Strong Electronic Effects in the *cis*-Selective Asymmetric Cyclopropanation of Olefins Catalyzed by [RuCl(PNNP)]$^+$

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Dedicated to the memory of Professor *Luigi M. Venanzi*

The cationic [RuCl(PNNP)]$^+$ catalysts containing tetradentate ligands with a P_2N_2 donor set (PNNP) show strong electronic effects in the cyclopropanation of *para*-substituted styrenes. The reactivity trend confirms that the carbene transfer to the olefin has electrophilic character. Linear free-energy relationships are observed for the relative reactivity, the *cis*/*trans* selectivity, and for the enantioselectivity (of the *cis*-cyclopropane). The linear correlation between log (k_X/k_H) and σ shows a large value of ρ (-2.4), which is indicative of significant charge buildup in the transition state of the carbene transfer to the olefin. All the relevant parameters (reactivity, diastereoselectivity, and enantioselectivity) increase with the increasing electron density at the C=C bond. To define the scope of the [RuCl(PNNP)]$^+$ catalysts, 1- and 2-substituted styrenes, and oct-1-ene were also investigated.

Introduction. – The 'electronic tuning' of the ligands has emerged as a field of intense investigation devoted to optimizing the performance of enantioselective catalysts [1][2][3]. This concept is particularly relevant to catalytic reactions that occur without substrate precoordination and are, therefore, less sensitive to the steric effects of the ligands. The latter reactions encompass atom-transfer reactions such as epoxidation and cyclopropanation. In their pioneering work, *Jacobsen* and co-workers have investigated the electronic effects on the enantioselectivity of asymmetric epoxidation of olefins in the Mn(salen)-catalyzed (salen = bis(salicylidene)ethylenediamine) epoxidation [2]. In these systems, electronic effects are thought to determine the position of the transition state along the reaction coordinate, which is the critical factor that determines enantioselectivity. Electronic effects that obey a linear free-energy relationship have been observed also in the Cu-catalyzed asymmetric cyclopropanation of olefins. In general, such effects can be based on the catalyst [4] or on the substrate [5–8]. There is general agreement that the intermediate carbene complex has electrophilic character, which is reflected by the higher reactivity of electron-rich olefins [9][10].

We have recently reported some five-coordinate Ru complexes of general formula [RuCl(PNNP)]$^+$ (**2**), where PNNP is a chiral tetradentate ligand with a P_2N_2 donor set (**1**; *Scheme 1*). These complexes catalyze the asymmetric epoxidation of olefins with H_2O_2 as oxidant with enantiomeric excesses (ee) up to 42% [11], as well as the asymmetric cyclopropanation of olefins by decomposition of diazo esters [12]. The latter catalytic reaction gives the *cis*-cyclopropane derivative with high diastereo- and

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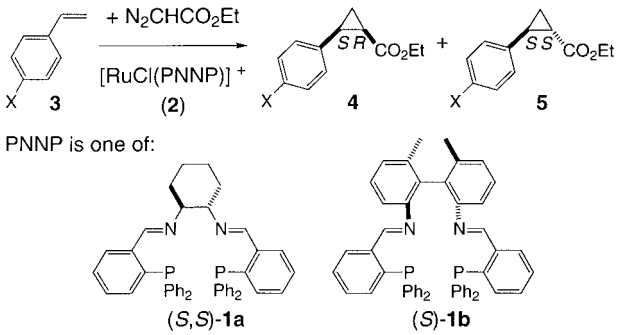
Scheme 1



enantioselectivity. With styrene, the *cis*-product is formed with 95% selectivity and 92% ee. Together with *Katsuki*'s salen-based catalysts [13], our system is one of the very few that give high *cis*-selectivity in the cyclopropanation of olefins.

In view of the formal analogy between the salen complexes mentioned above and our [RuCl(PNNP)]$^+$ systems, we started an investigation of the electronic effects in asymmetric cyclopropanation. Our aim is the electronic tuning of the PNNP ligands to improve the stereo- and enantioselectivity of the atom-transfer reactions, starting with the cyclopropanation reaction. To direct the synthesis of the new PNNP ligands, we decided to study first the electronic effects of the substrates. We describe herein the activity and selectivity trends observed in the cyclopropanation of *para*-substituted styrenes. Further, we investigated the scope of the reaction in terms of the substitution pattern of the C=C bond.

Results and Discussion. – The substrates used for the investigation of the *electronic effects* were the *para*-substituted styrenes *p*-X–C_6H_4–C(H)=CH_2 (X = H (**3a**), MeO (**3b**), ^{t}Bu (**3c**), Cl (**3d**), CF_3 (**3e**)). The PNNP ligands used were (1*S*,2*S*)-*N*,*N*′-bis[2-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine (**1a**) [14][15] and (*S*)-*N*,*N*′-bis[2-(diphenylphosphino)benzylidene]-6,6′-dimethyl-1,1′-biphenyl-2,2′-diamine [12], (**1b**) (*Scheme 1*). The five-coordinate complexes [RuCl(PNNP)]PF_6 (PNNP = **1a** : **2a**; PNNP = **1b** : **2b**) were prepared *in situ* from the corresponding dichloro

Table 1. *Cyclopropanation of* para-*Substituted Styrenes* p-$XC_6H_4C(H)=CH_2$ *Catalyzed by* **2b**[a])

Run	Olefin	X	Yield[b]) [%]	*cis*/*trans*	ee *cis* [%][c])
1	**3b**	MeO	71	37 : 63	71
2	**3c**	^{t}Bu	61	53 : 47	88
3	**3a**	H	51	51 : 49	92
4	**3d**	Cl	32	35 : 65	89
5	**3e**	CF_3	23	25 : 75	94

[a]) See *Exper. Part* for reaction conditions. [b]) Yields of isolated product refer to the sum of *cis*- and *trans*-isomers. [c]) The absolute configuration of ethyl *cis*-2-phenylcyclopropane-1-carboxylate is (1*R*,2*S*) [12]. The enantiomers of the *trans*-isomer could not be resolved by GC on several different chiral columns.

derivatives [$RuCl_2$(PNNP)] as described in [12]. We first carried out the cyclopropanation reaction with **2b** as the catalyst (*Table 1*), which usually gives the higher reaction yields [12]. This allowed us to isolate the cyclopropanation products and use them as GC reference (see *Exper. Part*).

Next, we performed pairwise competition experiments (*Scheme 2*) between styrene (**3a**) and the *para*-substituted derivatives, in which X is MeO ($\sigma = -0.28$), ^{t}Bu ($\sigma = -0.15$), Cl ($\sigma = 0.24$), or CF_3 ($\sigma = 0.53$), with **2a** as the catalyst (*Table 2*). These experiments were aimed at disclosing the electronic effects (if any) on the selectivity and on the reactivity of the previously detected carbene intermediate [12]. We chose catalyst **2a** as it gives *both* good enantioselectivity *and* high *cis*-selectivity. The results in *Table 2* show that the more electron-rich olefins are more reactive, which is in agreement with the electrophilic character of the carbene intermediate, as generally accepted in the case of the catalytic systems based on Ru [4], Fe [5], and Cu [6–8]. The relative rates follow a linear free-energy relationship. Indeed, the plot of log (k_X/k_H) *vs.* the *Hammett* σ parameter shows a linear correlation (*Fig. 1*)[2]). The fit gives $R^2 = 0.982$ with $\rho = -2.4$. The latter value indicates significant charge buildup at the benzylic C-atom in the transition state, as observed for the stoichiometric carbene transfer from the highly electrophilic iron-carbene complex [Fe=CH(Me)$(CO)_2$(Cp)]$^+$ ($\rho = -2.2$) [16]. Interestingly, [RuCl(PNNP)]$^+$ is more sensitive to substrate-based electronic effects than the catalytic systems based on iron-porphyrins ($\rho = -0.68$) [5] and Cu complexes ($\rho = -0.85$) [6]. This suggests a late transition state for the carbene transfer in the case of **2b** [5], as will be discussed below.

Scheme 2

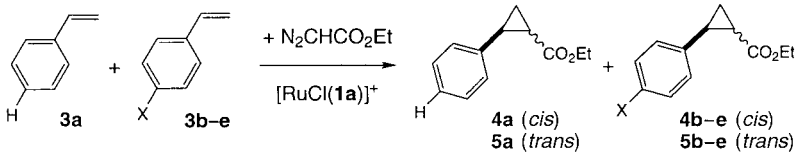


Table 2. *Pairwise Competition Cyclopropanation Experiments with* para-*Substituted Styrenes* p-$X-C_6H_4C(H)=CH_2$ *Catalyzed by* **2a**[a])

Run	Olefins	X	Conversion [%]		Yield [%][b])		*cis*/*trans*	
			3a	*p*-X–Styrene	**3a**	*p*-X–Styrene	**3a**	*p*-X–Styrene
1	**3b**/**3a**	MeO	7	99	4	28	83 : 17	95 : 5
2	**3c**/**3a**	^{t}Bu	13	31	7	25	91 : 9	94 : 6
3	**3d**/**3a**	Cl	30	9	15	6	87 : 13	82 : 18

[a]) See *Exper. Part* for reaction conditions. Olefin conversion and yields were determined by GC. In the **3e**/**3a** competition experiment, the GC peaks of **4a** and **4e**, and of **5a** and **5e** were not resolved. [b]) Yields of the cyclopropanation product are based on the olefin.

[2]) The relative reactivity k_X/k_H is defined as [(**4b**–**4e**) + (**5b**–**5e**)]/[(**4a**) + (**5a**)], the ratio between the total yield (in mol) of the X-substituted product and that of the styrene-derivative. This takes into account the total yield of the *trans*- and *cis*-isomers. The slow and continuous addition of the diazoacetate to the reaction solution rules out the measurement of initial rates. For an analogous treatment, see [5a]. We assume that the difference between conversion and yield in *Table 2* is due to olefin polymerization.

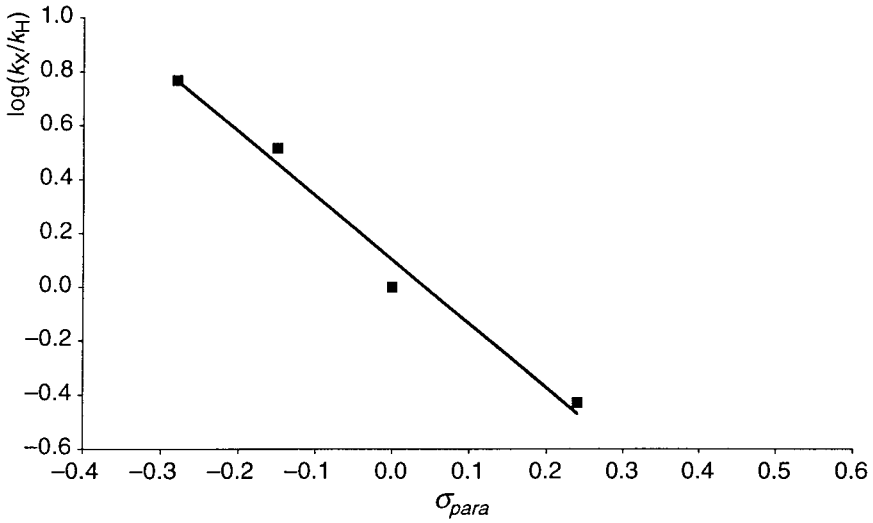


Fig. 1. Hammett *σ/ρ correlation for relative rates of cyclopropanation, log* (k_X/k_H) vs. σ_{para} *for* **3a**–**3d**

Further, each substrate **3** was tested singularly as to assess whether electronic factors affect the diastereo- and enantioselectivity. We chose catalyst **2a** to optimize the already good diastereo- and enantioselectivity[3]). The reactivity trend summarized in *Table 3* is analogous to that observed with catalyst **2b** (*Table 1*) and further confirms the electrophilic character of the intermediate carbene as discussed above. Both $[RuCl(PNNP)]^+$ catalysts, *i.e.*, **2a** and **2b**, distinctly show electronic effects of the substrate on the *cis*-selectivity. However, the dependence of the diastereoselectivity on the σ parameter is not linear for **2b** (*Table 1*). In contrast, the *cis*-selectivity of **2a** increases with increasing nucleophilicity of the olefin and is highest for X = MeO, *i.e.*, with the most reactive olefin (*Table 3*). A *Hammett* plot of log (*cis*/*trans*) (*cis*/*trans* is the ratio of *trans*- and *cis*-diastereoisomers) *vs.* σ shows a linear correlation ($R^2 = 0.991$) with $\rho = -0.83$ (*Fig. 2*). Interestingly, the trend reported above contrasts with that

Table 3. *Cyclopropanation of* para-*Substituted Styrenes* p-$X-C_6H_4C(H)=CH_2$ **3** *Catalyzed by* **2a**[a])

Run	Olefin	X	σ	Conversion [%]	Yield[b]) [%]	*cis*/*trans*	ee (*cis*)[c]) [%]
1	**3b**	OMe	–0.28	100	48	89 : 11	83
2	**3c**	^{t}Bu	–0.15	90	86	87 : 13	81
3	**3a**	H	0	65	25	83 : 17	81
4	**3d**	Cl	0.24	36	29	75 : 25	78
5	**3e**	CF_3	0.53	34	7	62 : 38	69

[a]) See *Exper. Part* for reaction conditions. [b]) Yields (GC) refer to the sum of *cis*- and *trans*-isomers. [c]) See *Footnote c* of *Table 1*.

[3]) As the diazo ester is consumed by the competitive homocoupling reaction, we used 2 equiv. of the diazoester to obtain reasonable yields also with the less-reactive olefins.

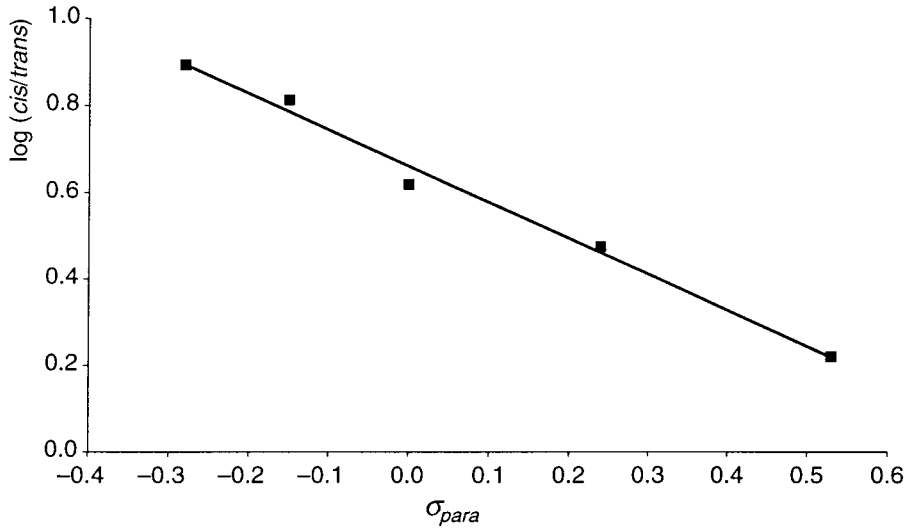


Fig. 2. Hammett *σ/ρ correlation for the* cis/trans *ratio, log (*cis/trans*)* vs. σ_{para} *for* **3a**–**3e**

observed for other cyclopropanation catalysts based on Ru [4] and Cu [7][8][13a], in which the *cis*/*trans*-ratio remains essentially constant over all the range of electronic properties of the substrate and ligand.

Finally, the electronic effects on the enantioselectivity obtained with catalyst **2a** are nearly independent of the σ parameter of the *para*-substituted styrene. A plot of log [(1*R*,2*S*)/(1*S*,2*R*)] *vs.* σ ((1*R*,2*S*)/(1*S*,2*R*) is the ratio of (*R*)- and (*S*)-enantiomers) is very roughly linear (with a poor R^2 value of 0.936), but ρ is as low as -0.35 (*Fig. 3*).

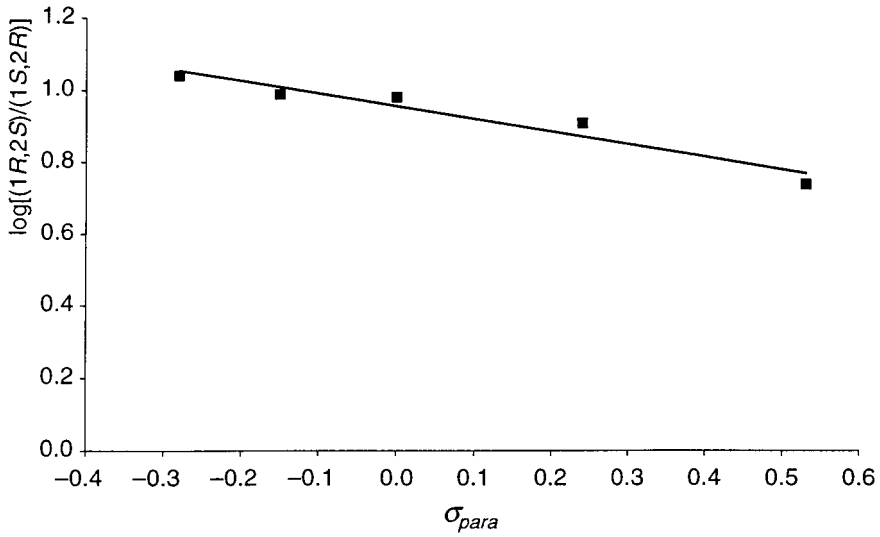


Fig. 3. Hammett *σ/ρ correlation for the enantiomeric ratio, log [(1*R,2S*)/(1*S,2R*)]* vs. σ_{para} *for* **3a**–**3e**

This effect is smaller than that observed with the Cu-catalyzed cyclopropanation of *para*-substituted styrenes ($\rho = 0.5$) [8]. Interestingly, the direction of the effect is reversed, and the Cu system gives the highest enantioselectivity with the most electron-poor olefin. Also, the electronic effect on the enantioselectivity is smaller than the ligand-based effects observed with chiral Ru pybox catalysts [4]. Despite its modest size, it goes in the right direction, as all three parameters (activity, *cis*-selectivity, and enantioselectivity) increase with the nucleophilicity of the olefin. Whatever the mechanistic implications of this trend might be, it suggests that the electronic tuning of the PNNP ligand should be appropriate.

Taken together, the above results allow some comments. Most importantly, all data confirm the electrophilic nature of the putative carbene intermediate. Then, the fact that the trends of enantioselectivity *vs.* ρ are opposite (at least qualitatively) for catalysts **2a** and **2b** (*Tables 3* and *1*, resp.) lend further support to our previous suggestion that catalysts **2a** and **2b** follow different mechanisms [12]. This was based on a model for the stereochemical course of the reaction catalyzed by **2a**, in which the carbene intermediate is assumed to be *trans*-[RuCl(C(H)COOEt)(PNNP)]$^+$. The latter species has been prepared by the reaction of **2a** with $N_2C(H)COOEt$ and characterized in solution. We tentatively suggest that, with catalyst **2b**, the configuration of the intermediate carbene could be different (for instance, *cis* instead of *trans*). The fact that we never observed a carbene intermediate in the reaction of **2b** with diazo esters [12] might also be a hint thereof.

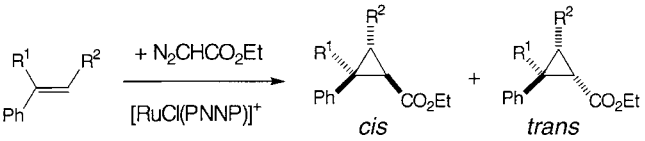
Finally, it should be noted that a parallel trend between reactivity and selectivity in cyclopropanation, as described above for the substrate-based effects with catalyst **2a**, has also been described for ligand-based effects in the case of pybox systems of *Nishiyama* and co-workers [4]. It is interesting that the Mn-catalyzed epoxidation of olefins, which is a strictly related atom-transfer reaction, shows the opposite trend, as the enantioselectivity decreases with increasing reactivity of the oxo intermediate. *Jacobsen*'s explanation was that the (ligand-based) electronic effects determine the position of the transition state along the reaction coordinate. Thus, the steric effects are maximized in a 'later' transition state, that is with the less reactive Mn=O intermediate, which, therefore, gives the higher enantioselectivity [2].

Clearly, the situation is apparently much less clear-cut in the Ru-catalyzed cyclopropanation with [RuCl(PNNP)]$^+$. This can be probably ascribed (at least in part) to the fact that four diastereoisomers are involved. However, we suggest *as a working hypothesis* that the lower intrinsic reactivity of the carbene intermediate as compared to the oxo complex (for a discussion of the relative reactivities of carbene and oxo ligands, see [17]) might be responsible for the different trend observed with cyclopropanation as compared to epoxidation. Indeed, the large ρ values observed in the competition reactions suggests that the carbene transfer to the olefin implies a late transition state, as observed for Fe(porphyrin)-catalyzed cyclopropanation [5]. In contrast, Rh-porphyrins are thought to give very early transition states [18]. It might be speculated that, when the transition state is a late one, the closeness of approach of the substrate is roughly independent of the electronic effects. Thus, the steric interactions between the carbene complex and the *p*-X-substituted styrene are similar with all substituents X. In other words, the electronic factors of the olefin do not affect significantly the steric crowding of each diastereoisomeric transition state (and, thus, its

energy). Eventually, the selectivity is determined by the difference of the reaction rates associated to the diastereoisomeric transition states. In this hypothesis, the more reactive substrate can be expected to give the larger rate difference for the formation of the diastereoisomeric products, as it gives the largest absolute energy difference between the diastereoisomers.

To determine the *scope* of the catalyst, we tested a variety of substituted aromatic and nonaromatic olefins (*Table 4*). As a model for a (*E*)-1,2-disubstituted olefin, we tested (*E*)-(prop-1-enyl)benzene (**8**). Catalyst **2a** was not active (*Run 1*), whereas **2b** gave low yield (15%, *Run 2*), but high stereoselectivity, as pure *trans*-isomer was formed (99.7% selectivity). However, the enantioselectivity is low (34%). This follows the general observation that the $[RuCl(PNNP)]^+$ catalysts give the *trans*-product with low or moderate enantioselectivity. Changing the substrate-to-catalyst ratio to 5 mol-% did not give any improvement. Interestingly, a Ru catalyst closely related to the $[RuCl(PNNP)]^+$ system gave the *trans*-cyclopropane-carboxylate with good yield and enantioselectivity [19]. However, also Cu-based catalysts lead to cyclopropanation of **8** with low or moderate diastereo- and enantioselectivity [20][21], which can be explained by the larger steric demand of this olefin as compared to styrene.

Table 4. *Cyclopropanation of Styrene Derivatives Catalyzed by* **2a** *and* **2b**[a])



8 R^1= H, R^2= Me
9 R^1= Me, R^2= H
10 R^1= Ph, R^2= H

Run	Catalyst	mol-%	Substrate	Yield [%]	*cis*/*trans*	ee [%] *cis*	ee [%] *trans*
1	**2a**	5	**8**	0	–	–	–
2	**2b**	1	**8**	15	0.3 : 99.7	n.d.[b])	34
3	**2a**	5	**9**	83	86 : 14	49[b])	7
4	**2a**[d])	5	**9**	90	76 : 24	23[b])	18
5	**2b**	1	**9**	89	49 : 51	75[b])	27
6	**2b**[d])	1	**9**	84	69 : 31	85[b])	48
7	**2b**[e])	1	**9**	87	70 : 30	85[b])	51
8	**2a**	5	**10**	57	–	26 (*S*)[c])	
9	**2b**	1	**10**	82	–	21 (*S*)[c])	

[a]) See *Exper. Part* for reaction conditions. Yields of isolated product refer to the sum of *cis*- and *trans*-isomers. [b]) Absolute configuration not determined. [c]) Absolute configuration (in parentheses) determined by the sign of the optical rotation [20]. [d]) $[Et_3O]PF_6$ was used as chloride scavenger instead of $TlPF_6$. [e]) Isolated **2b** as catalyst.

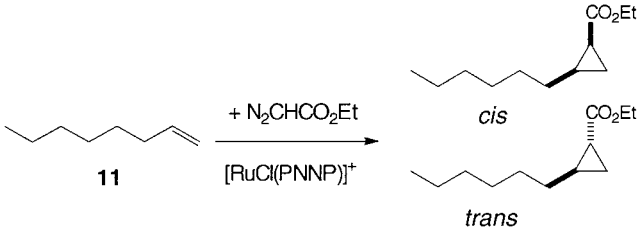
In agreement with the latter interpretation, 1,1-disubstituted olefins are more reactive. Thus, (1-methylethenyl)benzene (**9**) and 1,1-diphenylethene (**10**) give high (isolated) reaction yields with fair enantioselectivities (*Table 4*). Olefin **9** is cyclopropanated by **2a** with 86% *cis*-selectivity, but only 49% ee (7% ee for the *trans*-product, *Run 3*). Complex **2b** gives nearly quantitative yields (89%) and fair

enantioselectivity (75% ee for the *cis*-product), but the *cis*/*trans* ratio is 49 : 51 (*Run 5*), that is, in the range observed for styrene with this catalyst. In the case of **2b**, the diastereo- and enantioselectivity was improved by using $[Et_3O]PF_6$ for chloride abstraction from $[RuCl_2(\mathbf{1b})]$ instead of $TlPF_6$ (*Run 6*), or the preformed five-coordinate complex **2b** [11b]. In contrast, there is a slight loss of selectivity when the catalyst is formed *in situ* from $[RuCl_2(\mathbf{1a})]$ and $[Et_3O]PF_6$ (*Run 4*). This can be related to the formation of an ether adduct, which was monitored by ^{31}P-NMR [11b]. We have previouly observed that the aqua complex $[RuCl(OH_2)(\mathbf{1a})]^+$ (**2c**) is less selective than **2a** in the asymmetric epoxidation of olefins with H_2O_2 [11]. Thus, $[Et_3O]PF_6$ is a suitable chloride scavenger only for the synthesis of **2b**, which does not bind strongly to O-donors (including H_2O) [12].

Overall, these results suggest that the $[RuCl(PNNP)]^+$ catalysts are more sensitive to steric factors than *Katsuki*'s [RuCl(salen)(NO)], which gave good enantio- and *cis*-selectivity with **9** [13b]. In contrast, Cu-based catalysts [21][22], but also Ru-porphyrins [23], generally display *trans*-selectivity in the cyclopropanation of **9**. The related olefin 1,1-diphenylethene (**10**) is cyclopropanated in the presence of **2a** and **2b** with good yields, but the ee values are generally low and do not exceed 26% (*Table 4*; *Runs 8* and *9*). This confirms the detrimental effect of bulky substituents with the $[RuCl(PNNP)]^+$ catalysts, which are less effective with **10** than other Ru [19][23] and Cu [24] catalysts.

We have recently reported that **2b** cyclopropanates 2,5-dimethylhexa-2,4-diene with high *cis*- and enantioselectivity (up to 94 and 80%, resp.) [12]. The high selectivity, but also the low reaction yields (20%), can be explained by the steric requirements of the Me groups on the substrate. To verify this hypothesis, we tested a linear, nonaromatic olefin, *i.e.*, oct-1-ene (**11**). Indeed, **11** is more reactive than 2,5-dimethylhexa-2,4-diene, as the cyclopropanation product is formed with up to 65% isolated yield with catalyst **2b** (*Table 5*, *Run 2*). However, the diastereoselectivity is

Table 5. *Cyclopropanation of Oct-1-ene Catalyzed by* **2a** *and* **2b**[a])



Run	Catalyst	mol-%	Yield [%]	*cis*/*trans*	ee [%][b])	
					cis	*trans*
1	**2a**	5	20	60 : 40	64 (1*R*,2*S*)	18 (1*S*,2*S*)
2	**2b**	1	65	24 : 76	86 (1*R*,2*S*)	57 (1*S*,2*S*)
3[c])	**2b**	1	65	31 : 69	85 (1*R*,2*S*)	60 (1*S*,2*S*)
4[d])	**2b**	1	62	28 : 72	85 (1*R*,2*S*)	61 (1*S*,2*S*)

[a]) See *Exper. Part* for reaction conditions. Yields of isolated product refer to the sum of *cis*- and *trans*-isomers. [b]) Absolute configurations (in parentheses) were determined by the sign of the optical rotation [21]. [c]) $[Et_3O]PF_6$ was used as chloride scavenger instead of $TlPF_6$. [d]) Isolated **2b** as catalyst.

reversed as compared to 2,5-dimethylhexa-2,4-diene, as the *trans*-isomer is the major product (76%), which is formed with moderate enantioselectivity (57% ee). Again, the *cis*-cyclopropanation product (24%) shows the higher ee value (86% ee). However, in contrast with 2,5-dimethylhexa-2,4-diene, also catalyst **2a** was active with **11**, and gave a *cis*/*trans*-ratio of 60:40 and 64% ee for the *cis*-product (*Run 1*), which can be considered as a useful starting point. The same results are obtained with $Et_3O \cdot PF_6$ as chloride scavenger and with isolated **2b** as catalyst (*Runs 3* and *4*). To the best of our knowledge, no examples of *cis*-selective cyclopropanation of terminal olefins have been reported so far. The Cu-based catalysts generally give *trans*-selectivity with alk-1-enes [7][22][25].

In conclusion, the $[RuCl(PNNP)]^+$ complexes are viable catalysts for a wide spectrum of olefins. As generally observed with styrene derivatives, the enantioselectivity is higher for the *cis*-product than for the *trans*-isomer. Catalyst $[RuCl(\mathbf{2a})]^+$ shows strong electronic effects with *para*-substituted styrenes. It is encouraging that both enantio- and diastereoselectivity increase with the electron density at the olefinic C=C bond. Although ligand-based effects are generally smaller than substrate-based ones, we expect that electron-withdrawing substituents at the PPh_2 groups will improve reaction yield, selectivity, and enantioselectivity at the same time. Thus, the electronic tuning of the PNNP ligand will be the next step of our investigation.

Experimental Part

General. Reactions with air- or moisture-sensitive materials were carried out under Ar by *Schlenk* techniques. Styrene, 4-(trifluoromethyl)styrene and (+)-(1*S*,2*S*)-cyclohexane-1,2-diamine were obtained from *Fluka AG*, 2-(diphenylphosphino)benzaldehyde, 4-methoxystyrene, 4-chlorostyrene, and 4-(*tert*-butyl)styrene were purchased from *Aldrich*, $Tl[PF_6]$ from *Strem Chemicals*, and ethyl *trans*-2-phenylcyclopropane-1-carboxylate from *Lancaster*. (*S*)-6,6′-dimethyl-1,1′-biphenyl-2,2′-diamine was obtained from *Solvias AG* (Basel). Optical rotations: *Perkin-Elmer 341* polarimeter with a 1 dm-cell. ^{1}H- and ^{31}P-NMR spectra: *Bruker DPX* spectrometers; ^{1}H positive chemical shifts in ppm are downfield from TMS; ^{31}P-NMR spectra were referenced against external 85% H_3PO_4. MS: MS service of the Laboratorium für Organische Chemie; ETH-Zürich; a 3-NOBA (3-nitrobenzyl alcohol) matrix and a Xe-atom beam with a translational energy of 8 KeV were used for FAB^+-MS. Elemental analyses were carried out by the Laboratory of Elemental Analysis, ETH-Zürich.

Catalytic Cyclopropanation with 2b. – The reactions with all olefins and **2b** as catalyst were carried out according to the following procedure. Complex **2b** (20 mg, 21 μmol) and $Tl[PF_6]$ (7.5 mg, 21 μmol, 1 mol-% *vs.* olefin) were stirred in CH_2Cl_2 overnight. The resulting brown soln. was filtered over *Celite* (to remove the precipitated TlCl) and added to the corresponding olefin (2.16 mmol). A CH_2Cl_2 soln. (1 ml) of distilled ethyl diazoacetate (280 μl, 2.66 mmol, 1.25 equiv.) was added to the mixture over 6 h by syringe pump. The soln. was stirred for additional 14 h. After evaporation of the solvent, the product was isolated by column chromatography (CC; alumina; with hexane/AcOEt 9:1). Isolated yields, *cis*/*trans*-ratios, and ee values are reported in *Tables 1*, *4*, and *5* for **3a**–**3e**, **8**–**10**, and **11**, resp. Anal. and spectroscopic data are given below.

Ethyl 2-(4-Methoxyphenyl)cyclopropane-1-carboxylate. Yield (based on **3b**) 338 mg (71%) as a white, crystalline solid with a *cis*/*trans*-ratio of 37:63 (by GC analysis and ^{1}H-NMR integration). Achiral GC analysis: *Macherey-Nagel SE 54*, 30 m, carrier 92 kPa He. Temp. program: 50° isotherm for 5 min, then to 200° at 3° min^{-1}. t_R [min]: decane, 16.6; 4-methoxystyrene, 25.0; ethyl *cis*-2-(4-methoxyphenyl)cyclopropane-1-carboxylate, 48.6; ethyl *trans*-2-(4-methoxyphenyl)cyclopropane-1-carboxylate, 52.0. Chiral GC analysis: *Supelco beta-DEX 120*, 1.4 ml He min^{-1}; temp. program: 150° isotherm, t_R [min]: *cis*-(1*R*,2*S*), 46.6; *cis*-(1*S*,2*R*), 48.2; *trans*-(1*R*,2*R*) and *trans*-(1*S*,2*S*), 60.6 (not resolved). $[\alpha]_S^{20} = +32.1$ ($c = 1.135$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$; see [13b][13d] for literature values of the *cis*- and *trans*-isomers, resp.): 7.26–6.75 (*m*, 4 arom. H); 4.15 ([13d]: 4.16) (*q*, $J = 7.1$, MeCH_2 of *trans*-isomer); 3.90 ([13b]: 3.90) (*q*, $J = 7.1$, MeCH_2 of *cis*-isomer); 3.78 ([13d]: 3.78) (*s*, MeO of *trans*-isomer); 3.77 ([13b]: 3.77) (*s*, MeO of *cis*-isomer); 2.58–2.43 ([13b]: 2.52, *cis*) (2*ddd*, 1 + 1 H, cyclopropane H of *cis*- and *trans*-isomers, overlapped); 2.03 ([13b]: 2.03) (*ddd*, $J = 5.6, 7.8, 9.2$, 1 H, cyclopropane H of *cis*-isomer);

1.81 ([13d]: 1.82) (*ddd*, $J = 4.2$, 4.9, 8.3, 1 H, cyclopropane H of *trans*-isomer); 1.66 (*ddd*, $J = 5.0$, 5.6, 7.5, 1 H, cyclopropane H of *trans*-isomer); 1.56 ([13d]: 1.55) (*ddd*, $J = 4.6$, 4.9, 9.2, 1 H, cyclopropane H of *trans*-isomer); 1.40–1.20 ([13b]: 1.30 (*cis*); [13d]: 1.25 (*trans*)) (1 + 1 H, cyclopropane H of *trans*- and *cis*-isomers, buried under the signal of the Me of *trans*-isomer); 1.31 (*t*, $J = 7.3$, *Me*CH_2 of *trans* isomer); 1.02 ([13b]: 1.02) (*t*, $J = 7.3$, *Me* CH_2 of *cis*-isomer). EI-MS: 220.1 (M^+).

*Ethyl 2-[4-(*tert*-Butyl)phenyl]cyclopropane-1-carboxylate.* Yield (based on **3c**) 322 mg (61%) of a colorless oil with a *cis*/*trans*-ratio of 53 : 47 (by GC analysis and ^{1}H-NMR integration). Achiral GC analysis: *Macherey-Nagel SE 54*, 30 m, carrier 92 kPa He. Temp. program: 50° isotherm for 5 min, then to 200° at 3° min^{-1}. t_R [min]: decane, 16.6; 4-(*tert*-butyl)styrene, 27.9, ethyl *cis*-2-[4-(*tert*-butyl)phenyl]cyclopropane-1-carboxylate, 51.1; ethyl *trans*-2-[4-(*tert*-butyl)phenyl]cyclopropane-1-carboxylate, 54.0. Chiral GC analysis: *Supelco beta-DEX 120*, 1.4 ml He min^{-1}; temp. program: 150° isotherm, t_R [min] *cis*-(1*R*,2*S*), 48.4; *cis*-(1*S*,2*R*), 50.6; *trans*-(1*R*,2*R*) and *trans*-(1*S*,2*S*), 74.8 (not resolved). $[\alpha]_S^{20} = +52.9$ ($c = 0.99$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 7.33–7.03 (*m*, 4 arom. H); 4.16 (*q*, $J = 7.1$, Me*CH*$_2$ of *trans*-isomer); 3.85 (*AB* of *ABX*$_3$, $J = 2.7$, 7.1, Me*CH*$_2$ of *cis*-isomer); 2.61–2.44 (*m*, 1 + 1 H, cyclopropane H of *trans*- and *cis*-isomers); 2.05 (*ddd*, $J = 5.6$, 7.8, 9.3, 1 H, cyclopropane H of *cis*-isomer); 1.87 (*ddd*, $J = 4.1$, 5.3, 8.4, 1 H, cyclopropane H of *trans*-isomer); 1.69 (*ddd*, $J = 5.0$, 5.6, 7.5, 1 H, cyclopropane H of *cis*-isomer); 1.58 (*ddd*, $J = 4.5$, 5.2, 9.2, 1 H, cyclopropane H of *trans*-isomer); 1.4–1.2 (*m*, 1 + 1 H, cyclopropane H of *trans*- and *cis*-isomers, buried under the signal of *t*-Bu); 1.30 (*s*, *t*-Bu of *trans*-isomer); 1.29 (2*s*, 2 × 9 H, *t*-Bu of *cis*-isomer); 1.26 (*t*, $J = 7.3$, *Me*CH_2 of *trans*-isomer); 0.92 (*t*, X_3 of *ABX*$_3$, $J = 7.1$, *Me*CH_2 of *cis*-isomer. MS: 246 (M^+). Anal. calc. for $C_{16}H_{22}O_2$ (246): C 78.01, H 9.00, O 12.99; found: C 78.03, H 8.79, O 12.86.

Ethyl 2-(4-Chlorophenyl)cyclopropane-1-carboxylate. Yield (based on **3d**) 154 mg (32%) as a colorless oil with a *cis*/*trans*-ratio of 35 : 65 (by GC analysis and ^{1}H-NMR integration). Achiral GC analysis: *Macherey-Nagel SE 54*, 30 m,carrier 92 kPa He. Temp. program: 50° isotherm for 5 min, then to 200° at 3° min^{-1}. t_R [min]: decane, 16.6; 4-chlorostyrene, 20.8 ethyl *cis*-2-(4-chlorophenyl)cyclopropane-1-carboxylate, 46.7; ethyl *trans*-2-(4-chlorophenyl)cyclopropane-1-carboxylate, 49.4. Chiral GC analysis: *Supelco beta-DEX 120*, 1.4 ml He min^{-1}; temp. program: 150° isotherm, t_R [min]: *cis*-(1*R*,2*S*), 33.3; *cis*-(1*S*,2*R*), 34.0; *trans*-(1*R*,2*R*) and *trans*-(1*S*,2*S*), 41.8 (not resolved). $[\alpha]_S^{20} = +52.9$ ($c = 0.99$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$; see [13b] and [13d] for literature values of the *cis*- and *trans*-isomers, resp.): 7.26–7.0 (*m*, 4 arom. H); 4.17 ([13d]: 4.17) (*q*, $J = 7.1$, Me*CH*$_2$ of *trans*-isomer); 3.90 ([13b]: 3.90) (*q*, $J = 7.1$, Me*CH*$_2$ of *cis*-isomer); 2.56–2.43 (2*ddd*, 1 + 1 H, cyclopropane H of *trans*- and *cis*-isomers, overlapped); 2.08 ([13b]: 2.08) (*ddd*, $J = 5.5$, 7.9, 9.1, 1 H, cyclopropane H of *cis*-isomer); 1.86 ([13d]: 1.86) (*ddd*, $J = 4.3$, 5.2, 8.5, cyclopropane H of *trans*-isomer); 1.67 ([13b]: 1.67) (*ddd*, $J = 5.1$, 5.6, 7.5, 1 H, cyclopropane H of *cis*-isomer); 1.60 ([13d]: 1.60) (*ddd*, $J = 4.6$, 5.2, 9.2, 1 H, cyclopropane H of *trans*-isomer); 1.20–1.40 ([13b]: 1.33 (*cis*); [13d]: 1.28 (*trans*)) (2*ddd*, 1 + 1 H, cyclopropane H of *trans*- and *cis*-isomers, overlapped); 1.29 ([13d]: 1.28) (*t*, $J = 7.2$, *Me*CH_2 of *trans*-isomer); 1.02 ([13b]: 1.02) (*t*, $J = 7.2$, *Me*CH_2 of *cis*-isomer). EI-MS: 224 (M^+). Anal. calc. for $C_{12}H_{13}O_2$ (224): C 64.15, H 5.83, O 14.24; found: C 64.07, H 5.90, O 14.24.

Ethyl 2-[4-(Trifluoromethyl)phenyl]cyclopropane-1-carboxylate. Yield (based on **3e**) 121 mg (23%) of a colorless oil with a *cis*/*trans*-ratio of 25 : 75 (by GC analysis and ^{1}H-NMR integration). Achiral GC analysis: *Macherey-Nagel SE 54*, 30 m, carrier 92 kPa He. Temp. program: 50° isotherm for 5 min, then to 200° at 3° min^{-1}, t_R [min]: 4-(Trifluoromethyl)styrene, 12.3; decane, 16.6; ethyl *cis*-2-[4-(trifluoromethyl)phenyl]cyclopropane-1-carboxylate, 38.6; ethyl *trans*-2-[4-(trifluoromethyl)phenyl]cyclopropane-1-carboxylate, 41.5. Chiral GC analysis: *Supelco beta-DEX 120*, 1.4 ml He min^{-1}; temp. program: 110° for 10 min, 5° min^{-1} to 160°, isotherm for 20 min, t_R [min]: *cis*-(1*R*,2*S*), 22.8; *cis*-(1*S*,2*R*), 23.0; *trans*-(1*R*,2*R*) and *trans*-(1*S*,2*S*), 24.7 (not resolved). $[\alpha]_S^{20} = +173.2$ ($c = 1.55$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$); see [6] for literature values): 7.51–7.13 (*m*, 4 arom. H); 4.16 (*q*, $J = 7.1$, Me*CH*$_2$ of *trans*-isomer); 3.86 (*q*, $J = 7.1$, Me*CH*$_2$ of *cis*-isomer); 2.5–2.6 (*m*, 1 + 1 H, cyclopropane H of *trans*- and *cis*-isomers); 2.11 (*ddd*, $J = 5.7$, 7.9, 9.3, 1 H, cyclopropane H of *cis*-isomer); 1.94 (*ddd*, $J = 4.0$, 5.3, 8.6, 1 H, cyclopropane-H of *trans*-isomer); 1.74 (*ddd*, $J = 5.3$, 5.6, 7.5, 1 H, cyclopropane H of *cis*-isomer); 1.66 (*ddd*, $J = 4.7$, 5.4, 9.2, 1 H, cyclopropane H of *trans*-isomer); 1.45–1.30 (2*ddd*, 1 H, cyclopropane-H of *trans*- and *cis*-isomers, overlapped); 1.29 (*t*, $J = 7.1$, *Me*CH_2 of *trans*-isomer); 1.00 (*t*, $J = 7.1$, *Me*CH_2 of *cis*-isomer). MS: 258 (M^+).

Ethyl 3-Methyl-2-phenylcyclopropane-1-carboxylate. Yield (based on **8**) 70 mg (15%) of the colorless oil with a *cis*/*trans*-ratio of 0.7 : 99.3, as determined by GC analysis. Only the *trans*-isomer was observed by ^{1}H-NMR spectroscopy. Achiral GC analysis: *Macherey-Nagel SE 54*, 30 m, carrier 92 kPa He. Temp. program: 50° isotherm for 5 min, then to 200° at 5° min^{-1}. t_R [min]: ethyl *cis*-3-methyl-2-phenylcyclopropane-1-carboxylate, 29.2, ethyl *trans*-3-methyl-2-phenylcyclopropane-1-carboxylate, 30.8. Chiral GC analysis: *Supelco beta-DEX 120*, 1.4 ml He min^{-1}; temp. program: 110° isotherm, t_R [min]: *trans*-I, 83.08; *trans*-II, 84.95. Absolute

configuration was not determined. $[\alpha]_S^{20} = +149.2$ ($c = 0.45$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 7.3–7.0 (m, 5 arom. H); 4.18 (AB of ABX_3, $J = 1.0$, 7.1, MeCH_2); 2.41 (dd, $J = 5.0$, 6.5, 1 H, cyclopropane H); 2.02 (dd, $J = 5.0$, 9.2, 1 H, cyclopropane H); 1.67 (ddd, $J = 6.3$, 6.5, 9.2, 1 H, cyclopropane H); 1.36 (d, $J = 6.3$, *Me*CH_2); 1.28 (t, X_3 of ABX_3, $J = 7.1$, *Me*CH_2). EI-MS: 204 (M^+).

Ethyl 2-Methyl-2-phenylcyclopropane-1-carboxylate. Yield (based on **9**) 392 mg (89%) of a colorless oil with a *cis*/*trans*-ratio of 51:49 (by GC analysis and ^{1}H-NMR integration). Achiral GC analysis: *Macherey-Nagel SE 54*, 30 m, carrier 92 kPa He. Temp. program: 50° isotherm for 5 min, then to 200° at 5° min^{-1}. t_R [min]: ethyl *cis*-2-methyl-2-phenylcyclopropane-1-carboxylate, 28.2; ethyl *trans*-2-methyl-2-phenylcyclopropane-1-carboxylate, 29.5. Chiral GC analysis: *Supelco beta-DEX 120*, 1.4 ml He min^{-1}; temp. program: 140° isotherm, t_R [min]: *cis*-I, 16.0; *cis*-II, 16.5; *trans*-I, 19.6, *trans*-II, 19.8. $[\alpha]_S^{20} = +44.7$ ($c = 1.08$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$; see [13b] and [13d] for literature values of the *cis*- and *trans*-isomers, resp.): 7.4–7.2 (m, 5 arom. H); 4.22 ([13d]: 4.20) (q, $J = 7.1$, MeCH_2 of *trans*-isomer); 3.86 (AB of ABX_3, $J = 3.0$, 7.1, MeCH_2 of *cis*-isomer); 2.00 ([13d]: 1.96) (dd, $J = 6.0$, 8.3, 1 H, cyclopropane H of *trans*-isomer); 1.93 ([13b]: 1.90) (dd, $J = 5.4$, 7.6, 1 H, cyclopropane H of *cis*-isomer); 1.81 ([13b]: 1.78) (dd, $J = 4.9$, 5.6, 1 H, cyclopropane H of *cis*-isomer); 1.56 ([13d]: 1.52) (s, *Me*CH_2 of *trans*-isomer); 1.49 ([13b]: 1.46) (s, *Me*CH_2 of *cis*-isomer); 1.51–1.40 ([13d]: 1.41) (m, 2 H, cyclopropane CH_2, buried under Me signal of the *cis*-isomer); 1.33 ([13d]: 1.30) (t, $J = 7.1$, *Me*CH_2, of *trans*-isomer); 1.15 (dd, $J =$ 4.6, 7.7, 1 H, cyclopropane H of *cis*-isomer); 0.97 ([13b]: 0.94) (t, X_3 of ABX_3, $J = 7.1$, *Me*CH_2 of *cis*-isomer). EI-MS: 204 (M^+). Anal. calc. for $C_{13}H_{16}O_2$ (204.27): C 76.44, H 7.89, O 15.67; found: C 76.52, H 7.71, O 15.82.

Ethyl 2,2-Diphenylcyclopropane-1-carboxylate. Yield (based on **10**) 472 mg (82%) of a colorless oil. ^{1}H-NMR ($CDCl_3$; see [19b] for literature values): 7.38–7.16 (m, 10 arom. H); 4.03–3.81 (AB of ABX_3, $J = 1.6$, 7.0, MeCH_2); 2.54 (dd, $J = 5.9$, 8.1, 1 H, cyclopropane H); 2.19 ([19b]: 2.16) (dd, $J = 4.8$, 5.9, 1 H, cyclopropane H); 1.60 (dd, $J = 4.8$, 8.1, 1 H, cyclopropane H); 1.02 (t, X_3 of ABX_3, $J = 7.1$, *Me*CH_2). EI-MS: 266 (M^+). $[\alpha]_S^{20} = 165.6$ ($c = 1.12$, $CHCl_3$). Anal. calc. for $C_{18}H_{18}O_2$ (266.34): C 81.17, H 6.81, O 12.01; found: C 81.34, H 6.66, O 11.93. HPLC: *OJ*, 0.5 ml min^{-1}. hexane/AcOEt 98:2, t_R [min]: 16.7 (1*R*), 23.2 (1*S*).

Ethyl 2-Hexylcyclopropane-1-carboxylate. Yield (based on **11**) 279 mg (65%) of a colorless oil as a 24:76 mixture of the *cis*- and *trans*-isomers. Achiral GC analysis: *Macherey-Nagel SE 54*, 30 m, carrier 92 kPa He. Temp. program: 50° isotherm for 5 min, then to 200° at 5° min^{-1}. t_R [min]: ethyl *cis*-2-hexylcyclopropane-1-carboxylate, 26.1; ethyl *trans*-2-hexylcyclopropane-1-carboxylate, 26.6. Chiral GC analysis: *Supelco beta-DEX 120*, 1.4 ml He min^{-1}; temp. program: 90° isotherm, t_R [min]: *cis*-(1*R*,2*S*), 96.9; *cis*-(1*S*,2*R*), 100.9; *trans*-(1*R*,2*R*), 113.7, *trans*-(1*S*,2*S*), 114.9. $[\alpha]_S^{20} = -32.7$ ($c = 1.07$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 4.21 (q, $J = 7.1$, MeCH_2 of *cis*-isomer); 4.06 (q, $J = 7.1$, MeCH_2 of *trans*-isomer); 1.61 (ddd, $J = 5.5$, 7.9, 8.8, 1 H, cyclopropane H of *cis*-isomer); 1.53–1.14 (m, 10 H (hexyl CH_2 of *cis*-and *trans*-isomers) + 2 H (cyclopropane CH_2) + 3 H (*Me*CH_2)); 1.40–1.04 (m, 1 H, cyclopropane H of *trans*-isomer); 0.93 (ddd, $J = 4.4$, 7.9, 12.5, 1 H, cyclopropane H of *cis*-isomer); 0.84 (t, hexyl Me of *cis*- and *trans*-isomers; *Me*CH_2 signals are buried under this signal); 0.63 (ddd, $J =$ 4.1, 5.8, 7.8, 1 H, cyclopropane H of *trans*-isomer). EI-MS: 199 (M^+).

Competition Experiments. – A CH_2Cl_2 soln. (1 ml) ethyl diazoacetate (51 µl, 0.48 mmol, 1.0 equiv.) was added over 6 h to a CH_2Cl_2 soln. (1 ml) containing equimolar amounts (0.72 mmol, 1.5 equiv. *vs.* diazo ester) of styrene and one of the *para*-substituted derivatives **3**, as well as decane (as internal GC standard) and **2a** as catalyst (5 mol-% *vs.* diazo ester). The resulting red-brown soln. was stirred for an additional 14 h. Yields were determined by GC with decane as internal standard and the isolated cyclopropanation products as calibration standards. GC Analysis on chiral column: as described above. Results are reported in *Table 2*.

Catalytic Cyclopropanation with 2a. – Complex **2a** (20 mg, 24 µmol, 5 mol-% *vs.* olefin) and Tl[PF_6] (8.5 mg, 24 µmol) were stirred in CH_2Cl_2 overnight. The resulting brown soln. was filtered over *Celite* (to remove the precipitated TlCl) and added to the corresponding olefin (**3b**–**3e**, **8**, **9**, **10**, or **11**, 0.48 mmol). A CH_2Cl_2 soln. (1 ml) of distilled ethyl diazoacetate (100 µl, 0.96 mmol, 2 equiv. *vs.* olefin) was added to the mixture over 6 h by syringe pump. The soln. was stirred for additional 14 h. The reactions with olefins **3b**–**3e** were quantified by GC as described above. GC Yields, *cis*/*trans*-ratios, and ee values are given in *Table 3*. The products of the reaction with olefins **8**–**11** were isolated as described above. Yields and other data are reported in *Tables 4* and *5*.

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