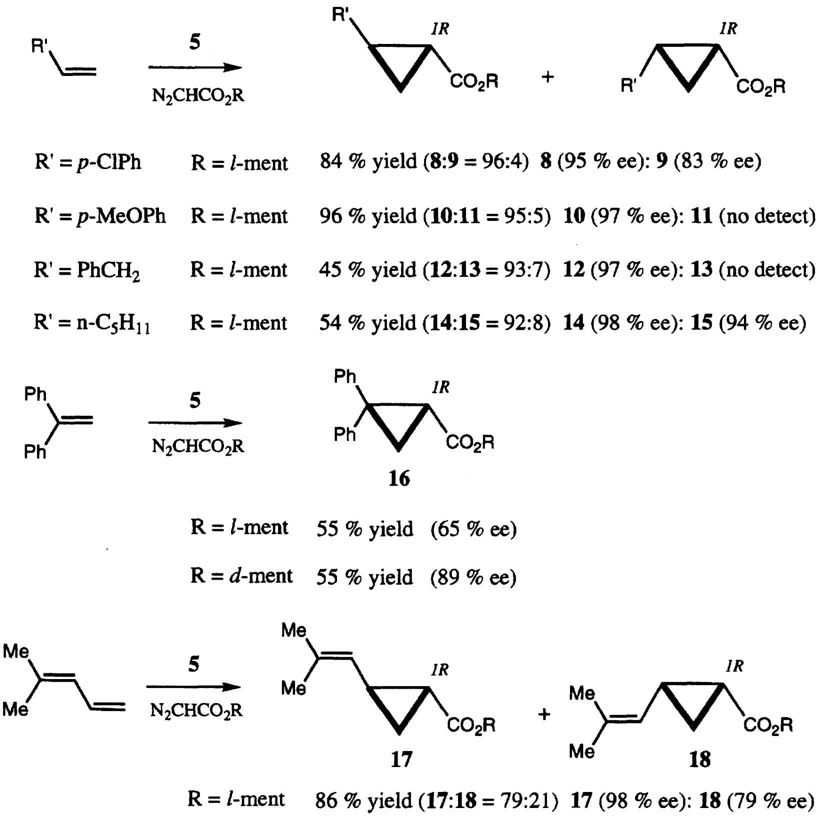
other substituted Pybox ligands. It was pointed out by Doyle that the octahedral geometry of the intermediate metal-carbene species can place their ligands in closest proximity to the carbene substituents.[1d)]

We also applied the 2,6-di-*t*-butyl-4-methylphenyl group (BHT) as a bulky ester, which exhibited the high *trans*-stereoselectivity reported by Doyle[14)] and Evans.[5b)] However, we could observe no reaction of BHT-diazoacetate and styrene with $RuCl_2$–Pybox catalysts below 60 °C.

The predominant formation of the *trans*-cyclopropane left us with one question: The isomerization by rotation of the olefin moiety during the carbene transfer may occur after the *cis*-approach of an olefin. However, we could determine no loss in the stereochemistry of the product cyclopropanes, **3** and **4**, with PhCH=CHD and methyl diazoacetate. This phenomenon can be explained by the fact that the carbene transfer from the Ru–Pybox moiety proceeds in a concerted manner. In this respect, a concerted mechanism was reported by Kodadek for the rhodium–porphyrin catalyzed cyclopropanation.[15)] However, Nakamura reported that isomerization occurred during the carbene-transfer via cobaltacyclobutane formation.[2)] Brookhart has also observed the same isomerization during the reaction of $Cp(CO)2FeCHPh^+$ and *cis*-styrene-d_1 that explains the bond rotation of the olefin moiety after attachment to the metal-carbene center.[16,1c)]

We have applied asymmetric cyclopropanation with the Ru–Pybox-*ip* complex **5** to other olefins, such as *p*-chlorostyrene, *p*-methoxystyrene, 3-phenyl-1-propene, 1-heptene, 1,1-diphenylethylene, and 4-methyl-1,3-pentadiene, for cyclopropanation with *l*-and *d*-menthyl diazoacetates under the same reaction conditions as those already described (Scheme 3). We obtained the corresponding cyclopropanes **8–18** in high %ees up to 98%. The highest % ee of 98% was observed for the *trans*-isomers **14** and **17**. *d*-Menthyl diazoacetate gave a higher % ee for 1,1-diphenylethylene rather than *l*-menthyl diazoacetate, due to stereochemical matching similar to the high % ees for the *cis*-product **4** from styrene and *d*-menthyl ester in Runs 4 and 9 in Table 1. Under the same reaction conditions, *β*-methylstyrene, 2,5-dimethyl-2,4-hexadiene, cyclopentene, and indene could not be cyclopropanated.

The applicability of the asymmetric catalytic cyclopropanation to intramolecular reactions is an attractive



R' = *p*-ClPh R = *l*-ment 84 % yield (**8**:**9** = 96:4) **8** (95 % ee): **9** (83 % ee)

R' = *p*-MeOPh R = *l*-ment 96 % yield (**10**:**11** = 95:5) **10** (97 % ee): **11** (no detect)

R' = $PhCH_2$ R = *l*-ment 45 % yield (**12**:**13** = 93:7) **12** (97 % ee): **13** (no detect)

R' = n-C_5H_{11} R = *l*-ment 54 % yield (**14**:**15** = 92:8) **14** (98 % ee): **15** (94 % ee)

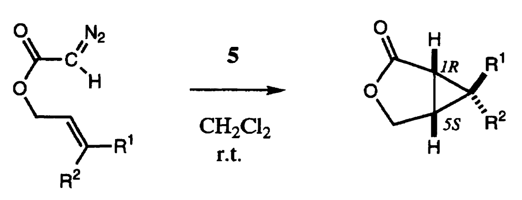
R = *l*-ment 55 % yield (65 % ee)

R = *d*-ment 55 % yield (89 % ee)

R = *l*-ment 86 % yield (**17**:**18** = 79:21) **17** (98 % ee): **18** (79 % ee)

Scheme 3.

subject for synthetic chemistry.[7c,17,18] We therefore examined the intramolecular cyclization of the allyl diazoacetates **19**, **20**, and **21** with the complex catalyst **5** (5 mol%). In spite of no reaction during intermolecular cyclopropanation with 1,2-disubstituted and trisubstituted olefins, as already described, the allyl diazoacetates **19**—**21** were easily cyclopropanated at room temperature to give the corresponding 3-oxabicylco-[3.1.0]hexan-2-one derivatives, **22**, **23**, and **24**, in high yields of 93% (86 % ee) for **22**, 79% (24% ee) for **23**, and 91% (76% ee) for **24**, respectively, with a (1*R*)-configuration for the all products (Scheme 4). The *cis*-cinnamyl diazoacetate **20** was cyclized, but at a low enantioselectivity (24%), compared to 86% ee of the *trans*-isomer **19**. The stereospecificity producing only from **19** to **22** and from **20** to **23** with no isomerization of the olefin moiety during the reaction also supports the concerted reaction mechanism of the hypothetical carbene transfer.



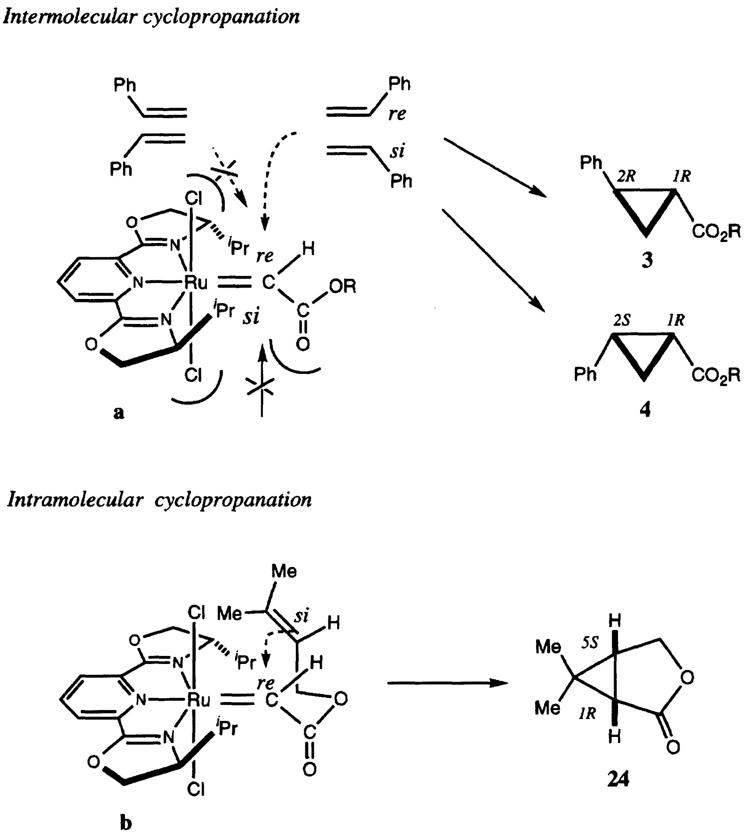
Substrate	R^1	R^2	Product	Yield (% ee)
19	Ph	H	**22**	93% (86)
20	H	Ph	**23**	79% (24)
21	Me	Me	**24**	91% (76)

Scheme 4.

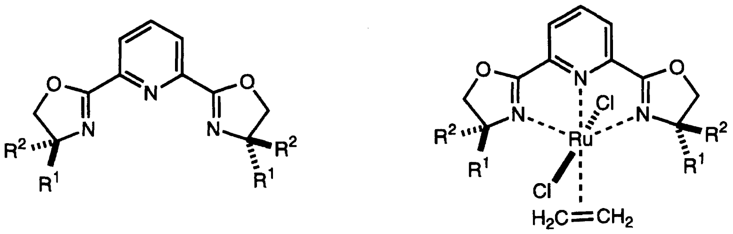
The critical steps of the carbene transfer for both intermolecular and intramolecular cyclopropanation are illustrated in Scheme 5. The (*S*,*S*)-absolute configuration of Pybox-*ip* produced the (1*R*)-absolute configuration on the cyclopropanes and the bicyclo-compounds, as already described, so that the *re*-faces of the metal-carbene centers in **a** and **b** were attacked by styrene to give the (2*R*)-isomer, i.e., the *trans*-isomer **3** by the attack of the *re*-face of styrene and the (2*S*)-isomer, i.e., the *cis*-isomer **4** by the attack of the *si*-face of styrene.

As active intermediates for metal-catalyzed cyclopropanations, several metal-carbene species have been reported in the chemistry of metal-porphyrins.[19] In this respect, we recently reported the isolation of a stable trimethylsilylcarbene complex of ruthenium–Pybox, $RuCl_2$(Pybox-*ip*) [=CH($SiMe_3$)], which has the ability of silylcarbene transfer to styrene, and also catalyzes the asymmetric cyclopropanation of styrene and diazoacetate.[20]

Ru–Pybox-X Catalysts. The isopropyl group on the oxazoline ring of Pybox-*ip*-(*S*,*S*) **2** can produce a good steric and chiral environment around the reaction site, as already described. Our further interest was focussed on several ligands **25**—**31**[8b,21] having a variety of groups on the oxazoline rings in place of the isopropyl group (Scheme 6). The preparation of the correspond-



Scheme 5.



Pybox-X X=	R^1	R^2
25, *ethyl-(R,R)*	H	Et
26, *s-butyl-(S,S)*	*s*-Bu	H
27, *t-butyl-(S,S)*	*t*-Bu	H
28, *benzyl-(S,S)*	Bz	H
29, *phenyl-(R,R)*	H	Ph
30, *dihydro*	H	H
31, *dimethyl*	Me	Me

	R^1	R^2
32	H	Et
33	*s*-Bu	H
34	Bz	H
35	H	Ph
36	H	H

Scheme 6.

ing ethylene-complexes **32**—**36** was successful with each Pybox-X, X =*ethyl-(R,R)* (**25**), *s-butyl-(S,S)* (**26**), *benzyl-(S,S)* (**28**), *phenyl-(R,R)* (**29**), *dihydro* (**30**). However, the corresponding ethylene-complexes of *t-butyl-(S,S)* (**27**) and *dimethyl* (**31**) could not be obtained using the same procedure, presumably due to the small mono-vacant site of the $RuCl_2$(Pybox-X)moiety, which does not have sufficient space to capture one ethylene molecule on the ruthenium center.

Cyclopropanation of styrene and diazoacetates with the Ru(Pybox-X)(ethylene) complexes **32**—**36** was carried out as previously described. The results are summarized in Table 2. Unexpectedly, the *ethyl-(R,R)*-complex **32** exhibited strong activity at 25 °C to give a 91 : 9 ratio of *trans*- and *cis*-cyclopropanes **3** and **4**; 82% ee for the (1*S*,2*S*)-*trans*-cyclopropane **3** with ethyl diazoacetate was obtained (Run 1). Moreover, a 95% ee of **3** was obtained using *d*-menthyl diazoacetate (Run 2). Thus, the ethyl group on Pybox proved to be sufficiently effective for enantioselection. The *s-butyl-(S,S)*-complex **33** gave almost the same results as those with **5** (Runs 4—6).

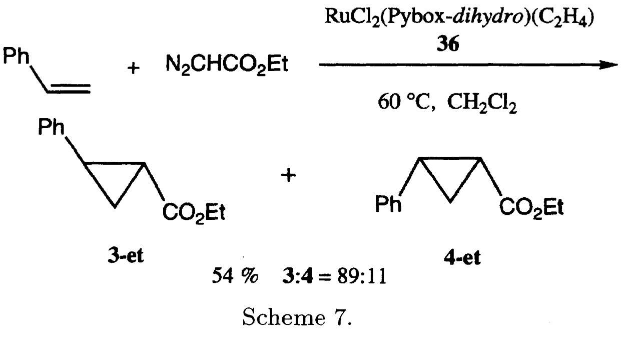
Table 2. Asymmetric Cyclopropanation of Styrene and Diazoacetates with Ru(Pybox-X) Catalysts[a)]

Run	Catalyst	N_2CHCO_2R R=	React. temp	Product: **3** (*trans*) and **4** (*cis*)			
			°C	Yield	Ratio	% ee (abs config)	
				%	**3**:**4**	**3**	**4**
1	**32**	Et	25	50	91:9	82 (1*S*,2*S*)	54 (1*S*,2*R*)
2	**32**	*d*-Ment	25	77	98:2	95 (1*S*,2*S*)	74 (1*S*,2*R*)
3	**32**	*l*-Ment	25	77	96:4	72 (1*S*,2*S*)	86 (1*S*,2*R*)
4	**33**	Et	25	82	94:6	91 (1*R*,2*R*)	79 (1*R*,2*S*)
5	**33**	*d*-Ment	25	86	97:3	80 (1*R*,2*R*)	93 (1*R*,2*S*)
6	**33**	*l*-Ment	25	89	99:1	96 (1*R*,2*R*)	66 (1*R*,2*S*)
7	**34**	Et	30	66	90:10	68 (1*R*,2*R*)	24 (1*R*,2*S*)
8	**34**	*d*-Ment	30	78	93:7	71 (1*R*,2*R*)	86 (1*R*,2*S*)
9	**34**	*l*-Ment	30	82	98:2	93 (1*R*,2*R*)	64 (1*R*,2*S*)
10	**35**	Et	35	38	89:11	69 (1*S*,2*S*)	41 (1*S*,2*R*)
11	**35**	*d*-Ment	35	51	95:5	84 (1*S*,2*S*)	14 (1*S*,2*R*)
12	**35**	*l*-Ment	35	56	97:3	14 (1*S*,2*S*)	66 (1*S*,2*R*)
13	**36**	Et	60	54	89:11	—	—
14	**36**	*d*-Ment	60	72	94:6	39 (1*S*,2*S*)	5 (1*R*,2*S*)
15	**36**	*l*-Ment	60	83	97:3	39 (1*R*,2*R*)	17 (1*S*,2*R*)

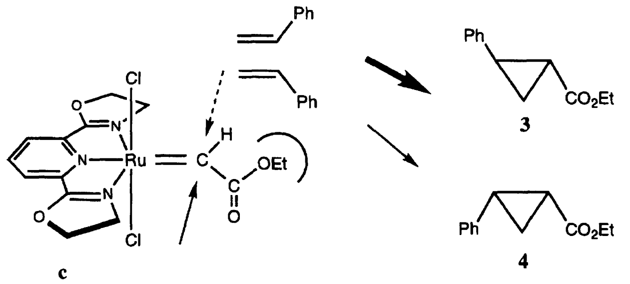
a) Styrene (15 mmol), diazoacetate (3.0 mmol), $RuCl_2$(Pybox-X)(C_2H_4) (**32**—**36**) (0.06 mmol), CH_2Cl_2 (1 mL) for Runs 1—13, $ClCH_2CH_2Cl$ (1 mL) for Runs 13—15, ca. 8 h for addition of diazoacetate then stirring for 4—12 h. Isolated yields. The ratios by ^1H NMR. The % ee's by chiral capillary GLPC (column: Astec B-DA, 30 m) with the corresponding methyl ester.

The *benzyl-*(*S*,*S*)-complex **34** and the *phenyl-*(*R*,*R*)-complex **35** required a slightly higher reaction temperature at 30—35 °C for a smooth reaction to give parallel, or slightly lower, stereo- and enantio-selectivities (Runs 7—12). Especially the *phenyl*-complex **35** showed a drastic stereochemical mismatching with the menthyl esters for the enantioselectivities, decreasing to 14% ees for **3** and **4** (Runs 11 and 12).

Most surprisingly, we have found that the non-chiral Pybox-*dihydro* complex **36** afforded a high *trans*–*cis* selectivity of 89:11 with ethyl diazoacetate (Run 13) (Scheme 7). Therefore, we can conclude that *the octahedral structure of the $RuCl_2$–Pybox system has an inherent potentiality for the trans-stereoselection* (Scheme 8). Moreover, the use of the menthyl diazoacetates increased the *trans*:*cis* selectivity up to 94:6 and 97:3 (Runs 14 and 15). Asymmetric induction, i.e., *diastereoselection*, was also observed in the *trans*-cyclopropane **3** in 39% ees; (1*S*,2*S*)-**3** from the *d*-menthyl ester and (1*R*,2*R*)-**3** from the *l*-menthyl ester (Runs 14 and 15).



Scheme 7.



Scheme 8.

This phenomenon can explain why the *l*-menthyl ester can increase the % ees of (1*R*,2*R*)-*trans*-cyclopropane **3** with Pybox-(*S*,*S*) ligands, while the *d*-menthyl diazoacetate decreased them. A similar diastereoselective cyclopropanation was reported using *d*- and *l*-menthyl diazoacetates and non-chiral rhodium acetates.[7d)]

Noteworthy is that cyclopropanation with **36** managed to proceed when the temperature was raised up to 60°C. We think that this may be attributed to the stability of **36**, which needs a higher temperature to dissociate ethylene to form an active species.

An X-ray analysis of **36** was successfully carried out to show that the ethylene moiety on **36** is coordinated perpendicular to the Cl–Ru–Cl plane (Fig. 1) (Table 3). We assume that the ethylene molecule on the chiral substituted-Pybox complexes **5**, **32**—**35** may also be placed perpendicular to the Cl–Ru–Cl plane. However, their sterically congested circumstances around the ruthenium atom for the chiral complexes might make the ethylene molecule readily dissociate to exibit the catalytic activity at around ambient temperature.

$RuCl_2$(Pybox-*ip*) Carbonyl Complexes. A solution of $[RuCl_2(p\text{-cymene})]_2$ (**1**) and Pybox-*ip* **2** in acetone at ambient temperature was exposed to carbon monoxide (1 atm) for 2 h, and gave air-stable black solids of *trans*-$RuCl_2$(Pybox-*ip*)(CO) (**37**) in 93% isolated yield as the sole product (Scheme 9). No further addition of CO was observed, even upon heating a solution of **37** in refluxing ethanol under a carbon monoxide atmosphere. No *cis*-isomer was produced. The carbonyl-complex **37** was also obtained from the ethylene-complex **5** at 50 °C in acetone under CO (1 atm). An X-ray analysis could be carried out with the corresponding diacetate complex **38**, showing its distorted octahedral structure with C_2-symmetry; N(1)–Ru–N(3) =153.7° (Fig. 2) (Table 4).

The carbonyl-complex was also employed for an asymmetric cyclopropanation of styrene with ethyl diazoacetate. Although a reaction with **37** below 40 °C did not take place, but a reaction with **37** proceeded at 75 °C in 1,2-dichloroethane giving the cyclopropane products **3** and **4** in 60% yield (ratio =69 : 31), but with a low asymmetric induction (Table 5). While the carbonyl complex **37** by a treatment with AgOTf (1.1 molar amounts) exhibited catalytic activity at 40 °C, the reaction resulted in low yields (25—38%)(Runs 2—4). Interestingly, methyl diazoacetate gave a slightly higher %ee for **3** (Run 2), rather than *t*-butyl diazoacetate (Run 4). The hypothetical carbonyl complex generated from **37** with Ag cation can easily provide one vacant site at one axial position, as illustrated for **d** in Scheme 10, where the carbene moiety opens its *si*-face for styrene giving mainly the (1*S*,2*S*)-configuration

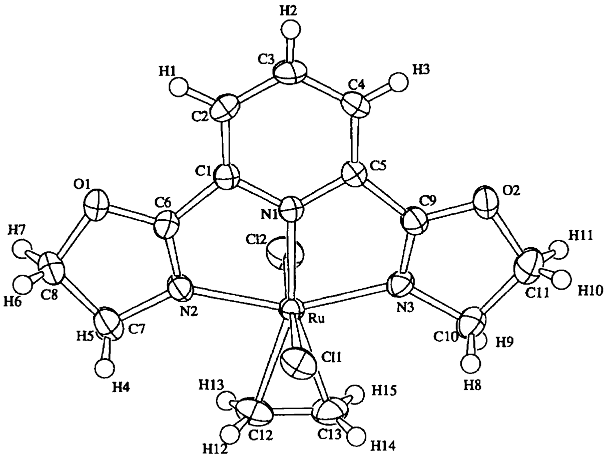
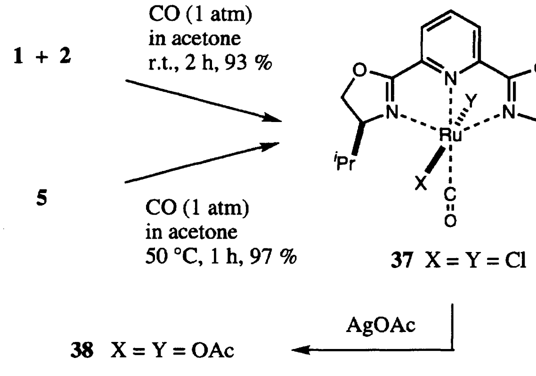


Fig. 1. Molecular structure of *trans*-$RuCl_2$(Pybox-*dihydro*)(C_2H_4) (**36**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for *trans*-$RuCl_2$(Pybox-*dihydro*)(C_2H_4) **36**

Distances (Å)			
Ru–C(1)	2.3908(9)	Ru–Cl(2)	2.3897(9)
Ru–N(1)	2.004(3)	Ru–N(2)	2.077(3)
Ru–N(3)	2.060(3)	Ru–C(12)	2.199(4)
Ru–C(13)	2.201(4)	C(12)–C(13)	1.377(5)
Angles (deg)			
Cl(1)–Ru–Cl(2)	179.65(3)	N(1)–Ru–N(2)	76.9(1)
N(1)–Ru–N(3)	76.7(1)	N(1)–Ru–Cl(1)	91.23(7)
N(1)–Ru–Cl(2)	88.58(7)	N(2)–Ru–N(3)	153.5(1)
N(2)–Ru–Cl(12)	85.1(1)	N(3)–Ru–C(13)	84.9(1)
C(12)–Ru–C(13)	36.5(1)	Ru–C(12)–C(13)	71.9(2)
Ru–C(13)–C(12)	71.7(2)		



Scheme 9.

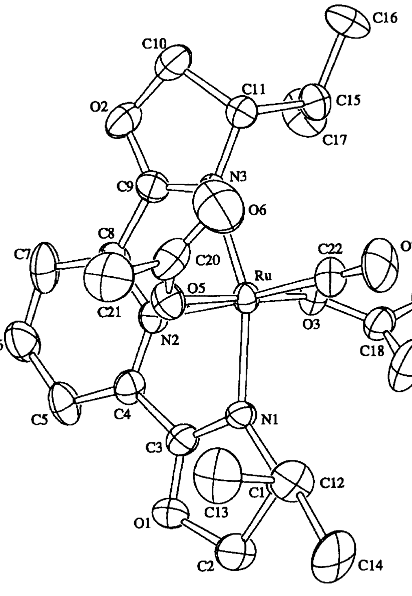


Fig. 2. Molecular structure of *trans*-$Ru(OAc)_2$(Pybox-*ip*)(CO) (**38**).

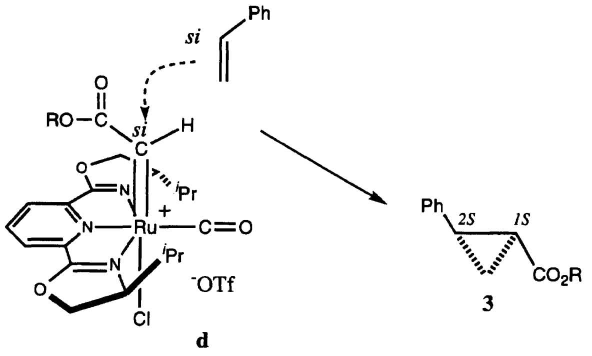
Table 4. Selected Bond Distances (Å) and Angles (deg) for *trans*-$Ru(OAc)_2$(Pybox-*ip*)(CO) **38**

Distances (Å)			
Ru–O(3)	2.071(4)	Ru–O(5)	2.069(5)
Ru–N(1)	2.097(6)	Ru–N(2)	2.073(5)
Ru–N(3)	2.083(5)	Ru–C(22)	1.877(7)
O(7)–C(22)	1.140(8)		
Angles (deg)			
O(3)–Ru–O(5)	172.5(2)	O(3)–Ru–N(2)	89.3(2)
O(5)–Ru–N(2)	83.3(2)	N(1)–Ru–N(2)	76.9(2)
N(1)–Ru–N(3)	153.7(2)	N(1)–Ru–C(22)	104.5(3)
N(2)–Ru–N(3)	76.8(2)	N(3)–Ru–C(22)	101.8(3)

Table 5. Asymmetric Cyclopropanation of Styrene and Diazoacetates with Ru(Pybox-*ip*)(co) Catalysts[a)]

Run	Catalyst	N_2CHCO_2R R=	React. temp	Product: **3** (*trans*) and **4** (*cis*)			
			°C	Yield (%)	Ratio **3**:**4**	% ee (abs config) **3**	**4**
1	**37**	Et	75	60	69:31	14 (1*R*,2*R*)	4 (1*R*,2*S*)
2	**37**/AgOTf[b)]	Me	40	34	52:48	44 (1*S*,2*S*)	3 (1*R*,2*S*)
3	**37**/AgOTf[b)]	Et	40	38	55:45	33 (1*S*,2*S*)	9 (1*R*,2*S*)
4	**37**/AgOTf[b)]	*t*-Bu	40	33	77:23	5 (1*S*,2*S*)	20 (1*R*,2*S*)

a) Styrene (15 mmol), diazoacetate (3.0 mmol), $RuCl_2$(Pybox-*ip*)(CO) (**37**) (0.06 mmol), $ClCH_2CH_2Cl$ (2 mL), ca. 8 h for addition of diazoacetate then stirring for 4—12 h. Isolated yields. The ratios by ^{1}H NMR. The % ee's by chiral capillary GLPC (column: Astec B-DA, 30 m) with the corresponding methyl ester. b) AgOTf (0.07 mmol).



Scheme 10.

for the *trans*-cyclopropane.

Conclusions. We have found that the in-situ catalyst and the ethylene-complex of $RuCl_2$(Pybox-*ip*) produce an extremely high level of *trans*:*cis* selectivity with high enantioselectivity for the asymmetric cyclopropanation of olefins and diazoacetates. The mode of cyclopropanation with the $RuCl_2$(Pybox) system could be explained as a concerted carbene-transfer. We have clarified that the inherent high *trans*-selectivity is attributable to the octahedral structure of the $RuCl_2$(Pybox) system.

Experimental

General Methods. All reactions were carried out under N_2. Dichloromethane was distilled under nitrogen from diphosphorus pentoxide. ^{1}H and ^{13}C NMR spectra were recorded at 270 and 67.8 MHz, respectively, on a JEOL JNM-GX 270 spectrometer using tetramethylsilane as the internal reference in $CDCl_3$. Infrared spectra were recorded on a JASCO A-3 spectrometer. Microanalyses were performed with a Yanagimoto MT-3 CHN corder. Column chromatography was performed with silica-gel (Merck, Art 7734). Analytical TLC was performed on Merck (Art 5715) precoated silica gel plates (0.25 mm). The optical purity was determined using a Shimadzu Capillary Gas Chromatograph 14A with a chiral capillary column (Astec Chiraldex B-DA and B-PH, 30 m). The optical rotation was measured on a JASCO DIP-140 polarimeter. Pybox ligands, 2,6-bis[X-2-oxazolin-2-yl]pyridine, were prepared by our method.[8b,21)] All alkyl diazoacetates were prepared by a method described in the literature by Pfaltz.[3b)] Allyl diazoacetates **19**—**21** were prepared with *trans*-cinnamyl alcohol, *cis*-cinnamyl alcohol, and 3-methyl-2-butenol by Blankley's method;[22)] after purified by silica-gel column chromatography, yield: 70% for **19**, 53% for **20**, 57% for **21**. ^{1}H NMR (270 MHz): **19**, δ=4.79 (broad s, 1H, C*H*N_2), 4.82 (d, J=6.3 Hz, 2H), 6.30 (dt, J=6.3, 15.6 Hz, 1H), 6.65 (d, J=15.6 Hz, 1H), 7.24—7.45 (m, 5 H); **20**, δ=4.78 (broad s, 1 H, C*H*N_2), 4.94 (d, J=6.4 Hz, 2 H), 5.82 (dt, J=11.7, 6.4 Hz, 1 H), 6.68 (d, J=11.7 Hz, 1H), 7.20—7.40 (m, 5 H); **21**, δ=1.72 (s, 3 H), 1.76 (s, 3 H), 4.66 (d, J=7.4 Hz, 2 H), 4.74 (s, 1 H), 5.35 (t, J=7.4 Hz, 1H).

***trans*-$RuCl_2$(Pybox-*ip*)(C_2H_4) (5).** A solution of Pybox-*ip* (301 mg, 1.0 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (306 mg, 0.50 mmol)[13)] in dichloromethane (10 mL) was stirred at room temperature under ethylene atmosphere for 1 h. After the solvent was removed under reduced pressure, the residue was purified by silica-gel column chromatography (SiO_2, ca. 20 g) with dichloromethane and methanol (100:1). The purple-band forerun was collected and concentrated to give **3** as dark-red solids in 93% yield (467 mg, 0.93 mmol); decomp 102—105 °C; IR (KBr disk) 2960, 1590, 1490, 1395, 1385 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.78 (d, J=6.8 Hz, 6H), 1.01 (d, J=7.3 Hz, 6 H), 2.47 (m, 2 H), 4.43 (m, 2 H, NC*H*), 4.82 (m, 2 H, *H* of OC*H*), 4.89 (m, 2 H, *H* of OC*H*), 4.94 (m, 2 H, ethylene), 5.26 (m, 2 H, ethylene), 7.89 (broad, 3H); ^{13}C NMR (67.8 MHz) δ=14.30 (q), 19.08 (q), 29.46 (d), 70.46 (d, NCH), 71.00 (t, O*C*-H_2, by selective decoupling), 71.68 (t, ethylene, by selective decoupling), 123.2 (d), 133.4 (d), 145.9 (s), 163.6 (s). Found: C, 43.97; H, 5.41; N, 8.31%. Calcd for $C_{19}H_{27}Cl_2N_3O_2Ru(H_2O)$: C, 43.93; H, 5.63; N, 8.09%. TLC, R_f 0.75 (dichloromethane : methanol=10 : 1).

***trans*-$RuBr_2$(Pybox-*ip*)(C_2H_4) (6).** With Pybox-*ip* (122 mg, 0.40 mmol) and [$RuBr_2$(*p*-cymene)]$_2$ (161 mg, 0.20 mmol)[13)] in dichloromethane (2 mL), as described above for **5**, the bromo-complex **6** was obtained as dark-red solids in 85% yield (203 mg, 0.34 mmol); decomp 117—120 °C; IR (KBr disk) 2950, 1590, 1565, 1490, 1440, 1395, 1385, 950 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.83 (d, J=6.8 Hz, 6 H), 1.02 (d, J=7.3 Hz, 6 H), 2.51 (m, 2 H), 4.42 (m, 2 H, NC*H*), 4.80 (m, 2 H, *H* of OC*H*), 4.90 (m, 2 H, *H* of OC*H*), 5.05 (m, 2 H, ethylene), 5.39 (m, 2 H, ethylene), 7.91 (broad s, 3H); ^{13}C NMR (67.8 MHz) δ=14.67, 19.24, 29.44, 69.43, 70.67, 71.93, 123.4, 133.5, 146.0, 163.8. Found: C, 38.70; H, 4.68; N, 6.80%. Calcd for $C_{19}H_{27}Br_2N_3O_2Ru$: C, 38.66; H, 4.61; N, 7.12%. TLC, R_f 0.87 (dichloromethane : methanol=10 : 1).

***trans*-RuI_2(Pybox-*ip*)(C_2H_4) (7).** With Pybox-*ip* (47 mg, 0.16 mmol) and $[RuI_2(p\text{-cymene})]_2$ (38 mg, 0.078 mmol)[13] in dichloromethane (1.5 mL), as described above for **5**, the iodo-complex **7** was obtained as dark-red solids in 94% yield (100 mg, 0.15 mmol); decomp 145—150 °C; IR (KBr disk) 2950, 1588, 1565, 1490, 1440, 1395, 1385, 950 cm^{-1}; ^{1}H NMR (270 MHz), δ=0.89 (d, J=6.8 Hz, 6 H), 1.04 (d, J=7.3 Hz, 6 H), 2.54 (m, 2 H), 4.40 (m, 2 H, NC*H*), 4.80 (m, 2 H, *H* of OC*H*), 4.92 (m, 2 H, *H* of OC*H*), 5.15 (m, 2 H, ethylene), 5.58 (m, 2 H, ethylene), 7.91 (broad s, 3 H); ^{13}C NMR (67.8 MHz) δ=15.28, 19.48, 29.36, 66.19, 71.16, 72.31, 123.5, 133.5, 146.0, 163.8. Found: C, 33.33; H, 4.05; N, 6.15%. Calcd for $C_{19}H_{27}I_2N_3O_2Ru$: C, 33.35; H, 3.98; N, 6.14%. TLC, R_f 0.88 (dichloromethane : methanol=40 : 1).

Cyclopropanation of Styrene and Methyl Diazoacetate with 5 (Run 6, Table 1). To a solution of *trans*-$RuCl_2$(Pybox-*ip*)(ethylene) (**5**) (30 mg, 0.06 mmol) and styrene (1.7 mL, 15 mmol) in dichloromethane (2.0 mL) was added a dichloromethane solution of methyl diazoacetate (3.0 mmol, ca. 1 M) through a microsyringe controlled by a mechanical feeder (ca. 4 μL/drop, ca. 0.4 mL h^{-1}) for 8 h at 20—25 °C under an argon atmosphere. After stirring for an additional 10 h, the mixture was concentrated under reduced pressure. The residual oil was subjected to silica-gel colunm chromatography with hexane-ether as an eluent to give an oily mixture of methyl *trans*-2-phenylcylopropane-1-carboxylate **3-me** and the *cis*-isomer **4-me** (390 mg, 74% yield, 90 : 10): TLC (R_f), 0.65 for **3-me** and 0.62 for **4-me** (hexane : ether=3 : 2): ^{1}H NMR δ=3.71 (2.70 H, s, CH_3-O) for **3-me** and 3.44 (0.30 H, s, CH_3-O) for **4-me**.[4b] Their enantiomeric purities, 88%ee for (1*R*,2*R*)-**3-me** and 70%ee for (1*R*,2*S*)-**4-me**, were measured by GLPC (Astec, Chiraldex B-DA, 30 m×0.25 mm): He (1.0 kg cm^{-2}), 110 °C; retention time (min), 43.3 for (1*R*,2*S*)-**4-me**, 45.1 for (1*S*,2*R*)-**4-me** (α=1.05, *R*=1.40), 50.7 for (1*S*,2*S*)-**3-me**, 51.9 for (1*R*,2*R*)-**3-me** (α=1.02, *R*=1.00). $[\alpha]_D$: negative for **3-me** and **4-me**: lit,[4b] positive for (1*S*,2*S*)-**3-me** and (1*S*,2*R*)-**4-me**. Cyclopropanation of deuterated styrene was performed using the same procedure: Products **3-me** and **4-me**, 47% yield, 88 : 11; 89% ee and 74% ee. ^{1}H NMR: for the starting styrene, δ=5.23 (0.69 H, *trans*-H_β to Ph) and 5.74 (0.31 H, *cis*-H_β to Ph). For **3-me**; $H_{c(3)}$, δ=1.32 (0.31±0.02 H) and 1.60 (0.69±0.02 H). For **4-me**; $H_{c(3)}$, δ=1.45 (0.69±0.02 H) and 1.71 (0.31±0.02 H).

With Ethyl Diazoacetate. Using the same procedure described above, a mixture of ethyl *trans*-2-phenylcyclopropane-1-carboxylate **3-et** and the *cis*-isomer **4-et** (416 mg, 73% yield, 91 : 9) was obtained: TLC (R_f), 0.66 for **3-et** and 0.57 for **4-et** (hexane : ether=3 : 1): ^{1}H NMR δ=4.17 (1.82 H, q, CH_2-O) for **3-et** and 3.87 (0.18 H, q, CH_2-O) for **4-et**. A small amount of diethyl maleate was contaminated. The ethyl esters were converted to the corresponding methyl esters by methanolysis in MeOH/NaOH to determine the enantiomeric purities by GLPC: 89% ee for (1*R*,2*R*)-**3-me** and 79%ee for (1*R*,2*S*)-**4-me**.

With *t*-Butyl Diazoacetate. Using the same procedure as that described above, a mixture of *t*-butyl *trans*-2-phenylcyclopropane-1-carboxylate **3-tb** and the *cis*-isomer **4-tb** (424 mg, 65%, 97 : 3) was obtained: TLC (R_f), 0.73 for **3-tb** and 0.62 for **4-tb** (hexane : ether=3 : 1): ^{1}H NMR δ=1.39 (8.73 H, s, CH_3) for **3-tb** and 1.06 (0.27 H, s, CH_3) for **4-tb**. The *t*-butyl esters were treated in methanol/*p*-TsOH at 50 °C to give the corresponding methyl esters: by GLPC, 94% ee for (1*R*,2*R*)-**3-me** and 87% ee for (1*R*,2*S*)-**4-me**.

With *d*-Menthyl Diazoacetate. Using the same procedure as that described above, a mixture of *d*-menthyl *trans*-2-phenylcyclopropane-1-carboxylate **3-*d*-ment** and the *cis*-isomer **4-*d*-ment** (741 mg, 82%, 97 : 3) was obtained: TLC (R_f), 0.65 for **3-*d*-ment** and 0.55 for **4-*d*-ment** (hexane : ether=6 : 1): ^{1}H NMR δ=4.71 (0.97 H, ddd, COOC*H*) for **3-*d*-ment** and 4.48 (0.03 H, ddd, COOC*H*) for **4-*d*-ment**. The *d*-menthyl esters were treated with NaOH in EtOH-H_2O at 70 °C, and then esterification with diazomethane to give the corresponding methyl esters: by GLPC 87% ee for (1*R*,2*R*)-**3-me** and 97% ee for (1*R*,2*S*)-**4-me**.

With *l*-Menthyl Diazoacetate. Using the same procedure as that for methyl diazoacetate, a mixture of *l*-menthyl *trans*-2-phenylcyclopropane-1-carboxylate **3-*l*-ment** and the *cis*-isomer **4-*l*-ment** (745 mg, 83%, 97 : 3) was obtained: TLC (R_f), 0.70 for **3-*l*-ment** and 0.60 for **4-*l*-ment** (hexane : ether=6 : 1): ^{1}H NMR δ=4.71 (0.97 H, ddd, COOCH) for **3-*l*-ment** and 4.48 (0.03 H, ddd, COOC*H*) for **4-*l*-ment**: by GLPC with the corresponding methyl esters, 96% ee for (1*R*,2*R*)-**3-me** and 80% ee for (1*R*,2*S*)-**4-me**.

Cyclopropanation with the in-situ Catalyst (Runs 1—5, Table 1). The in-situ catalyst was prepared by stirring of $[RuCl_2(p\text{-cymene})]_2$ (**1**) (18.4 mg, 0.03 mmol) and Pybox-*ip* (**2**) (72.4 mg, 0.24 mmol, 4 molar amounts to Ru) in dichloromethane (2.0 mL) for 30 min at room temperature. After the addition of styrene (1.7 mL, 15 mmol), the corresponding diazoacetate (3.0 mmol) in dichloromethane was added slowly, as described above. The work up and the characterization method were the same as that mentioned above.

Cyclopropanation of *p*-Chlorostyrene and *l*-Menthyl Diazoacetate with 5. Using the same procedure as that for Run 6 in Table 1: **5** (30 mg), *l*-menthyl diazoacetate (3.0 mmol), *p*-chlorostyrene (1.9 mL, 15 mmol), at 25 °C. A mixture of *l*-menthyl *trans*-2-(4-chlorophenyl)cyclopropane-1-carboxylate **8** and the *cis*-isomer **9** was obtained (847 mg, 84%, 96 : 4). The menthyl esters were converted to the corresponding methyl esters by reduction with $LiAlH_4$, Jones oxidation, then methylation with diazomethane. The enantiomeric purities, 95% ee for (1*R*,2*R*)-**8** and 83% ee for (1*R*,2*S*)-**9**, were measured by GLPC (Astec, Chiraldex B-DA, 30 m×0.25 mm): He (1.5 kg cm^{-2}), 120 °C; retention time (min), 108.2 for (1*S*,2*S*)-**8-me**, 113.2 for (1*R*,2*R*)-**8-me** (α=1.05, *R*=2.36); 81.0 for (1*S*,2*R*)-**9-me**, 83.3 for (1*R*,2*S*)-**9-me** (α=1.03, *R*=1.36).

Cyclopropanation of *p*-methoxystyrene and *l*-Menthyl Diazoacetate with 5. **5** (30 mg), *l*-menthyl diazoacetate (3.0 mmol), *p*-methoxystyrene (2.0 mL, 15 mmol), at 25 °C. A mixture of *l*-menthyl *trans*-2-(4-methoxyphenyl)cyclopropane-1-carboxylate **10** and the *cis*-isomer **11** was obtained (860 mg, 96%, 95 : 5). The menthyl esters were converted to the corresponding methyl esters by reduction with $LiAlH_4$, Jones oxidation then methylation with diazomethane. The enantiomeric purity, 97% ee for (−)-(1*R*,2*R*)-**10-me** was measure by GLPC (Astec, Chiraldex B-DA, 30 m×0.25 mm): He (1.75 kg cm^{-2}), 135 °C; retention time (min), 95.5 for (1*S*,2*S*)-**10-me**, 99.0 for (1*R*,2*R*)-**10-me** (α=1.03, *R*=1.56). The % ee of **11** could not be determined.

Cyclopropanation of 3-Phenyl-1-propene and *l*-Menthyl Diazoacetate with 5. **5** (30 mg), *l*-menthyl diazoacetate (3.0 mmol), 3-phenyl-1-propene (2.0 mL, 15 mmol), $\mathrm{ClCH_2CH_2Cl}$ (2.0 ml) at 50 °C. A mixture of *l*-menthyl 2-benzylcyclopropane-1-carboxylate **12** and the *cis*-isomer **13** was obtained (422 mg, 45%, 93 : 7). The menthyl esters were converted to the corresponding methyl esters by reduction with $\mathrm{LiAlH_4}$, Jones oxidation then methylation with diazomethane. The enantiomeric purity, 97% ee for (−)-(1*R*,2*R*)-**12-me** was measured by GLPC (Astec, Chiraldex B-DA, 30 m×0.25 mm): He (1.5 kg cm^{-2}), 110 °C; retention time (min), 55.1 for (1*S*,2*S*)-**12-me**, 56.1 for (1*R*,2*R*)-**12-me** (α=1.01, *R*=0.92). The %ee of **13** could not be determined.

Cyclopropanation of 1-Heptene and *l*-Menthyl Diazoacetate with 5. **5** (30 mg), *l*-menthyl diazoacetate (3.0 mmol), 1-heptene (3.4 mL, 24 mmol), at 35 °C. A mixture of *l*-menthyl *trans*-2-*n*-pentylcyclopropane-1-carboxylate **14** and the *cis*-isomer **15** was obtained (478 mg, 54%, 92 : 8). After transformation of the menthyl esters to the corresponding methyl esters, the ratio was determined by ^{1}H NMR δ=3.66 (2.76 H, s, C*H*$_3$-O) for **14-me** and 3.67 (0.24 H, s, C*H*$_3$-O) for **15-me**; ^{1}H NMR, in accordance with Ref. 4b. The enantiomeric purities, 98% ee for (1*R*,2*R*)-**14** and 94% ee for (1*R*,2*S*)-**15**, were measured by GLPC (Astec, Chiraldex B-DA, 30 m×0.25 mm): He (1.5 kg cm^2), 160 °C; retention time (min), 58.2 for (1*S*,2*S*)-**14-*l*-ment**, 62.2 for (1*R*,2*R*)-**14-*l*-ment** (α=1.08, *R*=3.5); 49.7 for (1*S*,2*R*)-**15-*l*-ment**, 65.8 for (1*R*,2*S*)-**15-*l*-ment** (α=1.35, *R*=10.0). $[\alpha]_\mathrm{D}$: negative for **14-me** and **15-me**: lit,[4b)] positive for (1*S*,2*S*)-**14-me** and (1*S*,2*R*)-**15-me**. A mixture of the corresponding maleate and the fumarate was obtained in ca. 40%.

Cyclopropanation of 1,1-Diphenylethylene with 5. With *l*-Menthyl Diazoacetate. **5** (30 mg), *l*-menthyl diazoacetate (3.0 mmol), 1,1-diphenylethylene (2.65 mL, 15 mmol), at 30—35 °C. *l*-Menthyl 2,2-diphenylcyclpropane-1-carboxylate **16-*l*-ment** (621 mg, 55%): TLC (R_f), 0.53 for **16-*l*-ment** (hexane : ether=10 : 1); by GLPC with the corresponding methyl ester **16-me**, 65% ee (1*R*), (Astec, Chiraldex B-DA, 30 m×0.25 mm): He (2.0 kg cm^{-2}), 150 °C; retention time (min), 44.0 for (1*S*)-**16-me**, 46.1 for (1*R*)-**16-me** (α=1.07, *R*=1.6). $[\alpha]_\mathrm{D}$ with the ethyl ester: negative for **16-et**: lit,[5b)] positive for (1*S*)-**16-et**. A mixture of the corresponding maleate and the fumarate was obtained in ca. 40%.

Cyclopropanation of 4-Methyl-1,3-pentadiene and *l*-Menthyl Diazoacetate with 5. **5** (30 mg), *l*-menthyl diazoacetate (3.0 mmol), 4-methyl-1,3-pentadiene (1.71 mL, 15 mmol). A mixture of *l*-menthyl *trans*-(2-methylpropen-1-yl)cyclopropane-1-carboxylate **17** and the *cis*-isomer **18** was obtained (742 mg, 86%, 79 : 21); ^{1}H NMR δ=4.63 (0.79 H, broad d, C=C*H*) for **17** and 5.13 (0.21 H, broad d, C=C*H*) for **18**; ^{1}H NMR, in accordance with Ref. 4b. TLC (R_f), 0.7 for **17**+**18** (hexane : ether=10 : 1). The diastereoselectivity was measured with their menthyl forms by GLPC: 98% for (1*R*,2*R*)-**17** and 79% for (1*R*,2*S*)-**18** (Astec, Chiraldex B-PH, 30 m×0.25 mm): He (1.0 kg cm^{-2}), 150 °C; retention time (min), 39.3 for (1*S*,2*S*)-**17**, 42.4 for (1*R*,2*R*)-**17** (α=1.07, *R*=2.2), 43.4 for (1*R*,2*S*)-**18**, 45.0 for (1*S*,2*R*)-**18** (α=1.04, *R*=2.4). $[\alpha]_\mathrm{D}$ with the methyl esters: negative for **17-me** and **18-me**; lit,[4b)] positive for (1*S*,2*S*)-**17-me** and (1*S*,2*R*)-**18-me**.

Intramolecular Cyclopropanation. With *trans*-Cinnamyl Diazoacetate (19) and 5. To a solution of *trans*-$\mathrm{RuCl_2}$(Pybox-*ip*)(ethylene) (**5**) (37.6 mg, 0.075 mmol) in dichloromethane (2.0 mL) was added a solution of *trans*-cinnamyl diazoacetate (**19**) (304 mg, 1.5 mmol) in dichloromethane (1.5 mL) for 3 h at room temperature under an argon atmosphere. After stirring for further 4 h, the reaction mixture was concentrated and purified by silica-gel column chromatography to give the desired product, [1*R*,5*S*-(1α,5α,6β)]-(−)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (**22**) (243 mg, 93%) as white solids; mp 114—115°C; IR (KBr disk) 1740 cm^{-1}; ^{1}H NMR (270 MHz) δ=2.30—2.40 (m, 2 H), 2.55 (m, 1H), 4.40—4.52 (m, 2 H), 7.07 (m, 2 H), 7.20—7.35 (m, 3 H); TLC (R_f), 0.65 for **19** and 0.3 for **22** (hexane : ether=1 : 1); $[\alpha]_\mathrm{D}^{25}$ =−138.3 (c=1.03, $\mathrm{CH_2Cl_2}$) 86% ee by GLPC (Astec, Chiraldex B-PH, 30 m×0.25 mm): He (1.5 kg cm^{-2}), 160 °C; retention time (min), 85.7 for (1*S*,5*R*)-**22**, 89.3 for (1*R*,5*S*)-**22** (α=1.04, *R*=2.7). The absolute configuration of (−)-**22** was tentatively assigned to (1*R*,5*S*) comparing to the sign of the rotation of **24**; also see, Ref. 7e.

With *cis*-Cinnamyl Diazoacetate (20) and 5. The procedure was the same as that described above for **13**; $\mathrm{RuCl_2}$(Pybox-*ip*)(ethylene) (**5**) (37.6 mg, 0.075 mmol), dichloromethane (2.0 mL), the *cis*-cinnamyl diazoacetate (**20**) (304 mg, 1.5 mmol), dichloromethane (1.5 mL). [1*R*,5*S*-(1α,5α,6α)]-(−)-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (**23**) (205 mg, 79%) was obtained as white solids; mp 79—80 °C; IR (KBr disk) 1750 cm^{-1}; ^{1}H NMR (270 MHz) δ=2.55—2.65 (m, 2 H), 2.78 (t, J=8.6 Hz, 1 H), 4.05 (d, J=9.8 Hz, 1H), 4.37 (dt, J=9.8, 2.5 Hz, 1 H), 7.25—7.4 (m, 5 H), also see Ref. 7f: TLC (R_f), 0.70 for **20** and 0.2 for **23** (hexane : ether=1 : 1): $[\alpha]_\mathrm{D}^{25}$=−52.0 (c=1.01, $\mathrm{CH_2Cl_2}$); by GLPC, 24% ee (Astec, Chiraldex B-DA, 30 m×0.25 mm): He (1.5 kg cm^{-2}), 160 °C; retention time (min), 44.6 for (1*S*,5*R*)-**20**, 45.5 for (1*R*,5*S*)-**20** (α=1.03, *R*=1.1). The absolute configuration of (−)-**20** was also tentatively assigned to (1*R*,5*S*).

With 3-Methyl-2-buten-1-yl Diazoacetate (21) and 5. The procedure was the same as that described above for **13**; $\mathrm{RuCl_2}$(Pybox-*ip*)(ethylene) (**5**) (37.6 mg, 0.075 mmol), dichloromethane (2.0 mL), the 3-methyl-2-buten-1-yl diazoacetate (**21**) (231 mg, 1.5 mmol), dichloromethane (3.0 mL). (1*R*,5*S*)-(−)-6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (**24**) (171 mg, 91%) was obtained as an oil; IR (film) 1760 cm^{-1}; ^{1}H NMR (270 MHz) δ=1.18 (s, 3H), 1.19 (s, 3H), 1.95 (d, J=6.3 Hz, 1 H), 2.05 (dd, J=6.3, 5.5 Hz, 1 H), 4.15 (d, J=9.8 Hz, 1 H), 4.37 (dd, J=9.8, 5.5 Hz, 1 H); TLC (R_f) 0.70 for **21** and 0.3 for **24** (hexane : ether=1 : 1); after Kugelrohr distillation, $[\alpha]_\mathrm{D}^{22}$=−95.5 (c=1.04, $\mathrm{CHCl_3}$); lit,[7e,23)] $[\alpha]_\mathrm{D}^{25}$=+89.9 (c=1.4, $\mathrm{CHCl_3}$) for (1*S*,5*R*); by GLPC, 76% ee (Astec, Chiraldex B-DA, 30 m×0.25 mm): He (1.0 kg cm^{-2}), 100 °C; retention time (min), 43.9 for (1*R*,5*S*)-**24**, 46.8 for (1*S*,5*R*)-**24** (α=1.07, *R*=1.6).

***trans*-$\mathbf{RuCl_2}$(Pybox-*ethyl*)($\mathbf{C_2H_4}$) (32).** A solution of Pybox-*ethyl* (**25**) (270 mg, 1.0 mmol) and $[\mathrm{RuCl_2}(p\text{-cymene})]_2$ (306 g, 0.5 mmol) in dichloromethane (9.0 mL) was stirred at room temperature under ethylene atmosphere for 1 h. After the same purification as that described above

Table 6. Crystallographic Data for *trans*-$RuCl_2$(Pybox-*dihydro*)(C_2H_4) **36**

Molecular formula	$C_{13}H_{15}Cl_2N_3O_2Ru$
Formula weight	417.26
Crystal color, habit	Dark red, prismatic
Crystal dimensions/mm	0.25×0.40×0.40
Crystal system	Monoclinic
Lattice type	C-centered
No. of reflections used for unit Cell determination (2θ range)	25 (53.9—54.9°)
Omega scan peak width at half-height	0.33°
Lattice parameters	a=27.758(3) Å b=8.433(2) Å c=13.188(3) Å β=93.03(1)° V=3082(1) Å^3
Space group	$C2/c$ (♯15)
Z value	8
D_{calcd}	1.798 g cm^{-3}
F_{000}	1664.00
μ(Mo $K\alpha$)	13.70 cm^{-1}
Radiation	Mo $K\alpha$ (λ=0.71069 Å)
Temperature	20°C
Scan type	ω–2θ
Scan rate	3.2 ° min^{-1}
Scan width	(1.47+0.30 tan θ)°
Scan range	$5<2\theta<55°$
No. of reflections measured	3857
Unique data	3778 (R_{int}=0.011)
Observed data, $I>3\sigma(I)$	3026
No. of variables	250
Reflection/parameter ratio	12.10
$R=\sum\|\|F_o\|-\|F_c\|\|/\sum\|F_o\|$	0.031
$R_w=\sum\|\|F_o\|-\|F_c\|\|w^{1/2}/\sum\|F_o\|w^{1/2}$	0.031
Goodness of fit	2.72
Minimum, maximum peak in final diff. map	−0.62, 0.85 e$^-$ Å^{-3}

for **5**, dark-purple solids **32** in 89% yield (421 mg, 0.89 mmol) was obtained; mp 98—100 °C decomp; IR (KBr disk) 1595, 1570, 1395 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.98 (t, J=7.3 Hz, 6 H), 1.73 (m, 2 H), 2.02 (m, 2 H), 4.41 (m, 2 H, NC*H*), 4.80 (m, 2 H, OC*H*), 4.90—4.97 (m, 4 H), 5.22 (m, 2 H), 7.89 (s, 3 H); ^{13}C NMR (67.8 MHz) δ=8.15, 26.00, 65.99, 69.99, 74.97, 123.4, 132.6, 145.2, 163.0. Found: C, 42.12; H, 4.85; N, 8.61%. Calcd for $C_{17}H_{23}Cl_2N_3O_2Ru$($0.2CH_2Cl_2$): C, 42.13; H, 4.81; N, 8.57%. TLC, R_f 0.35 (ethyl acetate : methanol=20 : 1).

***trans*-$RuCl_2$(Pybox-*s-butyl*)(C_2H_4) (33).** A solution of Pybox-*s-butyl* (**26**) (265 mg, 0.80 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (246 mg, 0.40 mmol) in dichloromethane (8.0 mL) was stirred at room temperature under ethylene atmosphere for 1 h. After the same purification as described above for **5**, dark-purle solids **33** in 74% yield (314 mg, 0.59 mmol) were obtained; mp 104—107 °C decomp; IR (KBr disk) 1592, 1570, 1395 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.77 (d, J=7.3 Hz, 6H), 1.05 (t, J=7.3 Hz, 6 H), 1.36 (quint, J=7.3 Hz, 6 H), 2.25 (m, 2 H), 4.56 (m, 2 H), 4.77—4.89 (m, 4H), 4.96 (m, 2 H), 5.29 (m, 2 H), 7.88 (s, 3 H); ^{13}C NMR (67.8 MHz) δ=11.96, 12.53, 26.76, 36.54, 68.94, 71.15, 72.01, 123.4, 133.5, 146.2, 163.9. Found: C, 45.97; H, 5.76; N, 7.78%. Calcd for $C_{21}H_{31}Cl_2N_3O_2Ru(H_2O)$: C, 46.07; H, 6.08; N, 7.68%. TLC, R_f 0.53 (CH_2Cl_2 : methanol=20 : 1).

***trans*-$RuCl_2$(Pybox-*benzyl*)(C_2H_4) (34).** A solution of Pybox-*benzyl* (**28**) (199 mg, 0.50 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (153 mg, 0.25 mmol) in dichloromethane (5.0 mL) was stirred at room temperature under an ethylene atmosphere for 1 h. After the same purification as that described above for **5**, dark-purple solids **34** in 93% yield (279 mg, 0.47 mmol) was obtained; mp 109—113 °C decomp; IR (KBr disk) 1592, 1570, 1395 cm^{-1}; ^{1}H NMR (270 MHz) δ=2.73 (m, 2 H), 3.60 (d, J=14.5 Hz, 2 H), 4.75—4.85 (m, 6 H), 5.18 (m, 2 H), 5.50 (m, 2 H), 7.28—7.40 (m, 10 H), 7.93 (s, 3 H); ^{13}C NMR (67.8 MHz) δ=39.89, 66.87, 71.13, 75.73, 123.5, 127.0, 128.9, 129.2, 133.7, 136.3, 146.2, 164.6. Found: C, 53.01; H, 4.49; N, 6.89%. Calcd for $C_{27}H_{27}Cl_2N_3O_2Ru$($0.2CH_2Cl_2$): C, 53.17; H, 4.49; N, 6.84%. TLC, R_f 0.48 (ethyl acetate : methanol=20 : 1).

***trans*-$RuCl_2$(Pybox-*phenyl*)(C_2H_4) (35).** A solution of Pybox-*phenyl* (**29**) (234 mg, 0.61 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (188 mg, 0.31 mmol) in dichloromethane (6.0 mL) was stirred at room temperature under ethylene atmosphere for 1 h. After the same purification as that described above for **5**, dark-purple solids **35** in 73% yield (260 mg, 0.45 mmol) was obtained; mp 88—92 °C

Table 7. Positional and Equivalnet Isotropic Thermal Parameters for *trans*-$RuCl_2$(Pybox-*dihydro*)(C_2H_4) **36**

Atom	x	y	z	$B_{eq}^{a)}/Å^2$
Ru	0.129023(9)	0.09289(3)	−0.18811(2)	1.783(5)
Cl(1)	0.07406(3)	−0.0298(1)	−0.30981(6)	2.92(2)
Cl(2)	0.18360(3)	0.2168(1)	−0.06626(7)	3.18(2)
O(1)	0.22456(8)	0.2104(3)	−0.4061(2)	2.87(5)
O(2)	0.02042(8)	0.4114(3)	−0.1300(2)	3.10(5)
N(1)	0.12377(9)	0.2999(3)	−0.2624(2)	1.92(5)
N(2)	0.18426(9)	0.0798(3)	−0.2880(2)	2.18(6)
N(3)	0.07045(9)	0.2001(3)	−0.1271(2)	2.09(6)
C(1)	0.1553(1)	0.3352(4)	−0.3336(2)	2.13(7)
C(2)	0.1529(1)	0.4780(4)	−0.3856(3)	2.90(8)
C(3)	0.1178(1)	0.5860(4)	−0.3621(3)	3.06(8)
C(4)	0.0854(1)	0.5514(4)	−0.2885(3)	2.66(8)
C(5)	0.0894(1)	0.4065(4)	−0.2395(2)	2.13(6)
C(6)	0.1887(1)	0.2040(4)	−0.3428(2)	2.15(7)
C(7)	0.2232(1)	−0.0313(5)	−0.3133(3)	3.34(9)
C(8)	0.2494(1)	0.0561(4)	−0.3953(3)	3.10(9)
C(9)	0.0601(1)	0.3380(4)	−0.1622(2)	2.22(7)
C(10)	0.0318(1)	0.1523(5)	−0.0606(3)	2.70(8)
C(11)	0.0005(2)	0.3002(5)	−0.0566(3)	3.70(10)
C(12)	0.1551(1)	−0.1401(4)	−0.1345(3)	2.94(8)
C(13)	0.1159(2)	−0.0997(5)	−0.0804(3)	3.21(9)
H(1)	0.178(1)	0.498(4)	−0.429(3)	3.6(8)
H(2)	0.115(1)	0.674(4)	−0.392(3)	3.3(8)
H(3)	0.063(1)	0.620(4)	−0.270(2)	2.0(7)
H(4)	0.210(1)	−0.130(5)	−0.339(3)	4.0(9)
H(5)	0.243(1)	−0.043(4)	−0.255(3)	3.3(9)
H(6)	0.248(1)	0.004(4)	−0.455(3)	3.2(8)
H(7)	0.282(1)	0.087(4)	−0.373(2)	3.2(8)
H(8)	0.014(1)	0.062(4)	−0.094(2)	1.6(6)
H(9)	0.044(1)	0.121(3)	0.001(2)	1.5(6)
H(10)	−0.033(1)	0.283(5)	−0.076(3)	4.1(9)
H(11)	0.003(1)	0.352(5)	0.011(3)	4.5(10)
H(12)	0.151(1)	−0.204(5)	−0.192(3)	3.8(9)
H(13)	0.187(1)	−0.128(3)	−0.107(2)	1.3(6)
H(14)	0.083(1)	−0.144(4)	−0.105(2)	2.4(7)
H(15)	0.122(1)	−0.049(4)	−0.013(2)	2.0(7)

a) $B_{eq}=(8/3)\pi^2(U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha)$.

decomp; IR (KBr disk) 1592, 1570, 1395 cm^{-1}; ^{1}H NMR (270 MHz) δ=4.19 (m, 2 H, ethylene), 4.43 (m, 2 H, ethylene), 4.68 (m, 2 H), 5.28 (m, 2 H), 5.43 (m, 2 H), 7.29—7.39 (m, 10 H), 7.92—8.04 (m, 3 H); ^{13}C NMR (67.8 MHz) δ=69.98, 73.33, 76.53, 124.0, 127.7, 128.6, 128.8, 133.0, 138.8, 146.2, 165.5. Found: C, 49.80; H, 4.00; N, 6.97%. Calcd for $C_{25}H_{23}Cl_2N_3O_2Ru(0.5CH_2Cl_2)$: C, 50.05; H, 3.95; N, 6.87%. TLC, R_f 0.32 (ethyl acetate : methanol=20 : 1).

***trans*-$RuCl_2$(Pybox-*dihydro*)(C_2H_4) (36).** A solution of Pybox-*dihydro* (**31**) (279 mg, 1.28 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (393 mg, 0.64 mmol) in dichloromethane (20 mL) was stirred at room temperature under ethylene atmosphere for 2 h. After the same purification as that described above for **5**, dark-purple solids **36** in 49% yield (260 mg, 0.62 mmol) was obtained, mp (decomp) >250 °C; IR (KBr disk) 1597, 1570, 1392 cm^{-1}; ^{1}H NMR (270 MHz) δ=4.31 (t, J=9.8 Hz, 4 H), 4.95 (s, 4 H), 5.05 (t, J=9.8 Hz, 4 H), 7.88 (s, 3 H); ^{13}C NMR (67.8 MHz) δ=52.99, 65.77, 71.67, 123.1, 133.6, 146.0, 164.9. Found: C, 36.76; H, 3.65; N, 9.92%. Calcd for $C_{13}H_{17}Cl_2N_3O_2Ru$: C, 36.63; H, 3.78; N, 9.86%. TLC, R_f 0.25 (CH_2Cl_2 : methanol=20 : 1).

***trans*-$RuCl_2$(Pybox-*ip*)(CO) (37).** A solution of Pybox-*ip* (1.51 g, 5.0 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (1.52 g, 2.5 mmol) in degassed acetone (100 mL) was stirred at room temperature under a carbon monoxide atmosphere for 2 h. After the solvent was removed under reduced pressure, the residue was purified by silica-gel column chromatography (SiO_2, ca. 100 g) with dichloromethane and methanol (100 : 1). The black-band forerun was collected and concentrated to give almost pure **37** as black solids in 92% yield (2.32 g, 4.6 mmol); mp 267—268 °C decomp; IR (KBr disk) 1965 cm^{-1} for $\nu_{C=O}$; ^{1}H NMR (270 MHz) δ=0.95 (d, J=6.8 Hz, 6 H), 1.03 (d, J=6.8 Hz, 6 H), 2.53 (m, 2 H), 4.19 (m, J=3.4, 6.8, 10.3 Hz, 2 H, NC*H*), 4.71 (m, J=8.3, 8.8 Hz, 2 H, OC*H*), 4.83 (m, J=8.8, 10.3 Hz, 2 H, OC*H*), 7.86 (d, J=8.3 Hz, 2 H), 8.11 (t, J=8.3(×2) Hz, 1 H); ^{13}C NMR (67.8 MHz) δ=15.30, 19.08, 29.50, 70.82, 72.08, 123.5, 139.2, 146.8, 163.5, 204.6 ($\underline{C}$O). Found: C, 42.82; H,

Table 8. Crystallographic Data for *trans*-Ru(OAc)$_2$(Pybox-*ip*)(CO) **38**

Molecular formula	$C_{22}H_{29}N_3O_7Ru$
Formula weight	548.56
Crystal color, habit	Dark red, plate
Crystal dimensions/mm	0.25×0.40×0.50
Crystal system	Monoclinic
Lattice type	P
No. of reflections used for unit Cell determination (2θ range)	22 (48.7—52.3°)
Omega scan peak width at half-height	0.30°
Lattice parameters	a=8.9558(9) Å
	b=16.478(2) Å
	c=9.1534(9) Å
	β=115.479(5)°
	V=1219.4(2) Å^3
Space group	$P2_1$ (♯4)
Z value	2
D_{calcd}	1.494 g cm^{-3}
F_{000}	564.00
μ(Mo $K\alpha$)	6.73 cm^{-1}
Radiation	Mo $K\alpha$ (λ=0.71069 Å)
Temperature	23°C
Scan type	ω–2θ
Scan rate	3.2 ° min^{-1}
Scan width	$(1.12+0.30 \tan\theta)°$
Scan range	$5<2\theta<55°$
No. of reflections measured	3086
Unique data	2911 (R_{int}=1.37)
Observed data, $I>3\sigma(I)$	2629
No. of variables	297
Reflection/parameter ratio	8.85
$R=\sum\|\|F_o\|-\|F_c\|\|/\sum\|F_o\|$	0.037
$R_w=\sum\|\|F_o\|-\|F_c\|\|w^{1/2}/\sum\|F_o\|w^{1/2}$	0.031
Goodness of fit	4.01
Minimum, maximum peak in final diff. map	−0.83, 0.90 e$^-$ Å^{-3}

4.60; N, 8.38%. Calcd for $C_{18}H_{23}Cl_2N_3O_3Ru$: C, 43.12; H, 4.62; N, 8.38%. TLC, R_f 0.6 (ethyl acetate : methanol=5 : 1).

***trans*-Ru(OAc)$_2$(Pybox-*ip*)(CO) (38).** A suspension of **37** (251 mg, 0.50 mmol) and silver acetate (417 mg, 2.5 mmol) in methanol (15 mL) was stirred at 40 °C under a nitrogen atmosphere for 2 d. After filtration and concentration, the residue was purified by silica-gel column chromatography with ethyl acetate and methanol to give **20** as black solids in 87% yield (239 mg, 0.436 mmol); mp 210 °C decomp; IR (KBr disk) 1960, 1920 cm^{-1} for $\nu_{C=O}$; ^{1}H NMR (270 MHz) δ=0.75 (d, J=6.8 Hz, 6 H), 0.97 (d, J=6.8 Hz, 6 H), 1.62 (s, 6 H, COCH_3), 2.50 (m, 2 H), 4.53 (m, 2 H), 4.66 (m, 2 H), 4.79 (m, 2 H), 7.79 (d, J=8.3 Hz, 2 H), 8.07 (t, J=8.3×2 Hz, 1 H); ^{13}C NMR (67.8 MHz) δ=14.55, 18.90, 23.32, 29.68, 71.11, 72.11, 122.60, 139.0, 148.0, 163.5, 178.4, 207.3. Found: C, 48.06; H, 5.35; N, 7.64%. Calcd for $C_{22}H_{29}N_3O_7Ru$: C, 48.71; H, 5.33; N, 7.66%. TLC, R_f 0.3 (ethyl acetate : methanol=5 : 1) for **38**. The corresponding monoacetate was detected at R_f 0.4 (ethyl acetate : methanol=5 : 1); black solids, mp 132—133 °C; its ^{1}H and ^{13}C NMR showed unsymmetrical patterns.

Cyclopropanation of Styrene and Ethyl Diazoacetate with 39 (Run 3, Table 5). After a mixture of **37** (30 mg, 0.06 mmol) and AgOTf (18.0 g, 0.07 mmol) in CH_2Cl_2 (2 mL) was left at room temperature over night, the mixture was filtered through a Celite-545 column with dichloromethane; the mono-triflate complex was detected by TLC as a single product. Then, the filtrate was concentrated in a reaction flask to give a black solid. Cyclopropanation on the same scale was performed at 40 °C. A mixture of **3-et** and **4-et** was obtained (217 mg, yield 38%, 55 : 45): by GLPC, 33%ee for (1*S*,2*S*)-**3-me** and 9%ee for (1*R*,2*S*)-**4-me**.

X-Ray Crystallography of 36 and 38. Crystals suitable for X-ray diffraction were grown in a solution of ethyl acetate for **36** and benzene for **38**. Their prisms were mounted for data collection on a Rigaku AFC-7R diffractometer, respectively (Tables 6, 7, 8, and 9). Lorentz, polarization, no absorption correction, and no decay correction were applied to the data. The structure was solved by heavy-atom Patterson methods (DIRDIF92PATTY). The non-hydrogen atoms were refined anisotropically for **36** and **38**. Hydrogen atoms were refined isotropically for **36**, but not refined for **38**.

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Table 9. Positional and Equivalent Isotropic Thermal Parameteres for *trans*-Ru$(OAc)_2$(Pybox-*ip*)(CO) **38**

Atom	x	y	z	$B_{eq}^{a)}$ Å
Ru	0.18858(6)	0.2500	0.34386(5)	2.150(9)
O(1)	0.3739(6)	0.0219(3)	0.3164(6)	3.2(1)
O(2)	0.4106(6)	0.3691(3)	0.7846(6)	3.9(1)
O(3)	0.0211(5)	0.2007(3)	0.4198(5)	2.5(1)
O(4)	−0.1617(6)	0.1575(4)	0.1770(6)	5.0(2)
O(5)	0.3796(6)	0.2946(3)	0.2971(6)	3.3(1)
O(6)	0.2735(8)	0.4159(4)	0.221(1)	8.0(2)
O(7)	−0.0814(7)	0.3330(4)	0.0588(7)	5.3(2)
N(1)	0.2203(7)	0.1379(3)	0.2526(6)	2.2(1)
N(2)	0.3798(6)	0.1971(4)	0.5413(6)	2.5(1)
N(3)	0.2405(7)	0.3359(4)	0.5263(7)	2.6(1)
C(1)	0.1469(9)	0.0897(5)	0.1038(8)	3.1(2)
C(2)	0.2502(10)	0.0097(5)	0.1466(8)	4.5(2)
C(3)	0.3422(8)	0.0946(5)	0.3599(8)	2.6(2)
C(4)	0.4359(8)	0.1254(4)	0.5224(8)	2.4(2)
C(5)	0.5689(9)	0.0890(5)	0.6519(9)	3.6(2)
C(6)	0.6428(9)	0.1319(6)	0.7969(9)	4.4(2)
C(7)	0.5872(9)	0.2076(5)	0.8100(8)	4.2(2)
C(8)	0.4501(8)	0.2411(8)	0.6769(7)	3.0(2)
C(9)	0.3624(8)	0.3176(5)	0.6599(8)	3.1(2)
C(10)	0.3027(10)	0.4400(5)	0.720(1)	5.1(2)
C(11)	0.1694(9)	0.4105(5)	0.5522(9)	3.3(2)
C(12)	0.1435(10)	0.1349(5)	−0.0417(8)	3.8(2)
C(13)	0.312(1)	0.1611(7)	−0.015(1)	6.6(3)
C(14)	0.065(1)	0.0794(6)	−0.1913(9)	6.2(3)
C(15)	−0.0021(9)	0.3966(5)	0.5456(8)	3.1(2)
C(16)	−0.0830(10)	0.4775(5)	0.5547(10)	4.6(2)
C(17)	−0.001(1)	0.3383(6)	0.676(1)	5.1(3)
C(18)	−0.1199(8)	0.1722(5)	0.3224(8)	2.9(2)
C(19)	−0.2418(8)	0.1602(5)	0.3938(9)	3.8(2)
C(20)	0.378(1)	0.3659(6)	0.2402(10)	3.7(2)
C(21)	0.535(1)	0.3818(6)	0.206(1)	6.0(3)
C(22)	0.0188(9)	0.3012(5)	0.1672(9)	3.2(2)
H(1)	0.6088	0.0352	0.6399	
H(2)	0.7345	0.1072	0.8886	
H(3)	0.6447	0.2396	0.9103	
H(4)	0.0300	0.0770	0.0810	
H(5)	0.1565	0.4503	0.4652	
H(6)	0.0706	0.1816	−0.0656	
H(7)	−0.0734	0.3719	0.4439	
H(8)	0.3005	0.0019	0.0705	
H(9)	0.1792	−0.0385	0.1288	
H(10)	0.2500	0.4585	0.7864	
H(11)	0.3616	0.4878	0.7060	
H(12)	0.3821	0.1170	0.0066	
H(13)	0.3062	0.1898	−0.1096	
H(14)	0.3533	0.1990	0.0737	
H(15)	−0.0412	0.0589	−0.2087	
H(16)	0.0594	0.1024	−0.2877	
H(17)	0.1357	0.0293	−0.1726	
H(18)	−0.0173	0.5035	0.6577	
H(19)	−0.0921	0.5129	0.4711	
H(20)	−0.1914	0.4687	0.5505	
H(21)	−0.1098	0.3339	0.6732	
H(22)	0.0424	0.2888	0.6737	
H(23)	0.0674	0.3639	0.7839	
H(24)	−0.2651	0.2094	0.4343	
H(25)	−0.3442	0.1374	0.3170	
H(26)	−0.1993	0.1219	0.4855	
H(27)	0.6303	0.3747	0.3004	
H(28)	0.5332	0.3403	0.1271	
H(29)	0.5256	0.4323	0.1594	

a) $B_{eq}=(8/3)\pi^2(U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha)$.

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