Aryloxycarbonylcarbene Complexes of Bis(oxazolinyl)pyridineruthenium as Active Intermediates in Asymmetric Catalytic Cyclopropanations

Soon-Bong Park, Naoya Sakata and Hisao Nishiyama*

Dedicated to Professor Henri Brunner on the occasion of his 60th birthday

Abstract: The reaction of $[RuCl_2(pybox)(C_2H_4)]$ (**1**) (pybox = 2,6-bis[(4′*S*)-isopropyloxazolin-2′-yl]pyridine) and 2,6-di-*tert*-butyltolyl diazoacetate (**4**) (DBT-DA) in benzene at 50 °C gave a stable 2,6-di-*tert*-butyltolylcarbonylcarbene–ruthenium complex **5** in 94% yield. The structure of **5** was characterized by NMR spectroscopy. 2,6-Diisopropylphenyl diazoacetate (**6**) and 2,4,6-trimethylphenyl diazoacetate (**7**) also gave the corresponding carbene complexes **9** and **10**, respectively. Asymmetric carbene transfer from the carbene complexes to styrene resulted in formation of the *trans* isomer of phenylcyclopropanecarboxylates **2** with high enantioselectivity: **2** was obtained as the sole product in 80% yield (55% *ee*) from **5** at 80 °C and in 82% yield (97% *ee*) from **9** at 60 °C; from **10** at 40 °C, a mixture of **2** and **3** in a ratio of 97:3 was formed in 91% yield (97% *ee* for **2** and 99% *ee* for **3**). After the carbene transfer reaction, the ethylene complex **1** could be regenerated and isolated by treatment of the reaction mixture under an ethylene atmosphere. The carbene complexes **9** and **10** (2 mol%) exhibited catalytic activity in the asymmetric cyclopropanation of styrene with the corresponding diazoacetates.

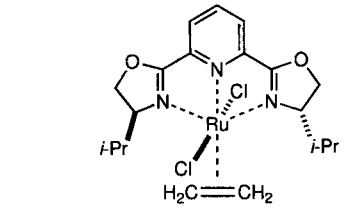
Keywords
asymmetric syntheses · carbene complexes · cyclopropanations · diazoacetates · ruthenium complexes

Introduction

The asymmetric cyclopropanation of olefins with diazoacetates catalysed by various transition metals complexed to nitrogen-based ligands has recently been explored.[1] We have reported on a chiral catalytic system of this type consisting of dichlororuthenium complexed to pybox [pybox = 2,6-bis(4-isopropyloxazolinyl)pyridine], which gives extremely high *trans*–*cis* selectivities of up to 98:2 with high enantioselectivities (Scheme 1).[2] We have also shown that the high *trans* selectivity can be attributed to the octahedral structure of the pybox–ruthenium system.

Asymmetric induction in the catalytic asymmetric cyclopropanation of olefins with diazoacetates has so far been explained in terms of a mechanism involving the formation of an alkoxycarbonylcarbene complex and subsequent carbene transfer to the olefin. However, such carbene complexes have not yet been isolated as intermediates for chiral copper or rhodium catalysts, which exhibit high asymmetric induction. Very recently some alkoxycarbene complexes have been reported for osmium and ruthenium porphyrin systems, which induce high *trans* selectivity in the carbene transfer to olefins.[3, 4]

We have been intrigued by the idea of obtaining a carbene complex of Ru–pybox, in order to explain the catalytic mechanism of this system.[5] We disclose herein the details of the isolation of chiral *aryloxycarbonylcarbene–ruthenium complexes* and their role as active intermediates in the asymmetric carbene transfer to styrene. We also discuss the reaction mechanism of the cyclopropanation with pybox–ruthenium catalysts.



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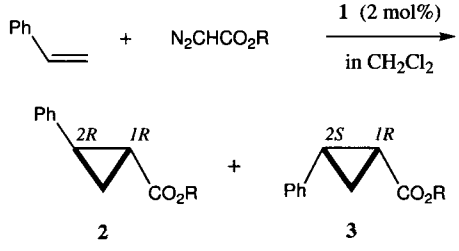

2 **3**

R = ethyl: **2**:**3** = 91:9, 89 %ee and 79 %*ee*
R = D-menthyl: **2**:**3** = 97:3, 87 %ee and 97 %*ee*
R = L-menthyl: **2**:**3** = 97:3, 96 %ee and 80 %*ee*

Scheme 1. Catalytic asymmetric cyclopropanation with the Ru–pybox catalyst.

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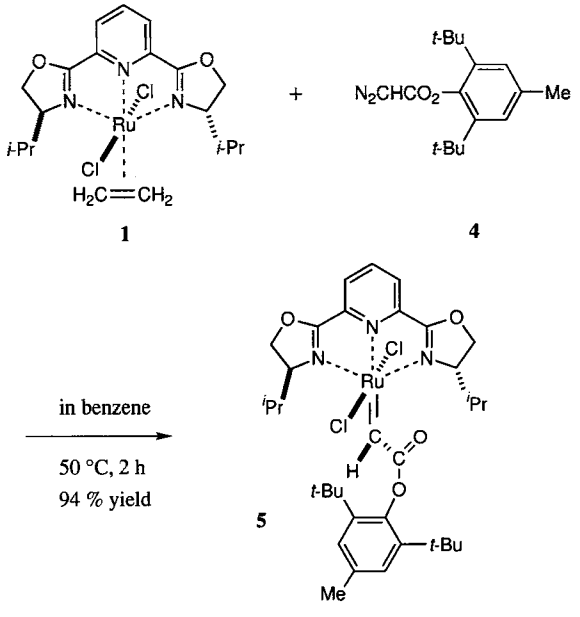
  0947-6539/96/0203-0303 $ 15.00+.25/0

Results and Discussion

We have already demonstrated the efficiency of our system in the asymmetric cyclopropanation with a variety of alkyl diazoacetates (Scheme 1). In general, it is reported that diazoacetates with bulky ester groups afford a high *trans* selectivity with any catalytic system. We therefore started with 2,6-di-*tert*-butyltolyl diazoacetate (DBT-DA) (**4**), which was previously reported by Doyle[6] and Evans,[7] as a promising candidate. However, no reaction was observed between **4** and styrene in dichloroethane in the presence of $[RuCl_2(pybox)(C_2H_4)]$ (**1**) (2 mol%), even at 60 °C, that is, none of the desired cyclopropanes or even dimerization products of the diazoacetates were detected. We supposed that the corresponding stable carbene complex had been formed. Indeed, by careful examination of the reaction mixture by TLC, we were able to observe the disappearance of the complex **1** and the formation of a new ruthenium complex.

The mixture of the complex **1** (0.3 mmol) and **4** (0.32 mmol) in benzene (5 mL) was heated at 50 °C for 2 h under an argon atmosphere. After concentration, the residue was purified on silica gel column at 0 °C with dichloromethane/methanol as eluent to give the new aryloxycarbonylcarbene complex **5** as a dark brown solid in 94% yield (Scheme 2). The complex **5** is thermal-



Scheme 2.

ly and air stable in the solid state but decomposes gradually in solution. ^1H and ^{13}C NMR spectra of **5** exhibited characteristic signals for the metal–carbene moiety ($Ru{=}CHCO_2$): a signal at $\delta = 21.67$ for $H_{carbene}$ and $\delta = 305.7$ for $C_{carbene}$ (Fig. 1.). The C–H coupling constant ($^1J_{C-H}$) is 142.4 Hz, indicating that hybridization of the carbene–carbon atom is close to sp^2.

Less bulky esters **6** and **7**, with 2,6-diisopropylphenyl and 2,4,6-trimethylphenyl substituents, respectively, reacted with **1** at somewhat lower temperature (45 and 40 °C) to give the corresponding aryloxycarbonylcarbene complexes **9** and **10**, respectively (Table 1). Phenyl diazoacetate **8** reacted with **1** at 0 °C to give the unstable carbene complex **11** in low isolated yield.

Our interest then turned to the carbene transfer experiments with the complexes **5**, **9** and **10** and to the degree of *trans*:*cis* selectivity and asymmetric induction that could be achieved with these complexes. The carbene transfer was examined in

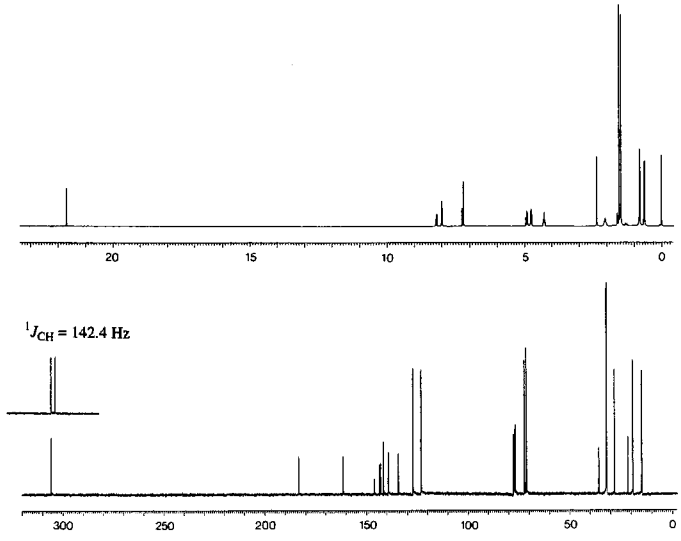
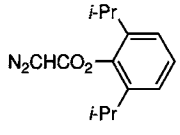
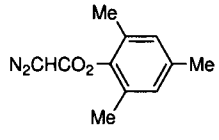
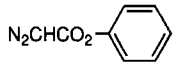


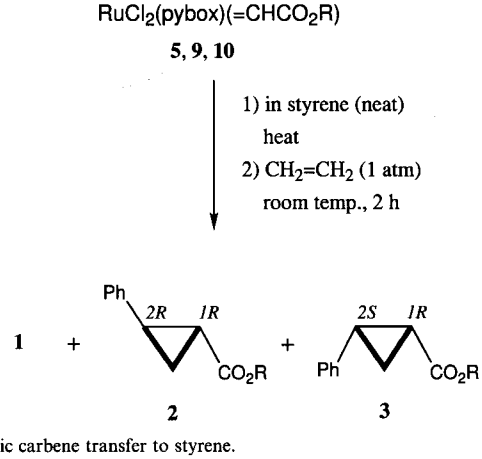
Fig. 1. ^1H (top) and ^{13}C NMR spectra (bottom) of the carbene complex **5** in $CDCl_3$.

Table 1. Some carbene complexes isolated by reaction of $[RuCl_2(pybox)(C_2H_4)]$ (**1**) with aryl diazoacetates.

Aryl diazoacetate		Carbene complex (yield, %)
	**6**	**9** (90)[a]
	**7**	**10** (92)[b]
	**8**	**11** (30)[c]

[a] 45 °C, 2 h. [b] 40 °C, 2 h. [c] 0 °C, 2 h.

neat styrene (ca. 80 equiv to the complex) with heating. The reaction of **5** and styrene proceeded at 80 °C to produce only the *trans*-cyclopropane derivative **2** (R = DBT) in 80% isolated yield (Scheme 3, Table 2). The enantiomeric excess of the



Scheme 3. Asymmetric carbene transfer to styrene.

0947-6539/96/0203-0304 $ 15.00+.25/0 Chem. Eur. J. 1996, 2, No. 3

Table 2. Carbene transfer from complexes **5**, **9** and **10** to styrene to give cyclopropanes **2** and **3** [a].

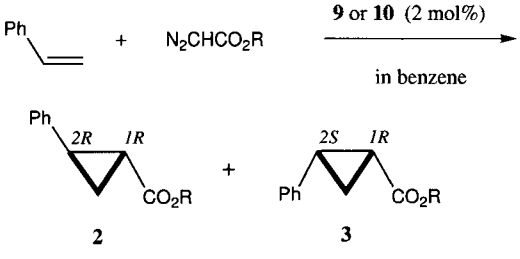
	T/°C	t/h	Yield/%	**2**:**3**	% *ee* **2**	% *ee* **3**
5	80	2	80	100:0	55	–
9	60	2	82	100:0	97	–
10	40	2	91	99:1	97	99

[a] Carbene complex (0.2 mmol) in styrene (ca. 2 mL); the ethylene complex **1** is recovered in 60–88% yields.

(1*R*,2*R*) product was 55% (Scheme 3). The reaction of the diisopropyl ester complex **9** proceeded smoothly at 60 °C and also gave the *trans* isomer **2** as the sole product in 82% yield and with high enantiomeric excess (97%). The trimethylphenyl ester complex **10** gave a mixture of **2** and **3** (99:1) with high enantiomeric excesses. When the reaction mixtures were treated with ethylene (1 atm) at room temperature after heating, the ethylene complex **1** could be isolated in 60–80% yield. This indicates that the skeleton of [$RuCl_2$(pybox)(vacant or styrene)] was maintained in the reaction mixture.

Thus asymmetric carbene transfer reactions from the aryloxycarbonyl carbene complexes **5**, **9** and **10** proceeded with high *trans* selectivity and asymmetric induction under stoichiometric conditions. These complexes are also expected to be intermediates in catalytic asymmetric cyclopropanations with the Ru–pybox system. Moreover, we observed that the carbene transfer requires higher reaction temperatures than the formation of the corresponding carbene complexes. Therefore, the rate-determining step of the catalytic reaction must occur as part of the carbene transfer pathway.

Finally, the carbene complexes **9** and **10** (0.04 mmol, turnover number = 50) were found to act as catalysts in the reaction of styrene (10 mmol) with the corresponding diazoacetate **6** and **7** (2.0 mmol), respectively (Scheme 4). The *trans*-cyclopropane **2**



Scheme 4.

was obtained exclusively with **9** and a mixture of the *trans*- and *cis*-cyclopropanes **2** and **3** with **10** (Table 3). However, the enantioselectivity with which **2** was formed decreased slightly to around 92–93% with multiple use of the catalysts, because of unanticipated decomposition of the catalysts. The results obtained with **9** and **10** are almost as good as those obtained with the ethylene complex **1** as catalyst (Table 3).

Table 3. Catalytic asymmetric cyclopropanations of styrene with aryl diazoacetates **6** and **7** to give cyclopropanes **2** and **3** [a].

Cat.	Diazoacetate	T/°C	Yield/%	**2**:**3**	% *ee* **2**	% *ee* **3**
9	**6**	60	90	100:0	92	–
1	**6**	60	92	100:0	92	–
10	**7**	50	95	98:2	93	>98
1	**7**	50	95	98:2	93	>98

[a] Catalyst (0.04 mmol, 2 mol%, styrene (10 mmol), diazoacetate (2 mmol), benzene.

Conclusion

We have explained the mechanism of the asymmetric cyclopropanation of olefins with diazoacetates catalysed by Ru–pybox complexes, by isolation of the corresponding carbene complexes as active intermediates and realization of the asymmetric carbene transfer to styrene.

Experimental Section

General: All reactions were carried out under nitrogen. ^1H and ^{13}C NMR spectra were recorded at 270 and 67.8 MHz, respectively, on a JEOL JNM-GX270 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 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). Optical purity was determined by Shimadzu Capillary Gas Chromatograph 14A with a chiral capillary column (Astec Chiraldex B-DA, 30 m). Pybox (2,6-bis[(4'*S*)-isopropyloxazolin-2'-yl]pyridine and [$RuCl_2$(pybox)(C_2H_4)] were prepared by our previously reported method [2]. Aryloxycarbonyl diazoacetates **6** and **7** were prepared by a literature method [6]. **6**: yellow solid, m.p. 77 °C; ^1H NMR: δ = 1.22 (d, J = 7.3 Hz, 12H), 3.00 (m, 2H), 5.02 (br, 1H), 7.10–7.25 (m, 3H). **7**: yellow solid, m.p. 66 °C; ^1H NMR: δ = 2.14 (s, 6H), 2.25 (s, 3H), 5.00 (br, 1H), 6.86 (s, 2H).

[$RuCl_2$(pybox)(=$CHCO_2$DBT)] (**5**): A solution of [$RuCl_2$(pybox)(C_2H_4)] (**1**) (150 mg, 0.30 mmol) and 2,6-di-*tert*-butyltolyl diazoacetate (**4**) (91 mg, 0.32 mmol) in benzene (5 mL) was heated at 50 °C for 2 h. The reaction was monitored by TLC (R_f = 0.53 for the product **5** and 0.60 for **1** with *i*PrOH:CH_2Cl_2:hexane 1:3:5). After concentration of benzene, the residue was transferred onto a silica gel (20 g) column at 0 °C with CH_2Cl_2:MeOH (100:1) as eluent. The dark brown band was collected and concentrated to give **5** as a brown solid (208 mg, 0.28 mmol) in 94% yield: m.p. 149 °C (decomp.): ^1H NMR: δ = 0.63 (d, J = 7.3 Hz, 6H), 0.76 (d, J = 7.3 Hz, 6H), 1.46 (s, 9H), 1.54 (s, 9H), 2.04 (m, 2H), 2.35 (s, 3H), 4.27 (m, 2H), 4.78 (t, J = 8.6 Hz, 2H), 4.94 (t, J = 8.6 Hz, 2H), 7.21 (s, 2H), 7.99 (d, J = 8.6 Hz, 2H), 8.20 (t, J = 8.6 Hz, 1H), 21.68 (s, 1H); ^{13}C NMR: δ = 14.63, 18.99, 21.41, 27.86, 31.70, 31.89, 35.59, 71.22, 72.23, 122.9, 127.0, 134.2, 139.0, 141.4, 142.9, 143.4, 145.9, 161.1, 183.2, 305.7 ($^1J_{CH}$ = 142.4 Hz); IR (KBr disk): 1705 cm^{-1}; Analysis calcd for $C_{34}H_{47}N_3O_4RuCl_2$ (0.5CH_2Cl_2): C, 53.39; H, 6.23; N, 5.41; found: C, 53.48; H, 6.26; N, 5.30.

[$RuCl_2$(pybox)(=$CHCO_2$-2,6-diisopropylphenyl)] (**9**): The procedure was similar to that described above for **5**: [$RuCl_2$(pybox)(C_2H_4)] (**1**) (150 mg, 0.30 mmol), 2,6-diisopropylphenyl diazoacetate (**6**) (81 mg, 0.33 mmol), benzene (5 mL), 45 °C, 2 h; monitored by TLC (R_f = 0.53 for the product **9** with *i*PrOH:CH_2Cl_2:hexane 1:3:5). Silica-gel column chromatography: 0 °C with CH_2Cl_2:MeOH (100:1). **9**: brown solid (186 mg, 0.27 mmol) in 90% yield: m.p. 113 °C (decomp.): ^1H NMR: δ = 0.76 (d, J = 7.3 Hz, 6H), 0.83 (d, J = 7.3 Hz, 6H), 1.26–1.28 (m, 12H), 2.2 (m, 2H), 3.64 (m, 2H), 4.19 (m, 2H), 4.78 (t, J = 7.3 Hz, 2H), 4.95 (t, J = 7.3 Hz, 2H), 7.20–7.30 (br, 3H), 8.01 (d, J = 7.3 Hz, 2H), 8.19 (t, J = 7.3 Hz, 1H), 21.11 (s, 1H); ^{13}C NMR: δ = 14.22, 18.66, 22.69, 23.31, 23.64, 26.72, 27.48, 29.16, 36.38, 70.83, 71.91, 122.6, 123.4, 125.0, 125.9, 138.6, 140.9, 144.4, 160.8, 184.9, 301.8 ($^1J_{CH}$ = 143.4 Hz); IR (KBr disk): 1713 cm^{-1}; Analysis calcd for $C_{31}H_{41}N_3O_4RuCl_2$ (0.4CH_2Cl_2): C, 51.97; H, 5.81; N, 5.79; found: C, 51.85; H, 5.98; N, 5.65.

[$RuCl_2$(pybox)(=$CHCO_2$-2,4,6-trimethylphenyl)] (**10**): The procedure was similar to that described for **5**: [$RuCl_2$(pybox)(C_2H_4)] (**1**) (150 mg, 0.30 mmol), 2,4,6-trimethylphenyl diazoacetate (**7**) (74 mg, 0.36 mmol), benzene (5 mL), 40 °C, 2 h; monitored by TLC (R_f = 0.52 for the product **10** with *i*PrOH:CH_2Cl_2:hexane 1:3:5). Silica-gel column chromatography at 0 °C with CH_2Cl_2:MeOH (100:1). **10** (180 mg, 0.28 mmol) in 92% yield: m.p. 120 °C (decomp.): ^1H NMR: δ = 0.71 (d, J = 7.9 Hz, 6H), 0.84 (d, J = 7.9 Hz, 6H), 2.21 (m, 2H), 2.28 (s, 3H), 2.36 (s, 6H), 4.13 (m, 2H), 4.77 (t, J = 7.9 Hz, 2H), 4.93 (t, J = 7.9 Hz, 2H), 6.91 (s, 2H), 8.08 (d, J = 7.9 Hz, 2H), 8.20 (t, J = 7.9 Hz, 1H), 21.11 (s, 1H); ^{13}C NMR: δ = 14.71, 17.25, 19.09, 20.69, 27.91, 71.34, 72.29, 122.9, 129.1, 130.9, 135.0, 138.6, 141.37, 145.3, 161.2, 184.7, 302.8 ($^1J_{CH}$ = 143.4 Hz); IR (KBr disk): 1706 cm^{-1}; Analysis calcd for $C_{28}H_{35}N_3O_4RuCl_2$: C, 51.77; H, 5.43; N, 6.47; found: C, 51.78; H, 5.41; N, 6.26.

Carbene transfer from 5 to styrene: A solution of the carbene complex **5** (147 mg, 0.2 mmol) in styrene (2 mL) was heated at 80 °C for 3 h under an argon atmosphere. After cooling to room temperature, the mixture was stirred under an ethylene atmosphere for 1 h. The mixture was concentrated and purified on a silica gel column with dichloromethane then dichloromethane/methanol. The last run (brown band) was collected to give **1** (82 mg, 0.164 mmol) in 82% yield. The first run was again purified with hexane/ether to give **2**–DBT (59 mg, 0.16 mmol) in

80% yield: $[\alpha]_D^{22} = -104$ ($c = 0.5$, CH_2Cl_2); ^{1}H NMR: $\delta = 1.37$ (br s, 18H), 1.52 (m, 1H), 1.73 (m, 1H), 2.18 (m, 1H), 2.32 (s, 3H), 2.70 (m, 1H), 7.10 (s, 2H), 7.15–7.35 (m, 5H). **2**–DBT was converted with $LiAlH_4$, CrO_3/H_2SO_4 (John's oxidation) and then diazomethane to the corresponding methyl ester **2**–Me for the determination of % *ee* by GLPC: 55% *ee* (1*R*,2*R*); see ref. [2b].

Carbene transfer of 9 to styrene: The procedure was similar to that for **5**: the carbene complex **9** (138 mg, 0.2 mmol), styrene (2 mL), 60 °C, 3 h, under an argon atmosphere. The ethylene complex **1** (61 mg, 0.12 mmol) was recovered in 61%. **2**–2,6-diisopropylphenyl (53 mg, 0.164 mmol) was obtained in 82% yield; ^{1}H NMR: $\delta = 1.15$–1.27 (m, 12H), 1.50 (m, 1H), 1.79 (m, 1H), 2.22 (m, 1H), 2.83 (m, 1H), 2.98 (m, 2H), 7.15–7.30 (m, 8H). The ester was converted to the methyl ester **2**–Me by hydrolysis with NaOH in refluxing ethanol followed by methylation with diazomethane for chiral GLPC analysis: 97% *ee* (1*R*,2*R*).

Carbene transfer of 10 to styrene: The procedure was similar to that for **5**: the carbene complex **10** (130 mg, 0.2 mmol), styrene (2 mL), 40 °C, 3 h, under an argon atmosphere. The ethylene complex **1** (89 mg, 0.177 mmol) was recovered in 88%. **2**–2,4,6-trimethylphenyl (51 mg, 0.18 mmol) was obtained in 91% yield; ^{1}H NMR of *trans* isomer: $\delta = 1.48$ (m, 1H), 1.78 (m,1H), 2.13 (s, 6H), 2.19 (m, 1H), 2.26 (s, 3H), 2.81 (m, 1H), 6.85 (s, 2H), 7.15–7.37 (m, 5H). A mixture of the *trans* and *cis* ester was converted to the methyl esters **2**–Me by hydrolysis with NaOH in refluxing ethanol followed by methylation with diazomethane for chiral GLPC analysis, 97% *ee* (1*R*,2*R*) for *trans*-**2**–Me and 99% *ee* (1*R*,2*S*) for *cis*-**2**–Me (*trans*:*cis* = 99:1).

Catalytic reaction of styrene and 6 in the presence of 9: To a solution of the carbene complex **9** (28 mg, 0.04 mmol) and styrene (1.1 mL, 10 mmol) in benzene (1 mL) was added a solution of 2,6-diisopropylphenyl diazoacetate **6** (493 mg, 2.0 mmol) in benzene (2 mL) through a microsyringe pump (ca. 4 μL per drop) over 6 h at 60 °C. After the mixture had been stirred for an additional 17 h, the benzene was removed under reduced pressure. The residual oil was purified by silica gel column chromatography with hexane/ether. The desired product *trans*-**2**–2,6-diisopropylphenyl (579 mg, 1.80 mmol) was obtained in 90%: $[\alpha]_D^{22} = -184$ ($c = 0.8$, CH_2Cl_2): 92% *ee* (1*R*,2*R*), by GLPC of the corresponding methyl ester.

Catalytic reaction of styrene and 7 in the presence of 10: To a solution of the carbene complex **10** (26 mg, 0.04 mmol) and styrene (1.1 mL, 10 mmol) in benzene (1 mL) was added a solution of 2,4,6-trimethylphenyl diazoacetate **7** (408 mg, 2.0 mmol) in benzene (2 mL) through a microsyringe pump (ca. 4 μL per drop) over 6 h at 50 °C. After the mixture had been stirred for an additional 19 h, benzene was removed under reduced pressure. The residual oil was purified by silica gel column chromatography with hexane/ether. The desired product **2**–2,4,6-trimethylphenyl (540 mg, 1.9 mmol) was obtained in 95% yield: 93% *ee* (1*R*,2*R*) for the *trans* isomer and >98% *ee* for the *cis* isomer (1*R*,2*S*) (ratio = 98:2) by GLPC of the corresponding methyl ester.

Catalytic reaction of styrene with 1: The procedure was the same as described above with **1** (20 mg, 0.04 mmol) instead of **9** and **10**.

Received: July 13, 1995 [F168]

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