Chiral Bis(dihydrooxazolyl)pyridineruthenium Complexes of *trans*-Cyclooctene and *trans*-Cycloheptene

Hisao Nishiyama,* Tomonari Naitoh, Yukihiro Motoyama, and Katsuyuki Aoki[a]

Abstract: Asymmetric reaction of an excess of *trans*-cyclooctene (**1**) with chiral bis(dihydrooxazolyl)pyridineruthenium (pybox-*ip*, **3**) complex selectively gives the corresponding ruthenium complex **4*R***, [$RuCl_2$(pybox-*ip*){(*R*)-*trans*-cyclooctene}], and (*S*)-*trans*-cyclooctene **2*S***. The X-ray crystal structure of complex **4*R*** shows a C25-C18-C19-C20 dihedral angle of 125° with a C18–C19 bond length of 1.41 Å. Complex **4*R*** can also be obtained by UV irradiation of a solution of *cis*-cyclooctene and [$RuCl_2$(pybox-*ip*)(C_2H_4)] (**8**) in THF in the presence of a photosensitizer. Even in the absence of the photosensitizer, **4*R*** is produced by irradiation in the presence of *cis*-cyclooctene. The photoreaction has been applied to *cis*-cycloheptene to give a 1:1 mixture of the diastereomeric complexes of [Ru(pybox-*ip*)-{*trans*-cycloheptene}].

Keywords: alkene complexes · enantiofacial selection · kinetic resolution · ruthenium

Introduction

Enantiofacial selection of substituted olefins by coordination is an important subject in the development of transition metal catalyzed asymmetric reactions and in the clarification of their mechanisms.[1] We have previously reported one mode of enantiofacially selective olefin coordination of α,β-unsaturated carbonyl compounds, such as dimethyl fumarate, methyl acrylate, vinyl methyl ketone, and acrolein, by use of the chiral bis(dihydrooxazolyl)pyridineruthenium fragment [$RuCl_2$(pybox)(vacant)] to produce the corresponding olefin complexes **A**.[2] It was proved that the {$RuCl_2$(pybox)} fragment can discriminate one enantioface (*si* face) of the substituted olefins. In connection with these findings, we have been interested in the kinetic resolution of the racemic olefin *trans*-cyclooctene **1** by complete discriminative coordination to the chiral {Ru–pybox} fragment. Isolation of chiral *trans*-cyclooctene and its transition metal complex was reported about thirty years ago by resolution of the diastereomeric complex **B** obtained from the platinum–benzylamine derivative and racemic *trans*-cyclooctene.[3] A few platinum, iron, and copper complexes (**C**, **D**, and **E**, respectively) of chiral or racemic *trans*-cyclooctene were also reported.[4] Here we present a new method for the direct trapping of one enantiomer of *trans*-cyclooctene from *cis*-cyclooctene by photochemical reaction. This process was also applied to the in situ trapping of the thermally unstable *trans*-cycloheptene from *cis*-cycloheptene.

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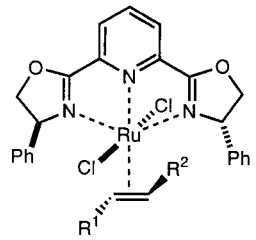
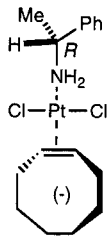
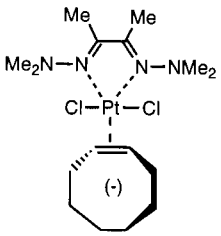


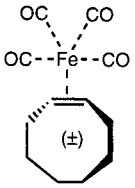
A[2]



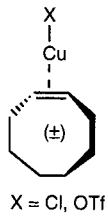
B[3b,3c]



C[3f]



D[4a]

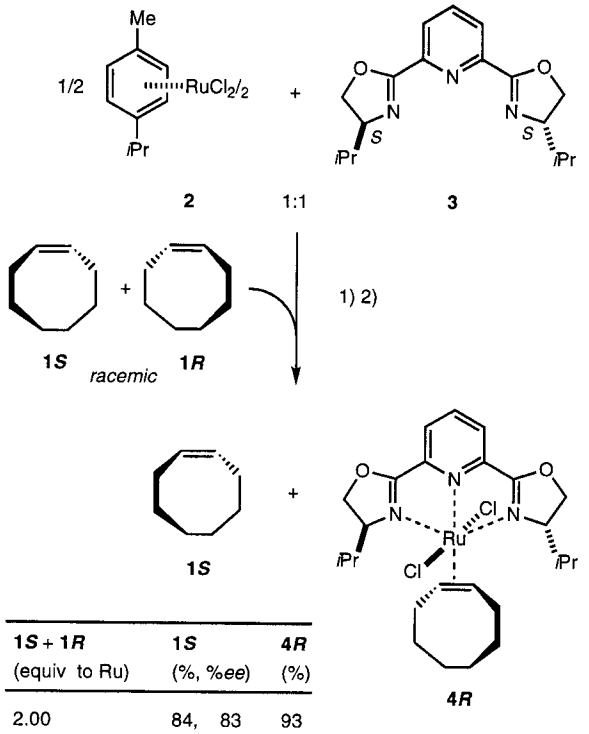


E[4b,4c]

Results and Discussion

First, we attempted a kinetic resolution, that is an enantioselective capture, of racemic *trans*-cyclooctene **1**[5] by reaction with a mixture of [{(*p*-cymene)$RuCl_2$}$_2$] (**2**)[6] and (*S*,*S*)-pybox-*ip* (**3**).[7] We eventually found the following optimal procedure: racemic *trans*-cyclooctene **1** (0.4 mmol, 2 equiv with respect to **2**) was added to a solution of [{(*p*-cymene)$RuCl_2$}$_2$] (**2**) and pybox-*ip* **3** (1 equiv with respect to **2**) in dichloro-

methane at 15 °C under an atmosphere of propylene and argon (1 atm). Propylene can accelerate the formation of the {$RuCl_2$(pybox)} fragment by coordination, but it readily dissociates. After stirring for 1 h under reduced pressure a distillate was obtained that contained (+)-(*S*)-*trans*-cyclooctene (**1*S***) in 84 % yield (83 % *ee*).[3] The solid residue was analyzed by ^{1}H NMR spectroscopy to be a mixture of [$RuCl_2$(pybox-*ip*){(−)-(*R*)-*trans*-cyclooctene}] (**4*R***) and probably [$RuCl_2$(pybox-*ip*){(+)-(*S*)-*trans*-cyclooctene}] (**4*S***) (ca. 95:5). Chromatographic separation of the residue through silica gel at 0 °C afforded only complex **4*R*** in 93 % yield, whereas complex **4*S*** could not be isolated because of decomposition (Scheme 1). Complex **4*R*** is thermally stable

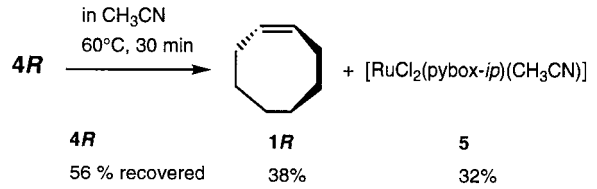


1S + 1R (equiv to Ru)	1S (%, %ee)	4R (%)
2.00	84, 83	93
1.73	65, 100	85

Scheme 1. Reaction procedure: 1) compounds **2** and **3** in CH_2Cl_2, propylene (1 atm), RT (25–30 °C), 2 h; 2) racemic olefin **1** was added at 15 °C, 1 h.

in solution or on exposure to air. Further attempts to isolate complex **4*S*** were not successful. A higher reaction temperature of over 15 °C and a reaction time of longer than 1 h caused isomerization (50–100 %) of the free *trans*-cyclooctene to *cis*-cyclooctene, which was catalyzed by unidentified ruthenium species; the yield of the desired complex also decreased to about 60 %. We also observed that *cis*-cyclooctene itself did not form the corresponding complex with the {Ru–pybox-*ip*} fragment. Use of 1.73 equiv of *trans*-cyclooctene (0.345 mmol) **1** to **2** (0.10 mmol) gave the optically pure (+)-(*S*)-*trans*-cyclooctene (**1*S***) in 65 % yield, as well as complex **4*R*** in 85 % yield based on **1**.

Recovery of another enantiomer (−)-(*R*)-*trans*-cyclooctene (**1*R***) from complex **4*R*** was attempted by heating **4*R*** in acetonitrile at 60 °C for 30 min, which yielded 38 % pure **1*R*** and 32 % [$RuCl_2$(pybox-*ip*)(CH_3CN)] (**5**); 56 % of complex **4*R*** was also reclaimed (Scheme 2). Thus, racemic *trans*-cyclooctene (**1**) was completely separated into its enantiomers by this method of enantioselective coordination and subsequent separation.[8]



Scheme 2. Recovery of (*R*)-*trans*-cyclooctene **1*R*** from complex **4*R***.

The molecular structure of the complex **4*R*** was solved by single-crystal X-ray analysis (Figure 1). The coordinated olefin **1*R*** is captured on the C_2-chiral, monovacant site of the {$RuCl_2$(pybox-*ip*)} fragment by coordination of its *exo-si,si* olefinic face.

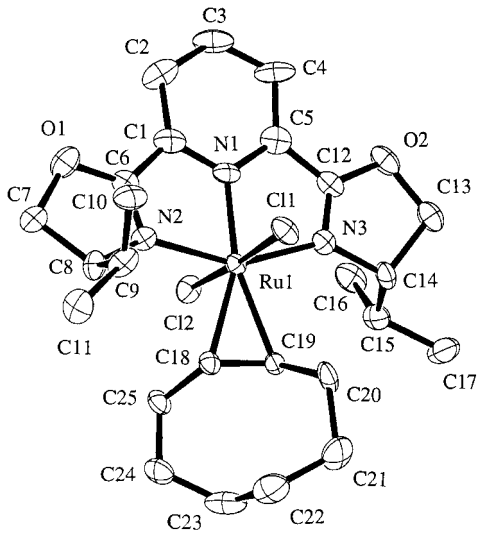


Figure 1. X-ray crystal structure of **4*R***; the CH_2Cl_2 molecule has been omitted.

The C18–C19 bond length in **4*R*** of 1.41 Å is similar to the value (1.42 Å) for the corresponding acrolein complex of the {Ru–pybox} fragment as previously reported by us (Table 1),[2] but is in contrast that of the corresponding Pt–benzylamine complex of *trans*-cyclooctene **B** (1.35 Å).[3] The

Table 1. Selected bond lengths [Å] and angles [°] of **4*R***.

Ru1–Cl1	2.396(4)	Ru1 – Cl2	2.408(4)
Ru1 – N1	1.99(1)	Ru1 – N2	2.11(1)
Ru1–N3	2.12(1)	Ru1–C18	2.22(2)
Ru1–C19	2.21(2)	C18–C19	1.41(2)
C18–C25	1.46(2)	C19–C20	1.50(2)
Cl1-Ru1-Cl2	174.8(2)	Cl1-Ru1-C18	96.2(4)
Cl1-Ru1-C19	90.7(5)	C18-Ru1-C19	37.2(5)
Ru1-C18-C19	70(1)	Ru1-C19-C18	71(1)
C18-C19-C20	120(1)	C25-C18-C19	122(1)
N2-Ru1-N3	151.9(5)	Ru1-C18-C25	123(1)
Ru1-C19-C20	121(1)	C20-C19-C18-C25	125(1)
N1-Ru1-C18-C19	175(1)		

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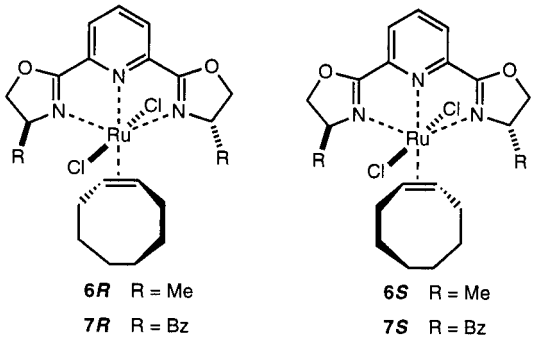
dihedral angle of C25-C18-C19-C20 is decreased to 125°, compared with a calculated dihedral angle of 139° for free *trans*-cyclooctene (Figure 1).[9] In other words, the cyclic side chains are bent away from the ruthenium center, so as to form a stable bond and reduce steric repulsion from the staggered isopropyl groups of the pybox ligand.

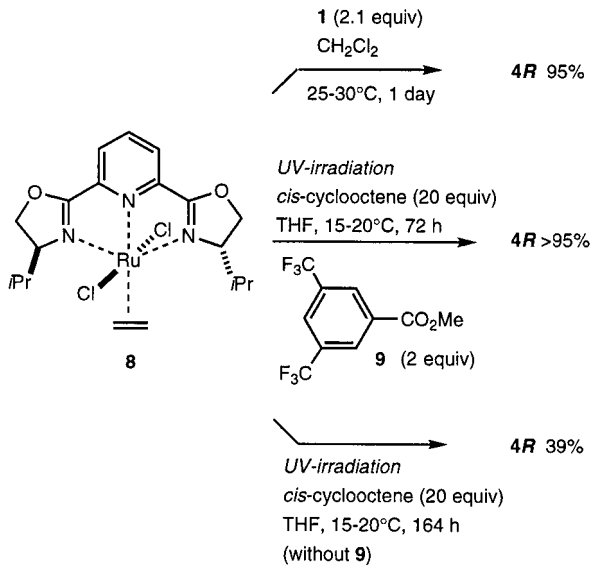
We have, so far, not obtained the corresponding olefin complex of [$RuCl_2$(pybox-*ip*)] with 1,2-alkyl- or aryl-disubstituted olefins such as *trans*-2-butene and *trans*-stilbene. In contrast, *trans*-cyclooctene forms a stable complex when coordinated at the vacant site of the octahedral {Ru–pybox} fragment.

However, the enantiofacial selectivity was changed by variation of the substituents on the pybox ligand, such as methyl and benzyl groups to give pybox-*me* and pybox-*bz*, respectively. A mixture of the complexes of (−)-(*R*)- and (+)-(*S*)-cyclooctene (**1*R*** and **1*S***) was obtained under the same reaction conditions as those for pybox-*ip*: with pybox-*me*, **6*R*** + **6*S*** (85% after column chromatography, 76:24), **1*S*** (97%, 25% *ee*); pybox-*bz*, **7*R*** + **7*S*** (87% after column chromatography, 78:22), **1*S*** (68%, 31% *ee*); the olefinic protons: ^{1}H NMR $\delta = 5.62$ and 5.50 for **6*R*** and **6*S***, $\delta = 5.82$ and 5.70 for **7*R*** and **7*S***.



Alternatively, we employed [$RuCl_2$(pybox-*ip*)(C_2H_4)] (**8**)[10] (0.2 mmol) as the starting ruthenium complex. The olefin-exchange reaction between *trans*-cyclooctene (**1**) (0.42 mmol) and complex **8** occurred smoothly to give the desired complex **4*R*** in high yield (95%) (Scheme 3). The recovered cyclooctene (66%) was mostly found in the *cis* form through isomerization, as the exchange reaction required more time (ca. 1 day) and a higher reaction temperature (25–30 °C).

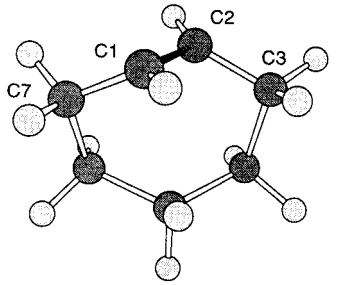
We next attempted to trap the chiral *trans*-cyclooctene in situ directly from the ethylene complex **8** and *cis*-cyclooctene by UV irradiation in the presence of methyl 3,5-ditrifluoromethylbenzoate (**9**) as a photosensitizer.[5] A solution of *cis*-cyclooctene (20 equiv with respect to **8**) and the ethylene complex **8** in THF with compound **9** (2 equiv with respect to **8**) was irradiated for 72 h at room temperature to produce the *trans*-cyclooctene complex **4*R*** in 95% yield based on **8**. In this reaction medium racemic *trans*-cyclooctene (**1**) generated in situ was thought to be enantioselectively trapped. The ethylene complex **8** itself is very stable and not changed by UV irradiation of its solution in THF over several days. Therefore, the release of the ethylene molecule from **8** was concluded to be induced by the olefin exchange reaction. Moreover, we found that the ethylene complex **8** itself acts as a photosensitizer to give the *trans*-cyclooctene complex **4R** (39%) by irradiation of *cis*-cyclooctene in THF for 164 h. The activity of **8** as a photosensitizer was below about 0.2 that of compound **9**.



Scheme 3. Ligand exchange reaction between ethylene complex **8** and *trans*-cyclooctene **1**, together with details of UV irradiation.

We have thus demonstrated enantiomeric discrimination of *trans*-cyclooctene by enantiofacially selective coordination. This phenomenon depends very much on the geometry of olefin coordination in the [$RuCl_2$(pybox-*ip*)] system. The parallel orientation of the olefin skeleton to the pybox plane (or N-Ru-N) brings one of the olefin enantiofaces toward the similar chiral cavity of the {$RuCl_2$(pybox-*ip*)} fragment.

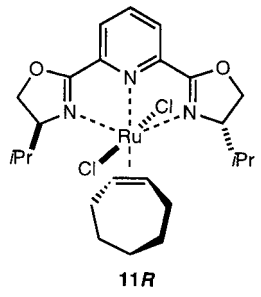
Finally, the method of irradiation and trapping in situ was applied to racemic *trans*-cycloheptene (**10**), which can not be isolated at ambient temperature. The sole case of its capture reported to date is found in a nonchiral copper complex.[11] Irradiation of (*cis*-cycloheptene)copper(I) trifluoromethanesulfonate [Cu^I(OTf)(*cis*-C_7H_{12})] at 254 nm in solution in hexane caused *cis* → *trans* isomerization of the coordinated *cis*-cycloheptene and gave a stable [Cu^I(OTf)(*trans*-cycloheptene)] analogue of complex **E** (X = OTf), which was well characterized on the basis of its NMR spectra (^{1}H and ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 5.51$ and 107.3 for the olefinic part of the *cis*-cycloheptene complex; $\delta = 4.55$ and 100.2 for those of the *trans*-cycloheptene complex[11]). We carried out the reaction with the Ru–pybox system under similar conditions to those used for *trans*-cyclooctene. A mixture of the ethylene complex **8**, *cis*-cycloheptene (30 equiv), and the photosensitizer **9** (10 equiv) in THF was irradiated for 180 h to give a new compound (75% yield) that proved to be a mixture (1:1) of the corresponding diastereomeric complexes **11*R*** and **11*S*** on the basis of NMR analysis (for the coordinated olefinic parts $\delta = 5.22$ and 5.38, $\delta = 80.3$ and 82.5). We also confirmed that *cis*-cycloheptene itself does not yield the corresponding complex with the {$RuCl_2$(pybox-*ip*)} fragment. Thus, we could successfully generate and capture racemic *trans*-cycloheptene with the [$RuCl_2$(pybox-*ip*)] species. The non-enantioselective capture may arise from the fact



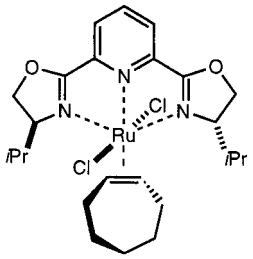
10

(*R*)-*trans*-cycloheptene

C7-C1-C2-C3 = 118°



11*R*



11*S*

that the cavity of the {$RuCl_2$(pybox-*ip*)} fragment is too wide to bind one of the enantiomers of **10** selectively, since free *trans*-cycloheptene has a smaller dihedral angle of 118° (based on calculations for a small molecule).[12]

Experimental Section

General: All reactions were carried out under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded at 270 and 67.8 MHz, respectively, on a JEOL JNM-GX 270 spectrometer with 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 recorder. 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). Optical purity was determined on a Shimadzu Capillary Gas Chromatograph 14A with a chiral capillary column (Supelco β-DEX 225, 30 m). The pybox and [$RuCl_2$(pybox)(C_2H_4)] reagents were prepared by our method.[10] *trans*-Cyclooctene was synthesized by photoisomerization of *cis*-cyclooctene with a photosensitizer.[5] The photoreaction was carried out under argon in a quartz-glass vessel with a low-pressure mercury lamp (32 W, Riko–Kagaku Sangyo Co. Ltd., UVL-32LP).

Reaction of the Ru(*p*-cymene) complex and pybox-*ip* with *trans*-cyclooctene: A mixture of [{(*p*-cymene)$RuCl_2$}$_2$] (**2**)[6] (61.2 mg, 0.10 mmol) and pybox-*ip* (**3**) (60.3 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature (25–30 °C) for 2 h under a propylene atmosphere (1 atm). The solution was cooled to 15 °C, after which a solution of racemic *trans*-cyclooctene (44 mg, 0.40 mmol; 66.7 μL, 6.0 N) in pentane was added. The reaction mixture was stirred for 1 h. The solvent was then removed under reduced pressure and trapped at −78 °C. The residue was redissolved in benzene (1 mL), and the resulting solution was evaporated and trapped (3 times). The solution was analyzed by gas chromatography with a chiral Supelco β-DEX (30 m) column and with *n*-nonane as an internal standard: 18.4 mg (0.167 mmol, 42%), 83% *ee* (*S*). At 55 °C, retention times were 46.5 min for the *cis* form, 47.6 min for (−)-(*R*)-*trans* form, and 49.0 min for (+)-(*S*)-*trans* isomer. The solution was analyzed with a polarimeter to show the (+)-sign of rotation. The residual solids were found by ^{1}H NMR spectroscopy to contain a 95:5 ratio of the isomers by integral of the coordinated olefin protons; $\delta = 5.59$ for **4*R*** and 5.40 for **4*S***. The solids were then passed through a silica gel column with CH_2Cl_2/CH_3OH solution as eluent to give only the pure complex **4*R*** (109 mg, 0.186 mmol, 93% yield). **4*R***: dark violet solid; $R_f = 0.58$ (CH_2Cl_2/CH_3OH = 10:1, silica gel plate Merck Art 5315); decomp. 175–177 °C; IR (KBr disk): $\tilde{\nu} = 2920$, 1488, 1449, 1395, 1252, 962 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si): $\delta =$ 0.76 (d, $J = 6.8$ Hz, 6H; CH_3), 1.01 (d, $J = 6.8$ Hz, 6H; CH_3), 1.43–1.54 (m, 2H), 1.82–2.00 (m, 2H), 2.17–2.50 (m 4H), 4.64 (m, 2H), 4.76–4.88 (m, 4H), 5.59 (m, 2H, olefinic), 7.88 (br s, 3H; protons of pyridine ring); ^{13}C NMR (67.8 MHz, C_6D_6): $\delta = 15.0$, 19.4, 30.0, 30.4, 37.1, 39.4, 70.8, 71.1, 87.7 (olefinic ^1J(C-H) = 148.7 Hz)*, 122.4, 132.4, 145.8, 163.7; $C_{25}H_{37}N_3O_2Ru(0.4\,CH_2Cl_2)$: calcd C 49.40, H 6.17, N 6.80; found C 49.31, H 6.12, N 6.93. (* cf. ^1J(C-H) = 150.6 Hz for the olefinic carbons in *trans*-cyclooctene).

X-ray analysis of 4*R*: A single crystal ($0.15 \times 0.2 \times 0.25$ mm) was obtained by recrystallization from CH_2Cl_2/*n*-pentane solution. Crystal data for **4*R***: $C_{25}H_{37}N_3O_2Cl_2Ru(CH_2Cl_2)$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 14.668(3)$, $b = 16.398(3)$, $c = 12.552(4)$ Å, $V = 3019.2(9)$ Å^3, $\rho_{calcd} =$ 1.471 g cm^{-3}, $Z = 4$, $\mu = 9.00$ cm^{-1}. The intensity data ($2\theta < 55°$) were collected on a Rigaku AFC-7R diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), and the structure was solved by heavy-atom Patterson methods (DIRDIF92 PATTY). The final cycle of refinement was based on 2009 observed reflections ($I > 3\sigma I$) and 325 variable parameters, and converged with $R = 0.055$ and $R_w = 0.061$. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114262. Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB12 1EZ (UK) (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Recovery of (−)-(*R*)-*trans*-cyclooctene from 4*R*: Complex **4*R*** (58.4 mg, 0.10 mmol) was heated at 60 °C for 30 min in solution in acetonitrile (1 mL). The solvent was removed under reduced pressure and trapped at −78 °C to give an evaporate that was analyzed by gas chromatography as described above. Optically pure (*R*)-*trans*-cyclooctene was obtained in 38% yield (0.038 mmol) in acetonitrile solution. The residue was passed through a silica gel column with CH_2Cl_2/CH_3OH solution as eluent to give the complex **4*R*** (32.8 mg, 0.056 mmol) and [$RuCl_2$(pybox-*ip*)(CH_3CN)] (**5**) (16.5 mg, 0.032 mmol).

Ligand exchange reaction with the ethylene complex 8 and *trans*-cyclooctene: A solution of the ethylene complex **8** (101 mg, 0.20 mmol) and *trans*-cyclooctene (46 mg, 0.42 mmol) in CH_2Cl_2 (2 mL) was stirred for 24 h. The same isolation procedure as described above yielded complex **4*R*** (95%, 111 mg, 0.19 mmol), together with cyclooctene (66%, 0.13 mmol, *cis*:*trans* = 86:14, 32% *ee* (*S*) for *trans*-cyclooctene) as detected by GC analysis.

UV irradiation of the ethylene complex 8 and *cis*-cyclooctene with photosensitizer 9: Complex **8** (50 mg, 0.10 mmol), photosensitizer **9** (55 mg, 0.20 mmol), and *cis*-cyclooctene (220 mg, 2.0 mmol) were placed in a quartz-glass vessel (50 mL) (held in a water bath) and dissolved in THF (1 mL) under an argon atmosphere. The solution was irradiated for 72 h at RT. The solution was concentrated and purified by silica gel column chromatography with CH_2Cl_2/CH_3OH solution as eluent to give complex **4*R*** (58 mg, 0.10 mmol, >95%) and a small amount of an organic polymeric impurity. The distillate from the solution was analyzed by GC and found to contain *trans*-cyclooctene (0.074 mmol, 33% *ee* (*S*)).

UV irradiation of the ethylene complex 8 and *cis*-cyclooctene (without photosensitizer 9): The irradiation reaction described above was carried out on the same scale for 72 h without the photosensitizer **9** to yield complex **4*R*** (20%). After 164 h, complex **4*R*** was obtained in 39% yield (23 mg, 0.039 mmol) together with some recovered ethylene complex **8** (23 mg, 0.046 mmol, 46%). A small amount of *trans*-cyclooctene was detected in the solution (3–9%, >90% *ee* (*S*)) by GC analysis.

UV irradiation of the ethylene complex 8 and *cis*-cycloheptene: Complex **8** (101 mg, 0.20 mmol), photosensitizer **9** (544 mg, 2.0 mmol), and *cis*-cycloheptene (577 mg, 6.0 mmol) were placed in a quartz-glass vessel (50 mL, held in a water bath) and dissolved in THF (2 mL) under an argon atmosphere. The solution was irradiated for 180 h at room temperature. The solution was subsequently concentrated and purified by silica gel column chromatography with CH_2Cl_2/EtOAc solution as eluent to give the complexes **11*S*** + **11*R*** (85 mg, 0.15 mmol, 75%); dark violet solid; $R_f =$ 0.56 (CH_2Cl_2/CH_3OH = 10:1, silica gel plate Merck Art 5315); ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si): $\delta = 0.70$ (d, $J = 6.8$ Hz, 3H; CH_3), 0.78 (d, $J =$ 6.8 Hz, 3H; CH_3), 0.98 (d, $J = 6.8$ Hz, 3H; CH_3), 1.02 (d, $J = 6.8$ Hz, 3H; CH_3), 1.95–2.20 (m, 7H), 2.35–2.57 (m, 4H), 4.32 (m, 1H), 4.54 (m, 1H), 4.70–4.90 (m, 4H), 5.22 (m, 1H; olefin), 5.38 (m, 1H; olefin), 7.85–8.00 (br, 3H; protons of pyridine ring); ^{13}C NMR (67.8 MHz, C_6D_6): $\delta = 14.7$ (×2), 18.6, 19.3, 26.7, 27.0, 28.7, 29.5, 31.3, 32.1, 33.9, 34.1, 71.4, 71.7, 71.8

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(×2), 80.3 (olefin), 82.5 (olefin), 122.0, 122.3, 133.3, 133.6, 144.7, 145.1, 163.1, 163.5; $C_{24}H_{35}N_3O_2Ru$: calcd C 50.61, H 6.19, N 7.38; found C 49.89, H 6.10, N 7.26.

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