36. Enantioselectivity and *cis*/*trans*-Selectivity in Dirhodium(II)-Catalyzed Addition of Diazoacetates to Olefins

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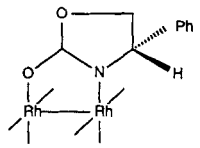
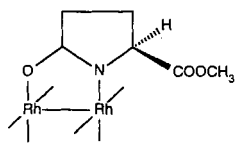
The Rh^{II}-catalyzed carbenoid addition of diazoacetates to olefins was investigated with $[Rh_2\{(4S)\text{-phox}\}_4]$ (**1**; phox = tetrakis[(4*S*)-tetrahydro-4-phenyloxazol-2-one]), $[Rh_2\{(2S)\text{-mepy}\}_4]$ (**2**; mepy = tetrakis[methyl (2*S*)-tetrahydro-5-oxopyrrole-2-carboxylate]), and $[Rh_2(OAc)_4]$ (**3**). While catalysis with **2** and **3** afford preferentially *trans*-cyclopropanecarboxylates, the *cis*-isomers are the major products with **1**. In general, the enantioselectivities achieved with **1** and **2** are comparable. Additions catalyzed by **1** are strongly sensitive to steric effects. Highly substituted olefins afford cyclopropanes in only poor yield. The preferential *cis*-selectivity observed in reactions catalyzed by **1** is attributed to dominant interactions between the ligand of the catalyst and the substituents of both olefin and diazoacetate, which overrule the steric interactions between olefin and diazoacetate in the transition state for carbene transfer.

Introduction. – Transition-metal-catalyzed carbenoid additions of diazoacetates to olefins may be highly enantioselective [1]. For example, the intramolecular cyclopropanation of allylic diazoacetates catalyzed by chiral 'rhodium pyrrolidinone carboxylates' [2] affords bicyclic lactones with ee's of up to 98% [3] [4]. Lactams are formed by analogy, albeit with somewhat lower selectivity [5]. The enantioselectivity of the intermolecular diazoacetate addition is highest with chiral Cu^I catalysts whose ligands have C_2 symmetry [6–9]. In the intermolecular addition of an (alkoxycarbonyl)carbene to a monosubstituted ethylene, formation of two stereoisomeric cyclopropanes are possible. In general, the *trans*-isomer predominates in the reaction mixture with catalysis by Cu^{II}, Rh^{II}, Pd^{II} [10], or Ru^{II} [11], although there are exceptions [12]. We have recently described a new chiral dirhodium(II) carboxamide catalyst, tetrakis[(4*S*)-tetrahydro-4-phenyloxazole-2-one]-dirhodium(II) (**1**; $[Rh_2\{(4S)\text{-phox}\}_4]$), which catalyzes the carbenoid addition of ethyl diazoacetate to styrene with preferential formation of the *cis*-cyclopropane isomer [13]. This is opposite to the stereochemistry of the diazoacetate addition catalyzed with other Rh^{II} catalysts such as $[Rh_2\{(2S)\text{-mepy}\}_4]$ (**2**), $[Rh_2\{(4S)\text{-bnox}\}_4]$ [2] [14] or $[Rh_2(OAc)_4]$ (**3**) [9], or with Cu catalysts. We have now investigated the diazo decomposition of a series of diazoacetates in the presence of olefins having different substitution patterns with $[Rh_2\{(4S)\text{-phox}\}_4]$ (**1**) in comparison to that catalyzed with **2** and **3** in order to examine the generality of this observation.

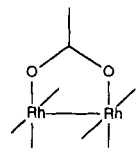
Results. – The carbene additions were effected under standard conditions in CH_2Cl_2 at room temperature, by adding a solution of the appropriate diazo ester to the olefin in the presence of 5 mol-% of catalyst by means of a syringe pump over 6–18 h. In some cases,



$[Rh_2\{(4S)\text{-phox}\}_4]$ (**1**)



$[Rh_2\{(2S)\text{-mepy}\}_4]$ (**2**)

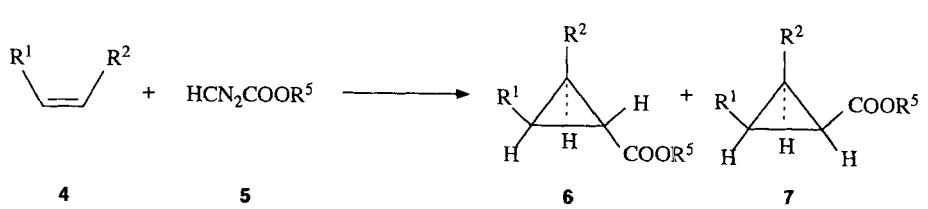


$[Rh_2(OAc)_4]$ (**3**)

when the yields of cyclopropanes were very low, reactions were also carried out in refluxing CH_2Cl_2 or in refluxing $ClCH_2CH_2Cl$, which resulted in somewhat improved yields. The cyclopropanes were separated from other reaction products by column chromatography and bulb-to-bulb distillation, and were identified by comparison of the NMR pattern of the cyclopropane H-atoms, which for most cyclopropanes obtained in this study is known, although sometimes with different ester groups. The *trans*/*cis* isomer ratio was determined by capillary GC and electronic integration. The isomer ratios from some carbene additions, catalyzed by $[Rh_2(OAc)_4]$ (**3**), are available in the literature, and these were all reproduced in our own experiments within experimental error. In general, the *cis*-cyclopropanecarboxylates were found to have shorter GC retention times than their *trans*-counterparts using a capillary methyl silicone column an observation consistent with that previously reported for FFAP columns [15].

The results for mono- and (*Z*)-disubstituted olefins **4** (*Scheme 1*) are summarized in *Table 1*. In general, diazoacetate additions catalyzed with $[Rh_2(OAc)_4]$ (**3**) led to preferential formation of the *trans*-cyclopropanes with the notable exception of the addition to butadiene, where, with all of the diazoacetates tried, the *cis*-isomers (**7h–7l**) were the major products. To verify this unexpected experimental results, the *cis*-isomer **7h** was synthesized independently from 3,3-diethoxypropyne *via* addition of methyl diazoacetate [16] followed by diimide reduction of the C=C bond, hydrolysis, and *Wittig* reaction [17]. The mixture of stereoisomers **6h** and **7h** obtained from addition of methyl diazoacetate (**5**, R^5 = Me) to buta-1,3-diene was equilibrated with MeO^- [18], and it was found that the major isomer was converted to minor one, so that the thermodynamically more stable *trans*-cyclopropanecarboxylate **6h** predominated in the equilibrated mixture. It is remarkable in this context that the thermal (uncatalyzed) addition of ethyl diazoacetate to butadiene occurs almost without any stereoselection (*trans*/*cis* isomer ratio 55:45) [19]. Since the *trans*-isomer is thermodynamically more stable [15], this result suggests an interaction between the non-reacting C=C bond and the attacking carbene in the $[Rh_2(OAc)_4]$ (**3**) catalyzed reaction, but which is absent in those catalyzed with Cu^I complexes, where the *trans*-cyclopropanecarboxylate is preferred by a factor of *ca.* 2 [6].

Scheme 1



4 **5** **6** **7**

Table 1. *Enantio- and Diastereoselectivity in Rh^{II}-Catalyzed Cyclopropene Formation from Mono- and (Z)-Disubstituted Olefins*

	Olefin (**4**)		Ester (**5**)	$[Rh_2(OAc)_4]$ (**3**)		NMR	$[Rh_2\{(2S)\text{-mepy}\}_4]$ (**2**)				$[Rh_2\{(4S)\text{-phox}\}_4]$ (**1**)			
	R^1	R^2	R^5	Yield [%]	**6**/**7**[a]	Ref.	Yield [%]	**6**/**7**[a]	ee (**6**)	ee (**7**)	Yield [%]	**6**:**7**[a]	ee (**6**)	ee (**7**)
a	Ph	H	Et	93	62:38[b]	[30]	59[c]	56:44[e]	58[c],[d]	33[c],[d]	41[e]	34:66[e]	24[d],[e]	57[d],[e]
b	Ph	H	*t*-Bu	68	66:34		49	52:48	56	77[d]	35	32:68	–	57[e]
c	Ph	H	*l*-menthyl	82[f]	68:32[f]	[6]	34[f]	52:48[f]	38[d],[f]	80[d],[f]	19[e]	27:73[e]	40[d],[f]	72[d],[e]
d	Ph	H	*d*-menthyl	79[f]	68:32[f]	[6]	74[f]	57:43[f]	31[f]	88[f]	24[e]	59:41[e]	4[e]	6[e]
e	Pr	H	Me	58	61:39[g]	[6]	55	58:42	44[h]	40[h]	21	38:62	42[h]	56[h]
f	Bu	H	*d*-menthyl	95[i]	60:40[i]		65	91:9	25	75	–	–	–	–
g	*t*-Bu	H	*d*-menthyl	87[i]	81:19[i]		62	80:20	53	82	–	–	–	–
h	CH_2=CH	H	Me	60	43:57	[6]	27	48:62	56[h]	60[h]	45	43:57	58[h]	47[h]
i	CH_2=CH	H	*t*-Bu	37	44:56		17	43:57	74[g]	–	20	52:48	46[k]	–
j	CH_2=CH	H	Ph	77	42:58		38	51:49	26[g]	–	60	51:49	48[k]	–
k	CH_2=CH	H	*l*-menthyl	90[l]	37:63		41	38:62	72[a]	60[a]	31[l]	49:51	54[a]	52[a]
l	CH_2=CH	H	*d*-menthyl	64[l]	38:62		22[l]	45:55	76[a]	50[a]	29[l]	43:57	14[a]	8[a]
m	Naphthalen-2-yl[m]	H	Et	56	63:37		–	–	–	–	32	42:58	–	–
n	Naphthalen-2-yl[m]	H	*t*-Bu	49	62:38		–	–	–	–	25	37:63	–	–
o	1,1′-Biphenyl-4-yl[n]	H	Et	55	60:40		–	–	–	–	31	36:64	–	–
p	1,1′-Biphenyl-4-yl[n]	H	*t*-Bu	51	67:33		–	–	–	–	28	37:63	–	–
q	$AcOCH_2$	H	Me	57	59:41		46	55:45	56	44	11	47:53	4	10
r	$AcOCH_2$	H	*l*-menthyl	49	68:32		26	70:30	38	26	5	51:49	34	50
s	EtO	H	*d*-menthyl	88[i]	63:37[i]		48	66:34	37	49	–	–	–	–
t	AcO	H	Me	60	63:37[o]		62	53:47	10[h]	55[h]	14	44:56	56[h]	68[h]
u	AcO	H	Et	42	65:35[p]		75	52:48	24[h]	60[h]	26	44:56	50[h]	48[h]
v	AcO	H	Ph	44	60:40		23	54:46	32[h]	35[h]	10	46:54	46[h]	44[h]
w	PhCOO	H	Me	54	62:38		40	50:50	22[h]	54[h]	22	38:62	32[h]	54[h]
x	PhCOO	H	*t*-Bu	49	67:33		24	63:37	28[h]	78[h]	10	53:47	76[h]	56[h]
y	Ph	Me	Me	60	69:31	[20] [32]	44	44:56	12[h]	16[h]	19	36:64	24[h]	18[h]
z	$-(CH_2)_3O-$		Me	71	82:18[q]	[32]	18	87:13	10[r]	49[r]	31	71:29	14[r]	76[r]

[a]) By capillary GC (methyl silicone column). [b]) 62:38 [10]. [c]) [14]. [d]) By GC, using *Chiraldex-γ*-cyclodextrine-TFA column. [e]) [13]. [f]) [34]. [g]) 60:40 [10]. [h]) By NMR, using $[Eu(hfc)_3]$. [i]) For ethyl ester [10]. [k]) By GC, *Lipodex E* column. [l]) In CH_2Cl_2 at reflux. [m]) 2-Vinylnaphthalene. [n]) 4-Vinylbiphenyl. [o]) For butyl ester [15]. [p]) 62:38 [23]. [q]) 87:13 [23]. [r]) By GC, *Lipodex C* column.

The enantiomeric (ee) or diastereoisomeric (de) excess of the cyclopropanes was determined either by capillary GC (*Lipodex C* or *E*, or *Chiraldex-γ*-cyclodextrin-TFA columns) or by ^{1}H-NMR, with a shift reagent ([Eu(hfc)$_3$]), respectively.

Inspection of *Table 1* reveals the following rough trends: the total yields of methyl and ethyl cyclopropanecarboxylates decrease from an average of *ca.* 60% with [$Rh_2(OAc)_4$] (**3**) to 50% with [Rh_2{(2*S*)-mepy}$_4$] (**2**) and to 30% with [Rh_2{(4*S*)-phox}$_4$] (**1**). The *trans*/*cis*-ratios (**6**/**7**) change in parallel from the catalyst having the least hindered access ([$Rh_2(OAc)_4$]; **3**), 60:40, to **2**, 50:50, and to that with the most hindered access (**1**), 30:70. An increase in size of the substituent of monosubstituted olefins **4** (R^1) produces minor variations in the *trans*/*cis*-ratios with all three catalysts, but enantioselectivity is almost unaffected. With **1**, the *cis*-cyclopropanecarboxylate **7** predominates always, independently from R^1, except when the ester group (R^5) is very bulky (*t*-Bu, Ph, or menthyl), in which case the *trans*-cyclopropanecarboxylate **6** may be the preferred form. We expected a substantial increase in the *trans*/*cis*-ratios with the sterically demanding 2-vinylnaphthalene (**4m**) and 4-vinyl-1,1′-biphenyl (**4o**) in comparison to styrene (**4a**), but this was not observed. Apparently, the additional benzene rings of **4m** and **4o** are too far away from the reacting center, and in spite of their different geometric orientations, they are unable to intervene in the reaction.

The *trans*/*cis*-selectivities are, in addition, subject to double diastereoselection. Thus, the addition of menthyl diazoacetate to styrene (**4a**), catalyzed by **1** having the (*S*)-configuration leads to **6**/**7** (*trans*/*cis*-ratio 27:73), but with *d*-menthyl diazoacetate the ratio changes to 59:41. With [Rh_2{(5*S*)-mepy}$_4$] (**2**) the effect is less spectacular: only 52:48 with *l*-menthyl and 57:43 with *d*-menthyl diazoacetate.

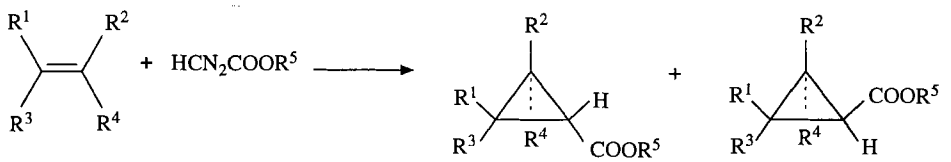
The diastereoselectivities achieved by [$Rh_2(OAc)_4$] (**3**) are consistent with weak steric interactions between R^1 and R^5, which favor the *trans*-cyclopropanecarboxylate **7**. The inverse preference for *cis*-cyclopropanecarboxylate formation observed with [Rh_2{(4*S*)-phox}$_4$] (**1**) may be attributed to interactions between R^1 and/or R^5 with the ligands of the catalyst (see below). [Rh_2{(5*S*)-mepy}$_4$] (**2**) is intermediate between **1** and **3**; the *trans*-cyclopropanecarboxylate predominates, but the preference for *trans*-cyclopropanation is weaker than with **3**. Of the two (*Z*)-disubstituted olefins investigated, β-methylstyrene (**4y**) reacts mainly to the *cis*-cyclopropanecarboxylate **6y** with both chiral catalysts **1** and **2**, while [$Rh_2(OAc)_4$] (**3**) favors the *trans*-isomer **7y**. The *trans*/*cis*-ratio of 36:64 obtained with **1** is, however, less remarkable than that of 11:89 reported for *Kodakek*'s Rh^{III}-(porphyrin) complex [20]. For comparison, the *trans*/*cis*-ratio **6y**/**7y** (R^5 = *t*-Bu) may reach 99:1 with chiral Cu^{II}(bipyridine) complexes [21]. The addition of methyl diazoacetate to dihydropyran, catalyzed by **1**, represents, with a *trans*/*cis*-ratio of 71:29 the exception to the general trend for preferential *cis*-addition with catalysis by **1**. However, this value must be seen in the light of the ratio of 87:13 with **2**, and 82:18 for **3**. It is, therefore, consistent with the general trend in favor of the *cis*-cyclopropanecarboxylate isomer produced with the more hindered catalyst.

The enatioselectivities reached with **1** and **2** are generally modest but reveal remarkable similarities. The average enantiomeric excess (ee) and diastereoisomeric excess (de) is *ca.* 40% for the *trans*-cyclopropanecarboxylates **6a**–**z** with both catalysts. For the *cis*-cyclopropanecarboxylates **7a**–**z**, the enantioselectivity is somewhat better (*ca.* 50%). [Rh_2{(2*S*)-mepy}$_4$] (**2**) is slightly more efficient than [Rh_2{(5*S*)-phox}$_4$]. The main discrepancies occur with *d*- and *l*-menthyl diazoacetates: With **2** and styrene, the diazoac-

etate having the *d*-configuration affords the *trans*- and *cis*-cyclopropanecarboxylate with de's of 31 and 88%, while the *l*-menthyl diazoacetate gives de's of 38 and 80%, respectively. The combination of **1** with *d*-menthyl diazoacetate is clearly a mismatch, giving de's of only 4 and 6%. In contrast, *l*-menthyl diazoacetates combined with **1** gives the *trans*-cyclopropanecarboxylate **6c** with 40, and the *cis*-isomer **7c** with 72% de. With the *d*-menthyl diazoacetate, even the achiral $[Rh_2(OAc)_4]$ (**3**) produces a modest asymmetric induction of 5 (*trans*-isomer) and 13% (*cis*-isomer) upon addition to styrene. A similar situation is found with butadiene, where a low de (*ca.* 10%) is observed for the addition of menthyl diazoacetate catalyzed by **3**. The data reveal no clear relationship between the bulk of R^1 or R^5 and ee.

The diazoacetate additions to 1,1- and (*E*)-1,2-disubstituted, and trisubstituted olefins (**8**) are summarized in *Table 2* and *Scheme 2*.

Scheme 2



8 **5** **9** **10**

The yields with $[Rh_2(OAc)_4]$ (**3**) are generally lower with all olefins in comparison to the monosubstituted ones, and they drop even more with **1** and **2**. Only the 1,1-disubstituted olefins afford cyclopropanes in moderate to high yields, but diastereoselection and/or enantioselection is low. (*E*)-*β*-Methylstyrene (**8g**), the only (*E*)-olefin investigated, underwent cyclopropanation in low yield with all of the Rh catalysts and furnished almost exclusively the *trans*-cyclopropanecarboxylates **9g** and **9h**. This contrasts with the diazoacetate addition to **8g** with Cu/bipyridine catalysts, where the *trans*/*cis*-ratio varies with the structure of the ligand in a narrow range from 68:32 to 40:60 [21]. Enantiomer separation was unsuccessful with this substrate, except in the case of **9h** (8% ee for **9h** obtained with *tert*-butyl diazoacetate and **1** as catalyst). The trisubstituted olefins gave acceptable yields with $[Rh_2(OAc)_4]$ (**3**) only. The *trans*/*cis*-ratios were unpredictably erratic, and so was the induction with the chiral catalysts. The addition of *l*-menthyl diazoacetate to 2,5-dimethylhexa-2,4-diene yielded the *trans*-cyclopropanecarboxylate **10l** with a de of 80% with **2** and 100% with **1**. The low yields of mere 5% makes this reaction, however, insignificant in view of synthetic applications.

Discussion. – The stereoselectivity of the transition-metal-catalyzed carbene addition to olefins varies according to the metal, the ligands, and the substituents of the carbene and of the olefin. Cu catalysts lead mainly to *trans*-cyclopropanes [6] [10]. The same applies to catalysts containing Pd [10]. A Co complex of camphorquinone-α-dioxime has been reported to provide *cis*/*trans*-ratios close to 1, with the *cis*-isomer slightly favored. *Kodakek*'s 'chiral wall' rhodium(III)-porphyrins, in turn, catalyze cyclopropane formation between diazoacetates and olefins with a slight preference for the *cis*-isomer, but with only modest enantiomeric excess [20]. *cis*-Selective cyclopropane formation from styrene with ethyl diazoacetate has been reported for an achiral iron-based catalyst $(\eta^5\text{-}C_5H_5)Fe^+(CO)_2(THF)BF_4^-$ [22].

Table 2. *Enantioselectivity and Diastereoselectivity in Rh^{II}-Catalyzed Cyclopropane Formation from 1,1- and (E)-1,2-Disubstituted, and Trisubstituted Olefins*

	Olefin (**8**)				Ester (**5**)	$[Rh_2(OAc)_4]$ (**3**)		NMR	$[Rh_2\{(5S)\text{-mepy}\}_4]$ (**2**)				$[Rh_2\{(4S)\text{-phox}\}_4]$ (**1**)			
	R^1	R^2	R^3	R^4	R^5	Yield [%]	**9**/**10**[a])	Ref.	Yield [%]	**9**/**10**[a])	ee (**9**)	ee (**10**)	Yield [%]	**9**/**10**[a])	ee (**9**)	ee (**10**)
a	Ph	H	Me	H	Et	42	59:41	[29] [31]	44	55:45	15[b])	5[b])	–			
b	Ph	H	Me	H	*l*-menthyl	80	53:47[c])		59	61:39[c])	5[a])	9[b])	–			
c	Ph	H	Me	H	*d*-menthyl	–	–		32	59:41	58	78				
d	Ph	H	Ph	H	Et	52	–	[29] [31]	37	–	20[b])	–	–			
e	Ph	H	Ph	H	*l*-menthyl	63	–		46	–	4[a])	–				
f	Ph	H	Me_3SiO	H	Me	23	47:53	[32]	80	45:55	30[b])	14[b])	44	47:53	14[b])	10[b])
g	Ph	H	H	Me	Me	33	95:5	[20] [31]	12	99:1	–	–	10	89:11	–	–
h	Ph	H	H	Me	*t*-Bu	10	92:8		–	–	–	–	17[d])	98:2	8[b])	
i	$Me_2C{=}CH$	Me	H	Me	Me	60	60:40[e])	[33]	70	49:51	6	20	24	53:47	16	14
j	$Me_2C{=}CH$	Me	H	Me	*t*-Bu	54	67:33		5	53:47	–	–	11	60:40	–	–
k	$Me_2C{=}CH$	Me	H	Me	Ph	42	62:38		5	54:49	–	–	5	60:40		
l	$Me_2C{=}CH$	Me	H	Me	*l*-menthyl	61[d])	64:36		5[d])	69:31	12[b])	80[b])	5[d])	64:36	12[b])	100[b])
m	Me_3SiO	H	$-(CH_2)_3-$		Me	37	47:53	[32]	36	43:53	50[b])	14[b])	5	57:43	–	–

[a]) By capillary GC (methyl silicone column). [b]) By NMR, using $[Eu(hfc)_3]$. [c]) By NMR. [d]) In $ClCH_2CH_2Cl$ at reflux. [e]) 64:36 [23].

The stereoselectivity of the $[Rh_2(OAc)_4]$ (**3**) catalyzed addition of diazo compounds to olefins has been investigated in the past [10] [23] [24]. A mechanism for cyclopropane formation has been proposed by analogy to the stoichiometric carbene transfer from $(CO)_5W = CHPh$ to olefins [25], in which the carbene resulting from decomposition of the diazo compound displaces a weakly bonded ligand from one of the axial coordination sites of the Rh. Carbene transfer occurs without disruption of the bonds of the ligands to the metal. The approaching olefin will interact with the p orbital of the carbene at the less substituted center so that the more substituted end points away from the plane defined by the O-atoms of the acetate ligands. In the transition state **11**, the C–C bond of the olefin lies parallel to the Rh–carbene bond and the more substituted C-atom of the olefin is oriented *anti* to the metal (*Fig. 1*). Bonding of the carbene to the less substituted terminal of the olefin is more advanced than to the more substituted one, where partial charge develops. Cyclopropane formation then occurs by dissociation of the carbon–metal bond by analogy to the backside displacement of R_3Sn^+ by the incipient carbenium ion upon solvolysis of γ-SnR_3 derivatives, which leads also to cyclopropanes [26].

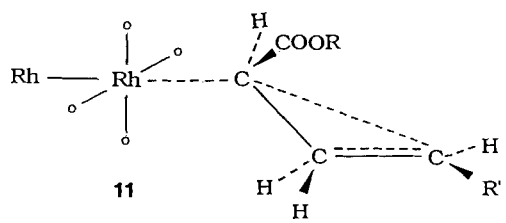


Fig. 1. *Model for transition state* **11** *for carbene transfer from* $[Rh_2(OAc)_4]$ (**3**) *to a monosubstituted olefin* (side-view)

The preferential stereochemistry of cyclopropanation is determined by the mutual interactions between the substituents of the carbene (COOR), the substituent of the olefin (R′), and the ligands of the complex. Carbene additions to olefins have early transition states, and, therefore, the interactions between COOR and R′ are weak. Although increased steric crowding of COOR and R′ should, in principle, favor the *trans*-cyclopropane, the effect is weak. In addition, the preferential formation of *trans*-cyclopropane in $[Rh_2(OAc)_4]$-catalyzed addition of diazoacetates is favored owing to a specific interaction between the C=O group of the carbene and the electrophilic center of the olefin [23] [24] upon going to the transition state, and stabilizing the latter. The hypothesis of this polar effect derives further support from the stereoselectivity of the Rh-catalyzed addition of nitrocarbenecarboxylates [27] and vinylcarbenecarboxylates [28].

The acetate ligands of **3** define a plane to which the carbene is coordinated, but they exert no steric influence into the half-space, where carbene transfer takes place. The situation is different, however, with the chiral catalysts **1** and **2**, where the substituents of the ligands protrude into this region, thereby limiting the possible orientations of the coordinated carbene and the approaching olefine. The enhanced steric hindrance leads to a decrease of the yield in the order $[Rh_2(OAc)_4]$ (**3**) > $[Rh_2\{(2S)\text{-mepy}\}_4]$ (**2**) > $[Rh_2\{(4S)\text{-phox}\}_4]$ (**1**), *i.e.*, in the order of increasing steric hindrance of the ligands. An electronic effect could account for the different trend observed with **3** in comparison to **1** and **2**, but should not significantly differentiate between **2** and **3**. At the same time, the *trans*/*cis*-ra-

tio decreases in the same order, and is inverted with **1**. This may be attributed to overruling of the attractive stabilization of the transition state leading to *trans*-products by the enhanced steric interactions of the ligands of **1** and **2** with COOR and R′.

The Ph groups of the oxazolidinone ligands of **1** define two approximately perpendicular planes which, together with the plane of the atoms bonded to the Rh, describe a half-box, in which the carbene transfer takes place. Extension of model calculations for **2** to **1** suggest two low-energy conformations, **12** and **13**, for the coordinated carbene, which allow attack of the olefin at the *re*- and *si*-face, respectively [13] (*Fig. 2*).

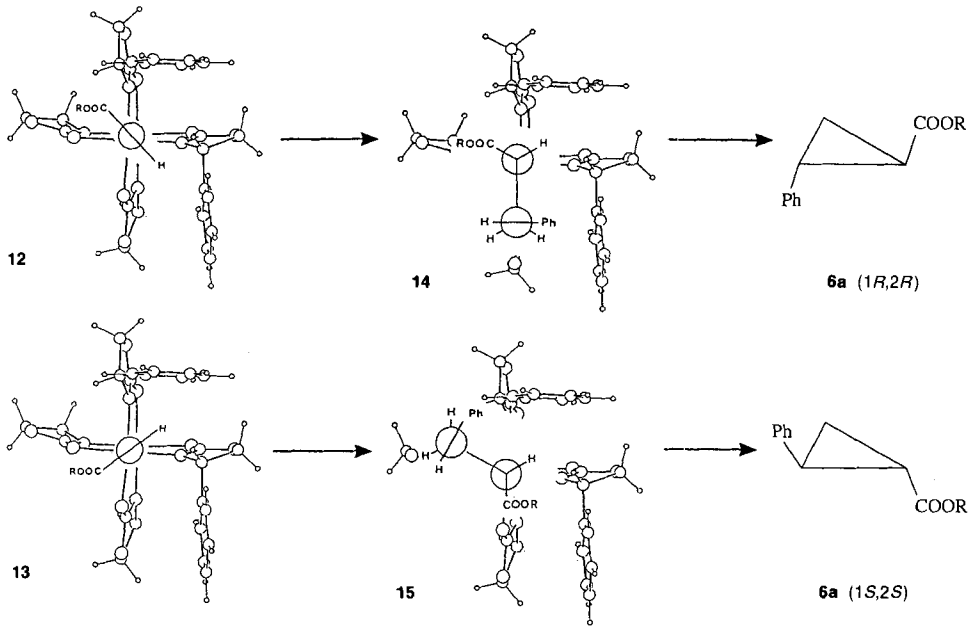


Fig. 2. *Projection of coordinated carbene on the X-ray structure of* **1** *along the Rh–Rh axis* (conformations of minimum energy, **12** and **13**, according to model calculations [13] and transition-state models leading to the sterically disfavored enantiomeric *trans*-cyclopropanecarboxylates **6a**. The rear Ph groups of the ligands are omitted for clarity)

The attacking olefin ($PhCH{=}CH_2$) will approach the coordinated carbene **12** from the open side of the half-box and orient the Ph substituent away from the coordination plane of the metal. Attack to the *re*-face of C(α) of the olefin leads to the transition state schematically represented by **14** in which the C=O substituent of the carbene (COOR) point outwards from the box, and the Ph group of the olefin is directed towards the inside. This transition state, which leads to the *trans*-cyclopropane with configuration (1*R*,2*R*), is destabilized owing to steric interactions between the Ph group of the olefin and the vertical Ph group of the oxazolidinone ligand. In the transition state resulting from attack of the *si*-face at C(α) of the olefin (not shown), which affords the *cis*-cyclopropane, the Ph and COOR groups point away both from the half-box. The steric interactions with the ligand are minimized, and the *cis*-cyclopropane is formed preferentially. Attack to the *si*-face of the coordinated carbene, in turn, occurs from the less hindered top side of conformation **13**. The transition state **15**, which leads to the *trans*-cyclopropane is again

destabilized, this time owing to interactions between the substituent of the olefin (Ph) and the horizontal Ph group of the oxazolidinone ligand. The transition state leading to the *cis*-cyclopropane is again sterically less hindered. The preferred *cis*-cyclopropanation in the $[Rh_2\{(4S)\text{-phox}\}_4]$ (**1**) catalyzed reactions is not unique even for Rh^{II} catalysts. Indeed *trans*/*cis*-ratios of up to 1:3 have been reported for cyclopropanations of (*Z*)-olefins with ethyl diazoacetate in the presence of $[Rh_2(OAc)\{\text{tris(triarylbenzoates)}\}]$ [29].

With **1** as catalyst, addition of ethyl diazoacetate to styrene produces the *cis*-cyclopropanecarboxylate with (1*R*,2*S*)-configuration [13] [30] with an ee of 57%. The configuration of the major *trans*-cyclopropanecarboxylate enantiomer from the same reaction is (1*R*,2*R*), indicating that it originates from **12**. The enantiomeric cyclopropanecarboxylates should, therefore, originate from **13**. However, the (*S*)-configuration at C(1) may also originate from a transition state analogous to **11**, in which the more substituted center of the olefin lies near the Rh-atom. Since (*Z*)-disubstituted olefins are only less reactive by a factor of *ca.* 2 than the mono-substituted counterparts in diazoacetate additions catalyzed by $[Rh_2(OAc)_4]$ [20], the possibility of still different transition states cannot be ruled out. The absolute configurations of other cyclopropanecarboxylates have not yet been determined, so that the generalization of this mechanistic model needs experimental confirmation.

In the reactions catalyzed with $[Rh_2\{(2S)\text{-mepy}\}_4]$ (**2**), the yields are higher than with **1**, and the *trans*-cyclopropanes are the predominant products [2] [14]. This may be attributed to decreased steric interactions in the transition state, owing to the smaller steric requirements of the protruding ligands in **2** (COOMe) in comparison to those of **1** (Ph). The *trans*-preference observed for $[Rh_2(OAc)_4]$ (**3**) applies also to **2**, although the *trans*/*cis*-ratio for **2** is intermediate between that observed for **1** and **3**. The absolute configurations of the cyclopropanecarboxylates obtained with **2** having the (*S*)-configuration at C(2) is opposite to that resulting from **1** with the (*S*)-configuration (at C(4)) owing to the sequence rule. The presence of the O-atom in the heterocyclic ring of **1** inverts the priority of the substituents of the asymmetric center in comparison to that of **2**, so that the orientation in space of the Ph group of **1** having (*S*)-configuration corresponds to that of **2** having (*R*)-configuration.

The inductions achieved in intermolecular Rh^{II}-catalyzed diazoacetate additions are generally lower than those obtained with Cu catalysts [6–9]. This could be due to the absence of additional free coordination sites of the Rh, which orient the olefin prior to carbene transfer. In the intramolecular Rh-catalyzed cyclopropanation (reaction of allyl- and homoallyl diazoacetates), the mobility of the olefin is much restricted, and high inductions result [3] [4]. However, an increase in steric crowing around the supposed coordination site of the carbene does not enhance enantioselection, but rather decreases the yields. In the intramolecular cyclopropanations, the presence of an O-atom in the allylic position seems crucial for enantioselection. While our mechanistic model accounts for the diastereoselectivity of the reaction, it does not explain this effect of O-substitution. Conceivably, the high inductions which have been realized with **2** in the intramolecular cyclopropanation may be due to a polar effect of the methoxycarbonyl substituent of the ligand. This hypothesis is currently under investigation.

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Experimental Part

General. ^{1}H-NMR Spectra were recorded from 200- and 300-MHz spectrometers. Mass spectra were obtained from *Varian-EM*, *Finnigan-4000*, *HP-5995*, or *VG-70-70* instruments at 70 eV. Microanalyses were performed at Texas Analytical Laboratories. Tetrakis[methyl (2*S*)-tetrahydro-5-oxopyrrole-2-carboxylate]dirhodium(II), ([Rh_2\{(2*S*)-mepy\}$_4$]) [2] and tetrakis[(4*S*)-tetrahydro-4-phenyloxazol-2-one]dirhodium(II) ([Rh_2\{(4*S*)-phox\}$_3$]) [13] were prepared from commercial [$Rh_2(OAc)_4$] according to published procedures. CH_2Cl_2 was distilled from CaH_2 prior to use. *tert*-Butyl diazoacetate [36] and *d*- or *l*-menthyl diazoacetate [7] were synthesized according to the published methods.

General Procedure for Cyclopropanation of Olefins with Diazoesters. To a light blue soln. of olefin (10.0 mmol; 2.0 mmol for 2-vinylnaphthalene and 4-vinyl-1,1'-biphenyl) Rh^{II} catalyst (0.010 mmol) in anh. CH_2Cl_2 (20 ml) under N_2 was added the diazoester (1.00 mmol) in CH_2Cl_2 (10 ml) through a syringe pump at a rate of 0.3–0.5 ml/h. After addition was complete, the mixture was filtered through a 1-cm plug of silica gel to separate the catalyst, and the plug was eluted with CH_2Cl_2 (30 ml). The excess olefin was removed by distillation at 25° or by bulb-to-bulb distillation at 60–80°/0.05 Torr. GC Analyses were performed prior to and following distillation without noticeable change in isomer rations. Diastereoisomer ratios were obtained from capillary phenyl silicone or methyl silicone column, and enantiomer separation was performed by the methods indicated in *Tables 1* and *2*. References to the ^{1}H-NMR spectra of the known cyclopropanes are also given in *Tables 1* and *2*. The cyclopropanecarboxylates **6** and **7m–p** were isolated by column chromatography on silica gel (hexane/AcOEt 98:2). The isomeric cyclopropanecarboxylates **6**/**7i–l** derived from addition to butadiene were identified *via* hydrolysis to the carboxylic acids (NaOH/MeOH) followed by conversion to methyl esters with (trimethylsilyl)diazomethane [37]. The same procedure was used for **9**/**10l**.

trans-*Ethyl 2-(Naphthalen-2-yl)cyclopropane-1-carboxylate* (**6m**). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.83–7.72 (*m*, 3 H); 7.57 (*s*, 1 H); 7.50–7.37 (*m*, 2 H); 7.20 (*dd*, *J* = 8.6, 1.8, 1 H); 4.19 (*q*, *J* = 7.1, 2 H); 2.70 (*ddd*, *J* = 9.4, 6.5, 4.2, 1 H); 2.01 (*ddd*, *J* = 8.6, 5.4, 4.2, 1 H); 1.67 (*ddd*, *J* = 9.4, 5.4, 4.6, 1 H); 1.41 (*ddd*, *J* = 8.6, 6.5, 4.6, 1 H); 1.29 (*t*, *J* = 7.1, 3 H).

cis-*Ethyl 2-(Naphthalen-2-yl)cyclopropane-1-carboxylate* (**7m**). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.81–7.72 (*m*, 4 H); 7.48–7.37 (*m*, 3 H); 3.82 (*q*, *J* = 7.0, 2 H); 2.72 (*ddd*, *J* = 9.3, 8.6, 7.4, 1 H); 2.15 (*ddd*, *J* = 9.3, 7.8, 5.7, 1 H); 1.85 (*ddd*, *J* = 7.4, 5.7, 5.1, 1 H); 1.40 (*ddd*, *J* = 8.6, 7.8, 5.1, 1 H); 0.90 (*t*, 7.0, 3 H). Analc. calc. for $C_{16}H_{16}O_2$ (*cis*/*trans*-mixture): C 79.97, H 6.71; found: C 79.89, H 6.74.

trans-tert-*Butyl 2-(Naphthalen-2-yl)cyclopropane-1-carboxylate* (**6n**). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.83–7.73 (*m*, 3 H); 7.56 (*s*, 1 H); 7.50–7.37 (*m*, 2 H); 7.20 (*dd*, *J* = 8.6, 1.8, 1 H); 2.61 (*ddd*, *J* = 9.4, 6.2, 4.1, 1 H); 1.94 (*ddd*, 9.4, 4.3, 4.1, 1 H); 1.60 (*ddd*, *J* = 9.4, 4.6 Hz, 4.3 Hz, 1 H); 1.49 (*s*, 9 H); 1.34 (*ddd*, *J* = 9.4, 6.2, 4.6, 1 H).

cis-tert-*Butyl 2-(Naphthalene-2-yl)cyclopropane-1-carboxylate* (**7n**). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.87–7.70 (*m*, 4 H); 7.48–7.36 (*m*, 3 H); 2.62 (*ddd*, *J* = 9.3, 8.4, 7.3, 1 H); 2.06 (*ddd*, *J* = 9.3, 7.8, 5.6, 1 H); 1.76 (*ddd*, *J* = 7.3, 5.6, 5.2, 1 H); 1.35 (*ddd*, *J* = 8.4, 7.8, 5.2, 1 H); 1.06 (*s*, 9 H). Anal. calc. for $C_{18}H_{20}O_2$: C 80.60, H 7.48; found: C 80.51, H 7.55

trans-*Ethyl 1-(1,1'-Biphenyl-4-yl)cyclopropane-1-carboxylate* (**6o**). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.58–7.27 (*m*, 8 H); 7.17 (*d*, *J* = 8.2, 1 H); 4.18 (*q*, *J* = 7.1, 2 H); 2.56 (*ddd*, *J* = 9.6, 6.5, 4.2, 1 H); 1.94 (*ddd*, *J* = 8.4, 5.2, 4.2, 1 H); 1.63 (*ddd*, *J* = 9.6, 5.2, 4.5, 1 H); 1.33 (*ddd*, *J* = 8.4, 6.5, 4.5, 1 H); 1.29 (*t*, *J* = 7.1, 3 H). MS: 267 (13, $[M + 1]^+$), 266 (75), 221 (28), 220 (40), 209 (25), 193 (98), 192 (51), 191 (96), 178 (100), 165 (87), 115 (46).

cis-*Ethyl 1-(1,1'-Biphenyl-4-yl)cyclopropane-1-carboxylate* (**7o**). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.58–7.27 (*m*, 8 H); 7.17 (*d*, *J* = 8.2, 1 H); 3.90 (*q*, *J* = 7.1, 2 H); 2.59 (*ddd*, *J* = 9.4, 9.2, 7.4, 1 H); 2.11 (*ddd*, *J* = 9.4, 7.8, 5.5, 1 H); 1.75 (*ddd*, *J* = 7.4, 5.6, 5.2, 1 H); 1.35 (*ddd*, *J* = 9.2, 7.8, 5.2, 1 H); 0.99 (*t*, *J* = 7.1, 3 H). MS: 267 (14, $[M + 1]^+$), 266 (71), 221 (23), 220 (37), 209 (22), 193 (99), 192 (46), 191 (91), 178 (100), 165 (76), 115 (40). Anal. calc. for $C_{18}H_8O_2$: C 81.17, H 6.81; found: C 81.06, H 6.90.

trans-tert-*Butyl 2-(1,1'-Biphenyl-4-yl)cyclopropane-1-carboxylate* (**6p**). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.58–7.26 (*m*, 8 H); 7.18 (*d*, *J* = 8.1, 1 H); 2.47 (*dd*, *J* = 9.5, 6.3, 3.9, 1 H); 1.87 (*ddd*, *J* = 8.6, 6.3, 3.9, 1 H); 1.58 (*ddd*, *J* = 9.5, 5.4, 4.4, 1 H); 1.48 (*s*, 9 H); 1.34 (*ddd*, *J* = 8.6, 6.3, 4.4, 1 H).

cis-tert-*Butyl 2-(1,1'-Biphenyl-4-yl)cyclopropane-1-carboxylate* (**7p**). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.58–7.26 (*m*, 8 H); 7.18 (*d*, *J* = 8.1, 1 H); 2.54 (*ddd*, *J* = 9.3, 8.5, 7.2, 1 H); 2.03 (*dd*, *J* = 9.3, 7.7, 5.6, 1 H); 1.68 (*ddd*, *J* = 7.2, 5.6, 5.3, 1 H); 1.28 (*ddd*, *J* = 8.5, 7.7, 5.3, 1 H); 1.15 (*s*, 9 H).

trans-*Methyl 2-(Acetoxymethyl)cyclopropane-1-carboxylate* (**6q**). IR ($CHCl_3$: *cis*/*trans*-mixture): 3030*m*, 1725*s*, 1441*m*, 1240*s*, 1441*m*, 1370*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.10 (*d*, *J* = 8, 1 H); 3.86 (*dd*, *J* = 12, 8, 1 H); 3.66 (*s*, 3 H); 2.05 (*s*, 3 H); 1.80–1.62 (*m*, 2 H); 1.31–1.23 (*m*, 2 H); 0.86 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 173.6 (*s*); 170.8 (*s*); 65.9 (*t*); 51.8 (*q*); 20.8 (*q*); 19.5 (*d*); 18.5 (*d*); 13.0 (*t*). MS (*cis*/*trans*-mixture): 172 (M^+, absent), 141 (3.5), 113 (32), 112 (100), 99 (65), 73 (28), 59 (21). HR-MS: 141.0546 ($C_7H_9O_3^+$, calc. 141.0549).

cis-*Methyl 2-(Acetoxymethyl)cyclopropane-1-carboxylate* (**7q**). ^{1}H-NMR ($CDCl_3$, 200 MHz): 4.45 (*dd*, J = 12, 6, 1 H); 4.10 (*d*, J = 6, 1 H); 3.69 (*s*, 3 H); 2.03 (*s*, 3 H); 1.60–1.55 (*m*, 1 H); 1.20–1.10 (*m*, 2 H); 0.86 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 172.5 (*s*); 170.8 (*s*); 65.9 (*t*); 51.8 (*q*); 20.4 (*q*); 19.5 (*d*); 17.4 (*d*); 12.0 (*t*).

trans-*1-Menthyl 2-(Acetoxymethyl)cyclopropane-1-carboxylate* (**6r**). IR ($CHCl_3$; *cis*/*trans*-mixture): 2927*m*, 1728*s*, 1457*m*, 1371*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.54–4.48 (*dd*, J = 14, 6.14, 1 H); 4.03–3.88 (*m*, 3 H); 2.03 (*s*, 3 H); 2.08–0.79 (*m*, 22 H). ^{13}C-NMR ($CDCl_3$): 172.6 (*s*); 167.3 (*s*); 74.3 (*d*); 65.8 (*t*); 47.0 (*d*); 40.9 (*t*); 34.0 (*t*); 31.3 (*d*); 26.4 (*d*); 23.5 (*t*); 21.9 (*q*); 20.7 (*q*); 20.6 (*q*); 19.5 (*d*); 18.9 (*q*); 16.3 (*q*); 12.6 (*t*). MS (*cis*/*trans*-mixture): 296 (M^+, absent), 141 (8), 138 (47), 99 (100), 95 (34), 81 (23).

cis-*1-Menthyl 2-(Acetoxy)methylcyclopropane-1-carboxylate* (**7r**). ^{1}H-NMR (200 MHz, $CDCl_3$): 4.03–3.88 (*m*, 3 H); 2.02 (*s*, 3 H); 2.08–0.79 (*m*, 22 H). ^{13}C-NMR ($CDCl_3$): 171.5 (*s*); 165.3 (*s*); 74.32 (*d*); 62.6 (*t*); 46.9 (*d*); 40.7 (*t*); 34.0 (*t*); 31.2 (*d*); 26.2 (*d*); 23.3 (*t*); 21.8 (*q*); 20.6 (*q*); 20.3 (*q*); 20.1 (*d*); 18.8 (*d*); 16.2 (*q*); 12.8 (*t*).

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