that there are no highly blocked sequences along the copolymer chains. The micellar nanospheres were prepared by dropwise addition of the various blend solutions of MAF/PCL in DMF into water, with moderate stirring. The appearance of a bluish hue signals the formation of micelles. The mixture was stirred for approximately 24 h at room temperature, and then DMF was removed by dialysis with pure water, which resulted in stable homopolymer/copolymer micelles in water. The micellar structure was locked by cross-linking the hydrophilic shell layer through condensation reactions between the carboxylic acid groups of poly(methylacrylic acid) (PMAA) and the amino groups of hexamethylenediamine in the presence of 1-(3-dimethyl-aminopropyl)-3-ethylcarbdiimide methiodide, which activates the carboxylic acid at room temperature.[3a] The cross-linked product was then dialyzed with distilled water for 3 days to remove the by-products of the reaction. The success of the cross-linking was confirmed by the fact that the resultant nanoparticles maintained their integrity upon switching the medium from water to a solvent mixture containing a large proportion of DMF. DLS (Malven Autosizer-4700) studies on the cross-linked particles found that no particle aggregation had taken place, which meant that there had been almost, zero interparticle cross-linking. For conducting biodegradation of the core, an appropriate amount of dust-free lipolase solution in water (Novozymes Co.) and dilute aqueous NaOH solution was added into the SCK nanoparticulate dispersion.[6] Typical reaction conditions: MAF-3/PCL (1:1, w/w), 50% cross-linked, $C = 2.9 \times 10^{-4}$ g mL^{-1}, pH 8–11 at 25 °C. TEM imaging was performed on a Philips CM 120 electron microscope at an accelerating voltage of 80 kV. The specimens were prepared on copper grids coated with a thin carbon film.

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An Efficient and Highly Enantio- and Diastereoselective Cyclopropanation of Olefins Catalyzed by Schiff-Base Ruthenium(II) Complexes**

Jason A. Miller, Wiechang Jin, and SonBinh T. Nguyen*

Dedicated to Professor Robert H. Grubbs on the occasion of his 60th Birthday

Compounds containing the cyclopropane fragment have received considerable attention because of their frequent occurrence in natural products and their importance as valuable synthetic intermediates.[1–3] Since the introduction of chiral cyclopropanation catalysts by Nozaki et al.,[4] Aratani et al.,[5] and Nakamura et al.,[6] transition-metal-catalyzed asymmetric cyclopropanation has emerged as one of the most efficient synthetic routes to the optically pure cyclopropane fragment.[2,7] Perhaps the most difficult aspect of these asymmetric cyclopropanations is the simultaneous control of yield and regio-, diastereo-, and enantioselectivity while maintaining functional group tolerance.[8,9] In cyclopropanation studies of chiral copper[10–15] and rhodium[16–18] complexes it was found that high enantioselectivities and high diastereoselectivities usually do not go hand-in-hand unless reactions were carried out in an intramolecular manner. Further, in the case of intermolecular cyclopropanation, best enantio- and diastereoselectivities are often only achieved with large diazo esters.

Since the early 1980s, a number of ruthenium complexes have been shown to catalyze olefin cyclopropanation.[1] In view of the advantages that ruthenium-based catalysts have over copper- and rhodium-based catalysts in functional-group tolerance and cost, respectively, the last decade has witnessed an increase in the number of reports on ruthenium-based cylopropanation catalysts, many of which are porphyrin-based.[19–21] Because of the well-known challenges associated with porphyrin synthesis, especially when chiral porphyrins are involved, non-porphyrin multidentate ligands have attracted a lot of attention from investigators over the last few years. In 1994, Nishiyama and co-workers employed a chiral Ru–pybox catalyst (pybox = bis(oxazolinyl)pyridine) for the cyclopropanation of styrene with *tert*-butyl diazoacetate (*t*BDA) and menthyl diazoacetate (MDA) which resulted in high enantio- and *trans*-selectivity.[22–25] However, when the smaller—and more common—diazo ester ethyl diazoacetate (EDA) is employed in this reaction, selectivities are much lower (see Table 1, entry 9). Recently, Katsuki and co-workers

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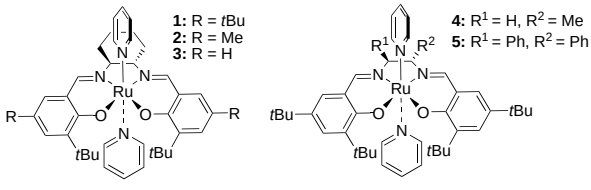
Table 1. Asymmetric cyclopropanation of styrene with EDA catalyzed by complexes **1**–**5**[a] in comparison to other catalysts. Bold-faced data indicate the best values.

Entry	[Ru] cat./ref.	Diazo ester	*t* [h]	*trans*:*cis*	Yield [%][b]	*trans* (% *ee*[c])	*cis* (% *ee*[c])
1	(*S*,*S*)-**1**	EDA	3	**10.8:1**	95	98 (1*S*,2*S*)	96 (1*S*,2*R*)
2	(*R*,*R*)-**1**	EDA	3	**10.8:1**	95	99 (1*R*,2*R*)	96 (1*R*,2*S*)
3	(*S*,*S*)-**2**	EDA	3	10.6:1	**96**	99 (1*S*,2*S*)	95 (1*S*,2*R*)
4	(*R*,*R*)-**2**	EDA	3	10.6:1	94	99 (1*R*,2*R*)	96 (1*R*,2*S*)
5	(*S*,*S*)-**3**	EDA	3	10.7:1	90	98 (1*S*,2*S*)	95 (1*S*,2*R*)
6	(*R*,*R*)-**3**	EDA	3	10.7:1	95	99 (1*R*,2*R*)	95 (1*R*,2*S*)
7	(*R*)-**4**	EDA	3	7.2:1	93	12 (1*R*,2*R*)	25 (1*R*,2*S*)
8	(*R*,*R*)-**5**	EDA	3	3.4:1	95	**> 99 (1*R*,2*R*)**	**> 99 (1*R*,2*S*)**
9	Nishiyama[22]	EDA[d]	12–20	11.5:1	69	88 (1*R*,2*R*)	78 (1*R*,2*S*)
10	Katsuki[39]	*t*BDA	24, irradiation	1:13.3	45[e]	N/A	97 (1*S*,2*R*)
11	Zheng[34]	EDA	14	1:1.9	15[f]	13 (1*R*,2*R*)	0

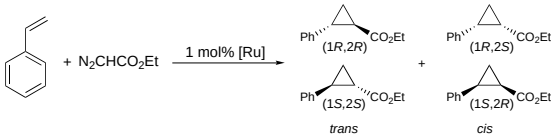
[a] Reaction conditions: EDA (0.5 mmol), styrene (2.5 mmol), catalyst (0.005 mmol), CH_2Cl_2, 3 h. [b] GC yield with undecane as an internal standard. [c] Determined by using Supelco β-DEX series chiral GC columns (see Supporting Information for method). Absolute configuration determined from known standards. [d] Slow addition of diazo ester over 4 h is required. [e] ^{1}H NMR yield. [f] GC yield with diethyl adipate as internal standard.

reported the use of a Ru(BINOL–derived salcen) complex as a catalyst in the photo-induced cyclopropanation of styrene with *t*BDA (salcen = *trans*-1,2-cyclohexanediamino-*N*,*N*′-bis-(salicylidene)).[26] In spite of the high enantio- and *cis*-selectivity reported, the reaction yields for Katsuki's catalyst were generally low (Table 1, entry 10). Further, owing to photolytic conditions reaction times for Katsuki's catalysts are generally long and optimal selectivity is only reported for the more bulky *t*BDA. Recently, Munslow and co-workers reported the use of nonplanar α-*cis* ruthenium biaryldiimine complexes to cyclopropanate olefins with EDA.[27] They reported good yields and diastereoselectivities and moderate to good enantioselectivities, however, the substrate scope was limited to styrene derivatives and tethered substrates and the ligand synthesis is quite complicated. More recently, Tang and co-workers have also reported a [Ru(pyridyldiimine)Cl_2] catalyst for the cyclopropanation of styrene with EDA.[28] Herein, we report the high-yield syntheses of the chiral Ru–salen complexes **1**–**5** containing *trans*-oriented pyridine ligands (H_2salen = *N*,*N*′-bis(salicylidene)ethylenediamine).[29,30] These compounds are very efficient catalysts for the asymmetric cyclopropanation of both electron-rich and electron-deficient olefins with EDA to give predominantly *trans* products with exceptionally high enantioselectivity. EDA was chosen as the test case because it is the most readily available diazoester and, because of its small size, one of the most difficult carbene precursors to employ in an enantioselective cyclopropanation reaction.



Complexes **1**–**5** were prepared from the reaction of the in situ prepared dilithium salt of the ligand, Li_2(salen), with [{$RuCl_2$(*p*-cymene)}$_2$], followed by the addition of excess pyridine at room temperature. Recrystallization of the dark-red crude products from toluene/hexanes mixtures afforded the analytically pure chiral ruthenium complexes in 48–86 % yield. ^{1}H and ^{13}C NMR (and X-ray diffraction[31]) studies revealed that these complexes contain two molecules of pyridine axially bound to the metal center in a *trans* coordination mode. Treatment of these pyridine complexes with excess PPh_3 resulted in no reaction which implies that pyridine binds tighter to the Ru center than PPh_3.

Complexes **1**–**5** were employed in catalytic amounts (1 mol %) for the cyclopropanation of styrene with EDA at ambient conditions [Eq. (1)]. Diastereo- and enantioselectivity results for these reactions are listed in Table 1 (entries 1–8). The presence of dimeric side products, such as diethyl fumarate and maleate, was negligible (< 1 %) for each reaction. For the cyclohexane-based system, the *trans*/*cis* ratio was found to be at least 10.6:1 in all cases, in stark contrast to that observed for Katsuki's Ru(BINOL–derived salcen) catalyst[26] where high *cis* selectivity is the norm. Katsuki's work (as well as current studies in our group) shows that substitution at the 3,3′-postitions of the salen ligand plays a large role in the diastereoselectivity of ruthenium(II)–salen catalysts, in contrast to that observed for the isoelectronic cobalt(III)–salen system.[32] The *trans*/*cis* selectivity for our salen-type catalysts decreases when other backbones are used which shows that the 3,3′-substituents are not the only factors governing diastereoselectivity. Exceptionally high enantiomeric excesses of cyclopropane products were found for both *trans* and *cis* isomers (Table 1). These remarkable *ee* values can be attributed to backbone substituents and the intrinsic properties of the highly effective salen ligand structure, which has also proven to be useful in other examples of asymmetric catalysis.[33] Interestingly, changing the substituent groups at the 5,5′-positions from H to Me to *t*Bu has little effect on the resulting product selectivity. Isolation of analytically pure catalyst is critical in our catalyst system. Zheng and co-workers have presumably generated the PPh_3 analogue of **1** in



(1)

situ but their cyclopropanation selectivities for styrene are quite low (Table 1, entry 11).[34]

The high *trans* selectivities of our ruthenium(II)–salen catalyst for the cyclopropanation of styrene can be rationalized by a ZINDO-minimized model structure calculation, which suggests that the olefin approach to the metal carbene intermediate (above the plane, as depicted in Figure 1) leads to a *trans* geometry between the olefin's substituent with

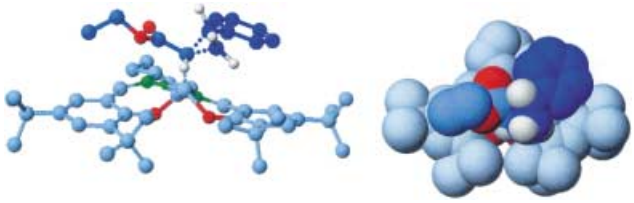


Figure 1. A ZINDO-optimized model structure of styrene as it approaches the putative (salen)Ru-EDA carbene intermediate. Left: a ball-and-stick model of this structure without a *trans* axial ligand. Right: a top-view space-filling model showing an optimal fit. A model structure with an additional *trans*-py axial ligand is given in the Supporting Information.

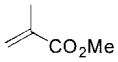
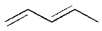
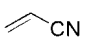
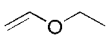
respect to the carbene group. This calculation supports our observations that substituents in the 5,5′-positions of the salen ligand do not significantly affect either diastereo- or enantioselectivity owing to their remote locations: the 5,5′-substituents are simply too far away from the metal carbene to influence its orientation. the 3,3′-substituents, however, are close enough to keep the singlet carbene locked in position while the olefin approaches.

The substrate scope of our catalyst system is quite remarkable and covers a whole range of conjugated, electron-rich, electron-poor, and aliphatic olefins with good enantioselectivity (Table 2). Methyl methacrylate (MMA) proves to be the most active substrate for our system: absolutely no carbene dimer was produced when only a 5:1 olefin:EDA ratio was used. However, all other substrates needed to be run at higher olefin concentrations to minimize carbene dimer formation. MMA is the substrate that gives the best diastereoselectivity (*trans*/*cis* = 100) and also shows opposite enantioselectivity from that for other olefins. These selectivities for MMA are the best observed to date.

Work carried out in the Doyle[35,36] and Nakamura[6,37] laboratories has shown that α,β-unsaturated carbonyl compounds and nitriles can yield racemic cyclopropanes through the decomposition of pyrazoline intermediates, which result from the noncatalyzed 1,3-dipolar cycloaddition of olefins with diazoesters. Although pyrazoline formation was a competing reaction in our ruthenium-catalyzed acrylonitrile cyclopropanation (Table 2), the enantiomeric excesses of the cyclopropane products are quite high which suggests that noncatalyzed cyclopropane formation from pyrazoline decomposition is only a minor pathway. In the case of MMA cyclopropanation catalyzed by our ruthenium–salen complexes, no evidence of the pyrazoline or olefin side-product formation normally associated with the 1,3-cycloaddition reaction[1] was observed and stereoselectivities are excellent. Thus, the 1,3-dipolar cycloaddition pathway is unlikely under our reaction conditions (dichloromethane, room temperature). Indeed, control reactions (0.5 mmol EDA, 2.5 mmol olefin, no catalyst, 5 mL CH_2Cl_2, 3 h, room temperature) show no evidence of pyrazoline formation when MMA was used. We have also taken steps to eliminate the possibility that pyrazoline adducts can be selectively decomposed to chiral cyclopropanes by our catalyst. Methyl methacrylate and acrylonitrile–2-pyrazoline adducts were separately synthesized[36] and then subjected to our catalyst under our typical cyclopropanation conditions. No tautomerization to 1-pyrazolines, pyrazoline decomposition, cyclopropane formation, or olefin side-product formation occurred. This leads us to believe that 1,3-dipolar cycloaddition is not a significant mechanistic pathway for our Ru^{II}–salen-type catalysts.

It is interesting to note that cyclopropanation of *trans*-piperylene with the nonsymmetrical catalyst (*R*)-**4** results in a

Table 2. Asymmetric cyclopropanation of other electron-rich and electron-deficient olefins with EDA catalyzed by complexes **1**, **4**, and **5**.[a] Bold-faced data indicate the best values.

Olefin	[Ru] cat.	*trans*:*cis*	Yield [%][b]	*trans* (% *ee*)[c]	*cis* (% *ee*)[c]
	(*R*,*R*)-**1**	100:1	26	2 (1*S*,2*S*)	Not observable
	(*R*)-**4**	**100:1**	**95**	**95 (1*S*,2*S*)**	Not observable
	(*R*,*R*)-**5**	100:1	53	91 (1*S*,2*S*)	Not observable
	(*R*,*R*)-**1**	1.8:1	57[d]	72 (1*R*,2*R*)	65 (1*R*,2*S*)
	(*R*)-**4**	1.6:1	93	39 (1*S*,2*S*)	44 (1*S*,2*R*)
	(*R*,*R*)-**5**	**1.9:1**	**97**	**89 (1*R*,2*R*)**	**90 (1*R*,2*S*)**
	(*R*,*R*)-**1**	**2.6:1**	26[e]	40 (1*R*,2*R*)	39 (1*R*,2*S*)
	(*R*)-**4**	2.1:1	**74**	15 (1*R*,2*R*)	38 (1*R*,2*S*)
	(*R*,*R*)-**5**	1.2:1	28	**58 (1*R*,2*R*)**	**62 (1*R*,2*S*)**
	(*R*,*R*)-**1**	4.1:1	80	**69 (1*R*,2*R*)**	**78 (1*R*,2*S*)**
	(*R*)-**4**	**4.4:1**	84	24 (1*R*,2*R*)	30 (1*R*,2*S*)
	(*R*,*R*)-**5**	3.8:1	**91**	68 (1*R*,2*R*)	67 (1*R*,2*S*)
	(*R*,*R*)-**1**	3.1:1	30	**90 (1*R*,2*R*)**	18 (1*R*,2*S*)
	(*R*)-**4**	2.9:1	**36**	49 (1*R*,2*R*)	26 (1*R*,2*S*)
	(*R*,*R*)-**5**	**4.3:1**	20	74 (1*R*,2*R*)	**56 (1*R*,2*S*)**

[a] Reaction conditions: 0.5 mmol EDA, neat olefin (used to minimize EDA dimer formation) with the exception of MMA (2.5 mmol olefin, 0.005 mmol catalyst, CH_2Cl_2, 12 h). Reactions are over within 2–3 h. [b] GC yield using undecane as an internal standard, with the exception of ethyl vinyl ether and 1-pentene where benzyl ether was used. [c] Determined by using Supelco β-DEX series chiral GC columns (see Supporting Information for method). Tentative absolute configurations determined by chiral GC elution orders.[40] [d] Only the terminal olefin of piperylene was cyclopropanated. [e] Pyrazoline formation was a competing reaction when acrylonitrile was cyclopropanated.[35]

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reversal of enantioselectivity in comparison to the use of (*R*,*R*)-**3** and (*R*,*R*)-**5**. This phenomenon has not been observed with any other olefin, including a variety of other conjugated olefins and olefins of similar size.[38] The reasons for this reversal of enantioselectivity are currently being investigated.

Although the cyclopropanation of the unactivated olefin 1-pentene with our catalysts affords quantitative EDA conversion, carbene dimerization is a significant competitor to cyclopropane production. Neither slow addition of the reactants (both olefin and EDA solutions) nor changing reaction conditions (temperature, solvent, and olefin concentrations) helped to reduce dimer formation. Nevertheless, the catalyst solution remains active for long periods in the presence of excess 1-pentene: successive addition of one equivalent EDA per day over four days continues to generate 2-propyl cyclopropanecarboxylic acid ethyl ester at the same rate and diastereoselectivity each time.

In summary, our ruthenium-based salen complexes constitute an important addition to the rank of modern asymmetric cycloproporation catalysts, as a result of their ease of synthesis, high activity/selectivity, and broad applicability to a wide range of electronically diverse terminal olefins.

Experimental Section

General procedures for the syntheses and characterizations of catalysts **1**–**5** and details of the calculation are available in the Supporting Information. Also included are all chiral GC methods and information regarding the characterization of cyclopropanes.

Preparation of complexes **1**–**5** (general procedure): Under an inert atmosphere, a THF solution (15 mL) of the salen ligand (1.5 mmol) was treated with lithium diisopropylamide (LDA; 2 mL of a 1.5 M solution of the monotetrahydrofuran complex in cyclohexane, 3.0 mmol) at 0 °C. After the addition was completed, the solution was allowed to warm up to room temperature and stirred for 1 h. This mixture was then added dropwise to a solution of $[\{RuCl_2(p\text{-cymene})\}_2]$ (460 mg, 0.75 mmol) and pyridine (1 mL) in THF (15 mL) at 0 °C. The reaction mixture was allowed to stir overnight. A dark-red solution was obtained, which was subsequently evaporated in vacuo. The residue was extracted into toluene (30 mL), filtered through a cannula, and evaporated under reduced pressure. Hexanes (20 mL) was then added to the residue to precipitate a dark red solid, which was filtered through a cannula and dried under vacuum. Further recrystallization with a toluene/hexanes mixture affords analytically pure compounds.

General procedure for the asymmetric cyclopropanation of styrene with EDA: A mixture of a chiral ruthenium–salen catalyst (0.005 mmol) and the olefin (2.5 mmol) in CH_2Cl_2 (1 mL) was placed in a 25-mL round-bottomed flask under N_2 in a glovebox. A CH_2Cl_2 solution (degassed three times) of EDA (0.50 mmol in 2.5 mL total volume) and internal standard (0.50 mmol) was slowly added through a gas-tight syringe over a period of 23 min under N_2. After the addition was complete the reaction mixture was allowed to stir for 12 h at room temperature. The solution was then passed through a short plug of silica gel to remove catalyst and washed with CH_2Cl_2 (15 mL). Samples were then analyzed by GC.

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